Semiclassical description of quantum effects in molecular dynamics

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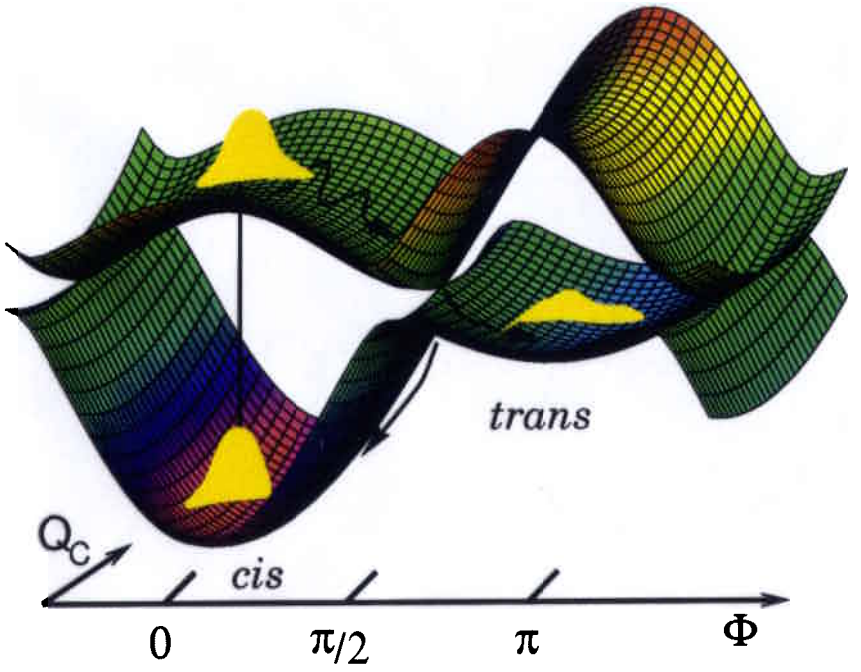
1. Introduction
2. Semiclassical initial-value representation methods
3. Coherent and dissipative vibrational dynamics
4. Nonadiabatic dynamics



Why semiclassical dynamics instead of quantum or classical dynamics?

- semiclassical concepts and methods can provide a more intuitive understanding than quantum dynamics

- semiclassical methods are supposed to overcome the exponential scaling problem of quantum basis-set calculations

	memory	CPU time
QM (basis set)	$\sim N^f$	$\sim fN^{f+1}$
semiclassical	$\sim f^2$	$\sim f^3$ (?)
(quasi)classical	$\sim f$	$\sim f$

- semiclassical theory is capable of describing quantum effects
  - tunneling
  - interference, recurrences
  - conservation of zero-point energy
  - nonadiabatic dynamics

Semiclassical Initial-Value Representation (IVR)

$$\langle\psi_f|e^{-iHt/\hbar}|\psi_i\rangle = \int \mathrm{d}q_f \mathrm{d}q_i \, \langle\psi_f|q_f\rangle\langle q_f|e^{-iHt/\hbar}|q_i\rangle\langle q_i|\psi_i\rangle$$

Semiclassical Van Vleck-Gutzwiller propagator

$$\langle q_f|e^{-iHt/\hbar}|q_i\rangle = \sum_{\text{class.paths}} \left[2\pi i\hbar \left|\frac{\partial q_f}{\partial p_i}\right|\right]^{-1/2} e^{iS/\hbar - i\pi\nu/2}$$

- involves boundary-value problem: $q(0) = q_i,\ q(t) = q_f$
- transformation from final coordinate to initial momentum

$$\sum_{\text{class.paths}} \int \mathrm{d}q_f = \int \mathrm{d}p_i \left|\frac{\partial q_f(p_i, q_i)}{\partial p_i}\right|$$

results in a simpler initial-value problem

$$\langle\psi_f|e^{-iHt/\hbar}|\psi_i\rangle = \int \mathrm{d}q_i \mathrm{d}p_i \, \langle\psi_f|q_t\rangle \left[\frac{\partial q_t}{\partial p_i}/(2\pi i\hbar)\right]^{1/2} e^{iS/\hbar}\langle q_i|\psi_i\rangle$$

$$q_t = q(p_i, q_i; t) \qquad S(p_i, q_i) = \int_0^t \mathrm{d}t'(p\dot{q} - H)$$

advantage:

- initial value problem, no nontrivial root search
- no singularities at caustics (i.e., zero of Jacobian is in numerator rather than denominator)

Miller, JCP **53**, 3578 (1970); Heller, JCP **95**, 9431 (1992)
Campolietti, Brumer, JCP **96**, 5969 (1992); Kay, JCP **100**, 4377 (1994)

Hermann-Kluk (coherent-state) IVR

(M. F. Herman and E. Kluk, Chem. Phys. **91**, 27 (1984))

- semiclassical propagator

$$e^{-iHt} = \int \frac{dq_0 dp_0}{(2\pi)^N} |q_t p_t\rangle C_t \; \langle q_0 p_0|$$

- pre-exponential factor

$$C_t = \sqrt{\det\left(\frac{1}{2}\left(\frac{\partial p_t}{\partial p_0} + \frac{\partial q_t}{\partial q_0} - i\gamma\frac{\partial q_t}{\partial p_0} + \frac{i}{\gamma}\frac{\partial p_t}{\partial q_0}\right)\right)}$$

monodromy matrix $\mathbf{M}_t = \begin{pmatrix} \frac{\partial p_t}{\partial p_0} & \frac{\partial p_t}{\partial q_0} \\ \frac{\partial q_t}{\partial p_0} & \frac{\partial q_t}{\partial q_0} \end{pmatrix}$

- action

$$S_t = \int_0^t d\tau \, (p_\tau \dot{q}_\tau \quad \cdot \cdot)$$

- Gaussian wave packet (coherent state)

$$\langle x|q_0 p_0\rangle = \left(\frac{\gamma}{\pi}\right)^{1/4} \exp\{-\gamma/2(x-q_0)^2 + ip_0(x-q_0)\}$$

Quasiclassical methods

In quasiclassical methods, the expectation value of an observable $\langle A\rangle(t) = \mathrm{tr}(\rho\, e^{iHt} A e^{-iHt})$ is described by the classical phase-space average

$$\langle A\rangle^{QC}(t) = \int \frac{dq_0 dp_0}{(2\pi)^N} A(q_t, p_t)\rho(q_0, p_0)$$

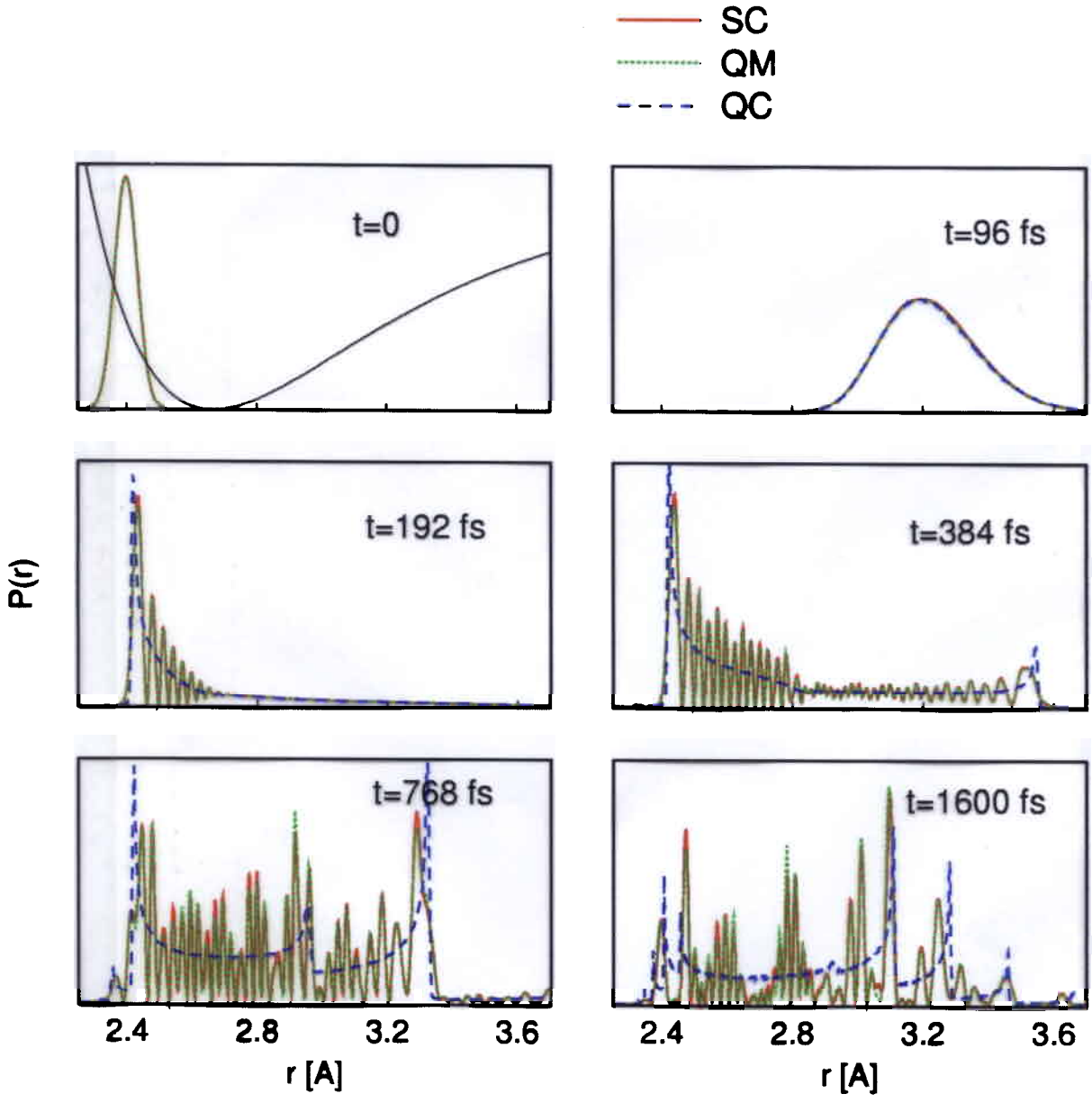
- dynamics is treated classically
- quantum mechanical nature of the initial state ρ is taken into account, e.g., by the Wigner function

$$\rho(q_0, p_0) = \int ds\, e^{isp_0} \langle q_0 - s/2|\rho|q_0 + s/2\rangle$$

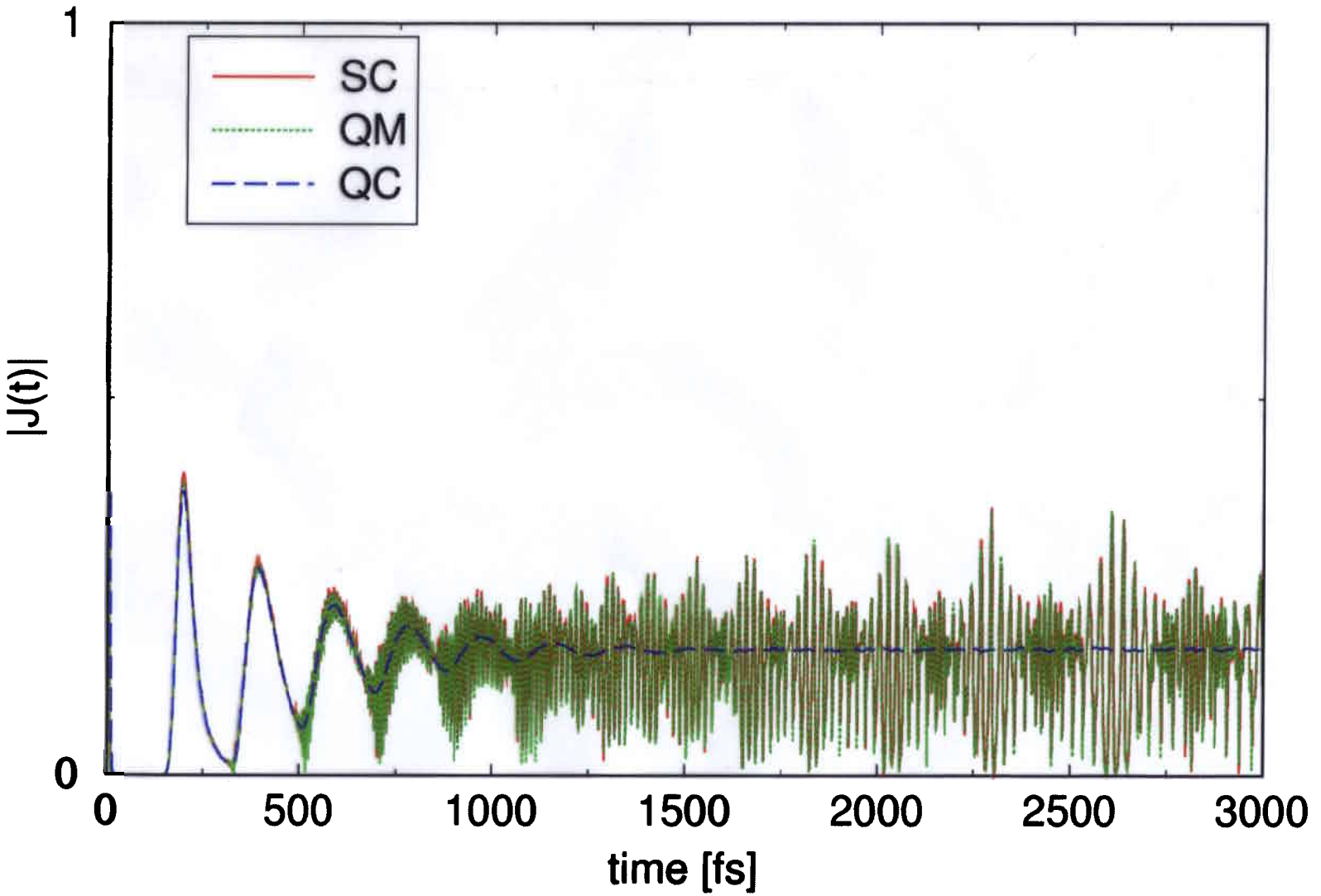
- low computational cost
- phase information is not included
- cannot describe quantum effects beyond very short time and beyond the harmonic approximation

Semiclassical wavepacket dynamics

- Vibrational wavepacket dynamics in the electronic ground state of I_2

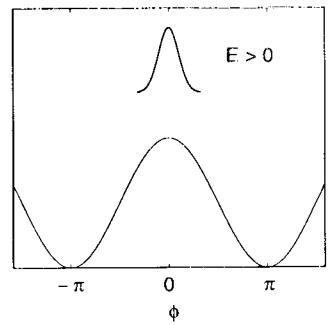


- autocorrelation function $J(t) = \langle q_\alpha p_\alpha | e^{-iHt} | q_\alpha p_\alpha \rangle = \int \frac{dq_0 dp_0}{2\pi} \langle q_\alpha p_\alpha | q_t p_t \rangle C_t e^{iS_t} \langle q_0 p_0 | q_\alpha p_\alpha \rangle$



Model for isomerization (hindered rotor)

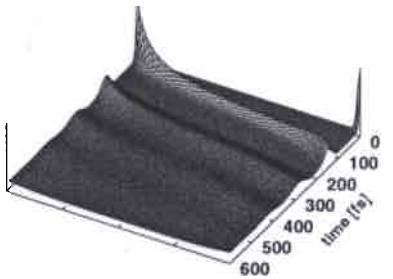
$$H = \frac{p^2}{2I} + W\cos(\phi)$$

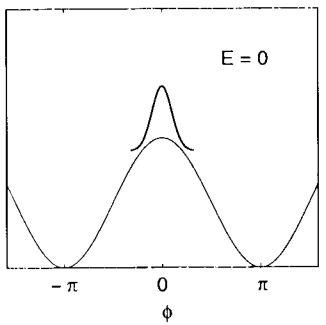


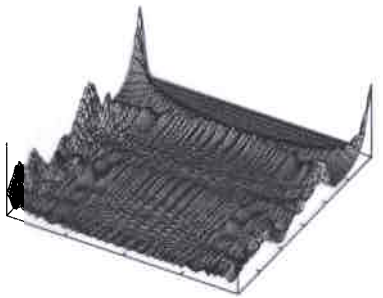
QM

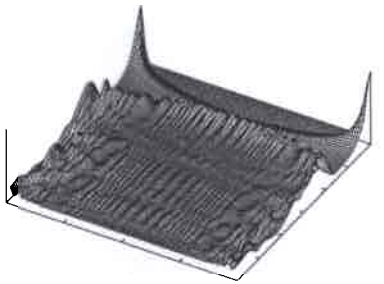
SC

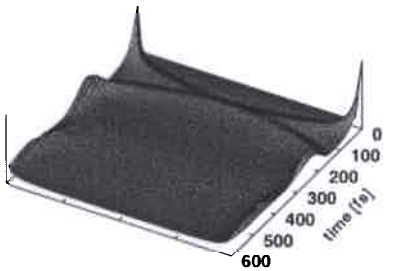
QC

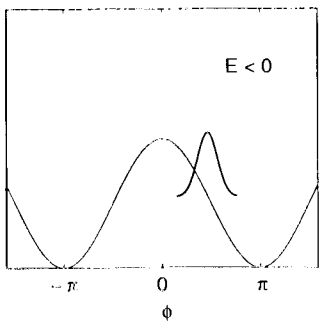


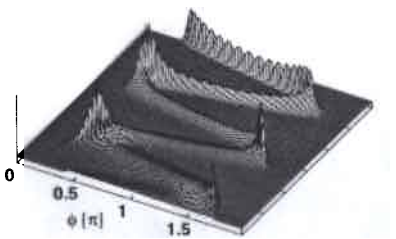


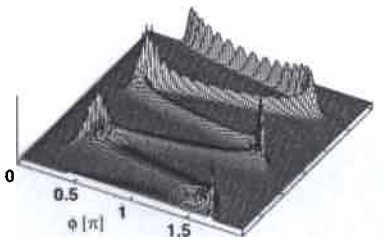


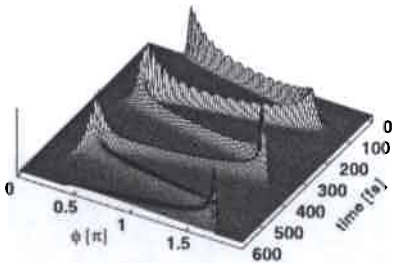






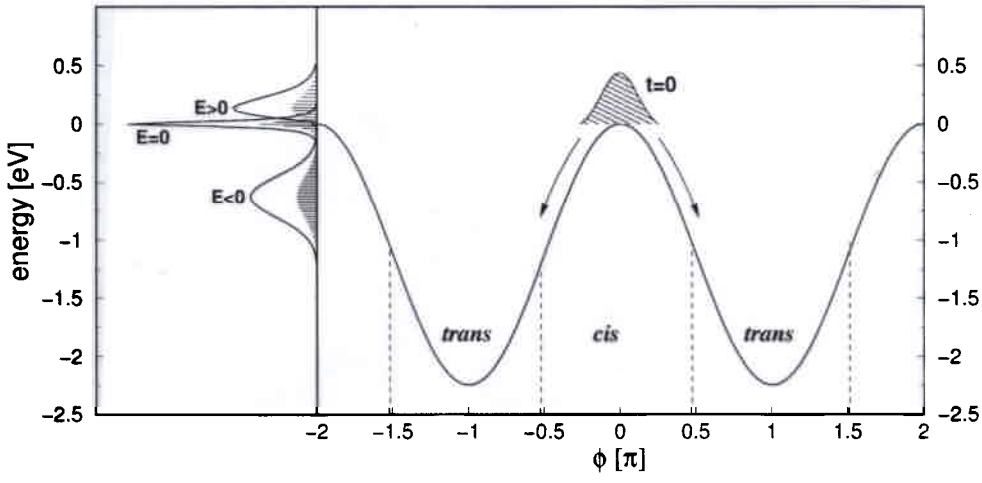




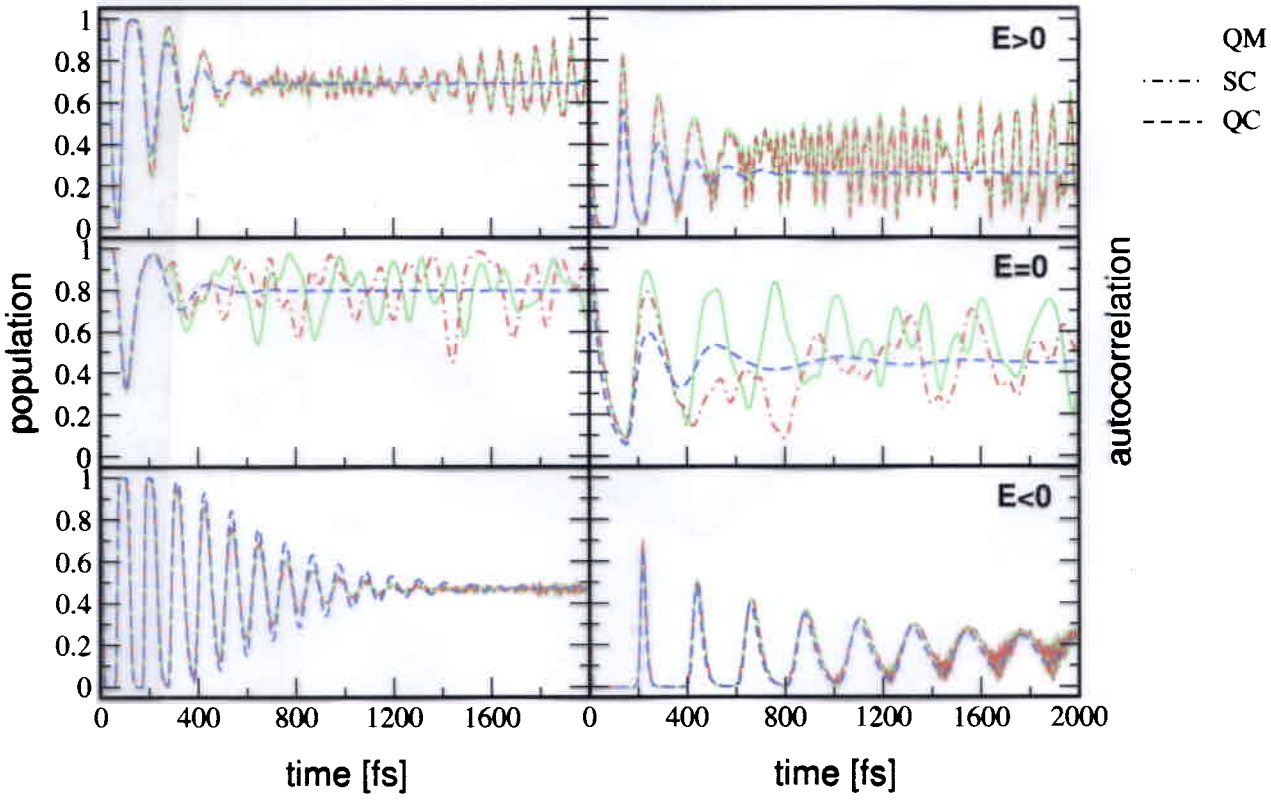


Model for isomerization (hindered rotor)

$$H = \frac{p^2}{2I} + W\cos(\phi)$$



$$\int_{-\pi/2}^{\pi/2} d\varphi |\langle\varphi|e^{-iHt}|\psi_i\rangle|^2 \qquad |\langle\psi_i|e^{-iHt}|\psi_i\rangle|$$

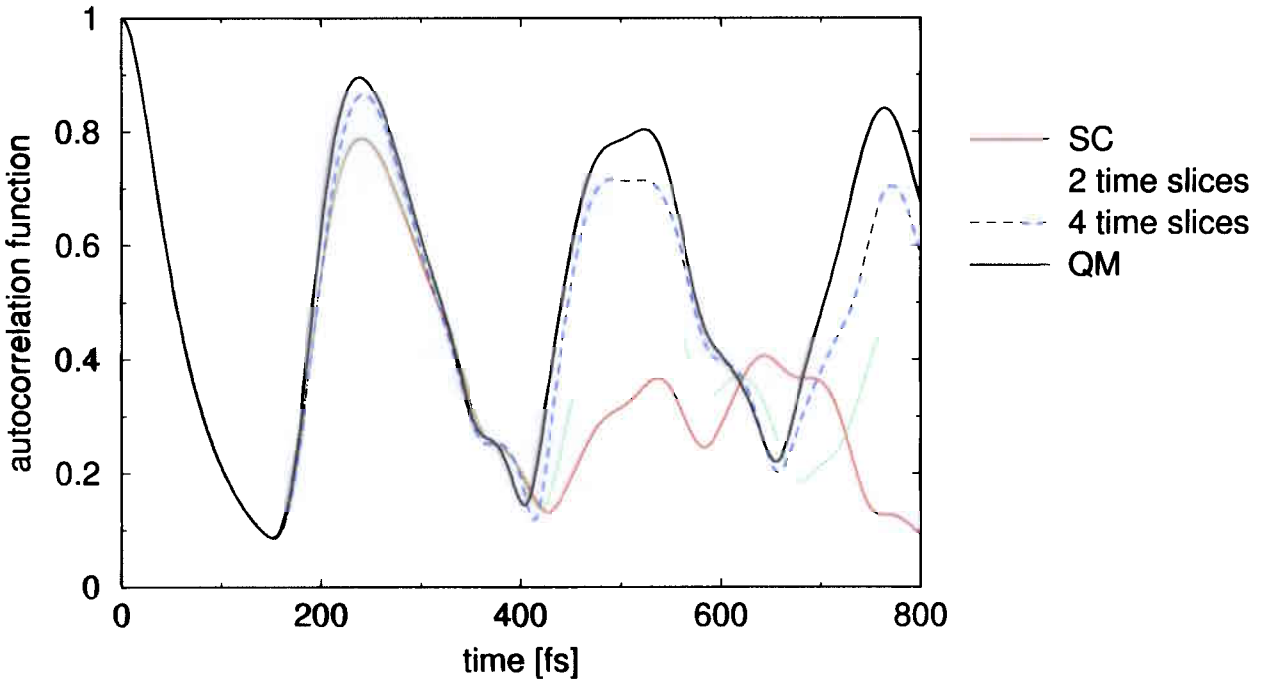


Model for isomerization (hindered rotor) $H = \frac{p^2}{2I} + W\ \cos(\phi)$

To obtain a better description of the dynamics close to the torsional barrier one can use the semiclassical propagator in the sense of a path integral

$$\langle \psi_f | e^{-iHt} | \psi_i \rangle = \langle \psi_f | e^{-iHt_2} e^{-iHt_1} | \psi_i \rangle$$

$$= \int \frac{dq_2 dp_2}{2\pi} \int \frac{dq_1 dp_1}{2\pi} \langle \psi_f | q_{t2} p_{t2} \rangle C_{t2} e^{iS_{t2}} \langle q_2 p_2 | q_{t1} p_{t1} \rangle C_{t1} e^{iS_{t1}} \langle q_1 p_1 | \psi_i \rangle$$



Numerical problems of semiclassical propagators in larger systems

Semiclassical Herman-Kluk IVR

$$\langle \psi_f | e^{-iHt} | \psi_i \rangle = \int \frac{\mathrm{d}q_0 \mathrm{d}p_0}{(2\pi)^N} \langle \psi_f | q_t p_t \rangle C_t e^{iS_t} \langle q_0 p_0 | \psi_i \rangle$$

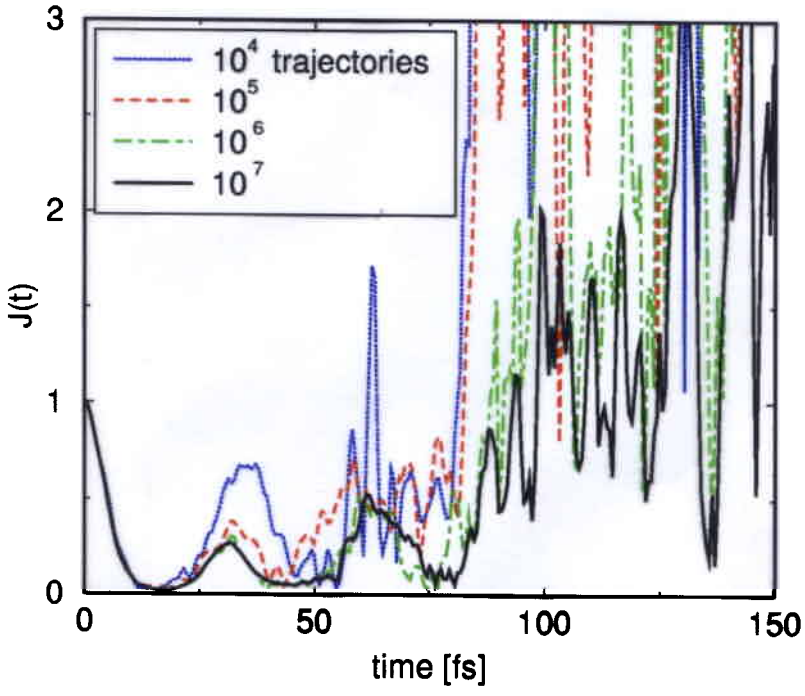
- For a high-dimensional system the phase-space integration is usually done employing Monte-Carlo methods
- Oscillatory nature of the integrand results in poor Monte-Carlo statistics (cf. 'sign problem' in real-time path-integral calculations). Therefore, many trajectories are needed to achieve convergence
- In chaotic systems, the pre-exponential factor C_t can become large, thereby amplifying the oscillations of the integrand

Methods to improve the convergence

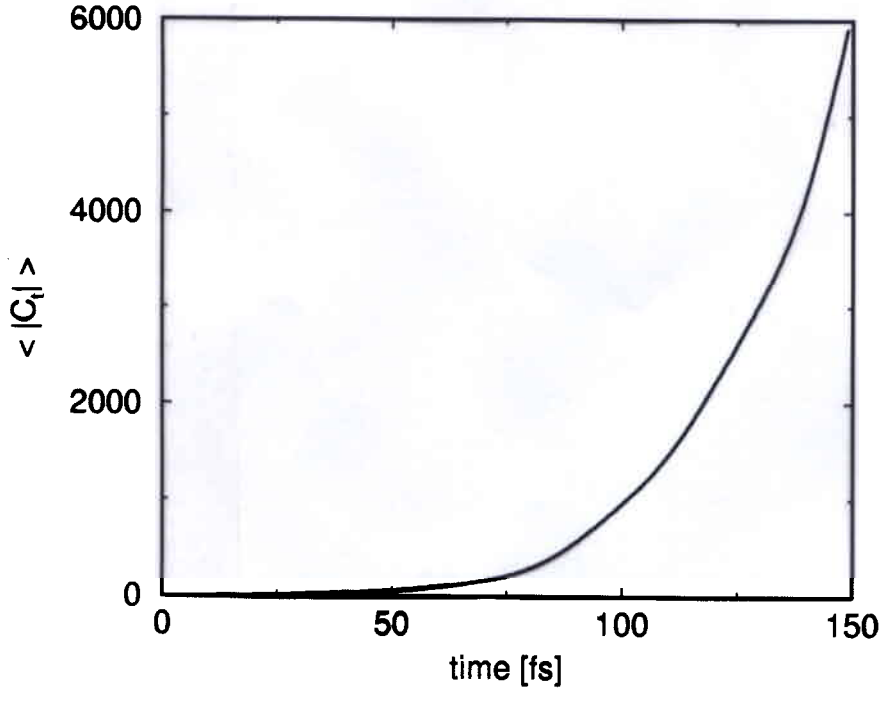
- discard trajectories with large pre-exponential factor
- Smoothing of the integrand using filtering techniques adapted from real-time path-integral methods
- Forward-backward methods

Numerical problems of semiclassical propagators in larger systems

- autocorrelation function of pyrazine after photoexcitation to the S_2 electronic state



- average modulus of the pre-exponential factor



Forward-Backward IVR for Correlation Functions

Consider the generic correlation function

$$C_{AB}(t) = \mathrm{tr}\left[Ae^{iHt}Be^{-iHt}\right]$$

Inserting the SC-IVR

$$e^{-iHt} = \int \frac{dq_0 dp_0}{(2\pi)^N} |q_t p_t\rangle C_t e^{iS_t} \langle q_0 p_0|$$

we obtain a double phase space SC-IVR for $C_{AB}(t)$

$$C_{AB}^{SC}(t) = \int \frac{dq_0 dp_0}{(2\pi)^N} \int \frac{dq_0' dp_0'}{(2\pi)^N} C_t(p_0, q_0) C_t(p_0', q_0')^* \times e^{i[S_t(p_0,q_0) - S_t(p_0',q_0')]} \langle p_0 q_0|A|p_0' q_0'\rangle \langle p_t' q_t'|B|p_t q_t\rangle$$

numerical problem: highly oscillatory integrand

Forward-Backward idea:

Combine the two propagators into one semiclassical time evolution

Makri, Thompson, CPL **291**, 101 (1998)
Sun, Miller JCP **110**, 6635 (1998)
Thoss, Wang, Miller JCP **114**, 9220 (2001)

Forward-Backward IVR

correlation function $C_{AB}(t) = \mathrm{tr}\left[Ae^{iHt}Be^{-iHt}\right]$

with local operator $B(s(\hat{q})) = \int \mathrm{d}p_s \tilde{B}(p_s) e^{ip_s s(\hat{q})}$

semiclassical approximation for the unitary operator

$$U = e^{iHt} e^{ip_s s(\hat{q})} e^{-iHt}$$

and stationary-phase approximation for the intermediate integration gives

$$U = \int \frac{\mathrm{d}q_0 \mathrm{d}p_0}{(2\pi)^N} |q_0' p_0'\rangle C e^{iS} \langle p_0 q_0|$$

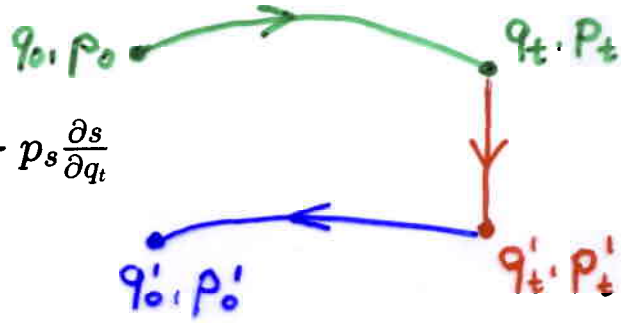
$$C_{AB}^{\mathrm{FB}}(t) = \int \mathrm{d}p_s \tilde{B}(p_s) \int \frac{\mathrm{d}q_0 \mathrm{d}p_0}{(2\pi)^N} \langle p_0 q_0 | A | q_0' p_0' \rangle C e^{iS}$$

action:

$$S = \int_0^t \mathrm{d}\tau (p_\tau \dot{q}_\tau - H) + p_s s(q_t) + \int_t^0 \mathrm{d}\tau (p_\tau' \dot{q}_\tau' - H)$$

trajectory:

- forward $q_0, p_0 \to q_t, p_t$
- jump $q_t' = q_t, \quad p_t' = p_t + p_s \frac{\partial s}{\partial q_t}$
- backward $q_t', p_t' \to q_0, p_0$

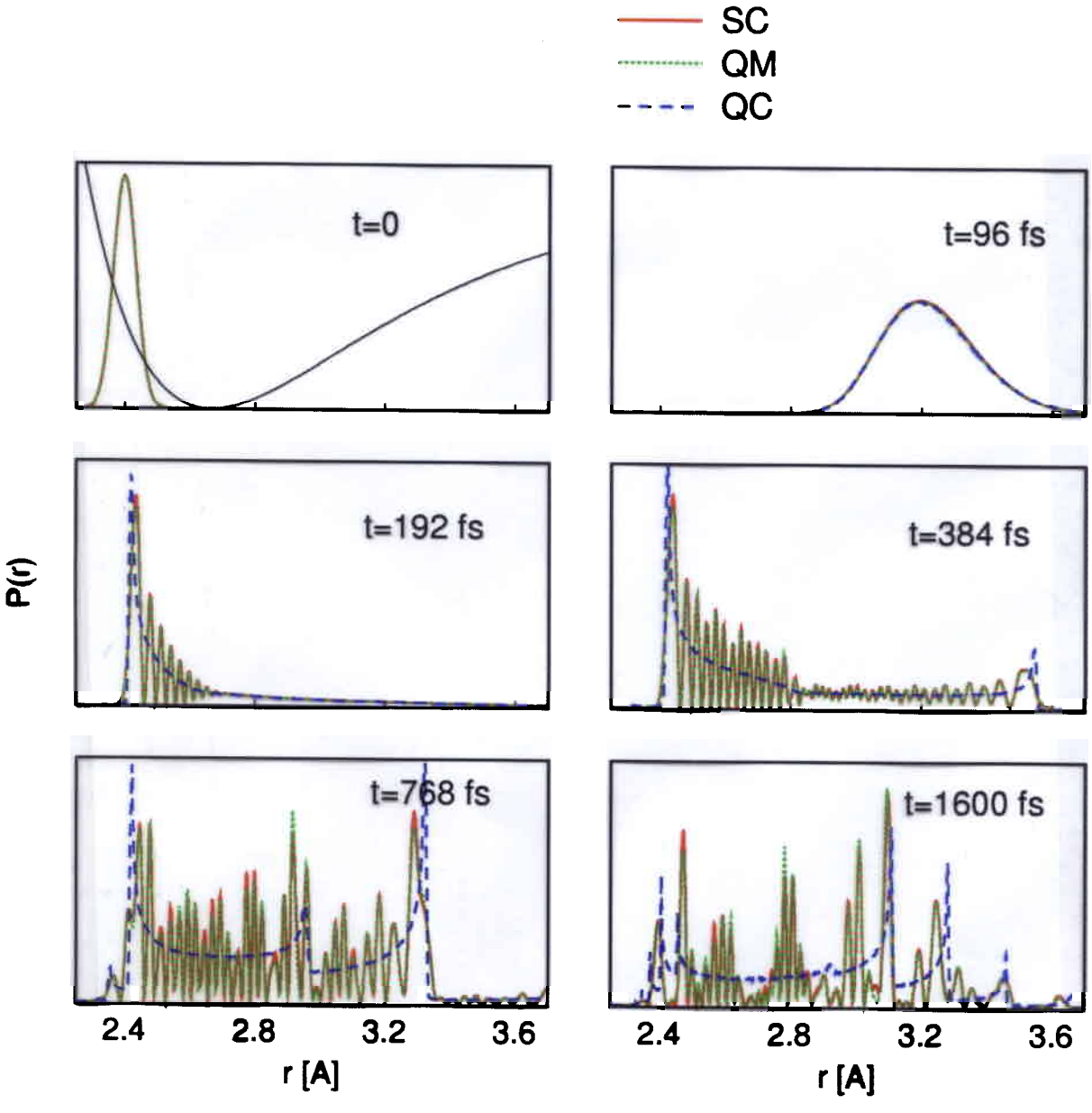


advantage:

- a single (rather than double) phase space integral
- partial cancellation of forward-backward phase results in a smoother integrand

Semiclassical wavepacket dynamics

- Vibrational wavepacket dynamics in the electronic ground state of I_2



Dissipative semiclassical wavepacket dynamics

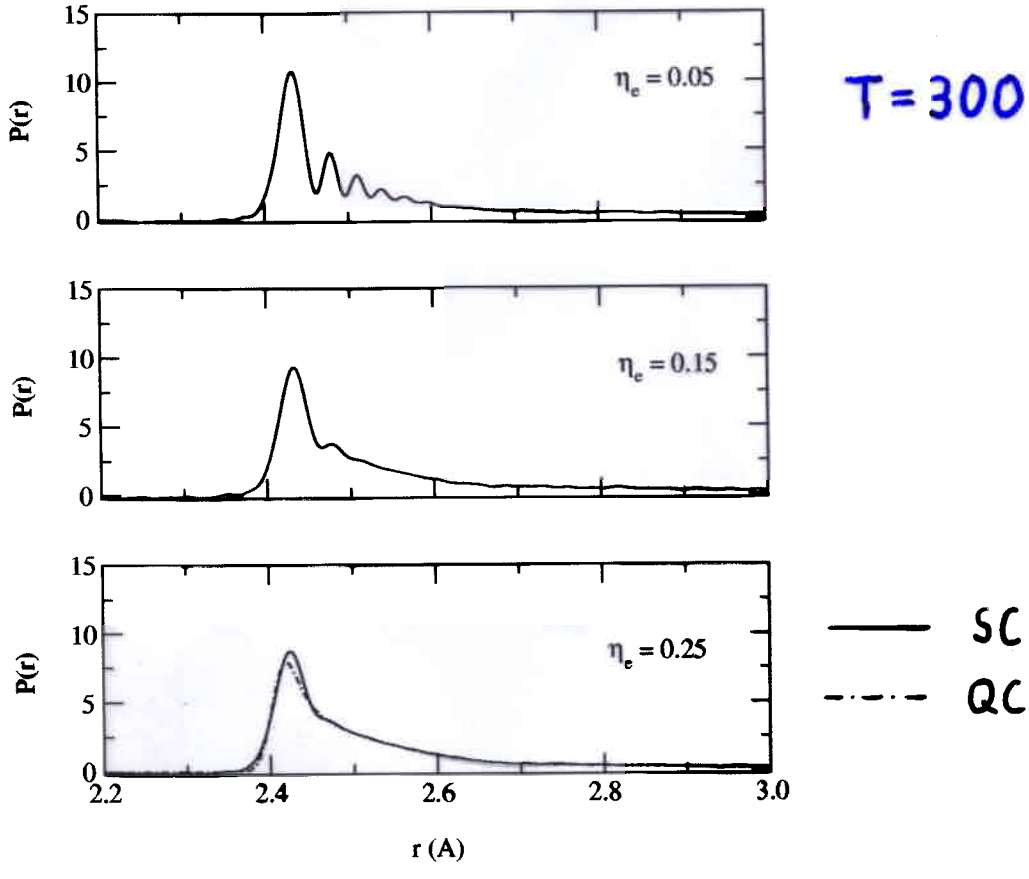
- Morse oscillator (corresponding to the electronic ground state of molecular I_2) coupled to a thermal bath:

$$H = \frac{p_r^2}{2m} + D(1-e^{-\alpha(r-r_e)})^2 + \sum_{j=1}^{N} \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left(q_j - \frac{c_j (r - r_e)}{m_j \omega_j^2} \right)^2$$

- spectral density:

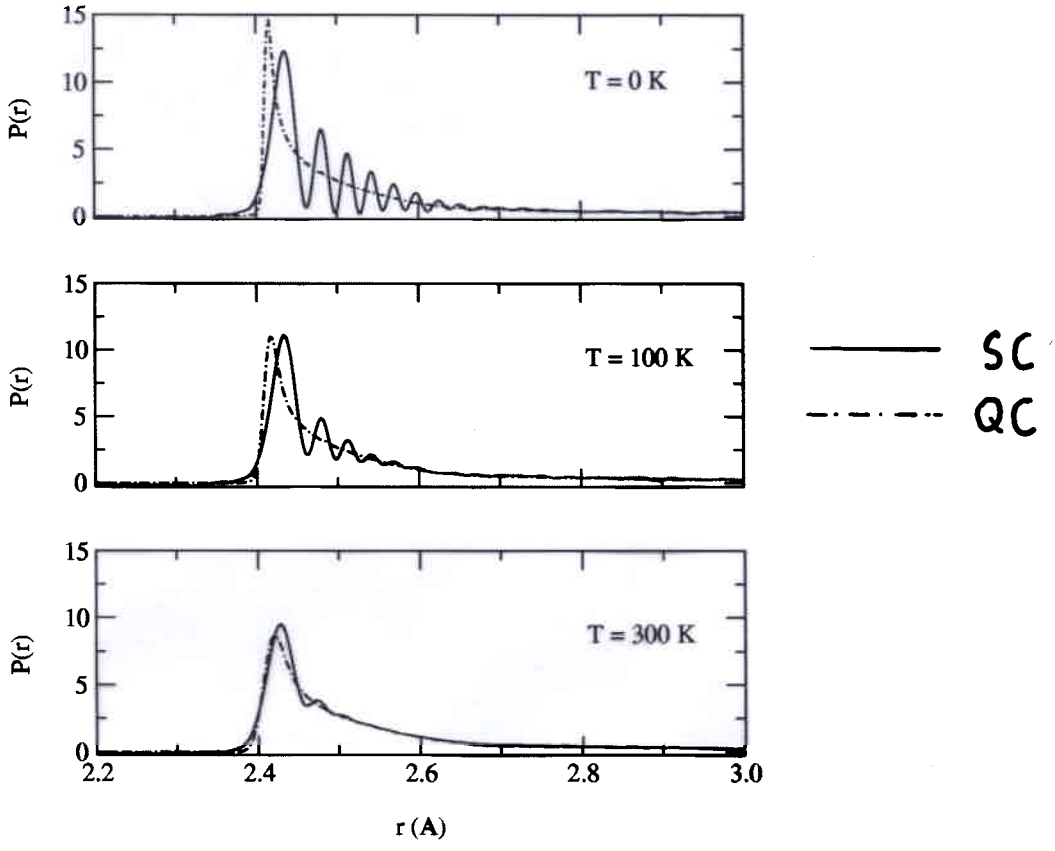
$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j) = \eta \omega e^{-\omega/\omega_c}$$

- Quenching of the coherent structure as a function of the coupling strength ($\eta_e = \eta / m\omega_r$)

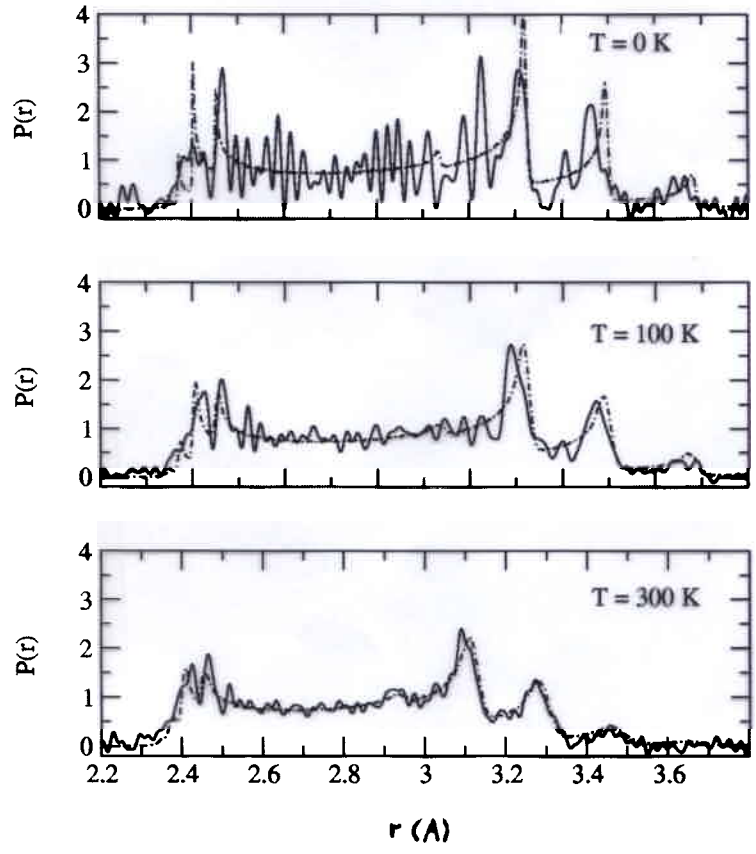


Wang, Thoss, Miller JCP **114**, 2562 (2001)

- Quenching of the coherent structure as a function of temperature after one vibrational period ($t = 192$ fs)

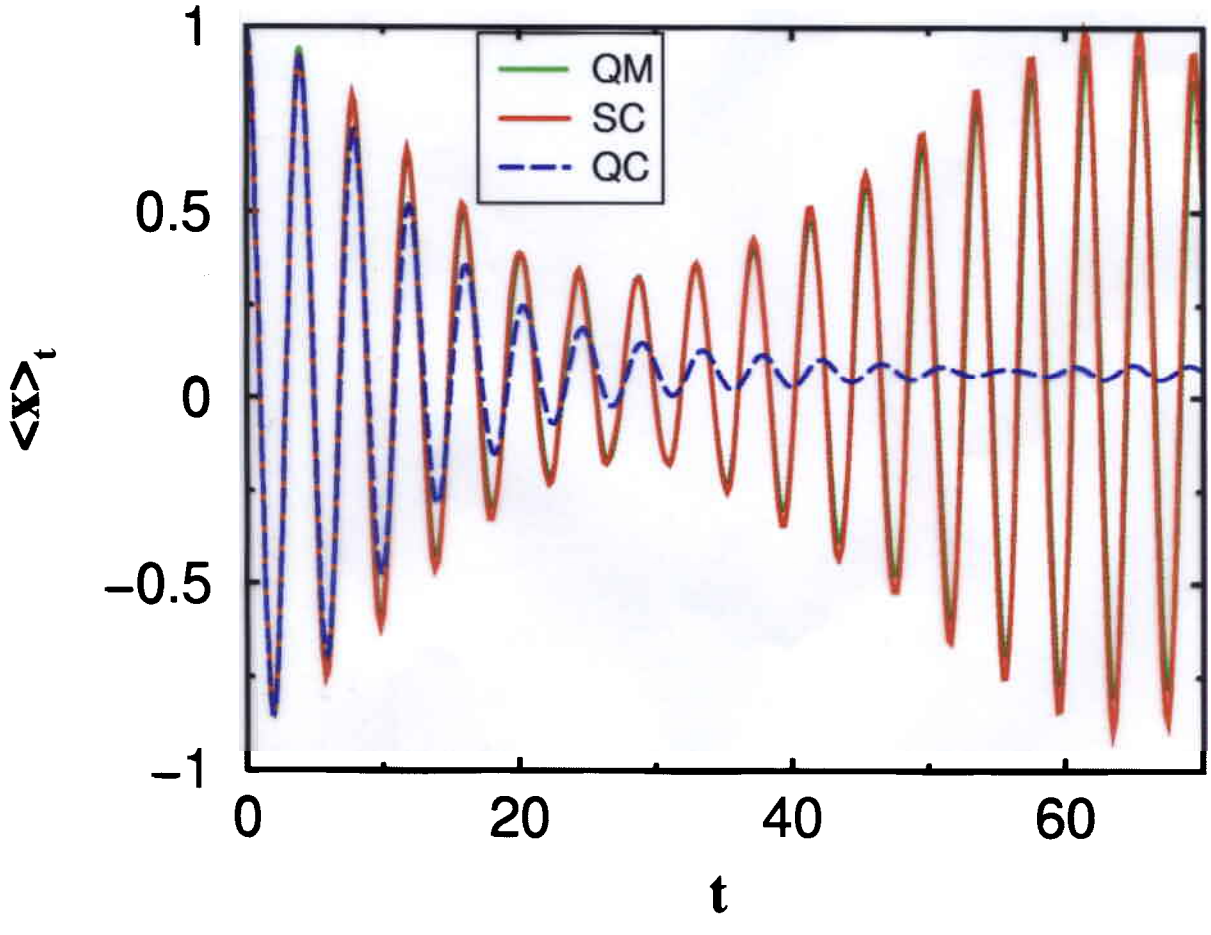


- after 8 vibrational periods ($t = 1600$ fs)



Recurrences in the dynamics of an anharmonic oscillator

- Hamiltonian: $H = \frac{p^2}{2m} + \frac{\omega^2}{2}x^2 + c_3x^3 + c_4x^4$
- initial state: $|\psi_i\rangle = |q_i = 1, p_i = 0\rangle$
- observable: $\langle x\rangle_t = \langle\psi_i|e^{iHt}xe^{-iHt}|\psi_i\rangle$



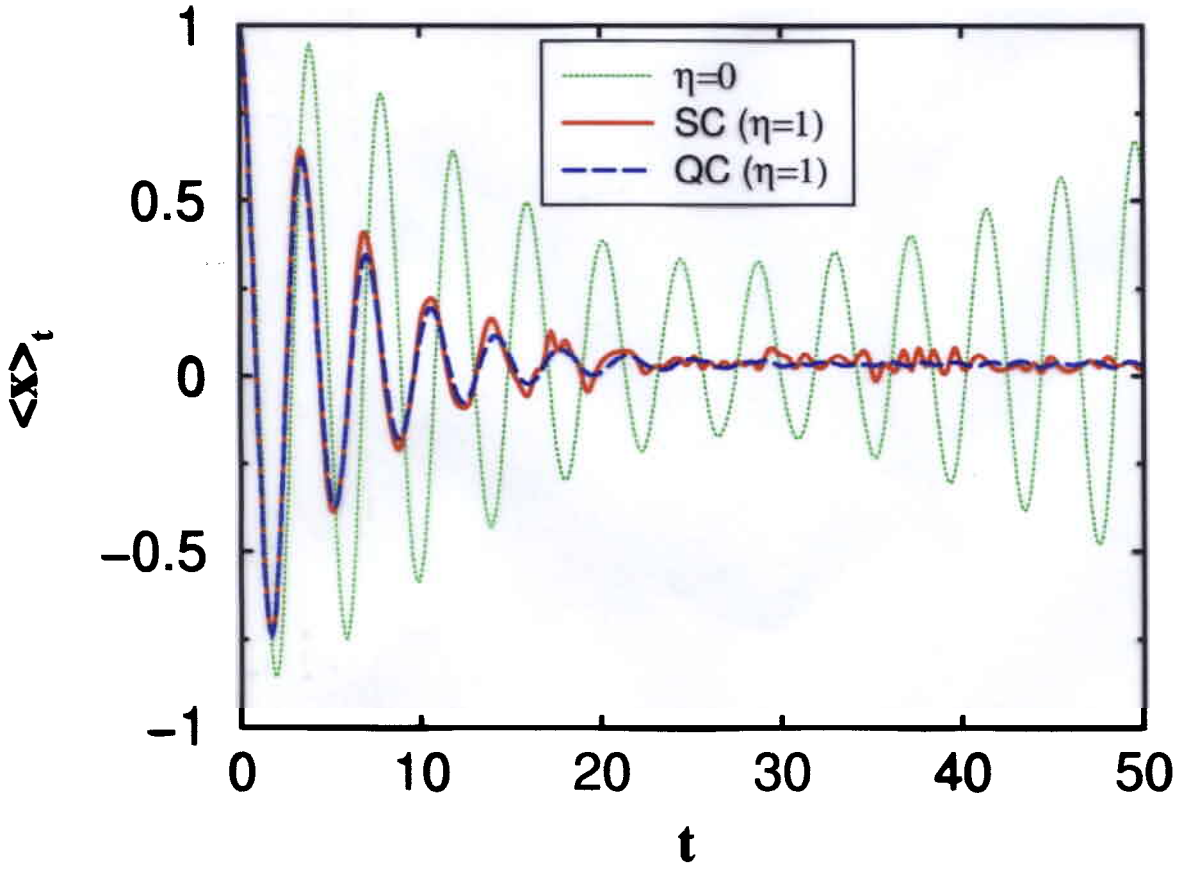
Damped anharmonic oscillator

- Hamiltonian:

$$H = \frac{p_x^2}{2m} + V_0(x) + \sum_{j=1}^{N} \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left(q_j - \frac{c_j x}{m_j \omega_j^2} \right)^2$$

- spectral density:

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j) = \eta \omega e^{-\omega/\omega_c}$$



Thoss, Wang, Miller JCP **114**, 9220 (2001)

Generalized FB-IVR

Although the FB-IVR as a rule is capable of describing quantum interference, it depends on the observable under consideration if all interference that can be described semiclassically is actually included in the calculation.

This problem is circumvented in a generalized FB-IVR which as a function of a parameter can tune between the full double phase space SC-IVR and the FB-IVR.

derivation: apply modified Filinov transformation to the full double phase space SC-IVR

$$C_{AB}^{GFB}(t) = \int \frac{\mathrm{d}q_0\mathrm{d}p_0}{(2\pi)^N} \int \frac{\mathrm{d}\Delta_q\mathrm{d}\Delta_p}{(2\pi)^N} \langle p_0 q_0|A|p_0' q_0'\rangle e^{iS} \times \bar{C}_0(p_0, q_0; \Delta_p, \Delta_q) e^{-\frac{1}{2}\Delta_q c_q \Delta_q} \langle p_t' q_t'|\bar{B}|p_t q_t\rangle$$

trajectory:

- forward $q_0, p_0 \to q_t, p_t$
- jump $q_t' = q_t + \Delta_q, \quad p_t' = p_t + \Delta_p$
- backward $q_t', p_t' \to q_0, p_0$

Filinov parameter: c_q, c_p

- $c_q, c_p \to 0$: double phase space SC-IVR
- $c_q, c_p \to \infty$: FB-IVR
- for finite c_q, c_p the GFB-IVR can combine the better convergence properties of the FB-IVR and the capability of the SC-IVR to describe quantum interference independent on the observable

Forward-Backward IVR

average position $\langle q\rangle(t) = \mathrm{tr}\left[\rho\, e^{iHt}\, q\, e^{-iHt}\right]$

Fourier representation $q = i\int \mathrm{d}p_s\, \delta'(p_s)\, e^{ip_s q}$

$$\langle q\rangle^{\mathrm{FB}}(t) = -i\frac{\partial}{\partial p_s}\Big[\int \frac{\mathrm{d}q_0\mathrm{d}p_0}{(2\pi)^N}\,\langle p_0 q_0|\rho|q_0' p_0'\rangle\, C\, e^{iS}\Big]_{p_s=0}$$

trajectory:

- forward $q_0, p_0 \rightarrow q_t, p_t$
- jump $q_t' = q_t, \quad p_t' = p_t + p_s$
- backward $q_t', p_t' \rightarrow q_0, p_0$

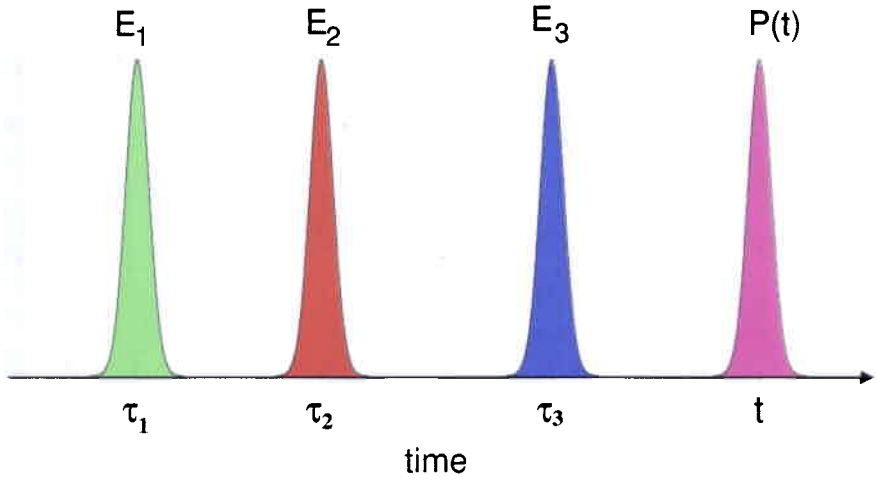
Since in this case the forward and backward trajectory differ only by an infinitesimal small momentum jump, the FB-IVR reduces to the quasiclassical expression

$$\langle q\rangle^{FB}(t) = \int \frac{\mathrm{d}q_0\mathrm{d}p_0}{(2\pi)^N}\, q_t\, \tilde{\rho}(q_0, p_0)$$

with $\tilde{\rho}(q_0,p_0) = [1 - \frac{1}{4}(\frac{\partial^2}{\partial q_0^2} + \frac{\partial^2}{\partial p_0^2})]\,\rho_H(q_0,p_0)$

- Husimi function $\rho_H(q_0,p_0) = \langle p_0 q_0|\rho|q_0 p_0\rangle$
- Wigner function $\rho_W(q_0,p_0) = \exp\left[-\frac{1}{4}\left(\frac{\partial^2}{\partial q_0^2} + \frac{\partial^2}{\partial p_0^2}\right)\right]\rho_H(q_0,p_0)$

Nonlinear optical spectroscopy



The third-order nonlinear polarization induced by the laser field is given by

$$P^{(3)}(t) = \int dt_3 \int dt_2 \int dt_1 \, E(t-t_3)\, E(t-t_3-t_2)\, E(t-t_3-t_2-t_1) \times S^{(3)}(t_3,t_2,t_2)$$

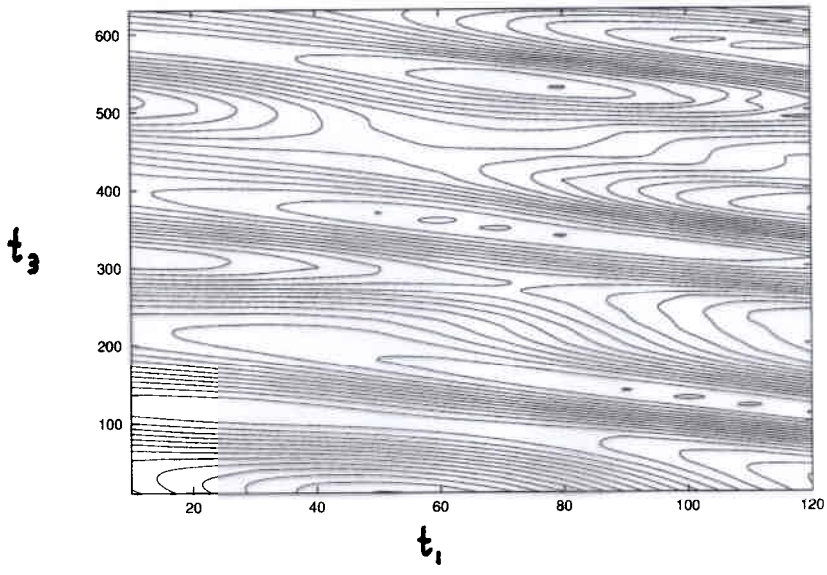
- laser field $E(t) = \sum_{j=1}^{3} E_j(t-\tau_j)\, \cos(\varphi_j - \omega_j t)$
- third-order response function

$$S^{(3)}(t_3,t_2,t_1) = i^3\, \mathrm{tr}\{\rho\, [[[\mu(t_3+t_2+t_1), \mu(t_2+t_1)], \mu(t_1)], \mu(0)]\}$$
$$= i^3 \sum_{j=1}^{4} \Big(R_j(t_3,t_2,t_1) - R_j^*(t_3,t_2,t_1) \Big)$$

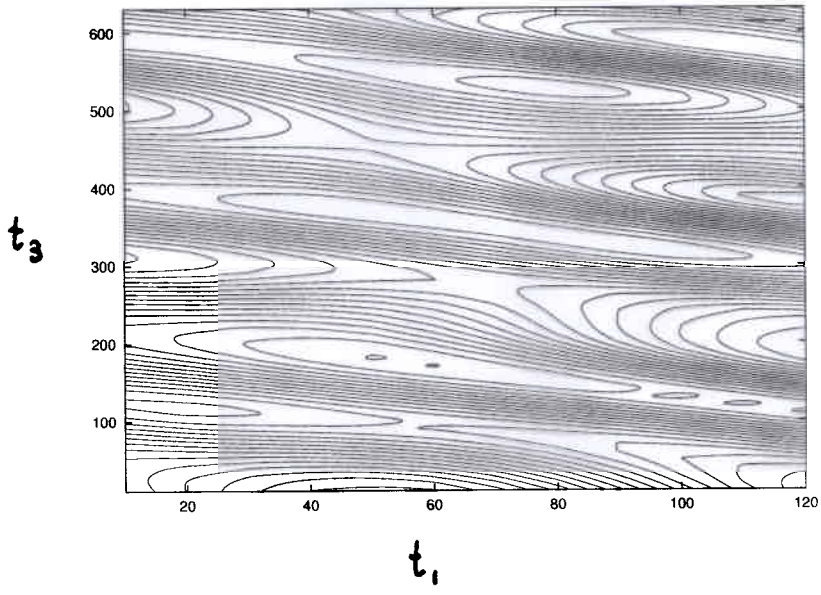
$$R_1(t_3,t_2,t_1) = \mathrm{tr}\{\rho\, e^{iHt_1}\mu\, e^{iHt_2}\mu\, e^{iHt_3}\mu\, e^{iH(t_1+t_2+t_3)}\mu\}$$

Nonlinear optical response of a Morse oscillator

$$S^{(3)}(t_3,t_2,t_1) \quad = \quad i^3\,\mathrm{tr}\{\,\rho\,[\,[\,[\,\mu(t_3+t_2+t_1),\mu(t_2+t_1)],\mu(t_1)],\mu(0)]\}$$

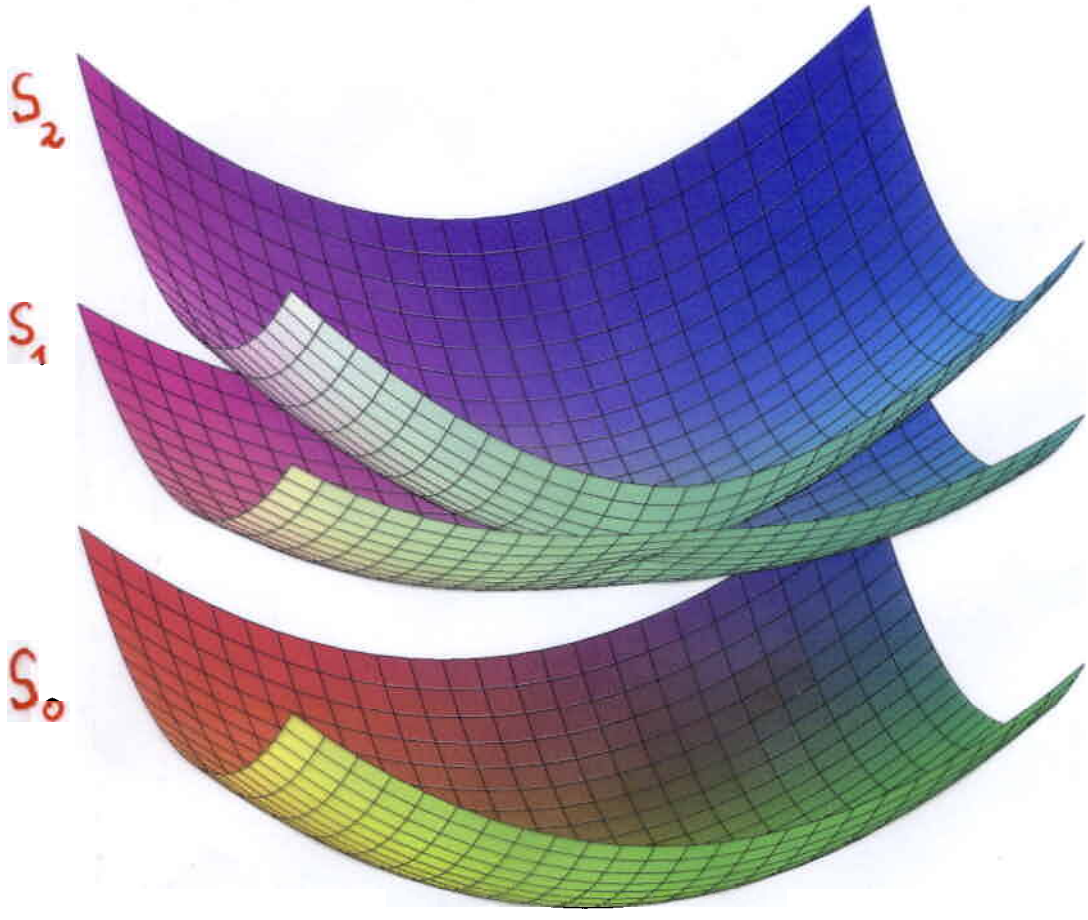


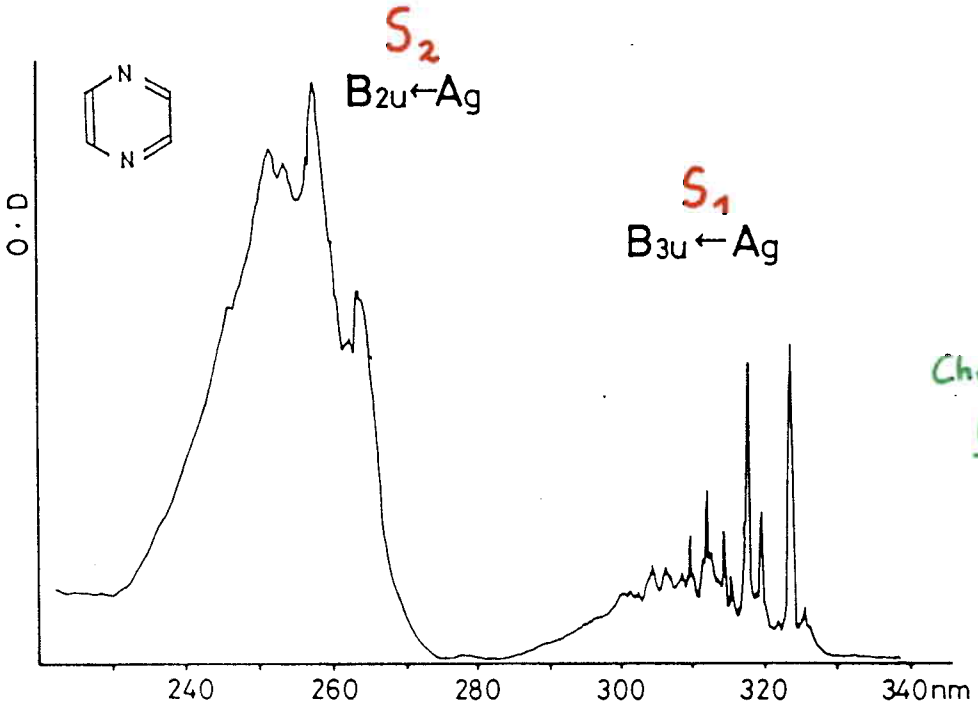
SC



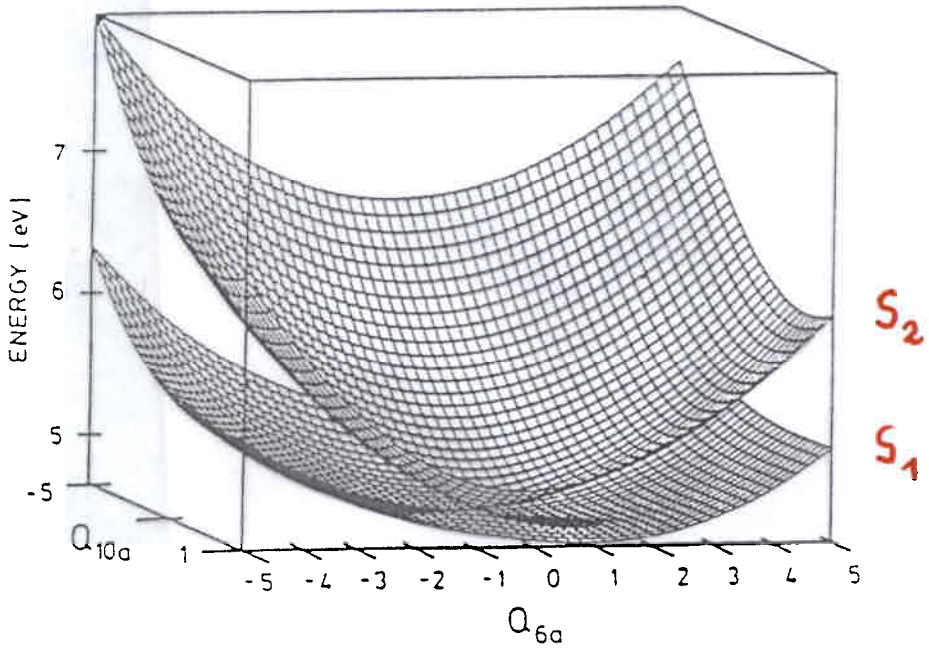
QM

Semiclassical description of nonadiabatic quantum dynamics





Suzuka et al.
Chem. Phys. Lett.
64 333 (1979)



Woywod, Domcke
J. Chem. Phys. 100, 1400 (1994)

Hamiltonian

molecular Hamiltonian represented in a basis of diabatic electronic states

$$\mathcal{H} = T(\mathbf{p}) + \sum_{n,m} |\phi_n\rangle V_{nm}(\mathbf{x}) \langle\phi_m|$$

- $T(\mathbf{p})$: kinetic energy operator of the nuclei
- V_{nm}: diabatic potential matrix

Observables

- autocorrelation function after photoexcitation to the S_2 electronic state

$$J(t) = \langle\Psi_i|e^{-i\mathcal{H}t}|\Psi_i\rangle \qquad |\Psi_i\rangle = |\phi_2\rangle|\mathbf{v}_i = \mathbf{0}\rangle$$

- absorption spectrum

$$I(\omega) \propto \omega \,\mathrm{Re} \int_0^\infty \mathrm{d}t \, e^{i(\omega+\varepsilon_0)t} J(t)$$

- population of the diabatic electronic states

$$P_j(t) = \langle\Psi_i|e^{i\mathcal{H}t}|\phi_j\rangle\langle\phi_j|e^{-i\mathcal{H}t}|\Psi_i\rangle$$

Semiclassical description

Standard semiclassical methods cannot be applied directly to nonadiabatic dynamics, because the Hamiltonian involves discrete DoF (discrete electronic states) which do not possess an obvious classical counterpart.

How can one incorporate discrete quantum degrees of freedom into a classical theory?

"Mapping Approach"

discrete DoF $\rightarrow$ continuous DoF

Examples:

- Holstein & Primakoff (PR 58 (1940) 1098)
- Schwinger's theory of angular momentum (1965)
  (see, e.g., Sakurai, *Modern Quantum Mechanics*)

spin system $\rightarrow$ harmonic oscillators

Mapping approach

discrete DoF → continuous DoF

$$[S_j, S_k] = i\epsilon_{jkl} S_l \qquad S_\pm = S_1 \pm i S_2$$

$$S_3|sm\rangle = m|sm\rangle \qquad -s \le m \le s$$

- Schwinger's theory of angular momentum
  (1965, see, e.g., Sakurai, *Modern Quantum Mechanics*)

$$S_+ \to a_1^\dagger a_2 \qquad S_- \to a_2^\dagger a_1 \qquad S_3 \to (a_1^\dagger a_1 - a_2^\dagger a_2)/2$$

$$|sm\rangle \to \frac{(a_1^\dagger)^{s+m}(a_2^\dagger)^{s-m}}{\sqrt{(s+m)!(s-m)!}}|0_1, 0_2\rangle = |(s+m)_1, (s-m)_2\rangle$$

$$[a_n, a_m^\dagger] = \delta_{n,m}$$

- Holstein-Primakoff transformation (PR 58 (1940) 1098)

$$S_+ \to \sqrt{2s}\, a^\dagger \sqrt{1 - a^\dagger a/2s} \qquad S_- \to \sqrt{2s}\, \sqrt{1 - a^\dagger a/2s}\, a$$
$$S_3 \to a^\dagger a - s$$

$$|sm\rangle \to \frac{(a^\dagger)^{s+m}}{\sqrt{(s+m)!}}|0\rangle = |s+m\rangle$$

Mapping approach

discrete DoF $\rightarrow$ continuous DoF

- molecular Hamiltonian in the discrete representation

$$\mathcal{H} = T(\mathbf{p}) + \sum_{n,m} |\phi_n\rangle V_{nm}(\mathbf{x}) \langle\phi_m|$$

- mapping relations

$$\begin{aligned} |\phi_n\rangle\langle\phi_m| &\rightarrow a_n^\dagger a_m, \qquad [a_n, a_m^\dagger] = \delta_{nm} \\ |\phi_n\rangle &\rightarrow |0_1, \ldots, 1_n, \ldots, 0_M\rangle \end{aligned}$$

- Cartesian electronic variables

$$X_n = (a_n^\dagger + a_n)/\sqrt{2}, \qquad P_n = i(a_n^\dagger - a_n)/\sqrt{2}$$

- molecular Hamiltonian in the continuous representation

$$H = T(\mathbf{p}) + \tfrac{1}{2} \sum_{n,m} (X_n X_m + P_n P_m - \delta_{nm}) V_{nm}(\mathbf{x})$$

- both Hamilton operators are equivalent in the physical subspace

$$\begin{aligned} & \langle\phi_n|\langle\mathbf{v}'|e^{-i\mathcal{H}t}|\mathbf{v}\rangle|\phi_m\rangle \\ = \; & \langle 0_1, \ldots, 1_n, \ldots, 0_M|\langle\mathbf{v}'|e^{-iHt}|\mathbf{v}\rangle|0_1, \ldots, 1_m, \ldots, 0_M\rangle \end{aligned}$$

The mapping approach therefore allows us to extend well-established semiclassical methods to general nonadiabatic problems.

(Stock & Thoss, PRL **78**, (1997) 578, PRA **59** (1999) 64)

Semiclassical autocorrelation function

$$
\begin{aligned}
J(t) &= \langle \phi_2 | \langle \mathbf{v}_i = \mathbf{0} | e^{-i\mathcal{H}t} | \mathbf{v}_i = \mathbf{0} \rangle | \phi_2 \rangle \\
&= \langle 0_1, 1_2 | \langle \mathbf{v}_i = \mathbf{0} | e^{-iHt} | \mathbf{v}_i = \mathbf{0} \rangle | 0_1, 1_2 \rangle \\
&\approx \int \frac{\mathbf{dX_0 dP_0}}{(2\pi)^M} \int \frac{\mathbf{dx_0 dp_0}}{(2\pi)^N} \langle 0 | X_{1t} P_{1t} \rangle \langle 1 | X_{2t} P_{2t} \rangle \langle \mathbf{0} | \mathbf{x}_t \mathbf{p}_t \rangle C_t \, e^{iS_t} \\
&\qquad \times \langle \mathbf{x_0 p_0} | \mathbf{0} \rangle \langle X_{10} P_{10} | 0 \rangle \langle X_{20} P_{20} | 1 \rangle
\end{aligned}
$$

Mapping approach

Related formulations

- classical "electron-analog" models
  Meyer & Miller, J. Chem. Phys. **70**, 3214 (1979),
  Sun & Miller, J. Chem. Phys. **106**, 916 (1997)

$$H_{MM} = T(\mathbf{p}) + \sum_j n_j V_{jj} + \sum_{j,k} \sqrt{\left(n_j + \tfrac{1}{2}\right)\left(n_k + \tfrac{1}{2}\right)}\, e^{i(q_j - q_k)}\, V_{jk}$$

$$|\psi_{el}(t)\rangle = \sum_j c_j(t)\, |\phi_j\rangle \qquad c_j = \sqrt{n_j}\, e^{-iq_j}$$

- spin-coherent state formulation
  Suzuki, Nucl. Phys. A **198**, 557 (1983),
  Thoss & Stock, PRA **59**, 64 (1999)

$$e^{-iHt} = N_t^{-1} \frac{2}{\pi} \int \frac{\mathrm{d}^2\mu_0}{(1 + |\mu_0|^2)^2}\, |\mu_t\rangle\, e^{iS_\mu}\, \langle\mu_0|$$

$$|\mu\rangle = \frac{|\phi_1\rangle + \mu\, |\phi_2\rangle}{\sqrt{1 + |\mu|^2}}$$

- Pechukas model for nonadiabatic transitions
  Pechukas, Phys. Rev. **181**, 174 (1969)

Relation to semiclassical spin-coherent state propagator

- semiclassical Herman-Kluk propagator based on mapping approach

$$\langle\phi_2|\langle \mathbf{v}_f|e^{-i\mathcal{H}t}|\mathbf{v}_i\rangle|\phi_1\rangle_{SC} = \int \frac{\mathrm{d}^2\mathbf{z_0}}{\pi^M}\int \frac{\mathrm{d}^2 Z_1}{\pi}\int \frac{\mathrm{d}^2 Z_2}{\pi}\,\langle 0,1|Z_{1_t},Z_{2_t}\rangle\,\langle \mathbf{v}_f|\mathbf{z_t}\rangle\,C_t\,e^{iS_t}\,\langle \mathbf{z_0}|\mathbf{v}_i\rangle\,\langle Z_{1_0},Z_{2_0}|1,0\rangle$$

- parametrisation

$$Z_1 = \sqrt{I}\sin\left(\frac{\theta}{2}\right)e^{i(\phi-\psi)/2} \qquad Z_2 = \sqrt{I}\cos\left(\frac{\theta}{2}\right)e^{-i(\phi+\psi)/2} \qquad |\mu\rangle = \frac{|\phi_1\rangle+\mu\,|\phi_2\rangle}{\sqrt{1+|\mu|^2}} \qquad \mu = e^{i\phi}\tan\left(\frac{\theta}{2}\right)$$

- integrate over ψ

$$\langle\phi_2|\langle \mathbf{v}_f|e^{-i\mathcal{H}t}|\mathbf{v}_i\rangle|\phi_1\rangle_{SC} = \int_0^\infty \mathrm{d}I\,\frac{I^2}{2}\,e^{-I}\,\frac{2}{\pi}\int \frac{\mathrm{d}^2\mu_0}{(1+|\mu_0|^2)^2}\int \frac{\mathrm{d}^2\mathbf{z_0}}{\pi^M}\,\langle\phi_2|\mu_t\rangle\,\langle \mathbf{v}_f|\mathbf{z_t}\rangle\,C_t\,e^{iS_t}\,\langle \mathbf{z_0}|\mathbf{v}_i\rangle\,\langle\mu_0|\phi_1\rangle$$

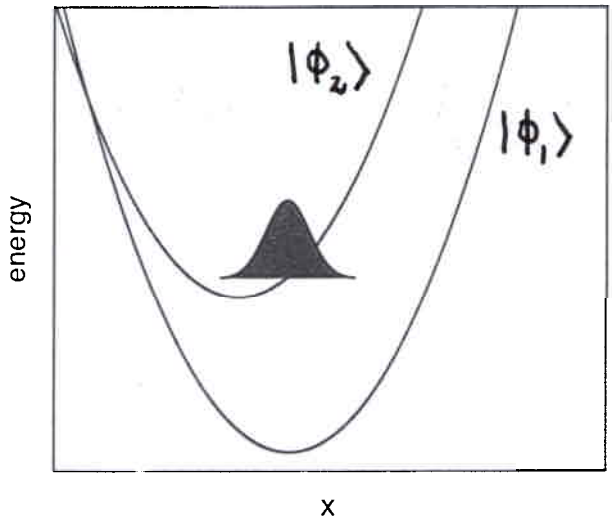
- replace sampling over I by fixed (quantum) value $I=1$

$$\langle\phi_2|\langle \mathbf{v}_f|e^{-i\mathcal{H}t}|\mathbf{v}_i\rangle|\phi_1\rangle_{SC} = \frac{2}{\pi}\int \frac{\mathrm{d}^2\mu_0}{(1+|\mu_0|^2)^2}\int \frac{\mathrm{d}^2\mathbf{z_0}}{\pi^M}\,\langle\phi_2|\mu_t\rangle\,\langle \mathbf{v}_f|\mathbf{z_t}\rangle\,C_t\,e^{iS_t}\,\langle \mathbf{z_0}|\mathbf{v}_i\rangle\,\langle\mu_0|\phi_1\rangle$$

$$S_t = \int_0^t \mathrm{d}\tau\left[\frac{i}{2}(\mathbf{z}_\tau^*\dot{\mathbf{z}}_\tau-\dot{\mathbf{z}}_\tau^*\mathbf{z}_\tau)+\frac{i}{2}\frac{(\mu_\tau^*\dot\mu_\tau-\dot\mu_\tau^*\mu_\tau)}{1+|\mu|^2}-h(\mathbf{z},\mu)\right] \qquad h(\mathbf{z},\mu)=\langle\mathbf{z}|\langle\mu|\mathcal{H}|\mu\rangle|\mathbf{z}\rangle$$

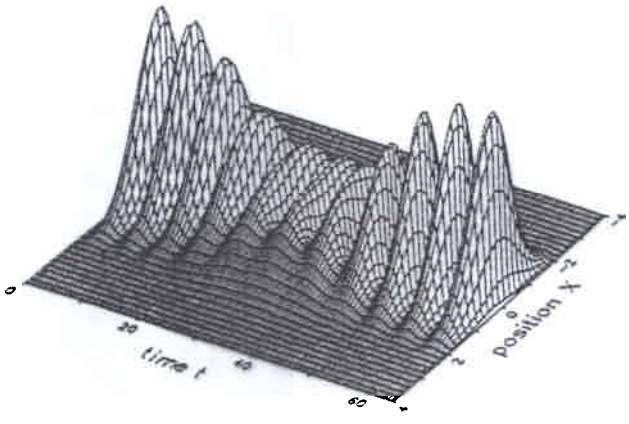
$$\dot\mu = -i\,(1+|\mu|^2)^2\,\frac{\partial h}{\partial\mu^*} \qquad \dot{\mathbf{z}} = -i\,\frac{\partial h}{\partial \mathbf{z}^*}$$

Thoss & Stock, PRA **59** (1999) 64



- Vibrational wave-function in the $|\phi_1\rangle$ electronic state

QM



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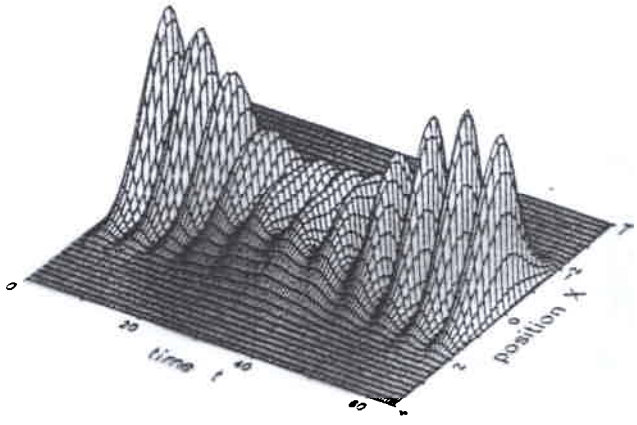
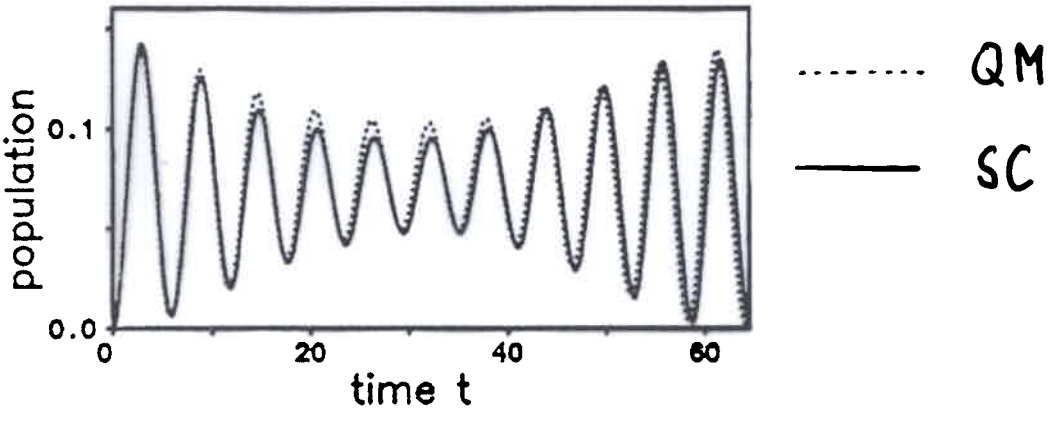


- population probability in the $|\phi_1\rangle$ electronic state



Four-mode pyrazine model

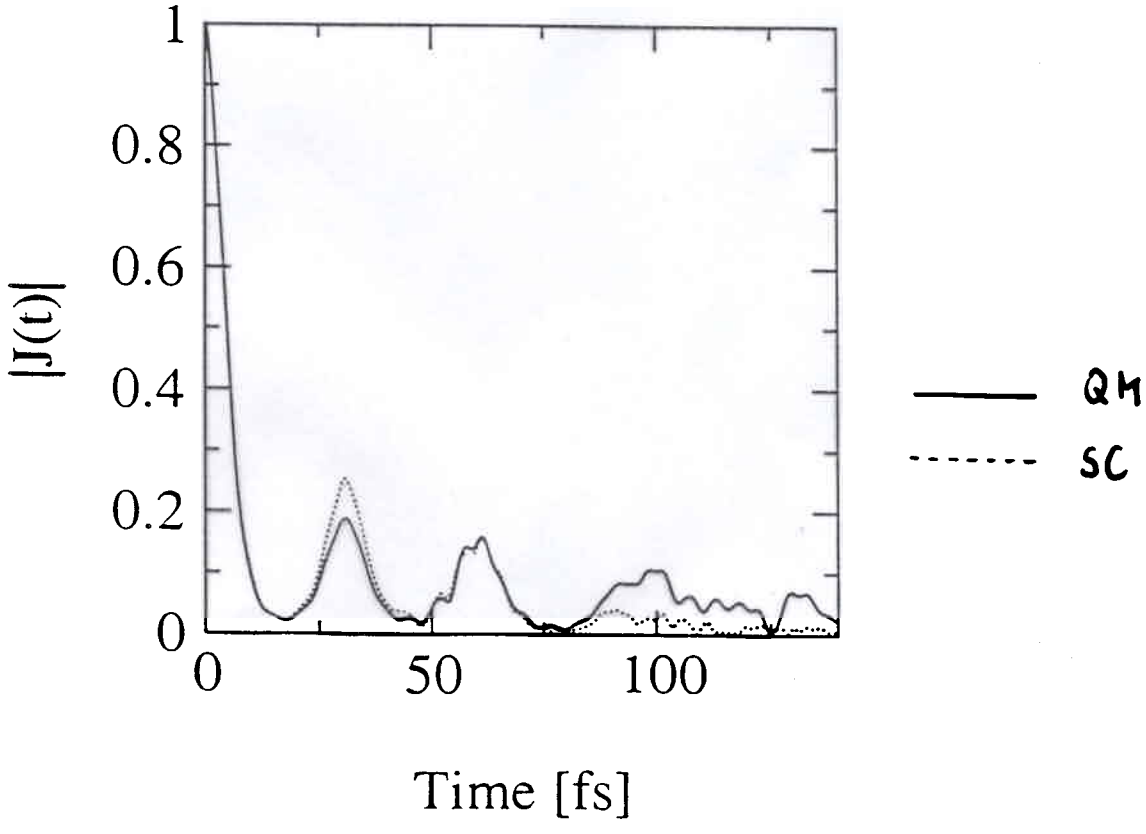
(C. Woywod, W. Domcke et al. JCP **100**, 1400 (1994))

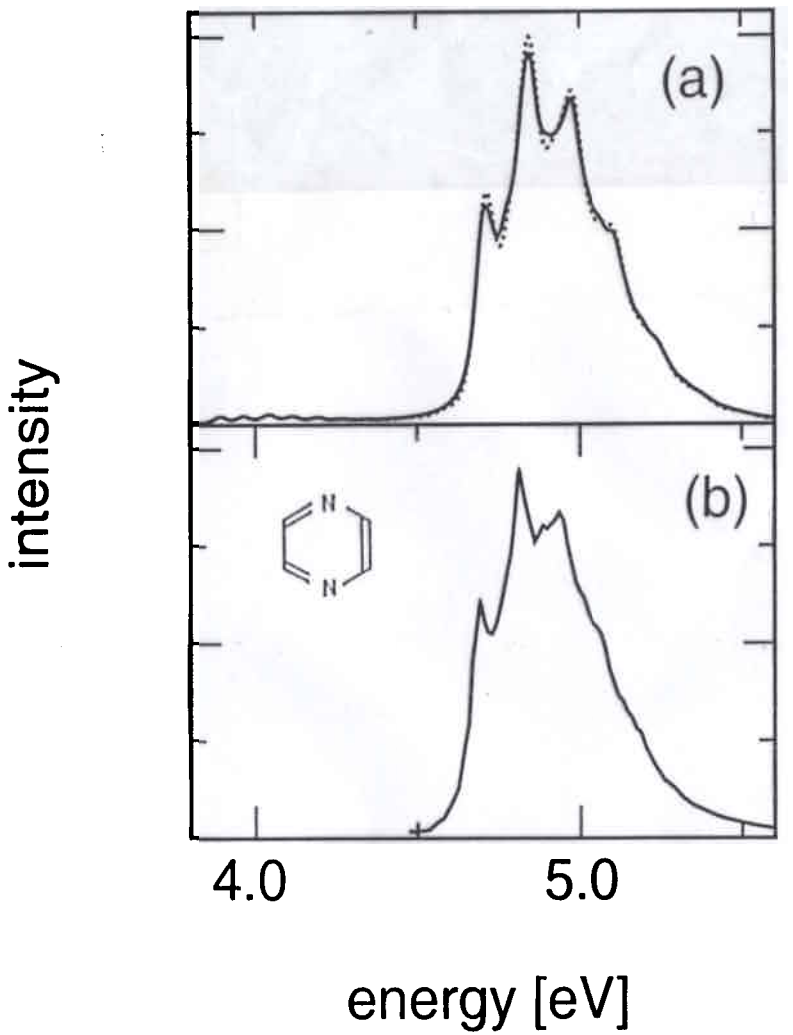
Besides the nontotally symmetric coupling mode ν_{10a}, the three most strongly coupled totally symmetric (Condon-active) modes are taken into account in this model ($G = \{\nu_1, \nu_{6a}, \nu_{9a}\}$).

- diabatic potential matrix

$$\mathbf{V} = \begin{pmatrix} E_1 + \sum_{j \in G} \kappa_j^{(1)} x_j & \lambda x_{10a} \\ \lambda x_{10a} & E_2 + \sum_{j \in G} \kappa_j^{(2)} x_j \end{pmatrix}$$

- autocorrelation function



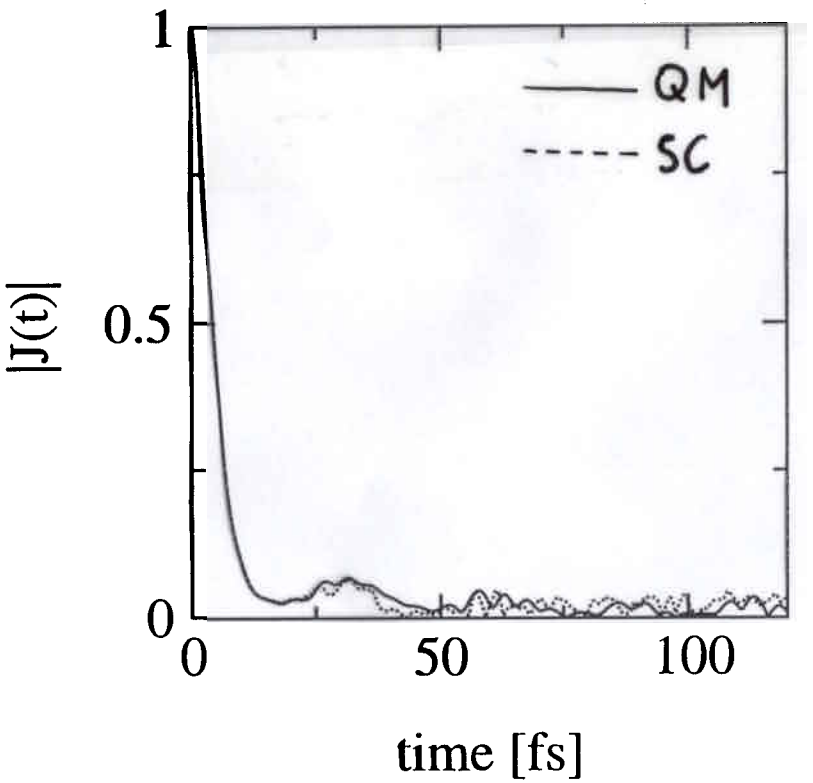


QM

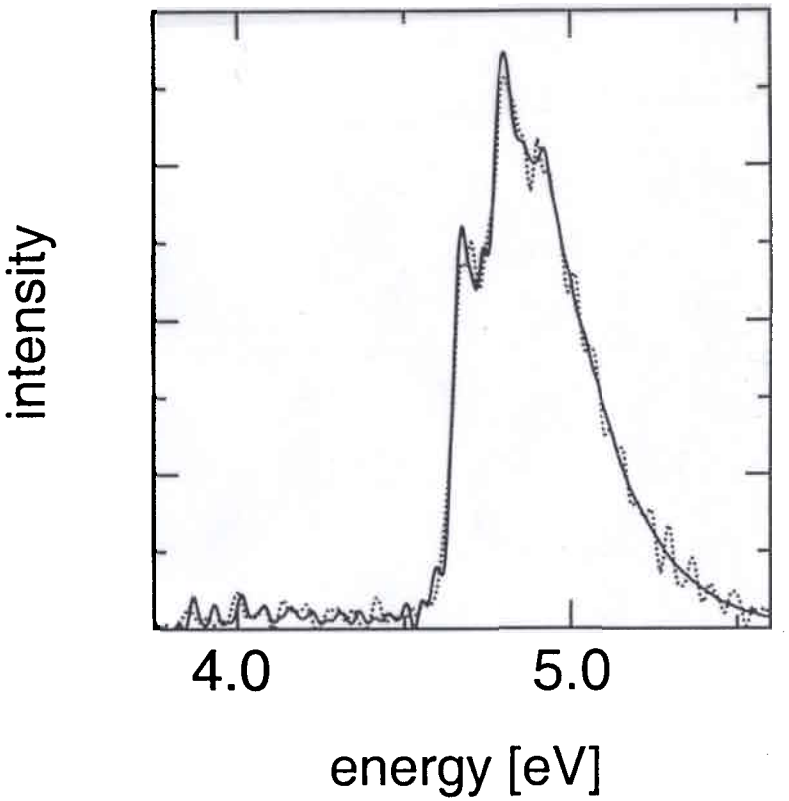
SC

Experiment:
I. Yamazaki et al.,
Faraday Discuss. 75, 395
(1983)

(a) Calculated and (b) experimental (Ref. [8]) absorption spectrum of the S_2 state of pyrazine. The semiclassical (dotted line) and the quantum (full line) results in (a) have been obtained by including a phenomenological electronic dephasing ($T_2 = 30$ fs).



Modulus of the autocorrelation function for the 24-mode pyrazine model. The full line is the quantum result [11] and the dotted line is the semiclassical result.



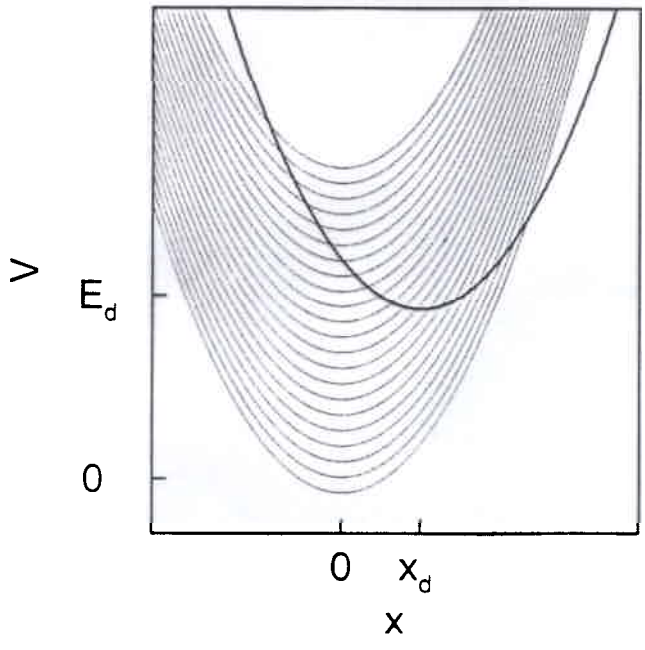
Absorption spectrum for the 24-mode pyrazine model. The full line is the quantum result [11] and the dotted line is the semiclassical result. In both spectra a phenomenological dephasing constant of $T_2 = 150$ fs was used.

QM-results: A. Raab, G.A. Worth, H.-D. Meyer, L.S. Cederbaum, JCP 110, 936 (1999)

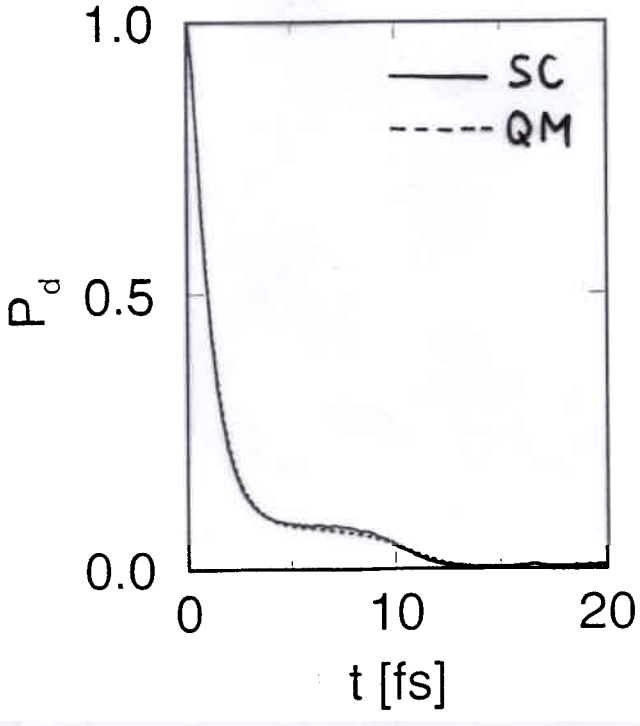
$^2\Pi_g$ d-wave shape resonance in electron–N_2 scattering

$$e^- + N_2(v) \rightarrow N_2^- \rightarrow e^- + N_2(v')$$

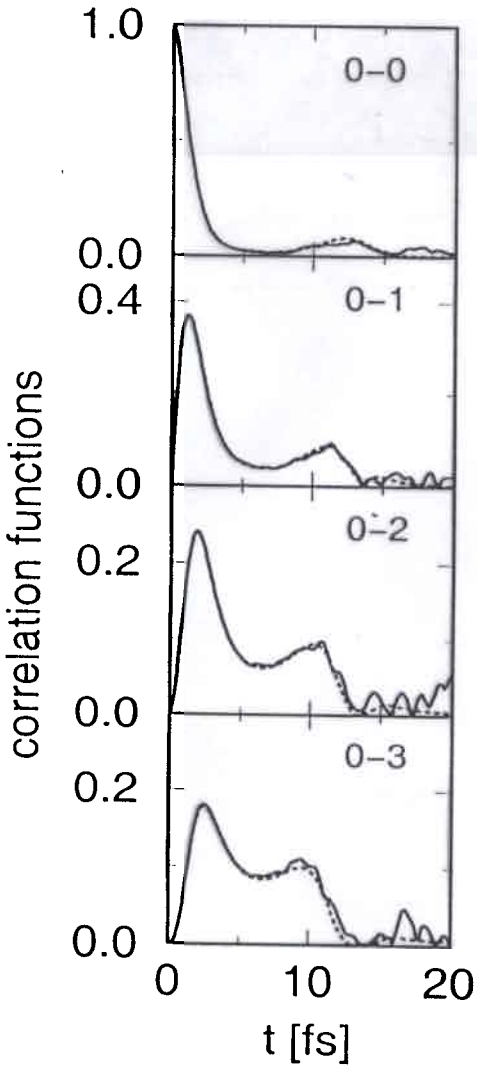
- Potential-energy curves of the resonance state and the target molecule for different values of the electron energy



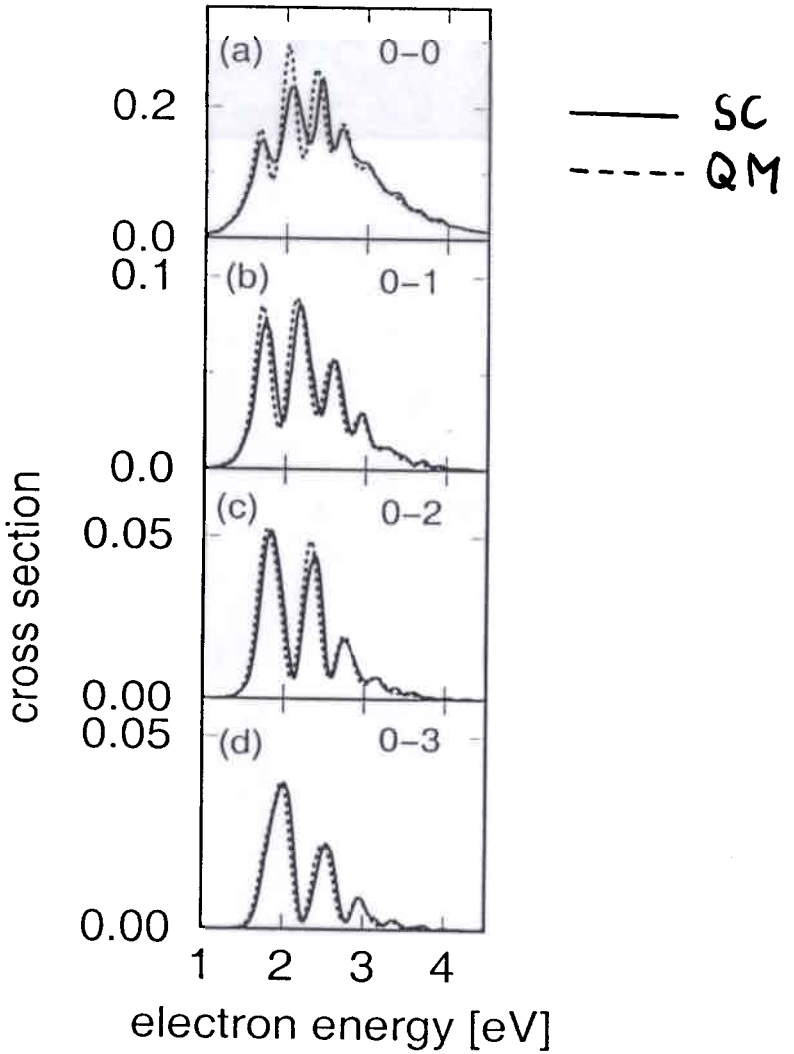
- Survival probability of the resonance state



vibrational excitation: $e^- + N_2(v=0) \rightarrow e^- + N_2(v')$



Modulus of the correlation functions in the resonance state corresponding to vibrational transition from the ground state to $v_f = 0 - 3$. The semiclassical results (full line) match the quantum results (dotted line) for times $t \leq 15$fs.



(a) Elastic ($v = 0 \rightarrow 0$) and (b)-(d) inelastic vibrational excitation ($v = 0 \rightarrow 1, 2, 3$) cross section for electron–N_2 scattering. The semiclassical results (full line) are seen to reproduce the quantum results better for a higher vibrational quantum number in the final state of the N_2-molecule.

Conclusions

- Semiclassical IVR methods are able to describe the dynamics in many molecular systems accurately
- With Filinov-Filtering and FB-IVR methods it is possible to treat rather large systems
- The mapping approach extends well-established semiclassical methods to nonadiabatic dynamics

problems:

- numerical effort
- semiclassical description of tunneling

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