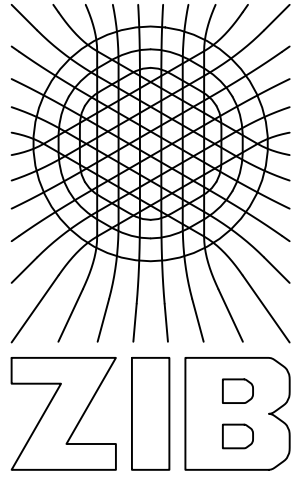
Computing expectation values for molecular quantum dynamics



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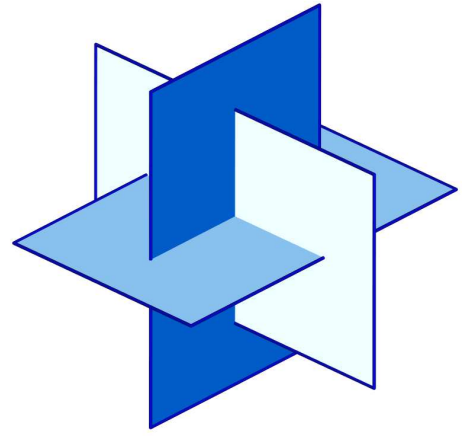


Moleküle im Rechner

February 16, 2010

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

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

properties of the solution: high-dimensional, highly oscillatory

Initial data

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

ψ_0 results from excitation of the ground state

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

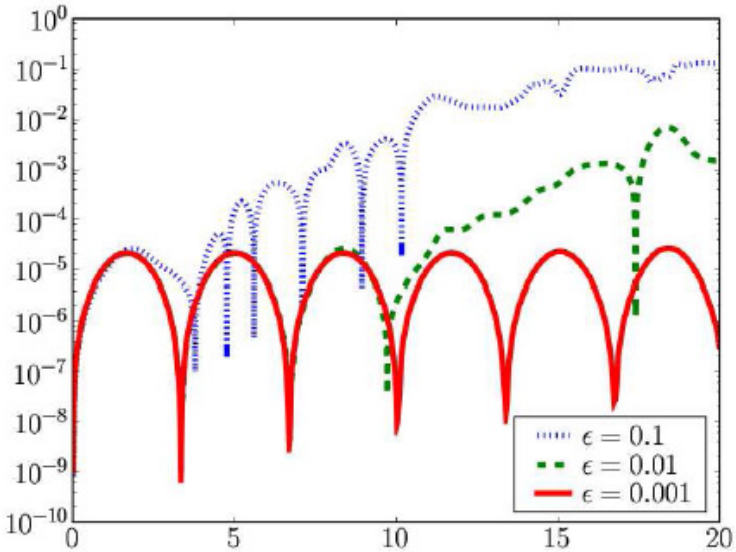
Example: Gaussian wave function

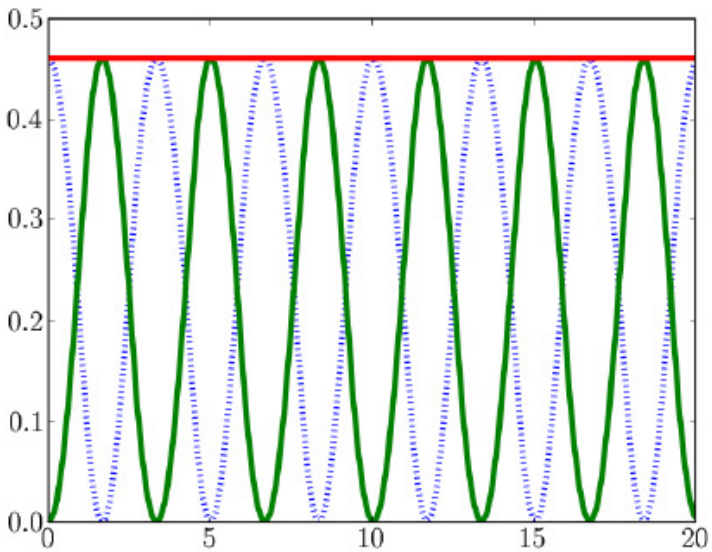
$$\psi_0(q) = g_0(q) = (\pi\varepsilon)^{-d/4}\exp(-\tfrac{1}{2\varepsilon}|q-q_0|^2 + \tfrac{i}{\varepsilon}p_0\cdot|q-q_0|)$$

Motivation

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

Approximation by Hagedorn wave packets





Expectation values

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

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

$$(\mathrm{Op}_\varepsilon(a)\psi)(q) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} a(\tfrac{1}{2}(q+y), p) \mathrm{e}^{ip\cdot(q-y)/\varepsilon} \psi(y) \mathrm{d}y \mathrm{d}p$$

	$a(q,p)$	$(\mathrm{Op}(a)\psi)(q)$
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

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

Wigner function

Properties:

$$\begin{aligned}\int_{\mathbb{R}^d} W(\psi)(q,p)\mathrm{d}p &= |\psi(q)|^2\\ \int_{\mathbb{R}^d} W(\psi)(q,p)\mathrm{d}q &= |(\mathcal{F}\psi)(p)|^2_{L^2}\\ \int_{\mathbb{R}^{2d}} W(\psi)(q,p)\mathrm{d}q\mathrm{d}p &= \|\psi\|^2_{L^2}\end{aligned}$$

$W(\psi)$ can take negative values:

$$W(\psi)(0,0) = -(\varepsilon\pi)^{-d}\|\psi\|^2_{L^2} \quad \text{for} \quad \psi(q) = -\psi(-q)$$

Example: Gaussians remain Gaussians

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

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 propagated sampling point

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

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

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

1. Initial sampling

Initial data

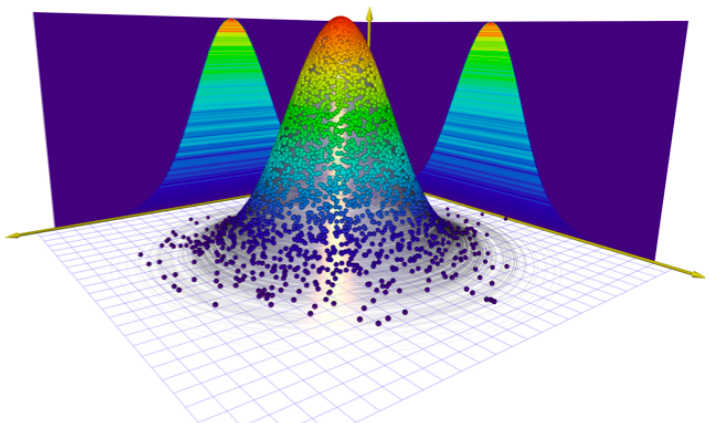
MATHEON ZIB

A. **Single Gaussian wave packet**

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

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

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



$$x_j \sim W(g_0)(z)$$

$$\langle a \circ \Phi^t \rangle_{\psi_0^\varepsilon} := \int_{\mathbb{R}^{2d}} (a \circ \Phi^t)(z) W(\psi_0^\varepsilon)(z)\, \mathrm{d}z \;\approx\; \frac{1}{N} \sum_{j=1}^{N} (a \circ \Phi^t)(x_j)$$

Initial data

MATHEON ZIB

B. **Superposition of two Gaussian wave packets**

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

$$W\left(\frac{1}{\sqrt{2}}(g_1^\varepsilon + g_2^\varepsilon)\right)(z) = \frac{1}{2}(W(g_1^\varepsilon)(z) + W(g_2^\varepsilon)(z)) + C(z)$$

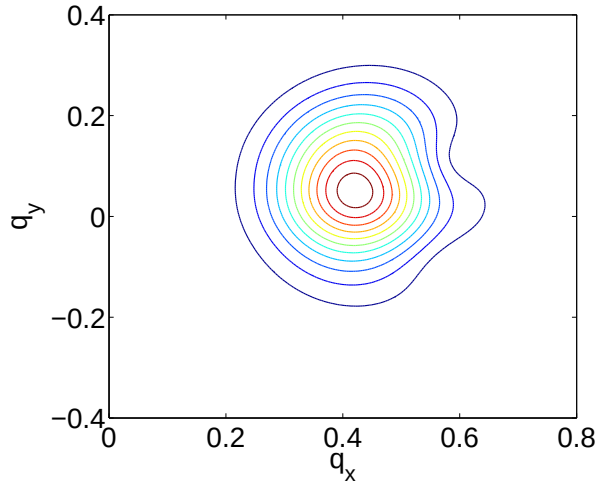
$$C(z) = (\pi\varepsilon)^{-d}\exp(-\frac{1}{\varepsilon}|z - z_+|^2)\cdot\cos(\frac{1}{\varepsilon}p_+ \cdot q_- - \frac{1}{\varepsilon}(z - z_+) \wedge z_-)$$

$$x_i \sim W(g_1)(z), \quad x_j \sim W(g_2)(z), \quad x_k \sim W(g_{12})(z)$$

$$\langle a\circ\Phi^t\rangle_{\psi_0^\varepsilon} \approx \frac{\sum_{i=1}^N (a\circ\Phi^t)(x_i) + \sum_{j=1}^N (a\circ\Phi^t)(x_j) + 2\sum_{k=1}^N (a\circ\Phi^t)(x_k)c(x_k)}{2(N + \sum_{k=1}^N c(x_k))}$$

Initial data

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



$$\langle a \circ \Phi^t \rangle_{\psi_0^\varepsilon} \approx \frac{1}{N} \sum_{j=1}^{N} (a \circ \Phi^t)(x_j) \frac{W(\psi_0^\varepsilon)(x_j)}{g(x_j)} \quad \text{with } x_j \sim g(z)$$

$$W(\psi_0^\varepsilon)(z) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^d} \mathrm{e}^{iy\cdot p/\varepsilon} \psi(q - \tfrac{1}{2}y) \overline{\psi}(q + \tfrac{1}{2}y) \mathrm{d}y \approx \frac{1}{M} \sum_{k=1}^{M} \frac{\Re I(q_k)}{h(q_k)}$$

Monte Carlo sampling

$f \equiv a \circ \Phi^t$

- Conventional Monte Carlo

$$\lim_{N\to\infty} \mathbb{P}\left(\left| \frac{1}{N} \sum_{j=1}^{N} f(x_j) - \int_{\mathbb{R}^{2d}} f(z) W(\psi_0^\varepsilon)(z) \mathrm{d}z \right| \leq \frac{c\,\sigma(f)}{\sqrt{N}} \right)$$
$$= \frac{1}{\sqrt{2\pi}} \int_{-c}^{c} \mathrm{e}^{-t^2/2} \mathrm{d}t,$$

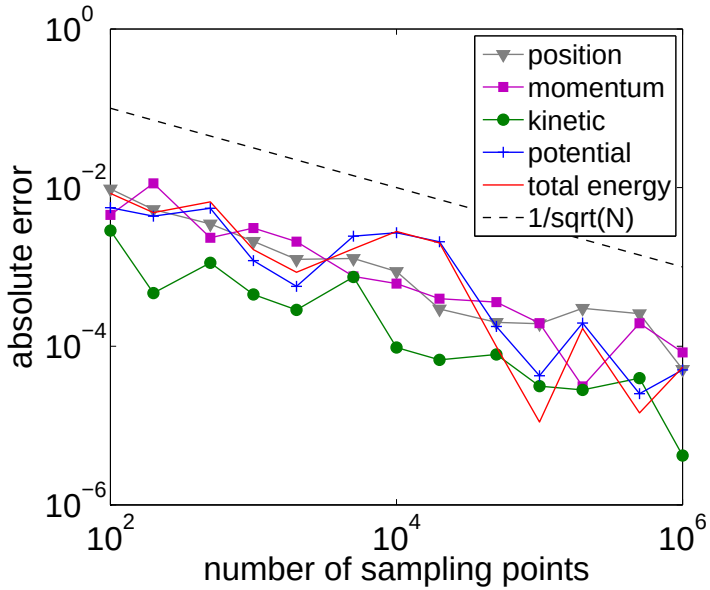
- Quasi Monte Carlo

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

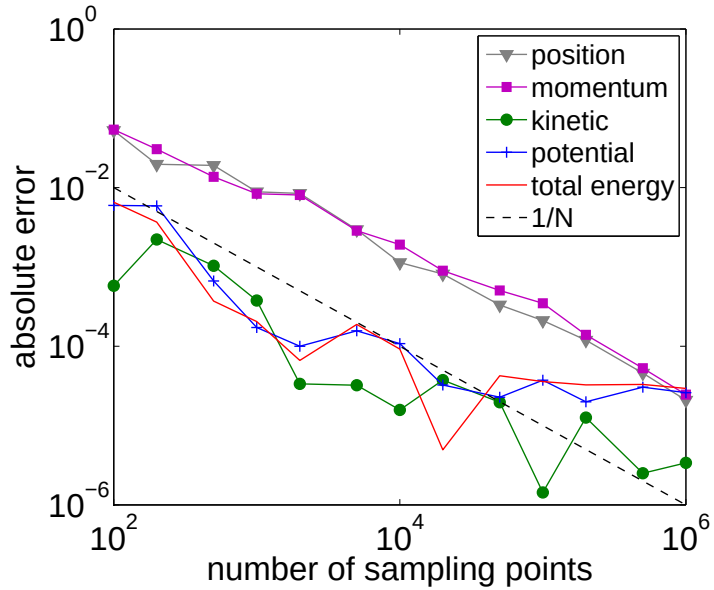
tranformation of well-known sequences (Halton, Sobol', ...) from the unit cube $[0,1)^{2d}$ to $\mathbb{R}^{2d}$

Convergence

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



(a) Conventional Monte Carlo



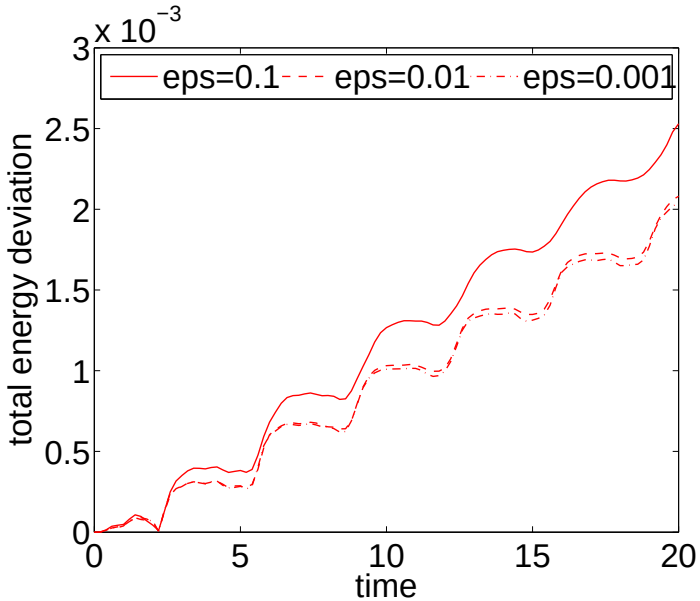
(b) Quasi-Monte Carlo

2. Classical transport

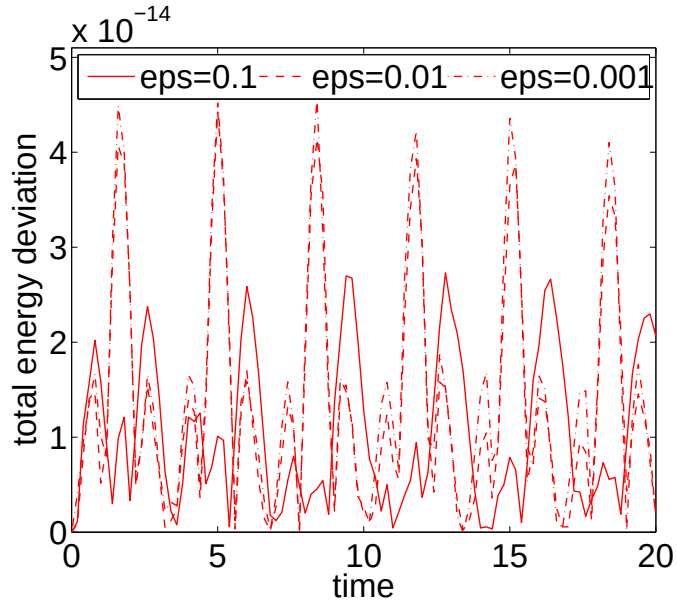
Energy conservation

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

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



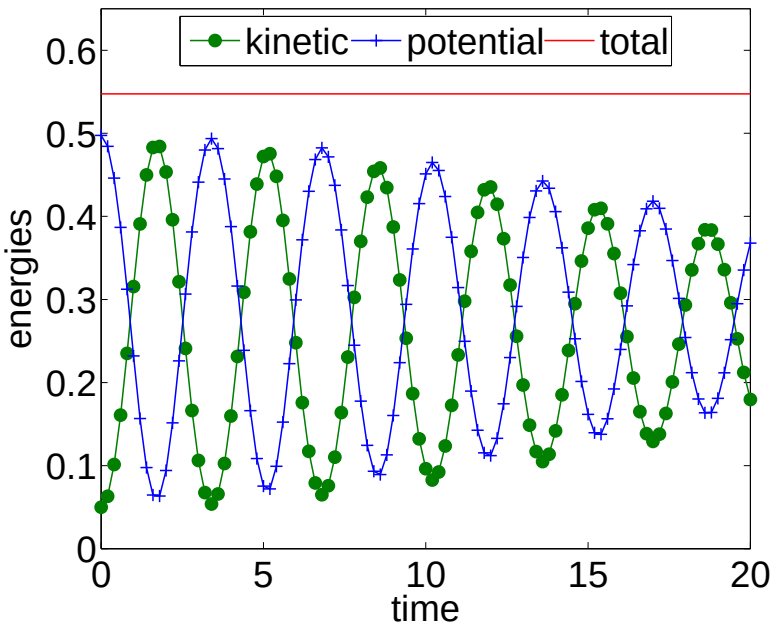
(c) Non-symplectic 4th order Runge-Kutta method



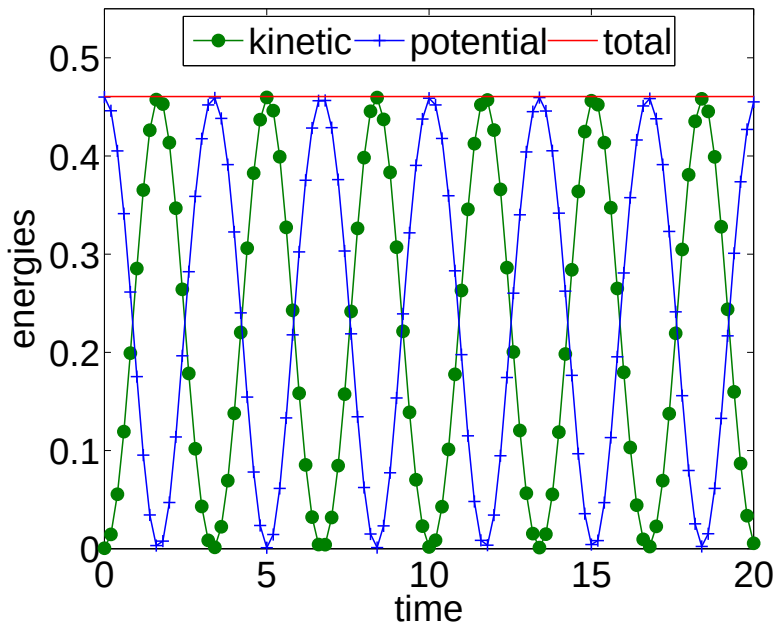
(d) 4th order symplectic partitioned Runge-Kutta method

3. Final evaluation and results

A. Single Gaussian wave packet



$\varepsilon = 0.1,\ N = 10^4$

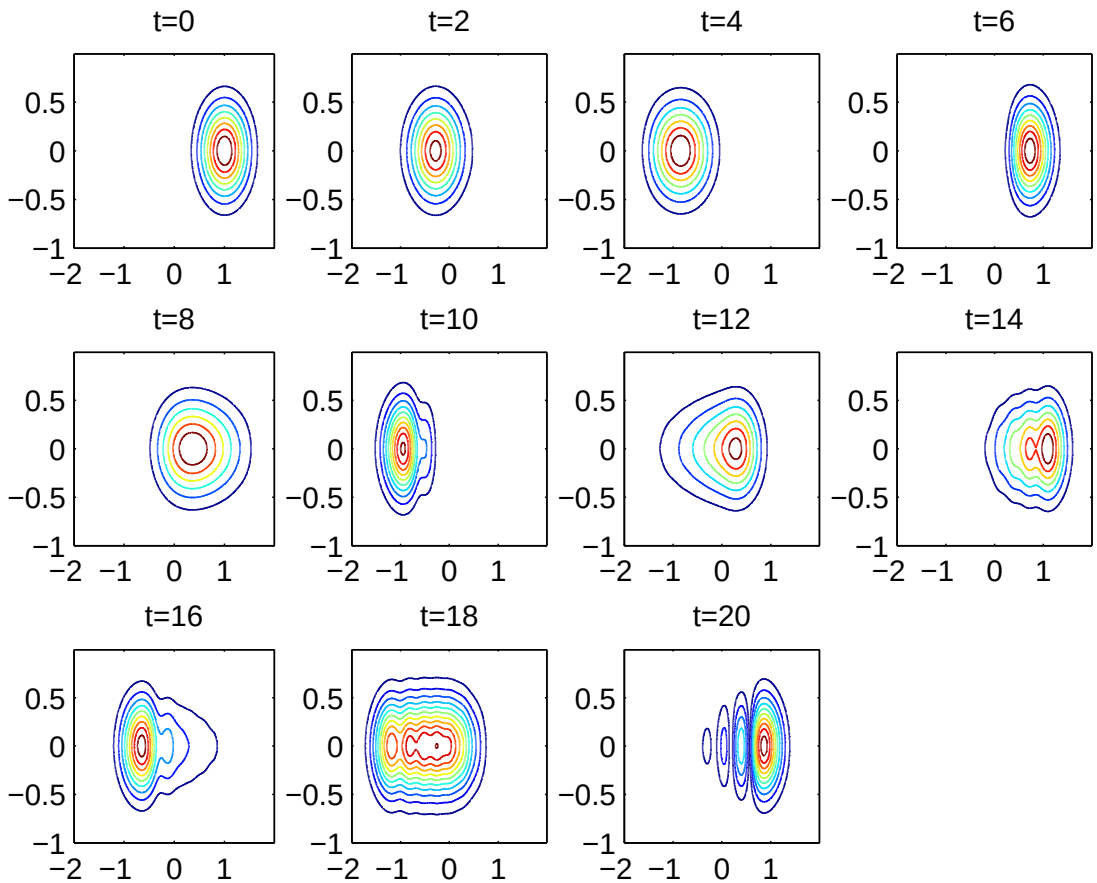


$\varepsilon = 0.001,\ N = 10^4$

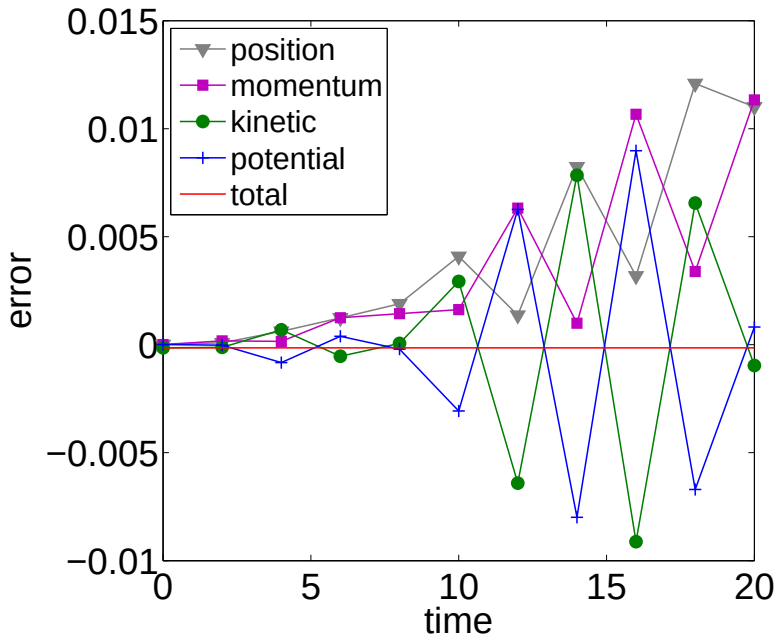
Reference solution

Strang splitting with Fourier differencing

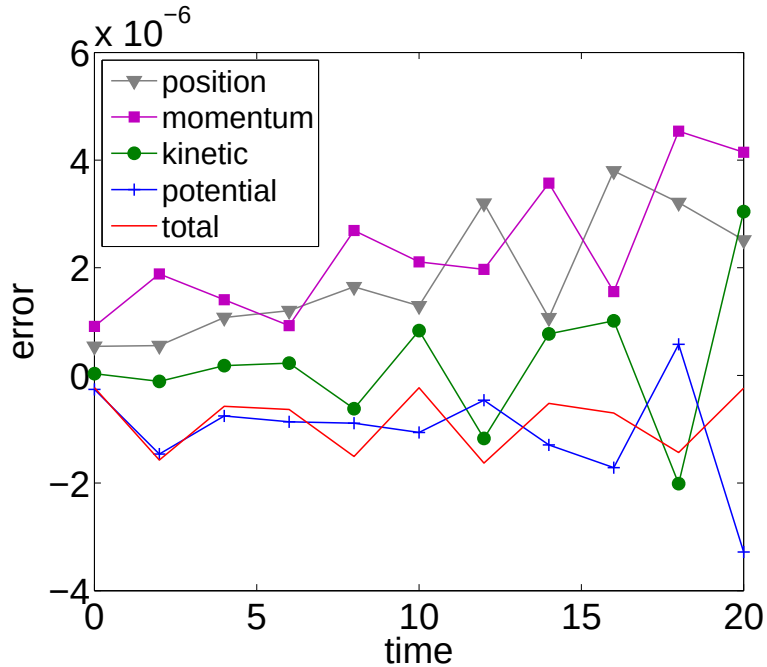
[Jahnke, Lubich, 2000]



Single Gaussian wave packet

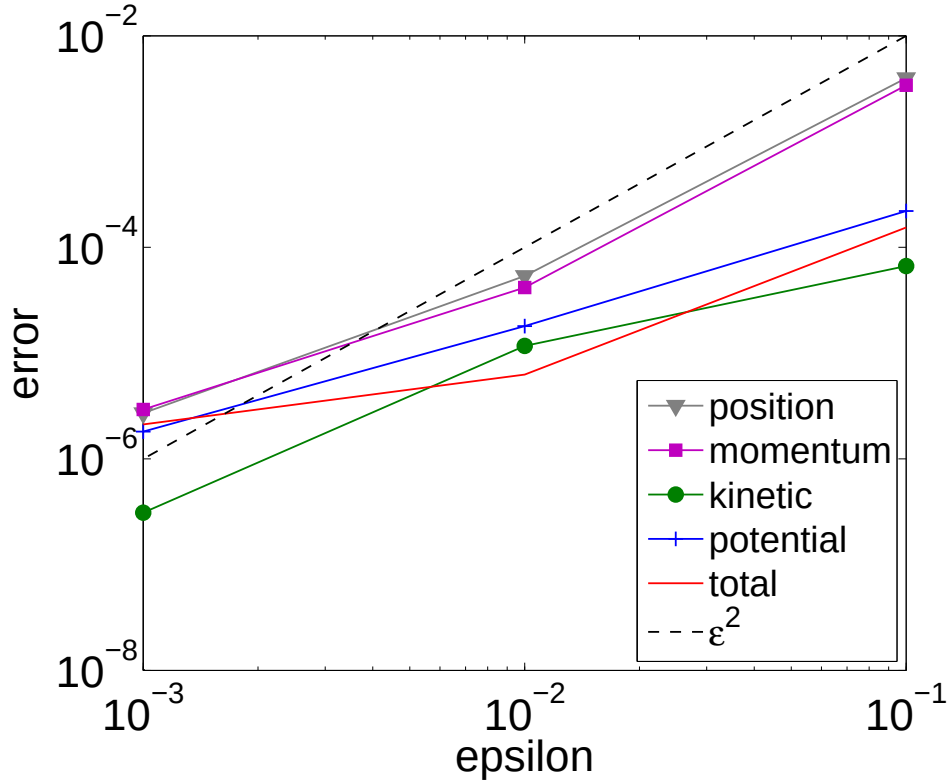


$\varepsilon = 0.1,\ N = 10^6$



$\varepsilon = 0.001,\ N = 10^6$

Single Gaussian wave packet

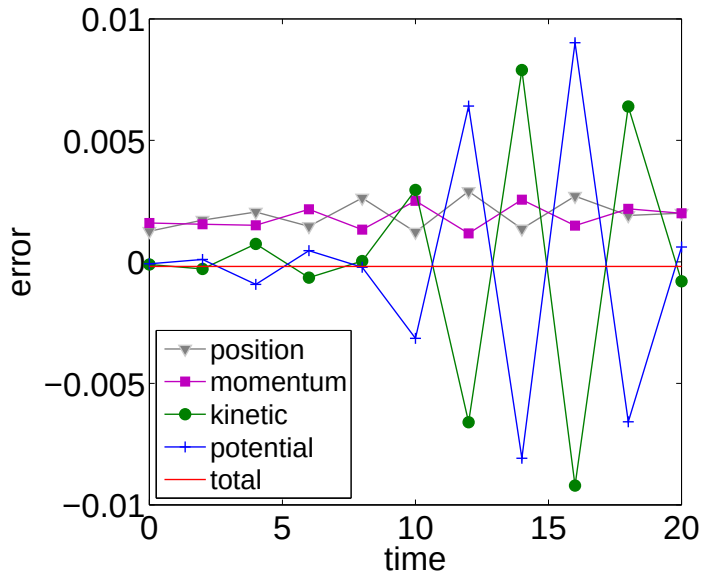


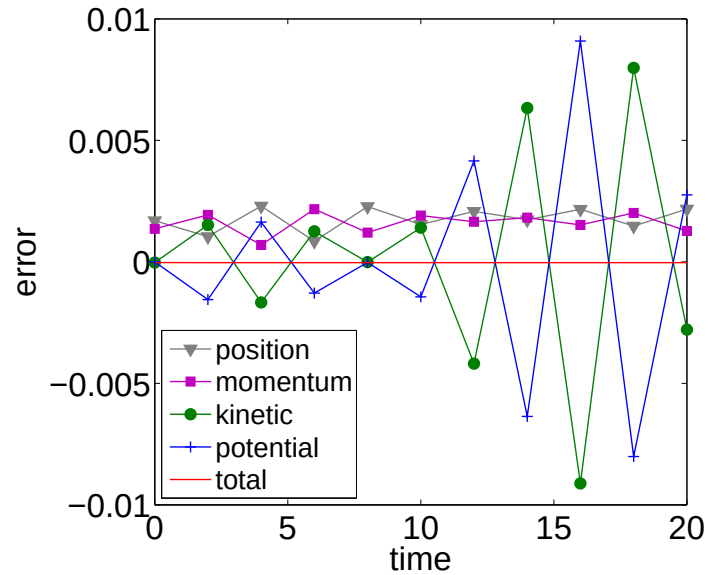
Method is of second order in ε

Superposition of Gaussian wave packets

$$\int_{\mathbb{R}^4} \tfrac{1}{2}|p|^2\, C(q,p)\,\mathrm{d}q\mathrm{d}p \;=\; \tfrac{1}{2}\,\mathrm{e}^{-1/\varepsilon}(\varepsilon-1),$$

$$\int_{\mathbb{R}^4} V(q)\, C(q,p)\,\mathrm{d}q\mathrm{d}p \;=\; \mathrm{e}^{-1/\varepsilon}(2-2\mathrm{e}^{-\varepsilon/4})$$

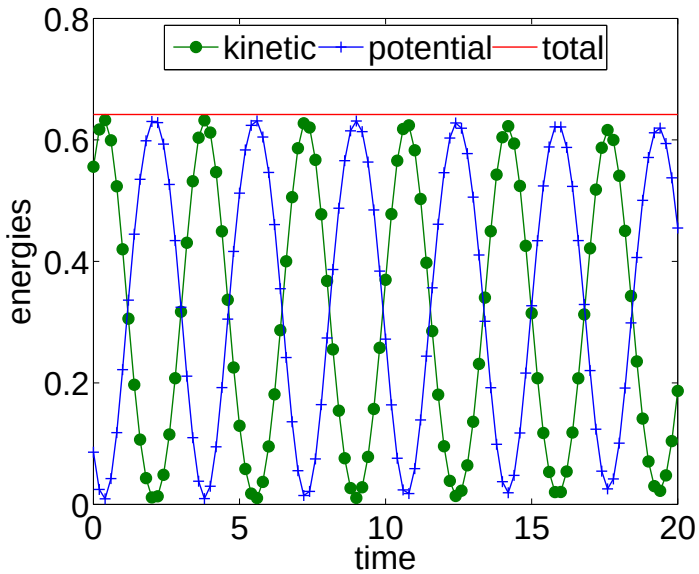


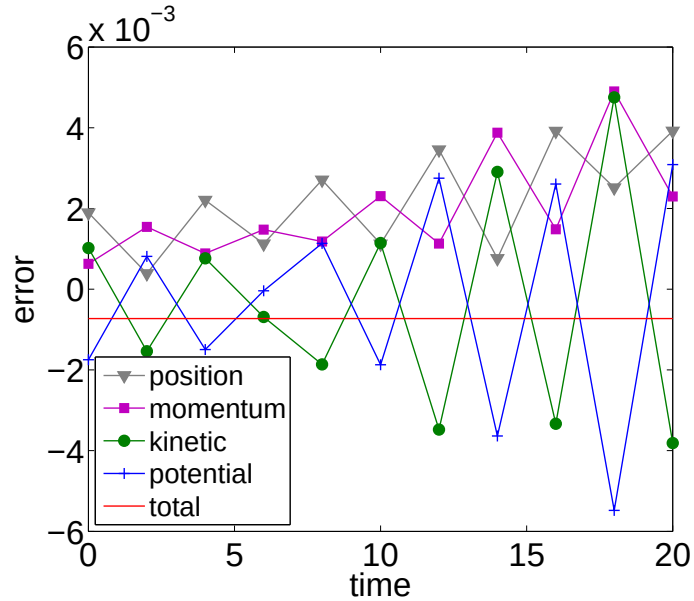


with cross term $(\varepsilon = 0.1, N = 10^4)$ without cross term

Grid based initial data

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



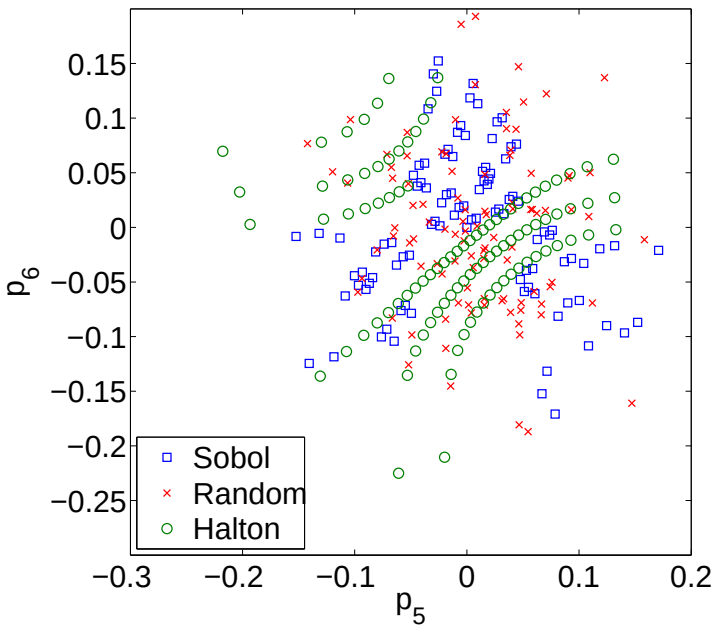


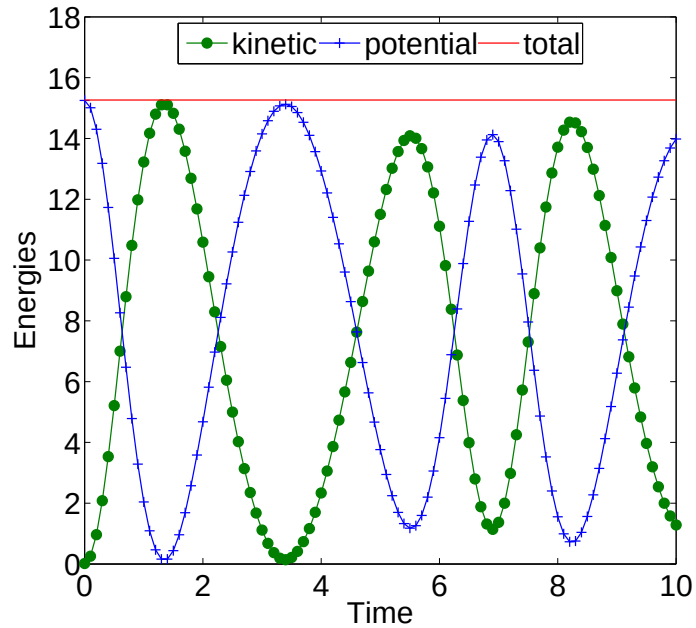
Computation of $W(\psi_0^\varepsilon)(q,p)$: quasi Monte Carlo with $M = 500$ and bicubic interpolation

The Henon-Heiles potential

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

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





$\varepsilon = 0.01,\ N = 10^2$, 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*. To be published in SIAM Journal on Scientific Computing, 2010. Preprint available as ZIB-Report 09-30, `http://opus.kobv.de/zib/volltexte/2009/1195/`.