LOBSTER: Chemical-Bonding Information from Plane Waves (and Orbitals)

Richard Dronskowski

H_2 within LCAO-MO Theory and Bloch States

Bands, DOS, COHP

Bonding Classics: Tellurium, Iron, Phase-Change Materials

Pseudopotentials & Plane Waves

Bonding Information projected from Plane Waves: LOBSTER

Charges and Orbital Mixing ($Pb_2Si_5N_8$)

Bond Indices (István Mayer's Heritage)

Tellurides and Phase-Change Materials, one more time

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

wigner

ab initio Computational Materials Science

MATERIALS PROJECT

NOMAD
NOVEL MATERIALS DISCOVERY

USPEX Computational Materials Discovery

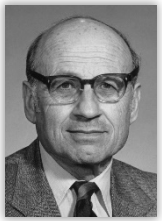
XtalOpt
Evolutionary Crystal Structure Prediction

CALYPSO

b-initio VASP icnna ackage imulation

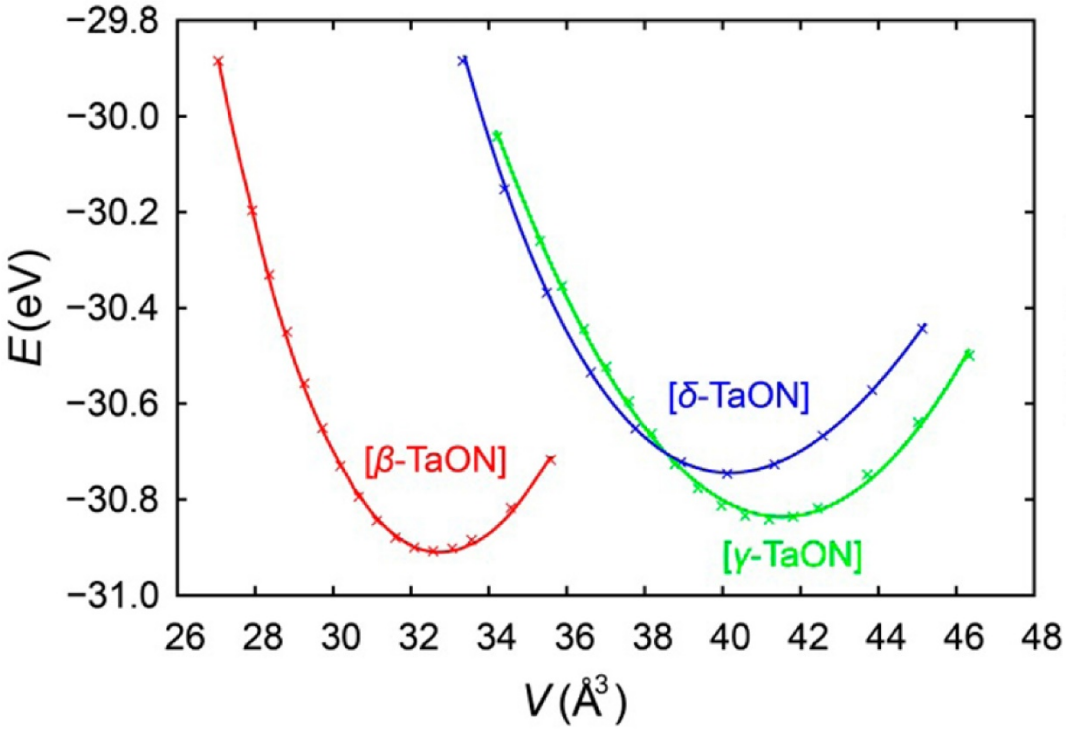
QUANTUMESPRESSO

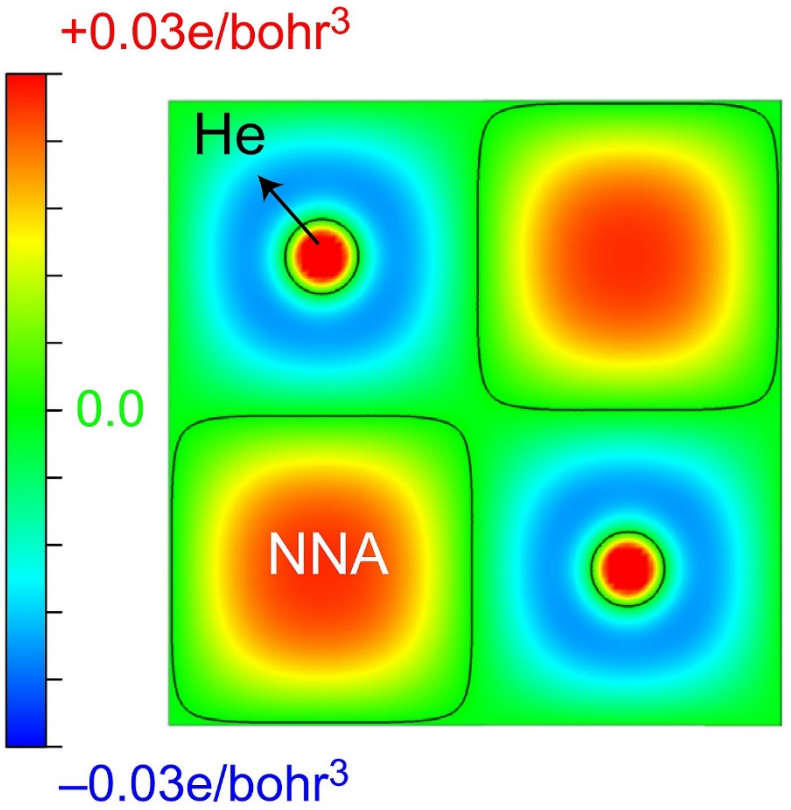
Abinit



$$v_{\mathrm{eff}}(\boldsymbol{r}) = v(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}' + v_{\mathrm{XC}}(\boldsymbol{r})$$

Total energy, ρ(*r*), *E* vs. *V*, DOS… is *insufficient*





Total energy, ρ(*r*), *E* vs. *V*, DOS… is *insufficient*

*To **understand** an observable means **being able to predict**, albeit qualitatively, the result that **a perfectly reliable calculation** would yield for that observable.*

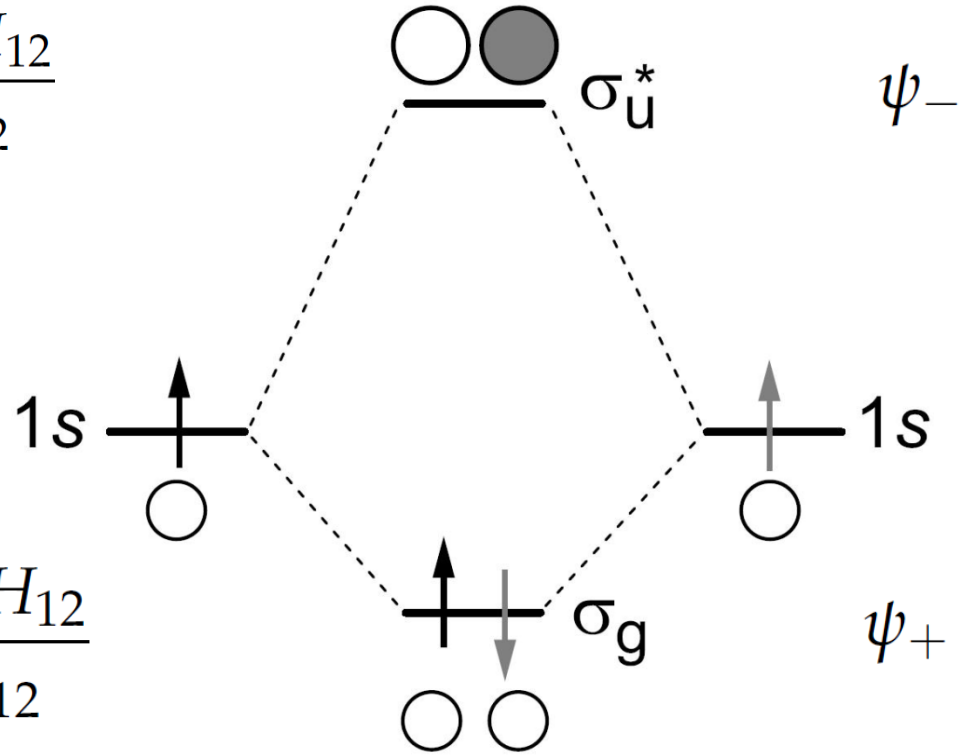
Roald Hoffmann,
Acc. Chem. Res.
1971, *4*, 1

LCAO-MO theory of the hydrogen molecule, H_2

$$\psi = c_1\phi_1 + c_2\phi_2$$

$$E_- = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

$$\psi_- = \frac{\phi_1 - \phi_2}{\sqrt{2(1 - S_{12})}}$$

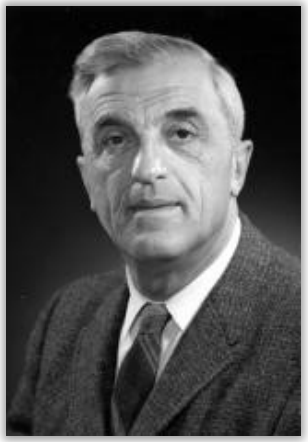


$$E_+ = \frac{H_{11} + H_{12}}{1 + S_{12}}$$

$$\psi_+ = \frac{\phi_1 + \phi_2}{\sqrt{2(1 + S_{12})}}$$

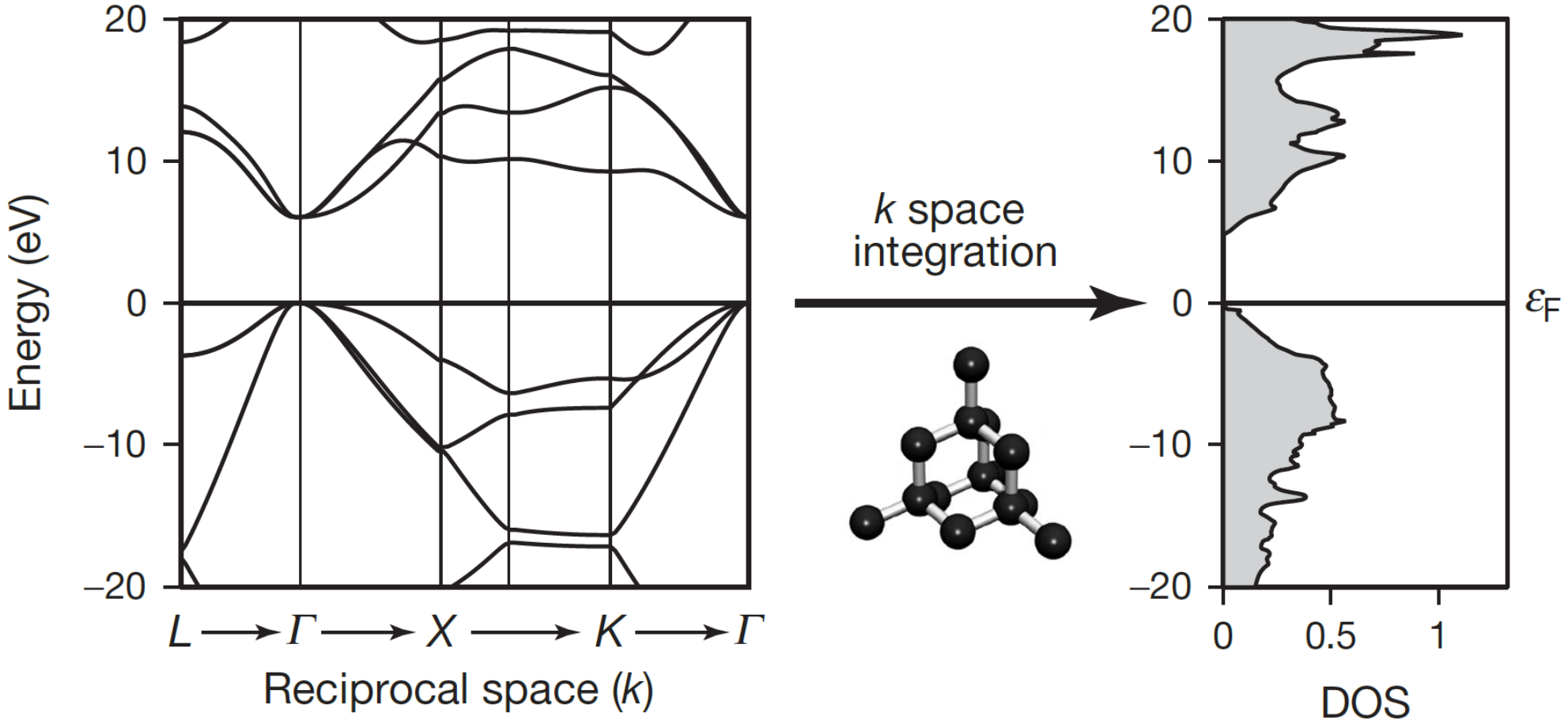
Felix Bloch's famous theorem

$$\psi(\boldsymbol{k}, \boldsymbol{r} + \boldsymbol{T}) = e^{i\boldsymbol{k}\boldsymbol{T}} \psi(\boldsymbol{k}, \boldsymbol{r})$$



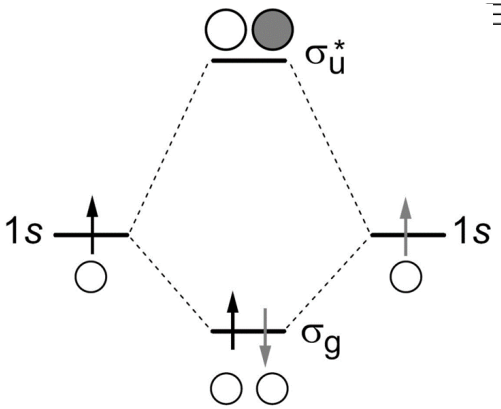
"When I started thinking about the problem, I realized that the main difficulty was to explain how the electrons could pass all the ions in the metal undisturbed [...] To my delight I found by a simple Fourier analysis that the wave differed from a plane wave of a free electron only by a periodic modulation."

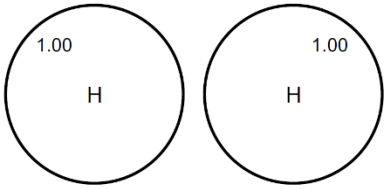
3dim diamond: bands and DOS (real system, DFT)

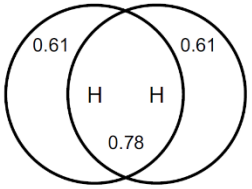


H_2: Population Analysis by Robert S. Mulliken

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



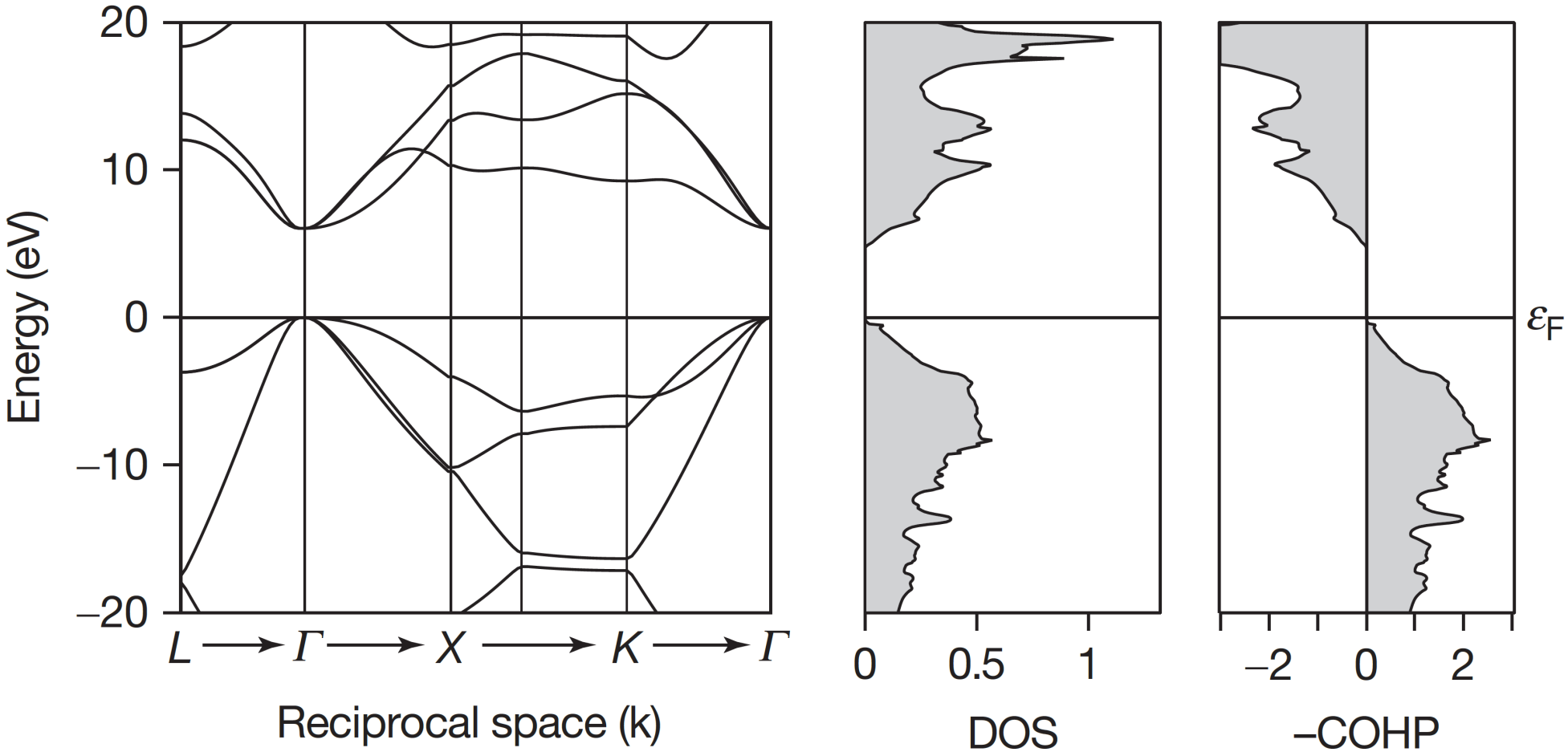




R. S. Mulliken,
J. Chem. Phys.
1955, *23*, 1833

none of the aforementioned plane-wave electronic-structure codes can do that because they are all lacking the atomic orbitals

3dim diamond: band structure, DOS, COHP



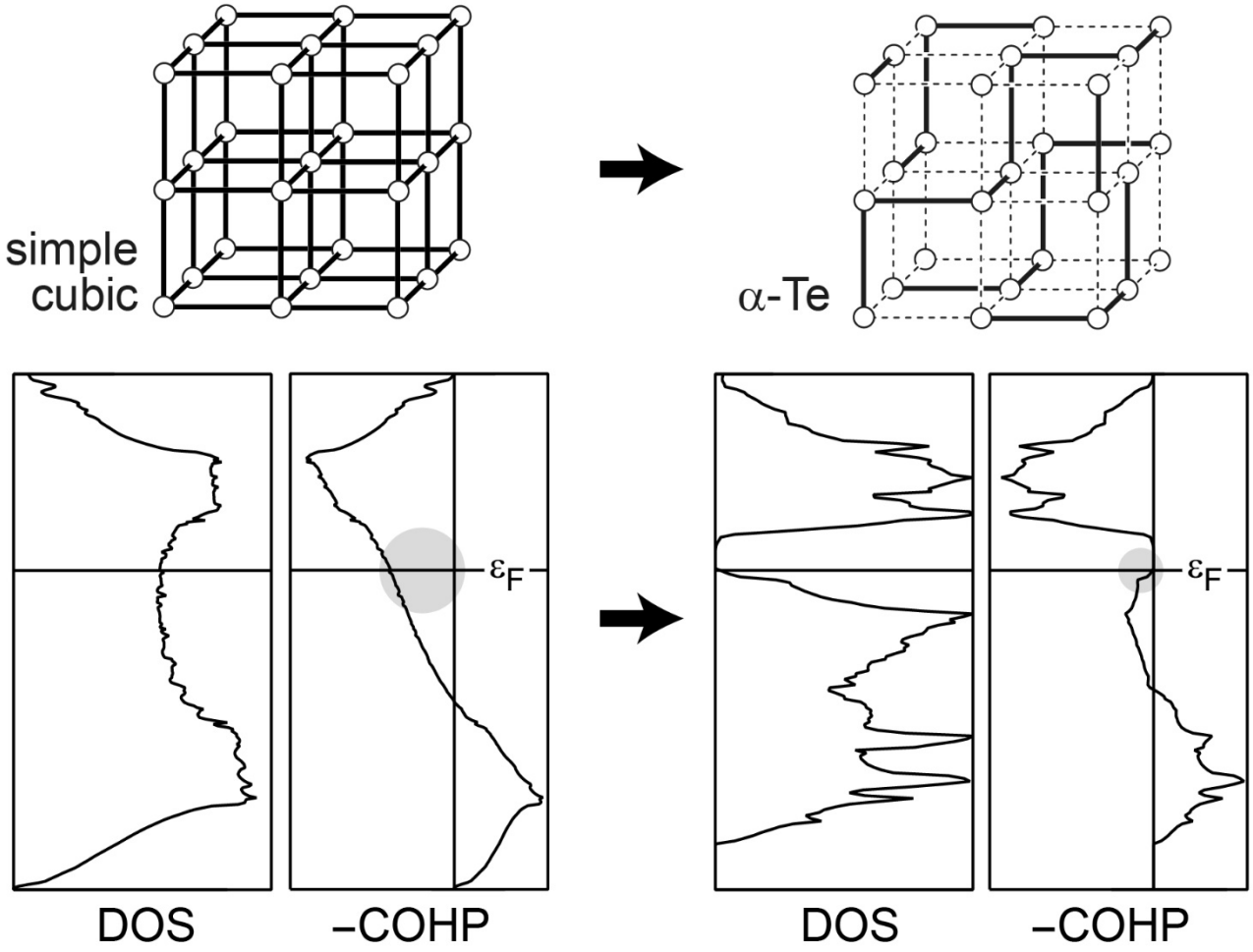
R. Dronskowski, P. E. Blöchl,
J. Phys. Chem. **1993**, *97*, 8617

DFT: Crystal Orbital Hamilton Population, COHP

$$E = \underbrace{\int^{\varepsilon_F} \sum_A \sum_{\substack{\mu \\ \mu \in A}} P_{\mu\mu}(E) H_{\mu\mu}(E)\, dE}_{\text{net atomic energies}} + \underbrace{\int^{\varepsilon_F} 2 \sum_A \sum_{B>A} \sum_{\substack{\mu \\ \mu \in A}} \sum_{\substack{\nu \\ \nu \in B}} \mathrm{Re}[P_{\mu\nu}(E) H_{\mu\nu}(E)]\, dE}_{\text{bonding energies}}$$

partitioning the energy, not the electrons, between the atoms and the bonds...

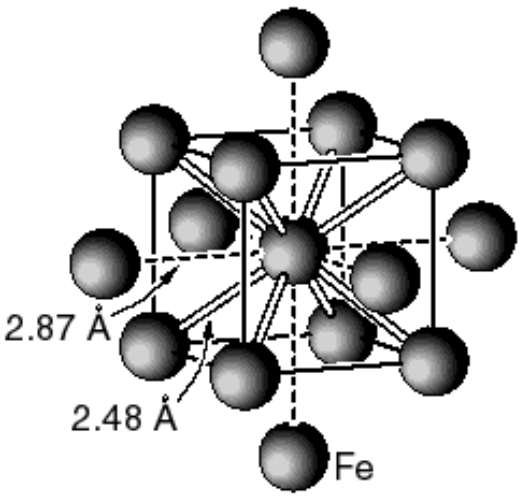
Example I: sc Tellurium is Peierls-unstable

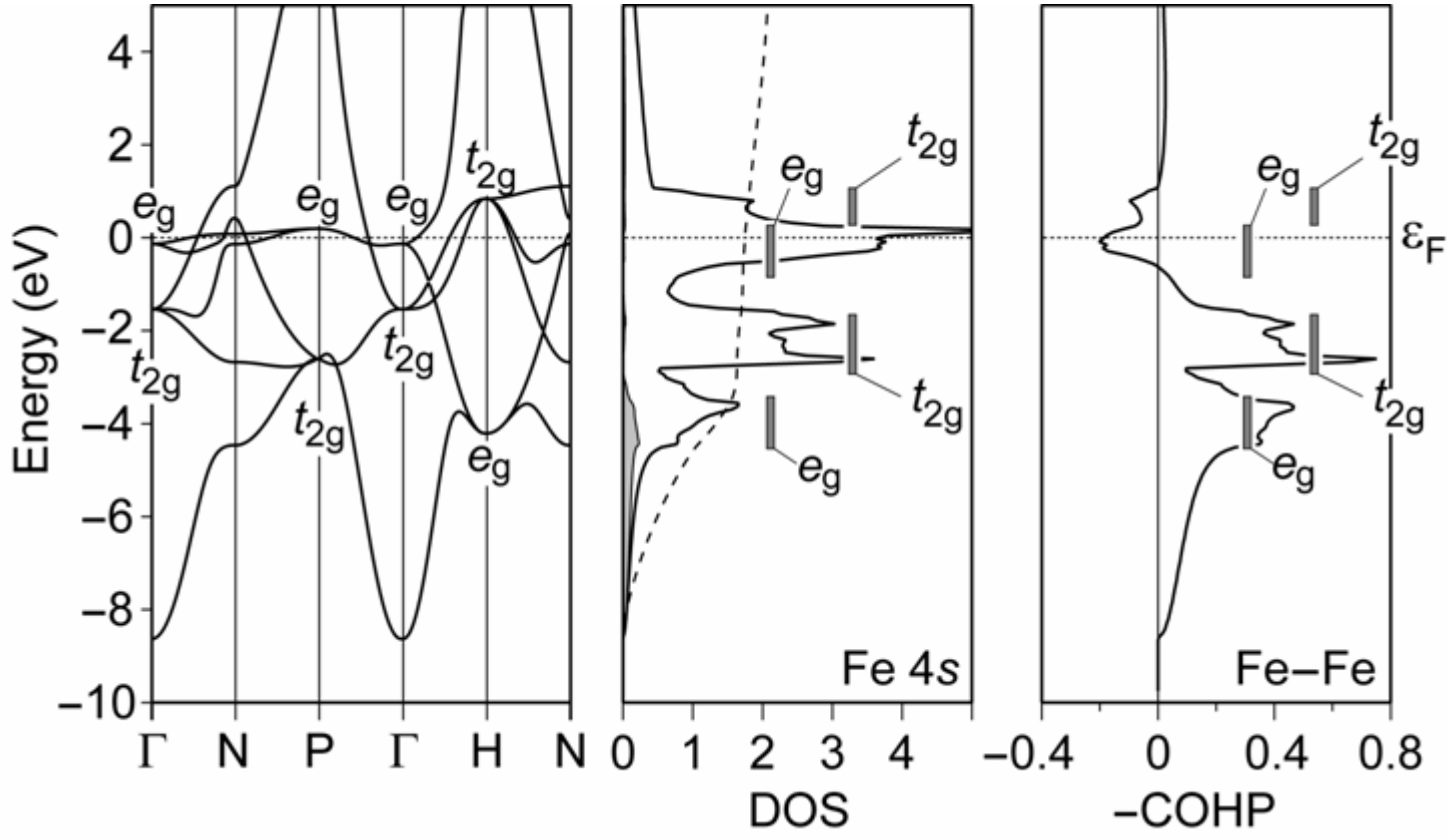


A. Decker, G. A. Landrum, R. Dronskowski,
Z. Anorg. Allg. Chem. **2002**, *628*, 295

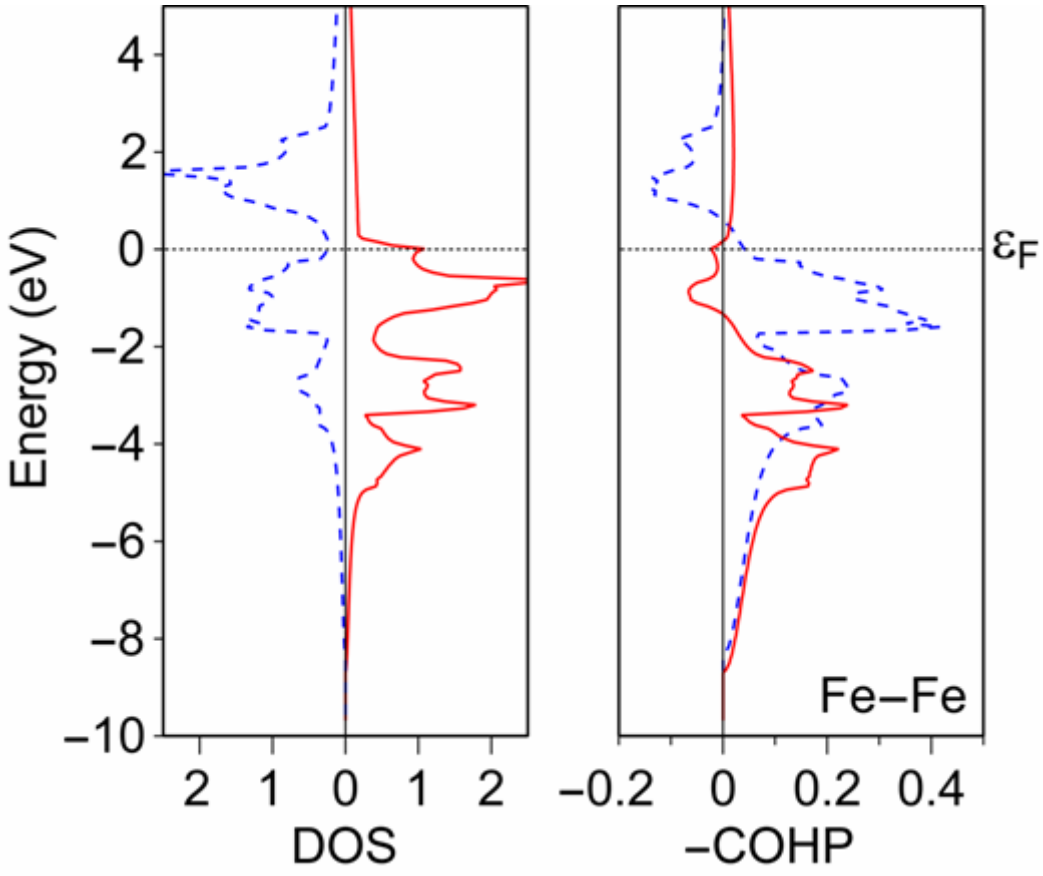
Example II: body-centered cubic Fe

and its corresponding non-realistic LDA band structure
without spin-polarization, on purpose:





Spin Polarization: Chemical Bonding



magnetic moment: 2.27 μ_B (exp.: 2.21 μ_B)

majority spin orbitals contract

minority spin orbitals expand

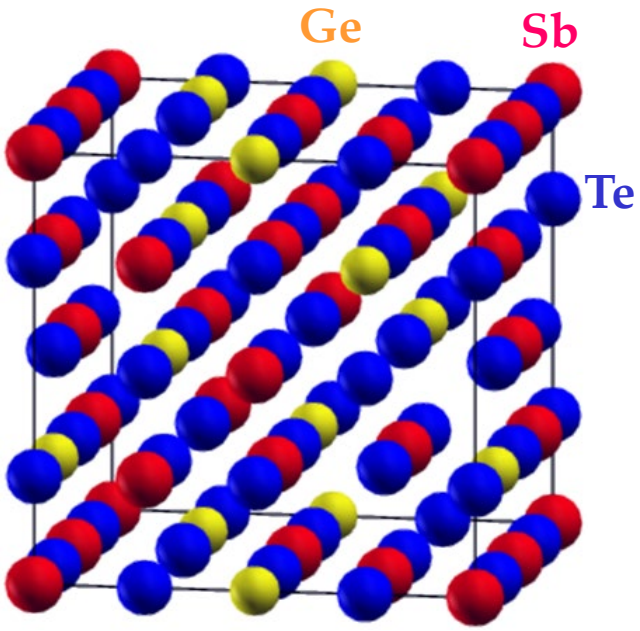
lowering of total energy by about 0.43 eV

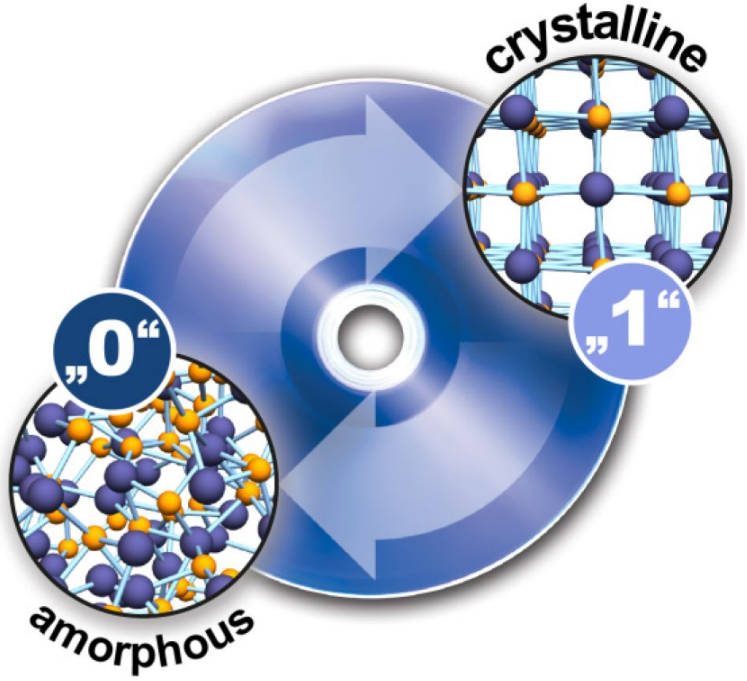
strengthening of iron–iron bonding by about 5%

minority spins roughly twice as strongly bonding as majority spins

G. A. Landrum, R. Dronskowski,
Angew. Chem. Int. Ed. **2000**, *39*, 1560

Example III: Ge–Sb–Te Phase-change Materials

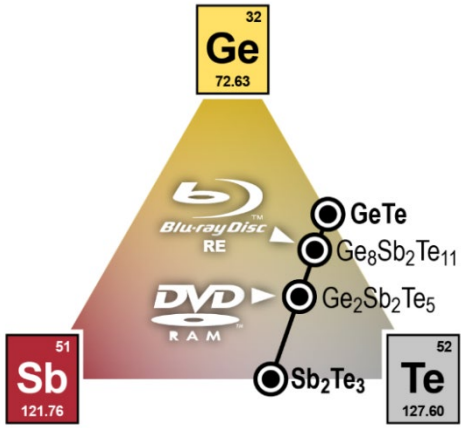


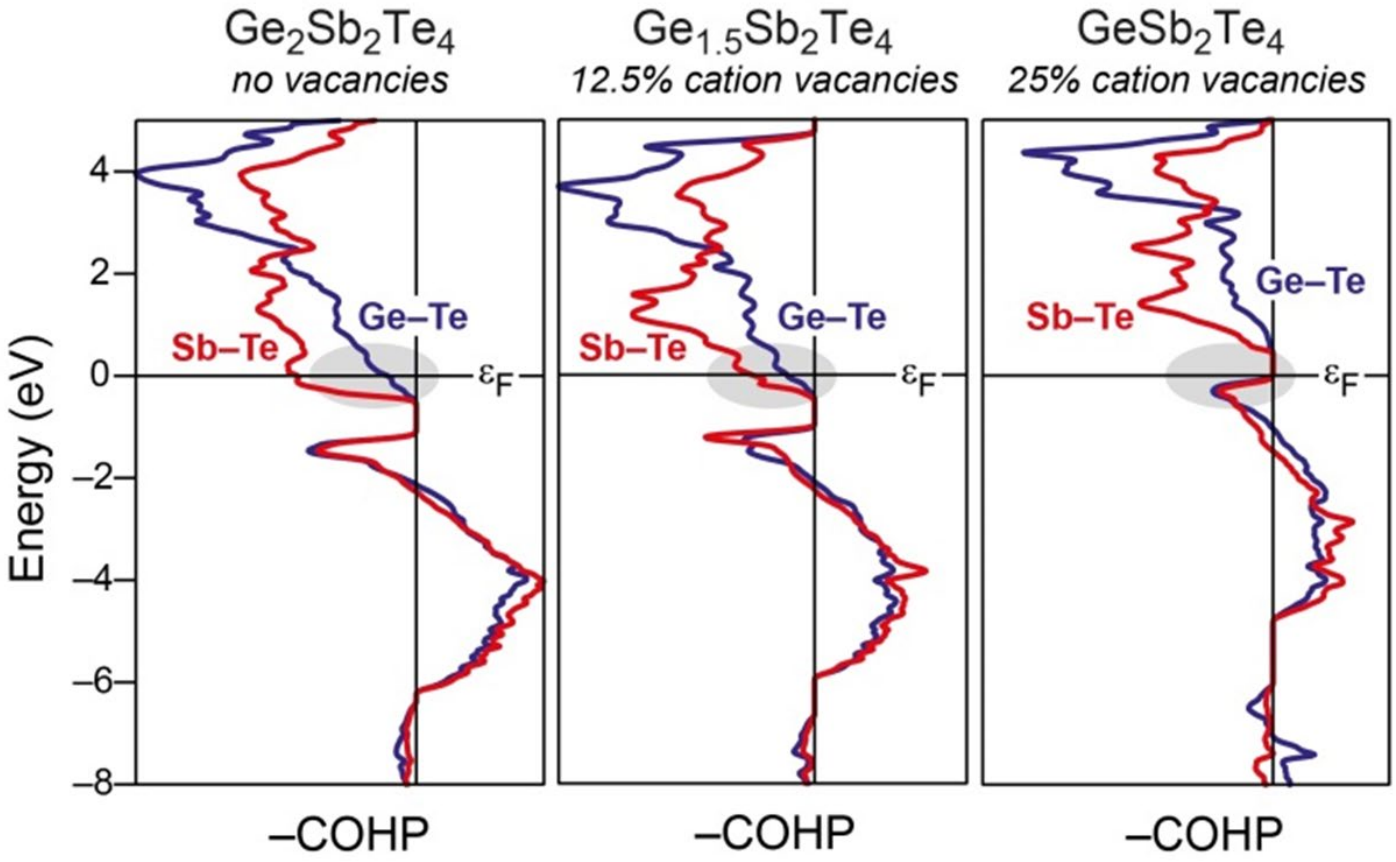


e.g., $Ge_2Sb_2Te_4$ with lots of Ge vacancies (≈ 20%) – **why?**

switching mechanism = *f*(vacancy nature)

Phase-change Materials: first COHP study

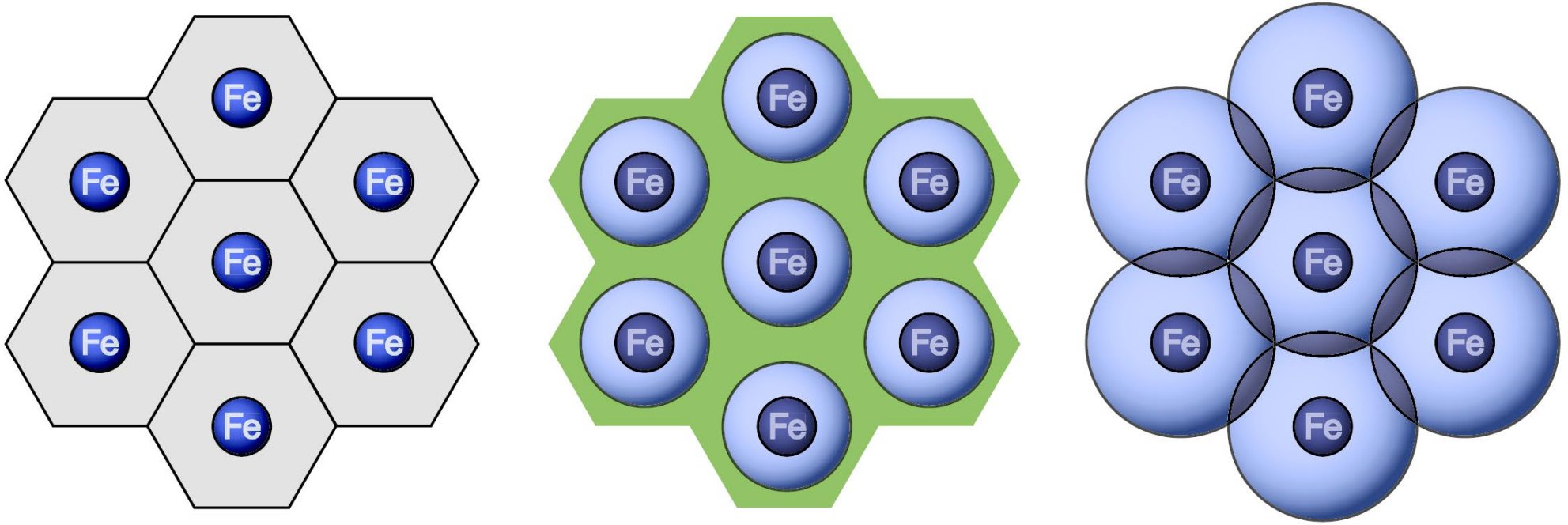




antibonding *Ge–Te and Sb–Te interactions in the highest bands; germanium vacancies annihilate antibonding states*

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

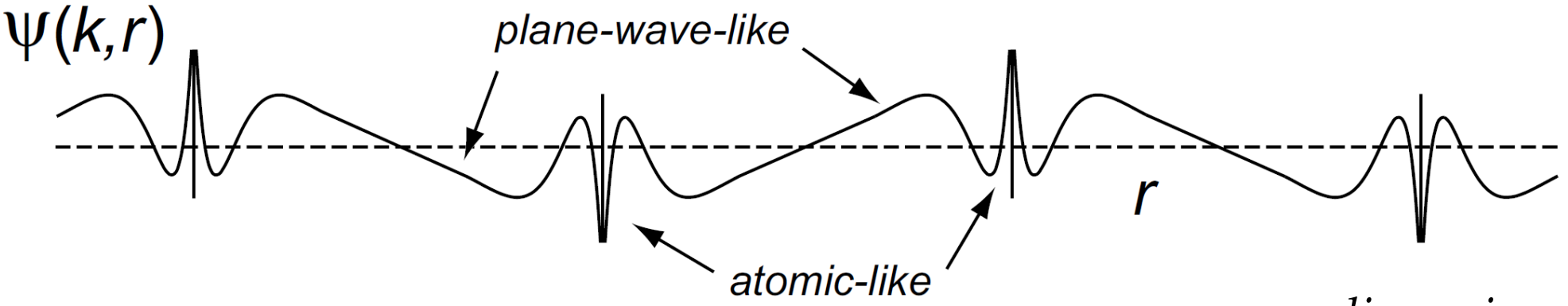
Wigner–Seitz, Muffin-Tin, Atomic Spheres → LMTO



Tight-Binding Linear-Muffin-Tin Orbitals
using the Atomic-Spheres-Approximation (ASA)

probably the most influential (among the chemists)
periodic ***orbital-based*** *electronic-structure method*

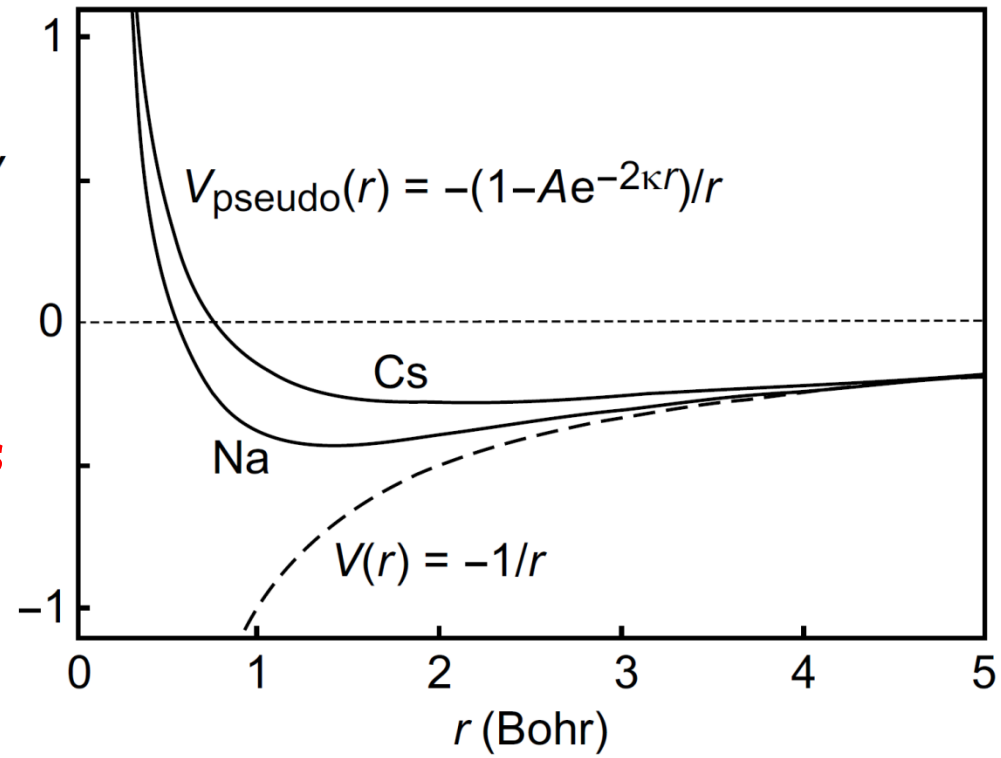
Hans Hellmann, *J. Chem. Phys.* 1935, *3*, 61



one-dimensional Na-3s Bloch function at **X**

the world's first pseudopotentials: Na and Cs

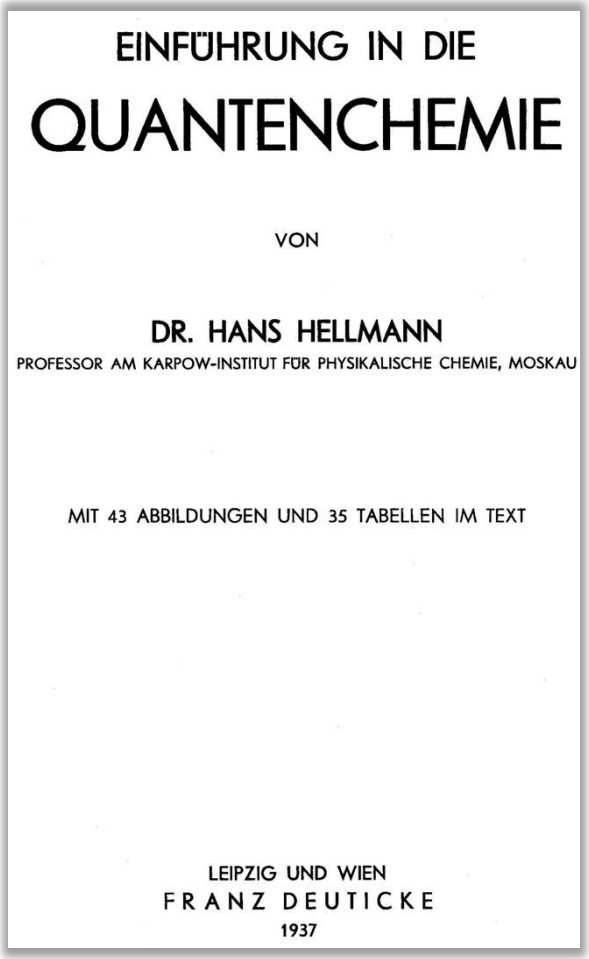
→ *plane waves, thus* ***reliable*** *forces!*

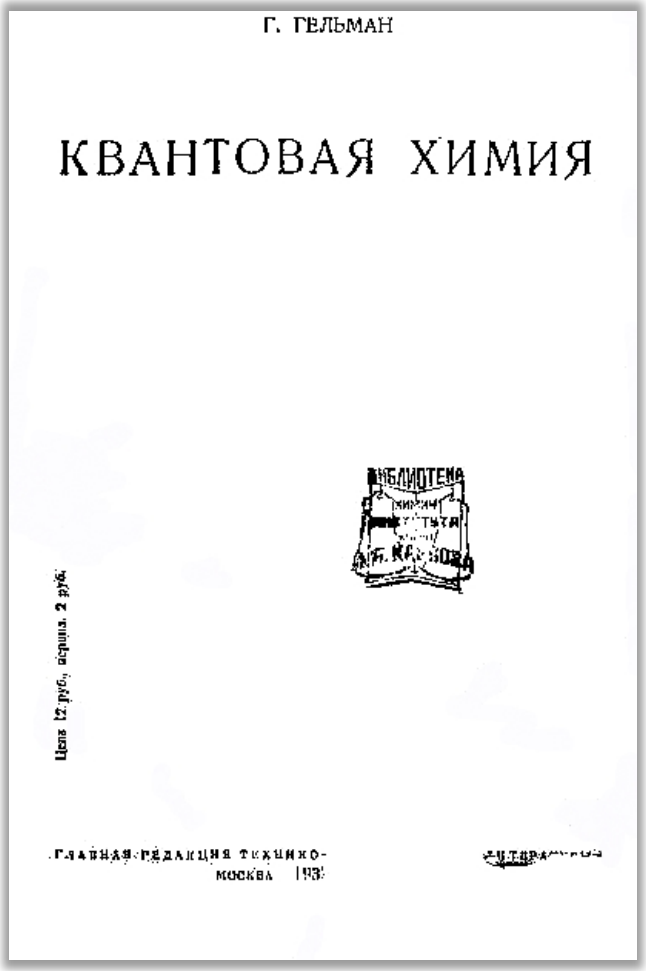


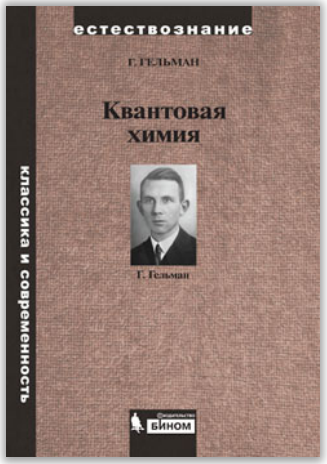
1933: Emigration to the Soviet Union

Greta Hermine Hans

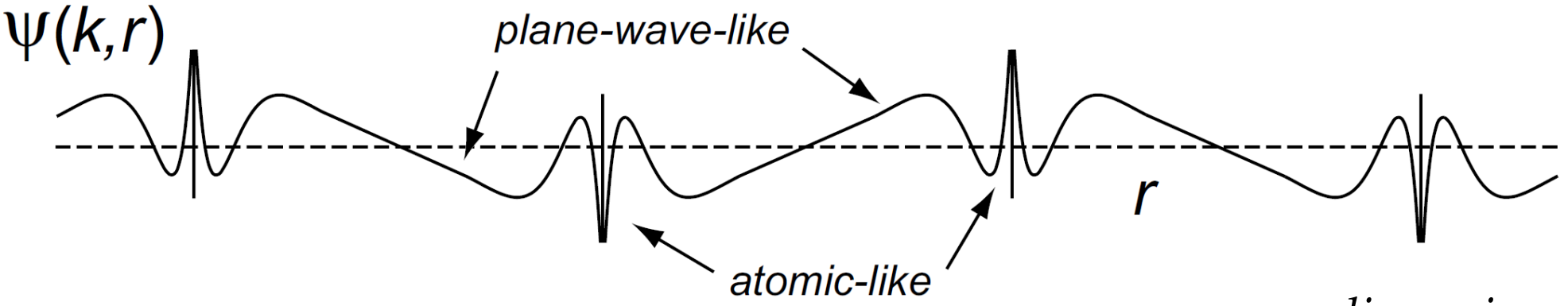
The World's first Quantum-Chemistry Textbooks







Hans Hellmann, *J. Chem. Phys.* 1935, *3*, 61



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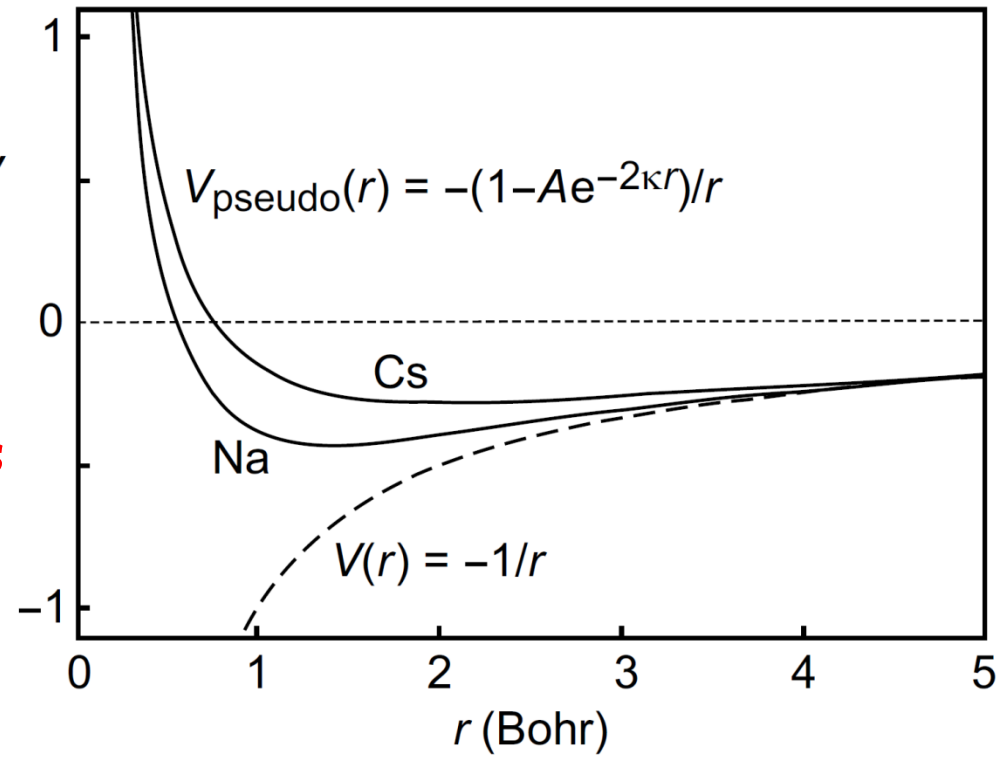
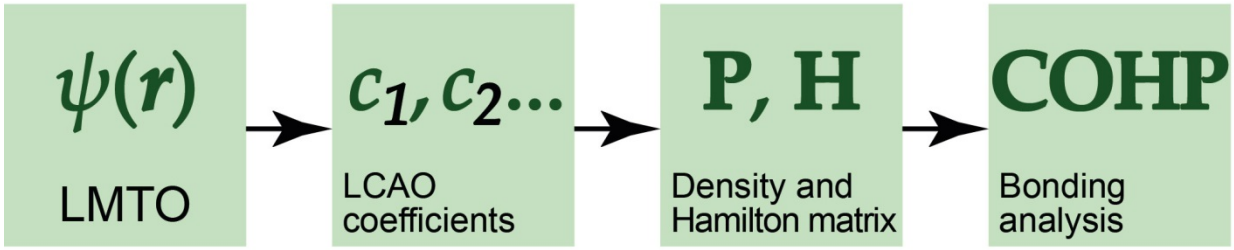
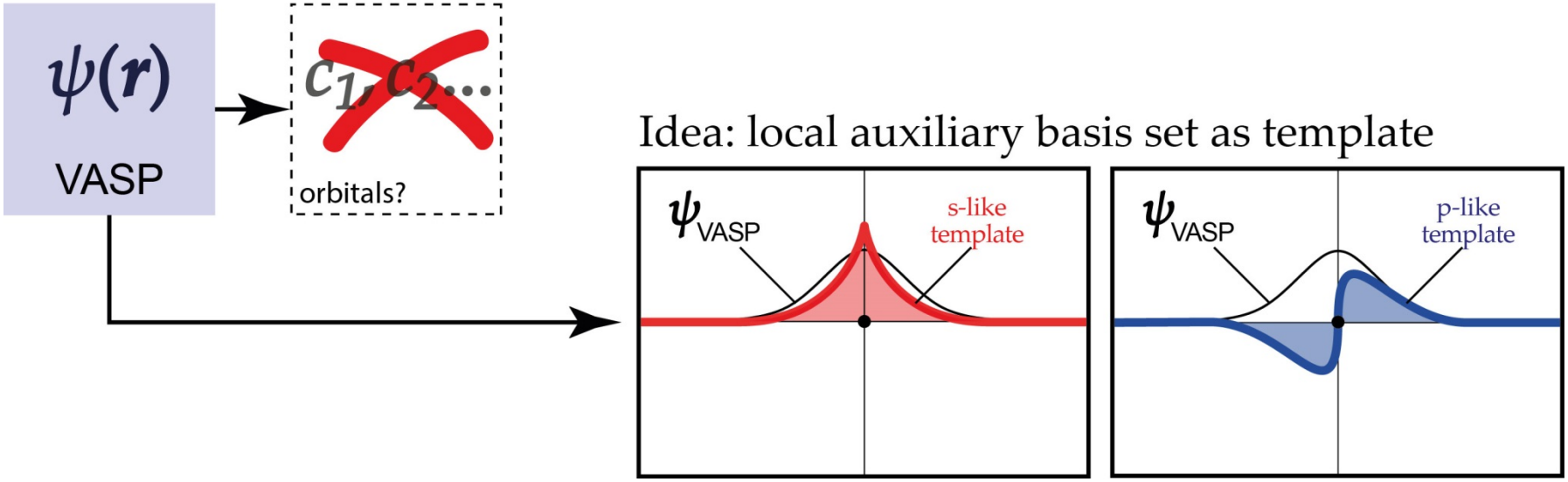


Retrieving the Chemistry

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



Modern: countless program packages with plane waves (e.g., VASP)



LOBSTER transforms plane-wave DFT data

PAW Output

$$|\psi_i\rangle = \left[1 + \Sigma_\mu \left(|\phi_\mu\rangle - |\tilde{\phi}_\mu\rangle \right) \langle \tilde{p}_\mu| \right] |\tilde{\psi}_i\rangle \, ; \, \varepsilon_i$$

VASP, QE, ABINIT

$$|\phi_\mu\rangle, |\tilde{\phi}_\mu\rangle, |\tilde{p}_\mu\rangle, |\tilde{\psi}_i\rangle, \varepsilon_i$$

LOBSTER
Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction

Slater-type orbitals

$$|\chi_\mu\rangle$$

(Bunge, Koga, pbeVaspFit2015)

Projection

$$T_{\mu j}(\boldsymbol{k}) = \langle \chi_\mu(\boldsymbol{k}) \,|\, \psi_i(\boldsymbol{k}) \rangle = \sum_\nu S_{\mu\nu}(\boldsymbol{k}) C_{\mu j}(\boldsymbol{k})$$

Chemical Bonding Analysis

$$|\psi_i\rangle = \sum_\mu C_{\mu j}(\boldsymbol{k}) \, |\chi_\mu\rangle$$

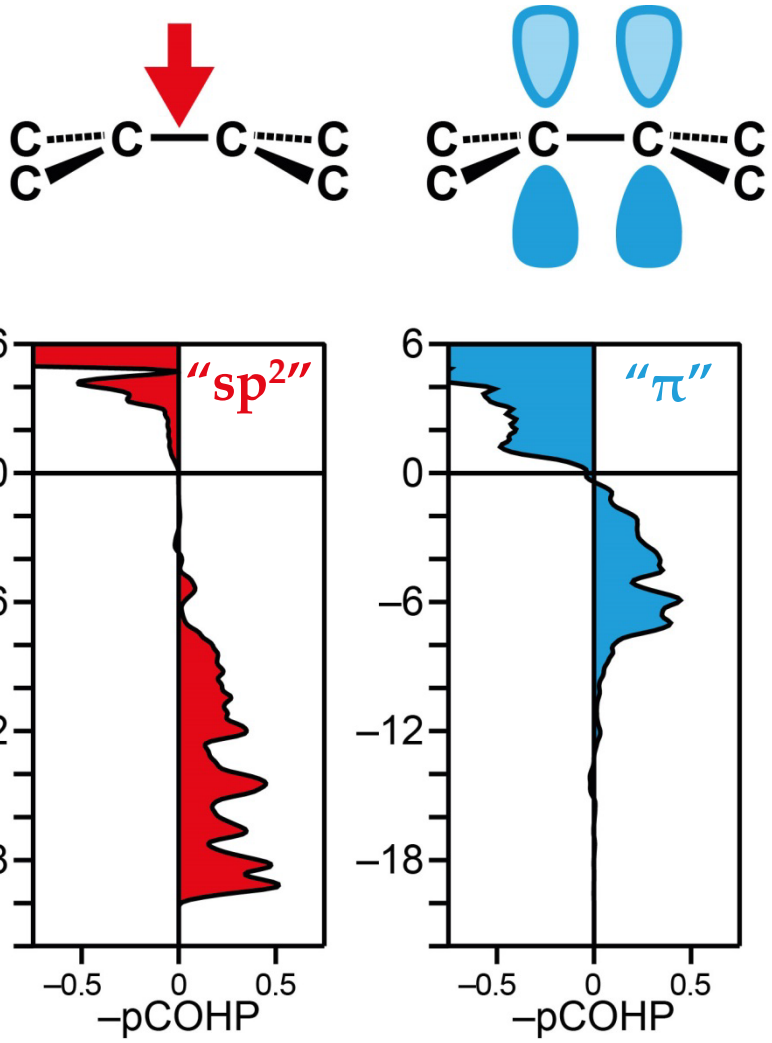
$C(\boldsymbol{k})$: pDOS, pCOOP, pCOHP, DOE, charge

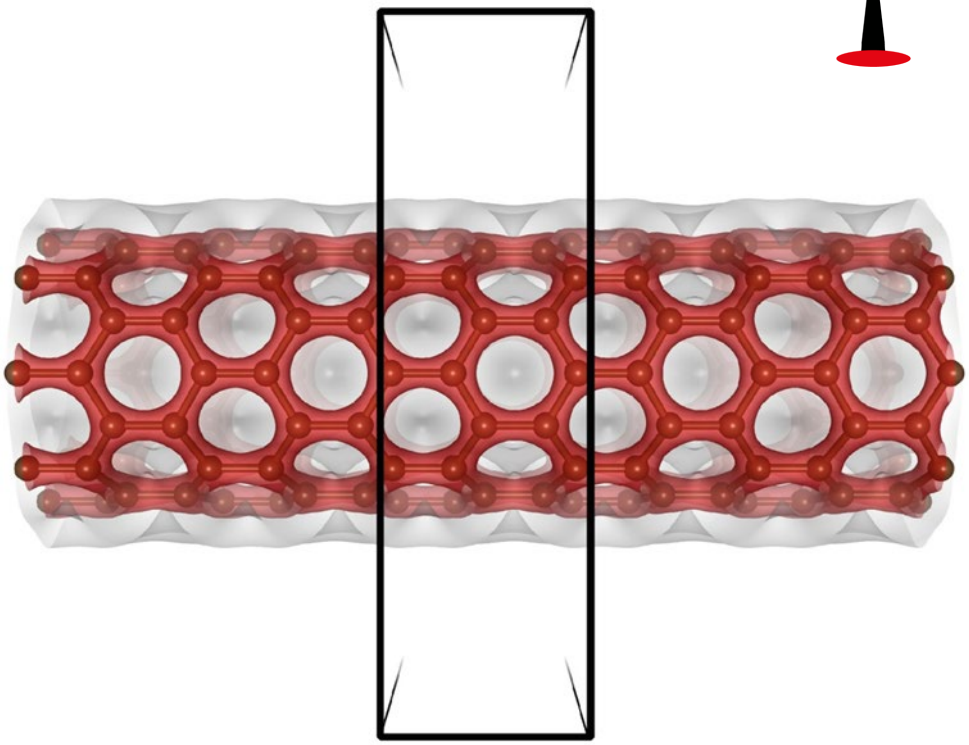
www.cohp.de

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

Wigner

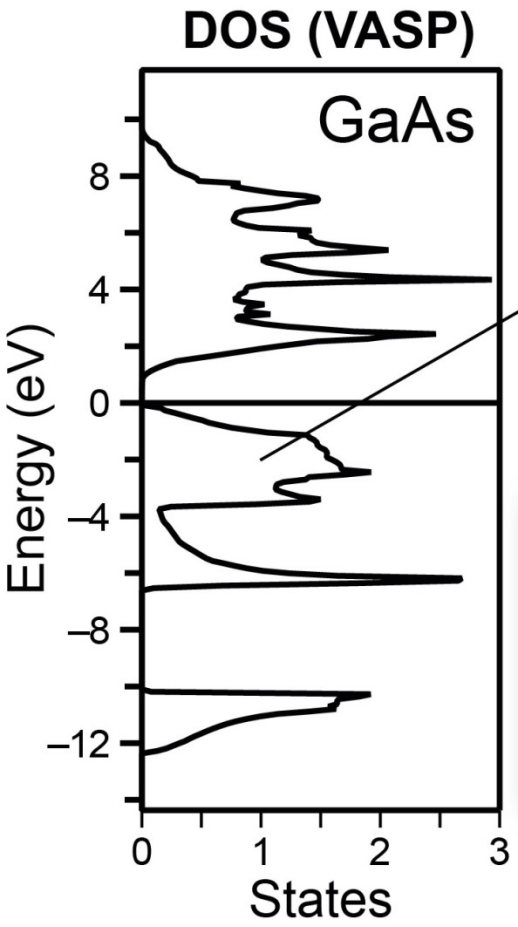
Chemical Bonding in the Carbon Nanotube





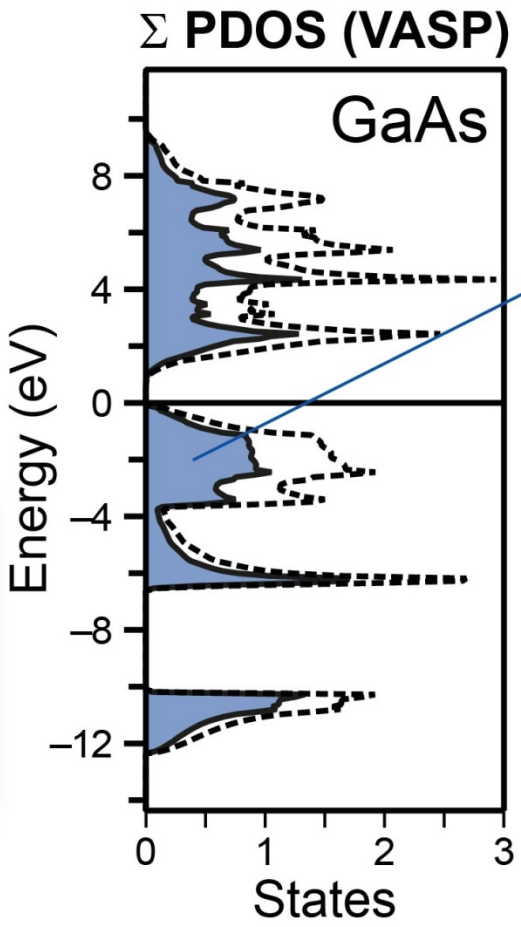
S. Maintz, V. L. Deringer,
A. L. Tchougréeff, R. Dronskowski,
J. Comput. Chem. **2016**, *37*, 1030

GaAs: fast & incorrect local DOS projections



Integral:
8.0 electrons

Ga: $4s^2\ 4p^1 \rightarrow$	**3 e⁻**
As: $4s^2\ 4p^3 \rightarrow$	**5 e⁻**
Total:	**8 e⁻**

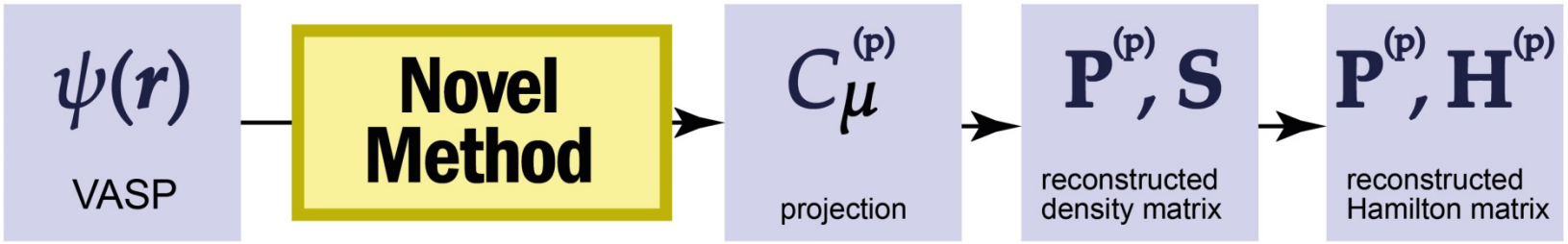


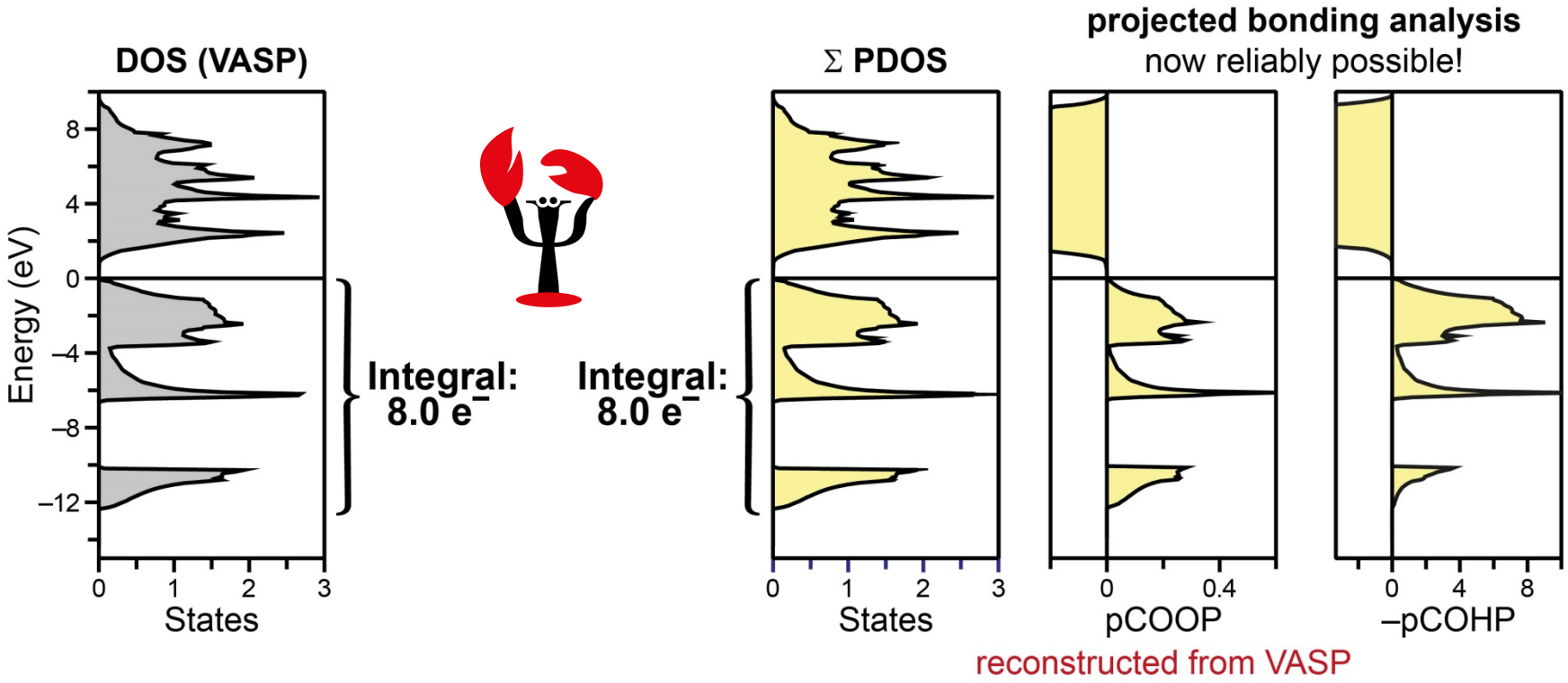
Integral:
4.8 electrons

40% lost!

*within VASP, the local DOS almost **never** add up to the total DOS due to the chosen algorithm*

Correct Local Projection for GaAs using LOBSTER





How to calculate atomic charges

Bader

Mulliken

Löwdin

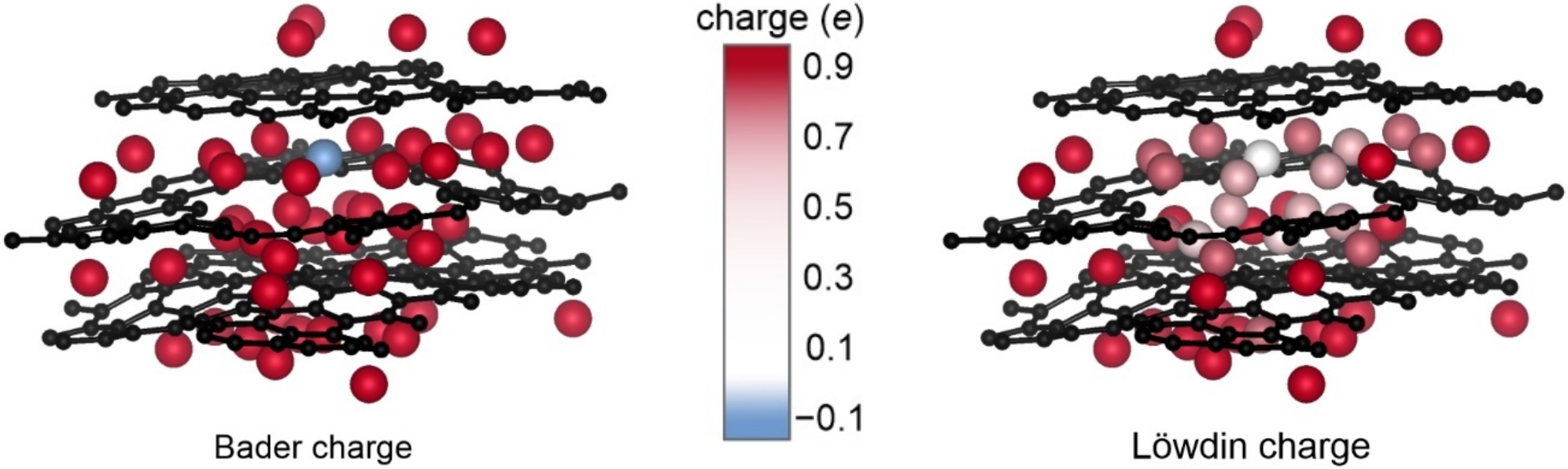
from the density

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N} f_i |\psi_i(\boldsymbol{x})|^2$$

from the wave function (orbitals)

$$\psi_i(\boldsymbol{x})$$

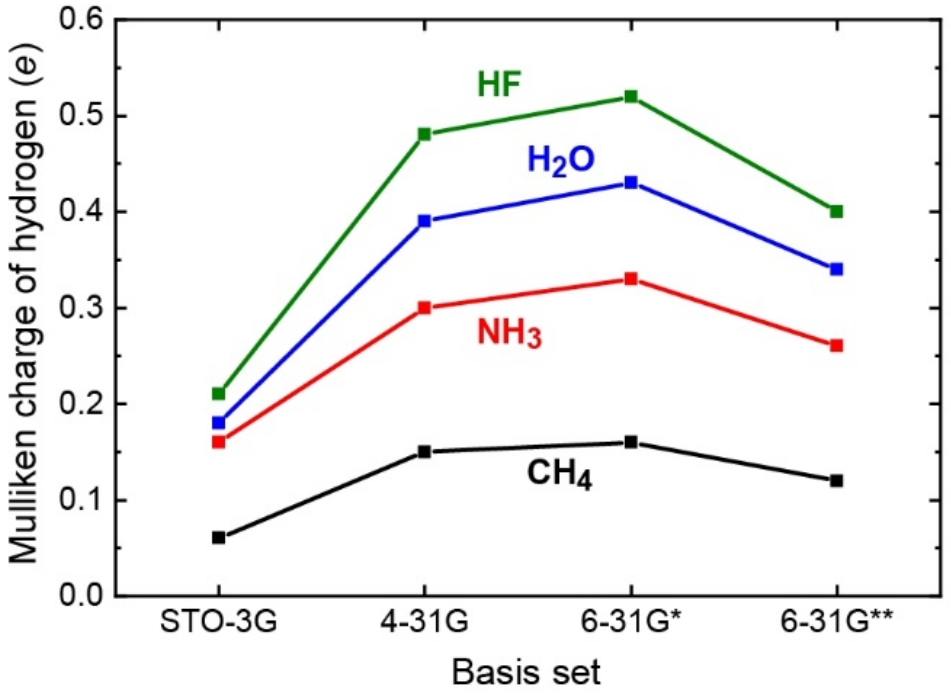
Amorphous $Li_{48}C_{216}$ – Bader *vs* Löwdin



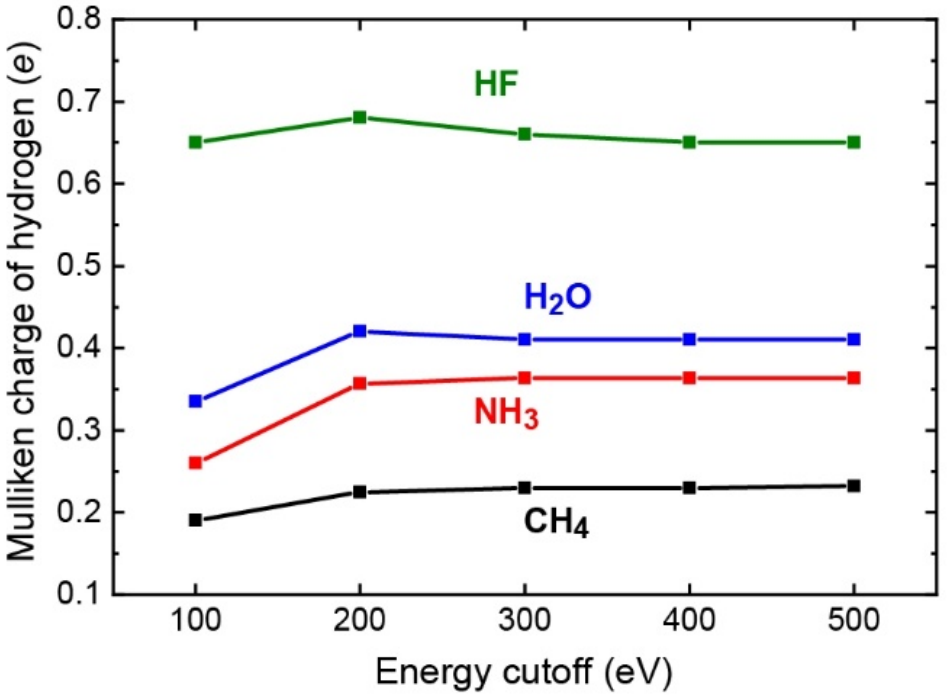
J.-X. Huang, G. Csányi, J.-B. Zhao, J. Cheng, V. L. Deringer, *J. Mater. Chem. A* **2019**, *7*, 19070

R. Nelson, C. Ertural, J. George, V. L. Deringer, G. Hautier, R. Dronskowski, *J. Comput. Chem.* **2020**, *41*, 1931

No basis-set dependency from plane waves



local basis sets (HF)



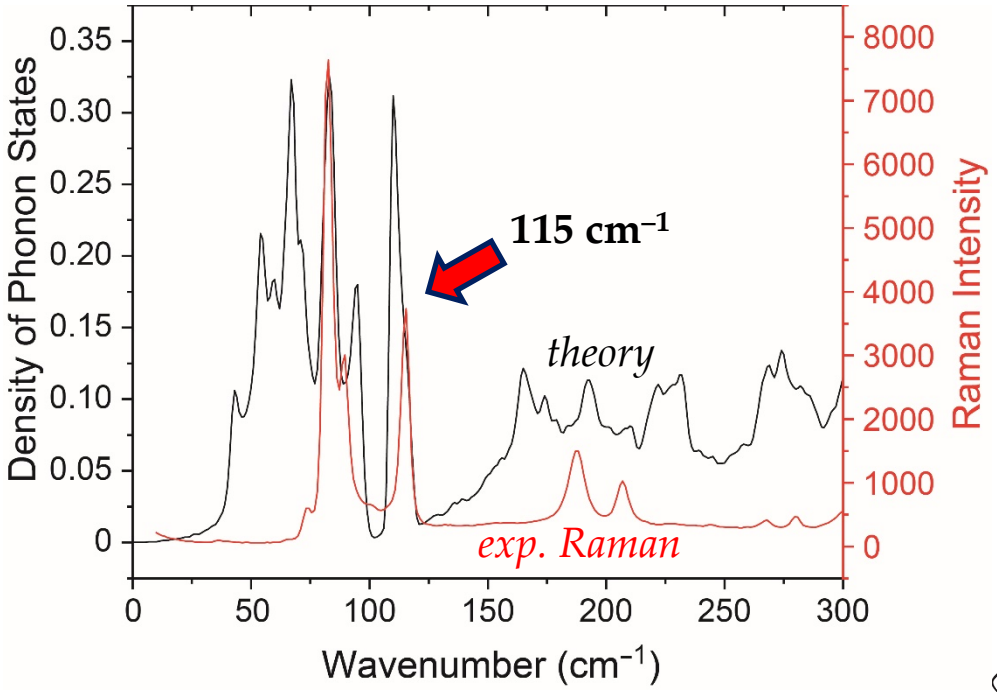
plane waves (LDA)

C. Ertural, S. Steinberg, R. Dronskowski,
RSC Advances **2019**, *9*, 29821

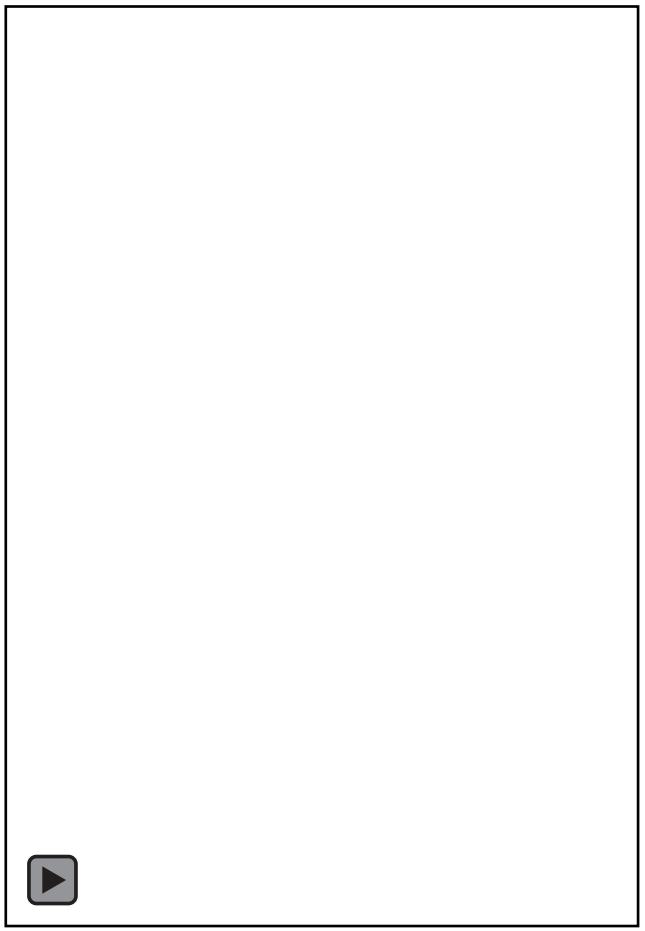
$Pb_2Si_5N_8$ from Schnick's group

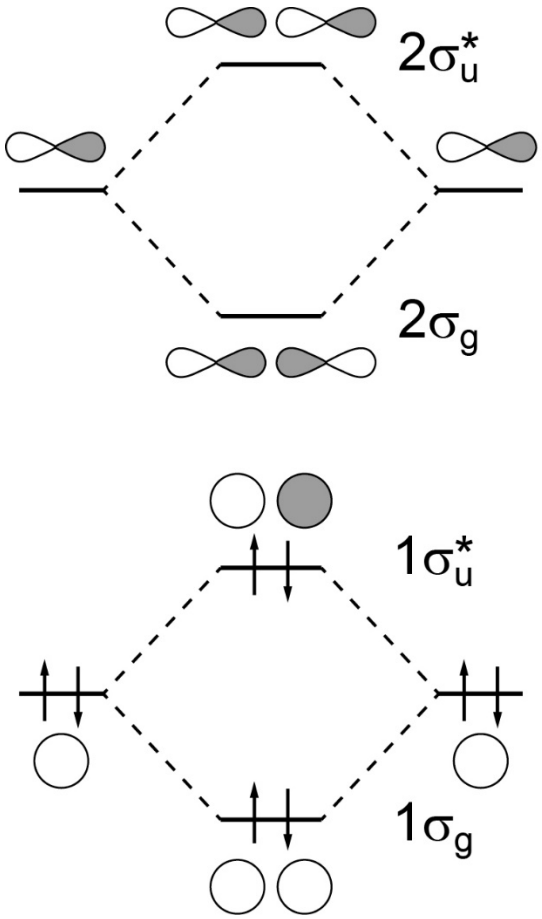
$$2\ PbCl_2 + Sr_2Si_5N_8 \rightarrow Pb_2Si_5N_8 + 2\ SrCl_2$$

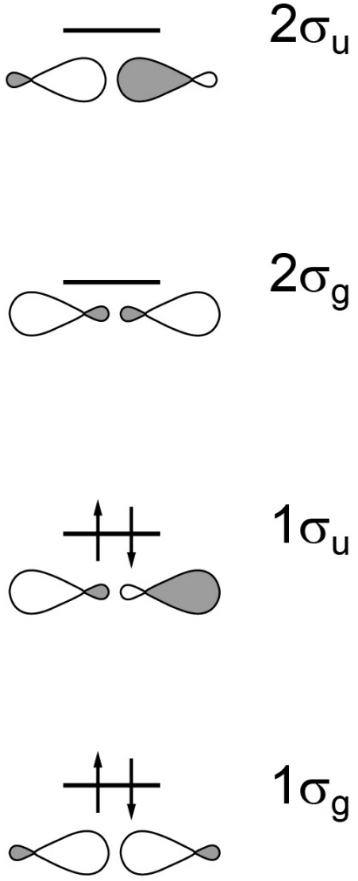
orthorhombic $Pmn2_1$,
$a = 5.774(1)$ Å,
$b = 6.837(1)$ Å,
$c = 9.350(1)$ Å, $Z = 2$



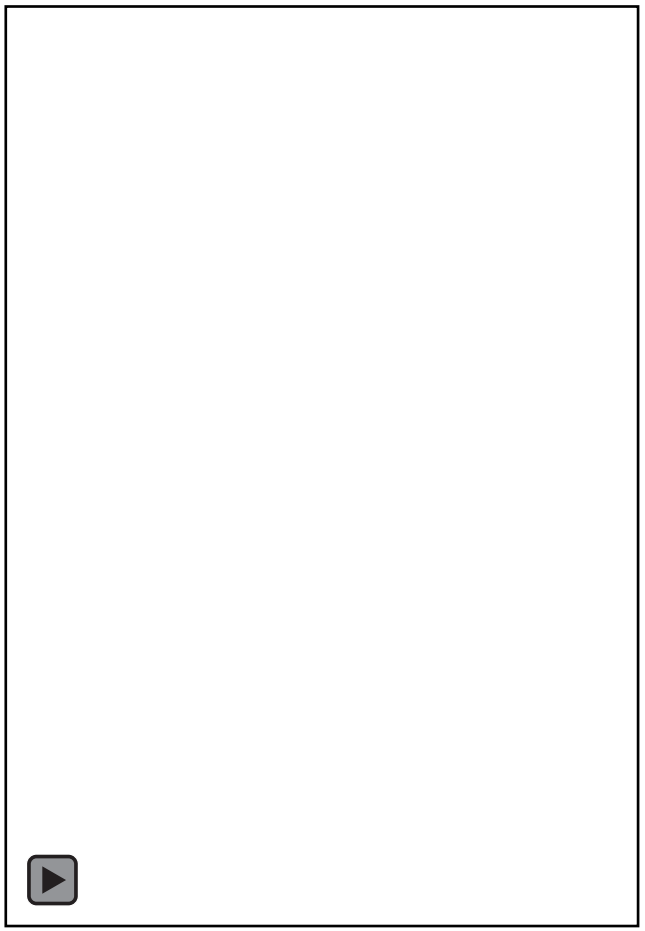
Attractive Pb^{2+}–Pb^{2+} ($6s^2$–$6s^2$) interactions

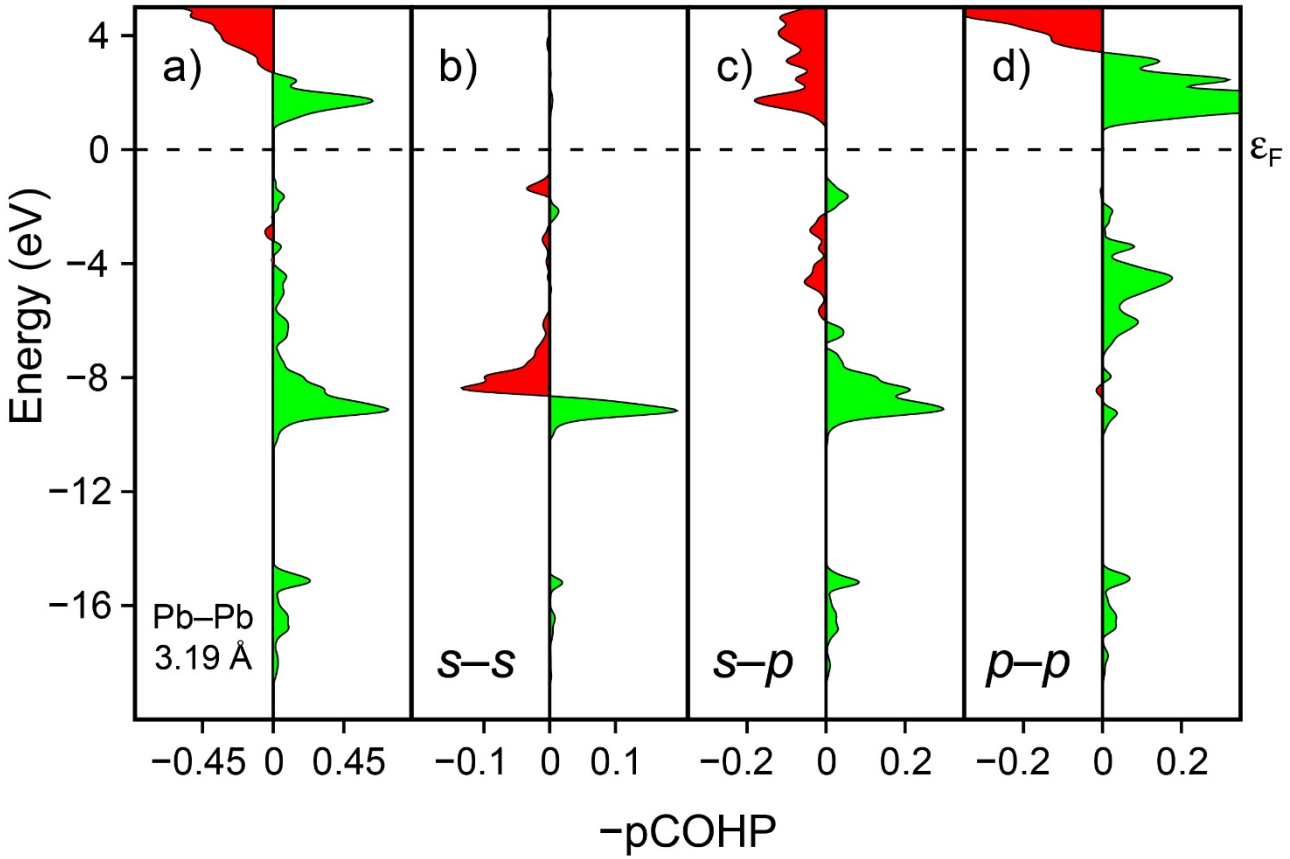


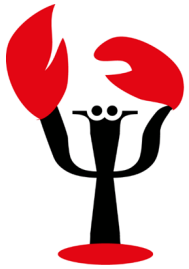




$Pb_2Si_5N_8$ with *attractive* Pb^{2+}–Pb^{2+} interactions

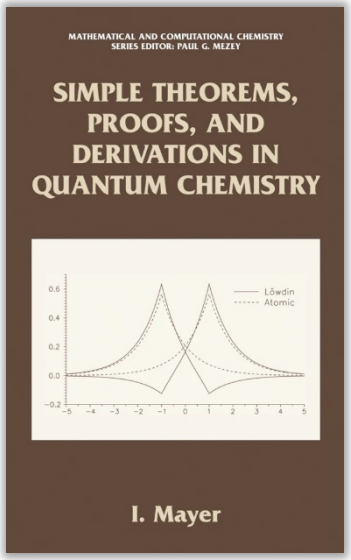


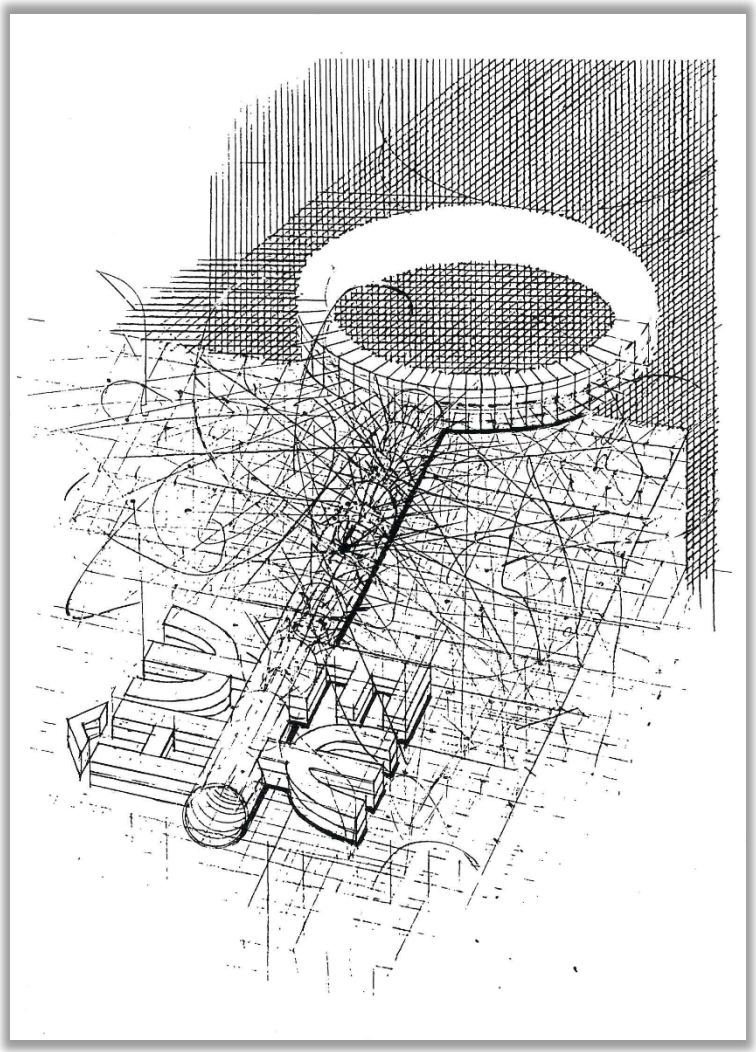




P. Bielec, R. Nelson, R. P. Stoffel,
L. Eisenburger, D. Günther, A.-K. Henß,
O. Oeckler, R. Dronskowski, W. Schnick,
Angew. Chem. Int. Ed. **2019**, *58*, 1432

Hungarian Quantum Chemist István Mayer





$$\mathrm{BI}_{\mathrm{Mayer}} = \mathrm{Tr}(P_{\mu\nu}.P_{\nu\mu})$$

I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270

Crystal-Orbital Bond Index (COBI)

$$\mathrm{COBI}_{\mu\nu}(E) = P_{\mu\nu} \sum_{j,\boldsymbol{k}} w_{\boldsymbol{k}} \mathrm{Re}(c^{*}_{\mu,j\boldsymbol{k}} c_{\nu,j\boldsymbol{k}}) \cdot \delta(\varepsilon_j(\boldsymbol{k}) - E)$$

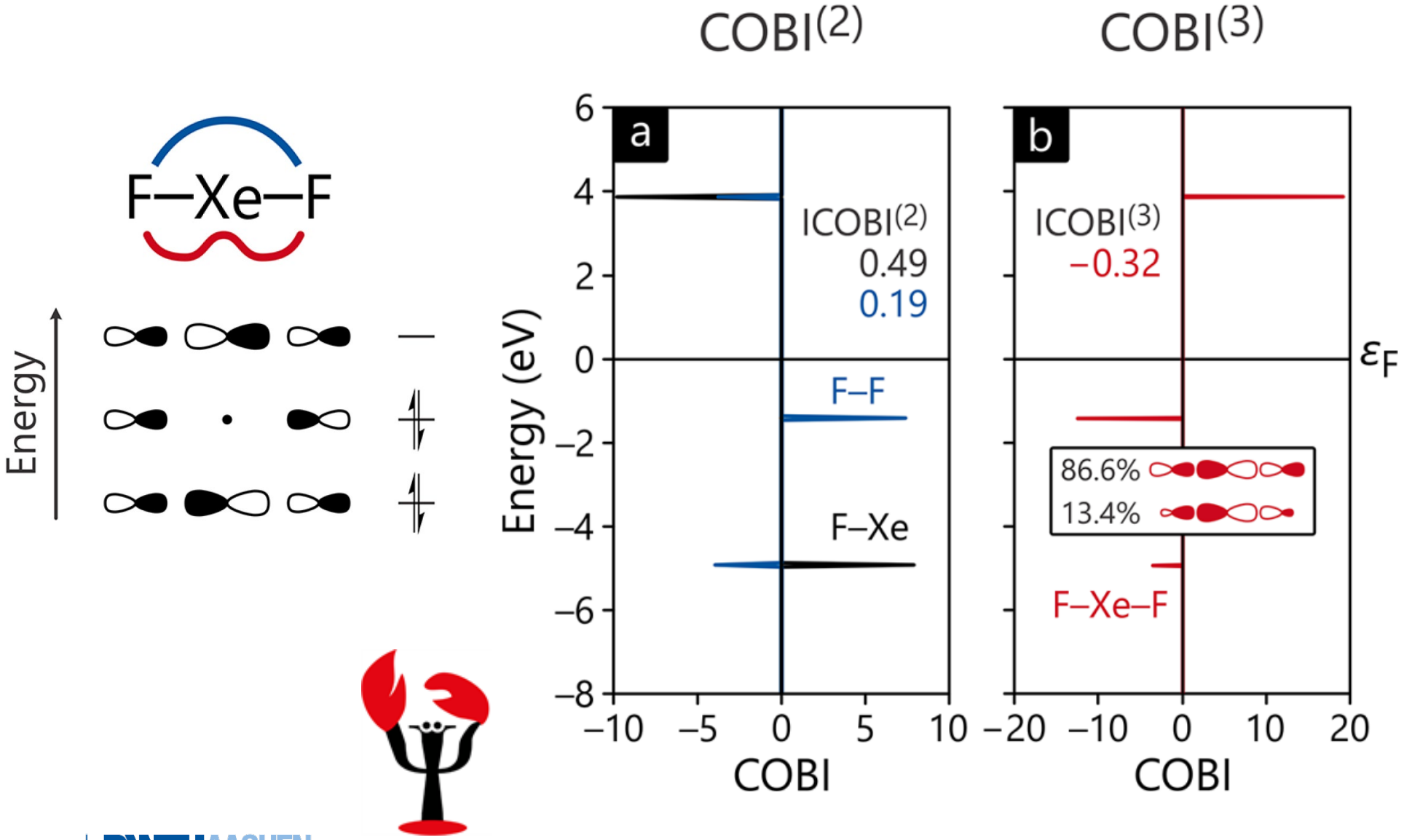
between **2** *atoms or orbitals*

$$\mathrm{COBI}^{(z)}(E) = \frac{1}{2^{z-1}} \sum_{p} P_{\mu\cdots\chi} \sum_{j} w_{\boldsymbol{k}} \mathrm{Re}(c^{*}_{\chi,j\boldsymbol{k}} c_{\mu,j\boldsymbol{k}}) \cdot \delta(\varepsilon_j(\boldsymbol{k}) - E)$$

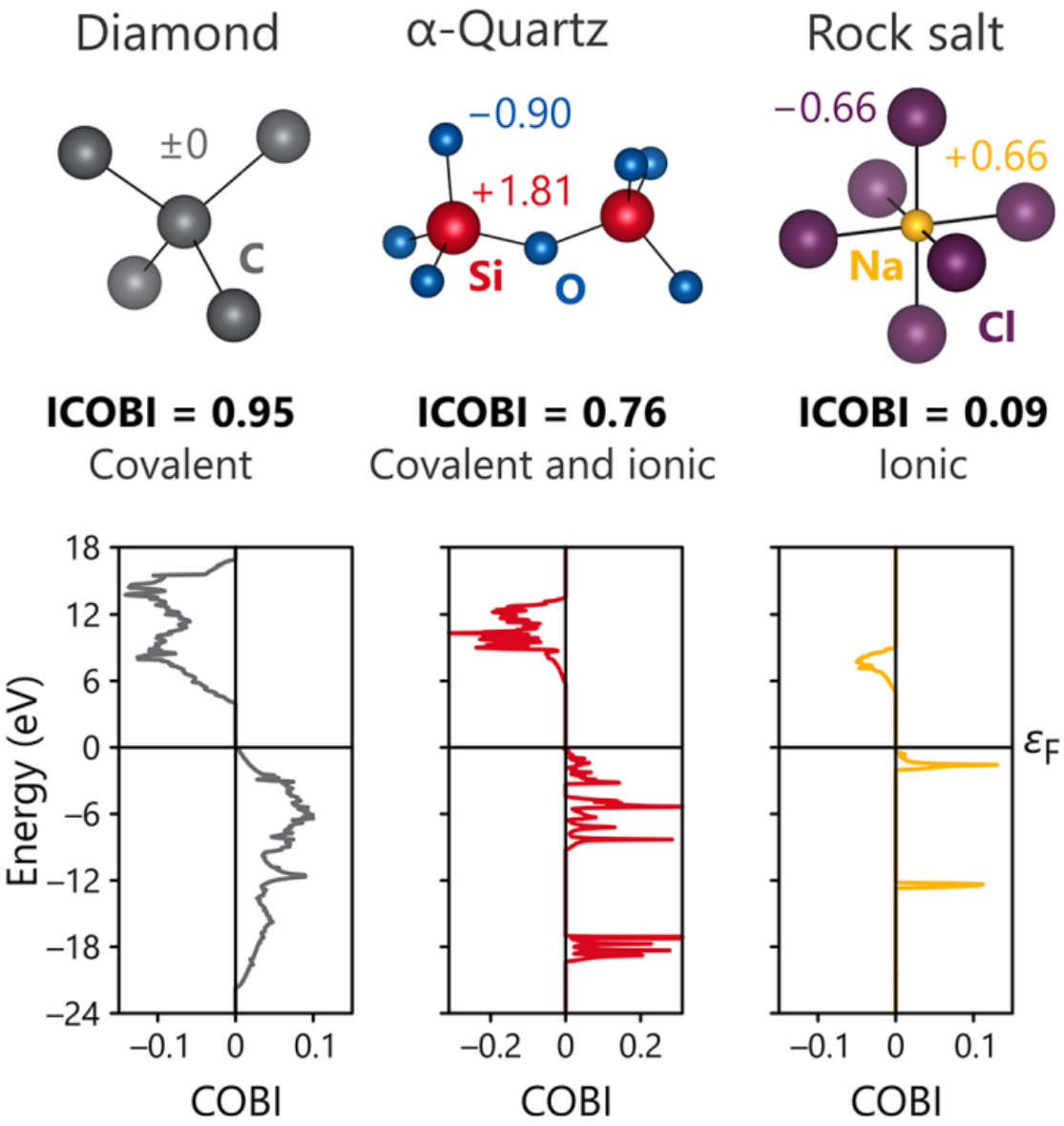
between **z** *atoms or orbitals*

P. C. Müller, C. Ertural, J. Hempelmann,
R. Dronskowski, *J. Phys. Chem. C* **2021**, *125*, 7959

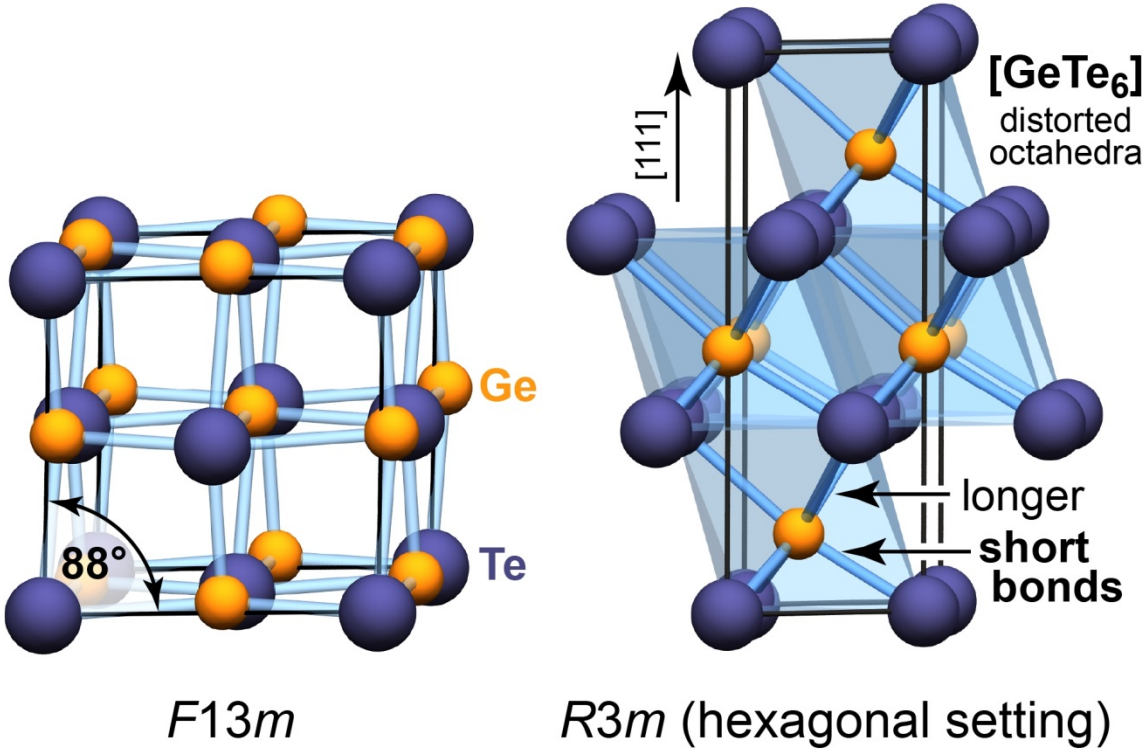
Xenon difluoride, a stable ten-electron species

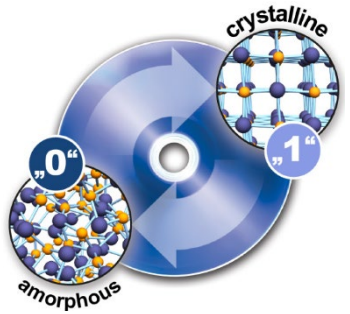


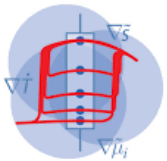
Covalency and ionicity in solids



(almost cubic) GeTe, a phase-change prototype



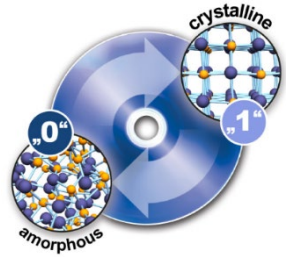




SFB 917
Nanoswitches

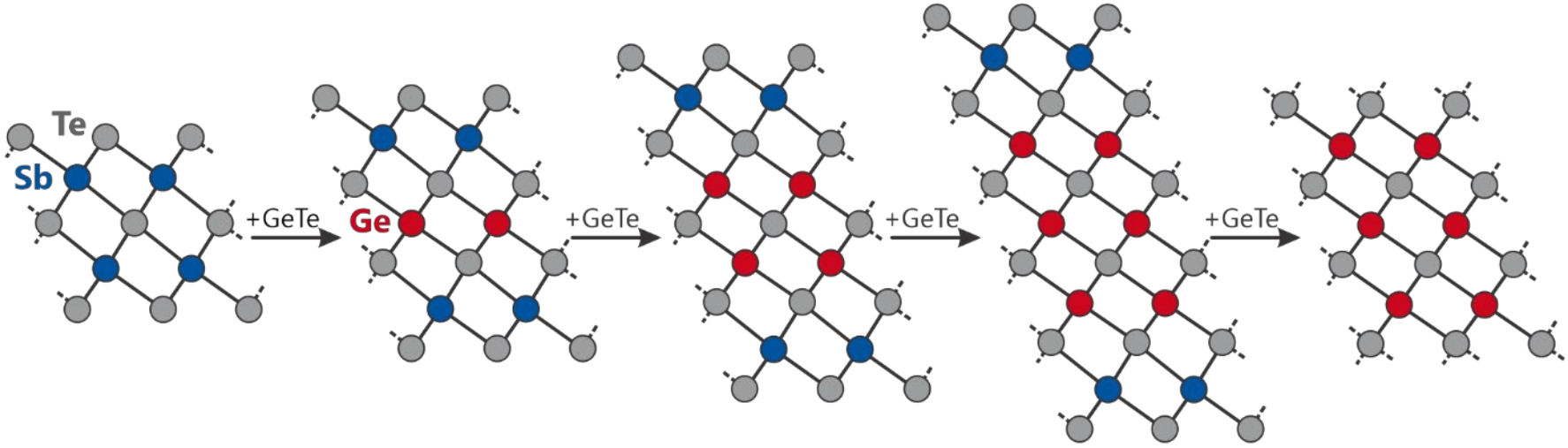
Synthesis: W. Klemm, G. Frischmuth, *Z. Anorg. Allg. Chem.* **1934**, *218*, 249
Structure: K. Schubert, H. Fricke, *Z. Naturforsch.* **1951**, *6a*, 781; J. Goldak, C. S. Barrett, D. Innes, W. Youdelis, *J. Chem. Phys.* **1966**, *44*, 3323; T. Chattopadhyay, J. X. Boucherle, H. G. von Schnering, *J. Phys. C: Solid State Phys.* **1987**, *20*, 1431

“GST” phase-change materials family



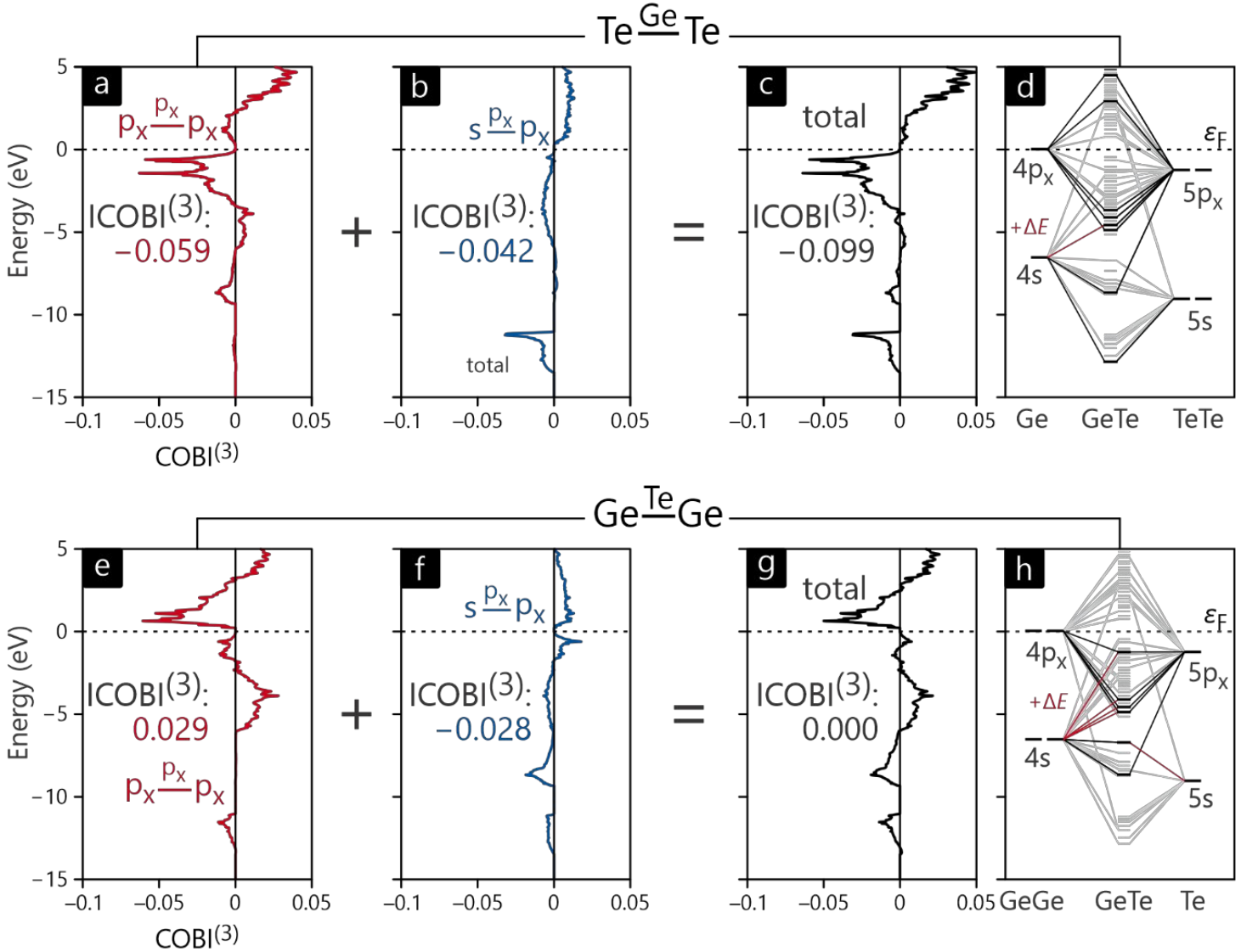
$(GeTe)_x(Sb_2Te_3)_y$

Sb_2Te_3	$GeSb_2Te_4$	$Ge_2Sb_2Te_5$	$Ge_3Sb_2Te_6$	GeTe
VEC: 5.6	5.43	5.33	5.27	5



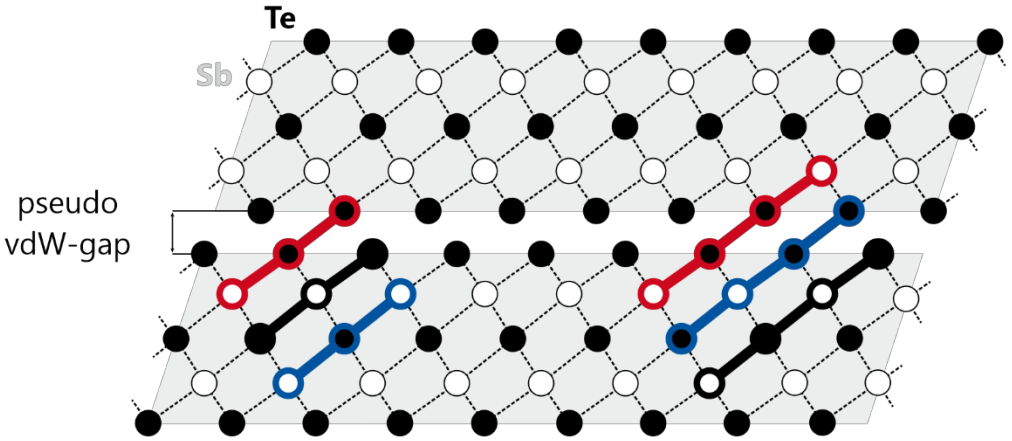
property portfolio: extraordinarily large optical dielectric constant / unusually large electrical conductivity / large Grüneisen parameter / **multiple-emission events in atom-probe tomography** / **12% too small van-der-Waals gaps**

Violating the 8 – *N* rule yields multicenter bonding

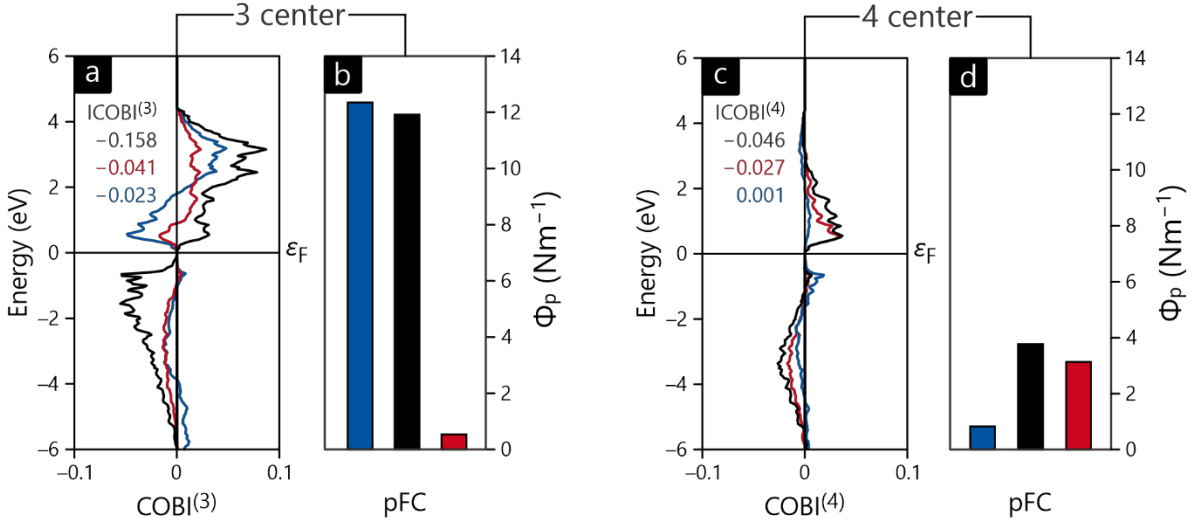


Ge^{2+} ($4s^2$ configuration) induces multicenter bonding, Te^{2-} (noble-gas shell) does not

Multicenter bonding closes the vdW gap (Sb_2Te_3)



ChemRxiv™



"The Orbital Origins of Chemical Bonding in Phase-Change Materials"

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

Summary

Chemical-bonding analysis (for H_2, solid Te, ferromagnetic Fe, phase-change materials) provides physical understanding.

Modern computational materials science operates with plane waves and pseudopotentials, so ***chemistry is hidden***.

LOBSTER digests plane-wave electronic structures and performs an analytical nonlocal-to-local ***unitary transformation*** (projection).

By directly working with the ***wave function*** (*not* with the density), atomic charges are both more accurate and faster to achieve; unexpected orbital mixing (say, Pb sp) is automatically detected.

The Crystal Orbital Bond Index, **COBI**, a solid-state variant of István Mayer's bond index, detects three- and more-center interactions; for *any* given material (or molecule).

Metavalency simply is ***multicenter bonding*** for electron-rich solids.

Emperor Karl and the Aachen Cathedral

Karl der Große
747–814 AD