Symmetry-constrained relaxation in FHI-aims

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Coffee Talk

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Overview

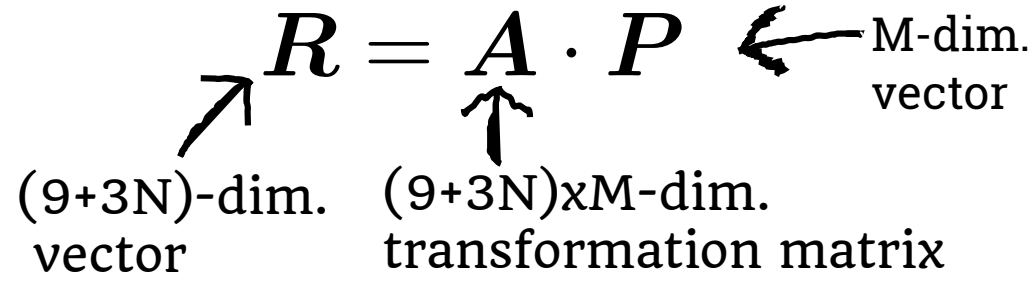
What do we have in FHI-aims?

- Full relaxation that *breaks* the symmetry in many cases
- Option to constrain
  - Full atoms
  - Individual Cartesian atom coordinates
  - Full lattice vectors
  - Individual lattice vector components
  - Angles between lattice vectors
- Option to use reciprocal lattice to initialize Hessian to relax cubic and hexagonal structures (Florian)

What do we want?

- Symmetry-constrained relaxation that *preserves*
  - Spacegroup
  - Pointgroup
  - Structure Prototype (Wyckoff positions)

Express structure through symmetry-reduced parameters



- Flattened vectors of full coordinates $\boldsymbol{R}$ and reduced parameter space $\boldsymbol{P}$ can be converted using transformation matrix $\boldsymbol{A}$
- Example: Orthorhombic lattice described by lattice parameters a, b and c

$$\boldsymbol{a} = \begin{pmatrix} a & 0 & 0 \end{pmatrix}$$
$$\boldsymbol{b} = \begin{pmatrix} 0 & b & 0 \end{pmatrix}$$
$$\boldsymbol{c} = \begin{pmatrix} 0 & 0 & c \end{pmatrix}$$

$$\rightarrow \text{flatten} \rightarrow \quad \begin{pmatrix} a \\ 0 \\ 0 \\ 0 \\ b \\ 0 \\ 0 \\ 0 \\ c \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

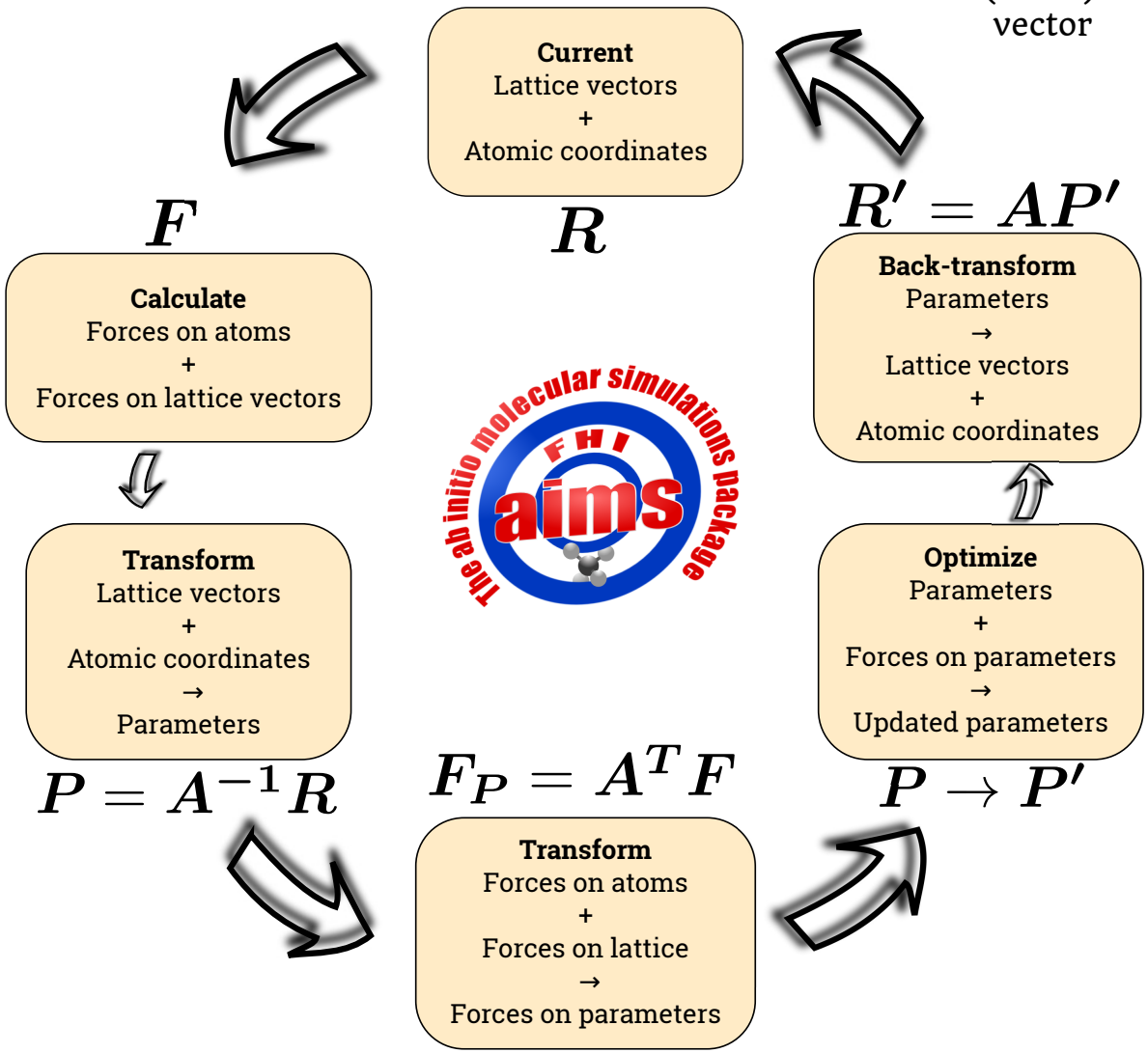
Workflow of the constrained relaxation

$$R = A \cdot P$$

M-dim. vector

(9+3N)-dim. vector

(9+3N)xM-dim. transformation matrix



Example input file: Rutile-Ti_2O_4

```
lattice_vector 4.5922000000000000 0.0000000000000000 0.0000000000000000
lattice_vector 0.0000000000000000 4.5922000000000000 0.0000000000000000
lattice_vector 0.0000000000000000 0.0000000000000000 2.9600000000000000
atom_frac    0.00000000000000    0.00000000000000    0.00000000000000  Ti
atom_frac    0.50000000000000    0.50000000000000    0.50000000000000  Ti
atom_frac    0.30000000000000    0.30000000000000    0.00000000000000  O
atom_frac   -0.30000000000000   -0.30000000000000    0.00000000000000  O
atom_frac    0.20000000000000    0.80000000000000    0.50000000000000  O
atom_frac    0.80000000000000    0.20000000000000    0.50000000000000  O

symmetry_n_params 3 2 1
symmetry_params a c x2
symmetry_lv     a ,  0 ,  0
symmetry_lv     0 ,  a ,  0
symmetry_lv     0 ,  0 ,  c
symmetry_frac   0           ,   0           ,   0
symmetry_frac   1./2        ,   1./2        ,   1./2
symmetry_frac   x2          ,   x2          ,   0
symmetry_frac   -x2         ,   -x2         ,   0
symmetry_frac   1./2 - x2   ,   1./2 + x2   ,   1./2
symmetry_frac   1./2 + x2   ,   1./2 - x2   ,   1./2
```

Symmetry paragraph:

- defines symmetry-reduced parameters
- gives form of structure in these parameters

We have only 3 free parameters instead of 27 ($9 + 3n_{\text{atoms}}$).

Capabilities of symmetry-constrained relaxation

- Relax even unstable or meta-stable structures within their symmetry
- Add or remove certain parameters to
  - Conserve / break a local symmetry
  - Create user-defined symmetries
- Monitor forces that would break the symmetry during standard relaxation

Relaxation in symmetry-reduced parameter space

Example: Si-bcc (not stable at 0K)

	Initial	standard	symm-constr.
Spacegroup	229	12	229
Pointgroup	m-3m	2/m	m-3m
ΔE (meV)	0	-243	-192
Volume (a_B^3)	18.5	14.6	14.7
# Steps		44	5

$\rightarrow$ Symmetry analysis using AFLOW with standard settings

Outlook

Integration with AFLOW Prototypes[1]

- geometry.in files can already be generated with AFLOW
- David Hicks (Curtarolo Group in Duke) works on outputting analytic expressions too
  Example: for TiO2 Rutile with parameters a,c/a,x1

```
aflow --proto=A2B_tP6_136_f_a:O:Ti --params=4,1.5,0.2 --aims
```

Implementation for monoclinic and triclinic crystal systems

- No linear matrix transformations possible because of expressions like $c \cdot \sin(\beta)$ $\rightarrow$ Ideas welcome...
  Substitution of variables as possible solution, e.g. for monoclinic case:

$$\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ c\cos(\beta) & 0 & c\sin(\beta) \end{pmatrix} \rightarrow \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ d & 0 & e \end{pmatrix} \qquad (1)$$

[1] M. J. Mehl, D. Hicks, C. Toher, O. Levy, R. M. Hanson, G. Hart, and S.