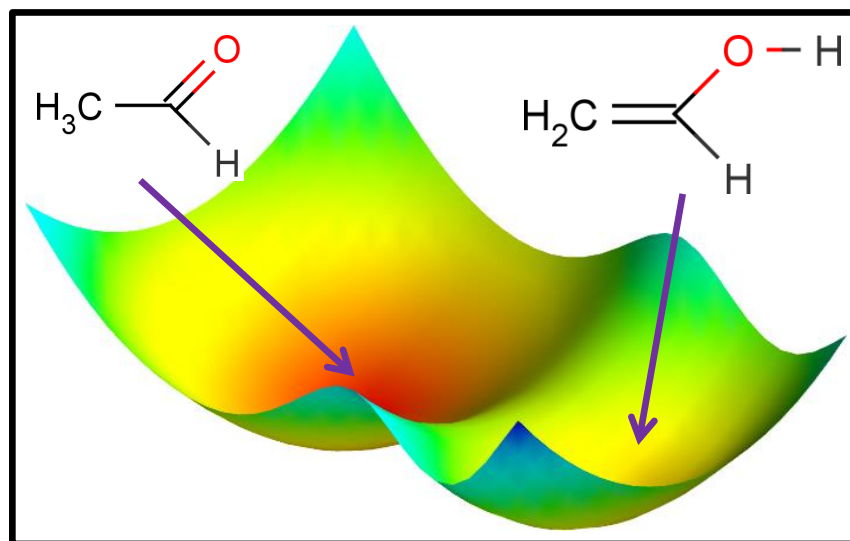# Applications of Electronic Structure Methods

Local Structure Optimization

Geometry update – (Quasi-)Newton Methods

Approximate PES by quadratic function

$$E(\Delta R) \approx E(R_{Min}) + \underbrace{\frac{\delta E}{\delta R}}_{F(R)}\Delta R + \frac{1}{2}\underbrace{\frac{\delta^2 E}{\delta R^2}}_{H}\Delta R^2$$
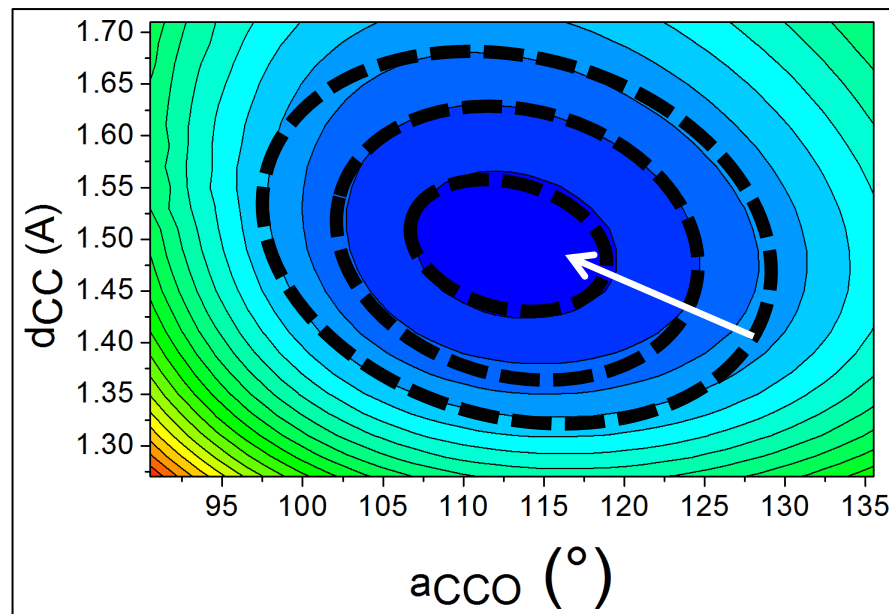
Forces   Hessian

Find minimum using

$$\Delta R = -H^{-1}F$$

Two variants:

- **Newton methods: calculate exact _H_**

- _Quasi-newton:_

  - approximate _H_

  - update as search progresses [1]

$$\tilde{H} \leftarrow \tilde{H} - \frac{\tilde{H}\Delta R(\tilde{H}\Delta R)^T}{\Delta R^T \tilde{H}\Delta R} - \frac{\Delta F \Delta F^T}{\Delta F^T \Delta R}$$

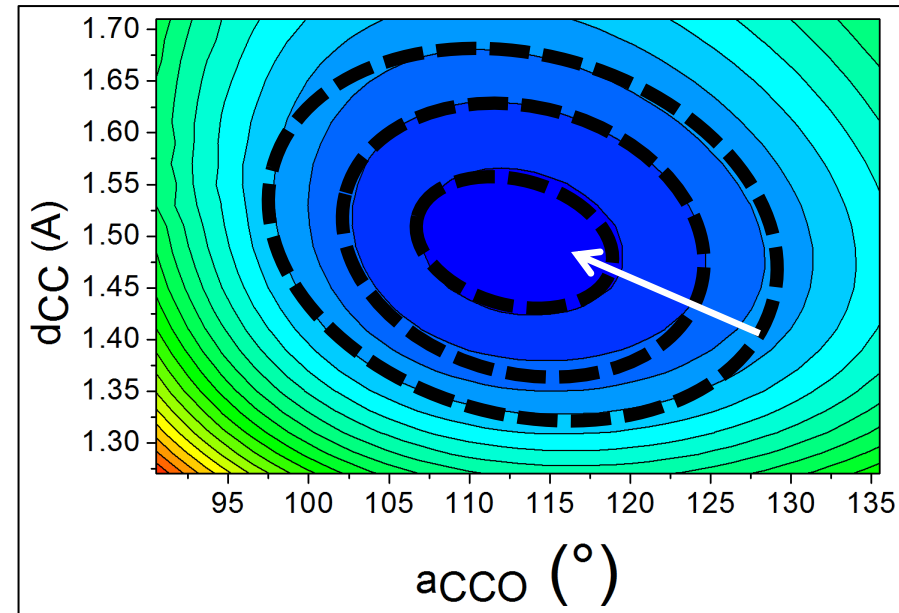[1] J. Nocedal and S. J. Wright, "Numerical optimization" (Springer, 2006)

(Quasi-)Newton Methods

De-facto standard method

$$\tilde{H} \leftarrow \tilde{H} - \frac{\tilde{H}\Delta R(\tilde{H}\Delta R)^T}{\Delta R^T \tilde{H}\Delta R} - \frac{\Delta F \Delta F^T}{\Delta F^T \Delta R}$$

Iterative, depends on:

- **Guess Hessian**
- **Step control**
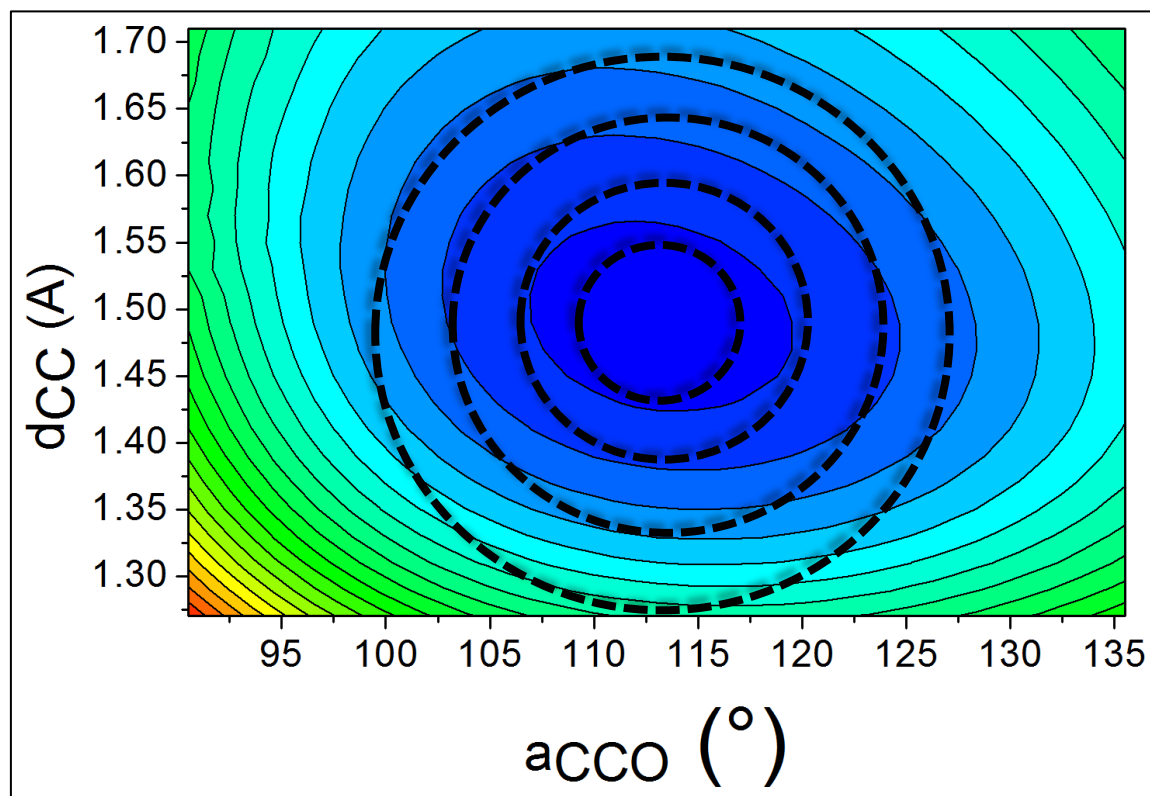- **Optimization History**
- **Starting point**

Note: Quasi-Newton methods converge to the closest stationary point → This can be a saddle point!

Guess Hessian: Scaled unit matrix

$$\tilde{H} = \beta\bar{\mathbf{1}}$$

Assumption: Each DoF has same force constant

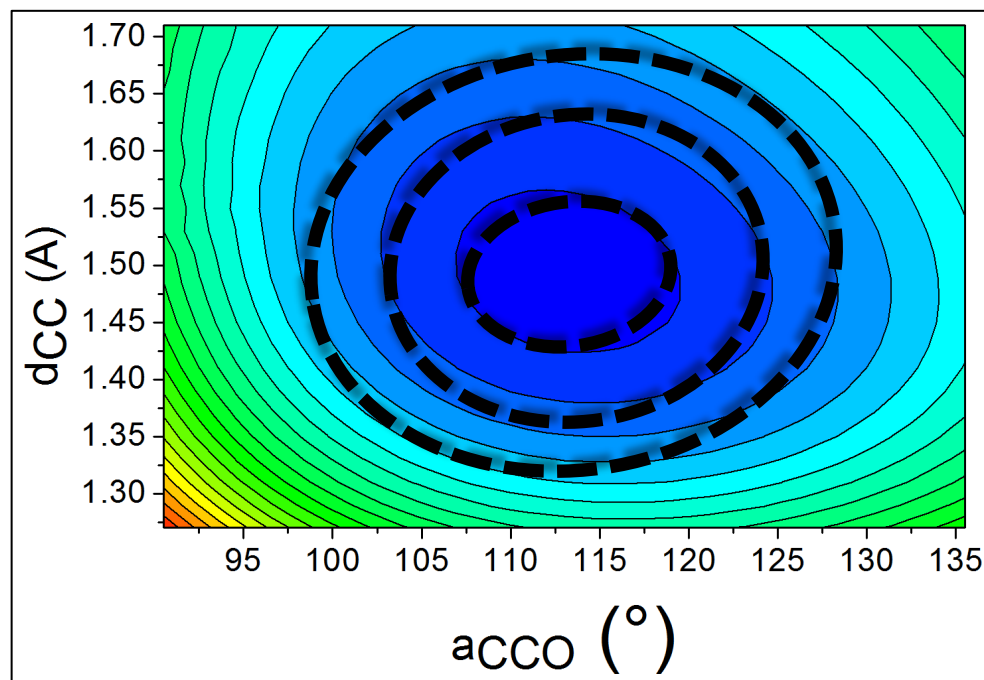- Typically good for bulk systems (esp. metals, vdW)
- Terrible for complex molecules

Guess Hessian: Chemically motivated

Properties:

- *k's* **parameterized [1]**
- **Different parameters exist**
  - **(e.g.: Lindh, Fischer)**
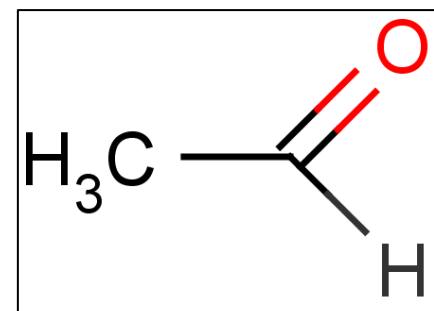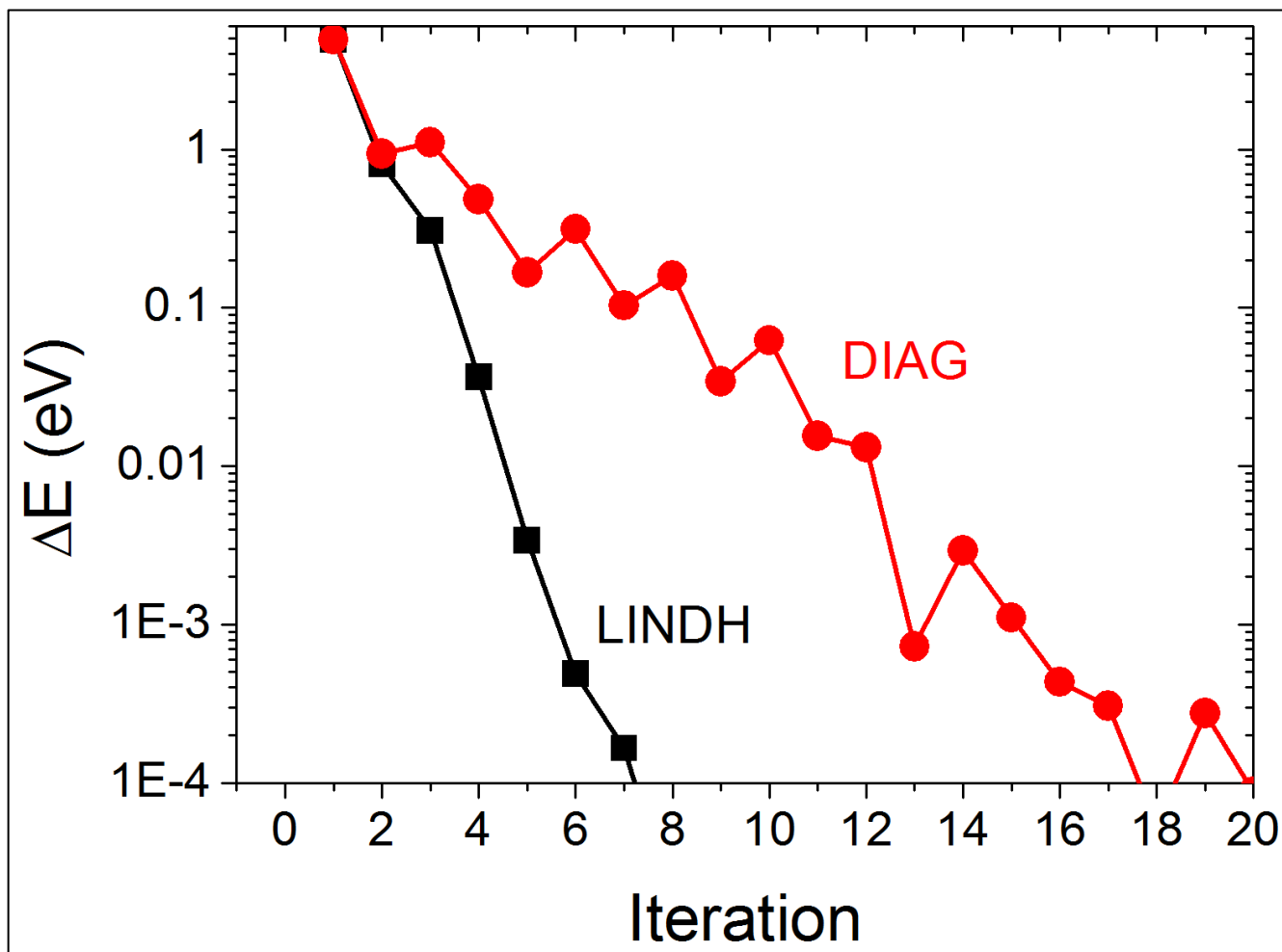- But not for everything
- Construction not unique

$$\tilde{E} = E + F\Delta R$$
$$+ \sum_{ij} k_{ij}\, d_{ij}^2 \quad \text{streching}$$
$$+ \sum_{ijl} k_{ijl}\, a_{ijl}^2 \quad \text{bending}$$
$$+ \sum_{ijlm} k_{ijlm}\, \tau_{ijlm}^2 \quad \text{torsion}$$
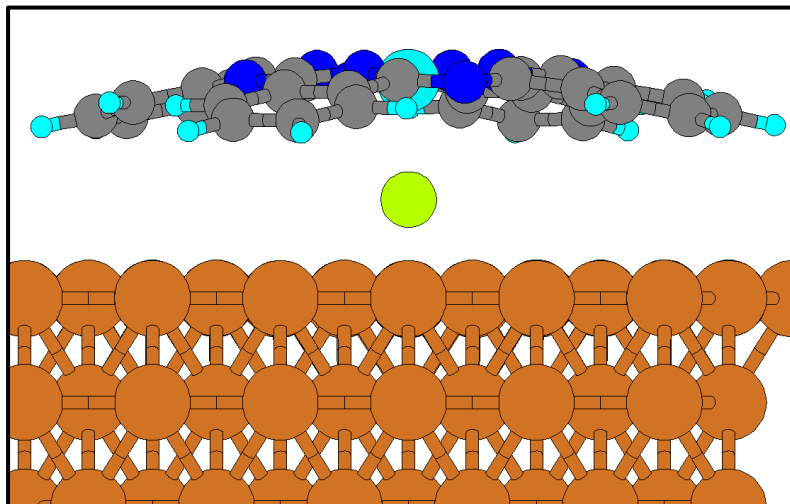

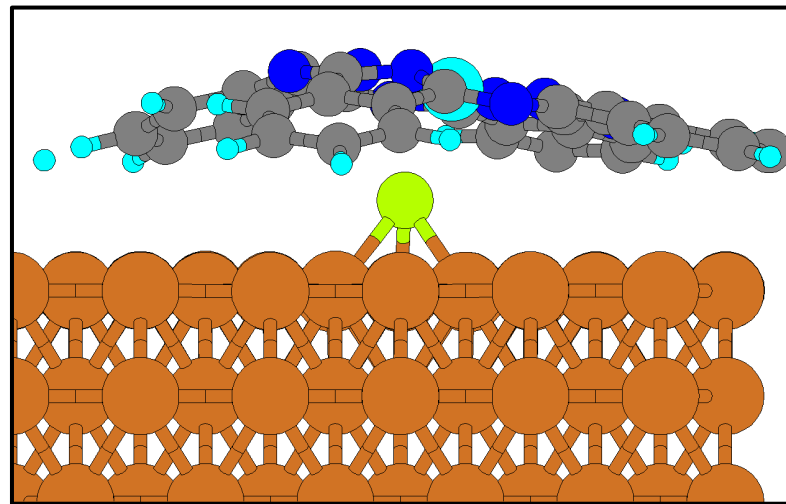[1] R. Lindh et al. , Chem. Phys. Lett. 241 , 423 (1995).

Effect of Guess Hessian

Speedup of calculation

Guess Hessian – Example 1
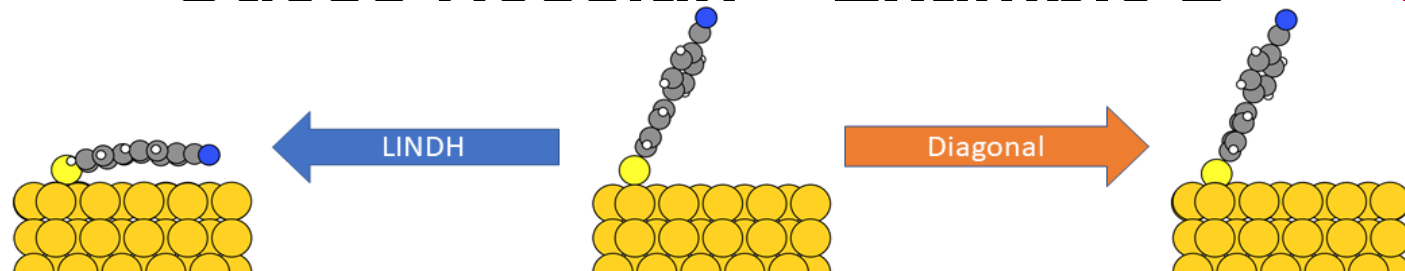

**Diagonal Hessian
[higher in energy]**

**Model Hessian (Fischer)
[lower in energy]**

Diagonal Hessian struggles with complex DoFs
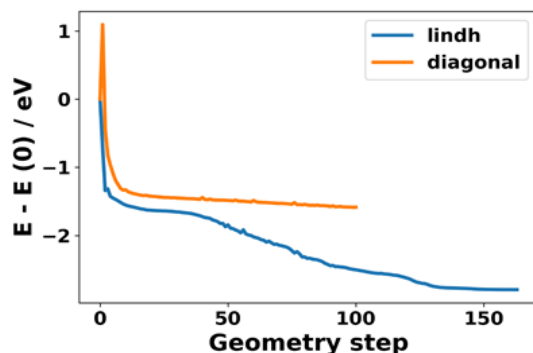### (e.g., bending of a planar molecule)
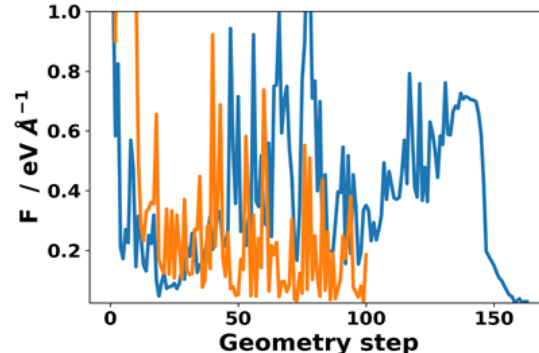
Courtesy of Elisabeth Wruss

Guess Hessian – Example 2
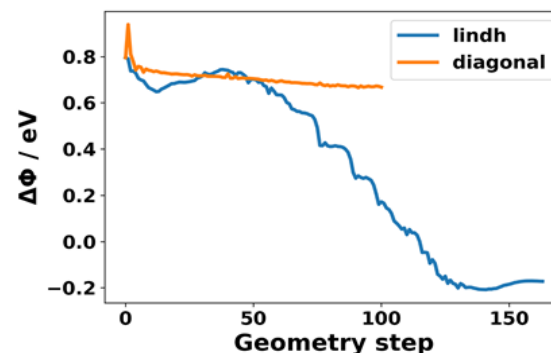

Diagonal Hessian struggles with complex DoFs

(e.g., falling over of a molecule)

==> Atoms which experience least forces have to move most!

Challenges of Quasi-Newton Methods

Soft degrees of freedom can cause large ΔR

$$\Delta R = \alpha \, H^{-1} F$$

Step control needed:
- **Line search method:**
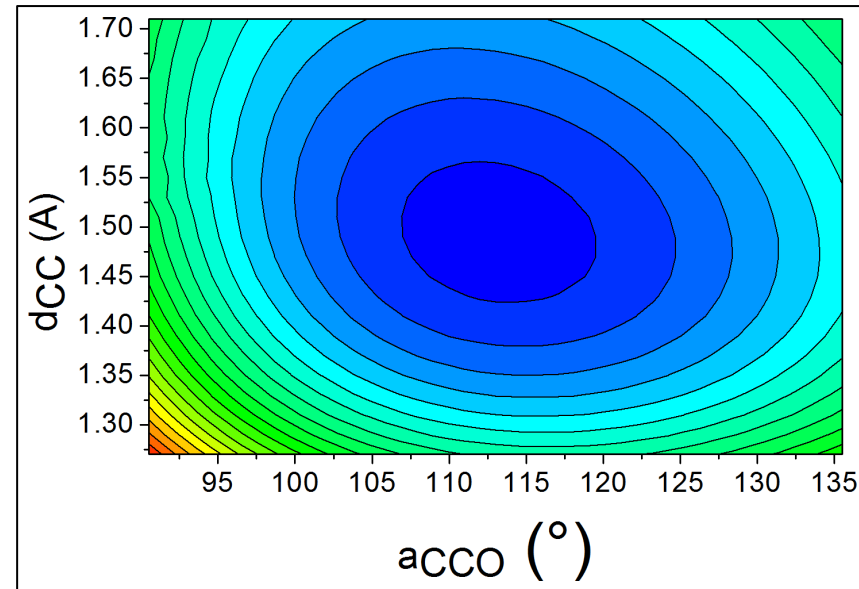 - If new point is worse than old, interpolate
- **Trust radius method**
  - Enforce upper limit for ΔR
  - Evaluate quality *q* of quadratic model
  - Adjust ΔR_{max} based on *q*
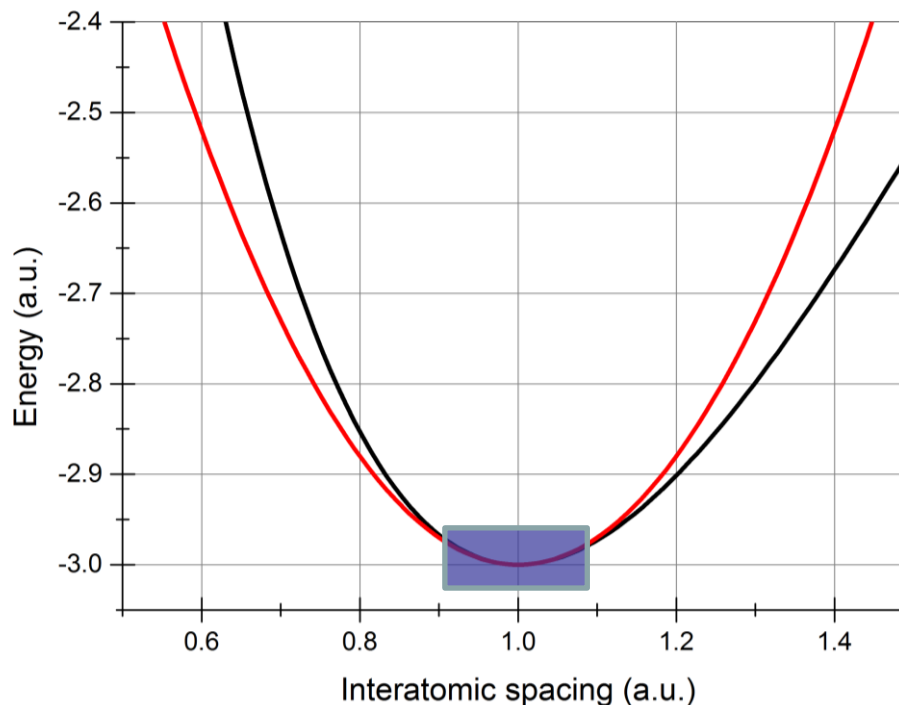
$$q = \frac{E_{true}}{E_{expected}}$$

Step size can become very small
- Far away from the minimum
- When Hessian is bad
- When convergence is bad

Search History

- **Points far away from minimum give „wrong" Forces/Hessian**
- **Errors accumulate, deteriorate Harmonic Expectation Value**
- **Only finite number of steps can/should be stored:**
  - Linear Dependency (#steps < DOFs)
  - Memory (H is 3N x 3N large)

Choice of the coordinate system

Coordinate system cannot affect physics, but numerics

$$E(x) = (1-y)^2 \xleftarrow{\quad y = e^{-x} \quad} E(x) = (1-e^{-x})^2 \xrightarrow{\quad y = e^{x} \quad} E(x) = \left(1 - \frac{1}{z}\right)^2$$

Position: y

Position: x

Position: z
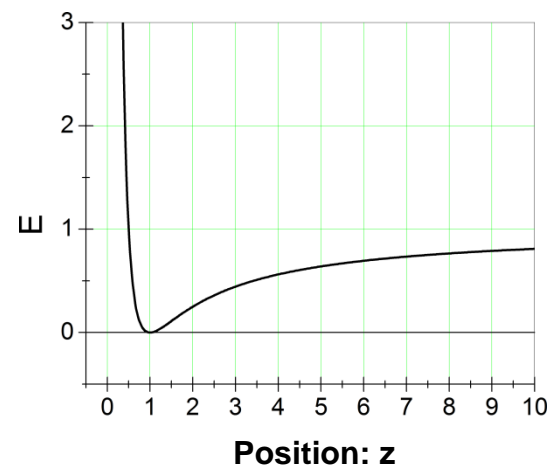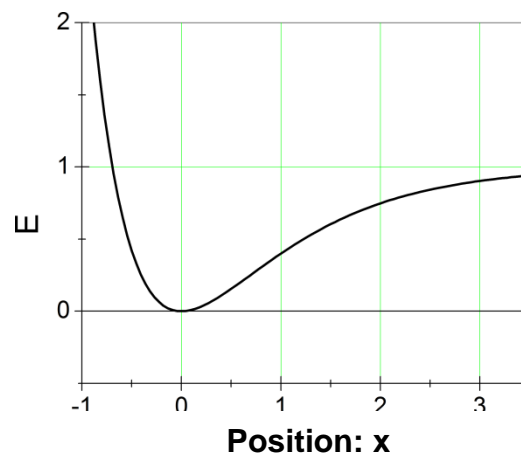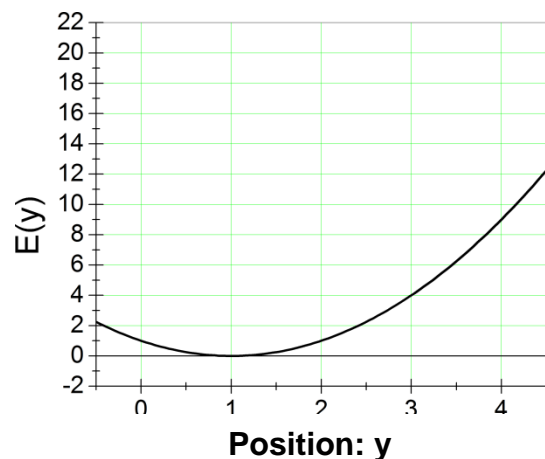
Table 12.2 Convergence for different choices of variables

Iteration	$x_{start} = 0.30$			$x_{start} = 1.00$		
	x	y	z	x	y	z
0	0.3000	0.7408	1.3499	1.0000	0.3679	2.7183
1	−0.2381	1.0000	−0.2229	3.3922	1.0000	4.6352
2	−0.0633		−0.3020	4.4283		7.3225
3	−0.0055		−0.4110	5.4405		11.2981
4	0.0000		−0.5628	6.4449		17.2354

Example taken from Jensen, Introduction to Computational Chemistry