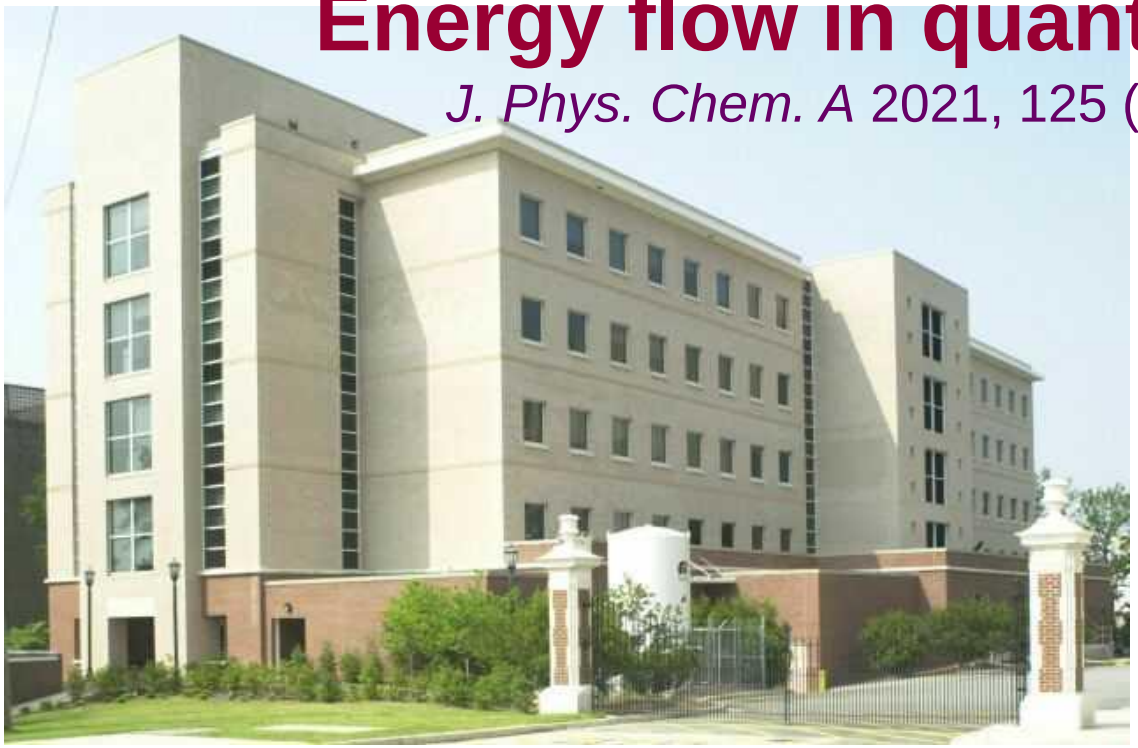
Energy flow in quantum systems

J. Phys. Chem. A 2021, 125 (21), 4653–4667



Sophya Garashchuk
Vitaly Rassolov

Covid explorations

Plan and main ideas

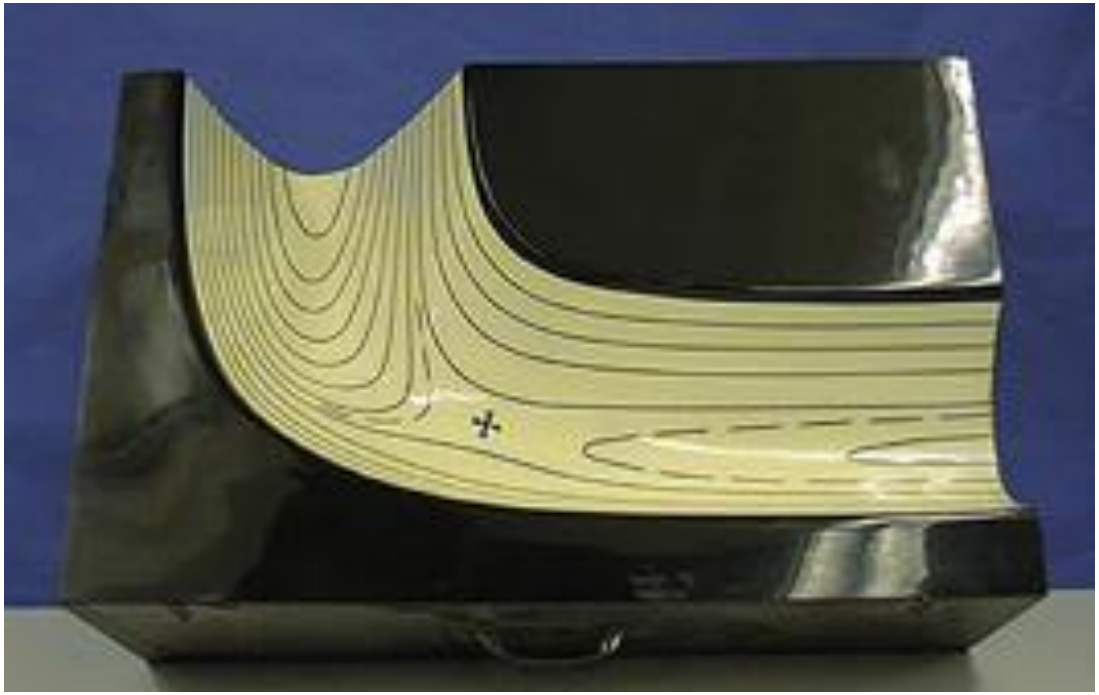
- Overview
  - Dynamics
  - Bohmian formulation
- Define and derive local energy
  - Not unique in quantum systems
    - This is general quantum feature
  - Our definition is consistent with classical limit
    - (still not unique)
  - And with Bohmian formalism
- Study four model systems
  - Mostly 1D
    - Simplified model double well (analytic)
    - Meta-stable well (numerical)
    - Also 2D Quantum-Classical
- Lessons for the quantum dynamics community
  - **Very hard to do exact quantum using Bohmian formalism**
  - **In transition to the classical regime, quantum effects become rare (rather than small)**

•Potential energy surface describes electronic energy and Coulomb repulsion between nuclei.

•Chemical reaction dynamics can be represented classically as motion of a marble on this surface

•In practice, one needs many marbles to gather statistics. To represent experimental conditions, marbles should start with different velocities and positions (*phase space sampling*)

•Simplest quantum effects are described by assigning individual marbles to particular quantum states (*quasiclassical description*).



The simplest quantum effect in nearly classical systems is zero-point-energy (ZPE) correction

Think of a quasiclassical picture, with the system represented by an ensemble of trajectories

At present, there is no simple way to account for ZPE along a reaction.
Important: ZPE is a property of the whole ensemble, not each trajectory.

What could be the way to describe ZPE-like quantum effects?

• A simple way is to compute the spread of trajectory ensemble, and "somehow" fit it to ZPE, then compute forces that come from ZPE.

• In effect, this is what we do in our approximate Bohmian formulation, except it is done in a rigorous way:

- ZPE dependence on spread is indirect; it is directly dependent on the average gradients of density
- we introduce non-classical momentum, and obtain ZPE from it.

Bohmian formulation

Substitution of a wave function in polar form

$$\psi(\mathbf{x},t) = A(\mathbf{x},t)\exp\left(\frac{\imath}{\hbar}S(\mathbf{x},t)\right)$$

into the Schrödinger equation

$$\imath\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\nabla^2\psi + V\psi$$

and separating real and imaginary parts gives

$$\frac{\partial S(\mathbf{x},t)}{\partial t} + \frac{(\nabla S(\mathbf{x},t))^2}{2m} + V = \frac{\hbar^2}{2m}\frac{\nabla^2 A(\mathbf{x},t)}{A(\mathbf{x},t)}$$

$$\frac{\partial A(\mathbf{x},t)}{\partial t} + \nabla A(\mathbf{x},t)\frac{\nabla S(\mathbf{x},t)}{m} = -\frac{A(\mathbf{x},t)}{2m}\nabla^2 S(\mathbf{x},t)$$

Bohmian formulation

In a moving frame, with $m\mathbf{v} = \nabla S(\mathbf{x}, t)$, the first equation is **local** with respect to $\{S, \nabla S\}$

$$\frac{d\nabla S}{dt} = \nabla[\frac{\hbar^2}{2m}\frac{\nabla^2 A(\mathbf{x}, t)}{A(\mathbf{x}, t)} - V]$$

and the second one is **local** with respect to $w = A(\mathbf{x}, t)^2 \delta\Omega$ (Ω is the volume element)

$$\frac{dw}{dt} = 0$$

All non-local effects are left in quantum potential

$$U = \frac{-\hbar^2}{2m}\frac{\nabla^2 A(\mathbf{x}, t)}{A(\mathbf{x}, t)}$$

Summary of traditional Bohmian approach

- Quantum equations are written in classical way: wavefunctions are represented by trajectories, each moving according to classical mechanics + additional forces from Quantum Potential

\+ Formulation is exact, and neatly compatible with molecular mechanics

\- Quantum potential is non-local, unbound, sometimes singular, and horribly unstable

New content. Derivations:

- Next, we introduce two operators
  1. Quantum trajectory operator
  2. Local energy operator

- Use these operators to introduce the "quantum power" expression
  - And apply it to model systems

Quantum Trajectory Operator

- Reminder: delta-function operator measures density at a point. Delta function operator can be thought as an infinitely narrow normalized Gaussian:

$$\rho(x_0) = \lim_{\varepsilon \to 0} \left\langle \psi(x) \right| \sqrt{\frac{\beta}{\pi\varepsilon}} \exp\left(\frac{-\beta(x - x_0)^2}{\varepsilon}\right) \left| \psi(x) \right\rangle$$

- Make
  - the point x_0 move: $\frac{dx_0(t)}{dt} = \frac{1}{m}\nabla S$
  - the Gaussian "breathe": $\frac{d\beta(t)}{dt} = \frac{-2\beta(t)}{m}\nabla^2 S$
  - Different normalization: $g_W = \lim_{\varepsilon \to 0} \exp\left(\frac{-1}{\varepsilon}\beta(t)\left(x - x_0(t)\right)^2\right)$
- One can show: $\frac{\partial \langle g_W \rangle}{\partial t} = 0$ in a quantum system.
- Basically, g_W is the quantum trajectory (weight) operator
  - It is linear, in Hilbert space
  - Can be used to study quantum behavior by non-Bohmian people

Local Energy Operator

- We use g_W to define the energy operator:

$$\hat{E}_w = \frac{1}{2}(g_w \hat{H} + \hat{H} g_W)$$

- One can show: $\langle \hat{E}_w \rangle = \langle g_w \rangle \left(\frac{p^2}{2m} + U(x_0) + V(x_0) \right)$
  - Which is a trajectory weight multiplied by Bohmian energy
- We define local energy as ratio of the expectation values of these two operators
  - $E(q_t) = \frac{\langle \hat{E}_w \rangle}{\langle g_w \rangle}$
- And define the central quantity of this talk: "quantum power" $\boldsymbol{Q} = \frac{\partial E(q_t)}{\partial t} = \frac{\partial \langle \hat{E}_w \rangle / \partial t}{\langle g_w \rangle}$

Local Energy Operator

- We use Heisenberg representation to derive time derivative of local energy:

$$\frac{\partial E(\boldsymbol{q}_t)}{\partial t} = \frac{\partial \left(\frac{\langle E_W \rangle}{\langle g_W \rangle}\right)}{\partial t} = \frac{\partial \left(\frac{\langle E_W^{\epsilon} \rangle}{\langle g_W^{\epsilon} \rangle}\right)}{\partial t} = \frac{\frac{\partial \langle E_W^{\epsilon} \rangle}{\partial t}}{\langle g_W^{\epsilon} \rangle}$$

$$= \Big(-(\boldsymbol{p} \cdot \boldsymbol{\nabla} U) + \hbar^2 Tr(\boldsymbol{M}^{-1} \cdot ((\boldsymbol{r} + \boldsymbol{\nabla}) \otimes \boldsymbol{r}) \cdot \boldsymbol{M}^{-1} \cdot (\boldsymbol{\nabla} \otimes \boldsymbol{\nabla} S))$$

$$+ \hbar^2 (\boldsymbol{r} \cdot \boldsymbol{\nabla} (\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} S)) + \frac{\hbar^2}{4} (\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} (\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} S)) \Big)_{\boldsymbol{q}_t}$$

Time derivative, 1D

$$\frac{d}{dt}\langle E_g\rangle = \sqrt{\frac{\pi}{\beta}}\frac{\hbar^2 a_0^2}{m^2}\left(\frac{s_4}{4}+\frac{s_3 a_1}{a_0}+\frac{s_2 a_2}{a_0}+\frac{s_1 a_3}{2a_0}-\frac{s_1 a_2 a_1}{2a_0^2}\right)$$

For a Gaussian WF this takes form ($s_3 = 0,\ s_4 = 0$):

$$a_1 = a_0 r,\ a_2 = -\frac{2ma_0}{\hbar^2}U, a_3 = -\frac{2ma_0}{\hbar^2}(\nabla U + rU),\ \frac{d}{dt}\frac{\langle E_g\rangle}{\langle g\rangle} = -\frac{s_1}{m}\nabla U - \frac{2s_2}{m}U.$$

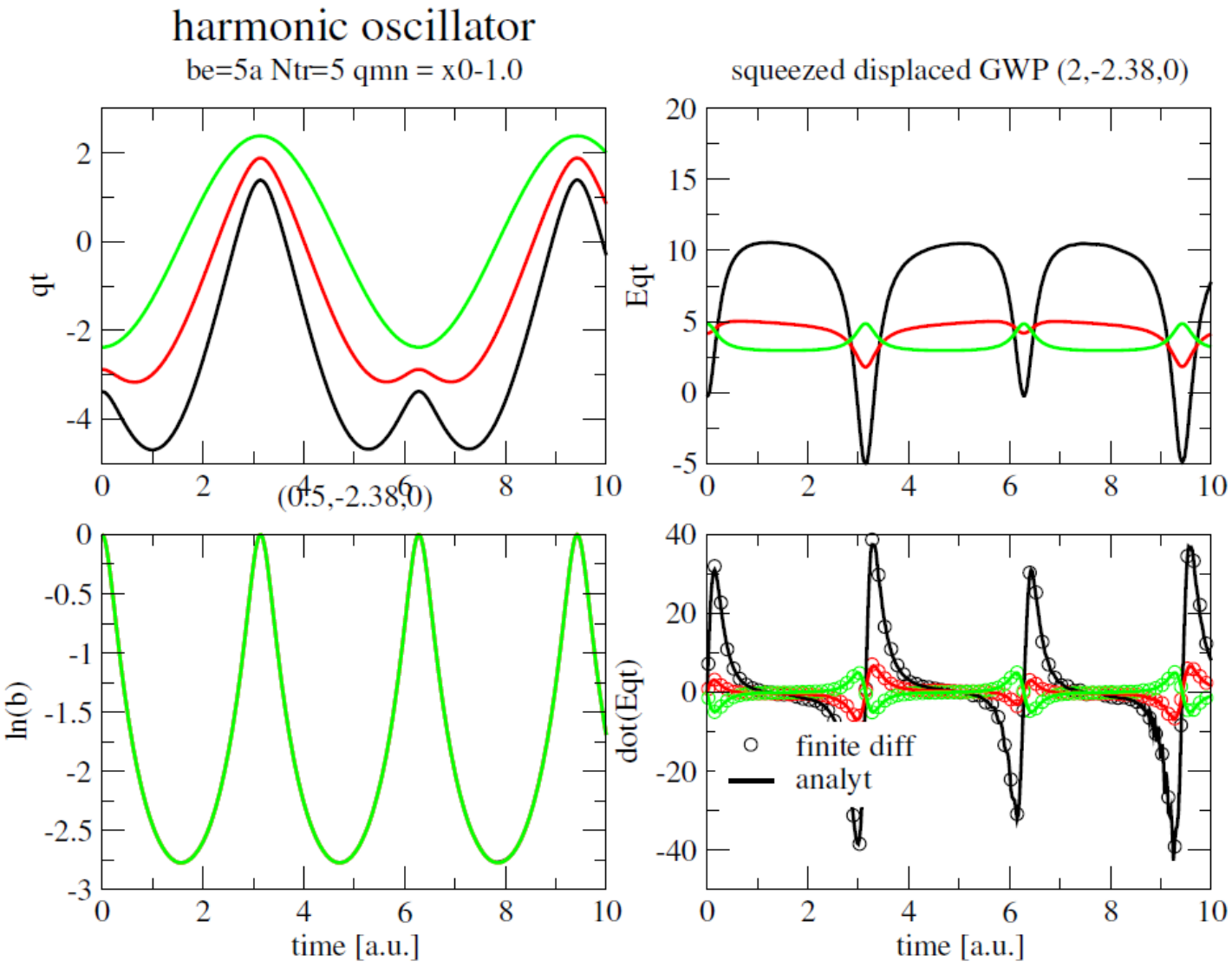
s_i and a_i are Taylor expansion coefficients of phase and amplitude. r is non-classical momentum, and U is quantum potential

Quantum power properties

- It is semiclassical (goes to zero when m $\rightarrow \infty$ or $\hbar \rightarrow 0$)
- It does not depend on the external potential V
- Given by a ratio of linear QM operators (i.e. meaningful even outside of Bohmian formalism, in traditional QM).

$$\frac{\partial E(\boldsymbol{q}_t)}{\partial t} = \frac{\hbar^2}{4\rho(\boldsymbol{q}_t)} \Bigg(Im(\psi^*(\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}\psi)) - 2Re\Big(\big(\boldsymbol{\nabla} S \cdot \boldsymbol{\nabla}(\psi^*(\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}\psi))\big) + \psi^*(\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} S)(\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}\psi) \Big) \Bigg)_{\boldsymbol{q}_t}$$

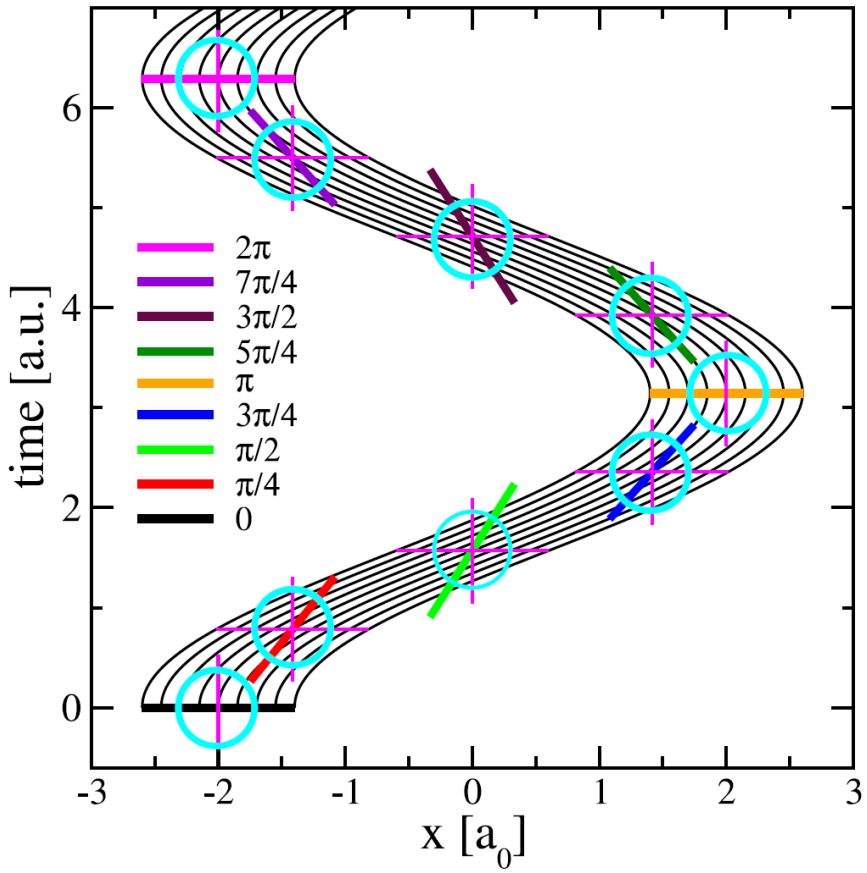
Systems (I): A Gaussian



Conclusion: periodic energy exchange among the trajectories, as expected

Systems (Ia): A Gaussian

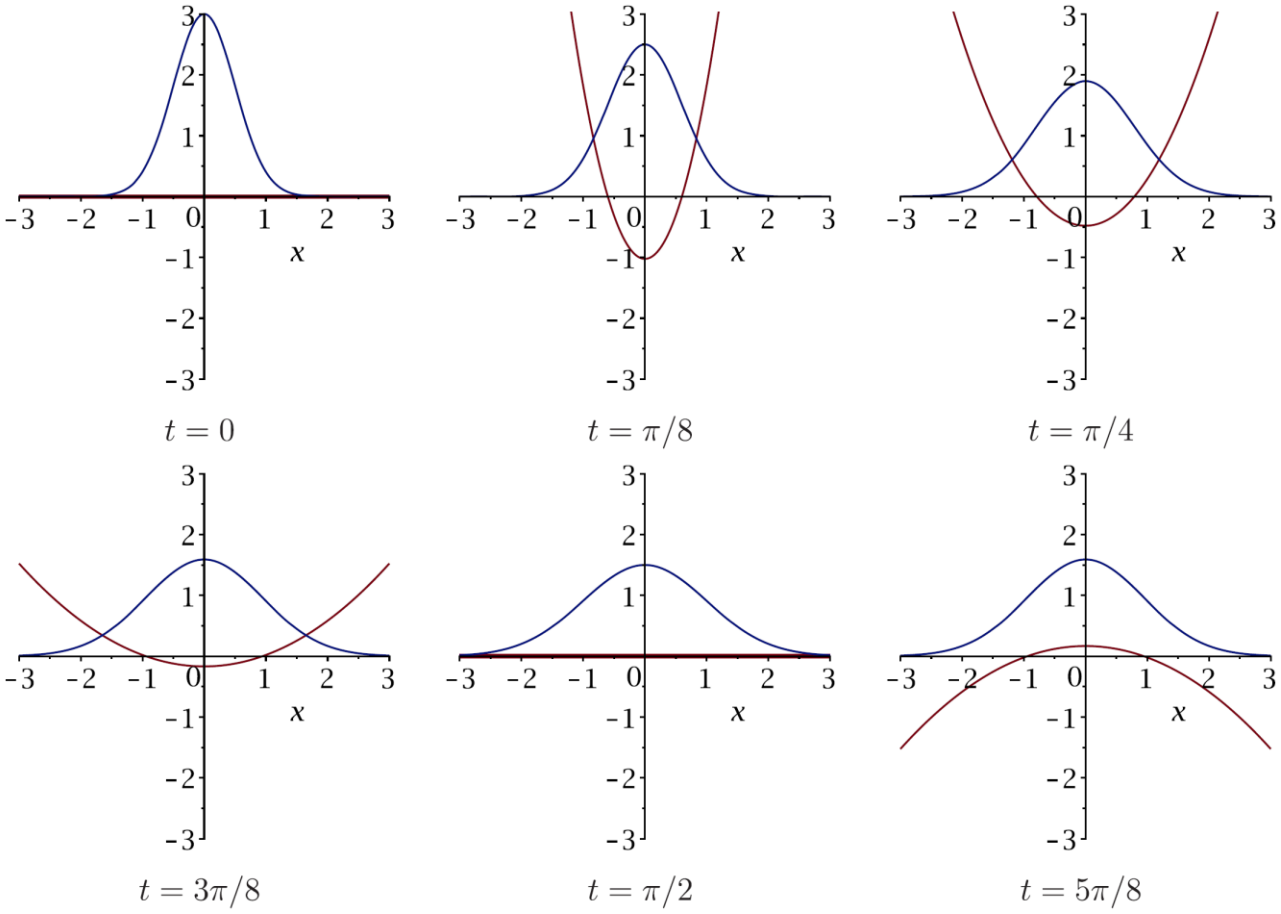
The translational motion of a coherent Gaussian wavepacket in a parabolic potential. The QTs, shown as thin solid lines, track the dynamics of the wavefunction, whose footprints are marked as circles. The corresponding **Q**, is plotted as straight line segments for nine instances of time listed in the legend.



Conclusion: Energy from the trailing edge flows into the leading edge

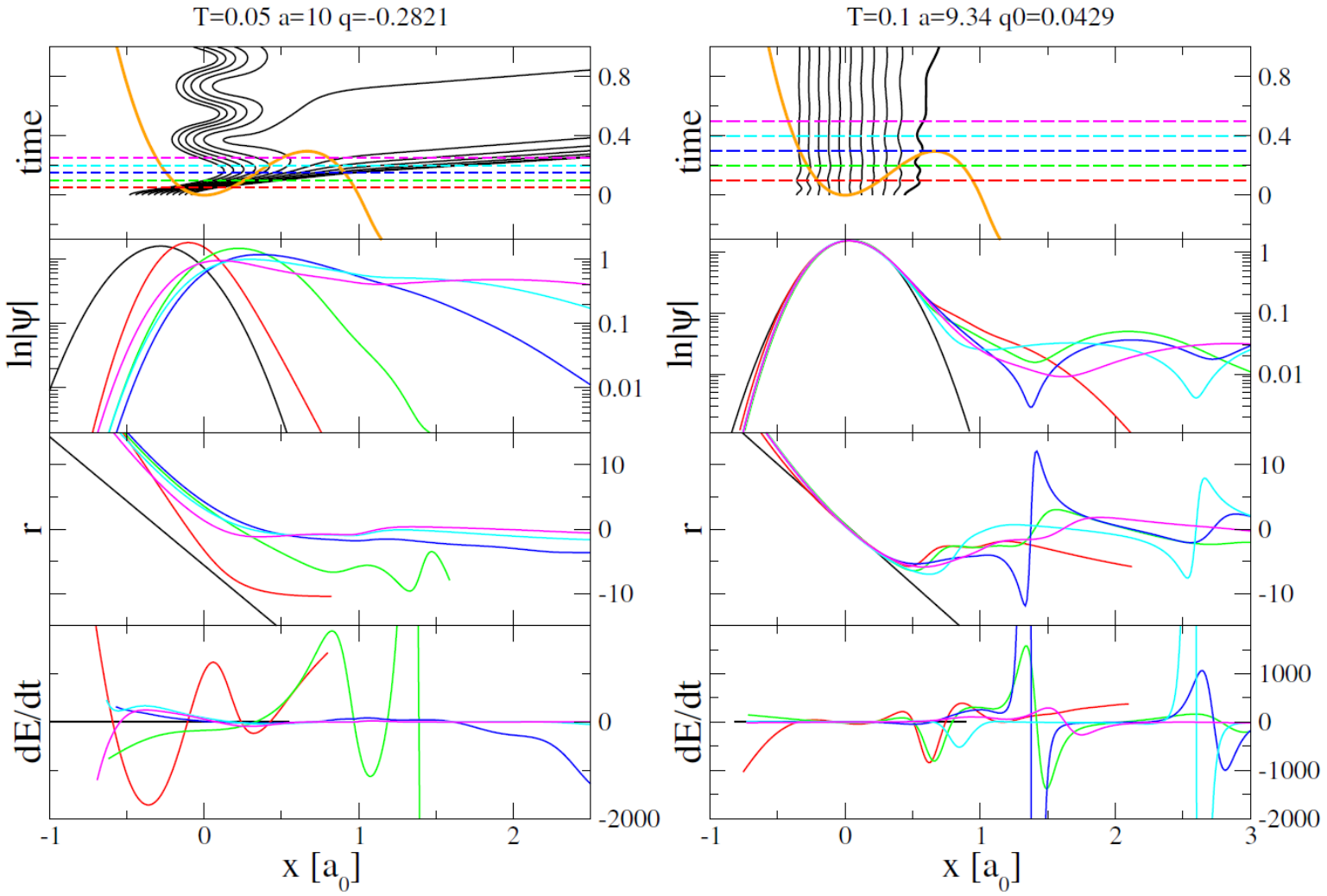
Systems (Ib): A Gaussian

The breathing motion of an otherwise stationary Gaussian wavepacket in a parabolic potential. The snapshots of **Q** and |Ψ| are plotted for times indicated at the bottom of each panel. The vertical axis corresponds to **Q** in a.u.



Conclusion: Again, energy from the “trailing edge” flows into the “leading edge”

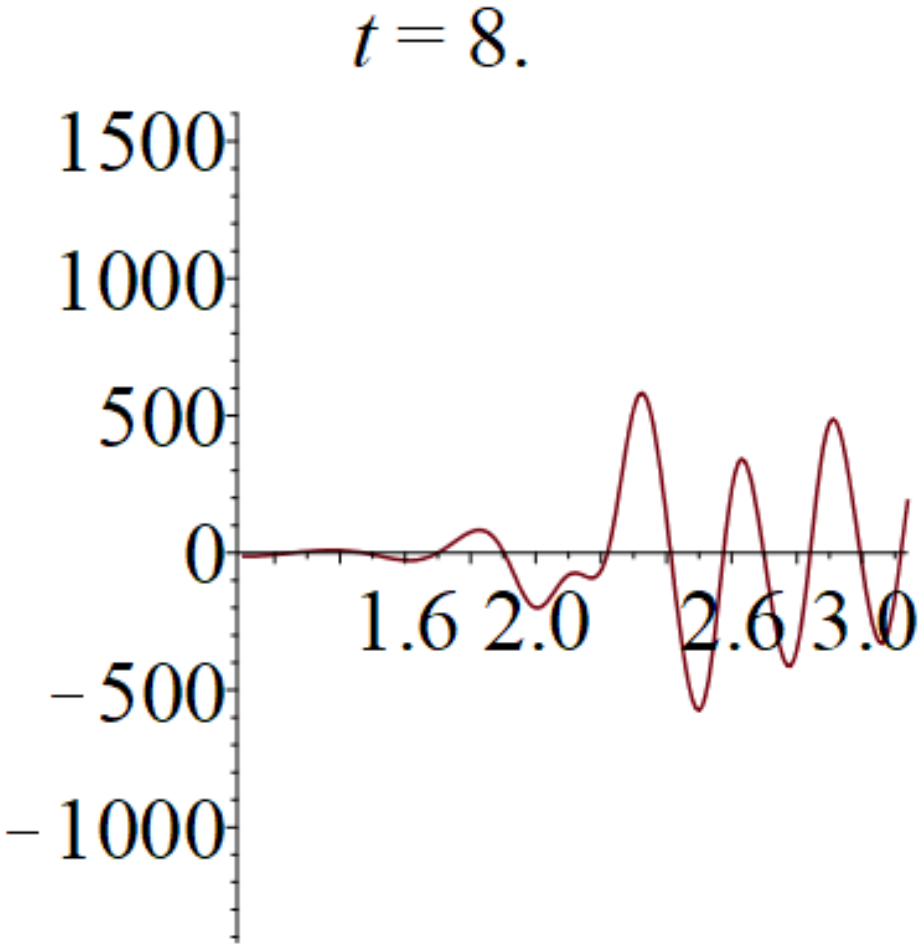
Systems (II): Metastable well



Conclusion: Energy exchange in the potential well helps trajectories to tunnel.

Systems (II): Metastable well

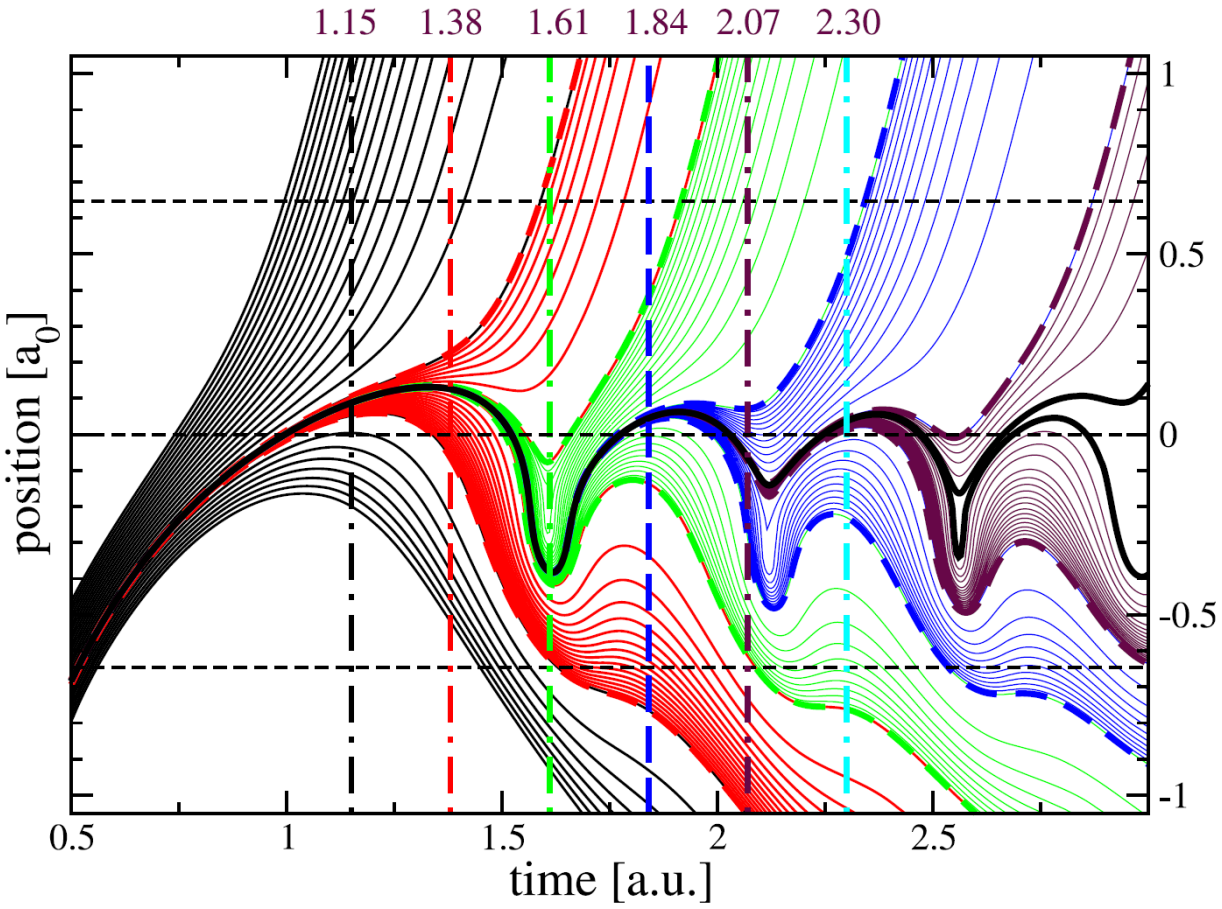
long time, large x quasistatic limit



Conclusion: Energy exchange in the potential well helps trajectories to tunnel.

Systems (II ½): Eckart Barrier

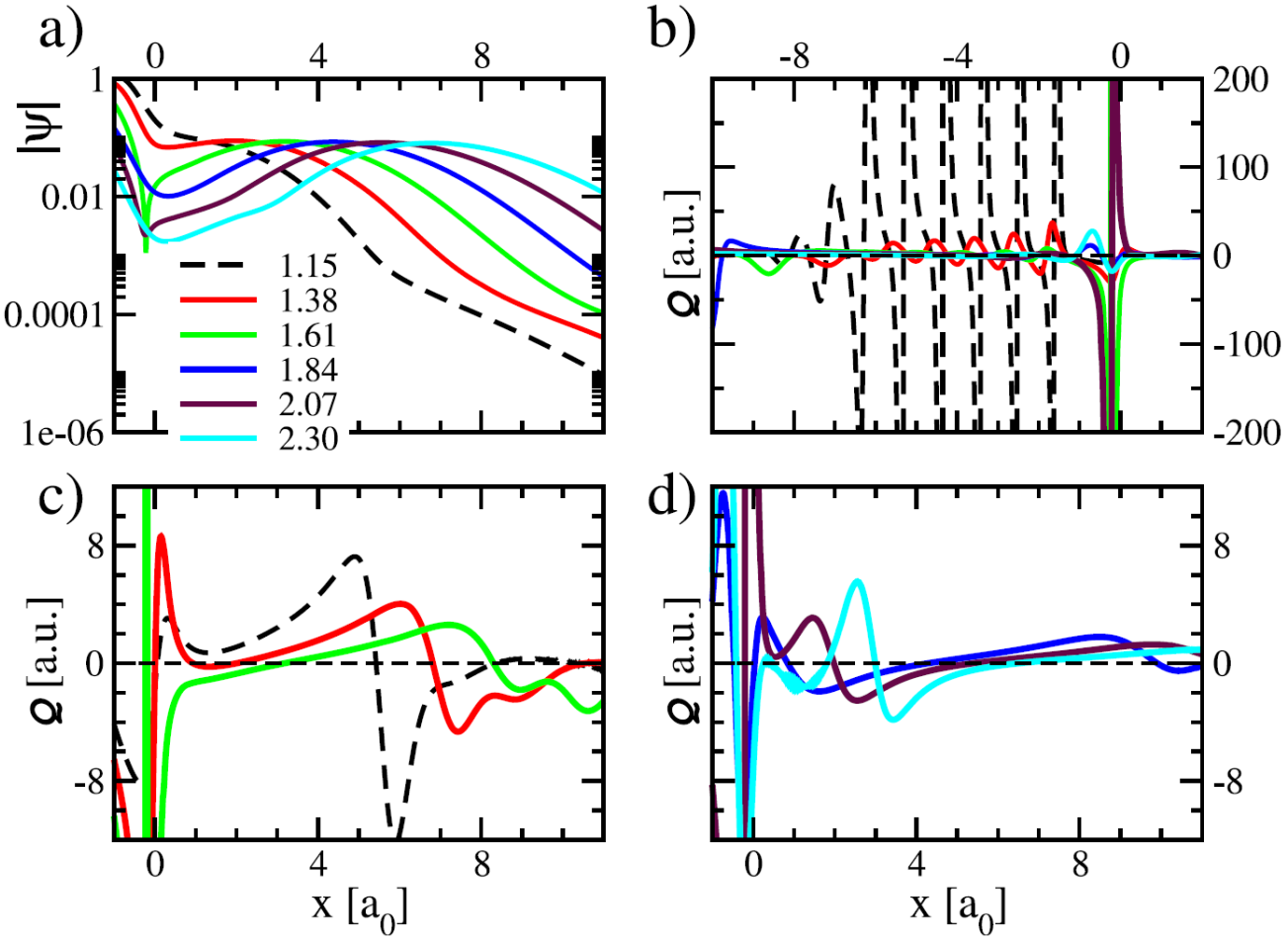
mimicking H + H_2 reaction barrier



Conclusion: Complicated dynamics at the barrier, constant recrossing

Systems (II ½): Eckart Barrier

mimicking H + H_2 reaction barrier



Conclusion: Complicated dynamics at the barrier, indeed

Systems(III): double well

Intro: Much work is done by others (**refs**), nobody did it analytically. Absence of external potential dependence in Eq. 42 permits simple two Gaussians model[vr]. We set up a time-dependent wavefunction in the space spanned by two identical normalized Gaussians, centered for convenience at $x = \pm 1$

$$\chi_L(x) = \left(\frac{\alpha}{\pi}\right)^{(1/4)} \exp\left(\frac{-\alpha(x+1)^2}{2}\right), \quad \chi_R(x) = \left(\frac{\alpha}{\pi}\right)^{(1/4)} \exp\left(\frac{-\alpha(x-1)^2}{2}\right). \tag{47}$$

We shift the diagonal Hamiltonian matrix elements to zero for convenience. Off-diagonal Hamiltonian matrix elements depend on the exact shape of the external double-well potential, and are taken as parameters $\langle \chi_L \hat{H} \chi_R \rangle = \epsilon$. Off diagonal overlap values are $\sigma = \langle \chi_L \chi_R \rangle = \exp(-\alpha)$. The solution of the Schrödinger equation localaized at time $t = 0$ in the left basis function is

$$\Psi(t,x) = \exp\left(\frac{\imath \epsilon t}{1+\sigma}\right)\left(\frac{1+\exp(\imath\phi)}{2}\chi_L(x) + \frac{1-\exp(\imath\phi)}{2}\chi_R(x)\right), \tag{48}$$

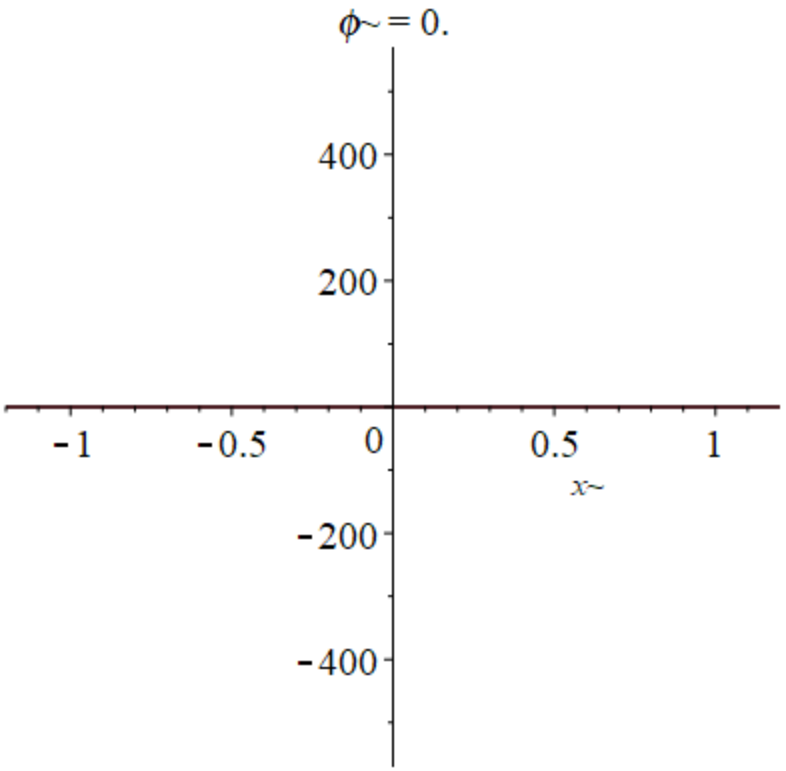
where $\phi = \frac{-2\sigma\epsilon t}{1-\sigma^2}$ is a dimensionless time.

$$p = \frac{-2\alpha \sin(\phi)}{(1+\cos(\phi))\exp(-2\alpha x) + (1-\cos(\phi))\exp(2\alpha x)}$$

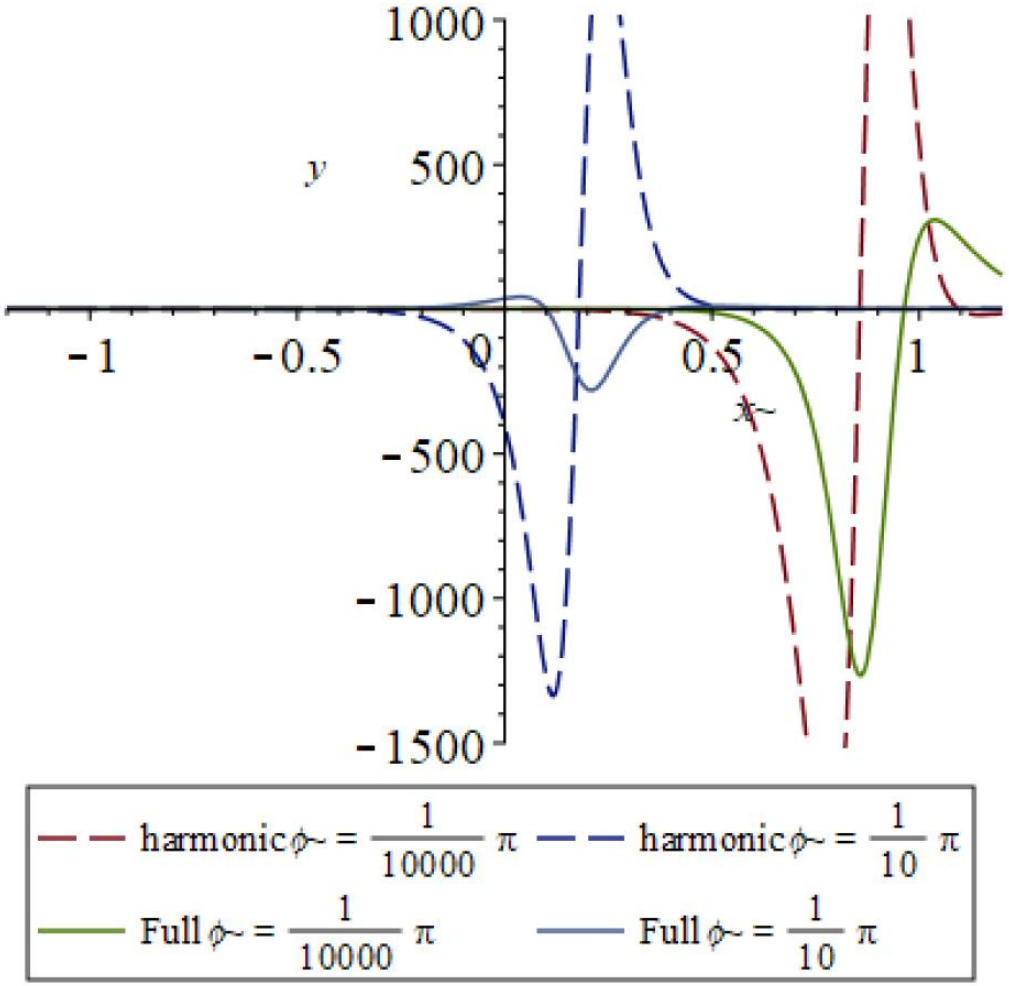
$$r = \frac{-\alpha\left((1+\cos(\phi))(x+1)\exp(-2\alpha x) + (1-\cos(\phi))(x-1)\exp(2\alpha x)\right)}{(1+\cos(\phi))\exp(-2\alpha x) + (1-\cos(\phi))\exp(2\alpha x)}$$

Double well: minima are at ±1.

Initial population (at φ=0) is in the **left** well



Systems: double well



Systems: double well
Conclusions

- Harmonic approximation is qualitatively incorrect for tunneling
- The energy redistribution for tunneling starts at the distant wall of the empty well [$x_0 \sim \ln(1/t)$ at short t]
  - To describe tunneling with trajectories, the whole space needs to be covered with them first. This is an intractable (at least NP) problem in a general multidimensional energy landscape

Systems (IV): 2D Quantum-Classical

$m_0=1$, $\lambda=m_0/m$

$$V(x_1,x_2)=\frac{k_1}{2}(x_1-x_2)^2+\frac{k_2}{2}x_2^2,\quad k_1=5,\quad k_2=15.$$

$$\tau=t\sqrt{k/m},$$

1D **2D**

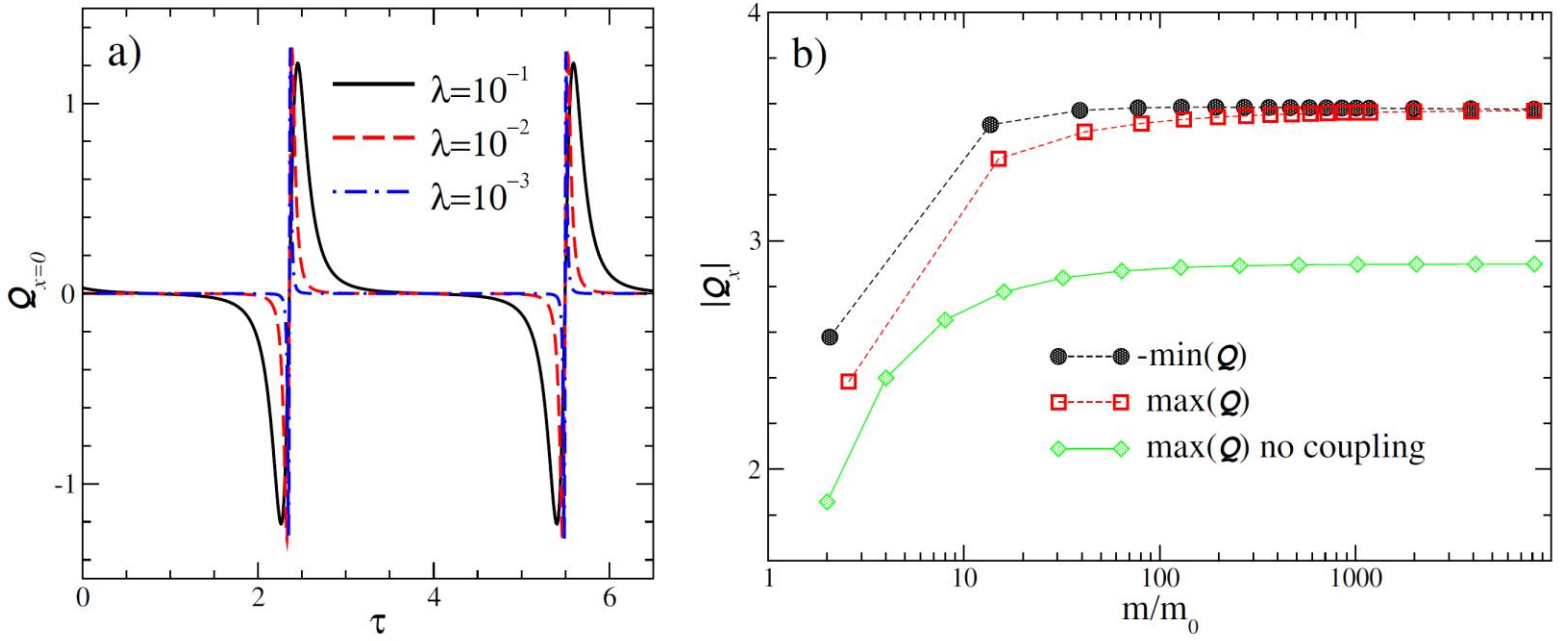


Figure 9: (a) The quantum power $\mathcal{Q}$, evaluated at $x=0$, for a GWP in one dimension as a function of the rescaled time, τ. The values of the mass ratio $\lambda=m_0/m$ are given in the legend. (b) The extrema of $\mathcal{Q}_x$ as a function of the relative mass of the heavy particle, m/m_0, for the two-dimensional quantum/classical model (Eq. (57)). The results from the uncoupled dynamics are displayed for comparison.

Systems (IV): 2D Quantum-Classical

$m_0=1$, $\lambda=m_0/m$

$$V(x_1,x_2)=\frac{k_1}{2}(x_1-x_2)^2+\frac{k_2}{2}x_2^2,\quad k_1=5,\quad k_2=15.$$

$$\tau=t\sqrt{k/m},$$

Conclusion: as $\lambda \to 0$ and system gets more classical, the quantum effects do not get smaller. Instead, they become less frequent.

To do:

- Find workable approximate expression for energy flow
  - To implement with quantum trajectories
- Study non-adiabatic dynamics
- Check WKB

Questions?