LOBSTER & ABINIT: perfect partners for chemical-bonding studies from plane waves

Richard Dronskowski

Population Analysis, COOP and COHP

Tellurium and other Materials (using good old LMTO)

Bonding Information projected from Plane Waves

The **LOBSTER** program: C & Nanotube & Ti

Ge–Ge bonds in Phase-Change Materials, Density-of-Energy (DOE)

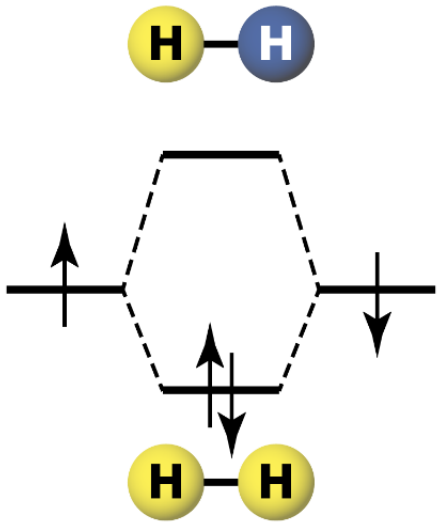
Plane-wave Benchmarking, **ABINIT** implementation

Correlated Stuff

Chair of Solid-State and Quantum Chemistry | RWTH AACHEN UNIVERSITY

H_2: Population Analysis by Robert S. Mulliken

$$\int \psi^* \psi d\tau = \underbrace{\int \psi^2 d\tau}_{\equiv 1} = c_1^2 \underbrace{\int \phi_1^2 d\tau}_{\equiv 1} + c_2^2 \underbrace{\int \phi_2^2 d\tau}_{\equiv 1} + 2c_1 c_2 \underbrace{\int \phi_1 \phi_2 d\tau}_{S_{12}}$$

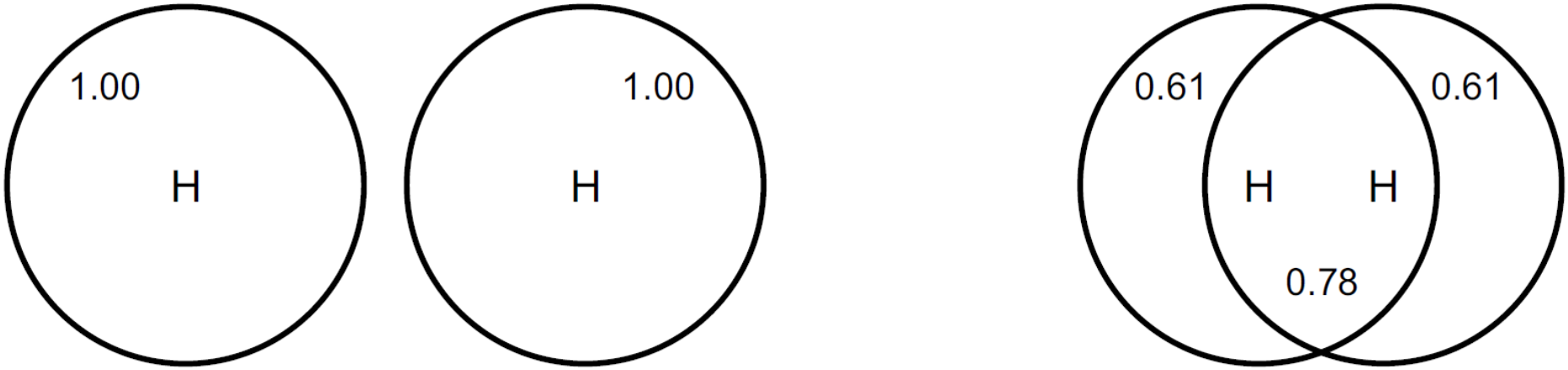


R. S. Mulliken,
J. Chem. Phys. **1955**, *23*, 1833

… plus population analyses by Roby, Löwdin, Davidson, Jug, Ahlrichs, and others…

Simplest Population Analysis for σ_g-MO of H_2

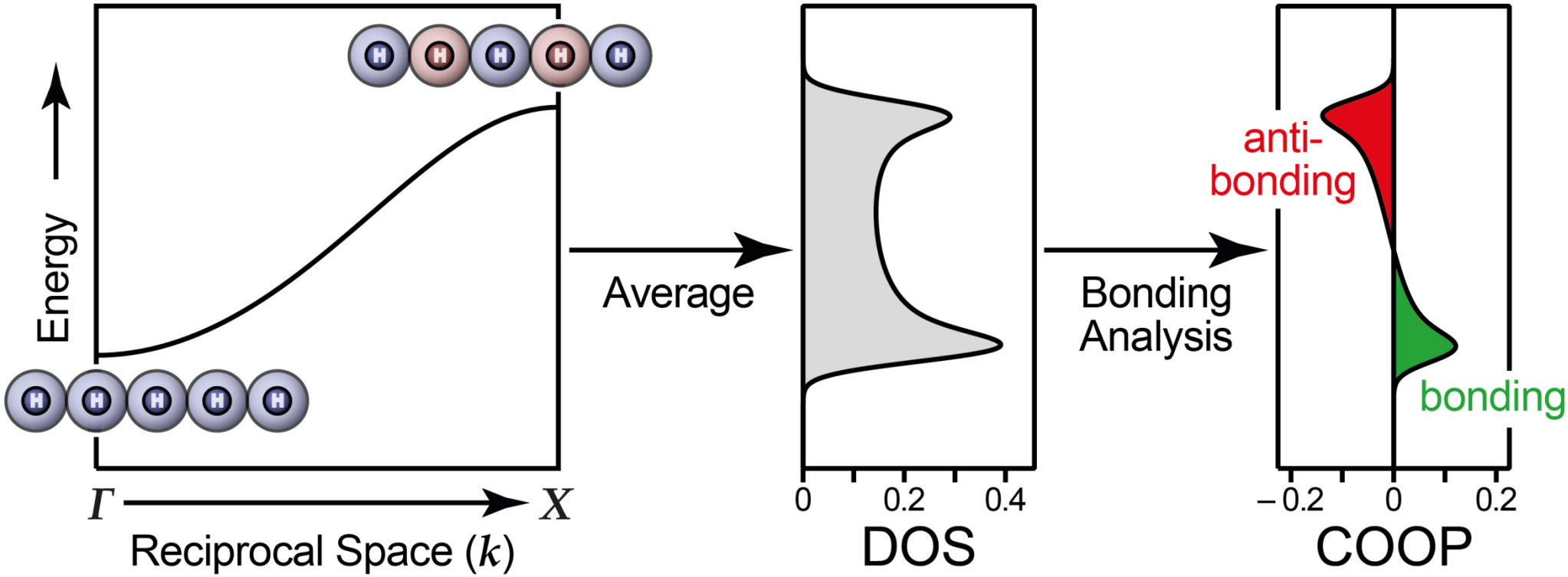
$$1 = \underbrace{\frac{1}{2(1+S_{12})}}_{=0.305} + \underbrace{\frac{1}{2(1+S_{12})}}_{=0.305} + \underbrace{\frac{2}{2(1+S_{12})}S_{12}}_{=0.390}$$

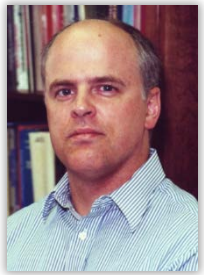


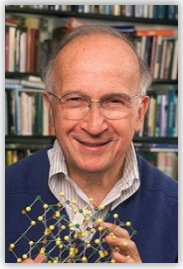
the two hydrogen atoms share 0.78 electrons

1dim H-chain: band structure, DOS, COOP

without any doubt (I guess) the icon of solid-state quantum chemistry:

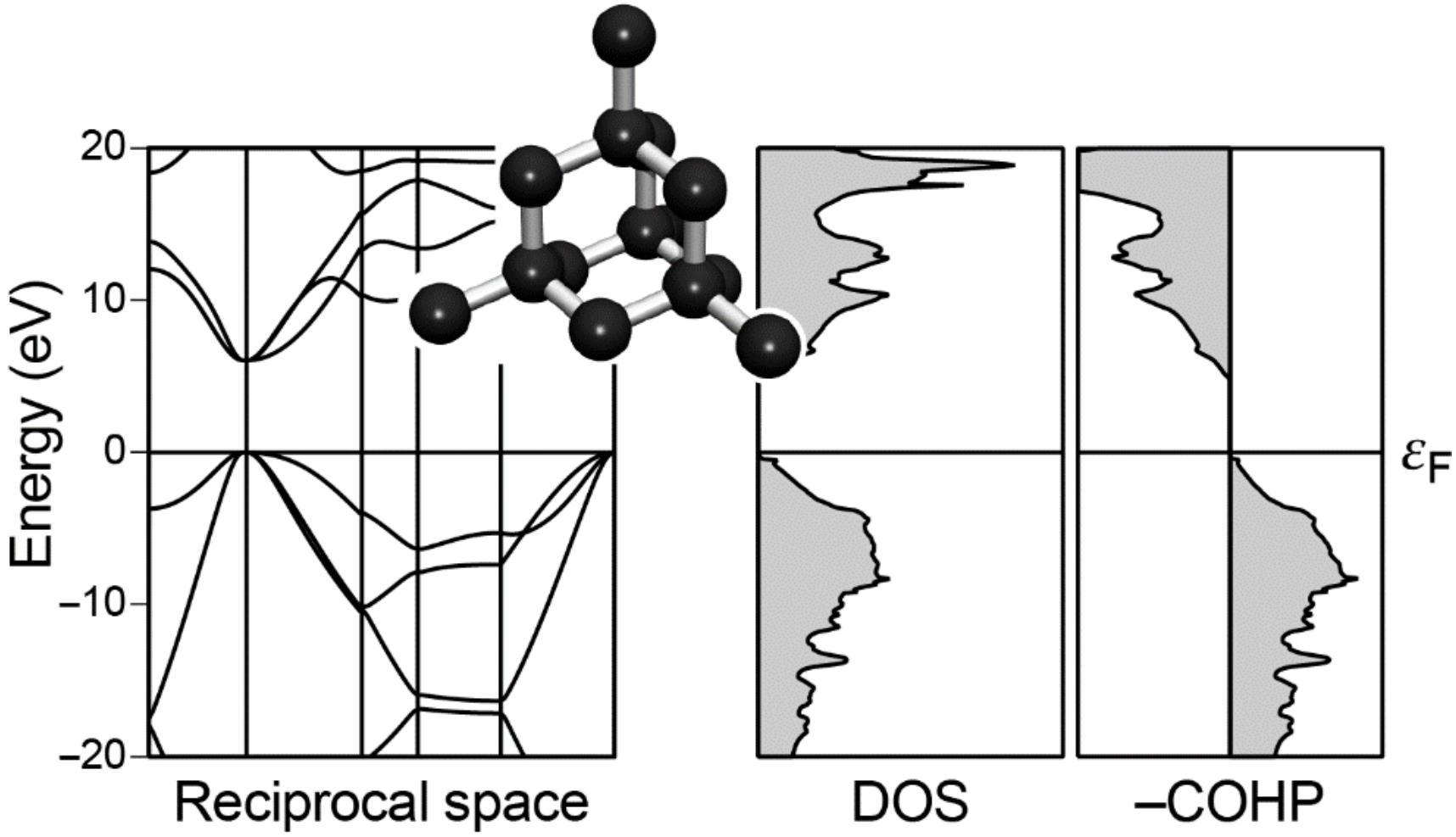






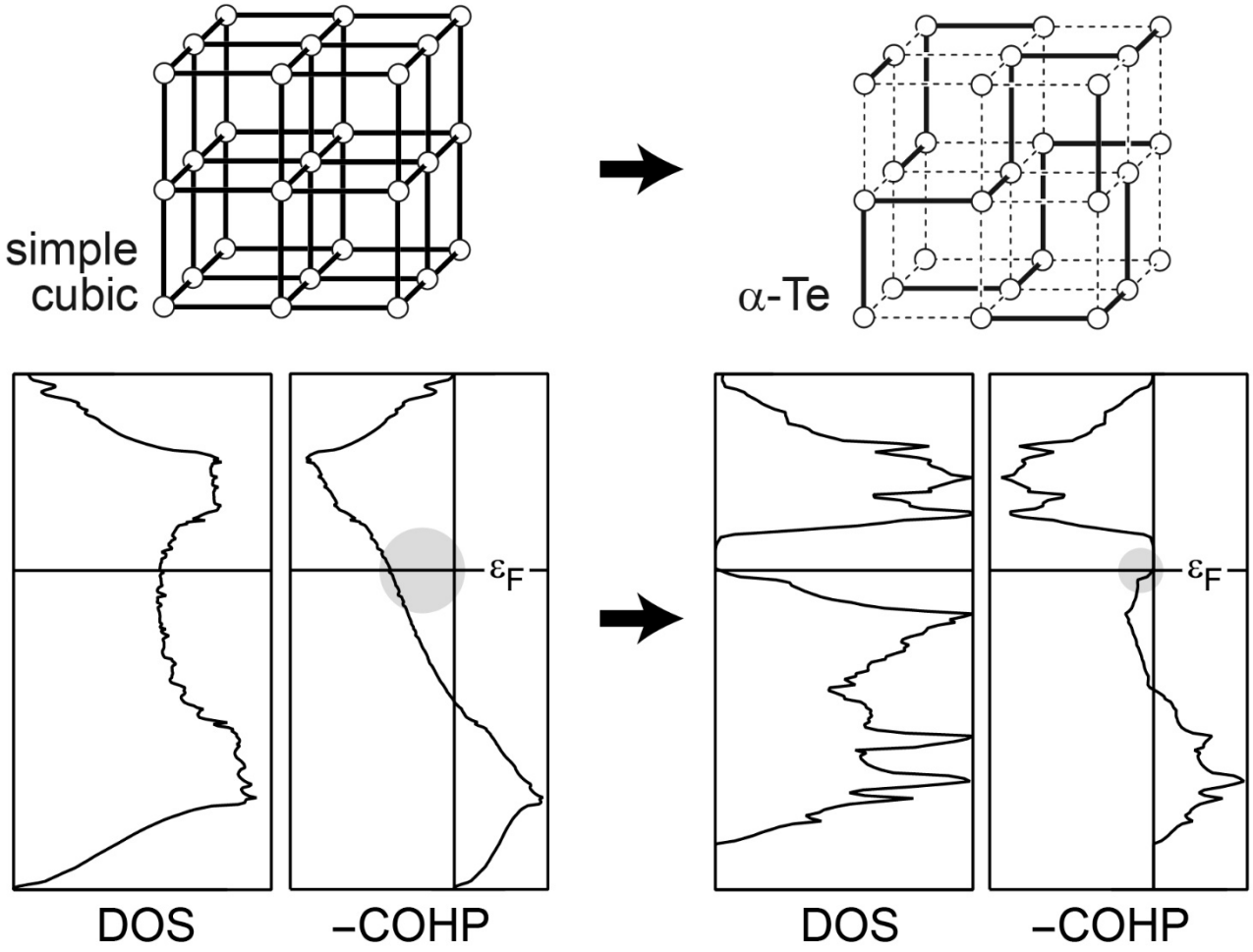
T. Hughbanks, R. Hoffmann,
J. Am. Chem. Soc. **1983**, *105*, 3528

DFT: Crystal Orbital Hamilton Population, COHP



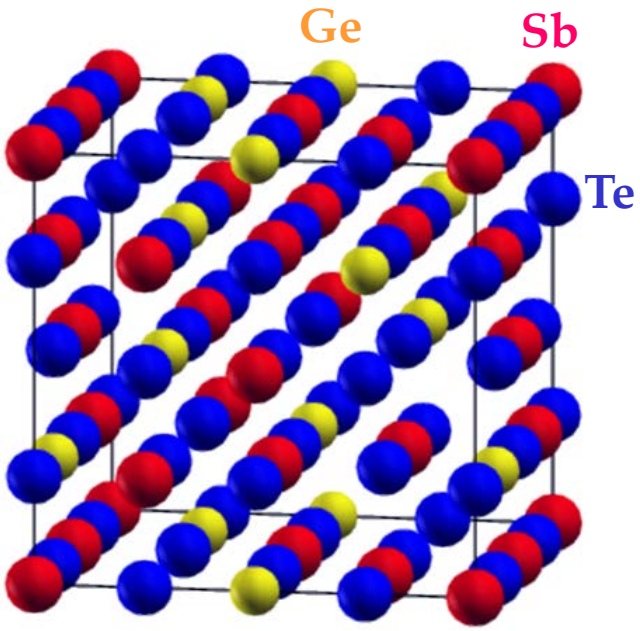
R. Dronskowski, P. E. Blöchl,
J. Phys. Chem. **1993**, *97*, 8617

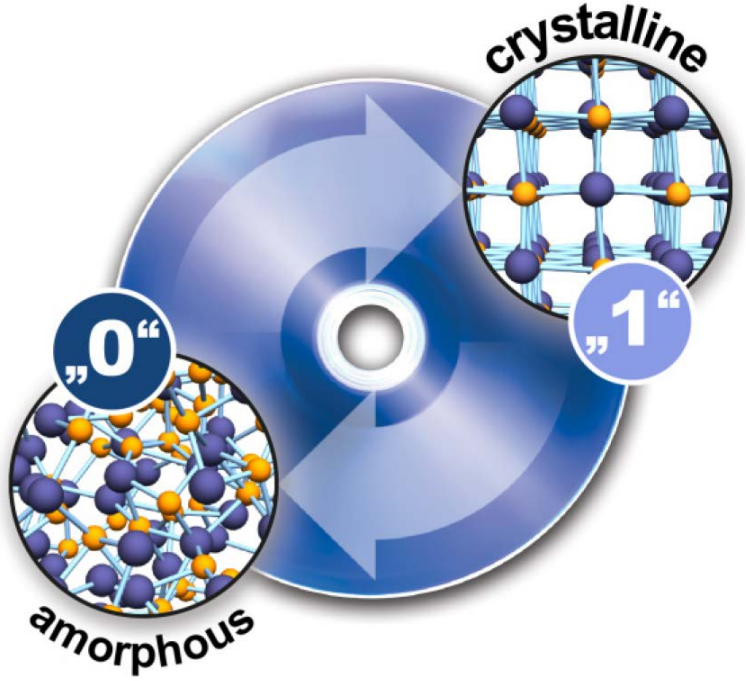
Example I: sc Tellurium is Peierls-unstable



A. Decker, G. A. Landrum, R. Dronskowski,
Z. Anorg. Allg. Chem. **2002**, *628*, 295

Example II: Phase-change Materials



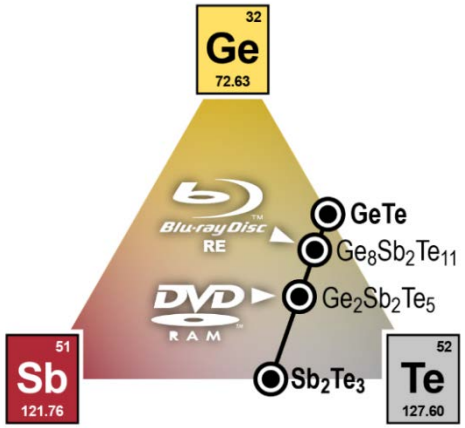


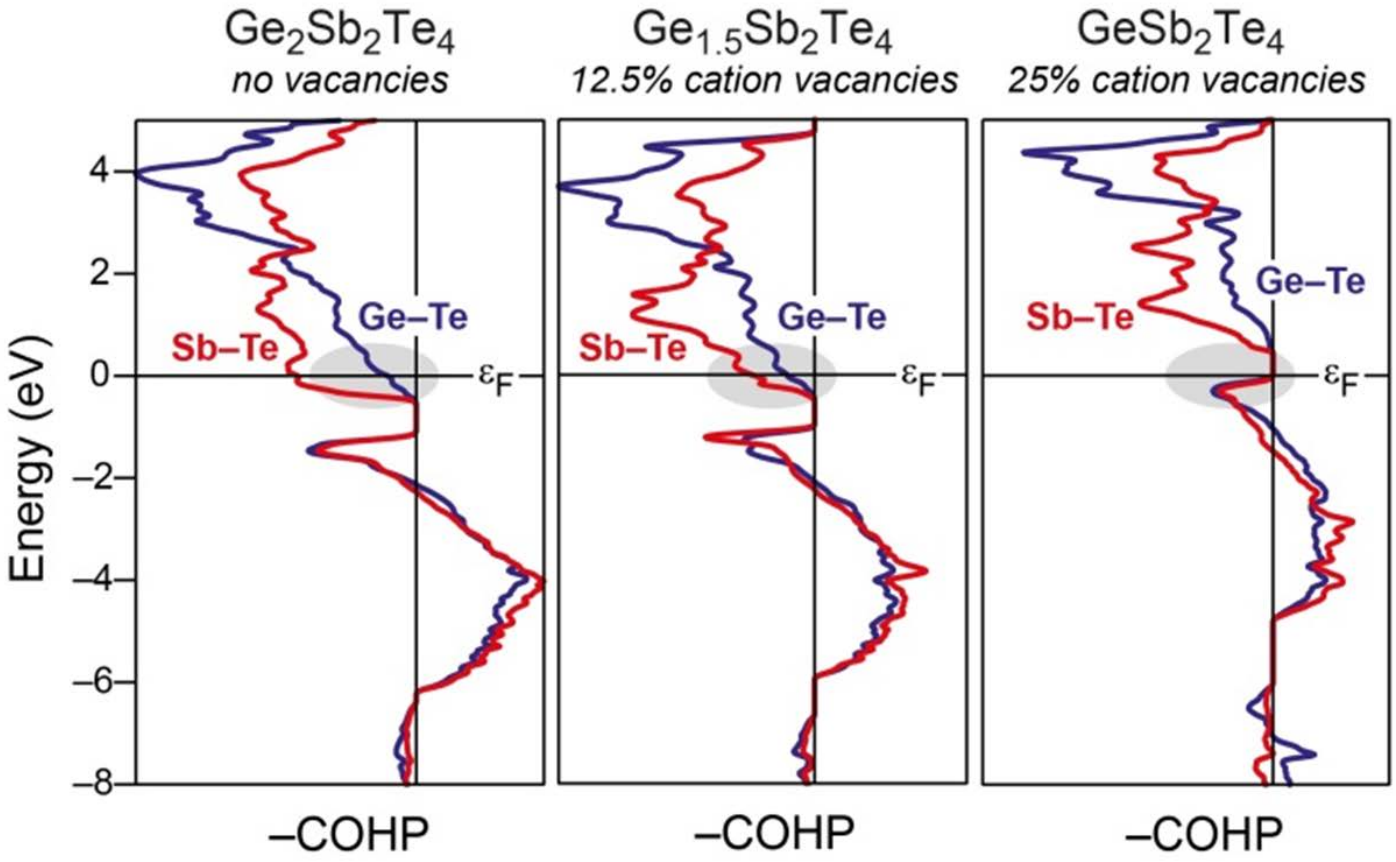
“GeSbTe” or “GST” ☠ with metastable [NaCl] structure

e.g., $Ge_2Sb_2Te_4$ with lots of Ge vacancies (≈ 20%) – **why?**

switching mechanism = *f*(vacancy nature)

Phase-change Materials: First COHP study

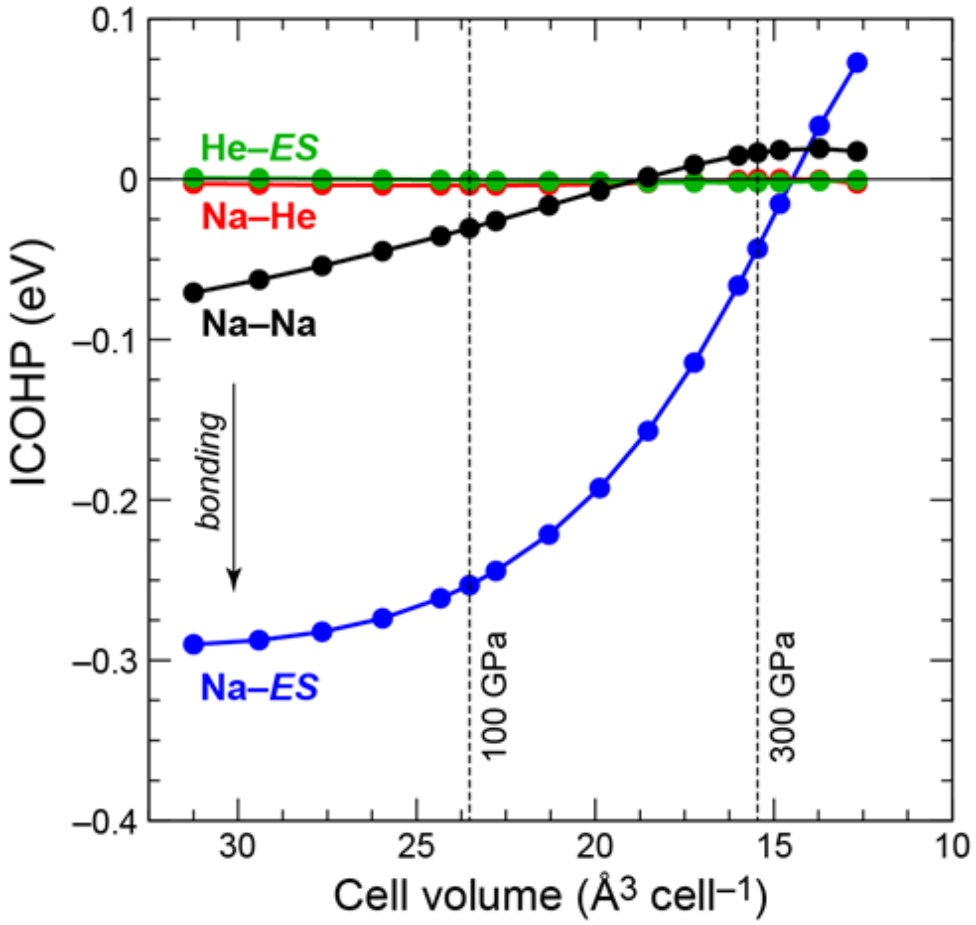


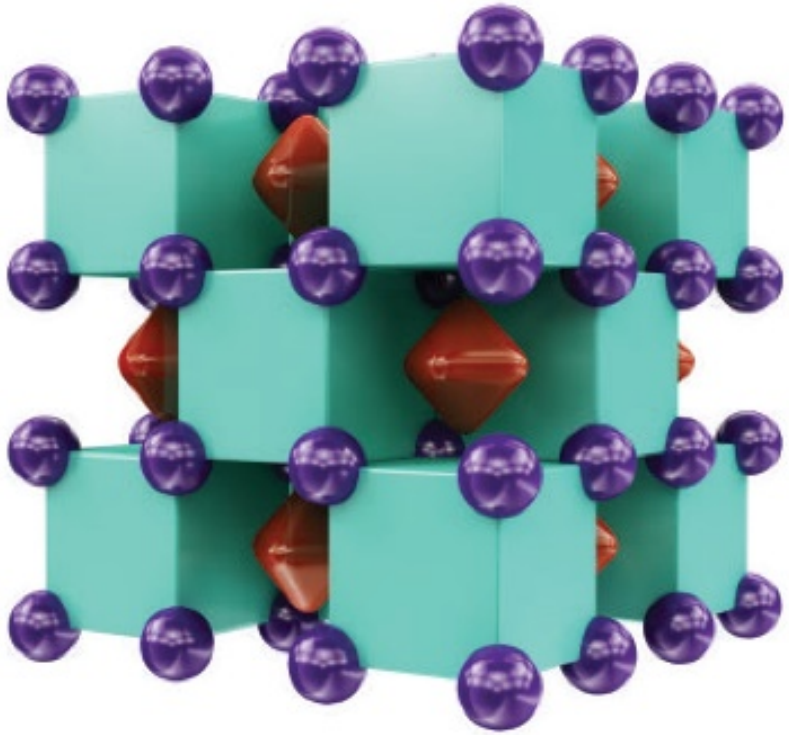


antibonding *Ge–Te and Sb–Te interactions in the highest bands; Ge/Sb vacancies annihilate antibonding states*

M. Wuttig, D. Lüsebrink, D. Wamwangi, W. Wełnic, M. Gilleßen, R. Dronskowski, *Nature Mater*. **2007**, *6*, 122

Example III: $Na_2He = (Na^+)_2He(e^-)_2$ @ 100 GPa

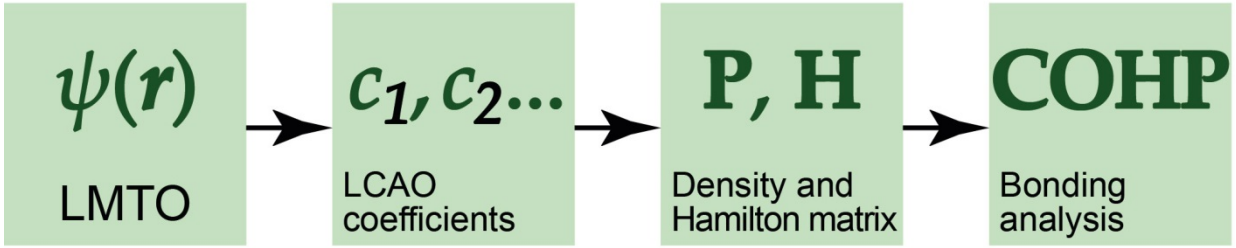




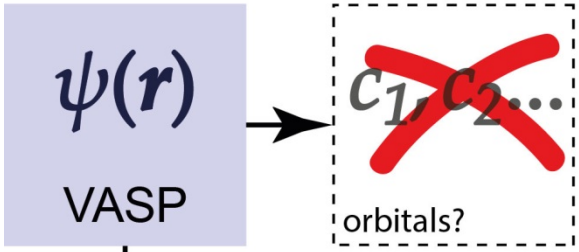
X. Dong, A. R. Oganov, A. F. Goncharov, E. Stavrou, S. Lobanov, G. Saleh, G.-R. Qian, Q. Zhu, C. Gatti, V. L. Deringer, R. Dronskowski, X.-F. Zhou, V. Prakapenka, Z. Konôpková, I. Popov, A. I. Boldyrev, H.-T. Wang, *Nature Chem.* **2017**, *9*, 440

Retrieving the Chemistry from Plane Waves

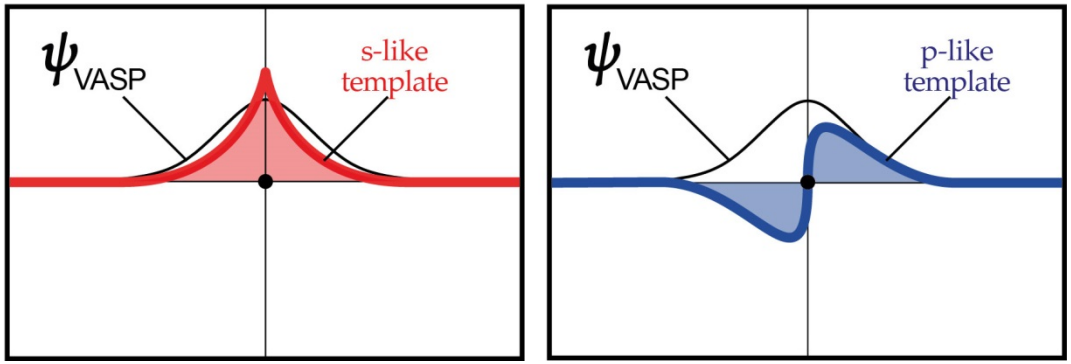
Traditionally: Tight-Binding LMTO-ASA (= densely packed atomic spheres)



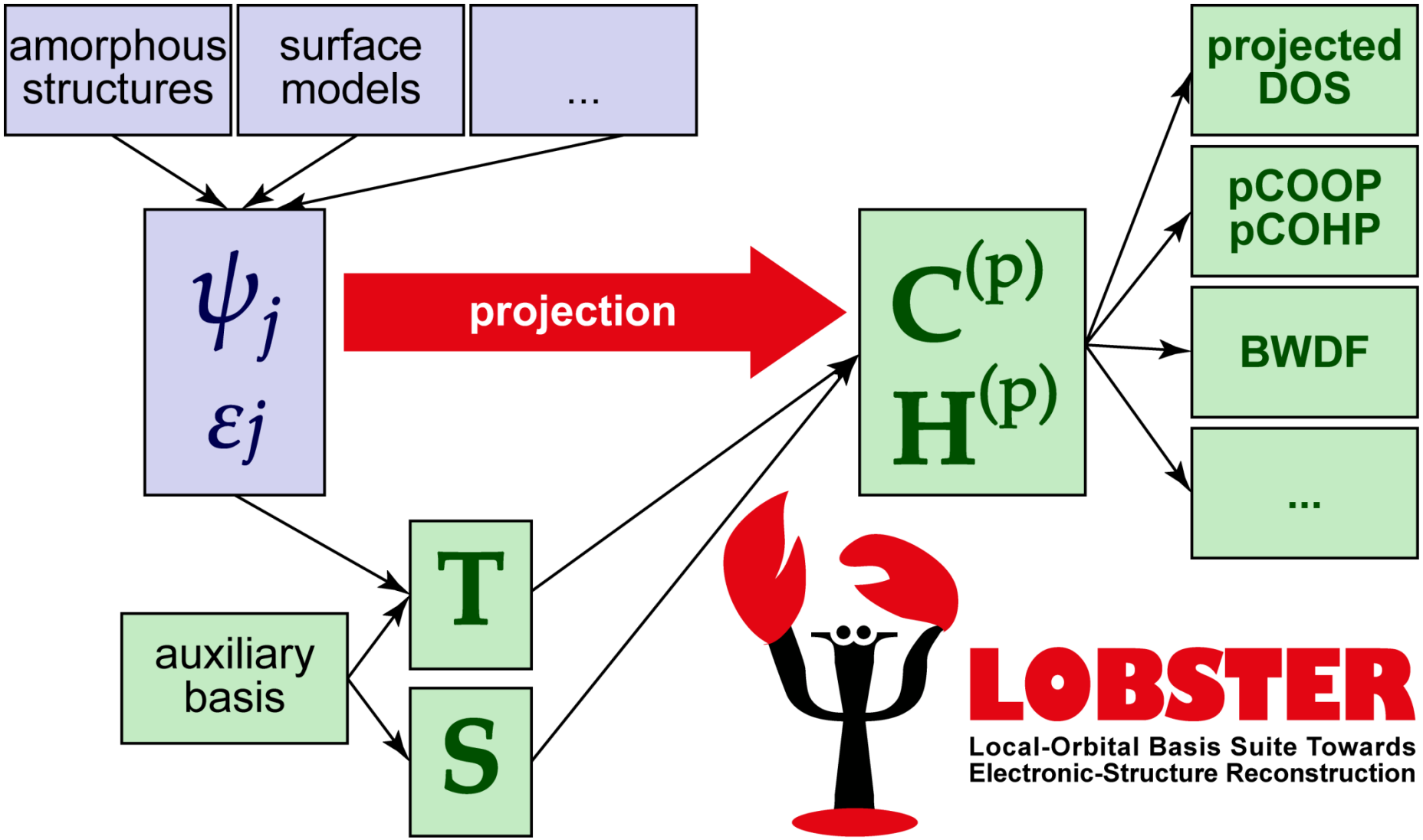
Modern: countless program packages with plane waves



Idea: local auxiliary basis set as template



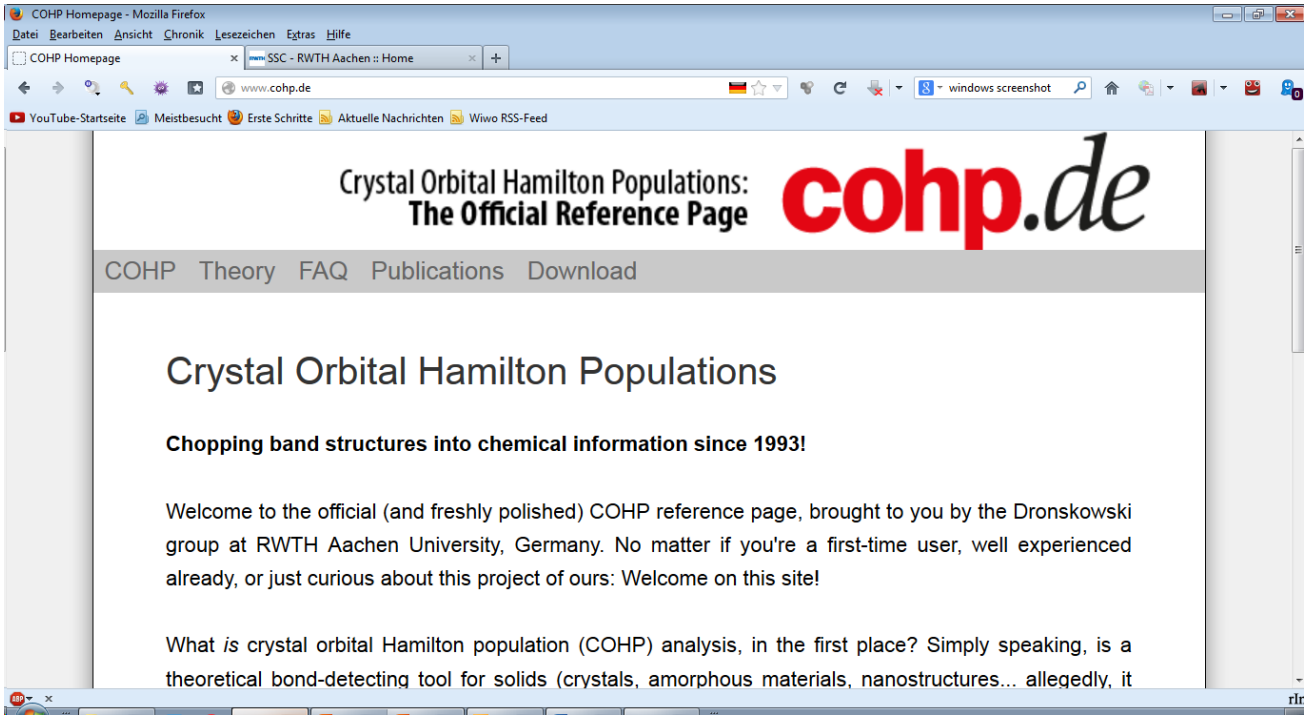
LOBSTER performs that…



freely available at www.cohp.de

Chair of Solid-State and Quantum Chemistry | RWTH AACHEN UNIVERSITY

www.cohp.de



b-initio VASP package Vienna Simulation

Abinit

QUANTUMESPRESSO

cecam Centre Européen de Calcul Atomique et Moléculaire

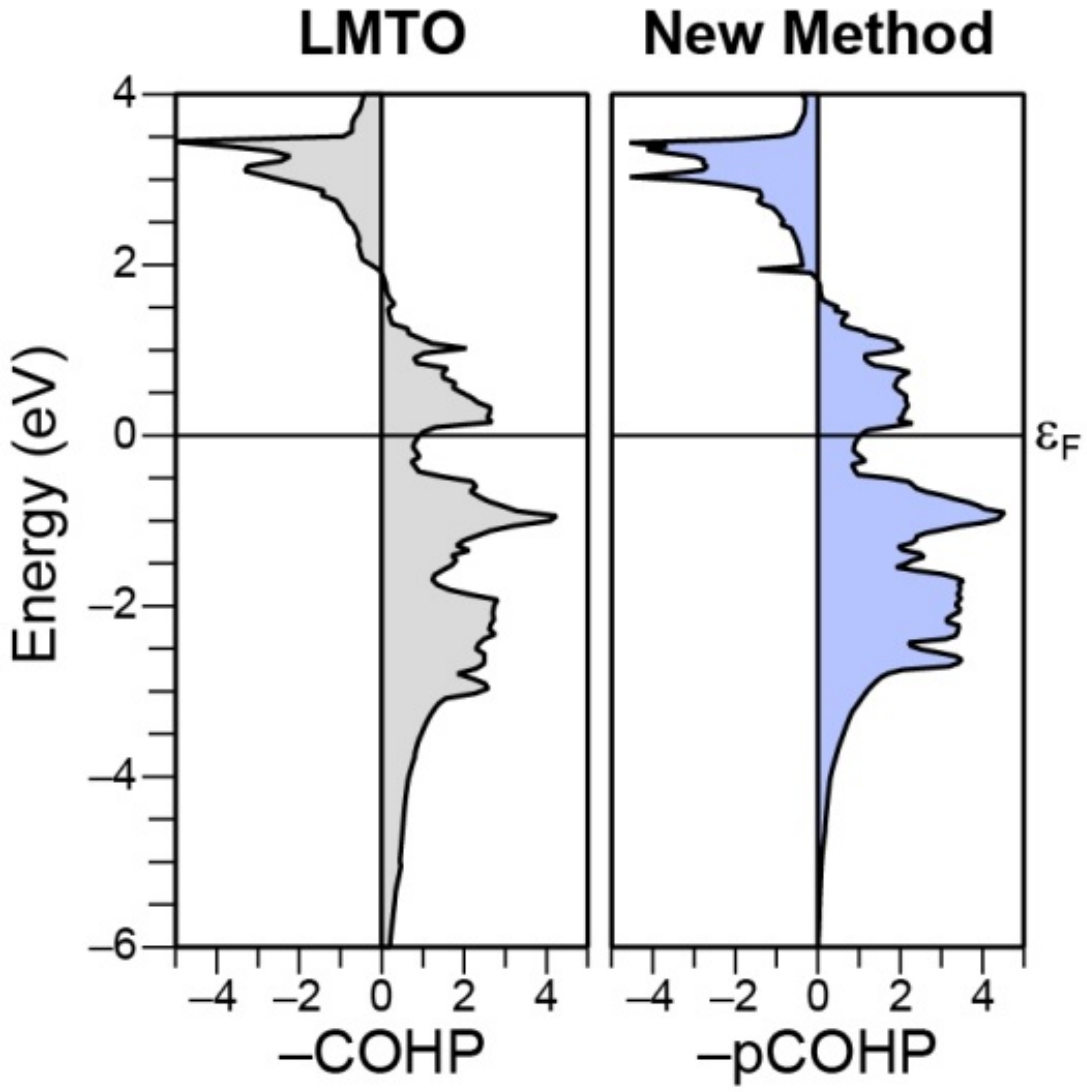
school:

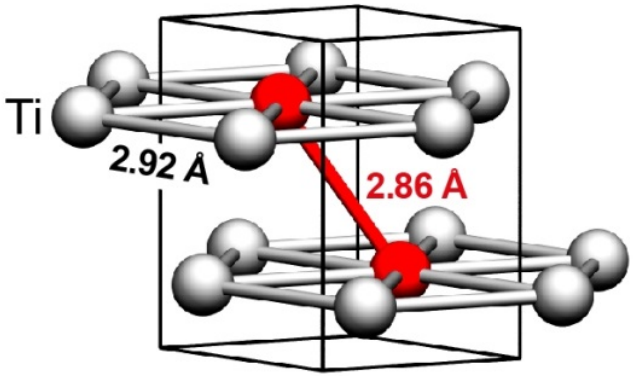
Explicit Chemical-Bonding Analysis of Materials from High-Performance First-Principles Simulations

September 25–29, Jülich

Chair of Solid-State and Quantum Chemistry | RWTH AACHEN UNIVERSITY

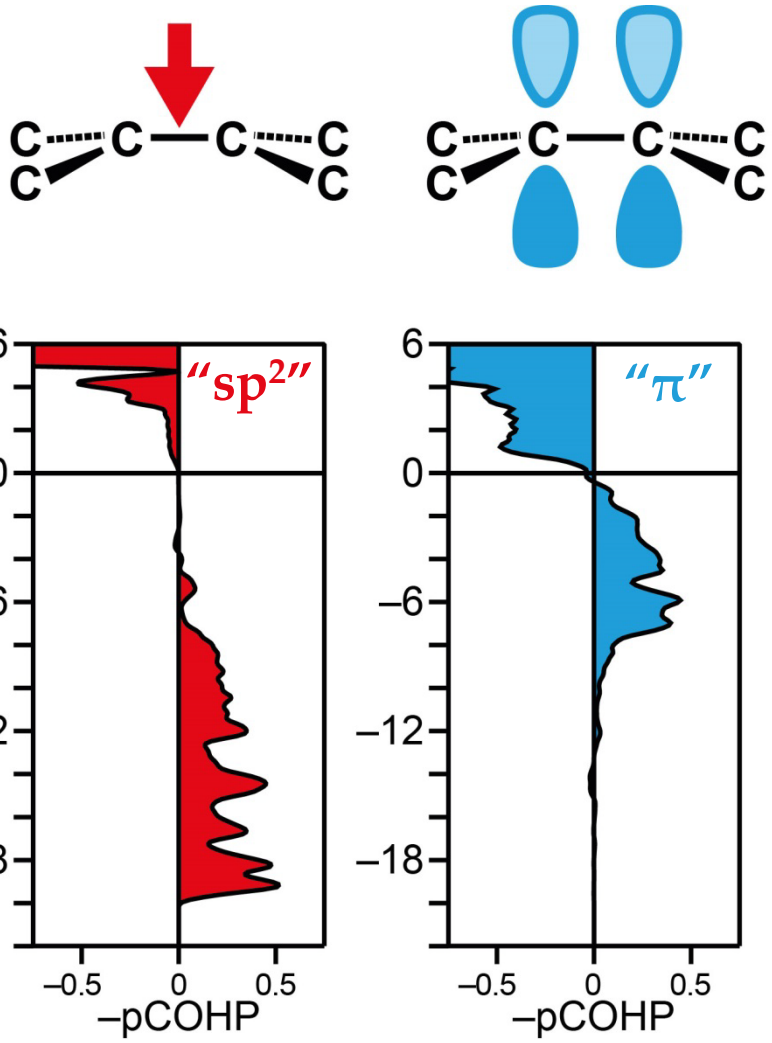
Titanium (hcp): Comparison with LMTO

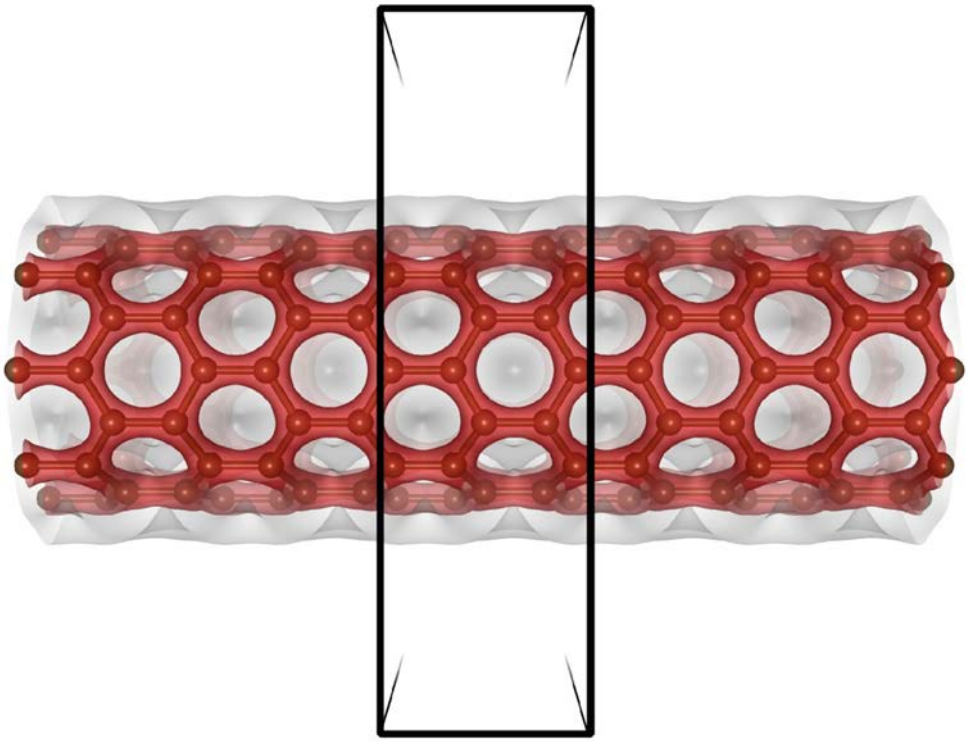




S. Maintz, V. L. Deringer,
A. L. Tchougréeff,
R. Dronskowski,
J. Comput. Chem. **2013**, *34*, 2557

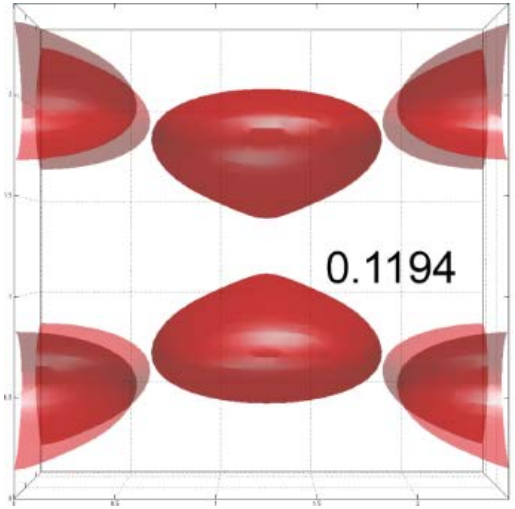
Chemical Bonding in the Carbon Nanotube



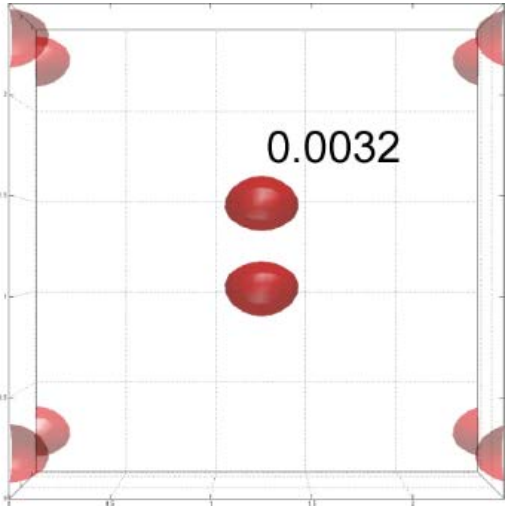


S. Maintz, V. L. Deringer,
A. L. Tchougréeff, R. Dronskowski,
J. Comput. Chem. **2016**, *37*, 1030

ABINIT: extended basis sets (e.g, for beryllium)



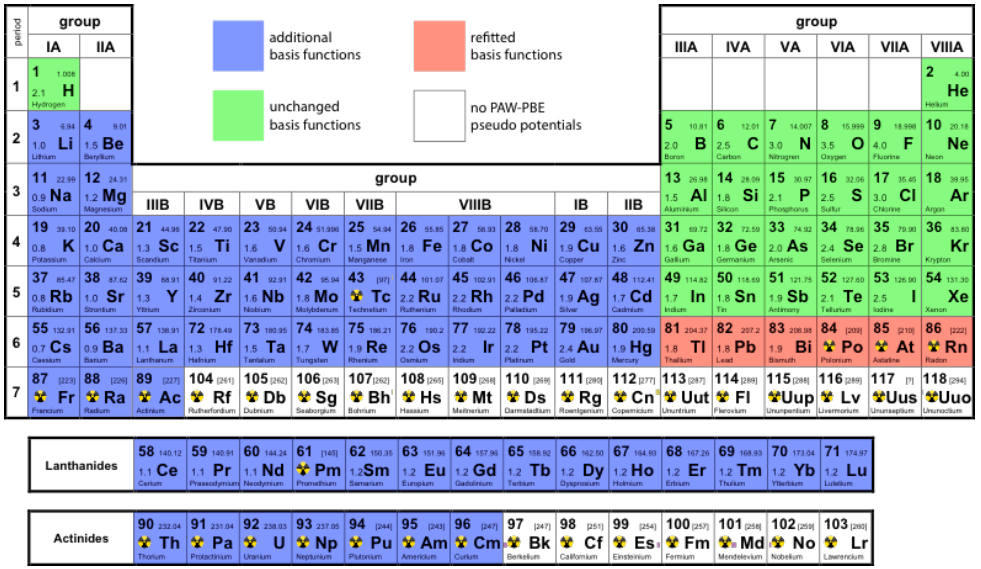
1s, 2s



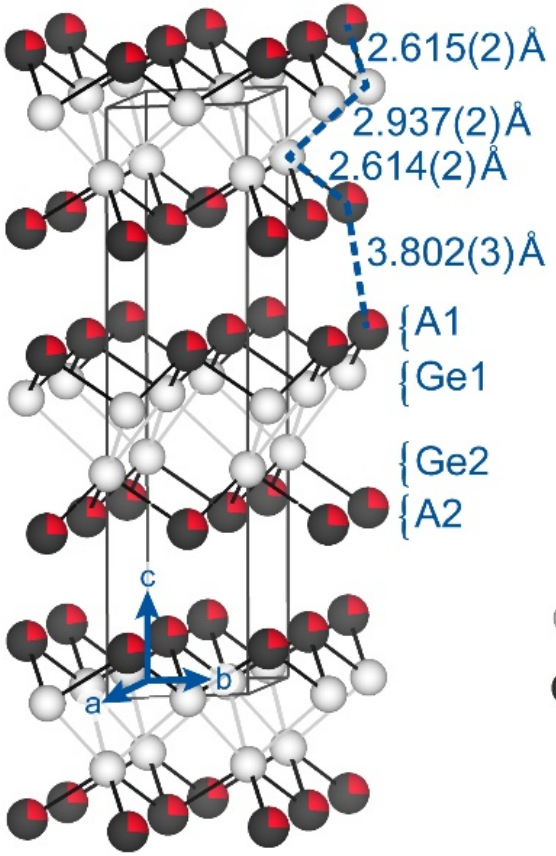
1s, 2s, 2p

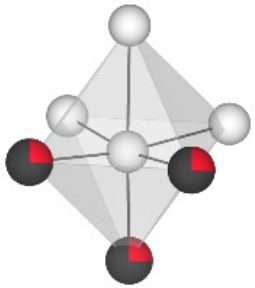
Isosurfaces (in Å^{-3}) at 65% of the differences between the ABINIT-based PAW densities and the LOBSTER-projected densities for the fourth band of β-Be at Γ

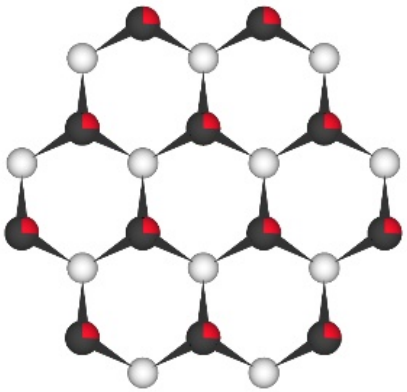
available since LOBSTER 2.1.0

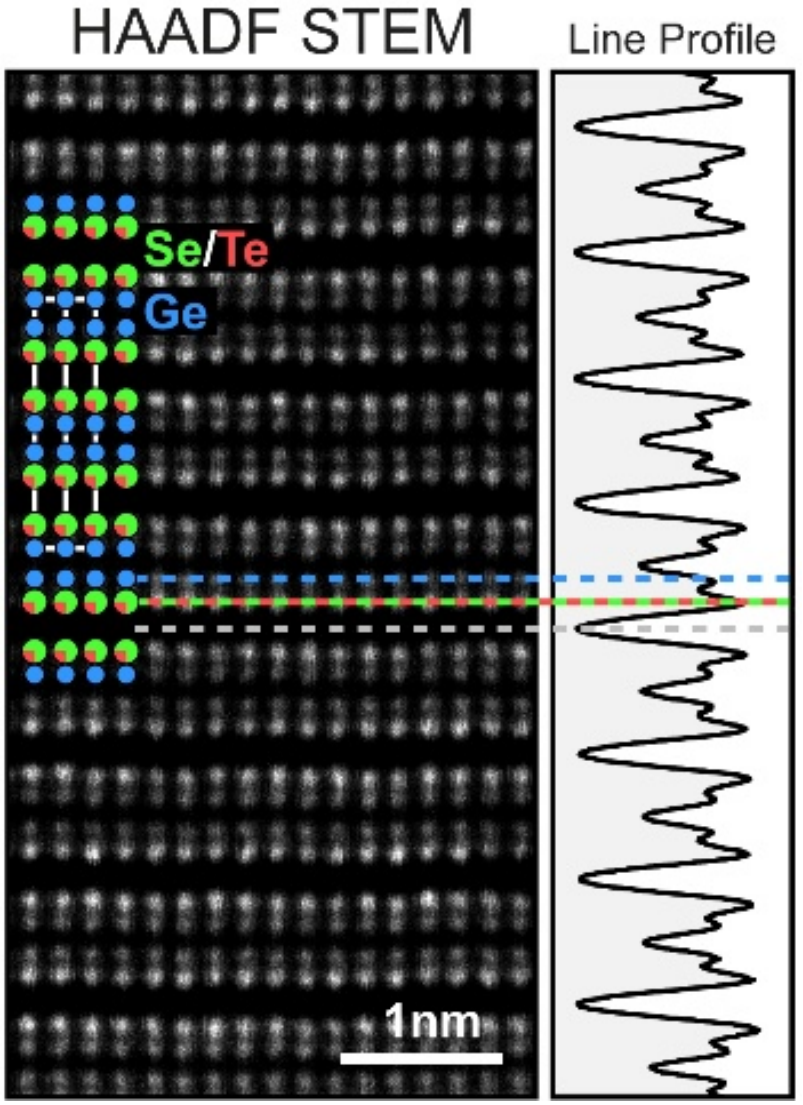


Ge_4Se_3Te, Structure & TEM: Ge–Ge = 2.94 Å

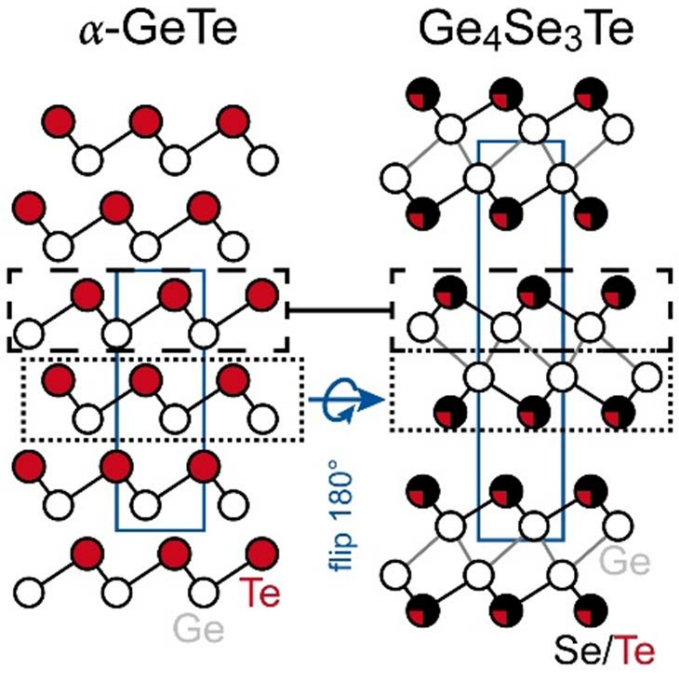


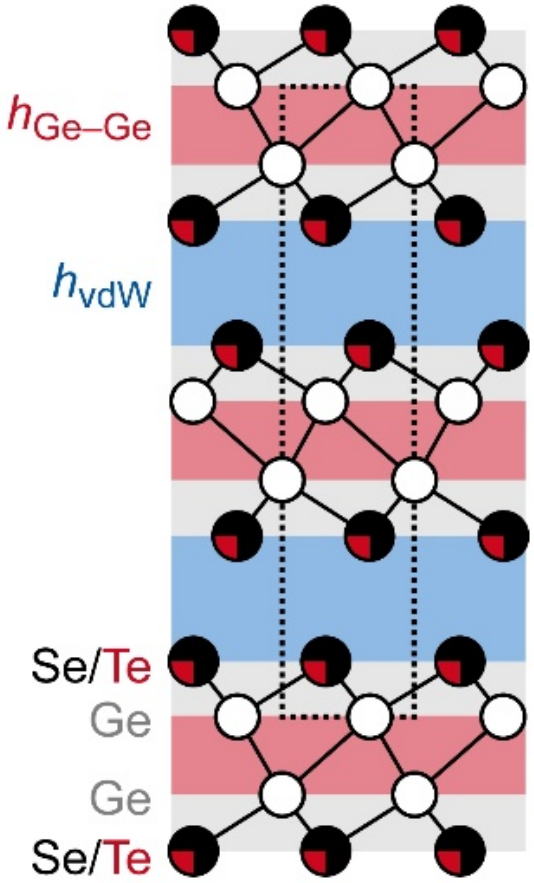


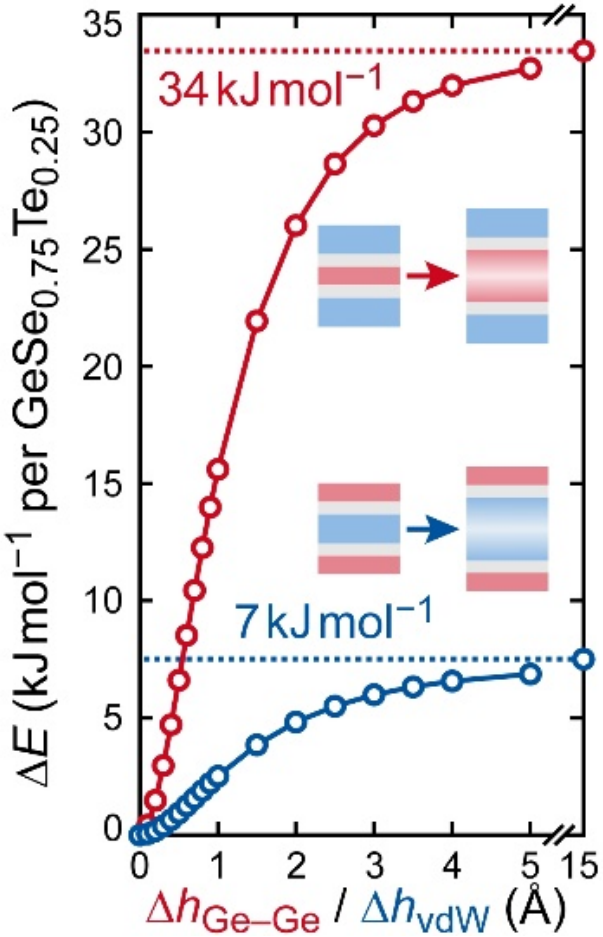




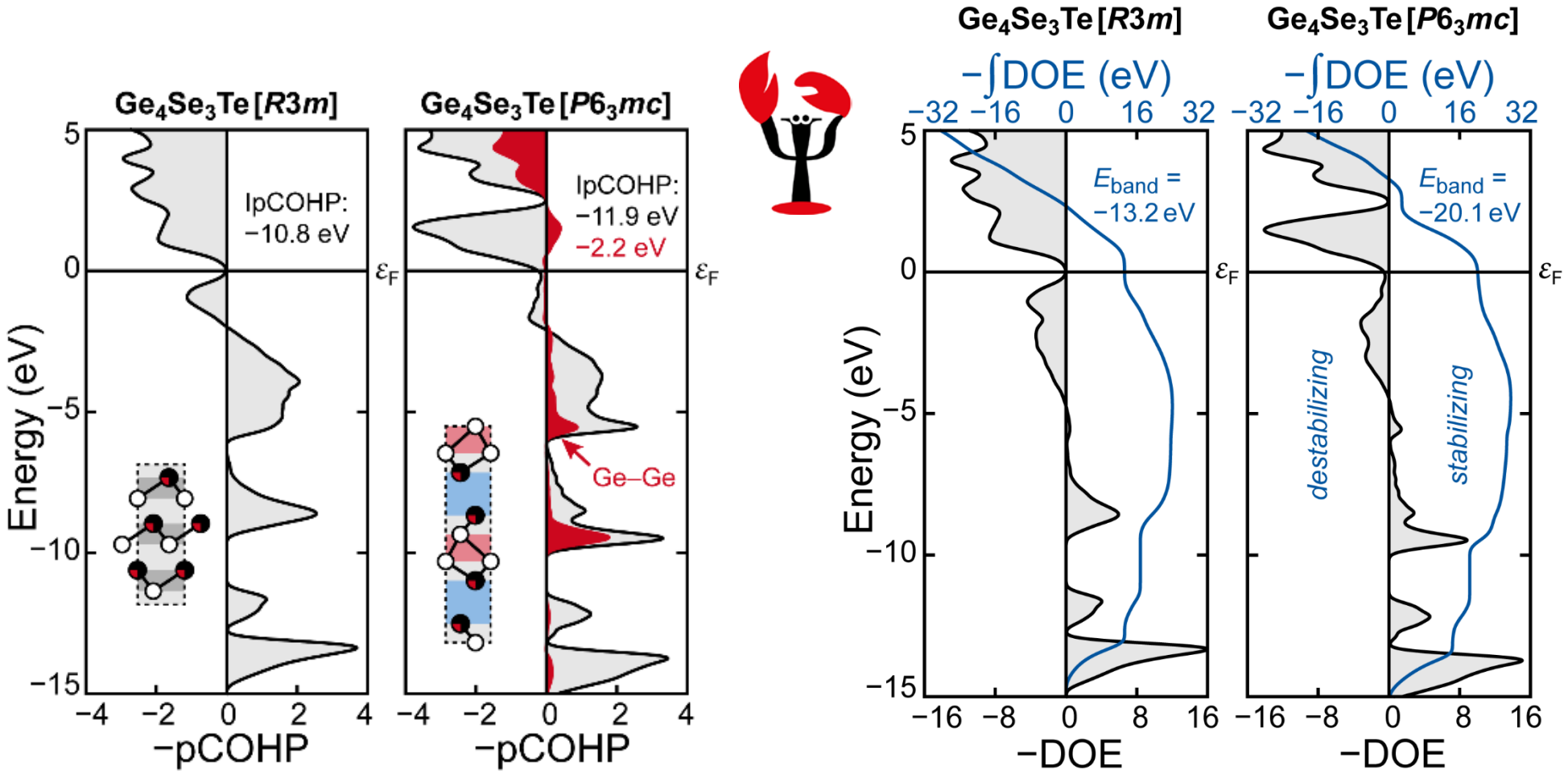
Ge_4Se_3Te: layers & forces (DFT+dispersion)







Ge_4Se_3Te: COHP & Density-of-Energy (DOE)



M. Küpers, P. M. Konze, S. Maintz, S. Steinberg, A. M. Mio, O. Cojocaru-Mirédin, M. Zhu, M. Müller, M. Luysberg, J. Mayer, M. Wuttig, R. Dronskowski, *Angew. Chem. Int. Ed.*, in press.

Benchmarking the Plane-wave Guys...

Basis: Bunge

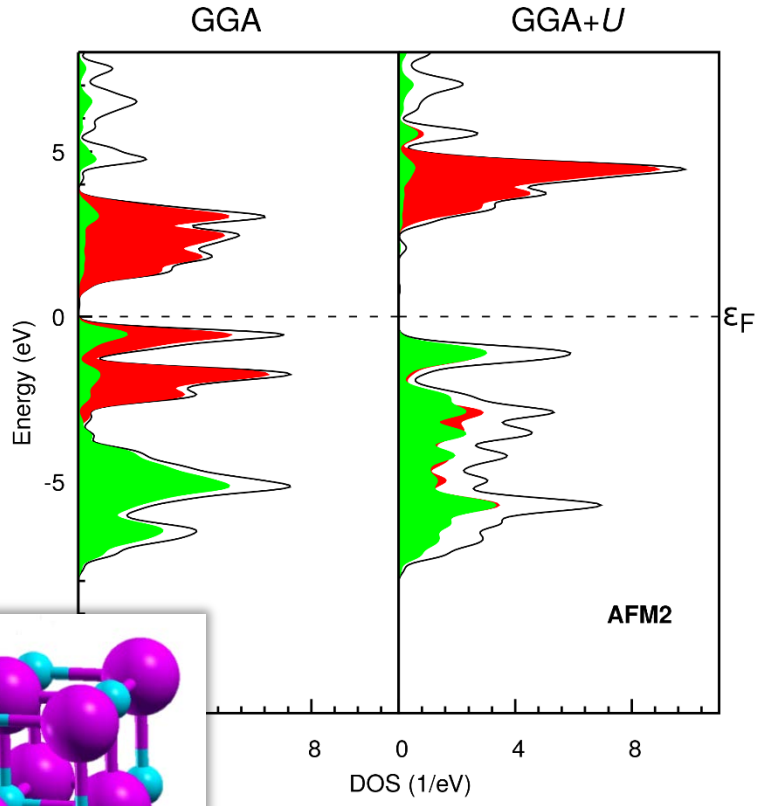
abs. charge spilling (%)

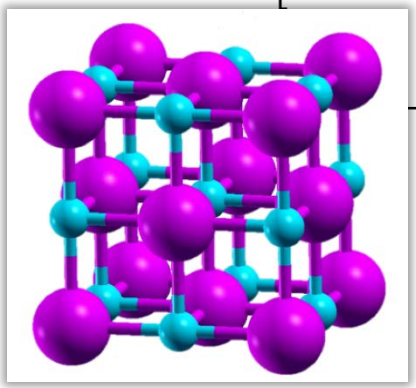
materials \ Interfaces	Espresso	VASP	ABINIT
Diamond	1.11	0.98	1.50
GaAs	0.73	0.88	0.56
Ti	2.01	7.83	3.07
fullerene	1.33	1.16	1.89
carbon-nanotube	1.27	1.10	1.80

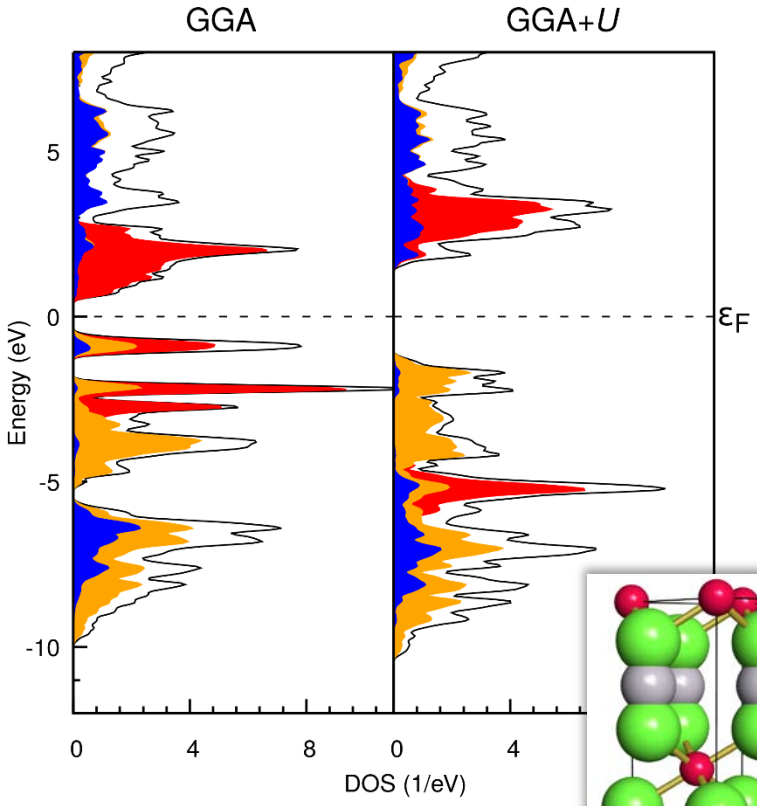
execution time (s)

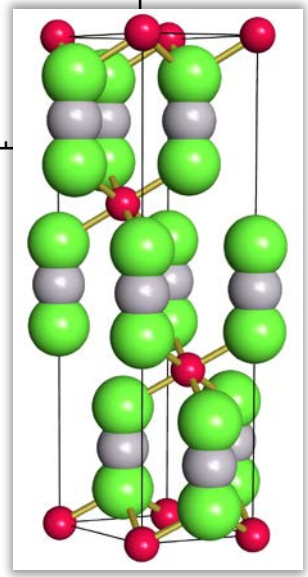
materials \ Interfaces	Espresso	VASP	ABINIT
Diamond	152	36	92
GaAs	611	170	504
Ti	102	33	105
fullerene	719	519	517
carbon-nanotube	114	332	176

Correlated Stuff: MnO and MnNCN

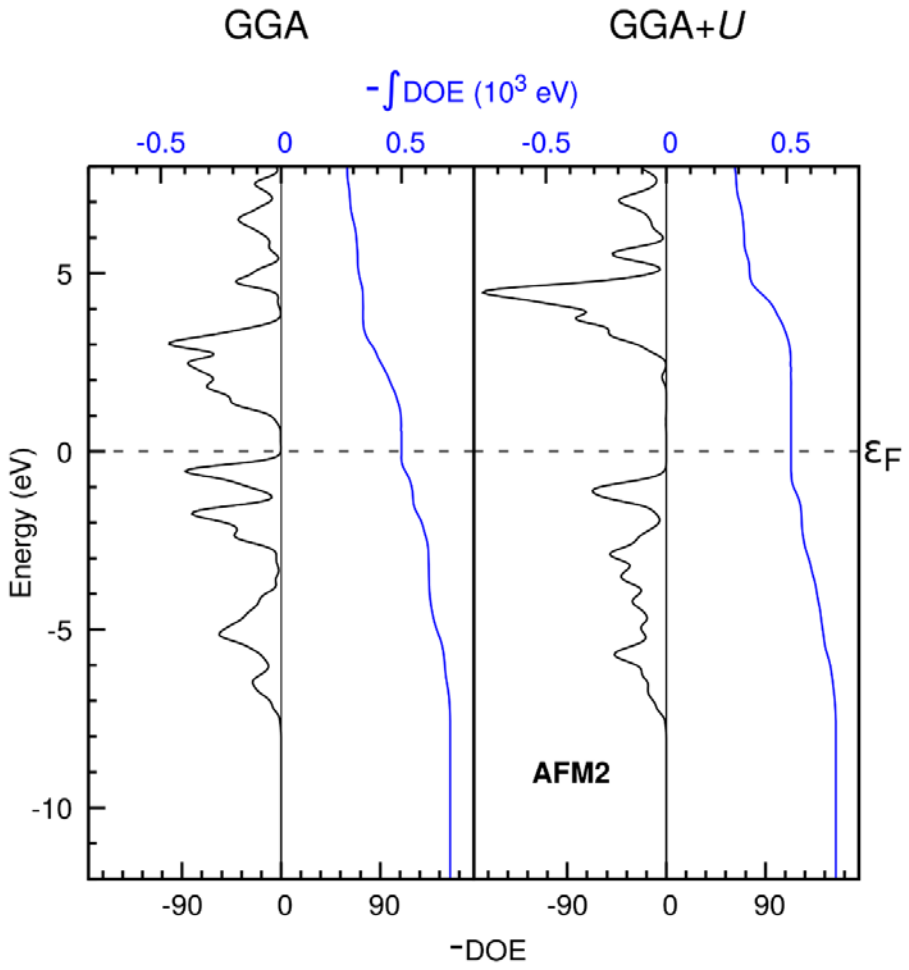


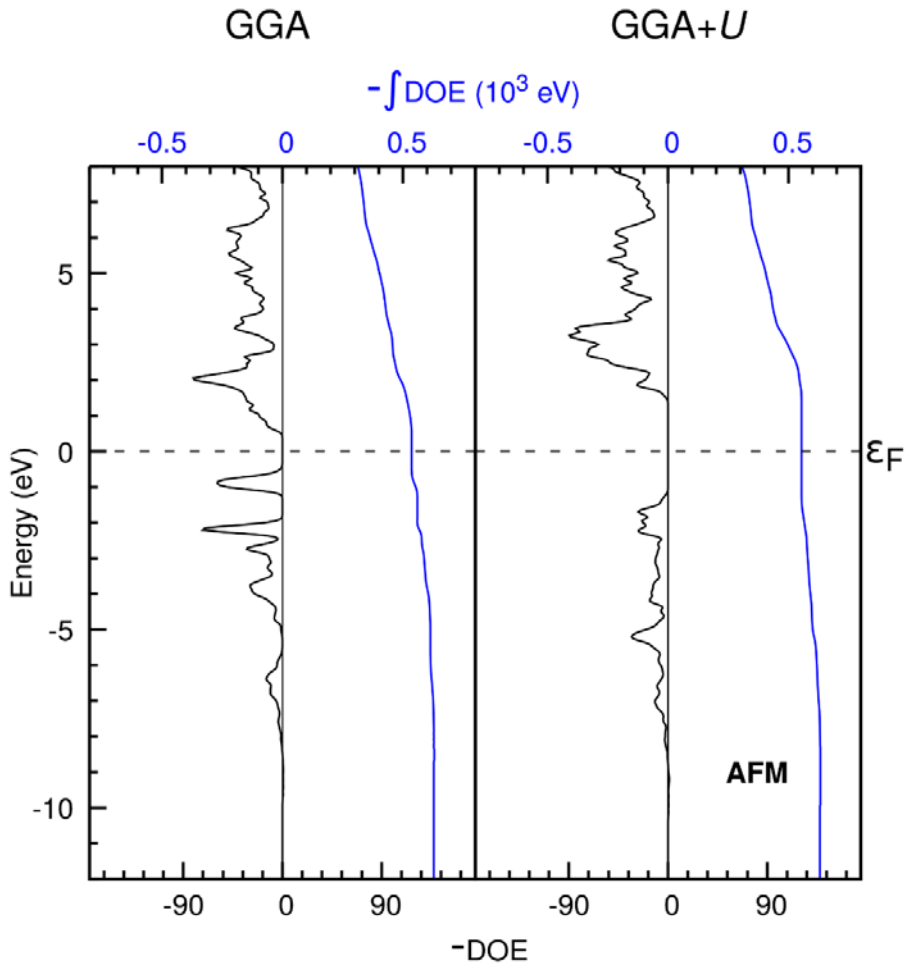






Density-of-Energy: MnO and MnNCN

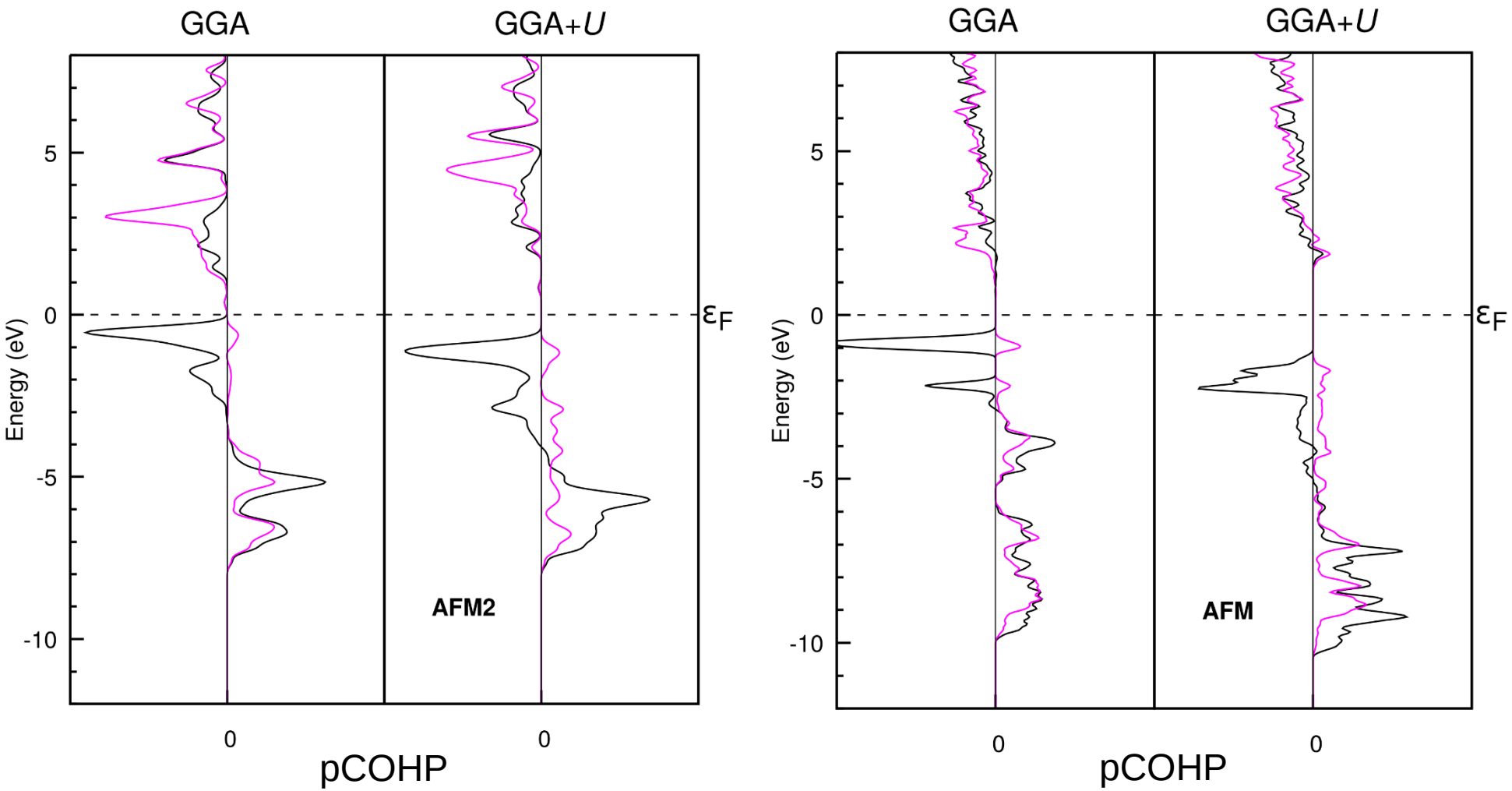




$$\mathrm{DOE}(E) = \sum_{k} \sum_{A} \sum_{\substack{\mu \\ \mu \in A}} \sum_{B} \sum_{\substack{\nu \\ \nu \in B}} P_{\mu\nu}(E,k)\, H_{\mu\nu}(k)$$

$$E_{\mathrm{band}} = \int_{-\infty}^{\varepsilon_{\mathrm{F}}} \mathrm{DOE}(E)\, dE$$

Mn–O versus Mn–N bonding



ABINIT Questions…

With respect to the next development of LOBSTER which shall include local orbitals from the pseudopotentials as a basis:

- *LOBSTER can only process ABINIT data that are calculated with PPs from the JTH PAW atomic dataset. How were these PPs in the JTH PAW dataset constructed/created?*
- *Can one construct his own PAW PPs with the ABINIT main binary?*
- *If not, how can one construct his own PAW PPs to be used for ABINIT calculations? What are the steps in detail?*

Finis