

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

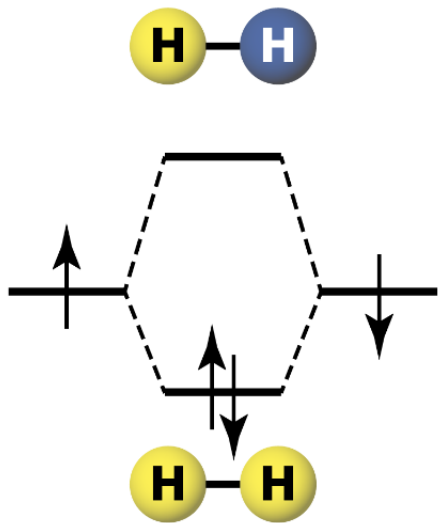
Ge-Ge bonds in Phase-Change Materials, Density-of-Energy (DOE)

Plane-wave Benchmarking, **ABINIT** implementation

Correlated Stuff

H₂: Population Analysis by Robert S. Mulliken

$$\int \psi^* \psi d\tau = \underbrace{\int \psi^2 d\tau}_{\equiv 1} = c_1^2 \underbrace{\int \phi_1^2 d\tau}_{\equiv 1} + c_2^2 \underbrace{\int \phi_2^2 d\tau}_{\equiv 1} + 2c_1c_2 \underbrace{\int \phi_1\phi_2 d\tau}_{S_{12}}$$



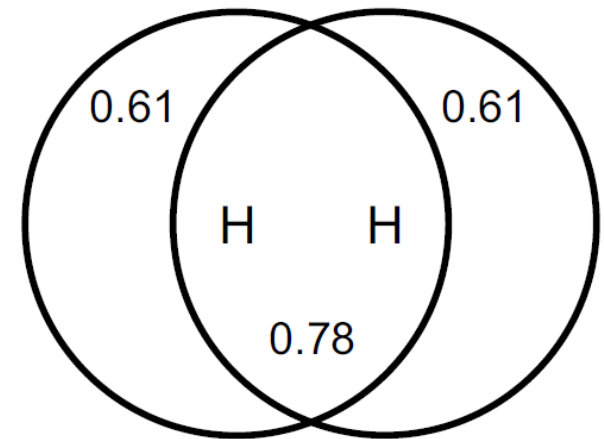
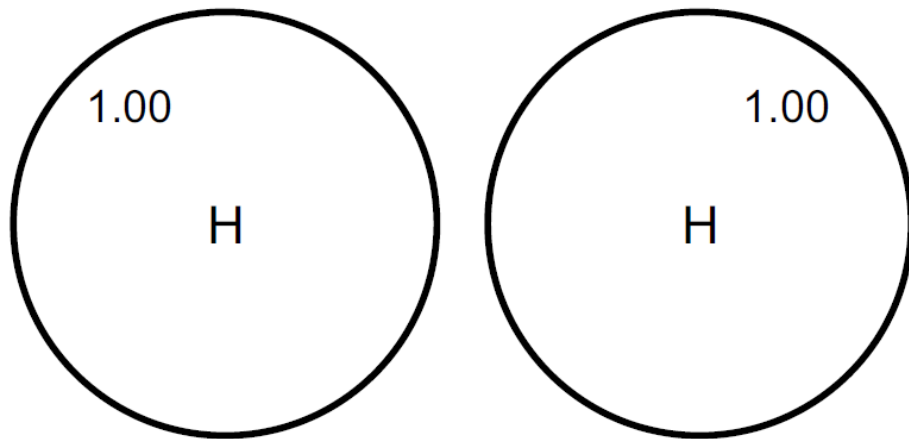
R. S. Mulliken,
J. Chem. Phys. **1955**, 23, 1833



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

Simplest **Population Analysis** for σ_g -MO of H_2

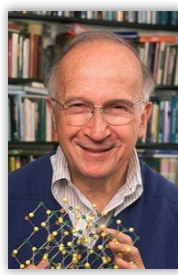
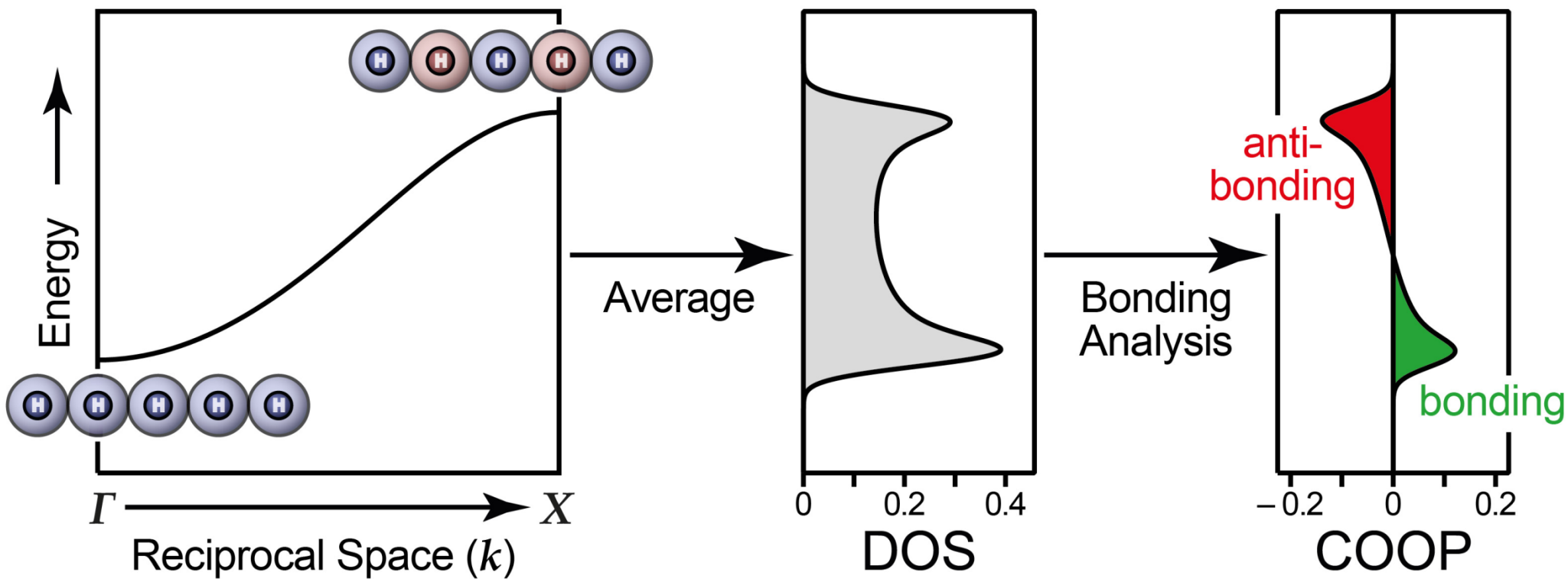
$$1 = \underbrace{\frac{1}{2(1 + S_{12})}}_{=0.305} + \underbrace{\frac{1}{2(1 + S_{12})}}_{=0.305} + \underbrace{\frac{2}{2(1 + S_{12})}}_{=0.390} S_{12}$$



the two hydrogen atoms share 0.78 electrons

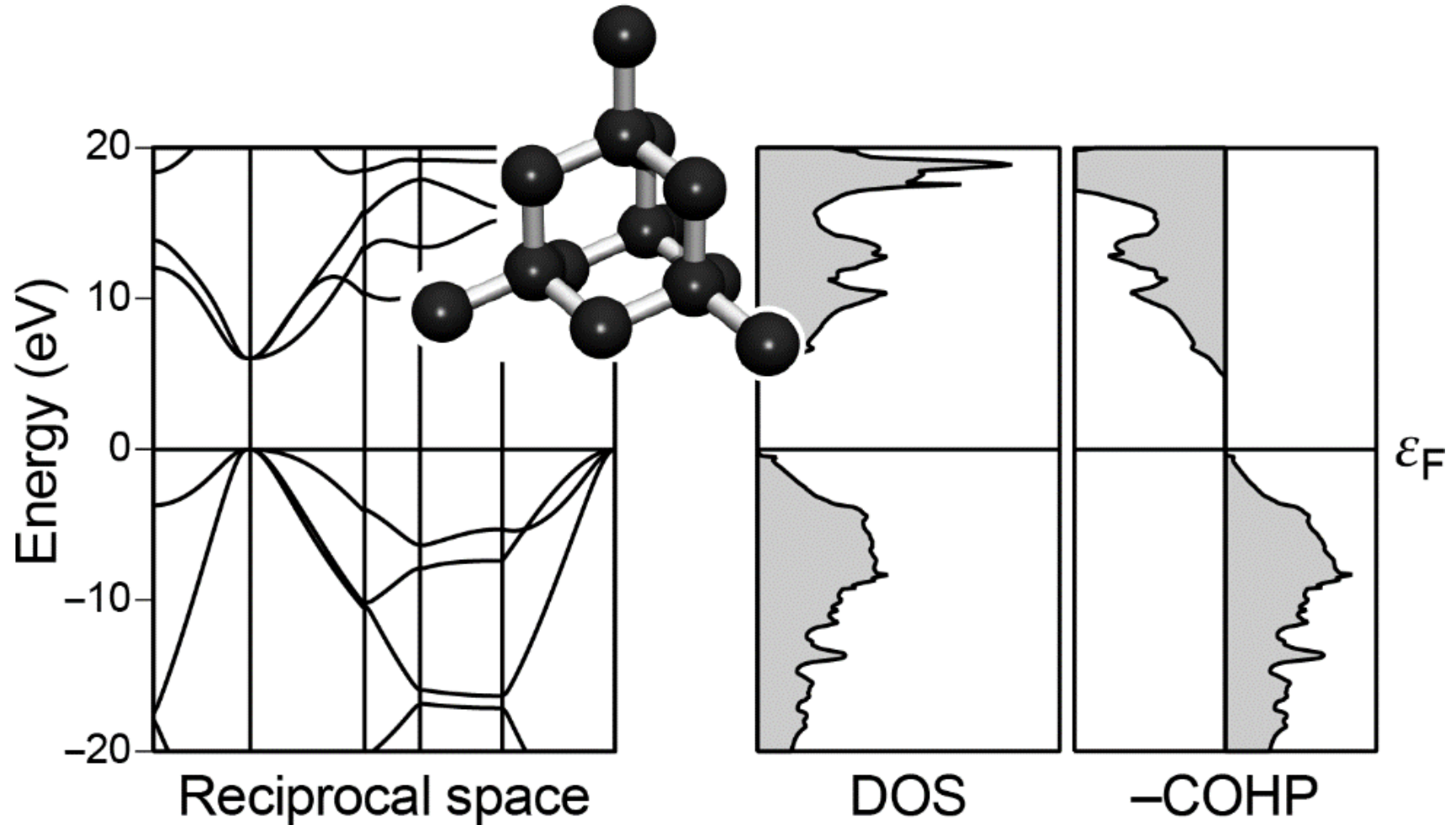
1dim H-chain: band structure, DOS, COOP

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



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

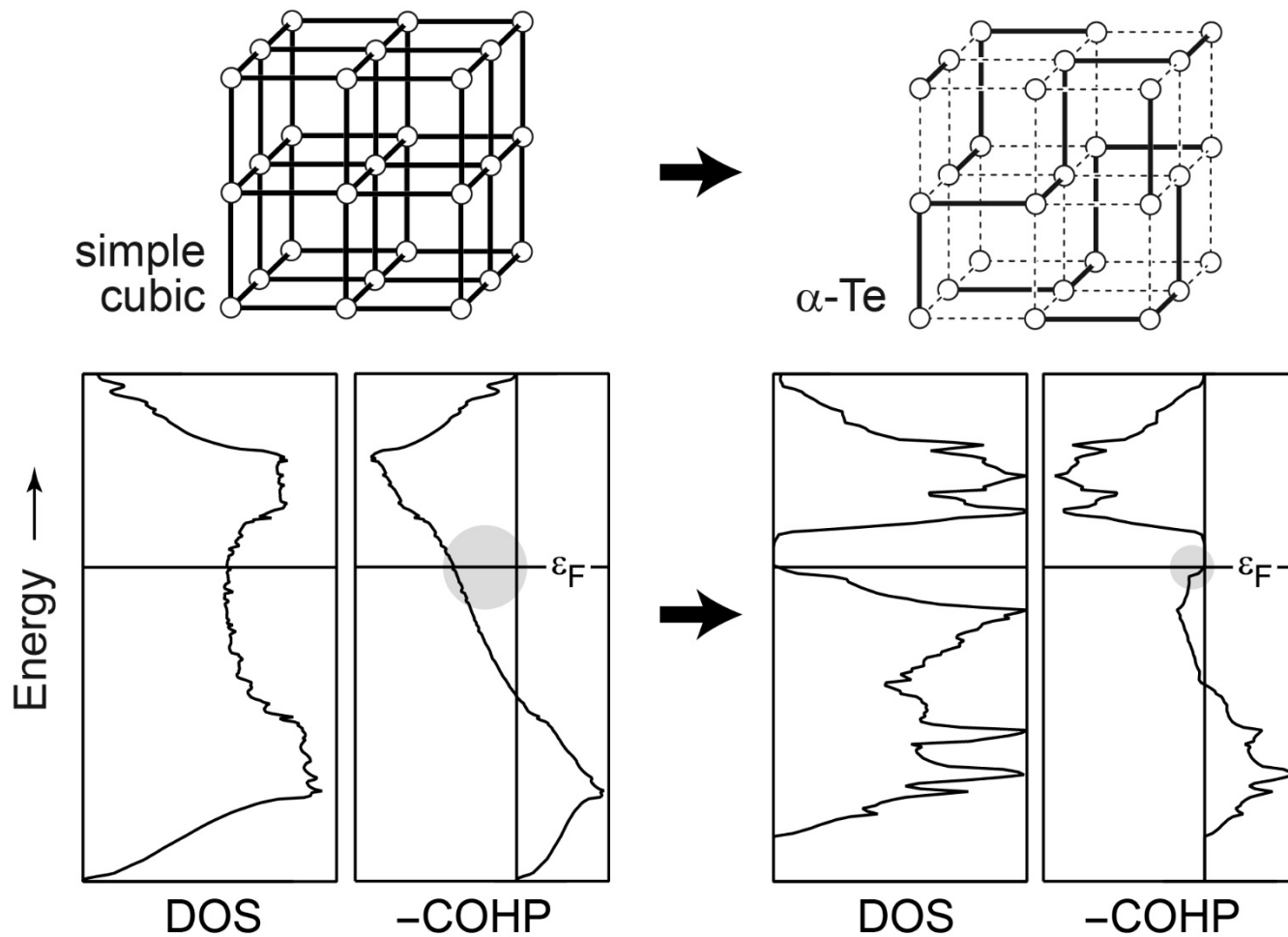
DFT: Crystal Orbital Hamilton Population, COHP



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

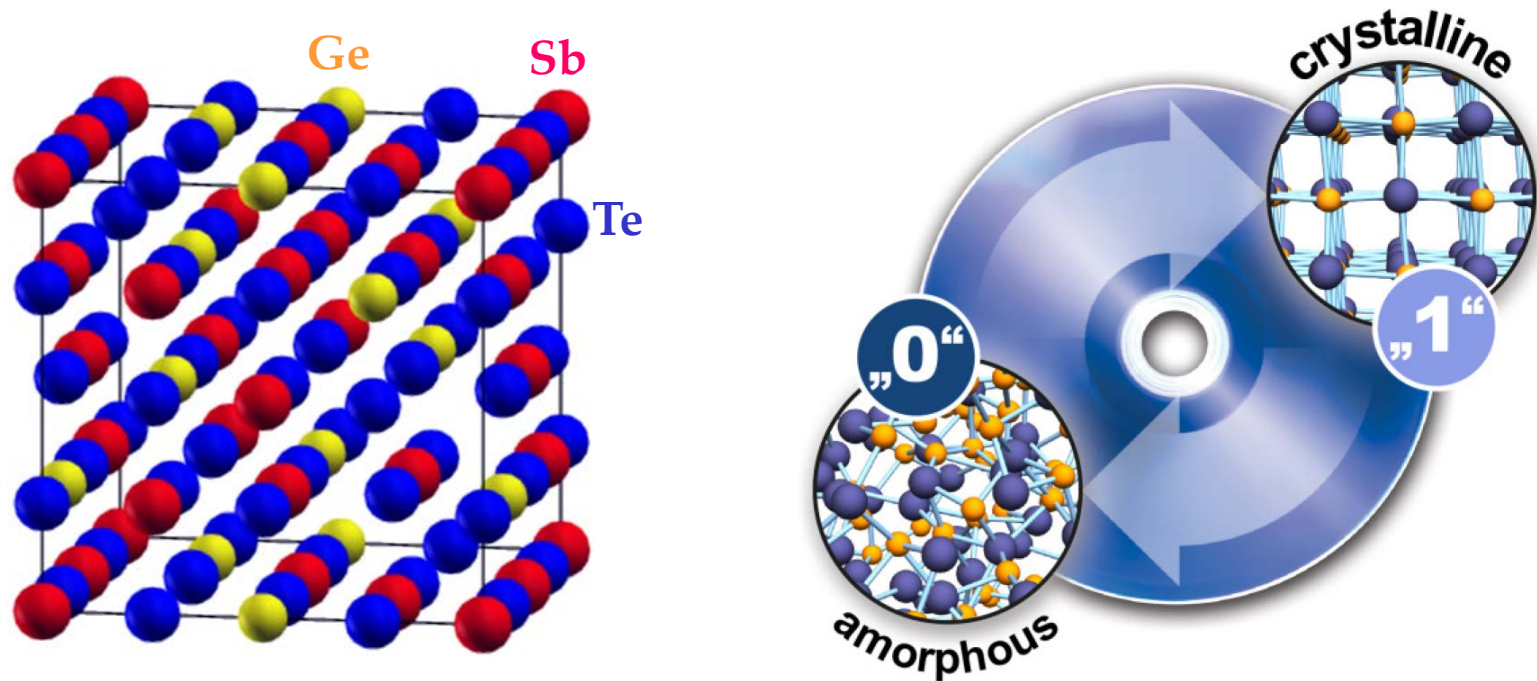


Example I: sc Tellurium is **Peierls-unstable**



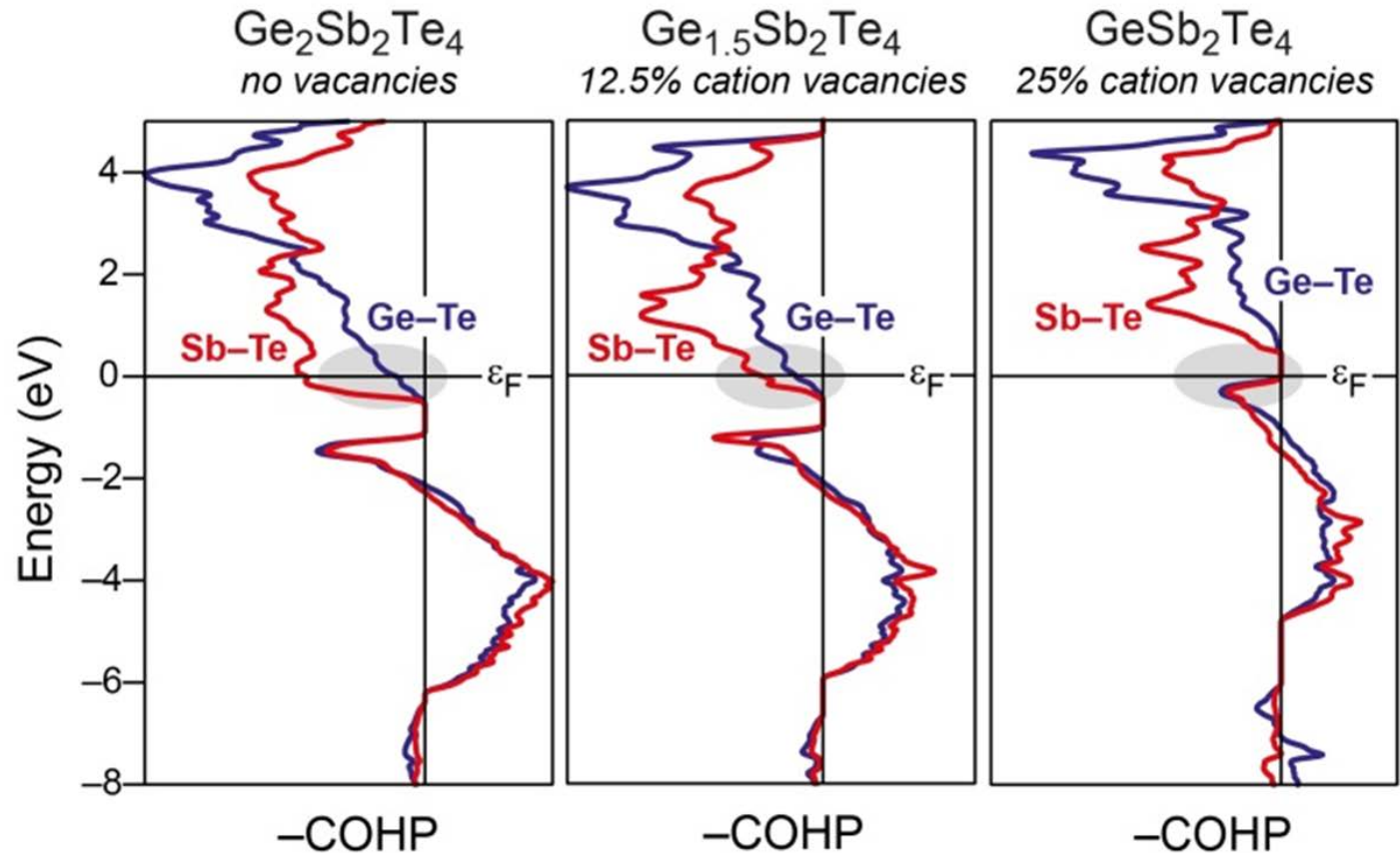
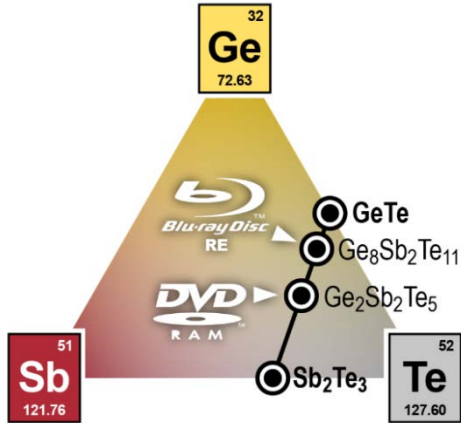
A. Decker, G. A. Landrum, R. Dronskowski,
Z. Anorg. Allg. Chem. **2002**, 628, 295

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

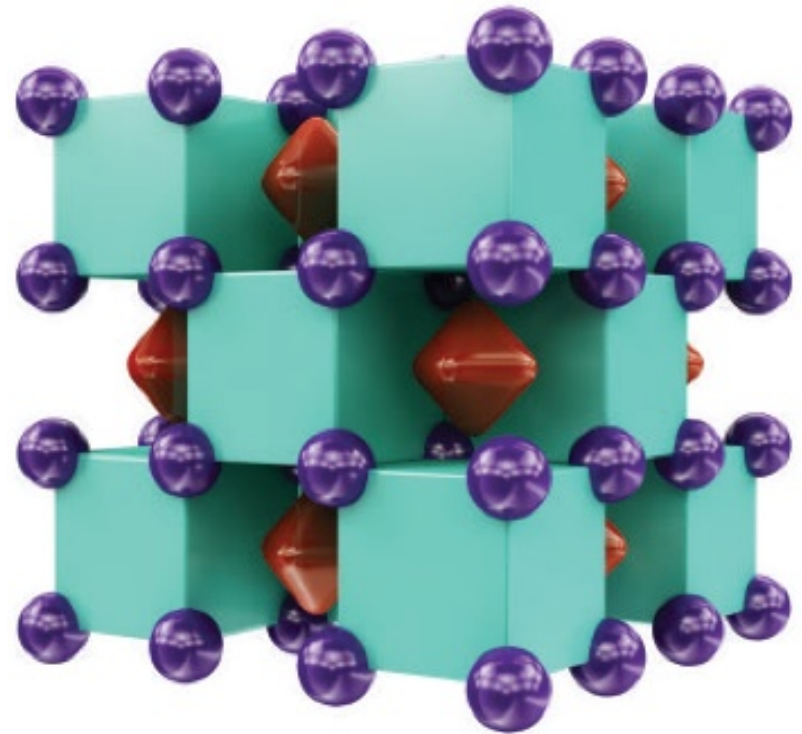
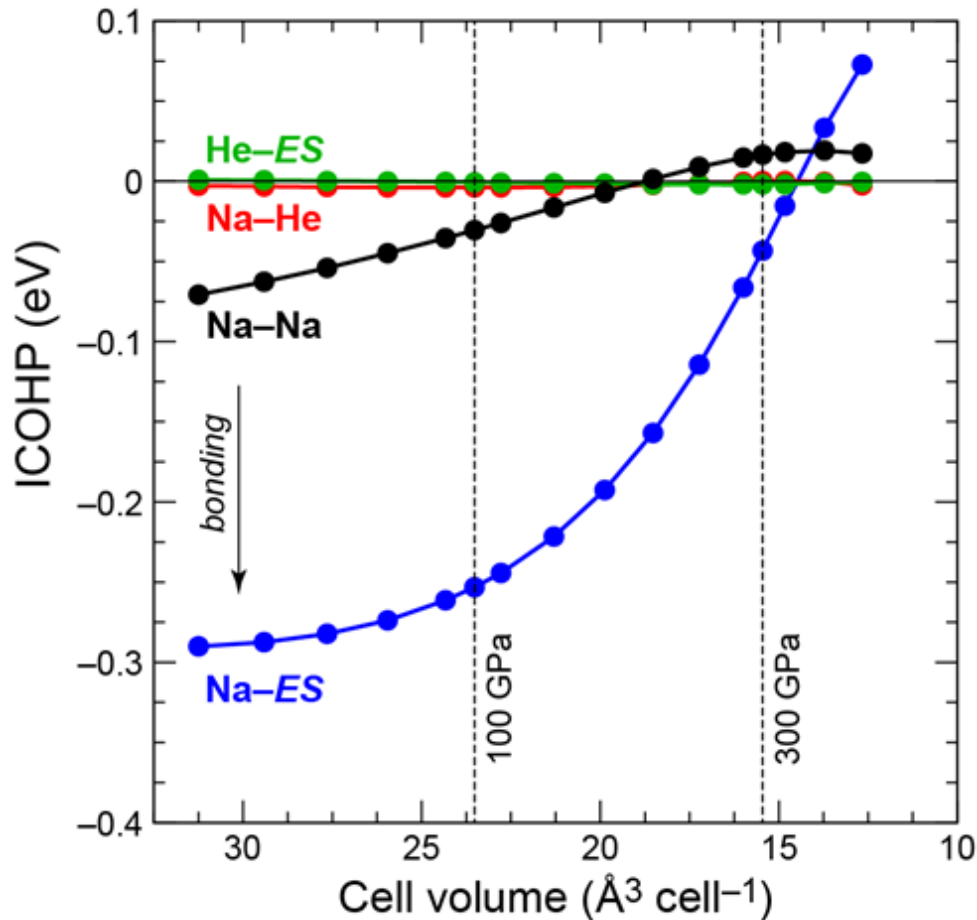
Phase-change Materials: First COHP study



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

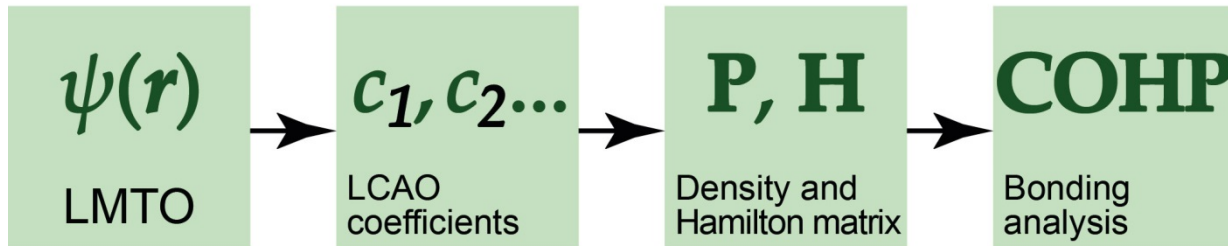
Example III: $\text{Na}_2\text{He} = (\text{Na}^+)_2\text{He}(\text{e}^-)_2 @ 100 \text{ GPa}$



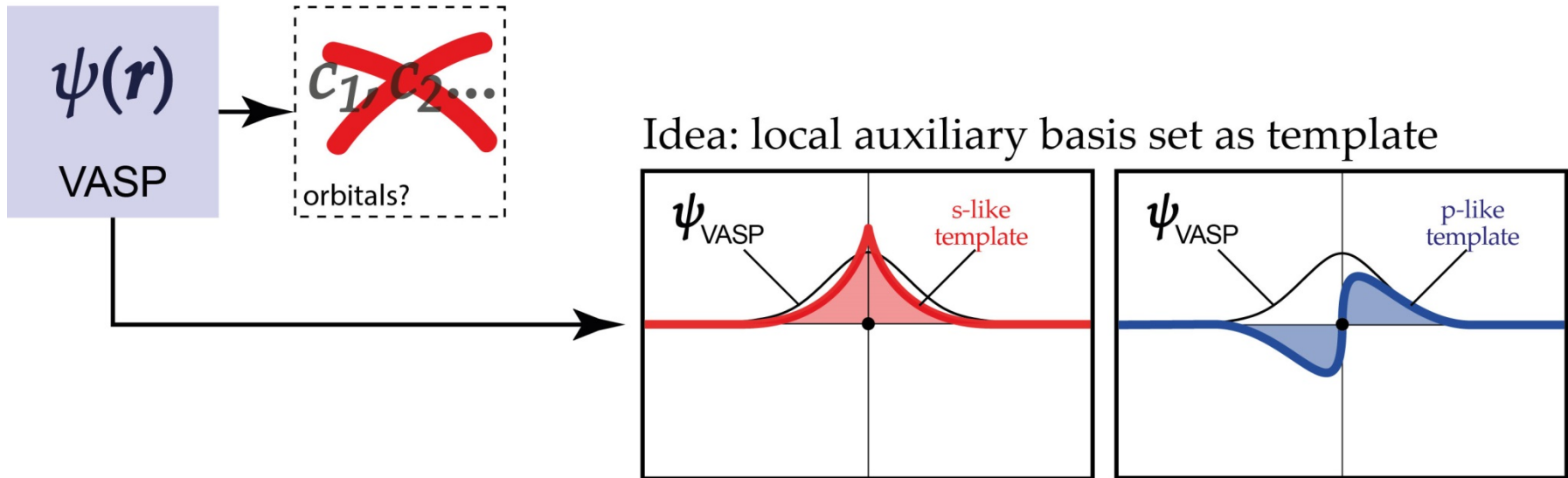
X. Dong, A. R. Oganov, A. F. Goncharov, E. Stavrou, S. Lobanov, G. Saleh, G.-R. Qian, Q. Zhu, C. Gatti, V. L. Deringer, R. Dronskowski, X.-F. Zhou, V. Prakapenka, Z. Konôpková, I. Popov, A. I. Boldyrev, H.-T. Wang, *Nature Chem.* **2017**, *9*, 440

Retrieving the Chemistry from Plane Waves

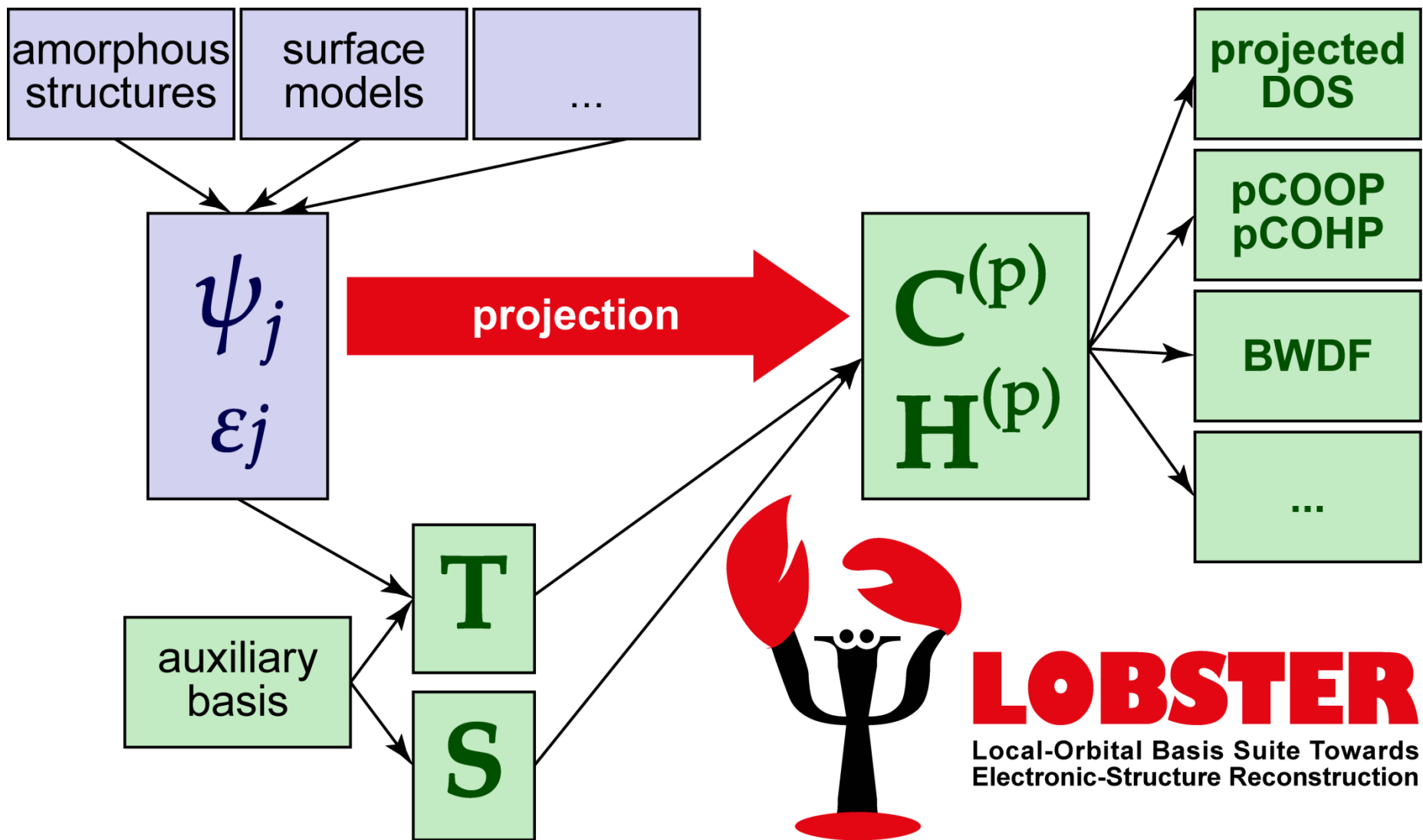
Traditionally: Tight-Binding LMTO-ASA (= densely packed atomic spheres)



Modern: countless program packages with plane waves

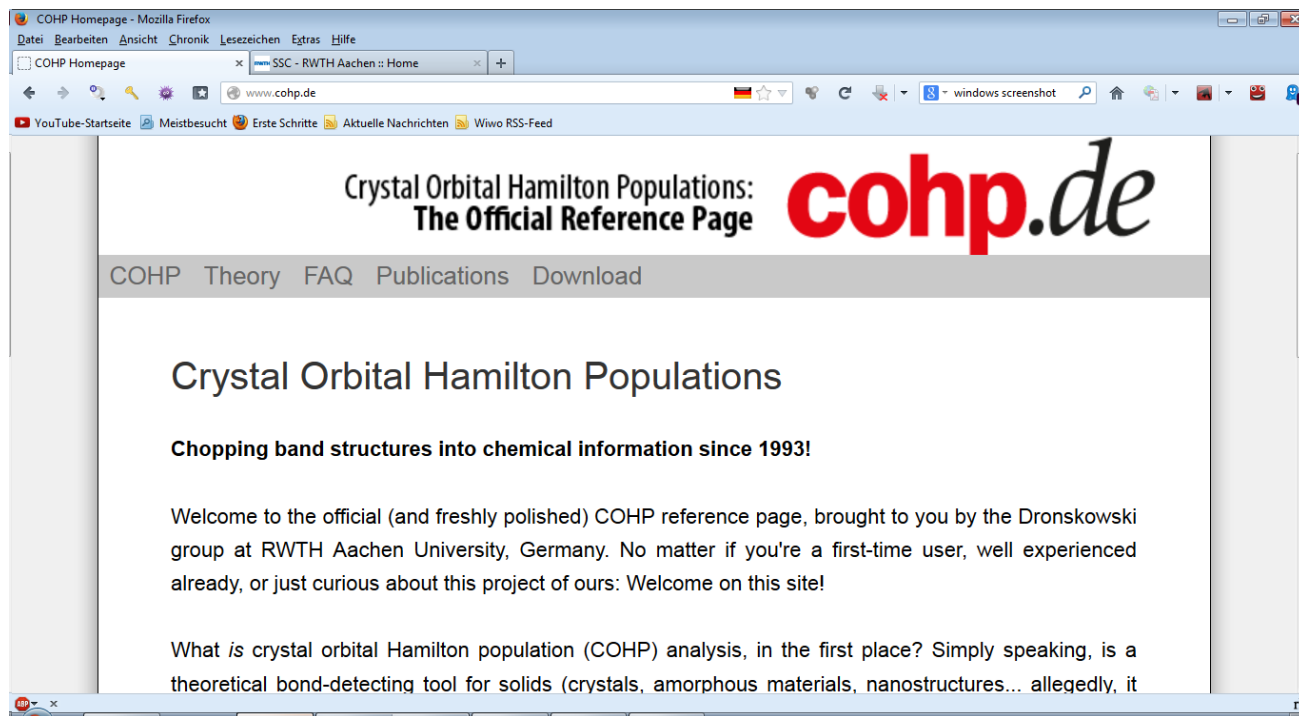


LOBSTER performs that...



freely available at www.cohp.de

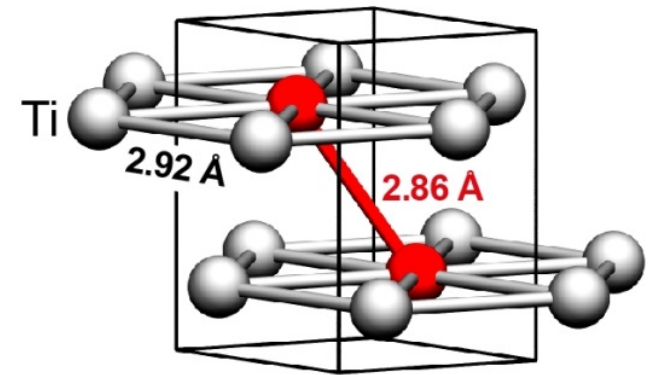
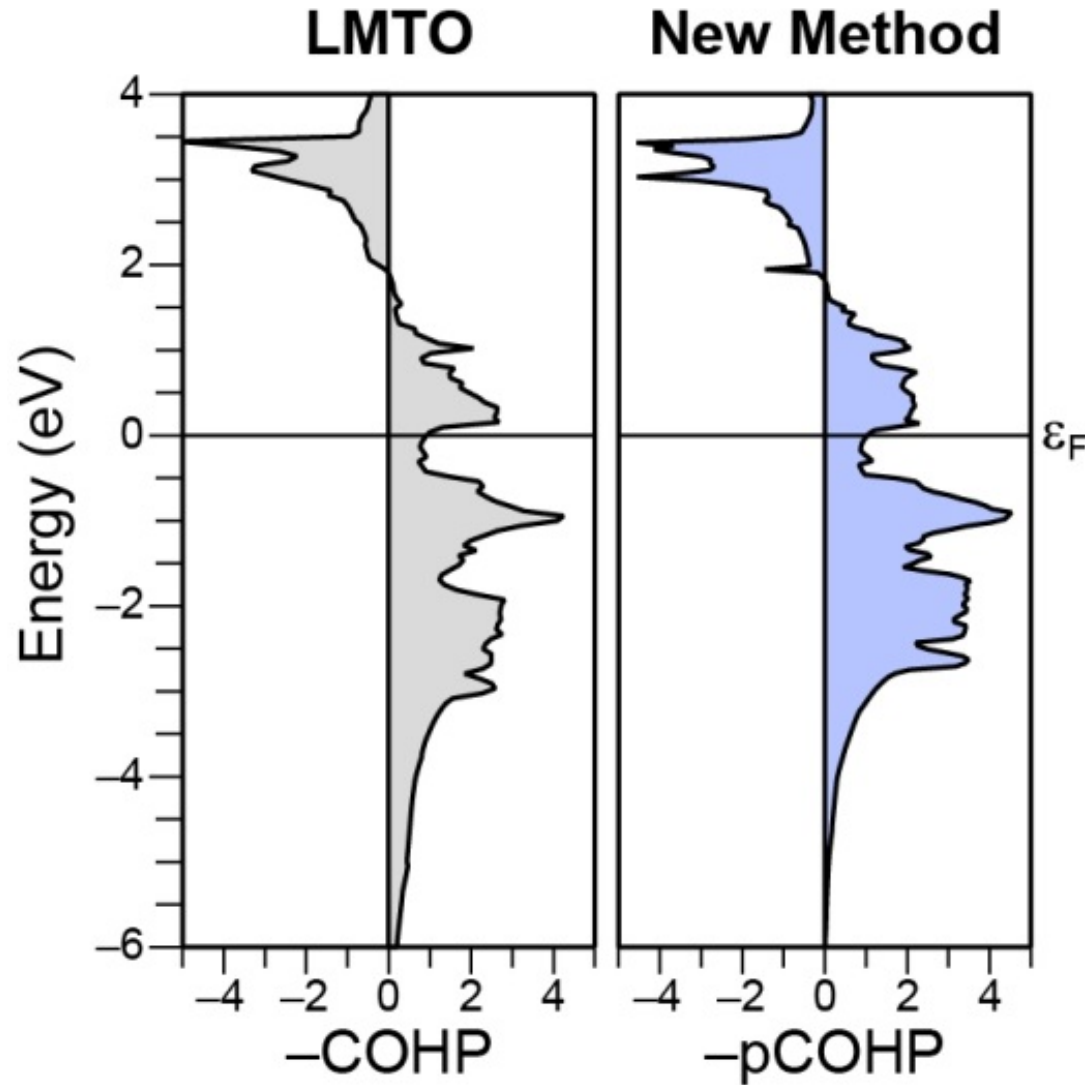
www.cohp.de



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

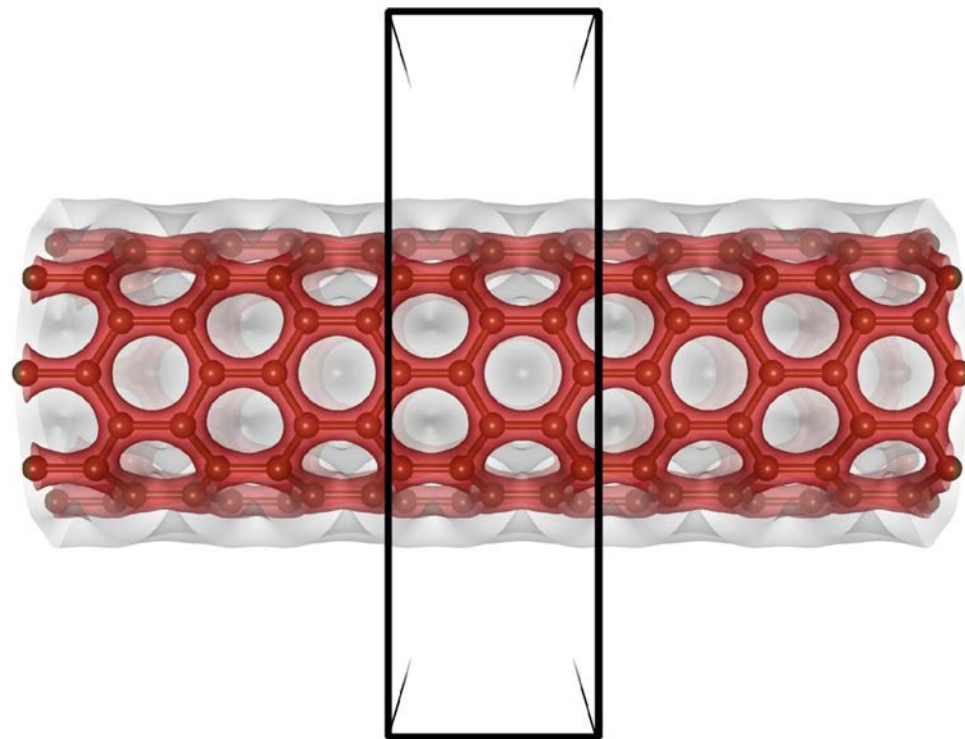
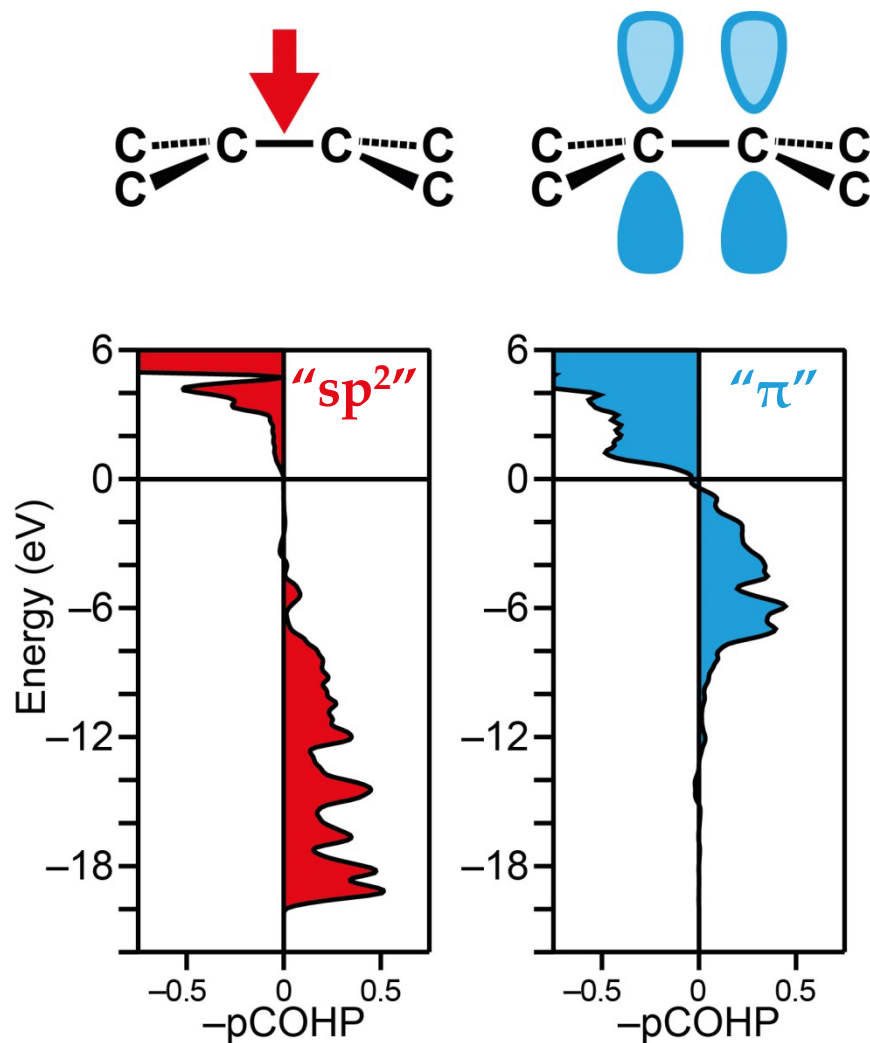
September 25–29, Jülich

Titanium (hcp): Comparison with LMTO



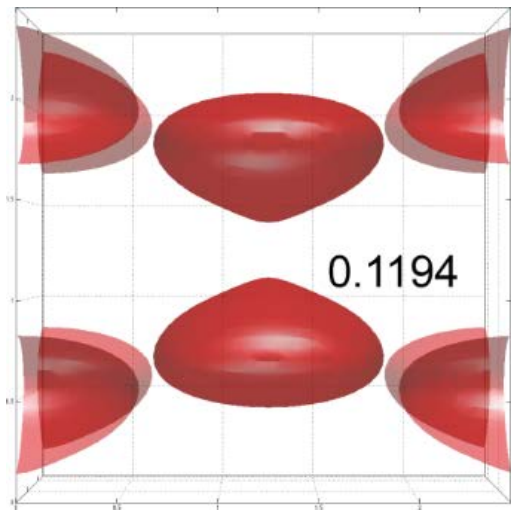
S. Maintz, V. L. Deringer,
A. L. Tchougréeff,
R. Dronskowski,
J. Comput. Chem. **2013**, *34*, 2557

Chemical Bonding in the Carbon Nanotube

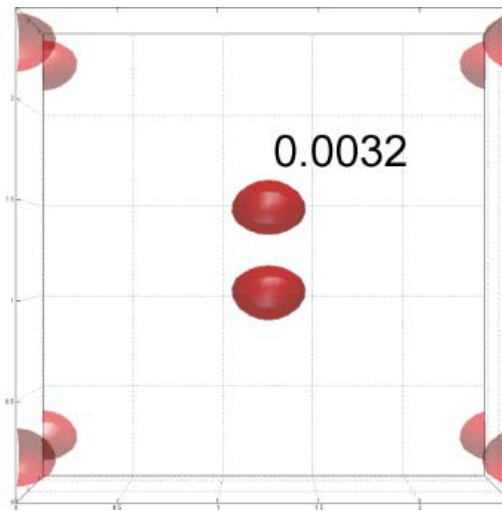


S. Maintz, V. L. Deringer,
A. L. Tchougréeff, R. Dronskowski,
J. Comput. Chem. **2016**, *37*, 1030

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



1s, 2s



1s, 2s, 2p

Isosurfaces (in \AA^{-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

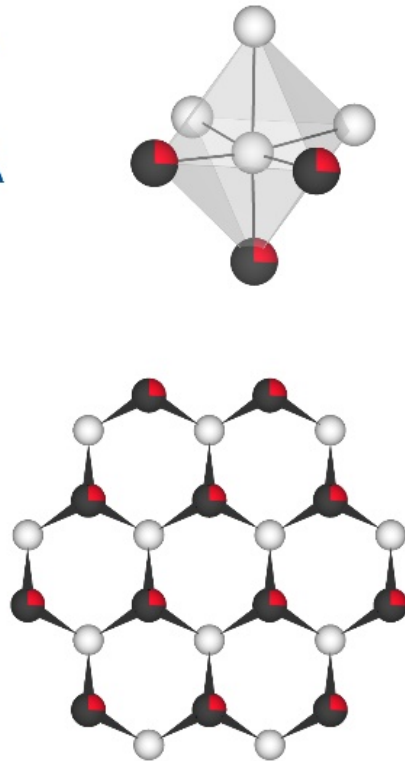
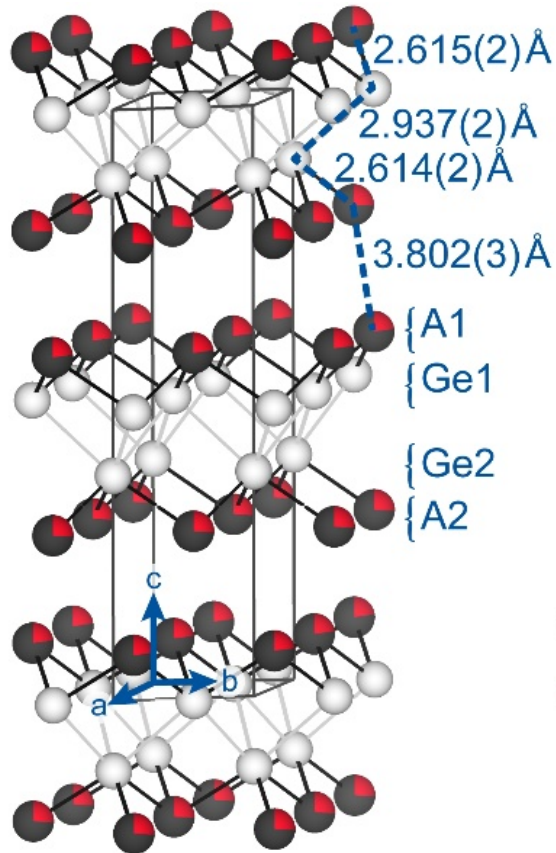
*available since
LOBSTER 2.1.0*

period	group		group																group																										
	IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	IIIA	IVA	VA	VIA	VIIA	VIIIA																							
1	1 1.008 H Hydrogen																						2 4.00 He Helium																						
2	3 6.94 Li Lithium	4 9.01 Be Beryllium																						5 10.81 B Boron																					
3	11 22.99 Na Sodium	12 24.31 Mg Magnesium																						13 26.98 Al Aluminum																					
4	19 39.10 K Potassium	20 40.08 Ca Calcium	21 44.96 Sc Scandium	22 47.88 Ti Titanium	23 50.94 V Vanadium	24 51.996 Cr Chromium	25 54.94 Mn Manganese	26 55.85 Fe Iron	27 58.93 Co Cobalt	28 58.70 Ni Nickel	29 63.55 Cu Copper	30 65.38 Zn Zinc	31 69.72 Ga Gallium	32 72.59 Ge Germanium	33 74.92 As Arsenic	34 78.96 Se Selenium	35 79.90 Br Bromine	36 83.80 Kr Krypton	37 85.47 Rb Rubidium	38 87.62 Sr Strontium	39 88.91 Y Yttrium	40 91.22 Zr Zirconium	41 92.91 Nb Niobium	42 95.94 Mo Molybdenum	43 97.91 Tc Technetium	44 101.07 Ru Ruthenium	45 101.07 Rh Rhodium	46 106.87 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium	49 114.82 In Indium	50 118.49 Sn Tin	51 121.75 Sb Antimony	52 127.60 Te Tellurium	53 126.90 I Iodine	54 131.30 Xe Xenon									
5	0.8 137.08 Cs Cesium	0.7 137.08 Ba Barium	55 137.08 La Lanthanum	56 137.33 Ce Cerium	57 138.91 Pr Praseodymium	58 140.91 Nd Neodymium	59 144.24 Pm Promethium	60 144.24 Sm Samarium	61 150.35 Eu Europium	62 151.96 Gd Gadolinium	63 157.25 Tb Terbium	64 158.93 Dy Dysprosium	65 162.50 Ho Holmium	66 164.93 Er Erbium	67 167.26 Tm Thulium	68 168.93 Yb Ytterbium	69 173.04 Lu Lutetium	70 173.04 Ce Cerium	71 173.04 Pr Praseodymium	72 175.04 Nd Neodymium	73 175.04 Pm Promethium	74 175.04 Sm Samarium	75 175.04 Eu Europium	76 175.04 Gd Gadolinium	77 175.04 Tb Terbium	78 175.04 Dy Dysprosium	79 175.04 Ho Holmium	80 175.04 Er Erbium	81 175.04 Tm Thulium	82 175.04 Yb Ytterbium	83 175.04 Lu Lutetium	84 175.04 Ce Cerium	85 175.04 Pr Praseodymium	86 175.04 Nd Neodymium	87 175.04 Pm Promethium	88 175.04 Sm Samarium	89 175.04 Eu Europium	90 175.04 Gd Gadolinium	91 175.04 Tb Terbium	92 175.04 Dy Dysprosium	93 175.04 Ho Holmium	94 175.04 Er Erbium	95 175.04 Tm Thulium	96 175.04 Yb Ytterbium	97 175.04 Lu Lutetium
7	87 223 Fr Francium	88 223 Ra Radium	89 223 Ac Actinium	90 223 Th Thorium	91 223 Pa Protactinium	92 223 U Uranium	93 223 Np Neptunium	94 223 Pu Plutonium	95 223 Am Americium	96 223 Cm Curium	97 223 Bk Berkelium	98 223 Cf Californium	99 223 Es Einsteinium	100 223 Fm Fermium	101 223 Md Mendelevium	102 223 No Nobelium	103 223 Lr Lawrencium	104 223 Th Thorium	105 223 Pa Protactinium	106 223 U Uranium	107 223 Np Neptunium	108 223 Pu Plutonium	109 223 Am Americium	110 223 Cm Curium	111 223 Bk Berkelium	112 223 Cf Californium	113 223 Es Einsteinium	114 223 Fm Fermium	115 223 Md Mendelevium	116 223 No Nobelium	117 223 Lr Lawrencium	118 223 Th Thorium	119 223 Pa Protactinium	120 223 U Uranium	121 223 Np Neptunium	122 223 Pu Plutonium	123 223 Am Americium	124 223 Cm Curium	125 223 Bk Berkelium	126 223 Cf Californium	127 223 Es Einsteinium	128 223 Fm Fermium	129 223 Md Mendelevium	130 223 No Nobelium	131 223 Lr Lawrencium

Lanthanides	58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 144.24 Pm Promethium	62 150.35 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Ytterbium	71 173.04 Lu Lutetium
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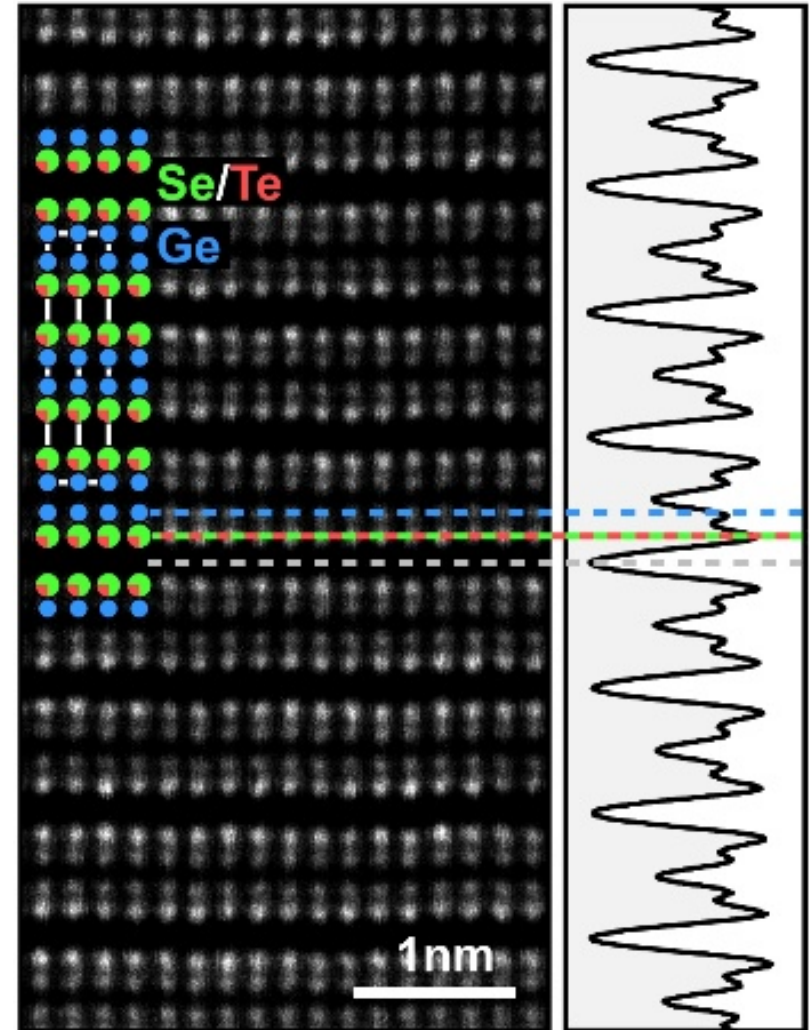
Actinides	90 232.04 Th Thorium	91 231.04 Pa Protactinium	92 238.03 U Uranium	93 237.05 Np Neptunium	94 237.05 Pu Plutonium	95 243 Am Americium	96 247 Cm Curium	97 247 Bk Berkelium	98 251 Cf Californium	99 254 Es Einsteinium	100 257 Fm Fermium	101 261 Md Mendelevium	102 265 No Nobelium	103 269 Lr Lawrencium
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Ge₄Se₃Te, Structure & TEM: Ge-Ge = 2.94 Å

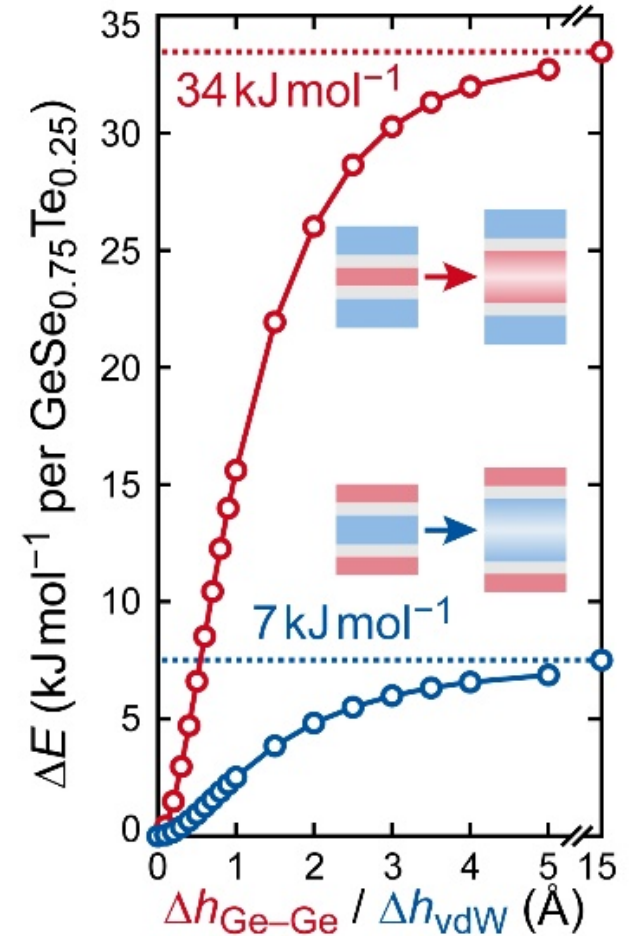
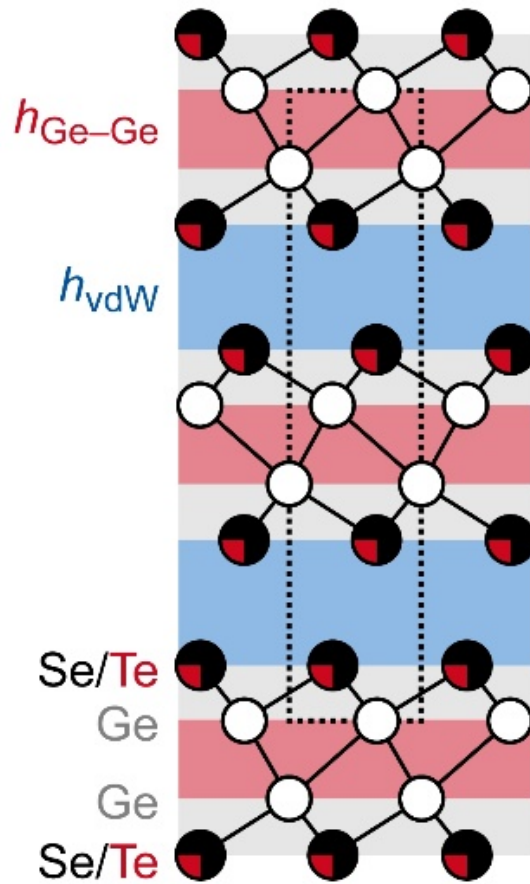
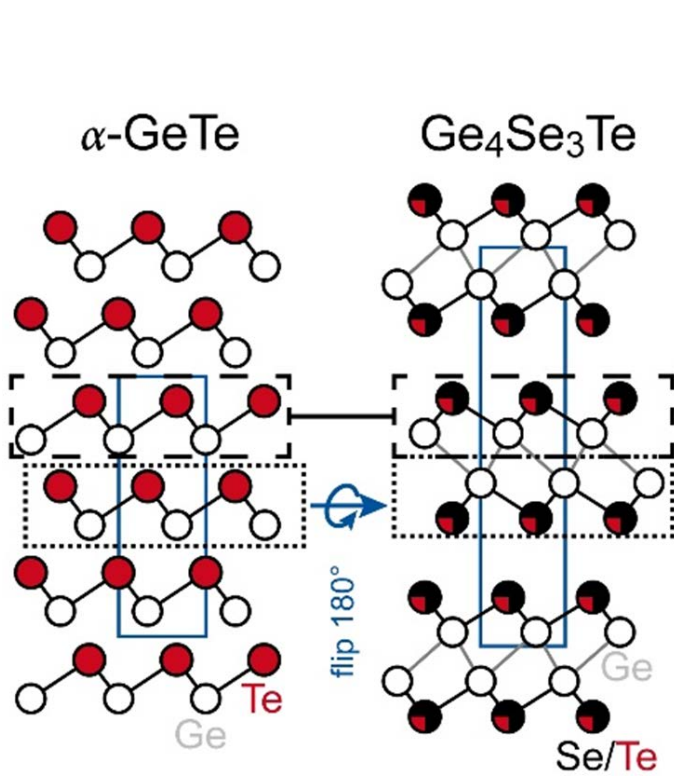


HAADF STEM

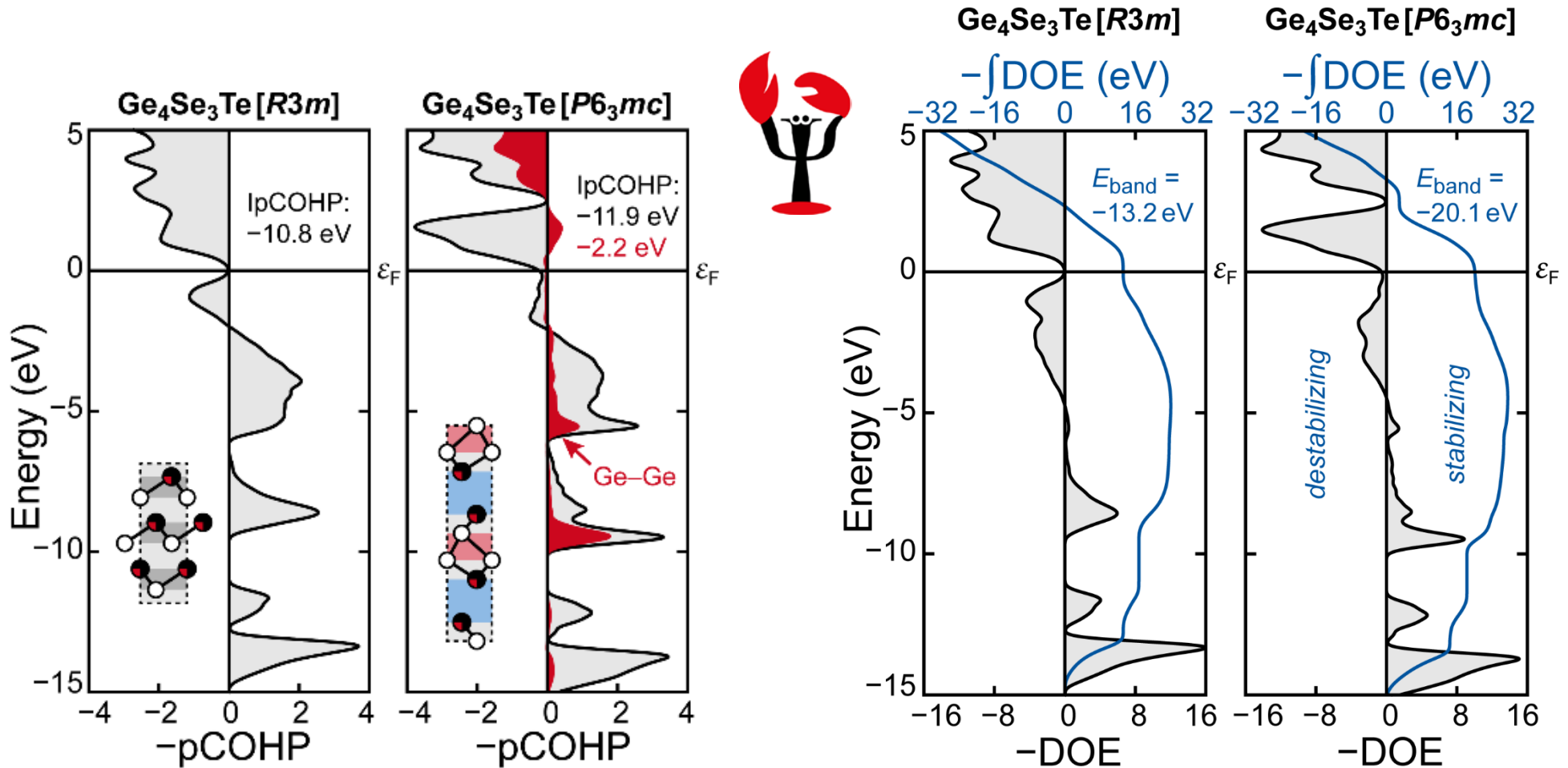
Line Profile



Ge₄Se₃Te: layers & forces (DFT+dispersion)



Ge₄Se₃Te: 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

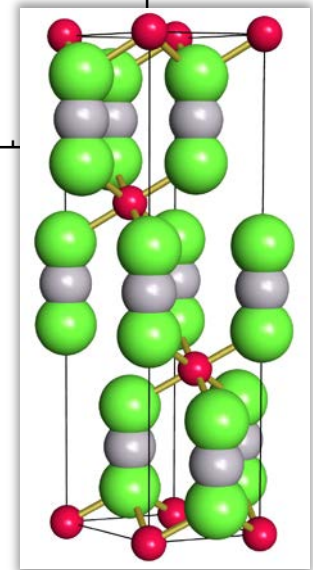
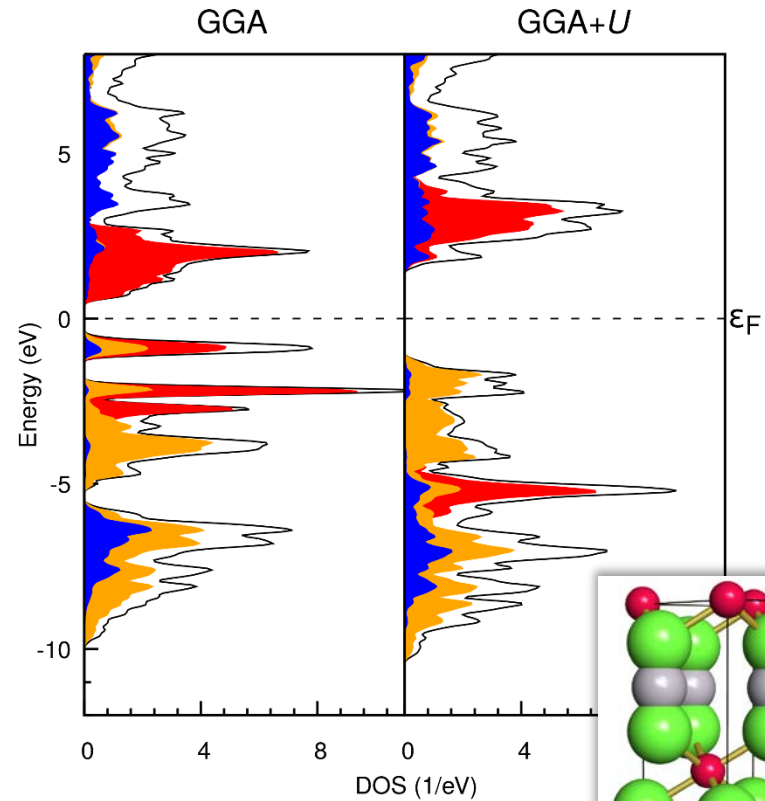
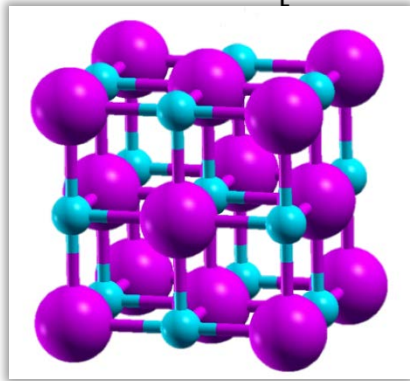
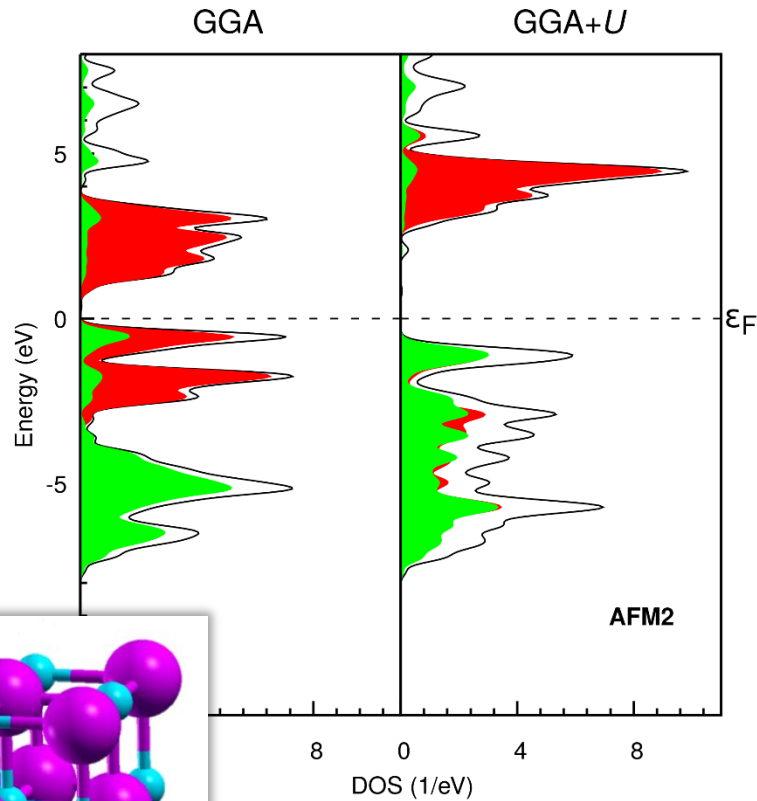


execution time (s)

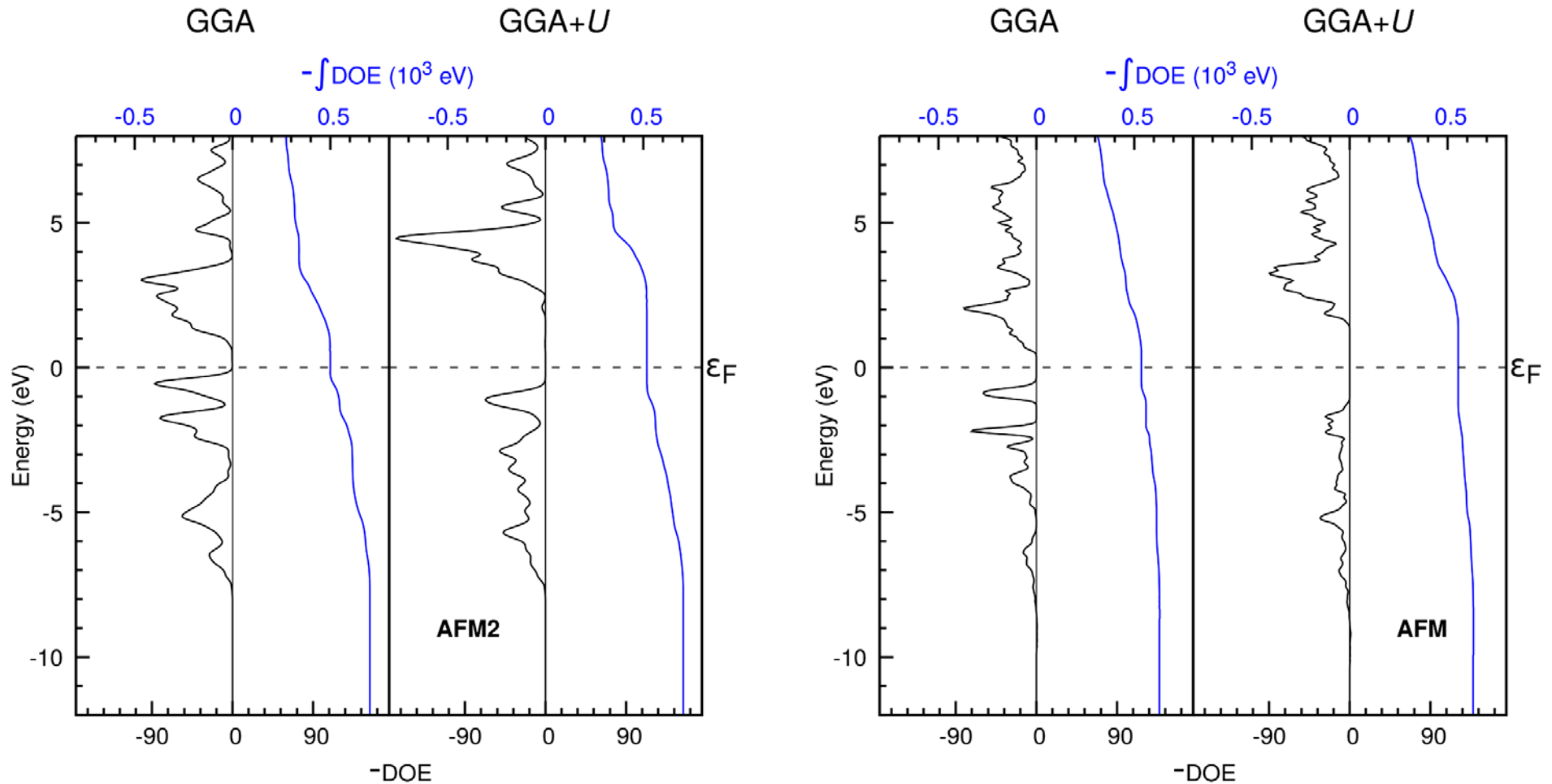
materials \ Interfaces	Espresso	VASP	ABINIT
Diamond	152	36	92
GaAs	611	170	504
Ti	102	33	105
fullerene	719	519	517
carbon-nanotube	114	332	176



Correlated Stuff: MnO and MnNCN



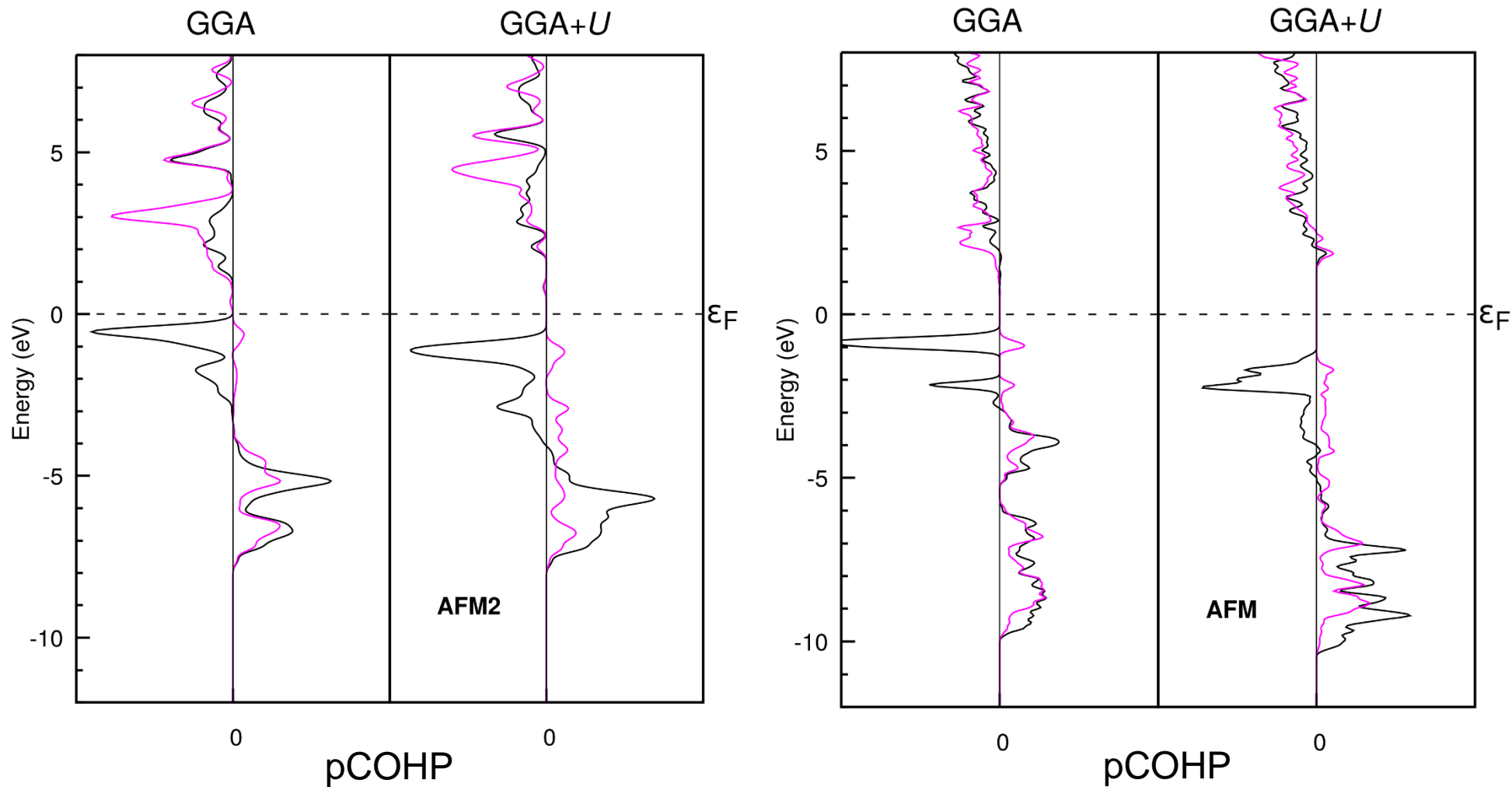
Density-of-Energy: MnO and MnNCN



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

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

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