Quasi-classical Liouville dynamics

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Introduction

Molecular dynamics between
quantum and classical mechanics

The goal

- Progress in molecular dynamics
  - Experiment: Ultrashort light pulses (ps $\rightarrow$ fs $\rightarrow$ as)
  - Simulations: Increasing computer power
  - Mathematics: Novel algorithms
- Exploring the limit of large molecular systems
  - Challenges in physical chemistry / chemical physics:
    Large molecules, clusters, liquids and solids/matrices
  - Challenges in biophysical chemistry:
    Photosynthesis, peptides$\rightarrow$proteins, conformations, ...

State of the art: quantum dynamics

- Small systems (2...4 atoms)
  - Exact quantum dynamics
  - Grid representations of wavefunctions, e. g., Fourier / DVR
- Medium systems (10...100 atoms)
  - Approximate quantum dynamics
  - Separable and nonseparable approaches, e. g., MCTDH
- Large systems (10^3...10^6 atoms)
  - Classical trajectory dynamics
  - Newton's / Hamiltonian's equations, e. g., leap frog

Classical Liouville dynamics

Classical limit of quantum dynamics

Quantum mechanics in phase space

- Concept of Wigner transform
  - E. P. Wigner (Szillard)
    Phys. Rev. **40**, 749-759 (1932)
  - W. Heisenberg
    Physik. Zeitschr. **32**, 737-740 (1931)
  - P. A. M. Dirac

    Proc. Camb. Phil. Soc. **26**, 376-385 (1930)
- Alternative approaches
  - K. Husimi
    Proc. Phys. Math. Soc. Jap. **22**, 264 (1940)

Wigner transform

- Quantum-mechanical operator→phase space function

$$A_W(R,P) = \int dS \exp(-\frac{i}{\hbar} P \cdot S) \left\langle R + \frac{S}{2} \middle| \hat{A} \middle| R - \frac{S}{2} \right\rangle$$

- Calculate quantum-mechanical expectation values

$$\left\langle \hat{A} \right\rangle = \int dR \int dP A_W(R,P) \rho_W(R,P)$$

- Wigner distribution function $\rho_W(R,P)$
  - Defined as Wigner transform of density operator

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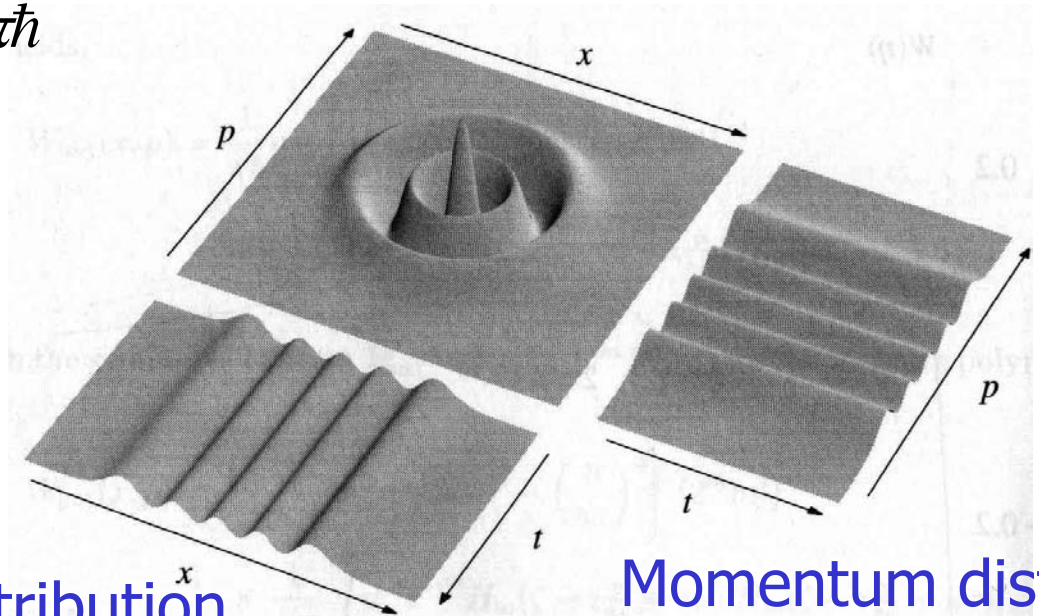
Wigner distribution function

Phase space distribution ⇒ „Quasi-distribution“

$$\left|\rho_W(R,P)\right| \le \frac{1}{\pi\hbar}$$



Position distribution

$$\rho(R) = \int dP \rho_W(R,P) \ge 0$$

Momentum distribution

$$\rho(P) = \int dR \rho_W(R,P) \ge 0$$

Dynamics of Wigner distribution

- Quantum Liouville-von Neumann equation (QLE)

$$\partial_t \hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}(t)]$$

- Wigner transform of QLE

$$\partial_t \rho_W(t) = -\frac{2}{\hbar} H_W \sin\left(\frac{\hbar}{2}\{\cdot,\cdot\}\right)\rho_W(t) = -\{H_W, \rho(t)\} + O(\hbar^2)$$

- Problems
  - Doubled dimensionality of Schrödinger equation
  - High powers of Poisson bracket operator $\{\cdot,\cdot\}$
  - Convergence of Taylor series problematic

Classical limit

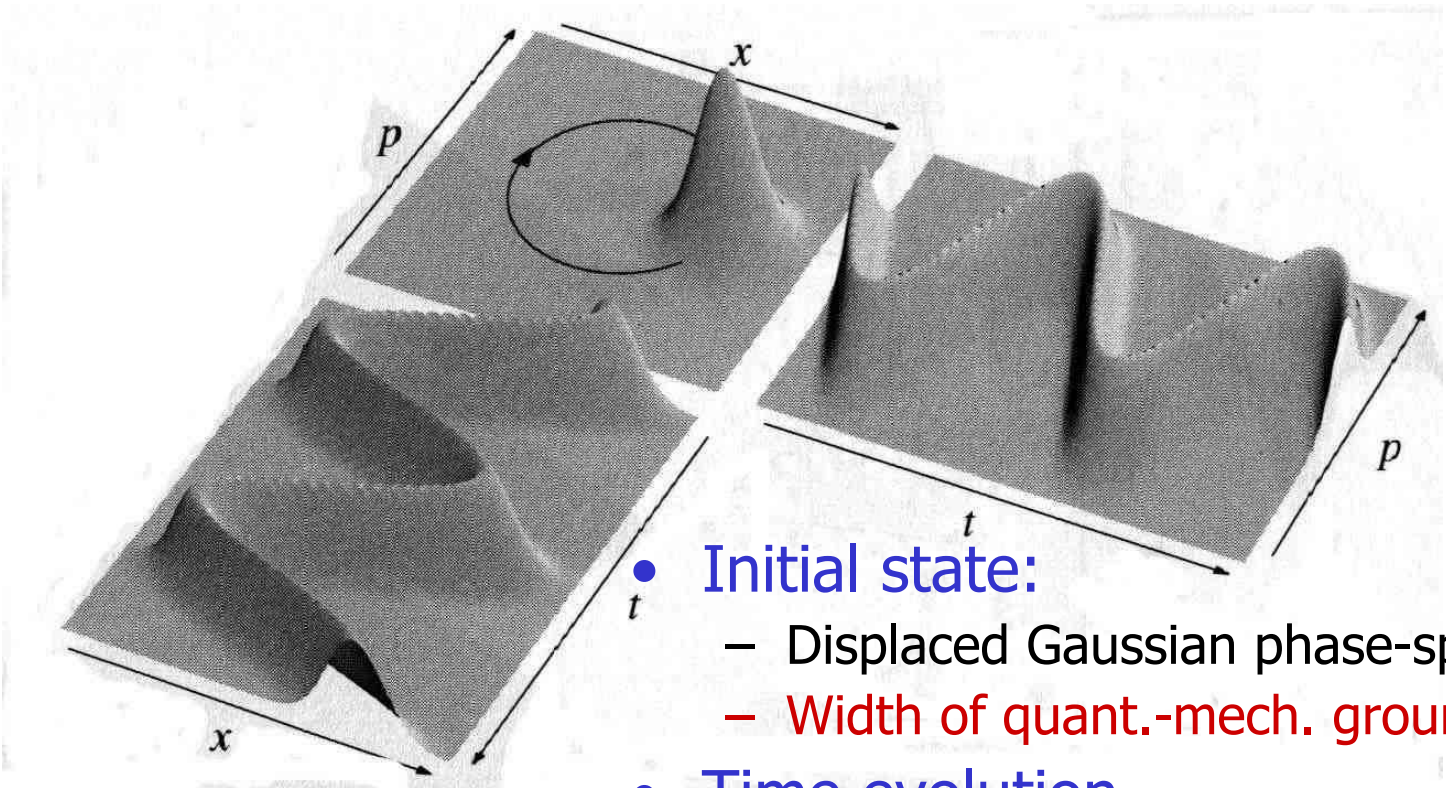
- Second order approximation (in Planck's constant)

$$\partial_t \rho_W(R,P,t) = -\{H_W(R,P), \rho_W(R,P,t)\}$$

  - Special case: exact for harmonic oscillator

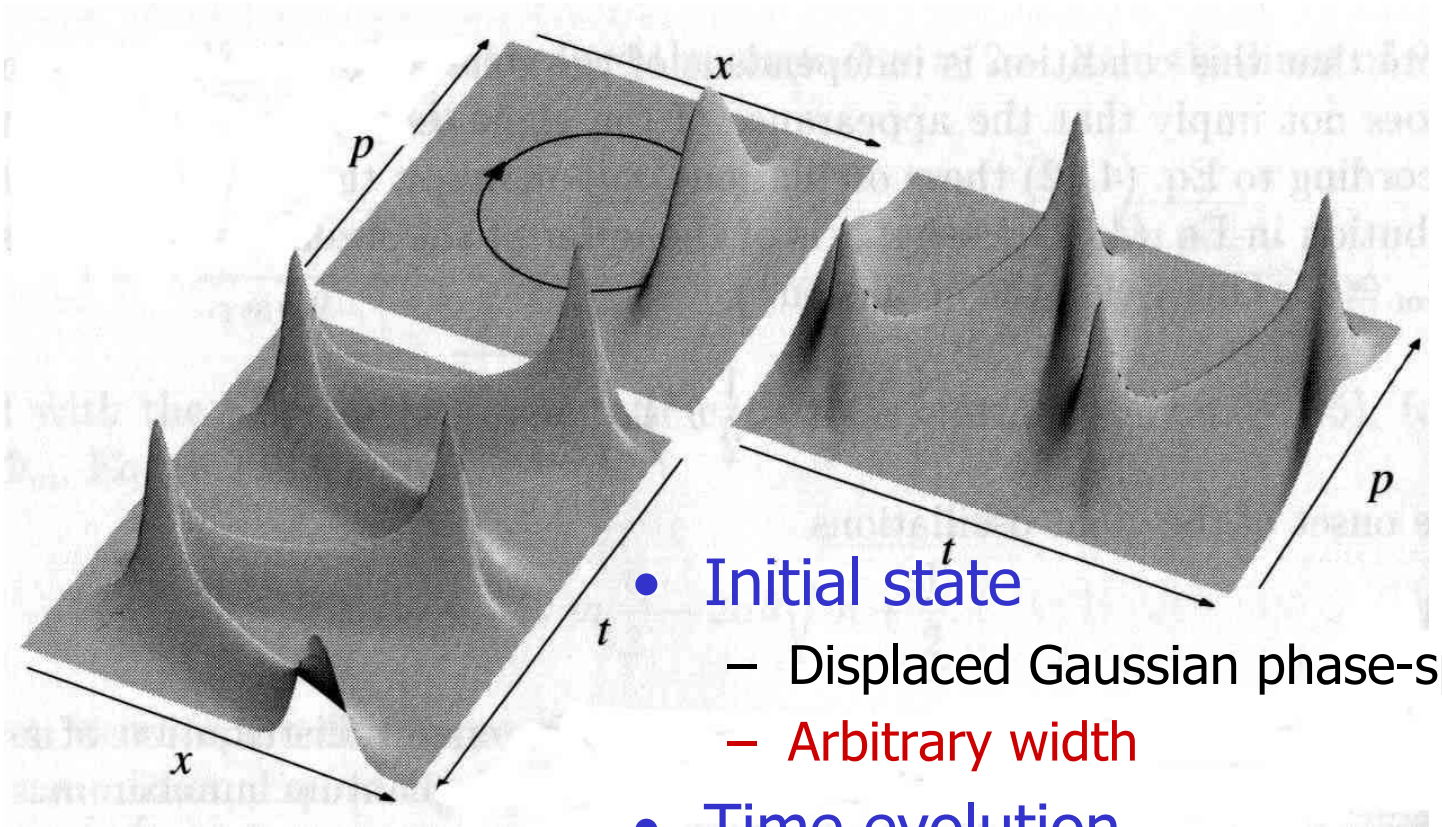
- Classical Liouville equation
  - Symplectic flow conserves phase space volume (continuity equation)
  - Motion according to Hamilton's class. equations of motion
  - „Classical and quantum dynamics coincide for harmonic oscillator"

Example: Coherent (Glauber) state



- Initial state:
  - Displaced Gaussian phase-space packet
  - Width of quant.-mech. ground state
- Time evolution
  - Center moves along classical trajectory
  - Constant width

Example: „Squeezed“ state



- Initial state
  - Displaced Gaussian phase-space packet
  - Arbitrary width
- Time evolution
  - Center moves along classical trajectory
  - Widths oscillate periodically

Guidelines for numerical work

- Representation of distribution functions
  - Particle methods (travelling basis set)
  - Finite width Gaussians instead of „delta" trajectories
  - Easy to implement in existing MD codes
- Adaptivity and control
  - Specified precision of representation
  - Adaptive control of basis size and time step
- Monte Carlo based approaches
  - Weak dependance of numerical effort on dimensionality
  - Applicability to multidimensional systems

Gaussian phasespace packets (GPPs)

- Optimal decomposition of dynamical Wigner function

$$\rho_n(R,P,t) = B_n(t)\exp\left[-\begin{pmatrix} R-R_n(t) \\ P-P_n(t) \end{pmatrix}^T \mathbf{G}_n(t) \begin{pmatrix} R-R_n(t) \\ P-P_n(t) \end{pmatrix}\right]$$

where $\mathbf{G}_n$ are positively definite matrices determining GPP shape

- Minimize global error functional for given global error

$$\xi(N;\rho_n) = \int dR \int dP \left| \rho_W(R,P) - \sum_{n=1}^{N} \rho_n(R,P) \right|^2$$

- Monte-Carlo based algorithm optimizes GPP parameters

Optimization strategy

Monte Carlo based algorithm

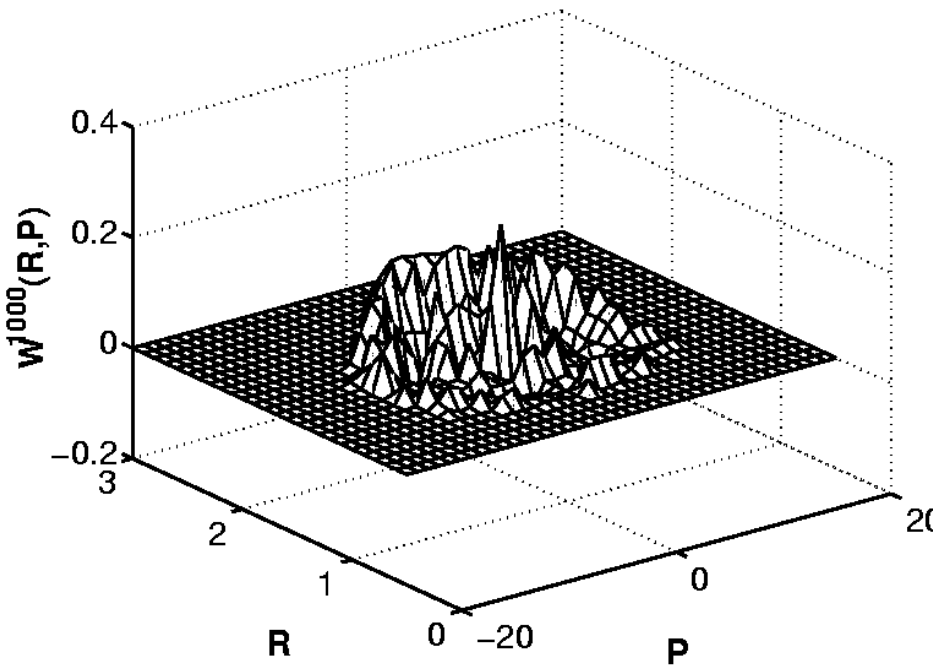
1. Randomly choose set of coord.'s where $|\rho_W(R,P)|>>0$
2. N=1: Pick initial phase space point (R_1, P_1) from this set
3. Minimization of error ξ: optimize R_i,P_i,B_i,G_i, i=1,...,N
   - Solve sparse set of linear equations to optimize B_i
   - Solve set of nonlinear equations to optimize G_i
4. If $\xi(N)>\varepsilon$ then N = N+1. Pick (R_{N+1} ,P_{N+1}) from set.
5. Redo minimization (steps 3-4) until $\xi(N)<\varepsilon$

Law of large numbers: $N \propto \sqrt{d}$

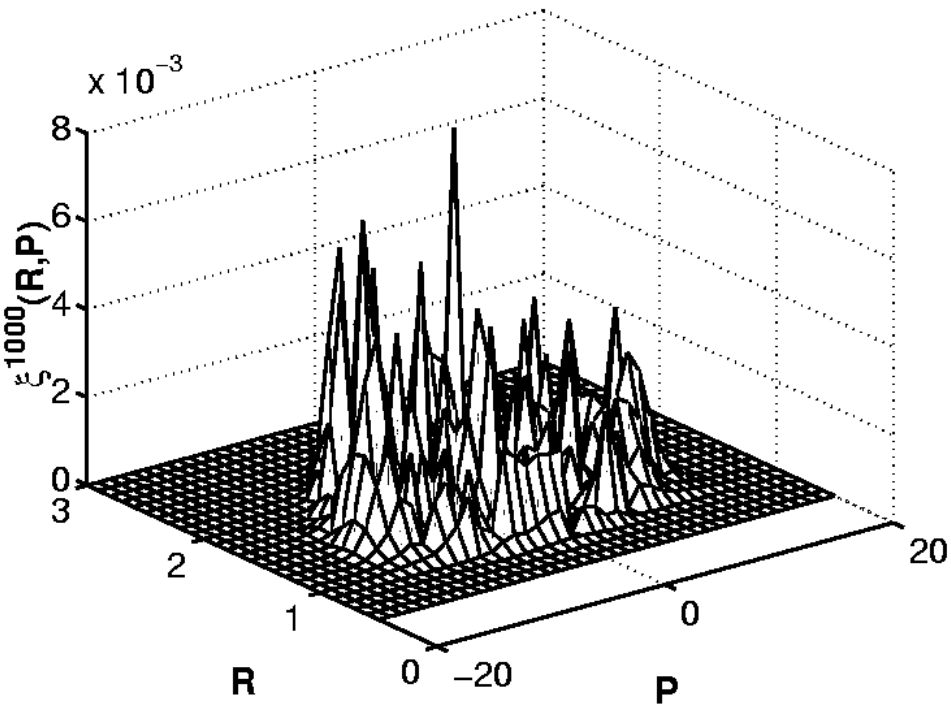
Example: Morse oscillator (v=4)

- 1000 GPP's for given global error: $\xi < \varepsilon = 0.001$

Wigner function



Local error



Classical GPP dynamics

- Basic assumptions
  1. Locally harmonic approximation of potential (LHA)
  2. Independent particle approximation (IPA)

- GPP centers follow class. trajectories in phase-space

$$\partial_t R_n = M^{-1} P_n \quad \text{and} \quad \partial_t P_n = -V^{(1)}$$

- GPP shape depends on Hessian of potential

$$\partial_t \mathbf{G}_n = \mathbf{C}\mathbf{G}_n + \mathbf{G}\mathbf{C}^T \quad \text{with} \quad \mathbf{C} = \begin{pmatrix} 0 & V^{(2)} \\ -M^{-1} & 0 \end{pmatrix}$$

see IH+BS+CS, JCP **117** (10), 4643-4650 (2002)

Explicit numerical integrator

- Strang splitting for Lie generators L = L_1 + L_2

$$\exp(iL\tau) = \exp(iL_1\tau/2)\exp(iL_2\tau)\exp(iL_1\tau/2) + O(\tau^3)$$

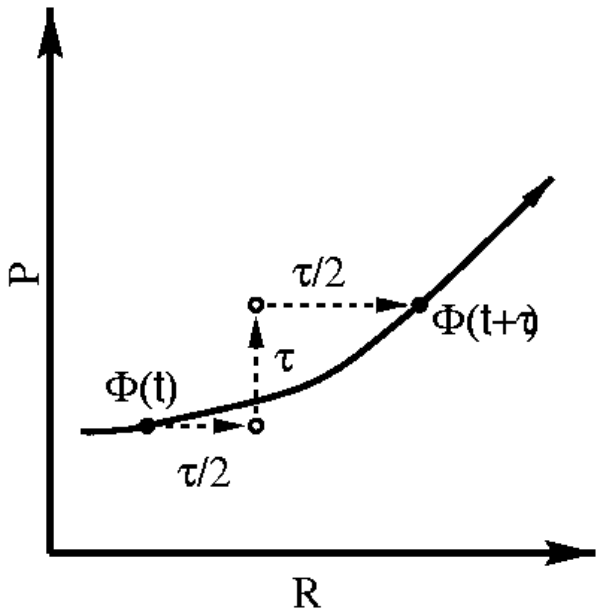
- Modified Leap frog

$$R_{1/2} = R_0 + \frac{\tau}{2} M^{-1} P_0$$

$$P_1 = P_0 - \tau V^{(1)}(R_{1/2})$$

$$\mathbf{G}_1 = \exp(\tau \mathbf{C}(R_{1/2}))\mathbf{G}_0 \exp(\tau \mathbf{C}^T(R_{1/2}))$$

$$R_1 = R_{1/2} + \frac{\tau}{2} M^{-1} P_1$$



- Quasi-conservation of energy and norm of GPP

Implicit numerical integrator

- Trapezoidal rule

$$\left(I - \frac{\tau}{2} L\right) \tilde{\rho}_W(t+\tau) = \left(I + \frac{\tau}{2} L\right) \rho_W(t)$$

Unknown:
GPP representation

Known:
Distribution function

- Error estimator (to be minimized)

$$\varepsilon_\tau = \| \tilde{\rho}_W(t+\tau) - \rho_W(t+\tau) \|$$

$\Rightarrow$ Least squares for GPP amplitudes

Adaptivity

- Adaptivity in phase-space

$$\varepsilon_\Gamma = \left\| \left(I - \frac{\tau}{2} L \right) \widetilde{\rho}_W (t+\tau) - \left(I + \frac{\tau}{2} L \right) \rho_W (t) \right\| \leq \mathrm{Tol}_\Gamma$$

Dynamic creation / annihilation of GPPs according to local error

- Adaptivity of time step

$$\tau_{\mathrm{opt}} \propto \sqrt{\frac{\mathrm{Tol}_\tau}{\varepsilon_\tau}}$$

see IH+MW, ZIB reprint 29 (2002)

Quasi-classical Liouville dynamics

Classical Liouville dynamics

with

Quantum initial conditions

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The problem

- Quantum initial conditions
  - Delocalized ground state (weak forces) **or**
  - Excited initial state (nodal structure)
- Wigner transform of initial wavefunction
  - Few analytically known cases (harmonic, Morse oscillator)
  - Grid methods limited to very low dimensionality
- Open questions ...
  - Numerical Wigner transform in high dimensionality
  - Choice of appropriate basis set ?!?

Gaussian wavepackets (GWPs)

- Optimal decomposition of initial wavefunction

$$\psi_j(R) = A_j \exp\left[-(R-R_j)^T a_j (R-R_j) + \frac{i}{\hbar} P_j^T (R-R_j) \right]$$

- Minimize error functional for given global error using minimal number of GWP basis functions

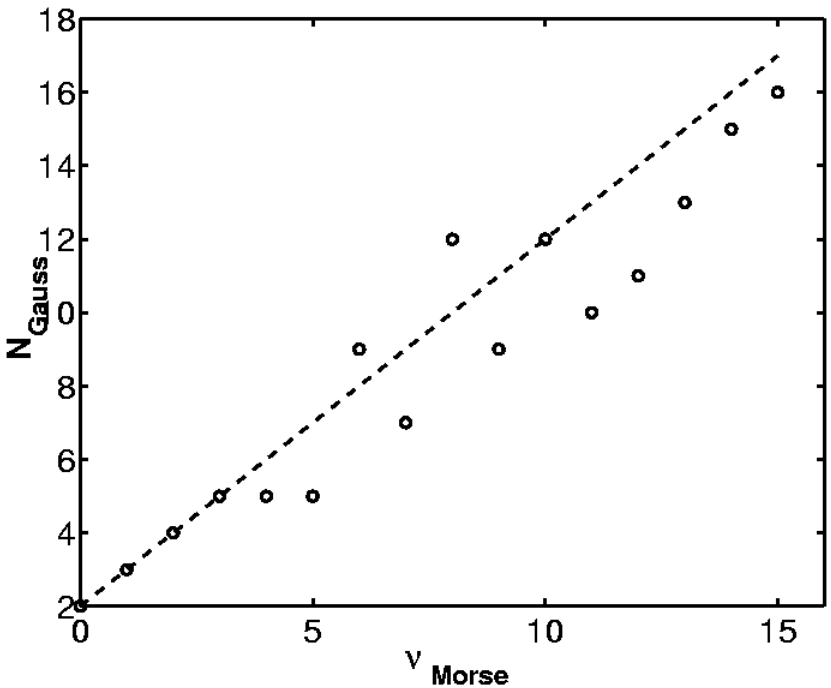
$$\Theta(N;\psi_j) = \int dR \left| \psi(R) - \sum_{j=1}^{N} \psi_j(R) \right|^2$$

- Monte Carlo based algorithm optimizes GWP parameters

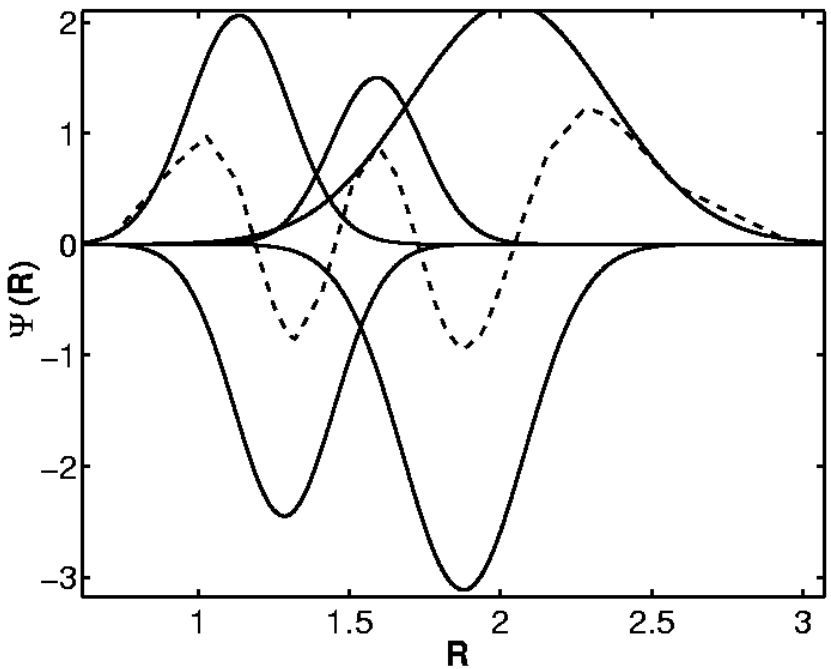
Example: Morse oscillator (H_2 vib)

- For given global error: $\Theta < \varepsilon = 0.001$

Number of GWPs



Example: v=4

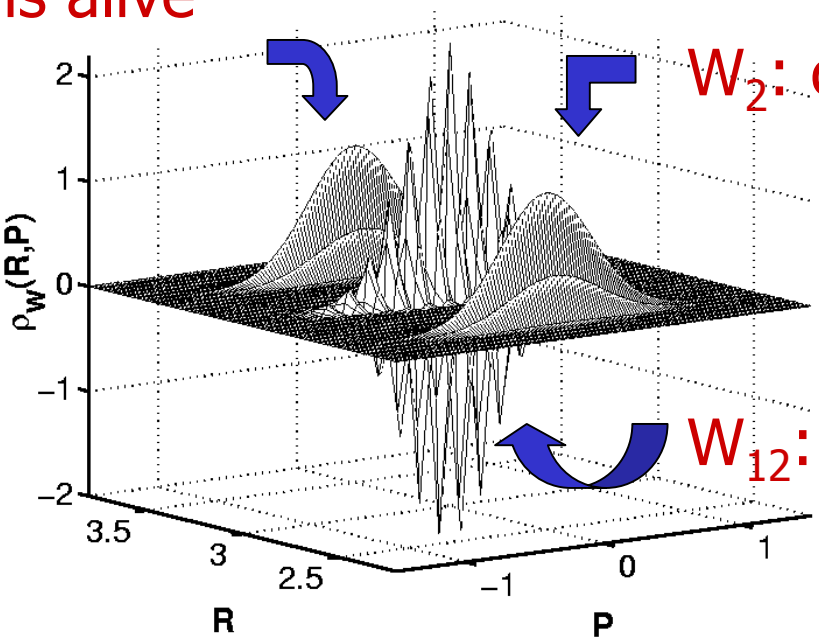


Wigner transform of superposition

- Analytical result for superpositions of GWPs

$$\rho_W(R,P) = \sum_j W_j(R,P) + \sum_{j<k} W_{jk}(R,P) + O(\varepsilon)$$

W_1: cat is alive



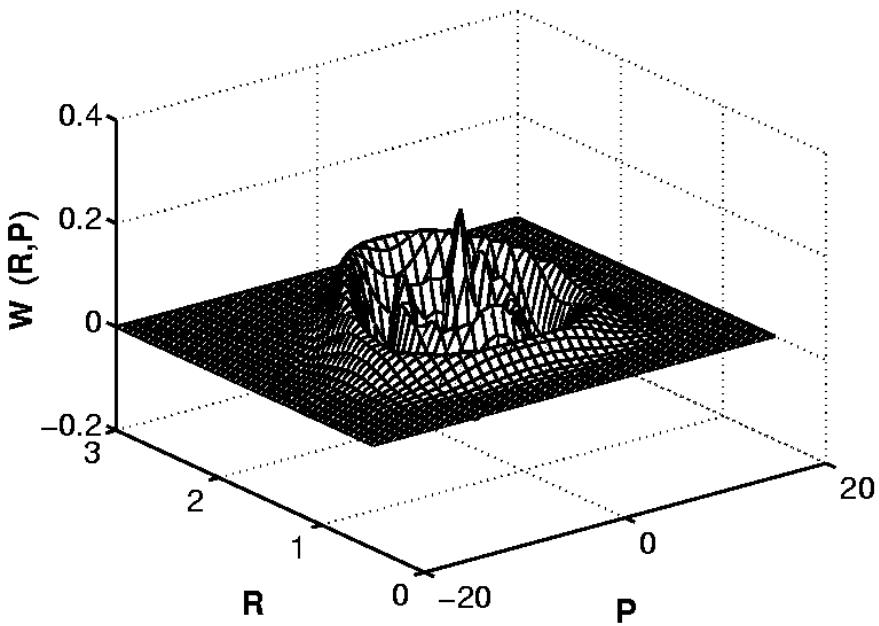
W_2: cat is dead

W_{12}: interference state

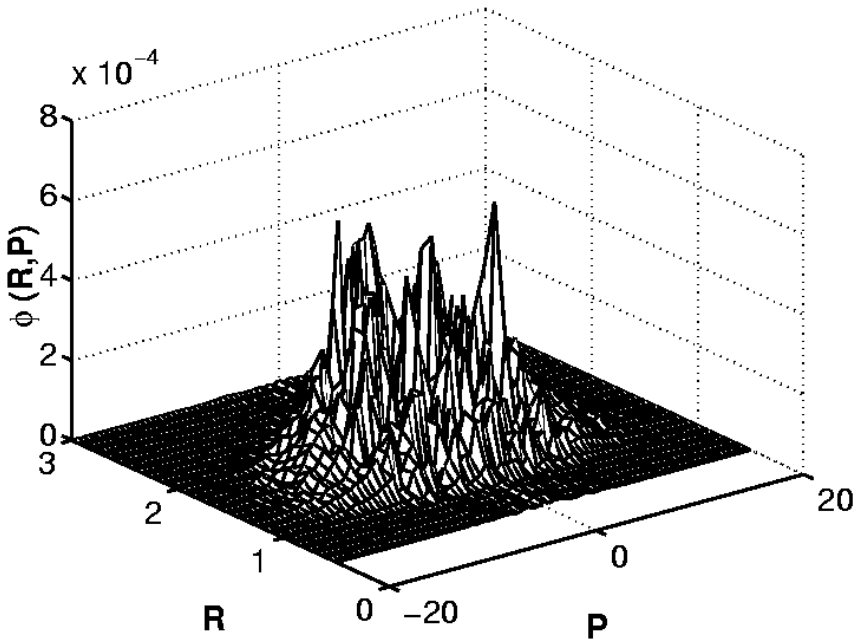
Example: Morse oscillator: v=4

- 5 Gaussian packets $\Rightarrow$ 15 terms in double sum

Wigner function

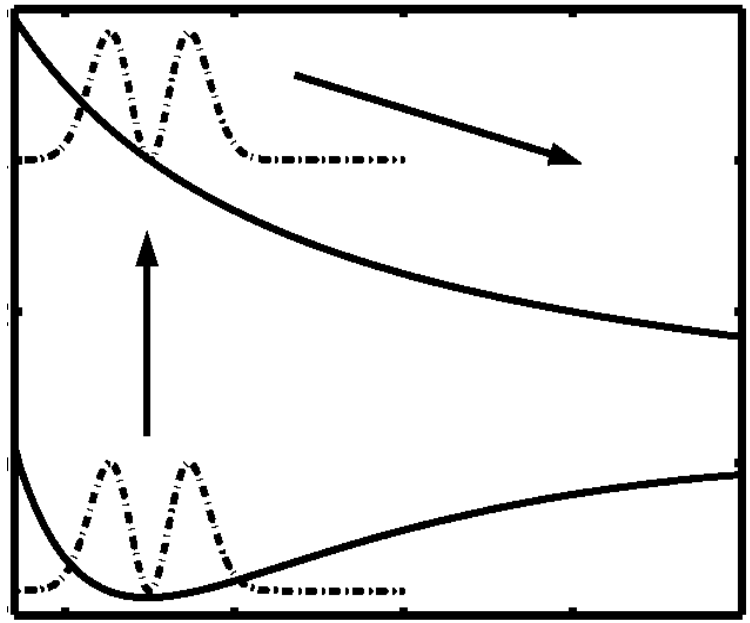


Local error



Example: Photodissociation

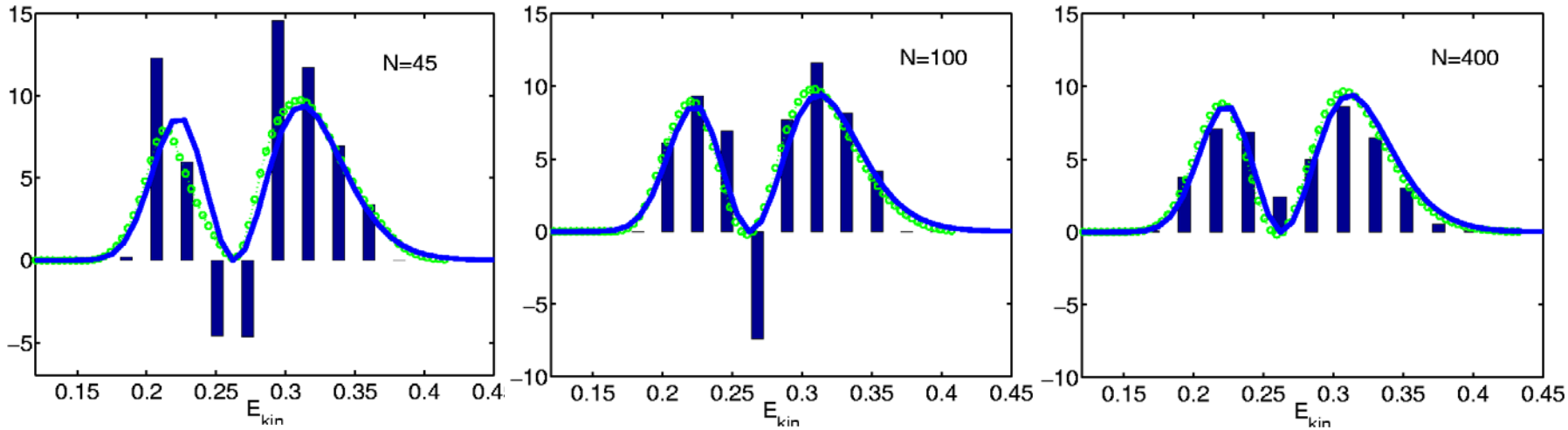
- Ground state (initial)
  - Shallow potential and/or
  - Vibrational pre-excitation
- Excited state dynamics
  - Instantaneous excitation
  - Direct fragment separation



- Reflection principle
  - Kinetic energy of fragments reflects initial density
- Classical Liouville dynamics with quantum initial conditions

Example: Photodissociation

Kinetic energy distribution after dissociation



- Deficiency of classical trajectories (bars)
- Improvement by Gaussian phase-space packets (circles)

⇒ Importance of dense sampling of phase space

Summary

- Representation of Wigner distribution function
  - Basis of Gaussian phase-space packets (GPPs)
  - Monte-Carlo algorithm: Optimal GPP representation
- Classical Liouville dynamics
  - Explicit Leap-Frog algorithm for GPP dynamics
  - Implicit trapezoidal rule: Time and space adaptivity
- Quantum initial condition
  - Use of Gaussian wave packets (GWPs)
  - Monte-Carlo algorithm: Optimal GWP representation
- Classical dynamics with quantum initial conditions

Outlook

- Quantum-classical Liouville dynamics JCP **117** 11075 (2002)
  - Nonadiabatic transitions in multistate Liouville dynamics
  - Surface-hopping Gaussian phase-space packets
- Photoinduced dynamics JCP **115**, 5733 (2001)
  - Intense, short pulses: beyond perturbation theory
  - Nonadiabatic transitions between „dressed states" (Floquet)
- Control of molecular dynamics ?!?
  - Error control through adaptive algorithms
  - Forward-backward propagation in optimal control theory

Further reading

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  Phys. Rep. **106**(3), 121-167 (1984)
- W. Schleich: Quantum optics in phase space
  Wiley-VCH, Berlin (2001)
- J. Ma, D. Hsu, and J. E. Straub: Approximate solution of the classical Liouville equation using Gaussian phase packets
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- I. Horenko and M. Weiser : Adaptive integration of multidimesional molecular dynamics
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