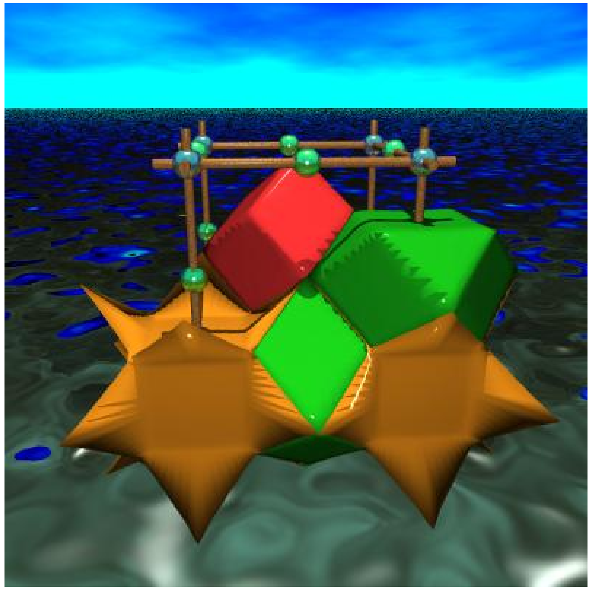
Chemical Bonding: Quantum Chemical Topology

Víctor Luaña

Departamento de Química Física y Analítica, Universidad de Oviedo

(http://web.uniovi.es/qcg/)



El enlace químico sin experimentos. 2009. Cálculos de estructura electrónica de sólidos en el cluster de computación de MALTA.

Oviedo, 21 y 22 de diciembre de 2009.

Quantum Chemical Topology (QCT)

Umbrella term coined by Popelier in 2005 to collect the many techniques and methods inspired and developed after the pioneering work of Bader and coworkers:

QTAIM or AIM: (Quantum Theory of Atoms in Molecules) Topological partition of the space induced by $\rho(\boldsymbol{r})$. Bader *et al.*. (ACC, PMS).

Full topology of the Laplacian: $L(\boldsymbol{r}) = -\nabla^2\rho(\boldsymbol{r})$. Bader, Popelier, Aray, . . . (AOR).

ELF: $\eta(\boldsymbol{r})$ (Electron Localizing Function). Becke, Bader, Silvi, Savin, . . . (JCG).

ELI: (Electron Localizability Indicator). Kohout, . . .

Localization and delocalization indices: Bader, Keith, Fradera, . . .

Source Function: Bader, Gatti.

Intra and extracule densities: Fradera *et al.*

IQA: (Interacting Quantum Atoms) Energy partition strictly based on QTAIM. Pendás, Blanco & Francisco.

The purpose of chemical bonding studies is understanding the complex factors relating chemical composition, molecular or crystal geometry, and chemical and physical properties.

Traditional successes: Pauling electronegativities, Lewis/VSEPR models, van Arkel-Ketelaar diagrams, radius ratio rules, Mooser-Pearson plots, Phillips-Van Vechten ionicity scales, Zunger/Villars/Pettifor/Miedema maps, Frontier Orbital Symmetry rules, . . .

(Empirical approaches and concepts, toy models, . . .).

The idea behind QTAIM/QCT is revolutionary and yet simple: Extract the chemical bonding information from the best available experimental or theoretical $|\Psi|^2$ by applying quantum mechanical operators in a way that is locally well defined.

QTAIM/QCT results may compare or not with traditional theories but the real purpose is to achieve permanent results that depend only on the quality of the wavefunction analyzed and not on arbitrarily defined concepts.

Quantum Mechanics Postulates (incomplete set)

1. All experimentally available information about a system is contained in the wavefunction Ψ. The information is available under the form of an statistical distribution $|\Psi|^2\, dq$.
2. Wavefunctions (kets, $|\Psi\rangle$) and their complex conjugates (bras, $\langle\Psi|$) form a dual vectorial space, such that any linear combination of well behaved wavefunctions (bounded, C^2 continuous and $|\Psi|^2$ integrable) is another wavefunction, and such that the scalar product $\langle\Psi|\Psi\rangle$ is a metric of the space.
3. Every observable A is represented by a *linear* and *hermitian* operator $\hat{\alpha}$ that acts on the dual space of kets and bras.
   Notice that the hermitian character of $\hat{p}$ and related operators depends on the wavefunction being bounded in the whole space.
4. The eigenstates, $\hat{\alpha}\,|\Phi_a\rangle = a\,|\Phi_a\rangle$, of a quantum mechanical operator, form a complete basis for the state space, that can be orthonormalized.
5. As a result of measuring the observable $\hat{\alpha}$, the initial state of the system, ψ, collapses into an eigenstate $|\Phi_a\rangle$ of the operator, and the measurement produces the corresponding eigenvalue a, with a probability given by $|\langle\Phi_a|\Psi\rangle|^2 \,/\, \langle\Psi|\Psi\rangle$.

What about the Molecular Orbital paradigm?

1. Molecular Orbital Theory is a fundamental part of the Quantum Chemistry hierarchical approach to solving the Schrödinger equation in molecular systems.
2. Orbitals, however, are not observable entities (remember: $|\Psi|^2$ and not Ψ provides the observable information).
3. Arbitrary unitary transformations can be applied to Ψ without modifying the observable properties of the quantum state.
4. Even *natural orbitals* (those that diagonalize $\rho(\boldsymbol{r})$) are not free from arbitrary elections (NO, NAO, NBO, NLMO, PNAO, PNBO, . . .).
5. The same can be said from canonical orbitals.
6. Most bonding concepts derived from MO theory come from a minimal basis simplification that works awfully in a quantitative sense and that do not remains stable towards improvements in the basis set and in the multielectronic properties of the wavefunction.

The electron density

$$\rho(\boldsymbol{r}) = \left\langle \Psi \middle| \frac{1}{N} \sum_{i=1}^{N} \delta(\boldsymbol{r}_i - \boldsymbol{r}) \middle| \Psi \right\rangle. \tag{1}$$

- $\rho(\boldsymbol{r})d\boldsymbol{r}$: probability that an arbitrary electron occupies a differential region around $\boldsymbol{r}$.
- $\rho(\boldsymbol{r})$ can be indirectly determined by fitting the experimental X-ray structure forms.
- In general: $\Psi(\boldsymbol{x}_1 \cdots \boldsymbol{x}_N, \boldsymbol{R}_1 \cdots \boldsymbol{R}_\nu, t)$.
- The two electron density function,

$$\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \left\langle \Psi \middle| \binom{N}{2}^{-1} \sum_{i>j}^{N} \delta(\boldsymbol{r}_i - \boldsymbol{r}_1)\delta(\boldsymbol{r}_j - \boldsymbol{r}_2) \middle| \Psi \right\rangle, \tag{2}$$

  describes the probability density of any two different electrons occupying differential regions around $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$.
- Diagonal terms of the density matrices $\Gamma^{(1)}(\boldsymbol{r}'; \boldsymbol{r})$, $\Gamma^{(2)}(\boldsymbol{r}'_1, \boldsymbol{r}'_2; \boldsymbol{r}_1, \boldsymbol{r}_2)$, ...

The complexity of the electron density versus the complexity of the wavefunction

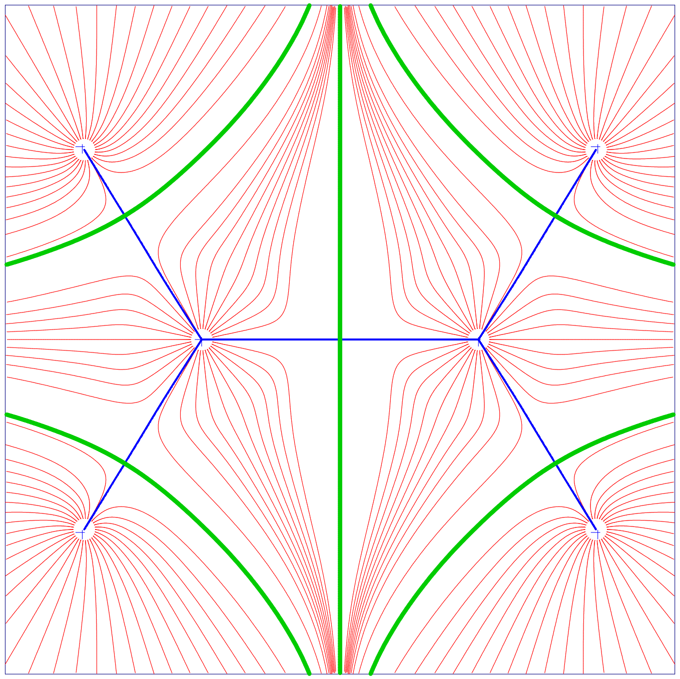
$\rho(\boldsymbol{r})$: $\mathbb{R}^3 \longrightarrow \mathbb{R}$. Let's assume a $10^4 \times 10^4 \times 10^4$ grid of `real*8` values: 8 TBytes (available as an external disk in 2010–2011!)

$\Psi(\boldsymbol{x}_1 \cdots \boldsymbol{x}_n, \boldsymbol{R}_1 \cdots \boldsymbol{R}_N)$: $\mathrm{H_2O}$, $n = 10$ electrons and $N = 3$ nuclei, $\mathbb{R}^{49} \longrightarrow \mathbb{R}^2$. Let's assume a grid with only 10 values per dimension: 16×10^{49} Bytes or 16×10^{37} TBytes or 160 EEBytes (available around 2134 assuming disks duplicate capacity every year!).

$\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)$: $\mathbb{R}^6 \longrightarrow \mathbb{R}$. Using a grid with 10^4 values per dimension: 8×10^{24} Bytes (find it around 2050 or your money back!!!).

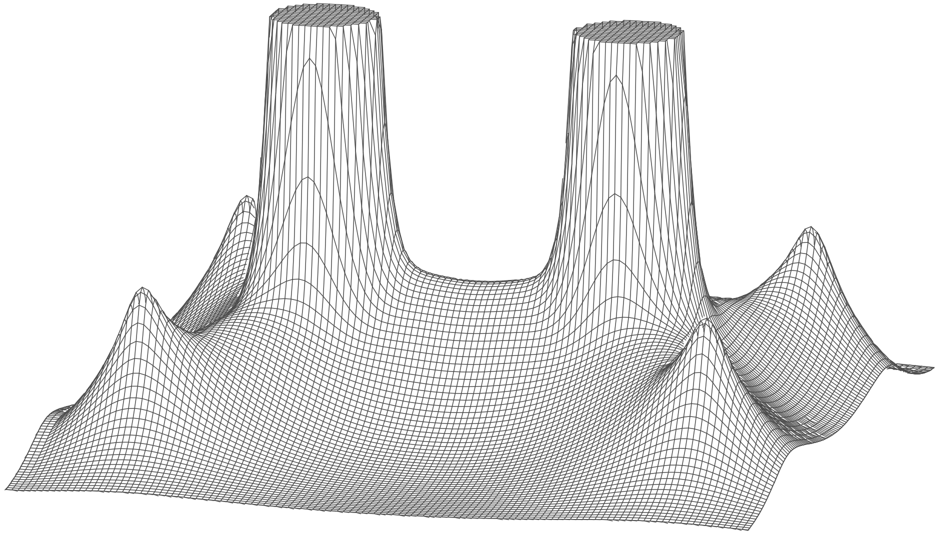
It is most useful that chemical bonding information resides in ρ and $\rho^{(2)}$ rather than $|\Psi|^2$, but the important point is why!

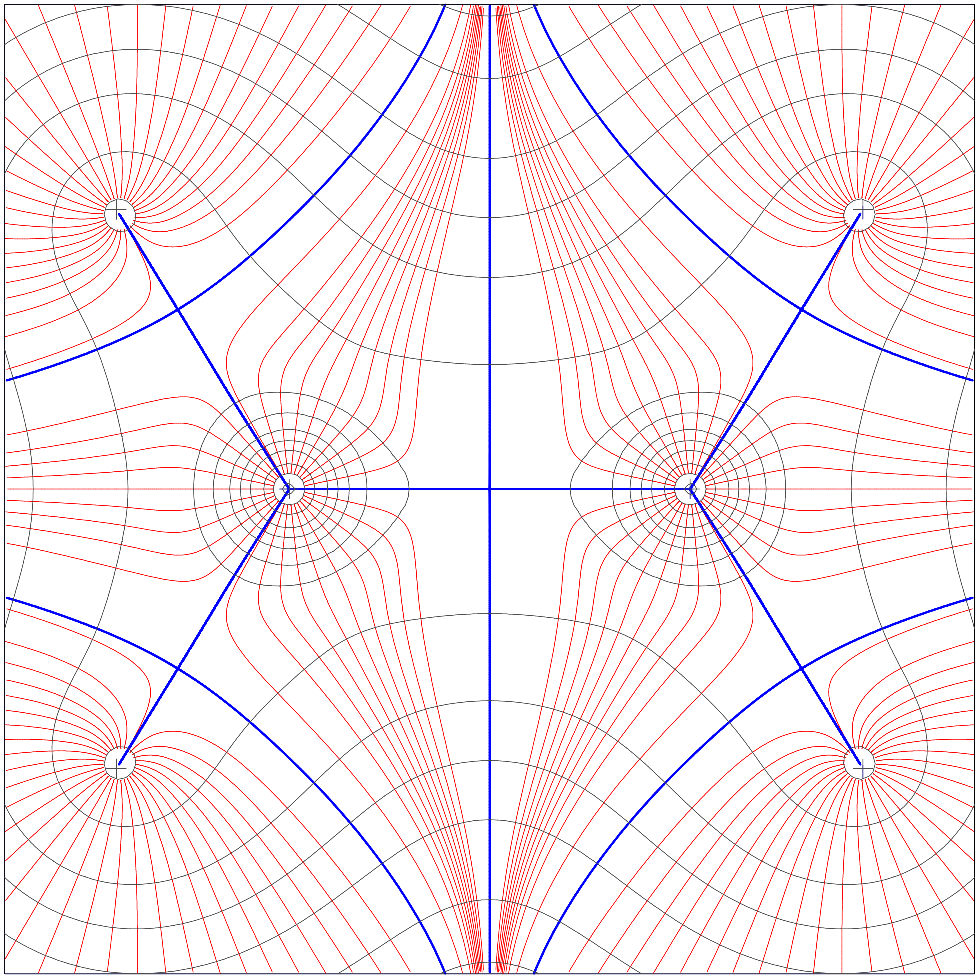
The classical QTAIM approach



$\mathrm{C_2H_4}$: ethylene

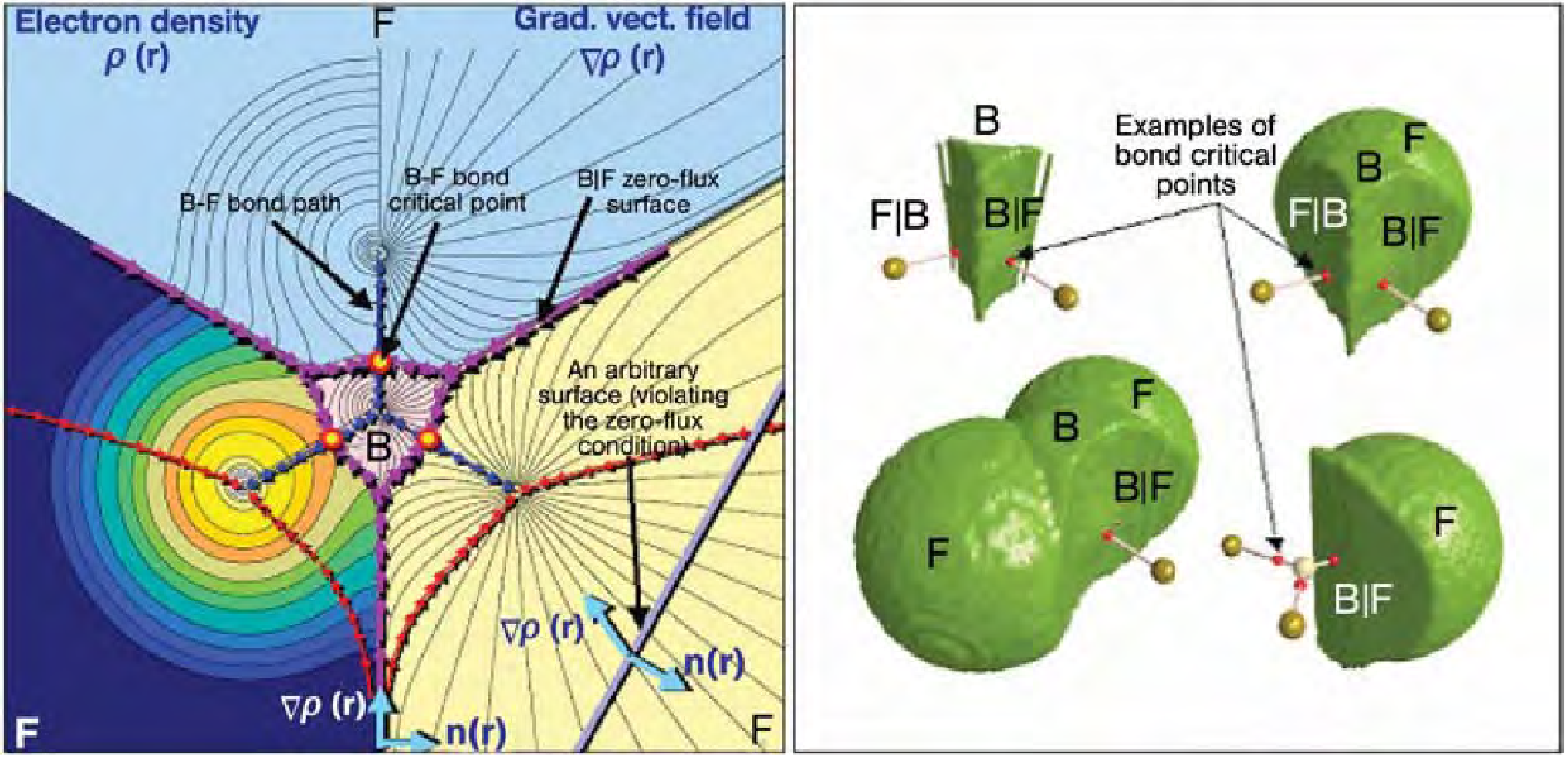
- 3D space is divided into *atomic basins* by the $\boldsymbol{\nabla}\rho(\boldsymbol{r})$ gradient vector field.
- Each basin is such that $\boxed{\boldsymbol{\nabla}\rho(\boldsymbol{r}_S)\cdot\boldsymbol{n}(\boldsymbol{r}_S)=0}$ (*zero flux condition*), i.e. gradient lines do not cross the *inter-atomic surface* (IAS) that separates two bonded basins.
- The only exception is a single *bond path*, the crest or ridge that connects two bonded nuclear peaks and crosses the IAS through the *bond critical point* or mountain pass.



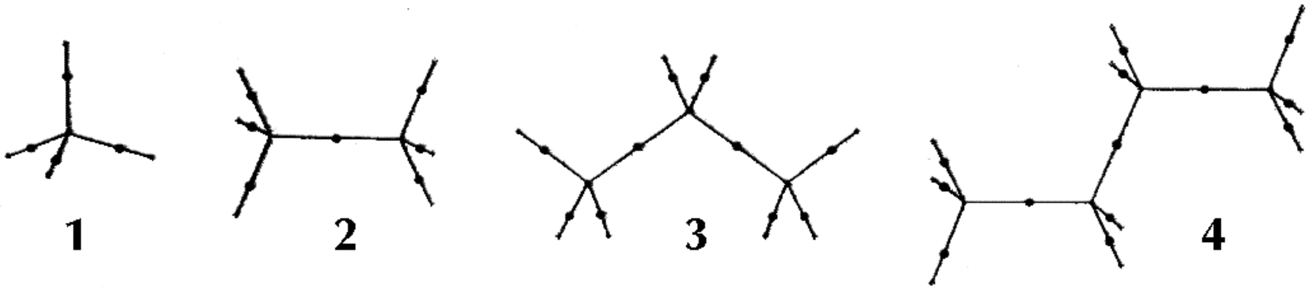


C_2H_4.

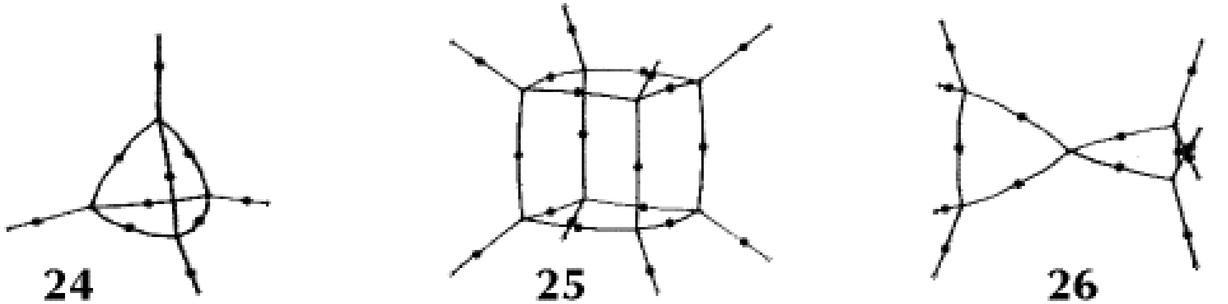
Most characteristic $\rho(\boldsymbol{r})$ feature: large nuclear peaks $\approx Z^3$.



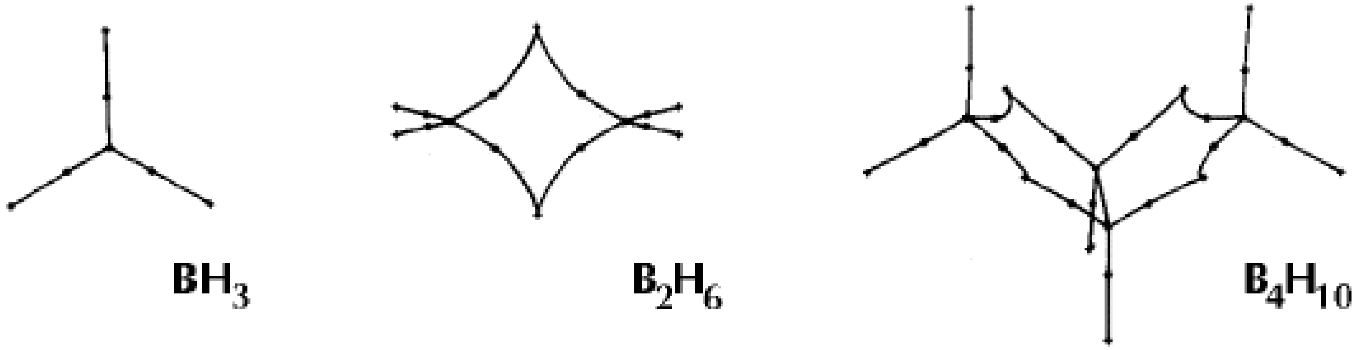
Boyd & Matta, 2007



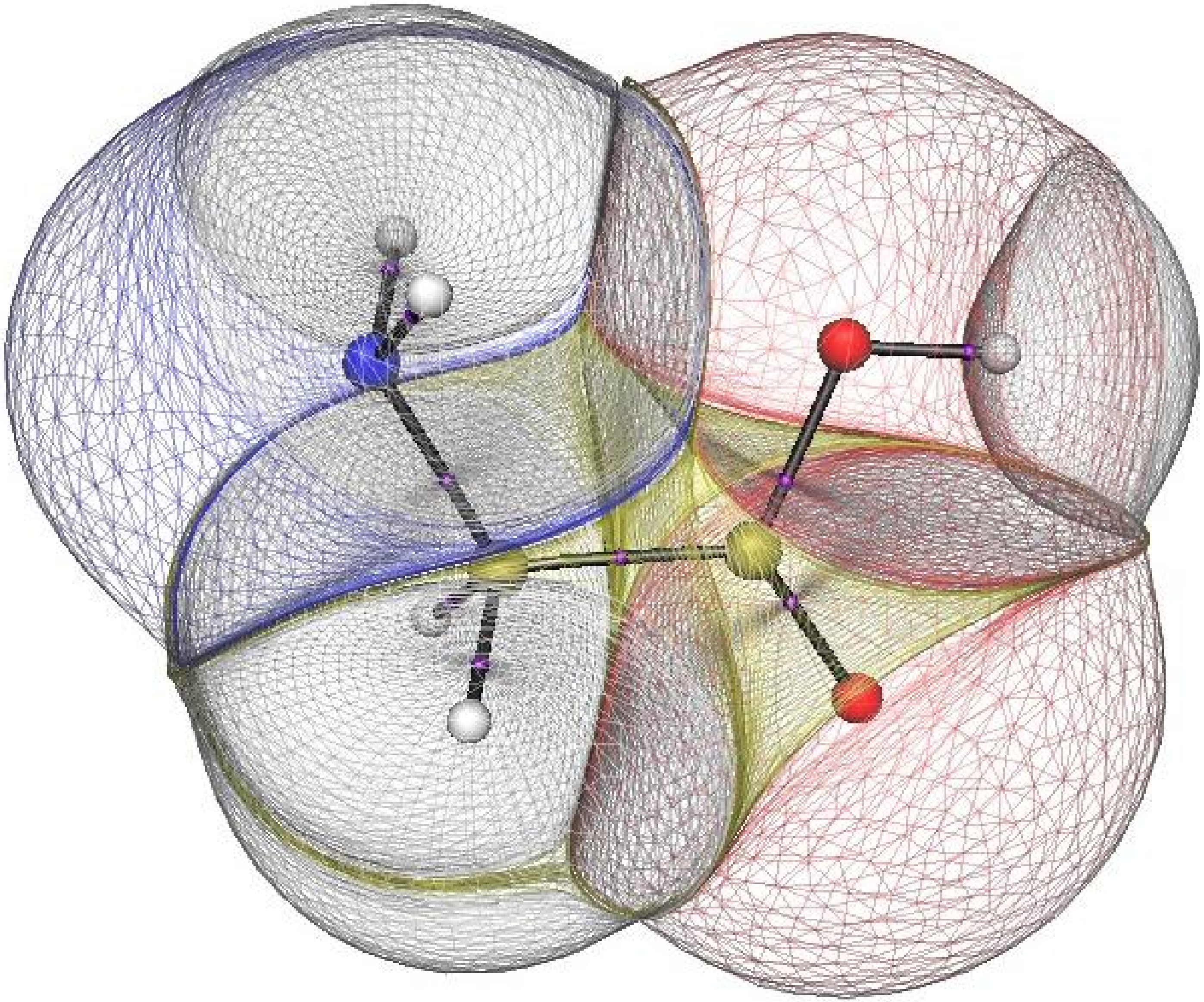
From CH_4 to C_4H_{10}.



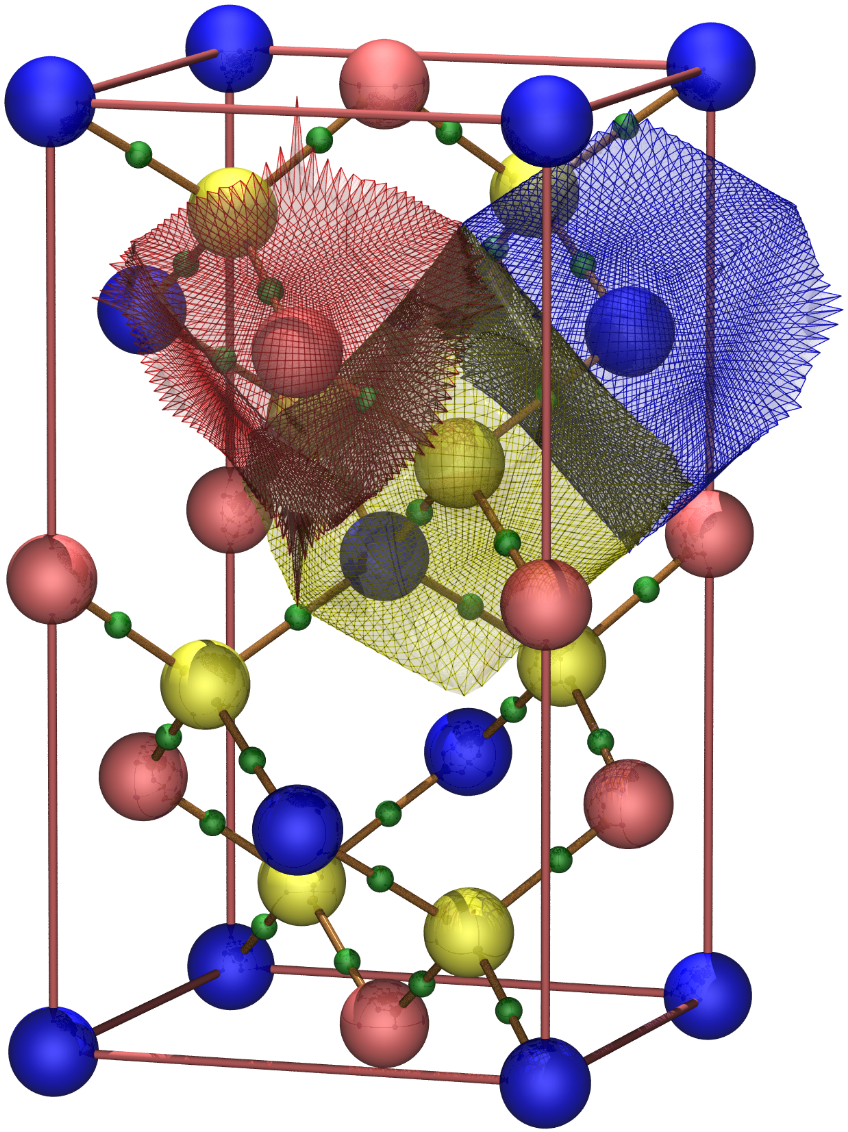
Small ring stress: tetrahedrane, cubane and spiropentane.



Electron deficient bonding in some boranes.

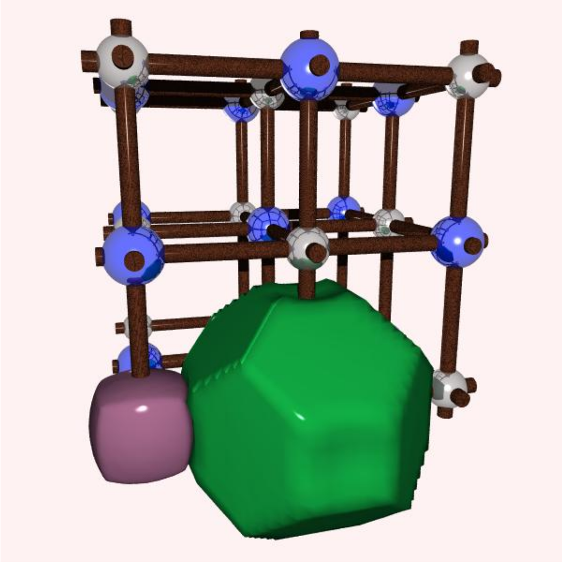


Popelier: glycine



$AgGaSe_2$ (chalcopyrite phase)

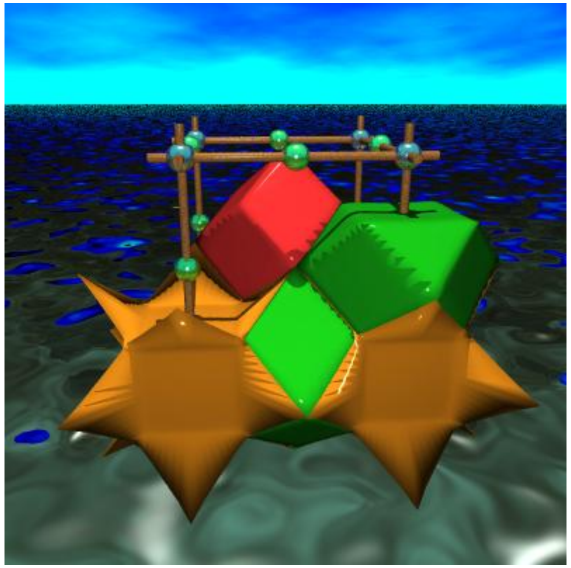
LiI basins



- All the sources and drains of the gradient lines are the critical points $\boldsymbol{\nabla}\rho(\boldsymbol{r}_c) = \mathbf{0}$. Those points can be classified according to the eigenvalues of the curvature matrix: $\boldsymbol{H}$ $(H_{\xi\zeta} = \partial^2\rho/\partial\xi\partial\zeta;\ \xi,\zeta = \{x,y,z\})$. In other words, critical points can be classified according to the dimensions of its attraction and repulsion basins:

(r,s)	Type	Where	attrac.	repul.
$(3,-3)$	Maximum	n: nucleus	3D	0D
$(3,-1)$	Saddle-1	b: bond cp.	2D	1D
$(3,+1)$	Saddle-2	r: ring cp.	1D	2D
$(3,+3)$	Minimum	c: cage cp.	0D	3D

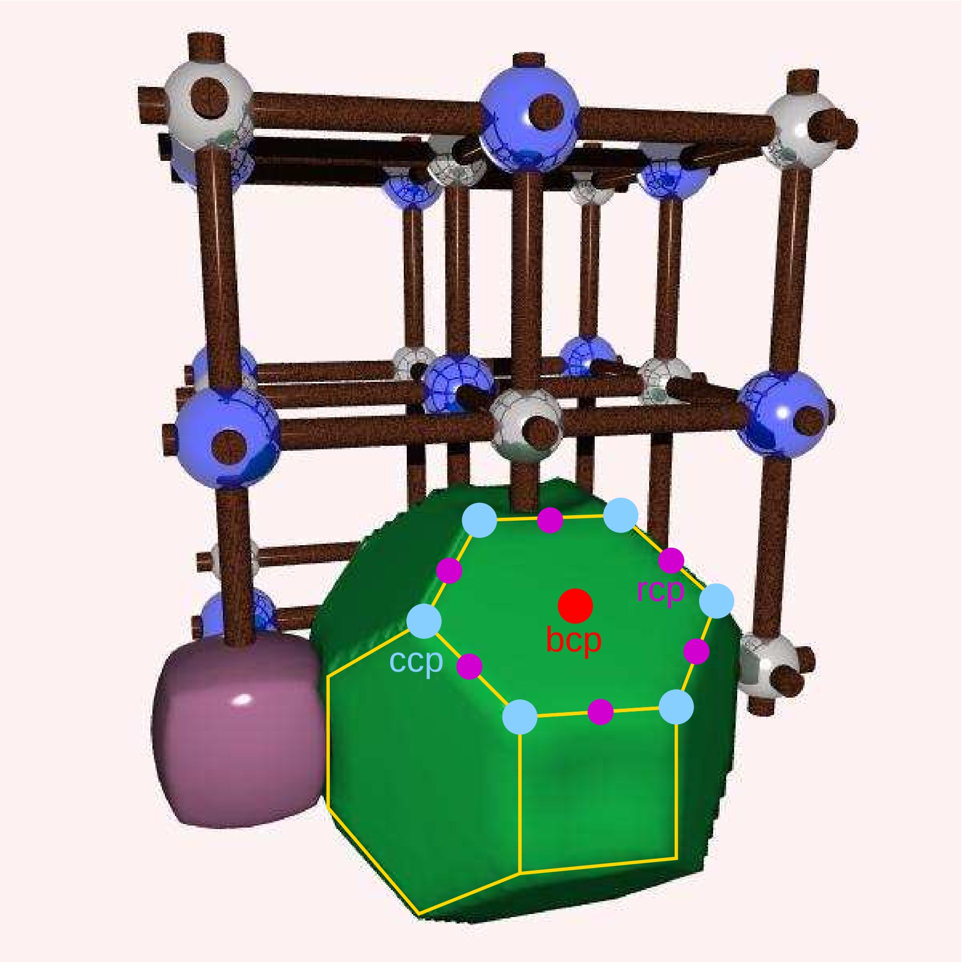
- Atomic basins in condensed matter are isomorphic to convex polyhedra: each face is an IAS created by a single bond cp, edges are the attraction basins of ring cp's, and vertices correspond to minima.
- Molecules: $n - b + r - c = 1$ (Euler-Poincaré).
- Crystals: $n - b + r - c = 0$, $n, c \geq 1$, $b, r \geq 3$ per unit cell (Morse relationships); $b + c = r + 2$ for each atomic basin (Euler relationship).



KCaF_3 basins

Atomic basins in crystals are equivalent to polyhedra:

- Inside: AB (3D) of a single ncp;
- Face: AB (2D) of a single bcp;
- Edge: AB (1D) of a single rcp;
- Vertex: AB (0D) of a single ccp;
- Euler relationship: $b + c = r + 2$.



The zero flux surface condition defining the atomic basins guarantees that all quantum mechanical operators are locally well defined, are hermitian, and can be integrated on each basin to produce the atomic contribution to the properties of the whole system. For instance:

- electronic population and charge:

$$\langle N\rangle_\Omega = \int_\Omega \rho(\vec r)\,d\vec r, \qquad \mathcal{Q}(\Omega) = Z_\Omega - \langle N\rangle_\Omega\,;$$

- multipolar moments:

$$N_\Omega^{lm} = \int_\Omega r^l S_{lm}(\theta,\phi)\rho(\vec r)\,d\vec r;$$

- electron kinetic energy:

$$\underbrace{-\frac{\hbar^2}{4m_e}\int_\Omega d\vec r\,[\nabla^2+\nabla'^2]\,\rho^1(\vec r\,';\vec r)}_{=K(\Omega)} = \underbrace{\frac{\hbar}{2m_e}\int_\Omega d\vec r\,[\vec\nabla'\cdot\vec\nabla]\,\rho^1(\vec r\,';\vec r)}_{=G(\Omega)}\underbrace{-\frac{\hbar^2}{4m_e}\oint_{S(\Omega)} dS\,\vec\nabla\rho(\vec r)\cdot\vec n(\vec r).}_{=0}$$

This equation is a consequence of $\nabla^2(\Phi^*\Phi) = (\nabla'^2+\nabla^2+2\vec\nabla'\cdot\vec\nabla)(\Phi^*\Phi)$. Notice that $K(\Omega)\neq G(\Omega)$ unless Ω is delimited by zero flux surfaces.

Basin contributions are strictly additive, $\langle O\rangle = \sum_\Omega \langle O\rangle_\Omega$, and they can be transferred from one compound to another as far as the shape of the basin do not change much.

- The zero flux condition $(\boldsymbol{\nabla}\rho(\boldsymbol{r}_S)\cdot\boldsymbol{n}(\boldsymbol{r}_S)=0)$ guarantees that $\mathcal{L}(\boldsymbol{r})=-\frac{\hbar^2}{4m_e}\nabla^2\rho(\boldsymbol{r})$ integrates to zero on the atomic basins and, from this, **every observable can be represented within the basin by a linear and hermitian operator**.
- Therefore: every molecular/crystal property can be decomposed into additive and non-overlapping contributions from the atomic basins. This is true for local properties (volume, charge, electrostatic field, . . .), and for non-local ones (linear momentum, kinetic energy, Fock exchange energy, . . .).
- Whereas local properties can be integrated on arbitrary regions this is not possible for non-local properties.
- The QTAIM basin partition is well defined, unique, and determined only by the observable electron density $\rho(\boldsymbol{r})$.
- Other scalar fields (laplacian, ELF, . . .) can give rise to basins, but only some properties can be calculated on them.

Properties at the bcp's provide a classification of bonding regimes

CC bcp	C_2H_6	C_6H_6	C_2H_4	C_2H_2
d (Å)	1.539	1.382	1.312	1.179
ρ_b (a.u.)	0.227	0.313	0.318	0.406
$\nabla^2\rho_b$ (a.u.)	-0.522	-0.944	-1.128	-1.233
n	1.0	1.5	2.0	3.0

Calc. HF/6-311G(3df,p):

$$n_{\text{CC}} = \exp\left\{\frac{\rho_b - 0.234}{0.163}\right\},$$

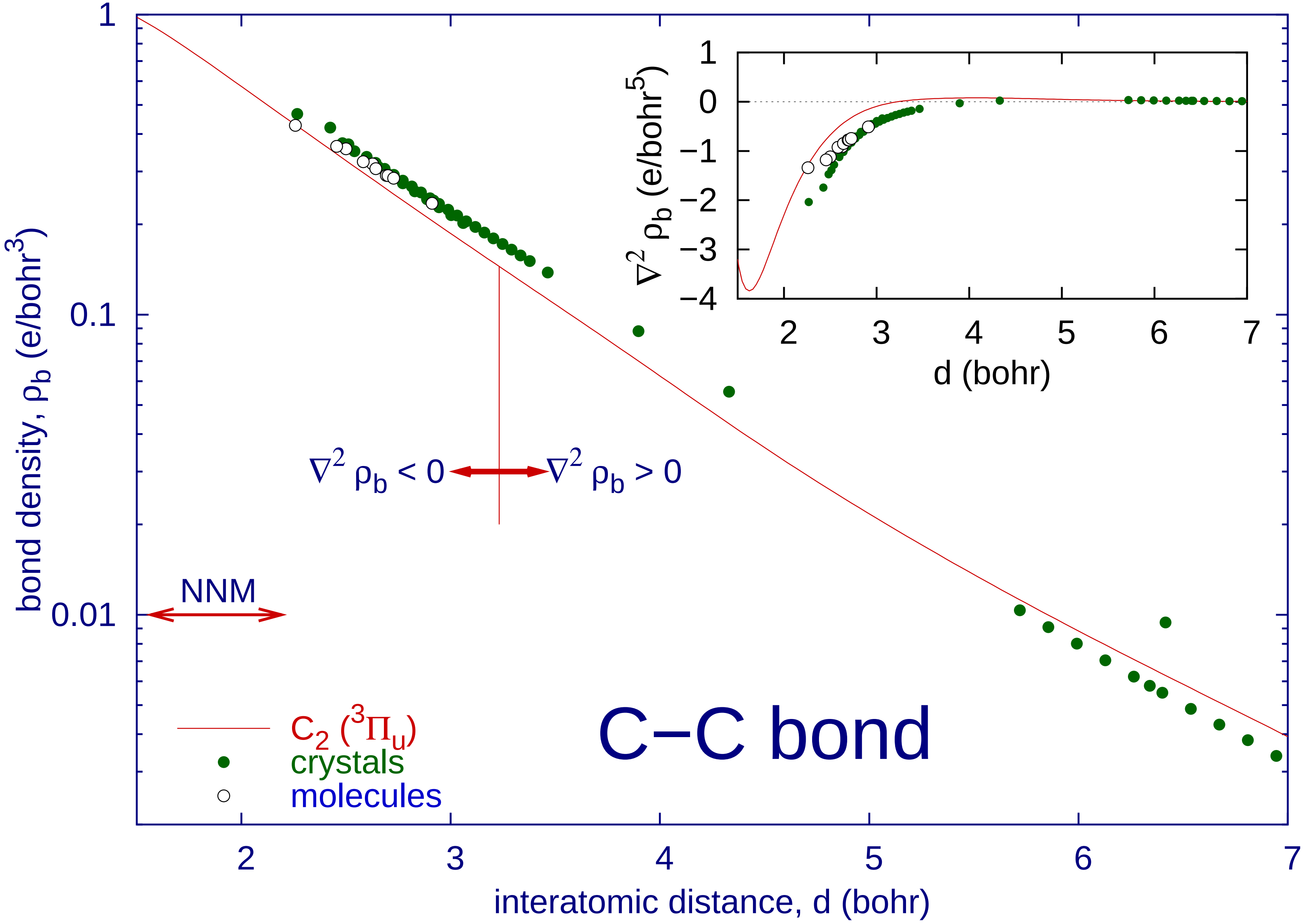
$$n_{\text{CC}} = \exp\left\{-\frac{\rho_b - 1.531}{0.325}\right\}.$$

- The $n_{AB} = F(\rho_b, \nabla^2\rho_b, \cdots)$ equation is specific for each AB pair (fine tuned for the calculation level).
- There exist a universal trend for the ρ_b and $\nabla^2\rho_b$ values as a function of the bond distance (JPhysChem A **108** (2004) 2794). For a homonuclear bond like CC:
  - long distance: $\rho_b \approx 0$, $\nabla^2\rho_b \gtrsim 0$, closed shell bonding: intermolecular.
  - medium dist.: $\nabla^2\rho_b < 0$, large ρ_b and $\left|\nabla^2\rho_b\right|$, shared shell: covalent bonding.
  - small dist.: non-nuclear maxima under adequate conditions (PhysRevLett **83** (1999) 1930).
  - smaller dist.: the sequence starts again for the inner shells.

Most heteropolar bonds are dominated by charge transfer (ionic bonding) on the medium distances. There are a few quite interesting low polarity combinations: BP, BAs, . . .

fpLAPW/GGA(PW91) (WIEN2K): diamond, graphite, CaC_2.

B3LYP/6-311G(3df,p) (GAUSSIAN): C_2, ethane, ethylene, acetylene, benzene, anthracene, alene.

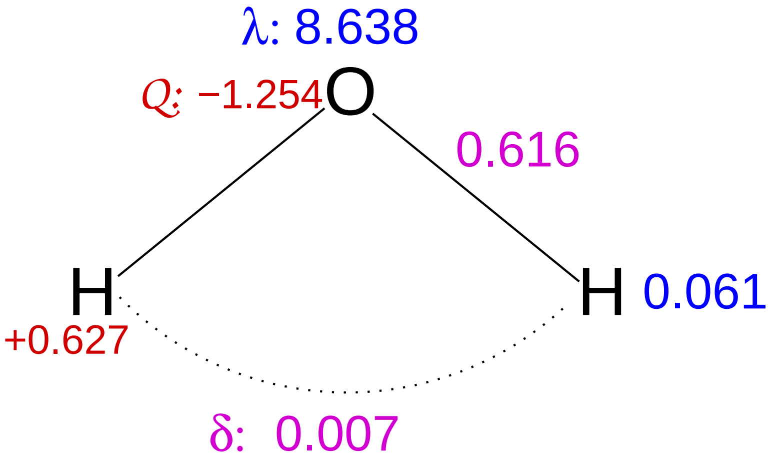


Multiple bonding is better determined from delocalization indices

$$N(A)=\int_A d\boldsymbol{r}_1\ \rho(\boldsymbol{r}_1),\ D_2(A,B)=\int_A d\boldsymbol{r}_1\int_B d\boldsymbol{r}_2\rho^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2),\ F(A,B)=2D_2(A,B)-N(A)N(B),$$

Localization index, $\lambda(A)=|F(A,A)|\leq N(A)$: average number of electrons localized in basin A.

Delocalization index, $\delta(A,B)=-F(A,B)-F(B,A)$: electrons shared between A and B.



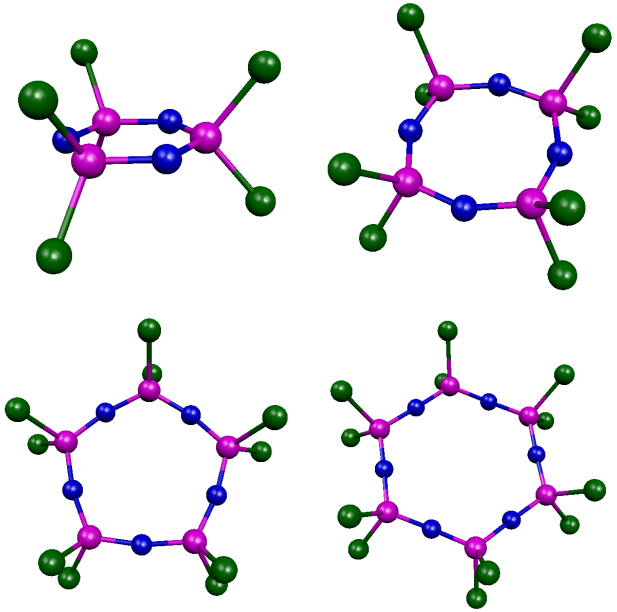
AB_n	$N(A)$	$N(B)$	$\lambda(A)$	$\lambda(B)$	$\delta(A,B)$
H_2	1.000	1.000	0.500	0.500	1.000
N_2	7.000	7.000	5.479	5.479	3.042
CO	4.646	9.354	3.860	8.567	1.574
LiF	2.060	9.940	1.971	9.851	0.178

Fradera *et al.* (2002)

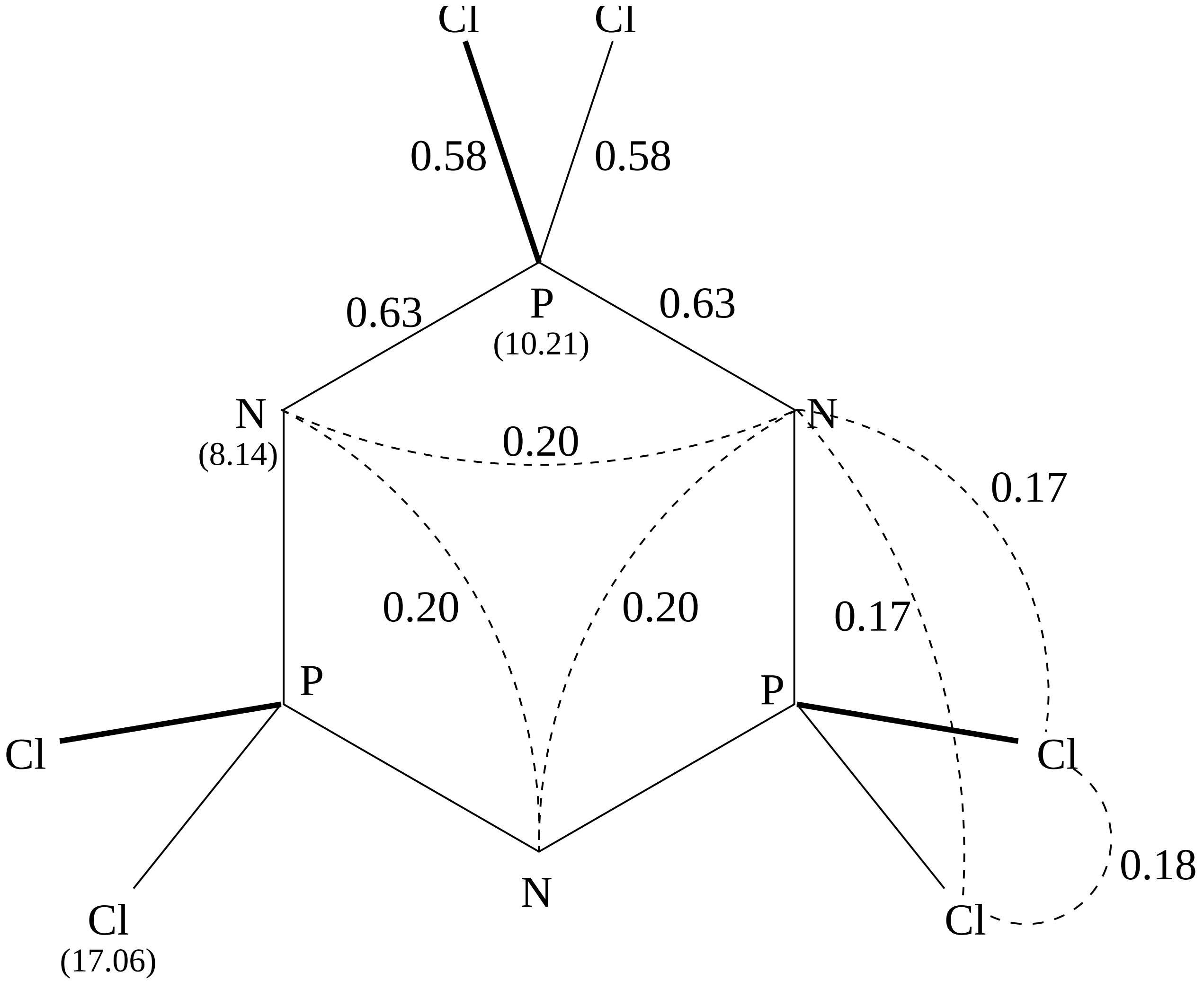
AB_n	LiH	BeH_2	BH_3	CH_4	NH_3	OH_2	FH
$\mathcal{Q}(A)$	0.912	1.725	2.114	0.175	-1.048	-1.254	-0.779
$\delta(A,B)$	0.197	0.272	0.503	0.982	0.894	0.616	0.398

Bonding in cyclophosphazenes, $[NPCl_2]_n$, n :2–7

JPhysChem A **105** (2001) 5280.
Very rigid NPN: 116–120°,
Flexible PNP: 123–168°,

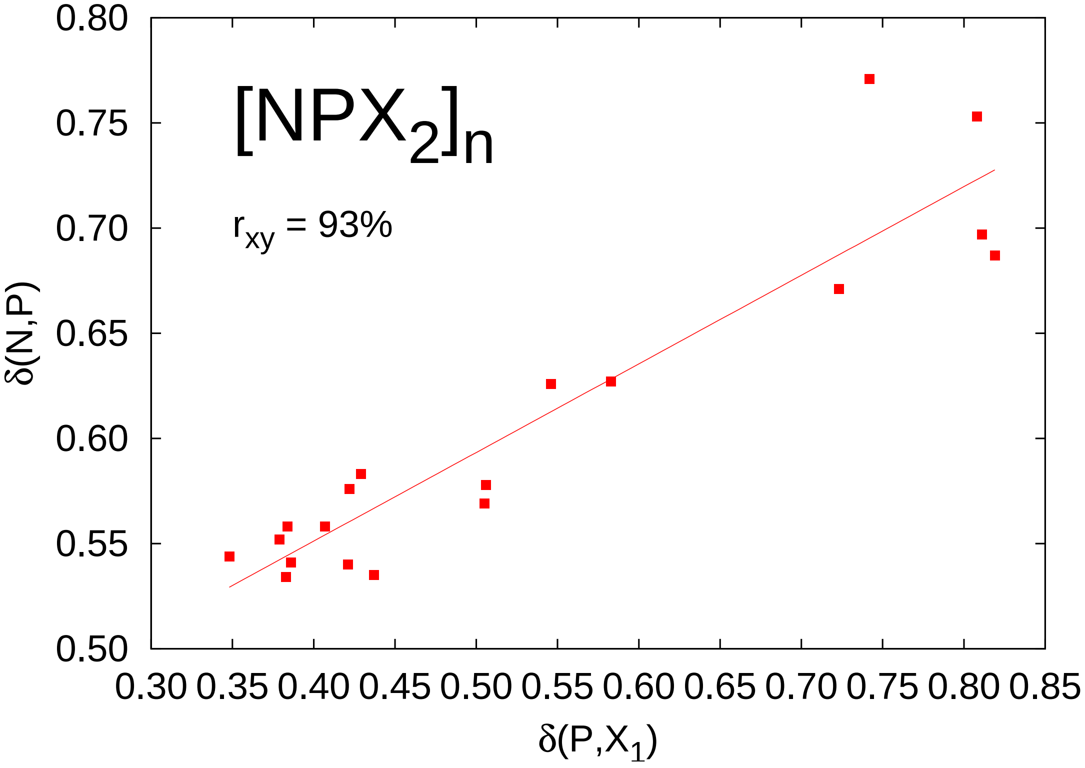


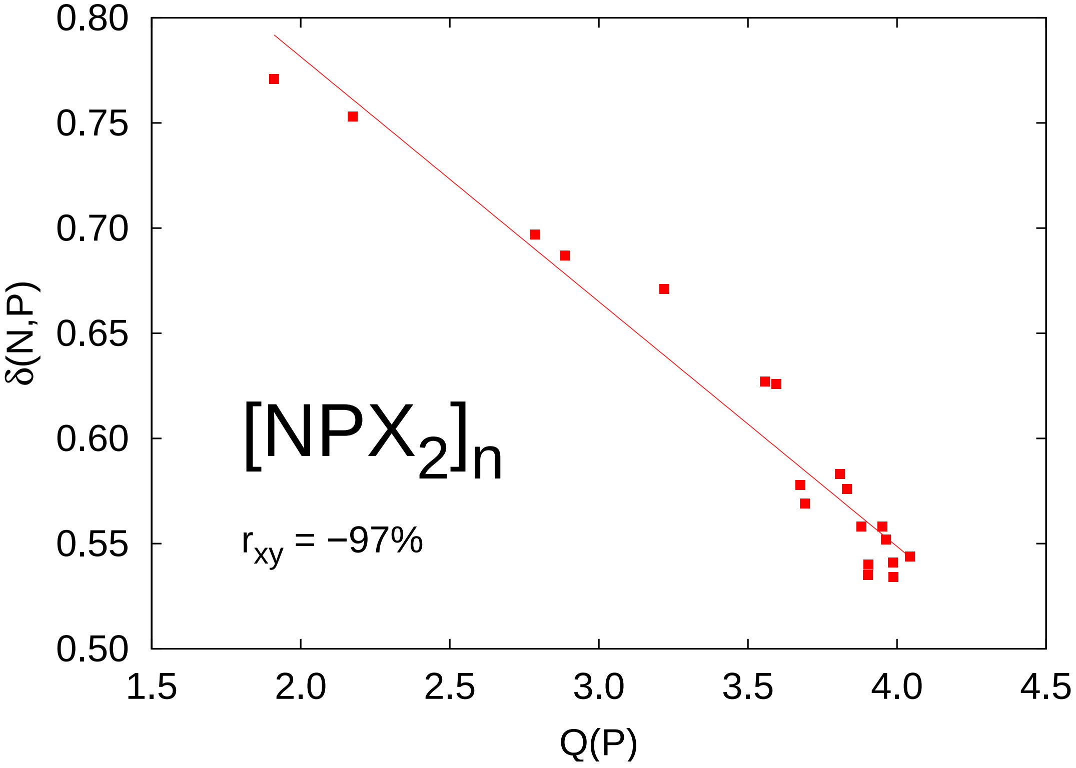
$\delta(\mathrm{N},\mathrm{P})$: 0.65–0.61, $\delta(\mathrm{P},\mathrm{Cl})$: 0.62–0.57,
$\mathcal{Q}$: $-2.2(4)$ (N), $+3.4(6)$ (P), -0.6 (Cl).



cycles: (NPX_2)$_3$:

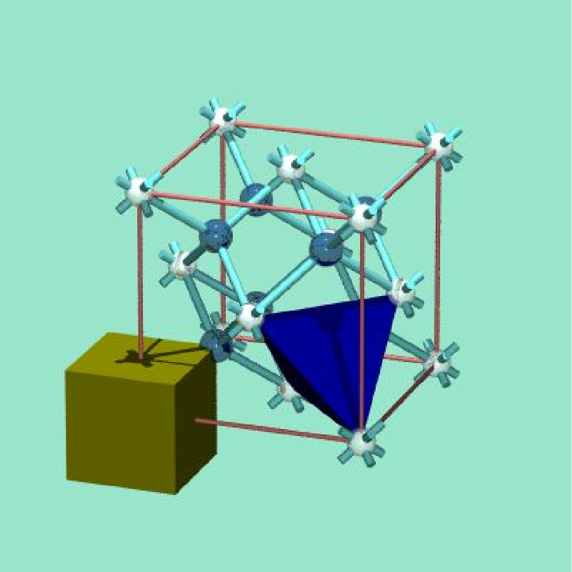
X: $-$H, $-$BH$_2$, $-$CH$_3$, $-$CH$=$CH$_2$, $-$C$\equiv$CH, $-$C$\equiv$N, $-$CNO, $-$NH$_2$, $-$NHNH$_2$, $-$NC, $-$NCS, $-$N$_3$, $-$OH, $-$OCH$_3$, $-$F, $-$SiH$_3$, $-$PH$_2$, $-$SH, $-$SCN, $-$Cl, $-$Br.

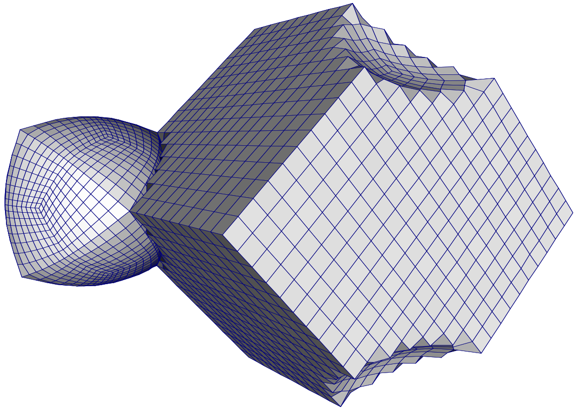




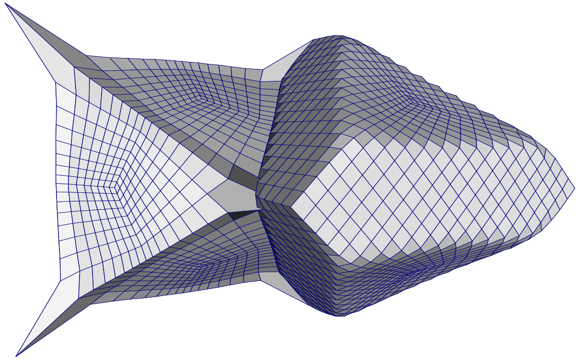
Electronic polymorphism

Crystals with the same structure can have different electron density topologies. Topological radii can be used to predict exactly this polymorphism [PRB 55(1997)4285; JPCB 102(1998)6937].

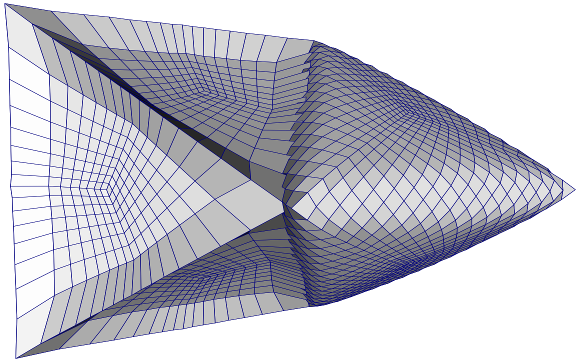




BeF$_2$ ($R_M/R_X \leq 0.6$)



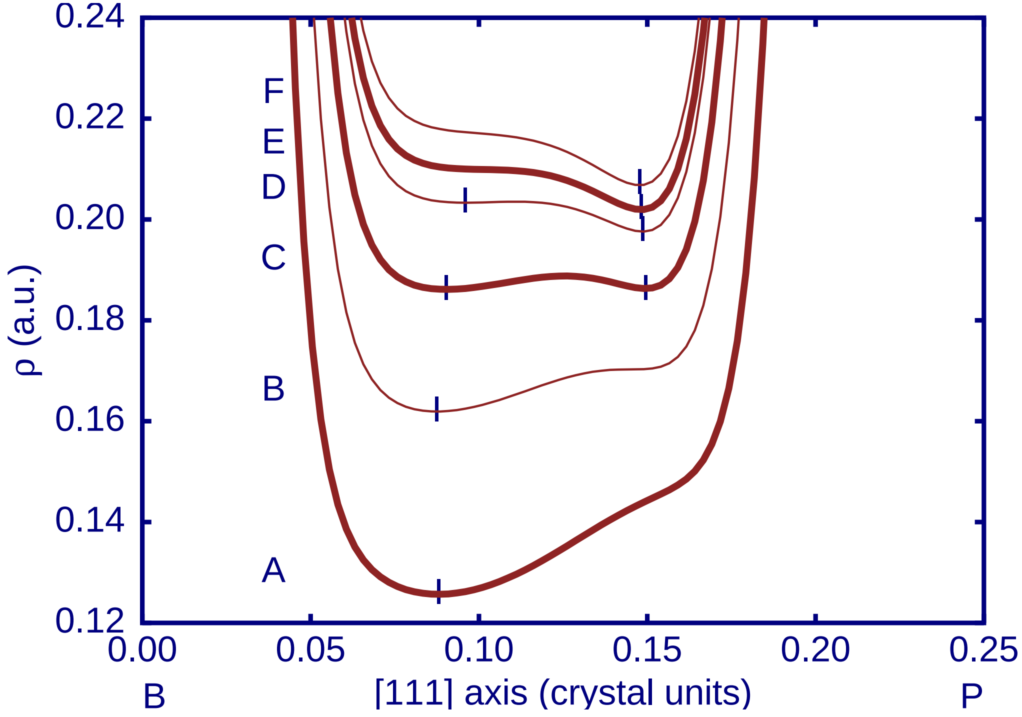
CaF$_2$ ($0.6 \leq R_M/R_X < 1.2$)

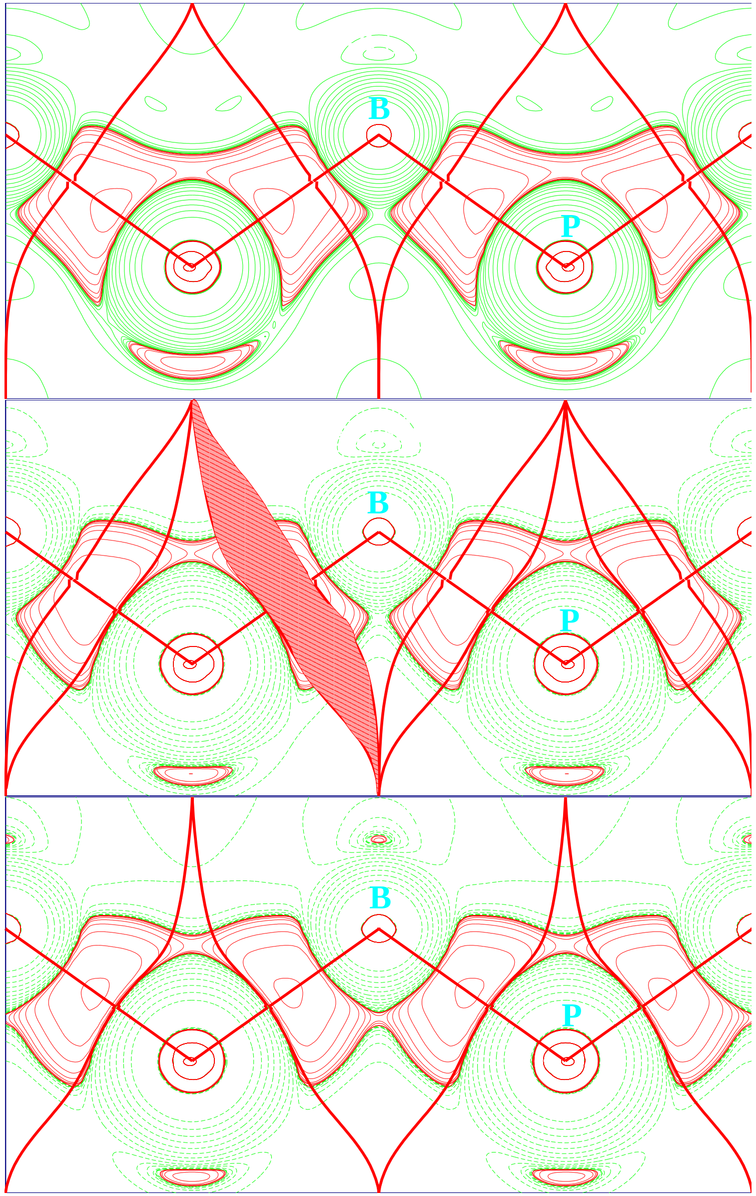


BaF$_2$ ($R_M/R_X \geq 1.2$)

Exotic topologies: The polarity inversion of BP

(HF-LCAO CRYSTAL, calc., PRB 63(2001)125103)



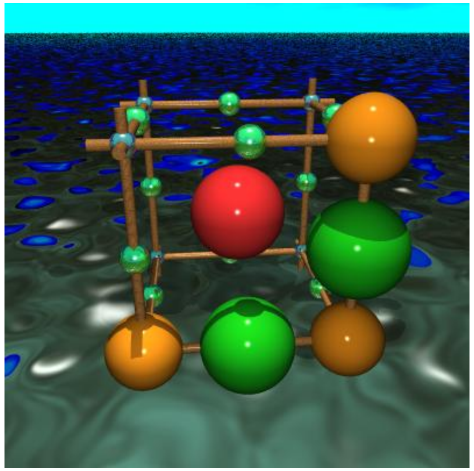


- The standard polarity, $B^{\delta+}P^{\delta-}$, is reversed under the application of hydrostatic pressure.
- The topology of most ionic/covalent crystals is determined by geometry and ion size ratios.

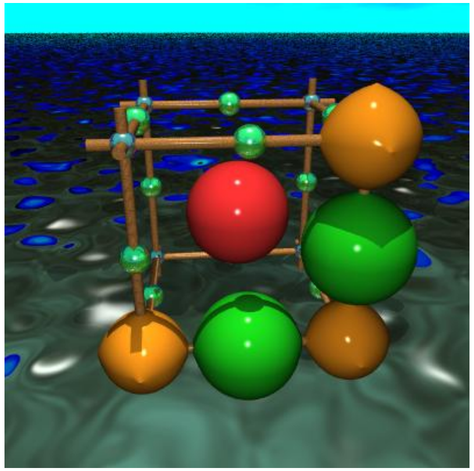
What happened to the spherical ion model?

Electron density is mostly spherically concentrated around nuclei [JPCM 11(1999)6329].

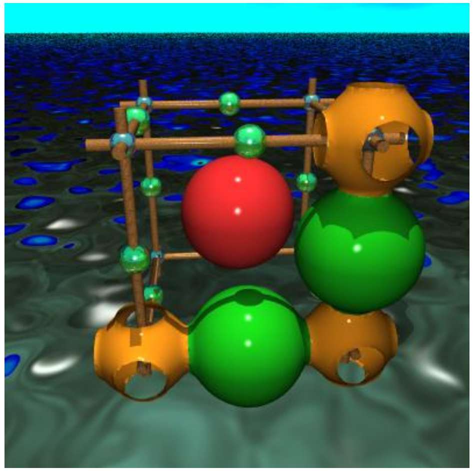
Ej. KMgF$_3$: ρ_{nuc} is 4.5×10^3 (K), 1.1×10^3 (Mg) & 4.5×10^2 e/bohr^3 (F), whereas ρ_b is 3.7×10^{-2} (Mg-F), 1.2×10^{-2} (K-F), & 9.9×10^{-3} e/bohr^3 (F-F).



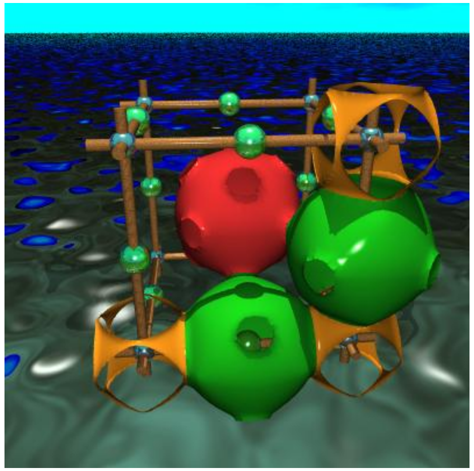
$\rho = 0.060\, e/\text{bohr}^3$



$\rho = 0.0366\, e/\text{bohr}^3$

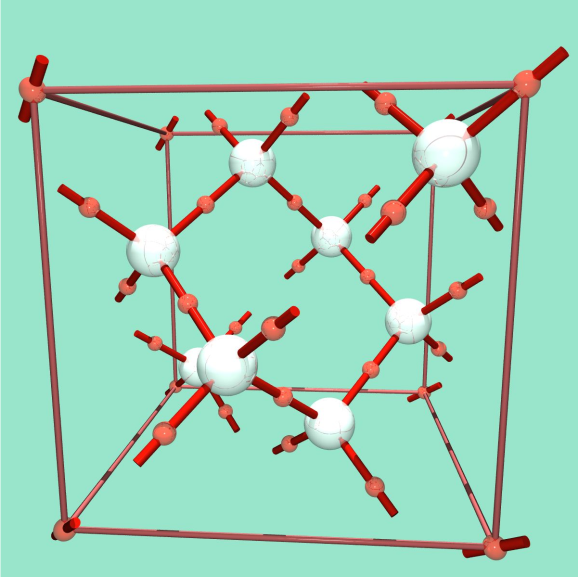


$\rho = 0.020\, e/\text{bohr}^3$



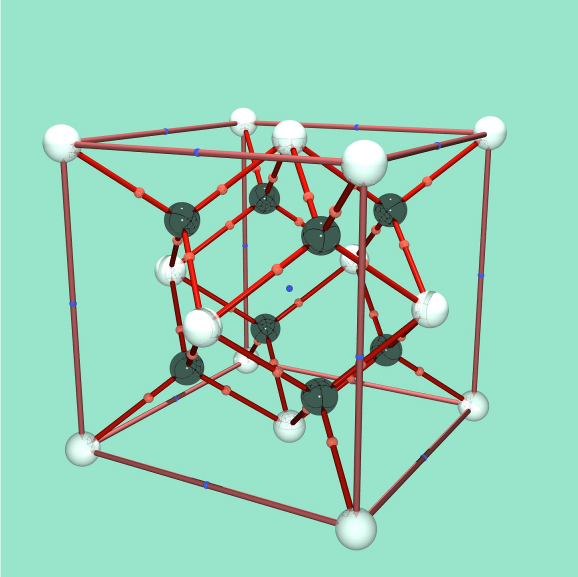
$\rho = 0.010\, e/\text{bohr}^3$

Some prototypical crystals



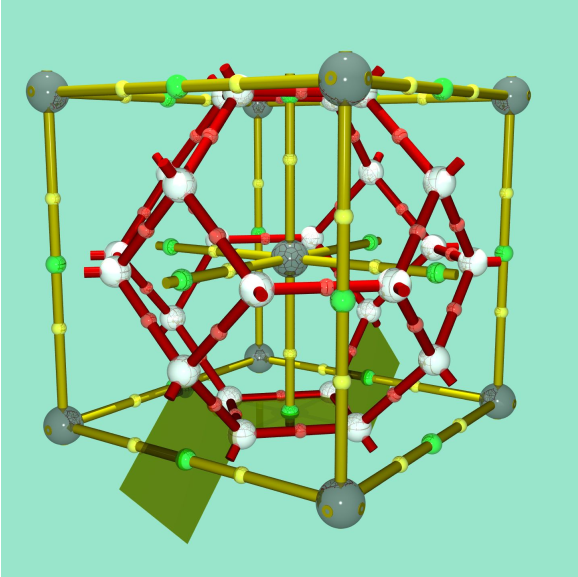
C diamond: share shell bonding.

$$\rho_b = 0.2659\, e/\text{bohr}^3$$
$$\nabla^2\rho_b = -0.9044\, e/\text{bohr}^5$$
$$q_C = 0$$



Li_2O: closed shell bonding.

$$R_{Li} = 1.402\,\text{bohr}$$
$$\rho_b = 0.0246\, e/\text{bohr}^3$$
$$\nabla^2\rho_b = +0.2076\, e/\text{bohr}^5$$
$$q_{Li} = 0.90$$
$$q_O = -1.80$$



Li: metal.

2 Li , 12 nnm in the cell

Volume: 24% Li, 76% nnm

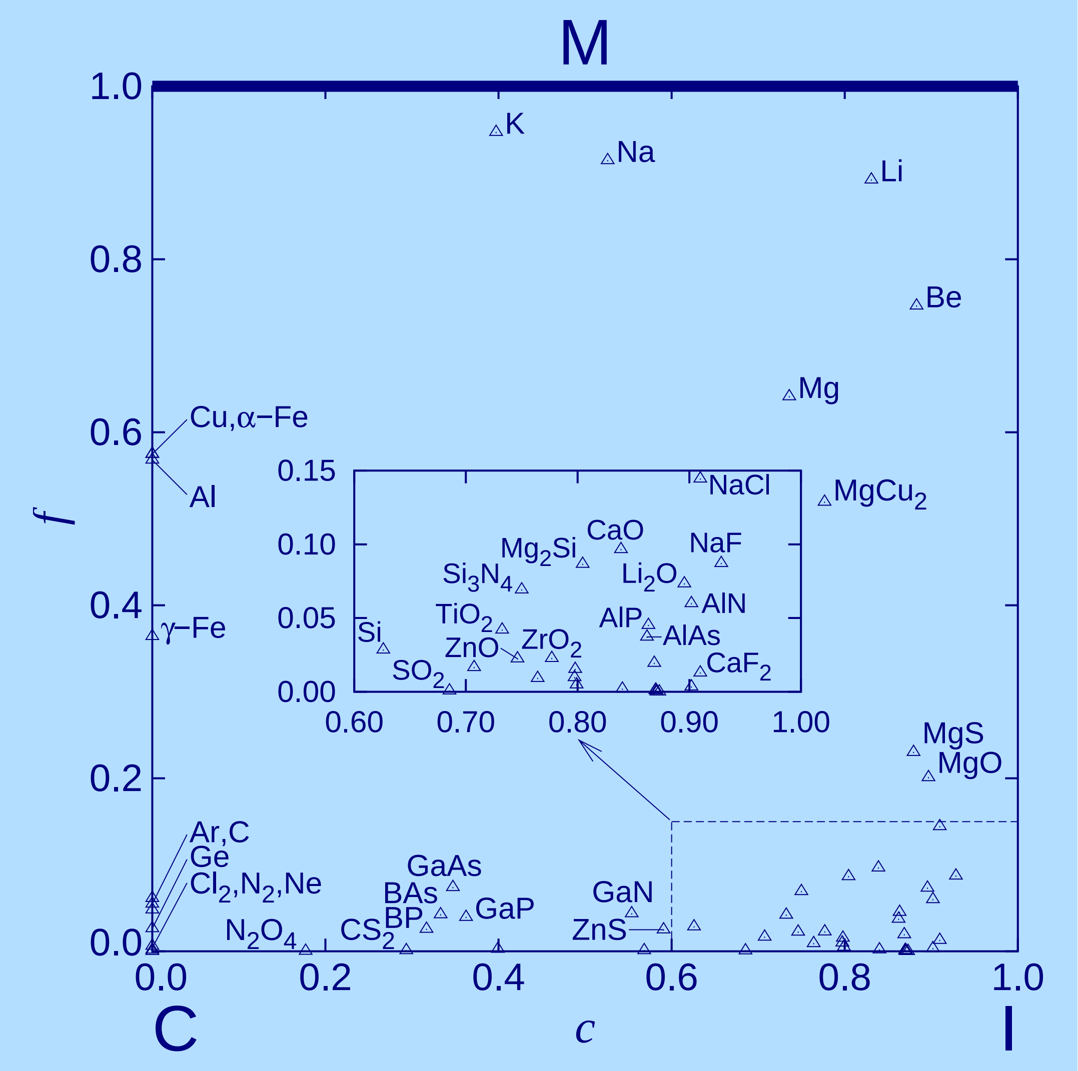
q: $+0.825$ Li, -0.137 nnm

Radius: 2.023 Li, 1.293 nnm

	Li-nnm	nnm-nnm
ρ_b	0.0072	0.0075
$\nabla^2\rho_b$	0.00526	-0.00024

Classification of covalent, ionic and metallic solids

- JACS **124** (2002) 14721.
- van Arkel-Ketelaar diagram is based on electronegativity: $|\chi_A - \chi_B|$ *vs.* $\langle \chi_i \rangle$.
- Appropriate ρ indices?
  - charge transfer: $\langle \mathcal{Q}_\Omega / \mathrm{OS}_\Omega \rangle$,
  - flatness: $\rho_{\min}/\rho_b^{\max}$,
  - molecularity: $\mu = (\rho_b^{\mathrm{max}} - \rho_b^{\mathrm{min}})/\rho_b^{\mathrm{max}}$ (if $\nabla^2\rho_b^{\mathrm{max}} \times \nabla^2\rho_b^{\mathrm{min}} < 0$ and $\mu = 0$ otherwise).
- Figure based on HF-LCAO CRYSTAL98 calculations.



Partition of thermodynamical properties

- The partition of atomic compressibility is simple:

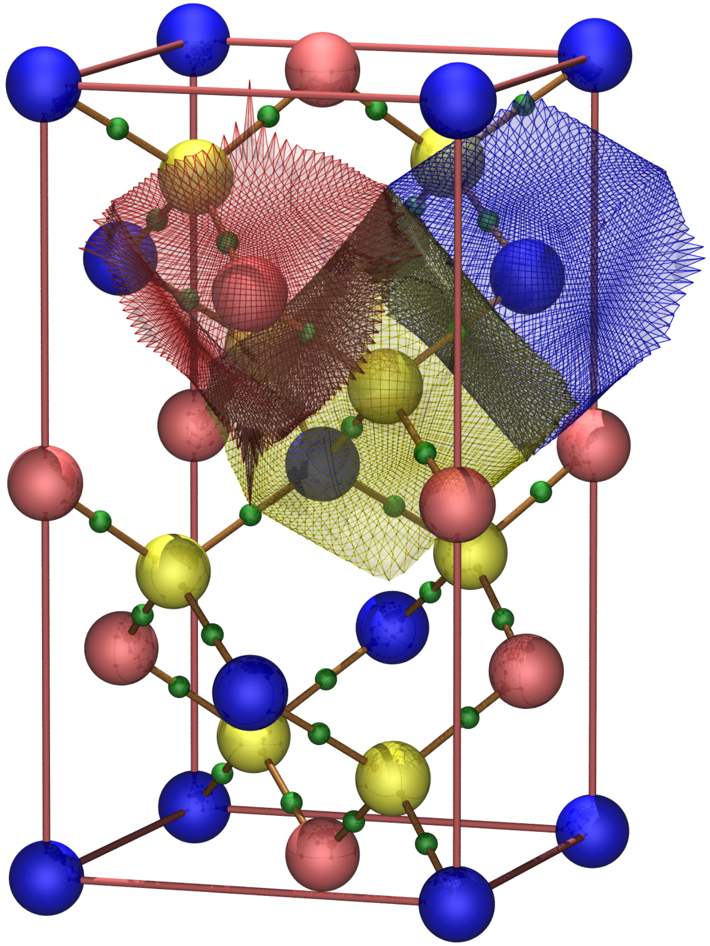
$$\kappa = \frac{1}{B} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right), \quad V = \sum_{\Omega} V_\Omega, \quad f_\Omega = V_\Omega / V,$$

$$\kappa_\Omega = \frac{1}{B_\Omega} = -\frac{1}{V_\Omega}\left(\frac{\partial V_\Omega}{\partial p}\right) \implies \boxed{\kappa = \sum_\Omega f_\Omega \kappa_\Omega}.$$

- This provides a very practical analytical tool. We can see, for instance, that the compressibility of spinels is controlled by the oxide ion (PhysRev B **62** (2000) 13970):

AB_2O_4	B (GPa)	B_A	B_B	B_O	f_O
$MgAl_2O_4$	215.2	282.1	331.9	201.6	0.8127
$MgGa_2O_4$	211.2	261.2	283.9	196.1	0.7486
$ZnAl_2O_4$	214.8	246.0	335.2	203.3	0.7690
$ZnGa_2O_4$	213.3	241.2	308.6	195.7	0.7070

- $B_O \approx B < B_{Zn} < B_{Mg} < B_{Ga} < B_{Al}$.
- In the static approximation ($T = 0$ K, no ZPE) all thermodynamic observables can be partitioned into basin contributions.



$AgGaSe_2$ (chalcopyrite phase)

	Ag	Ga	Se
$\mathcal{Q}$	$+0.28$	$+1.00$	-0.64

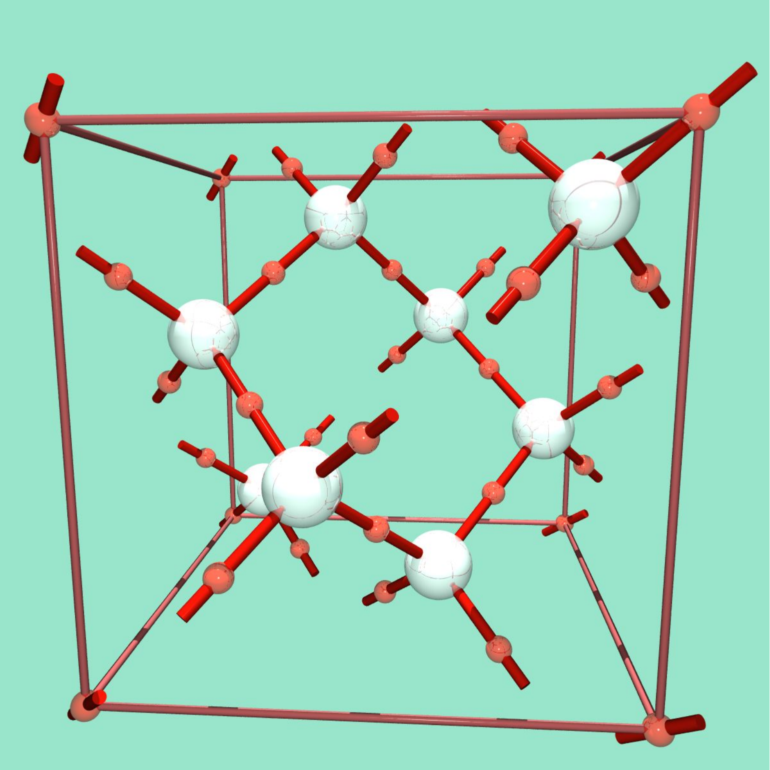
$$c = 31\%, \quad f = 2.6\%$$

Ω	f_Ω	κ_Ω (TPa^{-1})	B_Ω (GPa)
Ag	0.238	17.7	56.6
Ga	0.157	22.3	44.8
Se	0.603	19.6	51.1
	Total	19.5	51.2

Bonding in group IV semiconductors

1. Topology of $\rho(\boldsymbol{r})$:

The topology of all the elements (C–Pb) in the diamond phase is equivalent, but the properties at the bcp show a sequence from sharing (C, Si) to closed shell bonding (Sn, Pb).

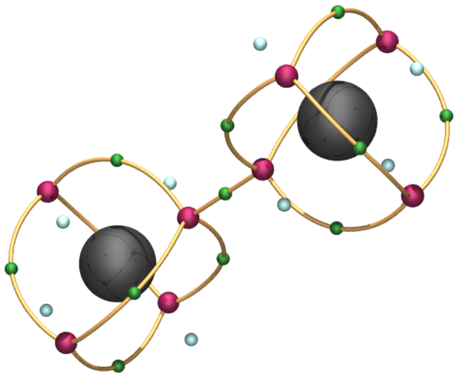


diamond:	ρ_b	$\nabla^2\rho_b$
C	0,240	$-0{,}551$
Si	0,084	$-0{,}123$
Ge	0,075	$-0{,}035$
Sn	0,054	$+0{,}003$
Pb	0,039	$+0{,}031$

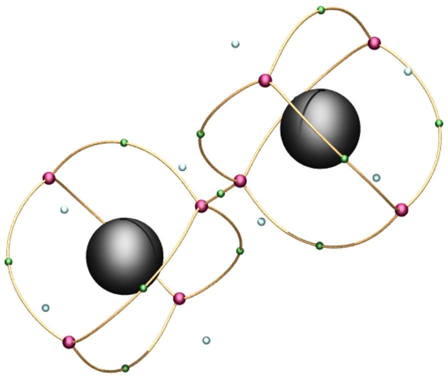
2. Topology of $L(\boldsymbol{r}) = -\nabla^2\rho(\boldsymbol{r})$:

$L(\boldsymbol{r}) \geq 0$: local e accumulation; $L(\boldsymbol{r}) < 0$: local e depletion.

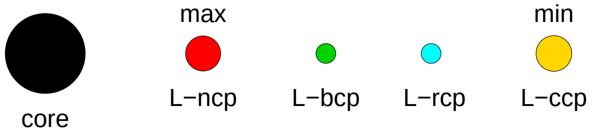
Three types of topology are clearly different: C–Si (covalent), Ge–Sn, and Pb (metallic?).

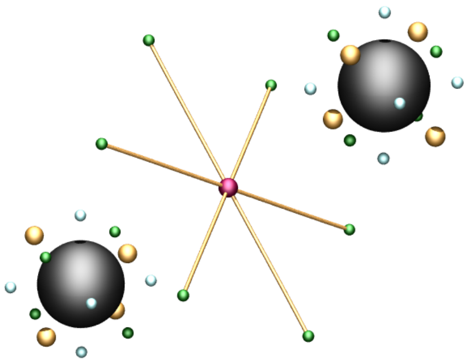


C:

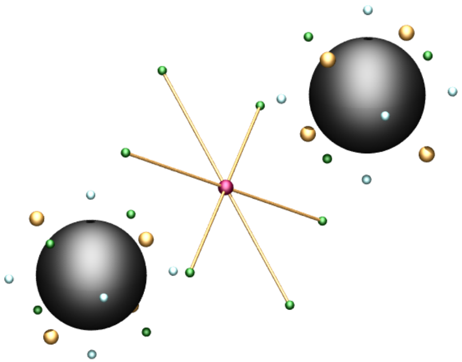


Si:

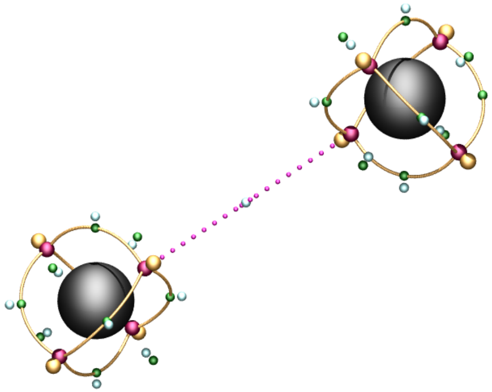




Ge:

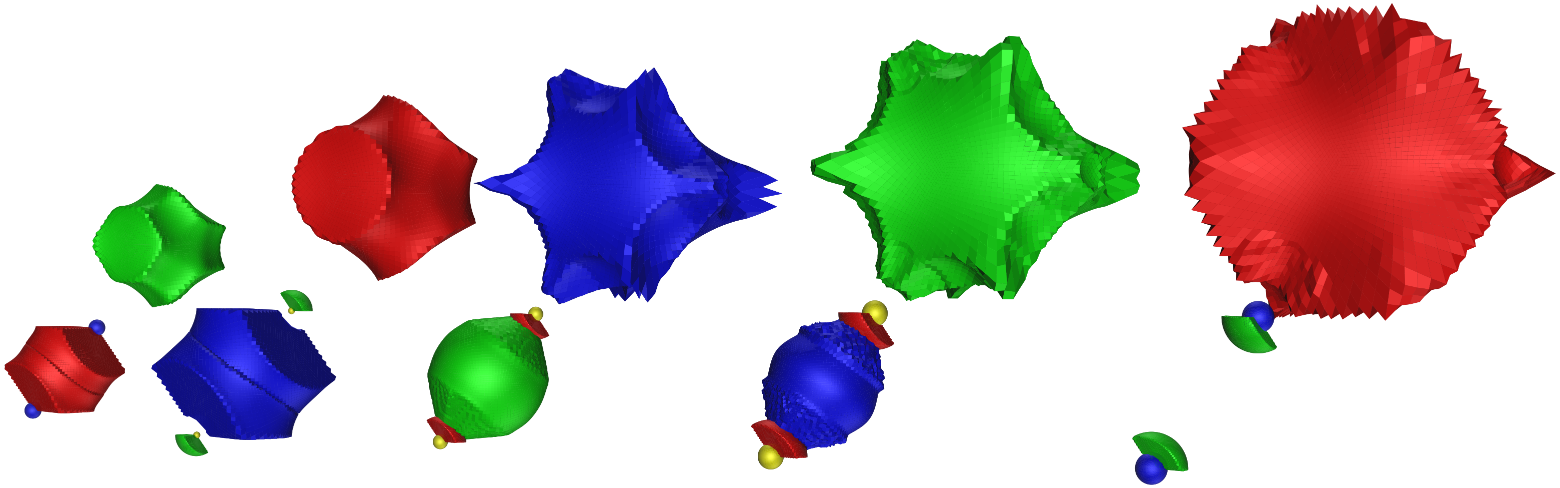


Sn:



Pb:

3. Population and volume of the L-ncp basins:



		V_Ω					$\mathcal{Q}_\Omega$				
		C	Si	Ge	Sn	Pb	C	Si	Ge	Sn	Pb
Core	$8a$	0.1	1	2	6	6	0.99	7.29	21.77	40.15	69.90
Twin-b	$32e$	5.1	19				1.08	1.51			
Sing-b	$16c$			22	23				3.16	2.33	
Inters	$8b$	17.6	59	107	180	291	0.71	0.66	3.93	5.06	11.96

4. Local compressibility of L-ncp basins:

Using $V = \sum_{\Omega} V_{\Omega}$, the static compressibility and bulk modulus, $\kappa = B^{-1} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)$, can be partitioned into basin contributions:

$$\kappa = \sum_{\Omega} f_{\Omega}\kappa_{\Omega} \quad \text{and} \quad B^{-1} = \sum_{\Omega} f_{\Omega} B_{\Omega}^{-1} \quad \text{with} \quad f_{\Omega} = \frac{V_{\Omega}}{V} \quad \text{and} \quad \kappa_{\Omega} = B_{\Omega}^{-1} = -\frac{1}{V_{\Omega}}\left(\frac{\partial V_{\Omega}}{\partial p}\right).$$

		C		Si		Ge		Sn		Pb	
		f_{Ω}	κ_{Ω}	f_{Ω}	κ_{Ω}	f_{Ω}	κ_{Ω}	f_{Ω}	κ_{Ω}	f_{Ω}	κ_{Ω}
Core	$8a$	0.1	0.01	0.7	0.02	1	0.02	2	0.08	2	0.21
Twin-b	$32e$	54	1.25	55	5.12						
Sing-b	$16c$					28	8.07	19	15.16		
Inters	$8b$	46	3.88	44	20.56	71	22.67	79	31.50	98	42.61
	κ_T	2.46(13)		11.93(5)		18.34($\bar{9}3$)		27.80(161)		41.92(239)	
	B_T	407($\bar{2}2$)		84(1)		55(3)		36(2)		24(1)	

Final Remarks

The real purpose of theory is producing insight, not numbers. Theory is not a substitute for experimentation, it is the way to understand the experiments.

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