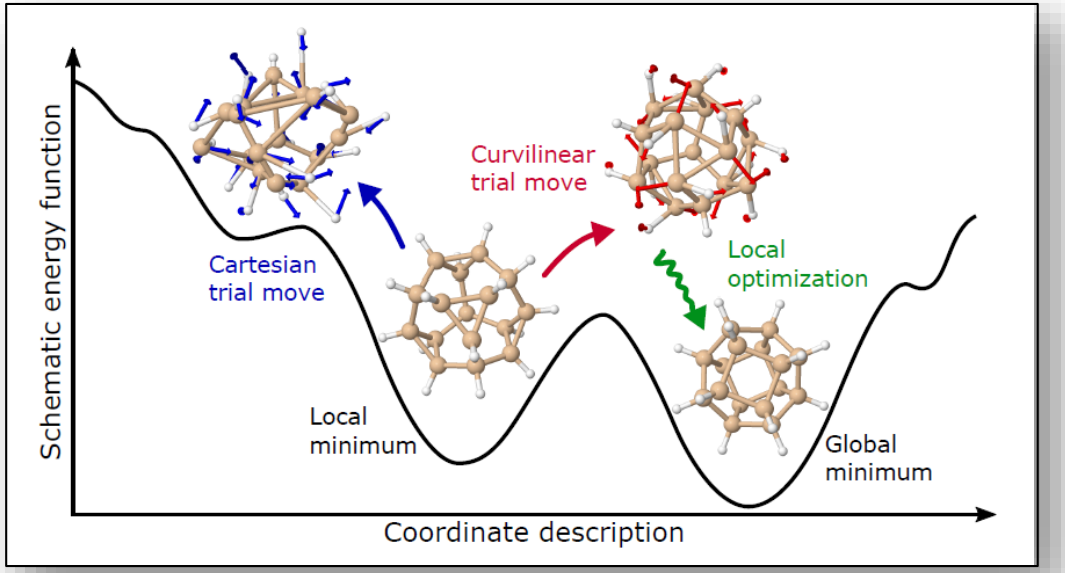
Exploring Discrete and Continuous Landscapes

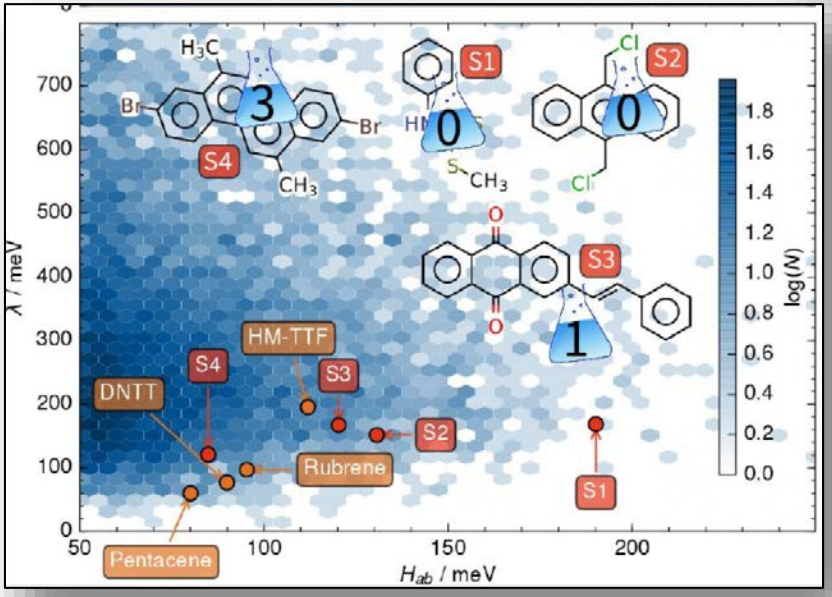
Karsten Reuter

Chemistry Department and Catalysis Research Center
Technische Universität München

$$f = f\left(\{\vec{R}_i\},\{Z_i\}\right)$$

Global materials structure search with chemically motivated coordinates

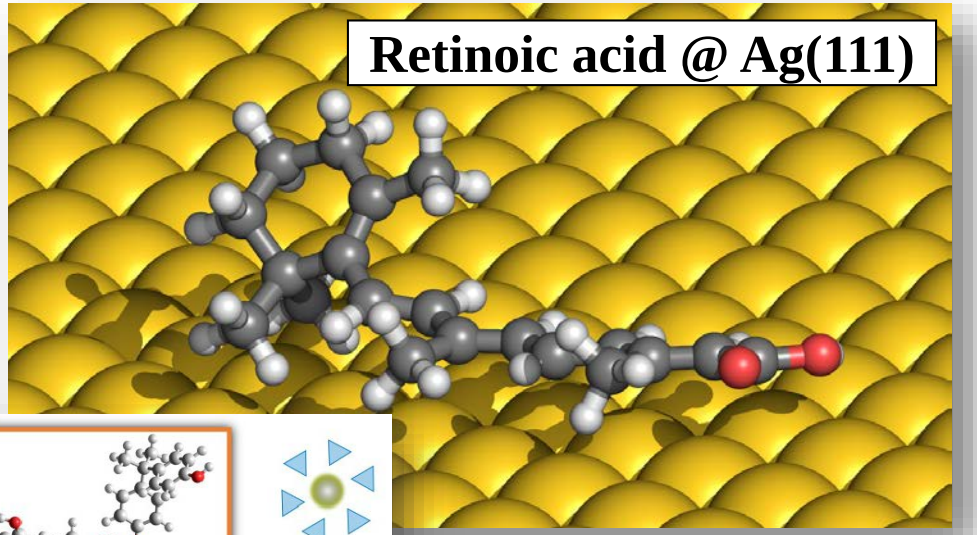


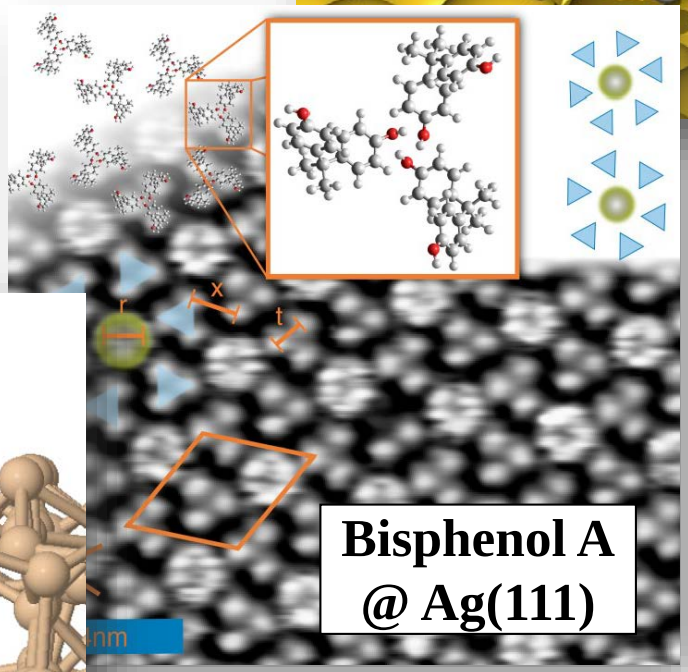


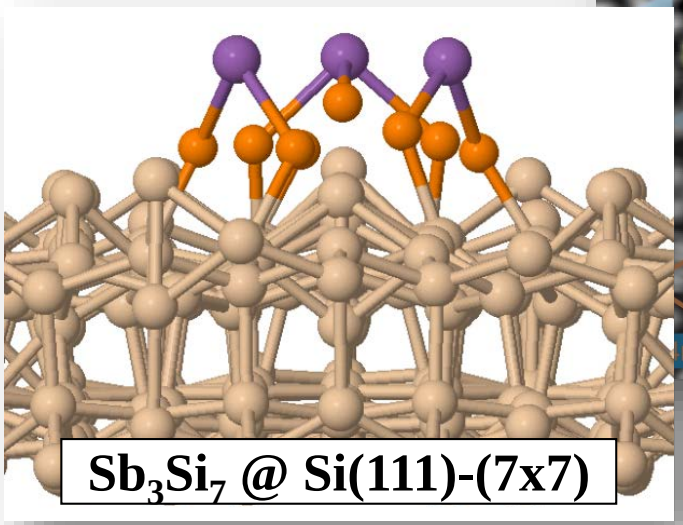
Computational screening for high carrier mobility in organic solar cells

Configurational spaces in the nanoworld

Functional molecules
Molecular networks
Surface reconstructions
…

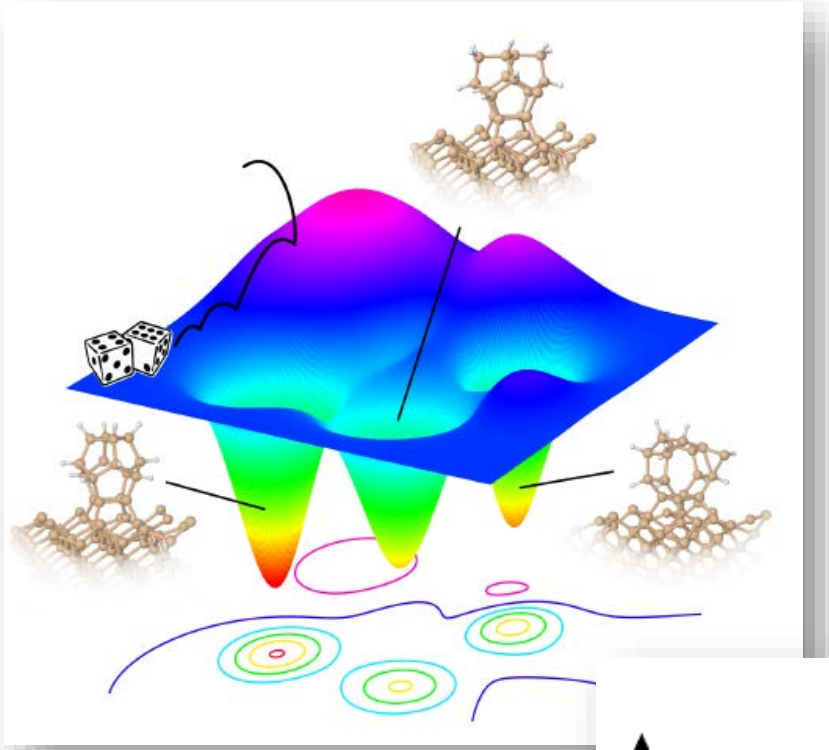




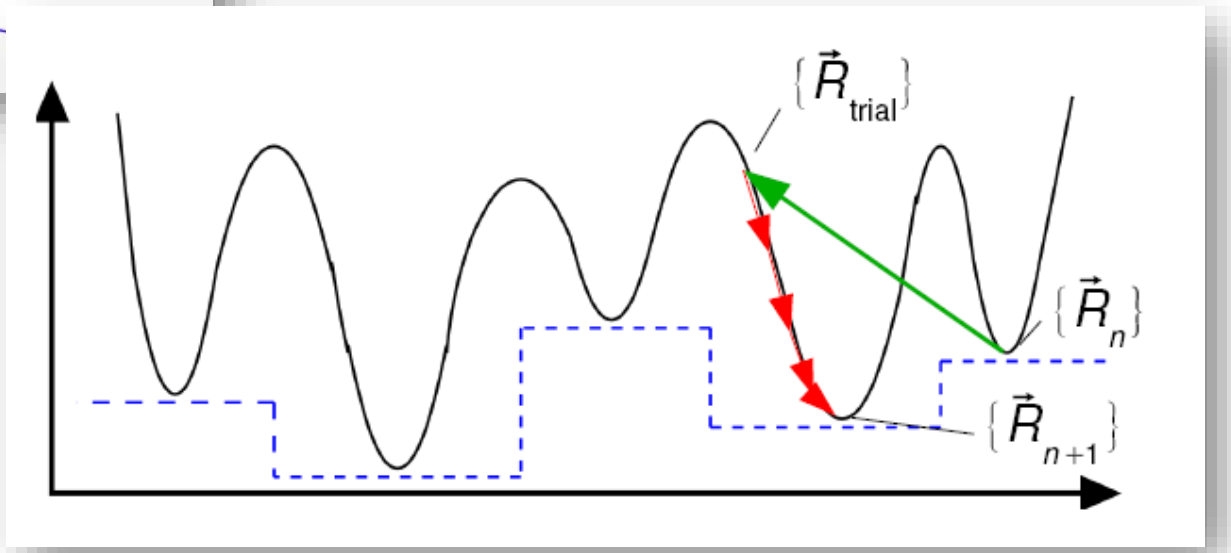


Structure is the key…

Navigating materials space: Global geometry optimization

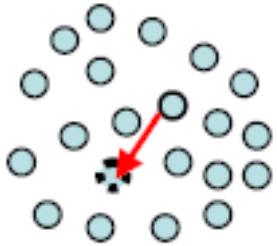


Basin hopping
Genetic algorithms
Minima hopping
…

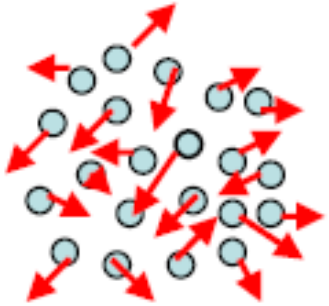


e.g. D. Wales *et al.*,
Adv. Chem. Phys. 115, 1 (2000)

A common, but chemically blind feature



single-particle move



collective move

Trial structure generation through discontinuous random „moves“

Cartesian coordinates (CCs):

✓ unbiased and universal

✓ intuitive (also from programmer‘s POV)

X can easily lead to unphysical configurations

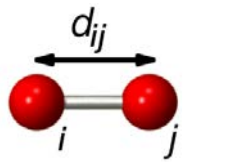
X difficult to „constrain“/“preserve“ structural motifs

A more “chemical” alternative?! Curvilinear displacements

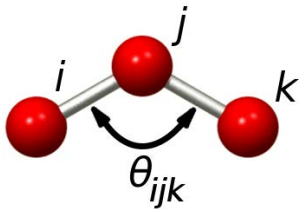
Internal Coordinates (ICs)

Automatic construction cumbersome

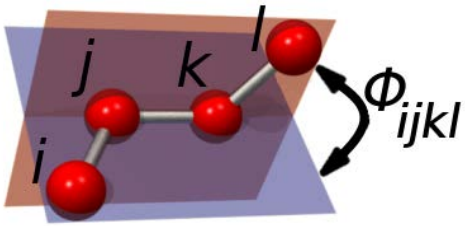
Delocalized ICs (DICs)



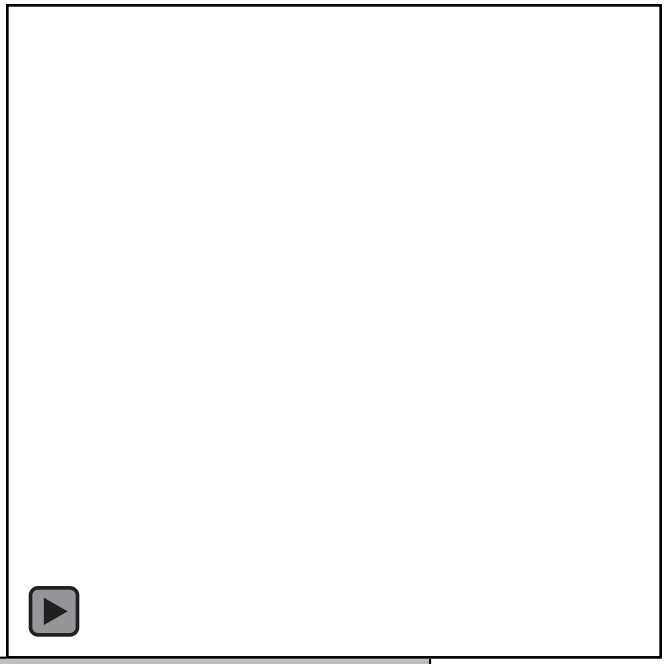
bond lengths



bond angles



torsions



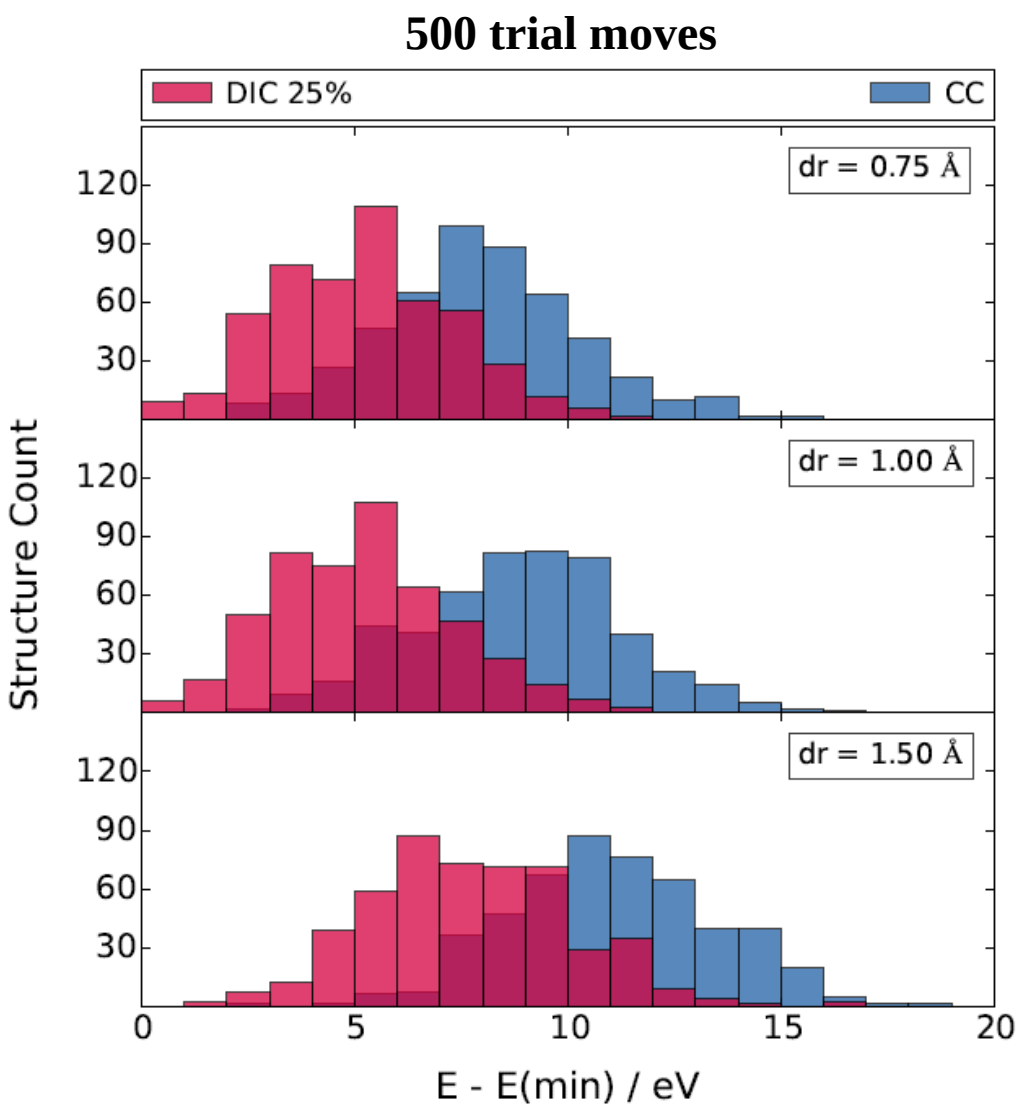
Non-redundant set of linear combinations of internal cordinates

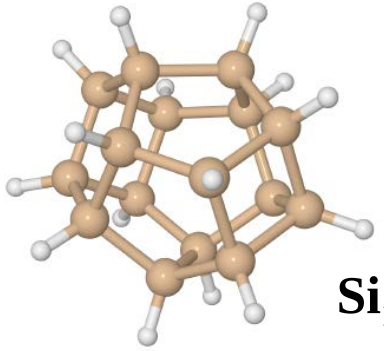
e.g.
C. Peng *et al.*, J. Comp. Chem. 17, 49 (1996)

Hydrogenated Si clusters: Do not break, but still sample…

$Si_{16}H$

Performance check



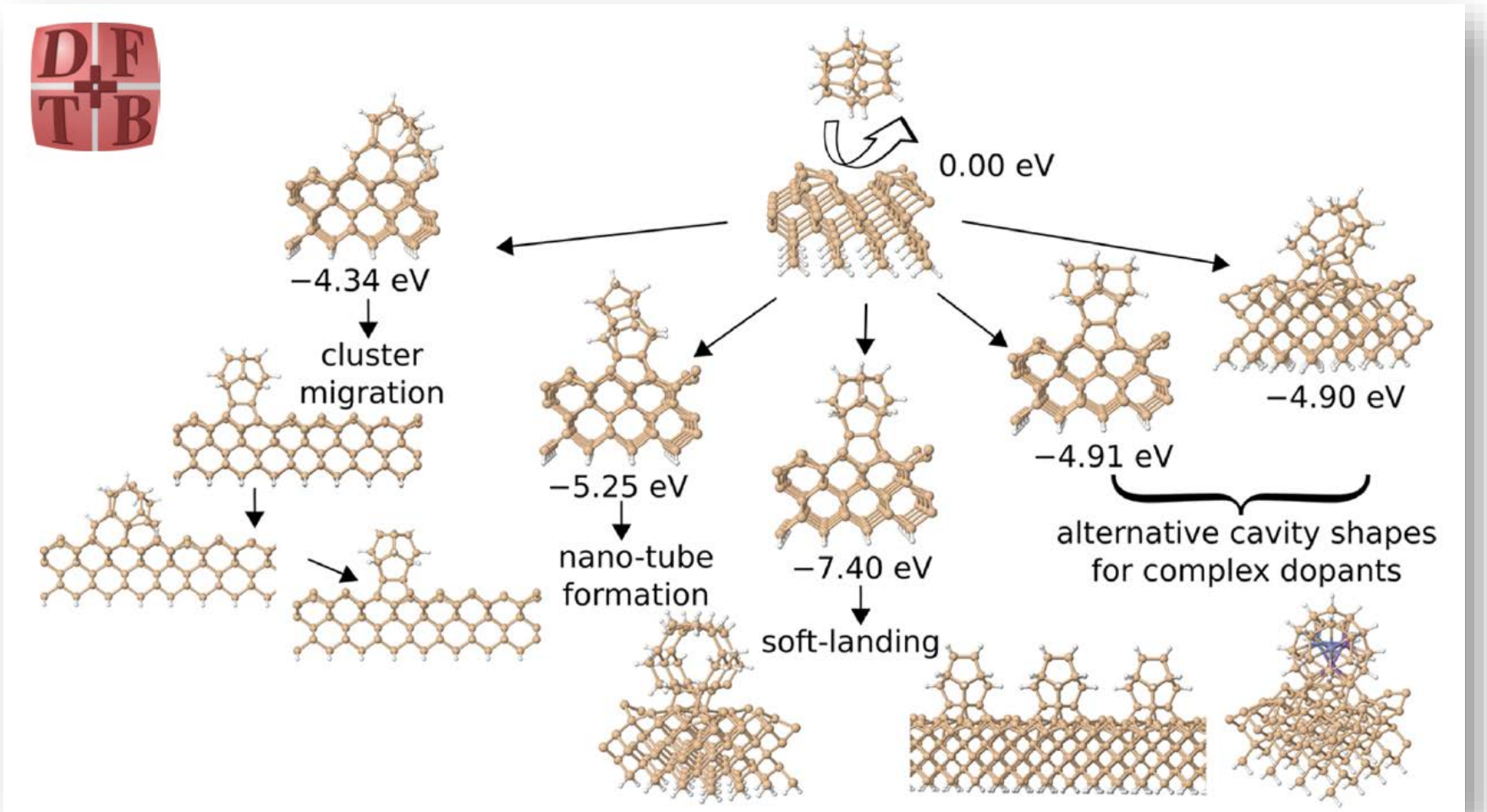


$Si_{16}H_{16}$

Preferential sampling of (intact!) low-energy structures

C. Panosetti *et al.*, Nano Lett. 15, 8044 (2015)

$Si_{16}H_{16}$ at Si(001)

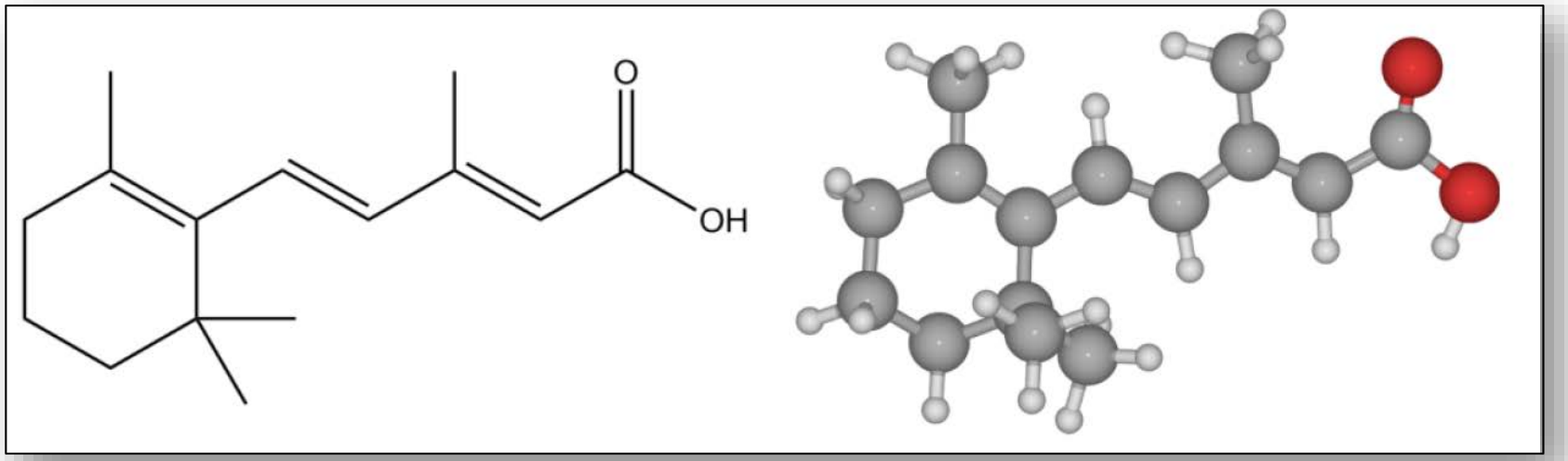


C. Panosetti *et al.*, Nano Lett. 15, 8044 (2015)

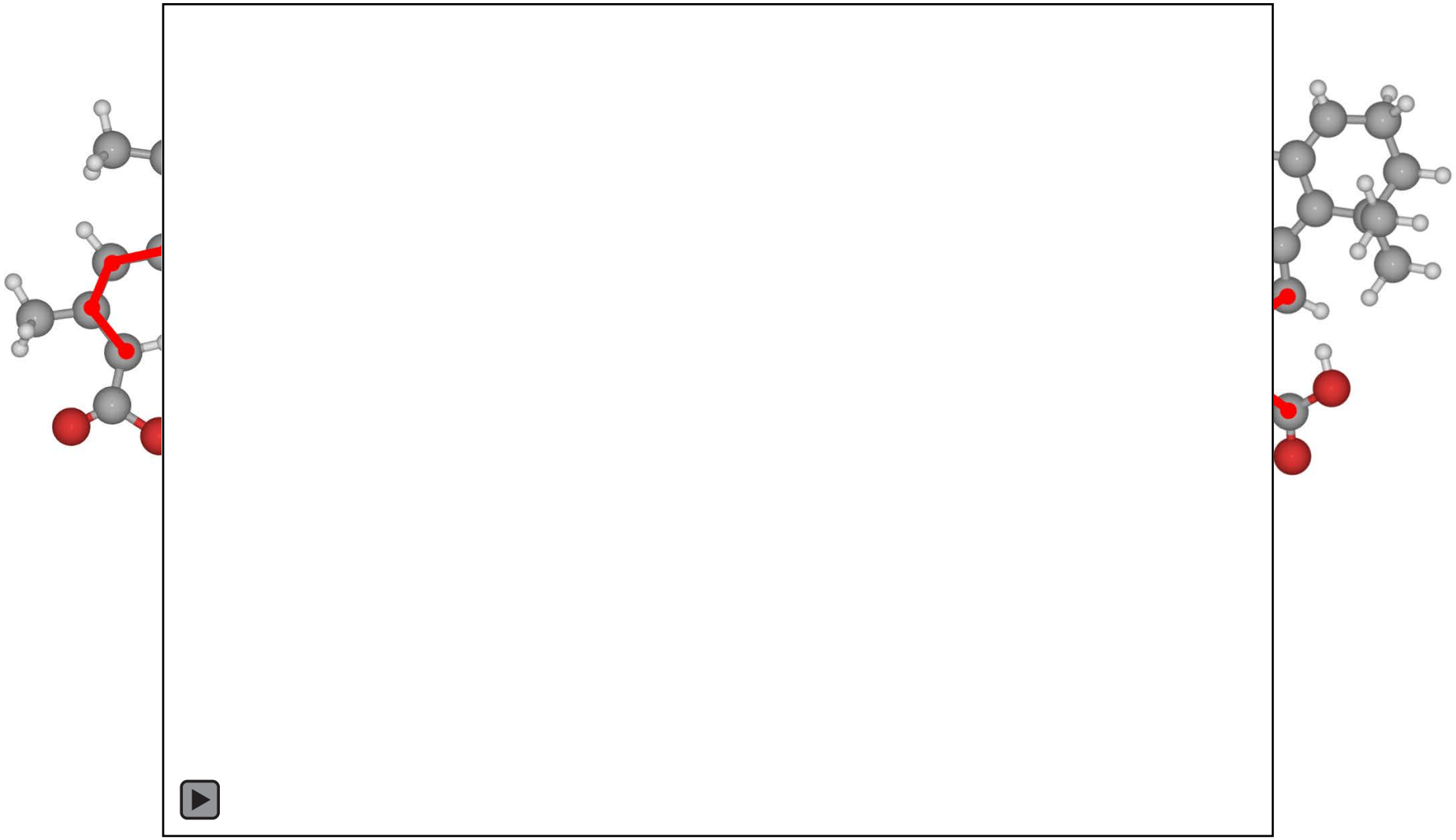
Constraint searches in chemical space

- **Structural integrity particularly important for (organic) molecules**
- **Application of bond-conserving constraints straightforward in DICs**

***trans*-β-ionylideneacetic acid (β-acid)**



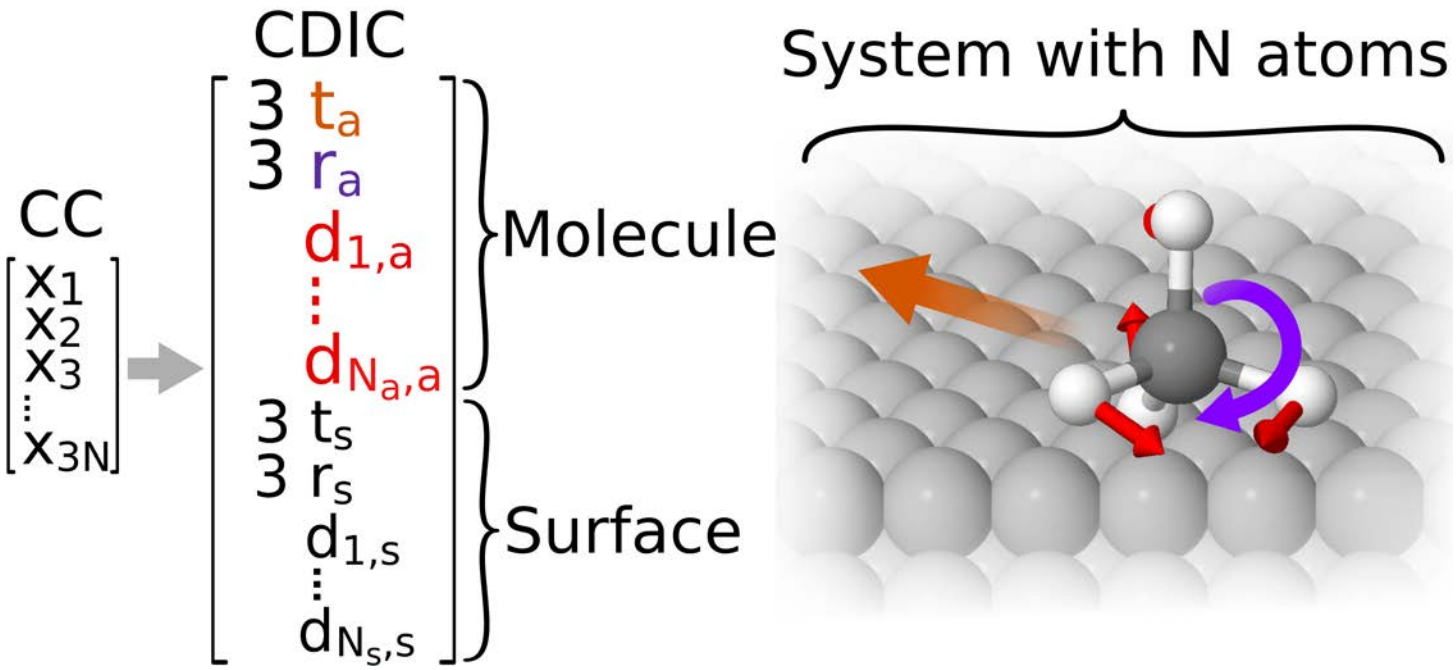
β-acid @ Au(111)



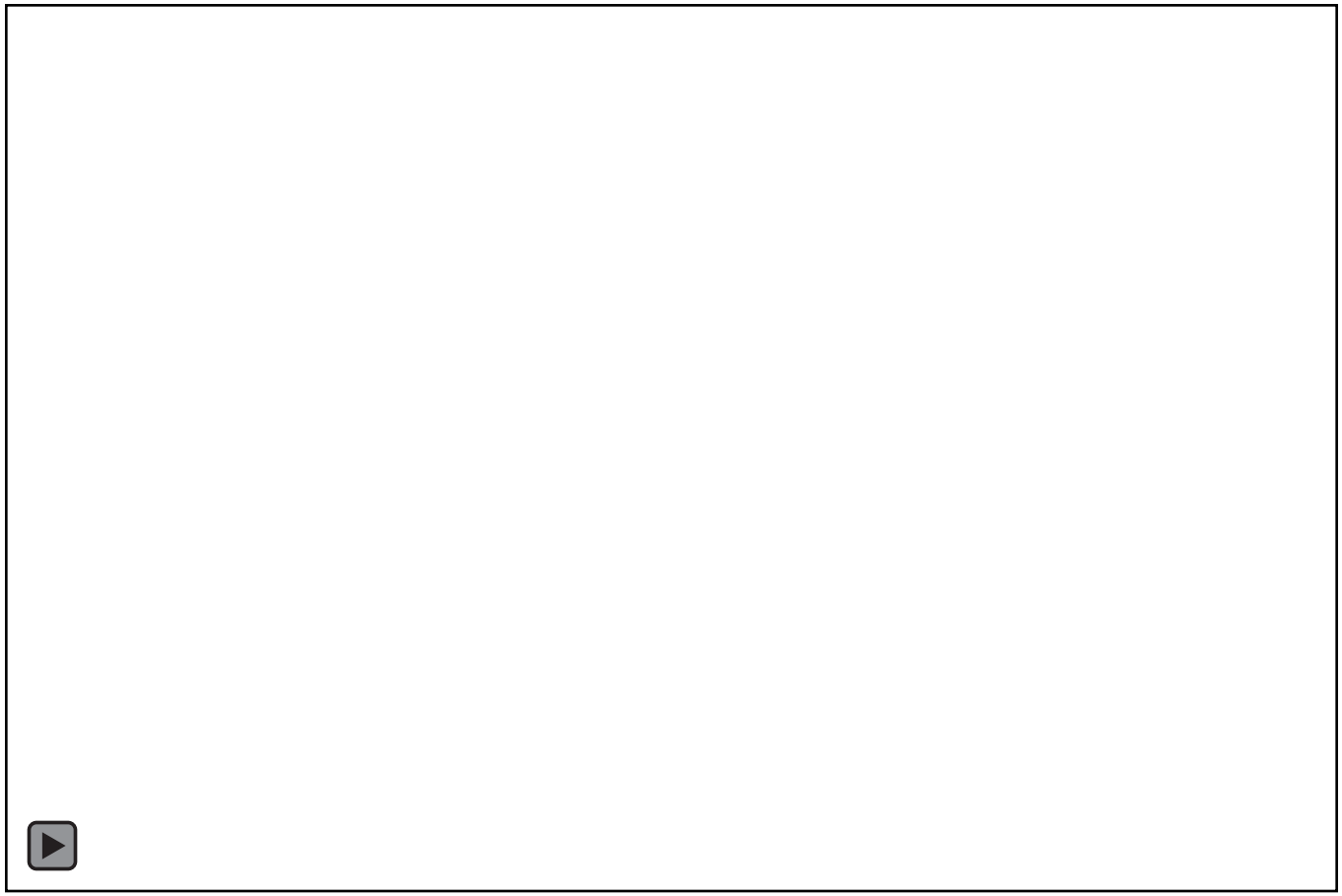
K. Krautgasser *et al*., J. Chem. Phys. 145, 084117 (2016)

Sub-system rotations and translations: Complete DICs

- **DICs filter out translations and rotations by construction**
- **Translations and rotations of sub-systems can be reintroduced by constructing DICs for sub-systems separately and building complete DICs (CDICs) from those**



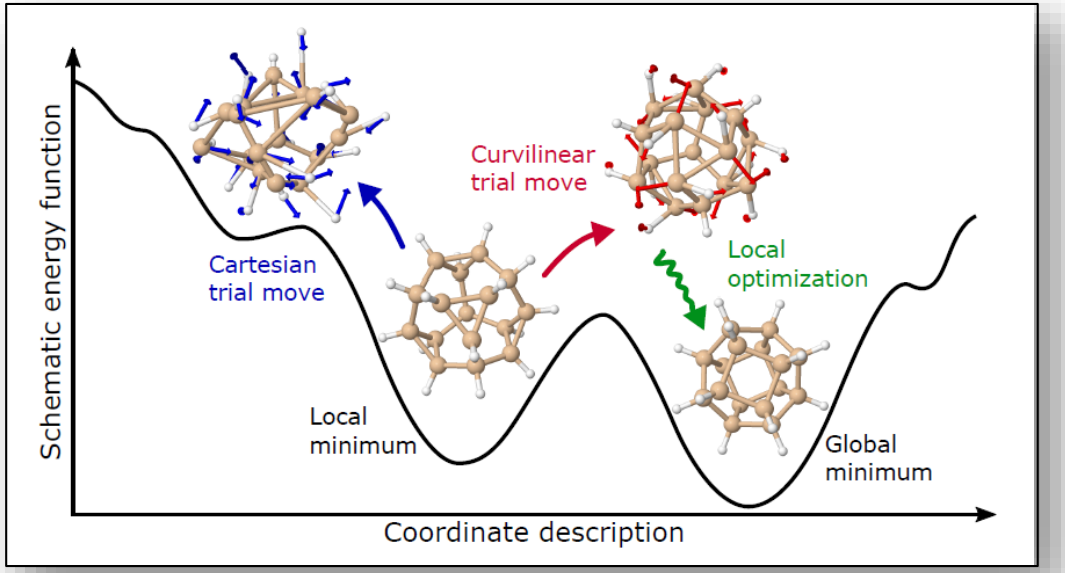
Lateral sampling: CH_4 @ Ag(111)

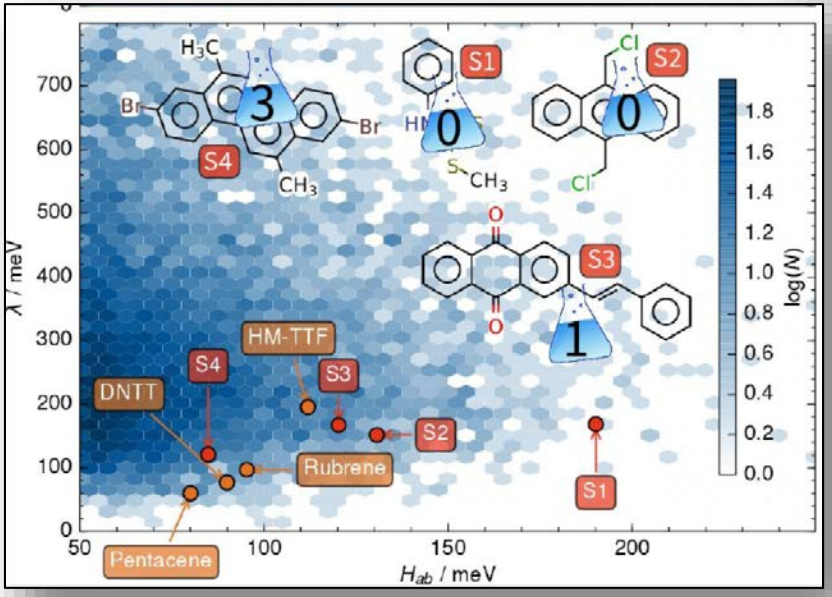


K. Krautgasser *et al*., J. Chem. Phys. 145, 084117 (2016)

$$f = f\left(\{\vec{R}_i\},\{Z_i\}\right)$$

Global materials structure search with chemically motivated coordinates

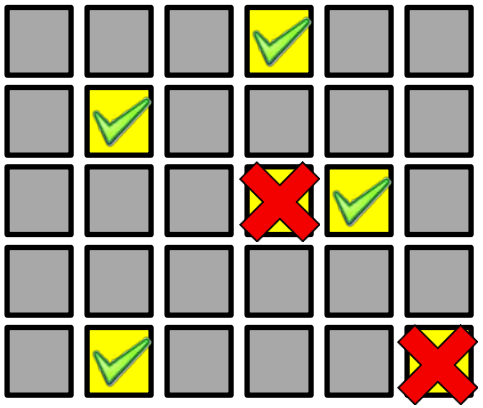


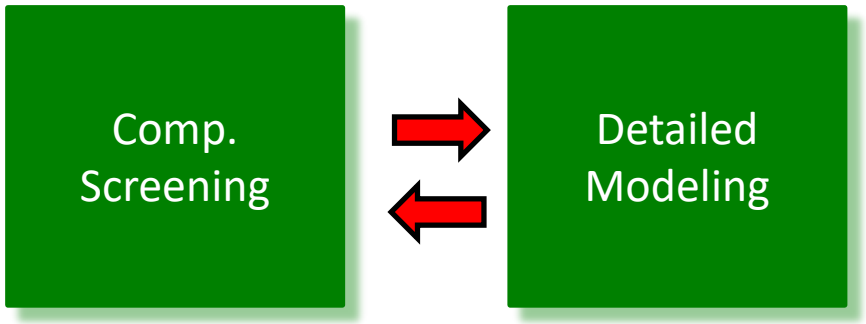


Computational screening for high carrier mobility in organic solar cells

Computational screening: Trends over accuracy

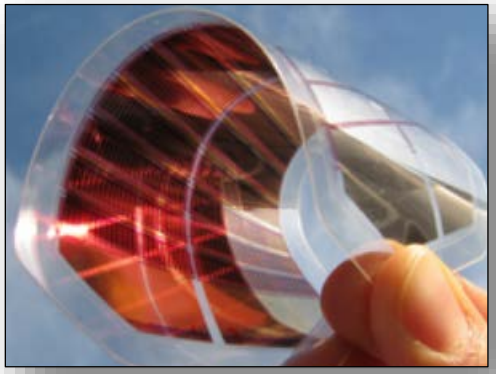
- Exploration of chemical space far beyond the capabilities of real synthesis
- Focus on numerically undemanding descriptors for efficient screening
- Multi-dimensional descriptors (data mining…)



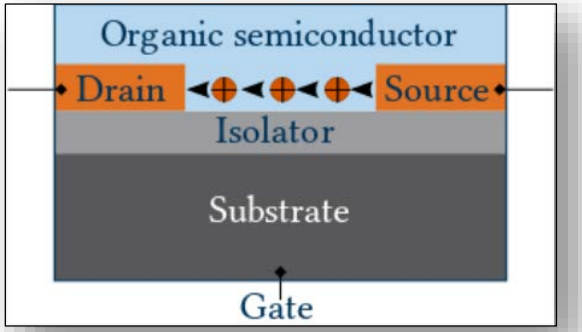


- Trends require lower accuracy
- Not every candidate must be correct (?!)
- As simple as possible, but not simpler…

Charge carrier mobility in organic solar cells: A key device parameter



$$\mu_{ij} = \frac{\partial \langle v_i \rangle}{\partial E_j}$$



Theories to calculate μ_{ij}:
Band theory – small polaron hopping – model Hamiltonians

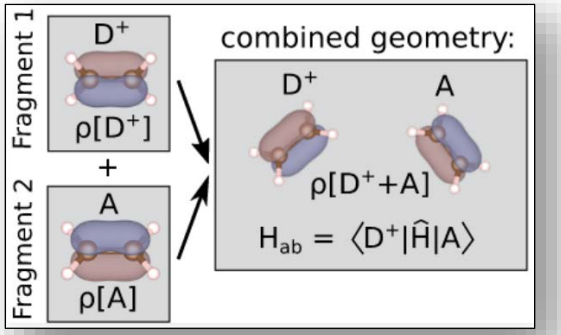
Common to all theories:

$\mu_{ij} \sim H_{ab}$ **Electronic coupling**
$\mu_{ij} \sim \lambda$ **Reorganization energy**

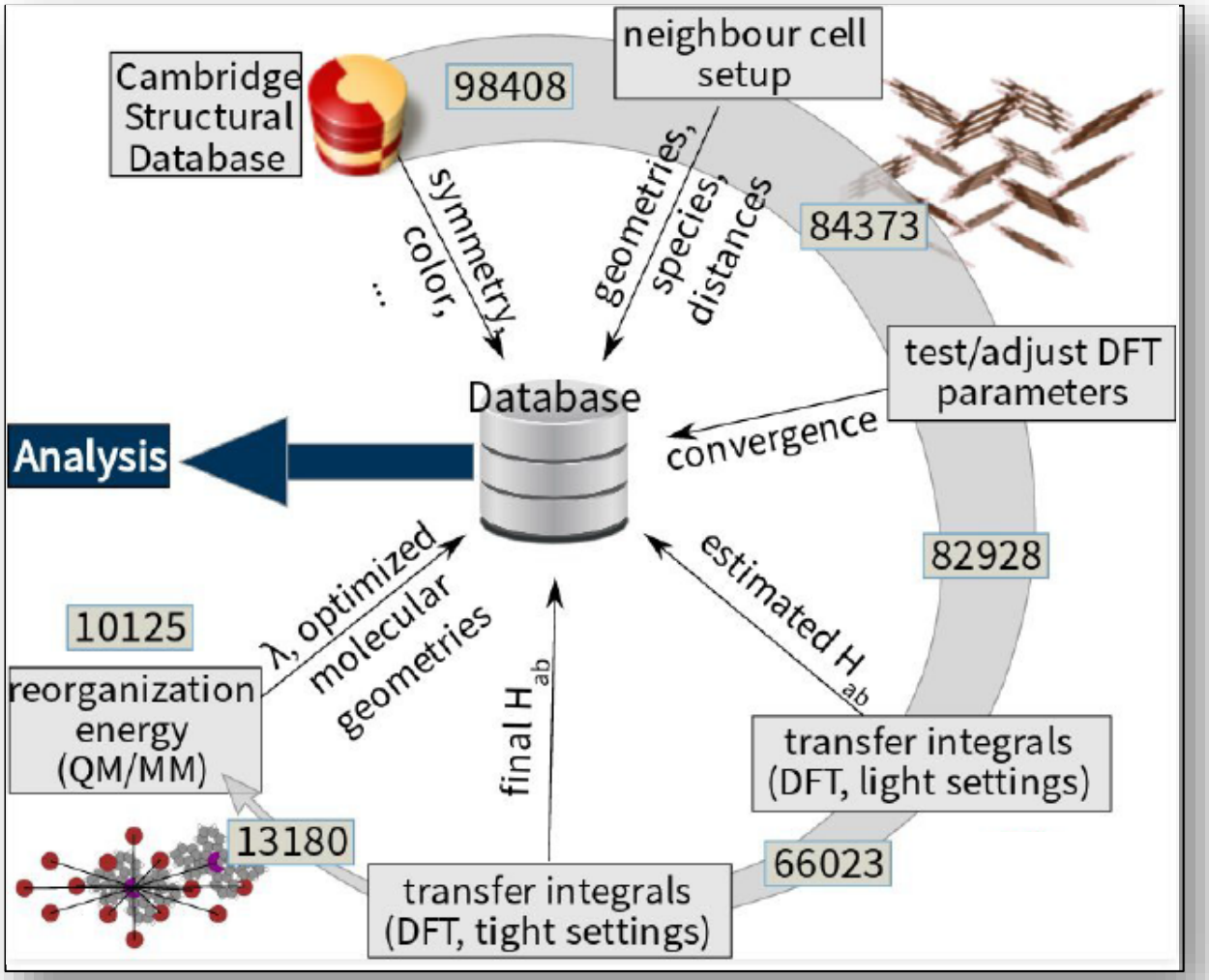
H. Oberhofer, K. Reuter, and J. Blumberger, Chem. Rev. 117, 10319 (2017)

Approximate, but efficient calculation of H_{ab}/λ_{intra} through fragment-orbital DFT:

C. Schober, K. Reuter, and H. Oberhofer
J. Chem. Phys. 144, 054103 (2016)

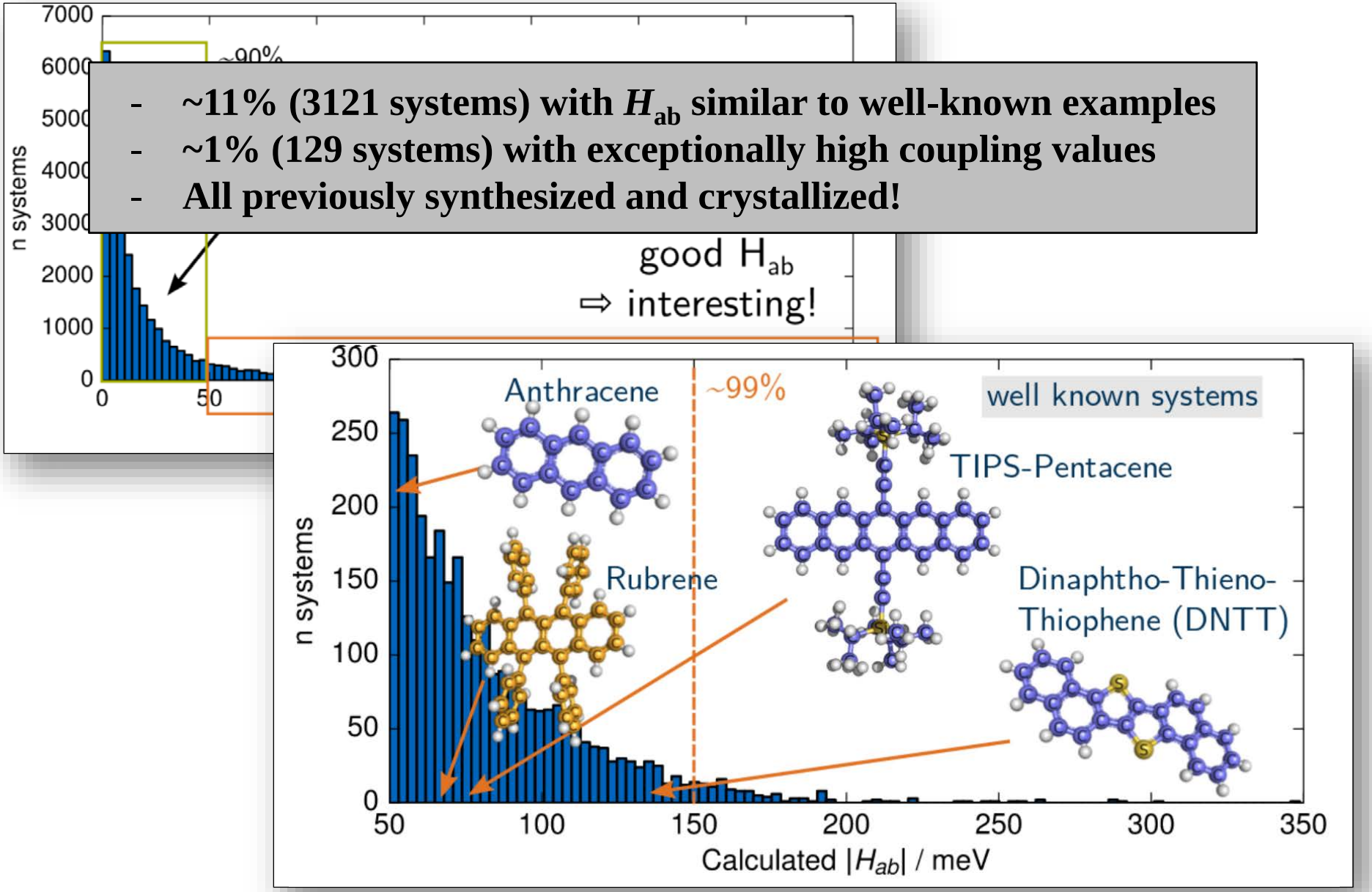


Automated materials screening

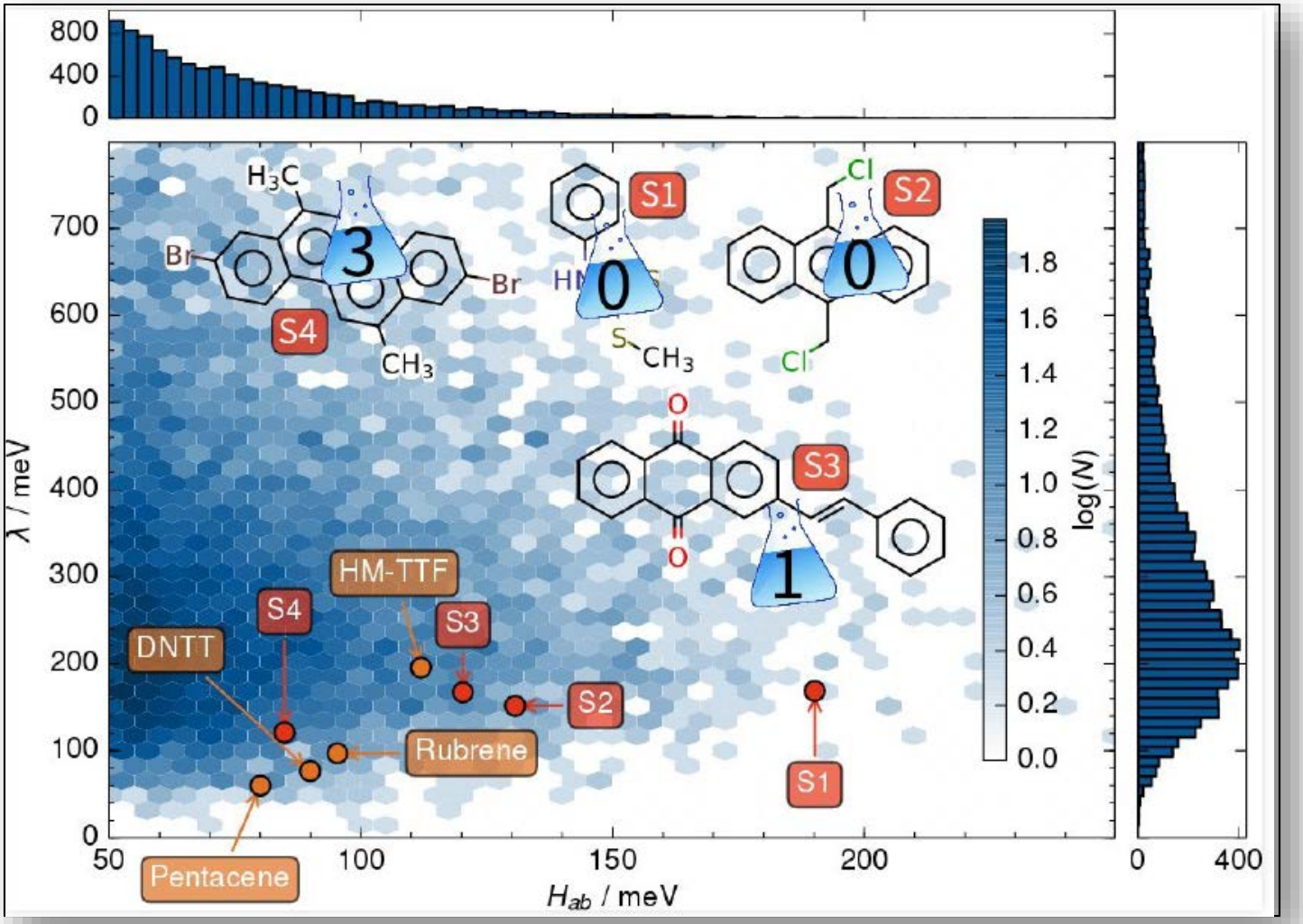


H_{ab} screening results

- **~11% (3121 systems) with H_{ab} similar to well-known examples**
- **~1% (129 systems) with exceptionally high coupling values**
- **All previously synthesized and crystallized!**

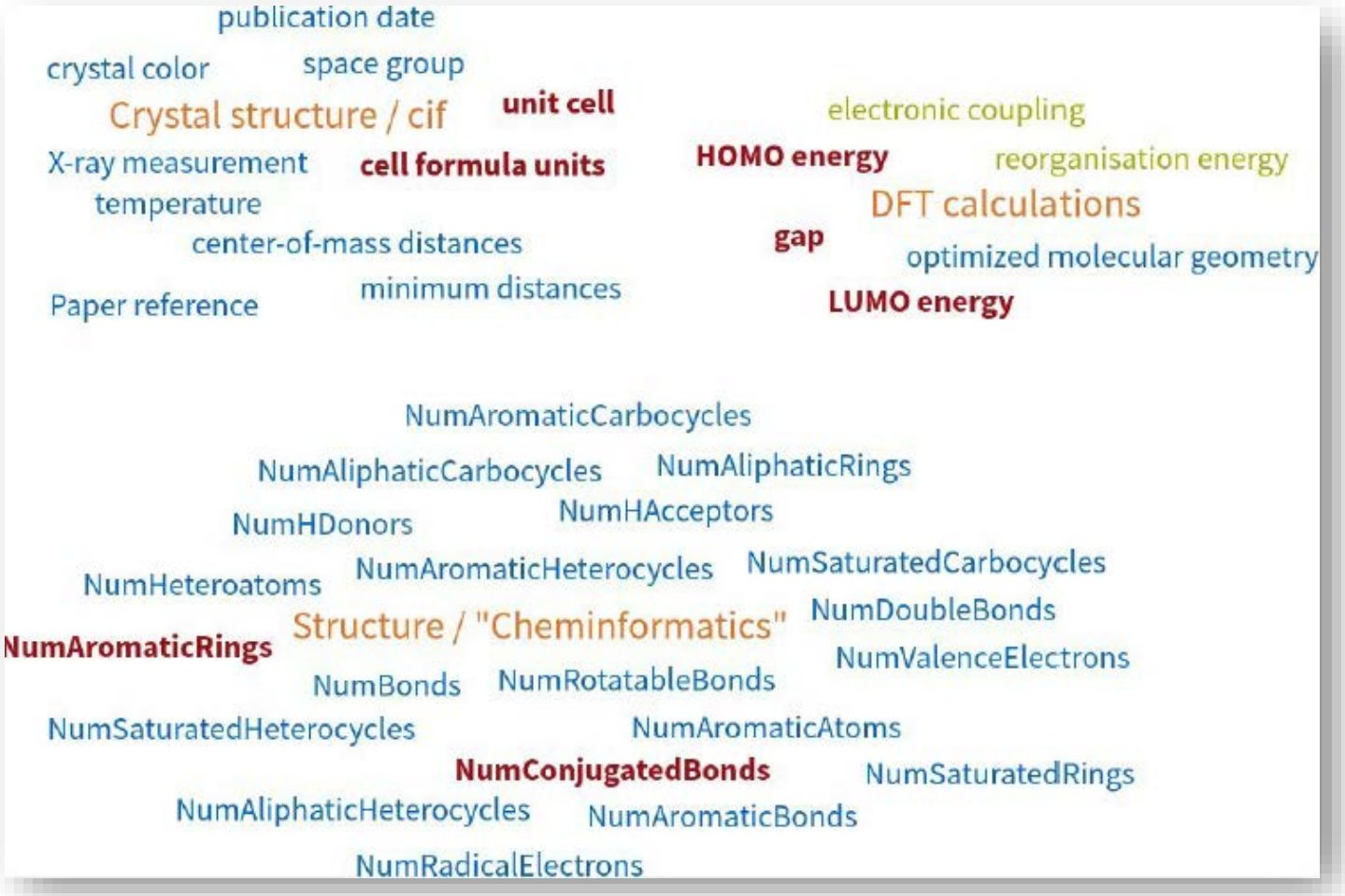


H_{ab} / λ_{intra} screening results



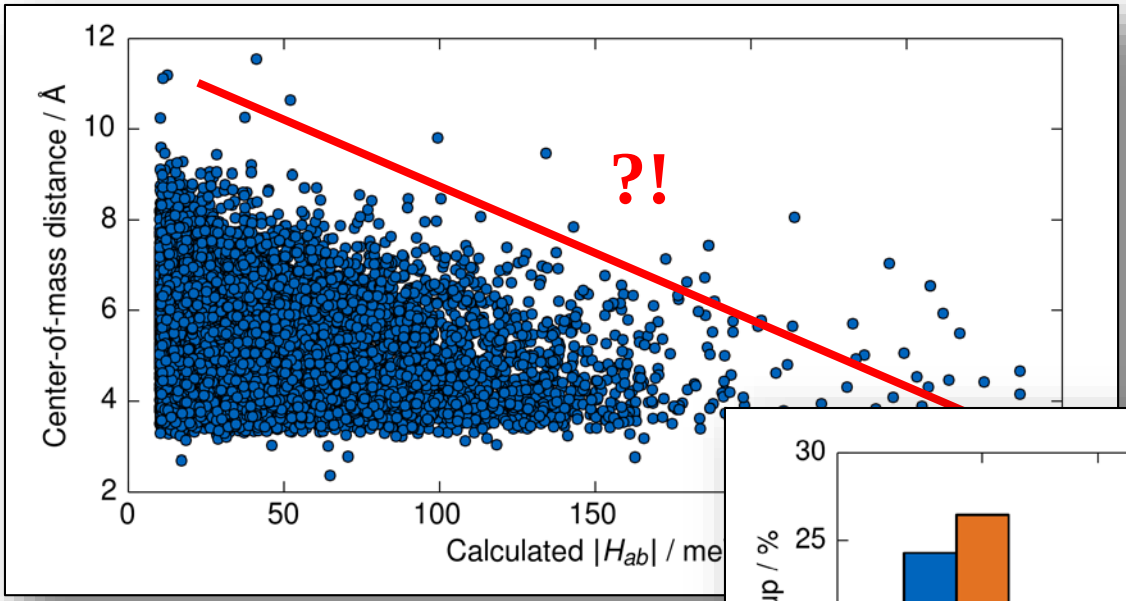
C. Schober, K. Reuter, and H. Oberhofer, J. Phys. Chem. Lett. 7, 3973 (2016)

What else can we learn?

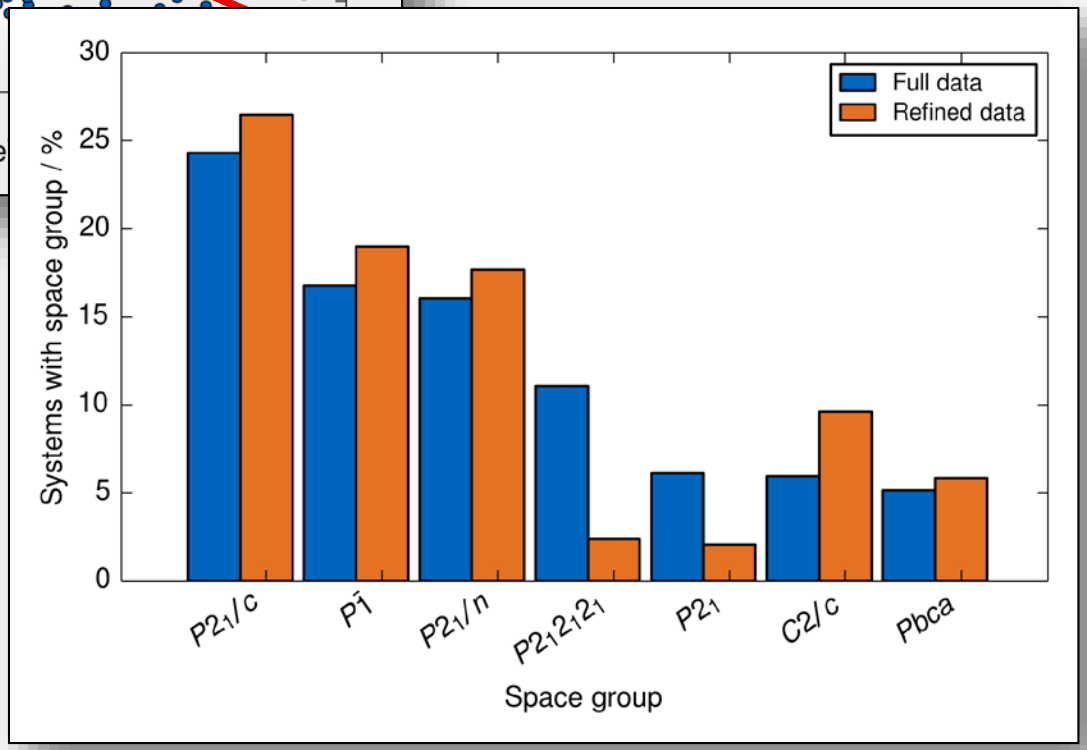


Correlations? Structure-property relationships? …

Scrutinizing simple indicators

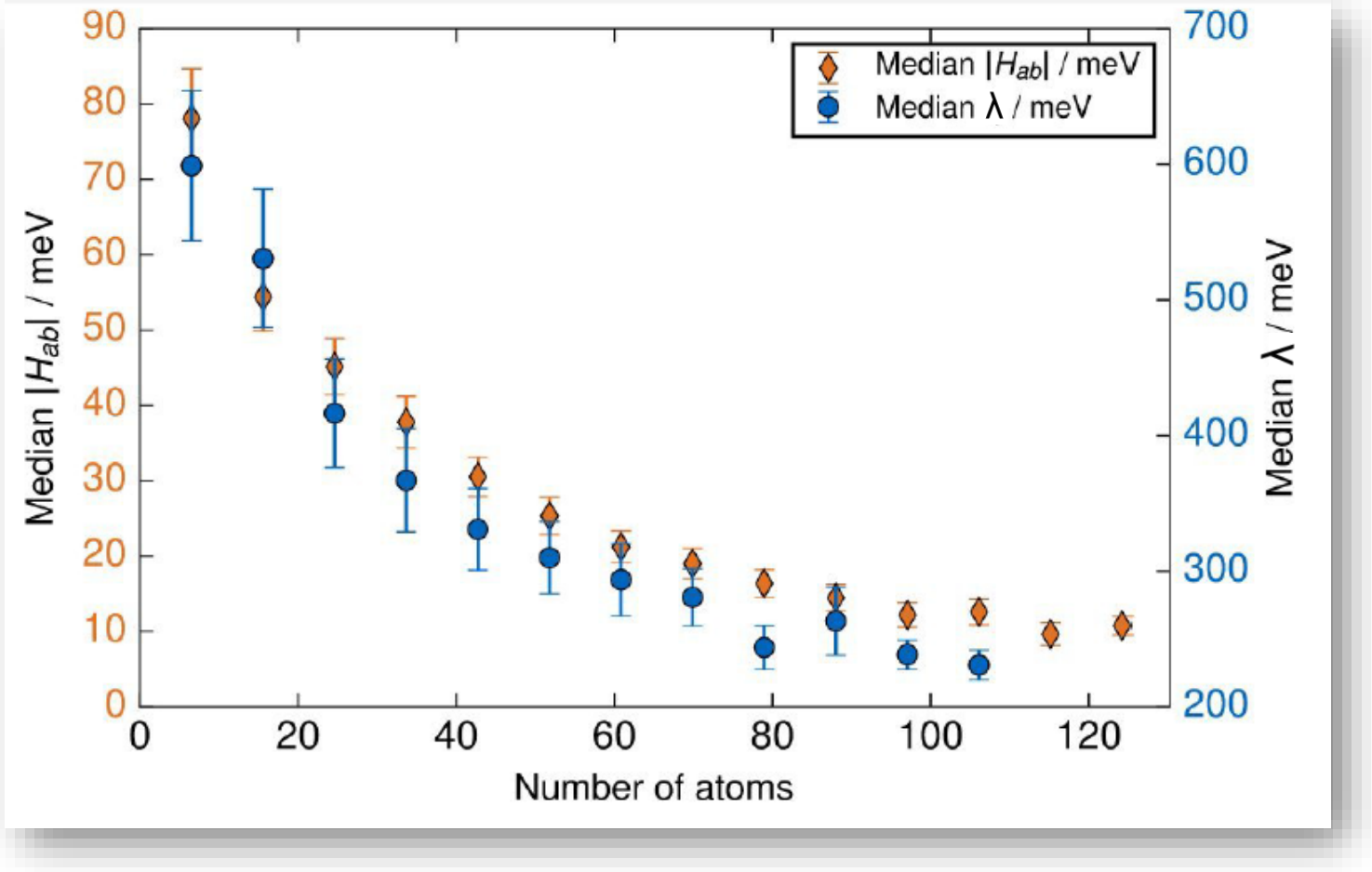


Close distances good for transport?



Particular space groups good for transport?

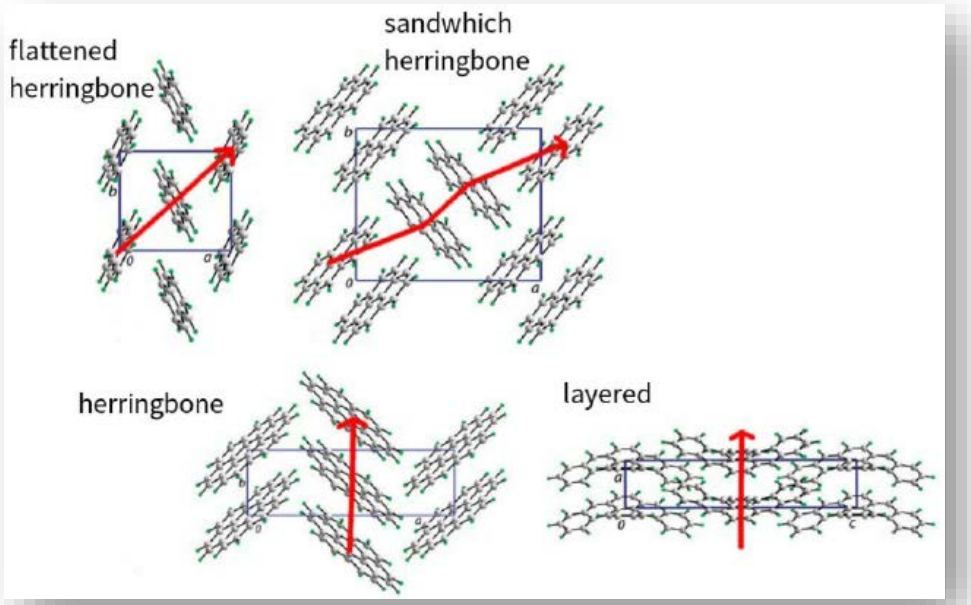
Size effects on H_{ab} and λ_{intra}

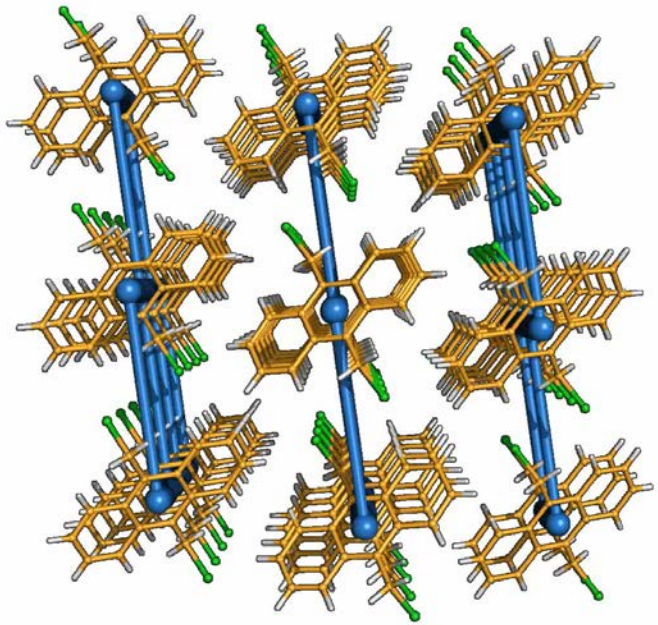


Interesting systems (high H_{ab} / low λ_{intra}) are outliers to this trend

Percolation pathways

Long-range charge percolation pathways are important for good mobility

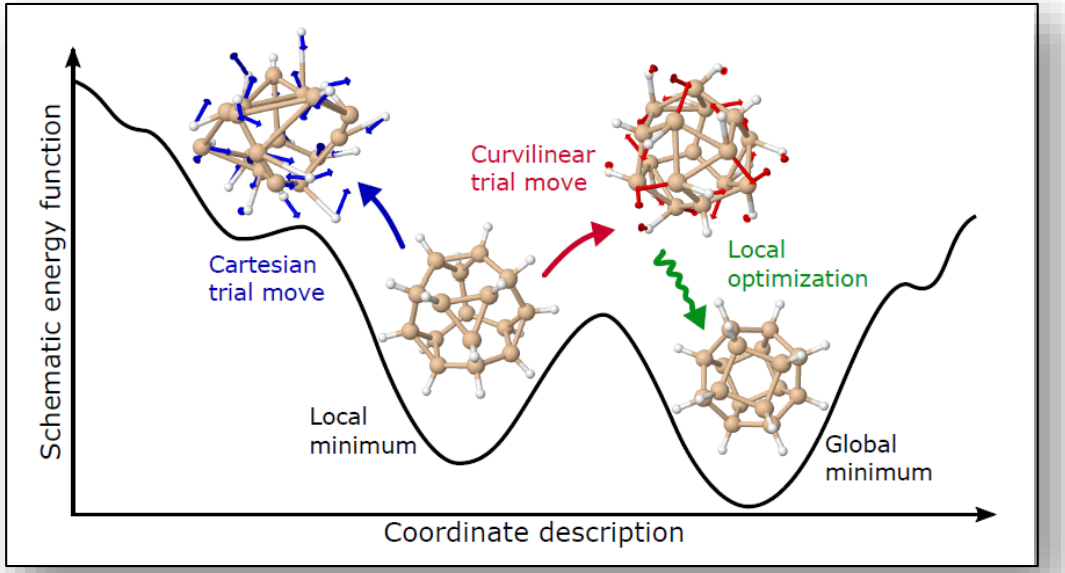


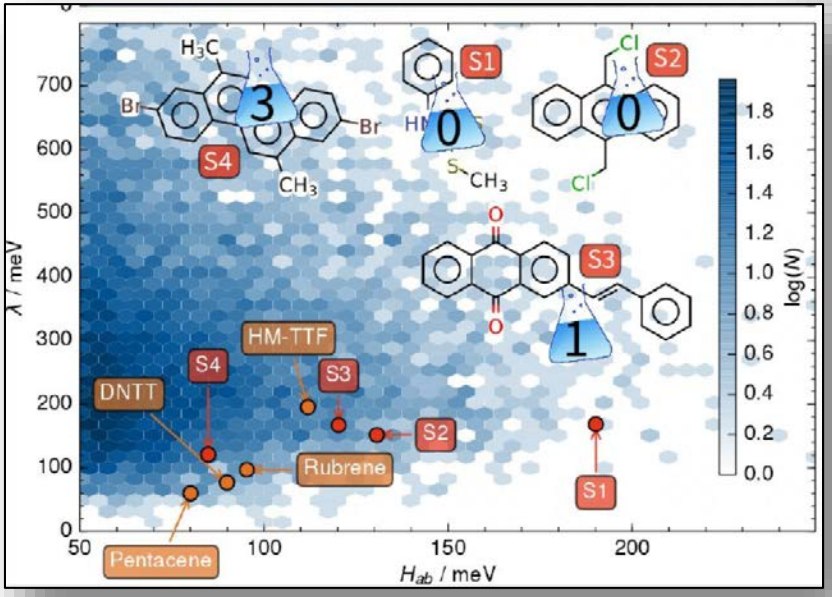


Automatized detection of pathways based on calculated H_{ab} and crystal structure

$$f = f\left(\{\vec{R}_i\},\{Z_i\}\right)$$

Global materials structure search with chemically motivated coordinates





Computational screening for high carrier mobility in organic solar cells

Thanks so much!






Chiara Panosetti

Konstantin Krautgasser

Reinhard Maurer (→ Warwick)

Christoph Schober

Christian Kunkel

Harald Oberhofer

www.th4.ch.tum.de

Alexander von Humboldt Stiftung/Foundation

DFG

Solar Technologies go Hybrid

lrz