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# **Quantum Mechanics Without Wavefunctions**

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Université de Montpellier et  
Centre Nationale de la Recherche Scientifique*



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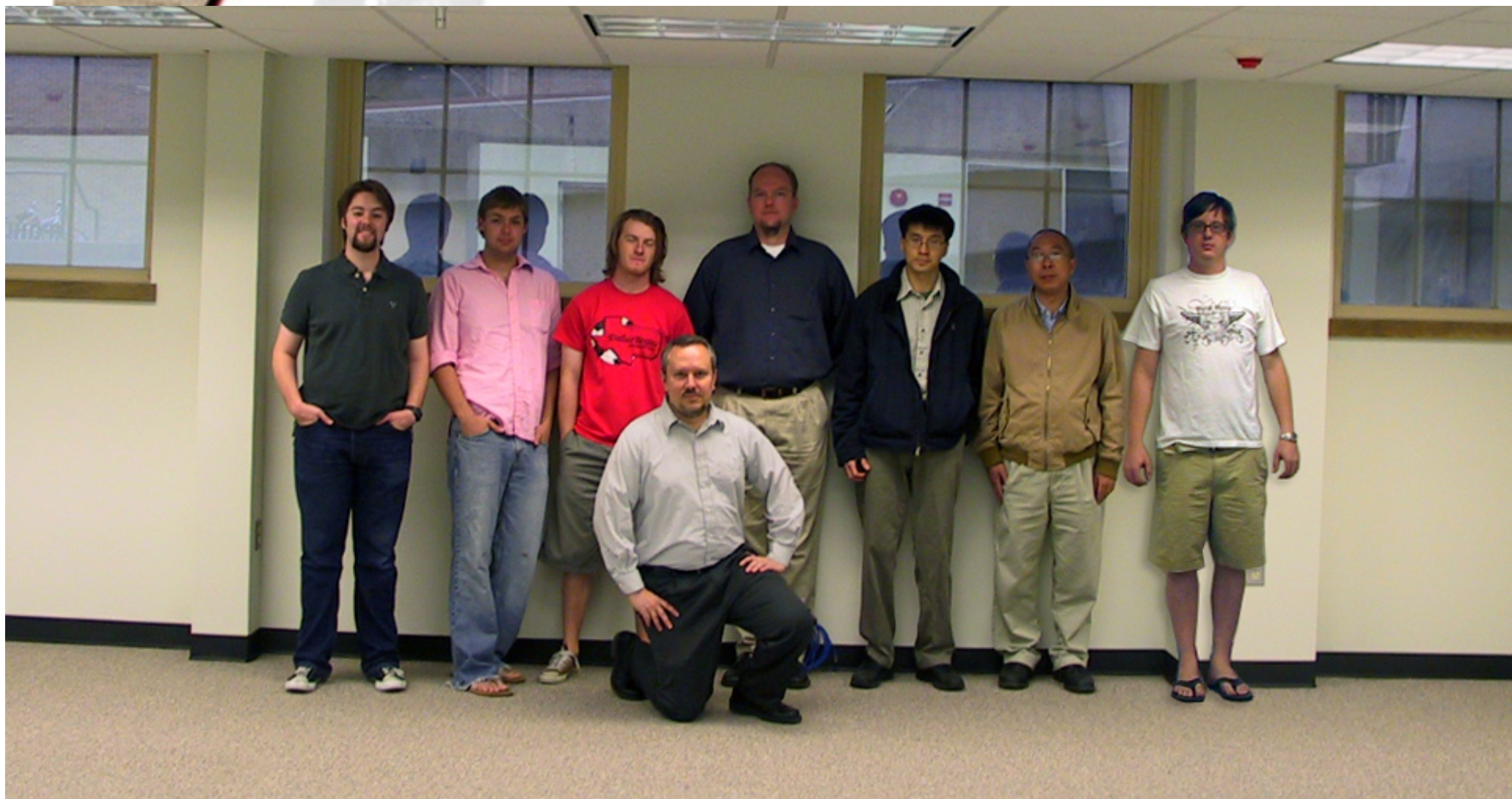
## Texas



Lubbock, Texas



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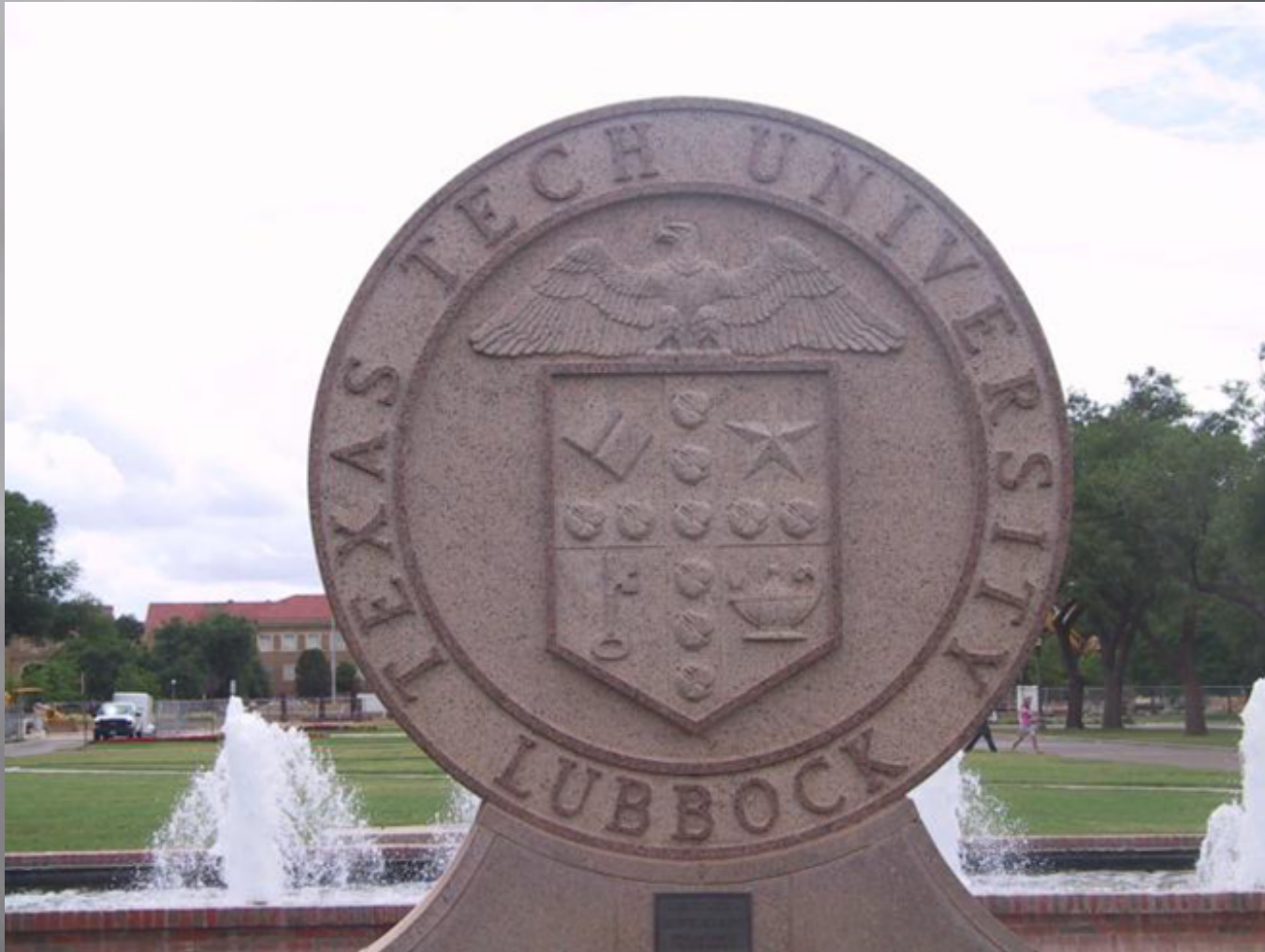






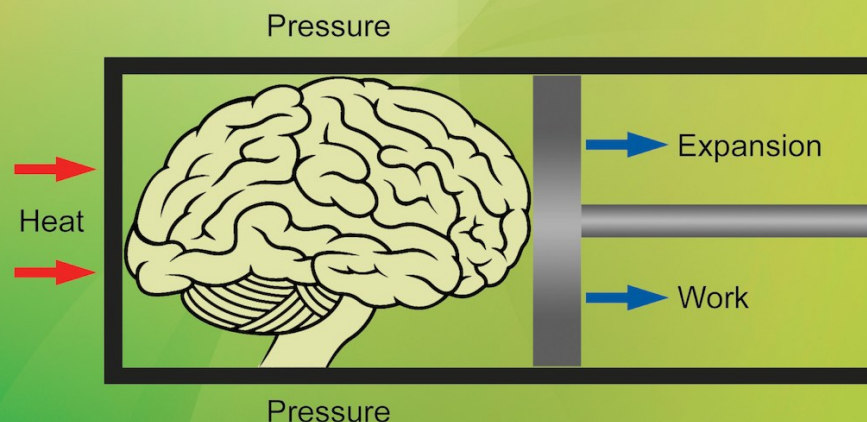


# Texas Tech University



Bill Poirier

# A Conceptual Guide to THERMODYNAMICS



WILEY

*"Poirier presents a concise and refreshingly transparent definition of entropy...perfectly suited for undergraduate students...**I will be adopting this next year**"*

*"What we have is a tremendously interesting take on entropy. It is fully interdisciplinary, drawing from information theory very nicely...Just great."*

*"... natural gift for analysing and expressing the essence of mathematical and scientific concepts."*

*"...using the molecular, statistical mechanical approach, but in a very simple way that will not repulse students...**the book will sell.**"*

*"I found the book to be quite excellent...finally explained concepts I have struggled with since my undergraduate days."*

*"I would have loved to have had this...It would also be helpful for instructors...writing their thermo lectures (and stat mech) for the first time."*

*"This book concept is **unique** in the field of thermodynamics."*

*"...appendices...add a certain dimension of "fun"*

Recommended by the Amer. Lib. Assoc.:

[www.conceptualthermo.com](http://www.conceptualthermo.com)





# Introduction

- Research Interest:
  - *“exact”* (accurate) quantum dynamics of molecular systems.
  - nuclear part of Born-Oppenheimer approximation.
- Research Scope:
  - quantum effects treated “exactly”.
  - *“large”* systems (so far up to benzene = 30D).
- What We Actually Calculate:
  - *“many”* vibrational states (energy levels & wavefunctions).
  - tunneling splittings and migration dynamics.
  - scattering cross sections and reaction rates.
  - quantum capture probabilities.
  - resonance lifetimes and widths.



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**Warning:** Exact quantum dynamics calculations are *extremely* challenging...

This is due to the “Curse of Dimensionality” or “Exponential Scaling Problem”.

All researchers in this area must somehow overcome, or at least deal with, this curse.

Our group is pursuing several strategies, including quantum trajectory methods based on “quantum mechanics without wavefunctions”.

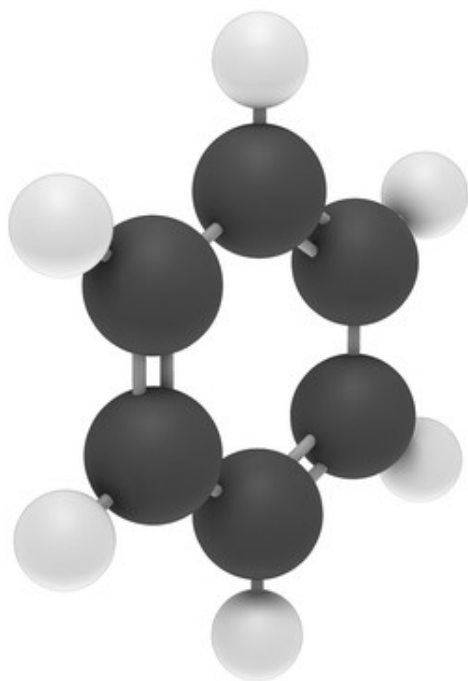




## Traditional Basis Set Methods

- Basis Set Methods are Used in Quantum Dynamics
  - Hamiltonian represented using finite set of  $N$  basis functions.
  - Leads to  $N \times N$  Hamiltonian matrix.
- Traditional (direct-product) basis sets:
  - $N$  grows exponentially with system dimensionality,  $d$ .
  - Calculation becomes intractable at large  $d$ .
- Computing vibrational states, phonons, excitons, etc. (energy levels & wavefunctions):
  - *number*  $K$  of dynamically relevant states *also* grows very rapidly with  $d$ .

# 250,000 Quantum States of Benzene (30D)

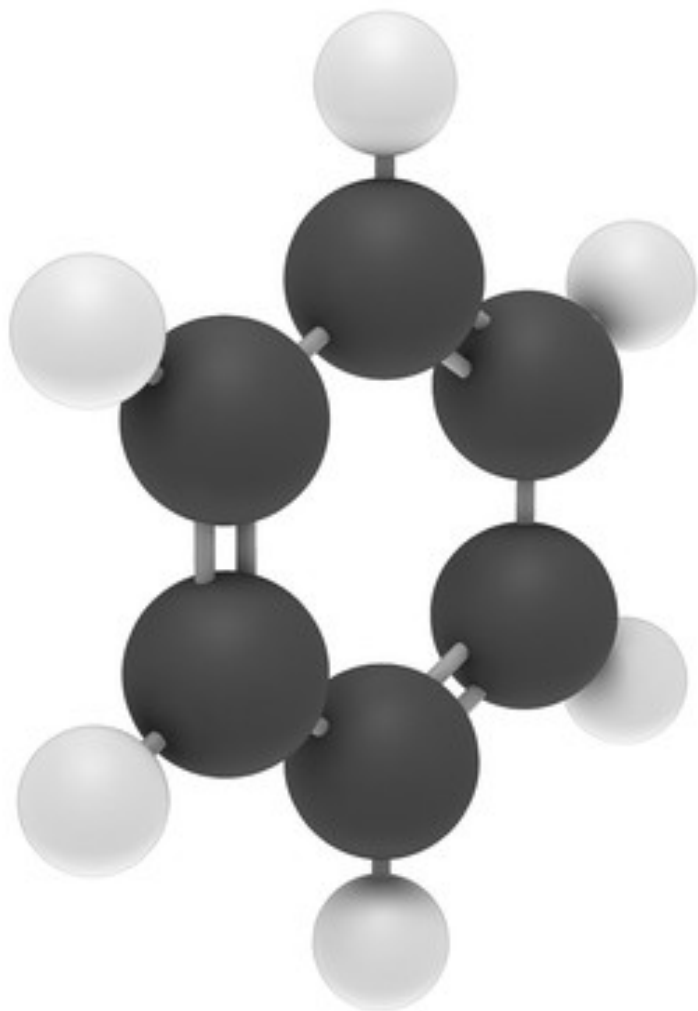


State (A1g)	State (Full List)	Eigenvalue N = 5276536	Error (cm <sup>-1</sup> )
1	3	614.772454	0.162
2	7	809.6288557	0.062
3	8	810.8874752	0.600
4	12	997.6635898	0.035
5	24	1112.1837	0.186
6	28	1195.480415	0.080
7	34	1226.890965	0.105
8	35	1226.896004	0.4396
9	49	1393.025453	0.469
10	51	1407.968252	0.274
30	163	1817.001	0.819
100	664	2389.344	0.500
200	2083	2716.141	3.186
1000	7465	3588.011	1.968
2000	23161	3947.823	3.806
10000	77564	4909.8180	2.918
20000	249101	5509.12173	1.120



# 30 Vibrational Modes of Benzene

1,000,000 Quantum Vibrational States of Benzene



v1 = 993;	v16 = 674;
v2 = 3074;	v17 = 1010;
v3 = 1350;	v18 = 3057;
v4 = 707;	v19 = 1309;
v5 = 990;	v20 = 1150;
v6 = 608;	v21 = 398;
v7 = 608;	v22 = 398;
v8 = 3057;	v23 = 967;
v9 = 3057;	v24 = 967;
v10 = 1601;	v25 = 1038;
v11 = 1601;	v26 = 1038;
v12 = 1178;	v27 = 1484;
v13 = 1178;	v28 = 1484;
v14 = 847;	v29 = 3047;
v15 = 847;	v30 = 3047;

# Tunneling Splittings and Migration Dynamics:

## Exact quantum dynamical treatment of hydrogen-material interactions

(5,5)SWNT-(H)<sub>n</sub>

Amber Allen

Stefan Estreicher

Jason McAfee

Bill Poirier

Fe(H)<sub>2</sub>(H<sub>2</sub>)(PEtPh<sub>2</sub>)<sub>3</sub>

Adelia Aquino

*Juergen Eckert\**

Megan Gonzalez

Reed Niemann

Bill Poirier

*\*MOFs also of interest:*

Introduced e.g. by J. Eckert and coworkers in *Science* **300**, 1127 (2003)  
(over 2500 citations)



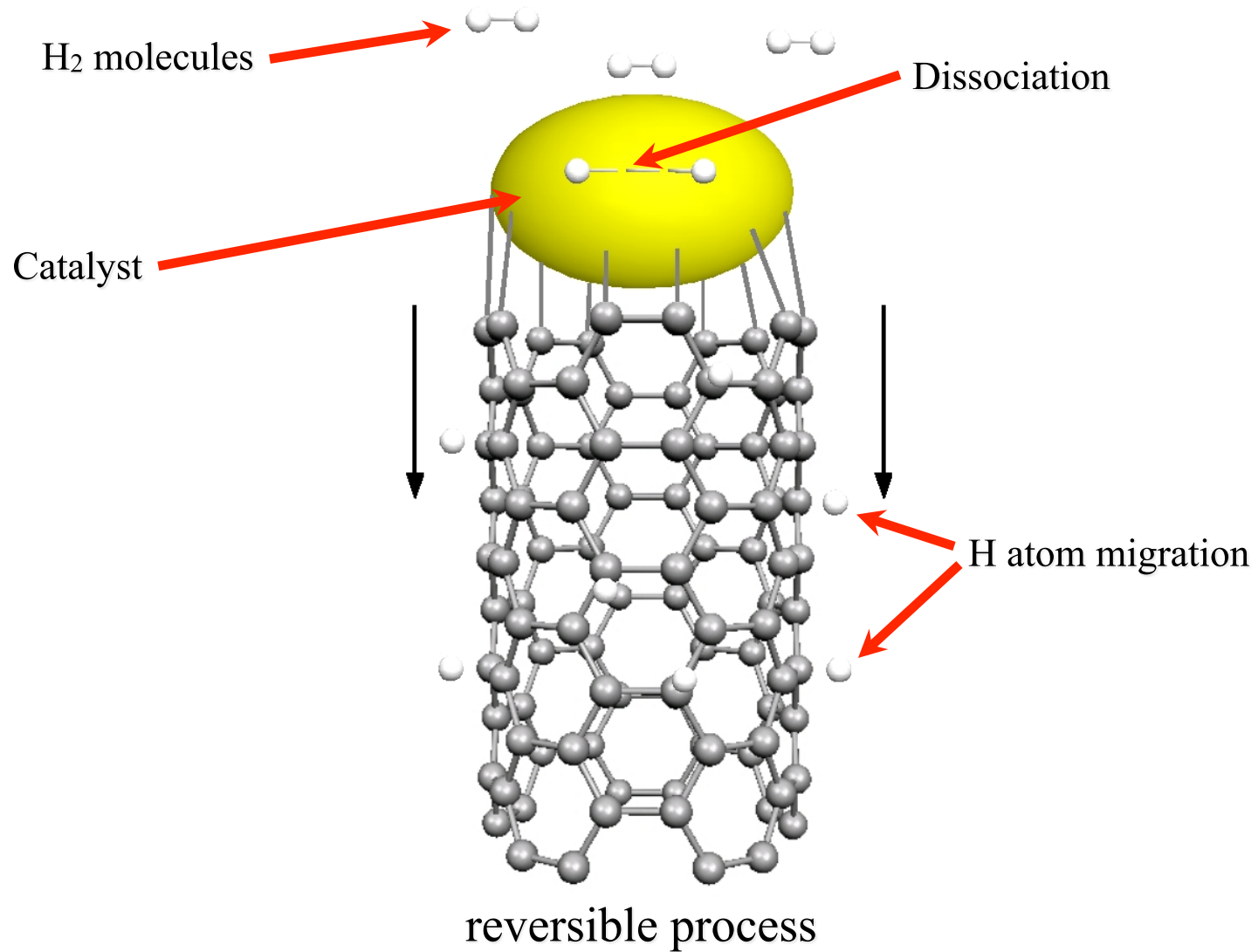


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## Goals and Motivation

- Evaluate CNTs in inorganic compounds as hydrogen storage materials.
- Use **accurate quantum methods** to obtain fundamental dynamical understanding of hydrogen-material interactions, including tunneling.
- Help develop a general language, methodology, framework, etc. for describing such interactions.

# “Spillover” Catalysis





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# Hydrogen Storage with SWNTs via Spillover Mechanism

## Previously Unanswered Questions

- Overall adsorption energetics:
  - energy gap much too large.
- Reversibility
  - H<sub>2</sub> formation and dissociation does not occur.
- Large migration rates at low T and P
  - experimental rates exceed classical diffusion rates by orders of magnitude.



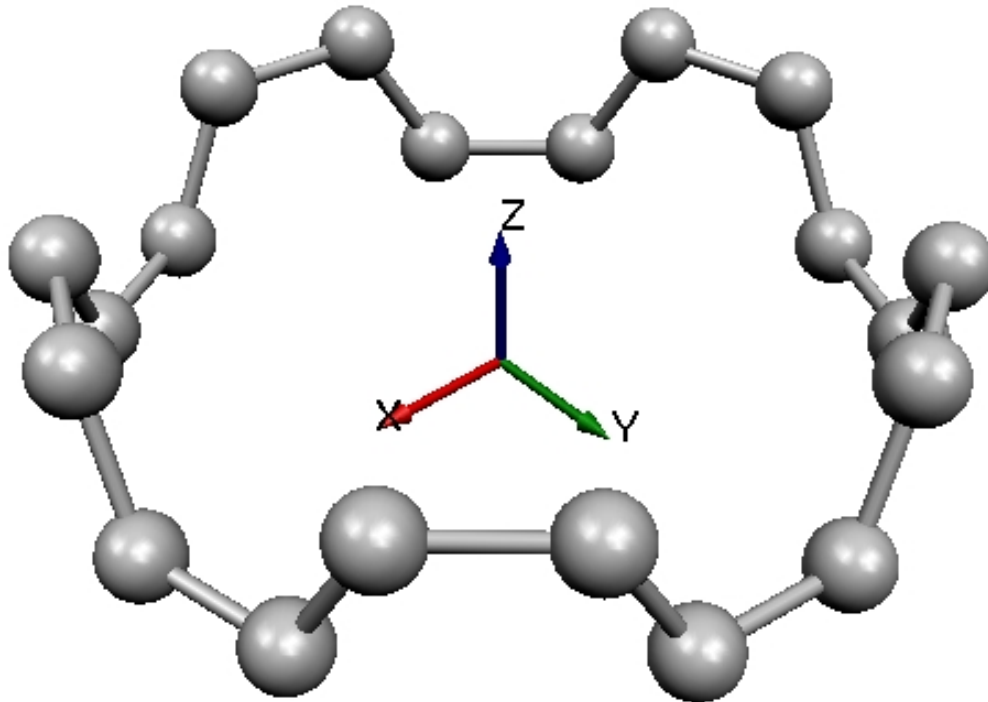


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## Project Overview

- DFT calculations of (5,5) SWNT–H system  
periodic, spin polarized  
supercells containing 3-5 unit cells  
no substrate relaxation or phonon interactions
- Fitting a 3D global analytic PES for H dof's.
- Quantum dynamics of all bound rovibrational states (primarily chemisorbed).
- Calculation of quantum migration rates
- Beyond single adsorbates

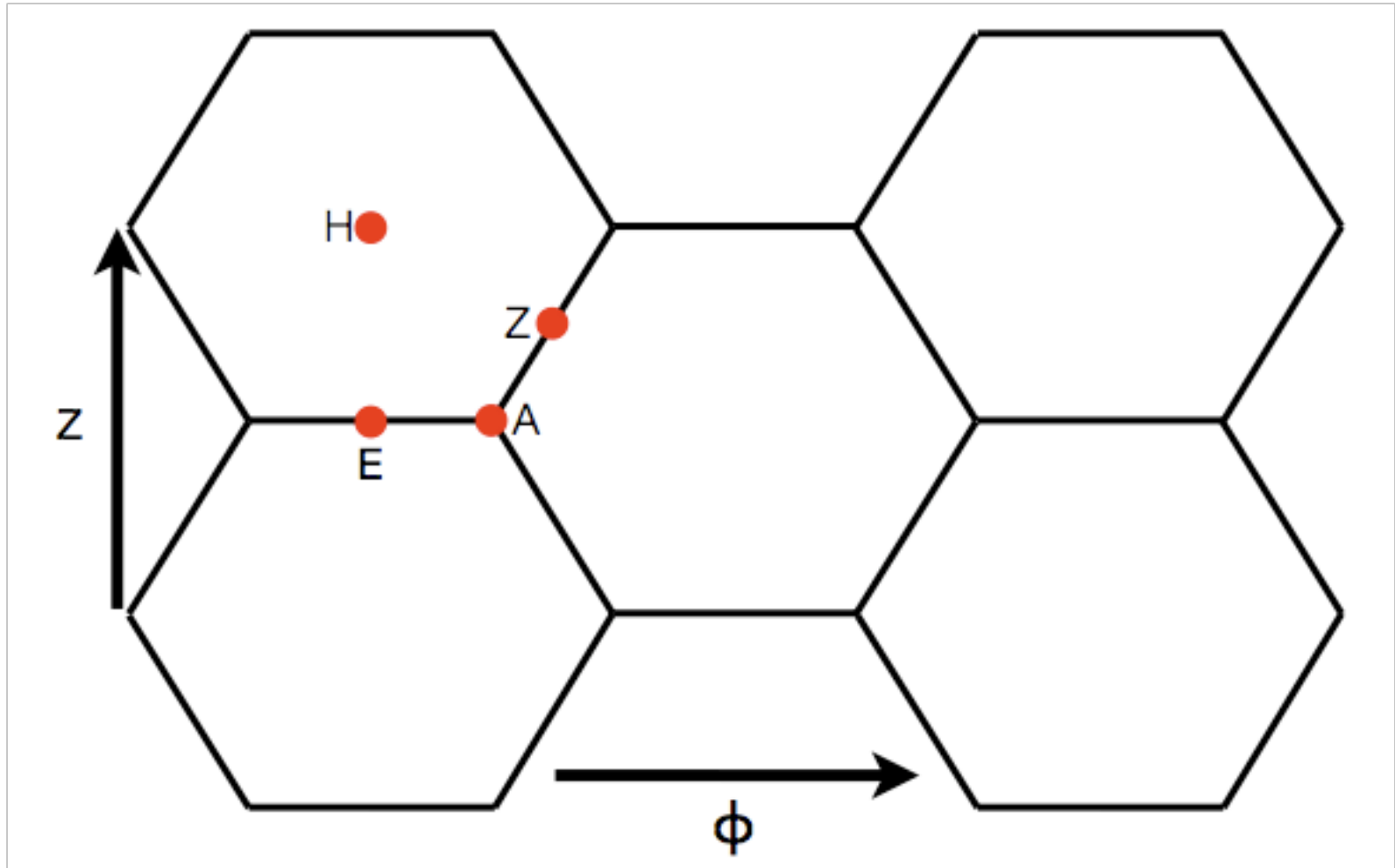
# (5,5)SWNT-H PES: Unit Cell



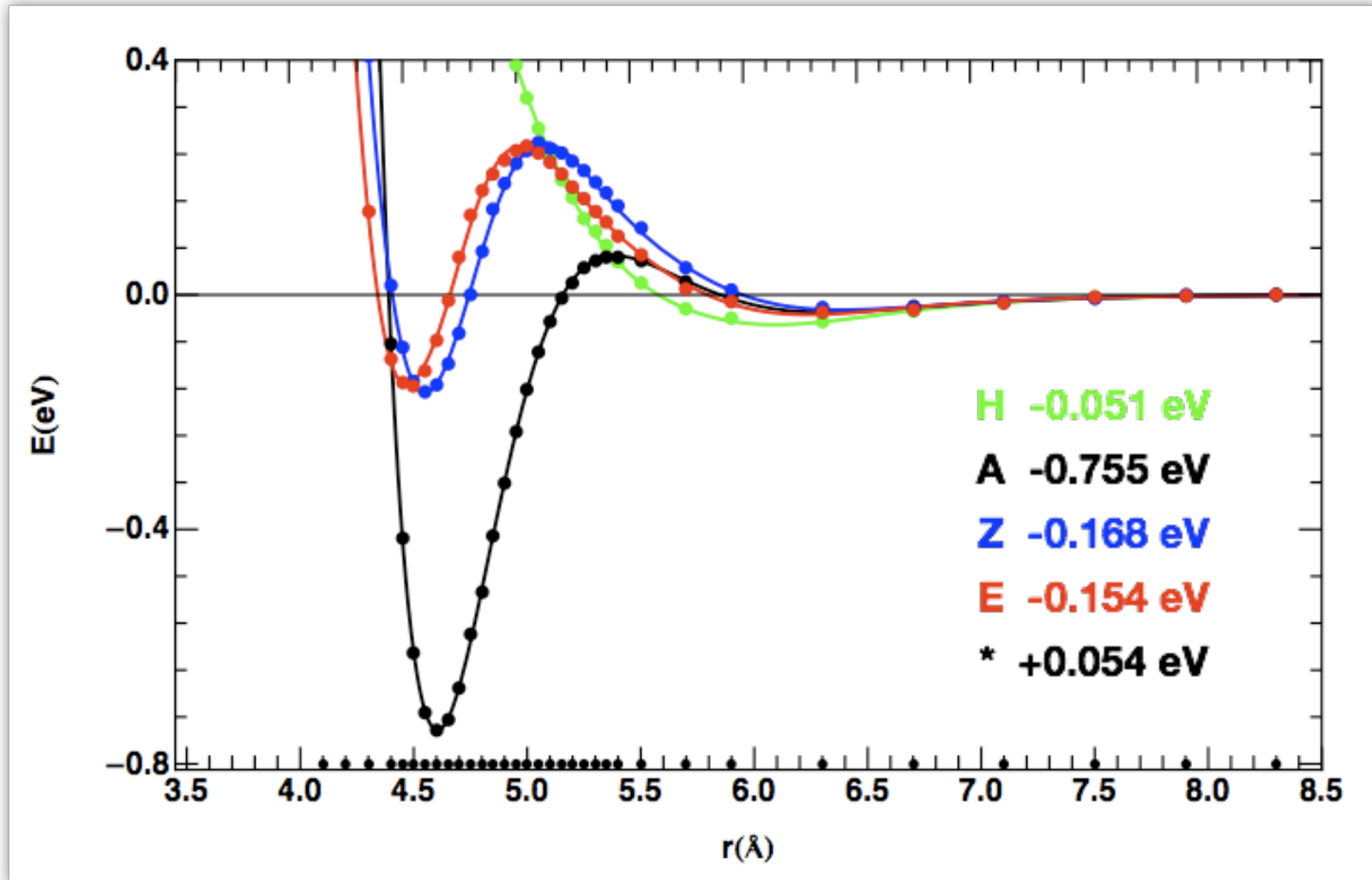
- unit cell
  - armchair shape
  - 20 atoms
  - $(r, z, \varphi)$  coordinates
  - $D_{10h}$  point group
- *reduced* unit cell
  - 4 atoms
  - restricted  $\varphi$  range
  - singly-degenerate irreps only

# (5,5)SWNT-H PES

## High Symmetry Sites



# (5,5)SWNT-H PES Radial Slices

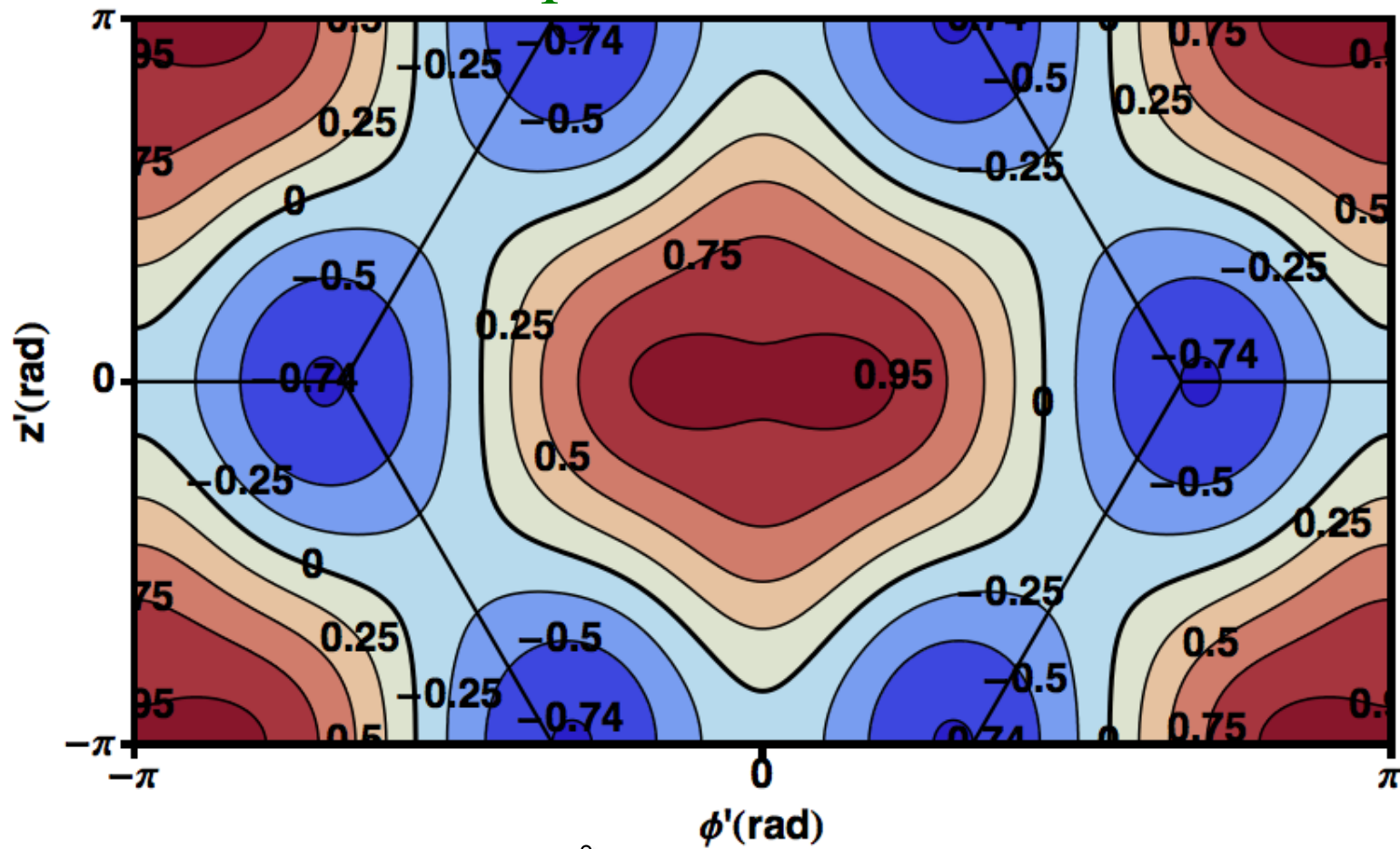


33 nonuniformly spaced radial grid points



# (5,5)SWNT-H PES

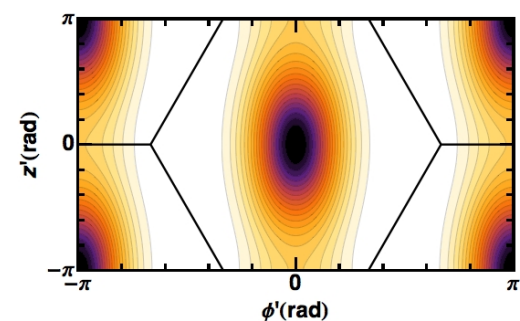
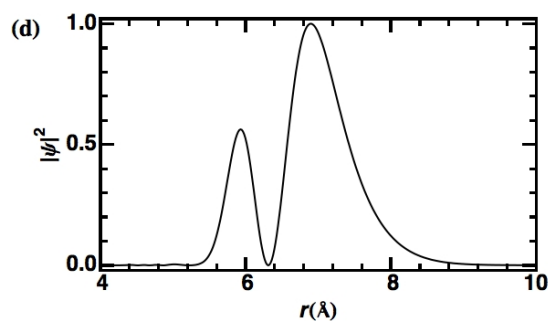
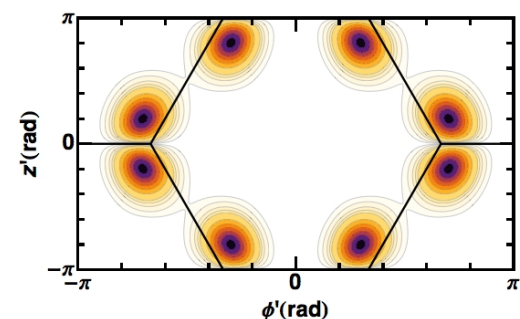
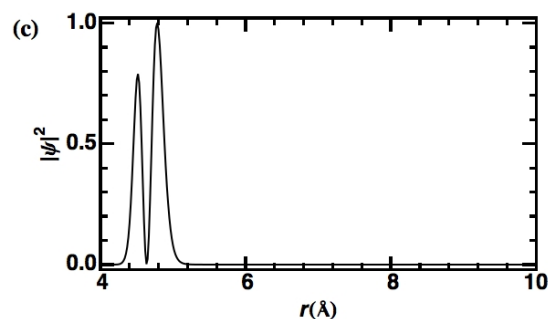
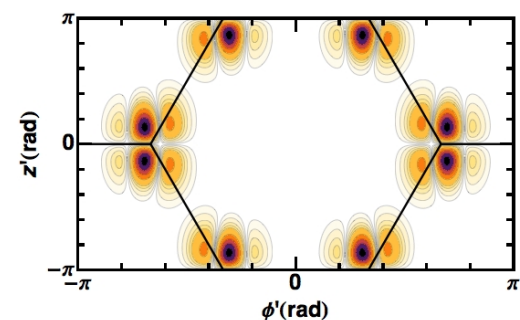
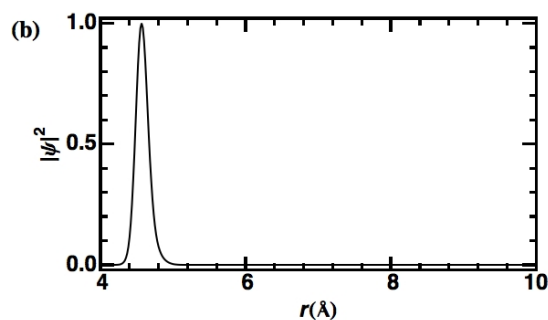
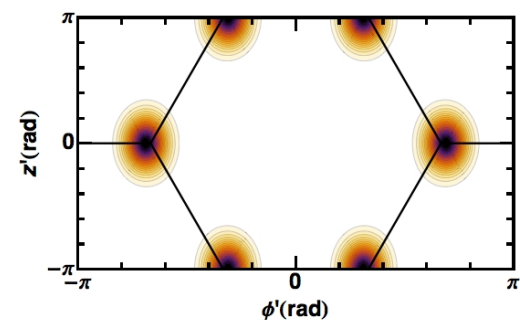
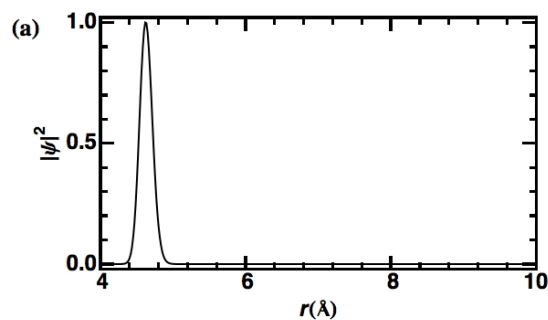
$r=r_{\text{eq}}$  contour plot



$$r = r_{\text{eq}} = 4.6 \text{ \AA}$$

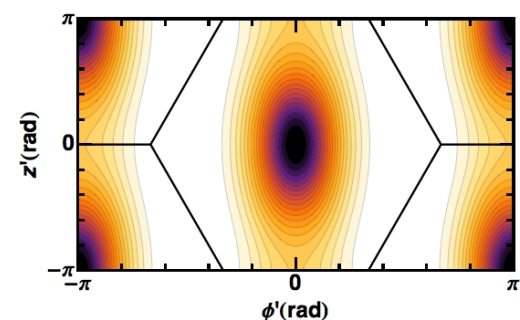
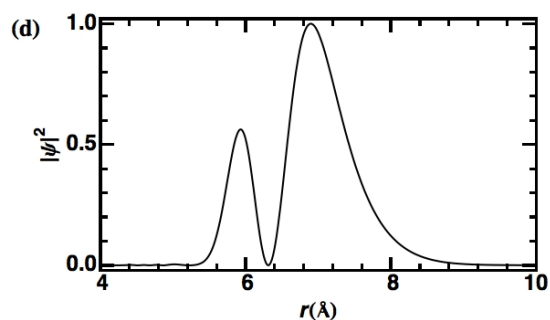
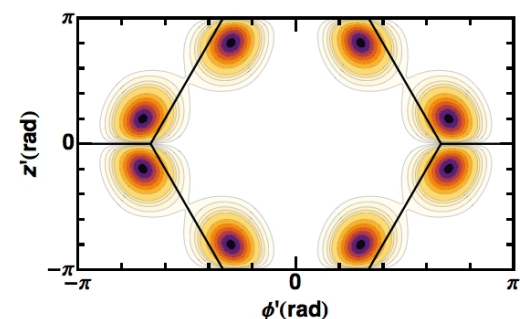
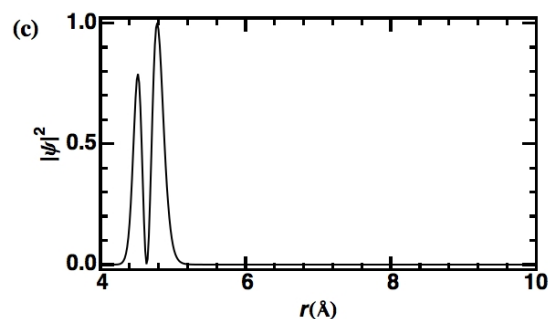
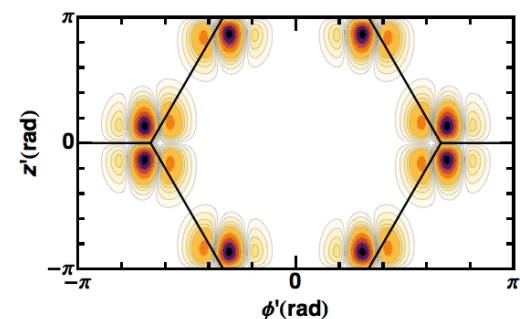
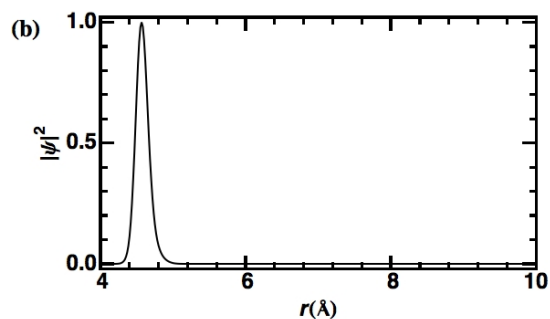
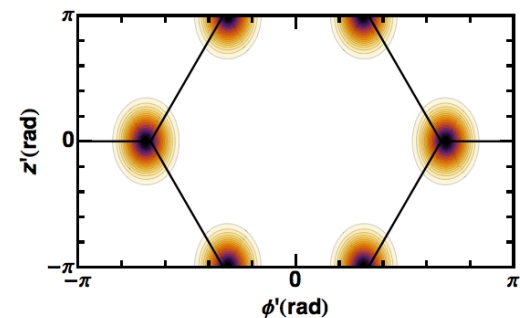
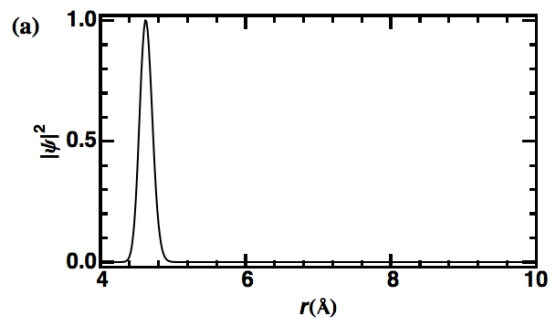
$|000\rangle$   
 -0.497 eV  
 0.258 eV ZPE

# Density Plots for Selected Rovibrational Eigenstates



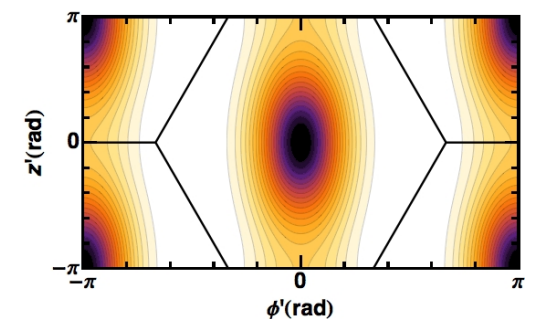
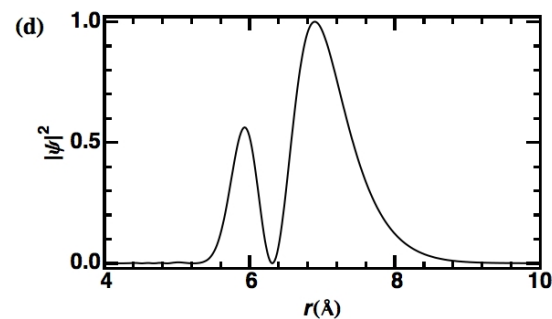
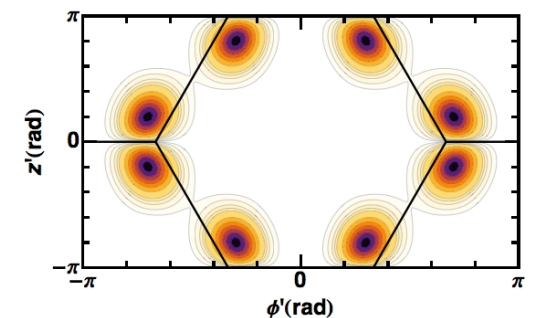
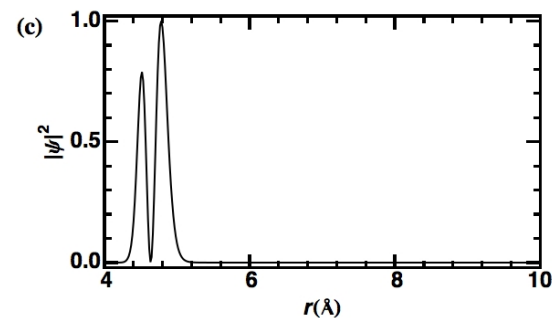
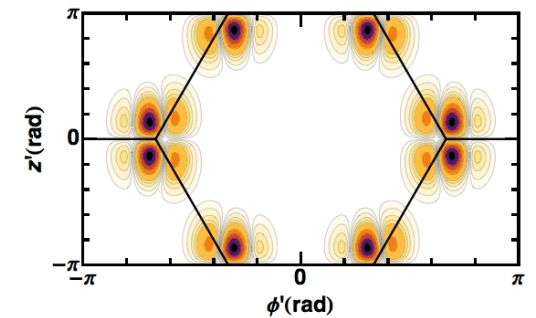
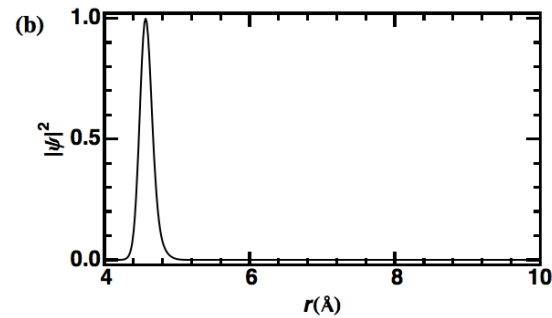
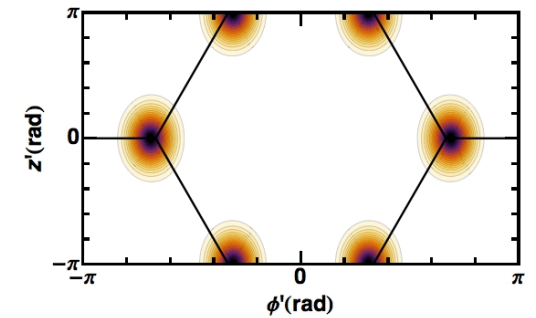
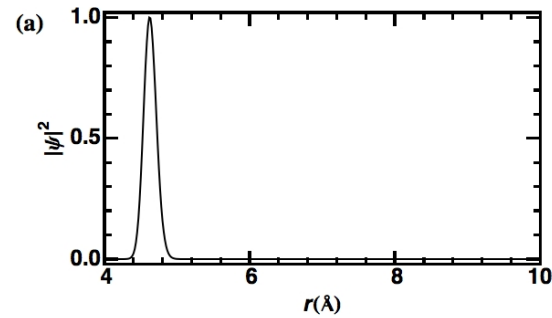
$|012\rangle$   
-0.159 eV

# Density Plots for Selected Rovibrational Eigenstates



# Density Plots for Selected Rovibrational Eigenstates

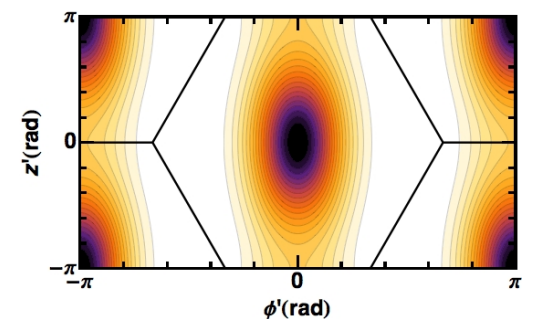
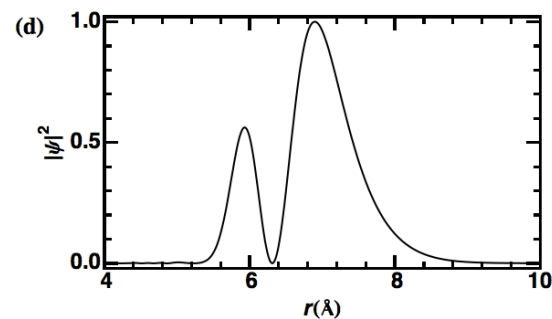
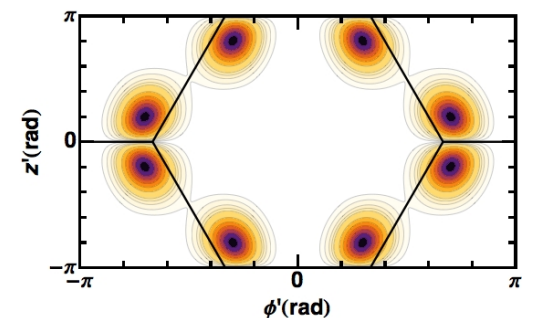
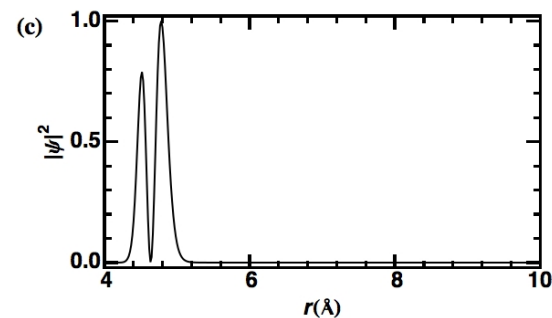
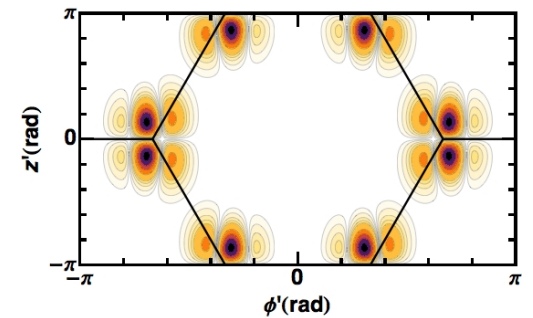
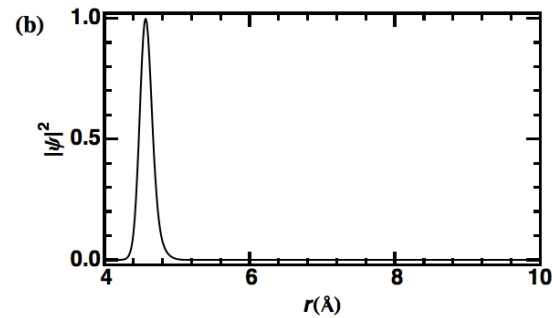
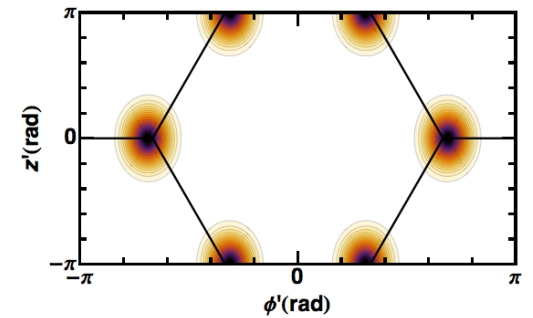
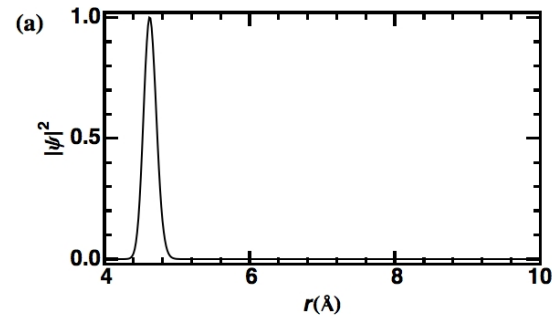
$|110\rangle$   
-0.128 eV





# Density Plots for Selected Rovibrational Eigenstates

$|1??\rangle$   
-0.039 eV



# E vs. Z Migration Rate ( $\text{s}^{-1}$ )

$ rz\phi\rangle$	E(eV)	$k_E^1$	$k_E^2$	$\bar{k}_E$	$k_Z^1$	$k_Z^2$	$\bar{k}_Z$
$ 000\rangle$	-0.4966244	$2.739 \times 10^6$	$2.739 \times 10^6$	$2.739 \times 10^6$	$1.640 \times 10^7$	$1.640 \times 10^7$	$1.640 \times 10^7$
$ 001\rangle$	-0.3841498	$8.869 \times 10^7$	$8.870 \times 10^7$	$8.870 \times 10^7$	$3.943 \times 10^8$	$3.943 \times 10^8$	$3.943 \times 10^8$
$ 010\rangle$	-0.3719295	$2.024 \times 10^6$	$2.025 \times 10^6$	$2.025 \times 10^6$	$5.977 \times 10^8$	$5.977 \times 10^8$	$5.977 \times 10^8$
$ 002\rangle$	-0.2764535	$4.007 \times 10^9$	$4.009 \times 10^9$	$4.008 \times 10^9$	$5.464 \times 10^9$	$5.466 \times 10^9$	$5.465 \times 10^9$
$ 011\rangle$	-0.2629459	$7.401 \times 10^7$	$7.381 \times 10^7$	$7.391 \times 10^7$	$1.469 \times 10^{10}$	$1.469 \times 10^{10}$	$1.469 \times 10^{10}$
$ 020\rangle$	-0.2550786	$3.220 \times 10^8$	$3.207 \times 10^8$	$3.213 \times 10^8$	$2.695 \times 10^9$	$2.694 \times 10^9$	$2.694 \times 10^9$
$ 100\rangle$	-0.2475234	$3.509 \times 10^7$	$3.556 \times 10^7$	$3.533 \times 10^7$	$6.491 \times 10^9$	$6.492 \times 10^9$	$6.491 \times 10^9$
$ 003\rangle$	-0.1735507	$4.141 \times 10^{10}$	$4.175 \times 10^{10}$	$4.158 \times 10^{10}$	$5.256 \times 10^{10}$	$5.289 \times 10^{10}$	$5.272 \times 10^{10}$
$ 012\rangle$	-0.1600243	$2.866 \times 10^9$	$2.810 \times 10^9$	$2.838 \times 10^9$	$1.953 \times 10^{11}$	$1.954 \times 10^{11}$	$1.953 \times 10^{11}$
$ 021\rangle$	-0.1477298	$7.558 \times 10^9$	$7.358 \times 10^9$	$7.458 \times 10^9$	$1.616 \times 10^{11}$	$1.614 \times 10^{11}$	$1.615 \times 10^{11}$
$ 101\rangle$	-0.1408521	$3.840 \times 10^9$	$3.731 \times 10^9$	$3.786 \times 10^9$	$6.311 \times 10^{10}$	$6.300 \times 10^{10}$	$6.306 \times 10^{10}$
$ 030\rangle$	-0.1397799	$4.152 \times 10^8$	$4.349 \times 10^8$	$4.250 \times 10^8$	$2.172 \times 10^9$	$2.153 \times 10^9$	$2.163 \times 10^9$
$ 110\rangle$	-0.1284453	$2.548 \times 10^5$	$7.654 \times 10^5$	$5.101 \times 10^5$	$6.824 \times 10^{10}$	$6.824 \times 10^{10}$	$6.824 \times 10^{10}$
$ 004\rangle$	-0.0763314	$4.979 \times 10^{11}$	$5.330 \times 10^{11}$	$5.154 \times 10^{11}$	$3.700 \times 10^{11}$	$4.050 \times 10^{11}$	$3.875 \times 10^{11}$
$ 013\rangle$	-0.0637028	$2.367 \times 10^{10}$	$1.866 \times 10^{10}$	$2.116 \times 10^{10}$	$1.726 \times 10^{12}$	$1.731 \times 10^{12}$	$1.728 \times 10^{12}$
$ 022\rangle$	-0.0510807	$1.105 \times 10^{11}$	$7.803 \times 10^{10}$	$9.426 \times 10^{10}$	$2.366 \times 10^{12}$	$2.334 \times 10^{12}$	$2.350 \times 10^{12}$
$ 200\rangle$	-0.0455344	$1.233 \times 10^{10}$	$1.110 \times 10^{10}$	$1.172 \times 10^{10}$	$2.209 \times 10^9$	$9.750 \times 10^8$	$1.592 \times 10^9$
$ 031\rangle$	-0.0363558	$9.146 \times 10^9$	$1.464 \times 10^{10}$	$1.189 \times 10^{10}$	$7.806 \times 10^{11}$	$7.751 \times 10^{11}$	$7.778 \times 10^{11}$
$ 102\rangle$	-0.0362710	$1.172 \times 10^{11}$	$1.124 \times 10^{11}$	$1.148 \times 10^{11}$	$1.211 \times 10^{11}$	$1.163 \times 10^{11}$	$1.187 \times 10^{11}$

J. L. McAfee and B. Poirier, J. Chem. Phys., **130**, 064701 (2009)



## Beyond single H-atom adsorbates

- Which picture is correct?
  - “molecular orbital” picture
  - chemical bonding picture
- Can we bind more than one H atom adsorbate to a single C atom? *NO.*
- Do adsorbates bound to different C atoms interact appreciably? *YES.*



## Full-coverage Binding Enhancement

1 unit cell of (5,5) SWNT  $\rightarrow$  20 CH units

Periodic reflections now desirable

SWNT and H geometries from single-adsorbate:

Binding energy per H atom now 1.58 eV.

Very pronounced multiple binding enhancement.

Fully relax SWNT and all H's

SWNT radius increases from 3.45 Å to 3.95 Å

Binding energy per H atom now 2.63 eV.

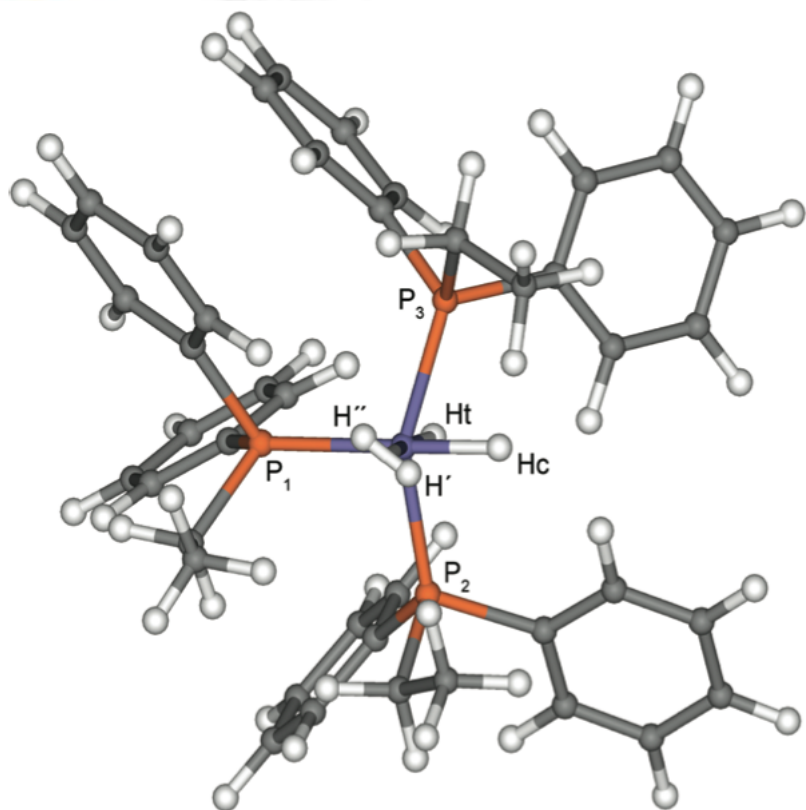
Relaxation yields additional  **$\sim 1$  eV**





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# $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ Complex: Motivation

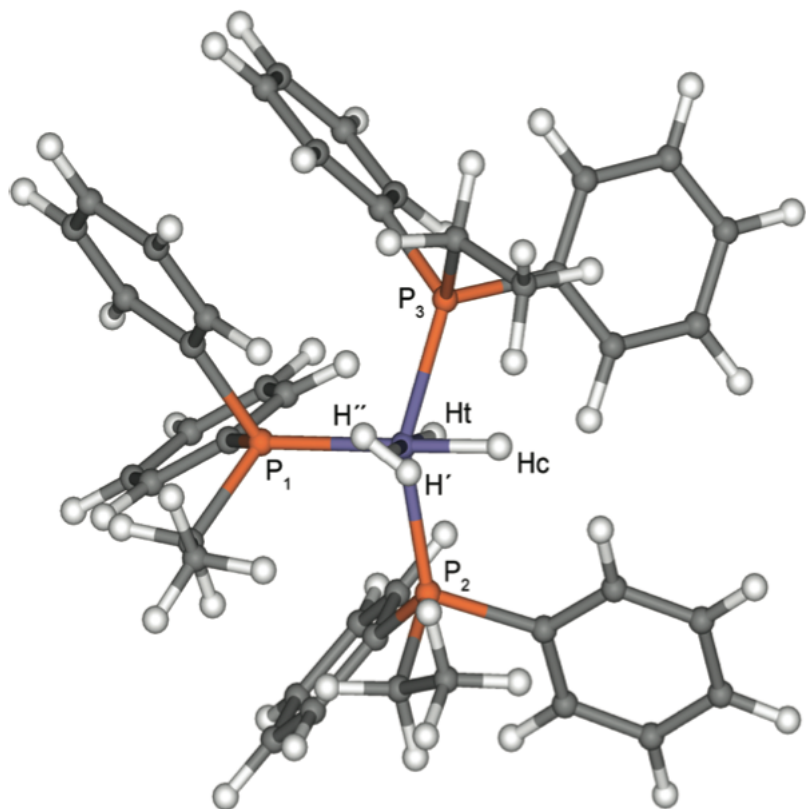


- $\text{H}_2$  forms sigma complex
- H atom ligands also relevant for hydrogen storage (spillover).
- $\text{H}_2$ —H exchange reactions very rapid (for Fe).
- $\text{H}_2$  rotational tunneling dynamics prevalent at low T.
- Theory (1D DFT) and Expt. (NMR, neutron scattering) disagree.



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# $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ Complex: Previous Work

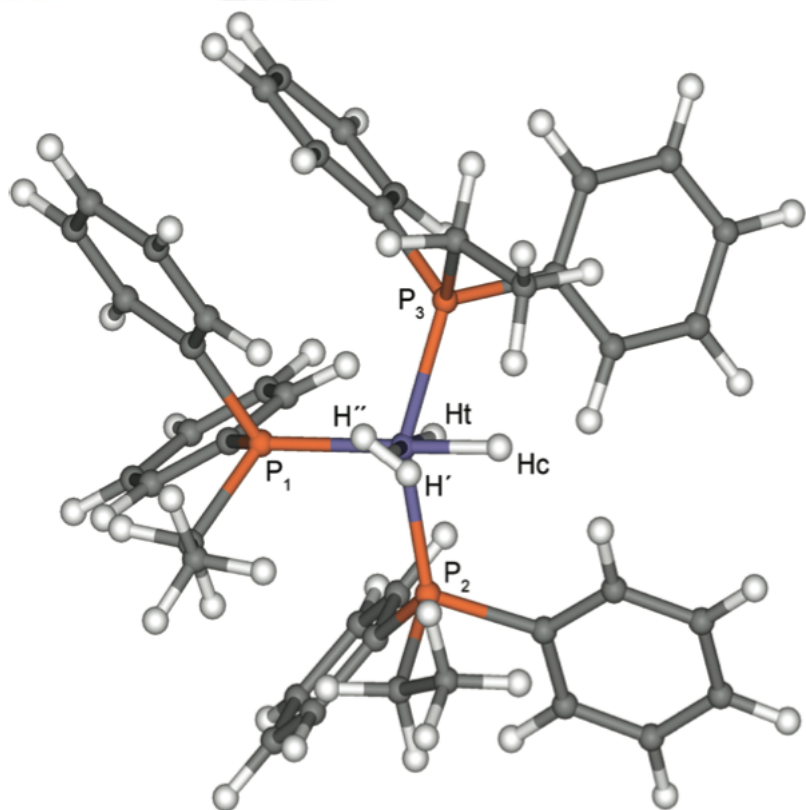


- N. Došlić, V. Gomzi, M. Mališ, I. Matanović, and J. Eckert, *Inorg. Chem.* **50**, 10740 (2011).
- L. S. van der Sluys, [J. Eckert](#), [O. Eisenstein](#), et. al, *J. Am. Chem. Soc.* **112**, 4831 (1990).
- S. Li, M. B. Hall, J. Eckert, C. M. Jensen, and A. Albinati, *J. Am. Chem. Soc.* **122**, 2903 (2000).
- K. W. Zilm et. al, *J. Am. Chem. Soc.* **112**, 920 (1990).
- J. Eckert, H. Blank, M. T. Bautista, and R. H. Morris, *Inorg. Chem.* **29**, 747 (1990).



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# $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ Complex: Our Goals



- Long Term:  $\text{H}_2$ —H exchange dynamics
  - minimum energy reaction path/profile
  - reduced dimensional quantum dynamics
  - full 12-dimensional quantum dynamics?
- ShortTerm:  $\text{H}_2$  rotation dynamics
  - conduct DFT ab initio calculations
  - build 2D rotational PES
  - conduct quantum dynamics calculations of rotational energy levels, tunneling splittings, etc.



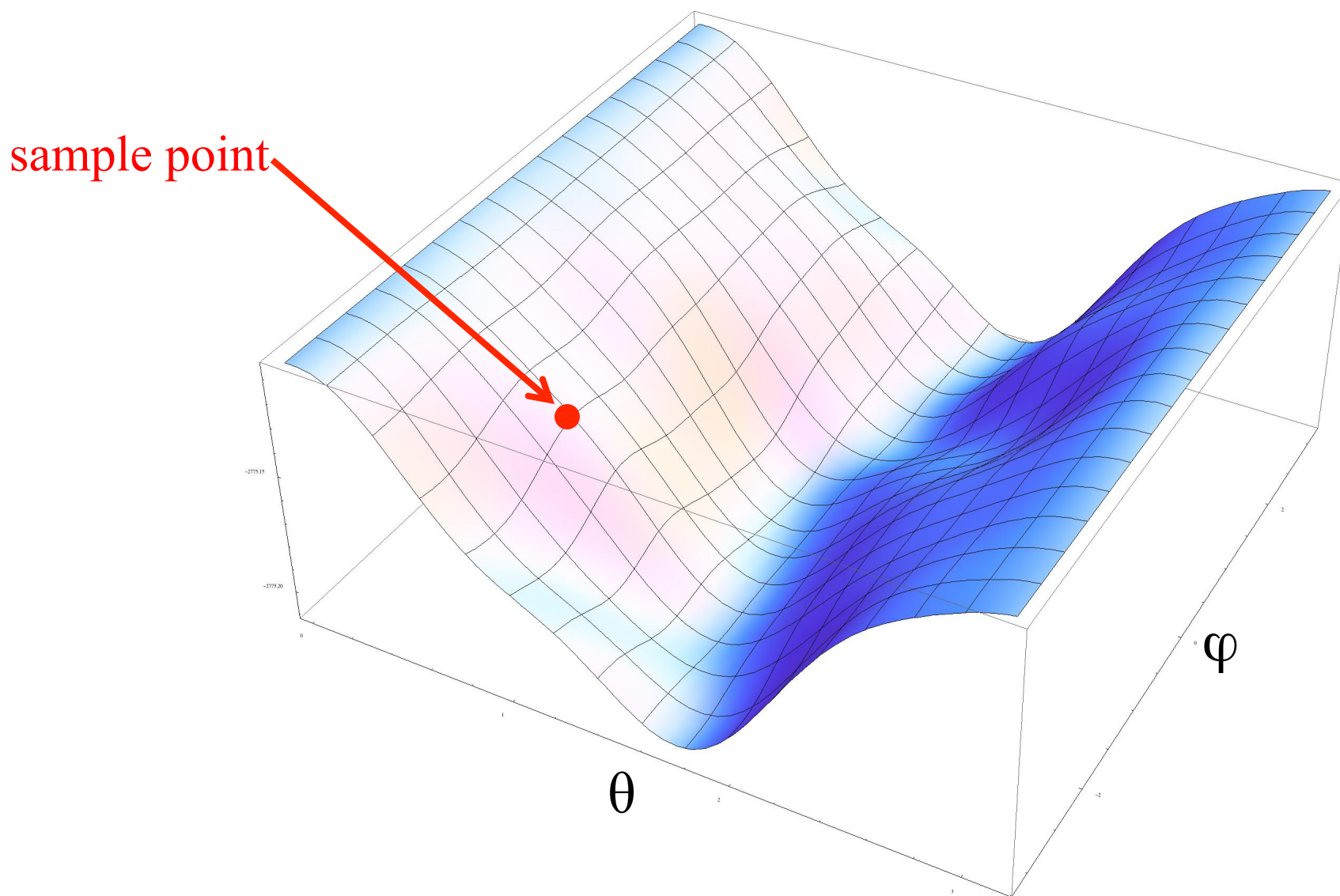
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# $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ Complex: $\text{H}_2$ rotation dynamics calculation

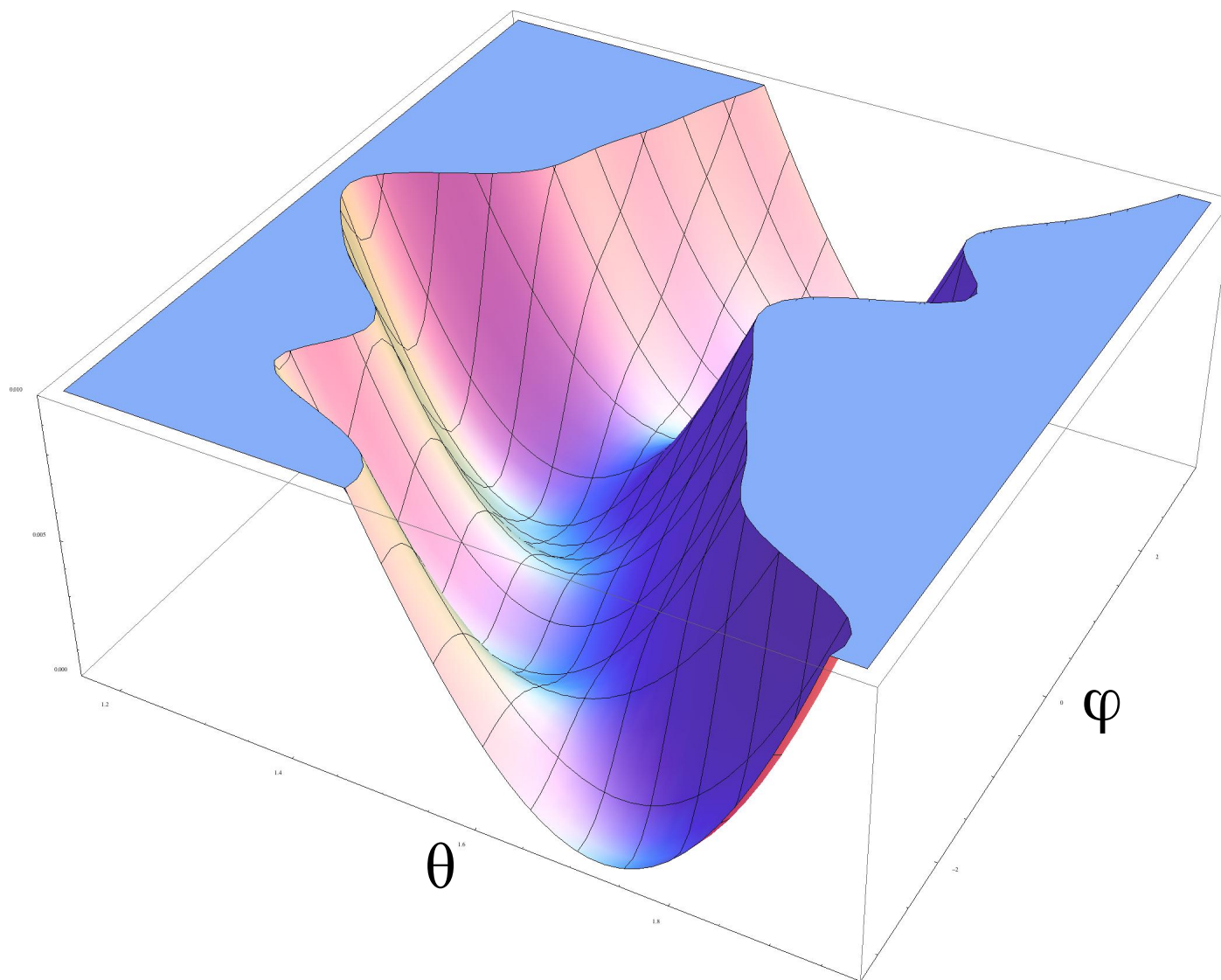
- Ab initio calculations using DFT
  - B3-LYP functionals; SV(P) basis; Stuttgart effective core potential (Fe).
  - full relaxation of all degrees-of-freedom except  $\text{H}_2$  orientation.
  - orientation  $(\theta, \phi)$  defined relative to Fe- $\text{H}_2$  axis.
  - 100 ab initio points thus far (10 polar angles  $\theta$ , 10 azimuthal angles  $\phi$ )
- Global Analytic Fit PES
  - expansion of global PES in spherical harmonics,  $Y_{lm}(\theta, \phi)$
  - $28 Y_{lm}(\theta, \phi)$  functions in all, up to  $l = 6$
  - only even  $l$  values considered, due to H atom permutation symmetry.
- Exact Quantum Dynamics Calculations
  - hindered rotor quantum states: energy levels and wavefunctions
  - tunneling splittings



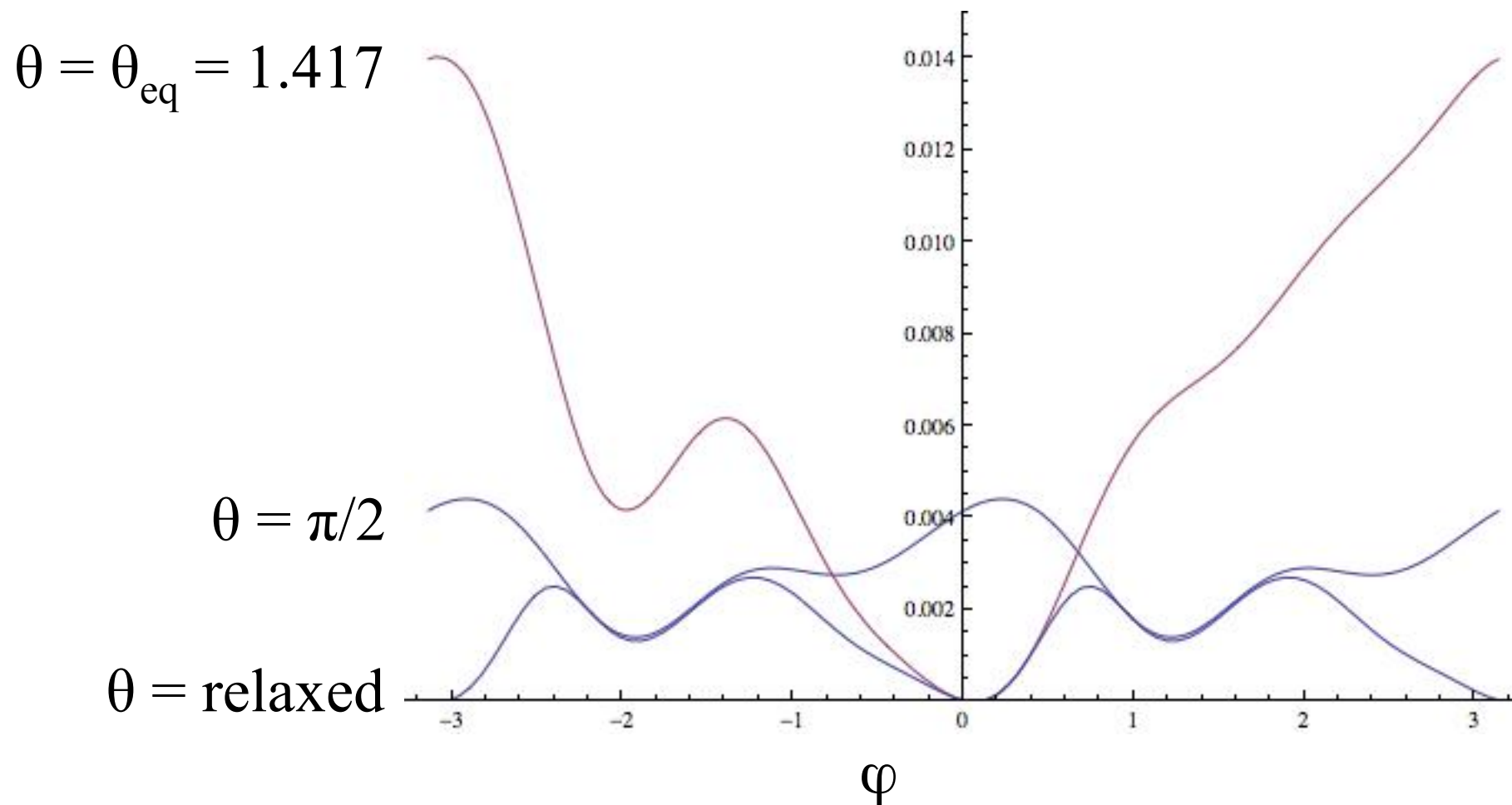
# $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ Complex: Global Analytic Fit PES



# $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ Complex: Global Analytic Fit PES



# Fe(H)<sub>2</sub>(H<sub>2</sub>)(PEtPh<sub>2</sub>)<sub>3</sub> Complex: Torsional Reaction Profiles:





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*November 18, 2015*

# **Quantum Mechanics Without Wavefunctions**

Bill Poirier

Texas Tech University

*Laboratoire Charles Coulomb (LCC) et  
Laboratoire Univers et Particules de Montpellier (LUPM)  
Université de Montpellier et  
Centre Nationale de la Recherche Scientifique*



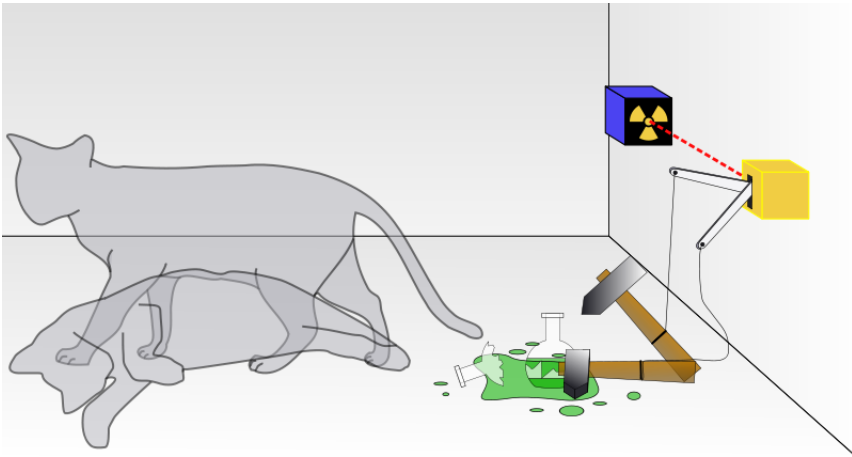
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# Getting Rid of $\Psi$ Altogether: *How can that even be possible?*

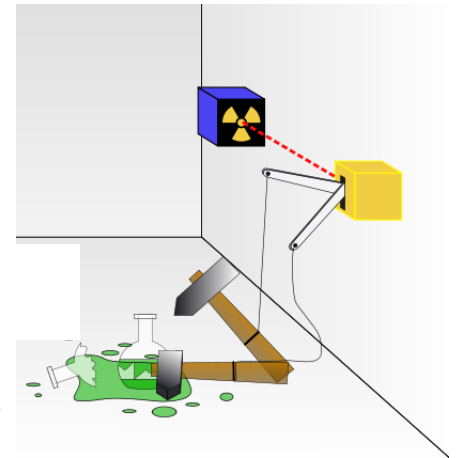
**Not**

,

**But**



$\Psi$



Is  $\Psi$  Alive or Dead ?



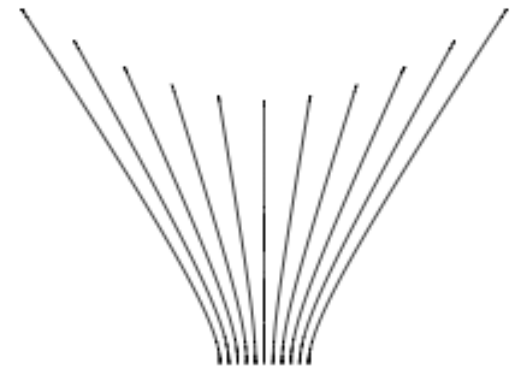
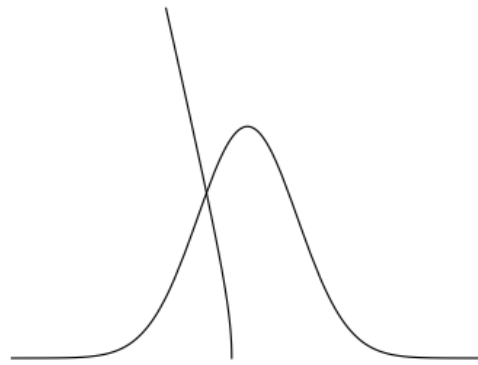
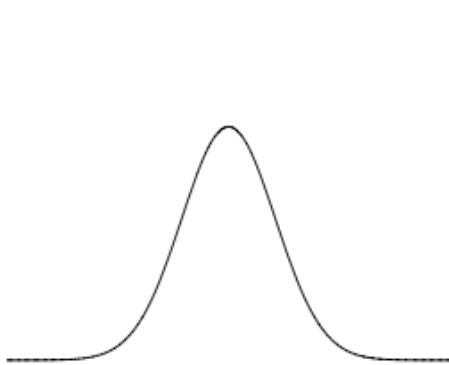


But if not  $\Psi$ , then what?

*Answer: Trajectories only*

- The wavefunction  $\Psi(x,t)$  is replaced with an *ensemble* (family) of trajectories,  $x(C,t)$ .
  - parameter  $C$  labels individual trajectories within the ensemble.
  - resembles classical statistical mechanics/trajectory simulations.
- The individual trajectories turn out to be the quantum trajectories of David Bohm. *However...*
- *This is NOT Bohmian Mechanics!*
  - Bohm uses a *single* trajectory,  $x(t)$ .
  - Bohm *also* uses the wavefunction,  $\Psi(x,t)$ .

Copenhagen quantum mechanics	Bohmian mechanics	Quantum trajectory-based formulation (non-relativistic)
$\Psi$ represents the state of the system. TDSE drives evolution of $\Psi(x,t)$ .	$\Psi$ and $x(t)$ together represent the state of the system. $\Psi$ leads to quantum potential $Q$ , driving trajectory dynamics via: $m\ddot{x} + \frac{\partial V(x)}{\partial x} + \frac{\partial Q(x,t)}{\partial x} = 0$	There is no $\Psi$ . $x(t, C)$ (trajectory ensemble) alone represents the state of the system, and leads to $Q$ . $x(t, C)$ satisfies its own PDE that replaces the TDSE (with ' denoting partial derivative w/ respect to $C$ .) $m\ddot{x} + \frac{\partial V(x)}{\partial x} + \frac{\hbar^2}{4m} \left( \frac{x''''}{x'^4} - 8 \frac{x'''x''}{x'^5} + 10 \frac{x''^3}{x'^6} \right) = 0$



- [1] A. Bouda, Int. J. Mod. Phys. A 18, 3347 (2003).
- [2] P. Holland, Ann. Phys. 315, 505 (2005).
- [3] B. Poirier, Chem. Phys. 370, 4 (2010).
- [4] J. Schiff and B. Poirier, J. Chem. Phys. 136, 031102 (2012).
- [5] B. Poirier, arXiv:1208.6260 [quant-ph], (2012).

# Reactive Scattering Calculations: Cross Sections & Rates

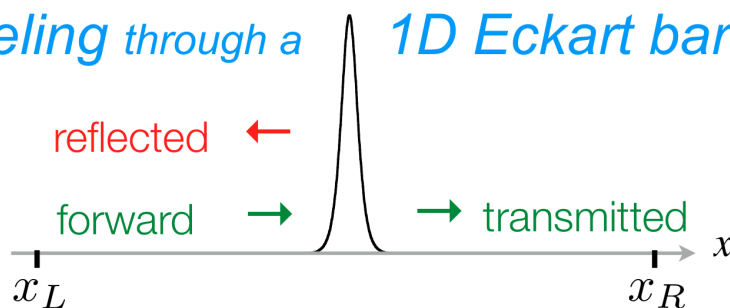
## *Time independent*

quantum trajectories (#5)

tunneling through a 1D Eckart barrier

Eckart potential:  
 $V(x) = V_0 \operatorname{sech}^2(\alpha x)$

$$\begin{aligned}\alpha &= 3.0 \text{ a.u.} \\ m &= 2000 \text{ a.u.} \\ V_0 &= 400 \text{ cm}^{-1}\end{aligned}$$



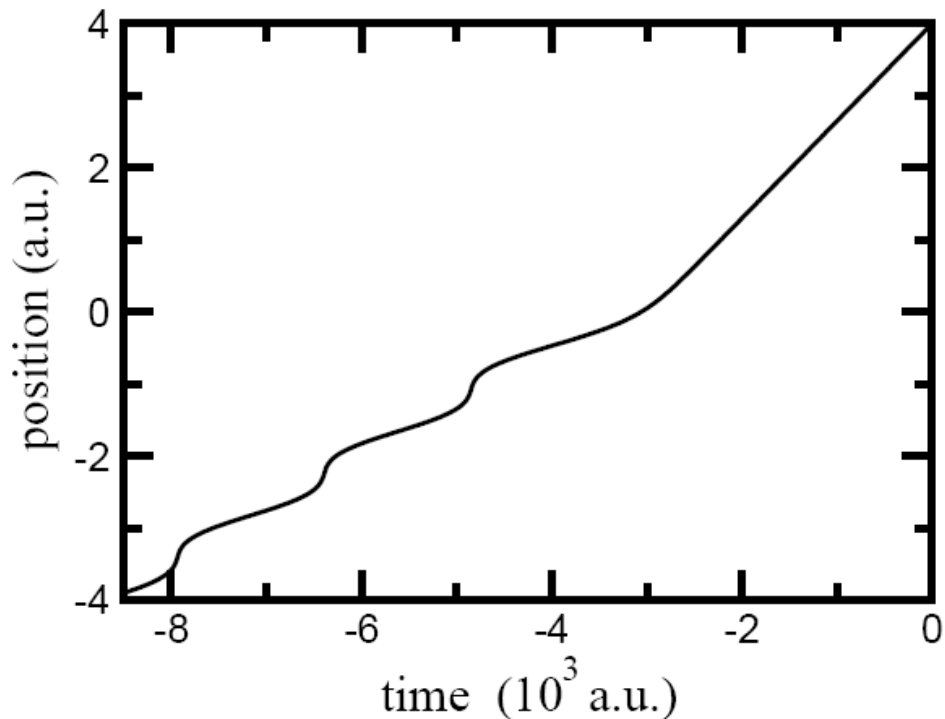
$$\Psi(x \rightarrow +\infty) = k_R^{-1/2} T \exp[ik_R x]$$

$$\Psi(x \rightarrow -\infty) = k_L^{-1/2} (\exp[ik_L x] + R \exp[-ik_L x])$$

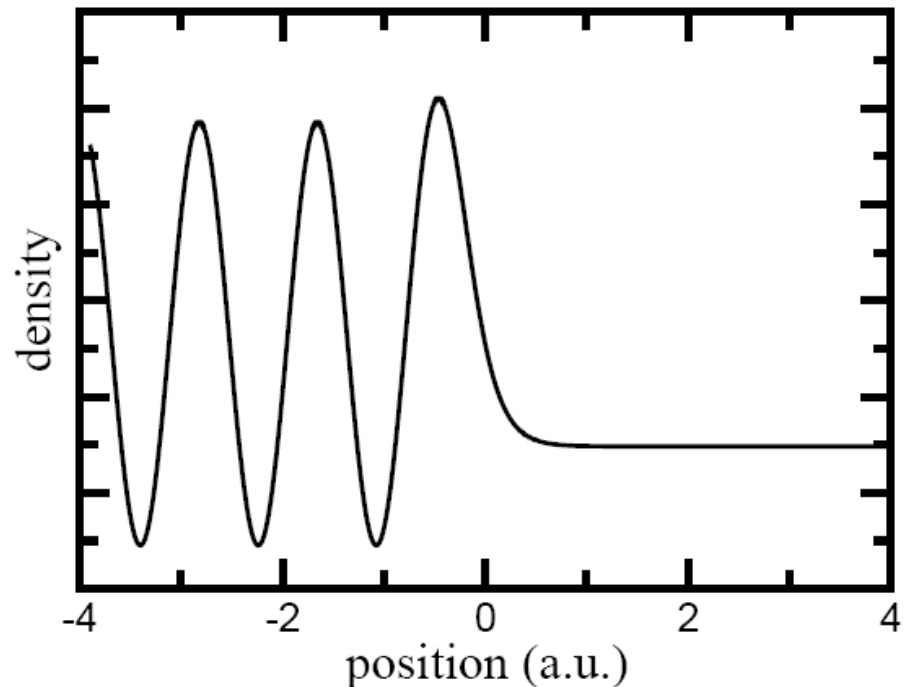
- Challenges in the continuum:

- Two linearly independent eigenstate solutions for each energy  $E$ , requiring imposition of special boundary conditions.
- Energy eigenstates extend infinitely far in both directions, necessitating use of optical potentials to absorb outgoing flux.
- Exact quantum dynamics calculation in the “deep” tunneling regime nearly impossible, even in 1D.

# Reactive Scattering Calculations: Cross Sections & Rates



Trajectory,  $x(t)$



Wavefunction density,  $\rho(x)$

Solve 4<sup>th</sup> order real-valued ODE in  $t$ , to obtain  $x(t)$ .

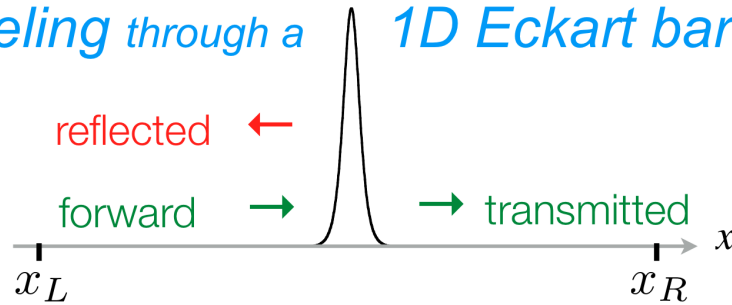
- similar to Newton's second law, w/ extra terms.
- two initial conditions specify  $E$  and  $x_0$ .
- remaining two specify boundary conditions of solution  $\psi$

# quantum trajectories (#5)

## tunneling through a 1D Eckart barrier

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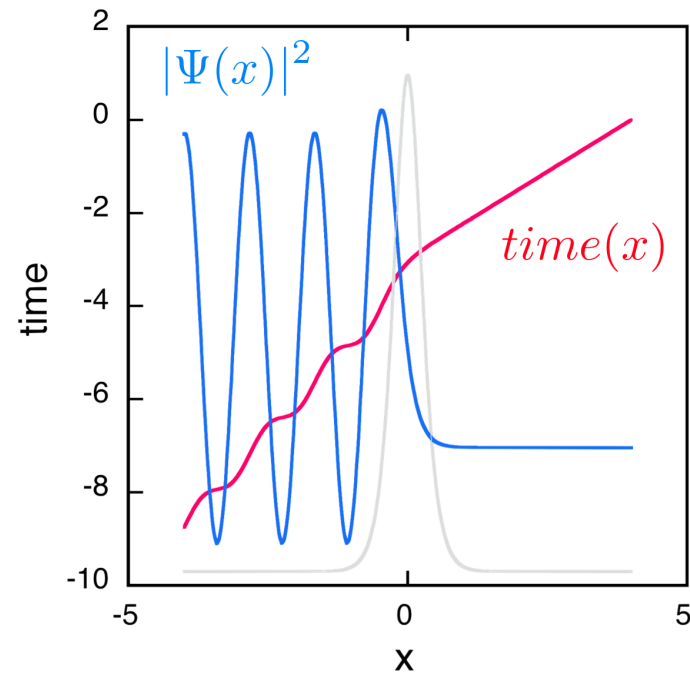


$$\begin{aligned}x_0 &= x_R \\ \dot{x}_0 &= \sqrt{2E/m} \\ \ddot{x}_0 &= \ddot{x}_0 = 0\end{aligned}$$

$$\Psi(x \rightarrow +\infty) = k_R^{-1/2} T \exp[ik_R x]$$

$$\Psi(x \rightarrow -\infty) = k_L^{-1/2} (\exp[ik_L x] + R \exp[-ik_L x])$$

- ODE integration by means of a simple Runge-Kutta propagator.





# scattering through a 1D Eckart barrier

- Main difference with classical trajectories on the left (reactant) asymptote:

- $p = m\dot{x}$  is **not** conserved.
- one can show that **Noether momentum**

$$p_{Noether} = m\dot{x} + \frac{\hbar^2}{4m} \left( \frac{\ddot{x}}{\dot{x}^4} - \frac{2\ddot{x}^2}{\dot{x}^5} \right)$$

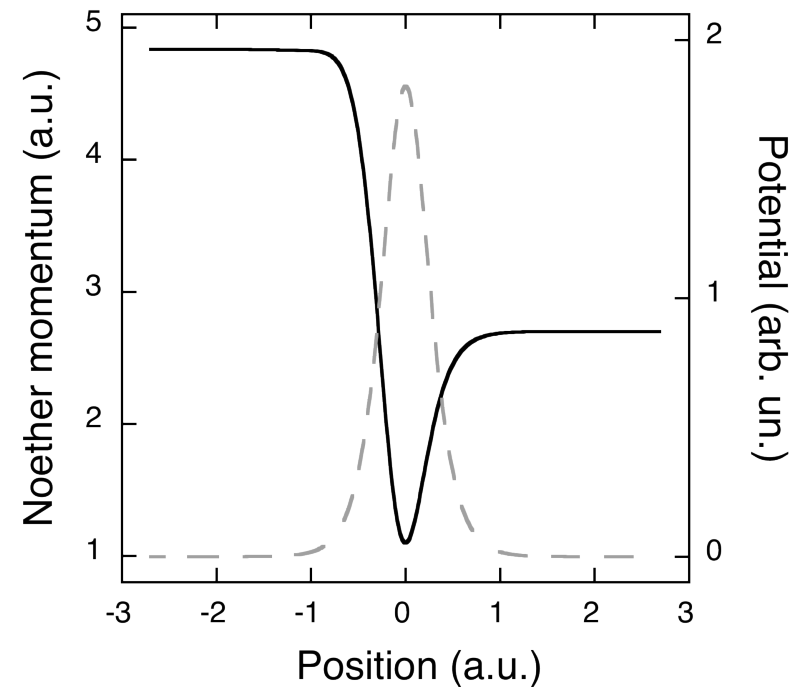
is conserved

- Asymptotic  $p_{Noether}$ :

$$p_L = p_{Noether}(t \rightarrow -\infty) = \hbar k_L \left( \frac{1 + |R|^2}{1 - |R|^2} \right)$$

- Transmission probability:

$$P_T = \frac{2\hbar k_L}{\hbar k_L + p_L}$$



# scattering through a 1D Eckart barrier

## Transmission as a function of Energy

$E/V_0$	Exact	Present calculation	Rel. error
1.(−12)	.28508(−12)	.28522(−12)	+5.(−04)
1.(−09)	.28507873(−09)	.28507863(−09)	−4.(−07)
1.(−06)	.28507940681(−06)	.28507940697(−06)	+5.(−10)
1.(−03)	.285757547947374(−03)	.285757547947352(−03)	−8.(−14)
1.(−01)	.356449541539905(−01)	.356449541539893(−01)	−4.(−14)
0.5	.318986860221912	.318986860221873	−1.(−13)
1.0	.716641955866101	.716641955866092	−1.(−14)
1.5	.900592641583308	.900592641583281	−3.(−14)
2.0	.963615495020163	.963615495020159	−4.(−15)
10.0	.999998078464427	.999998078464407	−2.(−14)



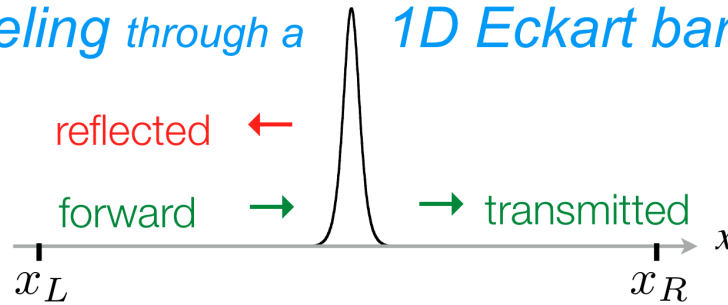
Can propagate for  $10^8$  a.u. of time with energy  
conservation  $\sim 1 \cdot 10^{-12}$

# quantum trajectories (#5)

## tunneling through a 1D Eckart barrier

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 $V(x) = V_0 \operatorname{sech}^2(\alpha x)$

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 $m = 2000 \text{ a.u.}$   
 $V_0 = 400 \text{ cm}^{-1}$



$$\begin{aligned} x_0 &= x_R \\ \dot{x}_0 &= \sqrt{2E/m} \\ \ddot{x}_0 &= \ddot{x}_0 = 0 \end{aligned}$$

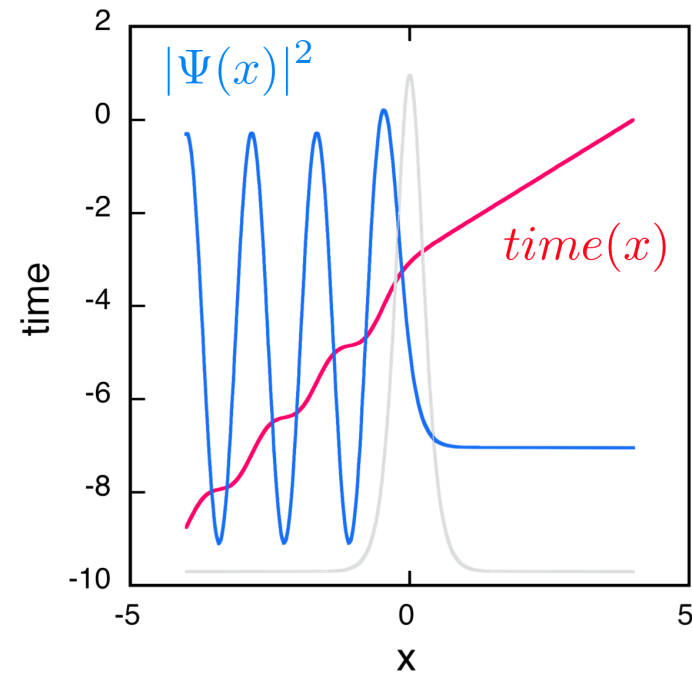
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$$\Psi(x \rightarrow -\infty) = k_L^{-1/2} (\exp[ik_L x] + R \exp[-ik_L x])$$

- ODE integration by means of a simple Runge-Kutta propagator.

deep tunneling

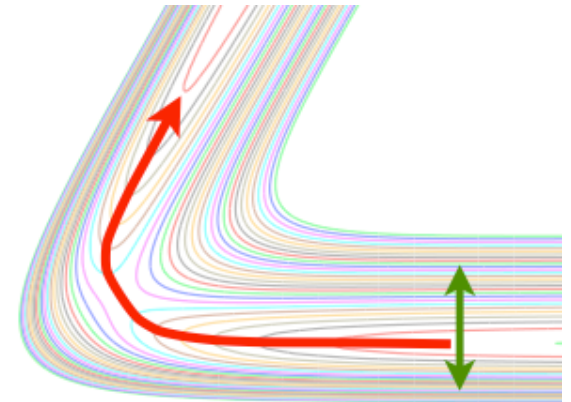
$E/V_0$	5.48 (− 43)
Exact PTransmission	1.5641888074199039 (− 43)
Computed PTransmission	1.5641888074199345 (− 43)
Relative Error	$\sim 2.0 (-14)$



# Multidimensional Applications:

*the best of both classical and quantum trajectories*

- ***Classical-like*** trajectory ensemble method.
- Individual ***exact quantum*** trajectory along reaction coordinate.
- Perpendicular modes treated classically.
  - Standard classical ***sampling*** of initial conditions...
  - ... modified to incorporate ***quantization of classical modes***.
- Computation of microcanonical quantum reactive scattering.
- Application:
  - cumulative reaction probabilities for a  $2D$  bottleneck potential.



# prototype 2D chemical system

## 2D bottleneck potential

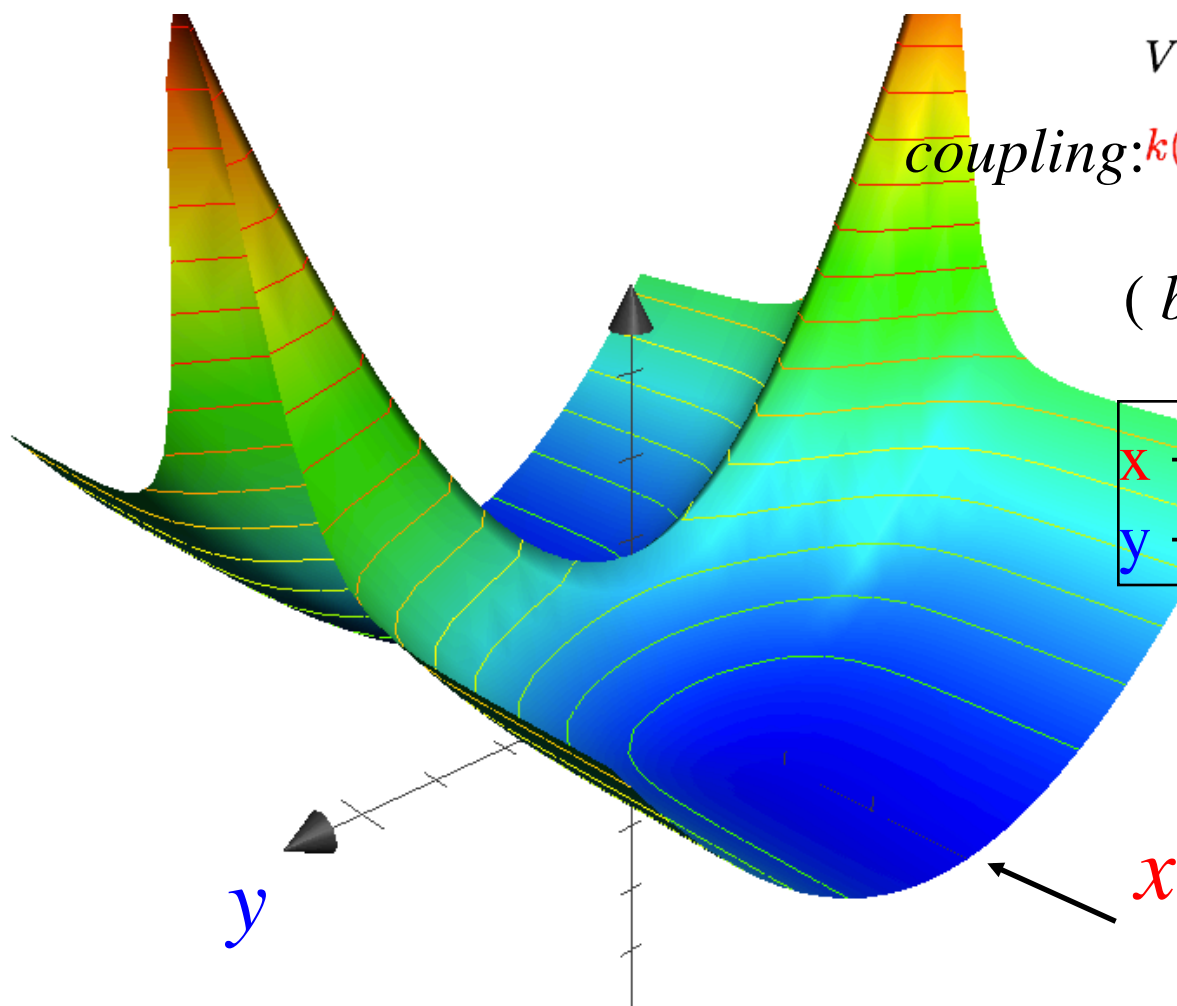
$x$ -Eckart barrier +  $y$ -harm. osc.

$$V(x, y) = V_0 / \cosh^2(\alpha x) + \frac{1}{2} k(x) y^2$$

coupling:  $k(x) = k_0 [1 + b / \cosh^2(\alpha x)]$

(  $b = 0 \Rightarrow x / y$  decoupled )

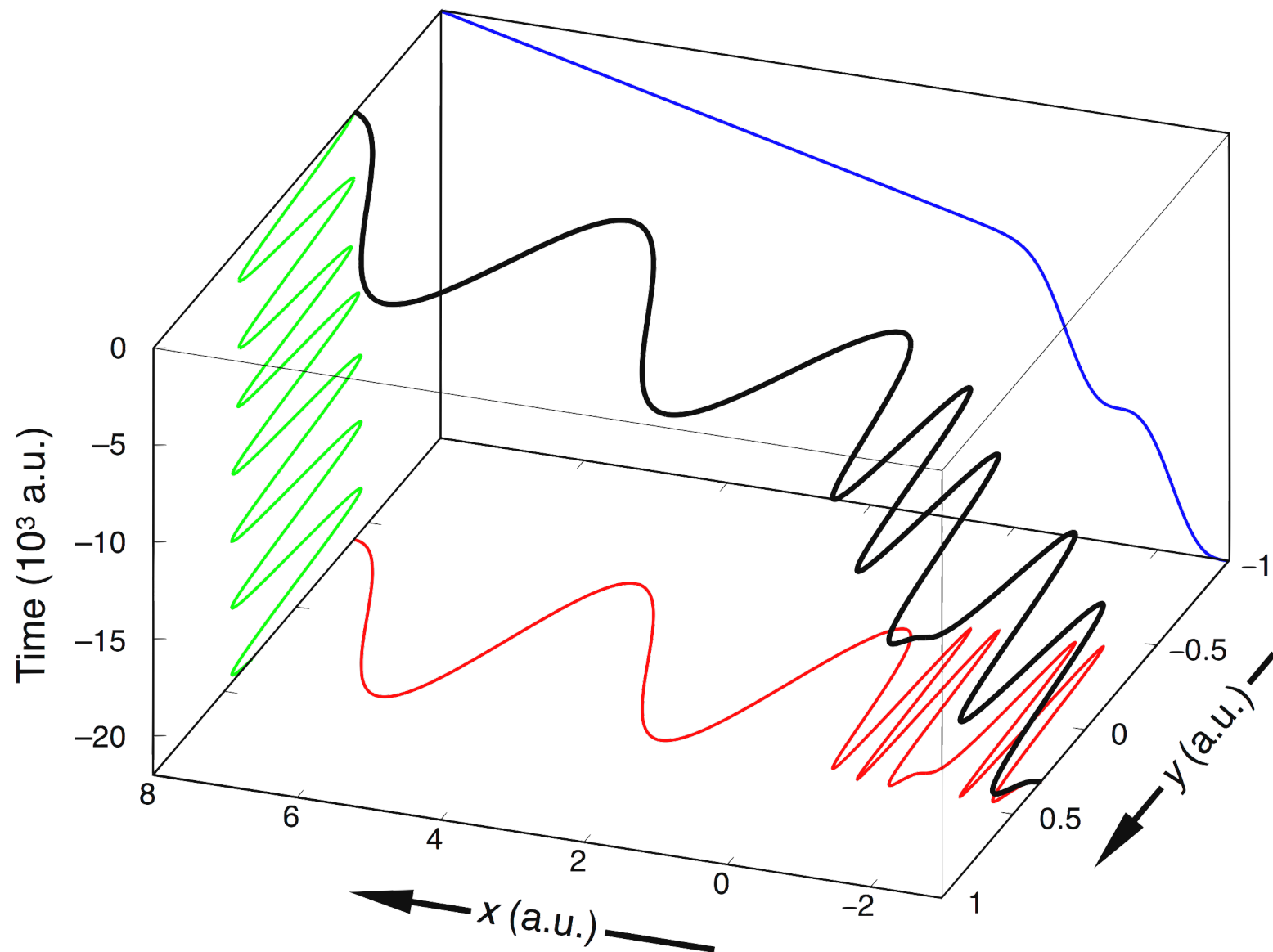
$x \rightarrow$  “no-wave” quantum traj.  
 $y \rightarrow$  classical motion.





# Quantum Trajectory Simulation (QTS)

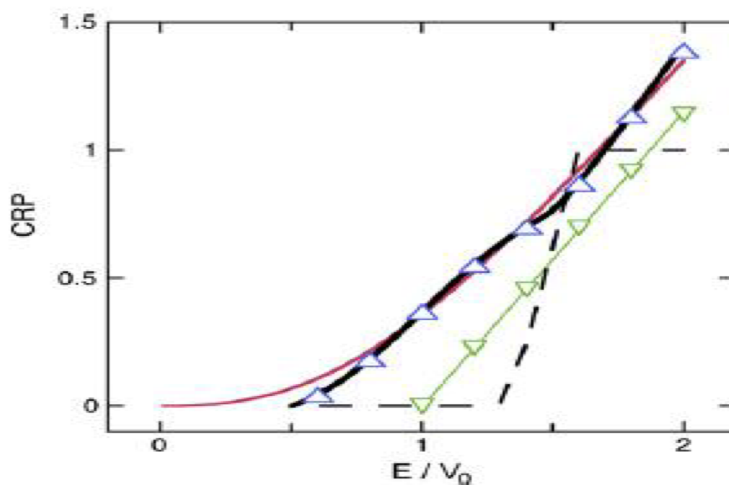
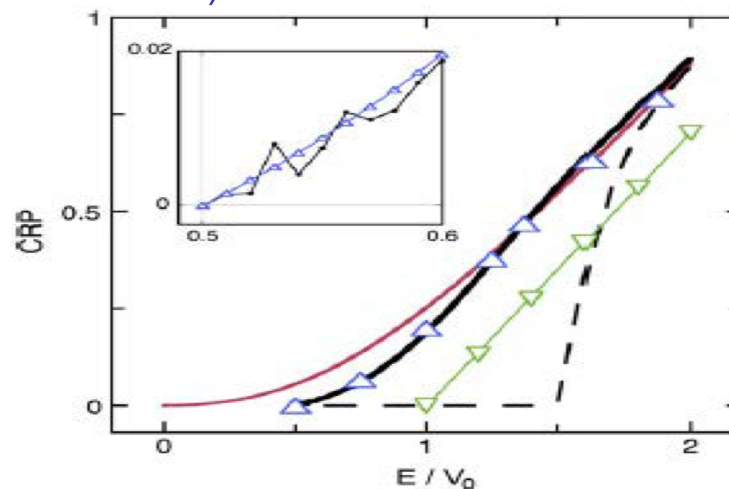
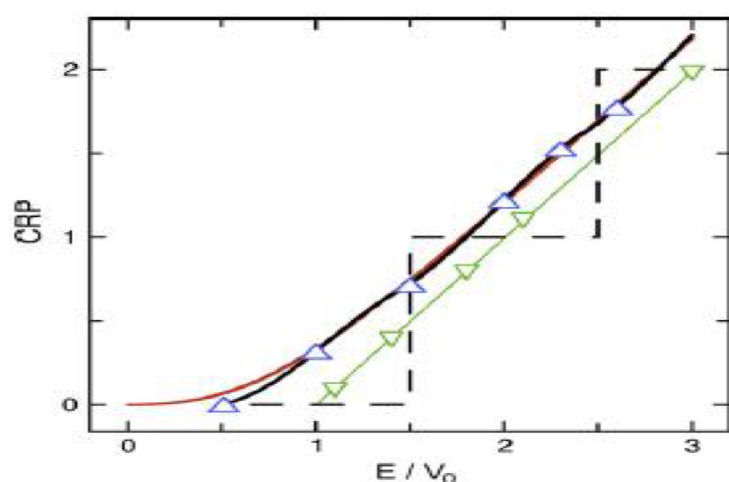
Results for 2D bottleneck potential system



# Quantum Trajectory Simulation (QTS)

## Results for 2D bottleneck potential system

Cumulative Reaction Probability(Microcanonical)<sup>2</sup>



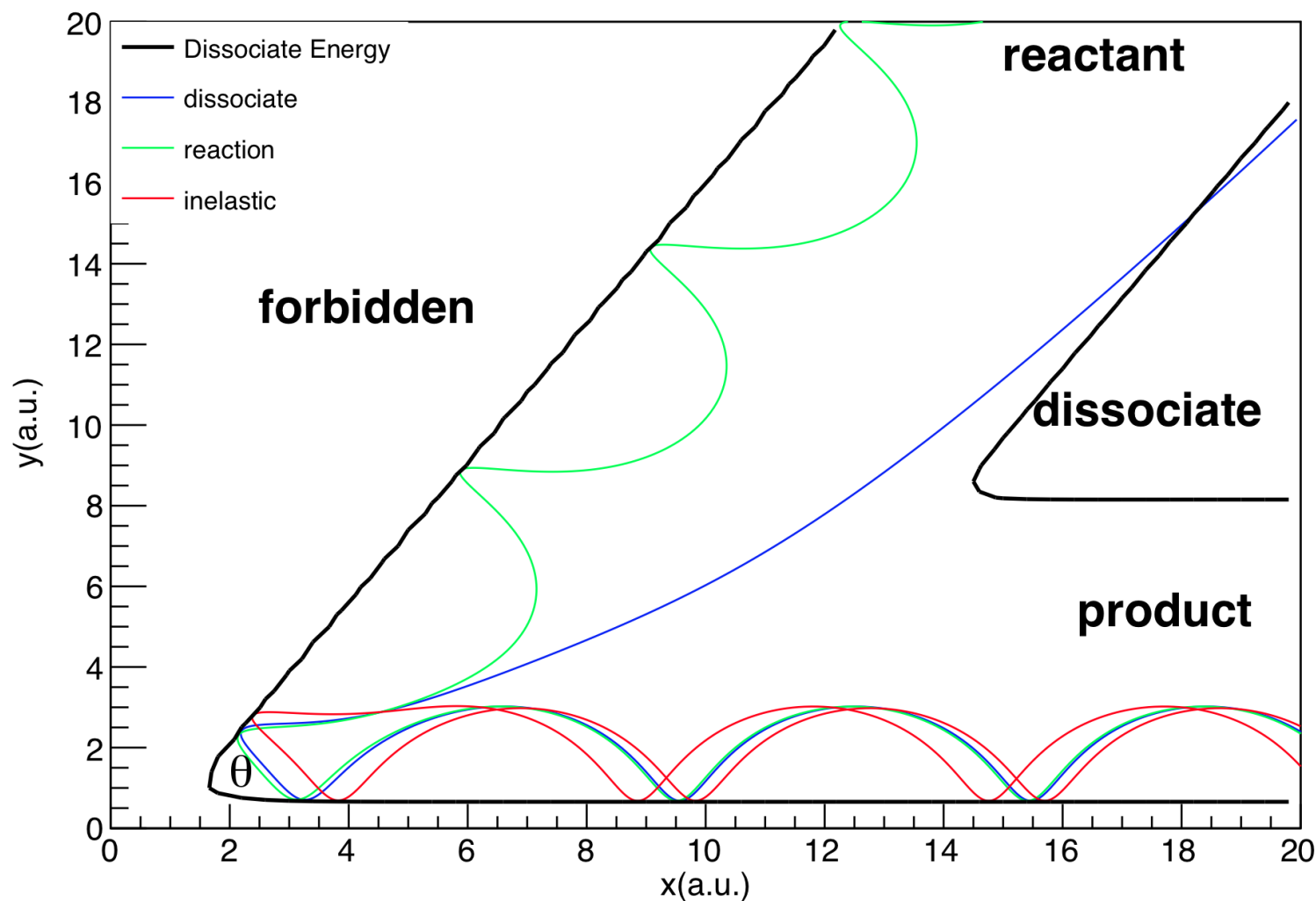
black:discrete variable rep.  
red:QTS standard  
blue:QTS PSA  
green:CTS standard  
dash:CTS PSA

<sup>2</sup>B.Poirier et al.Comput.Theor.Chem.990(2012)3

# Quantum Trajectory Simulation (QTS)

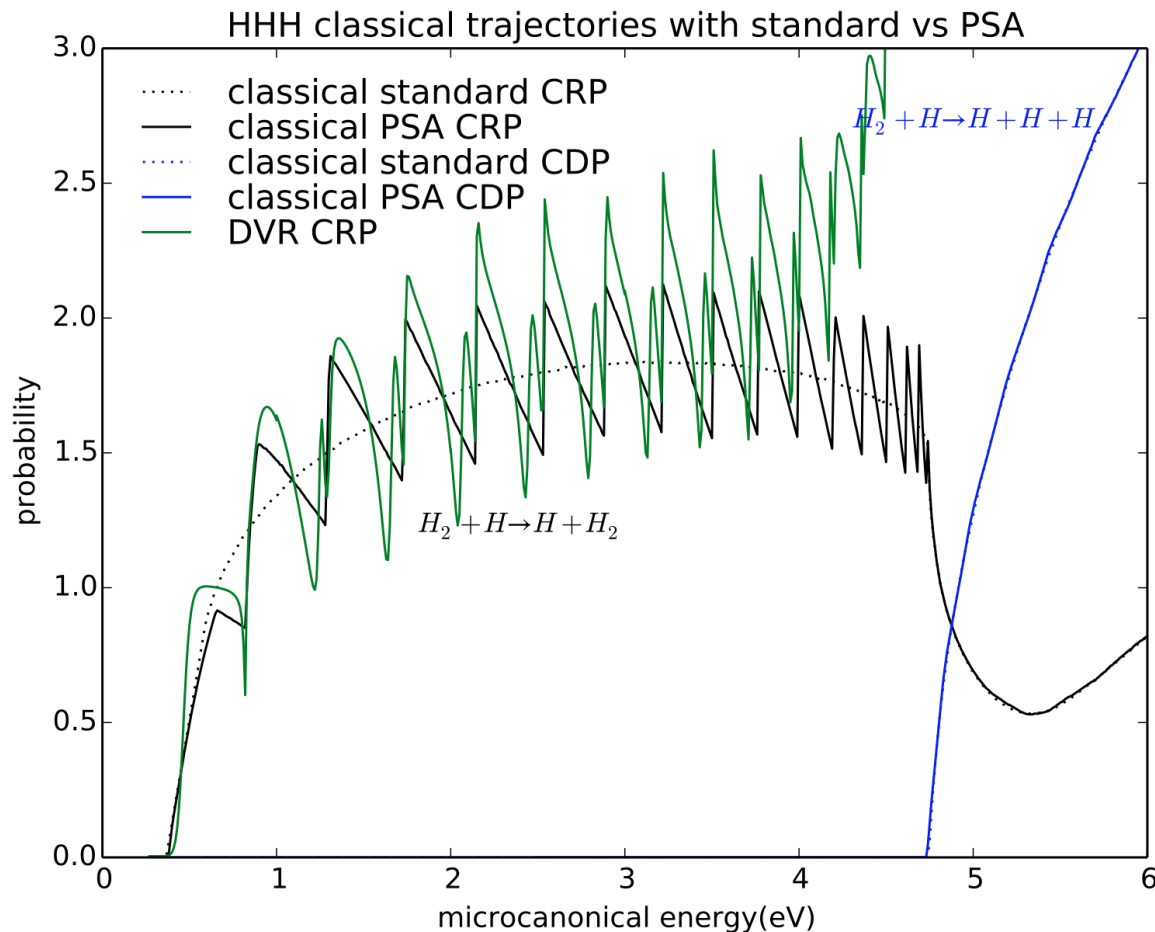
Results for collinear  $H+H_2$  reaction

LEPS trajectories



# Quantum Trajectory Simulation (QTS)

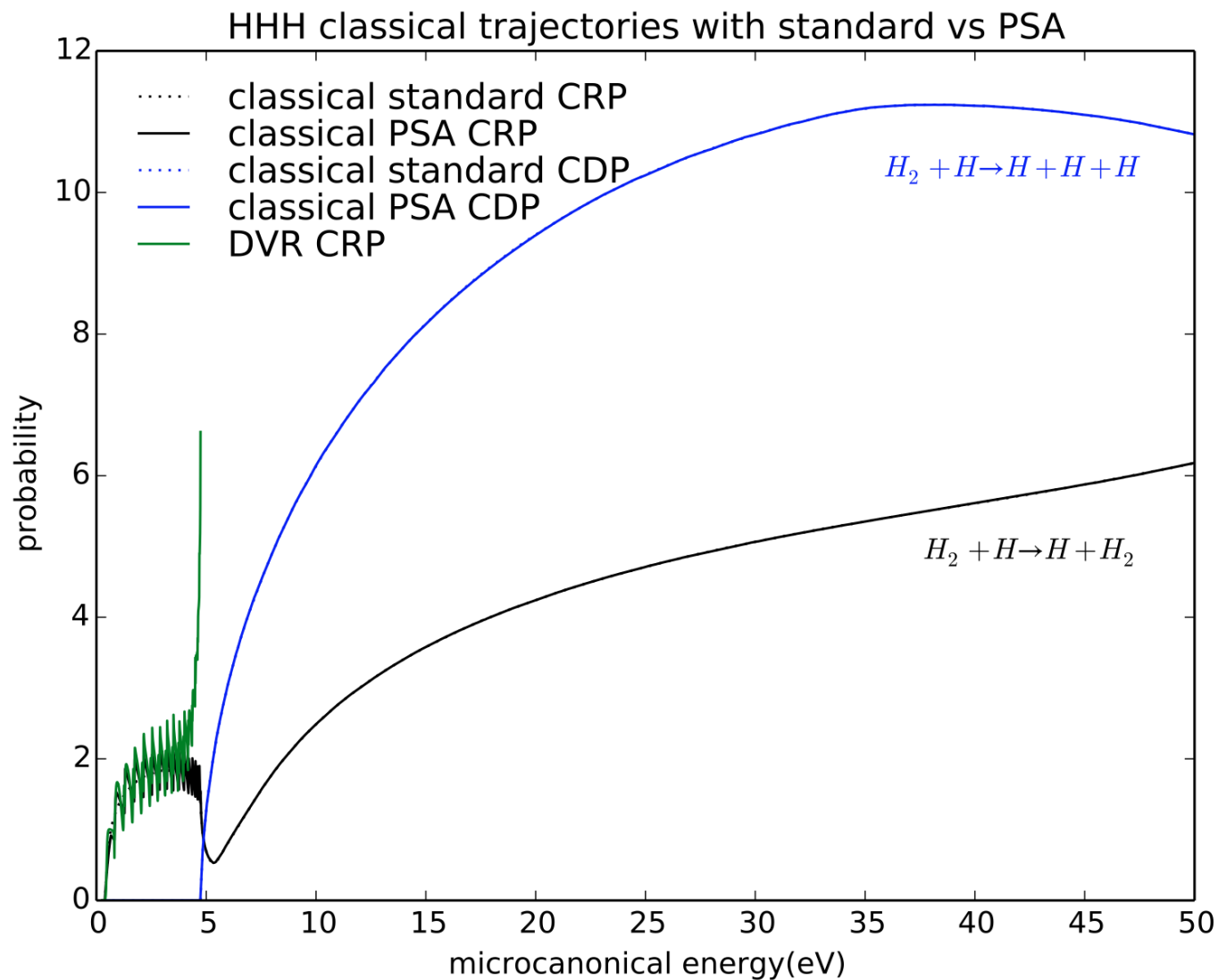
## Results for collinear $H+H_2$ reaction



e 13: In order to compare with other research, well depth is added to the microcanonical energy and the microcanonical energy is represented by eV.

# Quantum Trajectory Simulation (QTS)

## Results for collinear $H+H_2$ reaction



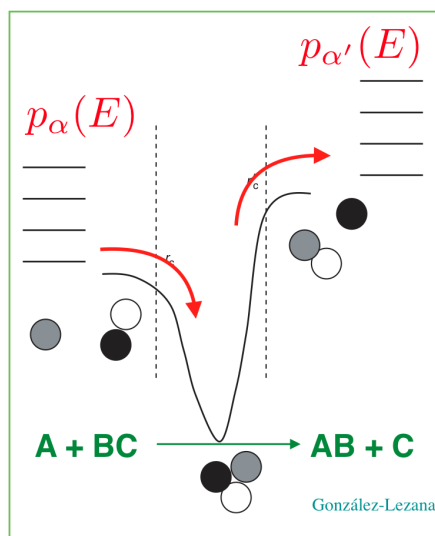


# the capture model (#1)

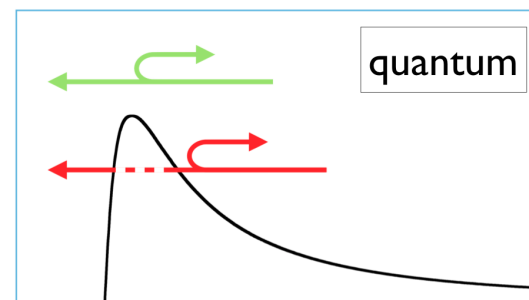
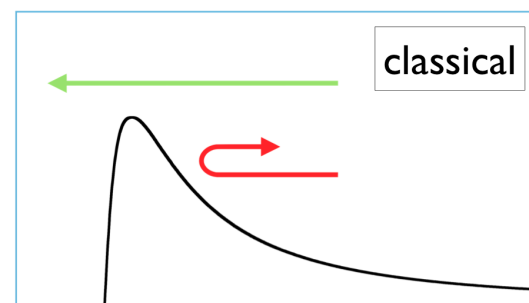
... for long-lived complex reactions

- Assumes all trajectories that cross the barrier actually proceed to form the products.
- Here is what's important at low collision energy:
  - long-range interactions,
  - the capture distance,
  - quantum tunneling & reflection ("suppression"),
  - ... more so as  $T \searrow$ .
- Theoretical approaches:
  - Quantum scattering (with approximations).
  - Statistical theories (quantum or classical):

$$P_{\alpha,\alpha'}(E) = \frac{p_{\alpha}(E) \times p_{\alpha'}(E)}{\sum p_{\alpha''}(E)}$$



## Scattering by a (centrifugal) barrier



# quantum trajectory capture (#1)

## capture distance and protocol

- (1) Propagate the trajectory.
- (2) Stop at “capture distance”  $x_C$
- (3) Get the *capture probability* from the “asymptotic” eq. at  $x_C$ :

$$P_T = \frac{2\hbar k_C}{\hbar k_C + p_C}$$

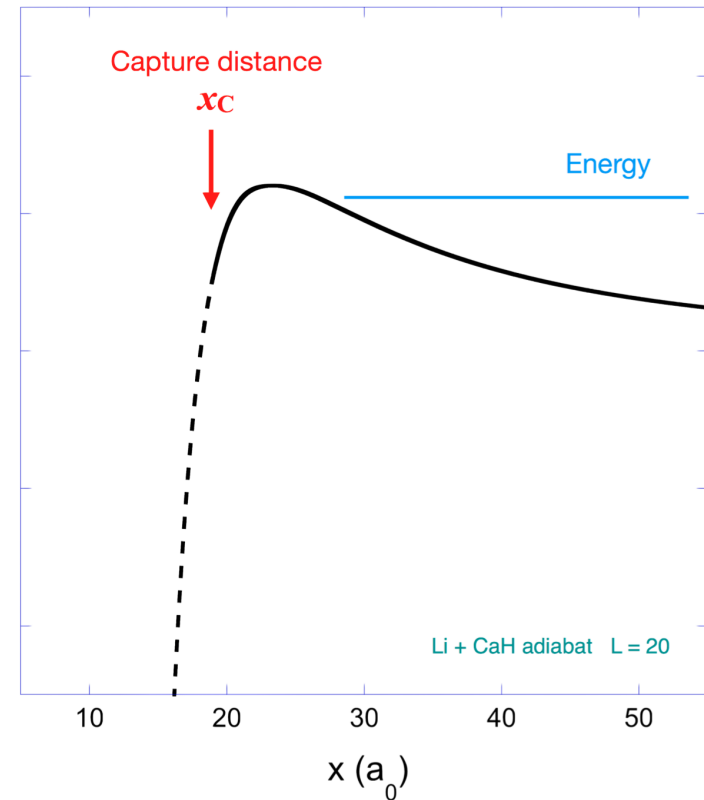
- with

$$p_C = p_{\text{Noether}}(x_C)$$

$$\hbar k_C = \sqrt{2m(E - V(x_C))}$$

Is this protocol valid?

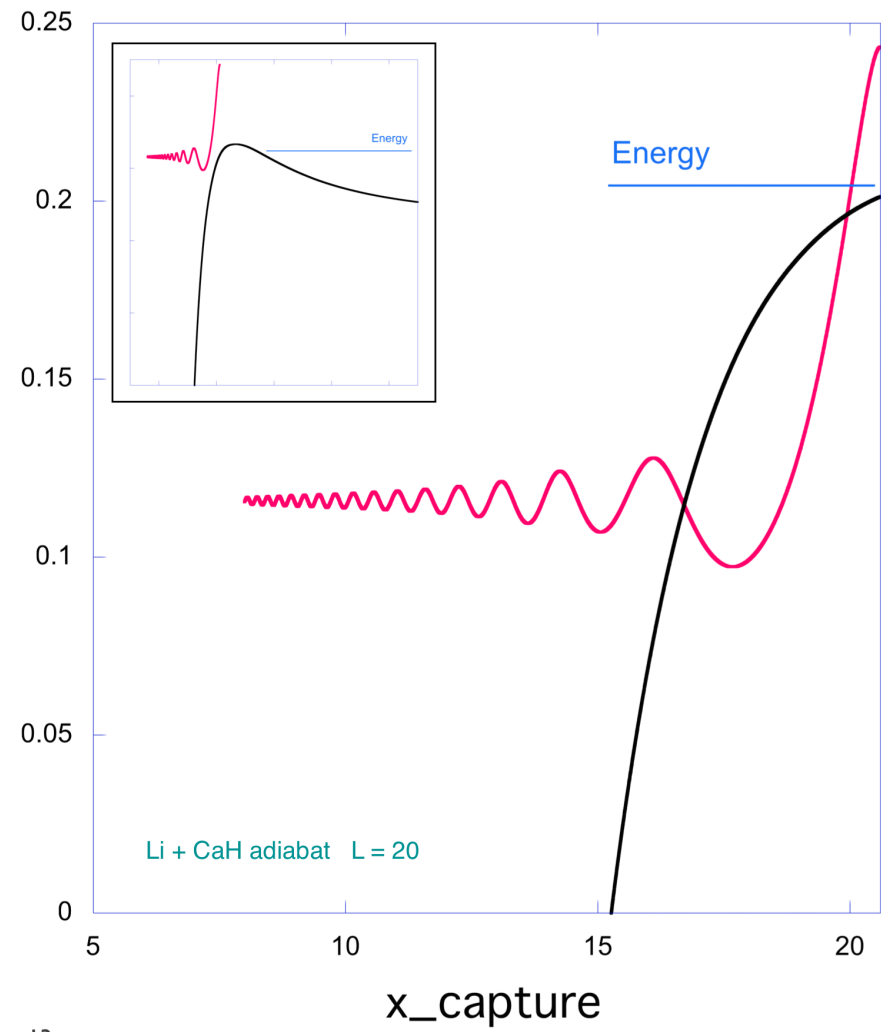
Stopping the propagation at  $x_C$  may introduce large errors???



# quantum trajectory capture (#2)

transmission probability vs capture distance

- Good convergence of probability.
- Can be used to monitor end of propagation.

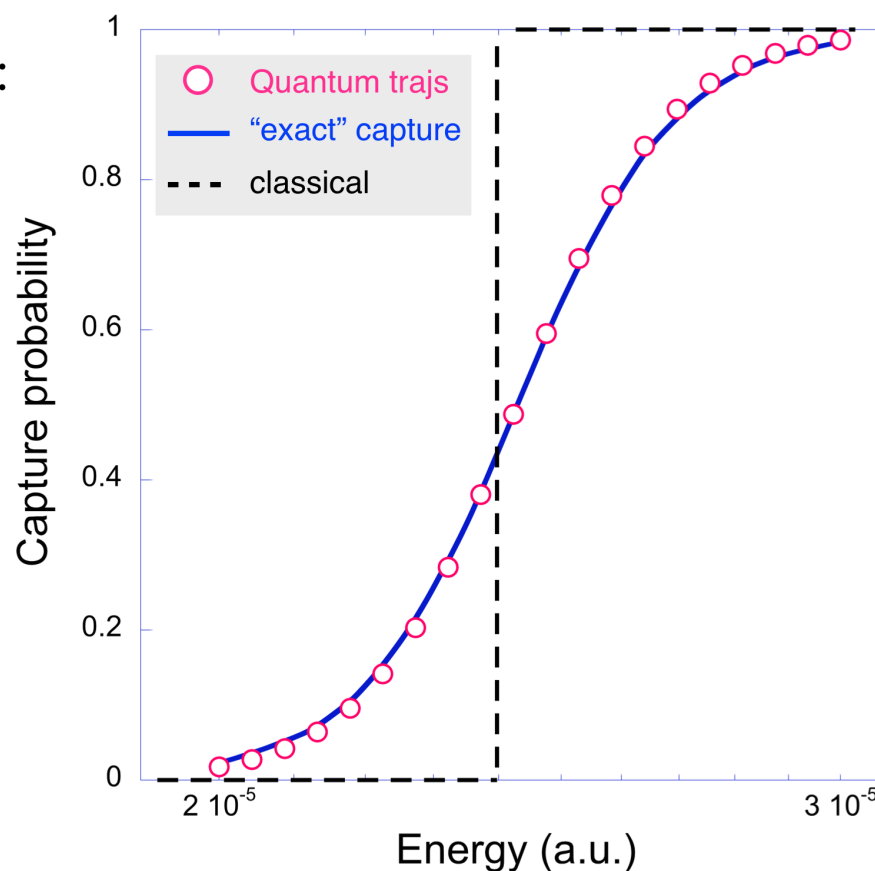


# Adiabatic channel capture on $\text{Li} + \text{CaH} \rightarrow \text{LiH} + \text{Ca}$

capture probability vs energy

T. V. Tscherbul & A. A. Buchachenko,  
*New J. Phys.* **17**, 035010 (2015).

- Centrifugal barrier  $L = 20$ ,
  - barrier top:  $E = 2.4 \cdot 10^{-5}$  a.u.
- Quantum trajectory calculation:
  - capture distance =  $8 a_0$ ,
  - max. distance =  $100 a_0$ ,
  - 20 energy points,
  - CPU (2.4GHz Intel) = 0.6 s.

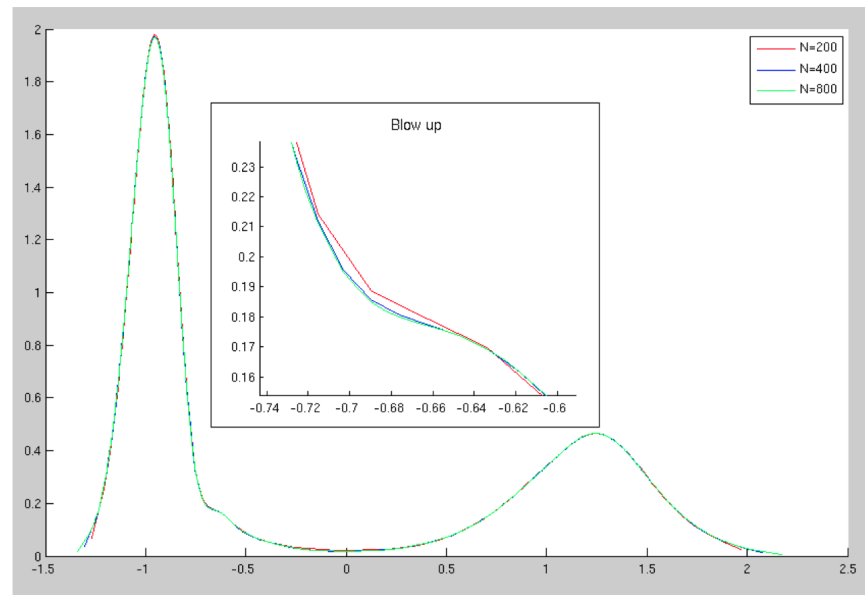




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# Time-Dependent Scattering

## 1D Time-dependent Wavepackets



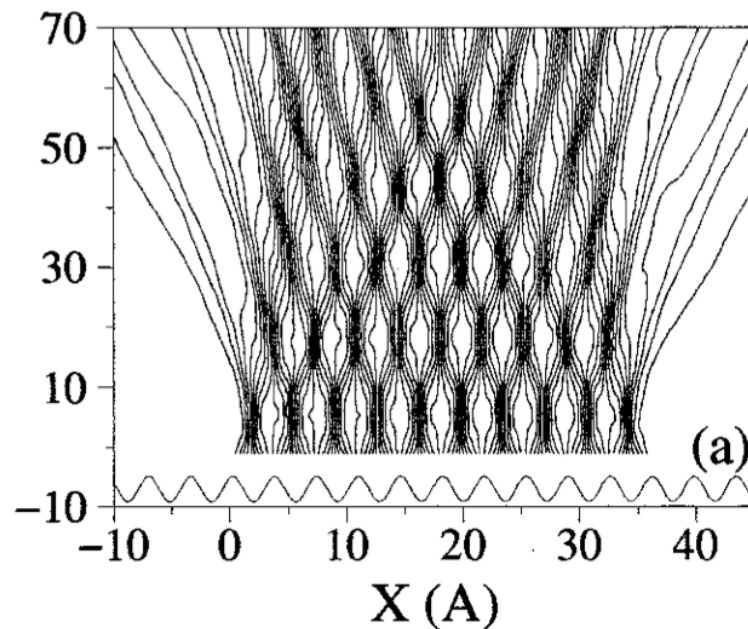
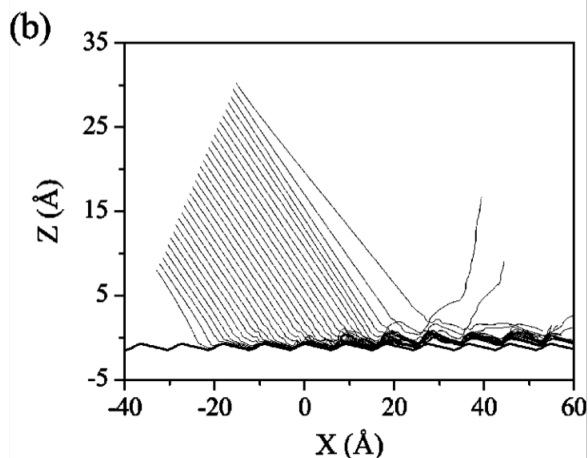
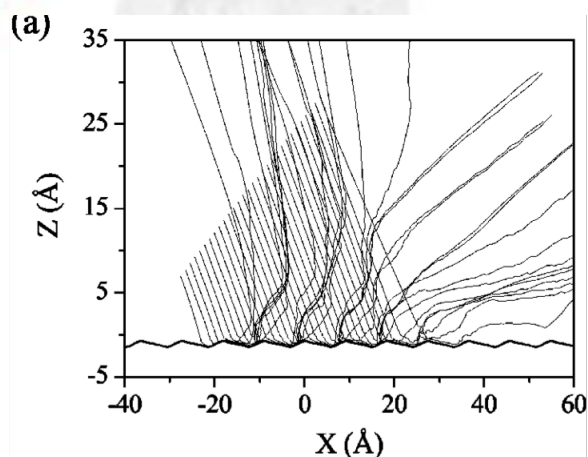
Density  $\frac{1}{x'} = \psi^2$  against  $x$  at  $t = 1$  for  $p_c = 30$ , using  $N = 200, 400, 800$  trajectories, and a time step close to the stability limit.





# Time-Dependent Scattering

## Many-D He-Cu Atom-Surface



• A. S. Sanz and S. Miret-Artés, *J. Chem. Phys.* **122**, 014702 (2005).

• A. S. Sanz, F. Borondo, and S. Miret-Artés, *Phys. Rev. B*, **61**, 7743 (2000).

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  - Yong-Cheng Ou
- Graduate Students:
  - Chaowen Guo

## Computer Resources:

- Texas Tech University
- Texas Advanced Computing Center

## Support:

- Robert A. Welch Foundation
- TRIP Match Fund
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- Gérard Parlant
- Yohann Scribano