Exploring dissipative excitonic dynamics: a consistent treatment from weak to strong environmental coupling

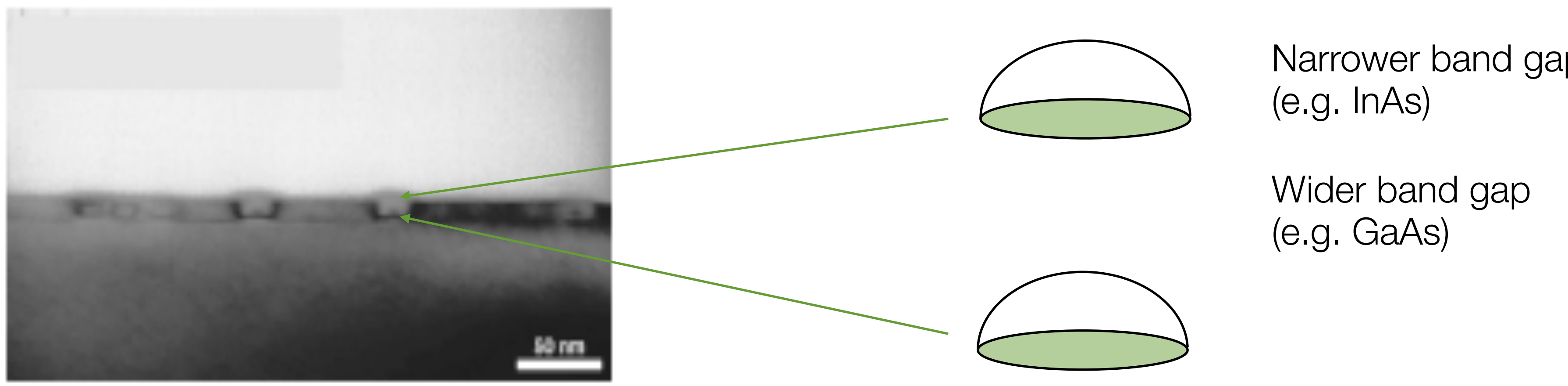
Ahsan Nazir

Junior Research Fellow
Imperial College London

Imperial College London

Semiconductor quantum dots

- Semiconductor QDs: Nanoscale islands of narrower band gap material embedded in a surrounding wider band gap material



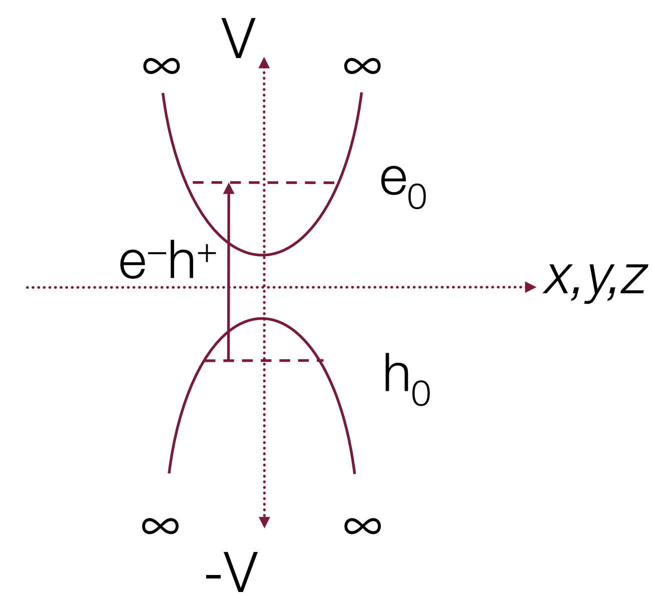
- 3D confinement leads to atomic-like carrier states with discrete energy levels

- For our purpose - 2-level system (pseudo-spin) which is **influenced by the solid-state environment,** here we consider phonons

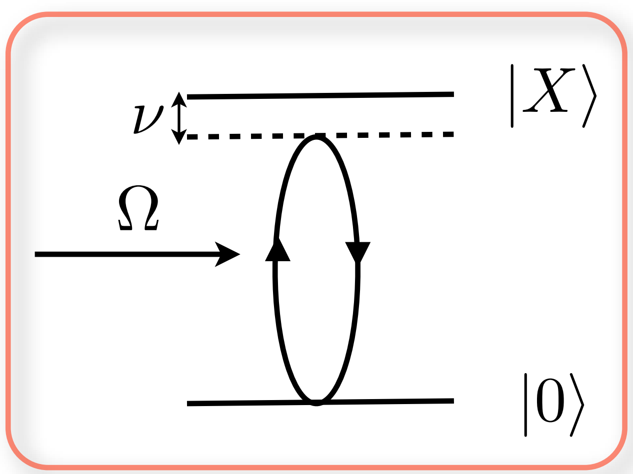
- How must we **modify** the standard quantum optics treatments to account for the solid-state nature of the system? e.g. influence of phonons on Rabi oscillations, resonance fluorescence spectrum, etc.

Excitonic two-level system

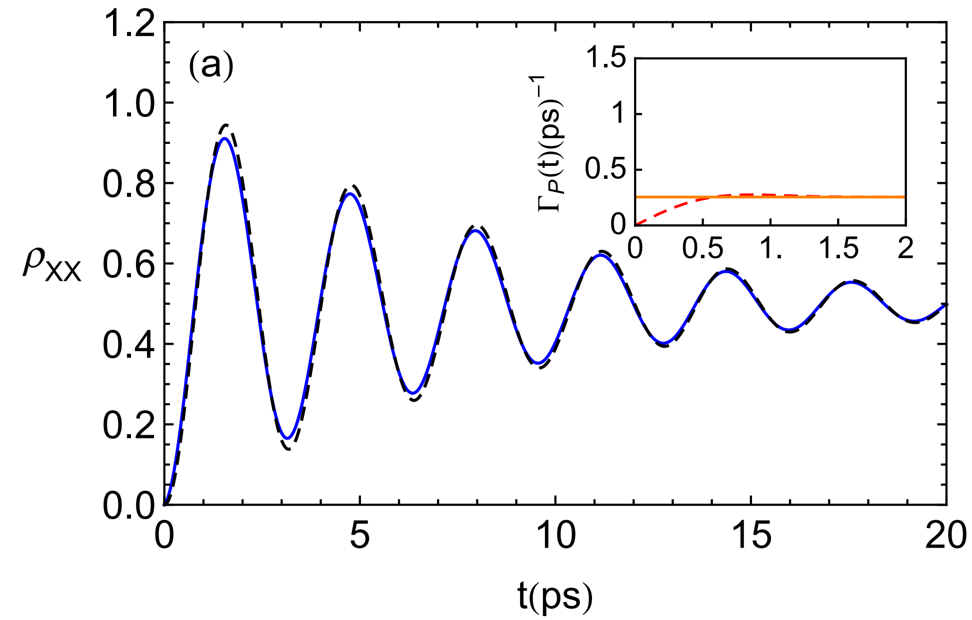
- Excitons: electron-hole pair states formed under excitation of electron from valence band to conduction band



- Two level system (strong confinement): absence $|0\rangle$ or presence $|X\rangle$ of an exciton defines the basis



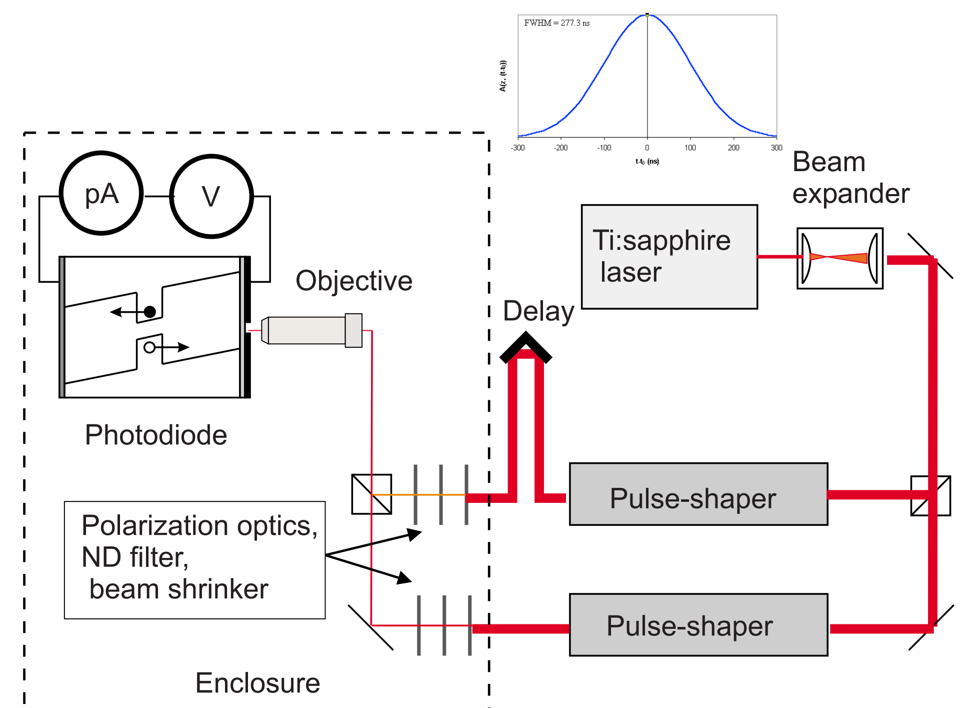
- Coherent manipulations through external laser addressing e.g. driving Rabi rotations. Rabi frequency (QD-laser coupling) Ω sets timescale of coherent population oscillations



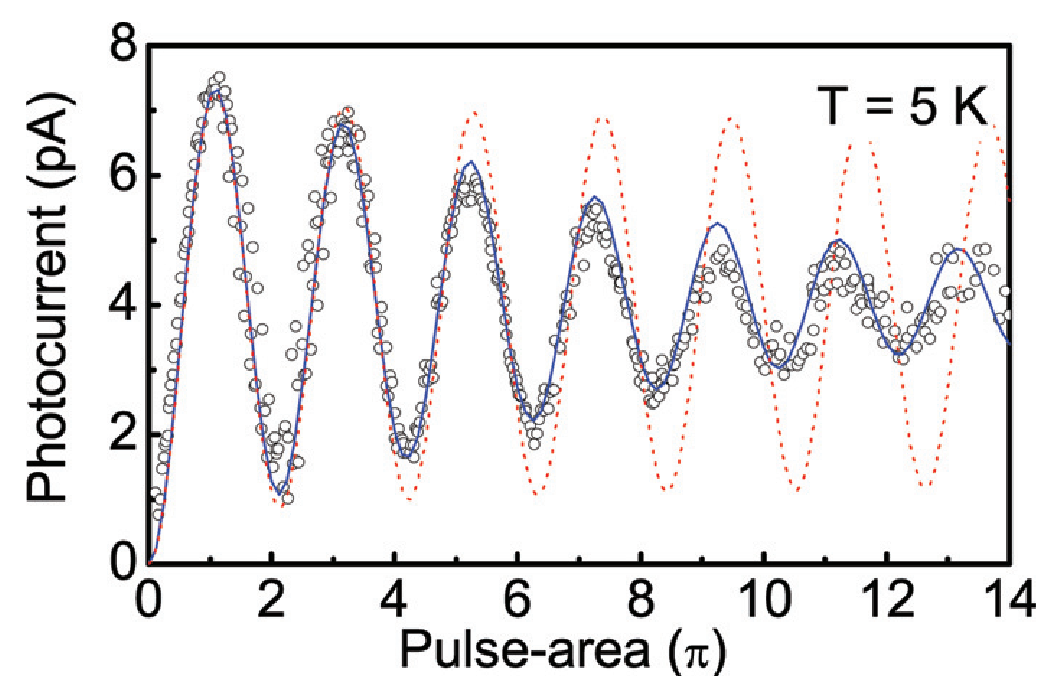
McCutcheon and Nazir, New J. Phys. 12, 113042 (2010)

Motivation - experimental data from Sheffield

- Single InGaAs/GaAs QD (2LS) resonantly driven by a single laser pulse of Gaussian envelope
- Photocurrent detection: photocurrent is proportional to the final occupation of the exciton state following resonant excitation
- Rabi rotations measured as a function of **pulse area**, with **duration fixed** - i.e. pulse area controlled by incident power
- Damping not simply fixed by pulse duration, **pulse area dependent damping** of Rabi rotations observed: $\boxed{\Gamma \propto \Omega^2}$
- What mechanism is responsible for Rabi rotation damping? A consequence of exciton-phonon interactions?

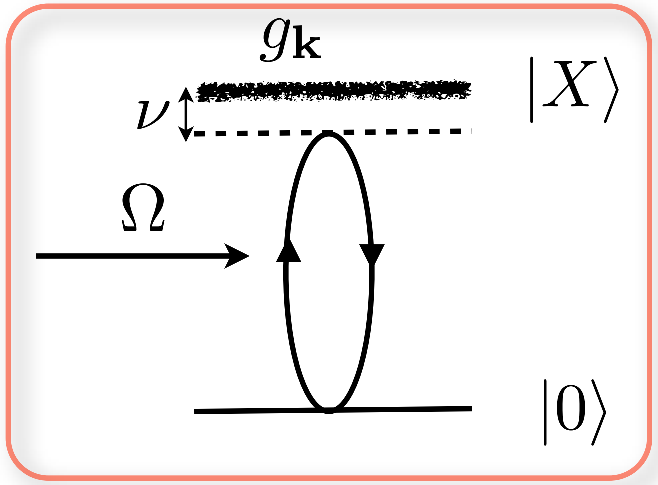


S. J. Boyle et al., PRB 78, 075301 (2008)



Quantum dot dynamics: master equations

$$H = \nu|X\rangle\langle X| + \frac{\Omega}{2}\sigma_x + \sum_{\mathbf{k}} \omega_{\mathbf{k}} b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + |X\rangle\langle X| \sum_{\mathbf{k}} g_{\mathbf{k}}(b_{\mathbf{k}}^\dagger + b_{\mathbf{k}})$$



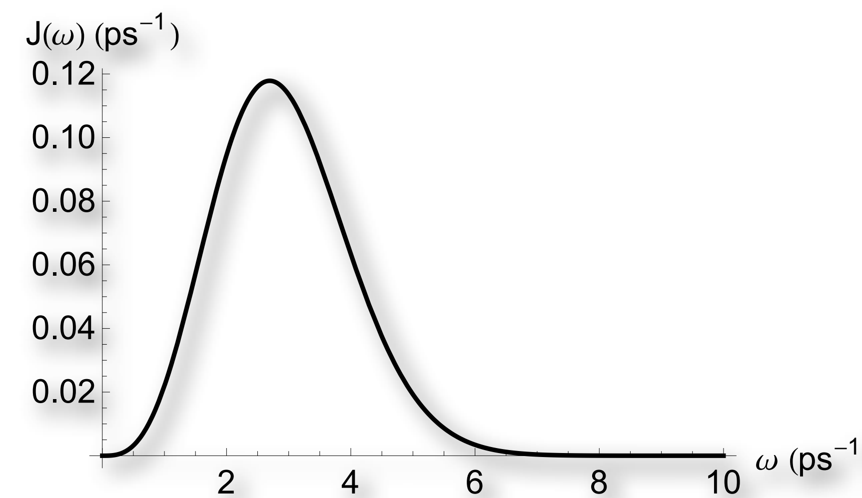
- Generally, we write $H = H_0 + H_I$ H_0 - solution known; H_I - treat as small perturbation

- Derive 2nd order (in H_I) master equation for the dynamics of the excitonic system, under influence of the phonon bath (Born approx. or projection operators)

$$\frac{d}{dt}\rho(t) = -\int_0^t ds tr_B[H_I(t), [H_I(s), \rho(t)\rho_B]]$$

  - Reduced description in terms of **system degrees of freedom only** - intuitive, efficient and relatively straightforward to work with

  - Important definition - **spectral density**, measure of the exciton-phonon coupling, weighted by the phonon density of states at a particular frequency



$J(\omega) \propto \omega^s$

$$J(\omega) = \sum_{\mathbf{k}} |g_{\mathbf{k}}|^2 \delta(\omega - \omega_{\mathbf{k}})$$

$$R = \int_0^\infty \omega^{-1} J(\omega) d\omega$$

Reorganisation energy

Experiment-theory comparison

- On resonance we find a simple (approximate) master equation, with **driving frequency dependent** rate

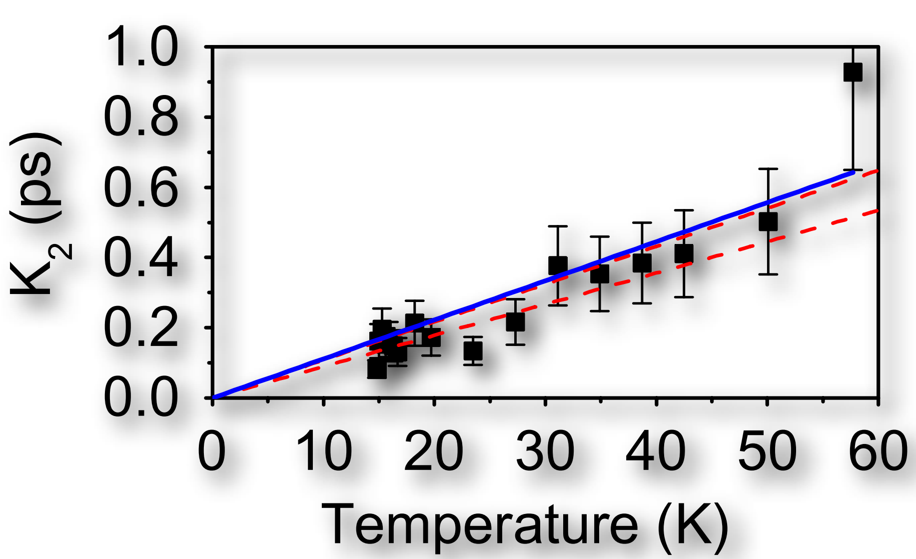
$$\boxed{\frac{d}{dt}\rho(t) = -i\frac{\Omega}{2}[\sigma_x,\rho(t)] - \Gamma\big[\sigma_z,[\sigma_z,\rho(t)]\big]}$$

$$\Gamma \propto J(\Omega)\coth\left(\Omega/k_B T\right)$$

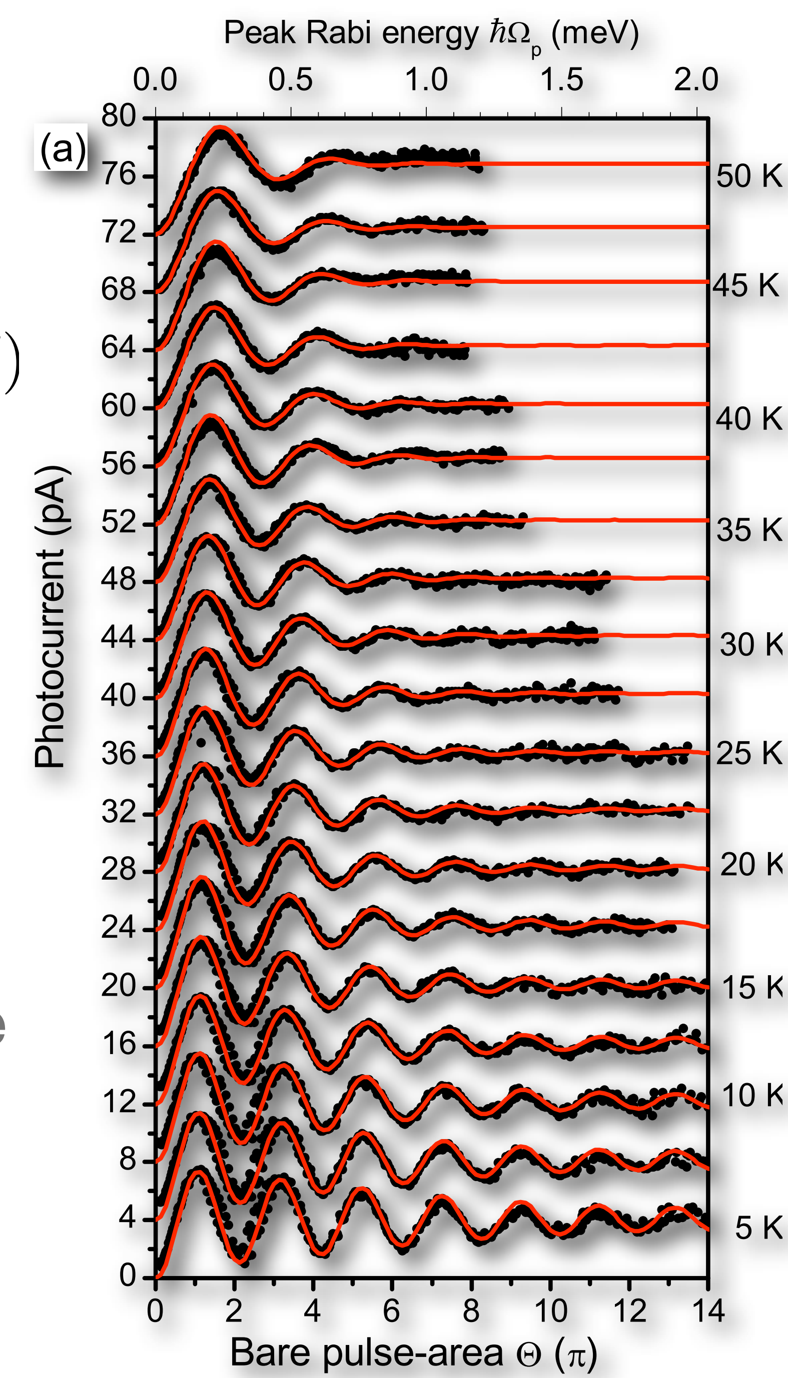
- Dominant coupling (acoustic phonons) has form

$$J(\omega) \propto \omega^3$$

- Hence, $\Gamma \approx K_2(T)\Omega^2 \propto \Omega^2 T$



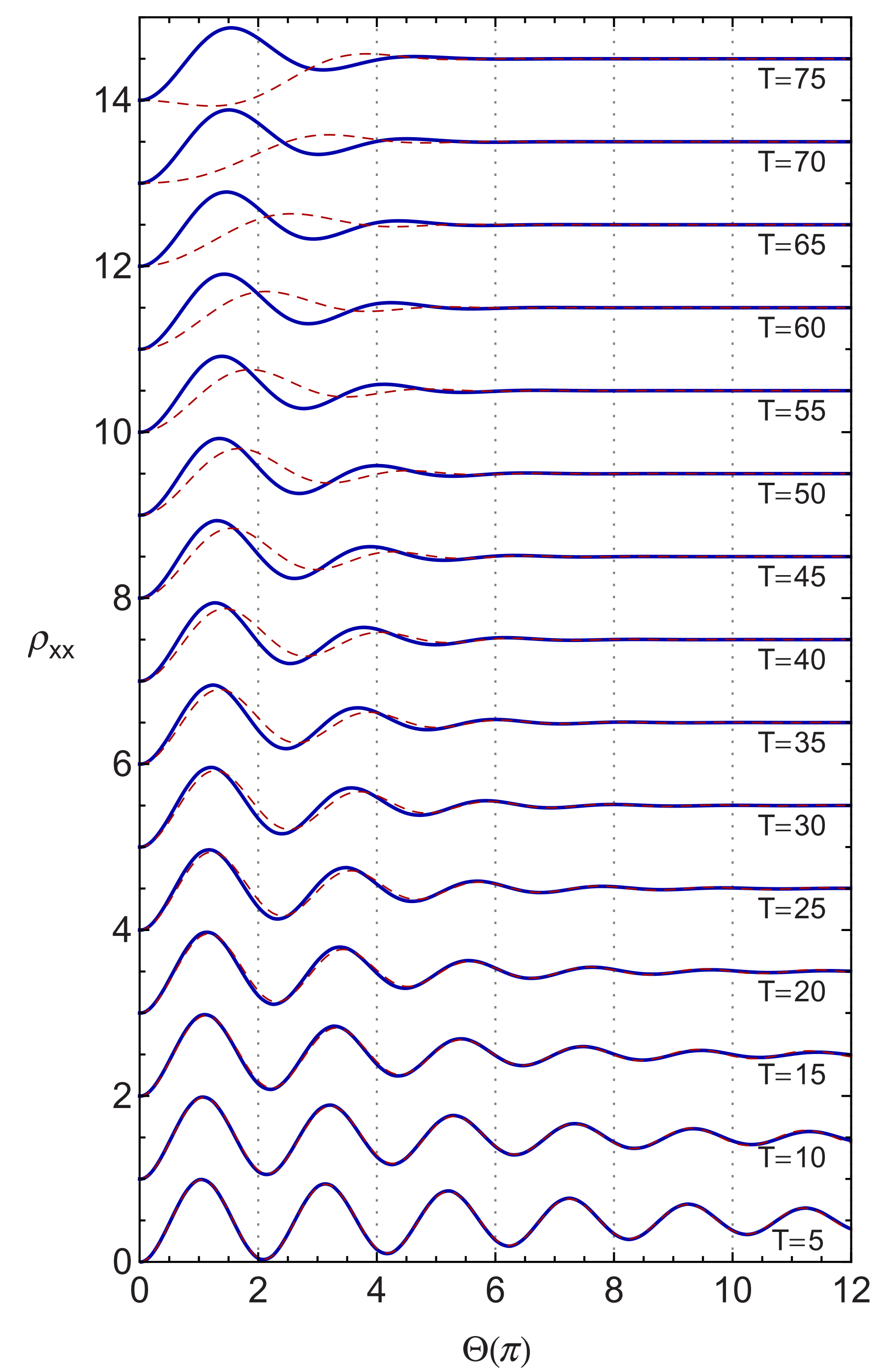
- Excellent agreement suggests exciton-phonon interactions are indeed the dominant source of decoherence in these experiments



Theory: Nazir, Phys. Rev. B 78, 153309 (2008)
Experiments: Ramsay, Gopal, Gauger, Nazir, Lovett, Fox, Skolnick, Phys. Rev. Lett. 104, 017402 (2010)
Ramsay, Godden, Boyle, Gauger, Nazir, Lovett, Fox, Skolnick, Phys. Rev. Lett. 105, 177402 (2010)

Limitations? Beyond weak-coupling theory

- Weak-coupling theory captures only single phonon processes, might be a problem as temperature (or system-bath coupling increases)
- In fact, it can even become **unphysical** in some regimes
- We can derive a 2nd order master equation valid beyond the limitations of the weak exciton-phonon coupling approximation by employing a **polaron transformation**
- Polaron theory (solid curves) and weak-coupling theory (dashed curves)
- More details coming up



McCutcheon and Nazir, New J. Phys. 12, 113042 (2010)

Motivation - optimised perturbative approaches

- Assuming a system-bath description, master equation techniques are a useful tool with which to analyse these systems (and many others).
  - Reduced description in terms of system degrees of freedom only - intuitive, efficient and relatively straightforward to work with

- Yet, a practical master equation nearly always requires some kind of approximation

  $H = H_0 + H_I$ H_0 - solution known, treat to all orders
  H_I - treat as a small perturbation

  - Hence, they are often valid only for rather restrictive parameter regimes.
  - However, we would like to explore dynamics over a wide range of parameters

- **Question: What is the 'best' we can do with a perturbative, second-order master equation?**
  - i.e. how do we engineer our interaction term so that it remains small over a large regime of parameters.

Other systems - Energy transfer

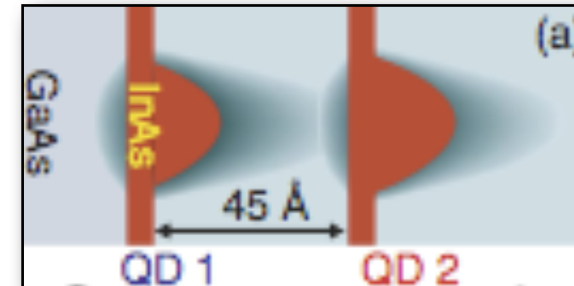
- Energy transfer is ubiquitous - under what **conditions** do we expect quantum coherent or incoherent transfer? Need a **consistent treatment**

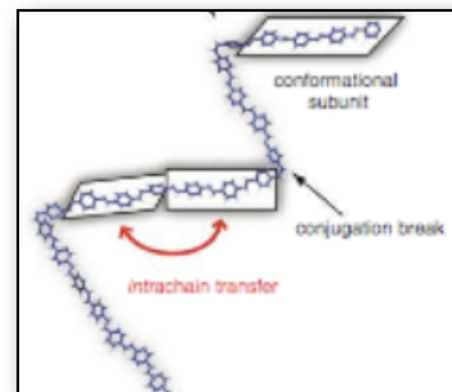
- Recent experiments interpreted in terms of quantum coherent energy transfer - e.g. in some light harvesting complexes coherence is observed at **room temperature**, and can last for hundreds of fs

- These systems can couple strongly to their surroundings (and at high temp.) - how can coherence survive? How do we deal **efficiently** with strong bath coupling?

- Are system-bath models sufficient?

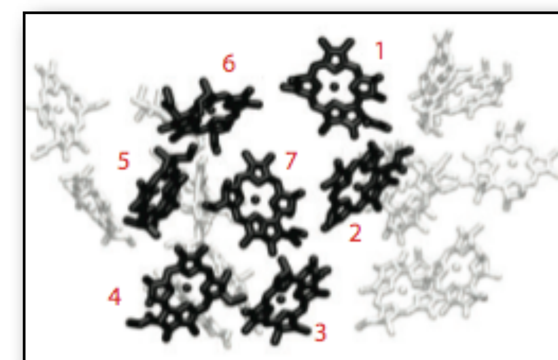
QDs: B. D. Gerardot et al., Phys. Rev. Lett. 95, 137403 (2005)

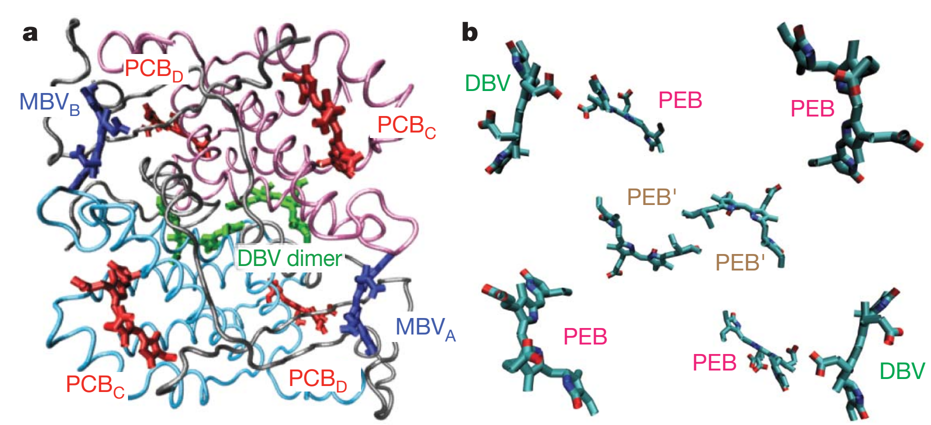




Conjugated Polymers: E. Collini and G. D. Scholes, Science 323, 369 (2009)

FMO: Fig. courtesy of Y.-C. Cheng and G. R. Fleming, Annu. Rev. Phys. Chem. 60, 241 (2009), G. S. Engel et al., Nature 446, 782 (2007); G. Panitchayangkoon et al., PNAS 107, 12766 (2010)



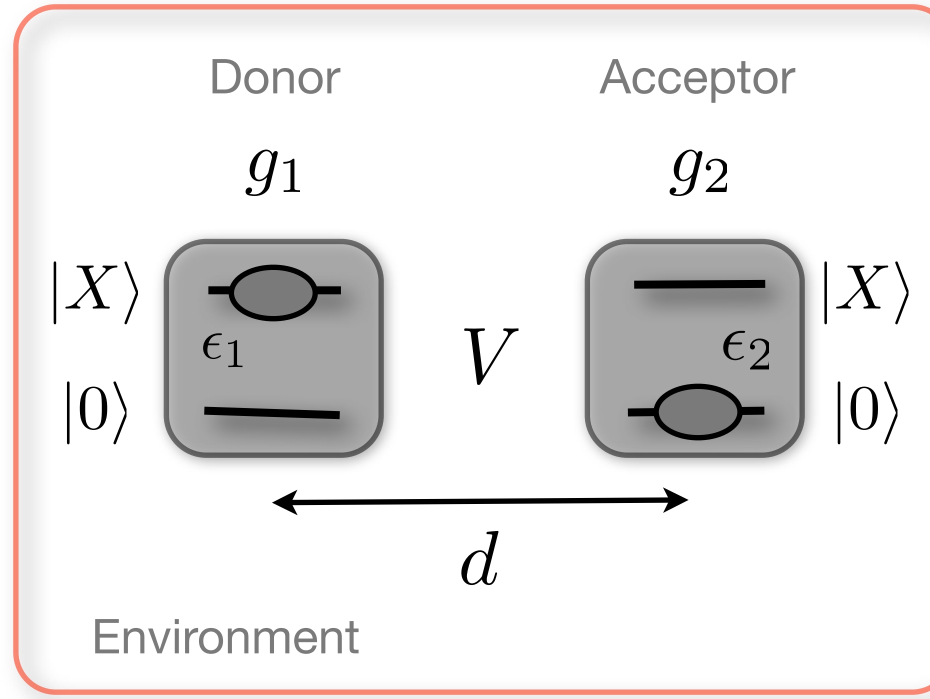


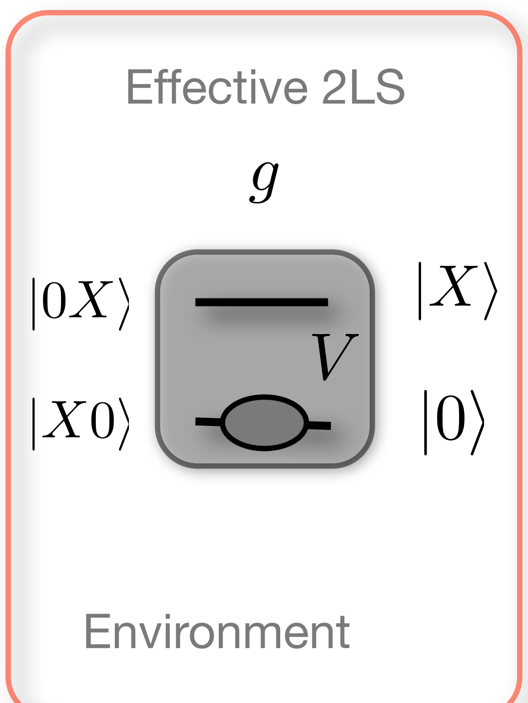
PC645/PE545: E. Collini et al., Nature 463, 644 (2010)

Dimer Model: Mapping to spin-boson

- Electronically coupled dimer (donor-acceptor pair) in a bosonic environment

$$H = \epsilon_1 |X\rangle_1\langle X| + \epsilon_2 |X\rangle_2\langle X| + V(|0X\rangle\langle X0| + |X0\rangle\langle 0X|) + \sum_k \omega_k b_k^\dagger b_k$$
$$+|X\rangle_1\langle X| \sum_k (g_{k,1} b_k^\dagger + g_{k,1}^* b_k) + |X\rangle_2\langle X| \sum_k (g_{k,2} b_k^\dagger + g_{k,}^* b_k)$$





- Working in single-excitation subspace reduces our problem to that of a **driven two-level system** in a bosonic bath (spin-boson model)

$$\boxed{H = \frac{\epsilon}{2}\sigma_z + V\sigma_x + \sum_{\mathbf{k}} \omega_{\mathbf{k}} b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + \sigma_z \sum_{\mathbf{k}} (g_{\mathbf{k}} b_{\mathbf{k}}^\dagger + g_{\mathbf{k}}^* b_{\mathbf{k}})}$$

$$\sigma_z = |X0\rangle\langle X0| - |0X\rangle\langle 0X| \qquad \epsilon = \epsilon_1 - \epsilon_2$$
$$\sigma_x = |X0\rangle\langle 0X| + |0X\rangle\langle X0|$$

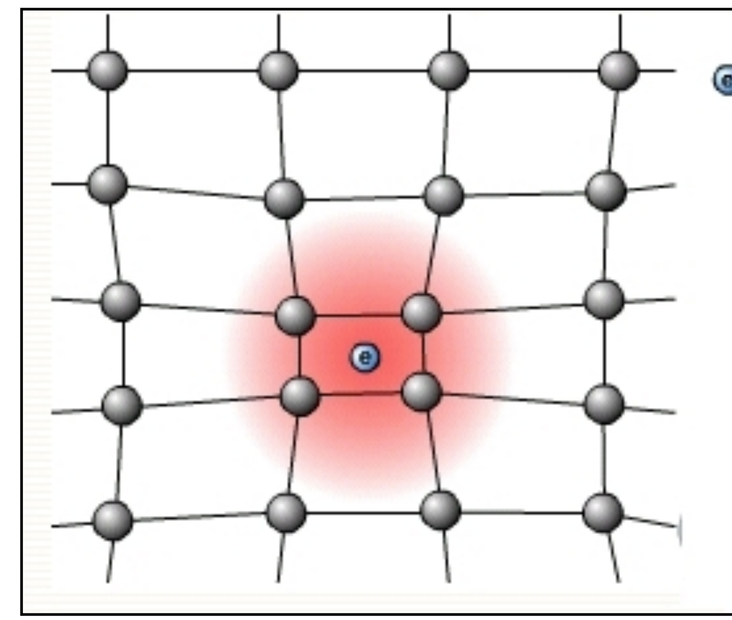
Exactly solvable limits

$$H = \frac{\epsilon}{2}\sigma_z + V\sigma_x + \sum_{\mathbf{k}} \omega_{\mathbf{k}} b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + \sigma_z \sum_{\mathbf{k}} (g_{\mathbf{k}} b_{\mathbf{k}}^\dagger + g_{\mathbf{k}}^* b_{\mathbf{k}})$$

- (I) Trivially, when system-bath coupling goes to zero
  - Undamped oscillations at a frequency $\eta = \sqrt{\epsilon^2 + 4V^2}$
- (II) Consider the case when electronic coupling $V = 0$

$$\begin{aligned} H = &|X0\rangle\langle X0| \left(\epsilon/2 + \sum_{\mathbf{k}} \omega_{\mathbf{k}} (b_{\mathbf{k}}^\dagger + g_{\mathbf{k}}^*/\omega_{\mathbf{k}})(b_{\mathbf{k}} + g_{\mathbf{k}}/\omega_{\mathbf{k}}) \right) \\ &+ |0X\rangle\langle 0X| \left(-\epsilon/2 + \sum_{\mathbf{k}} \omega_{\mathbf{k}} (b_{\mathbf{k}}^\dagger - g_{\mathbf{k}}^*/\omega_{\mathbf{k}})(b_{\mathbf{k}} - g_{\mathbf{k}}/\omega_{\mathbf{k}}) \right) \\ &- \sum_{\mathbf{k}} |g_{\mathbf{k}}|^2/\omega_{\mathbf{k}} \end{aligned}$$

- So, when electronic coupling is zero, excitation state dependent displacement **(polaron transformation)** will remove system-bath coupling



$$H_P = e^S H e^{-S}$$

$$S = \sigma_z \sum_{\mathbf{k}} (\alpha_{\mathbf{k}} b_{\mathbf{k}}^\dagger - \alpha_{\mathbf{k}}^* b_{\mathbf{k}})$$

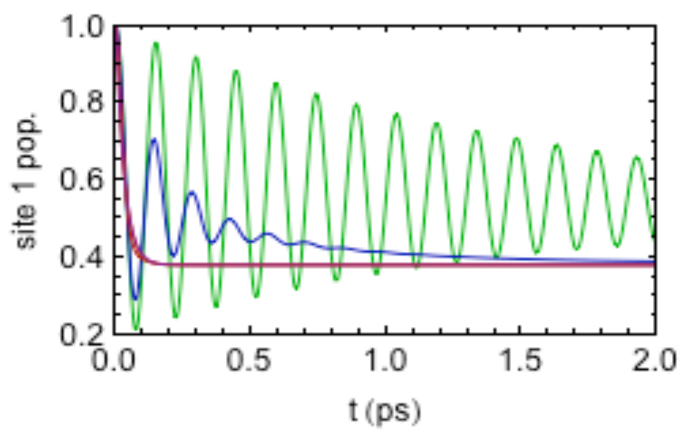
$$\alpha_{\mathbf{k}} = g_{\mathbf{k}}/\omega_{\mathbf{k}}$$

Common approximations

$$H = \frac{\epsilon}{2}\sigma_z + V\sigma_x + \sum_{\mathbf{k}} \omega_{\mathbf{k}} b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + \sigma_z \sum_{\mathbf{k}} (g_{\mathbf{k}} b_{\mathbf{k}}^\dagger + g_{\mathbf{k}}^* b_{\mathbf{k}})$$

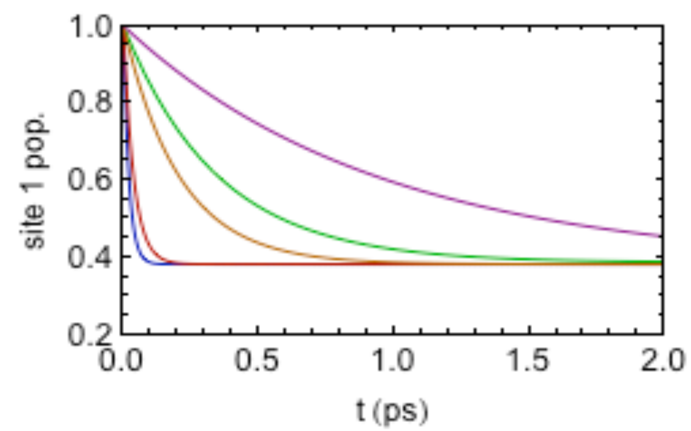
- We can approximate the dynamics around these two solvable limits:

Redfield



$$H_I = \sigma_z \sum_{\mathbf{k}} (g_{\mathbf{k}} b_{\mathbf{k}}^\dagger + g_{\mathbf{k}}^* b_{\mathbf{k}})$$

Foerster



$$H_I = V\sigma_x$$

T = 300 K
γ = 53 cm^{-1}
R = 1 cm^{-1}
R = 10 cm^{-1}
R = 10^2 cm^{-1}
R = 5x10^2 cm^{-1}
R = 1x10^3 cm^{-1}

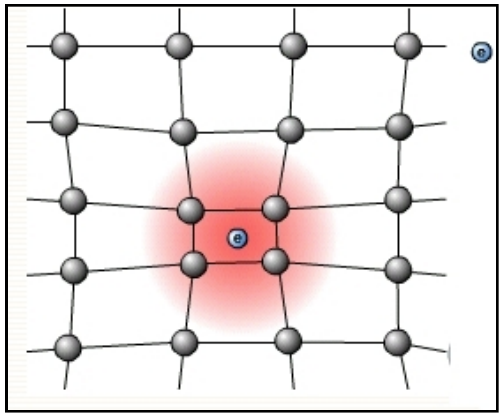
- Redfield master equation captures only single phonon processes, only valid at weak system-bath coupling (small reorganisation energy) and low temperature - cannot properly capture incoherent dynamics

- Foerster theory captures only incoherent processes, not valid at weak system-bath coupling

Polaron transformation

- Let's look at the full Hamiltonian after a polaron transformation

$$H_P = e^S H e^{-S} = \frac{\epsilon}{2}\sigma_z + V_R\sigma_x + H_B + V(\sigma_+(B_+ - B) + \sigma_-(B_- - B))$$

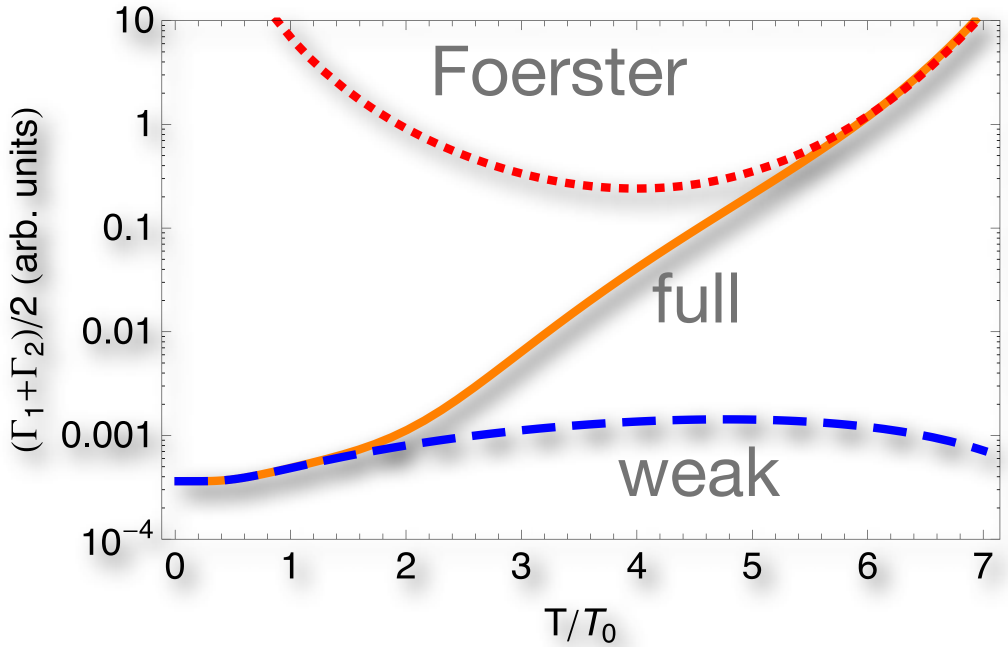


- We have now identified a new interaction Hamiltonian

$$H_I = V(\sigma_+(B_+ - B) + \sigma_-(B_- - B)) \qquad B_\pm = \mathrm{e}^{\pm\sum_{\mathbf{k}}\alpha_{\mathbf{k}}(b_{\mathbf{k}}^\dagger - b_{\mathbf{k}})}$$

- and a renormalised energy transfer strength $V_R = VB = Ve^{-\int_0^\infty d\omega \frac{J(\omega)}{\omega}\coth\omega/2k_BT}$

- For super-Ohmic environments, polaron master equation theory can interpolate between the weak-coupling and Foerster limits



- Nazir, Phys. Rev. Lett. 103, 146404 (2009), Jang et al., J. Chem. Phys. 129, 101104 (2008), McCutcheon and Nazir, Phys. Rev. B 83, 165101 (2011)
- Kolli, Nazir, Olaya-Castro, J. Chem. Phys. 135, 154112 (2011), Jang, J. Chem. Phys. 135, 034105 (2011)

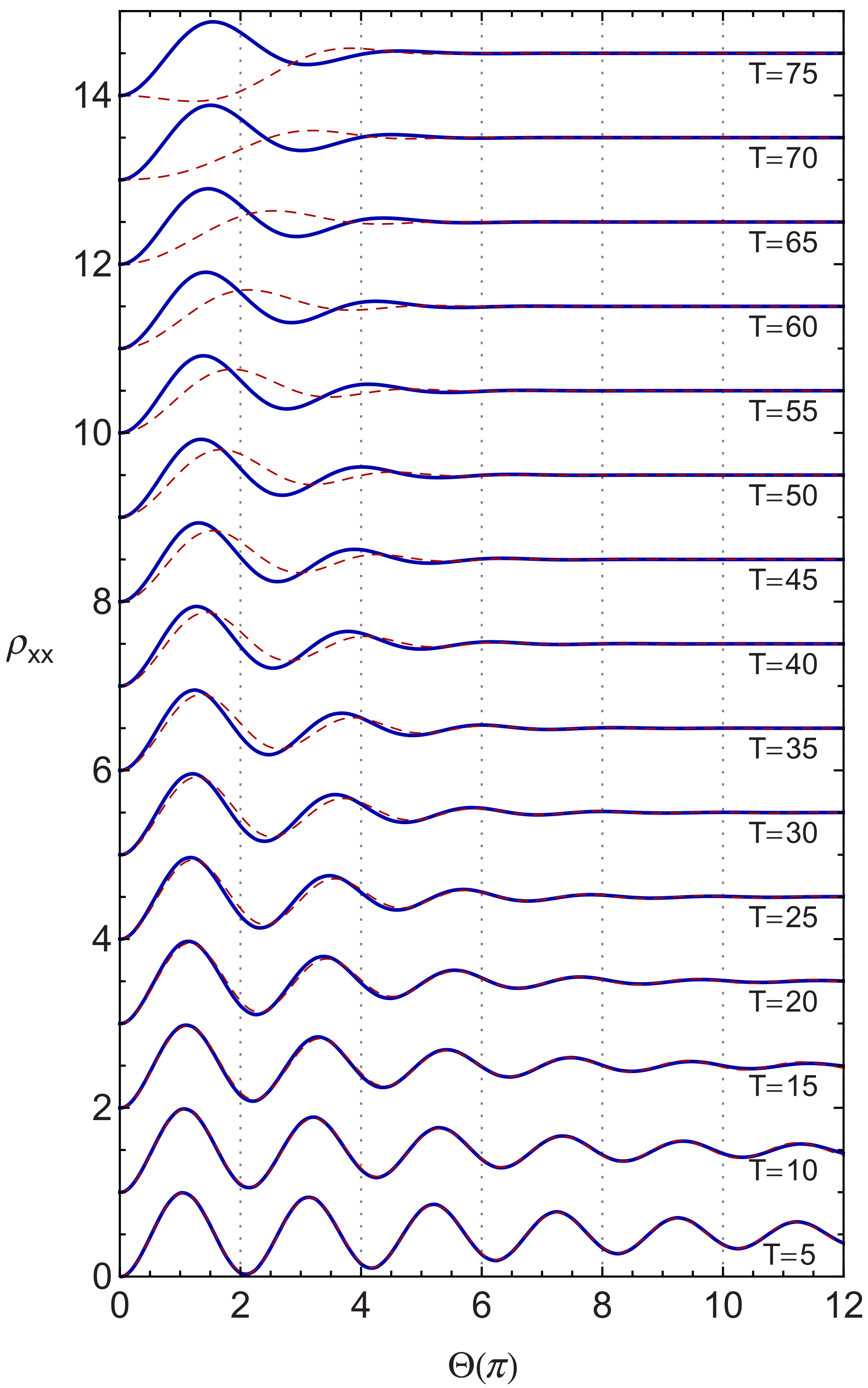
Back to the driven QD

- Exciton population as a function of pulse area, for varying temperatures

- 2nd order master equation

$$\dot{\rho}(t) = -i[H_S, \rho(t)] + \mathcal{L}_P(t)(\rho(t))$$

- Polaron theory (solid curves) and weak-coupling theory (dashed curves)



McCutcheon and Nazir, New J. Phys. 12, 113042 (2010)

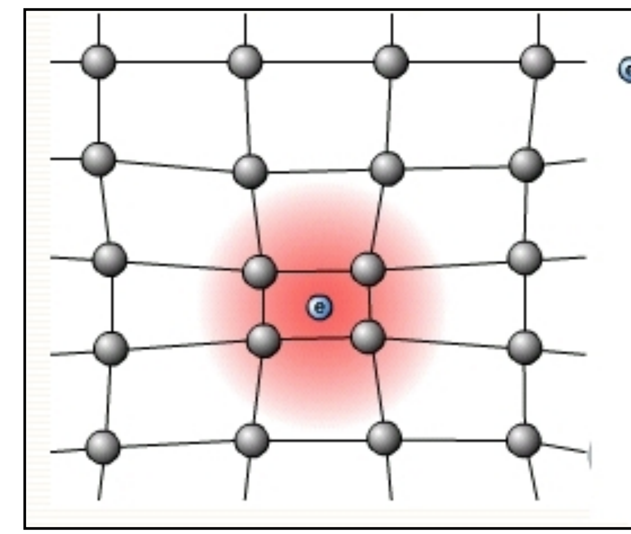
Polaron transformation - limitations

- But, the theory has some serious limitations
  - (I) For Ohmic environments, there is an infra-red divergence

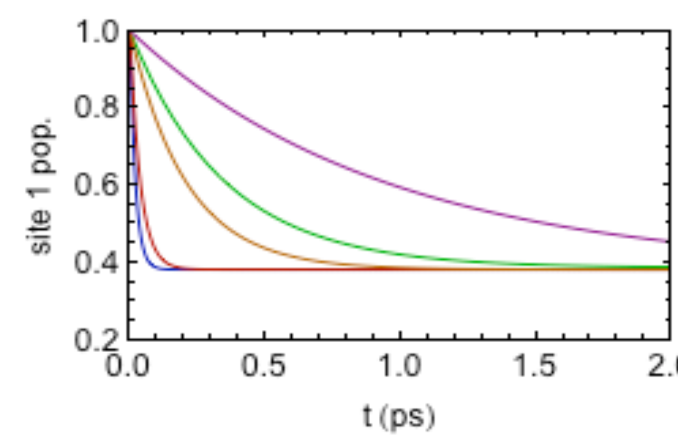
$$V_R = VB = Ve^{-\int_0^\infty d\omega \frac{J(\omega)}{\omega} \coth \omega/2k_B T} \to 0$$

$$H_P \to \frac{\epsilon}{2}\sigma_z + H_B + V(\sigma_+ B_+ + \sigma_- B)$$

  - Master equation no longer captures coherent energy transfer dynamics (essentially reduces to Foerster theory)
  - (II) For large V, similar to or greater than cutoff frequency in the spectral density, the theory predicts too much damping, even for super-Ohmic spectral densities
- Both problems related to the same physics, low frequency (sluggish) bath modes should not be fully displaced

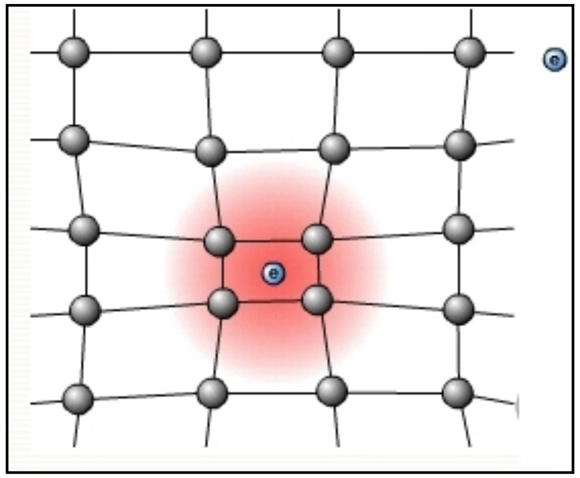


Polaron/Foerster



$J(\omega) \propto \omega$

Variational theory



- Let's again apply an excitation state dependent displacement to the bath, but now with a **tuneable magnitude**

$$H_V = e^{S(f_{\mathbf{k}})} H e^{-S(f_{\mathbf{k}})} \qquad S(f_{\mathbf{k}}) = \sigma_z \sum_{\mathbf{k}} (f_{\mathbf{k}}/\omega_{\mathbf{k}})(b_{\mathbf{k}}^\dagger - b_{\mathbf{k}})$$

$f_{\mathbf{k}} \to 0$ no transformation, weak-coupling theory

$f_{\mathbf{k}} \to g_{\mathbf{k}}$ polaron transformation

- In general, the transformed Hamiltonian contains both weak-coupling (Redfield) and polaron-type (Foerster) terms

- We **optimise** the transformation by minimising an upper bound on the system free energy (Silbey and Harris, JCP 80, 2615 (1984))

$$\boxed{f_{\mathbf{k}} = F(\epsilon, V, \omega_{\mathbf{k}}, T) g_{\mathbf{k}}}$$

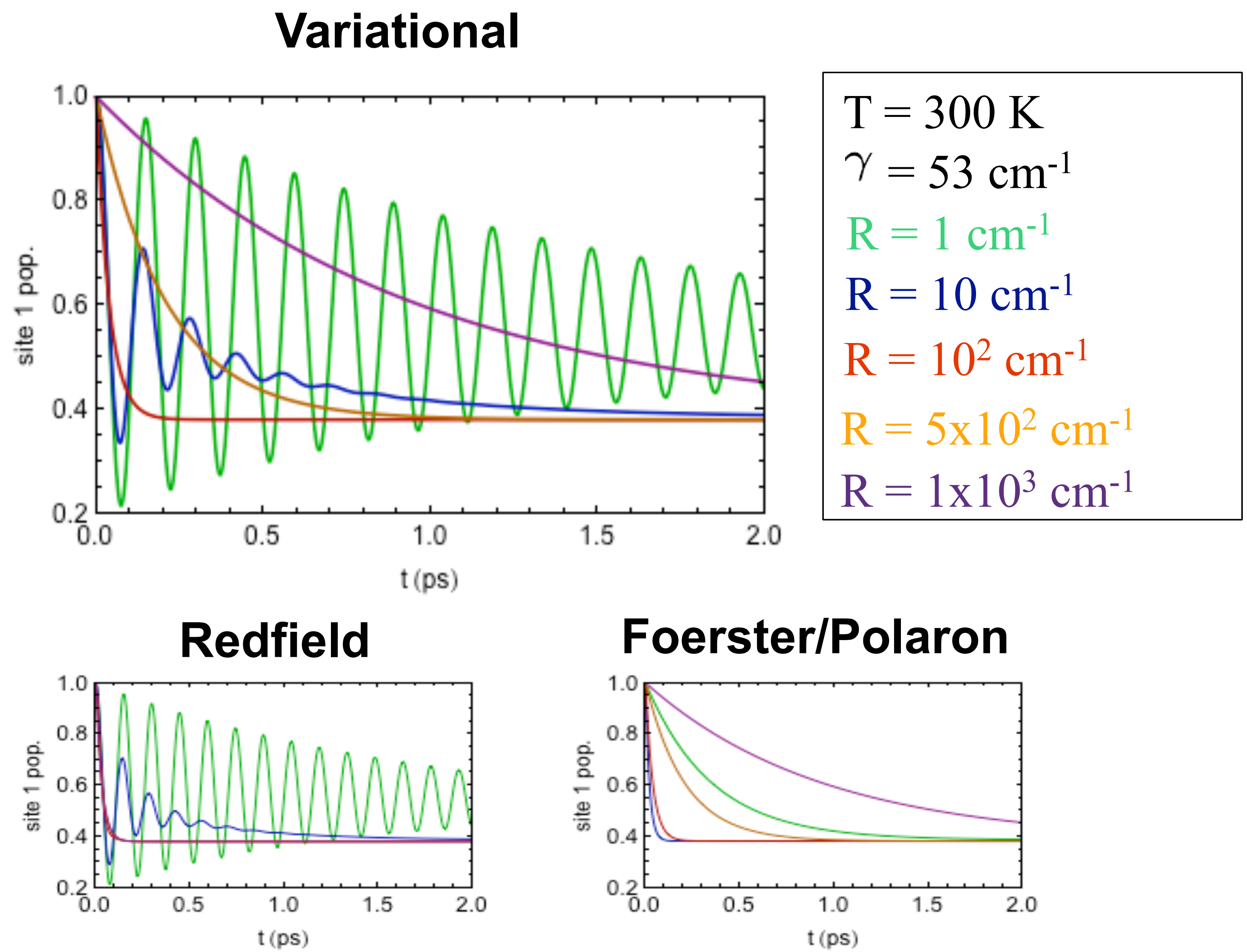
$V/\omega_{\mathbf{k}}$ small $f_{\mathbf{k}} \to g_{\mathbf{k}}$ full displacement

$V/\omega_{\mathbf{k}}$ large $f_{\mathbf{k}} \to 0$ no displacement

Variational dynamics - Ohmic

$$\dot{\rho}(t) = -i[H_S, \rho(t)] + \mathcal{L}_W(t)(\rho(t)) + \mathcal{L}_V(t)(\rho(t)) + \mathcal{L}_P(t)(\rho(t))$$

- Correctly captures both the Redfield and Foerster limits and interpolates between
- Comparison with numerically exact calculations shows quantitative agreement in many regimes



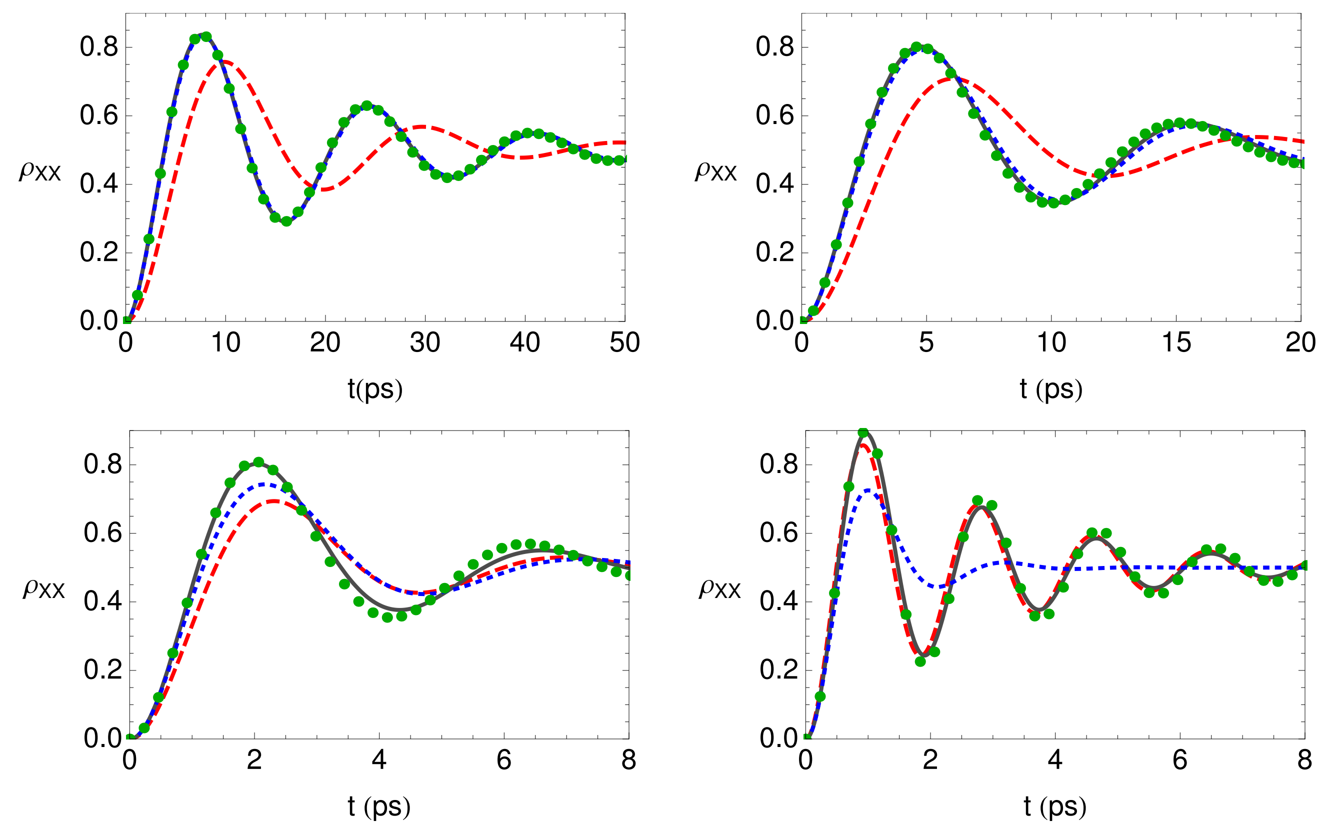
McCutcheon and Nazir, J. Chem. Phys. 135, 114501 (2011)

Variational dynamics - super-Ohmic

- super-Ohmic bath, increasing Rabi frequency (or electronic coupling strength)

- Comparison with (numerically exact) path integral calculations shows that variationally-optimised transformation leads to a master equation valid over a wide range of parameters

- Weak coupling (red dashed)
- polaron (blue dotted)
- variational (grey solid)
- path integral (green points)



$$J(\omega) \propto \omega^3$$

McCutcheon, Dattani, Gauger, Lovett, and Nazir, Phys. Rev. B 84, 081305(R) (2011)

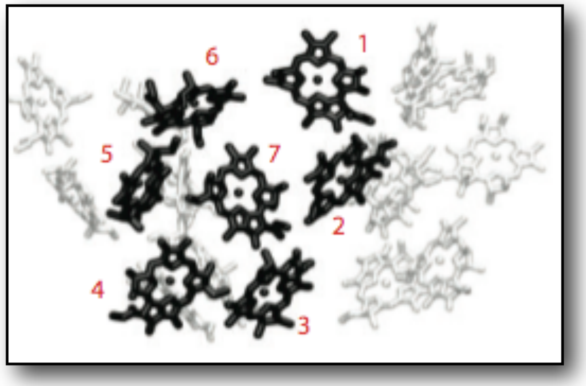
Multi-site generalisation

$$H = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{n\neq m} V_{nm}|n\rangle\langle m| + \sum_{n,k}\omega_{n,k} b^\dagger_{n,k} b_{n,k} + \sum_{n,k}|n\rangle\langle n|(g_{n,k}b^\dagger_{n,k} + g^*_{n,k}b_{n,k})$$

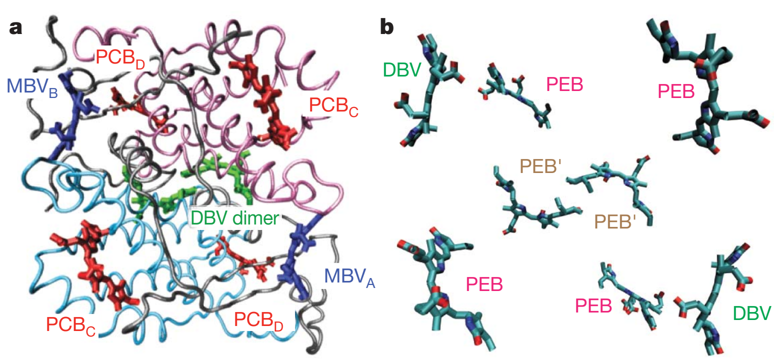
- Generalised unitary transformation: $H_V = e^S H e^{-S}$

$$e^{\pm S} = \exp\left[\pm\sum_{n,k}|n\rangle\langle n|(\alpha_{n,k}b^\dagger_{n,k} - \alpha^*_{n,k}b_{n,k})\right]$$

- As before, we **optimise** the transformation by minimising an upper bound on the system free energy
- Then derive a time-local master equation



FMO: Fig. courtesy of Y.-C. Cheng and G. R. Fleming



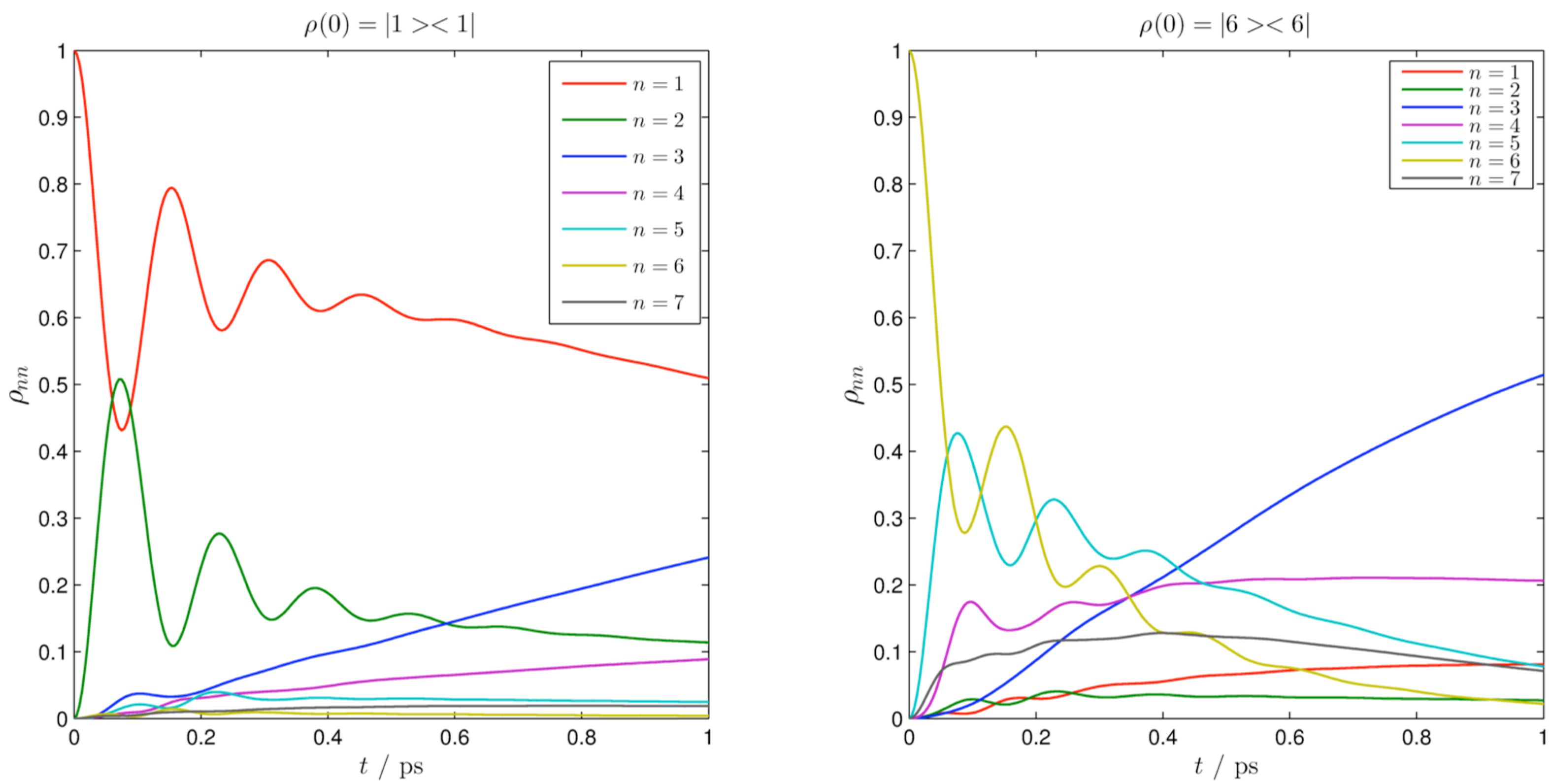
PC645/PE545: E. Collini et al.

$$\frac{\partial\rho}{\partial t} = -i[H_S,\rho] - \tfrac{1}{2}\sum_{ij}\sum_\omega \gamma_{ij}(\omega,t)[A_i, A_{j,\omega}\rho - \rho A^\dagger_{j,\omega}] - i\sum_{ij}\sum_\omega S_{ij}(\omega,t)[A_i, A_{j,\omega}\rho + \rho A^\dagger_{j,\omega}]$$

- Essentially as easy to apply as Redfield theory

Pollock, McCutcheon, Lovett, Gauger, and Nazir, arxiv:1212.5713

Multi-site generalisation: example results



Variational: 7-site FMO Hamiltonian, Lorentz-Drude spectral density, T = 77K

$$J(\omega) = \frac{2R\gamma\omega}{\pi(\omega^2 + \gamma^2)}$$

Pollock, McCutcheon, Lovett, Gauger, and Nazir, arxiv:1212.5713

Hierarchy: 7-site FMO Hamiltonian, Lorentz-Drude spectral density, T = 77K

Ishizaki and Fleming, PNAS 106, 17255 (2009)

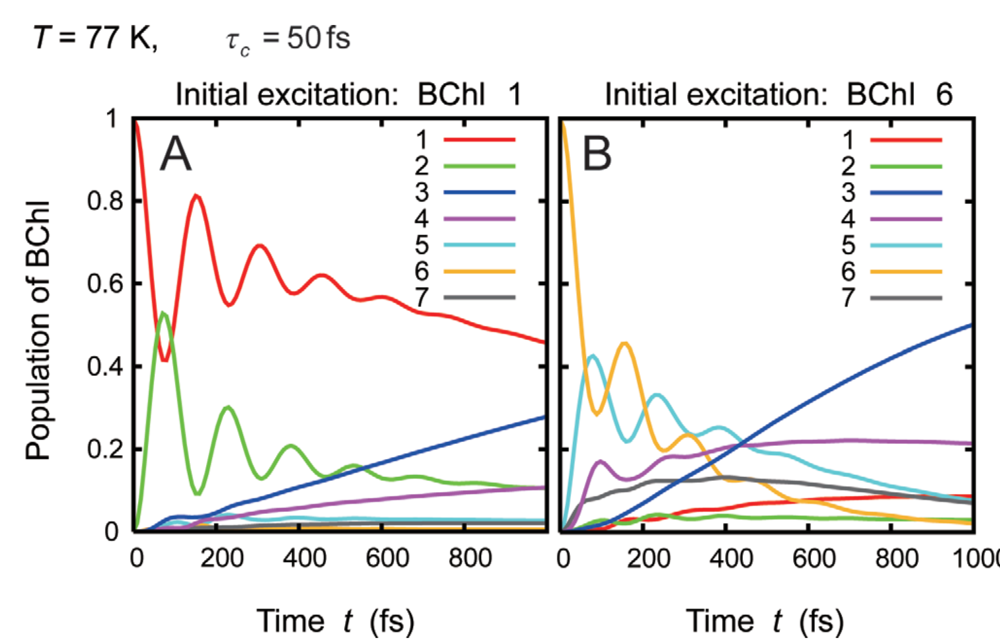
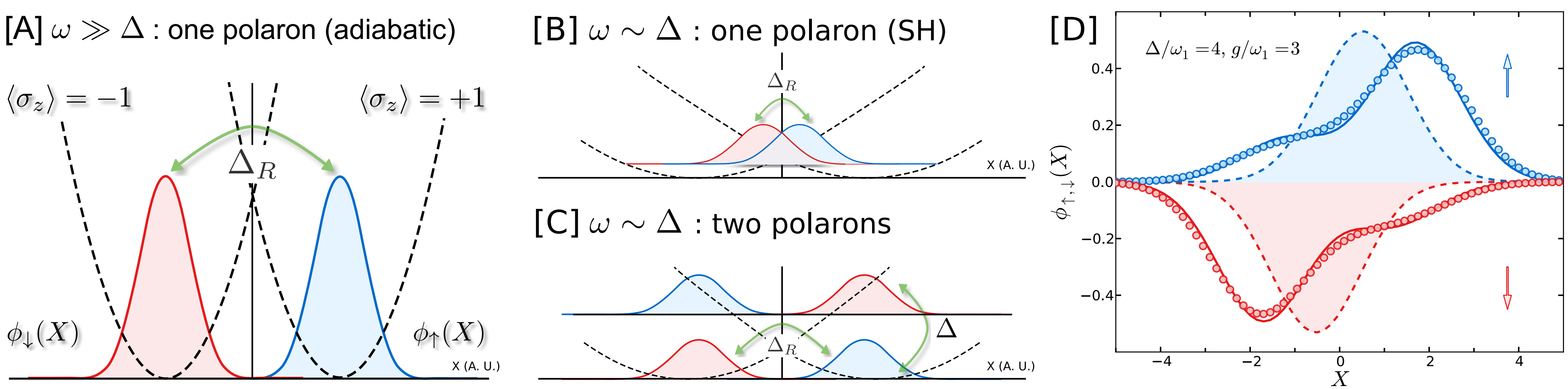


Fig. 2. Time evolution of the population of each BChl in the FMO complex. Calculations were done for cryogenic temperature, $T = 77$ K. The reorganization energy and the phonon relaxation time are set to be $\lambda_j = 35\,\mathrm{cm}^{-1}$ and $\tau_c = \gamma_j^{-1} = 50$ fs, respectively.

Beyond (variational) polaron approach



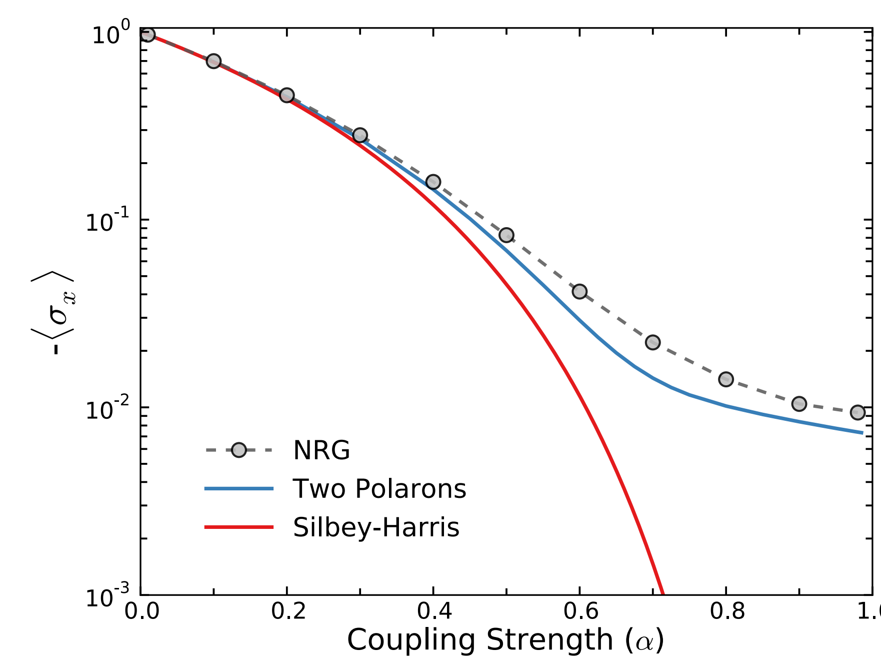
- Spin-boson model

$$H = \frac{\Delta}{2}\sigma_x + \sum_k \omega_k b_k^\dagger b_k - \frac{\sigma_z}{2}\sum_k g_k(b_k^\dagger + b_k)$$

- Allow for coherent state superposition in the ground state

$$|GS\rangle = |\uparrow\rangle\left[|+f_k^{\mathrm{pol.}}\rangle + p|+f_k^{\mathrm{anti.}}\rangle\right] - |\downarrow\rangle\left[|-f_k^{\mathrm{pol.}}\rangle + p|-f_k^{\mathrm{anti.}}\rangle\right]$$

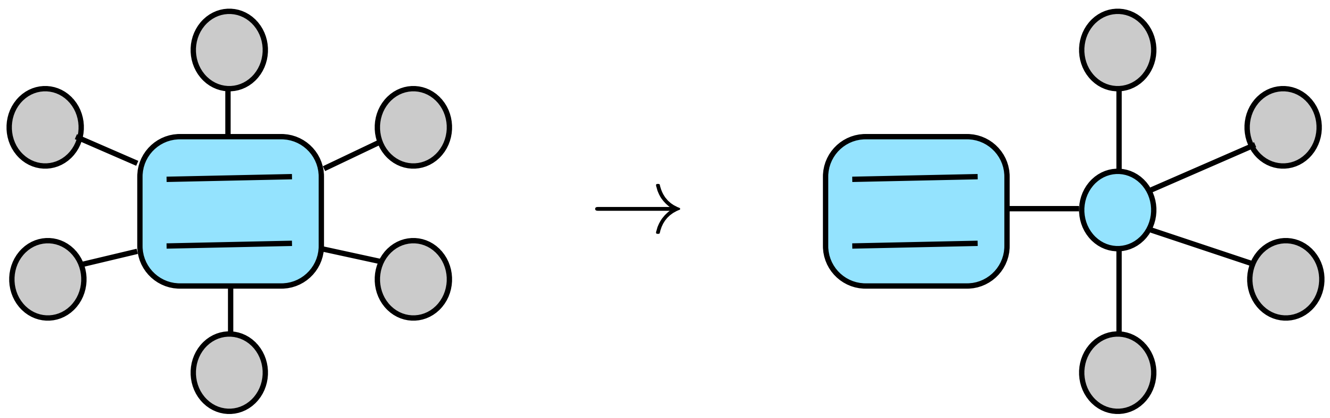
- Gives a lower ground state energy than the variational polaron state

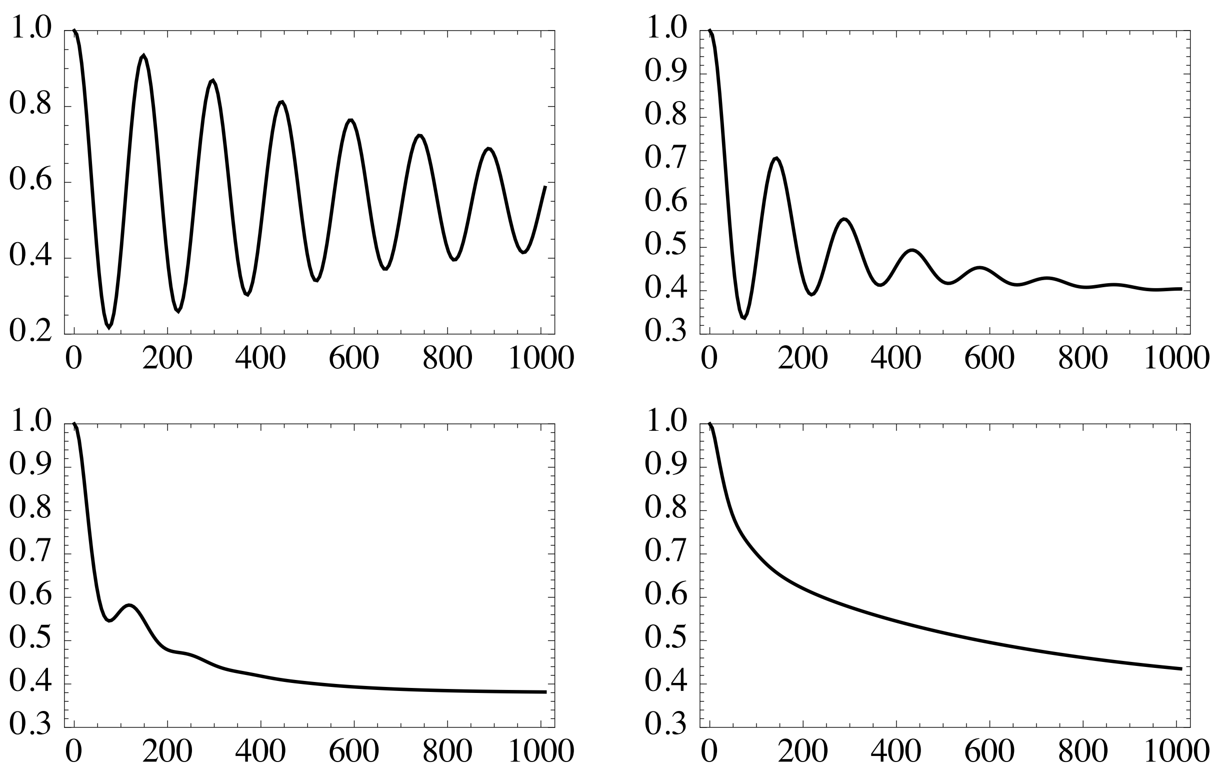


$$|\pm f_k\rangle = e^{\pm\sum_k f_k(b_k^\dagger - b_k)}|0\rangle$$

Bera, Florens, Baranger, Roch, Nazir, and Chin, arxiv:1301.7430

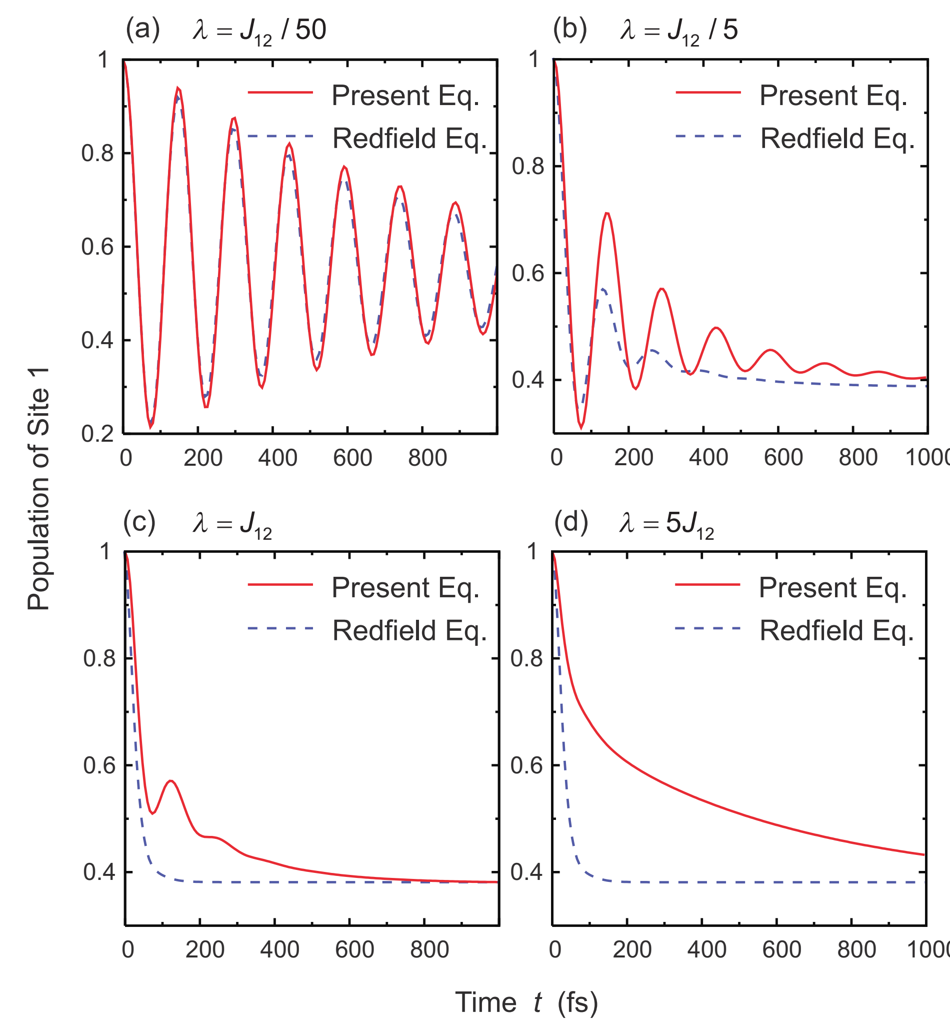
Reaction coordinate mapping





Thanks to Jake Iles-Smith

Hierarchy: Lorentz-Drude spectral density, T = 300K, varying coupling strength

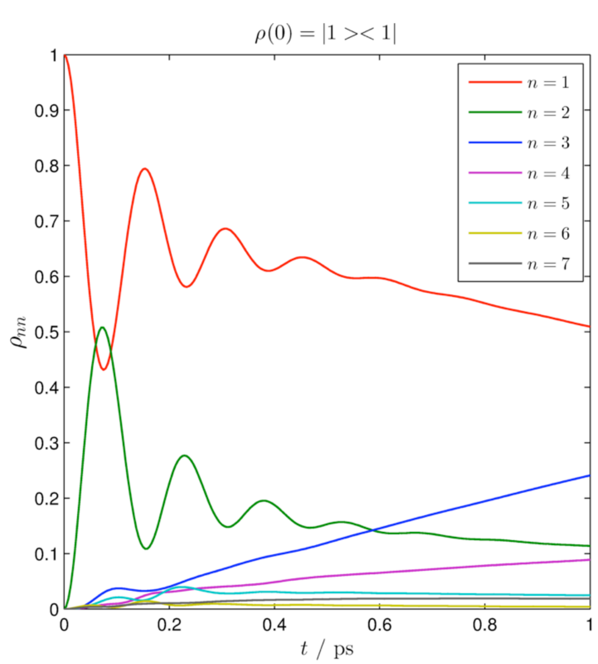


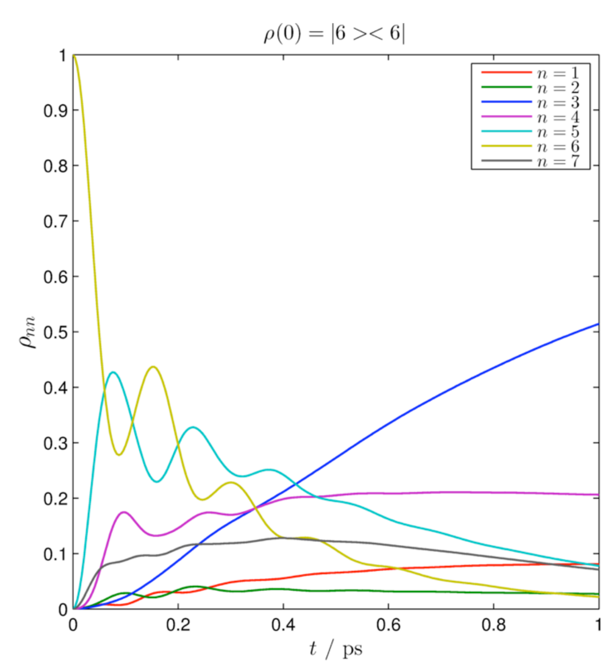
Ishizaki and Fleming, J. Chem. Phys. 130, 234111 (2009)

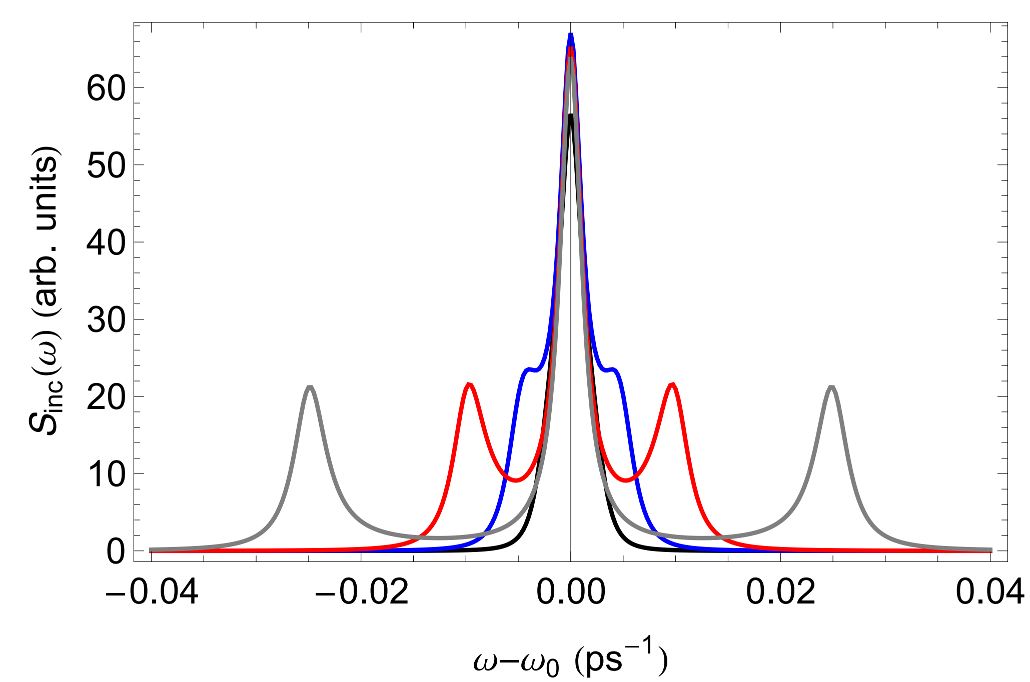
Summary and further work

- **Weak-coupling** master equation - experimental agreement: clear evidence that **exciton-phonon interactions** dominate exciton dephasing dynamics in self-assembled semiconductor QDs

- I also presented a **versatile variational master equation technique** - allows one to explore a **range** of system-bath coupling strengths, temperatures, and environmental spectral densities within a single formalism.







Phonon effects on emitted photon properties

McCutcheon and Nazir, arxiv:1208.4620

Acknowledgements

- Many thanks to:
  - Dara McCutcheon (Buenos-Aires)
  - Felix Pollock (Oxford)
  - Brendon Lovett (Heriot-Watt)
  - Erik Gauger (Oxford)
  - Ales Chin (Cambridge)
  - Serge Florens (Grenoble)
  - Harold Baranger (Duke)
  - Andrew Ramsay (Hitachi)
  - Maurice Skolnick (Sheffield)

- Funding

Imperial College London

Thanks very much for your attention!