# ‘Koopmon’ trajectories in nonadiabatic quantum-classical dynamics

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# Molecular dynamics: adiabatic vs nonadiabatic

- **Slow nuclear motion**: Born-Oppenheimer approximation (1927)

$$\Psi(r,x,t)=\chi(r,t)\psi(x;r), \qquad \partial_t\psi=0\text{: } \textit{adiabatic hypothesis}$$

  - Electronic spectral problem (difficult!): $\widehat{H}_e(r)\psi(r)=E(r)\psi(r)$
  - Lowest order expansion around *electronic-to-nuclear mass ratio*:

$$M_k\ddot{R}_k=-\nabla_{R_k}E(R_1,\dots,R_N)$$

BO: **classical nuclear trajectories + electronic steady state**

- The adiabatic hypothesis is often unsatisfactory → go **nonadiabatic**!

- The appearance of classical motion in BO leads to searching **mixed quantum-classical models** for nonadiabatic dynamics

- Standard approach: truncate Born-Huang expansion (electronic basis)

$$\Psi(r,x,t)=\sum_{k=1}^{\mathcal{N}}\chi_k(r,t)\,\psi_k(x;r) \quad \text{and pick} \quad \chi_k(r,t)\approx\underbrace{\chi_k(r;q_k(t),p_k(t))}_{\textit{Gaussian wavepacket}}$$

**Issues**: 1) difficult spectral problem for $\psi_k$; 2) not Hamiltonian; *etc.*

## Zoo of mixed quantum-classical models

- Mean-field theory (no correlations, more later):
- Surface hopping and its variants (widely accepted, violates uncertainty)
- Wavefunction factorizations (difficulties with classical limit)
- Bohmian/hydrodynamic approaches (inconsistent classical limit)
- Quantum-classical Liouville equation (violates uncertainty)
- Semiclassical Vlasov/Wigner eqns (insufficient/inadequate)

**Available approaches suffer from consistency issues → the search is open!**

*We consider methods involving a true classical component (no Born-Huang)*

# The quantum-classical Liouville equation (QCLE)

In 1981, Aleksandrov and Gerasimenko independently proposed an equation for the **hybrid quantum-classical density**

$$\hat{\rho} \otimes \rho(q,p) \qquad \longrightarrow \qquad \boxed{\widehat{\mathcal{P}}\,(q,p,t)}$$

The **quantum-classical Liouville equation** reads (see Kapral's work)

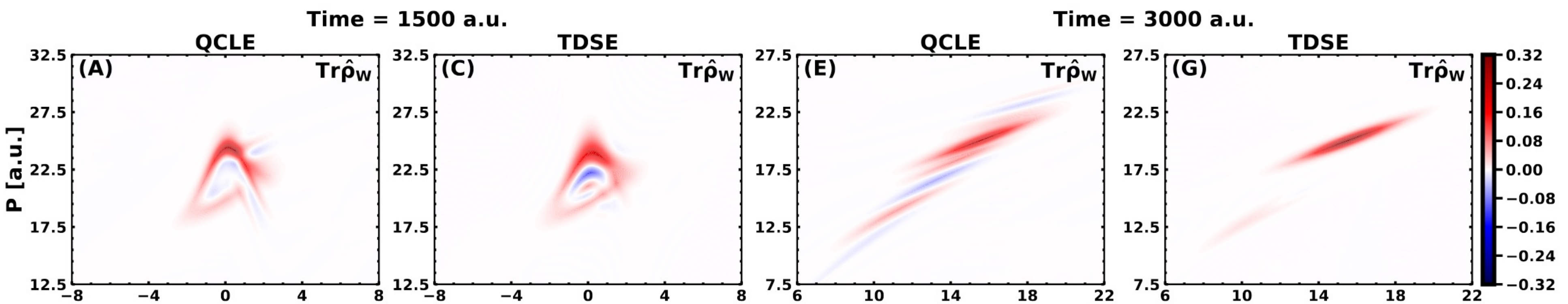
$$\boxed{\frac{\partial \widehat{\mathcal{P}}}{\partial t} = \underbrace{-i\hbar^{-1}[\widehat{H}, \widehat{\mathcal{P}}\,]}_{\textit{quantum-like term}} + \frac{1}{2}\Big(\underbrace{\{\widehat{H}, \widehat{\mathcal{P}}\} - \{\widehat{\mathcal{P}}, \widehat{H}\}}_{\textit{classical-like term}}\Big).}$$

- $\widehat{H} = \widehat{H}(q,p)$ is the Hamiltonian: $\widehat{H} = (m^{-1}\hat{P}^2 + M^{-1}p^2)/2 + V(q,\hat{Q})$

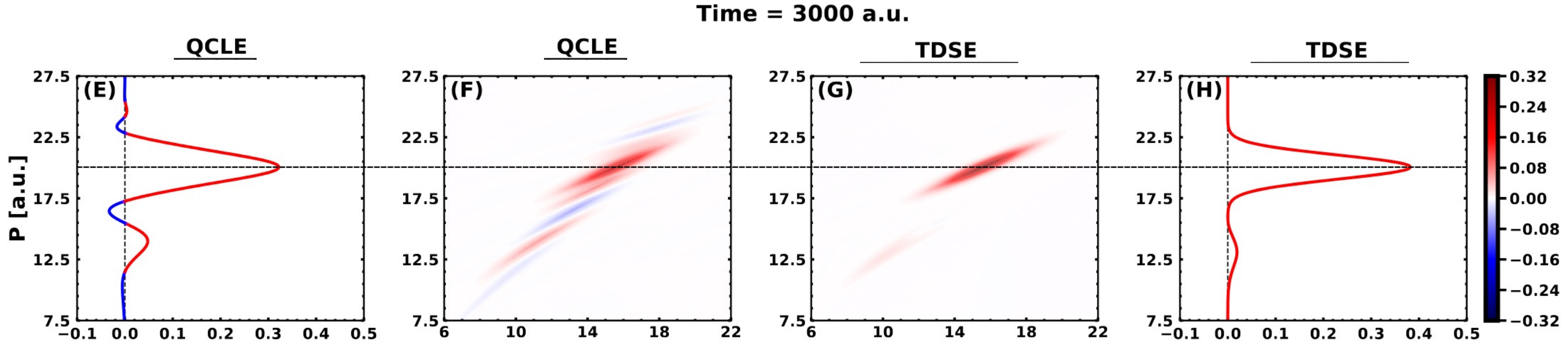
Several studies based on this eqn, which is a continuing source of inspiration

However, there are several issues [Agostini & Ciccotti, 07]. For example, the quantum (and classical) density may be unsigned, thereby **invalidating Heisenberg's principle**. *Also applies to surface hopping* [Bondarenko & Tempelaar '23].

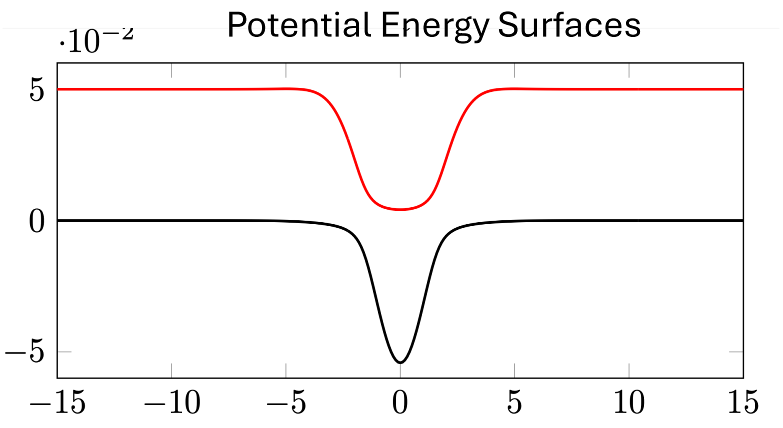
# QCLE results for dual avoided crossing [Gu & Schofield ’26]



Phase-space density Phase-space density Phase-space density Phase-space density

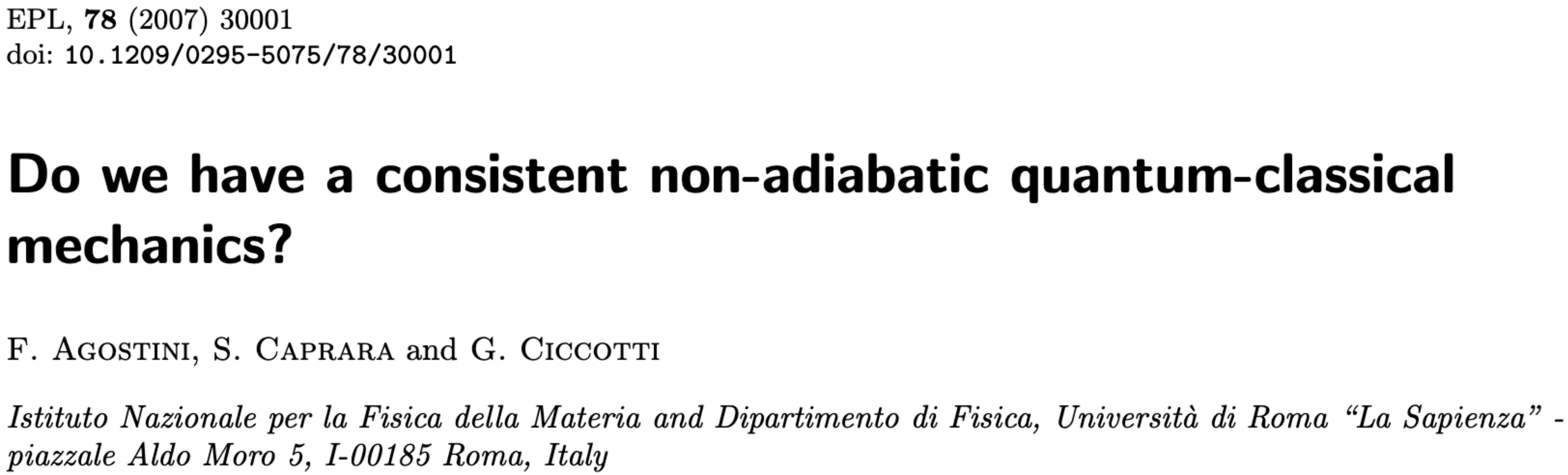


Momentum density Phase-space density Phase-space density Momentum density



QCLE dynamics generate spurious negativities in both phase-space and momentum space.

(Initial momentum: $p_0$=20 a.u.)



EPL, **78** (2007) 30001
doi: `10.1209/0295-5075/78/30001`

# Do we have a consistent non-adiabatic quantum-classical mechanics?

F. Agostini, S. Caprara and G. Ciccotti

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Yes! But it lacks accuracy! **Ehrenfest model** [Zimmerman & Vanicek '12]

$$\frac{\partial\widehat{\mathcal{P}}}{\partial t}+\frac{1}{M}\frac{\partial}{\partial q}(p\widehat{\mathcal{P}})+\frac{\partial}{\partial p}(\langle\widehat{\mathbf{F}}\rangle\widehat{\mathcal{P}})=-\frac{i}{\hbar}\Big[\widehat{V}(q),\widehat{\mathcal{P}}\Big]\,,\qquad\langle\widehat{\mathbf{F}}\rangle=-\frac{\mathsf{Tr}(\widehat{\mathcal{P}}\partial_q\widehat{V})}{\mathsf{Tr}\,\widehat{\mathcal{P}}}$$

*This model underestimates decoherence...* **NEED TO WORK HARDER!**

- Need to satisfy a series of stringent consistency criteria...
- Among others, we want **positivity** (quantum, classical) and **decoherence**
- We focus on modeling; computational performance to be addressed later

# A proposal by George Sudarshan [Sudarshan (1976)]

## Write classical mechanics in terms of (Schrödinger-like) wavefunctions

**Koopman-von Neumann theorem [Koopman, 1931].** Let $H(q,p)$ be a phase-space function and let $\chi \in L^2(\mathbb{R}^2)$ satisfy the

*KvN equation* $$\boxed{i\hbar\,\partial_t\chi = \{i\hbar H, \chi\}}$$

Then, $\rho = |\chi|^2$ satisfies the Liouville eqn $\partial_t\rho = \{H,\rho\}$. **Phase is arbitrary**.

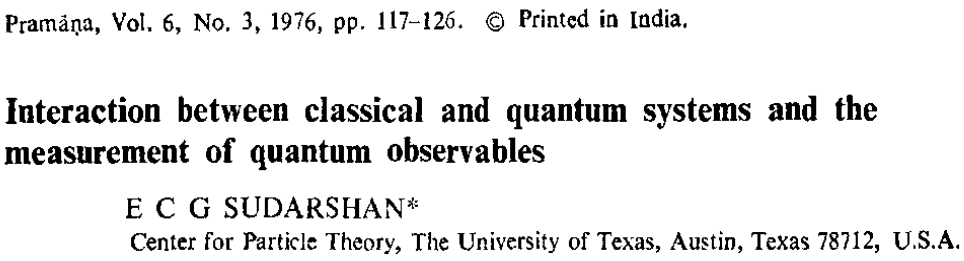
The Hermitian (self-adjoint) operator $\hat{L}_H := \{i\hbar H, \_\}$ is called the **Liouvillian**

$$i\hbar\,\partial_t\chi = \hat{L}_H\chi \quad \longrightarrow$$ *similarity with Schrödinger equation!*

Sudarshan proposed hybrid wavefunctions: $\chi(q,p)\otimes\psi(x) \to \Upsilon(q,p,x)$

# George Sudarshan's work from 1976

*George Sudarshan and Nikolay Bogolyubov with colleagues at the Institute of Theoretical Physics in Kyiv in 1971.*
*Courtesy of Viktor Gerasimenko, National Academy of Sciences in Ukraine, Kyiv.*



Pramāṇa, Vol. 6, No. 3, 1976, pp. 117–126. © Printed in India.

**Interaction between classical and quantum systems and the measurement of quantum observables**

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Sudarshan's hints:

- Take tensor product of Koopman and Schrödinger wavefunctions
- Make classical phases `unobservable' (we don't measure Hamilton-Jacobi functions!)

*Sudarshan's model attracted criticism from several authors [A. Peres & D. Terno '01]*

# Using math to overcome the issues in Sudarshan's theory

*We used math to blend Koopman wavefunctions with Hamilton's action principle:*

1. We replaced the original KvN theory with a variant (Koopman-van Hove, KvH) first appeared in quantization theory (yet fully classical!):
   $\boxed{i\hbar\,\partial_t\chi = \{i\hbar H,\chi\} - (p\partial_p H - H)\chi}$
   → this restores **information on the** **classical phases** (Hamilton-Jacobi)

2. After starting with two classical systems in the KvH description ($\chi = \chi(q,p,x,\pi)$), we quantized one of them: $\chi(q,p,x,\pi) \longrightarrow \Upsilon(q,p,x)$.
   $\boxed{i\hbar\,\partial_t\Upsilon = \{i\hbar\widehat{H},\Upsilon\} - (p\partial_p\widehat{H} - \widehat{H})\Upsilon}$
   → this corresponds to the **quantum-classical hybridization** step

3. We applied a gauge principle so that classical phases become a gauge freedom. Let $\mathbf{z} = (q,p)$ and use **exact factorization** [Abedi et al. '12]:
   $\Upsilon(\mathbf{z},x,t) = \sqrt{D(\mathbf{z},t)}e^{iS(\mathbf{z},t)/\hbar}\psi(x,t;\mathbf{z})$, with $\int|\psi(x,t;\mathbf{z})|^2\,\mathrm{d}x = 1$.
   → makes **classical phases** $S(\mathbf{z},t)$ **unobservable**.

# Mixed quantum-classical Hamiltonian model

Let $\widehat{\mathcal{P}}(q,p,x,x') = \Upsilon(q,p,x)\Upsilon(q,p,x')^*$, $\langle \widehat{A}\rangle = \operatorname{Tr}(\widehat{\mathcal{P}}\widehat{A})/\operatorname{Tr}\widehat{\mathcal{P}}$, and $\mathbf{X}_{\widehat{A}} = (\partial_p \widehat{A}, -\partial_q \widehat{A})$:

$$\boxed{i\hbar\frac{\partial\widehat{\mathcal{P}}}{\partial t} + i\hbar\underbrace{\operatorname{div}\Big(\widehat{\mathcal{P}}\big\langle \mathbf{X}_{\delta h/\delta\widehat{\mathcal{P}}}\big\rangle\Big)}_{\textit{probability transport}} = \underbrace{\left[\frac{\delta h}{\delta\widehat{\mathcal{P}}},\widehat{\mathcal{P}}\right]}_{\textit{unitary evolution}}, \quad \text{with} \quad h=\int\underbrace{\Big\langle \widehat{H}\operatorname{Tr}\widehat{\mathcal{P}} + i\hbar\{\widehat{\mathcal{P}},\widehat{H}\}\Big\rangle}_{\textbf{Ehrenfest + backreaction}} \mathrm{d}z}$$

The backreaction energy has an analogue in spin-orbit coupling [C.T. ’26].

Define $\mathcal{D} = \operatorname{Tr}\widehat{\mathcal{P}}$ (classical density) and $\widehat{\boldsymbol{\Gamma}} = i\hbar\mathcal{D}^{-1}[\widehat{\mathcal{P}}, \mathbf{X}_{\widehat{\mathcal{P}}}]/2$ [Mead ’92]:

$$\frac{\partial\widehat{\mathcal{P}}}{\partial t} + \frac{1}{2}\Big(\{\widehat{H},\widehat{\mathcal{P}}\} - \{\widehat{\mathcal{P}},\widehat{H}\}\Big) + \operatorname{div}\left(\frac{\widehat{\mathcal{P}}}{\mathcal{D}}\operatorname{Tr}\Big[\mathbf{X}_{\widehat{H}}, \widehat{\boldsymbol{\Gamma}}\Big]_{\mathsf{JL}}\right) = -\frac{i}{\hbar}\Big(\big[\widehat{H},\widehat{\mathcal{P}}\big] + \big[\widehat{\boldsymbol{\Gamma}}, \nabla\widehat{H}\big]\Big),$$

where $[\mathbf{A},\mathbf{B}]_{\mathsf{JL}} = \mathbf{A}\cdot\nabla\mathbf{B} - \mathbf{B}\cdot\nabla\mathbf{A}$.

Reduces to: *1) QCLE for $\widehat{\boldsymbol{\Gamma}} \simeq 0$. 2) Ehrenfest if backreaction is neglected.*

*The idea is not to use this formidable model for practical purposes; rather use* **its Hamiltonian structure as a platform for designing new algorithms***.*

# Koopmons – a coupled-trajectory particle method

- Given the system

$$i\hbar\frac{\partial\widehat{\mathcal{P}}}{\partial t}+i\hbar\,\mathrm{div}\Big(\widehat{\mathcal{P}}\Big\langle\mathbf{X}_{\delta h/\delta\widehat{\mathcal{P}}}\Big\rangle\Big)=\left[\frac{\delta h}{\delta\widehat{\mathcal{P}}},\widehat{\mathcal{P}}\right],\quad\text{with}\quad h=\mathrm{Tr}\int\widehat{\mathcal{P}}\Big(\widehat{\mathcal{H}}+i\hbar\{\widehat{\mathcal{P}},\widehat{\mathcal{H}}\}/\mathrm{Tr}\widehat{\mathcal{P}}\Big)\mathrm{d}z,$$

  the $\hbar-$term prevents point-particle solutions of the type

$$\widehat{\mathcal{P}}(\mathbf{z},t)=\sum_a w_a\hat{\rho}_a(t)\delta(\mathbf{z}-\boldsymbol{\zeta}_a(t))$$

- Our strategy: regularize the $\hbar$-term by replacing

$$\widehat{\mathcal{P}}\to\bar{\mathcal{P}}=\int K_\alpha(\mathbf{z}-\mathbf{z}')\widehat{\mathcal{P}}(\mathbf{z}')\,\mathrm{d}^6z.$$

  where $K_\alpha$ is a (Gaussian) mollifier depending on a regularization parameter $\alpha$

- The **regularized energy** reads: $\bar{h}=\mathrm{Tr}\int\Big(\widehat{\mathcal{P}}\widehat{\mathcal{H}}+i\hbar\bar{\mathcal{P}}\{\bar{\mathcal{P}},\widehat{\mathcal{H}}\}/\mathrm{Tr}\bar{\mathcal{P}}\Big)\mathrm{d}z$

- As the point-particle (*koopmon*) ansatz is now an exact solution, the latter yields the **Hamiltonian particle scheme** (w. $K_s(\mathbf{z})=K(\mathbf{z}-\boldsymbol{\zeta}_s)$)

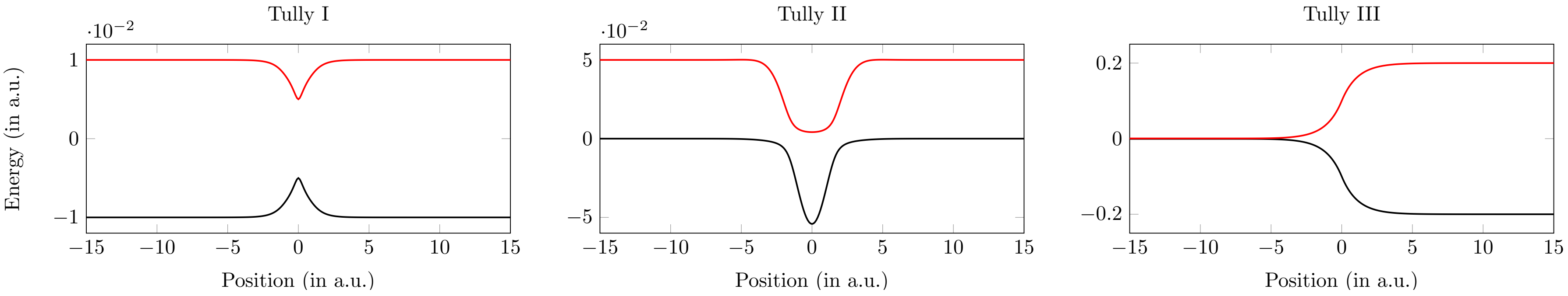
$$\dot{q}_a=w_a^{-1}\partial_{p_a}h,\qquad\dot{p}_a=-w_a^{-1}\partial_{q_a}h,\qquad i\hbar\dot{\rho}_a=w_a^{-1}[\partial_{\rho_a}h,\rho_a],$$

$$h=\sum_a w_a\Big\langle\rho_a,\widehat{H}_a+i\hbar\sum_b w_b[\rho_b,\mathcal{I}_{ab}]\Big\rangle\,,\qquad\widehat{\mathcal{I}}_{ab}=\int\frac{K_a\{K_b,\widehat{H}\}-K_b\{K_a,\widehat{H}\}}{4\sum_c w_cK_c}\,\mathrm{d}^2z.$$

# Numerical validation: Tully models

In Pauli matrix notation: $\widehat{H}(r,p) = \dfrac{p^2}{2M} + H_0(r)\mathbf{1} + H_1(r)\widehat{\sigma}_z + H_2(r)\widehat{\sigma}_x$

- Tully 1 model: $H_0 = 0$, $H_1 = a\,\mathrm{sgn}(r)(1 - e^{-b|r|})$, and $H_2 = ce^{-dr^2}$
- Tully 2 model: $H_0 = e_0 - ae^{-br^2}$, $H_1 = -H_0$, and $H_2 = ce^{-dr^2}$
- Tully 3 model: $H_0 = 0$, $H_1 = a$, and $H_2 = 2b\Theta(r) - b\,\mathrm{sgn}(r)e^{-c|r|}$



**Initial condition:** Gaussian wavepacket $\otimes$ spin-up state

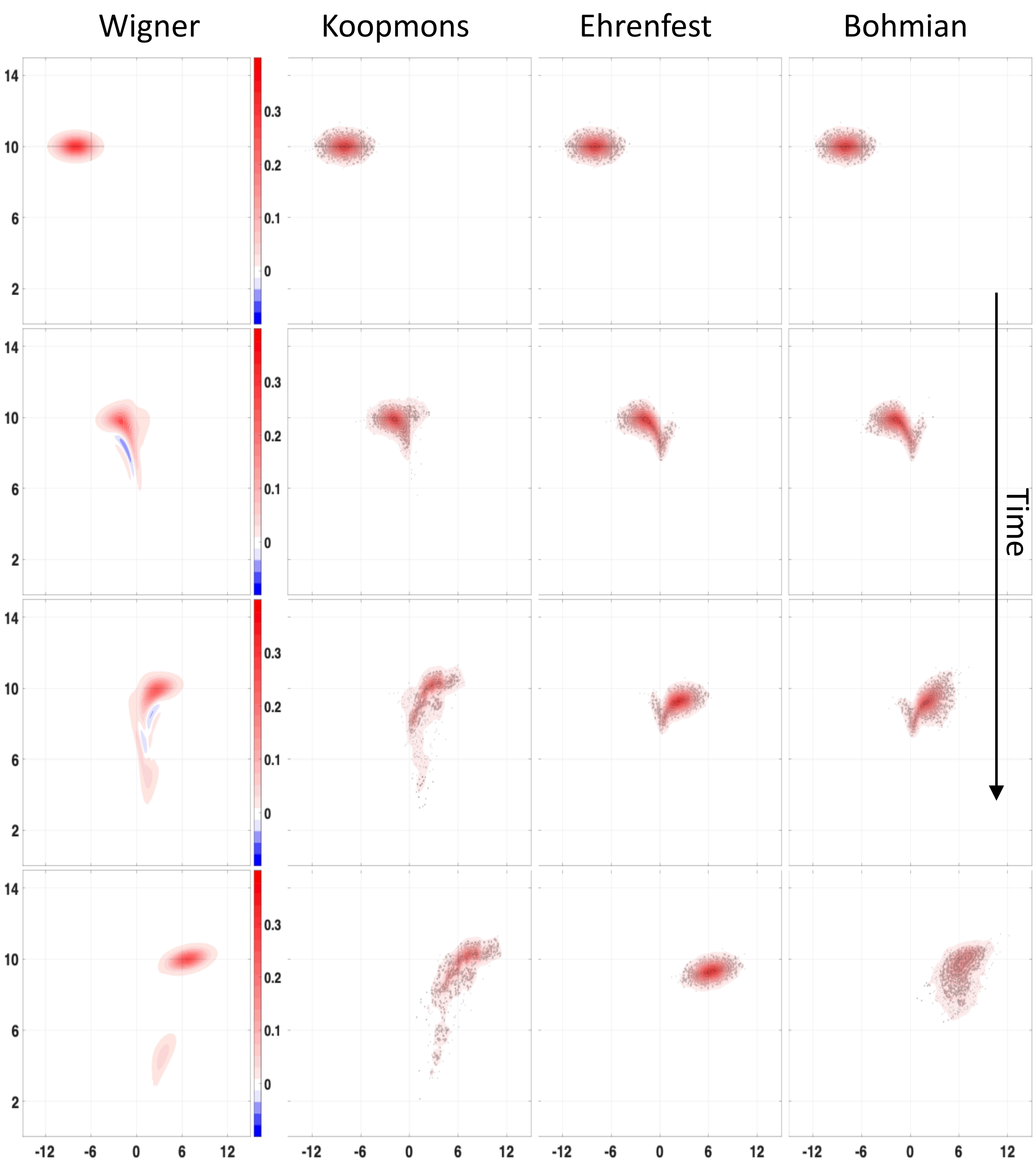
$$|\psi_0\rangle = (\pi\Delta_0^2)^{-1/4} \exp\left(-(r-r_0)^2/\Delta_0{}^2 + i2k_0 r\right)/2 \otimes |+\rangle, \quad \text{with} \quad \Delta_0 = 20/k_0$$

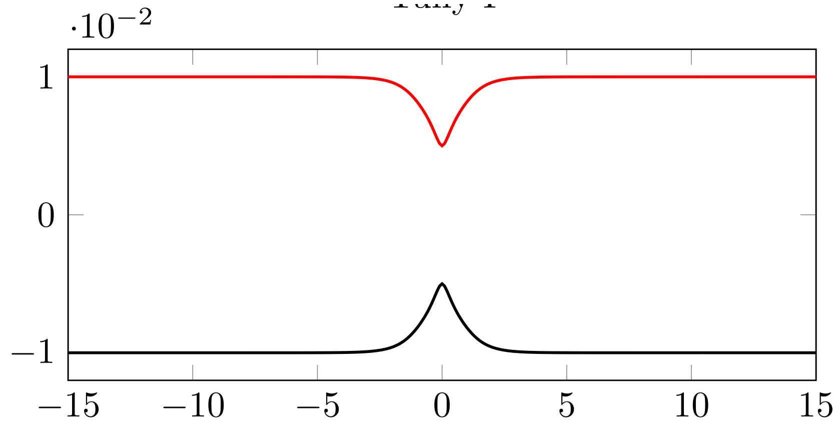
**Outputs:** we plot phase-space dynamics as well as

Population: $\hat{\rho}_{11} = 1 - \hat{\rho}_{22}$, purity: $\|\hat{\rho}\|^2 = \mathrm{Tr}\,\hat{\rho}^2$

**We also compared with a similar coupled-trajectory code based on Bohmian dynamics**

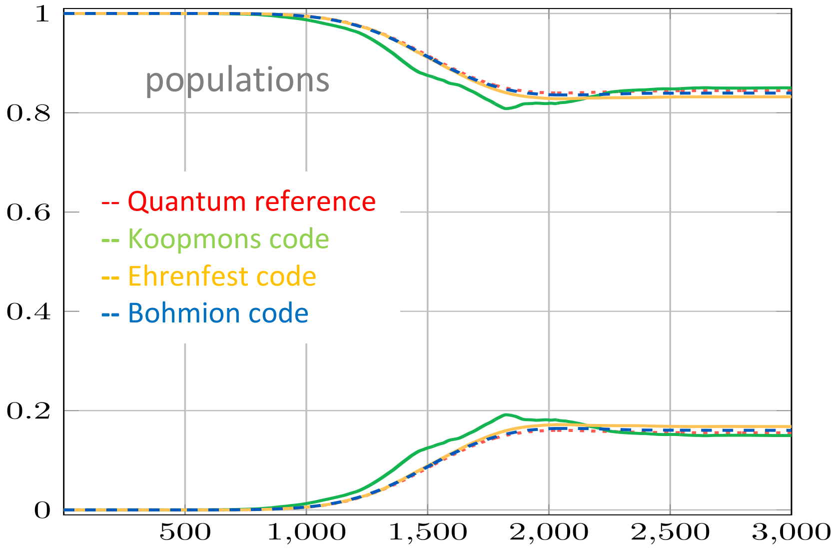
# Laptop simulations: single avoided crossing

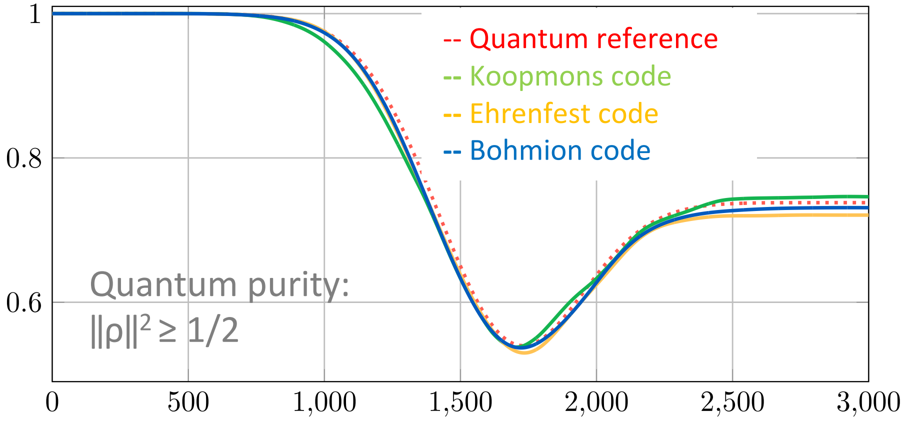




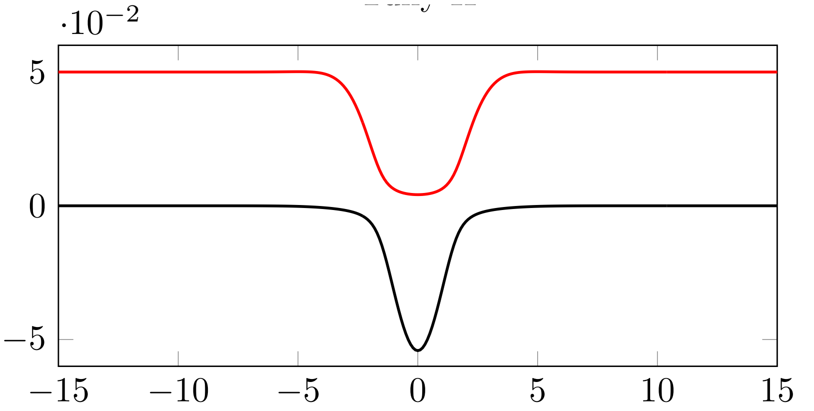
*Low initial momentum: $p_0 = 10$*

1000 particles; α=0.325; Δt=2



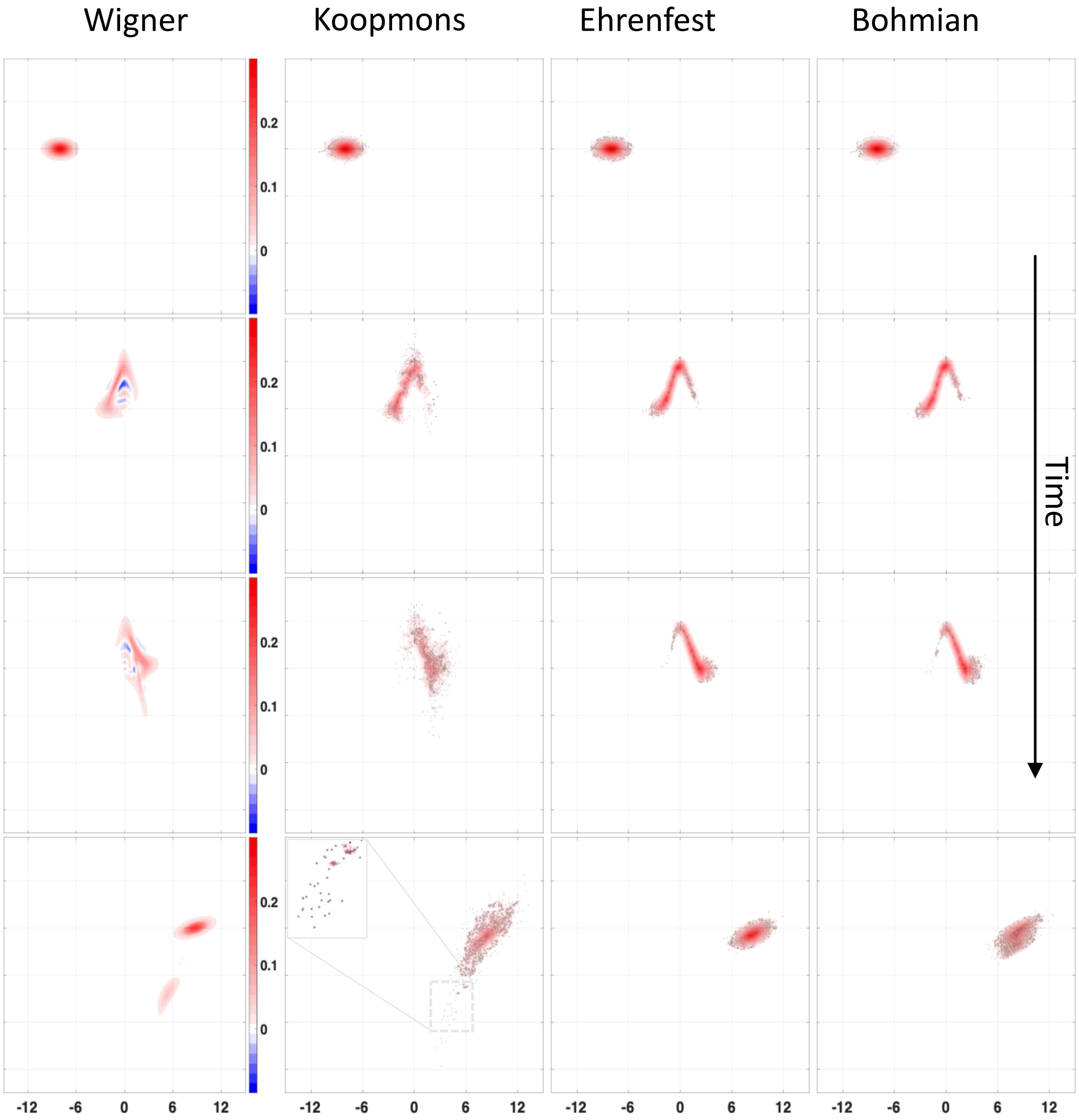


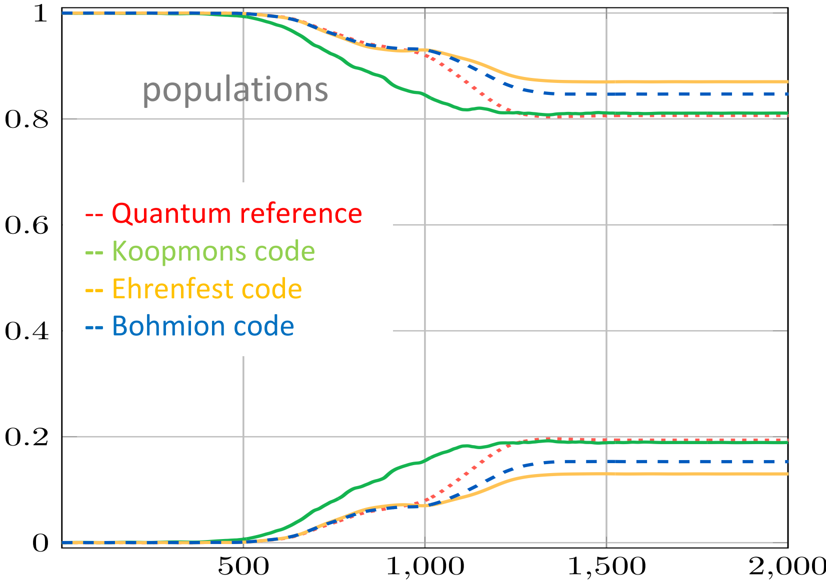
# Laptop simulations: dual avoided crossing

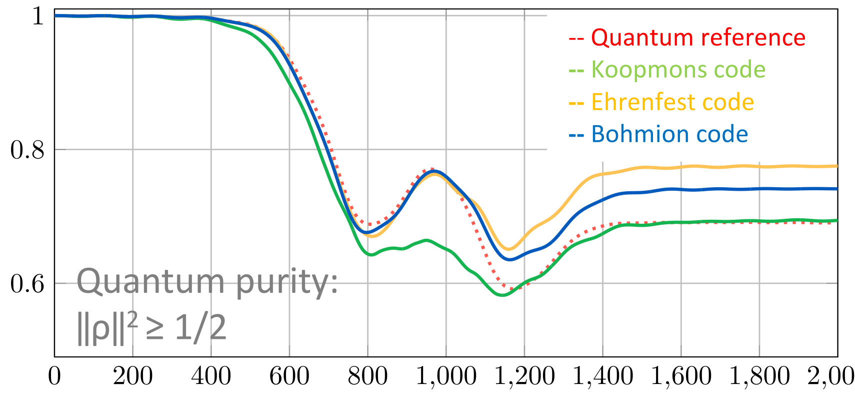


*Low initial momentum: $p_0 = 16$*

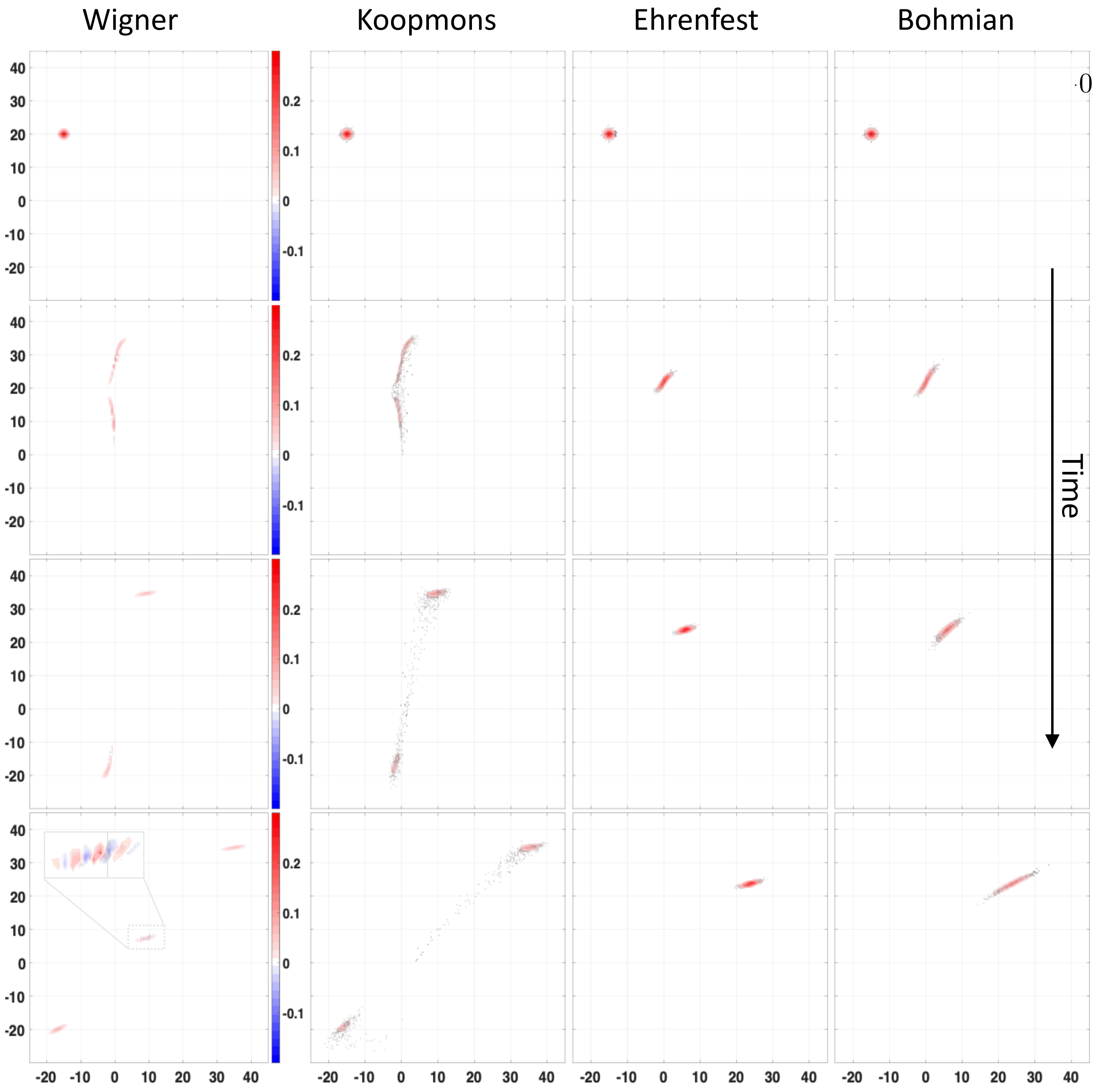
1000 particles; α=0.325; Δt=2

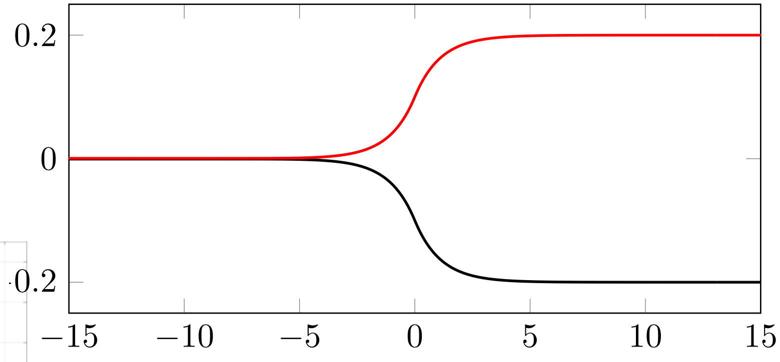






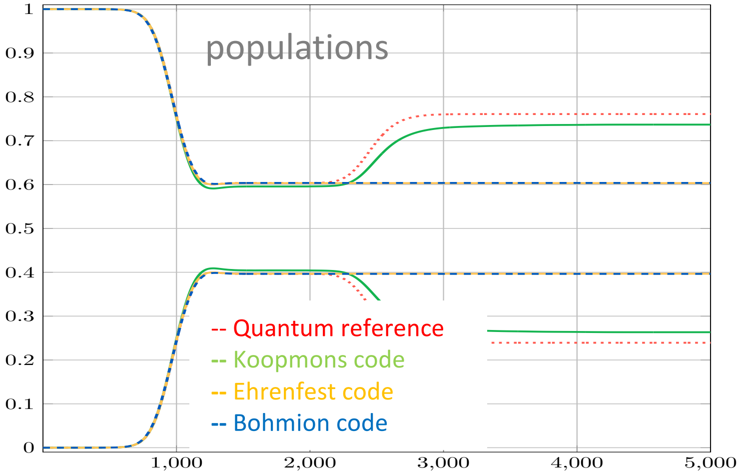
# Laptop simulations: extended coupling region

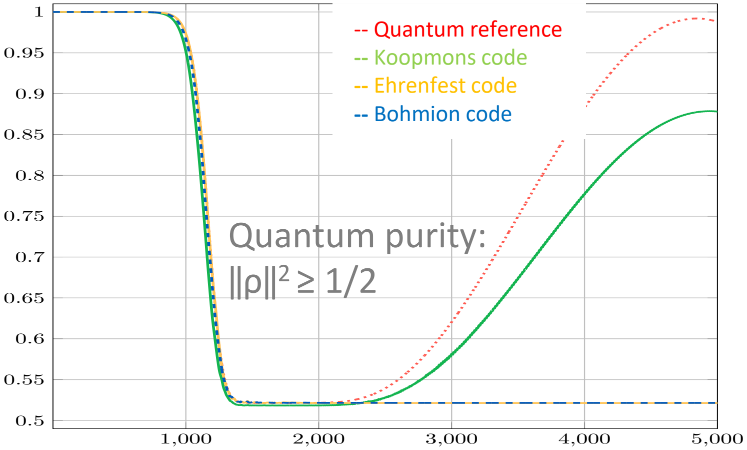




*Intermediate initial momentum: $p_0 = 20$*

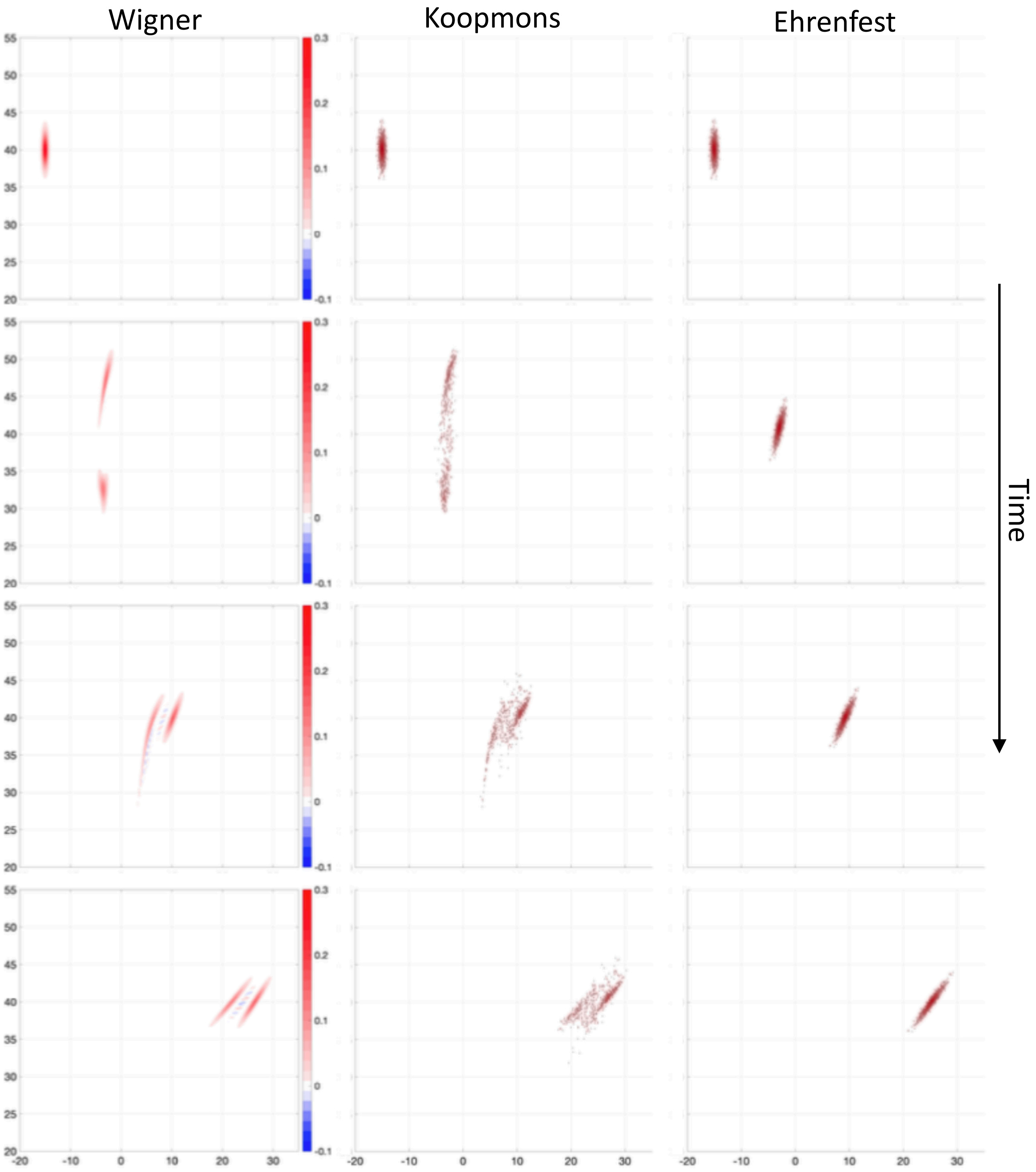
1000 particles; α=0.325; Δt=2

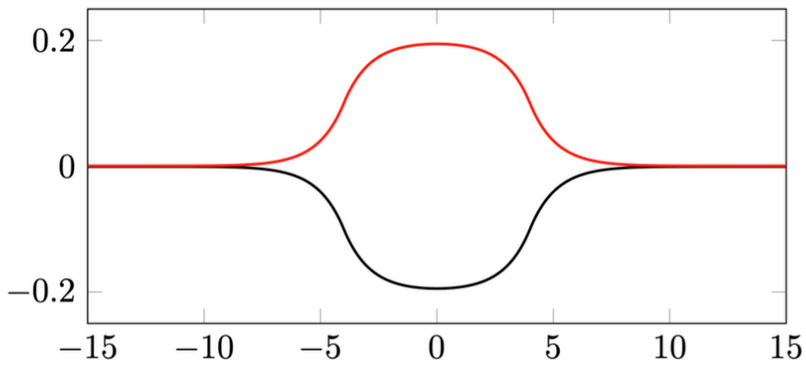




*Bohmian particle code necessitates a much finer integration grid parameter (α ~ 0.02) with resulting increased costs.*

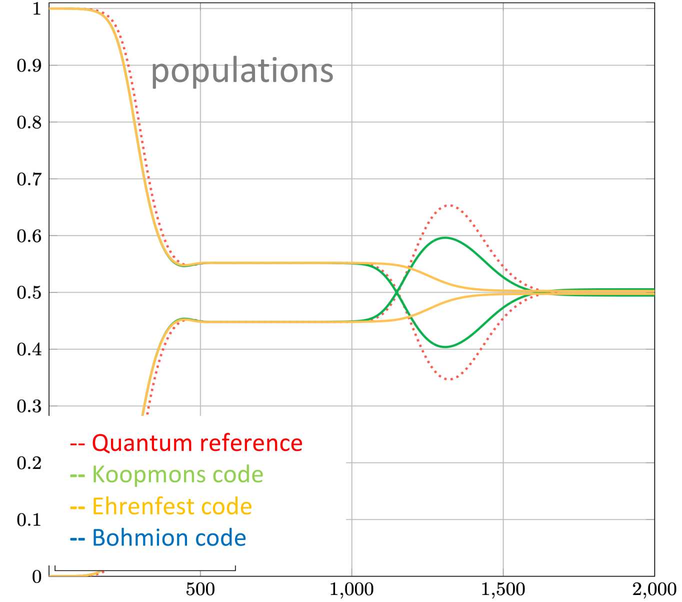
# Laptop simulations: double arch

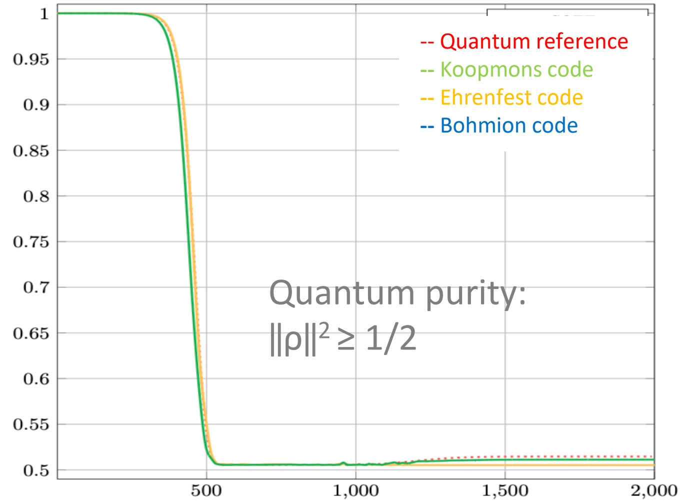




*Initial momentum: $p_0 = 40$*

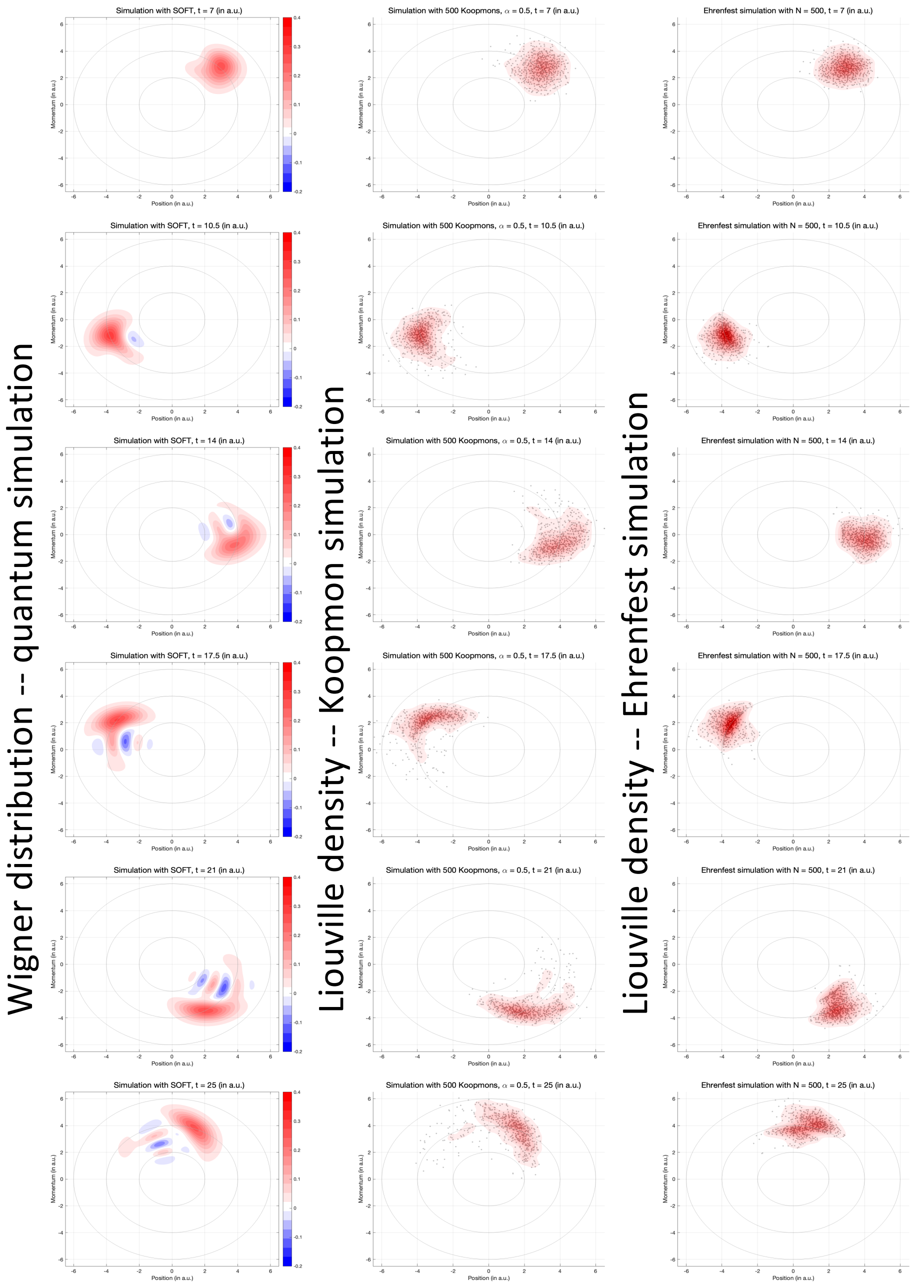
500 particles; α=0. 5; Δt=2



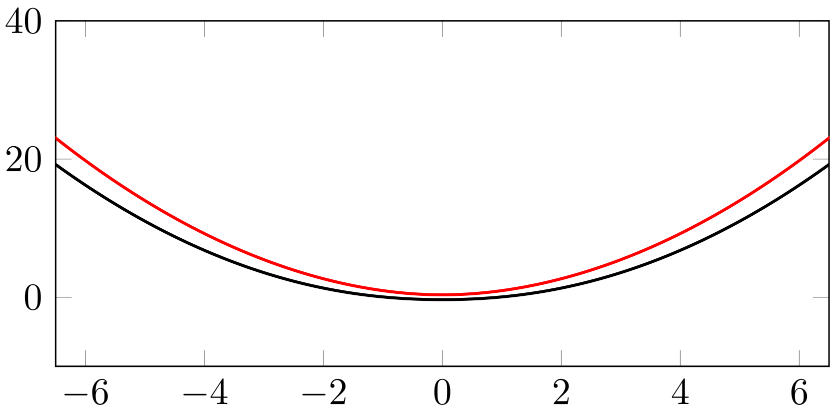


# Rabi Hamiltonian: *ultrastrong* coupling

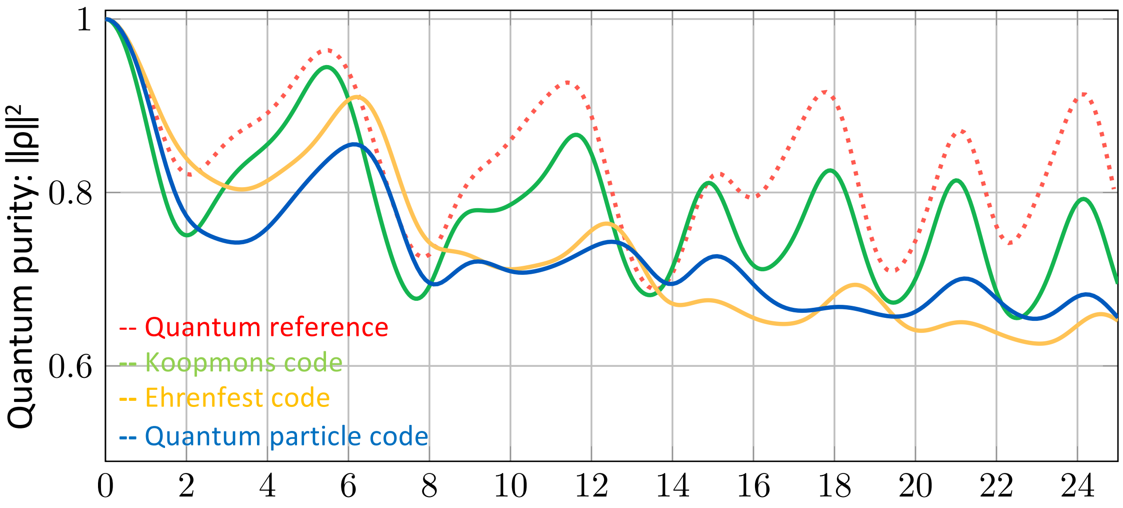
$$m = \omega = 1, \quad \gamma = 0.29, \quad C_0 = 0.35.$$



$$\hat{H}(q,p) = \frac{1}{2}\left(m\omega^2 q^2 + \frac{p^2}{m}\right)\hat{\sigma}_0 + \gamma q\hat{\sigma}_z + C_0\hat{\sigma}_x$$



500 particles; α=0.5; Δt=0.1



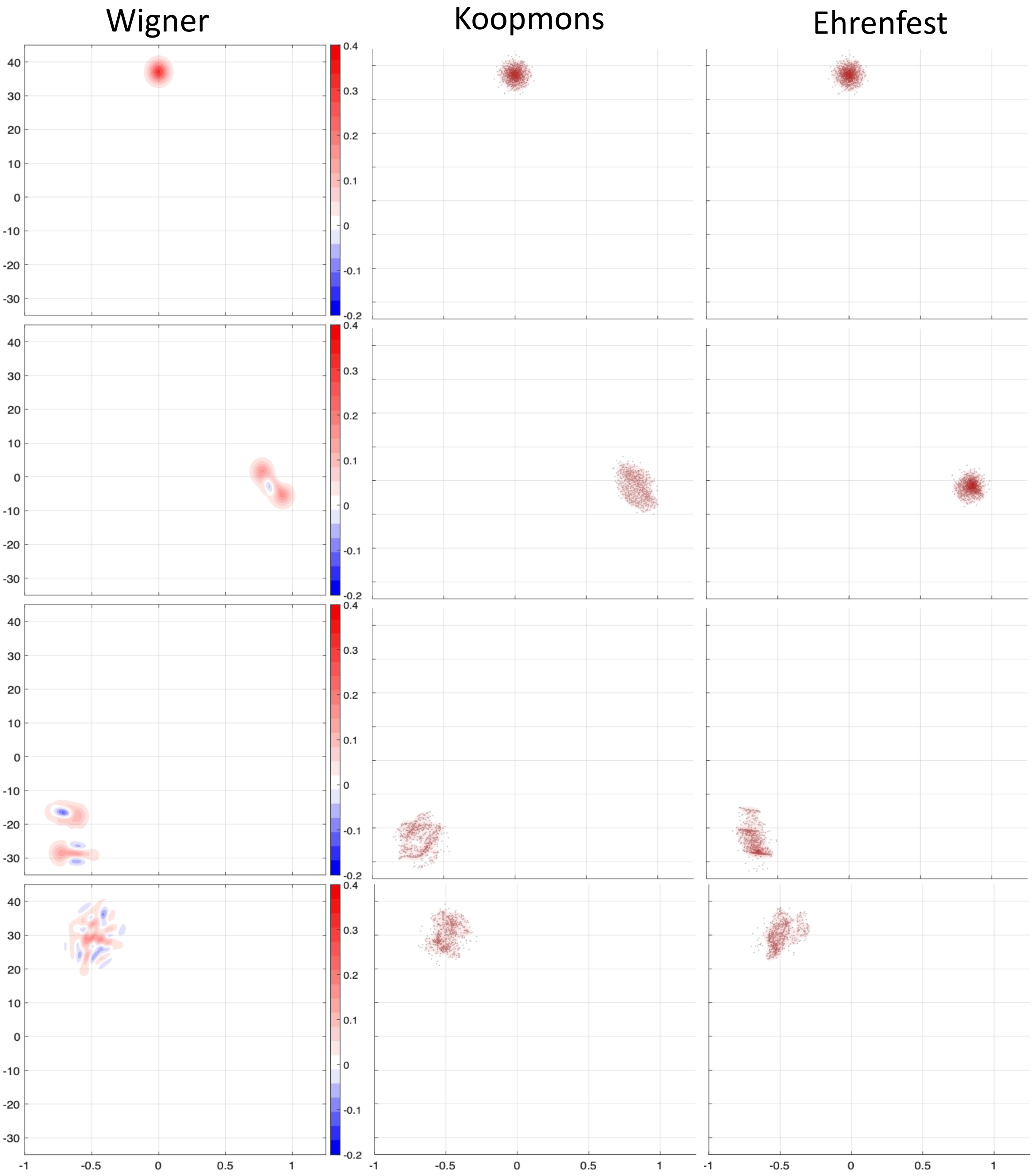
LONGER-TIME SIMULATION:

As the Wigner negative regions get wider, the hybrid results in the quantum sector start deviating from the fully quantum dynamics.

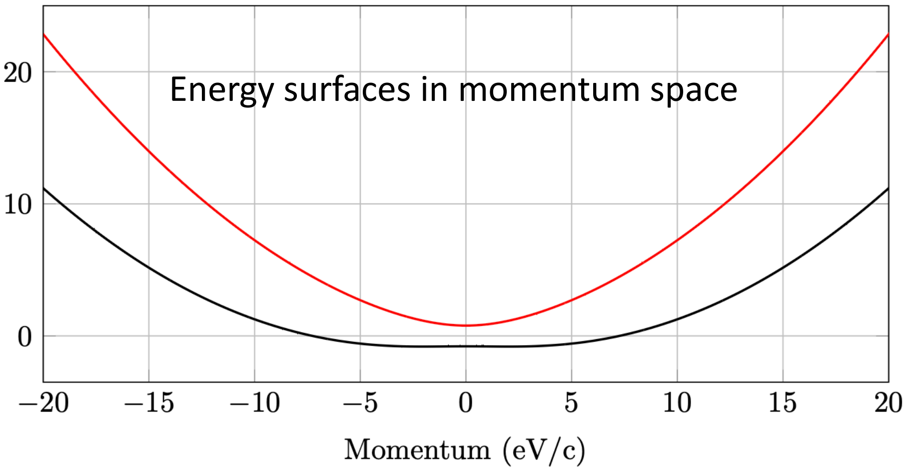
# Rashba-dominated InAs nanowire with quantum dot

High Rashba-coupling semiconductor:

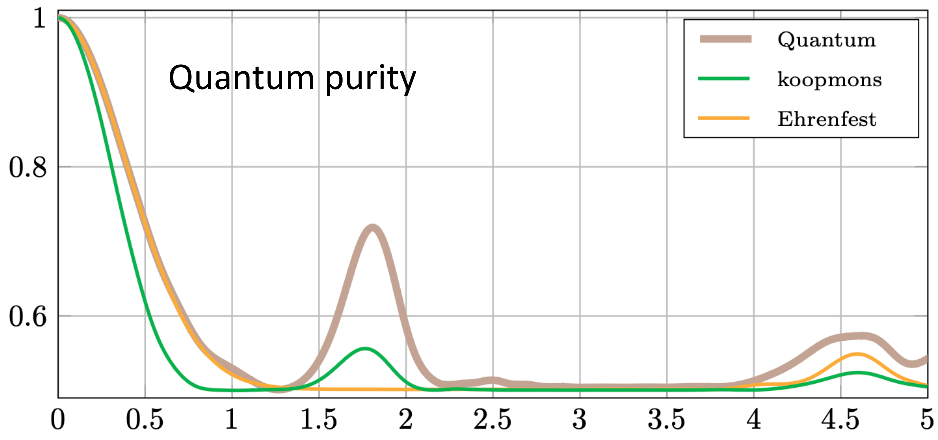
$E_{SO}=m\alpha_R^2/2$, $E_Z=g_e B_x/4$, $R=2E_{SO}/E_Z=1.26$, $\hbar\omega=178\text{GHz}$



$$\widehat{H}=\frac{1}{2m}p^2+\alpha_R\widehat{\sigma}_y p+\frac{1}{2}m\omega^2q^2+\frac{1}{4}g_eB_x\widehat{\sigma}_x$$



500 particles; $\alpha$=0.5. $p_0$=37.3 eV/c



*In this case, the quantum-classical methods are taken beyond their regime of validity: full quantum interference develops very quickly!*

*Unlike Ehrenfest, the koopmons still capture qualitative decoherence effects (early bump).*

# Tackling the curse of dimensions

- Take two dof's for simplicity:

$$\widehat{\mathcal{P}}(\mathbf{z}_1,\mathbf{z}_2,t)=\sum_{a,b}w_aw_b\,\hat{\varrho}_{ab}(t)\,\delta(\mathbf{z}_1-\zeta_1^{(ab)}(t))\,\delta(\mathbf{z}_2-\zeta_2^{(ab)}(t))$$

with $\zeta_1^{(a,b)}=\zeta_1^{(a,b')}$ and $\zeta_2^{(a,b)}=\zeta_2^{(a',b)}$, so that $f(\mathbf{z}_1,\mathbf{z}_2)=f(\mathbf{z}_1)f(\mathbf{z}_2)$.

- Consider the case (applies to most molecular models, can be extended)

$$\widehat{H}(\mathbf{z}_1,\mathbf{z}_2)=H_c(\mathbf{z}_1,\mathbf{z}_2)\mathbf{1}+\widehat{H}_Q+h_2(\mathbf{z}_2)\widehat{H}_1(\mathbf{z}_1)+h_1(\mathbf{z}_1)\widehat{H}_2(\mathbf{z}_2),$$

- Then, with the notation $K_\ell^{(s)}=K(\mathbf{z}_\ell-\zeta_\ell^{(s)})$, the 4D integral

$$\widehat{I}_{aba'b'}=\iint\left(\frac{K_1^{(a)}K_2^{(b)}K_2^{(b')}\{K_1^{(a')},\widehat{H}\}_1}{\sum_{c,d}w_cw_dK_1^{(c)}K_2^{(d)}}+\frac{K_1^{(a)}K_2^{(b)}K_1^{(a')}\{K_2^{(b')},\widehat{H}\}_2}{\sum_{c,d}w_cw_dK_1^{(c)}K_2^{(d)}}\right)\mathrm{d}^2z_1\mathrm{d}^2z_2.$$

becomes a **quadratic combination of 2D-integrals**

$$\widehat{I}_{aba'b'}=\widehat{\mathcal{I}}_1^{(aa')}\mathcal{J}_2^{(bb')}+\mathcal{I}_1^{(aa')}\widehat{\mathcal{J}}_2^{(bb')}+\mathcal{I}_2^{(bb')}\widehat{\mathcal{J}}_1^{(aa')}+\widehat{\mathcal{I}}_2^{(bb')}\mathcal{J}_1^{(aa')}.$$

with $\widehat{\mathcal{I}}_\ell^{(ss')}:=\displaystyle\int\frac{K_\ell^{(s)}\{K_\ell^{(s')},\widehat{H}_\ell\}_\ell}{\sum_c w_cK_\ell^{(c)}}\,\mathrm{d}^2z_\ell,\qquad \widehat{\mathcal{J}}_\ell^{(ss')}:=\int\frac{K_\ell^{(s)}K_\ell^{(s')}\widehat{H}_\ell}{\sum_d w_dK_\ell^{(d)}}\,\mathrm{d}^2z_\ell,$

## Ongoing directions:

- Higher-dimensional implementation
- Problems with multiple-level systems (electron/proton transfer models)
- Hydrodynamic closures (solute-solvent interaction)
- Mixed quantum-classical entropies (von Neumann doesn't work!)
- Mixed quantum-classical spin systems (radical pairs, spintronics)

# Need for more initiatives at the math/chemistry interface

- The new level of computational capability promises to accelerate molecular sciences across countless fields and profoundly benefit society
- Need to optimize balance between accuracy and computational cost
- The current mainstream approach develops data science/machine learning tools to **optimize the computational efficiency of existing schemes**
- However, many current schemes hinge on **mathematical models from 39–99 years ago** (BOMD, DFT, SH), when the accuracy, transferability, and approximations were dictated by a much lower computer power
- Prioritizing computational speed, the current approach overlooks questions of transferability and validity of the approximations. These questions call for **new flexible mathematical methods** retaining the nonlinear dynamics at different scales while allowing computational feasibility
- A pathway for the required paradigm shift involves **research programs for chemists and mathematicians to talk** beyond computational speed
- While chemists need to benefit from the **guidance of mathematical structure**, mathematicians need to accept **flexibility in the use of rigor**

# That's all – thank you!

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