Eulerian semiclassical computational methods in quantum dynamics

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outline

- Classical mechanics: Hamiltonian system, discontinuous Hamiltonian, transmission and reflection (J-Wen)
- Quantum barriers: quantum-classical coupling, interference (J-Novak)
- Diffraction: use GTD (J-Yin)
- Surface hopping (J-Qi-Zhang)
- Gaussian beam method (J-Wu-Yang)
- conclusion

I: Classical Mechanics for singular Hamiltonians

- a Hamiltonian system:

$$d\mathbf{x}/dt = \nabla_\xi H$$
$$d\xi/dt = -\nabla_{\mathbf{x}} H$$

$H=H(x, \xi)$ is the Hamiltonian

Classical mechanics: $H=1/2\ |\xi|^2+V(\mathbf{x})$ (=> Newton's second law)
Geometrical optics: $H = c(\mathbf{x})\ |\xi|$

computational method based on solving the Hamiltonian system is referred to as the particle method, or a Lagrangian method

- Phase space representation:

$$f_t + \nabla_\xi H\cdot \nabla_{\mathbf{x}} f - \nabla_{\mathbf{x}} H \cdot \nabla_\xi f = 0$$

$f(t, x, \xi)$ is the density distribution of a classical particle at position x, time t, with momentum ξ

Computational methods based on solving the Liouville equation will be refereed to as the Eulerian method

The Liouville equation can be solved by method of characteristics if H is smooth

Lagrangian vs Eulerian

- Lagrangian: simple, efficient in high dimension

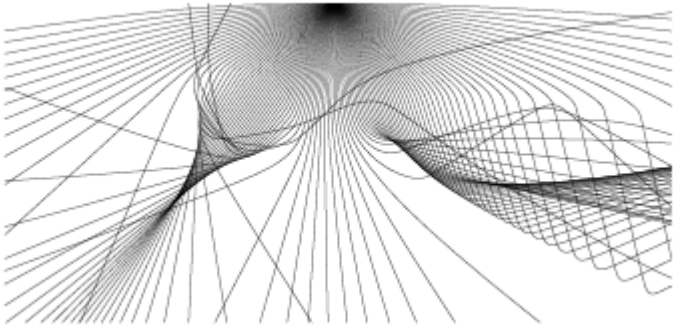
  particles (rays) may diverge: loss of accuracy, remeshing (increasing particles) is needed which may be complicated

- Eulerian: solving PDEs on a fixed mesh--high order accuracy; computational cost higher (reducing cost: moment closure, level set method)

A ray tracing result

- Rays or particles may diverge, so it becomes highly inaccurate to reconstruct quantities of interests: fields (electric or electromagnetic, Bohm potential, etc)

- Figure by O. Runborg



Discontinuous Hamiltonians

- $H=1/2|\xi|^2+V(x)$: $V(x)$ is **discontinuous-** potential barrier,
- $H=c(x)|\xi|$: $c(x)$ is discontinuous-different index of refraction
- quantum tunneling effect, semiconductor device modeling, plasmas, geometric optics, interfaces between different materials, etc.
- Modern theory (KAM theory) and numerical methods (symplectic scheme) for Hamiltonian system all assume smooth Hamiltonian

Analytic issues

$$f_t + \nabla_\xi H \cdot \nabla_{\mathbf{x}} f - \nabla_{\mathbf{x}} H \cdot \nabla_\xi f = 0$$

- The PDE does not make sense for discontinuous H. What is a weak solution?

$$d\mathbf{x}/dt = \nabla_\xi H$$
$$d\xi/dt = -\nabla_{\mathbf{x}} H$$

- How to define a solution of systems of ODEs when the RHS is discontinuous or/and measure-valued? (DiPerna-Lions-Ambrosio renormalized solution does not apply here—only work for BV RHS)

How do we extend the mathematical theory to singular Hamiltonian system

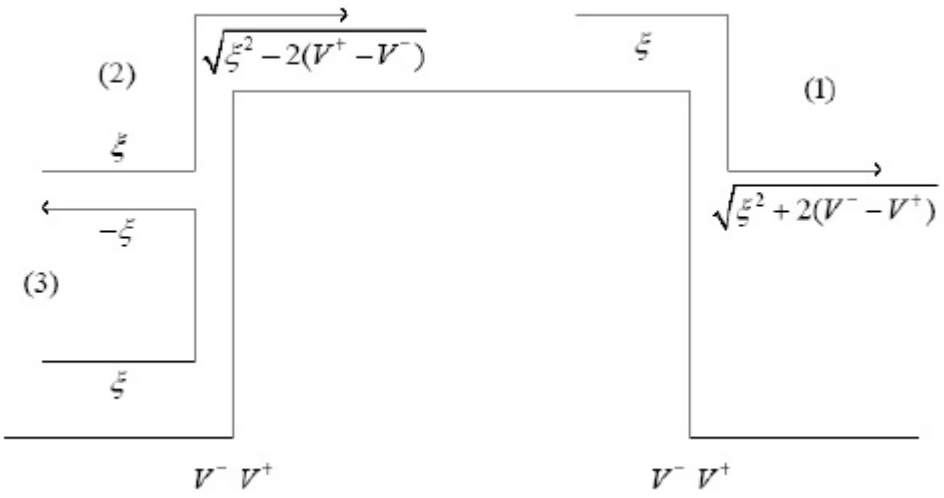
Our approach: build in correct physics at the singularity: transmission, reflection, diffraction, quantum tunneling, surface hopping, …

Classical particles at barriers

Particles either transmit or reflect

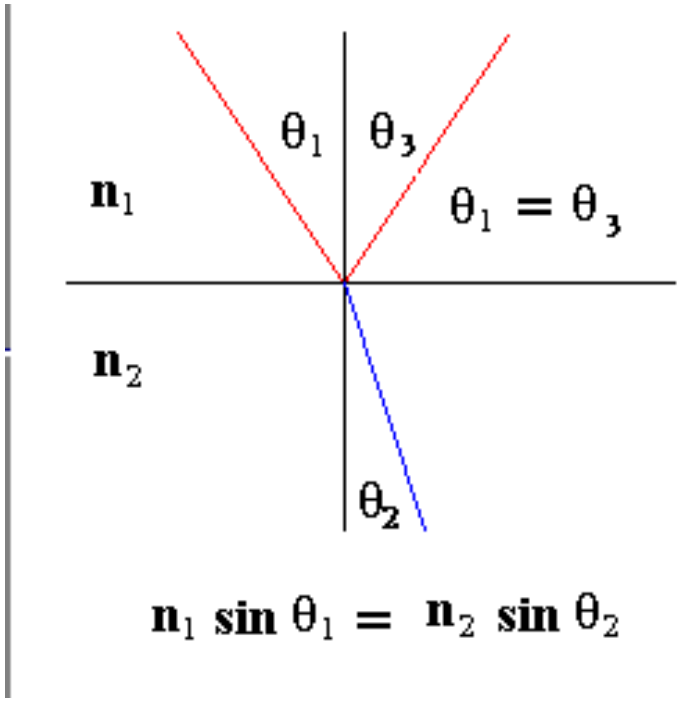
Hamiltonian is conserved:

$H^+ = H^-$

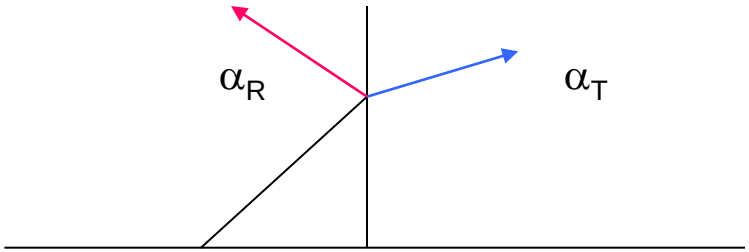


Snell-Decartes Law of refraction

- When a plane wave hits the interface, $H=c|\xi|$ is conserved: the angles of incident and transmitted waves satisfy ($n=c_0/c$)



Solution to Hamiltonian System with discontinuous Hamiltonians



- Particles cross over or be reflected by the corresponding transmission or reflection coefficients (probability)
- Based on this definition we have also developed particle methods (both deterministic and Monte Carlo) methods

Eulerian picture: An interface condition

an interface condition for f should be used to connect
(the good) Liouville equations on both sides of the interface.

$$f(x^+, \xi^+)=\alpha_T f(x^-,\xi^-)+\alpha_R\, f(x^+, -\xi^+) \quad \text{for } \xi^+>0$$

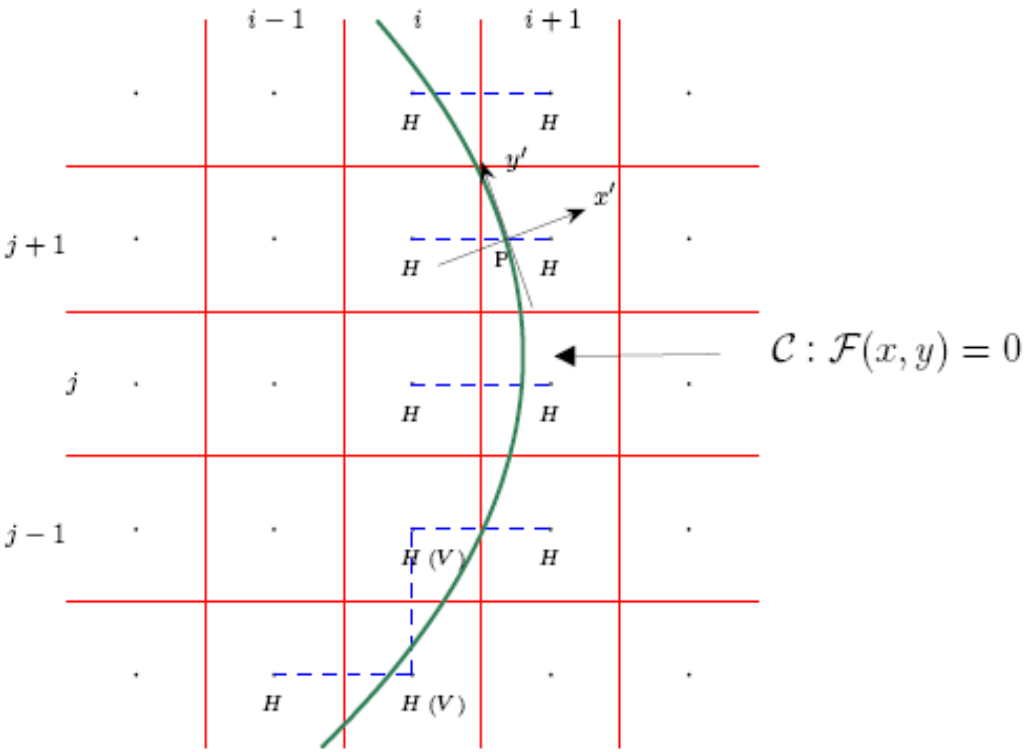
$$H(x^+, \xi^+)=H(x^-,\xi^-)$$

α_R: reflection rate α_T: transmission rate

$$\alpha_R+\alpha_T=1$$

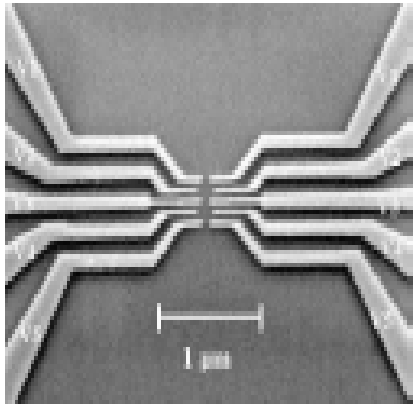
- α_T, α_R defined from the original "microscopic" problems
- This gives a mathematically well-posed problem that is physically relevant
- We can show the interface condition is equivalent to Snell's law in geometrical optics
- A new method of characteristics (bifurcate at interfaces)

Curved interface



II. Quantum barrier: a multiscale approach (with *K. Novak*, MMS, JCP)

We want to study quantum scale phenomena using a largely classical scale model.



- Nanotechnology
- Electron transport in semiconductors
- Tunneling diodes
- Quantum dot structures
- Quantum computing

A quantum-classical coupling approach for thin barriers

- Barrier width in the order of De Broglie length, separated by order one distance
- Solve a time-independent Schrodinger equation for the local barrier/well to determine the scattering data
- Solve the classical liouville equation elsewhere, using the scattering data at the interface

A step potential (V(x)=1/2 H(x))

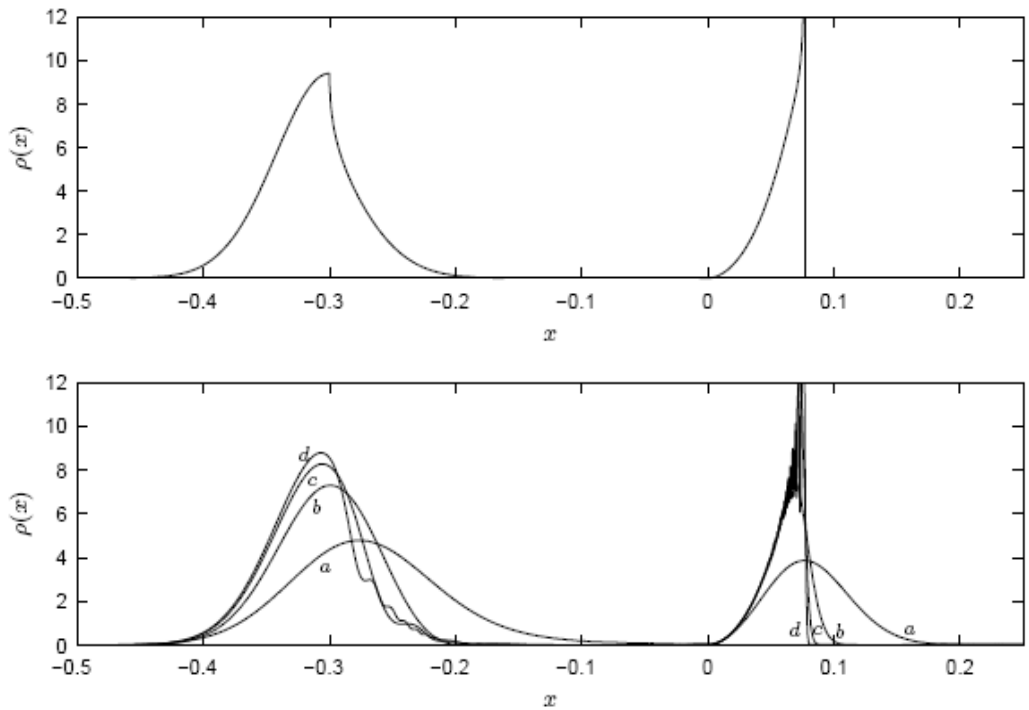
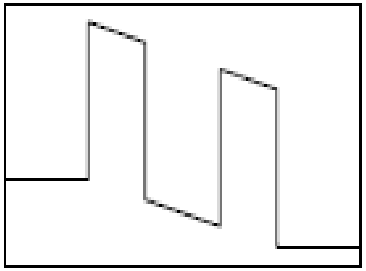


FIG. 5.1. *Position densities for the semiclassical Liouville (top) and Schrödinger (bottom) solutions of Example 5.1. The Schrödinger solution shows* $\varepsilon =$ *(a)* 200^{-1}, *(b)* 800^{-1}, *(c)* 3200^{-1} *and (d)* 12800^{-1}. *The position density of Liouville solution exhibits a caustic near* $x = 0.08$ *and the peak is unbounded. For the Schrödinger solution the peak reaches a height of 19 for the* $\varepsilon = 12800^{-1}$. *The plots are truncated for clarity.*

Resonant tunnelling



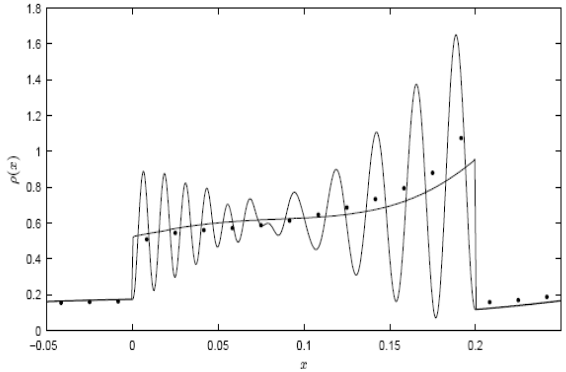


FIG. 5.4. *Detail of Fig. 5.3 showing position densities for the numerical semiclassical Liouville and von Neumann solutions. The • shows the numerical solution for with 150 grid points over the domain* $[-1.25, 1.25]$. *The solid line shows the "exact" Liouville solution and the von Neumann solution using* $\varepsilon = 0.002$.

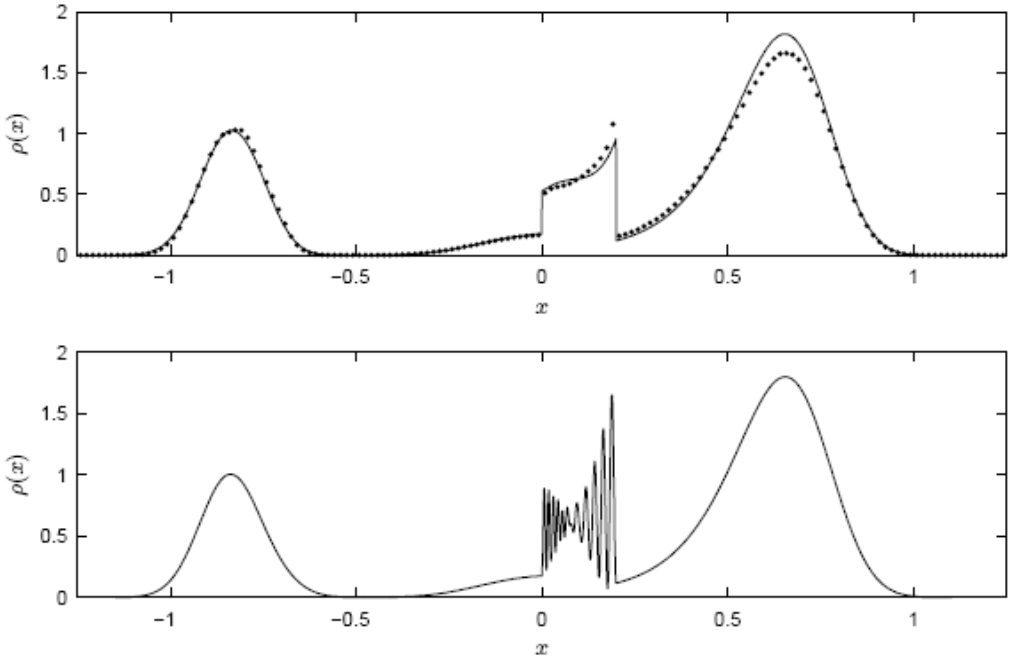
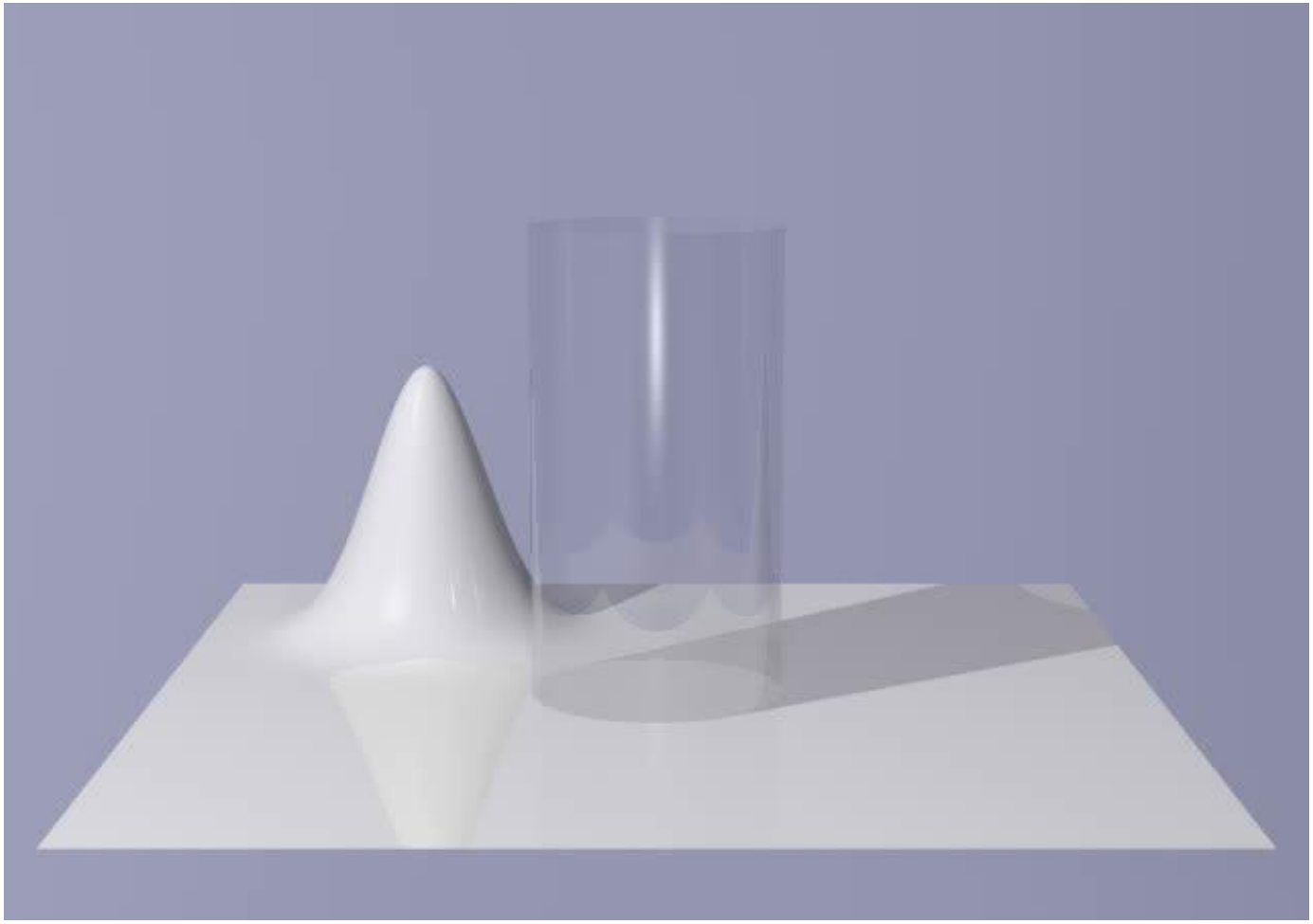
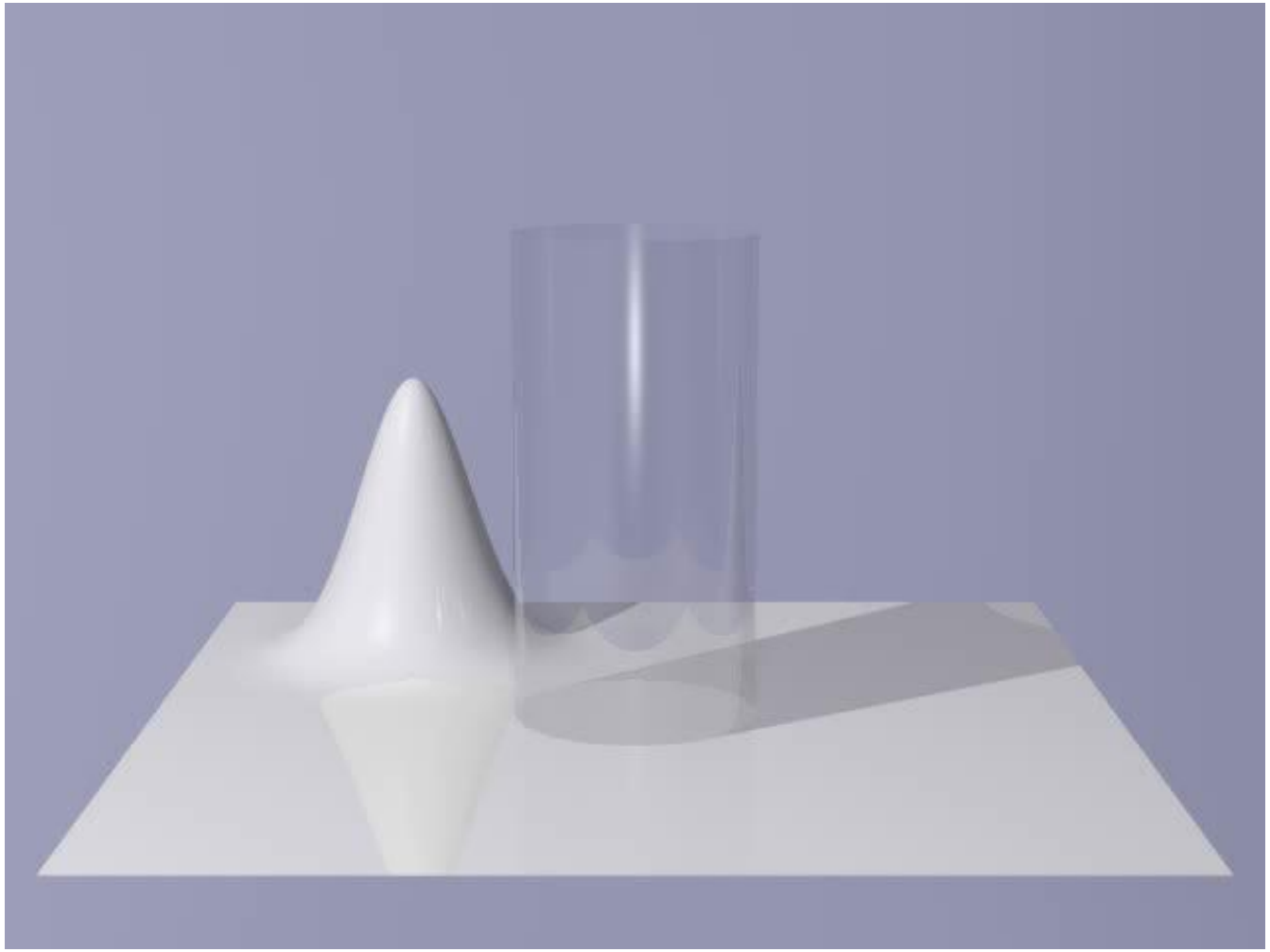


FIG. 5.3. *Position densities for the numerical semiclassical Liouville (top) and von Neumann (bottom) solutions of Example 5.3. The • in the Liouville plot shows the numerical solution for with 150 grid points over the domain* $[-1.25, 1.25]$. *The solid line shows the numerical solution for 3200 grid points. The von Neumann solution is for* $\varepsilon = 0.002$.

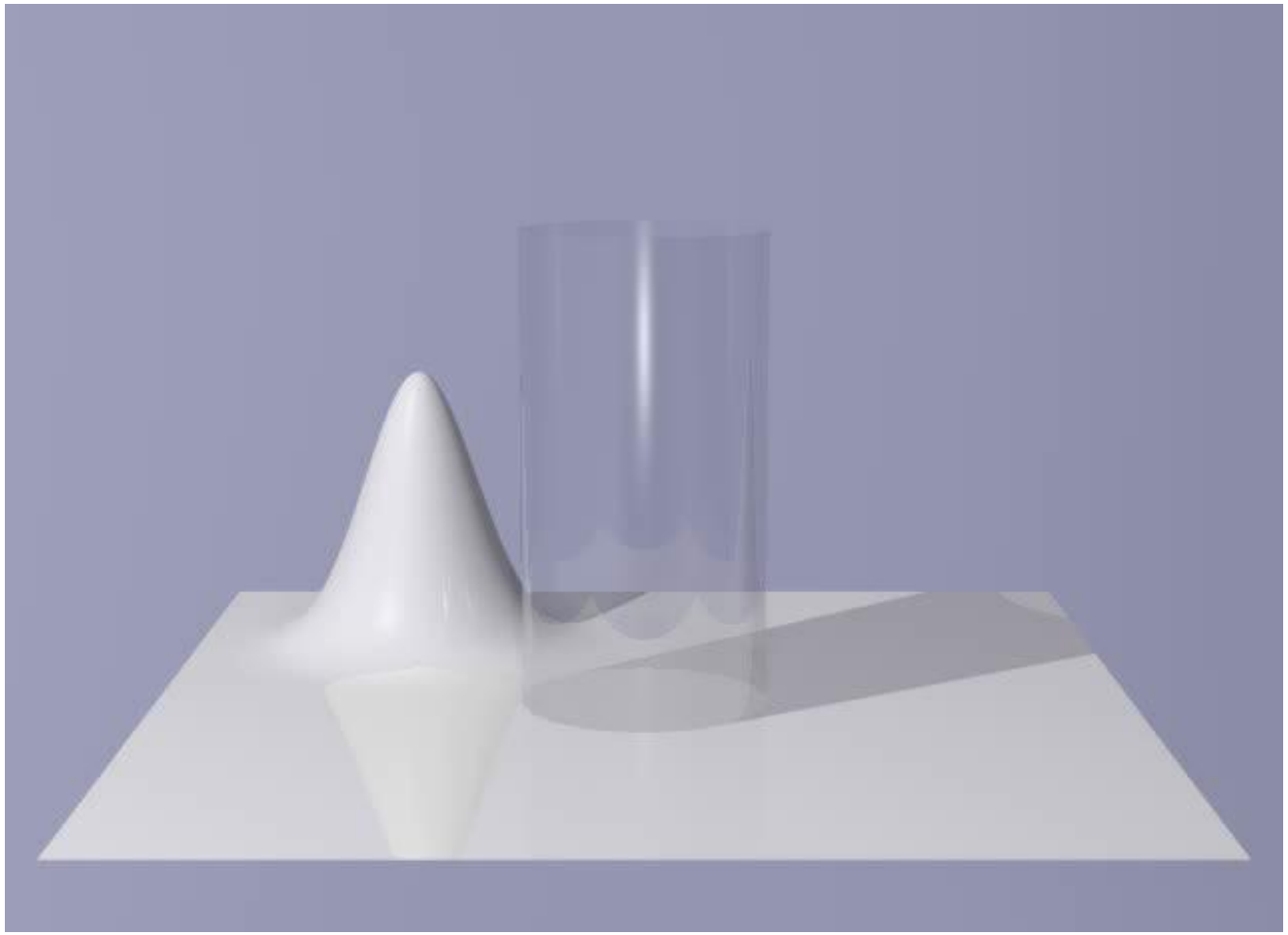
Circular barrier (Schrodinger with ε=1/400)



Circular barrier (semiclassical model)



Circular barrier (classical model)



Entropy

- The semiclassical model is time-irreversible.

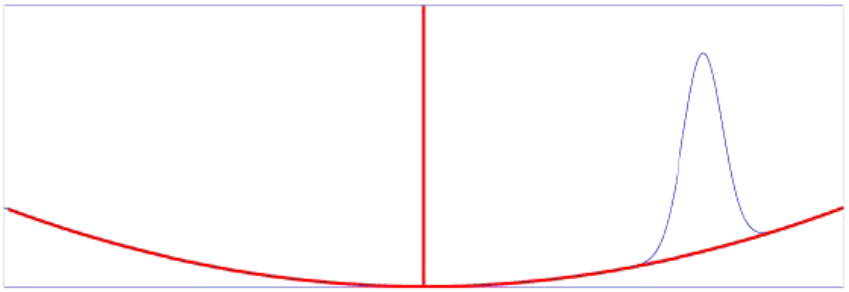
Loss of the phase information

cannot deal with inteference

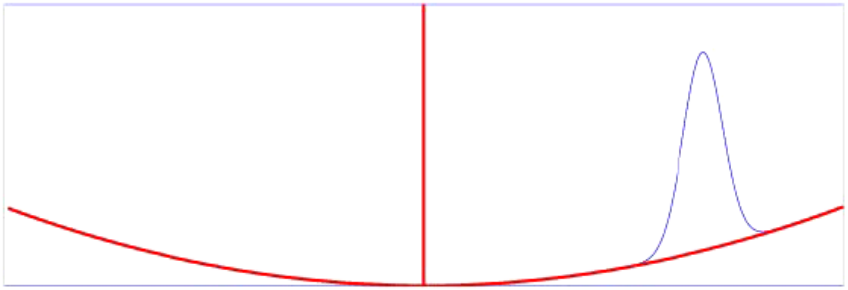
decoherence

$V(x) = \delta(x) + x^2/2$

Quantum



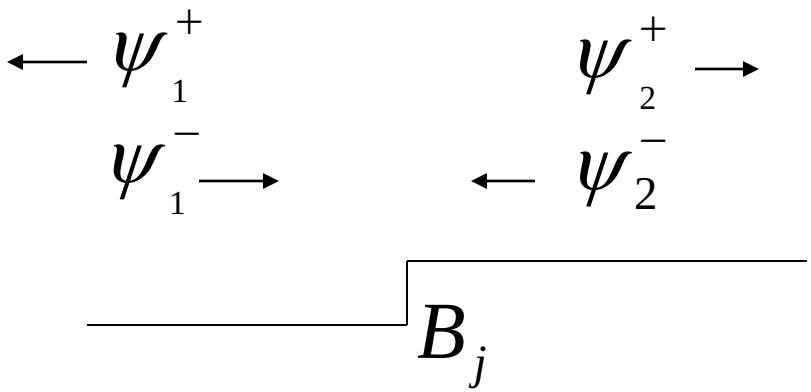
semiclassical



A Coherent Semiclassical Model

Initialization:

- Divide barrier into several thin barriers $B_1, B_2, \ldots, B_n$
- Solve stationary Schrödinger equation



- Matching conditions

$$\begin{pmatrix} \psi_1^+ \\ \psi_2^+ \end{pmatrix} = \begin{pmatrix} r_1 & t_2 \\ t_1 & r_2 \end{pmatrix} \begin{pmatrix} \psi_1^- \\ \psi_2^- \end{pmatrix} = S_j \begin{pmatrix} \psi_1^- \\ \psi_2^- \end{pmatrix}$$

A coherent model

- Initial conditions $\Phi(x, p, 0) = \sqrt{f(x, p, 0)}$
- Solve Liouville equation

$$\frac{d\Phi}{dt} = \frac{\partial \Phi}{dt} + p\frac{\partial \Phi}{dx} - \frac{dV}{dx}\frac{\partial \Phi}{dp} = 0$$

- Interface condition

$$\begin{pmatrix} \Phi^{+}_{j-1} \\ \Phi^{+}_{j} \end{pmatrix} = S_j \begin{pmatrix} \Phi^{-}_{j-1} \\ \Phi^{-}_{j} \end{pmatrix}$$

- Solution $f(x, p, t) = \left|\Phi(x, p, t)\right|^2$

Interference

Define the semiclassical probability amplitude as

$$\Phi(x,p,t) = \sqrt{f(x,p,t)}e^{i\theta(x,p)}$$

where $\theta(x,p)$ is the phase offset from the initial conditions $\Phi(x,p,0) = \sqrt{f(x,p,0)}$.

Hence, if $\Phi(x,p,t)$ is a solution to the Liouville equation for initial condition $\Phi(x,p,0)$, then $f_{\text{coh}}(x,p,t)$ is a solution to the Liouville equation for initial condition $f_{\text{coh}}(x,p,0)$. Furthermore, for two solutions Φ_1 and Φ_2 with $f_1 = |\Phi_1|^2$ and $f_2 = |\Phi_2|^2$,

$$|\Phi_1 + \Phi_2|^2 = f_1 + f_2 + 2\sqrt{f_1 f_2}\cos(\theta_1 - \theta_2). \tag{10}$$

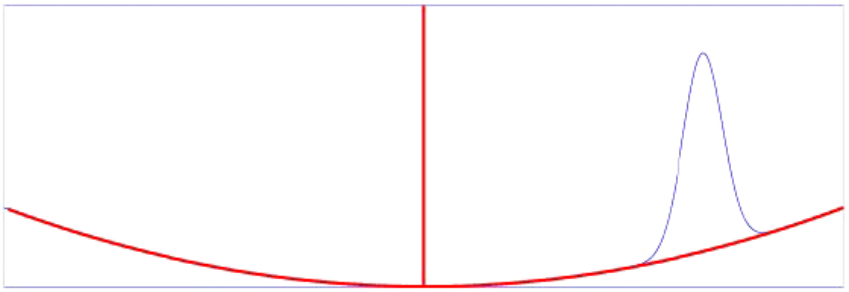
For any two probability densities ψ_1 and ψ_2 with with $\rho_1 = \int f_1\, dp = |\psi_1|^2$ and $\rho_2 = \int f_2\, dp = |\psi_2|^2$,

$$|\psi_1 + \psi_2|^2 = \rho_1 + \rho_2 + 2\sqrt{\rho_1 \rho_2}\cos(\theta_1 - \theta_2). \tag{11}$$

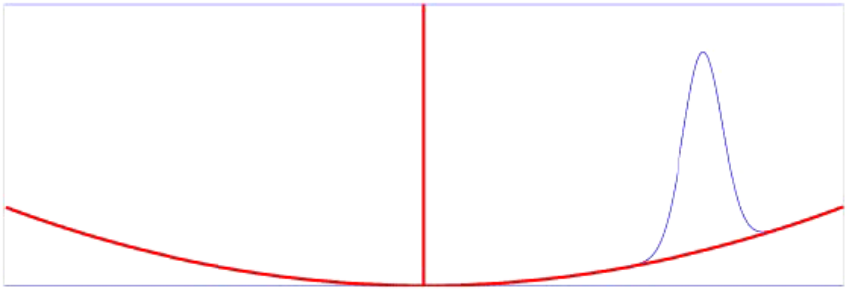
The coherent model

- $V(x) = \delta(x) + x^2/2$

Quantum

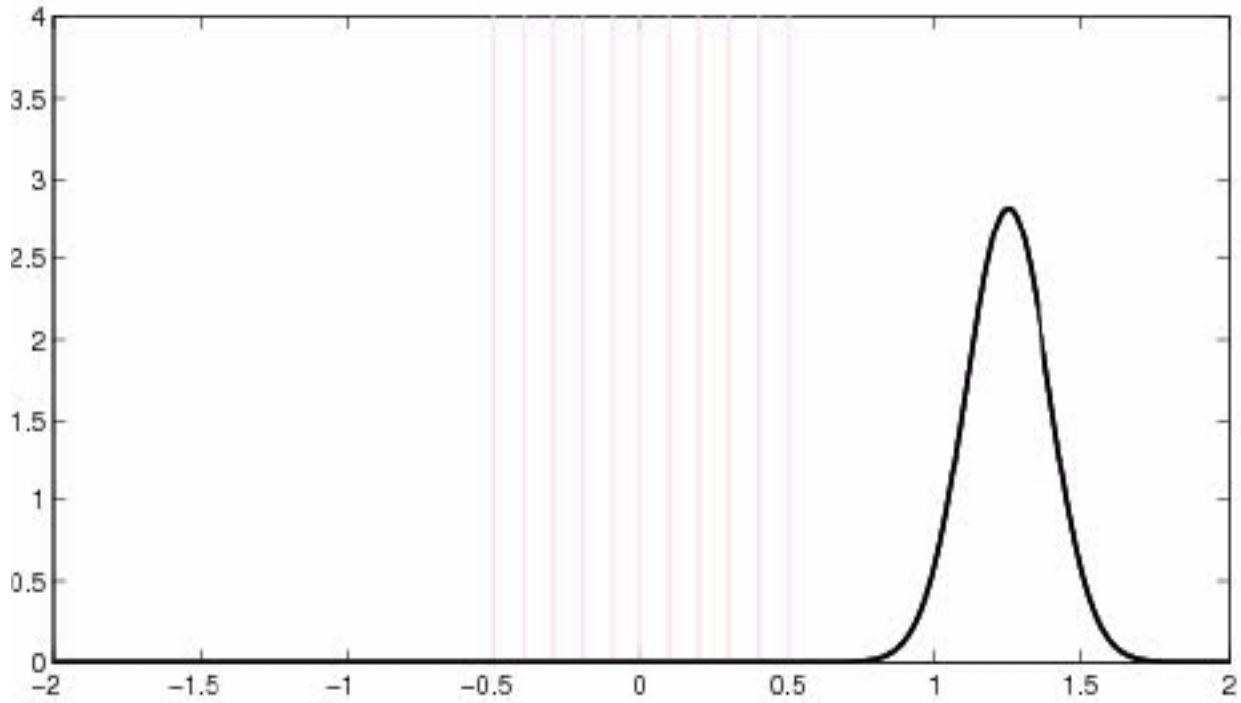


semiclassical

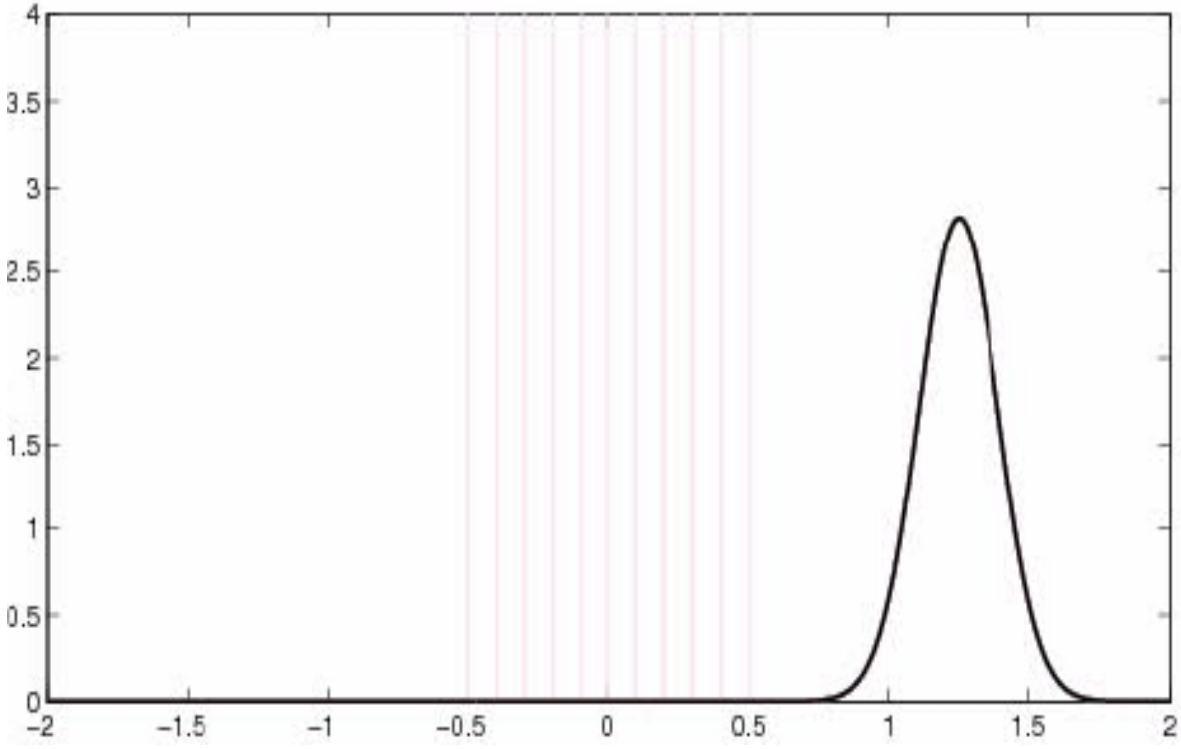


multiple delta barrier (Kronig-Penney)

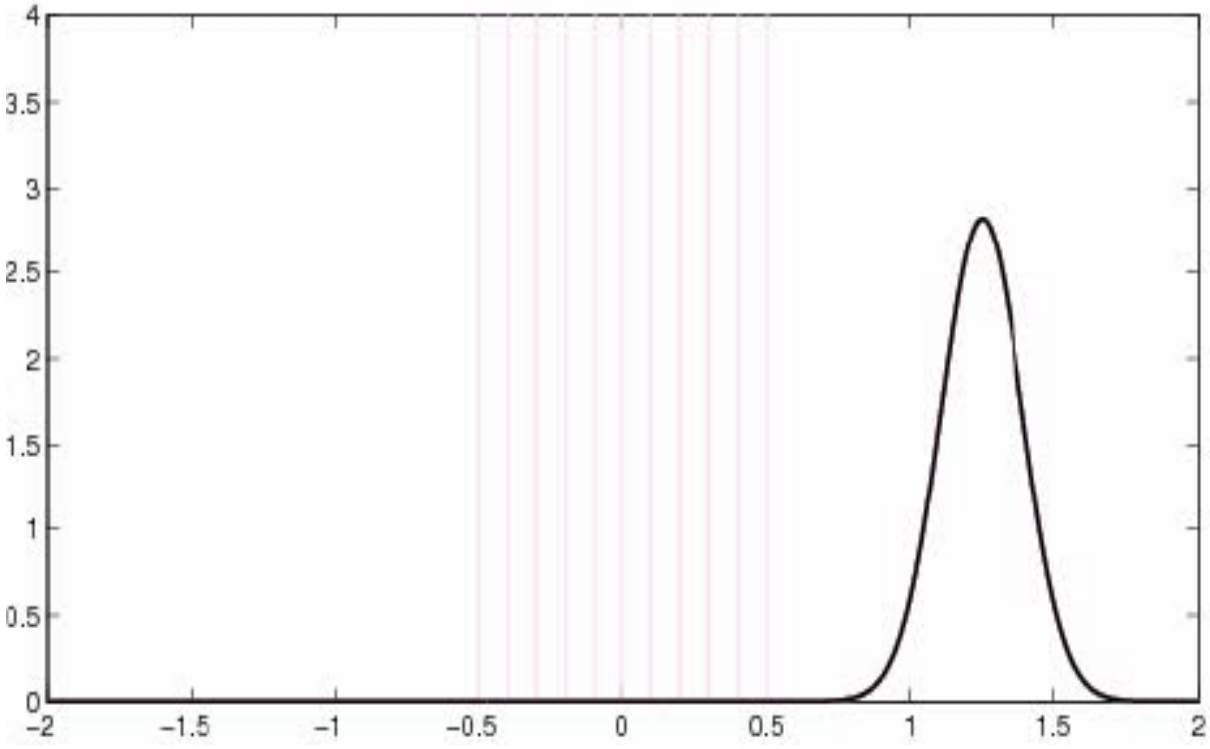
decoherent model vs Schrodinger



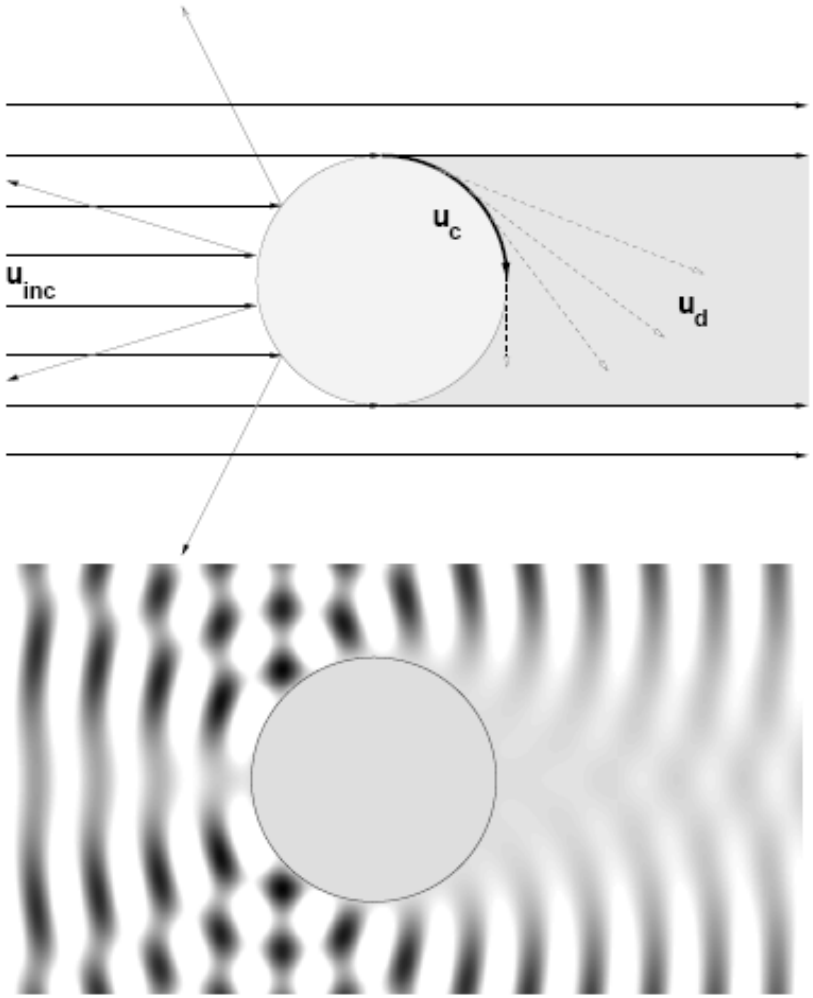
multiple delta barrier (Kronig-Penney) coherent model vs Schrodinger



multiple delta barrier (Kronig-Penney)
average soln of coherent model vs Schrodinger



III. Computation of diffraction (with *Dongsheng Yin*)



Transmissions, reflections and diffractions (Type A interface)

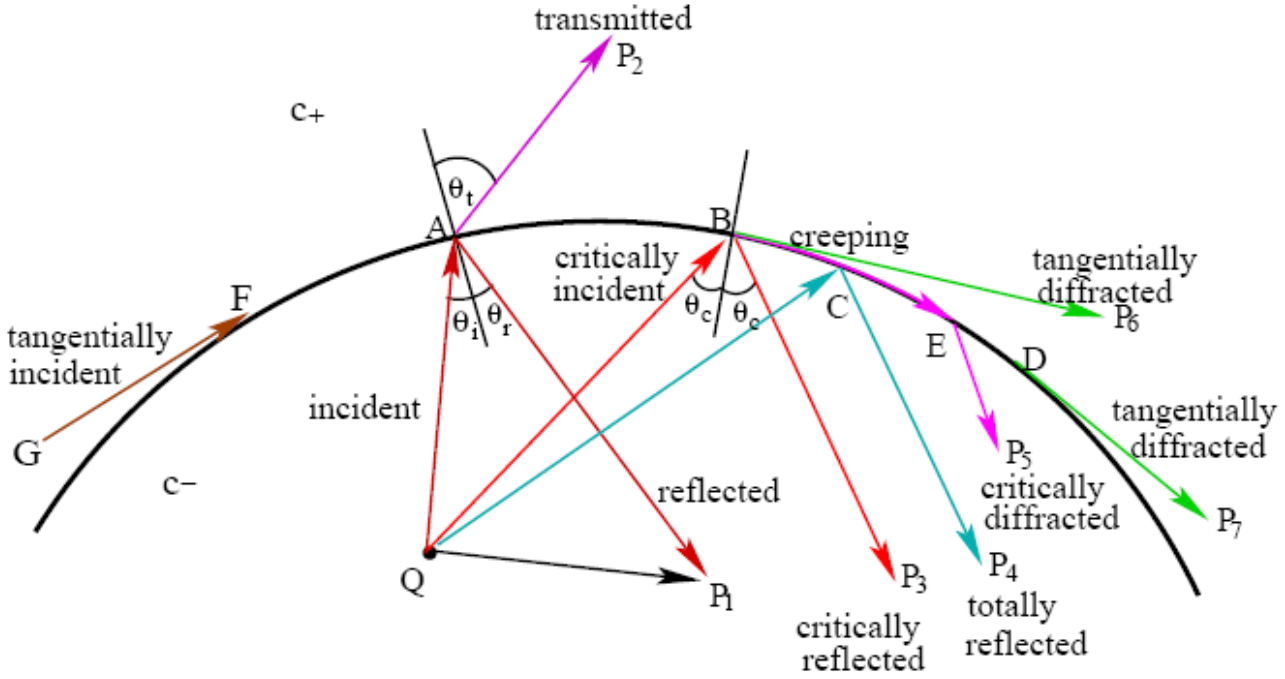


Figure 1: wave reflection, transmission and diffraction at a Type A interface

Type B interface

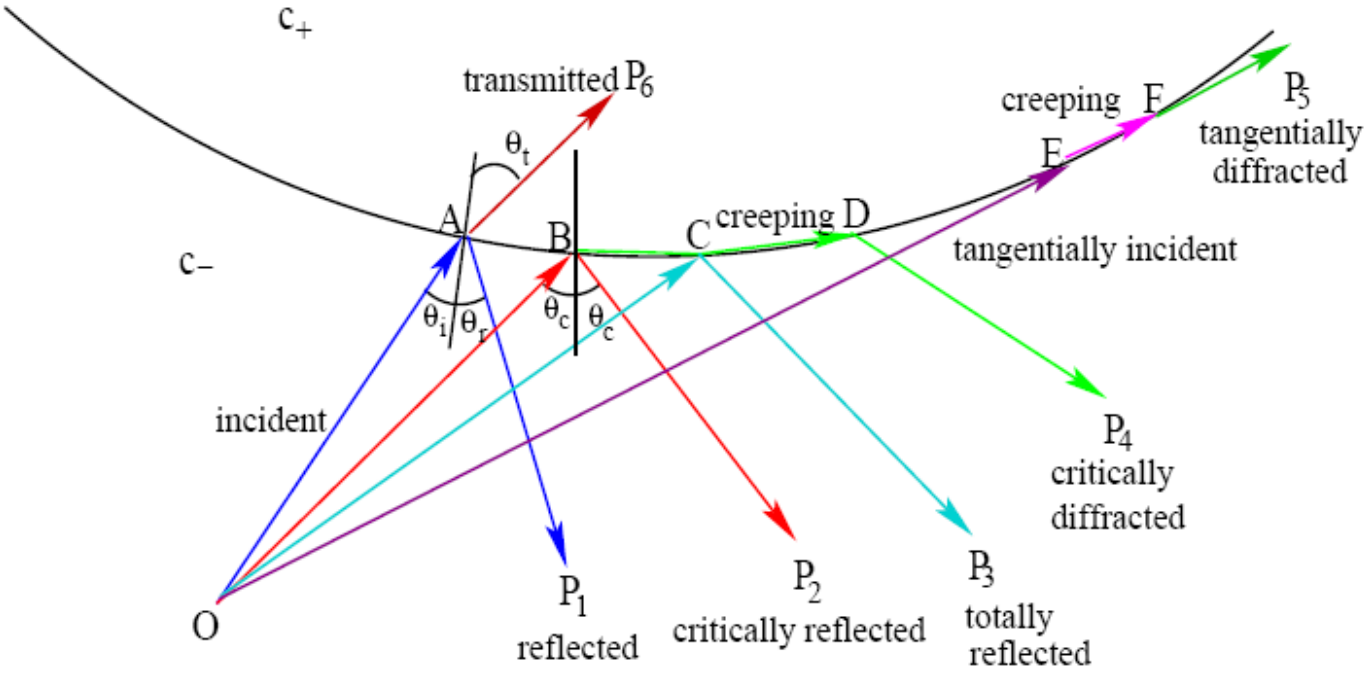


Figure 2: wave reflection, transmission and diffraction at a Type B interface

Hamiltonian preserving+Geometric Theory of Diffraction

- We uncorporate Keller's GTD theory into the interface condition:

$$\tau = \left(\frac{c^-}{c^+}\right)^2 (\xi')^2 + \left[\left(\frac{c^-}{c^+}\right)^2 - 1\right](\eta')^2 . \tag{4.1}$$

4.1 The Type B interface

We first discuss the **Type B** interface. For $\xi' > 0$, we use the following partial transmission and reflection condition at the interface:

$$f(t, \mathbf{x}^+, \xi', \eta') = \alpha_+^T f(t, \mathbf{x}^-, \xi_t', \eta_t') + \alpha_+^R f(t, \mathbf{x}^+, -\xi', \eta'), \ \ \xi_t' > 0. \tag{4.2}$$

with $\eta_t' = \eta'$ and ξ_t' obtained from ξ' through the constant condition (1.5).

For $\xi' < 0$, there are three possibilities:

1. if $\tau > 0$ (partial reflection and transmission), then
$$f(t, \mathbf{x}^-, \xi', \eta') = \alpha_-^R f(t, \mathbf{x}^-, -\xi', \eta') + \alpha_-^T f(t, \mathbf{x}^+, \xi_t', \eta_t') . \tag{4.3}$$
2. if $\tau < 0$ (complete reflection), the interface condition is
$$f(t, \mathbf{x}^-, \xi', \eta') = f(t, \mathbf{x}^-, -\xi', \eta'). \tag{4.4}$$
3. if $\tau = 0$ (**Case I**), there will be some diffractions, so the interface condition is
$$f(t, \mathbf{x}^-(s), \xi', \eta') = \alpha_{B_1}^D(\mathbf{x}(s)) \int_{s_b}^{s} \alpha_{B_1}^D(\mathbf{x}(s_q)) e^{-\int_{s_q}^{s} \beta_{B_1}(\mathbf{x}(z))dz}$$
$$\cdot \int_{\Gamma_q} f(t - \bar{t}_q, \mathbf{x}^-(s_q), \xi_q', \eta'(\xi_q')) d\xi_q' ds_q + (1 - \alpha_{B_1}^D(\mathbf{x}(s))) f(t, \mathbf{x}^-(s), -\xi', \eta'), \tag{4.5}$$
here Γ_q is the *line of critical angle*
$$\frac{\xi_q'}{\eta_q'} = \mathrm{sgn}(\eta') \sqrt{\left(\frac{c^+(\mathbf{x}(s_q))}{c^-(\mathbf{x}(s_q))}\right)^2 - 1}. \tag{4.6}$$

If $\xi' = 0$ (**case II**), there will be some tangentially diffracted waves, so

$$\begin{aligned} f(t, \mathbf{x}^-, \xi', \eta') &= \alpha^D_{B_2}(\mathbf{x}) \int_{s_b}^{s} \alpha^D_{B_2}(\mathbf{x}_q) e^{-\int_{s_q}^{s} \beta_{B_2}(\mathbf{x}(z))dz} \mathrm{sgn}(\eta') \int_0^{\mathrm{sgn}(\eta')\infty} f_-(t - \overline{t}_q, \mathbf{x}_q^-, 0, \eta'_q) d\eta'_q ds \\ &\quad + \big(1 - \alpha^D_{B_2}(\mathbf{x})\big) f_-(t, \mathbf{x}^-, \xi', \eta'), \end{aligned} \tag{4.7}$$

where $\overline{t}_q = |\int_{s_q}^{s} \frac{dz}{c^-(z)}|$ is the average time,

$$f_-(t, \mathbf{x}, \xi', \eta') = \lim_{\omega \to 0^+} f(t, \mathbf{x} - \omega \mathbf{k}', \xi', \eta') \,.$$

In this case, the incident wave tangentially hits the interface from the slow side. Part of the incident wave transforms into the creeping wave with coefficient $\alpha^D_{B_2}$, and part of the incident wave travels through tangentially with coefficient $1 - \alpha^D_{B_2}$.

A type A interface

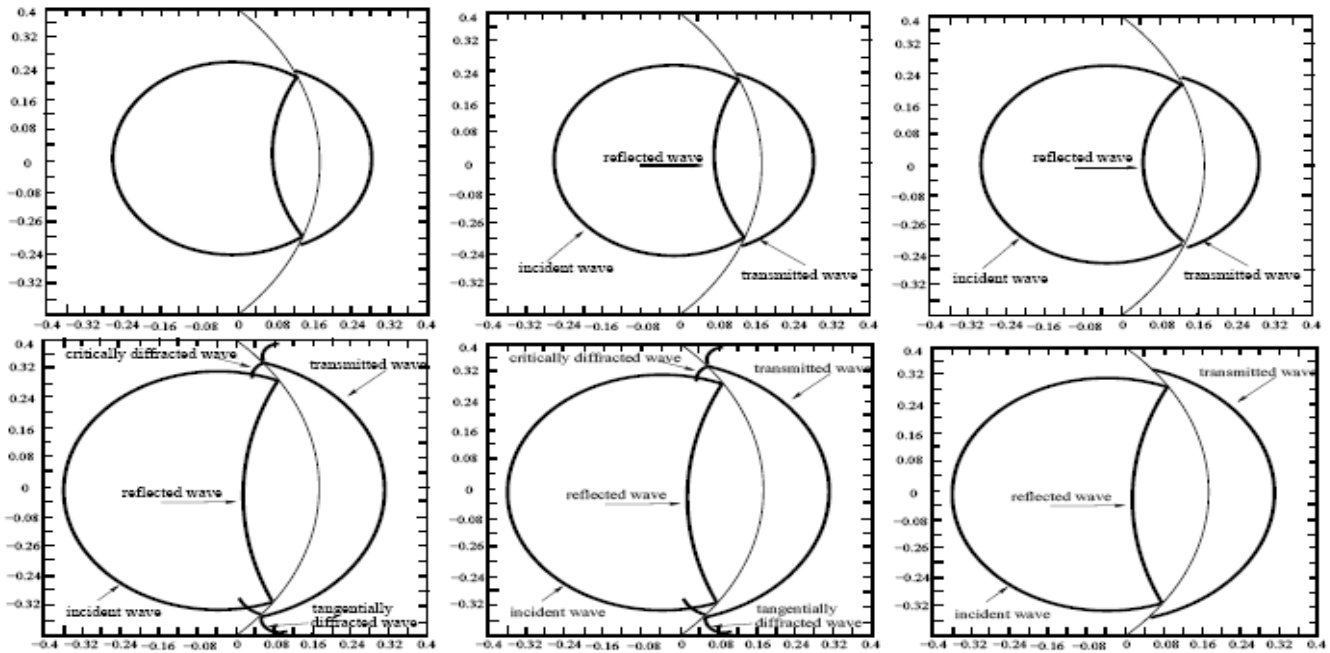


Figure 8: Example 5.3, wavefront of energy density $\mathcal{E}$ and $\mathcal{E}^{(0)}$ at $t = 0.1$ (top) and 0.2 (bottom). Left: $\mathcal{E}$; middle: $\mathcal{E}^{(0)}$ by GTD; right: $\mathcal{E}^{(0)}$ by GO.

Another type B interface

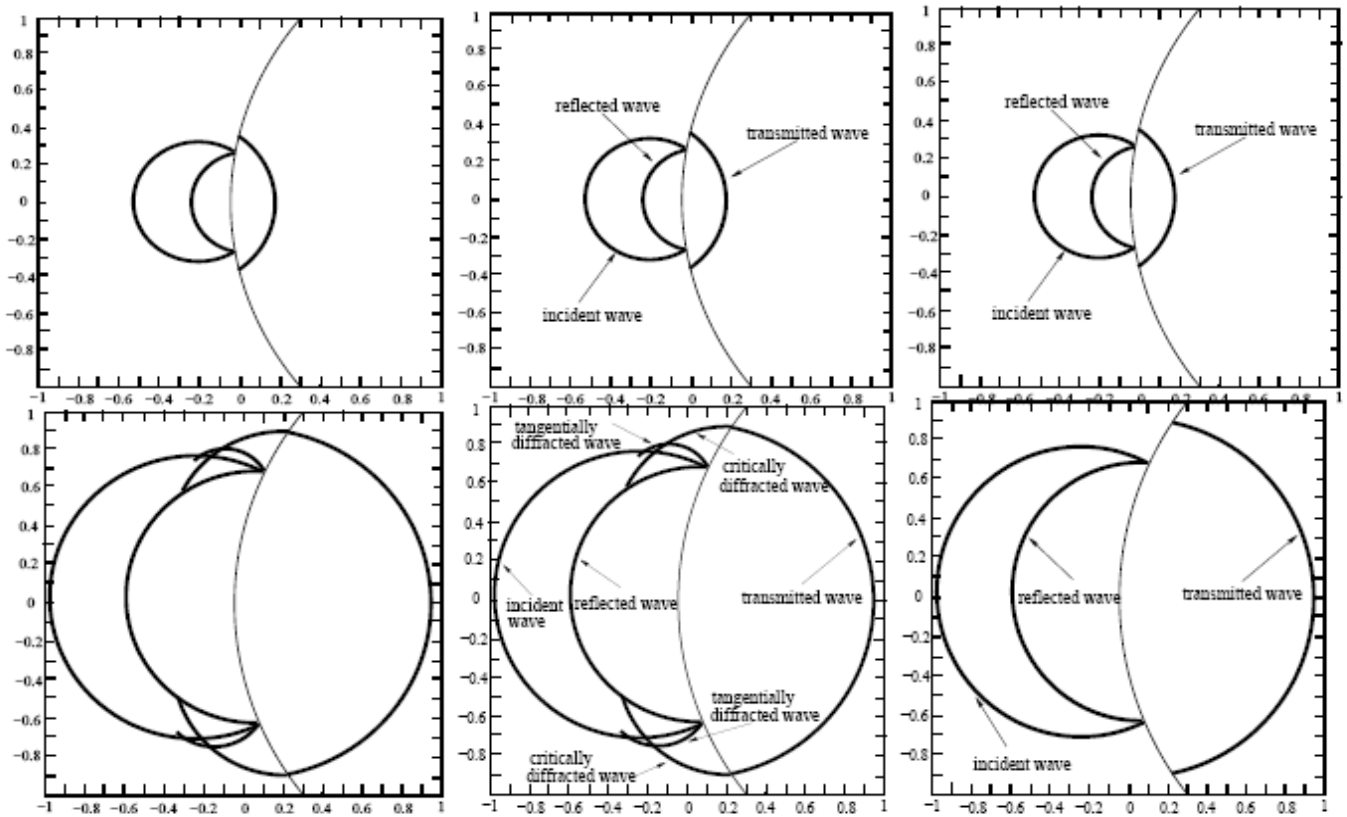


Figure 6: Example 5.2, wavefront of energy density $\mathcal{E}$ and $\mathcal{E}^{(0)}$ at $t = 0.15$ (top) and 0.5 (bottom). Left: $\mathcal{E}$; middle: $\mathcal{E}^{(0)}$ by GTD; right: $\mathcal{E}^{(0)}$ by GO.

Half plane

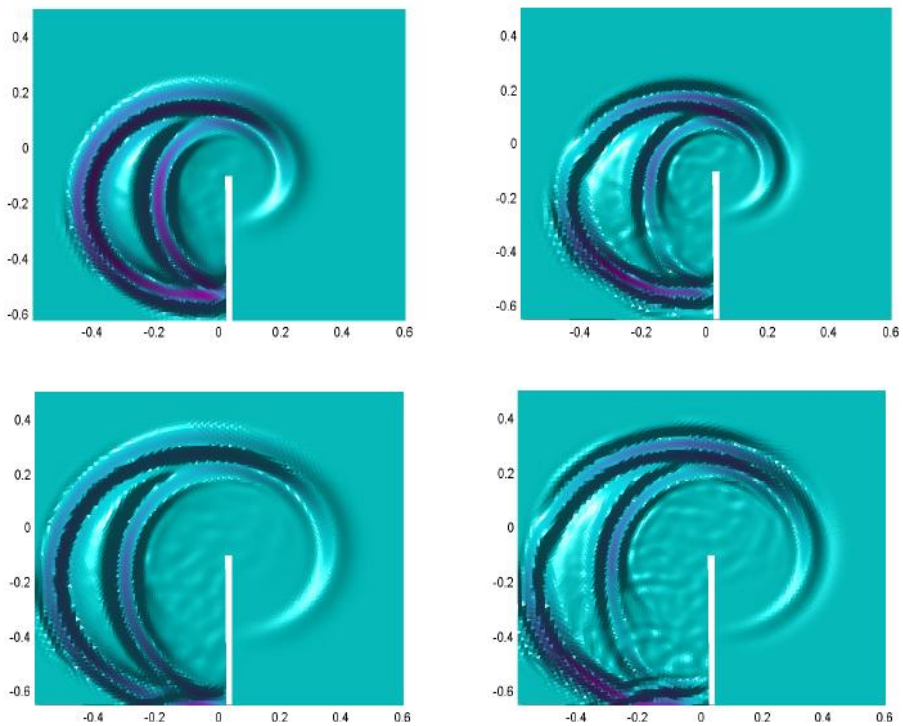
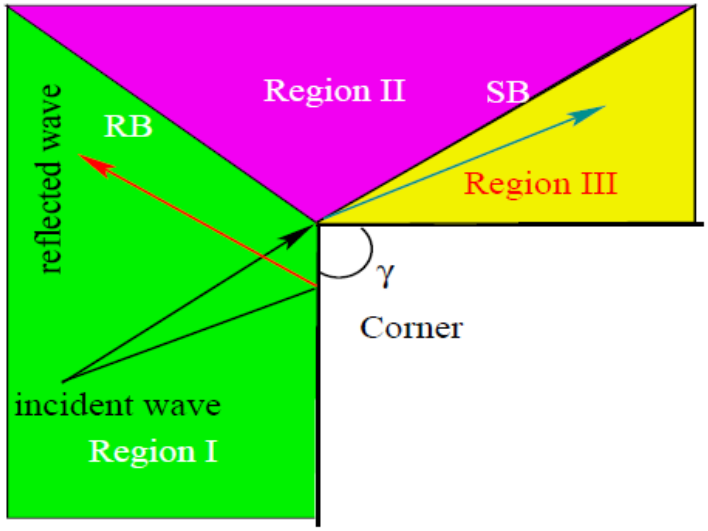


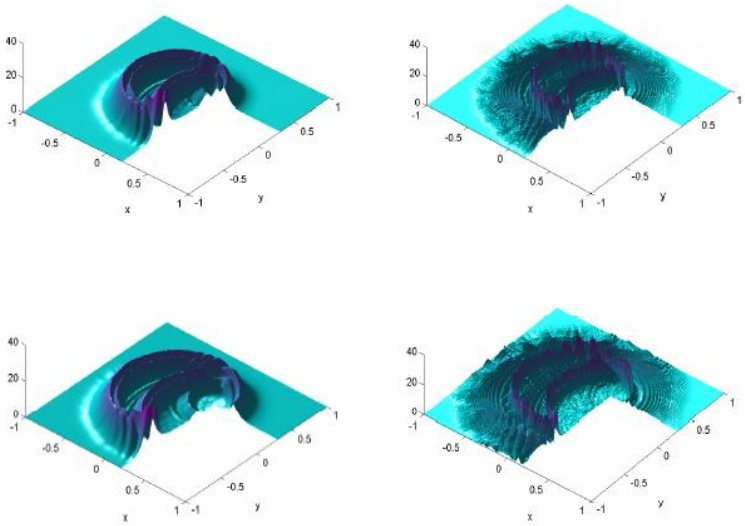
Figure 4: Example 5.1, energy density $\mathcal{E}^{(0)}$ and $\mathcal{E}$ at $t = 0.2$ (top) and 0.3 (bottom). Left: $\mathcal{E}^{(0)}$ by GTD; right: $\mathcal{E}$.

Corner diffraction

Illustrative figure



GTD vs full wave simulation



VI: surface hopping (J-Qi-Zhang)

- Born-Oppenheimer (*adiabatic)* approximation

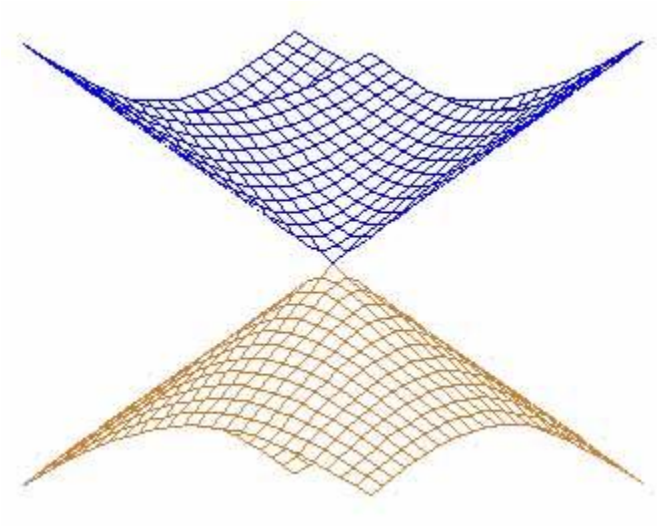
high ratio between the nuclear and electronic masses;

electronic Schrodinger equation is first solved, given electronic energy states that serve as the potential functions for the nuclear Schrodinger equation;

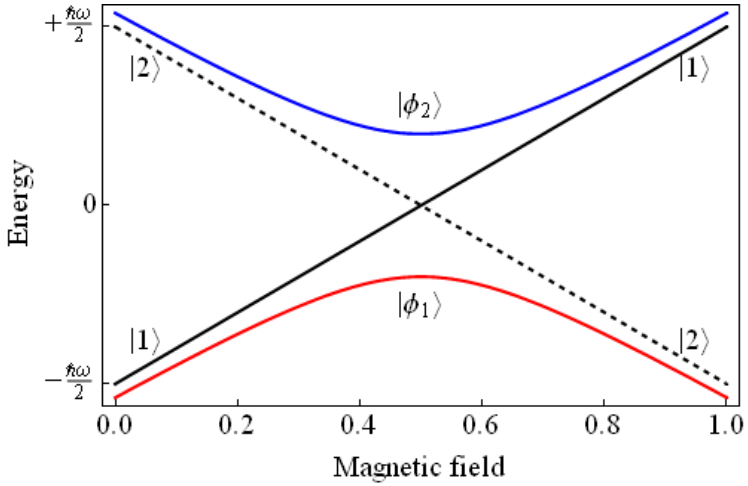
when energies of different electronic states are close , transitions between different energy states occur and the BO breaksdown

Transition between electronic states

Conical crossing



Avoided crossing



The Landau-Zener formula

- gives the probability of a diabatic transition between the two energy states

$$P_D = e^{-2\pi\Gamma}$$

$$\Gamma = \frac{a^2/\hbar}{\left|\frac{\partial}{\partial t}(E_2 - E_1)\right|} = \frac{a^2/\hbar}{\left|\frac{dq}{dt}\frac{\partial}{\partial q}(E_2 - E_1)\right|}$$

$$= \frac{a^2}{\hbar|\alpha|}$$

The surface hopping method (Tully ‘71)

- Particles follow the classical trajectory determined by the classical Hamiltonian; at avoided crossing region they “hop” with transition probability to different energy level (Hamiltonian system for different potential surfaces)
- A Monte-Carlo procedure; or particle splitting

An Eulerian Surface Hopping method

- For two-energy level system we use two Liouville equations, corresponding to two Hamiltonians, with an interface condition for Landau-Zener transition

$$\partial_t u_\tau + \nabla_{\mathbf{k}} \lambda_\tau \cdot \nabla_{\mathbf{x}} u_\tau - \nabla_{\mathbf{x}} \lambda_\tau \cdot \nabla_{\mathbf{k}} u_\tau = 0, \quad (t, \mathrm{x}, \mathrm{k}) \in R^+ \times \Omega, \quad \tau = 1, 2,$$

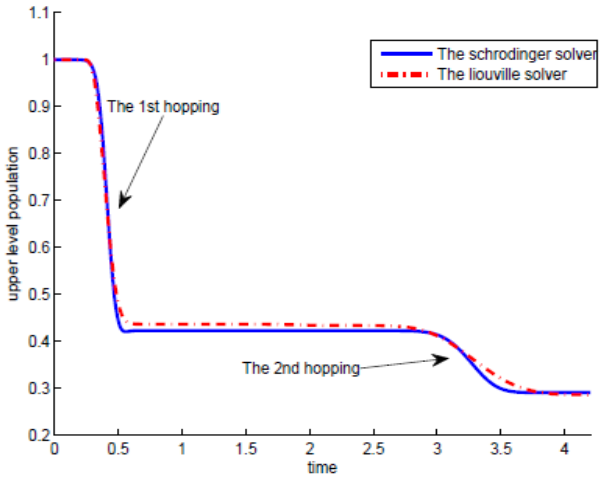
$$j_\tau(\mathrm{x}, \mathrm{k}) = \nabla_{(\mathrm{x},\mathrm{k})} u_\tau(\mathrm{x}, \mathrm{k}), \ \tau = 1, 2,$$

$$\begin{pmatrix} j_1(\mathrm{x}_0^+, \mathrm{k}_0^+) \cdot \vec{n} \\ j_2(\mathrm{x}_0^+, \mathrm{k}_0^+) \cdot \vec{n} \end{pmatrix} = \begin{pmatrix} 1 - T(\mathrm{x}_0, \mathrm{k}_0) & T(\mathrm{x}_0, \mathrm{k}_0) \\ T(\mathrm{x}_0, \mathrm{k}_0) & 1 - T(\mathrm{x}_0, \mathrm{k}_0) \end{pmatrix} \begin{pmatrix} j_1(\mathrm{x}_0^-, \mathrm{k}_0^-) \cdot \vec{n} \\ j_2(\mathrm{x}_0^-, \mathrm{k}_0^-) \cdot \vec{n} \end{pmatrix}$$

Numerical Examples

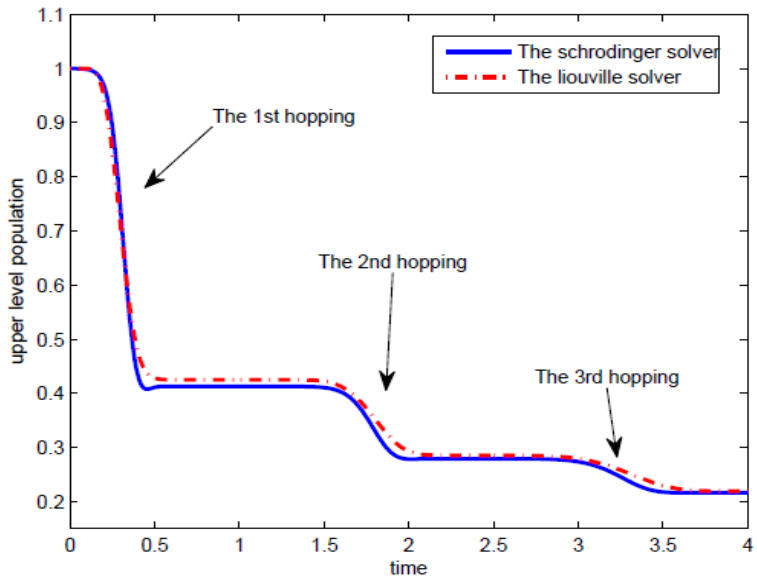
Linear isotropic potential

$$V_{iso}(\mathbf{x}) = \begin{pmatrix} x & y \\ y & -x \end{pmatrix}$$



John-Teller potential

$$V_{JT}(\mathbf{x}) = |\mathbf{x}|^2 + \begin{pmatrix} x & y \\ y & -x \end{pmatrix}$$



Advantage of Eulerian method

- No Monte-Carlo procedure
- High order accuracy
- Easily adopted to any number of energy states—number of Liouville equations fixed
- Arise naturally from semiclassical limit of systems of Schrodinger equation via the Wigner transform (Spohn, Teufel, Hagedorn, Lasser, Schutte, etc.)

V. An Eulerian Gaussian-Beam Method (J-Wu-Yang)

- Geometric optics or semiclassical limit blows up density at caustics. Gaussian beam is more accurate at caustics and preserves the Maslov-Keller phase shift

$$\varphi_{la}^{\varepsilon}(t, \boldsymbol{x}, \boldsymbol{y}_0) = A(t, \boldsymbol{y}) e^{iT(t,\boldsymbol{x},\boldsymbol{y})/\varepsilon}, \tag{2.1}$$

where $\boldsymbol{y} = \boldsymbol{y}(t, \boldsymbol{y}_0)$ and $T(t, \boldsymbol{x}, \boldsymbol{y})$ is given by the Taylor expansion

$$T(t, \boldsymbol{x}, \boldsymbol{y}) = S(t, \boldsymbol{y}) + \boldsymbol{p}(t, \boldsymbol{y}) \cdot (\boldsymbol{x} - \boldsymbol{y}) + \frac{1}{2}(\boldsymbol{x} - \boldsymbol{y})^\top M(t, \boldsymbol{y})(\boldsymbol{x} - \boldsymbol{y}) + O(|\boldsymbol{x} - \boldsymbol{y}|^3), \tag{2.2}$$

in which $(\boldsymbol{x} - \boldsymbol{y})^\top$ is the transpose of $(\boldsymbol{x} - \boldsymbol{y})$. Here $S \in \mathbb{R}$, $\boldsymbol{p} \in \mathbb{R}^n$, $A \in \mathbb{C}$, $M \in \mathbb{C}^{n \times n}$. The imaginary part of M will be chosen so that (2.1) has a Gaussian beam profile. We call (2.1) as the beam-shaped ansatz.

Lagrangian formulation (Popov, Hill, Heller)

$$
\begin{aligned}
\frac{\mathrm{d}\boldsymbol{y}}{\mathrm{d}t} &= \boldsymbol{p}, \\
\frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} &= -\nabla_{\boldsymbol{x}} V, \\
\frac{\mathrm{d}M}{\mathrm{d}t} &= -M^2 - \nabla_{\boldsymbol{x}}^2 V, \\
\frac{\mathrm{d}S}{\mathrm{d}t} &= \frac{1}{2}\,|\boldsymbol{p}|^2 - V, \\
\frac{\mathrm{d}A}{\mathrm{d}t} &= -\frac{1}{2}\big(\mathrm{Tr}(M)\big)A.
\end{aligned}
$$

$$
\begin{aligned}
\boldsymbol{y}(0,\boldsymbol{y}_0) &= \boldsymbol{y}_0, \\
\boldsymbol{p}(0,\boldsymbol{y}_0) &= \nabla_{\boldsymbol{x}} S_0(\boldsymbol{y}_0), \\
M(0,\boldsymbol{y}_0) &= \nabla_{\boldsymbol{x}}^2 S_0(\boldsymbol{y}_0) + iI, \\
S(0,\boldsymbol{y}_0) &= S_0(\boldsymbol{y}_0), \\
A(0,\boldsymbol{y}_0) &= A_0(\boldsymbol{y}_0).
\end{aligned}
$$

The Lagrangian beam summation

$$\Phi_{la}^{\varepsilon}(t,\boldsymbol{x}) = \int_{\mathbb{R}^n} \left(\frac{1}{2\pi\varepsilon}\right)^{\frac{n}{2}} r_\theta(\boldsymbol{x} - \boldsymbol{y}(t,\boldsymbol{y}_0))\varphi_{la}^{\varepsilon}(t,\boldsymbol{x},\boldsymbol{y}_0)\mathrm{d}\boldsymbol{y}_0. \qquad (:$$

The discrete form of (2.28) in a bounded domain is given by

$$\Phi_{la}^{\varepsilon}(t,\boldsymbol{x}) = \sum_{j=1}^{N_{\boldsymbol{y}_0}} \left(\frac{1}{2\pi\varepsilon}\right)^{\frac{n}{2}} r_\theta(\boldsymbol{x} - \boldsymbol{y}(t,\boldsymbol{y}_0^j))\varphi_{la}^{\varepsilon}(t,\boldsymbol{x},\boldsymbol{y}_0^j)\Delta\boldsymbol{y}_0, \qquad (:$$

The Eulrian formulation

$\boldsymbol{L}\, f = \partial_t f + \xi \cdot \nabla_y f - \nabla_y V \cdot \nabla_\xi f$

- For velocity or phase:

  Solve $\boldsymbol{L}\, \phi = 0 \quad \phi \in C^n$

  with $\phi(0,y,\xi) = -i\, y + (\xi - \nabla_y S_0)$

  (note $\mathrm{Re}(\phi)=0$ at $\xi = u = \nabla_y S$)
- For Hessian: $M = -\nabla_y \phi\, (\nabla_\xi \phi)^{-1}$
- For amplitude: Solves $\boldsymbol{L}\, \psi = 0$, $\psi \in R$

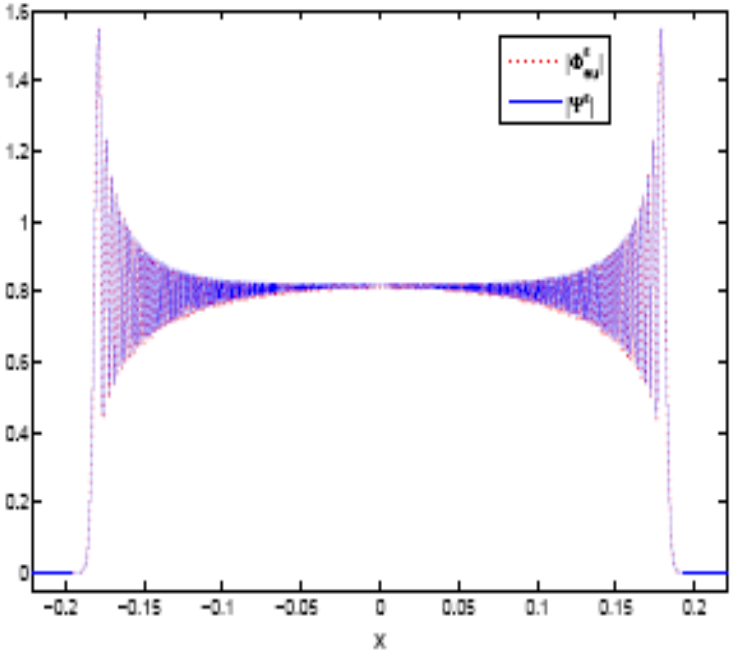
  with $\psi(0, y, \xi) = |A_0|^2$

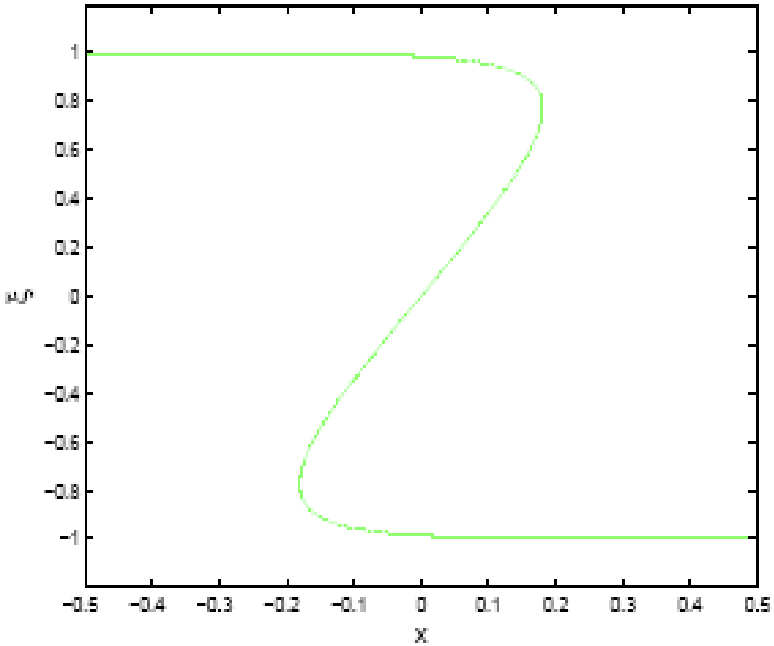
  then $A(t, x) = (\det (\nabla_\xi \phi)^{-1})\, \psi)^{1/2}$ (principle value)

The complexity is comparable to geometric optics or semiclassical limit; only now that $\phi \in C^n$ rather than R^n

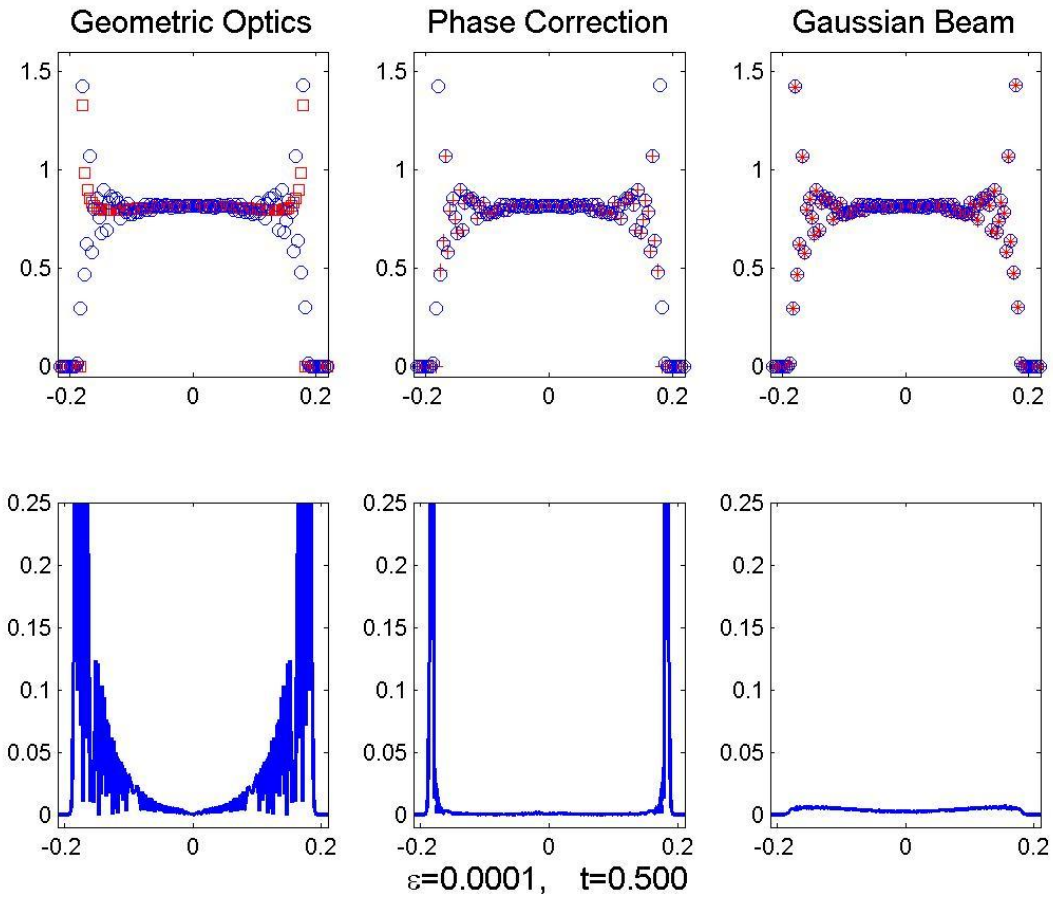
A numerical example ($\varepsilon=10^{-4}$)

- Density
- Velocity





Error comparison



Summary

Liouville equation based Eulerian computational methods for quantum dynamics:

- Partial transmissions and reflections, diffractions, and quantum barriers
- Surface hopping
- Gaussian beam methods as an improvement of the classical solver
- Computational cost is classical, yet certain important quantum information are captured
- can use local level set method to further reduce the cost

Future projects

- Gaussian beam for interface and quantum barriers
- Coherant semiclassical models for multi-D quantum barriers
- Gaussian beam or coherent quantum-classical coupling for surface hopping

Computational cost ($\varepsilon=10^{-6}$)

- Full simulation of original problem for

$$\Delta x \sim \Delta t \sim O(\varepsilon)=O(10^{-6})$$

Dimension	total cost
2d,	$O(10^{18})$
3d	$O(10^{24})$

- Liouville based solver for diffraction

$$\Delta x \sim \Delta t \sim O(\varepsilon^{1/3}) = O(10^{-2})$$

Dimension	total cost
2d,	$O(10^{10})$
3d	$O(10^{14})$

Can be much less with local mesh refinement