The Tensorial Cluster Expansion

- Needed to express configurational-dependence of many important properties:
  - elastic constants, equilibrium strain/stress
  - dielectric constant
  - ferroelectric vector
  - piezoelectric tensor
  - (electro/magneto)striction
  - optoelectric coupling, etc.

Scalar Cluster Expansion

$$q(\sigma) = \sum_{\alpha} J_\alpha \Gamma_\alpha(\sigma) \qquad \text{(without symmetry)}$$

$$q(\sigma) = \sum_{\nsim\alpha} J_\alpha m_\alpha \langle \Gamma_{\alpha'}(\sigma) \rangle_\alpha \qquad \text{(with symmetry)}$$

where

- $q(\sigma)$ a scalar function of configuration $\sigma \equiv (\sigma_1, \sigma_2, \ldots)$
- α is a *cluster* (i.e. a set of lattice sites)
- Sum: over all symmetrically distinct α
- $\Gamma_{\alpha'}(\sigma) = \prod_{i \in \alpha'} \sigma_i$ (“cluster functions”)
- $\langle \cdots \rangle_\alpha$: average over α' equivalent by symmetry to α
- m_α: multiplicities (# of terms in average/unit cell)
- J_α are coefficients to be determined.

$$\boxed{\text{The } \langle \Gamma_{\alpha'}(\sigma) \rangle_\alpha \text{ form a basis for the space of scalar functions of configuration.}}$$

Bases and Tensors

$$Q = \sum_{\beta} c_\beta \beta$$

$$Q_{ijk\ldots} = \sum_{\beta} c_\beta \beta_{ijk\ldots}$$

where
- β is a "basis tensor"
- c_β are coefficients to be determined

Example: A basis for symmetric rank 2 tensors in 3D is:

$$\beta = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\begin{bmatrix} 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 1/\sqrt{2} \\ 0 & 0 & 0 \\ 1/\sqrt{2} & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 \end{bmatrix}$$

$\boxed{\text{The } \beta \text{ form a basis for the space of tensors.}}$

“Tensor-product” basis

Basis a_i for space A

$$\sum_i c_i a_i$$

Basis b_j for space B

$$\sum_j c_j b_j$$

Basis $a_i b_j$ for space $A \otimes B$

$$\sum_i \sum_j c_{ij} a_i b_j$$

$$\boxed{\neq c_i c_j}$$

To obtain a basis for tensor-function $Q(\sigma)$ of configuration,

form every possible pairwise product of β’s and $\Gamma_\alpha(\sigma)$:

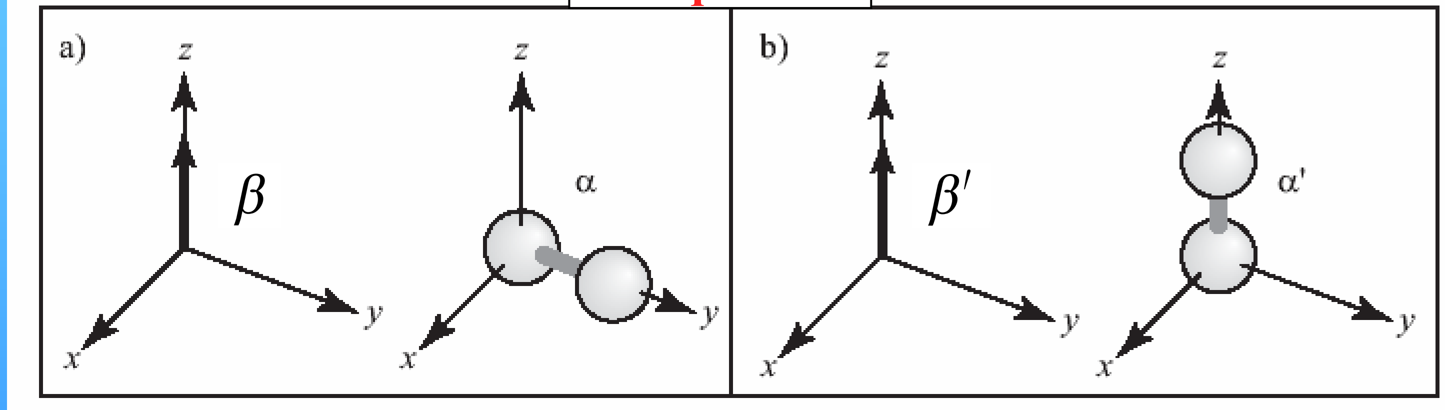
$$Q(\sigma) = \sum_\alpha \sum_\beta J_{\alpha\beta} \Gamma_\alpha(\sigma) \beta$$

Still need to exploit symmetry…

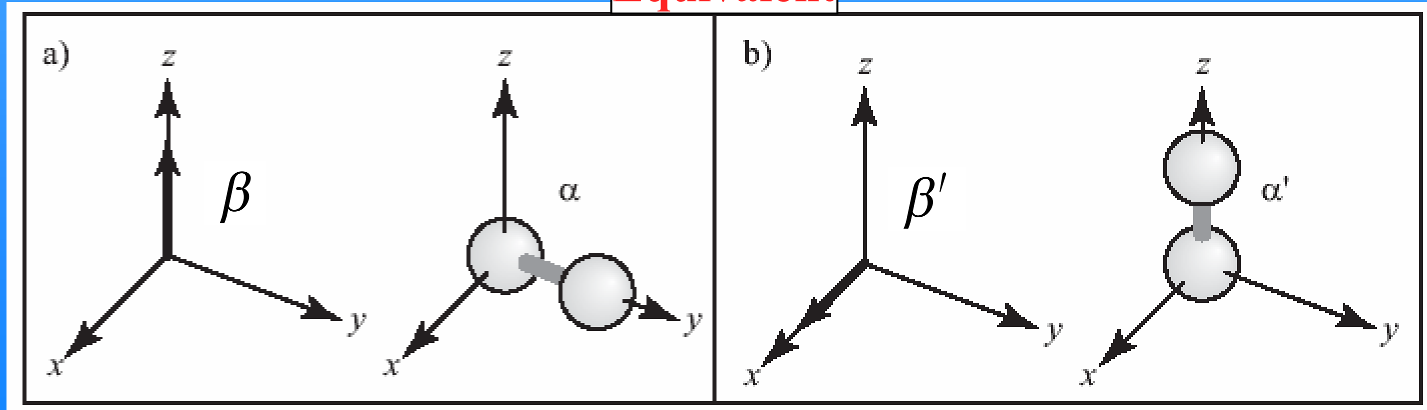
Exploiting symmetry

$J_{\alpha\beta} = J_{\alpha'\beta'}$ if (α, β) is equivalent by symmetry to (α', β').

Not equivalent



Equivalent



Re-grouping...

$$Q(\sigma) = \sum_{\alpha,\beta} J_{\alpha\beta}\Gamma_{\alpha}(\sigma)\beta$$

$$= \sum_{\nsim(\alpha,\beta)} \sum_{S} \sum_{P:P(\alpha)=\alpha} J_{S(P(\alpha))S(P(\beta))}\,\Gamma_{S(P(\alpha))}(\sigma)\; S(P(\beta))$$

Sum over sym. distinct (α,β)

Sum over sym. op. that move clusters around ("Space" group)

Sum over sym. op. mapping α onto α ("Point" group)

Re-grouping...

$$Q(\sigma) = \sum_{\sim(\alpha,\beta)} \sum_{S} \sum_{P : P(\alpha)=\alpha} J_{S(P(\alpha))S(P(\beta))}\, \Gamma_{S(P(\alpha))}(\sigma)\, S(P(\beta))$$

$$= \sum_{\sim(\alpha,\beta)} \sum_{S} \sum_{P : P(\alpha)=\alpha} J_{\alpha\beta}\, \Gamma_{S(\alpha)}(\sigma)\, S(P(\beta))$$

$J_{\alpha\beta} = J_{\alpha'\beta'}$ if $(\alpha,\beta) \sim (\alpha',\beta')$

$$= \sum_{\sim(\alpha,\beta)} J_{\alpha\beta} \sum_{S} \Gamma_{S(\alpha)}(\sigma)\, S\left(\sum_{P : P(\alpha)=\alpha} P(\beta) \right)$$

(Reordering)

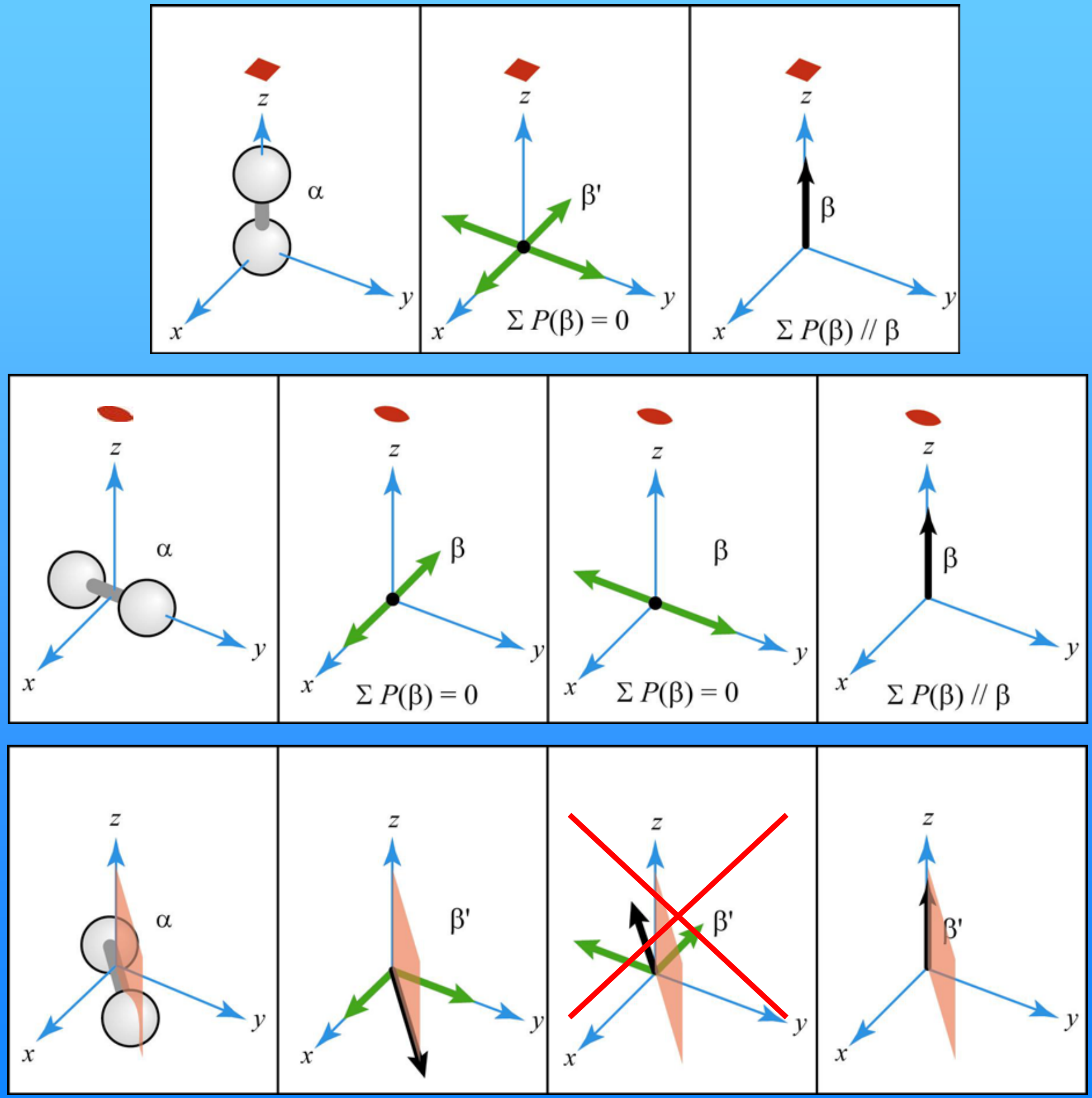
Disappears if β
is not allowed by symmetry
of cluster α

Symmetry restrictions

Example 1

Example 2

Example 3



Simplifying...

$$Q(\sigma) = \sum_{\nsim\alpha} \sum_{\beta\in C(\alpha)} J_{\alpha\beta} \sum_{S} \Gamma_{S(\alpha)}(\sigma) S(\beta)$$

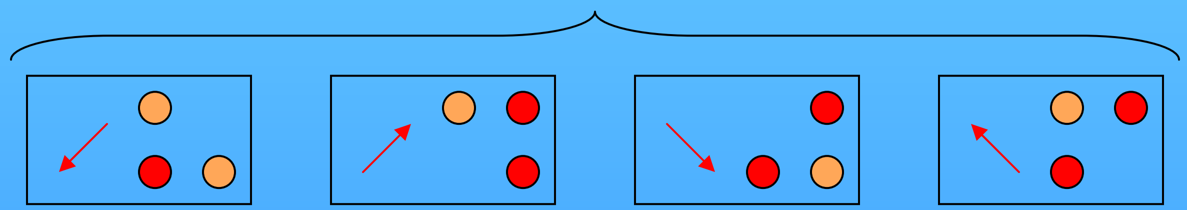
$C(\alpha)$: set of β allowed for cluster α

$$= \sum_{\nsim\alpha} \sum_{\beta\in C(\alpha)} J_{\alpha\beta} m_{\alpha} \underbrace{\left(\frac{1}{m_{\alpha}} \sum_{S} \Gamma_{S(\alpha)}(\sigma) S(\beta) \right)}_{\langle \Gamma_{\alpha'}(\sigma) \beta' \rangle_{(\alpha,\beta)}}$$

Multiplicities
(same as for conventional CE)

Tensorial Cluster Expansion

$$Q(\sigma) = \sum_{\sim\alpha} \sum_{\beta \in C(\alpha)} J_{\alpha\beta} m_\alpha \langle \beta' \Gamma_{\alpha'}(\sigma) \rangle_{(\alpha,\beta)}$$



- Outer sum: over all symmetrically distinct α
- $\Gamma_{\alpha'}(\sigma) = \prod_{i \in \alpha'} \sigma_i$ (“cluster functions”)
- m_α: multiplicities

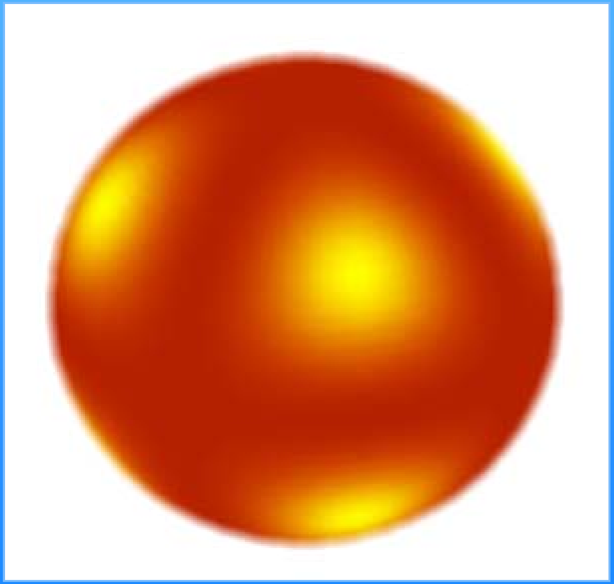
Same as in conventional cluster expansion

- β: basis tensor
- $C(\alpha)$: set of basis tensors compatible with point group of cluster α
- $\langle \cdots \rangle_{\alpha,\beta}$: average over all (α', β') equivalent to (α, β) by symmetry
- $J_{\alpha\beta}$ are coefficients to be determined.

A graphical representation of tensors

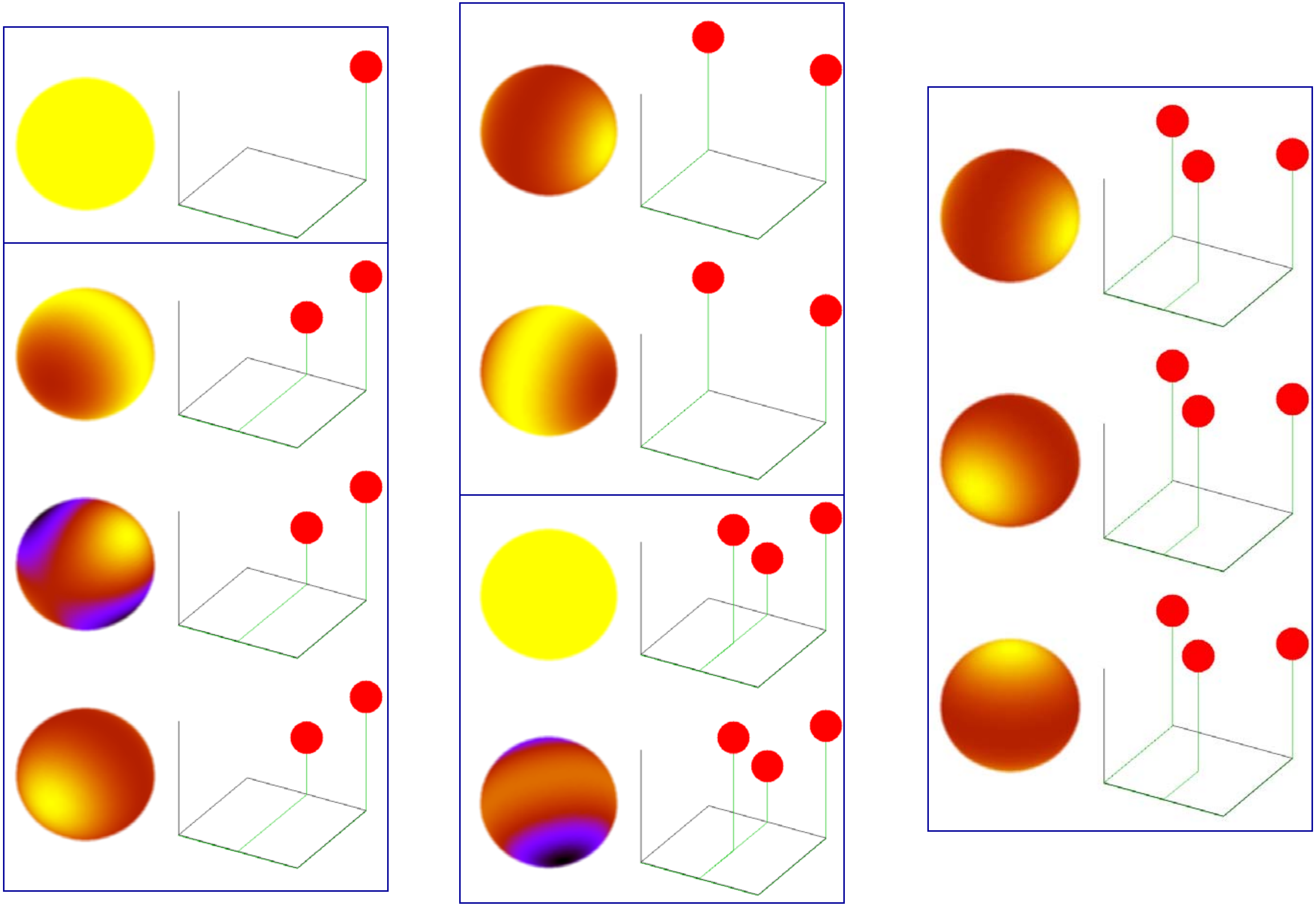
Plot $f(\mathbf{u})$ as a function of unit vector $\mathbf{u}$.

$$f(\mathbf{u}) = \sum_{i,j,k,\ldots} Q_{ijk\ldots} u_i u_j u_k \cdots$$

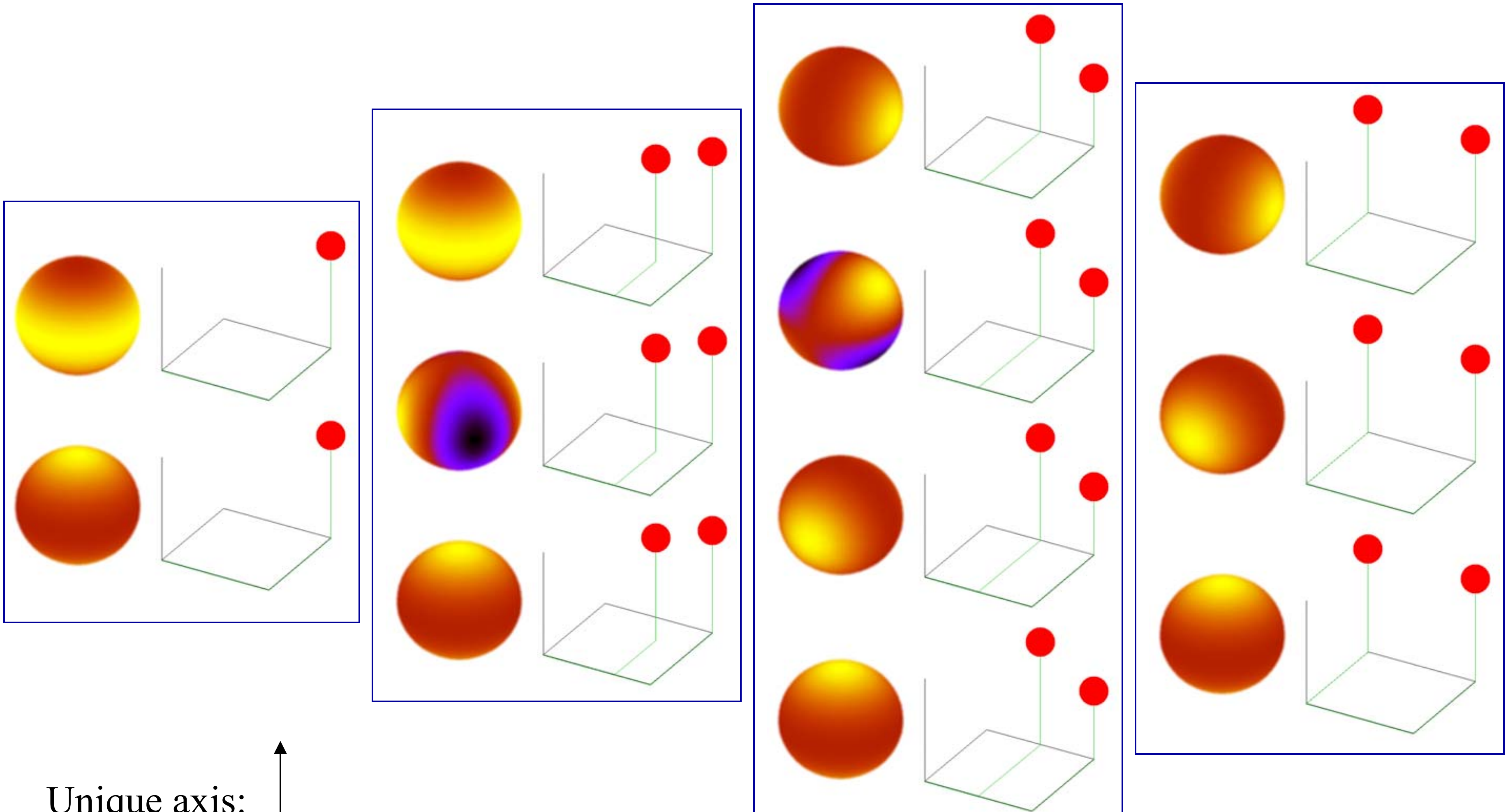


Works for any symmetric tensors (two different antisymmetric tensors could give same plot).

fcc with symmetric 2nd rank tensor



Tetragonal body-centered lattice with symmetric 2nd rank tensor



Unique axis:

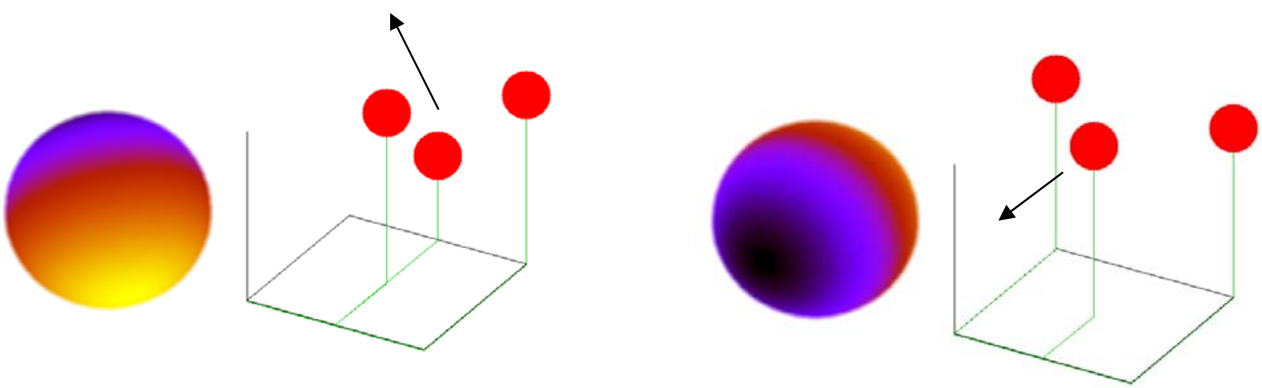
Can fcc superstructures be ferroelectric?

empty
point
pairs

Do not couple with vector-valued quantities on the fcc lattice.

All pairs are also lattice vectors "*v*" (in fcc).
v and –*v* are equivalent
⇒ pair has inversion symmetry
⇒ no unique axis possible

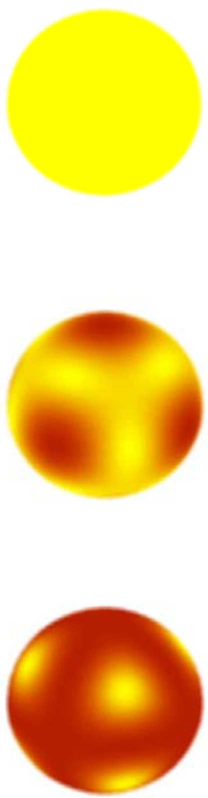
Triplets do couple with vector-valued quantities:



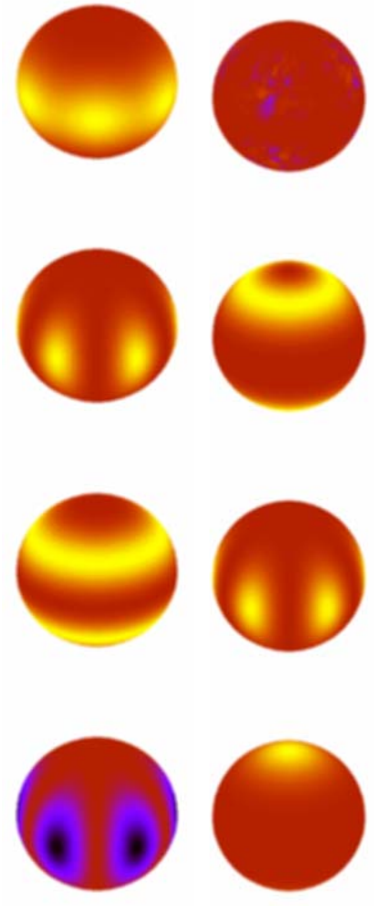
Yes, ferroelectricity possible

Special cases

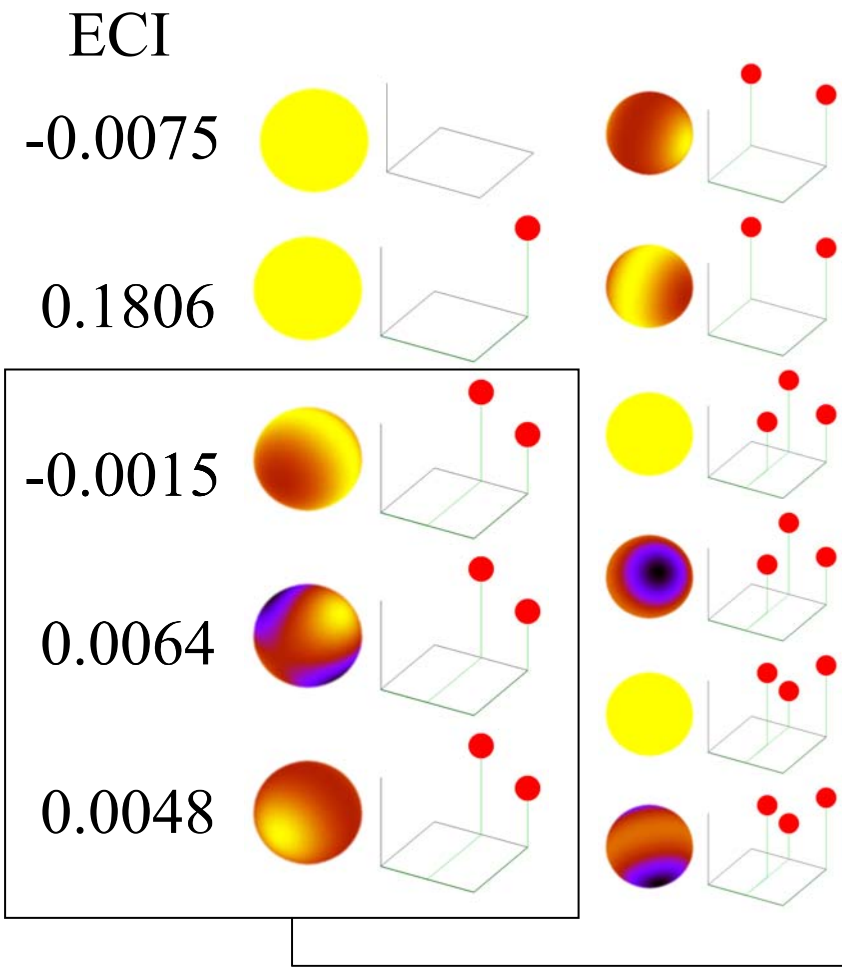
Cubic harmonics



Hexagonal harmonics

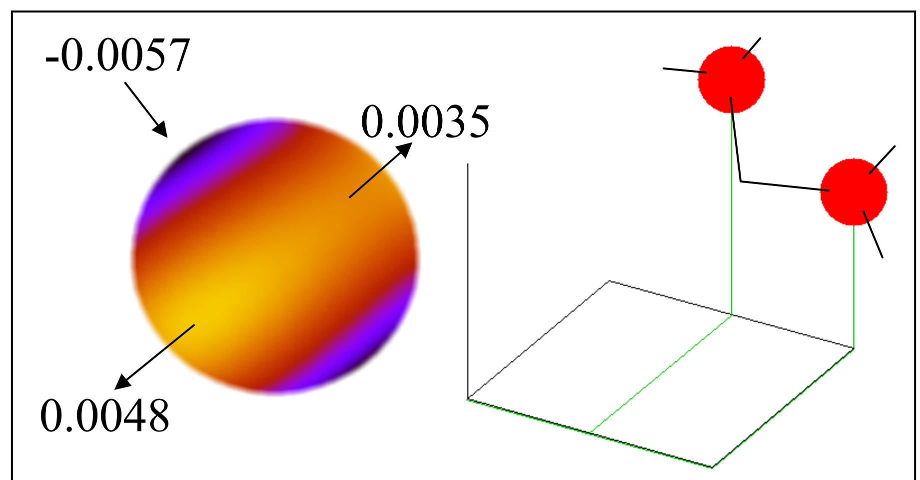


Example configuration-strain coupling in $(Ga_xIn_{1-x}N)$



Bond between alike atoms causes

- contraction along bond
- expansion perpendicular to bond

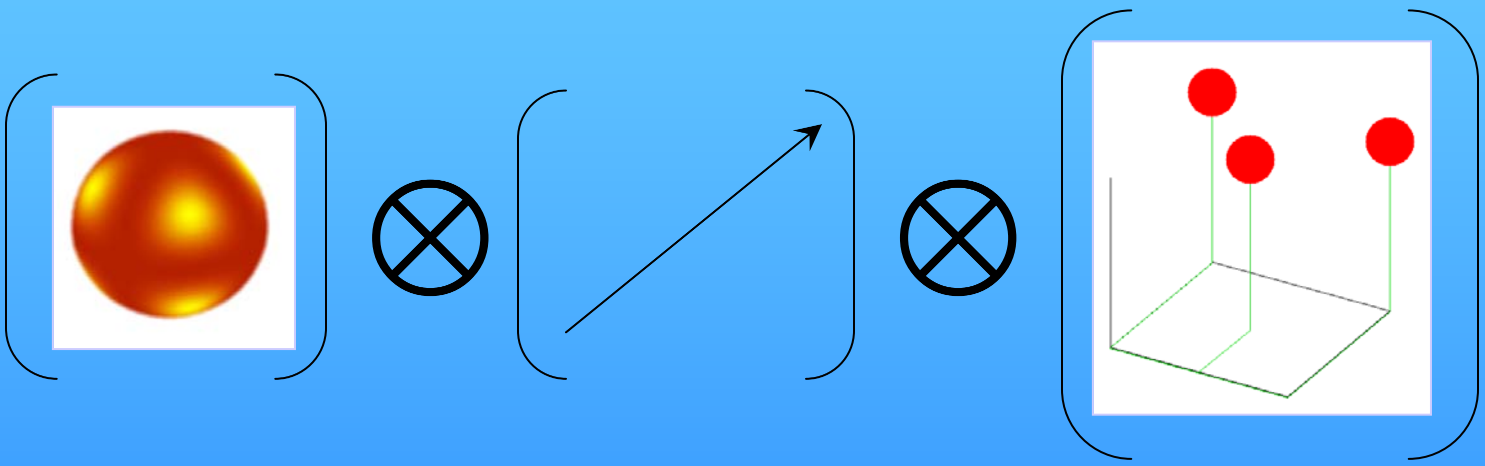


(Ga-In sublattice shown)

Extensions

Can combine any number of “Symmetry obeying objects”:

Local tensorial cluster expansion (e.g. environment-dependent force constants):



Code enables these generalizations, through object-oriented programming: