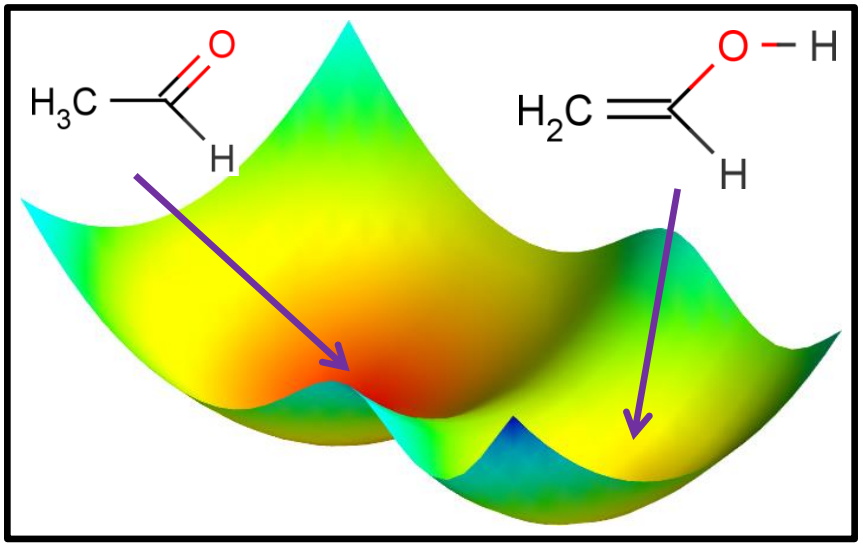
Local Structure Optimization



Structure Determines Property

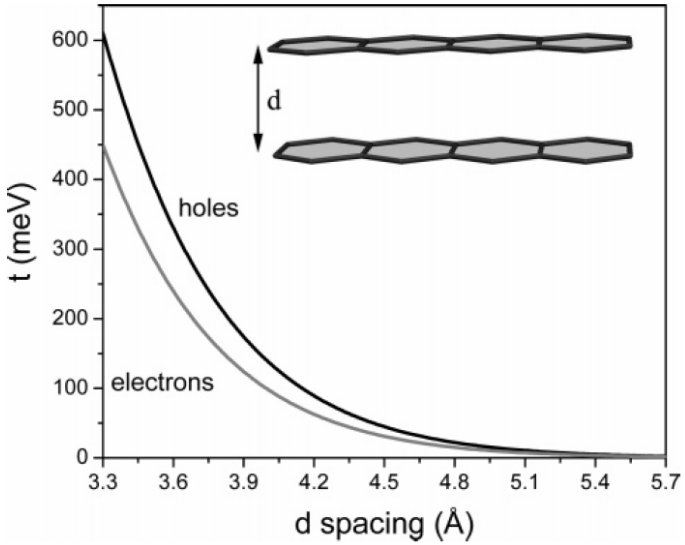
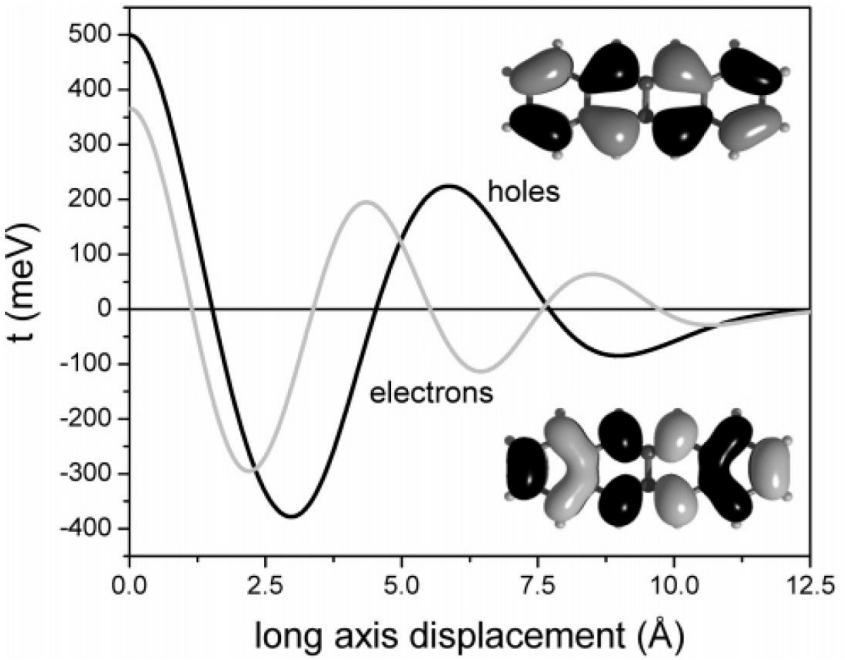


Figure 10. Evolution of the INDO-calculated transfer integrals for electron and hole transfer in a tetracene cofacial dimer, as a function of intermolecular distance.



Example: Even small changes in the geometry have a large impact on band width → carrier mobility!

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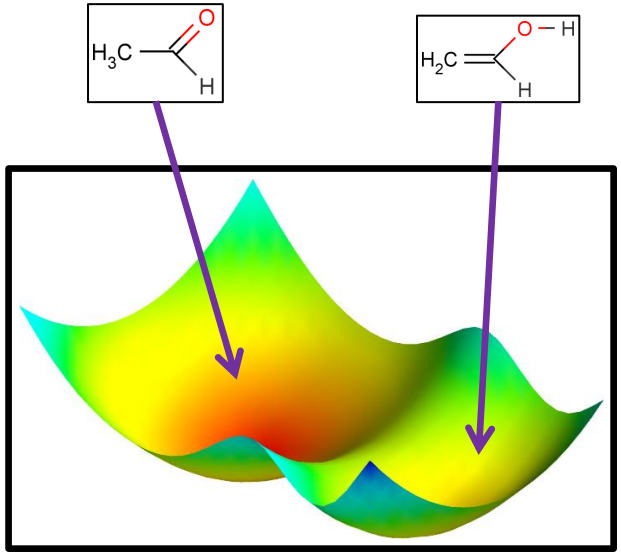
Global Structure Search

Multiple minima in PES

System in equilibrium is given by ensemble average over all minima



Methods to find the global minimum:

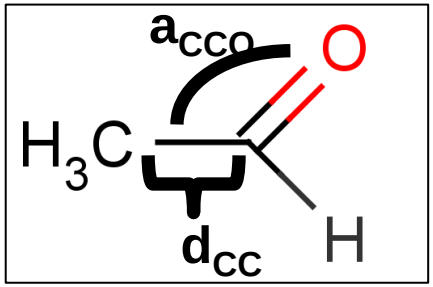
- **(Experiment)**
- **Stochastical or Monte-Carlo**
- **Basin Hopping**
- **Molecular dynamics**
- **Cluster expansion**
- **Genetic algorithm**
- **Diffusion methods**

Separate Lecture

Local Structure

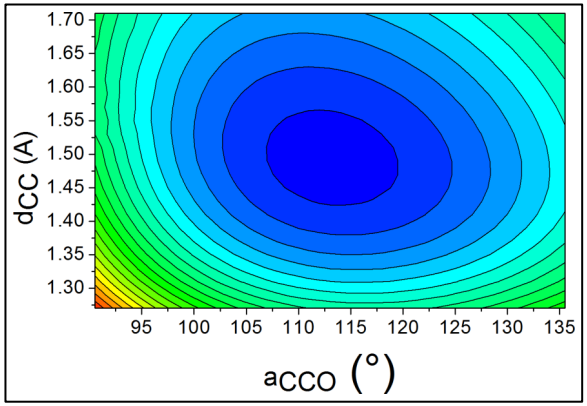
Properties of a material:

- In theory determined by average of geometry
- In practise, the (local) minimum geometry contributes most



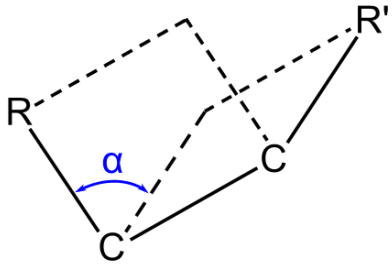
Target:

Find any (preferably: the closest) minimum on the potential energy surface



Different approaches possible:

- Mapping of the whole potential energy surface
- Gradient free methods: e.g,. Simplex method [1]
- Gradient-based methods



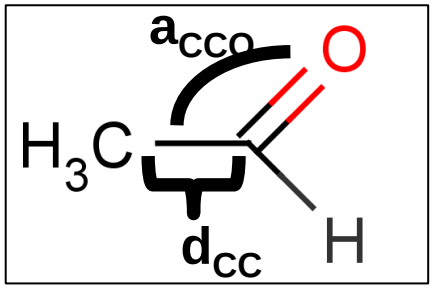
[1]: J. Nelder and R. Mead, Comp J (1965), 308

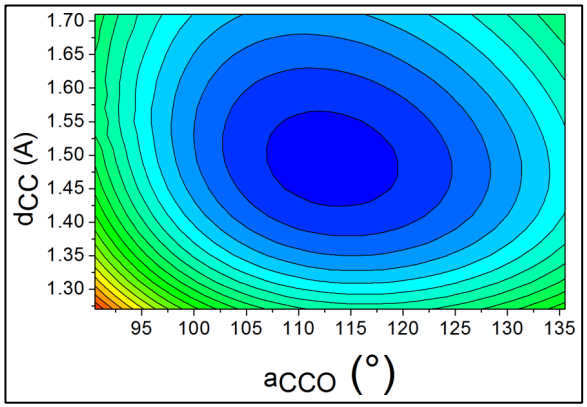
Mapping the potential energy surface

Degrees of freedom (DoF): $3N - 6$

Points per DoF: p

Calculations required: p^{3N-6}





Example: 5 atoms, 10 points: $10^{15-6} = 10^9$

Intractable for anything realistic!

In practice:

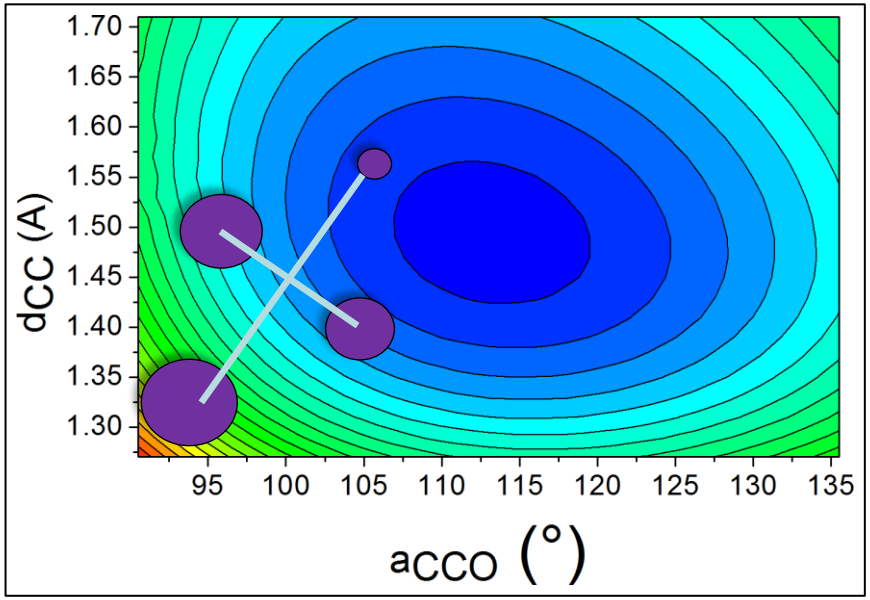
- **Cuts through PES (freeze DoFs)**
- **Parameterized PES**
- **Partial PES (molecular dynamics)**

Full PESs are hardly needed

[1]: J. Nelder and R. Mead, Comp J (1965), 308

Gradient-Free Methods

- Choose *n+1* start points
- Determine best and worst energy
- Remove worst point
- Project new point by reflection
- Expand, contract, compress
- Repeat until self-consistent



In practice:

- Only certain DoFs
- Only when gradients are not available or too expensive (highly correlated methods)
- Rarely used