CENTER FOR MOLECULAR MODELING

GHENT UNIVERSITY

Systematic coarse-graining in metal-organic frameworks

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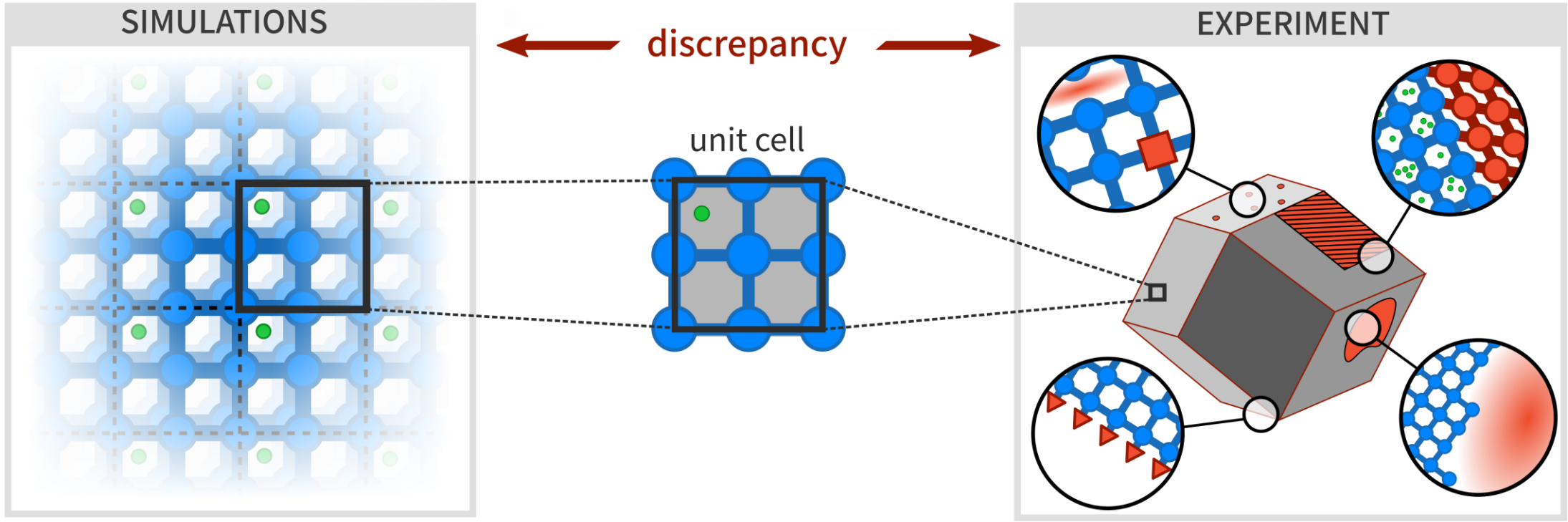
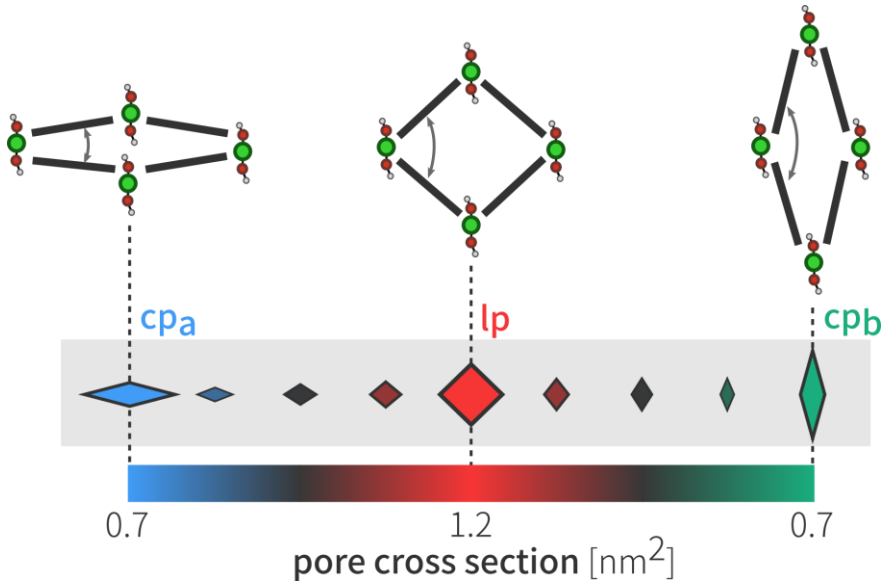
fwo Research Foundation Flanders
Opening new horizons

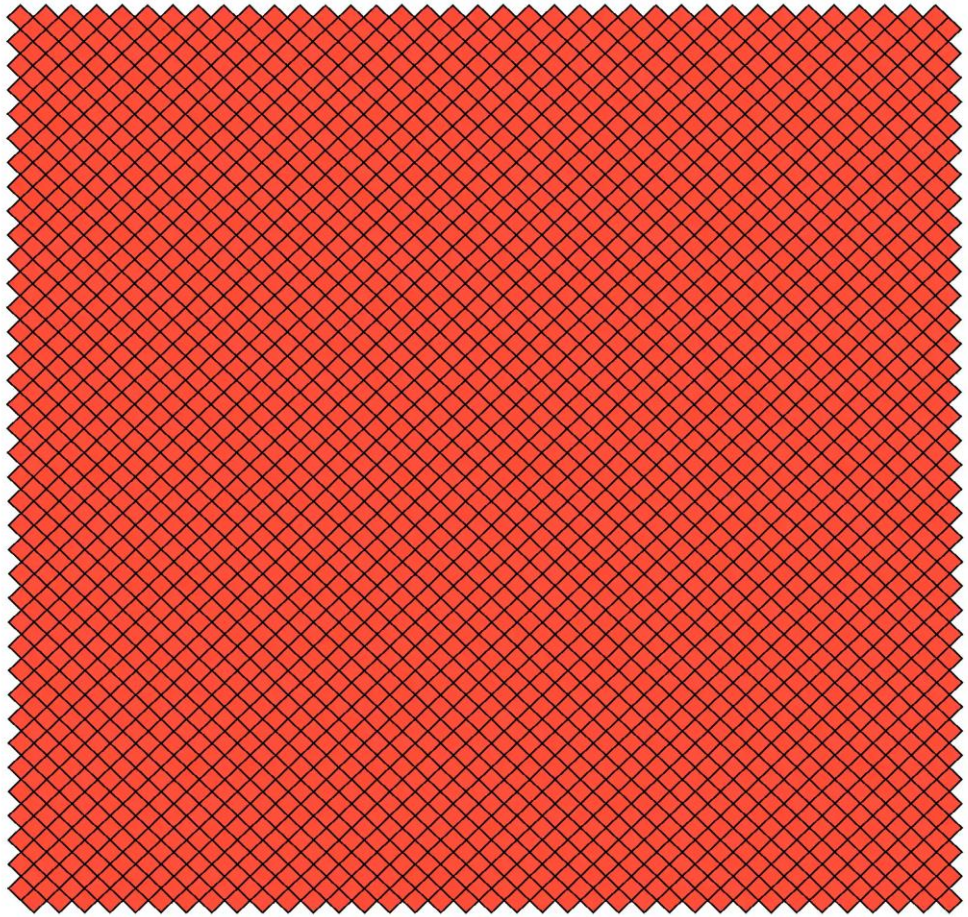
erc European Research Council

Why?



Beyond one million atoms





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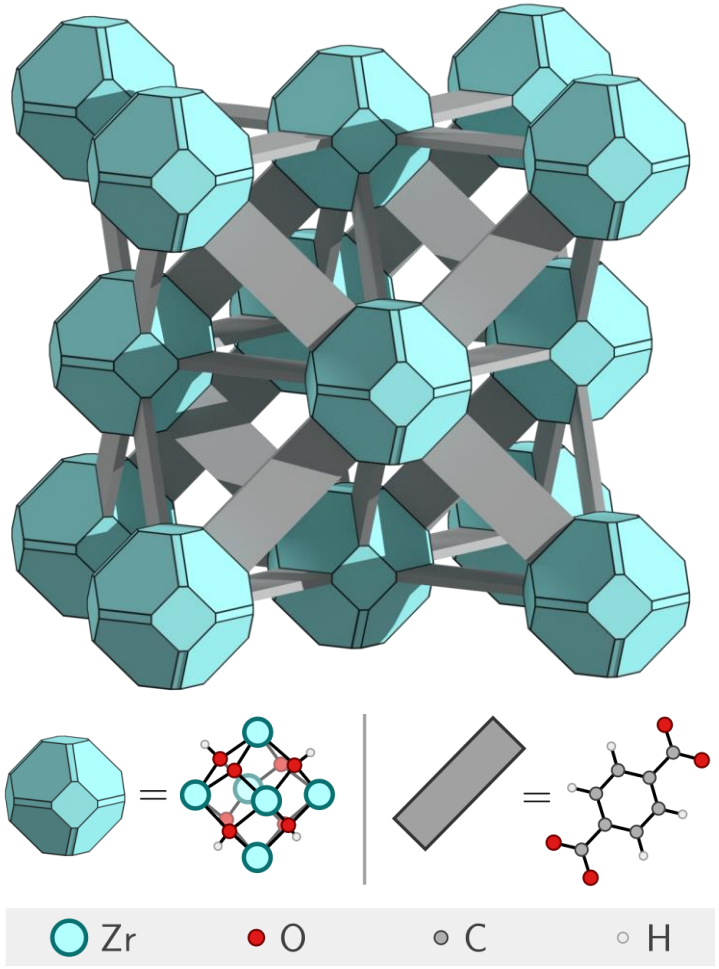
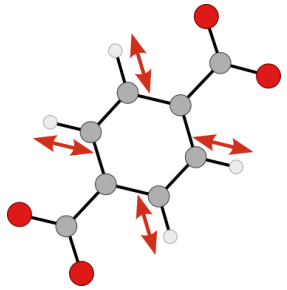
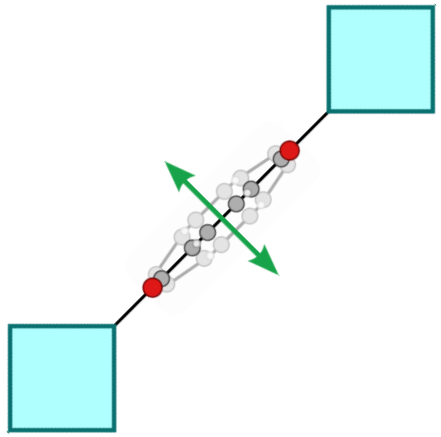
Coarse-graining in MOFs

an example: UiO-66(Zr)





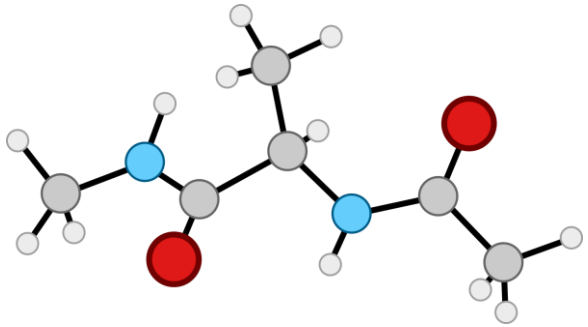
rigid, high-frequency modes
irrelevant



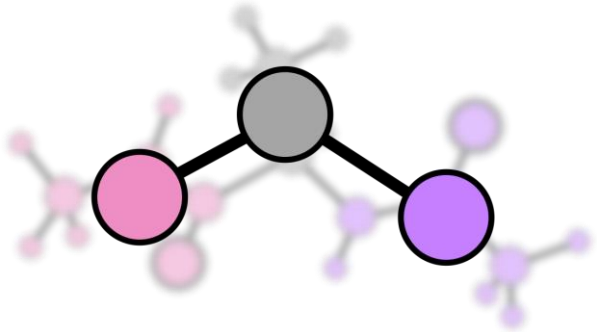
flexible, low-frequency modes;
relevant

1. partition atoms into CG beads
2. determine effective interaction potentials

The mapping entropy



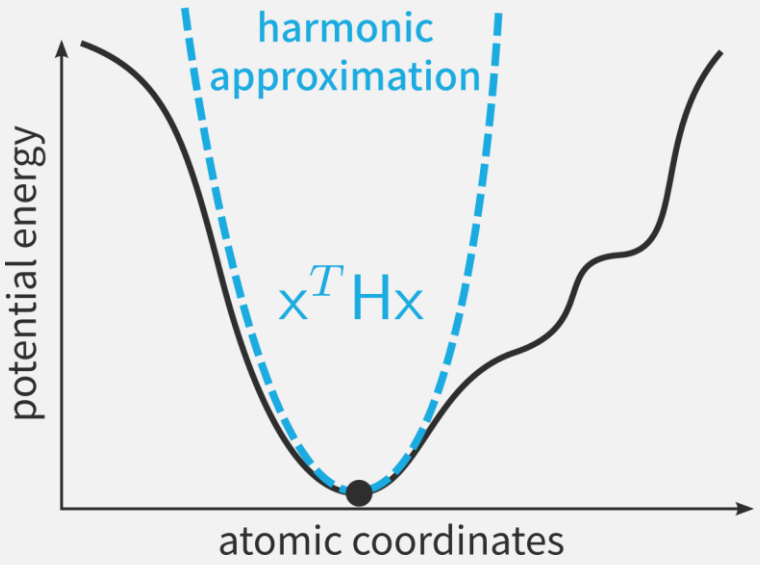
mapping ***M***



$$S_{\text{aa}} \geq S_{\text{cg}} + S_{\text{map}}$$

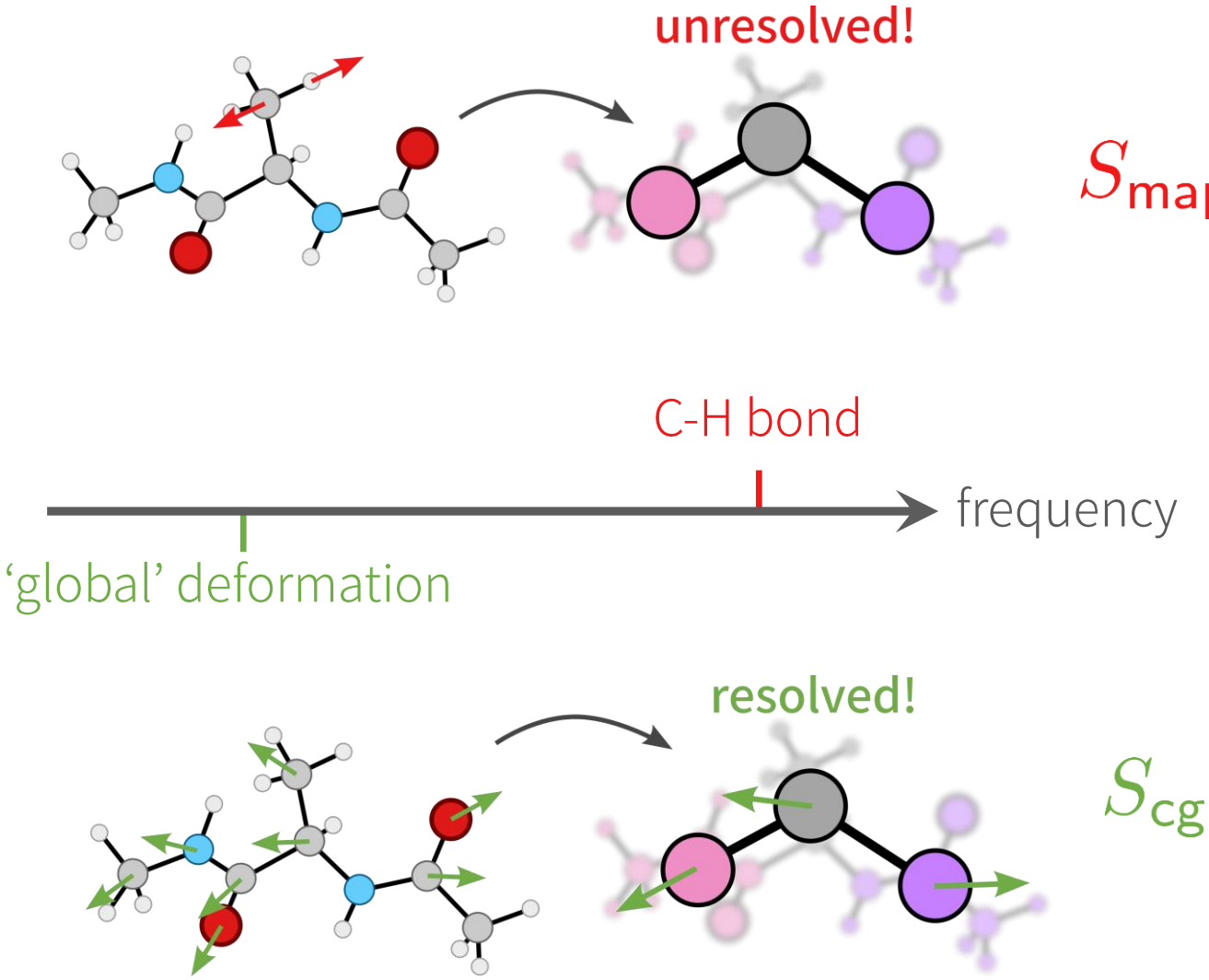
total atomic entropy | total CG entropy | **mapping entropy** ideally very small!

Physical intuition about the mapping entropy



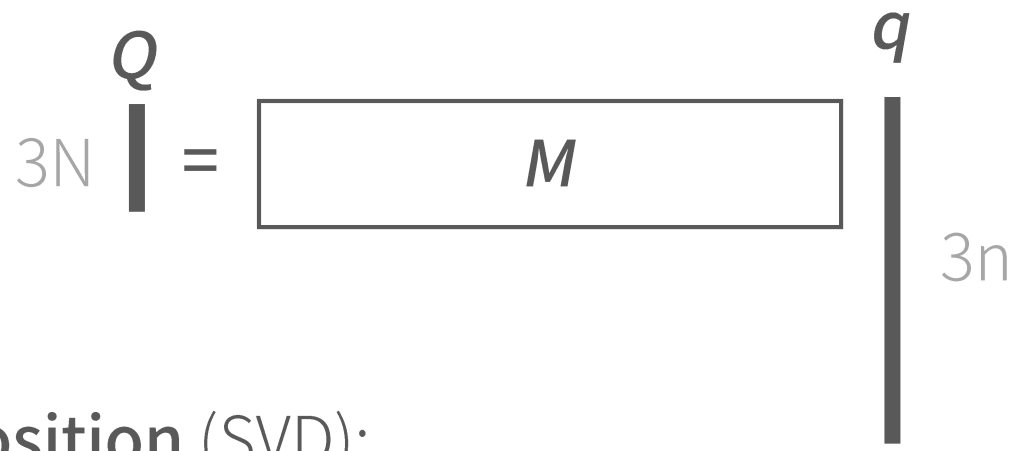
diagonalize Hessian matrix to obtain eigenmodes and eigenfrequencies

$$S_{\mathrm{aa}} = \sum_i S_{\mathrm{qm}}(\omega_i)$$

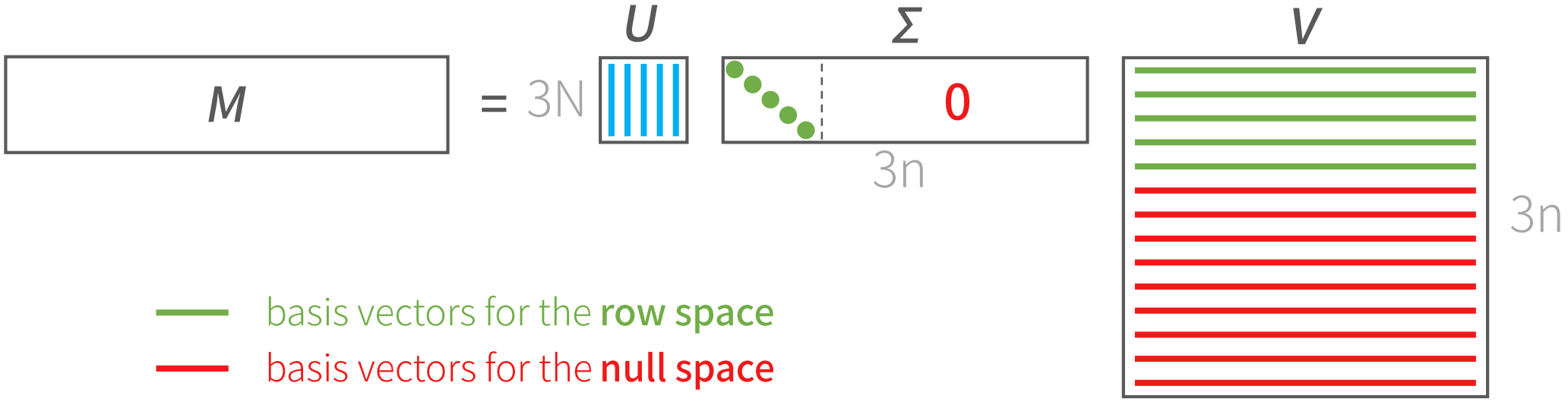


Cool... how do we formalize this intuition?

the mapping is a **linear** operator!



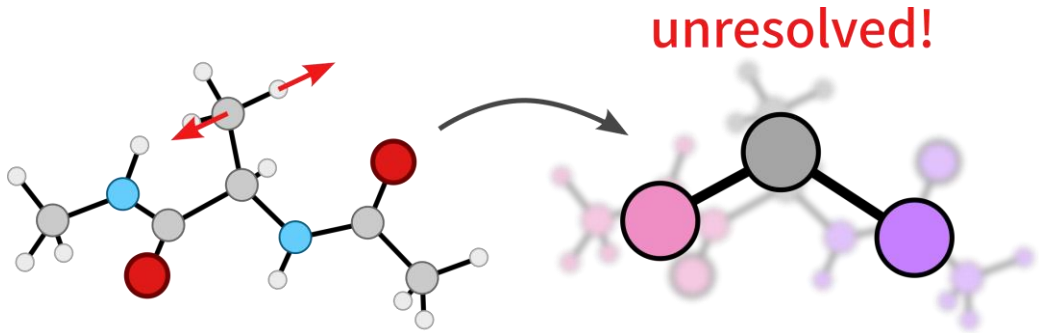
consider its **singular value decomposition** (SVD):



basis vectors for the **row space**

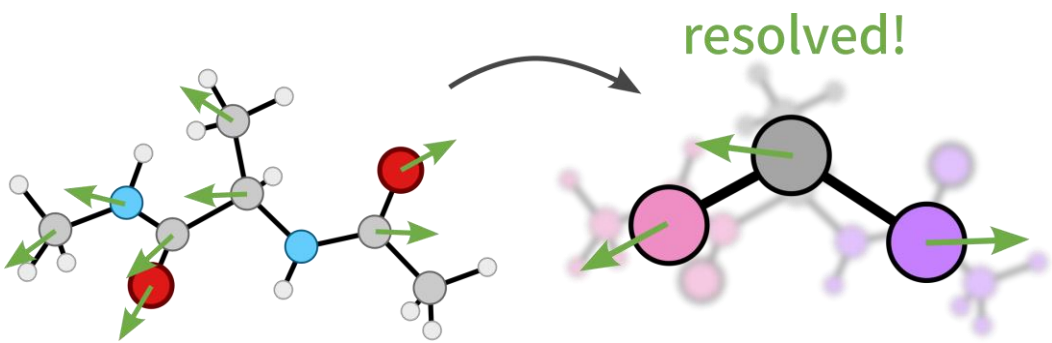
basis vectors for the **null space**

Unresolved modes reside in the null space



$$M\,q = (U\Sigma V)q \approx 0$$

unresolved modes reside in the null space of ***M***

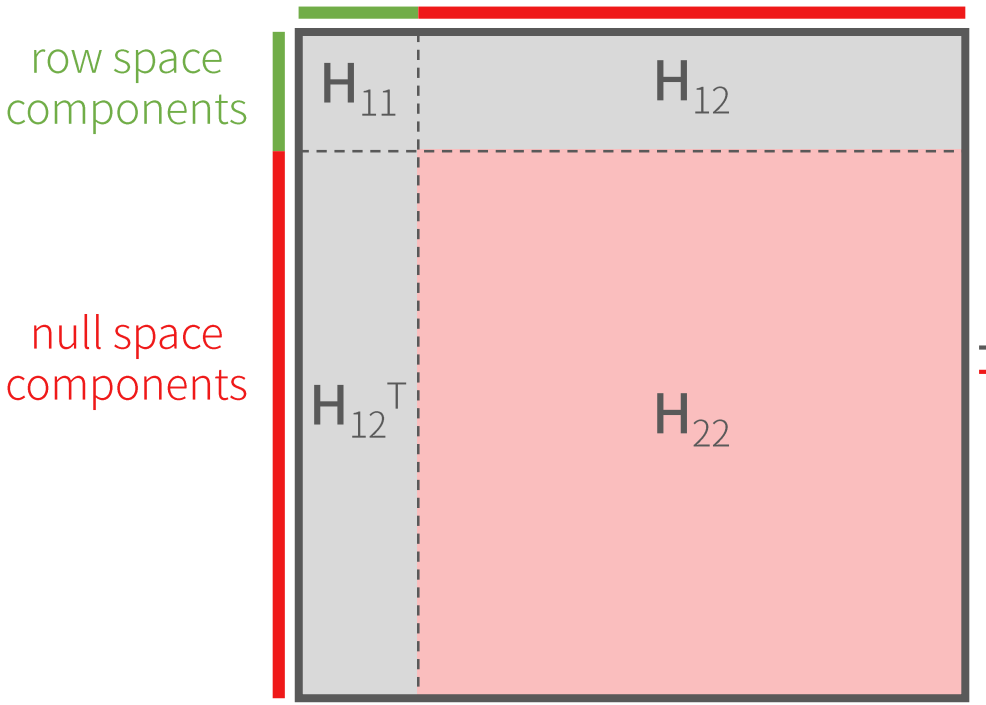


$$M\,q = (U\Sigma V)q \neq 0$$

resolved modes reside in the row space of ***M***

Represent the Hessian in the SVD basis!

transform the Hessian using $\boldsymbol{V}$:



$$S_{\mathsf{aa}} = \sum_{i}^{3n} S(\omega_i)$$

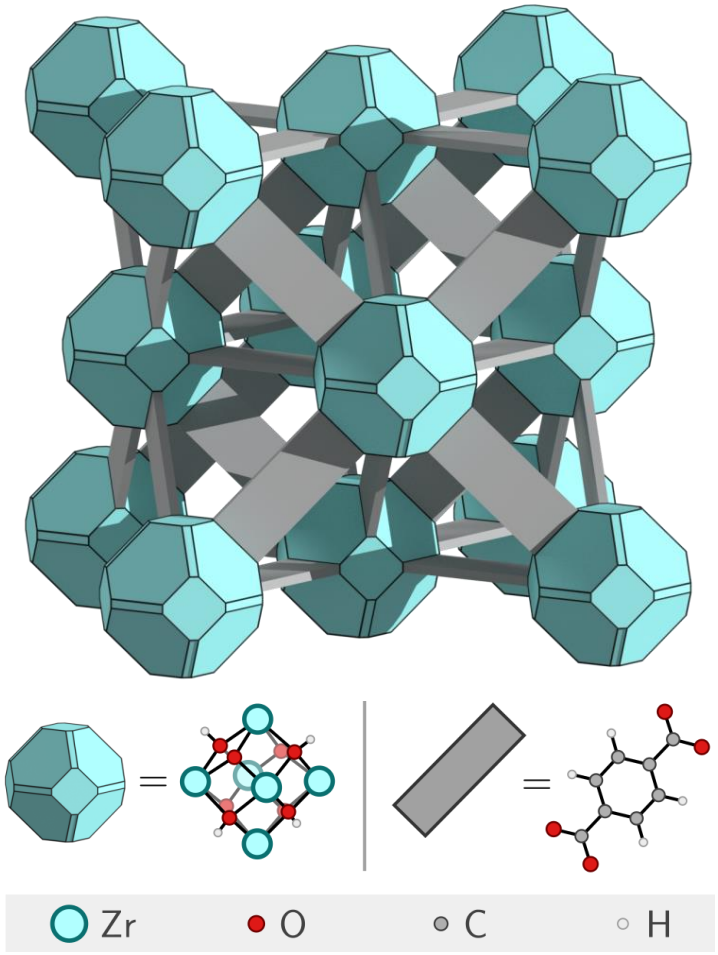
depends on:

I. the Hessian
II. the SVD of the mapping

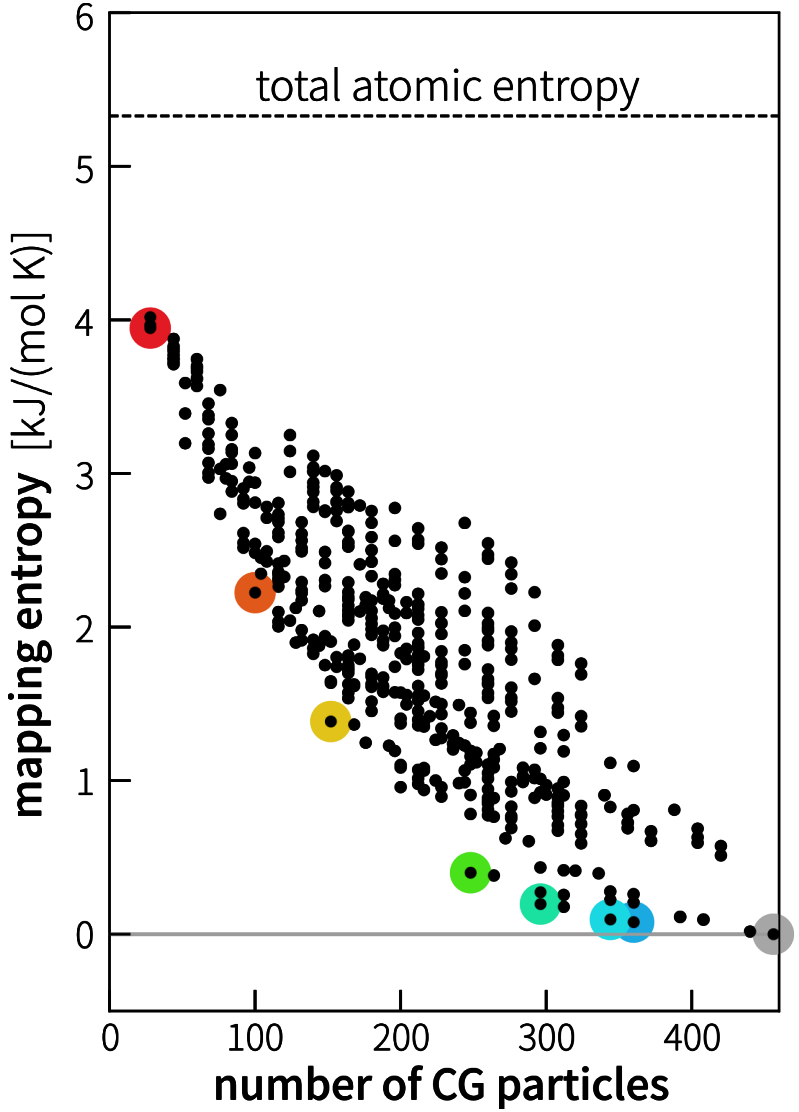
$$S_{\mathsf{map}} = \sum_{i}^{3n-3N} S(\omega_i)$$

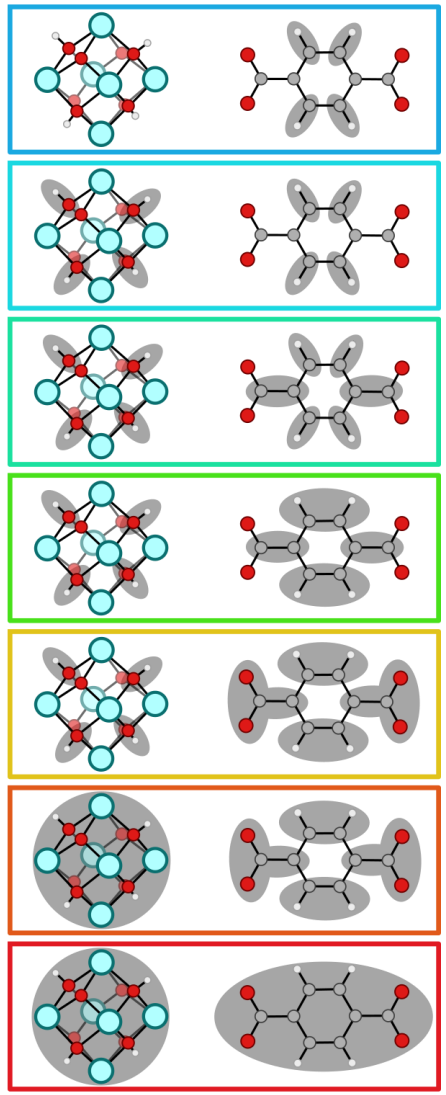
(proof based on linear algebra and stat. mech.)

UiO-66(Zr): evaluate all possible mappings



456 atoms in the unit cell;
~ 512 possible mappings!

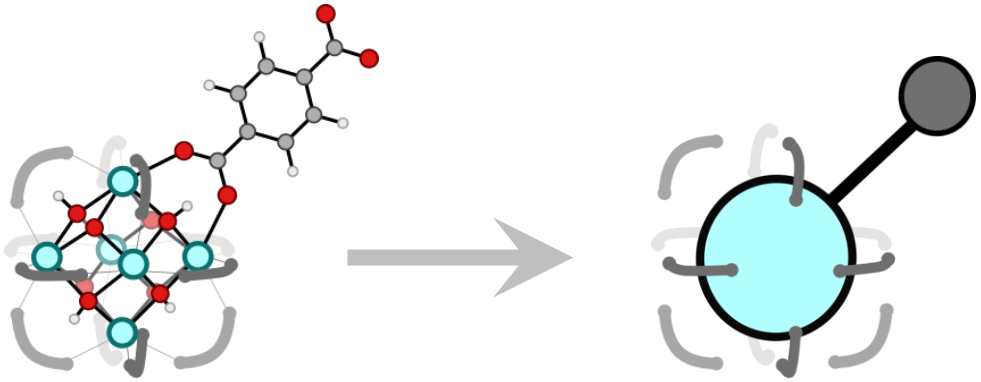


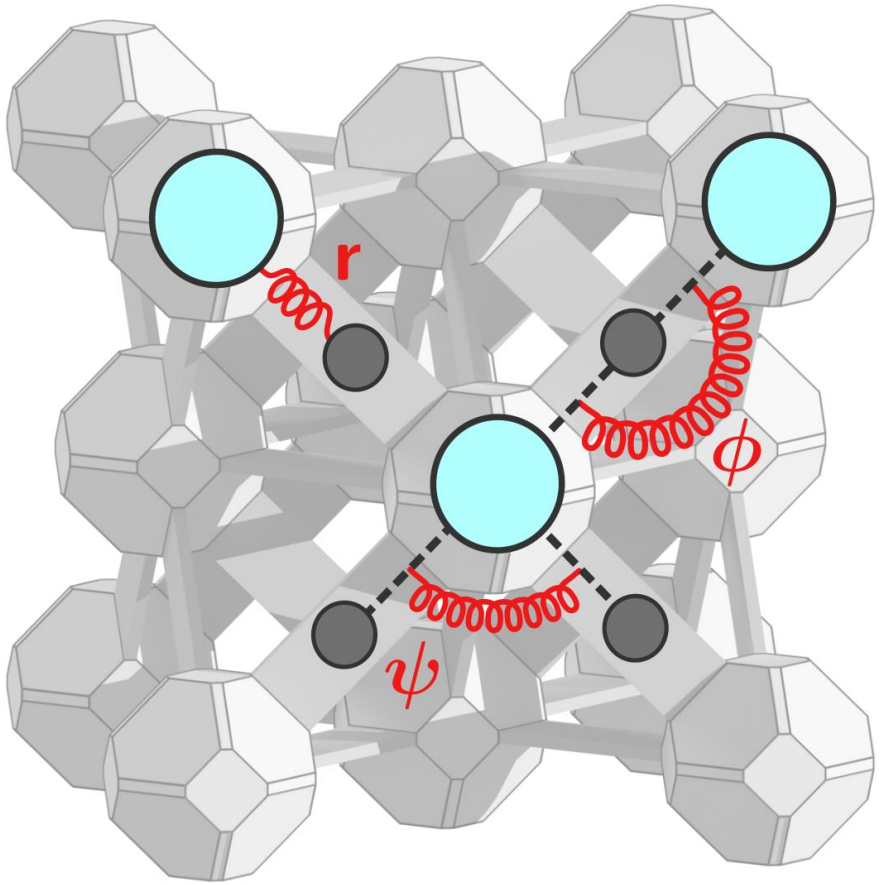


1. partition atoms into CG beads
2. determine effective interaction potentials

A minimal model for UiO-66(Zr)

consider the minimal mapping for UiO-66(Zr):





how do we parameterize the interactions?

Interactions determined by the free energy surface

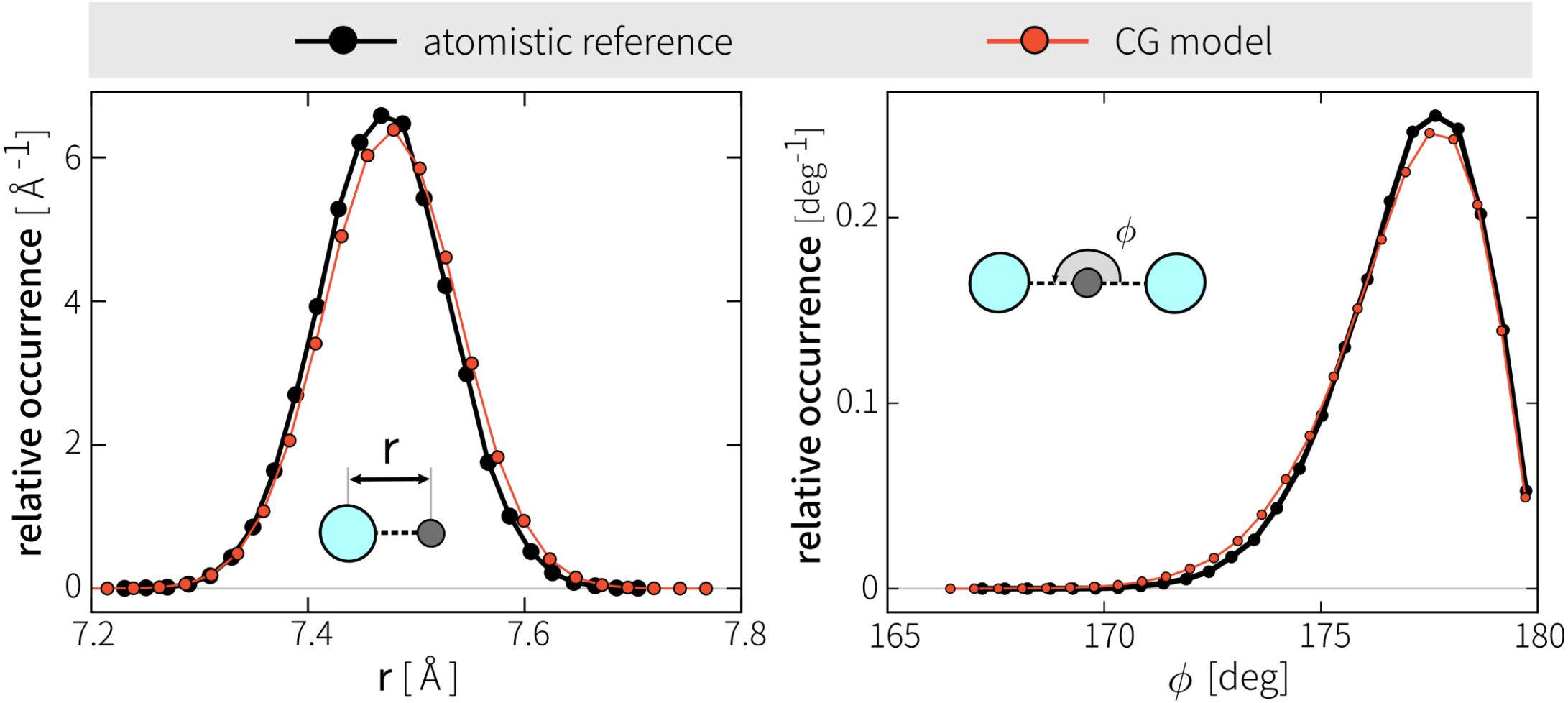
$$F(\boldsymbol{R}) = -kT \log \int e^{-\beta U_{\mathrm{aa}}(\boldsymbol{r})} \delta\left(\boldsymbol{M}(\boldsymbol{r}) - \boldsymbol{R}\right) \mathrm{d}\boldsymbol{r}$$

$$= U(\boldsymbol{R}) - TS(\boldsymbol{R})$$

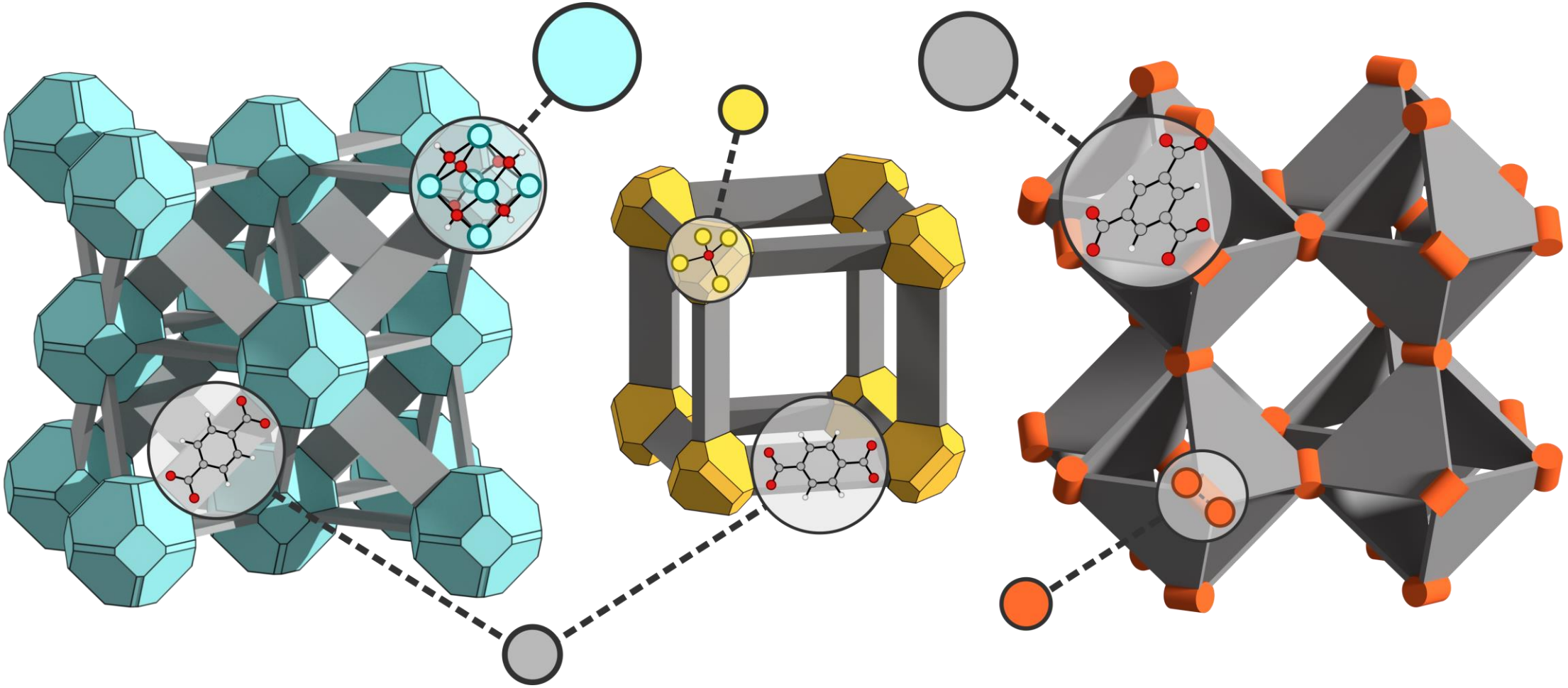
easy to approximate using energy matching!

if the atomic interactions are **harmonic**, then the entropic contribution to F(***R***) is constant!

This works quite well ...



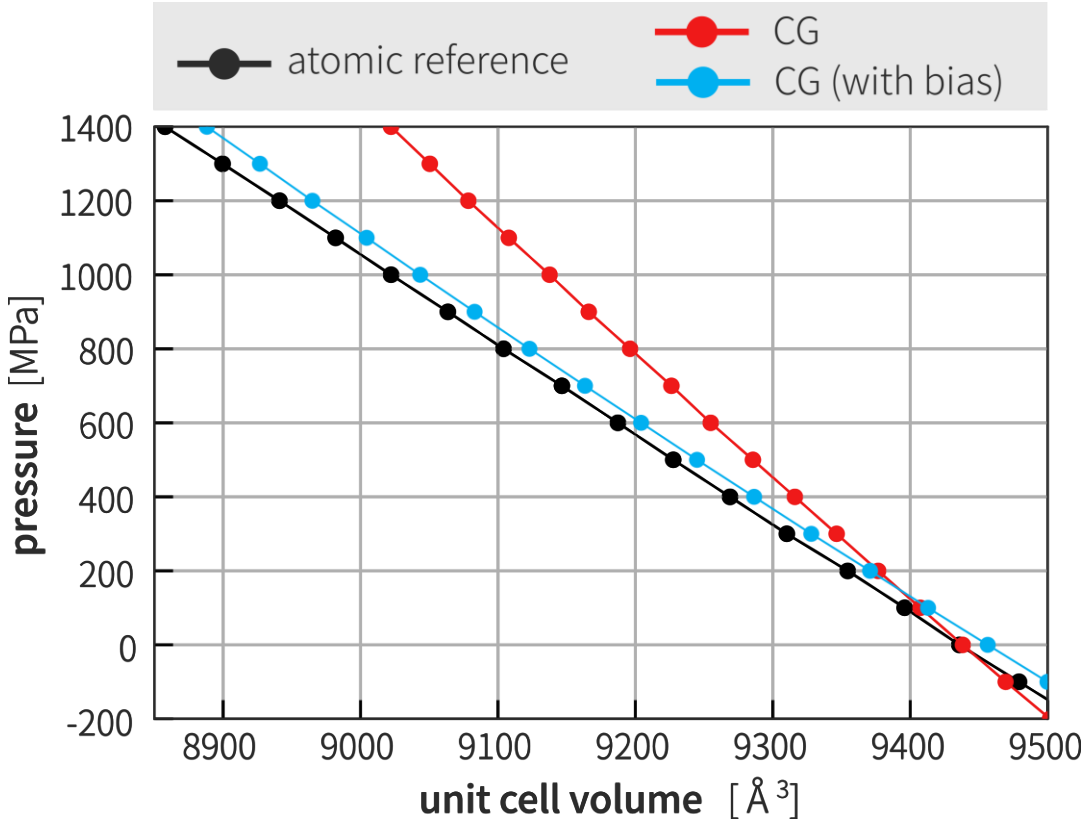
… and is generally applicable

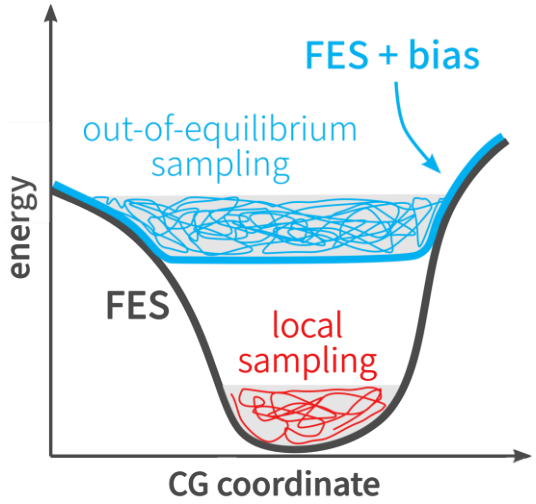


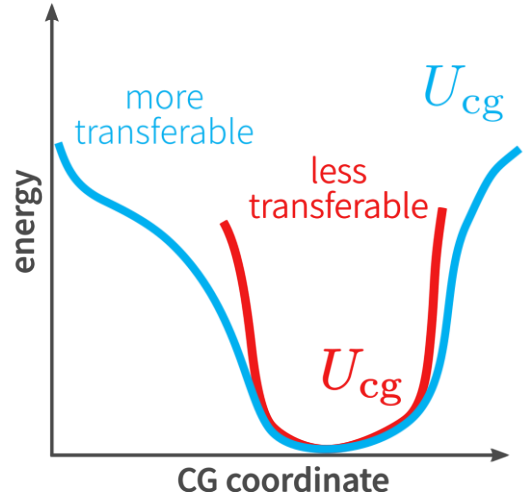
Aye, there's the rub

are these CG models **transferable**?

yes, but we need **enhanced sampling**!







1. partition atoms into CG beads

   transform the **Hessian** using the **eigendecomposition** of the mapping

2. determine effective interaction potentials

   incorporate **enhanced sampling** to obtain **transferable** models

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