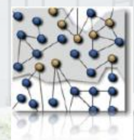
Coherence & Vibrations in Biology

Simulating System-Environment Interaction

Martin B Plenio



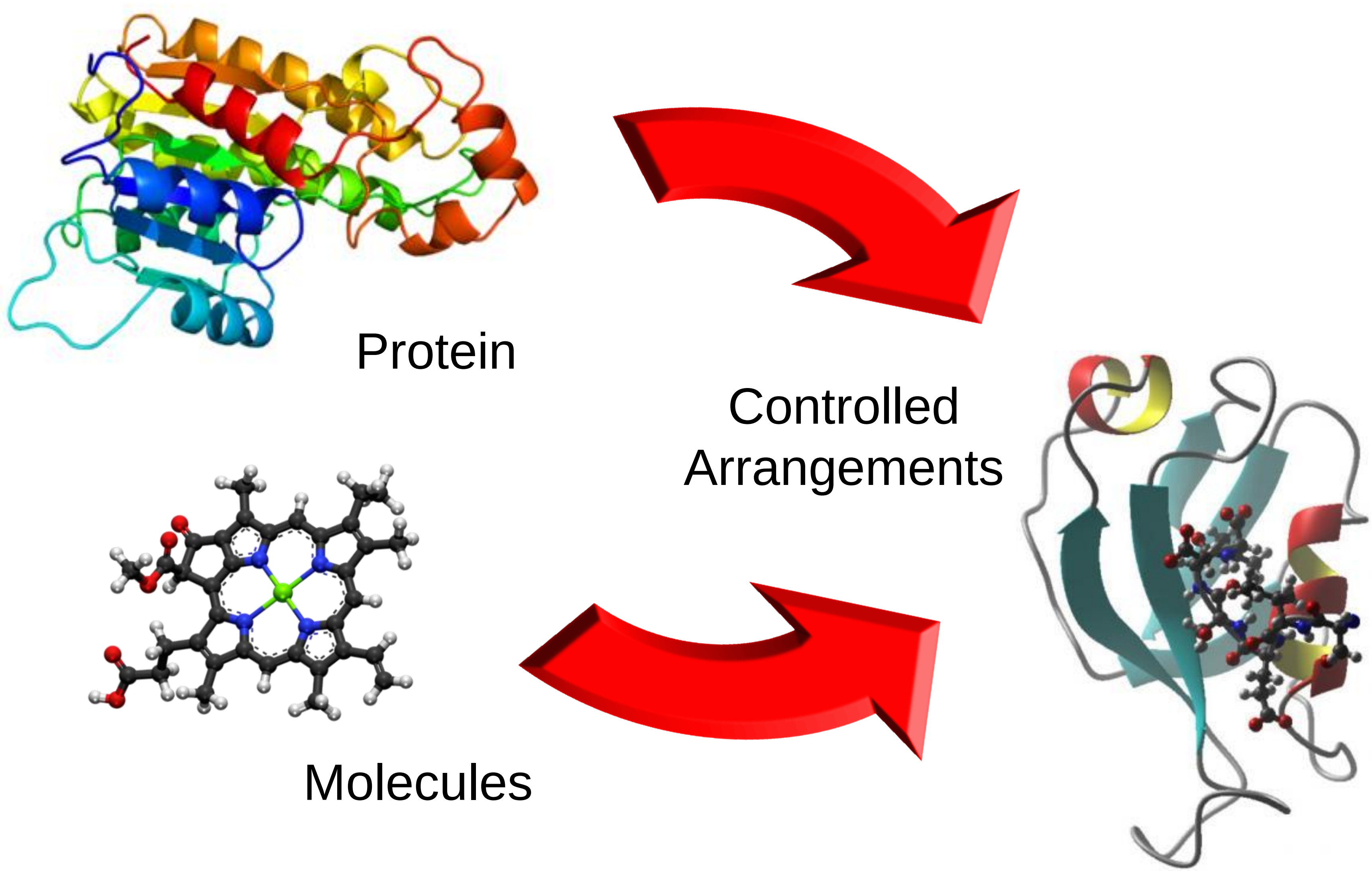


Institute of Theoretical Physics
&
Center for Quantum-BioSciences

Ulm University

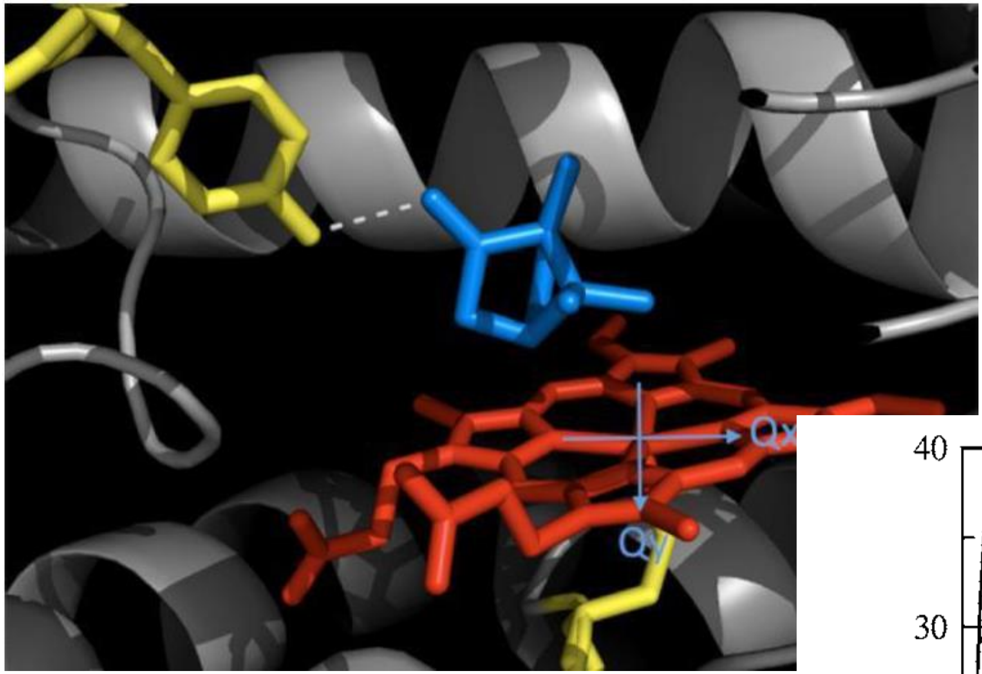
Coherence in Biology

Tuning Electronic and Vibrational Structures

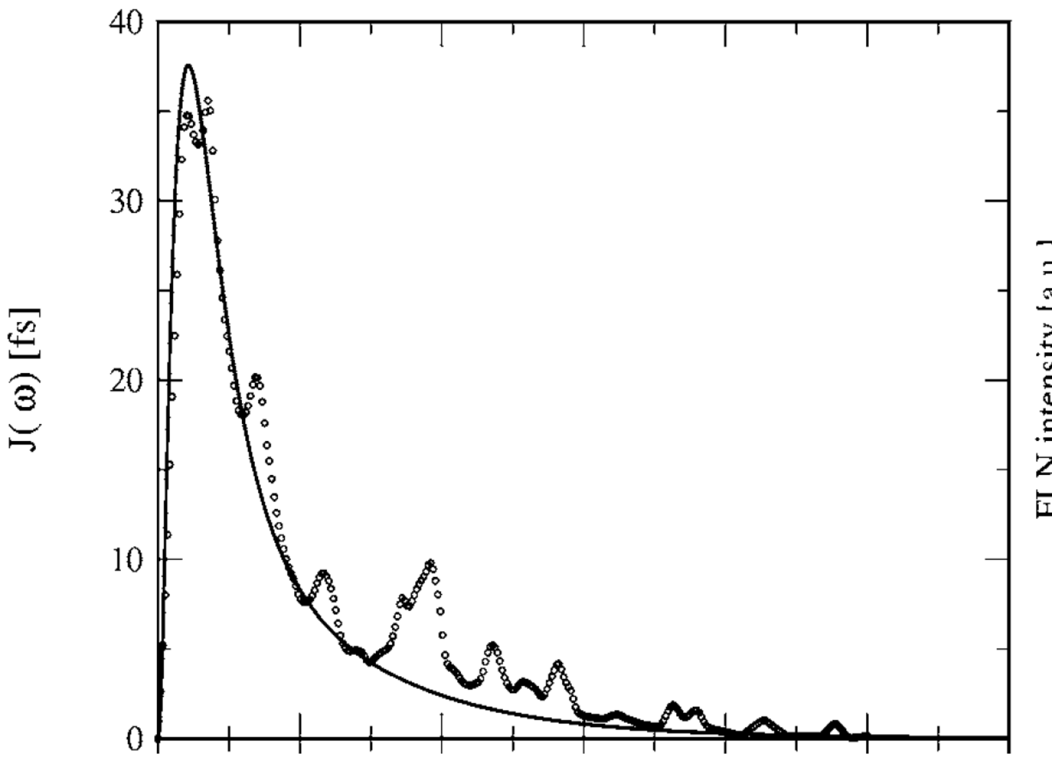


Coherence in Biology

Tuning Electronic and Vibrational Structures



- Coupling is neither weak nor strong
- Spectral density is highly structured



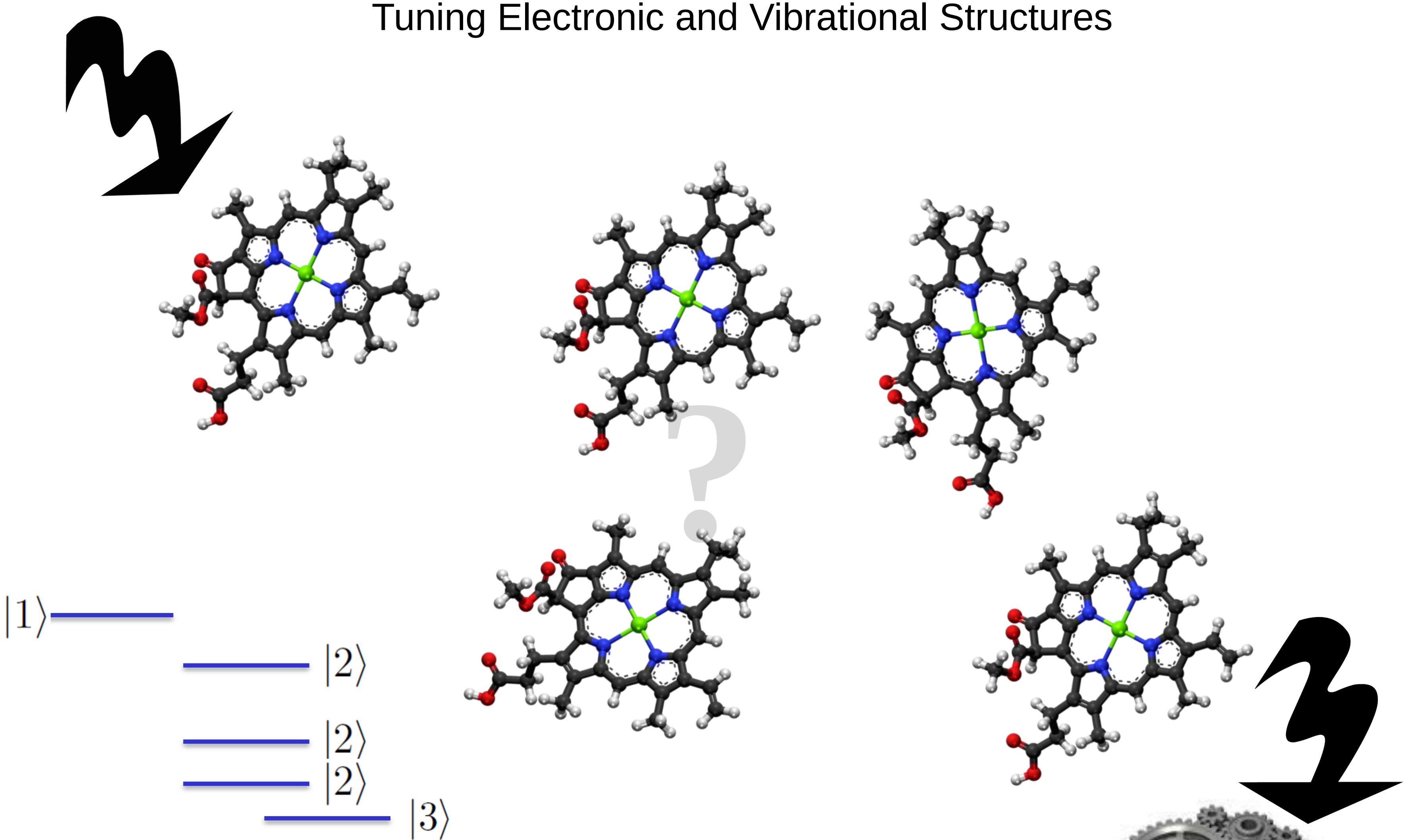
Vibrations affects local environment

⇨ excitation energy fluctuates

⇨ dephasing

Environment Assisted Quantum Dynamics

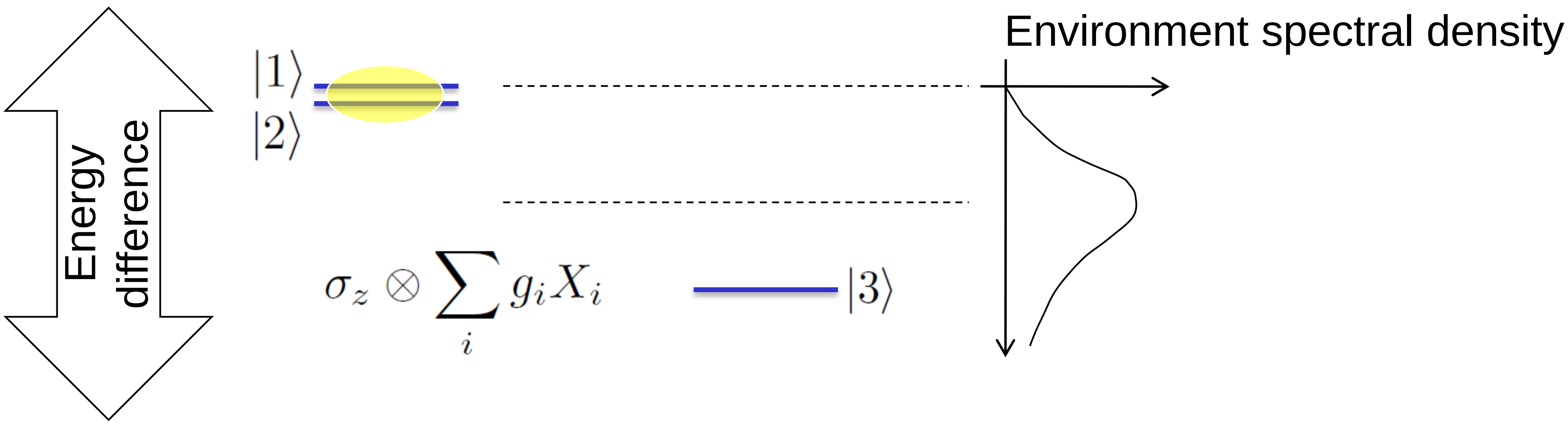
Tuning Electronic and Vibrational Structures

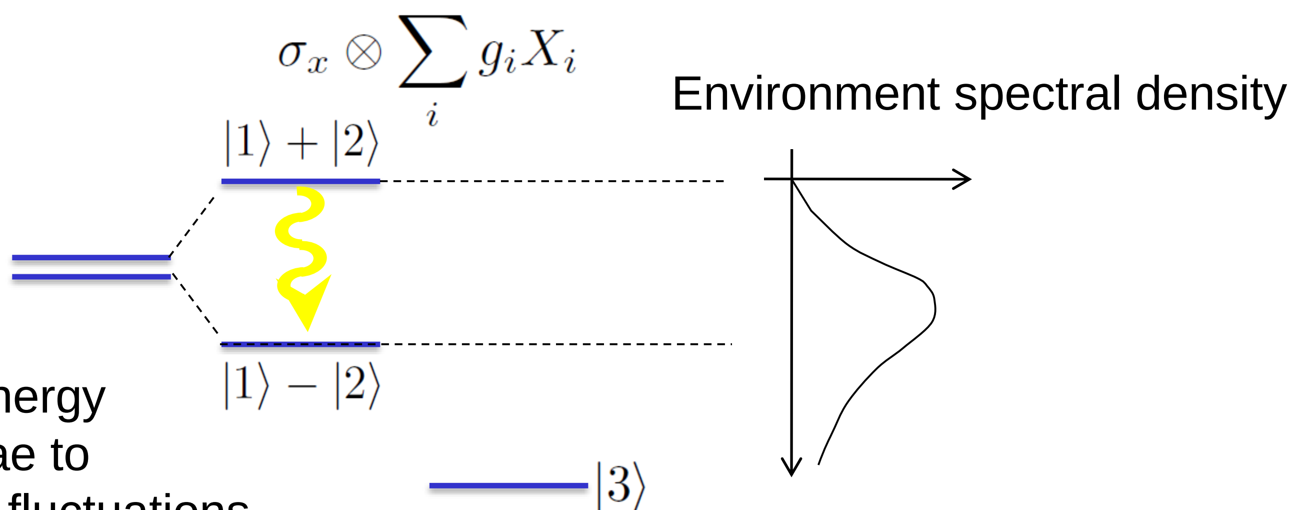


Chin, Datta, Caruso, Huelga & Plenio, NJP 2010
Chin, Huelga, Plenio, Phil. Trans. Roy. Soc. 2012
del Rey, Chin, Huelga, Plenio, J. Phys. Chem. Lett. 2013

Environment Assisted Quantum Dynamics

Tuning Electronic and Vibrational Structures



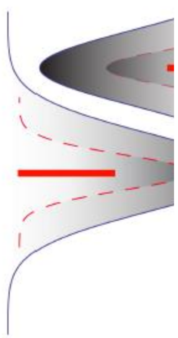


Coherently shifted energy levels act as antennae to harvest environment fluctuations

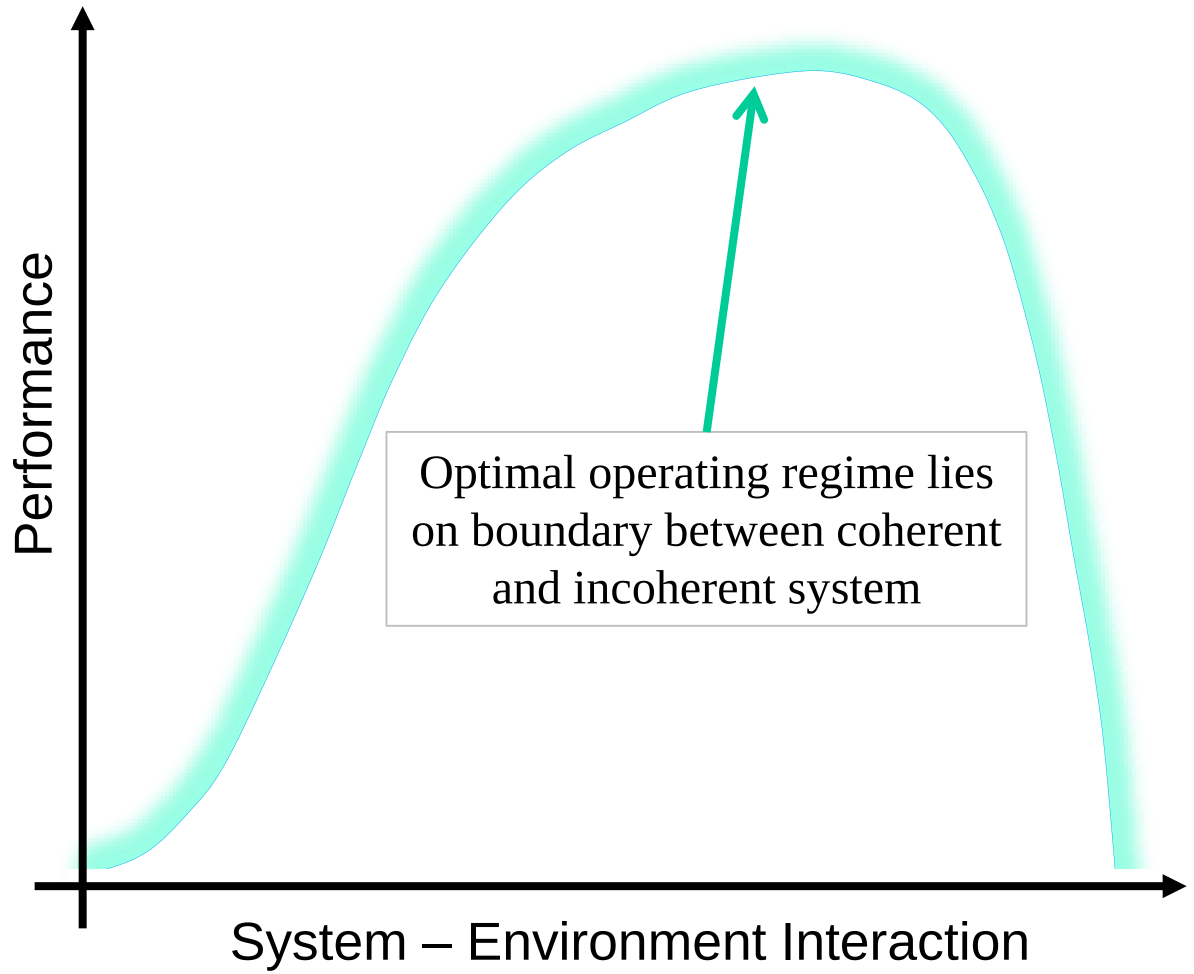
Chin, Datta, Caruso, Huelga & Plenio, NJP 2010
Chin, Huelga, Plenio, Phil. Trans. Roy. Soc. 2012
del Rey, Chin, Huelga, Plenio, J. Phys. Chem. Lett. 2013

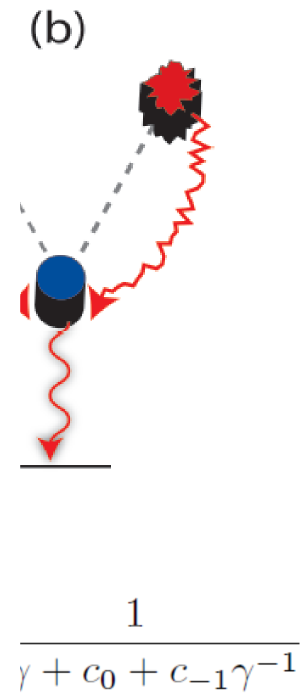
Environment Assisted Quantum Dynamics

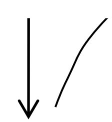
Design Principles



Effectiv
Rate ≅



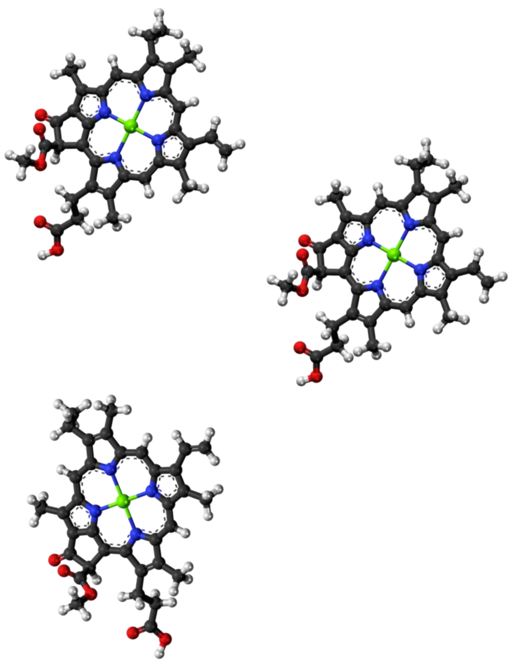


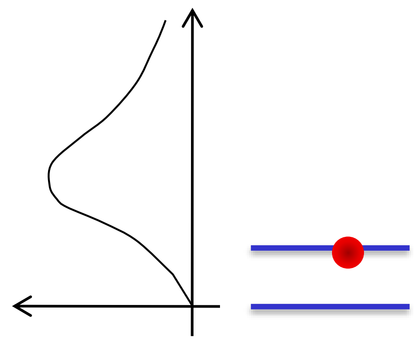


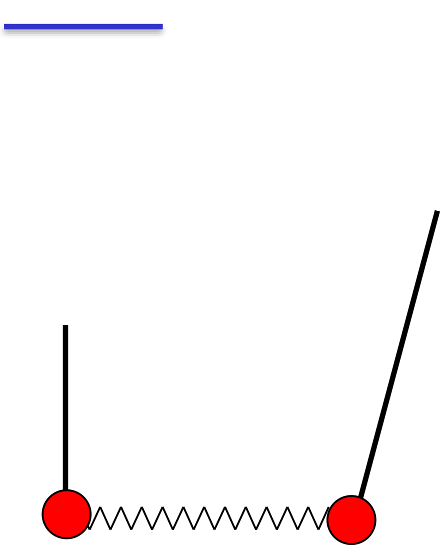
Plenio & Huelga, NJP 2008 Caruso, Chin, Datta, Huelga, Plenio, JCP 2009 Chin, Datta, Caruso, Huelga & Plenio, NJP 2010 Prior, Chin, Huelga & Plenio, PRL 2010

Environment Assisted Quantum Dynamics

Electronic & Vibrational Motion





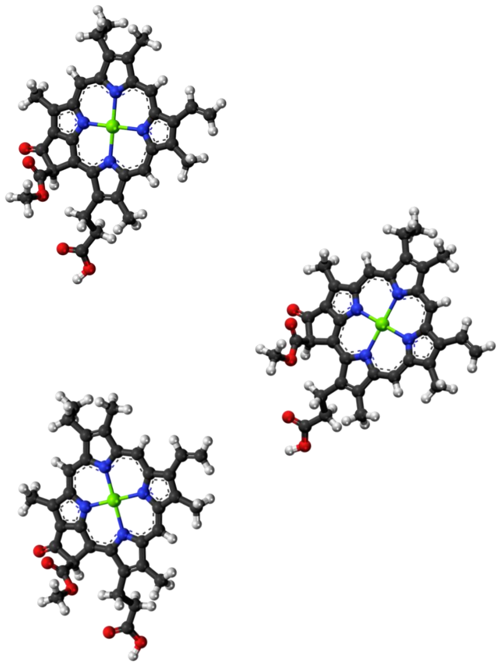


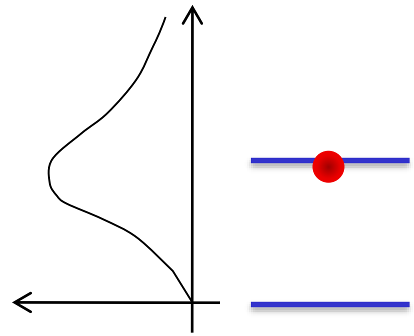
$$\omega_e \gg \omega_{vib}$$

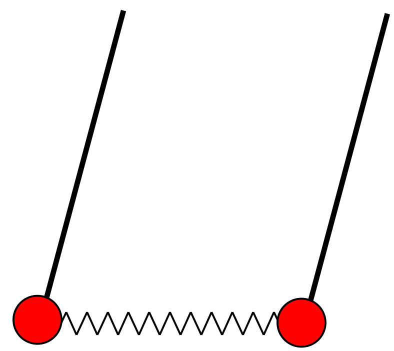
Plenio & Huelga, NJP 2008
Mohseni, Rebentrost, Lloyd, Aspuru-Guzik, JCP 2008
Caruso, Chin, Datta, Huelga, Plenio, JCP 2009
Chin, Datta, Caruso, Huelga & Plenio, NJP 2010
Del Rey, Chin, Huelga & Plenio, JPCL 2013
Moix, Khasin & Cao, NJP 2013

Environment Assisted Quantum Dynamics

Electronic & Vibrational Motion







$$\omega_e = \omega_{vib}$$

Plenio & Huelga, NJP 2008
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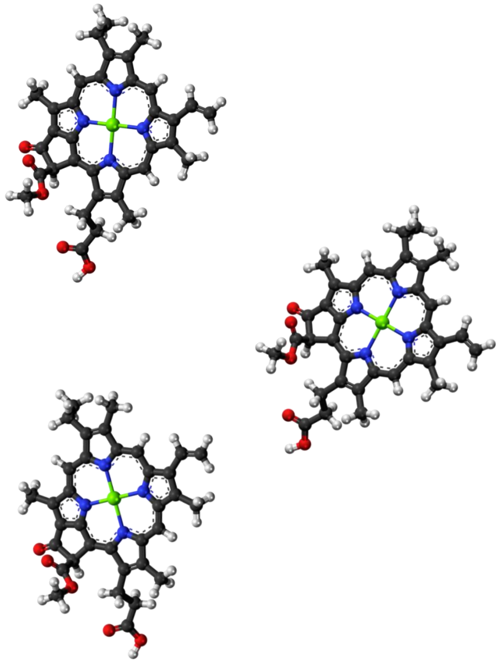
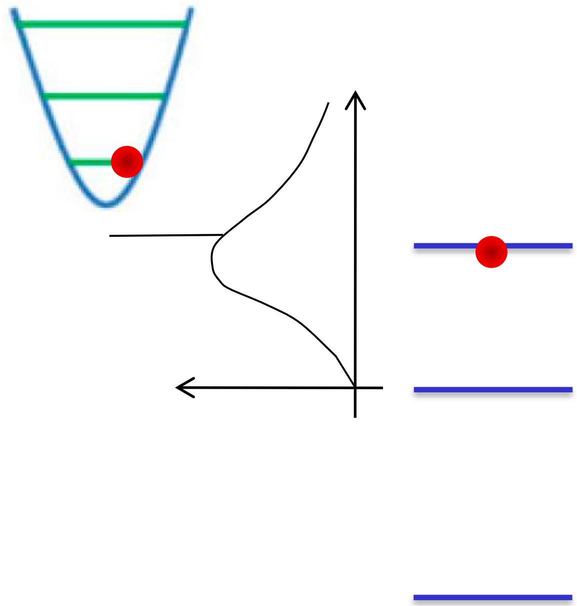
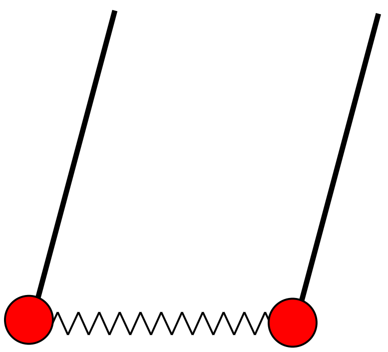
Environment Assisted Quantum Dynamics

Electronic & Vibrational Motion





Excitonic and vibrational resonance allows for periodic exchange of excitation and maintains electronic oscillatory dynamics

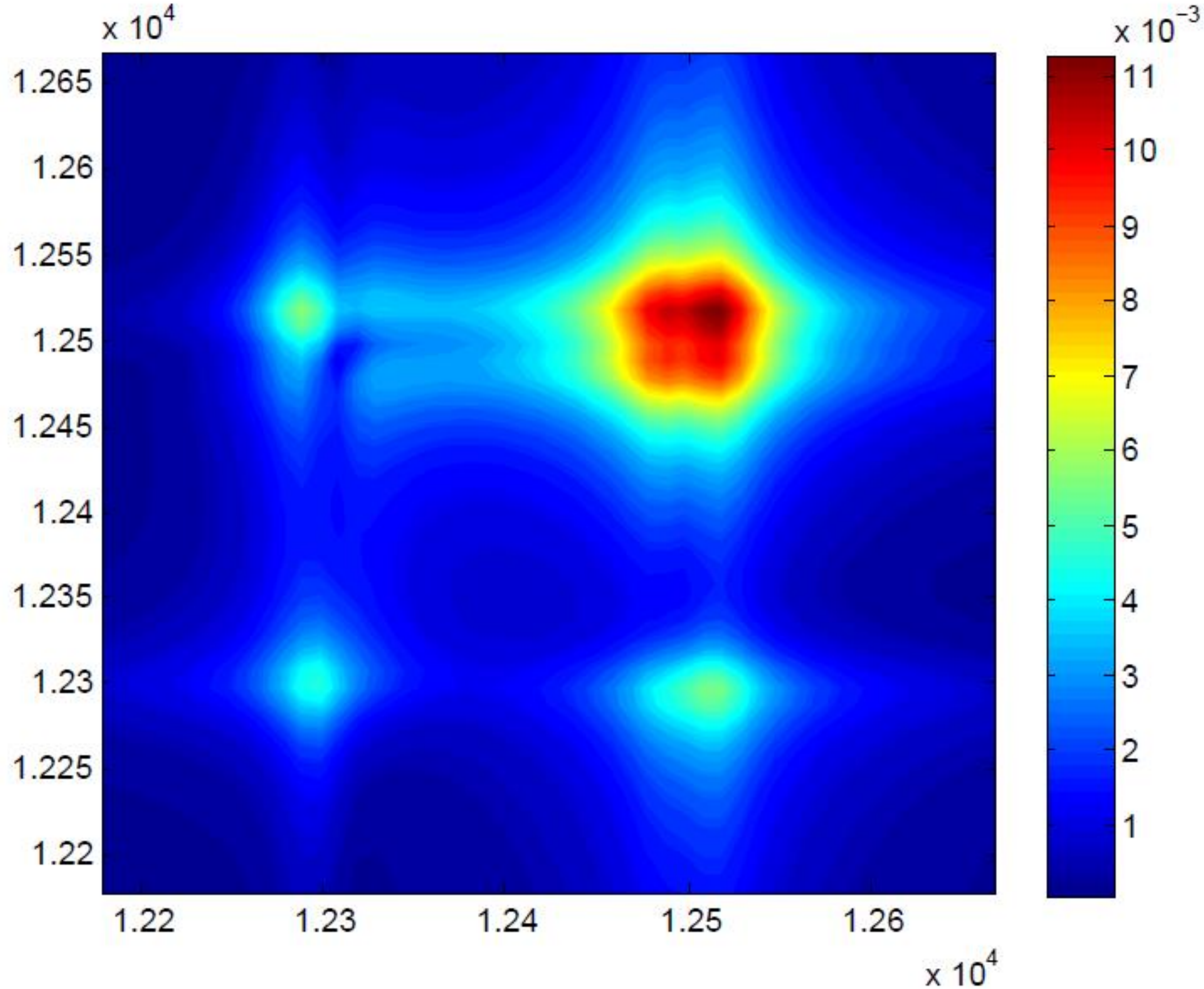


$$\omega_e = \omega_{vib}$$

Chin, Datta, Caruso, Huelga & Plenio, NJP 2010
Prior, Chin, Huelga, Plenio, PRL 2010
Chin, Prior, Rosenbach, Caycedo-Soler, Huelga & Plenio, Nat. Phys. 2013

Non-equilibrium System-Environment Dynamics

Long-lived Coherence at 277K



Plenio, Almeida, Huelga, J. Chem. Phys. 2013
Kreisbeck, Kramer, Aspuru-Guzik, NJP 2013
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Tiwari, Peters, Jonas, PNAS 2013

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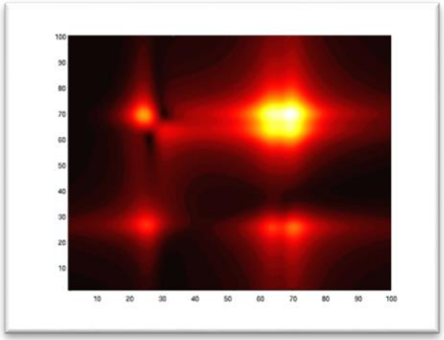

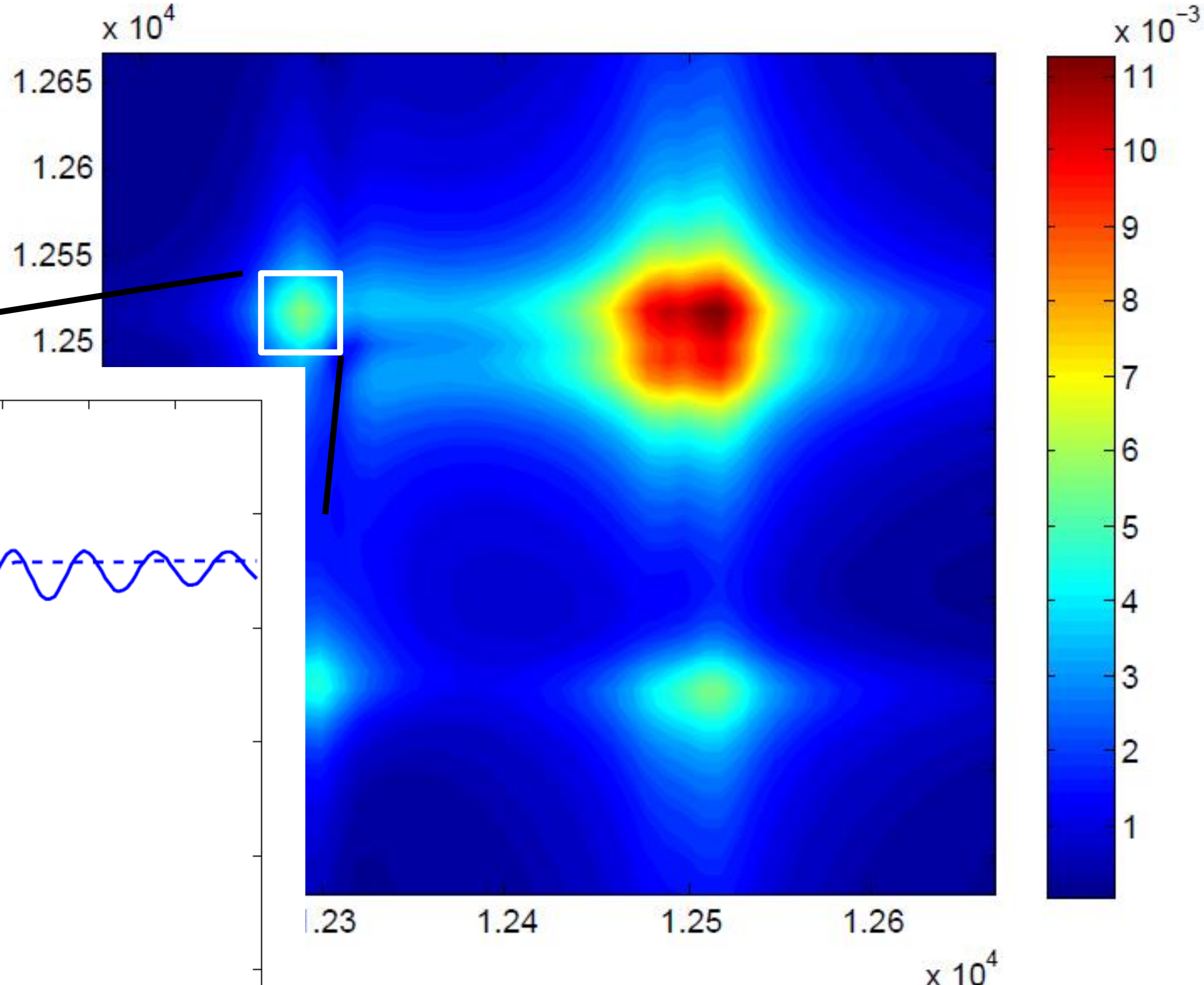

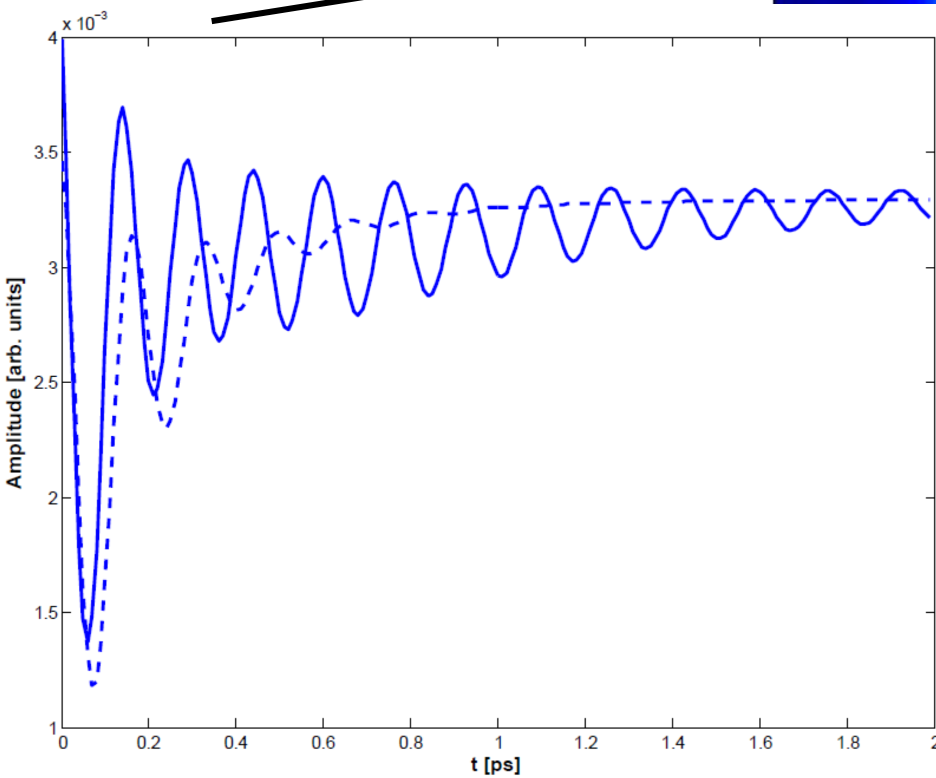

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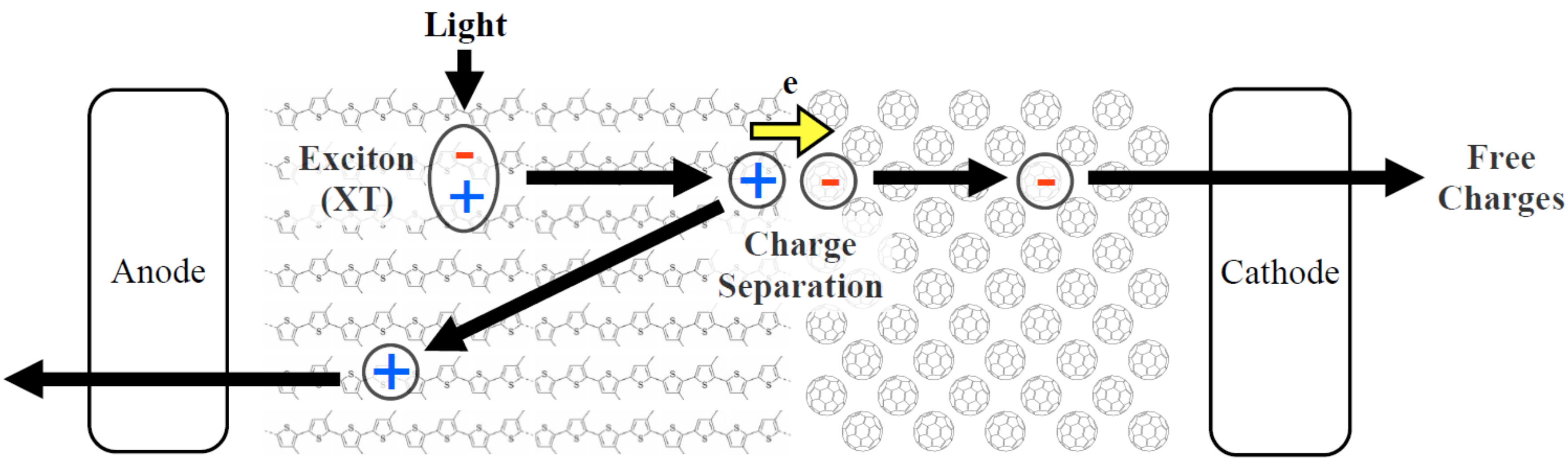
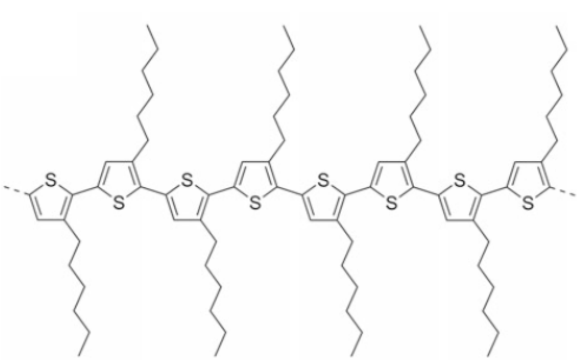
Vibronics in Organic Photovoltaics

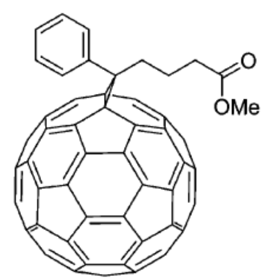
Vibronic Coupling Accelerates Polaron Pair Formation



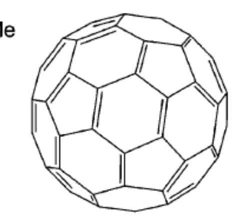
Donor
(Polymers, regioregular P3HT)

Acceptor
(Fullerenes)





PCBM



C_{60}

De Sio, Troiani, Rehault, Sommer, Lim, Huelga, Plenio, Maiuri, Cerullo, Molinari & Lienau. Nature Comm. **7**, 13742 (2016)

Vibronics in Organic Photovoltaics

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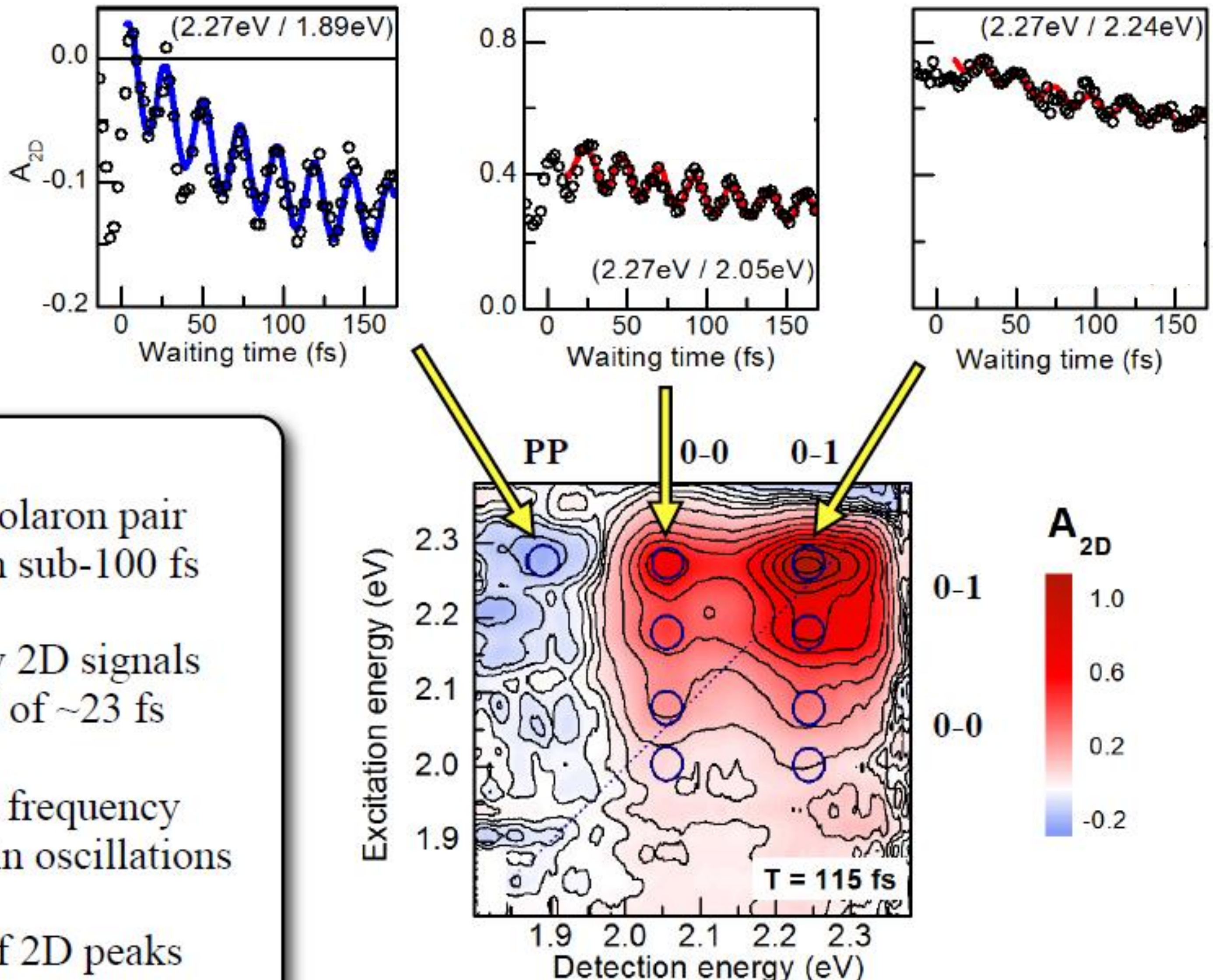

1. Ultrafast polaron pair generation on sub-100 fs

2. Oscillatory 2D signals with a period of ~23 fs

3. Additional frequency components in oscillations

4. Splitting of 2D peaks

De Sio, Troiani, Rehault, Sommer, Lim, Huelga, Plenio, Maiuri, Cerullo, Molinari & Lienau. Nature Comm. **7**, 13742 (2016)

Vibronics in Organic Photovoltaics

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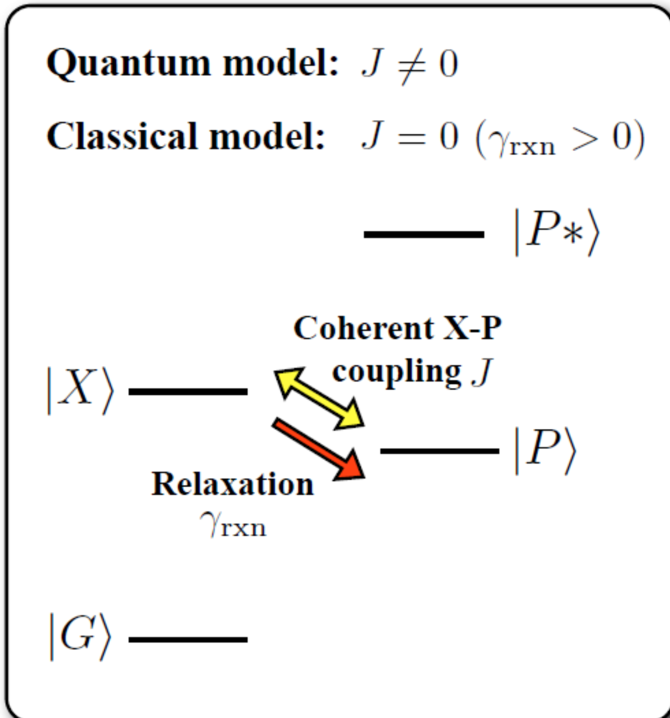
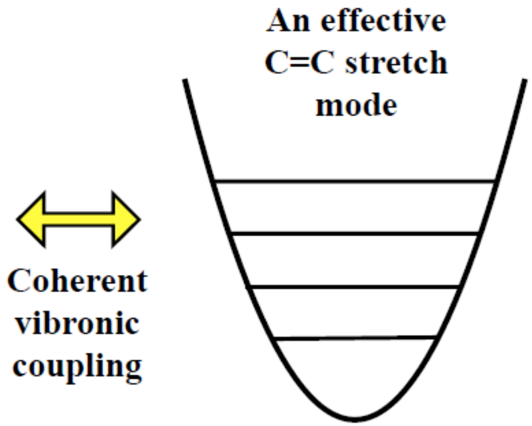
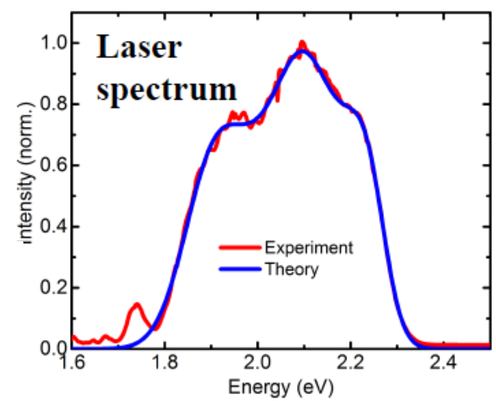






$$H = |G\rangle\langle G|(\hbar\omega a^\dagger a) + |X\rangle\langle X|(\hbar\Omega_X + \hbar\omega a^\dagger a + \hbar\omega\sqrt{S_X}(a^\dagger + a) + \hbar\omega S_X)$$
$$+ |P\rangle\langle P|(\hbar\Omega_P + \hbar\omega a^\dagger a + \hbar\omega\sqrt{S_P}(a^\dagger + a) + \hbar\omega S_P)$$
$$+ (|X\rangle\langle P| + |P\rangle\langle X|)(\hbar J + \hbar\omega\sqrt{S_{XP}}(a^\dagger + a))$$
$$+ |P*\rangle\langle P*|(\hbar\Omega_{P*} + \hbar\omega a^\dagger a + \hbar\omega\sqrt{S_{P*}}(a^\dagger + a) + \hbar\omega S_{P*}).$$

$$L_{dep}[\rho(t)] = \sum_{k=G,X,P,P*} \gamma_{dep}\left(|k\rangle\langle k|\rho(t)|k\rangle\langle k| - \frac{1}{2}\{|k\rangle\langle k|, \rho(t)\}\right)$$

$$L_{vib}[\rho(t)] = \gamma_{vib}\left(2\tilde{a}\rho(t)\tilde{a}^\dagger - \{\tilde{a}^\dagger\tilde{a}, \rho(t)\}\right),$$

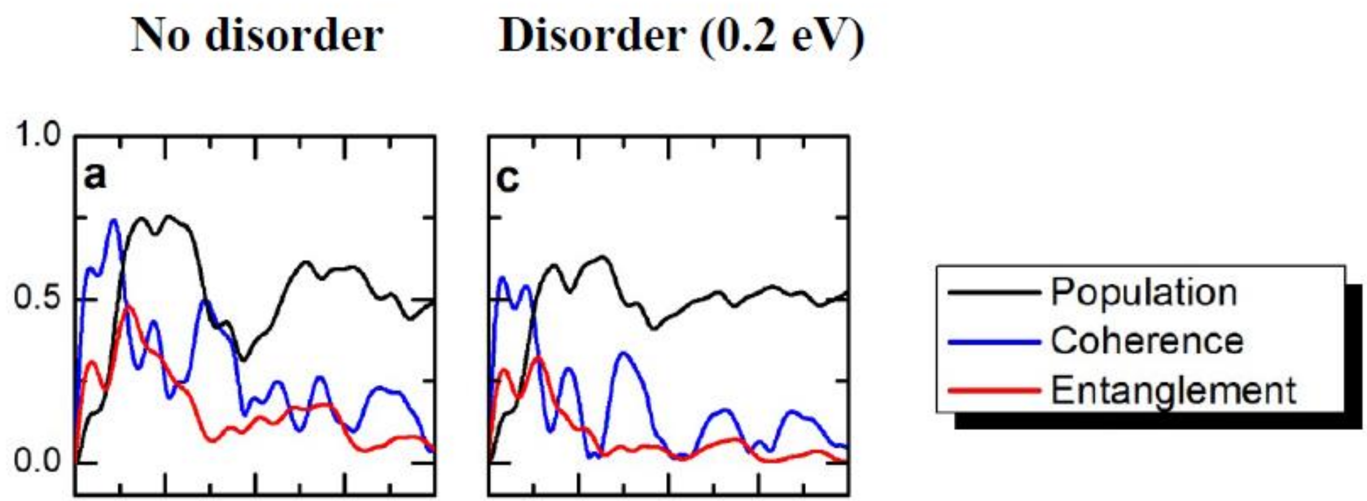
$$L_{rxn}[\rho(t)] = \gamma_{rxn}\left(|P\rangle\langle X|\rho(t)|X\rangle\langle P| - \frac{1}{2}\{|X\rangle\langle X|, \rho(t)\}\right)$$

De Sio, Troiani, Rehault, Sommer, Lim, Huelga, Plenio, Maiuri, Cerullo, Molinari & Lienau. Nature Comm. **7**, 13742 (2016)

Vibronics in Organic Photovoltaics

Vibronic Coupling Accelerates Polaron Pair Formation

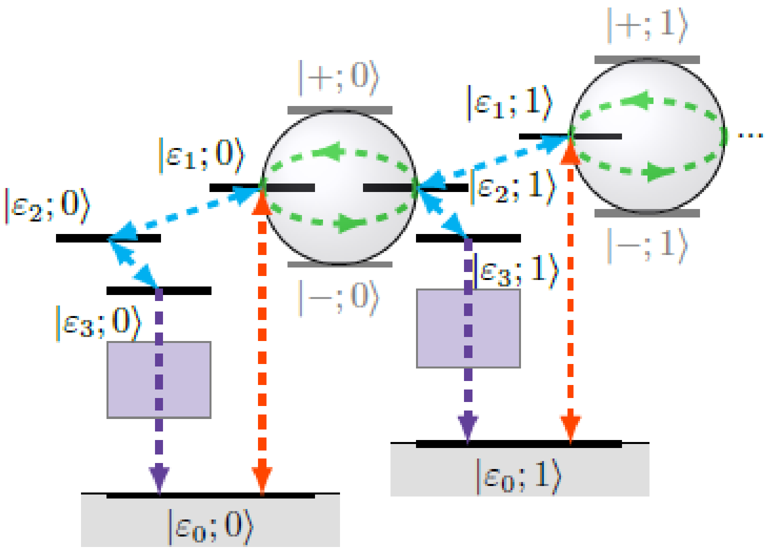
Non-equilibrium vibrational motions

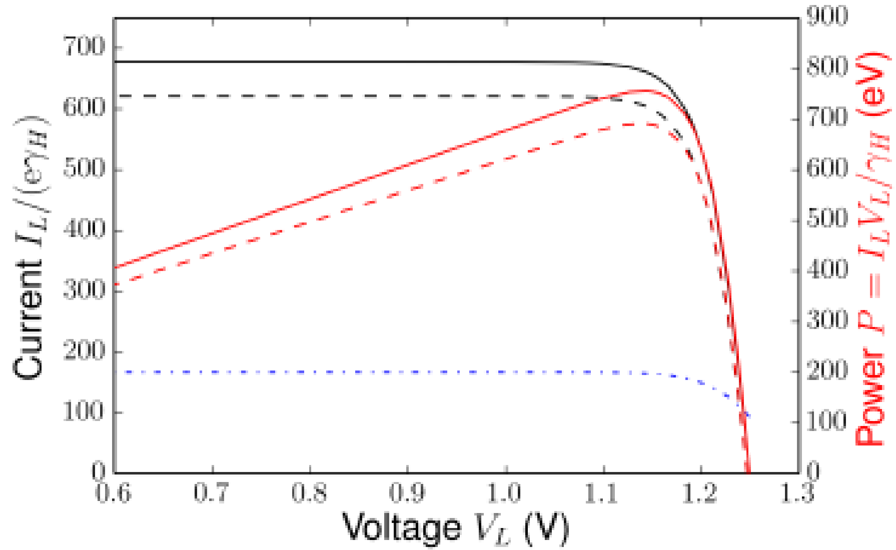


De Sio, Troiani, Rehault, Sommer, Lim, Huelga, Plenio, Maiuri, Cerullo, Molinari & Lienau. Nature Comm. **7**, 13742 (2016)

Non-equilibrium System-Environment Dynamics

Transport, Phonon Antennae & Long-lived Oscillations





Resonant vibrational modes can enhance power of nano-thermodynamical engine

Killoran, Huelga, Plenio, J Phys Chem. 2015

Coherence in Biology

The Thermodynamics of Small Engines

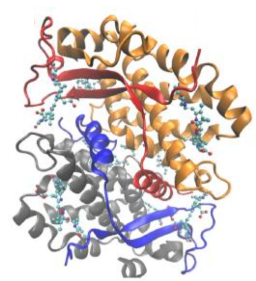
Quantum machines at the nanoscale

Faster, smaller, more quantum

Fluctuations grow

Interplay of Coherent Dynamics and Environment

How to verify principles in experiment ?



How to model these systems numerically

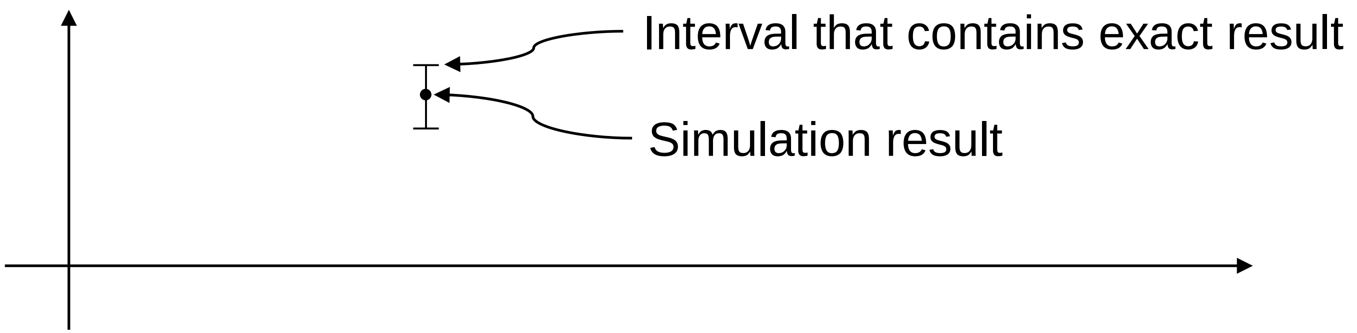
Design Principles for optimal performance

Certified Simulation of System-Environment Dynamics

Orthogonal Polynomials & t-DMRG

Ideal simulation method should satisfy:

- Method numerically tractable
- Possible to increase precision systematically
- Provide rigorous, assumption-free, error bounds on result

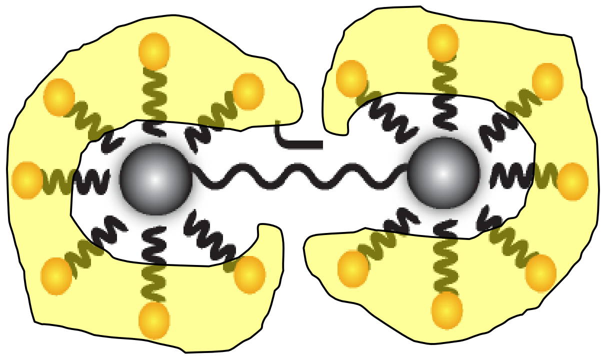


Prior, Chin, Huelga, Plenio, PRL 2010
Chin, Rivas, Huelga, Plenio, J. Math. Phys. 2010
Woods, Groux, Chin, Huelga, Plenio, J. Math. Phys. 2014
Rosenbach, Cerrillo, Huelga, Cao, Plenio, NJP 2016
Woods, Cramer, Plenio, PRL 2015
Mascherpa, Smirne, Huelga, Plenio, PRL 2017

Certified Simulation of System-Environment Dynamics

Orthogonal Polynomials & t-DMRG

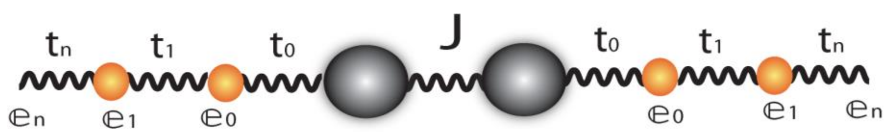
$$H_{res} = \int dx\, g(x) a_x^\dagger a_x$$



$$V = \int dx\, h(x) \hat{A}(a_x^\dagger + a_x)$$

$$b_n^\dagger = \int dx\, U_n(x) a_x^\dagger$$

Exact, thanks to theory of orthonormal polynomials



$$c_0 \hat{A}(b_0 + b_0^\dagger) + \sum_{n=0}^{\infty} \omega_n b_n^\dagger b_n + t_n b_{n+1}^\dagger b_n + t_n b_n^\dagger b_{n+1}$$

t-DMRG yields dynamics for general spectral densities

Prior, Chin, Huelga, Plenio, PRL 2010
Chin, Rivas, Huelga, Plenio, J. Math. Phys. 2010
Woods, Groux, Chin, Huelga, Plenio, J. Math. Phys. 2014
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Mascherpa, Smirne, Huelga, Plenio, PRL 2017

Certified Simulation of System-Environment Dynamics

Orthogonal Polynomials & t-DMRG

$$b_n^\dagger = \int dx\, U_n(x) a_x^\dagger$$

- Different rows of U (different n) are mutually orthogonal
- Each row of U can be considered proportional to a polynomial

$$U_n(x) = h(x)\tilde{p}_n(x)$$

$\tilde{p}_n(x)$ are some set of orthonormal polynomials with respect to the measure $d\mu(x) = h^2(x)dx$

Orthonormality:

$$\int dx\, U_n(x) U_m^*(x) = \int dx\, h^2(x)\tilde{p}_n(x)\tilde{p}_m(x) = \delta_{nm}$$

Three term recursion relation:

$$x\,\tilde{p}_n(x) \;=\; \frac{1}{C_n}\tilde{p}_{n+1}(x) + \frac{A_n}{C_n}\tilde{p}_n(x) + \frac{B_n}{C_n}\tilde{p}_{n-1}(x) \qquad p_0(x) = 1$$

Certified Simulation of System-Environment Dynamics

Orthogonal Polynomials & t-DMRG

$$V = \int dx\, h(x) \hat{A}(a_x^\dagger + a_x)$$

⇓

$$V = \hat{A} \sum_n \int dx\, h(x) U_n(x)(b_n + b_n^\dagger)$$

$$= \hat{A} \sum_n \int dx\, h^2(x) \tilde{p}_n(x)(b_n + b_n^\dagger)$$

$$= \hat{A} \sum_n \int dx\, h^2(x) \tilde{p}_n(x) p_0(x)(b_n + b_n^\dagger)$$

$$= \quad c_0 \ \hat{A}(b_0 + b_0^\dagger)$$

$$H_{res} = \int dx\, g x a_x^\dagger a_x$$

⇓

$$H_{res} = \sum_{n,m} \int dx\, g x U_n(x) U_m(x) b_n^\dagger b_m$$

$$= \sum_{n,m} \int dx\, g h^2(x) x \tilde{p}_n(x) \tilde{p}_m(x) b_n^\dagger b_m$$

$$= g \sum_{n,m} \int_0^{x_{\max}} dx h^2(x) \left[\frac{1}{C_n} \tilde{p}_{n+1}(x) + \frac{A_n}{C_n} \tilde{p}_n(x) + \frac{B_n}{C_n} \tilde{p}_{n-1}(x) \right] \tilde{p}_m(x) b_n^\dagger b_m$$

$$= g \sum_n \frac{1}{C_n} b_n^\dagger b_{n+1} + \frac{A_n}{C_n} b_n^\dagger b_n + \frac{B_{n+1}}{C_{n+1}} b_{n+1}^\dagger b_n$$

Certified Simulation of System-Environment Dynamics

Orthogonal Polynomials & t-DMRG

- Constructions of orthogonal polynomials

For each choice of scalar product (hence spectral density) these are uniquely determined and there are recursion relations.

⇓ ⇓

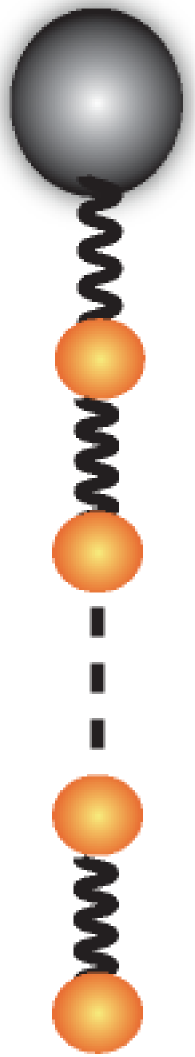
Numerics: OrthPol determines these and is numerically stable

W. Gautschi, ACM Trans Math Soft. 1994

Analytics: For many spectral densities we know recursions exactly

Certified Simulation of System-Environment Dynamics

Orthogonal Polynomials & t-DMRG



$$J(\omega) = 2\pi\alpha\omega_c^{1-s}\omega^s\Theta(\omega_c - \omega) = \pi h^2(g^{-1}(\omega))\frac{dg^{-1}(\omega)}{d\omega}$$

$$g(x) = \omega_c x,$$

$$h(x) = \sqrt{2\alpha}\omega_c x^{s/2}$$

OPs are Jacobi Polynomials

Recurrence coefficients known analytically

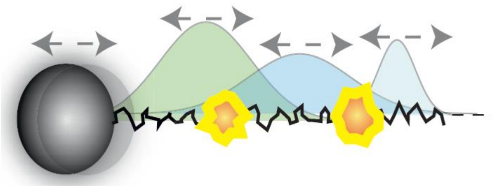
$$\omega_n = \frac{\omega_c}{2}\left(1 + \frac{s^2}{(s+2n)(2+s+2n)}\right),$$

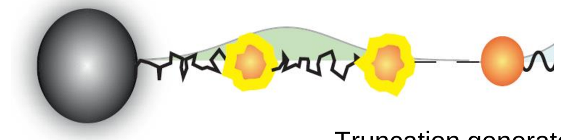
$$t_n = \frac{\omega_c(1+n)(1+s+n)}{(s+2+2n)(3+s+2n)}\sqrt{\frac{3+s+2n}{1+s+2n}}$$

Certified Simulation of System-Environment Dynamics

Orthogonal Polynomials & t-DMRG

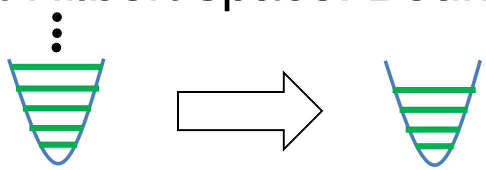
Error Budget DMRG :
- DMRG truncation in each step: can be upper bounded
- DMRG Trotterization in each step: can be upper bounded





Truncation generates optimal discretization of environment Woods & Plenio. J. Math. Phys. 2016

Error Budget Chain :
- Chain termination: Bounded by Lieb-Robinson techniques
- Local Hilbert space: Bounded by fidelity bound



Woods, Cramer & Plenio, PRL 2016

$$\frac{\Delta^2(t,L)}{4\|\hat{O}\|^2\|\hat{h}\|/c} \leq C\left(\|\gamma_0\|^{1/2} + t\|\hat{h}\|\right)\frac{(ct)^{L+1}(e^{ct}+1)}{(L+1)!}$$ esult

$$\Delta(t,L) = |\mathrm{tr}[\hat{O}e^{-i\hat{H}t}\hat{\varrho}_0 e^{i\hat{H}t}] - \mathrm{tr}[\hat{O}e^{-i\hat{H}_L t}\hat{\varrho}_0 e^{i\hat{H}_L t}]|$$

Simulation of System-Environment Dynamics

Dependence on Spectral Densities

General question: If two spectral densities differ by ΔJ, by how much will the expectation of spin observables differ?

Spin-Boson Model:

$$\hat{H} = \hat{H}_S \otimes \mathbb{I}_B + \mathbb{I}_S \otimes \hat{H}_B + \hat{H}_I$$
$$= \left(\frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x\right) \otimes \mathbb{I}_B + \mathbb{I}_S \otimes \int_0^\infty dk\omega_k \hat{a}_k^\dagger \hat{a}_k$$
$$+ \frac{\lambda}{2}\sigma_z \otimes \int_0^\infty dk h(k)(\hat{a}_k^\dagger + \hat{a}_k),$$

Observable:

$$\langle \hat{O}(t) \rangle = \mathrm{Tr}(\hat{O} e^{-i\hat{H}t} \hat{\rho}_0 e^{i\hat{H}t})$$

Result:

$$|\Delta\langle \hat{O}(t)\rangle| \leq \|\hat{O}\|(e^{\lambda^2 C t^2/2} - 1)^{lt''|\Delta\xi(t'-t'')|} - 1\Big)$$

$$\xi_J(t) := \int_0^\infty \frac{d\omega}{\pi} J(\omega)\left[\coth\left(\frac{\beta\omega}{2}\right)\cos(\omega t) + i\sin(\omega t)\right]$$

$$|\Delta\langle \hat{O}(t)\rangle| \leq \|\hat{O}\|(e^{\lambda^2[\gamma(\beta)+\eta]t} - 1) \qquad \int_0^\infty dt|\Delta\xi(t)| = c < \infty$$

Mascherpa, Smirne, Huelga, Plenio, PRL 2017

Simulation of System-Environment Dynamics

Hierarchies Equations of Motion

Decompose spectral density in antisymmetrized Lorentzians

$$\xi_L(t;\Omega,\Gamma) = \frac{e^{-\Gamma t}}{8\Omega\Gamma}\left[\coth\left(\frac{\beta}{2}(\Omega+i\Gamma)\right)e^{i\Omega t} + \coth\left(\frac{\beta}{2}(\Omega-i\Gamma)\right)e^{-i\Omega t} + 2i\sin(\Omega t)\right] - \frac{2}{\beta}\sum_{k=1}^{\infty}\frac{\nu_k e^{-\nu_k t}}{(\Omega^2+\Gamma^2-\nu_k^2)^2+4\Omega^2\nu_k^2},$$

Truncate at finite N

$\epsilon\beta$	N	$[\lvert\Delta\langle\sigma_z\rangle(t_{\max})\rvert^{\mathrm{an}}/\lVert\sigma_z\rVert](N)$	$[\lvert\Delta\langle\sigma_z\rangle(t_{\max})\rvert^{\mathrm{num}}/\lVert\sigma_z\rVert](N)$	$N^{\mathrm{an}}_{20\%}$	$N^{\mathrm{num}}_{20\%}$
0.4	2	27.94%	9.43%	3	2
1.4	7	62.39%	23.77%	10	8
10.0	48	111.69%	45.34%	70	56

Mascherpa, Smirne, Huelga, Plenio, PRL 2017

Summary

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Center for QuantumBioSciences
with dedicated Research Building
to be completed by end of 2018