

# Effective mode representation of structured environments

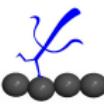
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○ School of Chemistry, Bangor University, Bangor, United Kingdom

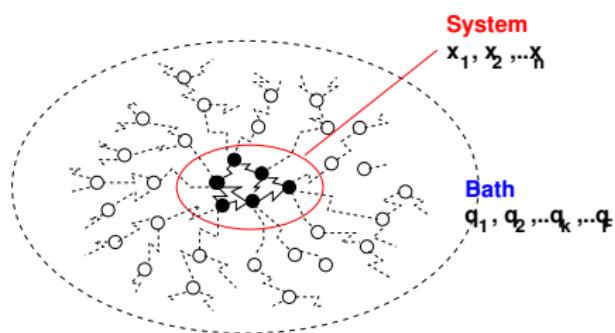
‡ Inst. of Physical and Theoretical Chemistry, Goethe University, Frankfurt, Germany

Rome - RSOSQCB, Apr 08, 2013

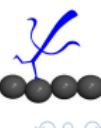


# System-bath dynamics

- **System:** relevant part, **experimentally probed**  
⇒ Few, important DOFs
- **Bath:** irrelevant part, but responsible for **decoherence** and **energy transfer**  
⇒ Large number of DOFs of no direct relevance



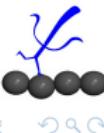
Quantum description is mandatory for inherently quantum systems and/or low-temperature baths..



# System-bath dynamics

..e.g.

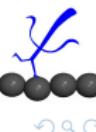
- **sticking, vibrational relaxation, and diffusion** of hydrogen atoms on cold surfaces
- **non-radiative decay** of photoexcited molecular systems
- **excitation energy and charge transfer** in condensed phase



## System-bath dynamics

$$H = \frac{p^2}{2M} + V(s) + \sum_k \left\{ \frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left( x_k - \frac{c_k s}{\omega_k^2} \right)^2 \right\}$$

- $\omega_k$  and  $c_k$  can be obtained from **atomistic** (*first principles*) potentials
- $\omega_k$  and  $c_k$  can be used to **model environments** which are known from e.g. spectroscopic data or molecular dynamics simulations
- the Hamiltonian suits well to **high-dimensional quantum dynamics calculations**, e.g. MCTDH and its variants



Basics  
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Effective modes  
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Calculations  
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# Outline

## 1 Basics

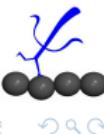
- Generalized Langevin Equation
- Independent Oscillator Model
- Spectral density

## 2 Effective modes

- Linear Chain representation
- Universal Markovian reduction
- Unraveling the memory kernel

## 3 Calculations

- LC-based MCTDH ansatz
- Summary



Basics

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Effective modes

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Calculations

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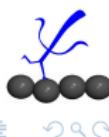
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Calculations

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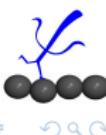
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## Effective modes

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## Calculations

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# Outline

1

## Basics

- Generalized Langevin Equation
- Independent Oscillator Model
- Spectral density

2

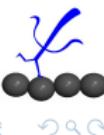
## Effective modes

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## Calculations

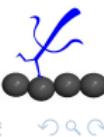
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## Generalized Langevin Equation

$$M\ddot{s}(t) + M \int_{-\infty}^{\infty} \gamma(t-t') \dot{s}(t') dt' + V'(s(t)) = \xi(t)$$

- $V'(s)$ : deterministic force
  - $\gamma(t)$ : dissipative memory kernel
  - $\xi(t)$ : Gaussian, stationary stochastic noise



## GLE: causality

$$\gamma(t) = 0 \text{ for } t < 0$$

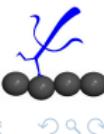
$$\tilde{\gamma}(\omega) \equiv \int_0^{\infty} \gamma(t) e^{i\omega t} dt$$

$\omega \rightarrow z$  in the upper half complex plane ( $\text{Im}z > 0$ )



General Kramers-Kronig relation

$$\tilde{\gamma}(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im}\tilde{\gamma}(\omega)}{\omega - z} d\omega = \frac{1}{\pi i} \int_{-\infty}^{+\infty} \frac{\text{Re}\tilde{\gamma}(\omega)}{\omega - z} d\omega$$



# GLE: positivity

$$\operatorname{Re} \tilde{\gamma}(\omega) \geq 0$$

$f$  external force,  $u = \langle v \rangle$  average velocity

$$M\dot{u}(t) + M \int_{-\infty}^{\infty} \gamma(t-t')u(t')dt' = f(t)$$

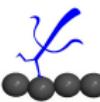
$\dot{W} = u(t)f(t)$ : power of the force  $f$

$$W = \int_{-\infty}^{\infty} u(t)^\dagger f(t) dt = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{u}(\omega)^\dagger \tilde{f}(\omega) d\omega$$

Second Law of Thermodynamics:  $W \geq 0$



$$W = \frac{M}{2\pi} \int_{-\infty}^{\infty} \tilde{u}(\omega)^\dagger \operatorname{Re} \tilde{\gamma}(\omega) \tilde{u}(\omega) d\omega \geq 0$$



## GLE: Fluctuation-Dissipation

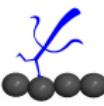
$$I(\omega) = 2Mk_B T \operatorname{Re} \tilde{\gamma}(\omega)$$

$$I(\omega) = \int_{-\infty}^{+\infty} \langle \xi(t) \xi(0) \rangle e^{i\omega t} dt$$

For a **free** particle ( $V' \equiv 0$ ) in a **stationary** state (i.e.  $t \rightarrow \infty$ )

$$C(t) = \langle v(t) v(0) \rangle = \frac{1}{2\pi M^2} \int_{-\infty}^{+\infty} \frac{I(\omega)}{| -i\omega + \tilde{\gamma}(\omega) |^2} e^{-i\omega t} d\omega$$

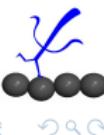
**Equipartition Law:**  $C(0) \equiv \frac{k_B T}{M}$



# GLE: Spectral density

$$J_0(\omega) = M\omega \operatorname{Re} \tilde{\gamma}(\omega)$$

- $J_0(\omega)$  is a real, odd function of  $\omega$
- $J_0(\omega) \geq 0$  for  $\omega \geq 0$  Positivity
- $\gamma(t) = \frac{\Theta(t)}{\pi M} \int_{-\infty}^{+\infty} \frac{J(\omega)}{\omega} e^{-i\omega t} d\omega$  Kramers-Kronig
- $\langle \xi(t)\xi(0) \rangle = Mk_B T \gamma(|t|)$  Fluctuation-Dissipation



# IO Hamiltonian

$$H = \frac{p^2}{2M} + V(s) + \sum_k \left\{ \frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left( x_k - \frac{c_k s}{\omega_k^2} \right)^2 \right\}$$

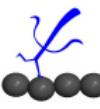
$$H \equiv H^{\text{sys}} + \Delta V(s) + H^{\text{int}} + H^{\text{bath}}$$

$H^{\text{sys}} = \frac{p^2}{2M} + V(s)$ : system Hamiltonian

$\Delta V(s) = \frac{1}{2} \left( \sum_k \frac{c_k^2}{\omega_k^2} \right) s^2 = \frac{1}{2} M \delta \Omega^2 s^2$ : "renormalization" potential

$H^{\text{int}} = - \sum_k c_k x_k s$ : interaction term

$H^{\text{bath}} = \sum_k \frac{p_k^2}{2} + \frac{\omega_k^2}{2} x_k^2$ : "bath" Hamiltonian





# IO Hamiltonian

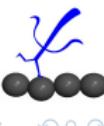
$$M\ddot{s}(t) + M \int_{t_0}^{\infty} \gamma(t-t') \dot{s}(t') dt' + V'(s(t)) = \xi(t)$$

$$\rho(x_1, x_2, \dots, p_1, p_2, \dots) = \frac{1}{Z} e^{-\beta H_{z_0}^{\text{env}}}$$

$$H_{z_0}^{\text{env}} = \sum_k \left\{ \frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left( x_k - \frac{c_k z(t_0)}{\omega_k^2} \right)^2 \right\}$$

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t) \xi(0) \rangle = \frac{k_B T}{M} \kappa(t)$$

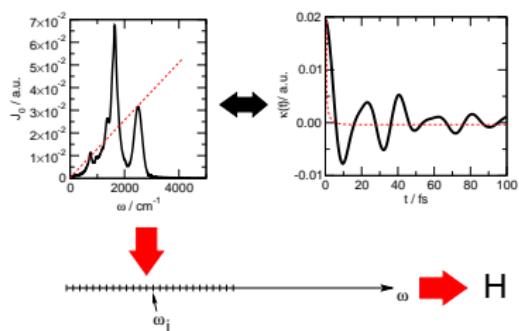
$$\Rightarrow J_0(\omega) = \frac{\pi}{2} \sum_k \frac{c_k^2}{\omega_k} (\delta(\omega - \omega_k) - \delta(\omega + \omega_k))$$



# IO Hamiltonian

Conversely..

$$J_0(\omega) \Rightarrow \omega_k = k\Delta\omega \text{ and } c_k = \sqrt{\frac{2\omega_k \Delta\omega J_0(\omega_k)}{\pi}} \quad (k = 1, \dots, N)$$



..discretized model which is equivalent to the GLE for times less than the Poincaré recurrence time,

$$t < T_{rec} = \frac{2\pi}{\Delta\omega} = \frac{2\pi}{\omega_N} N$$



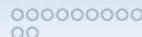
Basics



Effective modes

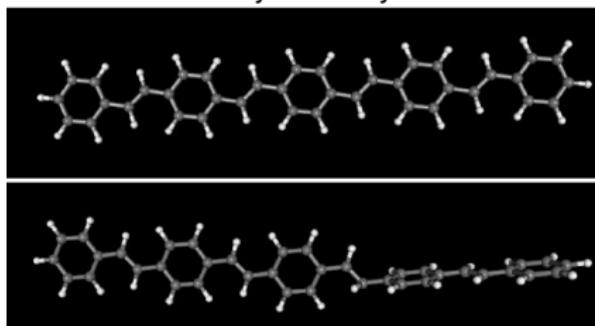


Calculations



# SD: torsional dynamics in PPV oligomers

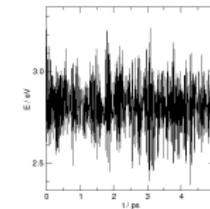
4-Phenylene-Vinylene



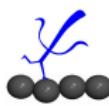
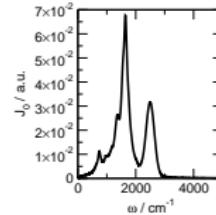
Canonical Molecular Dynamics at temperature  $T$

$\Rightarrow \langle \xi(t) \xi(0) \rangle$

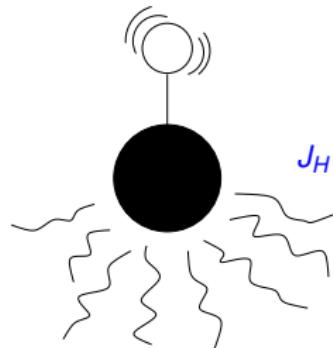
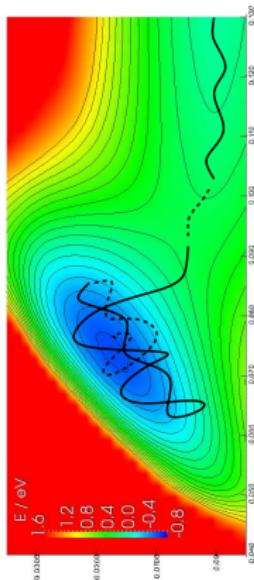
F. Sterpone *et al.*, Z. Phys. Chem., 225 (2011) 441



$$\langle \xi(t) \xi(0) \rangle \xrightarrow{\text{FT}} I(\omega) \Rightarrow J(\omega) = \frac{\omega}{2k_B T} I(\omega)$$



# SD: H chemisorption on graphene



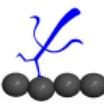
Canonical MD (AIMD in the near future):  $\delta z_H^i(t)$

$$\delta \tilde{z}_H^i(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} \delta z_H^i(t) dt$$

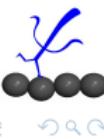
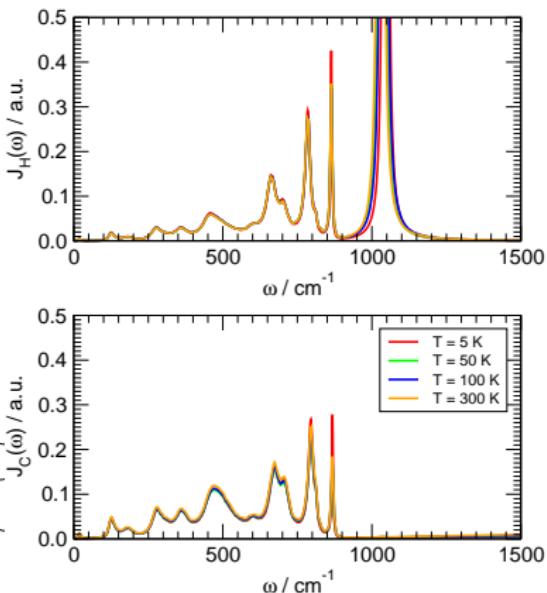
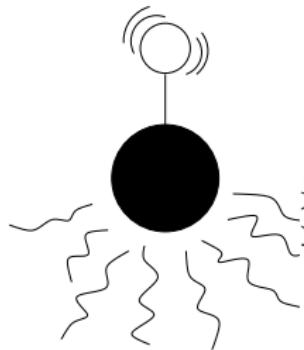
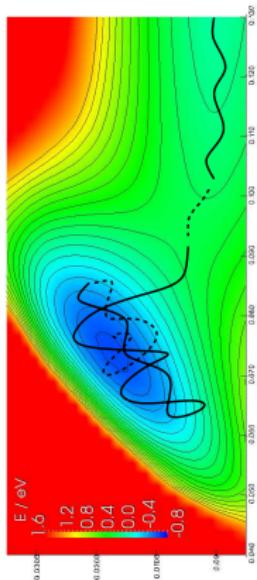
$$\tilde{C}(\omega) = \frac{1}{N} \sum_{i=1}^N |\delta \tilde{z}_H^i(\omega)|^2$$

$$J_H(\omega) = k_B T \frac{\sigma(\omega)}{|S^+(\omega)|^2} \quad \sigma(\omega) = \tilde{C}(\omega)\omega/2$$

$$\dots \Rightarrow J_C(\omega)$$



# SD: H chemisorption on graphene



Basics  
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Effective modes  
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Calculations  
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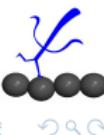
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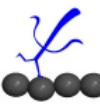


# Effective modes

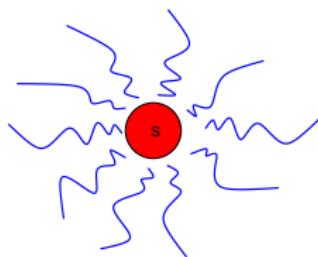
$$H^{\text{int}} = - \sum_k c_k x_k s = -D_0 X_1 s$$

- $D_0^2 = \sum_k c_k^2$ : effective mode coupling
- $X_1 = \sum_k x_k T_{k1}$ , ( $T_{k1} \equiv c_k$ ): effective mode
- $(X_1, X_2, \dots, X_N) = (x_1, x_2, \dots, x_N) T$ : (quasi-arbitrary) orthogonal transformation
- $(T^t \omega^2 T)_{ij} = \Omega_{ij}^2$   $i, j = 2, N$ : frequency matrix of the “residual” bath

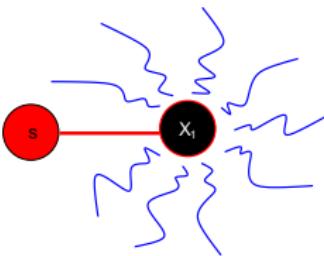
$\Rightarrow T$  can be fixed by requiring  $\Omega_{ij}^2 = \delta_{ij} \bar{\Omega}_i^2$



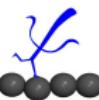
# Effective modes



$s$	$x_1$	$x_2$	$x_3$	..	..	$x_k$
$s$	$-c_1$	$-c_2$	$-c_3$	..	..	$-c_k$
$x_1$	$-c_1$	$\omega_1^2$	0	0	..	..
$x_2$	$-c_2$	0	$\omega_2^2$	0	..	..
$x_3$	$-c_3$	0	0	$\omega_3^2$	..	..
..	..	..	..	..	..	..
..	..	..	..	..	..	..
$x_k$	$-c_k$	0	0	0	..	$\omega_k^2$



$s$	$X_1$	$X_2$	$X_3$	..	..	$X_k$
$s$	$-D_0$	0	0	..	..	0
$X_1$	$-D_0$	$\Omega_1^2$	$-C_2$	$-C_3$	..	$-C_k$
$X_2$	0	$-C_2$	$\bar{\Omega}_2^2$	0	..	..
$X_3$	0	$-C_3$	0	$\bar{\Omega}_3^2$	..	..
..	..	..	..	..	..	..
..	..	..	..	..	..	..
$X_k$	0	$-C_k$	0	0	..	$\bar{\Omega}_k^2$



## Effective modes

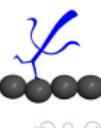
$$H = \left( \frac{p^2}{2M} + V(s) \right) + \Delta V(s) - D_0 s X_1 + \left( \frac{P_1^2}{2} + \frac{\Omega_1^2 X_1^2}{2} \right) - X_1 \sum_{k=2}^N C_k X_k + \\ + \sum_{k=2}^N \left( \frac{P_k^2}{2} + \frac{\bar{\Omega}_k^2 X_k^2}{2} \right)$$

In the **continuum limit**  $N \rightarrow \infty$  (with  $N\Delta\omega \equiv \omega_c$ ):

$$D_0^2 \rightarrow \frac{2}{\pi} \int_0^{+\infty} J_0(\omega) \omega d\omega$$

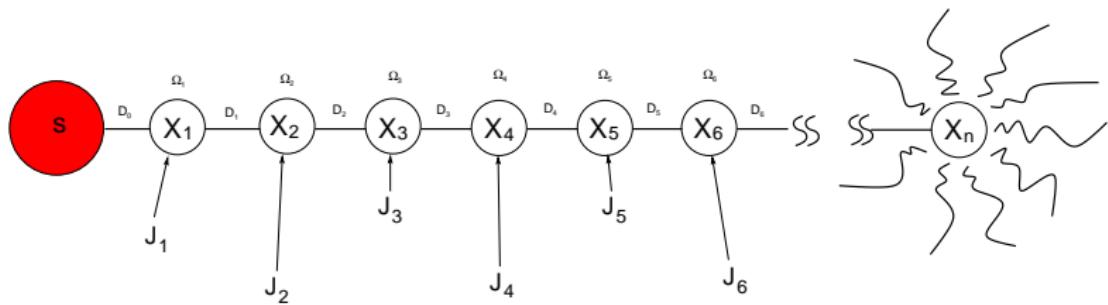
$$\Omega_1^2 \rightarrow \frac{2}{\pi D_0^2} \int_0^{+\infty} J_0(\omega) \omega^3 d\omega$$

..and the procedure can be **indefinitely** iterated  
**without** knowing the eigenfrequencies at each step

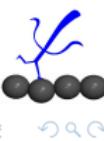


## Effective modes

$$H = \left( \frac{p^2}{2M} + V(s) \right) + \Delta V(s) - D_0 s X_1 - \sum_{n=1}^{\infty} D_n X_n X_{n+1} + \sum_{n=1}^{\infty} \left( \frac{P_n^2}{2} + \frac{\Omega_n^2 X_n^2}{2} \right)$$

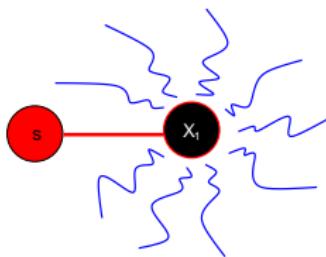


- How to obtain  $J_{n+1}(\omega)$  from  $J_n(\omega)$ ?
  - What is the **limiting** spectral density?



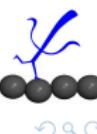
## A recursive relation

$$\begin{aligned}
 H = & \left( \frac{p^2}{2M} + V(s) \right) + \Delta V(s) - D_0 s X_1 + \left( \frac{P_1^2}{2} + \frac{\Omega_1^2 X_1^2}{2} \right) - X_1 \sum_{k=2}^N C_k X_k + \\
 & + \sum_{k=2}^N \left( \frac{P_k^2}{2} + \frac{\bar{\Omega}_k^2 X_k^2}{2} \right)
 \end{aligned}$$

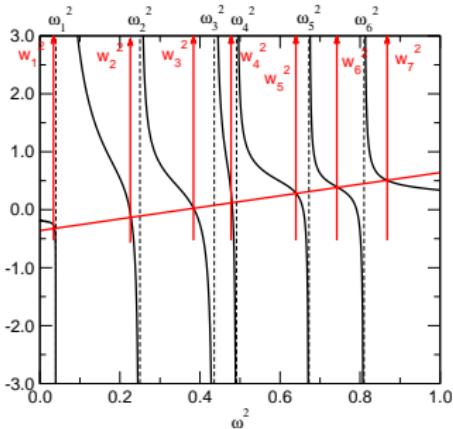


We can use the **Leggett's trick**<sup>1</sup> to obtain  $J_0(\omega)$  from  $J_1(\omega)$

<sup>1</sup> A.J. Leggett, *Phys. Rev. B* **30**, 1208 (1984); A. Garg, J.N. Onuchic and V. Ambegaokar, *J. Chem. Phys.* **83**, 4491 (1985); K.H. Hughes, C.D. Christ, and I. Burghardt, *J. Chem. Phys.* **131**, 024109 (2009); *ibid.* **131**, 124108 (2009)



# A recursive relation



$$\omega_1^2 \leq \bar{\Omega}_2^2 \leq \omega_2^2 \leq \bar{\Omega}_3^2 \dots \bar{\Omega}_N^2 \leq \omega_N^2$$

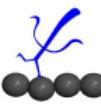
$$J_0(\omega) = \lim_{\epsilon \rightarrow 0} \operatorname{Im} W_0(\omega + i\epsilon)$$

$$W_0(z) = \frac{D_0^2}{\Omega_1^2 - z^2 - W_1(z)}$$

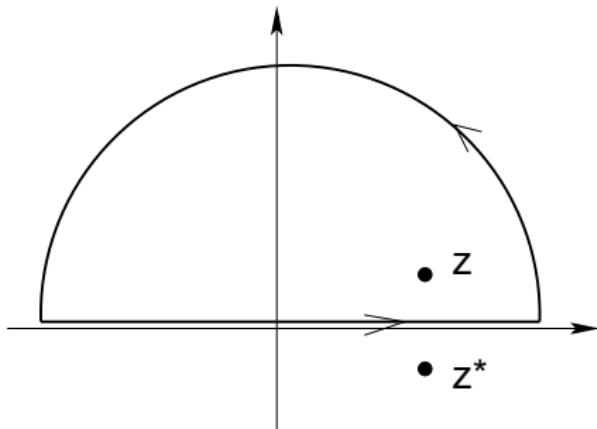
where

$$W_1(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{J_1(\omega)}{\omega - z} d\omega$$

$$(J_1(\omega) = \lim_{\epsilon \rightarrow 0} \operatorname{Im} W_1(\omega + i\epsilon))$$



## A recursive relation



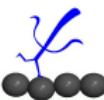
$$f(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im} f(\omega)}{\omega - z} d\omega$$

$$J_0(\omega) = \lim_{\epsilon \rightarrow 0} \text{Im} W_0(\omega + i\epsilon)$$

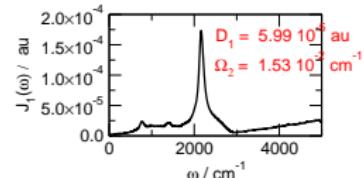
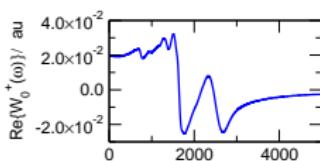
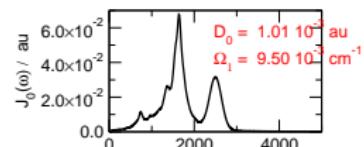
$$W_0(z) = \frac{D_0^2}{\Omega_1^2 - z^2 - W_1(z)}$$

$W_0(z)$  is **analytic** in the u.h.p  
and vanishes as  $z^{-2}$

$$W_0(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{J_0(\omega)}{\omega - z} d\omega$$



# A recursive relation



$$D_n^2 = \frac{2}{\pi} \int_0^{+\infty} J_n(\omega) \omega d\omega$$

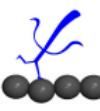
$$\Omega_{n+1}^2 = \frac{2}{\pi D_n^2} \int_0^{+\infty} J_n(\omega) \omega^3 d\omega$$

$$W_n(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{J_n(\omega)}{\omega - z} d\omega$$

$$W_{n+1}(z) = \Omega_{n+1}^2 - z^2 - \frac{D_n^2}{W_n(z)}$$

$$J_{n+1}(\omega) = \lim_{\epsilon \rightarrow 0} \text{Im} W_{n+1}(\omega + i\epsilon)$$

R. Martinazzo, B. Vacchini, K.H. Hughes and I. Burghardt, *J. Chem. Phys.* **134**, 011101 (2011)



Basics



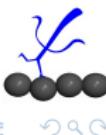
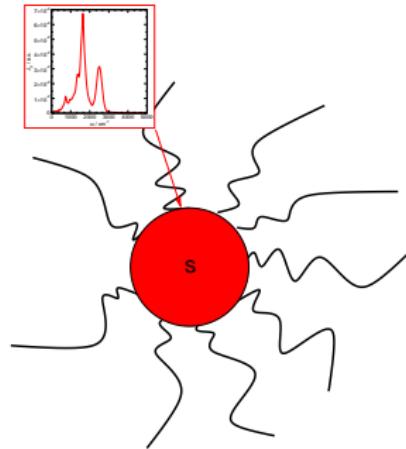
Effective modes



Calculations



# A recursive relation



Basics



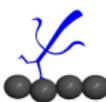
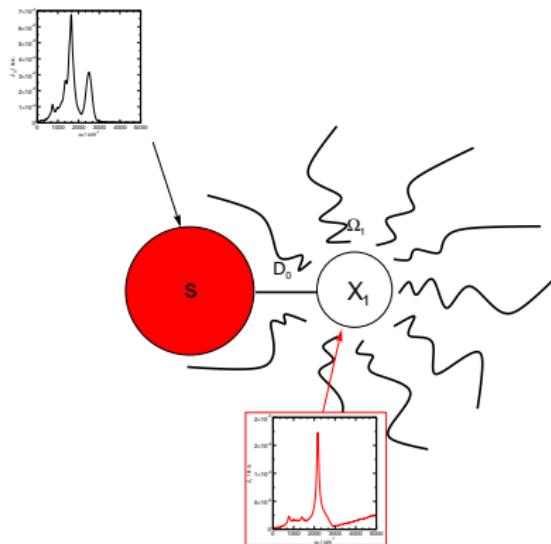
Effective modes



Calculations



# A recursive relation



Basics



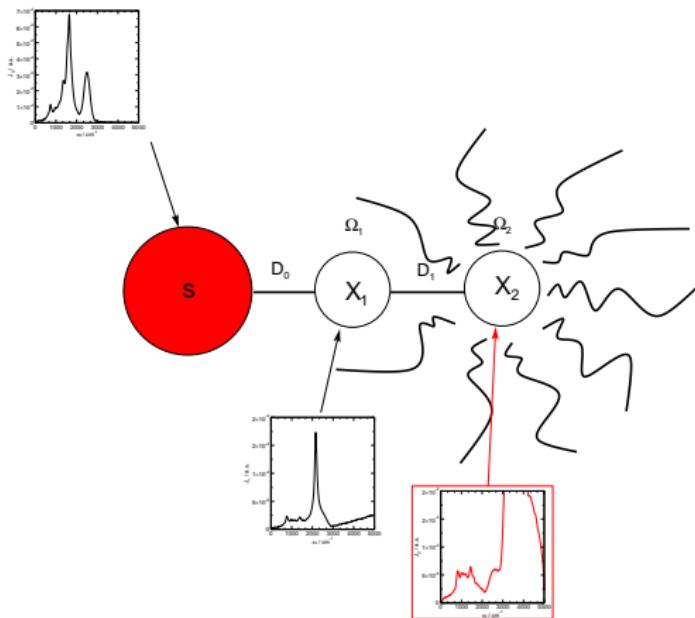
Effective modes



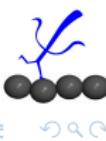
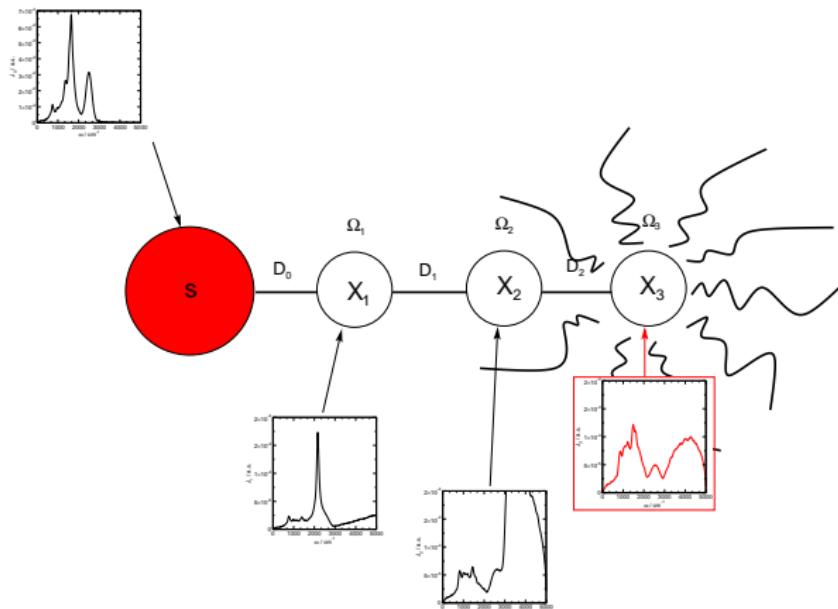
Calculations



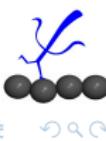
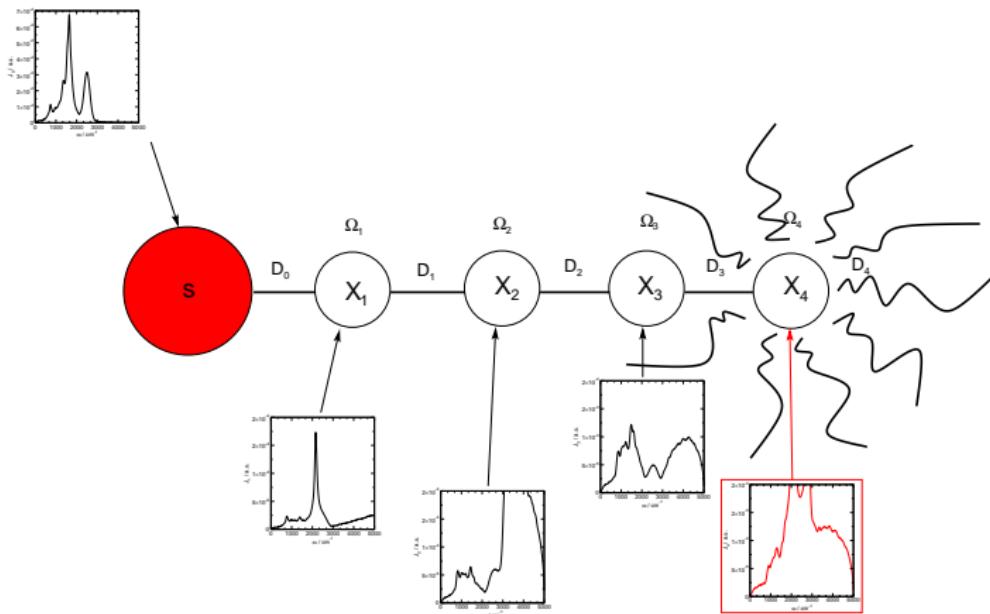
## A recursive relation



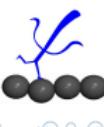
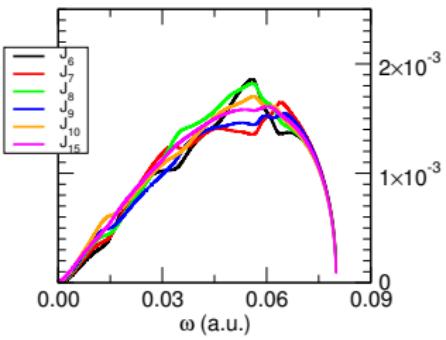
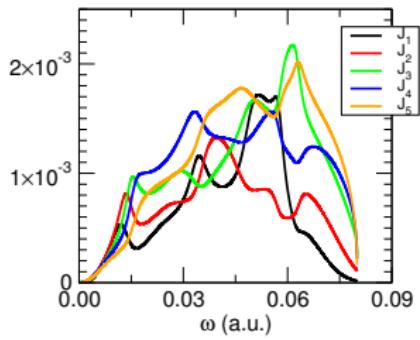
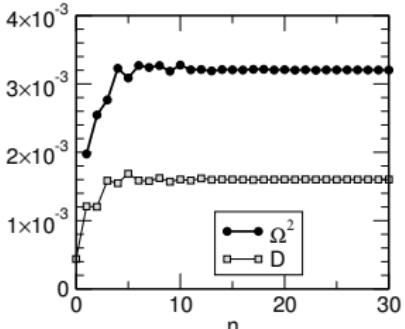
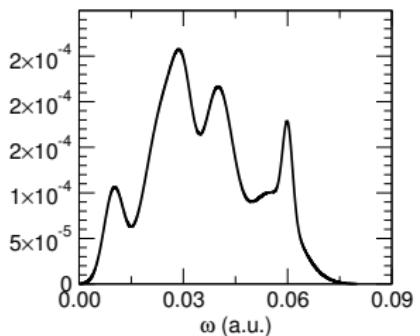
# A recursive relation



# A recursive relation

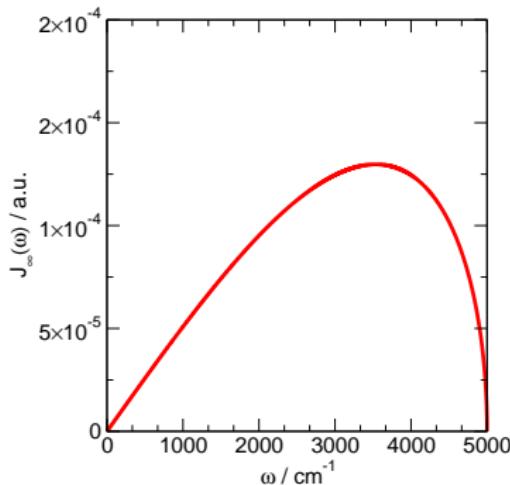


# A recursive relation



# Limiting behaviour

Provided  $D_n, \Omega_n \rightarrow D, \Omega$   
the **limiting chain** is **uniform**



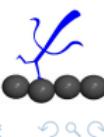
$$W_{\infty}(z) = \Omega^2 - z^2 - \frac{D^2}{W_{\infty}(z)}$$

i.e. if  $J_0(\omega) > 0$  in  $(0, +\omega_c)$  one gets the **Rubin SD**

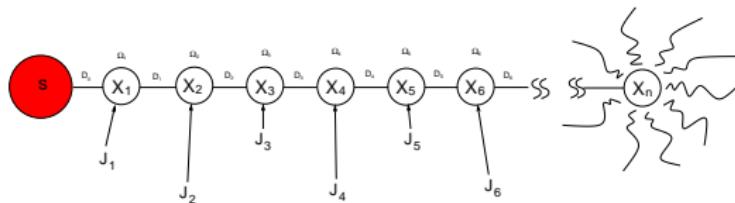
$$J_{\infty}(\omega) = \frac{\omega \omega_c}{2} \sqrt{1 - \frac{\omega^2}{\omega_c^2}} \Theta(\omega_c - \omega)$$

where  $\Omega^2 = 2D = \frac{\omega_c^2}{2}$  and the chain is **translationally invariant**

**(Quasi)-Ohmic behaviour!**



## Short-time behaviour



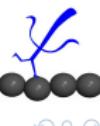
$$J_{n+1}(\omega) \Rightarrow J_n(\omega), \dots \Rightarrow J_0(\omega)$$

K.H. Hughes, C.D. Christ, and I. Burghardt, *J. Chem. Phys.* **131**, 024109 (2009); *ibid.* **131**, 124108 (2009)

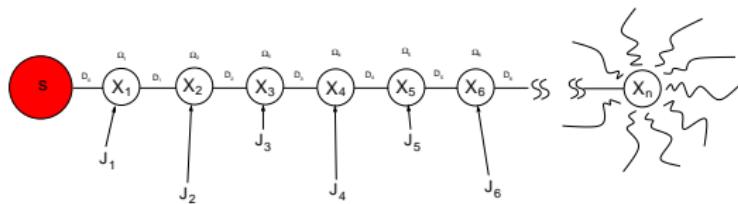
$$W_0(z) = \frac{D_0^2}{\Omega_1^2 - z^2 - \frac{D_1^2}{\Omega_2^2 - z^2 - \frac{D_2^2}{\Omega_3^2 - z^2 - W_4(z)}}}$$

What if **truncating** or **closing** the chain after introducing  $n$  modes?

$$W_{n+1} \rightarrow \dots \Rightarrow W_0(z) \rightarrow W_0(z) + \delta W_0(z)$$



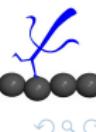
## Short-time behaviour



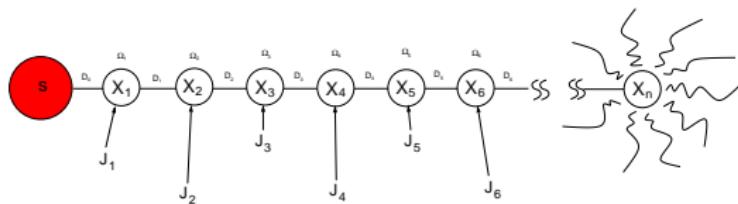
For  $z \rightarrow \infty$  where  $W_n(z) \rightarrow 0$ , 'errors' propagate as

$$\delta W_{n-1}(z) \approx D_{n-1}^2 \left(\frac{1}{z}\right)^4 \delta W_n(z)$$

i.e. with ***n* modes**  $W_0(z) = a_2 \left(\frac{1}{z}\right)^2 + a_4 \left(\frac{1}{z}\right)^4 + \dots$  is correct up to the ***4n*-th order**



## Short-time behaviour



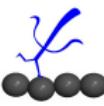
$$(|z| > \omega_c) \quad W_0(z) = \sum_{m=1}^{\infty} \mu_{2m-1}^{(0)} \left(\frac{1}{z}\right)^{2m} \quad \text{where} \quad \mu_k^{(0)} = \frac{2}{\pi} \int_0^{\infty} J_0(\omega) \omega^k d\omega$$

$$\{\mu_1^{(0)}, \mu_3^{(0)}\} \Leftarrow \{D_0, \Omega_1\}$$

$$\{\mu_1^{(0)}, \mu_3^{(0)}, \mu_5^{(0)}, \mu_7^{(0)}\} \Leftarrow \{D_0, \Omega_1; D_1, \Omega_2\}$$

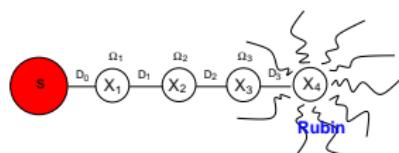
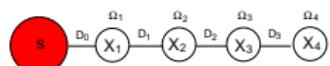
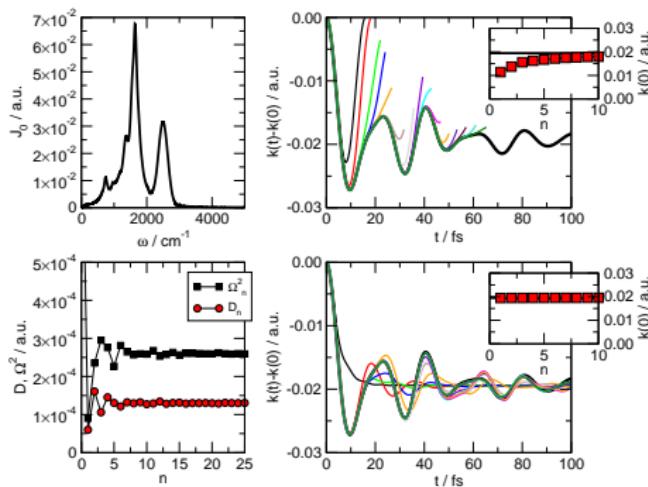
...

$$\{\mu_{2m-1}^{(0)}\}_{m=1}^{2n} \Leftarrow \{D_m, \Omega_{m+1}\}_{m=1}^n$$



# Short-time behaviour

$$\kappa(t) - \kappa(0) = \kappa_n(t) - \kappa_n(0) + \mathcal{O}(t^{4n})$$



R. Martinazzo, K.H. Hughes and I. Burghardt, *Phys. Rev. E* **84**, 030102(R) (2011)

Basics



Effective modes

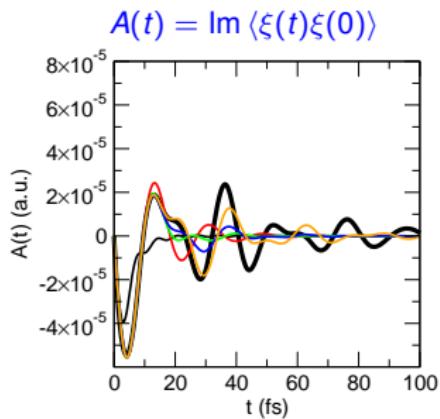
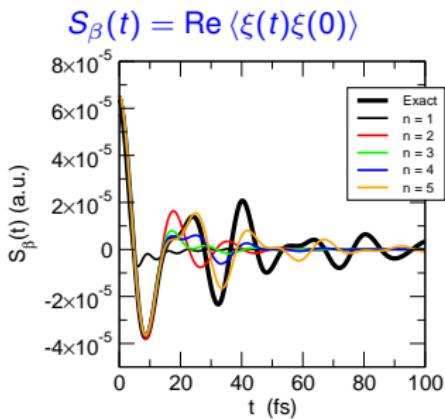


Calculations

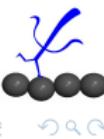


## Short-time behaviour

$$\kappa(t) - \kappa(0) = \kappa_n(t) - \kappa_n(0) + \mathcal{O}(t^{4n})$$



R. Martinazzo, K.H. Hughes and I. Burghardt, *Phys. Rev. E* **84**, 030102(R) (2011)



# Outline

## 1 Basics

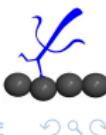
- Generalized Langevin Equation
- Independent Oscillator Model
- Spectral density

## 2 Effective modes

- Linear Chain representation
- Universal Markovian reduction
- Unraveling the memory kernel

## 3 Calculations

- LC-based MCTDH ansatz
- Summary



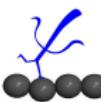
# Quantum dynamics with MCTDH

$$\Psi(x_1, x_2, \dots, x_N) = \sum_{i_1, i_2, \dots, i_N} c_{i_1, i_2, \dots, i_N} \phi_{i_1}^{(1)}(x_1) \phi_{i_2}^{(2)}(x_2) \dots \phi_{i_N}^{(N)}(x_N)$$

- $c_{i_1, i_2, \dots, i_N} = c_{i_1, i_2, \dots, i_N}(t)$  are time-evolving **amplitudes** for the configurations
- $\phi_i^{(k)}(x) = \phi_i^{(k)}(x, t)$  are time-evolving **single-particle functions**
- $\langle \phi_i^{(k)} | \phi_j^{(k)} \rangle = \delta_{ij}$  for any  $k = 1, \dots, N$

Equations of motion from DF variational principle

M.H. Beck, A. Jackle, G.A. Worth, H.-D. Meyer, *Phys. Rep.* **324** 1 (2000)



# A simple MCTDH *ansatz*

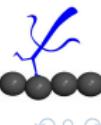
System + Primary + Secondary modes

$$\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}) = \sum_{IJ} c_{IJ} \phi_{i_1}(x_1) \dots \phi_{j_1}(y_1) \dots \psi_1(z_1) \psi_2(z_2) \dots \psi_N(z_N)$$

- Linear scaling
- Accuracy depends on the primary modes only
- Recurrence times can be enormously increased
- Effective-mode based variants for G-MCTDH<sup>1</sup>, LCSA<sup>2</sup>, etc. are possible

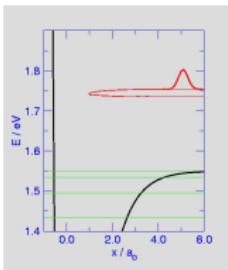
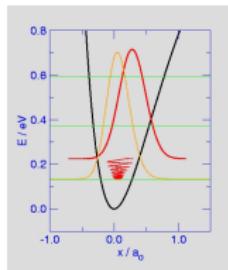
[1] I. Burghardt *et al.*, *J. Chem. Phys.* **111** 29727 (1999)

[1] R. Martinazzo *et al.*, *J. Chem. Phys.* **125** 194102 (2006)

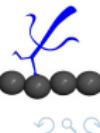


# Model systems

$$H = \frac{p^2}{2M} + V(s) + \sum_k \left\{ \frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left( x_k - \frac{c_k f(s)}{\omega_k^2} \right)^2 \right\}$$



- $f(s) = \frac{1-e^{-\alpha s}}{\alpha} \rightarrow s$  for  $s \rightarrow 0$
- $V(s) = D_e e^{-\alpha s} (e^{-\alpha s} - 2)$ ,  
with  $D_e = 1.55\text{eV}$
- $M = m_H$
- Several  $J(\omega)s$



Basics



Effective modes



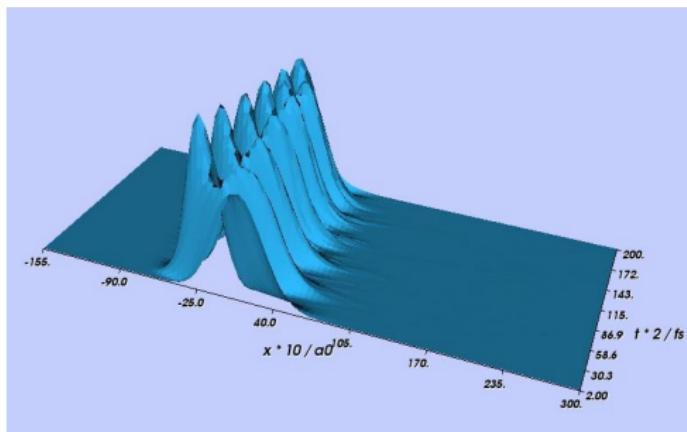
Calculations



# Model systems

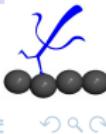
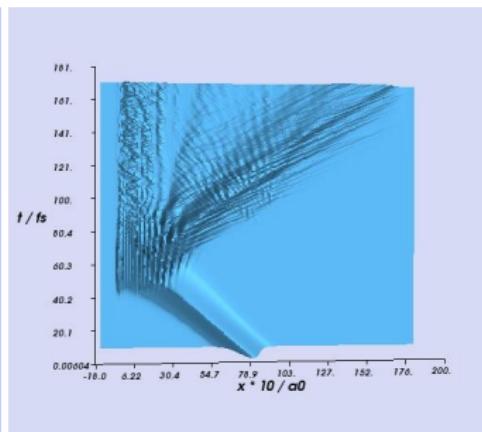
## Vibrational relaxation

$$\rho_t(s|s)$$



## Sticking

$$\rho_t(s|s)$$



Basics

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○○○○  
○○○

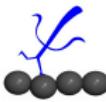
Effective modes

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Calculations

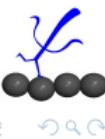
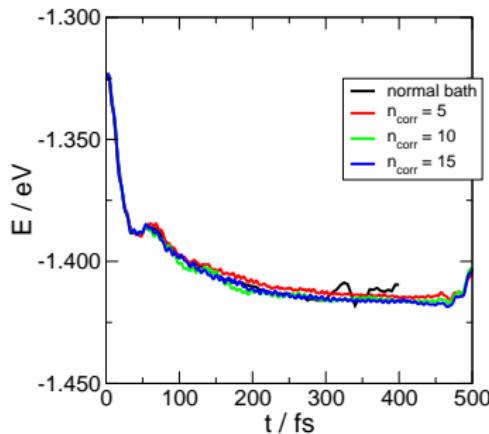
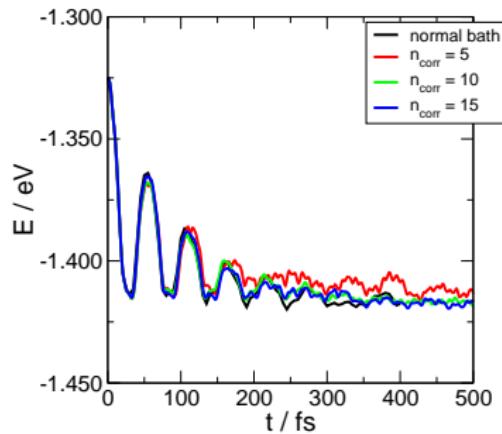
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# Chain dynamics: an example



## A simple MCTDH *ansatz*: vib relax

## Non-Markovian SDs, $N = 100$



Basics

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○○○  
○○○

Effective modes

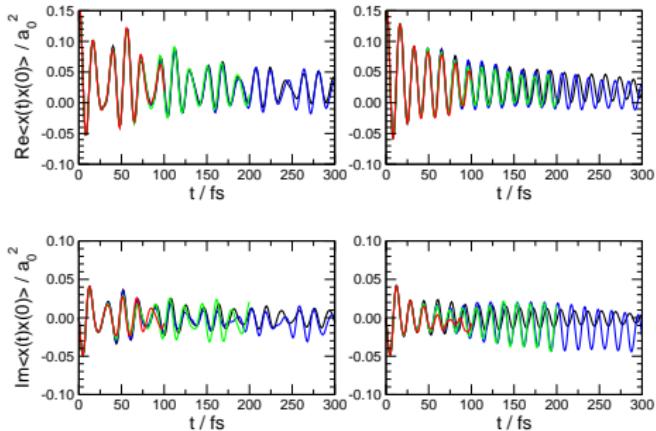
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Calculations

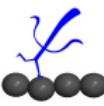
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○○○

# A simple MCTDH *ansatz*: vib relax

Non-Markovian SDs,  $N = 100$



M. Bonfanti, G.F. Tantardini, K.H. Hughes, R. Martinazzo and I. Burghardt, *J. Phys. Chem. A*, 11406 116 (2012)



Basics



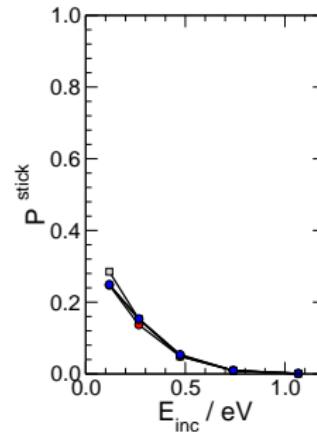
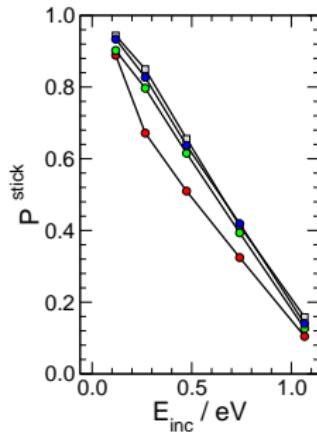
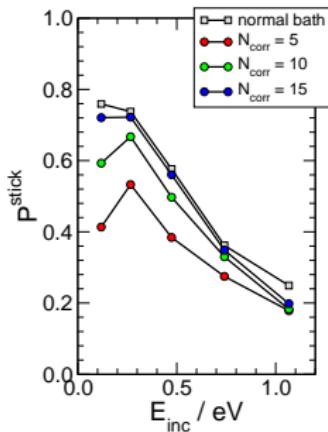
Effective modes



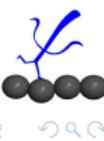
Calculations



# A simple MCTDH *ansatz*: sticking



M. Bonfanti, G.F. Tantardini, K.H. Hughes, R. Martinazzo and I. Burghardt, *J. Phys. Chem. A*, 11406 116 (2012)



Basics

A 3x5 grid of 15 small circles, arranged in three rows and five columns.

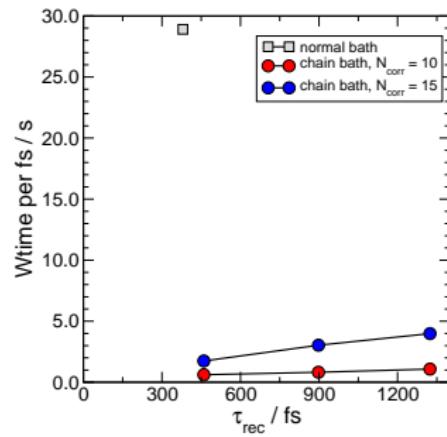
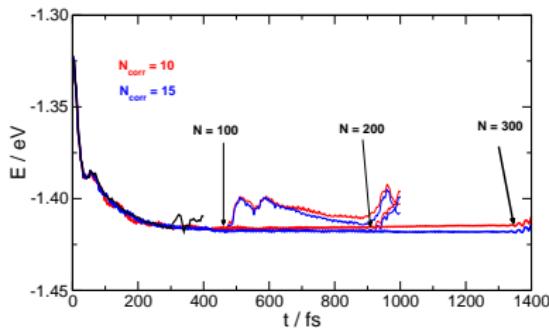
## Effective modes

A diagram consisting of three rows of small circles. The top row contains 3 circles, the middle row contains 8 circles, and the bottom row contains 3 circles, representing the numbers 3, 8, and 3 respectively.

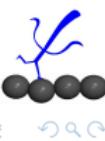
## Calculations

10

## A simple MCTDH *ansatz*: timings

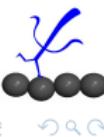


M. Bonfanti, G.F. Tantardini, K.H. Hughes, R. Martinazzo and I. Burghardt, *J. Phys. Chem. A*, 11406–116 (2012)



## Summary

- The IO model can be handled with **high-dimensional quantum** methods
- **Effective modes** considerably enlarge the range of applicability of quantum IO models
- **Classical mechanics** can be used to build a **quantum** IO model
- No need to build a potential: (equilibrium) **AIMD** can be used to obtain the necessary **correlation functions**



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**Thank you for your attention!**

