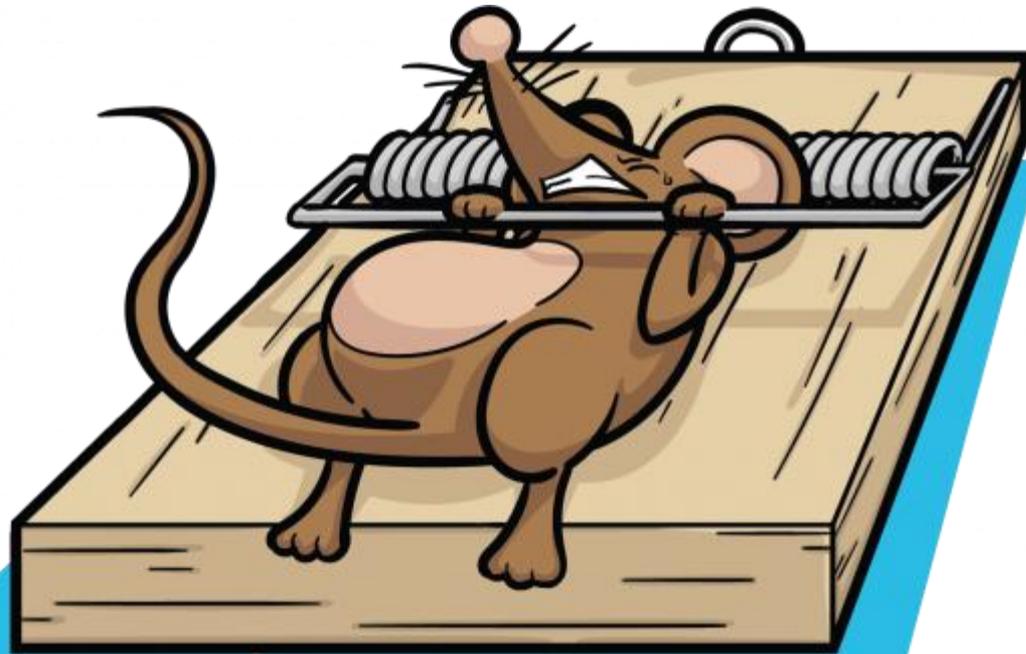
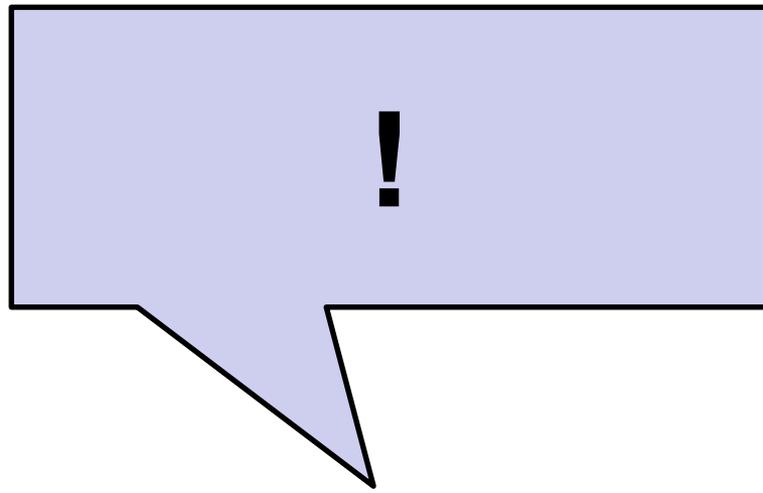
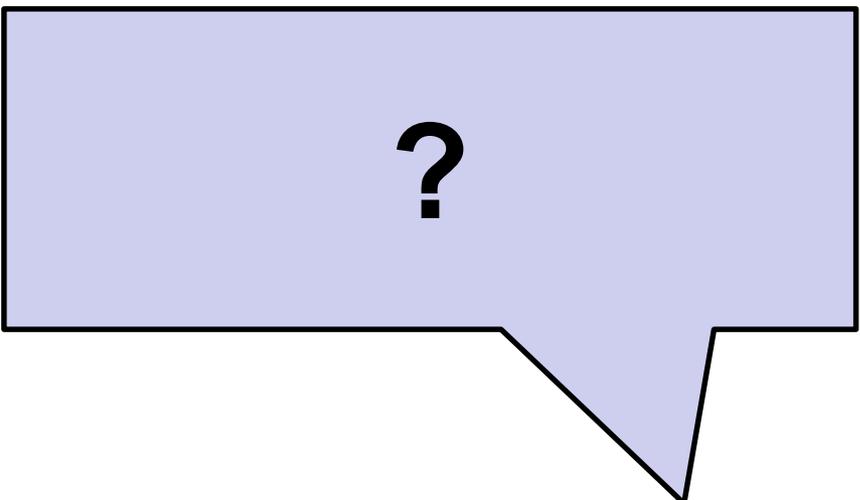


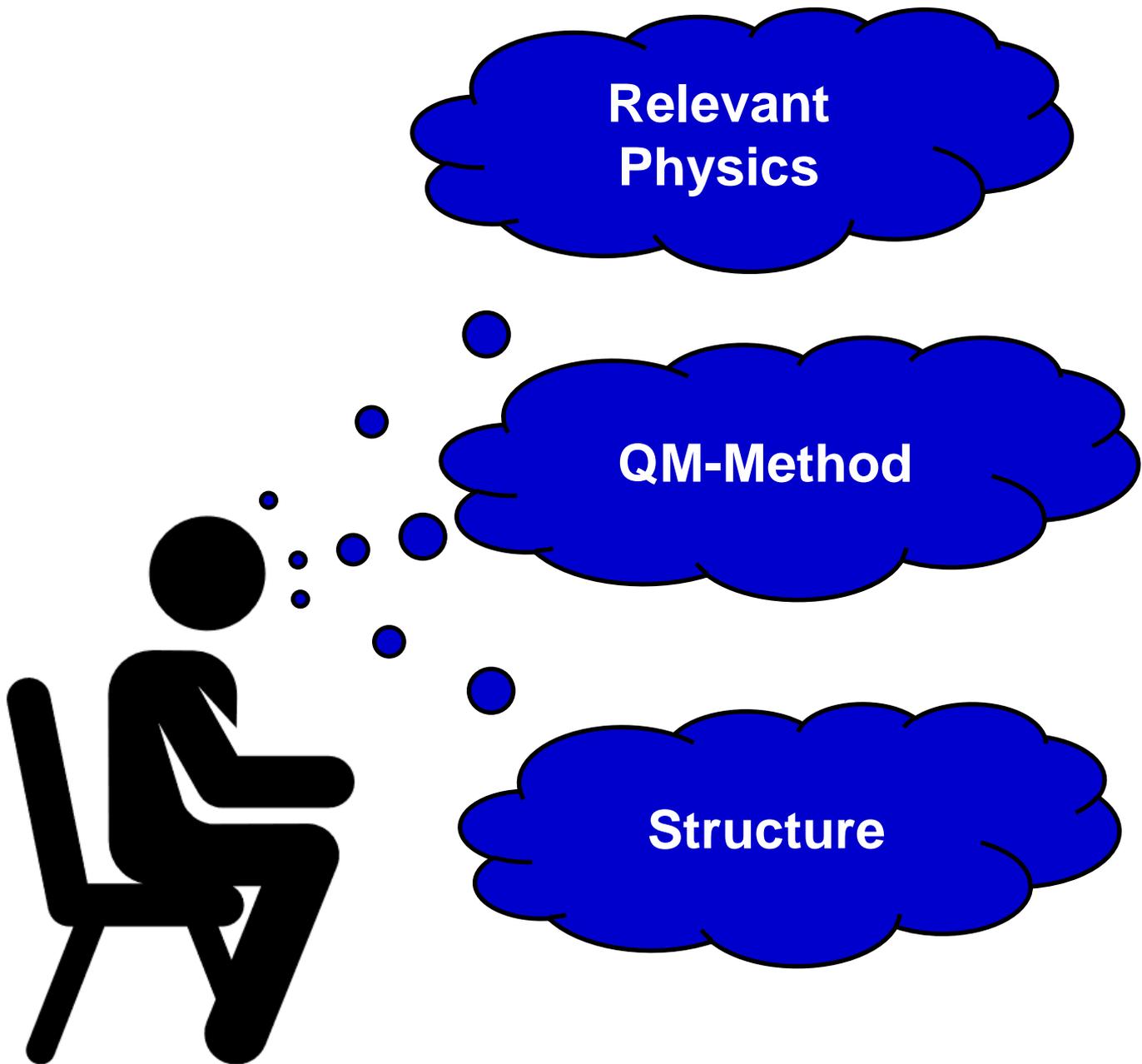
Approaching Material Simulations in Practice



Oliver T. Hofmann

Graz University of Technology
Institute of Solid State Physics





Purpose of this lecture:

- Repeat basic technical knowledge
- Demonstrate common failures and mistakes
- Raise awareness for plausibility checks

Experienced Audience

Interactive Examples

Example: Calculate the binding energy of F₂

```
#qm settings
xc b3lyp
charge 0

#convergence
sc_accuracy_etot 1e-6
```

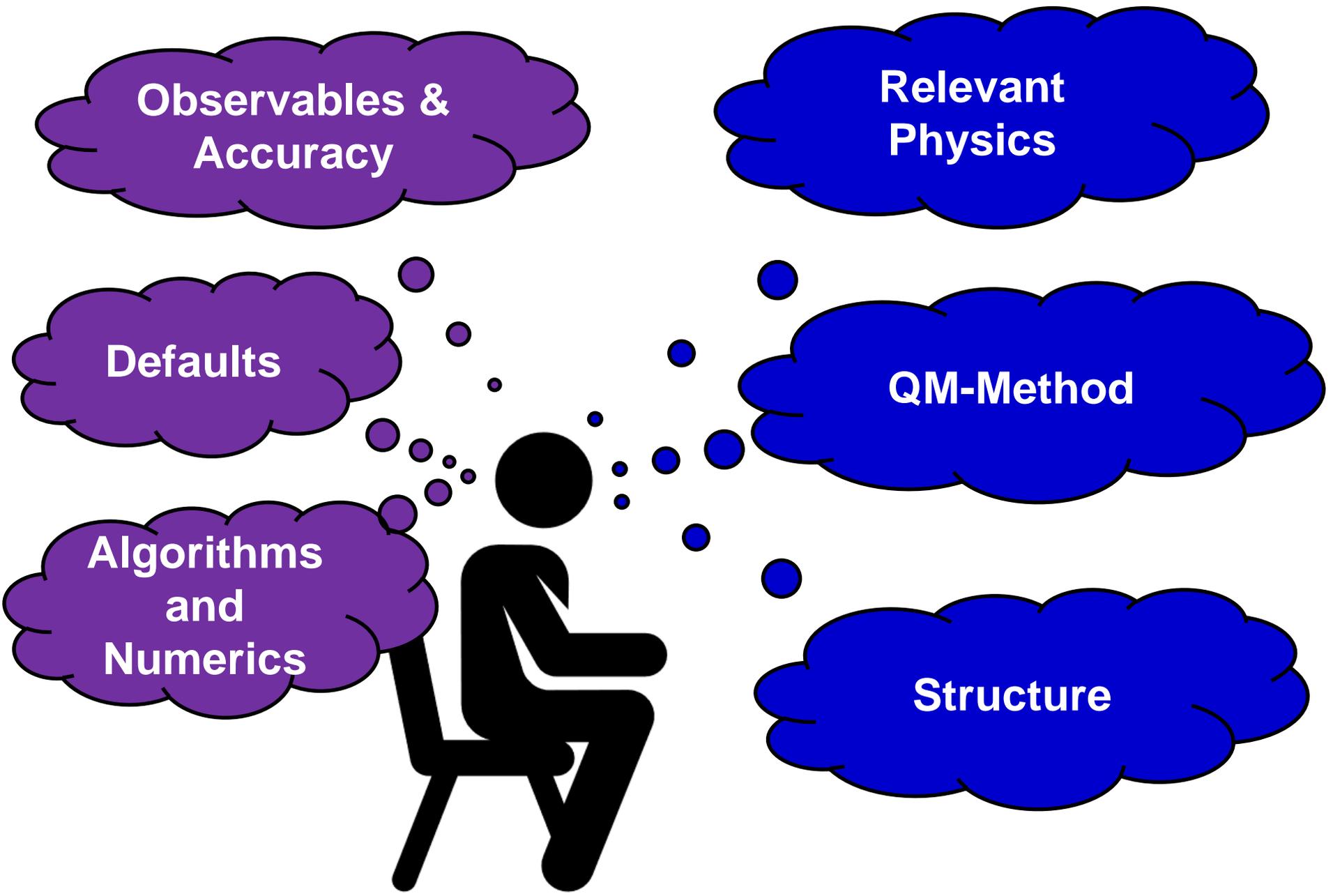


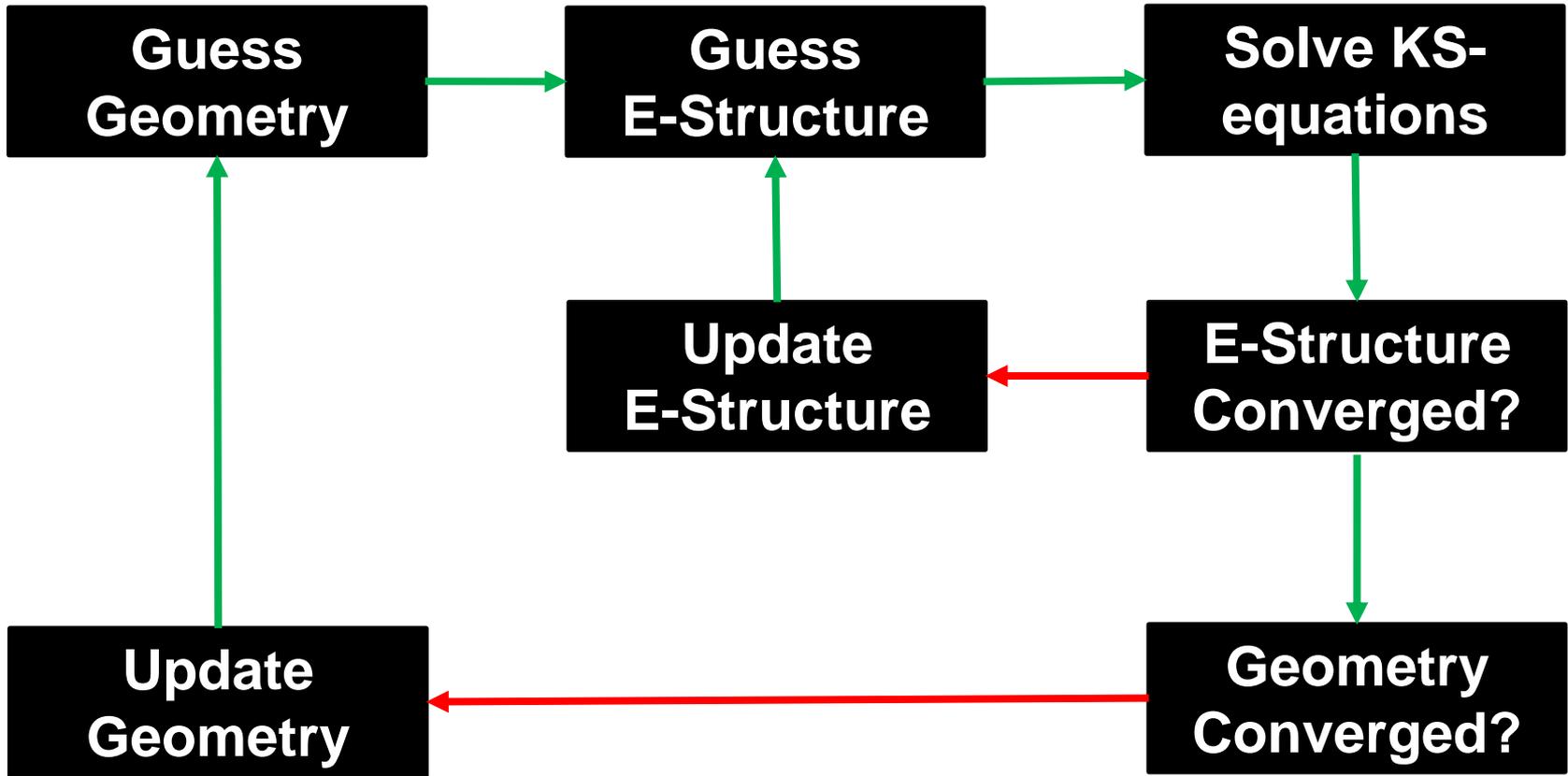
| | Energy (eV) |
|-------------------------|-------------|
| F ₂ molecule | -5439.43 |
| F atom | -2716.54 |
| Bond energy | 6.36 |
| Experiment | 1.64 |

| F ₂ |
|---------------------------|
| #Geometry from experiment |
| atom 0.0 0.0 0.0 F |
| atom 0.0 0.0 1.4 F |

| F |
|--------------------|
| atom 0.0 0.0 0.0 F |

What went wrong?





Example: Inorganic/Organic Interfaces

(De)localization
of States

(An)isotropy of
bonds

Interaction
Strength

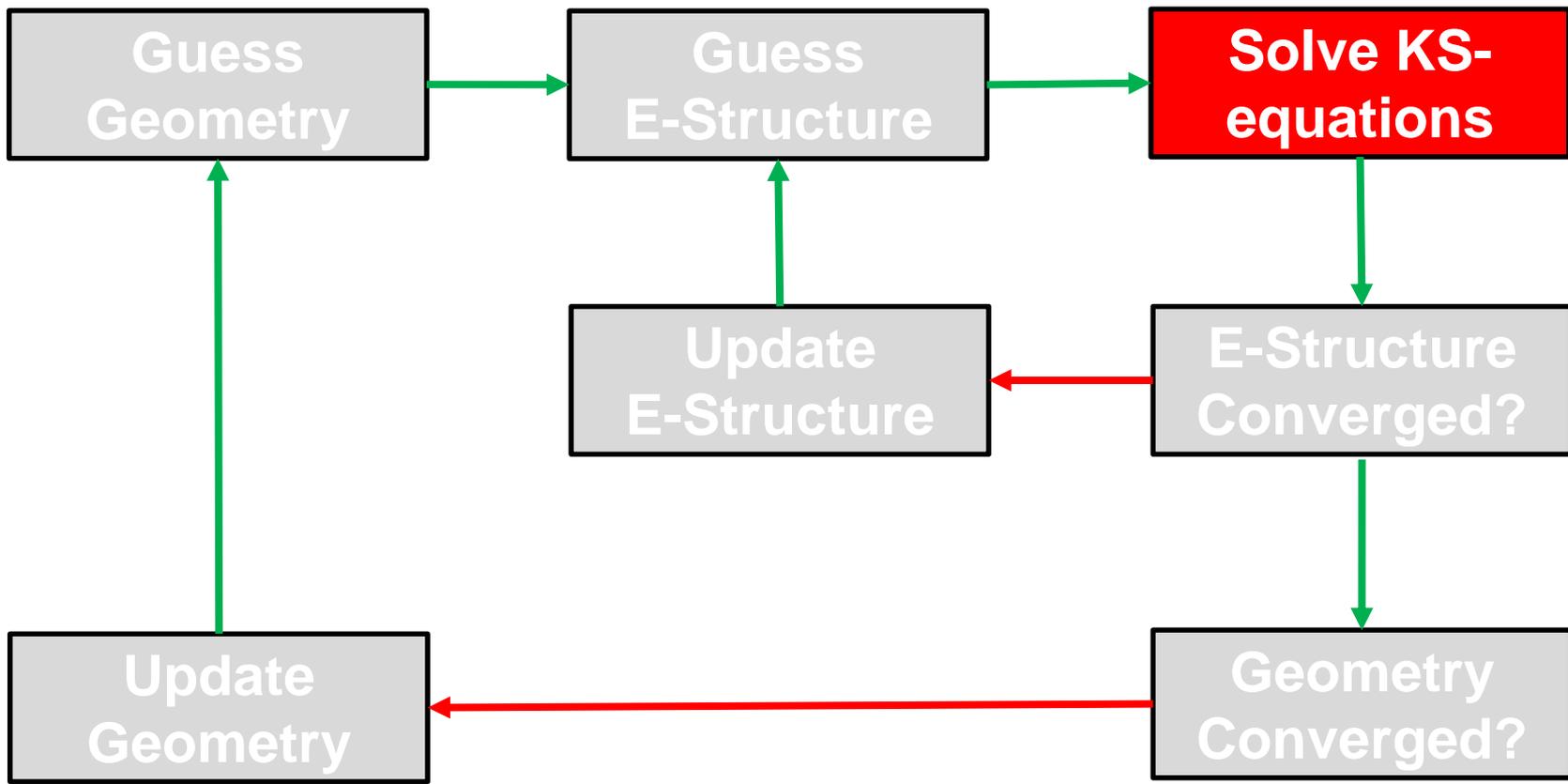


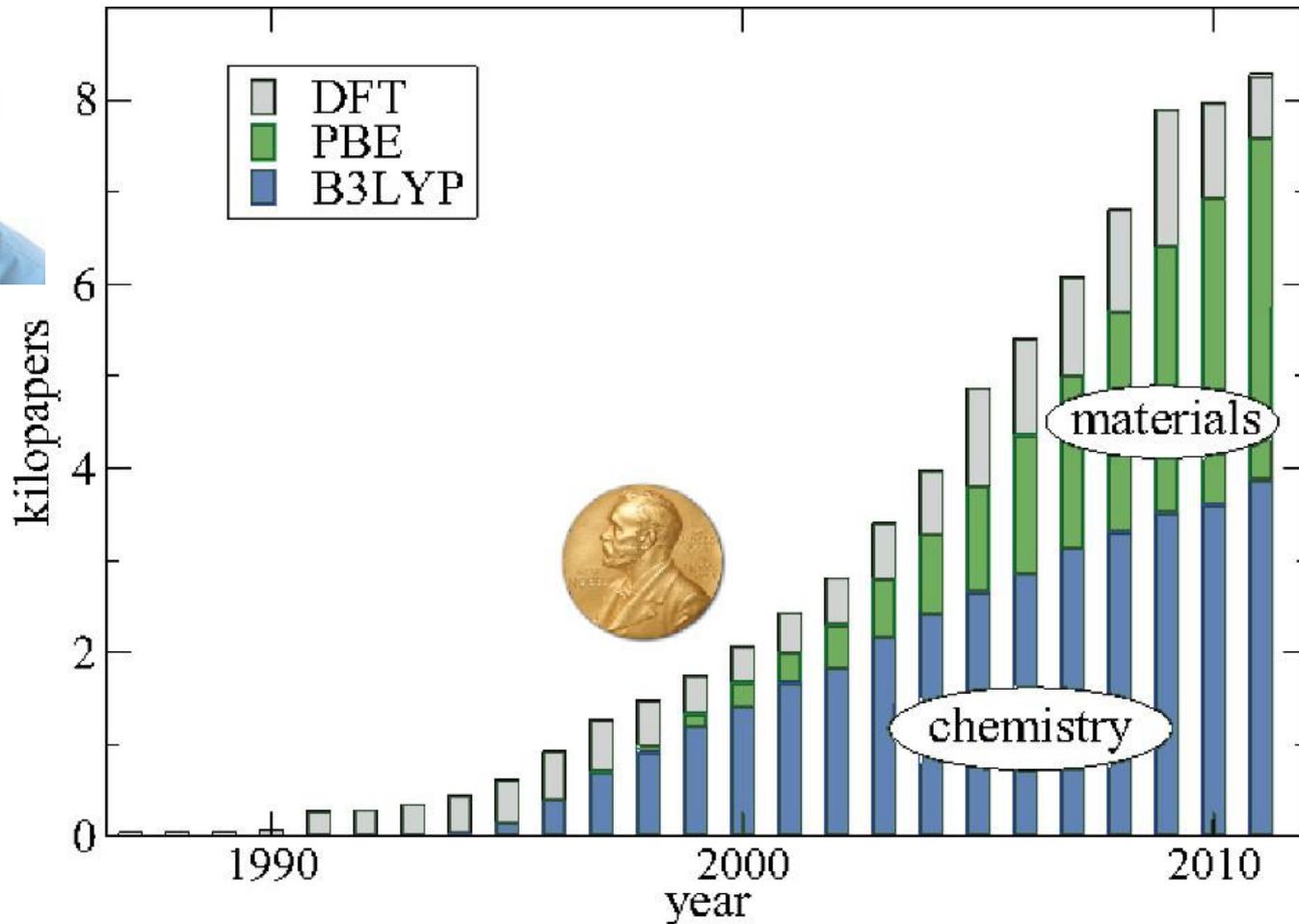
Charge Transfer

Typical Targets

Determine Adsorption Geometry

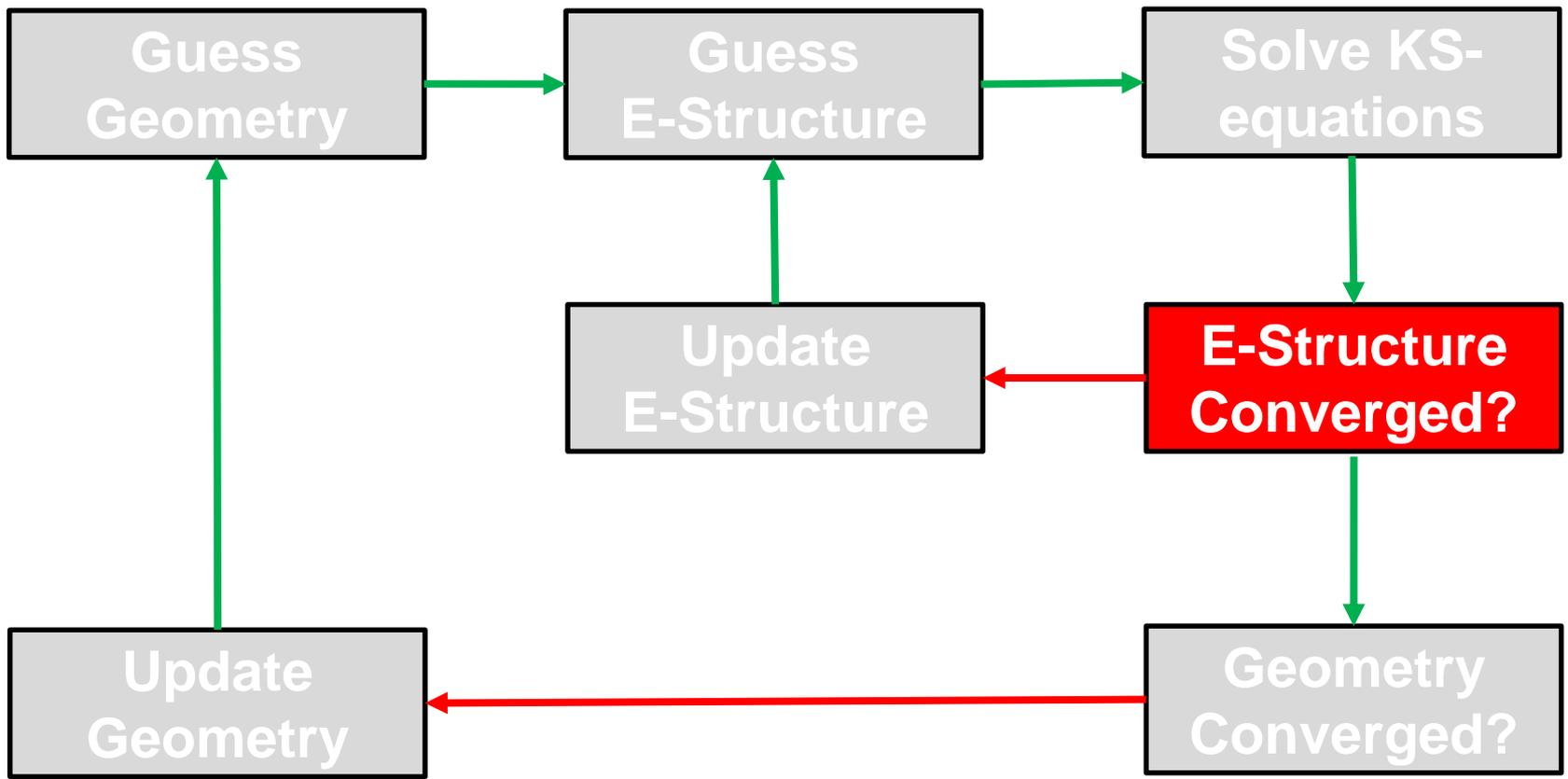
Determine Interface Dipole





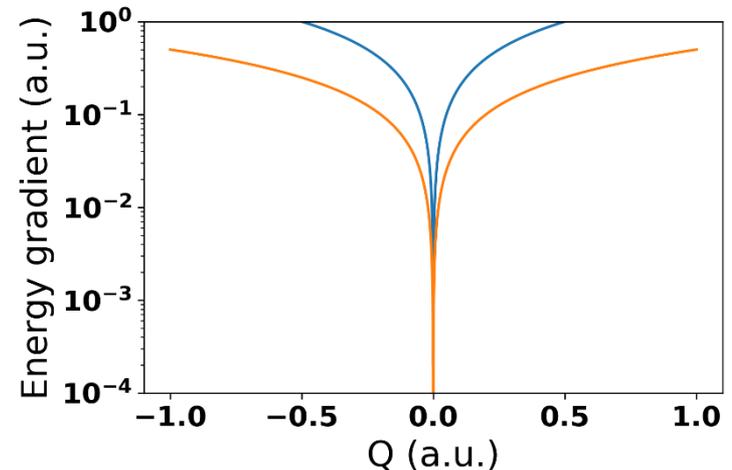
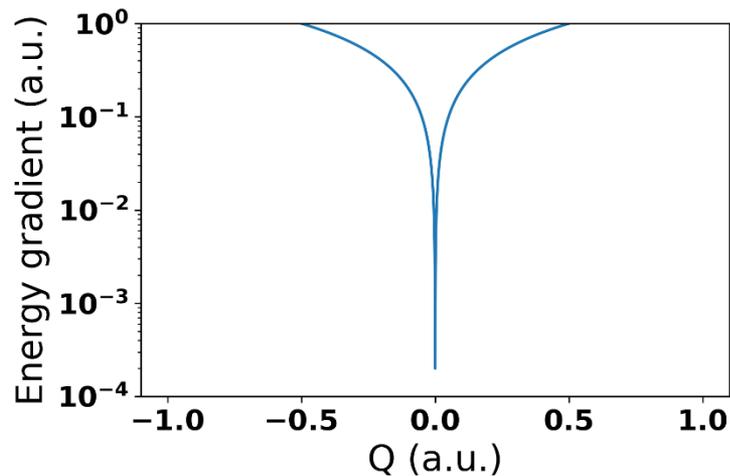
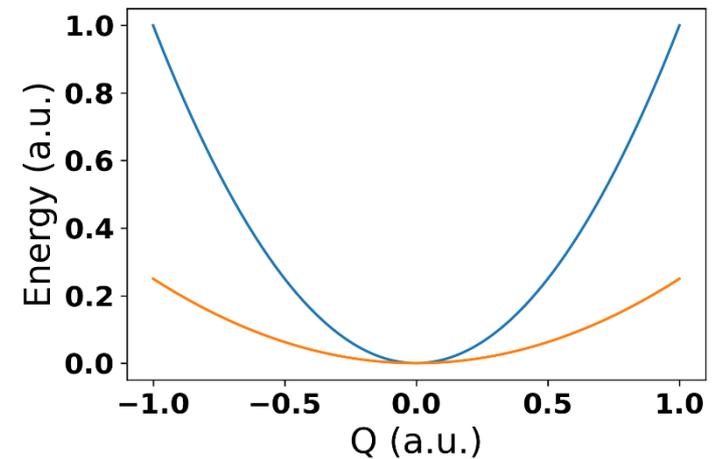
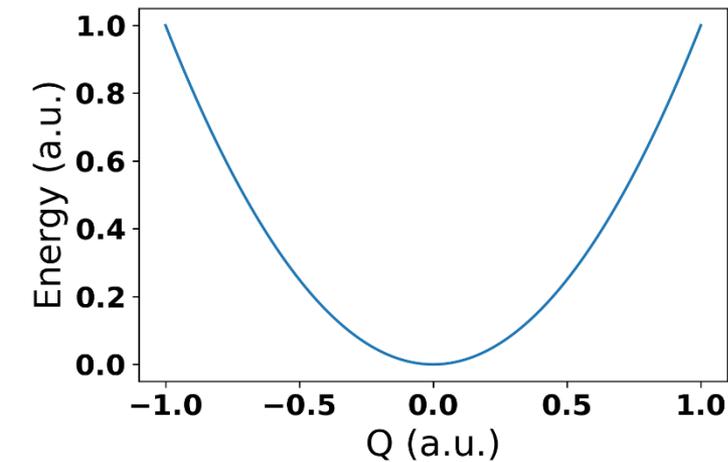
“Users should stick to the standard functionals [...] or explain very carefully why not.” (Kieron Burke, 2012)

[... + a van-der-Waals correction]



When is the calculation finished?

find the minimum



When is the calculation finished?

Answer: When „*property*“ does not change

Very loose

Convergence threshold

Very strict

Random
number

Inaccurate
result

Converged
result

Wasted
time

Numerical
instabilities

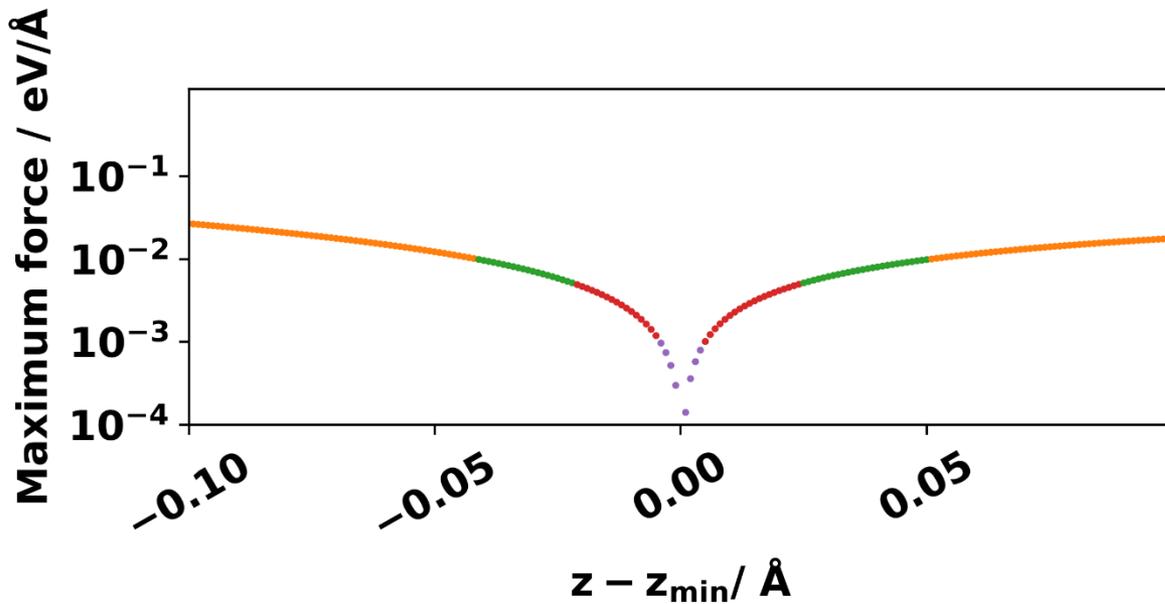
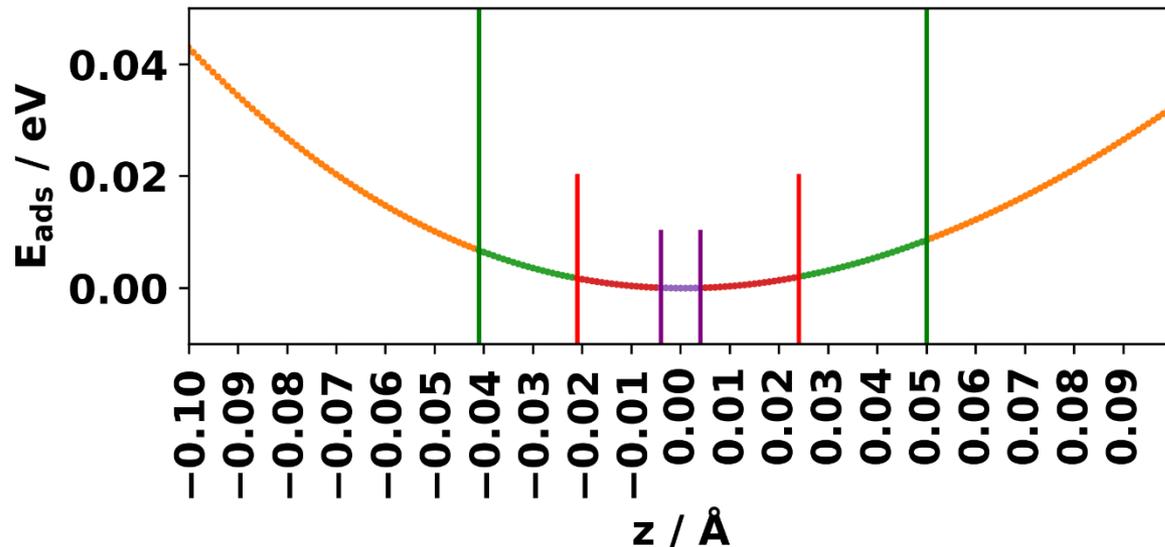
**Adjusting knob between
error bar and invested CPU time**

What are good thresholds?

Short answer: It depends.

Problem I: Connection between parameters and observables

- **Adsorption / Cohesive / [...] energy** ↔ **Total energy (1:1)**
- **Dipole moment** ↔ **Electron density (size dependent)**
- **Maximum force** ↔ **Adsorption height (interaction dependent)**



| Threshold (eV/Å) | Δz (Å) |
|------------------|----------------|
| 0.1 | n/a |
| 0.01 | ~ 0.1 |
| 0.005 | ~ 0.05 |
| 0.001 | 0.01 |

What are good thresholds?

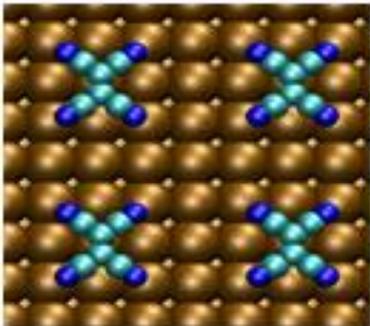
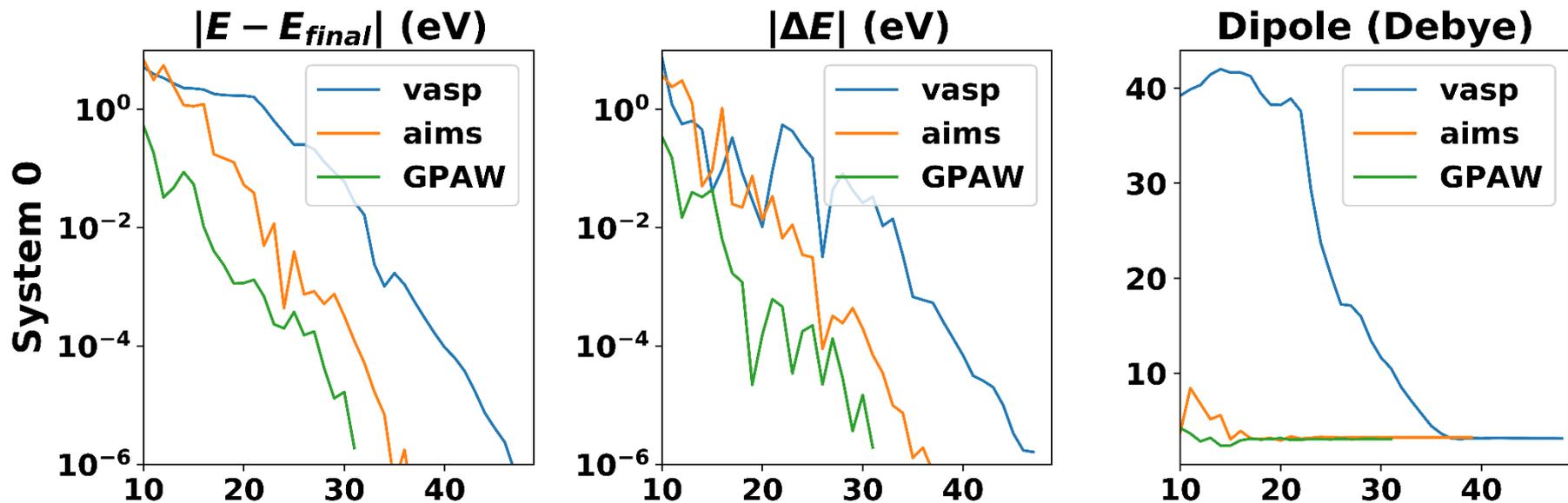
Short answer: It depends.

Problem I: Connection between parameters and observables

- **Adsorption / Cohesive / [...] energy** ↔ **Total energy (1:1)**
- **Dipole moment** ↔ **Electron density (size dependent)**
- **Maximum force** ↔ **Adsorption height (interaction dependent)**

Problem II:

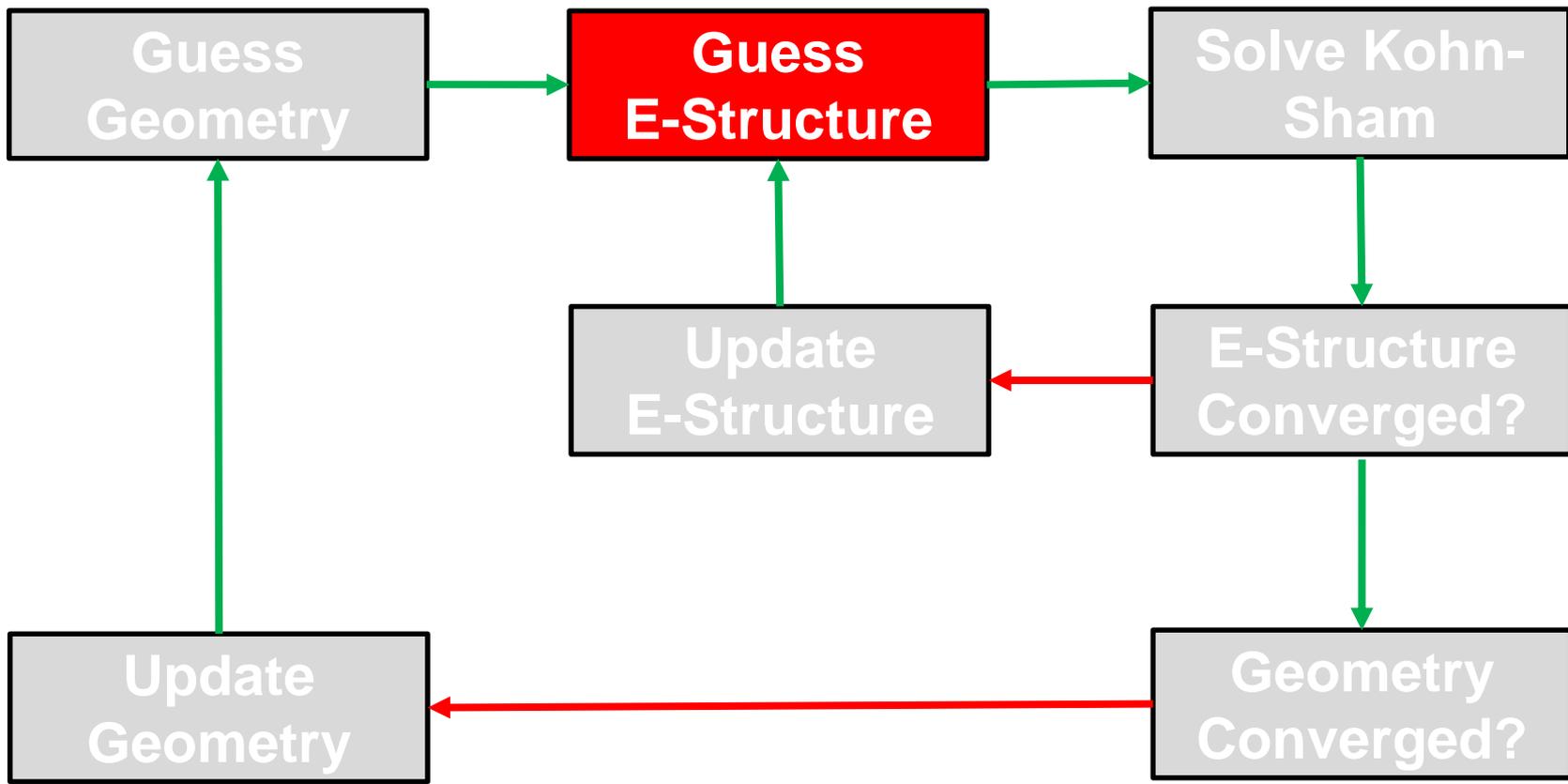
- **Not transferrable between different systems (size dependence)**
- **Not necessarily transferrable between different codes**
- **Sometimes not even transferrable between different algorithms within the same code**



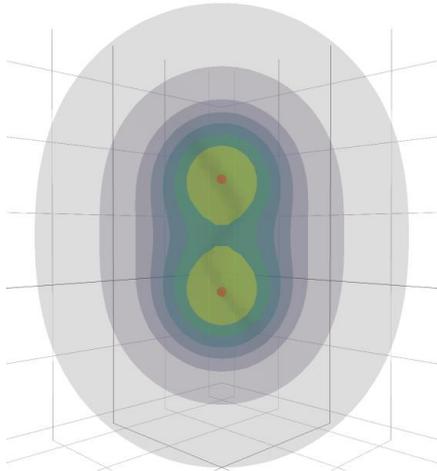
Weak correlation between total energy and energy gradient

No clear correlation between dipole moment and energy gradient

→ Converge observables explicitly!

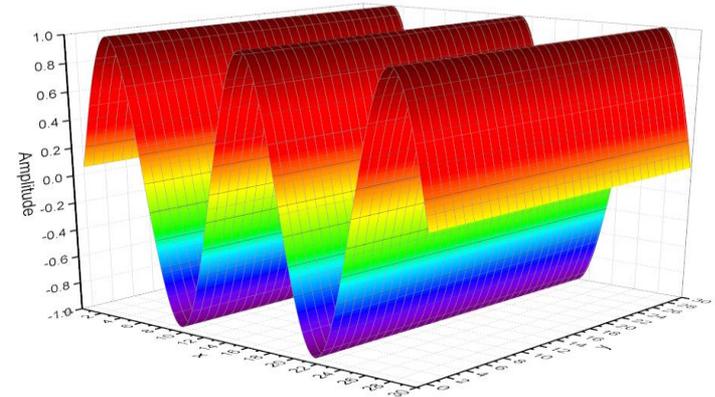


Atom-centered



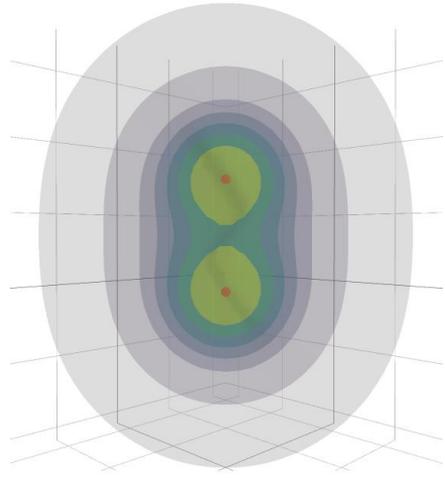
- **Hardly systematic**
- **Depends on #atoms**
- **BSSE-afflicted**
- **Overly confined**

Plane waves

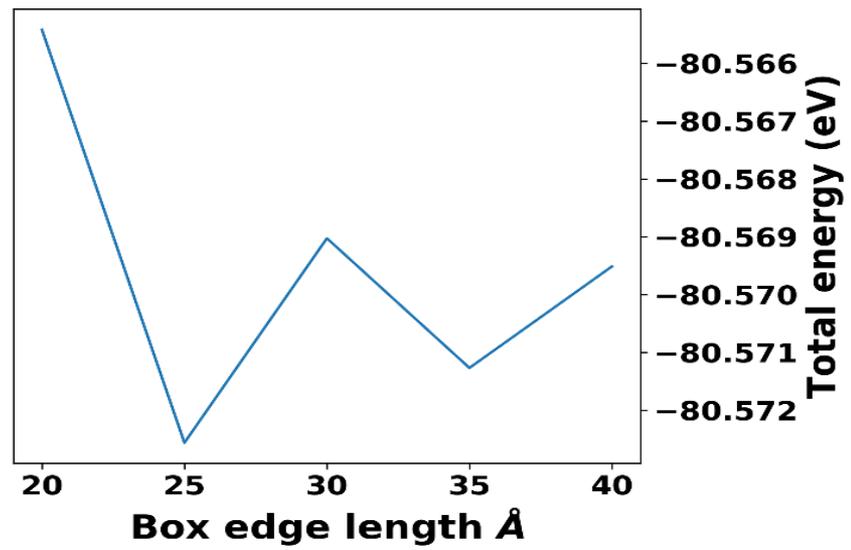
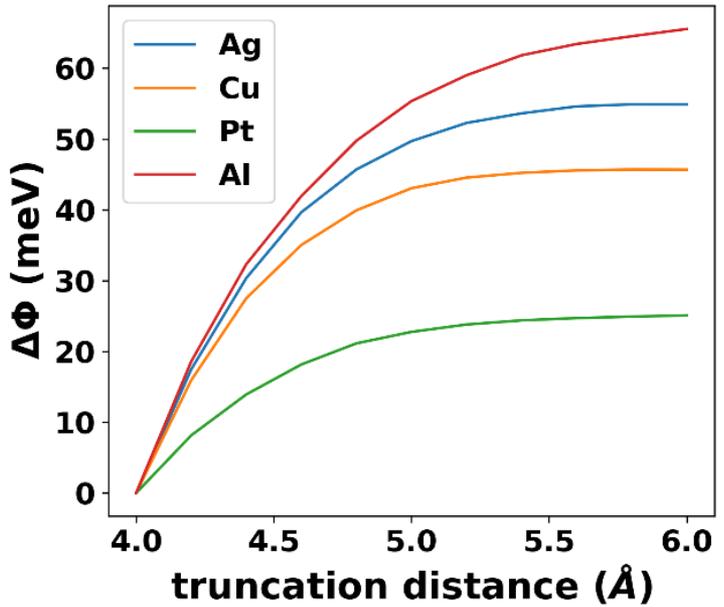
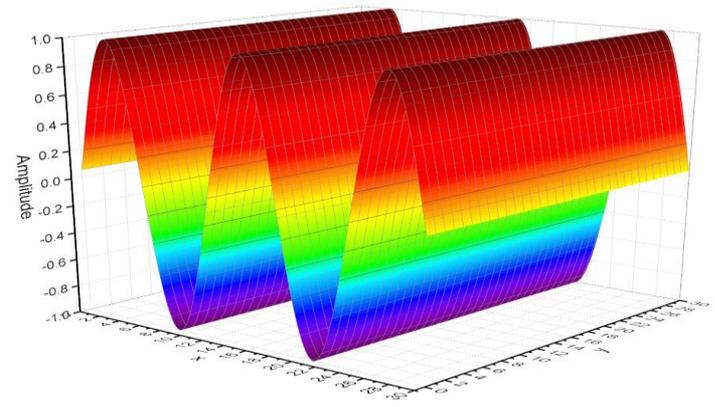


- **Highly systematic (cutoff)**
- **Depends on unit cell size**
- **Pseudopotentials**
- **Overly delocalized**

Atom-centered

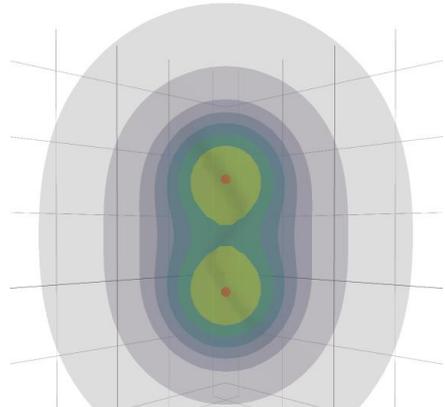


Plane waves

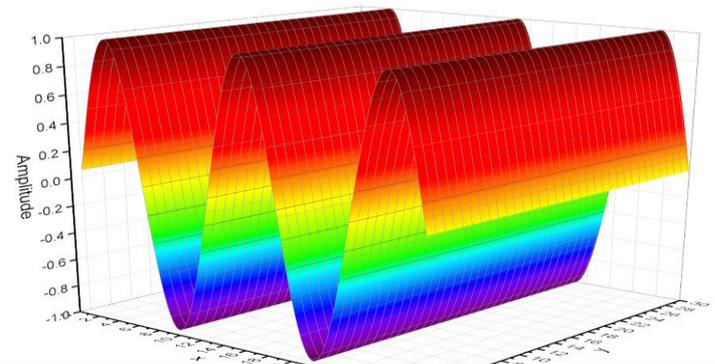


Dipole moments and Basis Sets

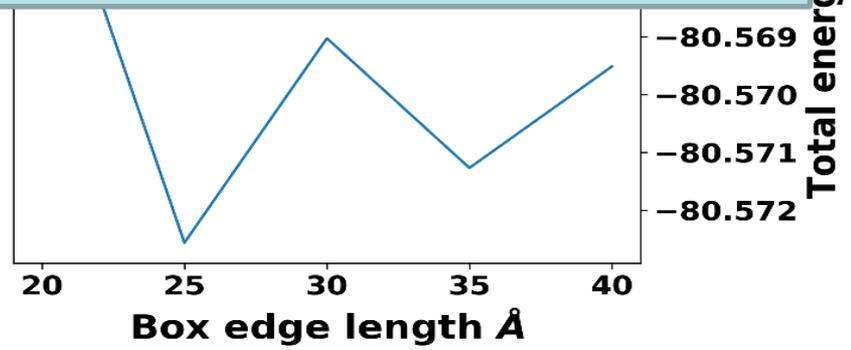
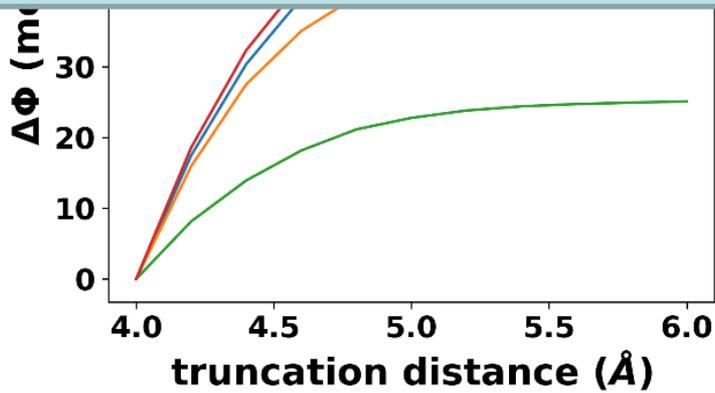
Atom-centered

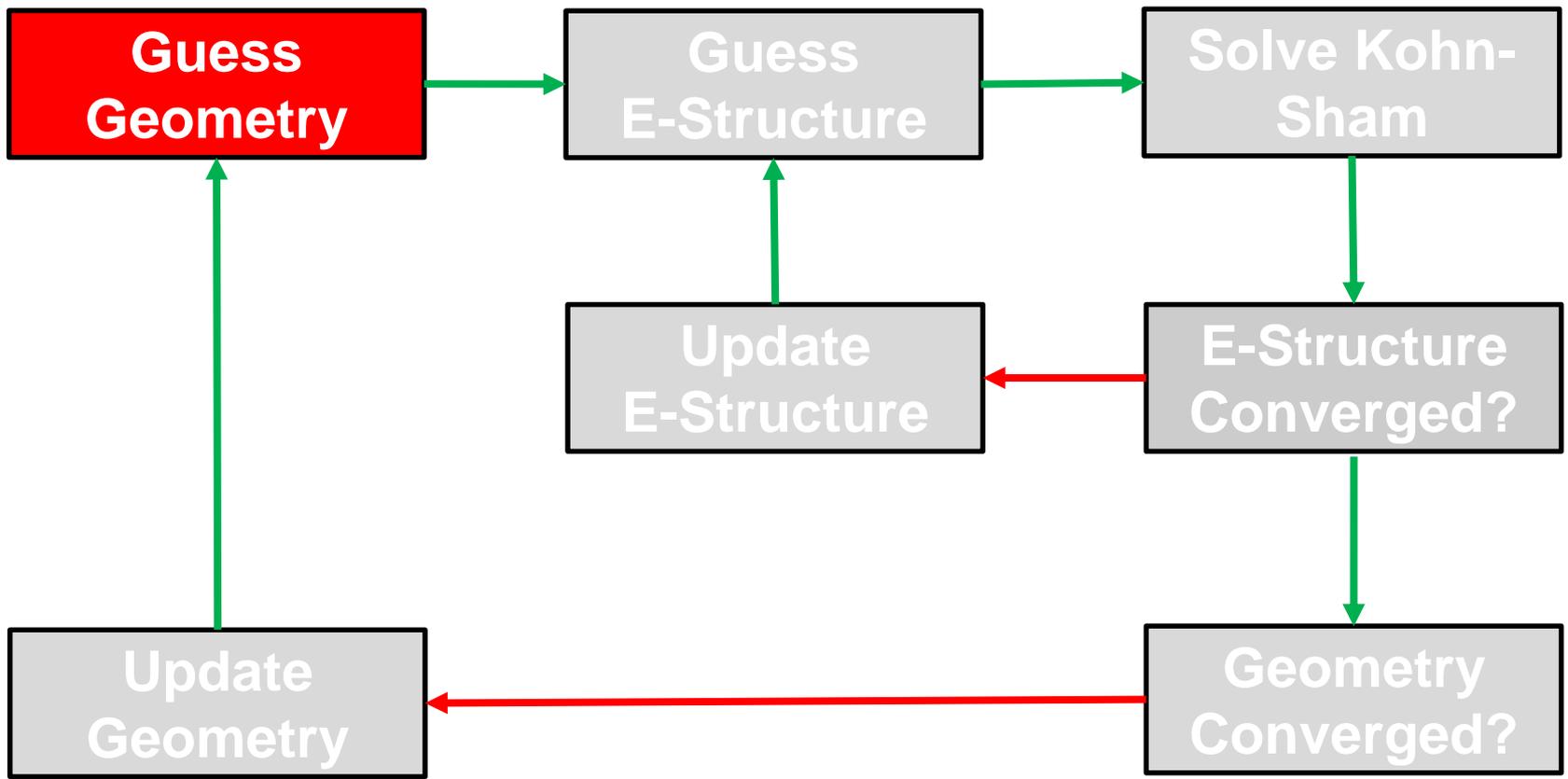


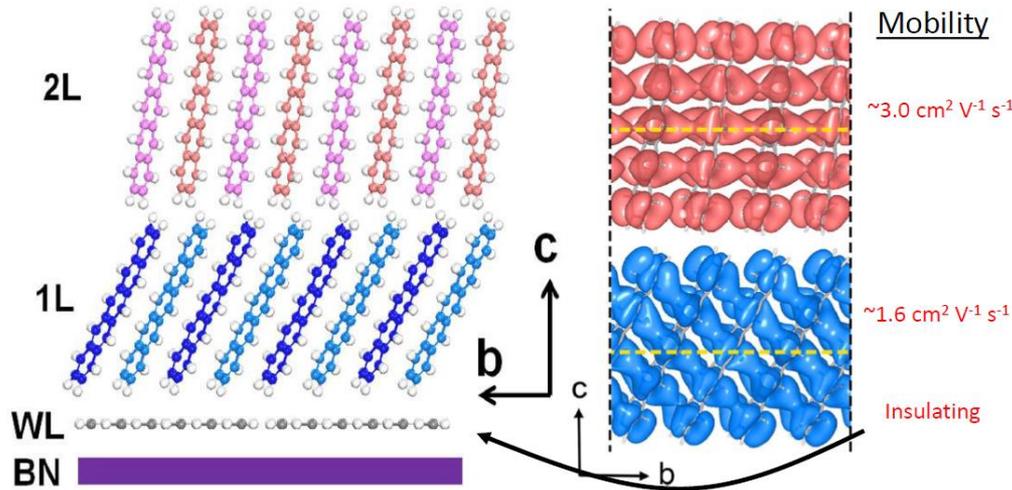
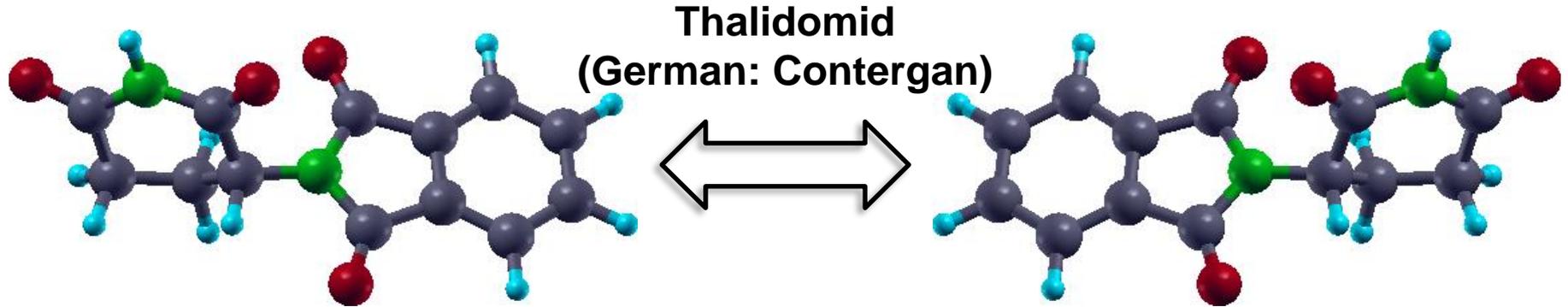
Plane waves



**Today, all modern code yield the same result
If overconverged and used correctly**

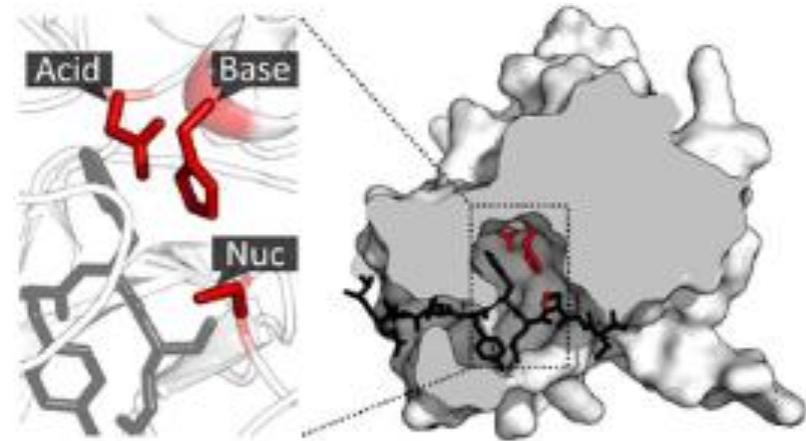






Y. Zhang et al., *Phys. Rev. Lett.*, 2016, **116**, 016602.

Mobilities in Pentacene



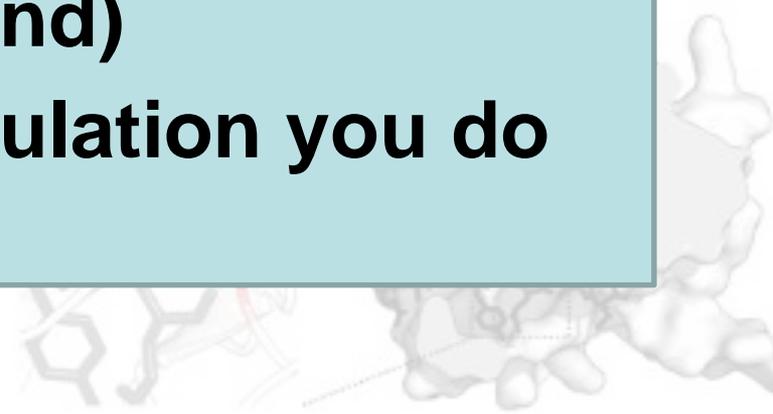
Catalytic Triade



**Global Structure Search
(of some kind)
is always the first calculation you do**

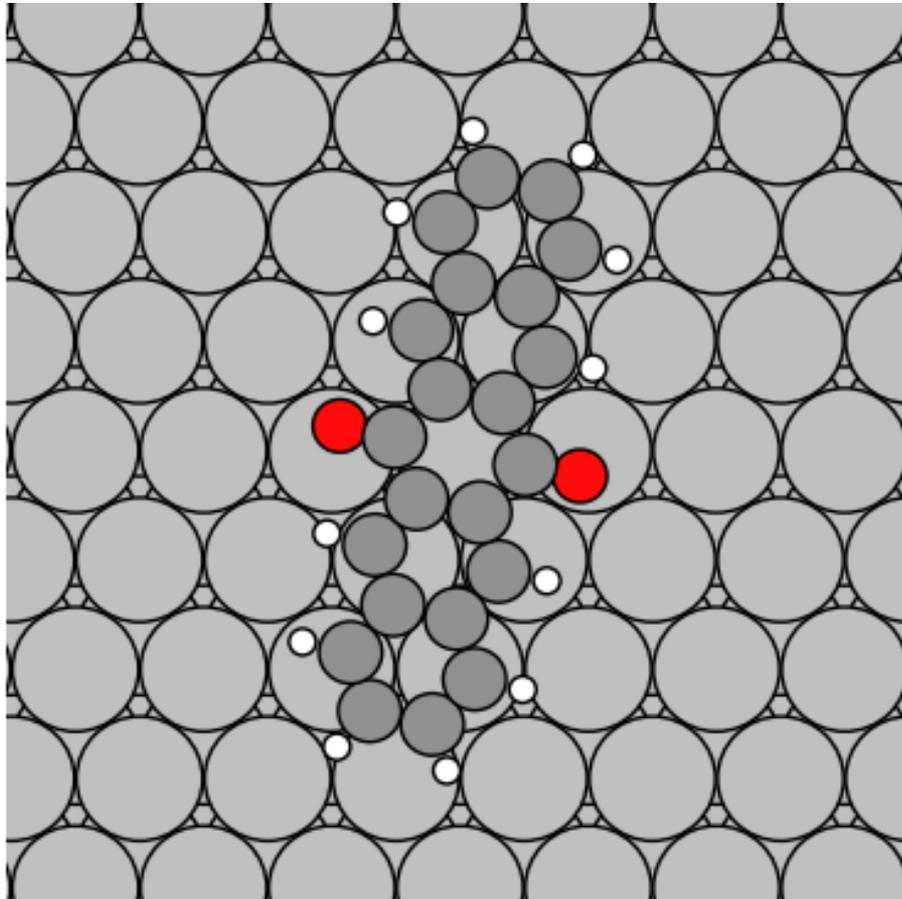


Mobilities in Pentacene

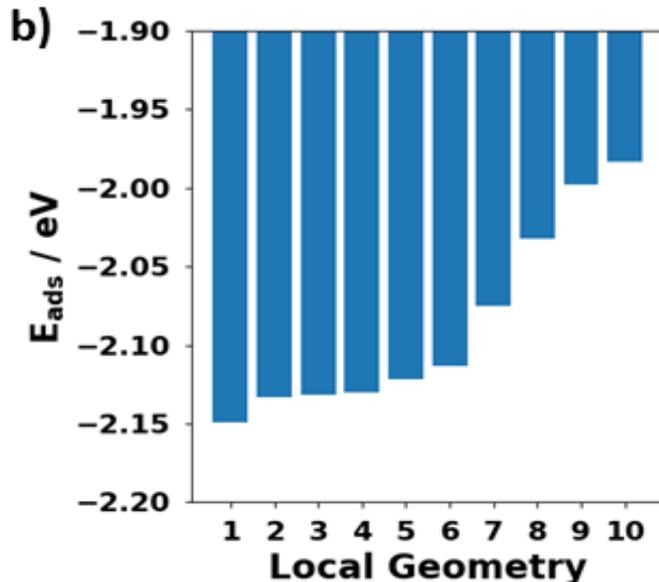
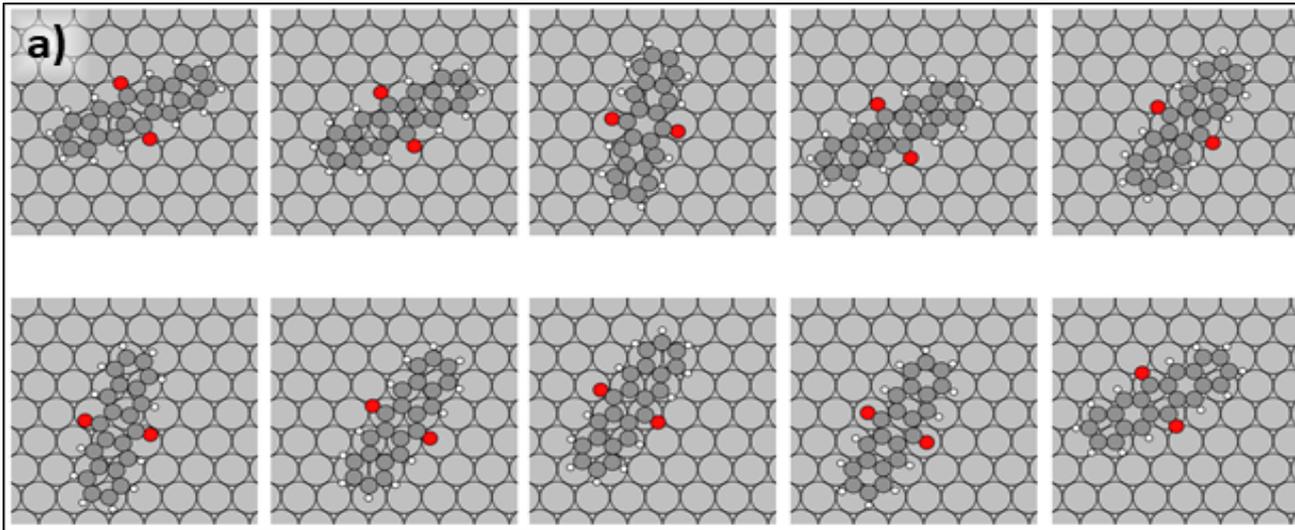


Catalytic Triade

Complex geometries: How many minima exist?



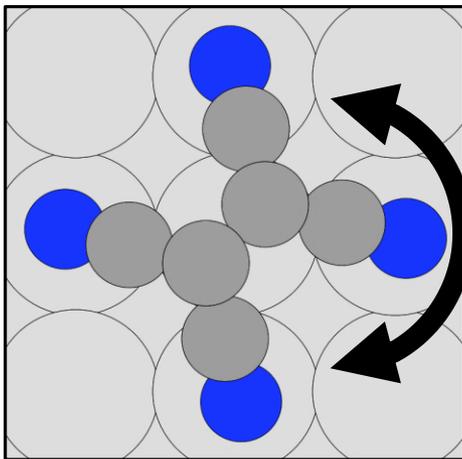
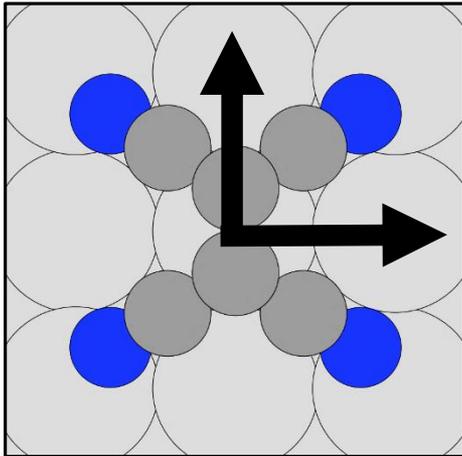
Guess Geometry: How many minima exist?



**Many non-trivial minima.
Hard to find by trial and error!**

**Can we trust the differences?
(Coordinate system)**

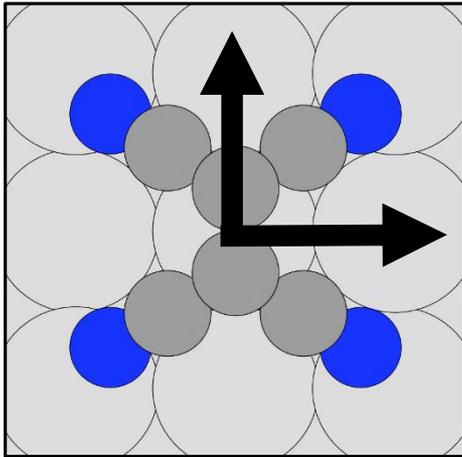
Traditional approach: Point and Click



- **Requires experience**
- **Easy to miss relevant minima**
- **Guess geometries far from harmonic part of PES**

Inefficient Strategy

Systematic Exploration: Expensive



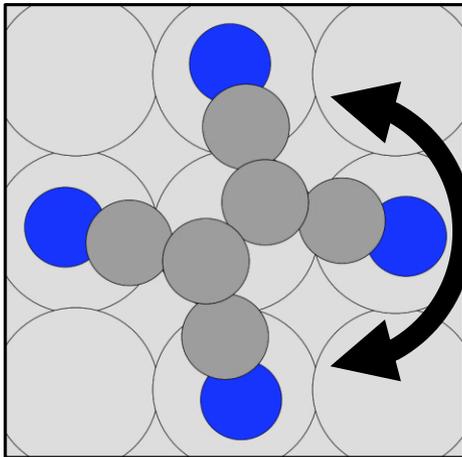
For each molecule:

Translation x: ~ 10 steps

Translation y: ~ 10 steps

Rotation: ~ 10 steps

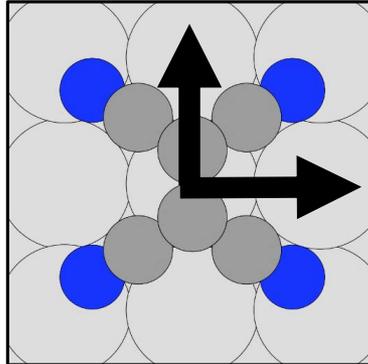
3 mol.: $(10 \times 10 \times 10)^3 = 1 \text{ billion}$



Solution: **Machine Learning**

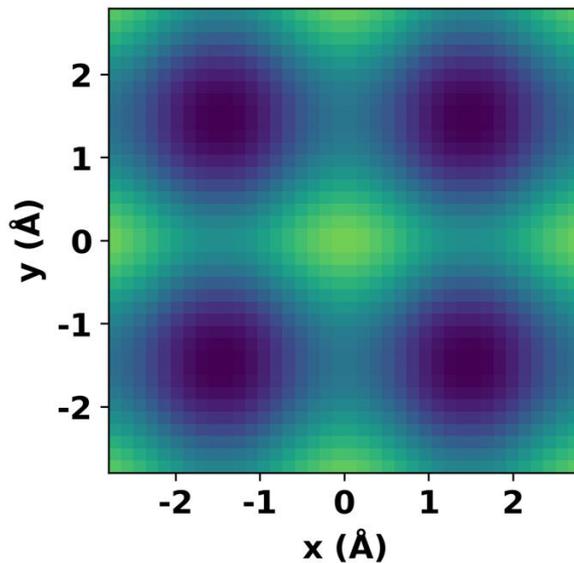
Systematic Exploration: Machine Learning

**100 x 100 DFT
evaluations**

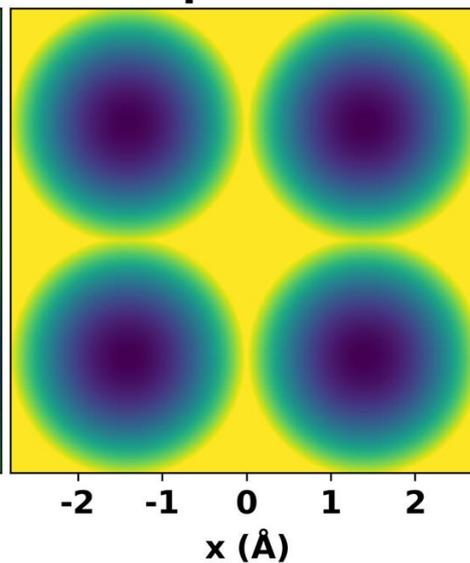


**16 DFT
evaluations**

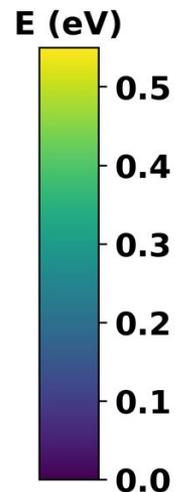
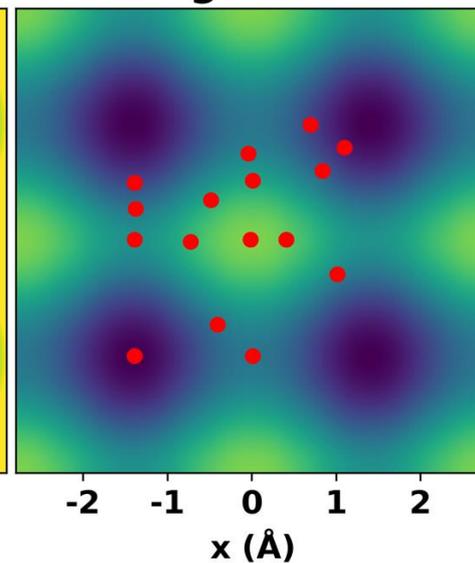
**Brute Force
Calculation**



**Harmonic
Expansion**



**Gaussian Process
Regression**



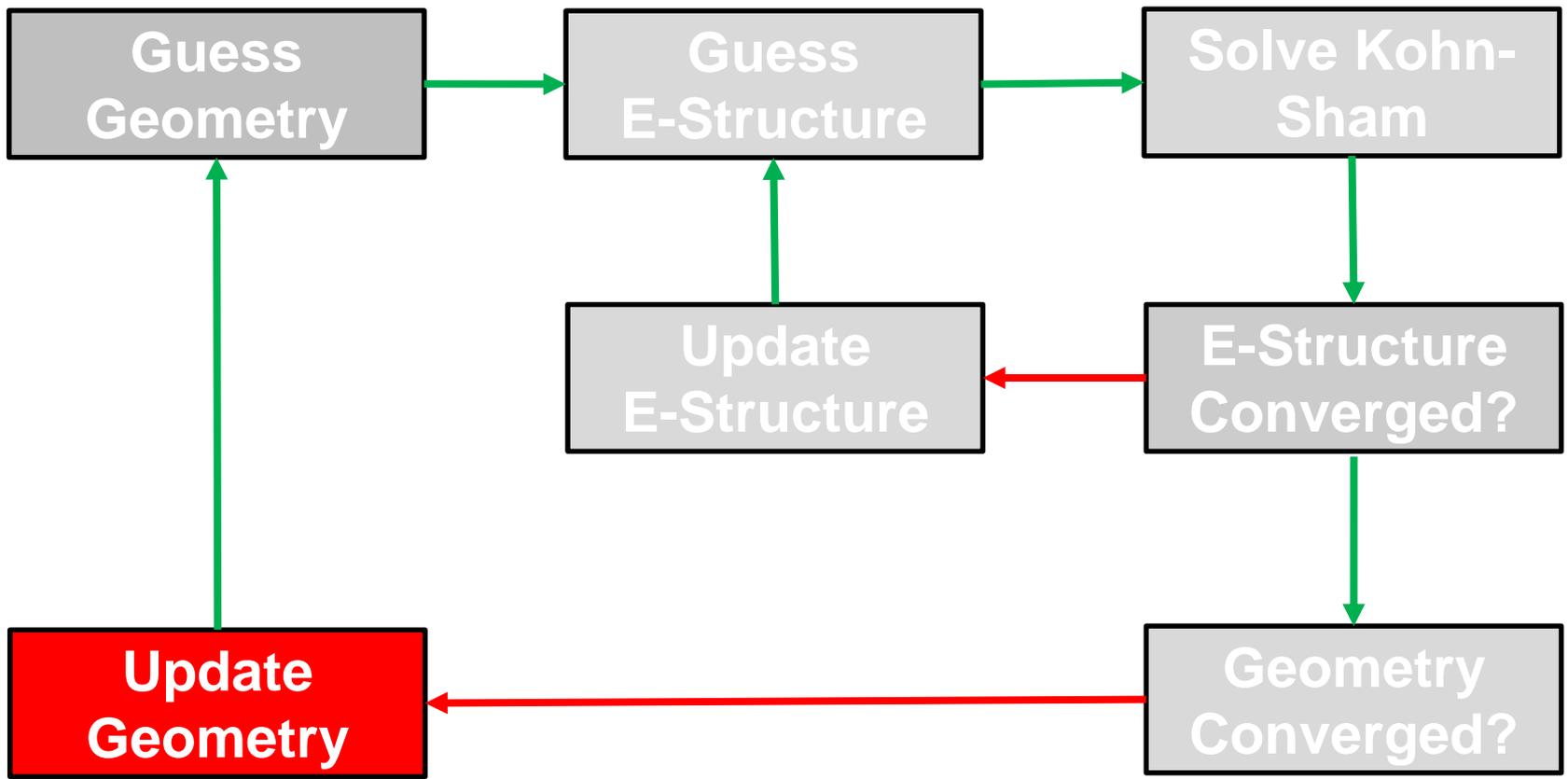
Pre-Optimization with Bayes Optimizers / GPR

Advantages:

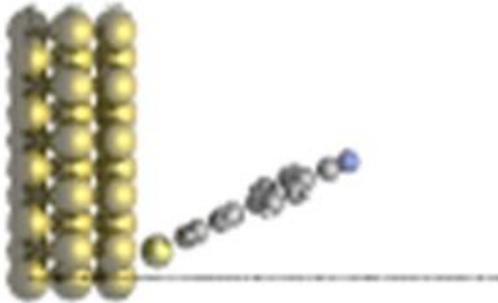
- Very few calculations required (~10-50 force evaluations)
- Large movements possible
- More information about the potential energy surface (Barriers, attraction basin size, ...)

Disadvantages:

- Hyperparameters!
- Manual identifications of soft degrees of freedom
- „freezing“ of DoFs can alter potential energy surface

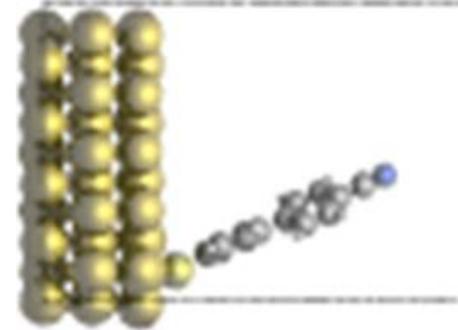


Initial Guess



$E = \text{reference}$
 $\Phi = 5.54 \text{ eV}$

Converged Result

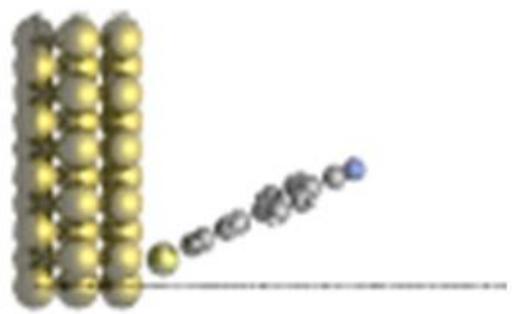


$E = -0.13 \text{ eV}$
 $\Phi = 5.54 \text{ eV}$

```
Net remaining forces (excluding translations, rotations) in present geometry:  
|| Forces on atoms || = 0.897187E-02 eV/A.  
Maximum force component is 0.897187E-02 eV/A.  
Present geometry is converged.
```

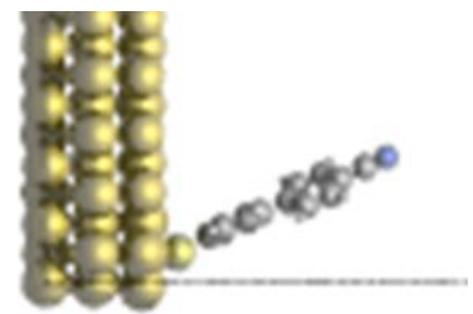
Plausible Result?

Initial Guess



$E = \text{reference}$
 $\Phi = 5.54 \text{ eV}$

Converged Result

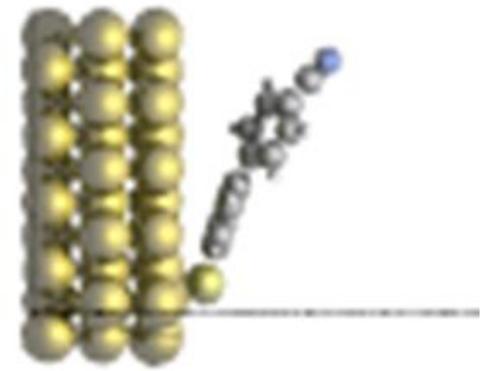


$E = -0.13 \text{ eV}$
 $\Phi = 5.54 \text{ eV}$

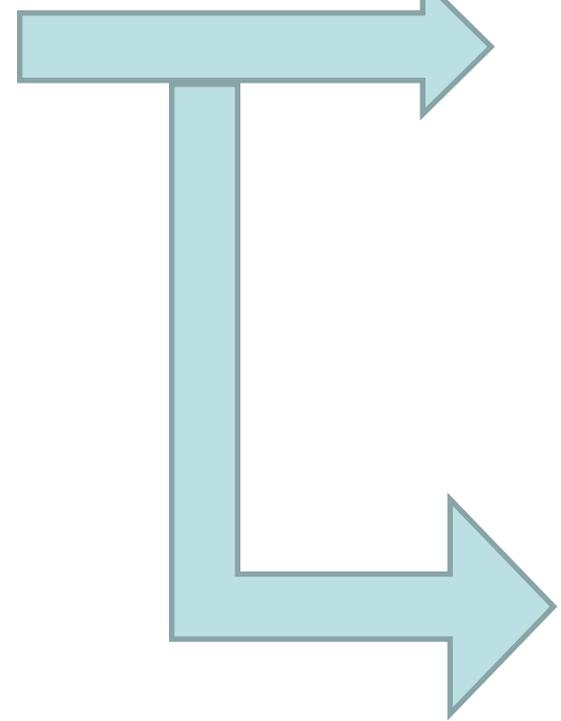
Diagonal Guess



Lindh Guess



$E = -1.95 \text{ eV}$
 $\Phi = 5.25 \text{ eV}$



Geometry update – (Quasi-)Newton Methods

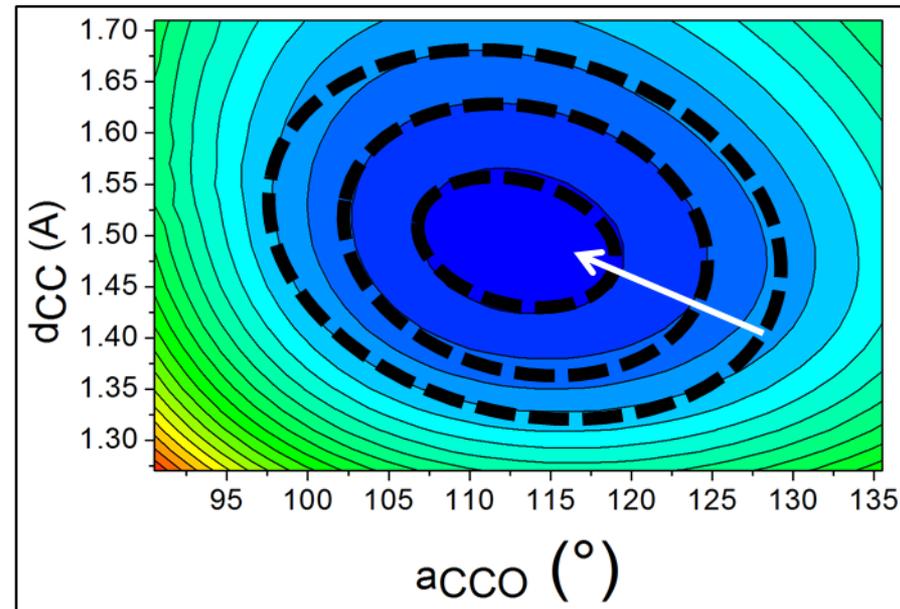
Approximate PES by quadratic function

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

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]

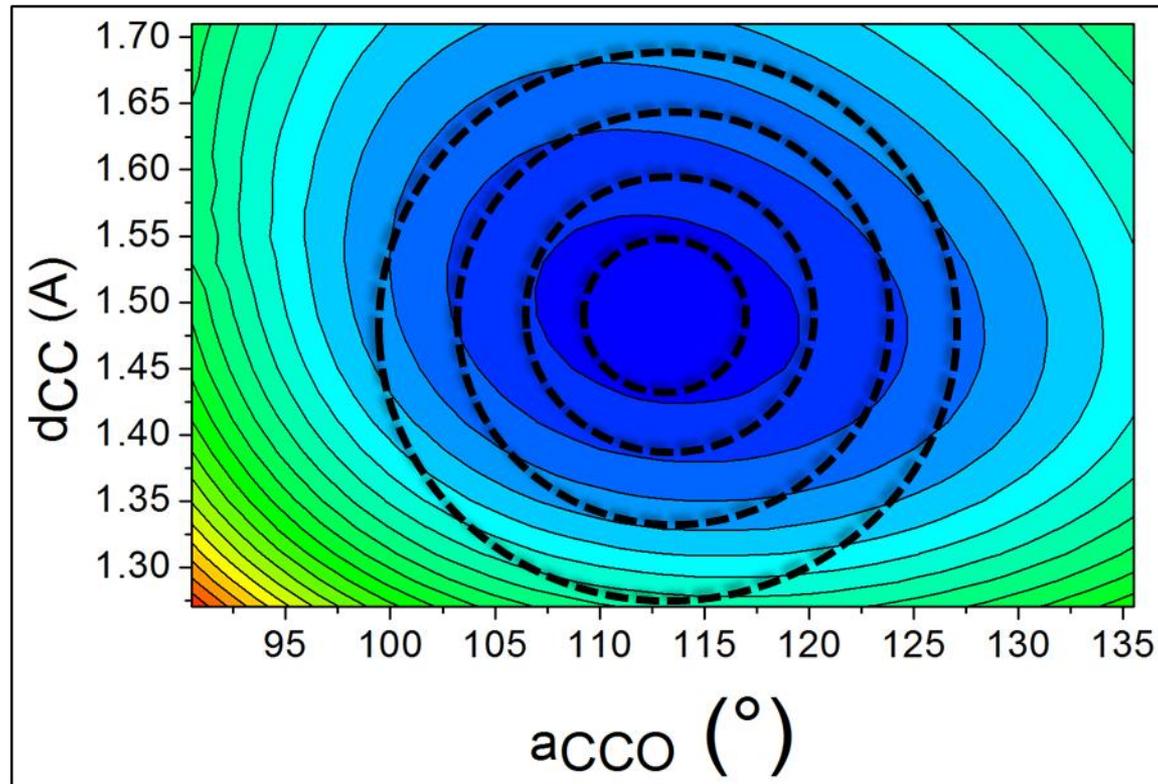
$$\tilde{H} \leftarrow \tilde{H} - \frac{\tilde{H} \Delta R (\tilde{H} \Delta R)^T}{\Delta R^T \tilde{H} \Delta R} - \frac{\Delta F \Delta F^T}{\Delta F^T \Delta R}$$

Guess Hessian: Scaled unit matrix

$$\tilde{H} = \beta \bar{I}$$

Assumption: Each DoF has same force constant

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

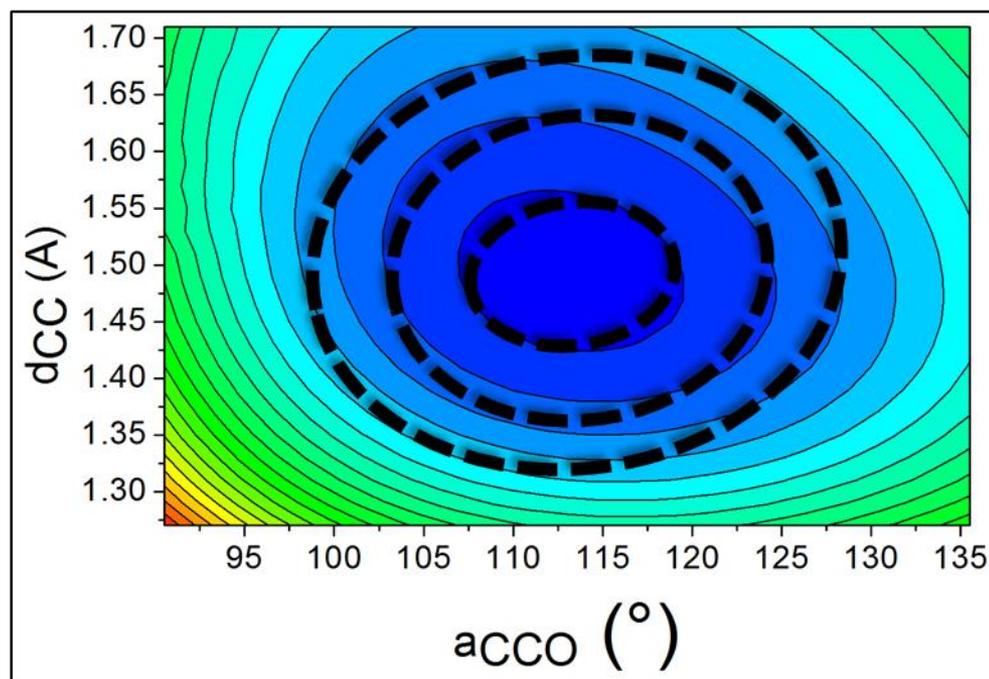


Guess Hessian: Chemically motivated

Properties:

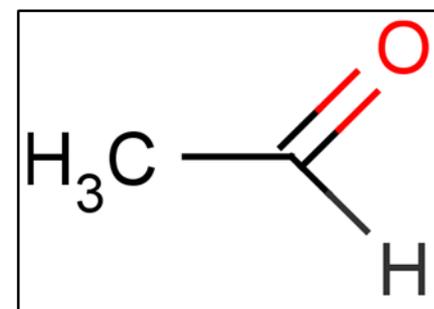
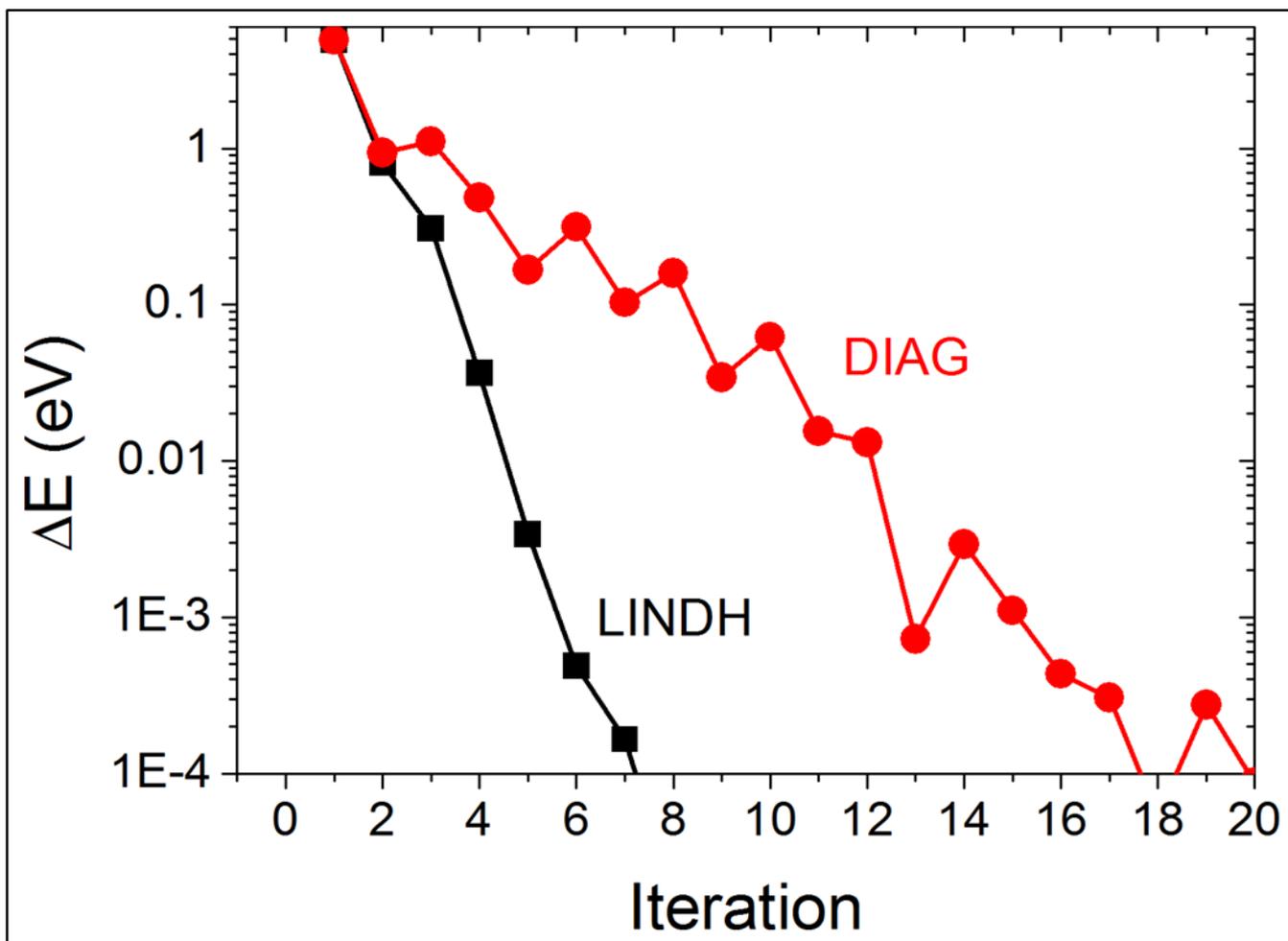
- k 's parameterized [1]
- Different parameters exist
 - (e.g.: Lindh, Fischer)
- But not for everything
- Construction not unique

$$\begin{aligned}\tilde{E} &= E + F\Delta R \\ &+ \sum_{ij} k_{ij} d_{ij}^2 \quad \text{stretching} \\ &+ \sum_{ijl} k_{ijl} a_{ijl}^2 \quad \text{bending} \\ &+ \sum_{ijlm} k_{ijlm} \tau_{ijlm}^2 \quad \text{torsion}\end{aligned}$$



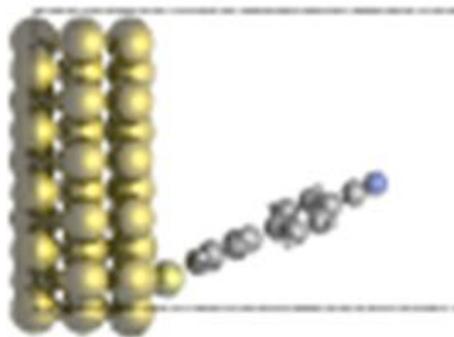
Effect of Guess Hessian

Speedup of calculation



Diagonal

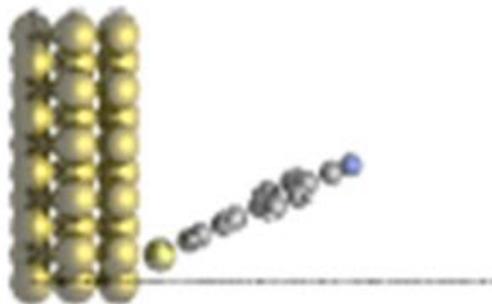
Default in most codes!



$$E = -0.13 \text{ eV}$$

$$\Phi = 5.54 \text{ eV}$$

Initial

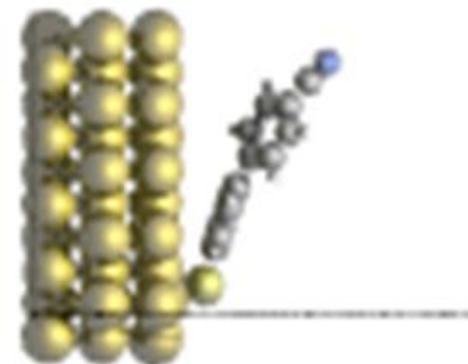


$$E = \text{reference}$$

$$\Phi = 5.54 \text{ eV}$$

Lindh

n/a in most codes!



$$E = -1.95 \text{ eV}$$

$$\Phi = 5.25 \text{ eV}$$

Challenges:

- hard and soft degrees of freedom present
- large movements prevented by step control
- Initial Hessian sub-optimal (no vdW)

Summary

- Mind defaults and algorithms
- Pre-screen geometries (if applicable), use modern technologies
- Select converged convergence thresholds
- Converge observables explicitly
- Check results for plausibility

