Computational Semiclassics

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$$\psi : \mathbb{R}_t \times \mathbb{R}_x^d \to \mathbb{C}^M$$

with

$$d \gg 1 \quad \text{and} \quad \|\nabla_{t,x}\psi\| \gg 1$$

Self-adjoint operator $\widehat{H}$

Schrödinger equation: $i\varepsilon\partial_t\psi = \widehat{H}\psi$

Unitary propagator $U_t = \mathrm{e}^{-i\widehat{H}t/\varepsilon}$

$0 < \varepsilon \ll 1$

Energy function H smooth, subquadratic

Hamilton equation: $\dot{z}_t = \Omega \nabla H(z_t)$

Symplectic flow $\Phi_t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$

Herman–Kluk propagator

cf. Herman/Kluk '81, Kay '06,

Swart/Rousse '09,

L/Sattlegger '16

$$\psi = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \langle g_z, \psi \rangle g_z \, dz$$

$$g_z(x) = (\pi\varepsilon)^{-d/4} \exp\Big(-\frac{1}{2\varepsilon}|x-q|^2 + \frac{i}{\varepsilon} p \cdot (x-q)\Big)$$

$$U_t\psi = (2\pi\varepsilon)^{-d}\int_{\mathbb{R}^{2d}} \langle g_z,\psi\rangle\, U_t g_z\, dz$$

$$\stackrel{!}{\approx} (2\pi\varepsilon)^{-d}\int_{\mathbb{R}^{2d}} u_t(z)\langle g_z,\psi\rangle\, \mathrm{e}^{iS_t(z)/\varepsilon} g_{z_t(z)}\, dz$$

$$u_t(z) = \sqrt{2^{-d}\det\left(\partial_q q_t(z) + \partial_p p_t(z) + i[\partial_p q_t(z) - \partial_q p_t(z)]\right)}$$

$$I_t = (2\pi\varepsilon)^{-d} \int\limits_{\mathbb{R}^{2d}} u_t(z) \langle g_z, \bullet \rangle \, \mathrm{e}^{iS_t(z)/\varepsilon} g_{z_t(z)} \, dz$$

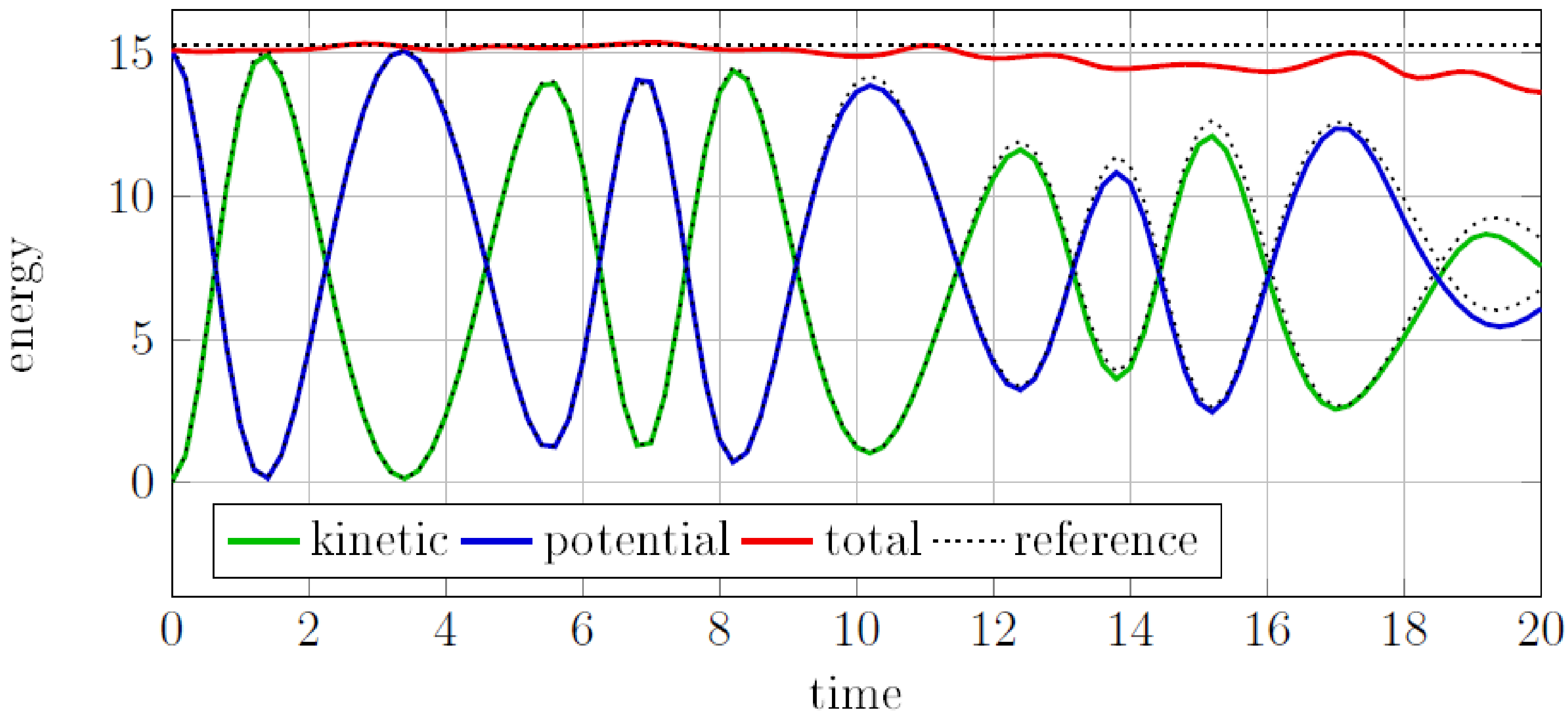
satisfies $\|I_t - U_t\| \leq C_{t,H}\, \varepsilon$.

If $|\widetilde{\Phi}^\tau - \Phi^\tau| \leq c\, \tau^\gamma$ is symplectic, then $\|I_\tau - \widetilde{I}_\tau\| \leq \widetilde{C}_{c,H}\, \tau^\gamma/\varepsilon$.

$$
\begin{aligned}
I_t\psi &= (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} u_t(z) \langle g_z, \psi\rangle \, \mathrm{e}^{iS_t(z)/\varepsilon} g_{z_t(z)} \, dz \\
&\approx \frac{1}{N} \sum_{j=1}^{N} \widetilde{u}_t(z_j) \, r_\psi(z_j) \, \mathrm{e}^{i\widetilde{S}_t(z_j)/\varepsilon} \, g_{\widetilde{z}_t(z_j)}
\end{aligned}
$$

with $z_1, \ldots, z_N \sim \mu_\psi$.

$d = 6$, $\varepsilon = 0.01$



computing time on a desktop computer: 5 resp. 30 minutes

LSC-IVR

cf. Miller ’74, Lee & Scully ’80, Heller ’81,
. . . , L & Röblitz ‘10

Egorov's theorem,

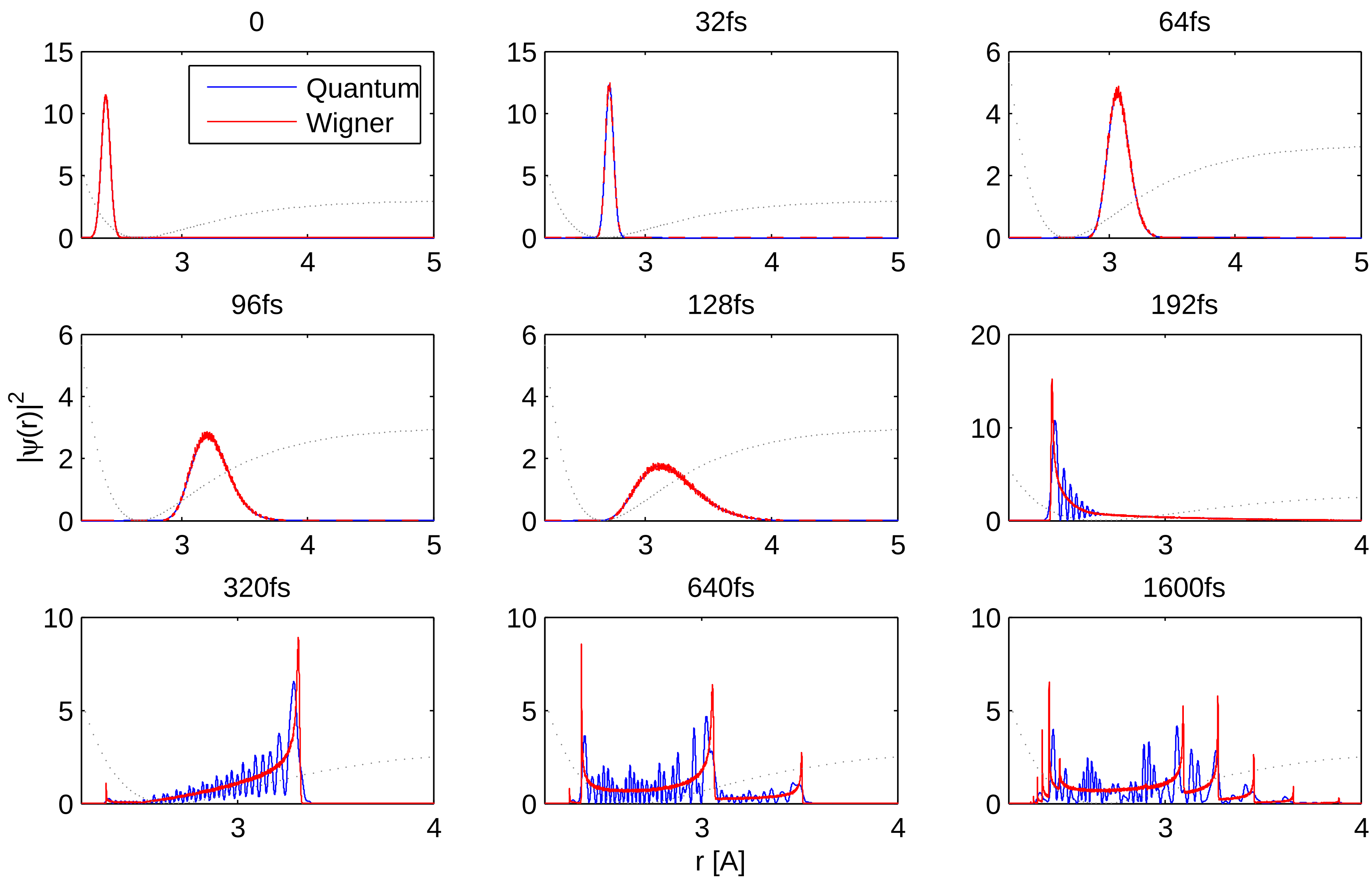
$$\left\| U_t^* \, \widehat{A} \, U_t - \widehat{A \circ \Phi_t} \right\| \leq C_{t,A,H} \, \varepsilon^2,$$

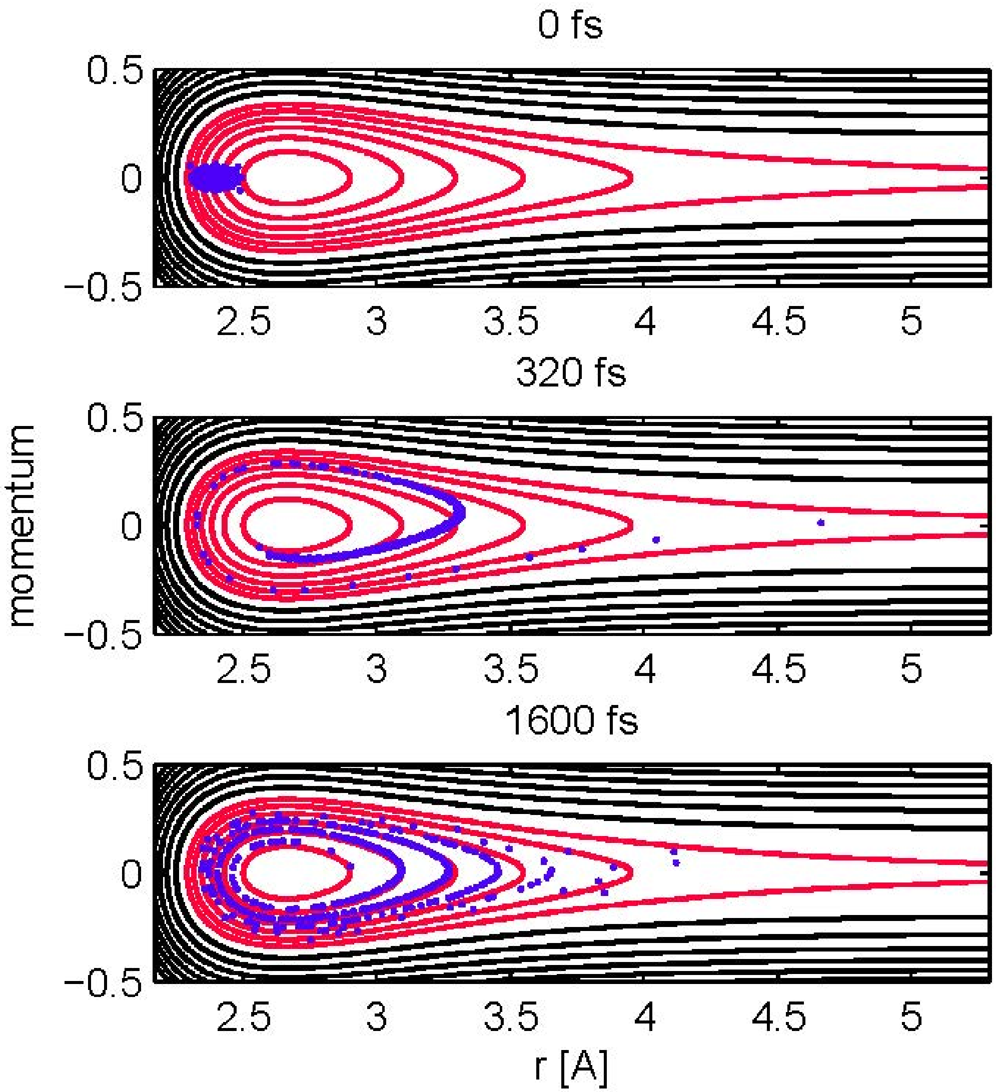
implies

$$\left\langle U_t \psi, \widehat{A} \, U_t \psi \right\rangle \approx \left\langle \psi, \widehat{A \circ \Phi_t} \, \psi \right\rangle .$$

$$
\begin{aligned}
\left\langle \psi, \widehat{A \circ \Phi_t} \psi \right\rangle &= \int_{\mathbb{R}^{2d}} (A \circ \Phi_t)(z) W_\psi(z) dz \\
&\approx \frac{1}{N} \sum_{j=1}^{N} (A \circ \widetilde{\Phi}_t)(z_j)
\end{aligned}
$$

with $z_1, \dots, z_N \sim W_\psi$.


0
32fs
64fs
96fs
128fs
192fs
320fs
640fs
1600fs
Quantum
Wigner
|ψ(r)|^2
r [A]

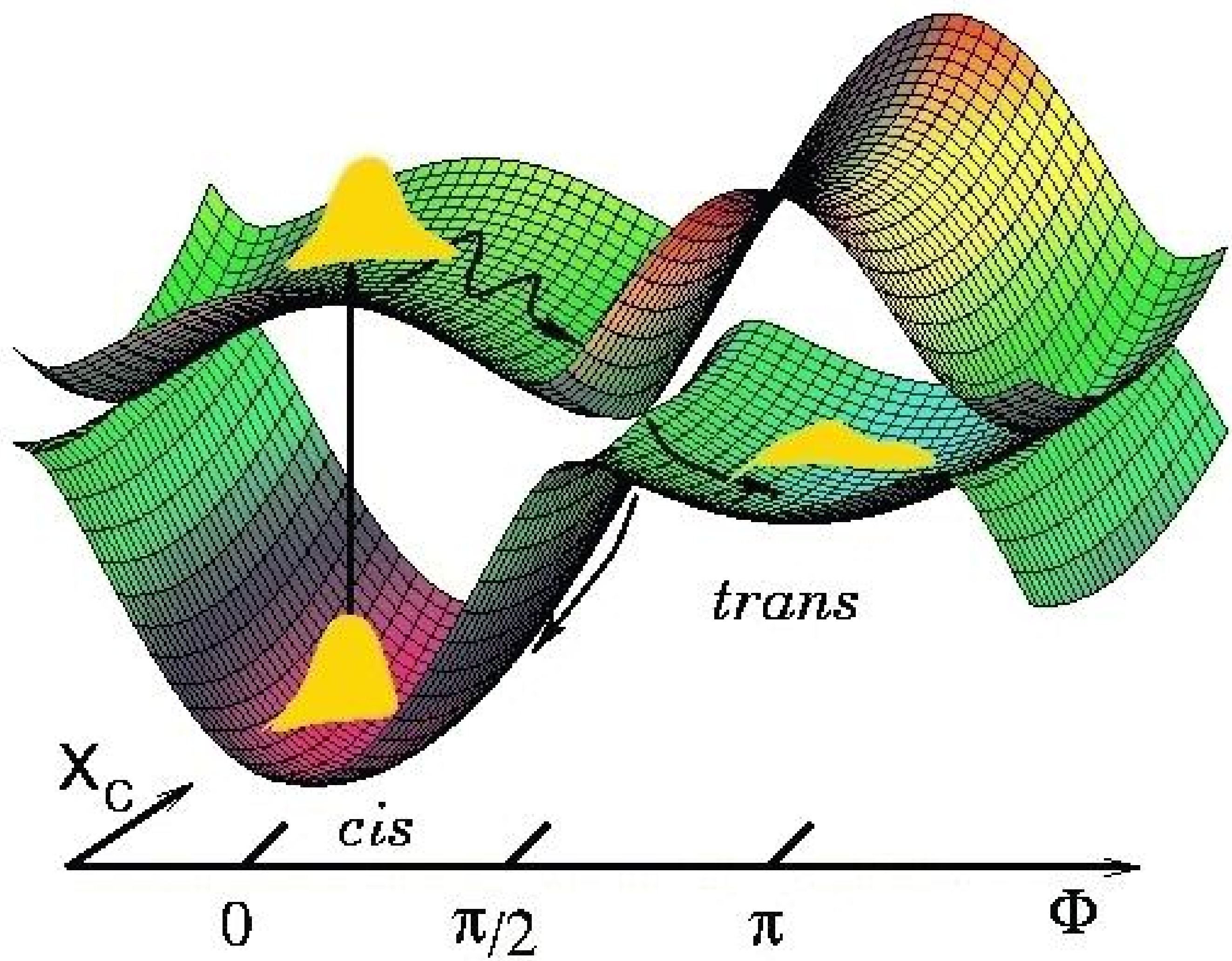

0 fs
320 fs
1600 fs
momentum
r [A]
0.5
0
−0.5
2.5
3
3.5
4
4.5
5

Surface hopping

cf. Bjerre/Nikitin ’67, Tully/Preston ’71,

Voronin/Marques/Varandas ’98,

L/Teufel/Fermanian ’03 –’16



trans
X_C
cis
0
$\pi/2$
π
Φ

Let $H = \lambda^+ \Pi^+ + \lambda^- \Pi^-$.

If $A = \Pi^\pm A \Pi^\pm$ and $(\dots)$, then

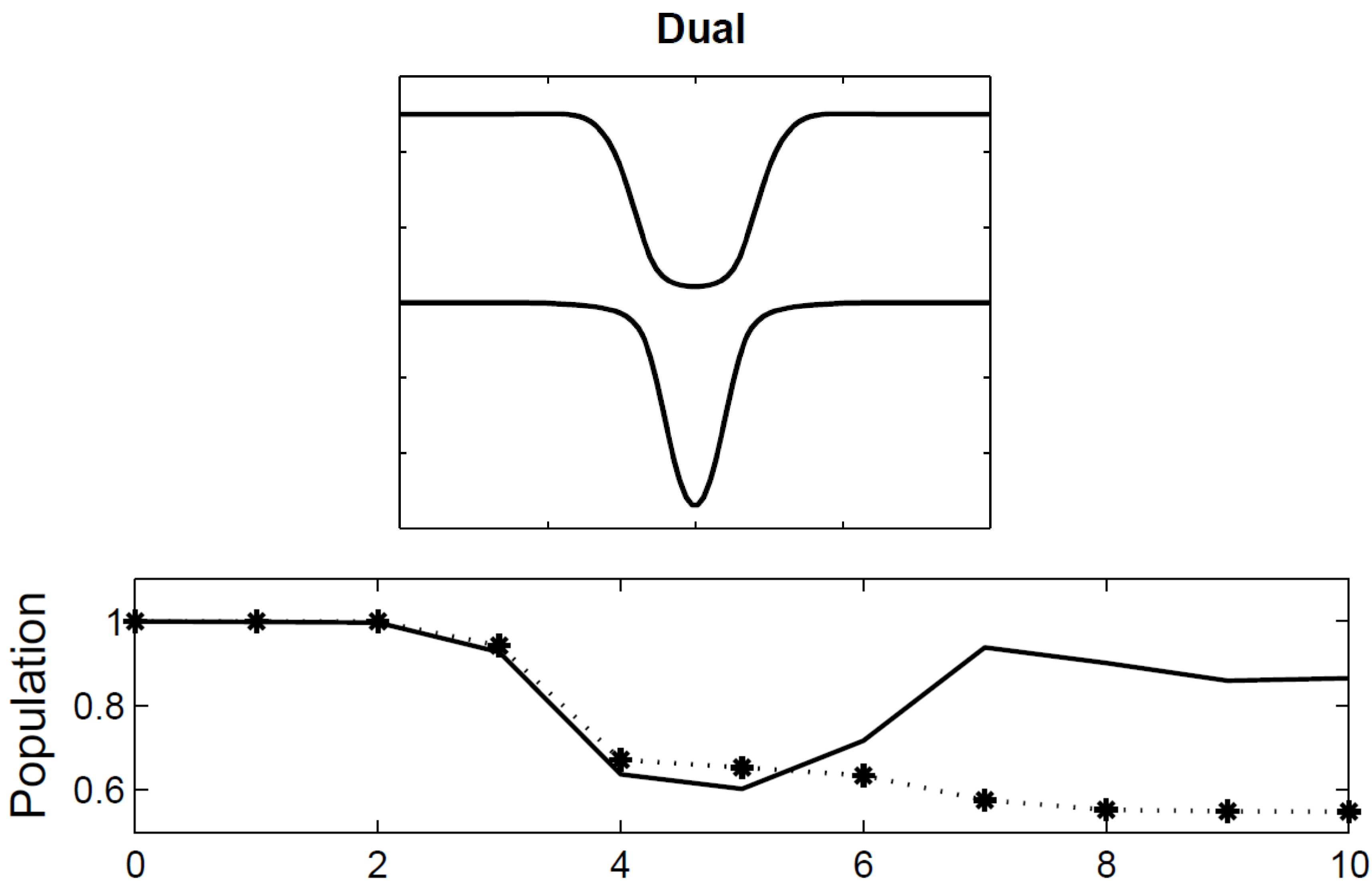
$$\left| \int_0^T \Big(\big\langle U_t\psi, \widehat{A}\, U_t\psi \big\rangle - \int_{\mathbb{R}^{2d}} (\mathcal{L}_t A)(z) W_\psi(z) dz \Big) dt \right| \leq C_{T,A,H}\, \varepsilon^{1/8}.$$

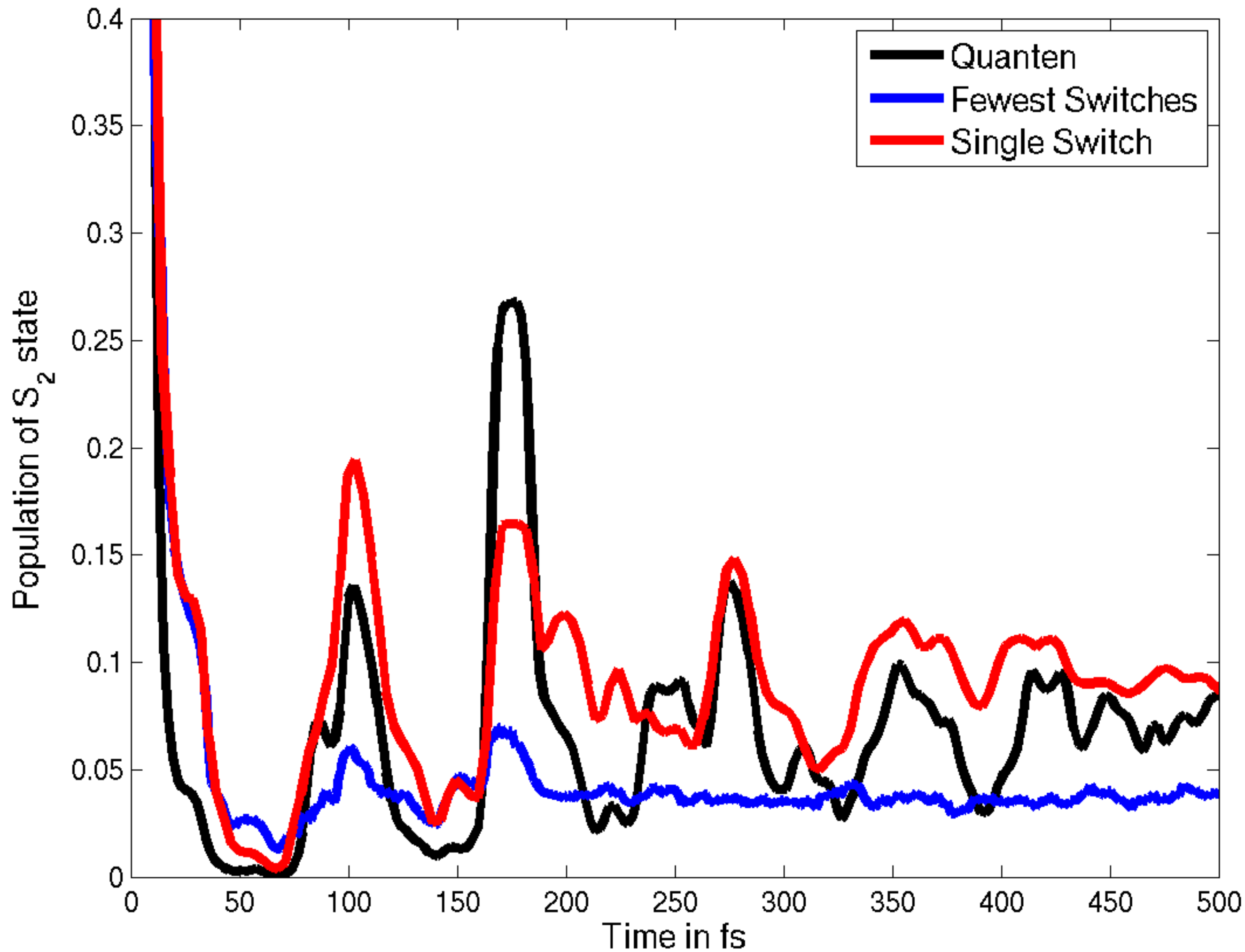
The semigroup $\mathcal{L}_t$ combines

$\oplus$ classical transport along λ^+ and λ^-,

$\oplus$ hops between the surfaces, when $t \mapsto (\lambda^+ - \lambda^-)(z_t)$ is minimal.

The hopping probability comes from a Landau–Zener formula.


Dual
Population
1
0.8
0.6
0
2
4
6
8
10



Quanten
Fewest Switches
Single Switch
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Population of S_2 state
0
50
100
150
200
250
300
350
400
450
500
Time in fs

Computational semiclassics
(Summary)

1. Herman–Kluk propagator
2. LSC-IVR (Egorov's theorem)
3. Surface hopping