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Stochastic dynamics of open quantum systems

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Decoherence in Quantum Dynamical Systems, Trento, April 2010

Outline

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1. Introduction: Decoherence and robust states

2. Open quantum system dynamics:
   stochastic Schrödinger equation   ("applied decoherence")

3. Applications:

- Vibrational quantum dynamics on Helium nanodroplets
  [M Schlesinger, M Mudrich, F Stienekmeyer, WTS, Chem. Phys. Lett. 490 (2010) 245]
- Energy transfer dynamics in molecular aggregates
  [J Roden, A Eisfeld, W Wolff, WTS, Phys. Rev. Lett. **103,** 058301 (2009)]
- Quantum decoherence of qubits
  [J Helm and WTS, Phys. Rev. A **80**, 042108 (2009), Phys Rev A **81** 042314 (2010)]

4. Conclusions

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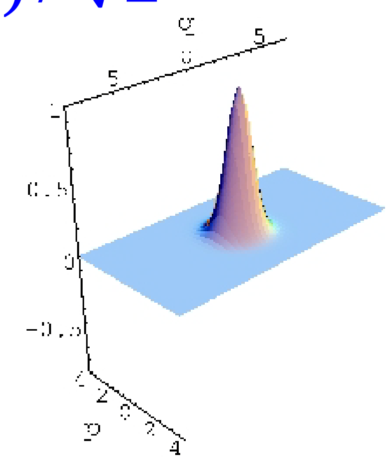
Harmonic oscillator (field mode)

Equation of motion:

$$\partial_t \,|\psi\rangle = -i\omega\, a^+ a \,|\, \psi\rangle \quad \text{or} \quad \dot{\rho} = -i\omega[a^+ a, \rho]$$

$$a = (q + ip)/\sqrt{2} \qquad q = Q\sqrt{m\omega/\hbar},\, p = P/\sqrt{\hbar m\omega}$$



Coherent states:

$$a\,|\,\alpha\rangle = \alpha\,|\,\alpha\rangle$$

$$|\,\psi(t)\rangle = |\,\alpha e^{-i\omega t}\rangle$$

Schrödinger, 1926: **„... Ich zeige, daß eine Gruppe von Energieeigenschwingungen ... Einen „Massenpunkt“ darzustellen vermag, welcher die nach der gewöhnlichen Mechanik zu erwartende „Bewegung“ ausführt.**

Damped oscillator (T=0)

Equation of motion:

$$\dot{\rho} = -i\omega[a^{+}a,\rho] + \tfrac{\gamma}{2}\left([a\rho,a^{+}] + [a,\rho a^{+}]\right)$$

Coherent („classical“) states are singled out, because they are the only states that remain pure under time evolution:

$$\rho(t) = |\alpha(t)\rangle\langle\alpha(t)| \quad \text{with} \quad \alpha(t) = \alpha e^{-i\omega t - \gamma t/2}$$

Relevant time scales:

- system time scale $\tau_{\mathrm{sys}} = \omega^{-1}$
- relaxation time scale $\tau_{\mathrm{diss}} = \gamma^{-1}$

However: *Superposition* of coherent states becomes mixture.

This may happen on a *new* time scale τ_{dec}

Initial superposition:

$\rho(0) = |\psi\rangle\langle\psi|$ with $|\psi\rangle = (|\alpha\rangle + |\beta\rangle)/\sqrt{2}$ and $D = |\alpha - \beta| \gg 1$

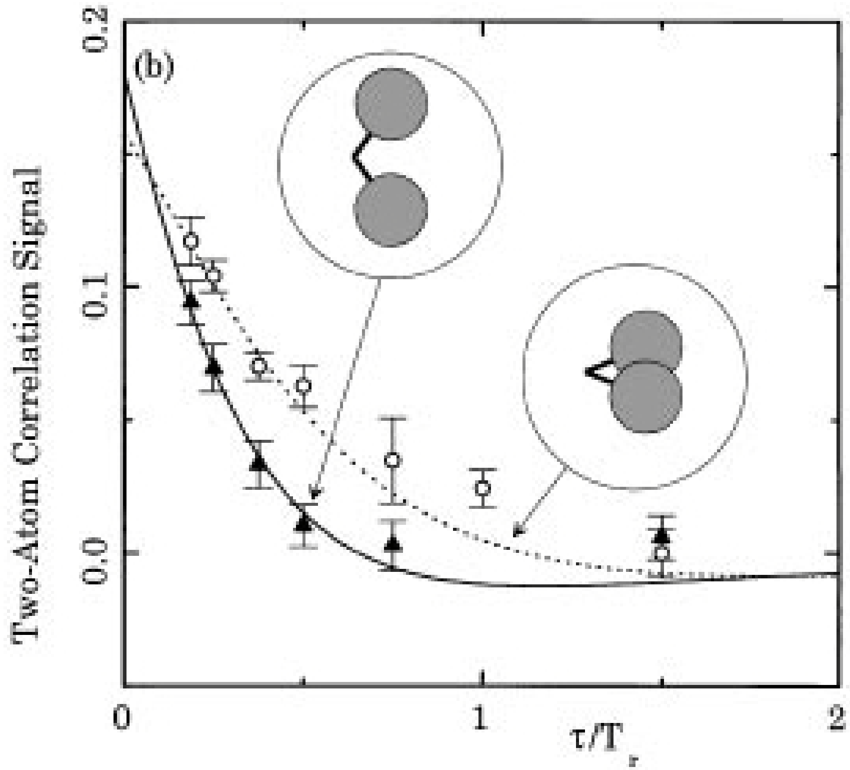
$$\rho(t) = \tfrac{1}{2}\big(|\alpha(t)\rangle\langle\alpha(t)| + |\beta(t)\rangle\langle\beta(t)|\big) + \frac{f(t)}{2}|\alpha(t)\rangle\langle\beta(t)| + \frac{f^*(t)}{2}|\beta(t)\rangle\langle\alpha(t)|$$

Here $|f(t)|^2 = e^{-\gamma|\alpha-\beta|^2 t} = e^{-\gamma D^2 t}$

Decoherence time: $\tau_{\text{dek}} = (\gamma D^2)^{-1} = \tau_{\text{diss}} / D^2 \ll \tau_{\text{diss}}$

Result of the Paris experiment:

M. Brune et. al.,
PRL **77**, 4887 (1996)



The larger D, the faster the coherence between the two coherent states is lost.

Message: state of an open quantum system will be a mixture of
time dependent „localized“ states

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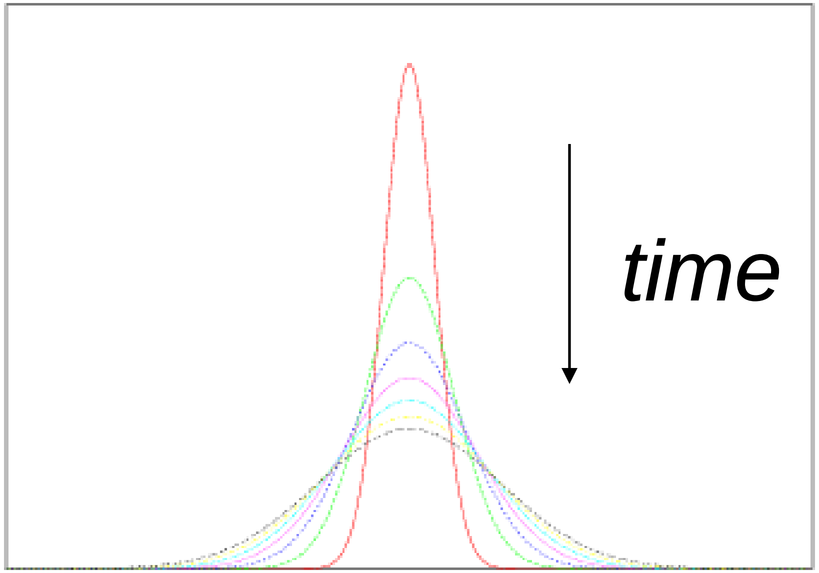
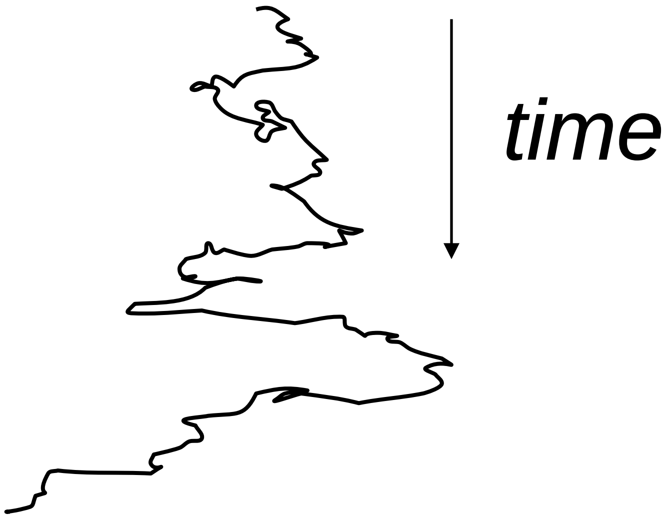
Classical Brownian motion





Individual Brownian particle:
stochastic trajectory $x(t)$

$$m\ddot{x} + \gamma m\dot{x} + V'(x) = F(t)$$

$$\mathrm{M}\left[F(t)F(s)\right] = 2m\gamma kT\delta(t-s)$$

(Langevin equation)

Ensemble description:
density $\rho(x,p,t)$

$$\dot{\rho} = \{H,\rho\} + \gamma \tfrac{\partial}{\partial p}(p\rho) + m\gamma kT \tfrac{\partial^2}{\partial p^2}\rho$$

(Einstein's approach: Diffusion-, Fokker-Planck-equation)

Quantum Brownian motion (‚Caldeira-Leggett')

Classical Brownian motion $m\ddot{Q} + \gamma m\dot{Q} + V'(Q) = F(t)$

may be derived from

$$H_{\text{tot}} = P^2/2m + V(Q) \;+\; Q\sum_i g_i q_i \;+\; \sum_i (p_i^2/2m_i + \tfrac{1}{2} m_i \omega_i^2 q_i^2)$$

$$m\ddot{Q}(t) + \int_0^t c(t-s)\dot{Q}(s)ds + V'(Q) = F(t)$$

$$\mathrm{M}\left[F(t)F(s)\right] = kTc(t-s) \approx 2m\gamma kT\delta(t-s)$$

$$c(t-s) = \sum_i (g_i^2/(m_i\omega_i^2))\cos(\omega_i(t-s))$$

Quantum Brownian motion (‚Caldeira-Leggett‘)

Classical Brownian motion $m\ddot{Q} + \gamma m\dot{Q} + V'(Q) = F(t)$

may be derived from

$$H_{\text{tot}} = P^2/2m + V(Q) \; + \; Q\sum_i g_i q_i \; + \sum_i (p_i^2/2m_i + \tfrac{1}{2} m_i \omega_i^2 q_i^2)$$

$$\dot{\rho}_{\text{tot}}(t) = \tfrac{1}{i\hbar}\left[H_{\text{tot}}, \rho_{\text{tot}}(t)\right]$$

$$\rho(t) = \mathrm{Tr}_{\text{env}}\left[\rho_{\text{tot}}(t)\right]$$

?

(Einstein, Fokker-Planck)

(Langevin)

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Solving the total Schrödinger equation (T=0):

Expand total state in a fixed (Bargmann) coherent state basis for the environmental degrees of freedom: [L.Diosi, WTS, Phys. Lett. A 235, 569 (1997)]

$$|\Psi_t\rangle = \int \frac{d^2 z}{\pi}\, e^{-|z|^2}\, |\psi_t(z^*)\rangle \otimes |z\rangle$$

System state $|\psi(z^*)\rangle$ **corresponds to a certain fixed configuration** $z = (z_1,\ z_2,\ z_3, \ldots, z_\lambda,\ \ldots)$ **of the environment.**

Find:

$$\dot{\psi}_t = -\tfrac{i}{\hbar} H_{sys}\psi_t + q z_t \psi_t - q \int_0^t ds\ \alpha(t-s) \frac{\delta \psi_t}{\delta z_s}$$

with $z_t = \sum_\lambda g_\lambda z_\lambda^* e^{i\omega_\lambda t}$ and $\alpha(t-s)$ the quantum bath correlation function

$$\alpha(t-s) = \langle B(t) B^+(s)\rangle = \int d\omega\ J(\omega) e^{-i\omega t}$$

(here T=0)

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(non-Markovian) "stochastic" Schrödinger equation

Total state:

$$|\Psi_t\rangle = \int \frac{d^2 z}{\pi}\, e^{-|z|^2}\, |\psi_t(z^*)\rangle \otimes |z\rangle$$

System state relative to $|z\rangle$

$$\dot{\psi}_t = -\tfrac{i}{\hbar} H_{\text{sys}} \psi_t + q z_t \psi_t - q \int_0^t ds\; \alpha(t-s) \frac{\delta \psi_t}{\delta z_s}$$

with $z_t = \sum_\lambda g_\lambda z_\lambda^* e^{i\omega_\lambda t}$

Reduced density operator:

$$\rho(t) = \mathrm{Tr}_{\text{env}}\left[|\Psi(t)\rangle\langle\Psi(t)|\right] =$$

$$= \int \frac{d^2 z}{\pi}\, e^{-|z|^2}\, |\psi_t(z^*)\rangle\langle\psi_t(z^*)| = \mathrm{M}\left[\,|\psi_t(z^*)\rangle\langle\psi_t(z^*)|\,\right]$$

Monte-Carlo integration over coherent state labels $z = (z_1,\ z_2,\ z_3, \ldots, z_\lambda,\ \ldots)$

⇨ z_t **Gaussian** ***stochastic process*** **with**

$$\mathrm{M}[z_t] = 0, \quad \mathrm{M}[z_t z_s] = 0, \quad \mathrm{M}[z_t z_s^*] = \alpha(t-s)$$

Non-linear "stochastic" Schrödinger equation

Total state: $$|\Psi_t\rangle = \int \frac{d^2z}{\pi}\, e^{-|z|^2}\, |\psi_t(z^*)\rangle \otimes |z\rangle$$

$|\psi_t(z^*)\rangle$ is a solution of the linear stochastic Schrödinger equation

Its norm contains information about its relevance in the expansion.

Better: Let environmental state move according to

total dynamics (Ehrenfest): $$\dot z_\lambda(t) = i g_\lambda e^{-i\omega_\lambda t} \langle \tilde\psi(t) | L^+ | \tilde\psi(t)\rangle$$

with $$|\tilde\psi(t)\rangle = \frac{|\psi_t(z(t))\rangle}{\sqrt{\langle \psi_t(z(t)) | \psi_t(z(t))\rangle}}$$

Nonlinear stochastic Schrödinger equation for $|\tilde\psi(t)\rangle$

[WTS, L Diosi, N Gisin, PRL 82, 1801 (1999)]

Reduced density operator: $$\rho(t) = \mathrm{M}[\,|\tilde\psi_t\rangle\langle\tilde\psi_t|\,]$$

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Coupled „quantum-classical“ dynamics:

Total state: $$|\Psi_t\rangle = \int \frac{d^2z}{\pi}\, e^{-|z|^2}\, |\psi_t(z^*)\rangle \otimes |z\rangle$$

$$|\tilde{\psi}(t)\rangle = \frac{|\psi_t(z(t))\rangle}{\sqrt{\langle \psi_t(z(t)) | \psi_t(z(t))\rangle}}$$

is the solution of the nonlinear stochastic Schrödinger equation.

Consider product states: $$|\Phi(t)\rangle = |\tilde{\psi}(t)\rangle \otimes |z(t)\rangle$$

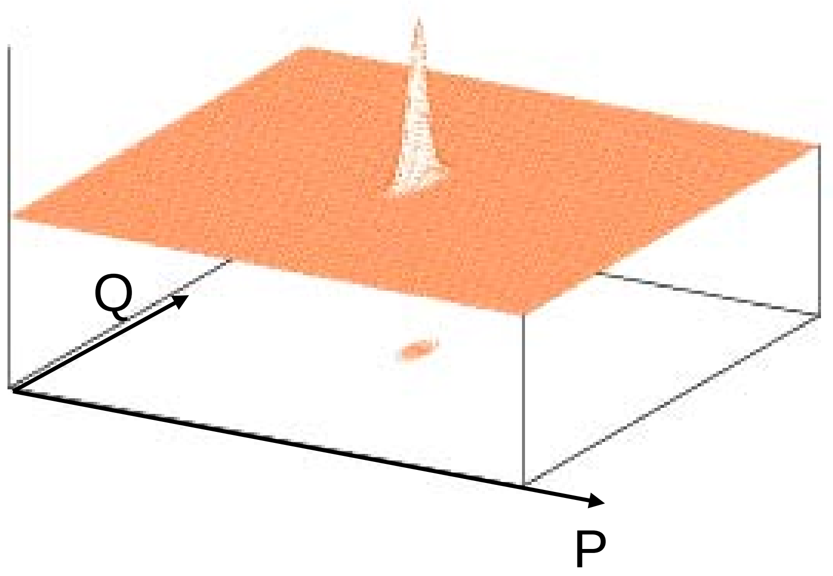
The states $\{|\Phi(t)\rangle\}$ are close to being solutions of the full dynamics:

$$\langle \Phi(t+\Delta t)|\exp(-\tfrac{i}{\hbar} H_{\text{tot}} \Delta t)|\Phi(t)\rangle = 1 + \bigcirc(\Delta t^2)$$

„quantum-classical“ dynamics!

Coherent wave packet dynamics: driven, nonlinear pendulum

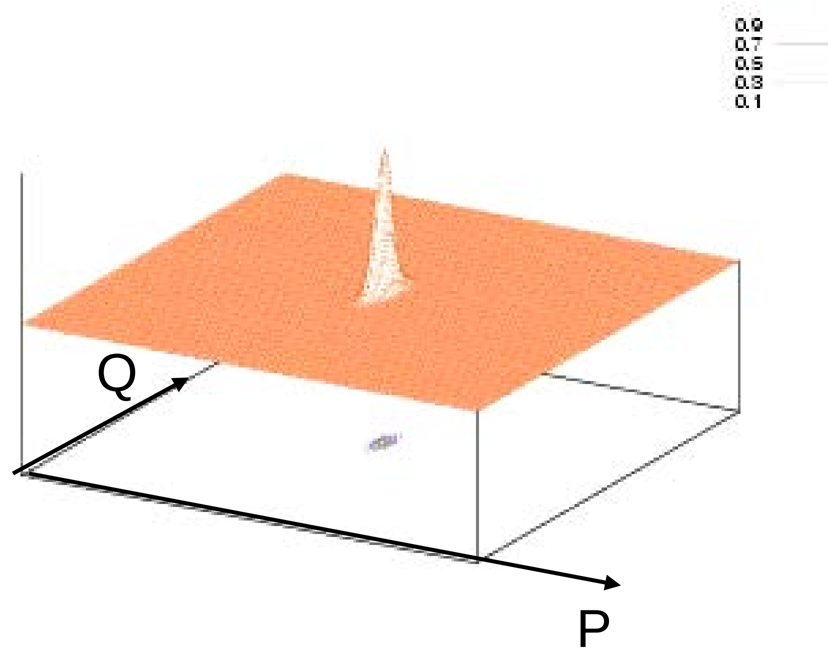
$$H = P^2/2M - AQ^2 + BQ^4 + CQ\cos(Dt)$$



Unitary dynamics:
fully coherent wave function spreads over whole phase space.

Quantum-Brownian motion:

Dynamics including damping and fluctuations:
Localized single run of the stochastic Schrödinger equation:



For $\hbar \to 0$: classical Langevin-dynamics of point particle!

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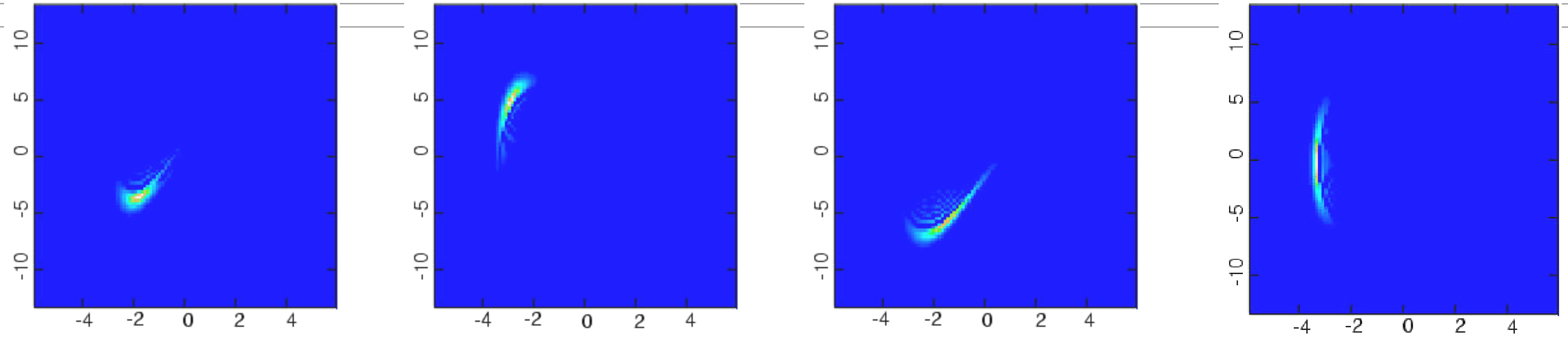
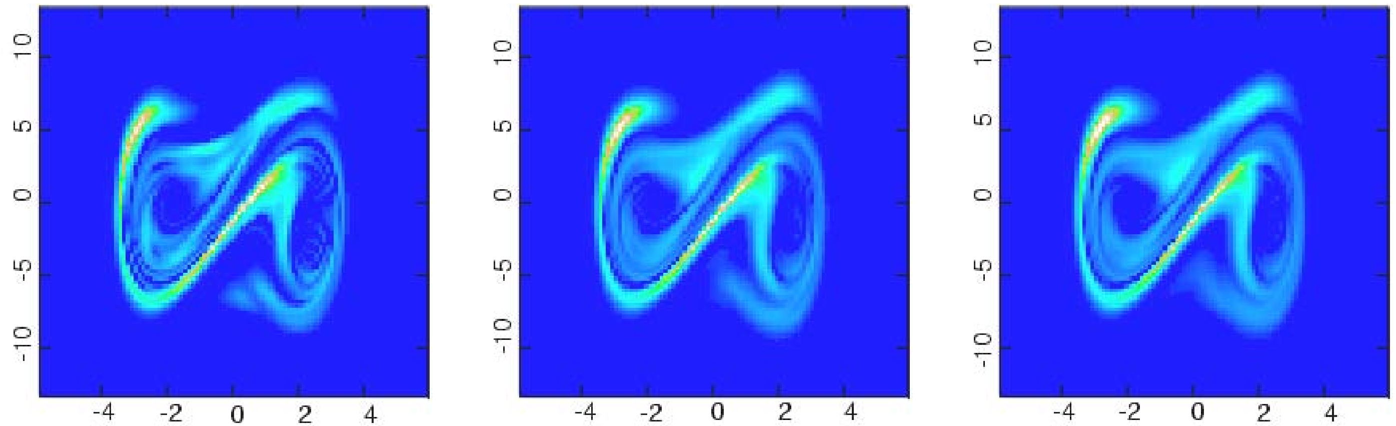
Quantum Brownian motion: Ensemble

ψ



ρ



250 **1000** **5000**

- **Single equation covers dynamics from fully coherent ($\gamma \to 0$) to fully incoherent (classical), as $\hbar \to 0$**
- **more(!) information available than in ρ.**

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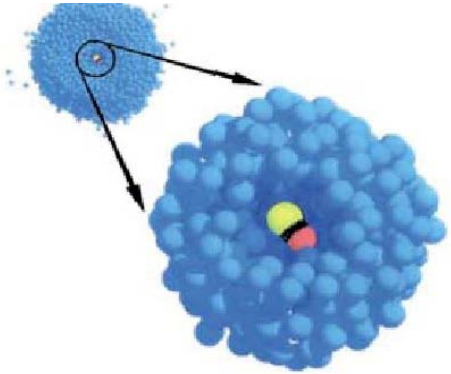
Helium nanodroplets (He_N)

He nanodroplet = aggregation of He atoms. Contains a few ten up to 10^6 He atoms

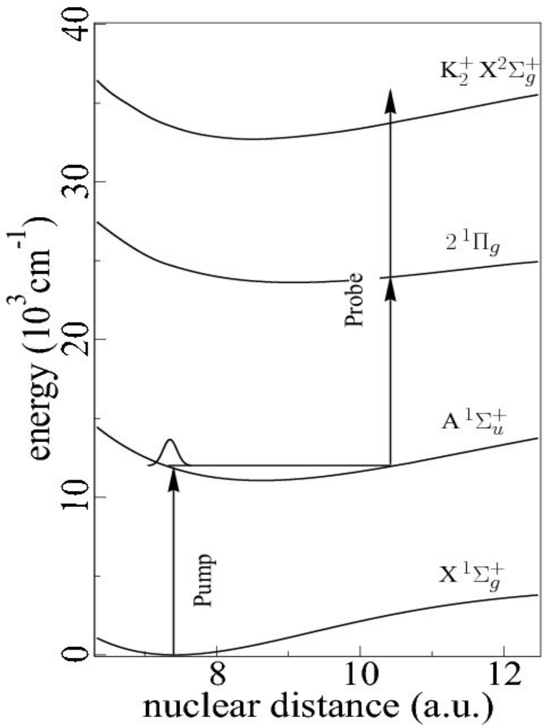
- Provide ideal “refrigerator” for high precision spectroscopy of embedded species at “zero” temperature
- Allow to study influence of collective degrees of freedom (phonons etc.) on molecular dynamics through shifts/broadening of spectral lines
- Show properties of superfluidity in a finite-sized quantum system. Embedded objects might move unhindered below a certain critical velocity.
- Femtosecond pump-probe experiments in Freiburg (Stienkemeyer group)



OCS molecule solvated in helium nanodroplet (from JP Toennies and AF Vilesov, Angew. Chemie (2004))

Femtosecond pump-probe spectroscopy

- Excitation: First pulse excites the dynamics, creates vibrational wave packet
- Probing: After certain time delay, second pulse leads to ionization of dimer
- Position of wave packet determines ion rate (Franck Condon window) – the nuclear dynamics is followed in real time
- Laser wavelength determines excitation pathway

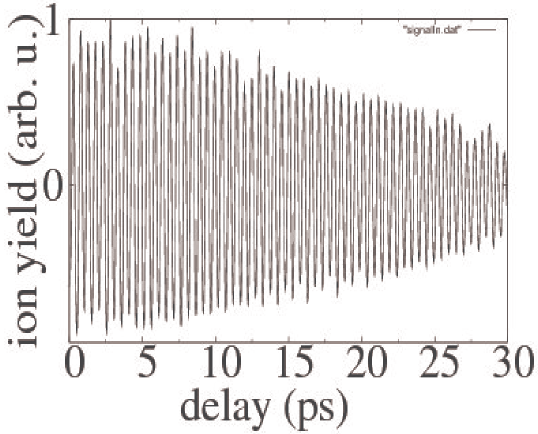


BO surfaces potassium, excitation at 833 nm

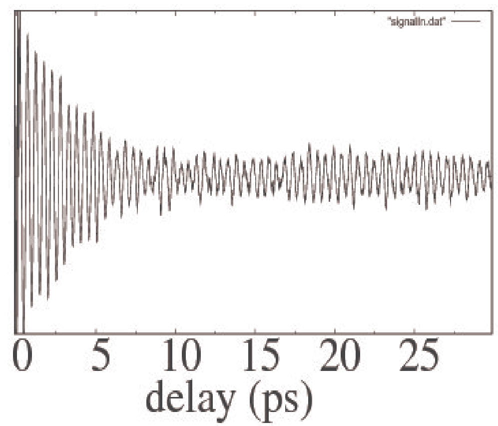
(for K_2 in gas phase, see Nicole et. al., JCP **111** (1999))

Comparison

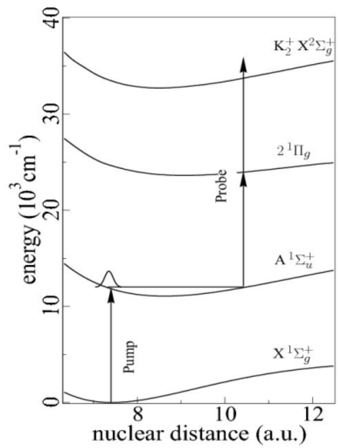
"simple" theory (free dimer)

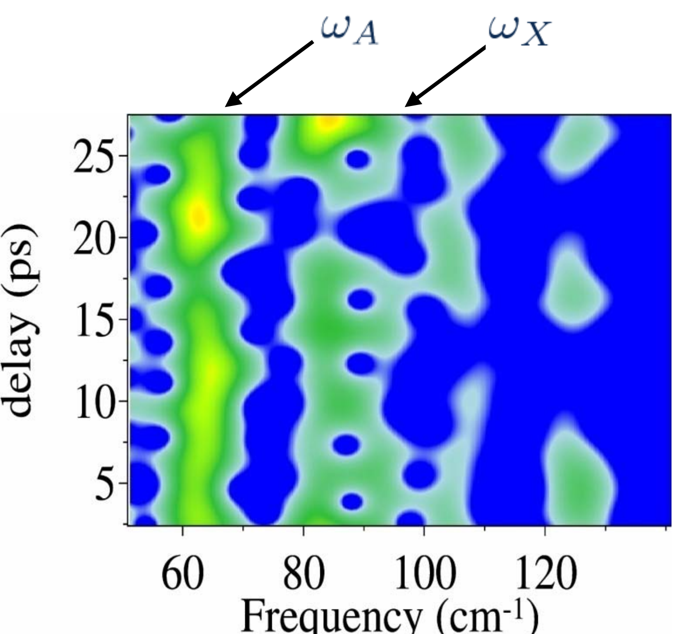


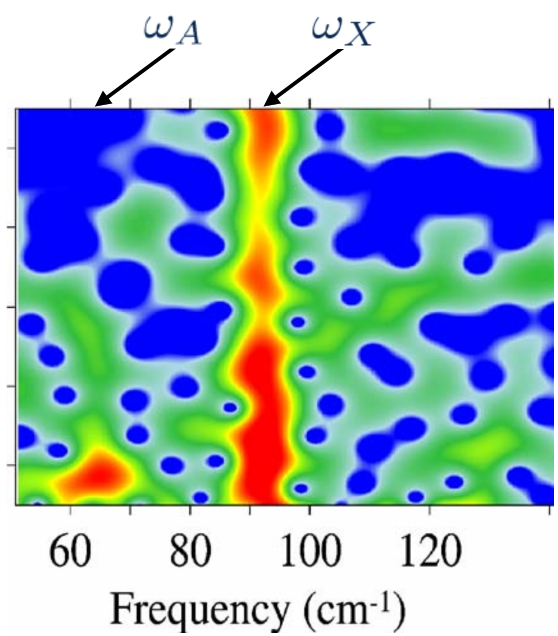
Experiment



(@ 833 nm)







(@ 800 nm)

Model for helium influence

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Influence of droplet on dimer dynamics described phenomenologically by including

Solvational shift

of particular BO surface within a reasonable range

Parameter Δ

Dissipative dynamics (Lindblad)

- Interaction of vibrational – with collective degrees of freedom of droplet (phonons) leads to dissipation
- Assume phenomenological damping of vibrational wave packet (damping constant γ

Dissipation on timescale $1/\gamma$

-> quantum fluctuations

Parameter γ

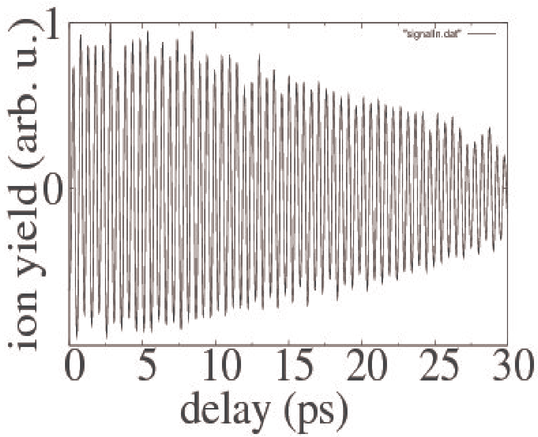
Desorption

Helium influence vanishes upon (statistical) desorption.

Parameter τ_D

Comparison (833 nm)

Free dimer



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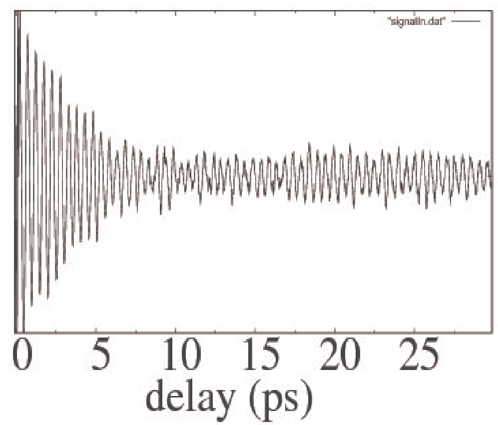
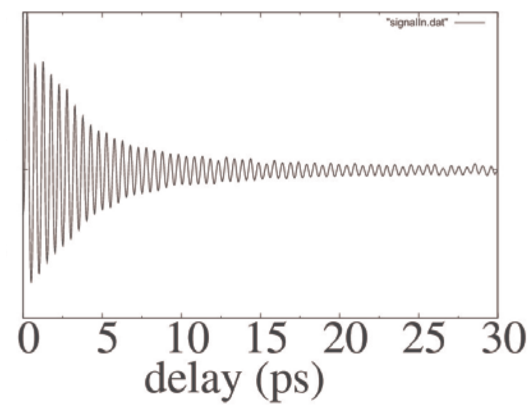


Damping model

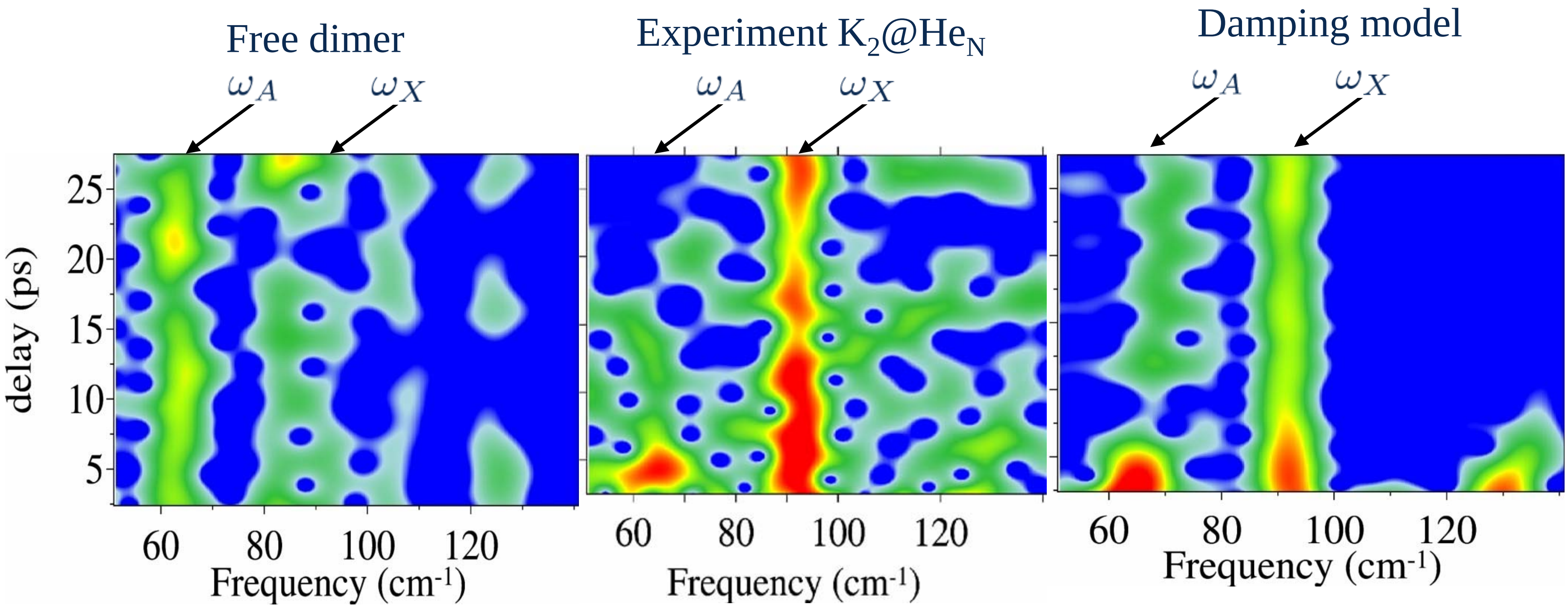


Damping model parameters: $\Delta = -50\mathrm{cm}^{-1}, \gamma = 0.15\mathrm{ps}^{-1}, \tau_D = 10\mathrm{ps}$

- Closing of Franck-Condon window in damped molecules:
  Initial decrease of signal amplitude.
- Some dimers desorb very early (and do not suffer from dissipation):
  Oscillatory behavior remains at later delay times ($\tau > 10\mathrm{ps}$

Same parameters, but different excitation wavelength....

Comparison (800 nm)



- Frequency component ω_A :dominant in gas phase spectrum, suppressed in experiment + model
- Frequency component ω_X :Absent in gas phase spectrum, visible in experiment + model

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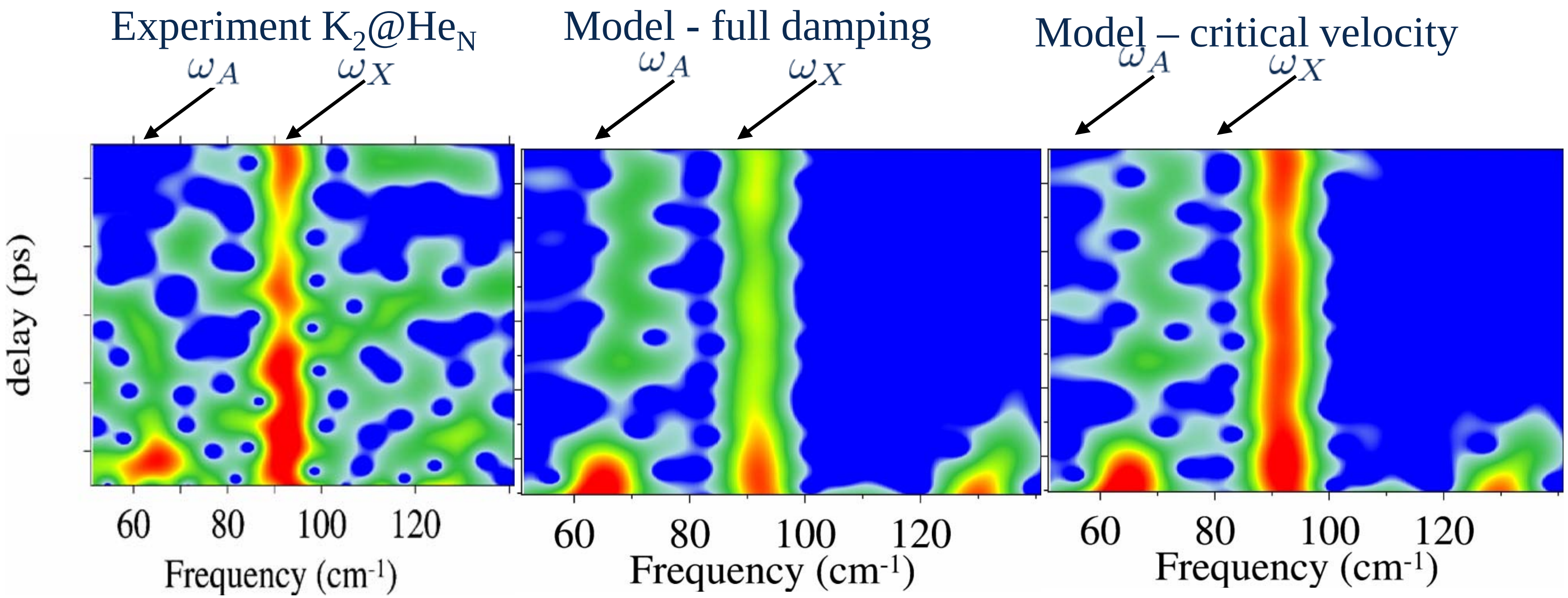
Frictionless motion in the ground state ?

- In a superfluid, an object may move frictionless as long as its velocity is low enough ("Landau critical velocity" with bulk value 60m/s).
- Allow for frictionless motion of slowly moving ground state wave packet.
- Effects of superfluidity might be observable.



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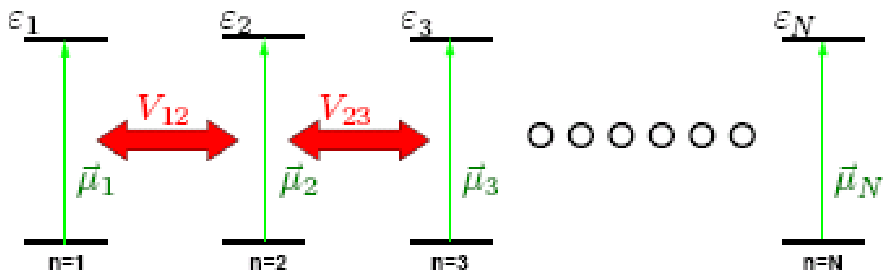
Energy transfer in molecular aggregates

Assemblies of monomers which largely retain their character on aggregation.

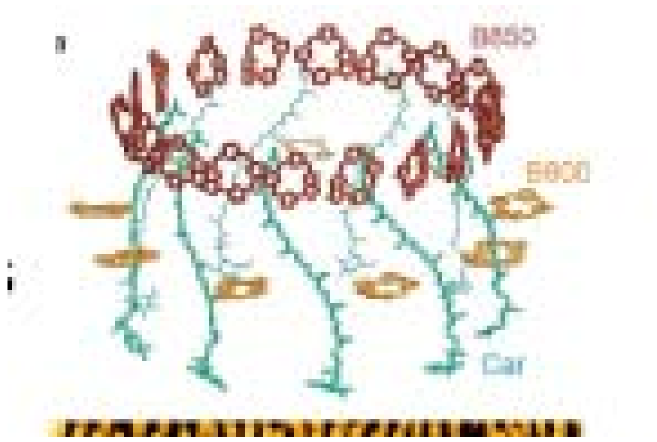
No overlap of electronic wavefunctions. The monomers interact via dipole-dipole interaction on excitation.



Examples:

Light-harvesting units in photosynthesis

Molecular aggregates (organic dyes)



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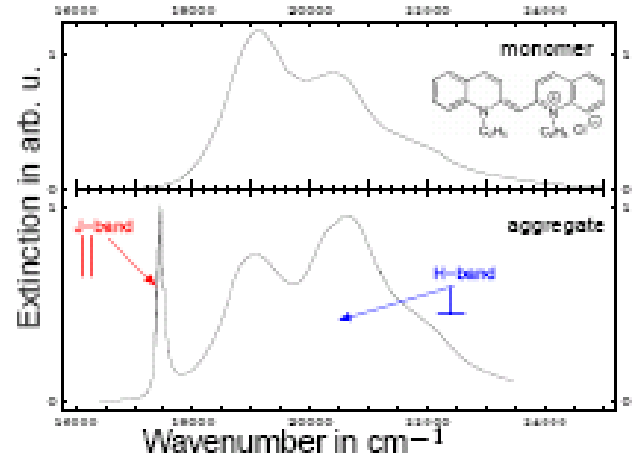
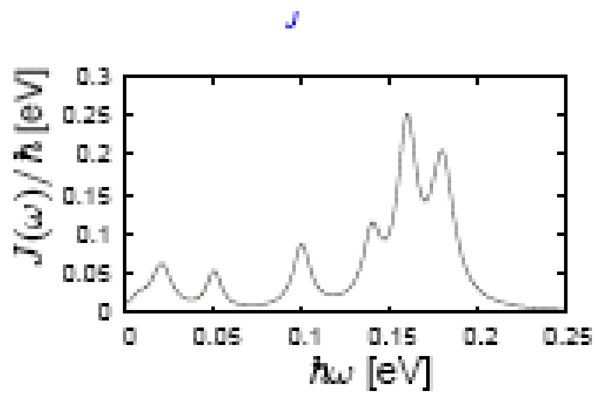
Absorption spectroscopy

Pseudoisocyanin (PIC):

(Jelly, Scheibe 1936)



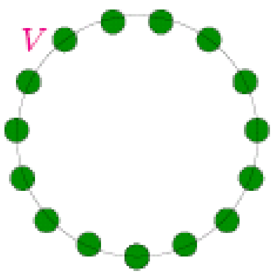
Electronic excitation couples to *structured* „bath“ of phonons:

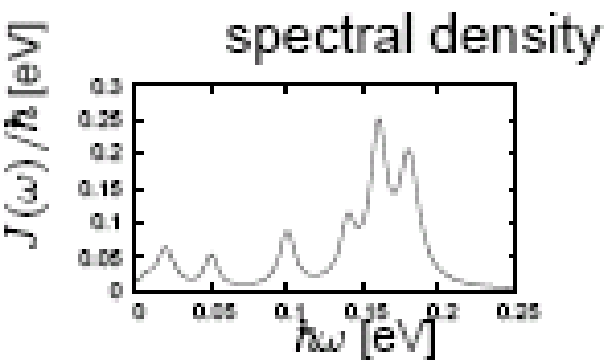


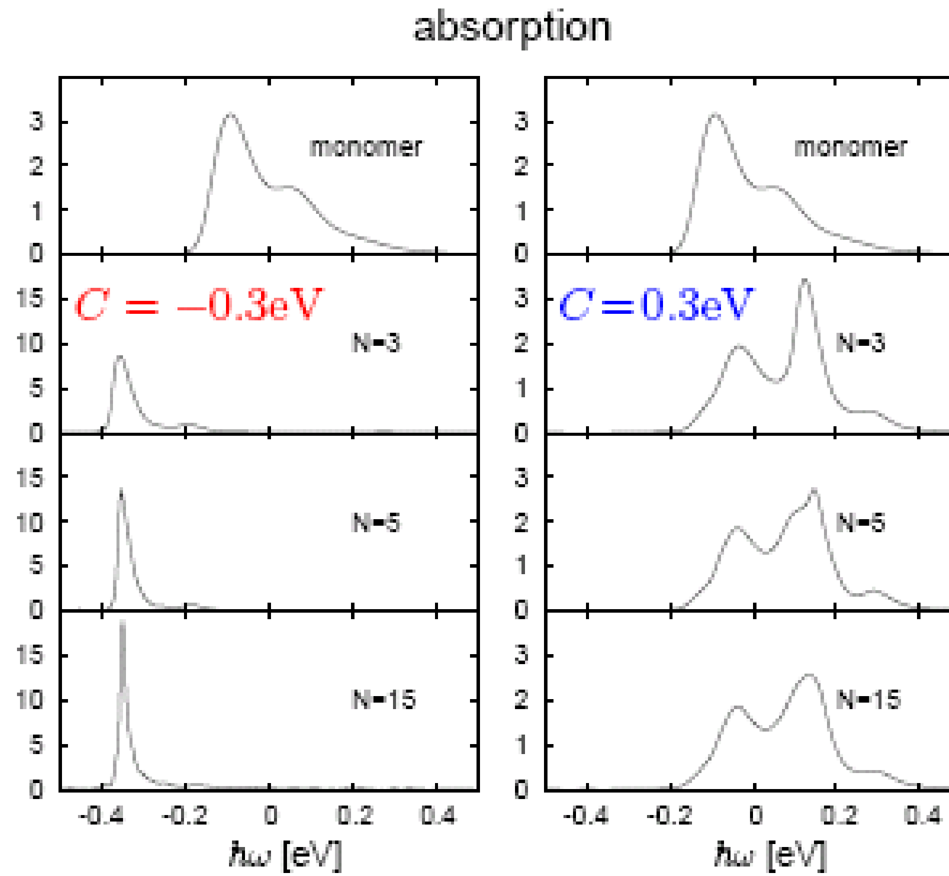
Apply our stochastic theory in „zeroth order noise expansion“!

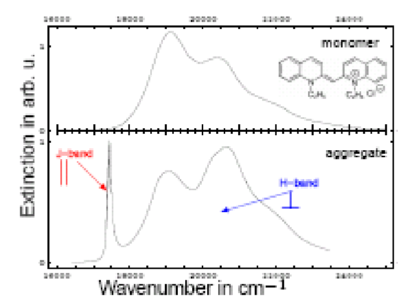
Our calculations

Ring-shaped aggregate



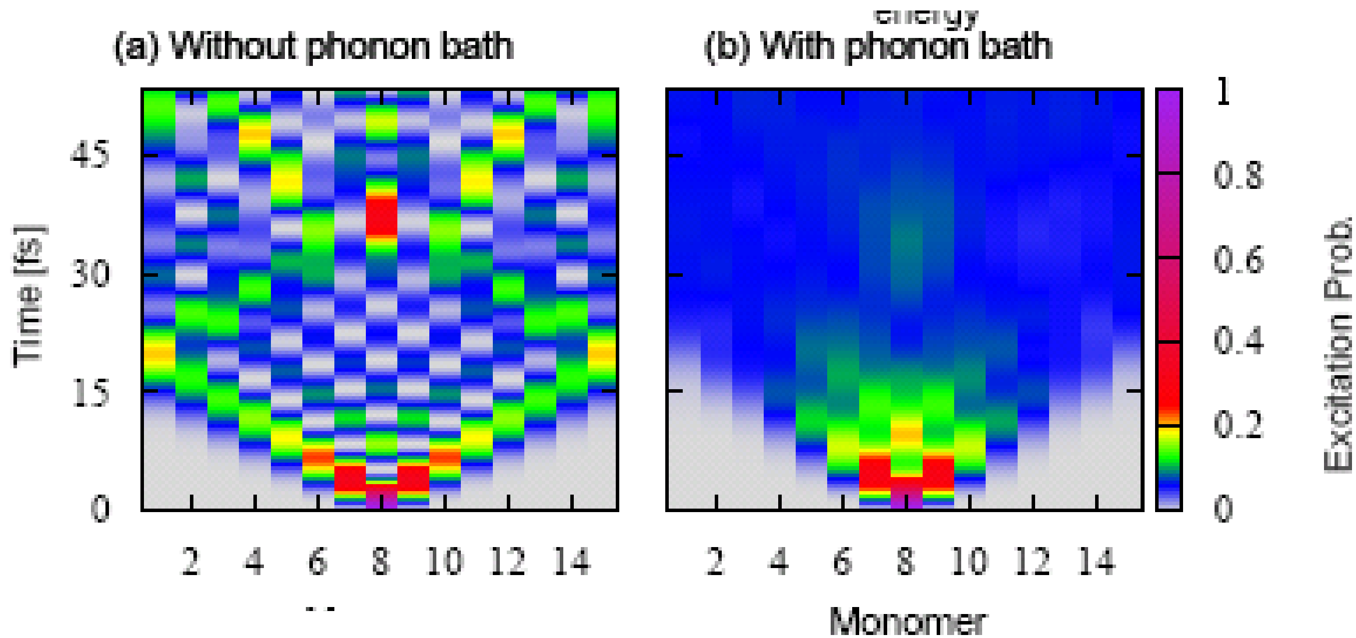


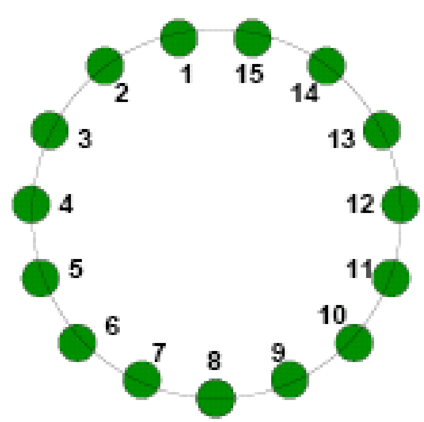




Influence of structured phonon bath on energy transfer

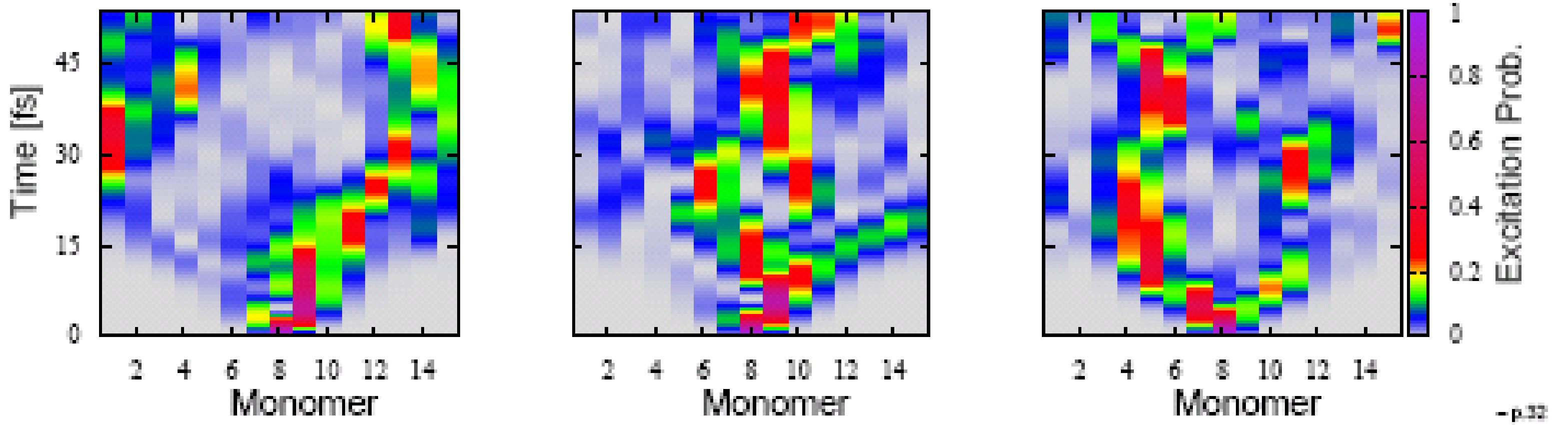
From ballistic (coherent) to Diffusive (incoherent):



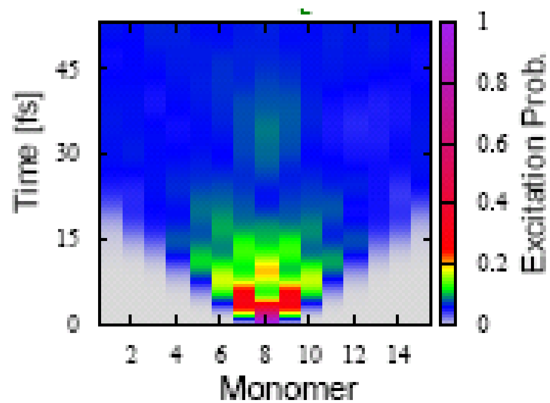


Coherence length in energy transfer:

Single realisations reveal coherence length:



Ensemble mean:



TECHNISCHE UNIVERSITÄT DRESDEN

Outline

1. Introduction: Decoherence and robust states

2. Open quantum system dynamics:
   stochastic Schrödinger equation ("applied decoherence")

3. Applications:

- Vibrational quantum dynamics on Helium nanodroplets
  [M Schlesinger, M Mudrich, F Stienekmeyer, WTS, Chem. Phys. Lett. 490 (2010) 245]
- Energy transfer dynamics in molecular aggregates
  [J Roden, A Eisfeld, W Wolff, WTS, Phys. Rev. Lett. **103,** 058301 (2009)]
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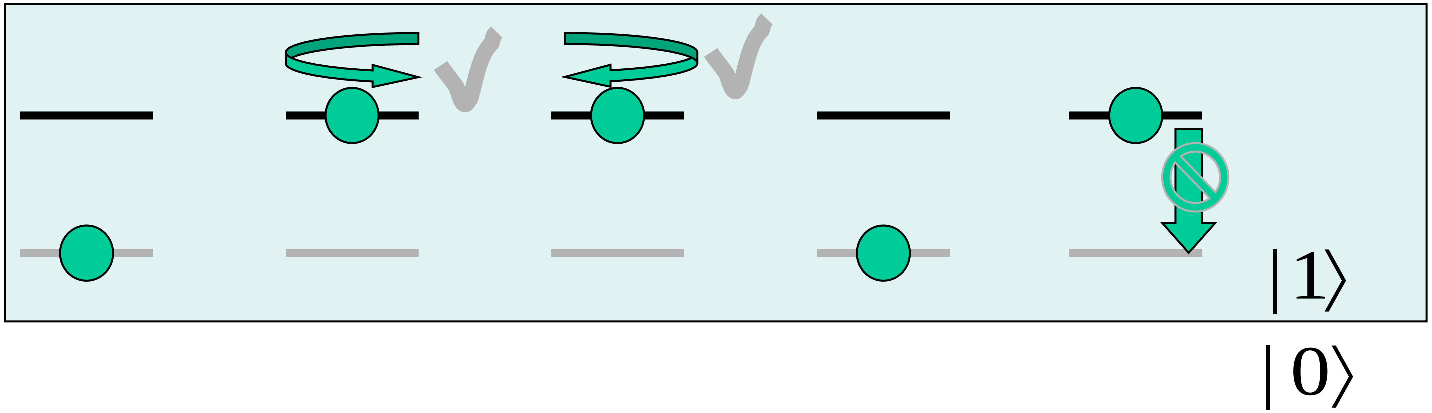
  [J Helm and WTS, Phys. Rev. A **80**, 042108 (2009), Phys Rev A **81** 042314 (2010)]

4. Conclusions

Most general „Qubit decoherence“

„pure dephasing“, no decay:



For any state $|n\rangle = |01101\rangle$ $(n = 1 \ldots 2^N)$ of the physical basis,

$$\langle n | \rho(t) | n \rangle = \text{const}$$

HUGE restriction/simplification!

(anything interesting left?)

„classical“ vs. „quantum“ decoherence

Decoherence caused by classical, fluctuating fields (Hamiltonians) („random external field“ (REF)-channels):

$$\rho(t) = \int d\mu(\omega) U_\omega(t)\rho(0)U_\omega^+(t)$$

„classical“

Decoherence caused by genuine interaction with a „quantum environment“ *(entanglement):*

$$H_{\text{tot}} = H_{\text{sys}} \otimes \mathbf{1} + H_{\text{int}} + \mathbf{1} \otimes H_{\text{env}}$$

$$\rho(t) = \text{Tr}_{\text{env}}\left[U_{\text{tot}}(t)(\rho(0) \otimes \rho_{\text{env}}(0))U_{\text{tot}}^+(t)\right]$$

„quantum“

„classical“ vs. „quantum“

Is a dephasing channel always REF?
(can pure dephasing always be described without entanglement?)

- 1 qubit: yes!
- More qubits: no!

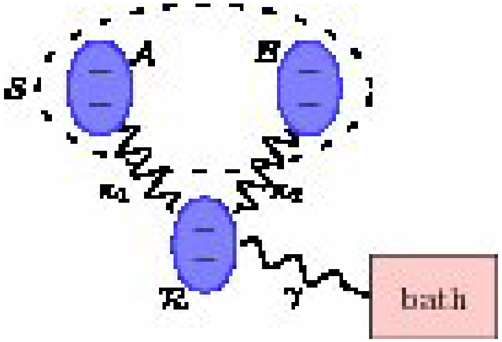
(Key idea: dephasing channels form convex set.
Find „extremal“ channels: some cannot be written as REF-channels …)

See: Landau and Streater, Linear Algebra Appl. 193: 107-127 (1993)

„true quantum“ decoherence of two qubits

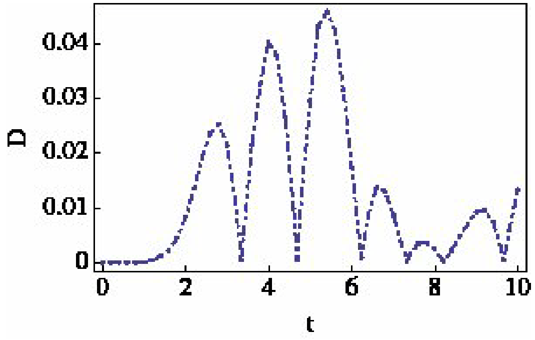
2 Qubits coupled to 1 „environmental qubit“:

$$H_{\text{tot}} = \sum_{j=1..4} |\, j \rangle\langle j \,| \otimes H_{\text{env}}^{j}$$

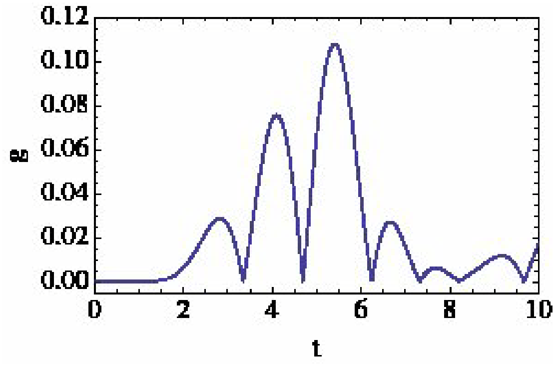


Four environmental qubit-states $|\Psi_j\rangle$ with corresponding Bloch-vector $\vec{r}_j$

This 2-qubit dephasing channel is **not REF**, if the four Bloch vectors do not point onto a plane.



Determine „distance“ of dynamics from REF dynamics



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4. Conclusions

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Conclusions

(1) Open quantum systems: borderline between “classical” and “quantum” dynamics set by efficiency of decoherence

(2) Stochastic description well suited to reveal localization of states i.e. loss of coherence: numerical tool for complex quantum dynamics

(3) Quantum fluctuations (=entanglement with environment) may also be described by classical noise.

(4) Applications to

- vibrational molecular dynamics on superfluid Helium droplets
- energy transfer dynamics in structured phonon baths
- decoherence in quantum information