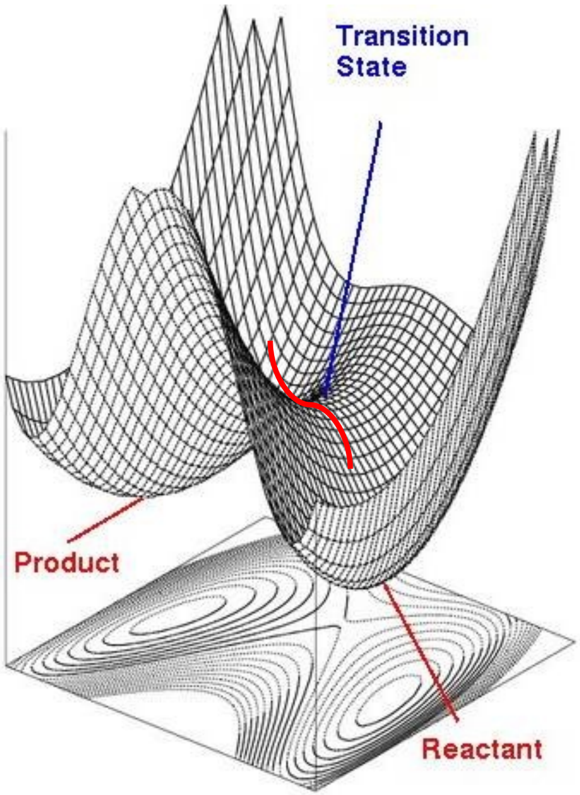
Forces and Structure Relaxation

Marivi Fernandez-Serra
Stony Brook University
Physics and Astronomy Department

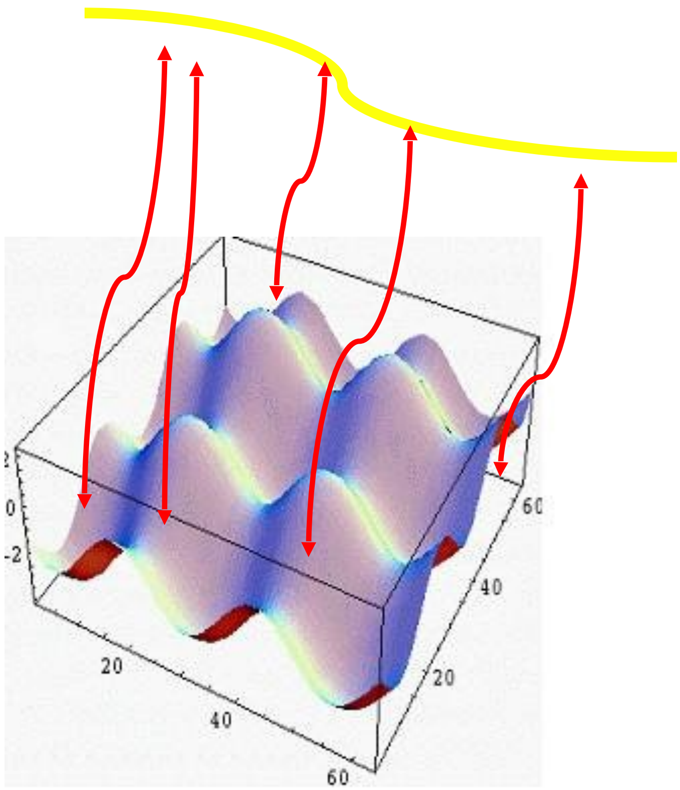
Stony Brook
University

Potential Energy Surface (PES)



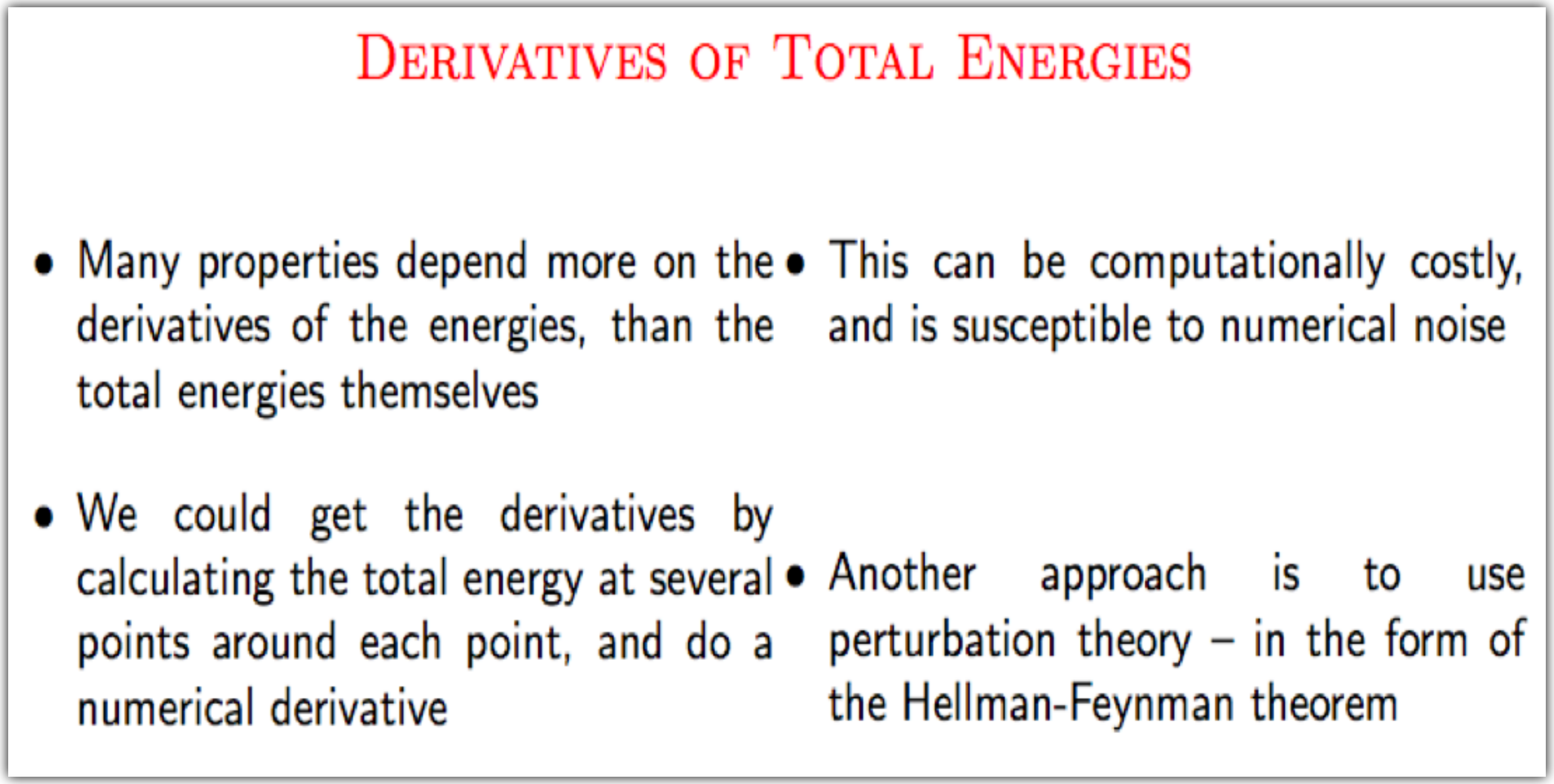
Optimizations and Phonons:

- We move on the PES
- Local vs global minima
- PES is harmonic close to minima



MD

- We move over the PES
- Good Sampling is required!!



Derivatives of Total Energies

- Many properties depend more on the derivatives of the energies, than the total energies themselves
- We could get the derivatives by calculating the total energy at several points around each point, and do a numerical derivative
- This can be computationally costly, and is susceptible to numerical noise
- Another approach is to use perturbation theory – in the form of the Hellman-Feynman theorem

The Hellman–Feynman theorem

- A way to calculate forces in quantum mechanics is provided by the *Hellman–Feynman theorem*
- In a general form, consider Hamiltonian $H(\lambda)$, depending on a continuous parameter λ.
- If $|\psi(\lambda)\rangle$ is an eigenvector of $H(\lambda)$ with eigenvalue $E(\lambda)$ then

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle \tag{1}$$

- Assume $|\psi(\lambda)\rangle$ is normalized:

$$\langle\psi(\lambda)|\psi(\lambda)\rangle = 1 \tag{2}$$

- Therefore

$$\frac{d}{d\lambda}\langle\psi(\lambda)|\psi(\lambda)\rangle = 0 \tag{3}$$

The Hellman–Feynman theorem

- The Hellman–Feynman theorem then states that

  $$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle \tag{4}$$

  i.e. the derivative of the *total energy* with respect to λ equals the expectation value of the derivative of the *Hamiltonian* with respect to λ. For the proof, we can write

  $$E(\lambda) = \langle \psi(\lambda) \left| H(\lambda) \right| \psi(\lambda) \rangle \tag{5}$$

- Differentiate both sides

  $$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle + \left\langle \frac{d\psi(\lambda)}{d\lambda} \left| H \right| \psi(\lambda) \right\rangle + \left\langle \psi(\lambda) \left| H \right| \frac{d\psi(\lambda)}{d\lambda} \right\rangle \tag{6}$$

The Hellman–Feynman theorem

- Because $|\psi(\lambda)\rangle$ is an eigenvector of $H(\lambda)$, we can write

$$\begin{aligned} \frac{dE}{d\lambda} = \left\langle \psi(\lambda) \middle| \frac{dH}{d\lambda} \middle| \psi(\lambda) \right\rangle + \\ E(\lambda)\left\langle \frac{d\psi(\lambda)}{d\lambda} |\psi(\lambda) \right\rangle + E(\lambda)\left\langle \psi(\lambda)| \frac{d\psi(\lambda)}{d\lambda} \right\rangle = \\ \left\langle \psi(\lambda) \middle| \frac{dH}{d\lambda} \middle| \psi(\lambda) \right\rangle + \\ E(\lambda)\left[\left\langle \frac{d\psi(\lambda)}{d\lambda} |\psi(\lambda) \right\rangle + \left\langle \psi(\lambda)| \frac{d\psi(\lambda)}{d\lambda} \right\rangle\right] \end{aligned} \qquad (7)$$

- Due to the normalization, the term in the brackets vanishes. We therefore have the Hellman–Feynman theorem

The Hellman–Feynman theorem

- Associate parameter λ with the nuclear coordinates $\mathbf{R}$.
- The forces acting on atoms can therefore be calculated as

$$\mathbf{F}_I = \nabla_I \varepsilon(\mathbf{R}) = \langle \psi_0 | \nabla_I H(\mathbf{R}) | \psi_0 \rangle \tag{8}$$

- The only term in the KS Hamiltonian which depends on the atomic coordinates is the external potential. Therefore

$$\mathbf{F}_I = - \int \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial \mathbf{R}_I} n(\mathbf{r}) d\mathbf{r} \tag{9}$$

- One can therefore do classical dynamics of ions using forces derived from *ab initio* electronic structure
- If the basis set depends on the ionic positions (*e.g.* atomic orb. Gaussians), the terms in the brackets in (7) will not go exactly to zero ⇒ *Pulay forces*

Forces on the atoms

Hellman-Feynmann theorem:

$$F_I = -\frac{\partial\langle\psi|H|\psi\rangle}{\partial R_I} = -\cancel{\left\langle\frac{\partial\psi}{\partial R_I}\middle|H\middle|\psi\right\rangle} - \cancel{\left\langle\psi\middle|H\middle|\frac{\partial\psi}{\partial R_I}\right\rangle} - \left\langle\psi\middle|\frac{\partial H}{\partial R_I}\middle|\psi\right\rangle$$

Using an atomic-like basis:

$$\psi(\mathbf{r}) = \sum_{\mu} c_{\mu}\phi_{\mu}(\mathbf{r})$$

$$F_I = -\frac{\partial\langle\psi|H|\psi\rangle}{\partial R_I} = -\frac{\partial}{\partial R_I}\sum_{\mu\nu} c_{\mu}c_{\nu}\langle\phi_{\mu}|H|\phi_{\nu}\rangle$$

$$= -\sum_{\mu\nu}\left[\cancel{\frac{\partial c_{\mu}}{\partial R_I}c_{\nu}} + \cancel{c_{\mu}\frac{\partial c_{\nu}}{\partial R_I}}\right]\langle\phi_{\mu}|H|\phi_{\nu}\rangle - \sum_{\mu\nu} c_{\mu}c_{\nu}\left\langle\phi_{\mu}\middle|\frac{\partial H}{\partial R_I}\middle|\phi_{\nu}\right\rangle -$$

$$-\sum_{\mu\nu} c_{\mu}c_{\nu}\left[\left\langle\frac{\partial\phi_{\mu}}{\partial R_I}\middle|H\middle|\phi_{\nu}\right\rangle + \left\langle\phi_{\mu}\middle|H\middle|\frac{\partial\phi_{\nu}}{\partial R_I}\right\rangle\right]$$

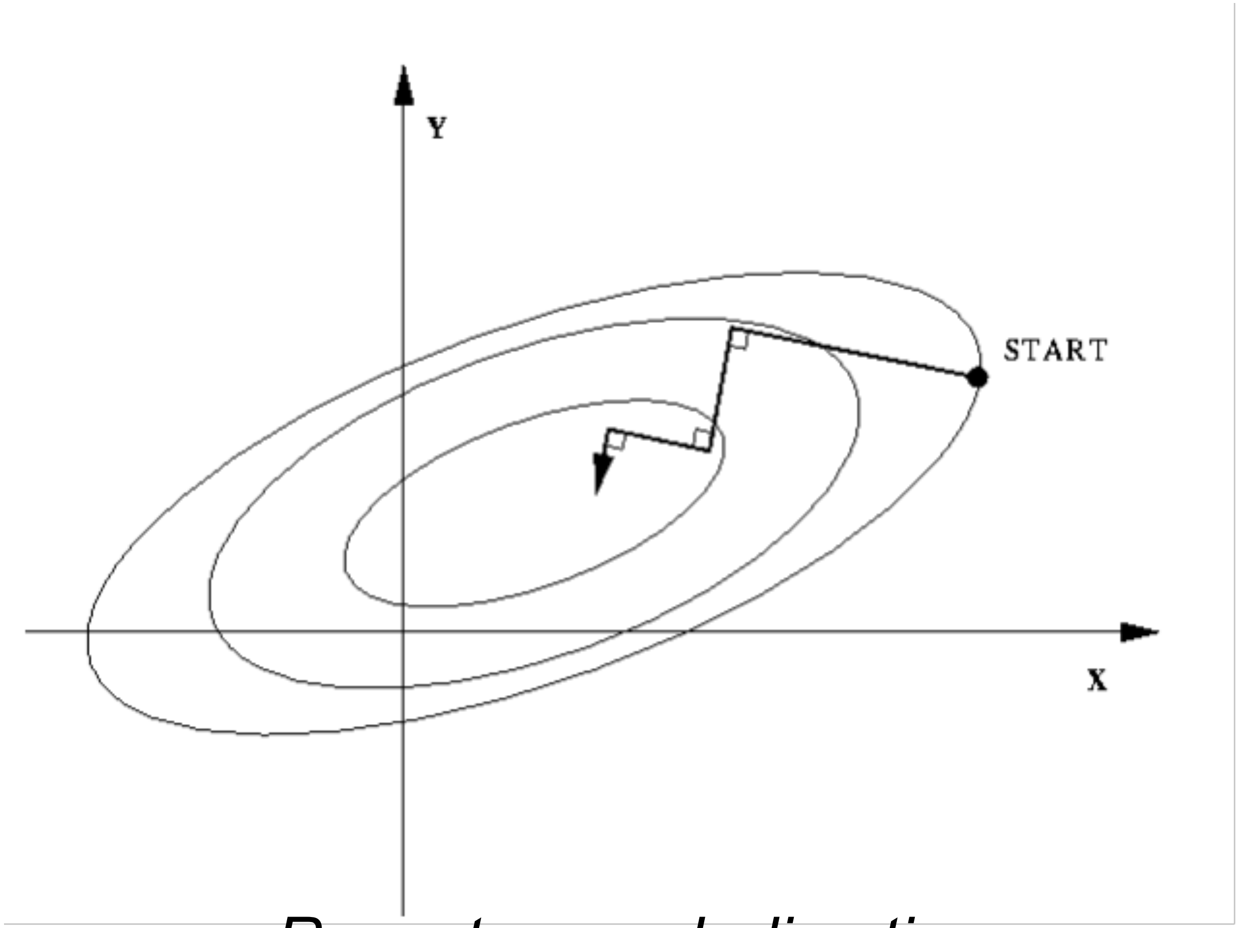
Pulay forces

The Hellman-Feynman Theorem and Density Functional Theory

$$\boxed{H_{\mathbf{R}} = -\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{\mathrm{e-e}}(\mathbf{r}) + V_{\mathrm{ion-e}}(\mathbf{r},\mathbf{R}) + V_{\mathrm{xc}}(\mathbf{r}) + V_{\mathrm{ion-ion}}(\mathbf{R})}$$

- The DFT Hamiltonian is parameterised in $\mathbf{R}$
- We get a contribution from the ion-electron (pseudo)potential
- We get a contribution from the ion-ion Couloumb interaction (from the Ewald sum)
- For the stresses, there are contributions from the kinetic energy and the Hartree terms
- While the total energy is correct to second order in the errors, the forces are only good to first order

Structural optimisation: Steepest descent

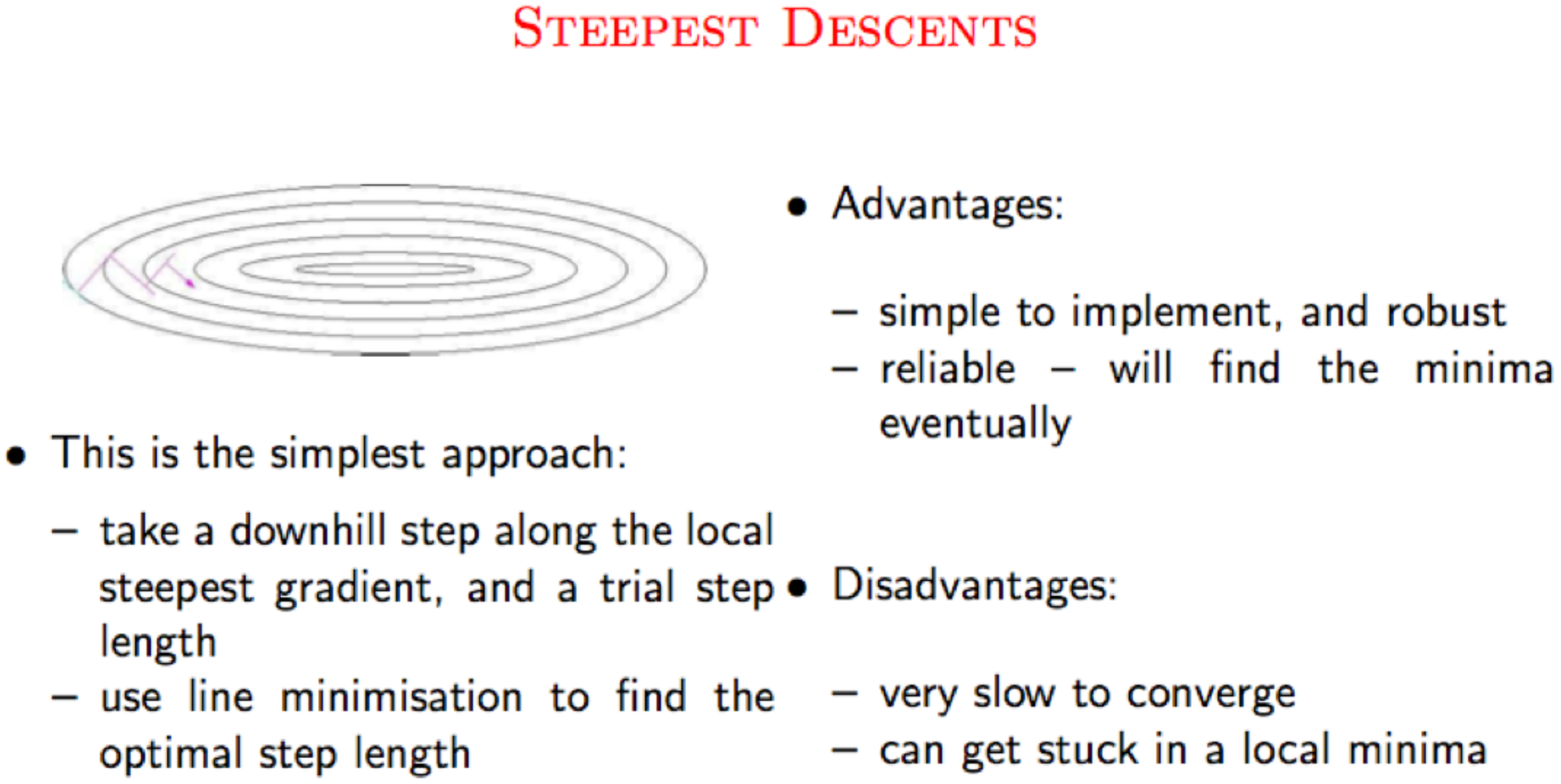


Repeats search directions

Structural optimisation:

minimum E vs atomic positions

Follow forces on atoms (gradient of function)



Steepest Descents

- This is the simplest approach:
  - take a downhill step along the local steepest gradient, and a trial step length
  - use line minimisation to find the optimal step length

- Advantages:
  - simple to implement, and robust
  - reliable – will find the minima eventually

- Disadvantages:
  - very slow to converge
  - can get stuck in a local minima

Theory for (local) geometry optimization

$$E(x+\delta x)=E(x)+\underset{\substack{\uparrow\\ \textit{Gradients}}}{G(x)}\delta x+\frac{1}{2}\underset{\substack{\uparrow\\ \textit{Hessian}}}{H(x)}\delta x^{2}$$

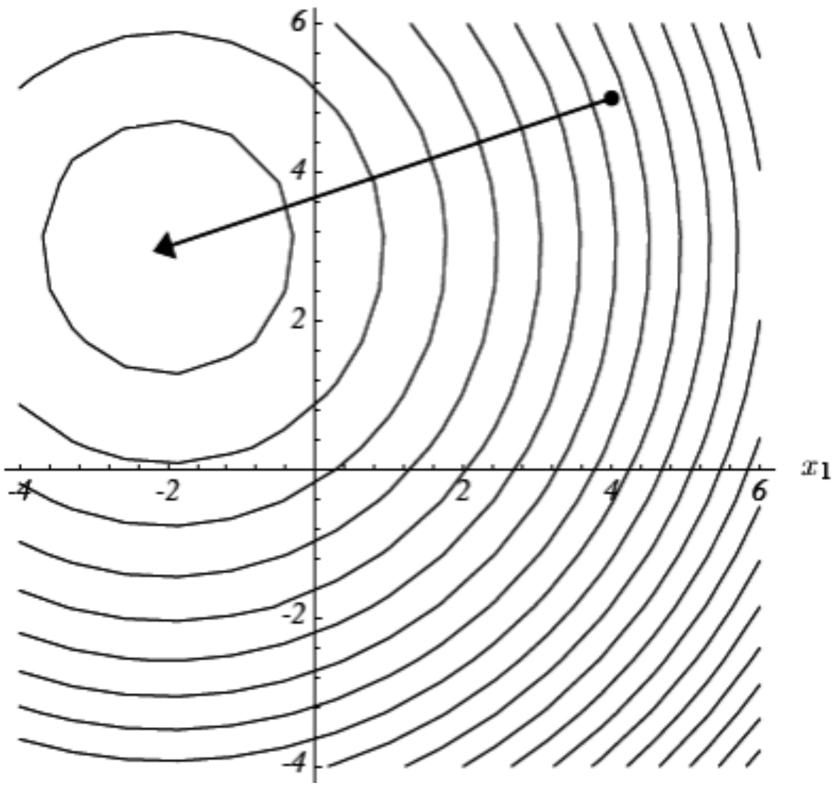
$$\delta x=-\underset{\substack{\uparrow\\ \alpha\ \textit{= 1 for quadratic region}}}{\alpha}H(x)^{-1}G(x)$$

Energy minimisation within a basin

Conditioning

Given eigenvalues of Hessian $$H\vec{\chi}_i = \omega_i \vec{\chi}_i$$

Condition number: $\kappa \propto \dfrac{\omega_i^{max}}{\omega_i^{min}}$ *Determines convergence*



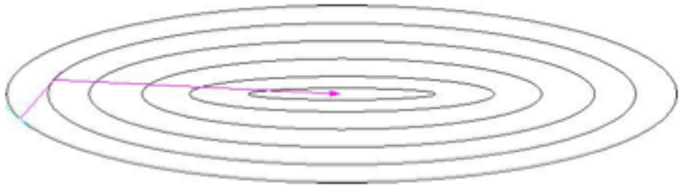
It converges on the first iteration If all ω are equal

Structural optimisation:

minimum E vs atomic positions

Follow forces on atoms (gradient of function)

Conjugate Gradients



- This improves on steepest descents:
  - the gradient is constructed to be conjugate to all previous directions
  - does not undo previous minimisation
  - a line minimisation is performed

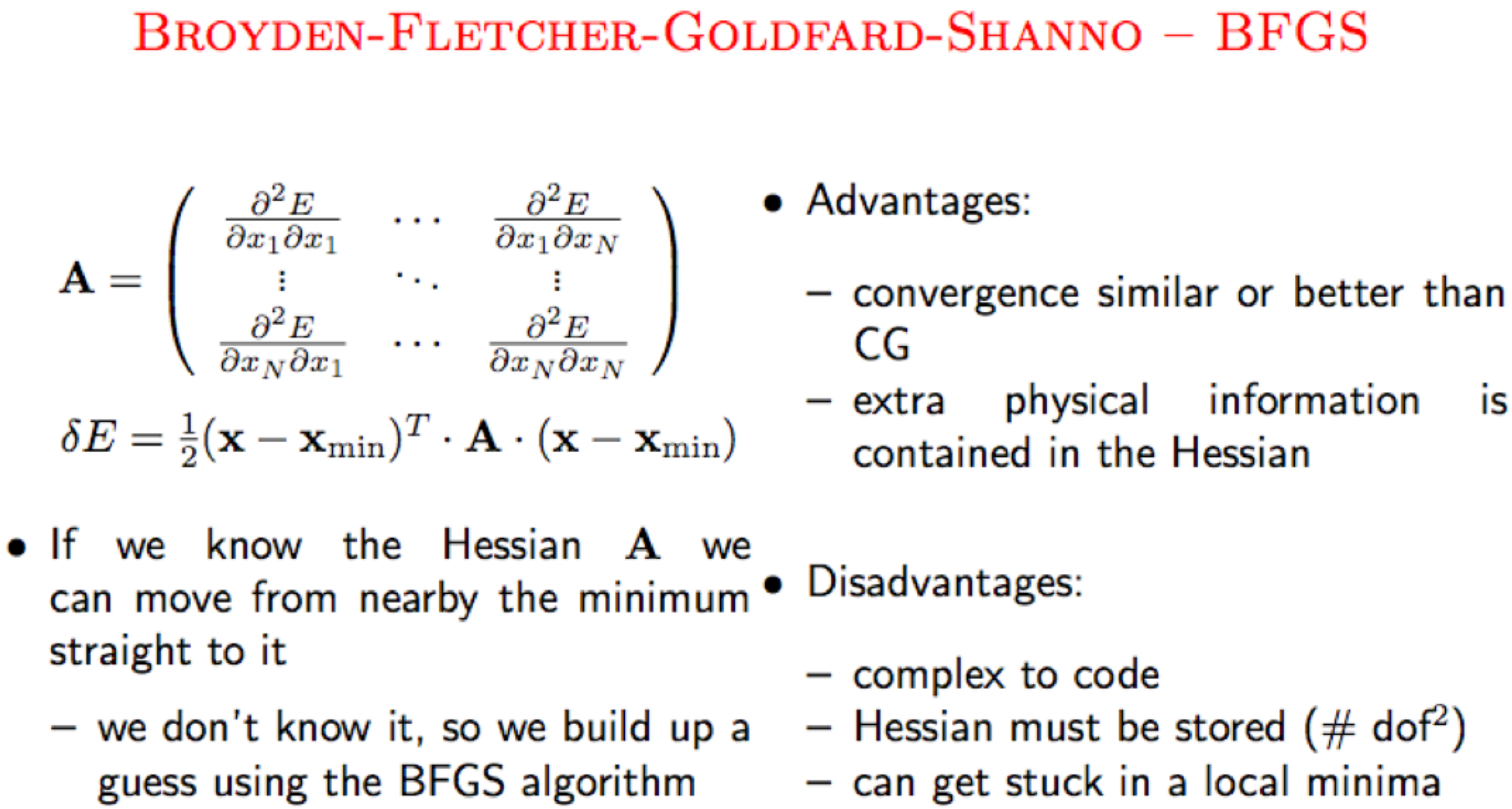
- Advantages:
  - rapid convergence – in a quadratic energy landscape, one dof per iteration
  - low storage requirements

- Disadvantages:
  - more complex to implement than SD
  - Hessian not explicitly calculated
  - can get stuck in a local minima

Structural optimisation:

minimum E vs atomic positions

Follow forces on atoms (gradient of function)



Broyden-Fletcher-Goldfard-Shanno – BFGS

$$\mathbf{A} = \begin{pmatrix} \frac{\partial^2 E}{\partial x_1 \partial x_1} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial x_N} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial x_N \partial x_1} & \cdots & \frac{\partial^2 E}{\partial x_N \partial x_N} \end{pmatrix}$$

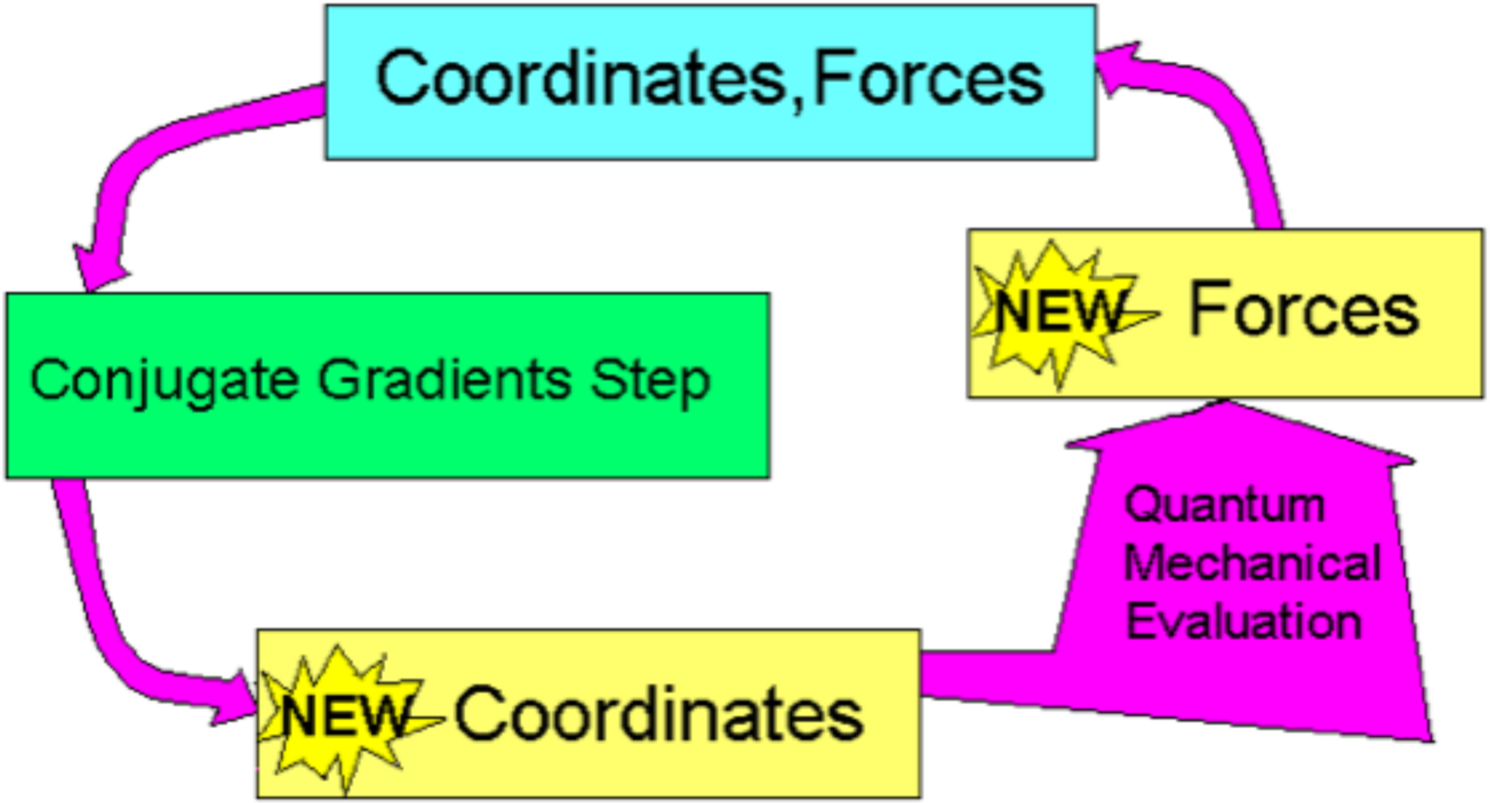
$$\delta E = \tfrac{1}{2}(\mathbf{x} - \mathbf{x}_{\mathrm{min}})^T \cdot \mathbf{A} \cdot (\mathbf{x} - \mathbf{x}_{\mathrm{min}})$$

- If we know the Hessian $\mathbf{A}$ we can move from nearby the minimum straight to it
  - we don't know it, so we build up a guess using the BFGS algorithm

- Advantages:
  - convergence similar or better than CG
  - extra physical information is contained in the Hessian

- Disadvantages:
  - complex to code
  - Hessian must be stored (# dof^2)
  - can get stuck in a local minima

Optimization (and MD) general basic Step



Coordinates,Forces

Conjugate Gradients Step

NEW Coordinates

Quantum Mechanical Evaluation

NEW Forces

Optimization in SIESTA(1)

- *Set runtype to conjugate gradients:*

  MD.TypeOfRun CG, Broyden

- *Set maximum number of iterative steps:*

  MD.NumCGsteps 100

- *Optionally set force tolerance:*

  MD.MaxForceTol 0.04 eV/Ang

- *Optionally set maximum displacement:*

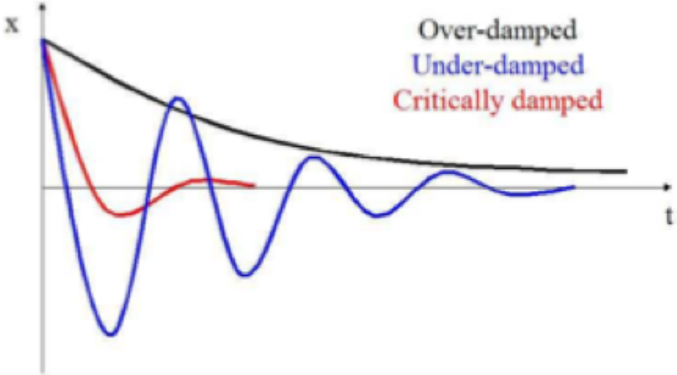
  MD.MaxCGDispl 0.2 Bohr

Structural optimisation:

minimum E vs atomic positions

Follow forces on atoms (gradient of function)

DAMPED MOLECULAR DYNAMICS



- This improves on steepest descents:
  - use velocities as well as forces
  - start with $\mathbf{v} = \mathbf{0}$ and add damping term to forces $-\gamma\mathbf{v}$
  - adjust γ and time step to obtain optimal convergence

- Advantages:
  - simple to implement, robust and more efficient than SD
  - can use wavefunction extrapolation (or Car-Parinello)

- Disadvantages:
  - convergence rate depends on damping factor γ
  - can get stuck in a local minima

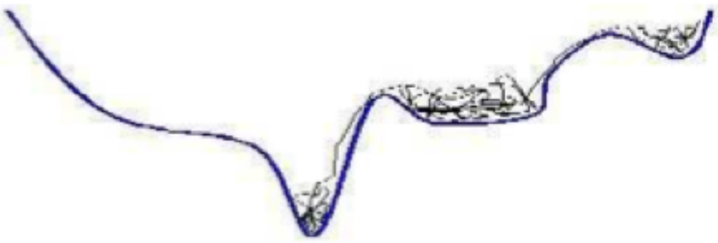
Structural optimisation:

global minimum E vs atomic positions

Follow forces on atoms (gradient of function)

SIMULATED ANNEALING

MD



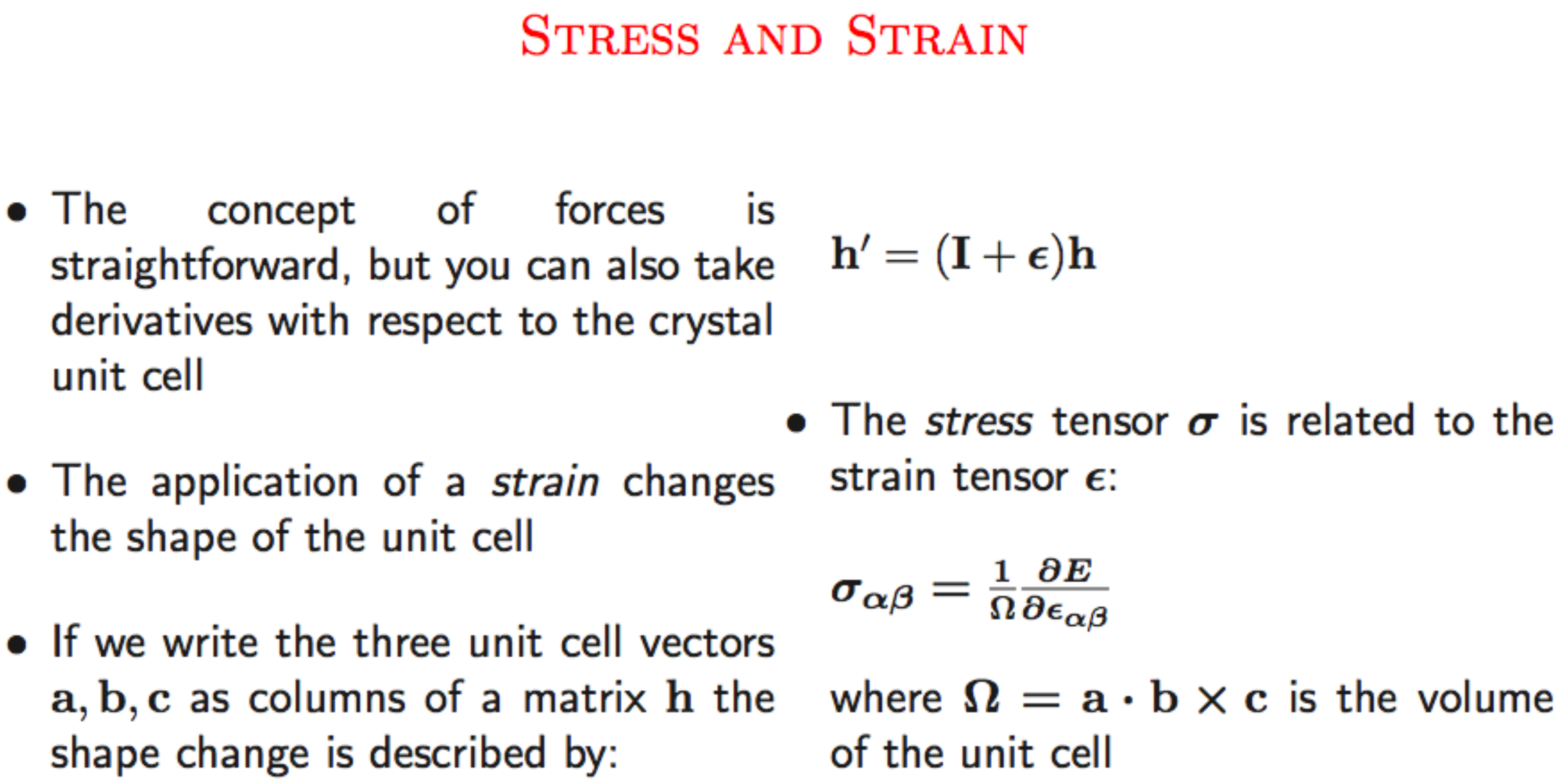
- Advantages:
  - very robust and reliable
  - reasonably immune to getting stuck in local minima

- This is a stochastic method:
  - always accept steps that lower the energy, and sometimes accept upward steps, using a Boltzman distribution
  - slowly reduce temperature, and iterate to the goundstate

- Disadvantages:
  - incredibly slow convergence
  - the cooling rate must be carefully adjusted to avoid quenching into local minima
  - no guarantee that the true global minima will be found

Structural optimisation:

Variable cell



Stress and Strain

- The concept of forces is straightforward, but you can also take derivatives with respect to the crystal unit cell
- The application of a *strain* changes the shape of the unit cell
- If we write the three unit cell vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$ as columns of a matrix $\mathbf{h}$ the shape change is described by:

$$\mathbf{h}' = (\mathbf{I} + \boldsymbol{\epsilon})\mathbf{h}$$

- The *stress* tensor $\boldsymbol{\sigma}$ is related to the strain tensor $\boldsymbol{\epsilon}$:

$$\boldsymbol{\sigma}_{\alpha\beta} = \frac{1}{\Omega}\frac{\partial E}{\partial \epsilon_{\alpha\beta}}$$

where $\boldsymbol{\Omega} = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ is the volume of the unit cell

Stress tensor and pressure

$$r_\alpha \rightarrow \sum_\beta \varepsilon_{\alpha\beta} r_\beta \qquad \alpha,\beta = \{x,y,z\}$$

$$u_{i\alpha} \rightarrow \sum_\beta \varepsilon_{\alpha\beta} u_{i\beta}$$

Strain tensor

$$\sigma_{\alpha\beta} \equiv \frac{1}{\Omega}\frac{\partial E}{\partial \varepsilon_{\alpha\beta}}$$

Stress tensor (Siesta)

$$P = -\frac{1}{3}\sum_\alpha \sigma_{\alpha\alpha}$$

Hydrostatic pressure

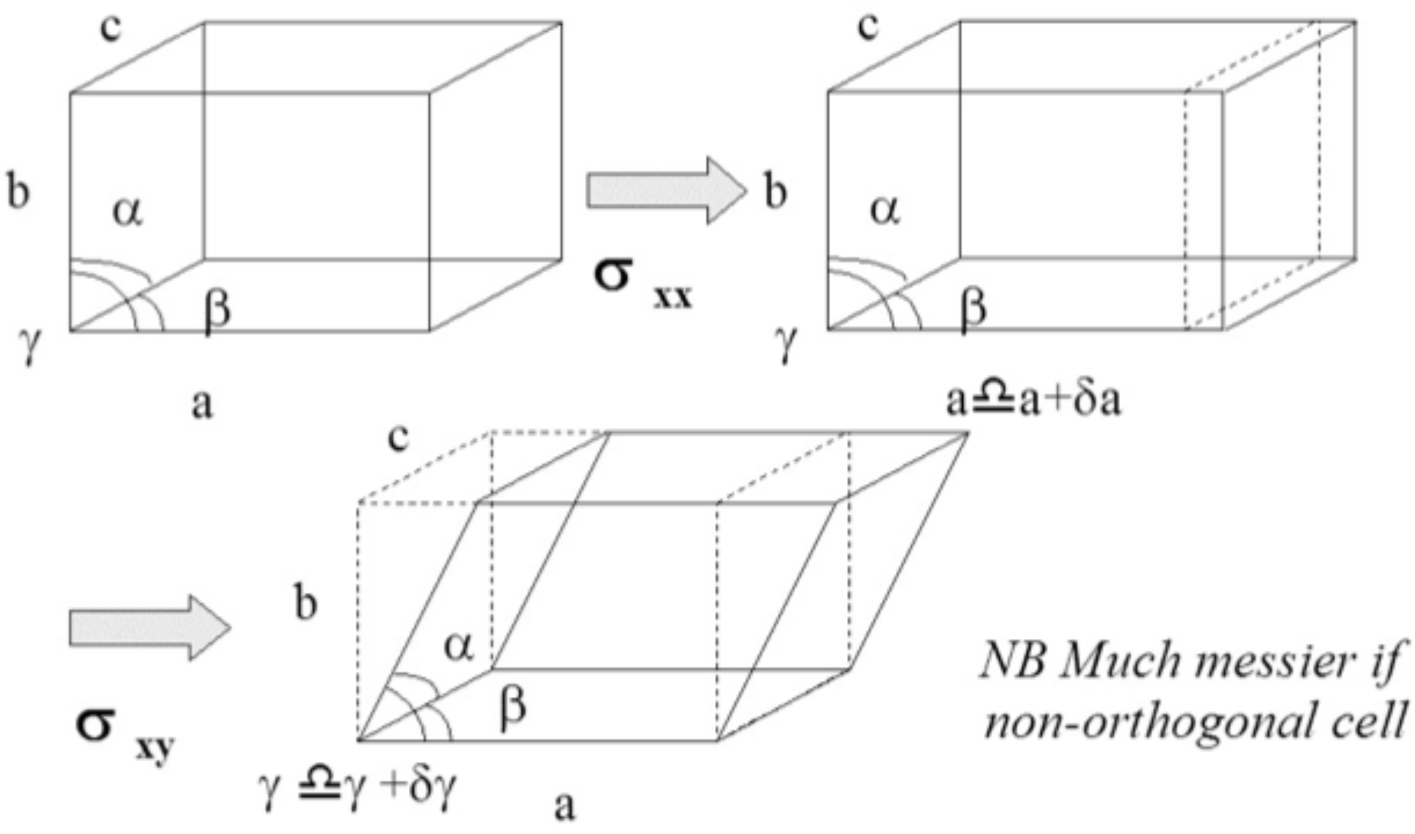
$$P_{mol} = P - \frac{1}{\Omega}\sum_I \mathbf{R}_I \mathbf{F}_I$$

Corrected pressure

Structural optimisation:

Variable cell

Stress and Strain



NB Much messier if non-orthogonal cell

Optimizations in SIESTA(2)

By default optimisations are for a fixed cell

- *To allow unit cell to vary:*
  MD.VariableCell true

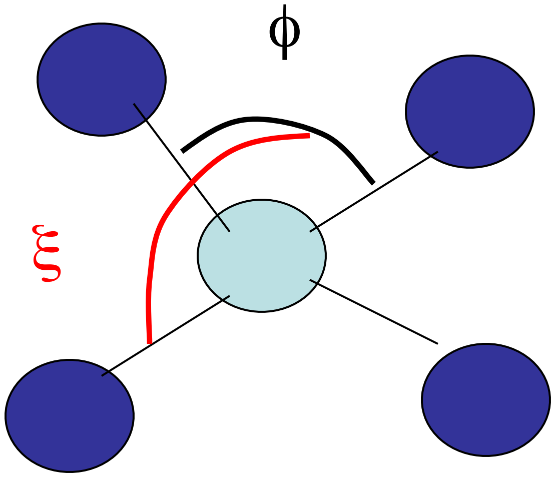
- *Optionally set stress tolerance:*
  MD.MaxStressTol 0.1 Gpa

- *Optionally set cell preconditioning:*
  MD.PreconditionVariableCell 5.0 Ang

- *Set an applied pressure:*
  MD.TargetPressure 5.0 GPa

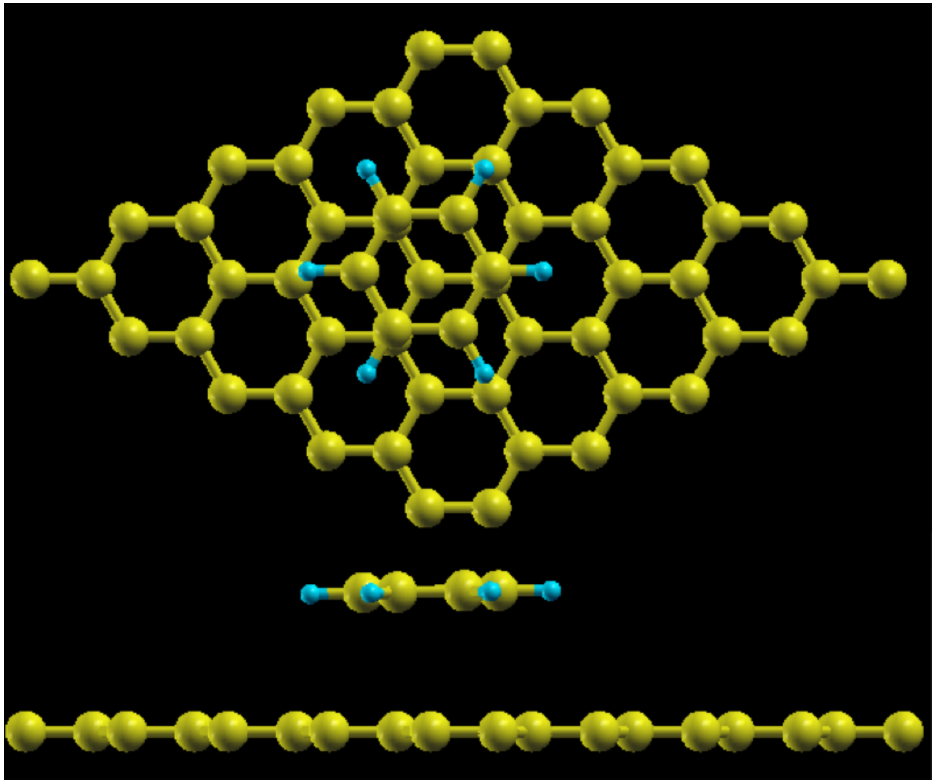
Z-Matrix coordinate format

- *Internal coordinates: Molecules represented by :*
  - *Bond lengths* χ_i
  - *Bending angles* ϕ_i
  - *Dihedral angles* ξ_i



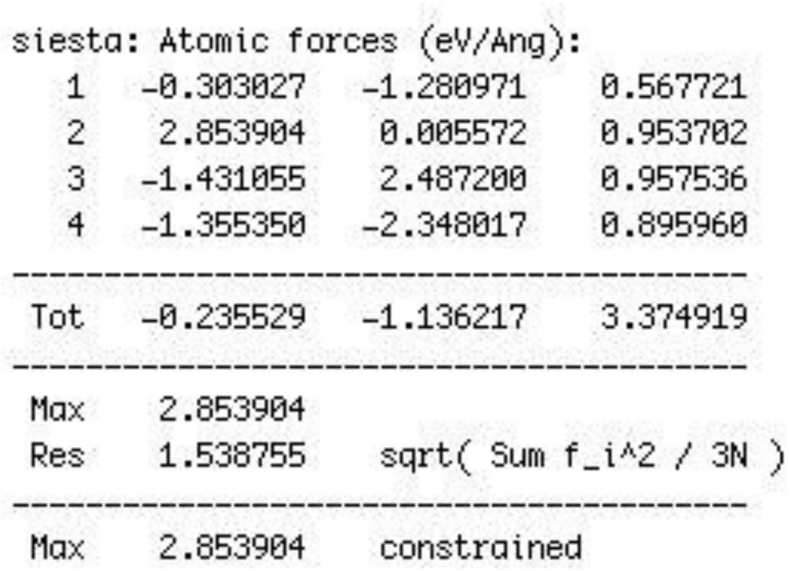
Z-Matrix

- *Allows for mixing of generalised and Cartesian coordinates: Useful for constrained relaxations*



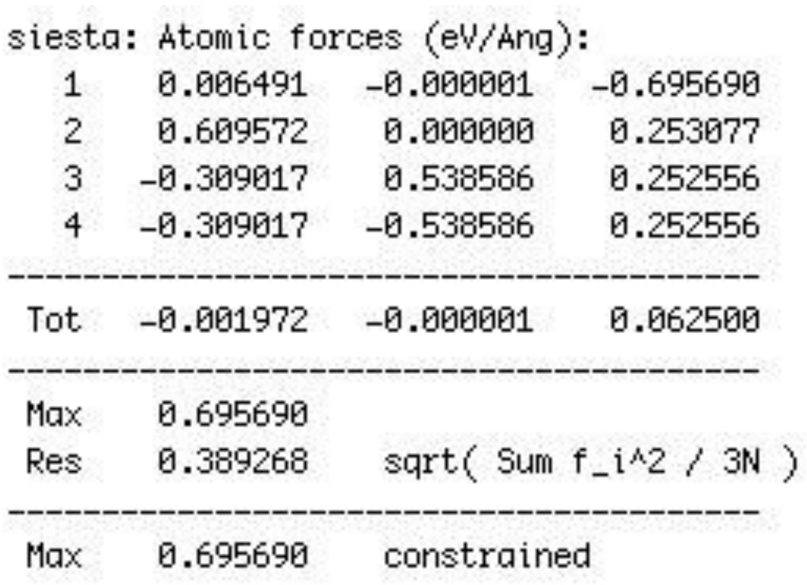
Explore the PES by using
A relevant coordinate:
Useful for estimating
barriers

Advice on optimizations in SIESTA(I)



```
siesta: Atomic forces (eV/Ang):
    1   -0.303027   -1.280971    0.567721
    2    2.853904    0.005572    0.953702
    3   -1.431055    2.487200    0.957536
    4   -1.355350   -2.348017    0.895960
----------------------------------------
  Tot   -0.235529   -1.136217    3.374919
----------------------------------------
  Max    2.853904
  Res    1.538755    sqrt( Sum f_i^2 / 3N )
----------------------------------------
  Max    2.853904    constrained
```

×



```
siesta: Atomic forces (eV/Ang):
    1    0.006491   -0.000001   -0.695690
    2    0.609572    0.000000    0.253077
    3   -0.309017    0.538586    0.252556
    4   -0.309017   -0.538586    0.252556
----------------------------------------
  Tot   -0.001972   -0.000001    0.062500
----------------------------------------
  Max    0.695690
  Res    0.389268    sqrt( Sum f_i^2 / 3N )
----------------------------------------
  Max    0.695690    constrained
```

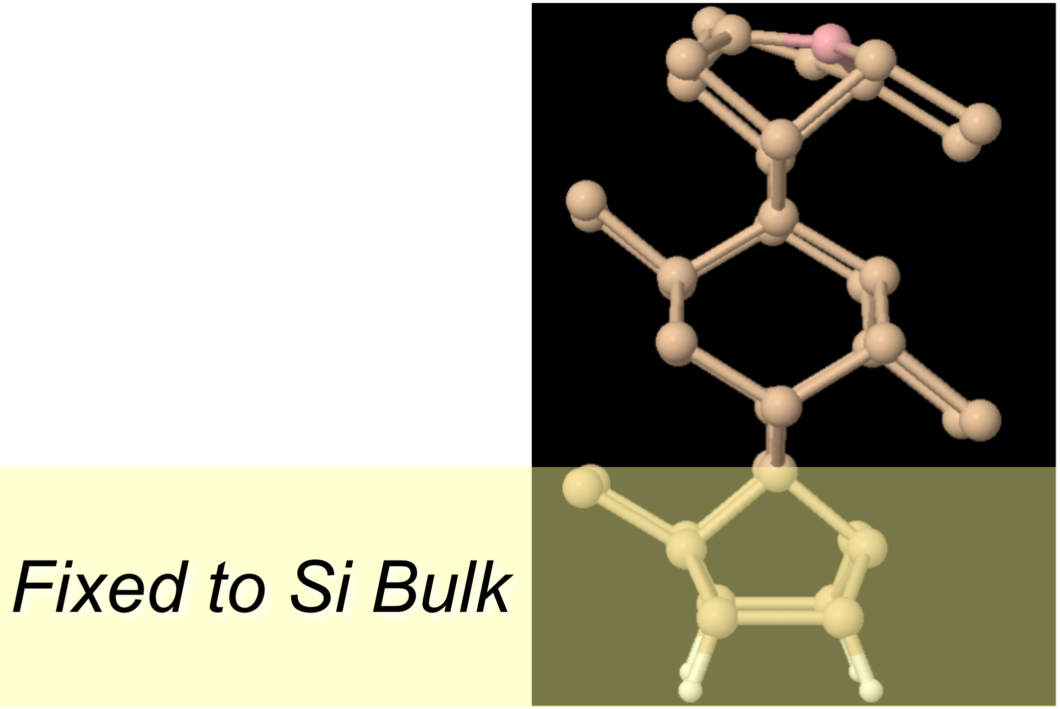
✓

Eggbox ….

Advice on Optimizations in SIESTA(II)

Ill-conditioned systems (soft modes) can slow down optimizations, very sensitive to mesh cutoff.

Use constraints when relevant.

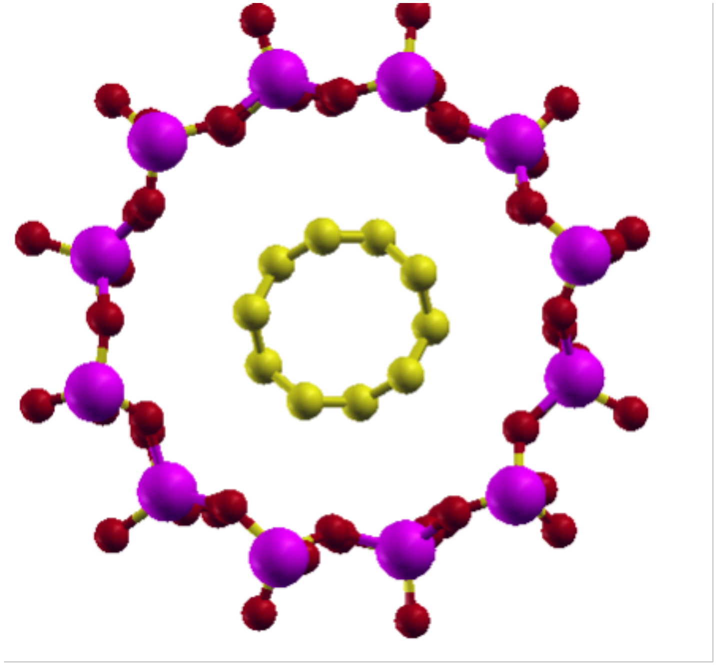


Fixed to Si Bulk

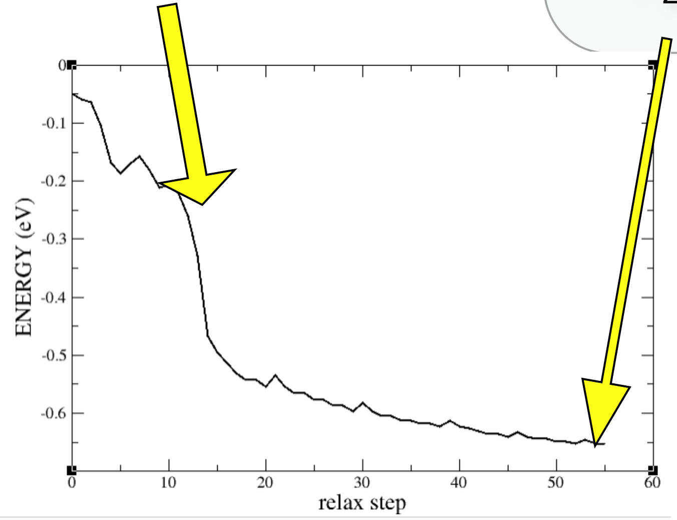
Advice on Optimizations in SIESTA(III)

- *Decouple Degrees of freedom (relax separately different parts of the system).*

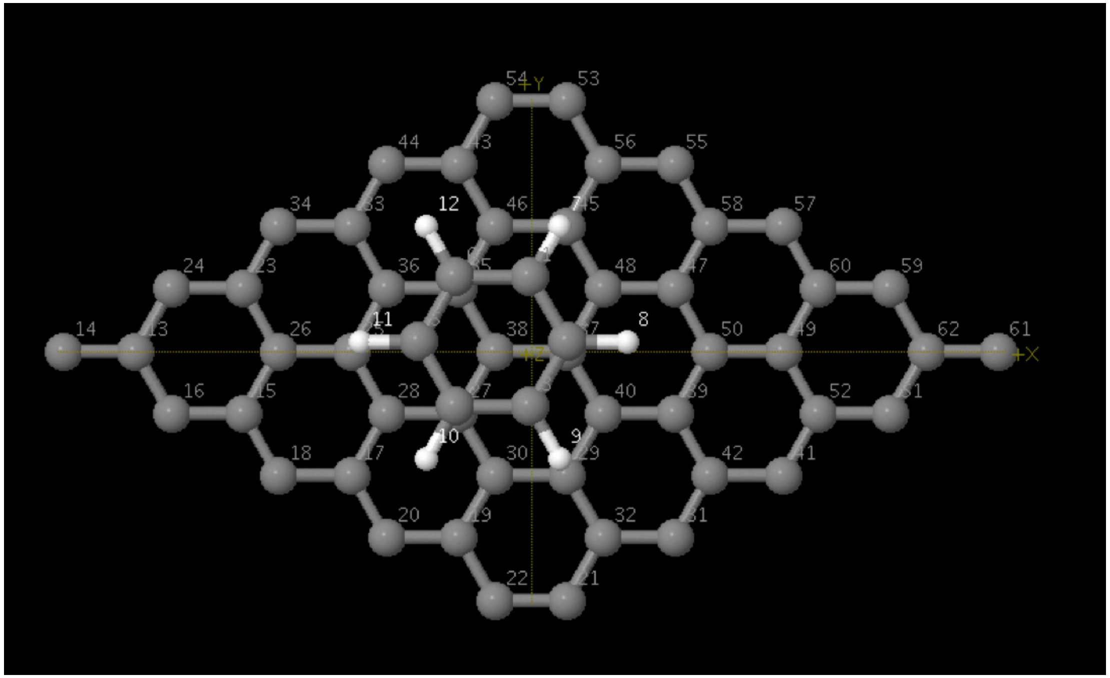
Look at the evolution of relevant physics quantities (band structure, Ef).

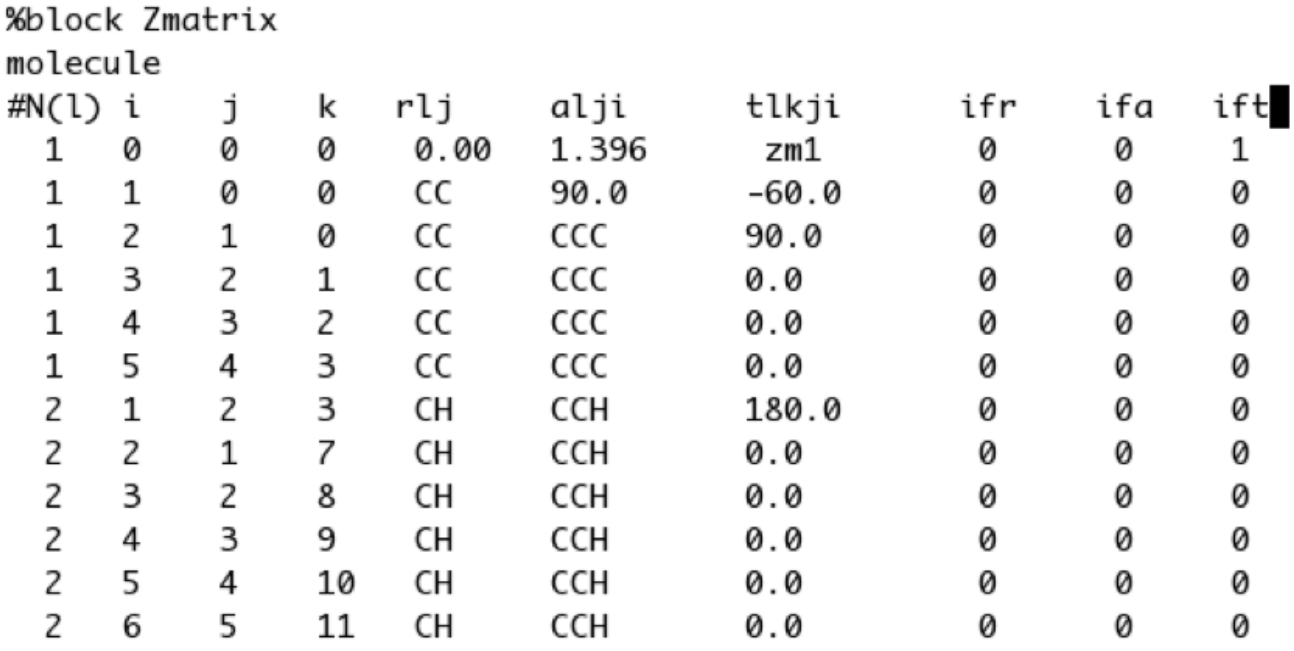


No constraints



Fix the Zeolite,
Its relaxation is no
Longer relevant.
F_{tube}<0.04 eV/A
F_{zeol}>0.1 eV/A





```
%block Zmatrix
molecule
#N(l) i     j     k    rlj       alji        tlkji       ifr      ifa     ift
  1   0     0     0     0.00     1.396        zm1         0        0       1
  1   1     0     0     CC       90.0        -60.0        0        0       0
  1   2     1     0     CC       CCC         90.0         0        0       0
  1   3     2     1     CC       CCC         0.0          0        0       0
  1   4     3     2     CC       CCC         0.0          0        0       0
  1   5     4     3     CC       CCC         0.0          0        0       0
  2   1     2     3     CH       CCH         180.0        0        0       0
  2   2     1     7     CH       CCH         0.0          0        0       0
  2   3     2     8     CH       CCH         0.0          0        0       0
  2   4     3     9     CH       CCH         0.0          0        0       0
  2   5     4     10    CH       CCH         0.0          0        0       0
  2   6     5     11    CH       CCH         0.0          0        0       0
```