Ab initio study of tungsten metal from linear-scaling density functional theory methods

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Unió Europea
Fons Europeu de Desenvolupament Regional

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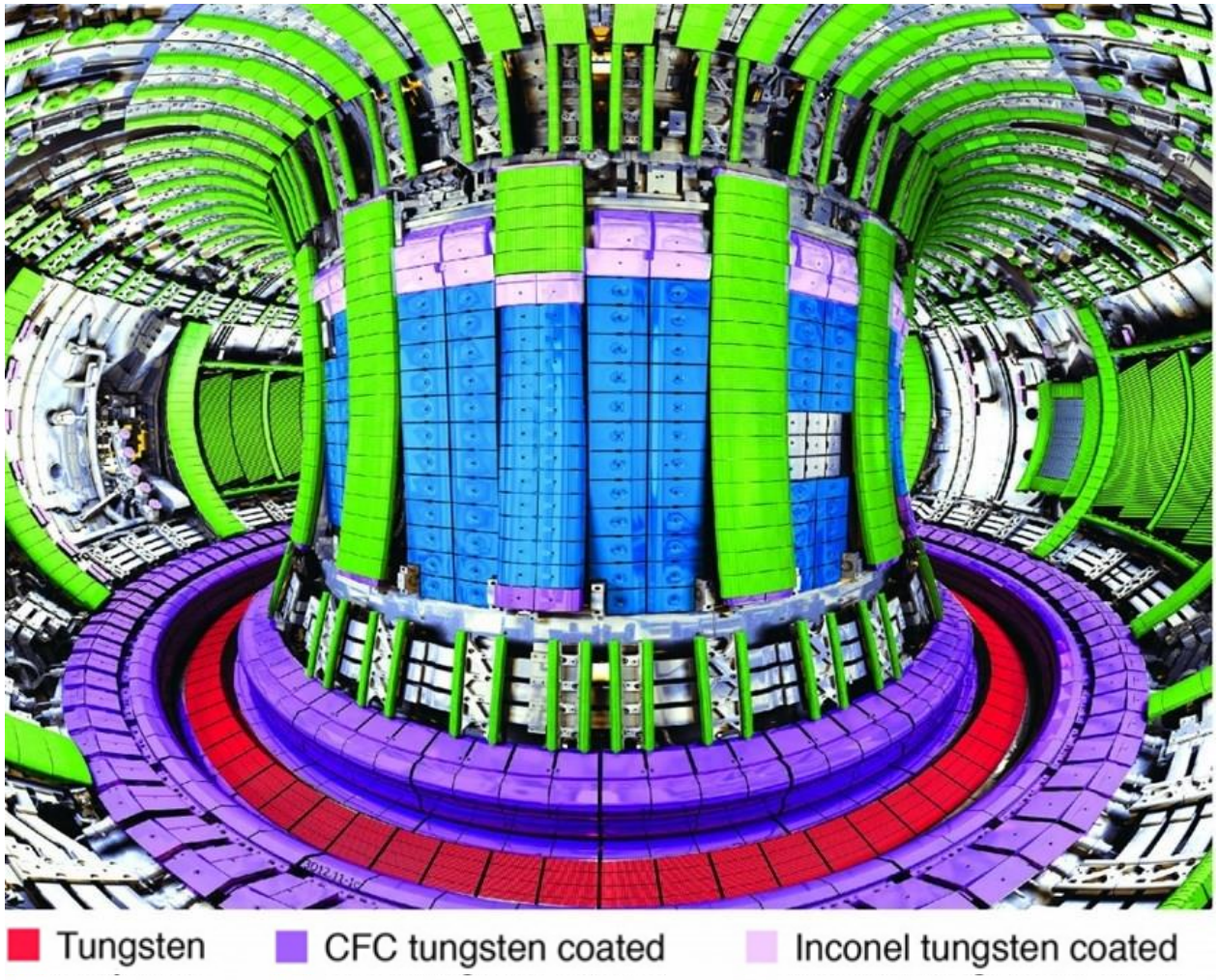
Plasma Facing Materials

W as armour material

- ***Tungsten*** (W): reference plasma facing material (e.g. ITER divertor)
- High strength, low yield
- High melting point (3700 K)
- **Defects** can deteriorate stability, thermal conductivity and mechanical properties

Defective materials from atomistic modelling

- QM methods (DFT): simple defects, small atomic structures
- Classical methods (MD): complex interatomic potentials.



J. Nucl. Mater., 486 (2017) 267-273
J. Nucl. Mater., 432 (2013) 482-500
Fusion Sci. Technol., 54 (2008) 891-945
Phys. Scripta, T159 (2014) 014009 (Adapted image)

What is large-scale DFT?

Systems' size: 1000s atoms

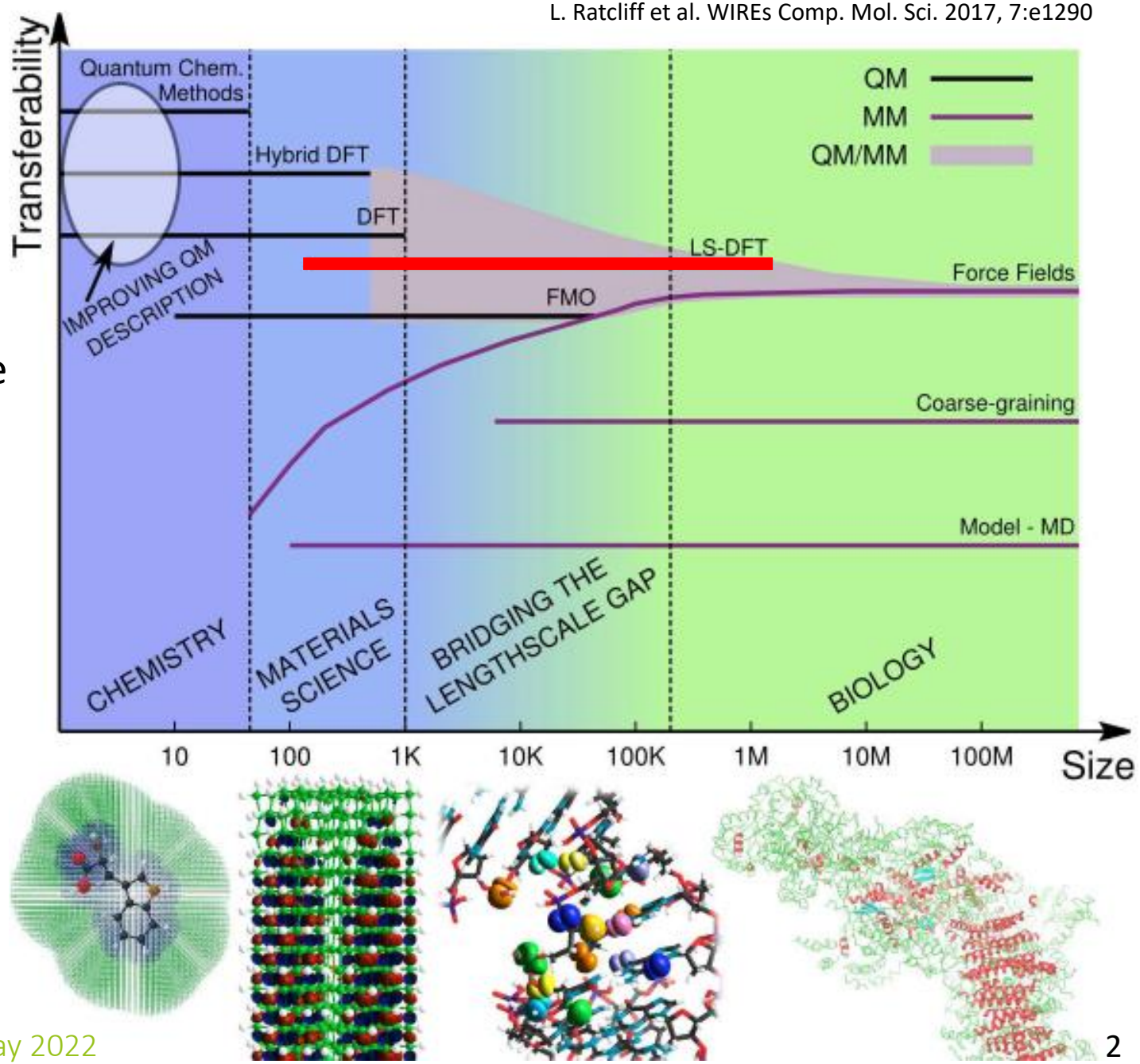
Ab-initio Density Functional Theory (DFT)

- Any element / High accuracy / Transferable
- (N_e^3) scaling, ~ 100s atoms

QM for Large Systems?

- Bridges QM - MD
- Complex morphologies, statistics
- QM properties: electronic structure, charge transfer, excited states…
- Validate empirical models

L. Ratcliff et al. WIREs Comp. Mol. Sci. 2017, 7:e1290

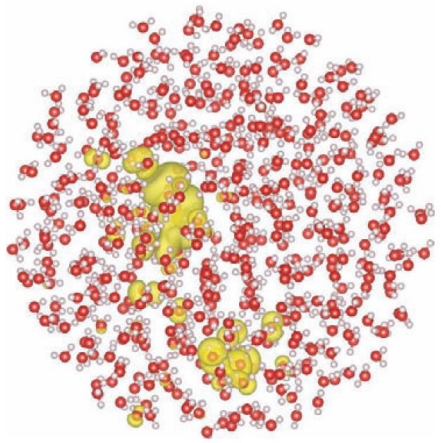


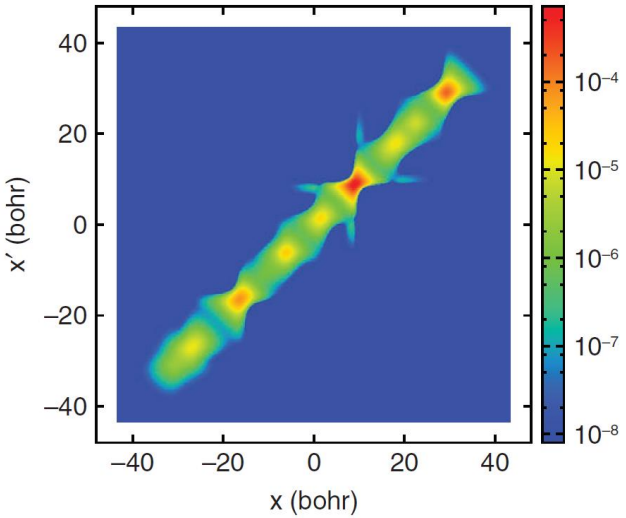
Methodology: Linear-Scaling DFT

Linear Scaling - Density Functional Theory (LS-DFT)

- W. Kohn's *nearsightedness* principle: electronic properties only act locally
- Electrons within a **threshold radius** (truncated)
- Algorithm **directly on the density matrix**, avoids Kohn–Sham orbitals $O(N_e^3)$ diagonalization
- **Linear scaling** with respect to system's size

$$\rho(r) = F(r,r') = \sum_i f_i \cdot |\psi_i(r)|^2 = \sum_{\alpha,\beta} \Phi_\alpha(r)\, K_{\alpha,\beta} \Phi_\beta(r)$$

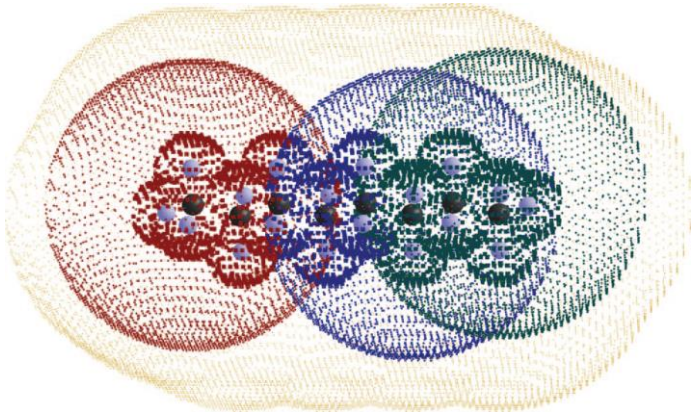


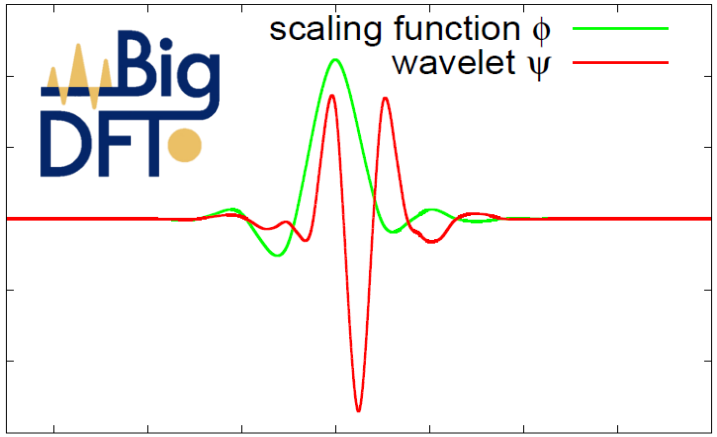


Methodology: Linear-Scaling DFT

Linear Scaling - Density Functional Theory (LS-DFT)

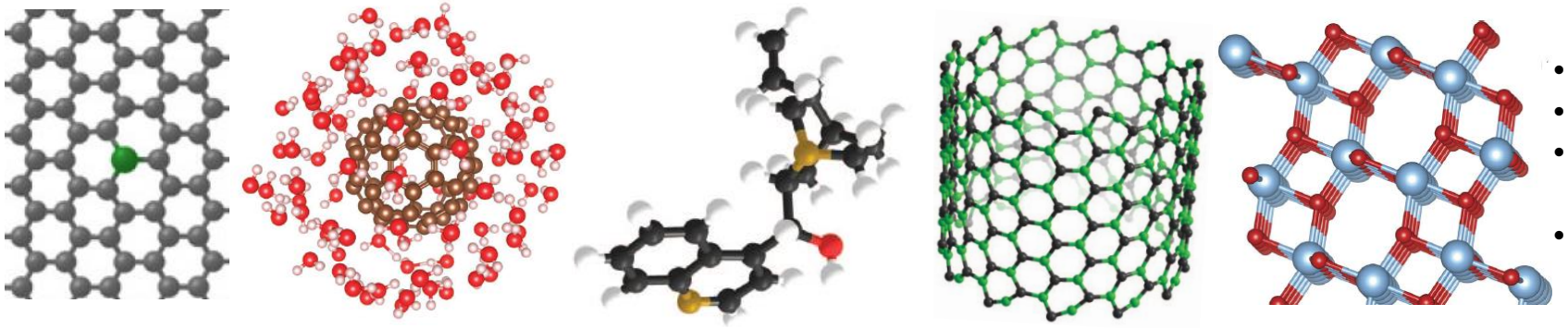
- BigDFT - localized basis functions (support functions - SFs): **wavelet basis set**
- Combine properties from plane waves and Gaussian orbitals:
  - compact, orthogonal → systematic convergence
- Adaptive mesh, finer sampling close to the atoms
- Standard boundary conditions—free, wire, surface or 3D periodic.





W simulations with LS-BigDFT

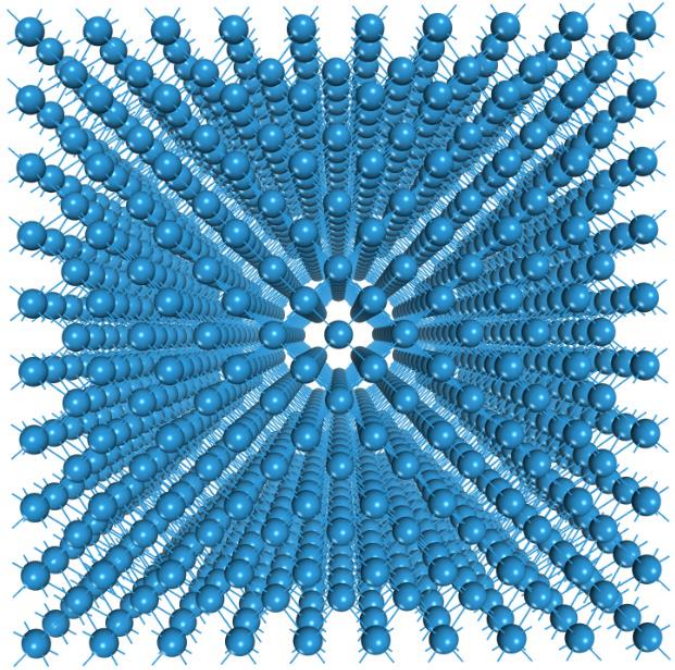
Accuracy for non-metallic systems shown during the past years



- J. Chem. Phys. 140, 204110 (2014)
- Phys. Chem. Chem. Phys. 17, 31360 (2015))
- Theory and Simul. in Phys. Mat. Appl. Springer Series in Materials Science 296 (2020)
- J. Chem. Phys. 152, 194110 (2020)

Metals simulations: computational setup

- BCC periodic structure (a=3.23 Å)
- Krack HGH Pseudopotentials (W $6s^2$ $5d^4$)
- Wavelet grid: 0.38 bohr
- Multipliers: Fine=6 & Coarse=8
- 9 SF per atom (including the unoccupied W 6p states), localization radii 7.5 bohr
- Density kernel 11 bohr
- PBE XC
- Finite electronic T: 0.005 Ha
- Γ-point sampling grid



Methodology: Linear-Scaling DFT

Challenges of LS-DFT

- Metals are difficult
- Semiconductors & insulators ($E_{gap} > 0$) → rapid matrix decay
- Metals ($E_{gap} = 0$) : bad localization → slow matrix decay (hard to converge)
  - Many support functions
  - Finite temperature
- Large computational overhead: O(N) slow for small systems
  - Large computing power

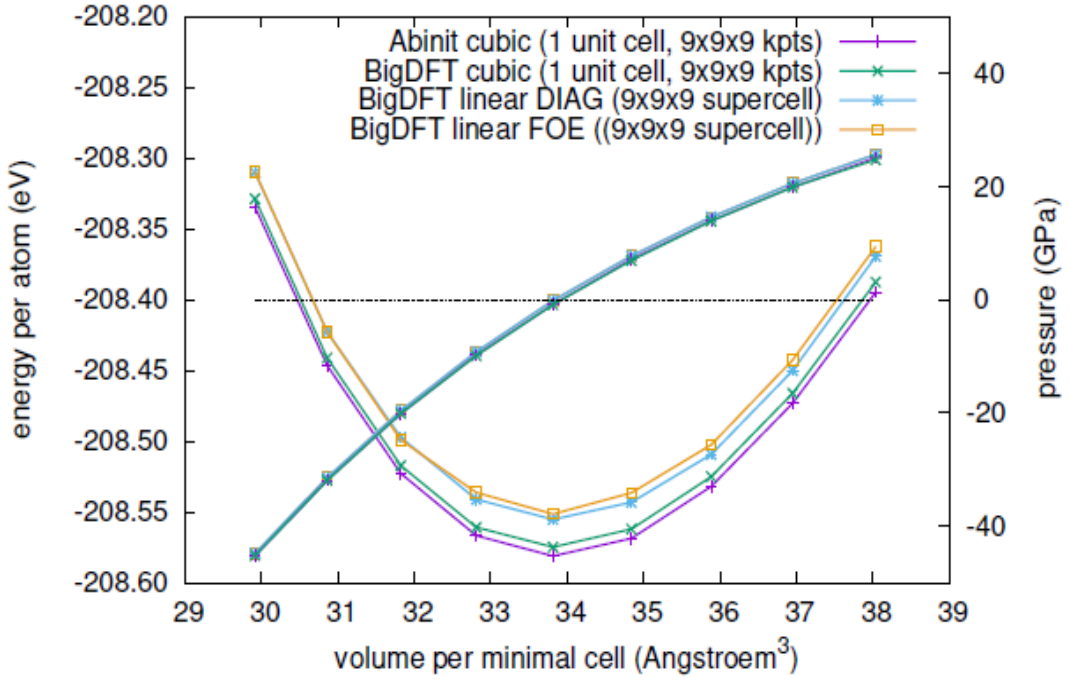
LS-DFT vs. traditional DFT

Is it possible to simulate metallic systems?

RESULTS: BigDFT calculations of W

- Scalability & Convergence tests
- Defect formation
- Pseudofragment approach
- Electronic structure

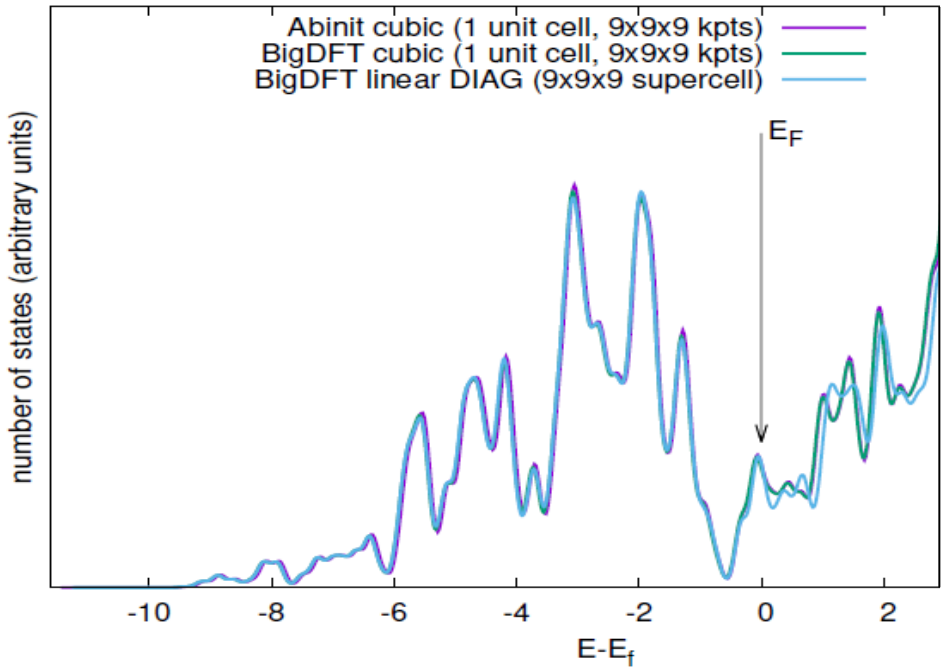
LS-BigDFT for W: Convergence & Scalability



E vs. Vol: same trend, shifted E

Pressure: Perfect agreement

Density of States (DOS)

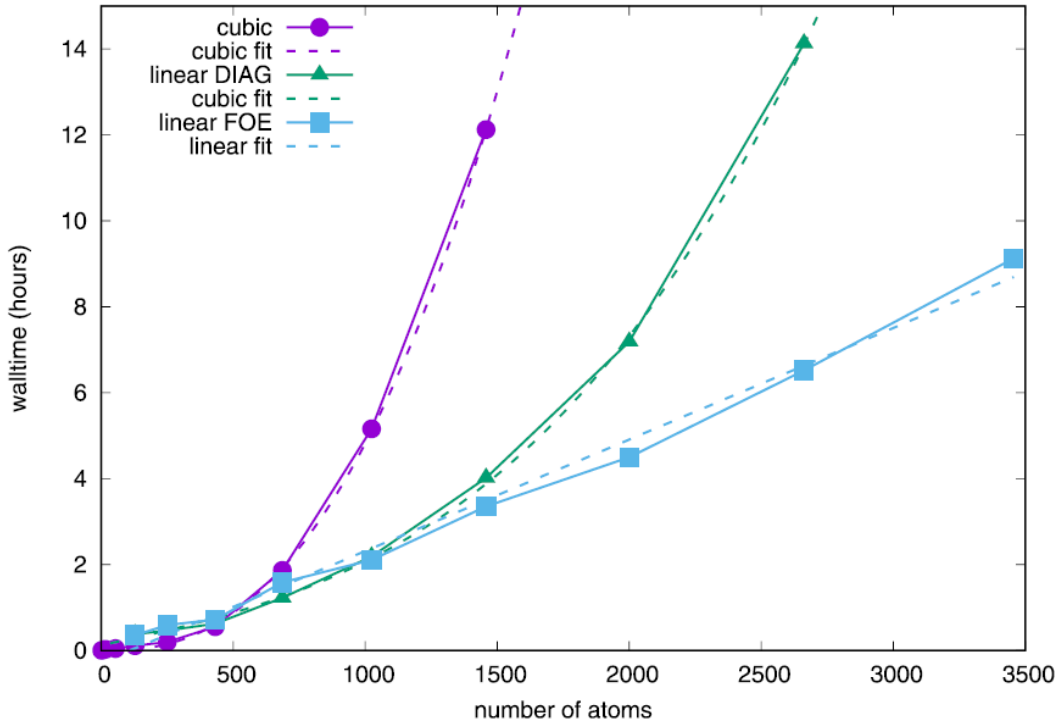


Accurate DOS below E_F

(SF not optimized for unoccupied states)

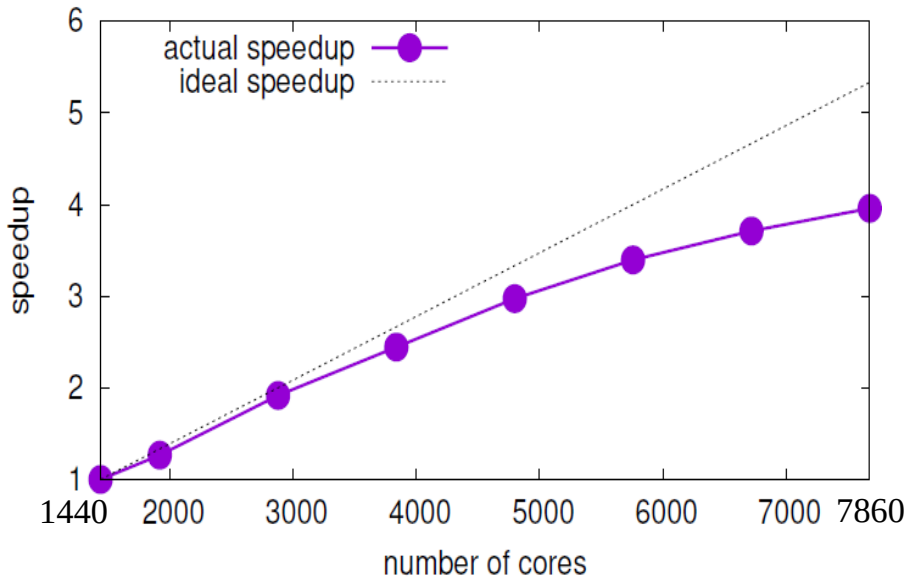
S. Mohr, M. Eixarch, M. Amsler, M.J. Mantsinen, L. Genovese. Nucl. Mater. Energy 15 (2018) 64–70

LS-BigDFT for W: Convergence & Scalability



- Crossover points:
  - cubic - DIAG: 500 atoms
  - **DIAG – linear FOE (Fermi Operator Expansion): 1000 atoms**

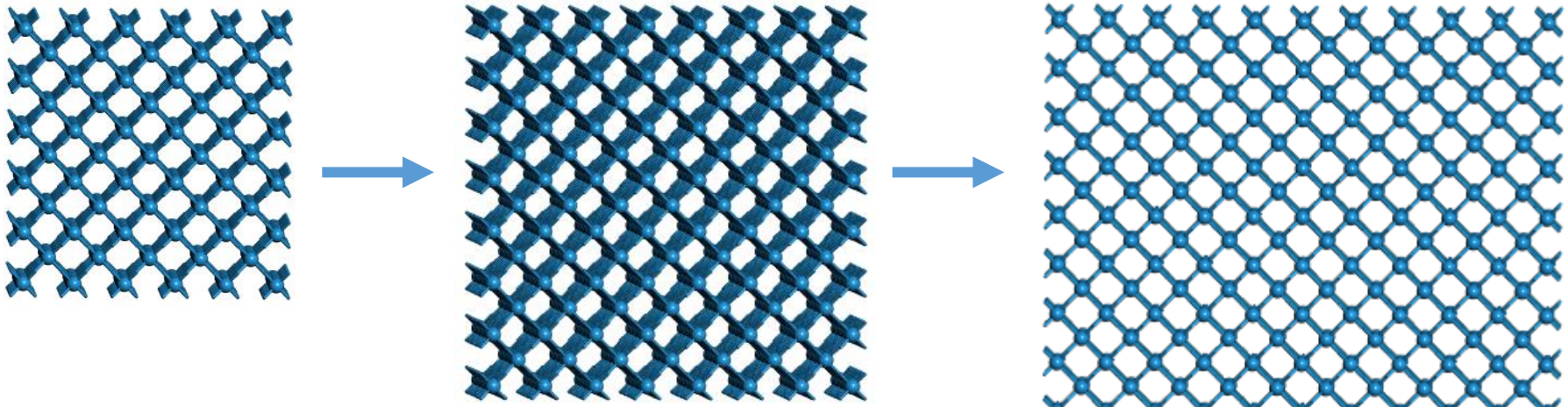
Linear Scaling (FOE) Scalability

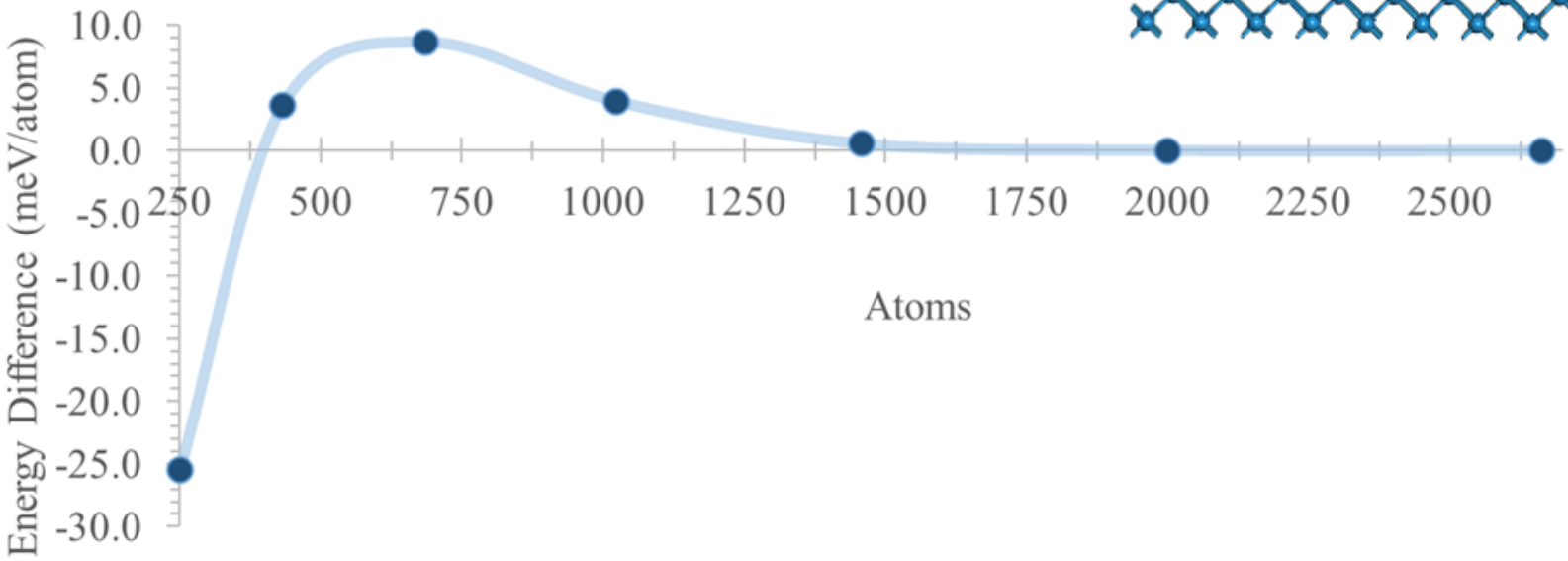


- 1024 atoms
- 74% for 7860 cores

S. Mohr, M. Eixarch, M. Amsler, M.J. Mantsinen, L. Genovese. Nucl. Mater. Energy 15 (2018) 64–70

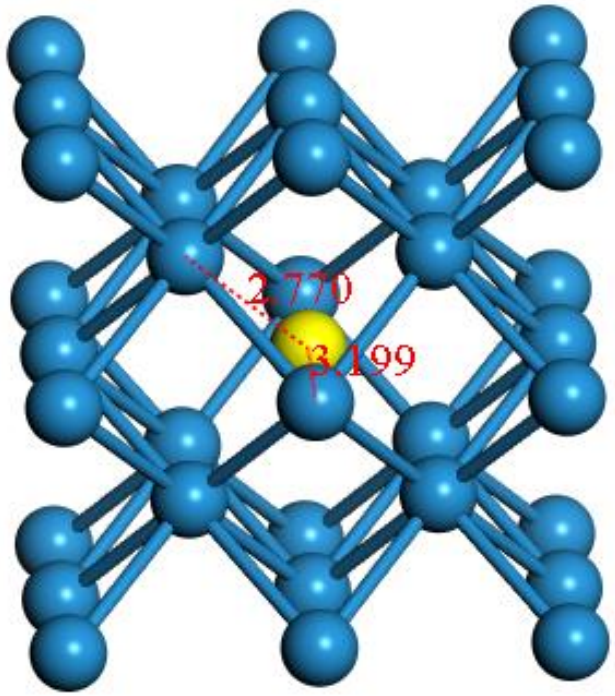
LS-BigDFT for W: Size convergence





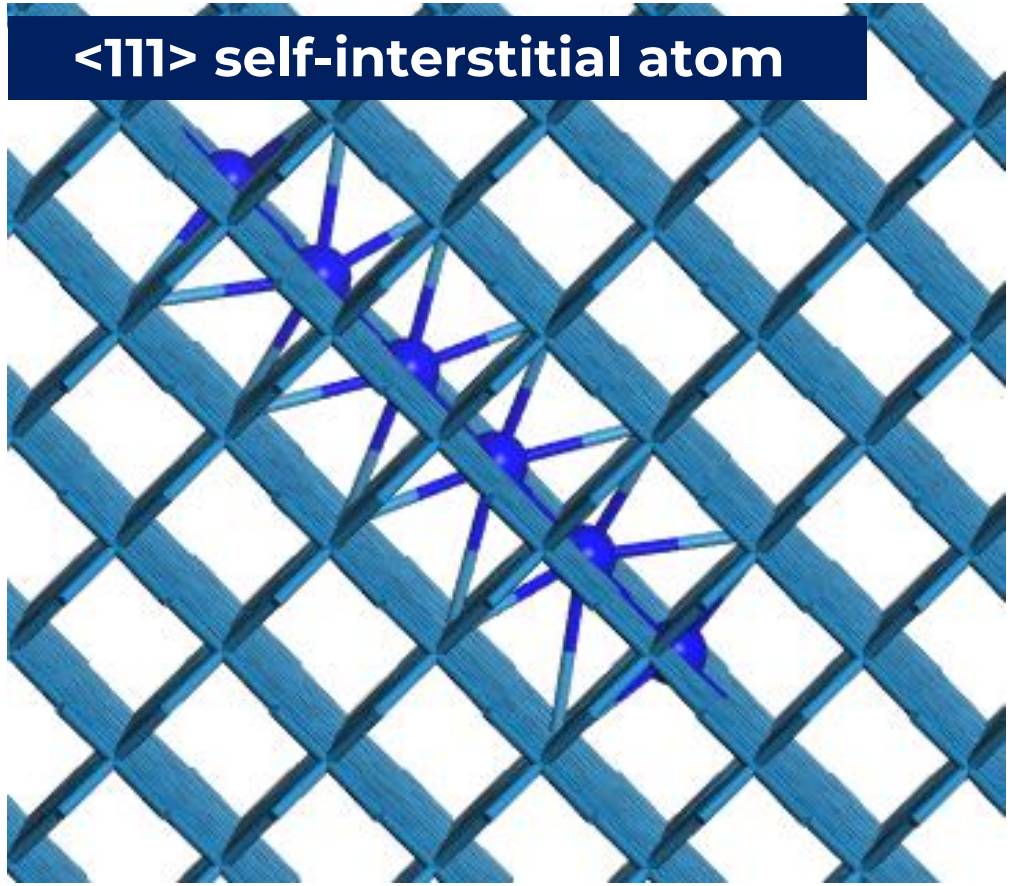
LS-BigDFT for W: Geometry

Vacancy



- Interatomic distances: 1st and 2nd neighbours decrease by 1%
- Common behaviour even for smaller systems

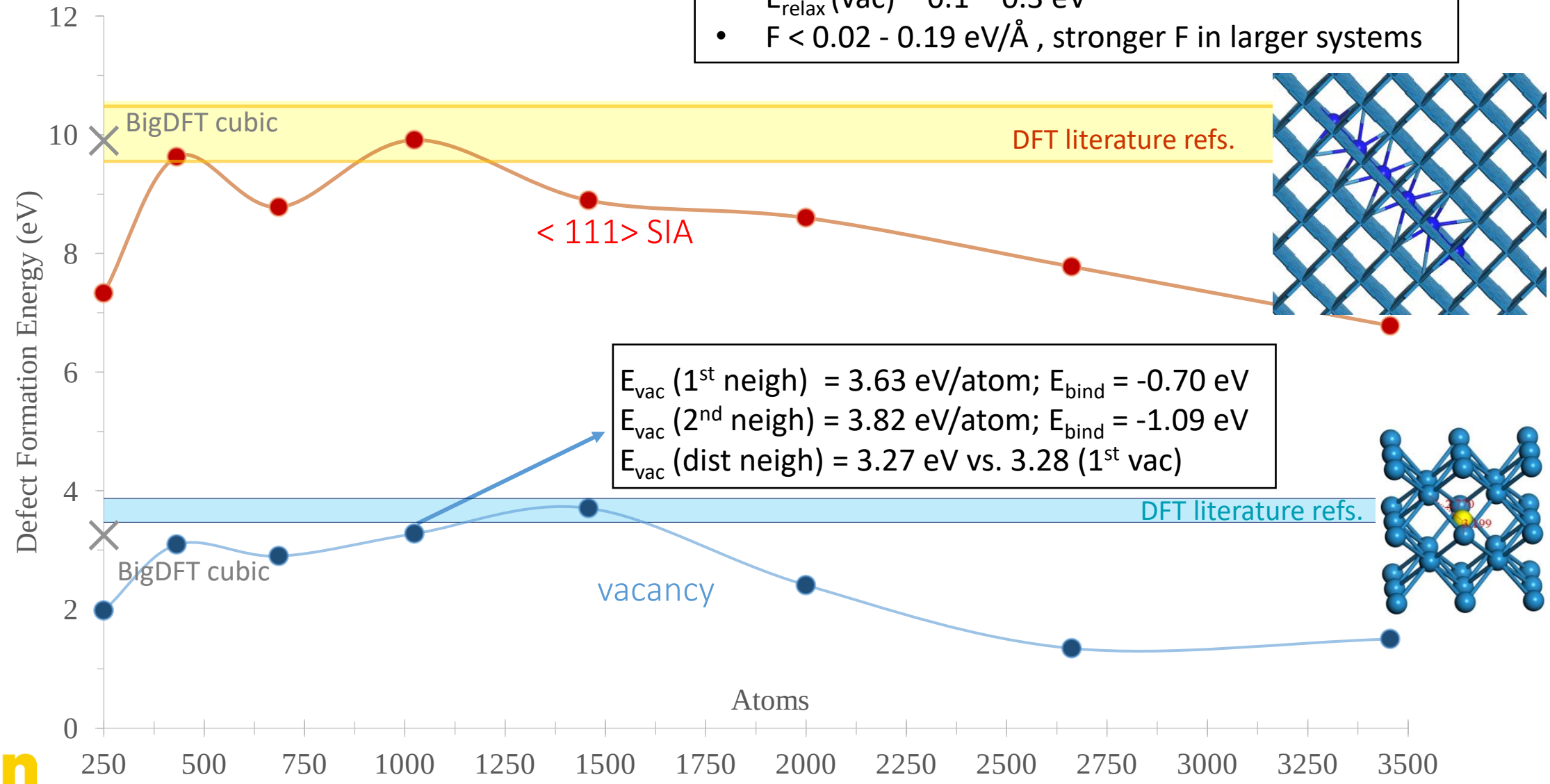
<111> self-interstitial atom



- Extended defect – needs at least 4 bcc unit-cells to accommodate relaxation

LS-BigDFT for W: Defects

- E not converged for smaller systems
- E_{relax} (vac) ~ 0.1 – 0.3 eV
- F < 0.02 - 0.19 eV/Å , stronger F in larger systems



E_{vac} (1st neigh) = 3.63 eV/atom; E_{bind} = -0.70 eV
E_{vac} (2nd neigh) = 3.82 eV/atom; E_{bind} = -1.09 eV
E_{vac} (dist neigh) = 3.27 eV vs. 3.28 (1st vac)

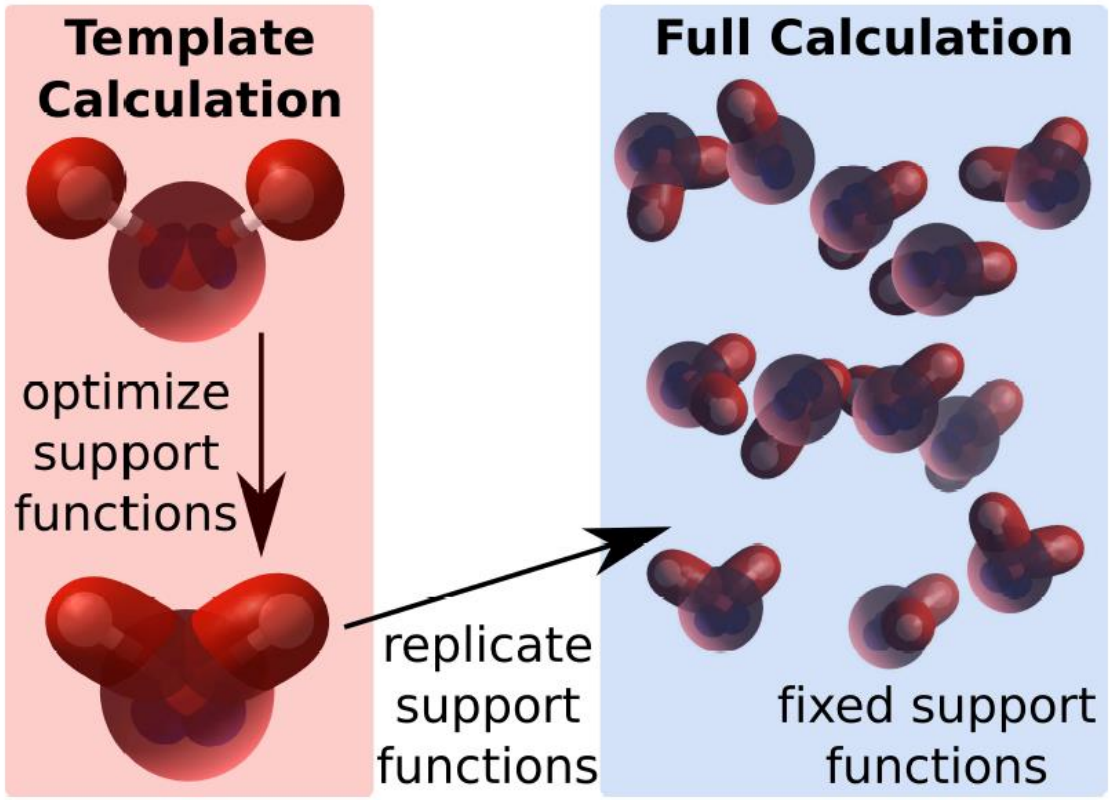
Ref. Values: Phys. Rev. B 76 (2007) 054107, Phys. Res. B 255 (2007) 23–26, **Phys. Res. B** 73 (2006) 020101, **Phys. Res. B** 94 (2016) 024103, Nucl. Fusion 58 (2018) 026004

Pseudofragment approach

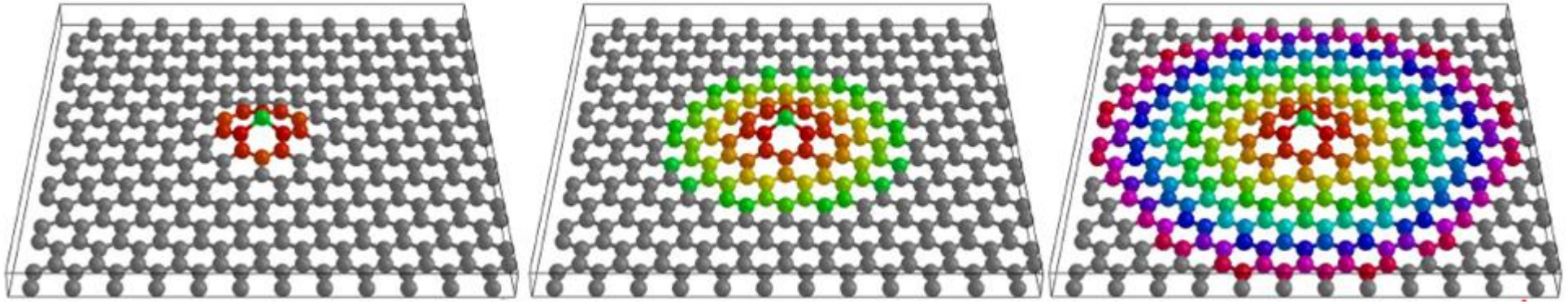
(1) template calculation: **optimize support functions** (SFs) for isolated fragment

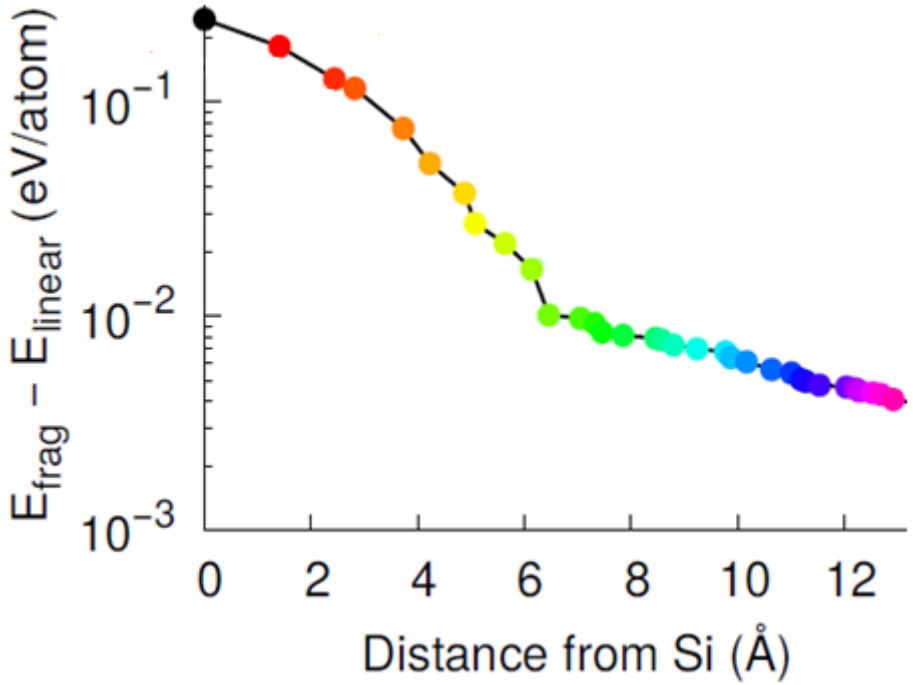
(2) reformatting: **replicate** and rototranslate templates

(3) full calculation: **SFs as fixed-basis** (or input for opt), opt density kernel only



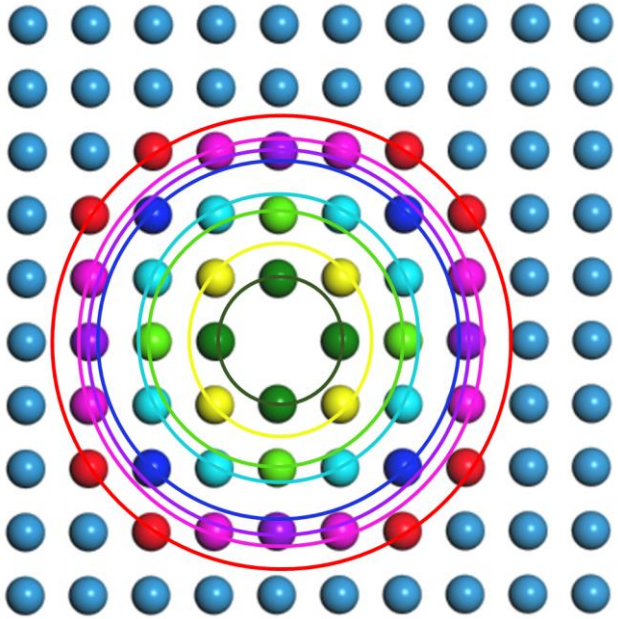
Pseudofragment approach

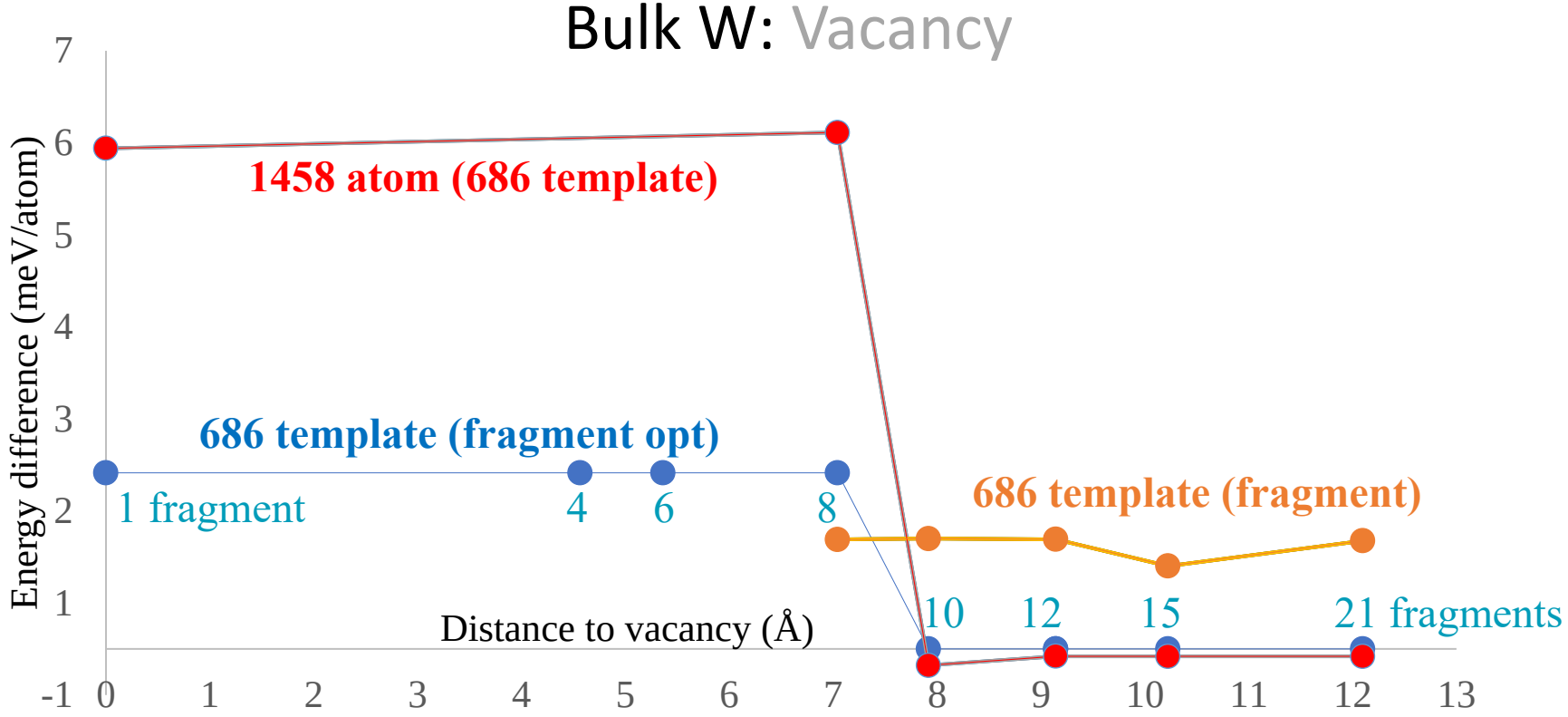




L.E. Ratcliff et al. Theory Simul. Phys. Mater. Appl. 2020 (adapted)

LS-BigDFT for W: Pseudofragment approach



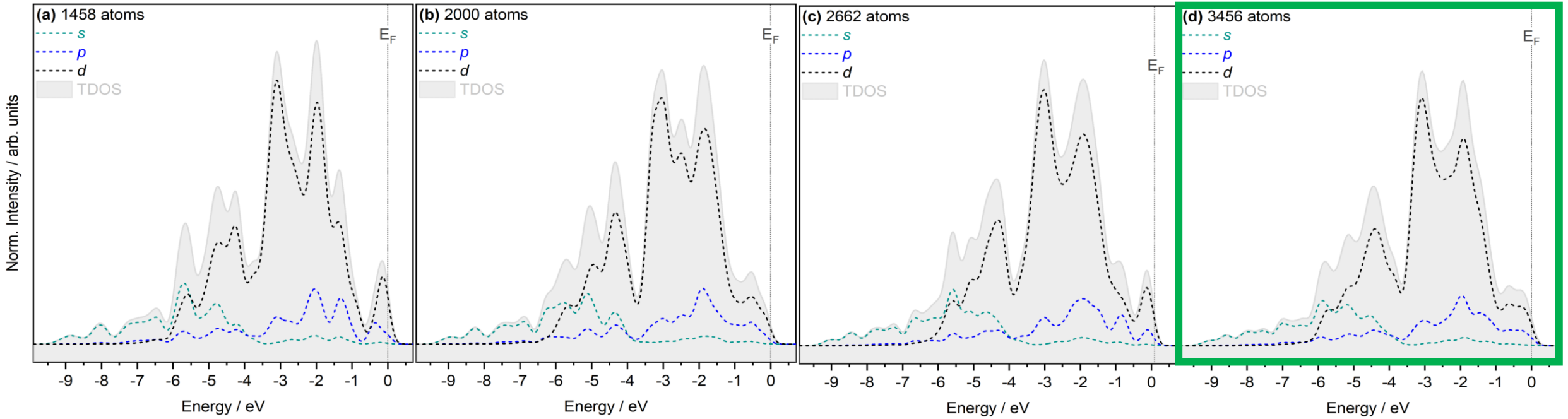


Fragopt: good energies, moderated speed-up

Frag: excellent performance, larger error in E

LS-BigDFT: PDOS convergence

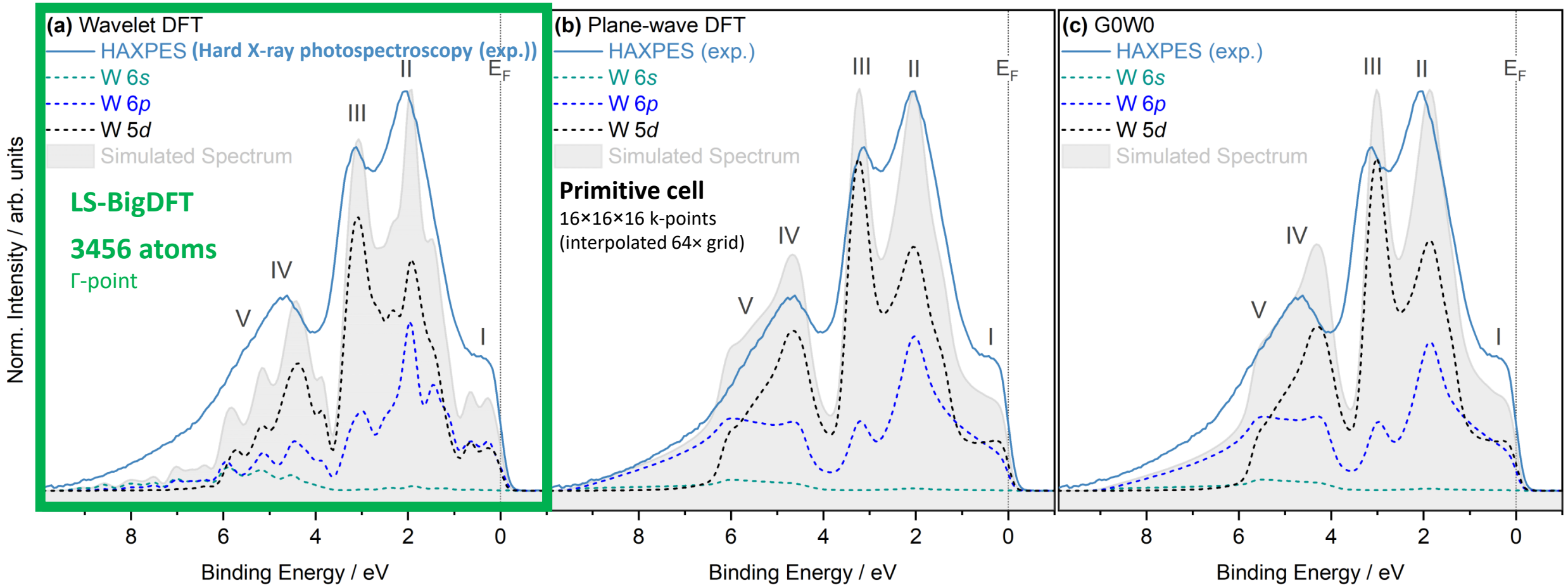
Partial and Total Partial Density of States / supercell sizes



- **Supercell size** (or k-point) affects DOS
- Pseudofragments: improve performance with high accuracy
- Up to **3456 atoms**, for now…

- Kalha et. al, J. Appl. Phys. 129 (2021) 195302
- Kalha et. al, Phys. Rev. B 105 (2022) 045129

LS-BigDFT: DOS comparison



- Kalha et. al, J. Appl. Phys. 129 (2021) 195302
- Kalha et. al, Phys. Rev. B 105 (2022) 045129

Summary

- BigDFT: accurate calculations of metals. Overcoming size limitation of standard DFT.
- Large-scale calculations of vacancy & self-interstitials (SIA) from LS-BigDFT.
- 1000s atoms needed for convergence.
- Accurate Density of States (DOS), also with pseudofragments.
- Pseudofragment approach: accuracy vs. computing time.
- More testing required…
- Atomic Simulation Environment (ASE) calculator.
- Classical MD simulations of thermal conductivity in defective W.
- Initial work with doped and alloyed W.
- Initiated benchmarks for JFRS-1 2022 project.

Dissemination

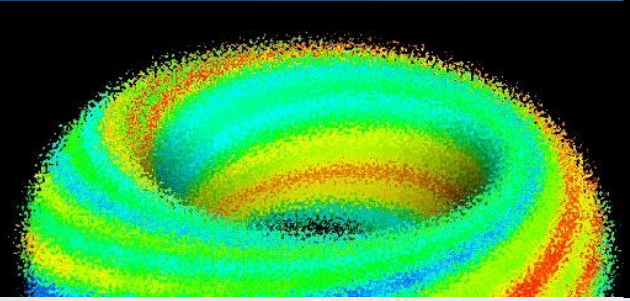
- Two journal publications: J. Appl. Phys. 129 (2021) 195302 & Phys. Rev. B 105 (2022) 045129 + 2 in preparation
- 13 presentation at workshops / conferences

Next steps

- New JFRS-1 project for 2022 term
  - Thermal & mechanical properties from lattice dynamics
  - ML interatomic potentials
  - LS-BigDFT validation.

Fusion Group

Barcelona Supercomputing Center
Centro Nacional de Supercomputación



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- **HPC access at**
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- BSC Fusion group & FusionCAT network
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- XPS: Anna Regoutz and Curran Kalha (UCL)
- JFRS-1 support team

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