Stable long-time semiclassical dynamics of multidimensional systems

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Goal: Dominant QM effects on nuclear dynamics of large molecular systems in the SC regime on a long-time scale

- Efficient and accurate for SC systems

- Well-defined QM and classical limit, error assessment

- Systematically improvable and **stable** for long times

- Energy and norm conserving

- Invariant under standard coordinate transformation

Method: Bohmian trajectory framework and semiclassical implementation

Interacting (coherent) trajectories are essential for long-time dynamics (to avoid "sign" problem etc)

Features of implementation

- Use trajectory weights rather than solve for $A(x,t)$
  $w = A^2(x,t)dx_t$: $\quad dw/dt = 0$ for closed systems. Normalization is conserved

- *Approximate Quantum Potential*
  based on $\widehat{p}\psi = \left(-\imath\hbar A^{-1}\nabla A + \nabla S\right)\psi$
  $p = \nabla S$ – classical component
  $r = \nabla A/A$ – nonclassical component

- Approximate r rather than $A(x,t)$; averaging over density avoids singularity problem

AQP from nonclassical momentum:

Represent r in a small basis $\vec{f}(x)$; $\tilde{r} = \vec{s} \cdot \vec{f}$

Find $\vec{s}$ by minimizing I; equivalent to minimizing AQP

$$I = \langle (r - \tilde{r})^2 \rangle \quad \nabla_s I = 0$$

- Linear algebra
- Coefficients $\vec{c}$ are in terms the moments of trajectory distribution
- Single sums over trajectories $\rightarrow$ scales as classical propagation
- The only addition to classical trajectory propagation – cheap in many dimensions

AQP $$\tilde{U} = -\frac{\hbar^2}{2m}(\tilde{r}^2 + \tilde{r}')$$

– *Energy is conserved*

– $\tilde{r} = 0, \quad \tilde{U} = 0$ – classical limit

– complete basis $\vec{f}(x)$ – QM limit

– linear basis (Gaussian wavepacket) – Linearized Quantum Force

Model description of quantum effects using approximate nonclassical momentum

- Wavefunction energy distribution, basic bifurcation - linear approximation

- Tunneling/description of reaction channels - domains/subspaces

- Excited states prefactors to the polar part

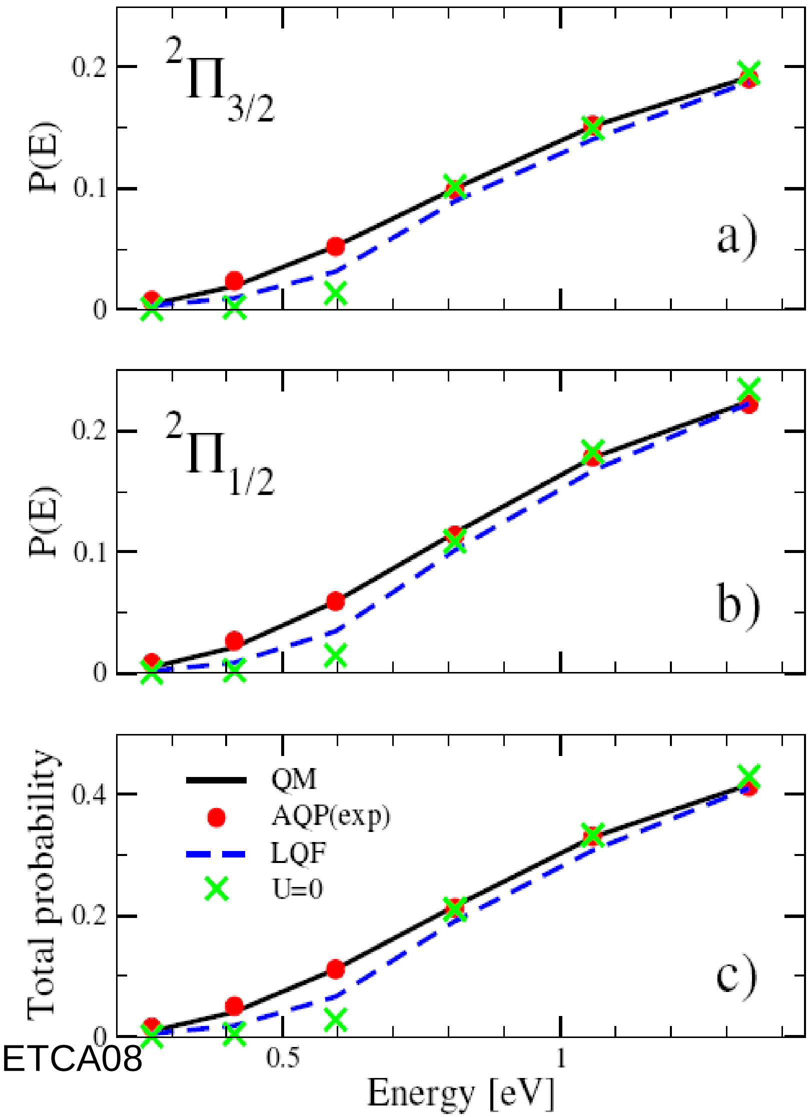
- Nonadiabatic dynamics prefactors + matrix formulations

- Description of zero point energy in anharmonic potentials take a suitable (beyond linear) basis

$O+H_2$ performed as the standard QM calculation
Ground state-to-all probability vs collision energy

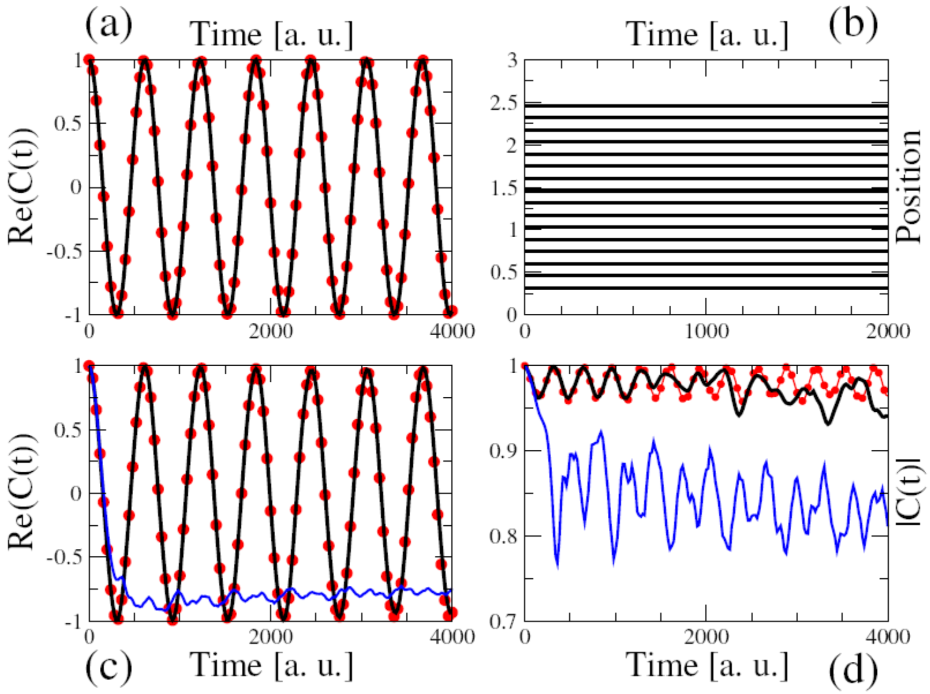
Theory was generalized to arbitrary coordinate systems

Reaction probabilities for the wavepacket initialized on $^3P_1$ obtained using QM (solid line), AQP with (circles) and without (dash) exponential function, and classical (crosses) propagation methods: a) Probability to $^2\Pi_{3/2}$; b) Probability to $^2\Pi_{1/2}$; c) Probability summed over all electronic states.



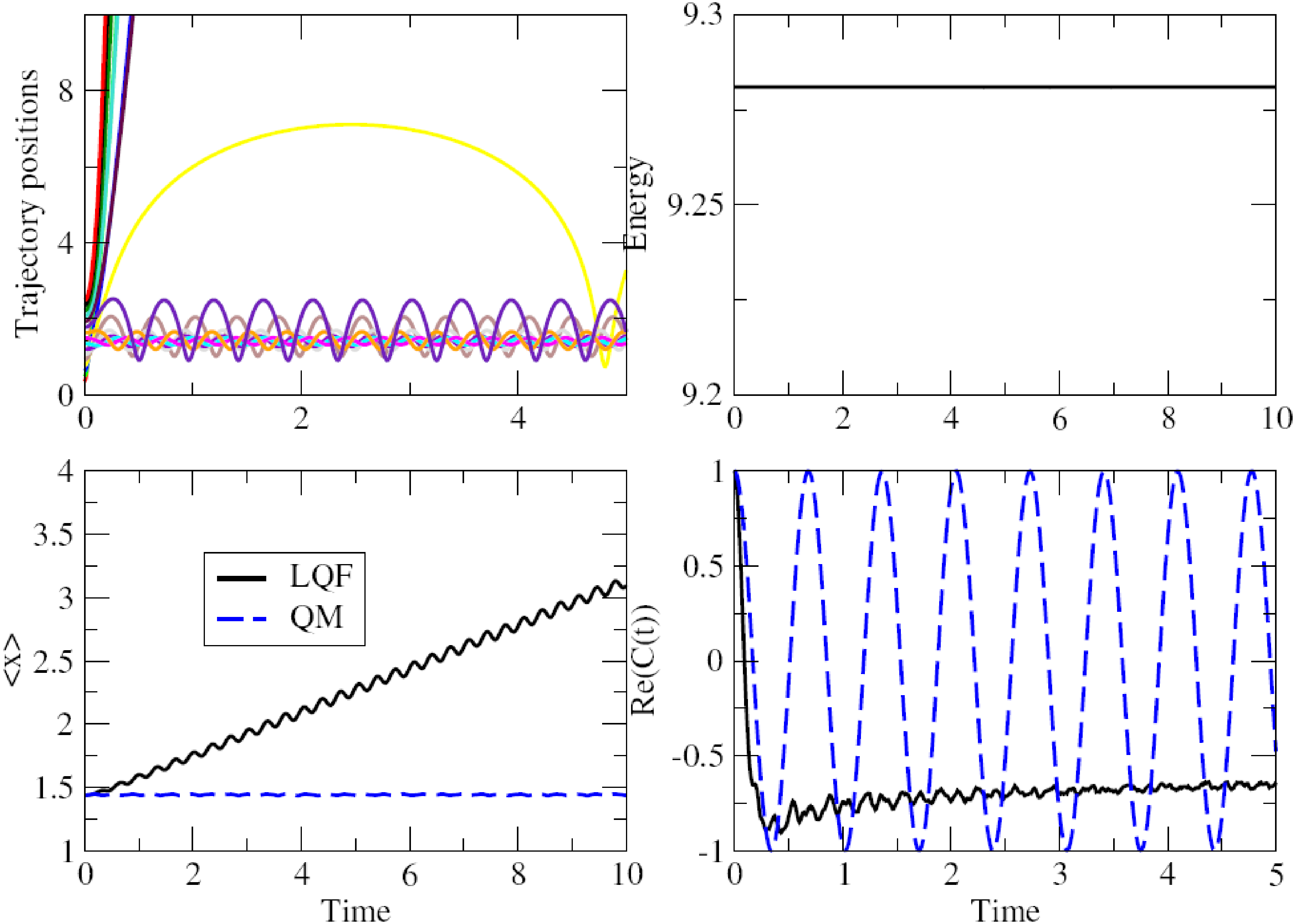
The main challenge: long time stability

(a) Ground state QM (circles) and AQP with exponential basis function (line). (b) AQP trajectories. (c) Gaussian WP: QM (circles), AQP with (thick line) and without (thin line) exponential basis function. (d) $|C(t)|$ of the Gaussian wavepacket.



1D Morse (from $H+H_2$, x_{min}=1.44)

x_0=1.45, a_0=9.6, p_0=0, m=1



General solution for stable long-time description of ZPE?

Improving ZPE with semi-empirical friction

In anharmonic systems looses ZPE or quantum potential energy due to unphysical decoherence of trajectories

Requirements on the correcting force:

(i) Galilei invariant

(ii) vanish when the propagation is exact

(iii) vanish in the classical limit of zero quantum potential

(iv) in case of separable motion, this force should not influence the exact degrees of freedom

Functional form

In anharmonic potential error in momentum $\delta p(t)$ and in position

$$\delta x(t) = \int_0^t \frac{\delta p(\tau)}{m} d\tau. \tag{1}$$

Error in quantum potential due to $\delta x(t)$

$$U[x(t) + \delta x(t)] \approx U[x(t)] + U'[x(t)] \int_0^t \frac{\delta p(\tau)}{m} d\tau, \tag{2}$$

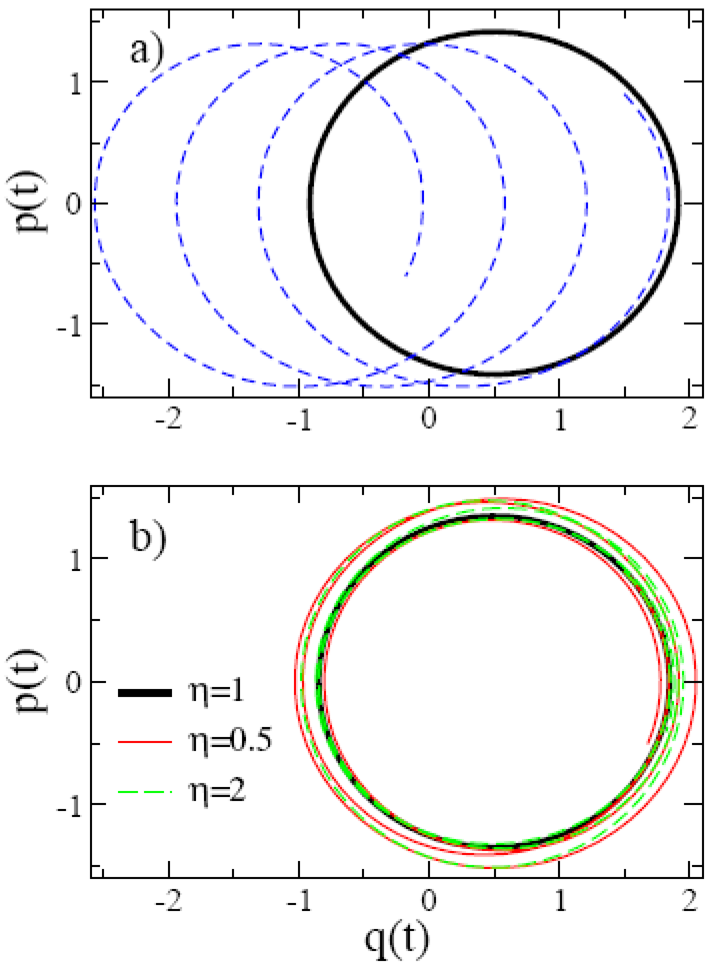
resulting in a deviation δF of the force

$$\delta F = -\frac{d}{dx}\left(U'[x(t)] \int_0^t \frac{\delta p(\tau)}{m} d\tau\right). \tag{3}$$

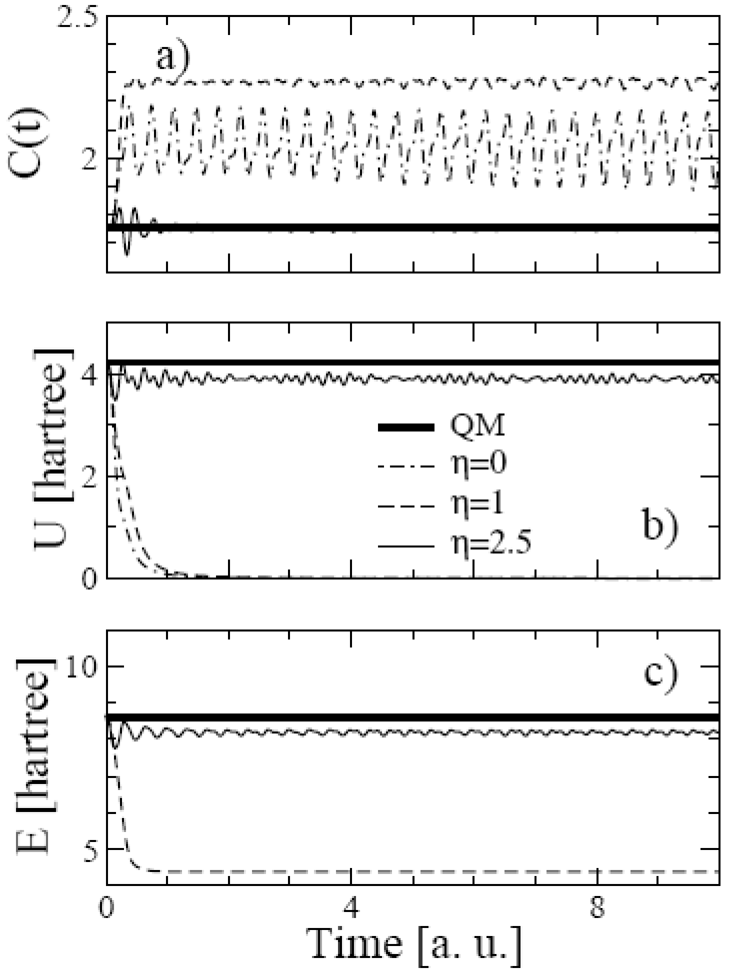
To compensate introduce a friction-like force, $F_{fr} \approx -\delta F$

$$F_{fr} = \eta \left(\nabla \cdot \nabla^T U[\vec{x}(t)]\right) \int_0^t (\vec{v}(\tau) - \tilde{v}(\tau)) d\tau. \tag{4}$$

The friction coefficient $\eta = 1$ if expansion is exact, otherwise η is **adjustable**.



Displaced quantum trajectories for a coherent Gaussian wavepacket: (a) momenta vs positions of trajectories without (solid line) and with the initial displacement (dash); (b) momenta vs positions of the initially displaced trajectories with the friction force coefficient $\eta = \{1,\ 0.5,\ 2\}$.



Dynamics in the Morse potential. (a) The amplitude of the density correlation function, $C(t) = \langle\rho(0)|\rho(t)\rangle$, (b) quantum energy, $\langle U\rangle$, and (c) total energy of the system as a function of time are obtained with the LQF method for $\eta = 0$ (dot-dash line), $\eta = 1$ (dash line) and $\eta = 2.5$ (thin solid line). The quantum result is shown with a thick solid line on all panels. On panel c) result for $\eta = 0$is indistinguishable from the exact energy.

Balancing approximation errors in a more rigorous (compared to semi-empirical friction) way

Linear $\tilde{r}$ is cheap, robust but describes ZPE on short time-scale
$\tilde{U} \to 0$ once trajectories "dissociate"

"Graceful" handling of approximated diff equations based on the analytical solutions to models

$$p = p_0 + p_1 x + \epsilon x^2, \quad |\psi|^2 = \exp(-\alpha x^2)(1 + \delta(x - x_0))^2$$

Stabilize with respect to small nonlinearities by using **both**, classical and nonclassical momenta

$$\begin{aligned} -m\dot{r} &= (r\nabla + \nabla^2/2)p \approx \mathrm{C}^p r + 2\mathrm{C}^r(p - \tilde{p}) \\ m(\dot{p} + V') &= (r\nabla + \nabla^2/2)r \approx \mathrm{C}^r r + 2\mathrm{C}^r(r - \tilde{r}) \end{aligned}$$

Technical details

Conservation of energy is a bit trickier: **r** and **p** are coupled

$$\tilde{r}_x = \vec{c}_x^{\ r} \cdot \vec{f},$$

$$\mathbf{C}^r = [\vec{c}_x^{\ r}, \vec{c}_y^{\ r} \ldots]$$

$$\frac{dE}{dt} = \frac{\langle \vec{r}^{\ 0} \cdot (\mathbf{C}^r \vec{p} - \mathbf{C}^p \vec{r}) \rangle}{m} = 0$$

$\mathbf{M}$ is block diagonal, with blocks

$$\mathbf{S} = \langle \vec{f} \otimes \vec{f} \rangle$$

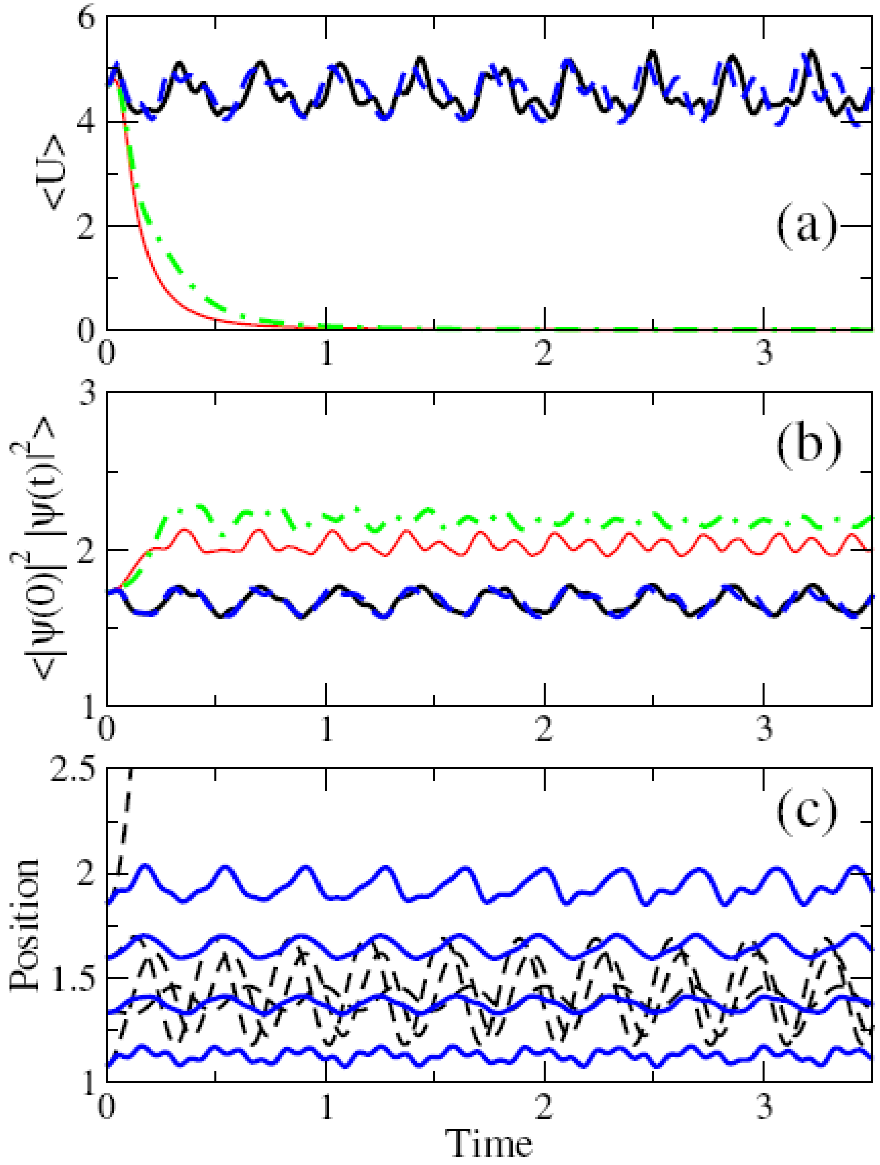
Only S needs to be inverted

$$\begin{pmatrix} \mathbf{M} & \mathbf{O} & \vec{\mathbf{D}}^p \\ \mathbf{O} & \mathbf{M} & \vec{\mathbf{D}}^r \\ \vec{\mathbf{D}}^p & \vec{\mathbf{D}}^r & 0 \end{pmatrix} \cdot \begin{pmatrix} \vec{\mathbf{C}}^r \\ \vec{\mathbf{C}}^p \\ \lambda \end{pmatrix} = \begin{pmatrix} \vec{\mathbf{B}}^r \\ \vec{\mathbf{B}}^p \\ 0 \end{pmatrix}$$

For example, $\mathbf{B}^r = -\frac{1}{2} \langle (\nabla \otimes \vec{f})^T \rangle$

Size of matrix $2N_{dim}N_{bas}+1$, computational complexity $N_{traj}N_{dim}^2$

Hydrogen molecule



1 a. u.=1/40 fs

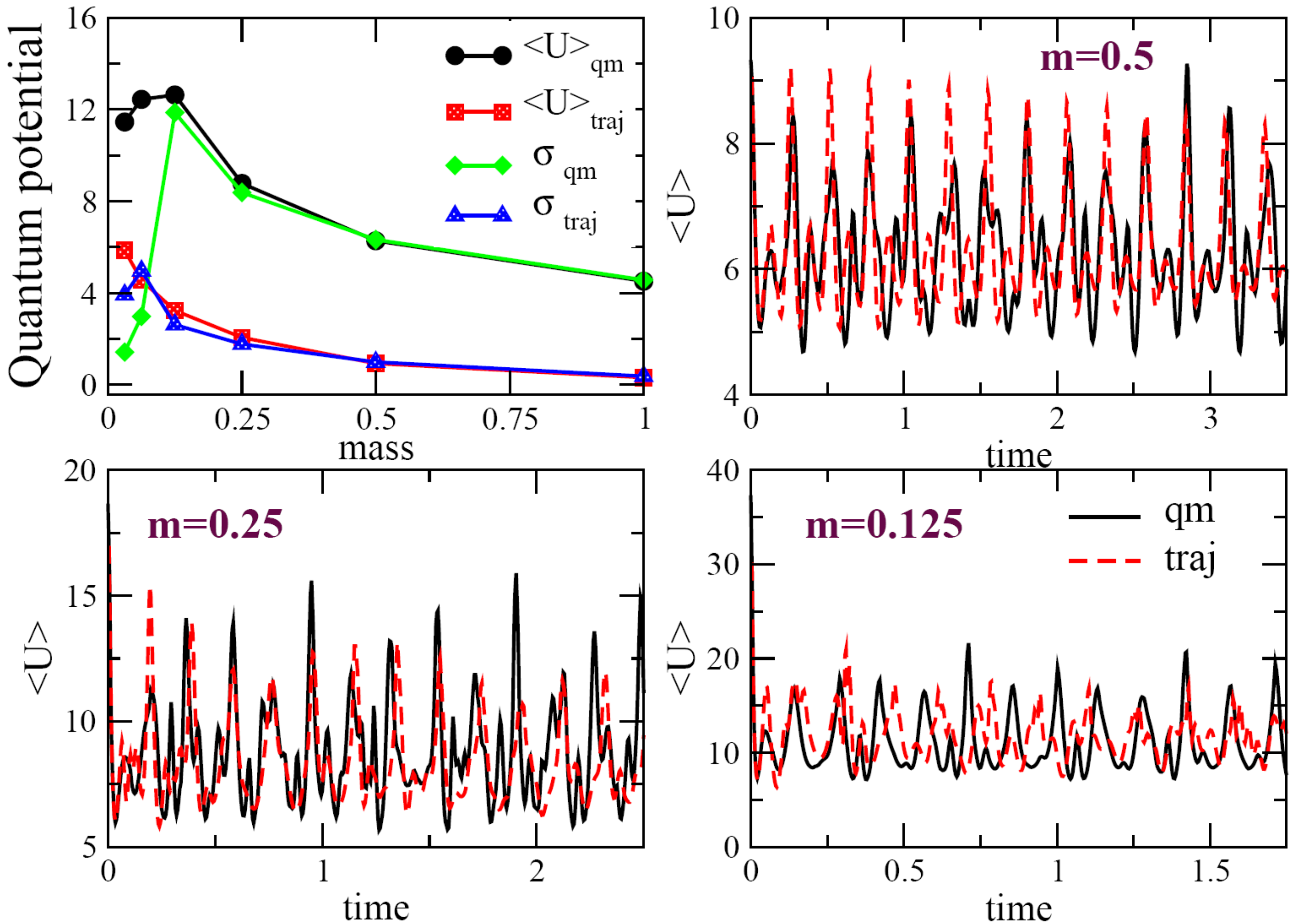
Quantum energy

Trajectory location

Trajectories; up to 200 oscillations or 1.5 ps

Rescaled (more quantum!) hydrogen molecule

Morse oscillator

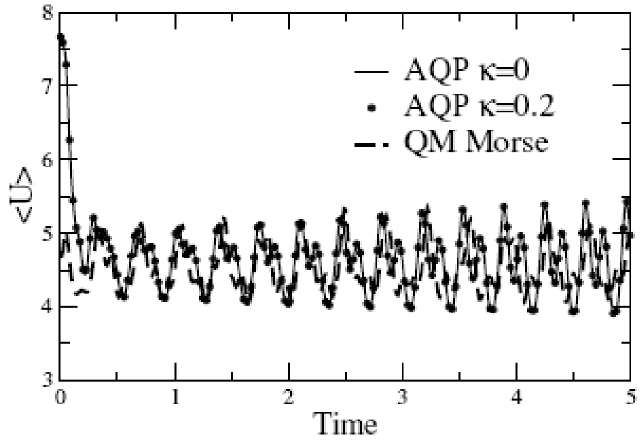


Good tests for multidimensional systems? nothing to compare with

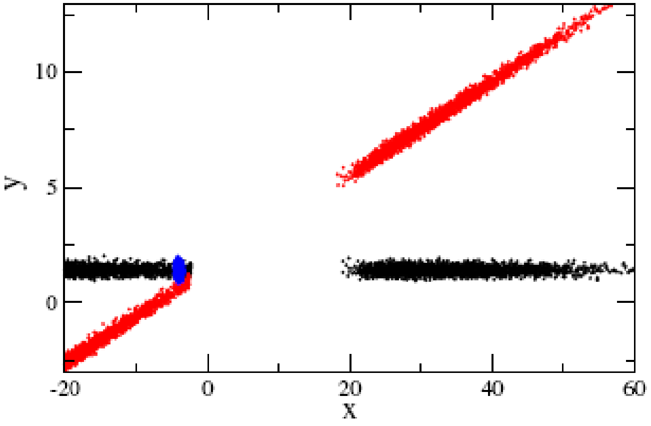
We use our own model of a single reactive Eckart potential and many Morse oscillators (N_{bound}=17), all “coupled” by a unitary transformation

$$\boldsymbol{\Omega} = \begin{pmatrix} \alpha & -\kappa & -\kappa & -\kappa \\ \kappa & 1+\beta & \beta & \beta \\ \kappa & \beta & 1+\beta & \beta \\ \kappa & \beta & \beta & 1+\beta \end{pmatrix}$$

Rective coordinate + environment (oscillator)



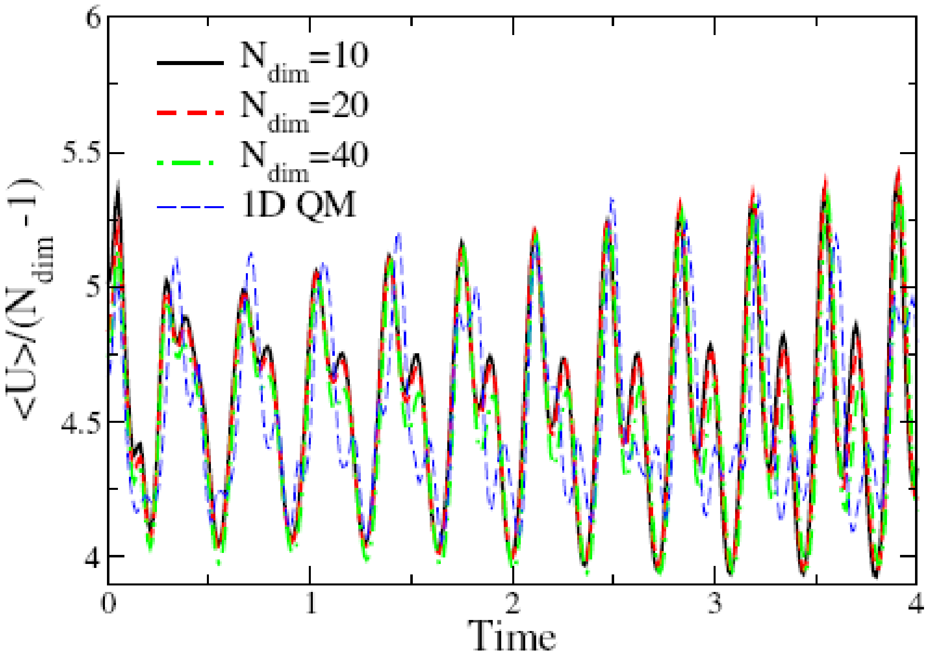
Quantum energy



“Coupling” by rotation: positions after 15 vibrations

Rotation: Quantum energy for $N_{dim} = 2$ and positions of trajectories after 14 oscillation periods

High dimensionality



Quantum energy per vibrational degree of freedom $N_{dim} = \{10, 20, 40\}$. QM result for a single Morse oscillator is shown with a thin solid line.

Achieved long-time ZPE description in high dimension
for open reaction coordinate
Need to do double well to model proton transfer

Convergence with the number of trajectories

TABLE I: Accuracy of the average quantum potential $\langle U\rangle$ over 15 oscillation periods for 10−, 20− and 40−dimensional systems. Number of trajectories is given in the top row. Δ is the relative average difference and σ is the standard deviation for $\langle U\rangle$ obtained with $N_{traj} \leq 2\times 10^4$ trajectories compared to the $N_{traj} = 4\times 10^4$ calculation.

N_{traj}	5×10^3	1×10^4	2×10^4	5×10^3	1×10^4	2×10^4	4×10^4
N_{dim}	Δ [%]			σ [%]			$\langle U\rangle$
10	1.68	0.84	0.52	2.16	1.21	0.62	41.44
20	2.07	1.09	0.40	2.92	1.59	1.09	87.07
40	–	0.89	0.32	–	2.58	1.22	177.5

Summary

- Bohmian formulation is an excellent foundation for a semiclassical method in coordinate space
- Long time stabilitiy requires modification of the differential equation (is it a general conclusion?)
- MULTI-dimensional anharmonic systems are now easy to do
- Next step: systems with multiple minima (double well). At present the multiple minima DOF quickly become nearly classical
  - We plan to use subspaces, but balancing all errors is so far too tricky for us