Weak Field Control employing the Stochastic Surrogate Hamiltonian

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If you want to simulate Everything you get nothing.

We therefore limit the number of observables.

For a system bath scenario there are infinite ways to realize the same system dynamics.

We will try to use the easiest.
Reduced dynamics

\[ H = H_s + H_B + H_{SB} \]
Reduced dynamics

\[ \hat{\rho}(0) = \hat{\rho}_s \otimes \hat{\rho}_B \quad \longrightarrow \quad \hat{\rho}(t) = \hat{U}(t) \hat{\rho}(0) \hat{U}^\dagger(t) \]

\[ \hat{\rho}_s = \text{tr}_B\{\hat{\rho}(0)\} \quad \longrightarrow \quad \hat{\rho}_s(t) = \Gamma(\hat{\rho}_s(0)) = \text{tr}_B\{\hat{\rho}(t)\} \]

Quantum operations

\[ \Gamma(\hat{\rho}_s(0)) = \sum_j \hat{K}_j \hat{\rho}_s \hat{K}_j^\dagger \]

\[ \hat{K}_j = \langle e_j | U | e_0 \rangle \]

operator sum representation or Kraus operator


where \( |e_j\rangle \) is a complete set in the bath and \( |e_0\rangle \) is a purified initial state.
Quantum dynamical semigroup. Density operator description


\[ \Gamma(\hat{\rho}_s(0)) = \sum K_j \hat{\rho}_s \hat{K}^\dagger_j \]

Markovian property

\[ \Gamma(t)\Gamma(s) = \Gamma(t+s) \]

\[ \Gamma(t) = e^{\mathcal{L}t} \]

\[ \mathcal{L} = \mathcal{L}_H + \mathcal{L}_D . \]

\[ \mathcal{L}_H^*(\hat{A}) = i[\hat{H},\hat{A}] . \]

\[ \mathcal{L}_D^*(\hat{A}) = \sum_j \left[ \hat{F}_j \hat{A} \hat{F}_j^\dagger - \frac{1}{2} (\hat{F}_j \hat{F}_j^\dagger \hat{A} + \hat{A} \hat{F}_j \hat{F}_j^\dagger) \right] , \]

Generator of a completely positive map
Stochastic wavefunction

\[ \dot{\rho} = -\frac{i}{\hbar}[H, \rho] + \sum_{m} \left( 2 L_m \rho L_m^\dagger - L_m^\dagger L_m \rho - \rho L_m L_m^\dagger \right) \]

\[ |d\psi\rangle = -\frac{i}{\hbar} H|\psi\rangle dt + \sum_{m} \left( 2 \langle L_m \rangle_\psi L_m - L_m^\dagger L_m - \langle L_m \rangle_\psi \langle L_m \rangle_\psi \right) |\psi\rangle dt \]

\[ + \sum_{m} (L_m - \langle L_m \rangle_\psi)|\psi\rangle d\xi \]

where \( \langle L_m \rangle_\psi = \langle \psi | L_m | \psi \rangle \) is the expectation of \( L_m \) for state \( |\psi\rangle \).

\[ M(\text{Re}(d\xi_n), \text{Re}(d\xi_m)) = M(\text{Im}(d\xi_n), \text{Im}(d\xi_m)) = \delta_{nm} dt \]

\[ M d\xi_m = 0 \quad M(\text{Re} d\xi_n, \text{Im} d\xi_m) = 0 \]

\[ \rho \approx \sum_{s} \frac{1}{s_m} \rho_s = \sum_{s} \frac{1}{s_m} |\phi_s\rangle \langle \phi_s | / \langle \phi_s | \phi_s \rangle \]

# of realizations is very large!

The surrogate Hamiltonian approach

\[ H = H_s + H_{int} + H_B \]

\[ H = H_s + \tilde{H}_{int} + \tilde{H}_B \]

If our measurements apply to system operators \( A = A_s \otimes I_B \)

\[ \langle A \rangle = \text{tr}\{ \rho_s \cdot A \} \quad \text{where} \quad \rho_s = \text{tr}\{ \rho_{SB} \} \]

For sufficiently short times we can dilute the spectrum of the bath Hamiltonian.

Then we look for a compact bath Hamiltonian which generates an equivalent system dynamics.
The surrogate Hamiltonian approach

\[ H = H_s + H_{\text{int}} + H_B \]

\[ H_s = T + V_s(R) \]

\[ H_B = \sum \epsilon_j b_j^* b_j \]

\[ H_{\text{int}} = f(R) \sum \kappa_j (b_j + b_j^*) \]
### III Discrete bath approximation

\[ H_{\text{int}} = f(R) \sum U_m (B_m + B_m^*) \]

\[ H_B = \sum \epsilon_m B_m^* B_m \]

**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**

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

**Representative bath modes**

**Interface**

**System**

**Short time approximation**

\[ \Delta E = \frac{\hbar}{\Delta t} \]
IV Alternative spin bath representation

\[ H_s = T + V_s(R) \]

\[ H_B = \sum \varepsilon_j \sigma_j^+ \sigma_j^- + \sum \Delta_{jk} \sigma_j^+ \sigma_k^- \]

\[ H_{int} = f(R) \sum \kappa_j (\sigma_j^+ + \sigma_j^-) \]

Baer, Zeiri & Kosloff PRB 55 10952 (1997)

Baer & Kosloff JCP 106 8862 (1997)
Vibrational relaxation

energy relaxation

![Graph showing vibrational relaxation](image)
Vibrational relaxation

energy relaxation
Vibrational relaxation

energy relaxation
Direct simulation of system bath dynamics

Example: Simulation of ultrafast photodissociation of $\text{Na}^-$ in solution

3D $32 \times 32 \times 32$ grid
2 electronic surfaces
10 bath modes (TLS)
32 M words $\approx 528$ Mb

3D $32 \times 32 \times 32$ grid
2 electronic surfaces
20 bath modes (TLS)
32 G words $\approx 528$ Gb

1 ps of propagation $5 \Delta E \sim 5$ eV $\sim 3200$ Tflop

This is the limit of current computational ability
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 \( \beta = 1/k_bT \), \( \hat{H}_0 \) the stationary Hamiltonian and \( Z = Tr\{e^{-\beta \hat{H}_0}\} \)

\( L \) is the size of the Hilbert space.

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

We can approximate \( \rho_\beta \) by using only \( J \) terms such that \( e^{-\beta E_j} \ll \) error

Evaluation of the sum will scale as \( O(J^3) \)
Finite Temperature

Correlated initial state

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

- Diagonalization of \( \hat{H}_0 = \hat{H}_S \otimes \hat{H}_B \)
  
  \[ E_i \{\psi_i\} \]

- Separate simulations for every eigenstate
  
  \[ e^{-i\hat{H}t} \psi_i(0) \]

- Boltzmann averaging
  
  \[ \langle \hat{A} \rangle_T = \text{tr}\{\hat{r}_b \hat{A}\} \]

The number of eigenstates grows with temperature and \textit{exponentially} with the number of the bath modes.
The random phase wavefunction $\Phi$

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

$\phi_k$ is any complete set of eigenvalues, $\theta$ 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

$$\langle e^{i(\theta_n - \theta_m)} \rangle = \frac{1}{2\pi} \int_{0}^{2\pi} e^{i(n-m)\theta} d\theta = \delta_{nm}$$

The identity operator:

$$\hat{I} = \lim_{K \to \infty} \left( \frac{1}{K} \sum_{k=1}^{K} |\Phi(\vec{\theta}_k)\rangle\langle\Phi(\vec{\theta}_k)| \right)$$
Decomposing the thermal state into a sum of random projections:

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

The thermal random wavefunction:

Correlated initial state

\[ |\Phi(\frac{\beta}{2}, \theta)\rangle = e^{-\frac{\beta}{2} \hat{H}_0} |\Phi(\theta)\rangle. \]

An average thermal expectation value:

\[ \langle \hat{A} \rangle_\beta = tr \{ \hat{\rho}_\beta \hat{A} \} = \lim_{K \to \infty} \frac{1}{Z} \left( \sum_{k=1}^{K} \frac{1}{K} \langle \Phi(\frac{\beta}{2}, \theta_k) | \hat{A} | \Phi(\frac{\beta}{2}, \theta_k) \rangle \right). \]

David Gelman and Ronnie Kosloff
Simulating dissipative phenomena with a random phase thermal wavefunctions, high temperature application of the Surrogate Hamiltonian approach.

M. Nest, R. Kosloff,
Quantum Dynamical Treatment of Inelastic Scattering of Atoms at a Surface at Finite Temperature: The Stochastic Thermal Wave Function Approach
Journal of Chemical Physics 127134711 (2007)
The scaling of the statistical error:

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

Fig. 2. (Left) The error \( \sigma(P)/\langle P \rangle \) in the power absorbed at \( \omega_{max} \) 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** \( \lambda(L) \sim 1/L \)
Extending the time scale: adding a stochastic layer

Gil Katz, David Gelman, Mark A. Ratner, and Ronnie Kosloff
Replacing the bath modes $H_T = H_S + H_B + H_B' + H_{SB} + H_{BB'}$.

- $\hat{\rho}_S$ System

- $\lambda_j$ System bath coupling

- $\omega_j$ Energy levels of the bath

- $\Gamma_j$ Rate of swap

- $S \psi_k \otimes \phi_k = \phi_k \otimes \psi_k$ Swap operation

- $\phi_k = \left( e^{-\frac{\hbar \omega_k}{2 kT} + \phi_1} \right)^{1/\sqrt{Z}}$
Homogenizer

$$\rho_{s(1)} = \text{Tr} \left\{ U \rho_{s(0)} \otimes \sigma_B U^\dagger \right\}$$
$$\rho_{s(N)} = \text{Tr} \left\{ U_N \ldots U_1 \rho_{s(0)} \otimes \sigma_B U_1^\dagger \ldots U_N^\dagger \right\}$$

Swap operation:  \( S |\psi\rangle \otimes |\phi\rangle = |\phi\rangle \otimes |\psi\rangle \)

Partial swap operation:  \( P(\eta) = \cos(\eta) I + i \sin(\eta) S \)

Decay of an oscillator to a bath

\[ \hat{H}_S = \frac{\hat{P}^2}{2M} + D \left( e^{-2\alpha \hat{\mathcal{R}}} - 2e^{-\alpha \hat{\mathcal{R}}} \right) \]
\[ \hat{H}_{SB} = \hat{A}_S \otimes \sum_j^N \lambda_j (\hat{\sigma}_j^+ + \hat{\sigma}_j) \]
\[ \hat{H}_B = \sum_j \omega_j \hat{\sigma}_j^+ \hat{\sigma}_j \]

\[ f(\hat{\mathcal{R}}) = \frac{1 - e^{-\alpha \hat{\mathcal{R}}}}{\alpha} \]

\[ J(\omega) = M \gamma \omega \]

9 bath modes

12 bath modes

15 bath modes + swap

9 bath modes + swap
Cooling to thermal equilibrium

Coordinate representation

Phase space Wigner function
Approaching thermal equilibrium

9 bath modes + swap
6 realizations
Convergence properties of the stochastic surrogate Hamiltonian

$\text{M} = \text{total # of states}$

$\text{N}=6$

$\text{N}=9$

$\text{N}=12$

$\text{N}=15$

$\text{K}^{-1/2}$

Number of realizations
1) The Surrogate Hamiltonian method is a consistent non-Markovian system-bath reduction.

It can deal with
- Time dependent Hamiltonians such as coherent control
- Finite temperature bath.

Problem: good for only short time dynamics.

2) The stochastic secondary bath extends the timescale up to equilibrium.

If the Hilbert space is large the # of realizations n be very small.

The swap operation limits the growth of entanglement. Classical limit induced by noise.
Model system for weak field control

Target: change the branching ratio on the excited state

Phase only control
Phase only control with relaxation compared to free propagation

With relaxation

Branching ratio of excited states at 7 psec

Chirp rate

-1 -0.5 0 0.5 1
Coherent control of a branching ratio in weak field scenario ("one photon")

Phase only control (timing). The frequency spectrum stays intact.

Dissipation introduces a new time scale
The Surrogate Hamiltonian

\[ H = H_S + H_B + H_{SB} \]

- \textit{implicit} description of the bath
- replace:

\[ \hat{H}_B = \sum_{k=1}^{\infty} \hat{n}_k^{\text{true}} \rightarrow \sum_{k=1}^{N} \hat{n}_k^{\text{rep}} \]

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

\( \Delta E = \hbar / \Delta t \)

The interaction between system and bath: Relaxation

Energy exchange between system and bath

Nuclear relaxation

\[
\hat{H}_{S \leftrightarrow B}^{nr} = \left( \begin{array}{cc} f_g(\hat{Q}) & 0 \\ 0 & f_e(\hat{Q}) \end{array} \right) \otimes \sum_i \alpha_i^{nr} (\hat{\sigma}_i^+ + \hat{\sigma}_i) ;
\]

\[
\alpha_i^{nr} = \sqrt{J(\varepsilon_i) / \rho(\varepsilon_i)} .
\]
Absorption of the probe pulse

\[ \hat{H}_S = \left( \begin{array}{cc} \hat{H}_g & V_d(\hat{Q}) \\ V_d(\hat{Q}) & \hat{H}_e \end{array} \right) \otimes I_B \]

\[ \mathcal{P} = \left\langle \frac{\partial \hat{H}_{SF}}{\partial t} \right\rangle = \text{tr}_S \left\{ \hat{\rho}_S \frac{\partial}{\partial t} \hat{A}_{SF} \right\} . \]

\[ \Delta E = \int \mathcal{P} dt = -\hbar \omega L \Delta N_g . \]

Effect of electronic dephasing

Dynamical hole

Filter diagonalization
Excitation by pump pulse

Wigner plot of excited state

\[ \hat{A}_{SF} = \begin{pmatrix} 0 & -E(t)\hat{\mu}_{tr} \\ -E^*(t)\hat{\mu}_{tr} & 0 \end{pmatrix} \otimes 1_B \]

\[ E(t) = E_0 e^{-\frac{(t-t_{	ext{max}})^2}{2\sigma^2}} e^{-i\omega_L t} \]

10% excitation

Wigner plot of ground state
The turnover Quantum Zeno effect

![Graphs showing time delay and rate vs. electronic dephasing and nuclear dephasing.]

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 Hamiltonian
The surrogate Hamiltonian for the conical intersection case
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 excited state population

Convergence of velocity distribution
Decoherence

\[ \gamma_{\text{coh}} = \frac{\gamma M \omega_0 \delta^2}{2\pi} \]