http://exciting-code.org

Structure Optimization and Elasticity

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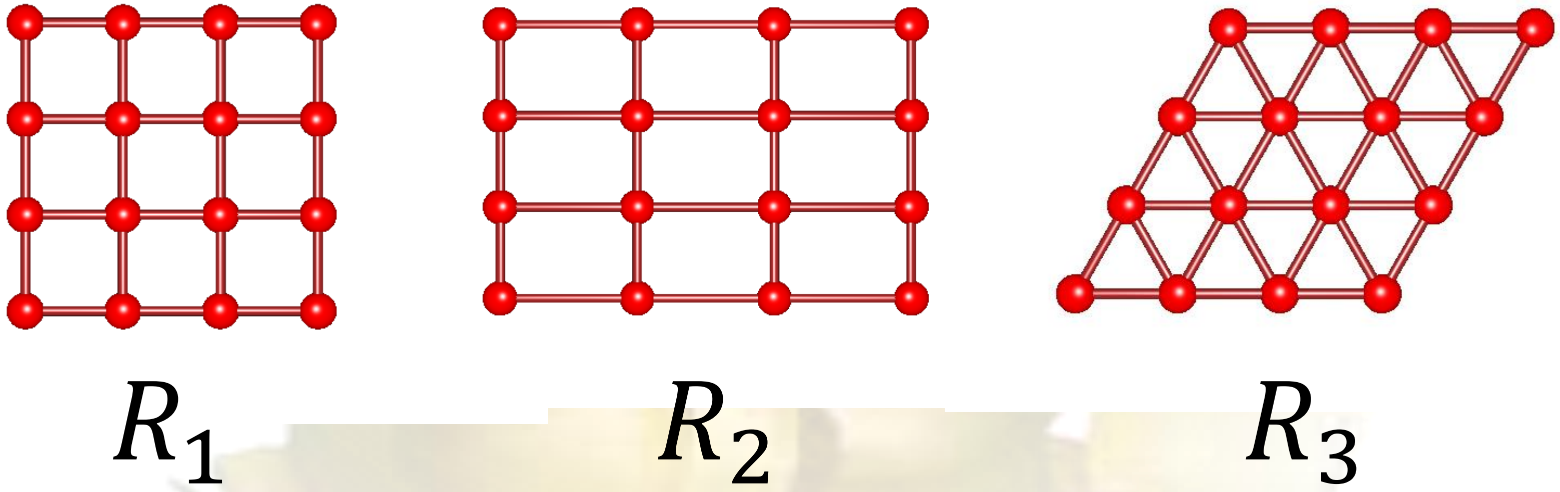
Outline

- Structure optimization
  - Cell optimization
  - Internal degrees of freedom
- Elasticity

Structure Optimization

Structure Optimization

Atomic configurations:



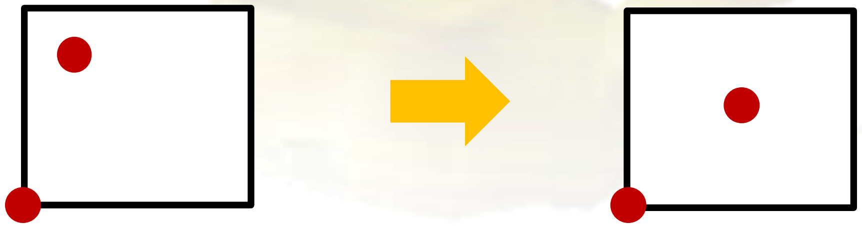
Which configuration has the lowest DFT total energy?

Structure Optimization

- (a): **Cell shape**

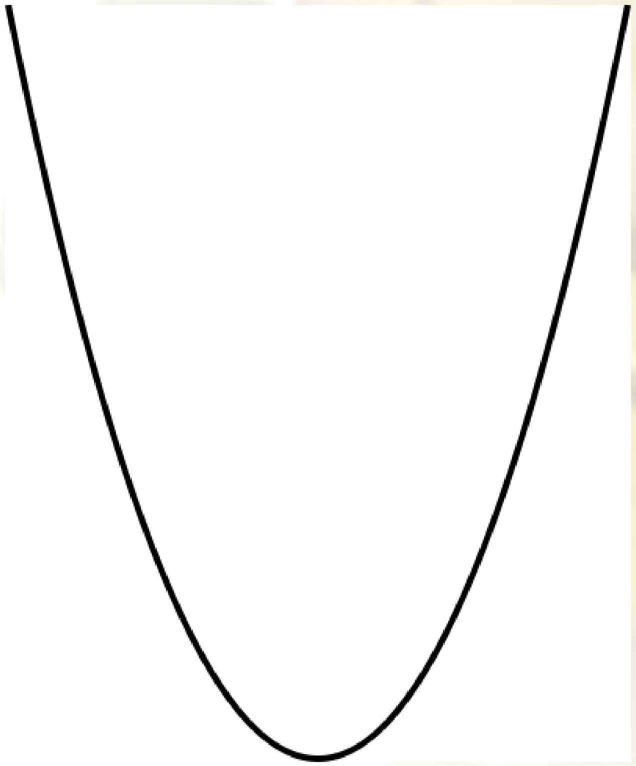
stress

- (b): **(Relative) atomic positions**

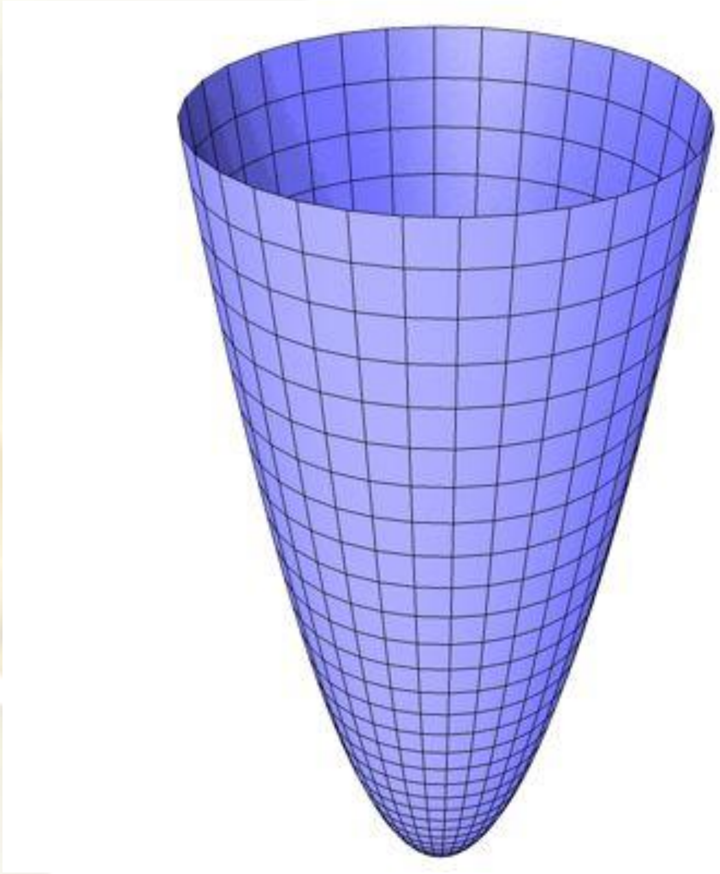


force

Energy Minimization

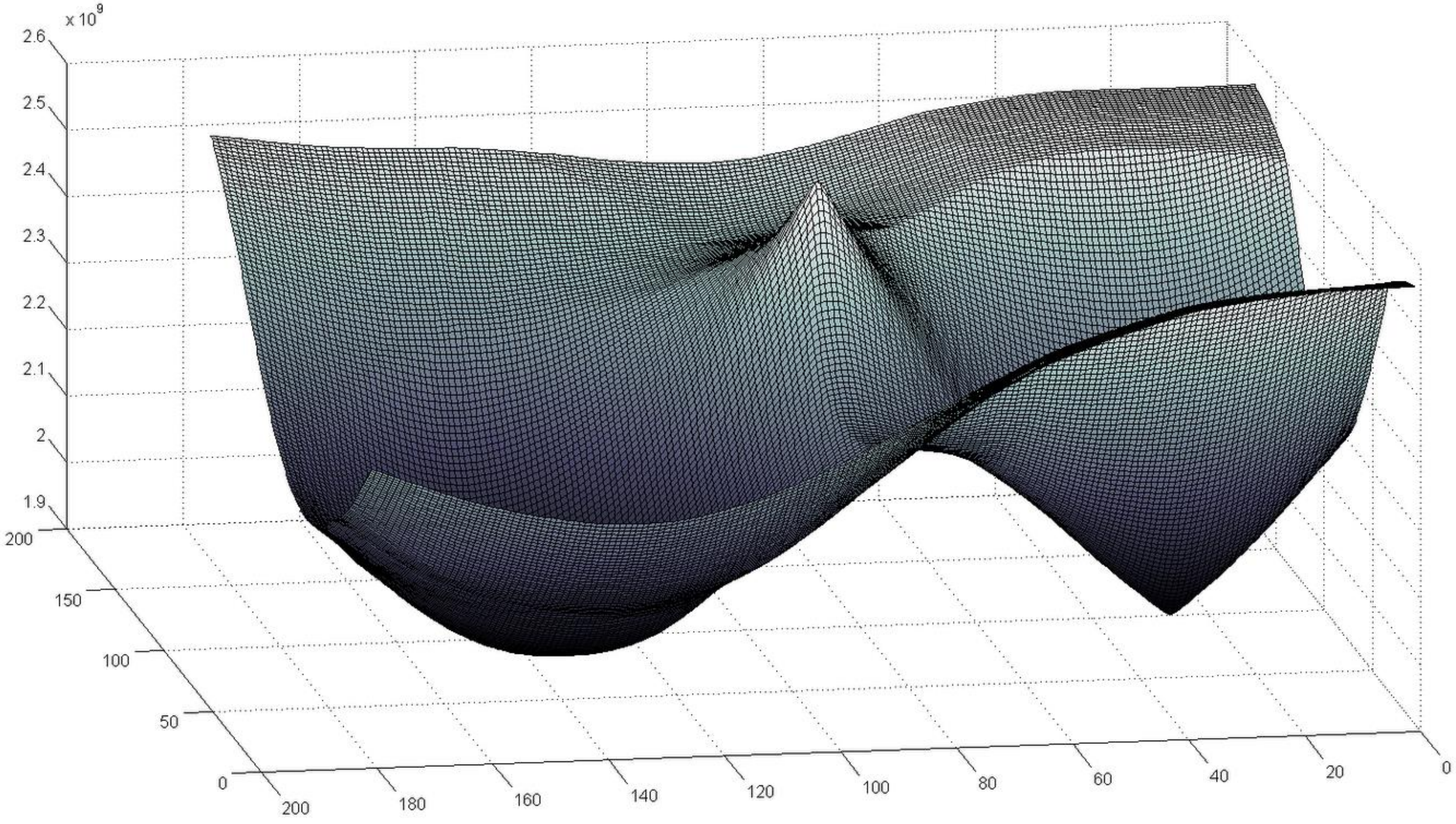


parabola

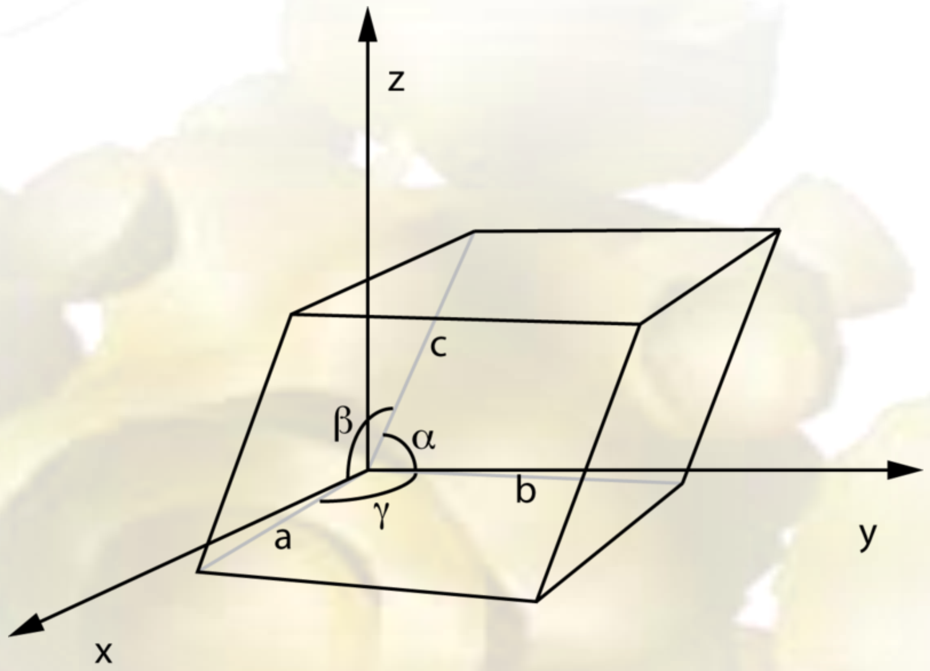


paraboloid

Energy Minimization



Lattice (Cell) Optimization



$$E = E(\mathbf{a}, \mathbf{b}, \mathbf{c}, \alpha, \beta, \gamma)$$

↕

$$E = E(\mathbf{V}, \mathbf{b}/\mathbf{a}, \mathbf{c}/\mathbf{a}, \alpha, \beta, \gamma)$$

Equation of State (EOS)

$$E = E(\mathbf{V})$$

- [ ] Murnaghan EOS
- [x] Birch-Murnaghan EOS
- [ ] Vinet EOS
- [ ] Polynomial EOS

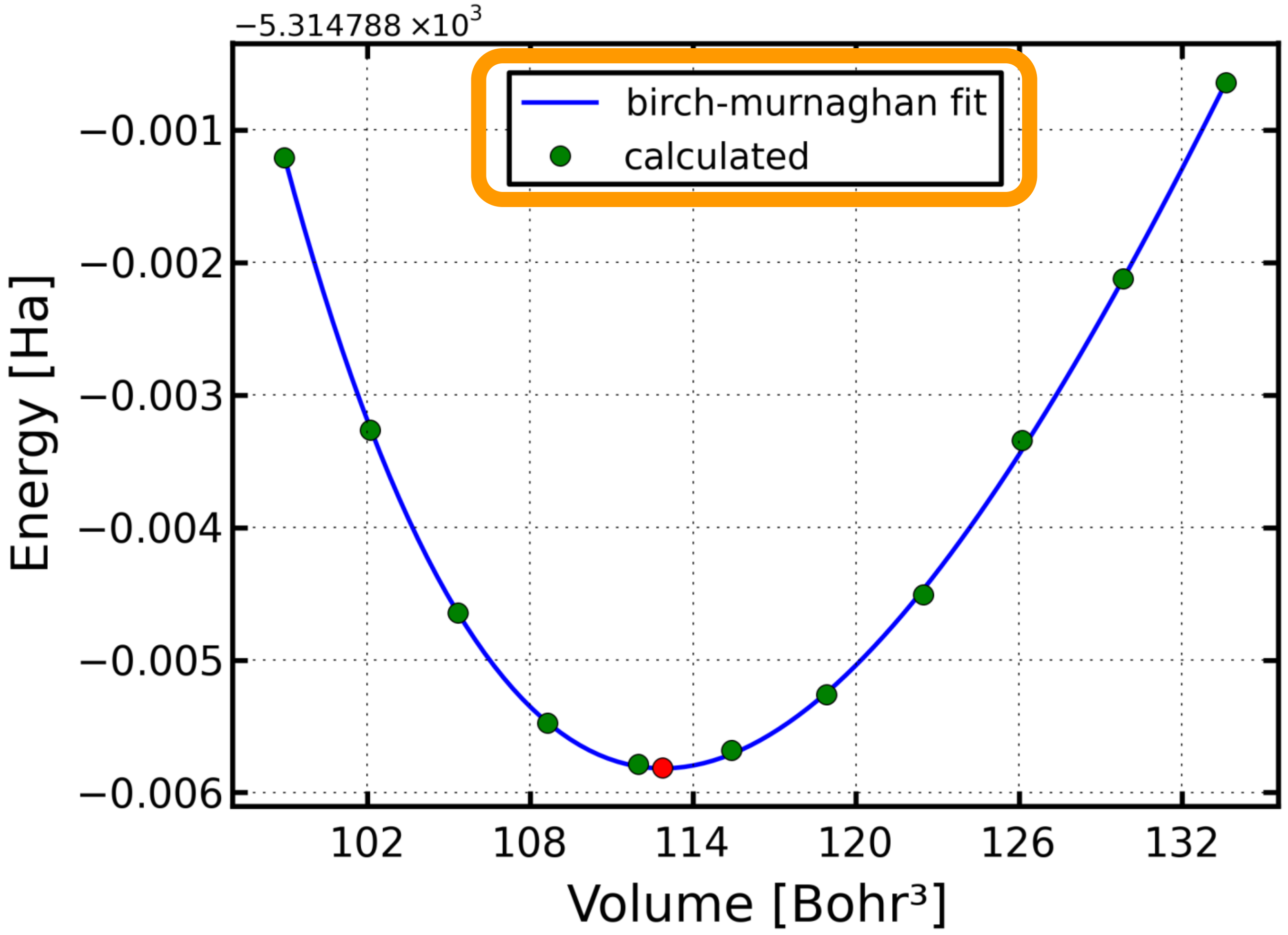
Birch-Murnaghan EOS

$$B_0 = -V\left(\frac{\partial P}{\partial V}\right)_{P=0} \qquad B_0' = \left(\frac{\partial B}{\partial P}\right)_{P=0}$$

$$P(V) = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right]\left\{1 + \frac{3}{4}\left(B_0' - 4\right)\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]\right\}.$$

$$E(V) = \boxed{E_0} + \frac{9V_0\boxed{B_0}}{16}\left\{\left[\left(\frac{\boxed{V_0}}{V}\right)^{2/3} - 1\right]^3\boxed{B_0'} + \left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]^2\left[6 - 4\left(\frac{V_0}{V}\right)^{2/3}\right]\right\}.$$

Equation of State of Silver

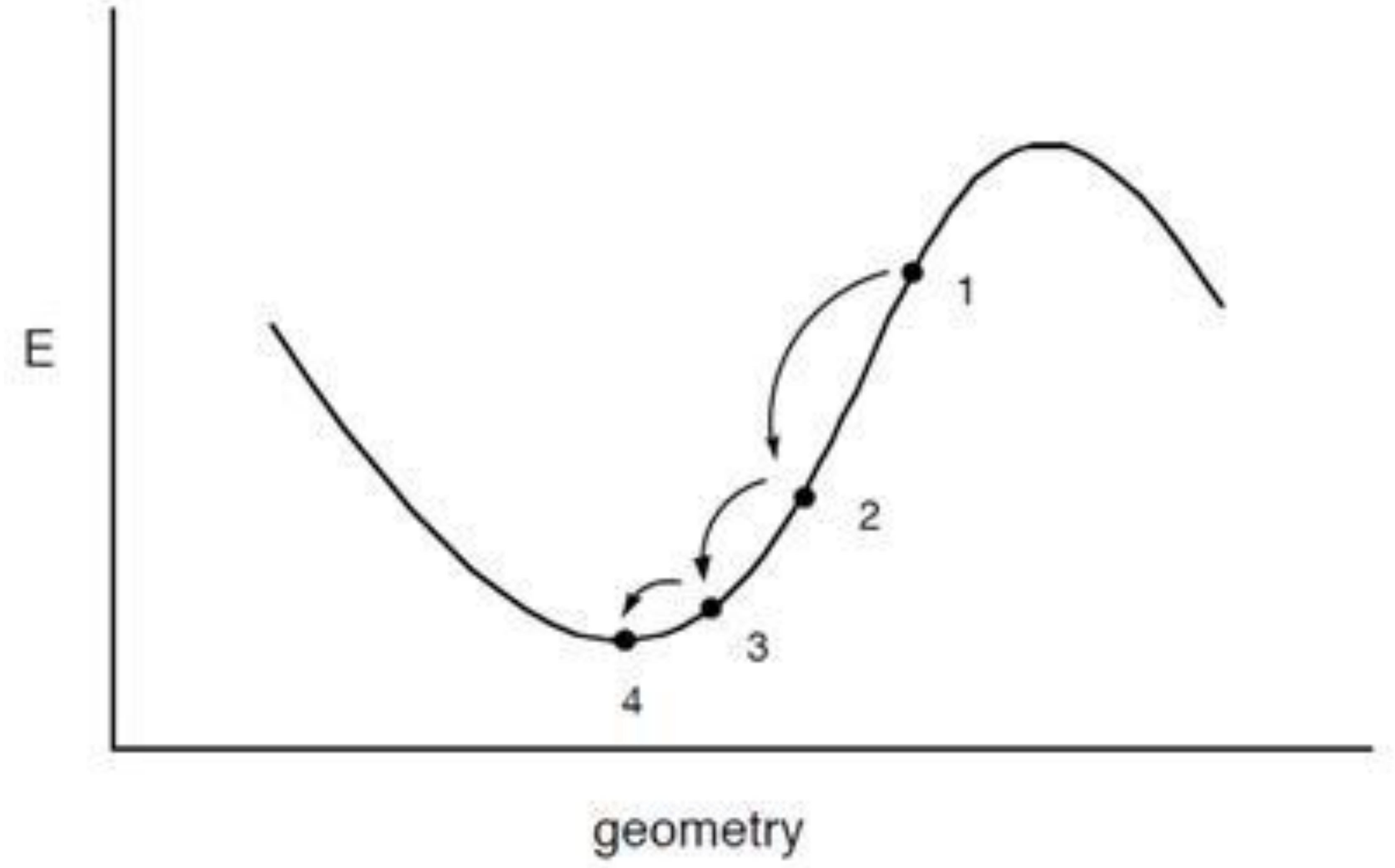


Lattice Optimization in exciting

- Tool: **OPTIMIZE-lattice.sh**

- Example $E = E(V, c/a)$
  - STEP1: opt. V at fixed $(c/a)_0$: get V_1
  - STEP2: opt. c/a at fixed V_1: get $(c/a)_2$
  - STEP3: opt. V at fixed $(c/a)_2$: get V_3
  - ...

Energy Minimization: Relaxation

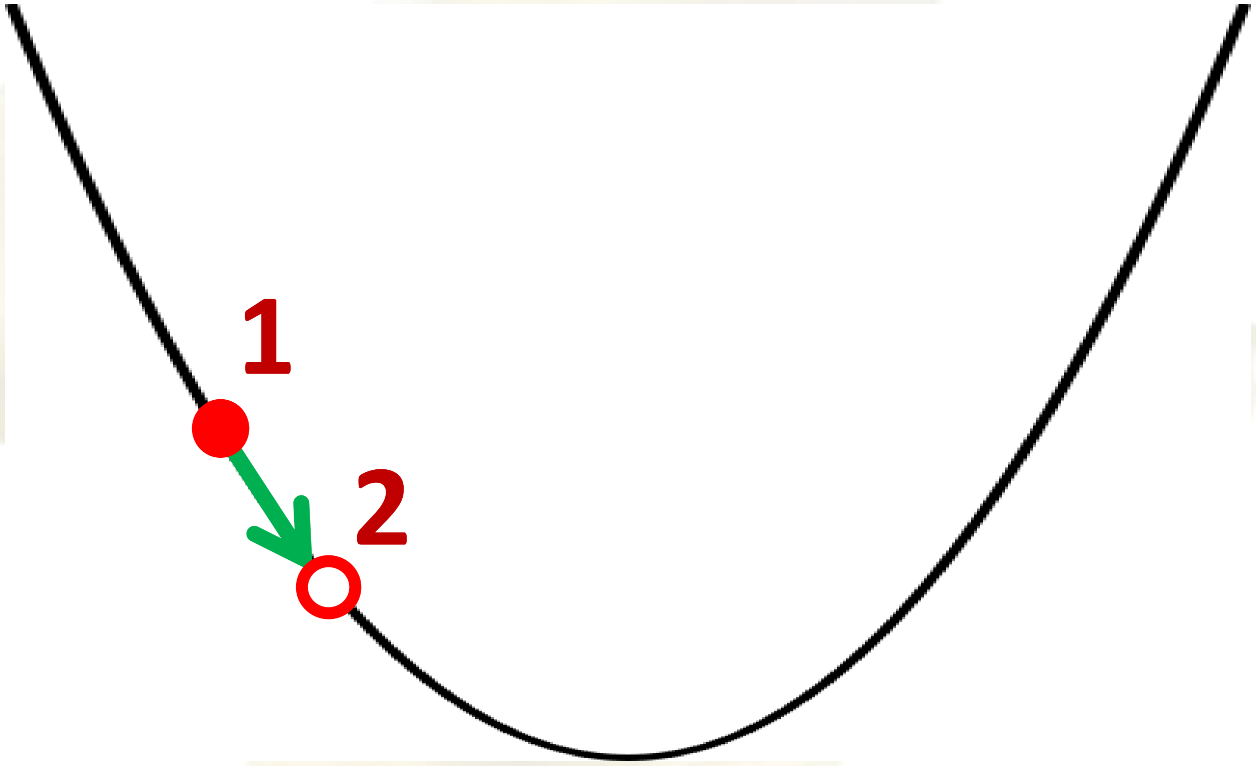


Internal degree of freedom: atomic positions

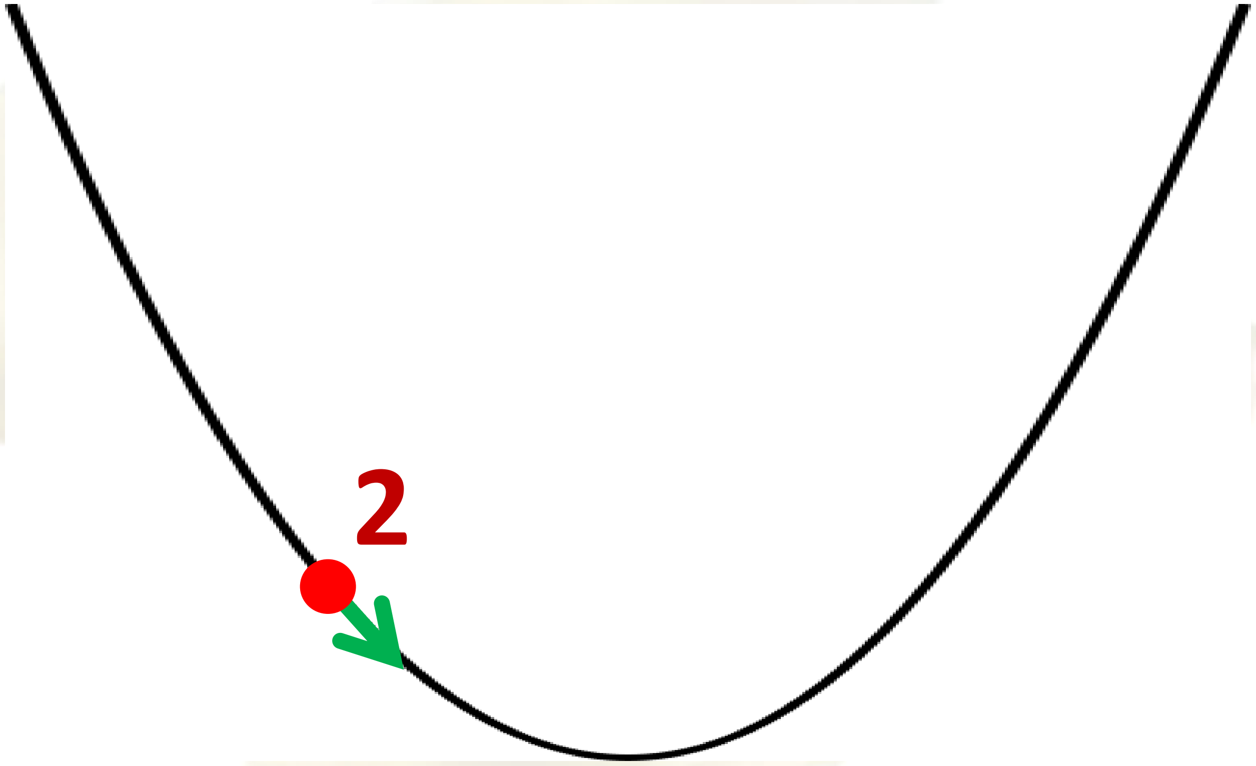
Relaxation methods in exciting

- newton
- harmonic
- bfgs

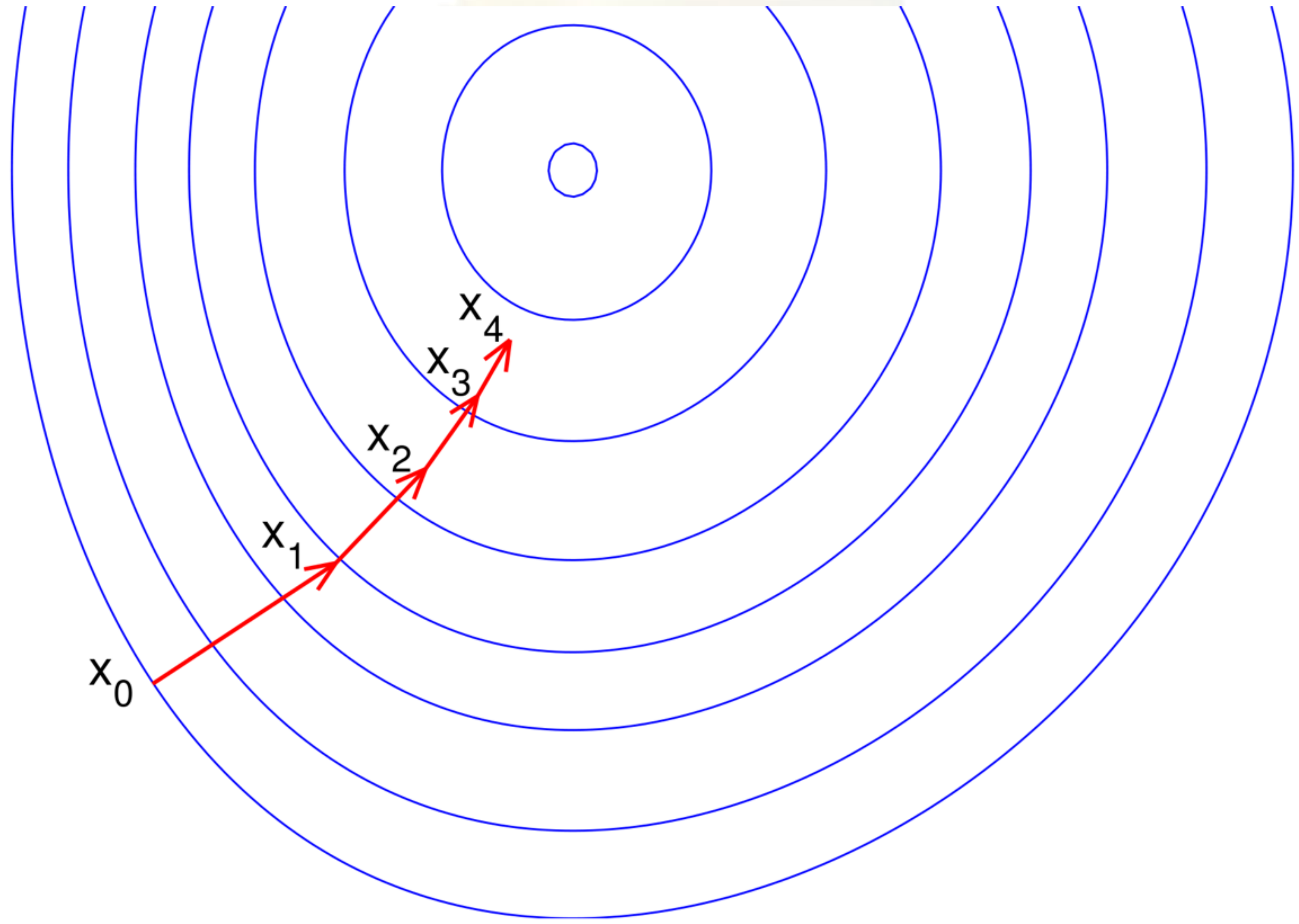
newton



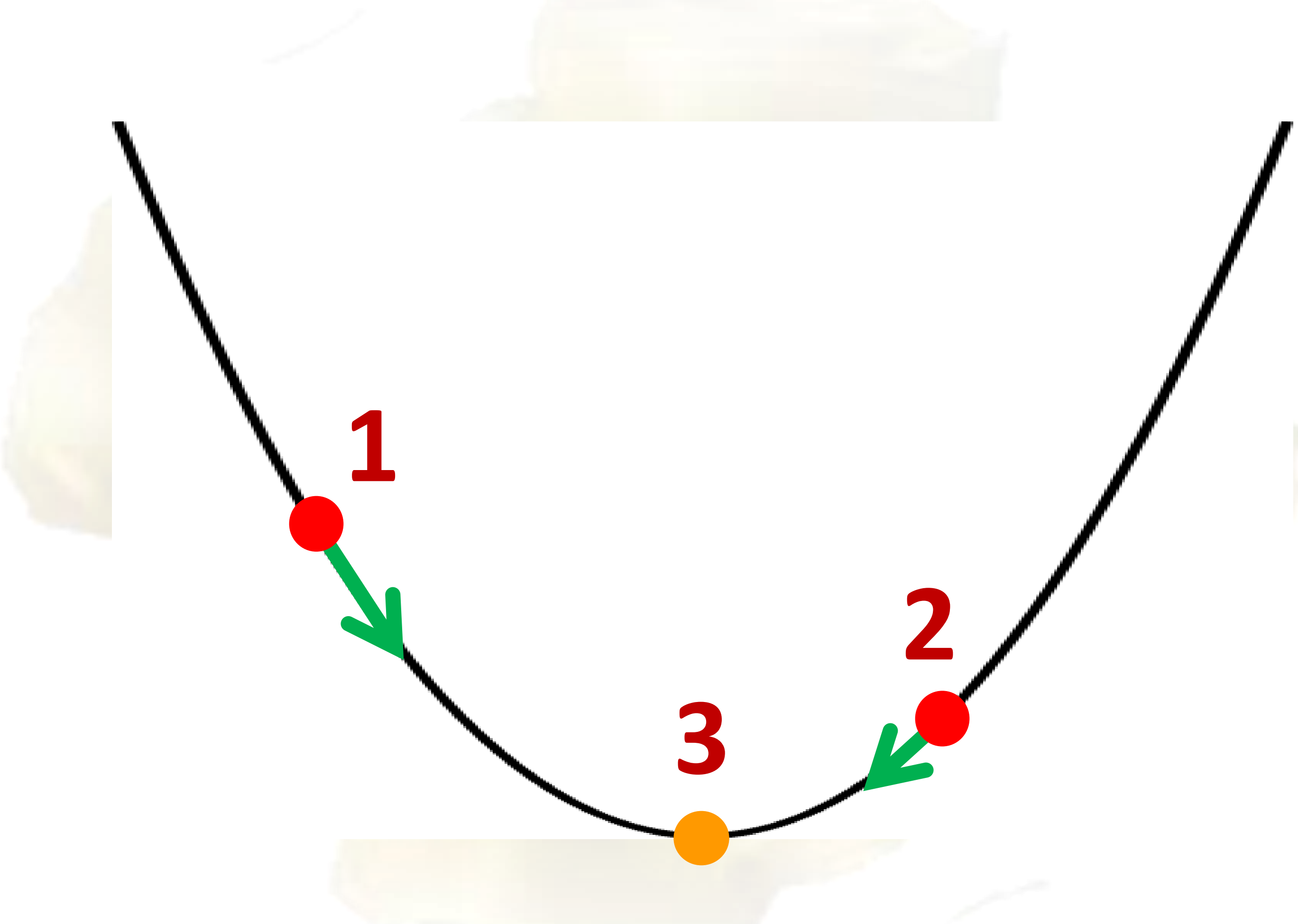
newton



newton (steepest descent)



harmonic

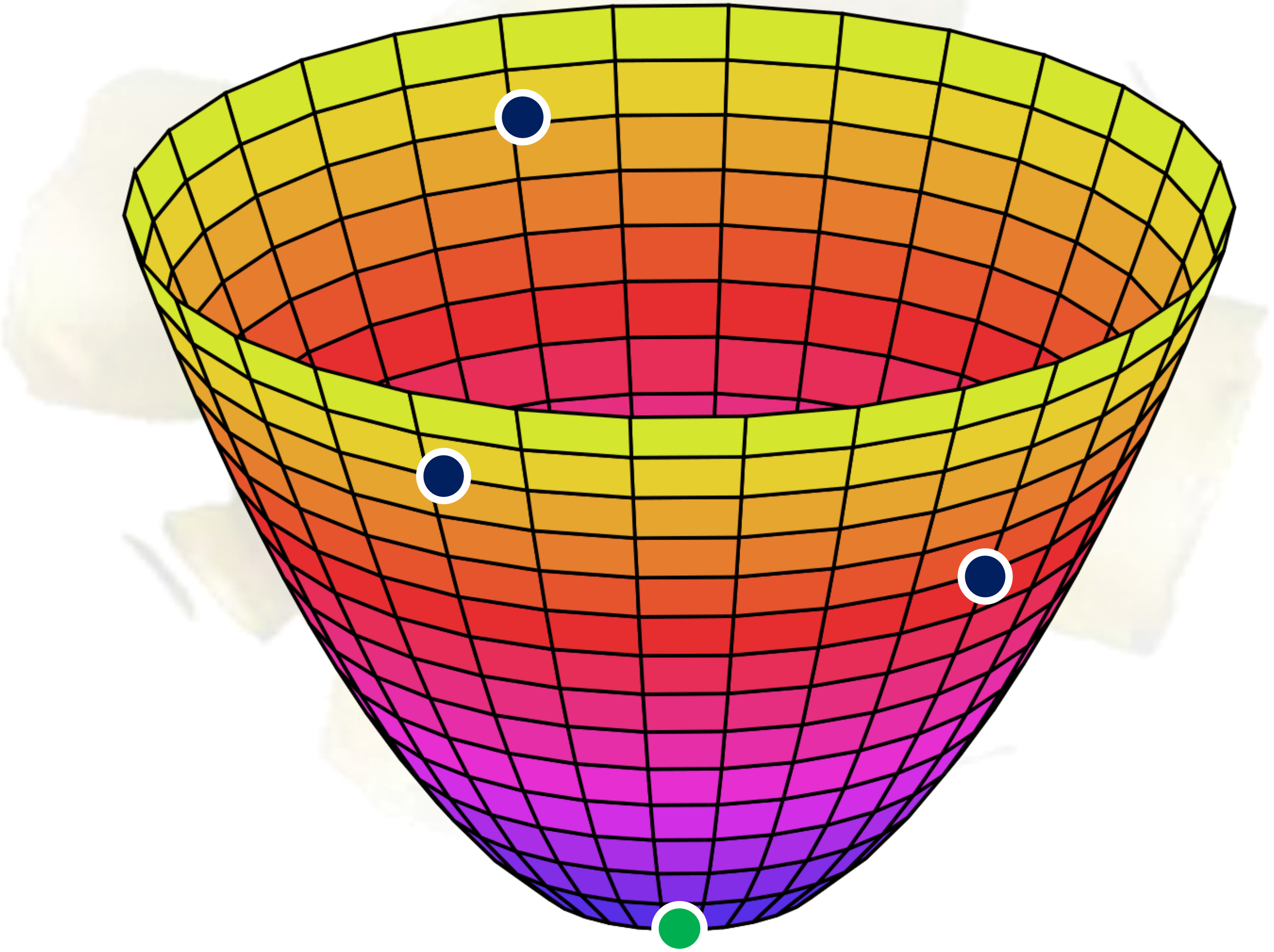


A parabola has a constant 2nd derivative

bfgs

Broyden, Fletcher, Goldfarb, Shanno

bfgs



bfgs

- Extension to N-degrees of freedom:
  - Similar to **harmonic**
  - Hessian matrix vs. 2nd derivative
  - Very efficient if close to minimum
  - Default in **exciting**

input.xml

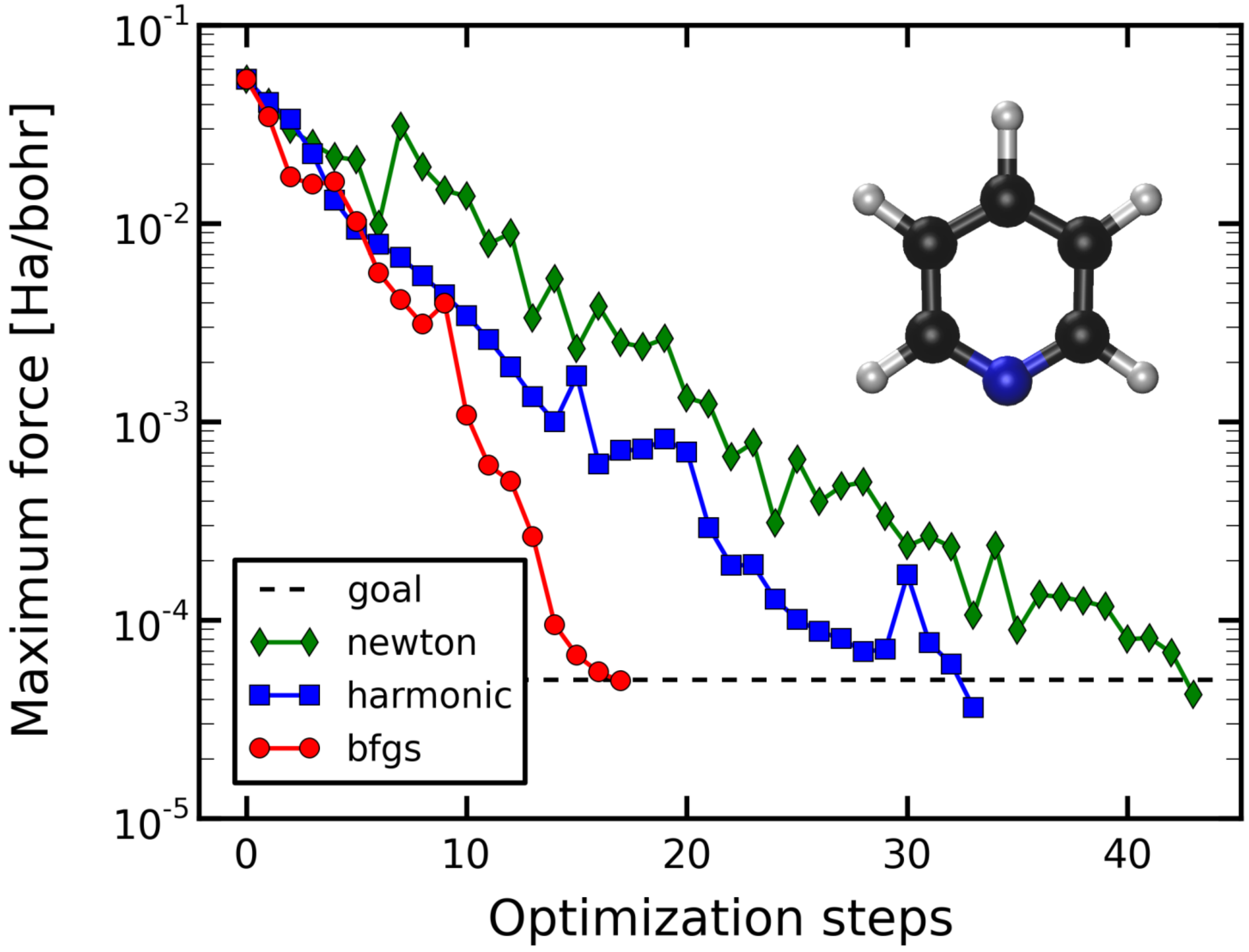
```
<input>
    …
    <structure … />

    <groundstate … />

    <relax method=´´bfgs´´/>

</input>
```

Relaxation of Pyridine



Elasticity

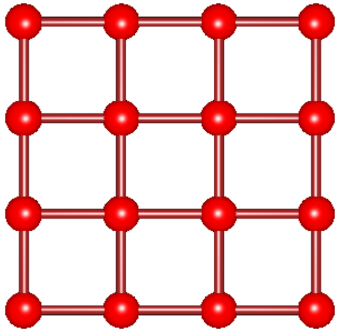
What Is Elasticity?

- Description of distorsions of rigid bodies and of the energy, forces, and fluctuations arising from these distorsions.
- Describes mechanics of extended bodies from the macroscopic to the microscopic.
- Generalizes simple mechanical concepts

Force → Stress

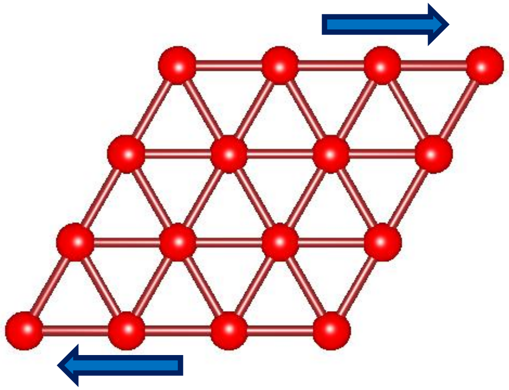
Displacement → Strain

Strain: State of deformation

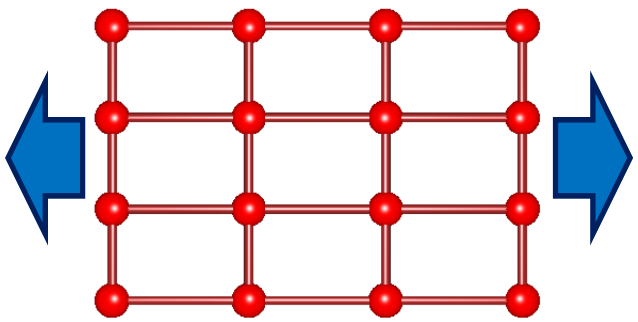


Equilibrium:
- Zero strain
- Zero forces
- Zero stress
- Zero displacements

Shear strain



Uniaxial strain



Homogeneous strain

$\boldsymbol{r}$ = unstrained position

$\boldsymbol{r}_s$ = strained position

$$\boldsymbol{r}_s = \boldsymbol{F} \cdot \boldsymbol{r} = (1 + \boldsymbol{\varepsilon}) \cdot \boldsymbol{r}$$

$\boldsymbol{F}$ = Deformation Matrix

$\boldsymbol{\varepsilon}$ = Physical Strain Matrix

Voigt notation

$$\begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{xy} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{xz} & \varepsilon_{yz} & \varepsilon_{zz} \end{pmatrix} \equiv \begin{pmatrix} \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & \varepsilon_3 \end{pmatrix}$$

Voigt indices:

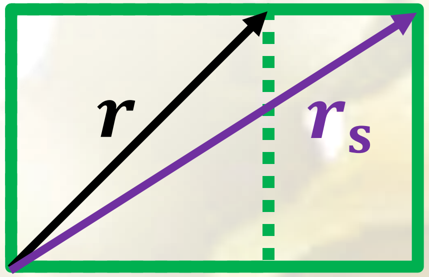
i, j	$=$	xx	yy	zz	yz or zy	xz or zx	xy or yx
α	$=$	1	2	3	4	5	6

Representative vector:

$$\boldsymbol{\varepsilon} = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6)$$

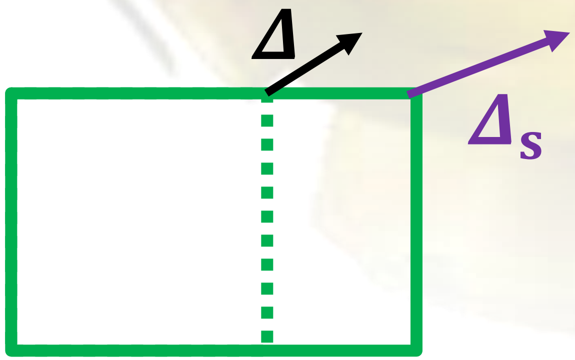
Strain definitions

Physical strain:



$$\boldsymbol{r}_s = (1 + \boldsymbol{\varepsilon}) \cdot \boldsymbol{r}$$

Lagrangian strain:



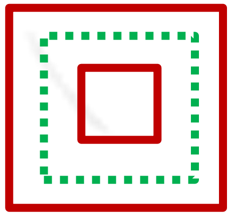
$$\boldsymbol{\eta} = \boldsymbol{\varepsilon} + \frac{1}{2}\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}$$

$$|\boldsymbol{\Delta}_s|^2 - |\boldsymbol{\Delta}|^2 = \boldsymbol{\Delta} \cdot 2\boldsymbol{\eta} \cdot \boldsymbol{\Delta}$$

Examples of strain (2D)

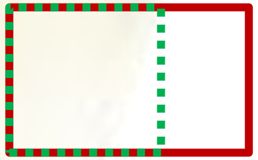
$$\begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_1 \end{pmatrix}$$

Expansion, compression:



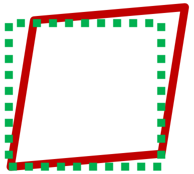
$$\begin{pmatrix} \varepsilon_1 & 0 \\ 0 & 0 \end{pmatrix}$$

Uniaxial strain:

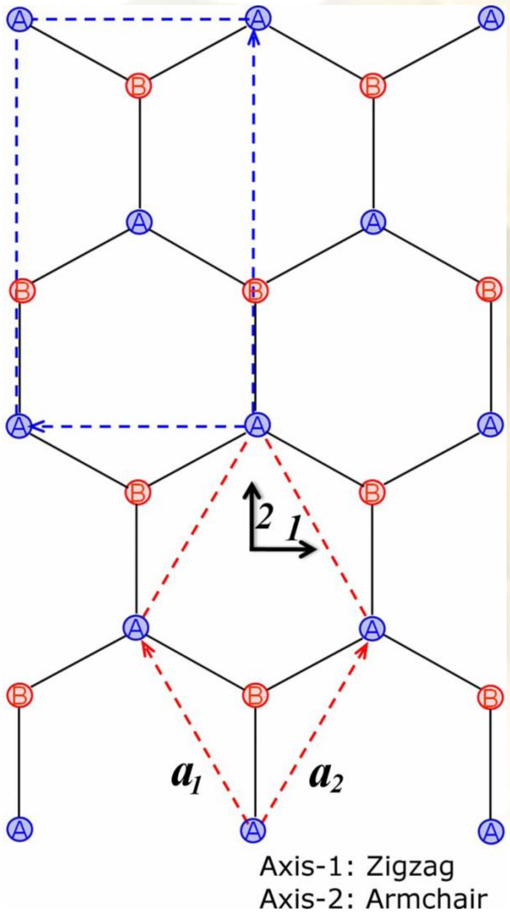


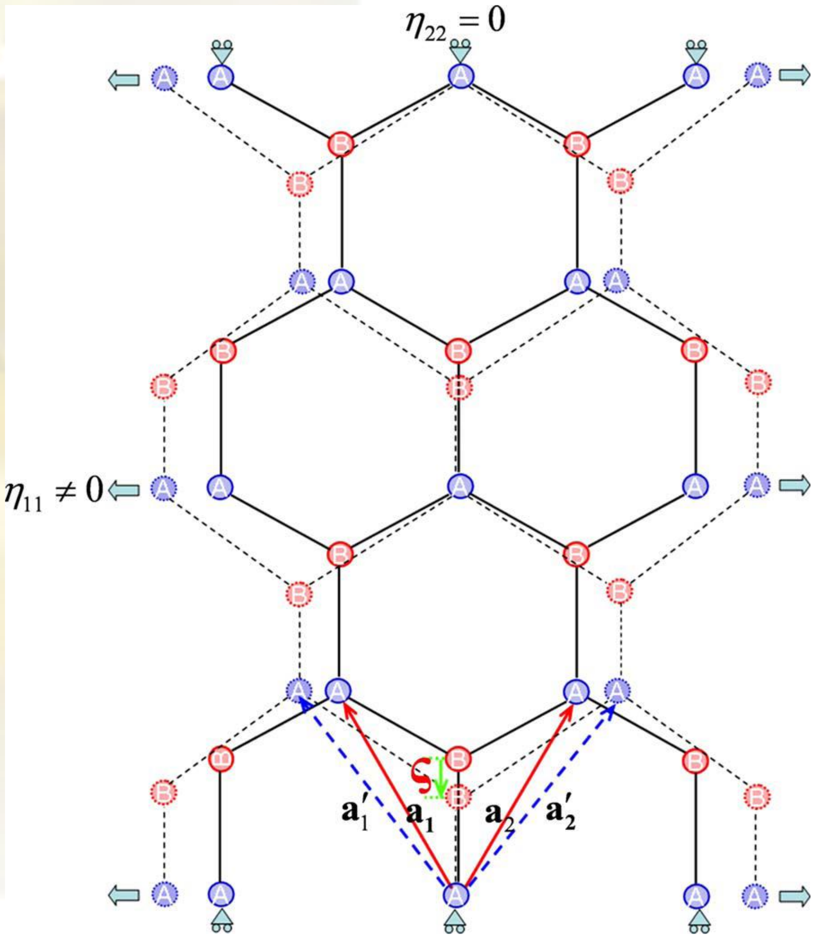
$$\begin{pmatrix} 0 & \varepsilon_6/2 \\ \varepsilon_6/2 & 0 \end{pmatrix}$$

Shear strain:



Uniaxial strain in graphene





Linear elastic response

Low pressure expansion in terms of Lagrangian strain $\boldsymbol{\eta}$:

$$E(\boldsymbol{\eta}) = E_0 + \frac{V_0}{2!}\boldsymbol{\eta}\cdot\boldsymbol{C}^{(2)}\cdot\boldsymbol{\eta} + \cdots$$

$E_0, V_0 =$ Reference (equilibrium) energy and volume

Linear elastic constant (2nd order):

$$\boldsymbol{C}^{(2)} = \frac{1}{V_0}\left[\frac{\partial^2 E(\boldsymbol{\eta})}{\partial\boldsymbol{\eta}\partial\boldsymbol{\eta}}\right]_{\eta=0}$$

Diamond

C_{11}, C_{12}, C_{44}

Stress

Physical Stress:

$$\sigma_\alpha = \frac{1}{V}\frac{\partial E(\boldsymbol{\varepsilon})}{\partial \varepsilon_\alpha}$$

Lagrangian Stress:

$$\tau_\alpha = \frac{1}{V_0}\frac{\partial E(\boldsymbol{\eta})}{\partial \eta_\alpha}$$

$$\boldsymbol{\tau} = \det(\mathbf{1}+\boldsymbol{\varepsilon})\;(\mathbf{1}+\boldsymbol{\varepsilon})^{-1}\cdot\boldsymbol{\sigma}\cdot(\mathbf{1}+\boldsymbol{\varepsilon})^{-1}$$

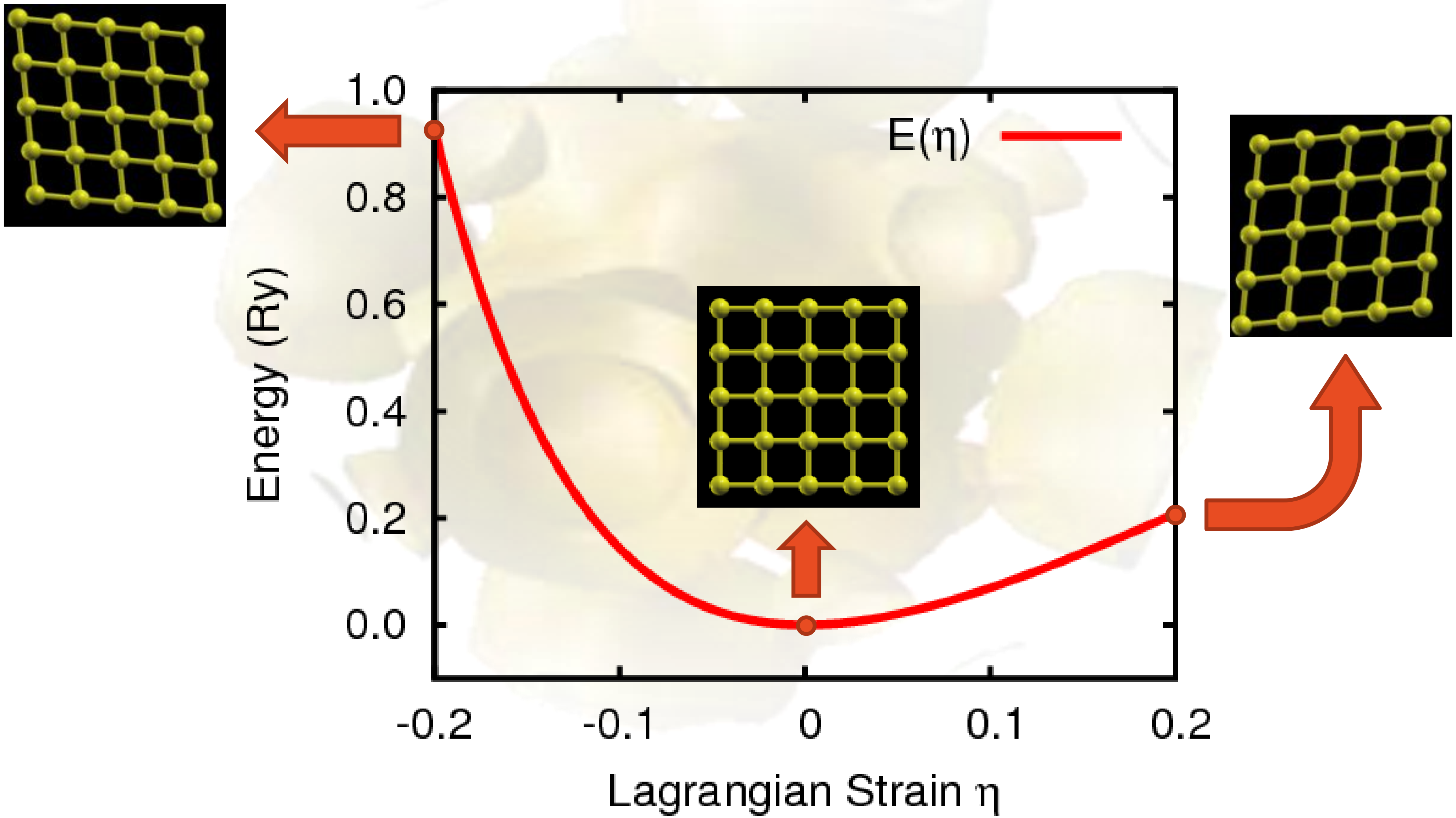
Stress vs strain

Using the definition of Lagrangian Stress and the expansion of the Elastic Energy in terms of Lagrangian strains:

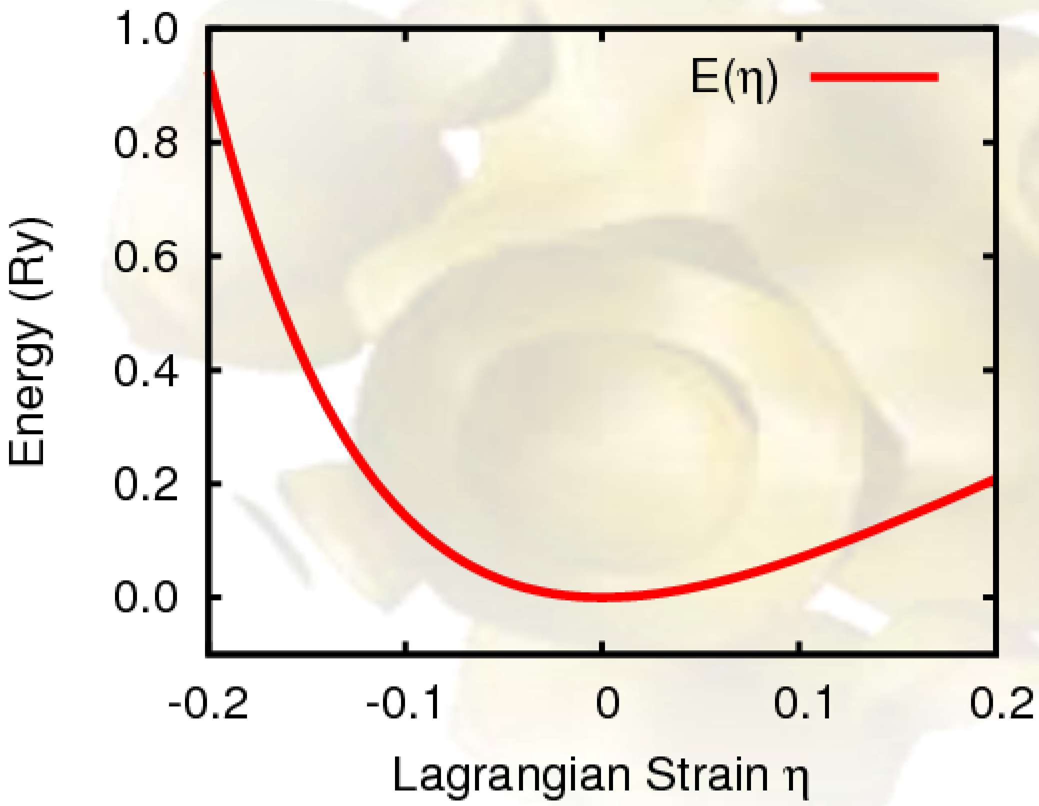
$$\tau_\alpha = \frac{1}{V_0}\frac{\partial E(\boldsymbol{\eta})}{\partial \eta_\alpha}$$

$$\boldsymbol{\tau}(\boldsymbol{\eta}) = \boldsymbol{C}^{(2)} \cdot \boldsymbol{\eta} + \frac{1}{2!}\boldsymbol{\eta} \cdot \boldsymbol{C}^{(3)} \cdot \boldsymbol{\eta} + \cdots$$

Generic **strain** deformation

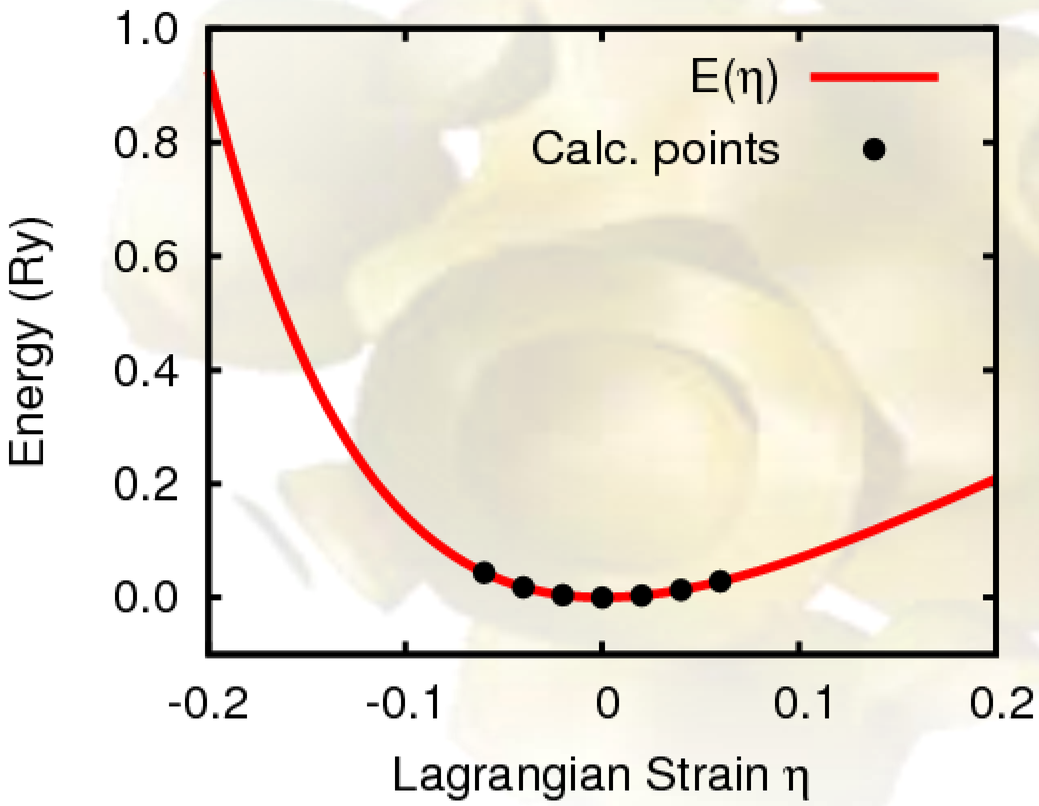


Elastic constants calculations



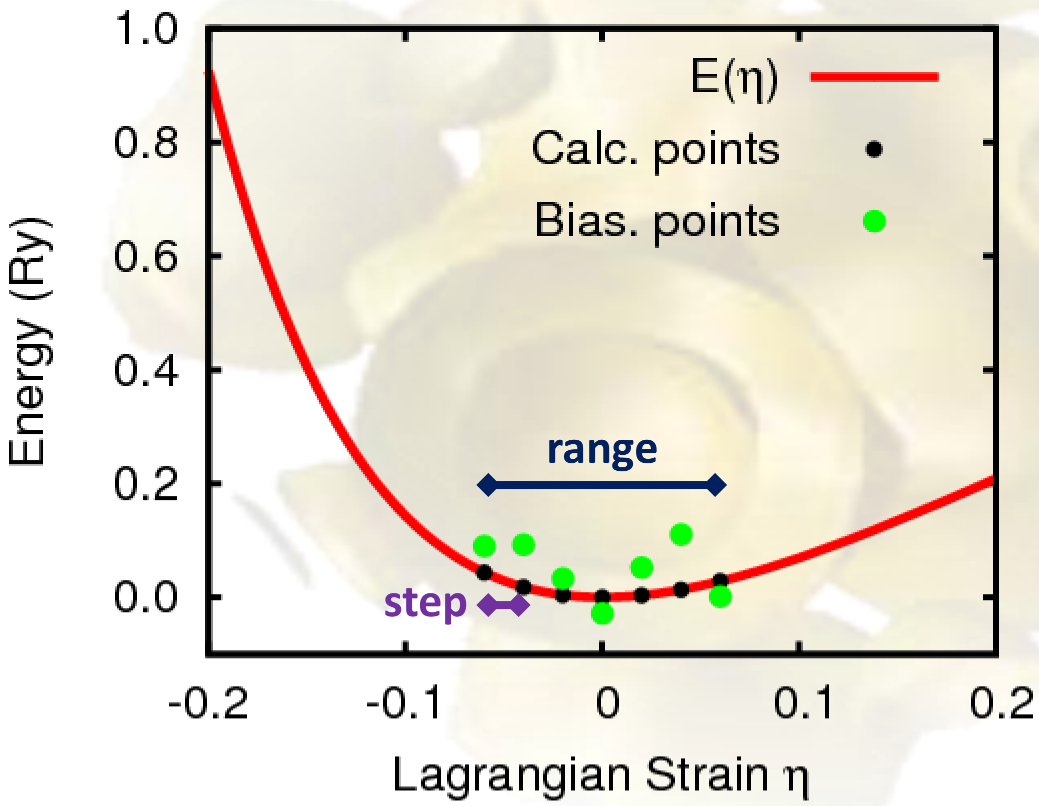
- Select deformation type: E=E(η)
- Elastic constants are derivatives of E(η) taken at η=0

Numerical calculations



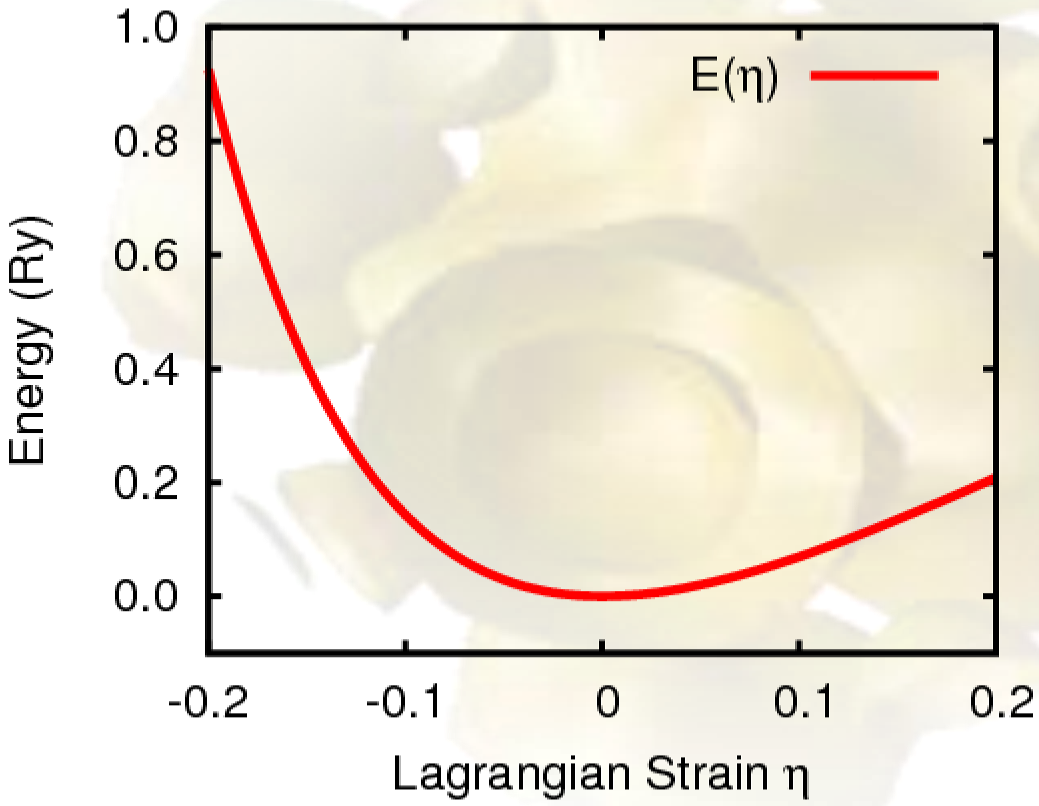
- Fitting a polynomial to the calculated points
- Error sources!

Numerical derivatives: Error sources



- Numerical errors in fitting procedure:
  # of points
  Points step
  Points range
  Polynomial order
- Biased set of calculated points

Numerical derivatives: A toy model

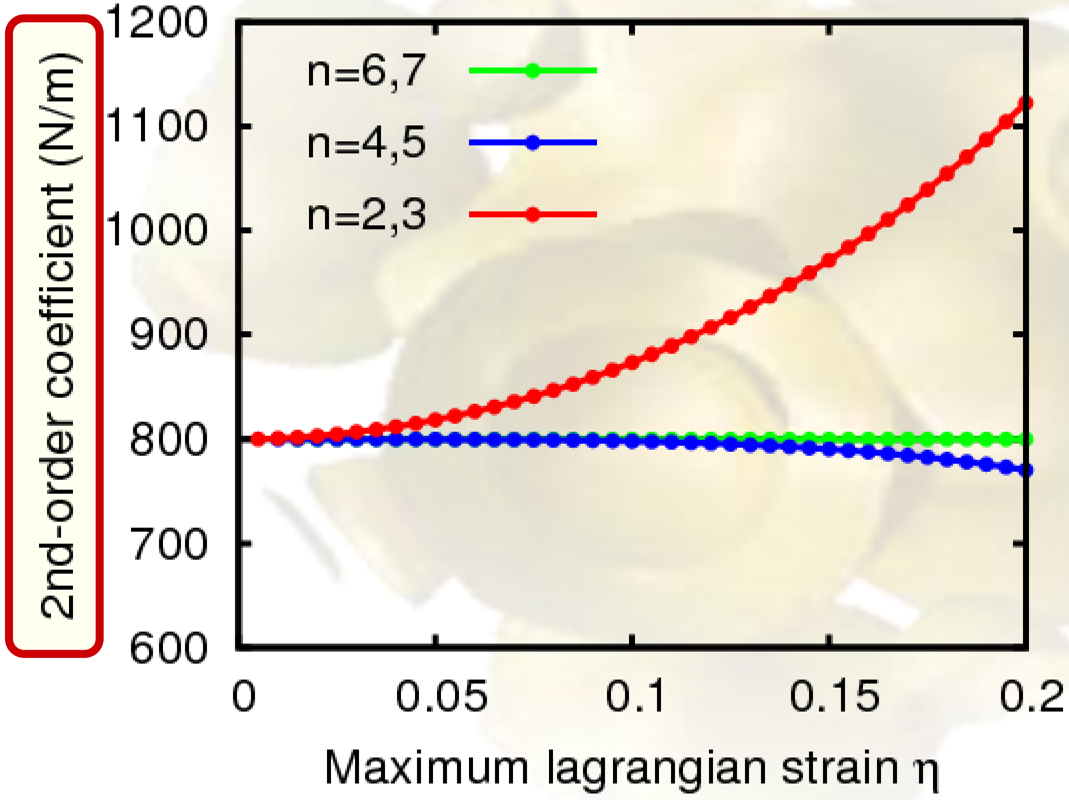


- E=E(η) is a known function: 6th-order polynomial with known coefficients

$$E(\eta) = E_0 + \sum_{i=2}^{6} A_i \, \eta^i$$

$$A_2 = 800 \text{ Ry}$$

Numerical determination of A_2

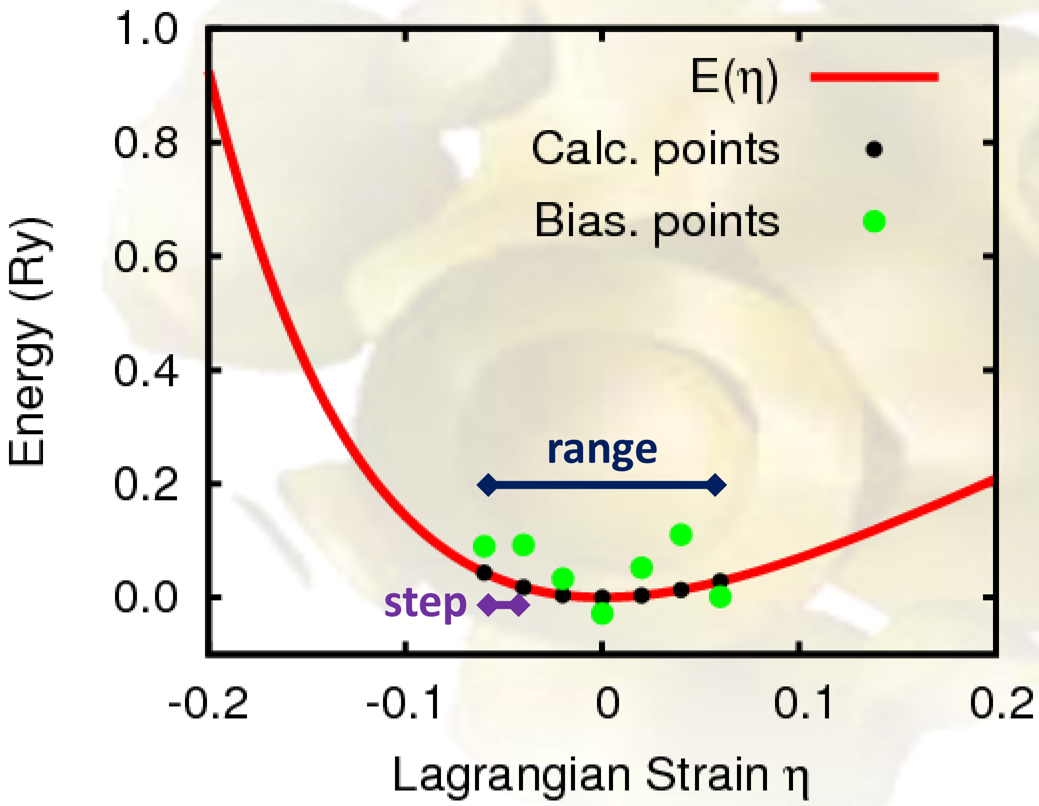


(range)

- Using polynomial fitting of order n

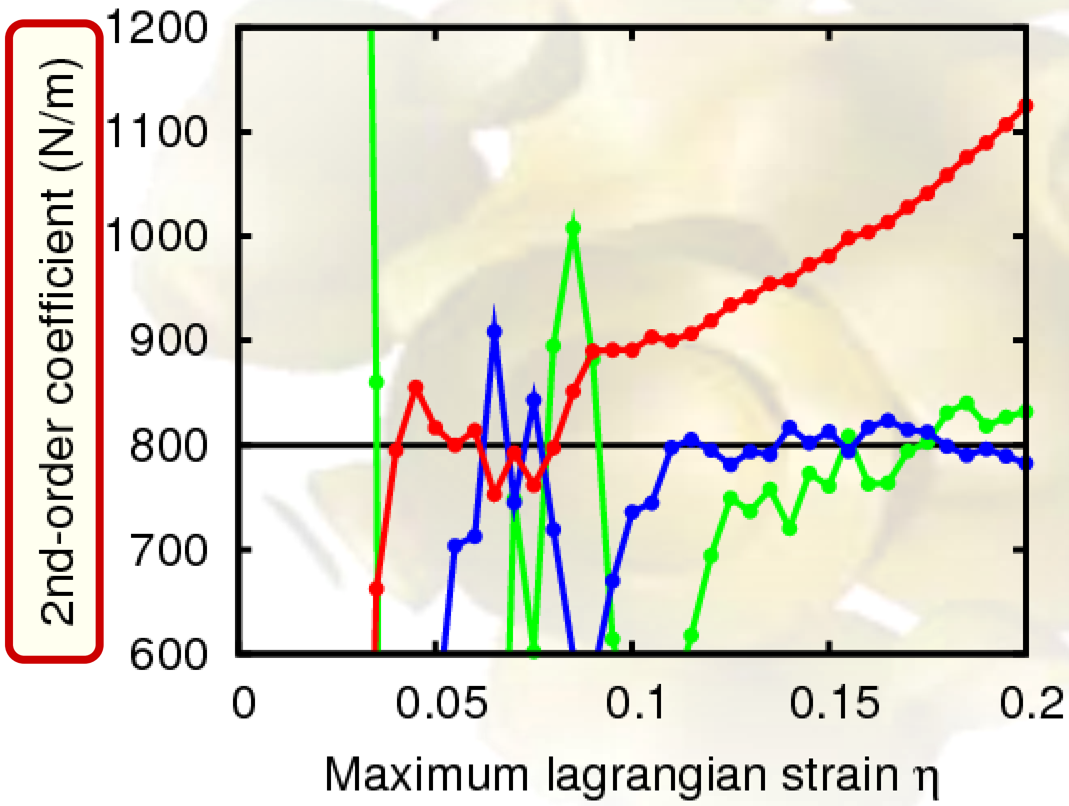
Ideal: no noise

Numerical derivatives: Error sources



- Biased set of calculated points

Numerical determination of A_2

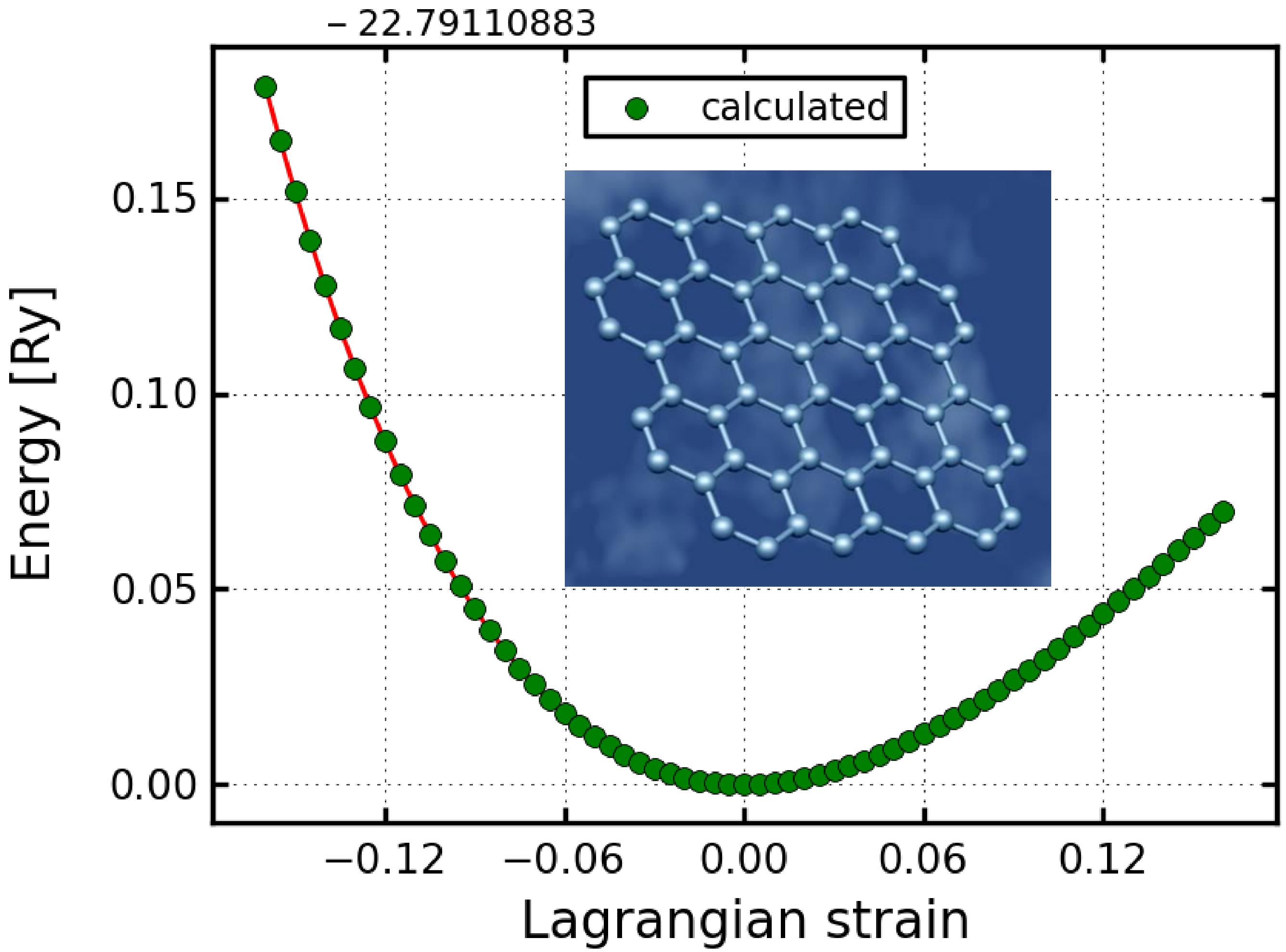


(range)

- Using polynomial fitting of order n

+ noise

Graphene (100) Strain



Number of independent elastic constants

Structure	Space group number	$c_{\alpha\beta}$	$c_{\alpha\beta\gamma}$
Cubic I	207 to 230	3	6
Cubic II	195 to 206	3	8
Hexagonal I	177 to 194	5	10
Hexagonal II	168 to 176	5	12
Trigonal I	149 to 167	6	14
Trigonal II	143 to 148	7	20
Tetragonal I	89 to 142	6	12
Tetragonal II	75 to 88	7	16
Orthorhombic	16 to 74	9	20
Monoclinic	3 to 15	13	32
Triclinic	1 to 2	21	56

exciting: Tools & more

- ElaStic (talk)
- CELL (talk)
- LayerOptics
- NOMAD project

Main ElaStic Reference

Computer Physics Communications 184 (2013) 1861–1873

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COMPUTER PHYSICS COMMUNICATIONS

ElaStic: A tool for calculating second-order elastic constants from first principles

CrossMark

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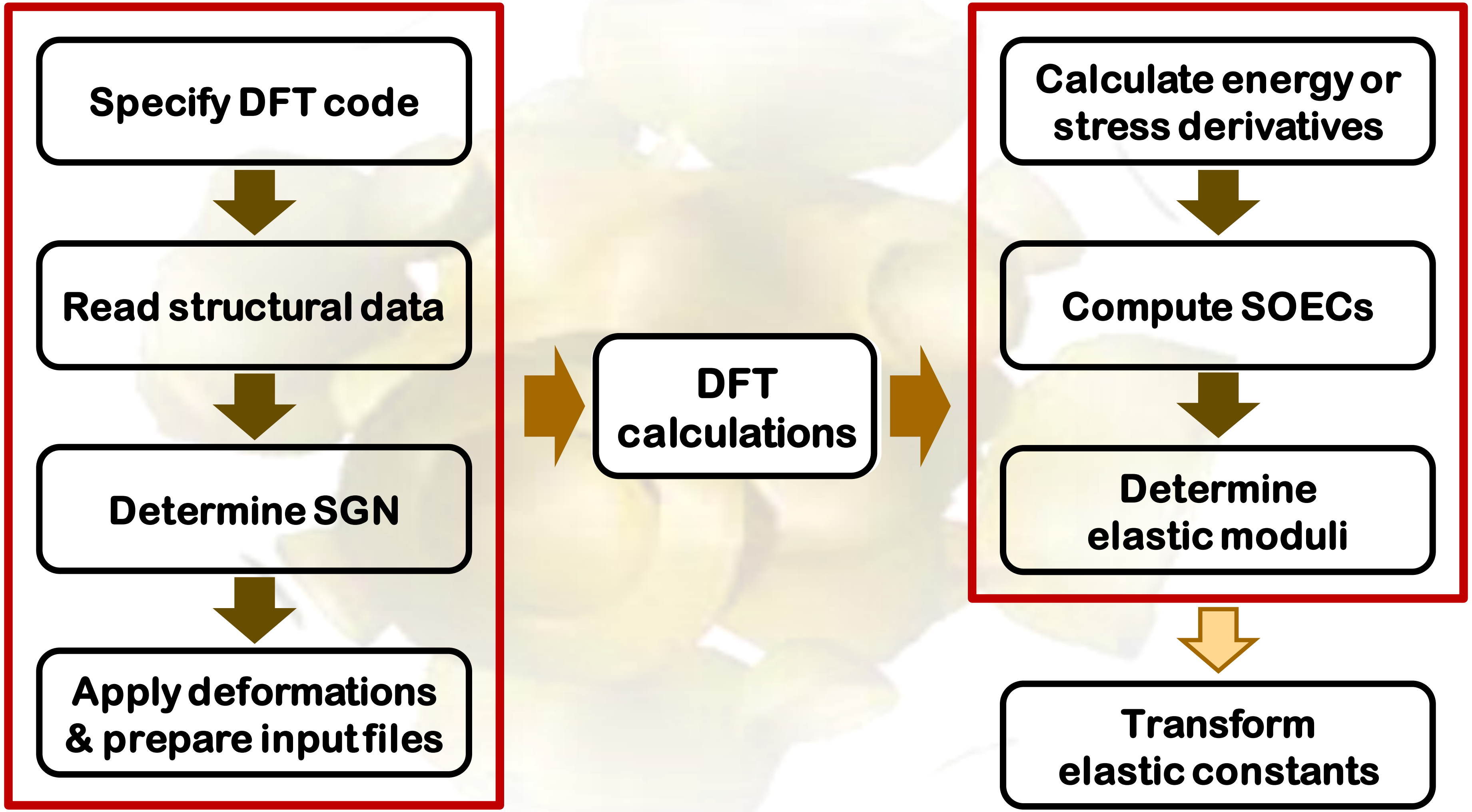
ElaStic



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☛ LATTICE OPTIMIZATION:

【b】 Volume optimization for cubic systems
【b】 Simple examples of structure optimization
【b】 General lattice optimization

☛ ELASTIC PROPERTIES:

【b】 Energy vs. strain calculations
【a】 How to calculate the stress tensor

☛ TOOLS AND PACKAGES

【a】 ElaStic@exciting: How to calculate elastic constants

The Last Slide: We are still so Excited!