DFTB+
The Fast Way of Doing Quantum Mechanics

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Bremen Center for Computational Materials Science

University of Bremen

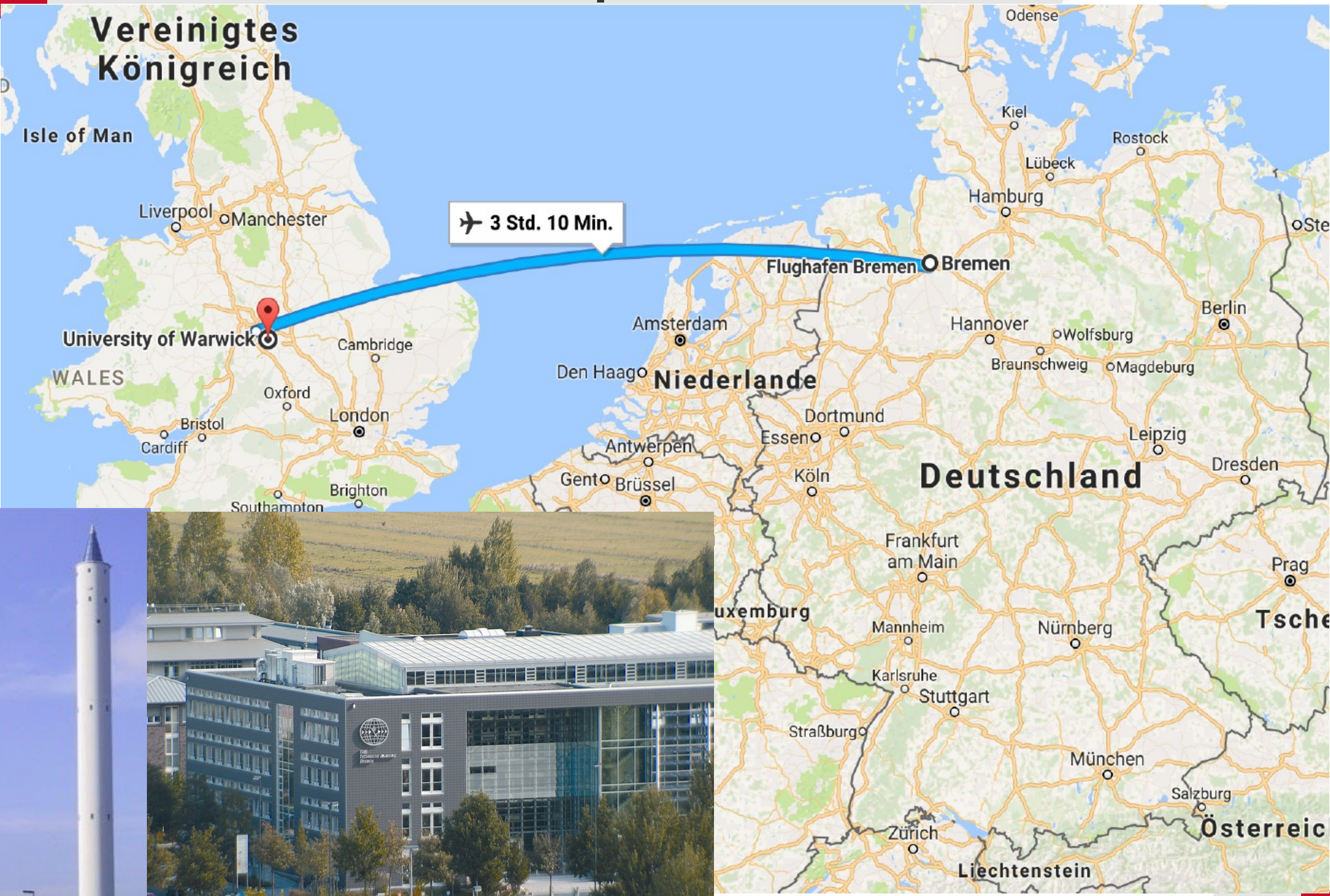
Scientific Computing Seminars

Warwick, 2017

Outline

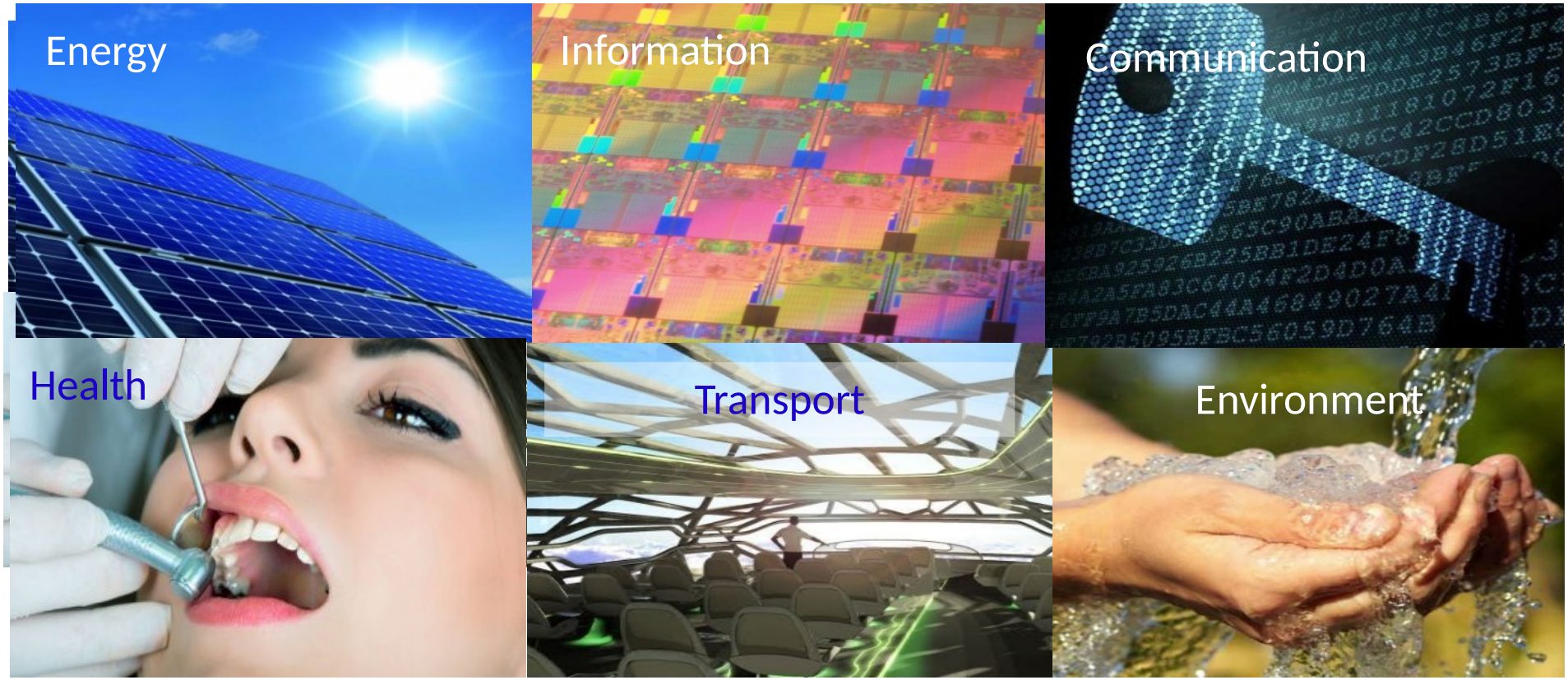
- Introduction
- DFTB-theory
- Parameterisation
- Extended Lagrangian Bohr-Oppenheimer molecular dynamics
- Basic Matrix Library

Bremen Center of Comp. Mat. Science



Mission of the BCCMS

Functional materials are the basis of key technologies



Atomic scale control requires **Quantum Mechanical Materials Modelling**

Research Training Group QM³ http://www.rtg-qm3.de/

Chairs in the BCCMS

Founding Chair - 2006
Computational Materials Science

Thomas Frauenheim

Vasily Ploshikhin

Conrad-Naber Endowed Chair - 2008
Hybrid Materials Interfaces

Lucio Colombi Ciacchi

Airbus Endowed Chair – 2009/2010
Integrative Materials and Process Simulation & Engineering

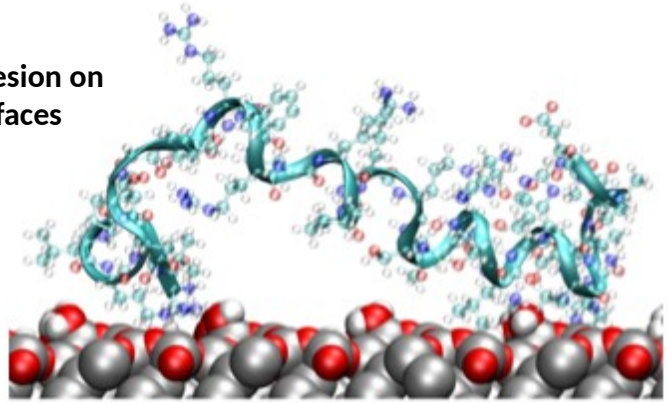
Tim Wehling

Electronic Structure and Correlated Nanosystems – ECN 2012

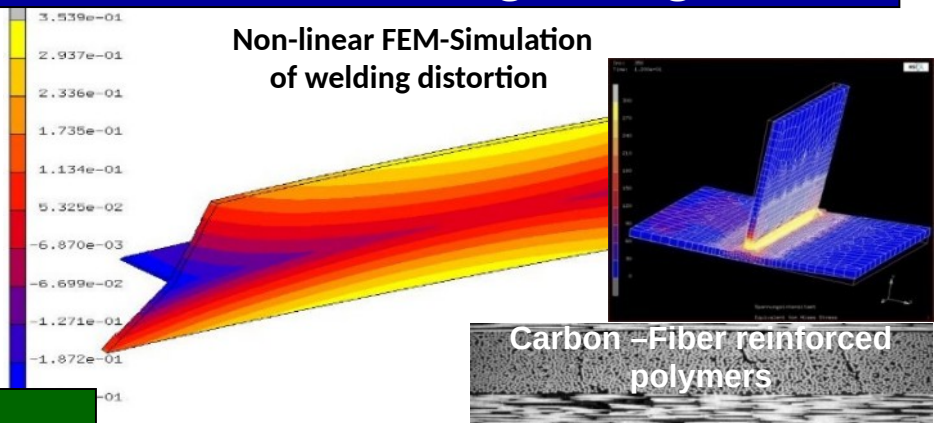
Research focus of the BCCMS

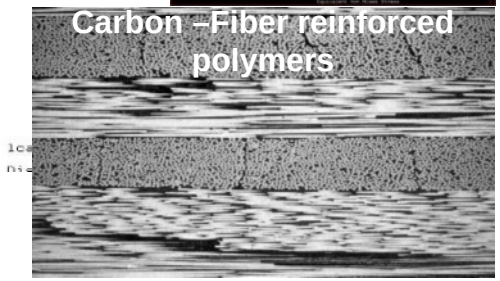
Integrative Materials and Process Simulation & Engineering

Collagen adhesion on silicon surfaces

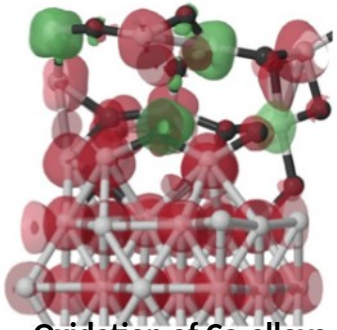


Non-linear FEM-Simulation of welding distortion

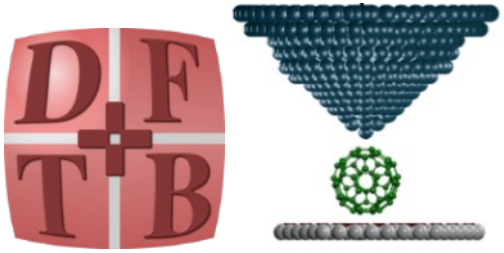




Hybrid Materials Interfaces

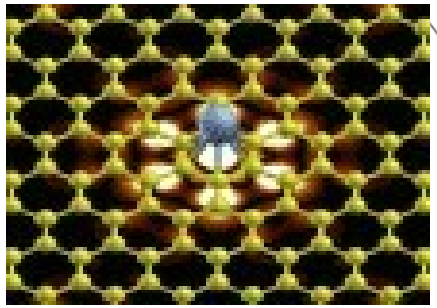


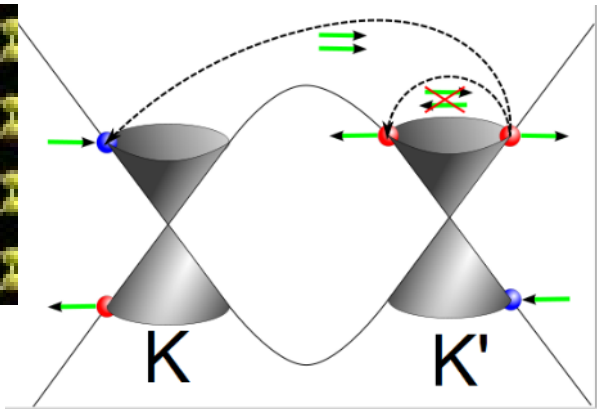
Oxidation of Co-alloys



Chemical reactive processes

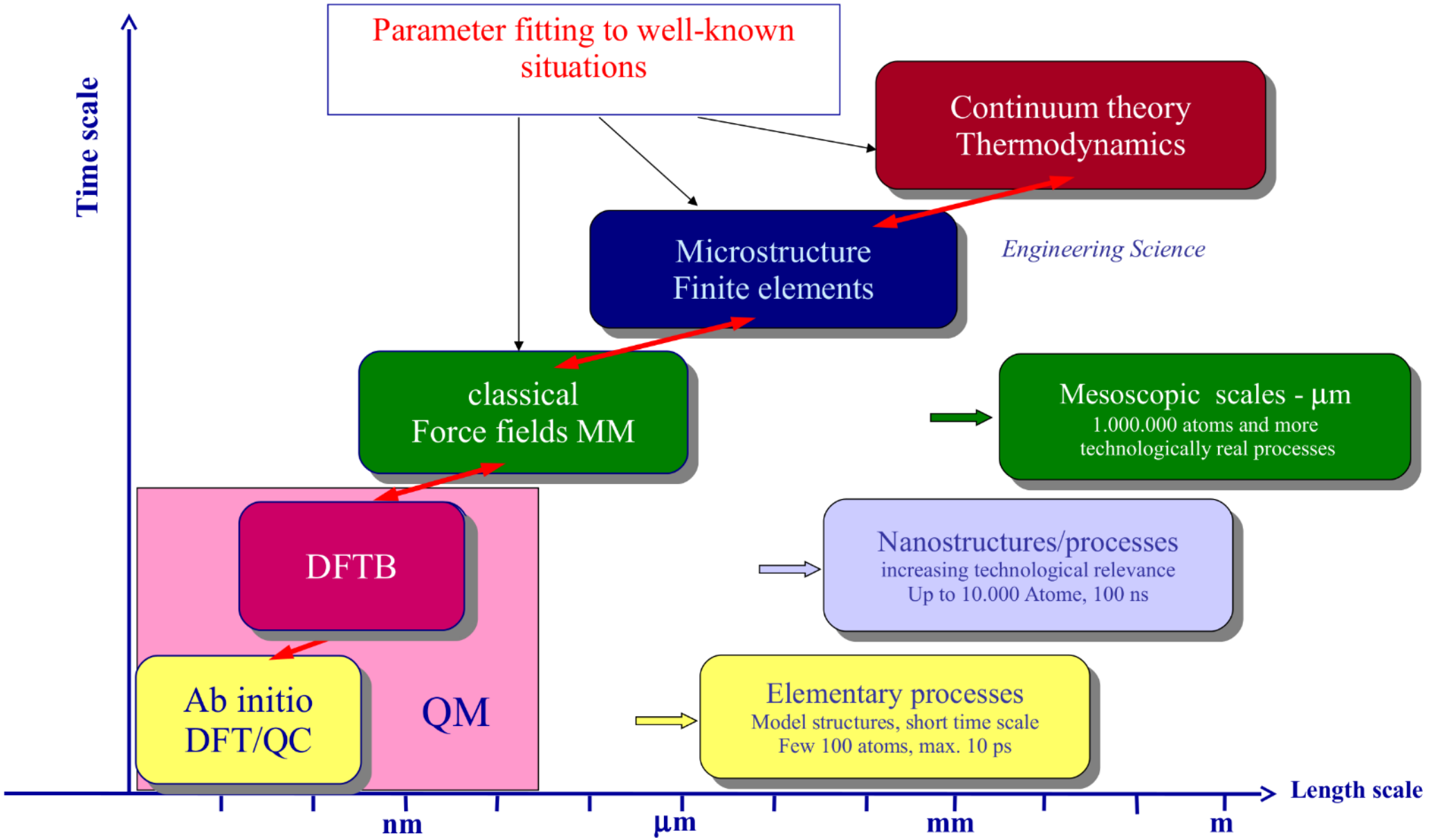
ES & Correlated Nanosystems





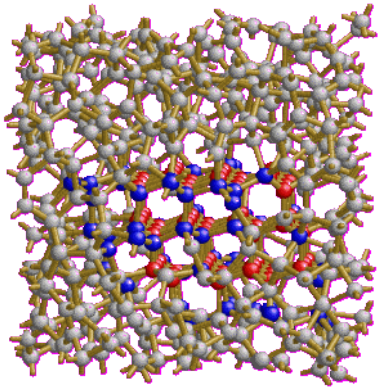
Computational Materials Science

DFTB in the method zoo

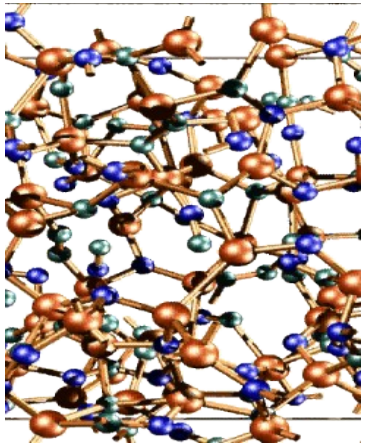


Approximate DFT for materials science

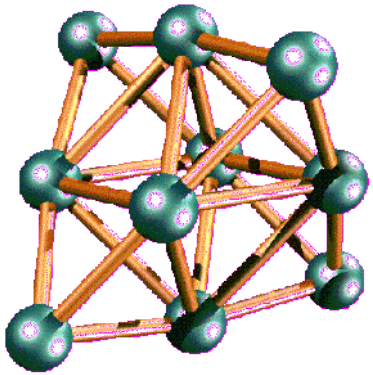
Diamond nucleation



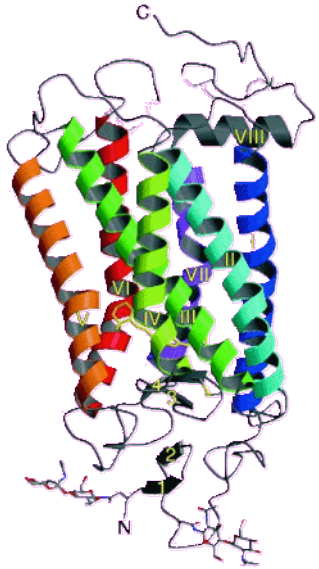
SiCN-ceramics



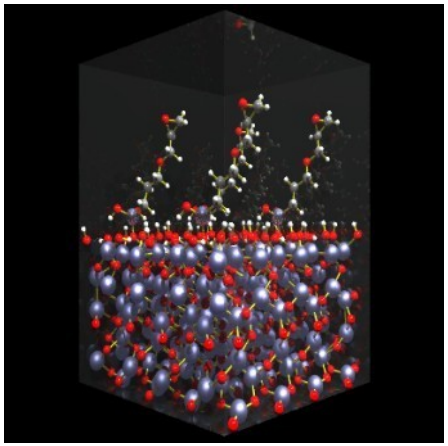
Si-cluster growth



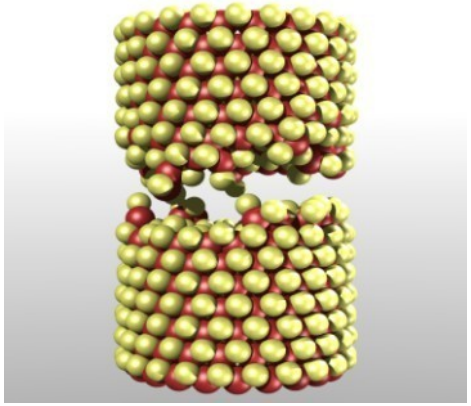
Retinal proteins



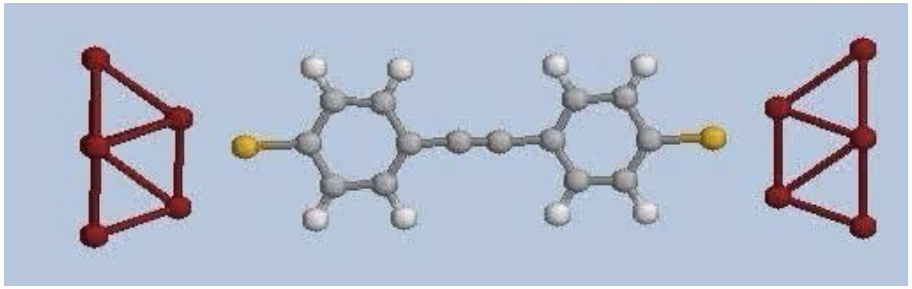
Hybrid interfaces



Inorganic nanotubes



Molecular electronics



From DFT to DFTB

- Density Functional Theory

$$E = E[n(\boldsymbol{r})]$$

- Kohn—Sham-picture

$$n(\boldsymbol{r}) = \sum_i f_i |\psi_i(\boldsymbol{r})|^2$$

- Foulkes—Haydock

$$n(\boldsymbol{r}) = n_0(\boldsymbol{r}) + \delta n(\boldsymbol{r})$$

- Expansion of total energy up to second (or third) order in the fluctuation

$$E_{\text{tot}}[n_0 + \delta n] = E_{\text{bs}}[n_0] + E_{\text{rep}}[n_0] + E_2[n_{0,} \delta n^2] + O(\delta n^3)$$

From DFT to DFTB

$$E_{bs}[n_0] = \sum_{i}^{occ} f_i \langle \psi_i | -\frac{\Delta}{2} + V_{eff}[n_0] | \psi_i \rangle$$

$$V_{eff}[n_0] = V_{ext} + \int' \frac{n_0(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{r}'|} + V_{xc}[n_0]$$

$$E_{rep}[n_0] = -\frac{1}{2} \int \int' \frac{n_0' n_0}{|\boldsymbol{r} - \boldsymbol{r}'|} + E_{xc}[n_0] - \int V_{xc}[n_0] n_0 + \frac{1}{2} \sum_{A} \sum_{B \neq A} \frac{Z_A Z_B}{R_{AB}}$$

Like KS-DFT, but depends only on reference density

$$E_2[n_0, \delta n] = \frac{1}{2} \int \int' \left(\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} + \frac{\delta^2 E_{xc}}{\delta n \delta n'} \bigg|_{n_0} \right) \delta n \delta n'$$

- Reference density = sum of compressed atomic densities
- E_{bs} and $E_2[n_0, \delta n]$ calculated explicitly (with approximations)
- E_{rep} fitted in order to correct errors due to approximations

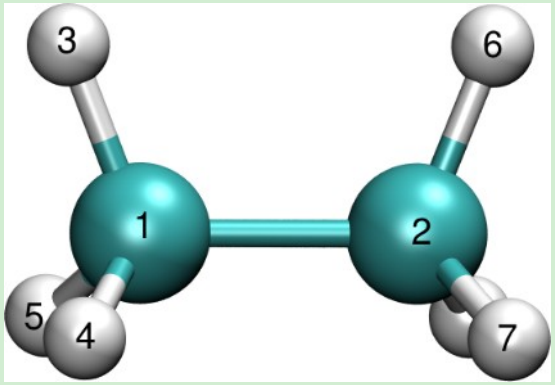
Repulsive energy

- Repulsive energy as superposition of pairwise interactions

$$E_{\text{rep}} = \frac{1}{2} \sum_{A} \sum_{B \neq A} E_{\text{rep}}^{AB}\left(|\boldsymbol{R}_A - \boldsymbol{R}_B|\right)$$

- Deviation from *ab initio* calculation tabulated as function of distance for every species pair in advance

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



$$\begin{aligned} E_{\text{rep}} = \quad & E_{\text{rep}}^{CC}\left(|\boldsymbol{R}_1 - \boldsymbol{R}_2|\right) + \ldots \\ & E_{\text{rep}}^{CH}\left(|\boldsymbol{R}_1 - \boldsymbol{R}_3|\right) + \ldots \\ & E_{\text{rep}}^{HH}\left(|\boldsymbol{R}_3 - \boldsymbol{R}_4|\right) + \ldots \end{aligned}$$

Band structure energy

- To be calculated

$$E_{\text{bs}} = \sum_i f_i \left\langle \psi_i \middle| -\frac{\Delta}{2} + V_{\text{eff}} \middle| \psi_i \right\rangle \qquad \text{with} \qquad \left[H + V_{\text{eff}} \right] \psi_i = \varepsilon_i \psi_i$$

- LCAO-Ansatz (usually with minimal basis)

$$\psi_i = \sum_\mu c_{i\mu} \phi_\mu \left(\boldsymbol{r} - \boldsymbol{R}_{A(\mu)} \right) \longrightarrow \sum_\nu \left(H_{\mu\nu} - \varepsilon_i S_{\mu\nu} \right) = 0$$

$$H_{\mu\nu} = \left\langle \phi_\mu \middle| H \middle| \phi_\nu \right\rangle \qquad S_{\mu\nu} = \left\langle \phi_\mu \middle| \phi_\nu \right\rangle$$

- Potential as sum of atomic contributions

$$V_{\text{eff}}[n_0] = \sum_A V_{\text{eff}}[n_0^A] = \sum_A V_{\text{eff}}^A$$

Band structure energy

- Neglecting crystal field and three center terms

$$H_{\mu_A \nu_A} = \left\langle \phi_\mu \left| -\frac{\Delta}{2} + V^A_{\text{eff}} \right| \phi_\nu \right\rangle + \sum_{B \neq A} \left\langle \phi_\mu \left| V^B_{\text{eff}} \right| \phi_\nu \right\rangle$$

$$H_{\mu_A \nu_B} = \left\langle \phi_\mu \left| -\frac{\Delta}{2} + V^A_{\text{eff}} + V^B_{\text{eff}} \right| \phi_\nu \right\rangle + \sum_{C \neq A \neq B} \left\langle \phi_\mu \left| V^B_{\text{eff}} \right| \phi_\nu \right\rangle$$

- On-site elements = free atom eigenvalues

$$H_{\mu_A \nu_A} = \varepsilon_\mu \delta_{\mu\nu} \longrightarrow \text{correct dissociation limit}$$

- Potential superposition versus density superposition

$$V_{\text{eff}}[n_0^A] + V_{\text{eff}}[n_0^B] \longleftrightarrow V_{\text{eff}}[n_0^A + n_0^B]$$

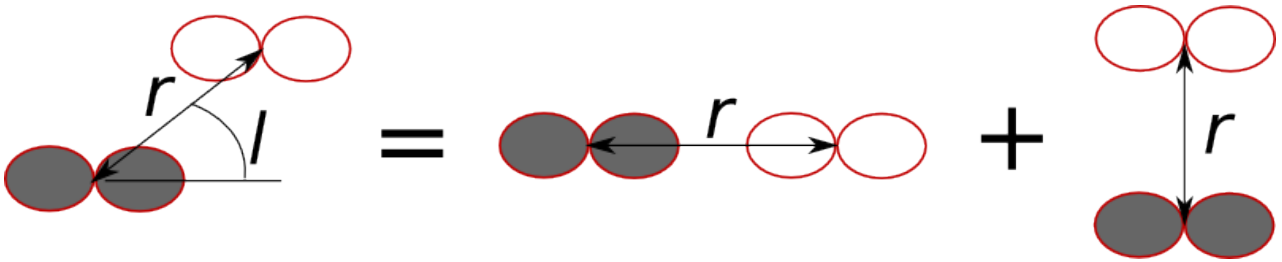
Band structure energy

- Final Hamiltonian

$$H_{\mu_A \nu_A} = \varepsilon_\mu \delta_{\mu\nu}$$

$$H_{\mu_A \nu_B} = \left\langle \phi_\mu \left| -\frac{\Delta}{2} + V_{\text{eff}}\left[n_0^A + n_0^B\right] \right| \phi_\nu \right\rangle$$

- Can be tabulated as function of distance for every species pair in advance



$$H_{p_x p_x}(l, r) = l^2 H_{pp}^{\sigma}(r) + (1 - l^2) H_{pp}^{\pi}(r)$$

Non-SCC DFTB Workflow

Input

- Geometry
- Tabulated *H* and *S*
- Tabulated E_{rep}

Calculation

- Table lookup for H and S
- Diagonalisation
- Table lookup for E_{rep}

Output

- Energy, forces
- Band structure
- Eigenvectors, density
- :

Charge transfer between atoms not considered yet

Describing charge transfer (SCC-DFTB)

- To be calculated

$$E_2 = \frac{1}{2}\int\int' \left(\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + \left.\frac{\delta^2 E_{\mathrm{xc}}}{\delta n(\boldsymbol{r})\delta n(\boldsymbol{r}')}\right|_{n=n_0} \right) \delta n(\boldsymbol{r})\delta n(\boldsymbol{r}')$$

- Density fluctuation = sum of atomic contributions

$$\delta n(\boldsymbol{r}) = \sum_A \delta n_A(\boldsymbol{r})$$

$$E_2 = \frac{1}{2}\sum_A \sum_B \int\int f^{\mathrm{hxc}}(\boldsymbol{r},\boldsymbol{r}')\delta n_A(\boldsymbol{r})\delta n_B(\boldsymbol{r}')$$

- Atomic charge fluctuation should be a charge monopole

$$\delta n_A(\boldsymbol{r}) = \Delta q_A f(r) \longrightarrow E_2 = \frac{1}{2}\sum_A \sum_B \gamma_{AB}\Delta q_A \Delta q_B$$

Describing charge transfer (SCC-DFTB)

- Monopole charges calculated in Mulliken-approximation

$$q_A = \frac{1}{2} \sum_{\mu \in A} \sum_{\nu} \left(P_{\mu\nu} S_{\nu\mu} + S_{\mu\nu} P_{\nu\mu} \right) \qquad P_{\mu\nu} \sum_i f_i c_{i\mu} c_{i\nu}^*$$

- Hamiltonian depends on the solution (wave function coefficients)

$$H_{\mu_A \nu_B} = \frac{1}{2} S_{\mu_A \nu_B} \sum_C \left(\gamma_{AC} + \gamma_{BC} \right) \Delta q_C$$

- Charges iterated until self consistency has been reached

$$q_A^{(0)} \rightarrow H_{\mu\nu}^{(0)} \rightarrow c_{i\mu}^{(1)} \rightarrow q_A^{(1)} \rightarrow H_{\mu\nu}^{(1)} \rightarrow c_{i\mu}^{(1)} \rightarrow \ldots \rightarrow$$

SCC iteration

Problem: Some (e.g. X—H interactions) overestimated

Describing spin polarization

- Fluctuation in the magnetization in monopole approximation

$$E_{\delta m} = \frac{1}{2} \sum_{A} \sum_{l \in A} \sum_{l' \in A} p_{Al}\, p_{Al'}\, W_{All'} \qquad p_{Al} = q_{Al}^{\text{up}} - q_{Al}^{\text{down}}$$

$$H^{\sigma}_{\mu_{Al}\, \nu_{Bk}} = \frac{1}{2} \left(\sum_{m \in A} W_{Alm}\, p_{Am} + \sum_{m \in B} W_{Bkm}\, p_{Bm} \right)$$

- Spin coupling constants couple magnetizations on the same atom only
- Spin coupling constants from *ab initio* atom calculations (no adjustable parameters)

$$W_{Alm} = \frac{1}{2} \left(\frac{\partial\, \varepsilon_l^{\text{up}}}{\partial\, f_m^{\text{up}}} - \frac{\partial\, \varepsilon_l^{\text{up}}}{\partial\, f_m^{\text{down}}} \right)$$

- Have been also extended to non-colinear spin

3rd order expansion in density (DFTB3)

- Third order expansion in the density

$$E_3[n_0,\delta n]=\frac{1}{6}\int''\int'\int \left.\frac{\delta^3 E_{xc}[n]}{\delta n\delta n'\delta n''}\right|_{n_0,n_0',n_0''}\delta n\delta n'\delta n''$$

$$E_3\approx\frac{1}{2}\sum_A\sum_B \Delta q_A^2\Delta q_b\Gamma_{AB} \qquad \Gamma_{AB}=\left.\frac{\partial\gamma_{AB}}{\partial q_A}\right|_{q_A^0}$$

- Damping of the electrostatic interaction for hydrogen

$$\gamma_{AB}=\frac{1}{R_{AB}}-F(R_{AB},U_A,U_B)h(R_{AB},U_A,U_B)$$

$$h_{AB}=\exp\left[-\left(\frac{U_A+U_B}{2}\right)^{\zeta}R_{AB}^2\right]$$

- Improved geometries and binding properties for biological molecules

M. Gauss et al, J. Chem. Theory Comput. **7,** 931 (2011)

Going beyond monopole approximation

- Traditional SCC model

$$E_2 = \frac{1}{2} \sum_A \sum_{B \neq A} \gamma_{AB} \delta q_A \delta q_B$$

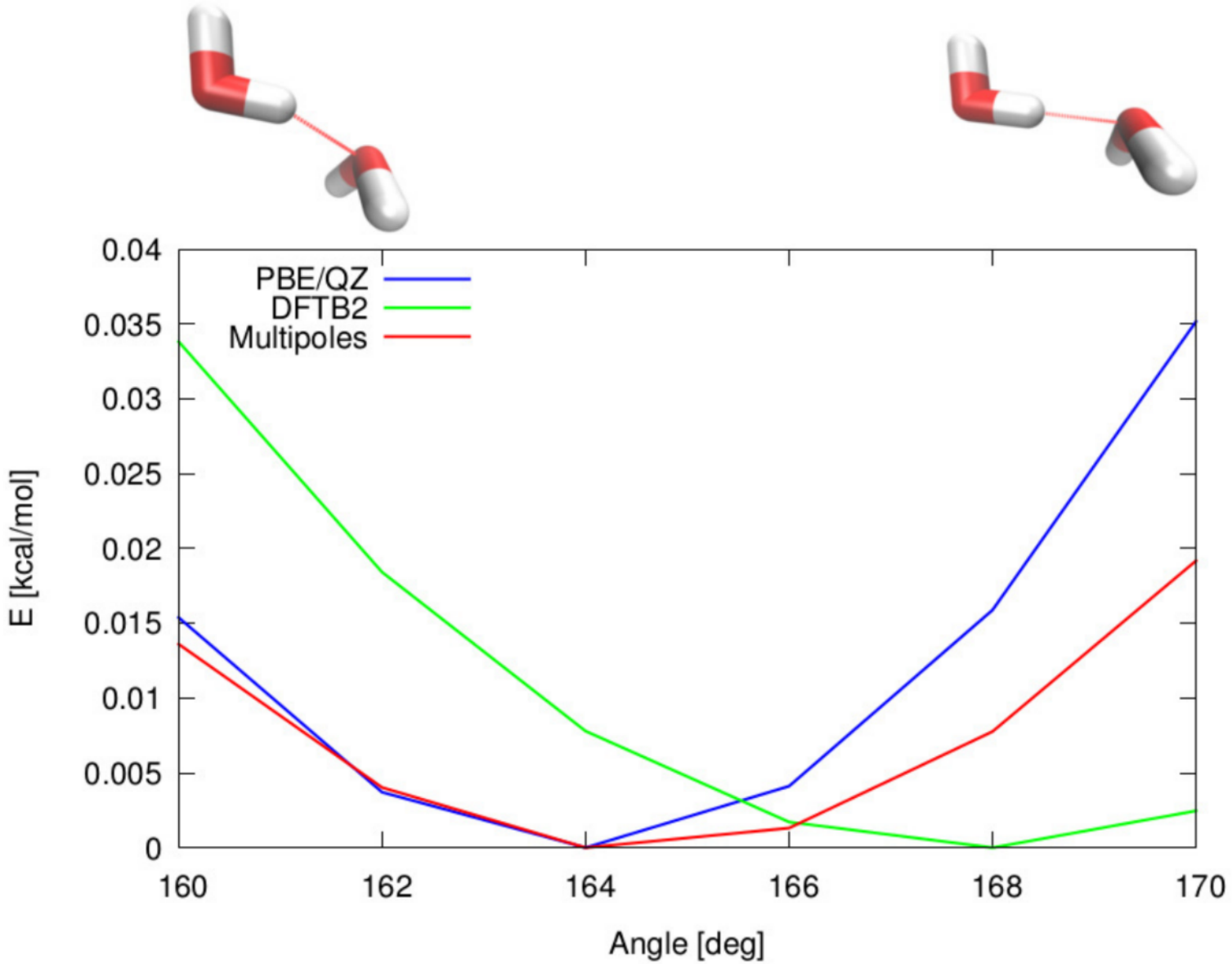
- Expansion up to higher moments

$$E_{\text{multi}} = \frac{1}{2} \sum_{A,B} \left[\gamma_{AB}^{(00)} \Delta q_A \Delta q_B + \gamma_{AB}^{(10)} \Delta \boldsymbol{d}_A \Delta q_B + \gamma_{AB}^{(01)} \Delta q_A \Delta \boldsymbol{d}_B + \gamma_{AB}^{(11)} \Delta \boldsymbol{d}_A \circ \Delta \boldsymbol{d}_B + \gamma_{AB}^{(20)} \Delta Q_A \Delta q_B + \gamma_{AB}^{(02)} \Delta q_A \Delta Q_B + \ldots \right]$$

- First and second order contains:
  - Monopole-dipole interaction
  - Dipole-dipole and monopole-quadrupole interaction
- Improves electrostatic interaction between atoms

Multipoles – first benchmarks

- Water dimer angle scan, varying intermolelucar angle without molecule distortion (no repulsive contribution)



Extending DFTB

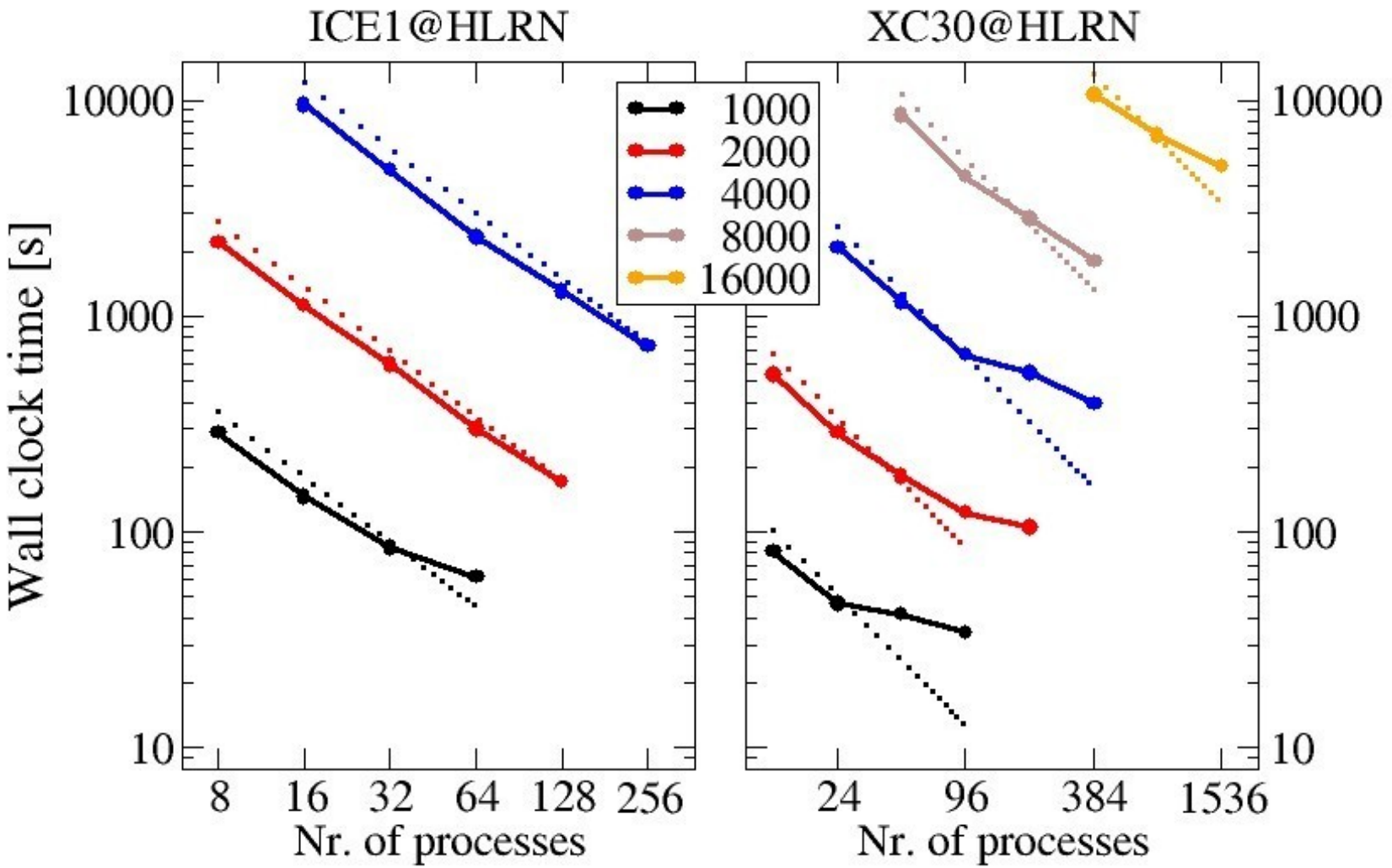
- DFTB = Approximated DFT
- Extensions of DFT can be usually carried over to DFTB
- Several extensions already available (e.g. in DFTB+)
  - Linear response TD-DFT (Casida-formulation)
  - Electron transport via Greens function formalism
  - Range separated xc-functionals
  - (GW)
  - :

When porting a DFT-feature to DFTB

- Is accuracy of DFTB enough
- Is the computational effort justifiable (e.g. can integral evaluation at run-time avoided)

Performance of DFTB+ (dense diag.)

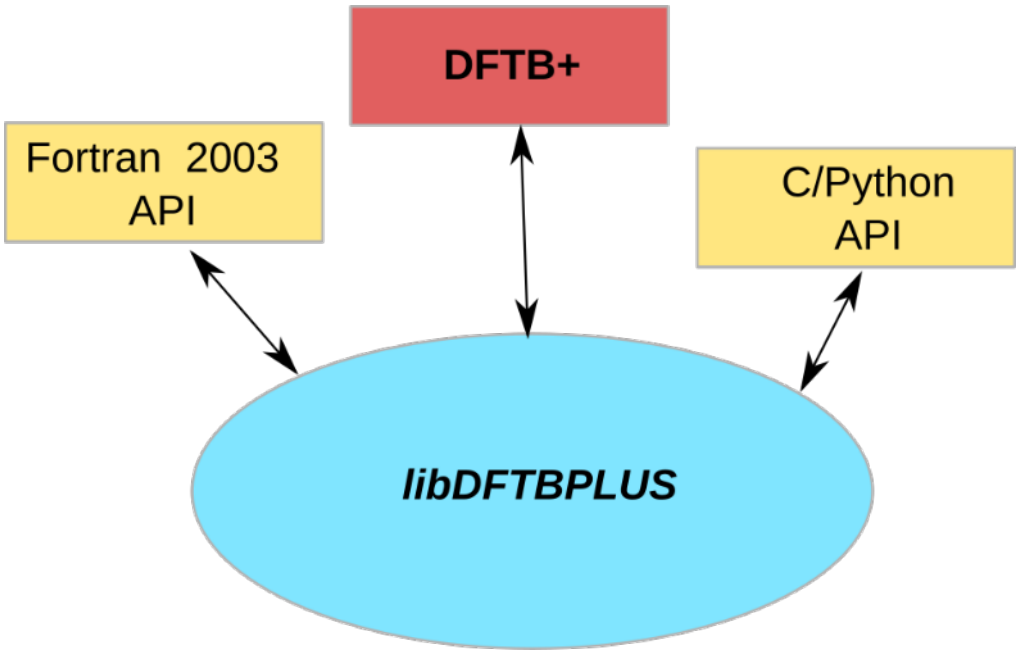
One total energy calculation (11 SCC) + force



www.dftbplus.org

libDFTB+

- Separate core DFTB-functionality into a standalone library
- Two level API
  - Full (black box) DFTB-calculator (QM/MM codes)
    Currently being integrated into CHARMM, Gromacs, Amber
  - Low-leve API, e.g. Hamiltonian element generator (for QM codes)
- Permissive **L-GPL** license (non-commercial/commercial usage possible)



www.dftbplus.org

github.com/dftbplus

Bottlenecks in DFTB

Creating parameters

- Number of repulsives goes with N_{TYPE}^{2}
- Various “automatic” fitting techniques
- Creating repulsive from atomic parameters

Electrostatics

- Currently conventional Ewald-summation: O(N^2)
- Could be replace with particle mesh Ewald or fast multipole: N log(N)

Solving the generalised eigenvalue problem

- Currently via LAPACK / ScaLAPACK: O(N^3)
- Various approximative techniques as in DFT can reach O(N)

Self-consistency iterations

- Constant prefactor of about 10 during MD simulation
- Extended Born-Oppenheimer Lagrangian can make it superfluous

Parameterization

- Electronic parameters
- Repulsive term

Electronic parameters

- To be calculated

$$H^0_{\mu_A \nu_B} = \left\langle \phi_{\mu_A} \left| -\frac{1}{2}\Delta + V_{\text{eff}}\left[n_0^A + n_0^B\right] \right| \phi_{\nu_B} \right\rangle$$

compressed wave functions compressed densities

- Free isolated atom with compression potential

$$\left[-\frac{1}{2}\Delta + V_{\text{A}} + \left(\frac{r}{r_A}\right)^n \right] \psi_i^A(\boldsymbol{r}) = E_i^A \, \psi_i^A(\boldsymbol{r})$$

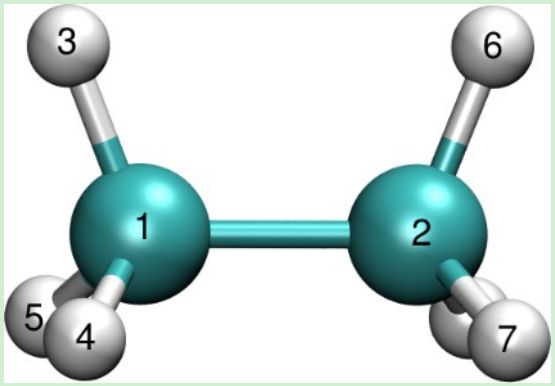
- Two types of compression radii for every species
  - Density compression $r^{\text{d}}_A,\ r^{\text{d}}_B, \ldots$
  - Wave function compression $r^{\text{w}}_{A,l},\ r^{\text{w}}_{A,l'},\ \ldots,\ r^{\text{w}}_{B,l},\ r^{\text{w}}_{B,l'},\ \ldots$

- Sanity check: Band structure

Repulsive term

- To be calculated

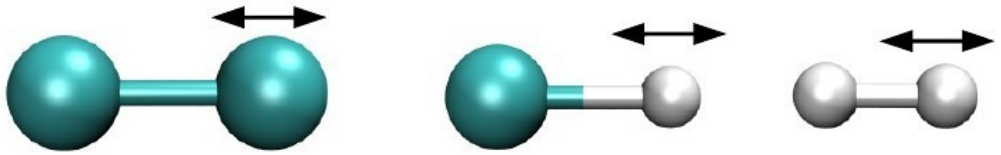
$$E_{\text{rep}} = \frac{1}{2} \sum_{A} \sum_{B \neq A} E_{\text{rep}}^{AB}\left(|\boldsymbol{R}_A - \boldsymbol{R}_B|\right)$$



$$\begin{aligned} E_{\text{rep}} = \quad & E_{\text{rep}}^{CC}\left(|\boldsymbol{R}_1 - \boldsymbol{R}_2|\right) + \ldots \\ & E_{\text{rep}}^{CH}\left(|\boldsymbol{R}_1 - \boldsymbol{R}_3|\right) + \ldots \\ & E_{\text{rep}}^{HH}\left(|\boldsymbol{R}_3 - \boldsymbol{R}_4|\right) + \ldots \end{aligned}$$

- Individual repulsive interaction for each dimer interaction

$$E_{\text{rep}}^{AB}(R_{AB}) = E_{\text{ab}\,initio}(R_{AB}) - \left[E_{\text{bs}} + E_2 + E_{\delta m} + \ldots\right](R_{AB})$$



Repulsive term

Fitting difficulties

- Choosing right fit system(s)
- Choosing right test systems, evaluting quality of parametrization
- Nr. of interactions to fit increases quadratically with number of elements

Automated fitting frameworks available

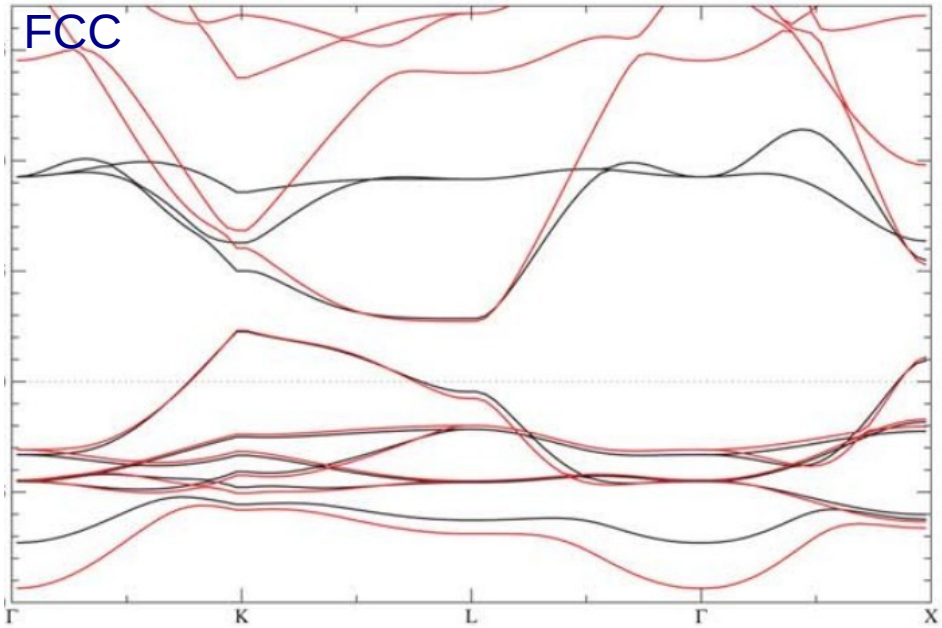
- **ADPT**: Chien-Pin Chou, Henryk Witek and colaborators
  https://bitbucket.org/solccp/adpt_core
- **SKOPT**: Stanislav Markov in colaboration with BCCMS
  https://bitbucket.org/stanmarkov/skopt

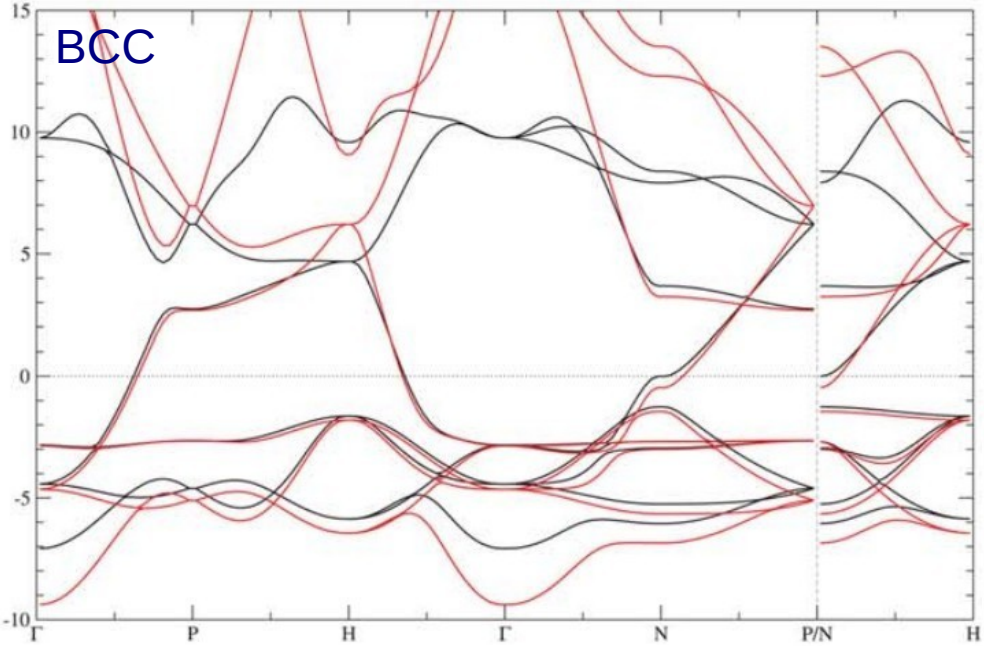
Alternative approach: Pairwise repulsive from (fitted) atomic parameters

- Theoretically, entire periodic table can be “easily” covered
- Quality usually lower than specially tuned sets

Parameters for Au-thiolates compounds

Au-Au bulk phases





	$E_{formation}$ (eV)		d (Å)	
Phase	PWs-DFT	DFTB	PWs-DFT	DFTB
FCC	0 by definition		2.936	2.887
BCC	+0.012	+0.023	2.854	2.819
A15	+0.127	+0.147	2.645–3.240	2.618–3.207
SC	+0.178	+0.051	2.740	2.695
Diamond	+0.710	+0.397	2.663	2.627

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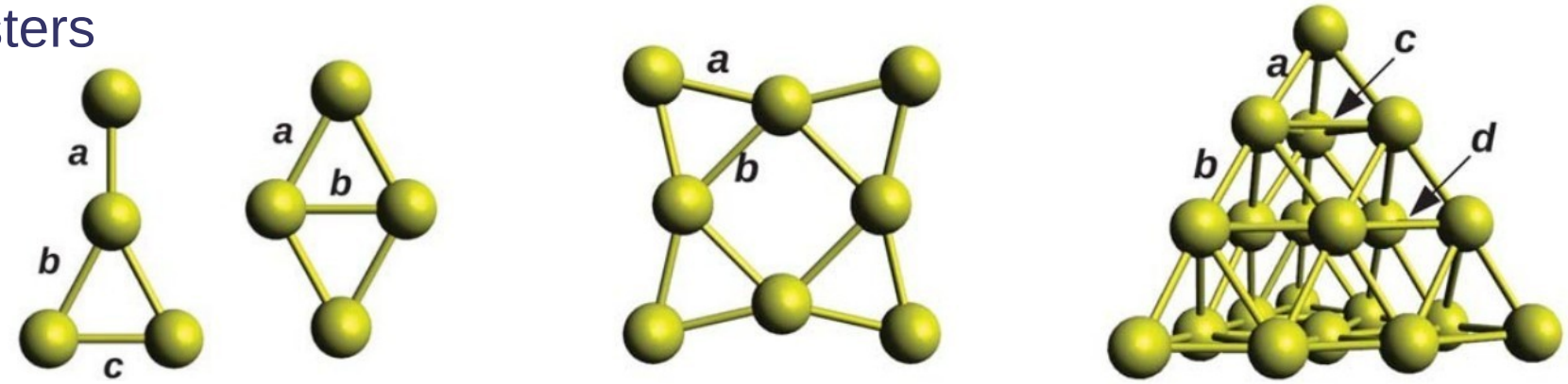
Parameters for Au-thiolates compounds

Au clusters



	Au_2	Au_{4a}	Au_{4b}	Au_8	Au_{20}
Au–Au (Å), DFT	2.54	a: 2.55 b: 2.71 c: 2.61	a: 2.71 b: 2.65	a: 2.65 b: 2.78	a: 2.73 b: 2.69 c: 2.96 d: 2.83
Au–Au (Å), DFTB	2.53	a: 2.54 b: 2.59 c: 2.57	a: 2.59 b: 2.59	a: 2.58 b: 2.66	a: 2.60 b: 2.65 c: 2.73 d: 2.69
HLG (eV), DFT	2.01	0.95	0.99	1.46	1.76
HLG (eV), DFTB	2.05	1.08	0.82	1.20	1.96
$E_{formation}$ (eV), DFT	−1.11	−1.45	−1.47	−1.91	−2.25
$E_{formation}$ (eV), DFTB	−1.42	−1.94	−2.00	−2.49	−2.97
$E_{formation}$ (eV), exp	−1.10[67], −1.15[68]				

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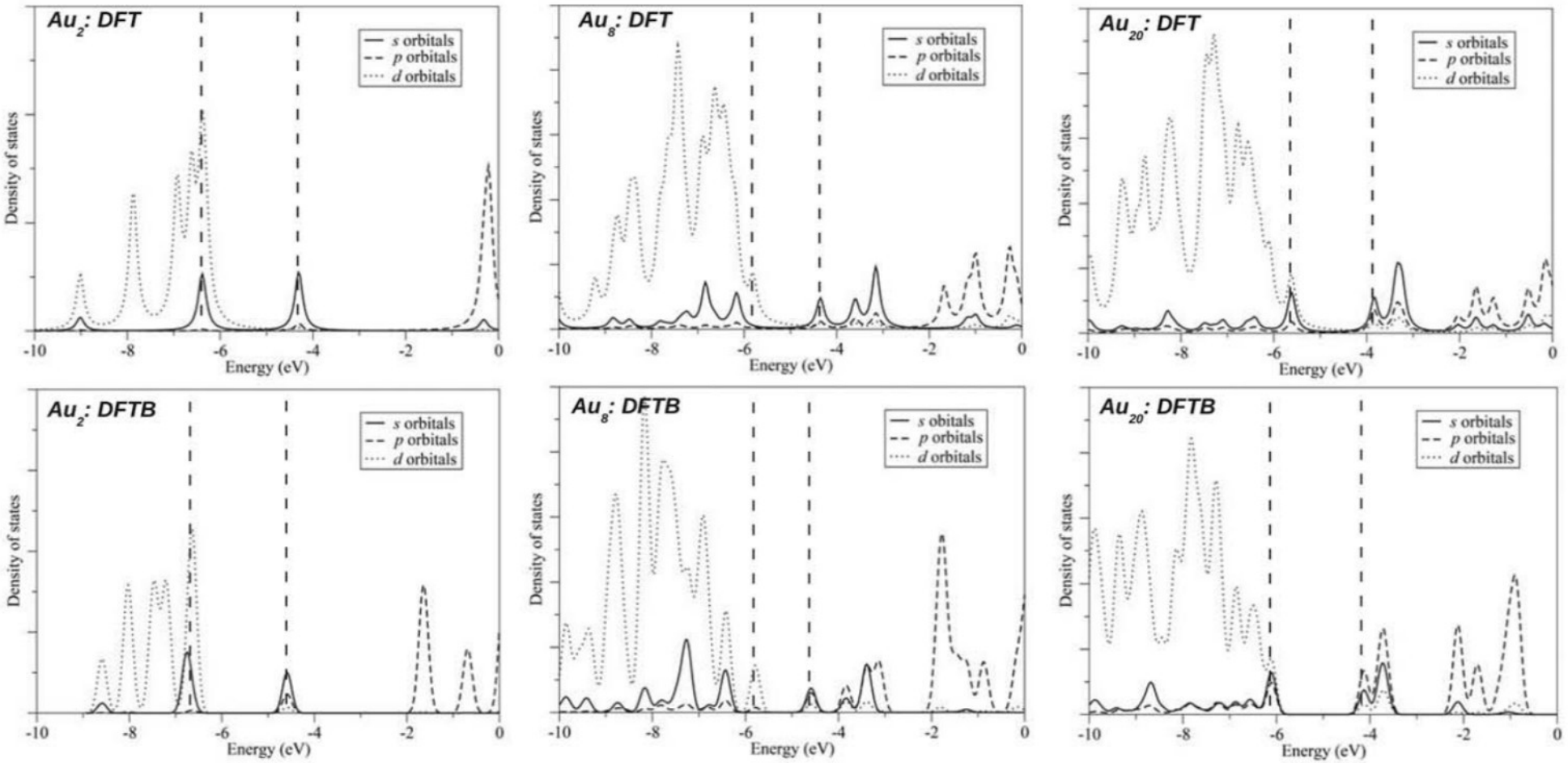
Parameters for Au-thiolates compounds

PDOS



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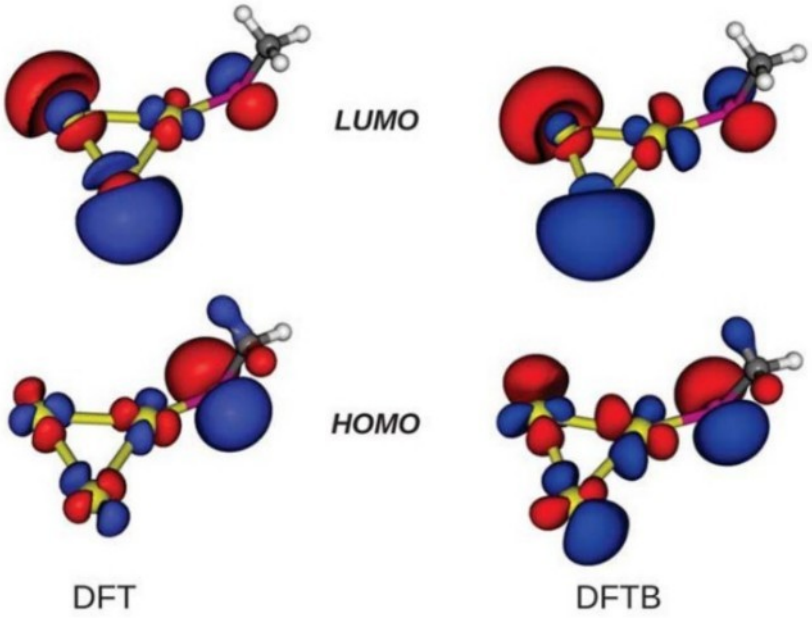
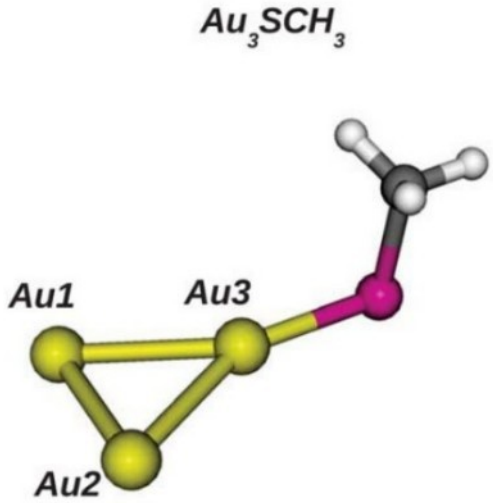
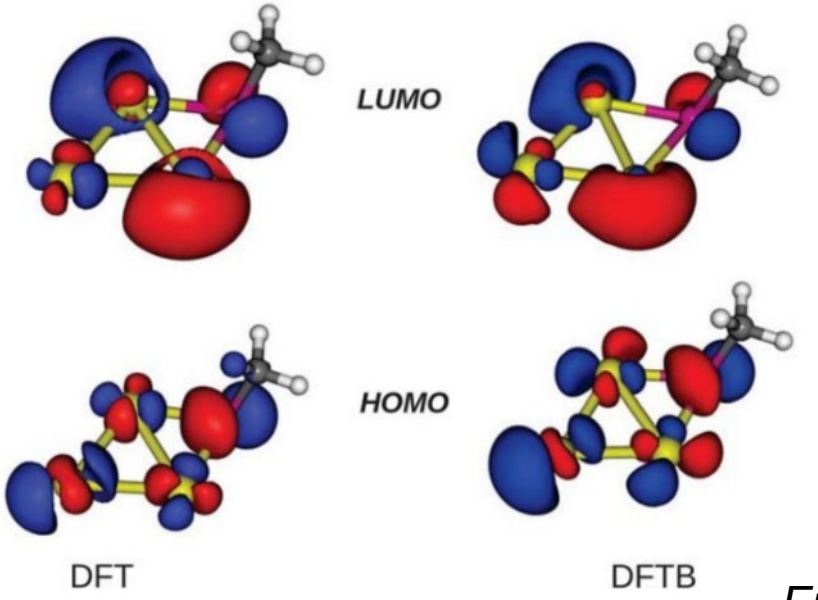
Parameters for Au-thiolates compounds

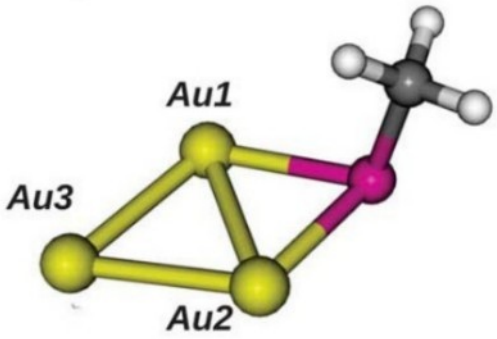
Frontier orbitals





Top conformation





Bridge conformation

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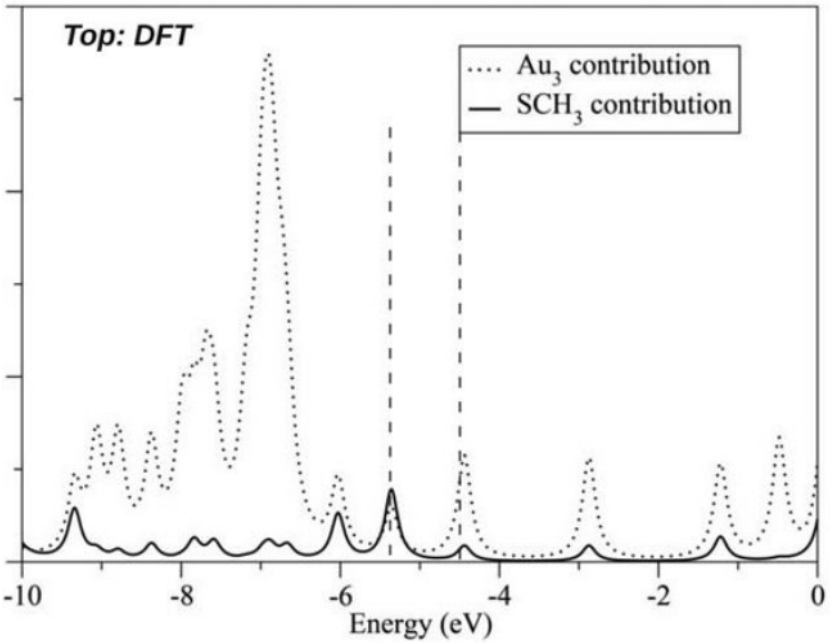
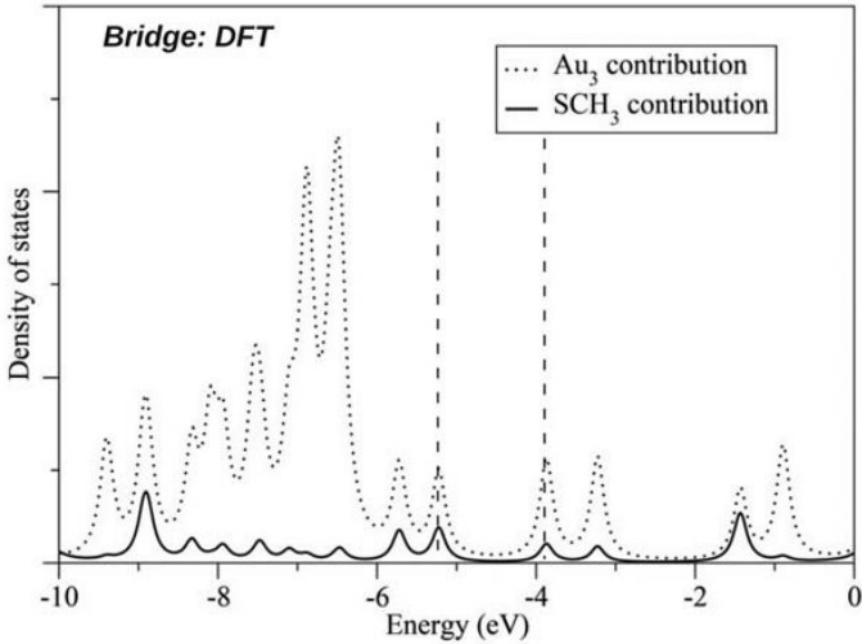
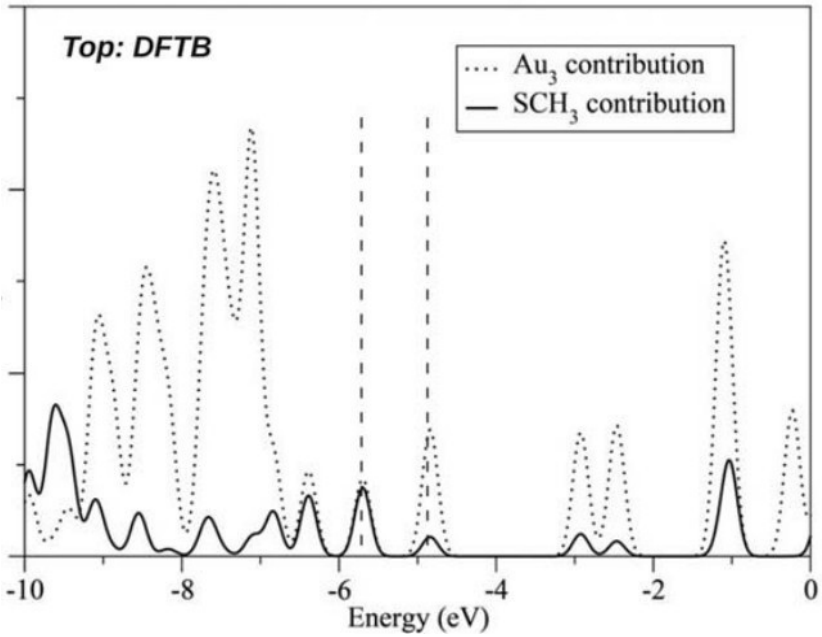
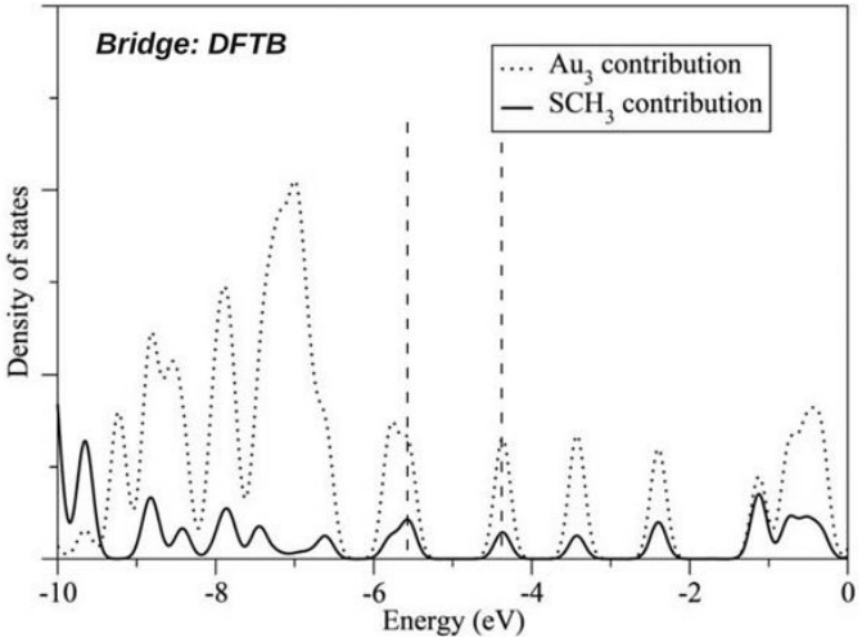
Parameters for Au-thiolates compounds

PDOS









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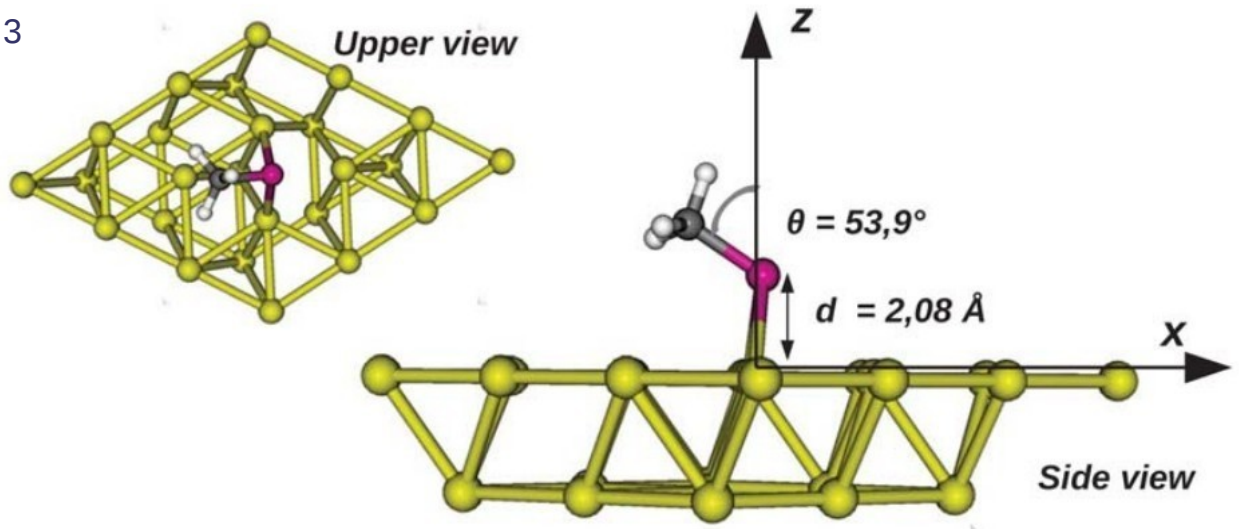
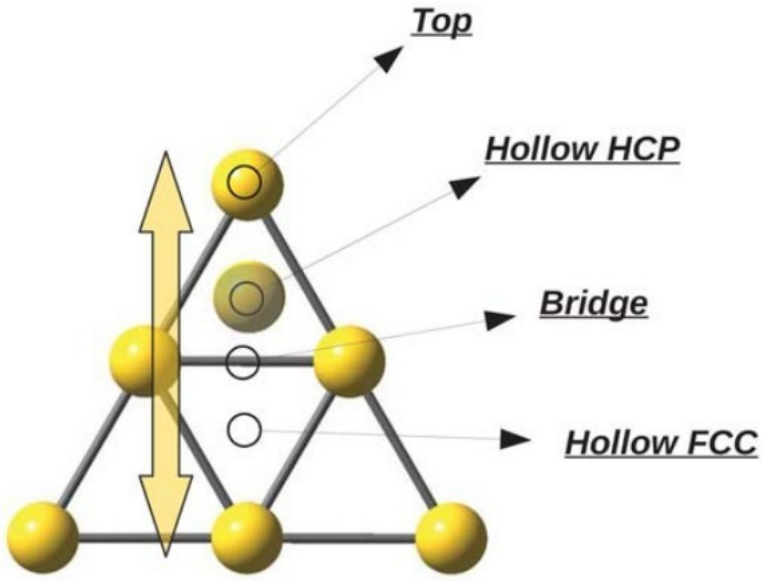
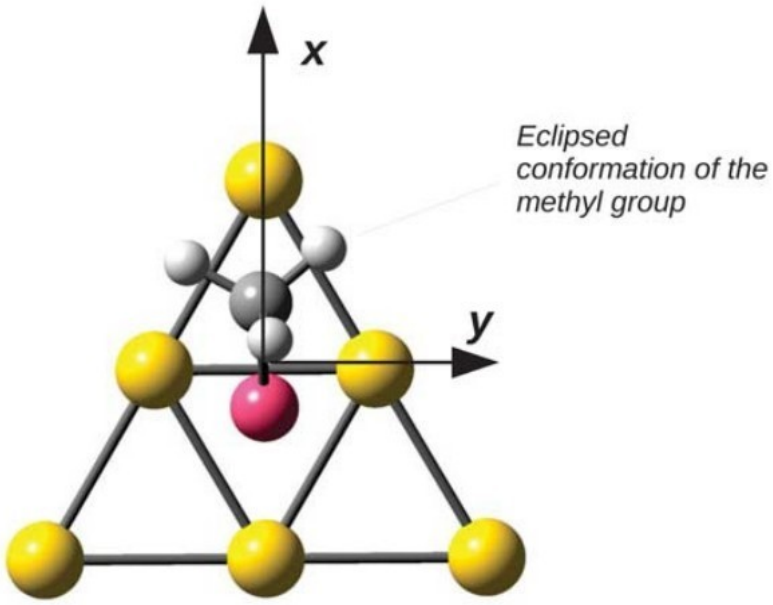
Parameters for Au-thiolates compounds

$Au_{25}SCH_3$







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Parameters for Au-thiolates compounds

	Top	
	DFT	DFTB
Au–Au (Å)	Au1-Au2: 2.64 Au1-Au3: 2.69 Au2-Au3: 2.69	Au1-Au2: 2.57 Au1-Au3: 2.59 Au2-Au3: 2.59
Au–S (Å)	Au3-S: 2.26	Au3-S: 2.28
S–C (Å)	1.84	1.83
Au–S–C (°)	Au3-S-C: 105.3	Au3-S-C: 111.2

	Bridge	
	DFT	DFTB
Au–Au (Å)	Au1-Au2: 2.72 Au1-Au3: 2.72 Au2-Au3: 2.72	Au1-Au2: 2.61 Au1-Au3: 2.58 Au2-Au3: 2.58
Au–S (Å)	Au1-S: 2.47 Au1-S: 2.47	Au2-S: 2.45 Au2-S: 2.45
S–C (Å)	1.84	1.83
Au–S–C (°)	Au1-S-C: 105.0 Au2-S-C: 105.8	Au1-S-C: 111.4 Au2-S-C: 110.9

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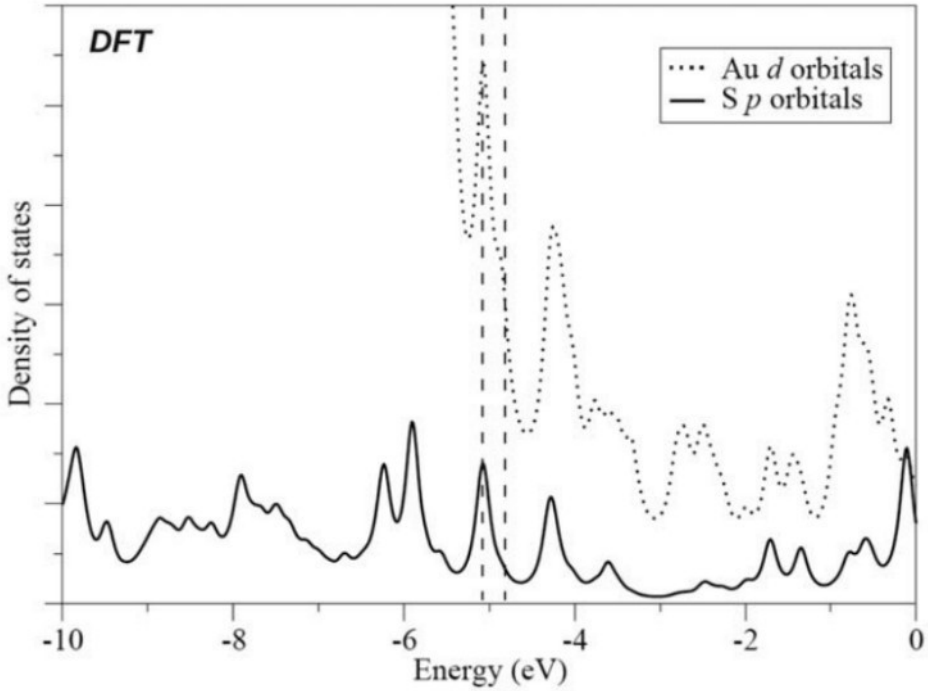
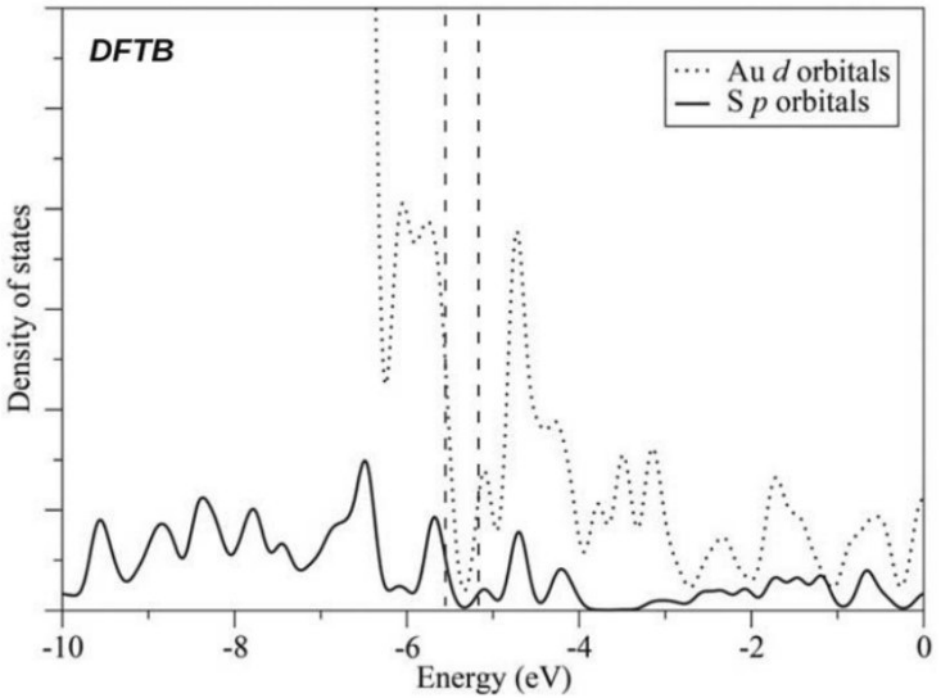
Parameters for Au-thiolates compounds

PDOS





Relative stability (kcal/mol)

	Tilt angle: 53.9°		Tilt angle: −53.9°	
	DFT	DFTB	DFT	DFTB
Bridge	0	0	0	0
Hollow HCP	4.85	3.43	8.32	9.68
Hollow FCC	16.2	11.3	5.55	3.23
Top	42.9	44.2	43.0	46.1

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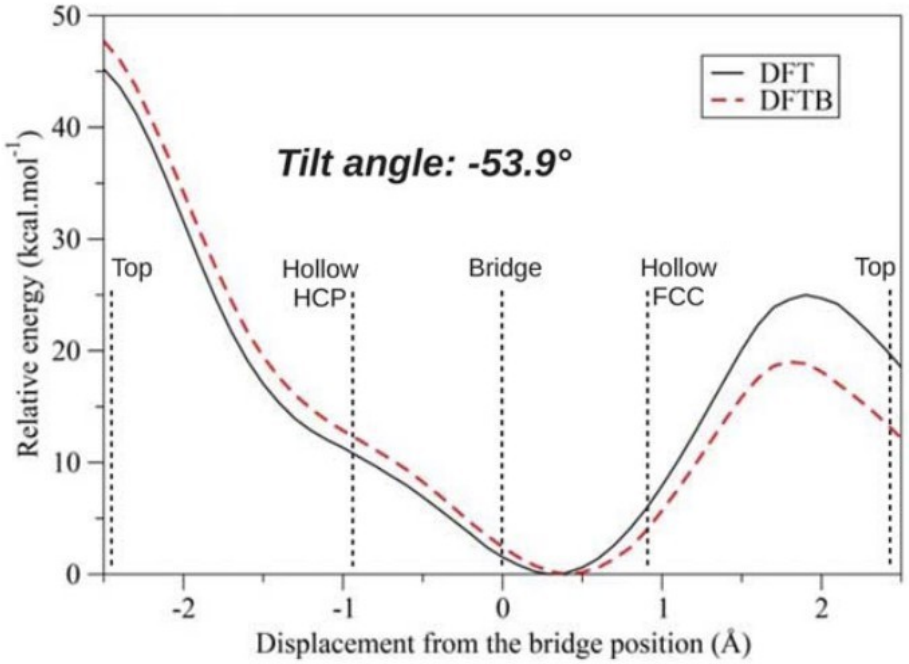
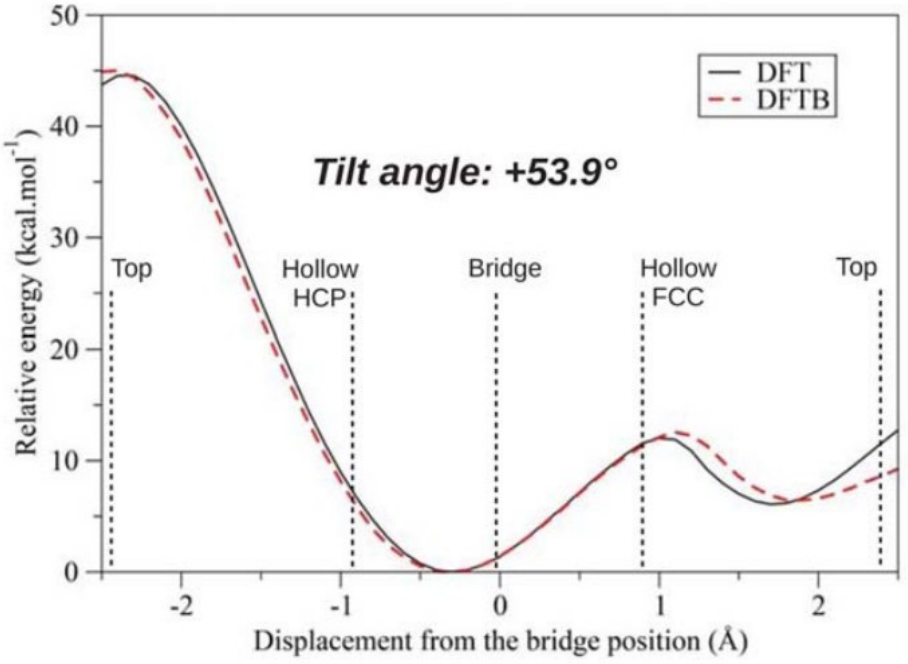
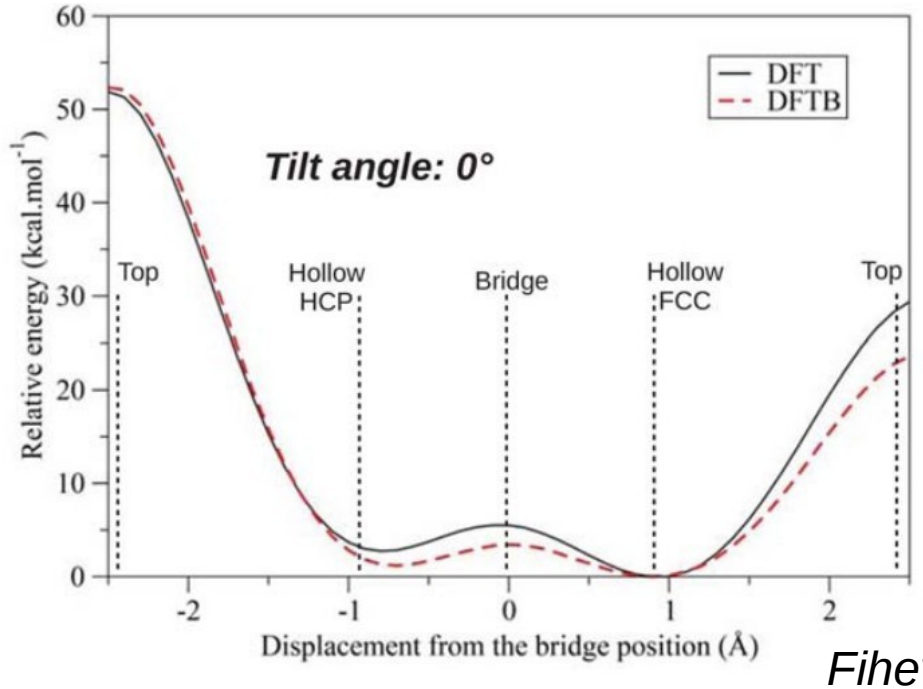
Parameters for Au-thiolates compounds



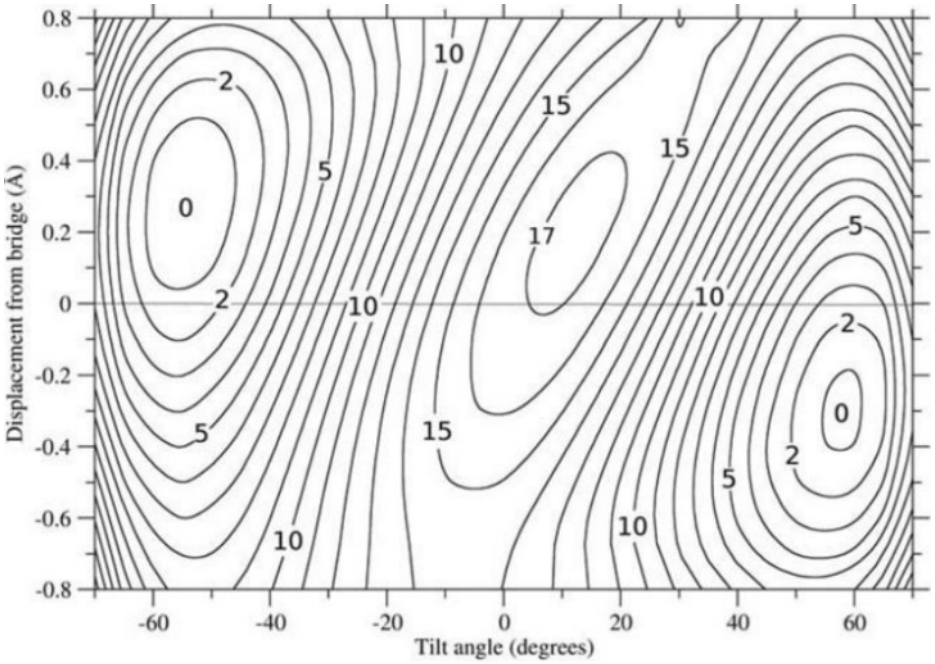




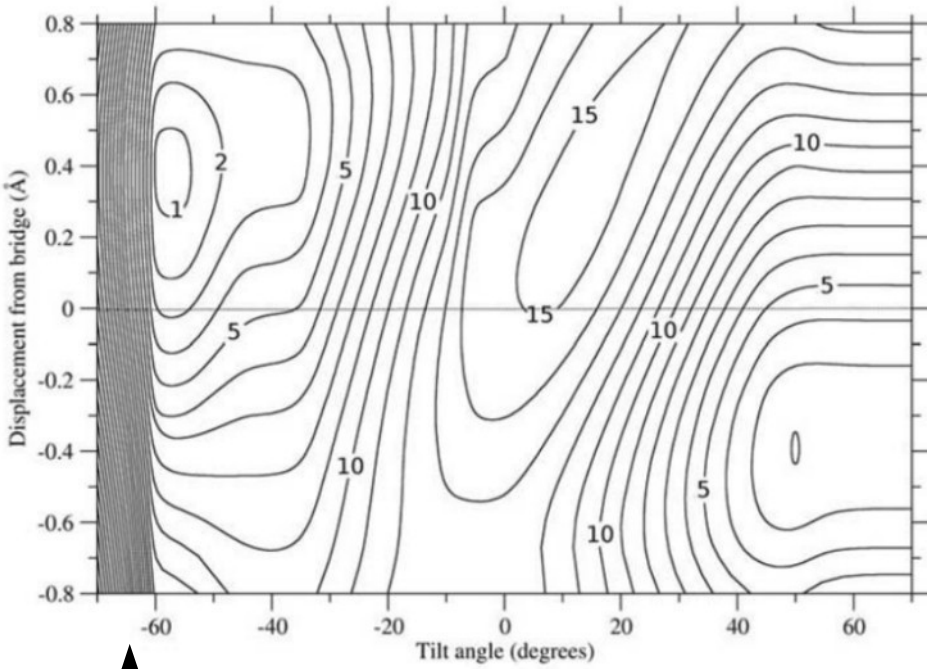
Fihey et al, J. Comp. Chem, ***36*** *2075 (2015)*

Parameters for Au-thiolates compounds

DFT



DFTB



Unphysical high energy region

Fihey et al, J. Comp. Chem, ***36*** *2075 (2015)*

Limits of DFTB

Can you trust DFTB?

- No!
- Unless it has been validated (method + parameterization) for your problem

Problematic cases

- Situations, which are problematic for DFT
  (although sometimes DFTB is better due to error compensation, c.f. band gap of semiconductors)
- Configurations which are very different from those used to obtain the parameters (e.g. bulk vs. surface vs. molecule)

How to apply DFTB for your problems

- Check on small system sizes agains ab initio (or experiment)
- Scale up to large system sizes or long time scales

Born-Oppenheimer MD

MD on the Born-Oppenheimer surface

- Geometry at t_0
- SCF (SCC) to get electronic ground state (energy, forces)
- Integration of equations of motion
- New geometry at $t_0 + \delta t$

Problem

Good accuracy requires many (~ 10 – 20) SCC iterations

Task

Given the last k geometries and converged densities/charges:

$$\boldsymbol{R}(t-\delta t),\ldots,\boldsymbol{R}(t-k\,\delta t) \quad \text{and} \quad n(t-\delta t),\ldots,n(t-k\,\delta t)$$

predict a good charge guess for current geometry $\boldsymbol{R}(t)$

Lagrangian of the Born-Oppenheimer-MD

- Usual BO-Lagrangian

$$L^{\mathrm{BO}}(\boldsymbol{R},\dot{\boldsymbol{R}}) = \frac{1}{2}\sum_A M_A \dot{\boldsymbol{R}}_A^2 - U_{\mathrm{SCF}}[\boldsymbol{R};n]$$

U_{SCF} converged energy of electronic system

n converged charges for given geometry (not a dynamic variable)

- Equation of motion

$$M_A \ddot{\boldsymbol{R}} = \frac{-\partial U_{\mathrm{SCF}}[\boldsymbol{R};n]}{\partial \boldsymbol{R}_A}$$

Note:

- SCC convergence only reached up to a certain limit
- $U_{\mathrm{SCF}}[\boldsymbol{R}; n]$ (and consequently forces) never exact

Extended Lagrangian BO-MD

Goal: Propagating el. Degrees of freedom in time while **staying on the Born-Oppenheimer-surface**

- Auxiliary dynamical variable (approx. density): D

  → D should evolve in quadratic potential around true density n

$$L^{\mathrm{XBO}}(\boldsymbol{R},\dot{\boldsymbol{R}},D,\dot{D}) = L^{\mathrm{BO}} + \frac{\mu}{2}\mathrm{Tr}[\dot{D}^2] - \frac{\mu\omega^2}{2}\mathrm{Tr}[(n-D)^2]$$

μ Fictitious mass for electronic degrees

ω Steepness of potential

- Equations of motion

$$\begin{aligned} M_A\ddot{\boldsymbol{R}} &= -\frac{\partial U_{\mathrm{SCF}}}{\partial \boldsymbol{R}_A} - \mu\omega^2\mathrm{Tr}[(n-D)\frac{\partial n}{\partial \boldsymbol{R}_A}] \\ \mu\ddot{D} &= \mu\omega^2(n-D) \end{aligned}$$

Extended Lagrangian BO-MD

- Setting fictitious mass to zero:

$$L^{\mathrm{XBO}} \rightarrow L^{\mathrm{BO}}$$

$$M_A \ddot{\boldsymbol{R}} = -\frac{\partial U_{\mathrm{SCF}}[\boldsymbol{R};n]}{\partial \boldsymbol{R}_A}$$

$$\ddot{D} = \omega^2 (n - D)$$

- D does not change the nuclear motion (auxiliary)
- Dynamics of D independent from fictitious mass
- If $D(t)$ and $n(t)$ close: $D(t)$ **good initial guess** for SCC procedure

Stability

- Optimal (highest) $\kappa = \delta t^2 \omega^2 = \kappa_0$ can be calculated for which procedure is still stable
- $\kappa > \kappa_0$: Method can become unstable (D diverging from n)
- $\kappa << \kappa_0$: Average distance between D and n big (leaving BO-surface)

Fast (SCC-free) XLBOMD

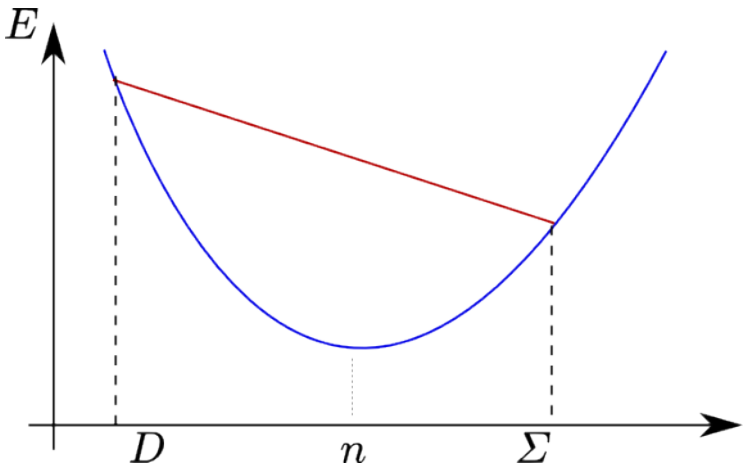
- Integration of equation of motion (Verlet algorithm):

$$D_{n+1} = 2D_n - D_{n-1} + \kappa(n_n - D_n)$$

- If energy functional convex in the vicinity of n:

$$n \rightarrow (1-c)D + c\,\Sigma$$

$$D_{n+1} = 2D_n - D_{n-1} + c\,\kappa(\Sigma_n - D_n)$$

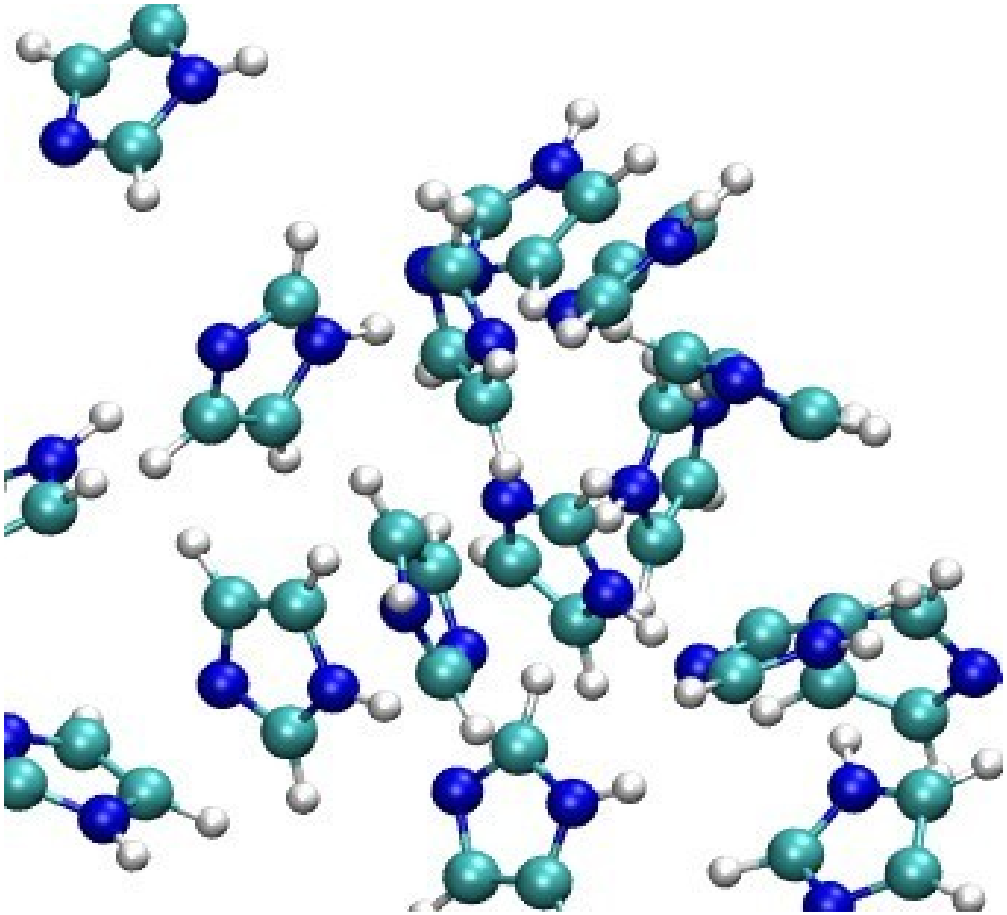


- Integration scheme stable, as long as charges after first diagonalisation yield lower energies as before
- Only **one diagonalisation per time** step necessary

Note: Not supposed to work for systems with SCC-instabilities

Fast XLBOMD at work: Liquid imidazol

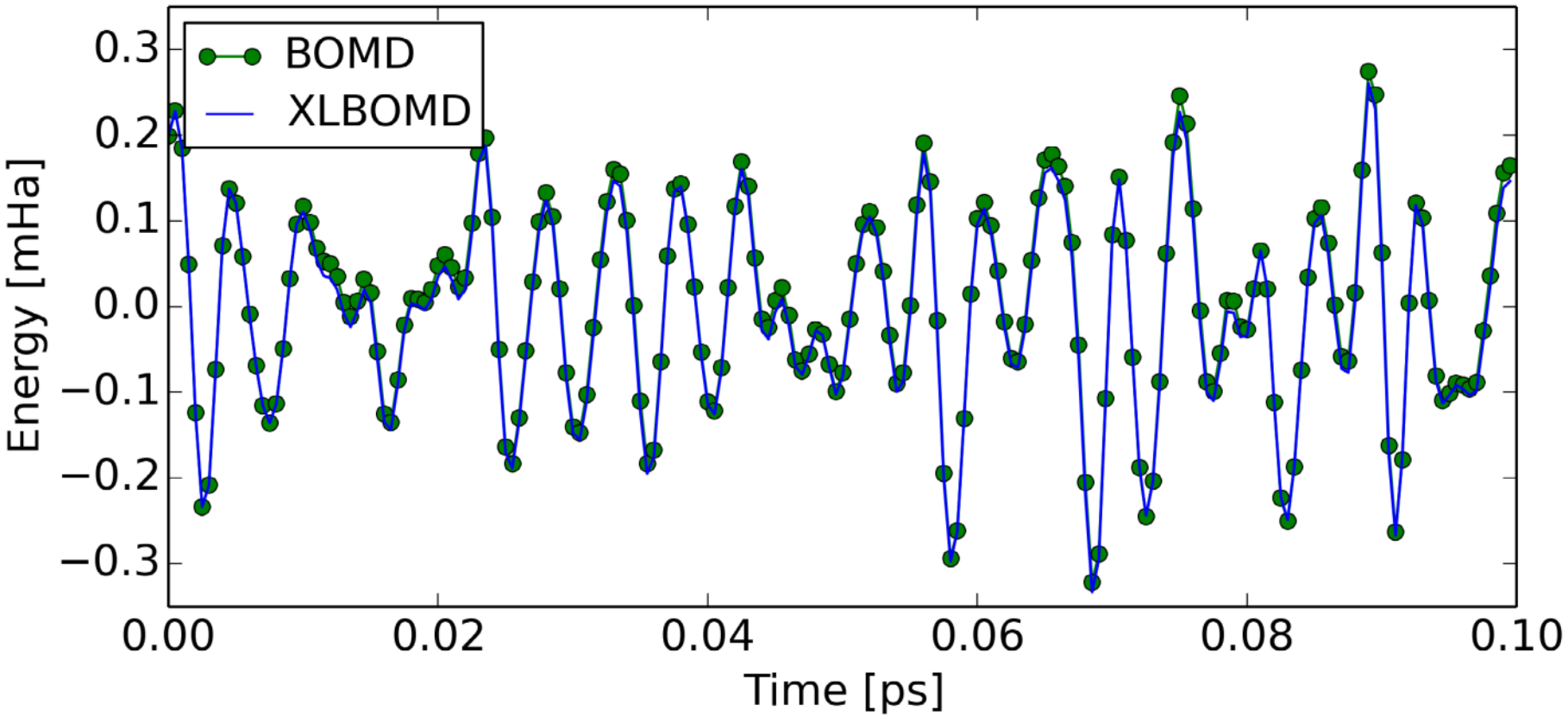
- 16 imidazol molecules
- Periodic boundary conditions
- Γ-point sampling
- Timestep: 0.5 fs
- *c*: 0.5



- Thermalization at 400 K with Nosé-Hoover chain
- NVE dynamics with SCC-free XLBOMD (one diagonalisation per time step) for 50 ps

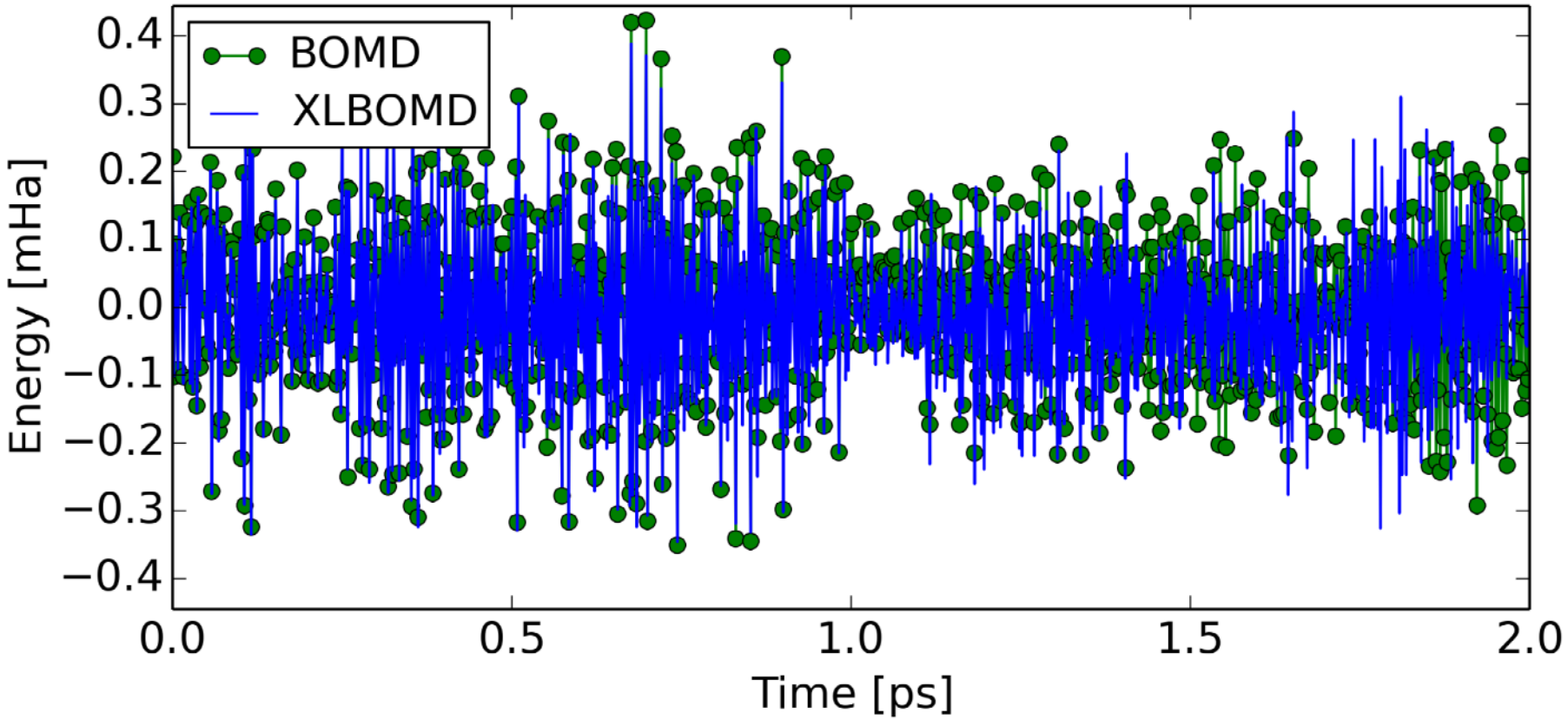
Fast XLBOMD at work: Liquid imidazol

Total energy fluctuation (T_e = 300 K)



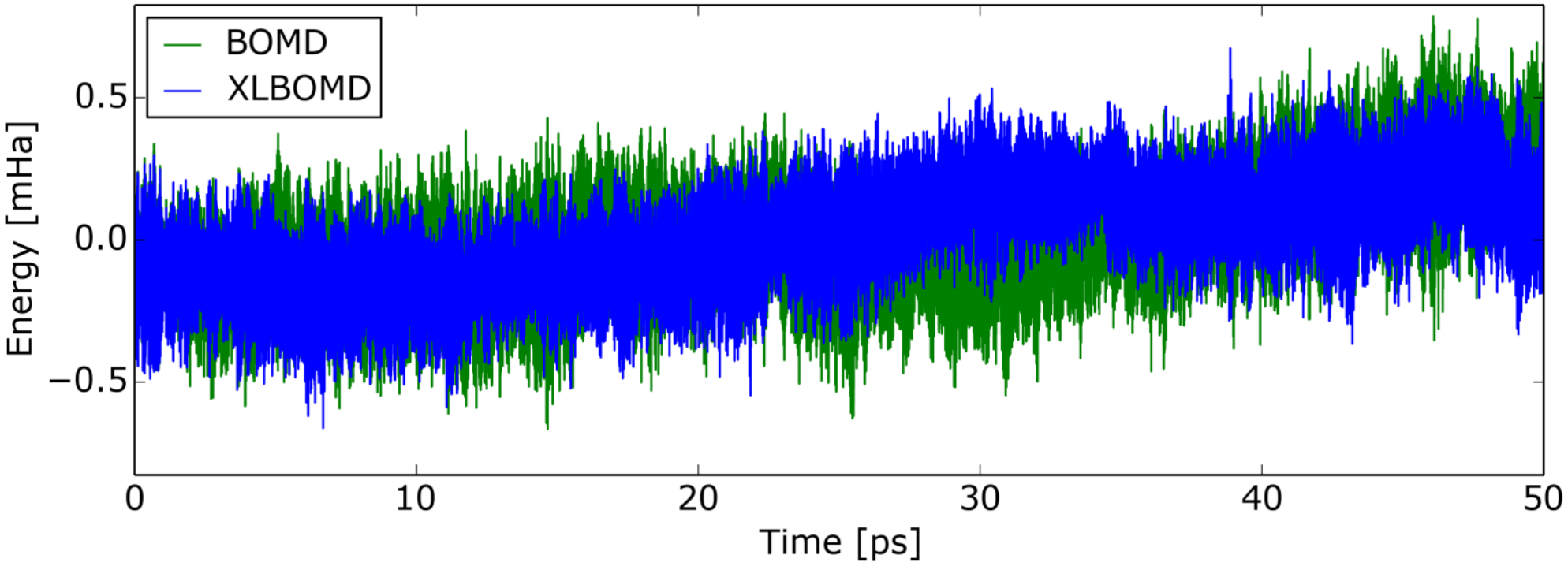
Fast XLBOMD at work: Liquid imidazol

Total energy fluctuation (T_e = 300 K)



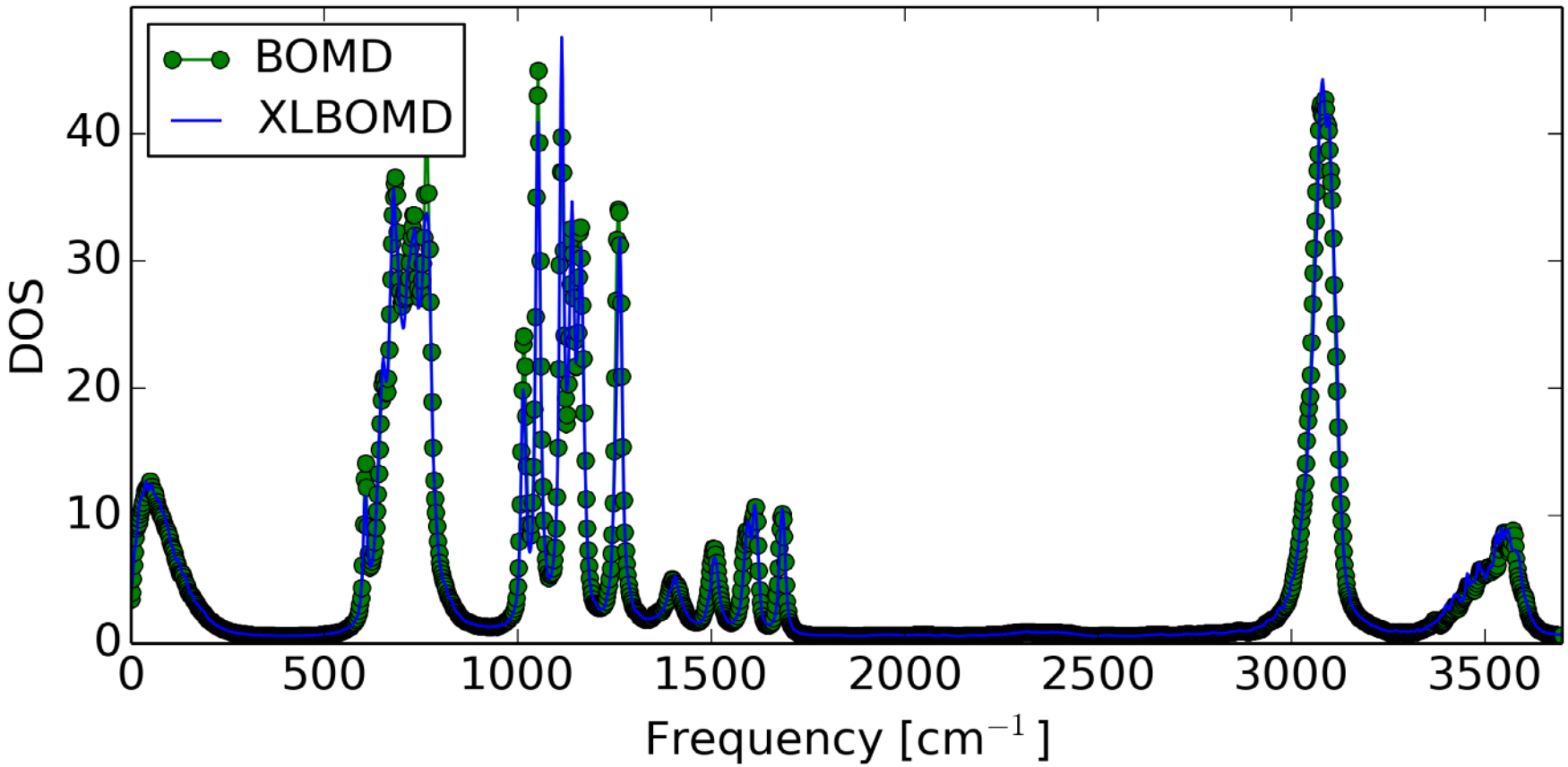
Fast XLBOMD at work: Liquid imidazol

Total energy fluctuation (T_e = 300 K)



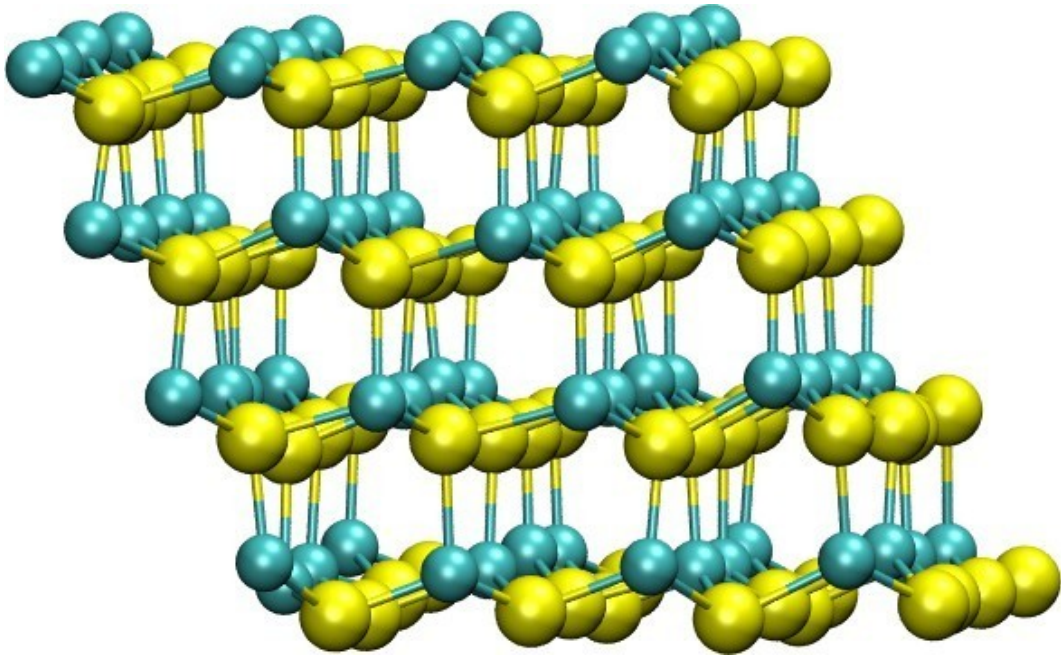
Fast XLBOMD at work: Liquid imidazol

Vibrational DOS from velocity autocorrelation (T_e = 300 K)



Fast XLBOMD at work: 3C-SiC bulk

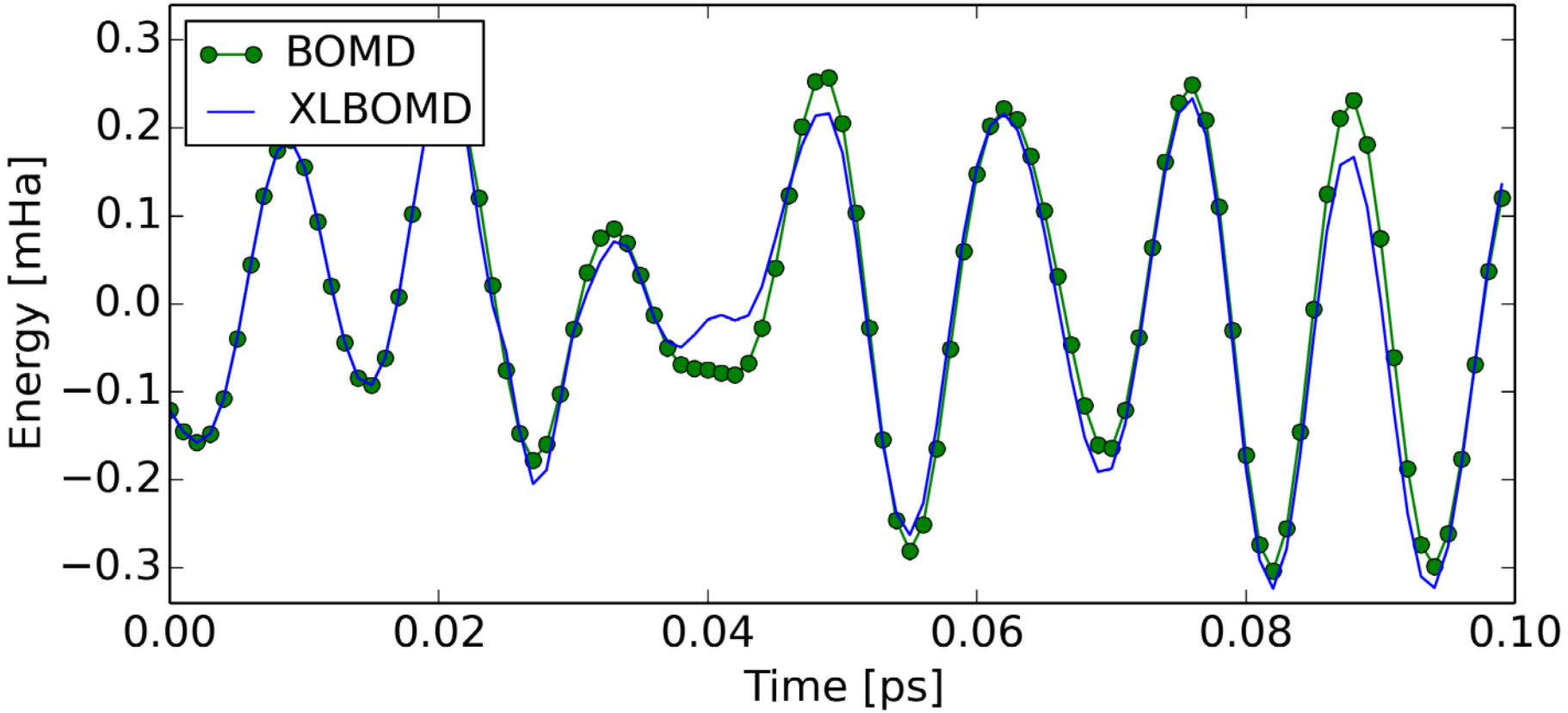
- 128 atom supercell
- Periodic boundary conditions
- 2 x 2 x 2 Monkhorst-Pack sampling
- Timestep: 1.0 fs
- *c*: 0.25



- Thermalization at 2000 K with Nosé-Hoover chain
- NVE dynamics with SCC-free XLBOMD (one diagonalisation per time step) for 50 ps

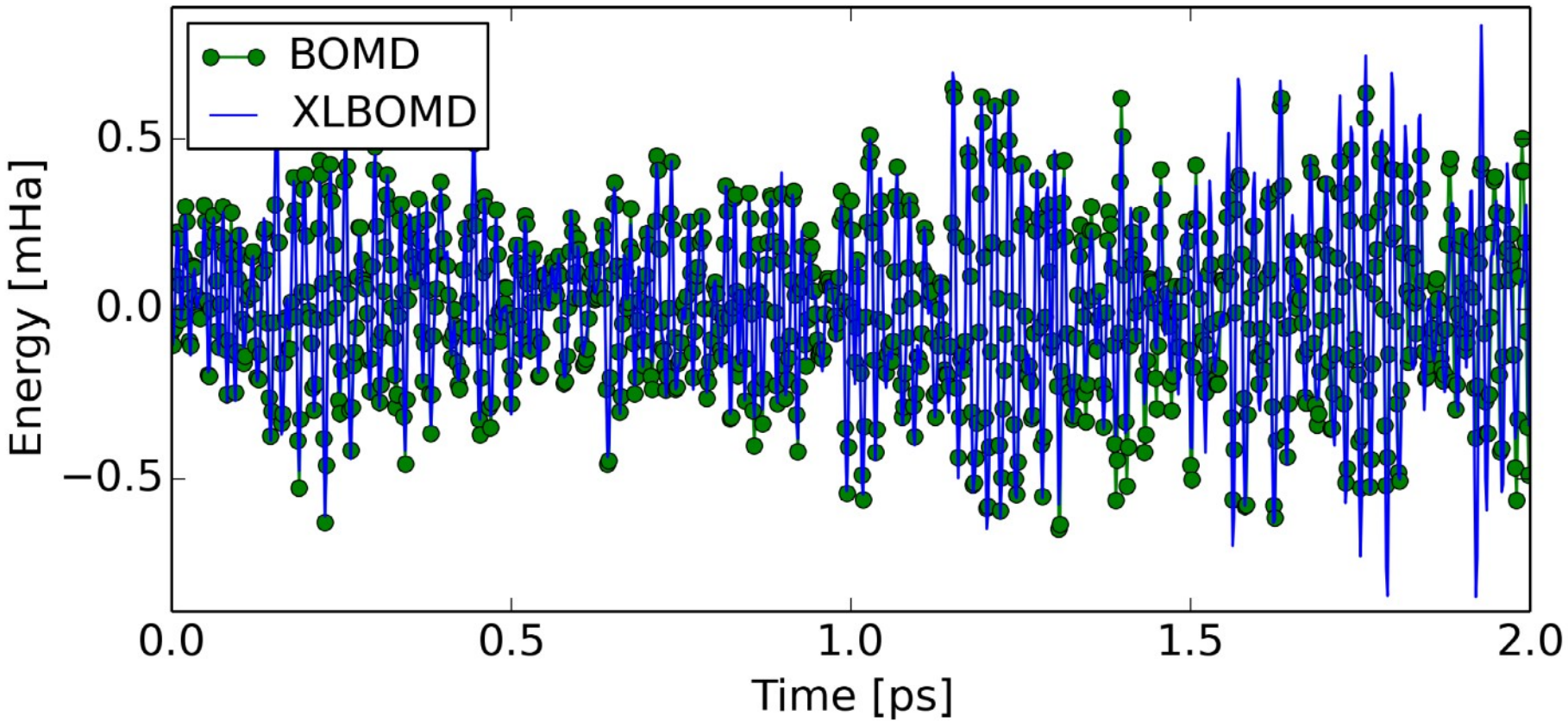
Fast XLBOMD at work: 3C-SiC bulk

Total energy fluctuation:



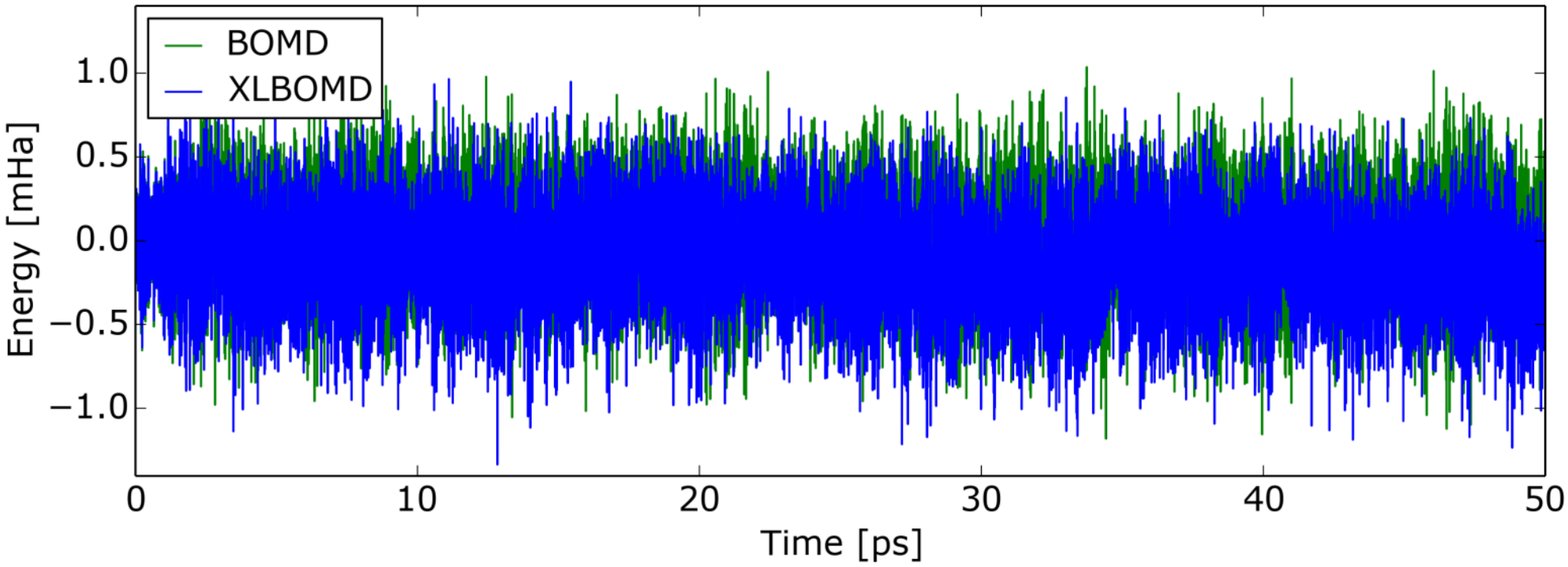
Fast XLBOMD at work: 3C-SiC bulk

Total energy fluctuation:



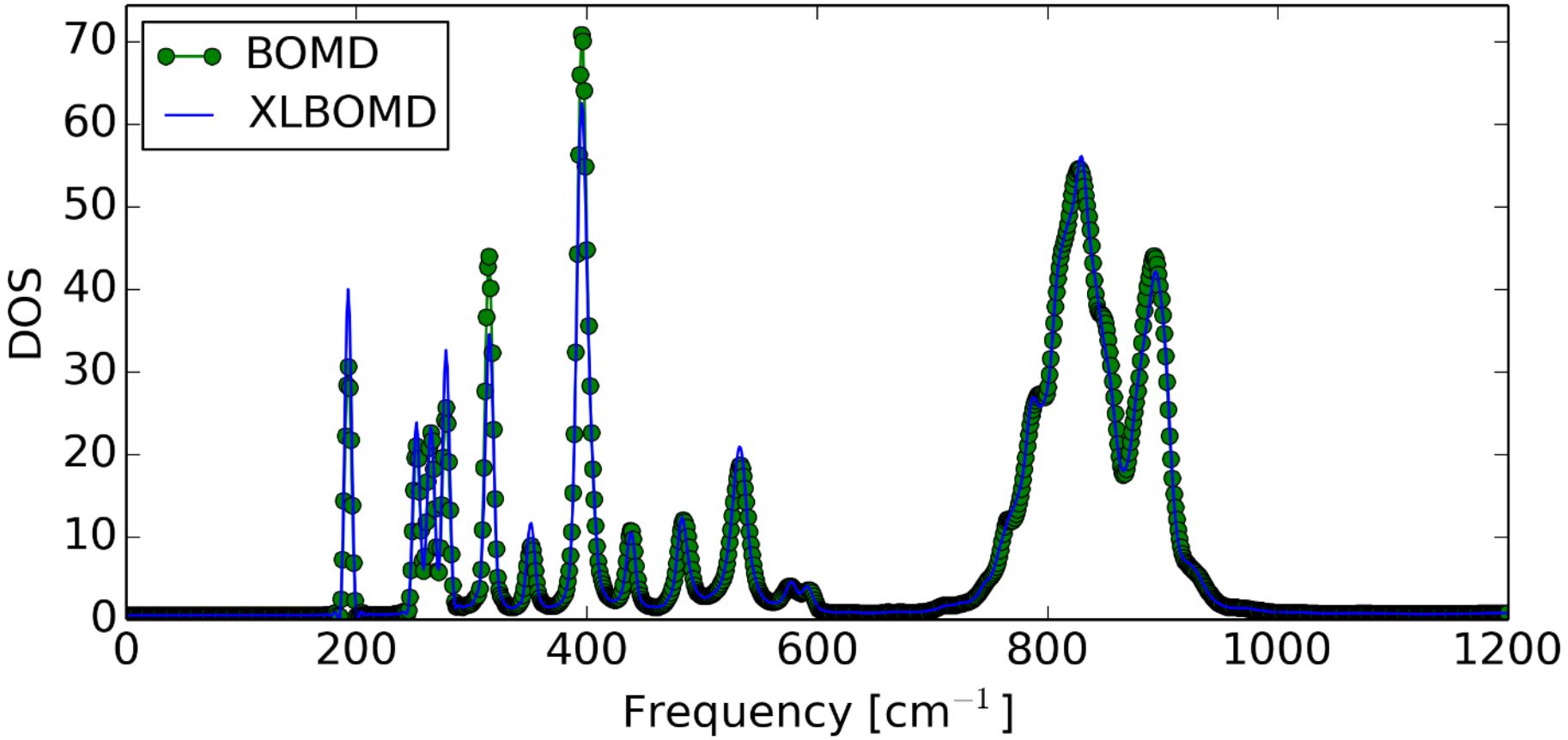
Fast XLBOMD at work: 3C-SiC bulk

Total energy fluctuation:



Fast XLBOMD at work: 3C-SiC bulk

Vibrational DOS from velocity autocorrelation



Getting density without diagonalisation

SP2-algorithm

- Recursive expansion of the Fermi-operator

$$\boldsymbol{P} = \theta[\mu \boldsymbol{I} - \boldsymbol{H}]$$

$$\theta[\mu \boldsymbol{I} - \boldsymbol{H}] = \lim_{i \to \infty} f_i(f_{i-1}(\ldots f_0(\boldsymbol{X_0})))$$

$$f_i(\boldsymbol{X}_i) = \begin{cases} \boldsymbol{X}_i^2 & \text{if } \mathrm{Tr}(\boldsymbol{X}) \leqslant N_{\mathrm{occ}} \\ 2\boldsymbol{X}_i - \boldsymbol{X}_i^2 & \text{if } \mathrm{Tr}(\boldsymbol{X}) > N_{\mathrm{occ}} \end{cases}$$

$$\boldsymbol{X_0} = \frac{\epsilon_{\max} \boldsymbol{I} - \boldsymbol{H}}{\epsilon_{\max} - \epsilon_{\min}}$$

- Recursively applied until $\mathrm{Tr}(\boldsymbol{X}) \simeq N_{\mathrm{occ}}$

$$\boldsymbol{P} \simeq \boldsymbol{X}$$

Gershgorin circle theorem

A. M. N. Niklasson, Phys. Rev. B 66, 155115 (2002)

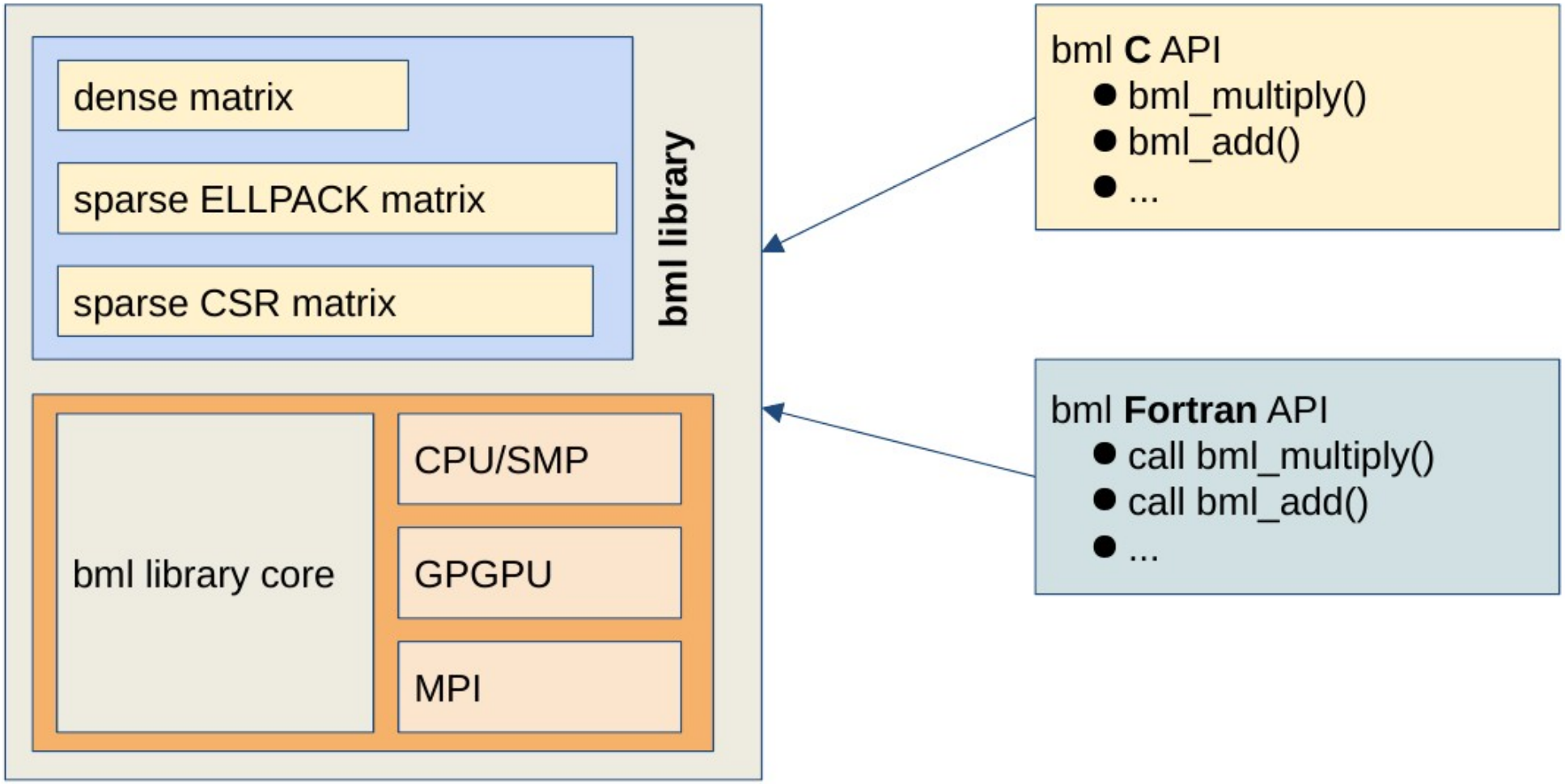
Getting density without diagonalisation

Algorithm 1 Pseudocode for the SP2 algorithm.

procedure SP2(tol, $\mathbf{H}$, $\mathbf{P}$, N_{occ})
  Estimate ϵ_{min} and ϵ_{max} from $\mathbf{H}$
  $\mathbf{X} = (\epsilon_{\text{max}}\mathbf{I} - \mathbf{H})/(\epsilon_{\text{max}} - \epsilon_{\text{min}})$
  TraceX = Tr[$\mathbf{X}$]
  for $i = 1 : i_{\text{max}}$ **do**
    TraceXold = TraceX
    $\mathbf{X}_{\text{tmp}} = \mathbf{X}^2$
    if (TraceX $- N_{\text{occ}}$) $\leqq 0$ **then**
      $\mathbf{X} = 2\mathbf{X} - \mathbf{X}_{\text{tmp}}$
    else
      $\mathbf{X} = \mathbf{X}_{\text{tmp}}$
    end if
    if $|$TraceX $- N_{\text{occ}}| \leqq$ tol **then**
      break
    end if
  end for
  $\mathbf{P} = \mathbf{X}$

end procedure

BML matrix library



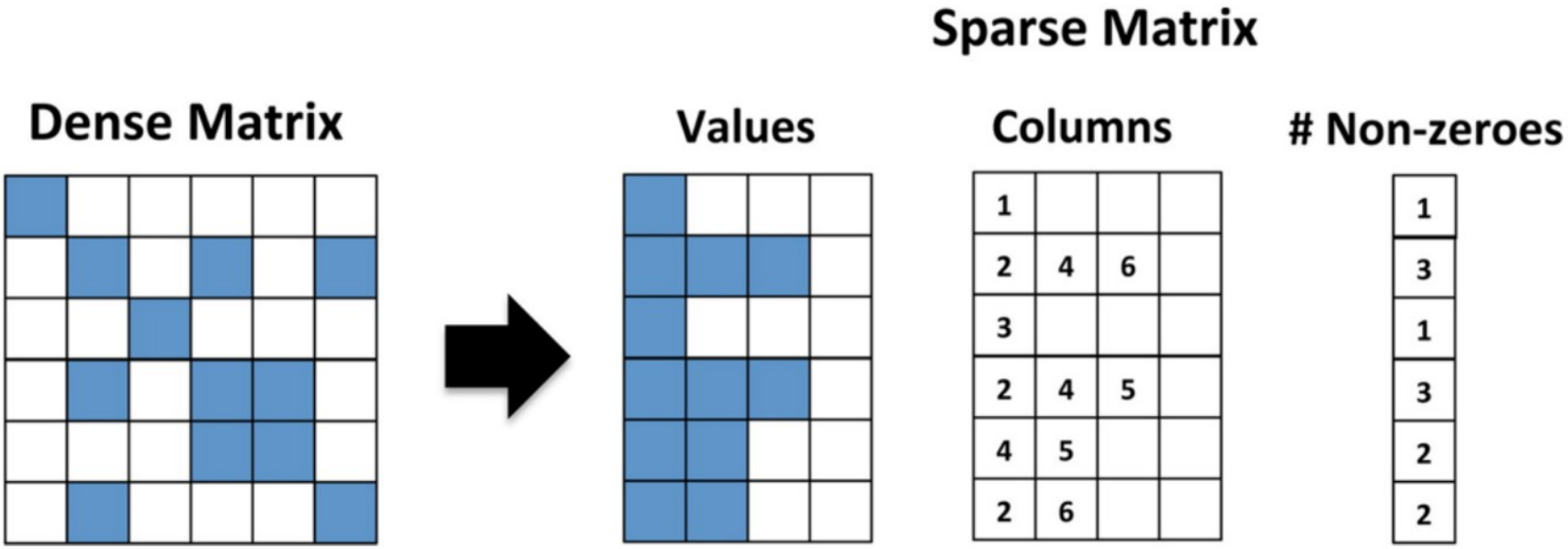

```
type(bml_matrix) :: a
call bml_zero_matrix(bml_matrix_dense, bml_precision_double,&
    & 100, a)
```

https://github.com/lanl/bml

N. Bock et al., Comput. Softw. Big Sci., submitted

BML matrix library

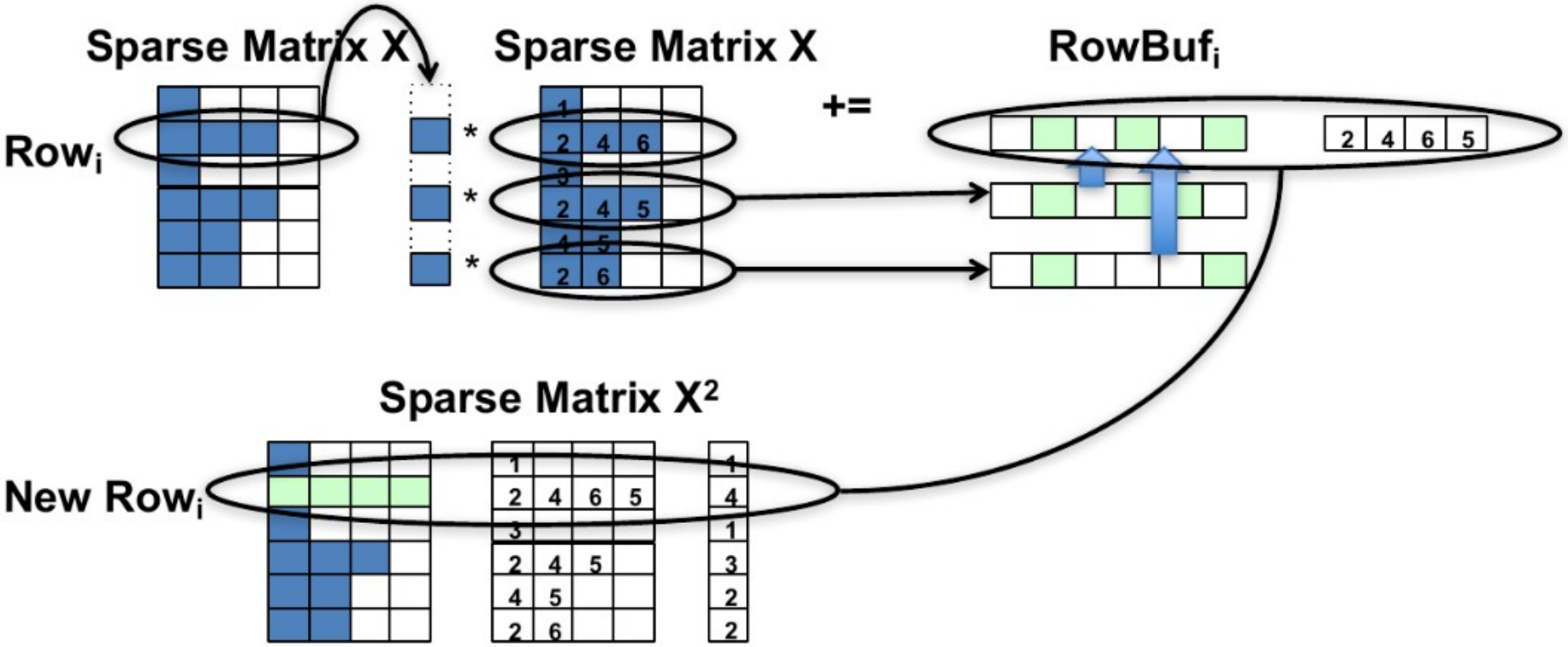
ELLPACK-R format



- Less compact than other sparse formats (e.g. compressed sparse format)
- Simple strided access for each row
- Simplified parallelism
- No insertion costs

BML matrix library

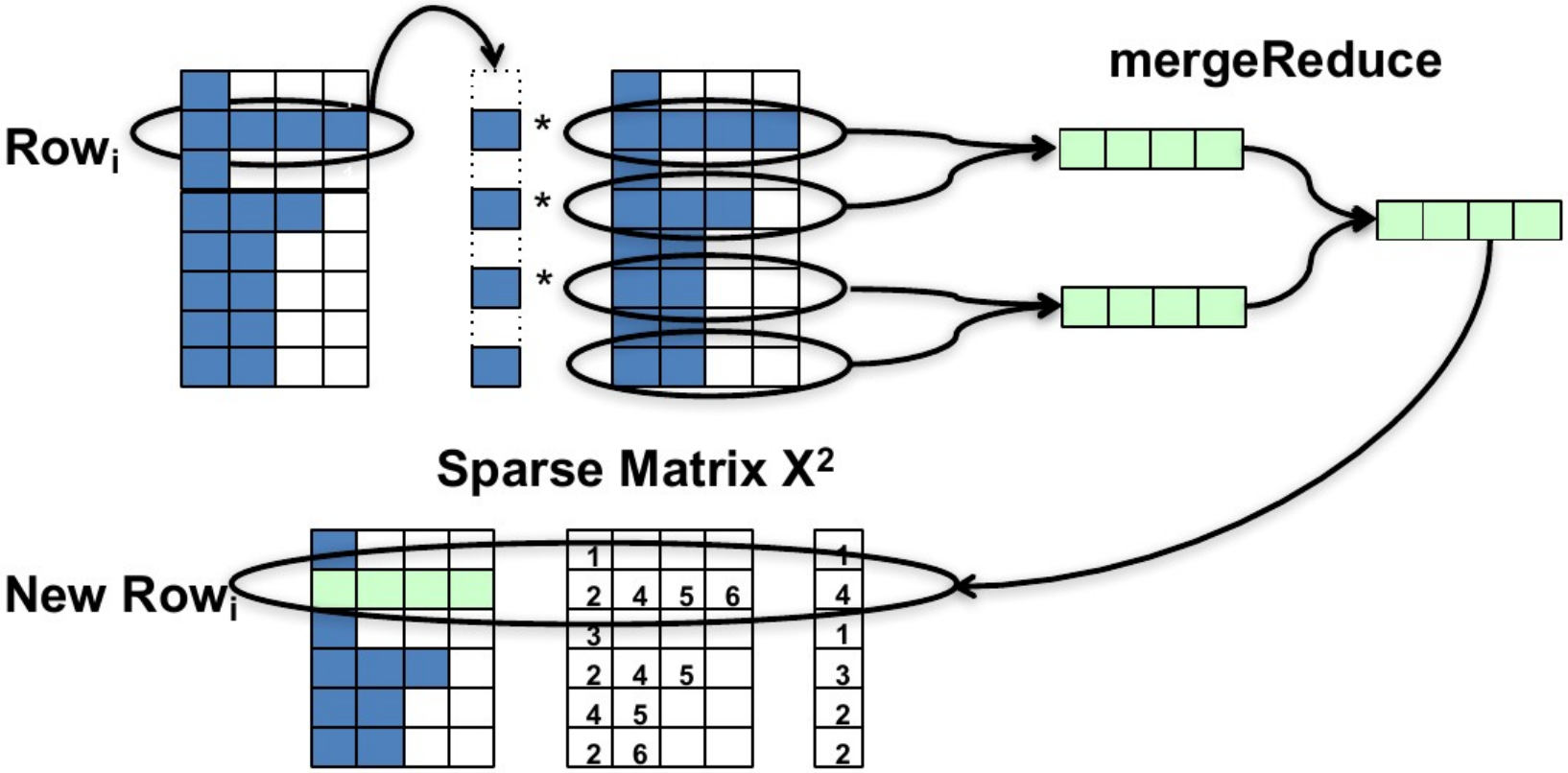
Gustavson algorithm for matrix-matrix multiplication



- Optimal for multi-core architectures
- Parallelises well over rows on shared memory architectures
- Requires large row buffers (may not fit into the cache)
- Matrix elements may become unordered

BML matrix library

Merged based matrix-matrix multiplication



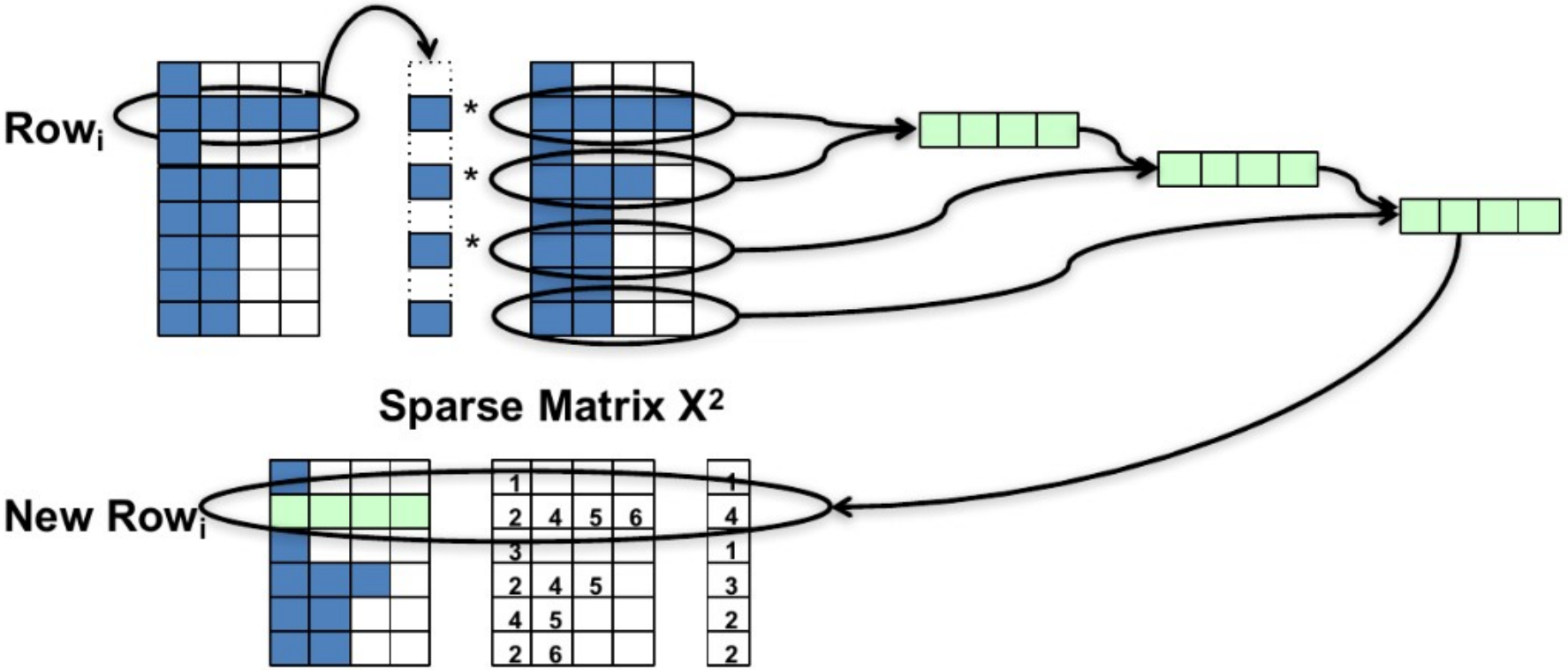
- Requires only O(m^2) storage
- Completes in log(m) steps
- Memory access regular, requires only contiguous blocks of size m
- Good when cache sizes are rather small

https://github.com/lanl/bml

N. Bock et al., Comput. Softw. Big Sci., submitted

BML matrix library

Low-storage merge based matrix-matrix multiply



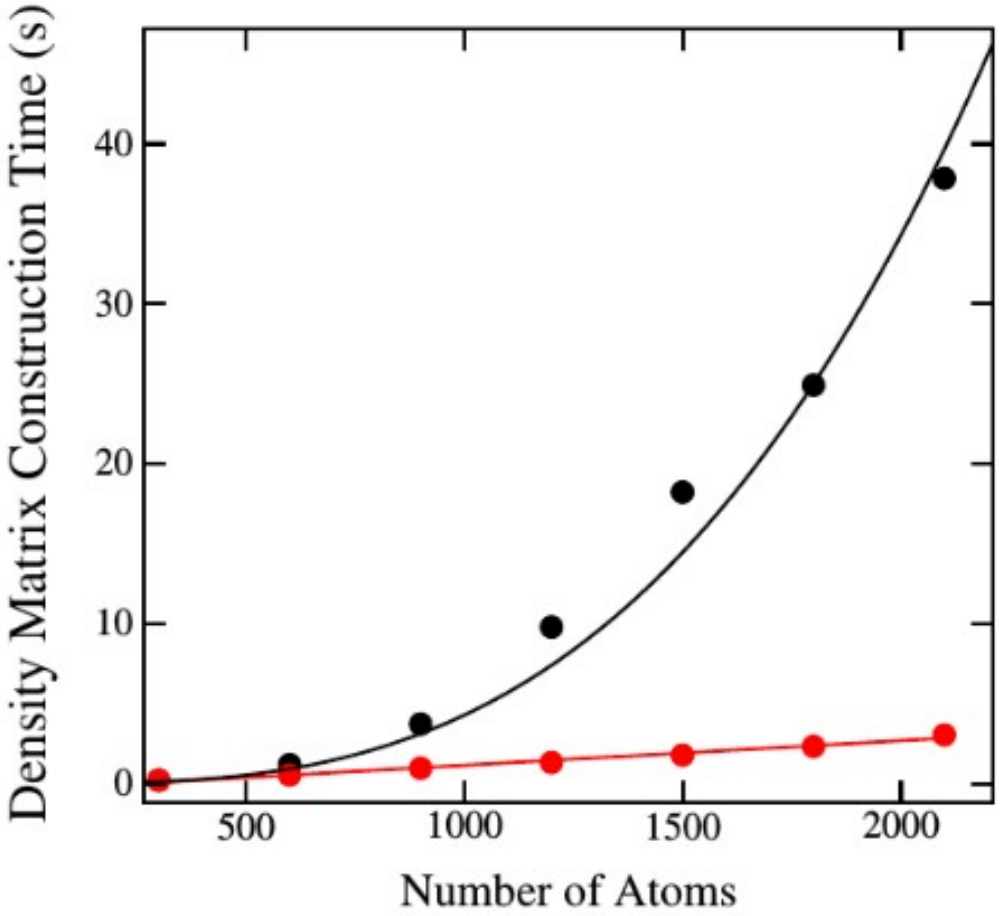
- Requires only O(*m*) storage
- Completes in *m* - 1 steps
- Memory access regular, requires only contiguous blocks of size *m*
- Good when cache sizes are extremely small

https://github.com/lanl/bml

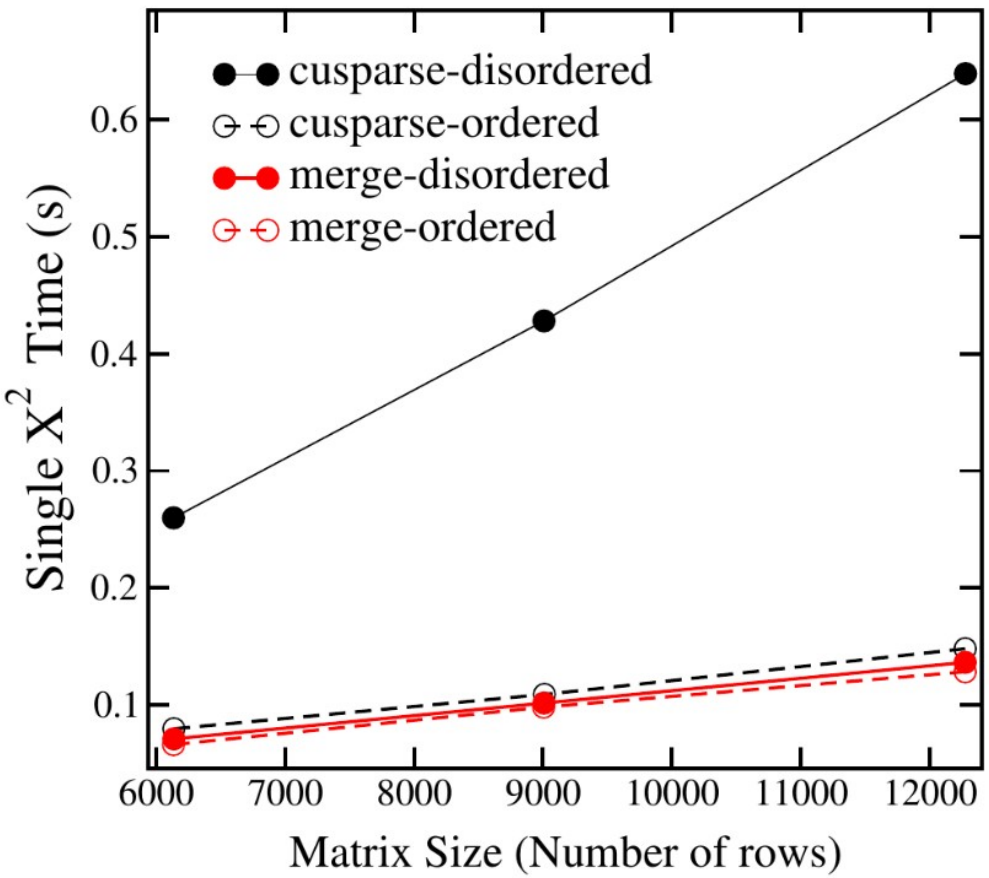
N. Bock et al., Comput. Softw. Big Sci., submitted

BML matrix library

Sparse versus dense scaling



GPU performance



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Summary

- Density Functional Tight Binding is an efficient and versatile QM simulation framework
- DFTB offers DFT-like calculations at much lower costs
- Due to approximations and fitted parameters less transferable than DFT
- Extended Lagrangian Born-Oppenheimer MD can be used to speed up molecular dynamics simulations by sparing self-consistency cycles
- SP2-algorithm based on the BML-library enables O(*N*)-scaling with system size.