# Experiences with Self-Consistent Tight Binding and ELSI

Ben Hourahine

*benjamin.hourahine@strath.ac.uk*

# Motivation via computational cost

| Method | Eform. (eV) | Time | |
|---|---|---|---|
| Orthogonal TB | 3.2 | 1 | |
| Self-Consistent Orthogonal TB | 3.2 | 13 | |
| Non-orthogonal TB | 3.1 | 2 | (~DFTB) |
| SC non-orthogonal TB | 3.4 | 19 | (~SCC-DFTB) |
| 3 centre non-orthogonal TB | 4.3 | 72 | |
| 3 centre SC non-orthogonal TB | 4.4 | 87 | |
| LCAO LDA DFT | 3.8 | 44 | |
| SC LCAO LDA DFT | 4.1 | 110 | |

Si vacancy formation, 64 atoms periodic Γ-point minimal basis

A. P. Horsfield and A. M. Bratkovsk, J. Phys. Cond. Mat. 12 R1–R24 (2000).

# DFTB

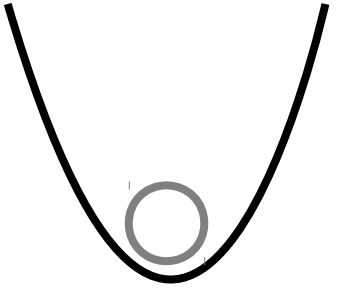
Semi-empirical DFTB modelling (DFT-*lite* descended from the Harris functional)

- Non-orthogonal tight-binding minimal basis (usually)
- Approximate expansion of Kohn-Sham around a reference density
- Higher order terms give charge transfer and spin contributions
  - Behaves like (S)GGA/LDA
- Parameterised integrals/repulsives but no integration after that (Open parameters : http://www.dftb.org )
- Standard DFT-like properties (Janak's theorem works), vibrational modes/intensities/Raman/...
- Time dependent and transport extensions (following DFT)

J. Phys. Chem. A 111, issue 26 (2007)
pssb 249 issue 2 (2012)

# DFTB – underlying idea

Sum of neutral **confined** atomic densities (Confinment dictated by physical environment)



$$n_0(r) = \sum_\alpha n_0^\alpha |r - R_\alpha| \qquad E_{tot} = E_{bs}[n_0] + E_{rep}[n_0] + E_{2nd}[n_0, \delta n^2]$$

$E_{bs}[n_0]$ and $E_{2nd}[n_0,\delta n^2]$ **calculated explicitely**

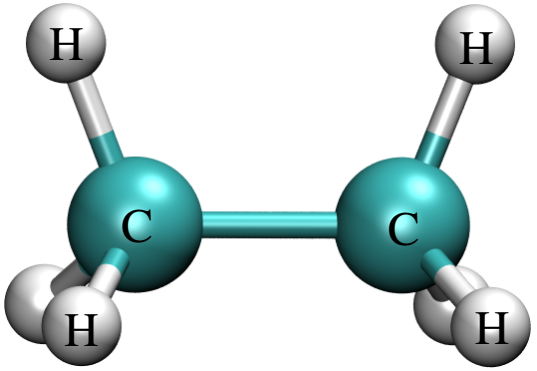
(approximations: yes, adjustable parameters: no)

Superposition of pairwise interactions

$$E_{rep} = \frac{1}{2} \sum_\alpha \sum_{\beta \neq \alpha} E_{rep}^{\alpha\beta}(|R_\alpha - R_\beta|)$$

Deviation from *ab initio* calculation tabulated as function of distance **in advance**

$$E_{rep}^{\alpha\beta}(R_{\alpha\beta}) = E_{\text{ab initio}}(R_{\alpha\beta}) - [E_{bs} + E_2](R_{\alpha\beta})$$



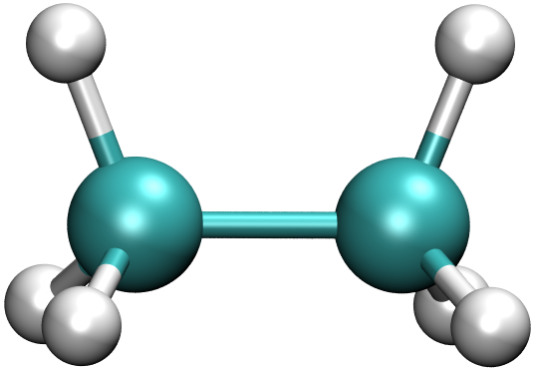

Repulsives needed:
- C – C
- C – H
- H – H

$E_{rep}[n_0]$ **fitted to *ab initio* calculations**
(corrects energyerrors due to approximations)

# Repulsive parameterization

$$E_{\text{rep}}^{\alpha\beta}(R_{\alpha\beta}) = E_{\text{ab initio}}(R_{\alpha\beta}) - [E_{\text{bs}} + E_2](R_{\alpha\beta})$$

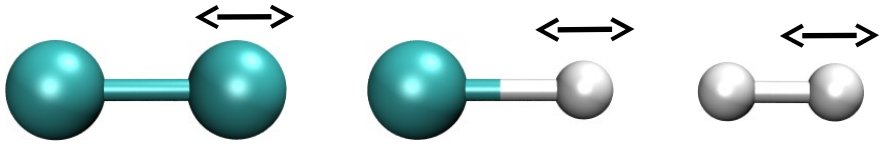
Tabulating difference between *ab initio* and DFTB without repulsives as function of distance



Historically needed a lot of expertise

- Choosing right fit system(s)

  Stretching/compressing dimers usually not enough



- Choosing test systems

  Wide spectrum of systems and properties reasonable

  (e.g. biological systems, solids, hybrid systems)

Repulsives needed:
- C – C
- C – H
- H – H

- Several diatomic repulsives must be co-optimised at the same time

Automatic (black box) fitting difficult, **semi-automatic fitting currently possible**:

https://bitbucket.org/stanmarkov/skopt https://bitbucket.org/solccp/adpt_core

# DFTB SCC contribution

In the late 1990's several groups all started considering how to account more realistically for charge transfer effects in tight binding.

The DFTB approach is to use Mulliken charges to model of the electrostatics present in the system. This then adds terms to the total energy and potential that depend on *fluctuations* from neutrality of the local charges.

$$q_\alpha = \sum_i f_i \sum_{\mu \in \alpha} \sum_\nu c_{i\mu} c_{i\nu} S_{\mu\nu}$$

$$\Delta q_\alpha = q_\alpha - q_\alpha^0$$

$$E_{2\mathrm{nd}} = \frac{1}{2} \sum_\alpha \sum_{\beta \neq \alpha} \gamma_{\alpha\beta} \Delta q_\alpha \Delta q_\beta \qquad H_{\mu\nu}^{2\mathrm{nd}} = \frac{1}{2} S_{\mu\nu} \sum_\xi (\gamma_{\alpha\xi} + \gamma_{\beta\xi}) \Delta q_\xi$$

Elstner, Porezag, Jungnickel, Elsner, Haugk, Frauenheim, Suhai and Seifert, Phys. Rev. B 58 7260 (1998).

# SCC-DFTB (DFTB2) – accuracy

| | DFTB | cc-pVDZ | cc-pVTZ | G2 |
|---|---|---|---|---|
| $H_2+CH{\equiv}CH \rightarrow CH_2{=}CH_2$ | −38.8 | −41.0 | −37.9 | −40.1 |
| $H_2+CH_2{=}CH_2 \rightarrow CH_3{-}CH_3$ | −37.0 | −28.5 | −26.5 | −30.5 |
| $3H_2+HCN \rightarrow NH_3+CH_4$ | −47.9 | −47.1 | −48.5 | −53.7 |
| $H_2+CO \rightarrow H_2CO$ | +10.9 | +0.1 | +0.7 | +3.1 |
| $2H_2+CO \rightarrow CH_3OH$ | −7.8 | −12.6 | −13.1 | −15.5 |
| $H_2+CH_3OH \rightarrow CH_4+H_2O$ | −25.7 | −20.6 | −24.6 | −26.2 |
| $2H_2+N_2 \rightarrow NH_2{-}NH_2$ | +32.7 | +31.6 | +31.9 | +30.7 |
| $H_2+NH_2{-}NH_2 \rightarrow 2NH_3$ | −47.4 | −38.3 | −43.1 | −46.7 |
| $H_2+H_2O_2 \rightarrow 2H_2O$ | −81.7 | −63.3 | −71.1 | −82.8 |
| $2H_2+CO_2 \rightarrow H_2O+H_2CO$ | +15.6 | +26.6 | +21.9 | +14.5 |
| $CH_4+CO \rightarrow CH{\equiv}CH+H_2O$ | +55.9 | +51.5 | +43.7 | +44.3 |
| $CH_4+H_2CO \rightarrow CH_2{=}CH_2+H_2O$ | +6.2 | +10.4 | +5.2 | +1.1 |
| $CH_4+CH_3OH \rightarrow CH_3{-}CH_3+H_2O$ | −12.1 | −5.4 | −7.6 | −10.8 |
| $2CH_4+N_2 \rightarrow NH_2{-}NH_2+CH_2{=}CH_2$ | +83.3 | +75.4 | +75.4 | +76.6 |
| $CH_4+H_2O_2 \rightarrow CH_3OH+H_2O$ | −56.0 | −42.6 | −46.4 | −56.6 |
| $2NH_3+CH{\equiv}CH \rightarrow NH_2{-}NH_2+CH_2{=}CH_2$ | +8.7 | −2.8 | +5.1 | +6.7 |
| $2NH_3+CH_2{=}CH_2 \rightarrow NH_2{-}NH_2+CH_3{-}CH_3$ | +10.4 | +9.7 | +16.6 | +16.2 |
| $NH_3+HCN \rightarrow CH_4+N_2$ | −33.1 | −40.5 | −37.4 | −37.6 |
| $NH_3+CO \rightarrow HCN+H_2O$ | +14.3 | +13.8 | +10.8 | +12.0 |
| $2NH_3+H_2CO \rightarrow NH_2{-}NH_2+CH_3OH$ | +28.8 | +25.5 | +29.3 | +28.2 |
| $H_2+H_2CO \rightarrow CH_3OH$ | −18.7 | −12.8 | −13.8 | −18.6 |
| $Oxirane+H_2O \rightarrow OH{-}CH_2{-}CH_2{-}OH$ | −30.9 | −20.5 | −16.7 | −19.6 |
| $Oxirane+NH_3 \rightarrow NH_2{-}CH_2{-}CH_2{-}OH$ | −33.1 | −20.4 | −17.5 | −22.6 |
| $HNCO+H_2O \rightarrow NH_2{-}COOH$ | −4.3 | −17.3 | −11.1 | −16.1 |
| $CH_2{=}NH+CH_4+NH_3 \rightarrow 2CH_3NH_2$ | −2.7 | +1.1 | +4.3 | −0.6 |
| $H_2CO+CH_4+H_2O \rightarrow 2CH_3OH$ | +7.1 | +7.9 | +10.9 | +7.6 |
| $HCN+2CH_4+2NH_3 \rightarrow 3CH_3NH_2$ | +17.4 | +14.1 | +21.4 | +14.6 |
| $CO+2CH_4+2H_2O \rightarrow 3CH_3OH$ | +43.6 | +28.6 | +36.2 | +36.8 |

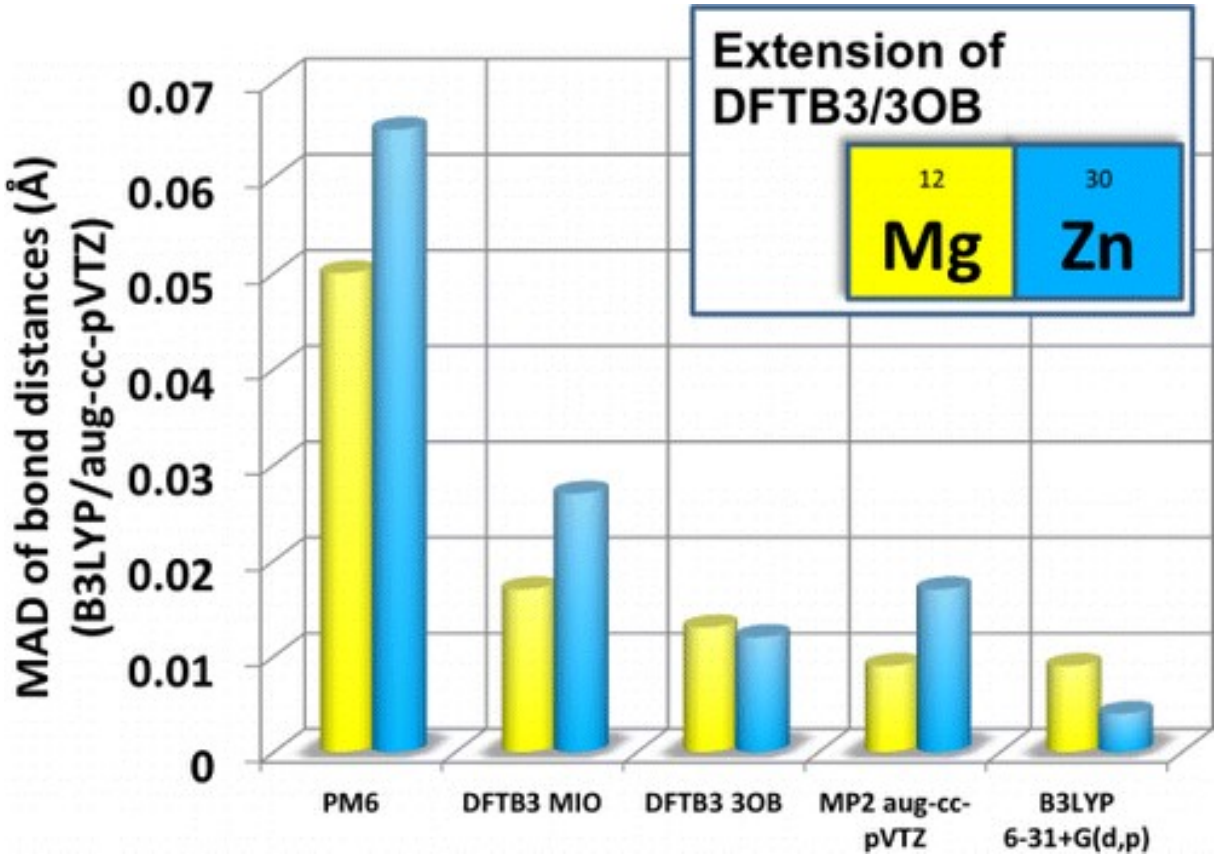
With respect to G2 set:

mean ave. dev.: 4.3 kcal/mole

Krueger, *et al.*, J. Chem. Phys. 122 (2005) 114110.

# DFTB3 – accuracy

Expand the DFT energy to 3rd order in charge fluctuations



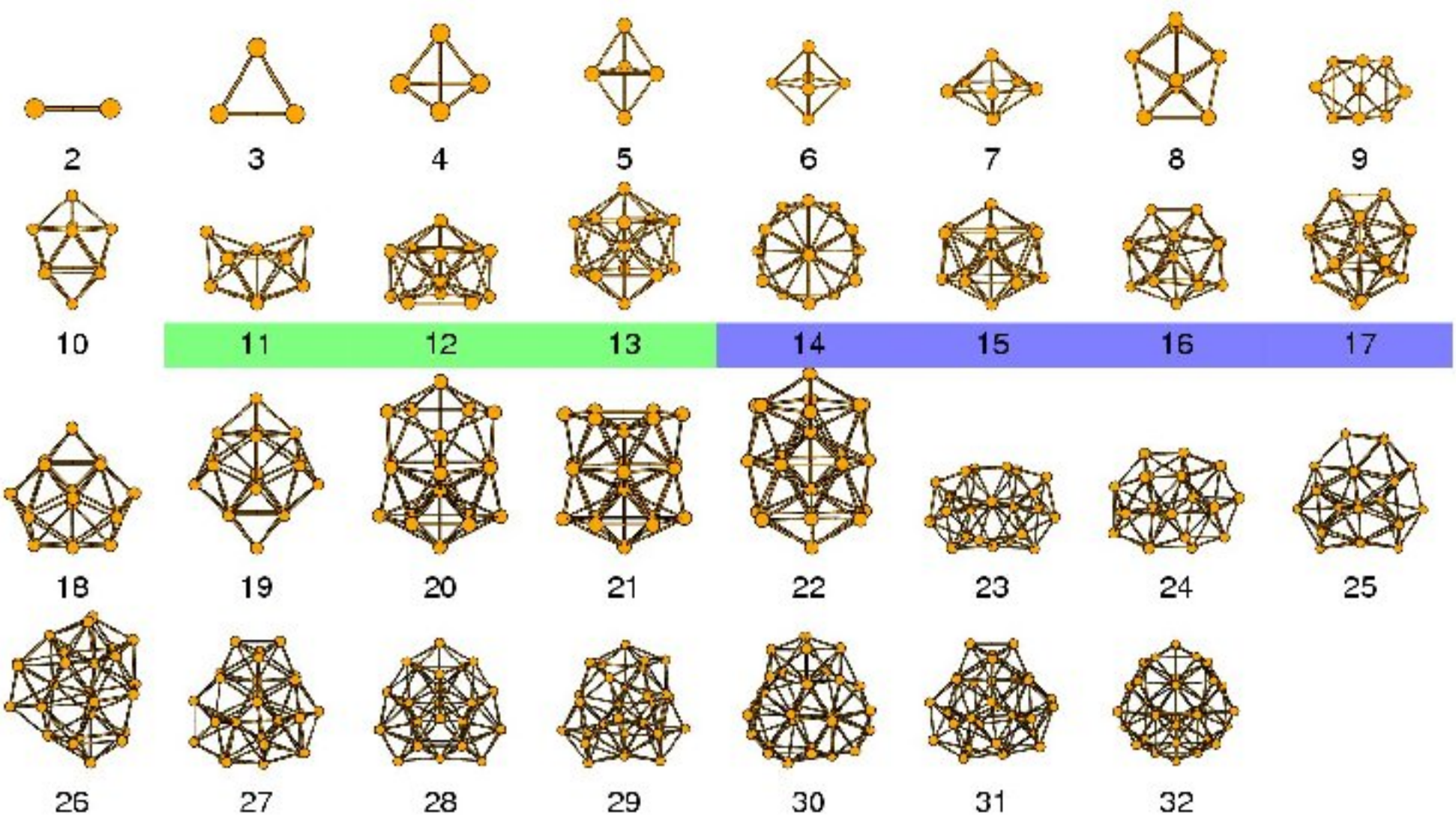

Small molecule test set

Paper includes peptides and other larger systems at DFTB3 level

Typical mean absolute deviation (MAD) of ~3–5 kcal/mol

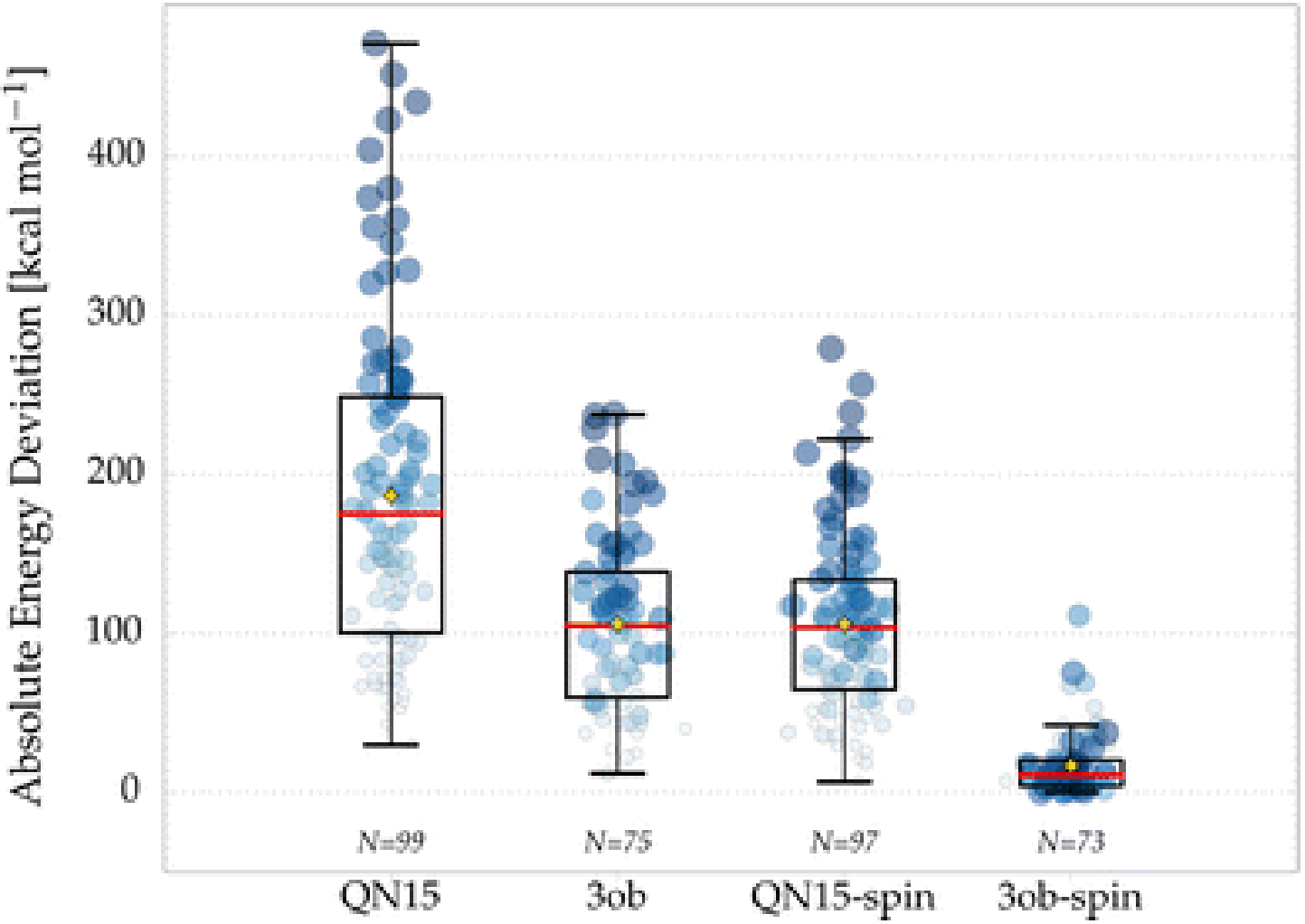
X. Lu, M. Gaus, M. Elstner, Q. Cui, *J. Phys. Chem B* **2015**, 119, 1062−1082.

# Spin




Köhler et al. Chem. Phys 309 23 (2005)

# Spin – accuracy




GMTKN30 test set

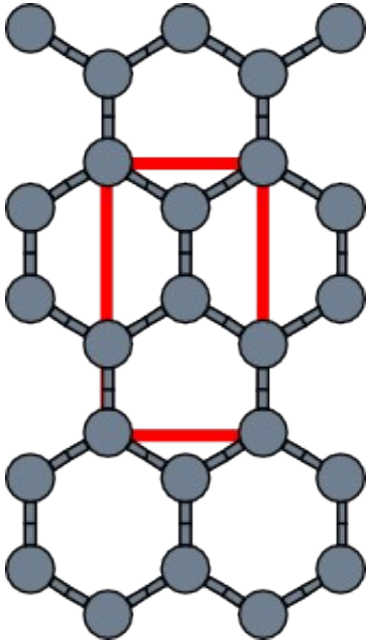
3ob set technically intended for DFTB3 level model

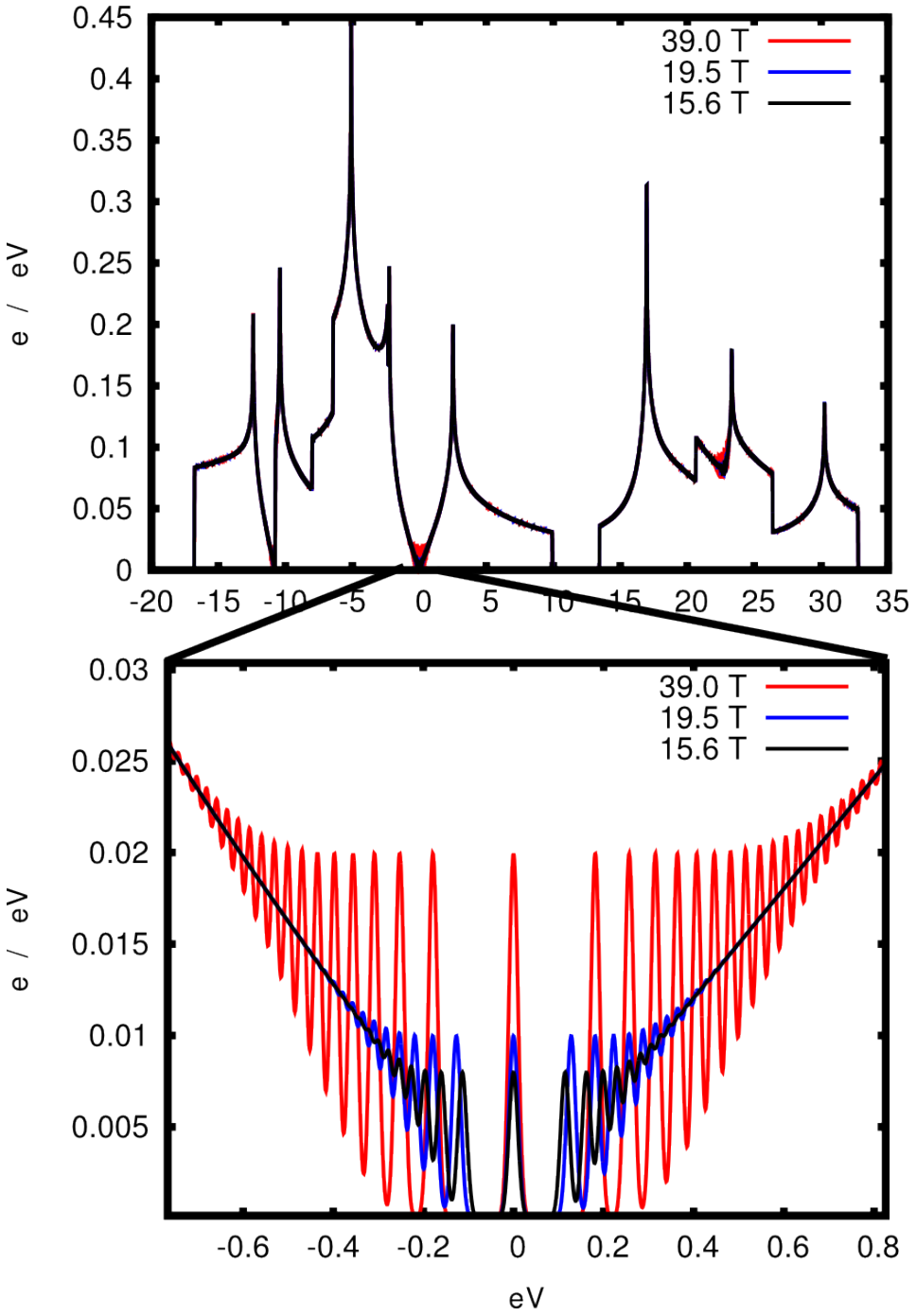
Melix, P., Oliveira, A.F., Rüger, R. et al. Theor Chem Acc (2016) 135: 232.

# Graphene

Bulk states of this system with DFTB+ – Landau levels

Problem: supercell has a  minimum of 1 flux quantum of B field threading through. The bigger the cell the smaller the applied field can be






| Field | length | Atoms |
|---|---|---|
| 39 T | 0.8 μm | 8000 |
| 19.5 T | 1.7 μm | 16000 |
| 15.6 T | 2.1 μm | 20000 |

Calculations performed on SUPERMUC in Bavaria via PRACE scheme, ScaLAPACK D&C, QR solvers 96 nodes x16 cores; 92% strong scaling

# Previous low scaling DFTB implementations

linear scaling DFTB technologies – either
In the literature, 'current' or legacy  DFTB codes:

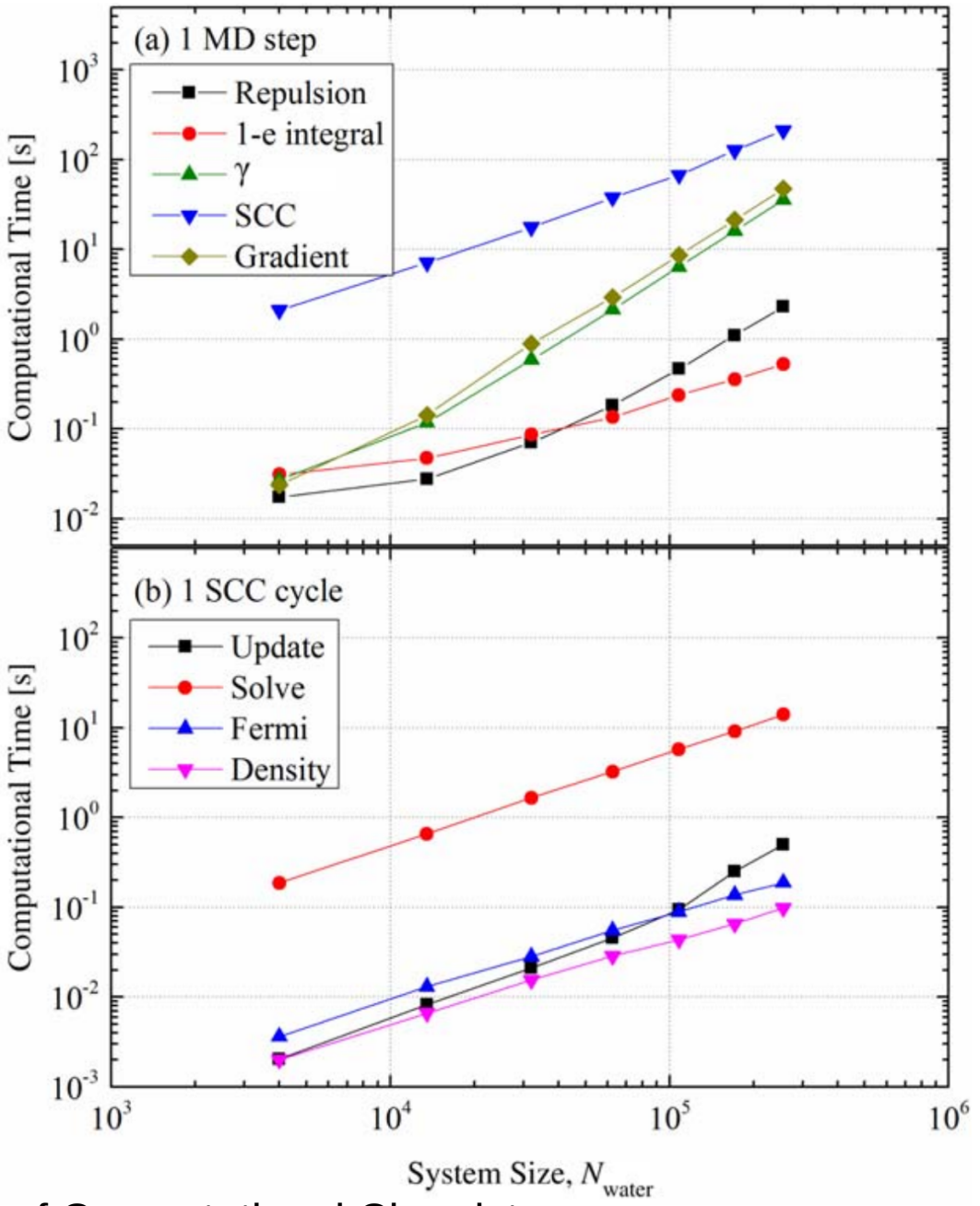
- Yang's divide and conquer (at least x3 versions)
- Galli functional
- Fermi operator expansion (at least x2 versions)
- Time dependent DFTB from [H,SP]
- Green's function solutions (NEGF for 1D)

Quadratic scaling –
- Car-Parinello + sparsity (Heine)
- SIPPS (Sternberg)
- PEXSI (Bremen Student project)

# Current size limits: DC-DFTB-K code

Liquid water simulation using
Divide and conquer to build the density matrix, and a (very) large supercomputer

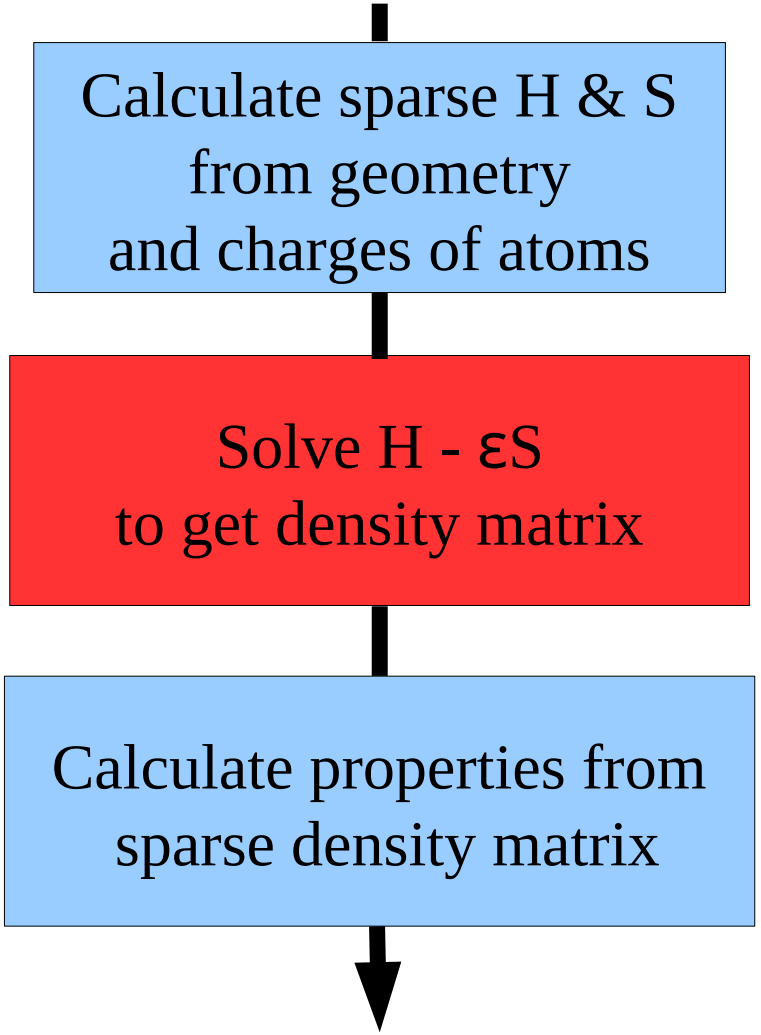
– wide HOMO-LUMO
– disordered
– localised density matrix




Nishizawa et al. Journal of Computational Chemistry 2016, 37, 1983–1992

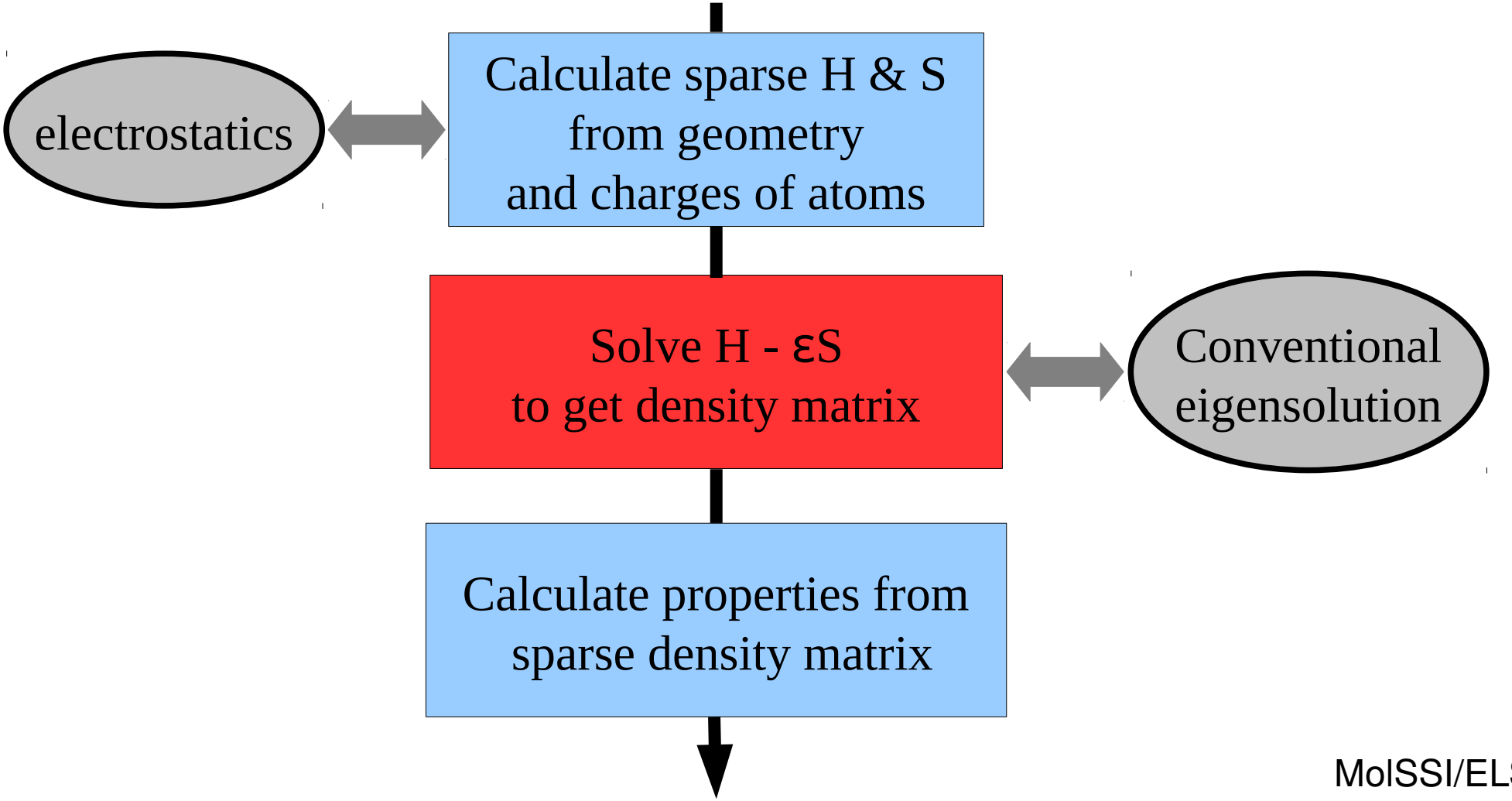
# DFTB+

Internally designed to use a sparse representation for as much as possible (well, easy…).



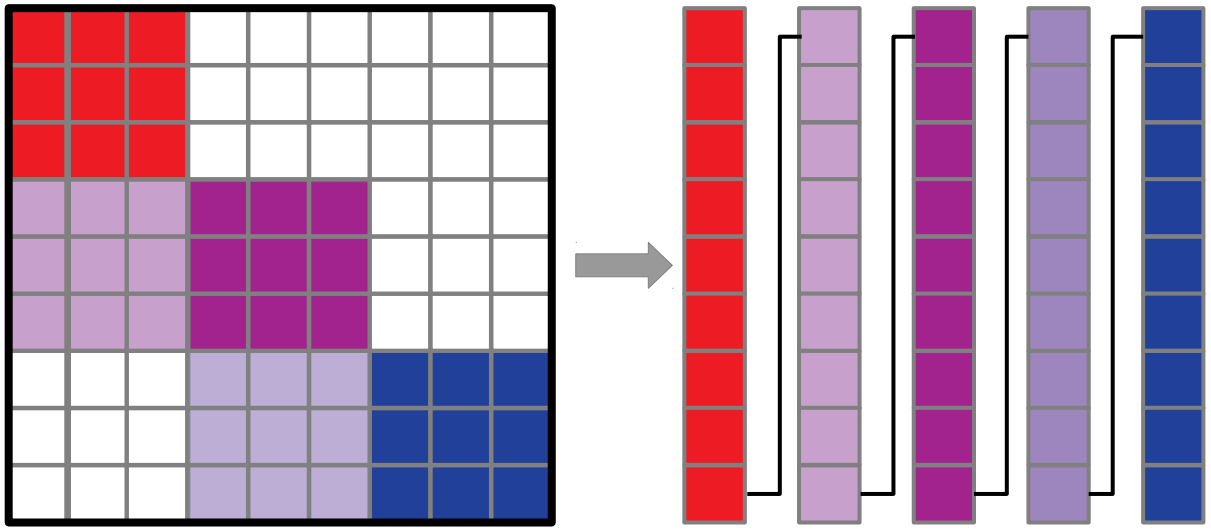
# DFTB+

Internally designed to use a sparse representation for as much as possible (well, easy…).
Only at two point in its calculation are there dense calculations to solve the ground state hamiltonian



# Internal sparse data structure

## Compressed block lower triangle format

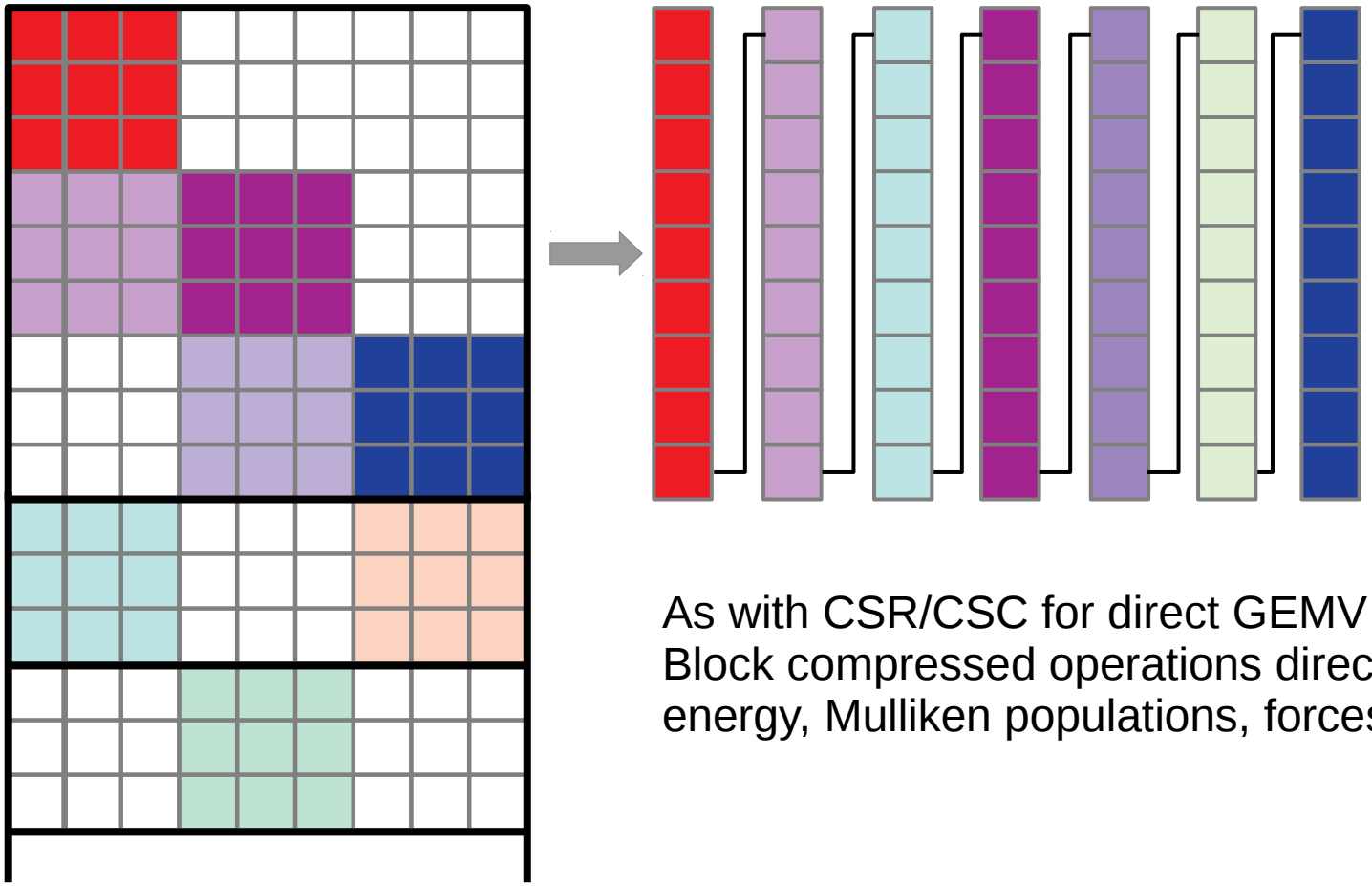


As with CSR/CSC for direct GEMV operations;
Block compressed operations directly for band energy, Mulliken populations, forces, stress, ...

B. Aradi, B. Hourahine, and Th. Frauenheim.
DFTB+, a sparse matrix-based implementation of the DFTB method,
J. Phys. Chem. A, 111 5678 (2007)

# Internal sparse data structure

Compressed block lower triangle format – includes boundary conditions in format (non central cell atoms in lower triangle) so not quite Harwell



As with CSR/CSC for direct GEMV operations; Block compressed operations directly for band energy, Mulliken populations, forces, stress, ...

B. Aradi, B. Hourahine, and Th. Frauenheim.
DFTB+, a sparse matrix-based implementation of the DFTB method,
J. Phys. Chem. A, 111 5678 (2007)

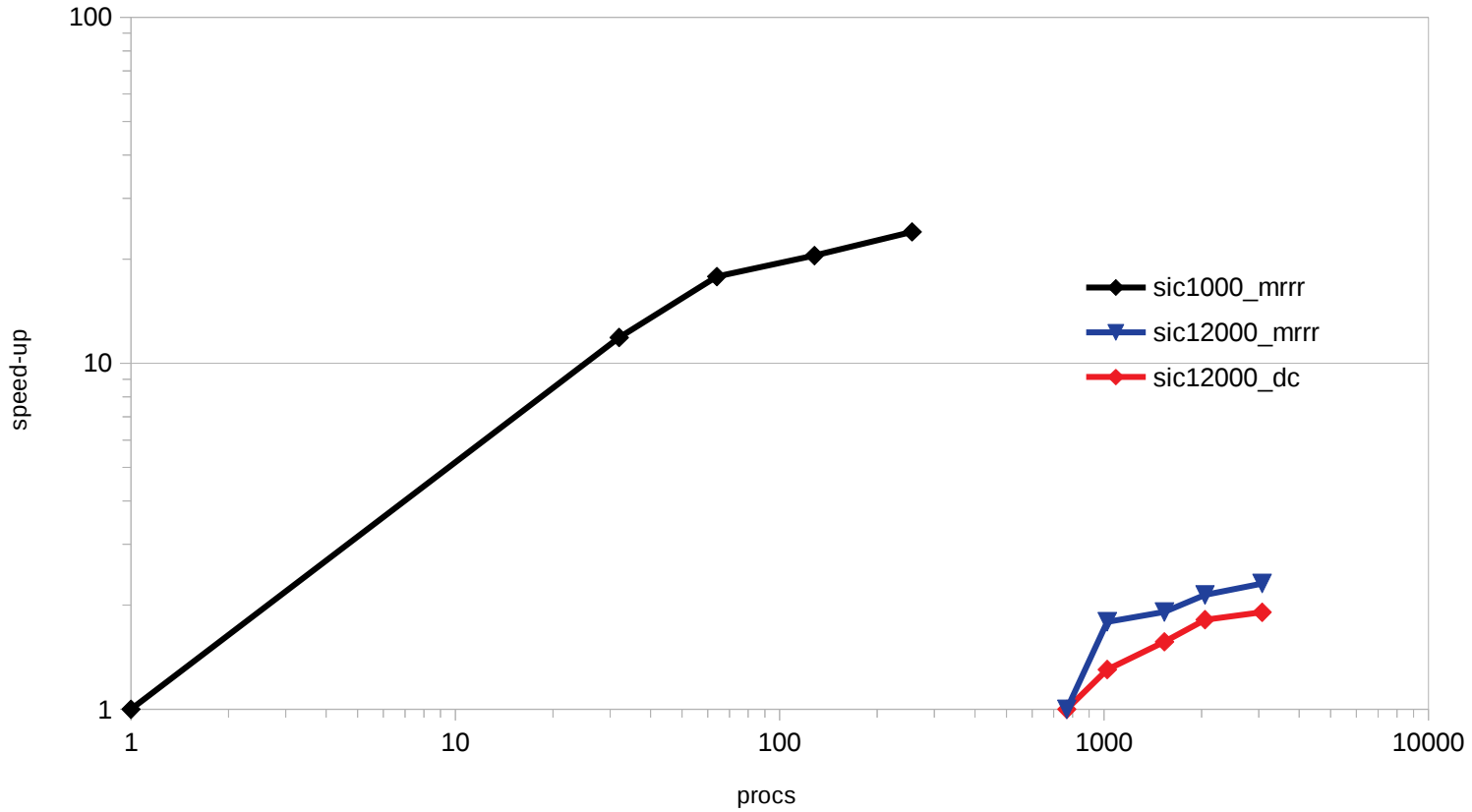
# DFTB+ as of today

http://www.dftbplus.org + http://www.dftb.org

- 17.1 onwards LGPL 3 licence; 18.1 is dual openMP and MPI parallel (and hybrid); 18.2 bugfix release
- LAPACK / ScaLAPACK eigensolvers
- DFTB 1, 2 and 3 models (+ spin)
- LDA+U, spin orbit, Casida exited state (molecules, Γ point partly)
- Various MD and geometry drivers (XL-BOMD, L-BFGS, …)
- Socket interface to drive with other codes (path-integral MD and REMD from I-Pi code https://github.com/i-pi/i-pi, ...)
- Various software engineering: FYPP preprocessor used – Fortran meta-programming; Doxygen / ford literate; regression testing; ...

# DFTB+ Parallel performance

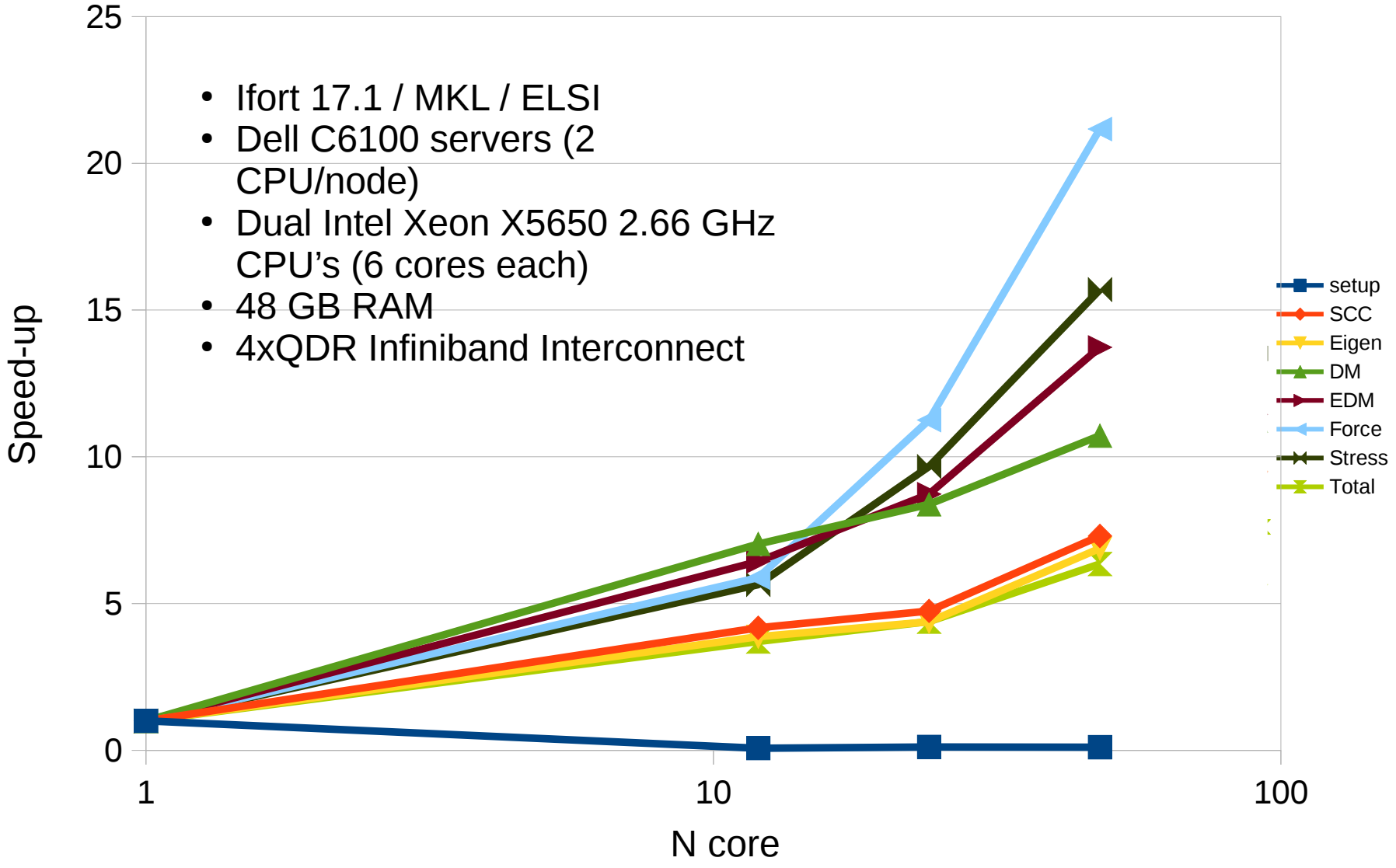
# ScaLAPACK (Pre-ELSI)




Γ point SCC
7 iterations
+ forces

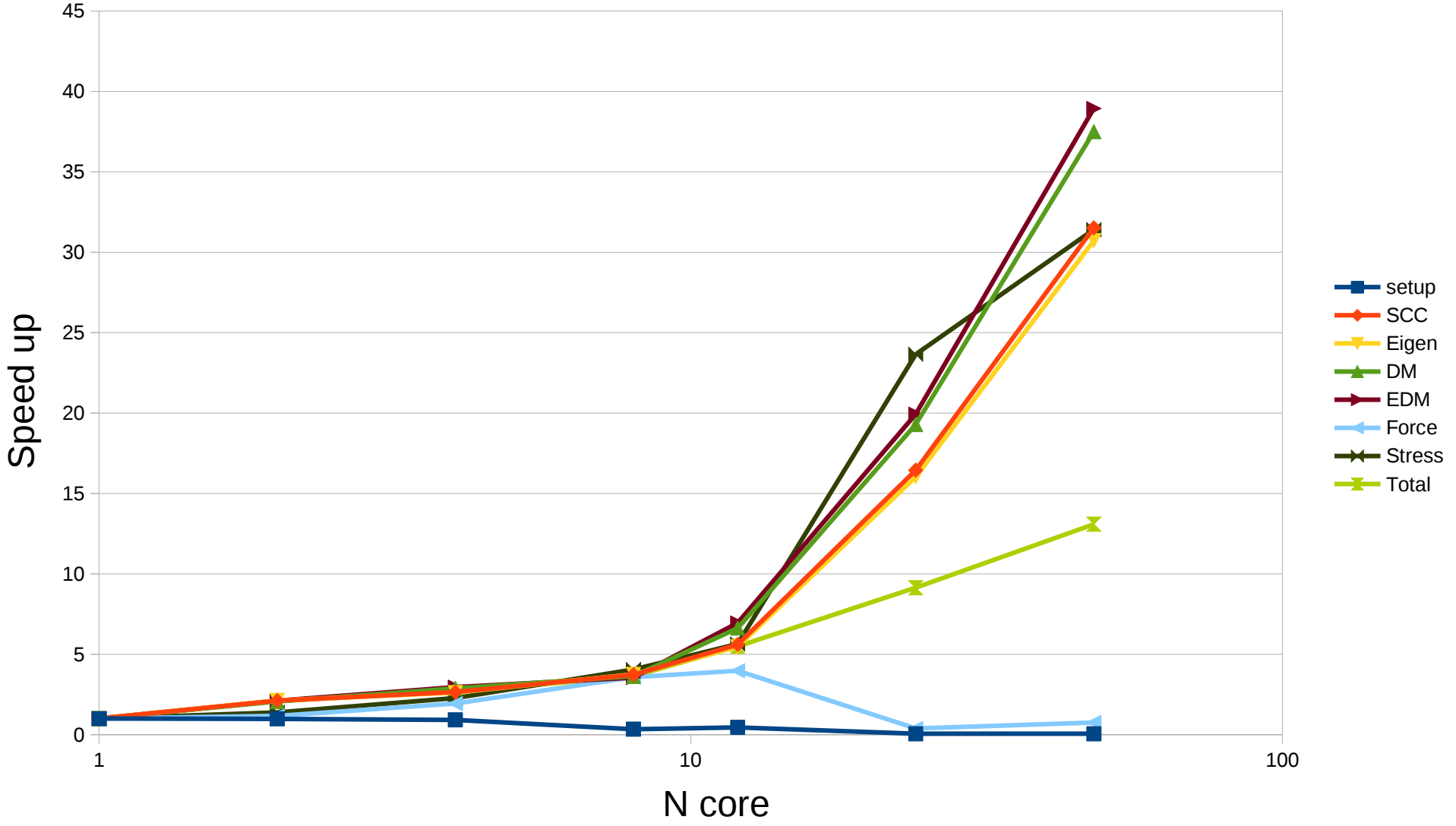
SuperMUC, Munich – Intel Xeon Sandy Bridge-EP Infiniband interconnect

# ScaLAPACK (MRRR) – Jan ‘18 old hardware



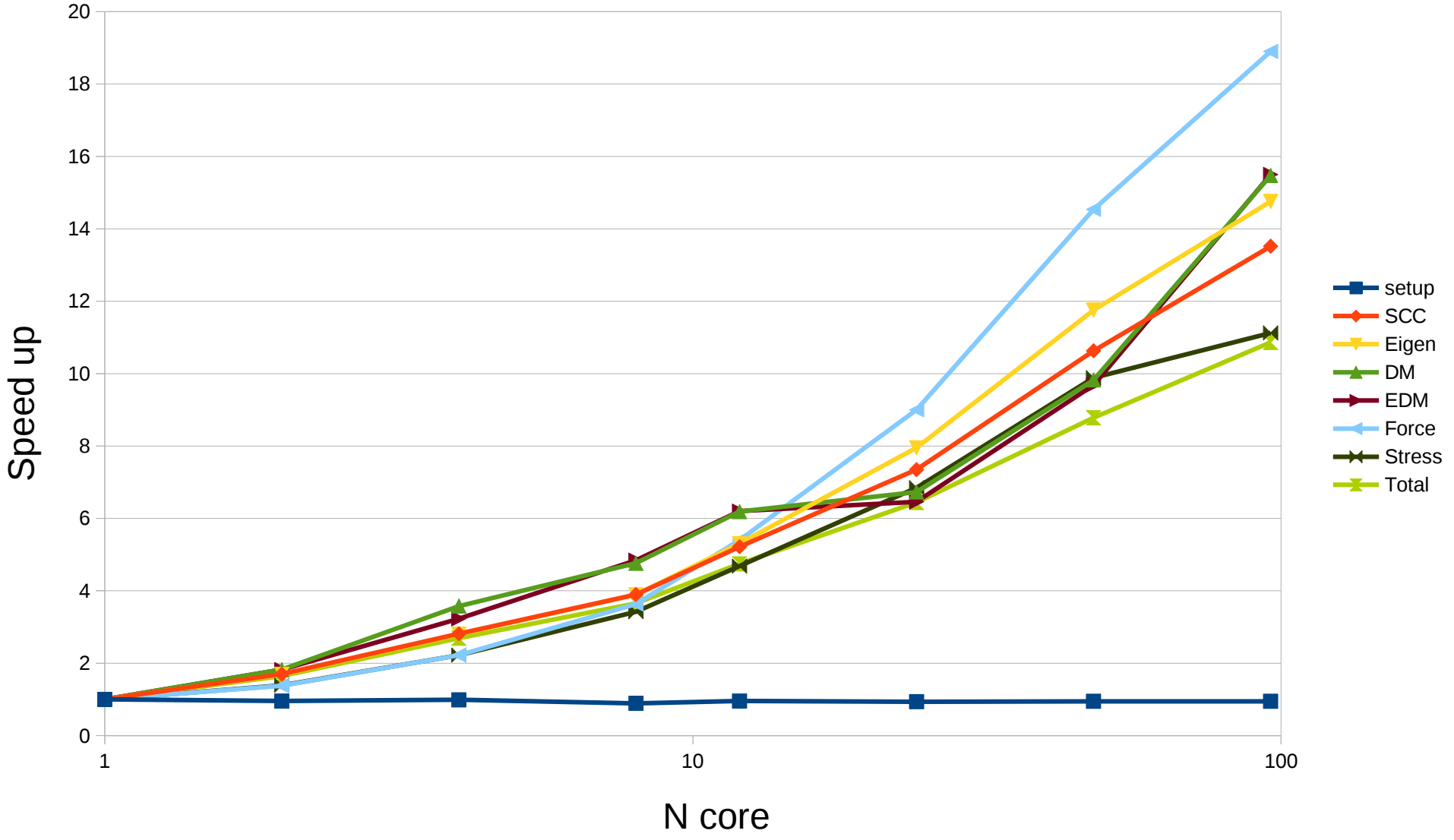

$Si_{2048}C_{2048}$ supercell, Γ point, 4 self consistent cycles + forces / stresses
(Dual Intel Xeon X5650 2.66 GHz)

# ELSI (ELPA2) – Jan'18 old hardware



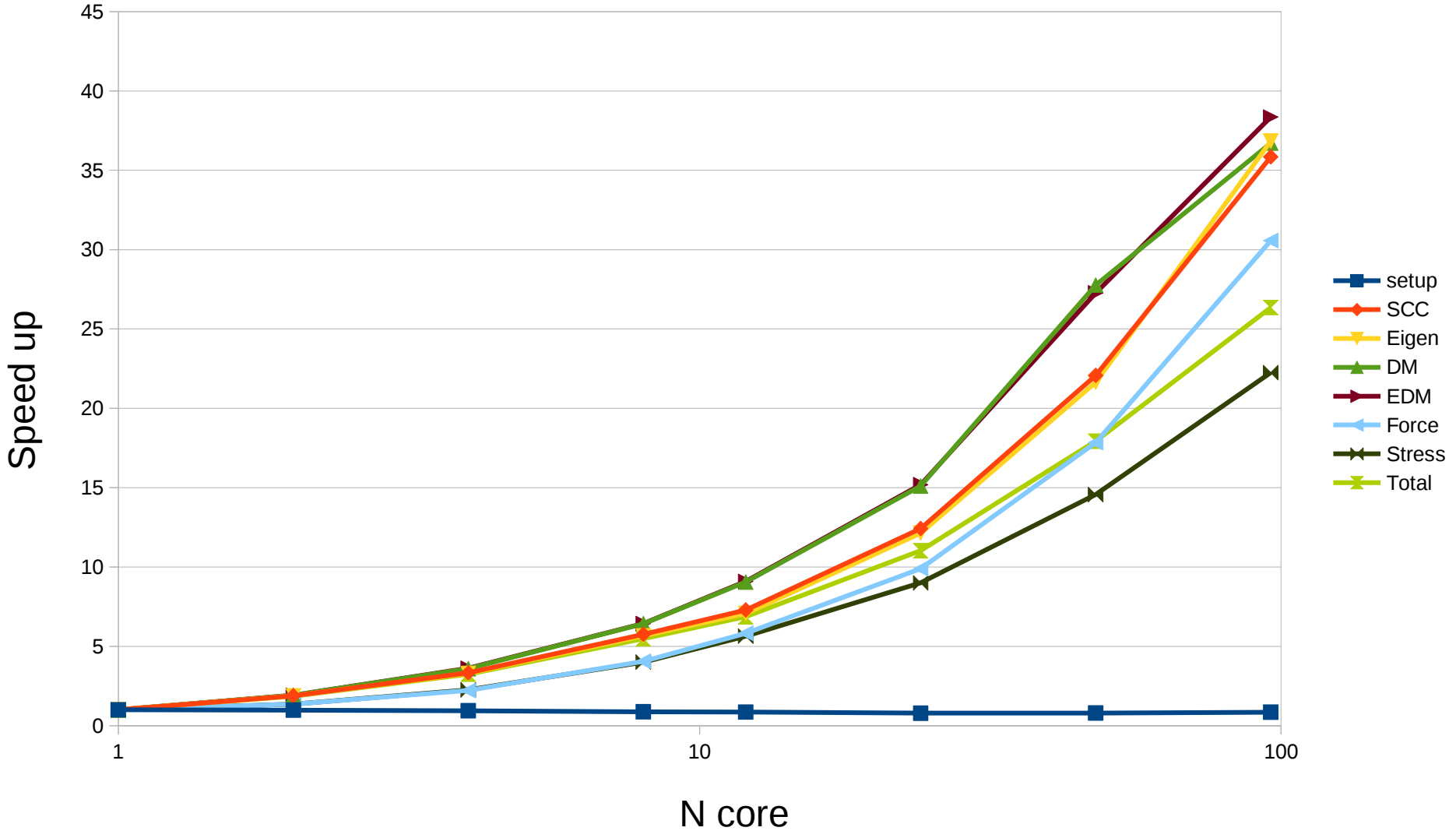

$Si_{2048}C_{2048}$ supercell, Γ point, 4 self consistent cycles + forces / stresses
(Dual Intel Xeon X5650 2.66 GHz)

# ELPA2



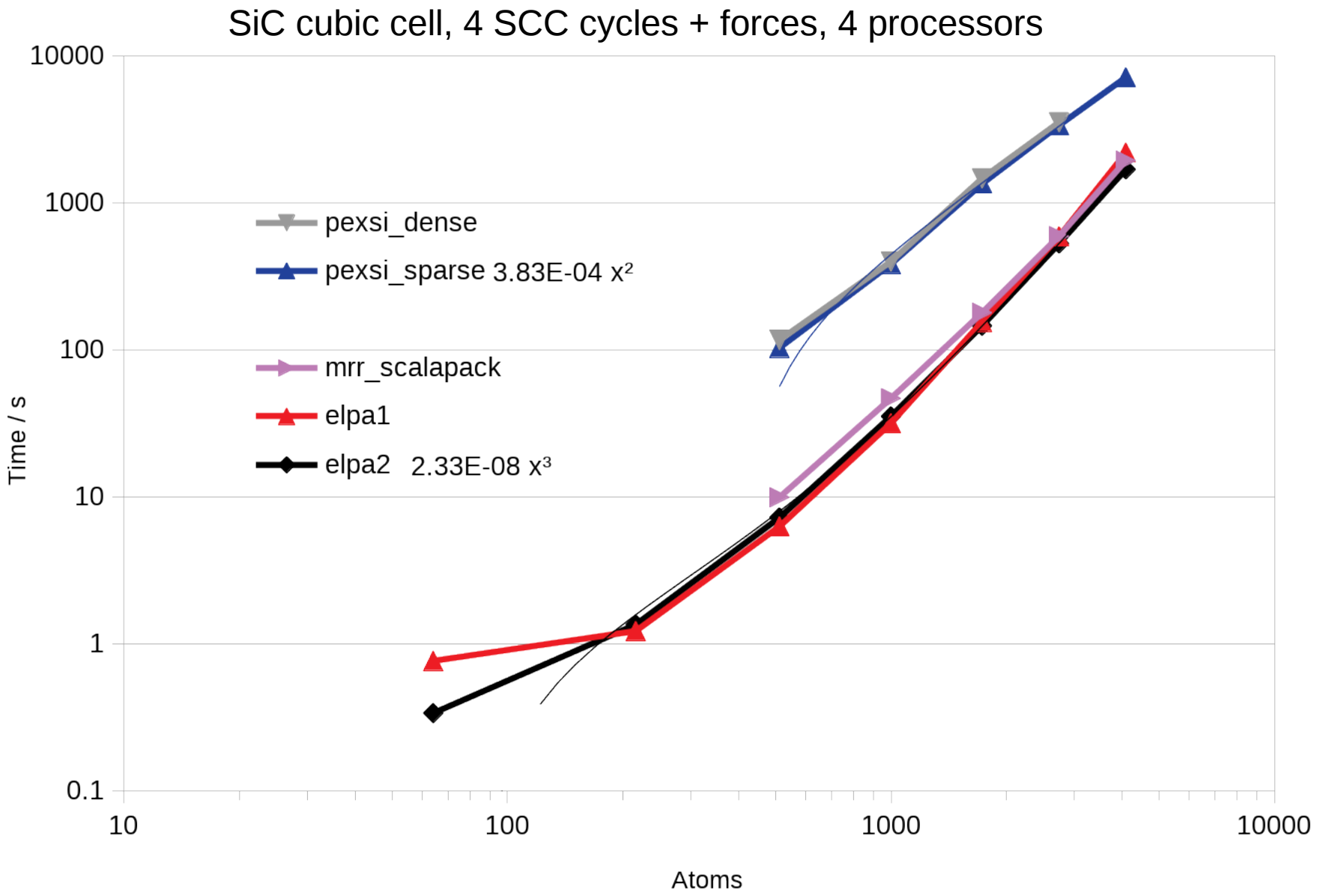

$Si_{216}C_{216}$ supercell, Γ point, 4 self consistent cycles + forces / stresses
(Dual Intel Xeon X5650 2.66 GHz)

# ELPA2



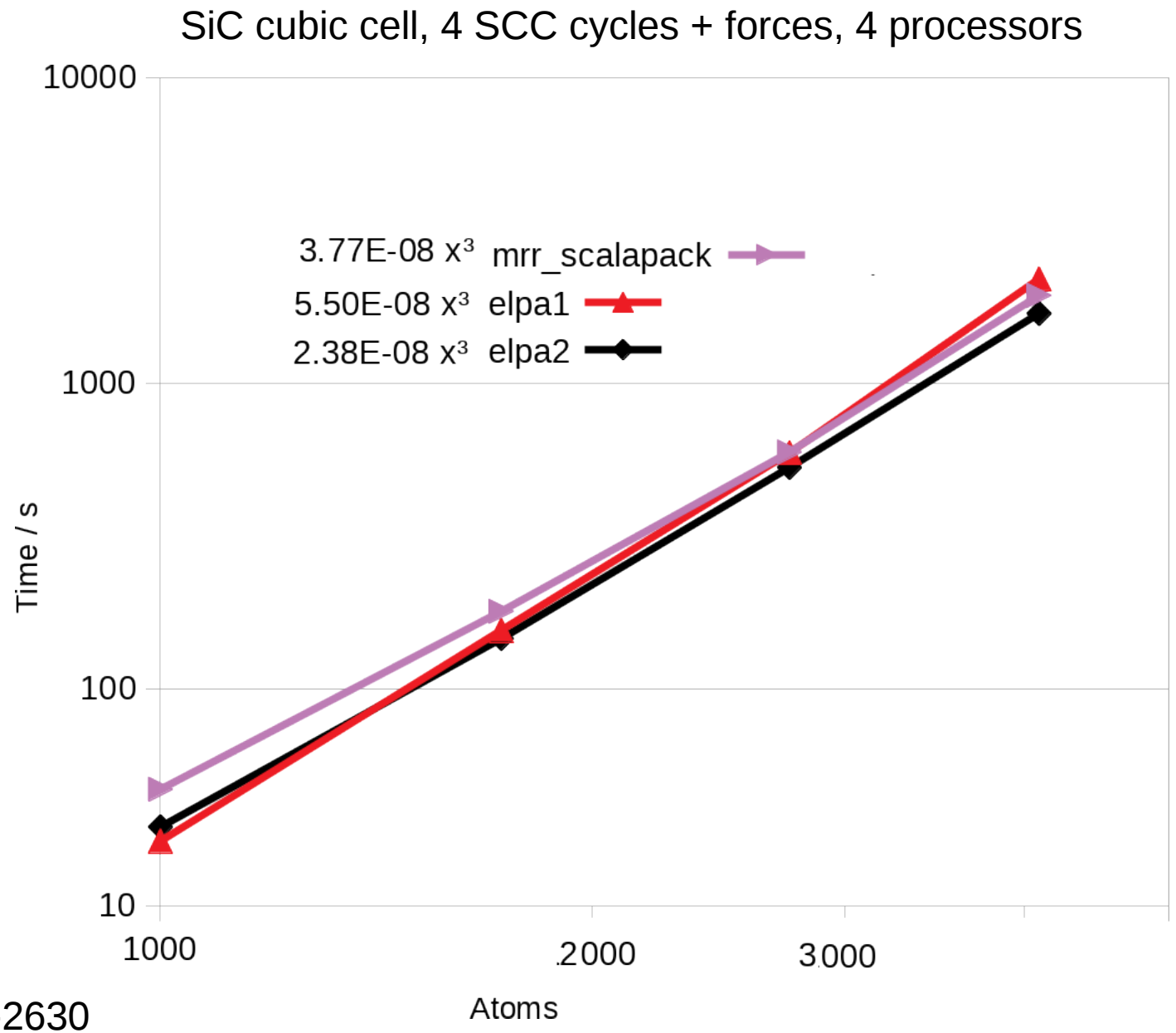

$Si_{864}C_{864}$ supercell, Γ point, 4 self consistent cycles + forces / stresses
(Dual Intel Xeon X5650 2.66 GHz)

# Recent ELSI (July ‘18)




Xeon E5-2630

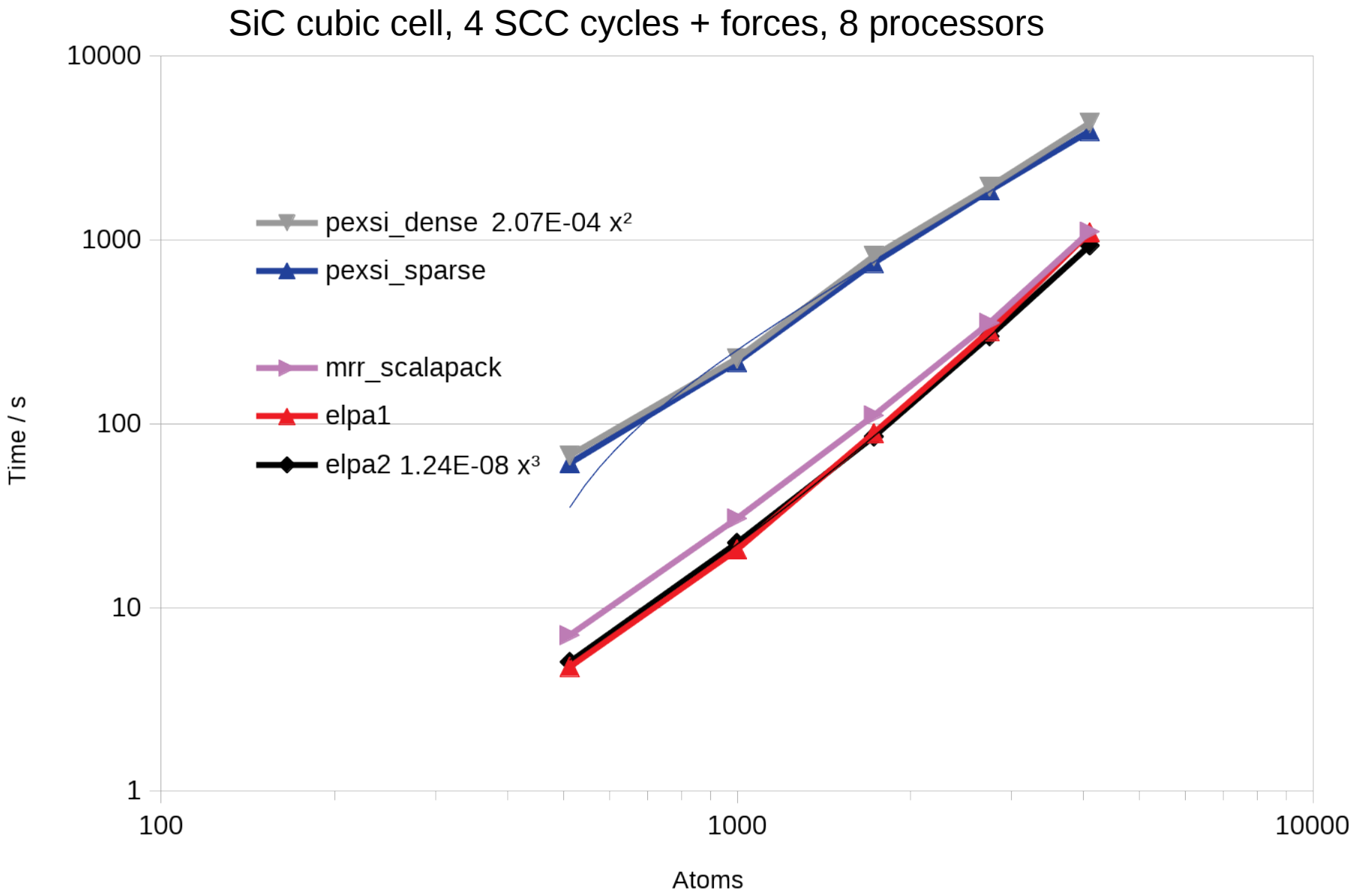
# Just the eigensolvers...




Xeon E5-2630

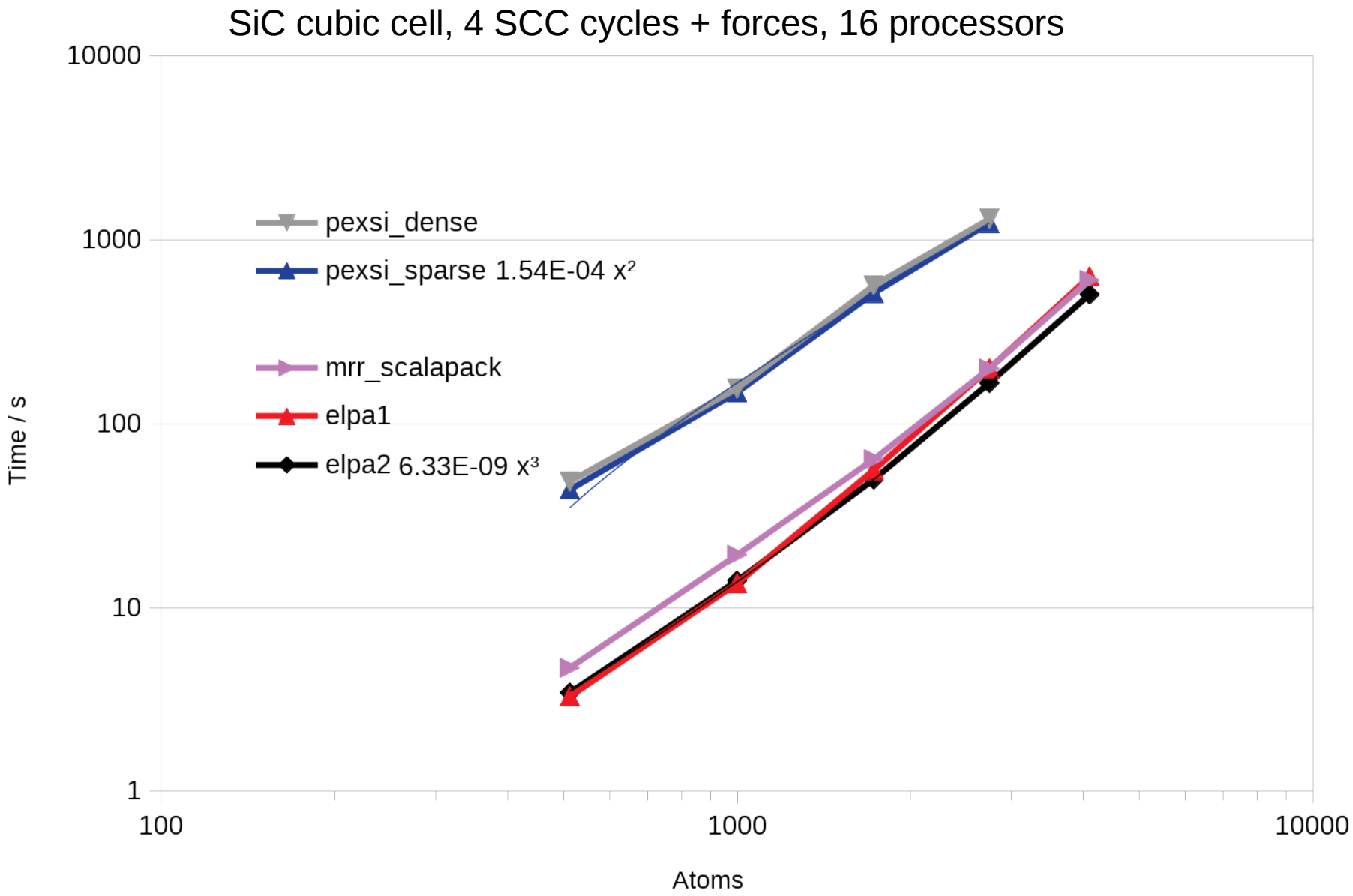
MolSSI/ELSI

# A bit larger systems




Xeon E5-2630

# System size scaling

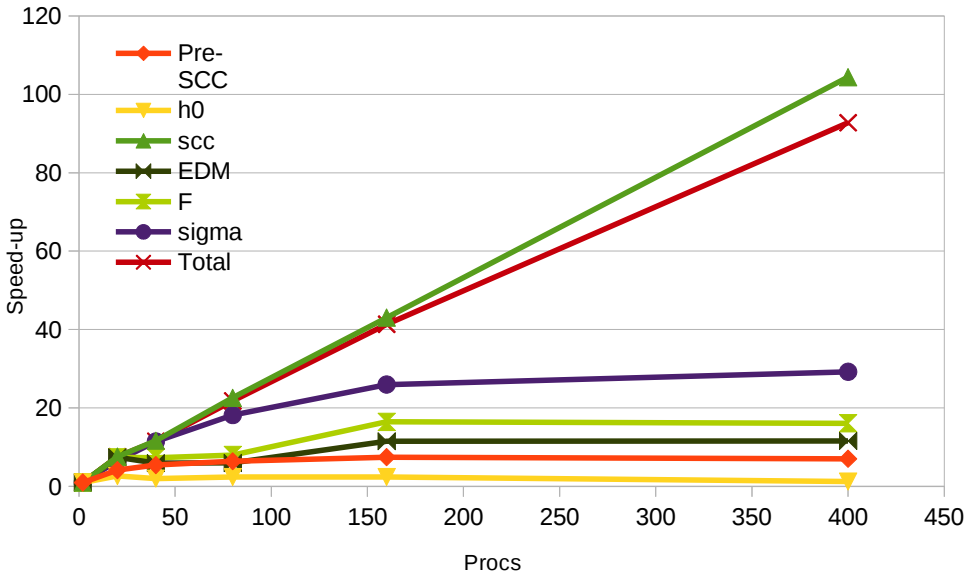


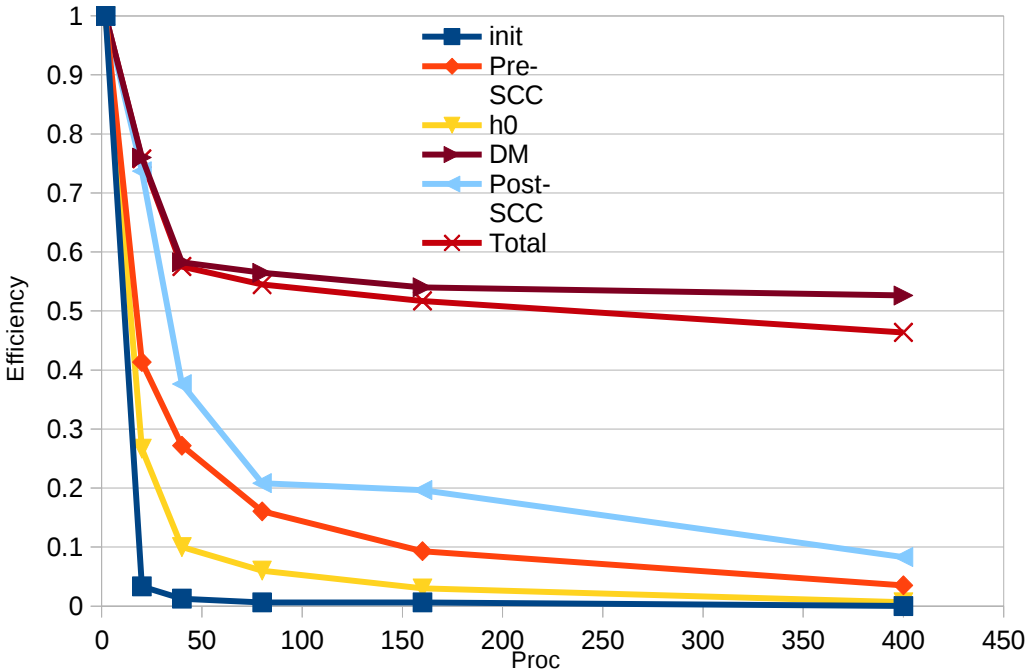

Xeon E5-2630

MolSSI/ELSI

# Speed-up and parallel efficiency

$Si_{2048}C_{2048}$ cubic cell, 4 SCC cycles + forces PEXSI



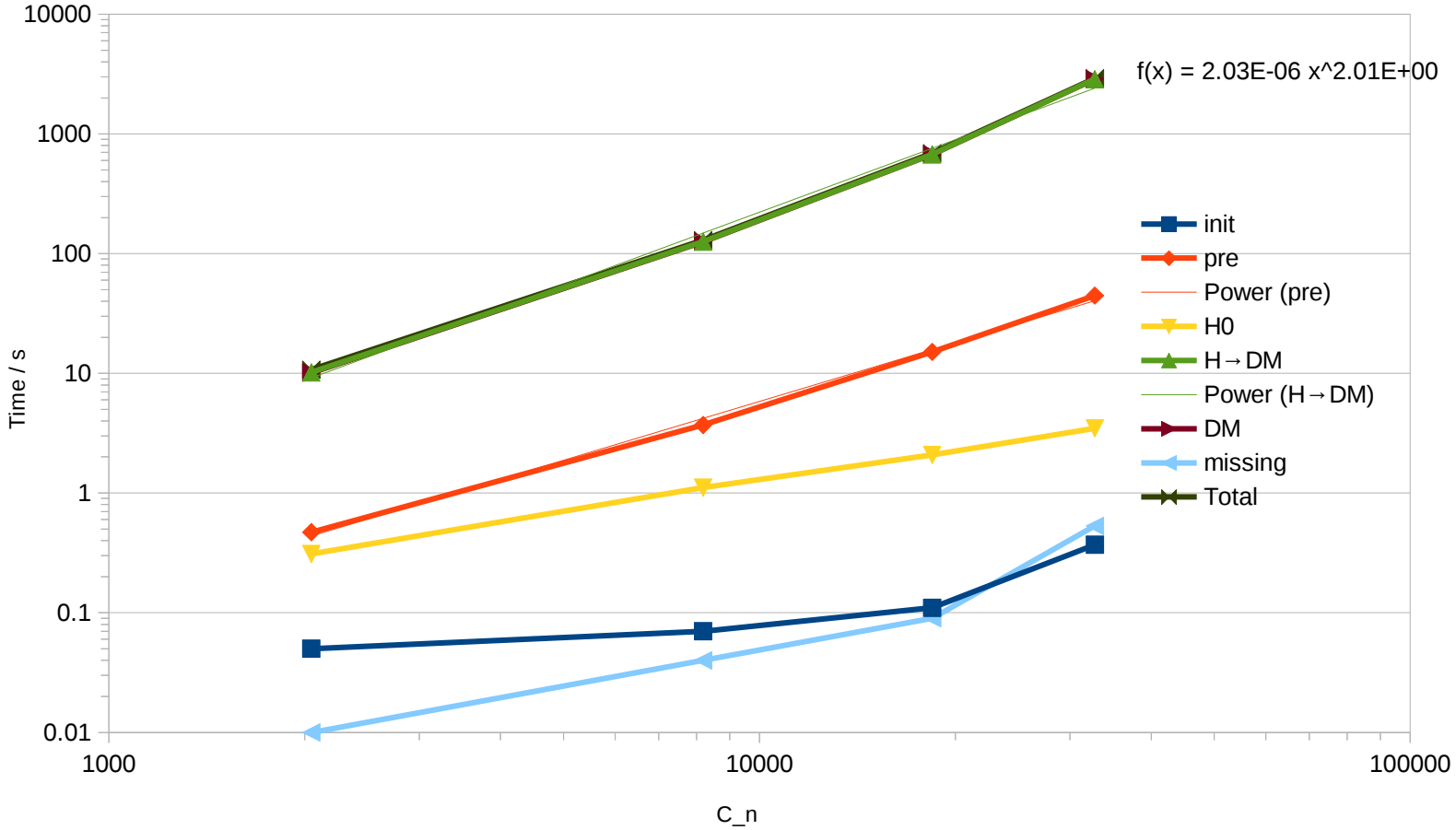

~94% parallel
– solver is  better than surrounding code but dominates total time
– not a surprise

- PEXSI is nested parallel over the poles (x20), then the matrix inversion for each pole
- solving inversion on 10 cores

> 45% efficient in this case up to 400 cores
Again the solver dominates and is better scaling than the rest of the code

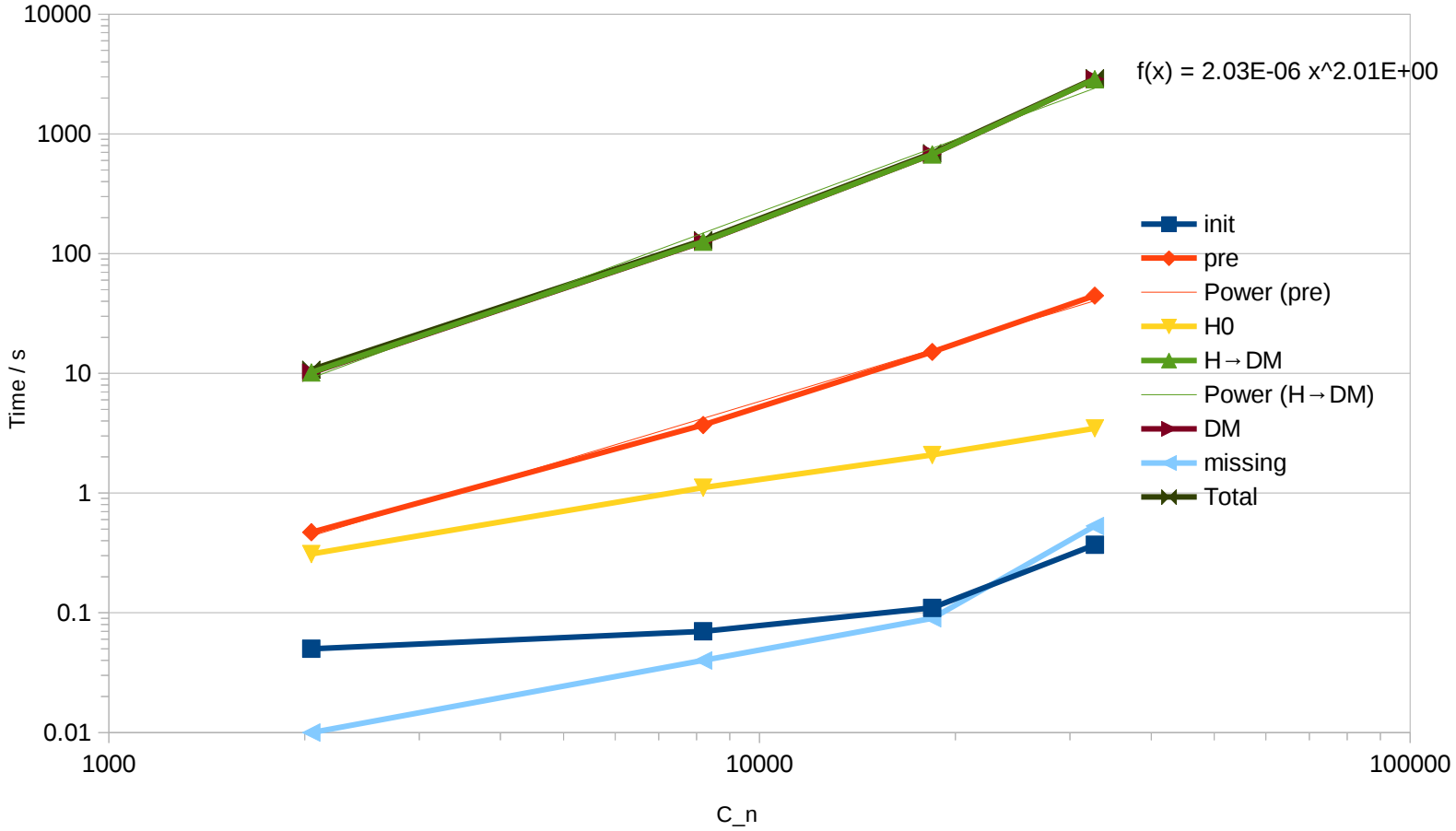
2 x Intel Xeon Gold 6138 20 core 2.0GHz CPU / Node (~ Skylake)

# 2D case – periodic graphene with PEXSI




2 x Intel Xeon Gold 6138 20 core 2.0GHz CPU / Node (~ Skylake)

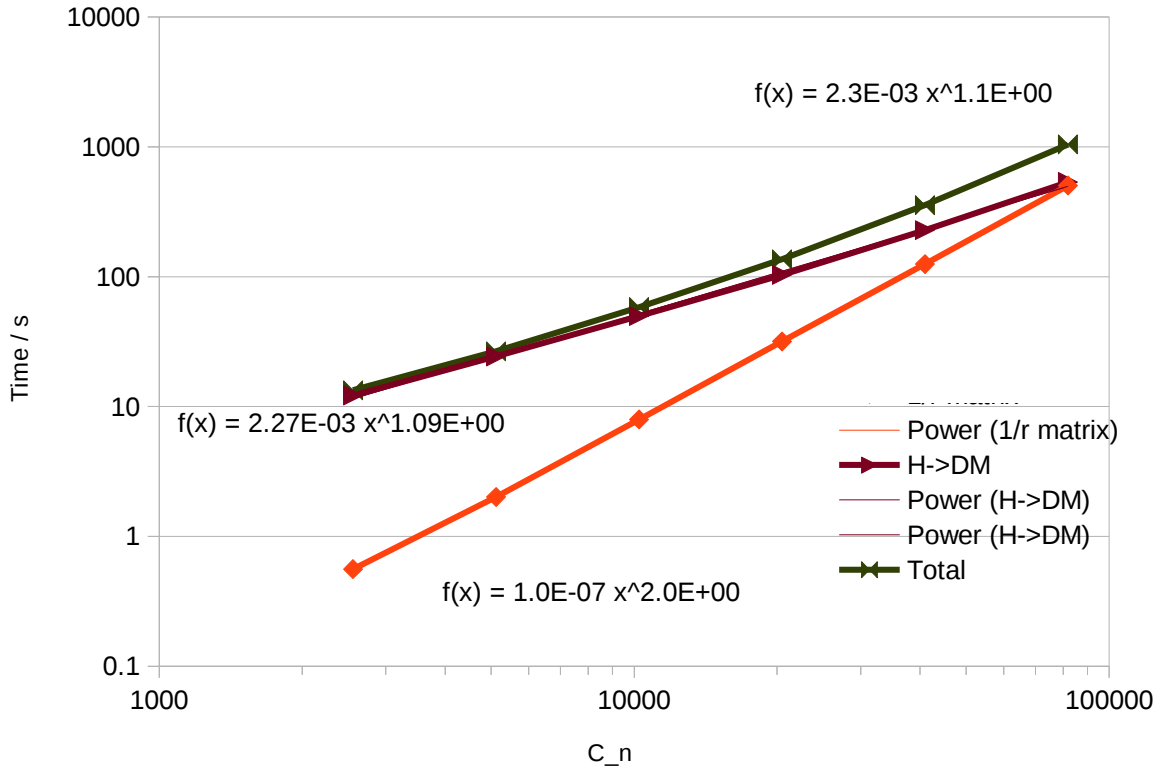
# 2D case – periodic graphene with PEXSI




Fill-in worse than expected – hoping for $O(N^{1.5})$, got $O(N^2)$

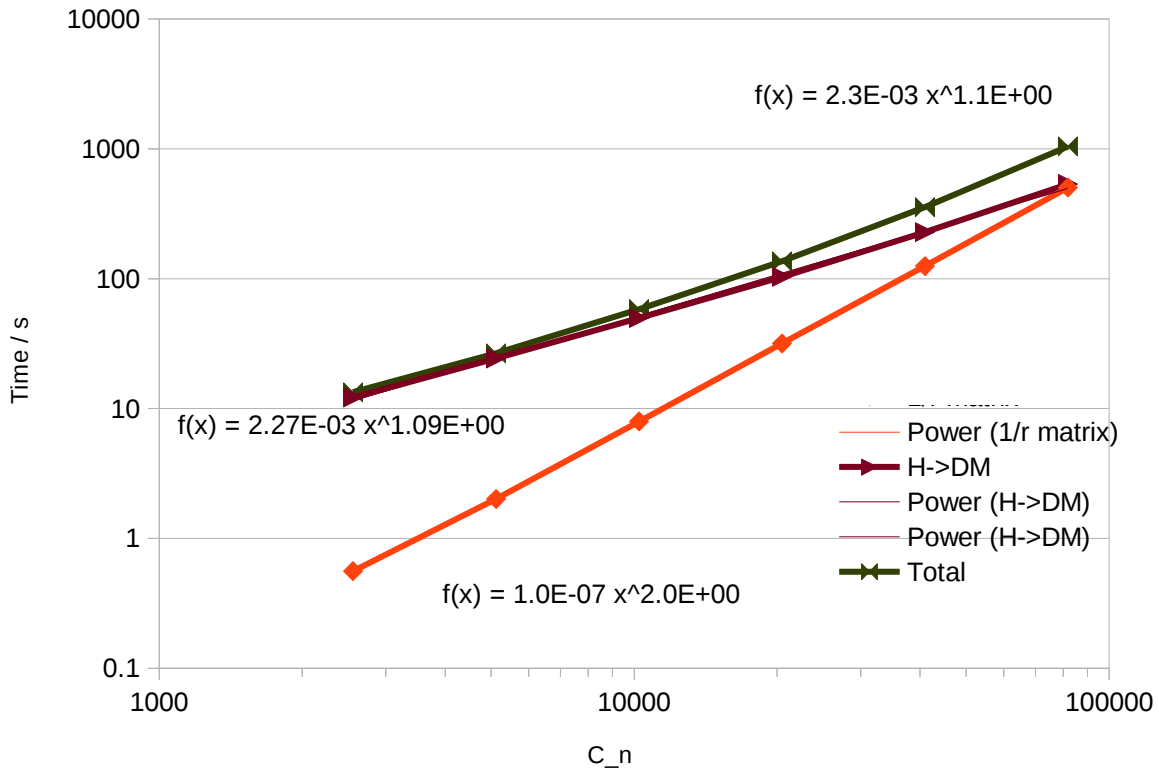
2 x Intel Xeon Gold 6138 20 core 2.0GHz CPU / Node (Broadwell)

# 1D case – 10,10 nanotube with PEXSI




CNT on 40 processors, 20 proc/pole
non-SCC energy + forces
8 proc./pole
Ifort 18.2 / MKL / ELSI
Skylake
192 GB RAM / node

# 1D case – 10,10 nanotube with PEXSI




CNT on 40 processors, 20 proc/pole
non-SCC energy + forces
8 proc./pole
Ifort 18.2 / MKL / ELSI
Skylake
192 GB RAM / node

Geometry and neighbour set-up

- electrostatics (if used) are similar costs (depends on periodic / molecular boundary)

# Interactions with the ELSI team

Definitely recommend working with ELSI

- Victor's Advice on DFTB+ ↔ CSC format
  - Contributed DFTB+ ↔ Siesta CSC code < 1 week
  - Also answered a lot of my stupid API questions
- Complex Hamitonians with PEXSI
  - Turns out transpose of DM was being returned
  - Lin fixed this within ~3 days
- ...

# Acknowledgements

The Volker and the ELSI team (special thanks to Victor Yu, Lin Lin and his group)

Thomas Frauenheim and the BCCMS Bremen group (Bálint Aradi, Christof Köhler,…)

Partly supported by:

EPSRC grant No. EP/P015719/1

EPSRC funded ARCHIE-WeSt High Performance Computer
( http://www.archie-west.ac.uk ), EPSRC grant No. EP/K000586/1.

This work was granted access to the HPC resources of SuperMUC made available within the Distributed European Computing Initiative by the PRACE-2IP, receiving funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement RI-283493.