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Bipolar Quantum Wavepacket Dynamics for Multidimensional Systems

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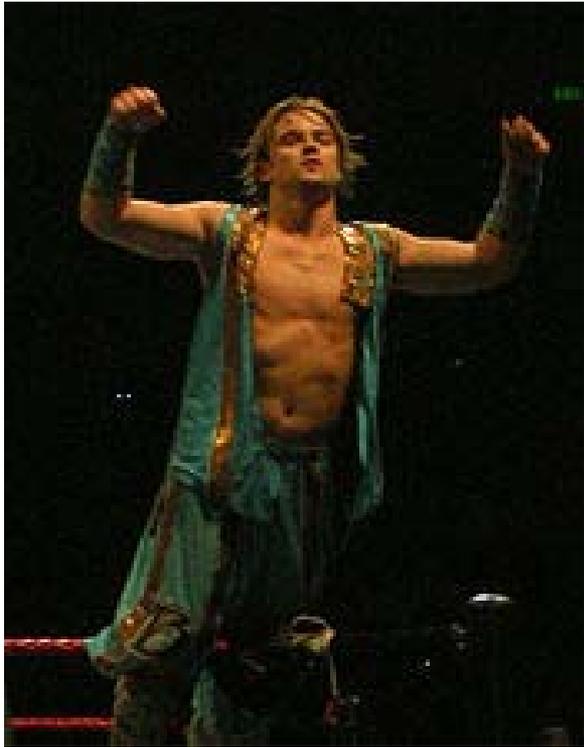
"Brian Kendrick is one of the more unusual and eccentric young Superstars on Raw…

Definition of Terms

- "*real-valued, bipolar, analytic, time-dependent*" in the BM BM

  (Briggs-Meyers Bohmian Mechanics)

- "Bohmian Mechanics"
  - exact, trajectory-based formulation of quantum mechanics.
  - quantum wavefunction, ψ, represented by ensemble of trajectories.
  - amplitude phase decomposition of ψ.

- "Quantum Trajectory"
  - phase determines trajectory *velocity* at each point, x.
  - amplitude determines *quantum potential*, Q, at each point, x.
  - quantum trajectories obtained from $V_{\text{eff}} = V + Q$
  - *different meaning for bipolar stationary states*.

- "Bipolar"

  $\psi = \psi_+ + \psi_-$

  ψ_+ is "forward" or "incident" or "reacting" wave

  ψ_- is "backward" or "reflecting" or "non-reacting" wave

- "Wavepacket Dynamics"
  - non-stationary state solutions of the time-dependent Schrödinger equation.
  - ψ , ψ_+ , and ψ_- must be localized at all time t.

The Quantum Potential

- *1 Dimension* $$Q(x) = -\frac{\hbar^2}{2m}\frac{1}{R}\left(\frac{\partial^2 R}{\partial x^2}\right)$$ where $R = |\psi|$

- *Classical limit*:

  $\hbar \to 0 \Rightarrow Q = 0$ *(ideally, but often in practice, $Q \neq 0$)*
  The correspondence principle is not satisfied at the trajectory level, so that classical and quantum trajectories are completely different in the classical limit.

- *It can even happen that Q diverges!!!*
  This is associated with the so-called "node problem", which makes it impossible to propagate quantum trajectories for realistic molecular applications, for which there is always some interference.

Correspondence Principle

- PROBLEM: appears to *violate correspondence principle!*

  – classical limit = large action = many nodes = divergent Q!

  – correspondence principle suggests $Q \rightarrow 0$.

- Resolution: bipolar expansion of ψ :

  – unique exact quantum decomposition can be specified:

  $$\psi = \psi_+ + \psi_-$$

  $Q_+ = Q_-$ approaches *zero* in the classical limit.
  CORRESPONDENCE PRINCIPLE SATISFIED

Overview of Bipolar Decomposition Schemes (1D)

- Stationary bound states:

  ψ_+ and ψ_- are themselves solutions of TISE.

  ψ_+ and ψ_- complex conjugates ($R_+ = R_-$; $S_+ = -S_-$).
  dynamical equations decoupled.

- Stationary scattering states:

  ψ_+ and ψ_- are *not* solutions of TISE.
  $R_+ \neq R_-$; $p_+ = -p_-$
  dynamical equations *coupled*, by interaction potential.

- Localized wavepacket dynamics:

  ψ_+ and ψ_- are *not* solutions of TDSE.
  $R_+ \neq R_-$; $S_+ \neq -S_-$
  dynamical equations *coupled*, by interaction potential.

Bipolar Velocities for
1D Stationary Scattering States

Momentum field definition: $p_\pm(x) = \pm\sqrt{2m[E - V_{\mathrm{eff}}(x)]}$
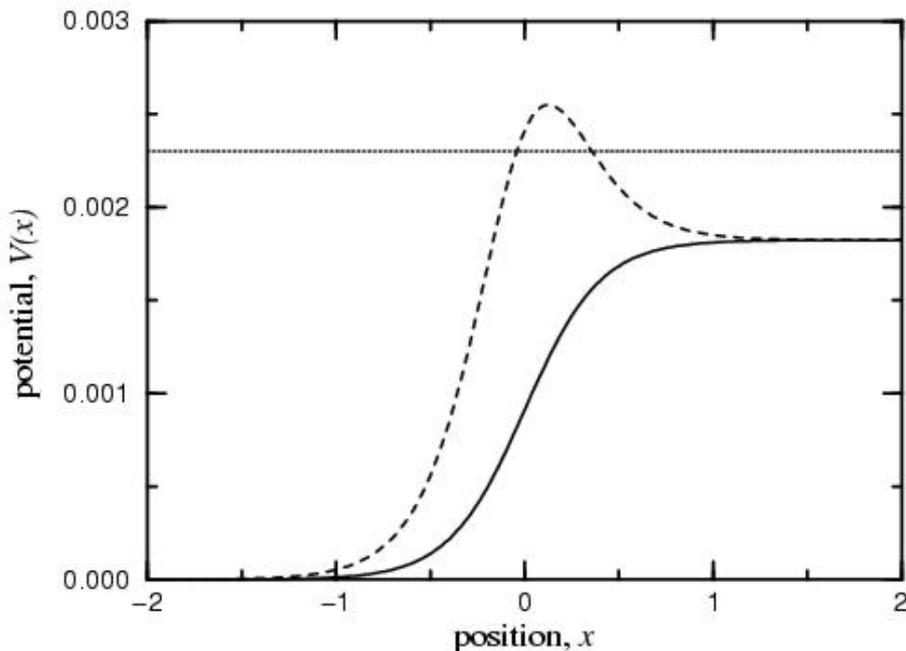
- Classical trajectories (dashed line)

  $V_{\mathrm{eff}}(x) = V(x)$

  barriers give rise to turning points.

- Constant velocity trajectories

  $V_{\mathrm{eff}}(x) = 0$

  asymptotic coupling (interference).

- Monotonic trajectories (solid line)

  $V_{\mathrm{eff}}(x \to \pm\infty) = V(x \to \pm\infty)$

  no turning points or asymp. coupling.

Combined Continuity Relation

$$\partial \rho_\pm / \partial t = -\, j'_\pm \pm \dot{\rho}_{cpl}$$

$$j_+^{in} \longrightarrow \boxed{\rho_+} \longrightarrow j_+^{out}$$

$$\uparrow \dot{\rho}_{cpl}$$

$$j_-^{out} \longleftarrow \boxed{\rho_-} \longleftarrow j_-^{in}$$
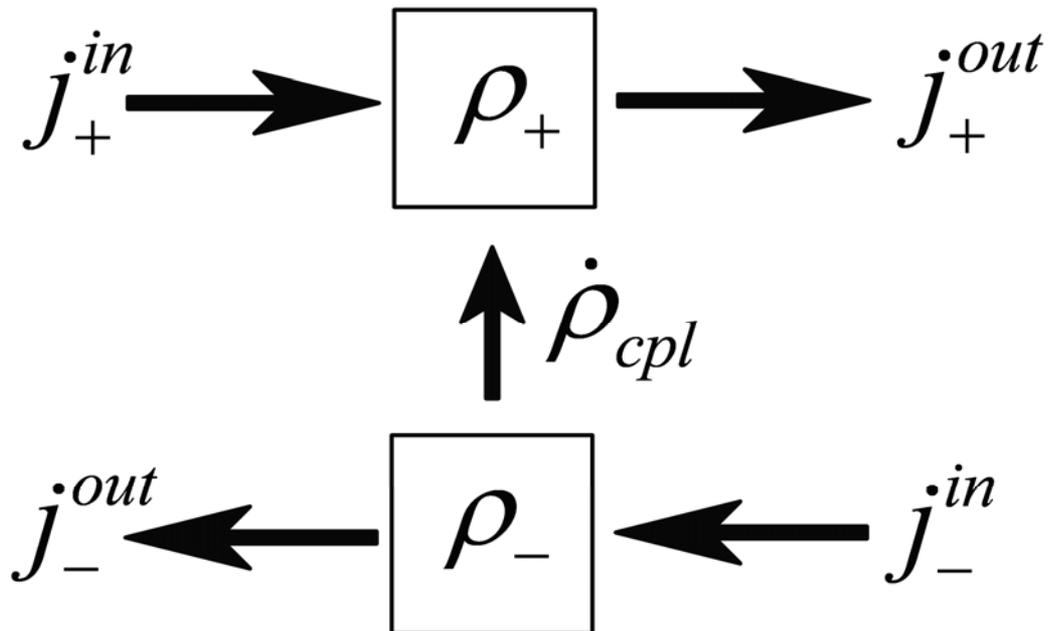
Detailed balance relation between
"forward reaction" and "reverse reaction"

1D Wavepacket Dynamics

- Basic bipolar approach:
    - generalize time-dependent stationary state approach.
    - satisfy bipolar continuity equation: $\partial\rho_\pm / \partial t = -j'_\pm \pm \dot\rho_{cpl}$

$$j_+^{in} \longrightarrow \boxed{\rho_+} \longrightarrow j_+^{out}$$

$$\uparrow \dot\rho_{cpl}$$

$$j_-^{out} \longleftarrow \boxed{\rho_-} \longleftarrow j_-^{in}$$
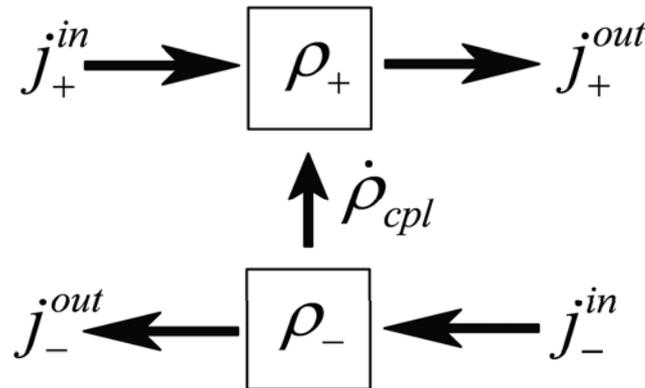
    - *FAILS,* where requirements for success are:
        1) perfect asymptotic separation (time and space).
        2) localized $\psi_\pm$, if ψ itself is localized.
        3) components $\psi_\pm$ themselves exhibit no interference.

Bipolar Stationary State Expansion

- Let $\varphi^E(x) = \varphi_+^E(x) + \varphi_-^E(x)$ be the (unique) left-incident stationary scattering solution of the TISE, with energy E:

$$\hat{H}\varphi^E = E\varphi^E$$

- Bipolar components, $\varphi_\pm^E(x)$, obtained using constant-velocity trajectories, must satisfy the following coupled equations:

$$\varphi_\pm^{E\,'} = \pm\left(\frac{i}{\hbar}\right)p\,\varphi_\pm^E \mp \left(\frac{i}{\hbar}\right)\left(\frac{m}{p}\right)V\left[\varphi_+^E + \varphi_-^E\right]$$

- Differentiating w/ respect to x, and substituting yields:

$$\hat{H}\varphi_\pm^E = E\varphi_\pm^E \pm \left(\frac{i\hbar}{2p}\right)V'\left[\varphi_+^E + \varphi_-^E\right]$$

Time-Independent WKB
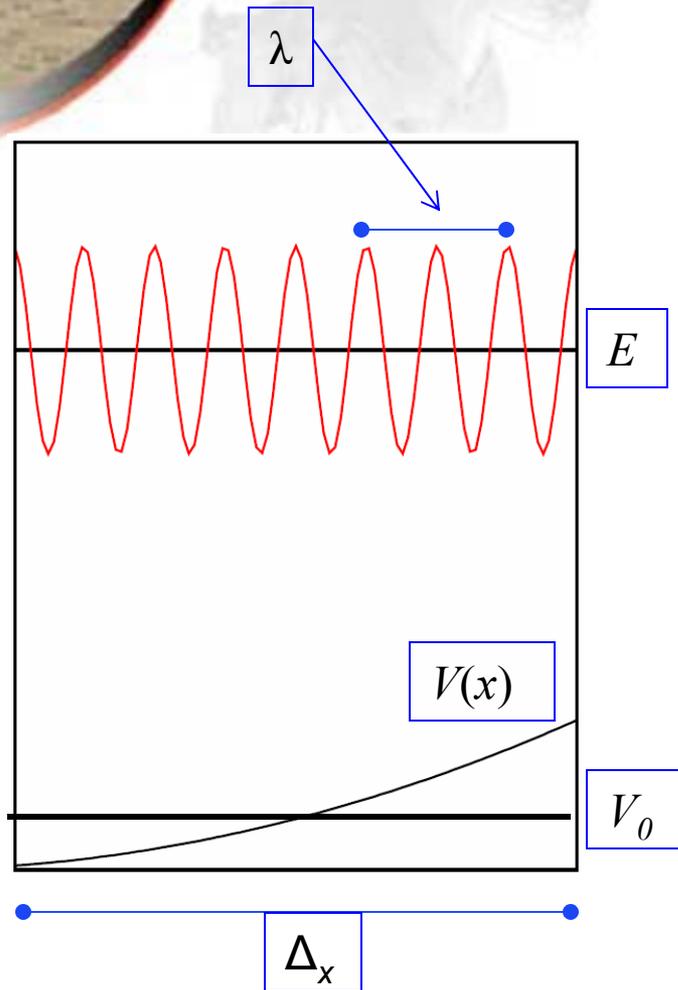
- Application to energy eigenstates of 1D Hamiltonians.
- Fundamental WKB assumption:
  (small wavelength assumption)
  $\lambda << \Delta x$, range over which V varies appreciably compared to $E-V$.
  increasingly well satisfied in classical limit
  ($\hbar \rightarrow 0$ *OR* $m \rightarrow \infty$ *OR* $E \rightarrow \infty$)
- Equivalent conditions:
  $\lambda |V'(x)| << E-V = p^2/2m$
  $4\pi \hbar m |V'(x)| / p^3 << 1$
- Treat potential as constant, V_0, over region of width Δx.
  Local WKB solutions are plane waves:
  $A_+ e^{ipx/\hbar}$ and $A_- e^{-ipx/\hbar}$ where $p^2 = 2m(E-V_0)$

Bipolar Stationary State Expansion

- Obtain $\varphi^E(x,t)$ evolution equations as follows:

$$\frac{\partial \varphi_\pm^E}{\partial t} = -\left(\frac{i}{\hbar}\right)\hat{H}\varphi_\pm^E \mp \left(\frac{V'}{2p}\right)\left[\varphi_+^E + \varphi_-^E\right]$$

$$\text{identity}: \quad \left[\varphi_+^E + \varphi_-^E\right]' = \left(\frac{i}{\hbar}\right)p\left[\varphi_+^E - \varphi_-^E\right]$$

$$\frac{\partial \varphi_\pm^E}{\partial t} = -\left(\frac{i}{\hbar}\right)\left[\hat{H}\varphi_\pm^E \pm \left(\frac{V'}{2}\right)\left(\Phi_+^E - \Phi_-^E\right)\right]$$

$$\text{where} \quad \Phi_\pm^E(x) = \int_{-\infty}^{x} \varphi_\pm^E(x')dx'$$

- Expand wavepacket $\Psi(x)$ as sum over stationary states $\varphi^E(x)$:
  $\psi(x) = \int a(E)\,\varphi^E(x)\,dE$
  bipolar $\varphi^E(x) = \varphi_+{}^E(x) + \varphi_-{}^E(x)$ leads to $\psi(x) = \psi_+(x) + \psi_-(x)$,
  $\psi_\pm(x) = \int a(E)\,\varphi_\pm{}^E(x)\,dE$

1D Bipolar Wavepacket Dynamics

- Substitute into $\psi_\pm(x,t)$ expansion:

$$\frac{\partial \psi_\pm}{\partial t} = -\left(\frac{i}{\hbar}\right)\left[\hat{H}\psi_\pm \pm \left(\frac{V'}{2}\right)(\Psi_+ - \Psi_-)\right]$$

$$\text{where} \quad \Psi_\pm(x) = \int_{-\infty}^{x} \psi_\pm(x')dx'$$

- "Good" wavepacket conditions for initial $\psi(x,t=0)$:
  a) localized in reactant asymptotic region of position space, x.
  b) localized in positive region of momentum (Fourier) space, p.

- Formal properties of $\Psi_\pm(x,t)$ time evolution:
  a) implies $a(E)$ are Fourier components; b) implies initial $\psi = \psi_+$.
  $|a(E,t)|^2$ = const. then implies perfect sep'n at large t [condition (1)].
  b) also implies $\Psi_\pm$ localized [condition (2)].
  no formal proof for condition (3) (no nodes).

- Combined continuity equation **not** satisfied.

1D Eckart Barrier:
bipolar wavepacket scattering
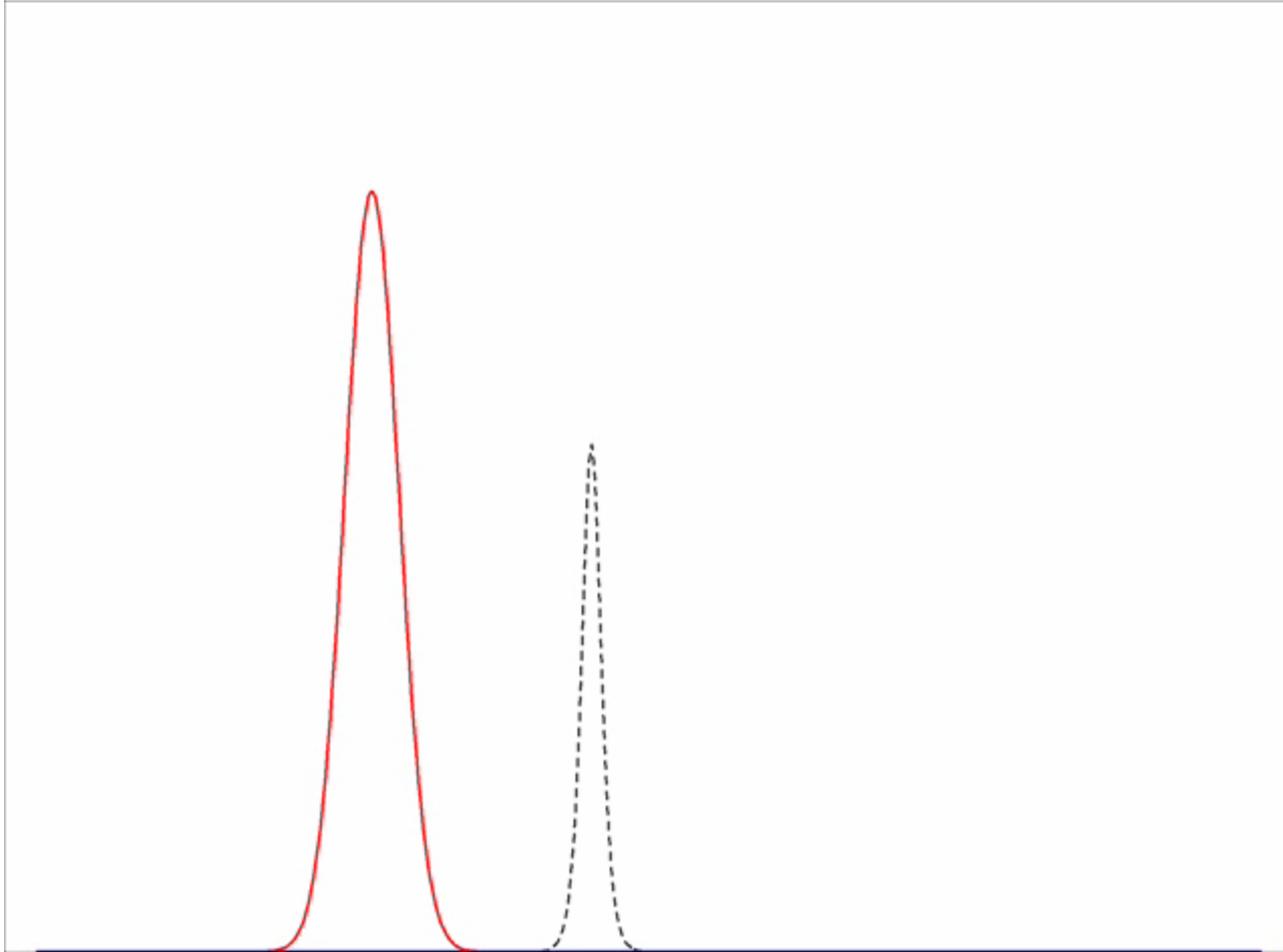
Density Plot

1D Ramp Barrier:
bipolar wavepacket scattering
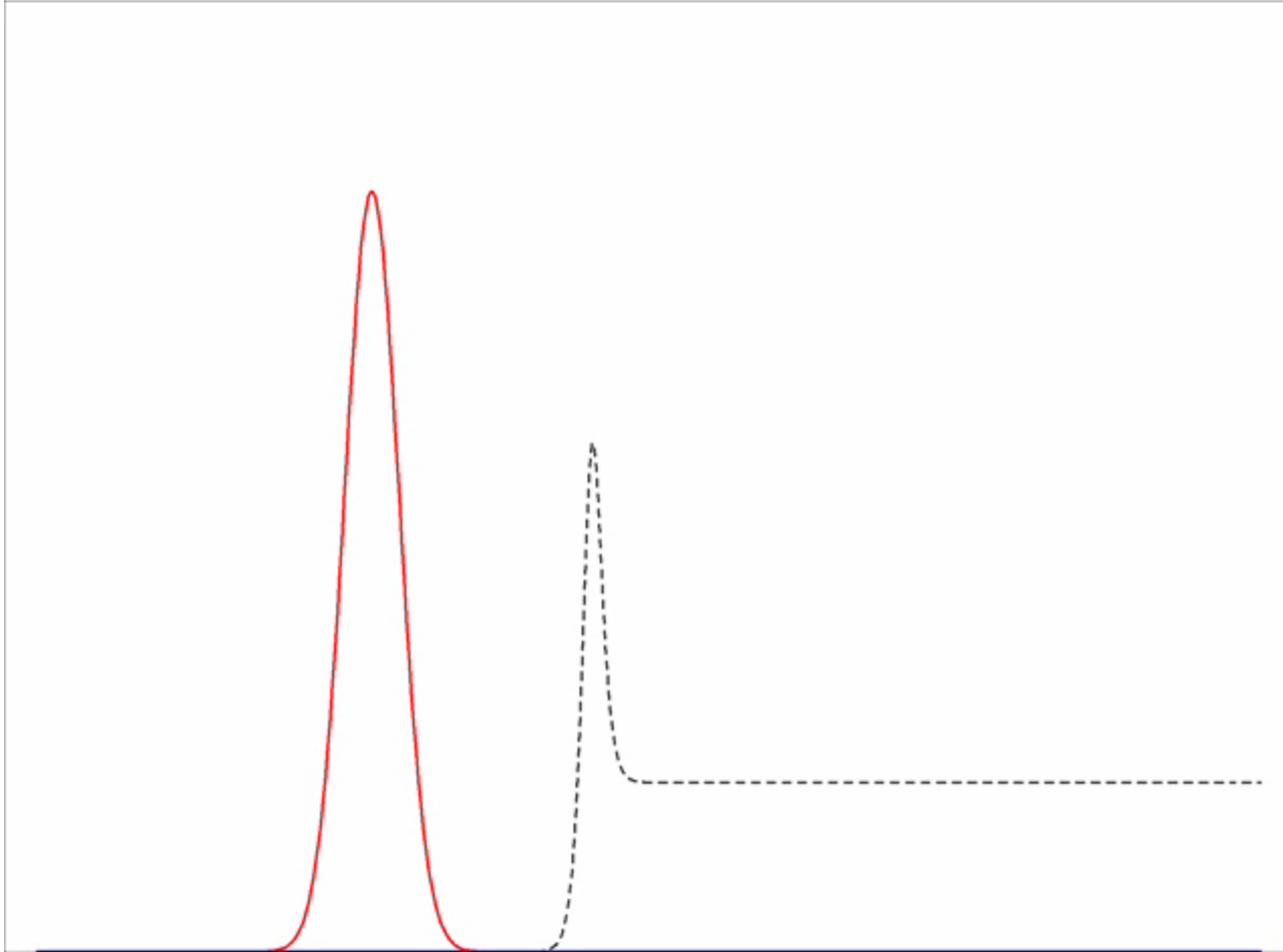
Density Plot

Multiple Surface Dynamics

- All of above can be generalized for multisurface problems:
  - unified framework for handling multiple components *and* surfaces.
  - in both cases, *interaction potentials induce transitions*, trajectory hops.
- Underlying condition essentially the same as before:
  - $\varphi_i{}' = a_{i+}(\varphi_{i+}{}^{sc}){}' + a_{i-}(\varphi_{i-}{}^{sc}){}'$ for each component, *i*.
  - sufficient to determine unique decomposition for stationary state.
- Two-surface example (symmetric potential wavepacket dynamics):

$$\dot{\vec{\psi}} = -\left(\frac{i}{\hbar}\right)\widetilde{H}\cdot\vec{\psi}, \qquad \text{with} \qquad \dot{\vec{\psi}} = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \quad ; \quad \widetilde{H} = \begin{pmatrix} \hat{H}_1 & \hat{D} \\ \hat{D} & \hat{H}_2 \end{pmatrix}$$

$$\frac{\partial\psi_{1\pm}}{\partial t} = -\left(\frac{i}{\hbar}\right)\left[\hat{H}_{11}\psi_{1\pm} + D\psi_{2\pm} \pm \left(\frac{V_1'}{2}\right)(\Psi_{1+} - \Psi_{1-}) \pm \left(\frac{D'}{2}\right)(\Psi_{2+} - \Psi_{2-})\right]$$

$$\frac{\partial\psi_{2\pm}}{\partial t} = -\left(\frac{i}{\hbar}\right)\left[\hat{H}_{22}\psi_{2\pm} + D\psi_{1\pm} \pm \left(\frac{V_2'}{2}\right)(\Psi_{2+} - \Psi_{2-}) \pm \left(\frac{D'}{2}\right)(\Psi_{1+} - \Psi_{1-})\right]$$

Multiple Surface Dynamics: bipolar wavepacket scattering
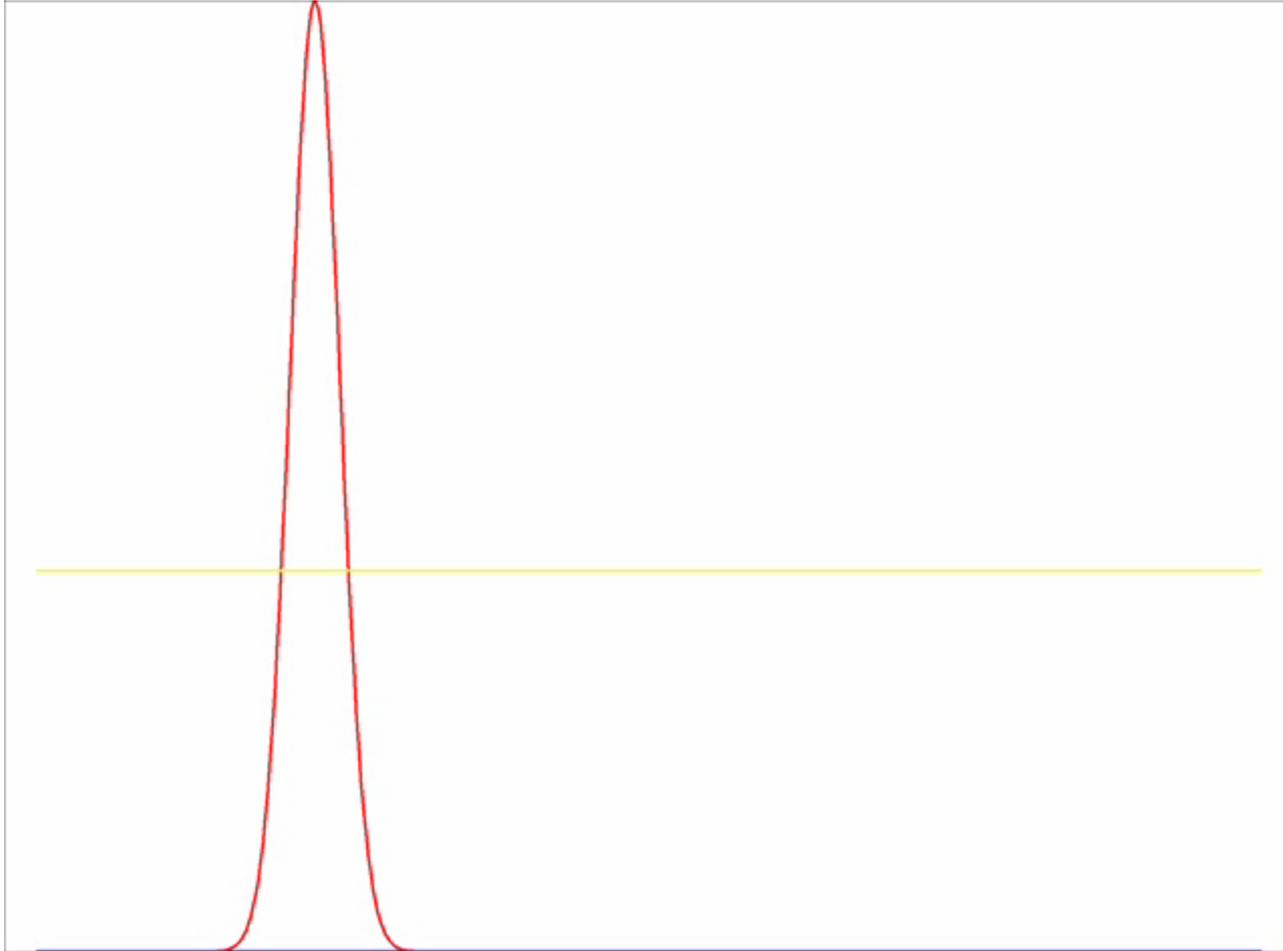
Density Plot

Multidimensional Wavepacket Scattering

- **How many components?**

  2 or 2^f, where f = # degrees of freedom? *Only 2 needed.*

  $\psi_\pm$ interpretation: forward/backwards along reaction path.

  Integrated quantity, $\Psi_\pm$ is a *line* integral.

- Linear reaction paths in Cartesian coordinates:

  spatial coordinates are $(x,\mathbf{y})$, x = rxn coord, $\mathbf{y}$ = $\perp$ modes

- Time evolution equations:

$$\frac{\partial \psi_\pm}{\partial t} = -\left(\frac{i}{\hbar}\right)\left[\hat{H}\psi_\pm \pm \frac{1}{2}\left(\frac{\partial V(x,\mathbf{y})}{\partial x}\right)\Psi_\Delta\right]$$

$$\text{where } \Psi_\Delta(x,\mathbf{y}) = \int_{-\infty}^{x}\left[\psi_+(x',\mathbf{y}) - \psi_-(x',\mathbf{y})\right]dx'$$

Bottleneck Potential System: unipolar wavepacket scattering
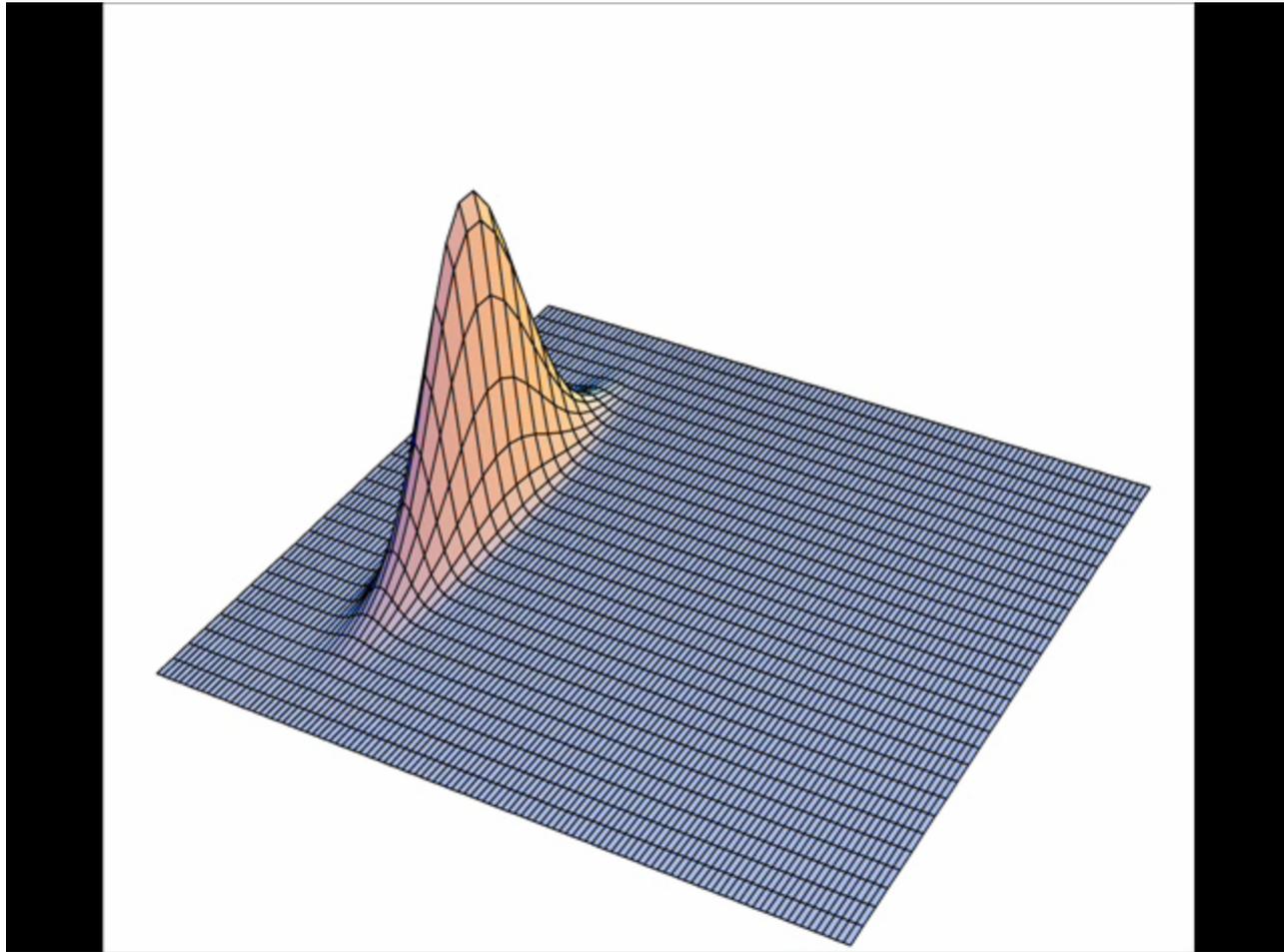
Density Plot

Bottleneck Potential System: bipolar wavepacket scattering
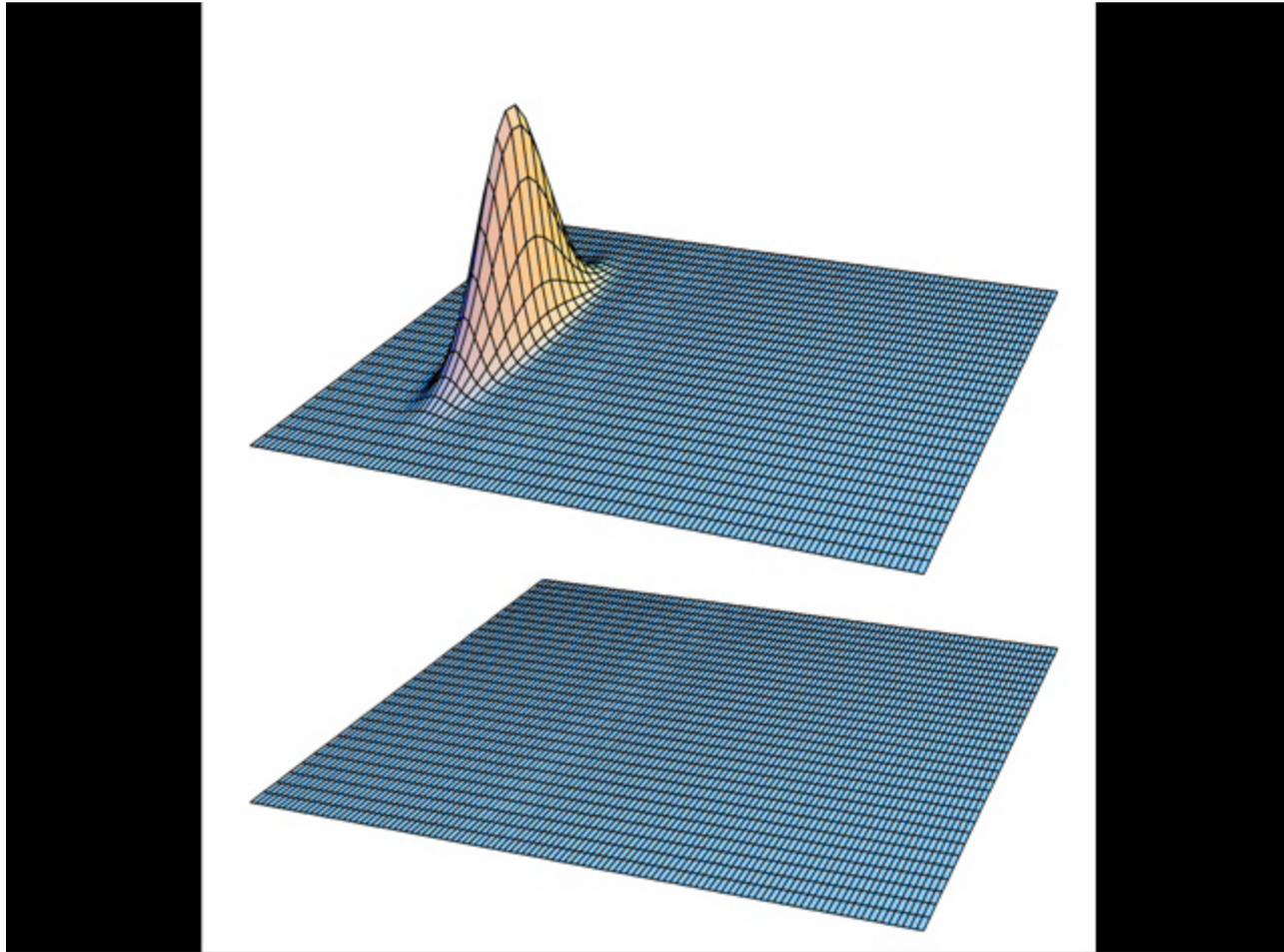
Density Plot

Multidimensional Wavepacket Scattering

- Curvilinear reaction paths

  Ψ_Δ still a *line* integral, taken around curvilinear path.

  $$\Psi_\Delta(\vec{x}) = \int_{-\infty}^{0} \left(\psi_+ - \psi_-\right) d\vec{x}'[s]$$

  Time evolution equations now have commutator terms

- How should reaction paths be defined?

position y / position x vs.   position y / position x
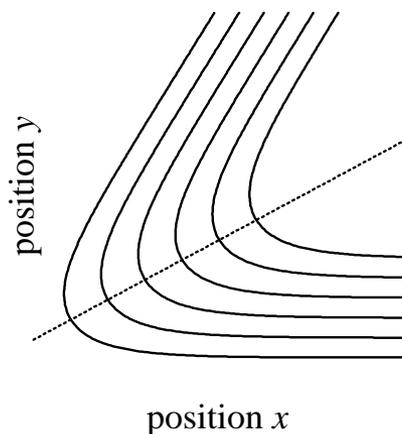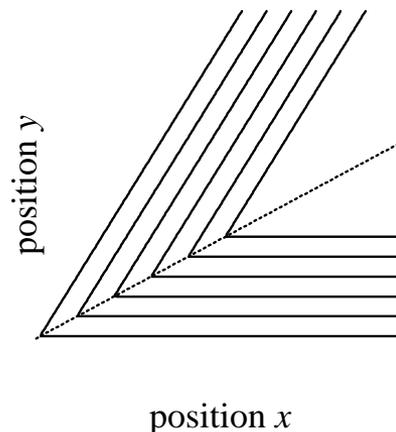
Universality of $\Psi_\Delta = (\Psi_+ - \Psi_-)$

- It can be shown that Ψ_Δ is the same for *all* reaction path definitions that agree asymptotically.

- It can be shown that

$$\frac{\partial \Psi_\Delta}{\partial t} = -\left(\frac{i}{\hbar}\right)\hat{H}\Psi_\Delta$$

  Ψ_Δ evolves as an ordinary TDSE wavepacket, without coupling to ψ.
  initial $\Psi_\Delta(x,t=0) = \Psi(x,t=0)$ known analytically for Gaussian $\psi(x,t=0)$

- Numerical propagation scheme:
  - propagate $\psi(x,t)$ and $\Psi_\Delta(x,t)$ completely independently.
  - no coupling or numerical integration required.
  - use conventional, efficient TDSE techniques (e.g. Crank-Nicholson).
  - compute bipolar components at any time obtained via

$$\psi_\pm = (1/2)\left[\psi \pm \hat{s}\cdot\vec{\nabla}\Psi_\Delta\right]$$

Collinear H+H2 in Jacobi Coordinates: unipolar wavepacket scattering
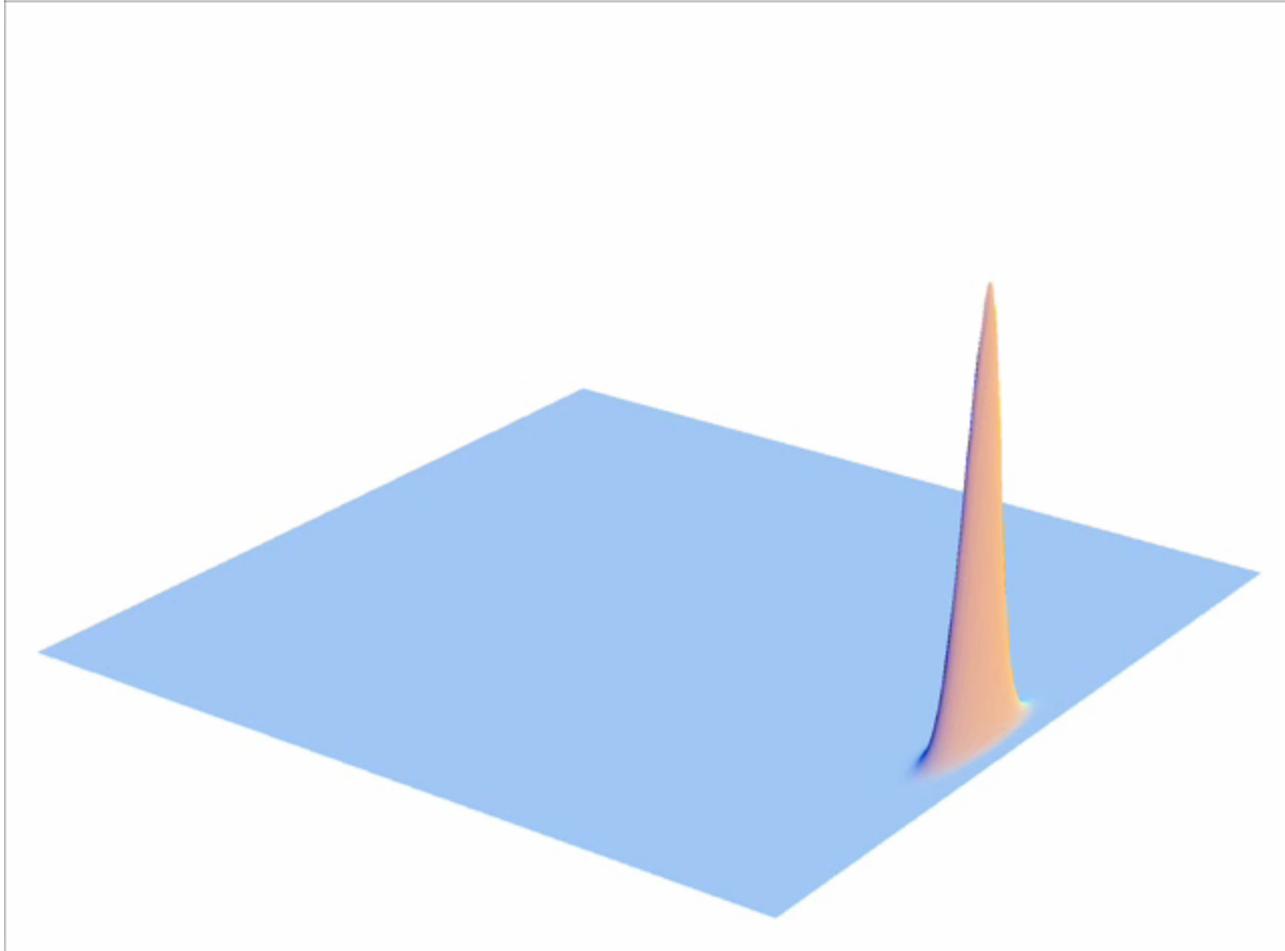
Density Plot

Collinear H+H2 in Jacobi Coordinates: bipolar wavepacket scattering
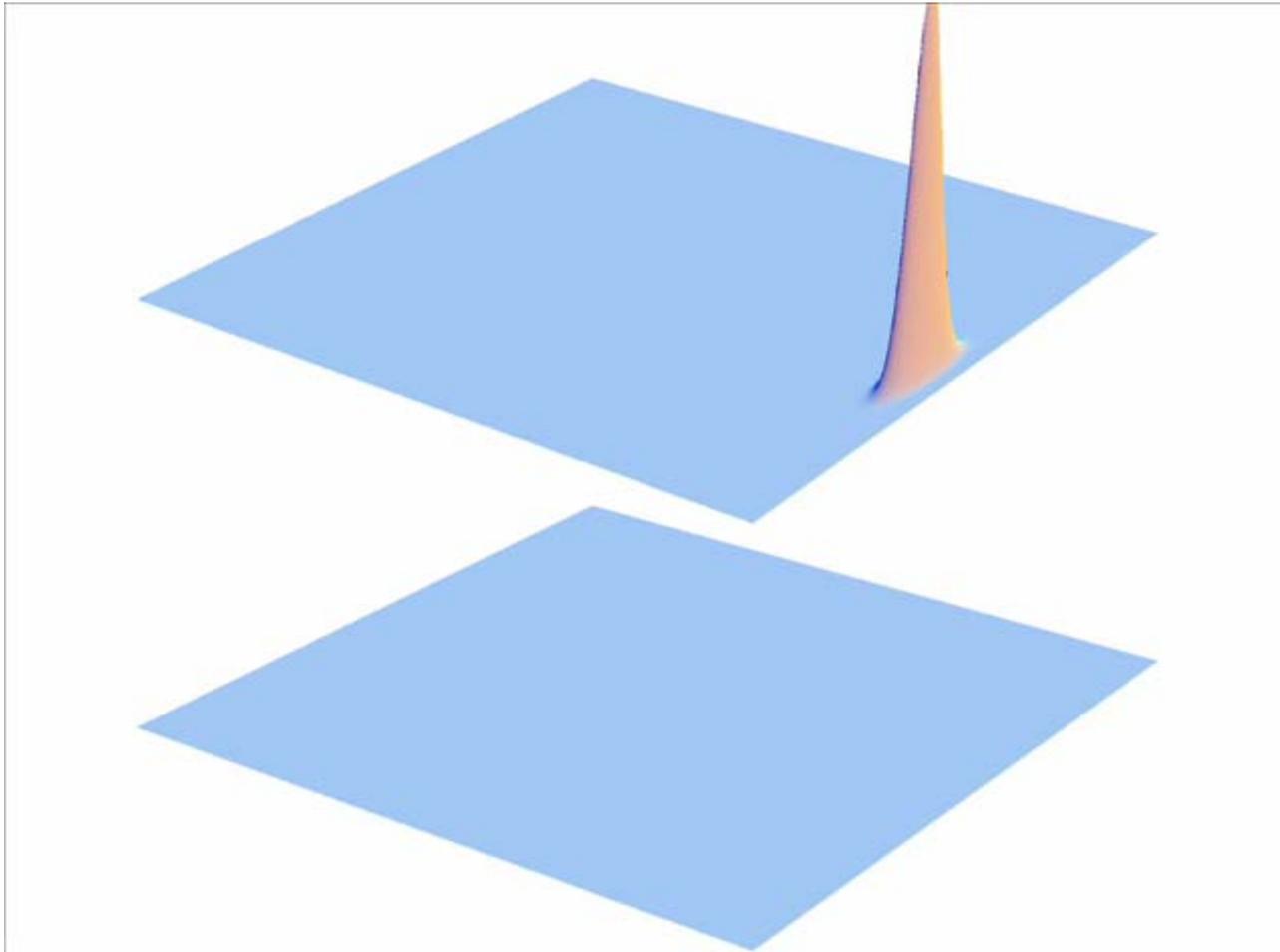
Density Plot

Curvilinear Eckart + Harmonic Oscillator
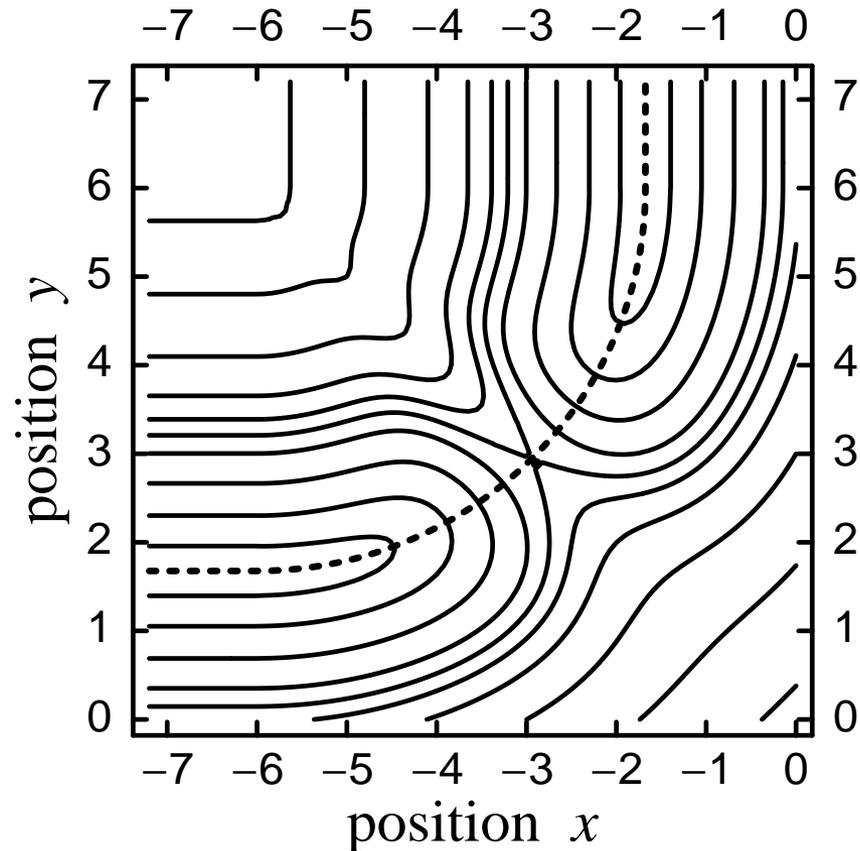
Contour Plot of Potential Surface

Curvilinear Eckart + Harmonic Oscillator: bipolar wavepacket scattering
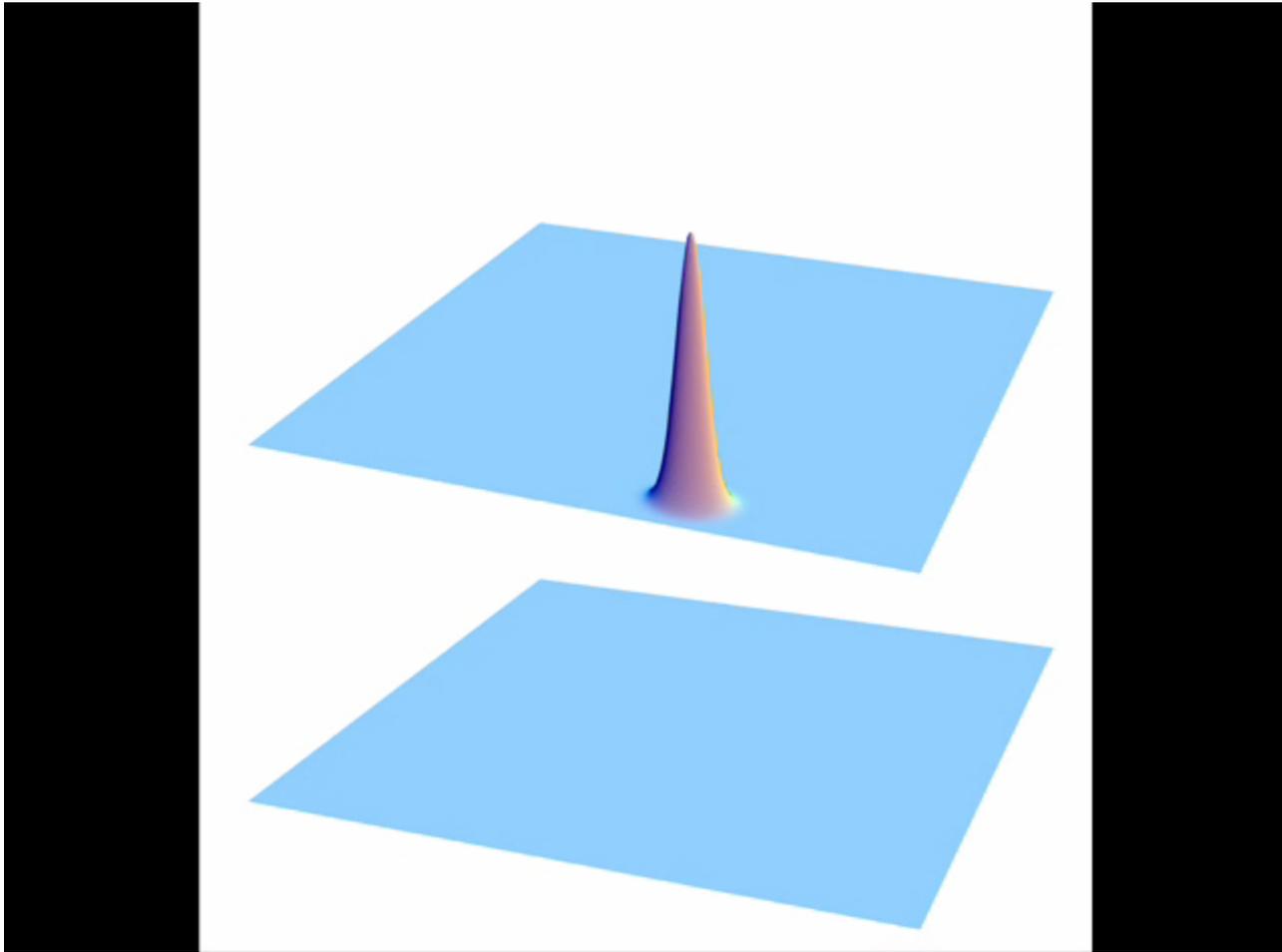
Density Plot

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