Time-dependent semiclassical hybrid approach to many particle quantum dynamics

Frank Großmann

Institut für Theoretische Physik, TU Dresden

Overview

Semiclassical initial value representations

- Thawed Gaussian Wavepacket Dynamics: TGWD
- Frozen GWD: multiple trajectories

Semiclassical hybrid dynamics

- Combination of FGWD and TGWD
- A first application: Secrest Johnson model

Semiclassical Initial Value Representations

A Gaussian

Semiclassical Initial Value Representations

A Gaussian times a plane wave

Heller's TGWD

$$\Psi(x,t) = \left(\frac{\gamma_0}{\pi}\right)^{1/4} \exp\left\{-\frac{\gamma_t}{2}(x-q_t)^2 + \frac{i}{\hbar}p_t(x-q_t) + \frac{i}{\hbar}\delta_t\right\}$$

$$\gamma_0, p_t, q_t \in \mathbf{R}, \qquad \gamma_t, \delta_t \in \mathbf{C}$$

Ansatz for the solution of the time-dependent Schrödinger equation

$$i\hbar\dot{\Psi}(x,t) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)\right]\Psi(x,t)$$

E. J. Heller, J. Chem. Phys. **62**, *1544 (1975)* second order Taylor expansion of potential around $q_t \Rightarrow$

$$\boxed{\dot{q}_t = \frac{p_t}{m} \qquad \dot{p}_t = -V'(q_t, t)}$$

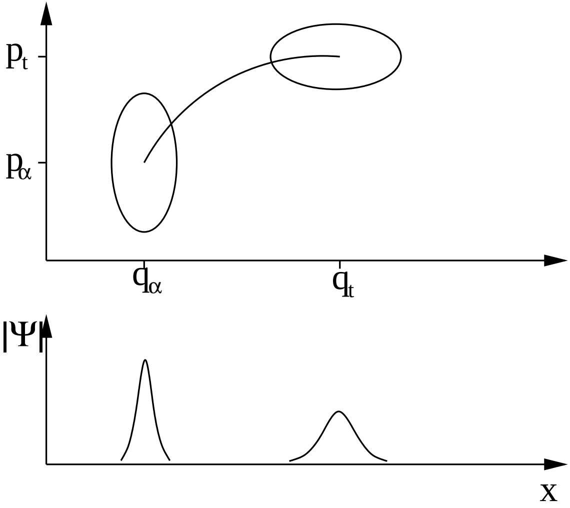
Hamilton's equations with initial conditions $(q_t, p_t) = (q_\alpha, p_\alpha)$

$$-i\hbar\dot{\gamma}_t = -\frac{\hbar^2}{m}{\gamma_t}^2 + V''(q_t, t)$$

time dependent width parameter γ_t with IC $\gamma_{t=0} = \gamma_0$

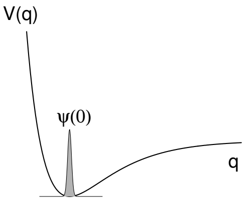
$$\dot{\delta}_t = \frac{p_t^2}{2m} - V(q_t, t) - \frac{\hbar^2}{2m}\gamma_t$$

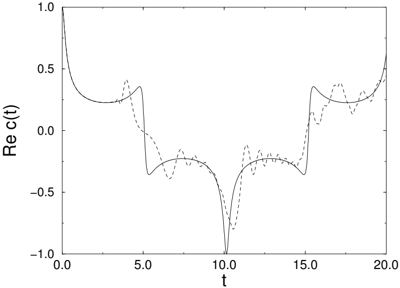
TGWD: Phase- and position space



single trajectory method

A simple example: Morse oscillator





$$c(t) = \langle \Psi(0) | \Psi(t) \rangle = \langle \Psi(0) | e^{-i\hat{H}t/\hbar} | \Psi(0) \rangle$$

Semiclassical multiple trajectory method for N DOF: FGWD

$$\Psi(\mathbf{x},t) = \int d\mathbf{x}' K(\mathbf{x},t;\mathbf{x}',0)\Psi(\mathbf{x}',0)$$

Can the propagator be constructed with initial value solutions?

$$K(\mathbf{x},t;\mathbf{x}',0) = \int \frac{d\mathbf{p}'d\mathbf{q}'}{(2\pi\hbar)^N}\langle\mathbf{x}|\ldots\exp\{iS(\mathbf{p}',\mathbf{q}',t)/\hbar\}\ldots|\mathbf{x}'\rangle$$

- $\mathbf{x},\mathbf{x}'$ just "dummy variables"
- Hamilton's principal function $S(\mathbf{p}',\mathbf{q}',t) = \int_0^t L dt'$
- $\cdots$: initial value solutions $\mathbf{p}_t(\mathbf{p}',\mathbf{q}'),\mathbf{q}_t(\mathbf{p}',\mathbf{q}')$

Coherent state representation of unity: γ=const

$$\hat{1} = \int \frac{d\mathbf{p}d\mathbf{q}}{(2\pi\hbar)^N} |g_\gamma(\mathbf{p},\mathbf{q})\rangle\langle g_\gamma(\mathbf{p},\mathbf{q})|$$

Herman-Kluk "Frozen" Gaussian Approximation (FGA, HHKK)

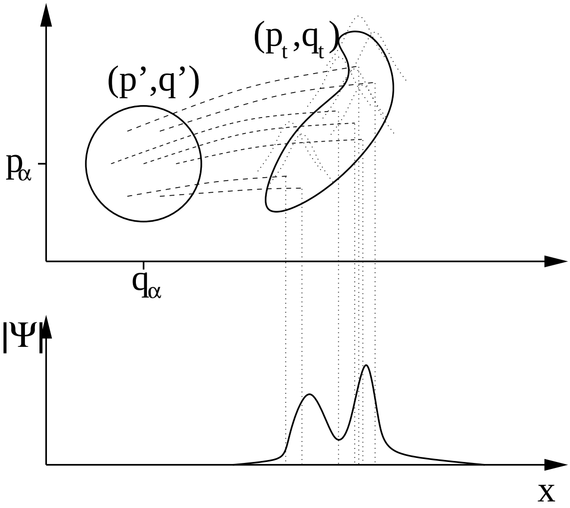
$$K(\mathbf{x},t;\mathbf{x}',0) \approx \int \frac{d\mathbf{p}'d\mathbf{q}'}{(2\pi\hbar)^N} \langle \mathbf{x}|g_\gamma(\mathbf{p}_t,\mathbf{q}_t)\rangle R e^{iS(\mathbf{p}',\mathbf{q}',t)/\hbar} \langle g_\gamma(\mathbf{p}',\mathbf{q}')|\mathbf{x}'\rangle$$

$$R = \sqrt{\det \frac{1}{2}\left(\mathbf{m}_{pp} + \mathbf{m}_{qq} - \gamma i\hbar \mathbf{m}_{qp} - \frac{1}{\gamma i\hbar}\mathbf{m}_{pq}\right)}$$

$\mathbf{m}_{pp}, \mathbf{m}_{qq}, \ldots$ are elements of the stability (monodromy) matrix $\mathbf{M}$

Herman and Kluk (1984), K.G. Kay (1994), F.G. and A. Xavier (1998)

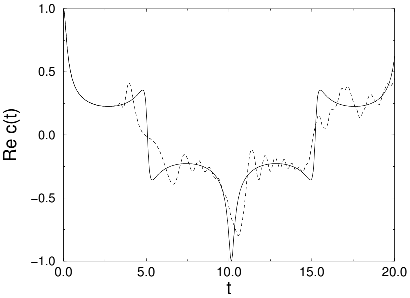
FGWD: Phase- and position space



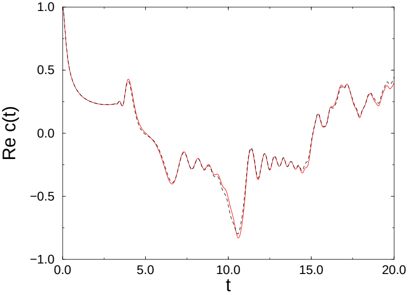
*multi*trajectory method

Simple example revisited

TGWD/QM



FGWD/QM



- Time-dependent method for *arbitrary* dynamics
- SPA $\rightarrow$ Van Vleck-Gutzwiller propagator

$$K(\mathbf{x}, t; \mathbf{x}', 0) \sim \sum_j \left| \frac{1}{\det \mathbf{m}_{qp}} \right|^{1/2} \exp\{iS_j(\mathbf{x}, \mathbf{x}', t)/\hbar - i\pi\nu_j/2\}$$

- "Maslov-Phase" is already incorporated
- no problems at caustics, FGA is uniform $\Rightarrow$Kay (2006)
- FGA is unitary (in SPA) $\Rightarrow$Herman (1986)
- iterative improvement is possible $\Rightarrow$Pollak group, Kay group

Semiclassical hybrid dynamics

problem: exponential scaling of numerical effort in qm

Frozen Gaussian Wavepacket Dynamics

$$\Psi_\alpha(\mathbf{x},t) = \int d\mathbf{x}' K^{\mathrm{FGA}}(\mathbf{x},t;\mathbf{x}',0)\langle \mathbf{x}'|\Psi_\alpha(0)\rangle$$

$$\boxed{\Psi_\alpha(\mathbf{x},t) = \int \frac{d\mathbf{p}'d\mathbf{q}'}{(2\pi\hbar)^N}\langle \mathbf{x}|g(\mathbf{p}_t,\mathbf{q}_t)\rangle R e^{\frac{i}{\hbar}S(\mathbf{p}',\mathbf{q}',t)}\langle g(\mathbf{p}',\mathbf{q}')|\Psi_\alpha(0)\rangle}$$

- ☺ no storage problems due to locality of cm
- ☹ linear scaling not generic *M. L. Brewer, JCP* **111**, *6168 ('99)*
- ☺ expanding the exponent around $(\mathbf{p}_\alpha, \mathbf{q}_\alpha)$ $\Rightarrow$TGWD (too crude)

Correlated many particle dynamics

$$\mathbf{q}' = (\mathbf{q}'_1, \mathbf{q}'_2)$$

- $\mathbf{q}'_2$ are n "nearly harmonic" DOFs $\Rightarrow$TGWD
- $\mathbf{q}'_1$ are $N-n$ "strongly anharmonic" DOFs $\Rightarrow$FGWD

$$\Psi_\alpha(\mathbf{x}, t) = \int \frac{d\mathbf{p}'_1 d\mathbf{q}'_1}{(2\hbar)^N \pi^{N-n}} \sqrt{\frac{\sqrt{\det \gamma}}{\pi^{N/2} \det \mathbf{A}_2}} R \exp\left\{\frac{1}{4}\mathbf{b}_2^{\mathrm{T}} \cdot \mathbf{A}_2^{-1} \cdot \mathbf{b}_2 + c_2\right\}$$

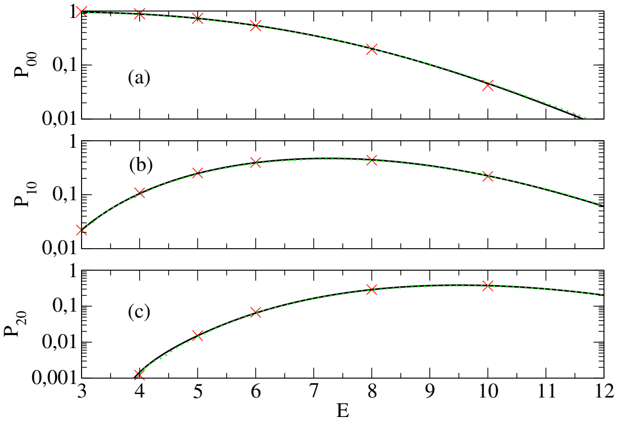
$\mathbf{A}_2, \mathbf{b}_2, c_2$ contain fully coupled classical dynamics

FG, J. Chem. Phys. **125**, *014111 (2006)*

Inelastic scattering: Secrest-Johnson model

$$H(\mathbf{p},\mathbf{q}) = \frac{p_1^2}{2\mu} + \frac{p_2^2}{2} + \exp\{\alpha(q_2 - q_1)\} + \frac{1}{2}q_2^2$$

collinear He-H_2 scattering: $\mu = 2/3$, $\alpha = 0.3$



S-matrix extraction

cross correlation function

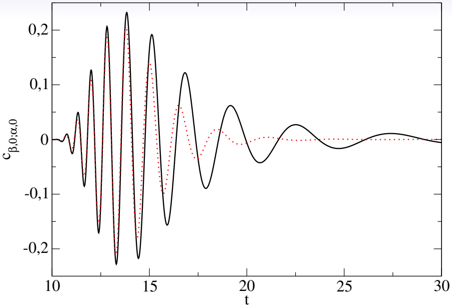
$$c_{\beta,n';\alpha,n}(t) = \langle \Psi_{\beta,n'} | \exp\{-iHt/\hbar\} | \Psi_{\alpha,n} \rangle$$

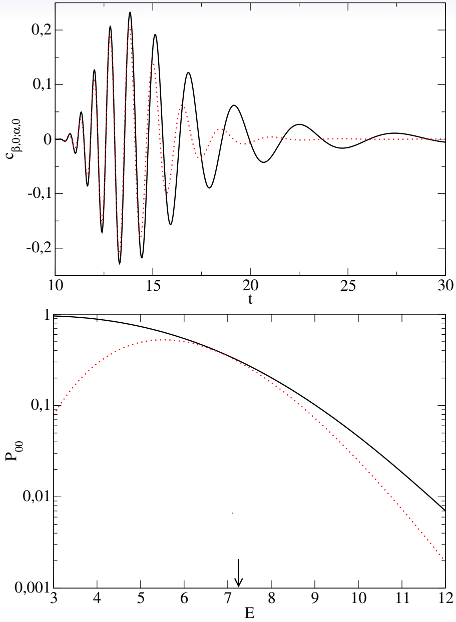
Fourier transform

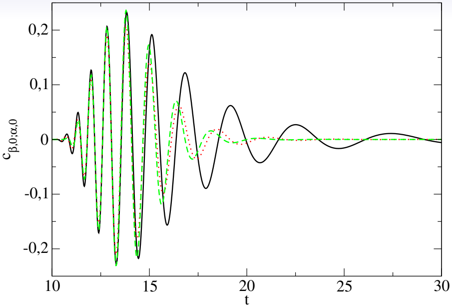
$$\boxed{S_{\beta,n';\alpha,n}(E) = \frac{(2\pi\hbar)^{-1}}{\eta^*_{\beta,n'}(E)\eta_{\alpha,n}(E)} \int c_{\beta,n';\alpha,n}(t) e^{iEt/\hbar} dt}$$

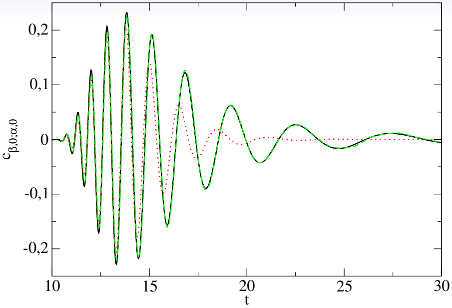
FT to be performed numerically!

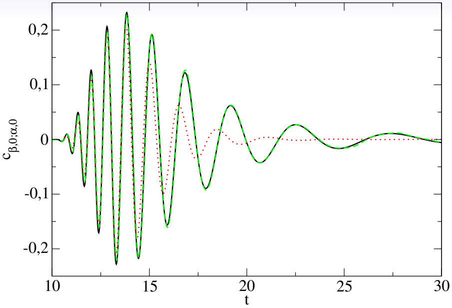
D. J. Tannor and D. E. Weeks, J. Chem. Phys. **98**, *3884 (1993)*

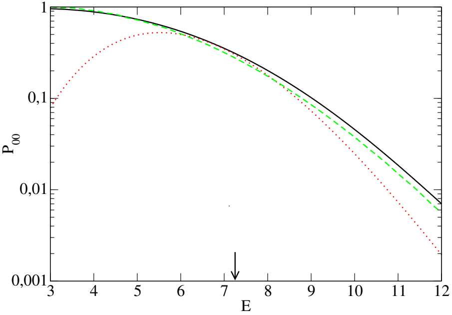

0,2
0,1
0
-0,1
-0,2
$c_{\beta,0;\alpha,0}$
10
15
20
25
30
t


0,2
0,1
0
-0,1
-0,2
10
15
20
25
30
t
$c_{\beta,0;\alpha,0}$
1
0,1
0,01
0,001
3
4
5
6
7
8
9
10
11
12
E
P_{00}


0,2
0,1
0
-0,1
-0,2
$c_{\beta,0;\alpha,0}$
10
15
20
25
30
t


0,2
0,1
0
-0,1
-0,2
$c_{\beta,0;\alpha,0}$
10
15
20
25
30
t


0,2
0,1
0
-0,1
-0,2
$c_{\beta,0;\alpha,0}$
10
15
20
25
30
t


1
0,1
0,01
0,001
P_{00}
3
4
5
6
7
8
9
10
11
12
E

Conclusions

Semiclassical initial value representation of the quantum propagator

- “Thawed” versus “Frozen” GWD
- interacting many particle systems:

“Frozen” and “Thawed” GWD combined!