Theoretical Chemical Dynamics Studies of Elementary Combustion Reactions

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Objectives

We have two prime objectives:

- **More accurate predictions of reaction rates**
- **A better understanding of chemistry at high pressures**

Today:

- Approaches (some sausage making)
- Preliminary results for developing and validating methods
  Pressure effects: HO_2
  Polyatomic PESs: C_2H_5
  (Immediate target $C_2H_5O_2$; ultimately larger systems)

Predicting Reaction Rates*

Most practical methods are based on classical mechanics

(Quantum dynamics limited to ~ 5 or fewer atoms).

Although the classical approximation can be problematic, it is valid for many applications and at least provides insights in almost all cases.

Accurate potential energy surfaces is crucial:

Dynamics simulations are now done (mostly) with approximate analytical PESs or direct dynamics.

A few highly accurate PESs are available but have been produced at high cost. Many are not flawless.

Direct dynamics commonly done with DFT.

* Particularly nonstatistical rates

Taking Advantage of High-level Electronic Structure Theory

- Quantum chemistry theory, properly applied, can reliably and accurately predict the energetics of many gas-phase reactions

We want methods to:

- **Take full advantage of current quantum chemistry theory**
- **Limit costs**
- **Generate accurate global PESs fit to a minimum number (100's – 1000's) of *ab initio* points**
- **Make direct dynamics feasible for the highest levels of quantum chemistry methods (for which gradients may not be directly available)**

As "blackbox" as possible

Our Approach

Interpolating Moving Least Squares (IMLS)

- Expensive, but cheaper than high level quantum chemistry
- Doesn't need gradients, but can use gradients and Hessians
- Can use high-degree polynomials

Enhancing efficiency:

- Optimally place minimum number of points
- Weight functions
- Reuse fitting coefficients
- Use zeroth-order PES and fit differen**ce**
- Other techniques

We have demonstrated its utility for several atoms (CH_2, HO_2, H_2O_2, CH_4);* we are now focusing on larger systems.

* Supported by DOE

IMLS Methods

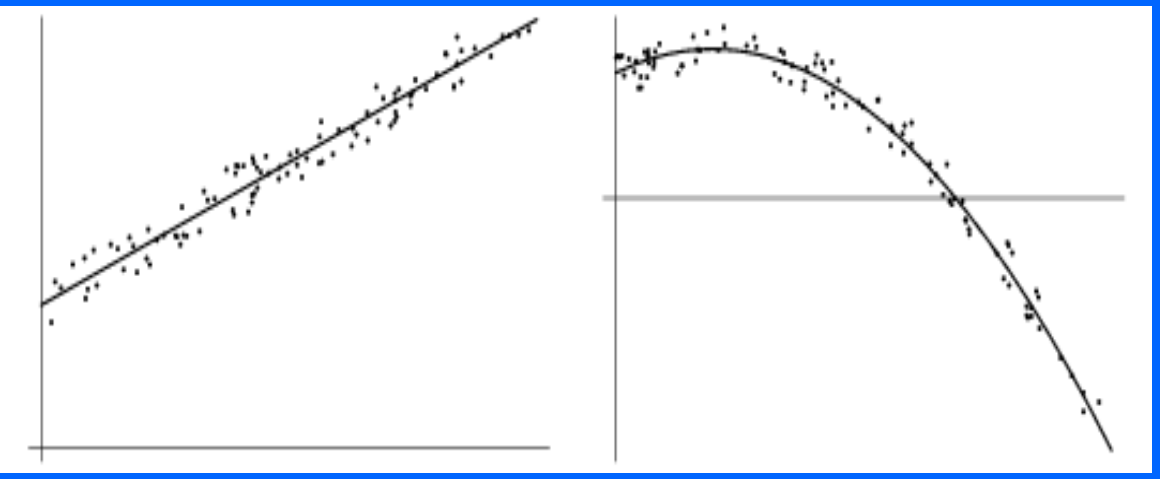
Two general approaches:

- **Global driver: uses energy or coordinate ranges**
  - **Start with "seed" points to provide crude shape**
  - **Add points determined automatic point-placement method – most "value" for each point and allows fitting without "holes" and other flaws.**

- **Trajectories driver: Determine dynamically accessible configuration space & point distribution**
  - **Accelerated direct dynamics**
  - **"on the fly" fitting**

I'll describe a few of the more important aspects of the methods

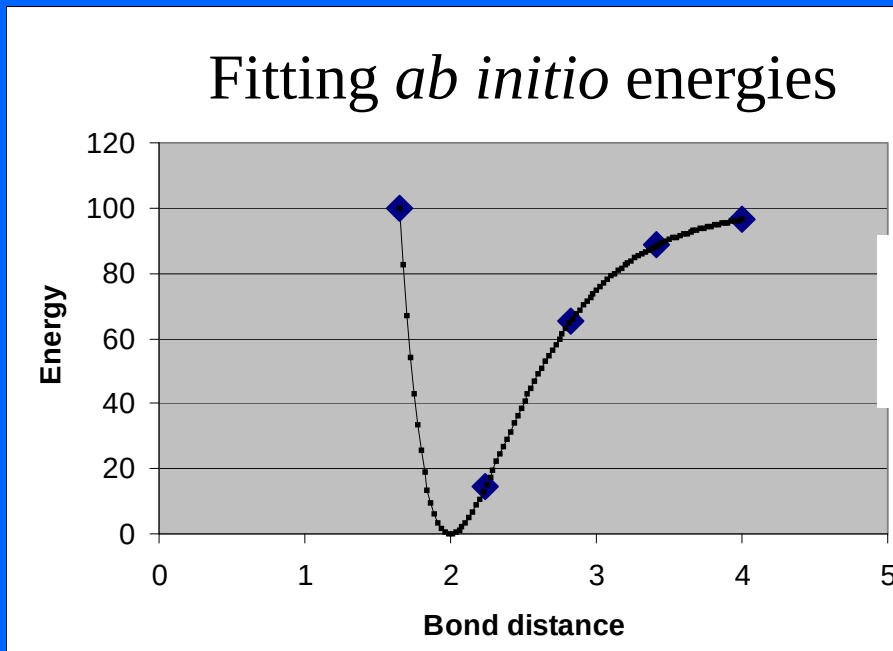
Least-Squares Fitting



Usual applications are for data with experimental errors & trends following known functional forms.

- ***Ab initio* energies do not have random errors**
- **A PES does not have a precisely known functional form**

  ⇒ the energy points lie on a surface of unknown shape
- **Thus, fit with a general basis set (e.g., polynomials)**
- **Basis functions closely resembling the true function provide a more compact representation**



Weighted least squares equations

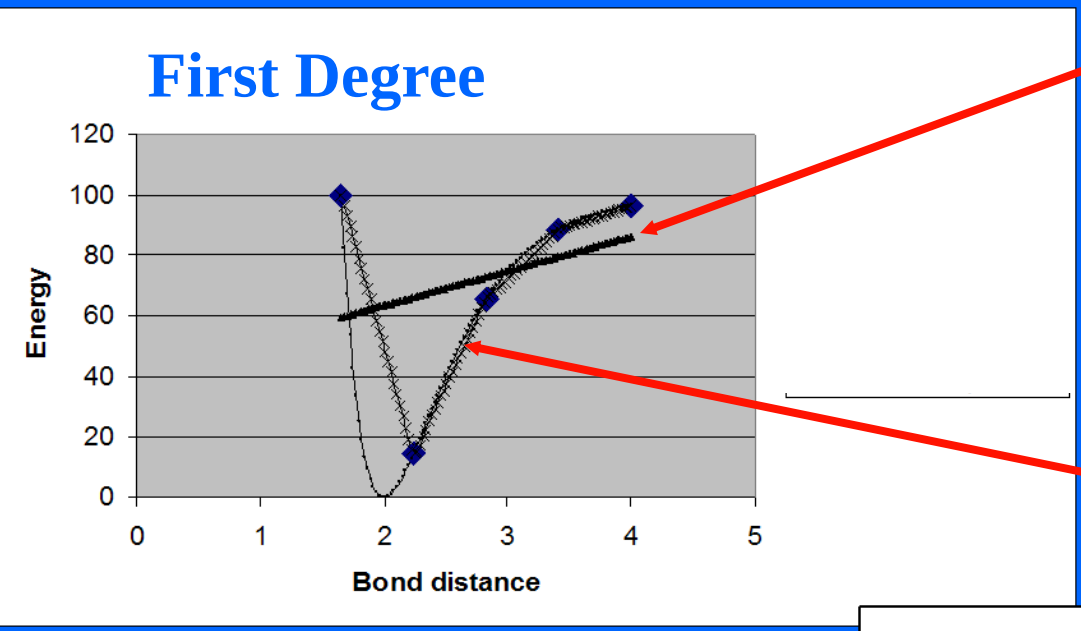
$$V_{fitted}(\mathbf{z}) = \sum_{j=1}^{m} a_i^T(\mathbf{z})\, b_i(\mathbf{z})$$

$$D[V_{fitted}(\mathbf{z})] = \sum_{j=1}^{N} w_i(\mathbf{z})[V(\mathbf{z}^{(\mathbf{i})}) - V_{fitted}(\mathbf{z}^{(\mathbf{i})})]^2$$

$$B^T W(z)\, B\, a(z) = B^T W(z) V$$

$$\mathbf{B} = \begin{pmatrix} b_1(\mathbf{z}^{(1)}) & b_2(\mathbf{z}^{(1)}) & \cdots & b_m(\mathbf{z}^{(1)}) \\ b_1(\mathbf{z}^{(2)}) & b_2(\mathbf{z}^{(2)}) & \cdots & b_m(\mathbf{z}^{(2)}) \\ \vdots & \vdots & \ddots & \vdots \\ b_1(\mathbf{z}^{(n)}) & b_2(\mathbf{z}^{(n)}) & \cdots & b_m(\mathbf{z}^{(n)}) \end{pmatrix}$$

Weighted vs. standard least squares



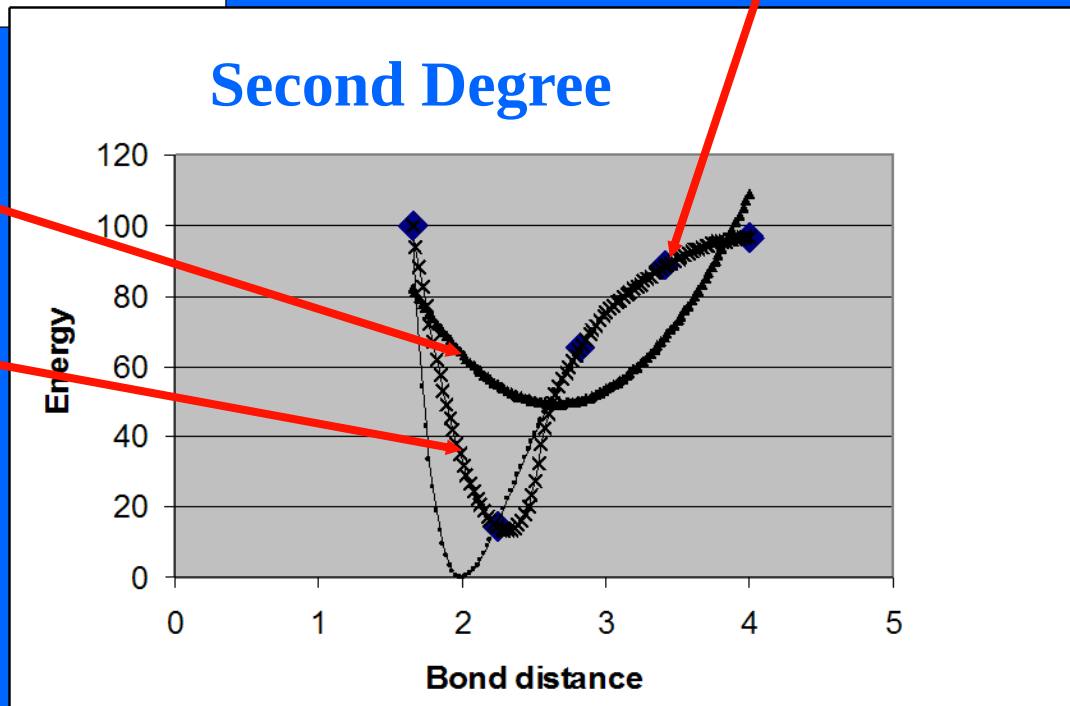
Standard, first degree

Weighting causes IMLS to fit perfectly at each point

IMLS, first degree

Standard, second degree

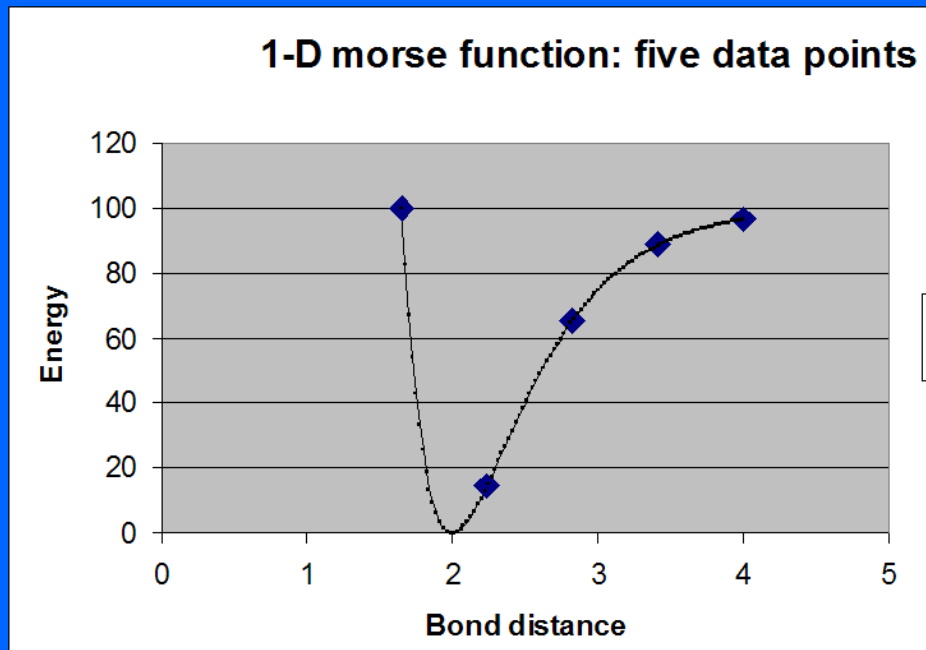
IMLS, second degree



Optimum Point Placement

- We want to do the fewest number of *ab initio* calculations
- A non-uniform distribution of points is best
- We can use the fact that IMLS fits perfectly at each point to determine where to place points for the most accurate fit using the fewest possible points
- Use fits of different degree IMLS fits

Illustration: 1-D
Morse potential
5 "seed" points
arbitrarily placed



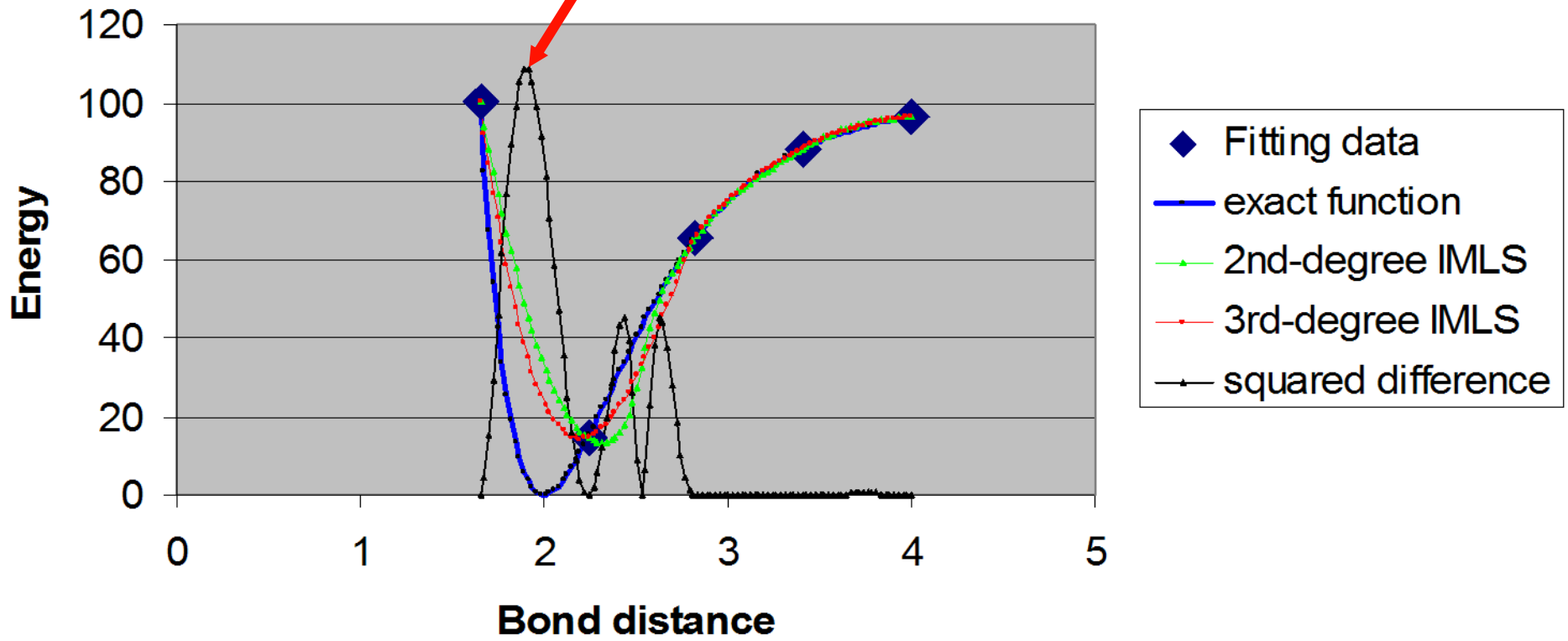
Automatic Point Placement: 1-D Illustration

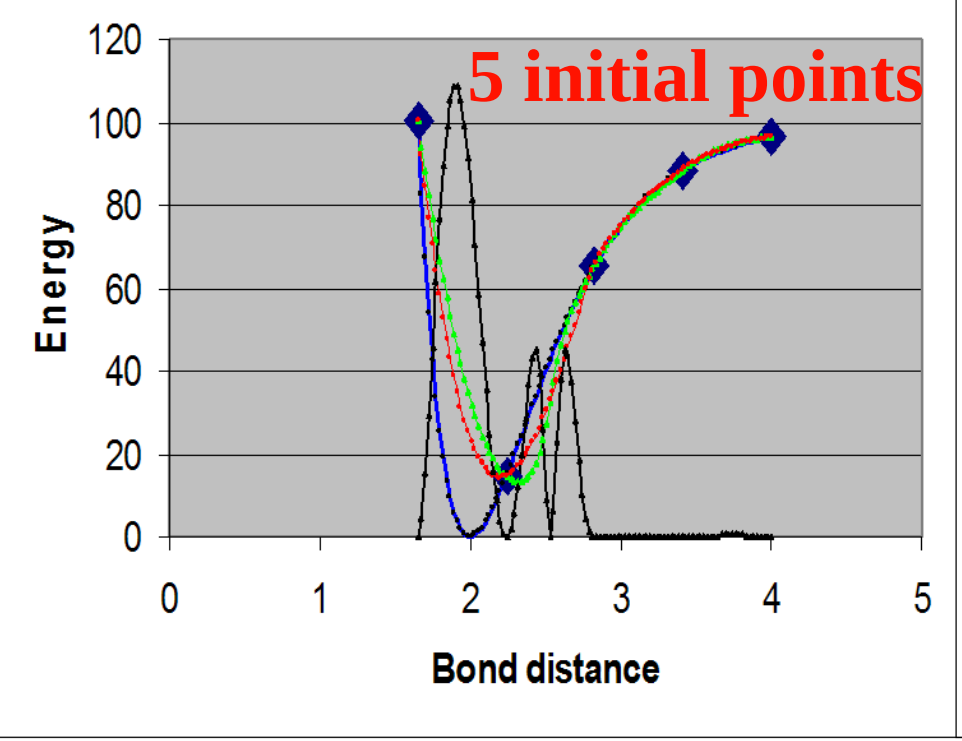
Start with 5 uniformly placed points

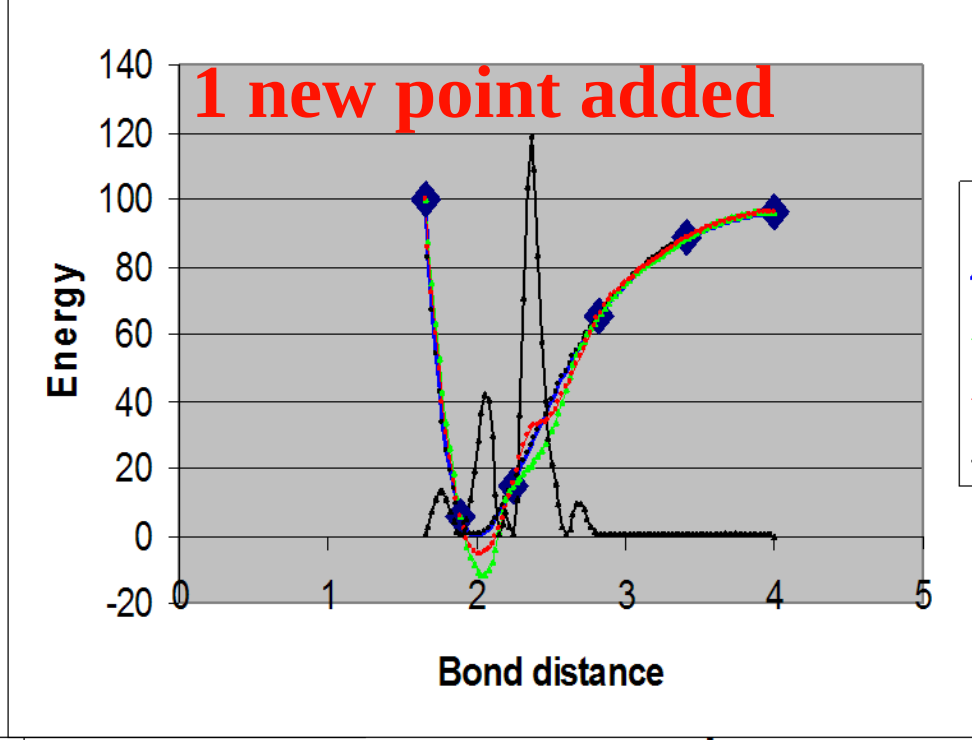
Fit with 2nd & 3rd degree IMLS

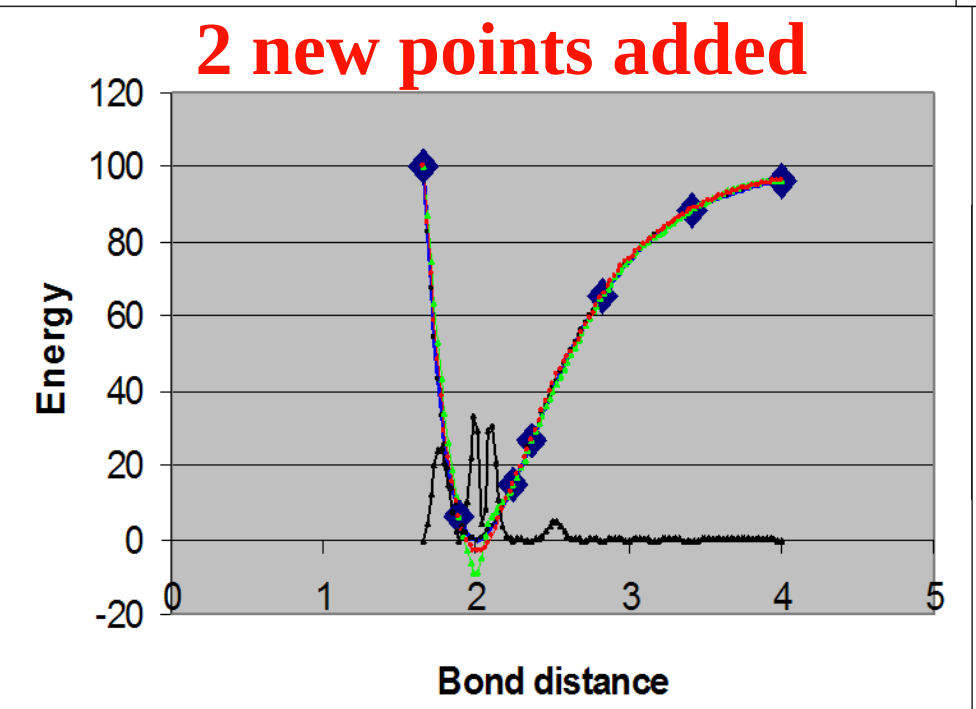
Add new point where they differ the most

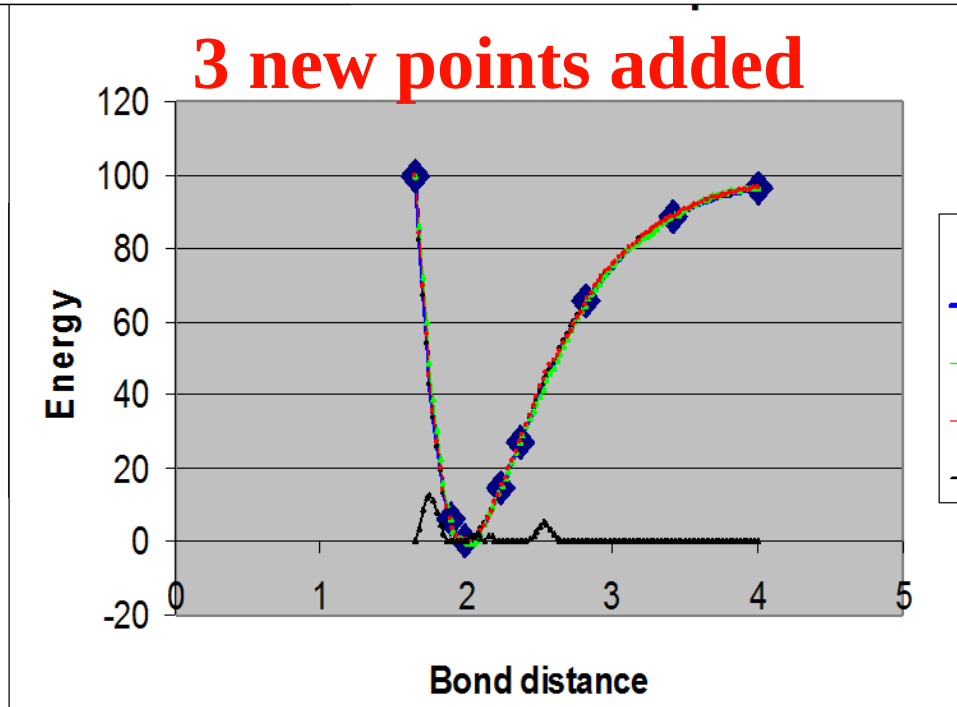
Squared difference indicates where new points are needed




5 initial points
Energy
Bond distance
120
100
80
60
40
20
0
0
1
2
3
4
5

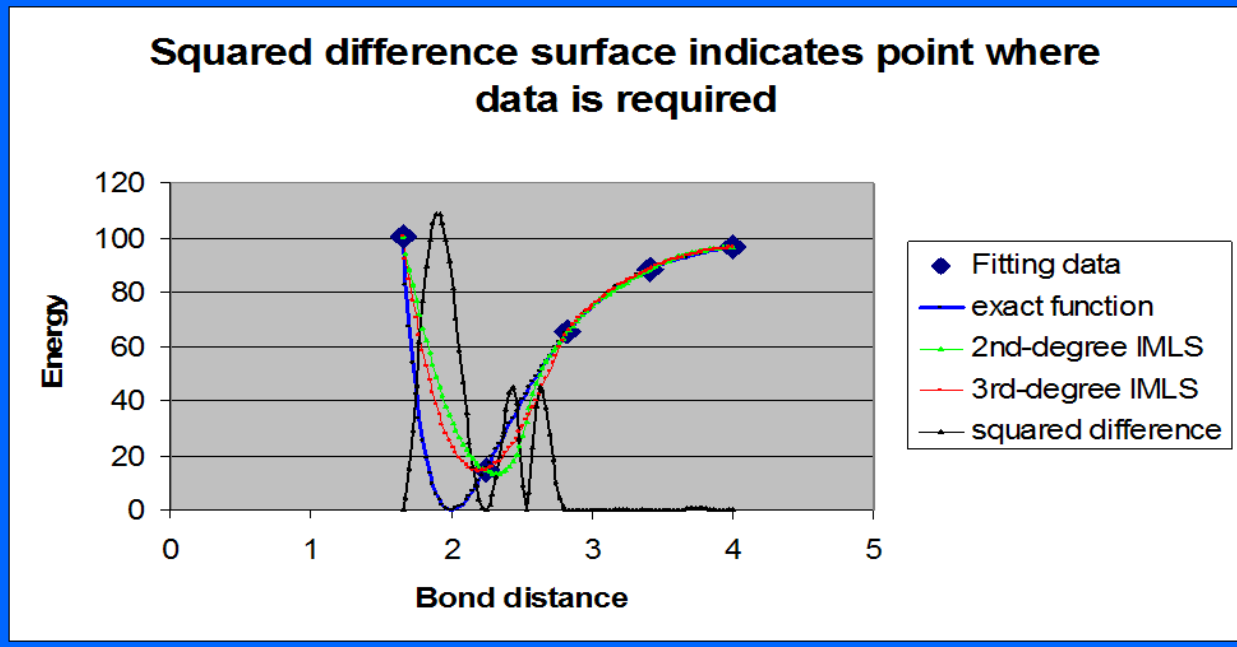

1 new point added
Energy
Bond distance
140
120
100
80
60
40
20
0
-20
0
1
2
3
4
5


2 new points added
Energy
Bond distance
120
100
80
60
40
20
0
-20
0
1
2
3
4
5


3 new points added
Energy
Bond distance
120
100
80
60
40
20
0
-20
0
1
2
3
4
5

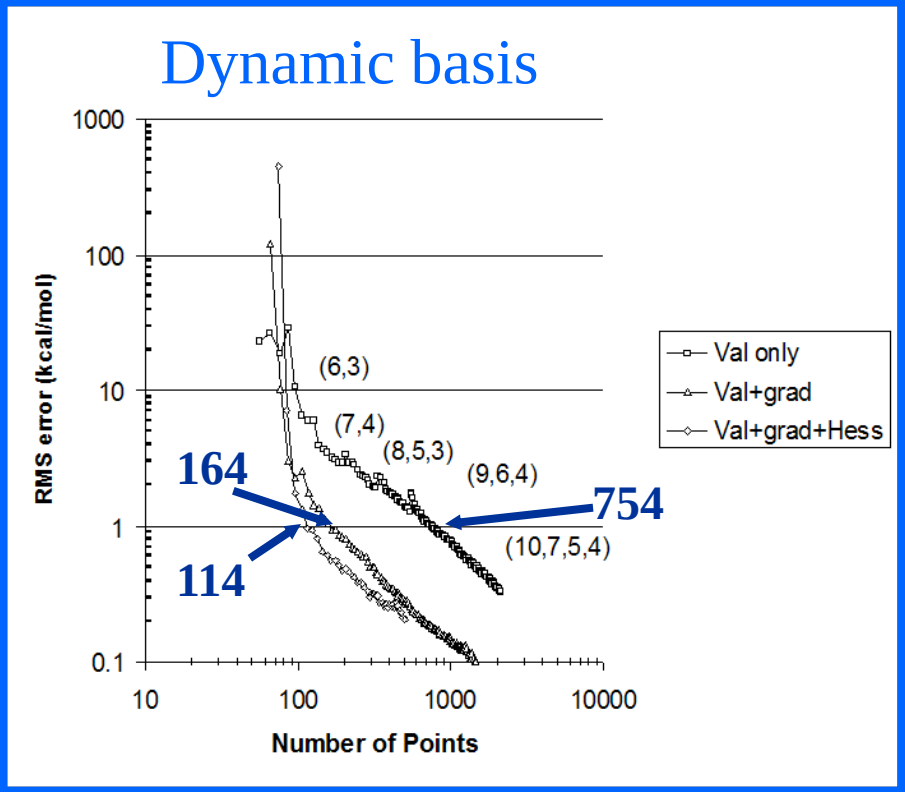
Automatic point selection

- We can find the optimum place to add each *ab initio* point – high fidelity to the "true" surface – no "holes"
- Trivial in 1-D
- Also Practical in many dimensions although a bit difficult



- Define negative of the squared-difference surface
- We can use efficient minimization schemes such as conjugate gradient to find local minima

Dynamic Basis Procedure



Kuhn *et al*. H_2O_2 PES*

[JCP 111, 2565 (1999)]

Fit up to 100 kcal/mol

A min. of 591 pts. would be needed if we started with the (10,7,5,4) basis. <u>We started with 108 points.</u> Convergence also much faster

RMS error based on randomly selected test points

Avoids including points in the seed data that are not optimally located.

Start with very small initial grid of points & use automatic surface generation with a small basis, successively increasing the basis as points are added.

IMLS & Classical Trajectories
Preliminary Applications

Two different approaches:

- **Using IMLS in direct dynamics**
- **Using classical trajectories to grow a PES (under development)**

In both cases IMLS "intercepts" *ab initio* PES calls & the electronic structure code is called only if necessary (based on error estimate)

Effects of extreme temperatures & pressures on elementary combustion reactions

A better knowledge of combustion chemistry at high pressures can facilitate the design of ultra-lean fuel, high-pressure engines.

This is an area of chemistry that is relatively unexplored
– experimentally the measurements are difficult
– little theoretical effort has been expended.
– Even for relatively simple reactions it is often difficult to model the reactions or interpret experimental rate data as functions of pressure [For example: $H + O_2 + M \rightarrow HO_2 + M$]

Fernandes, Luther, Troe, & Ushakov Phys. Chem. Chem. Phys. 10, 4313 (2008).
Sellevåg, Georgievskii, & Miller, J. Phys. Chem. A 112, 5085 (2008).

HO_2 in Ar bath

- HO_2 is one of the critical reaction intermediates in combustion because
  - its dissociation is chain branching
  - its reactions HO_2+X (not chain branching) lead to low-T, high-P combustion

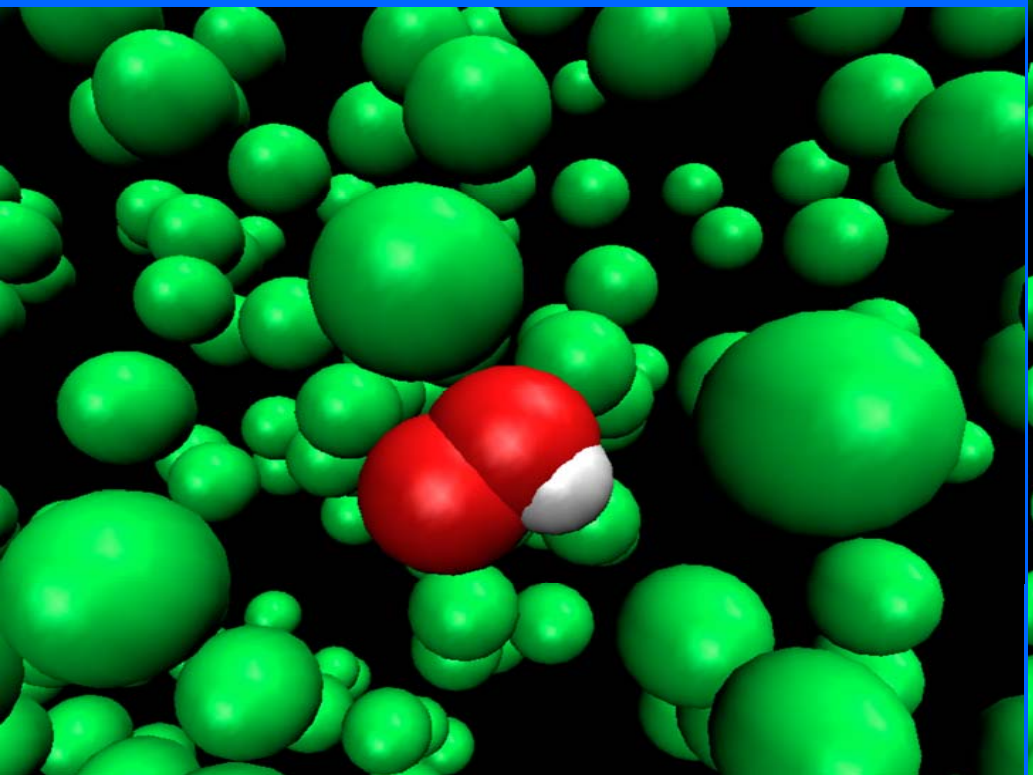
- Frequently studied both experimentally and theoretically but not at very high pressures

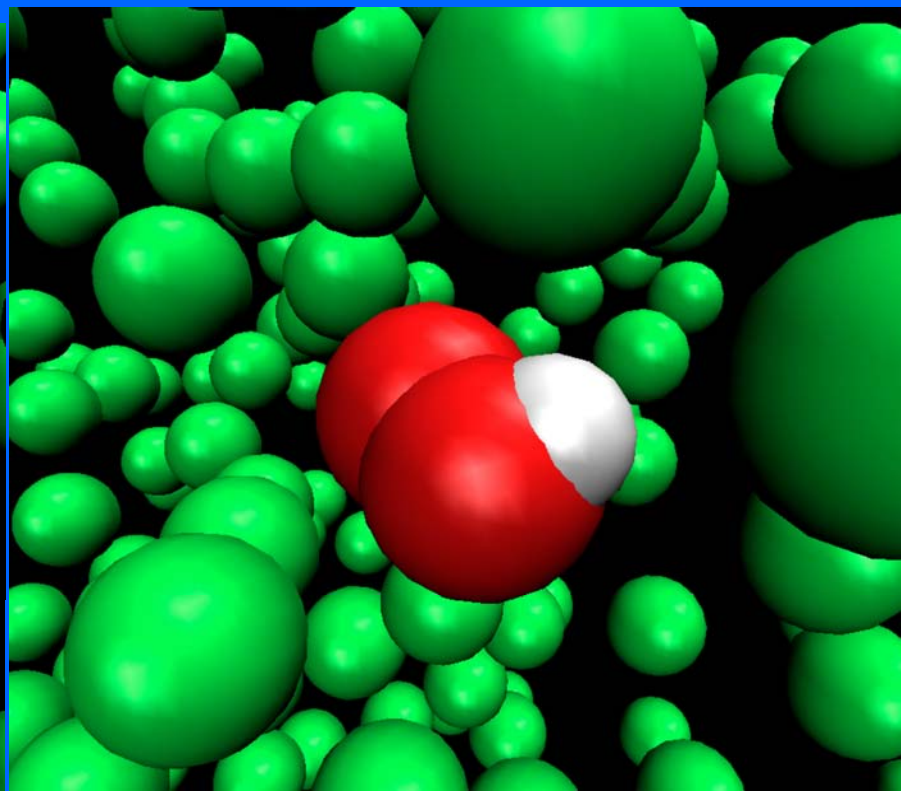
- HO_2/Ar-buffer-gas MD study can examine
  - multiple mechanisms to dissociation/relaxation (e.g., chaperon mechanism)
  - breakdown in isolated bimolecular collision assumption
  - exponential down model
    (collisional vibrational excitation/relaxation)

Our initial studies are being done with an approximate analytical PES & with a new approach to the dynamics calculations

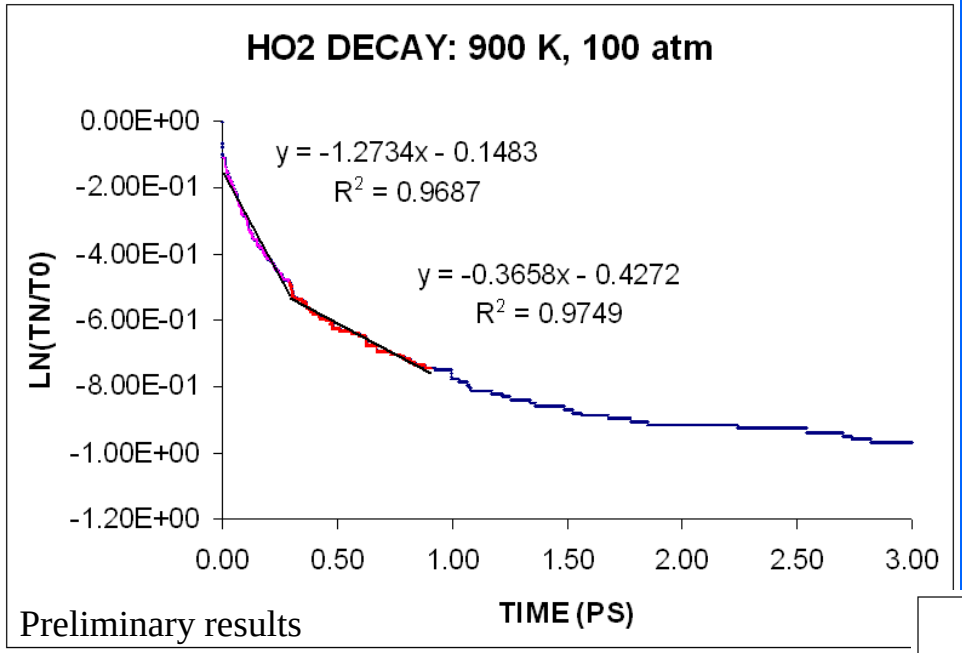
HO_2 in Ar bath

We are performing MD simulations of HO_2 in an Ar bath as functions of T & P over the ranges 400 K – 900 K & 100 atm – 900 atm, respectively. The HO_2 is placed in a sphere, with soft reflecting walls, filled with Ar. The Ar-Ar interactions are Lennard-Jones forces and the HO_2 potential is the DMBE approximate PES due to Varandas *et al*. This PES was selected because it allows us to perform a large number of preliminary studies.





HO_2 Unimolecular Decay in Ar-buffer gas

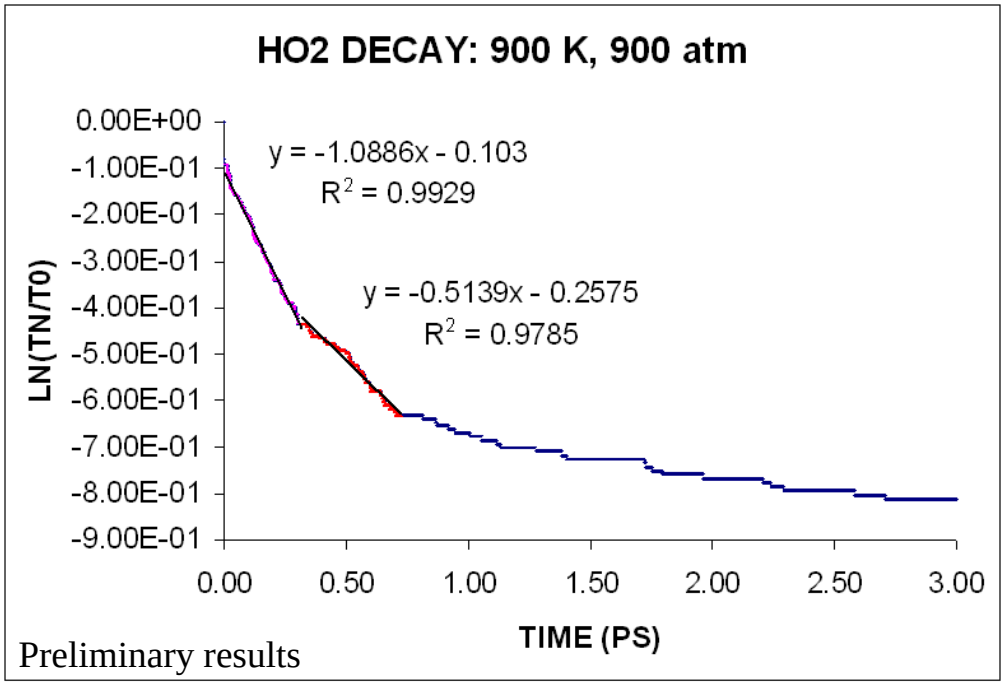


Preliminary results

Biexponential decay would suggest separate decay mechanisms – non-statistical (dynamical) effects

We are looking into this but beyond the behavior of the decay curves we have yet to see a causes

Others have seen similar decay, but discovered no cause ➔



Preliminary results

HO_2 Complexes in H + O_2 Collisions

Lendvay *et al*. Chem. Phys. 349, 181 (2008).

They examined individual trajectories, found what they charactrized as instantaneous and slow dissociations, but the transition between the two to be completely smooth – no boundary to suggest two different mechanisms.

But note that the shapes of some of their curves suggest a stretched exponential ➔

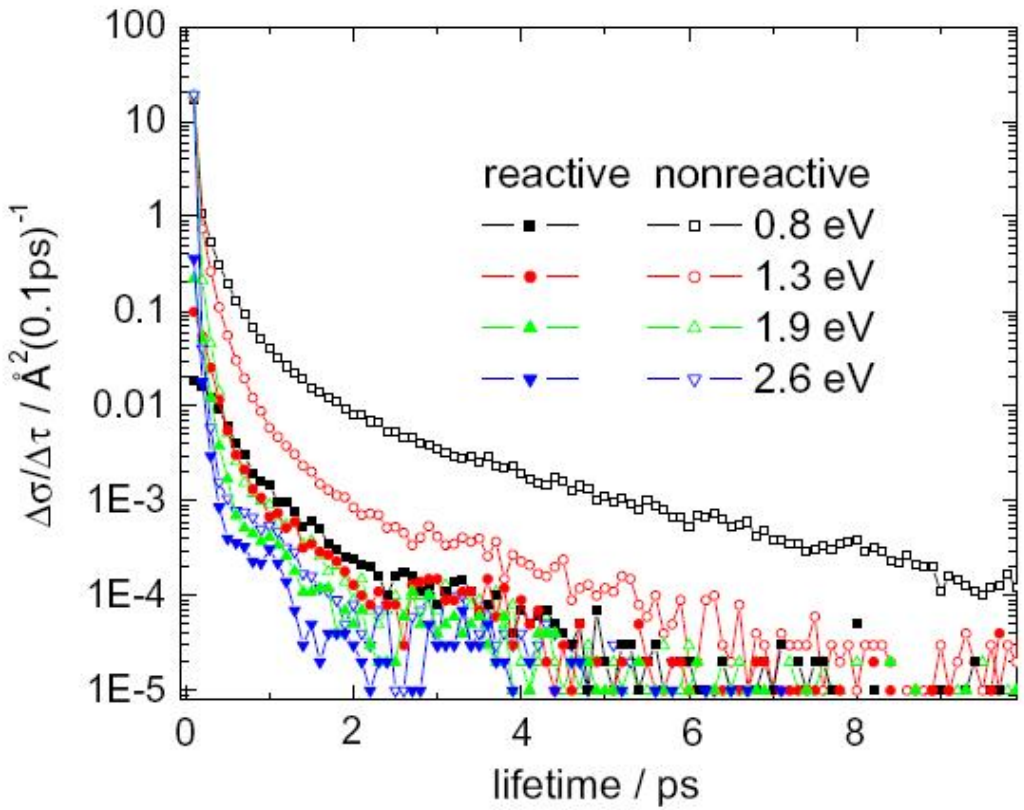


Fig. 5. Lifetime distributions in terms of contributions to the reactive and nonreactive cross sections at initial translational energies 0.8, 1.3, 1.9 and 2.6 eV.

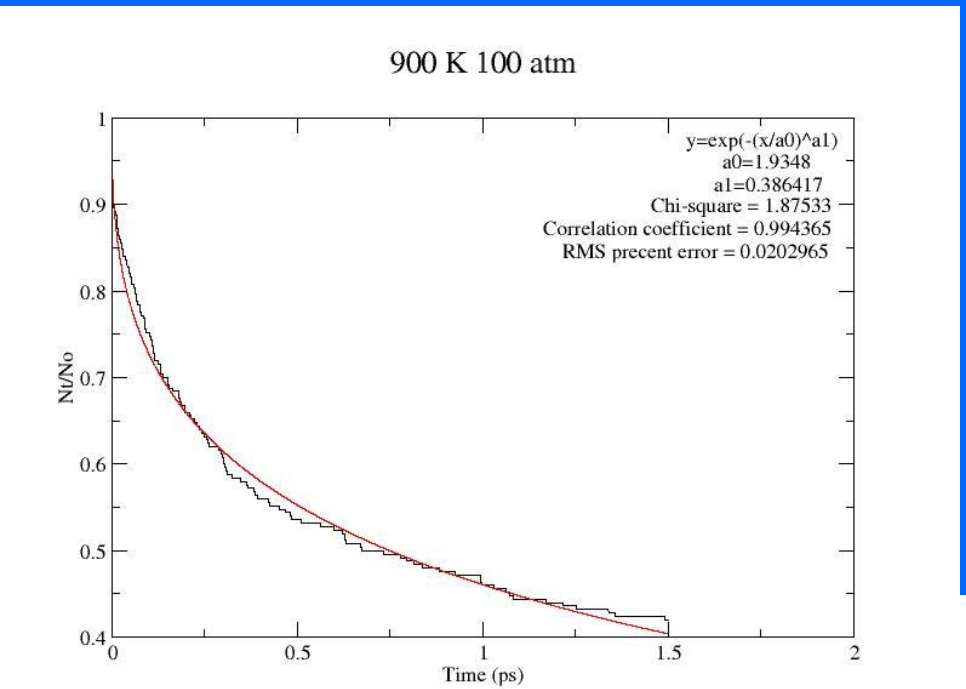
Stretched exponential

- We have attempted fits with the Kohlrausch–Williams–Watts function (aka stretched exponential):

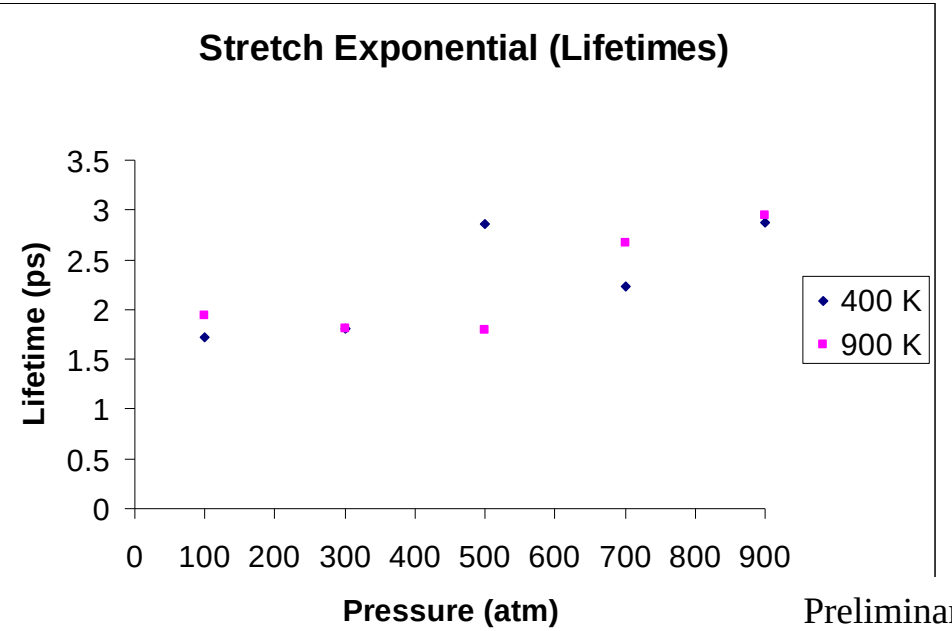
  $$y=\exp(-(t/\tau)^{**}\beta)$$

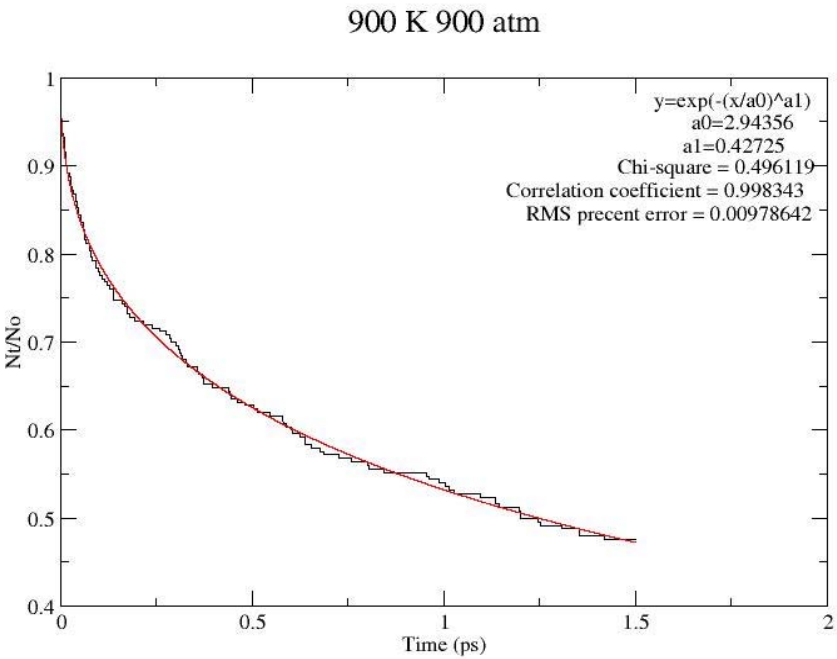
  - τ : The long time, or macroscopic relaxation time. This is referred to as fitting parameter a0.
  - β exponent, referred to as fitting parameter a1.
- The fitting was applied to the 400 K: 100 atm, 300 atm, 500 atm, 700 atm, 900 atm data sets
- The x ordinate refers to time
- The y ordinate refers to the ratio N_t/N_0
  - N_t : the number of unreacted NO_2 at time t
  - N_0: the total number of NO_2 in the ensemble

Stretched exponential fits of decay curves



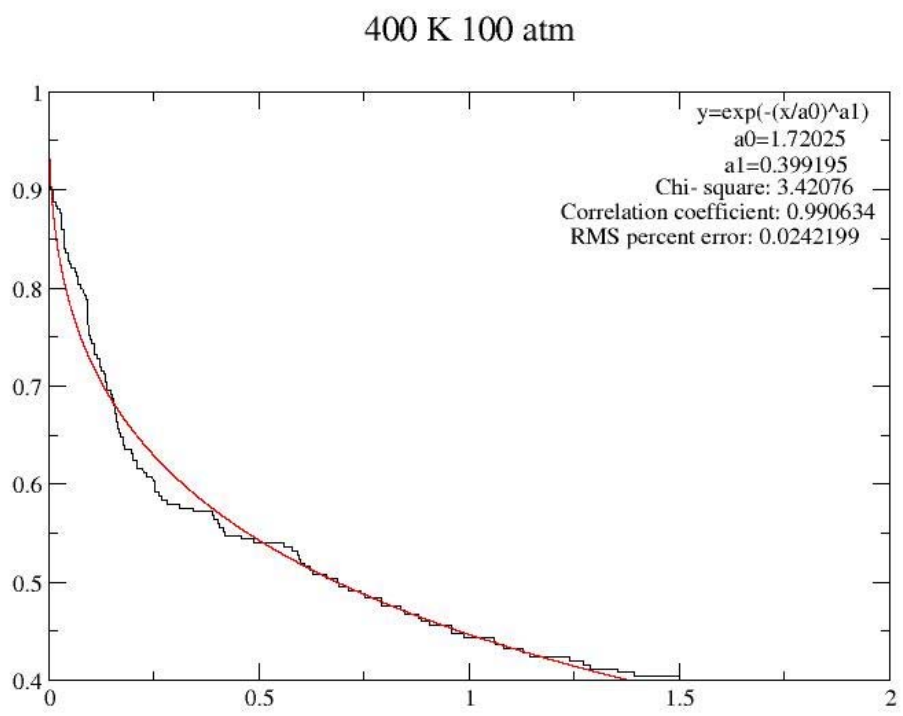
Some of the curves are well fit by the stretched exponential, and the fitting parameter indicates that the lifetime increases with pressure, but not all the curves can be fit by this function – see next slide





Preliminary results

Stretched exponential fits of decay curves



Preliminary results

Clearly not a good fit.

Insufficient statistics?

Simply different behavior?

Our analysis is incomplete. We will also be performing simulations using our IMLS PES & the XXZLG PES.

Recent PESs for HO_2

- MRCI PES of Xu *et al.* (known as XXZLG)[1] improves on other ab initio PESs going back to the well-known Melius and Blint[2] PES
- XXZLG: >18,000 spline-fitted points

  (*ab initio*: aug-cc-pVQZ basis set)

[1] C. Xu, D. Xie, D. H. Zhang, S. Y. Lin, and H. Guo, J. Chem. Phys. **122,** 244305 (2005).
[2] C. F. Melius and R. J. Blint, Chem. Phys. Lett. **64,** 183 (1979).

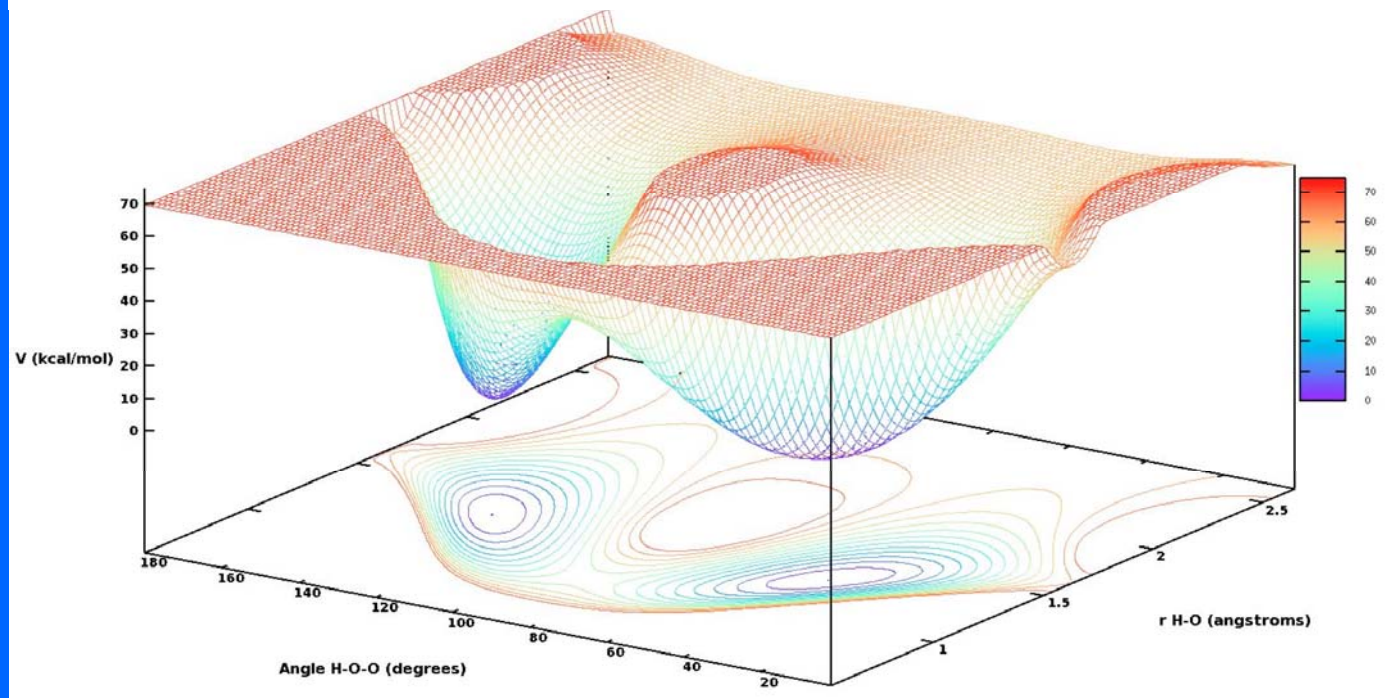
We have developed a new, highly accurate IMLS PES for HO_2 MRCI, Complete basis set (CBS) extrapolation, correlation of all electrons (no frozen core approximation), 18 electronic states included in dynamic weighting (Molpro option), includes Renner-Teller coupling region of linear spatial configuration

1609 *ab initio* points (for somewhat smaller configuration range than XXZLG)

New IMLS PES for HO_2

- Dissociation energy: $HO_2 \longrightarrow H+O_2$
  - Experiment: D_0 = 16790+-13 cm^{-1} IMLS: 16717 cm^{-1}
- Subsequent dissociation energy: $O_2 \longrightarrow O + O$
  - Experiment: D_0 = 41269.1+-0.2 cm^{-1} IMLS: 41282.8 cm^{-1}

Surface plot at equilibrium O-O distance in HO_2



New HO_2 PES

The IMLS PES required only 1609 points (energy & gradients) generated automatically with no convergence problems

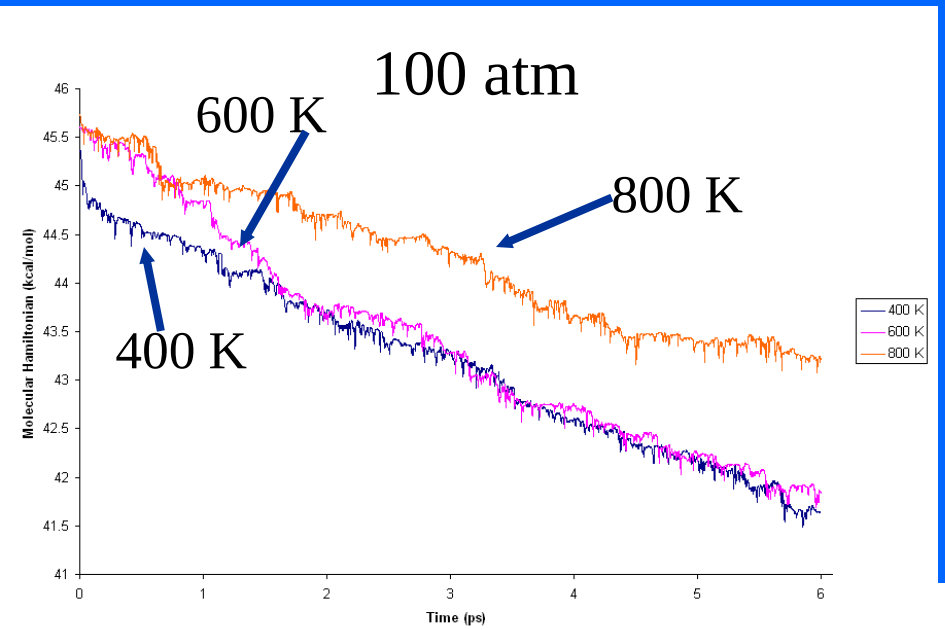
Excellent geometries:

Geometry	rOO (bohr)	rOH (bohr)	Theta (degrees)
IMLS	1.8315	2.5113	104.21
expt	1.8344(38)	2.5144(16)	104.29(31)

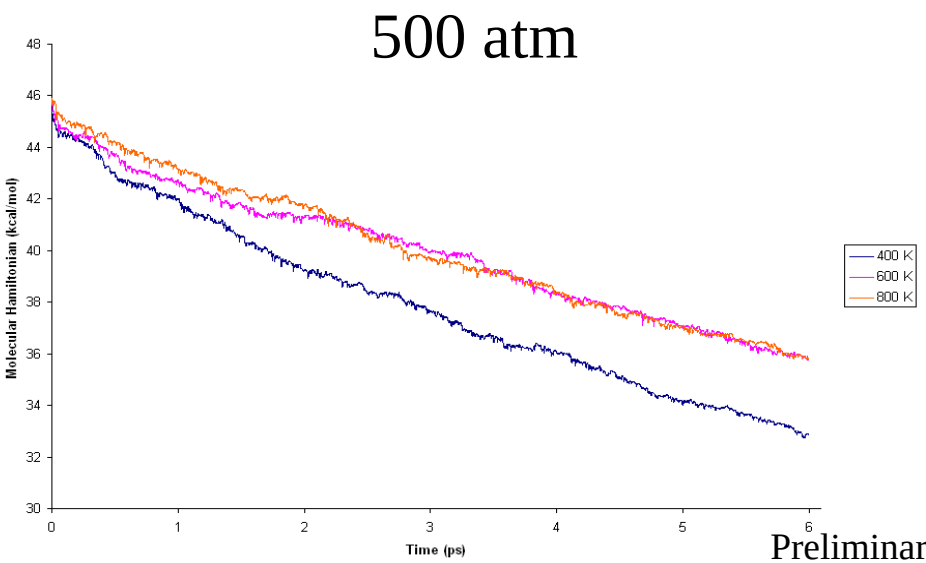
Excellent frequencies:

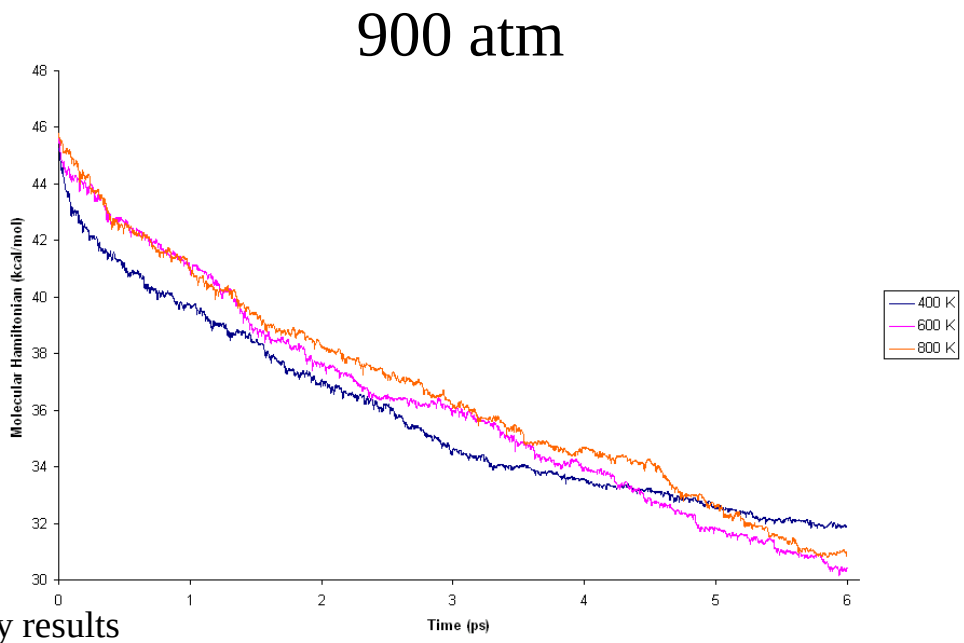
Vibrational level	(0,0,1)	(0,1,0)	(1,0,0)
IMLS	1101.7	1390.2	3439.4
expt	1097.6	1391.8	3436.2

Collisional Relaxation of HO2: Results for our IMLS PES



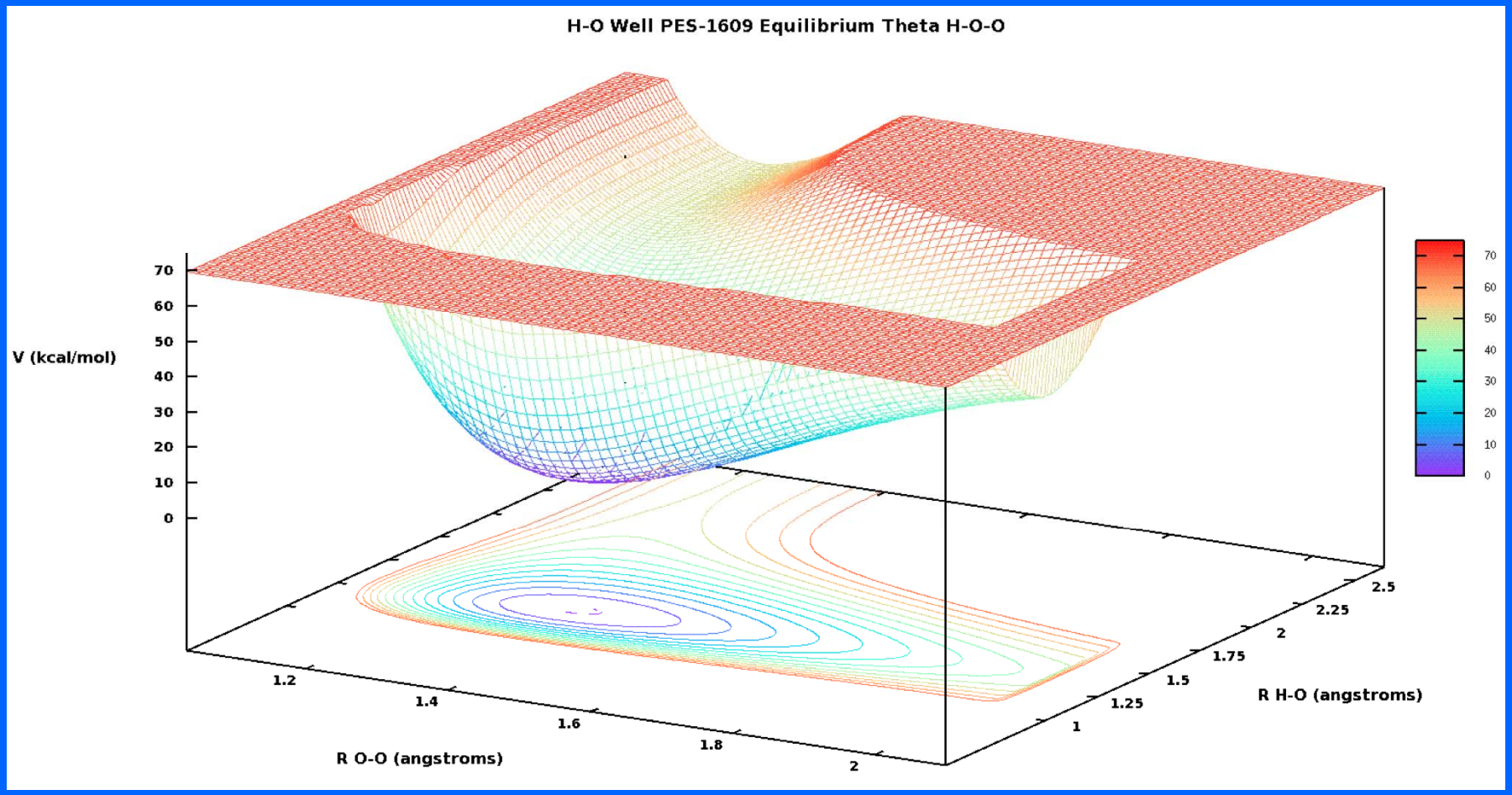
Initial results: P & T effects on loss of internal energy





Preliminary results

IMLS PES

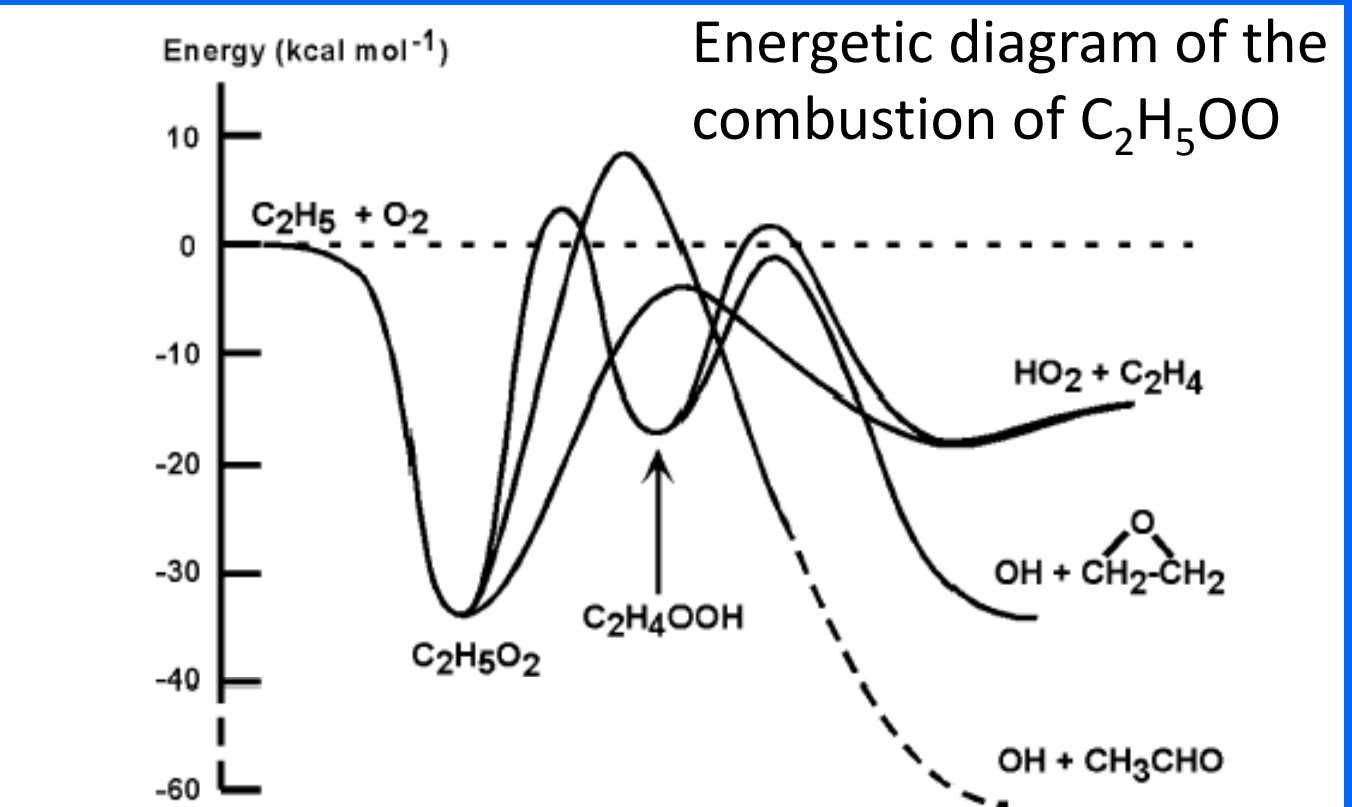


Our fit to date has focused on the spectroscopy. We will extend the PES further out the dissociation channels, and use it in studies of the effects of pressure.

Peroxy radicals

Our broader interest is the R+O2 family of reactions (of which $H+O_2$ is a member). They are important in low-T, high-P operating conditions of internal combustion engines

We begin with $\mathbf{C_2H_5O_2}$



Energetic diagram of the combustion of C_2H_5OO

DeSain et al. *J. Phys. Chem. A*, ***107***, 4415 *(2003)*

Miller *et al*. Int.J.Chem.Kin **33**, 654 (2001)

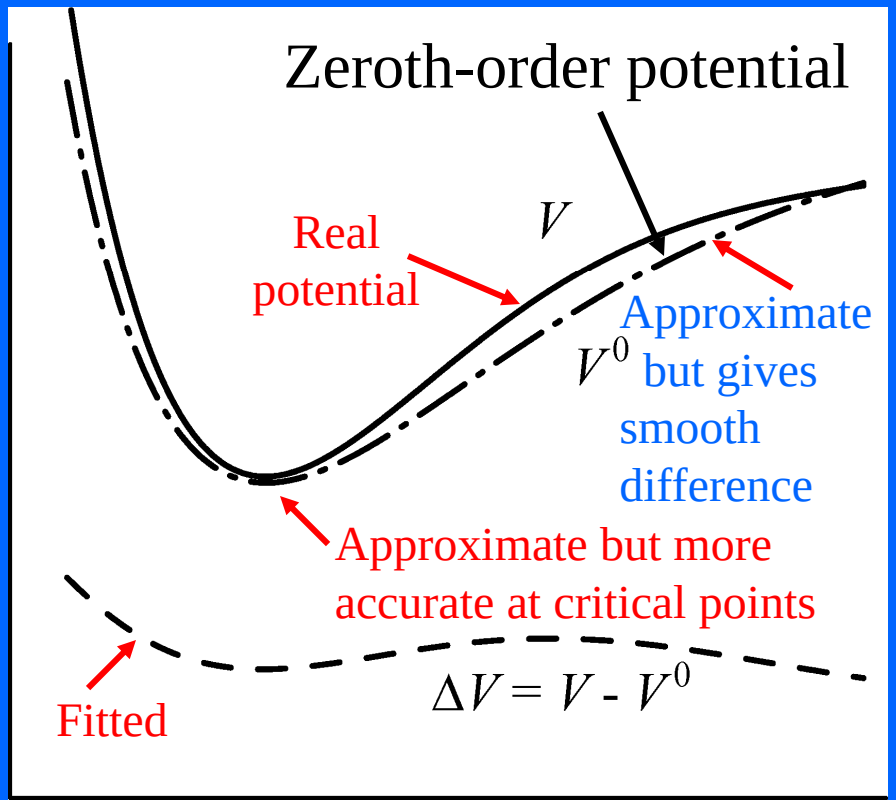
Miller *et al*. Proc.comb.inst. **28**, 1479 (2000)

Reducing the anount of *Ab Initio* data

For so many degrees of freedom we need to use a zeroth-order potential. By fitting the difference between the *ab initio* PES and one that approximates the true PES allows for fitting a much smoother topology, thus greatly reducing the number of *ab initio* data needed for a good fit.

Options:
Empirical global force field
or
Inexpensive electronic structure method

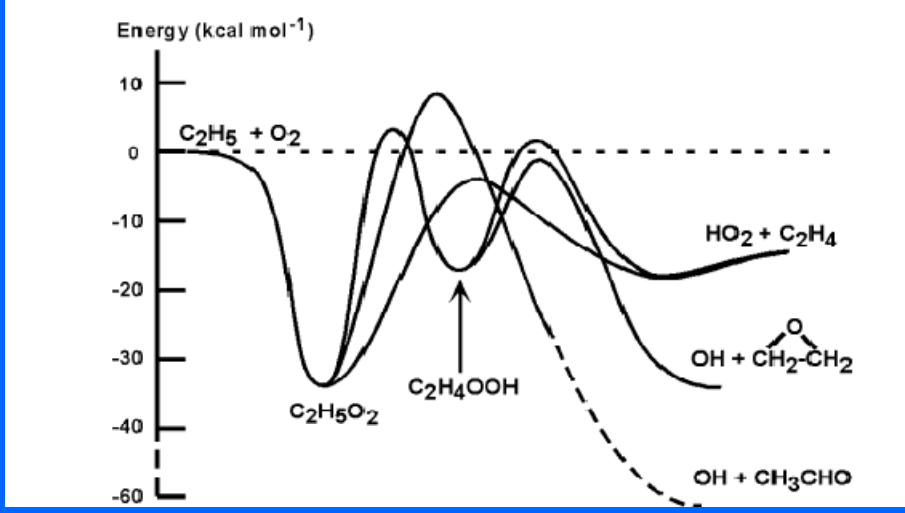
We first checked the available reactive force fields



Semiempirical Force Fields

Possibilities: AIREBO or Reaxff

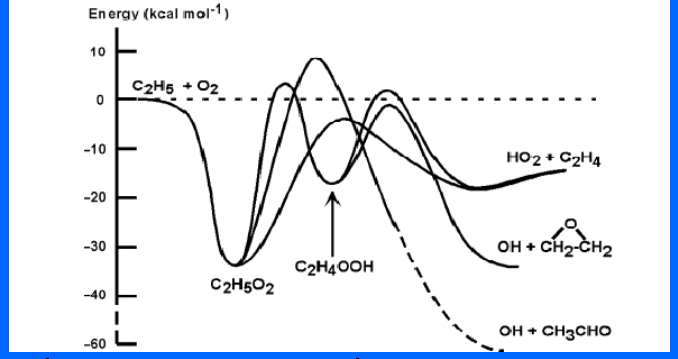
- **The AIREBO does not yet include Oxygen**



kcal/mol (origin $C_2H_5 + O_2$)	Cbs-qb3	Reaxff
$C_2H_5 + O_2$	0.000	0.00
$C_2H_5O_2$	-39.697	-47.39
$HO_2 + C_2H_4$	-15.044	-24.72
HO + ethylene oxide	-35.090	-35.95
$HO + CH_3CHO$	-61.007	-116.01
C_2H_4OOH	-20.610	-44.28

- Reaxff has erratic Energetics - Unacceptable

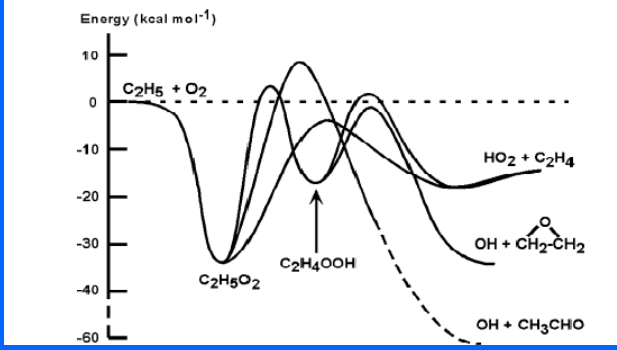
DFT with "common" functionals – not accurate enough.



PE Kcal/mol	CBS-QB3	Pw91/ aug-cc-pVTZ	PBE/ aug-cc-pVTZ	B3LYP/ aug-cc-pVTZ
$C_2H_5 + O_2$	0.000	0.000	0.000	0.000
$C_2H_5O_2$	-39.697	-37.503	-36.822	
$HO_2 + C_2H_4$	-15.044	12.028	-15.965	49.311
HO + ethylene oxide	-35.090	65.195	50.709	84.857
HO + CH_3CHO	-61.007	40.522	26.483	57.337
C_2H_4OOH	-20.610	-16.164	-15.142	-12.925
Maximum Absolute error		>100	>80	>65

Inexpensive electronic structure method

PE Kcal/mol	CBS-QB3	M05/ CBSB7	M05-2X/ CBSB7
$C_2H_5 + O_2$	0.000	0.000	0.000
$C_2H_5O_2$	-39.697	-32.583	-37.718
$HO_2 + C_2H_4$	-15.044	-3.707	-10.050
HO + ethylene oxide	-35.090	-29.992	-31.511
HO + CH_3CHO	-61.007	-53.802	-56.515
C_2H_4OOH	-20.610	-10.069	-16.688
Maximum Absolute error		11.3	5.0



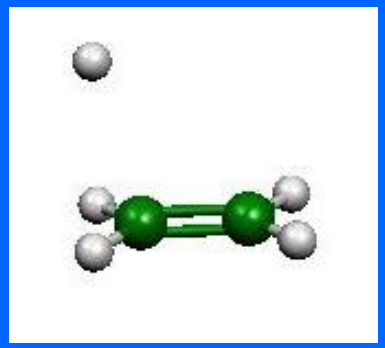
Also, accurately Predicts frequencies

M05-2X/CBSB7 Truhlar *et al.* is method of choice

Using to develop methods

DFT/MO5 Energetics

DFT/MO5 serves as an inexpensive electronic structure method



$^{-}CH_2CH_3$

Isomerization
M05-2X/CBSB7:
43.2 kcal/mol
Ab initio:
(1) 46.7 kcal/mol
(2) 42.7 kcal/mol

TS
M05-2X/CBSB7:
45.6 kcal/mol
Ab initio:
(1) 48.2 kcal/mol
(2) 40.2 kcal/mol

$CH_2CH_2(^1S)+H$

Dissociation
M05-2X/CBSB7:
41.5 kcal/mol
Ab initio:
(1) 40.9 kcal/mol
(2) 39.6 kcal/mol

CH_3CH_2

0.0

Ab-initio :
(1) MP4SDQ/6-311++G**
(2) CBS-QB3

Direct dynamics simulations of C_2H_5

Benchmark studies

• Use DFT/MO5-2X/CBSB7 in direct dynamics simulation of C_2H_5 dissociation/isomerization

- GENDYN linked to Gaussian
- 0.12 fs time step with RK4 integration
- initial energy randomized with 500 initial time steps
- typical trajectory at 150 kcal/mol energy:
  - runs 20,000 time steps
  - takes ~2 weeks on our cluster => ~1 minute / time step
  - generates ~80,000 points on the DFT/M05-2X/CBSB7 PES
- calculated trajectories undergo both isomerization and dissociation

These simulations will generate >10**6 DFT/M05-2X/CBSB7 points which can be used to

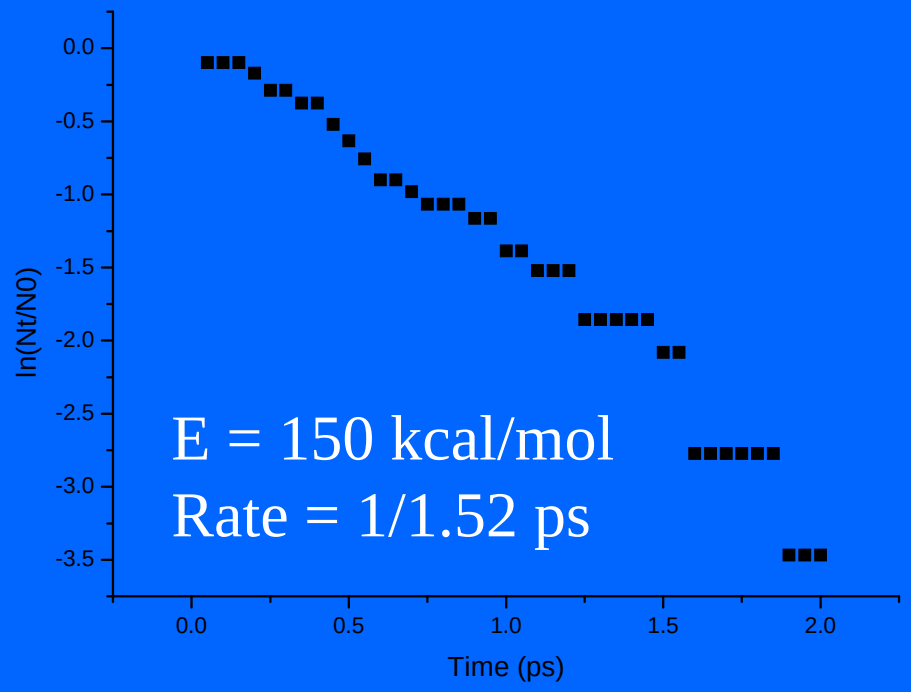
Develop a zeroth-order PES

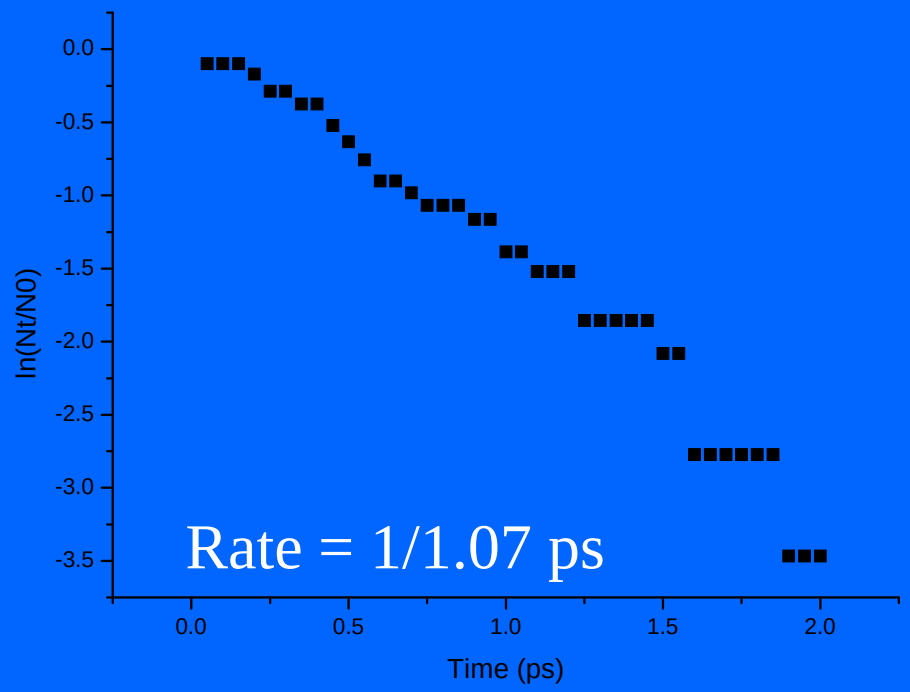
Test IMLS fitting methods for multi-D PESs

This DFT method will be used to develop direct dynamics/IMLS methods

Direct Dynamics Simulations of C_2H_5: Preliminary results

Direct dynamics simulation of C2H5 dissociation/isomerization using the DFT/MO5-2X/CBSB7 electronic structure method





Very preliminary results

The work continues

- Pressure effects in chemical reactions, particularly R-O_2 dissociations

  (Beyond the bimolecular collision limit)
- Exponential down model
- Accurate global PESs for some key radicals

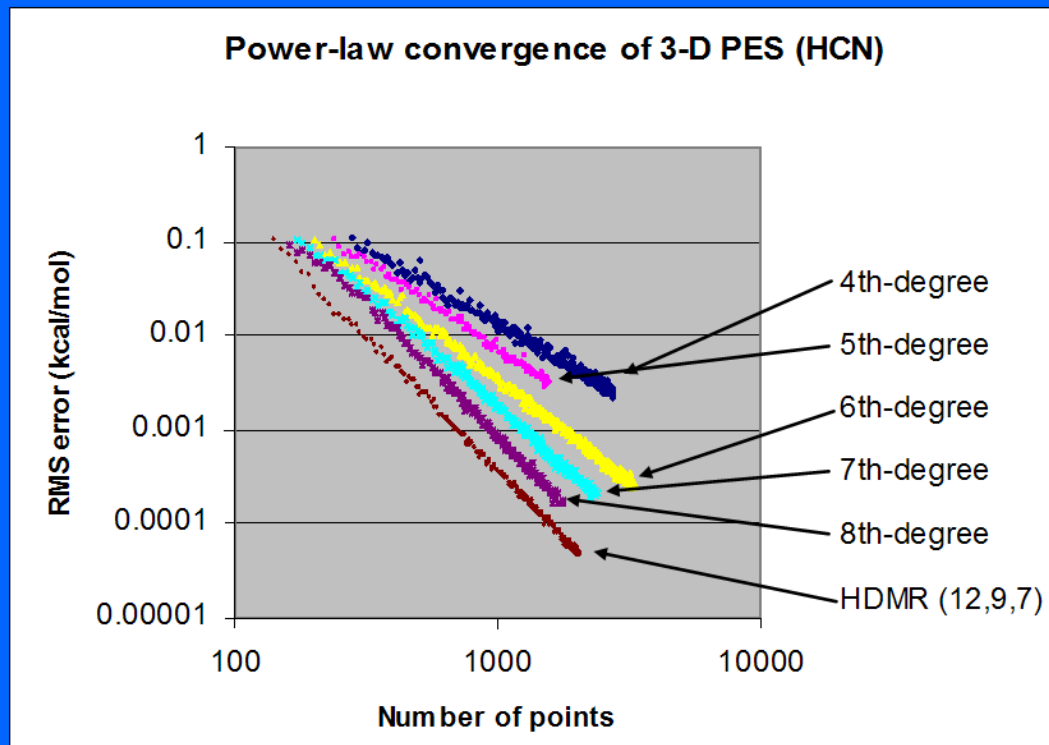
  (Several barriers and valleys)
- Methods for direct dynamics with IMLS enhanced *ab initio* forces calculations
- Take full advantage of current electronic structure theory for predicting chemistry

High Dimensional Model Representation (HDMR) basis set

- Represent high-D function with lower order terms

$$V(Q_1, Q_2 \ldots Q_N) = \sum_i V_i^{(1)}(Q_i) + \sum_{i,j} V_{i,j}^{(2)}(Q_i, Q_j) + \ldots$$

- Can also use full dimensional expansion but restrict the order of terms differently
- Evaluation scales as NM^2. HDMR greatly reduces M.
- Reduces the number of points required.

Automatic surface generation Using (12,9,7) & (11,8,6) bases

We fit a 3-D HCN-HNC PES using (12,9,7) HDMR basis:
1-coordinate term truncated at 12th degree
2-coordinate term truncated at 9th degree
3-coordinate term truncated at 7th degree
180 basis functions