Modelling weak and strong matter-light coupling with organic molecules

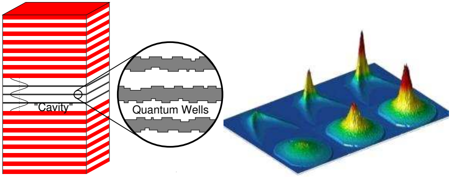
Jonathan Keeling

University of St Andrews 1413-2013

Telluride, July 2015

Motivation: polariton condensates

- CdTe Polariton Condensate
  $T \sim 20$K. [Kasprzak *et al.* Nature, '06]



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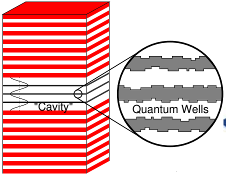

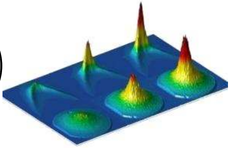

Models:

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  - Statistical mechanics
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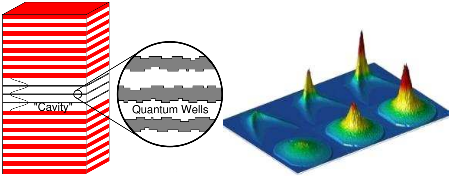

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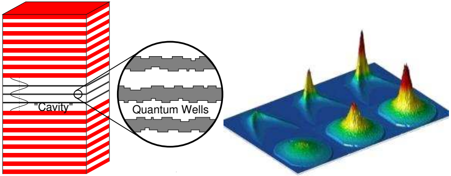

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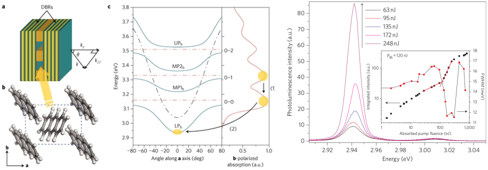

[Kena Cohen and Forrest, Nat. Photon '10]

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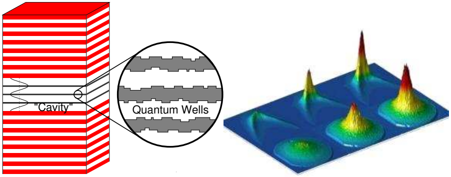

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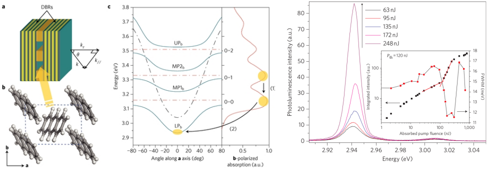

Q1. Vibrational replicas?

Q2. Relevance of disorder?

Q3. Lasing vs condensation?

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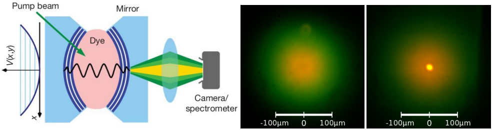

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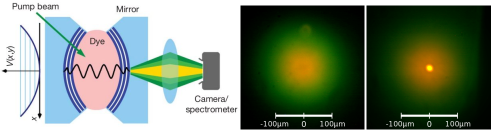

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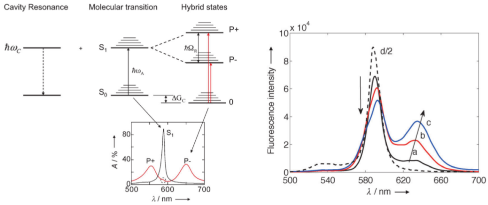
Q1. Relation to dye laser?

Q2. Relation to polaritons?

Q3. Thermalisation breakdown?

Motivation: vacuum-state strong coupling

- Linear response (no pump, no condensate): effects of matter-light coupling alone.



[Canaguier-Durand *et al.* Angew. Chem. ’13]

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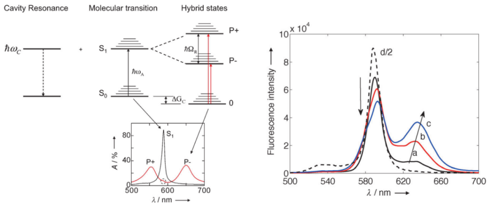

[Canaguier-Durand *et al.* Angew. Chem. '13]

Q1. Can **ultra-strong** coupling to light change:
- charge distribution?
- vibrational configuration?
- molecular orientation?
- crystal structure?

Q2. Are changes collective ($\sqrt{N}$ factor) or not?

Q3. If not, what is data showing?

1. Modelling photon BEC & organic polaritons

2. (Ultra-)strong coupling, weak pumping
   - Ultra strong coupling & reconfiguration
   - Vibrational sidebands in spectrum

3. Driven dissipative systems
   - Limitations of rate equation model
   - Toy problem – two bosonic modes

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What kinds of modelling

- Bottom up
  - DFT (or quantum chemistry)
    $\rightarrow$ electronic structure
  - Time-dependent DFT /MD
    $\rightarrow$ vibrational spectra
  - FDTD/transfer-matrix
    $\rightarrow$ cavity modes
- Tractable microscopic toy models
- Top-down
  - Equilibrium stat. mech.
  - (complex/stochastic/. . .)GPE (+ Boltzmann)
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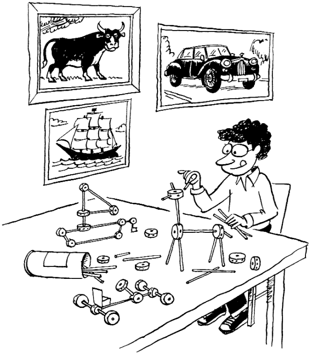

Illustration by Dick Codor.

[From Auerbach, Interacting electrons and quantum magnetism]

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Toy models

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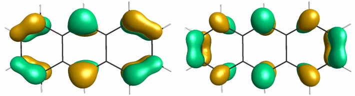

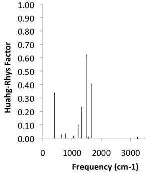

2. Simplified archetypal model: Dicke-Holstein

- *Each* molecule: two DoF
  - Electronic state: 2LS
  - Vibrational state: harmonic oscillator

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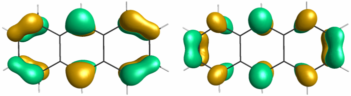

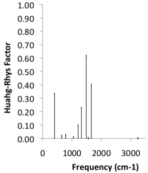

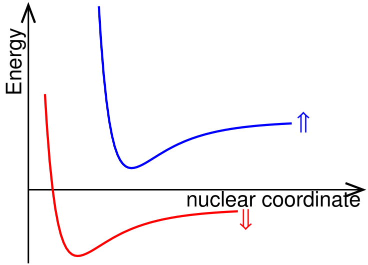

2. Focus on low-energy effective theory
   - Two-level system, HOMO/LUMO
   - Single DoF PES

See also [Galego, Garcia-Vidal, Feist. arXiv:1506:03331]

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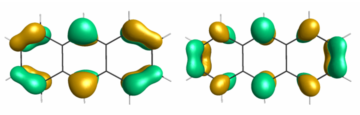

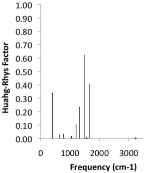

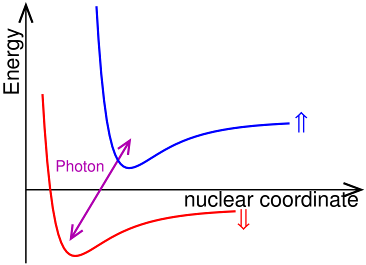

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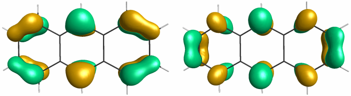

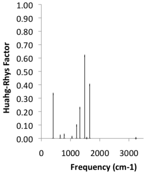

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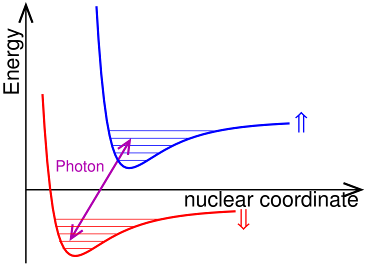

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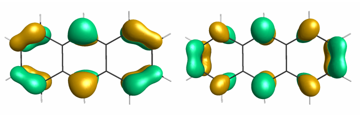

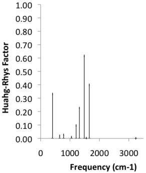

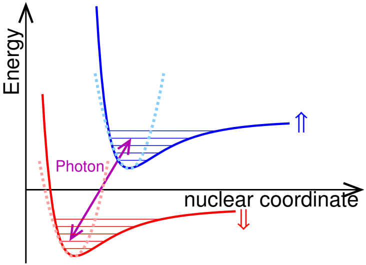

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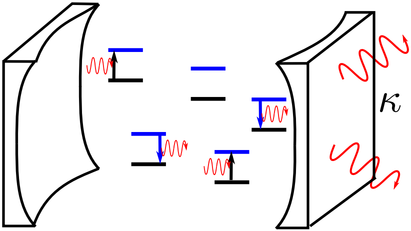

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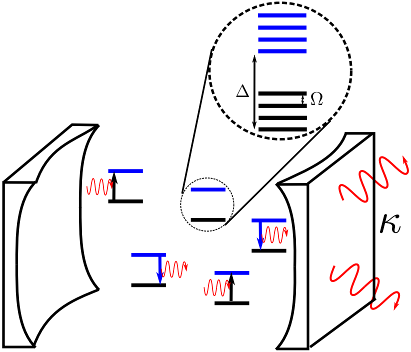

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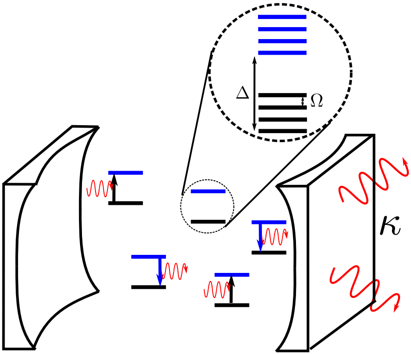

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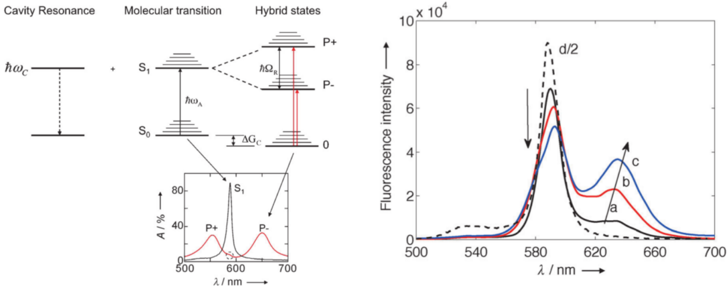

[Canaguier-Durand *et al.* Angew. Chem. '13]

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- Temperature dependent

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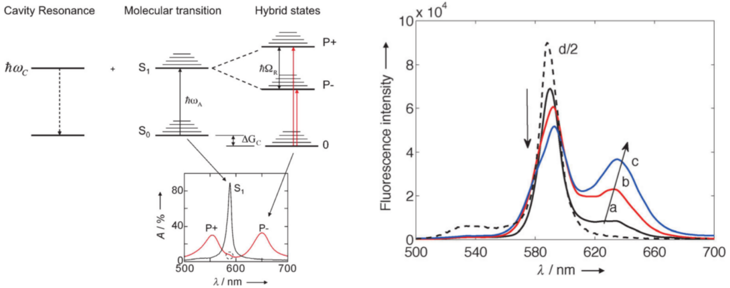

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Disordered molecules — spectrum

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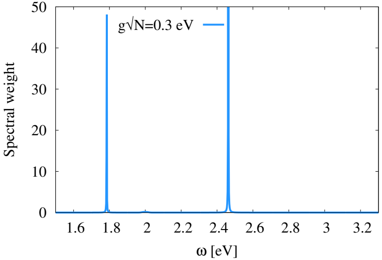

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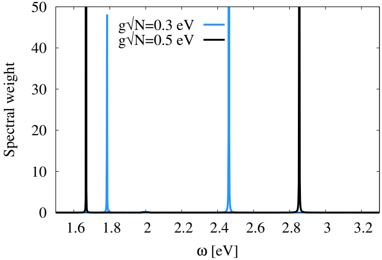

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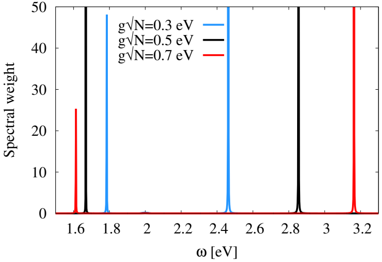

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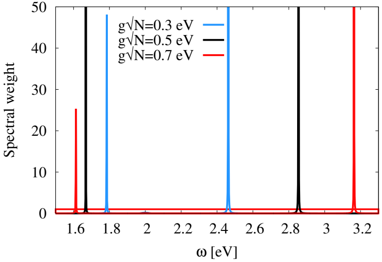

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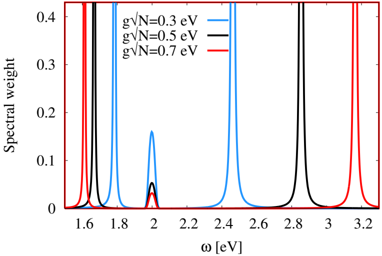

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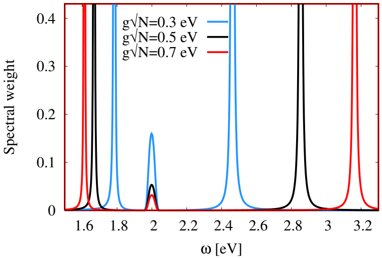

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[Houdré *et al.* , PRA '96]

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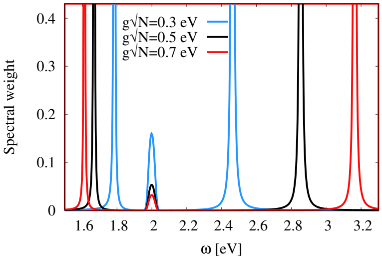

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Molecular adaptation

- Central peak — depends on g, not T.
- Can g_{eff} depend on T?
- Rotational degrees of freedom

$$H = \ldots + \sum_\alpha \left[\ldots + g_{\alpha,k}\cos(\theta_\alpha)(\psi_k^\dagger + \psi_{-k})\sigma_\alpha^x + E_0(\theta_\alpha)\right]$$

- Schrieffer-Wolff, $\delta H = \sum_{\alpha,k} g_{\alpha,k}(\psi_k^\dagger \sigma_\alpha^+ + \text{H.c.})$:

$$H_{\text{eff}} = \ldots + \sum_\alpha \left[-K_0\cos^2(\theta_\alpha) + E_0(\theta)\right], \quad K_0 = \sum_k \frac{g_k^2}{\omega_k + \epsilon}$$

[Cwik *et al.* , `arXiv:1506.08974`]

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Molecular adaptation

- Central peak — depends on g, not T.
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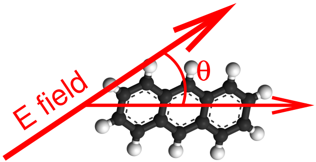

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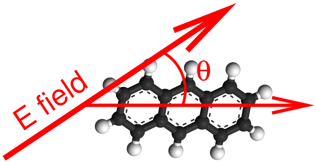

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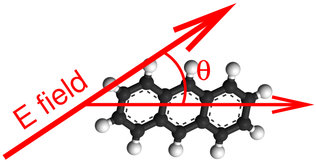

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$$S \to S(1-2K_1), \quad K_1 = \sum_k \frac{g_k^2}{(\omega_k+\epsilon)^2}$$

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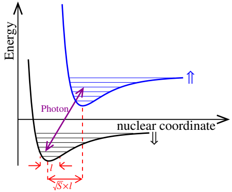

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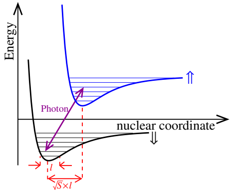

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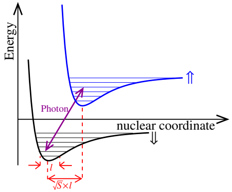

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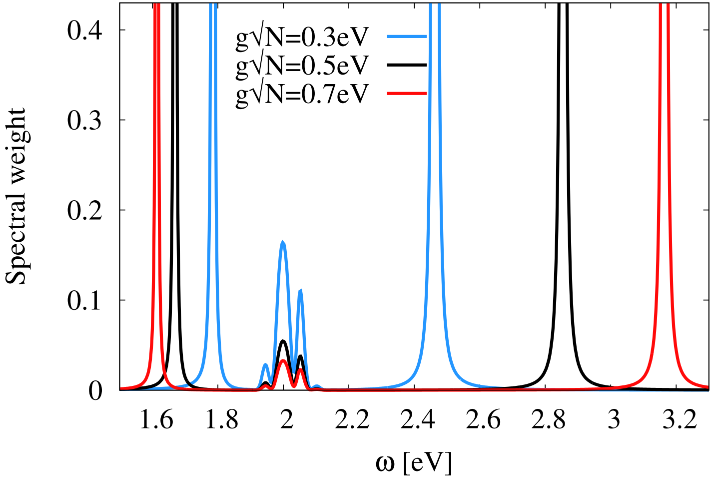

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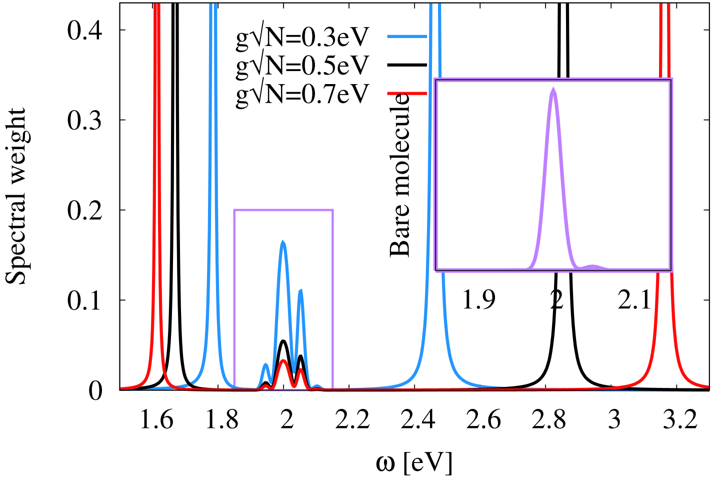
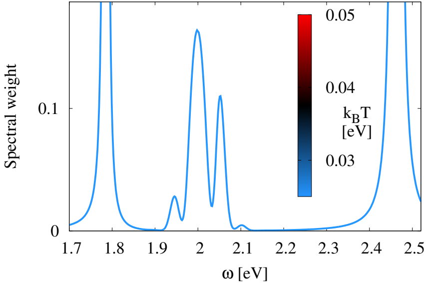


Disordered molecules + vibrations – *vs* temperature

- *vs* vs temperature

- Stronger disorder & $S = 0.5, \sigma = 0.025$eV



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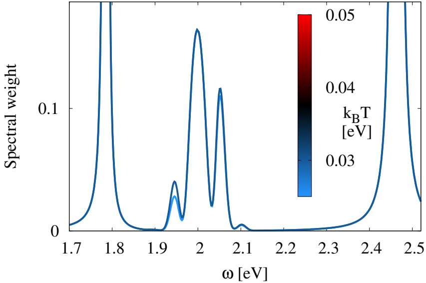

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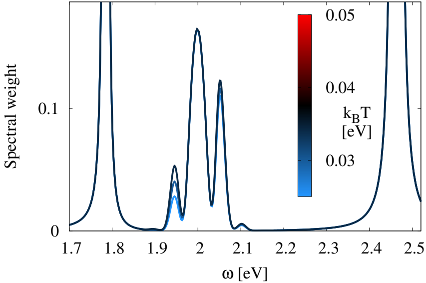

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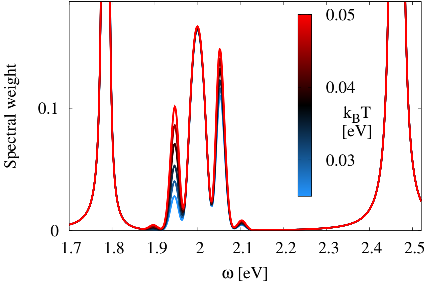

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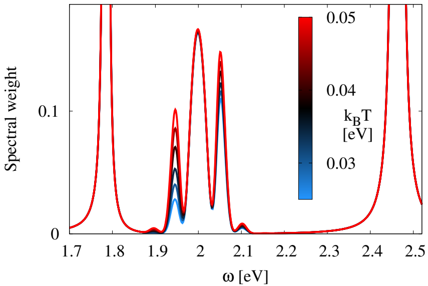

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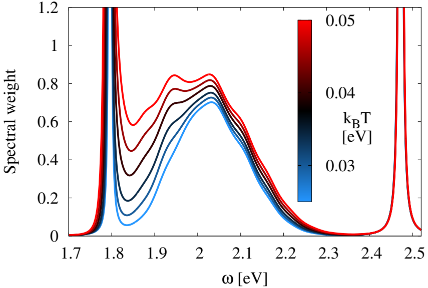

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Driven dissipative systems

1. Modelling photon BEC & organic polaritons

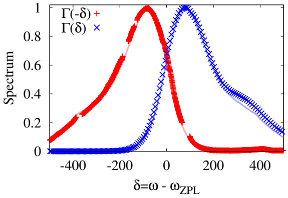
2. (Ultra-)strong coupling, weak pumping
   - Ultra strong coupling & reconfiguration
   - Vibrational sidebands in spectrum

3. Driven dissipative systems
   - Limitations of rate equation model
   - Toy problem – two bosonic modes

Photon BEC, rate equations & oscillations

- Photon BEC: can derive photon rate equation [See Kirton talk]

$$\partial_t n_m = -\kappa n_m + \Gamma(-\delta_m)(n_m + 1)N_\uparrow - \Gamma(\delta_m) n_m N_\downarrow$$



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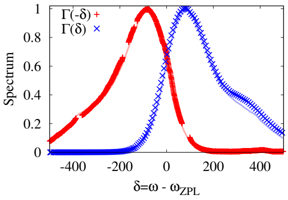

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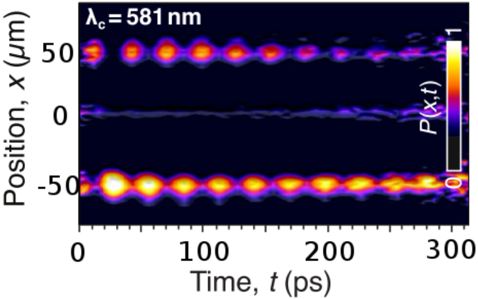
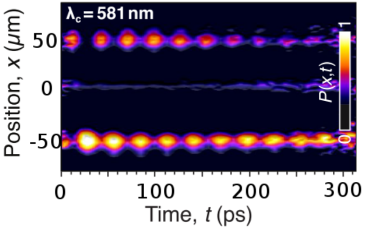


Photon BEC rate equations



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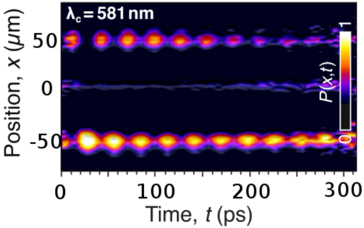

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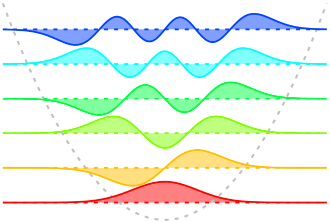

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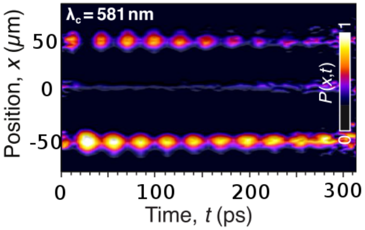

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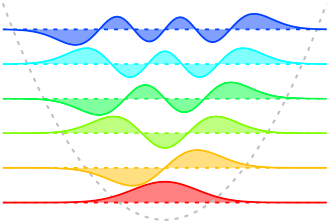

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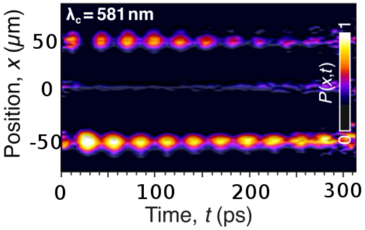

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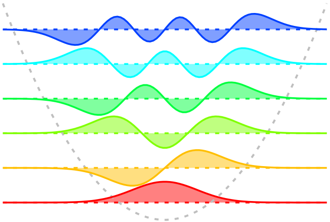

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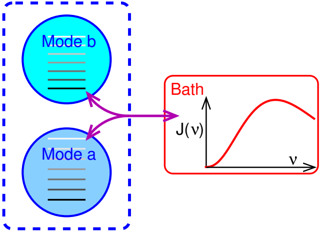
Emission must create coherence between non-degenerate modes.

Toy problem: two bosonic modes

- Basic problem: Emission from thermal bath



$$H = \omega_a \hat{\psi}_a^\dagger \hat{\psi}_a + \omega_b \hat{\psi}_b^\dagger \hat{\psi}_b + H_{\text{Bath}}$$
$$+ (\varphi_a^* \hat{\psi}_a^\dagger + \varphi_b^* \hat{\psi}_b^\dagger) \sum_i g_i \hat{c}_i + \text{H.c.}$$

Toy problem: naïve solutions

Two "expected" behaviours:

- At resonance: "weak lasing" — coupling to bath dominates

$$\frac{d}{dt}\rho = \Gamma^{\downarrow}\mathcal{L}[\varphi_a\hat{\psi}_a + \varphi_b\hat{\psi}_b] + \Gamma^{\uparrow}\mathcal{L}[\varphi_a^*\hat{\psi}_a^\dagger + \varphi_b^*\hat{\psi}_b^\dagger]$$

- Far from resonance: pointer states are eigenstates

$$\frac{d}{dt}\rho = \sum_{i=a,b} \Gamma_i^{\downarrow}\mathcal{L}[\hat{\psi}_i] + \Gamma_i^{\uparrow}\mathcal{L}[\hat{\psi}_i^\dagger]$$

- Questions:
  - How does crossover work?
  - Are these actually right?

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- Solve via Laplace transform. Find $F_{ij}(t) = \langle \hat{\psi}_i^\dagger(t)\hat{\psi}_j(t)\rangle$
- Steady state:
- Time evolution —
  $F_{ab}(t) \sim \exp(-\alpha\Delta^2 t)$

- Always some coherence
  - (individual always wrong)
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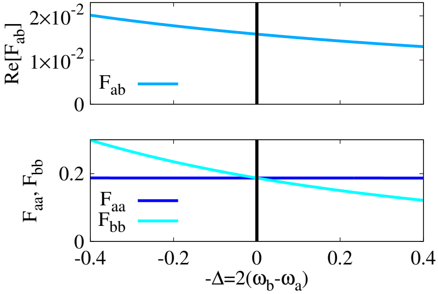

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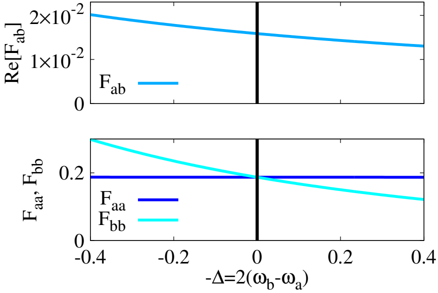

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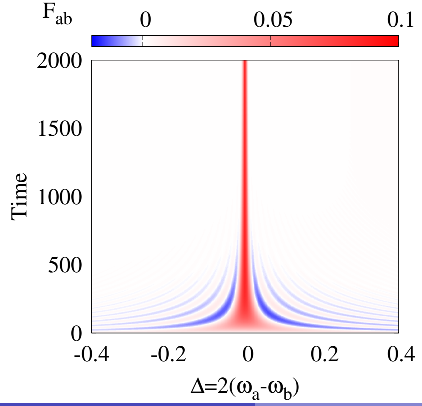

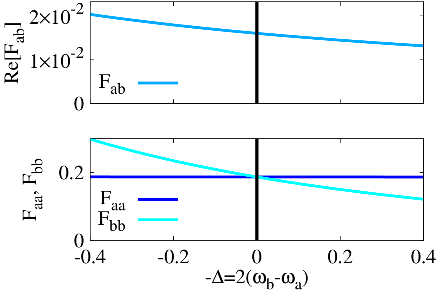

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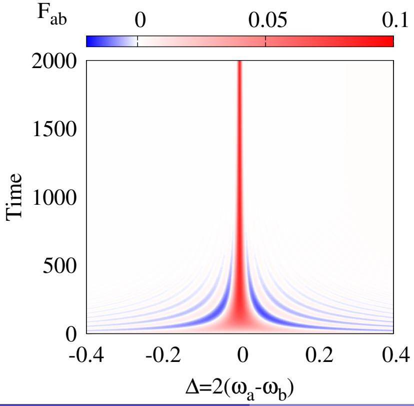

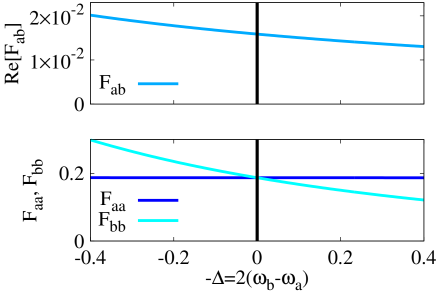

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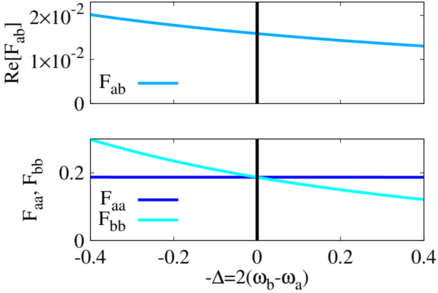

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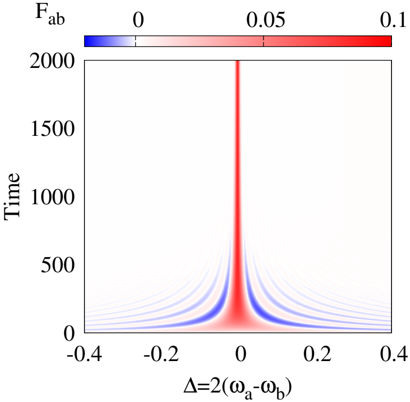

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Toy problem: Bloch-Redfield theory

Unsecularised Bloch-Redfield theory:

$$\partial_t \rho = -i[\hat{H}, \rho] + \sum_{ij} L^{\downarrow}_{ij} \varphi^*_i \varphi_j \left(2\hat{\psi}_j \rho \hat{\psi}^\dagger_i - [\rho, \hat{\psi}^\dagger_i \hat{\psi}_j]_+ \right) + \sum_{ij} L^{\uparrow}_{ij} \varphi^*_i \varphi_j \left(2\hat{\psi}^\dagger_j \rho \hat{\psi}_i - [\rho, \hat{\psi}_i \hat{\psi}^\dagger_j]_+ \right).$$

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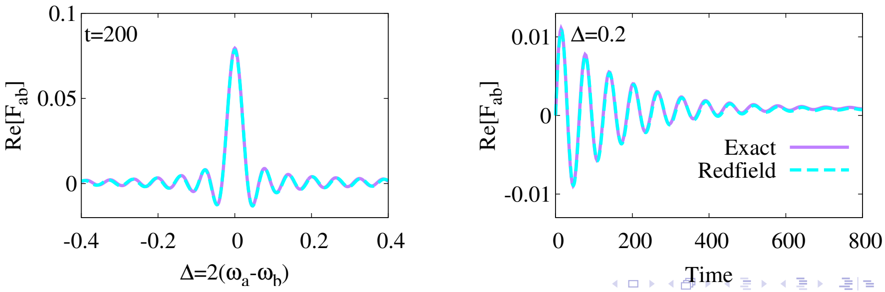
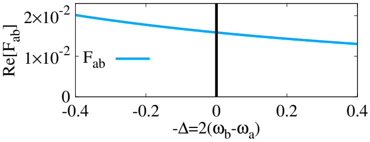


Toy problem: Secularisation

- Secularisation (in eigenbasis of $\hat{H}$): $L_{ij}^{\uparrow,\downarrow} \rightarrow L_{ii}^{\uparrow,\downarrow}\delta_{ij}$



- Leads to $F_{ab}(t \rightarrow \infty) = 0$. Exact:
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- Check stability: consider $f = (F_{aa}, F_{bb}, \Re[F_{ab}], \Im[F_{ab}])$

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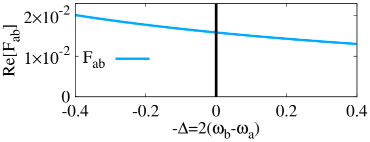

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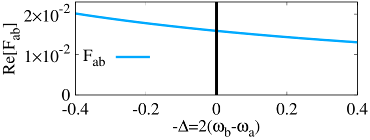

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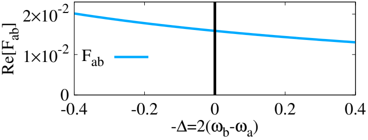

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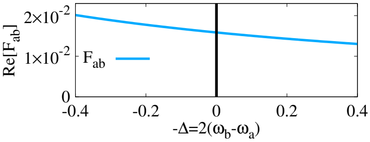

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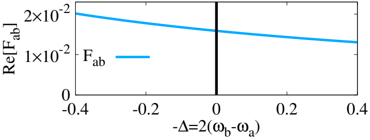

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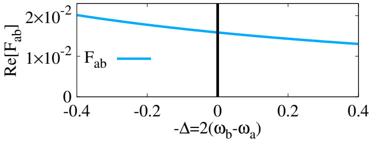

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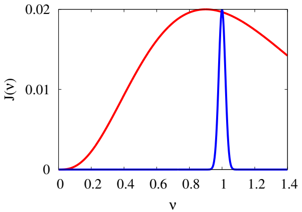

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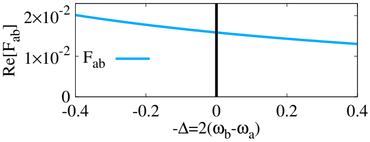

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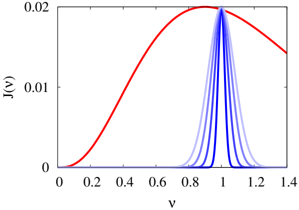

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- Is BR the best (time-local) theory we can find?
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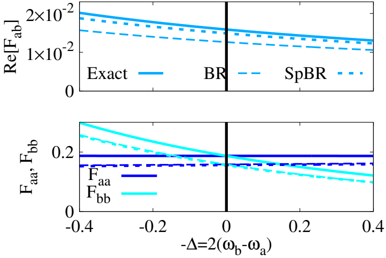

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Acknowledgements

GROUP:

  

COLLABORATORS:

   

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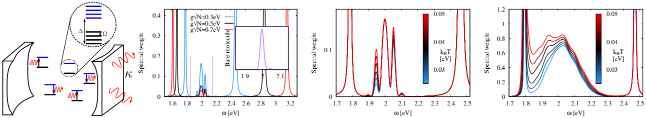
topnes — Topological Protection and Non-Equilibrium States in Strongly Correlated Electron Systems

EPSRC — Engineering and Physical Sciences Research Council

The Leverhulme Trust

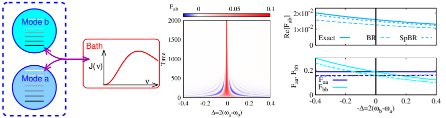
Summary

- Vibrational configuration



[Cwik, Kirton, De Liberato, JK `arXiv:1506.08974`]

- Modelling incoherent emission into non-degenerate modes



[Eastham, Kirton, Cammack, Lovett, JK `arXiv:1508.XXXX`]

Extra Slides