Numerical analysis of dynamics in minimal models for cavity-coupled molecules

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CENTRE EUROPÉEN DE SCIENCES QUANTIQUES

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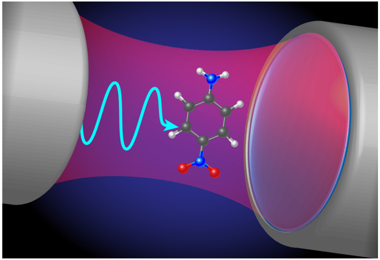
Goal : Describe quantum dynamics of polaritonic systems

Eugene WIGNER

Hermann WEYL

Hilbert space $\mathcal{H}$ → Phase space $\{q,p\}$



T. S. Haugland et al., "Coupled cluster theory for molecular polaritons: Changing ground and excited states," Phys. Rev. X 10, 041043 (2020), adapted by APS

Wigner formalism of Quantum Mechanics

- A phase space representation of Quantum Mechanics, Weyl symbols :

$$\Omega_W(q,p) = \int \mathrm{d}\xi \left\langle q - \frac{\xi}{2} \middle| \hat{\Omega}(\hat{q},\hat{p}) \middle| q + \frac{\xi}{2} \right\rangle e^{\frac{i}{\hbar}p\xi}$$

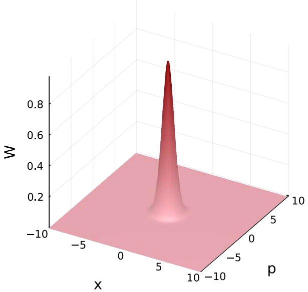
- The Wigner function, a quasi-probability distribution :

$$\mathbf{W}(\mathbf{q},\mathbf{p}) = \rho_{\mathbf{W}}(\mathbf{q},\mathbf{p})$$

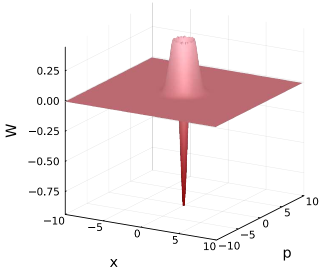
- Mean value of any Quantum Mechanical operator :

$$\left\langle \hat{\Omega}(\hat{q},\hat{p}) \right\rangle = \int \mathrm{d}q\mathrm{d}p\, W(q,p)\Omega_W(q,p)$$

Wigner function = Quasi-probability distribution



Wigner function for $\hat{\rho} = |0\rangle\langle 0|$



Wigner function for $\hat{\rho} = |1\rangle\langle 1|$

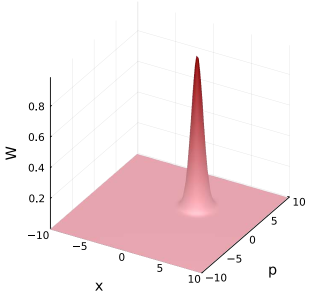
Initial state choice

Coherent state : $|\alpha\rangle$

- Displaced vacuum :

$$|\alpha\rangle = \hat{D}(\alpha)\,|0\rangle \qquad (1)$$

- Wigner function always positive for every alpha
- Reproduces the classical motion



Wigner function for $\hat{\rho} = |\alpha\rangle\langle\alpha|$

From Liouville-von Neumann equation :

$$i\hbar\dot{\hat{\rho}} = [\hat{H}, \hat{\rho}]$$

To Moyal equation :

$$\dot{W} = \frac{2}{\hbar} W \sin\left(\frac{\hbar}{2}\Lambda\right) H_W$$

Expansion :

$$\dot{W} = W\Lambda H_W - \frac{\hbar^2}{24} W\Lambda^3 H_W + o(\hbar^4)$$

Truncated Wigner Approximation

$$\dot{W} = W\Lambda H_W = \frac{\partial W}{\partial p}\frac{\partial H_W}{\partial q} - \frac{\partial H_W}{\partial p}\frac{\partial W}{\partial q}$$

Truncated Wigner Approximation

Mean value of an operator within the TWA :

$$\left\langle \hat{\Omega}(\hat{q},\hat{p}) \right\rangle = \int \mathrm{d}q\mathrm{d}p\, W(q(0),p(0))\Omega_W(q_{cl},p_{cl},t)$$

Statistical solving with classical trajectories!

Application :

- Choose initial points for N trajectories according to the initial Wigner probability distribution
- Evolve the points with the classical equations of motion
- Compute the time evolution of the observable

Mean value

$$\left\langle \hat{\Omega}(t) \right\rangle = \frac{1}{N}\sum_{i=1}^{N} \Omega_{W,cl,i}(t)$$

And for discrete systems? (Spin systems, Two level systems, ...)

$\hookrightarrow$ Coherent state representation

Spin coherent state Wigner function

$$W(s_\perp, s_z) = \frac{1}{\pi S} e^{-s_\perp / S} \delta\left(s_z - S\right)$$

$$S = \frac{N}{2}, \quad s_\perp = \left(s_x^2 + s_y^2\right)^{1/2}$$

Need for a new approach!

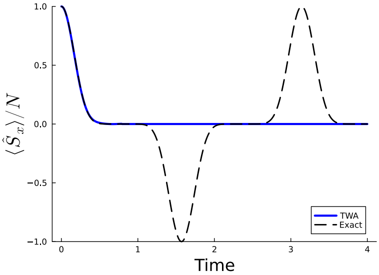


Figure 1 – Dynamics for Ising interactions with the TWA. Captures short time aspects (decay) but not revivals.

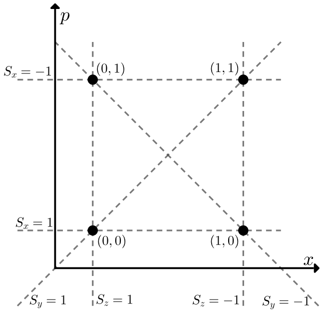
Discrete Phase Space

From Bloch vector $\vec{r}_\alpha$:

$$\begin{pmatrix}1\\1\\1\end{pmatrix}, \begin{pmatrix}1\\-1\\-1\end{pmatrix}, \begin{pmatrix}-1\\-1\\1\end{pmatrix}, \begin{pmatrix}-1\\1\\-1\end{pmatrix}$$

To phase space vector $\alpha = (x, p)$:

$$(0,0), (1,0), (0,1), (1,1)$$



Discrete Wigner function

$$w_\alpha = \frac{1}{4} Tr\left(\hat{\rho}_{init}(\mathbb{1} + \vec{r}_\alpha \cdot \vec{\hat{\sigma}})\right)$$

Discrete Truncated Wigner Approximation

Positivity of w_α depends on :

- Definition of the discrete phase space
- Initial state

Example :

- All spins starting in the z direction
- $w_{(0,0)} = w_{(0,1)} = 1/2$
  $w_{(1,0)} = w_{(1,1)} = 0$

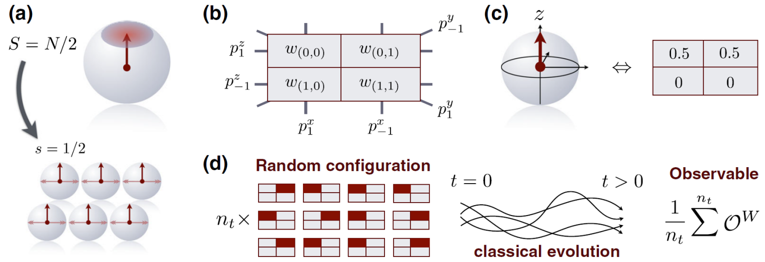


Figure 2 – Discrete Truncated Wigner Approximation application [3].

Discrete Truncated Wigner Approximation

Sampling for Ising, spins starting in x :

$$\begin{pmatrix}1\\1\\1\end{pmatrix},\begin{pmatrix}1\\-1\\1\end{pmatrix},\begin{pmatrix}1\\1\\-1\end{pmatrix},\begin{pmatrix}1\\-1\\-1\end{pmatrix}$$

$$\implies w_\alpha = 1/4$$

DTWA captures quantum dynamics of discrete systems

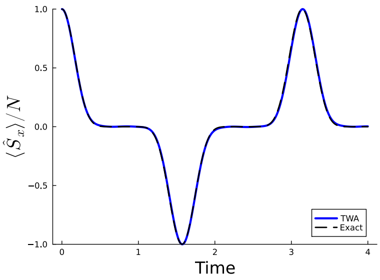


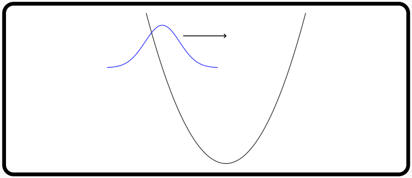
Figure 3 – Dynamics for Ising interactions with the DTWA.

General Hamiltonian

$$\hat{H} = \frac{1}{2}\sum_{i\neq j}\left[\frac{J_{ij}^{\perp}}{2}(\hat{\sigma}_i^x\hat{\sigma}_j^x + \hat{\sigma}_i^y\hat{\sigma}_j^y) + J_{ij}^z\hat{\sigma}_i^z\hat{\sigma}_j^z\right] + \Omega\sum_i \hat{\sigma}_i^x$$

Applications :

- Vibrational states of molecules
- Quantized EM field



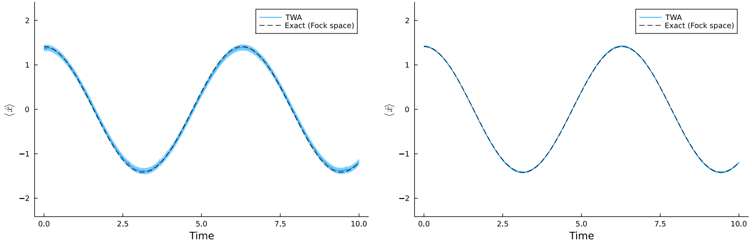


Figure 4 – TWA results for the Harmonic Oscillator for $N = 100$ and $N = 1000$ trajectories.

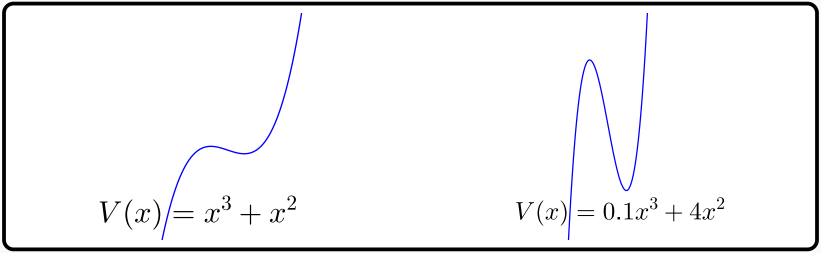
Limits of the TWA : Anharmonic Oscillator

Using TWA is neglecting :

$$\frac{\hbar^2}{24} W \Lambda^3 H_W$$

Initial state : Harmonic Oscillator coherent state

$$\hat{\rho} = |\alpha\rangle\langle\alpha|$$



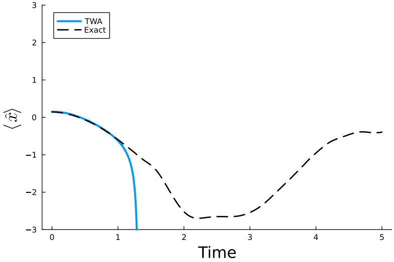
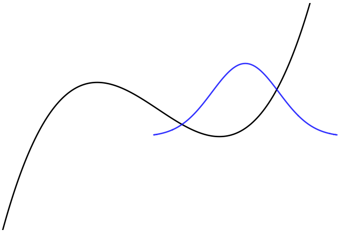


Figure 5 – TWA results for the Anharmonic Oscillator for $N = 1000$ trajectories and $\alpha = 0.1$ in $V(x) = x^3 + x^2$.



Potential and initial state used.

Limits of the TWA : Anharmonic Oscillator

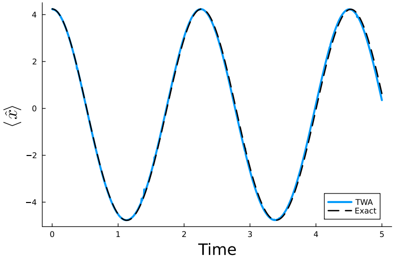
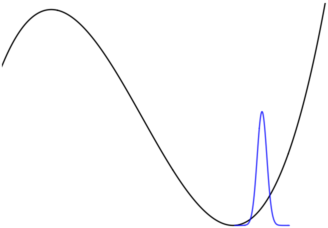


Figure 6 – TWA results for the Anharmonic Oscillator for $N = 1000$ trajectories and $\alpha = 3$ in $V(x) = 0.1x^3 + 4x^2$.



Potential and initial state used.

Quartic Potential

Quartic Potential :

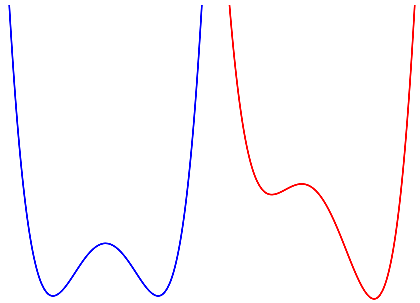
- $V(x) = ax^4 - bx^2 - cx$
- $a \ll b$

Applications :

- Diatomic molecules
- Atom optical trapping

Investigation :

- Position
- Quantum Tunneling



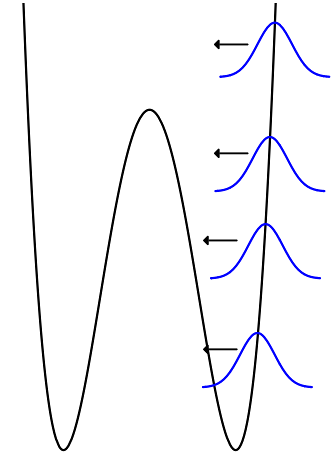
Corresponding potentials

Quartic potential : Wells

Investigation of the position dynamics in a well of the quartic potential

$$V(x) = 0.005x^4 - 3x^2$$

Initial state : Right well of the potential
$\implies \hat{\rho} = |\alpha\rangle\langle\alpha|\,,\ \alpha > 0$



Different initial states in a well of the quartic potential

Quartic potential : Well

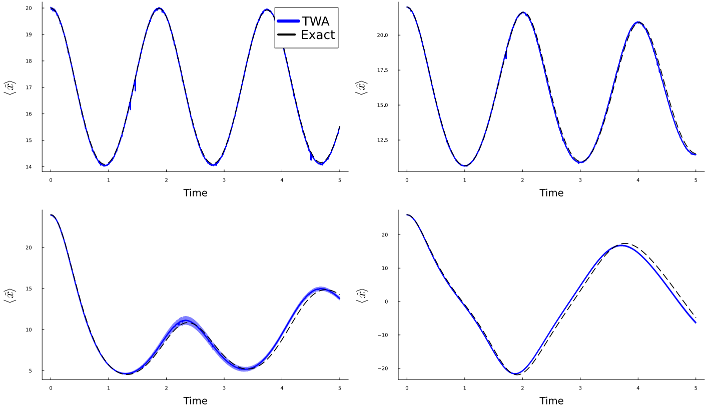


Figure 7 – TWA results for the symmetric quartic potential for $N = 1000$ trajectories and different values of α.

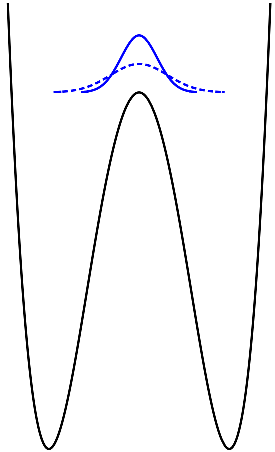
Quartic potential : Middle

Initial state : Middle of the potential

$\implies \hat{\rho} = |0\rangle\langle 0|$

Expectation : The wave function only spread around the center

$\implies \Delta x$ is the characteristic quantity



Initial state at the middle of the quartic potential

Quartic potential : Middle

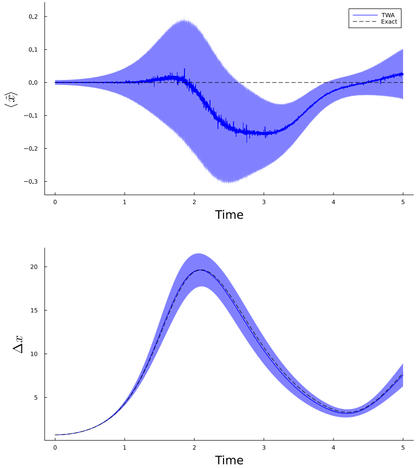
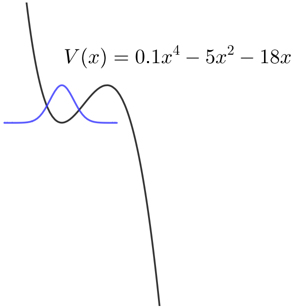


Figure 8 – TWA results for the symmetric quartic potential for $N = 10000$ trajectories and $\alpha = 0$.

Quartic potential : Quantum Tunneling



Potential used for Quantum Tunneling

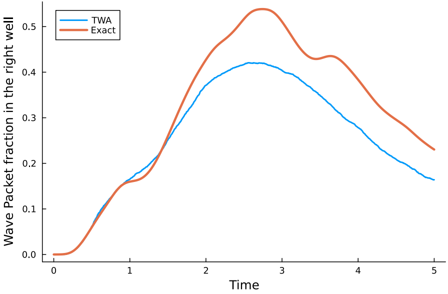


Figure 9 – Capability of the TWA to emulate Quantum Tunneling.

Toy model to describe polaritonic chemistry dynamics

Physical situation : a photon is incoherently absorbed by the cavity

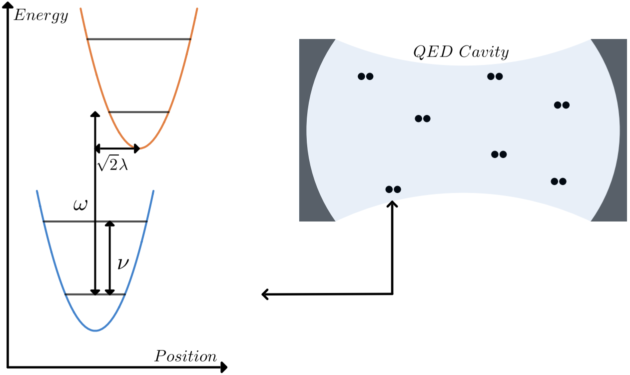


Figure 10 – Holstein-Tavis-Cummings model in picture.

Holstein-Tavis-Cummings Model

Holstein-Tavis-Cummings Hamiltonian

$$\hat{H} = \Delta \sum_n \hat{\sigma}_n^+ \hat{\sigma}_n^- + g \sum_n \hat{a}\hat{\sigma}_n^+ + \hat{a}^\dagger \hat{\sigma}_n^- + \nu \sum_n \hat{b}_n^\dagger \hat{b}_n$$
$$- \lambda\nu \sum_n \left(\hat{b}_n + \hat{b}_n^\dagger\right) \hat{\sigma}_n^+ \hat{\sigma}_n^- + \sum_n \epsilon_n \hat{\sigma}_n^+ \hat{\sigma}_n^-$$

Contains :

- Coupling to cavity
- Coordinates vibrations of molecules
- Coupling between coordinates and electronic states of the molecules
- Disorder of the electronic energy

TWA Computation of the HTC model

Physical situation : a photon is incoherently absorbed by the cavity

Simulation initial parameters :

- Physical parameters are defined by experimental results
- Vibrational state : $|0\rangle$
- Electronic state : $|0\rangle$
- Photonic state : $|1\rangle$

Problem : $W < 0$ for $\hat{\rho}_{phot} = |1\rangle\langle 1|$

Possibility : Consider the photonic state as a two-level system $\{|0\rangle, |1\rangle\}$

Not yet done!

Conclusion

Phase space quantum mechanics

TWA	DTWA
• Captures continuous systems dynamics • Works for very quadratic potentials	• Captures discrete systems dynamics • Works for two-body interaction

The two methods can be easily combined to describe complex systems

Bibliography

[1] Anatoli Polkovnikov. Phase space representation of quantum dynamics. Annals of Physics, 325(8) :1790–1852, August 2010.

[2] J. Schachenmayer. Numerical approaches to quantum manybody non-equilibrium. 2023.

[3] J. Schachenmayer, A. Pikovski, and A. M. Rey. Many-body quantum spin dynamics with monte carlo trajectories on a discrete phase space. Phys. Rev. X, 5 :011022, Feb 2015.

[4] D. Wellnitz, G. Pupillo, and J. Schachenmayer. Disorder enhanced vibrational entanglement and dynamics in polaritonic chemistry. Communications Physics, 5(1), May 2022.

Appendix : Equations of motion

Potentials

- Harmonic :

$$H = \frac{1}{2}\left(p^2 + x^2\right)$$

$$\dot{x} = p, \;\; \dot{p} = -x$$

- Anharmonic :

$$H = \frac{p^2}{2} + ax^3 + bx^2$$

$$\dot{x} = p, \;\; \dot{p} = -\left(3ax^2 + bx\right)$$

- Quartic :

$$H = \frac{p^2}{2} + ax^4 - bx^2 + cx$$

$$\dot{x} = p, \;\; \dot{p} = -\left(4ax^3 - bx^2 + c\right)$$

Discrete systems

- $\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$
- Assume a product ansatz for the density matrix :

$$\hat{\rho} = \prod_i \frac{1}{2}\left(\mathbb{1} + \vec{r}_i \cdot \hat{\vec{\sigma}}\right)$$

- Liouville-von Neumann equation :

$$\dot{\hat{\rho}} = -i[H, \hat{\rho}]$$

- Solve for $\vec{r}_i$

Appendix : Exact computation

- $\langle \hat{\Omega} \rangle (t) = \langle \Psi(t) | \hat{\Omega} | \Psi(t) \rangle$
- $|\Psi(t)\rangle = \hat{U}(t,0)\,|\Psi(0)\rangle = e^{-\frac{i}{\hbar}\hat{H}t}\,|\Psi(0)\rangle$
- $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})$
- Use x representation :

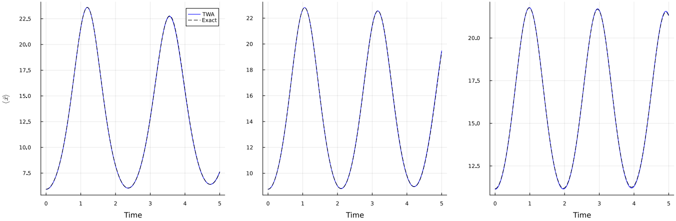
$$|\Psi\rangle = \sum_i \Psi(x_i)\,|x_i\rangle$$

$$\frac{\hat{p}^2}{2m} = -\lim_{a\to 0} \frac{1}{2ma^2} \sum_i |x_i\rangle\langle x_{i+1}| - 2\,|x_i\rangle\langle x_i| + |x_i\rangle\langle x_{i-1}|$$

$$\hat{V}(\hat{x}) = \sum_i V(x_i)\,|x_i\rangle\langle x_i|$$

- Matrix products

Appendix : More dynamics in the well



Dynamics of the coherent state in the well for different values of α. 1 : $\alpha = 4.2$, 2 : $\alpha = 6.2$, 3 : $\alpha = 7.9$.