FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

FAST GEOMETRY OPTIMIZATION OF LARGE-SCALE SYSTEMS WITH SMALL NUMERICAL BASIS SETS

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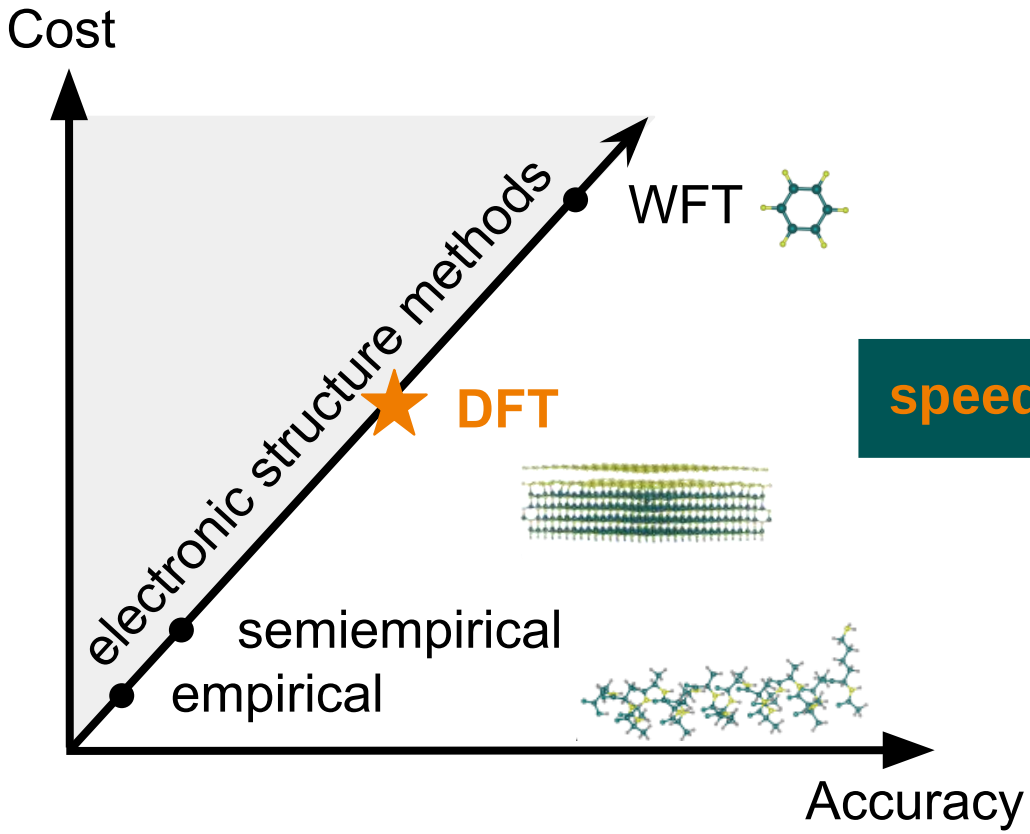
DFT – THE WORKHORSE OF MATERIALS MODELLING



speed-up

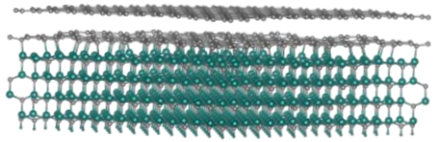
small basis + correction

- fast
- robust
- accurate

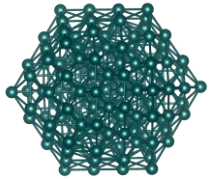
SMALL BASIS + CORRECTION IN MATERIALS MODELLING AREAS OF APPLICATIONS

- **systems with hundreds of atoms**
  speed-up molecular dynamics,
  geometry optimizations etc.
  use in composite methods

- **systems with >= 1000 of atoms**
  enable large-scale geometry
  optimization at DFT level



surfaces/interfaces

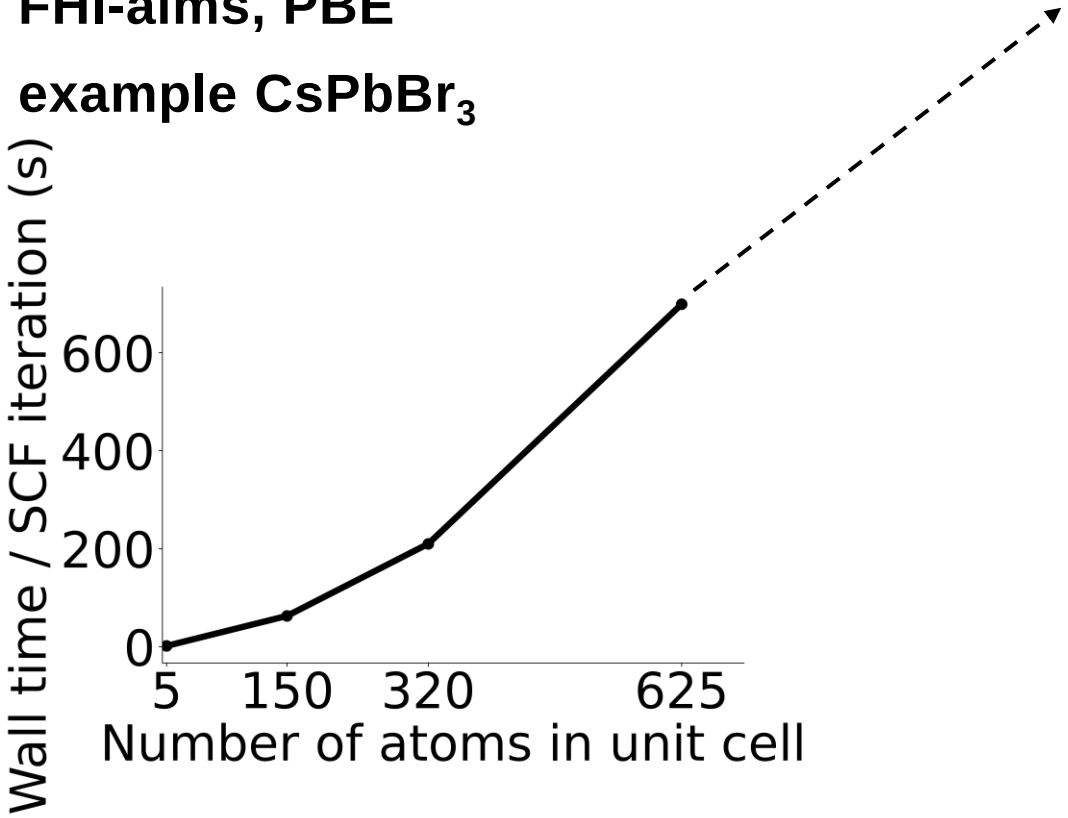


nanoparticles

KS-DFT BOTTLENECK

FHI-aims, PBE

example $CsPbBr_3$



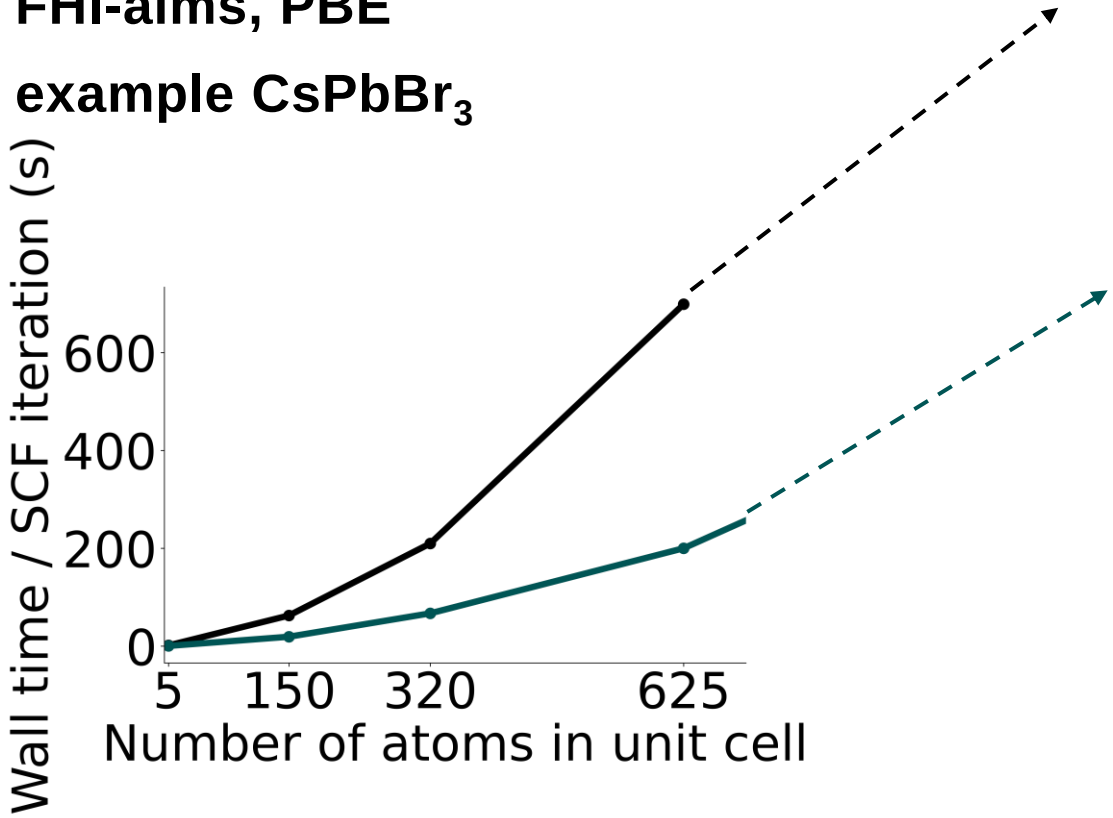
basis-set size: converged (‘tight’)

cubic-scaling $O(N^3)$ bottleneck

ENABLE LARGE-SCALE COMPUTATIONS WITH SMALL BASIS SET

FHI-aims, PBE

example $CsPbBr_3$



basis-set size: converged (‘tight’)

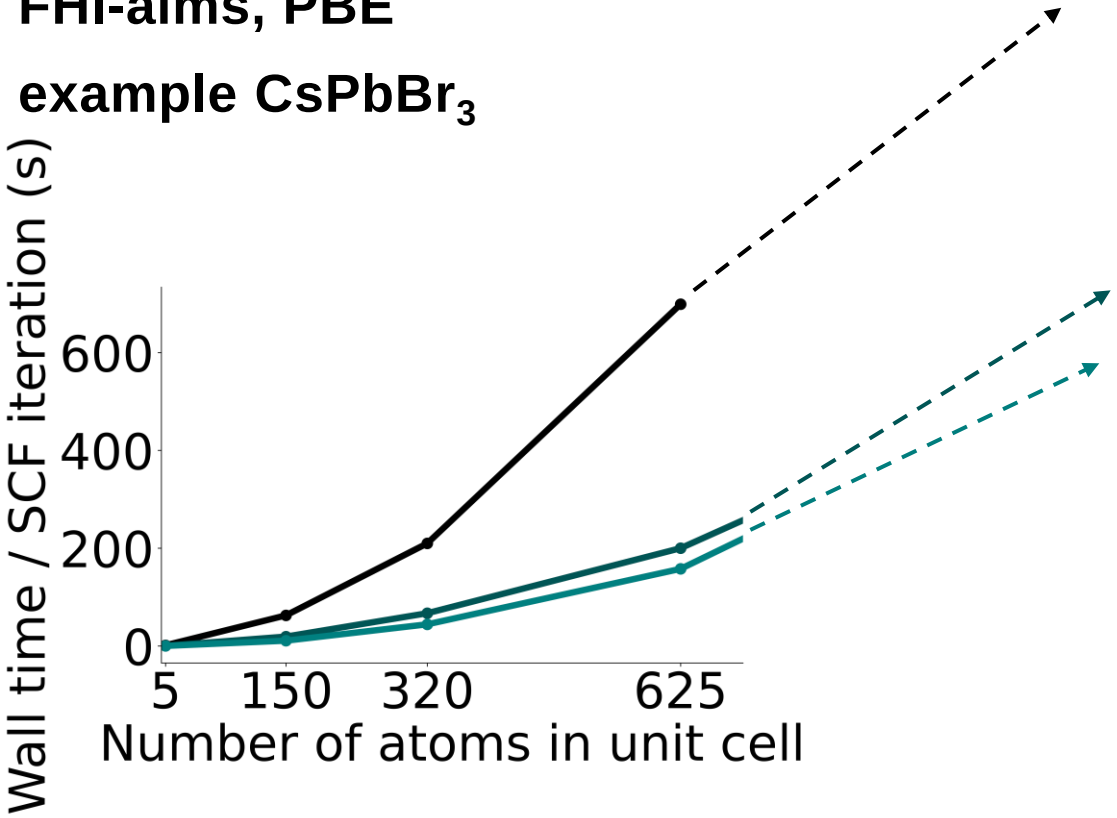
increase accessible system size with:

(1) basis-set size: ‘min+s’

ENABLE LARGE-SCALE COMPUTATIONS WITH SMALL BASIS SET

FHI-aims, PBE

example $CsPbBr_3$



basis-set size: converged (‘tight’)

increase accessible system size with:

(1) basis-set size: ‘min+s’

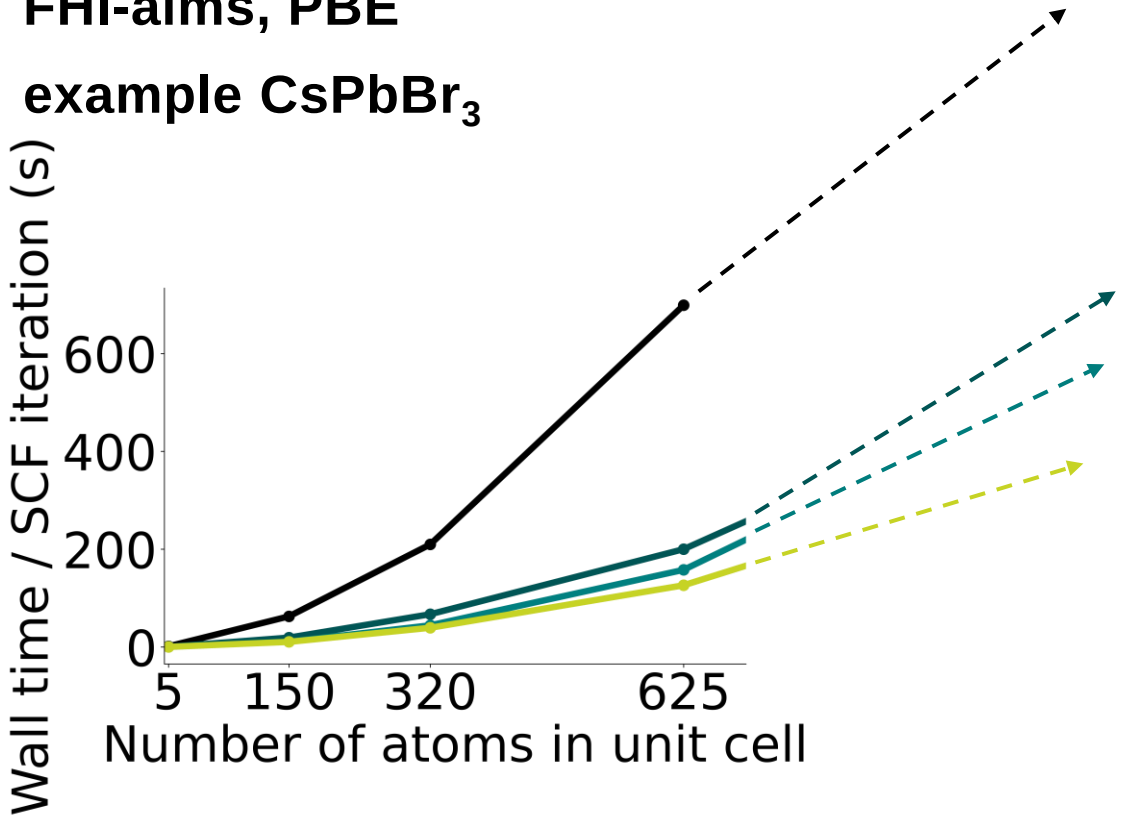
+(2) frozen core approximation [1]

[1] Yu et al., J. Chem. Phys. 154, 224107 (2021)

ENABLE LARGE-SCALE COMPUTATIONS WITH SMALL BASIS SET

FHI-aims, PBE

example $CsPbBr_3$



basis-set size: converged (‘tight’)

increase accessible system size with:

(1) basis-set size: ‘min+s’

+(2) frozen core approximation [1]

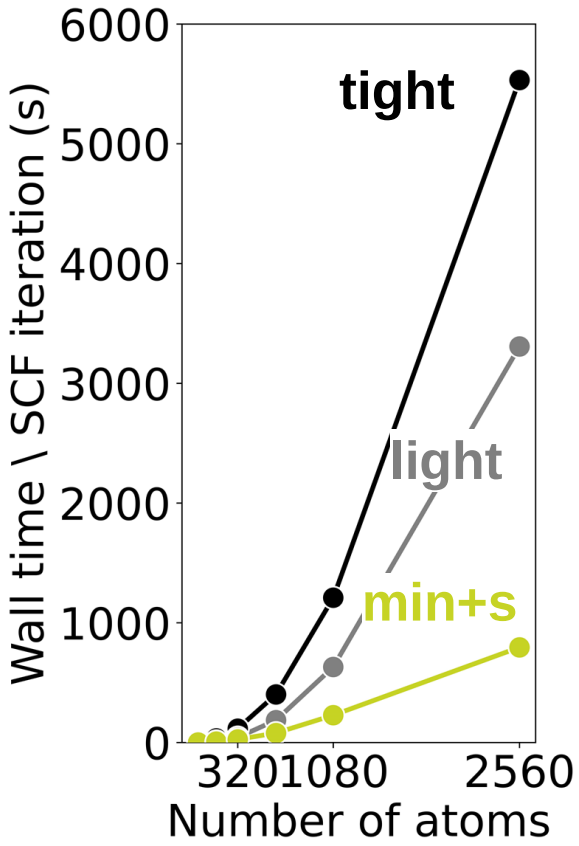
+(3) ‘light’ grid settings

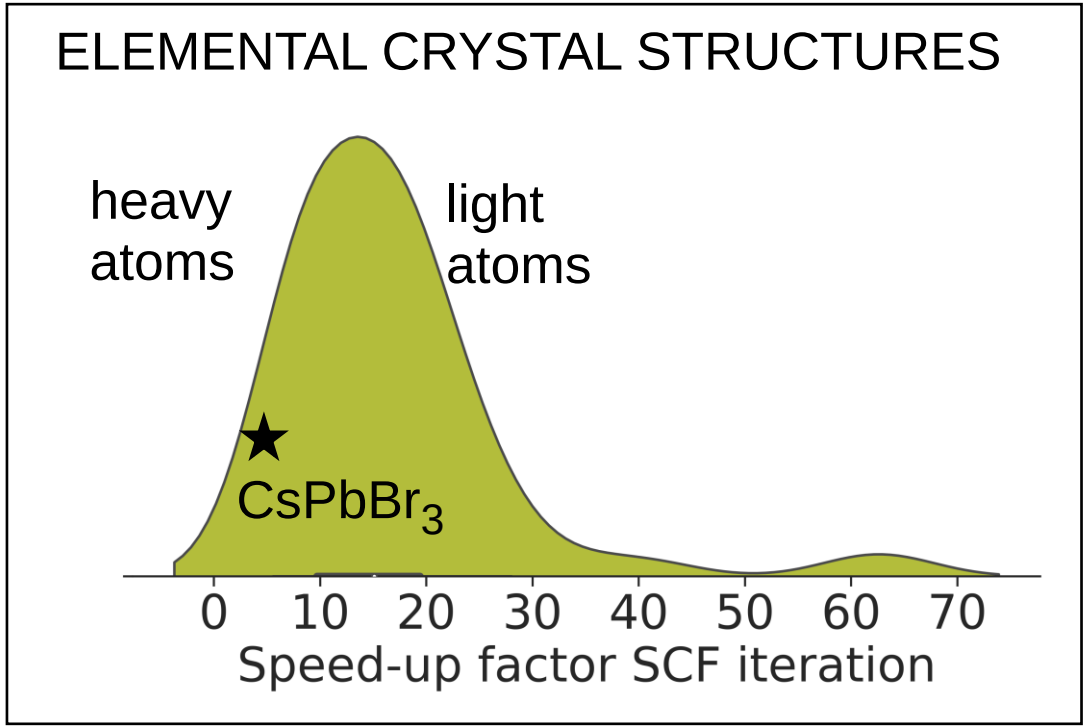
[1] Yu et al., J. Chem. Phys. 154, 224107 (2021)

PERFORMANCE SMALL BASIS SET
$CsPbBr_3$ WITH BASIS SET REDUCTION TO 53%

Time consumption ~O(N^3)

100% → 21%





Structures from Lejaeghere et al., Crit. Rev. Solid State Mater. Sci. 39, 1-24 (2014)

PERFORMANCE SMALL BASIS SET
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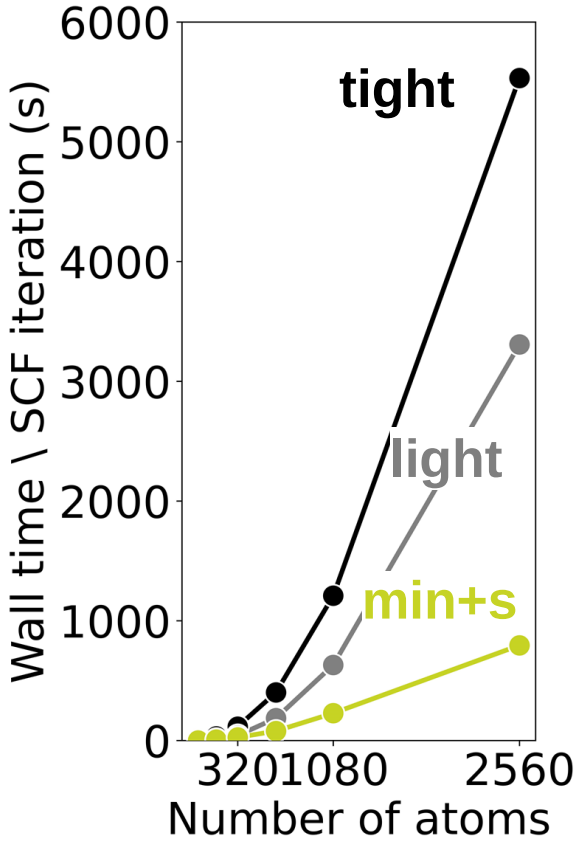
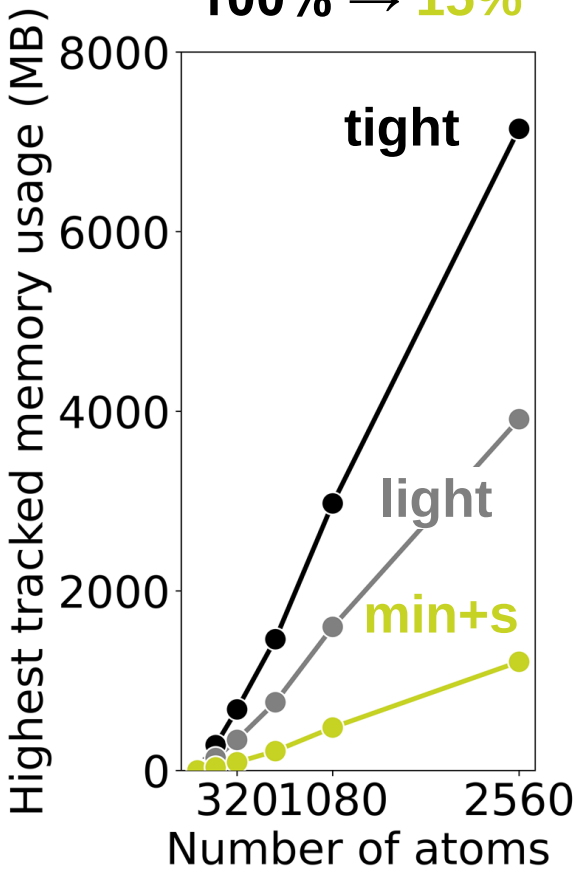
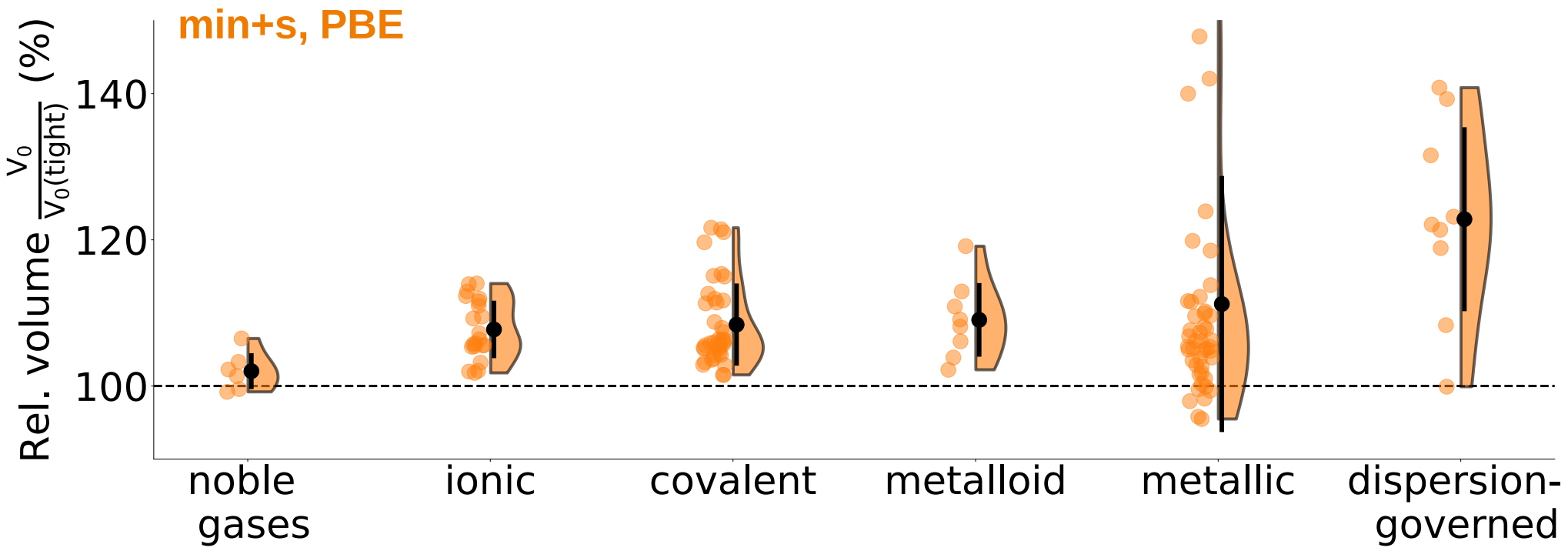


Memory usage ~O(N)

100% → 15%

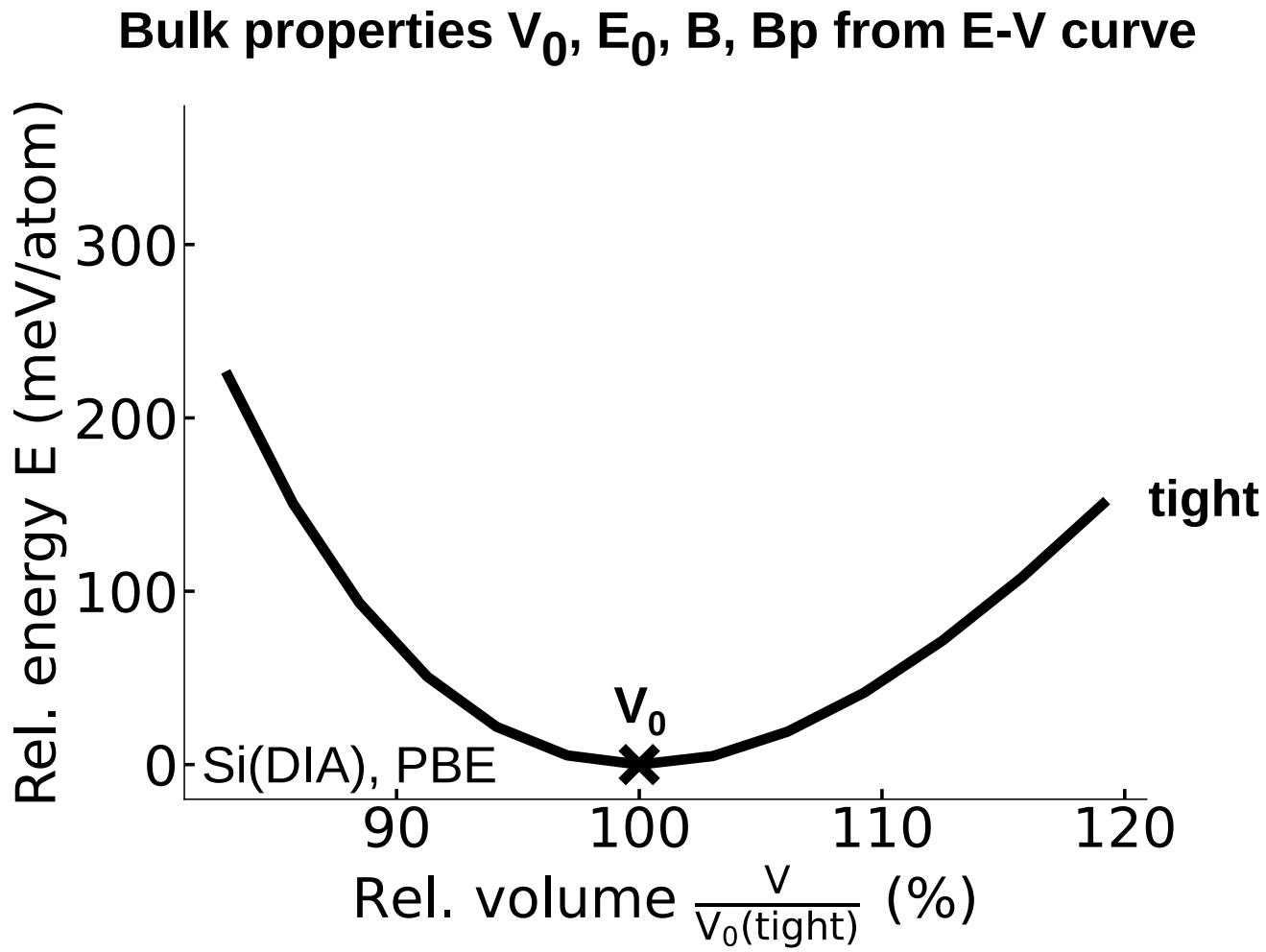


WHY NOT USE SMALL BASIS SETS ON A REGULAR BASIS ?
SMALL BASIS SET ERROR



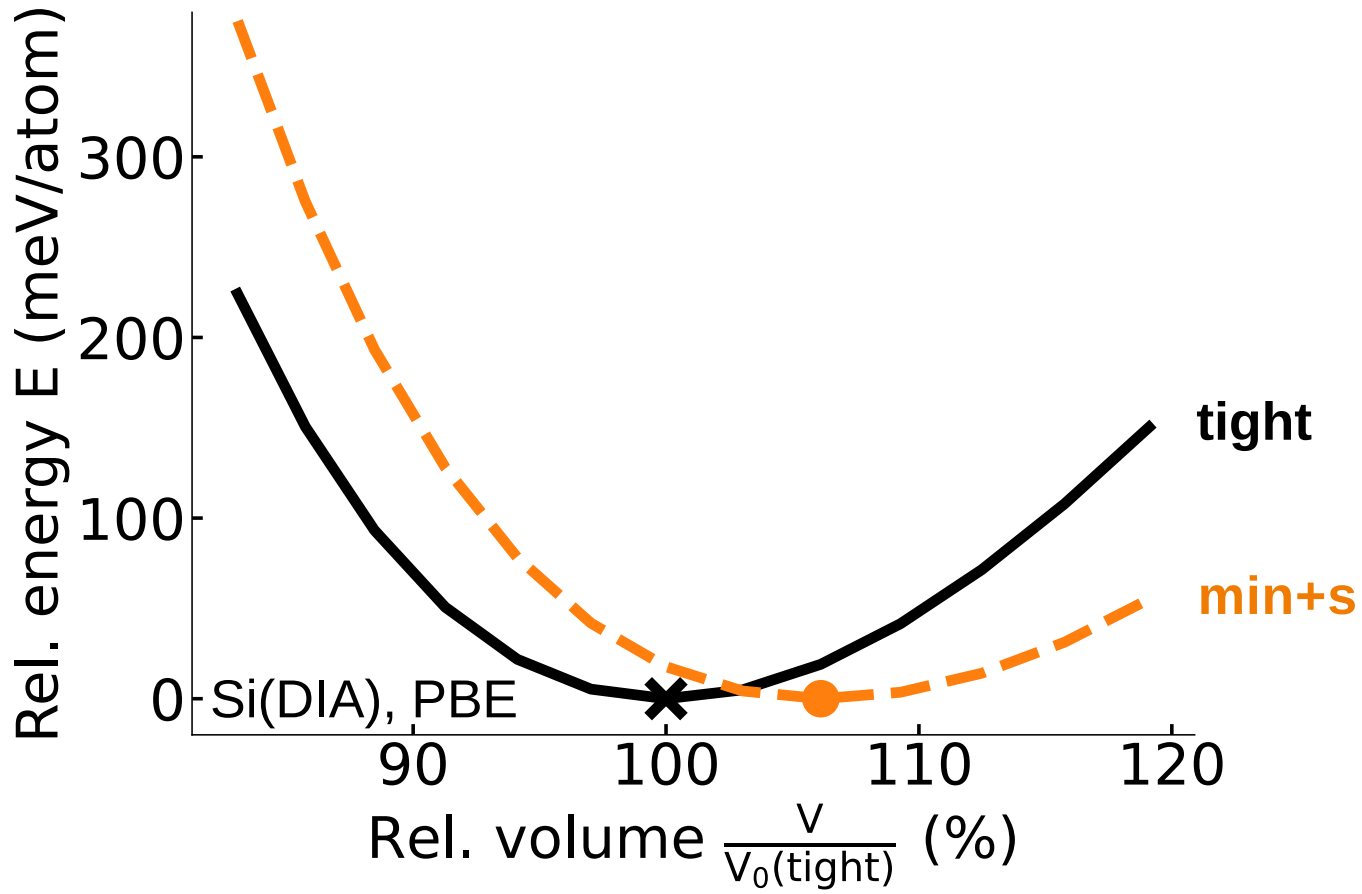
Structures from Lejaeghere et al., Crit. Rev. Solid State Mater. Sci. 39, 1-24 (2014), Huhn et al., Phys. Rev. Materials 1.3 (Aug. 2017)

MEASURE OF BASIS SET ERROR IN BULK SYSTEMS



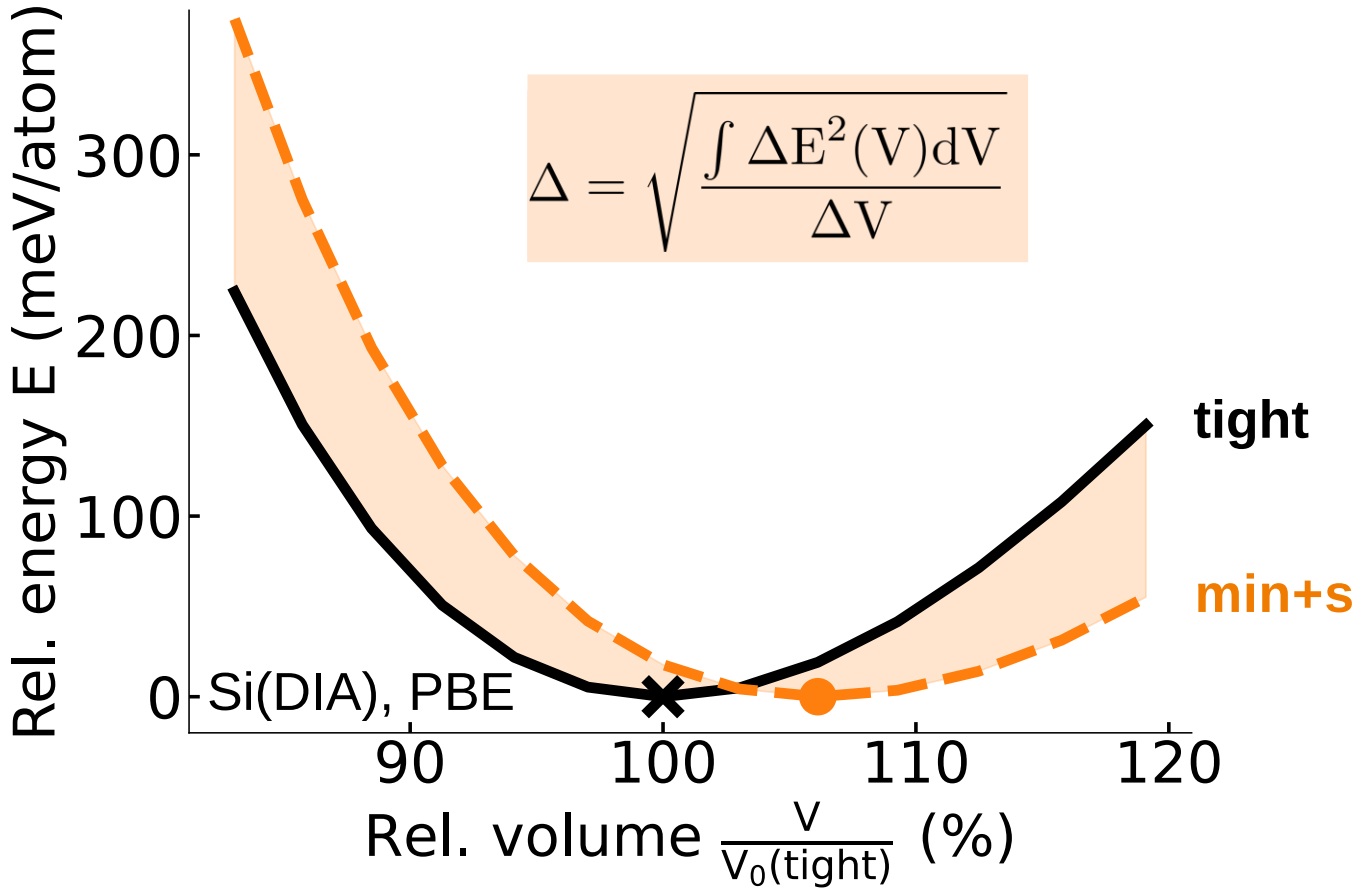
MEASURE OF BASIS SET ERROR IN BULK SYSTEMS

Small basis set alters V_0, E_0, B, Bp and shape of E-V curve



MEASURE OF BASIS SET ERROR IN BULK SYSTEMS

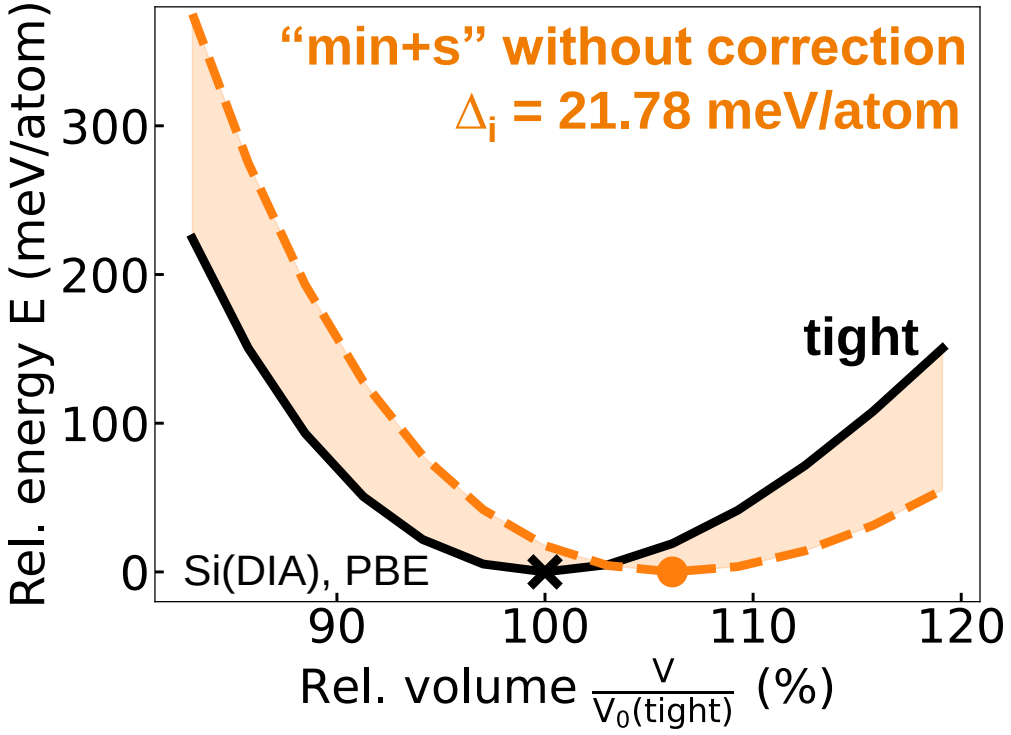
Similarity to “tight” E-V curve with Δ-value [2]

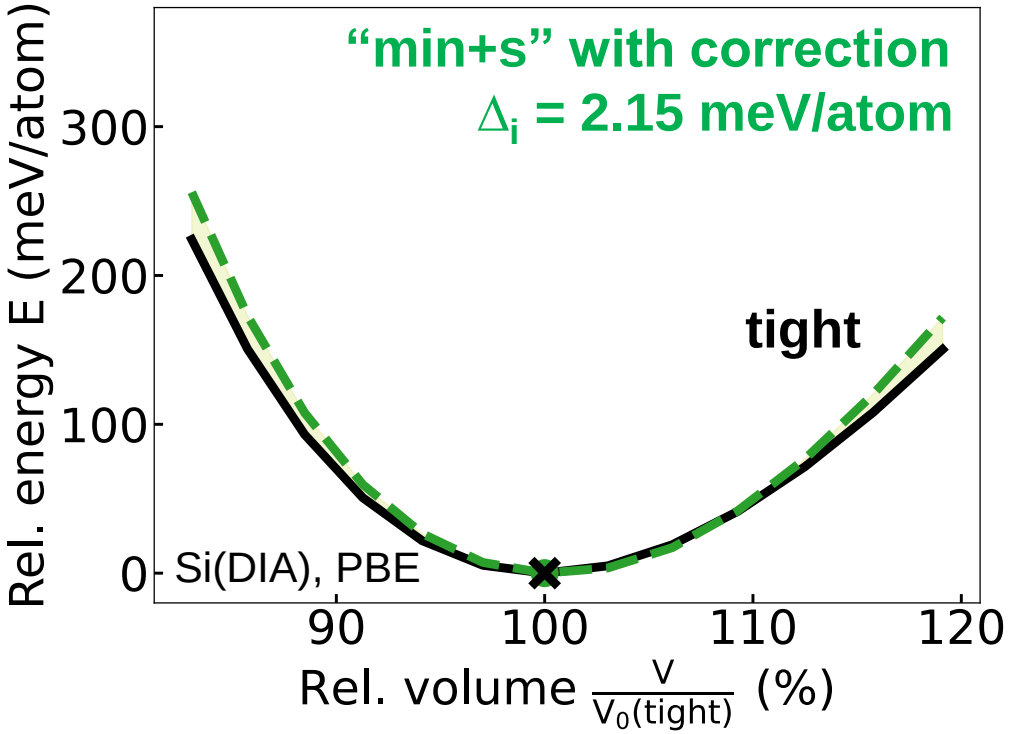


[2] Lejaeghere et al., Crit. Rev. Solid State Mater. Sci. 39, 1-24 (2014)

CORRECTION TO RECOVER ACCURATE GEOMETRIES
OBJECTIVE OF THE CORRECTION

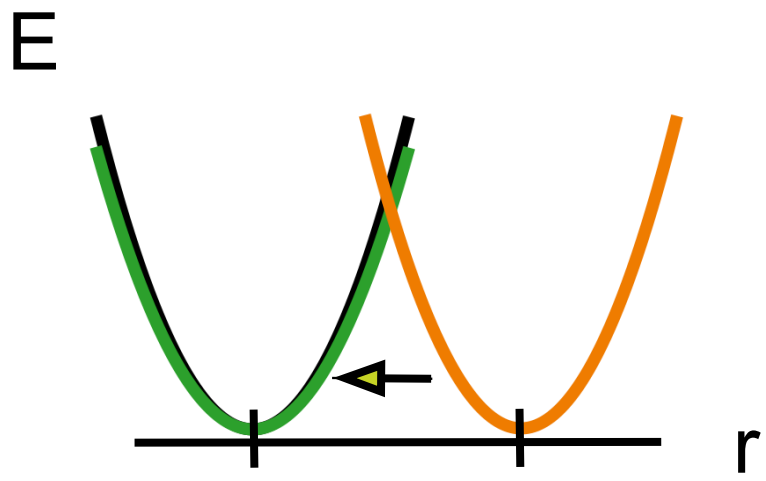
Increase similarity between the corrected "min+s“ and “tight” E-V curve



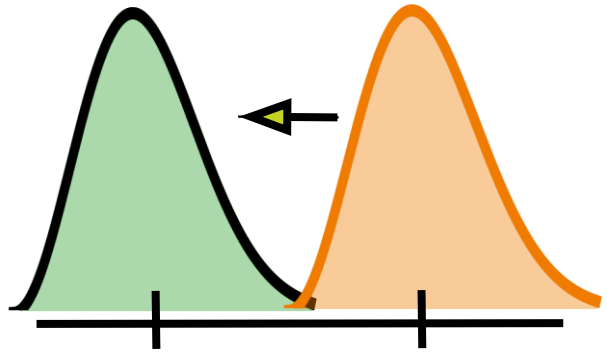


CORRECTION TO RECOVER ACCURATE GEOMETRIES
CHARACTERISTICS OF THE CORRECTION

Linear correction is most <u>minimally-invasive</u> [3]



correct equilibrium bond lengths



intact statistical ensemble

$$E_{total} = E_{small\ basis} + E_{correction}$$

[3] Pitera et al., J. Chem. Theory Comput. 8.10 (2012)

CORRECTION TO RECOVER ACCURATE GEOMETRIES
MINIMALLY INVASIVE LINEAR CORRECTION

Proposed method

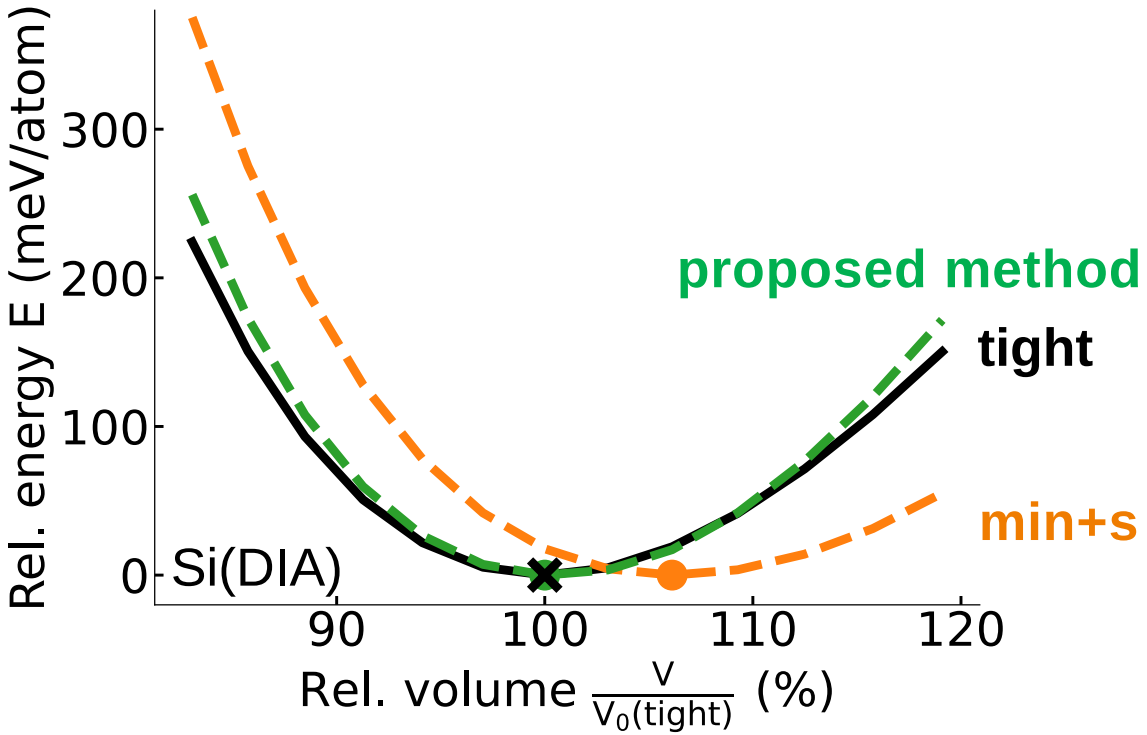
$E_{total} = E_{small\ basis} + E_{correction}$

$$E_{correction} = \frac{1}{2} \sum_{A}^{Nunit} \sum_{B \neq A}^{Nsuper} e_{AB}$$

$$e_{AB} = s(r_{AB} - r_{cut}) f_{switch}(r_{AB}, r_{cut})$$

with correction strength s

Proposed method E-V curve

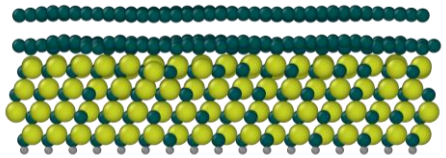


FITTING OF ELEMENT DEPENDENT CORRECTION STRENGTH S
FITTING SET

Transferability to different bonding situations

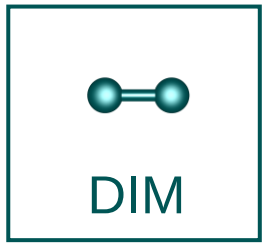
surface

bulk

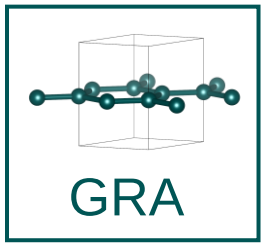


example: graphene on SiC(0001)[4]

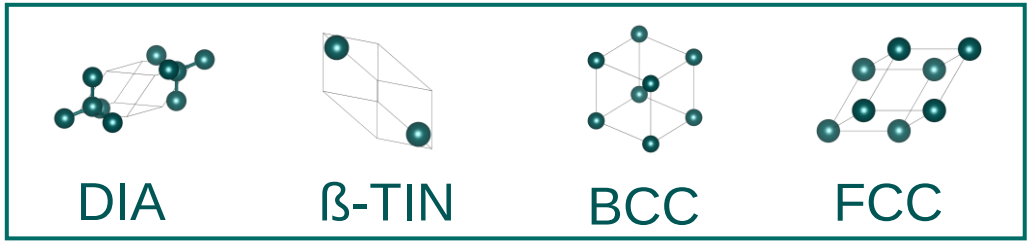
fitting set for Z = 1 - 86 [5]



non-periodic



semi-periodic



periodic

[4] Structures from Nemec et al., (2013) 5] Structures from Noam Bernstein

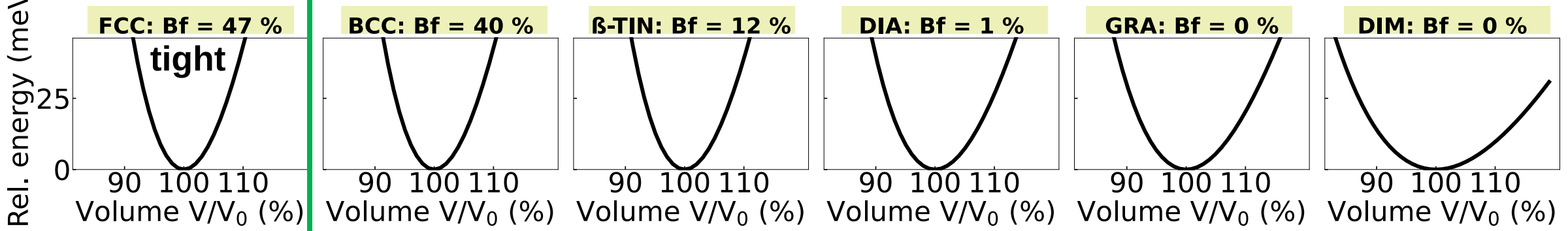
FITTING OF ELEMENT DEPENDENT CORRECTION STRENGTH S
FITTING SET

Energetic order given by Boltzmann factor

$$Bf(E_{0,i}) = e^{-\frac{(E_{0,i} - \min E_{0,i})}{kT=0.25eV}}$$

Ground-state

Example Cu

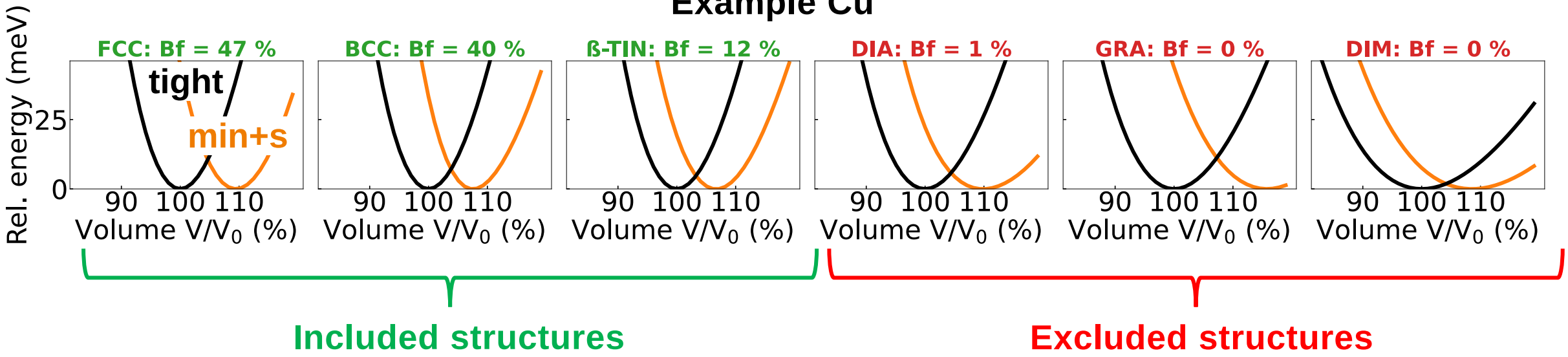


FITTING OF ELEMENT DEPENDENT CORRECTION STRENGTH S
FITTING SET

Include energetically most stable structures

$$Bf(E_{0,i}) = e^{-\frac{(E_{0,i} - \min E_{0,i})}{kT=0.25eV}} >= 10\%$$

Example Cu

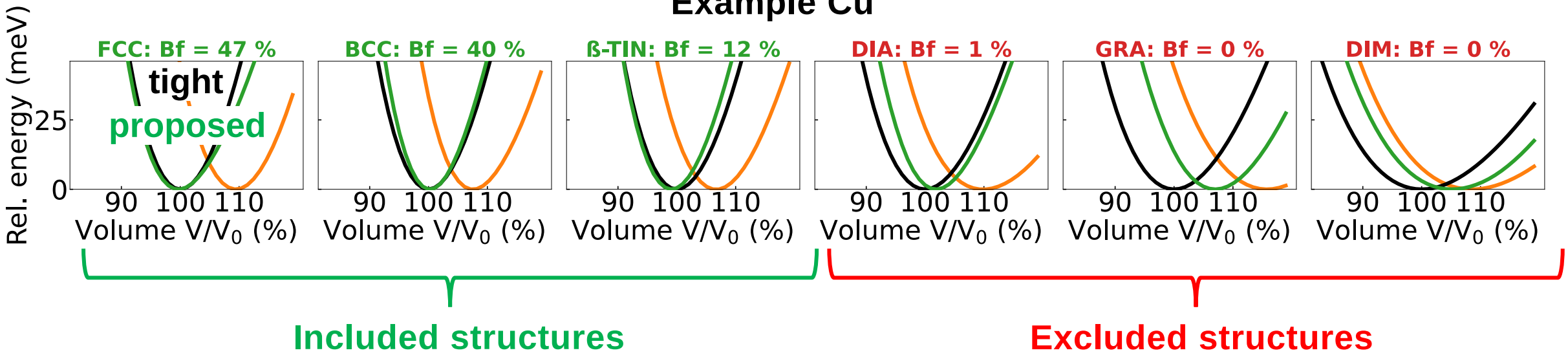


FITTING OF ELEMENT DEPENDENT CORRECTION STRENGTH S
E-V CURVES WITH FITTED CORRECTION STRENGTH

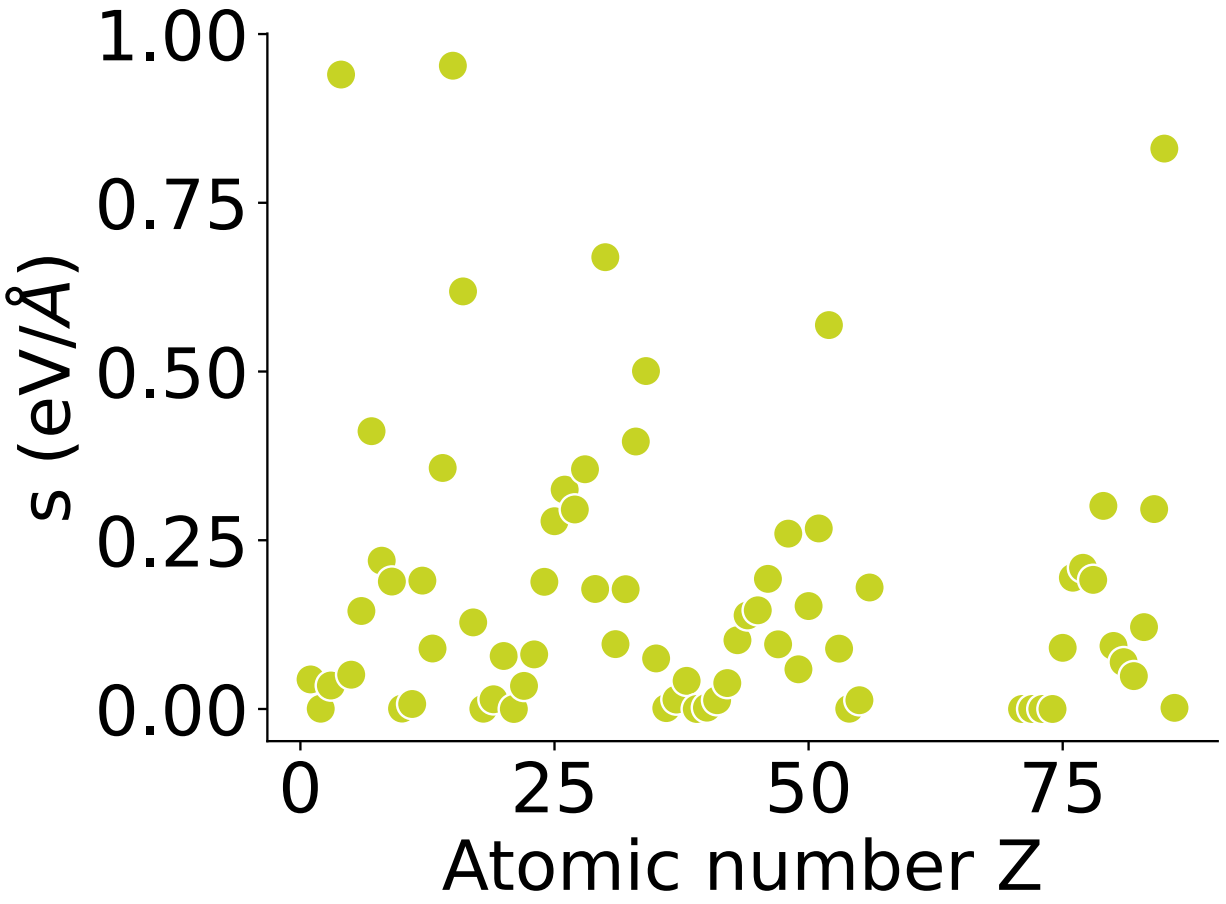
Include energetically most stable structures

$$Bf(E_{0,i}) = e^{-\frac{(E_{0,i} - \min E_{0,i})}{kT=0.25eV}} >= 10\%$$

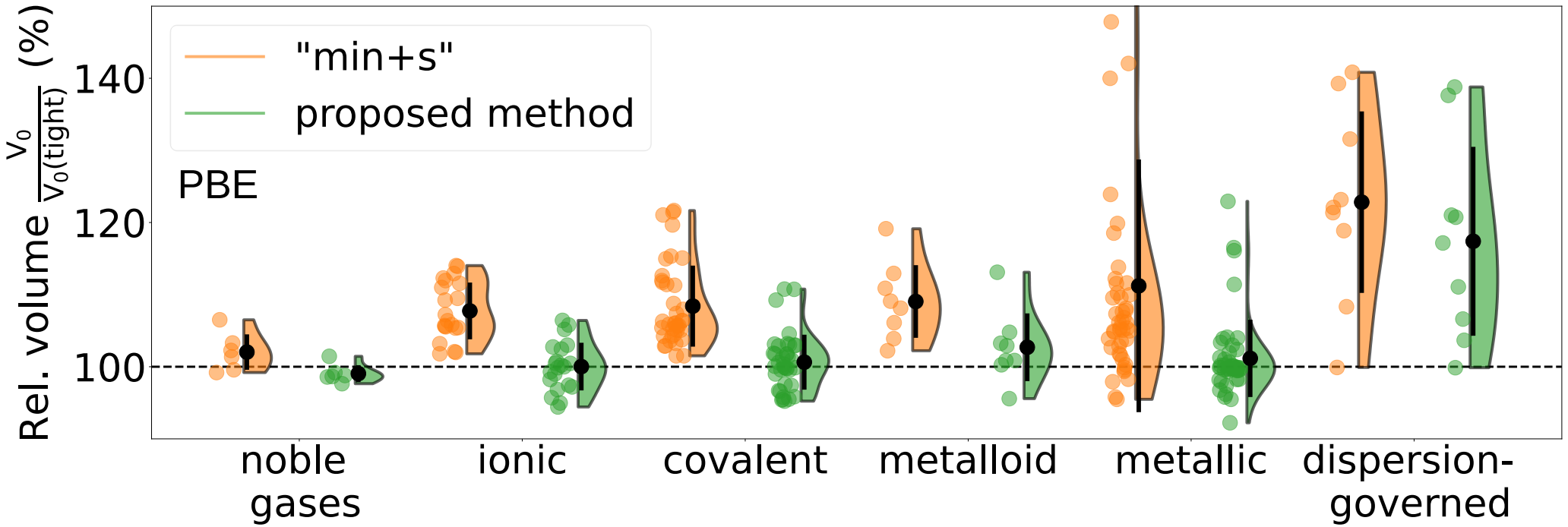
Example Cu



FITTED ELEMENT DEPENDENT CORRECTION STRENGTH S
Z = 1 - 86 (EXCLUDING LANTHANIDES)

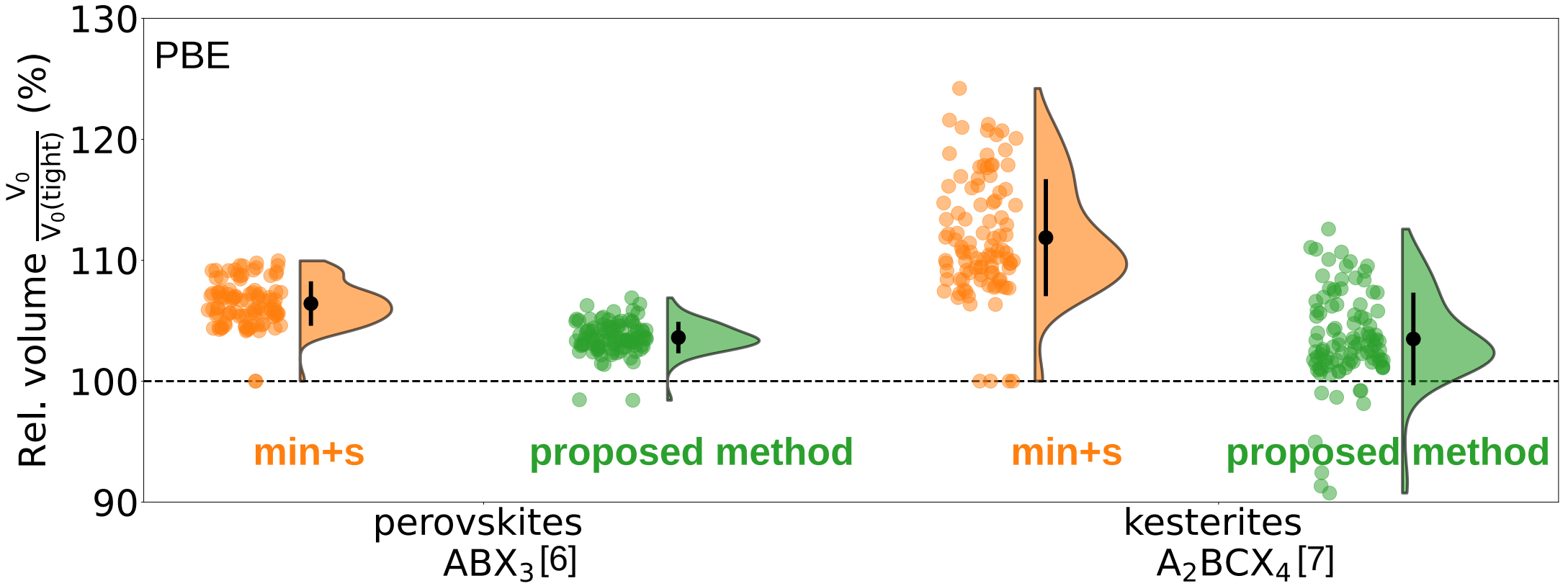


PERFORMANCE PROPOSED METHOD EQUILIBIRUM VOLUMES
MONOELEMENTAL MATERIALS AND BINARY COMPOUNDS



Structures from Lejaeghere et al., Crit. Rev. Solid State Mater. Sci. 39, 1-24 (2014), Huhn et al., Phys. Rev. Materials 1.3 (Aug. 2017)

CORRECTION TO RECOVER ACCURATE GEOMETRIES
TERNARY AND QUATERNARY COMPOUNDS

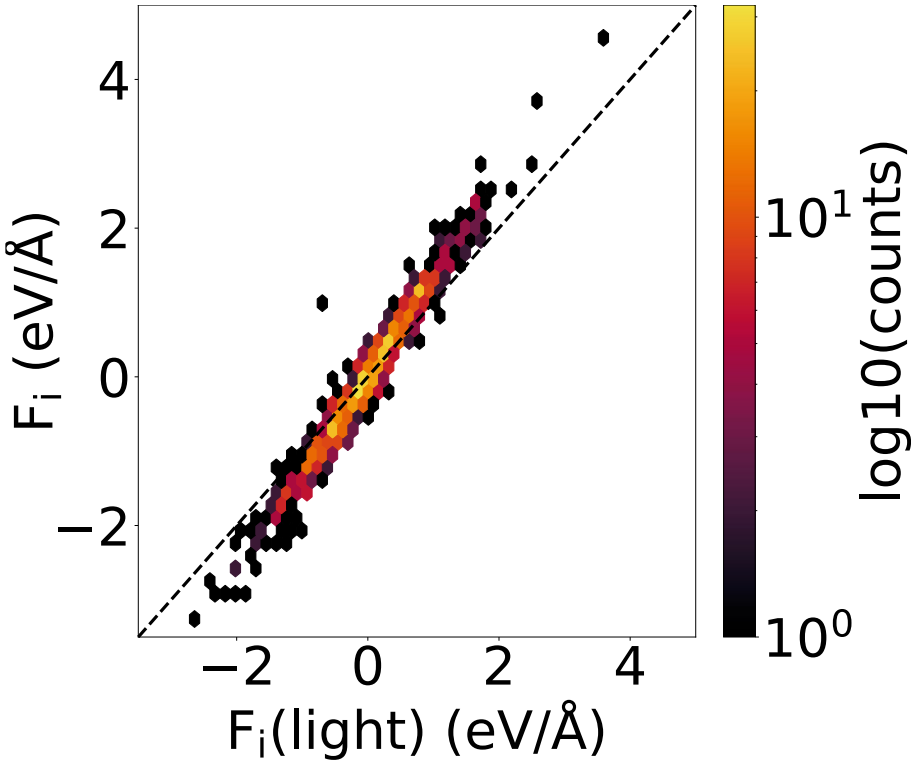


[6] 100 structures from Castelli et al., 2014 [7] 100 structures from Pandey et al., 2018

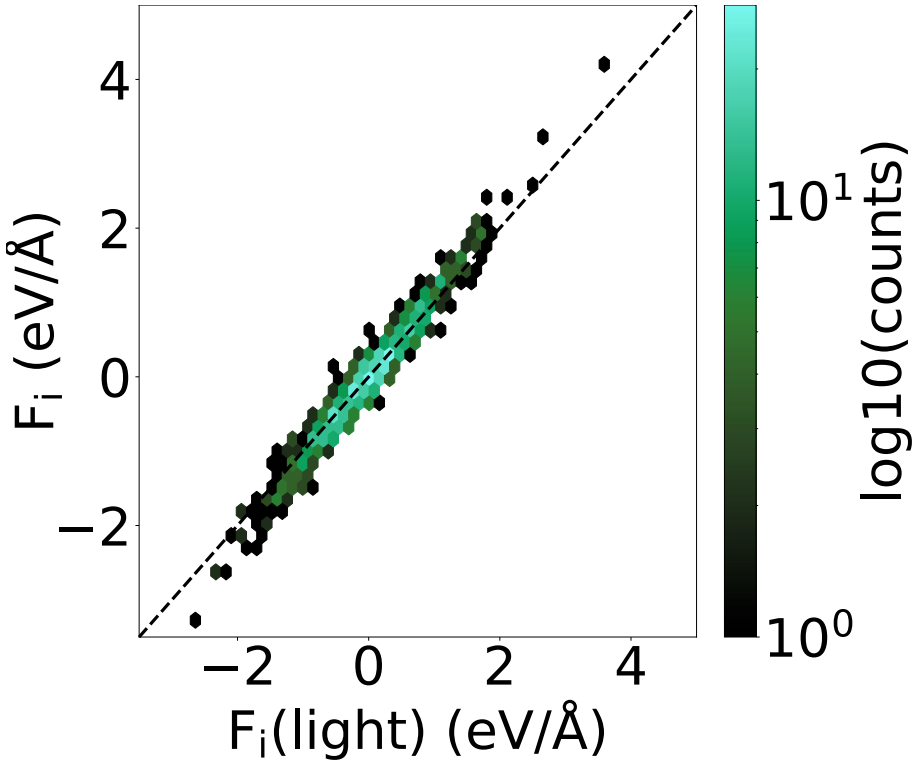
MOLECULAR DYNAMICS – FORCES

Cu, PBE, NPT N = 256 P = 0 eV/Å^3 T = 1600K

Small basis ‘min+s’ baseline

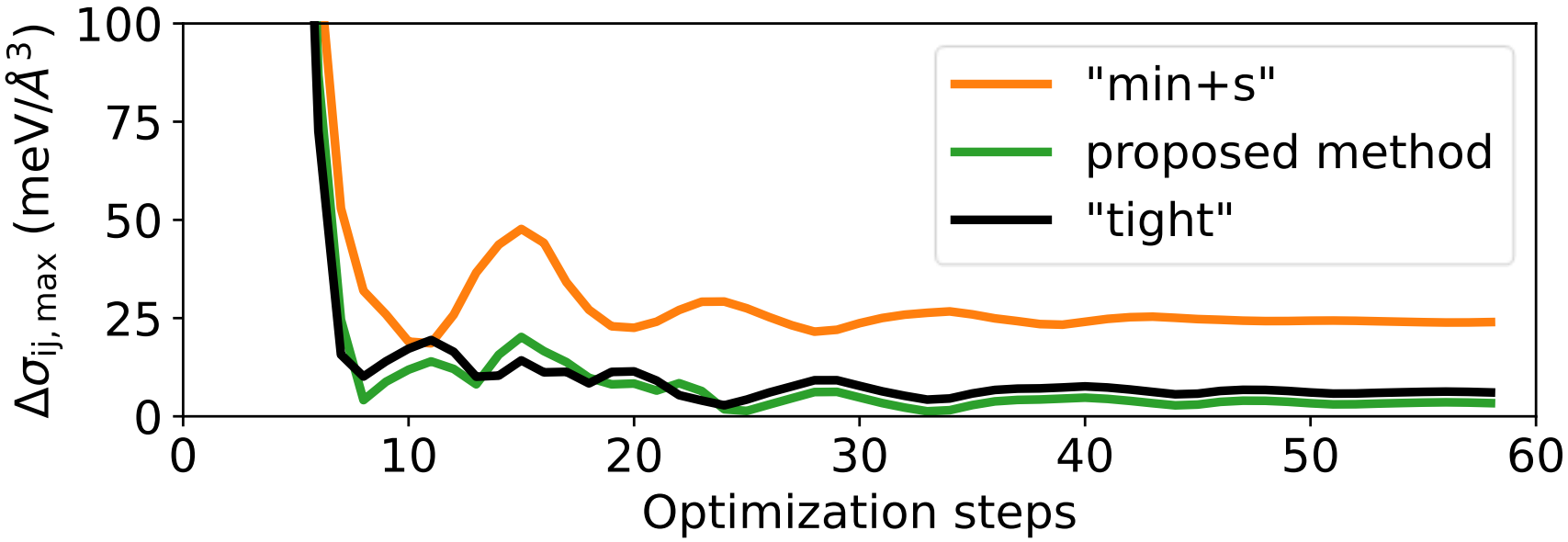


Proposed method



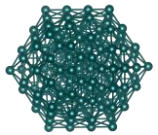
GEOMETRY OPTIMIZATION - STRESSES

System: stretched + rattled Si(DIA) unitcell std 0.11 Angström, PBE

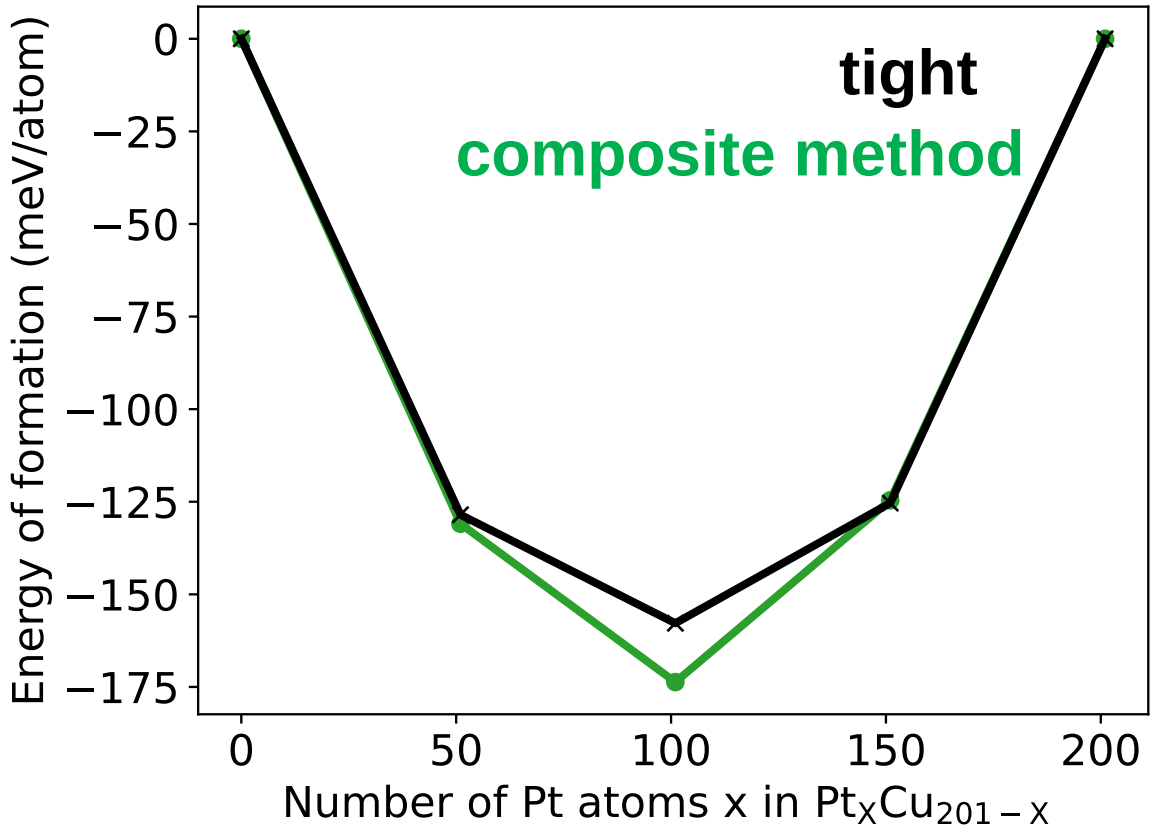


USE OF PROPOSED METHOD IN COMPOSITE METHODS

Nanoparticles Pt_xCu_{201-x}[8], PBE, |Fmax| <= 0.001 eV/Å³



Formation energy



[8] Initial structures from Vega, Mater. Adv. 2.20 (Oct. 2021)

STATUS SMALL BASIS DFT: PBE\”MIN+S” + CORRECTION

relative energies, forces, stresses for Z = 1-86 (excluding lanthanides)

Application areas

- **systems with hundreds of atoms**
  speed-up MD, pre-relaxations and geometry optimizations etc.
  use in composite methods

- **systems with >= 1000 of atoms**
  enable large-scale geometry optimization at DFT level