

Basics

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Effective modes

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Calculations

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Effective mode representation of quantum mechanical energy transfer to surfaces

Rocco Martinazzo

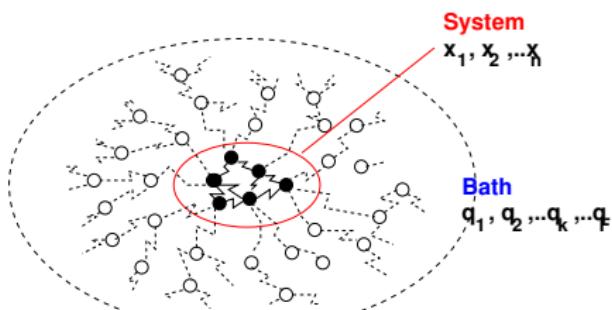
Dipartimento di Chimica Fisica ed Elettrochimica
Università degli Studi, Milano, Italy

Universiteit Leiden, Nov 25, 2011

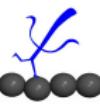


System-bath dynamics

- **System:** relevant part, experimentally probed
 \Rightarrow Few, important DOFs
- **Bath:** irrelevant part, but responsible for energy transfer
 \Rightarrow Large number of DOFs of non-direct relevance



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



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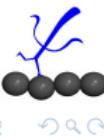
Calculations

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System-bath dynamics

..e.g. in surface science

- **sticking** of hydrogen atoms on cold surfaces
- **vibrational relaxation** of light adsorbates at surfaces
- surface **diffusion** of hydrogen atoms at low temperatures



System-bath dynamics

Reduced equations of motion

First **project**, then **evolve**

- Density operator, $\rho^{sb} \rightarrow \rho^{sys}$
- (Approximate) equation of motion for $\rho_{\sim}^{sys}(t)$

..also REOM for system observables if Heisenberg picture is preferred

Unitary (approximate) evolution

First **evolve**, then **project**

- Approximate time-evolution of the whole system $\rho_{\sim}^{sb}(t)$
- Project whole state onto system space, $\rho^{sb} \rightarrow \rho^{sys}$

..also exact evolution if the bath is not too large

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Outline

1 Basics

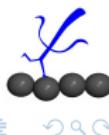
- Generalized Langevin Equation
- Independent Oscillator Model

2 Effective modes

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

3 Calculations

- LC-based MCTDH ansatz
- Outlook



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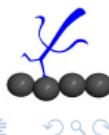
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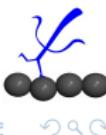
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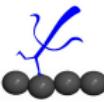
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Generalized Langevin Equation

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

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



GLE: causality

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

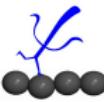
$$\tilde{\gamma}(\omega) \equiv \int_0^{\infty} \gamma(t) e^{i\omega t} dt$$

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



Kramers-Kronig relation(s)

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



GLE: positivity

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

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

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

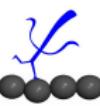
$\dot{W} = u(t)f(t)$: power of the force f

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

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

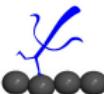
$$I(\omega) = 2Mk_B T \operatorname{Re} \tilde{\gamma}(\omega)$$

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

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

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

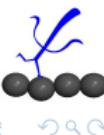
Equipartition Law: $C(0) \equiv \frac{k_B T}{M}$



GLE: Spectral density

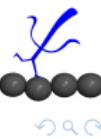
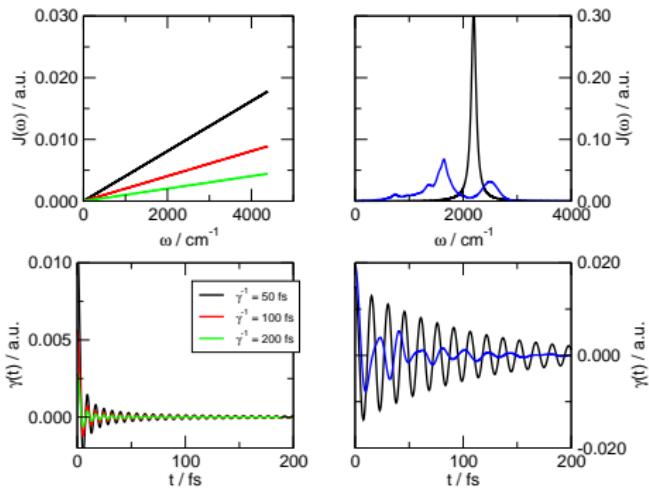
$$J(\omega) = M\omega \operatorname{Re} \tilde{\gamma}(\omega)$$

- $J(\omega)$ is a real, **odd** function of ω
- $J(\omega) \geq 0$ 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



GLE: Spectral density

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



Basics



Effective modes



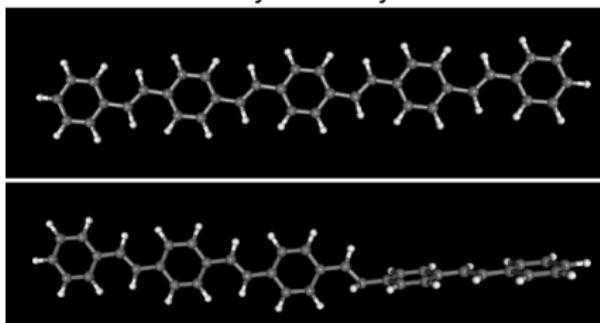
Calculations



GLE: Spectral density

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

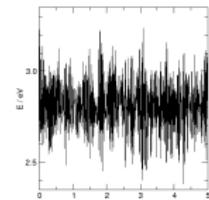
4-Phenylene-Vinylene



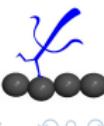
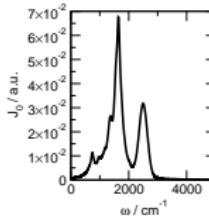
Canonical Molecular Dynamics at temperature T

$\Rightarrow \xi(t)$

F. Stpone, *unpublished*



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



IO Hamiltonian

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

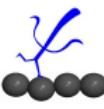
$$H \equiv H^{\text{sys}} + \Delta V(s) + H^{\text{int}} + H^{\text{bath}}$$

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

Classical (or Heisenberg quantum) equations of motions

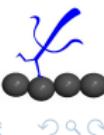
$$\ddot{s} = -\frac{\partial V}{\partial s} + M\delta\Omega^2 z + \sum_k c_k x_k$$

$$\ddot{x}_k = -\omega_k^2 x_k + c_k s$$

$F_{\text{ren}}^{\text{env}} = \sum_k c_k x_k$: force exerted by the bath on the system

$c_k s$: force felt by the k-th mode

⇒ Each $k - th$ HO is a forced Harmonic oscillator



IO Hamiltonian

Solving for $x_k(t)$...

$$x_k(t) = x(t_0) \cos(\omega_k t) + \frac{\dot{x}_k(t_0)}{\omega_k} \sin(\omega_k t) + \int_{t_0}^{+\infty} \Theta(t - t') \frac{\sin(\omega_k(t - t'))}{\omega_k} c_k z(t') dt'$$



"free solution"

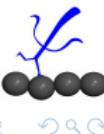


"response"

$x_k^0(t)$: free solution of the HO with initial conditions $x_k(t_0), \dot{x}_k(t_0)$

$\delta x_k(t)$: response of the HO to the external perturbation

$$F^{\text{env}} = \sum_k c_k x_k^0(t) + \sum_k c_k \delta x_k(t)$$



IO Hamiltonian

Upon rearranging

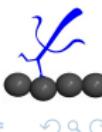
$$F^{\text{env}} = \xi(t) - M \int_{t_0}^{+\infty} \gamma(t-t') \dot{s}(t') dt'$$

where

$$\xi(t) = \sum_k \left\{ \left[x_k(t_0) - \frac{c_k}{\omega_k^2} s(t_0) \right] \cos(\omega_k t) + \frac{\dot{x}_k(t_0)}{\omega_k} \sin(\omega_k t) \right\} c_k$$

$$M \kappa(t) = \sum_k \frac{c_k^2}{\omega_k^2} \cos(\omega_k t)$$

$$\gamma(t) = \Theta(t) \kappa(t)$$



IO Hamiltonian

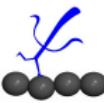
$$M\ddot{s}(t) + M \int_{t_0}^{\infty} \gamma(t-t') \dot{s}(t') dt' + V'(s(t)) = \xi(t)$$

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

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

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

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



IO Hamiltonian

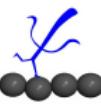
$$J(\omega) = \frac{\pi}{2} \sum_k \frac{c_k^2}{\omega_k} (\delta(\omega - \omega_k) - \delta(\omega + \omega_k))$$

Conversely, for a given GLE with spectral density $J(\omega)$,

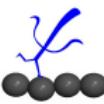
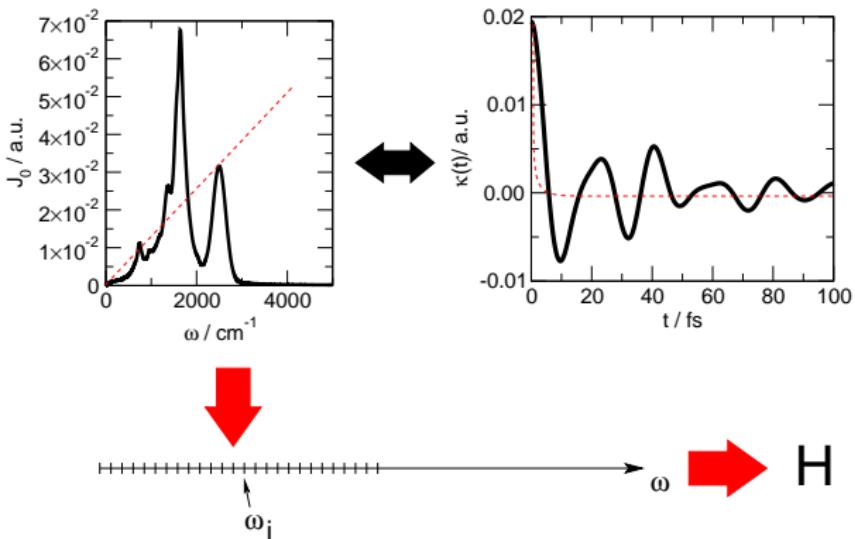
$$k = 1, \dots, N \quad \omega_k = k\Delta\omega \quad c_k = \sqrt{\frac{2\omega_k \Delta\omega J(\omega_k)}{\pi}}$$

provides a **discretized** model which is **equivalent** to the GLE for

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



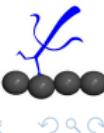
IO Hamiltonian



IO Hamiltonian

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

- * dissipative dynamics for $t < T_{\text{rec}}$
- * the bath can be obtained from small amplitude expansion of the exact Hamiltonian...
- * ...or used to model phenomenological $J(\omega)$
- * the Hamiltonian can be quantized to describe quantum dissipation



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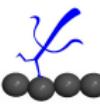


Effective modes

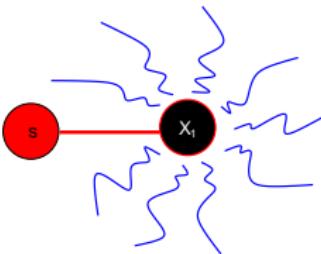
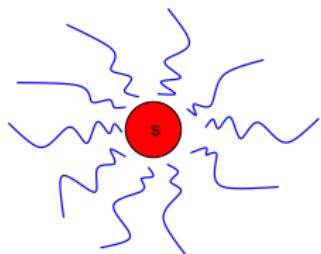
$$H^{\text{int}} = - \sum_k c_k x_k s = -D_0 X_1 s$$

- $D_0^2 = \sum_k c_k^2$: 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 Fix T by requiring $\Omega_{ij}^2 = \delta_{ij} \bar{\Omega}_i^2$



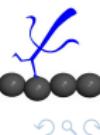
Effective modes



s	x_1	x_2	x_3	x_k
s	$-c_1$	$-c_2$	$-c_3$	$-c_k$
x_1	$-c_1$	ω_1^2	0	0
x_2	$-c_2$	0	ω_2^2	0
x_3	$-c_3$	0	0	ω_3^2
..
..
x_k	$-c_k$	0	0	0	..	ω_k^2



s	X_1	X_2	X_3	X_k
s	$-D_0$	0	0	0
X_1	$-D_0$	Ω_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

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

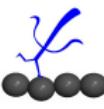
In the **continuum limit** $N \rightarrow \infty$ (with $N\Delta\omega \equiv \omega_c$):

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

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

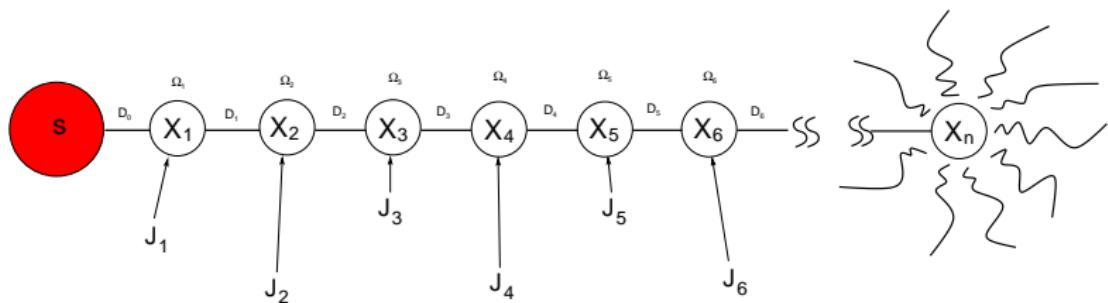
$$J_1(\omega) = \frac{\pi}{2} \sum_{k=2}^N \frac{c_k^2}{\bar{\Omega}_k} (\delta(\omega - \bar{\Omega}_k) - \delta(\omega + \bar{\Omega}_k))$$

..and the procedure can be **indefinitely** iterated

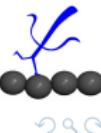


Effective modes

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

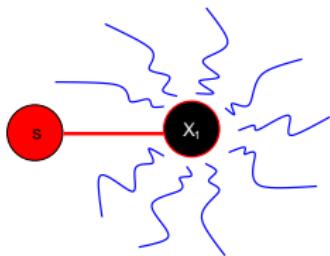


- Do we need the eigenfrequencies at each step?
- How to get $J_{n+1}(\omega)$ from $J_n(\omega)$?
- What is the limiting spectral density?



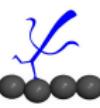
A recursive relation

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

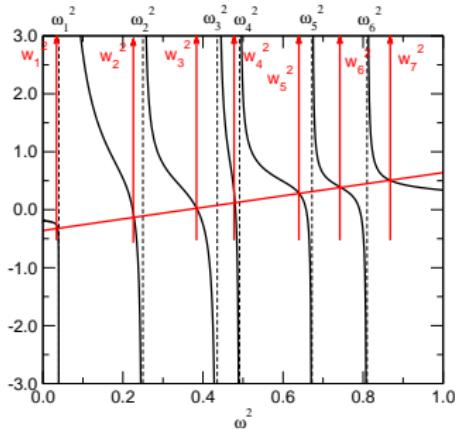


- We can use the Leggett's trick¹ to get $J_0(\omega)$ from $J_1(\omega)$
- There is no need to know the eigenfrequencies in the continuum limit

¹ 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



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

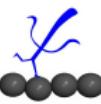
$$W_1(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{J_1(\omega)}{\omega - z} d\omega$$

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

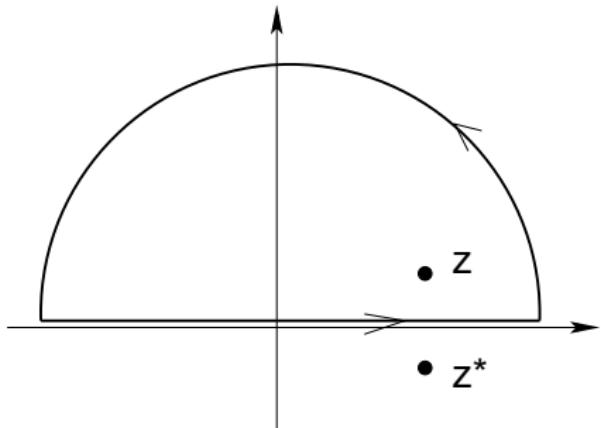


$$W_0(z) = \frac{D_0^2}{\Omega_1^2 - z^2 - W_1(z)}$$

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



A recursive relation



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

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

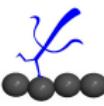
$$J_0(\omega) = \lim_{\epsilon \rightarrow 0} \text{Im} W_0(\omega + i\epsilon)$$



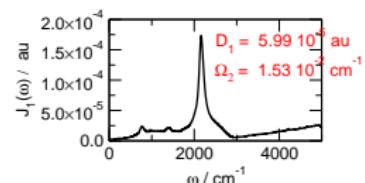
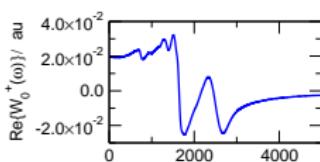
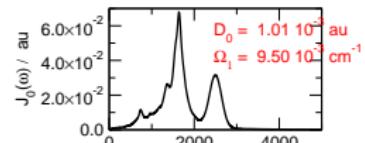
$W_0(z)$ is **analytic** in the u.h.p
and vanishes as z^{-2}



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



A recursive relation



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

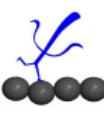
$$\Omega_{n+1}^2 = \frac{2}{\pi D_n^2} \int_0^{+\infty} J_n(\omega) \omega^3 d\omega$$

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

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

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

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



Basics



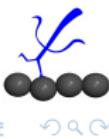
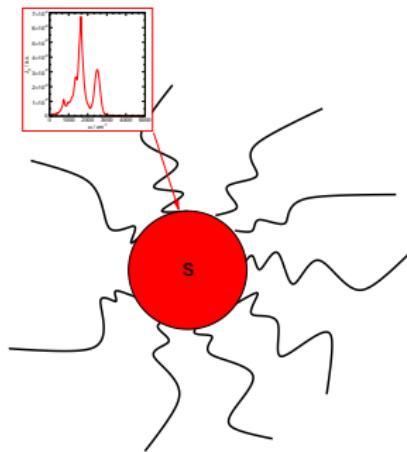
Effective modes



Calculations



A recursive relation



Basics

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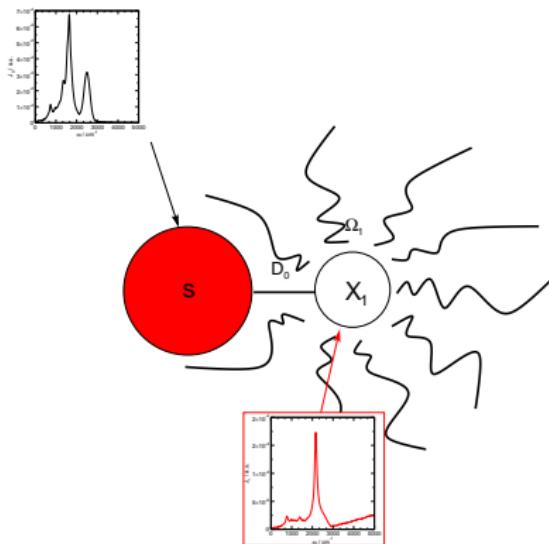
Effective modes

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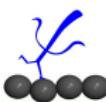
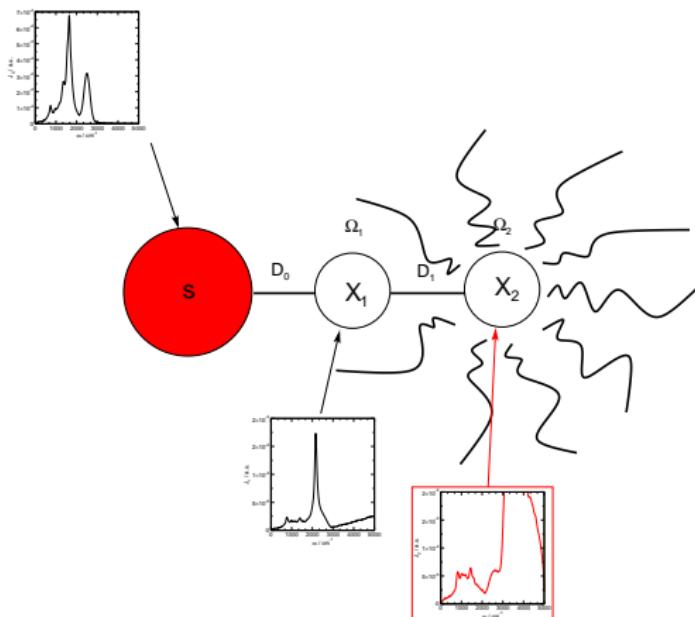
Calculations

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A recursive relation



A recursive relation



Basics

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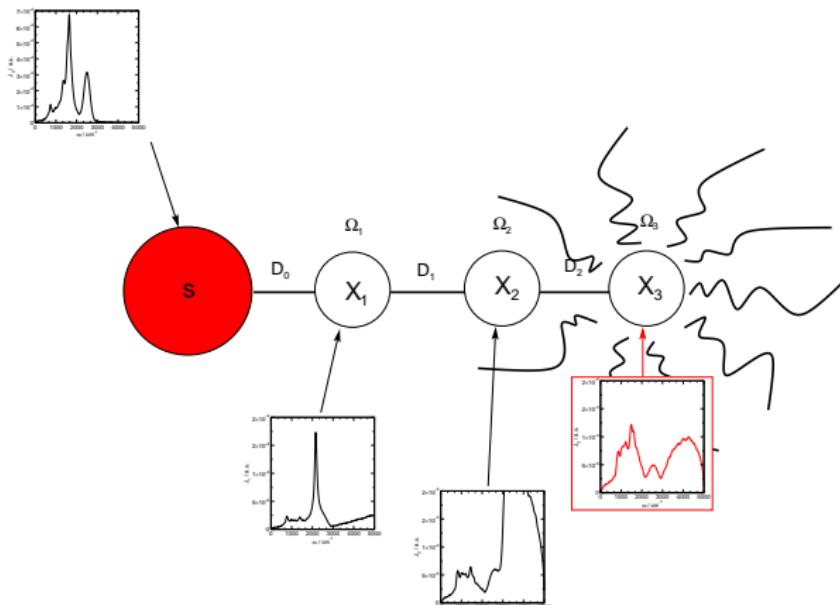
Effective modes

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Calculations

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A recursive relation



Basics



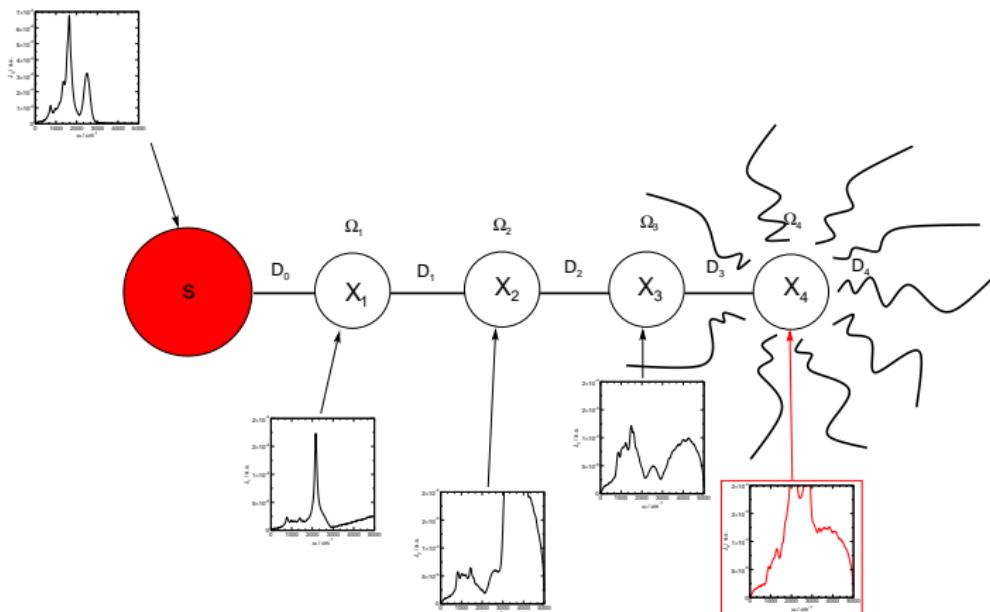
Effective modes



Calculations



A recursive relation



Basics

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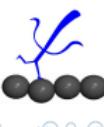
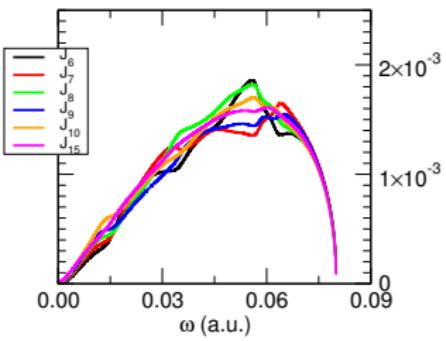
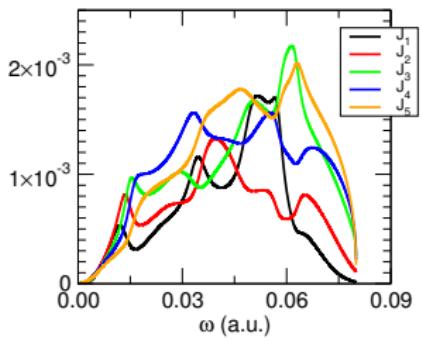
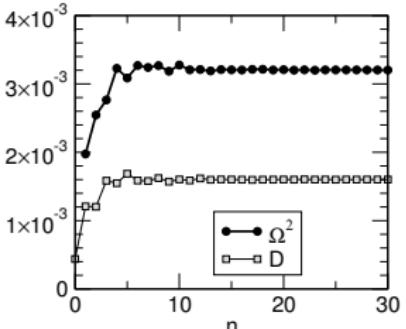
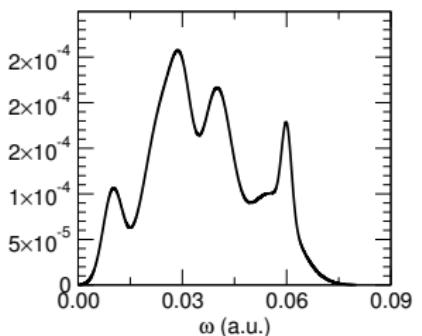
Effective modes

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Calculations

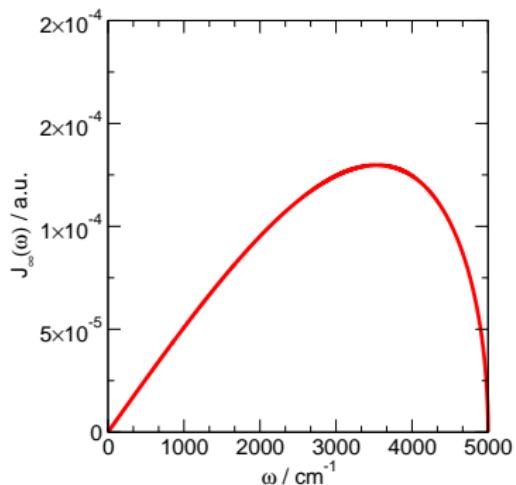
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A recursive relation



Limiting behaviour

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



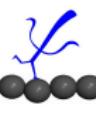
$$W_\infty(z) = \Omega^2 - z^2 - \frac{D^2}{W_\infty(z)}$$

i.e. if $J_0(\omega) > (0, +\omega_c)$ 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 $\Omega^2 = 2D = \frac{\omega_c^2}{2}$

(Quasi)-Ohmic behaviour!!



Short-time behaviour

Kramers-Kronig

$$\kappa(t) = \frac{1}{\pi M} \int_{-\infty}^{+\infty} \frac{J_0(\omega)}{\omega} e^{-i\omega t} d\omega$$

Fluctuation-Dissipation

$$\langle \xi(t)\xi(0) \rangle_\beta = \frac{\hbar}{\pi} \int_{-\infty}^{+\infty} \frac{J_0(\omega)}{1-e^{-\hbar\beta\omega}} e^{-i\omega t} d\omega$$

For $|z| > \omega_c$

$$W_0(z) = \sum_{m=1}^{\infty} \mu_{2m-1}^{(0)} \left(\frac{1}{z} \right)^{2m}$$

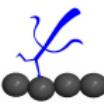
$$\{\mu_1^{(0)}, \mu_3^{(0)}\} \Leftarrow \{D_0, \Omega_1\}$$

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

...

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

$$\mu_k^{(0)} = \frac{2}{\pi} \int_0^\infty J_0(\omega) \omega^k d\omega$$



Basics

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○○○○○○○○○○

Effective modes

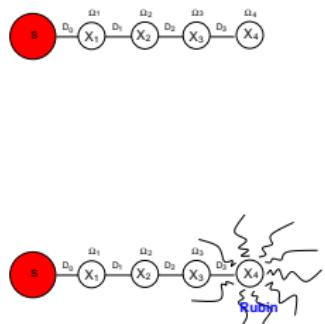
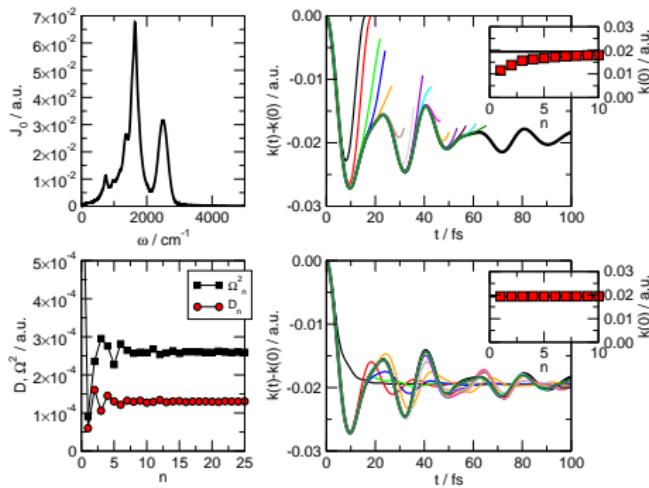
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Calculations

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Short-time behaviour

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

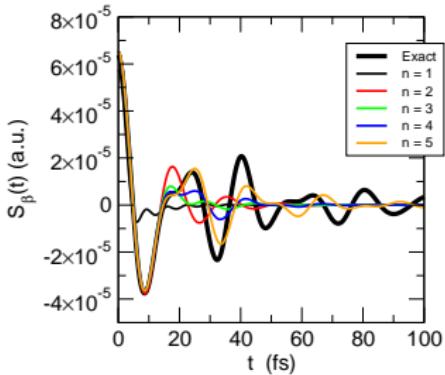


R. Martinazzo, K.H. Hughes and I. Burghardt, *Phys. Rev. E* **84**, 030102(R) (2011)

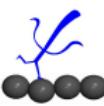
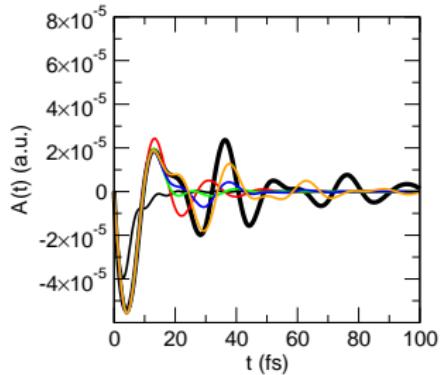
Short-time behaviour

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

$$S_\beta(t) = \text{Re} \langle \xi(t)\xi(0) \rangle$$



$$A(t) = \text{Im} \langle \xi(t)\xi(0) \rangle$$



Outline

1 Basics

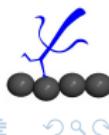
- Generalized Langevin Equation
- Independent Oscillator Model

2 Effective modes

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

3 Calculations

- LC-based MCTDH ansatz
- Outlook



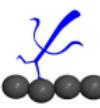
A simple MCTDH *ansatz*

System + Primary + Secondary modes

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

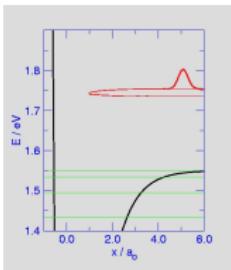
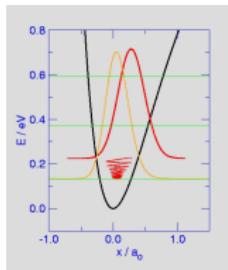
- Linear scaling
- Accuracy depends on the primary modes only
- Recurrence times can be enormously increased
- Effective-mode based variants for LCSA^{1–3} are possible

- [1] R. Martinazzo, M. Nest, G. F. Tantardini and P. Saalfrank, *J. Chem. Phys.* **125** 194102 (2006)
 [2] S. Lopez-Lopez, M. Nest, R. Martinazzo, *J. Chem. Phys.* **134** 014102 (2011)
 [3] S. Lopez-Lopez, R. Martinazzo, M. Nest, *J. Chem. Phys.* **134** 094102 (2011)

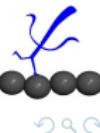


Model systems

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



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



Basics

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Effective modes

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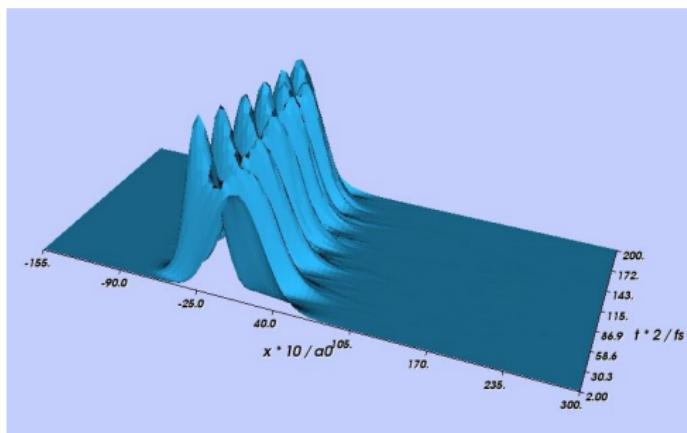
Calculations

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Model systems

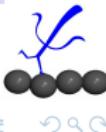
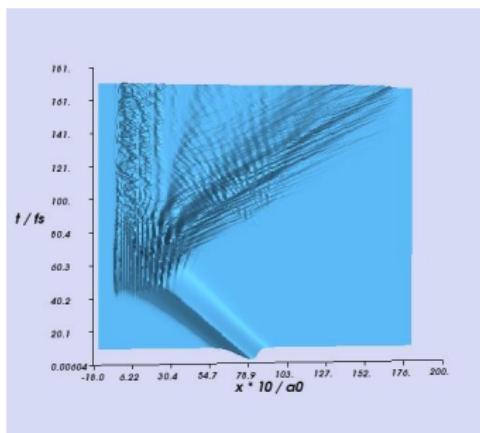
Vibrational relaxation

$$\rho_t(s|s)$$



Sticking

$$\rho_t(s|s)$$



Basics

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Effective modes

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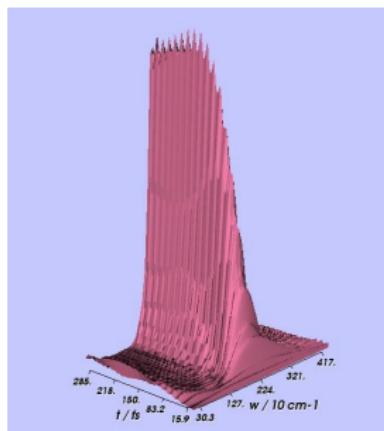
Calculations

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Model systems

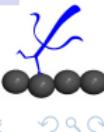
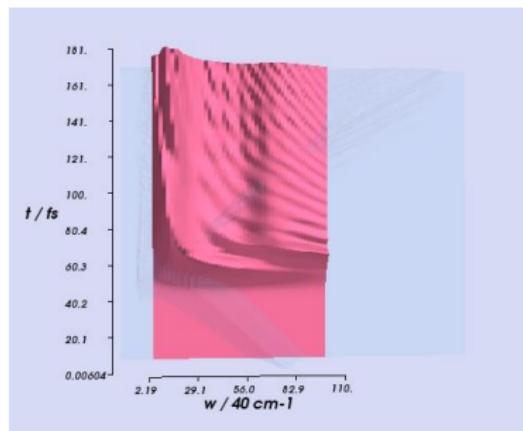
Vibrational relaxation

$$\langle a_\omega^\dagger a_\omega \rangle_t$$



Sticking

$$\langle a_\omega^\dagger a_\omega \rangle_t$$



Basics

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Effective modes

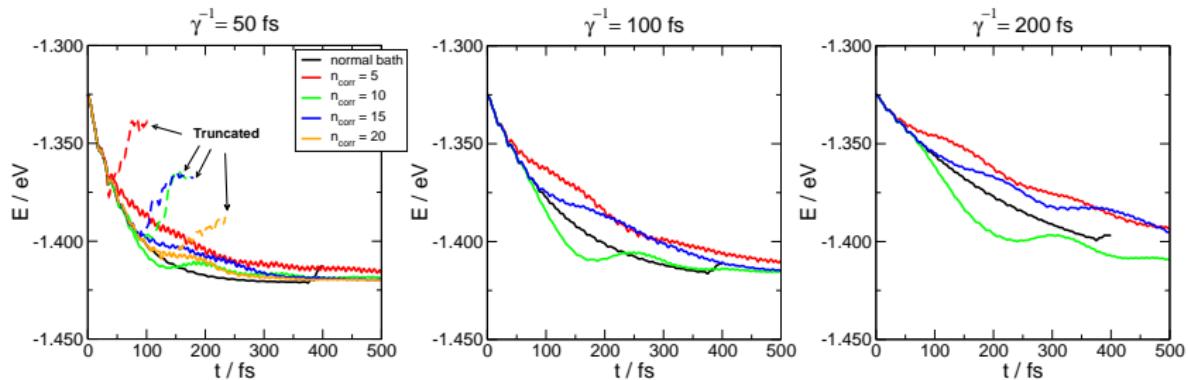
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Calculations

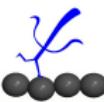
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A simple MCTDH *ansatz*: vib relax

Ohmic case, $N = 100$

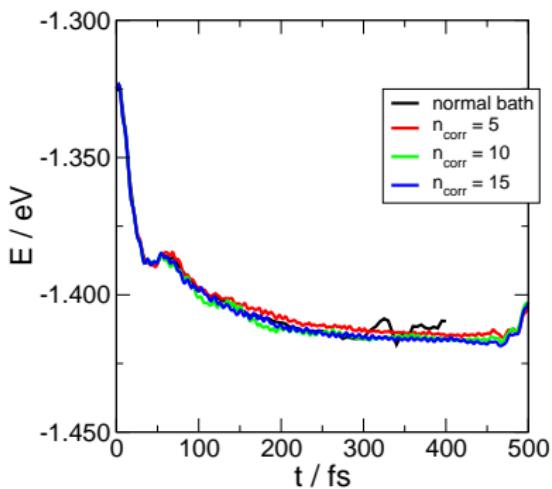
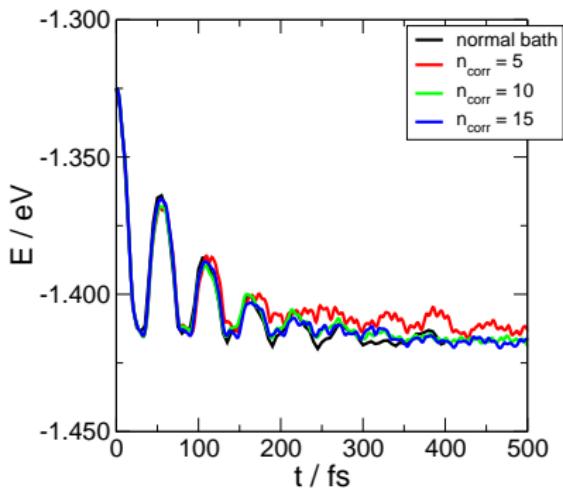


M. Bonfanti, G.F. Tantardini, K.H. Hughes, I. Burghardt and R. Martinazzo, *in preparation*



A simple MCTDH *ansatz*: vib relax

Non-Markovian case, $N \equiv 100$



Basics

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Effective modes

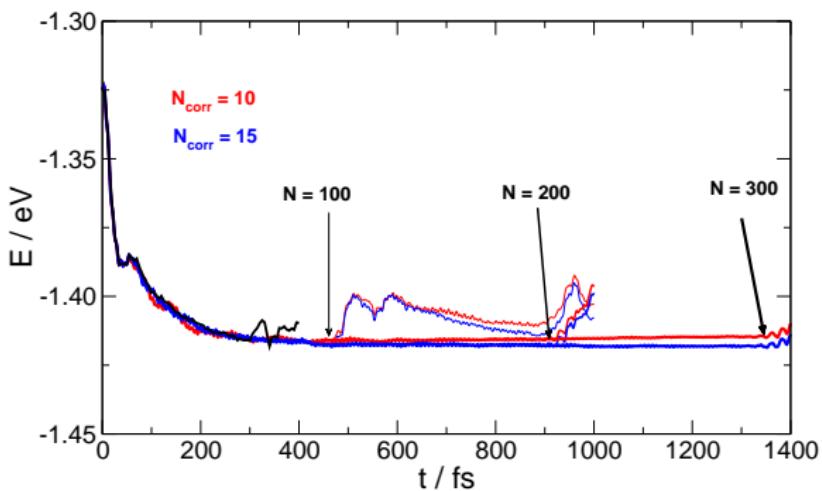
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Calculations

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A simple MCTDH *ansatz*: vib relax

Non-Markovian case, $N = 100 - 300$



Basics

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Effective modes

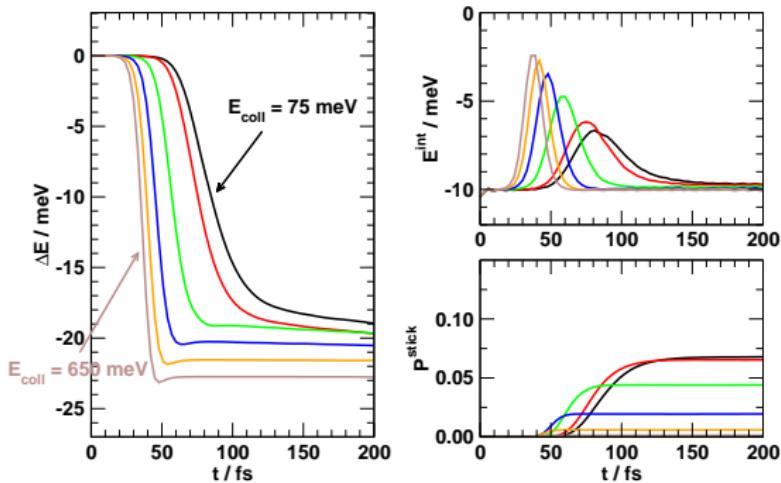
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Calculations

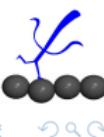
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A simple MCTDH *ansatz*: sticking

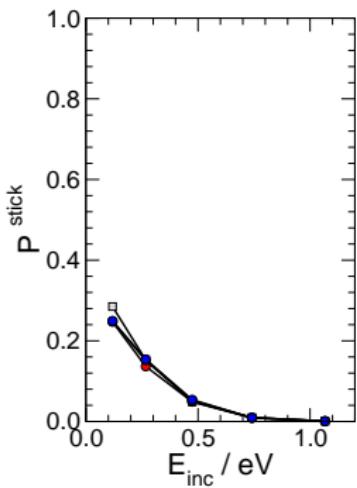
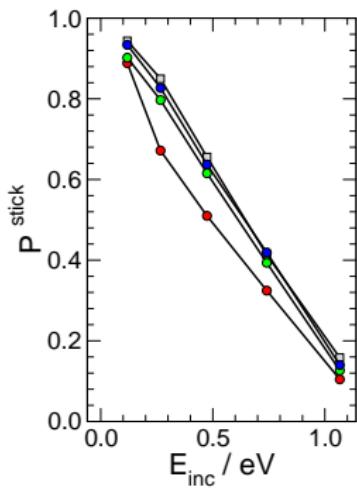
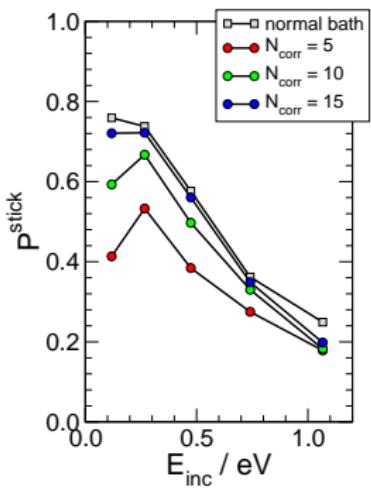
Overview, $N = 100$



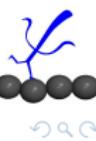
M. Bonfanti, G.F. Tantardini, K.H. Hughes, I. Burghardt and R. Martinazzo, *in preparation*



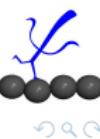
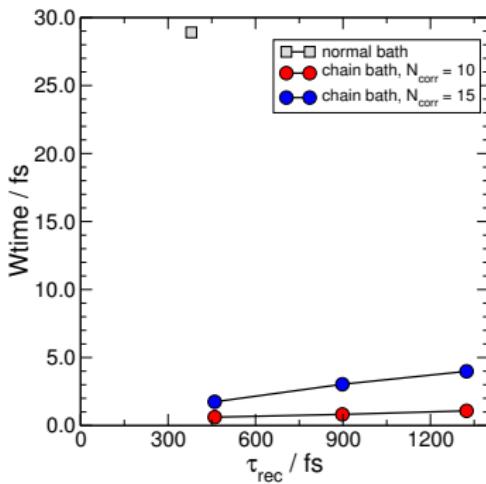
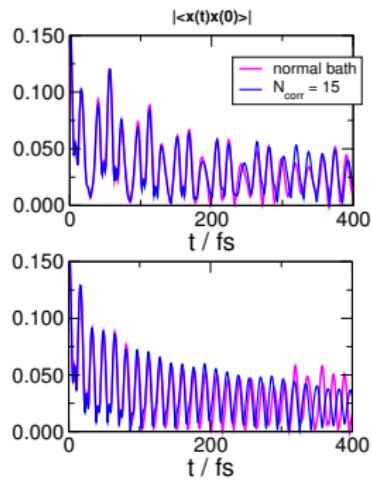
A simple MCTDH *ansatz*: sticking



M. Bonfanti, G.F. Tantardini, K.H. Hughes, I. Burghardt and R. Martinazzo, *in preparation*



A simple MCTDH *ansatz*: timings



Basics



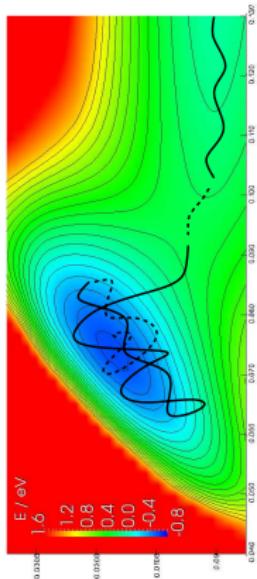
Effective modes



Calculations

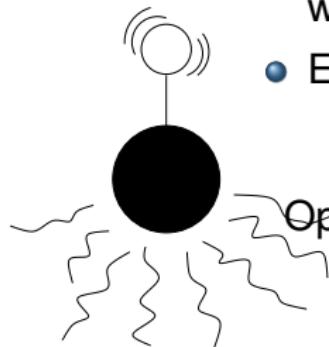


H Chemisorption

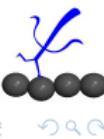


Low energy H atoms:

- Tunneling into the chemisorption well
- Energy relaxation



Open-system quantum problem



Basics



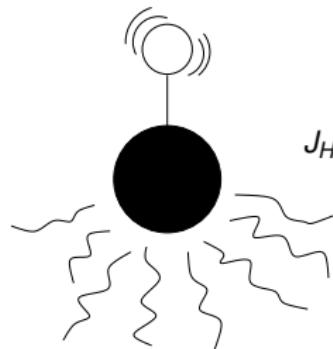
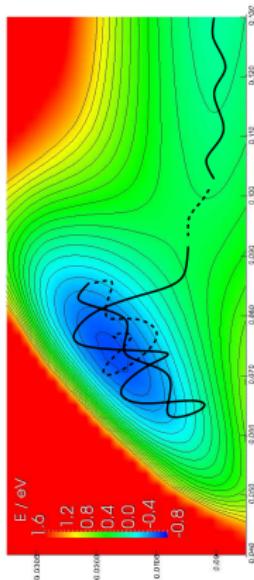
Effective modes



Calculations



H Chemisorption



$$H = \frac{p_H^2}{2m_H} + \frac{p_C^2}{2m_C} + V(z_C, z_H, \mathbf{q}^{eq}) + \sum_{k=1}^F \left[\frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left(x_k - \frac{c_k}{\omega_k^2} (z_C - z_C^{eq}) \right)^2 \right]$$

↑

$$J_C(\omega) = m_C \frac{D_0^2 J_H(\omega)}{|W^+(\omega)|}$$

↑

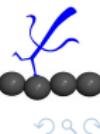
$$J_H(\omega) = k_B T \frac{\sigma(\omega)}{|S^+(\omega)|} \quad \sigma(\omega) = \tilde{C}(\omega) \omega / 2$$

↑

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

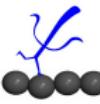
↑

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



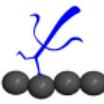
Summary

- 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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Basics

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○○○○○○○

Effective modes

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○○○○○○○○○○
○○○

Calculations

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Acknowledgements

Thank you for your attention!

