

A transformative approach for constructing anharmonic force fields

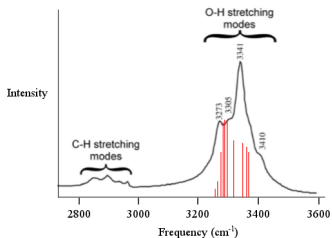
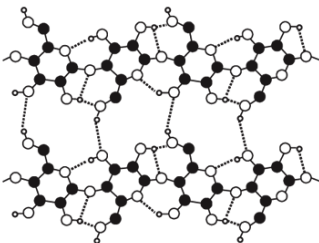
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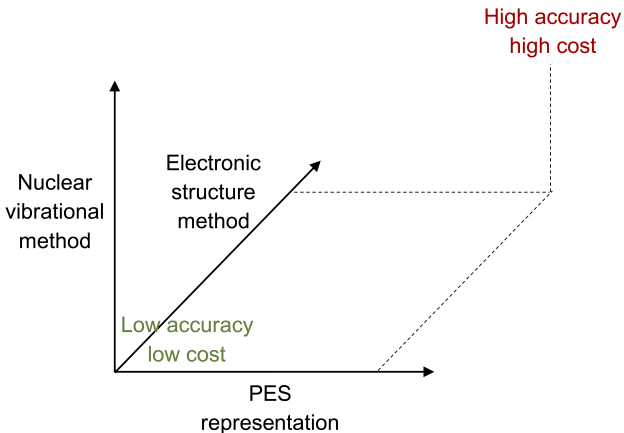
Primary goal

Routine, black-box calculation of anharmonic vibrational frequencies for semi-rigid molecules, extensible to selected vibrational modes of larger systems (clusters, materials).



Computational considerations

Overall trade-offs between accuracy and computational cost:



Electronic structure methods for vibrational frequencies

- Weak coupling between electronic and nuclear degrees of freedom in wavefunction
- Harmonic contribution to fundamentals \gg anharmonic contribution



Use harmonic frequencies for benchmarking the performance of different electronic structure methods

Electronic structure methods for vibrational frequencies

Benchmark data set

- Spectroscopically accurate potential energy surfaces for 50 small molecules (3-6 atoms) implemented from the literature
 - Ground and excited states
 - Anionic, cationic and uncharged
 - Organic and inorganic
- At least CCSD(T)/aug-cc-pVQZ quality
- Expanded in symmetry-adapted internal coordinates
- Anharmonic fundamentals within 5 cm^{-1} of experiment
- Harmonic frequencies calculated from anharmonic PES

Electronic structure methods for vibrational frequencies

Approximate electronic structure methods

- B3LYP/6-31G(d,p), B3PW91/6-31G(d,p), PBE0/6-311G(d,p)
- EDF2/(aug-)cc-pVTZ
- M05/6-311+G(2df,2p), M06/6-311+G(2df,2p)
- MP2/(aug-)cc-pVTZ

* All DFT calculations performed using ultra-fine grids and tight SCF convergence thresholds.

Electronic structure methods for vibrational frequencies

Method	Errors (cm ⁻¹)	
	Mean	Max
B3LYP	28	223
B3PW91	25	245
PBE0	27	228
EDF	27	238

Mean anharmonicity = 47 cm⁻¹

Max. anharmonicity = 237 cm⁻¹

Electronic structure methods for vibrational frequencies

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Electronic structure methods for vibrational frequencies

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M05	36	204
M06	32	178
MP2	23	128

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Electronic structure methods for vibrational frequencies

Take-home messages

- Don't use DFT for anharmonic frequency calculations
- Don't even use MP2
- Coupled-cluster models with at least at TZ basis required
- May be able to get away with a lower level of theory for the anharmonic part of the potential?
- If you can only afford a poor electronic structure model, you may as well use a poor anharmonicity model*

The importance of coordinate choice

Describing the potential energy surface

- Force field coordinates required for concise PES expansion
- Curvilinear internal coordinates - bond lengths, bond angles, dihedral angle, out-of-plane angles
- Redundant set

Solving the nuclear Schrödinger equation

- Normal mode coordinates diagonalize kinetic energy operator
- Rectilinear coordinates - Cartesian displacement vectors
- Non-redundant set

You can't have your cake and eat it too

Two possible solutions:

Transform coordinates in which PES is expanded

- low order expansion in internal coordinates → higher order expansions in Cartesian normal mode coordinates
- describes curvature of potential energy surface

Transform coordinates in which kinetic energy operator is expressed

- express KE operator in same non-redundant set of internal coordinates as PES
- describes curvature of internal coordinate set

You can't have your cake and eat it too

Two possible solutions:

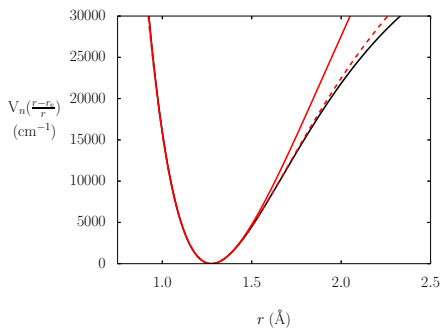
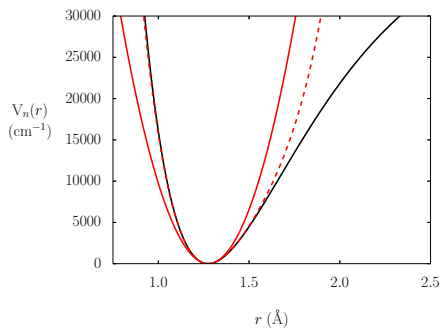
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PES expansions for HCl



Fundamental vibrational frequency of HCl (cm^{-1})

n	$V_n(r - r_e)$	$V_n\left(\frac{r-r_e}{r}\right)$
2	2990.9	2927.8
∞	2885.2	2885.2

Fundamental vibrational frequency of HCl (cm^{-1})

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3	2730.5	2911.8
4	2901.6	2886.1
5	2881.8	2885.2
6	2885.6	2885.2
∞	2885.2	2885.2

Moving on to molecules

- 1 Define redundant internal coordinate set, \mathbf{Z}_r
 - Simon-Parr-Finlan for stretches
 - Polynomial for bond angles, torsion angles, out-of-plane angles
- 2 Construct non-redundant internal coordinate set, \mathbf{Z}
 - Can use symmetry-adapted internal coordinates for simple, small, symmetrical molecules
 - Otherwise, how best to define appropriate linear combinations?
- 3 Generate concise PES in internal coordinates, $V_n(\mathbf{Z})$
- 4 Transform into higher order expansion in normal mode coordinates, e.g. $V_6(\mathbf{Q})$
- 5 Solve nuclear vibrational Schrödinger equation

Defining non-redundant internal coordinates

The simplest approach

- Use Wilson G matrix method:
 - $\mathbf{G} = \mathbf{B}_r \mathbf{B}_r^T$, $N_{\text{int}} \times N_{\text{int}}$ matrix
 - $\mathbf{B}_r = \frac{d\mathbf{Z}_r}{d\mathbf{X}}$, $N_{\text{int}} \times 3N_{\text{atom}}$ matrix
 - diagonalize \mathbf{G}
 - $\mathbf{U} = N_{\text{mode}} \times N_{\text{int}}$ transformation matrix comprising N_{mode} eigenvectors with non-zero eigenvalues
 - $\mathbf{Z} = \mathbf{UZ}_r$
- Calculate energy derivatives by numerical differentiation:
 - with respect to displacements along Z_i
 - analytic second derivatives derived from *ab initio* Hessian data
 - but what step sizes to take along each coordinate, Z_i ?
 - and what order of expansion will be required?

Defining non-redundant internal coordinates

An extra step

- Define curvilinear normal mode coordinates, $\tilde{\mathbf{Q}}$, as a linear combination of non-redundant internal coordinates, \mathbf{Z} , such that $\frac{d\tilde{\mathbf{Q}}}{d\mathbf{X}} = \frac{d\mathbf{Q}}{d\mathbf{X}}$
 - $\mathbf{L} = \frac{d\mathbf{X}}{d\mathbf{Q}}$ transforms between Cartesian and normal mode coordinates, derived from normal mode analysis
 - $\tilde{\mathbf{L}} = \frac{d\mathbf{X}}{d\tilde{\mathbf{Q}}} = \frac{d\mathbf{X}}{d\mathbf{Q}} = \mathbf{L}$, by definition
 - $\mathbf{B} = \frac{d\mathbf{Z}}{d\mathbf{X}} \rightarrow$ Wilson B-matrix for non-redundant coordinate set
 - $\tilde{\mathbf{Q}} = (\mathbf{B}\tilde{\mathbf{L}})^{-1}\mathbf{Z}$
- Calculate energy derivatives by numerical differentiation:
 - with respect to displacements along \tilde{Q}_i
 - analytic second derivatives derived from *ab initio* Hessian data
 - step size inversely proportional to frequency
 - can tailor order of expansion to character of vibrational mode

PES expansions

Concise expansion in curvilinear normal mode coordinates

$$V_4(\tilde{\mathbf{Q}}) = \frac{1}{2!} \sum_{i,j} \tilde{F}_{i,j} \tilde{Q}_i \tilde{Q}_j + \frac{1}{3!} \sum_{i,j,k} \tilde{F}_{i,j,k} \tilde{Q}_i \tilde{Q}_j \tilde{Q}_k + \frac{1}{4!} \sum_{i,j,k,l} \tilde{F}_{i,j,k,l} \tilde{Q}_i \tilde{Q}_j \tilde{Q}_k \tilde{Q}_l$$

↓ Coordinate transformation*

Higher order expansion in rectilinear normal mode coordinates

$$V_6(\mathbf{Q}) = \frac{1}{2!} \sum_{i,j} F_{i,j} Q_i Q_j + \frac{1}{3!} \sum_{i,j,k} F_{i,j,k} Q_i Q_j Q_k + \frac{1}{4!} \sum_{i,j,k,l} F_{i,j,k,l} Q_i Q_j Q_k Q_l + \frac{1}{5!} \sum_{i,j,k,l,m} F_{i,j,k,l,m} Q_i Q_j Q_k Q_l Q_m + \frac{1}{6!} \sum_{i,j,k,l,m,n} F_{i,j,k,l,m,n} Q_i Q_j Q_k Q_l Q_m Q_n$$

Coordinate transformation procedure

$$\left\{ \begin{array}{l} \tilde{F}_i = \frac{dV}{d\tilde{Q}_i} = 0 \\ \tilde{F}_{i,j} = \frac{d^2V}{d\tilde{Q}_i d\tilde{Q}_j} \\ \tilde{F}_{i,j,k} = \frac{d^3V}{d\tilde{Q}_i d\tilde{Q}_j d\tilde{Q}_k} \\ \tilde{F}_{i,j,k,l} = \frac{d^4V}{d\tilde{Q}_i d\tilde{Q}_j d\tilde{Q}_k d\tilde{Q}_l} \end{array} \right\} \Rightarrow \left\{ \begin{array}{l} F_i = \frac{dV}{dQ_i} = 0 \\ F_{i,j} = \frac{d^2V}{dQ_i dQ_j} \\ F_{i,j,k} = \frac{d^3V}{dQ_i dQ_j dQ_k} \\ F_{i,j,k,l} = \frac{d^4V}{dQ_i dQ_j dQ_k Q_l} \\ F_{i,j,k,l,m} = \frac{d^5V}{dQ_i dQ_j dQ_k Q_l Q_m} \\ F_{i,j,k,l,m,n} = \frac{d^6V}{dQ_i dQ_j dQ_k Q_l Q_m Q_n} \end{array} \right\}$$

Coordinate transformation procedure

Shorthand notation: $\left\{ \frac{dV}{d\tilde{\mathbf{Q}}} \right\}^4 \xrightarrow{\left\{ \frac{d\tilde{\mathbf{Q}}}{d\mathbf{Q}} \right\}^5} \left\{ \frac{dV}{d\mathbf{Q}} \right\}^6$

Requires:

- repeated application of chain rule*
- derivatives of $\tilde{\mathbf{Q}}$ with respect to \mathbf{Q} , to 5th order, themselves formed through a sequence of coordinate transformations:

$$\left\{ \frac{d\mathbf{Z}}{d\mathbf{X}} \right\}^5 \xrightarrow{\frac{d\mathbf{X}}{d\mathbf{Q}}} \left\{ \frac{d\mathbf{Z}}{d\mathbf{Q}} \right\}^5 \xrightarrow{\frac{d\tilde{\mathbf{Q}}}{d\mathbf{Z}}} \left\{ \frac{d\tilde{\mathbf{Q}}}{d\mathbf{Q}} \right\}^5$$

- required transformation matrices defined during normal mode analysis, construction of $\tilde{\mathbf{Q}}$

Coordinate transformation procedure

Reduced mode-representation variants:

- Restrict number of independent indices in \tilde{F} :
 - $V_4^{3\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$
 - $V_4^{2\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$
- Restrict number of independent indices in F :
 - $V_4(\tilde{\mathbf{Q}}) \rightarrow V_6^{5\text{MR}}(\mathbf{Q})$
 - $V_4(\tilde{\mathbf{Q}}) \rightarrow V_6^{4\text{MR}}(\mathbf{Q})$
 - $V_4(\tilde{\mathbf{Q}}) \rightarrow V_6^{3\text{MR}}(\mathbf{Q})$
- Both:
 - Sensible combinations of the above
 - \tilde{m} = mode-coupling in curvilinear normal mode potential
 - m = mode-coupling in rectilinear normal mode potential

Computational scaling

Step	Scaling law $O(\dots)$	Example: $V_4(\tilde{\mathbf{Q}}) \Rightarrow V_6(\mathbf{Q})$
<i>ab initio</i> calculations	$N_{\text{basis}}^7 N_{\text{mode}}^{\tilde{m}-2}$	$N_{\text{basis}}^7 N_{\text{mode}}^2$
construction of $\frac{d\tilde{\mathbf{Q}}}{d\mathbf{Q}}$	$N_{\text{mode}}^{m-1} N_{\text{int}}$	$N_{\text{mode}}^5 N_{\text{int}}$
coordinate transformation	$N_{\text{mode}}^{\tilde{m}+m}$	N_{mode}^{10}

- \tilde{m} = mode-coupling in curvilinear normal mode potential
- m = mode-coupling in rectilinear normal mode potential

Implementation details

- $\left\{ \frac{d\mathbf{Z}}{d\mathbf{X}} \right\}^5$ matrix elements obtained via:

	stretching	bending	torsional	out-of-plane
hard-coded expressions	r	$\cos \theta$	$\sin \phi$	τ
coordinate transformation	$1 - e^{-\alpha(r-r_e)}$	θ	ϕ	$\sin \tau$
symbolic differentiation	$(r - r_e)/r$ other	other	other	other

- All transformation formulae hard-coded
- Enables general non-linear transformations between any defined coordinate systems
- Interfaces with GAMESS and CFOUR program packages
- Code available on sourceforge: PyPES extensible library

PES validation

Transformed PES expansions validated by:

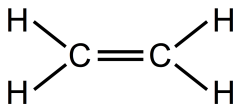
- calculating anharmonic vibrational fundamental frequencies, using VPT2-screened VCI algorithm
- comparing results against benchmark literature values
- internal comparison - choice of internal coordinate system, completeness of internal coordinate PES
- internal comparison - convergence with respect to expansion order, mode-representation

Nuclear vibrational structure method

VPT2-screened VCI

- 1 Construct harmonic oscillator basis states, according to maximum “excitation level” (total vibrational quanta)
- 2 Choose states for inclusion in VCI matrix based on their VPT2 corrections to harmonic frequencies, using loose screening threshold
- 3 Diagonalize newly formed sparse VCI matrix
- 4 Choose more states based upon their VPT2 contribution to new, anharmonic fundamentals, tightening screening threshold
- 5 Repeat steps (3) and (4) until no new states are selected, or fundamental transition energies don't change

Ethene

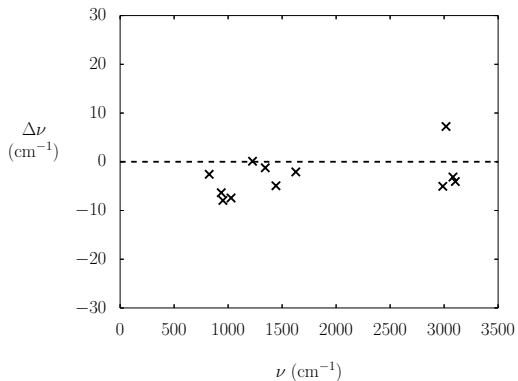


Redundant internal coordinates:

- 5 × bond lengths
- 6 × bond angles
- 4 × dihedral angles

Sextic force field in non-redundant set of symmetry-adapted internal coordinates, $V_6(\mathbf{Z}_{\text{ref}})$, implemented from the literature¹

Coordinate definition and PES truncation errors (cm^{-1})



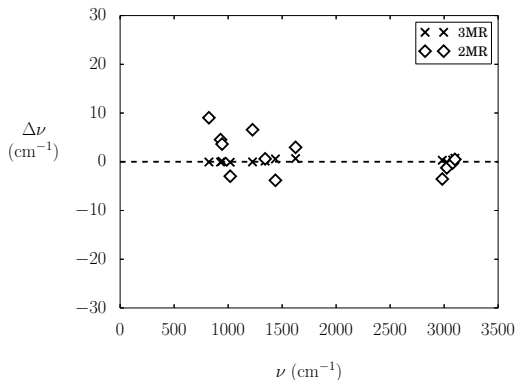
Reference:

$$V_6(\mathbf{Z}_{\text{ref}}) \rightarrow V_6(\mathbf{Q})$$

Approximation:

$$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$$

Reduced mode representation in internal coordinates



Reference:

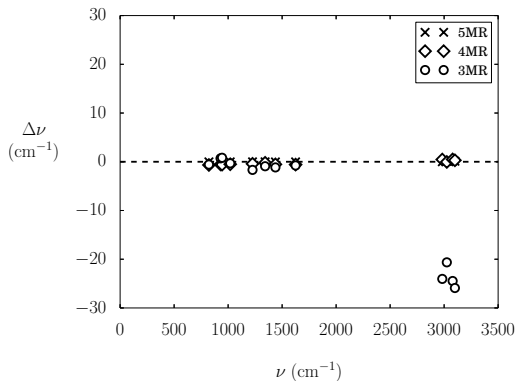
$$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$$

Approximations:

$$V_4^{3\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$$

$$V_4^{2\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$$

Reduced mode representation in normal mode coordinates



Reference:

$$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{R})$$

Approximations:

$$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6^{5\text{MR}}(\mathbf{Q})$$

$$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6^{4\text{MR}}(\mathbf{Q})$$

$$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6^{3\text{MR}}(\mathbf{Q})$$

Testing - molecules

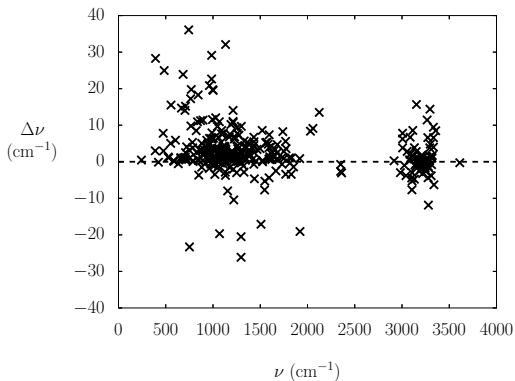
A series of internal coordinate force fields and higher order transformed normal mode force fields:

- $V_4(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$ (reference)
- $V_4^{3\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6^{4\text{MR}}(\mathbf{Q})$
- $V_4^{2\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6^{4\text{MR}}(\mathbf{Q})$

were generated for:

- 4 × 5-atom molecules
- 8 × 6-atom molecules
- 5 × 7-atom molecules
- 6 × 8-atom molecules

2MR QFF in internal coordinates



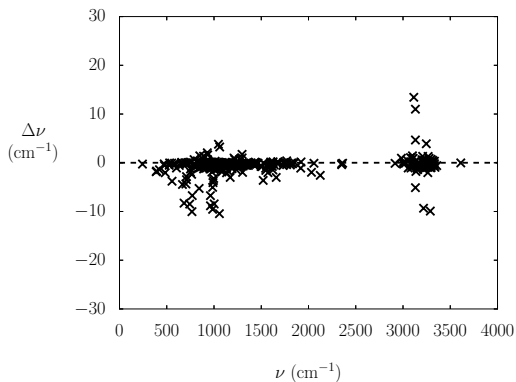
Reference:

$$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$$

Approximations:

$$V_4^{2\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6^{4\text{MR}}(\mathbf{Q})$$

3MR QFF in internal coordinates



Reference:

$$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$$

Approximations:

$$V_4^{3\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6^{4\text{MR}}(\mathbf{Q})$$

Accuracy vs computational cost

Potential	Mean Absolute Error (cm ⁻¹)	Scaling law, $O(\dots)$	
		PES construction	Coordinate transformation
$V_4^{2\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$	4.7	N_{basis}^7	N_{mode}^8
$V_4^{3\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$	0.7	$N_{\text{basis}}^7 N_{\text{mode}}$	N_{mode}^9
$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6^{3\text{MR}}(\mathbf{Q})$	4.7	$N_{\text{basis}}^7 N_{\text{mode}}^2$	N_{mode}^7
$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6^{4\text{MR}}(\mathbf{Q})$	0.6	$N_{\text{basis}}^7 N_{\text{mode}}^2$	N_{mode}^8
$V_4(\tilde{\mathbf{Q}}) \rightarrow V_6^{5\text{MR}}(\mathbf{Q})$	0.03	$N_{\text{basis}}^7 N_{\text{mode}}^2$	N_{mode}^9
$V_4^{3\text{MR}}(\tilde{\mathbf{Q}}) \rightarrow V_6^{4\text{MR}}(\mathbf{Q})$	1.0	$N_{\text{basis}}^7 N_{\text{mode}}$	N_{mode}^7

Summary

$V_4^{3MR}(\tilde{\mathbf{Q}}) \rightarrow V_6^{4MR}(\mathbf{Q})$ PES gives

- maximum error $< 12 \text{ cm}^{-1}$ and average error $< 1 \text{ cm}^{-1}$ relative to $V_4(\tilde{\mathbf{Q}}) \rightarrow V_6(\mathbf{Q})$
- optimal tradeoff between accuracy and computational cost - requires only $O(N_{\text{mode}})$ *ab initio* Hessian calculations
- first readily available numerically stable procedure for generating sextic force fields in rectilinear normal mode coordinates
- ability to accurately model anharmonic fundamentals for semi-rigid molecules with up to 15 atoms

Where to from here?

- Transform into localized modes
 - lower order transformations, expansions required?
- Transform kinetic energy operator rather than PES?
- Provide ability to specify 'spectator modes' to be modelled using second order expansion in curvilinear normal mode coordinates
 - only generate higher derivatives along 'active modes'
 - reduce computational cost to $N_{\text{basis}}^7 N_{\text{active}}$
- Improve stability of interpolated PES: transforming into high order expansions in Cartesian space avoids singularities associated with expanding PES in asymptotically-divergent internal coordinates.

Where to from here?

- Transform between different internal coordinate systems to exploit asymptotic behaviour
- Construct and test hybrid force fields using different levels of electronic structure theory
 - Harder than it sounds to do rigorously and cheaply - complex series of transformations required to find normal mode coordinates and equilibrium geometry for hybrid force field analytically from component parts
 - Could cheat and assume geometry and normal mode coordinates stay approximately constant and do literal replacement of force constants