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Energy transfer and dissociation in gas-phase collisions of N_2, O_2, NO, N, and O. Part 3. Local methods for constructing potential energy surfaces.

Jason Bender
Department of Aerospace Engineering and Mechanics, University of Minnesota

in collaboration with
Yuliya Paukku, Ke Yang, Zoltan Varga, and Donald G. Truhlar
Dept. of Chemistry, University of Minnesota
and
Sriram Doraiswamy and Graham V. Candler
Dept. of Aerospace Engineering and Mechanics, University of Minnesota

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Overview

- Local versus global fitting: a one-dimensional example
  - Least squares (LS)
  - Weighted least squares (WLS)
  - Local interpolating moving least squares (L-IMLS)
- ***Permutationally invariant local interpolating moving least squares*** (PI-L-IMLS) in six dimensions, for a four-atom system
  - Generalization of one-dimensional L-IMLS
  - Key features
    - Separation of pairwise interaction energy
    - Permutational invariance in the basis functions
    - Permutational invariance in the weight functions
    - Improved efficiency with a cutoff radius correlation
  - Results for the N_4 system
  - Error statistics

One-dimensional fitting

- Suppose we have a five-point data set, describing the dependence of potential energy on a single coordinate:

$$\begin{pmatrix} x_0 \\ x_1 \\ x_2 \\ x_3 \\ x_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 2 \\ 3 \\ 4 \end{pmatrix} \qquad \begin{pmatrix} f_0 \\ f_1 \\ f_2 \\ f_3 \\ f_4 \end{pmatrix} = \begin{pmatrix} 3 \\ -2 \\ 4 \\ 7 \\ 16 \end{pmatrix}$$

- $\{x_i\}$ are the one-dimensional ***coordinates***
- $\{f_i\}$ are the ***exact energies***
- We will construct a smooth ***fitting function*** $f(x)$ that approximates this data set.
- Consider three different approaches of increasing complexity.

The Least Squares (LS) method

- Consider a quadratic polynomial:

$$f(x) = p(x) = a_0(1) + a_1(x) + a_2(x^2)$$

coefficient ***basis function***

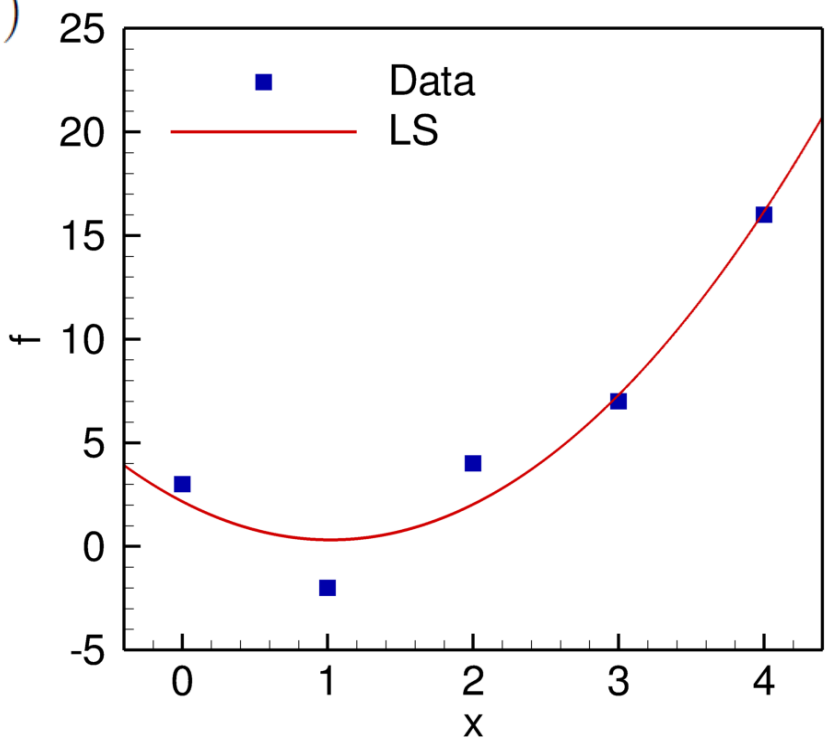
- Minimizing the error functional,

$$E(p(x)) = \sum_{k=0}^{N-1} (p(x_k) - f_k)^2$$

leads to the normal equations,

$$\mathbf{B}^T\mathbf{B}\mathbf{a} = \mathbf{B}^T\mathbf{f}$$

which can be solved for the coefficients.



The Weighted Least Squares (WLS) method

- The fit can be modified by introducing ***weights*** into the normal equations.
  - There are many ways to do this.
  - In one approach, we define the weight as a decreasing function of distance from a ***localization point.***

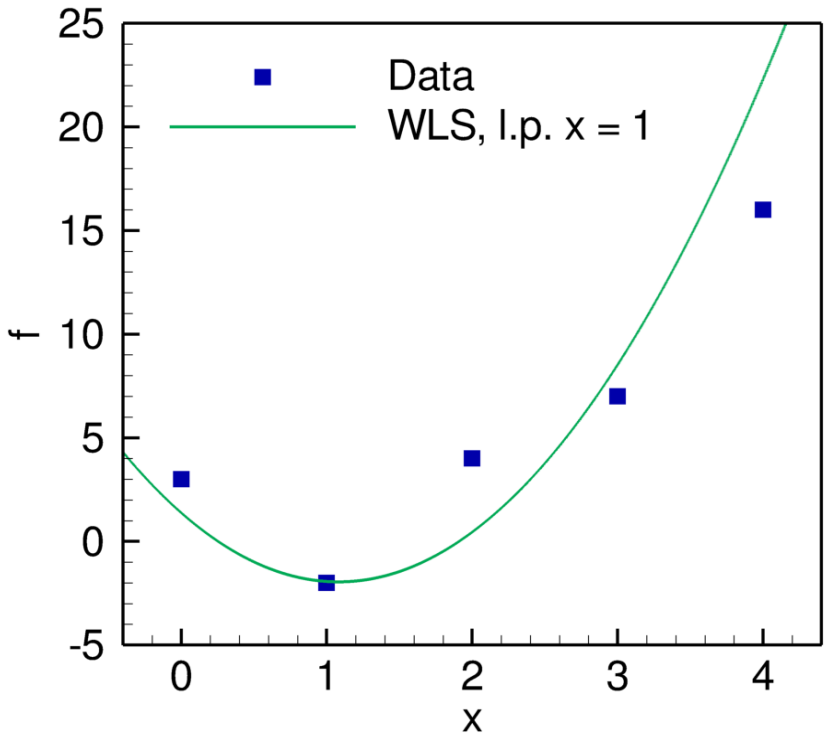
$\omega(x, x_o)$ ***is a function of***

$$\frac{|x - x_o|}{R}$$

localization point

scaling factor

  - The resulting fit will be highly accurate near the localization point.



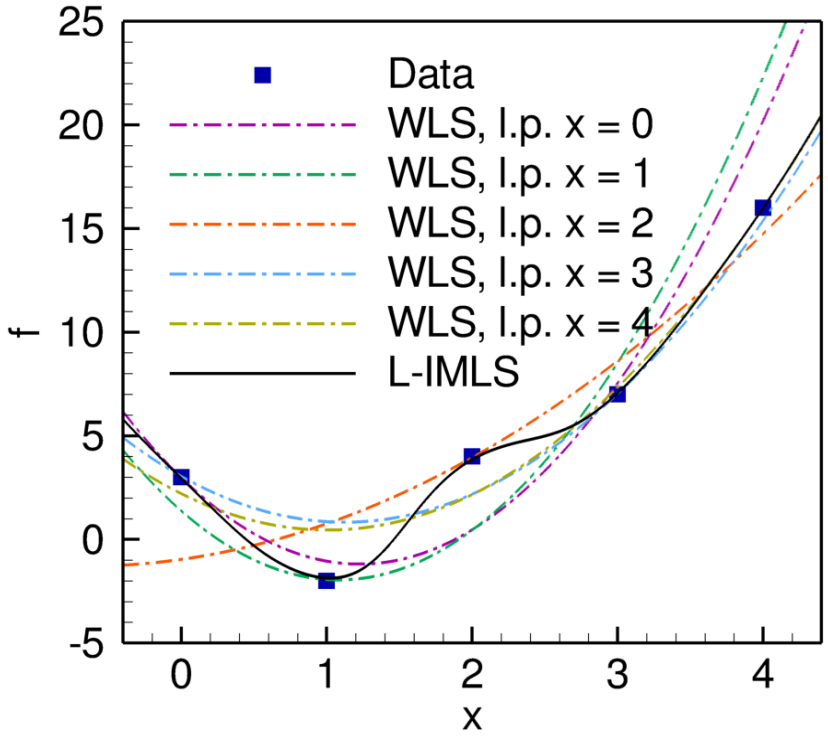
The Local Interpolating Moving Least Squares (L-IMLS) method

- A WLS fit can be constructed in this way for each point in the data set.
  - This defines a family of ***local fits.***
  - Each one fits the entire data set, but is especially accurate at its localization point.
- We define a smooth function as a weighted average of the local fits:

$$f(x) = \frac{\sum_{i=1}^{N} w(x, x_i)\, p_i(x)}{\sum_{i=1}^{N} w(x, x_i)}$$

weight on local fit i

local fit i



Y. Guo, I. Tokmakov, D. L. Thompson, A. F. Wagner, and M. Minkoff, J. Chem. Phys. 127, 214106 (2007).

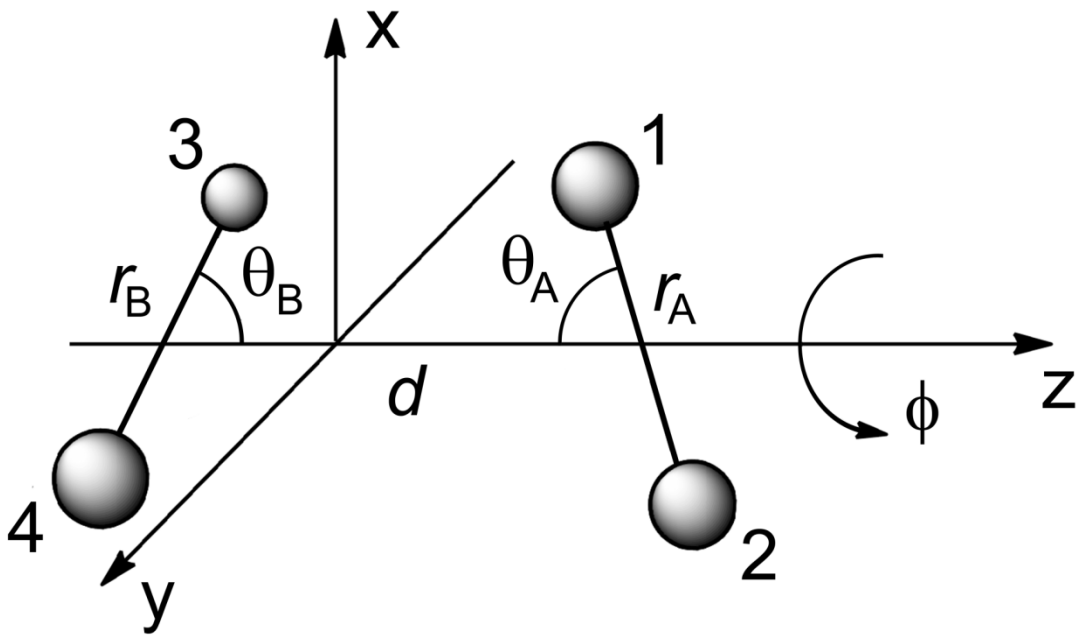
R. Dawes, D. L. Thompson, Y. Guo, A. F. Wagner, and M. Minkoff, J. Chem. Phys. 126, 184108 (2007).

L-IMLS – Key features

- L-IMLS consists of two distinct steps:
  - In the ***construction step***, we define a set of normal equations, solve them for the local fit coefficients, and store the results.
  - In the ***evaluation step***, we calculate a weighted average of the local fits.
- There are two weight functions in L-IMLS, ω and W.
- The LS and WLS methods are ***global*** methods. L-IMLS is a ***local*** method.
  - In a global method, each data point influences the fitting function uniformly.
  - In a local method, the influence of a data point on the fitting function may vary with evaluation location.

Extending the method to six dimensions

- A four-atom system has six internal degrees of freedom.



- To extend L-IMLS to a six-dimensional system, we must:
  1. Ensure correct asymptotic behavior
  2. Generalize the basis functions to 6D
  3. Generalize the weight functions to 6D
  4. Control computational cost

Preliminaries – Distances and Morse variables

- How do we specify a four-atom geometry?
  - Using a mixture of distances and angles is cumbersome.
  - Using the Cartesian coordinates of each of the four atoms introduces unnecessary degrees of freedom.
- The typical starting point for describing a four-atom geometry is the six internuclear distances:

distance from atom #1 to atom #2

$$\widetilde{\mathbf{q}} = (\widetilde{q}_1, \widetilde{q}_2, \widetilde{q}_3, \widetilde{q}_4, \widetilde{q}_5, \widetilde{q}_6) = (r_{12}, r_{13}, r_{14}, r_{23}, r_{24}, r_{34})$$

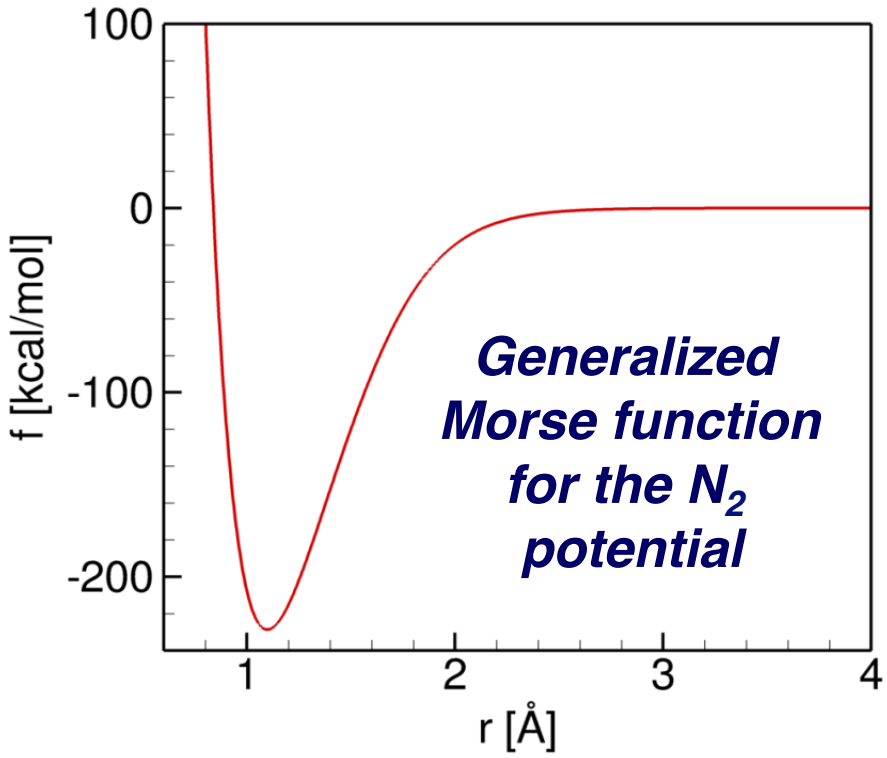
- Better behaved are the six corresponding ***Morse variables***.

$$\mathbf{q} = (q_1, q_2, q_3, q_4, q_5, q_6) \quad \textit{where} \quad q_l = \exp\left(-\frac{\widetilde{q}_l - \widetilde{q}_{\mathrm{eq}}}{a}\right)$$

equilibrium N_2 bond distance

scaling factor

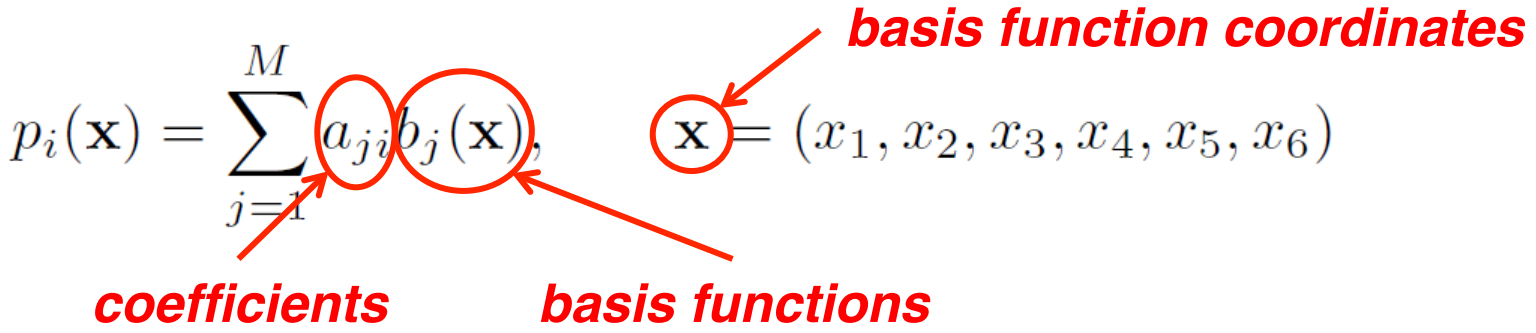
$2N_2 \rightarrow (N_4) \rightarrow N_2 + 2N$



- The N_2 potential energy curve has been studied extensively.
- We can model the N_2 potential with a generalized Morse function.
- ***If a system exhibits only pairwise interactions, then our N_4 potential must reduce to a sum of pairwise potentials.***
- To guarantee this, we:
  - Separate pairwise interaction energy from the total energy.
  - Fit only the remaining "many-body" component of the energy.

Generalizing the basis functions

- General form of a local fit:



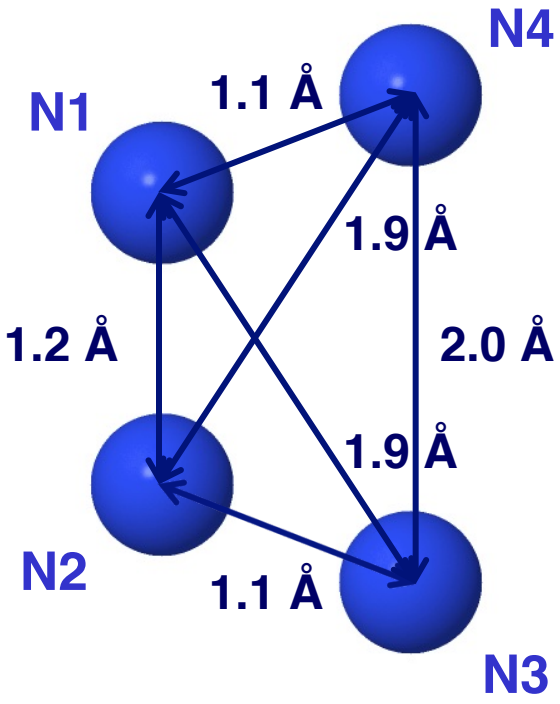
- Define the basis functions to be monomials in the six coordinates:

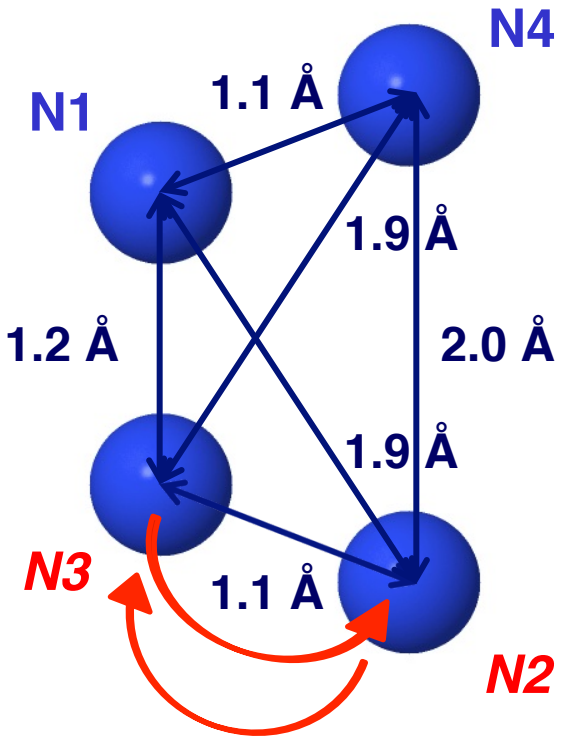
$$\{b_j(\mathbf{x})\} = \{1,$$
$$x_1,\ x_2,\ \ldots,\ x_6,$$
$$x_1^2,\ x_2^2,\ \ldots,\ x_6^2,\ x_1x_2,\ x_1x_3,\ x_1x_4,\ \ldots,\ x_5x_6,$$
$$x_1^3,\ x_2^3,\ \ldots,\ x_6^3,\ x_1^2x_2,\ x_1^2x_3,\ x_1^2x_4,\ \ldots,\ x_5^2x_6,\ x_1x_2x_3,\ x_1x_2x_4,\ \ldots\}$$

- It now remains to choose the six coordinates.
- What would happen if we used the six internuclear distances?

Permutational symmetry – An introduction

$$\mathbf{x} = (r_{12}, r_{13}, r_{14}, r_{23}, r_{24}, r_{34})$$





$$\mathbf{x} = (1.2, 1.9, 1.1, 1.1, 1.9, 2.0)$$

$$\mathbf{x} = (1.9, 1.2, 1.1, 1.1, 2.0, 1.9)$$

NOT equivalent

A permutationally invariant coordinate system

- The basis function coordinate system should be ***permutationally invariant:***
  - If one geometry can be obtained by a permutation of the atoms of a second geometry, then the two geometries should have identical coordinates.
  - The local fits will "inherit" permutational invariance from the coordinate system.
- Define the coordinates as a set of six permutationally invariant polynomials in Morse variables.
  - Three polynomials chosen to capture three-body interactions.
  - Three polynomials chosen to capture four-body interactions.
  - As a system approaches a geometry exhibiting only two-body interactions, all six polynomials approach zero.

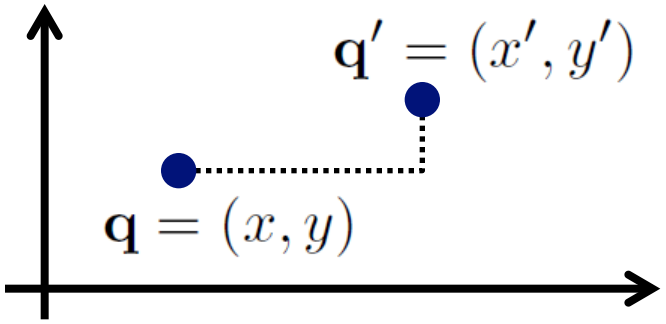
Generalizing the weight functions

- The weight function must be expressed using a six-dimensional ***distance metric***.

$\omega(x, x_o)$ *is a function of* $\dfrac{|x - x_o|}{R}$ ⇨ $\omega(\mathbf{q}, \mathbf{q}')$ *is a function of* $\dfrac{d(\mathbf{q}, \mathbf{q}')}{R(\mathbf{q})}$

One-dimensional weight function ***Six-dimensional weight function***

- We allow the scaling factor ***R*** to vary with one of the weight function's inputs.
- Naïve approach: generalize the usual distance metric used in a Cartesian coordinate system:



$$d(\mathbf{q}, \mathbf{q}') = \sqrt{(x - x')^2 + (y - y')^2}$$

Permutational invariance in the distance metric

$$d(\mathbf{q},\mathbf{q}') = \left[\sum_{l=1}^{6} |q_l - q'_l|^2\right]^{\frac{1}{2}} = |\mathbf{q}-\mathbf{q}'|$$

BAD!!

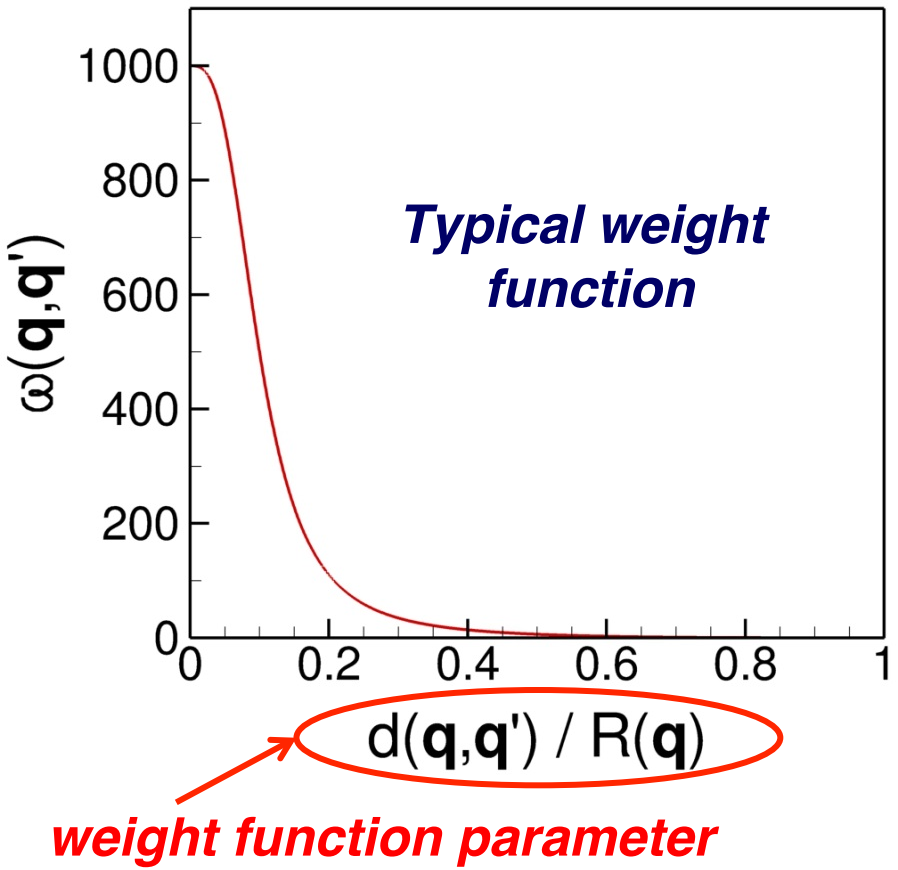
- The naïve approach ***fails***.
- If one geometry can be obtained by a permutation of the atoms of a second geometry, then the six-dimensional distance between the two geometries should be zero.
- A more sophisticated approach:
  - Consider all 24 (= 4!) possible permutations of the atoms.
  - Form a modified power mean of L^2 norms, one for each permutation.

permutation function

$$d(\mathbf{q},\mathbf{q}') = \left[\left(\sum_{k=1}^{24} \left(|\mathbf{q} - \chi_k(\mathbf{q}')|^2\right)^{-p_d}\right)^{\frac{-1}{p_d}}\right]^{\frac{1}{2}}$$

Controlling computational cost

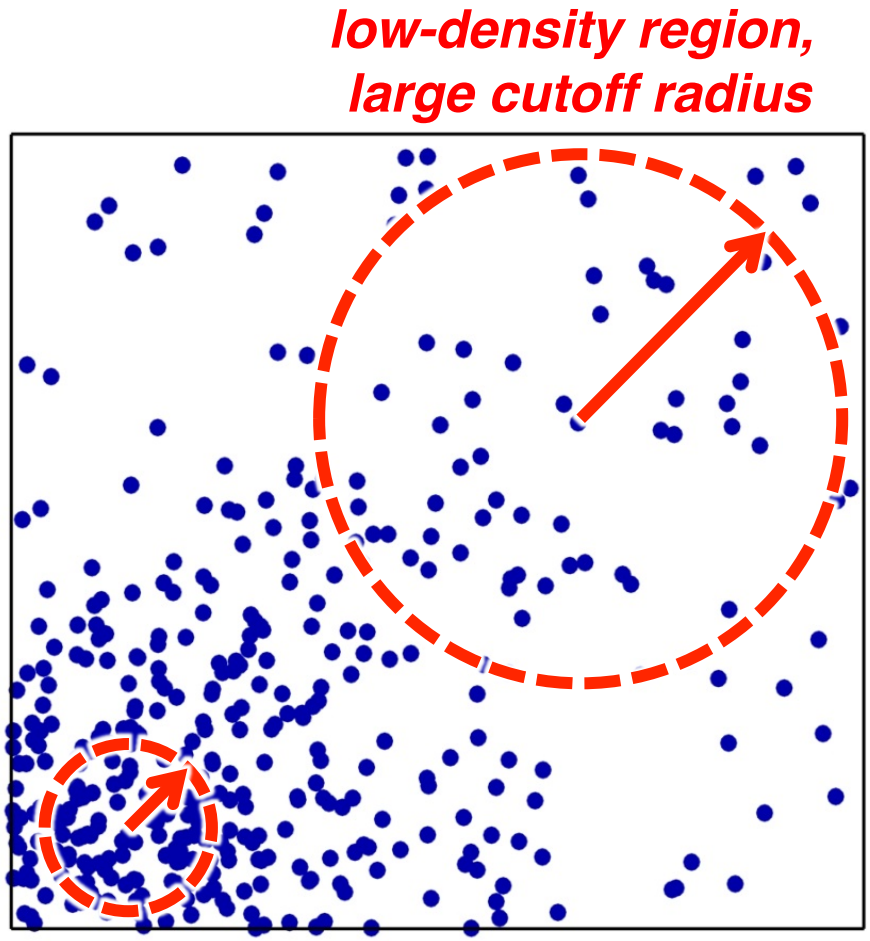
- It is inefficient and unnecessary to use all local fits for all cases.
  - We can define the weight function so that it decreases smoothly to zero, as the ***weight function parameter*** approaches one.
  - The scaling factor ***R*** will be called the ***cutoff radius***. If the distance to a data point is larger than the cutoff radius, then the weight on that point is zero.
- The cutoff radius should depend on the density of data points.



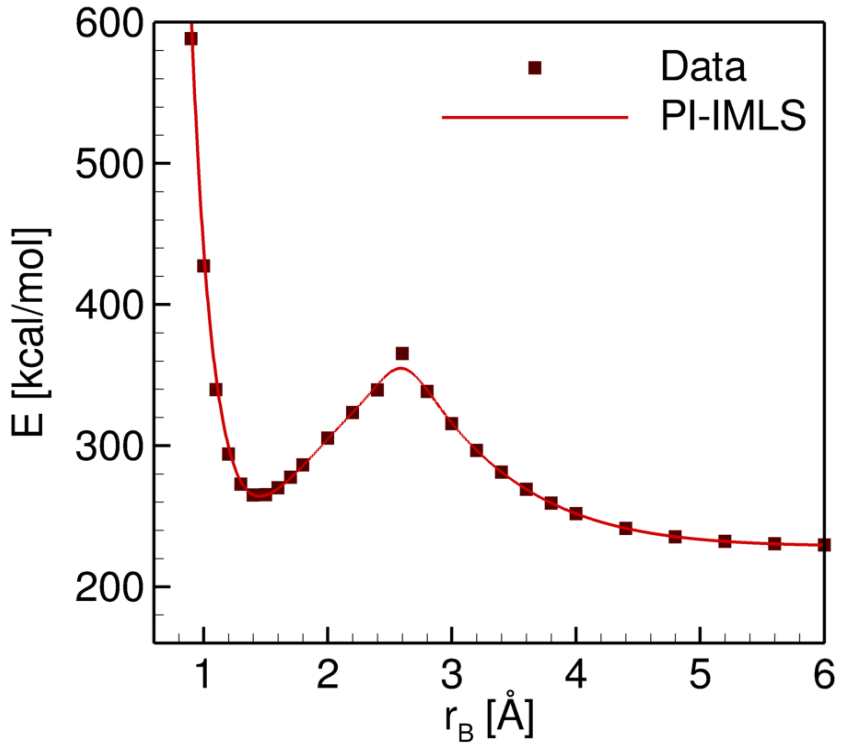
$$d(\mathbf{q}, \mathbf{q}') \geq R(\mathbf{q}) \Rightarrow$$
$$\omega(\mathbf{q}, \mathbf{q}') = 0$$

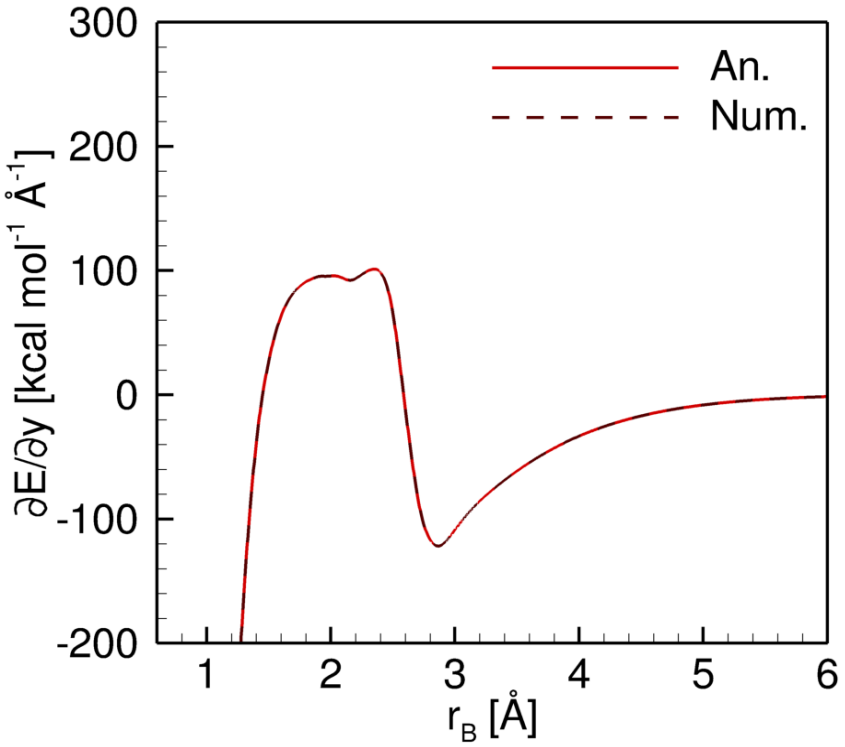
The cutoff radius correlation

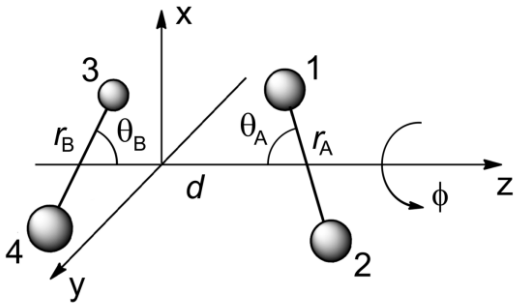
- The cutoff radius should be smaller in higher-density regions of space.
- A ***cutoff radius correlation*** can be constructed based on simple statistical methods:
  - The density of space is correlated to a single ***characteristic coordinate*** of the geometries.
  - The cutoff radius is expressed as a polynomial in the characteristic coordinate.
- Typical: 10x reduction in number of local fits used in an evaluation.



Results – Examples of 1D Cuts



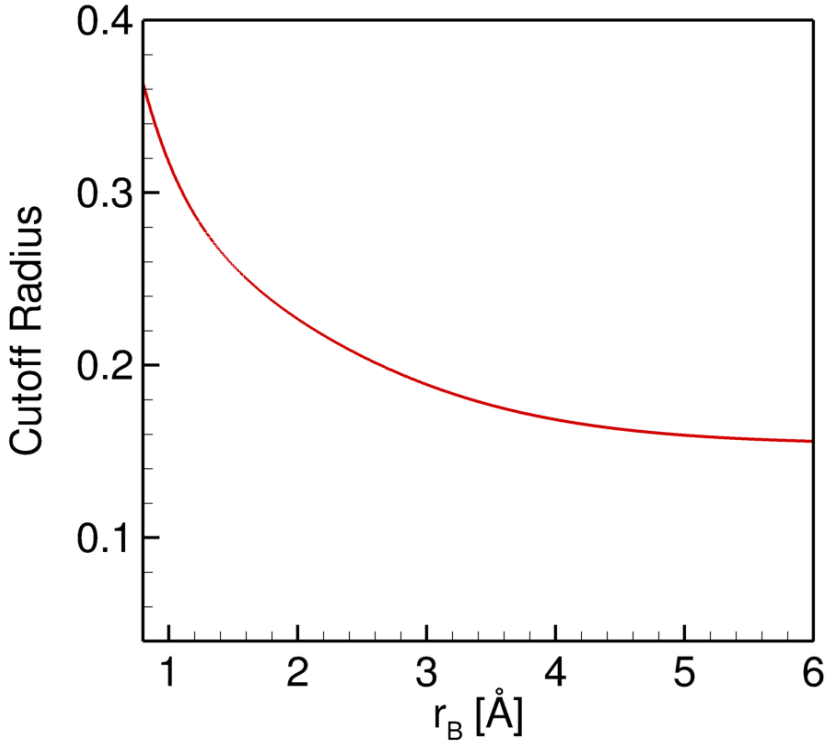


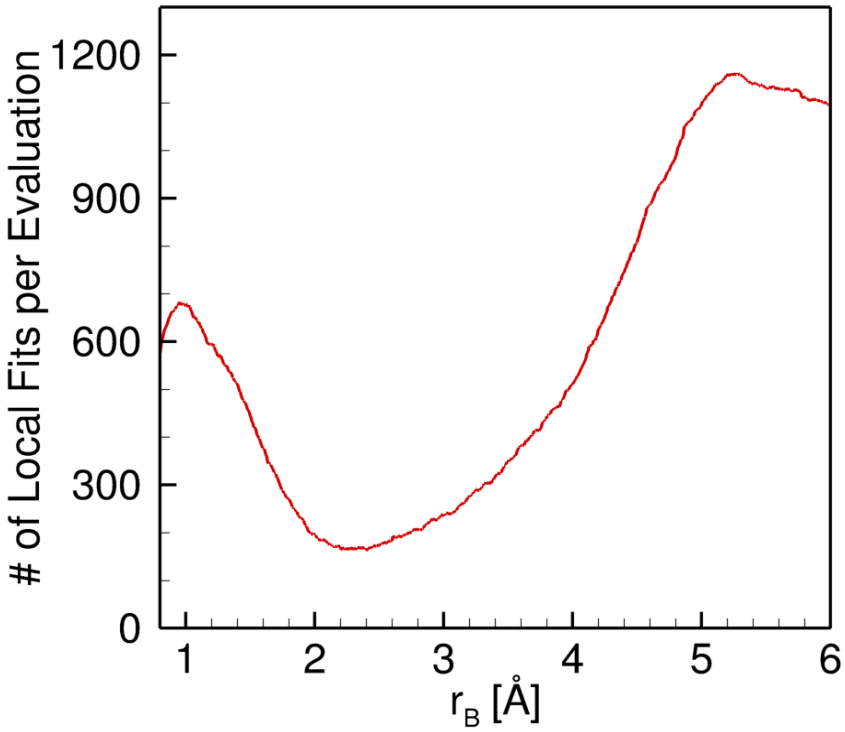


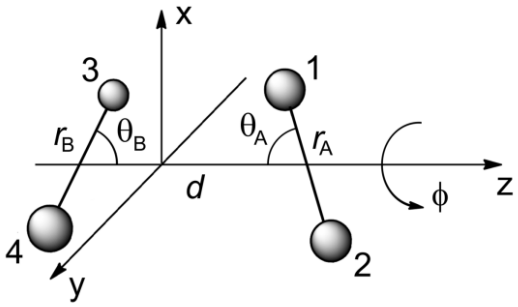
Fixed parameters: $\theta_A = \theta_B = \phi = 90^\circ \quad r_A = 1.098$ Å

(Gradient component reported for atom #3) $d = 1.2$ Å

Results – Examples of 1D Cuts



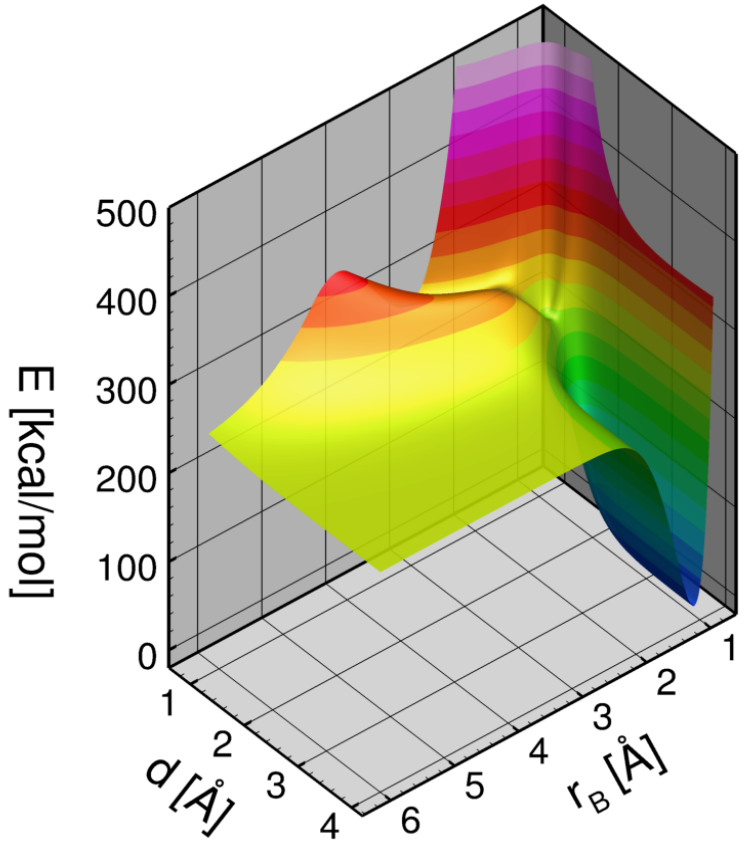


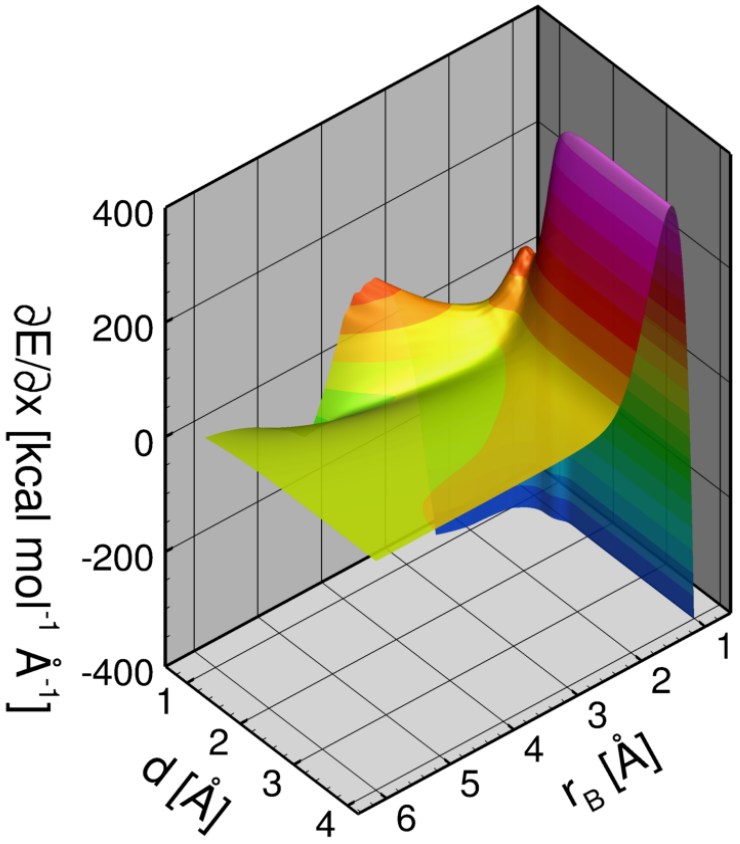


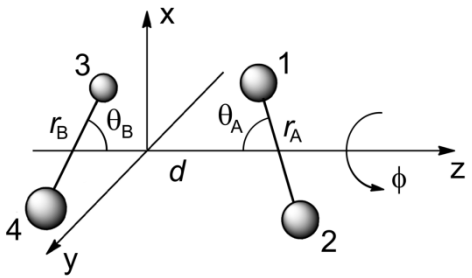
Fixed parameters: $\theta_A = \theta_B = \phi = 90^\circ \quad r_A = 1.098$ Å

(Gradient component reported for atom #3) $d = 1.2$ Å

Results – Examples of 2D Cuts







Fixed parameters: $\theta_A = \theta_B = 90^\circ \qquad \phi = 0^\circ$

$r_A = 1.098$ Å

Results – Error Statistics

Data subset	# of points	Fitting accuracy	Cross validation
$E < 100$	509	0.14	0.21
$100 \le E < 228$	1556	0.33	0.58
$228 \le E < 456$	9202	0.46	1.2
$456 \le E < 1000$	1542	2.3	4.0
$1000 \le E$	328	2.5	6.8
All data	***13137***	***0.71***	***1.5***

PI-L-IMLS mean unsigned error (MUE) statistics.
All energies in kcal/mol.

Next Steps

- ***This is only the beginning.***
- Presently, we are using the N_4 PESs in quasiclassical trajectory simulations to determine cross sections and reaction rates.
  - Using the ANT code, developed in the Truhlar group
  - Focus: nitrogen dissociation and vibrational energy exchange at extremely high temperatures
  - Results will serve as inputs to CFD codes and other tools to study hypersonic flow phenomena.
- Further phases of the project:
  - Excited state electronic structure calculations (already in progress)
  - Nonadiabatic trajectories

Acknowledgments

MURI Team

Donald G. Truhlar
Graham V. Candler
Zoltan Varga (Truhlar group)
Yuliya Paukku (Truhlar group)
Ke R. Yang (Truhlar group)
Sriram Doraiswamy (Candler group)

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Questions?

Backup

Weight functions

- One-dimensional L-IMLS:

$$\omega(x_1, x_2) \equiv \nu\left(z = \frac{|x_1 - x_2|^2}{R^2}\right) \quad \textit{where} \quad \nu(z) = \frac{\exp(-z)}{(z)^{p_\nu} + (\epsilon_\nu)^{p_\nu}}$$

$$w(x_1, x_2) \equiv u\left(z = \frac{|x_1 - x_2|^2}{R^2}\right) \quad \textit{where} \quad u(z) = \frac{1}{(z)^{p_u} + (\epsilon_u)^{p_u}}$$

Parameters used: $p_\nu = p_u = 1, \qquad \epsilon_\nu = \epsilon_u = 10^{-3}, \qquad R = 4$

- Six-dimensional EPI-IMLS:

$$\omega(\mathbf{q}_1, \mathbf{q}_2) \equiv \nu\left(z = \frac{d^2(\mathbf{q}_1, \mathbf{q}_2)}{R^2(\mathbf{q}_1)}\right) \quad \textit{where} \quad \nu(z) = \frac{\exp(-z)}{(z)^{p_\nu} + (\epsilon_\nu)^{p_\nu}}$$

$$w(\mathbf{q}_1, \mathbf{q}_2) \equiv u\left(z = \frac{d^2(\mathbf{q}_1, \mathbf{q}_2)}{R^2(\mathbf{q}_1)}\right) \quad \textit{where} \quad u(z) = \frac{s(z)}{(z)^{p_u} + (\epsilon_u)^{p_u}}$$

Parameters used:

$p_\nu = p_u = 3, \qquad \epsilon_\nu = \epsilon_u = 10^{-1}$

$$s(z) = \begin{cases} (1 - z^4)^4 & \text{if } 0 \le z \le 1 \\ 0 & \text{if } 1 < z \end{cases}$$

Basis function coordinate system

$$x_1 = \left[\left(q_1q_2 + q_1q_3 + q_1q_4 + q_1q_5 + q_2q_3 + q_2q_4 + q_2q_6 + q_3q_5 + q_3q_6 + q_4q_5 + q_4q_6 + q_5q_6\right)\frac{1}{12}\right]^{1/2}$$

$$x_2 = \left[\left(q_1q_2q_4 + q_1q_3q_5 + q_2q_3q_6 + q_4q_5q_6\right)\frac{1}{4}\right]^{1/3}$$

$$x_3 = \left[\left(q_1q_2(q_1+q_2) + q_1q_3(q_1+q_3) + q_1q_4(q_1+q_4) + q_1q_5(q_1+q_5) + q_2q_3(q_2+q_3) + q_2q_4(q_2+q_4) + q_2q_6(q_2+q_6) + q_3q_5(q_3+q_5) + q_3q_6(q_3+q_6) + q_4q_5(q_4+q_5) + q_4q_6(q_4+q_6) + q_5q_6(q_5+q_6)\right)\frac{1}{24}\right]^{1/3}$$

$$x_4 = \left[\left(q_1q_2q_3 + q_1q_4q_5 + q_2q_4q_6 + q_3q_5q_6\right)\frac{1}{4}\right]^{1/3}$$

$$x_5 = \left[\left(q_1q_3q_4 + q_2q_3q_4 + q_1q_2q_5 + q_2q_3q_5 + q_2q_4q_5 + q_3q_4q_5 + q_1q_2q_6 + q_1q_3q_6 + q_1q_4q_6 + q_3q_4q_6 + q_1q_5q_6 + q_2q_5q_6\right)\frac{1}{12}\right]^{1/3}$$

$$x_6 = \left[\left(q_1q_2q_5q_6 + q_1q_3q_4q_6 + q_2q_3q_4q_5\right)\frac{1}{3}\right]^{1/4}$$

Implementation – A permutationally invariant distance metric

- Consider two points in six-dimensional space:

$$\mathbf{q}_1 = (q_{1,1}, q_{1,2}, q_{1,3}, q_{1,4}, q_{1,5}, q_{1,6}) \qquad \mathbf{q}_2 = (q_{2,1}, q_{2,2}, q_{2,3}, q_{2,4}, q_{2,5}, q_{2,6})$$

- Naïve approach: ***(BAD)***

$$d^2(\mathbf{q}_1, \mathbf{q}_2) = \sum_{l=1}^{6} |q_{1,l} - q_{2,l}|^2 = |\mathbf{q}_1 - \mathbf{q}_2|^2$$

- Minimum approach: ***(BAD)***

permutation function

$$d^2(\mathbf{q}_1, \mathbf{q}_2) = \min\left\{|\mathbf{q}_1 - \chi_k(\mathbf{q}_2)|^2 : k = 1, ..., 24\right\}$$

- Modified power mean approach: ***(GOOD)***

$$d^2(\mathbf{q}_1, \mathbf{q}_2) = \left(\sum_{k=1}^{24} \left(|\mathbf{q}_1 - \chi_k(\mathbf{q}_2)|^2\right)^{-p_d}\right)^{\frac{-1}{p_d}}$$

Parameter used: $p_d = 2$

Implementation – The cutoff radius correlation

- Characteristic coordinate, in terms of Morse variables:

$$q_{ch} = q_{ch}(\mathbf{q}) = q_1^2 + q_2^2 + q_3^2 + q_4^2 + q_5^2 + q_6^2$$

- Cutoff radius correlation polynomial:

$$R(q_{ch}) = \sum_{c=1}^{C_{\max}} \alpha_c (q_{ch})^{c-1}$$

determined from weighted least squares fitting

Parameter used: $C_{\max} = 5$