Application of Tube Dynamics to Non-statistical Reaction Processes

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Acknowledgements

- T. Yanao
- C. Conley, R. McGehee, D. Appleyard
- C. Simó, J. Llibre, R. Martinez
- G. Gómez, A. Jorba, J. Masdemont
- N. De Leon, M. Mehta, R. Topper
- C, Jaffé, T. Uzer, L. Wiesenfeld, S. Wiggins
- R. Berry, T. Komatsuzaki
- M. Dellnitz, O. Junge, K. Grubbits, K. Padberg, B. Thiere

Outline of Presentation

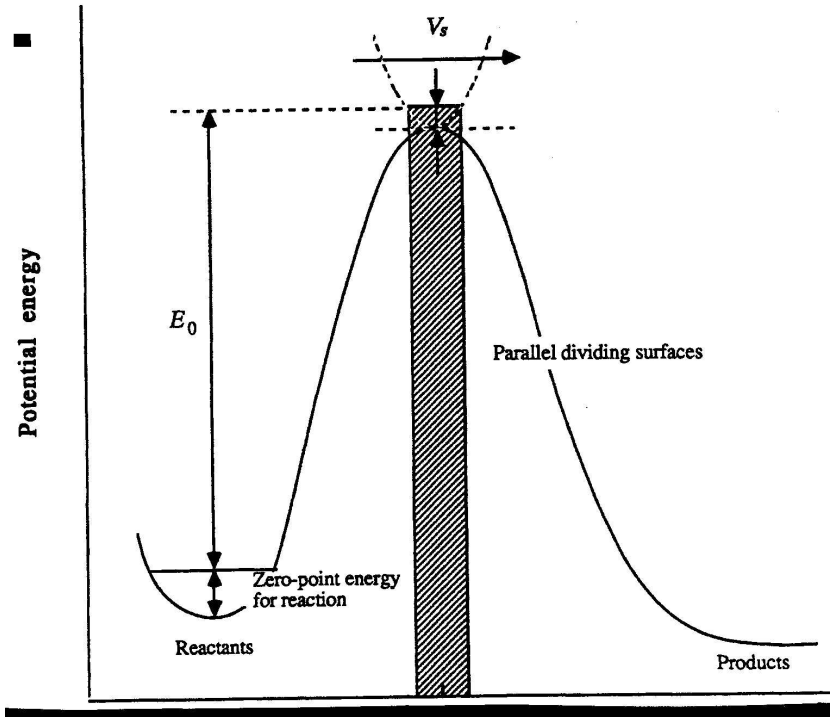
- **Main Focus**
  - merge **tube dynamics** with **Monte Carlo** methods to compute lifetime distributions and reaction rates, in systems that exihibit non-RRKM behavior.
- **Background**, **Motivation**, and **Main Results:**
  - limitations of conventional reaction rate theories.
  - need for accurate rate calculations in higher dof systems.
- **Theoretical** and **Computational Tools**.
  - Tube Dynamics of Rank One Saddles.
  - Monte Carlo methods as Efficient Way for Rate Calculations.
- **Application to a 3 DOF Model System**.
  - Formation and Ionization of Rydberg (Hydrogen) Atom.
  - method may be useful for more dof.
- **Conclusion** and **Ongoing Work**.

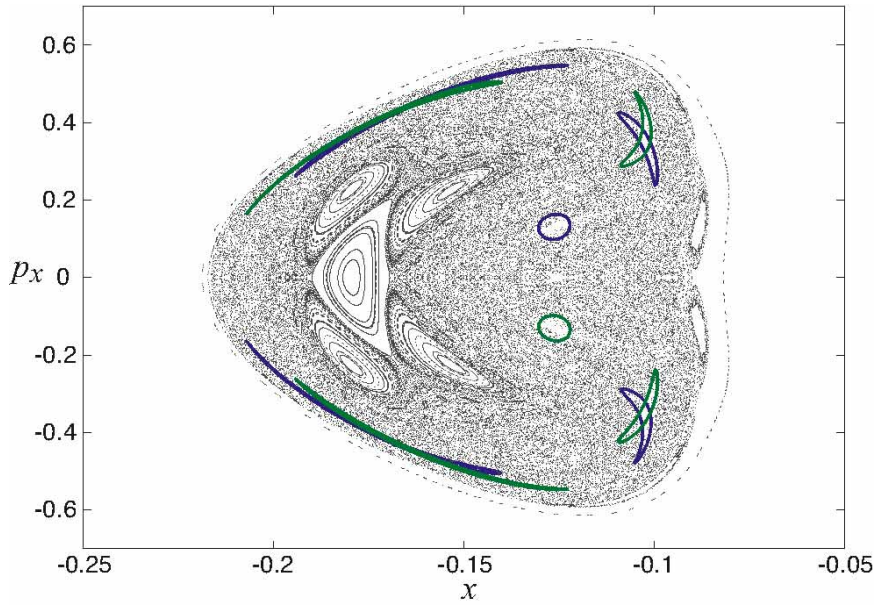
Limitation of Conventional Reaction Rate Theories

- Conventional reaction rate theories (e.g., transition state theory/RRKM) assume **phase space is structureless**.

$$\text{Reaction Rate} = \frac{\text{Flux across Transition State}}{\text{Phase Space Volume of Reactant}}$$

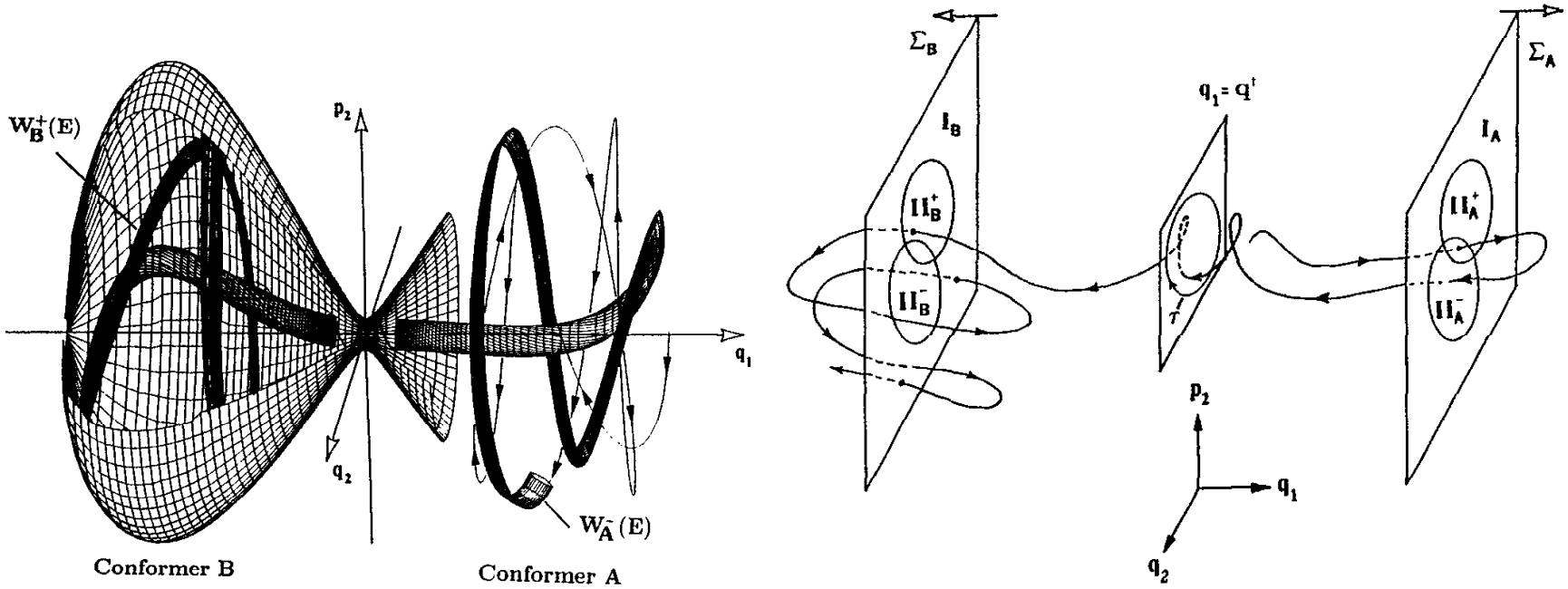
- Rates computed can be **several order** of magnitude off.
- While structureless assumption is useful in many circumstances, in general the phase space is **not structureless**.





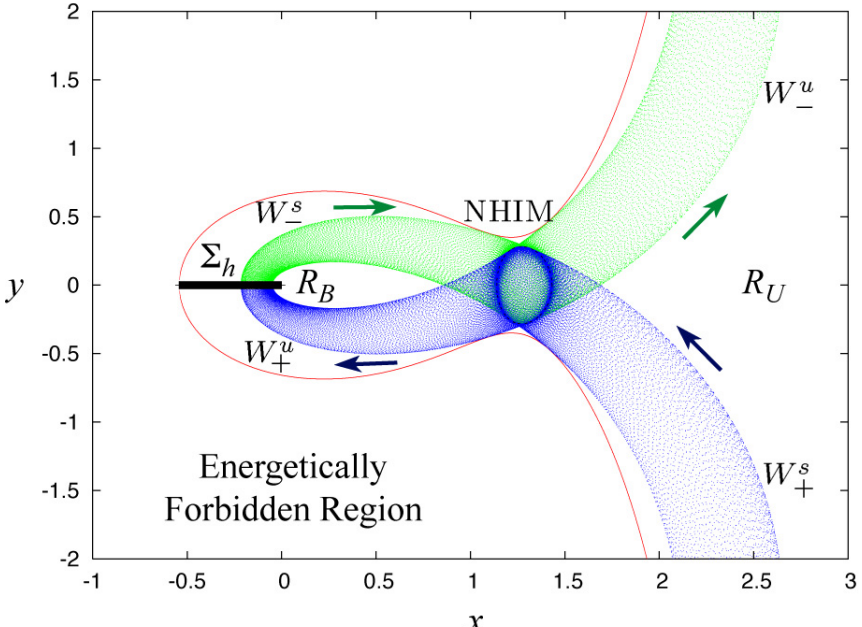
Reaction Island Theory and Theory of Tube Dynamics

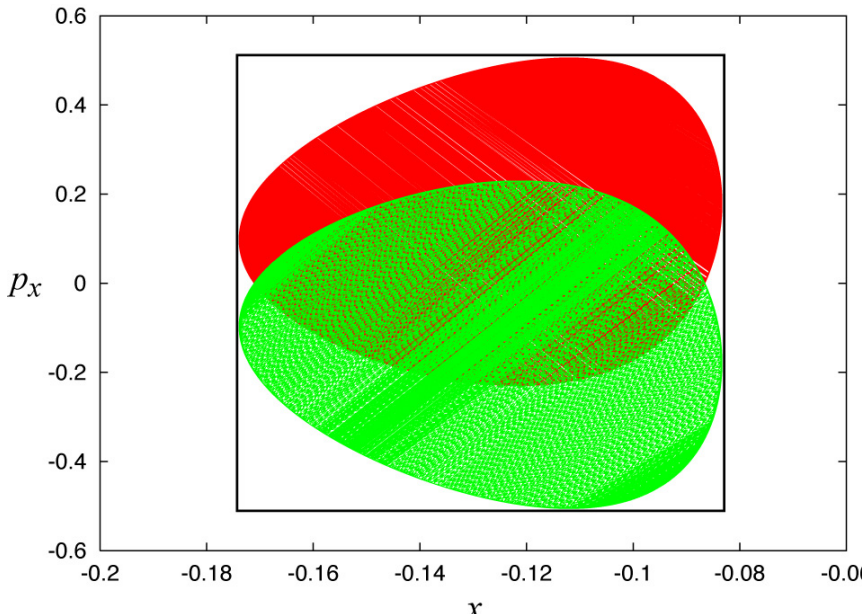
- De Leon et al [1991] extended local study near TS to global one, and used cylindrical manifold for rate calculation in 2dof (**reaction island theory**).
- Koon et al [2000, 2004] developed a global theory of **tube dynamics** in astrodynamical applications in 2 and 3 dof.
- Uzer et al [2002] studied local geometric structure of **rank-one saddle** that regulates reaction in 3+ dof.



Merge Tube Dynamics with Monte Carlo Methods

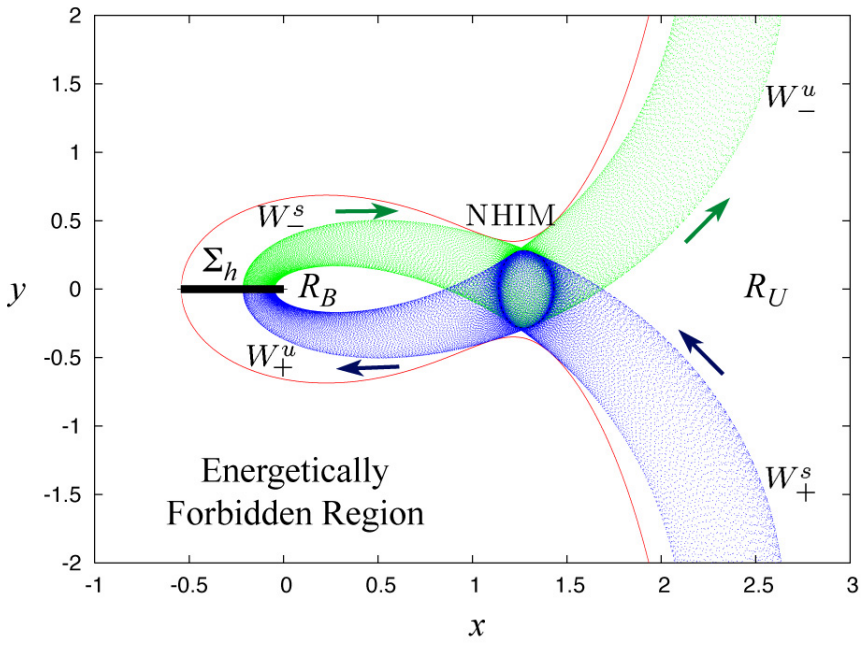
- Need a **comprehensive theory** of chemical reactions and **efficient computational tools** for rate calculations in 3+ dof.
- Current work which merges **tube dynamics** with **Monte Carlo methods** provides initial steps for this program.
  - Use invariant manifold tubes which mediate dynamcial process of reaction as a key theoretical tool.
  - Use Monte Carlo methods to compute high D volumes of tube intersections as a practical algorithm for rate calculation.

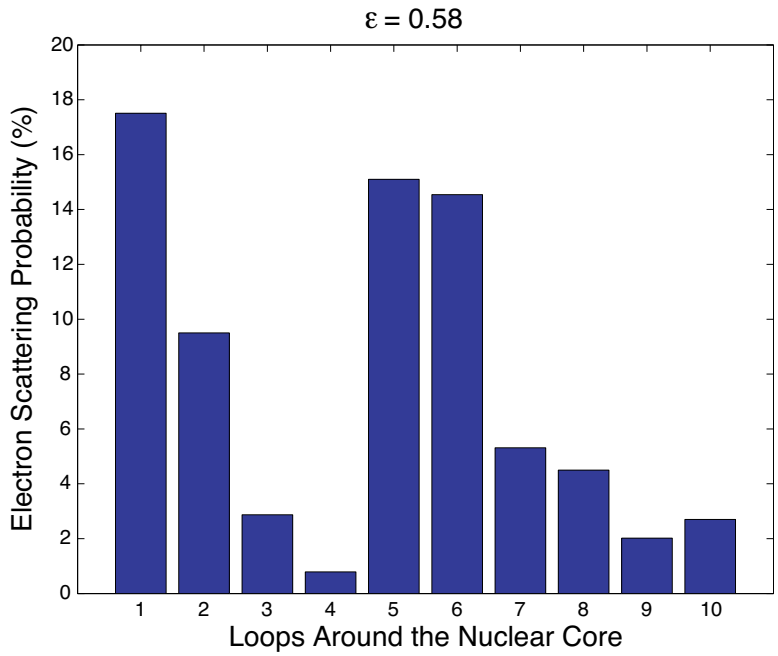




Scattering and Ionization of Rydberg Atom (3 DOF)

- Apply general method to a model problem:
  Scattering and **Ionization** of electrons in Rydberg atoms in crossed electric and magnetic fields.
  - Understand better the **transport mechanism** between large regions of phase space.
  - Obtain accurate **lifetime distribution** and reaction rate that is **non-exponential/non-RRKM**.



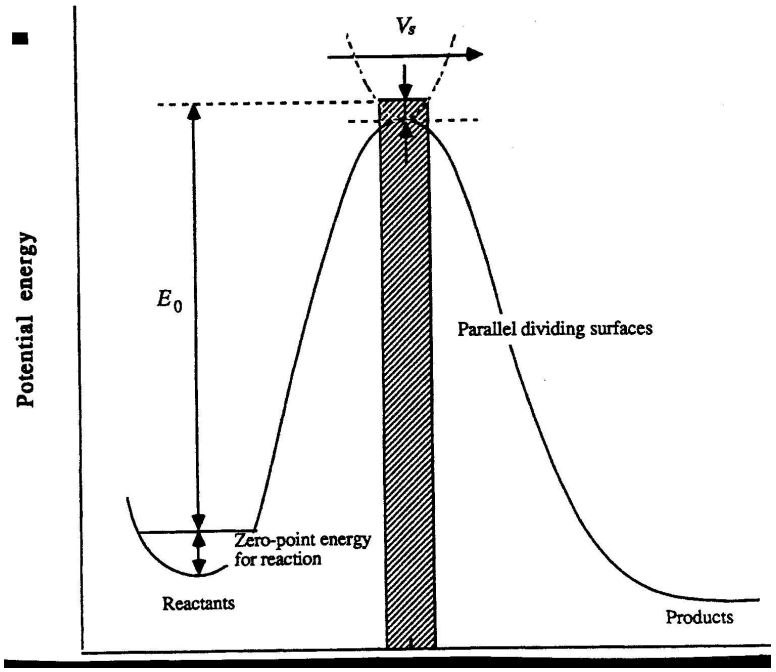


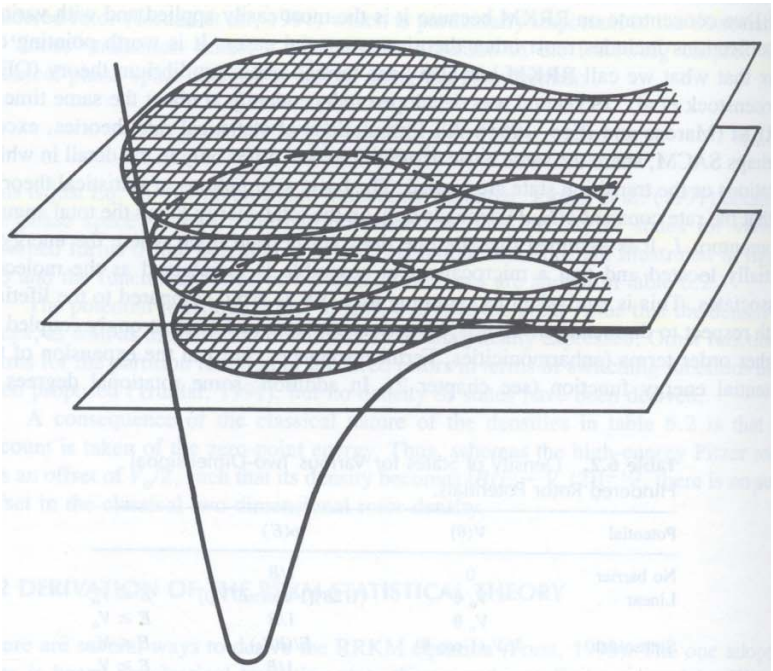
Phase Space, Energy Surface, Realms and Saddles

- Chemical reactions proceed through energy barriers.
- Described in **phase space** where **energy surface** determines **realms** connected by barriers, related to **rank-one saddles**.
- Consider Rydberg atom (3dof, 5D surface in 6D space)

$$H = \frac{1}{2}(p_x^2 + p_y^2 + p_z^2) - \frac{1}{r} + \frac{1}{2}(xp_y - yp_x) + \frac{1}{8}(x^2 + y^2) - \varepsilon x.$$

- 2 realms, 1 bound, 1 unbound.





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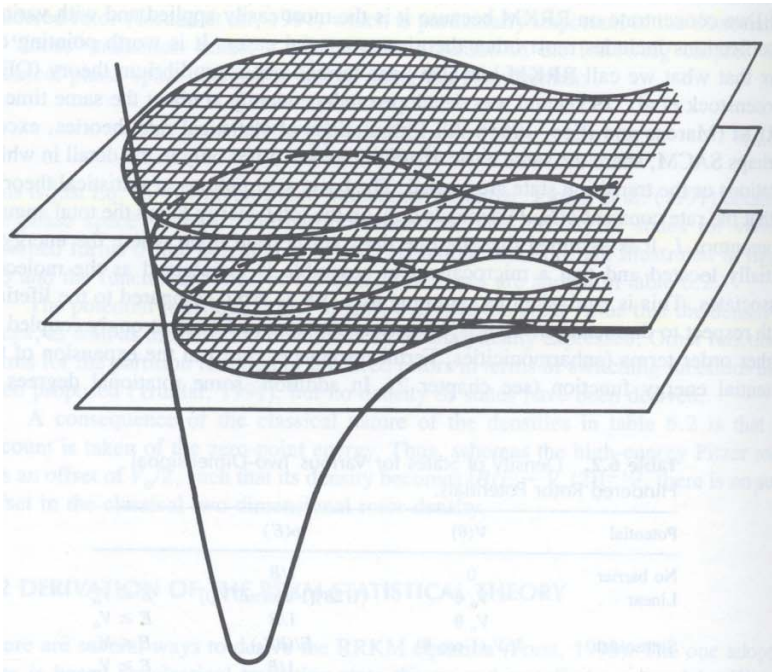
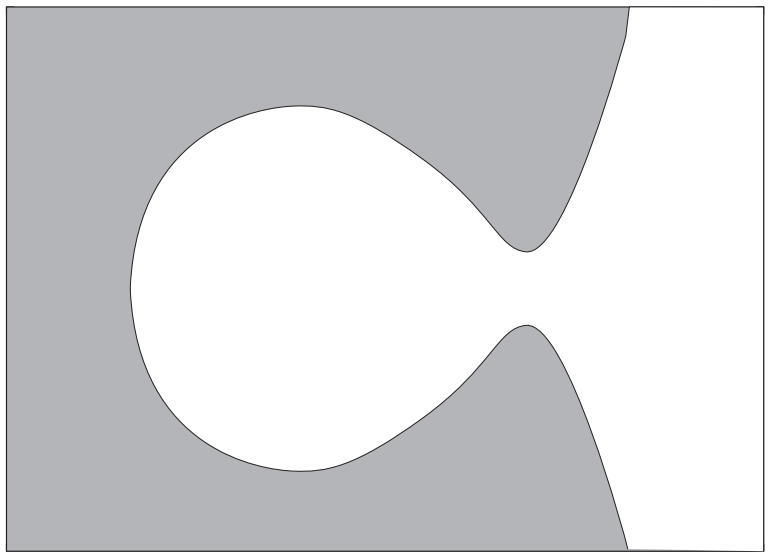
- 2 realms, 1 bound, 1 unbound.
- For energy value above that of a saddle $(\pm\lambda, i\omega_k)$, **bottleneck** opens and reaction becomes possible energetically.
- Figure shows projection of energy surface on xy plane.



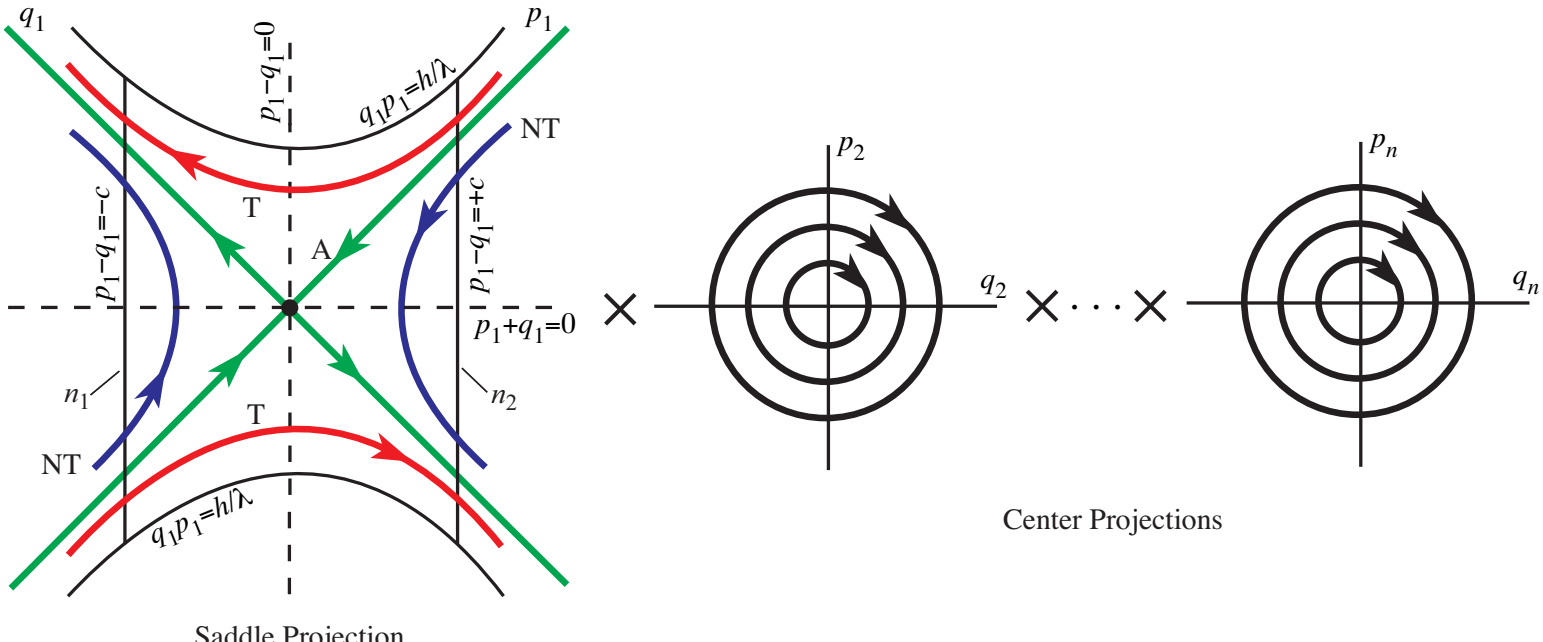


Dynamics Near A Rank-One Saddle

- Quadratic normal form at a **rank-1 saddle** $(\pm\lambda, i\omega_k)$

$$H_2(q_1, p_1, \ldots, q_n, p_n) = \lambda q_1 p_1 + \sum_{k=2}^{n} \frac{\omega_k}{2}(q_k^2 + p_k^2),$$

- 4 types of orbits:
  - **bound orbits**: S^{2n-3}, S^3 (**NHIM**)
  - **asympototic orbits** to **NHIM** (stable/unstable manifolds)
  - **reacting** and **non-reacting orbits**

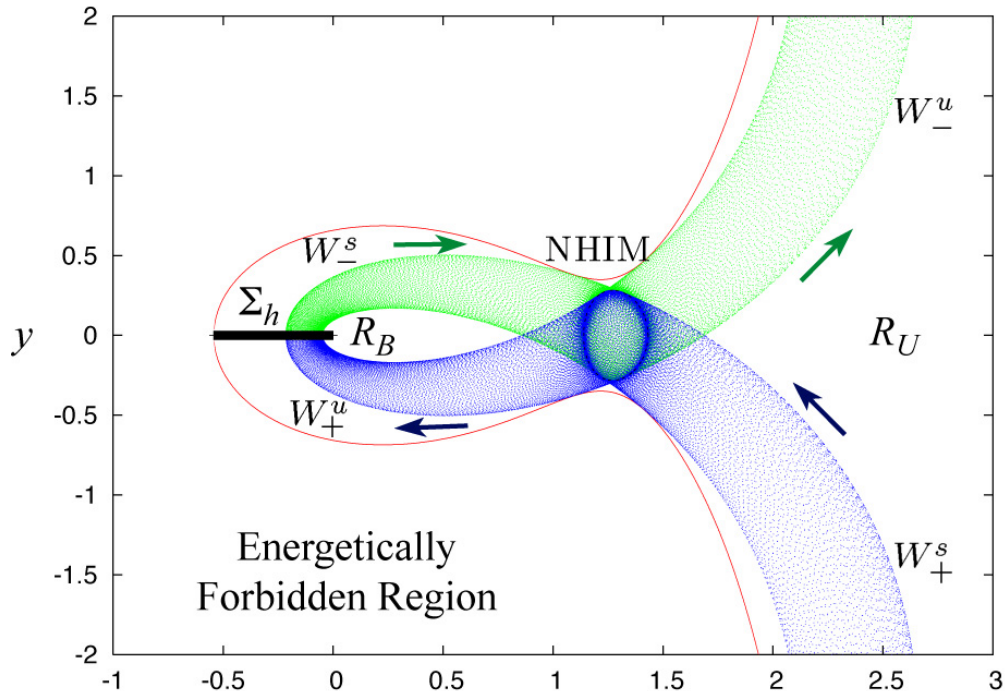


Computation of NHIM and Its Invariant Manifolds

- **Lie Transform** put Rydberg Hamiltonian into **normal form**

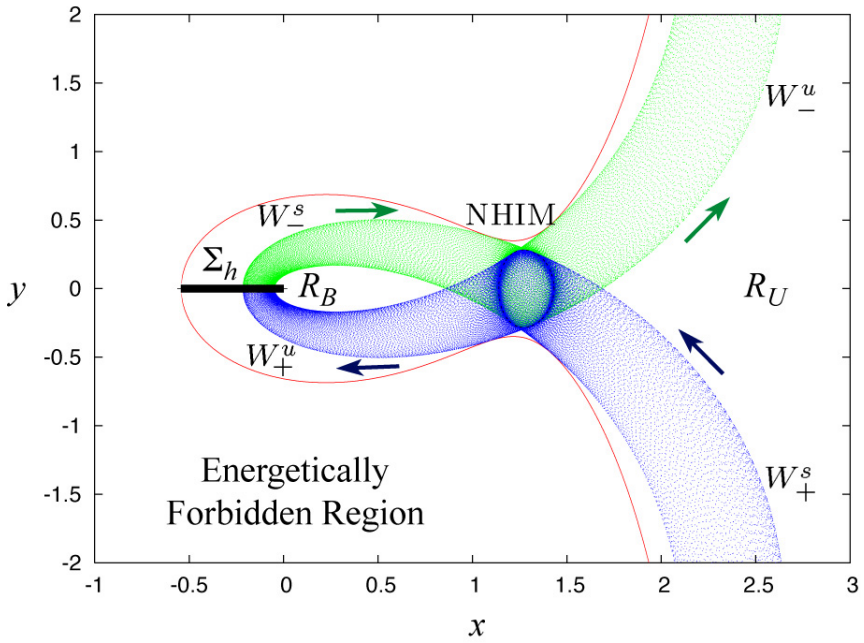
$$\bar{H}_N = \lambda q_1 p_1 + \frac{\omega_2}{2}(q_2^2+p_2^2) + \frac{\omega_3}{2}(q_3^2+p_3^2) + \sum_{n=3}^{N} H_n(q_1 p_1, q_2, p_2, q_3, p_3).$$

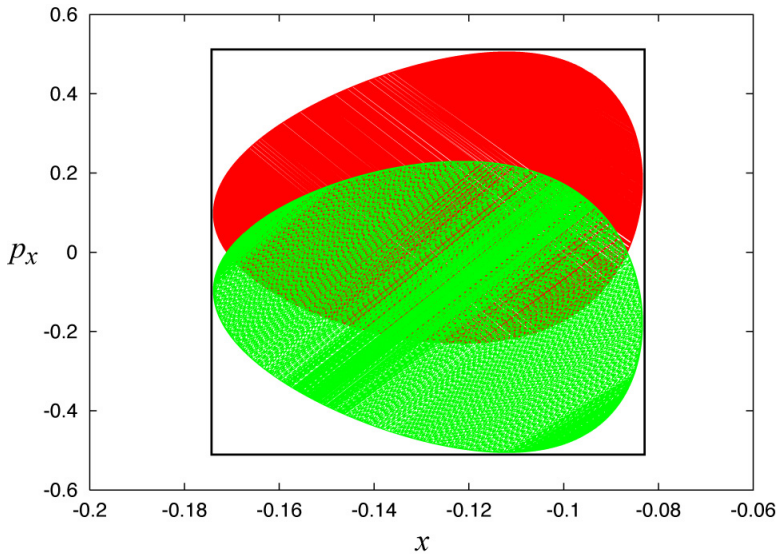
- Set $q_1 = p_1 = 0$, obtain **3D NHIM** (S^3).
- Set $q_1 = 0$ ($p_1 = 0$), integrate Hamiltonian equations, obtain global **4D stable** (**unstable**) **manifold**.



Invariant Manifold Tube as Separatrix

- Asymptotic orbits form **4D invariant manifold tubes** in **5D energy surface**.
- They separate reacting and non-reacting orbits:
  - **Reacting orbits** are those inside the tubes.
  - **Non-reacting orbits** are those outside the tubes.
- **Tubes** control transport between bound and unbound region, and chemical reaction rates and scattering lifetime distributions.

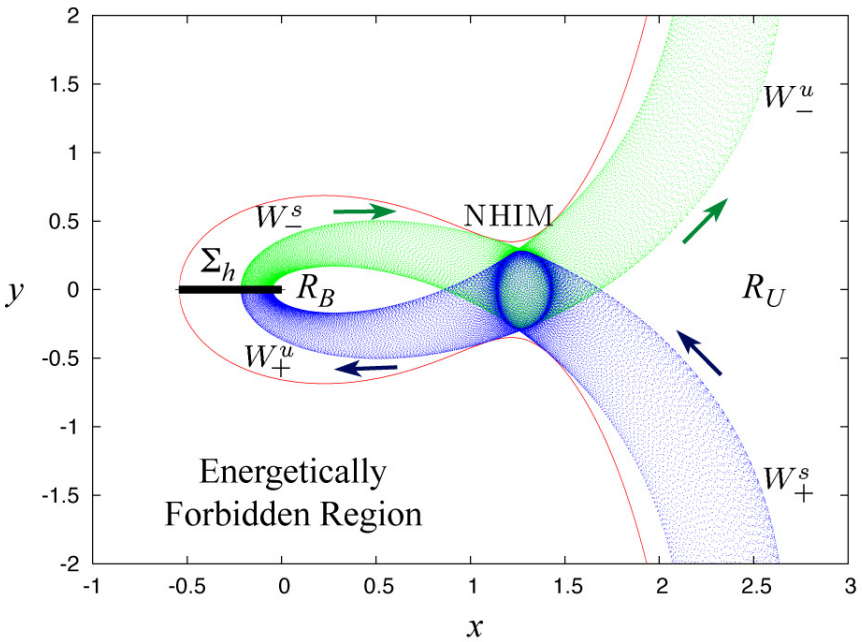


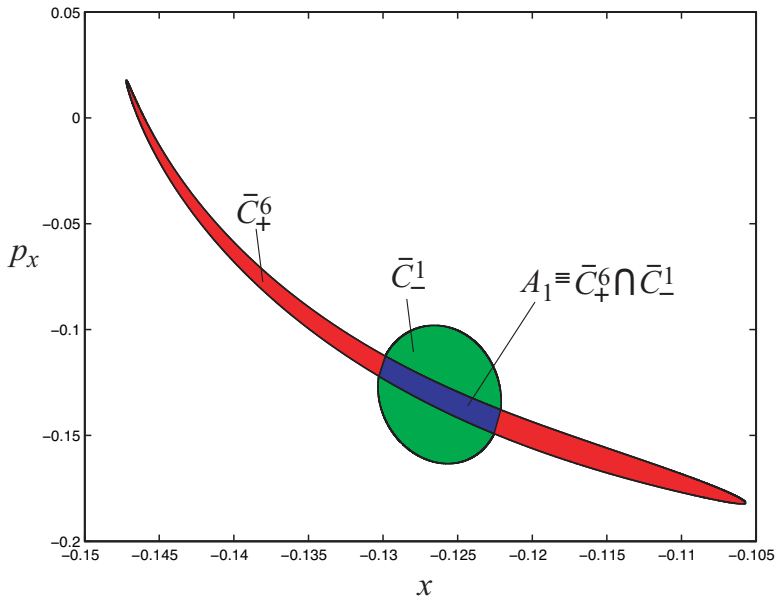


Global Transport and Poincaré Cuts

- Choose appropriate 4D **Poincaré sections** Σ_h
  - $W^s_+ \cup W^u_+$ constitute **capture reaction path** from R_U to R_B, first piercing Σ_h in **entrance** $\bar{C}^1_+$.
  - $W^s_- \cup W^u_-$ constitute **escape reaction path** from R_B to R_U passing through **exit** $\bar{C}^1_-$.
- **Reaction** is determined by intersection of images and pre-images

$$f^{j-1}(\bar{C}^1_+) \cap f^{-(k-1)}(\bar{C}^1_-) = f^{m-1}(\bar{C}^1_+) \cap \bar{C}^1_- = \bar{C}^m_+ \cap \bar{C}^1_-$$

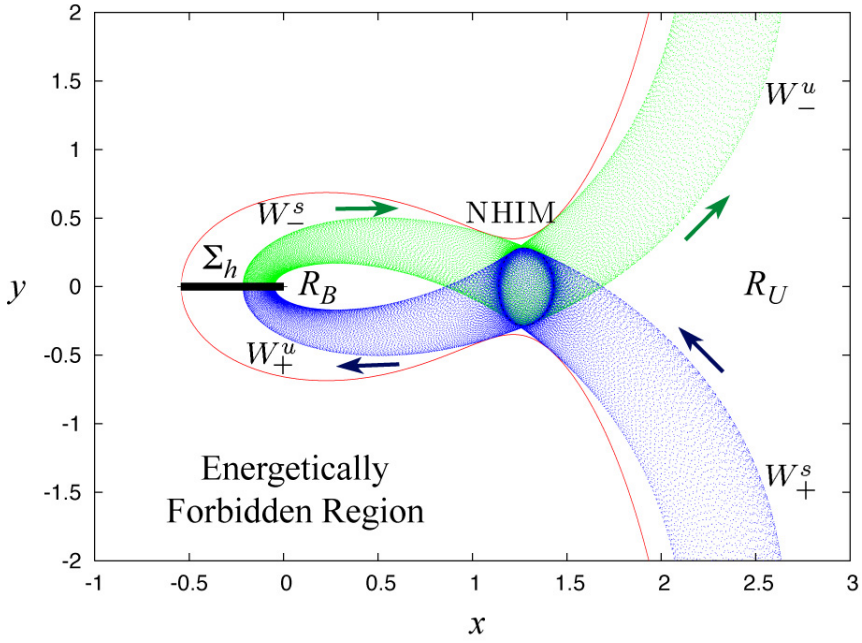


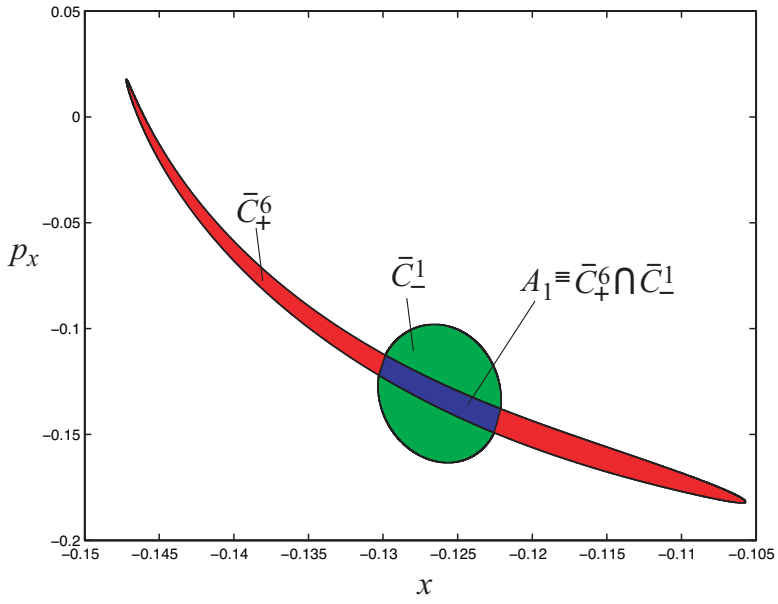


Computation of Lifetime Distribution Spectrum

- Evaluations of intersection volumes of **entrance** and its **images** with **exit** provide scattering lifetime distribution and reaction rates.
- Assume an uniform distribution of incoming **reactants** on $\bar{C}_+^1$, then fraction of **products** escaping after executing m loops around bound region is

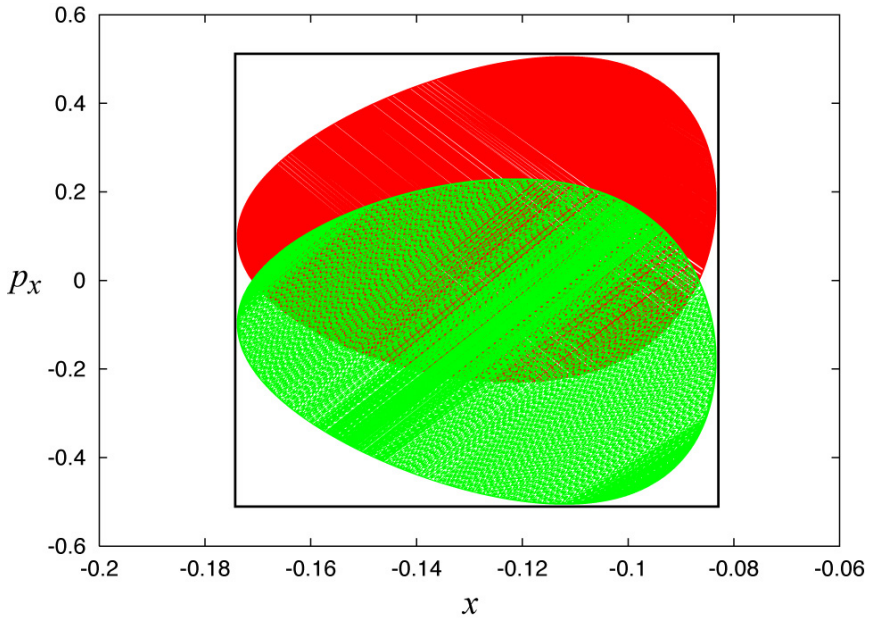
$$\frac{V(\bar{C}_+^m \cap \bar{C}_-^1)}{V(\bar{C}_+^1)}.$$

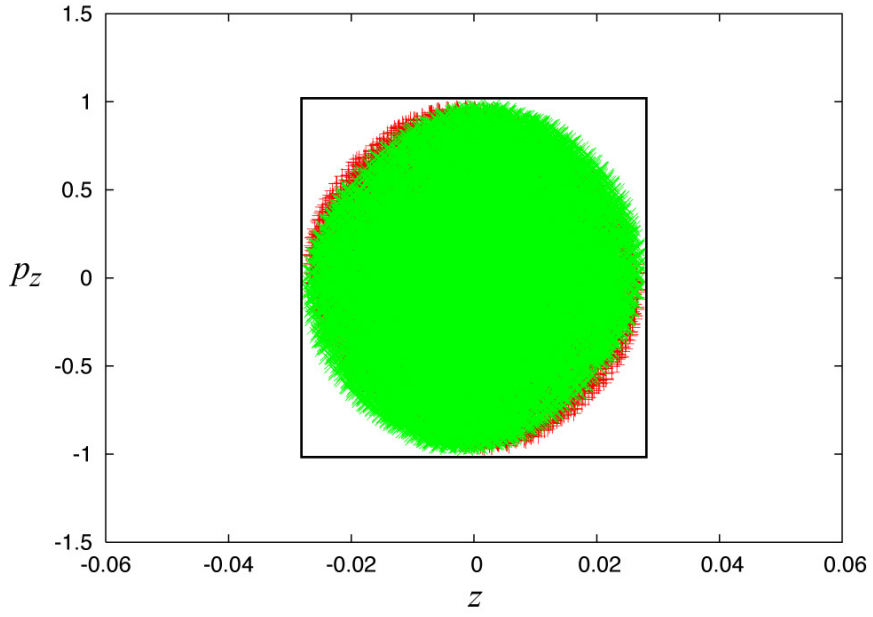




Volume Computation via Monte Carlo Methods

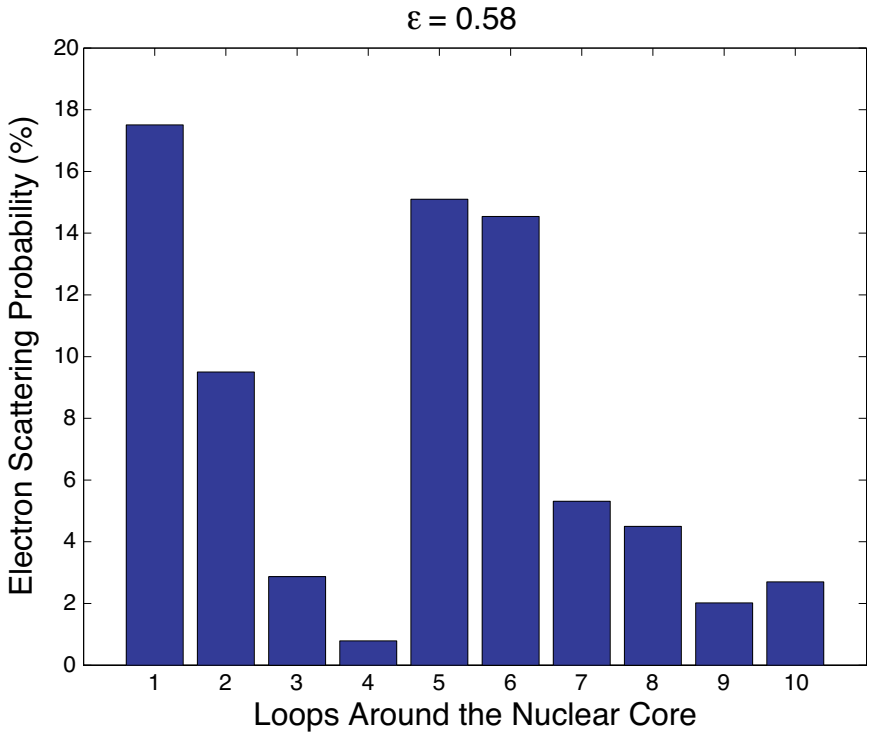
- For high DOF, direct computation of intersection volumes with a numerical quadrature is very difficult.
- Use **Monte Carlo methods** to compute numerically an approximate value of 4D volume (e.g., $V(\bar{C}^1_+ \cap \bar{C}^1_-)/V(\bar{C}^1_+)$)
  - Choose bounding box containing **Poincaré cuts** of stable and unstable manifolds.
  - Obtain an oracle distinguishing whether random chosen points inside this box belong to target object.

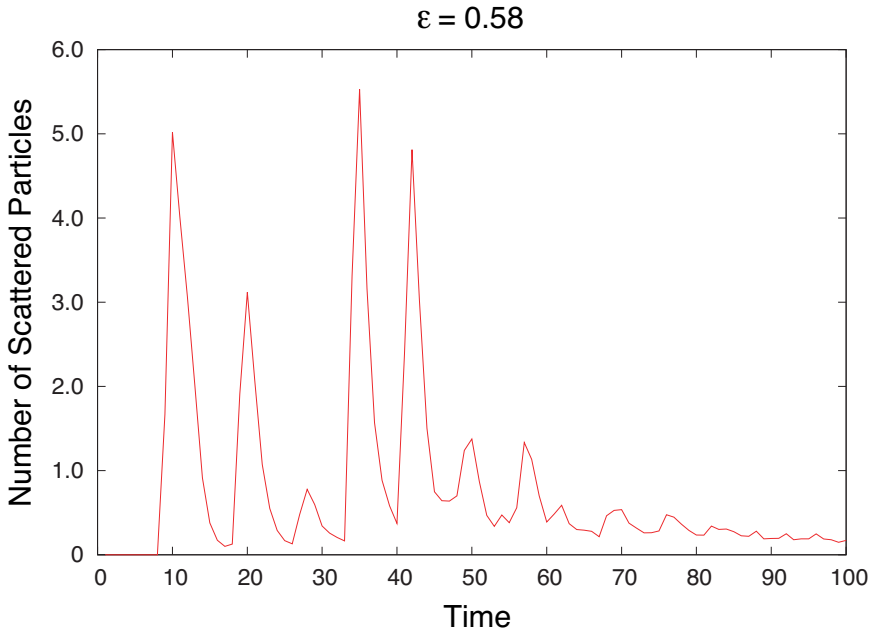




Scattering Profile is Structured and Non-RRKM

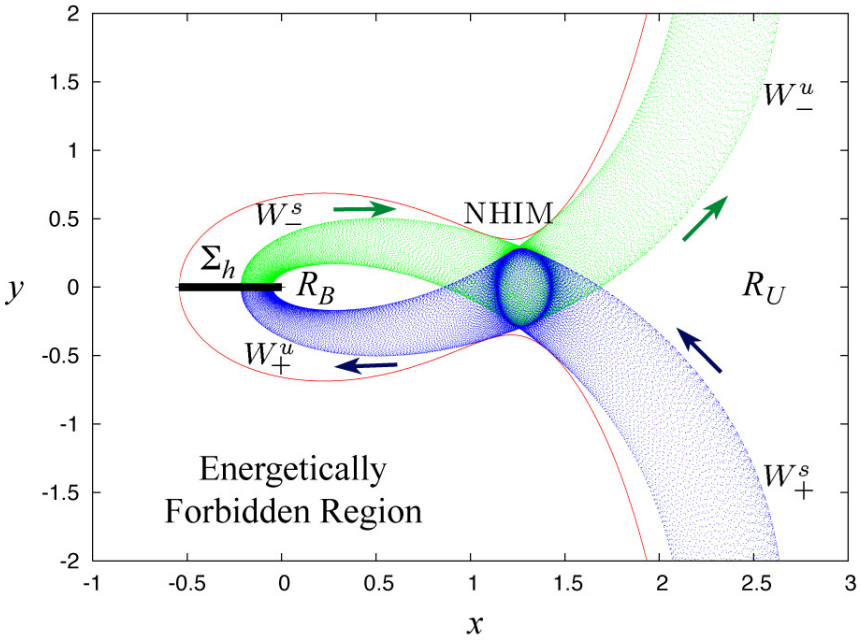
- **Scattering profile**, % of reactants escaping from bound state as a function of loops, is **structured** (not an exponential decay).
- Its temporal/**lifetime distribution** is similar to loop profile.
- Results stress: phase space is not structureless.
  Need to consider **tube dynamics** in computing reaction rates.

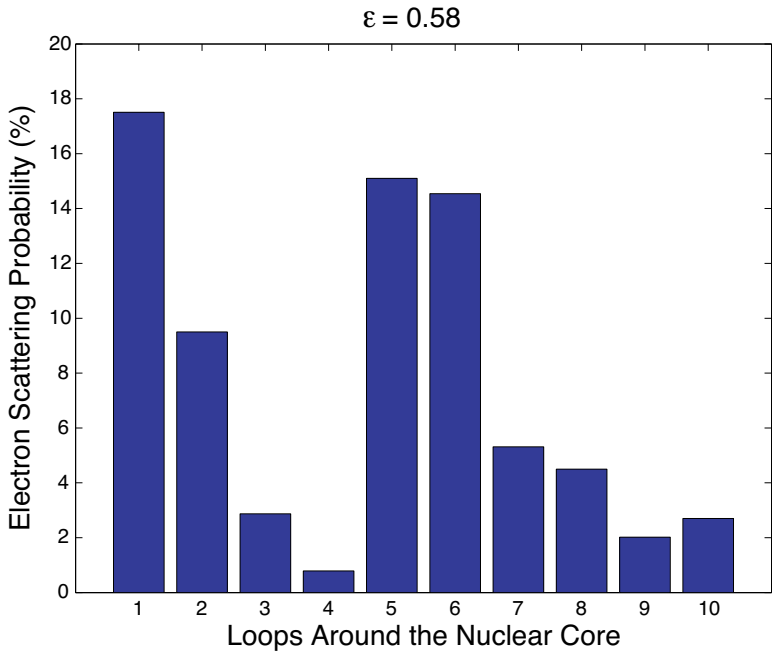




Conclusion

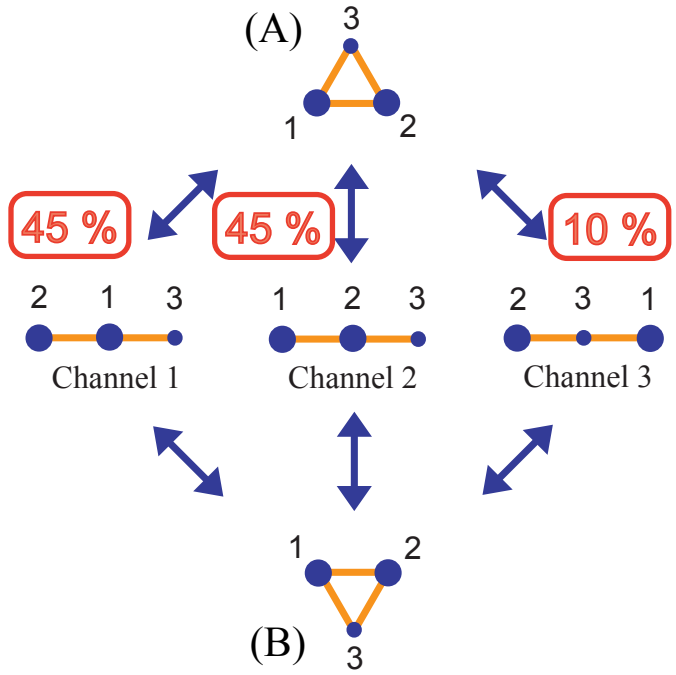
- Merge **tube dynamics** with **Monte Carlo** methods to compute lifetime distributions and rates, in systems that exihibit non-RRKM behavior.
- Apply to a 3 DOF Model System: Formation and Ionization of Rydberg Atom. But methodology may be useful for **more dof**.





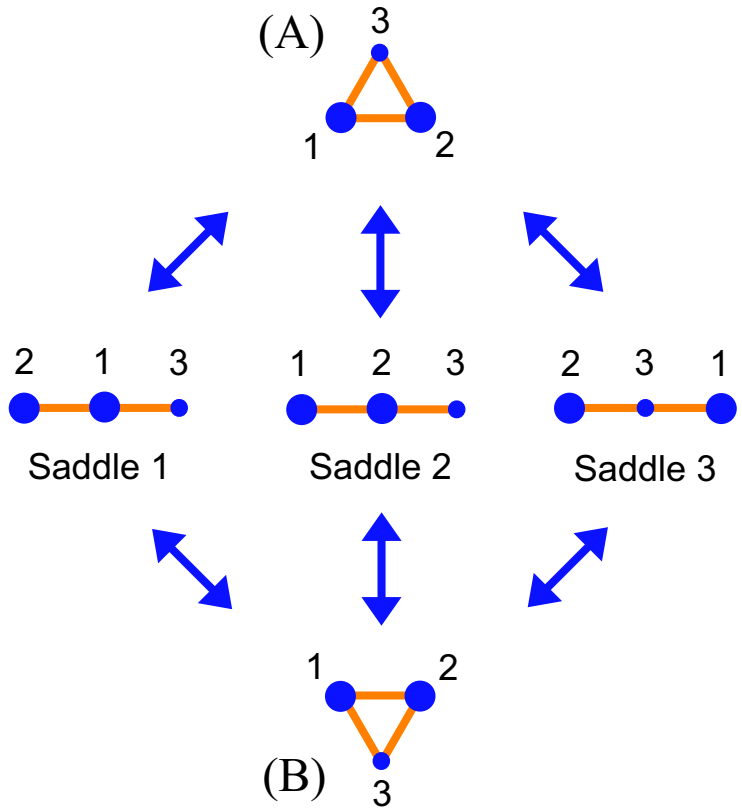
Ongoing Work

- Apply to systems with **rank one saddles**:
  - **isomerization** of polyatomic molecules, bimolecular reactions.
- Isomer. of triatomic cluster with **unequal masses**:
  2 triangular **isomers** connected by 3 collinear **rank one saddles**.
- Model constructed by **T. Yanao** to study
  importance of **mass effect** on **branching ratios**.
  Prototype for studying isotope effect.



Ongoing Work

- For multi-channel reactions (isomerization of polyatomic molecules), need to study **heteroclinic structures**.
- Choice of a suitable set of **Poicaré sections** will be important.
- Computation of volumes of different intersections via **Monte Carlo** methods still will be key in computing reaction rates.



Discussion

- View as a continuation of De Leon et al. (1991),
  solely for elementary reactions; for systems with rank one saddles.
- Jaffé, Uzer, and Farrelly (1999) suggests
  a classical treatment is appropriate for Rydberg atom.
- Believe a more careful averaging over energy level is needed for comparision with experiements.
  Possible to experimentally excite a Rydberg atom to a given level of energy (Held, Schlichter, Raithel and Walther [1998])