

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

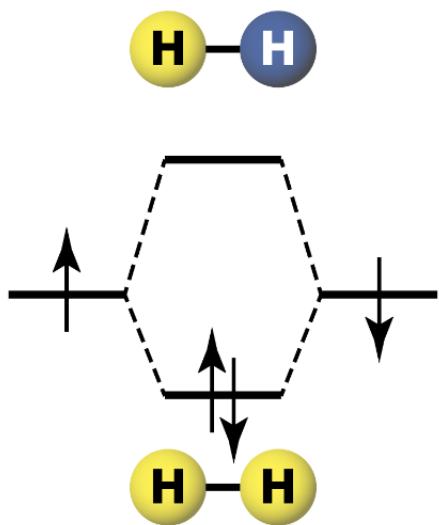
Ge-Ge bonds in Phase-Change Materials, Density-of-Energy (DOE)

Plane-wave Benchmarking, **ABINIT** implementation

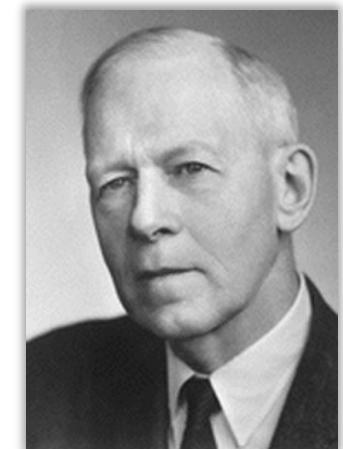
Correlated Stuff

H_2 : Population Analysis by Robert S. Mulliken

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



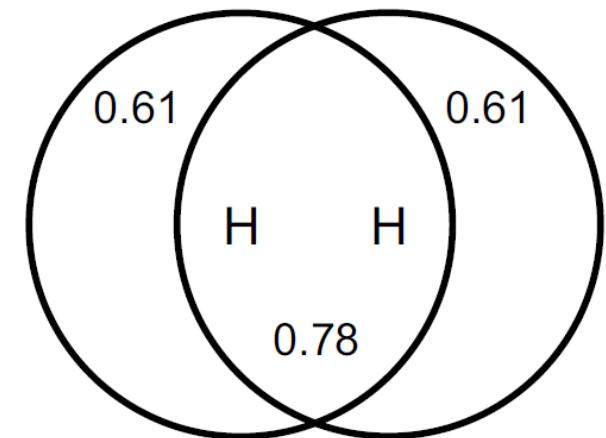
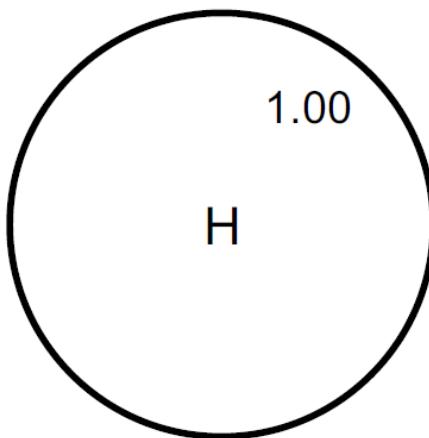
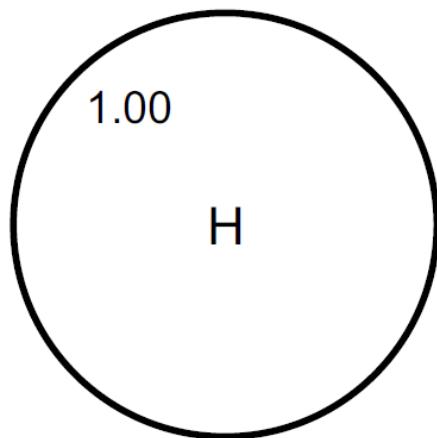
R. S. Mulliken,
J. Chem. Phys. **1955**, *23*, 1833



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

Simplest Population Analysis for σ_g -MO of H_2

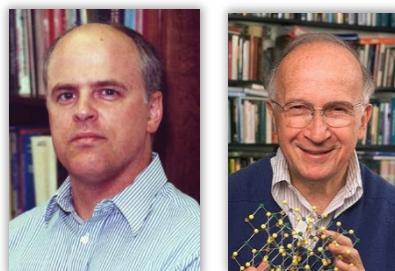
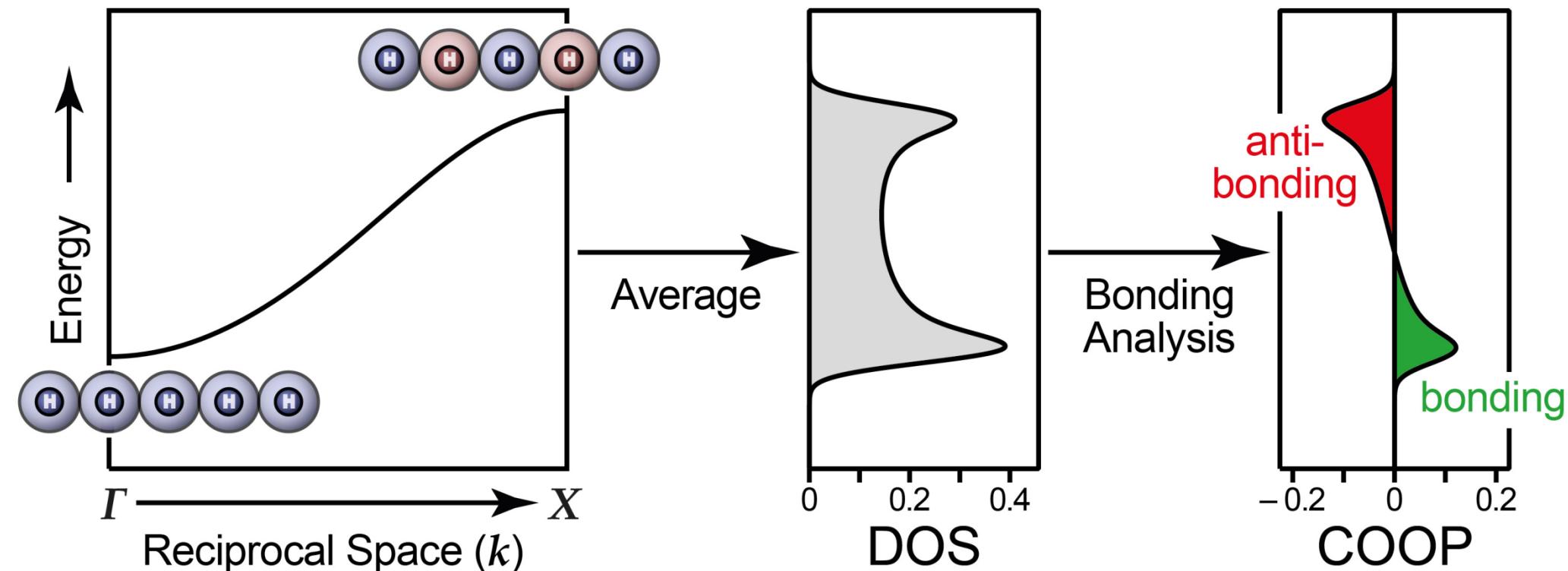
$$1 = \underbrace{\frac{1}{2(1 + S_{12})}}_{=0.305} + \underbrace{\frac{1}{2(1 + S_{12})}}_{=0.305} + \underbrace{\frac{2}{2(1 + S_{12})} S_{12}}_{=0.390}$$



the two hydrogen atoms share 0.78 electrons

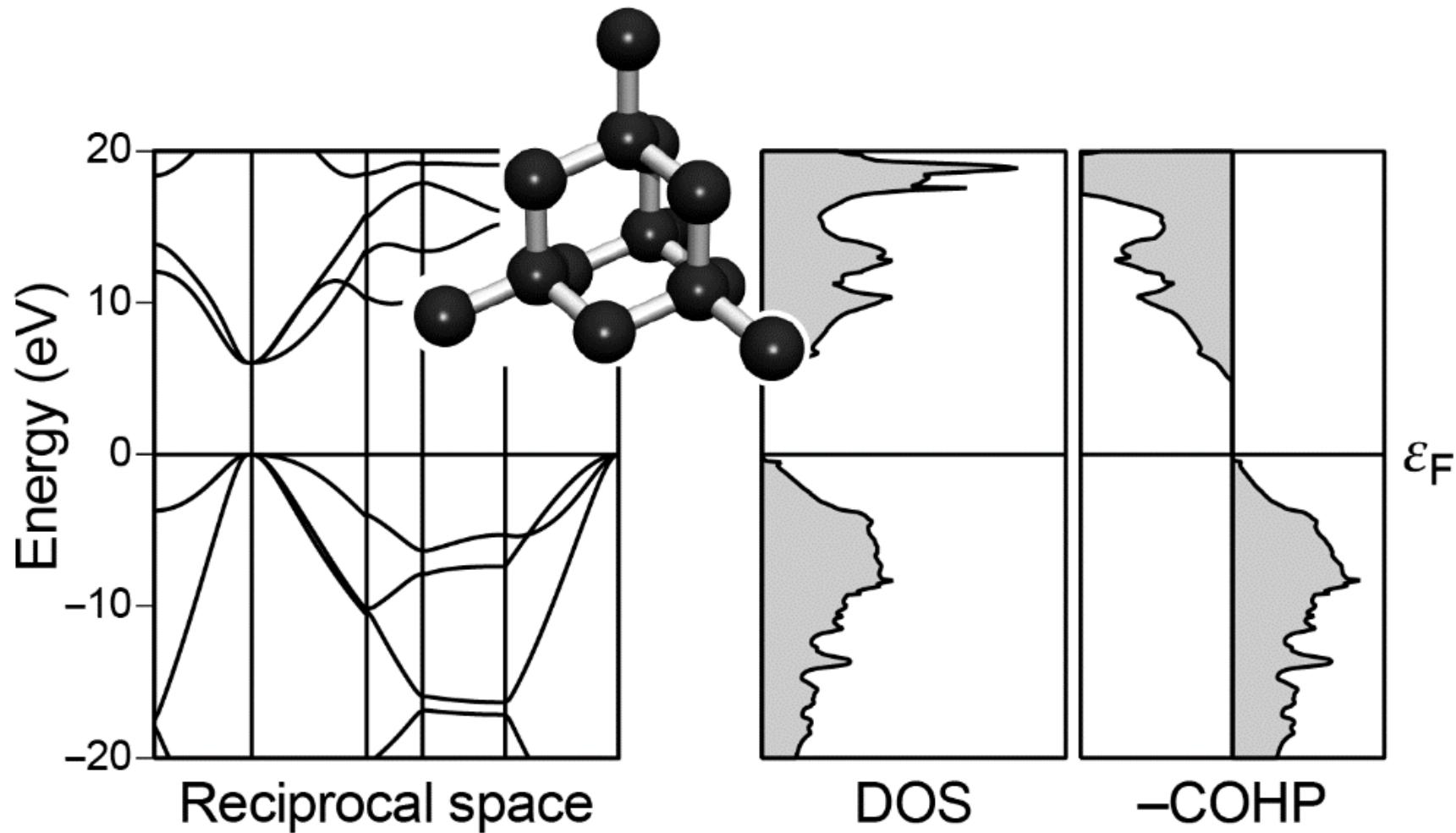
1dim H-chain: band structure, DOS, COOP

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



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

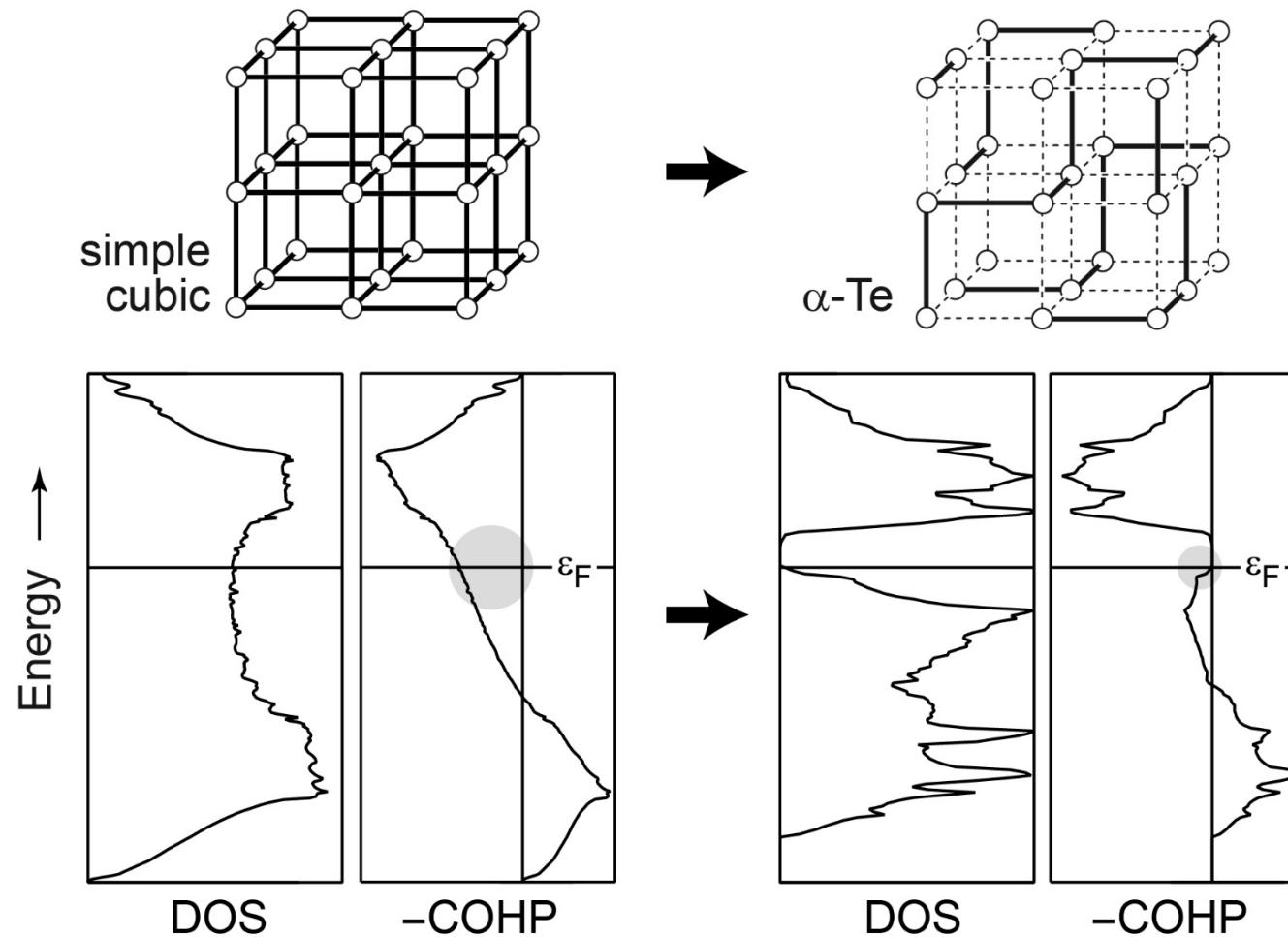
DFT: Crystal Orbital Hamilton Population, COHP



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

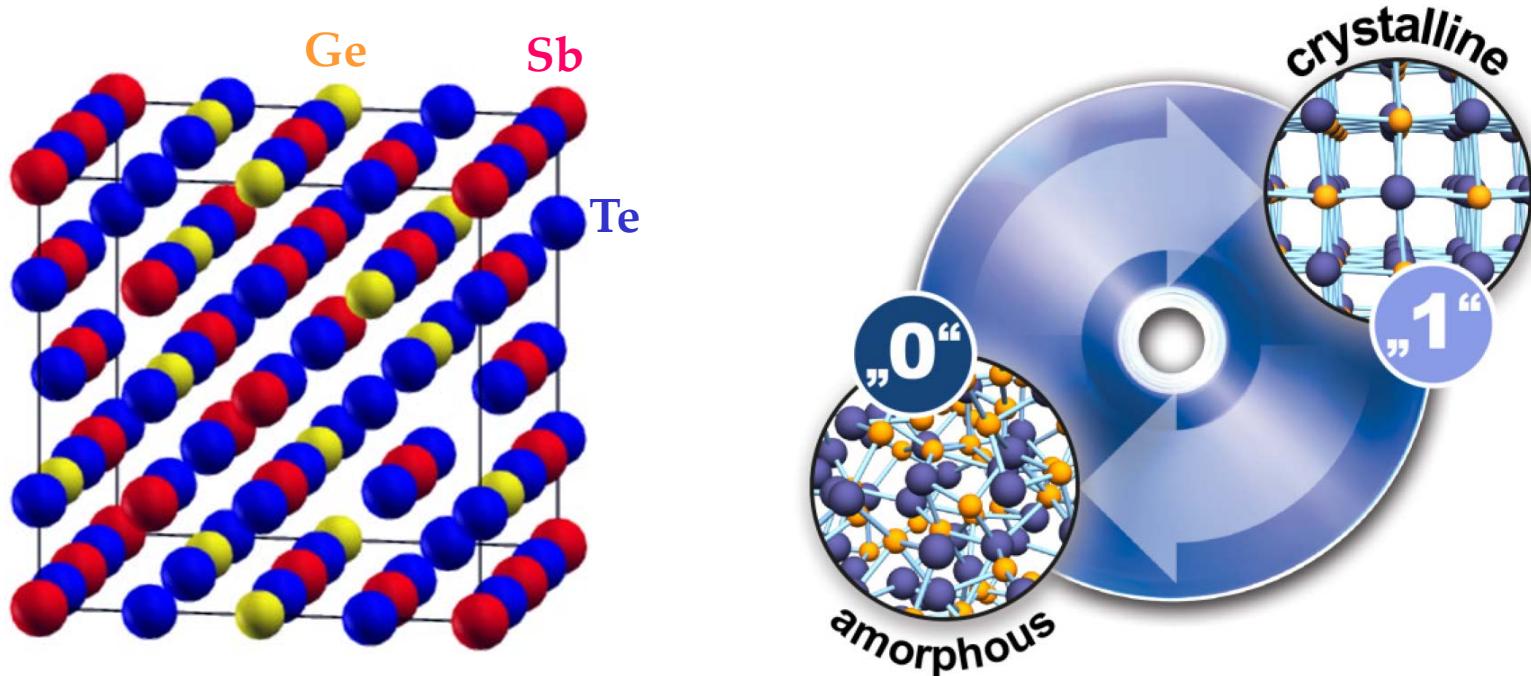


Example I: sc Tellurium is Peierls-unstable



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

Example II: Phase-change Materials

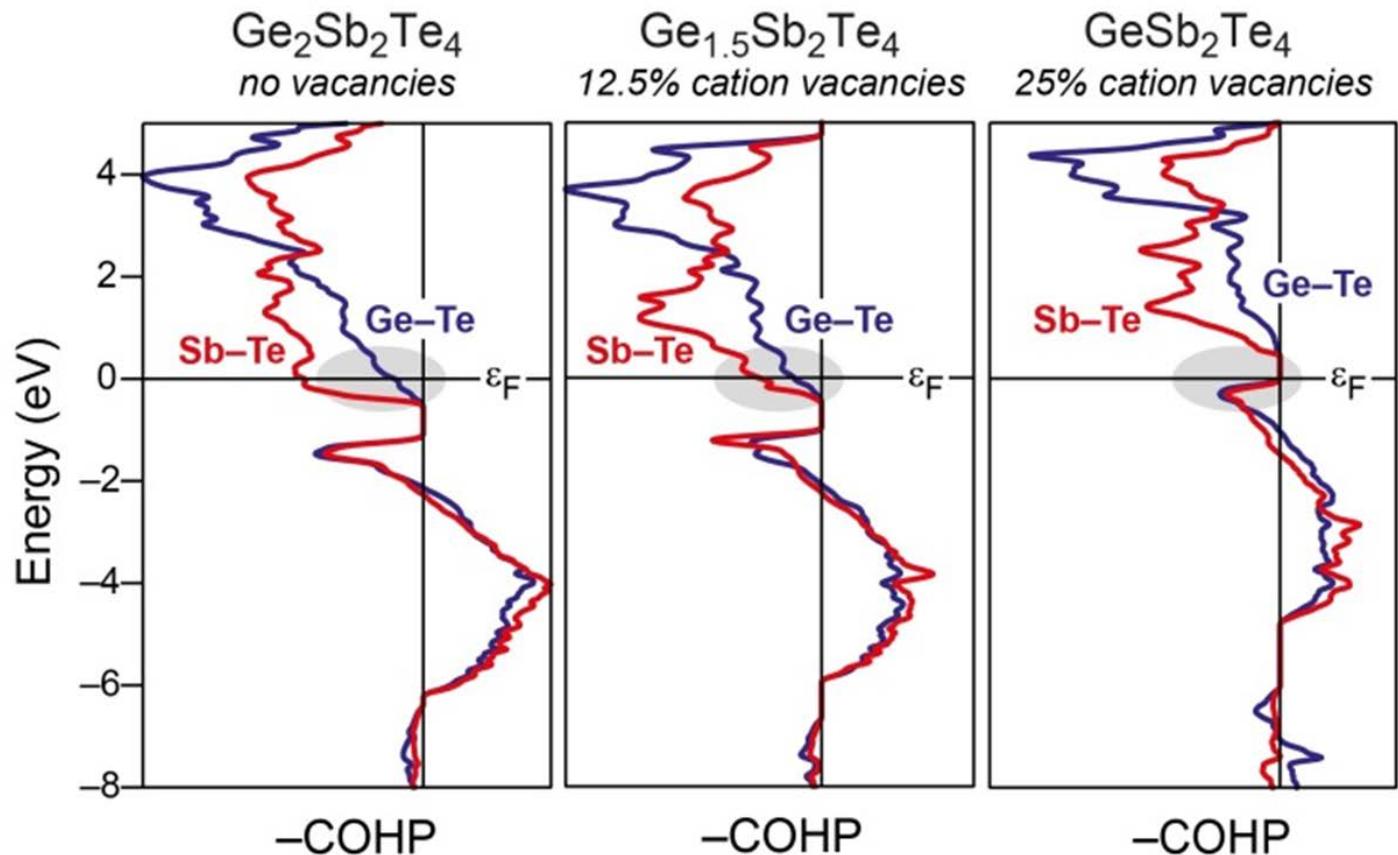
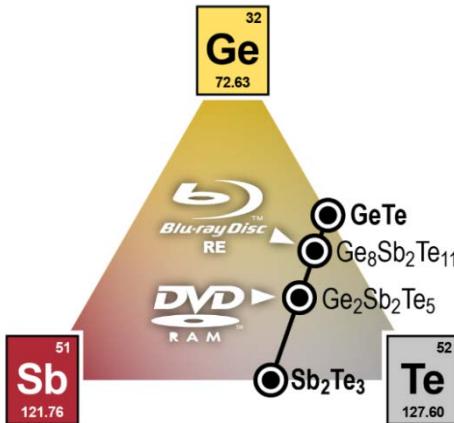


“GeSbTe” or “GST” ☠ with metastable [NaCl] structure

e.g., $\text{Ge}_2\text{Sb}_2\text{Te}_4$ with lots of Ge vacancies ($\approx 20\%$) – **why?**

switching mechanism = $f(\text{vacancy nature})$

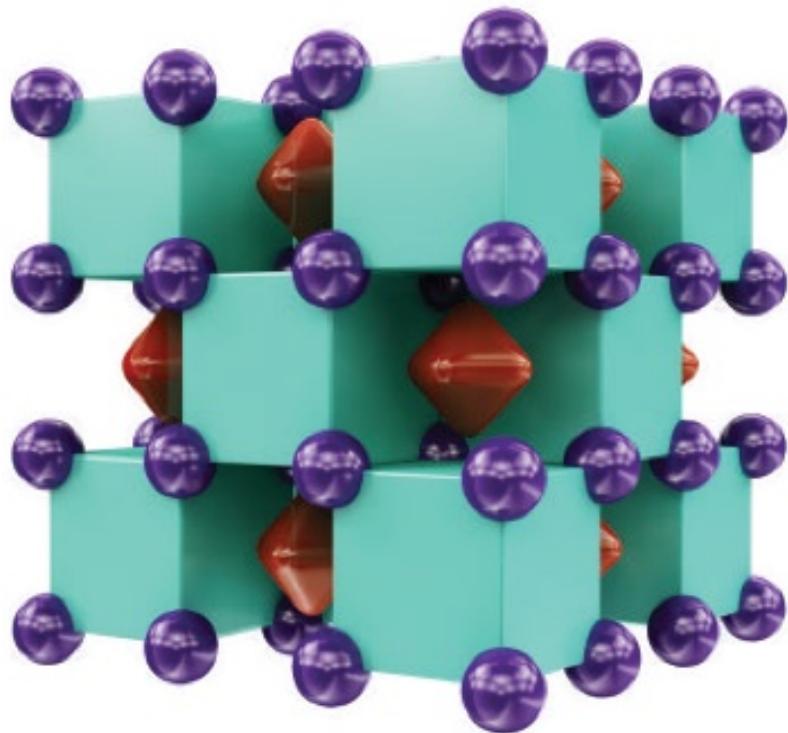
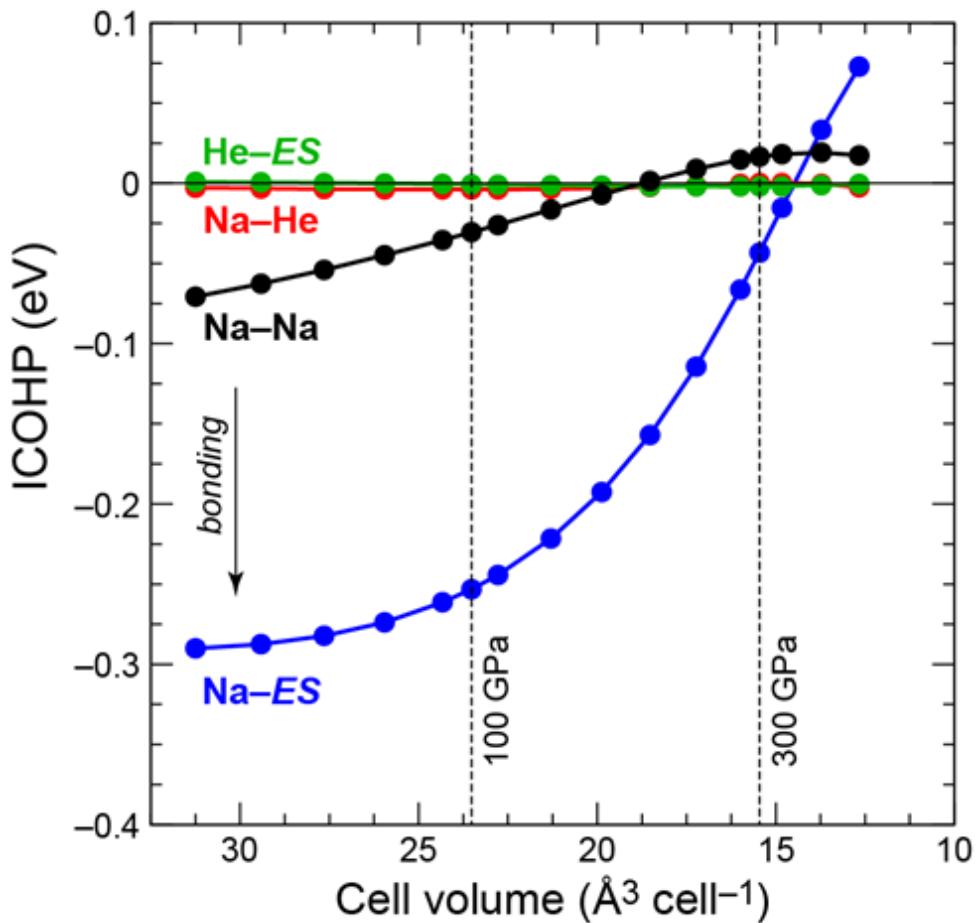
Phase-change Materials: First COHP study



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

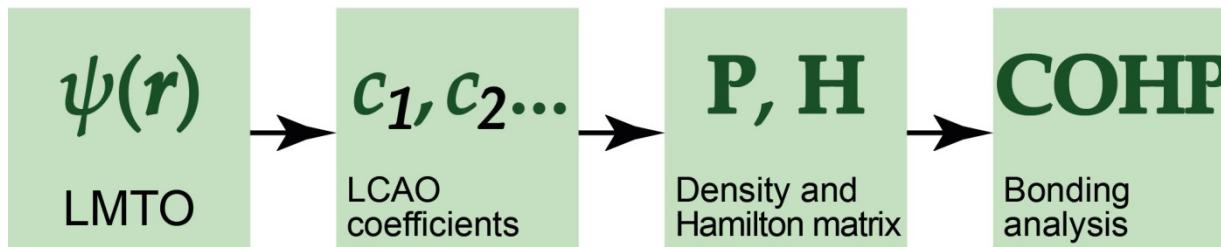
Example III: $\text{Na}_2\text{He} = (\text{Na}^+)_2\text{He}(\text{e}^-)_2$ @ 100 GPa



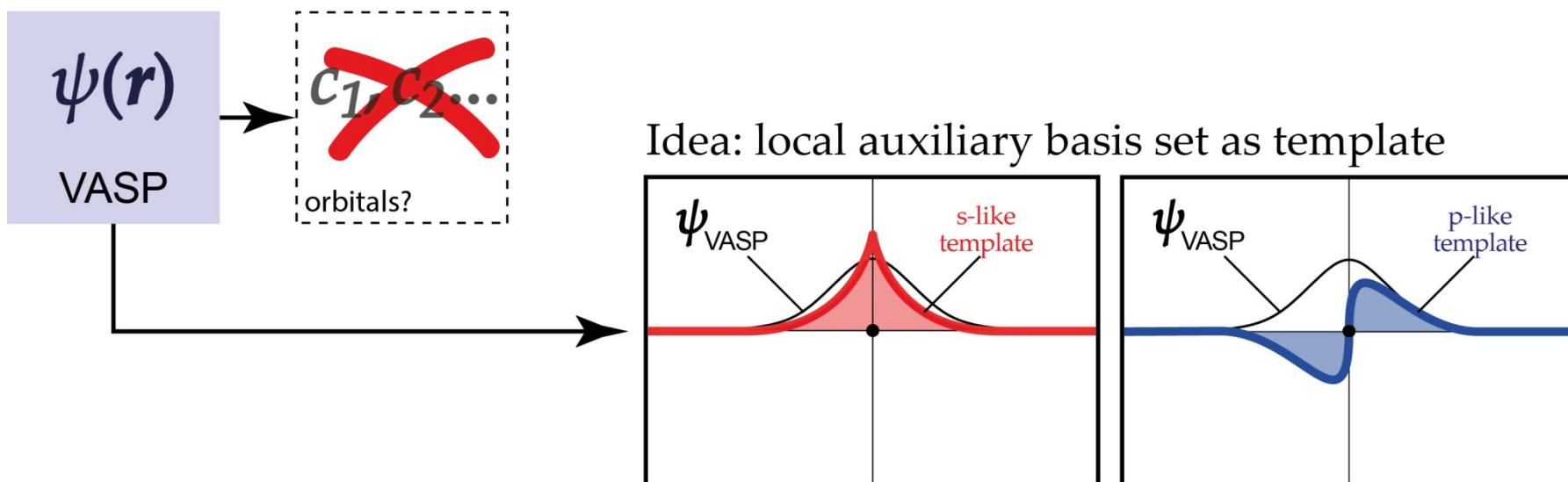
X. Dong, A. R. Oganov, A. F. Goncharov, E. Stavrou,
S. Lobanov, G. Saleh, G.-R. Qian, Q. Zhu, C. Gatti, V. L. Deringer,
R. Dronskowski, X.-F. Zhou, V. Prakapenka, Z. Konôpková,
I. Popov, A. I. Boldyrev, H.-T. Wang, *Nature Chem.* 2017, 9, 440

Retrieving the Chemistry from Plane Waves

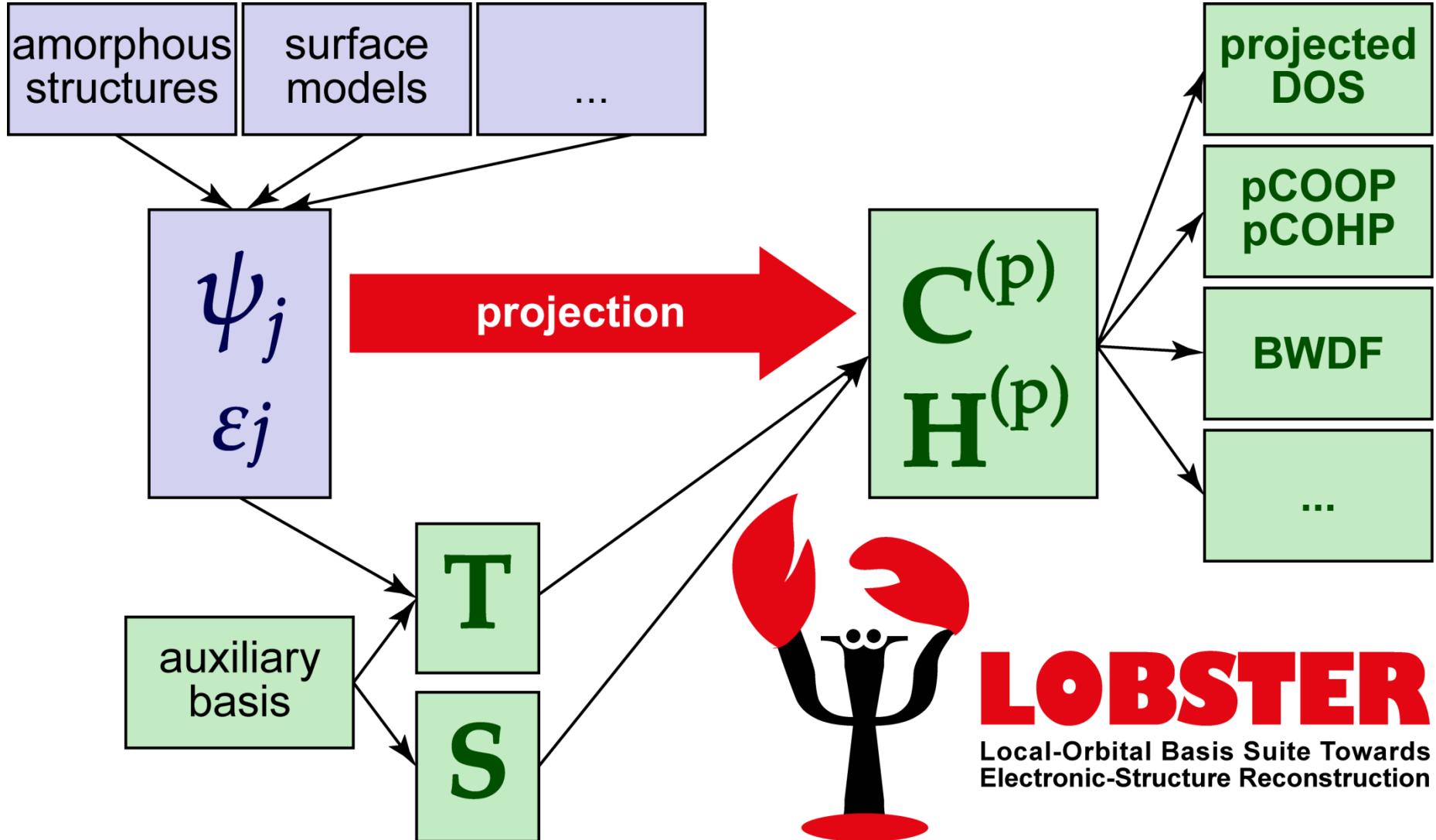
Traditionally: Tight-Binding LMTO-ASA (= densely packed atomic spheres)



Modern: countless program packages with plane waves



LOBSTER performs that...



LOBSTER
Local-Orbital Basis Suite Towards
Electronic-Structure Reconstruction

freely available at www.cohp.de

www.cohp.de

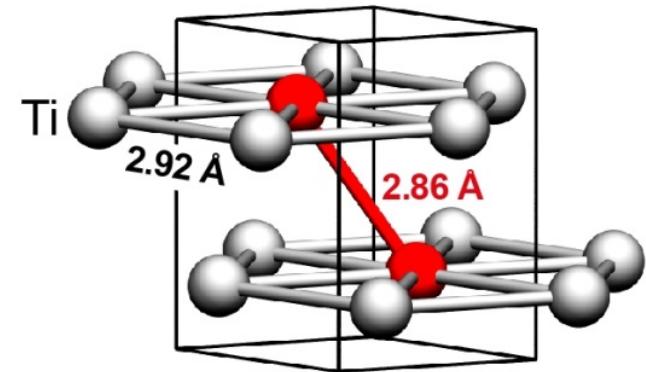
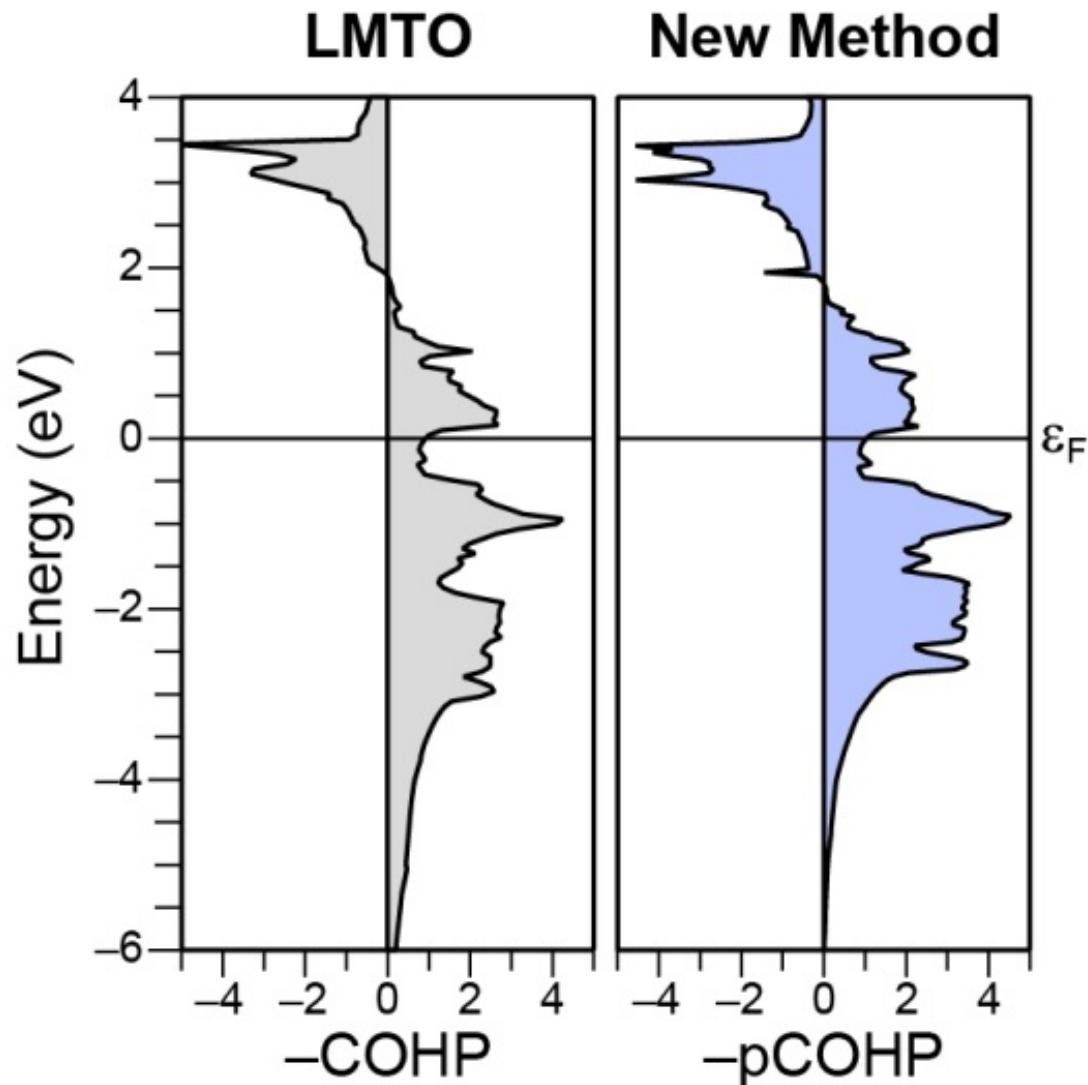


school:

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

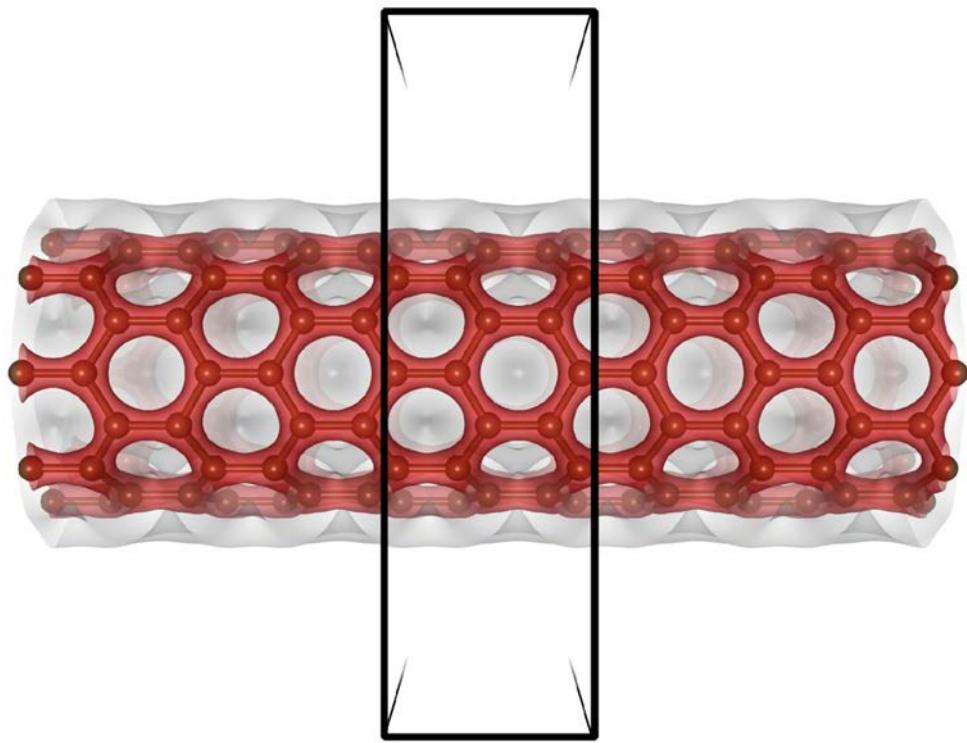
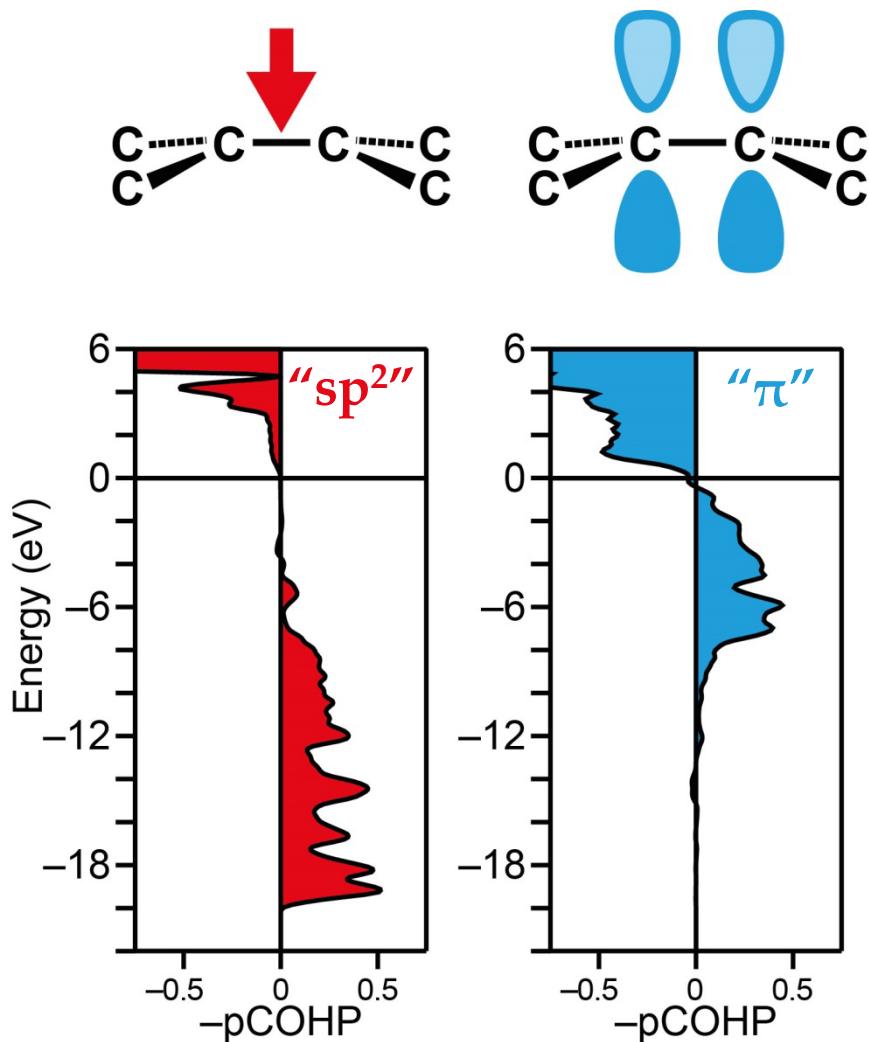
September 25–29, Jülich

Titanium (hcp): Comparison with LMTO



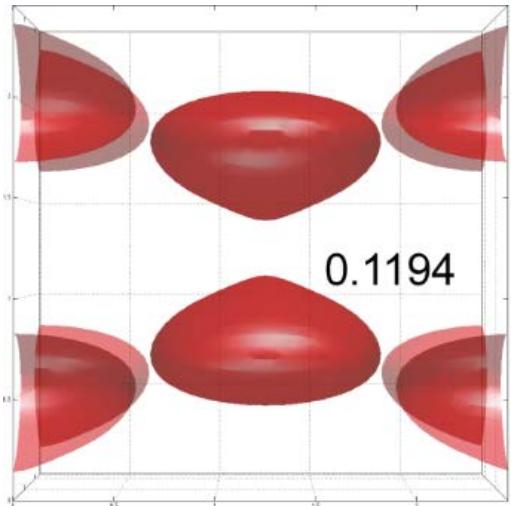
S. Maintz, V. L. Deringer,
A. L. Tchougréeff,
R. Dronskowski,
J. Comput. Chem. **2013**, *34*, 2557

Chemical Bonding in the Carbon Nanotube

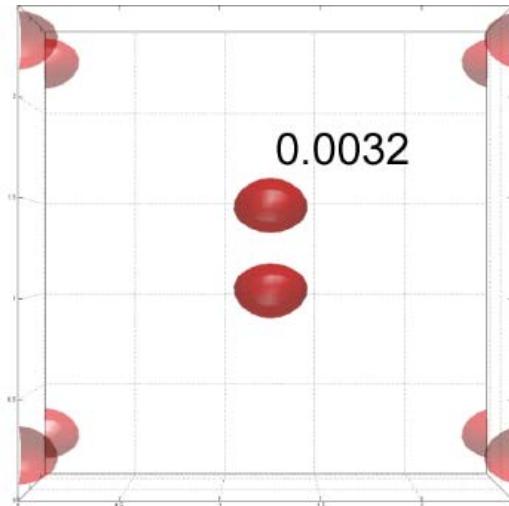


S. Maintz, V. L. Deringer,
A. L. Tchougréeff, R. Dronskowski,
J. Comput. Chem. 2016, 37, 1030

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



1s, 2s



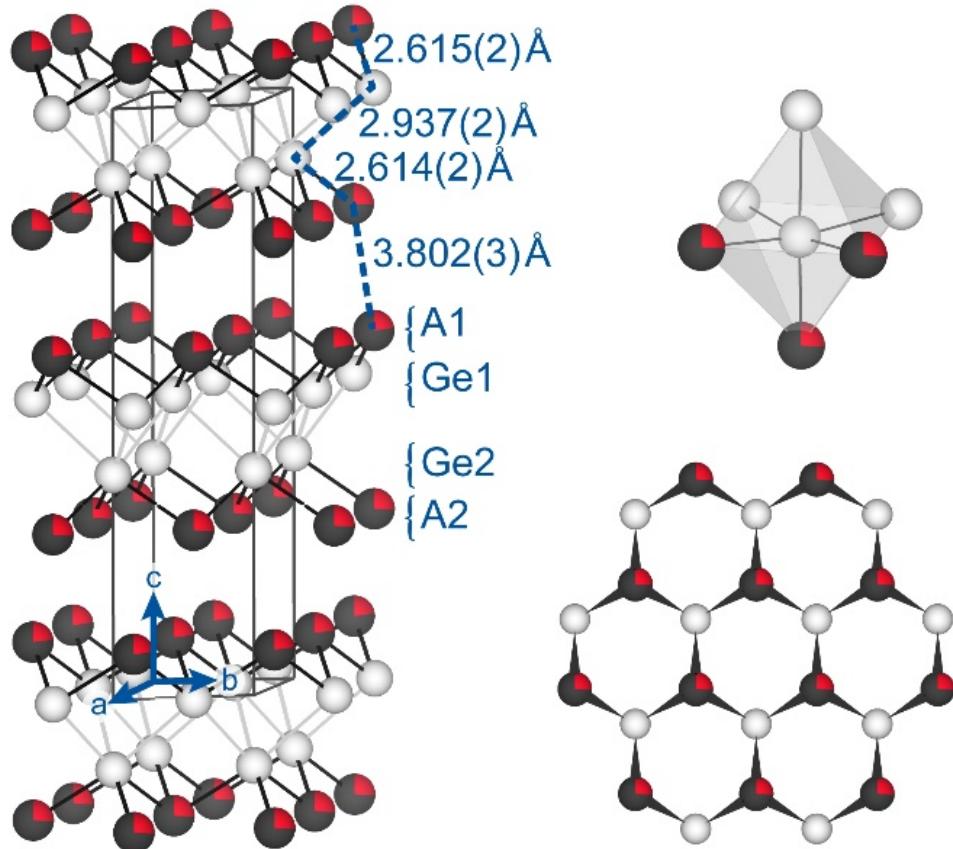
1s, 2s, 2p

*available since
LOBSTER 2.1.0*

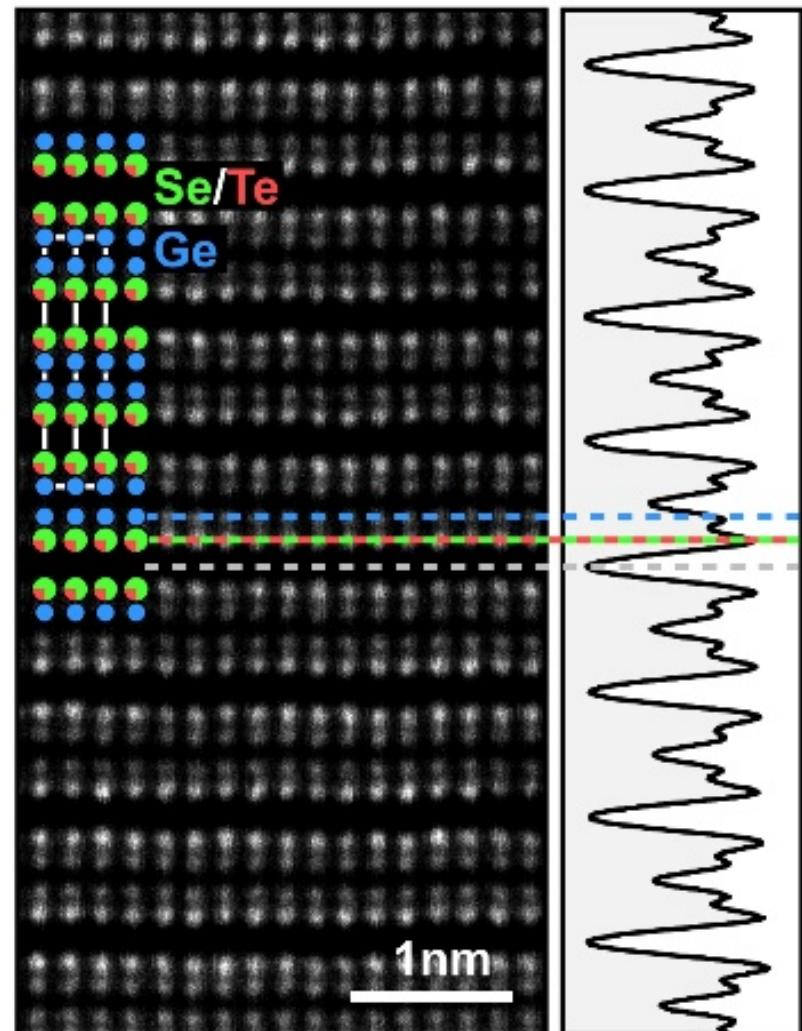
Isosurfaces (in Å⁻³) at 65% of the differences between the ABINIT-based PAW densities and the LOBSTER-projected densities for the fourth band of β-Be at Γ

group		group		group		group	
period	IA	IIA	III	IV	V	VI	VII
1	1.000 2.1 H						
2	3 5.94 Li Lithium	4 9.01 Be Beryllium					
3	11 22.99 Na Sodium	12 24.31 Mg Magnesium	IIIB	IVB	VB	VIB	VIIIB
4	19 39.18 K Potassium	20 40.08 Ca Calcium	21 44.96 Sc Scandium	22 47.90 Ti Titanium	23 50.94 V Vanadium	24 51.986 Cr Chromium	25 54.94 Mn Manganese
5	37 58.47 Rb Rubidium	38 57.82 Sr Strontium	39 58.91 Y Yttrium	40 51.26 Nb Niobium	41 52.31 Mo Molybdenum	42 56.94 Tc Tantalum	43 [97] Ru Ruthenium
6	55 132.91 Cs Cesium	56 137.33 Ba Barium	57 138.91 La Lanthanum	72 178.49 Hf Hafnium	73 195.25 Ta Tantalum	74 183.85 Tungsten	75 198.21 Rh Rhodium
7	87 223.49 Fr Francium	88 [226] Ra Radon	89 [227] Ac Actinium	104 [241] Rf Rutherfordium	105 [262] Db Dubnium	106 [283] Sg Bismuth	107 [282] Bh Hassium
Lanthanides		58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 [145] Eu Europium	62 150.35 Sm Samarium	63 151.96 Gadolinium
Actinides		90 232.04 Th Thorium	91 233.04 Pa Protactinium	92 238.03 U Uranium	93 237.05 Np Neptunium	94 [244] Pu Plutonium	95 [247] Am Americium
						96 [247] Cm Curium	97 [247] Bk Berkelium
						98 [265] Cf Californium	99 [264] Es Einsteinium
						100 [265] Fm Fermium	101 [264] Md Mendelevium
						102 [265] No Nobelium	103 [265] Lr Lawerentium

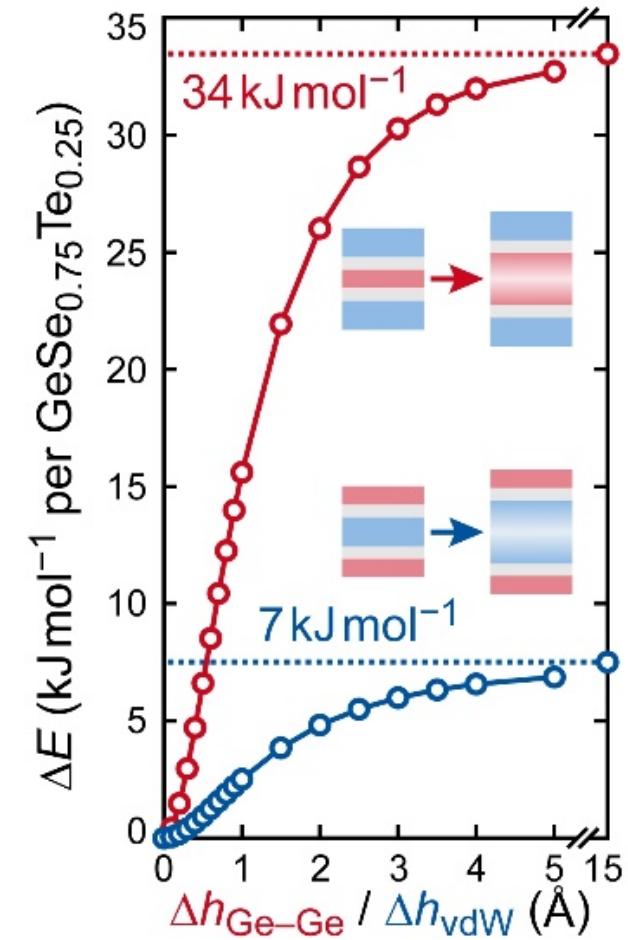
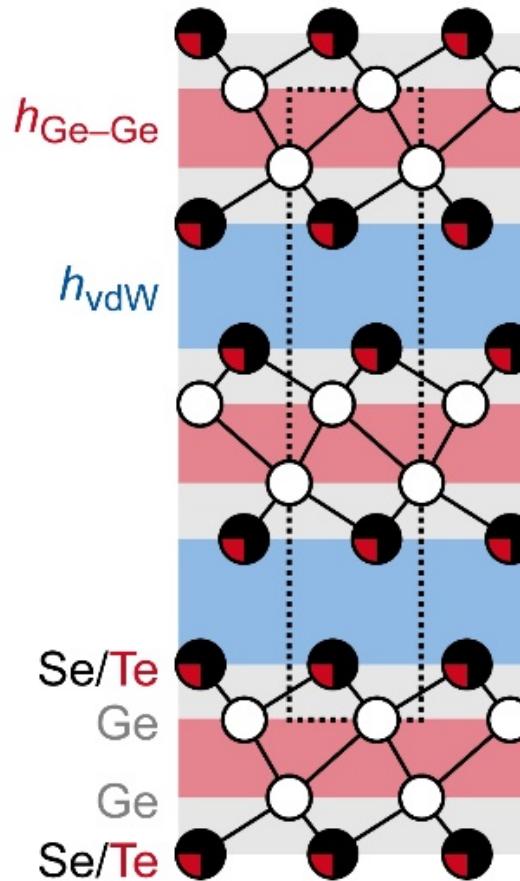
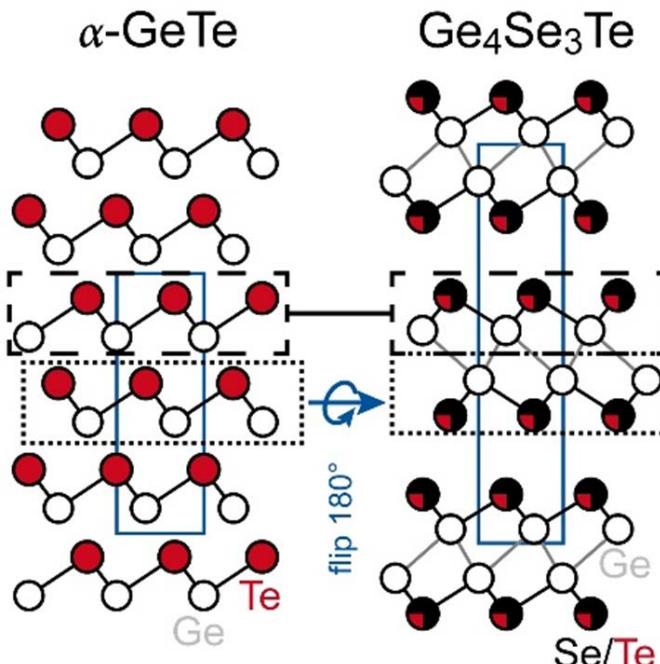
$\text{Ge}_4\text{Se}_3\text{Te}$, Structure & TEM: Ge–Ge = 2.94 Å



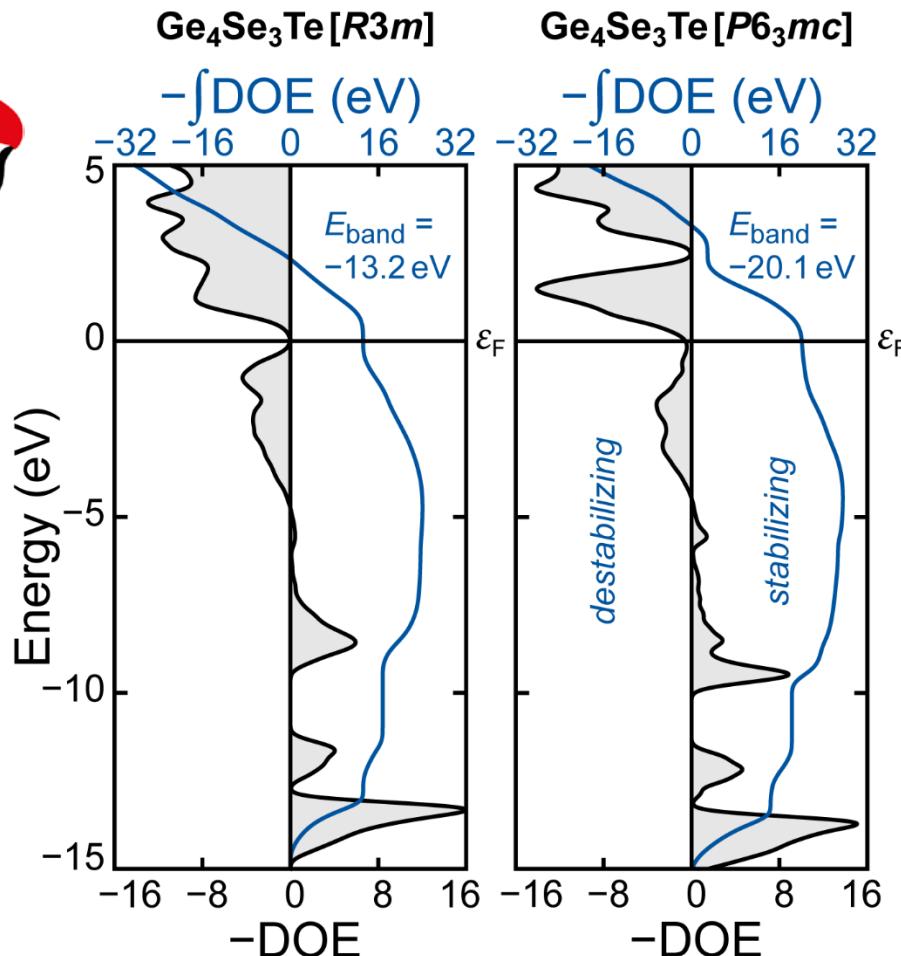
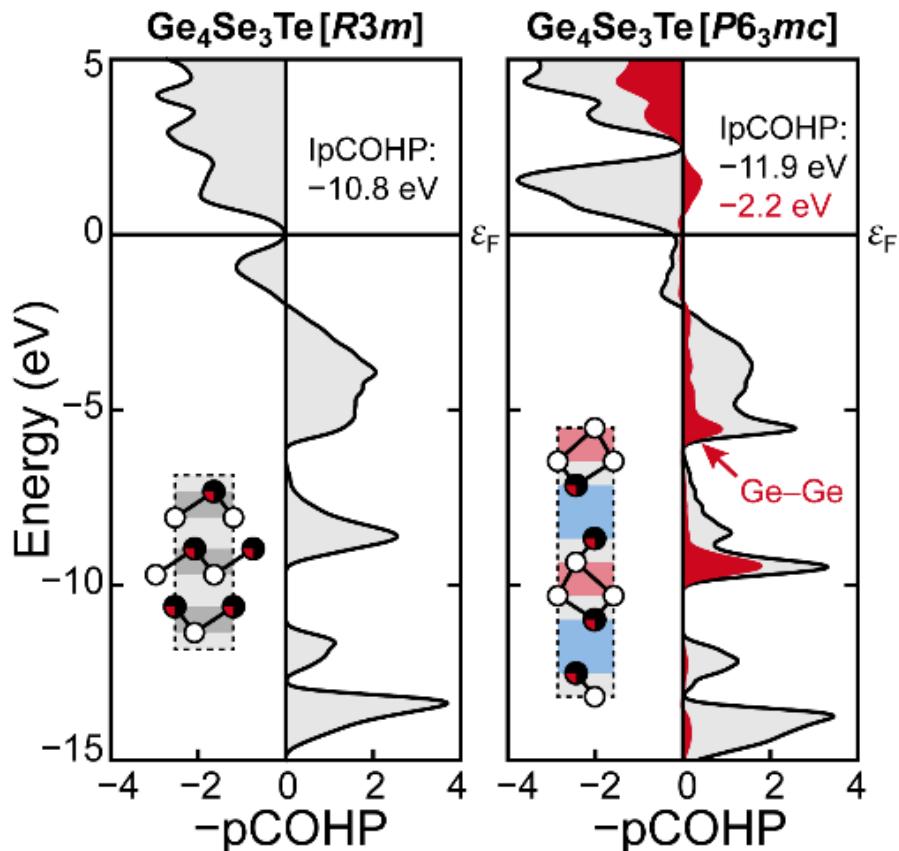
HAADF STEM Line Profile



$\text{Ge}_4\text{Se}_3\text{Te}$: layers & forces (DFT+dispersion)



$\text{Ge}_4\text{Se}_3\text{Te}$: 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 (%)

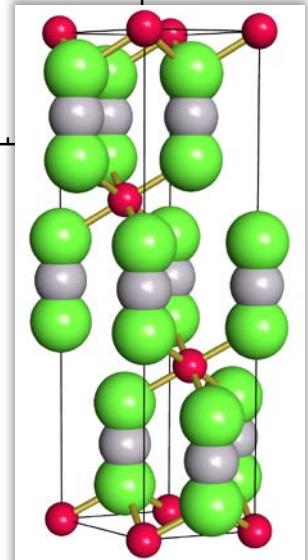
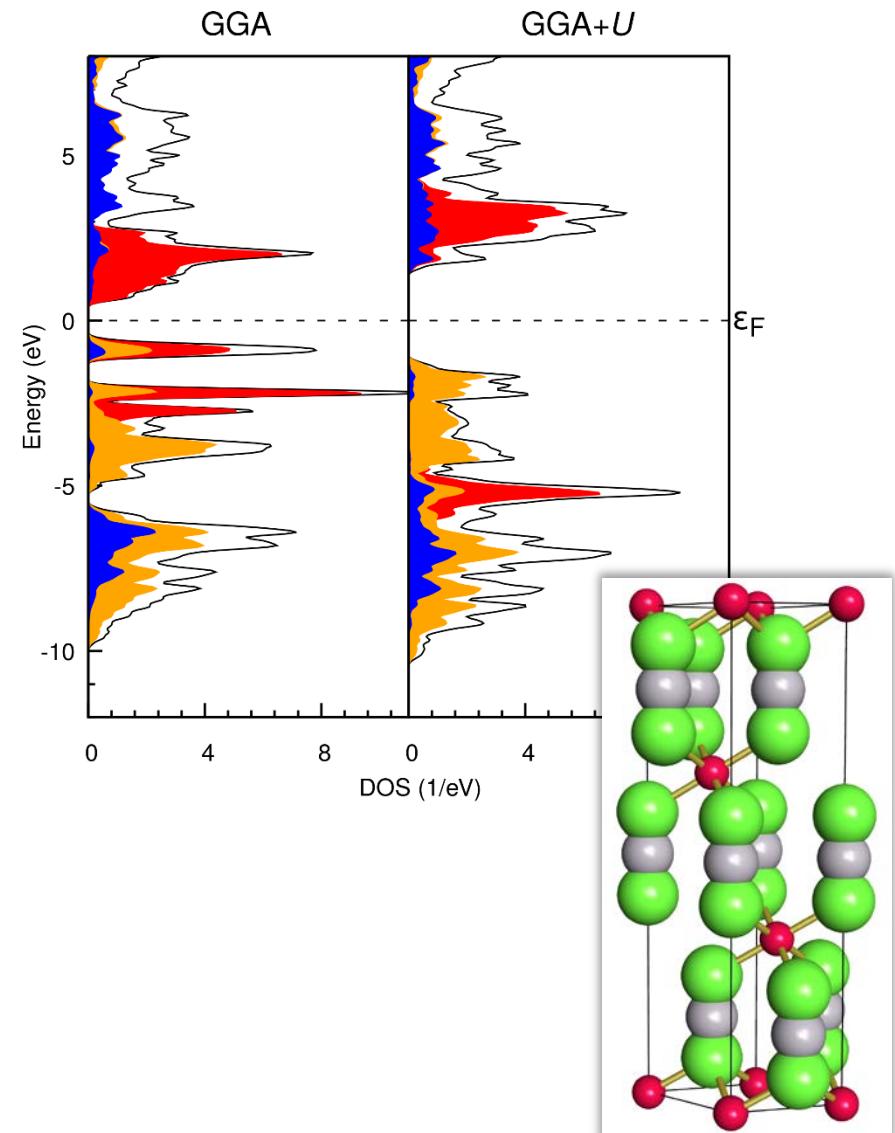
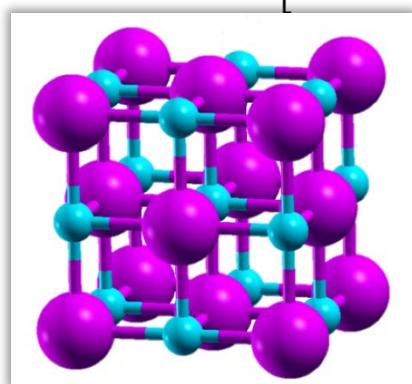
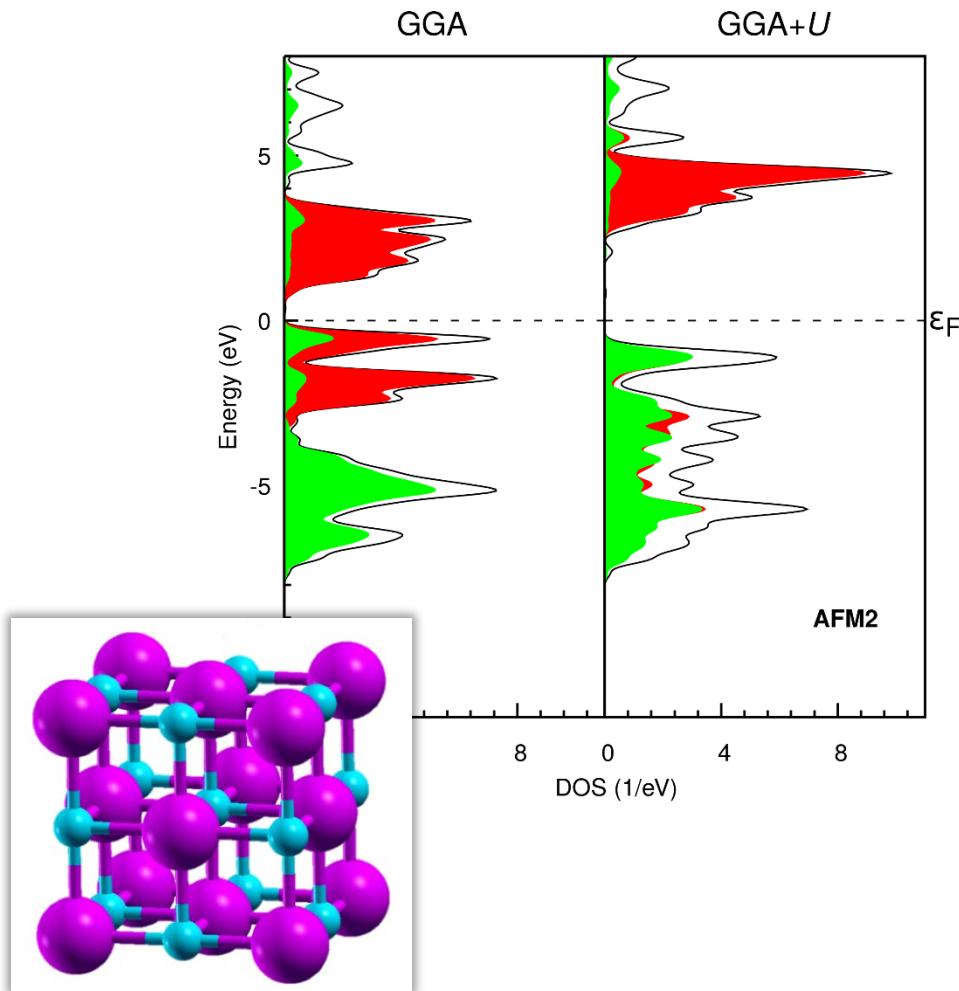
materials \ Interfaces	Espresso	VASP	ABINIT
Diamond	1.11	0.98	1.50
GaAs	0.73	0.88	0.56
Ti	2.01	7.83	3.07
fullerene	1.33	1.16	1.89
carbon-nanotube	1.27	1.10	1.80



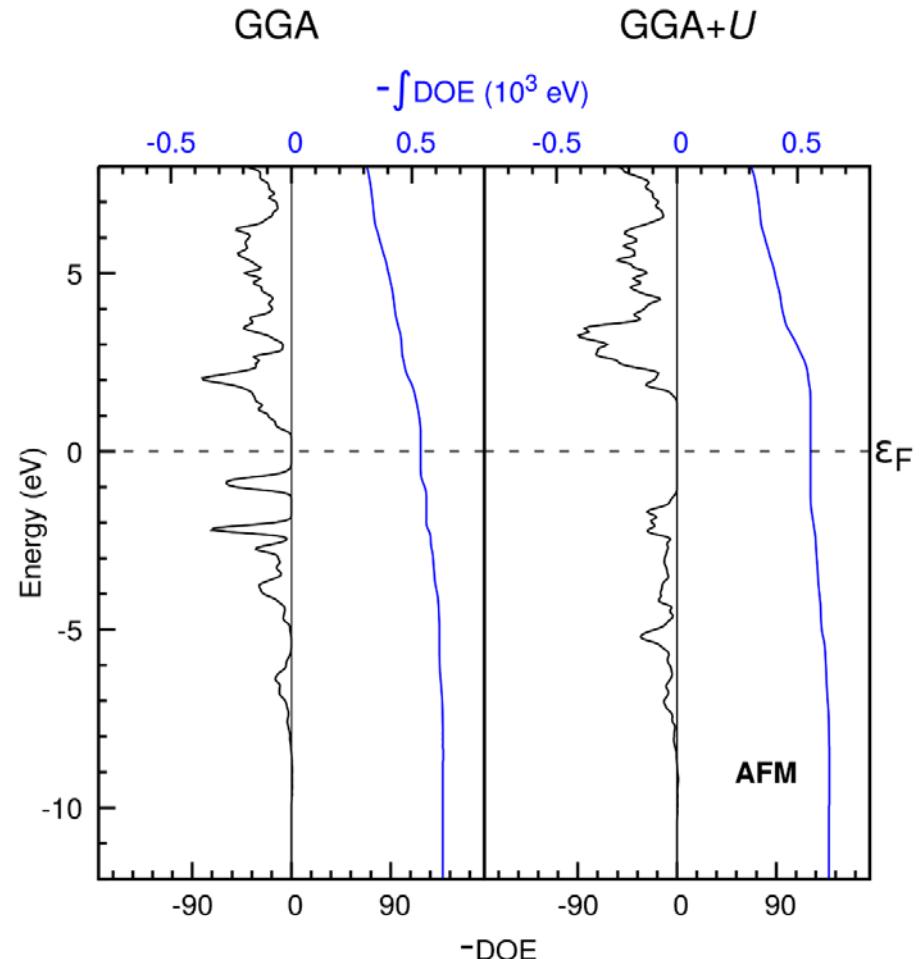
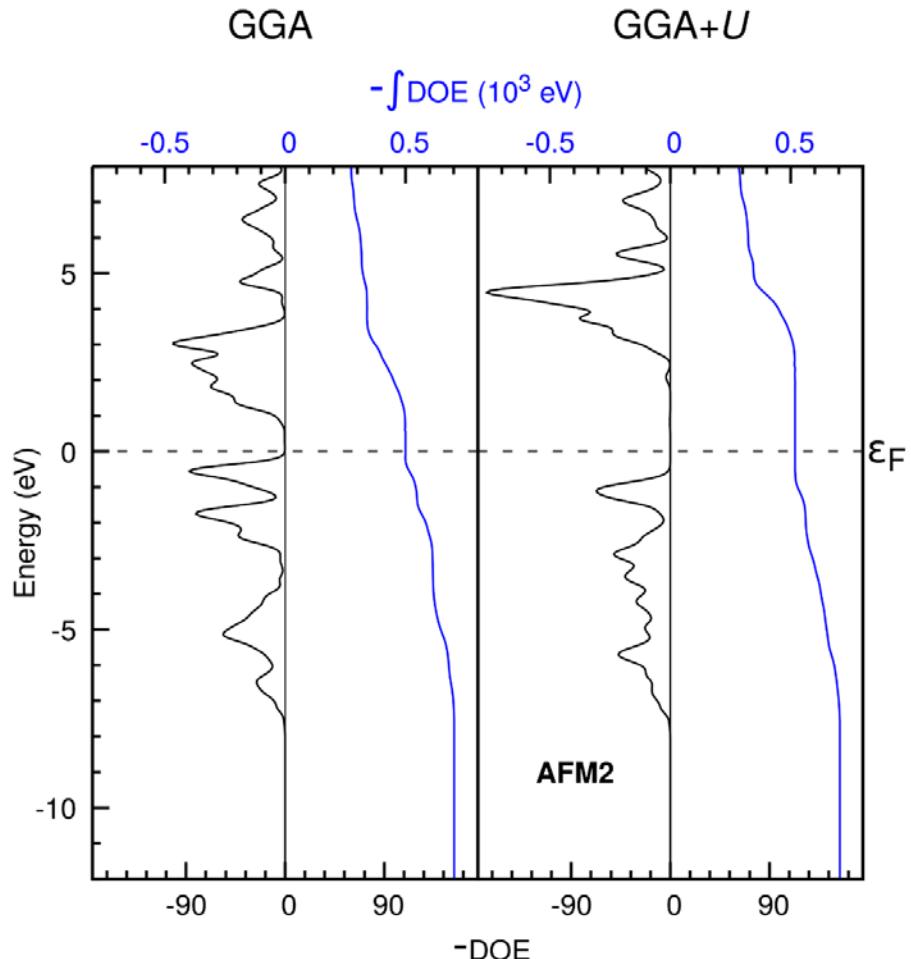
execution time (s)

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



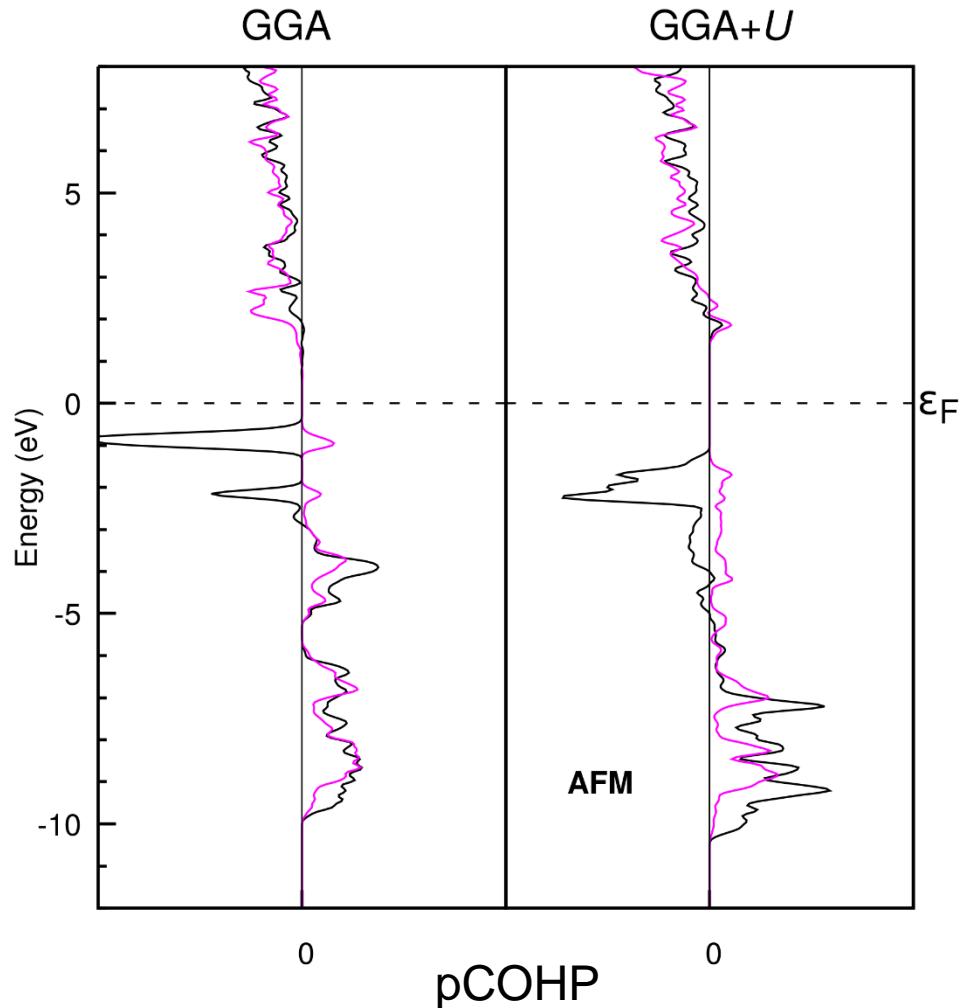
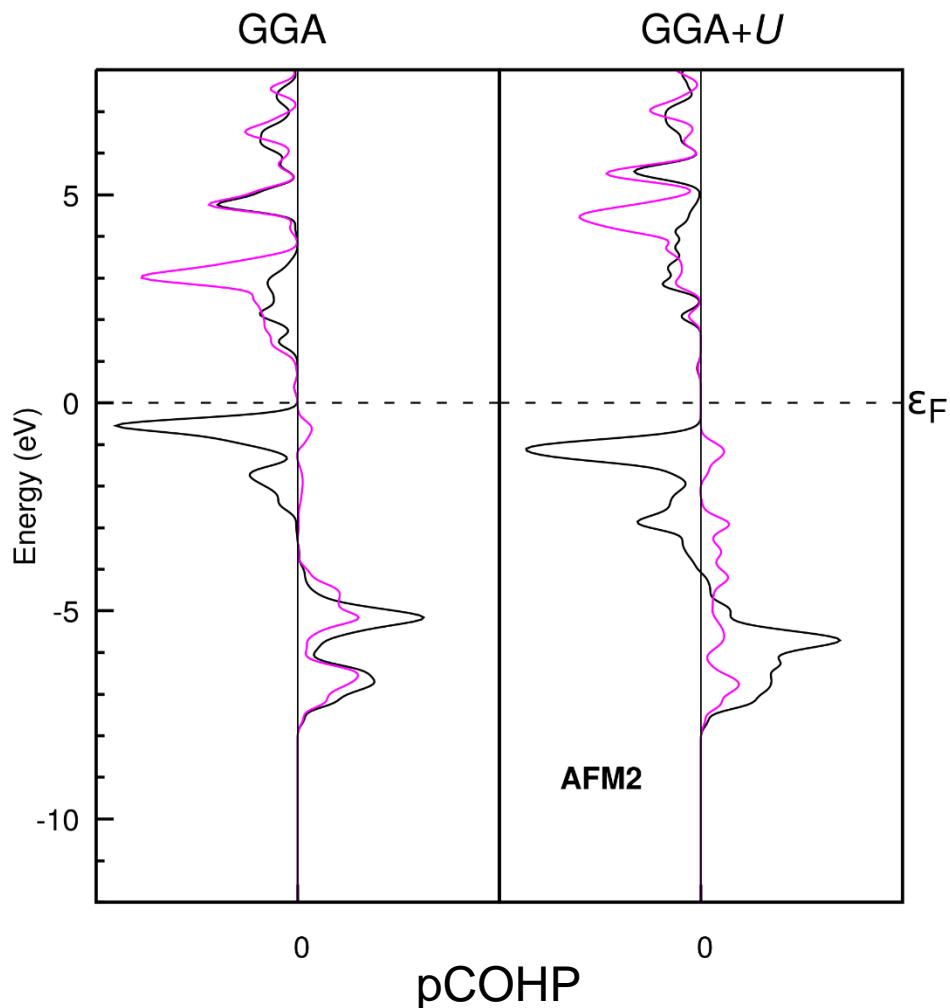
Density-of-Energy: MnO and MnNCN



$$\text{DOE}(E) = \sum_k \sum_A \sum_{\mu} \sum_{\mu \in A} \sum_{\nu} \sum_{\nu \in B} P_{\mu\nu}(E, k) H_{\mu\nu}(k)$$

$$E_{\text{band}} = \int_{-\infty}^{\epsilon_F} \text{DOE}(E) dE$$

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