The Surrogate Hamiltonian

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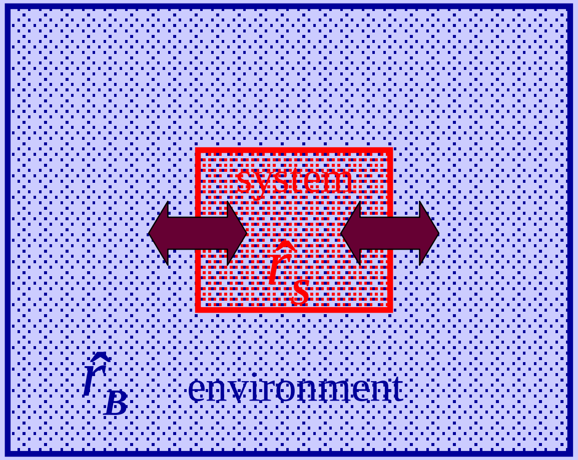
Safed Workshop on Quantum Dissipation
Open Problems in Open Quantum Systems

Problem
Reduced Vs Full Dynamics

$\hat{H}_S \otimes \hat{H}_B$



$$\hat{H} = \hat{H}_{SYSTEM} + \hat{H}_{BATH} + \hat{H}_{SB}$$

How to get $\hat{\rho}_S$

$$\hat{\rho}_S(t) = tr_B\left\{\hat{U}(t)\hat{\rho}(0)\hat{U}^{\dagger}(t)\right\}$$

Dynamics:

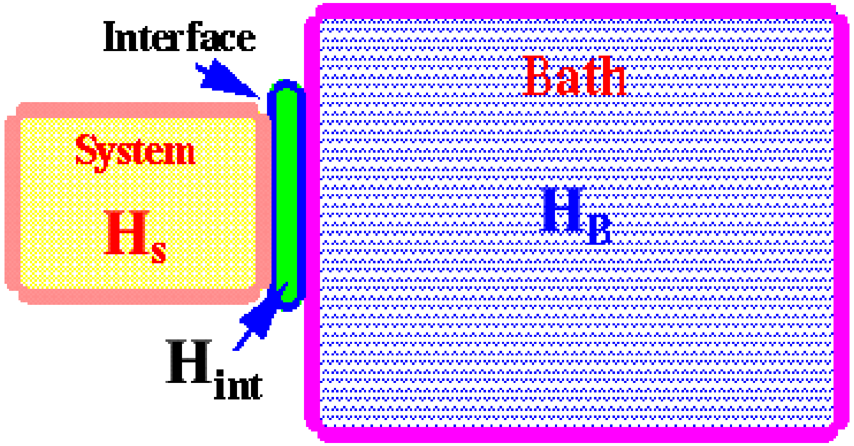
$$\hat{\rho}(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_B \xrightarrow[\text{evolution}]{\text{unitary}} \hat{\rho}_S(t) = \hat{U}(t)\,\hat{\rho}_S(0) \otimes \hat{\rho}_B\,\hat{U}^{\dagger}(t)$$

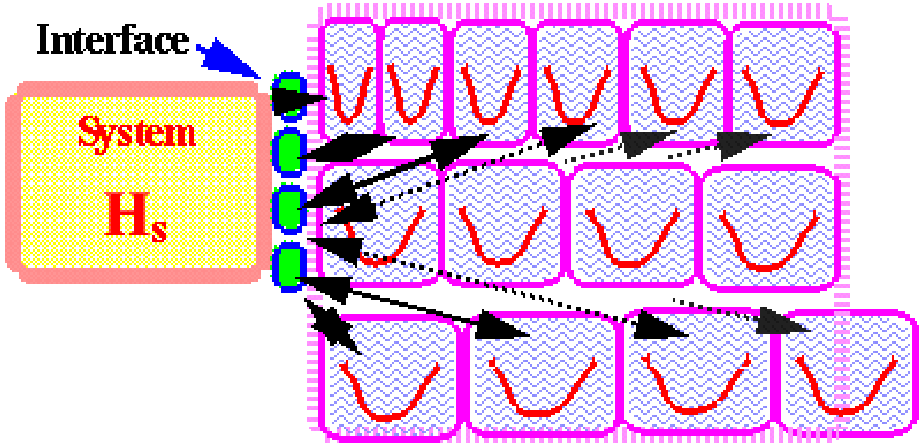
$\downarrow tr_B$ OR $\downarrow tr_B$

$$\hat{\rho}_S(0) \xrightarrow[\text{map}]{\text{dynamical}} \hat{\rho}_S(t) = \hat{V}(t)\,\hat{\rho}_S(0)$$

I The surrogate Hamiltonian approach

II Weak coupling limit





Normal mode analysis

$$H = H_s + H_{int} + H_B$$

$$\hat{H}_s = \hat{T} + V_s(\hat{R})$$

$$\hat{H}_{int} = f(\hat{R}) \sum_j V_j (\hat{b}_j^\dagger + \hat{b}_j)$$

$$\hat{H}_B = \sum_j \epsilon_j \hat{b}_j^\dagger \hat{b}_j$$

III Discrete bath approximation

$$\hat{\mathrm{H}} = \hat{\mathrm{T}} + V_s(\hat{\mathrm{R}}) + \sum_{m=0}^{N-1} \epsilon_m \hat{\mathrm{B}}^\dagger_{\mathrm{m}} \hat{\mathrm{B}}_{\mathrm{m}} + f(\hat{\mathrm{R}}) \sum_{m=0}^{N-1} U_m \hat{\mathrm{B}}^\dagger_{\mathrm{m}} + H.C.$$

Renormalizing the interaction

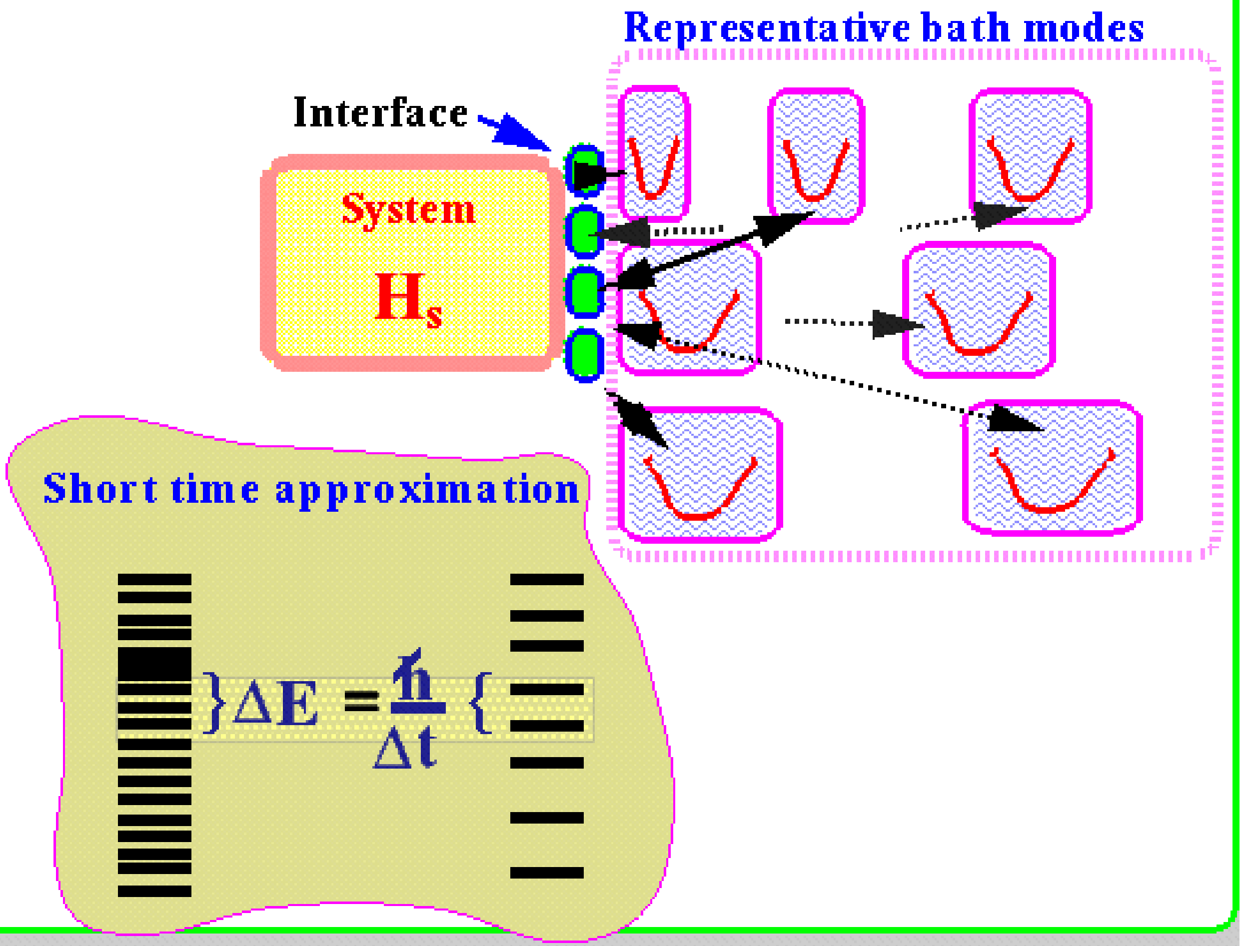
$$U_m = \sqrt{J(\epsilon_m)/\rho(\epsilon_m)}$$

Spectral density

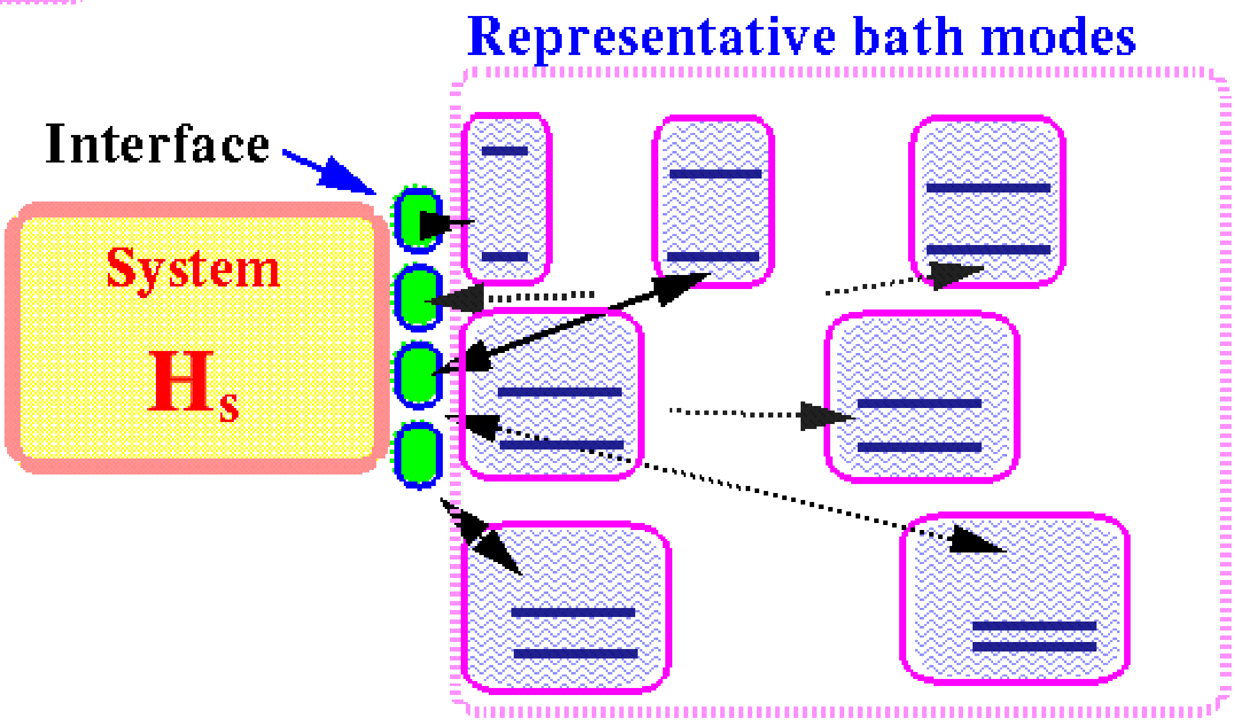
$$J(\epsilon) = \sum_j |V_j|^2 \delta(\epsilon_j - \epsilon)$$

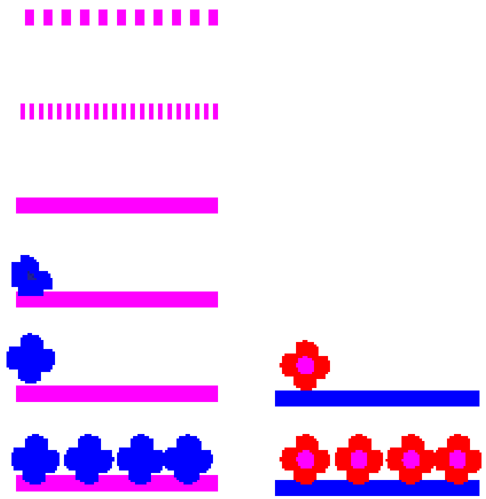
Density of states

$$\rho(\epsilon_m) \approx (\epsilon_{m+1} - \epsilon_m)^{-1}$$



IV Replacing the bath modes





Low temperature approximation

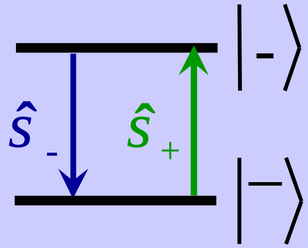
$$P_n = z^{-1} e^{-\beta E_n}$$

Fully correlated system bath representation !

Surrogate Hamiltonian

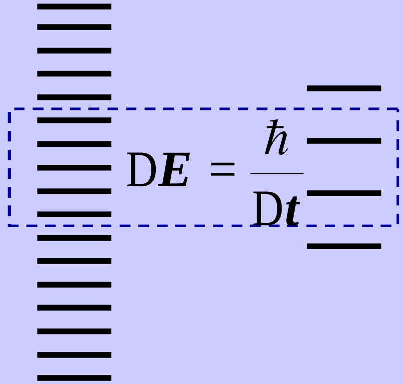
$$\hat{H} = \hat{H}_S \otimes \hat{I}_B + \hat{H}_{SB} + \hat{I}_S \otimes \hat{H}_B$$

- ***implicit*** **description of the bath: TLS** $\hat{H}_B = \sum \omega_i \hat{\sigma}_i^\dagger \hat{\sigma}_i$



- **for times $t \ll \infty$, $N \ll \infty$ is sufficient**

- **replace** $$\hat{H}_B \sim \sum_{i=1}^{\infty} \tilde{n}_i^{true} \rightarrow \sum_{i=1}^{N} \hat{n}_i^{rep}$$

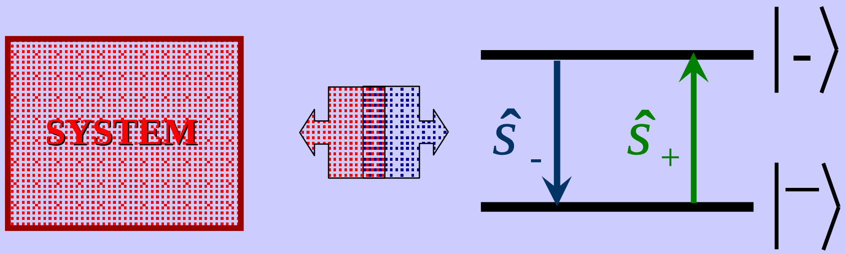


- **Hamiltonian dynamics**

$$\Psi(t) \xrightarrow[\text{evolution}]{\text{unitary}} e^{-i\hat{H}t}\,\Psi(0)$$

Surrogate Hamiltonian

How do we build the bath?



$$\hat{H}_{SB} = f(\hat{R}) \otimes \sum_i \lambda_i (\hat{\sigma}_i^{\dagger} + \hat{\sigma}_i)$$

Harmonic bath - spectral density function $J(\omega)$

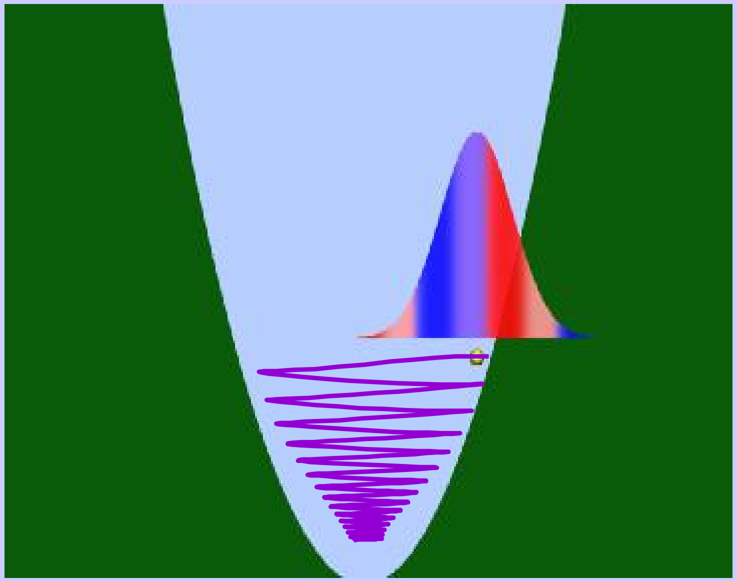
$$J(\omega) = \sum_i |\lambda_i|^2 \rho(\omega) \delta(\omega - \omega_i) \qquad \lambda_i = \sqrt{\frac{J(\omega_i)}{\rho(\omega_i)}}$$

from MD simulations (J.S. Bader and B.J. Berne, JCP 100, 8359 (1994))

Vibrational relaxation

Example: **Harmonic Oscillator linearly coupled to an Ohmic bath**

$$\hat{H} = \underbrace{\frac{\hat{P}^2}{2M} + M\omega_0^2 \hat{X}^2}_{\text{system}} + \underbrace{\sum_i \omega_i \hat{\sigma}_i^\dagger \hat{\sigma}_i}_{\text{bath}} + \underbrace{\hat{X} \sum_i \lambda_i (\hat{\sigma}_i^\dagger + \hat{\sigma}_i)}_{\text{interaction}}$$



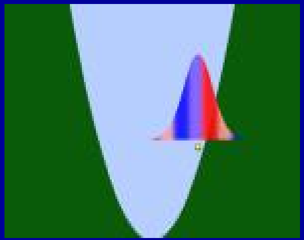
$$\lambda_i = \sqrt{\frac{J(\omega_i)}{\rho(\omega_i)}}$$

Ohmic spectral density

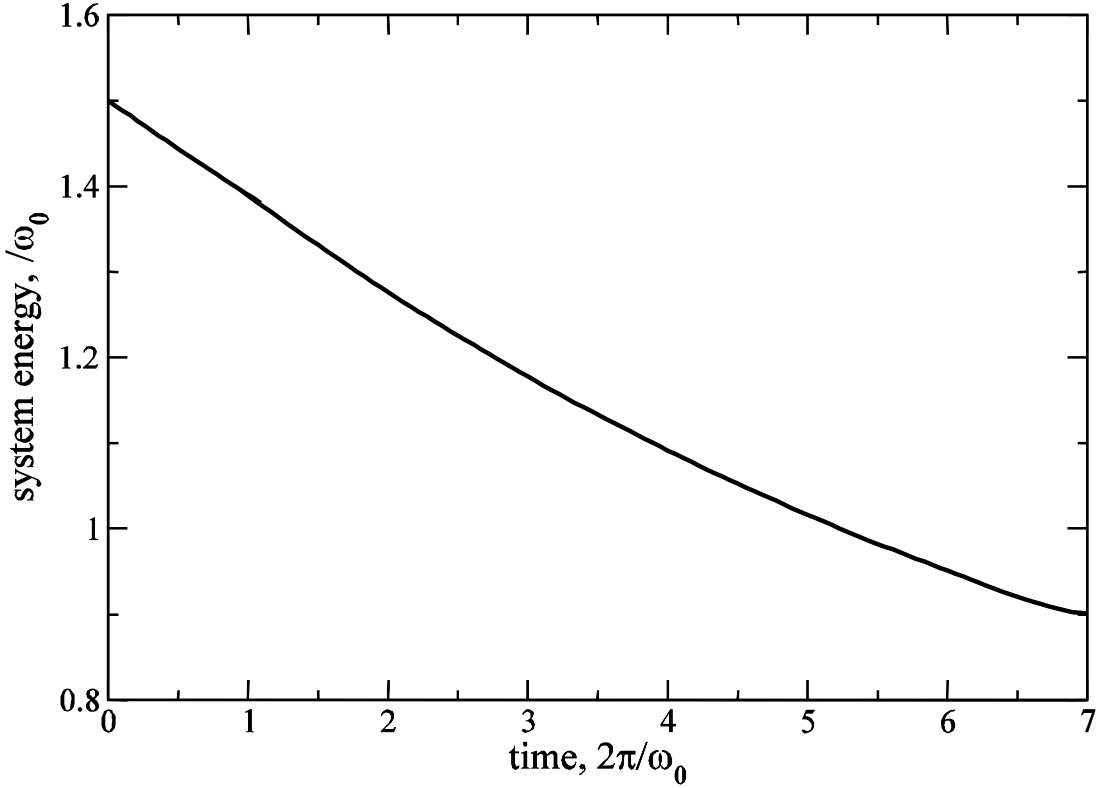
$$J(\omega) = \eta \omega e^{-\omega/\omega_c}$$

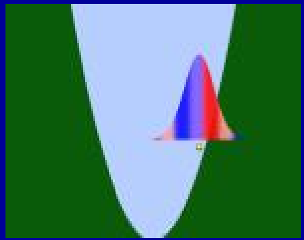
η **- coupling strength**

ω_c **- cutoff frequency**

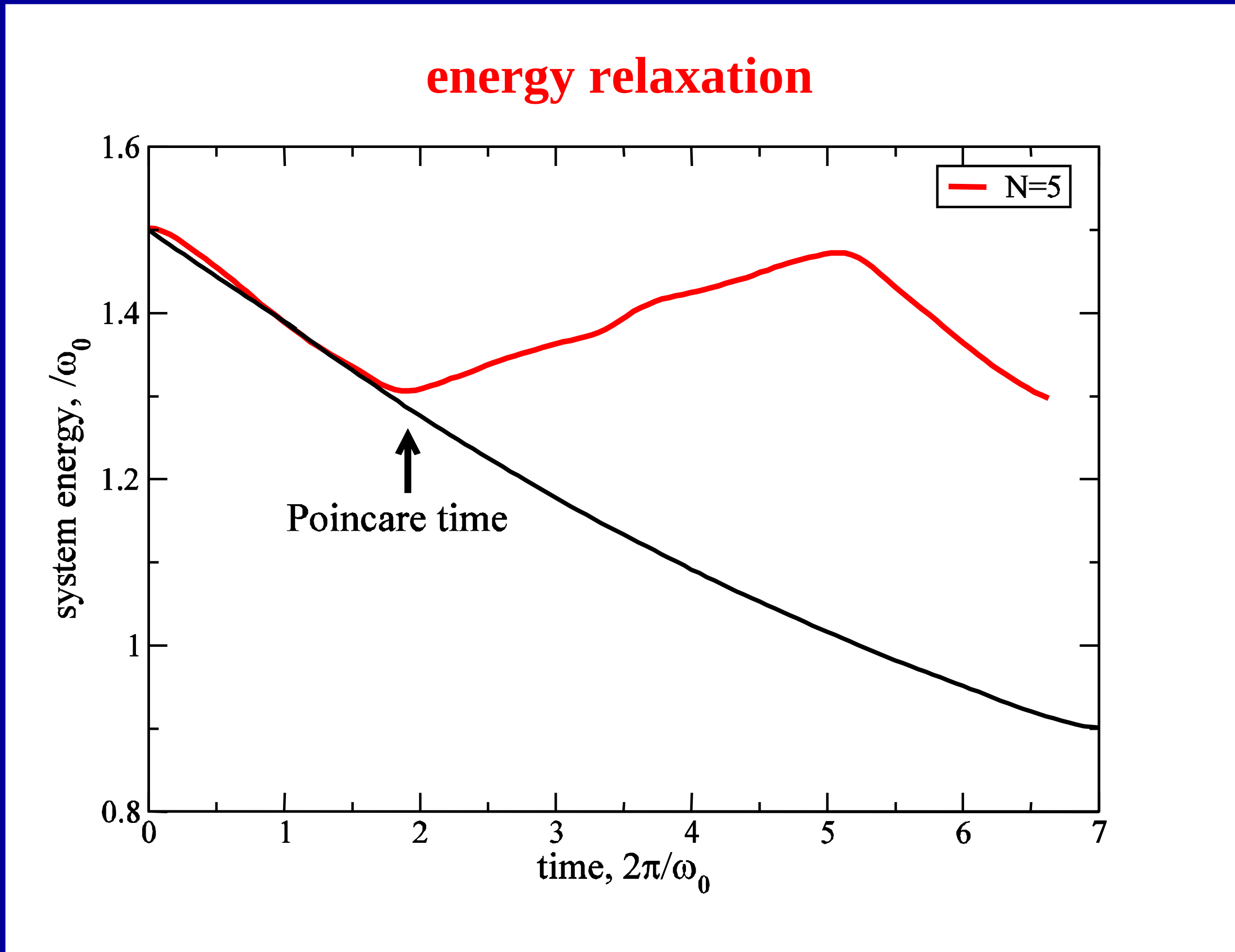


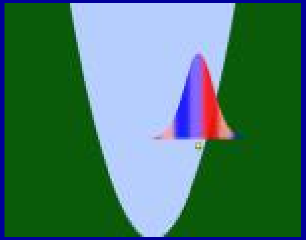
Vibrational relaxation



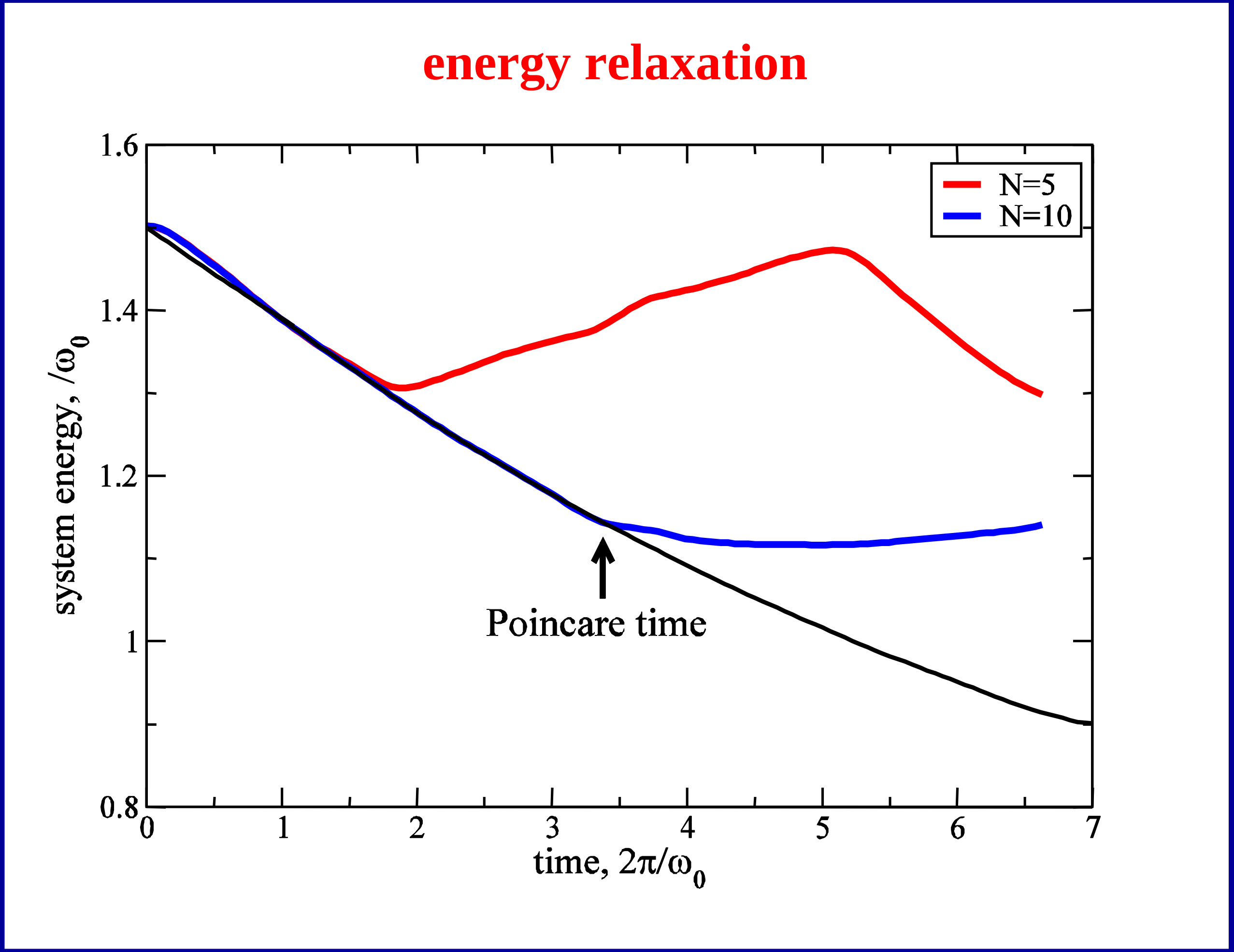


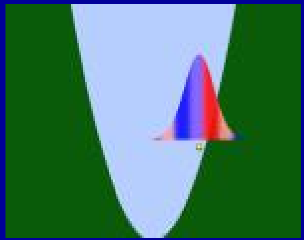
Vibrational relaxation



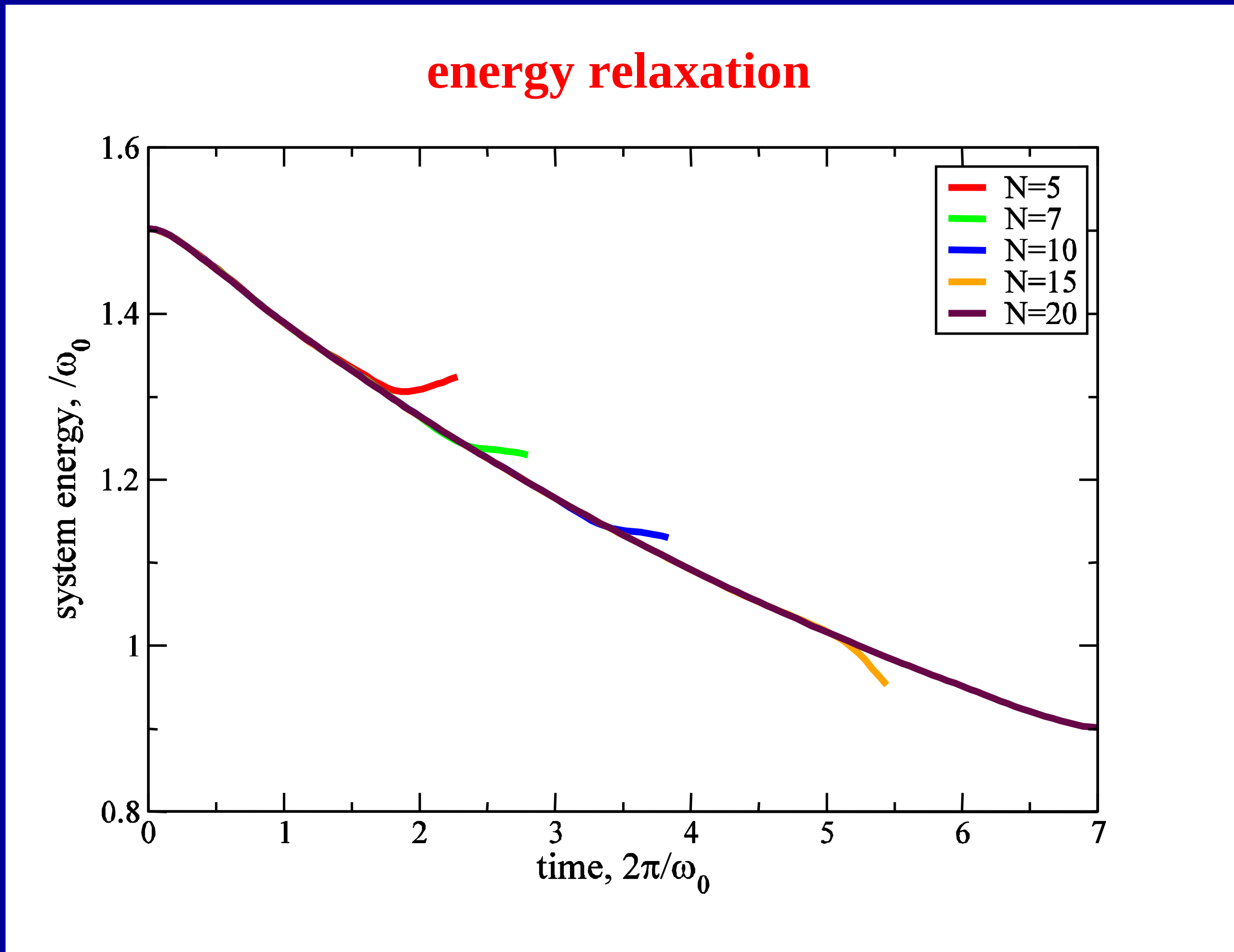


Vibrational relaxation





Vibrational relaxation



Surrogate Hamiltonian

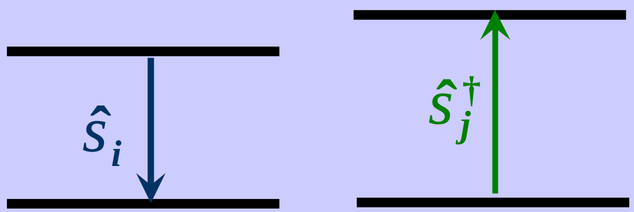
How do we build the bath?

From first principles …

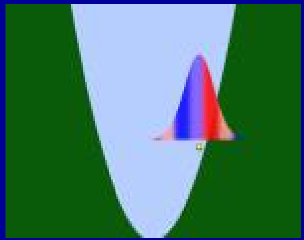
pure dephasing
(almost elastic interactions)

$$\hat{H}^{d}_{SB} = \hat{H}_{S} \otimes \sum_{ij} c_{ij}\left(\hat{S}_i^{\dagger}\hat{S}_j + \hat{S}_j^{\dagger}\hat{S}_i\right)$$

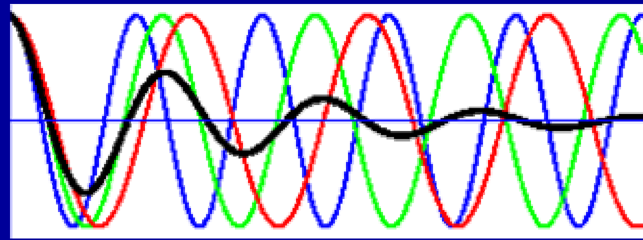
$$c_{ij} = \frac{\bar{c}}{N(N-1)} e^{-\frac{(\omega_i - \omega_j)^2}{2\sigma^2}}$$



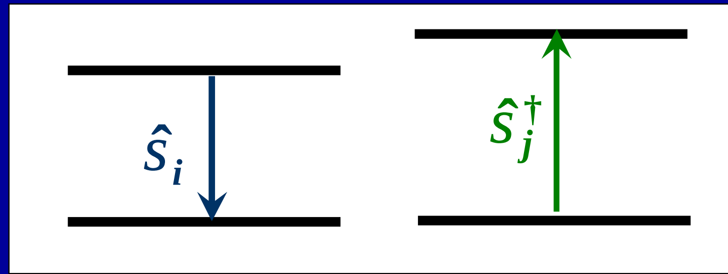
The bath has to be initially excited

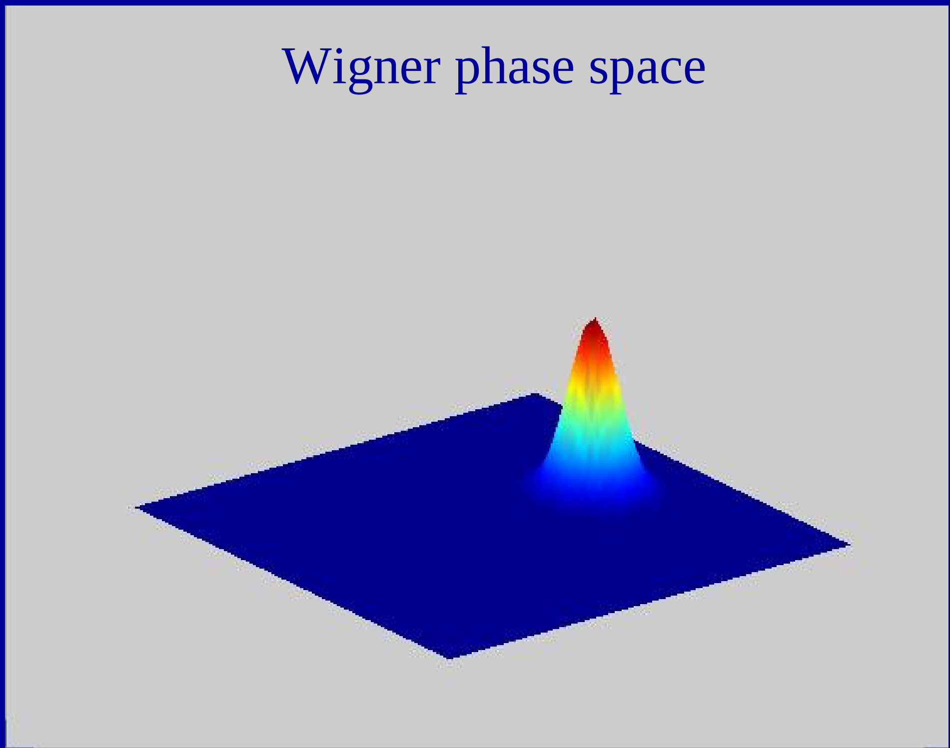


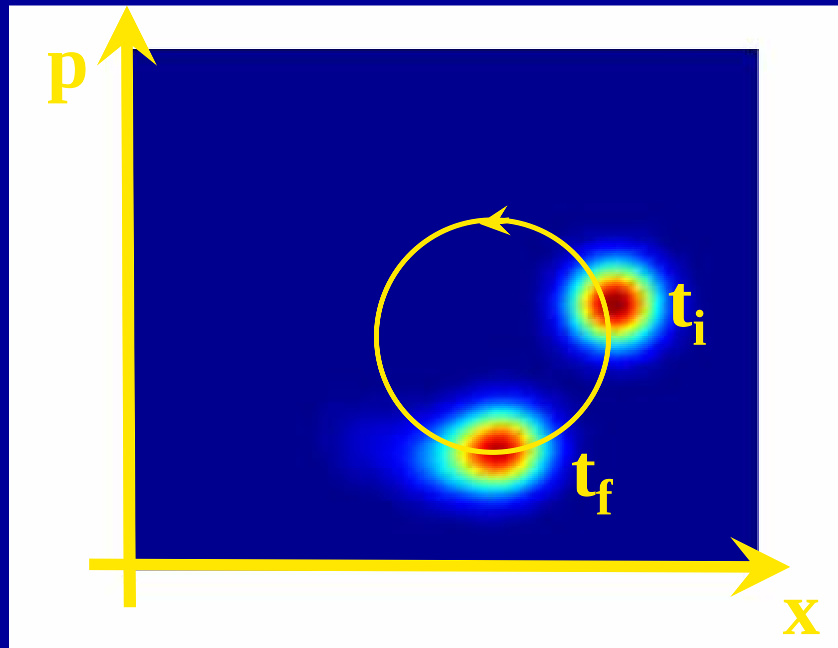
Pure dephasing



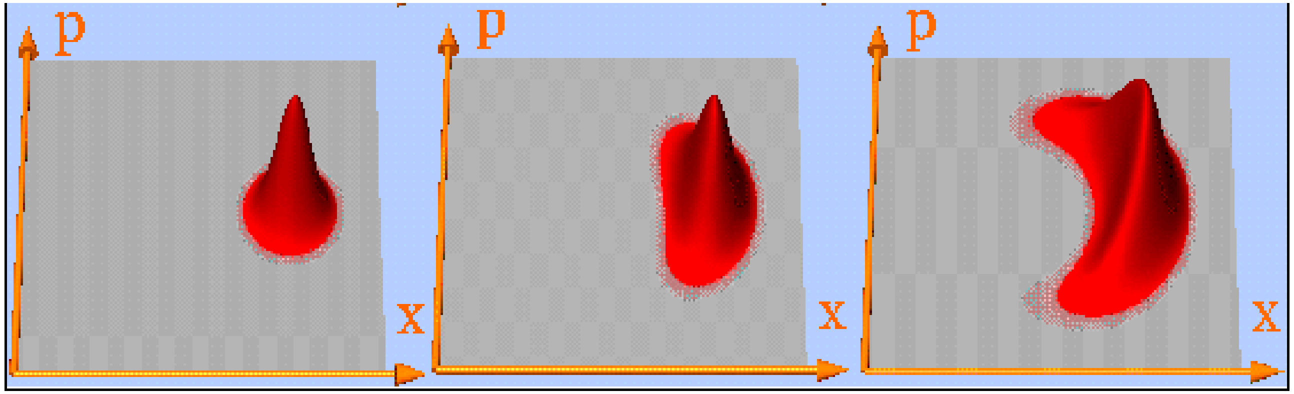
$$\hat{H}^{d}_{SB} = \hat{H}_{S} \otimes \sum_{ij} c_{ij}\left(\hat{s}_i^{\dagger}\hat{s}_j + \hat{s}_j^{\dagger}\hat{s}_i\right)$$







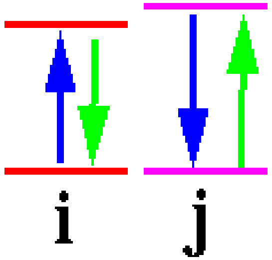
Dephasing: almost elastic system bath encounters



Nuclear dephasing

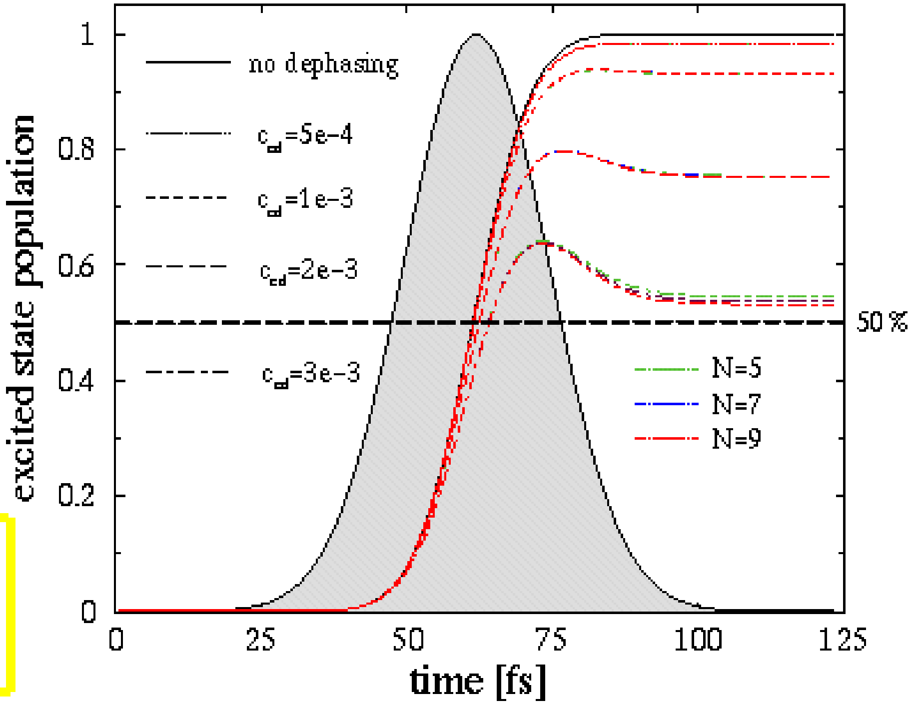
$$\hat{\mathbf{H}}_{SB}^{nd} = \begin{pmatrix} \hat{\mathbf{H}}_g & 0 \\ 0 & \hat{\mathbf{H}}_e \end{pmatrix} \otimes \sum_{ij} c_{ij}^{nd} (\hat{\sigma}_i^+ \hat{\sigma}_j + \hat{\sigma}_j^+ \hat{\sigma}_i) \, .$$

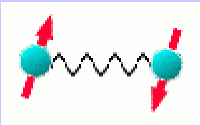
Almost elastic energy exchange



Electronic dephasing

$$\hat{\mathbf{H}}_{SB}^{ed} = \Delta_V(\hat{\mathbf{Q}}) \frac{1}{2} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \sum_{ij} c_{ij}^{ed} (\hat{\sigma}_i^+ \hat{\sigma}_j + \hat{\sigma}_j^+ \hat{\sigma}_i)$$





Spin bath Vs Harmonic bath

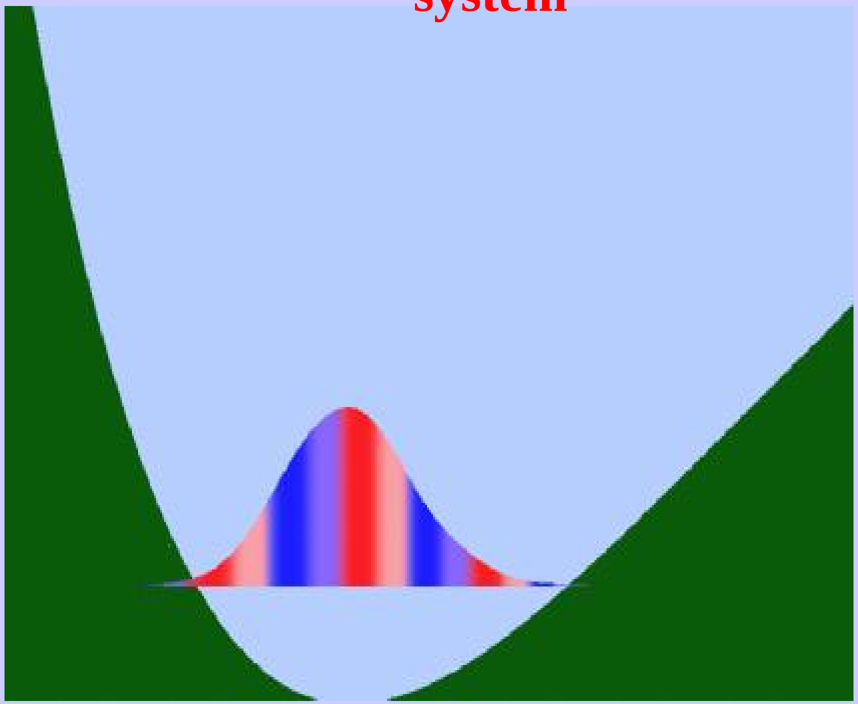
Spin bath Vs Harmonic bath

M. Nest and H.-D. Meyer, JCP 119, 24 (2003)

Morse Oscillator linearly coupled to an Ohmic bath

$$\hat{H} = \underbrace{\frac{\hat{P}^2}{2M} + D\left(1 - e^{-\alpha \hat{X}}\right)^2}_{\text{system}} + \underbrace{\sum_i \omega_i \hat{s}_i^\dagger \hat{s}_i}_{\text{bath}} + \underbrace{\hat{X} \sum_i \lambda_i (\hat{s}_i^\dagger + \hat{s}_i)}_{\text{interaction}} \quad \text{TLS}$$

$$\sum_i \omega_i \hat{a}_i^\dagger \hat{a}_i + \hat{X} \sum_i \lambda_i (\hat{a}_i^\dagger + \hat{a}_i) \quad \text{HO}$$



METHOD: MCTDH ⟷ SURROGATE HAMILTONIAN

BATH: HO ⟷ TLS

The same $J(\omega) = M\gamma\omega$

Spin bath Vs Harmonic bath

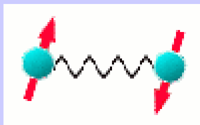
HARMONIC BATH WITH LINEAR COUPLING

$$\hat{r}_{BATH} = \hat{r}_1 \ \text{Ä} \ \hat{r}_2 \ \text{Ä} \ \hat{r}_3 \ \text{Ä} \ \ldots$$

SPIN BATH

$$\hat{r}_{BATH} \neq \hat{r}_1 \ \text{Ä} \ \hat{r}_2 \ \text{Ä} \ \hat{r}_3 \ \text{Ä} \ \ldots$$

ENTANGLEMENT

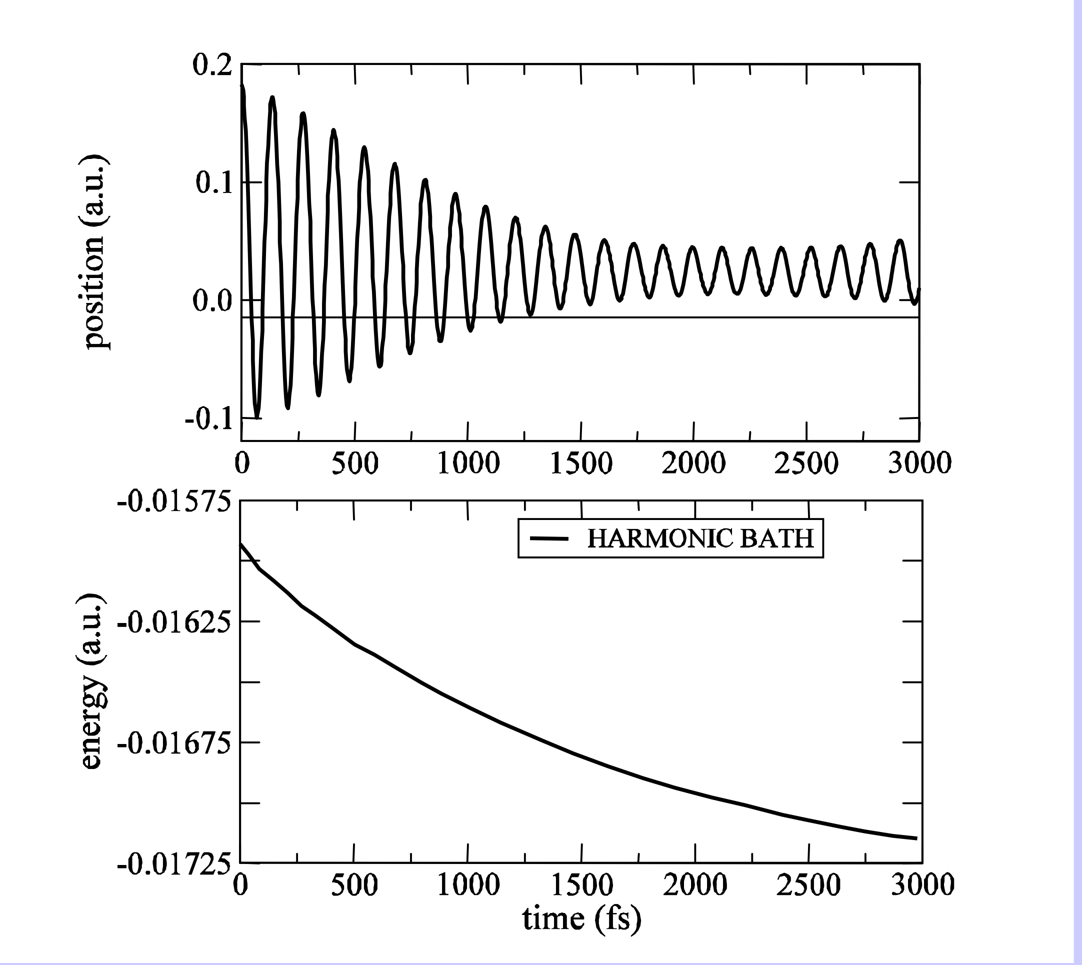


$$\hat{r}_B = tr_S \{\hat{r}\} \longrightarrow \hat{r}_{ij} = tr_{k\,^1 i,j} \{\hat{r}_B\}$$

$$\hat{r}_{ij} \overset{?}{=} \hat{r}_i \ \text{Ä} \ \hat{r}_j$$

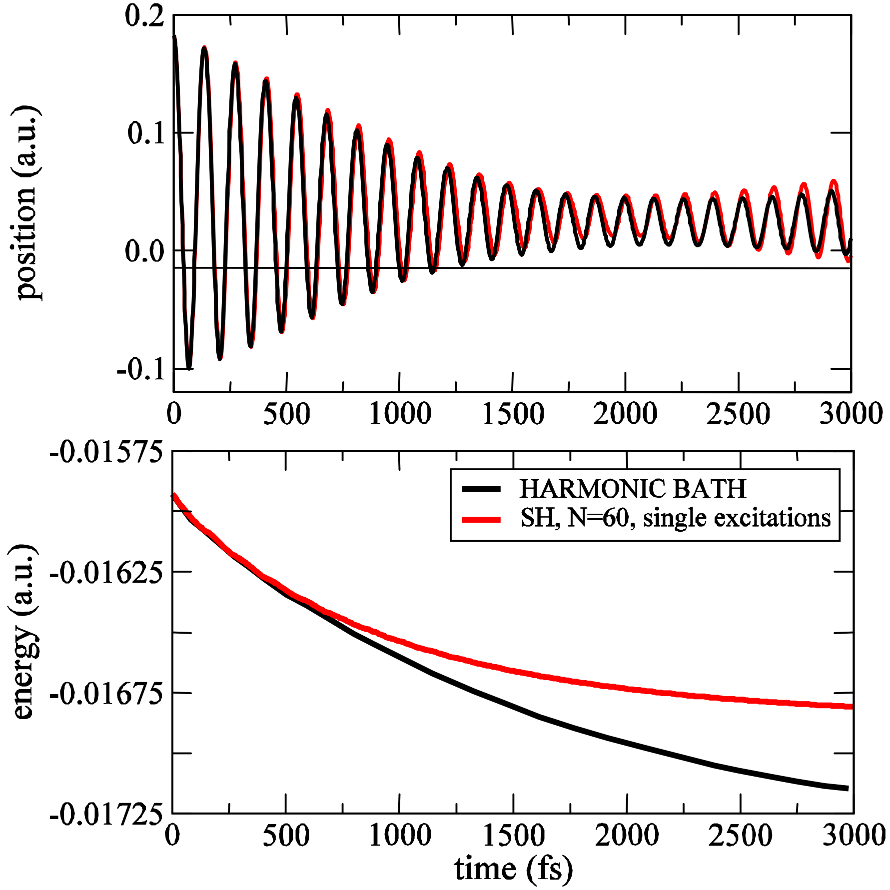
weak coupling limit

g^{-1}=1630 fs >> t_{osc}=127 fs, t_{bath}=54 fs



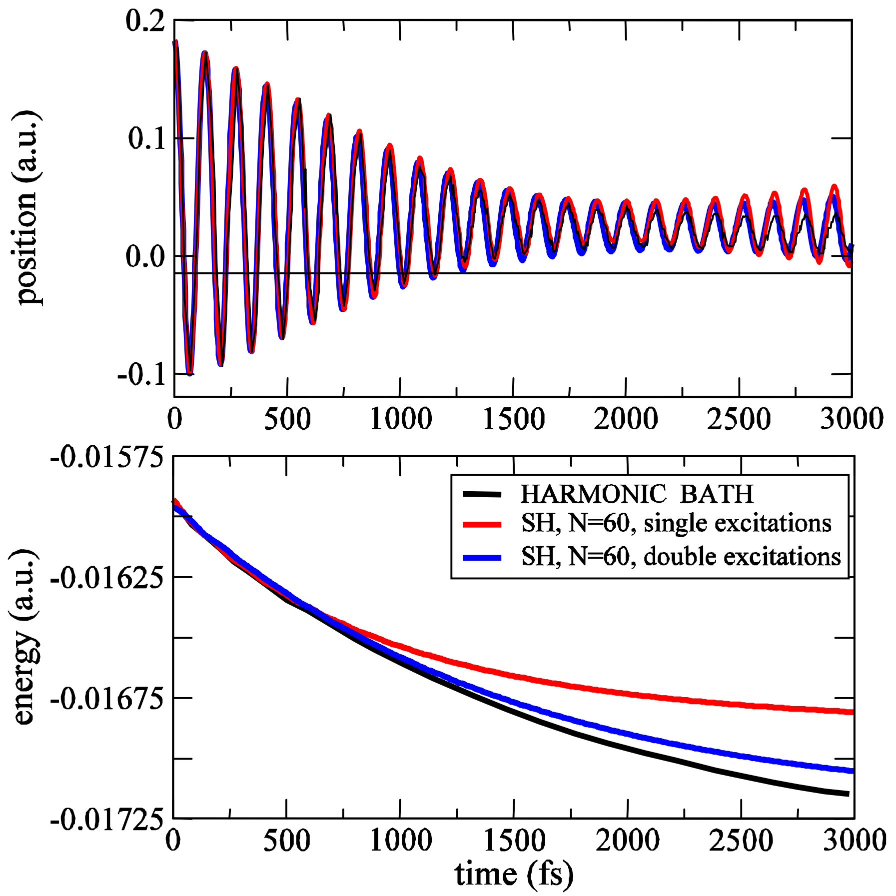
weak coupling limit

g^{-1}=1630 fs >> t_{osc}=127 fs, t_{bath}=54 fs



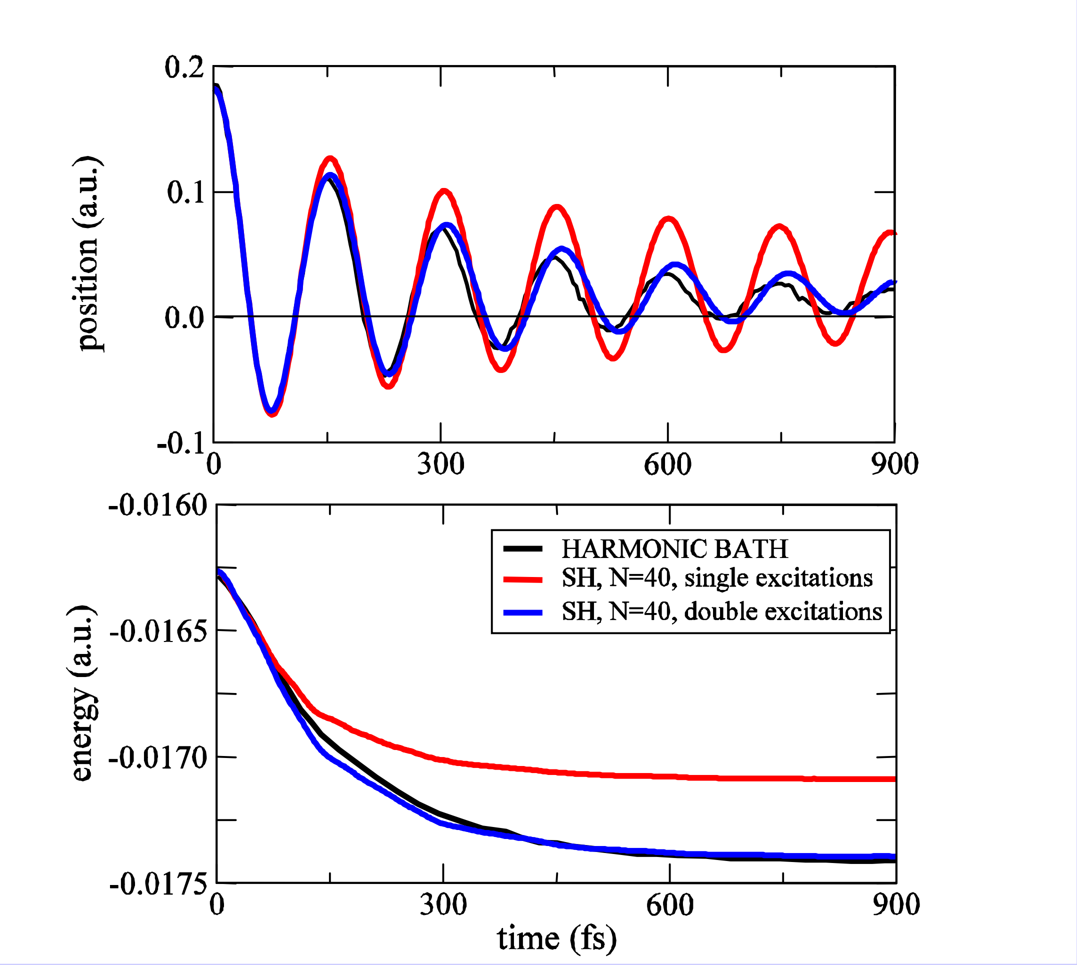
weak coupling limit

g^{-1}=1630 fs >> t_{osc}=127 fs, t_{bath}=54 fs



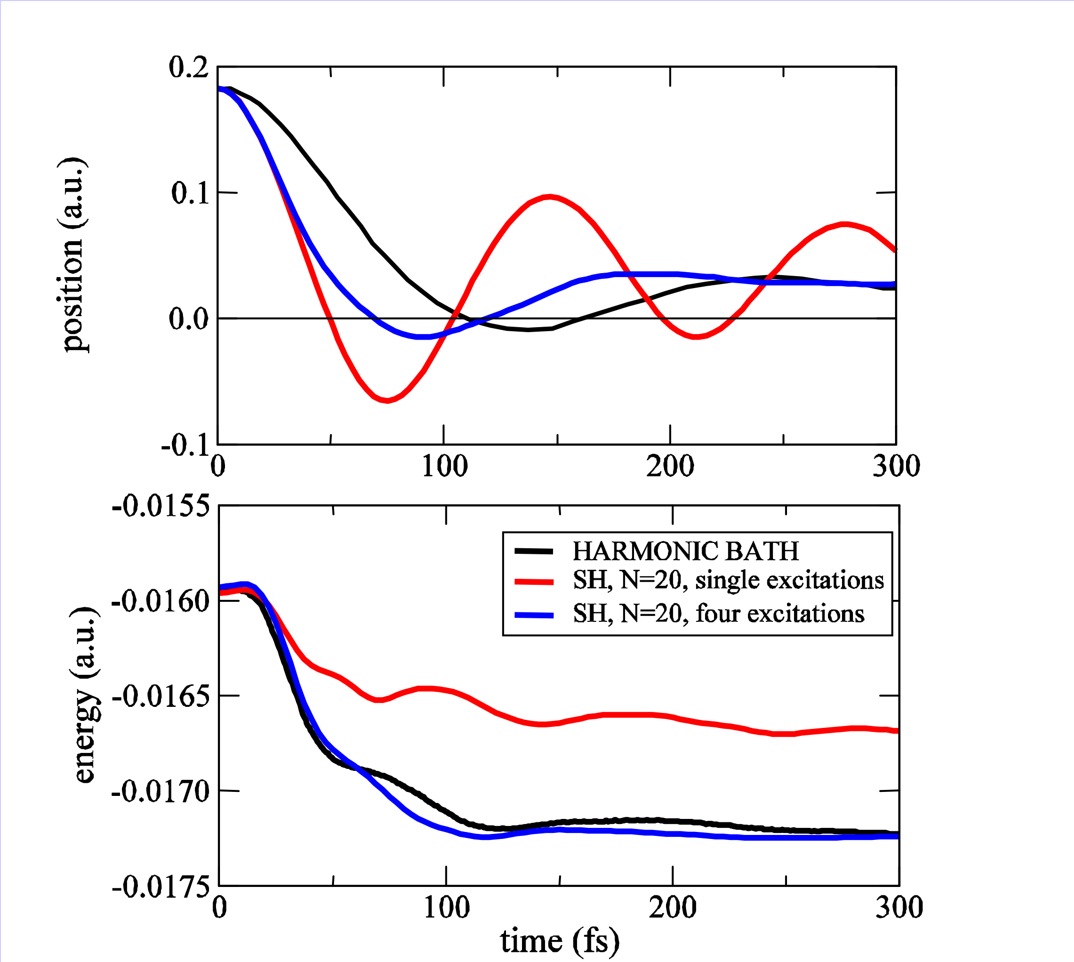
intermediate coupling

g^{-1}=163 fs ≈ t_{osc}=127 fs > t_{bath}=54 fs



strong coupling

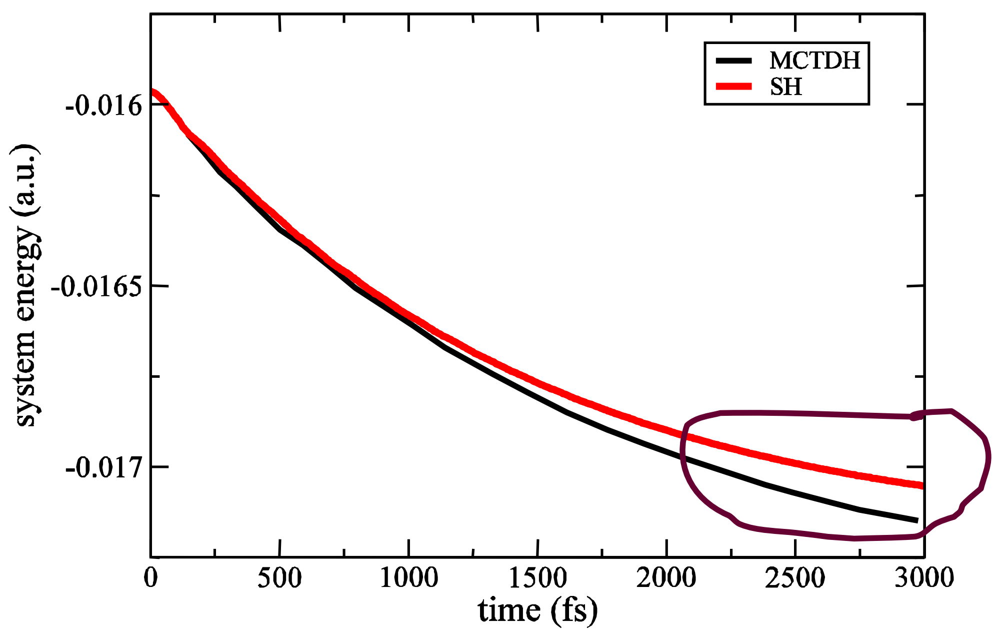
g^{-1} =54 fs ≈ t_{bath}=52 fs < t_{osc}=127 fs



Saturation

$$\Psi = \begin{pmatrix} \psi_0(R) \\ \psi_1(R) \\ \psi_2(R) \\ \psi_3(R) \\ \vdots \\ \psi_7(R) \end{pmatrix} \begin{matrix} \text{system} \\ 1^{st} \text{ mode} \\ 2^{nd} \text{ mode} \\ 1^{st} + 2^{nd} \\ \\ \text{three excitations} \end{matrix}$$

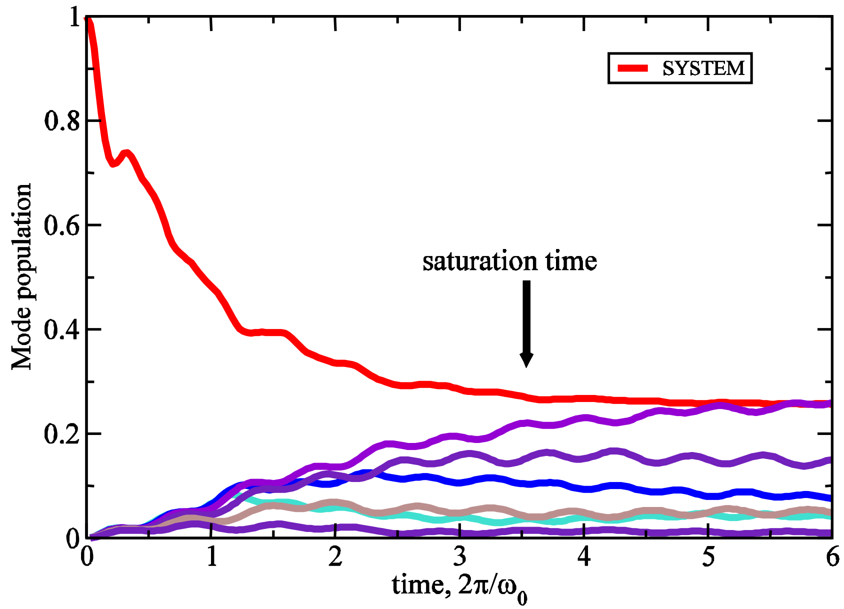
$T_{rec} \approx 3200$ fs



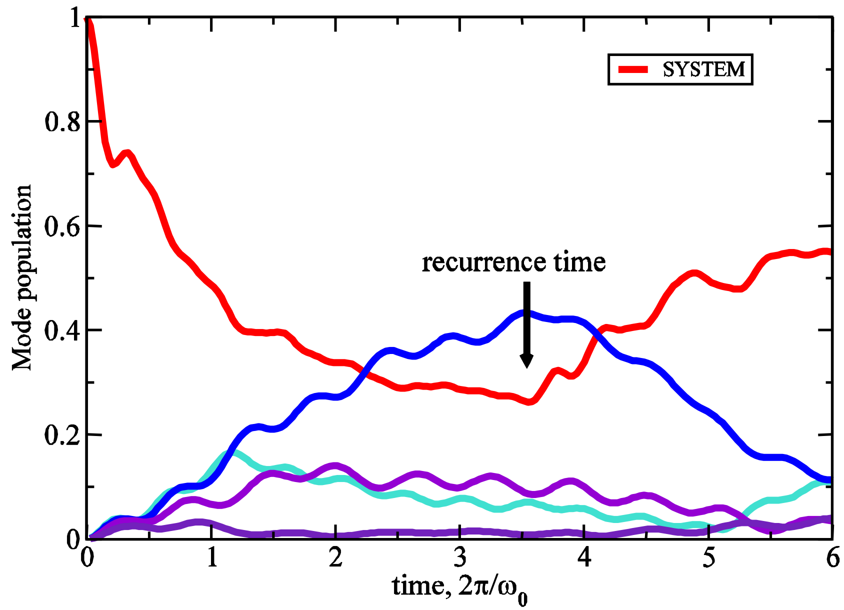
Saturation

Bath Dynamics

N=40, single excitations

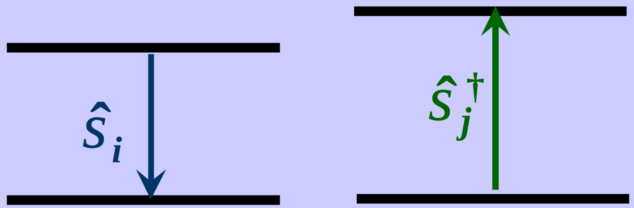


N=20, single excitations



inter-spin interactions

$$\hat{\tilde{H}}_B = \sum_i \omega_i \hat{s}_i^\dagger \hat{s}_i + \sum_{|i-j|=1} \kappa_{ij} \left(\hat{s}_i^\dagger \hat{s}_j + \hat{s}_j^\dagger \hat{s}_i \right)$$



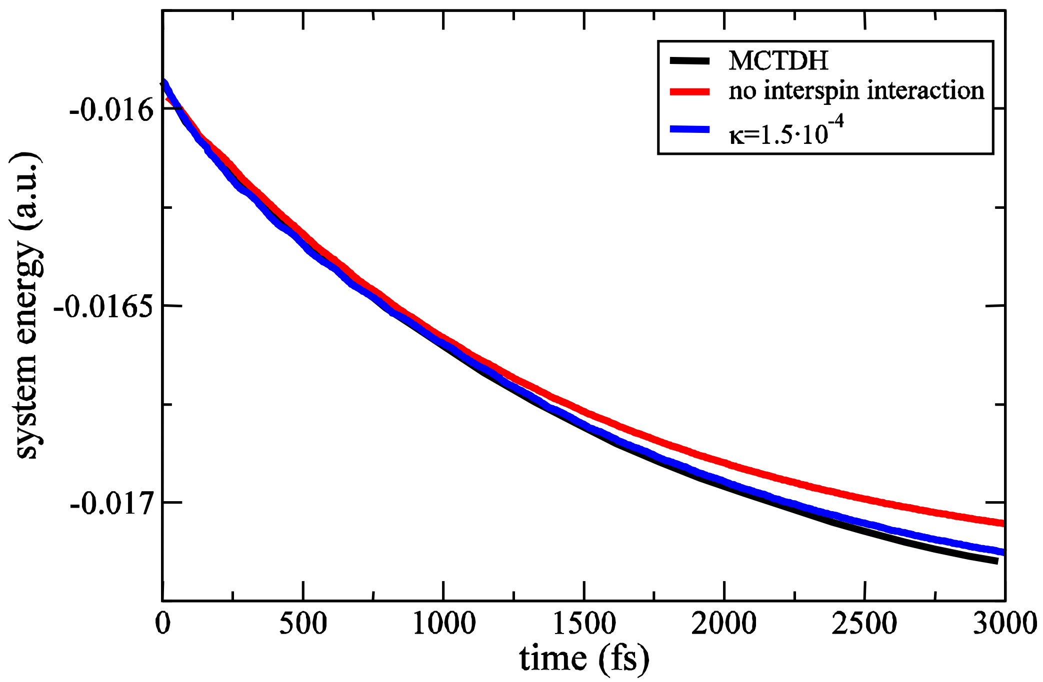
ALMOST ELASTIC ENERGY EXCHANGE BETWEEN TWO NEAREST NEIGHBORS

$$\hat{\tilde{H}}_B = \sum_i \tilde{\omega}_i \hat{\tilde{s}}_i^\dagger \hat{\tilde{s}}_i$$

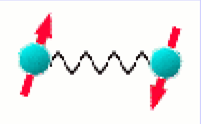
FOR SUFFICIENTLY SMALL κ

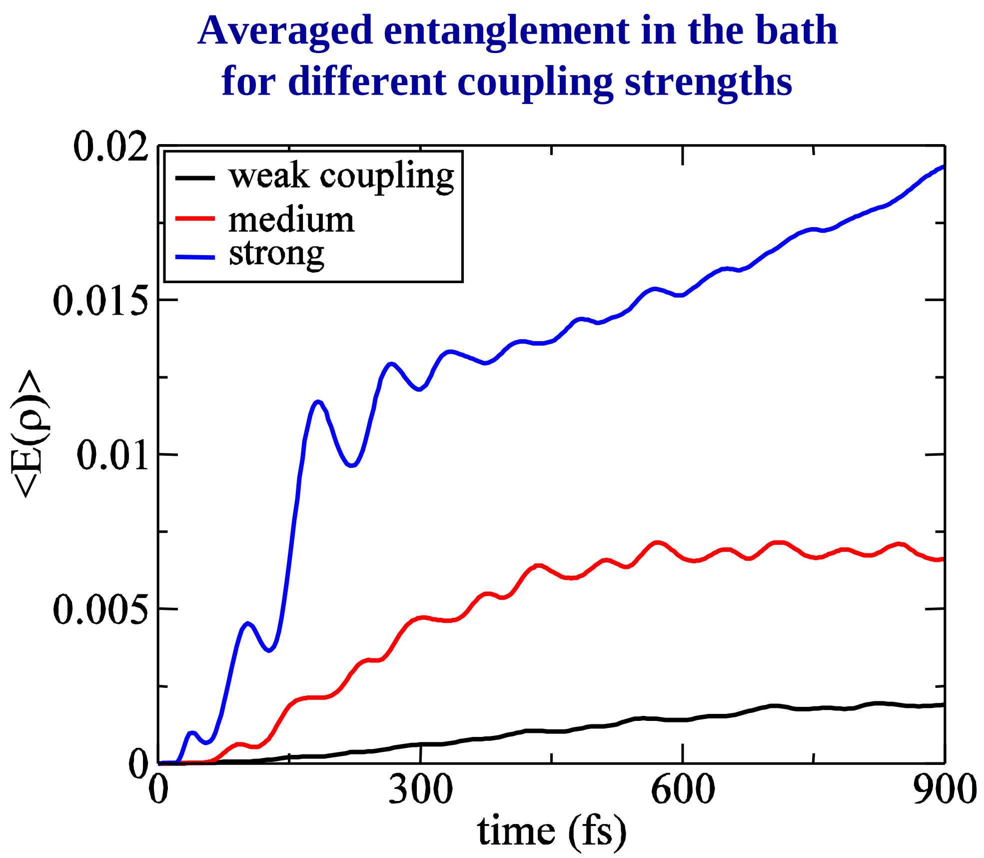
THE BATH'S SPECTRUM REMAINS ALMOST THE SAME

inter-spin interactions $\hat{H}_{\text{int}} = \sum_{ij} k_{ij}(\hat{s}_i^{\dagger}\hat{s}_j + \hat{s}_j^{\dagger}\hat{s}_i)$



Entanglement





The thermal wavefunction.

A thermal state diagonal in the energy representation

$$\rho_\beta = \frac{e^{-\beta H_0}}{Z} = \frac{1}{Z}\sum_{j=1}^{L} e^{-\beta E_j} |\Psi_j\rangle\langle\Psi_j|$$

with $\beta = 1/k_b T$, $\hat{\mathbf{H}}_0$ the stationary Hamiltonian and $Z = Tr\{e^{-\beta \hat{\mathbf{H}}_0}\}$

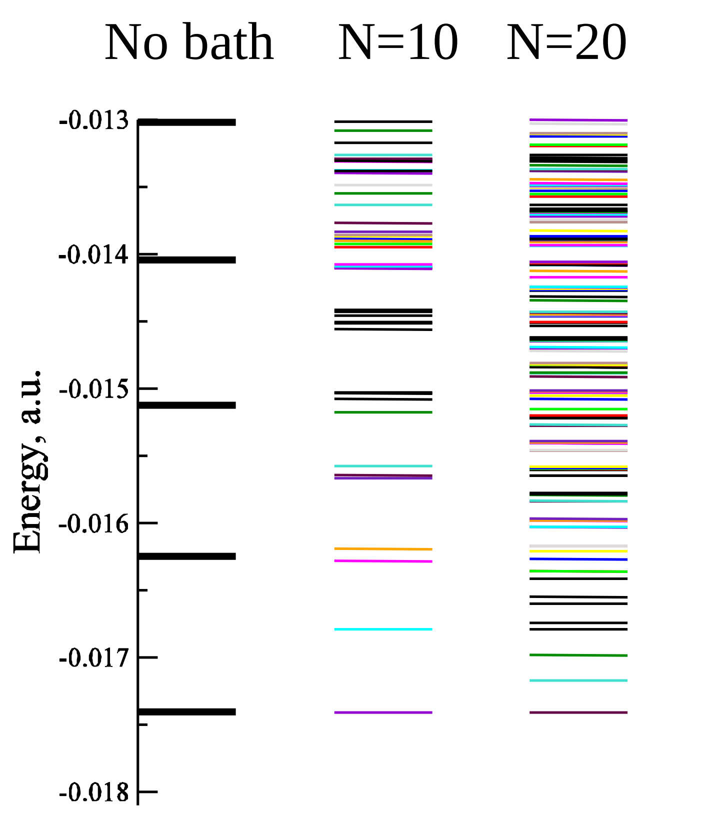
L is the size of the Hilbert space.

Evaluation of the sum will scale as $O(L^3)$

We can approximate ρ_β by using only J terms such that $e^{-\beta E_J} << \text{error}$

Evaluation of the sum will scale as $O(J^3)$

Finite Temperature



$\hat{H}_S \otimes \hat{H}_B$

$$\hat{H} = \hat{H}_0 + \hat{V}(t)$$

- **Diagonalization of $\hat{H}_0 = \hat{H}_S \otimes \hat{H}_B$**

$$E_i \quad \{\Psi_i\}$$

- **Separate simulations for every eigenstate**

$$e^{-i\hat{H}t}\,\Psi_i(0)$$

- **Boltzmann averaging**

$$\langle \hat{A} \rangle_T = \mathrm{tr}\{\hat{\rho}_b \hat{A}\}$$

The number of eigenstates grows with temperature and ***exponentially*** with the number of the bath modes

The random phase wavefunction Φ

$$|\Phi(\vec{\theta})\rangle = \sqrt{Q}\sum_{k=1}^{L} e^{i\theta_k}|\phi_k\rangle$$

ϕ_k is any complete set of eignevalues, θ is a set of random phases

The projection:

$$|\Phi(\vec{\theta})\rangle\langle\Phi(\vec{\theta})| = Q\sum_{n,m} e^{i(\theta_n-\theta_m)}|\phi_n\rangle\langle\phi_m| ,$$

The average of random phases

$$\left\langle e^{i(\theta_n-\theta_m)}\right\rangle = \frac{1}{2\pi}\int_0^{2\pi} e^{i(n-m)\theta}d\theta = \delta_{nm}$$

The identity operator:

$$\hat{\mathbf{I}} = \lim_{K\to\infty}\left(\frac{1}{K}\sum_{k=1}^{K}|\Phi(\vec{\theta}_k)\rangle\langle\Phi(\vec{\theta}_k)|\right)$$

Decomposing the thermal state into a sum of random projections:

$$\hat{\boldsymbol{\rho}}_\beta = \frac{1}{Z} e^{-\frac{\beta}{2}\hat{\mathbf{H}}_0}\ \hat{\mathbf{I}}\ e^{-\frac{\beta}{2}\hat{\mathbf{H}}_0} = \lim_{K\to\infty} \frac{1}{Z} \left(\frac{1}{K} \sum_{k=1}^{K} |\Phi(\frac{\beta}{2}, \vec{\theta}_k)\rangle\langle\Phi(\frac{\beta}{2}, \vec{\theta}_k)| \right)$$

The thermal random wavefunction:

$$|\Phi(\frac{\beta}{2}, \vec{\theta})\rangle = e^{-\frac{\beta}{2}\hat{\mathbf{H}}_0}|\Phi(\vec{\theta})\rangle \quad .$$

An average thermal expectation value:

$$\langle\hat{\mathbf{A}}\rangle_\beta = tr\{\hat{\boldsymbol{\rho}}_\beta\hat{\mathbf{A}}\} = \lim_{K\to\infty} \frac{1}{Z} \left(\frac{1}{K} \sum_{k=1}^{K} \langle\Phi(\frac{\beta}{2}, \vec{\theta}_k)|\hat{\mathbf{A}}|\Phi(\frac{\beta}{2}, \vec{\theta}_k)\rangle \right).$$

Random phase thermal wavepacket

For temperature T the initial state is described by the mixture:

$$\hat{\rho}_\beta = Z^{-1}\begin{pmatrix} e^{-\beta E_0} & 0 & 0 & \dots \\ 0 & e^{-\beta E_1} & 0 & \\ \vdots & & \ddots & \\ 0 & & & e^{-\beta E_j} \end{pmatrix}$$

Random phase thermal wavepacket

pure state $\hat{\rho}_\beta = \left|\Phi(\tfrac{\beta}{2},\theta)\right\rangle\left\langle\Phi(\tfrac{\beta}{2},\theta)\right|$

$$\left|\Phi(\tfrac{\beta}{2},\theta)\right\rangle = \sqrt{Q}\sum_k e^{-\frac{\beta}{2}E_k} e^{i\theta_k} \left|\varphi_k\right\rangle$$

$$\hat{\rho}_\beta = Z^{-1}\begin{pmatrix} e^{-\beta E_0} & e^{-\frac{\beta}{2}(E_0+E_1)} e^{i(\theta_1-\theta_0)} & \cdots \\ e^{-\frac{\beta}{2}(E_0+E_1)} e^{i(\theta_0-\theta_1)} & e^{-\beta E_1} & \\ \vdots & & \ddots \end{pmatrix}$$

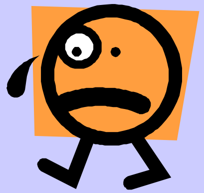
$$\left\langle e^{i(\theta_n-\theta_m)}\right\rangle = \frac{1}{2\pi}\int_0^{2\pi} e^{i(n-m)\theta}\,d\theta = \delta_{nm}$$

Random phase thermal wavepacket

How do we build $\left|\Phi(\tfrac{\beta}{2},\theta)\right\rangle = \sqrt{Q}\sum_{k} e^{-\frac{\beta}{2}E_k} e^{i\theta_k}\left|\varphi_k\right\rangle$ **?**

$$\left|\Phi(\theta)\right\rangle = \sqrt{Q}\sum_{k=1}^{L} e^{i\theta_k}\left|\varphi_k\right\rangle \xrightarrow{\;e^{-\frac{\beta}{2}\hat{H}_0}\;} \left|\Phi(\tfrac{\beta}{2},\theta)\right\rangle$$

Imaginary time propagation



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completeness

$$\hat{I} = \lim_{K\to\infty}\left(\frac{1}{K}\sum_{k=1}^{K}\left|\Phi(\theta_k)\right\rangle\left\langle\Phi(\theta_k)\right|\right) \Rightarrow \hat{\rho}_\beta = \frac{1}{Z} e^{-\frac{\beta}{2}\hat{H}_0}\,\hat{I}\,e^{-\frac{\beta}{2}\hat{H}_0}$$

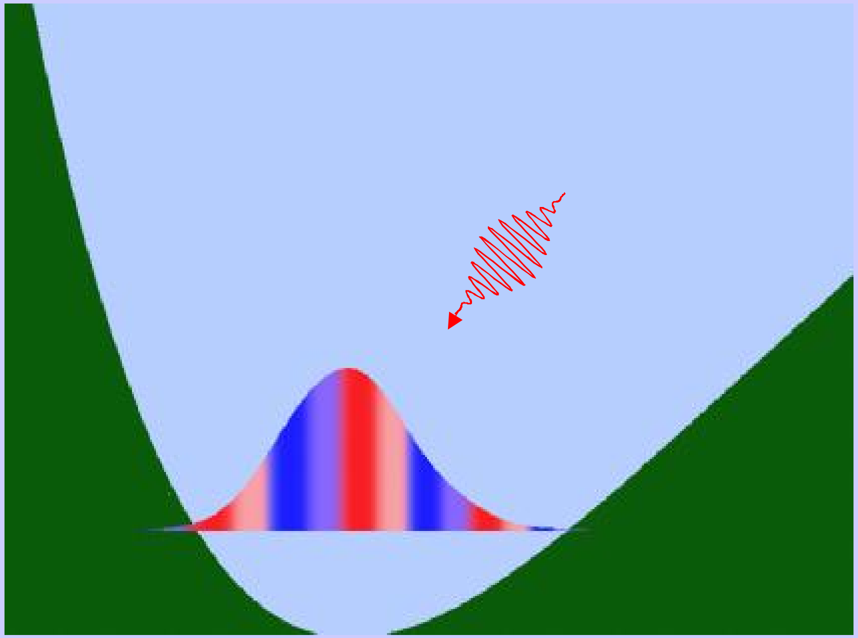
Random phase wavepackets can be expanded in any set of states !!!

Random phase thermal wavepacket

Example: Morse Oscillator linearly coupled to an Ohmic bath

$$\hat{H} = \frac{\hat{P}^2}{2M} + D\left(1 - e^{-\alpha \hat{X}}\right)^2 + \sum_i \omega_i \hat{\sigma}_i^\dagger \hat{\sigma}_i + \hat{X} \sum_i \lambda_i (\hat{\sigma}_i^\dagger + \hat{\sigma}_i) - \hat{\mu}\hat{E}(t)$$

system **bath** **interaction** **field**



Observables:

- $P = \left\langle \frac{\partial \hat{H}_{\text{int}}}{\partial t} \right\rangle \qquad \hat{H}_{\text{int}} = -\hat{\mu}\hat{E}(t)$
- $C(t) = Tr_S \{ \hat{\rho}_S \hat{M} \}$

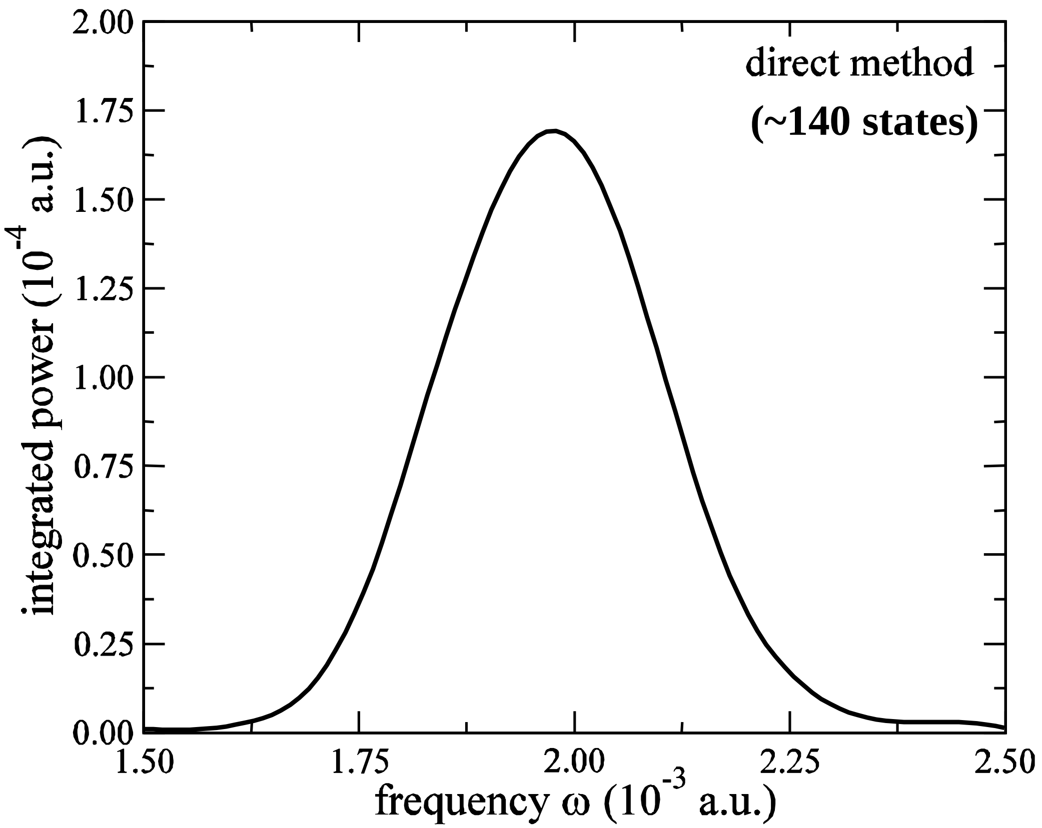
  $\hat{M} = \hat{\mu}^* e^{-i\hat{H}t} \hat{\mu} e^{i\hat{H}t}$

Direct Vs random phase method

$$\Delta E = \int_0 P\,dt \qquad kT = \omega_0$$

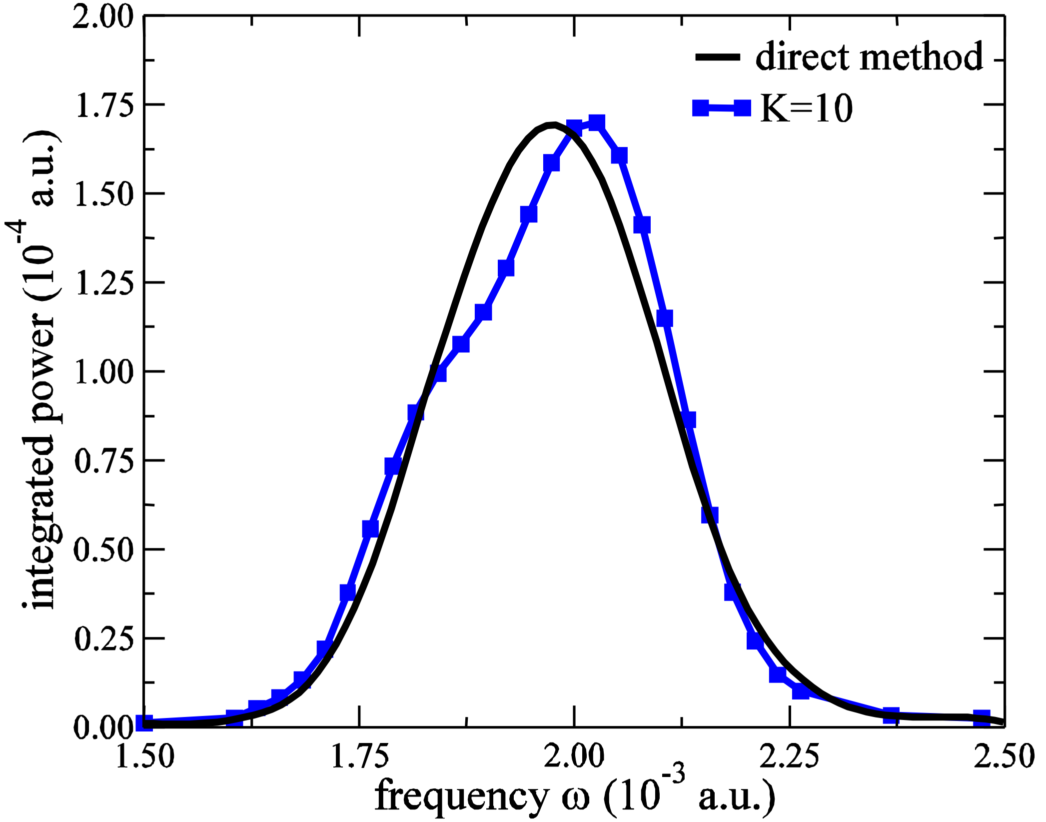
$$P = \left\langle \frac{\partial \hat{H}_{int}}{\partial t} \right\rangle$$

$$\hat{H}_{int} = -\hat{\mu}\hat{E}(t)$$



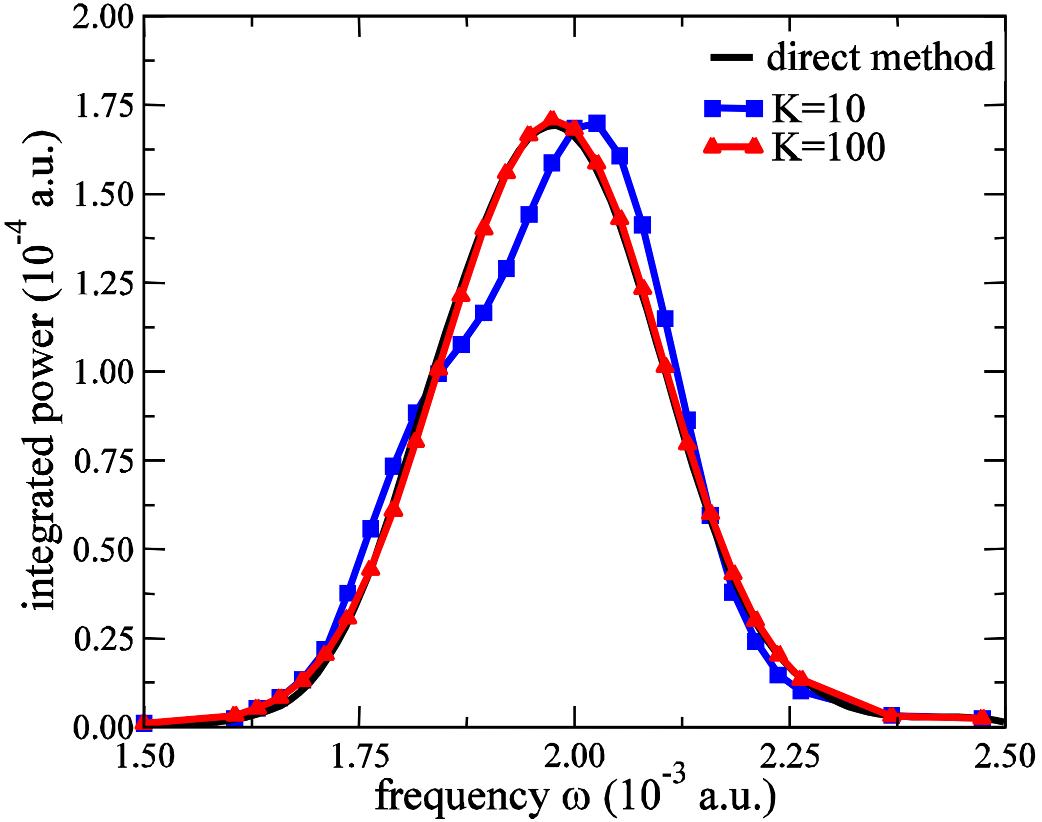
Direct Vs random phase method

$$\Delta E = \int_0 P\,dt \qquad kT = \omega_0$$



Direct Vs random phase method

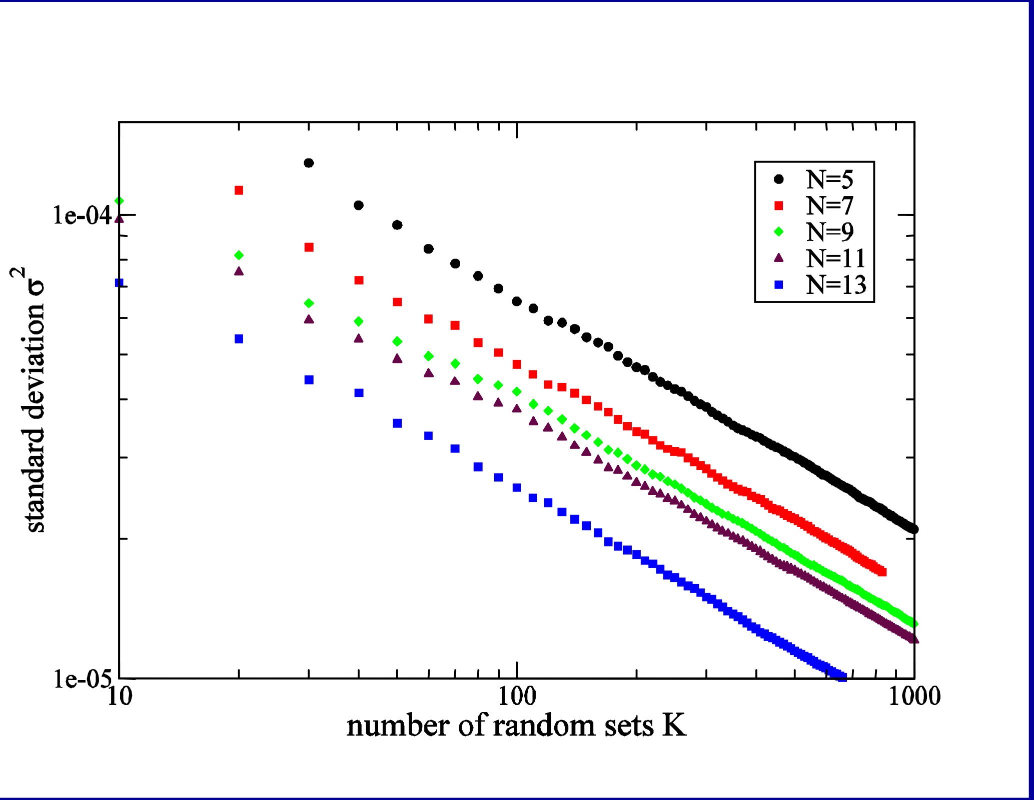
$$\Delta E = \int_0^{\infty} P\,dt \qquad kT = \omega_0$$



When is the random phase method preferable?

How many random sets (K) do we need to obtain the desired accuracy?

$$s^2 = \frac{l(L)}{K}$$



K **number of random sets**

L **system size**

l **may depend on**

- **system size**
- **temperature**
- **properties of the observable**

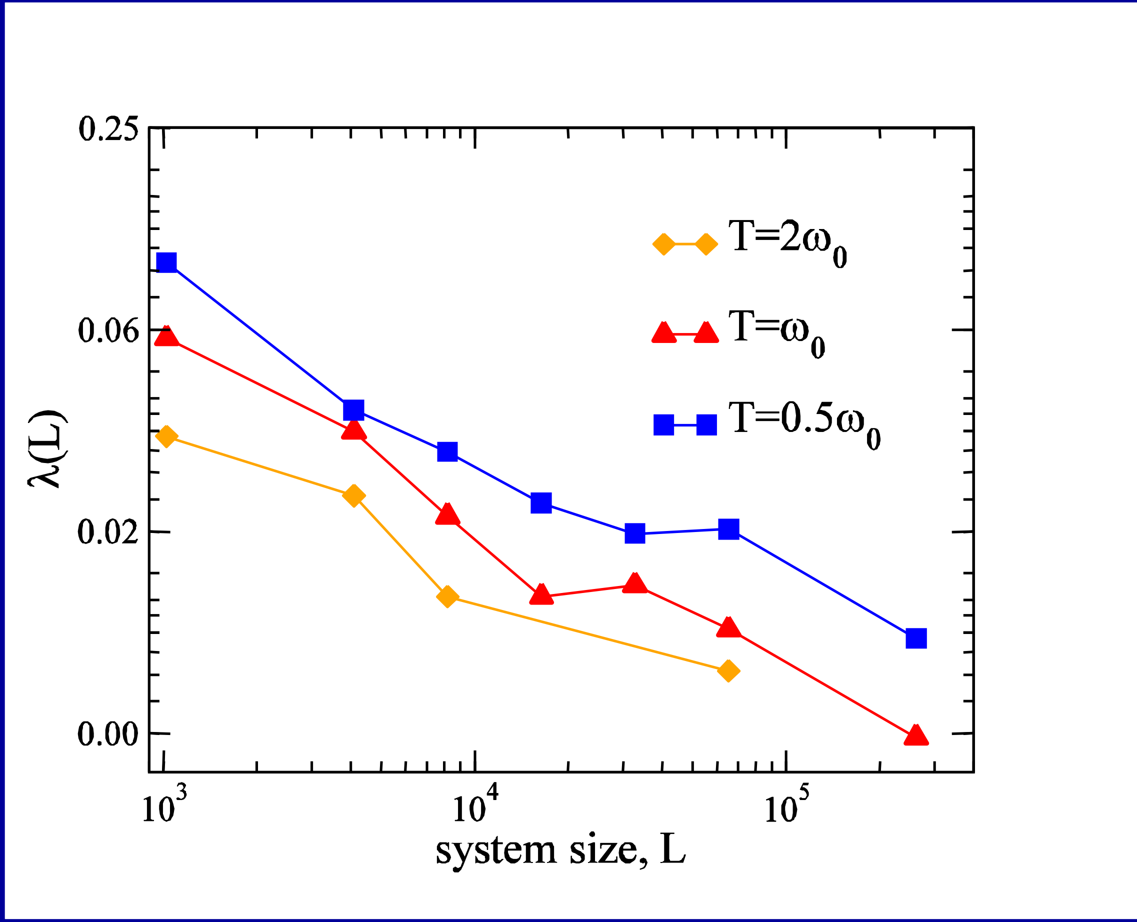
When is the random phase method preferable?

$$K(L) = \frac{l(L)}{s^2}$$

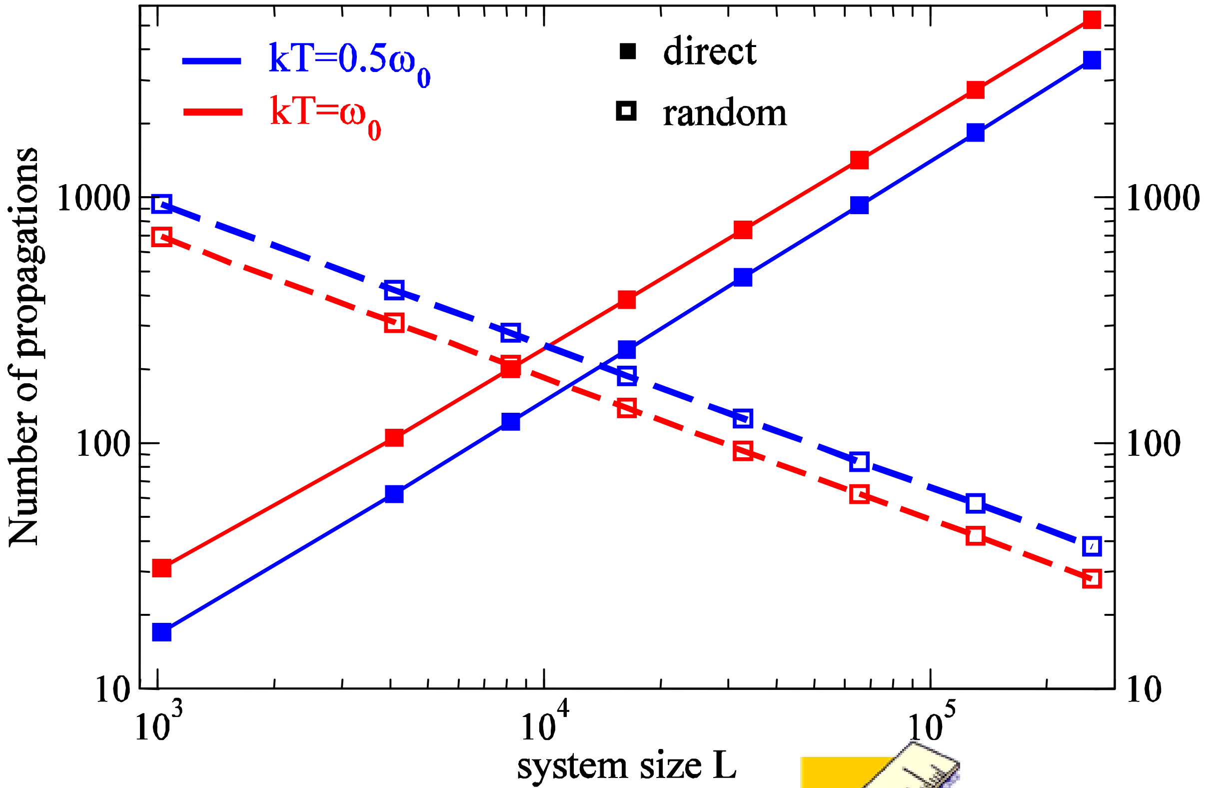
K **number of random sets**

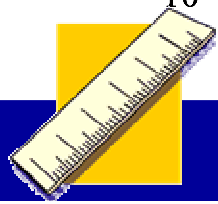
L **system size**

SELF-AVERAGING



When is the random phase method preferable?

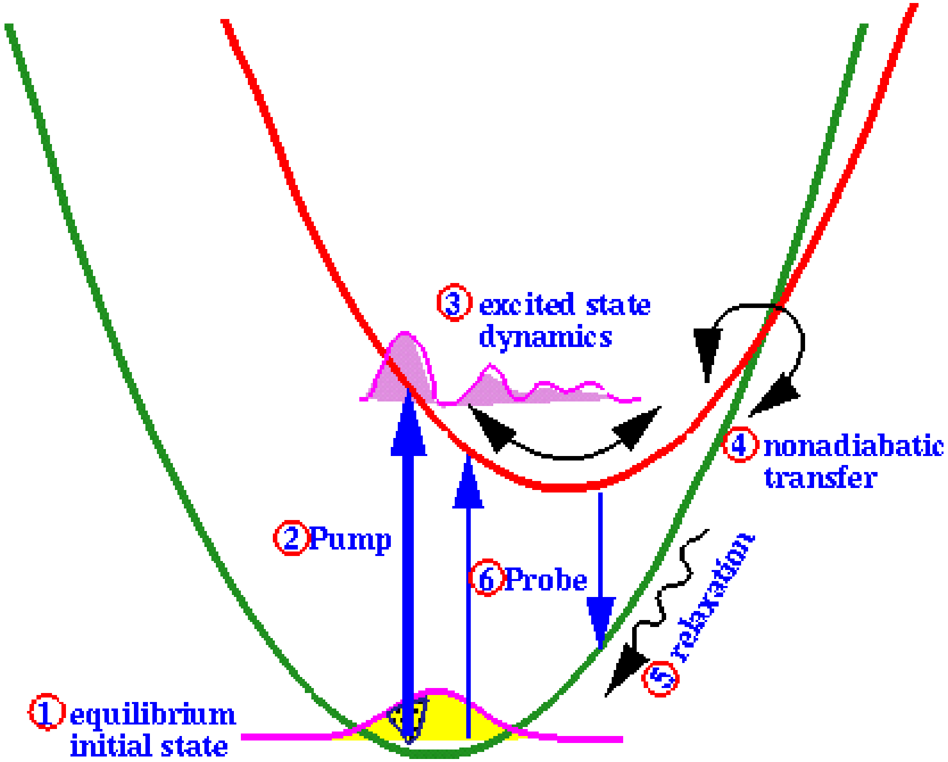




Open Questions

- Differences between the spin and harmonic bath. Finite temperature simulations? Saturation?
- Entanglement between the bath modes. How important? Where?
- What is the reason for the self-averaging in the random phase method?
- Constructing the bath from the first principles.

Charge transfer photoexcitation cycle



1. Equilibration of initial state

$$\rho \neq \rho_S \otimes \rho_B$$

2. Excitation by pump pulse

   Pump field influences the system–bath coupling

   Electronic dephasing

3. Dynamics of the ground and excited state

   Nuclear dephasing and relaxation

4. Nonadiabatic charge transfer

   Influenced by all dissipative mechanisms

5. Relaxation and recovery of equilibrium

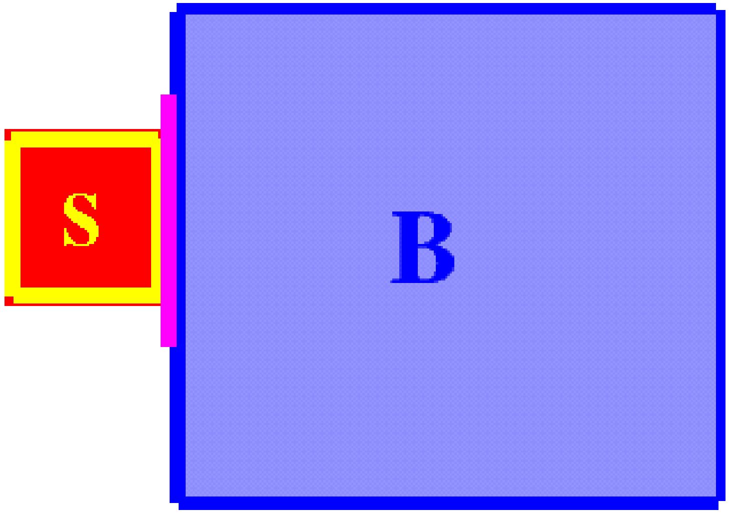
   Nuclear relaxation

6. Monitoring of cycle by probe pulse

   Electronic dephasing

The Surrogate Hamiltonian

$$\mathbf{H} = \mathbf{H}_S + \mathbf{H}_B + \mathbf{H}_{SB}$$



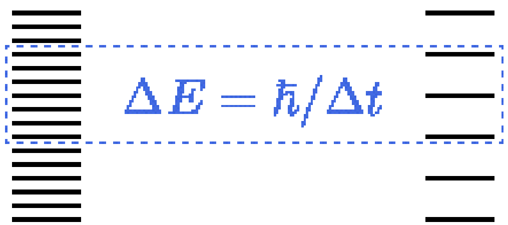
- *implicit* description of the bath
- replace:

$$\hat{\mathsf{H}}_B = \sum_{k=1}^{\infty} \hat{\mathsf{n}}_k^{\mathsf{true}} \longrightarrow \sum_{k=1}^{N} \hat{\mathsf{n}}_k^{\mathsf{rep}}$$

- Hamiltonian dynamics: $\Psi(\hat{\mathsf{Q}};t) = \mathsf{e}^{-i\hat{\mathsf{H}}t}\Psi(\hat{\mathsf{Q}};0)$.
- For times $t \ll \infty$, $N \ll \infty$ sufficient!

$\curvearrowright$ good for ultrafast events

R. Baer and R. Kosloff. J. Chem. Phys. 106 (1997), 8862–8875.



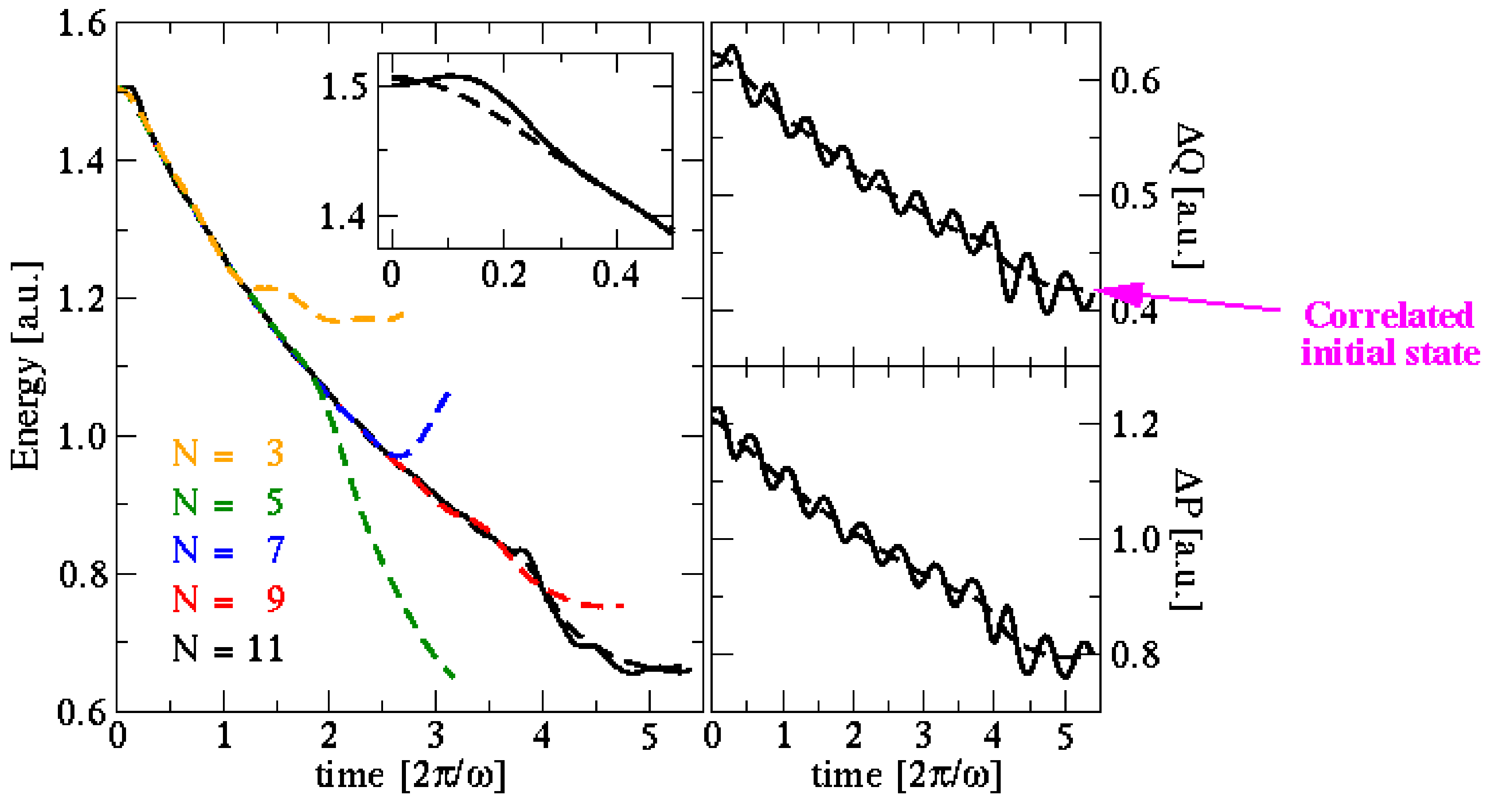
The interaction between system and bath: Relaxation

Energy exchange between system and bath

Nuclear relaxation

$$\hat{\mathbf{H}}_{SB}^{nr} = \begin{pmatrix} f_g(\hat{\mathbf{Q}}) & 0 \\ 0 & f_e(\hat{\mathbf{Q}}) \end{pmatrix} \otimes \sum_i d_i^{nr}(\hat{\boldsymbol{\sigma}}_i^+ + \hat{\boldsymbol{\sigma}}_i) \;,$$

$$d_i^{nr} = \sqrt{J(\varepsilon_i)/\rho(\varepsilon_i)} \;.$$

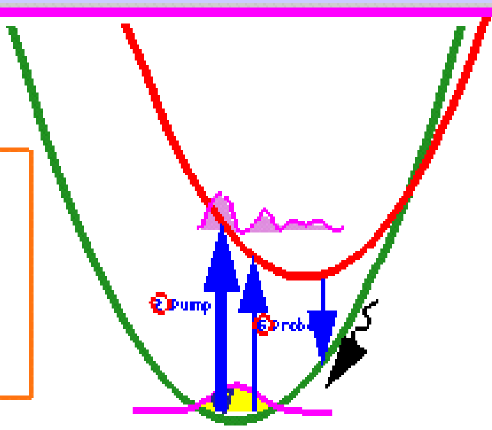


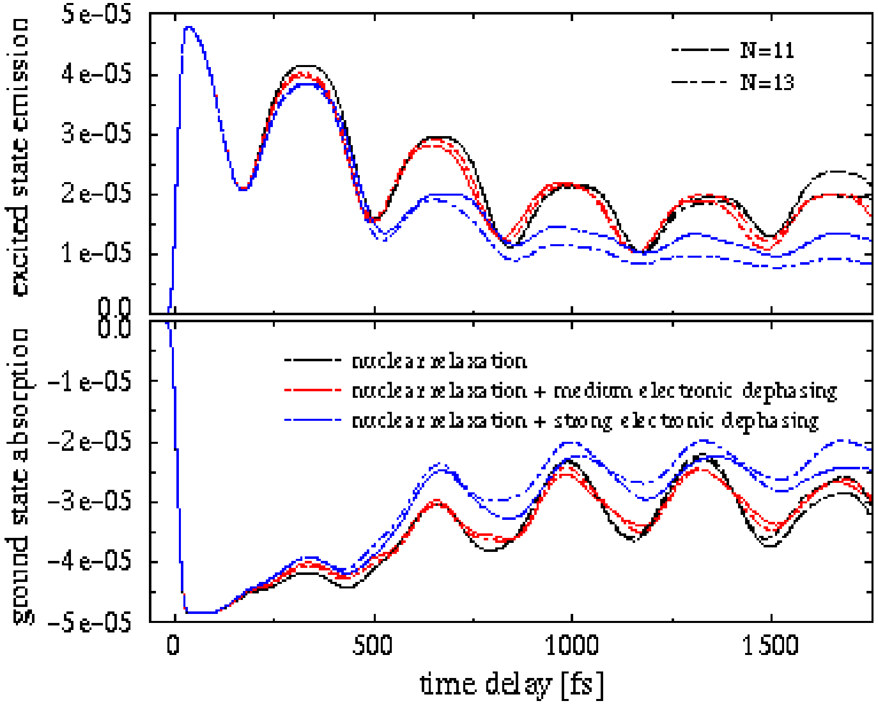
Absorption of the probe pulse

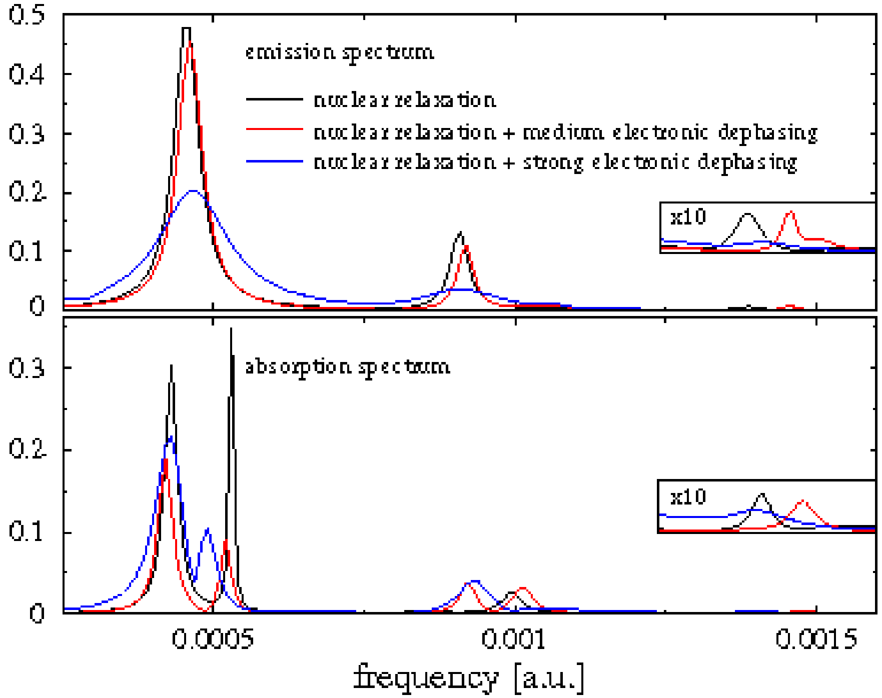
$$\hat{\mathbf{H}}_S = \begin{pmatrix} \hat{\mathbf{H}}_g & V_d(\hat{\mathbf{Q}}) \\ V_d(\hat{\mathbf{Q}}) & \hat{\mathbf{H}}_e \end{pmatrix} \otimes \mathbb{1}_B$$

$$\mathcal{P} = \left\langle \frac{\partial \hat{\mathbf{H}}_{SF}}{\partial t} \right\rangle = \mathrm{tr}_S \left\{ \hat{\rho}_S \frac{\partial}{\partial t} \hat{\mathbf{H}}_{SF} \right\} .$$

$$\Delta E = \int \mathcal{P} dt = -\hbar \omega_L \Delta N_g .$$





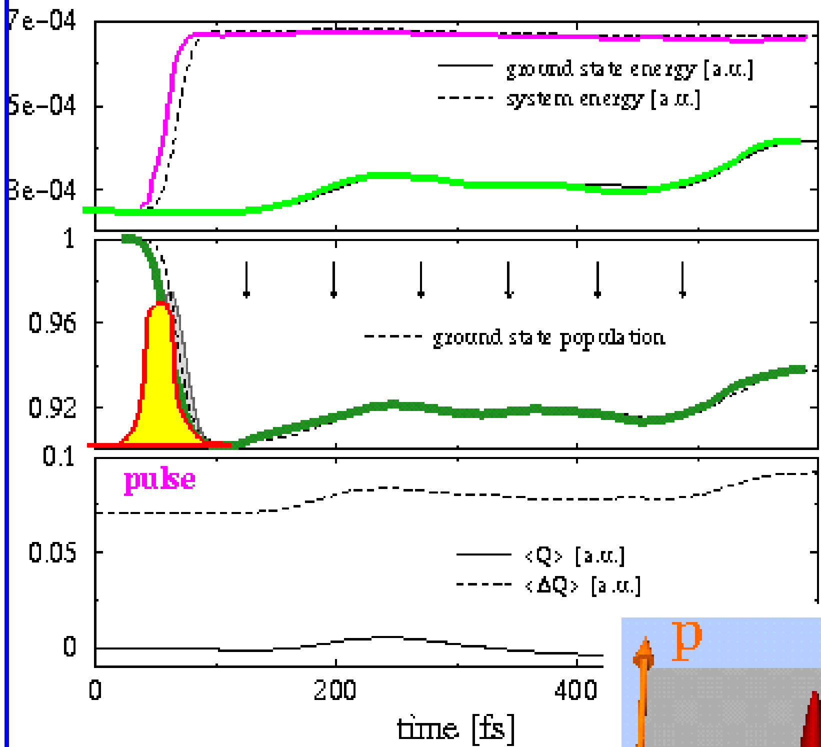


Effect of electronic dephasing

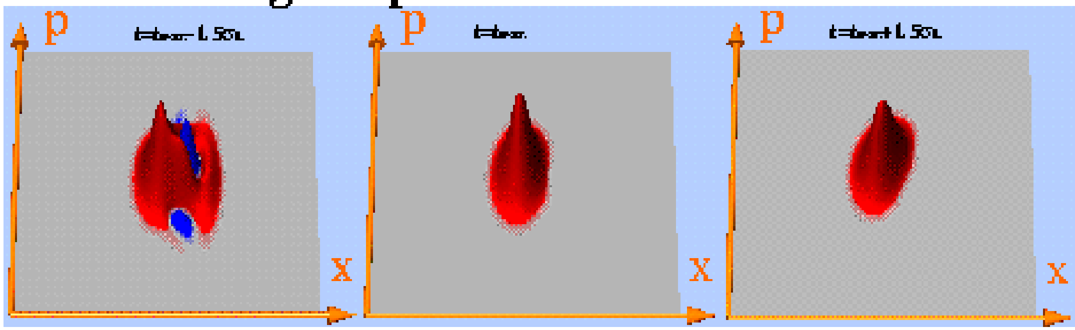
Dynamical hole

Filter diagonalization

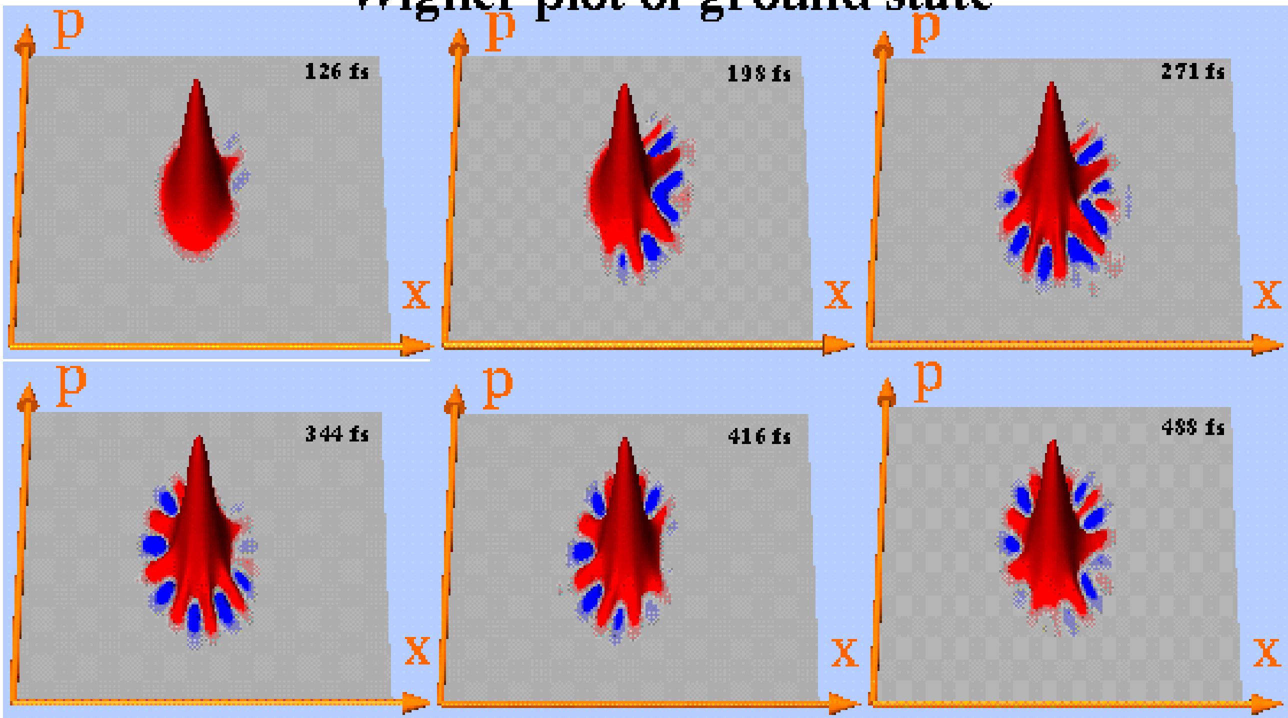
Excitation by pump pulse



Wigner plot of excited state



Wigner plot of ground state

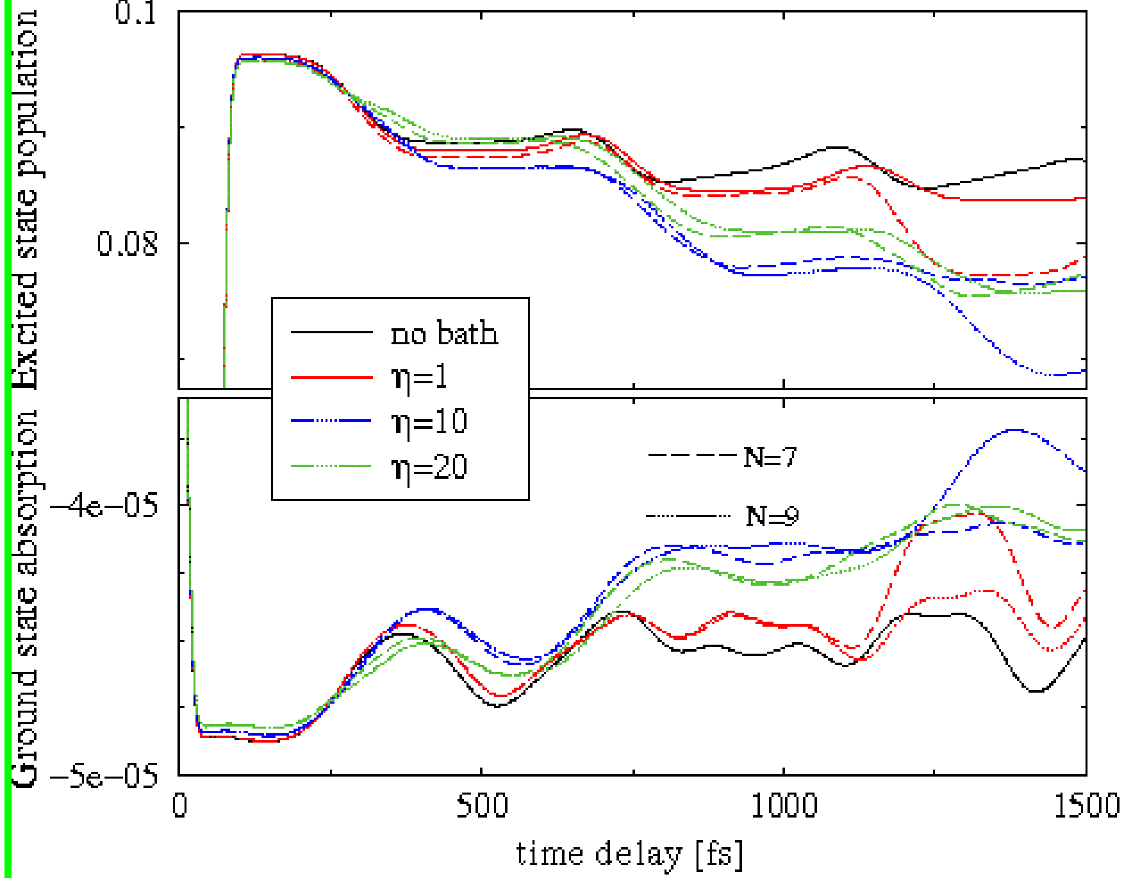


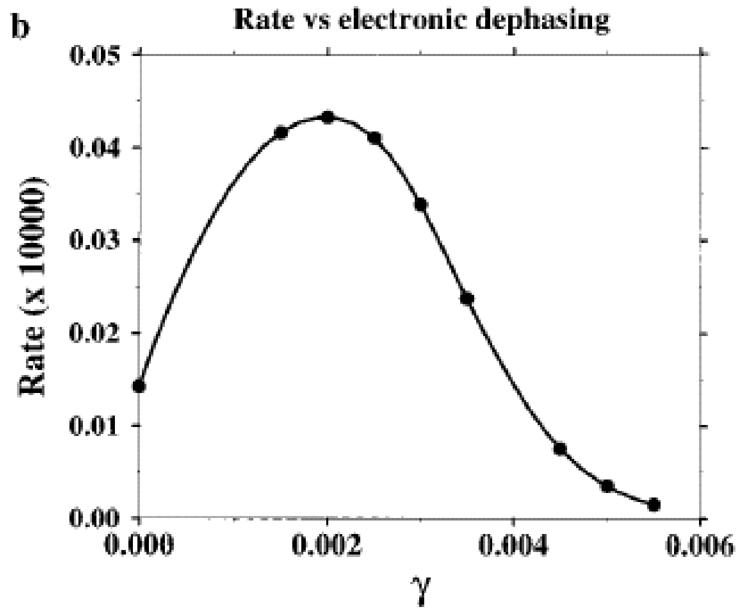
$$\hat{\mathbf{H}}_{SF} = \begin{pmatrix} 0 & -E(t)\hat{\boldsymbol{\mu}}_{tr} \\ -E^*(t)\hat{\boldsymbol{\mu}}_{tr} & 0 \end{pmatrix} \otimes \mathbb{1}_B$$

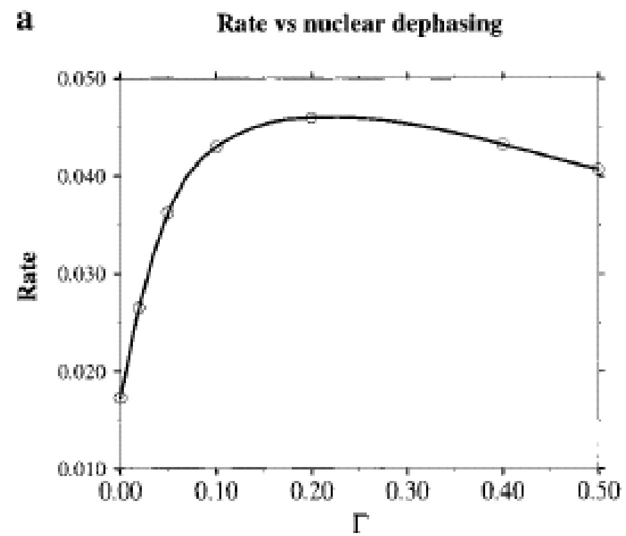
$$E(t) = E_0\, \mathrm{e}^{\frac{-(t-t_{max})^2}{2\sigma_L^2}}\, \mathrm{e}^{-i\omega_L t}\,.$$

10% excitation

The turnover Quantum Zeno effect







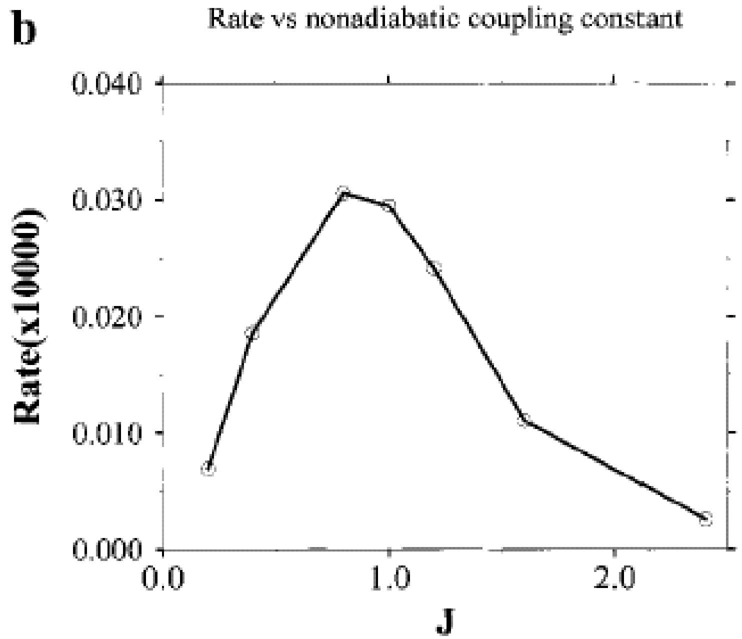
J. Am. Chem. Soc. **1999,** *121,* 3386–3395

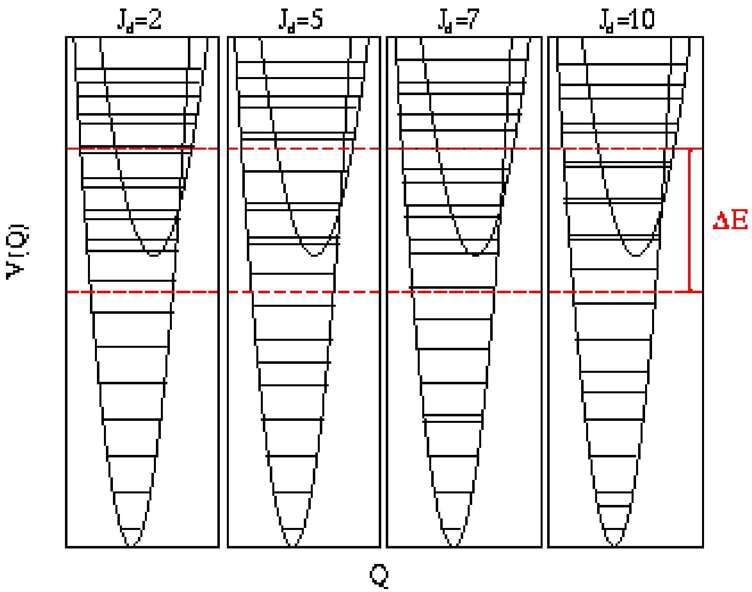
Photoexcited Electron Transfer: Short-Time Dynamics and Turnover Control by Dephasing, Relaxation, and Mixing

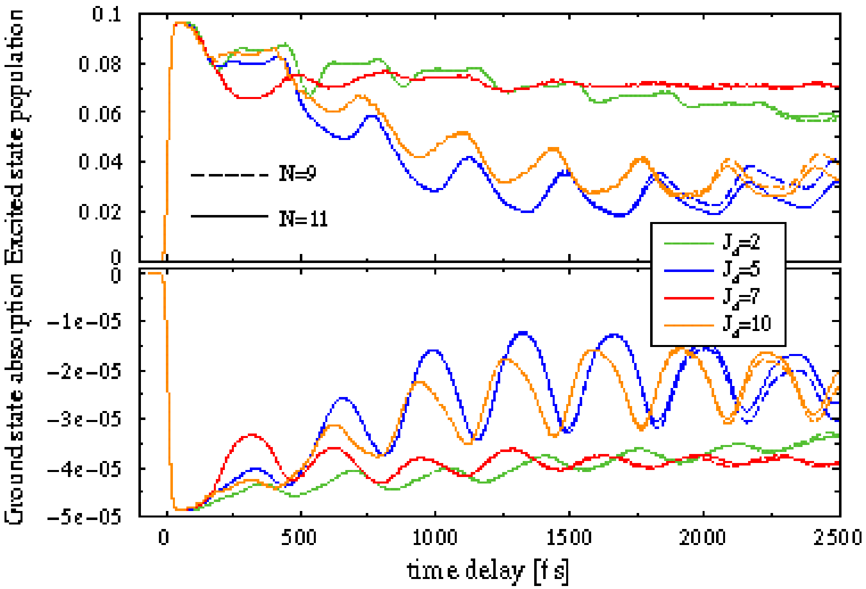
Guy Ashkenazi,† Ronnie Kosloff,*,† and Mark A. Ratner*,‡

Turnover with respect to the nonadiabatic coupling J

Semigroup vs Surrogate Hamiltonain







The scaling of the statistical error:

$$\sigma^2 = \frac{\lambda(L)}{K}$$

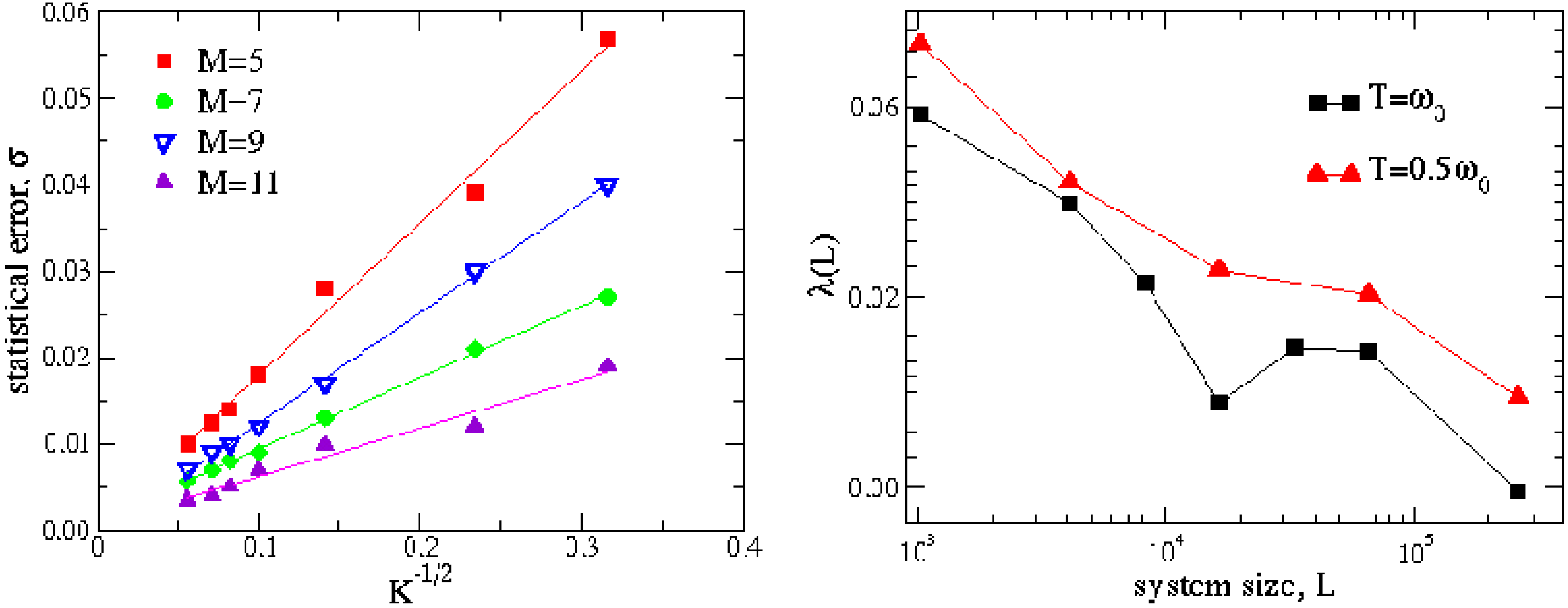
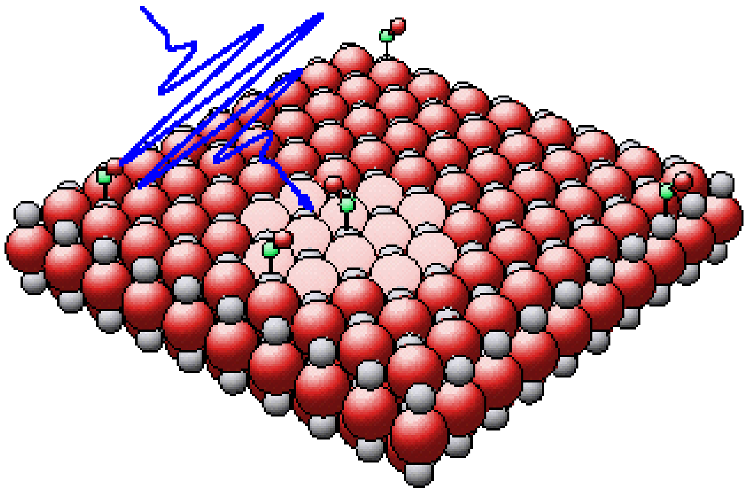
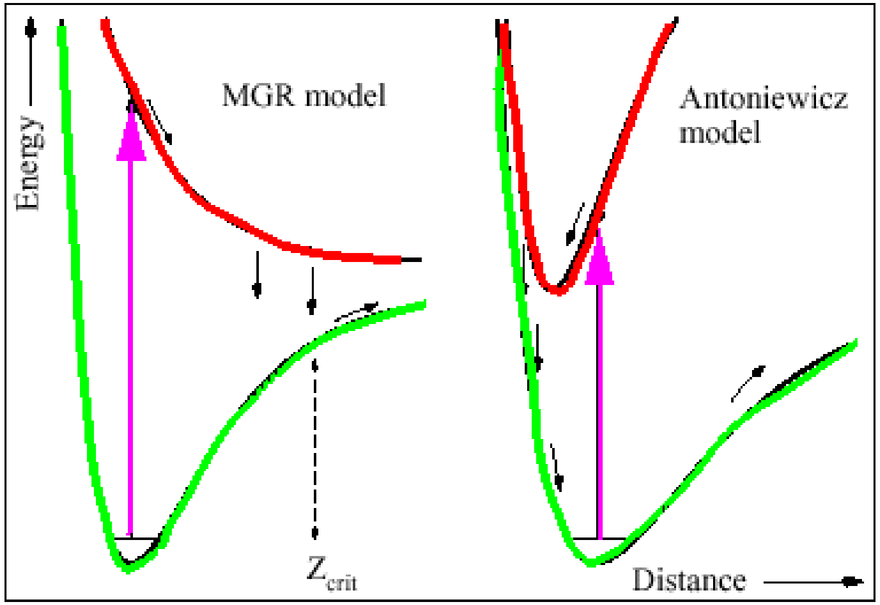


Fig. 2. (Left) The error $\sigma(\mathcal{P})/\langle\mathcal{P}\rangle$ in the power absorbed at ω_{max} as a function of $K^{-1/2}$, where K is the number of random phase sets. The calculations are made for an increasing number of bath modes. (Right) The function $\lambda(L)$ versus the system size for two different temperatures.

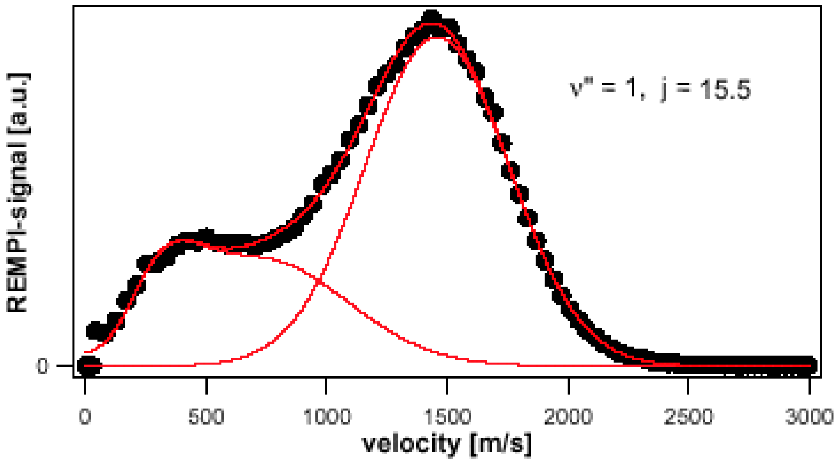
Self averaging $\lambda(L) \propto 1/L$

Laser induced desorption NO on NiO(100)



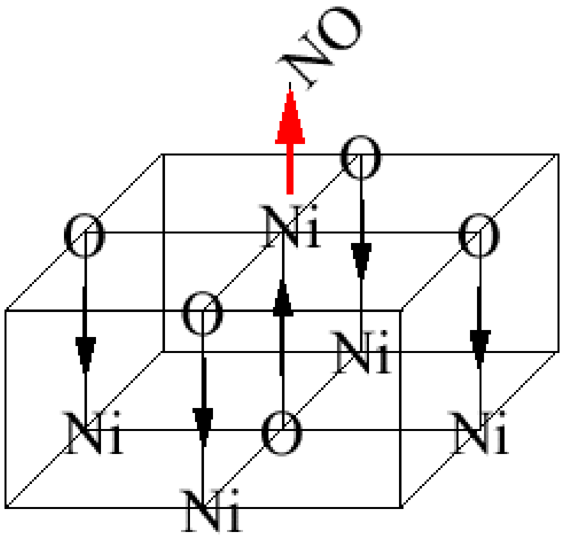


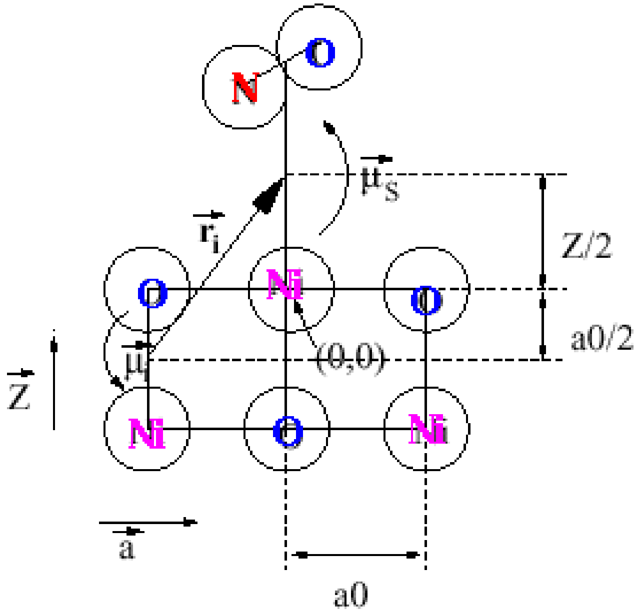
Experimental velocity distribution



Electronic quenching

NO/NiO(100) the surrogate Hamiltonian approach





A direct excitonic bath construction

$$\hat{\mathbf{H}}_B = \varepsilon \sum_i \hat{\boldsymbol{\sigma}}_i^+ \hat{\boldsymbol{\sigma}}_i + \frac{\eta}{\log(N)} \sum_{ij(NN)} (\hat{\boldsymbol{\sigma}}_i^+ \hat{\boldsymbol{\sigma}}_j + \hat{\boldsymbol{\sigma}}_j^+ \hat{\boldsymbol{\sigma}}_i) \ ,$$

System bath coupling

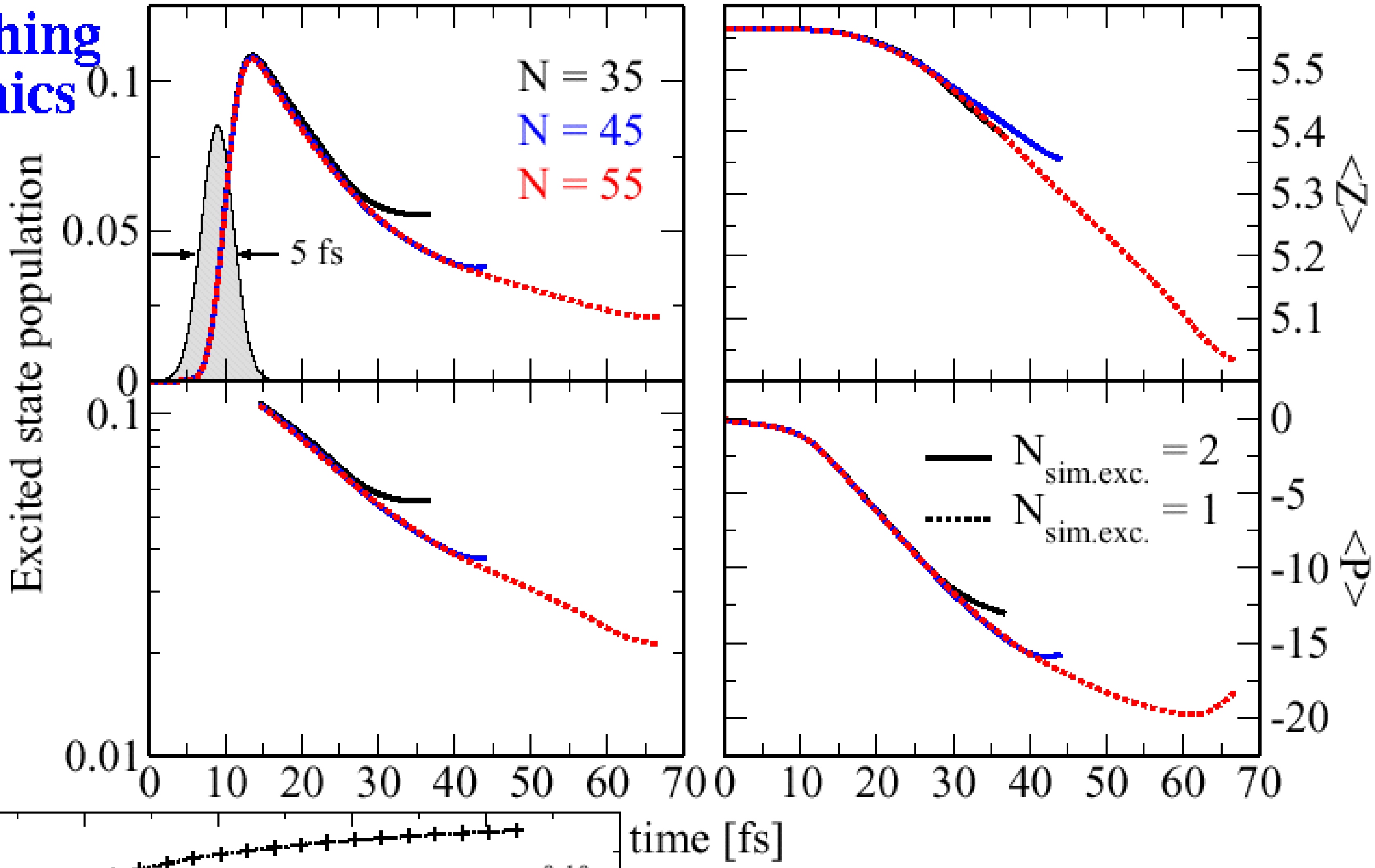
$$\hat{\mathbf{H}}_{SB} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \otimes \sum_i \hat{\mathbf{V}}_i (\hat{\boldsymbol{\sigma}}_i^+ + \hat{\boldsymbol{\sigma}}_i) \ ,$$

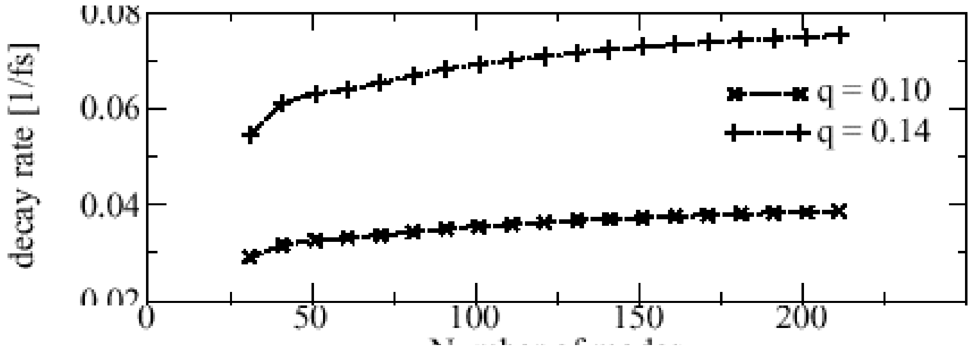
$$\hat{\mathbf{V}}_i = \hat{\vec{\mu}}_S \cdot \vec{E}_i = \frac{\hat{\vec{\mu}}_S \cdot \hat{\vec{\mu}}_i}{|\hat{\vec{\mathbf{r}}}_i|^3} - 3 \frac{(\hat{\vec{\mu}}_S \cdot \hat{\vec{\mathbf{r}}}_i)(\hat{\vec{\mu}}_i \cdot \hat{\vec{\mathbf{r}}}_i)}{|\hat{\vec{\mathbf{r}}}_i|^5} \ .$$

Dipole–dipole coupling

$$\hat{\mathbf{H}}_{BF}(t) = E(t) \sum_i \mu_i (\hat{\boldsymbol{\sigma}}_i^+ + \hat{\boldsymbol{\sigma}}_i) \ .$$

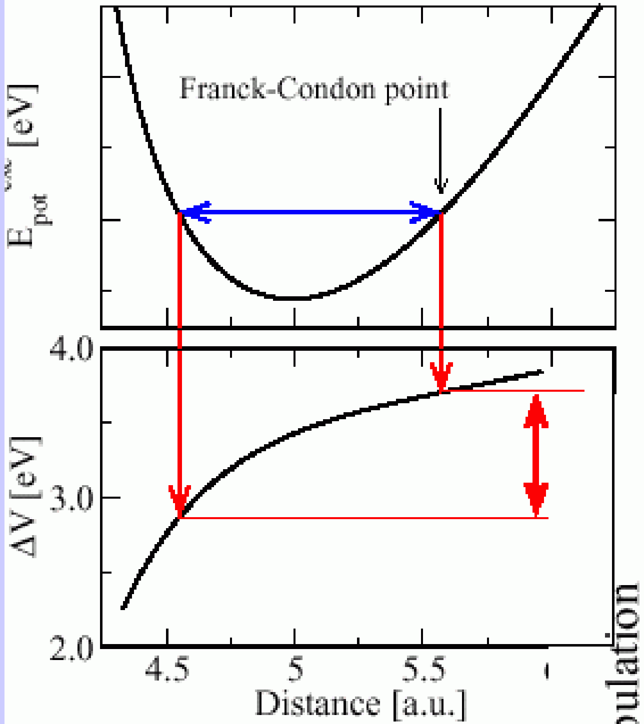
Quenching Dynamics



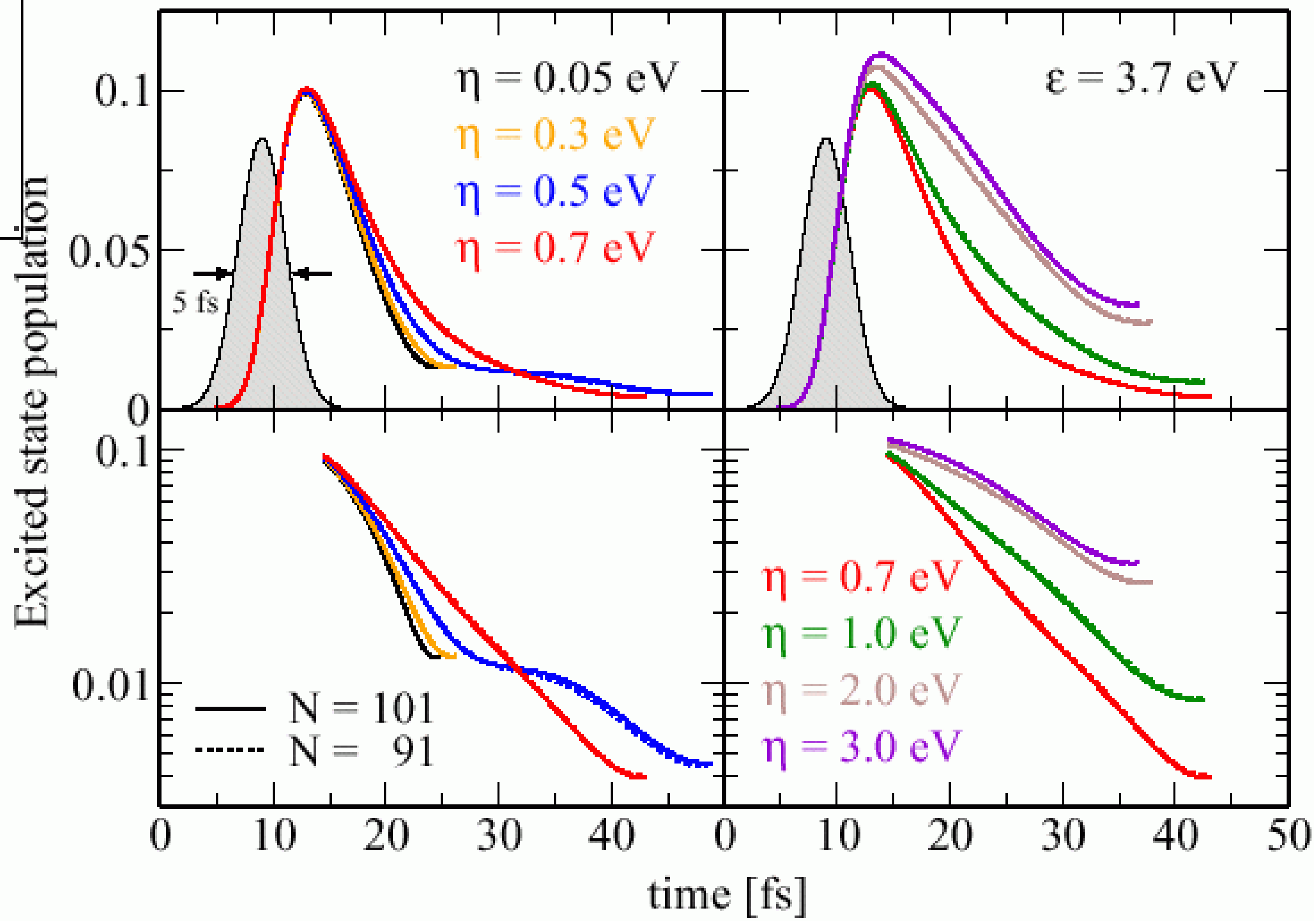


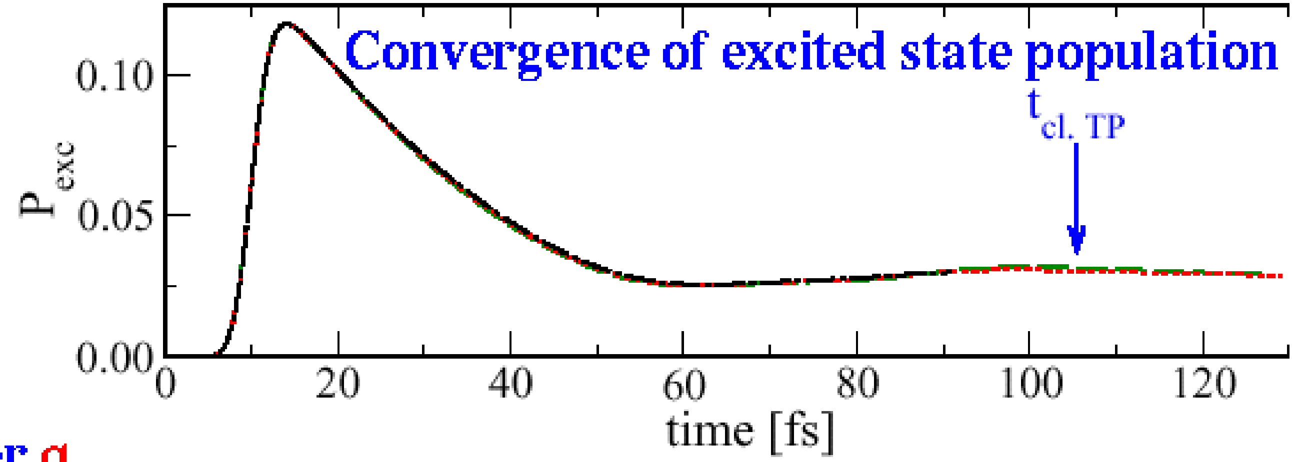
Convergence of decay rate as a function of charge transfer

Quenching dynamics

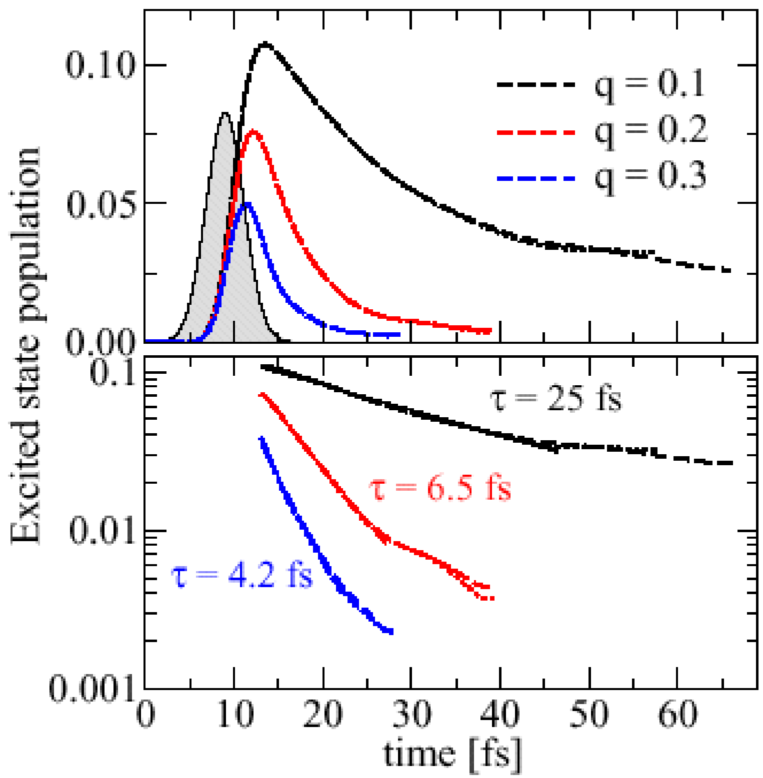


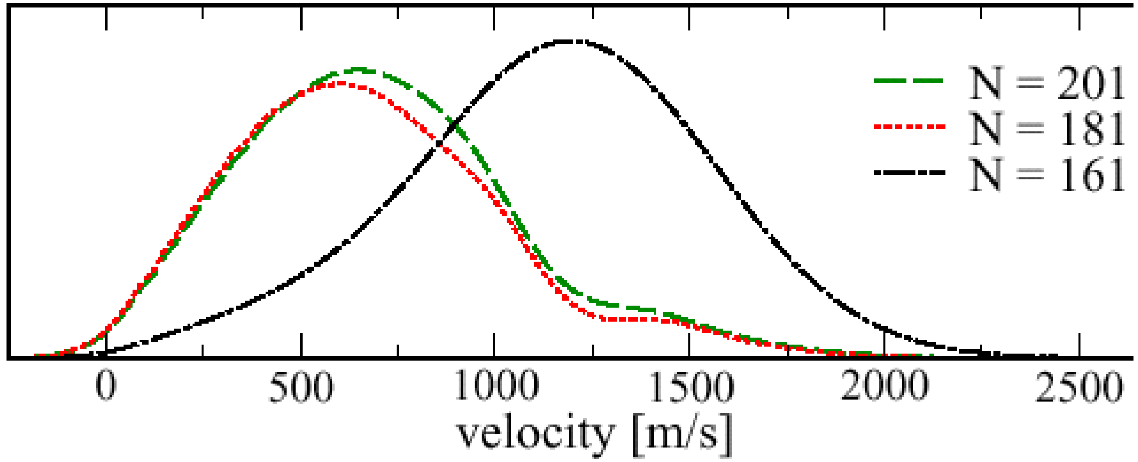
Influence of nearest neighbor coupling parameter





Lifetime as a function of effective charge transfer q

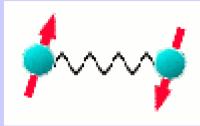


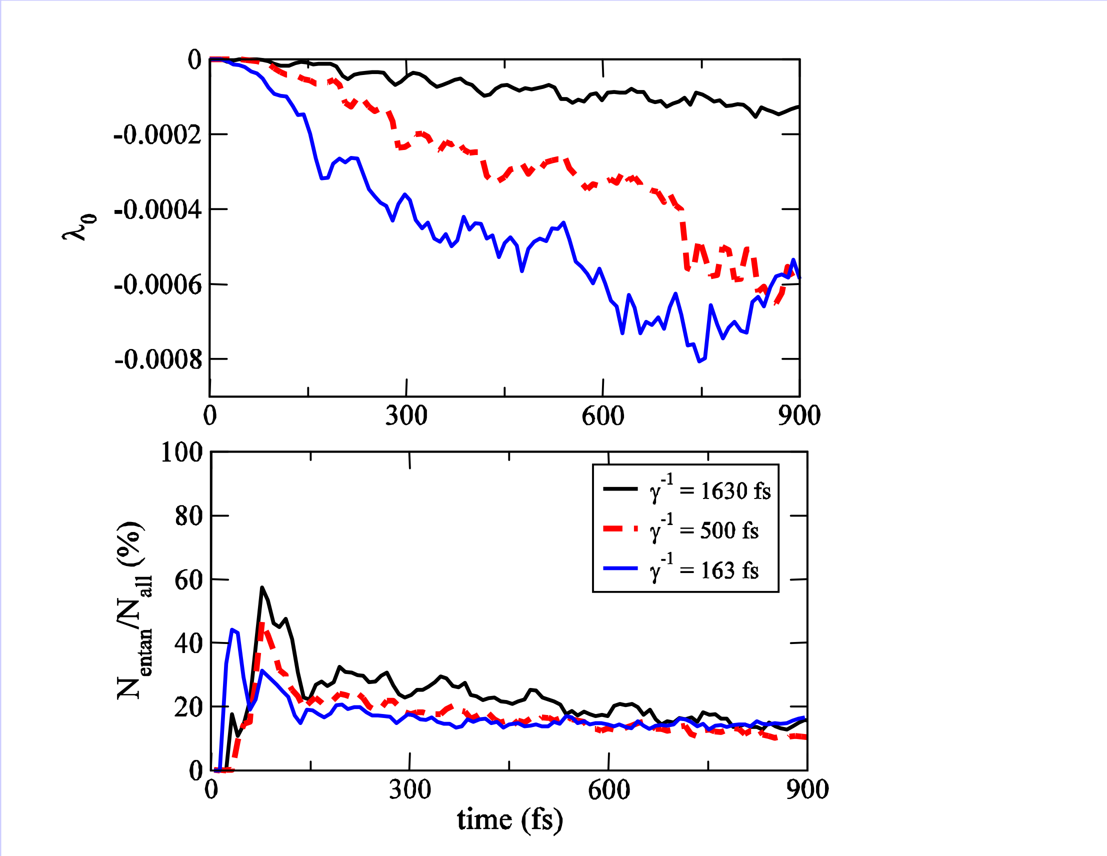


Convergence of velocity distribution

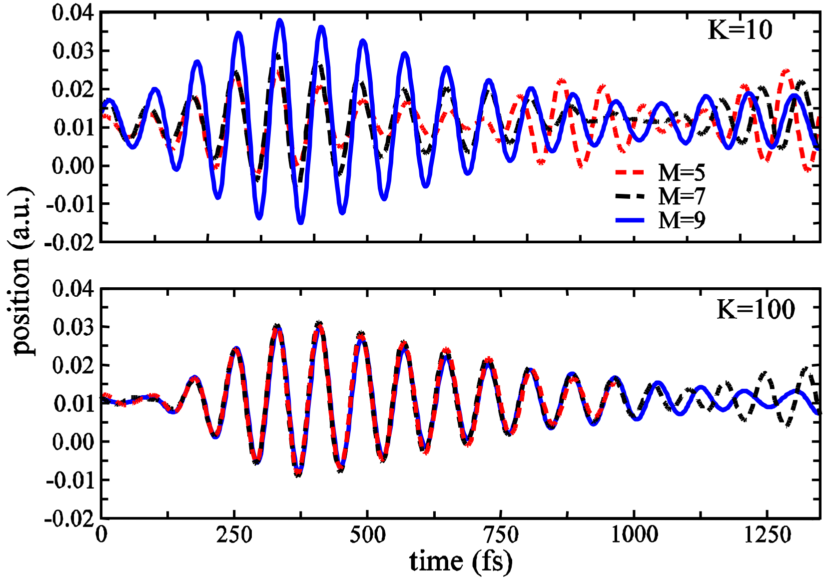
END

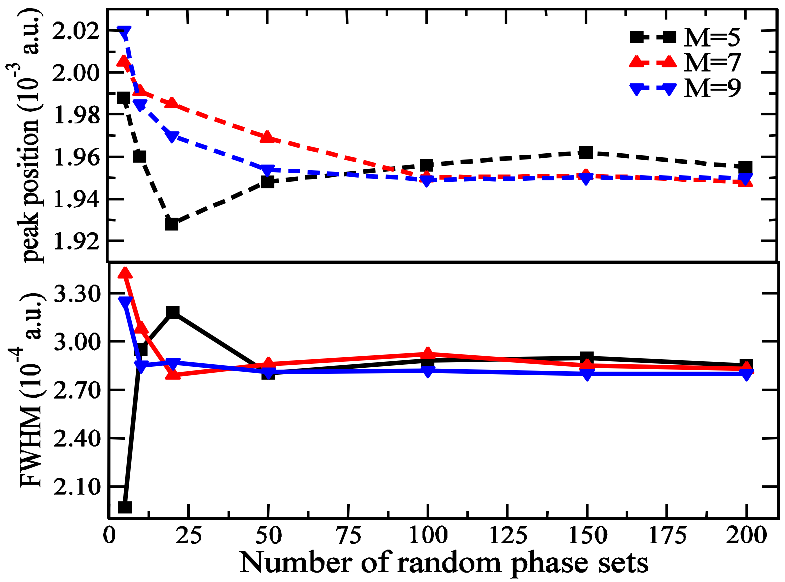
Entanglement





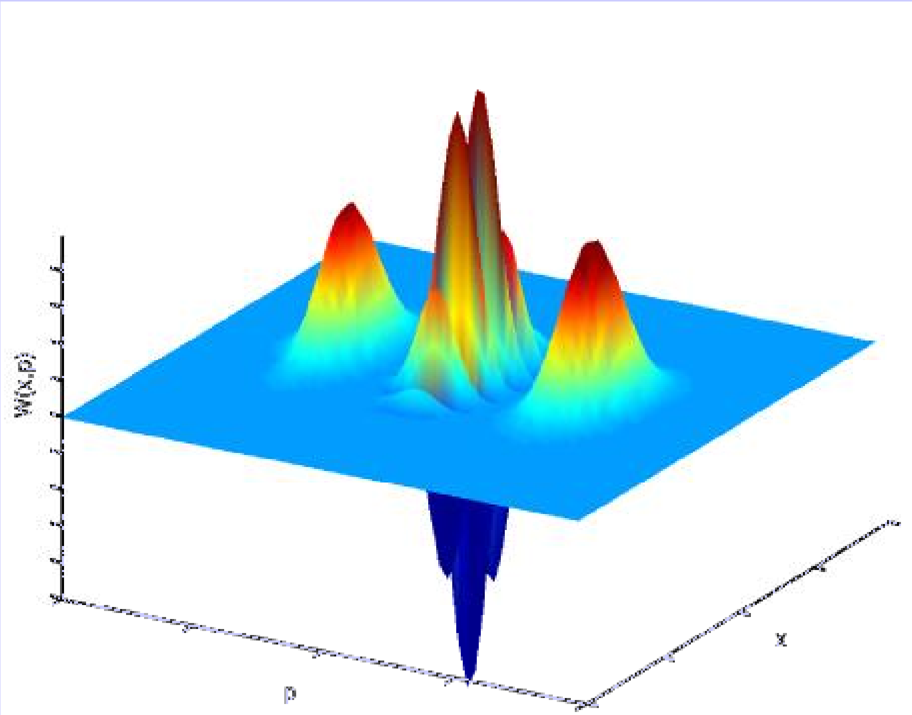
Random phase thermal wavepacket

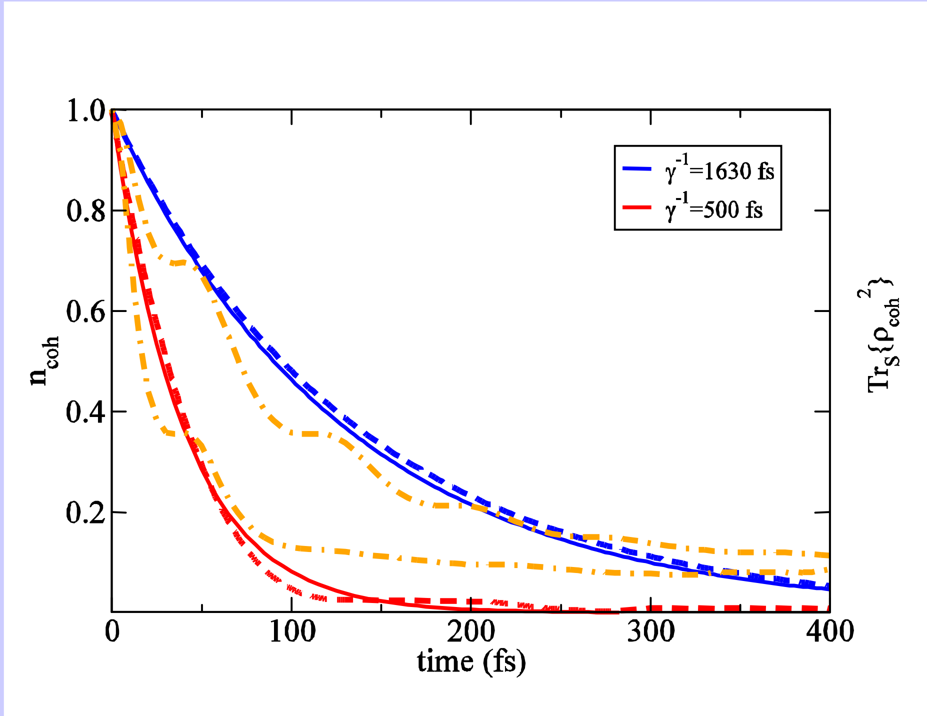




Decoherence

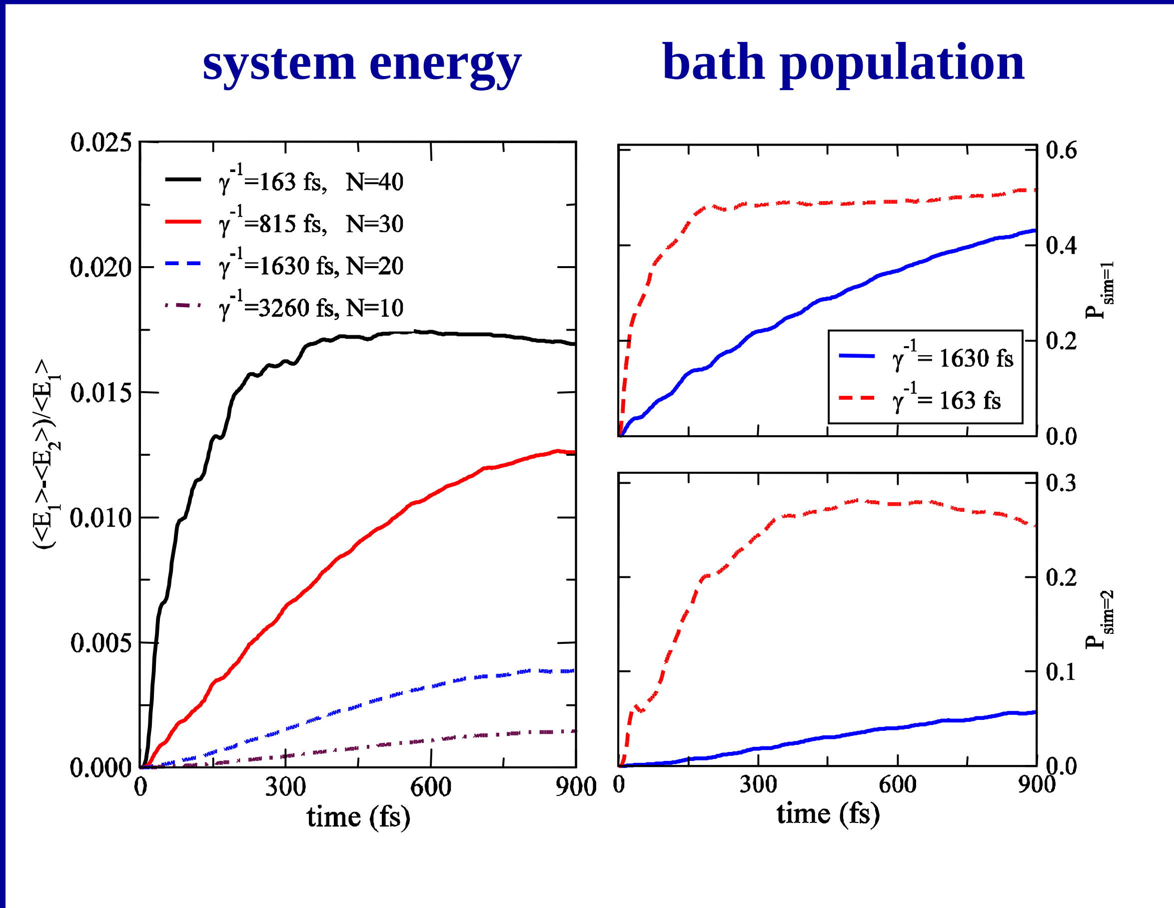
$$g_{coh} = \frac{g M w_0 d^2}{2\hbar}$$





single excitations vs double excitations

$$\Psi = \begin{pmatrix} \psi_0(R) \\ \\ \psi_2(R) \\ \psi_3(R) \\ \vdots \end{pmatrix} \quad \begin{matrix} \text{system} \\ \\ 2^{nd}\ \text{mode} \\ 1^{st} + 2^{nd} \\ \\ \end{matrix}$$



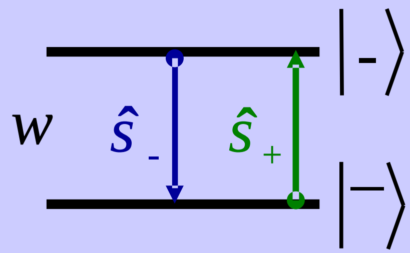
Surrogate Hamiltonian

BATH OF TWO-LEVEL SYSTEMS $\hat{H}_B = \sum w_i \hat{s}_i^\dagger \hat{s}_i$

lowering

$\hat{s}_- |{-}\rangle = |\bar{\ }\rangle$

$\hat{s}_- = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{1} & \mathbf{0} \end{pmatrix}$



raising

$\hat{s}_+ |\bar{\ }\rangle = |{-}\rangle$

$\hat{s}_+ = \begin{pmatrix} \mathbf{0} & \mathbf{1} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}$

$\hat{s}_+\hat{s}_- = |{-}\rangle\langle \bar{\ }|\bar{\ }\rangle\langle {-}| = \hat{\boldsymbol{n}}$ **a number operator**

Methods

Bloch-Redfield equation ← Markovian approximation ← **Quantum Master Equation**

$\hat{\rho}_S$ does not obey complete positivity

weak coupling ↑

$$\hat{\rho}(t) \approx \hat{\rho}_S(t) \otimes \hat{\rho}_B$$

$$\hat{H} = \hat{H}_{SYSTEM} + \hat{H}_{BATH} + \lambda \hat{H}_{SB}$$

secular approximation (Davies)

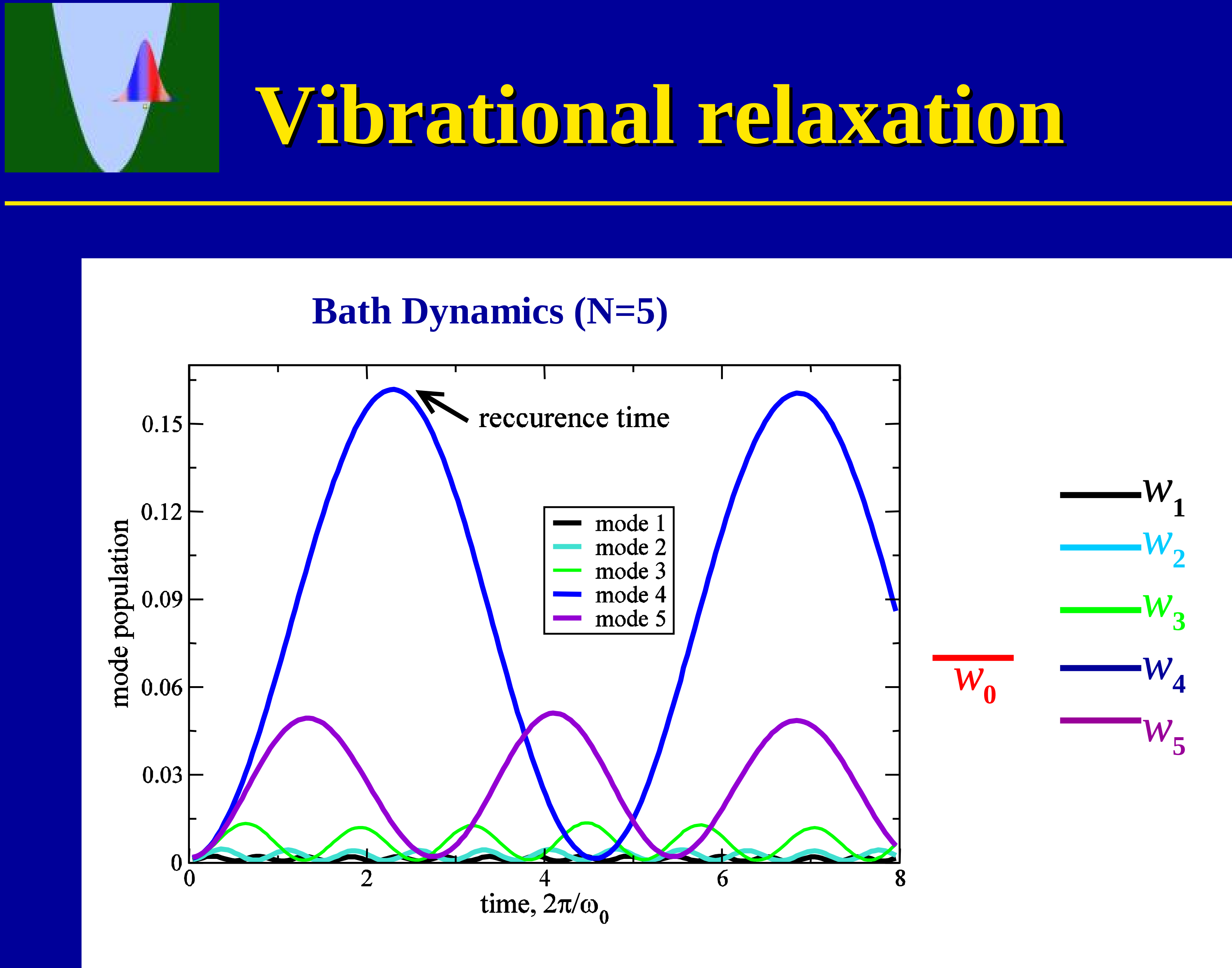
Dynamical semigroup ↓

$$\frac{d}{dt}\hat{\rho}_S(t) = \mathcal{L}\,\hat{\rho}_S(t)$$ Lindblad

Markovian Quantum Master Equation

Quantum Langevin equation

Vibrational relaxation



When is the random phase method preferable?

How many random sets (K) do we need to obtain the desired accuracy?

$$s^2 = \frac{l(L)}{K}$$

K **number of random sets**

L **system size**