UNIVERSITÉ DU LUXEMBOURG

UL HPC School - June 2017

# HPC in Theoretical Chemical Physics: Molecular Crystal Structure Prediction

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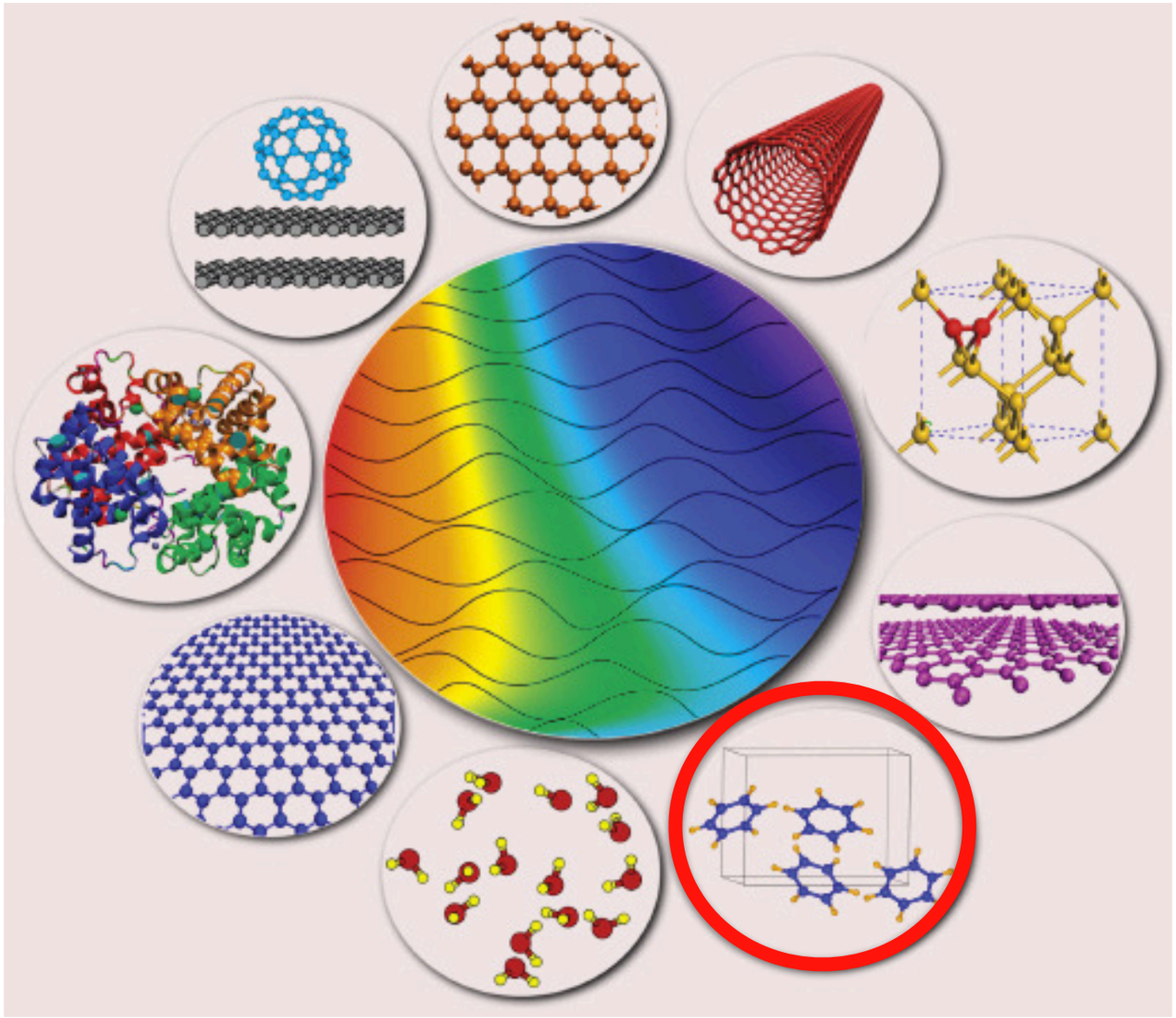
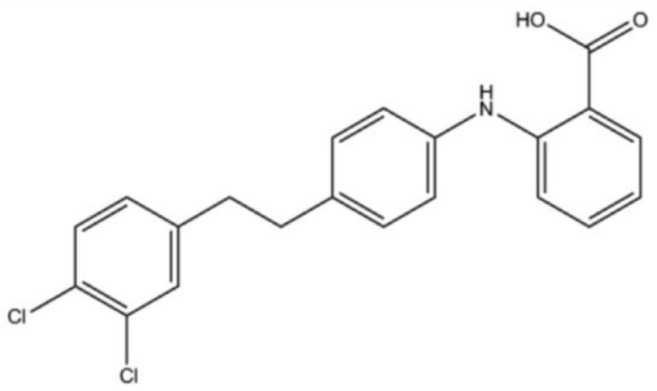
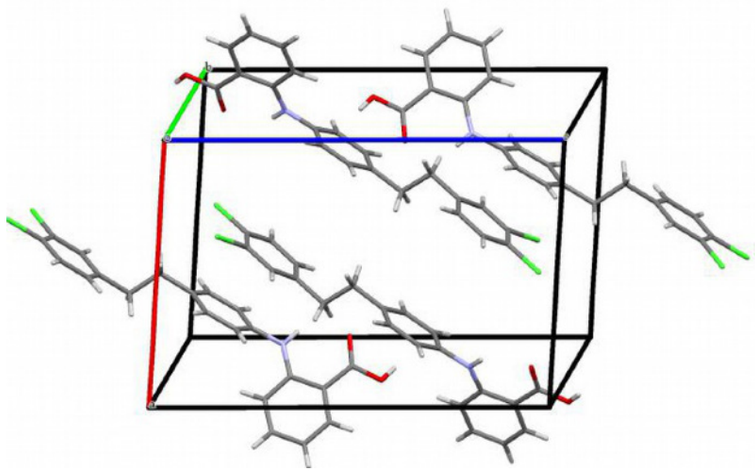
**We develop advanced quantum-mechanical first-principles methods and apply them to achieve increasingly reliable description of complex molecules and materials.**



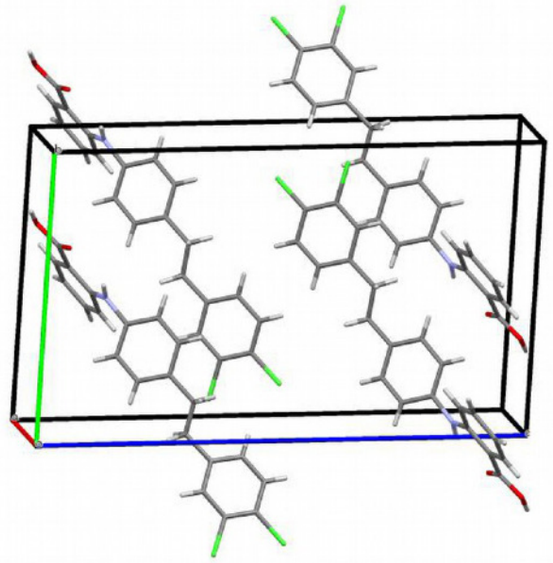
Treating van der Waals interactions as coupling between waves is a paradigm shift for chemistry and materials science © University of Luxembourg

# Molecular Crystals



or



?

- Solids composed of molecular moieties
- Held together by intermolecular interactions
- Different crystal-packing motifs (polymorphs) possible
- Used as pharmaceuticals, organic electronics, explosives, …
- Energy difference between polymorphs **~ 1 - 4 kJ/mol**

  ↳ **~ 1 - 2 % of lattice energy**

  ↳ **High accuracy required**

**Polymorphs can exhibit completely different**

- Kinetic stabilities
- Solubilities
- Densities
- Vibrational Spectra (THz)
- NMR chemical shifts
- Melting Points
- Conductivities
- Refractive Indices
- Vapor pressure
- Elastic constants
- Heat capacities
- …

# First-Principles Modeling of Molecular Crystals

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**Vibrational free energy**
**—polymorph stability at finite temperatures**

**Lattice energy**
**—relative stability of polymorphs**

**Structure**
**— molecular structure**
**— crystal packing**

**Crystal structure prediction (CSP)**

**Gibbs free energy**
**—phase diagram**

**Vibrational spectra**
**(IR/THz, Raman, INS)**

**Thermal expansion**

**Heat capacity**

**NMR chemical shifts**

**Elastic constants**
**—mechanical stability**

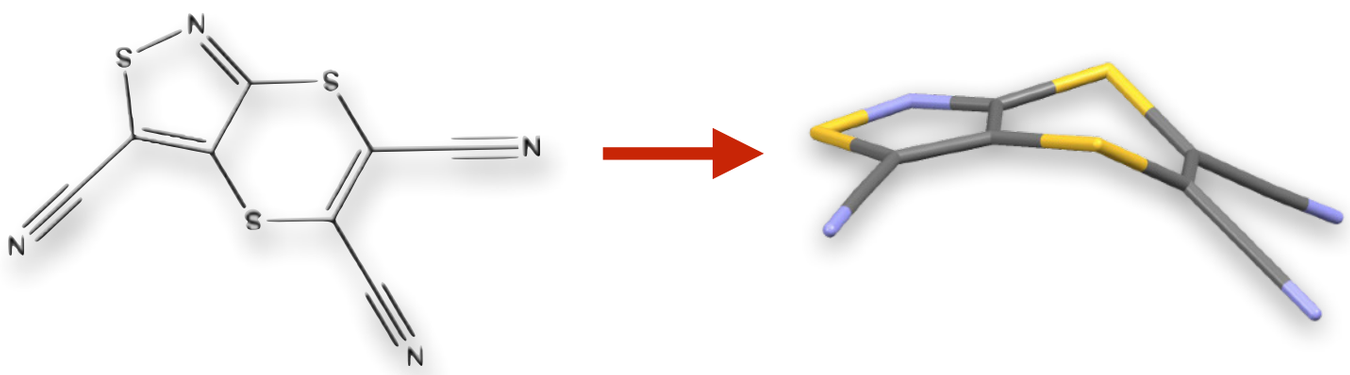
**Vibrational modes**

J. Hoja, A.M. Reilly, A. Tkatchenko, *WIREs Comput. Mol. Sci.*, 7, 1294 (2017).

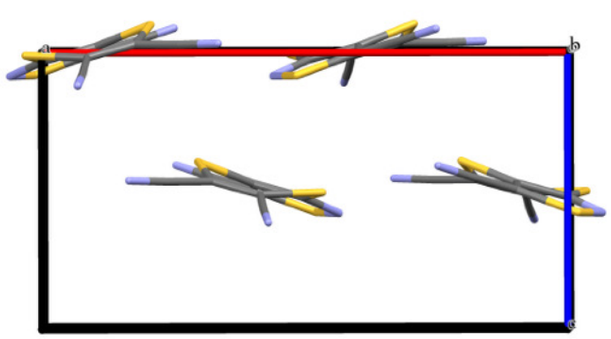
# Crystal Structure Prediction (CSP)

2D structural formula → molecular crystal structure

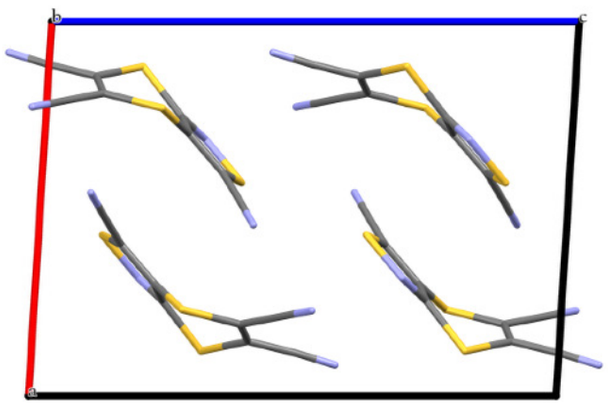
## Step 1: Generating Molecular Conformations



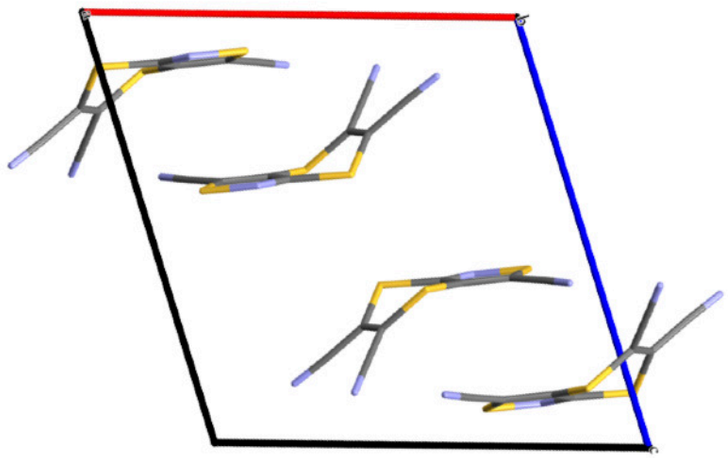

## Step 2: Crystal-Packing Arrangement



Structure 1

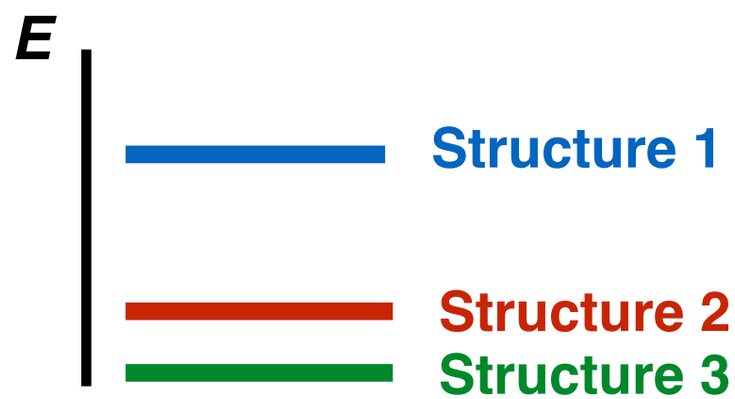


Structure 2



Structure 3

## Step 3: Stability Ranking



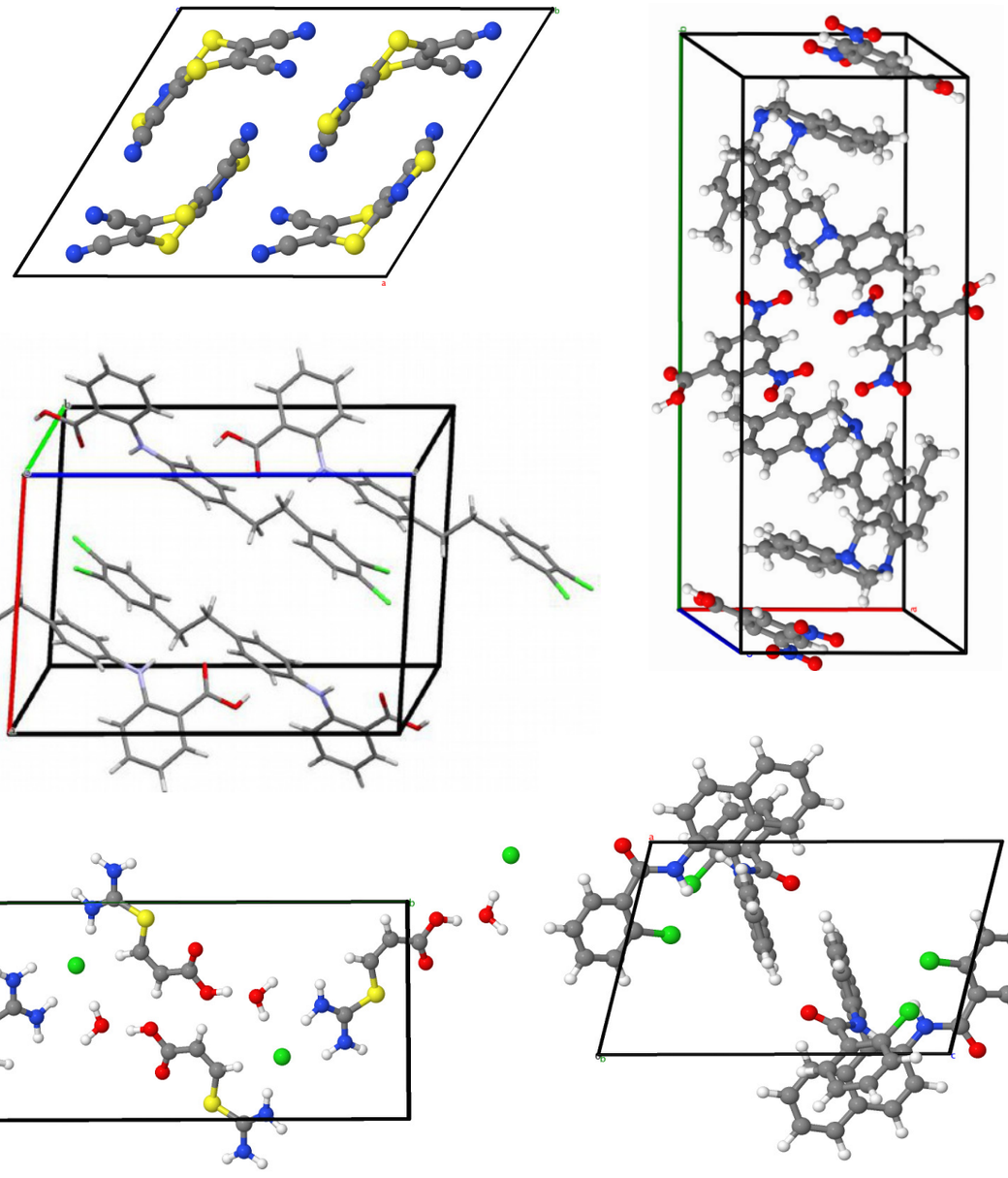
# Molecular Crystal Structure Prediction

- Pre-screening with first-principles-derived force field
- Hierarchical first-principles approach
- vdW-inclusive DFT + harmonic vibrational free energy

**Number and size of calculations for 5 model systems:**

- 500 initial structures
- 15 - 992 atoms per unit cell (average 193)
- For free energies on average
  ~ 300 finite displacements
  ~ 350 atoms in supercell

↳ **Large computational workload**



# Used Software: FHI-aims

## Fritz Haber Institute *ab initio* molecular simulations

- Accurate and efficient quantum mechanics for molecules and materials
- All-electron, numeric atom-centered basis functions
- Non-periodic and periodic structures within same framework
- Density Functional Theory (DFT)
- Various van der Waals models, e.g. many-body dispersion [2]
- Beyond DFT: RPA, GW, MP2, …
- Scalable: 1,000s of atoms on up to (ten)thousands of CPUs

**http://aims.fhi-berlin.mpg.de**


MAX-PLANCK-GESELLSCHAFT

[1] Blum, Gehrke, Hanke, Havu, Havu, Ren, Reuter, Scheffler, *Comput. Phys. Commun.* 180, 2175 (2009).
[2] A. Tkatchenko, R.A. DiStasio Jr., R. Car, and M. Scheffler, *Phys. Rev. Lett.* 108, 236402 (2012).

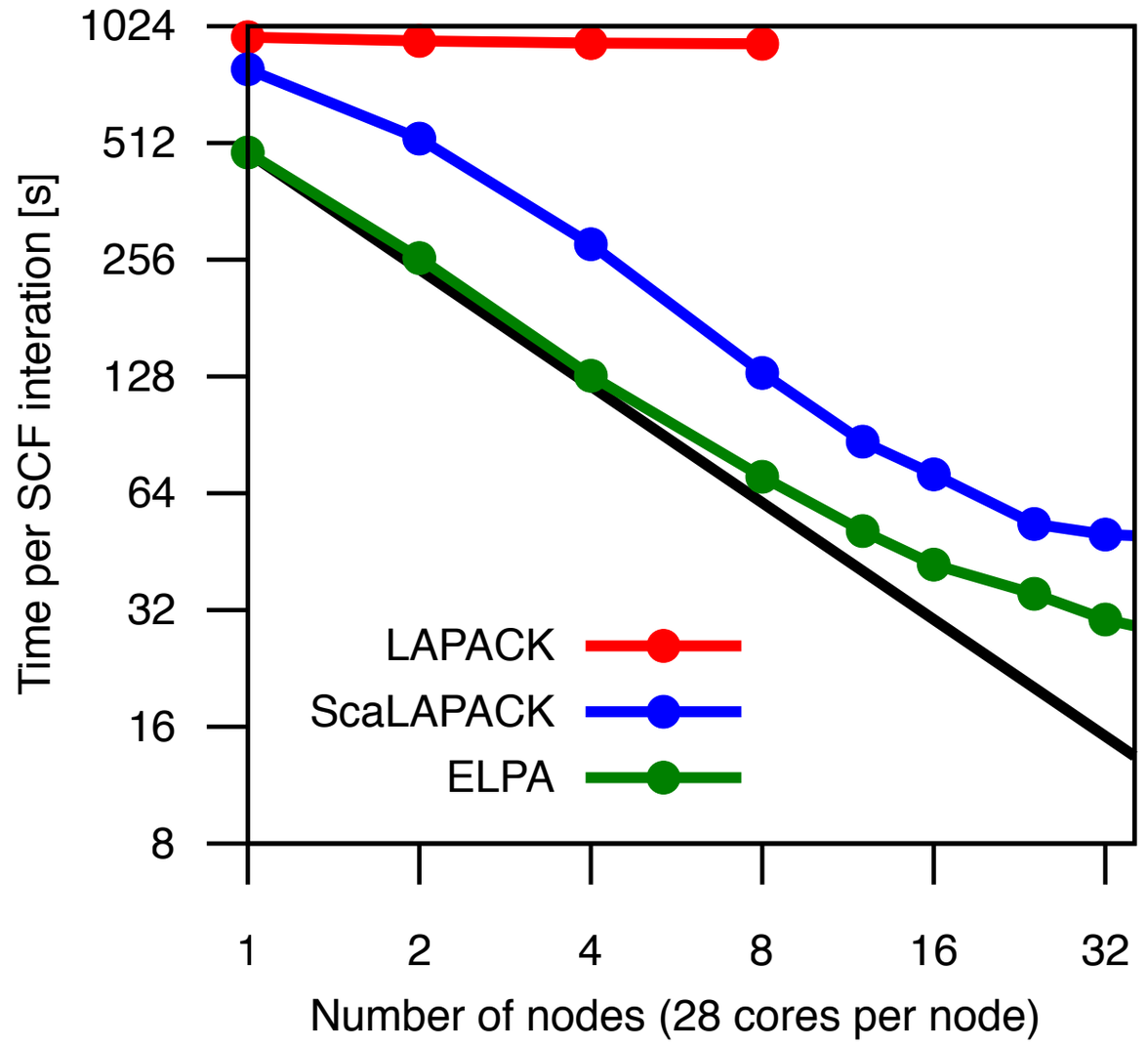
# Scaling of FHI-aims on Iris

**LAPACK — Linear Algebra PACKage**

- solving systems of linear equations
- linear least squares
- eigenvalue problems
- matrix factorizations
- singular value decomposition
- …

**ScaLAPACK — Scalable LAPACK**

- LAPACK routines redesigned for distributed memory




**ELPA - Eigenvalue SoLvers for Petaflop-Applications**

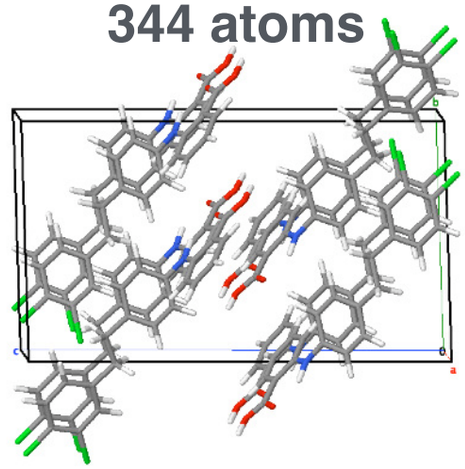
- highly efficient and highly scalable direct eigensolvers for symmetric matrices

**https://gitlab.mpcdf.mpg.de/elpa/elpa**

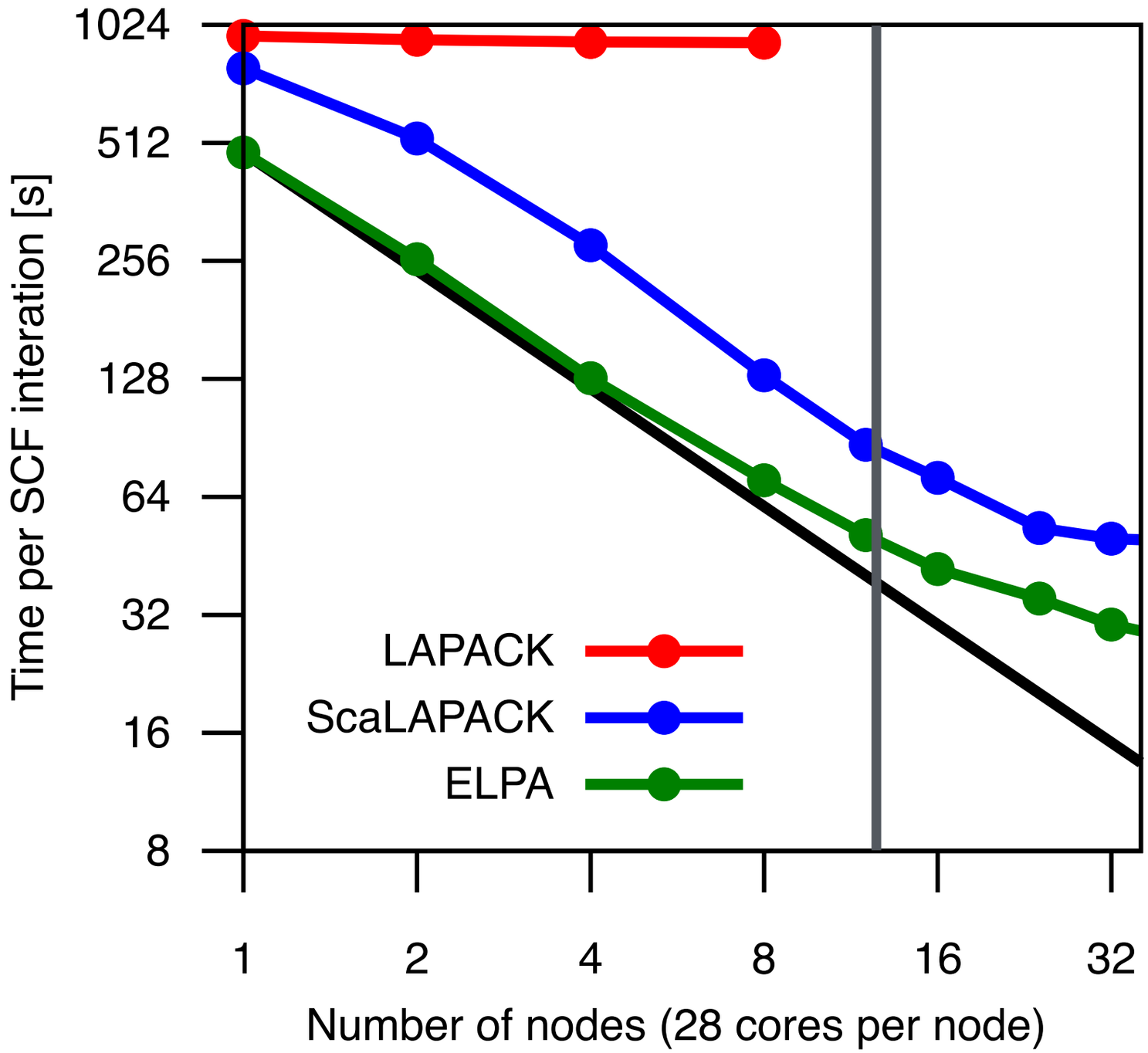
MPCDF

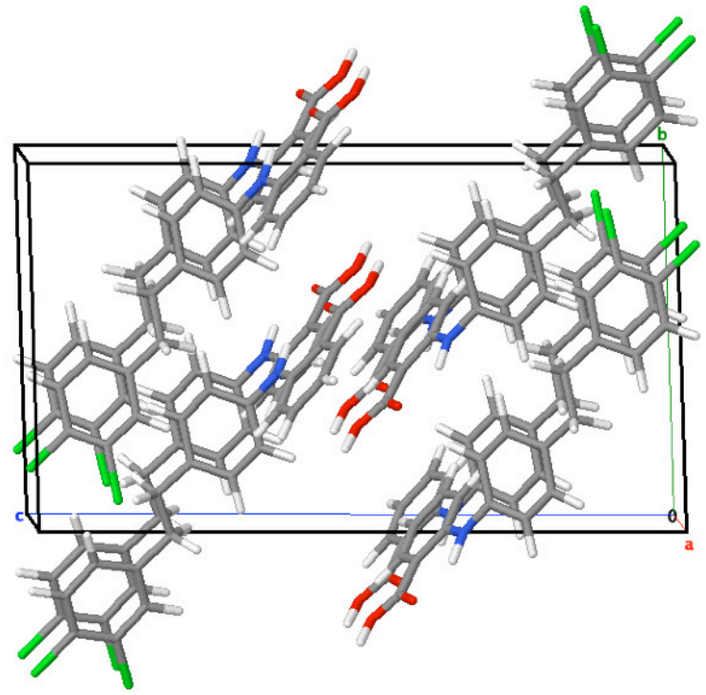
MAX-PLANCK-GESELLSCHAFT

**344 atoms**



# Scaling of FHI-aims on Iris



344 atoms

**Memory per core [GB]**

| | 1 N | 2 N | 8 N |
|---|---|---|---|
| **LAPACK** | ~4.0 | ~4.0 | ~4.0 |
| **ScaLAPACK ELPA** | ~1.6 | ~0.8 | ~0.3 |