DFT in practice – part II

Oliver T. Hofmann, Berlin August 1st
Solving the Schrödinger equation

\[ \hat{H} \Psi = E \Psi, \]  
with

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

\[ \hat{H} = \hat{T}^{Nuc} + \hat{V}^{Nuc-Nuc} + \hat{T}^{e} + \hat{V}^{Nuc-e} + \hat{V}^{e-e} \]

Full many body solution typically not attainable

→ Born-Oppenheimer Approximation

\[ \hat{H}^{e} \Phi_{\nu} = E_{\nu}^{e} \Phi_{\nu}, \]  
with

\[ \hat{H}^{e} = \hat{T}^{e} + \hat{V}^{e-Nuc} + \hat{V}^{e-e} \]

– Assumption: electrons are in an eigenstate of \( H^{e} \)

– Implication: separation of nuclear and electronic coordinates
Outline

Solving the electronic part
  - Self-consistent field method
  - Density mixing and preconditioner
  - Broadening of states

Nuclear Structure optimization
  - (Global structure optimization)
  - Local structure optimization
  - „Forces“ in DFT
  - Vibrations in the harmonic approximation
Where are the electrons?

All ground state properties related to electron distribution [1] \( \Phi(r_1, r_2, \ldots, r_N) \iff n(r) \)

- Relative energy of conformers, dipole moments, reactivities, etc.
- Density functional theory (DFT)

Kohn-Sham scheme [2]

- Map electron density on effective one-particle orbitals
  \[ n(r) \iff \sum_i f_i |\phi_i|^2 \]

Kohn-Sham DFT

\[
\left( \frac{1}{2} \nabla^2 + \int \frac{n(r')}{|r - r'|} d^3r' + V_{xc} + V_{ext} \right) \phi_i = \epsilon_i \phi_i
\]

\[
\hat{T}^e, \quad \hat{V}^{e-e}, \text{ depends on } n = \sum_i |\phi_i|^2
\]

We want to determine all \( \Phi_i \) such that

- \( E[n] \to \text{min} \)
- \( H \) is consistent with \( \Phi_i \)

Approaches

- Direct minimization (rarely used)
- Self-consistent field method
Self-consistent field method

Initial guess: e.g. density

Calculate potential

Update potential

Construct Hamiltonian

Obtain new eigenvalues, eigenvectors, and density

Update density / density matrix (mixer, preconditioner)

Converged?

No

Yes

Finished
Self-consistent field method (SCF)

1. **Initial guess**: e.g. density

2. Calculate potential

3. Update potential

4. Update density / density matrix (mixer, preconditioner)

5. Construct Hamiltonian

6. Obtain new eigenvalues, eigenvectors, and density

7. Converged?

   - **Yes**: Finished
   - **No**: Go back to step 2

**Equation:**

\[
 n^{j+1} = n^j + f(\Delta n)
\]

\[
 V^{j+1} = V^j
\]
Convergence

When is the calculation finished?

Answer: When "property" does not change

Typical "properties" to converge:
- Change of the density $\Delta n$
- Change of the sum of eigenvalues
- Change of the total energy

Options differ between codes
Thresholds often historically grown
What are safe convergence settings?

Short answer: It depends.

**Problem I: Connection between parameters and observables**
- Adsorption / Cohensive / [...] energy ↔ Total energy (1:1)
- Dipole moment ↔ Electron density (size dependent)
- Force constants of bonds ↔ sum of eigenvalues (?????)

**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
What are safe convergence settings?

**Overconverged settings:**
(Some) results are code-independent

**Underconverged settings or**
Non-trivial relation to observables: Error bar unknown!

Lejaeghere et al., Science 351 (2016)

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**Take-home messages**

**Solution I:** Converge your convergence parameters

**Solution II:** Define convergence for your observable
Self-consistent field method (SCF)

Initial guess: e.g. density

Calculate potential

Update potential

Construct Hamiltonian

Obtain new eigenvalues, eigenvectors, and density

Update density / density matrix (mixer, preconditioner)

Converged?

Finished
Importance of the initial guess

Electronic structure exhibits multiple minima
- Qualitative different behavior
- Which is found depends (mostly) on guess
- Common issue for magnetic solids

How do we find a stable, reasonable, fast-converging initial guess?
Random initialization

Traditional approach (for bandstructure codes)

\[ \Phi = \sum_i c_i \phi_i \quad c_i = RND \]

+ : Straightforward to implement
+ : Unbiased

- : Far from correct solution:
  - : No chemical motivation
  - : Density varies most strongly near nucleus

- Mostly used in plane wave codes to initialize wave-function (not density)
- Backup method

Superposition of spheric atomic densities

Most common (for bandstructure codes)

+ : Straightforward to implement

+/-: „Mostly sufficient“, but can overemphasize symmetry

- : No density matrix / orbital coefficients

- : Most atoms not really spherical objects

✔ Used in VASP, FHI-aims, etc.
Extended Hückel Model [1]

Semi-empirical method:

- Linear combination of atomic orbitals
  \[ \phi_i = \sum_j c_{ij} \psi_j \]

- Hamiltonian parameterized:
  \[ H_{ii} : \text{parameterized valence ionization energies} \]
  \[ H_{ij} = \frac{1}{2} KS_{ij} (H_{ii} + H_{jj}) \] [2,3]

- Density from orbitals:
  \[ n = \sum f_i \phi_i \]

+ : Controlled occupation of orbitals (flexibility)
+ : Consistent wave-function and density
- : Parameters not available for all elements

Used in Quantum Chemistry (Gaussian, Turbomole, ...)

Self-consistent field method (SCF)

1. **Initial guess**: e.g. density
   - Calculate potential
   - Update potential
   - Construct Hamiltonian
   - Obtain new eigenvalues, eigenvectors, and density
   - Update density / density matrix (mixer, preconditioner)

2. Check for convergence:
   - If converged, finish.
   - If not, iterate with updated density.

Mathematical expression:

\[ n^{j+1} = n^j + f(\Delta n) \]
Naive Mixing

- Calculate new density from Kohn-Sham orbitals
- Replace old density by new density

\[ n^{j+1} = n^j + \Delta n \]

**Example:** \( \text{H}_2, d=1.5\text{Å}, \) projected in 1 dimension

Typically does not work

- **Best case:** Oscillating, non-converging results
- **Worst case:** Bistable, apparently converged solution
Linear Mixing

- Calculate new density from Kohn-Sham orbitals
- Replace old density by new density

\[ n^{j+1} = n^j + \alpha \Delta n \]

Example: \( \text{H}_2 \), \( d=1.5\text{Å} \), projected in 1 dimension

\( \alpha=0.3 \): Converges quickly
Density Update

**Linear Mixing**

- Calculate new density from Kohn-Sham orbitals
- Replace old density by new density

\[ n^{j+1} = n^j + \alpha \Delta n \]

**Example:** \( \text{H}_2 \), \( d=1.5\text{Å} \), projected in 1 dimension

- \( \alpha = 0.3 \): Converges quickly
- \( \alpha = 0.8 \): Oscillates

![Graph showing electron density difference vs position](image)
Density Update

Linear Mixing

➢ Calculate new density from Kohn-Sham orbitals
➢ Replace old density by new density

\[ n^{j+1} = n^j + \alpha \Delta n \]

Example: \( \text{H}_2 \), \( d=1.5\text{Å} \), projected in 1 dimension

Ideal choice system dependent

No clear recipe to choose ideal \( \alpha \)

Guaranteed convergence

Converges slowly
Pulay Mixing [1]
(Direct Inversion of Iterative Subspace)

- Define residual: \( R^j(r) = n^j(r) - n^j_{KS}(r) \)

*Change between input and output density*

- Predict residual of next step from previous steps

\[
R^{j+1}(r) = \sum_{j=N-M}^{N-1} \beta_j R^j(r)
\]

*Idea*: obtain \( \beta \) from least-squares fit

*Pitfall*: Only use limited number of previous steps

Pulay Mixing [1]
(Direct Inversion of Iterative Subspace)

- Construct „optimal density“:
  \[ n^{j+1} = n^{opt} + \alpha R[n^{opt}] \]

- Use underrelaxation

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Charge preconditioning

Problem: *Charge Sloshing*

- Charge „bounces“ back and forth
- (Lack of) balance between long-range and short-range charge re-distribution
- Often encountered in defect-systems
  - Localized defects (vacancies, interstitials)
  - Surfaces, Slabs, Thin Films
  - Etc.
Charge preconditioning

**Solution:** Make $\alpha$ depend on $\Delta n(r)$

$$n^{j+1} = n^j + \hat{G} \Delta n$$

**Concept:**

- Treat density change in Fourier space
- Damp long-range oscillations

$$\Delta n(G) = \frac{1}{\Omega} \int \Delta n(r) e^{-iGr} dr$$
Charge preconditioning

Solution: Make $\alpha$ depend on $\Delta n(r)$

$$n^{j+1} = n^j + \hat{G} \Delta n$$

Concept:
- Treat density change in Fourier space
- Damp long-range oscillations

$$\Delta n(G) = \frac{1}{\Omega} \int \Delta n(r) e^{-iGr} \, dr$$

$$\hat{G} = \alpha \frac{\Delta^2}{\Delta^2 + q_0^2}$$

$q >> \Delta$: $G \approx \alpha$

Normal mixing

$q << \Delta$: $G \approx \alpha \Delta / q^2$

Damping

$\alpha$: Mixing parameter
$q_0$: Screening parameter
Charge preconditioning

\[ \hat{G} = \alpha \frac{\nabla^2}{\nabla^2 + q_0^2} \]

\( \alpha \): Mixing parameter  
\( q_0 \): Screening parameter

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8 layer Al slab, PBE calculation

no \textit{a priori} known ideal choice for \( q_0 \)

Reasonable guess from Thomas-Fermi:

\[ q_0 \approx \sqrt{\frac{4k_f}{\pi}} \]
A special problem: Metallic systems

Metallic properties determined by Fermi surface
Fermi-surface: Collection at k-points at which $\varepsilon = \varepsilon_{\text{Fermi}}$

- At $\varepsilon_{\text{Fermi}}$ occupation changes from 1 to 0
- Many-body self-interaction: Occupation changes energy of state
- Problem: Frequent „level switching“ during SCF
A special problem: Metallic systems

\[ n = \sum_i f(E_F - \epsilon_i) |\Psi_i|^2 \]

Solution: Replace step function by a more smooth function

Fermi [1]

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

Gaussian [2]

\[ f(x) = \frac{1}{2} \text{erfc}\left(\frac{x}{\sigma}\right) \]

Methfessel-Paxton [3]

\[ f(x) = \frac{1}{2} \text{erfc}\left(\frac{x}{\sigma}\right) + \sum_{m} A_m H_{2M+1} \times \frac{x}{\sigma} \exp\left(\frac{x}{\sigma}\right)^2 \]

Density Update

A special problem: Metallic systems

Numerical Implications

• Level switching is damped
• Much faster convergence
• Total energy now depends on $\sigma$, no longer variational
• Backextrapolation possible

Pitfall: Adsorption of molecules

Physical implications:

• States become fractionally occupied
• In DFT, well defined as ensemble average
• Do not confuse with fractional filling of bands
• Broadening is not electron temperature (except: Fermi)
• Chemical potential / $E_F$ in semiconductors not meaningful!

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 qualitatively

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


Slide courtesy of Andrew Jones
Global structure search

Born-Oppenheimer energy surface can contain several minima

- Constitution isomery
- Configuration isomery
- Conformation isomery
- Polymorphism

• 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:

- Experimental structure determination
- Stochastical or Monte-Carlo
- Basin Hopping
- Molecular dynamics:
  - Simulated annealing
  - Minima Hopping
  - Metadynamics
- Cluster expansion
- Genetic algorithm
- Diffusion methods
- Machine Learning / Bayes Optimization
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 structure 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 a 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

\[
\frac{\delta E}{\delta R} = \langle \Psi_0 | \frac{\delta \hat{H}}{\delta R} | \Psi_0 \rangle + \langle \frac{\delta \Psi_0}{\delta R} | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | \hat{H} | \frac{\delta \Psi_0}{\delta R} \rangle
\]
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 \( V^{\text{nuc-nuc}} \) and \( V^{\text{e-nuc}} \)

\[
F_i^{\text{Hellman–Feynman}} = Z_i \sum_j \nabla R_i \frac{Z_j}{|R_i - R_j|} + \int d^3r \ n(r) \nabla R_i \frac{Z_i}{|R_i - r|}
\]
Total energy gradient

Search for minimum by following the gradient

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

- First term vanishes
- Second term survives for atom-centered basis functions
Total energy gradient

Search for minimum by following the gradient

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

Additional contributions from atom-centered approximations
- Multipole expansion
- Relativistic corrections
- (Integration grids)

All straightforward but lengthy

Once we have the Force, how do we find the minimum?
Geometry update – Steepest descent

Follow negative gradient to find minimum

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

Steplength \( \alpha \) variable

Guaranteed but slow convergence

Oscillates near minimum

Not suitable for saddle points

Improved versions exists
- Linie minimization
  (optimal step length)
- Conjugated gradient [1]

Geometry update – (Quasi)Newton Methods

Approximate PES by quadratic function

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

Find minimum: \[ \Delta R = H^{-1} F \]

Newton: calculate exact \( H \)

Expansive! Cheaper method needed

Geometry update – (Quasi)Newton Methods

Approximate PES by quadratic function

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

Find minimum: \[ \Delta R = H^{-1} F \]

- Newton: calculate exact \( H \)
- Quasi-Newton: approximate \( H \)
  - Update as search progresses [1]

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

Geometry update – (Quasi)Newton Methods

Guess initial Hessian

➢ Naive choice: Scaled unit matrix \( \tilde{H} = \beta \mathbf{1} \)
➢ Chemically motivated choice (e.g.: Lindh [1])

\[
\tilde{E} = E + F \Delta R
\]
- stretching + \( \sum_{ij} k_{ij} d_{ij}^2 \)
- bending + \( \sum_{ijl} k_{ijl} a_{ijl}^2 \)
- torsion + \( \sum_{ijlm} k_{ijlm} \tau_{ijlm}^2 \)

\[ k \text{ parameterized} \ [1] \]

Update as search progresses [2]

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

Challenges of Quasi-Newton Methods

Soft degrees of freedom can cause large $\Delta R$

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 $\Delta R$
  - Evaluate quality of quadratic model

  - Adjust $\Delta R_{\text{max}}$ based on $q$

  $q = \frac{E_{\text{true}}}{E_{\text{expected}}}$
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 in the harmonic approximation
Why calculating vibrations?

Vibrations give important information about the system:

– Classification of stationary points (minimum / saddle point)

– If saddle-point: Provides search direction

– Thermodynamic data
  • Zero-point energy
  • Partition sum
  • Finite temperature effects

– Connection to experiment:
  • Infra-red intensities: derivative of dipole moment
  • Raman intensities: derivative of polarizability
How good is the harmonic approximatioino?

Morse-potential: \[ E = U_0 \left( e^{2a(r-r_0)} - 2e^{a(r-r_0)} \right) \]

Harmonic oscillator: \[ E = U_0 + \frac{1}{2} \gamma (r - r_0)^2 \]
How good is the harmonic approximation?

Morse-potential: \[ E = U_0 \left( e^{2a(r-r_0)} - 2e^{a(r-r_0)} \right) \]

Harmonic oscillator: \[ E = U_0 + \frac{1}{2} \gamma (r - r_0)^2 \]

Reasonable model for small displacements (~10% of bond length)

Maximum displacement:
\[ A = \max(x) = \sqrt{\frac{2k_B T}{\gamma}} \]

Ca. 0.1Å at room temperature
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 \( H \)
Solve Newton's equation of Motion:
- Exponential ansatz: \( \Delta R = u e^{i\omega t} \)
- Leads to generalized eigenvalue problem:

\[
F = M \Delta \ddot{R} \\
Hu = \omega^2 Mu
\]

**Interpretation of results:**
- **Negative \( \omega \): Transition state**
- **Large \( \omega \): large force constant, e.g., bond stretching**
- **Small \( \omega \): small force constant, e.g., out-of-plane vibrations**
From vibrations to thermodynamic data

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

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

Hessian from geometry optimization not sufficient

- Analytic second derivative using perturbation theory [1]
- Numerical differentiation
  - Computational very expensive
  - Contains parameter (displacement), needs to be checked carefully
  - Often single displacement not sensible to sample all vibrations

Conclusions

Often calculated in harmonic approximation

Yield information about stability of geometry

Required for temperature effects

Anharmonic effects via molecular dynamics
Summary

Electronic part

– Careful with convergence parameters

– Mixing: Guaranteed or fast convergence
  • DIIS / Pulay state of the art

– Convergence Acceleration: Preconditioner and Smearing

– Initial Guess important
  • Think first before starting a calculations
Summary

Nuclear Structure Optimization

- Local structure optimization
  - Gradient-free method
  - Gradients
  - Model Hesse-matrix generated during search

- Vibrations in the harmonic approximation
  - Model Hess-matrix not sufficient
Thank you for your attention
Visualization

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

Nuclear coordinates

Electron distribution

What else can we learn?

How can we visualize results that are not just „numbers“
Codes use different types of basis functions and grids to store $n / \Psi$. 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
- Orbitals
- Scanning tunneling microscopy

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 orbitals contain „chemical information“

Eigenstate densities
- tend to agree well with $\Delta\text{SCF}$

![Diagram](image)

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

Pentacene HOMO density

$\Delta\text{SCF}$ 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 \((\mu)\) and sample \((\nu)\)

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

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**

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]

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 acceleration: 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
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 – beyond harmonic

For high $T$ or double-well minima
  - Molecular dynamics: Luca Ghiringhelli

Re-introducting quantum nuclei:
  - See talk by Roberto Car

![Graph showing energy levels vs. nuclear displacement]