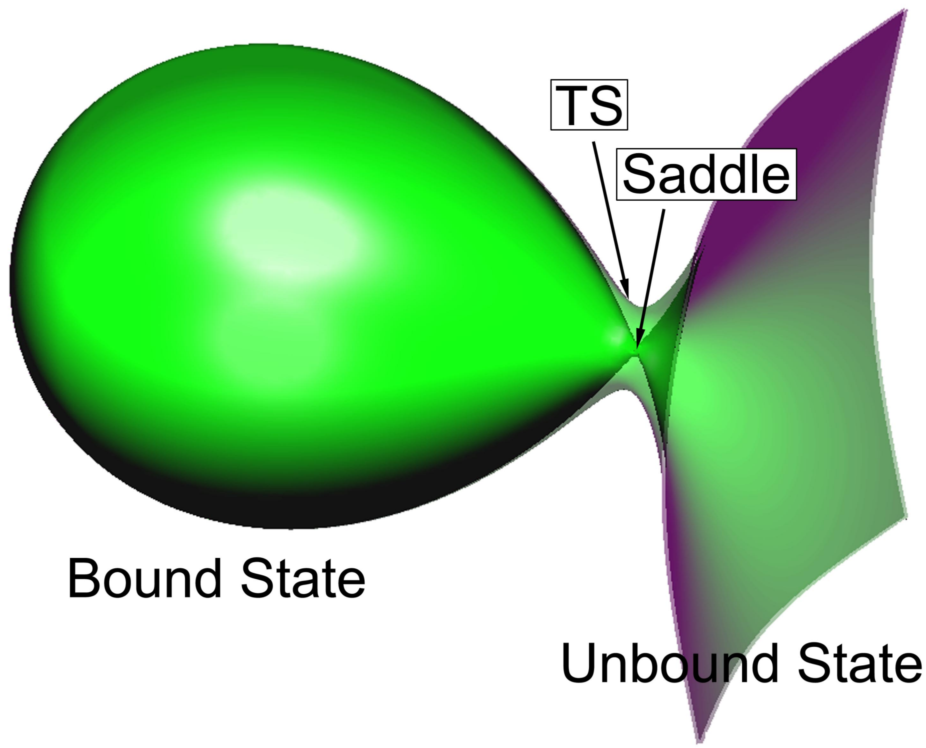
Rank-1 Saddle Transport

Scattering Reactions with 3 or more Degrees of Freedom



Steve Brunton

Organization of Talk

I. Saddle Transport & Chemical Reaction Rates

II. Transition State of a Scattering Reaction

III. Methods for Accurate Rate Calculation

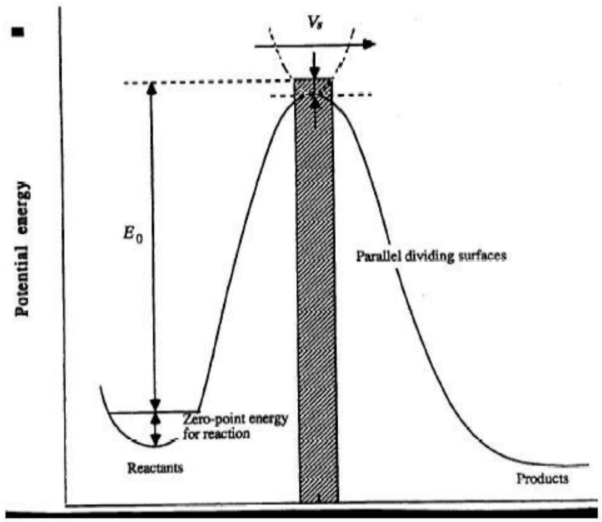
IV. Applications:

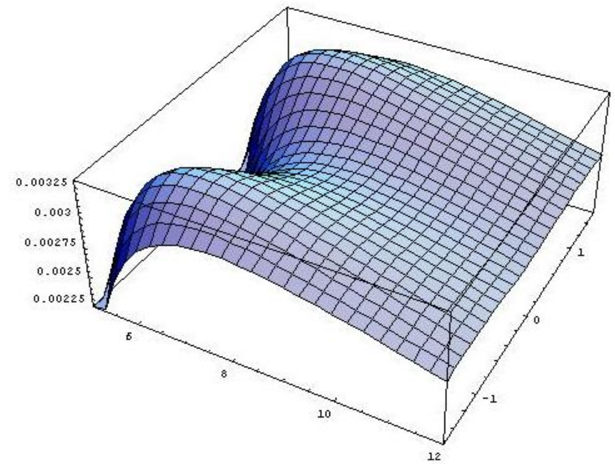
- **Electron Scattering in the Rydberg Atom**
- **Planar Scattering of H_2O with H_2**
- **Higher DOF systems, Rank-2 Saddle Transport, Experimental Verification**

V. Conclusions & Open Questions

VI. References

Transition State Theory





Schematic of potential saddle separating two wells (left) and the saddle of a scattering reaction (right) [Figures from /∼koon/presentations/chemical.pdf]

- Transition State: Joins Reactants & Products
  - **Bottleneck near rank-1 saddle**
  - **Opens for energies larger than saddle**
- TST Assumes Unstructured Phase Space
  - **Even Chaotic Phase Space is Structured**

Rank-1 Saddle Transport

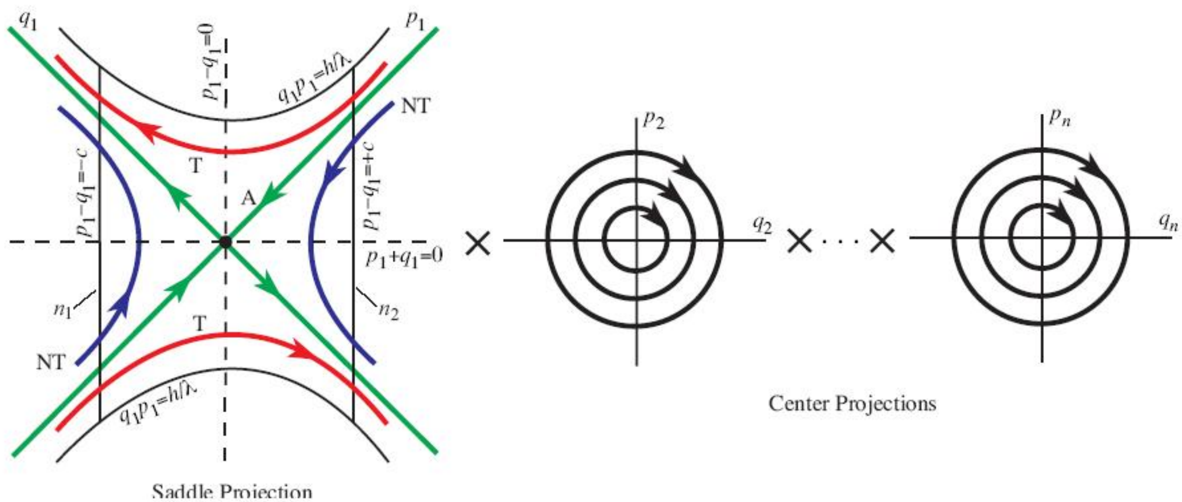
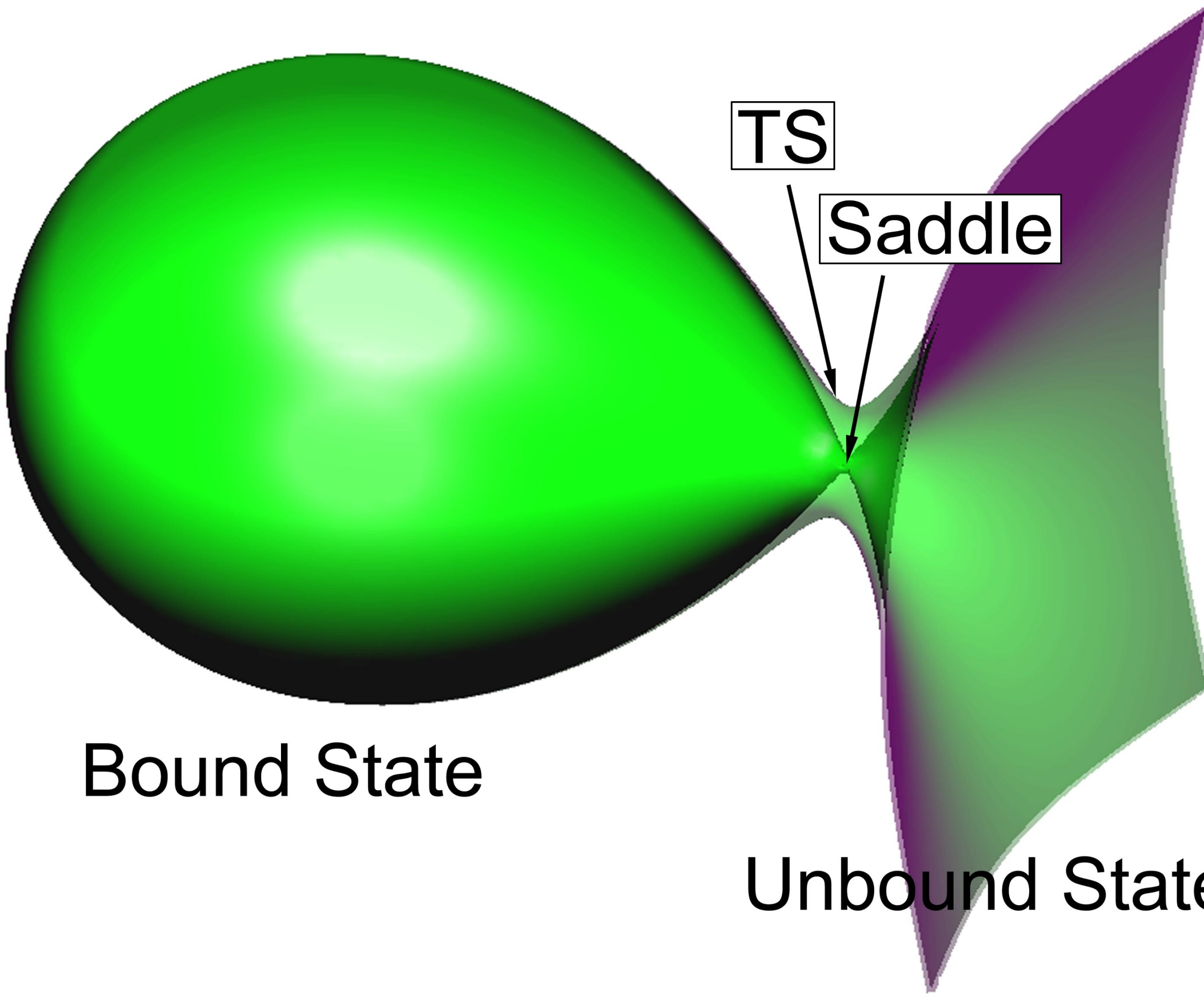


Figure from /∼koon/papers/specialist_final.pdf

- Saddle direction mediates transport
- Energy is shared between saddle and centers

$$S^{2DOF-3} \cong \left\{ \sum_{i=1}^{DOF-1} \frac{\omega_i}{2} \left(q_{i+1}^2 + p_{i+1}^2 \right) = H - \lambda q_1 p_1 \right\}$$

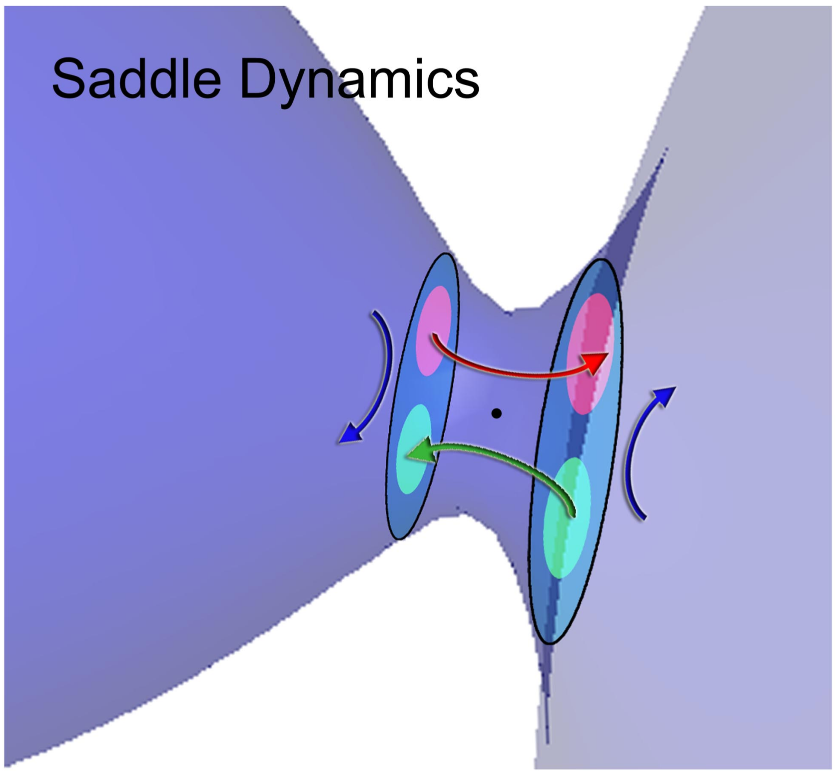
What is a Scattering Reaction?

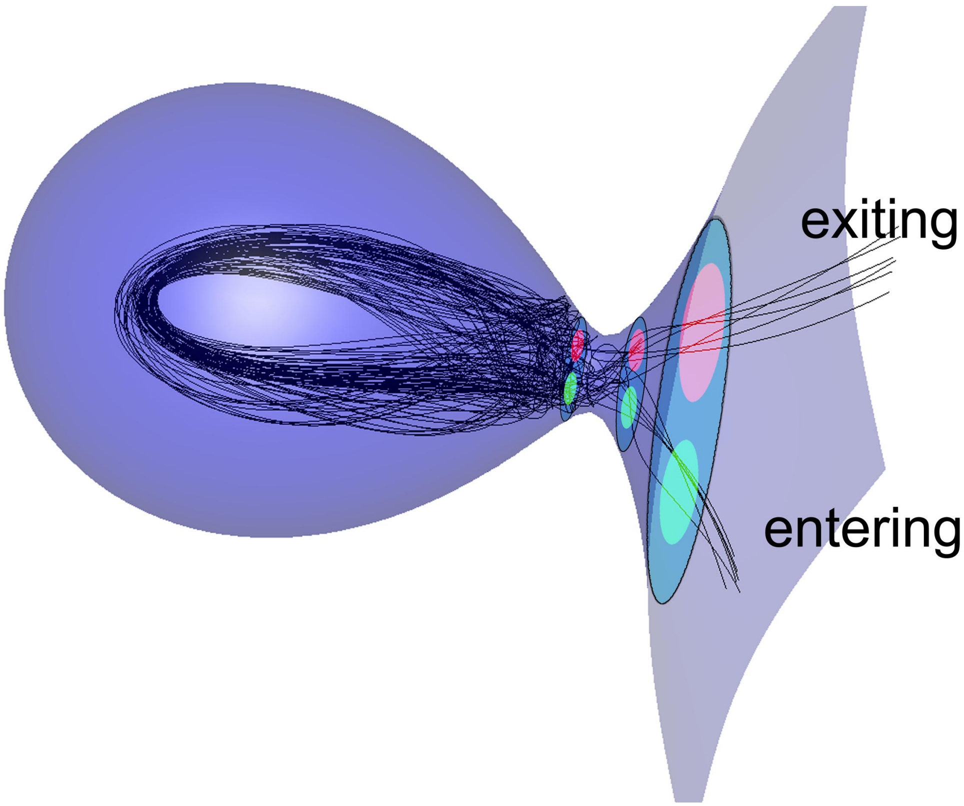


- Bound vs. Unbound States (Hill Region)
- Nonzero Angular Momentum not always valid

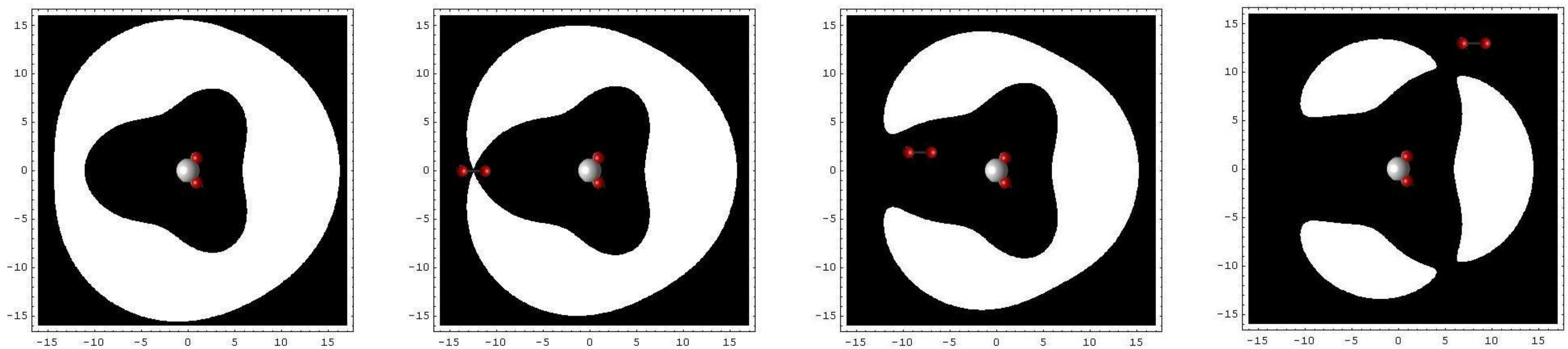
Overview of Method

- Identify Saddle/TS & Hill Region
- Find Box Bounding Reactive Trajectories (outcut)
  - **in & out cuts make "airlock"**
  - **Monte Carlo sample energy surface in box**
- Integrate traj's into bound state until escape





Identifying the Hill Region

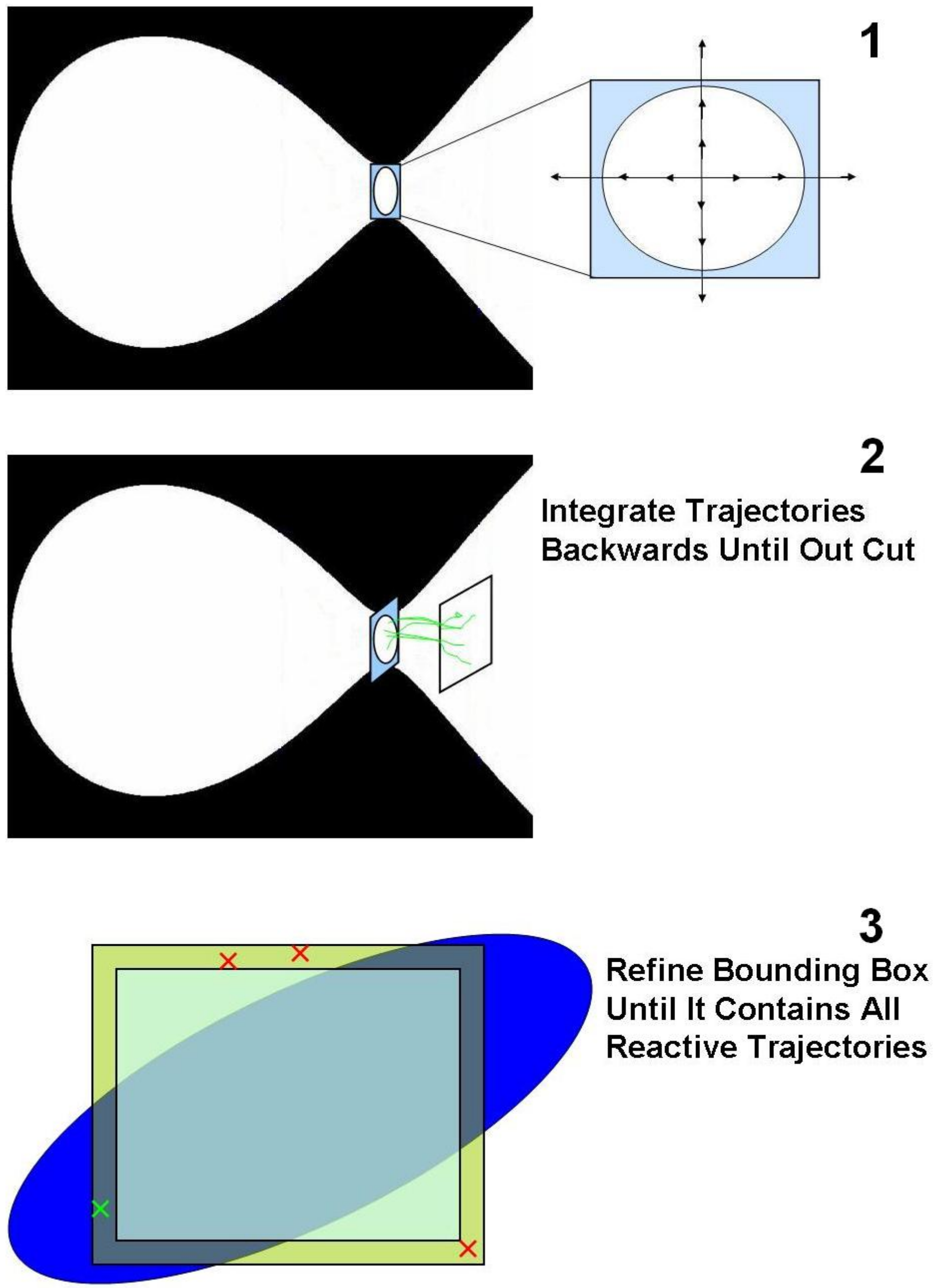


Hill Region for H_2O-H_2 at various energies (fixed H_2 orientation)

- Reduce out rotations and work at fixed ang. mom.
- Hill Region is in cartesian body-frame coordinates
- **Amended Potential:** For $\mu \in \mathfrak{g}^*$,

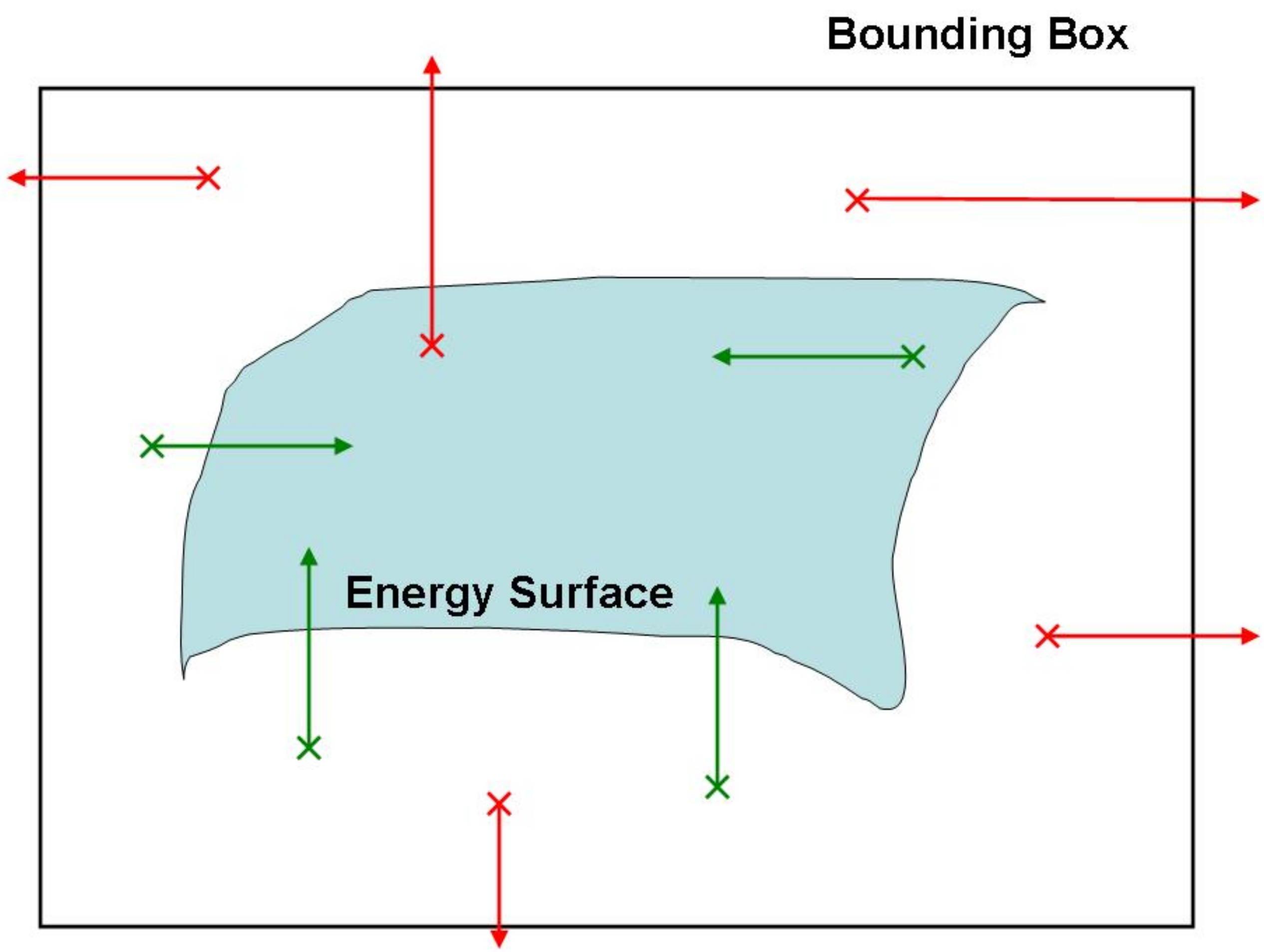
$$V_\mu(q) = V(q) + \frac{1}{2}\langle \mu, \mathbb{I}^{-1}(q)\mu \rangle = V(q) + \frac{1}{2} g_{00}^{-1} \mu^2$$

Bounding Box Method



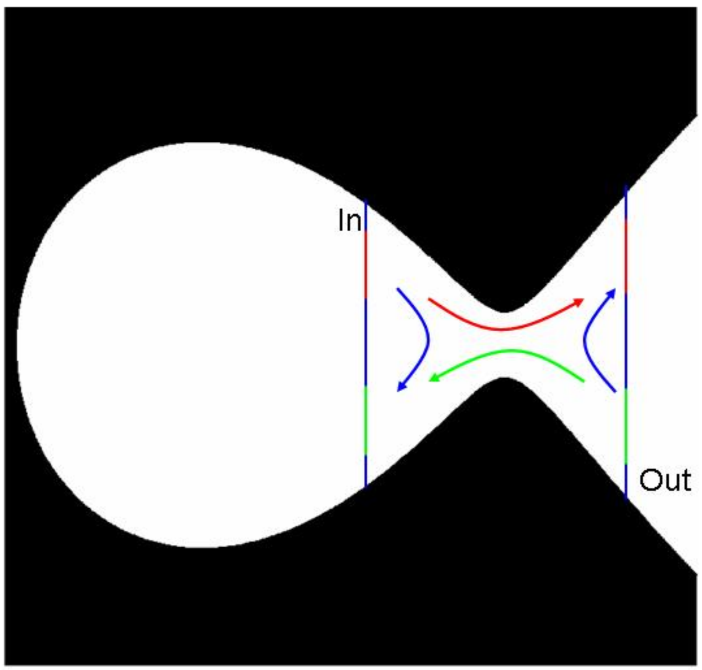
Sampling the Energy Surface

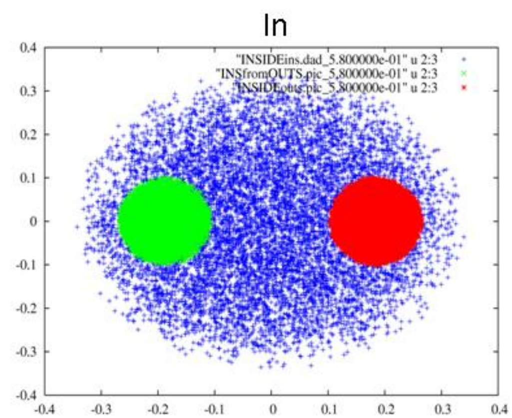
- Randomly select points in bounding box
- Project (using momentum variables) until intersects energy surface

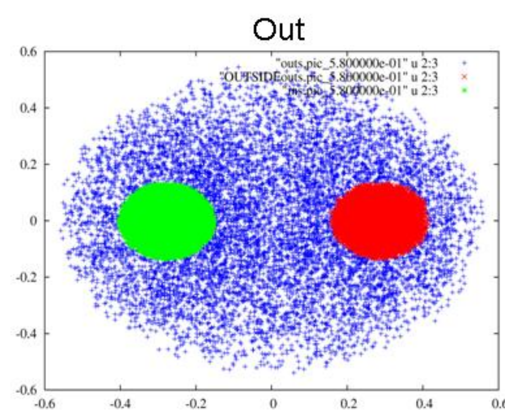


Example - Rydberg Atom

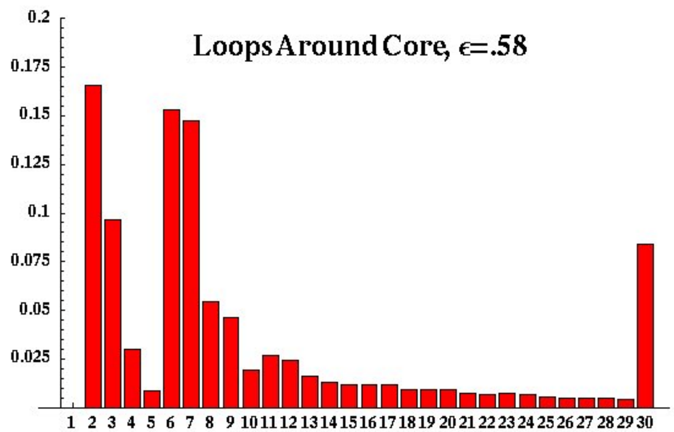
$$H = \frac{1}{2}\left(p_x^2 + p_y^2 + p_z^2\right) + \frac{1}{2}\left(xp_y - yp_x\right) + \frac{1}{8}\left(x^2 + y^2\right) - \epsilon x - \frac{1}{\sqrt{x^2 + y^2 + z^2}}$$

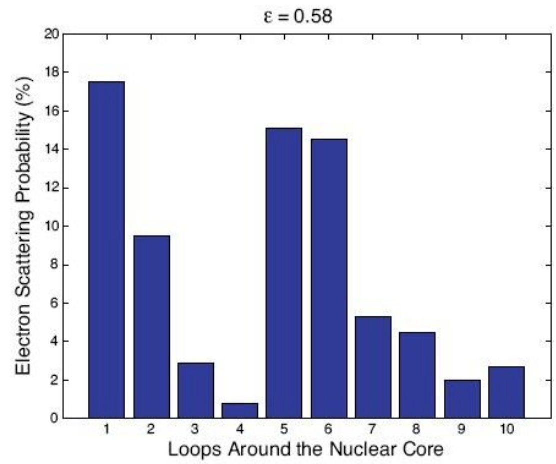


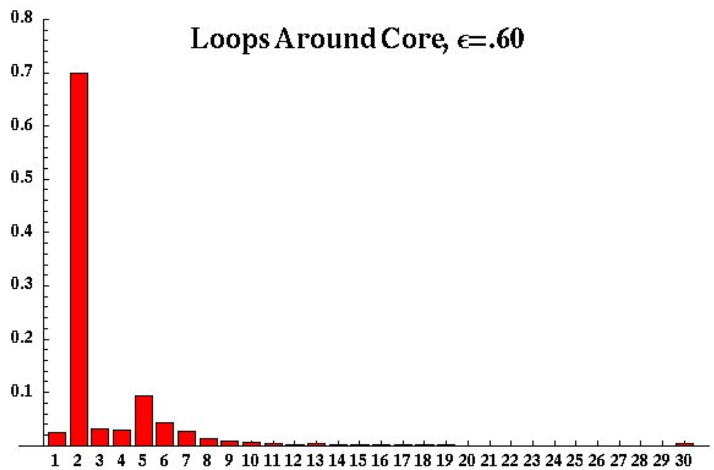


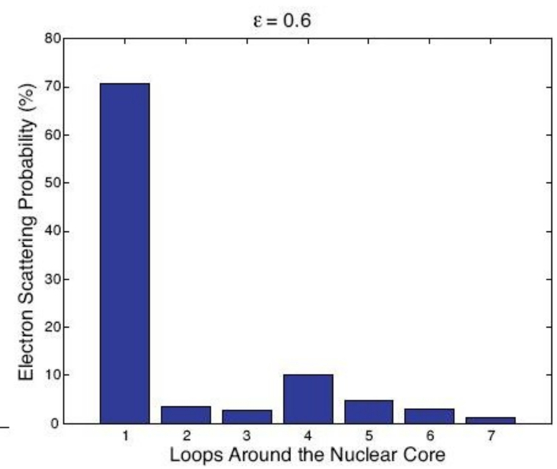


Rydberg Atom Cont'd









- $\sim$3 minutes :: 4,000 pts :: $< .5\%$ error
- $\sim$1 hour :: 140,000 pts :: $< .1\%$ error
- $\sim$2 days :: 1,000,000 pts ::

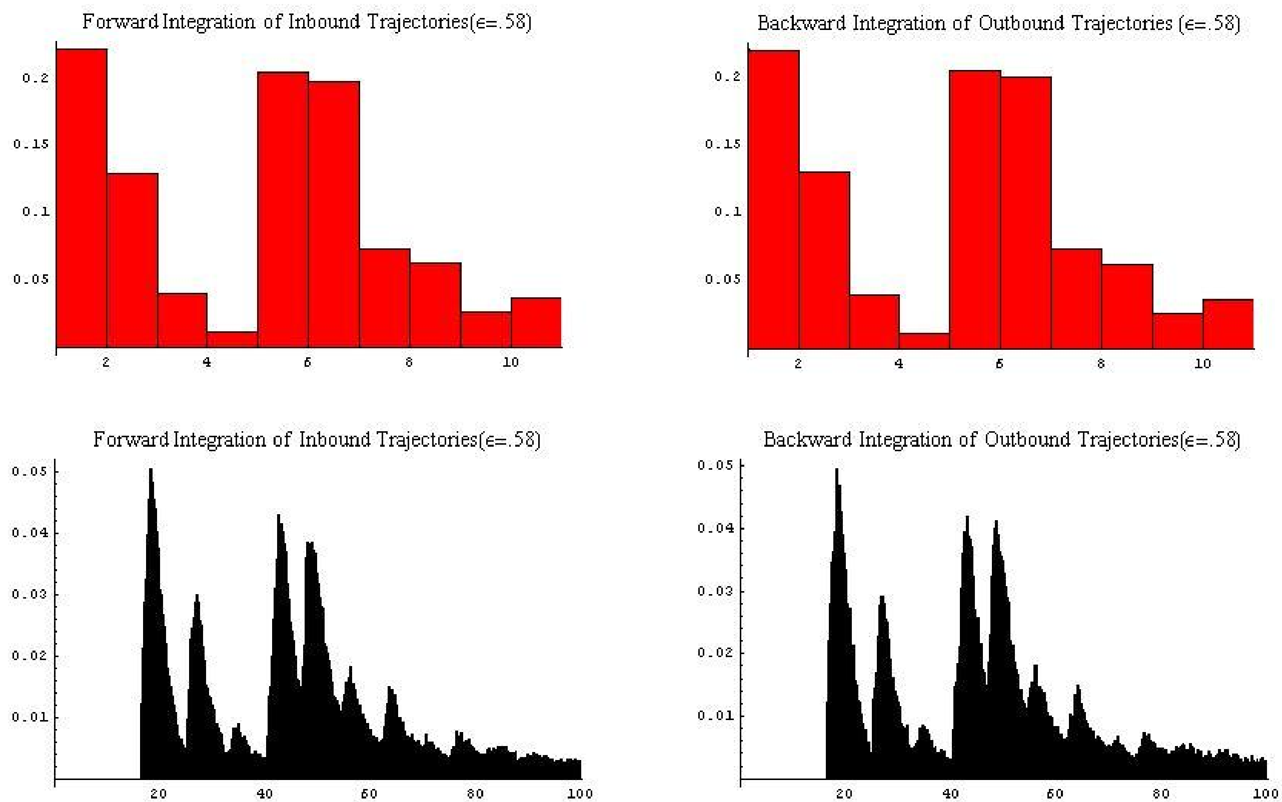
Controlling Standard Deviation

- Compute data in N chunks (size ∼1000pts):
  - $X_j(i)$ **- bin** i **for chunk** j
  - $\bar{X}(i)$ **- bin** i **for combined data**

$$SD(i) = \frac{1}{N}\sqrt{\left(X_1(i) - \bar{X}(i)\right)^2 + \ldots + \left(X_N(i) - \bar{X}(i)\right)^2}$$

- Keep computing chunks until $SD(i) <$tolerance $\forall i$
- Only necessary data is computed

Dual Method Test



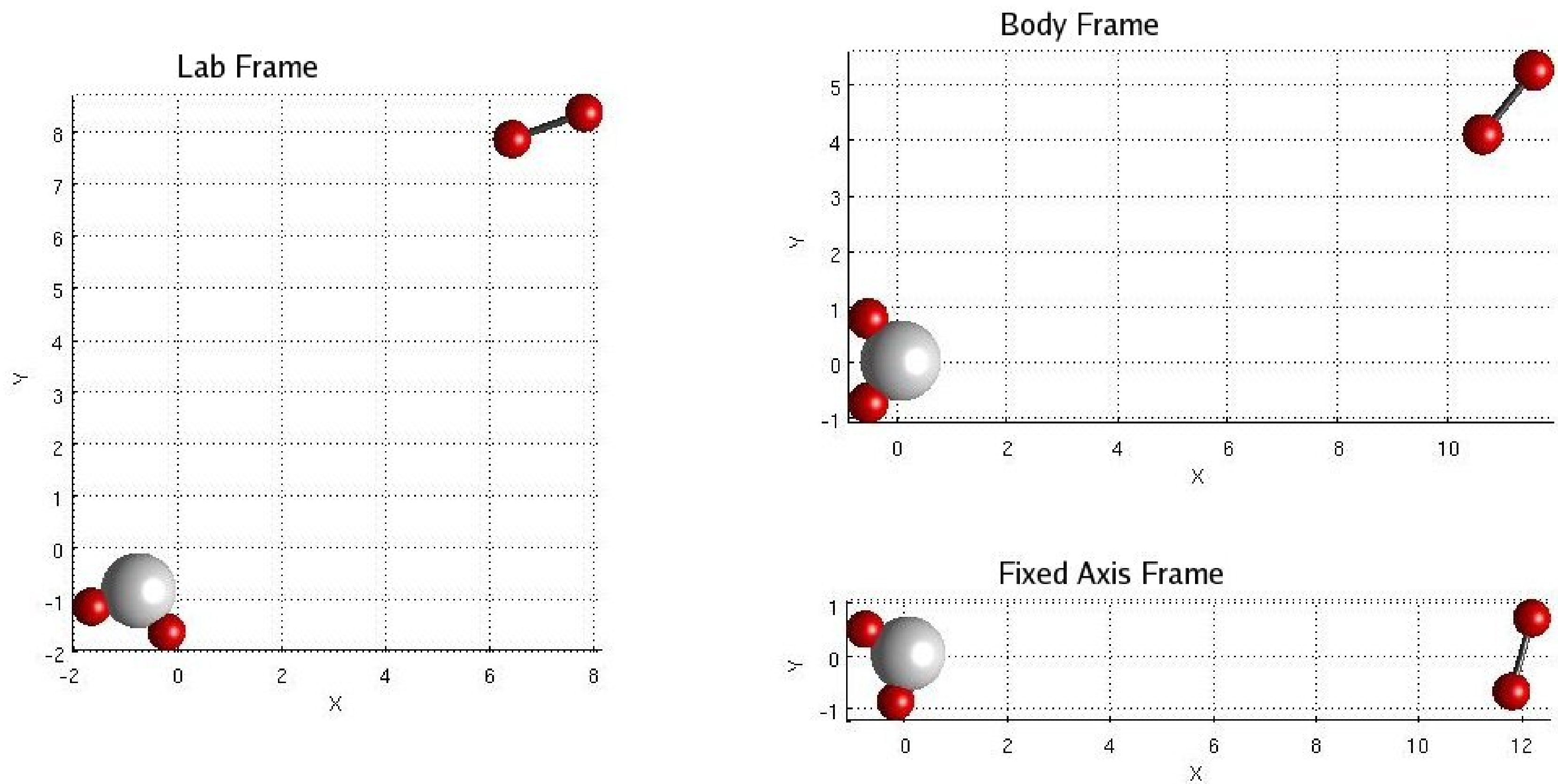
Comparison of LD using forward and backward integration

- Integrate trajectories backwards into bound state
  - **Detects error in bounding box, sampling error**

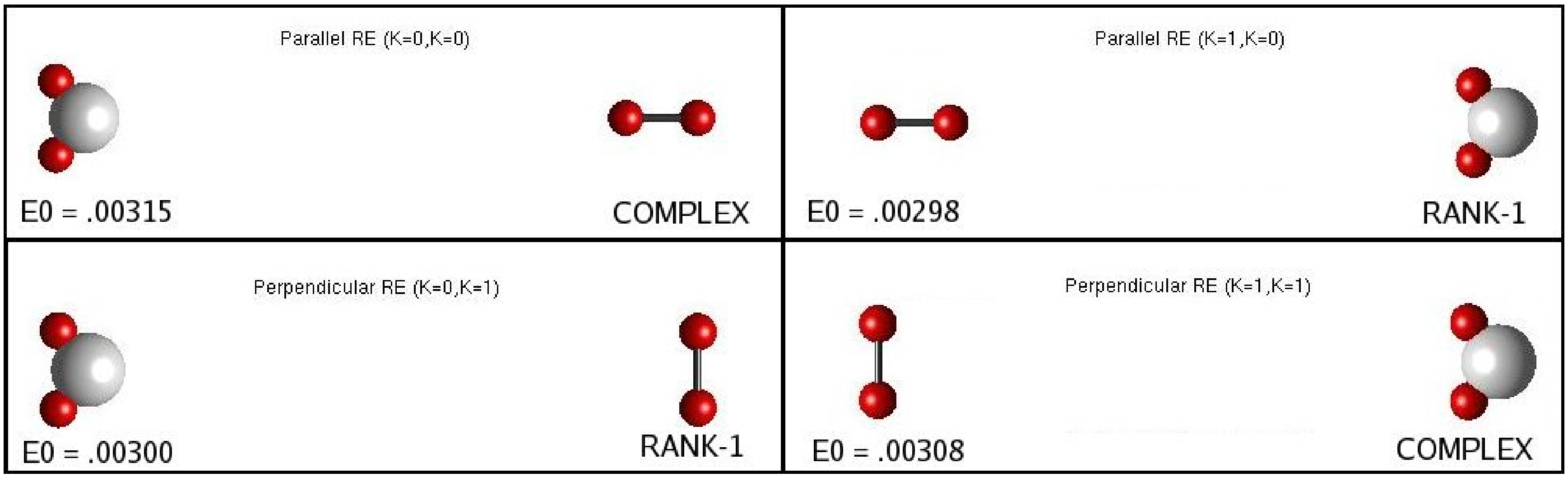
Planar Scattering of H_2O-H_2

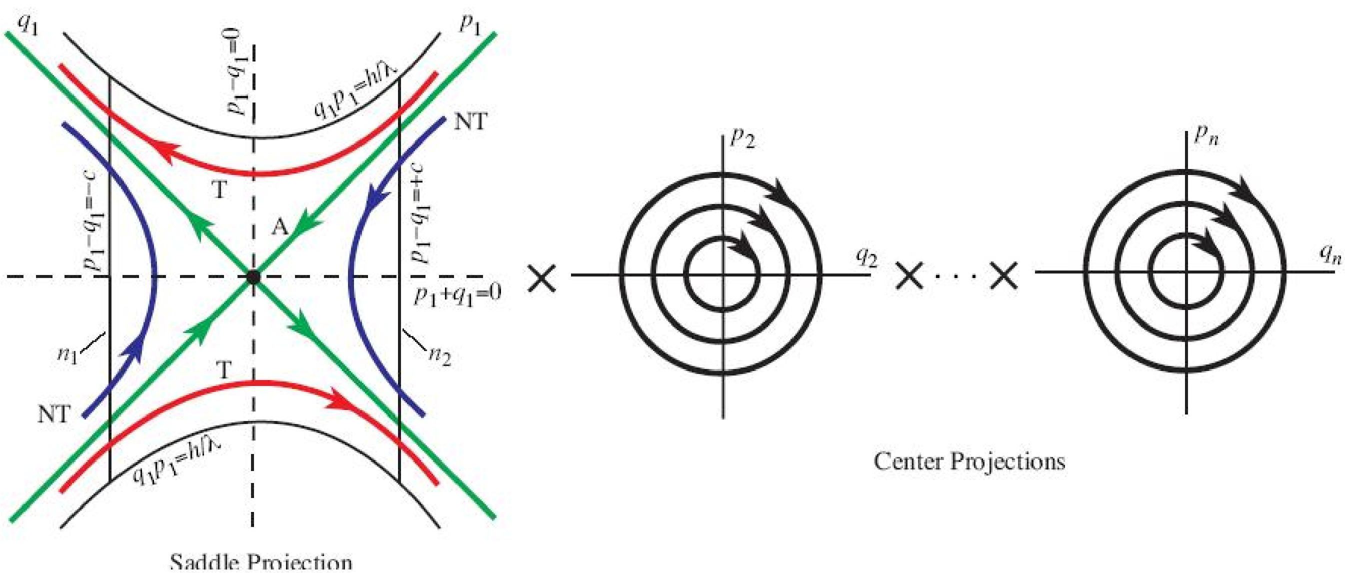
$$H = \frac{p_R^2}{2m} + \frac{(p_\theta - p_\alpha)^2}{2mR^2} + \frac{(p_\alpha - p_\beta)^2}{2I_a} + \frac{p_\beta^2}{2I_b} + V$$

- V = **dipole/quadrupole + dispersion + induction + Leonard-Jones. (Wiesenfeld, 2003)**
- **Reduce out** θ **and work on** $p_\theta \equiv J > 0$ **level set.**



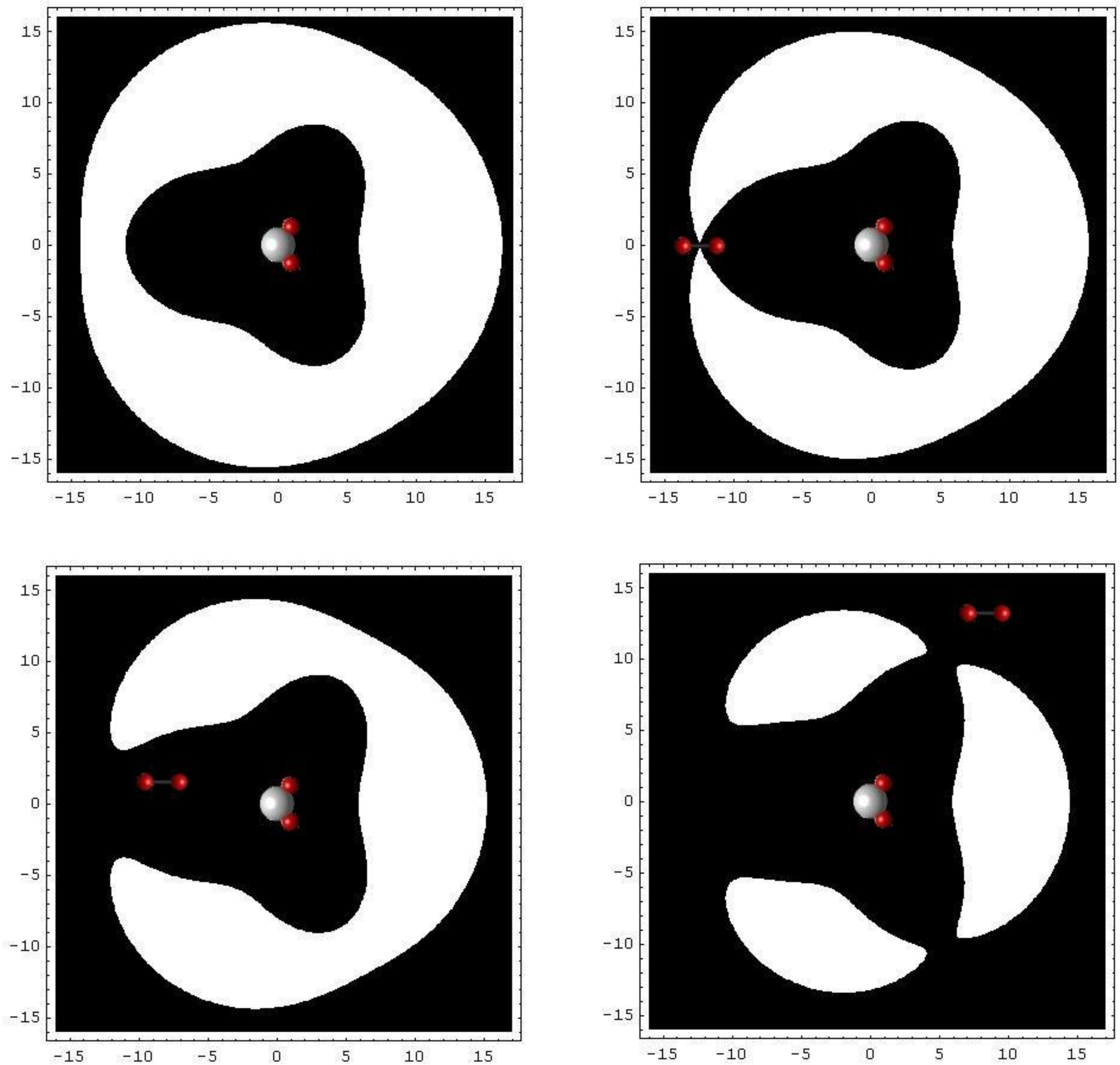
H_2O-H_2 Saddles



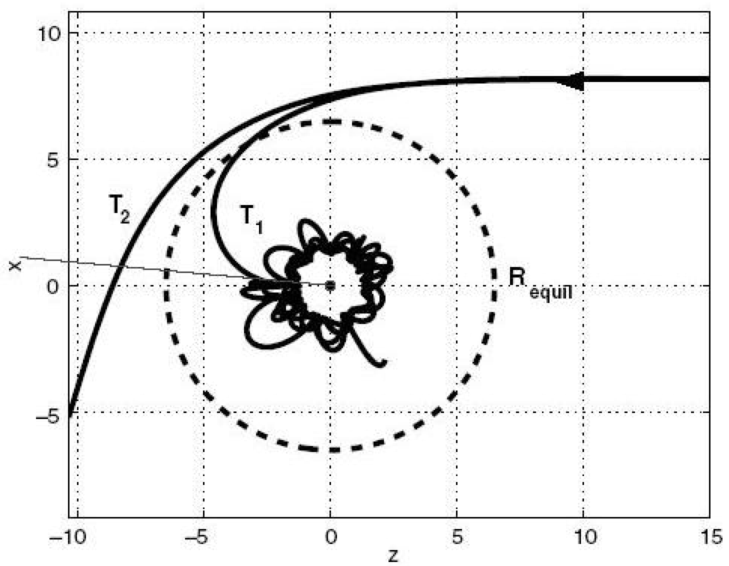


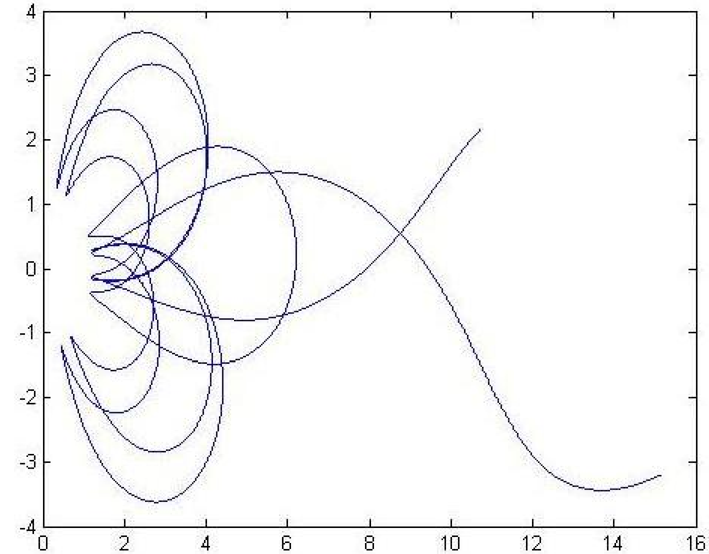
Linearization near rank-1 saddle

H_2O-H_2 Hill Region



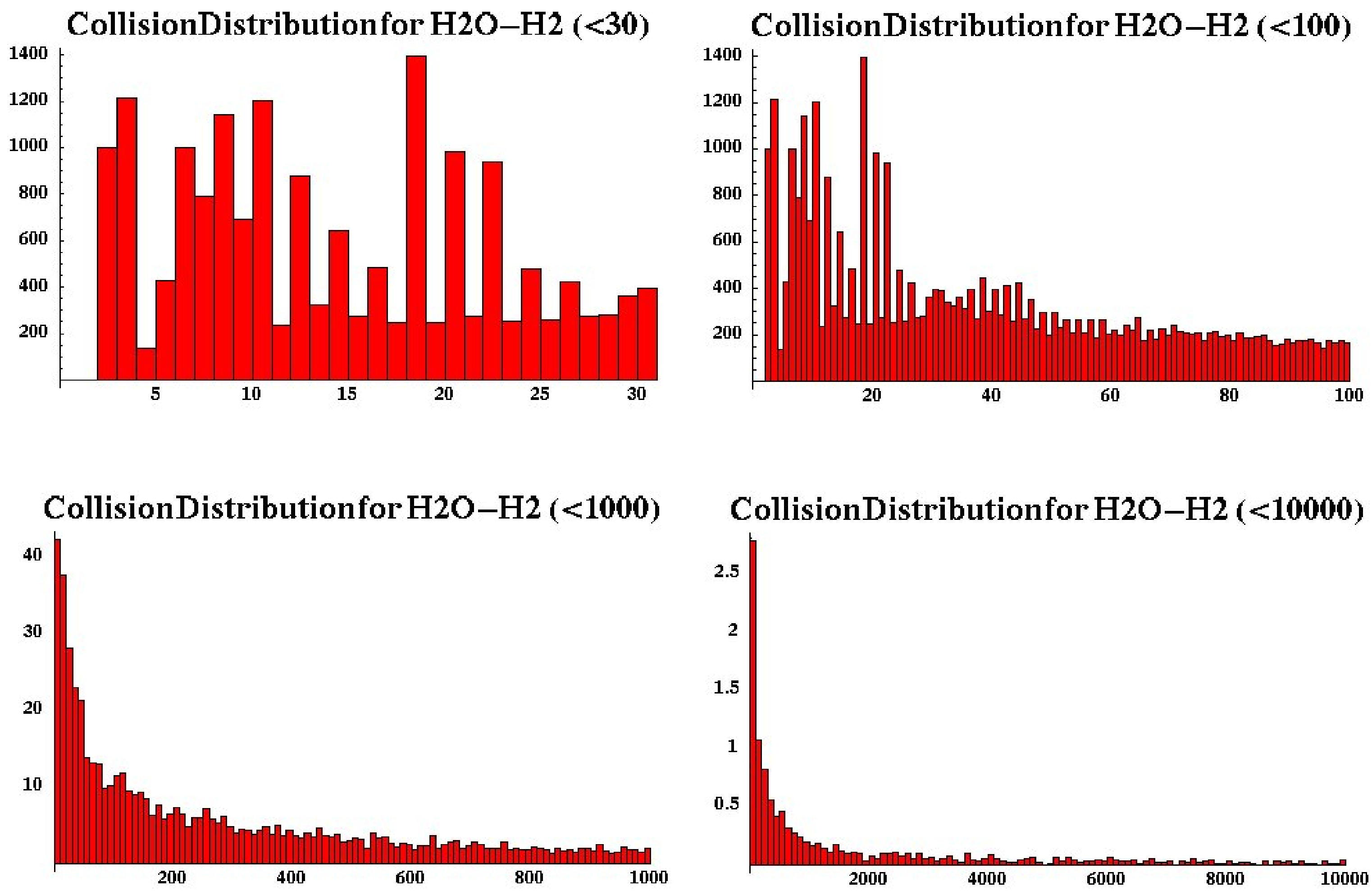
H_2O-H_2 Collision Dynamics





- Unrealistic Potential
- Numerically Volatile Collisions
- Is Non-Scattering Reaction Occurring?
- More Realistic Potential Surface (Wiesenfeld)

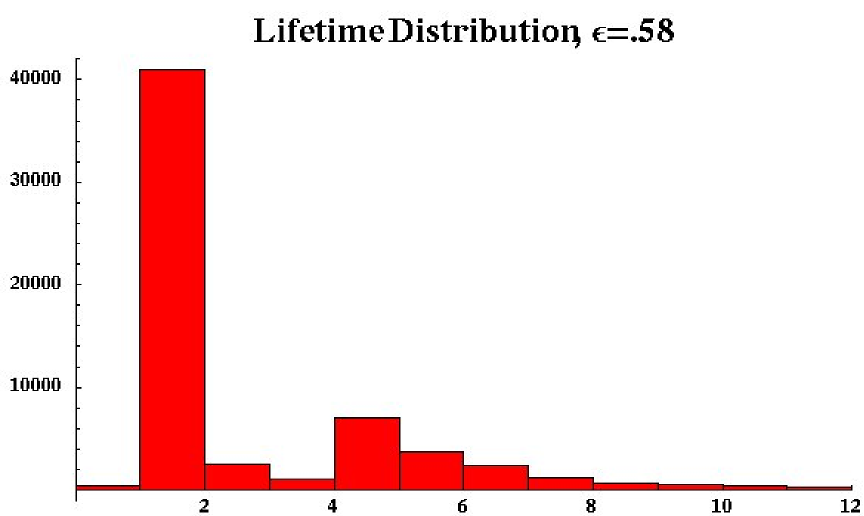
H_2O-H_2 Lifetime Distribution

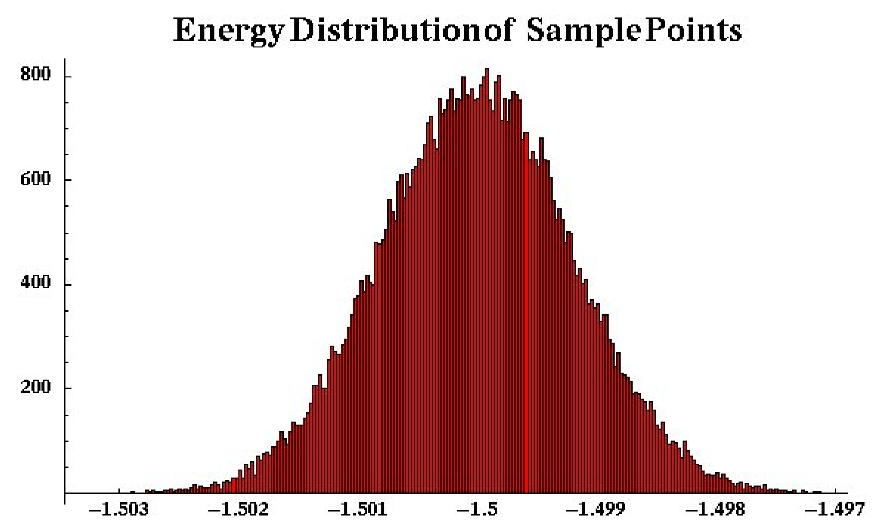


- **Locally structured (fine scale)**
- **Globally RRKM (coarse scale)**
  - Does structure persist w/ error in energy samples?

Gaussian Energy Sampling

- Experimental verification of lifetime distribution
  - **Fixed energy slice is not realistic**
  - **Gaussian around target energy is more physical**
  - **Do nonRRKM features persist?**

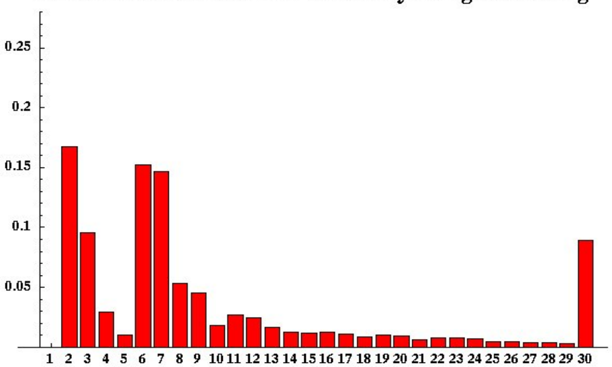




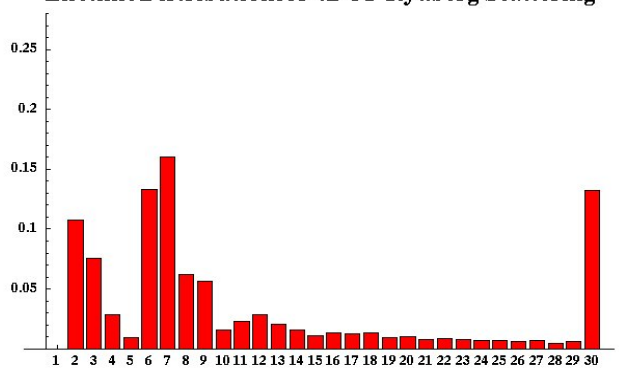
≥ 3 DOF Rydberg Analog

$$H = \frac{1}{2}\left(p_x^2 + p_y^2 + p_z^2 + p_w^2\right) + \frac{1}{2}\left(xp_y - yp_x\right) + \frac{1}{8}\left(x^2 + y^2\right) - \epsilon x - \frac{1}{\sqrt{x^2 + y^2 + z^2 + w^2}}$$

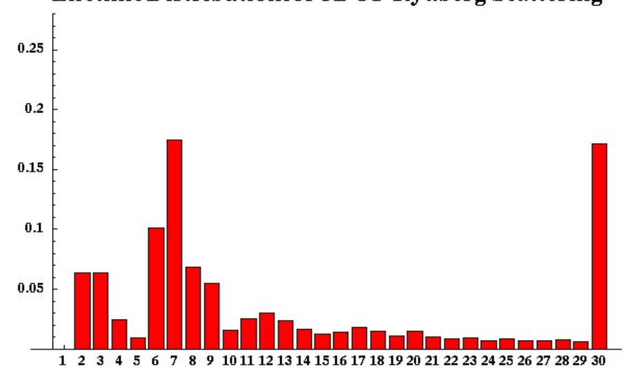
Lifetime Distribution for 3DOF Rydberg Scattering



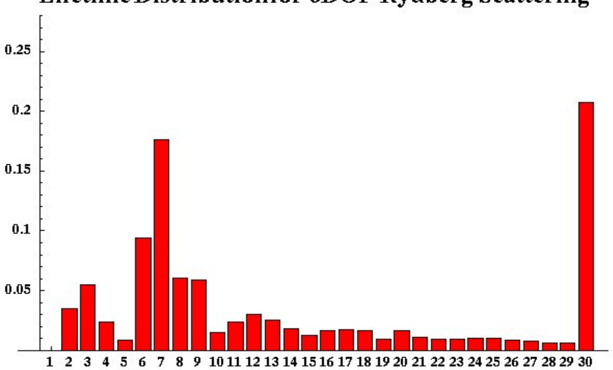
Lifetime Distribution for 4DOF Rydberg Scattering



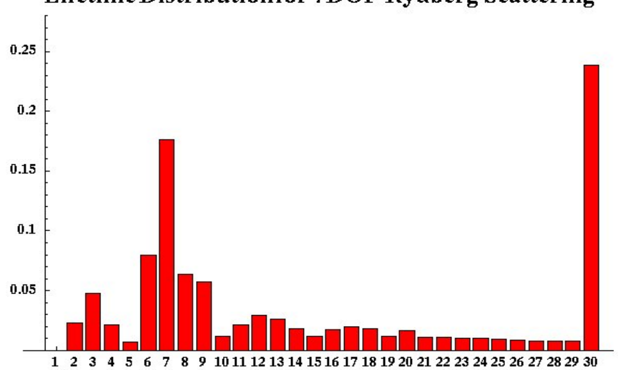
Lifetime Distribution for 5DOF Rydberg Scattering



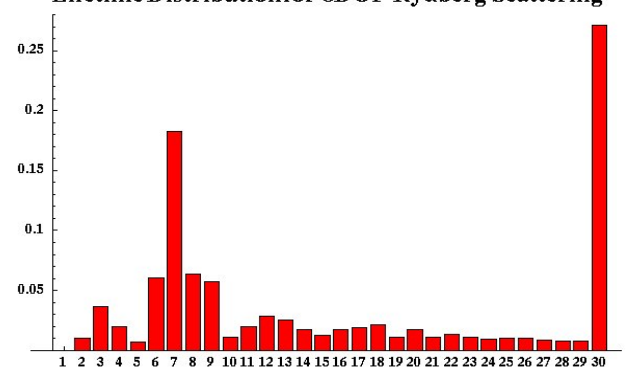
Lifetime Distribution for 6DOF Rydberg Scattering



Lifetime Distribution for 7DOF Rydberg Scattering

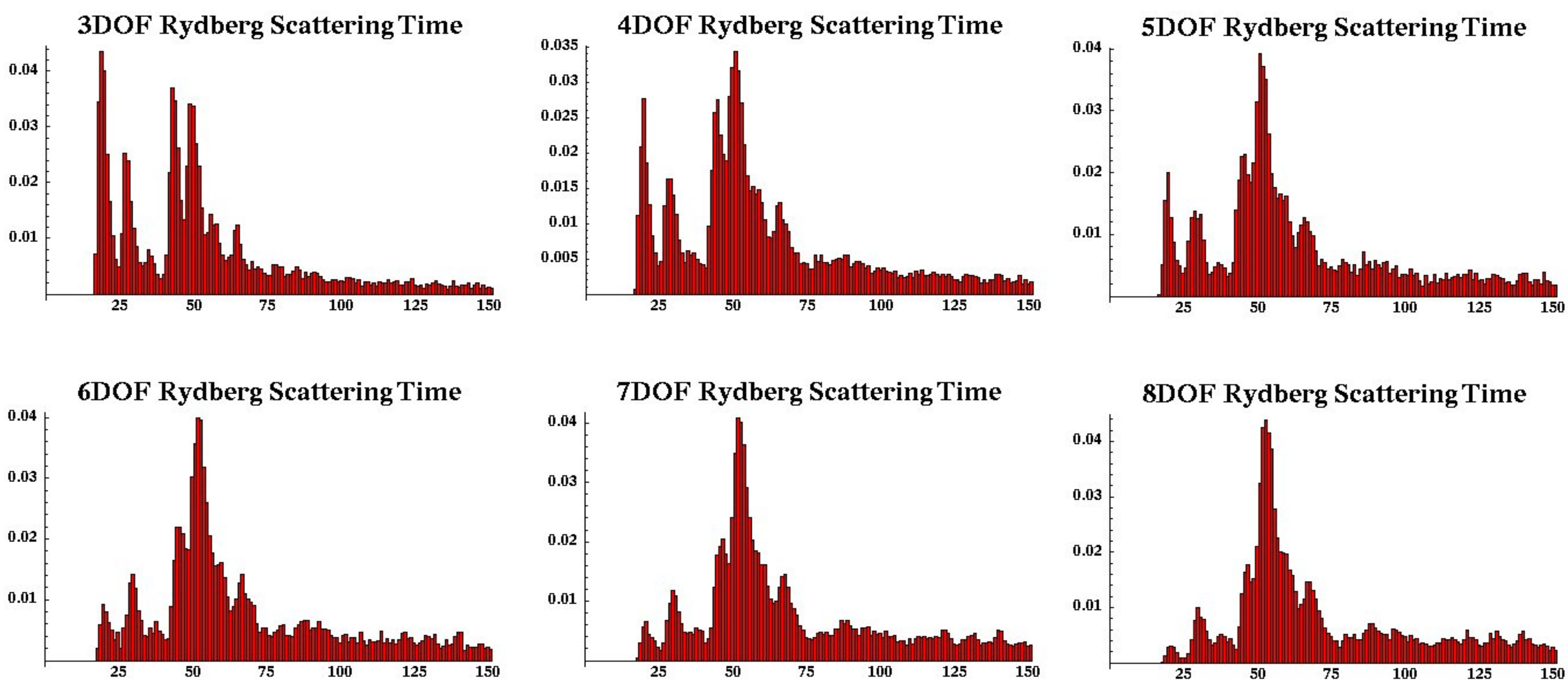


Lifetime Distribution for 8DOF Rydberg Scattering



$\geq$ 3 DOF Rydberg Analog

- x,y,z-like variables (w is z-like)
- Sampling takes 5-20min for $\leq$ 8 DOF

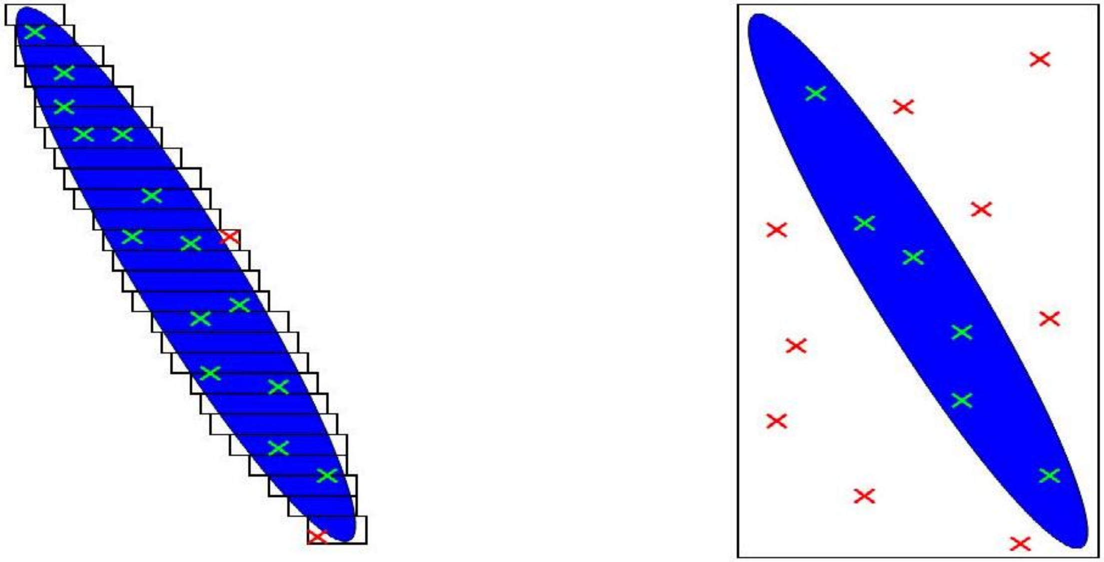


Comparison of Methods

- Almost Invariant Set Methods (GAIO)
  - **Transfer operators on box subdivisions**
  - **Increasing memory demands w/ higher DOF**
- High Order Normal Form Expansion
  - **Compute Transit Tubes directly**
  - **Manipulating expansion becomes involved for $>$ 3 DOF**
- Bounding Box Method
  - **Lifetime Distribution essentially 1D problem**
  - **Scales well to higher DOF systems**
  - **Integration & sampling become bottleneck**

Future Work

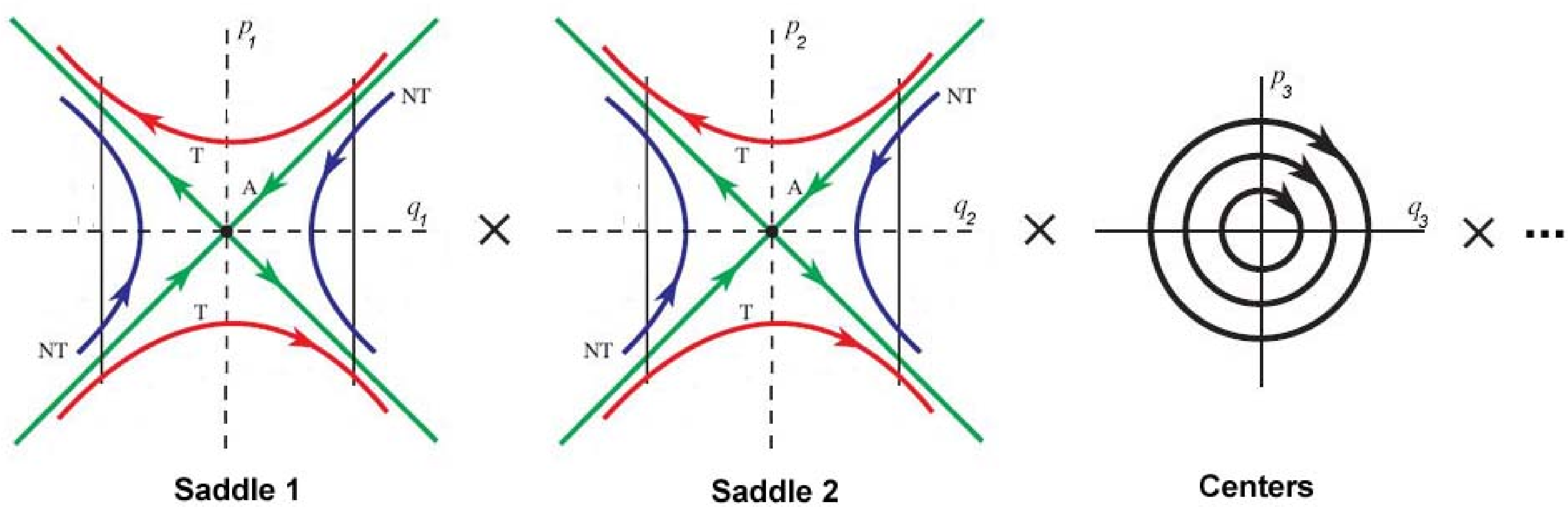
- Tighter Bounding Box



  - **Improvement is greater for higher DOF systems**

- Variational Integrator
  - **Larger time steps, faster runtime**
  - **Computes collisions more accurately**
  - **Bulk of computation is integration**

Rank-2 Saddles



- Reaction coordinate is ambiguous for rank-2 saddle
  - **Multi-channel reactions**
- Transit orbits exist for one or both saddles
- Topology of transit tubes isn't clear
  - **Non-compact intersection with transverse cut**
  - **Makes sampling difficult (or impossible?)**

Conclusions & Open Questions

- Conclusions
  - **Bounding Box Method is very efficient**
  - **Requires minor modification for new systems**
  - **Remains fast for high DOF systems**
- Next Steps
  - **Apply method to higher DOF chemical system**
  - **Obtain experimental verification of method**
- Open Problems
  - **Is there an estimate for how small energy must be for linear dynamics to persist?**
  - **Perron-Frobenius operator (coarse grained reaction coordinate)**
  - **Apply tube dynamics to stochastic models**
  - **Solve Rank-2 sampling problem (non-compact)**

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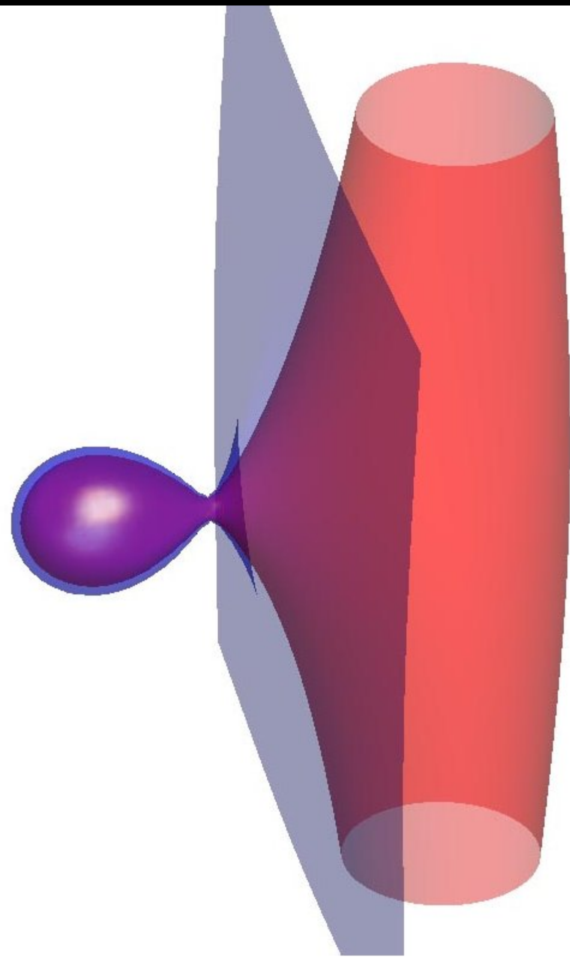
Questions...



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