Quantum Wavepacket Dynamics with Trajectories: Computational Issues

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Overview

- Quantum Hydrodynamics
  - Background and motivation
  - The de Broglie-Bohm equations of motion
  - The Quantum Trajectory Method
- Computational Issues
  - Accurate and stable derivatives
  - Unitarity
  - Node formation and singularities
- Applications
  - 1 and 2 dimensional tunneling (Eckart barrier)
  - 1 dimensional rounded square barrier (resonance)
  - N dimensional Eckart barrier (N=1, …, 100)

Background and Motivation

Goal: Quantum mechanical treatment of the nuclear motion in chemical reactions with a “large” number (> 4) of atoms

Applications: Proton transfer reactions in enzyme catalysis, vibrational energy transfer in liquid water, membranes, ionic solutions, combustion, atmospheric, and polymer chemistry

- Standard quantum mechanical methods scale exponentially with the number of atoms

- Quantum hydrodynamic equations contain both a classical and quantum force

Background and Motivation

- Significant computational advantages:
  - Moving reference frame eliminates large space fixed grids
  - Local fitting eliminates large basis set expansions
  - Different approximation schemes may be possible

- Non-trivial computational issues:
  - Accurate and stable derivatives
  - Non-uniform grids
  - Singularities can occur in quantum potential

The de Broglie-Bohm Equations of Motion

Express time-dependent wave function in polar form

[Madelung (1926), de Broglie (1927), Bohm (1952)]

$$\psi = R(\mathbf{x}, t)\, e^{i\, S(\mathbf{x},t)/\hbar}$$

Substitute into time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi(\mathbf{x}, t)}{\partial t} = \left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{x})\right] \psi(\mathbf{x}, t)$$

Separate into real and imaginary parts

The de Broglie-Bohm Equations of Motion

Continuity equation

$$\frac{\partial \rho(\mathbf{x},t)}{\partial t} + \nabla \cdot (\frac{\rho}{m} \nabla S) = 0$$

where $\rho = R(\mathbf{x},t)^2$

Quantum Hamilton-Jacobi Equation

$$\frac{1}{2m}|\nabla S|^2 + V(\mathbf{x}) + Q(\mathbf{x},t;\rho) = -\frac{\partial S(\mathbf{x},t)}{\partial t}$$

The de Broglie-Bohm Equations of Motion

Equation of motion (Lagrangian frame)

$$m\frac{d\mathbf{v}}{dt} = -\nabla(V+Q) = \mathbf{f}_c + \mathbf{f}_q$$

quantum force

classical force

where flow velocity $\mathbf{v} = \nabla S/m$

Quantum potential

$$Q(\mathbf{x},t;\rho) = -\frac{\hbar^2}{2m}\frac{1}{R}\nabla^2 R$$

Note: Q can become singular when R → 0

Quantum Hydrodynamics

$$\Psi(\mathbf{x},t) = \exp[C(\mathbf{x},t)]\exp[i\,S(\mathbf{x},t)/\hbar]$$

$$\frac{dC}{dt} = -\frac{1}{2}\nabla\cdot\mathbf{v} + (\dot{\mathbf{x}}-\mathbf{v})\cdot\nabla C$$

$$\frac{dS}{dt} = L_Q + (\dot{\mathbf{x}}-\mathbf{v})\cdot(m\mathbf{v})$$

$$m\frac{d\mathbf{v}}{dt} = -\nabla\,(V+Q) + (\dot{\mathbf{x}}-\mathbf{v})\cdot(m\nabla\mathbf{v})$$

$$L_Q = \frac{1}{2}m|\mathbf{v}|^2 - [V(\mathbf{x}) + Q(\mathbf{x},t;\rho)]$$

$\dot{\mathbf{x}} = 0$
Eulerian

$\dot{\mathbf{x}} = \mathbf{v}$
Lagrangian

$\dot{\mathbf{x}}$= user specified
Arbitrary Lagrangian Eulerian (ALE)

Note: quantum trajectories are well defined!

flow lines of the probability fluid: $\dot{\mathbf{x}} = \mathbf{v}$

The Quantum Trajectory Method

Until 1999, the quantum hydrodynamic approach was used only as an interpretative tool

Lopreore and Wyatt were the first to obtain a direct solution of the quantum hydrodynamic equations of motion for a one-dimensional tunneling problem [Phys. Rev. Lett. **82**, 5190 (1999)]

This method is called "The Quantum Trajectory Method" which is based on the Lagrangian frame of reference (i.e., the grid points were chosen to be the quantum trajectories, $\dot{\mathbf{x}} = \mathbf{v}$)

The key ingredient to the success of their approach is the Moving Least Squares (MLS) method for computing derivatives

The Moving Least Squares Method

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$$f(\mathbf{x}) = \sum_{j=1}^{n_b} a_j \, p_j(\mathbf{x} - \mathbf{x}_i)$$

The a_j are determined from a "local" least squares fit of $f(\mathbf{x})$ to a polynomial expansion about $\mathbf{x}_i$

1D $\quad p_j(x) = \{1, x, x^2/2\}$

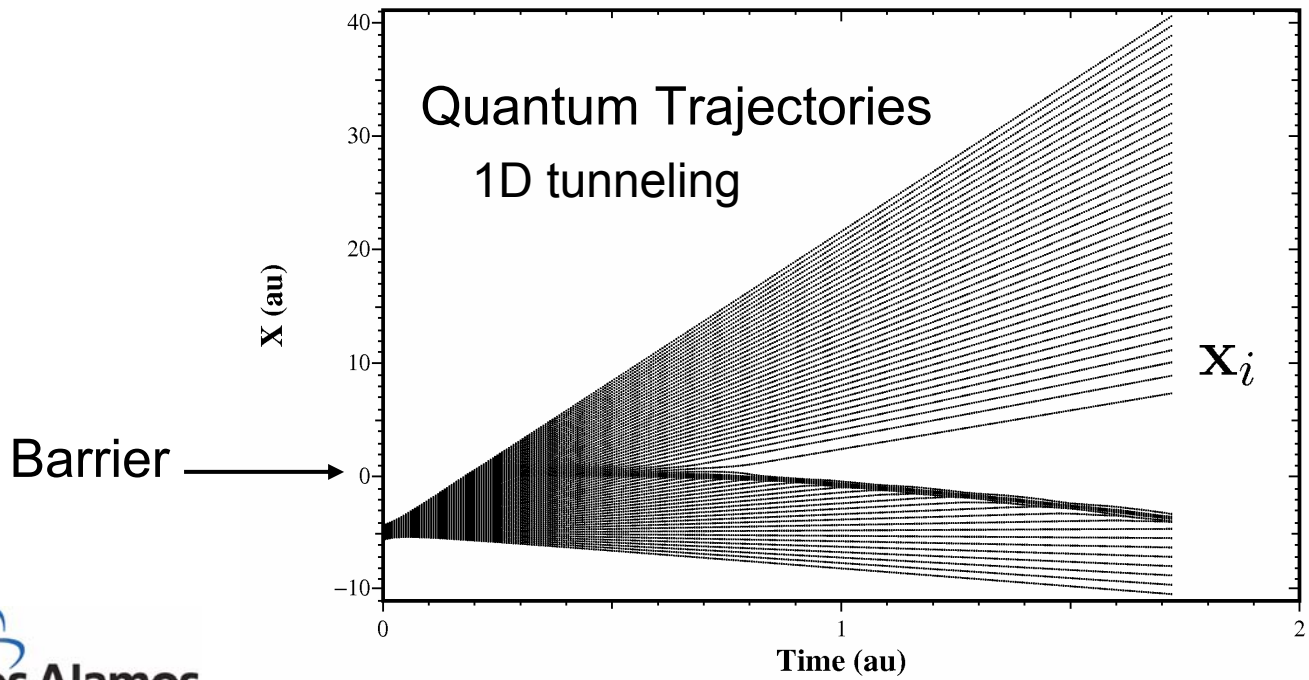
2D $\quad p_j(x, y) = \{1, x, y, x^2/2, xy, y^2/2\}$

$$(\nabla^2 f)_i = a_4 + a_6 \qquad \text{2D}$$

The Quantum Trajectory Method

Non-trivial computational problems:

- Lagrangian grid eventually becomes highly non-uniform
- Singularities in Q and f_q can occur when R → 0 (nodes)



Computational Issues: Accurate and Stable Derivatives

Use Arbitrary Lagrangian Eulerian (ALE) frame to maintain "uniform" grid:

1. Use Lagrangian frame to predict "edges" of wave packet at time t + Δt
2. Construct uniform grid between "edges" at time t + Δt
3. Compute grid velocities ($\dot{x}_i$) based on uniform grids at times t and t + Δt

$$\dot{x}_i = \frac{(x_i^{t+\Delta t} - x_i^t)}{\Delta t}$$

4. Propagate again using ALE frame from time t to t + Δt

Ensures uniform grid at each time step but grid spacing typically increases

Hughes and Wyatt, Chem. Phys. Lett. **366**, 336 (2002)

Computational Issues: Accurate and Stable Derivatives

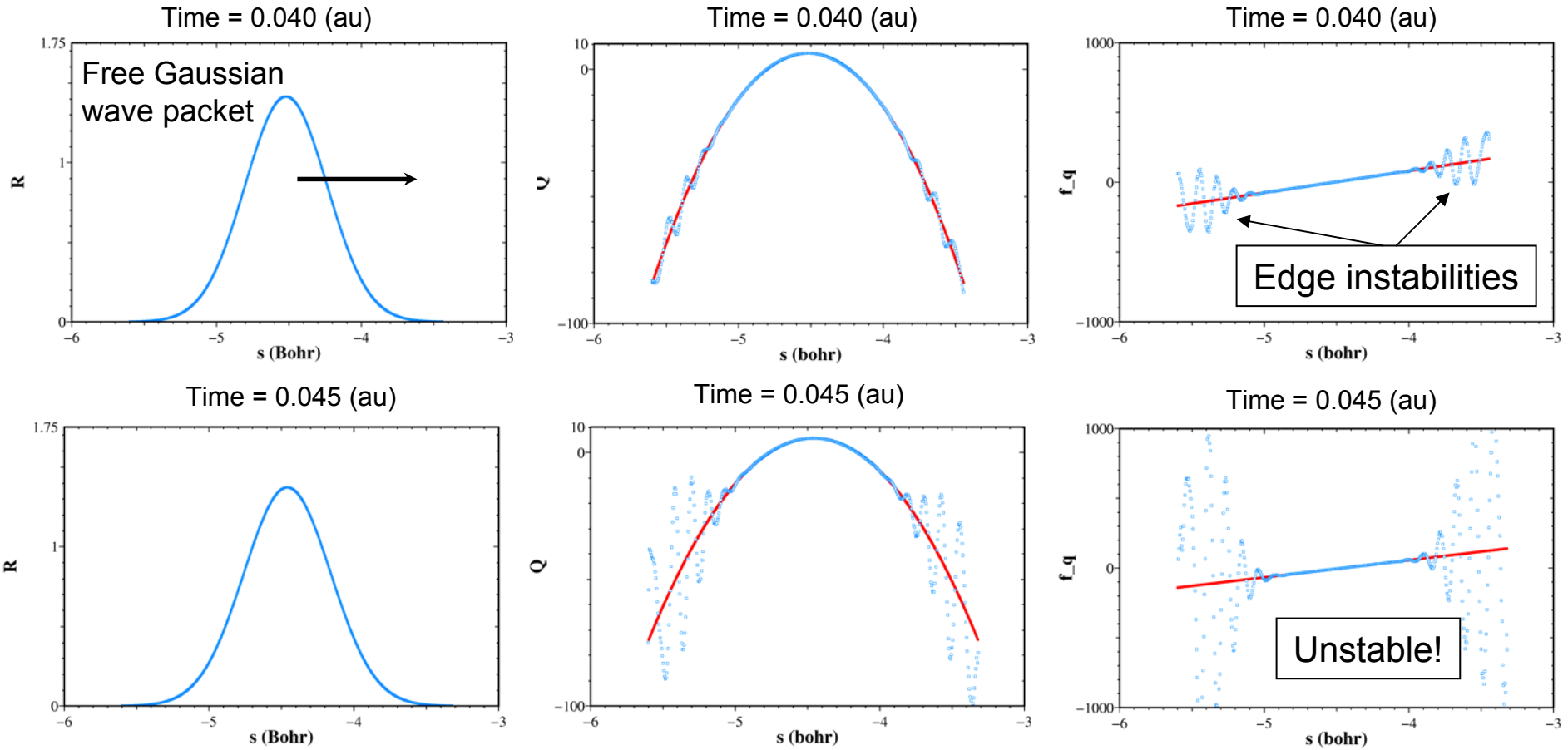
Regridding algorithm needed to maintain grid spacing:

- Add more points if the grid spacing becomes too large
- Delete points at edges if the density becomes too small

ALE + Regridding ensures a nearly constant grid spacing

- Dramatically improves accuracy and stability of derivatives
- Allows for implementation of implicit averaging (unitarity)
- Allows for implementation of artificial viscosity (node problem)

Computational Issues: Edge Instabilities



Red (stable) curve = MLS with **varying** radius of support
Blue (unstable) curve = MLS with **constant** radius of support

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Edge Instabilities: Solution

Edge instabilities can be eliminated by using a **variable** radius of support which increases near edges:

grid spacing

$$r^i_{\max} = \left[(\gamma_1 - \gamma_2)\exp(C_i)/\exp(C_{\max}) + \gamma_2\right]\Delta x$$

radius of support

$$\exp(C_i) \to \exp(C_{\max}) \qquad r^i_{\max} \to \gamma_1 \Delta x$$ "center"

$$\exp(C_i) \to 0 \qquad r^i_{\max} \to \gamma_2 \Delta x$$ "edges"

$$\gamma_1 \approx 15 \qquad \gamma_2 \approx 30$$

Kendrick, J. Chem. Phys. **119**, 5805 (2003)

Computational Issues: Unitarity

Implicit averaging … using information from the future:

1. Average all potentials, forces, and gradients at time t with those at time t + Δt

$$Q_{\mathrm{avg}} = [Q(t) + Q(t + \Delta t)]/2, \ldots$$

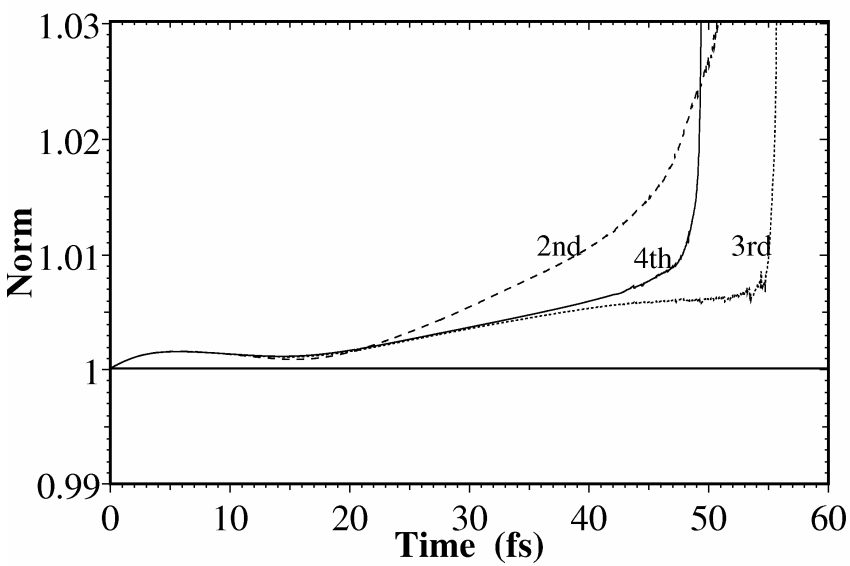
2. Repropagate from time t to t + Δt using averaged fields

Averaging cancels out a large portion of the numerical errors which accumulate at each time step

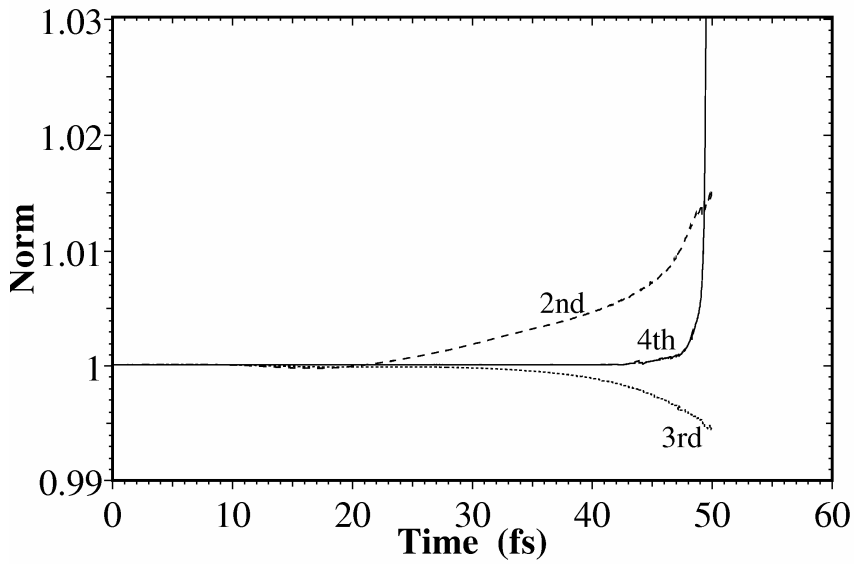
Dramatically improves accuracy and unitarity

Computational Issues: Unitarity (1D example)

without averaging

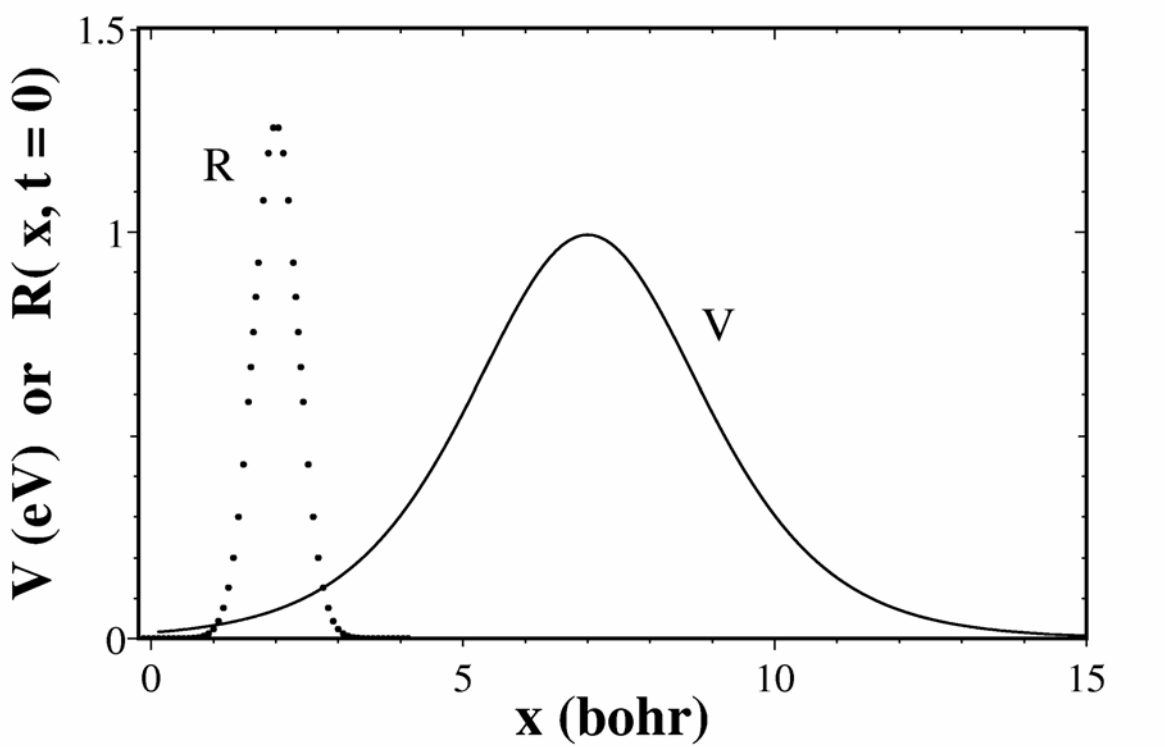


with averaging



Kendrick, J. Chem. Phys. **119**, 5805 (2003)

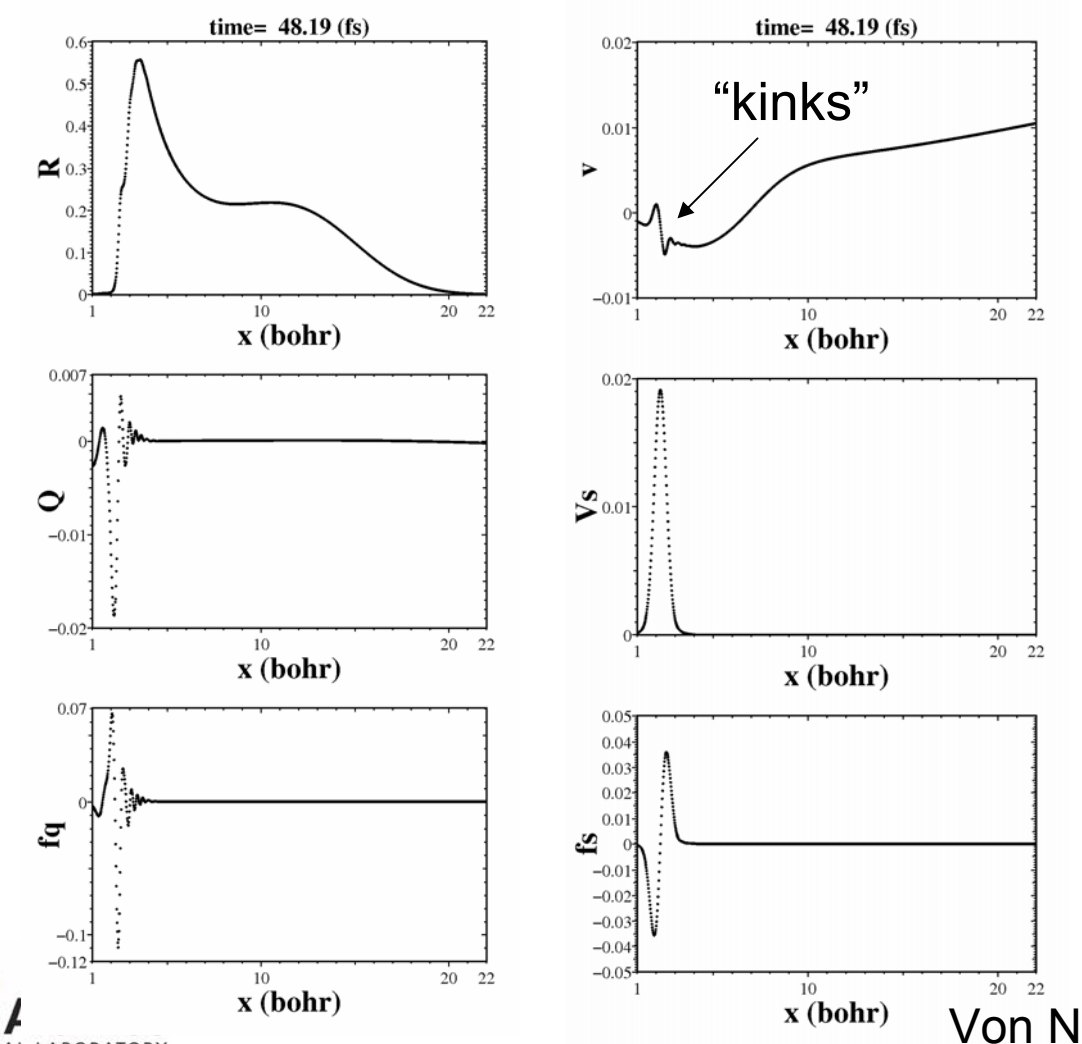
Example: 1D scattering off an Eckart barrier



$$V(x) = V_0 \,\mathrm{sech}^2[a\,(x - x_b)]$$

$$a = 0.4,\; x_b = 7\,\mathrm{a}_0,\; V_0 = 8000\,\mathrm{cm}^{-1}$$

Computational Issues: Artificial Viscosity (1D example)



"nodes" begin to form due to interference

gives rise to "kinks" or "shock fronts" in velocity

Viscosity potential:

when $\frac{\partial \mathrm{v}}{\partial x} < 0$

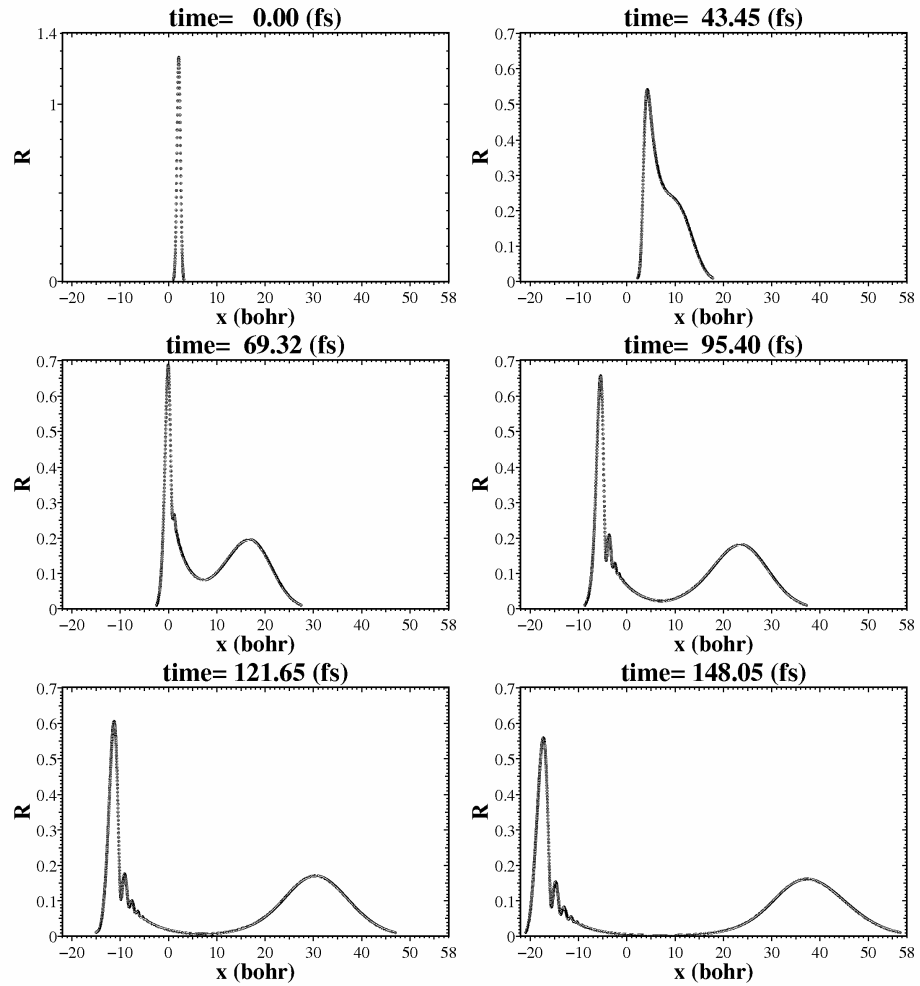
$$V_s = c_1 \left| \frac{\partial \mathrm{v}}{\partial x} \right| + c_2 \left| \frac{\partial \mathrm{v}}{\partial x} \right|^2$$

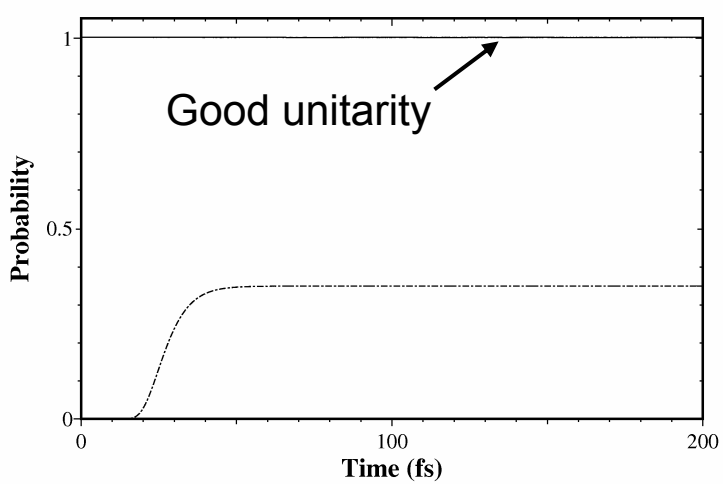
Viscosity force:

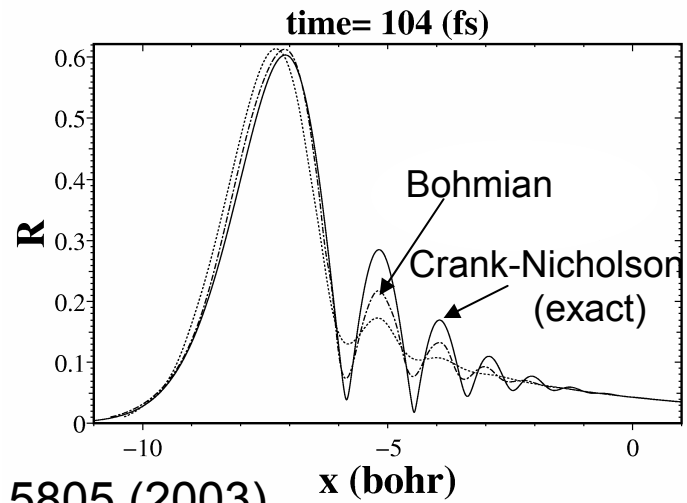
$$f_s = -\nabla V_s$$

Von Neumann and Richtmyer (1950)

1D wave packet time series (KE_{flow} = 0.8 eV)

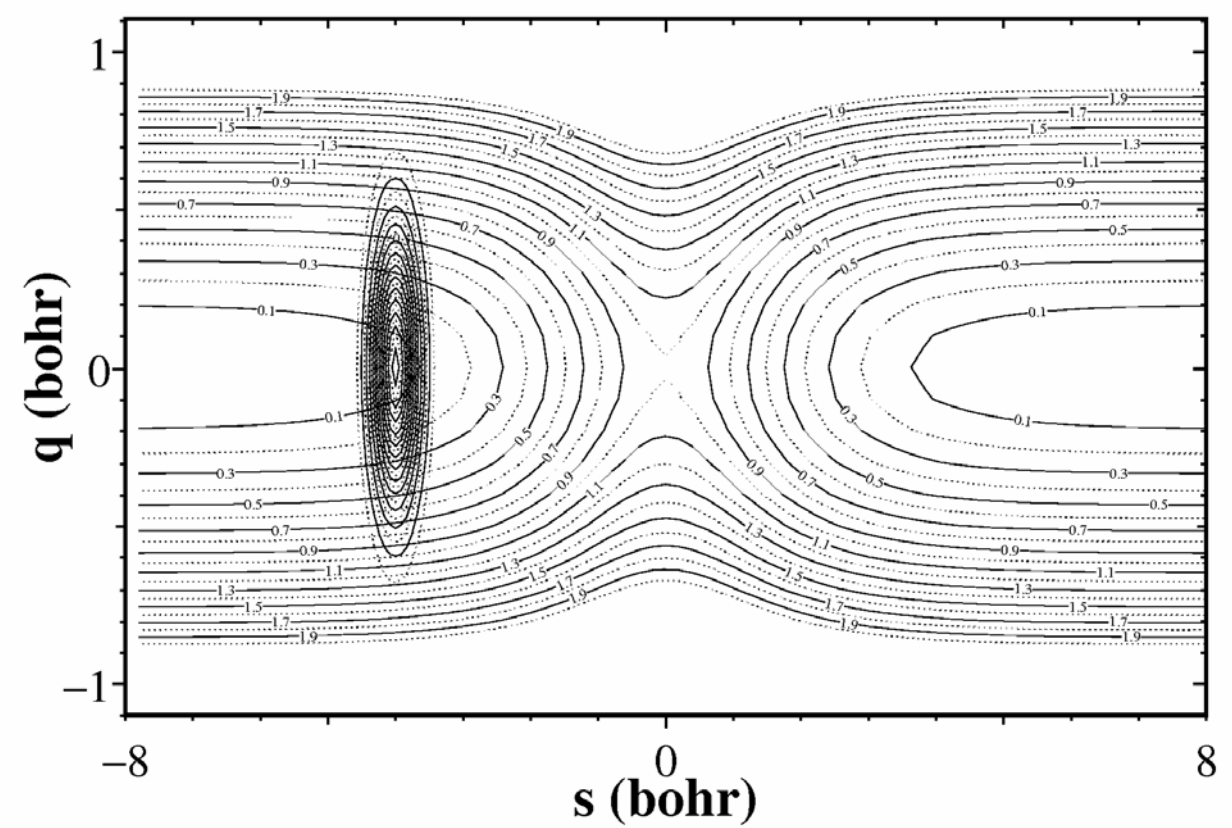






Kendrick, J. Chem. Phys. **119**, 5805 (2003)

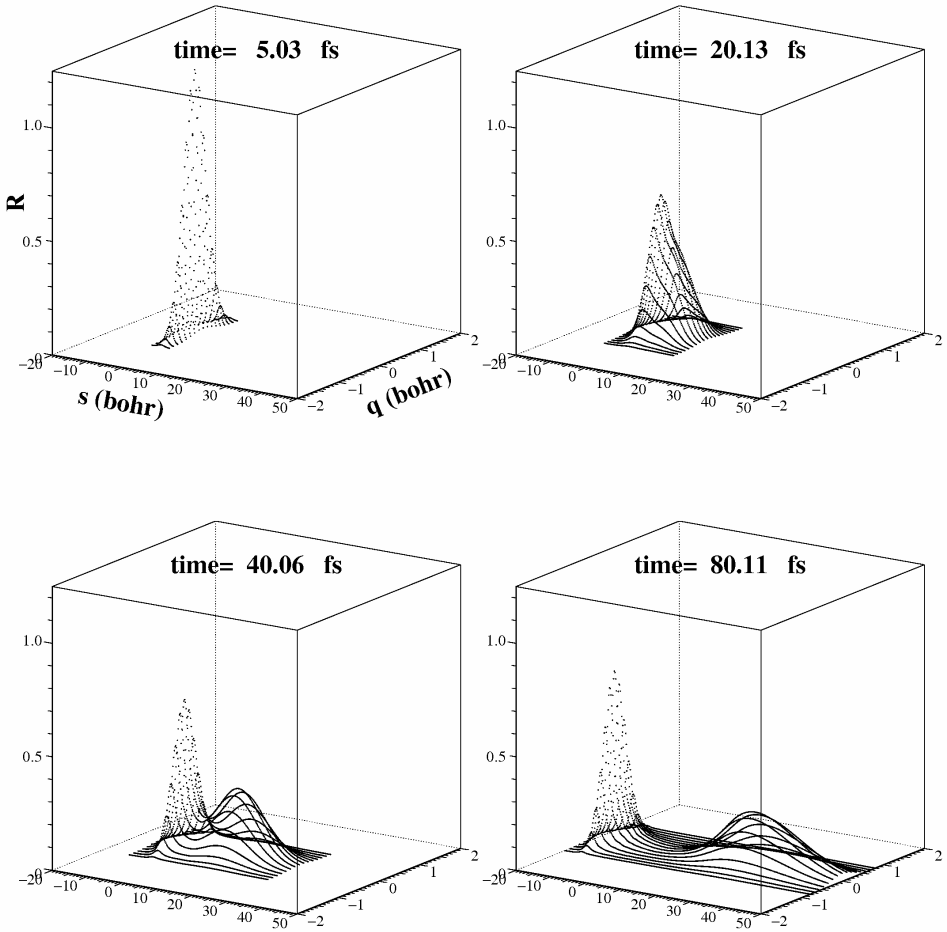
Example: 2D scattering off an Eckart barrier

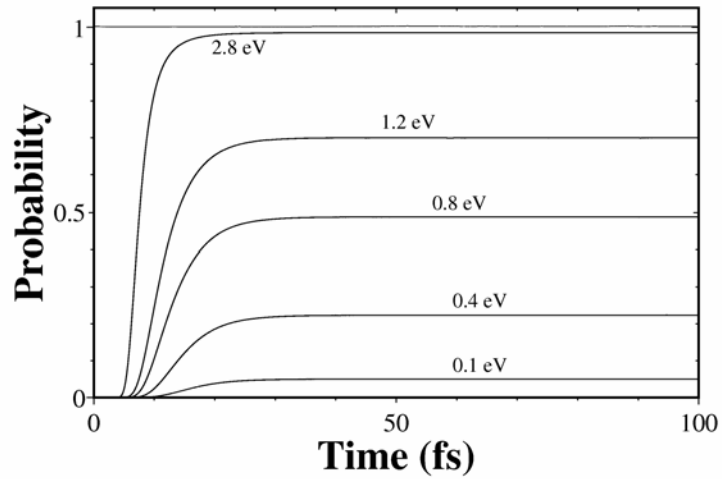


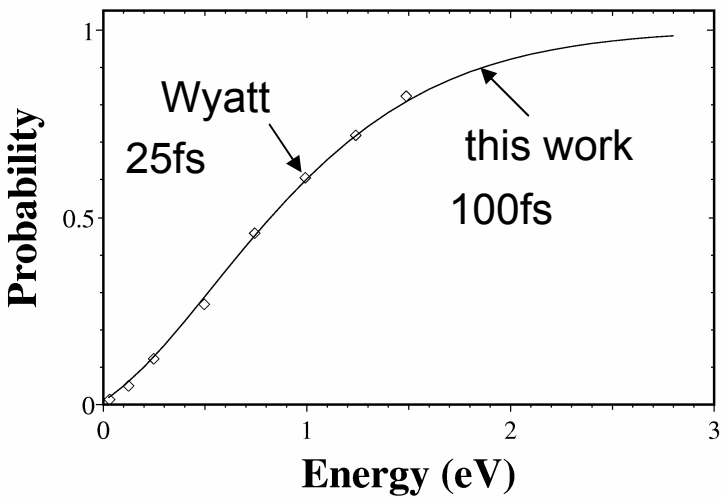
$$V(q,s) = V_0 \,\mathrm{sech}^2(a\,s) + \tfrac{1}{2}\,k(s)\,q^2$$

Pauler and Kendrick, J. Chem. Phys. **120**, 603 (2004)

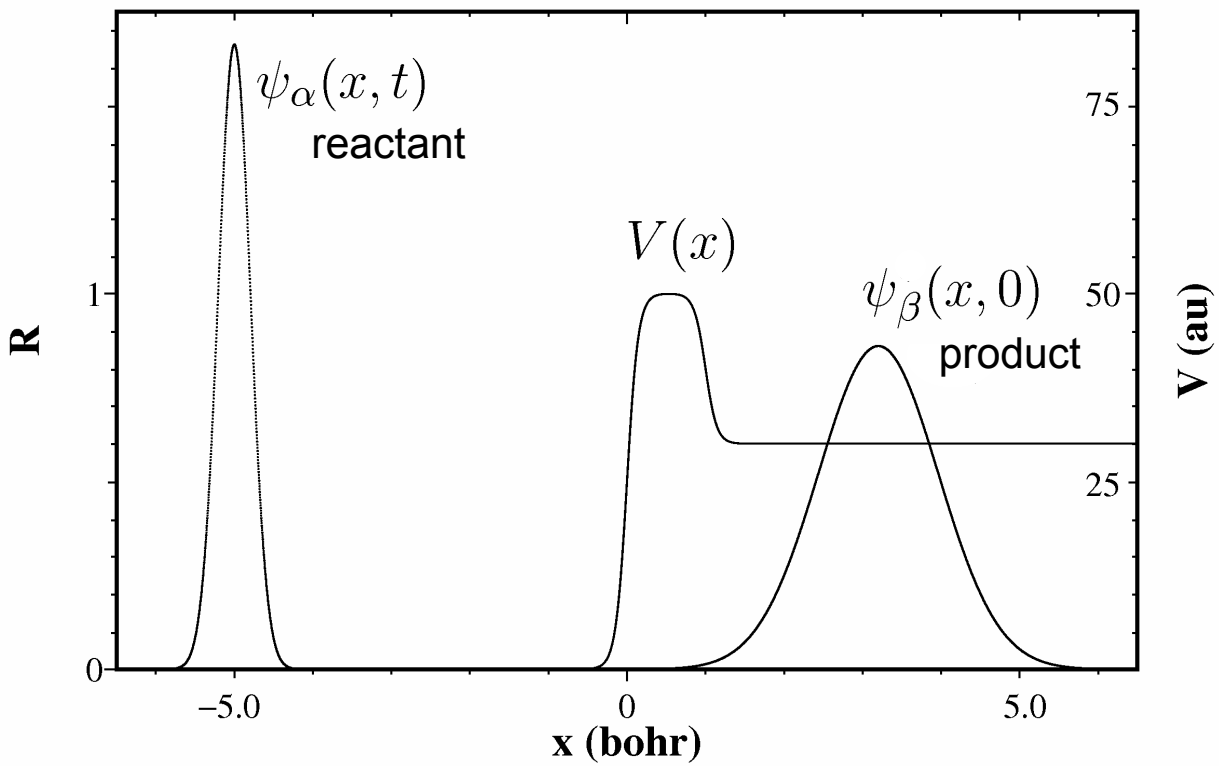
2D wave packet time series (KE_{flow} = 0.8 eV)







Example: 1D model chemical reaction with resonance



$$V(x) = \frac{V_1}{2}[\tanh(a\,(x - x_1)) + 1] - \frac{V_2}{2}[\tanh(b\,(x - x_2)) + 1]$$

$a = b = 0.7$, $V_1 = 50\,\text{au}$, $V_2 = 20\,\text{au}$, $x_1 = 0$, $x_2 = 1\,\text{au}$

Derrickson, Bittner, and Kendrick, J. Chem. Phys. **123**, 054107 (2005)

Wave packet correlation function approach

Overlap of propagated (reactant) wave packet with product wave packet

$$C_{\beta\,\alpha}(t) = \int \mathrm{dx}\, \psi_\alpha(x,t)\, \psi^*_\beta(x,0)$$

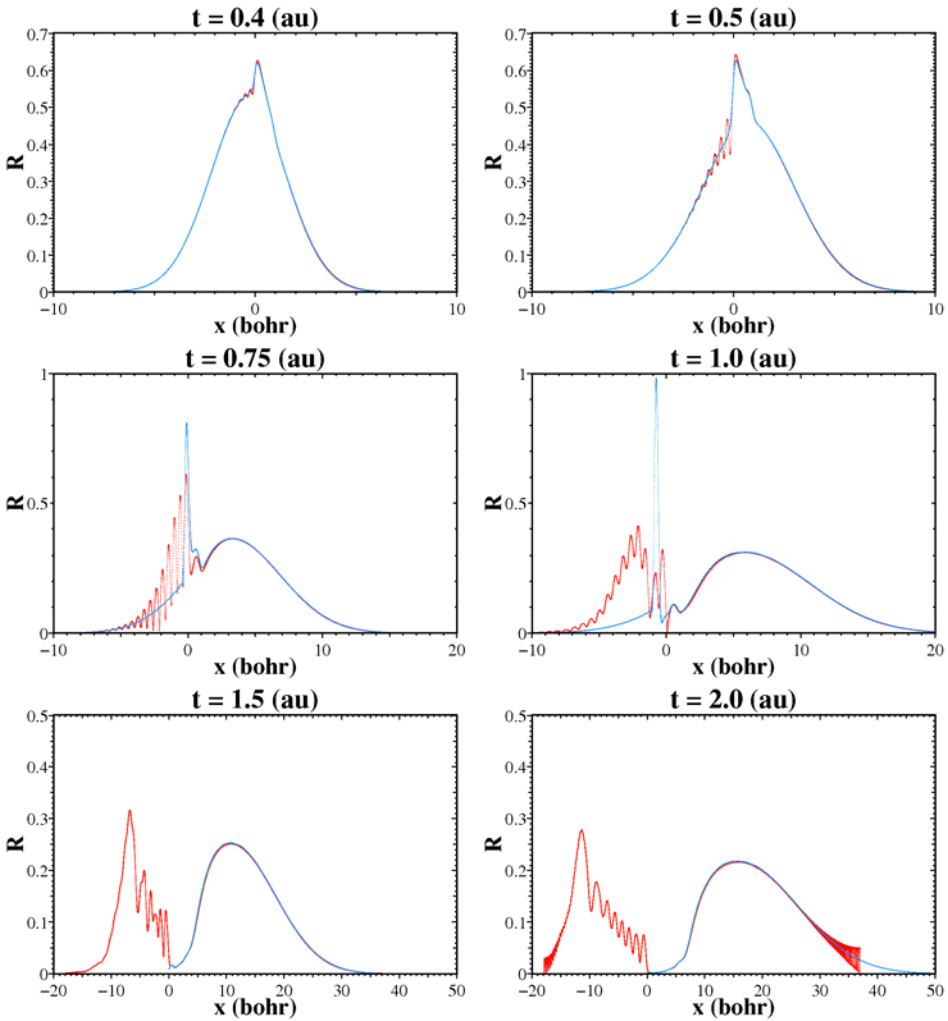
Fourier transform gives scattering matrix

$$S_{\beta\,\alpha}(E) = \frac{(2\pi\hbar)^{-1}}{\eta^*_\beta(E)\eta_\alpha(E)} \int_{-\infty}^{\infty} C_{\beta\,\alpha}(t)\, e^{iEt/\hbar}\, \mathrm{dt}$$

State-to-state reaction probabilities and time delays

$$P_{\beta\,\alpha}(E) = \mid S_{\beta\,\alpha}(E) \mid^2, \quad t_{\beta\,\alpha} = \hbar\, \mathrm{Im}\left(\frac{\mathrm{d}\ \ln\ S_{\beta\,\alpha}}{\mathrm{d}E}\right)$$

1D wave packet time series



Blue = Bohmian

Red = Crank-Nicholson "exact"

Dynamic "localized" artificial viscosity:

$$V_s = c_1 \left| \frac{\partial \mathrm{v}}{\partial x} \right| + c_2 \left| \frac{\partial \mathrm{v}}{\partial x} \right|^2$$

vary with time and location

$$c_i \propto |f_q|$$

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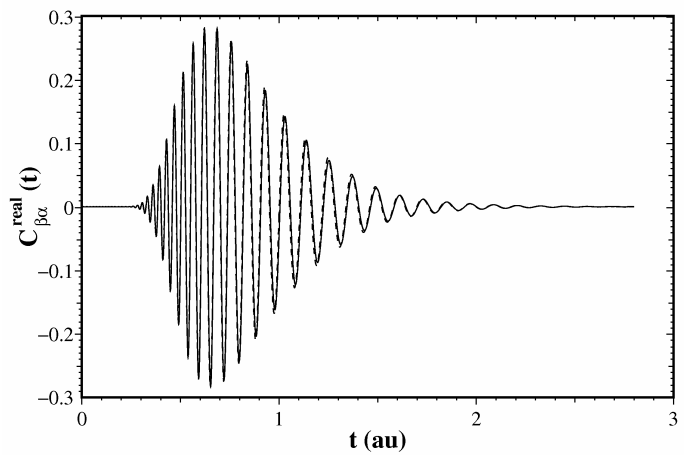
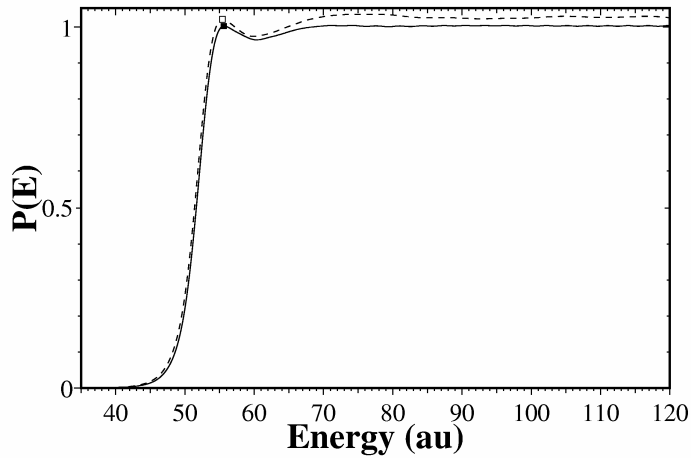
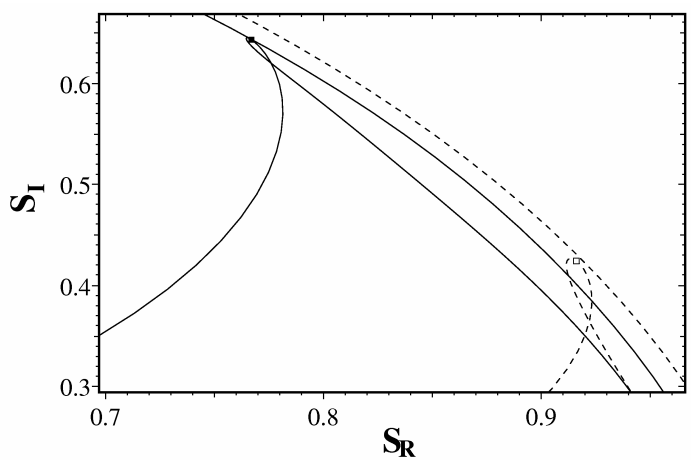
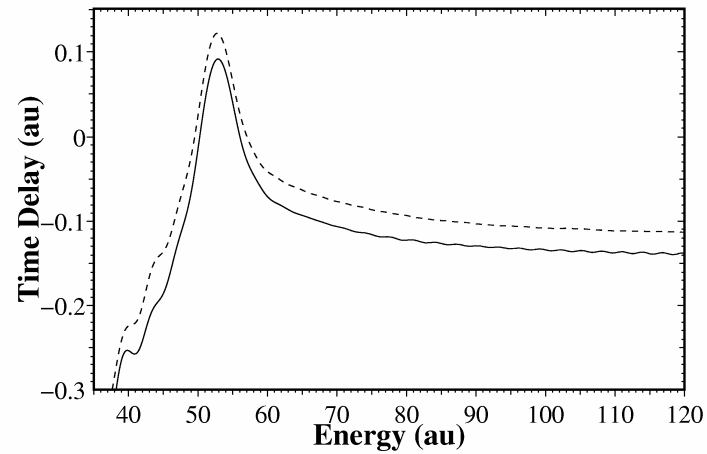
Scattering Results

Solid = Crank-Nicholson "exact" Dashed = Bohmian









N-Dimensional Model Problem

Natural collision coordinates:

Reaction Path = s

N – 1 Vibrational = q^i

Potential energy surface:

$$V(s,\mathbf{q}) = V(s) + \frac{1}{2}\sum_{i=1}^{N-1} k_i(s)\,(q^i)^2$$

Eckart

Harmonic

Metric tensor:

$$g_{ss} = [1 + \kappa(s)\,q^1]^2$$

$$g_{ii} = 1$$

reaction path curvature

Kendrick, J. Chem. Phys. **121**, 2471 (2004)

N-Dimensional Model Problem

Classical and Quantum forces exactly cancel for bound states

$$f_c^{q^i} + f_q^{q^i} = 0 \qquad (1)$$

Consistent with a stationary bound state

$$v^{q^i} = 0 \qquad \frac{\partial v^{q^i}}{\partial q^i} = 0 \qquad \frac{\partial v^{q^i}}{\partial s} = 0 \qquad (2)$$

Vibrational Decoupling Scheme (VDS)

(a) Equations (1) and (2) are assumed to hold for all s and q^i

Obtain decoupled set of $N_q(N-1)$ one-dimensional equations

(b) Reintroduce coupling terms as needed to obtain desired accuracy

N-dimensional Model Problem

$$\dot{C} = -\tfrac{1}{2}\,\partial_s v^s + (\dot{r}^s - v^s)\partial_s C - \tfrac{1}{2}\left[g^{-\frac{1}{2}}\,\kappa(s)\,v^{q^1} + \sum_i \partial_{q^i} v^{q^i}\right]$$

$$\dot{S} = \tfrac{1}{2}\,\mu\, g_{ss} v^s\, v^s - [V + Q] + g_{ss}\,(\dot{r}^s - v^s)\,\mu\, v^s + \tfrac{1}{2}\,\mu \sum_i v^{q^i}\, v^{q^i}$$

$$\mu\,\dot{v}^s = f_c^s + f_q^s + \mu\,(\dot{r}^s - v^s)\partial_s v^s$$

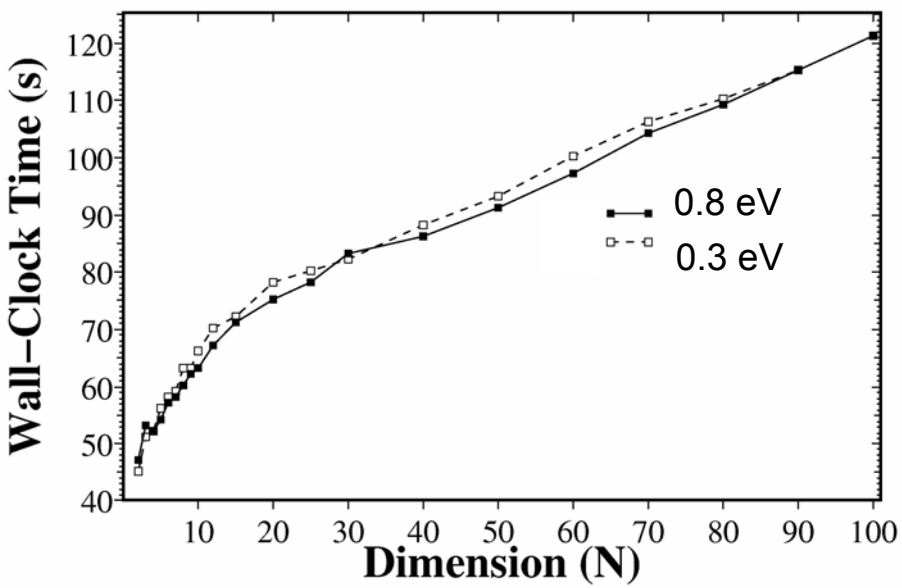
coupling terms

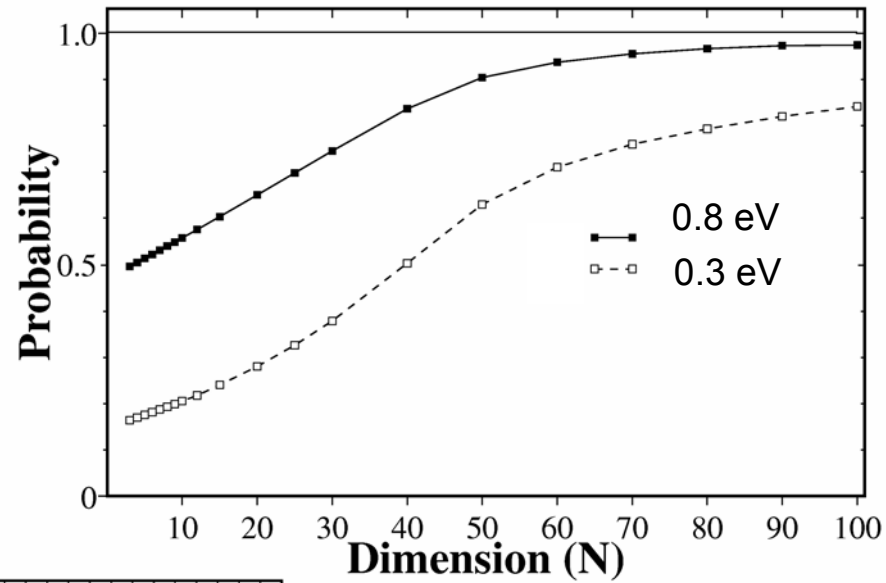
$$\mu\,\dot{v}^{q^i} = 0 + \mu\,(\dot{r}^s - v^s)\partial_s v^{q^i} + \Delta f^{q^i}(\partial_s k(s), \partial_s^2 k(s), \kappa(s))$$

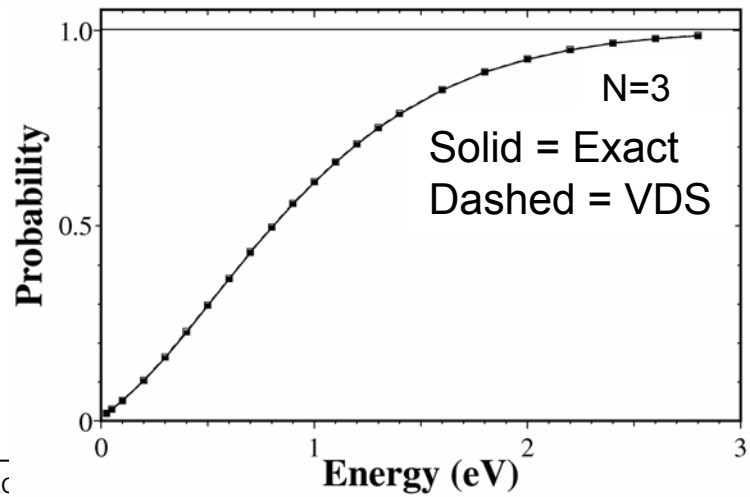
Investigating two approaches: Iterative and Direct

Issues: scaling, stability and convergence

Vibrational Decoupling Scheme
results for model problem







Summary

- Moving Least Squares + ALE + regridding + implicit averaging = stable, accurate, unitary wave packet propagation method
- Artificial viscosity suppresses node formation = stable propagation for long times
- Scattering applications:
  - 1D and 2D Eckart barrier
  - 1D “square” barrier with resonance
- Vibrational Decoupling Scheme (VDS)
  - N dimensional model problem (linear scaling N=100)

Future Work

- Generalize vibrational decoupling scheme to include coupling and anharmonicities
- Apply to real molecules

Extra Slides

Computational Issues: Edge Instabilities