

**Quantum-Classical Dynamics**  
**at Constant Temperature:**  
**An Application of Non-Hamiltonian**  
**Brackets**

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**In Chemical Physics Classical Statistical Mechanics is not  
enough!**

Classical Statistical Mechanics cannot treat situations where tunneling effects or non-adiabatic evolution are important:

- Electron and proton transfer either in isolated molecules, in solution, at electrochemical interfaces, or in biological molecules, etc.

Example: Coherent Chromophore dynamics in Bacteriorhodopsin.

## Coherent Control of Retinal Isomerization in Bacteriorhodopsin

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Optical control of the primary step of photoisomerization of the retinal molecule in bacteriorhodopsin from the all-trans to the 13-cis state was demonstrated under weak field conditions (where only 1 of 300 retinal molecules absorbs a photon during the excitation cycle) that are relevant to understanding biological processes. By modulating the phases and amplitudes of the spectral components in the photoexcitation pulse, we showed that the absolute quantity of 13-cis retinal formed upon excitation can be enhanced or suppressed by  $\pm 20\%$  of the yield observed using a short transform-limited pulse having the same actinic energy. The shaped pulses were shown to be phase-sensitive at intensities too low to access different higher electronic states, and so these pulses apparently steer the isomerization through constructive and destructive interference effects, a mechanism supported by observed signatures of vibrational coherence. These results show that the wave properties of matter can be observed and even manipulated in a system as large and complex as a protein.

Quantum mechanics dictates that all matter has an inherent wave property. On a molecular scale, this property can lead to destructive and constructive interferences that have a pronounced effect on transmission probabilities along reaction coordinates. Modern spectroscopic techniques have afforded direct evidence of such interferences and even exploited interference of the underlying wave properties to steer chemical reactions one way or another (*1*). For the most part, however, these studies have focused on small molecules and ions. In a protein, random fluctuations among the enormous number of degrees of freedom might be expected to cancel any interference effects. At the same time, proteins are highly evolved structures, and the question arises whether the phases of the underlying matter waves could play a role or even be manipulated in directing biological processes. This question can be addressed by determining the degree of conserved phase relationships, or quantum coherence, involved in a chemical process occurring within the confines of the protein environment. Experimental tests for coherence, as for any wave phenomena, must be able to demonstrate the creation of both constructive and destructive interference pathways, a process termed coherent control for molecular systems (*1, 2*).

Tests of quantum coherence are most readily accomplished for photoactive processes in which short, specifically shaped excitation pulses can be used to manipulate the process on a time scale faster than random thermal motions act to scramble

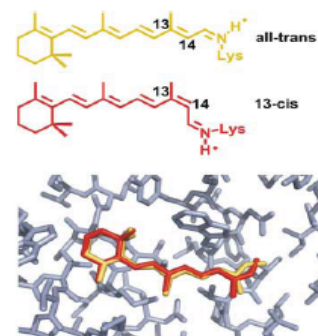
phase relationships (cause decoherence). In this regard, one of the fastest biological processes is the photoisomerization of the retinal molecule in rhodopsin proteins. This relatively simple photochemical reaction is the primary event for vision in higher organisms, photoreceptor response, and energy conversion in halobacteria. As such, the reaction has been subject to intense experimental and theoretical investigation (*3–11*). The possibility of manipulating the isomerization efficiency by excitation with tailored excitation light pulses has also been discussed from a theoretical standpoint in which a small subset of the total number of coupled motions is treated (*12, 13*). However, the full problem is computationally intractable and so requires direct experimental investigation for resolution.

Experimental manipulation of the relative photoisomerization yield of a molecule was recently reported for the cyanine dye NK88 in solution (*14*). These studies were conducted using excitation energies near saturation level for the absorption in question ( $1.5 \mu\text{J}$  per pulse); the primary action of the shaped light fields may have been to control the excited-state population (*15*) rather than the reaction coordinate itself. Under strong field excitation conditions, multiphoton processes inevitably access higher-lying excited states and so substantially perturb the state of interest. These issues are irrelevant if the objective is to induce a particular reaction outcome, but they become important in interpreting the correlation of the pulse shapes with the molecular processes.

Previous pulse-shaping studies of biological systems (*16*) were also performed under relatively strong excitation conditions and demonstrated the quenching of energy transfer from the carotenoids in light-harvesting systems. This effect was attributed to enhanced nonradiative relaxation of the carotenoid excited state; it was not possible to control the converse pathway to increase energy transfer. Our goal in the present study was to

control the absolute isomerization yield of the 13-cis retinal isomer in bacteriorhodopsin (bR). We sought specifically to control the degree of coherence in the protein environment in the weak field regime so as to ensure that the resultant dynamics would pertain to the protein's behavior under normal functional conditions. In this context, we report the manipulation of the absolute yield of 13-cis retinal over a 40% range, clearly demonstrating that a protein can manifest coherent interference effects. Through feedback-controlled amplitude and phase variation of the spectral components composing the excitation pulse, we could selectively enhance or suppress the isomerization yield by 20% in either direction.

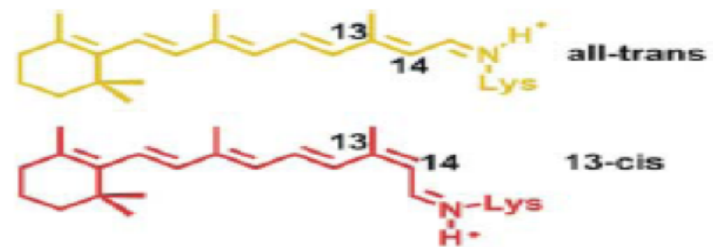
**Optimization of the isomerization yield.** Photoisomerization of the retinal chromophore in bR (Fig. 1) occurs with a relatively high quantum yield ( $\approx 65\%$ ) (*17, 18*) of the 13-cis isomer. Prior work has shown that the isomerization is complete within  $\approx 3$  ps (*6*), and the product, termed the K intermediate, has a well-resolved positive differential absorption ( $\Delta A$ ) band in the 630- to 640-nm range (*19, 20*). To ensure adequate vibrational cooling, we chose a 20-ps delay after the actinic pulse before targeting the 630-nm absorption feature for optimization (a detailed description of the materials and methods is given in the supporting online material). At this delay, the magnitude of measured signal  $\Delta A$ , weighted by actinic excitation energy (the amount of photons absorbed in a sample), directly reflects the isomerization



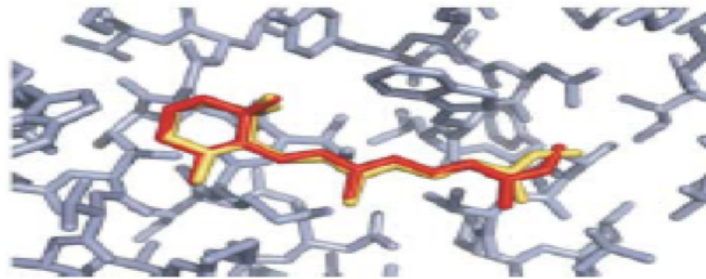
**Fig. 1.** Configurations of the retinal molecule (top) in bacteriorhodopsin (bottom) in the ground state (all-trans, yellow), and after isomerization (13-cis K form, red). [The bottom image is from the Protein Data Bank; identification numbers 1QH and 1QKP (*39*).] The photoisomerization process requires a torsional motion and bond stretching along the C13-C14 axis. The motion through the transition-state region connecting the excited reactant and product surfaces will involve a superposition of vibrations to give this localized displacement (*11, 12*).

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Configurations of the retinal molecule of the bacteriorhodopsin. Yellow: ground state, all-trans. Red: excited state, cis.



**Superimposition of the ground and excited configurations of the the retinal molecule in the bacteriorhodopsin environment. The motion through the transition state region involves a superposition of vibrations giving a localized displacement.**

## Full **Quantum** Mechanics is not affordable!

A full quantum formulation is neither computationally feasible nor conceptually necessary in situation where one is interested only in the quantum effects on a small number of degrees of freedom.

## **QUANTUM-CLASSICAL** DYNAMICS

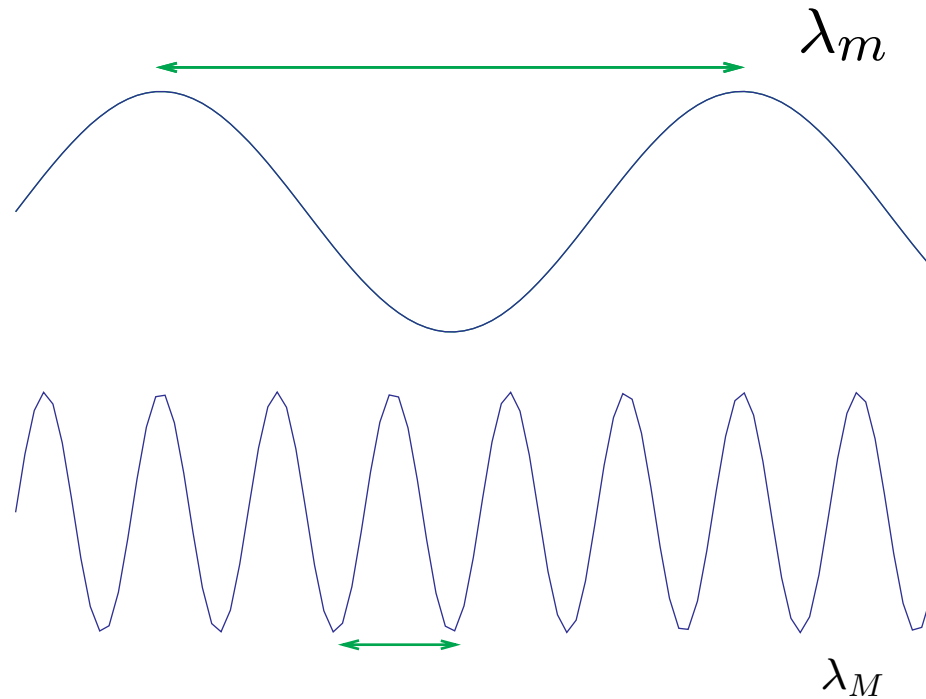
- R. Kapral and G. Ciccotti, Mixed Quantum-classical dynamics J. Chem. Phys., 110 8919 (1999)
- S. Nielsen, R. Kapral and G. Ciccotti, Statistical Mechanics of quantum-classical systems J. Chem. Phys., 115 5805 (2001)

## Features of the method

- Consistent coupling of quantum and classical degrees of freedom.
- The approach recovers, by means of controllable approximations, both surface-hopping and Ehrenfest mean field methods.
- Energy is conserved exactly.
- **RIGOROUS FORMULATION OF THE STATISTICAL MECHANICS OF QUANTUM-CLASSICAL SYSTEMS.**

## Quantum-Classical Systems

Light quantum particles and heavy bath particles:  $M \gg m$



thermal wave length:

$$\lambda_M = \hbar \left( \frac{\beta}{M} \right)^{1/2} = \left( \frac{m}{M} \right)^{1/2} \lambda_m$$

## Mixed **quantum**- **classical** Liouville equation

$$\begin{aligned}\frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} &= -\frac{i}{\hbar} [\hat{H}_W, \hat{\rho}_W(t)] + \frac{1}{2} (\{\hat{H}_W, \hat{\rho}_W(t)\} - \{\hat{\rho}_W(t), \hat{H}_W\}) \\ &\equiv -i\hat{\mathcal{L}}\hat{\rho}_W(t) \equiv (\hat{H}_W, \hat{\rho}_W(t))\end{aligned}$$

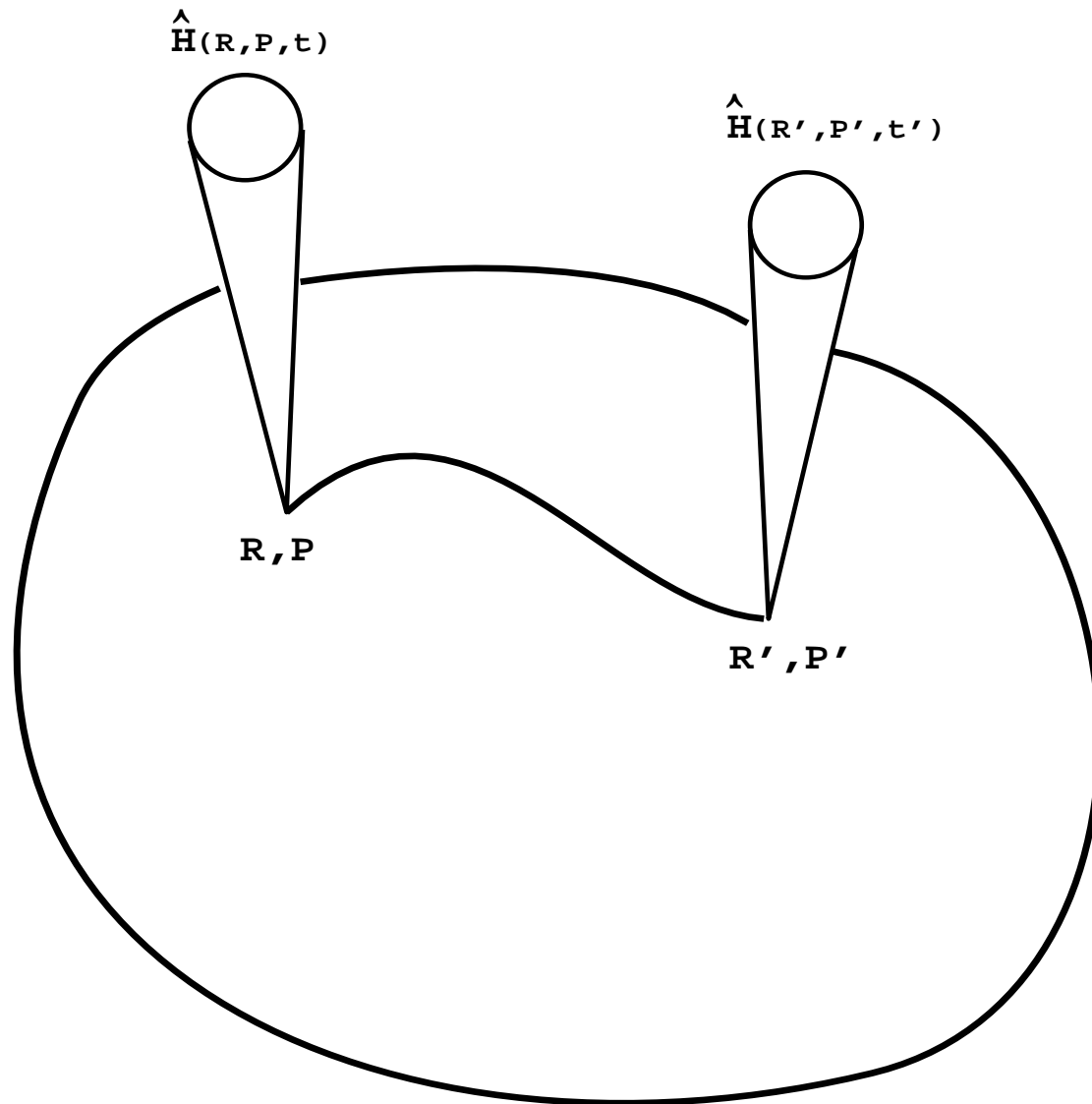
### Non-Hamiltonian bracket

$$(\hat{\chi}_1, (\hat{\chi}_2, \hat{\chi}_3)) + (\hat{\chi}_3, (\hat{\chi}_1, \hat{\chi}_2)) + (\hat{\chi}_2, (\hat{\chi}_3, \hat{\chi}_1)) \neq 0$$

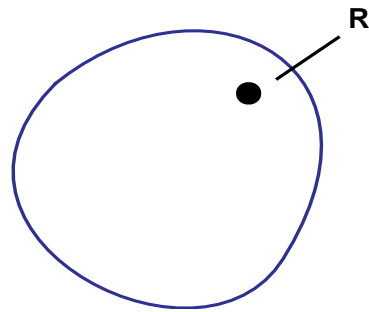
### Quantum-Classical Hamiltonian

$$\hat{H}_W(R, P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R)$$

# Quantum Classical World



## Adiabatic basis: Eulerian picture



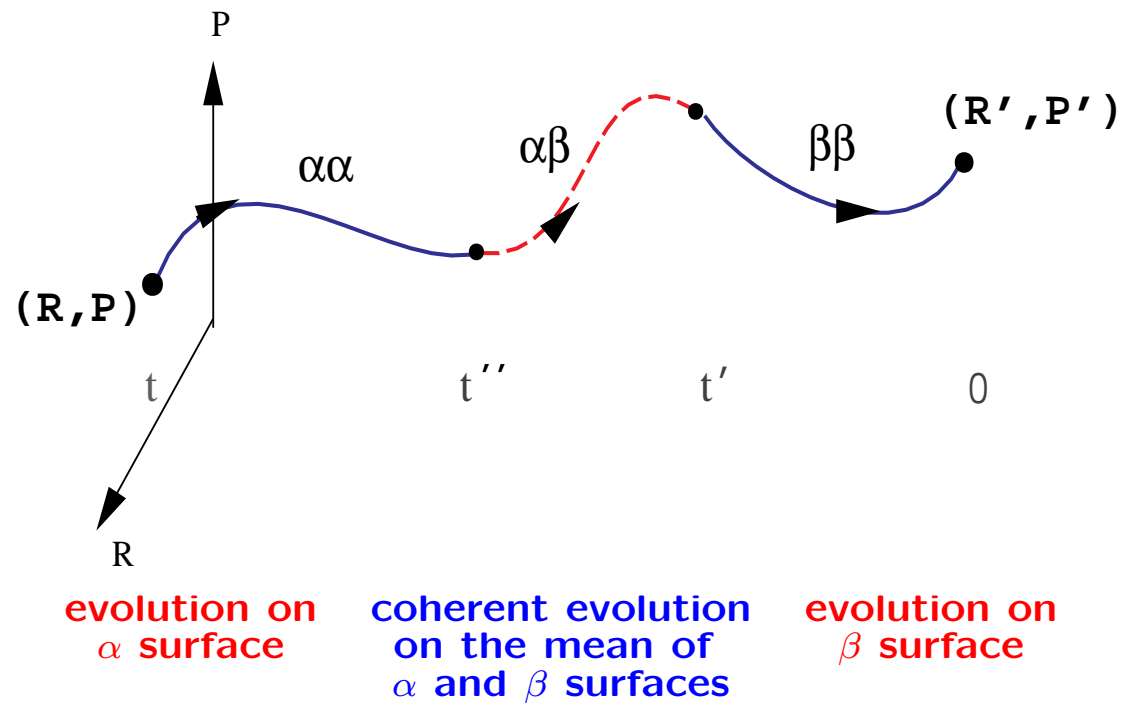
$$\hat{H}_W(R, P) = \frac{P^2}{2M} + \hat{h}_W(R)$$

Adiabatic eigenvalue problem :  $\hat{h}_W(R)|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle$

## Evolution of density matrix

$$\rho_W^{\alpha\alpha'}(R, P, t) = \sum_{\beta\beta'} (e^{-i\hat{\mathcal{L}}t})_{\alpha\alpha',\beta\beta'} \rho_W^{\beta\beta'}(R, P)$$

Schematic representation of a surface-hopping trajectory



## The Spin-Boson Model

- Dynamics of the dissipative two-state system  
A. J. Leggett *et al.*  
Rev. Mod. Phys. 59, 1 (1987).

$$H = -\hbar\Omega\hat{\sigma}_x - \sum_{J=1}^N c_J R_J \hat{\sigma}_z + \sum_{J=1}^N \left( \frac{P_J^2}{2M_J} + \frac{1}{2} M_J \omega_J^2 R_J^2 \right)$$

The  $c_J$  are chosen in such a way that the Spectral Density

$$J(\omega) \equiv \frac{\pi}{2} \sum_J \frac{c_J^2}{M_J \omega_J} \delta(\omega - \omega_J) \text{ is Ohmic } \rightarrow \eta \omega e^{-\omega/\omega_c}$$

- The spin-boson model can be solved by numerically "exact" Path Integral techniques (Makri and Thompson, Chem. Phys. Lett 291 101, (1998); J. Chem. Phys. 110, 1343 (1999)) and also by means of the quantum-classical approach which has been sketched previously.
- In this case, the simpler quantum-classical dynamics is exact and provides results that are indistinguishable from those obtained by the path integral approach.
- A cumulant analysis of the influence functional within the path integral approach shows that a large number of oscillators ( $N \geq 200$ ) is required to achieve a mapping of a manybody environment onto an effective harmonic environment.  
N, Makri J. Phys. Chem B 103 2823 (1999).
- Within the quantum-classical case, it might be interesting to represent the effects of the temperature also on the dynamical trajectories.

## Discussion

- Dissipation/Decoherence is introduced by sampling the initial conditions and by nonadiabatic transitions.
- Since energy is conserved along the quantum-classical trajectory, a huge number of classical degrees of freedom is required in order to represent correctly the statistics of the canonical ensemble.
- Is there a way to introduce dissipation and temperature effects within the time-evolution of quantum-classical trajectories so that the description of the bath can be simplified?

## Non-Hamiltonian Classical Dynamics at constant temperature: Nosè-Hoover method

$$H_N = \frac{P^2}{2M} + V(R) + \frac{p_s^2}{m_s} + 3Nk_B T s$$

$$\text{Equations of motion} \left\{ \begin{array}{l} \dot{R} = P/M \\ \dot{s} = p_s/m_s \\ \dot{P} = -\nabla_R V - P p_s/m_s \\ \dot{p}_s = P^2/M - k_B T \end{array} \right.$$

$$\text{Antisymmetric matrix } \mathcal{B} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -P \\ 0 & -1 & P & 0 \end{bmatrix}$$

$$X = (R, s, P, p_s) \quad \dot{X}_i = \sum_{kj} \frac{\partial X_i}{\partial X_k} \mathcal{B}_{kj} \frac{\partial H_N}{\partial X_j} = \{X_i, H_N\}_{\mathcal{B}}$$

## Matrix Structure of the Quantum-Classical Bracket

Rewrite the Quantum-Classical Bracket

$$(\hat{H}_W, \hat{\chi}) = \frac{i}{\hbar} [\hat{H}_W, \hat{\chi}] - \frac{1}{2} \{\hat{H}_W, \hat{\chi}\} + \frac{1}{2} \{\hat{\chi}, \hat{H}_W\}$$

as

$$(\hat{H}_W, \hat{\chi}) = \frac{i}{\hbar} \begin{bmatrix} \hat{H}_W & \hat{\chi} \end{bmatrix} \cdot \begin{bmatrix} 0 & 1 + \frac{\hbar \Lambda}{2i} \\ -1 - \frac{\hbar \Lambda}{2i} & 0 \end{bmatrix} \cdot \begin{bmatrix} \hat{H}_W \\ \hat{\chi} \end{bmatrix}$$

where  $\hat{H} \wedge \hat{\chi} \equiv -\{\hat{H}_W, \hat{\chi}\} = -$  Poisson bracket of  $\hat{H}$  and  $\hat{\chi}$

Let us exploit the matrix structure of the brackets in order to introduce the

## Quantum-Classical Nosè-Hoover Dynamics

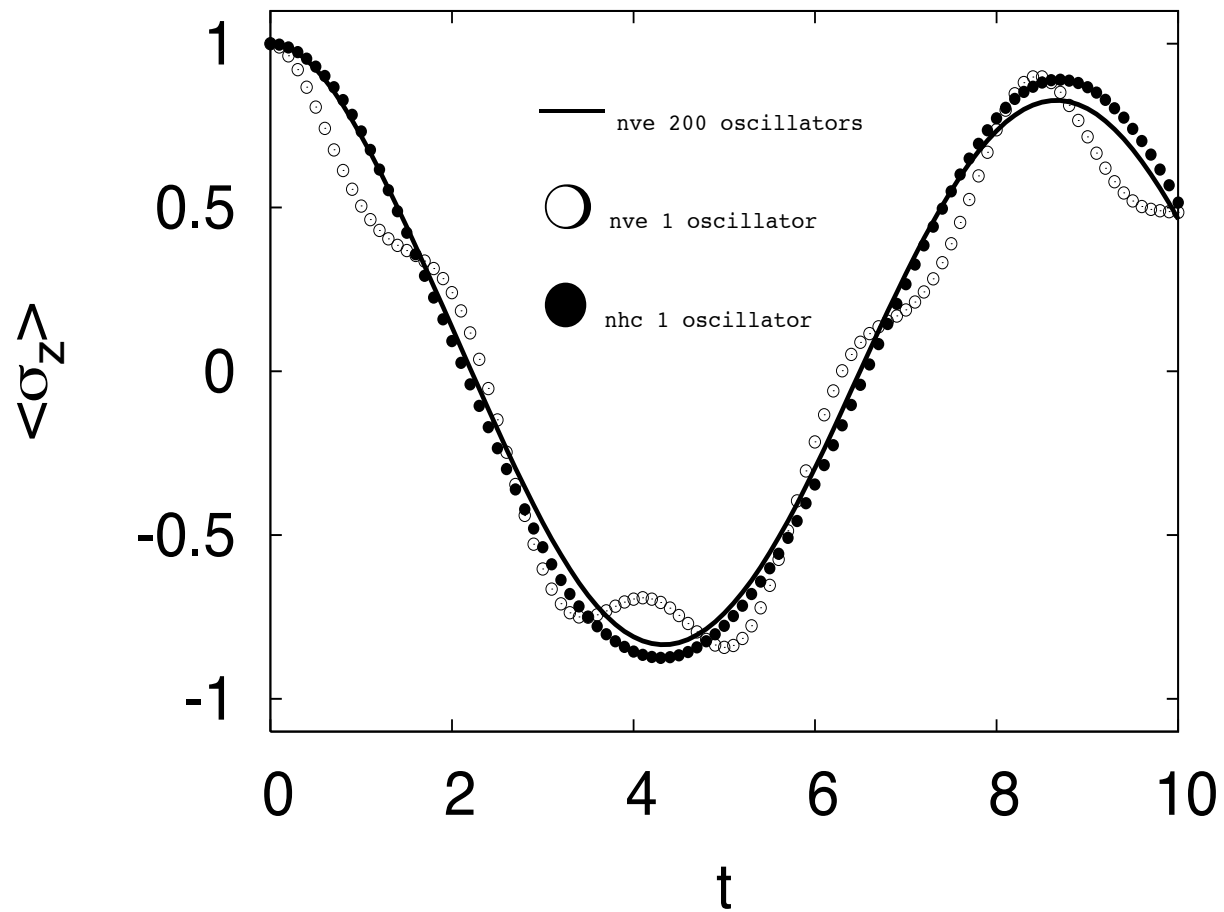
$$\hat{H}_N = \frac{P^2}{2M} + \frac{p_s^2}{2m_s} + 3Nk_B T s + \hat{h}(R)$$

$$\hat{H}_N \Lambda_N \hat{\chi} \equiv - \sum_{ij} \frac{\partial \hat{H}_N}{\partial X_i} \mathcal{B}_{ij} \frac{\partial \hat{\chi}}{\partial X_j}$$

$$\begin{aligned} \dot{\chi} &= \begin{bmatrix} \hat{H}_N & \hat{\chi} \end{bmatrix} \begin{bmatrix} 0 & 1 + \frac{\hbar \Lambda_N}{2i} \\ -1 & -\frac{\hbar \Lambda_N}{2i} \\ & & 0 \end{bmatrix} \cdot \begin{bmatrix} \hat{H}_N \\ \hat{\chi} \end{bmatrix} \\ &= \left( \hat{H}_N, \hat{\chi} \right)_{\mathcal{B}} = i \mathcal{L}_N \hat{\chi} \end{aligned}$$

## Features

- Stationary density matrix  $(\hat{H}_N, \hat{\rho}_{Ne})_{\mathcal{B}} = 0$  is easily written up to order  $\hbar$  (as in the constant energy case).
- Dynamics is represented in the adiabatic basis as classical-like **Nosè-Hoover trajectory segments** (with associated phase factors) interspersed by **nonadiabatic transitions**.
- Hellmann-Feynman forces are calculated from the energy surfaces  $1/2(E_{\alpha} + E_{\alpha'})$ .
- **Nosè quantum-classical Hamiltonian is exactly conserved.**



Time-decay of the population of a spin-boson model in an initial non-equilibrium state.

## Summary

- **Quantum-classical** dynamics is a useful approximation of **full quantum dynamics**.
- Such a scheme is designed to treat **arbitrary classical environments**. It can be applied to more realistic systems with many classical degrees of freedom and a larger number of quantum states
- I showed you **numerical evidence** that **temperature effects** can be directly introduced in the time propagation of **quantum-classical** trajectories by means of the **Nosè-Hoover thermostat**.
- This promises to provide an **alternative description of dissipative effects** in quantum and quantum-classical systems.
- **Non-Hamiltonian brackets** are interesting theoretical tools for introducing arbitrary (and useful) dynamics while keeping the statistical mechanical properties of the system under control.

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