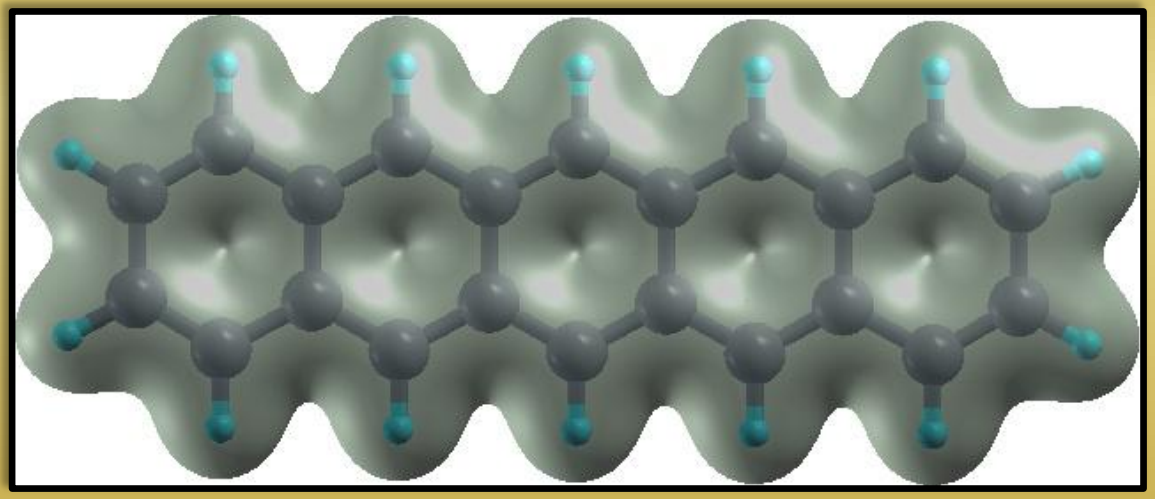
Electronic Structure Theory in Practice



Oliver T. Hofmann,
Trieste, Aug 7th 2013

Solving the Schrödinger equation

$$\hat{\mathrm{H}}\Psi = \mathrm{E}\Psi, \text{ with}$$

$$\Psi = \Psi(\{R_{Nuc}\}, \{r_{elec}, \sigma_{elec}\})$$

$$\hat{\mathrm{H}} = \hat{\mathrm{T}}^{\mathrm{Nuc}} + \hat{\mathrm{V}}^{\mathrm{Nuc-Nuc}} + \hat{\mathrm{T}}^{\mathrm{e}} + \hat{\mathrm{V}}^{\mathrm{Nuc-e}} + \hat{\mathrm{V}}^{\mathrm{e-e}}$$

- **Full many body solution typically not attainable**
- **→ Born-Oppenheimer Approximation**

$$\hat{\mathrm{H}}^{\mathrm{e}}\ \Phi_\nu = E^e_\nu \Phi_\nu, \text{ with}$$

$$\hat{\mathrm{H}}^{\mathrm{e}} = \hat{\mathrm{T}}^{\mathrm{e}} + \hat{\mathrm{V}}^{\mathrm{e-Nuc}} + \hat{\mathrm{V}}^{\mathrm{e-e}}$$

  - **Assumption: electrons are in an eigenstate of H^e**
  - **Separation of nuclear and electronic coordinates**

Outline

- **Solving the electronic part**
  - Self-consistent field method
  - Achieving and accelerating convergence
- **Structure optimization**
  - (Global structure optimization)
  - Local structure optimization
  - Vibrations
- **What can we learn from this?**
  - Visualization

Where are the electrons?

- **All ground state properties related to electron distribution [1]** $\Phi(r_1, r_2, ..., r_N) \Longleftrightarrow n(r)$
  - **Relative energy of conformers, dipole moments, reactivities, etc.**
  - **→ Density functional theory (DFT)**

- **Kohn-Sham scheme [2]**
  - **Map electron density on effective one-particle orbitals**

$$n(r) \Longrightarrow \sum_i f_i |\phi_i|^2$$

[1] P. Hohenberg, W. Kohn, Phys Rev. (1964), B864

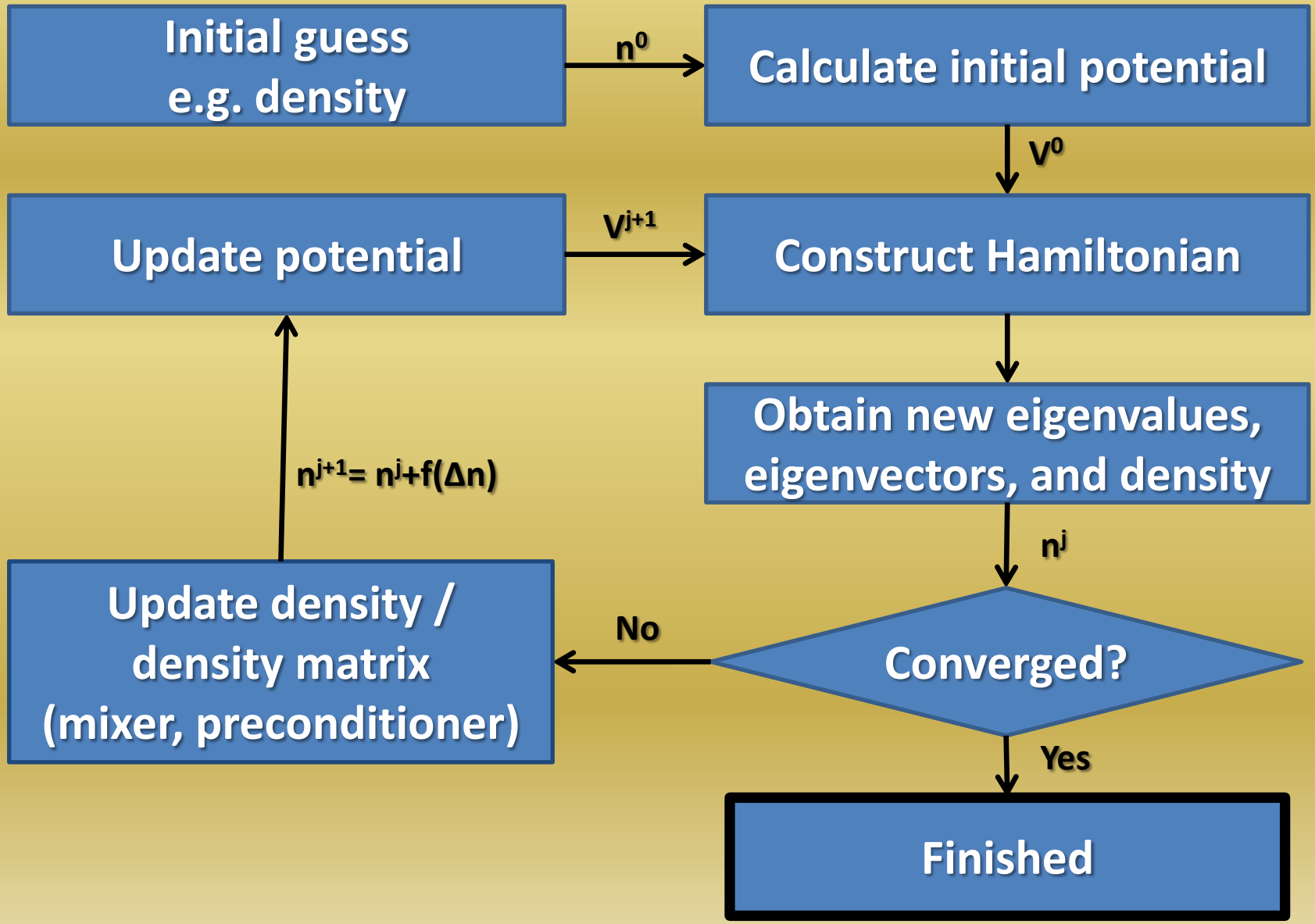
[2]: W. Kohn, L.J. Sham, Phys. Rev. (1965), A1133

Kohn-Sham DFT

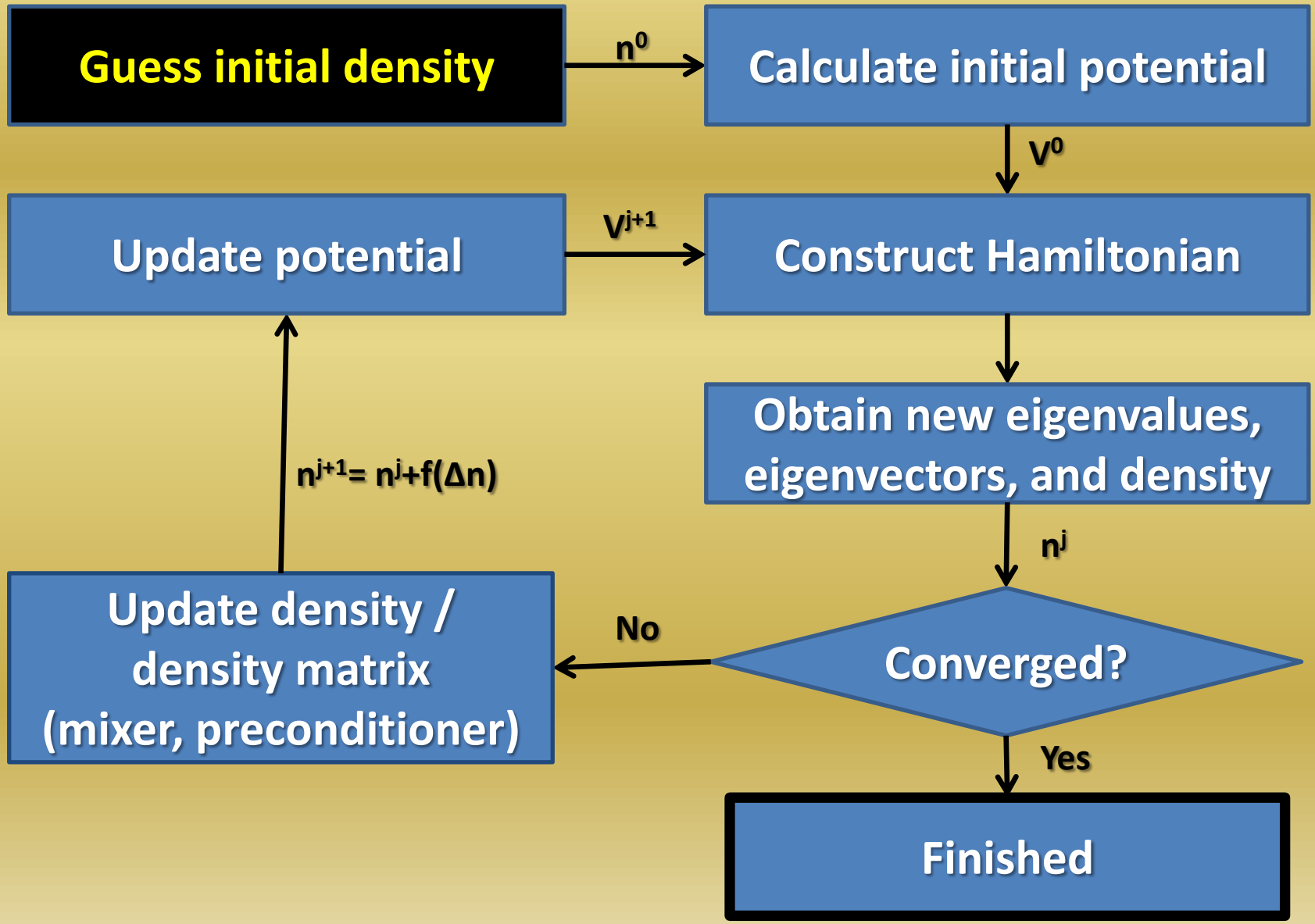
$$\left(\underbrace{\tfrac{1}{2}\nabla^2}_{\hat{T}^e} + \underbrace{\int \frac{n(r')}{|r-r'|}d^3r' + V_{xc} + V_{ext}}_{\hat{V}^{e-e},\ \text{depends on } n=\sum_i |\phi_i|^2}\right)\phi_i = \epsilon_i\phi_i$$

- **We want to determine all Φ_i such that**
  - **E[n] → min**
  - **H is consistent with Φ_i**
- **Approaches**
  - Direct minimization
  - **Self-consistent field method**

Self-consistent field method

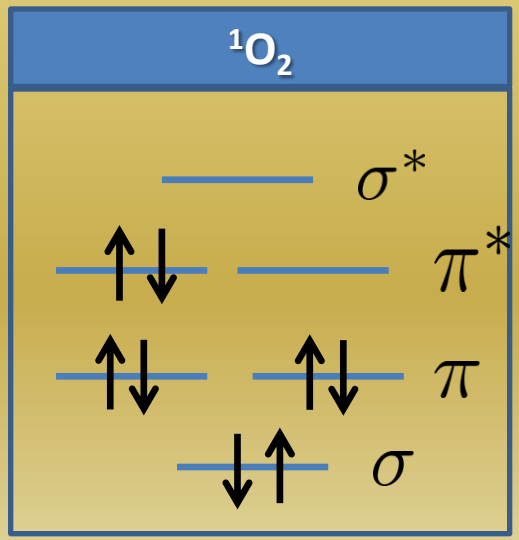


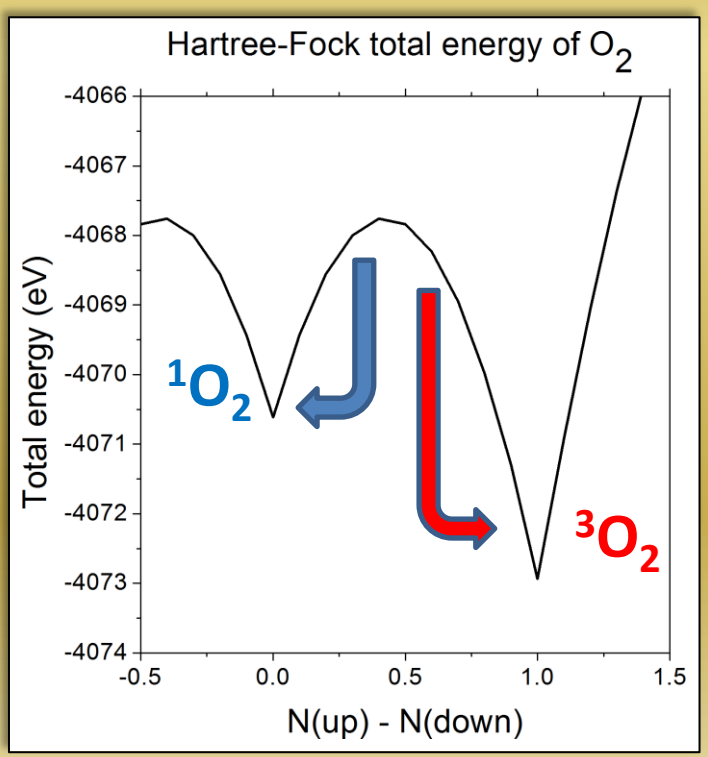
Self-consistent field method

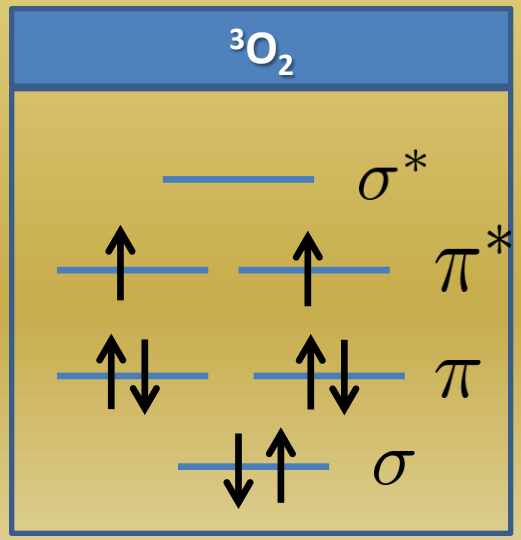


Importance of the initial guess

- Different minima might exist, qualitative changes
- Example: Two different stable spin-states for O_2
- Common issue, e.g., for magnetic solids

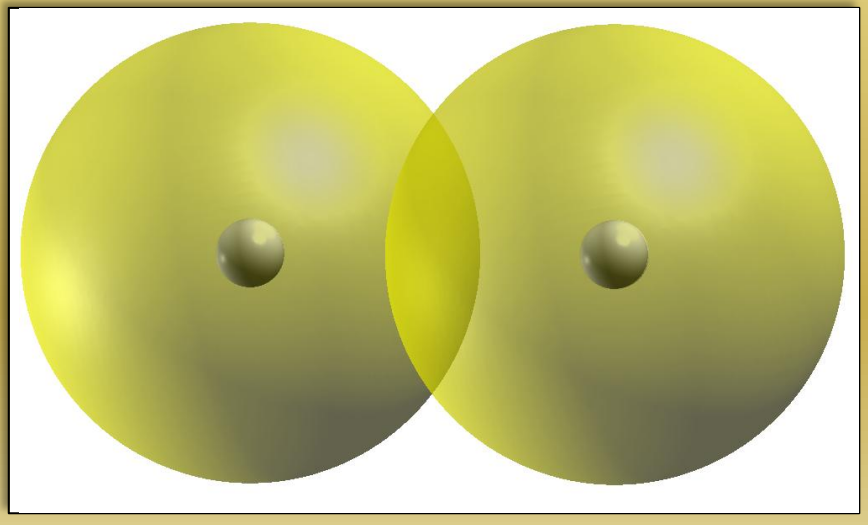






Finding an initial guess

- **Superposition of spheric atomic densities**
  - **Straightforward to implement**
  - **„Mostly sufficent“, but can overemphasize symmetry**
  - **No density matrix / orbitial coefficients**



Finding an initial guess

- **Extended Hückel Theory [1]**
  - **Linear combination of atomic orbtials:** $\phi_i = \sum_j c_{ij}\psi_j$
  - **Hamiltonian:**

$$H_{ii}: \quad \text{parameterized valence ionization energies}$$

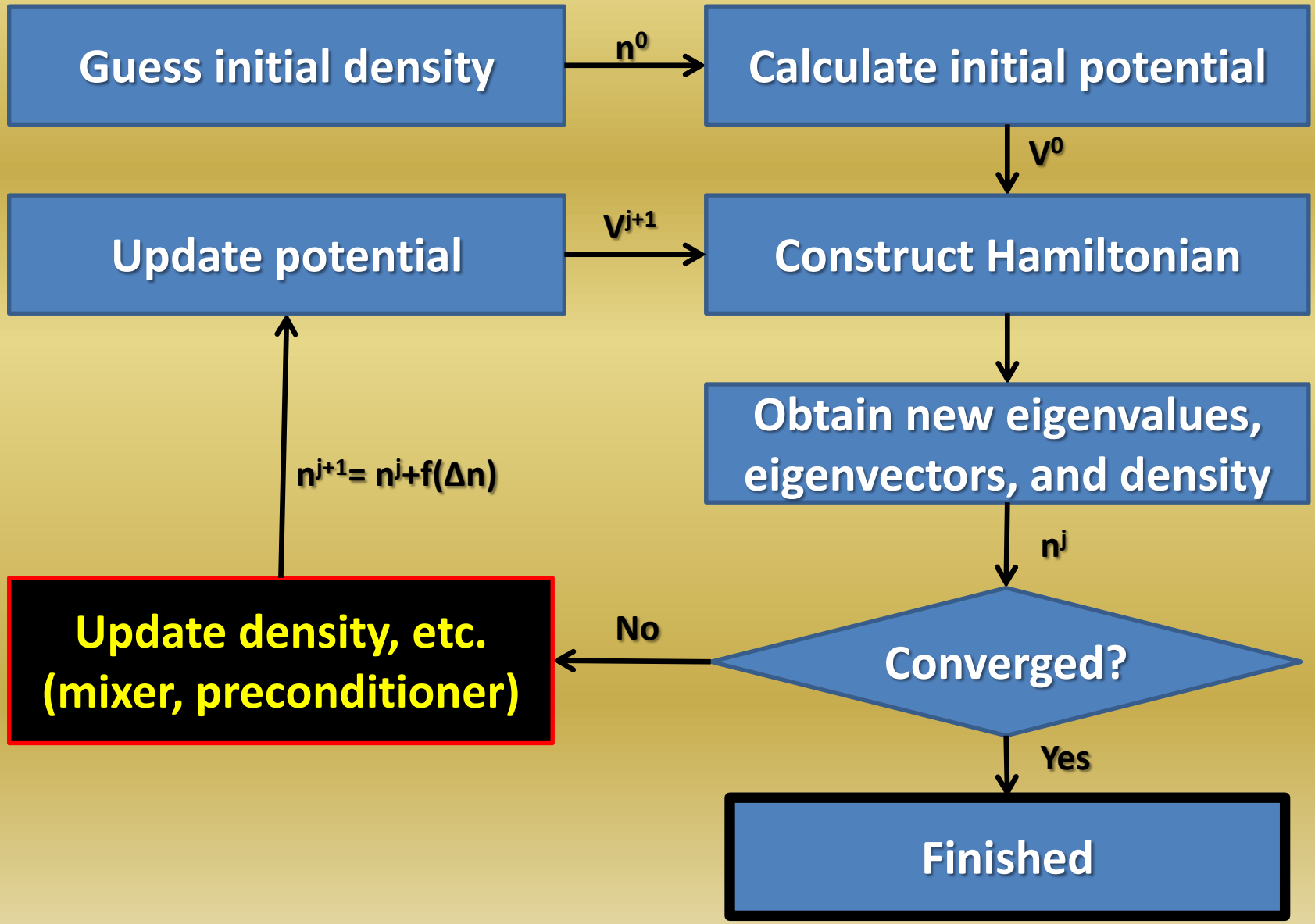
$$H_{ij} = \tfrac{1}{2}KS_{ij}\left(H_{ii} + H_{jj}\right) \text{ [2,3]}$$

  - **Solve set of linear equations:** $\sum_i [H_{ij} - ES_{ij}]c_{ij} = 0$
  - **Improved flexibility, specific orbitals can be populated**

- **Random basis set coefficients**
  - **Backup method**
  - **Usually plane-waves only**

[1] R. Hoffmann, J Chem. Phys (**1963**), 1397
[2] R. S. Mulliken, J. Chem. Phys. (**1946**) 497
[3] M. Wolfsberg and L. Helmholtz, J. Chem. Phys (**1952**), 837

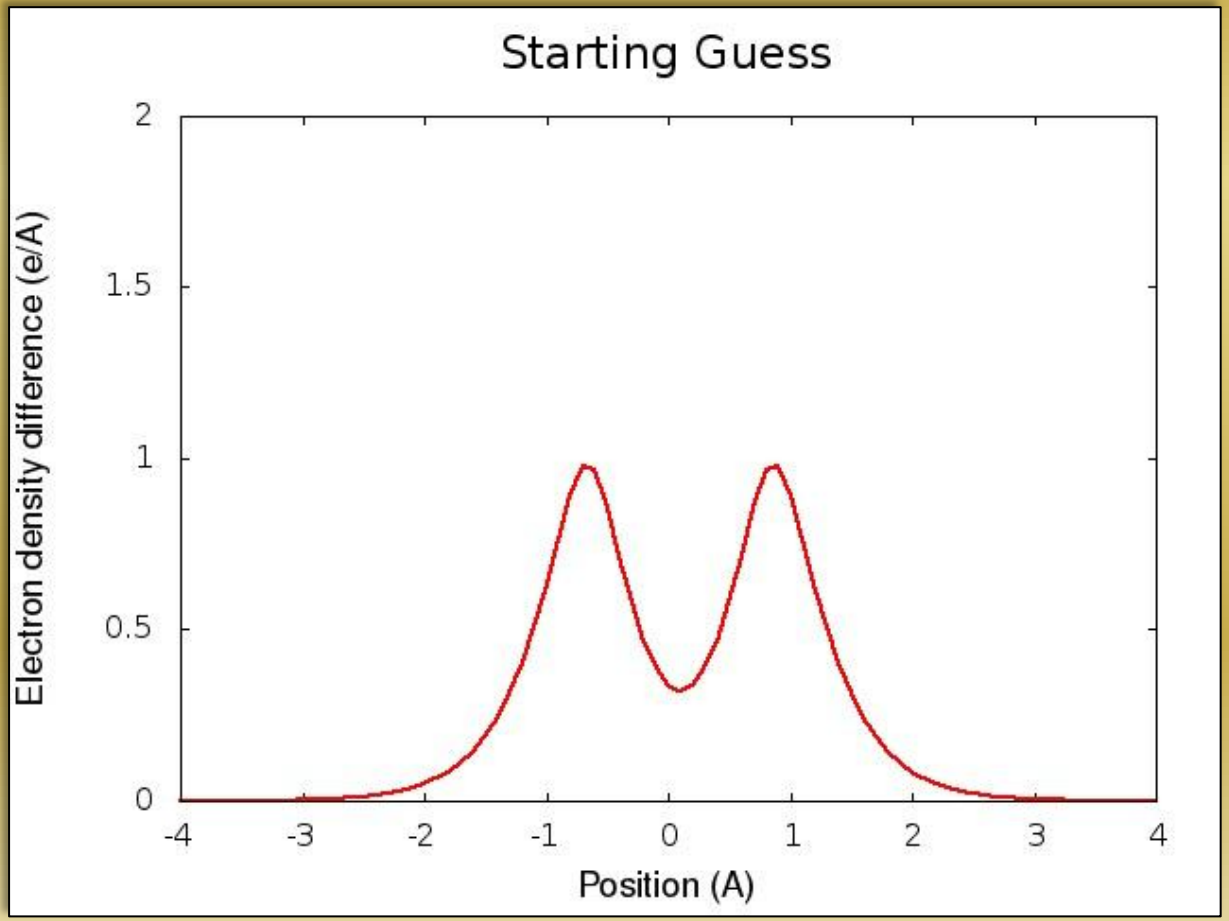
Self-consistent field method



Naive Mixing – Good guess

Naively take the newly calculated density: $n^{j+1} = n^j + \Delta n$

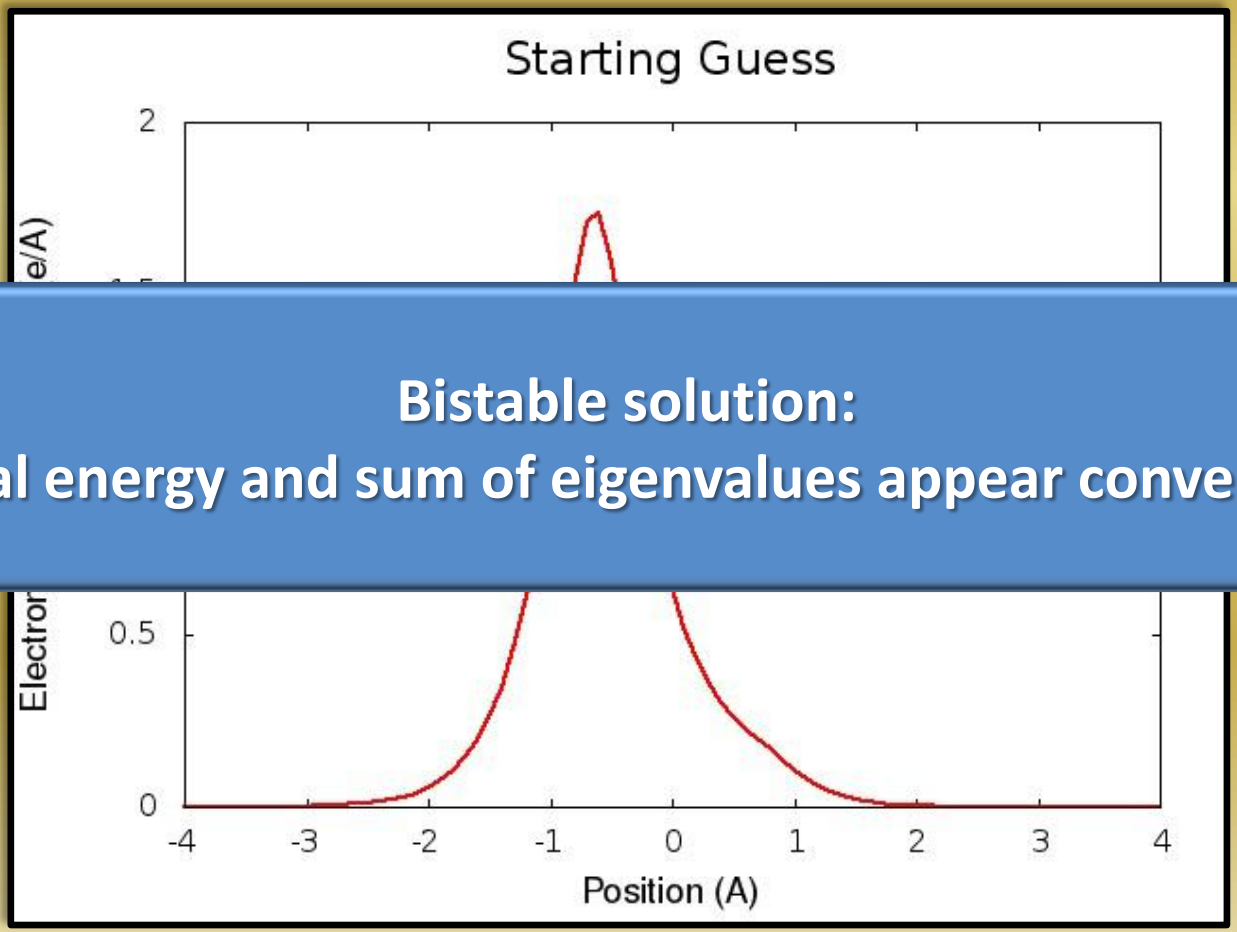
Example: H_2, d=1.5Å, projected in 1 dimension, PBE calculation



Naive Mixing – Bad guess

Naively take the newly calculated density: $n^{j+1} = n^j + \Delta n$

Example: H_2, d=1.5Å, projected in 1 dimension, PBE calculation

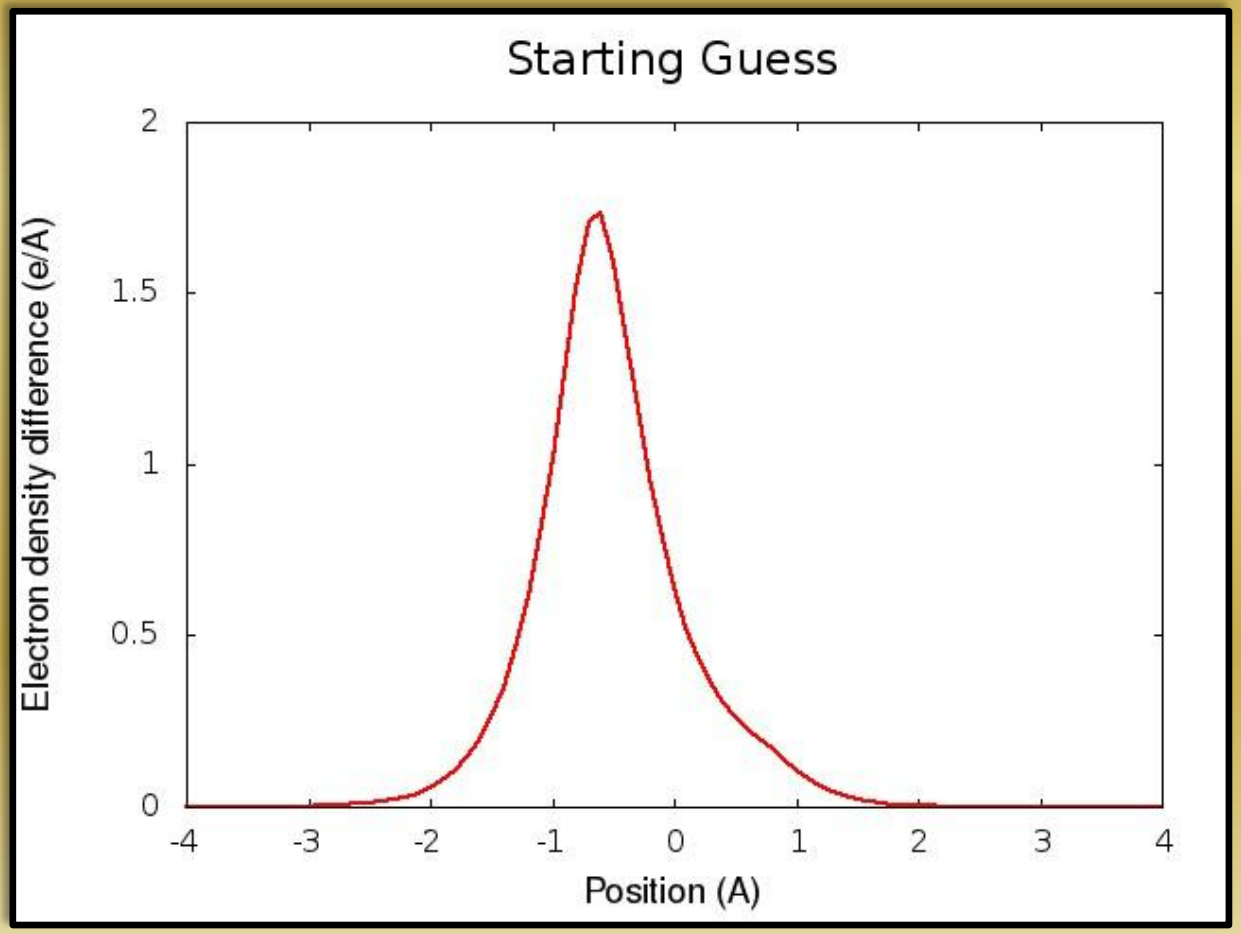


Bistable solution:
Total energy and sum of eigenvalues appear converged

Linear mixing

Damp oscillations by reducing steplength: $n^{j+1} = n^j + \alpha \Delta n$

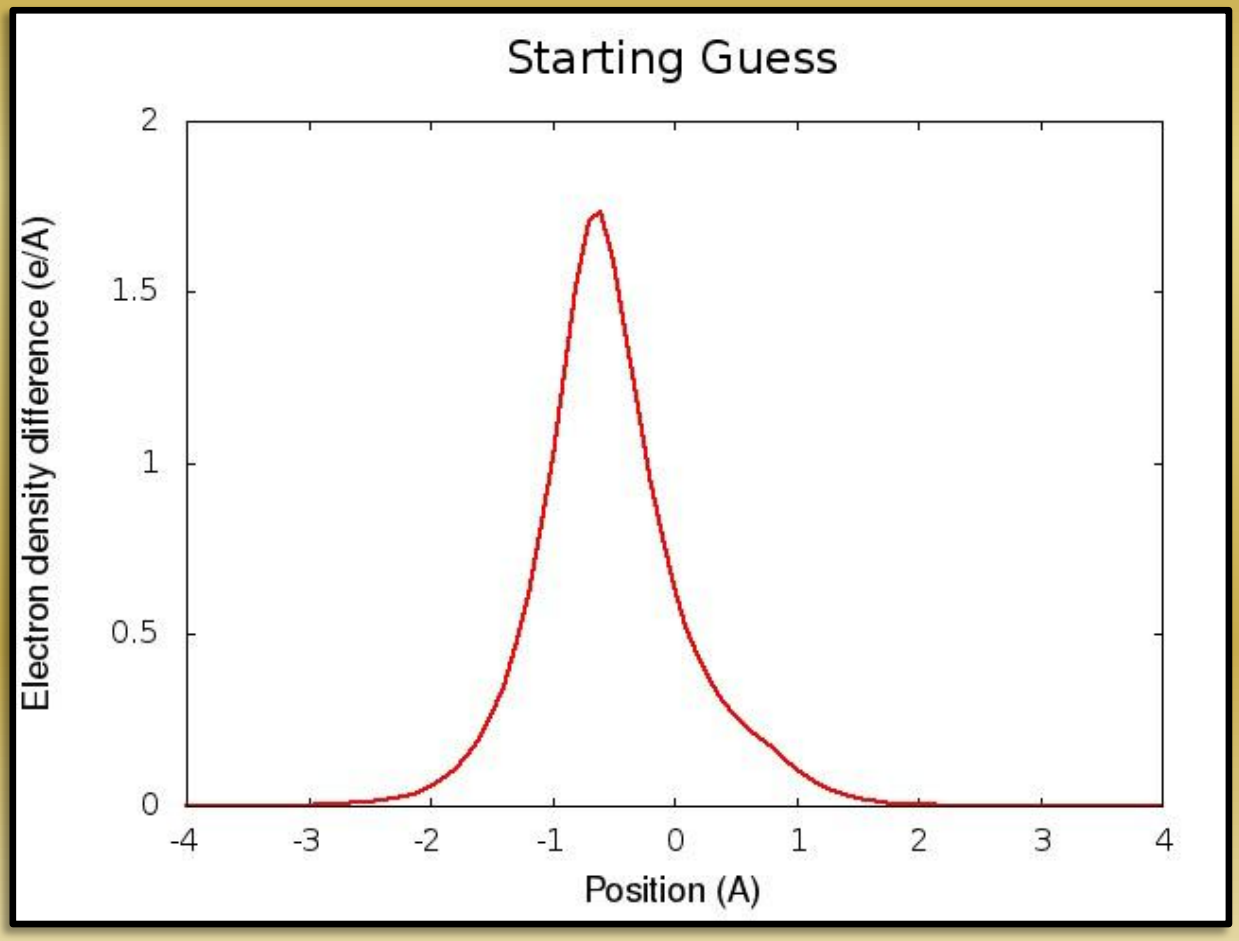
<u>Example:</u> As previous, α=0.3



Linear mixing

Damp oscillations by reducing steplength: $n^{j+1} = n^j + \alpha \Delta n$

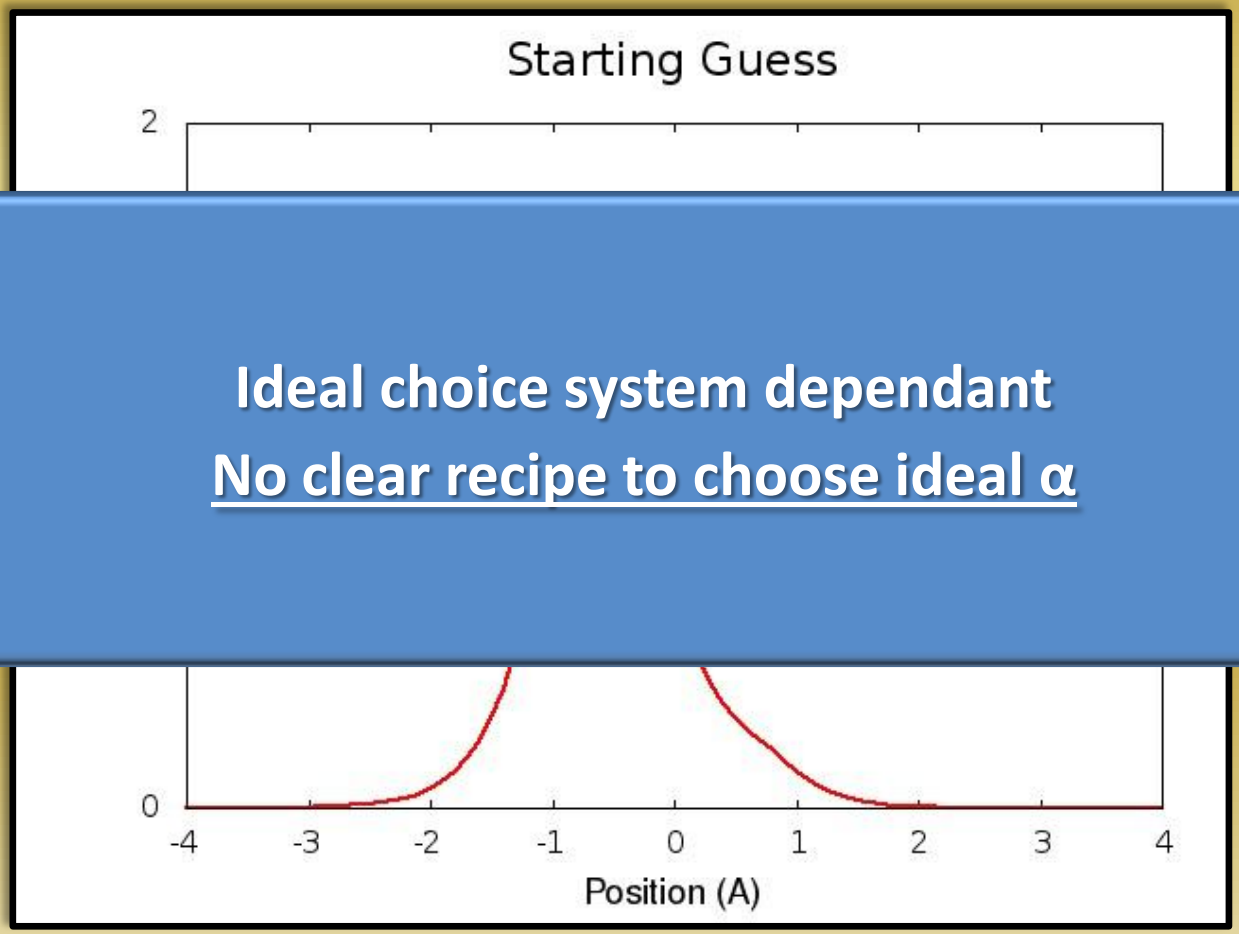
<u>Example:</u> As previous, α=0.8



Linear mixing

Damp oscillations by reducing steplength: $n^{j+1} = n^j + \alpha \Delta n$

<u>Example:</u> As previous, α=0.03



Ideal choice system dependant

<u>No clear recipe to choose ideal α</u>

Pulay mixing [1]

Generate optimized input density: $n^{j+1} = n^{opt} + \alpha R[n^{opt}]$

- **a.k.a. Direct Inversion in Iterative Subspace (DIIS) [1]**
- **Account for previous densities:**

$$n^{opt} = \sum_{\mu=1}^{j} \beta^{(\mu)} n^{(\mu)}, \text{ under the constrain that } \sum \beta = 1$$

- **Assuming linearity of residual ...**

$$R[n^{opt}] = R[\sum_{\mu} \beta^{(\mu)} n^{\mu}] = \sum_{\mu} \beta^{\mu} R[n^{\mu}]$$

- **... the residual is minimized and the new density is constructed**

[1] P. Pulay, Chem. Phys. Lett. 73 , 393 (1980).

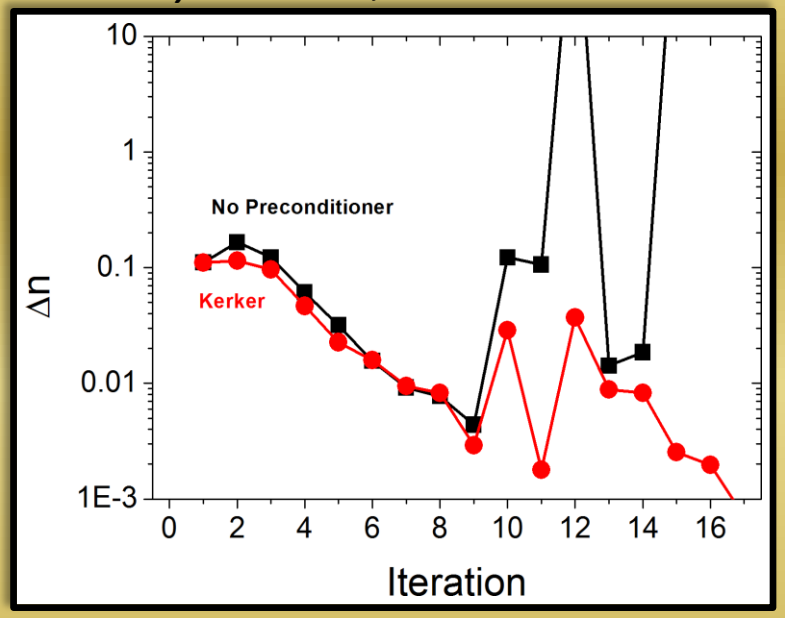
Preconditioning

- **Potential during SCF deviates from correct potential, causes spurious „charge overshooting“**
- **Often pathological for surfaces, slab, thin films, etc.**
- **Solution: Make α depend on Δn(r)** $n^{j+1} = n^j + \hat{G}\Delta n$
  - **Kerker preconditioning [1]:** $\hat{G} = \alpha \frac{\nabla^2}{\nabla^2 + q_0^2}$

[1] G. Kerker, Phys. Rev. B 23 , 3082 (1981).

Preconditioning

8 layer Al slab, PBE calculation



- **Again, no *a priori* known ideal choice for q_0**
- **Reasonable values close to Thomas-Fermi screening constant**

$$q_0 \approx \sqrt{\frac{4k_f}{\pi}}$$

Broadening of states

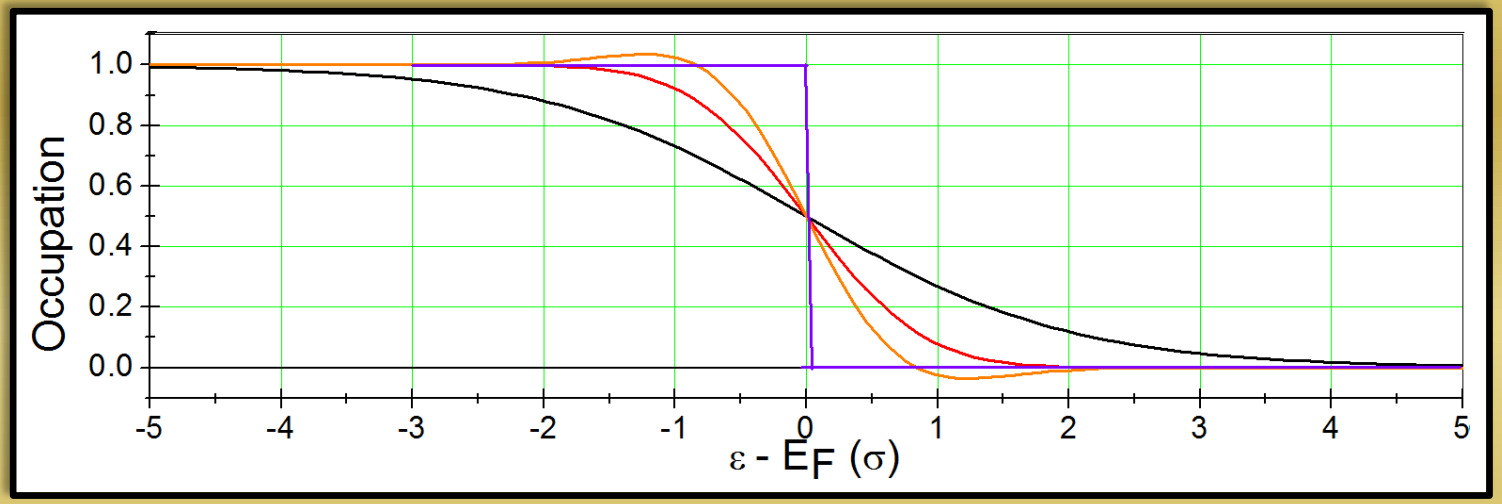
$$n = \sum_i f_i |\phi_i|^2$$

$$f = \Theta(\epsilon - E_F)$$

- **Stepfunction: Discontinuity for bands crossing E_F**
- **Solution: Replace Θ by an approximate, smooth function**

Broadening of states

$$n = \sum_i f(E_F - \epsilon_i)|\Psi_i|^2 \qquad f(x) = \Theta(-x)$$



$$f(x) = \left(exp(\frac{x}{\sigma} + 1)\right)^{-1}$$ **Fermi [1]**

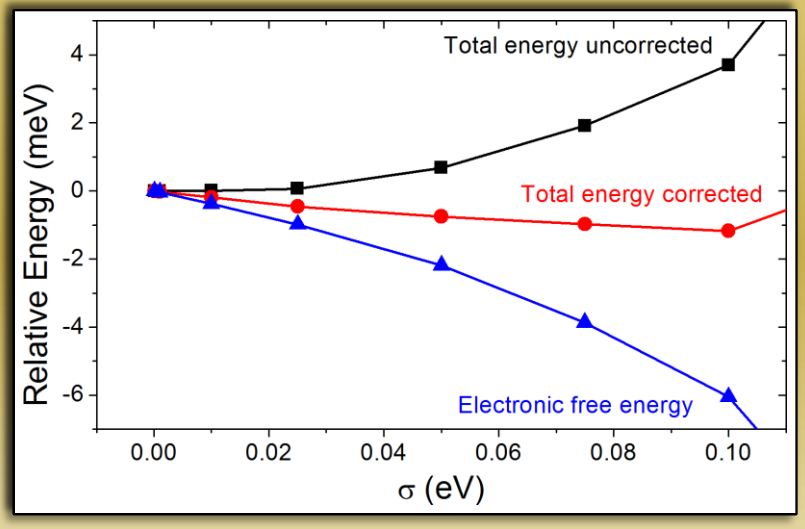
$$f(x) = \frac{1}{2}\mathrm{erfc}\left(\frac{x}{\sigma}\right)$$ **Gaussian [2]**

$$f(x) = \frac{1}{2}\mathrm{erfc}\left(\frac{x}{\sigma}\right) + \sum_m^n A_m H_{2M+1} \times \frac{x}{\sigma}\exp\left(\frac{x}{\sigma}\right)^2$$ **Methfessel-Paxton [3]**

[1] N. Mermin, Phys. Rev.137 , A1441 (1965).
[2] C.-L. Fu, K.-H. Ho, Phys. Rev. B 28 , 5480 (1983).
[3] M. Methfessel, A. Paxton, Phys. Rev. B 40 , 3616 (1989).

Broadening of states

- **Total energy now depends on σ, no longer variational**
- **Optimize free energy:** $\Omega = E_{tot} - \sigma S(\sigma)$
- **Backextrapolation to σ → 0**
- ***S* similar for different situations (absorption)**

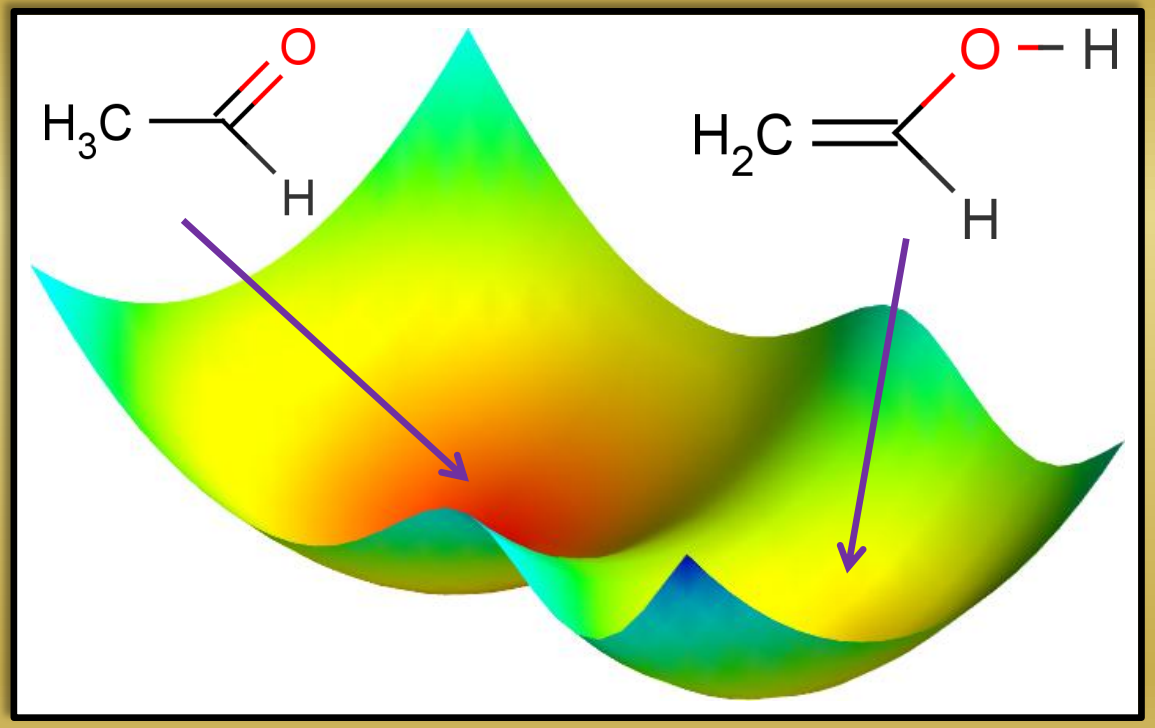


Cu (111)
- 5 layer slab
- Gaussian smearing
- PBE calculation
- 12x12x1 k-points

Summary SCF

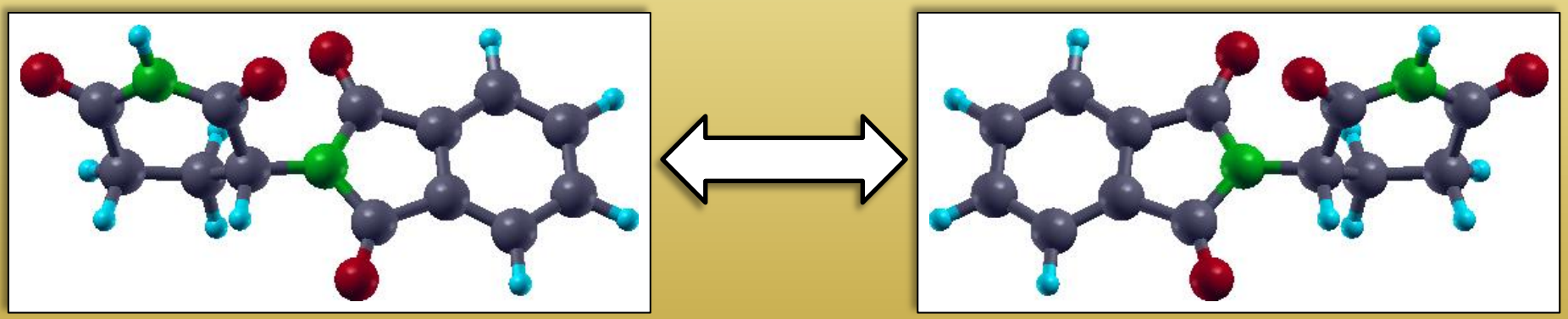
- **Ground state electron density determined iteratively**
- **Initial guess needs initial thought, can change results qualiatively**
- **Density update by**
  - Linear mixing (slow)
  - Pulay mixing
- **Convergence acceleration by**
  - Preconditioner
  - Broadening of states

Structure optimization



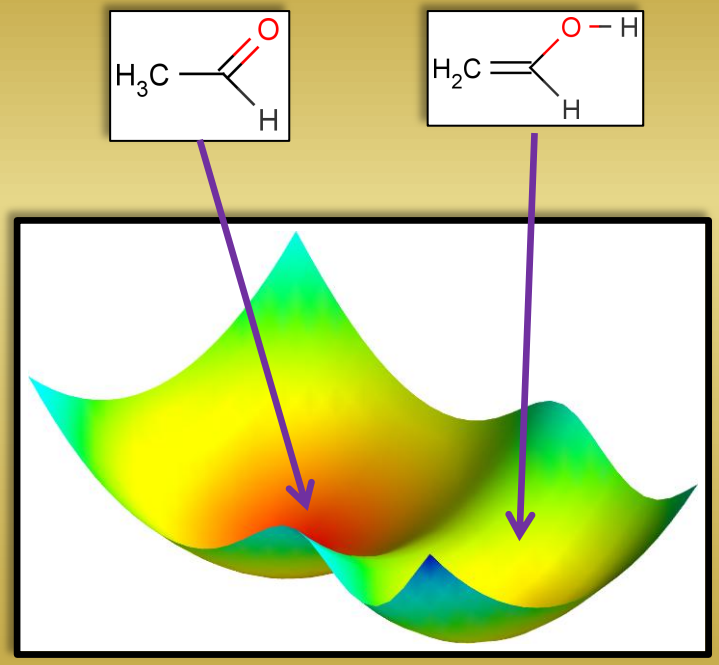
Structure optimization

- Most electronic properties sensitive to geometry
- „Geometry determines function“



Global structure search

- Born-Oppenheimer energy surface can contain several minima
  - Constitution isomery
  - Configuration isomery
  - Conformation isomery
- System in equilibrium is given by ensemble average over all minima
- Often dominated by global minimum (but watch out for tautomers)



Global structure search

- **Methods to find the global minimum:**

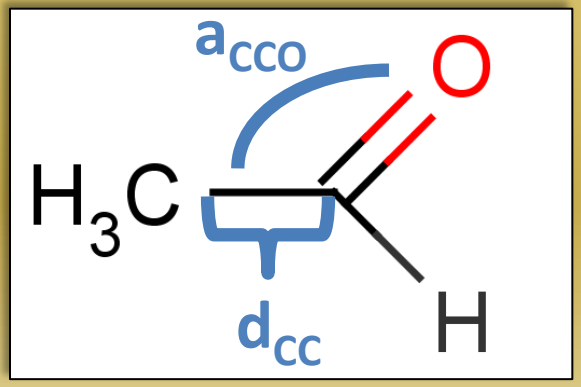
- **Stochastical or Monte-Carlo**
- **Molecular dynamics: Simulated annealing [1,2]**
- **Genetic algorithm [3]**
- **Diffusion methods [4]**
- **Experimental structure determination**

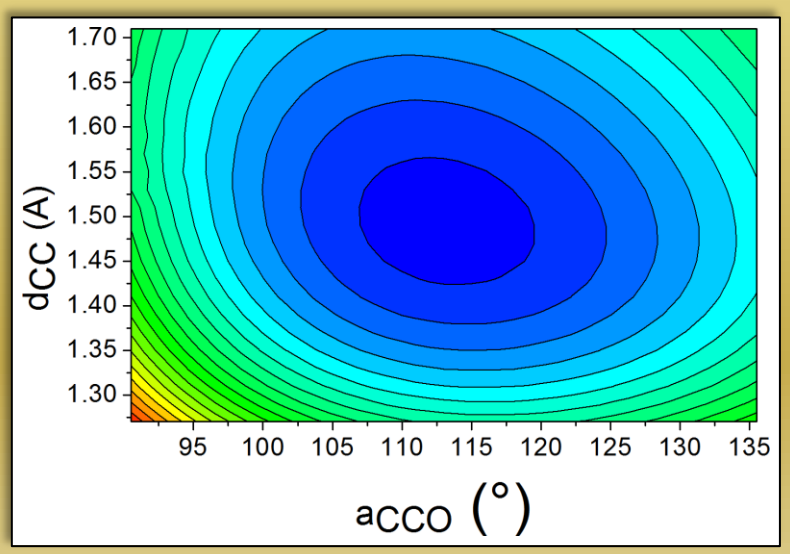
*[1]: S. Kirkpatrick, et al., Science, (**1983**), 671*
*[2]: S.R. Wilson and W. Cui, Biopolymers (**1990**), 225*
*[3]: R.S. Judson, Rev. Comput Chem., (**1997**), 1*
*[4] J. Konstrowicki, H. A. Scheraga, J Phys. Chem. (**1992**), 7442*

Local structure optimization

- **Once we have an reasonable guess, find closest minimum**

- **Different approaches possible:**
  - **Mapping of the potential energy surface**
    - **Requires a lot of calculations**
    - **Typically only for dynamics**

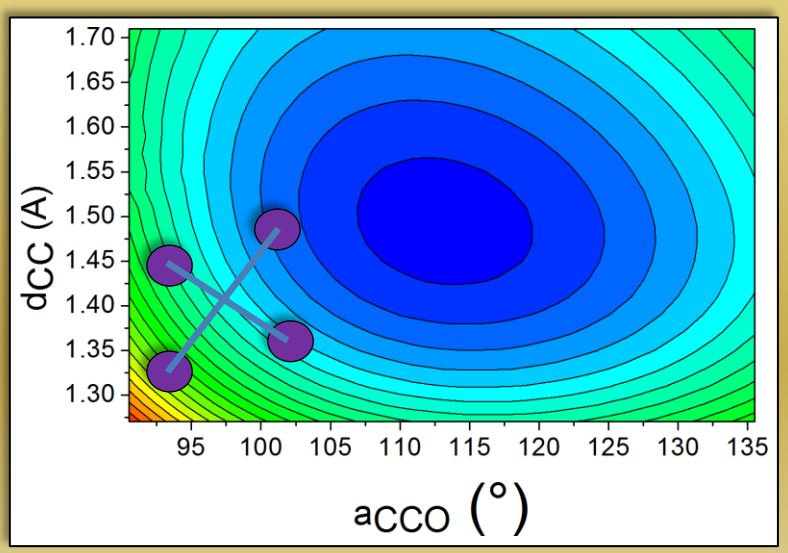




Local stucture optimization

- **Once we have an reasonable guess, find closest minimum**

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



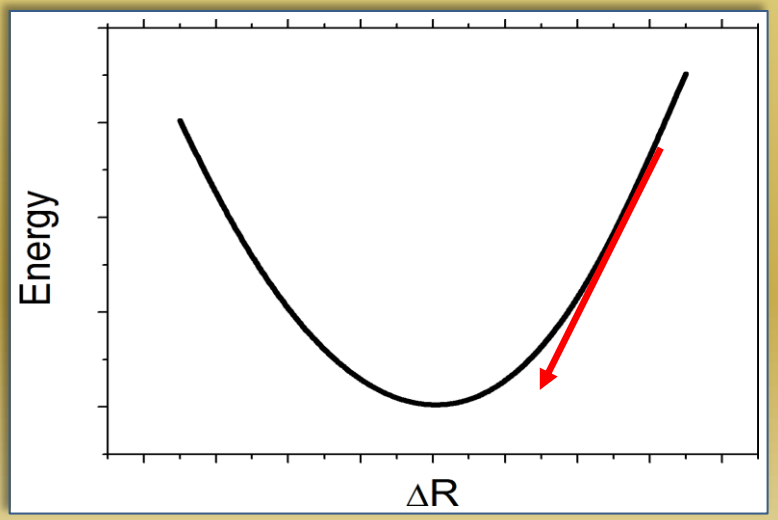
[1]: J. Nelder and R. Mead, Comp J (1965), 308

Local structure optimization

- **Once we have an reasonable guess, find closest minimum**

- **Different approaches possible:**
  - **Mapping of the whole potential energy surface**
  - **Gradient free method: e.g., simplex**
  - **Gradient-based methods**
    - **Calculate gradient (a.k.a. „forces“)**

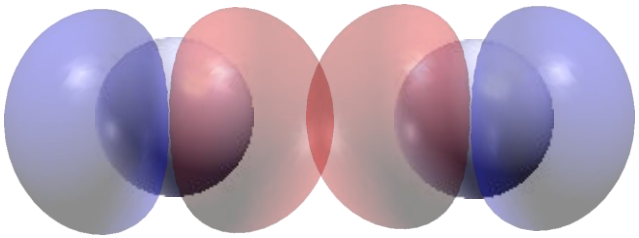
$$F = \frac{\delta E}{\delta R}$$



Total energy gradient

- **Search for minimum by following the gradient**

$$\frac{\delta E}{\delta R} = \langle \Psi_0 | \frac{\delta \hat{H}}{\delta R} | \Psi_0 \rangle + \langle \frac{\delta \Psi_0}{\delta R} | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 \rangle | \hat{H} | \frac{\delta \Psi_0}{\delta R} \rangle$$



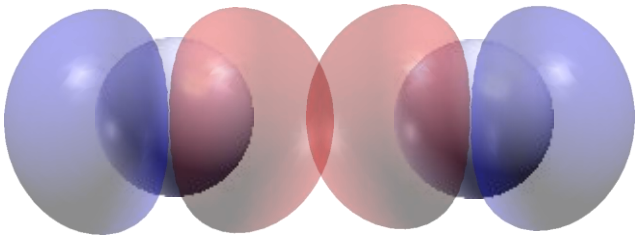
Total energy gradient

- **Search for minimum by following the gradient**

$$\frac{\delta E}{\delta R} = \langle \Psi_0 | \frac{\delta \hat{H}}{\delta R} | \Psi_0 \rangle + \langle \frac{\delta \Psi_0}{\delta R} | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | \hat{H} | \frac{\delta \Psi_0}{\delta R} \rangle$$

- **affects only $V^{nuc\text{-}nuc}$ and $V^{e\text{-}nuc}$**

$$F_i^{Hellman-Feynman} = Z_i \sum_j \nabla R_i \frac{Z_j}{|R_i - R_j|} + \int d^3r \; n(r) \nabla R_i \frac{Z_i}{|R_i - r|}$$



Total energy gradient

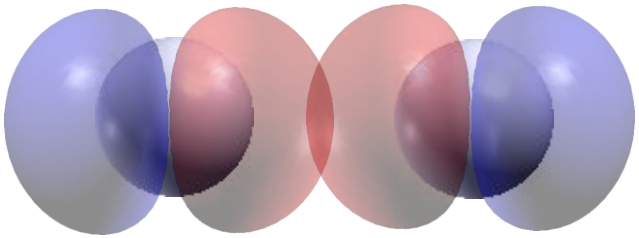
- **Search for minimum by following the gradient**

$$\frac{\delta E}{\delta R} = \langle \Psi_0 | \frac{\delta \hat{H}}{\delta R} | \Psi_0 \rangle + \langle \frac{\delta \Psi_0}{\delta R} | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 \rangle | \hat{H} | \frac{\delta \Psi_0}{\delta R} \rangle$$

$$\frac{\delta \Psi_0}{\delta R} = \frac{\delta \Psi_0}{\delta c} \frac{\delta c}{\delta R} + \frac{\delta \Psi_0}{\delta \phi} \frac{\delta \phi}{\delta R}$$

$$F^{Pulay} = -2 \sum_{i\sigma} \langle \frac{\delta \phi_{i\sigma}}{\delta R} | \hat{h} - \epsilon_{i\sigma} | \phi_{i\sigma} \rangle$$

- **First term vanishes**
- **Second term survives for atom-centered basis functions**



Total energy gradient

- **Search for minimum by following the gradient**

$$\frac{\delta E}{\delta R} = \langle \Psi_0 | \frac{\delta \hat{H}}{\delta R} | \Psi_0 \rangle + \langle \frac{\delta \Psi_0}{\delta R} | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 \rangle | \hat{H} | \frac{\delta \Psi_0}{\delta R} \rangle$$

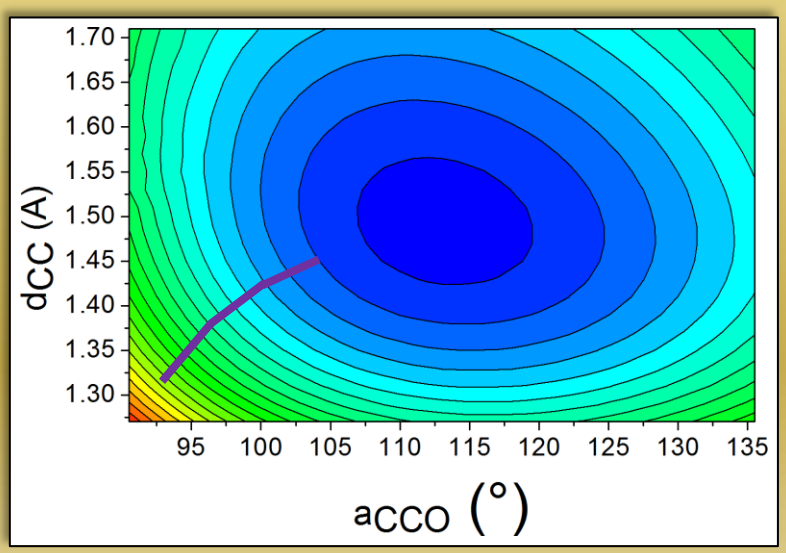
- **Additional contributions from atom-centered approximations**
  - **Multipole expansion**
  - **Relativistic corrections**
  - **(Integration grids)**
- **All straightforward but lengthy**

Geometry update – Steepest descent

- **Follow negative gradient to find minimum**

$$R^{n+1} = R^n - \alpha F(R^n)$$

- **Steplength α variable**
- **Guaranteed but slow convergence**
- **Oscillates near minimum**
- **Not suitable for saddle points**
- **Improved versions exists**
  - **Conjugated gradient [1]**



[1] M. Hestenes, E. Stiefel (1952). "Methods of Conjugate Gradients for Solving Linear Systems"

(Quasi)Newton methods

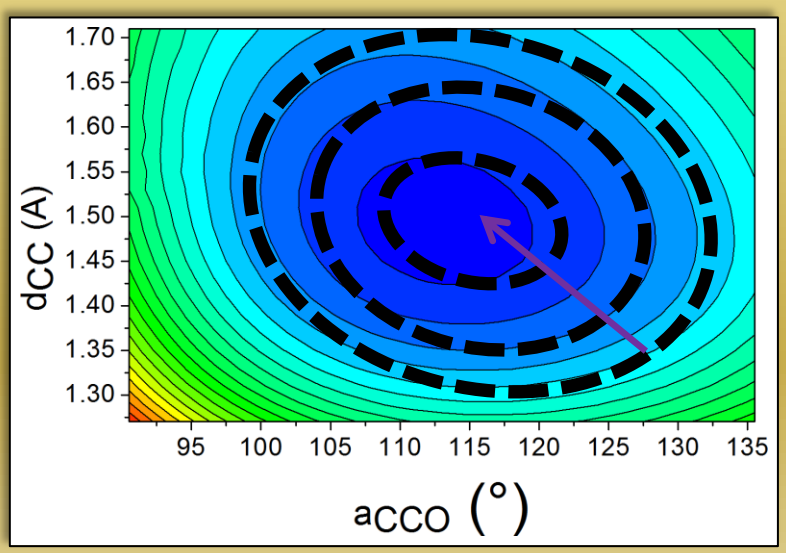
- **Approximate PES by quadratic function**

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

H … Hessian

- **Find minimum:** $\Delta R = H^{-1}F$
  - **Newton: calculate exact *H***
  - **Quasi-Newton: approximate *H***
    - **Update as search progresses [1]**

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



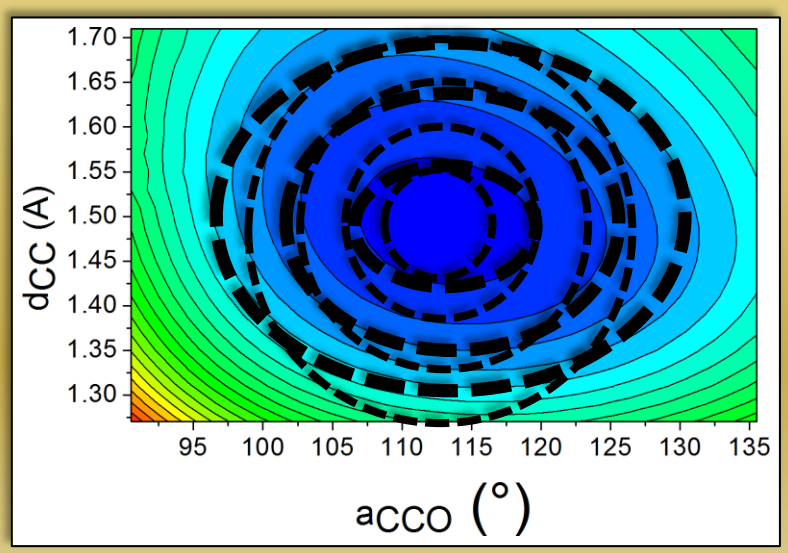
[1] J. Nocedal and S. J. Wright, "Numerical optimization" (Springer, 2006)

(Quasi)Newton methods

- **Initial Hessian critical for performance**
- **Naive choice: Scaled unit matrix** $\tilde{H} = \beta \bar{1}$
- **Improved version: Apply „penalties“ on different kind of coordinates**

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

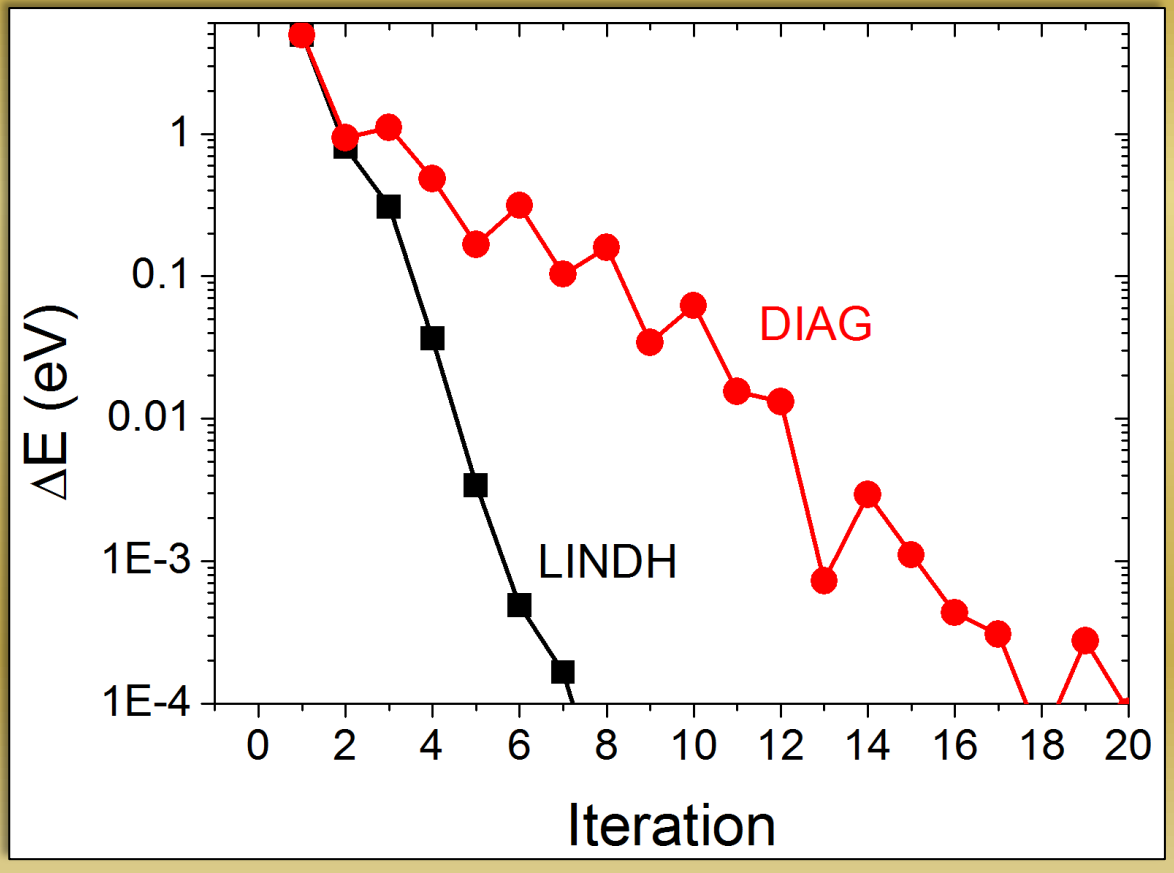
  - ***k* parameterized [1]**

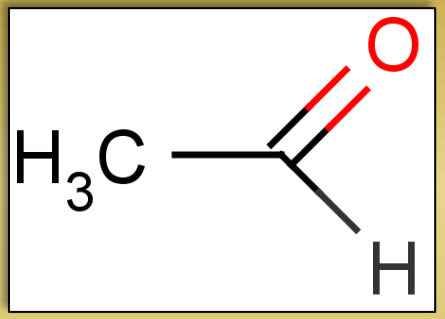


[1] R. Lindh et al. , Chem. Phys. Lett. 241 , 423 (1995).

Effect of the Initial Hessian

Proper initialization leads to significant speed-up





(Quasi)Newton methods

- **Soft degrees of freedom can cause large ΔR**

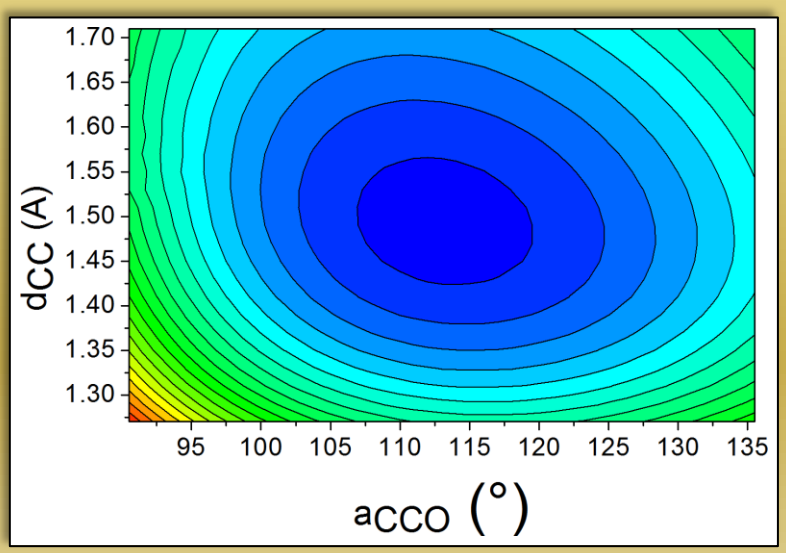
- **Step control needed:** $\Delta R = \alpha\, H^{-1} F$
  - **Line search method: If new point is worse than old, interpolate**

    $E(\alpha) = E(R + \alpha \Delta R)$

  - **Trust radius method**
    - **Enforce upper limit for ΔR**
    - **Evaluate quality of quadratic model**

      $$q = \frac{E_{true}}{E_{expected}}$$

    - **Adjust ΔR_{max} based on q**

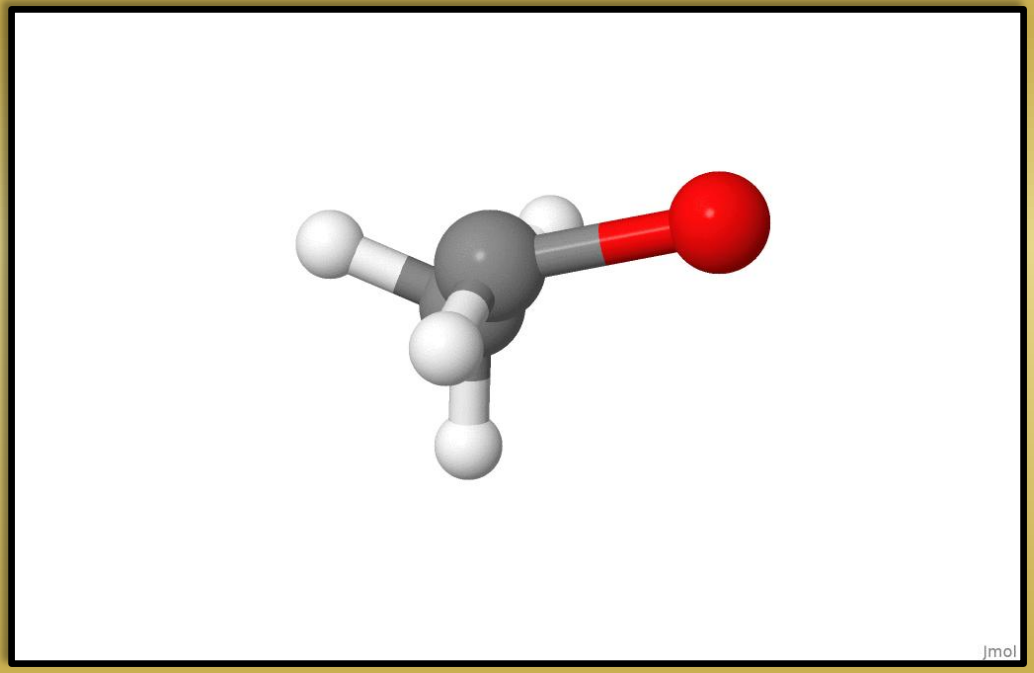


[1] R. Lindh et al. , Chem. Phys. Lett. 241 , 423 (1995).

Conclusions

- **(Global optimization: PES feature-rich, methods to find global minima exist)**
- **Local geometry optimization: Follow gradient**
  - **Hellman-Feynman from moving potentials**
  - **Pulay from moving basis functions**
  - **+ additional terms**
- **Quasi-Newton method *de-facto* standard**
  - **Require approximation and update of Hessian**
  - **Step control by line search or trust radius method**

Vibrations



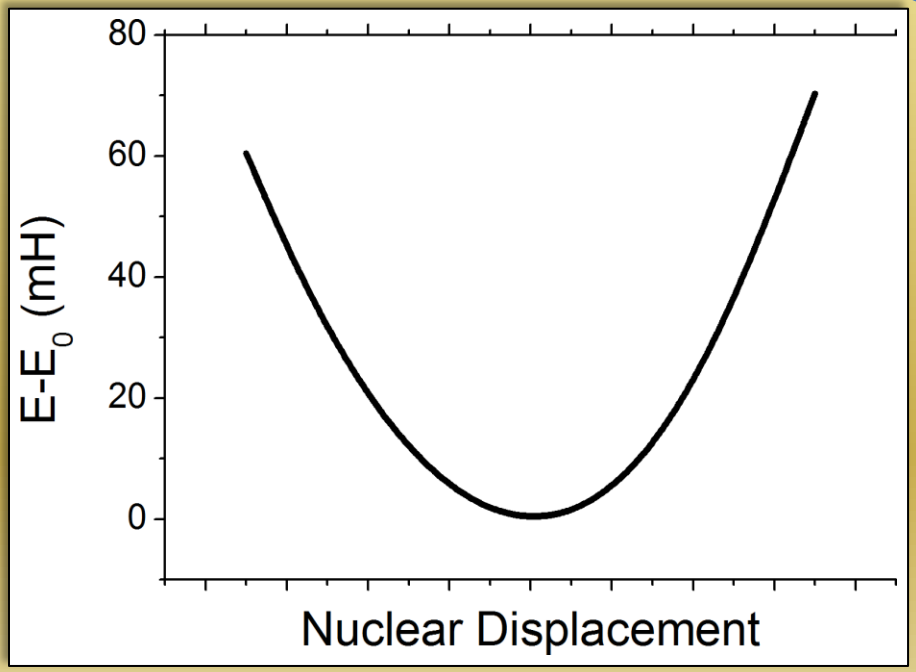
Vibrations

- **Vibrations give important information about the system:**
  - **Classification of stationary point (minimum / saddle point)**
  - **If saddle-point: Provides search direction**
  - **Thermodynamic data**
    - **Zero-point energy**
    - **Partion sum**
    - **Finite temperature effects**
  - **Connection to experiment:**
    - **Infra-red intensities: derivative of dipole moment**
    - **Raman intensities: derivative of polarizabilty**

Vibrations

- **Expand Energy in Taylor series:**

$$E(R) \approx E(R_0) + \sum_i \frac{\delta E}{\delta R_i} \Delta R_i + \sum_i \sum_j \frac{\delta^2 E}{\delta R_i \delta R_j} \Delta R_i \Delta R_j + \ldots$$



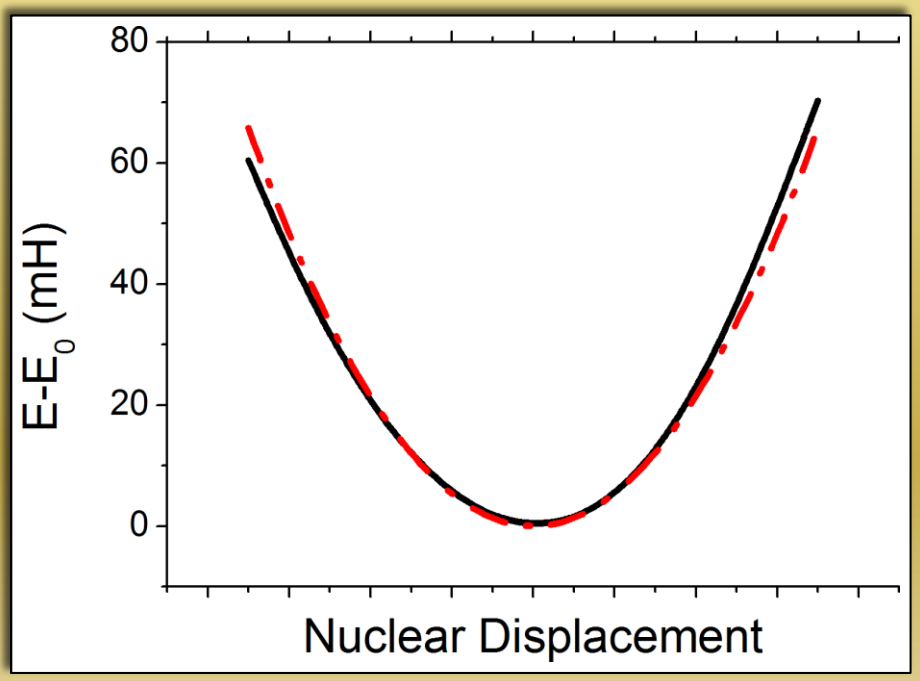
Vanishes for R_0

Vibrations

- **Expand Energy in Taylor series:**

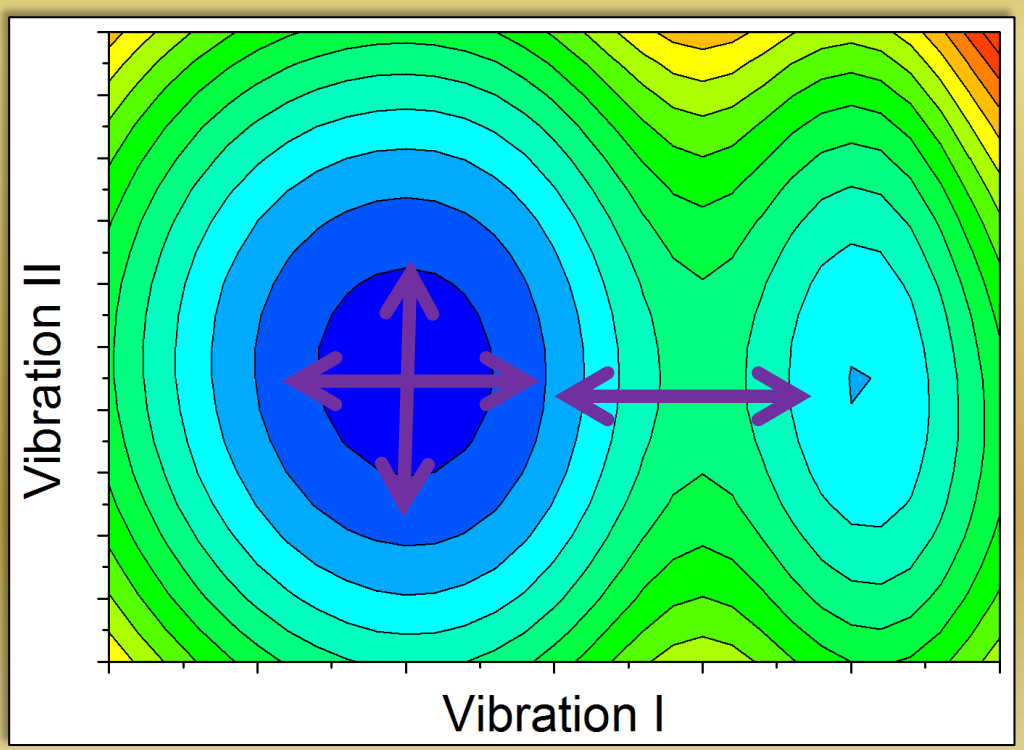
$$E(R) \approx E(R_0) + \sum_i \frac{\delta E}{\delta R_i}\Delta R_i + \sum_i \sum_j \frac{\delta^2 E}{\delta R_i \delta R_j}\Delta R_i \Delta R_j + \ldots$$

Hessian *H*



Vibrations

- **Solve Newtons equation of Motion:** $F = M\Delta\ddot{R}$
  - **Exponential ansatz:** $\Delta R = ue^{i\omega t}$
  - **Leads to generalized eigenvalue problem:** $Hu = \omega^2 Mu$



- **Negative ω: Transition state**
- **Large ω = large force constant, e.g., bond streching**
- **Small ω : small force constant, e.g., out-of-plane vibrations**

Vibrations

- **Free energy for finite temperature**

$$F(T) = E_{min} + \sum_{\nu} \left(\frac{\hbar\omega}{2} + k_b T \ln[1 - e^{\frac{\hbar\omega}{k_B T}}] \right)$$

- **Partition sum**

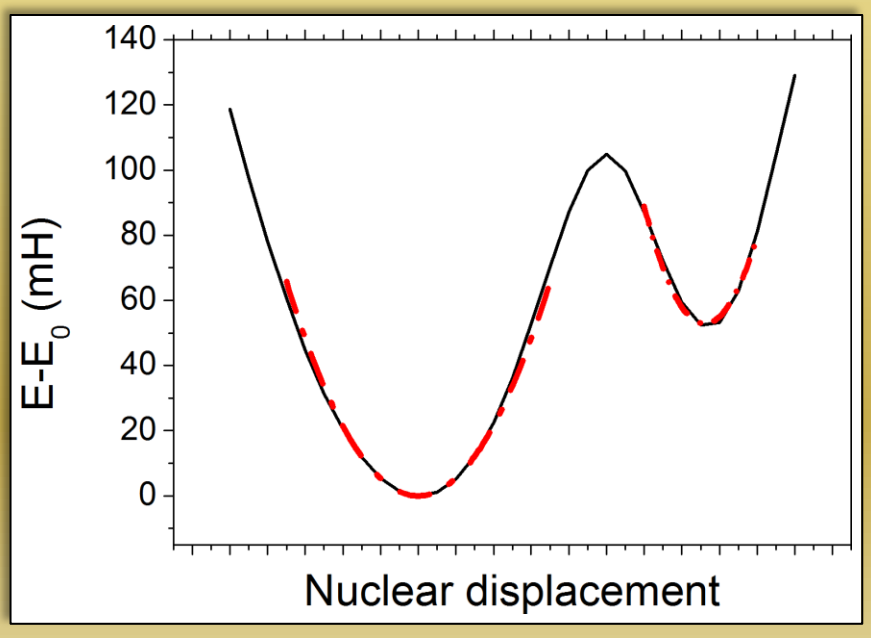
$$z_{vib} = \Pi_j \sum_{\nu} \exp\left(-\frac{\hbar\omega(\nu + \frac{1}{2})}{k_B T} \right)$$

- **Hessian from geometry optimization not sufficent**
  - **Analytic second derivative using perturbation theory [1]**
  - **Numerical differentiation**

[1] S. Baroni et al. , Rev. Mod. Phys. 73 , 515 (2001).

Vibrations – beyond harmonic

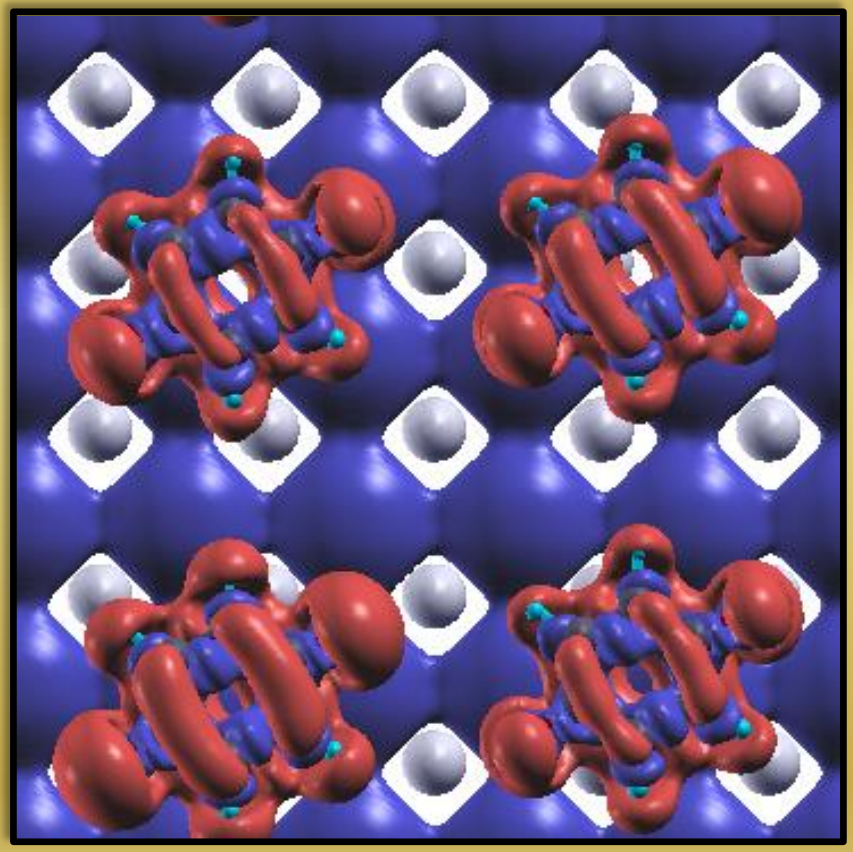
- **For high T or double-well minima**
  - **Molecular dynamics: Luca Ghiringhelli**
- **Re-introducting quantum nuclei:**
  - **See talk by Roberto Car**



Conclusions

- Often calculated in harmonic approximation
- Yield information about stability of geometry
- Required for temperature effects
- Anharmonic effects via molecular dynamics

Visualization



PBE: Electron density difference upon adsorption of p-bezoquinone on Li

Visualization

- Nuclear coordinates
- Electron distribution

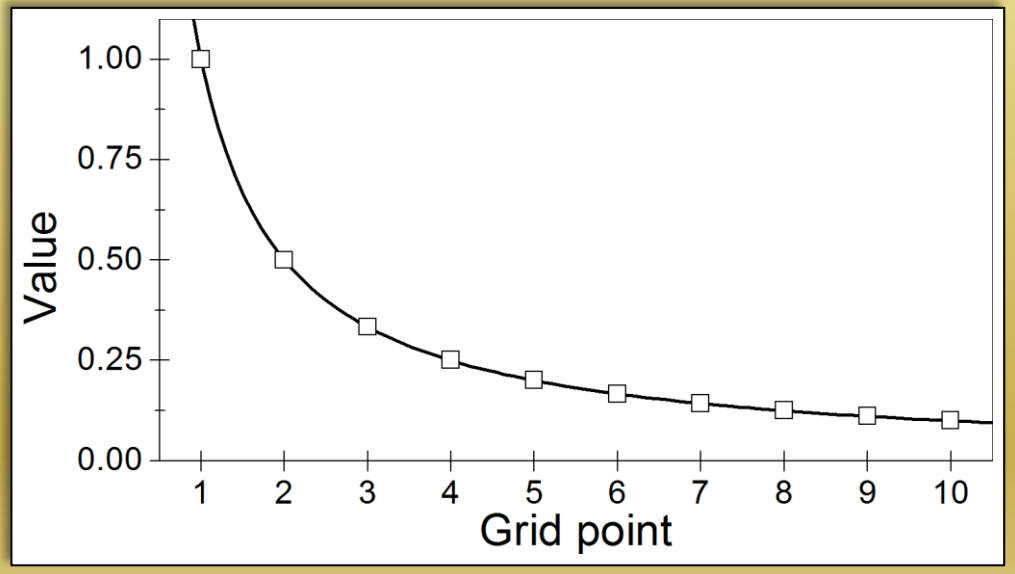
- What else can we learn?
- How can we visualize results that are not just „numbers“

Format for visualization

- **Codes use different types of basis functions and grids to store *n* / *Ψ*. No standard format to save information about custom grids**

- **Solution: Extrapolate and save quantities on evenly-spaced grids**
  - ***Common format: cube [1]***
  - ***Very memory intensive***

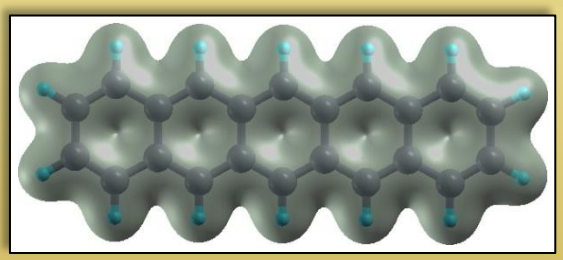
- **3 examples:**
  - ***Electron density***
  - ***Orbtials***
  - ***Scanning tunneling microcopy***



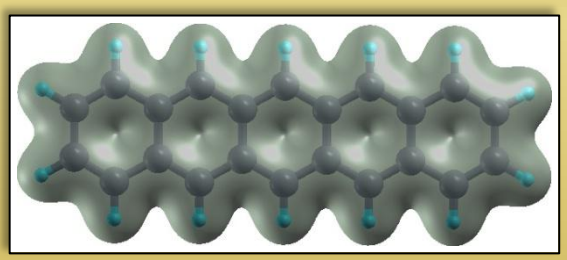
[1] P. Bourke http://paulbourke.net/dataformats/cube/

Electron density

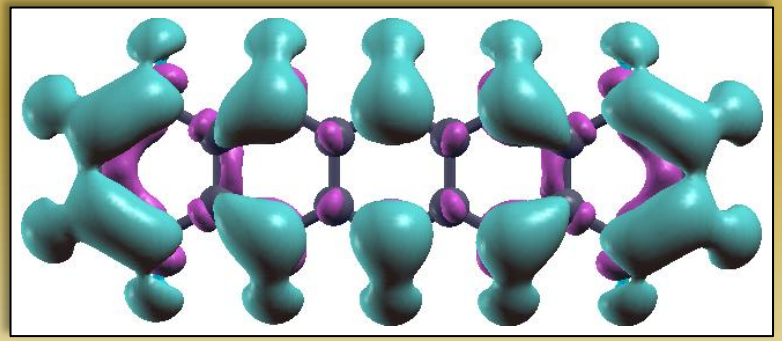
- **Contains core and valence electrons**
- **Resolution typically not sufficient for QM-postprocessing**
- **Even electron counting can be challenging**
- **Can be used, e.g., for charge differences (ΔSCF)**



Total density of neutral pentacene



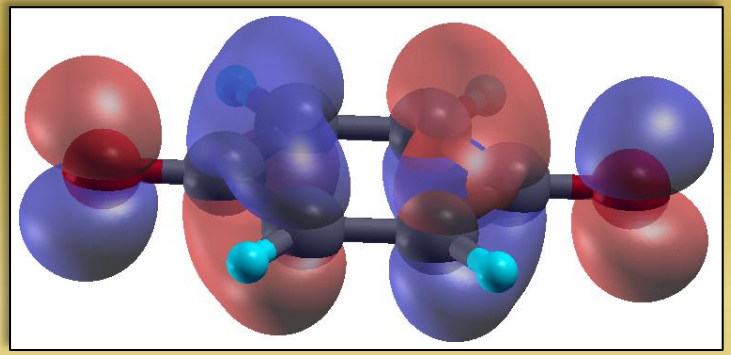
Total density of the pentacene cation



ΔSCF density. Cyan are negative values

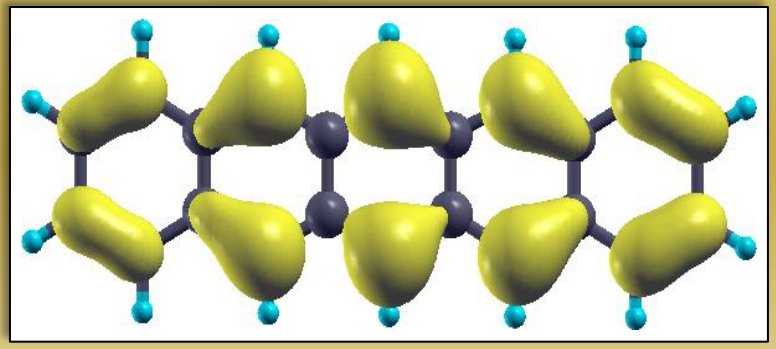
Orbitals

- **Valence orbtials contain „chemical information“**

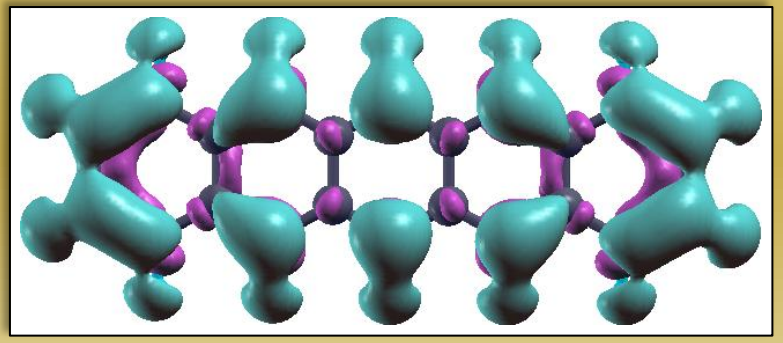


The LUMO of p-Benzoquinone exhibits nodes on the C=O double bond

- **Eigenstate densities** $n_i = |\psi_i|^2$
  - **tend to agree well with ΔSCF**



Pentacene HOMO density

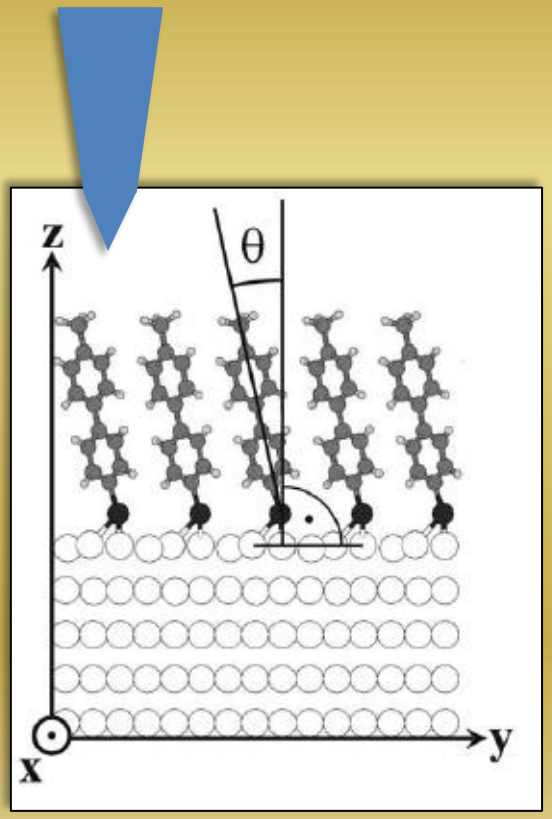


ΔSCF density for electron removal
Cyan: electron density reduced: Magenta: Increased

Scanning Tunneling Microscopy

- *Scan over (x,y) and measure tunnel current*
- *2 Modes:*
  - *Constant height*
  - *Constant current*
- *Tunnel current*
  - *Depends on energy (E) and tunnel matrix elements (M) of both tip (μ) and sample (v)*

$$I = \frac{2\pi e}{\hbar} \sum_{\mu,\nu} f(E_\nu)[1 - f(E_\nu - eV)|M_{\mu\nu}|^2 \delta(E_\mu - E_\nu)$$

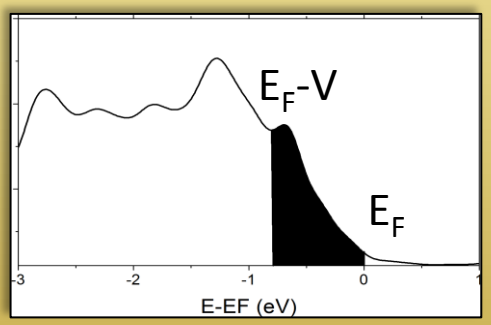


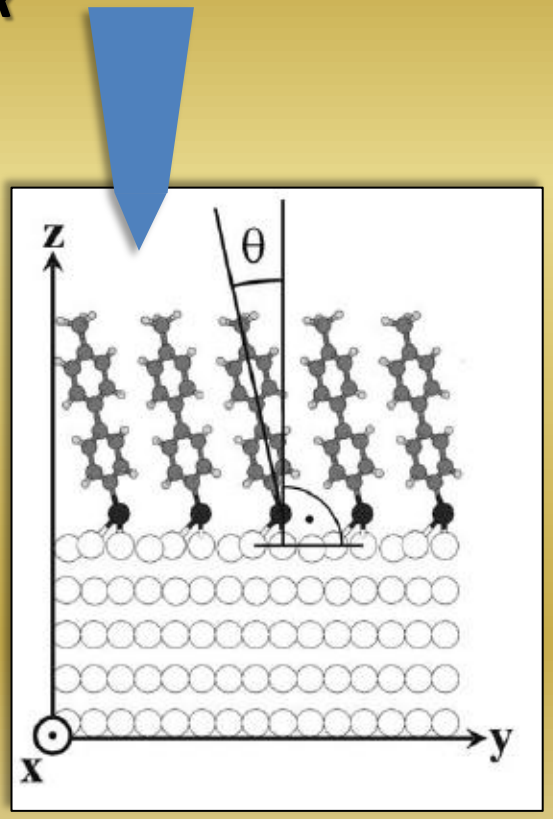
[1] OJ. Bardeen, Phys. Rev. Lett. 6, 57 (1961)
[2] J. Tersoff, Phys. Rev. B 40 (1989) 11990.

Scanning Tunneling Microscopy

- ***Simulation by Tersoff-Hamann [1]***
  - ***Neglect impact of tip***
  - ***Assume single point-like atom at apex***

$$I \approx \int_{E_f - V}^{E_f} \sum_\nu |\psi_\nu(r)|^2 \delta(\epsilon_\nu - E_F)$$



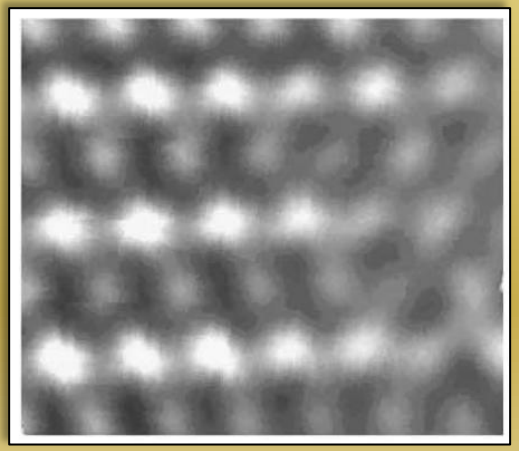


- ***Works only for s-type tips [2]***
  - ***CO-functionlized tips probe gradient***

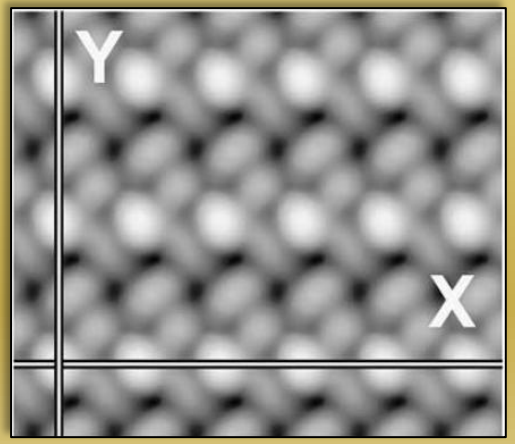
[1] J. Tersoff, Phys. Rev. B 40 (1989) 11990.
[2] L. Gross et al, Phys. Rev. Lett. (2011), 086101

Scanning Tunneling Microscopy

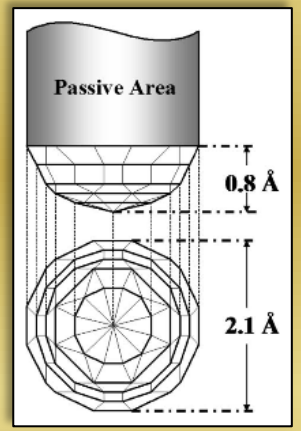
- ***Problem for adsorbate systems:***
  - ***Point-like tip can penetrate layer***
  - ***Resulting pictures too „crisp“***
  - ***Solution:***
    - ***Average over adjacent points***
    - ***Model tip as extended object [1]***

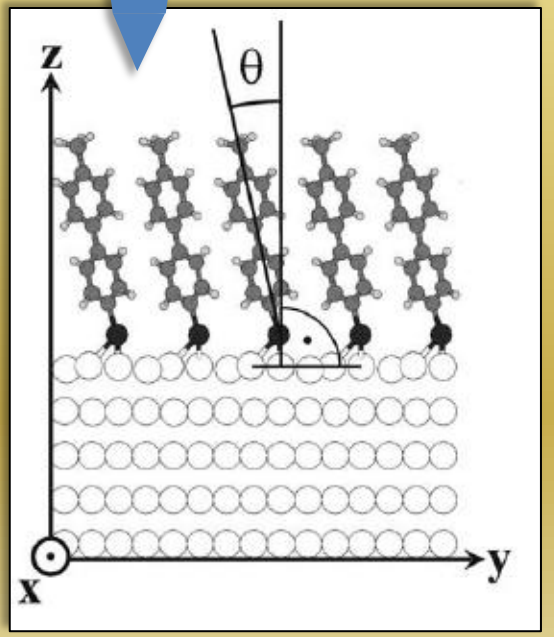


Experimental STM [2]



Simulated STM [1]





[1] G. Heimel et al., Surface Science 600 (2006) 4548–4562
[2] W. Azzam et al., Langmuir 19 (2003) 4958.

Conclusion

- Electronic Schrödinger equation
  - Solved by direct minimization or self-consistent field method
  - Initial guess requires some thought
  - Mixer: Tradeoff between stability and time
  - Convergence accelleration: Preconditioner, Broadening
- Structure optimization
  - Evaluate energy gradients
  - Contribution from Hellman-Feynman and Pulay forces
  - Solution by (Quasi)Newton-Methods

Conclusion

- Vibrations
  - Information about stability of geometry
  - Characterization of thermodynamic properties
  - Allow to account for temperature effects
- Visualization
  - Fields saved on regular grid
  - Helpful for direction connection with experiment, e.g.:
    - Scanning tunneling microscopy

Thank you for your attention