Sparse Interpolatory Reduced-Order Models for Simulation of Light-Induced Molecular Transformations

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Outline

Molecular Geometry

- Stationary nuclei in cloud of moving electrons.
- N atoms located by $3N - 6$ coordinates (Wilson et al 1955) torsion and bond angles
- Atoms move in response to external forces, such as light.
- Stable configurations (the only ones which occur in nature) are local minimizers of potential energy $\mathcal{E}$.

Potential Energy

$\mathcal{E}$ depends on

- Configuration $p \in R^N$.
- Quantum state $n = 0, 1, \ldots$

Quantum states are ordered

$$\mathcal{E}_0(p) \leq \mathcal{E}_1(p) \leq \mathcal{E}_2(p) \leq \ldots$$

and (as you will hear many more times) the local minimizers of $\mathcal{E}_n$ are the only configurations in nature.

2-Butene

2-butene has 2 stable geometries for $n = 0$

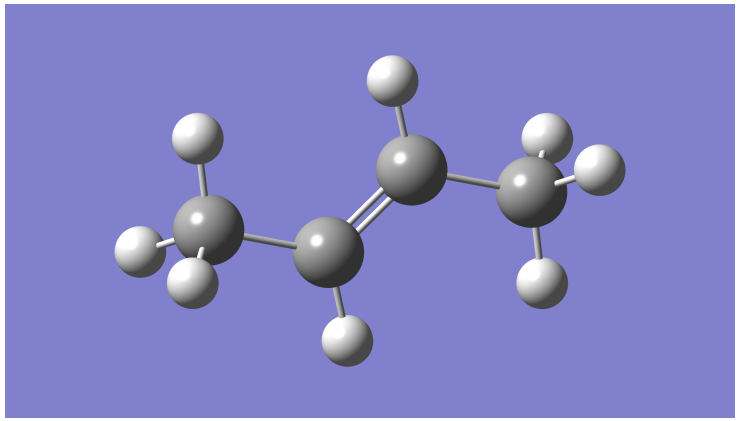


Figure: trans 2-butene

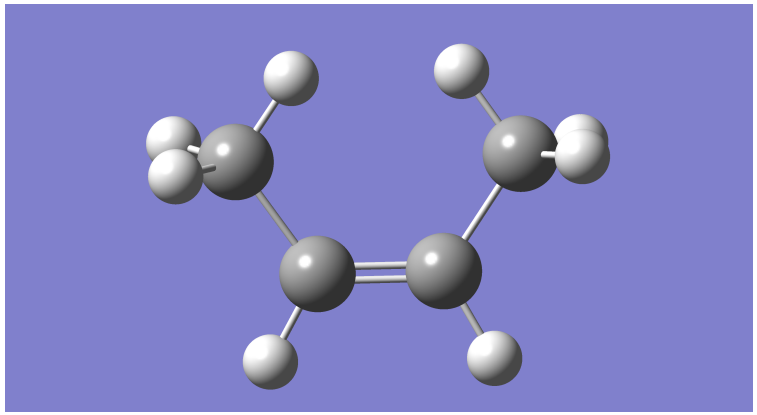


Figure: cis 2-butene

Excitations

- Begin with a stable ground state p local minimizer of $\mathcal{E}_0$
- Excite the molecule with light shifting the state to $n = 1$, say
- p may not be a local minimizer of $\mathcal{E}_1$

This is an opportunity to apply light to change the configuration.

Results of Excitation

Excitation changes orbital, thus changing interatomic forces

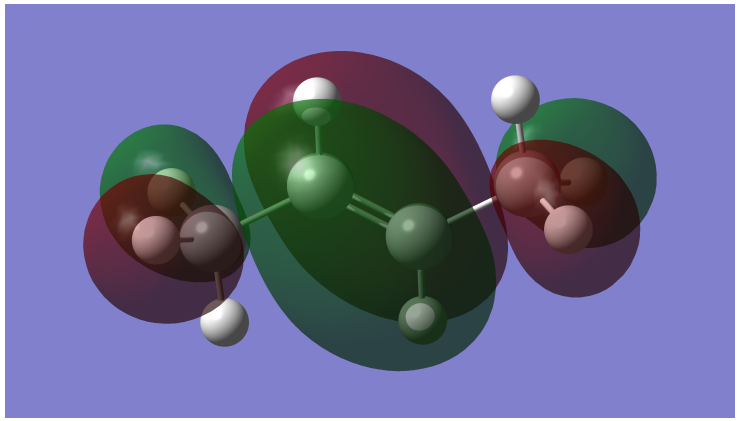


Figure: Highest Occupied Molecular Orbital

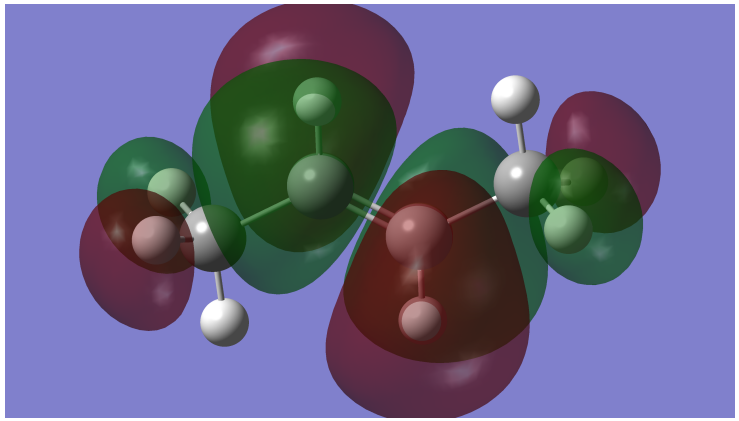


Figure: Lowest Unoccupied Molecular Orbital

Our Assignment

Simulate this:

- begin at p_0 in state 0
- excite to new state
- relax to local minimum in new state
- emit energy and return to state 0
- relax to minimum p_f
- Goal: $p_f \neq p_0$

Applications: sensors, solar power, ...

Fantasy Algorithm

- Compute $\mathcal{E}$ with a good quantum chemistry code.
  We use Gaussian.
- Compute relaxation after excitation by integrating

$$p' = -\nabla \mathcal{E}(p)$$

  and thereby optimize as nature does it.

Using dynamics-unaware method can lead to incorrect results.

Computational Reality: Reduction Step 1

- Molecules have 100s of atoms and
  100s of degrees of freedom (torsion angles)
- We can't vary all of them and must pick a few,
  and must solve an optimization problem to resolve the rest.
- So we need some collaborators to guide us as we reduce the number of degrees of freedom.
- The collaborators need us to tell them if they kept to many or omitted some degrees of freedom.

Reduction in Problem Size

- $p = (x, \xi)$ molecular coordinates; $\mathcal{E}(p)$ energy.
- x are the design coordinates
- $E(x)$ energy function of x
  - Fix x; let Gaussian solve

$$\min_{\xi} \mathcal{E}(x, \xi)$$

to find $\xi = \xi(x)$.

- Evaluation of E is very expensive; ∇E out of the question.
- Internal iteration requires good initial iterate. Failure is very costly.

2-butene Excitation

Success with a single DOF [Luo, Gelmont, Woolard (2007)]

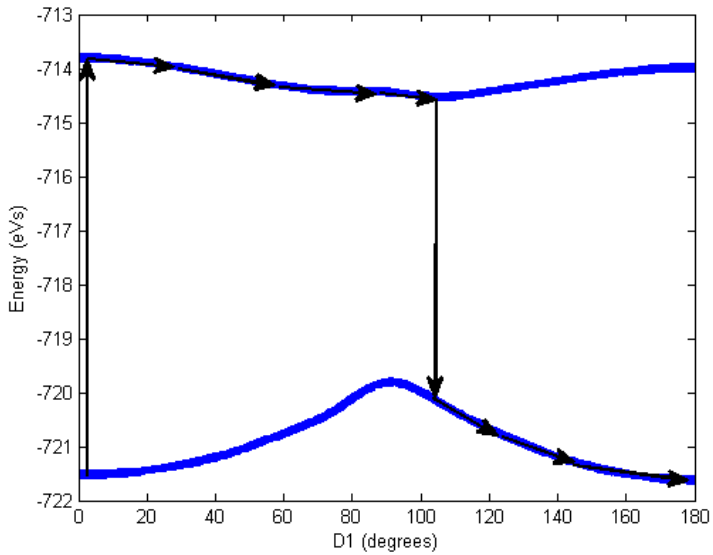


Figure: 1 variable simulation of 2-butene

Can you see why randomness might be needed?

Remarks

- Prior work used internal (expensive) Gaussian continuation.
- Gaussian will only handle one DOF.
- Internal Gaussian optimization can fail.

What we'd like to do.

- Begin with stable (local min) of $\mathcal{E}$ in the ground state.
- Excite the molecule and move through a sequence of excited states.
- Simulate relaxation in excited state via $x' = -\nabla E(x)$ and find local min.
- Interrupt dynamics in mid-stream if something interesting happens.
- Return to ground state and (maybe) find different stable state.
- Query the optimization landscape afterwards to
  - Look for design variables that did not change much or slave variables that did.
  - Add some randomness to capture thermal fluctuations.

What we can do. Reduction: Step 2

- Interpolate E in the region of interest with x_0 on boundary
  - Evaluate E on a mesh
  - Organize the evaluations so that
    - Internal optimization for ξ converges (ie has good initial data)
    - As many evaluations as possible done in parallel
- Interpolate E to get E^S
- Use the interpolant to drive the dynamics and solve

$$x' = -\nabla E^S$$

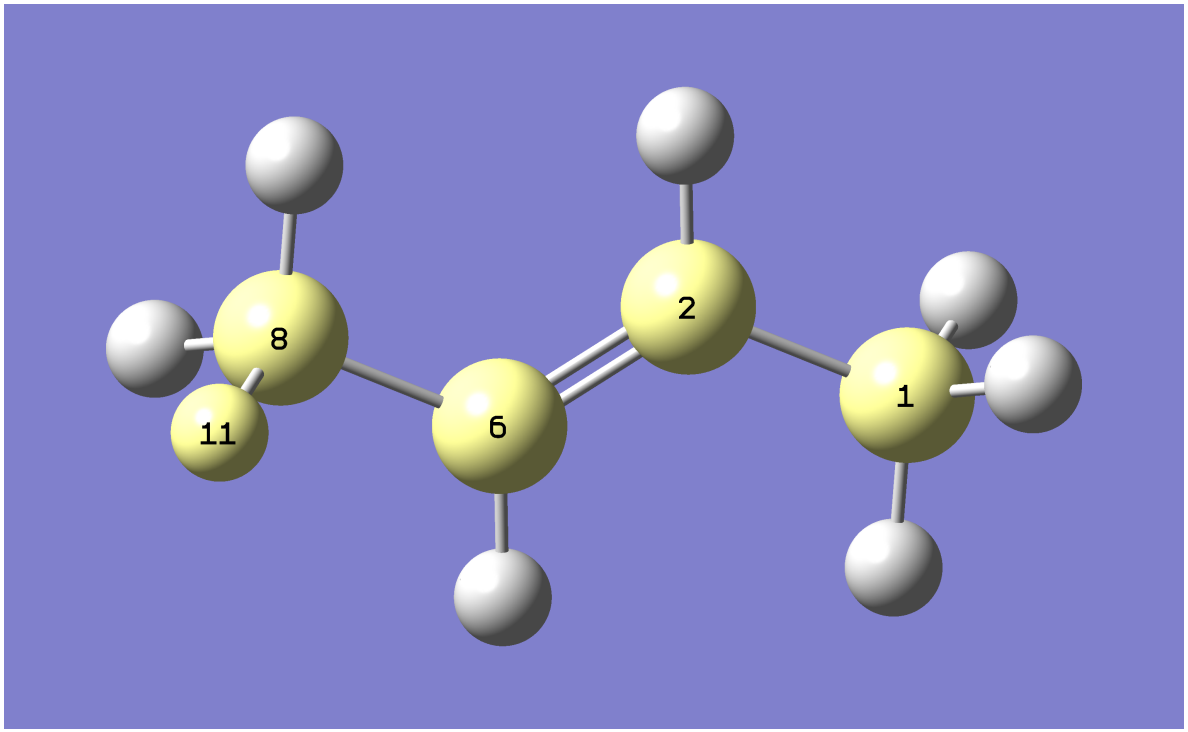
Your bad idea alarm may be going off because we have a ...

"Look-Ahead" IVP integrator

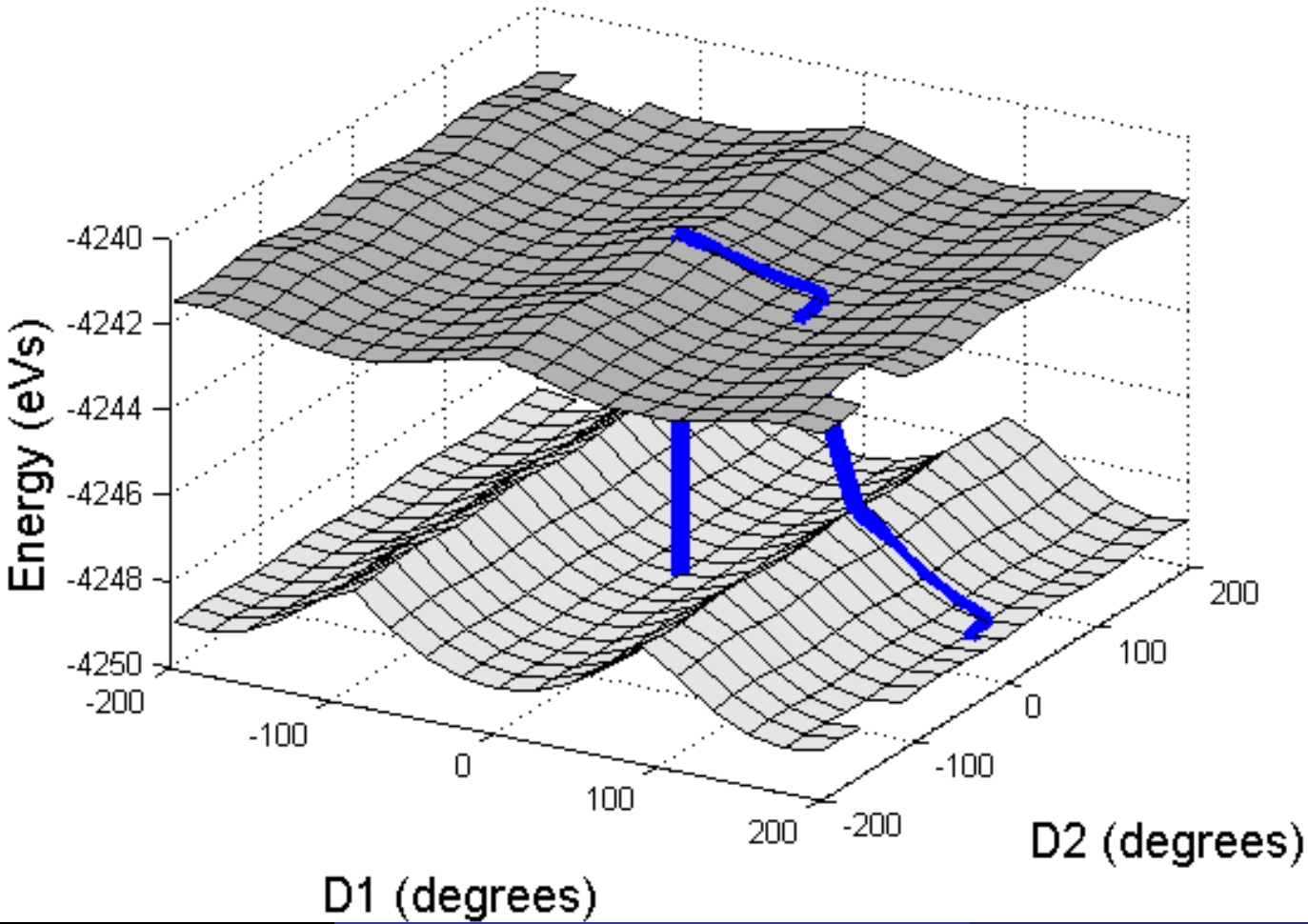
- Normally insane for $u' = f$ because
  - you'd visit places the dynamics never see,
  - waste many calls to f, and
  - the complexity would be a killer for high dimensional problems.
- But we do well with this because
  - serial evaluation of f in an normal integrator performs poorly,
  - our dimension ≤ 10 is low,
  - our function is REALLY expensive, and
  - look-ahead parallelizes easily.

Example Butene C_4H_8; D1/D2 coordinates

Rotate angles D1 (8,6 – 2,1) and D2 (11,8 – 6,2)



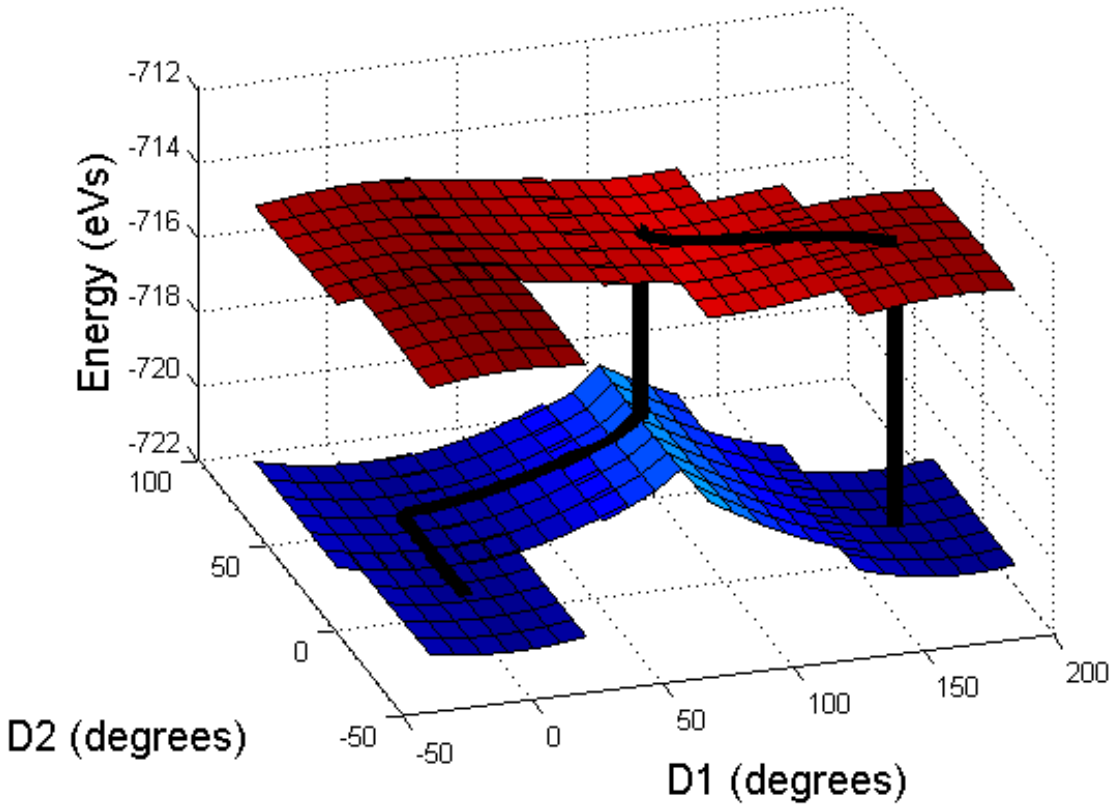
Tensor Product Mesh Results



Good Scalability, Too Many Gaussians, Reduction: step 3

- Solution: Local cubic interpolation, one patch at a time.
  - Integrate dynamics on each patch.
  - Locate and evalute on the next one.
  - Potential for error estimation and control.
- Timings: Full Surface $\approx 2\times$ patch
- Parallel performance was worse,
  but would improve with more degrees of freedom.
- Exponential complexity still there.

Faster Parallel Evaluation in Two Dimensions



Sparse Interpolation: Reduction: step 4

Tensor product grids are hopeless for more than two design variables.
We shamelessly steal an idea (Smolyak, 1963) from high-dimensional integration.

- Generate mesh in R^d so that integration has degree of exactness k
- Symmetric about coordinate lines and diagonals
- Nested meshes as k increases
  so we can estimate error efficiently.

Current approach: uses patches with sparse grids.

Building a Sparse Interplation: I

Barthelmann, Novak,Ritter (2000)

- Chebyshev extrema for $m_1 = 1, m_2 = 3, \ldots m_i = 2^{i-1} + 1$
- $\mathcal{X}^i = \{x_j^i\}_{j=1}^{m_i}$

$$x_j^i = -\cos\left(\frac{\pi(j-1)}{m_i}\right).$$

- Let $\mathcal{U}^i(f)(x) = \sum_{j=1}^{m_i} f(x_j^i) l_j^i(x)$ where l_j^i are the Lagrange interpolating polynomials.
- And now it's time for several variables ...

Building a Sparse Interpolation: II

- For $f : R^d \to R$, $\bar{\mathbf{i}} = (i_1, \ldots, i_d)$, $|\bar{\mathbf{i}}| = \sum_{j=1}^{d} i_j$, $x = (x_1 \ldots x_d)^T$

$$\mathcal{U}^{\bar{\mathbf{i}}}(f)(x) = \sum_{j_1=1}^{m_{i_1}} \cdots \sum_{j_d=1}^{m_{i_d}} f(x_{j_1}^{i_1} \ldots x_{j_d}^{i_d})(l_{j_1}^{i_1}(x_1) \ldots l_{j_d}^{i_d}(x_d))$$

- Combine a few of the $\mathcal{U}^{\bar{\mathbf{i}}}$ interpolants to get ...

Building a Sparse Interpolation: III

$$\mathcal{A}(k,d) = \sum_{k+1 \le |\bar{\mathbf{i}}| \le d+k} (-1)^{d+k-|\bar{\mathbf{i}}|} \begin{pmatrix} d-1 \\ d+k-|\bar{\mathbf{i}}| \end{pmatrix} \mathcal{U}^{\bar{\mathbf{i}}}$$

Does all kinds of good stuff:

- Interpolates polynomials of degree k exactly
- Many fewer high-order cross terms than tensor products
- Uses sparse grids

Complexity: $x \in R^d$

- Best possible for degree k

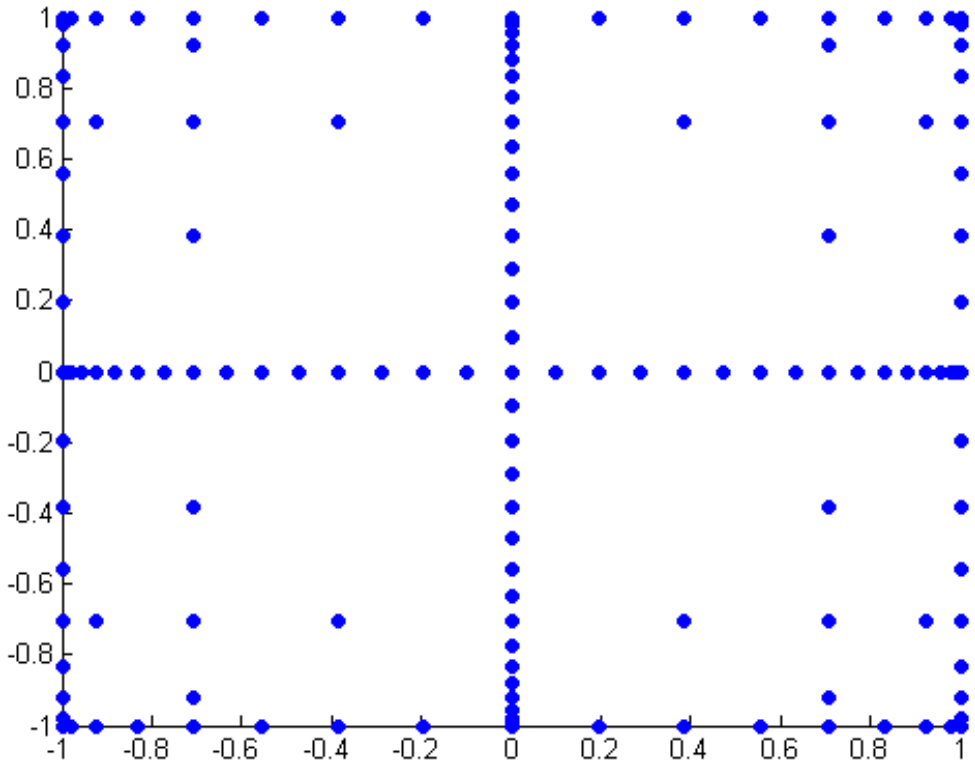
$$\left(\begin{array}{c} d+k \\ k \end{array} \right) \approx d^k/k! \text{ for large } d$$

- Tensor product grid has $(k+1)^d$ points.
- Sparse grid has $\approx 2^k d^k/k!$ points

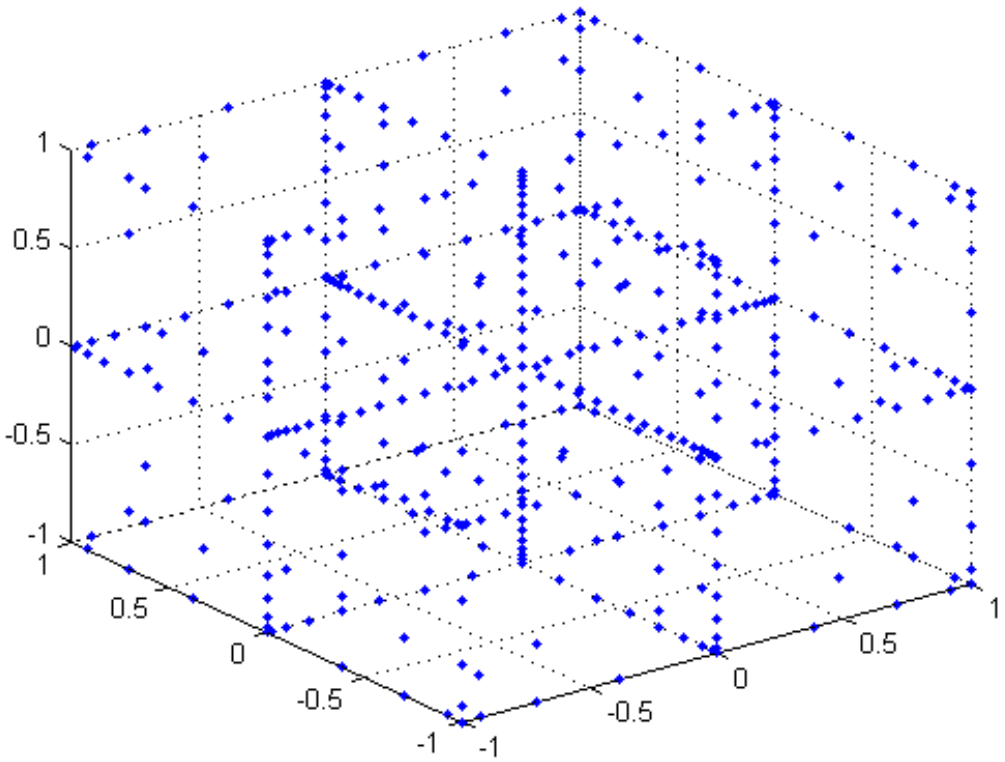
Cubic interpolation for varying d.

Dimension	2	3	4	5	6	7	8	9	10
Grid Size	29	69	137	241	389	589	849	1177	1581

Two-dimensional Sparse Grid



Three-dimensional Sparse Grid



Algorithm

- Begin with x_c, $E(x_c)$, and patch size h
- Interpolate on patch to build surrogate.
  If evaluation fails, reduce h and try again.
- Integrate dynamics using surrogate E^S until either
  - you hit a patch boundary or
  - the itegration terminates at a local minimum (of the surrogate).
- Figure out how well you did and adjust the patch size.

Patch Size Control I

Method until September 2011.

- Evaluate E at the end of the path x_+
- Compare $ared = E(x_c) - E(x_+)$ to $pred = E(x_c) - E^S(x_+)$
- We want $ared/pred$ to be near 1
  - If $ared/pred$ is near 1 and x_+ is on the boundary, $h \longrightarrow 2h$.
  - If $ared/pred$ is far from 1 $h \longrightarrow h/2$.
  - Otherwise leave h alone.

This is a crude form of error estimation.

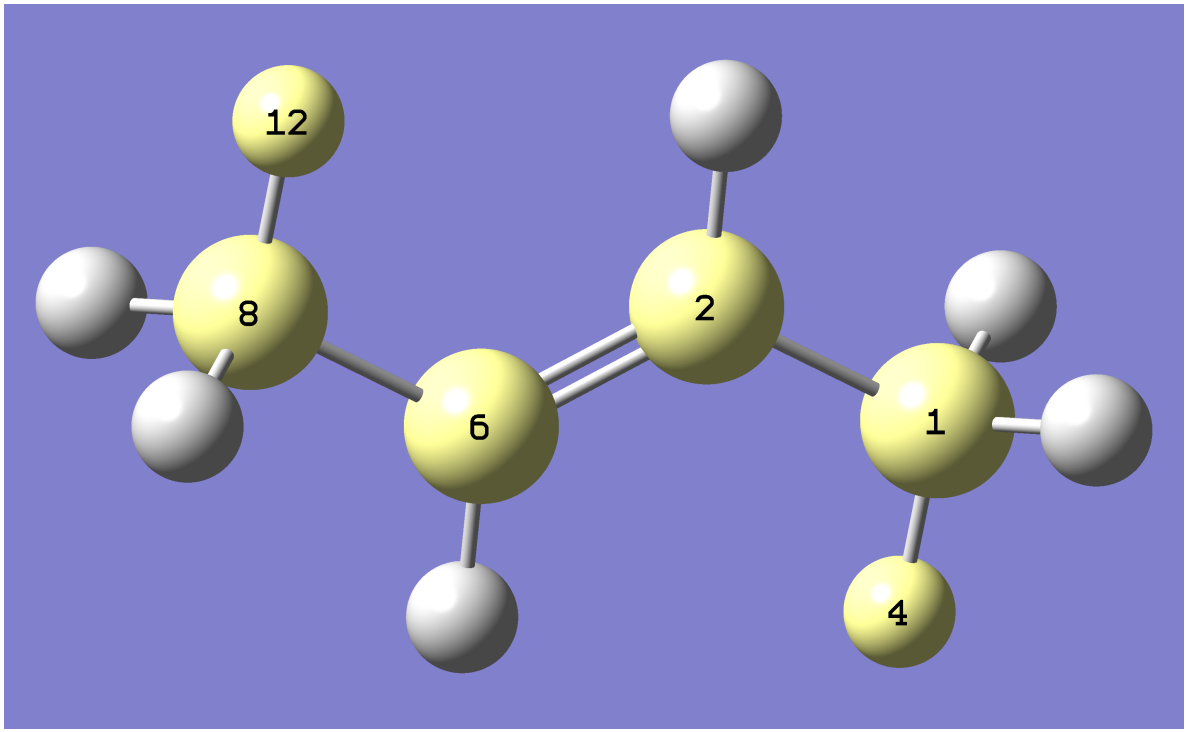
Problem: evaluation at interpolation nodes fails too often.

Computing: I

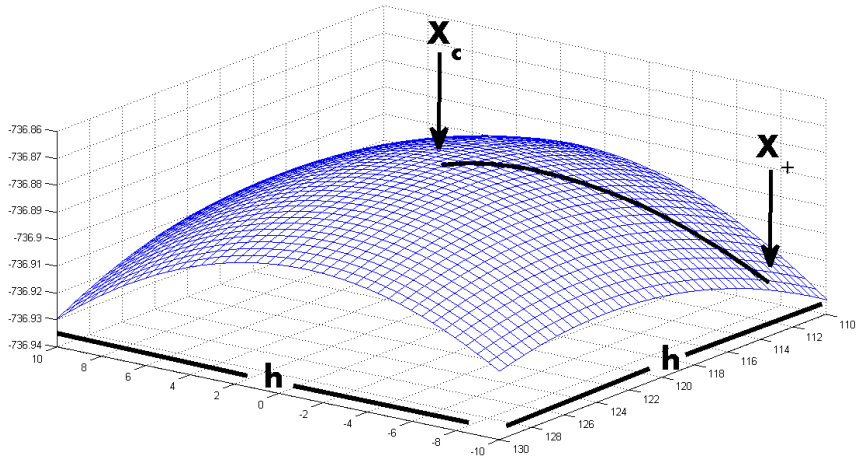
- Hardware: IBM Blade Center
  - 32 blades; dual quad-core Xenons = 256 cores
  - Infiniband network
- Parallelism:
  - Energy evaluations at each node in parallel.
  - Gaussian uses 4-way parallelism on each blade
  - 64 Gaussian calls at once. Managed with Python.

Example Butene C_4H_8; D1/D2/D3 coordinates

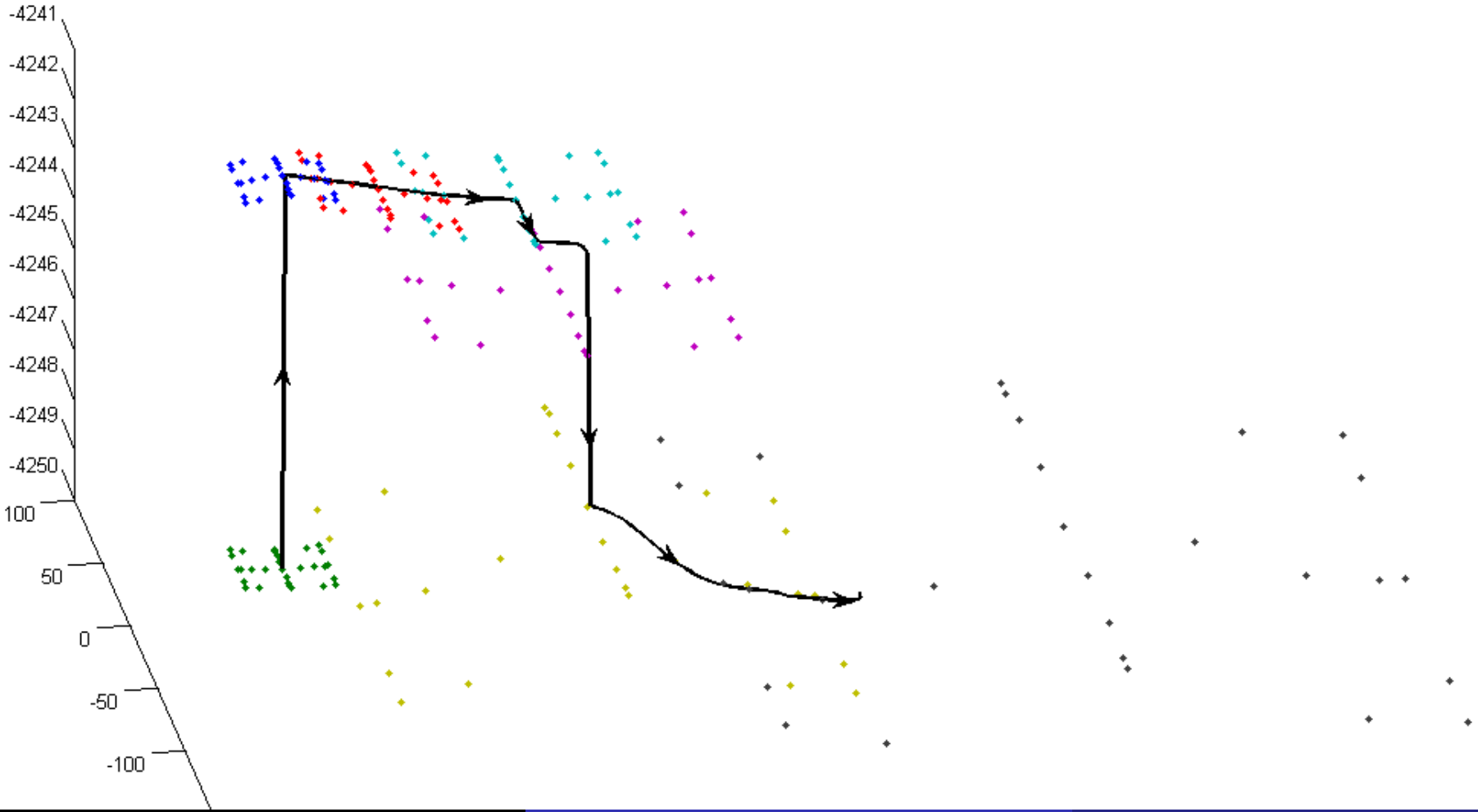
Rotate angles D1 (8,6 – 2,1), D2 (12,8 – 6,2), D3 (4,1 – 2,6)



Patch from 2-butene Computation



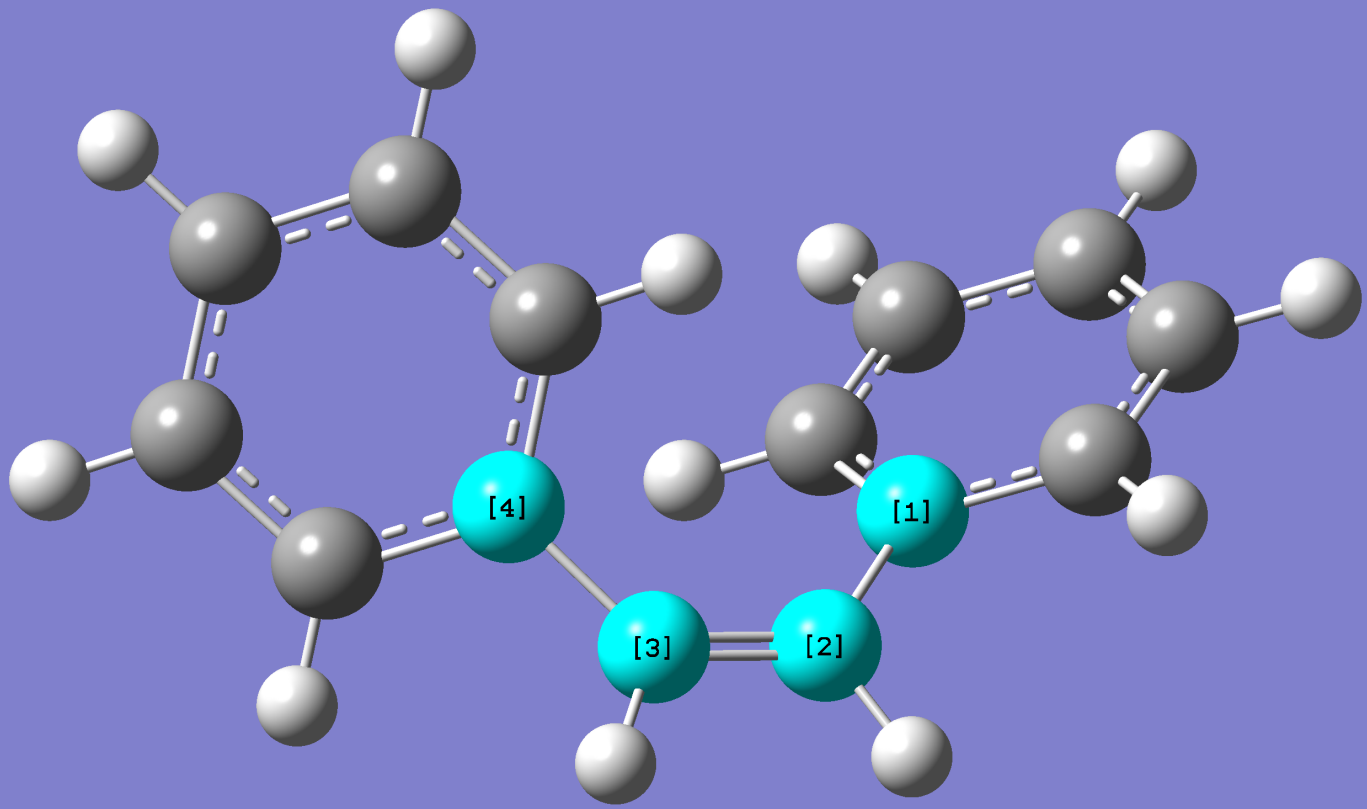
Success


-4241
-4242
-4243
-4244
-4245
-4246
-4247
-4248
-4249
-4250
100
50
0
-50
-100

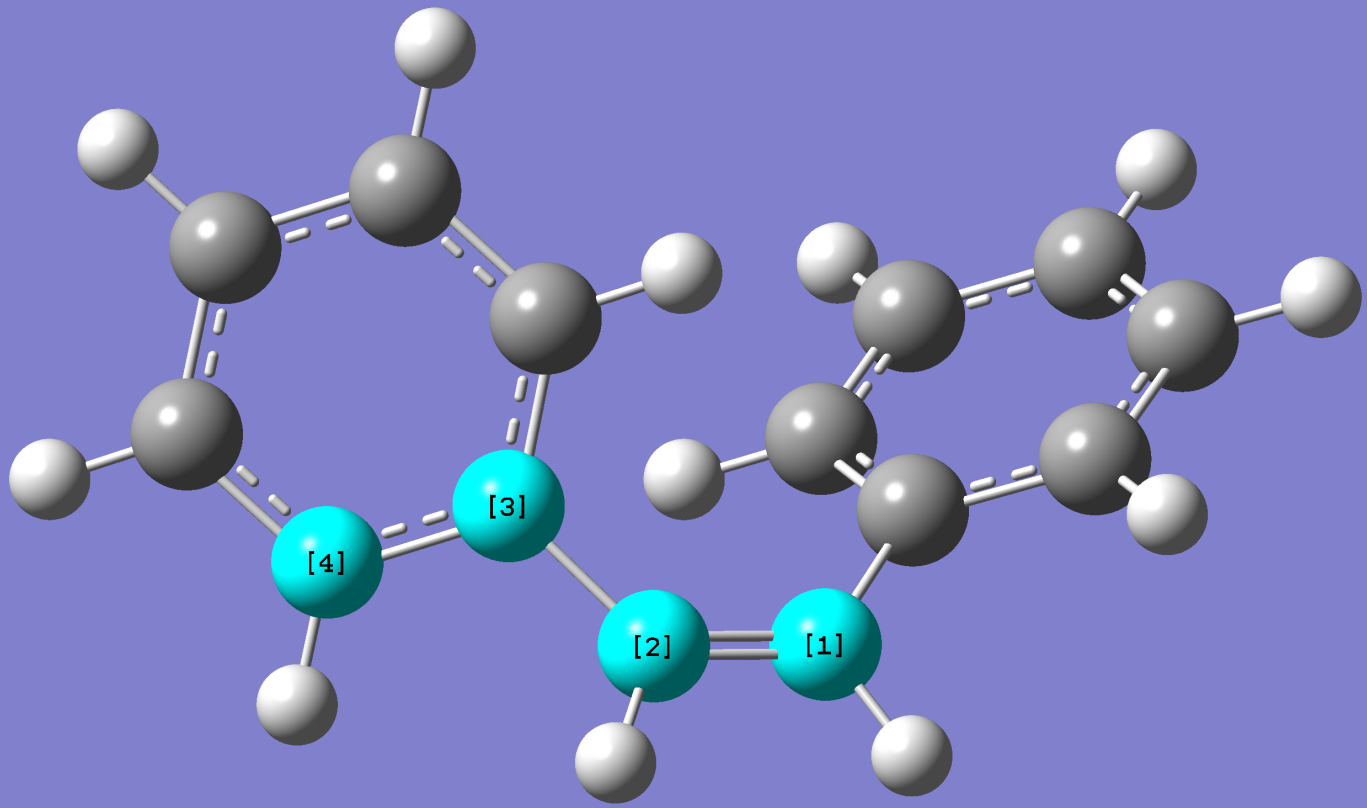
Parallel Performance

degree	# points	cores	time(sec)
2	25	13	190.96
3	69	39	194.05

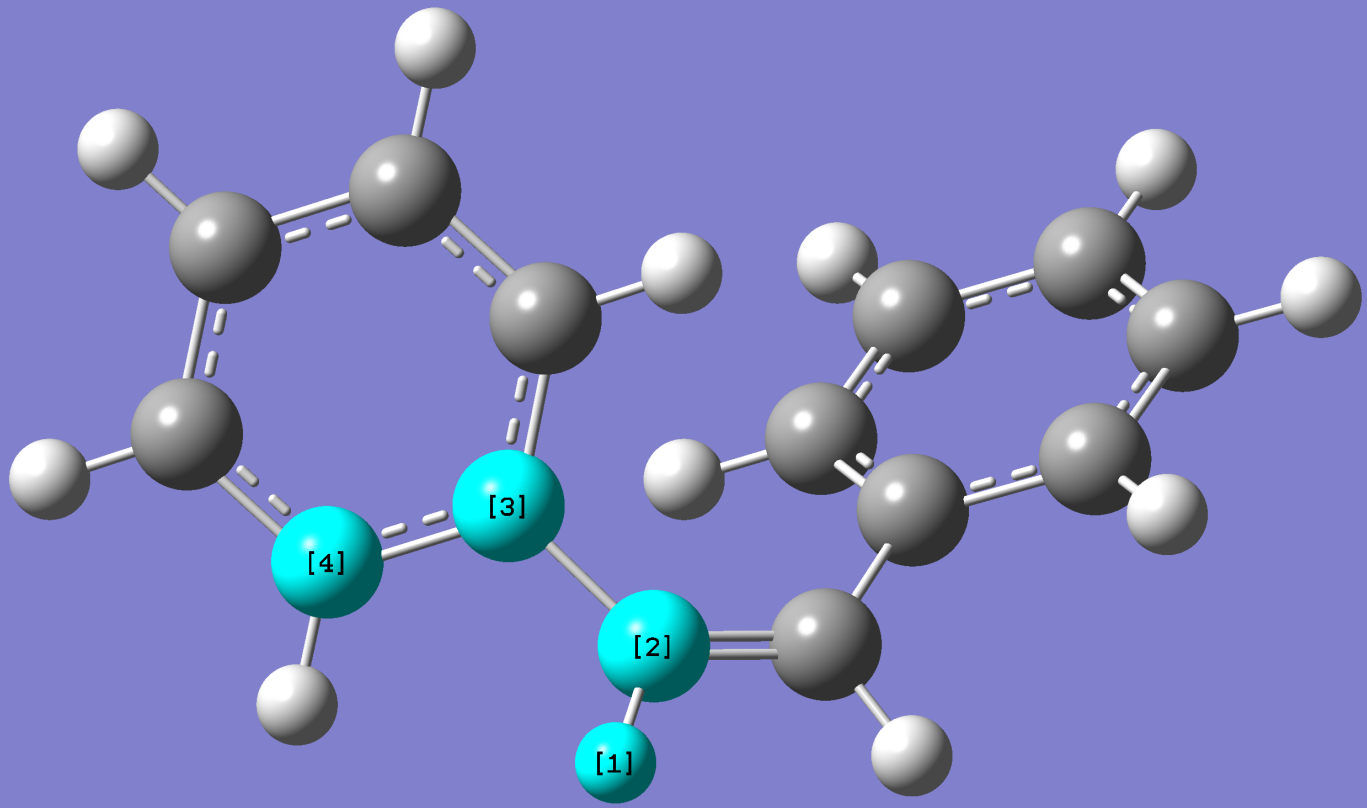
Something Larger: $(C_{14}H_{12})$ Stilbene-1



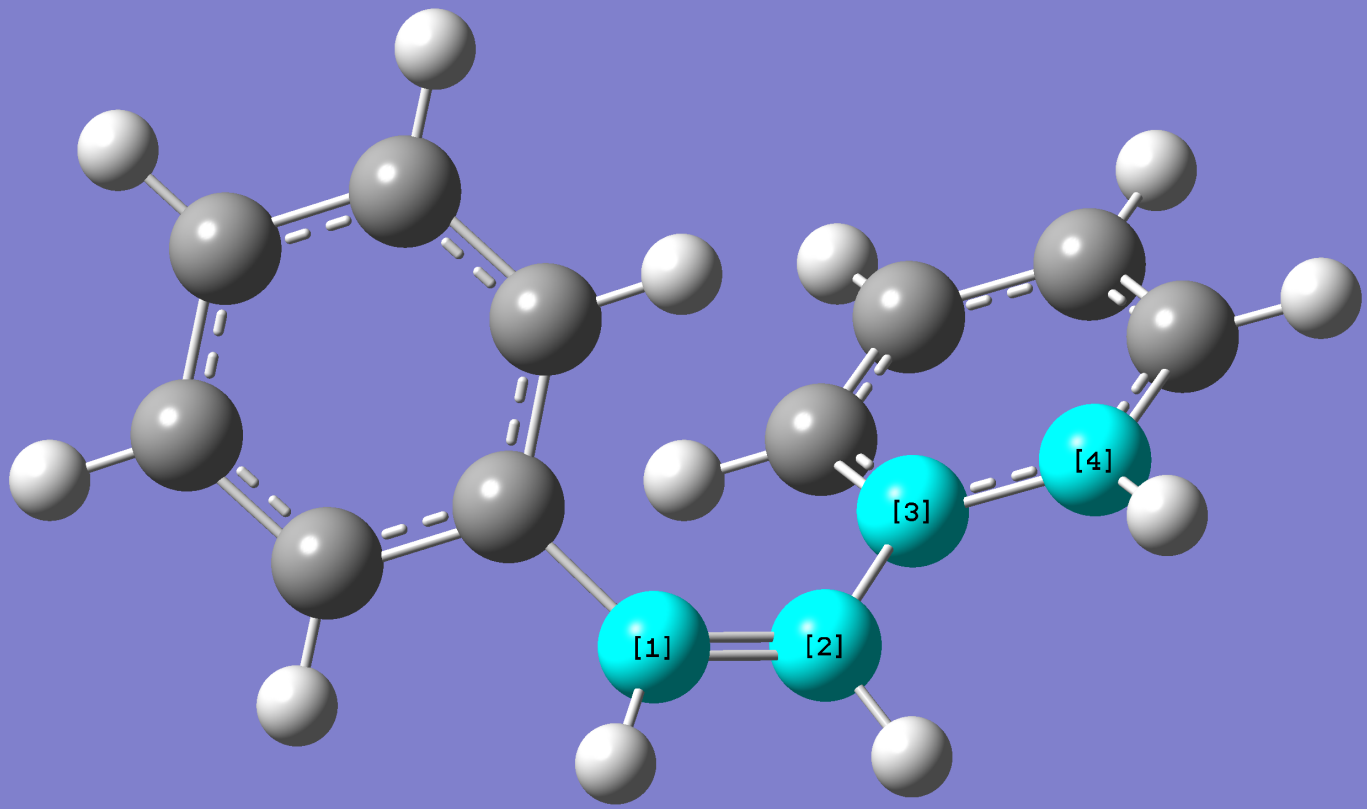
Something Larger: Stilbene-2



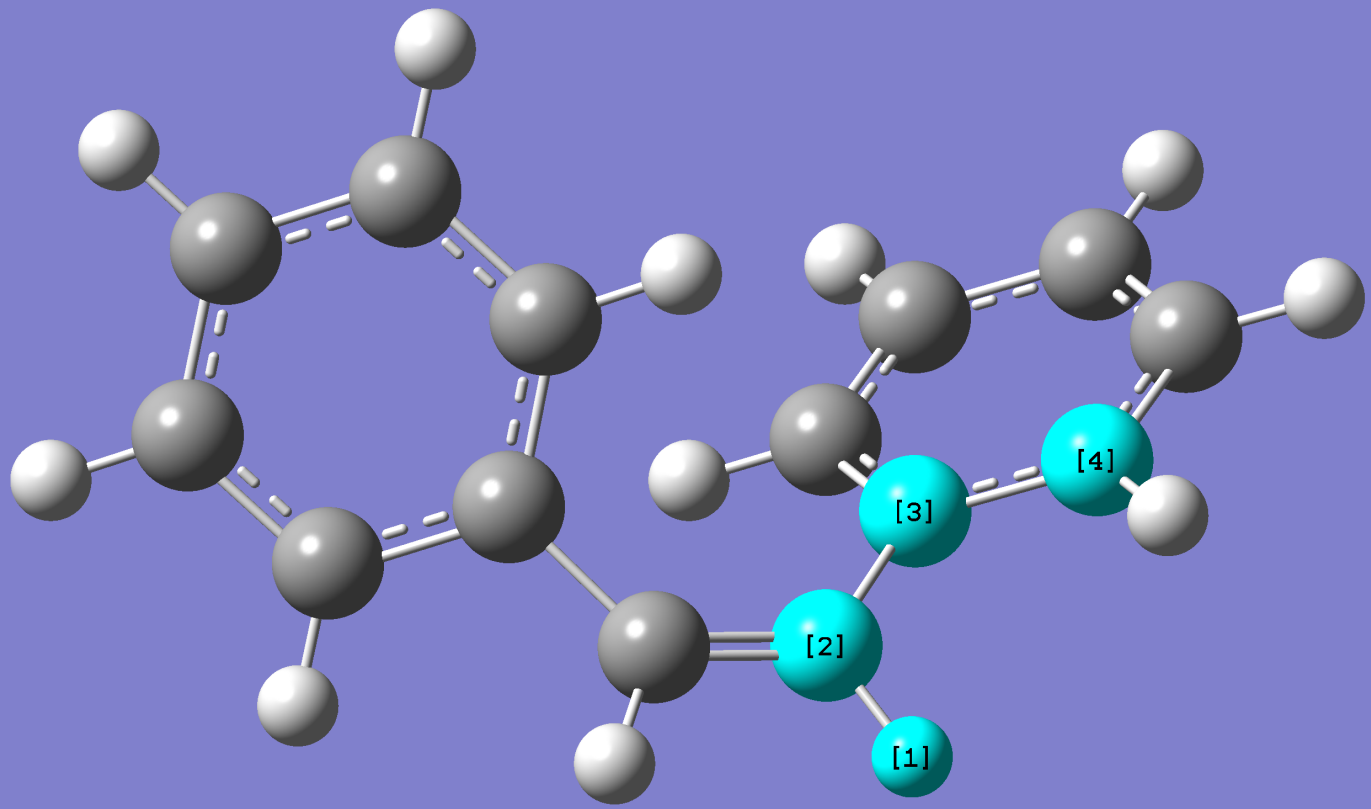
Something Larger: Stilbene-3



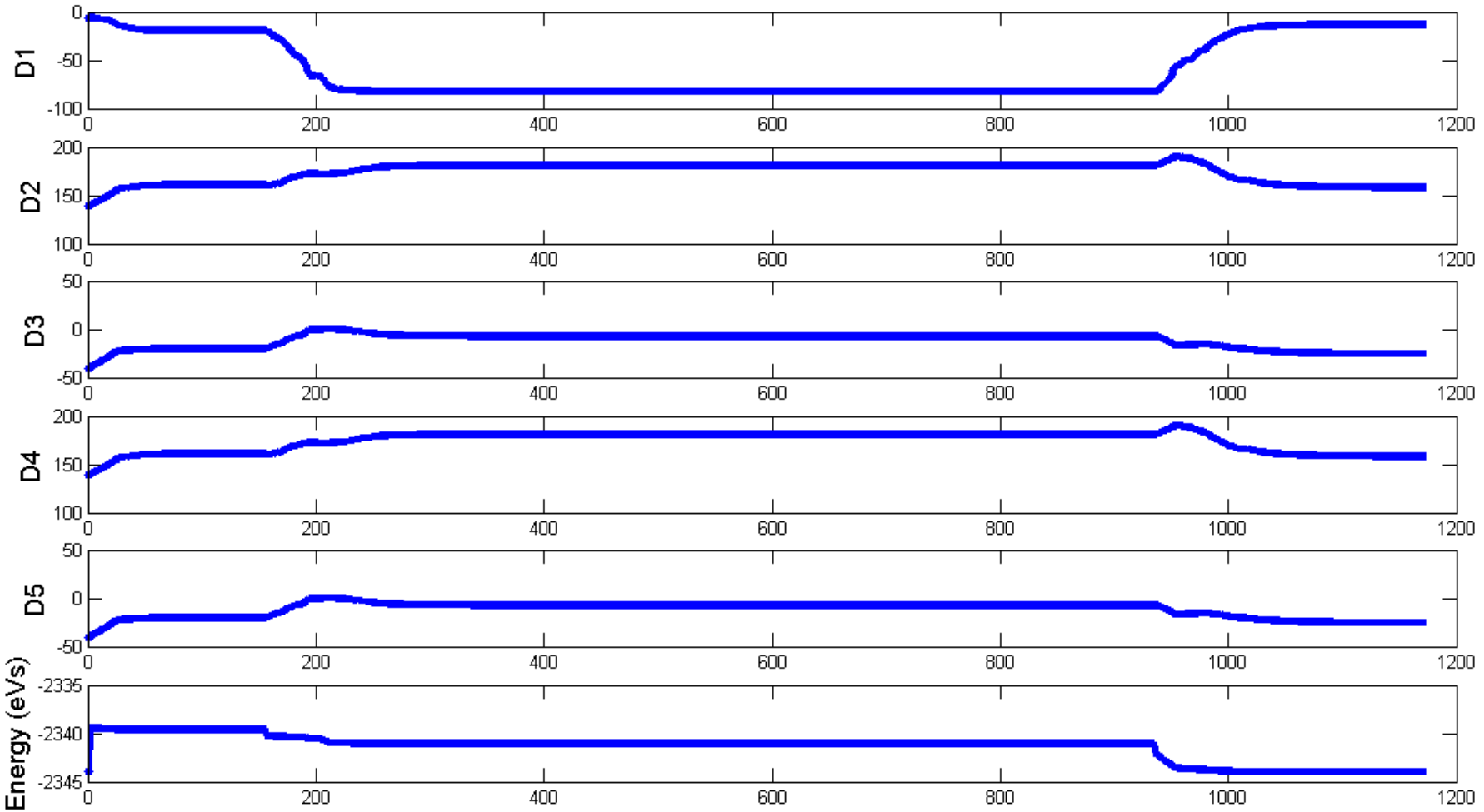
Something Larger: Stilbene-4



Something Larger: Stilbene-5



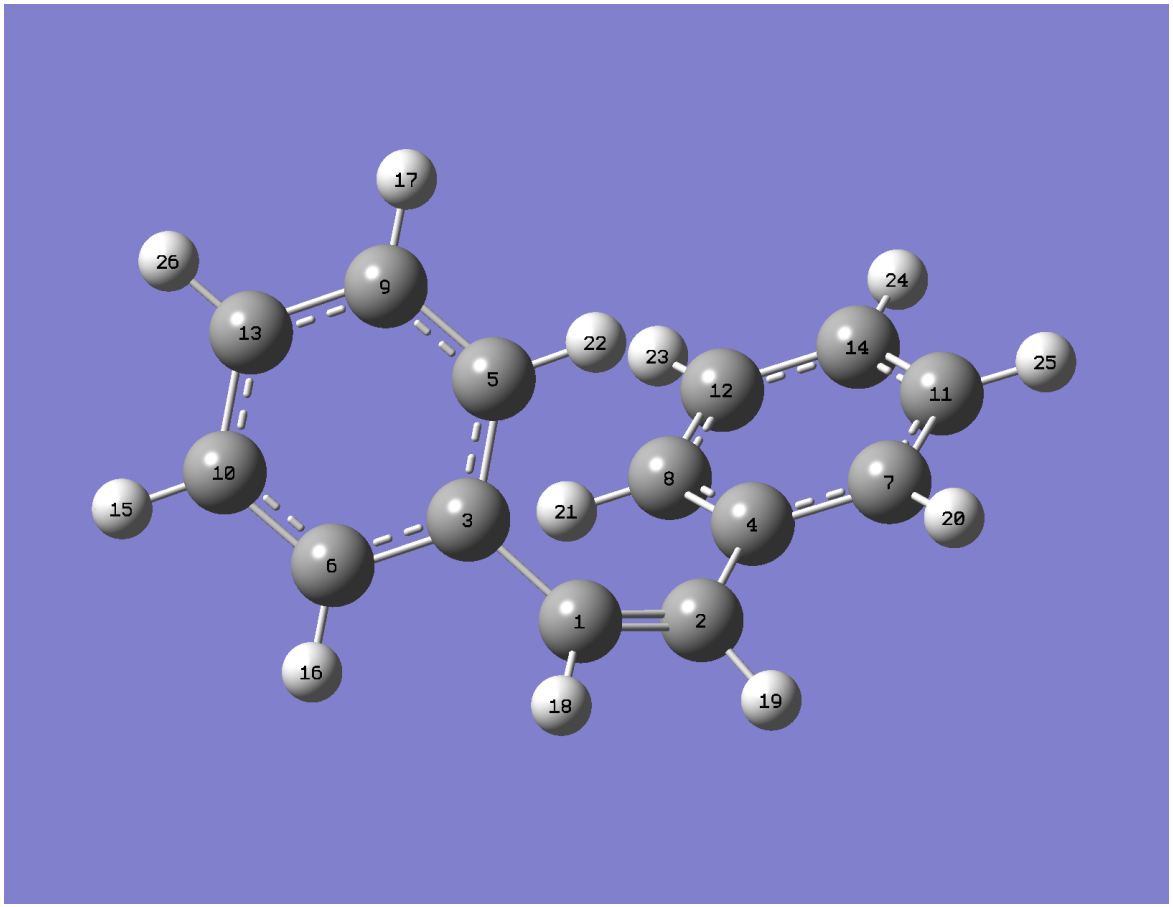
The Path


D1
D2
D3
D4
D5
Energy (eVs)
0
200
400
600
800
1000
1200
-100
-50
0
100
150
200
-2335
-2340
-2345

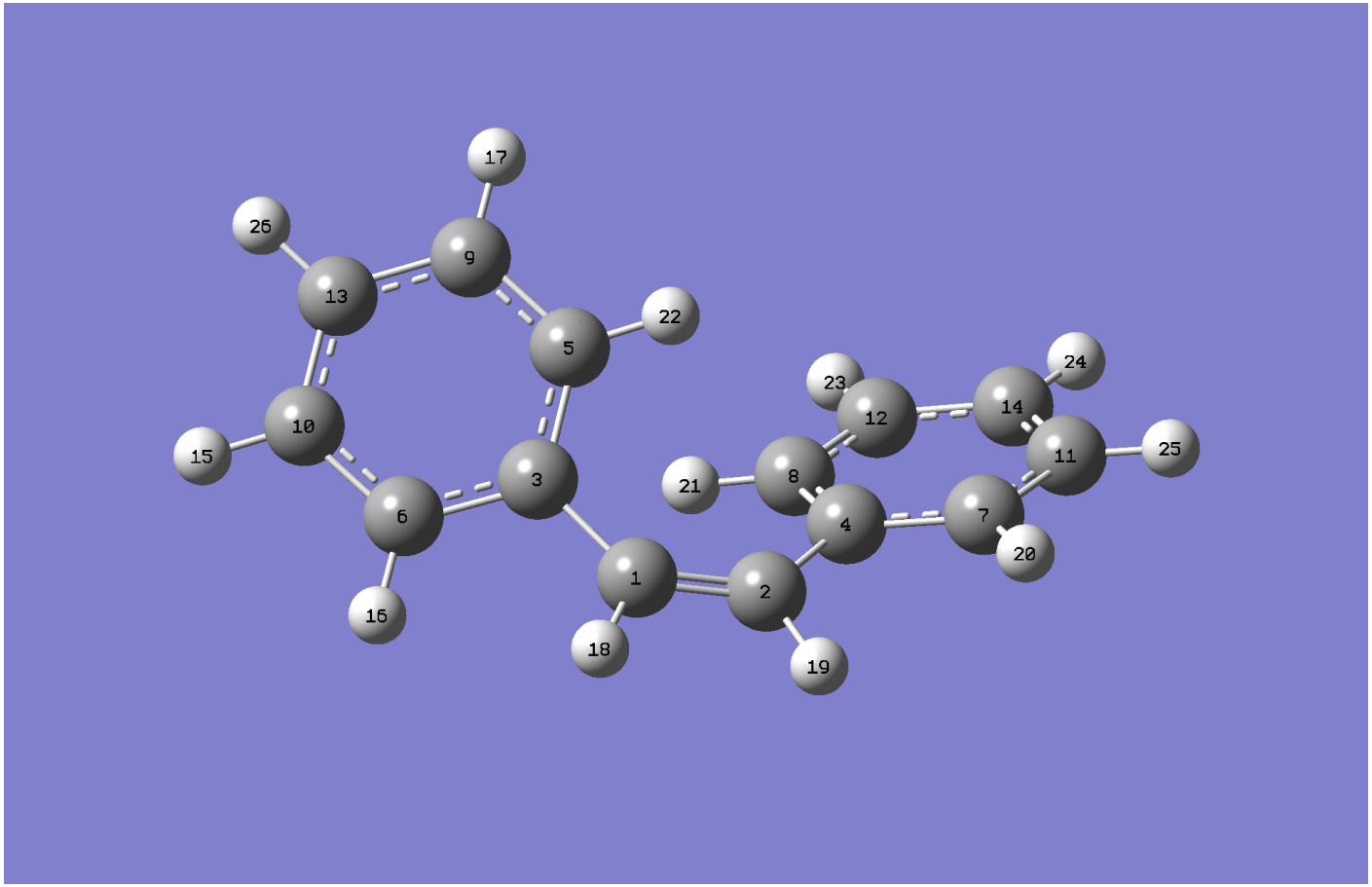
Bottom Line

	D1	D2	D3	D4	D5	Energy
Start	-6.00	140.00	-40.00	140.00	-40.00	-2343.94
End	-8.94	153.57	-28.23	153.58	-28.22	-2343.97

OLD



NEW



Patch Size Control II

Respond to Internal Optimization:

- Internal iteration limit (BFGS) of 30.
- Shrink patch when max observed count > 15
  Shrink by how much?
- Allow patch to grow when max observed count < 5
  Growth will also depend on error estimation.

Patch Size Control III

Degree k sparse interpolant E^k has error

$$\epsilon_k = O(h^{k+1})$$

and ∇E^k has order $O(h^k)$.
Grids Ω^k are nested ($\Omega^k \subset \Omega^{k+1}$).
Estimate error of degree k approximation before the integration:

- Compute E^k and E^{k+1} from the evaluations on Ω^{k+1},
- Computed estimate error $\bar{\epsilon}_k$ by $\|E^k - E^{k+1}\|_\infty$ over most recent trajectory

Patch Size Control IV

Then,

- Base the integration on ∇E^{k+1} (order extrapolation).
- Use RK45 ideas to control patch size from desired error.

Example: Want energy error $\leq \tau$.
If $\bar{\epsilon}_k \approx \epsilon_k \approx Ch^{k+1}$ then $C \approx \bar{\epsilon}_k / h^{k+1}$.
Pick h_{new} to force $\epsilon_k \leq \tau$ by $h_{new} < (\tau / C)^{1/(k+1)}$.

LITES

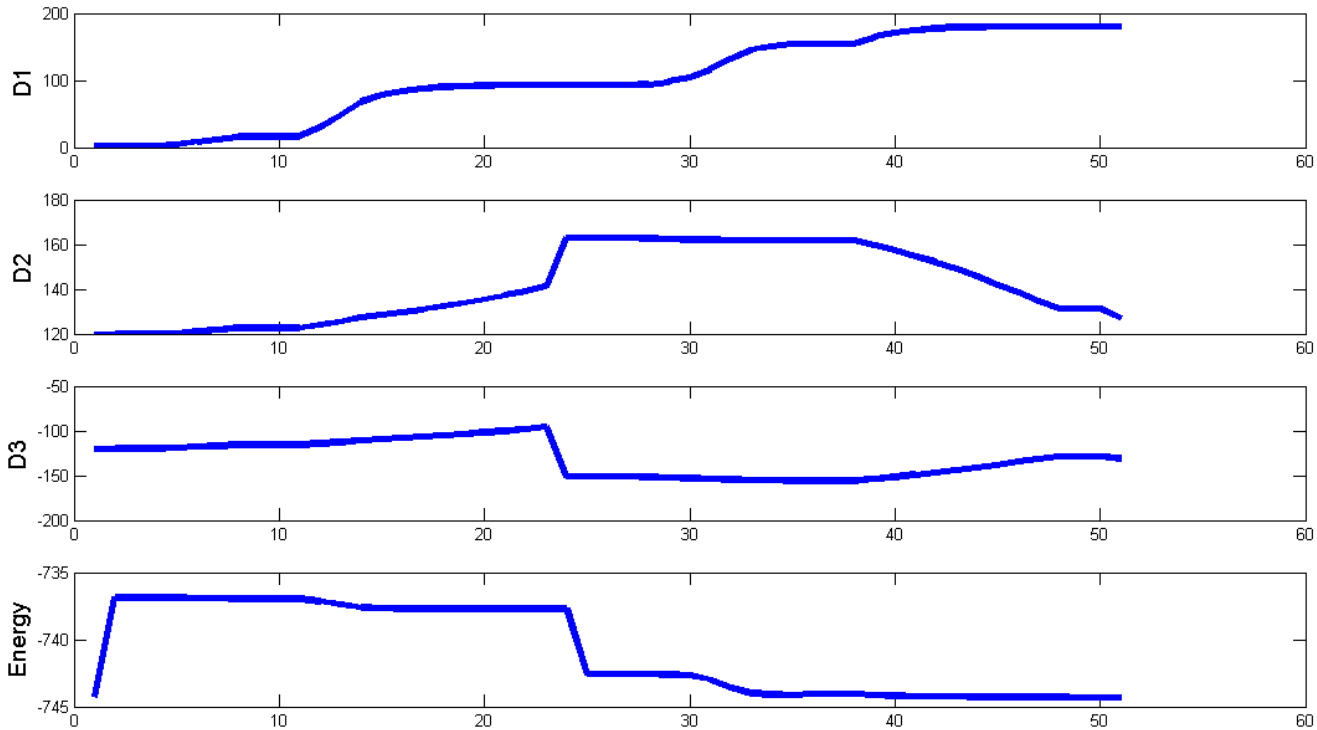
Light-Induced Transition Effects Simulator

- Phython driver + numerics
- Error and patch-size control
- Manages calls to Gaussian in parallel
- Documentation aimed at chemists.
  Now in beta-test with a real chemist.
- Uses Gaussian data structure: Z-matrix
  Easy to swap Gaussian for something else.

LITES I/O

- Input:
  - ordered list of excited states beginning and ending at 0
  - Initial ground state configuration
- Output:
  - Final point + energy + configuration
  - Z-matrix at each interpolation node
  - Z-matrix at start/end of each patch

LITES Results: 2-butene Revisited



2-butene 3D Simulation Accuracy

$$\delta = 10^{-3}$$

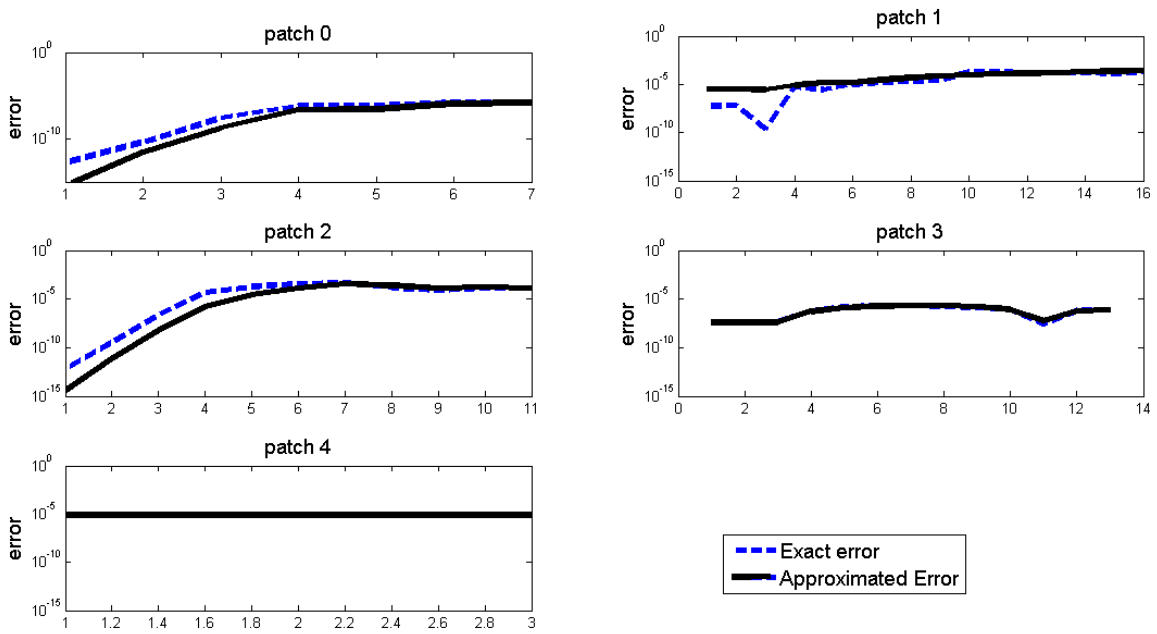


Figure: Actual vs Approximate Error on each Patch

LITES Results: Azobenze

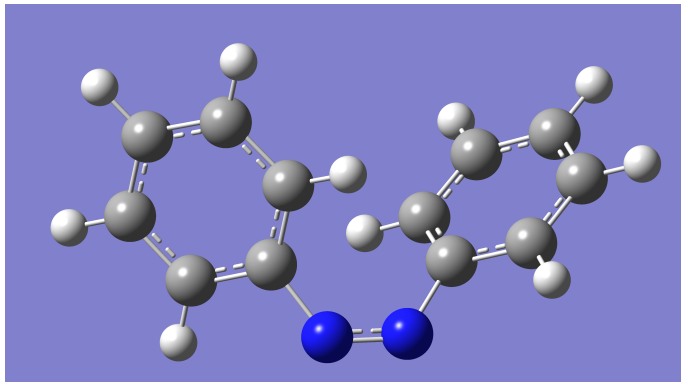


Figure: Cis-Azobenzene

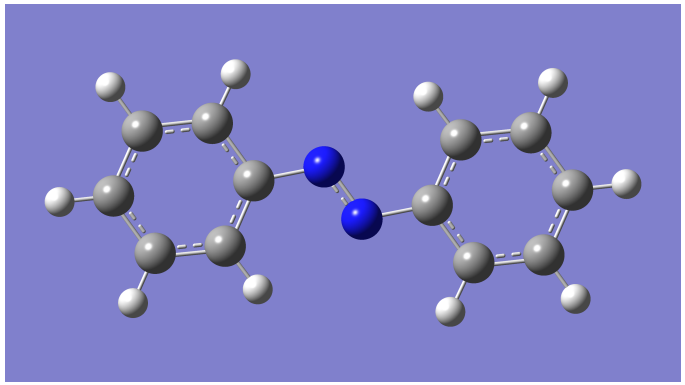


Figure:
Trans-Azobenzene

Cis-Azobenzene Simulation

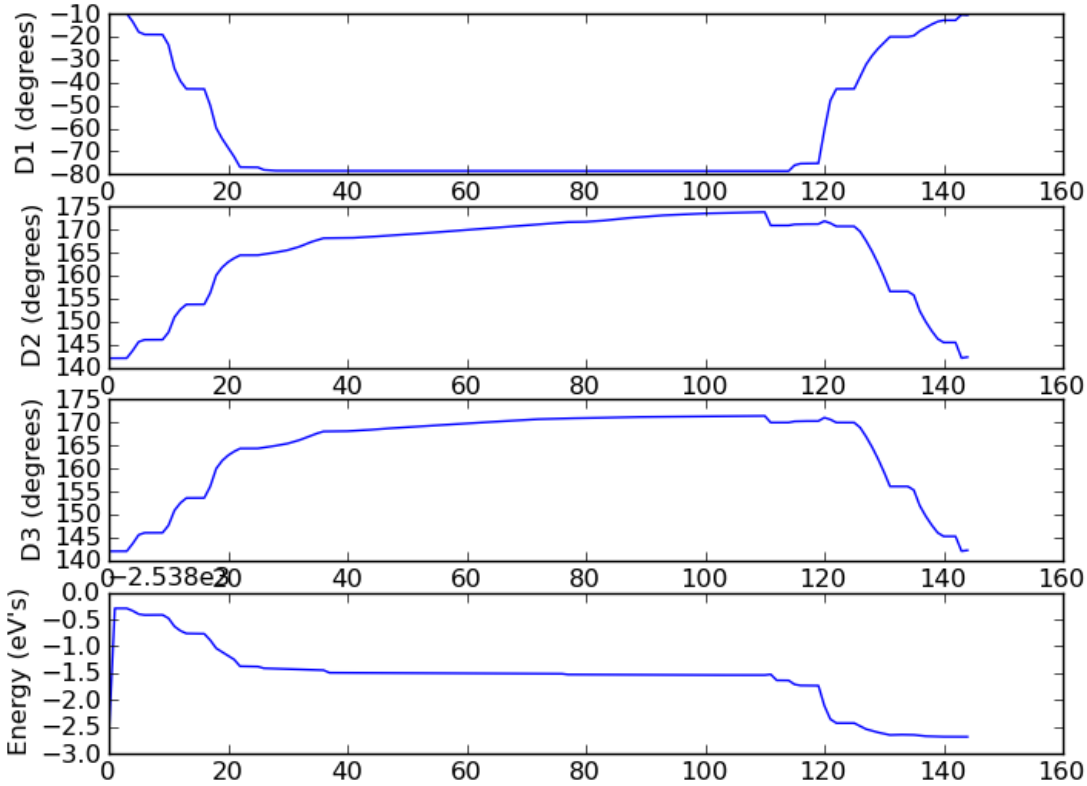


Figure: Cis returns to Cis

Trans-Azobenzene Simulation

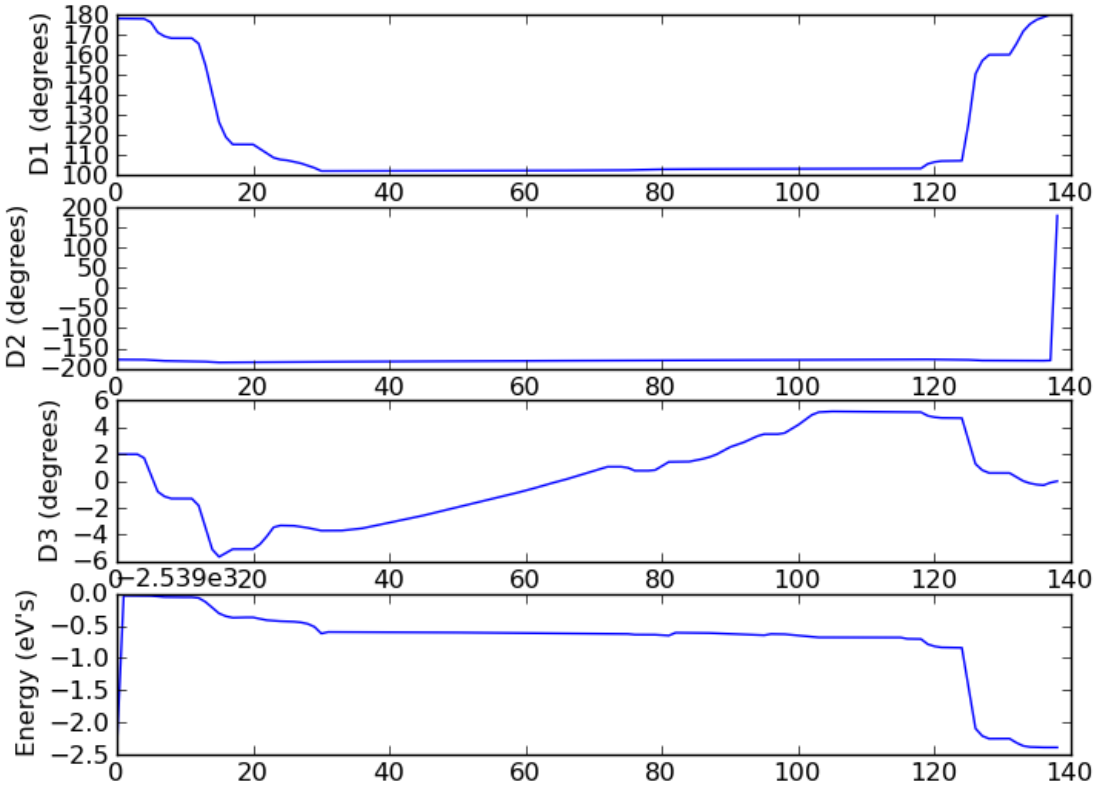


Figure: Trans returns to Trans

Remarks

- The tool works, but we did not get what we wanted.
- Chemistry expertise is needed to
  - identify the correct design variables,
  - chose the sequence of exited states, and
  - figure out the frequency and pulse rate to get to these states.

Future

- Include thermal effects (randomness).
- Query patches for low barriers (more randomness).
- Experiments.

Opportunities in Quantum Chemistry/Physics

- Many opportunities for mathematicians.
- You must have professional help (ie collaborators).
- Leaning curve is steep (be patient).
- You will function with very incomplete information.

Conclusions

- Sparse interpolatory surrogates for molecular simulation.
- Application: sensors, solar power
- Natural parallel evaluation of Gaussian.
- Good speedup for 100s of cores.