Computing expectation values for molecular quantum dynamics

Susanna Röblitz

joint work with C. Lasser, FU Berlin

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Zuse Institute Berlin

DFG Research Center

Matheon

Schrödinger equation

$$\begin{aligned} i\varepsilon\partial_t\psi(t,q) &= \left(-\frac{\varepsilon^2}{2}\Delta_q + V(q)\right)\psi(t,q), \\ \psi(0,q) &= \psi_0(q) \end{aligned}$$

$$\varepsilon = \sqrt{1/\text{average nuclear mass}} = 0.001, \ldots, 0.1$$

$V(q)$ solves the electron eigenvalue problem

$$\forall q \in \mathbb{R}^d : \quad H_{\mathrm{el}}(q)\chi(q,x) = V(q)\chi(q,x)$$

properties of the solution: high-dimensional, highly oscillatory

Initial data

$\psi_0 \in L^2(\mathbb{R}^d, \mathbb{C})$ mit $\|\psi_0\|_{L^2} = 1$.

ψ_0 results from excitation of the ground state

$$\left(-\frac{\varepsilon^2}{2}\Delta_q + V_0(q)\right)\varphi_0(q) = E_0\varphi_0(q)$$

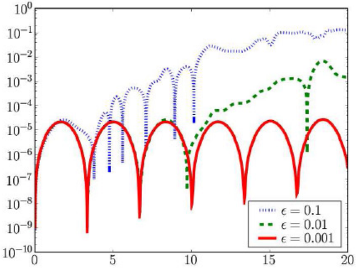
Example: Gaussian wave function

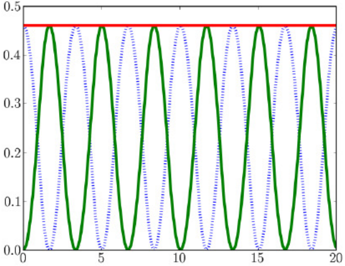
$$\psi_0(q) = g_0(q) = (\pi\varepsilon)^{-d/4}\exp(-\tfrac{1}{2\varepsilon}|q-q_0|^2 + \tfrac{i}{\varepsilon}p_0 \cdot |q-q_0|)$$

Motivation

[E. Faou, V. Gradinaru, C. Lubich, *SIAM J. Sci. Comput.*, 2009]

Approximation by Hagedorn wave packets





Expectation values

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$$\langle \mathrm{Op}(a)\psi, \psi \rangle_{L^2} = \int_{\mathbb{R}^d} (\mathrm{Op}(a)\psi)(q)\,\overline{\psi}(q)\mathrm{d}q,$$

$\mathrm{Op}(a)$ is obtained as Weyl quantization of smooth functions a

	$a(q,p)$	$(\mathrm{Op}(a)\psi)(q)$
position	q	$q\psi$
momentum	p	$-i\varepsilon\nabla_q\psi$
potential energy	$V(q)$	$V\psi$
kinetic energy	$\frac{1}{2}\lvert p\rvert^2$	$-\frac{\varepsilon^2}{2}\Delta_q\psi$

Egorov theorem

For the solution of the Schrödinger equation, $\psi(t)$, and Weyl quantized operators $\mathrm{Op}(a)$:

$$\left\langle \mathrm{Op}(a)\psi(t), \psi(t) \right\rangle_{L^2} = \left\langle \mathrm{Op}(a \circ \Phi^t)\psi_0, \psi_0 \right\rangle_{L^2} + O(\varepsilon^2 \partial_q^3 V)$$

with classical Hamiltonian flow $\Phi^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$

$$\dot{q} = p, \qquad \dot{p} = -\nabla_q V(q)$$

Conservation of total energy $h(q,p) = \frac{1}{2}|p|^2 + V(q)$:

$$\left\langle \mathrm{Op}(h)\psi(t), \psi(t) \right\rangle_{L^2} = \left\langle \mathrm{Op}(h \circ \Phi^t)\psi_0, \psi_0 \right\rangle_{L^2}$$

Wigner function

Expectation values for Weyl quantized operators $\mathrm{Op}(a)$:

$$\langle \mathrm{Op}(a)\psi, \psi \rangle_{L^2} = \int_{\mathbb{R}^{2d}} W(\psi)(q,p) a(q,p) \mathrm{d}q \mathrm{d}p$$

$W(\psi) : \mathbb{R}^{2d} \to \mathbb{R}$, continuous, real-valued

$$\int_{\mathbb{R}^{2d}} W(\psi)(q,p) \mathrm{d}q \mathrm{d}p = \|\psi\|_{L^2}^2$$

$$W(\psi)(q,p) \quad = \quad (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^d} \mathrm{e}^{iy\cdot p/\varepsilon} \psi(q - \tfrac{1}{2}y) \overline{\psi}(q + \tfrac{1}{2}y) \mathrm{d}y$$

Example:

$$W(g_0)(q,p) = (\pi\varepsilon)^{-d} \exp(-\tfrac{1}{\varepsilon} |(q,p) - (q_0,p_0)|^2)$$

Particle method

$$\begin{aligned}\langle \mathrm{Op}_\varepsilon(a)\psi^\varepsilon(t), \psi^\varepsilon(t)\rangle_{L^2} &= \int_{\mathbb{R}^{2d}} (a \circ \Phi^t)(z)\, W(\psi_0^\varepsilon)(z)\, \mathrm{d}z + O(\varepsilon^2) \\ &= \int_{\mathbb{R}^{2d}} (a \circ \Phi^t)(z)\, \frac{W(\psi_0^\varepsilon)(z)}{g(z)} g(z)\, \mathrm{d}z + O(\varepsilon^2) \\ &\approx \frac{1}{N} \sum_{j=1}^{N} a(\Phi^t(z_j)) \frac{W(\psi_0^\varepsilon)(z_j)}{g(z_j)}\end{aligned}$$

1. initial sampling of the importance sampling function $g(z)$
2. classical transport of sampling points

$$\dot{q} = p, \quad \dot{p} = -\nabla_q V(q)$$

3. final (weighted) summation over the propagated sampling points

Error propagation

perturbation

$$\langle \mathrm{Op}(a)\psi_0^\varepsilon, \psi_0^\varepsilon \rangle_{L^2} \quad \longrightarrow \quad \langle \mathrm{Op}(\tilde{a})\psi_0^\varepsilon, \psi_0^\varepsilon \rangle_{L^2}$$

but

$$\left| \langle \mathrm{Op}_\varepsilon(a)\psi^\varepsilon(t), \psi^\varepsilon(t) \rangle_{L^2} - \left\langle \mathrm{Op}_\varepsilon(\tilde{a} \circ \Phi^t)\psi_0^\varepsilon, \psi_0^\varepsilon \right\rangle_{L^2} \right| \leq C_\varepsilon \varepsilon^2 + \|\mathrm{Op}_\varepsilon(\delta_t)\|.$$

where δ_t is the mean deviation of $\tilde{a}$ from a along the classical flow

$$\delta_t(q,p) = \tfrac{1}{t} \int_0^t (\tilde{a} - a) \circ \Phi^s(q,p) \mathrm{d}s.$$

$\rightarrow$ asymptotic accuracy not altered by small initial sampling error

1. Initial sampling

Initial data

A. Single Gaussian wave packet

$$\psi_0^\varepsilon(q) = g_0^\varepsilon(q) = (\pi\varepsilon)^{-1/2} \exp(-\tfrac{1}{2\varepsilon}|q - q_0|^2),$$

$$z_0 = (q_0, p_0) = (1, 0, 0, 0)^T$$

B. Superposition of two Gaussian wave packets

$$\psi_0^\varepsilon = \frac{1}{\sqrt{2}}(g_1^\varepsilon + g_2^\varepsilon), \qquad z_1 = (1, 0, 0, 0)^T, \qquad z_2 = -z_1$$

$$W((g_1^\varepsilon + g_2^\varepsilon)/\sqrt{2})(z) = (W(g_1^\varepsilon)(z) + W(g_2^\varepsilon)(z))/2 + C(z)$$

C. Numerically computed laser excitation on a 1024×512 grid, $\varepsilon = 0.01$

Monte Carlo sampling

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- Conventional Monte Carlo

$$\lim_{N\to\infty} \mathbb{P}\left(\left| \tfrac{1}{N}\sum_{j=1}^{N} (a\circ\Phi^t)(x_j) - \langle a\circ\Phi^t\rangle_{\psi_0^\varepsilon} \right| \le \frac{c\,\sigma(a\circ\Phi^t)}{\sqrt{N}} \right) = \frac{1}{\sqrt{2\pi}}\int_{-c}^{c} \mathrm{e}^{-t^2/2}\mathrm{d}t,$$

- Quasi Monte Carlo

$$\left| \frac{1}{N}\sum_{j=1}^{N} f(x_j) - \int_{\mathbb{R}^{2d}} f(z)W(\psi_0^\varepsilon)(z)\mathrm{d}z \right| \le \mathrm{Var}(f)\, D_{\mathcal{N}}^{*}(x_1,\dots,x_N) \le CN^{-1}(\log N)^{3d}$$

tranformation of well-known sequences (Halton, Sobol', ...) from the unit cube $[0,1)^{2d}$ to $\mathbb{R}^{2d}$

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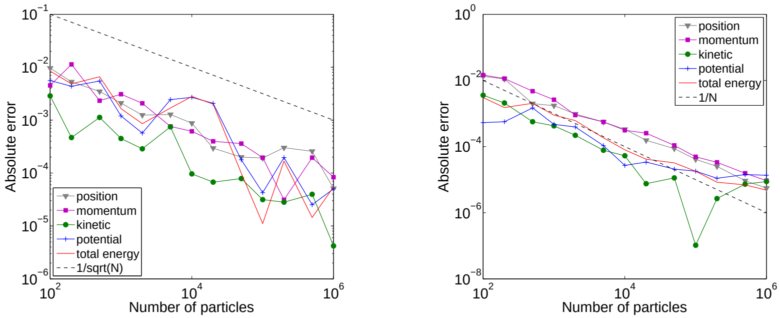
Superposition of two-dimensional Gaussian wave packets, $\varepsilon = 0.1$



(a) Conventional Monte Carlo (b) Quasi-Monte Carlo

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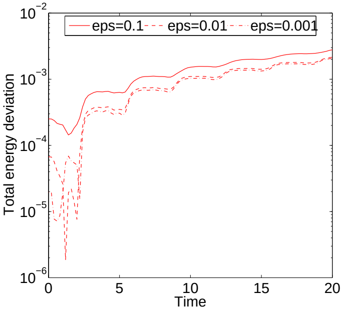
2. Classical transport

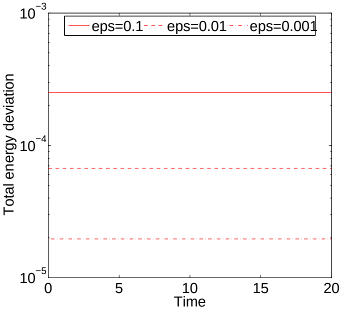
Energy conservation

$$\dot{q} = p, \quad \dot{p} = -\nabla_q V(q), \qquad V(q) = 2 - \cos(q_1) - \cos(q_2)$$

Single Gaussian wave packet, $N = 10^4$



(c) Non-symplectic 4th order Runge-Kutta method



(d) 4th order symplectic partitioned Runge-Kutta method

3. Final evaluation

Phase space summation

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B. Superposition of two Gaussian wave packets

$$\langle a \circ \Phi^t \rangle_{\psi_0^\varepsilon} \approx \frac{1}{2M}\Big(\sum_{j=1}^{N_1} (a \circ \Phi^t)(x_j(z_1)) + \sum_{j=1}^{N_2} (a \circ \Phi^t)(x_j(z_2))$$

$$+ \sum_{j=1}^{N_3} (a \circ \Phi^t)(x_j(z_+)) \cdot \tilde{c}(x_j(z_+)) \Big)$$

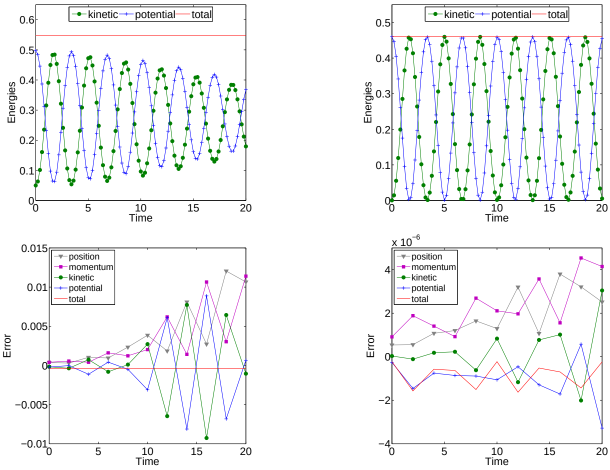
$$M = N_1 + N_2 + \sum_{j=1}^{N_3} \tilde{c}(x_j(z_+))$$

C. numerically computed laser excitation

$$\langle a \circ \Phi^t \rangle_{\psi_0^\varepsilon} \approx \frac{1}{M} \sum_{j=1}^{N} (a \circ \Phi^t)(x_j) W(\psi_0^\varepsilon)(x_j), \quad M = \sum_{j=1}^{N} W(\psi_0^\varepsilon)(x_j)$$

Results

Single Gaussian wave packet

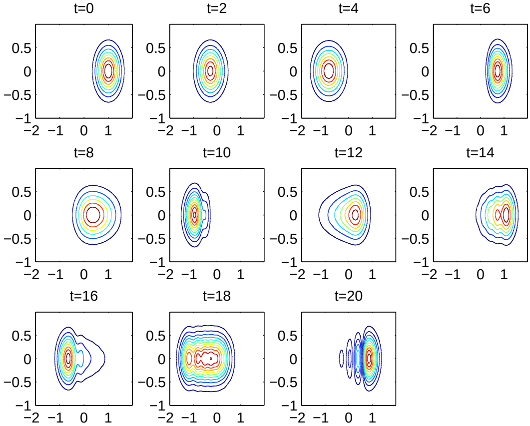


$\varepsilon = 0.1,\ N = 10^4$ $\quad$ $\varepsilon = 0.001,\ N = 10^6$

Reference solution

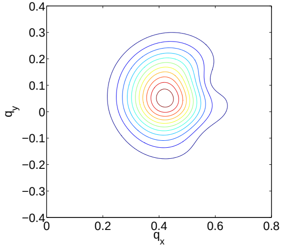
Strang splitting with Fourier differencing

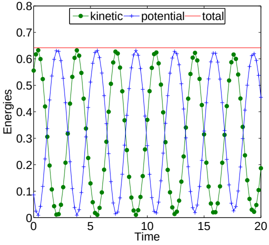
[Jahnke, Lubich, 2000]

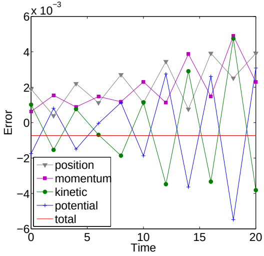


Grid based initial data

$\varepsilon = 0.01, \; N = 10^3$





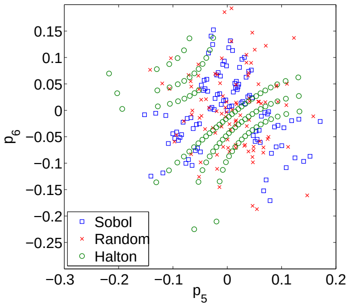


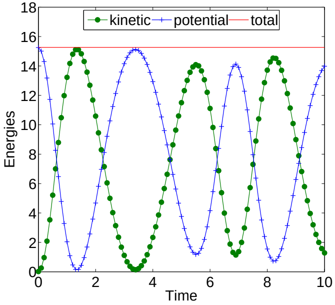
Computation of $W(\psi_0^\varepsilon)(q,p)$: quasi Monte Carlo with $n = 500$ and bicubic interpolation

The Henon-Heiles potential

$$V(q) = \sum_{j=1}^{6} \tfrac{1}{2} q_j^2 + \sum_{j=1}^{5} \sigma_* (q_j q_{j+1}^2 - \tfrac{1}{3} q_j^3) + \tfrac{1}{16} \sigma_*^2 (q_j^2 + q_{j+1}^2)^2$$

$$\psi_0^\varepsilon(q) = (\pi\varepsilon)^{-3/2} \exp(-\tfrac{1}{2\varepsilon}|q-q_0|^2),\ q_0 = (2,2,2,2,2,2)^T,\ \sigma_* = 1/\sqrt{80}$$





$\varepsilon = 0.01,\ N = 10^2$, accuracy of initial sampling: 10^{-3}

Overall computing times

MATLAB 7.5 on a 2.2 GHz AMD Opteron Dual Core 875 Processor

	A ($\varepsilon = 0.001$)	B ($\varepsilon = 0.1$)	C ($\varepsilon = 0.01$)
$N = 3 \cdot 10^3$	16.4 sec	15.9 sec	38.8 sec
$N = 3 \cdot 10^4$	2 min 45 sec	2 min 44 sec	6 min 39 sec
$N = 3 \cdot 10^5$	31 min 16 sec	31 min	64 min

Henon-Heiles potential ($N = 10^2$): 2.5 sec

Strang reference solution (2048×1024): 2h 47 min

Conclusion

- Summary
  - particle method as an efficient tool for computing expectation values in high dimensions
  - 2nd order accuracy with respect to the semiclassical parameter
  - computing time scales linearly with the number of sampling points
  - no curse of dimensionality
- open questions
  - long time propagation
  - adaptive sampling

Finally

Thank you for your attention!

Further information

C. Lasser, S. Röblitz: Computing expectation values for molecular quantum dynamics. *Submitted*.

2 open positions:

- parameter estimation for large complex systems, e. g. reaction networks
- qualification:
  - Bachelor or Master/Diploma/PhD in Mathematics
  - knowledge in numerical mathematics (ODEs,Newton methods)