

DFT in practice II

SCF, Forces, Structure Optimization

Hands on DFT Barcelona 2019

August 27

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Task: Solve the Schrödinger Equation

$$\hat{H}\Psi = E\Psi$$

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

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

- Full solution → Nobel prize
- Find reasonable **approximations!**

Previous Talks:

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

Born-Oppenheimer: Electrons move (much) faster

$$\Psi(\{R\}, \{r, \sigma\}) \approx \Phi_{\text{Nuc}}(\{R\}) \cdot \Psi_{\text{elec}}(\{r, \sigma\})$$

Electronic problem:

$$\hat{H}_{\text{el}} = \hat{T}^{\text{e}} + \hat{V}^{\text{e-e}} + \hat{V}^{\text{Nuc-e}} \longrightarrow \hat{V}^{\text{ext}} \Big|_R$$

Outline

Solving the electronic structure problem

- Self-consistent field method (SCF)
- Density mixing and preconditioner
- Broadening of states

Nuclear structure optimization

- Forces in DFT
- Local Structure Optimization
- Vibrations in harmonic approximation

Vibrational Analysis in Harmonic Approximation

DFT in a nutshell

Hohenberg-Kohn [1]: Ground state properties of matter determined by density

$$\Psi_{\text{el}}(r_1, r_2, \dots, r_{3N}) \iff n(x, y, z)$$

- Reduce degrees of freedom by a factor N (N can be $\sim 10^{23}$)
- Gives total energy, dipole moments, forces (more on this later), ...

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

$$n(r) \implies \sum_i f_i |\psi_i^{\text{KS}}|^2$$

Remark: Kohn-Sham orbitals ψ_i^{KS} are **not the electrons!**

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

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

Kohn-Sham DFT

KS equation:

$$\left(-\frac{1}{2} \nabla^2 + \int \frac{n(r')}{|r-r'|} d^3 r' + V_{\text{xc}} + V_{\text{ext}} \right) \psi_i^{\text{KS}} = \epsilon_i \psi_i^{\text{KS}}$$

$V_{\text{ext}}(\{\mathbf{R}\})$ defines the problem

Problem

- $\left(-\frac{1}{2} \nabla^2 + V^{\text{KS}}[\{\psi_i^{\text{KS}}\}] \right) \psi_i^{\text{KS}} = \epsilon_i \psi_i^{\text{KS}}$

Approach


- Solve **self-consistently**

Kohn-Sham DFT

KS equation:

$$\left(-\frac{1}{2} \nabla^2 + \int \frac{n(r')}{|r-r'|} d^3 r' + V_{\text{xc}} + V_{\text{ext}} \right) \psi_i^{\text{KS}} = \epsilon_i \psi_i^{\text{KS}}$$

$\hat{V}^{\text{e-e}}$

hard! 

more on xc functionals in the talks to come

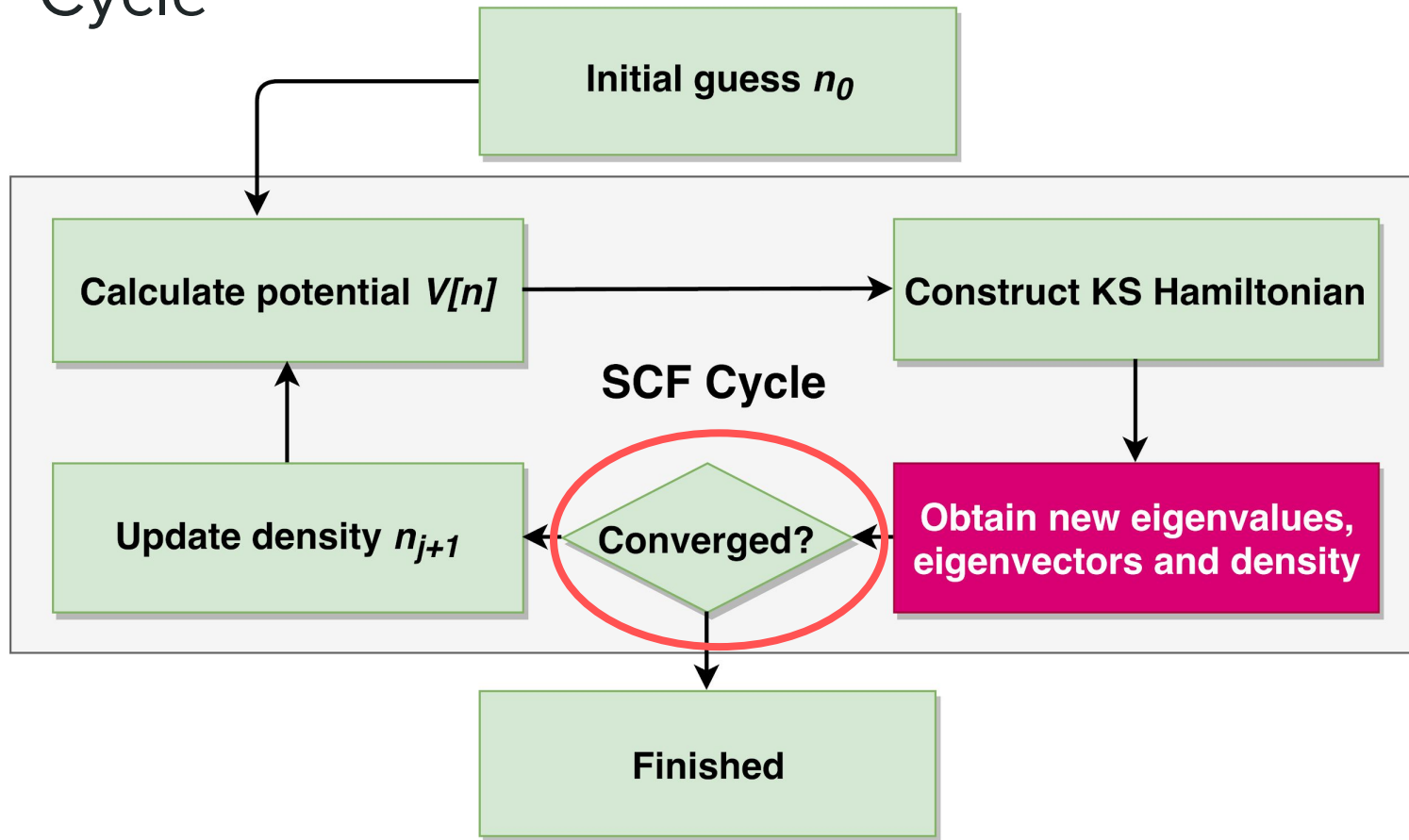
Problem

- $\left(-\frac{1}{2} \nabla^2 + V^{\text{KS}} \left[\left\{ \psi_i^{\text{KS}} \right\} \right] \right) \psi_i^{\text{KS}} = \epsilon_i \psi_i^{\text{KS}}$

Approach

- Solve **self-consistently**

SCF Cycle



When is the Calculation converged or finished?

Answer: **When the density and properties of interested do not change**

Main Convergence Parameter: **Change of density** $\Delta n(r)$

- Good density → good properties
- in FHIaims: **sc_accuracy_rho**

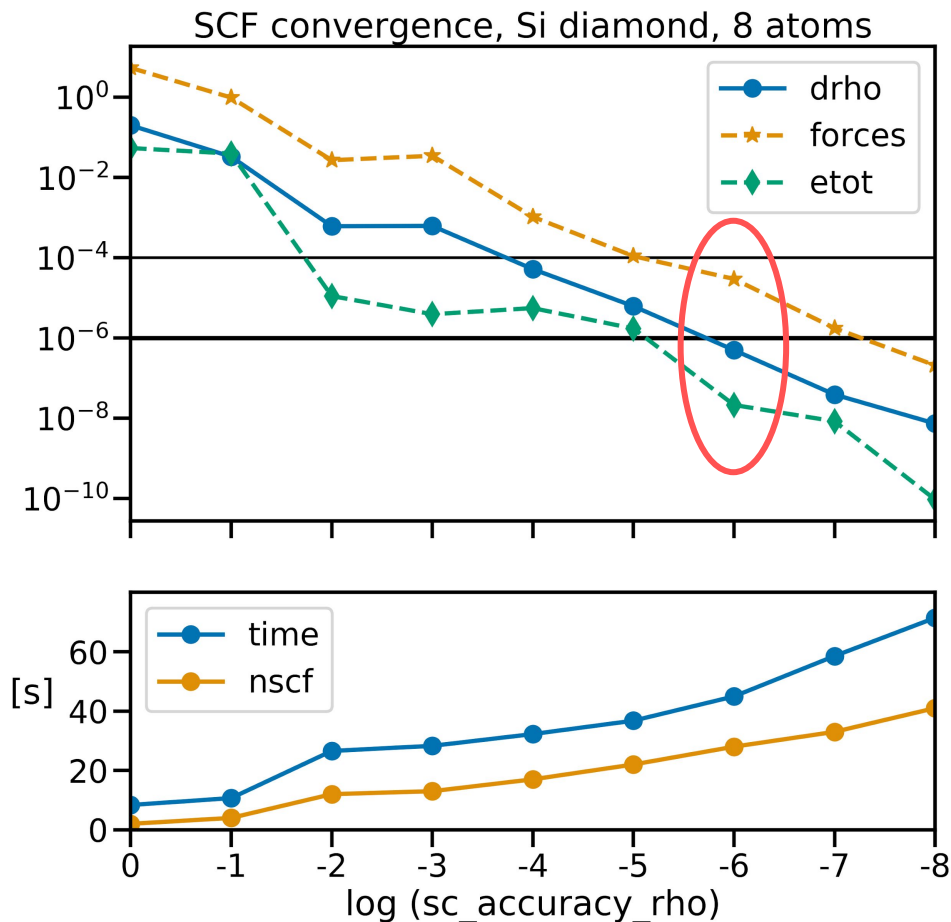
When is t

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Answer: Whe

Main Conver

- Good de
- in FHLaim

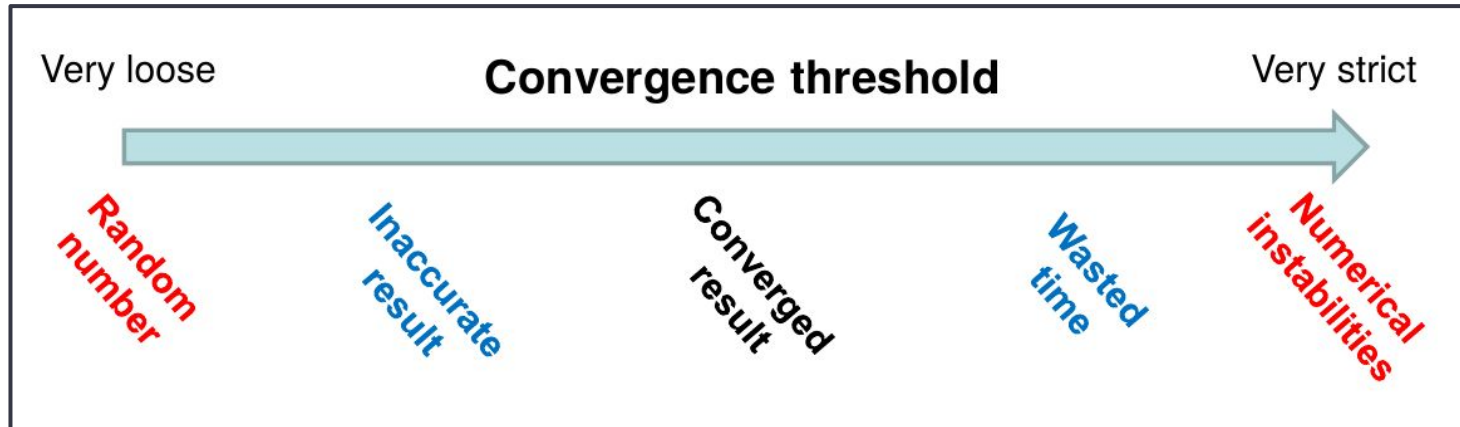


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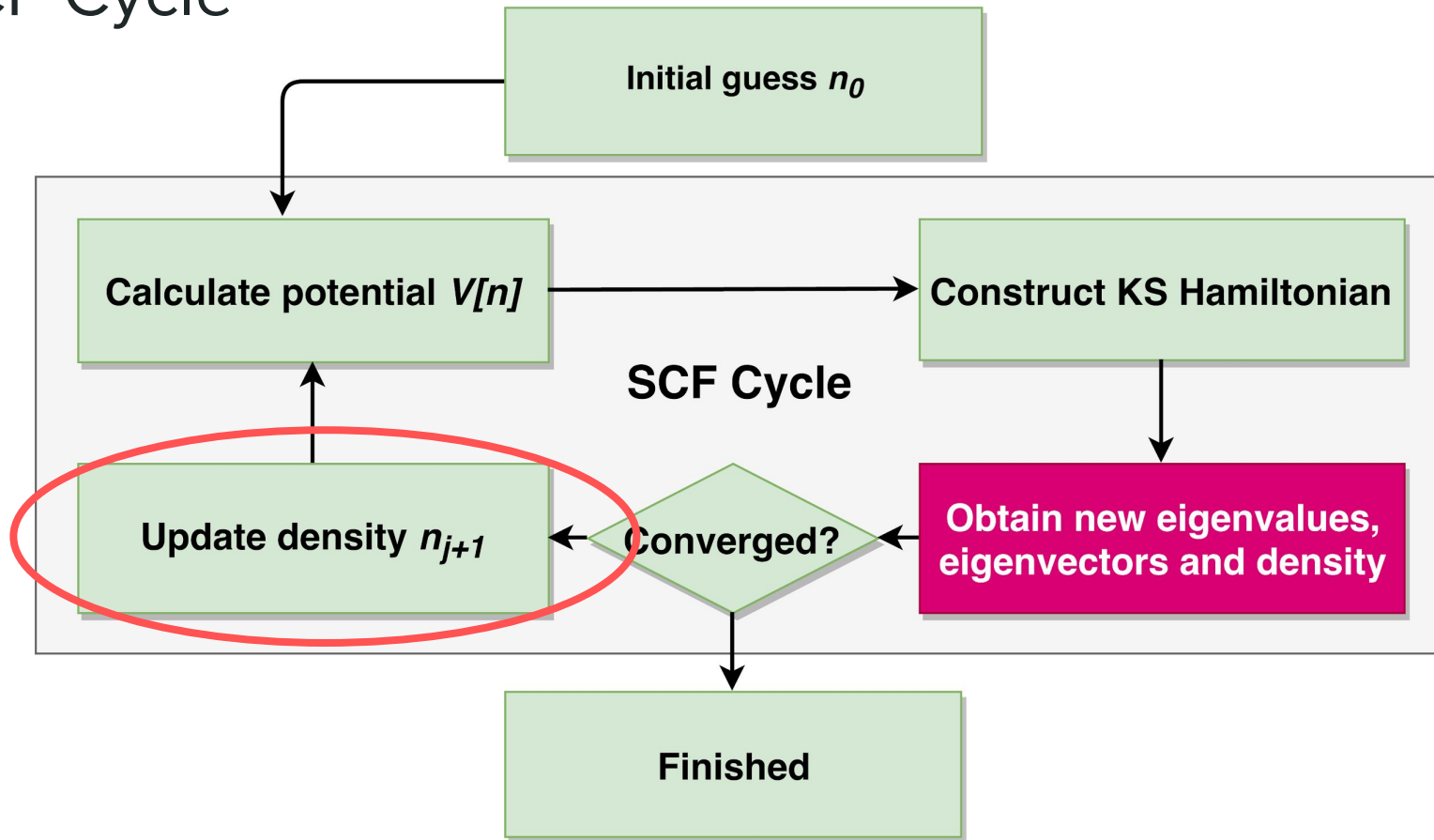


What are safe convergence settings?

Answer: **It depends.**

- Implementation: Different codes use different convergence criteria
- Best case: **default values are good enough!**
 - E.g. in FHI-aims

SCF Cycle



Density Update -- Naïve Mixing

Simple approach:

- Compute new density from Kohn-Sham orbitals
- replace old density by new density

$$n_{j+1} = n_j + \Delta n_j$$

Numerically not stable

- Best case: oscillating, non-converging results
- Worst case: wrong solution that appears converged

Density Update -- Linear Mixing

Next simple approach:

- Compute new density from Kohn-Sham orbitals
- add fraction of new density to old density

$$n_{j+1} = n_j + \alpha \Delta n_j$$

Not too bad

- Guaranteed convergence
- No clear recipe how to choose ideal α
 - possible: **slow convergence**

Density Update -- Pulay Mixing [1]

Standard approach:

- Compute new density from Kohn-Sham orbitals
- predict new residual Δn_j from **history of residuals**

$$\Delta n_{j+1}(r) = \sum_{j=N-M}^{N-1} \beta_j \Delta n_j(r)$$

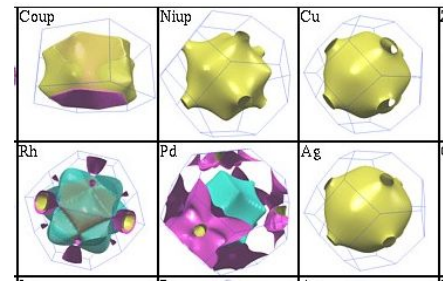
- determine β_i from least-squares fit

Best choice in most cases

- Convergence not guaranteed, *but*
- **Usually much faster** than linear mixing!
- If it didn't work \rightarrow linear mixing

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

Special Problem: Metallic Systems

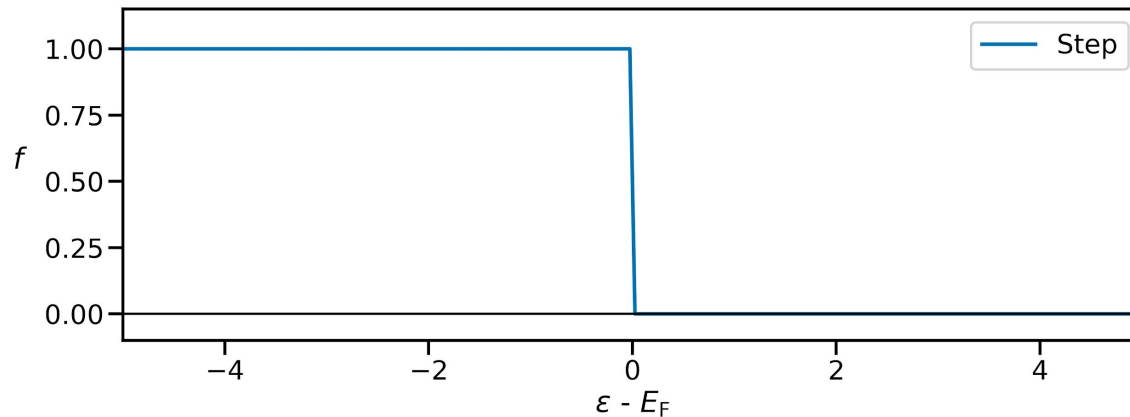


http://www.phys.ufl.edu/fermisurface/periodic_table.html

Problem: **Fermi function f is a step function at $T=0K$**

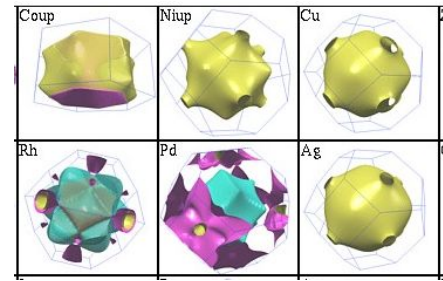
➤ **numerically unstable** to evaluate, especially for **metals**

$$n = \sum_i f(E_F - \epsilon_i) |\psi_i|^2 \equiv \int d^3k f(E_F - \epsilon(\mathbf{k})) |\psi(\mathbf{k})|^2$$



Special Problem: Metallic Systems

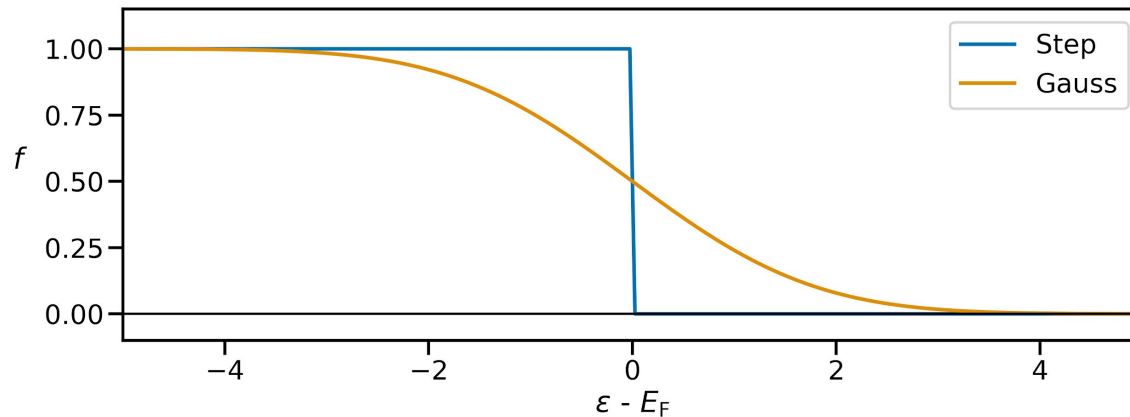
Problem: **Fermi function f is a step function at $T=0K$**



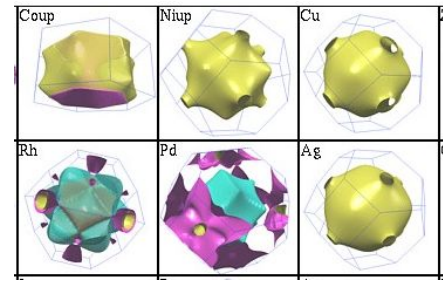
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Gaussian smearing: $f(\epsilon, \sigma) = \frac{1}{2} \operatorname{erfc} \left(\frac{\epsilon}{\sigma} \right)$



Special Problem: Metallic Systems

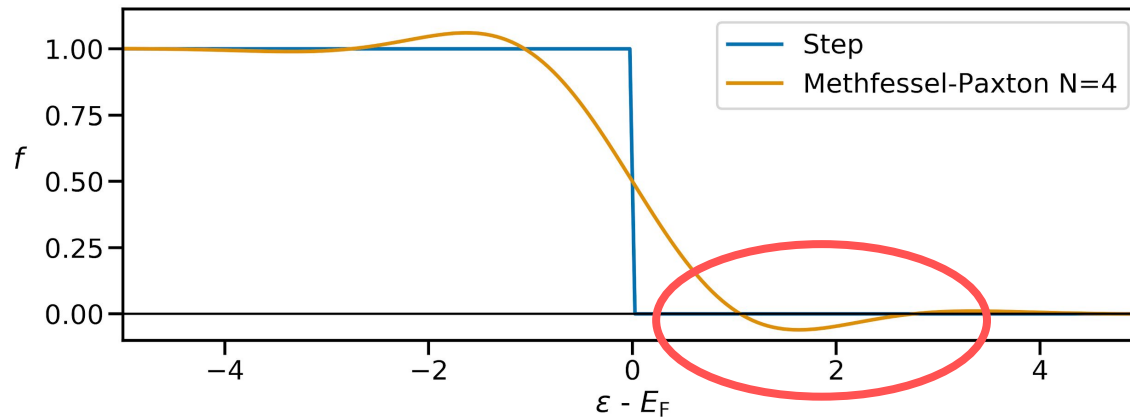


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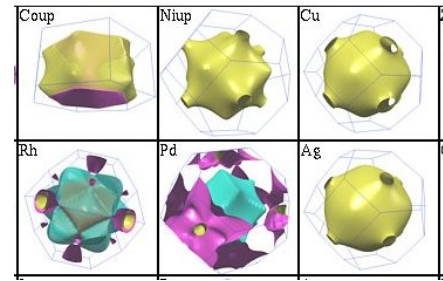
Methfessel-Paxton: $f(\epsilon, \sigma)|_N = \frac{1}{2} \operatorname{erfc}(\epsilon/\sigma) + \sum_{n=1}^N A_n H_{2n-1}(\epsilon/\sigma) e^{-(\epsilon/\sigma)^2}$



M. Methfessel, A. Paxton, *Phys. Rev. B* **40**, 3616 (1989).

Special Problem: Metallic Systems

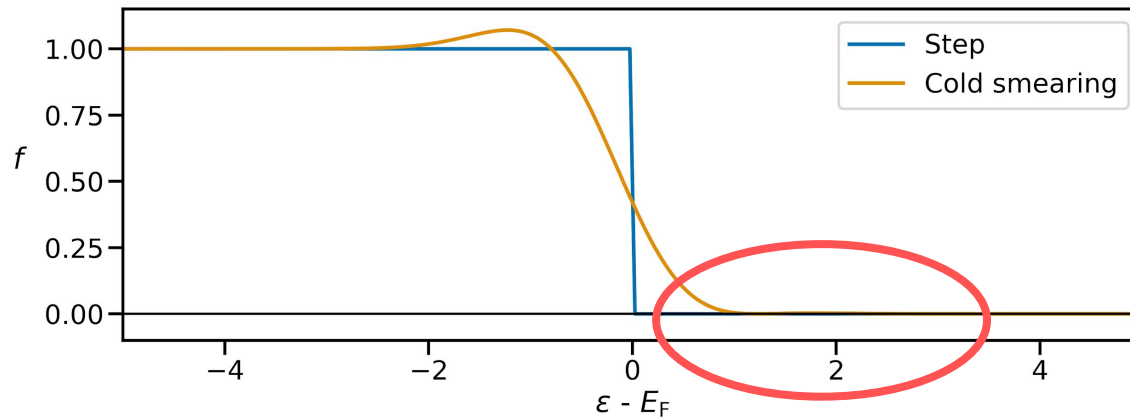
Problem: **Fermi function f is a step function at $T=0K$**



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➤ **numerically unstable** to evaluate, especially for **metals**

Cold smearing:
$$f(\epsilon, \sigma) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\epsilon/\sigma} \left(ax^3 - x^2 - \frac{3x}{2} + \frac{3}{2} \right) e^{-x^2} dx$$



Special I

Problem: Fe

➤ numeric

Cold smear

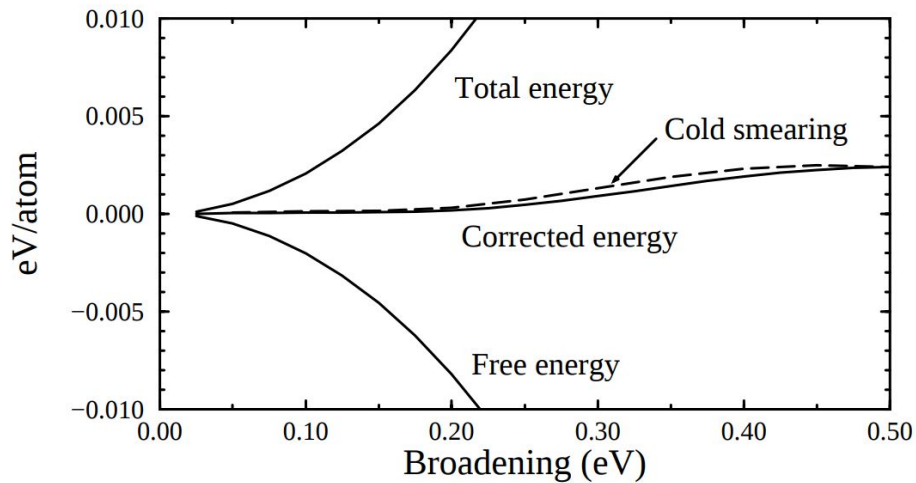
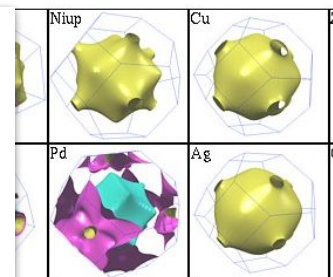


Figure 4.8: Comparison between the cold smearing and the corrected energy, in the model case of α -tin with 12 electrons, as discussed in the text.

Artificial Broadening needs to be corrected!



ufl.edu/fermisurface/periodic_table.html

Basissets

Basisset: Complete set of functions to represent KS states

$$\psi_i^{\text{KS}}(\mathbf{r}) = \lim_{K \rightarrow \infty} \sum_{k=1}^K c_k \phi_k(\mathbf{r})$$

Problem

- **Complete** basissets are typically of **infinite** size ($K = \infty$)

Solution

- Find *good enough* **approximation** $K < \infty$

Basissets | Popular Choices

Plane Waves

$$\phi_{\mathbf{k}}(\mathbf{r}) \propto \exp(i\mathbf{k} \cdot \mathbf{r})$$

- K corresponds to max. wave number, i.e., highest energy $E_{\text{Cut}} = \hbar K_{\text{max}}$
- used in: VASP, QuantumESPRESSO, *many* others
- → **Nicola Marzari after the coffee break**

Gaussian type orbitals

$$\phi_{k \equiv lmn; \alpha}(\mathbf{r}) \propto x^l y^m z^n \exp(-\alpha r^2)$$

- more cutoff parameter, need to choose α
- real space grid
- Pro: analytic integrals
- used in: Gaussian, Orca, FHI-aims, ...

Basissets

Numeric atom-centered functions (used in FHI-aims, discussed by Volker)

$$\phi_{k \equiv ilm}(\mathbf{r}) \propto \frac{u_i(r)}{r} Y_{lm}(\varphi, \vartheta)$$

- **Discretize** real space grid
- **Truncated** multipole expansion (l, m)
- Pro: Fewer basis functions needed, **linear scaling**
- used in: **FHI-aims**, SIESTA, DFTB+, ...
- Defaults available:
 - **light**: Get to know a system, geometry optimization, molecular dynamics, ...
 - **intermediate**: tighter grids, geometries should be converged
 - **tight**: Converged geometries and energies
 - **really_tight**: Overcomplete Benchmark basisset

Basissets

Si, fcc diamond	light	intermediate	tight	really_tight
r_{cut} [Å]	5	6	6	6
# Integration points	11,208	35,840	35,840	56,860
Multipole l_{max}	4	6	6	8
Max. # basis functions	36	68	78	78
Error [meV per atom]	28.1	11.6	0.6	0.0
Time per scf step [s] [*]	0.4	3.4	4.7	9.8

Learn in tutorials:

Summary

Ground state electron density determined iteratively

Density Update by

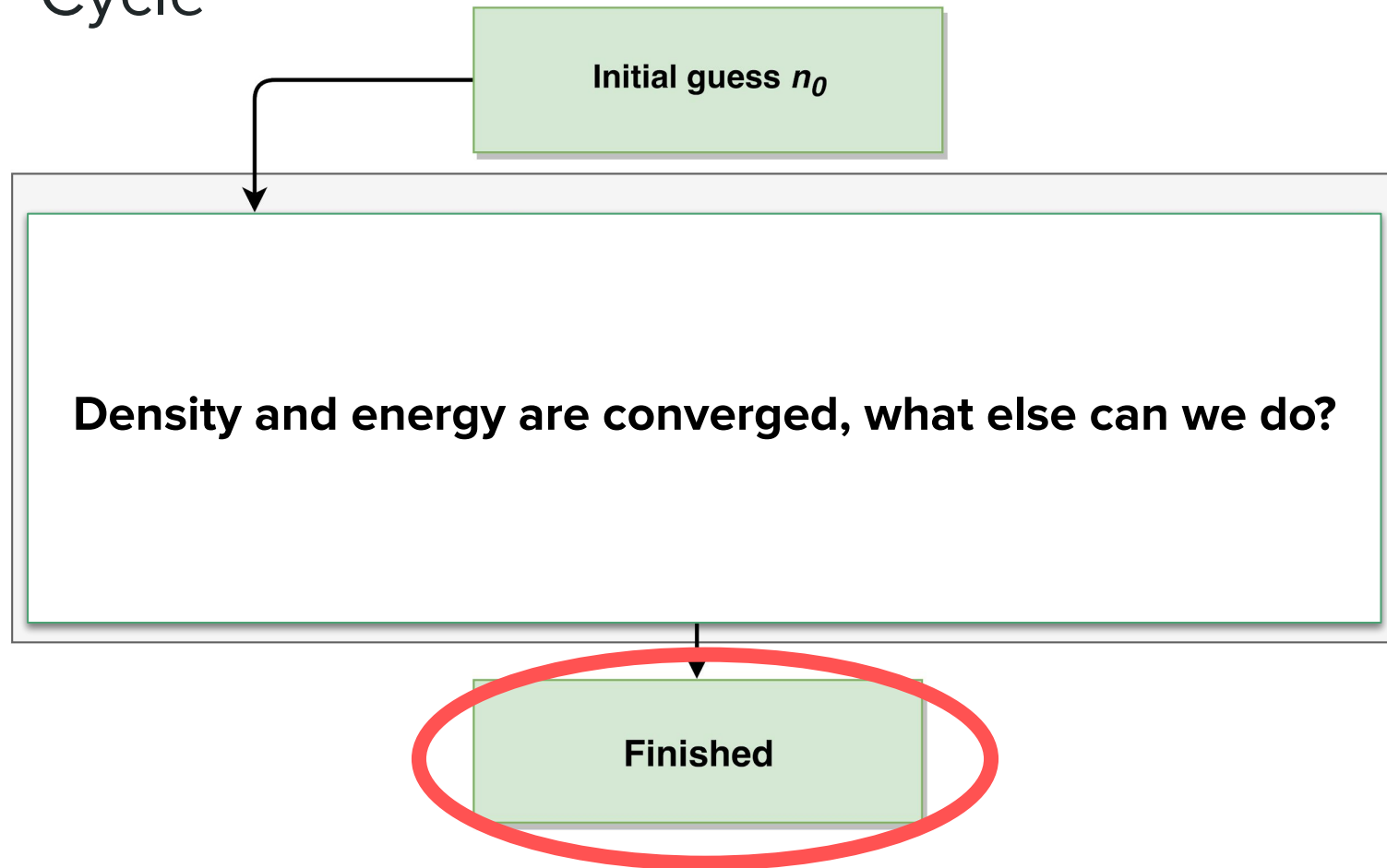
- Linear Mixing
- Pulay Mixing

Convergence acceleration by

- Preconditioner (not discussed)
- Broadening of states

Basis sets

SCF Cycle



Structure Search

Born-Oppenheimer energy surface or Potential Energy Surface (PES):

$$E_{\text{BO}} [n], n (V_{\text{ext}} (\{\mathbf{R}\})) \implies E_{\text{BO}} (\{\mathbf{R}\})$$

Typically there exists one or several minima

- System in thermal equilibrium: Ensemble average over all minima
- Often dominated by one global minimum, but depends

Global structure search → **S. Woodley** (Thu.)

Now: Local structure search!

Structure

Born-Oppenheimer

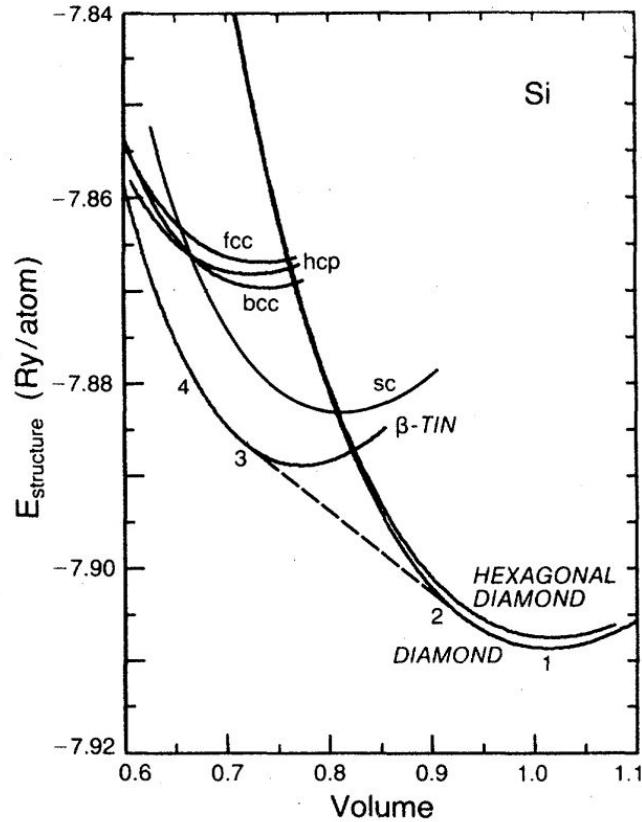
$$E_{\text{BO}}[n],$$

Typically the

- System
- Often c

Global structure

Now: Local



from: M. T. Yin and Marvin L. Cohen, *Phys. Rev. B* **26**, 5668 (1982)

PHES):

nima

Structure Search

Born-Oppenheimer energy surface or Potential Energy Surface

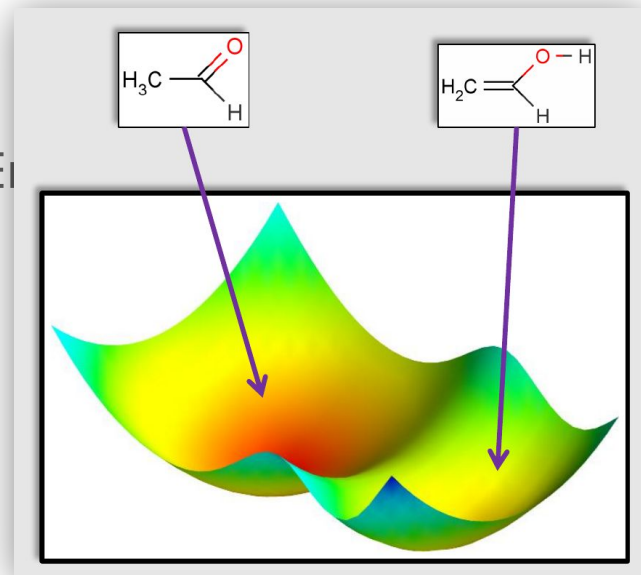
$$E_{\text{BO}} [n], n (V_{\text{ext}} (\{\mathbf{R}\})) \implies E_{\text{BO}} (\{\mathbf{R}\})$$

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Local Structure Search

Close enough to a minimum

- map out PES (expensive)
- follow the gradient a.k.a force

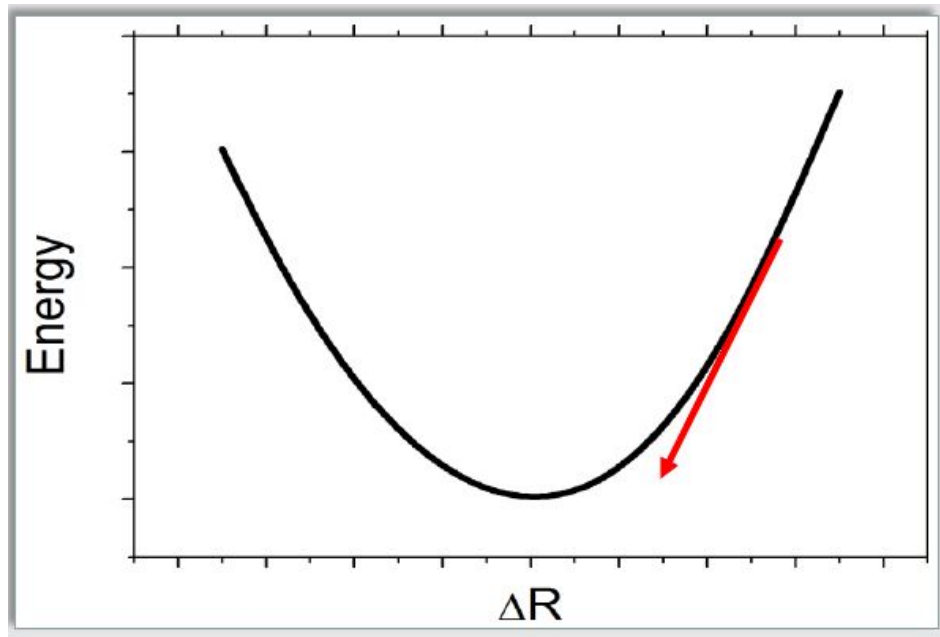
$$\mathbf{F} = -\frac{\delta E}{\delta \mathbf{R}}$$

- Finite differences (3N calculations!)

$$\frac{\delta E}{\delta \mathbf{R}} \approx \frac{\Delta E}{\Delta \mathbf{R}}$$

- *Hellmann-Feynman Theorem:*

$$\frac{d}{d\mathbf{R}_I} E_{\text{BO}} = \frac{d}{d\mathbf{R}_I} \left[E[n] + V^{\text{Nuc-Nuc}} \right]$$



Local Structure Search

Close enough to a minimum

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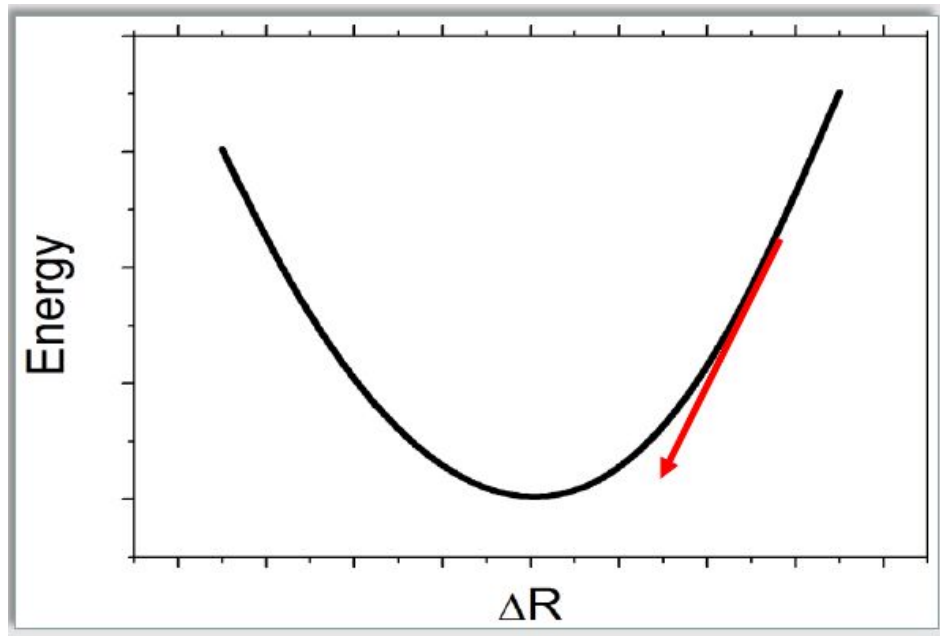
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- *Hellmann-Feynman Theorem:*

$$\frac{d}{d \mathbf{R}_I} E_{\text{BO}} = \int d r^3 \mathbf{n}(\mathbf{r}) \frac{e^2 Z_I (\mathbf{R}_I - \mathbf{r})}{|\mathbf{R}_J - \mathbf{r}|^3} - \sum_{J \neq K} \frac{e^2 Z_J Z_K (\mathbf{R}_I - \mathbf{R}_J)}{|\mathbf{R}_J - \mathbf{R}_K|^3}$$



Hellmann-Feynman Theorem - Remarks

Is it this easy?

In principle yes, **but:**

- More complicated in periodic case
 - nuclear terms can only be summed up together with electronic terms

- Additional terms in atom centered basis sets

- Pulay terms

- because the basis sets move with the atoms

- Multipole Expansion

- corrects error arising from truncation of multipole expansion of

\hat{V}_{Hartree}

- Relativistic corrections
- Integration grids

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

Geometry Optimization - Steepest Descent

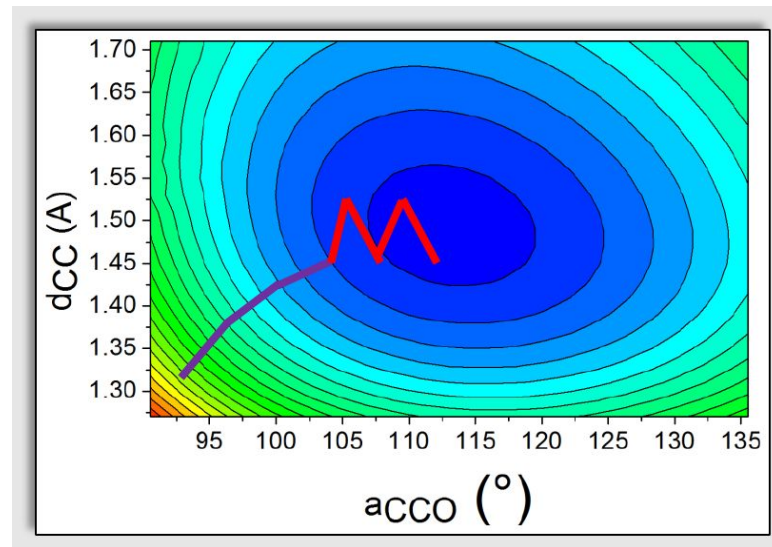
Follow negative gradient to find minimum

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

Variable step length α

Convergence guaranteed, but can be slow

Oscillates near minimum



Geometry Optimization - Newton

Local parabolic model for PES

$$E(\Delta R) \approx E(R_{\text{Min}}) + \boxed{\frac{\delta E}{\delta R}} \Delta R + \frac{1}{2} \boxed{\frac{\delta^2 E}{\delta R^2}} \Delta R^2$$

Step towards minimum:

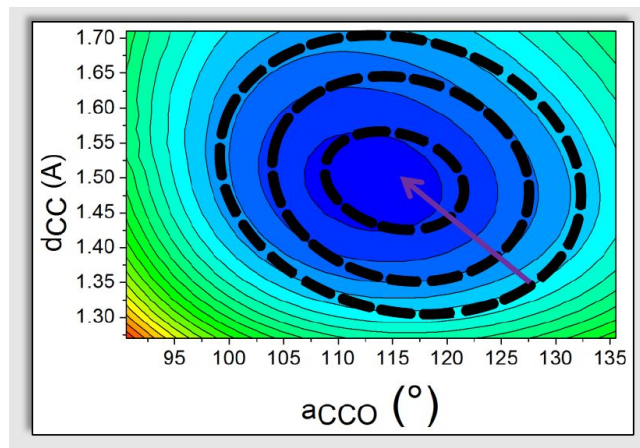
$$\Delta R = \mathbf{H}^{-1} F$$

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

$$\mathbf{H} = \frac{\delta^2 E}{\delta R^2}$$

Newton: Compute H

→ **expensive** in DFT, $\dim \mathbf{H} = 3N \times 3N$



Geometry Optimization - Quasi-Newton

Local parabolic model for PES

$$E(\Delta R) \approx E(R_{\text{Min}}) + \boxed{\frac{\delta E}{\delta R}} \Delta R + \frac{1}{2} \boxed{\frac{\delta^2 E}{\delta R^2}} \Delta R^2$$

Step towards minimum:

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

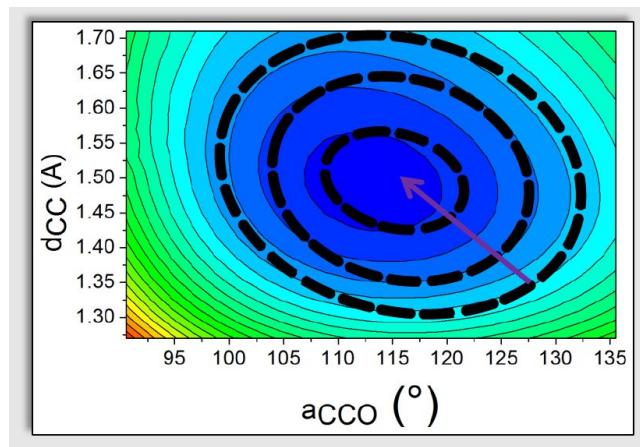
$$F = \frac{\delta E}{\delta R}$$

$$\mathbf{H} = \frac{\delta^2 E}{\delta R^2}$$

Quasi-Newton: Approximate $\hat{\mathbf{H}}$

BFGS: Update initial guess every step

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



Geometry Optimization - Quasi-Newton

Initial guess for approximate hessian

- Naïve choice: Scaled unit matrix $\tilde{H} = \beta \bar{\mathbf{1}}$
- Chemically motivated choice, e.g., Lindh [1]
- Periodic systems [2]
 - Lattice defines coordinate system
 - Generalized force on lattice: **Stress** σ
 - Non-orthogonal lattice: affects optimal choice for initial guess of hessian

More on periodic systems:

Lecture by **S. Levchenko** tomorrow 9am

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

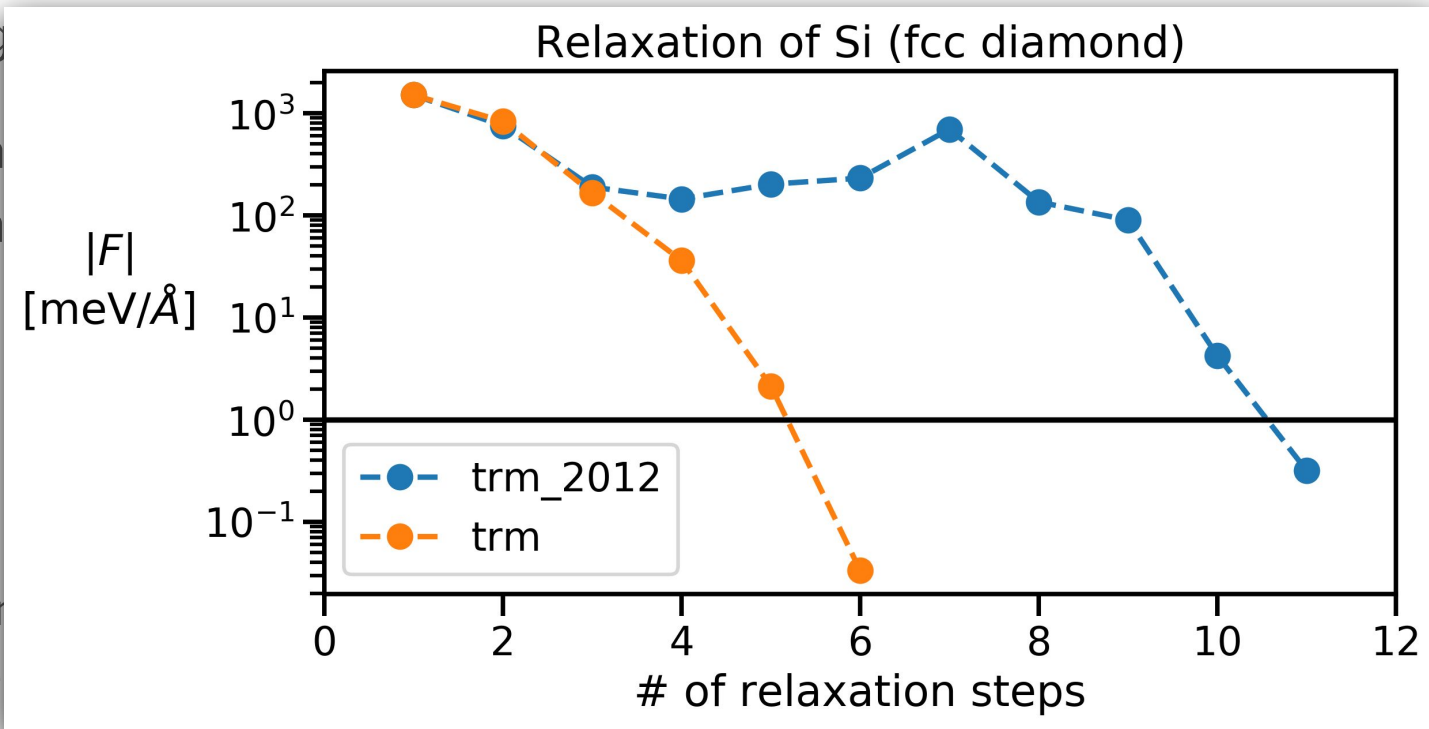
[2] B. Pfrommer et al., *Journal of Comp. Physics* **131**, 223 (1997)

Geometry Optimization - Quasi-Newton

Initial g

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- Ch
- Pe
-
-
-

More or
Lecture



ssian

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

[2] B. Pfrommer et al., *Journal of Comp. Physics* **131**, 223 (1997)

Geometry Optimization - Remarks

More tricks

- **Trust radius method:** estimate validity of parabolic model and enforce upper limit on step length ΔR

More approaches

- Bayesian optimization
 - local model of PES based on Gaussian functions (smooth, differentiable)
- Damped Molecular Dynamics
 - e.g. FIRE [1]

→ many implemented, documented, and readily available in [Atomistic Simulation Environment](#)

[1] Bitzek et al., *Phys. Rev. Lett.* **97**, 170201 (2006)

“Numerical Optimization”, J. Nocedal and S.J. Wright, Springer 1999

Vibrations in the Harmonic Approximation

Vibrations make Thermodynamics.

- Free energy
- Heat capacity, heat transport
- (Structural) Phase transitions
- Reaction pathways
- many more

Connection to experiment

- Infrared intensities: derivative of dipole moment
- Raman intensities: derivative of polarizability

$$Z_{\text{vib}} = \prod_j \sum_{\nu} \exp\left(-\frac{\hbar\omega_j\left(\nu + \frac{1}{2}\right)}{k_{\text{B}}T}\right)$$

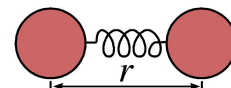
$$F(T) = k_{\text{B}}T \ln Z = \sum_j \left(\frac{\hbar\omega_j}{2} + k_{\text{B}}T \ln \left[1 - e^{-\frac{\hbar\omega_j}{k_{\text{B}}T}} \right] \right)$$

$$C_V = -T \left(\frac{\partial^2 F^{\text{ha}}(T, V)}{\partial T^2} \right)_V$$

Harmonic Approximation

Taylor expansion of PES about equilibrium configuration is parabolic to first approximation:

$$E(\Delta R) = E(R_0) + \cancel{\frac{\delta E}{\delta R} \Delta R} + \frac{1}{2} \frac{\delta^2 E}{\delta R^2} \Delta R^2 + \mathcal{O}(\Delta R^3)$$

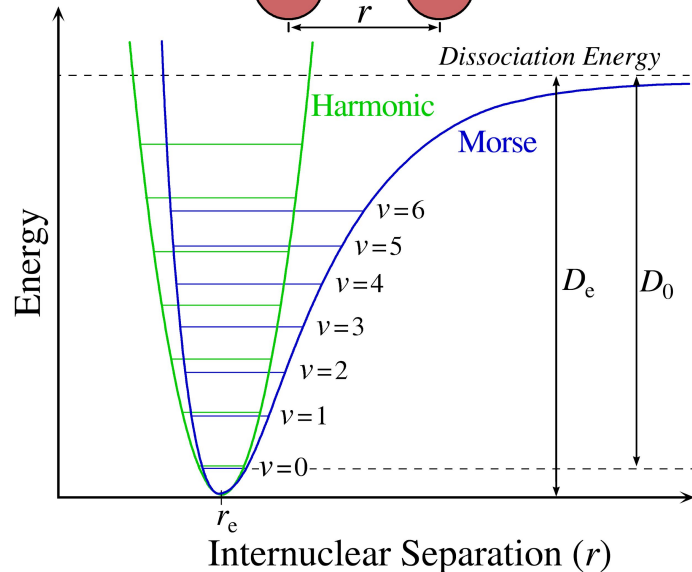


Example: **Morse potential**

$$V(R) = D_e \left(1 - e^{-a(R-R_0)} \right)^2$$

Second derivative: **exercise!**

We will meet it later today..



Harmonic Approximation (classical)

Hessian $\mathbf{H} \equiv \frac{\delta^2 E}{\delta R^2}$ can be used to compute forces from displacements:

$$\mathbf{F} = -\mathbf{H}(\mathbf{R} - \mathbf{R}_0)$$

Solve Newton's equation of motion analytically

$$\mathbf{F} = \mathbf{M}\ddot{\mathbf{R}}$$

Exponential ansatz

$$\Delta R(t) = u e^{i\omega t}$$

$$\longrightarrow \mathbf{H}u = \omega^2 \mathbf{M}u$$

Harmonic Thermodynamics (quantum)

Partition sum

$$Z_{\text{vib}} = \prod_j \sum_{\nu} \exp\left(-\frac{\hbar\omega_j\left(\nu + \frac{1}{2}\right)}{k_{\text{B}}T}\right)$$

Free energy

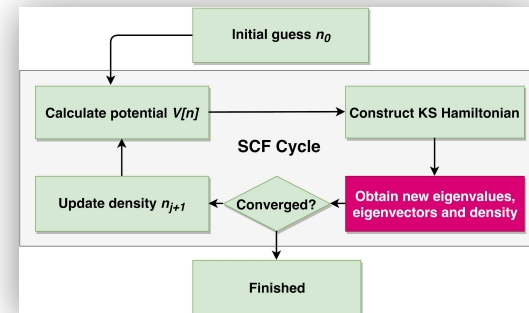
$$F(T) = k_{\text{B}}T \ln Z = \sum_j \left(\frac{\hbar\omega_j}{2} + k_{\text{B}}T \ln \left[1 - e^{-\frac{\hbar\omega_j}{k_{\text{B}}T}} \right] \right)$$

Heat capacity (exercise)

$$C_V = -T \left(\frac{\partial^2 F^{\text{ha}}(T, V)}{\partial T^2} \right)_V$$

Summary

Self-consistent solution of fundamental DFT equation

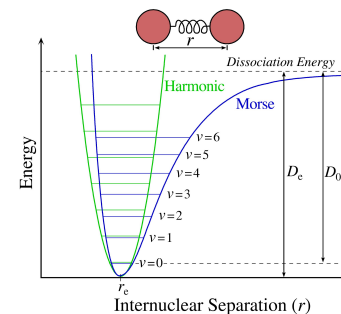


Gradients in DFT: Hellmann-Feynman Theorem

$$\frac{d}{d\mathbf{R}_I} E_{\text{BO}} = \int d\mathbf{r}^3 n(\mathbf{r}) \frac{e^2 Z_I (\mathbf{R}_I - \mathbf{r})}{|\mathbf{R}_J - \mathbf{r}|^3} - \sum_{J \neq K} \frac{e^2 Z_J Z_K (\mathbf{R}_I - \mathbf{R}_J)}{|\mathbf{R}_J - \mathbf{R}_K|^3}$$

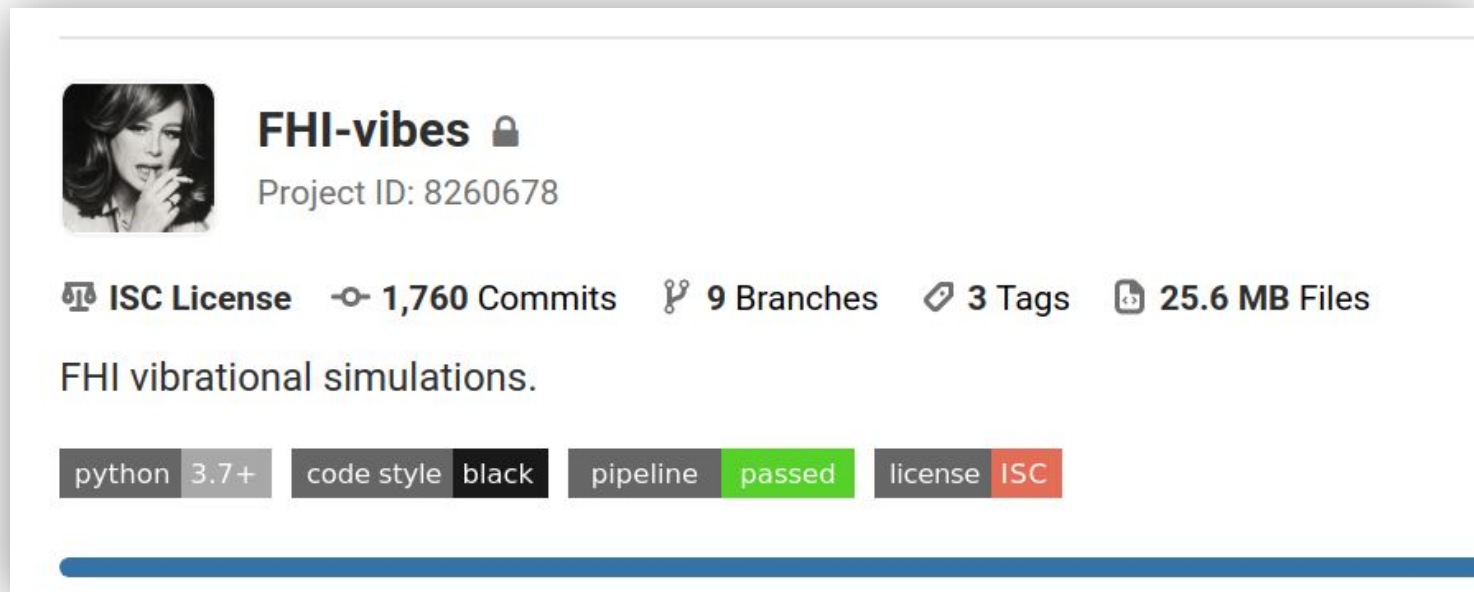
Geometry optimization: how to find the (structural) minimum

Harmonic approximation: first attempt at vibrational analysis










Outlook

Stay tuned for **Tutorial 6: Phonons with FHI-vibes**



The screenshot shows the GitHub repository page for FHI-vibes. It includes a profile picture of a woman, the repository name 'FHI-vibes' with a lock icon, and the Project ID '8260678'. Below this, there are statistics: 'ISC License', '1,760 Commits', '9 Branches', '3 Tags', and '25.6 MB Files'. A description reads 'FHI vibrational simulations.' At the bottom, there are several status boxes: 'python 3.7+', 'code style black', 'pipeline passed' (highlighted in green), and 'license ISC' (highlighted in red).

 **FHI-vibes** 
Project ID: 8260678

 **ISC License**  **1,760 Commits**  **9 Branches**  **3 Tags**  **25.6 MB Files**

FHI vibrational simulations.

python 3.7+ code style black pipeline **passed** license **ISC**

Thank you very much!