Towards a Parallel Implementation of The Growing String Method

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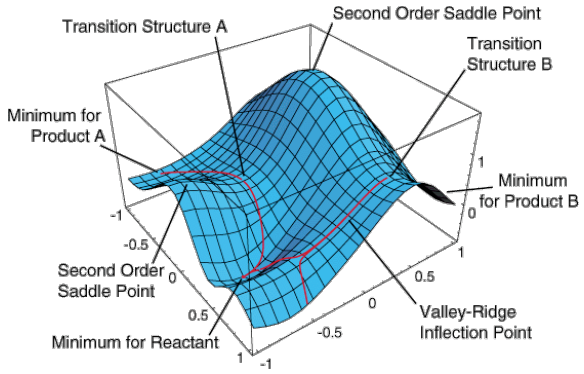
Transition State Finding Algorithms

- Utilize electronic structure calculations to determine potential energy surface and deduce reaction mechanisms and rates.
- Transition states are represented by first-order saddle points on the PES.
- $\partial E/\partial x = -F$
- $\partial^2 E/\partial x^2 = H$
- A transition state is characterized by a Hessian which has only one negative eigenvalue.

Flavors

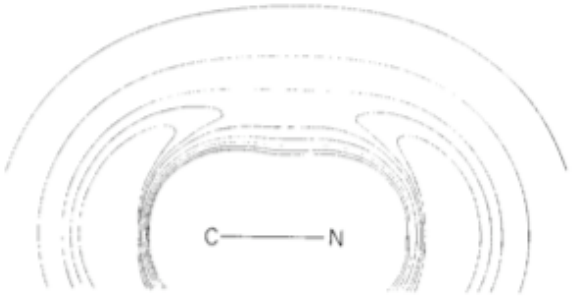
- Nudged Elastic Band - connects reactant and product with around 10-20 intermediate structures with Hookean springlike interactions between them. Requires good initial guess of the TS or calculations will fail to converge. Also, if Hooke's constants used to keep the nodes spaced along the path are chosen improperly, it will fail.
- Growing String Method - Linear synchronous transit line connects reactant and product. The GSM grows two independent strings from each end. They connect to one string when the arclength between the strings reaches zero. No initial TS guess required. The nodes are redistributed after each move instead of using springs.

Sample PES



http://www.chem.wayne.edu/~hbs/chm6440/PES.html

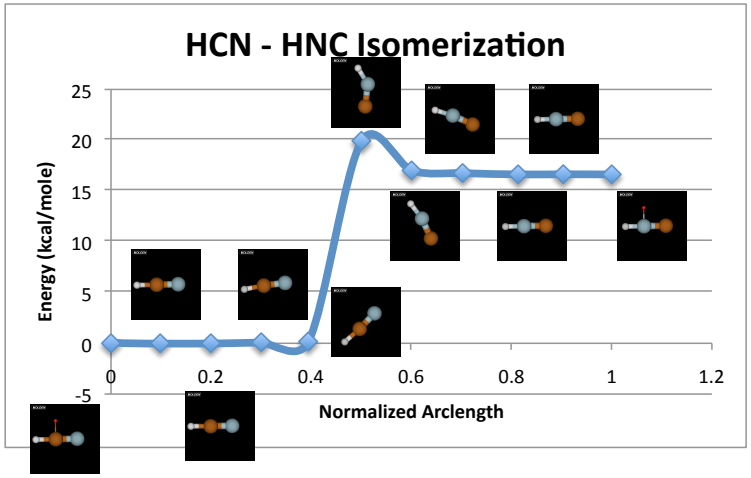
HCN→HNC PES



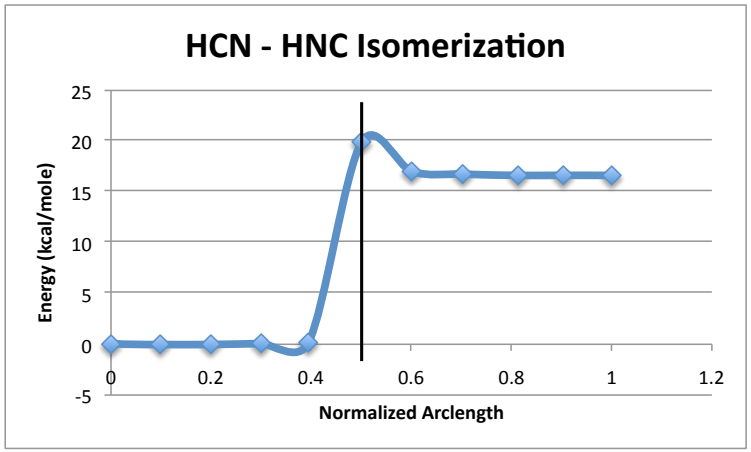
Contour plot approximately representing the potential energy surface for a hydrogen atom moving around a rigid CN radical. The two local minima located at opposite ends of the radical are not of equal depth, although they may appear so because their energies differ by less than the contour interval.[1]

[1] P. K. Pearson, H.F. Schaefer, J. Chemp. Phys. **62**, 350 (1975).

HCN→HNC Reaction Diagram

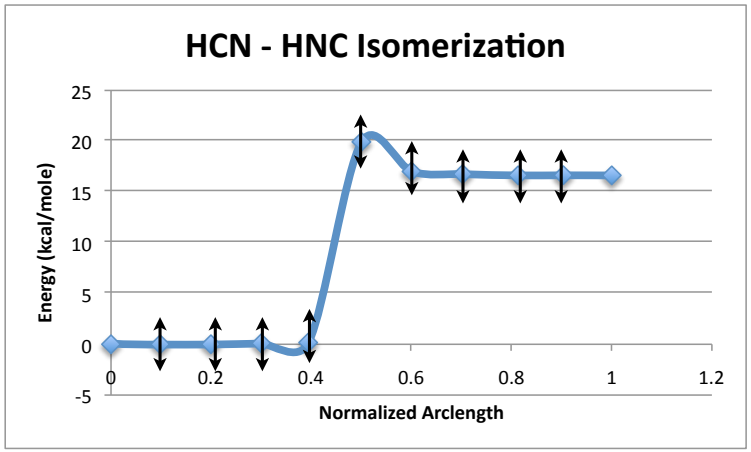


Parallelism



2x initial speedup from using
separate processors to grow string

Parallelism



After string is formed, nodes are redistributed and string evolves. Evolution is inherently parallel and constitutes lion's share of computational time. Expect speedup on up to 9 PEs. What about more?