~ 100 researchers

CNR-SCITEC, Istituto di Scienze e Tecnologie Chimiche «Giulio Natta»

CHIMICA VERDE

CHIMICA PER L'ENERGIA

CHIMICA E SALUTE

MATERIALI AVANZATI

CHIMICA PER I BENI CULTURALI

CHIMICA COMPUTA-ZIONALE

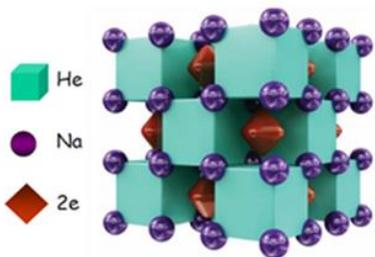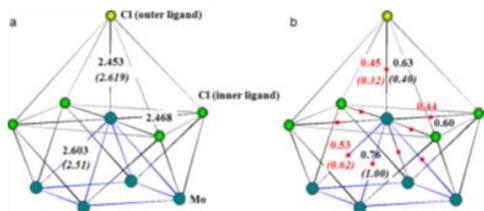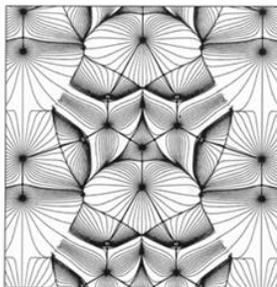Milano, 73          Roma, 9

Perugia, 10          Genova, 6

# My general expertise

Carlo Gatti

A.R. Oganov, Skoltech Institute Moscow, Russia

He
Na
2e

**High pressure evolution of structure and bonding**

**Li, Na batteries Organic electrodes; Phase-change materials**

**C. Frayret**, Jules Verne Univ. Amiens, France

**M. Wuttig**, RWTH, Aachen, Germany

CRYSTAL17

**S. Casassa**, **B. Civalleri**, **A. Erba** Univ. Torino, Italy

**Software code development, TOPOND, NCI_Milano**

**Chemical bonding**

**Molecular Recognition in HPLC**

σ-hole
Y—X····A
halogen bond
X = Cl, Br, I
A = Lewis base (O, N, S, halogen, π-donor, anion); Y = EWG

Ch
Y····A   A····Y
σ₁   σ₂
chalcogen bond
Ch = S, Se, Te
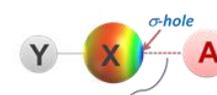
**P. Peluso**, CNR-ICB, Sassari, Italy
**V. Mamane**, Strasbourg University France

**Modern Pauling's Bond Valence Model Me-Me bonds**

**New Chemical descriptors: SF for SD, EP, SD topology**

CAUSE

$\nabla^2 s$

EFFECT

s

a
Cl (outer ligand)
2.453
(2.619)
Cl (inner ligand)
2.468
2.603
(2.51)
Mo

b
0.45  0.63
(0.32) (0.40)
0.44
0.53  0.60
(0.62)
0.76
(1.00)

**E. Levi, D. Aurbach**
Bar-Ilan University, Israel

**B.B. Iversen**, CMC project, Aarhus Univ. Denmark
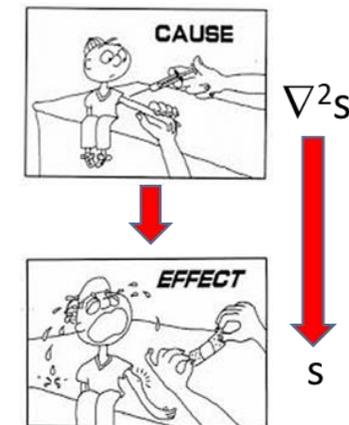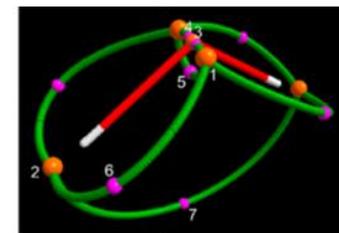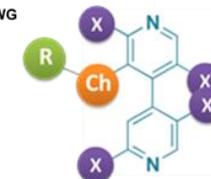
## Outline

➤ Retrieving chemical bonding information from the wf: compresses the information contained in the wf by using its probabilistic interpretation ➡ reduced densities

➤ Bond descriptors from reduced densities ($\rho$ and related quantities; first and second order matrices)

➤ How to analyse reduced densities. Pros and cons of deformation densities ➡ **topology**

➤ The theory of *Gradient dynamical systems* ➡ partitioning of the molecular space ➡ topological features/study of the scalar associated to the gradient field

➤ QTAIM as a specific very important case (topological basin ➡ topological atom ⬌ quantum atom)

➤ Some important hints on QTAIM chemical bonding classification and on the use of the density Laplacian

➤ Didactic example on the use of QTAIM to detect packing effects (urea crystal)

☐ Spin density topology

☐ Electrostatic potential Source Function (applied to enantioseparation outcome in HPLC)

☐ Do the peculiar physical properties of phase change materials entail unusual chemical bonding features? (LI and DI application)

**Why retrieving chemical (bonding) information from the model wavefunction of a material? (or, in general, of any investigated system of some fundamental and/or practical interest?)**

➢ Thoughtful searches for more and more performing materials or of materials with novel properties and functions require a profound understanding of their structure-property relationships

➢ The detailed knowledge of the *structure* of a material, either through experimental and/or *in silico* approaches, is a necessary and fundamental prerequisite for its study.

➢ Yet the geometrical, electronic and (magnetic) structure of a material is ultimately related to its *chemical bonding features*, which are just a function of its chemical composition/stoichiometry, and of external constraints (applied P, T and external fields)

**Material's properties** are determined by **chemical bonding**

GeSe: orthorhombic, **poor** thermoelectrics ➡ covalent bonding    (2c-2e)

GeTe: almost cubic,  **good** thermoelectrics ➡ *metavalent* bonding  (1c-2e)
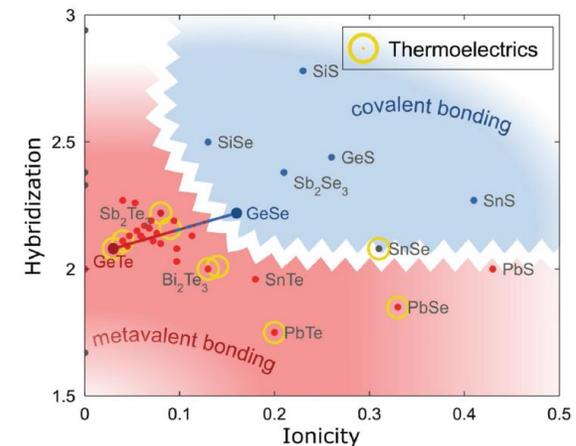
## How retrieving chemical (bonding) information from wavefunctions?

The amount of information stored in a wavefunction becomes soon so large with increasing number of electrons that it escapes human comprehension ➡️ an information compression technique is needed
Vleck JHV. Phys Rev. 1932;49:232

**Two main strategies**:

❑ **A**. Take advantage of the models/approximations used to solve Schrödinger's equation. In HF, e.g., $\psi$ is written as a Single Determinant (SD) constructed from one-electron functions or orbitals $\varphi$ ➡️ mean-field (MF) approach: $e^-$ move in the average potential created by the rest of the particles ($e^-$ and n) of the system ➡️ Knowledge and manipulation of the $N$ (number of $e^-$) 3D $\varphi$ of a system is much easier than that of the full wf. However, this simplification **comes at the expense of several problems and caveats:** *(a)* $\psi$ is invariant to unitary transformations of orbitals ➡️ orbital interpretations are method (MO, VB, etc. ) dependent; *(b)* when the MF is abandoned and electron correlation is taken into account, the pristine SD orbital concept vanishes and (MC approaches) many more than $N$ partially occupied functions appear

❑ **B**. compress the information contained in the wavefunction by using its probabilistic interpretation
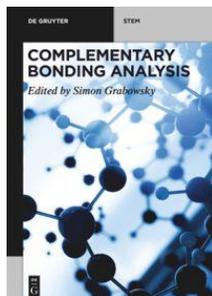
Ángel Martín Pendás and Carlo Gatti, **Chapter 3: Quantum theory of atoms in molecules and the AIMAll software** in *Complementary Bonding Analysis*, S. Grabowsky Ed, De Gruyter 2021

G. Saleh, D. Ceresoli, G. Macetti and C. Gatti*, **Chapter 5: Chemical Bonding Investigations for Materials**, in *Computational Materials Discovery*, A.R. Oganov, G. Saleh, A.G. Kvashnin Eds., RSC 2019

# From wavefunctions to chemical bond descriptors

Forget about the behavior of all e⁻ but 1 or 2 and get the density of finding e⁻ or e⁻ pairs at given positions of $R^3$ or $R^6$. These **reduced densities** are QM observables (experimentally accessed in principle), invariant under orbital transformations ➡ do not depend on models of computational methods, and have clear-cut interpretations

$$\Psi_{el}(\boldsymbol{r},\boldsymbol{r_2},...\boldsymbol{r_N};\boldsymbol{R})$$

System of $N_{el}$ and M nuclei; $\Psi_{el}$ : stationary *wf* for fixed nuclear space coordinates (BO approx.) $\boldsymbol{R}$ : ensemble of nuclear coordinates for the *M* nuclei

$$\Psi_{el}(\boldsymbol{r_1},\boldsymbol{r_2},...\boldsymbol{r_N};\boldsymbol{R})\cdot\Psi_{el}^*(\boldsymbol{r_1},\boldsymbol{r_2},...\boldsymbol{r_N};\boldsymbol{R})d\boldsymbol{r_1}d\boldsymbol{r_2},...d\boldsymbol{r_N}$$

Born's interpretation of the wf

$$\rho(\mathbf{r_1})d\mathbf{r_1}$$

*probability* of finding any of its electrons at $\mathbf{r_1}$ regardless of the exact position of the other e

where the corresponding *probability density* is the *position electron density* (ED) $\rho(\mathbf{r})$

$$\rho(\boldsymbol{r}) = N\int \Psi_{el}(\boldsymbol{r},\boldsymbol{r_2},...\boldsymbol{r_N};\boldsymbol{R})\cdot\Psi_{el}^*(\boldsymbol{r},\boldsymbol{r_2},...\boldsymbol{r_N};\boldsymbol{R})d\boldsymbol{r_2},...d\boldsymbol{r_N}$$

Density matrices are a convenient mathematical device for evaluating the expectation values of operators corresponding to physical observables, $<\psi_{el}| O | \psi_e>$

$$\gamma_p(r_1 r_2 ... r_p ; r_1' r_2' ... r_p') = \binom{N}{p} \int \psi_{el}(r_1 r_2 ... r_p r_{p+1} ... r_n) \psi_{el}^*(r_1' r_2' ... r_p' r_{p+1}' ... r_n') dr_{p+1} ... dr_n$$

A numerical value is assigned to $\gamma_p$ by two sets of indices. $\gamma_p$ may be seen as an element of a matrix and $\gamma_p(\{r\};\{r'\})$ as the corresponding matrix with infinite elements. The diagonal elements $(r_1 \equiv r_1')$ of this matrix, correspond to the probability of finding $p$ electrons with given space coordinates and regardless of those of the remaining ($N$-$p$) electrons. This is a $p$-particles density, motivating why $\gamma_p(\{r\};\{r'\})$ is called a *density matrix*

$\binom{N}{p}$ is a binomial coefficient ensuring proper normalization

$$\gamma_2(r_1 r_2 ; r_1' r_2') = \frac{N(N-1)}{2} \int \psi_{el}(r_1 r_2 r_3 ... r_n) \psi_{el}^*(r_1' r_2' r_3' . r_n') dr_3 ... dr_n$$

$$\gamma_1(r_1 ; r_1') = N \int \psi_{el}(r_1 r_2 ... r_n) \psi_{el}^*(r_1' r_2' . r_n') dr_2 ... dr_n$$

Since only one- and two-body interactions take place among electrons, we need just $\gamma_1$ and $\gamma_2$

$$\gamma_1(\mathbf{r}_1;\mathbf{r}_1') = N\int \psi_{el}(\mathbf{r}_1\mathbf{r}_2\,..\mathbf{r}_n)\psi_{el}^*(\mathbf{r}_1'\mathbf{r}_2'..\mathbf{r}_n')d\mathbf{r}_2...d\mathbf{r}_n$$
First order density matrix (DM)

$$\gamma_2(\mathbf{r}_1\mathbf{r}_2;\mathbf{r}_1'\mathbf{r}_2') = \frac{N(N-1)}{2}\int \psi_{el}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3...\mathbf{r}_n)\psi_{el}^*(\mathbf{r}_1'\mathbf{r}_2'\mathbf{r}_3'..\mathbf{r}_n')d\mathbf{r}_3...d\mathbf{r}_n$$
Second order DM

The expectation value of any one- and two-electron operators may be expressed as

$$\left\langle \hat{O}_1 \right\rangle = \left\langle \sum_i^N O_1(\mathbf{r}_i) \right\rangle = \int O_1(\mathbf{r}_1)\gamma_1(\mathbf{r}_1;\mathbf{r}_1')d\mathbf{r}_1 \bigg|_{\mathbf{r}_1'=\mathbf{r}_1}$$

$$\left\langle \hat{O}_2 \right\rangle = \left\langle \sum_{i,j}^N {}'O_2(\mathbf{r}_i\mathbf{r}_j) \right\rangle = \int O_2(\mathbf{r}_1\mathbf{r}_2)\gamma_2(\mathbf{r}_1\mathbf{r}_2;\mathbf{r}_1'\mathbf{r}_2')d\mathbf{r}_1 d\mathbf{r}_2 \bigg|_{\mathbf{r}_1'=\mathbf{r}_1;\mathbf{r}_2'=\mathbf{r}_2}$$

using the convention that the operators act only on functions of the unprimed variables and that **r'** is put equal to **r** after operating with the operators but before completing the integration

All 1-electron and all 2-electron properties may be obtained from the first and second order DMs

# From wavefunctions to chemical bond descriptors

$$\Psi_{el}(\boldsymbol{r}, \boldsymbol{r_2}, ... \boldsymbol{r_N}; \boldsymbol{R})$$

$$\gamma_1(\boldsymbol{r} = \boldsymbol{r}^{'}) \equiv \rho(\boldsymbol{r})$$

$$\rho(\boldsymbol{r}) = N \int \Psi_{el}(\boldsymbol{r}, \boldsymbol{r_2}, ... \boldsymbol{r_N}; \boldsymbol{R}) \cdot \Psi_{el}^{*}(\boldsymbol{r}, \boldsymbol{r_2}, ... \boldsymbol{r_N}; \boldsymbol{R}) dr_2, ... dr_N$$

**Derived from the ED $\rho$ :**    $\rho, \nabla^2\rho$, ESP, EF, SF, RDG, etc.

SF Source Function; ESP Electrostatic Potential; EF Electric Field, RDG Reduced Density Gradient

$$\gamma_1(\boldsymbol{r_1}; \boldsymbol{r_1}^{'}) = N \int \psi_{el}(\boldsymbol{r_1}\boldsymbol{r_2} ... \boldsymbol{r_n}) \psi_{el}^{*}(\boldsymbol{r_1}^{'}\boldsymbol{r_2}^{'}. \boldsymbol{r_n}^{'}) dr_2 ... dr_n$$

**Derived from $\gamma_1(\boldsymbol{r_1}; \boldsymbol{r_1}^{'})$ :**    G,V, H, LOL, ELF, etc.

G,V,H : kinetic, potential and energy densities, ELF : Electron Localization Function

**Derived from $\gamma_2(\boldsymbol{r_1}\boldsymbol{r_2}; \boldsymbol{r_1}^{'}\boldsymbol{r_2}^{'})$ :**    $\rho_2(\boldsymbol{r_1}, \boldsymbol{r_2}) \equiv \gamma_2(\boldsymbol{r_1}, \boldsymbol{r_2}; \boldsymbol{r_1}, \boldsymbol{r_2})$

$\rho_2(\boldsymbol{r_1}, \boldsymbol{r_2})$ Pair density    LI, DI, DAFH, ELI's family...

LI/DI: local/deloc indices; DAFH Domain Average Fermi Hole, ELI, Electron Localizability Indicators

# From wavefunctions to chemical bond descriptors: LI and DI

$\rho_2(\mathbf{r}_1,\mathbf{r}_2) \equiv \gamma_2(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1,\mathbf{r}_2)$  Pair Density : all information on the correlated motion of electrons

$\rho_2(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}[\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) -\rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2)]$

LI, DI, DAFH, ELI's family...

$\rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2)$  It is the so called *exchange-correlation density*, which incorporates all non classical effects and measures to which degree the density is excluded at $\mathbf{r}_2$ because of the presence of an electron at $\mathbf{r}_1$.

$\rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2)$ integrates to N, so that integration of $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$, $\frac{1}{2}(N^2-N) = \frac{1}{2} N(N-1)$, yields the total number of distinct pairs, $\frac{1}{2} N(N-1)$

The probability of finding one electron at $\mathbf{r}_1$ and another one at $\mathbf{r}_2$ deviates from the purely classical description of a product of independent EDs because of Coulomb and Fermi correlation of $e^-$ motions

$$\lambda(A) = \int_A \int_A \rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2)dr_1 dr_2$$  $\lambda(A)$ Electron localization index, **LI**

$$\delta(A,B) = 2 \cdot \int_A \int_B \rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$  $\delta(A,B)$ Electron delocalization index, **DI**

A and B are "atomic" basins (to be defined)

$$N(A) = \lambda(A) + \frac{1}{2}\sum_{B \neq A} \delta(A,B)$$

# Source of information

$\rho(\mathbf{r}) \equiv \rho_1(\mathbf{r},\mathbf{r}) \longrightarrow \nabla^2\rho, \text{ESP,EF,SF, RDG, etc.}$

Only indirect information on electron correlation

C. Gatti, PJ Mac Dougall and RFW Bader, Effect of electron correlation on the topological properties of molecular charge distributions, *J. Chem. Phys.* 88, 3792 (1988)

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$\rho_1(\mathbf{r},\mathbf{r}') \longrightarrow \text{G}(\mathbf{r}),\text{V}(\mathbf{r}), \text{H}(\mathbf{r}), \text{LOL, ELF,}$

$\rho_2(\mathbf{r}_1,\mathbf{r}_2) \equiv \rho_2(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1,\mathbf{r}_2)$

Pair Density : all information on the correlated motion of electrons

$\rho_2(\mathbf{r}_1,\mathbf{r}_2) = \tfrac{1}{2}[\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2)]$

$\longrightarrow$ LI, DI, DAFH, ELI's family…

$\lambda(A) = \int\limits_A \int\limits_A \rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$   Electron localization index, **LI**

$\delta(A,B) = 2 \cdot \int\limits_A \int\limits_B \rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$   $\delta(A,B)$ Electron delocalization index, **DI**

%loc(A) = [$\lambda$(A)/N(A)]·100          %deloc (A) =$\Sigma_{A \neq B}$ [0.5·$\delta$ (A,B)/N(A)]·100

# How to analyse reduced densities

❑ Reduced densities, are dominated by the nuclear positions

It was thus clear from the beginning that a theory of chemical bonding based on electron densities (or functions derived thereof) should focus on density differences, i.e. on how electrons redistribute in chemical processes

CF Matta, HDR thesis, Nancy 2009
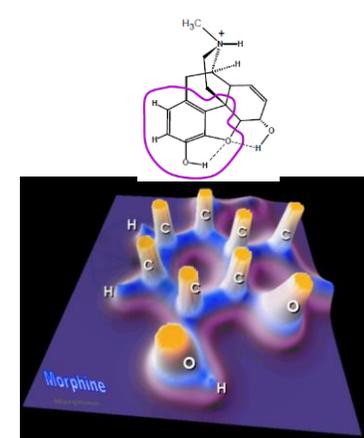
$$\Delta\rho = \rho - \rho_{ref}$$

❑ Yet, the "arbitrary choice of the reference density can completely alter the interpretation

❑ Analyse the density **itself**

❑ Examine its ***topology***. If we want to study the behavior of a scalar function without recourse to an external reference, only its value and that of its derivatives are available (Paul Mezey).

## Deformation densities: pros and cons

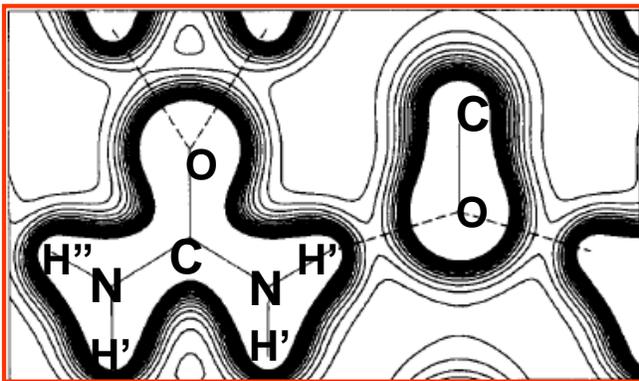$$\Delta\rho(\mathbf{r} ; \mathbf{X}) = \rho(\mathbf{r} ; \mathbf{X}) - \rho_{ref}(\mathbf{r} ; \mathbf{X})$$

$\Delta\rho$  standard deformation electron density

$\rho$  total electron density, either $\rho_{th}$ or $\rho_{exp,MM,static}$

$\rho_R$ reference density

*molecules* → promolecular density

*crystals* → procrystal density

$\rho_{ref} = \sum_{atoms} \rho_a(\mathbf{r}-\mathbf{R}_a)$  where $\rho_a$ is the ground state spherically averaged atomic electron density
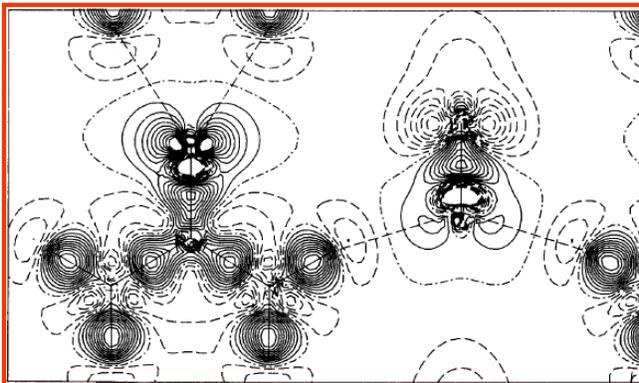
Total electron density
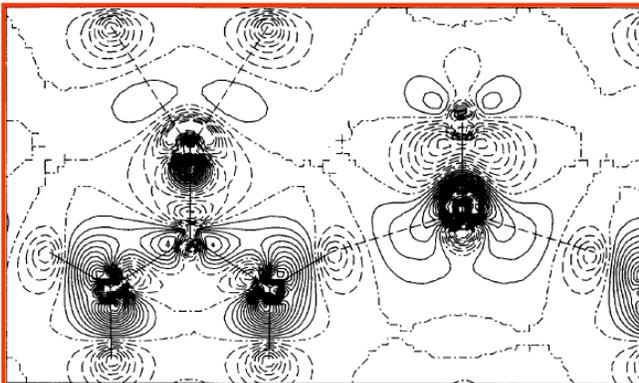
$\rho$, urea crystal
0.01 au contour intervals
Dovesi et al., JCP 92, 7402 (1990)



Deformation electron density
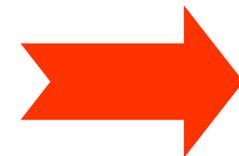
$\Delta\rho$ (bulk minus atoms)
**0.01** au cont. int.



Interaction electron density

$\Delta\rho$ (bulk minus molecular superposition) **0.002** au cont. int.

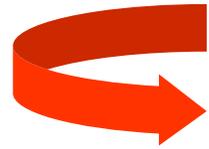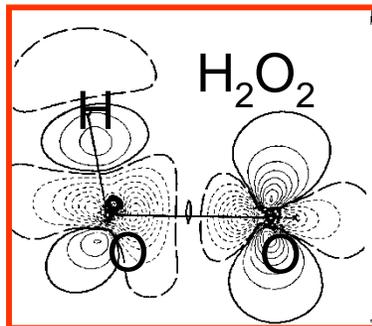Useful! Yet DD may have serious drawbacks......

■ $\rho_{ref}(\mathbf{r} ; \mathbf{X})$ is a non physical quantity: the antisymmetry requirement is only fulfilled separately by each $\rho_a$

■ $\rho_{ref}(\mathbf{r} ; \mathbf{X})$ is not unique

In the case of an atom with spatially degenerate or nearly degenerate GS (e.g. atoms with an open valence shell, like B, C, O or F) many alternative $\rho_a$ may be chosen.

$\Delta\rho$
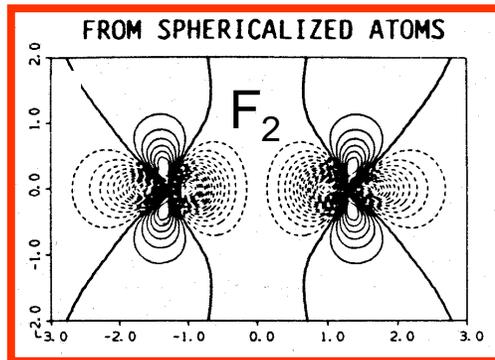
Orientational freedom exists for degenerate atomic GSs


FROM SPHERICALIZED ATOMS
$F_2$

The spherically averaged density might not be the best reference choice to give insight on the way an atom it is bonded to other atoms


$H_2O_2$

Some covalent bonds do not show the expected accumulation of the electron density along the internuclear axis

## $\Delta\rho$ in $F_2$

F———F $\longrightarrow$ z

$2p_\sigma$ : 5/3 e$^-$ for each F

10/3 e$^-$ in the promolecule

$2p_\sigma$ M.O. 2e$^-$ in the molecule

2 - 10/3 e$^-$ = -4/3 e$^-$



FROM SPHERICALIZED ATOMS
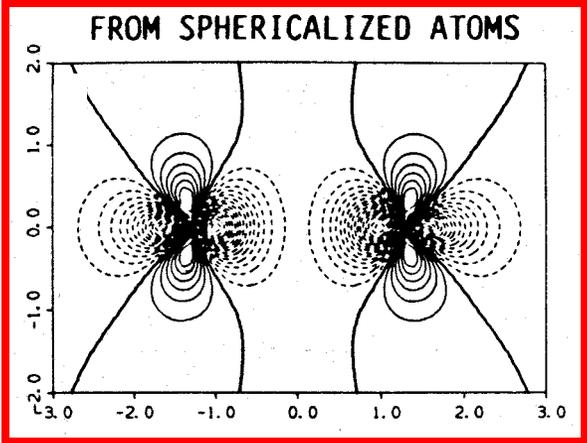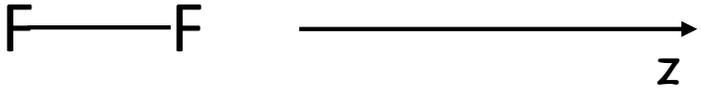
............ Depletion; interval 0.04 au
———— Accumulation

In the $p_\sigma$ region there are globally 4/3 e$^-$ less than for the promolecule $\longrightarrow$ depletion in the internuclear region (typical behaviour for atoms with more than half-filled valence shells



FROM ORIENTED ATOMS

$(2s)^2 (2p\pi_{x,y})^4 (2p_{z})^1$    F : $^2P_z$
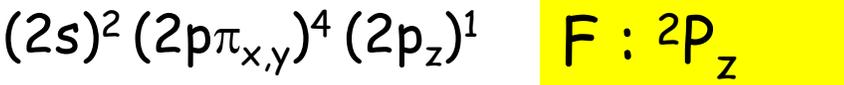
2 - 2 e$^-$ = 0 e$^-$ $\longrightarrow$ accumulation and depletion along z ($\Delta\rho_b$=0.05 au; $\Delta\rho_{lone\ pair\ maximum}$ =0.07 au)

Δρ and total ρ in strained hydrocarbons

Δρ

C-C,  1.87 Å

C-C,  1.54 Å
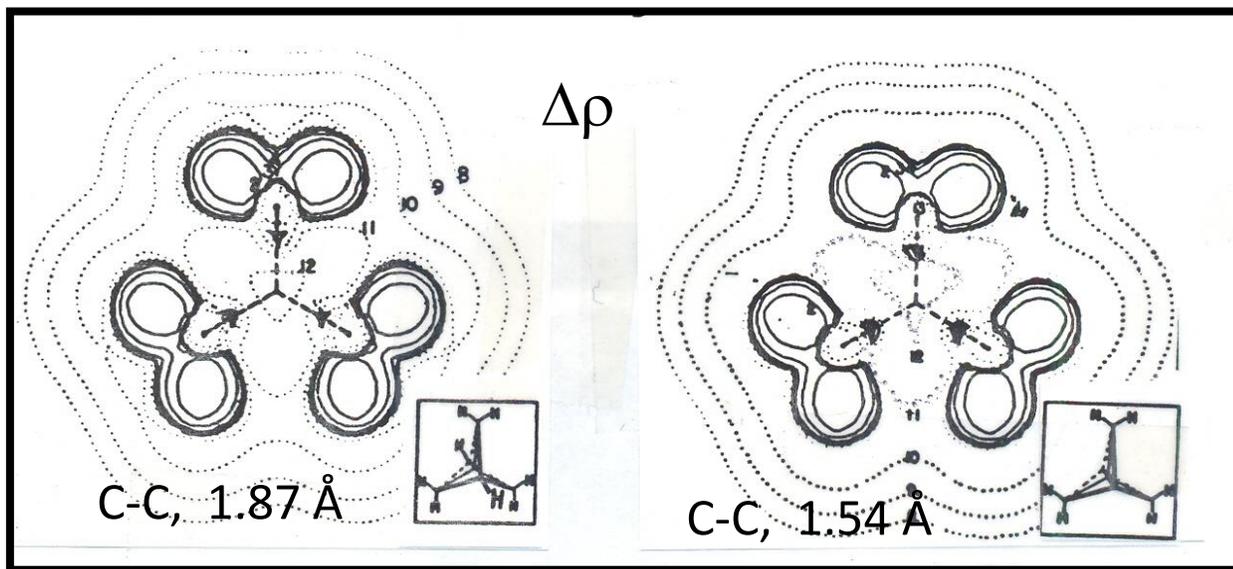
Bicyclo [1.1.1] pentane          1.1.1 propellane

Jackson J, Allen, LC
JACS, 106, 591 (1984)
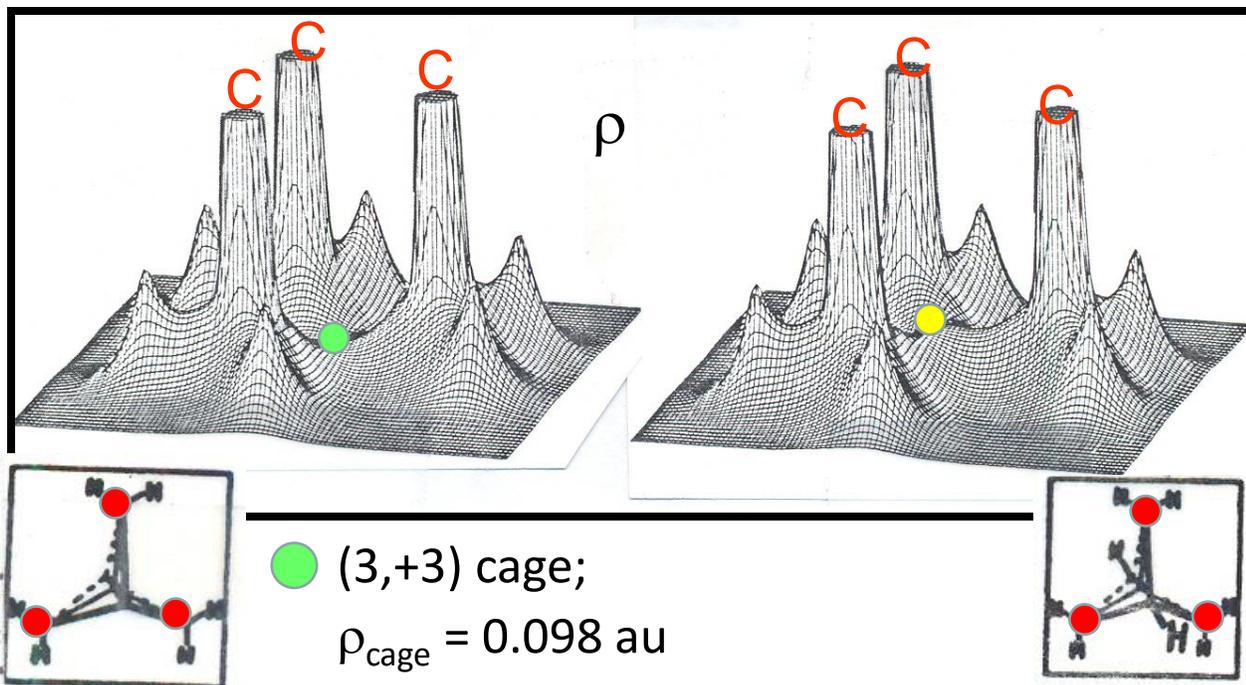
Wiberg KB, Bader RWF et al., JACS,109, 985 (1987)

ρ

C   C   C                    C   C   C

🟡 (3,-1) saddle;

$\rho_b$= 0.203 au $\cong$4/5 of a normal CC bond (in this plane is a local maximum)

🟢 (3,+3) cage;

$\rho_{cage}$ = 0.098 au

# The theory of gradient dynamical systems and scalar field topology

R. H. Abraham, C. D. Shaw *Dynamics: The Geometry of Behavior*; Addison Wesley: Redwood City, CA, 1992; (b) R. H. Abraham, J. E. Marsden, *Foundations of Mechanics,* Addison Wesley: Redwood City, CA, 1994.

- ❑ $y$  differentiable vector field

    Let's introduce a fictitious time coordinate $t$ and the system of equations

    $d\boldsymbol{r}/dt = \boldsymbol{y}$  (this trick transforms the field into a *gradient dynamical system*)

- ❑ Solution of this system of equations defines the **trajectories or field lines** of $\boldsymbol{r}(t)$ and the **theory of dynamical systems** allows us to fully classify their properties

- ❑ Let's turn to $R^3$ and take a scalar function $f$ (carrying the physical or chemical information, for instance it may be the ED, the ELF, etc) and define an associated vector field through its gradient $\nabla f$

    $d\boldsymbol{r}/dt = \nabla f$

    an explicit form for the field (or flux) lines of the gradient field is given by:

    $$\boldsymbol{r}(t) = \boldsymbol{r}(t_0) + \int_{t_0}^{t} \nabla f(\boldsymbol{r}(s))ds$$

    which is simply interpreted as a temporal movement guided by the gradient field $\nabla f$ at the position reached at the (fictitious) time t

$$\boldsymbol{r}(t) = \boldsymbol{r}(t_0) + \int_{t_0}^{t} \nabla f(\boldsymbol{r}(s)) ds$$

❑ Except that at special points (Critical Points, CPs)

a) Only one gradient line passes through each point $\boldsymbol{r}$

b) $\nabla f$ is tangent to the trajectory at every point

c) the trajectories are orthogonal to isoscalar surfaces of the field at any point

❑ every line must begin and end where $\nabla f(\mathbf{r}) = 0$. All other points are *wandering* points

❑ The points $\boldsymbol{r_c}$ where $\nabla f(\boldsymbol{r_c}) = 0$ are the so called Critical Points (CPs) of the field $f$. Their number and properties characterize its global structure (**or topology**)

❑ CPs are classified in terms of rank and signature

Hessian matrix $H(\boldsymbol{r_c}) = \begin{bmatrix} \dfrac{\partial f(\boldsymbol{r_c})}{\partial x^2} & \cdots & \dfrac{\partial f(\boldsymbol{r_c})}{\partial x \partial z} \\ \vdots & \ddots & \vdots \\ \dfrac{\partial f(\boldsymbol{r_c})}{\partial z \partial x} & \cdots & \dfrac{\partial f(\boldsymbol{r_c})}{\partial z^2} \end{bmatrix}$ $H$ Diagonalization $\longrightarrow$ Eigenvalues $\lambda_i$ Eigenvectors $v_i$ (i=1,3)

CP(**RANK**, SIGNATURE)

**RANK:** number of non zero $\lambda_i$     SIGNATURE: difference between the number of positive and negative curvatures $\lambda_i$

NON DEGENERATE CPs : (**3**, −3), (**3**, −1), (**3**, +1) and (**3**, +3)

□ Behaviour of the trajectories of the field along each eigendirection $v_i$ depends on the sign of its associated $\lambda_i$ value. Either they start or end at the CP when sgn $\lambda_i$ is positive or negative, respectively

□ Ordering $\lambda_i$ such that $\lambda_1 \leq \lambda_2 \leq \lambda_3$ :

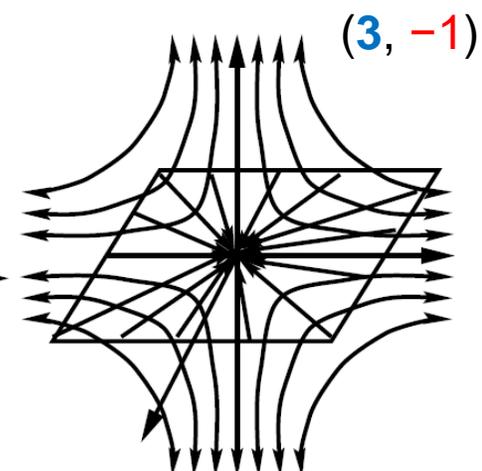a) all $\lambda_i < 0$, (**3**,-**3**) *sink or attractor*: all trajectories converge toward the CP

b) $\lambda_1$ and $\lambda_2 < 0$, $\lambda_3 > 0$, (**3**,-1) *saddle point of the first kind*; in the plane defined by $v_1$ and $v_2$ the gradient lines approach the CP, in the orthogonal direction $v_3$ direction escape from it

c) $\lambda_1 < 0$, $\lambda_2$ and $\lambda_3 > 0$, (**3**,+1) *saddle point of the second kind;* in the plane defined by $v_2$ and $v_3$ the gradient lines escape from the CP, while approach the CP in the orthogonal direction $v_1$

d) all $\lambda_i > 0$, (**3**,+**3**) *source or repellor*: every field line escapes the CP in all directions



(**3**, −**3**)  (**3**, −1)
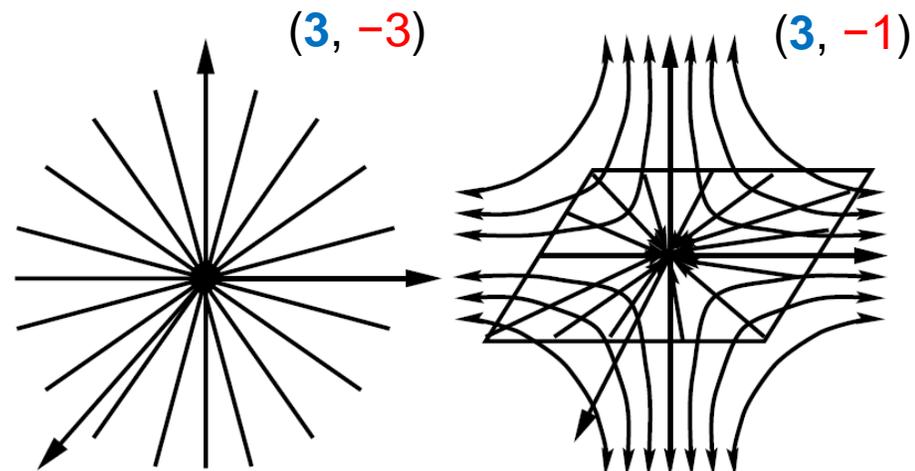
(a) Sink critical point    (b) Saddle of the first kind.

(**3**,+1)   (**3**,+**3**)
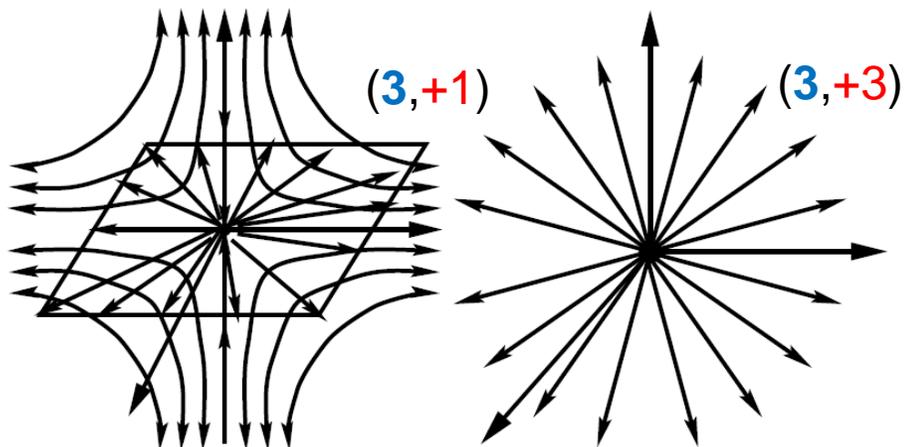
(c) Saddle of the second kind.    (d) Source.
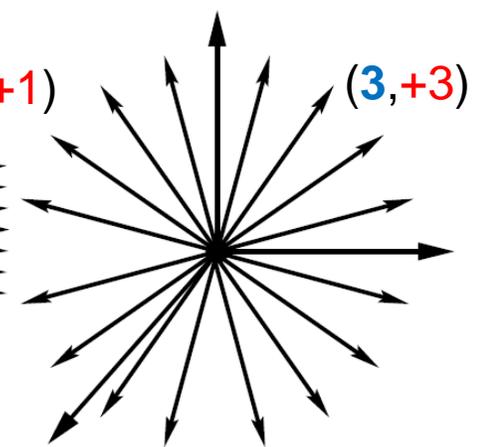
**Figure 3.1:** The four types of CPs of a 3D scalar field.

Ángel Martín Pendás and Carlo Gatti, Chapter 3: Quantum theory of atoms in molecules and the AIMAll software in Complementary Bonding Analysis, S. Grabowsky Ed., De Gruyter 2021

❑ Either the attraction basins of the (3,-3) CPs or the repulsion basins of the (3,+3) CPs are 3D regions. So, e.g., the union of all the (3,-3) attraction basins of the field is the full $R^3$ space, except a null measure set formed by the 2D surfaces or 1D lines which correspond to the attraction basins of the other CPs.

❑ The attraction (or repulsion) basins of a field induce a topology in $R^3$ , i.e. an exhaustive partition into disjoint regions

$$R^3 \equiv U_A \Omega_A \quad , A \text{ runs over all the attraction (repulsion) basins}$$

❑ Surfaces that separate the basins are called separatrices. At all their points $\nabla f$ is parallel to the surface, so :

$$\text{Separatrices are local zero-flux surfaces of } \nabla f: \quad \nabla f(r_s) \cdot n_s = 0$$

❑ The theory of gradient dynamical systems leads to a space partitioning analogous to the well-known partition made in hydrology in river basins delimited by watersheds.

❑ In our case the space is that of an *in vacuo* system or of the unit cell of a periodic system.

❑ Number and type of CPs of a given scalar field is limited through topological invariants, which depend only on the intrinsic properties of the space in which the field is defined

❑ In $R^3$ , the space where we embed finite molecules, the Euler-Poincaré or Morse invariant (Morse M. Trans Am Math Soc. 1931;33:72–91) reads:

$$n(3,-3) - m(3,-1) + i(3,+1) - k(3,+3) = 1$$

(n, m, i, k, being the number of CPs with signatures -3, -1,+1 and +3)

❑ For 3D periodic systems (e.g. crystal), the space in which the unit cell is embedded is not $R^3$, but a 3D torus, $S^3$, since each spatial direction is equivalent to a closed line or circumference. The invariant (Morse relations) reads:

$$n(3,-3) - m(3,-1) + i(3,+1) - k(3,+3) = 0$$

❑ Those Wyckoff positions of the space group that have three fixed coordinates must contain a critical point of the crystal structure ( For more details see: C. K. Johnson, M.M. Burnett and W. D. Dunbar, "Crystallographic Topology and Its Applications https://digital.library.unt.edu/ark:/67531/metadc675925/ and A. Martín Pendás, A. Costales, V. Luaña, PRB 55, 4275 (1997))

❑ In a periodic 3D crystal, $k \geq 1$, $i \geq 3$, $m \geq 3$ $n \geq 1$, so at least 8 CPs

# Quantum Theory of Atoms in Molecules (QTAIM) and crystals (QTAIMC)

❑ Uses as scalar $f$ the total $\rho$ as an information source from which to (re)formulate chemical concepts

❑ Provides a bridge between chemistry and QM and shows that all chemistry is already hidden in $\rho$ (no need to invoke any arbitrary reference density)

❑ QTAIM goes far beyond a simple topological study of $\rho$.

It provides a full consistent QM framework for the definition of the atoms or groups of atoms in a molecule or crystal and for the treatment of the mechanics of their interaction
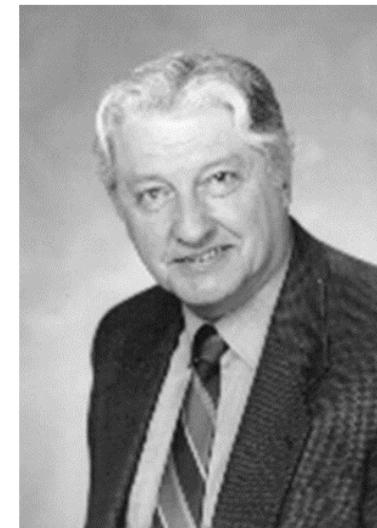


Richard Bader

**Topological study of $\rho(r;X)$**

$$\nabla\rho = \mathbf{i}\frac{d\rho}{dx} + \mathbf{j}\frac{d\rho}{dy} + \mathbf{k}\frac{d\rho}{dz}$$

🔵 $\nabla\rho(\mathbf{r}_c) = 0$      $\mathbf{r}_c$ = Critical Point, CP

**1) find CPs**

**H**   $H_{12} = \partial^2\rho/(\partial x \partial y)$      $H \equiv \nabla\nabla\rho =$

$$\begin{pmatrix} \frac{\partial^2\rho}{\partial x^2} & \frac{\partial^2\rho}{\partial x\partial y} & \frac{\partial^2\rho}{\partial x\partial z} \\ \frac{\partial^2\rho}{\partial y\partial x} & \frac{\partial^2\rho}{\partial y^2} & \frac{\partial^2\rho}{\partial y\partial z} \\ \frac{\partial^2\rho}{\partial z\partial x} & \frac{\partial^2\rho}{\partial z\partial y} & \frac{\partial^2\rho}{\partial z^2} \end{pmatrix}$$

**Hessian matrix**

🔵 Diagonalize H at $\mathbf{r}_c$

Allows to find a rotation of the coordinate axes to a new set such that all of the off-diagonal elements vanish ⟶ eigenvectors and eigenvalues:

principal axes of curvatures and curvatures

$$\begin{pmatrix} \frac{\partial^2\rho}{\partial x'^2} & 0 & 0 \\ 0 & \frac{\partial^2\rho}{\partial y'^2} & 0 \\ 0 & 0 & \frac{\partial^2\rho}{\partial z'^2} \end{pmatrix}_{\mathbf{r}'=\mathbf{r}_c} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}$$

$(\nabla\nabla\rho)\boldsymbol{v}_i = \lambda_i\boldsymbol{v}_i$ ; i=1,2,3

🔵 Get its eigenvalues $\lambda_i$ (curvatures)

🔶 Get **H** matrix eigenvalues $\lambda_i$ (curvatures)

$$\lambda_3 \geq \lambda_2 \geq \lambda_1$$

🔶 Non degenerate CPs (rank 3) ⟶

(3,-3) ⟶ NUCLEI (and in special cases NNA)

(3,-1) ⟶ BONDED ATOMS ( ∈"chemical bonds")

(3,+1) ⟶ RING

(3,+3) ⟶ CAGES

| Name | Acronym | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | (rank,signature) |
|---|---|---|---|---|---|
| Nuclear attractor | NA | - | - | - | (3, -3) |
| Bond Critical Point | BCP | - | - | + | (3, -1) |
| Ring Critical Point | RCP | - | + | + | (3, +1) |
| Cage Critical Point | CCP | + | + | + | (3, +3) |
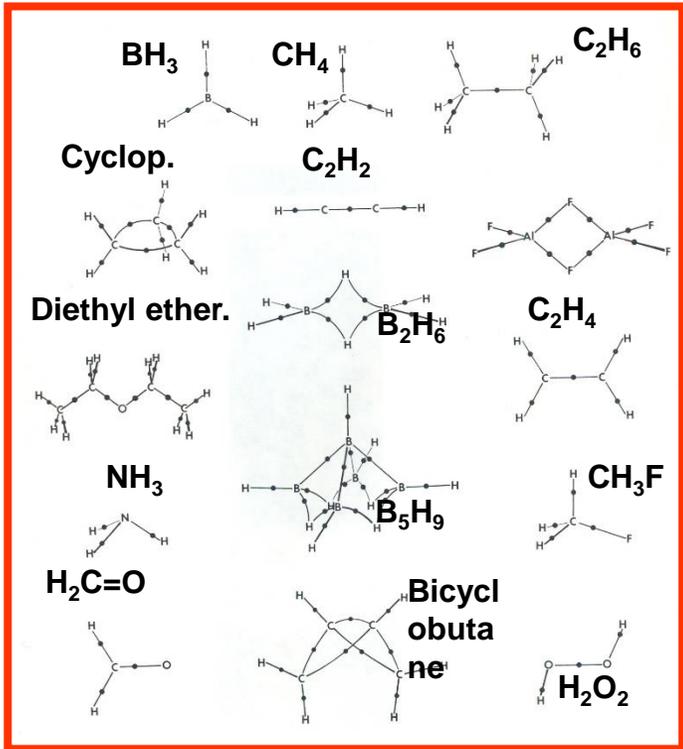
"Molecular graphs"
Molecular structure

Bond paths

- Bcp, $\nabla\rho = 0$
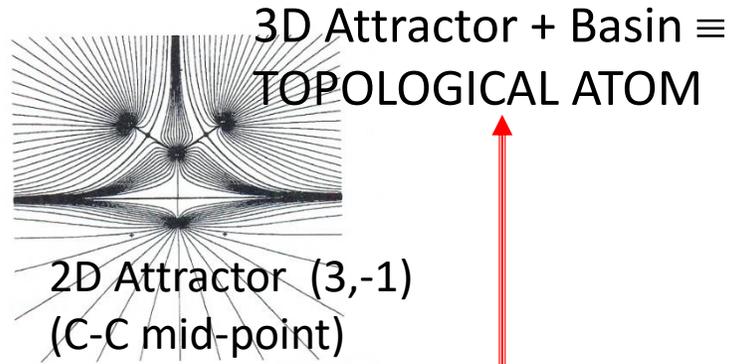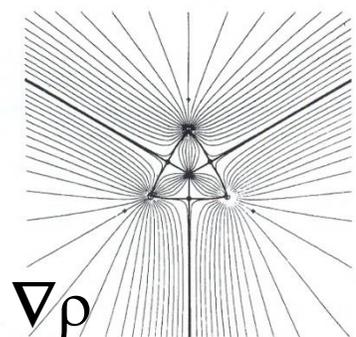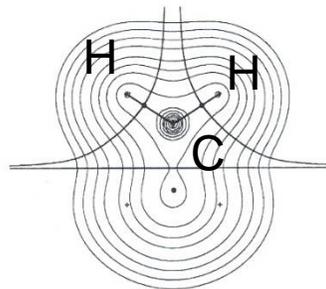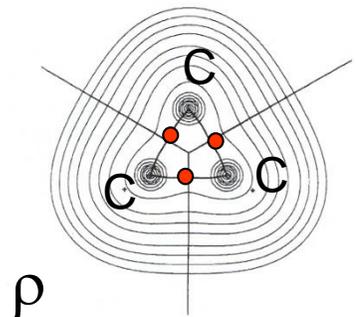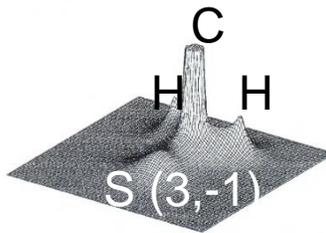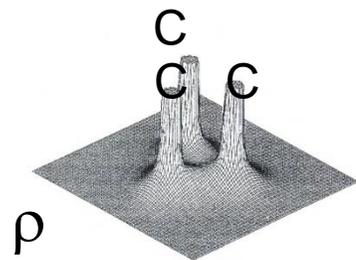
$\nabla\rho(\mathbf{r}_c) = 0$   $\mathbf{r}_c$ = Critical Point   1) Find

**H**   $H_{12} = \partial^2\rho/(\partial x \partial y)$   2) Classify

H eigenvalues $\lambda_i$ and eigenvectors   $\lambda_3 \geq \lambda_2 \geq \lambda_1$   Non degenerate CPs (rank 3)

(**3**, -3) - - - - - → NUCLEI

(**3**, -1) - - - - - → BONDED ATOMS ("chemical bonds")

(**3**, +1) - - - - → RING

(**3**, +3) - - - - - → CAGES

S (3,-1)

3D Attractor + Basin ≡ TOPOLOGICAL ATOM

2D Attractor (3,-1) (C-C mid-point)

"QUANTUM" ATOM

Classify by (**RANK**, SIGN) the CP of $\rho$ in R$^3$

# The ∇ρ vector field and the definition of the molecular structure

- dr(s)/ds = ∇ρ[r(s); X]  for a given r(0) ≡ r$_0$

- r(s) = r$_0$ + ∫ ∇ρ[ r(t); X]dt  Gradient Paths

3D, (3,-3) ● ∇ρ attractors

3D, (3,-3) ●

    +         ∇ρ attractors

2D (3,-1) ●

ρ contours + ∇ρ lines of 2D attractors :
molecular graph (BPs)  and intersections
of IAS



IAS inters.

C-C Bond Path

Basin + 3D attractor ≡ topological atom

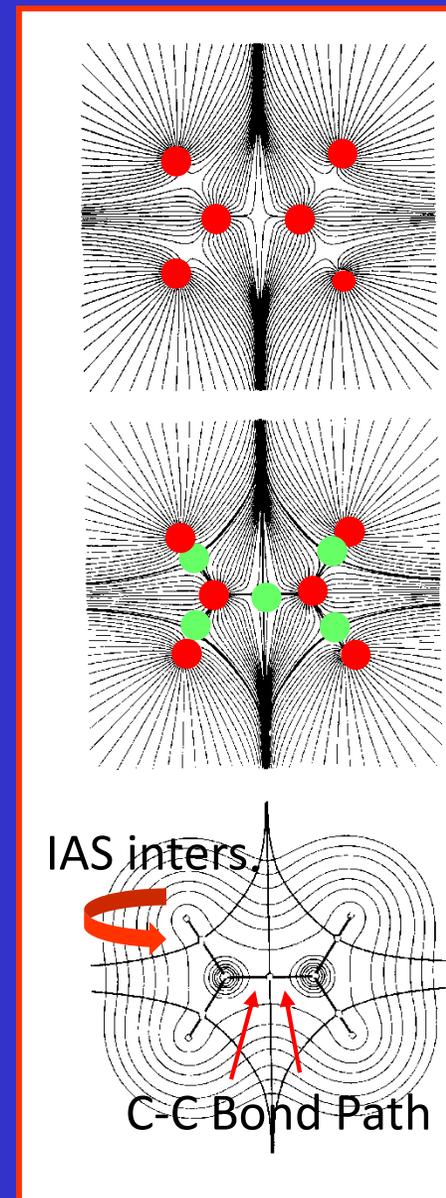$$\langle \hat{O} \rangle_{molecule} = \sum_i^{\substack{all\ atoms \\ in\ the \\ molecule}} \left( N \int_{\Omega_i} \left\{ \int \frac{1}{2} [\Psi^* \hat{O} \Psi + (\hat{O}\Psi)^* \Psi] d\tau' \right\} d\mathbf{r} \right)$$

$$= \sum_i^{\substack{all\ atoms \\ in\ the \\ molecule}} \left( \int_{\Omega_i} \rho_O d\mathbf{r} \right) = \sum_i^{\substack{all\ atoms \\ in\ the \\ molecule}} O(\Omega_i)$$

$\int d\tau'$ integration over the coordinates of all electrons but one and summation over all spins

Any molecular property O which can be expressed in terms of a corresponding property density in space $\rho_O(\mathbf{r})$ can be written as a sum of atomic contributions

### Atomic kinetic energy

Many alternative formulas for the kinetic energy density

$K(\mathbf{r}) = N\ k \int d\tau' [[\psi^* \nabla^2 \psi + (\nabla^2 \psi)^* \psi]$

$k = -h^2/(16\pi^2 m_e)$

In terms of the Laplacian operator

$G(\mathbf{r}) = N\ \frac{1}{2}\ k \int d\tau'\ \nabla\psi^* \bullet \nabla\psi$

$K(\mathbf{r}) - G(\mathbf{r}) = k\ \nabla^2\rho(\mathbf{r})$

In terms of the dot product of the moment operator

$\int_\Omega [K(\mathbf{r}) - G(\mathbf{r})]\ d\tau = K(\Omega) - G(\Omega) = k \int_\Omega \nabla^2\rho(\mathbf{r})\ d\tau = k \int_\Omega \nabla\cdot\nabla\rho(\mathbf{r})\ d\tau = \oint_{S(\Omega)} \nabla\rho\cdot\mathbf{n}(\mathbf{r_s})ds \equiv 0$

The local zero flux condition enables to define a kinetic energy for the atom $\equiv$ -E $(\Omega)$

Divergence theorem

virial fragment, as is for the whole system

**TOPOLOGICAL ATOM $\equiv$ "QUANTUM" ATOM**

## Atomic electron population and net charge

$$N(\Omega) = \int_\Omega \rho(\mathbf{r})\, d\tau$$

$$q(\Omega) = Z_\Omega - N(\Omega)$$

## Atomic moments

$$M_j(\Omega) = -\int_\Omega d\tau\, \rho(\mathbf{r})\, r_{j\Omega}\, ;\ j = 1\text{-}3$$

Atomic dipole

$$Q_{ij}(\Omega) = -\int_\Omega d\tau\, \rho(\mathbf{r})\, (3r_i r_j - r^2_\Omega\, \delta_{ij})\, ;\ i,j = 1\text{-}3$$



RFW Bader, Atoms in Molecules, Oxford Press 1990
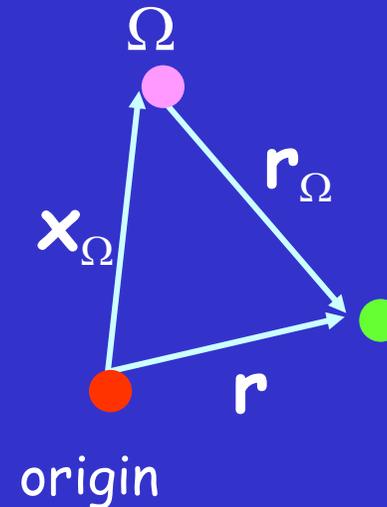
Atomic quadrupole moment tensor (traceless)

Real symmetric matrix which can be diagonalized

## Atomic volumes

$$V(\Omega) = \int_\Omega d\tau$$

$$\sum_{\Omega \text{ of all cell}} V(\Omega) = V_{cell}$$

Generally infinite in the molecular case; always finite in the crystalline case

Normally the atomic volume is however defined as the region of space enclosed by the intersection of the atomic zero-flux surface and a particular envelope of $\rho$

$$V_{0.001}(\Omega) \equiv V1 = \int_{\Omega*} d\tau ; \qquad \Omega^*: \ \forall \mathbf{r} \in \Omega \text{ where } \rho \geq 0.001 \text{ au}$$

$V_{0.001}$ yields molecular sizes in agreement with those determined from the analysis of the kinetic theory data for gas-phase molecules (van der Waals volumes)

$$V_{0.002}(\Omega) \equiv V2 = \int_{\Omega**} d\tau ; \qquad \Omega^{**}: \forall \mathbf{r} \in \Omega \text{ where } \rho \geq 0.002 \text{ au}$$

$V_{0.002}$ yields molecular sizes compatible with the closer packing found in the solid state

# $\nabla^2\rho$ and the local contributions to the energy

$$\frac{1}{4}\nabla^2\rho(\mathbf{r}) = 2G(\mathbf{r}) + V(\mathbf{r})$$

Local expression of quantum virial theorem

- $V(\mathbf{r})$ electronic potential energy density, $\leq 0$ always

  $$\int_\Omega V(\mathbf{r}) = V(\Omega) = 2E_e(\Omega)$$

- $G(\mathbf{r})$ positive definite kinetic energy density , $\geq 0$ always

  $$\int_\Omega G(\mathbf{r}) = T(\Omega) = -E_e(\Omega);$$

- $2T(\Omega) + V(\Omega) = -2E(\Omega) + 2 E_e(\Omega) = 0$ ; virial theorem

- Regions where $\nabla^2\rho$ <0, $V(\mathbf{r})$ dominates over $G(\mathbf{r})$

- Regions where $\nabla^2\rho$ >0 , $G(\mathbf{r})$ dominates over $V(\mathbf{r})$

$$G(r) = \tfrac{1}{2}(\nabla \bullet \nabla')\Gamma(1)(r,r')\big|_{r=r'} \approx$$

$$G(r) \approx (3/10)(3\pi^2)^{2/3}\rho(r)^{5/3} + (1/72)[\nabla\rho(r)]^2/\rho(r) + (1/6)\nabla^2\rho(r)$$

Yu A. Abramov, Acta Cryst. **A53** 264 (1997)

$\equiv 0$ at bcp

Assuming that the multipole derived electron distributions obey the local virial theorem (though they don't), one gets also V(**r**)

$$\tfrac{1}{4}\nabla^2\rho(r) = 2\,G(r) + V(r)$$

Relatively accurate description in the medium-range behaviour (1–4 a.u. from the atomic nucleus) of G(r)

Agreement with "exact" G(r) values nearly quantitative for closed-shell interactions (bcps at large distances from nuclei)

Agreement only qualitative and often rather poor ( Δ > 300%) for typical shared interactions

## Local expression of quantum virial theorem

$$\tfrac{1}{4}\,\nabla^2\rho\,(\mathbf{r}) = 2\,G(\mathbf{r}) + V(\mathbf{r})$$

$$\nabla^2\rho_b$$

$G(\mathbf{r}) > 0$

$V(\mathbf{r}) < 0$

Chemical Interactions

shared

Closed-shell

$\nabla^2\rho_b < 0$
$V(\mathbf{r}_b)$ in local excess
respect to the average
$2G(\Omega) = -V(\Omega)$

$\nabla^2\rho_b > 0$
$G(\mathbf{r}_b)$ in local excess
respect to the average
$2G(\Omega) = -V(\Omega)$

# The dicothomous classification based on the sign of $\nabla^2\rho$

| Property | Shared shell, $\nabla^2\rho_b < 0$ Covalent and polar bonds | Closed-shell, $\nabla^2\rho_b > 0$ Ionic, H- bonds and vdW molecules |
|---|---|---|
| $\lambda_I$ | $\lambda_{1,2}$ dominant ; $\|\lambda_{1,2}\|/\|\lambda_3 > 1$ | $\lambda_3$ dominant; $\|\lambda_{1,2}\|/\|\lambda_3 \ll 1$ |
| VSCC | The VSCCs of the two atoms form one continuous region of CC | $\nabla^2\rho > 0$ over the entire interaction region. The spatial display of $\nabla^2\rho$ is mostly atomic-like |
| $\rho_b$ | Large | Small |
| Energy Lowering | By accumulating $\rho$ in the interatomic region | Regions of dominant $V(r)$ are separately localized within the boundaries of interacting atoms |
| Energy components | $2G_b < \|V_b\|$; $G_b/\rho_b < 1$; $G_{b\|\|} \ll G_{b\perp}$; $H_b < 0$ | $2G_b > \|V_b\|$ ; $G_b/\rho_b > 1$, $G_{b\|\|} \gg G_{b\perp}$; $H_b$ any value |

Electron sharing is decreasing (ond polarity increasing) → ⟶

Electron sharing (covalency) is increasing (and polarity decreasing) ←

The classification based on the adimensional $|V_b|/G_b$ ratio
Espinosa, E. et al. , J. Chem. Phys. 117 (2002) 5529

| Shared shell (SS) $|V_b|/G_b > 2$ | Transit region, incipient covalent bond formation $1 < |V_b|/G_b < 2$ | Closed-shell (CS) $|V_b|/G_b < 1$ |
|---|---|---|
| $H_b < 0; \ \nabla^2 \rho_b < 0$ | $\mathbf{H_b < 0; \ \nabla^2 \rho_b > 0}$ | $H_b > 0; \ \nabla^2 \rho_b > 0$ |
| Bond degree (BD) = $H_b/\rho_b \equiv$ Covalence degree (CD)<br><br>BD large and negative<br><br>The larger is \|BD\| the more covalent is the bond | BD $\equiv$ CD<br><br>BD negative and smaller in magnitude than for SS interactions<br><br>BD Approaching zero at the boundary with CS region | BD $\equiv H_b/\rho_b \equiv$ Softness degree (SD)<br><br>SD positive and large<br><br>The larger is SD the weaker and closed-shell in nature is the bond |
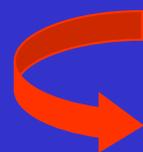
Identified with the region of incipient covalent bond formation using a NBO analysis

Formulated for X-H....F-Y systems. 79 cases with $d_{H...F}$ ranging from 0.8 to 2.5 Å.
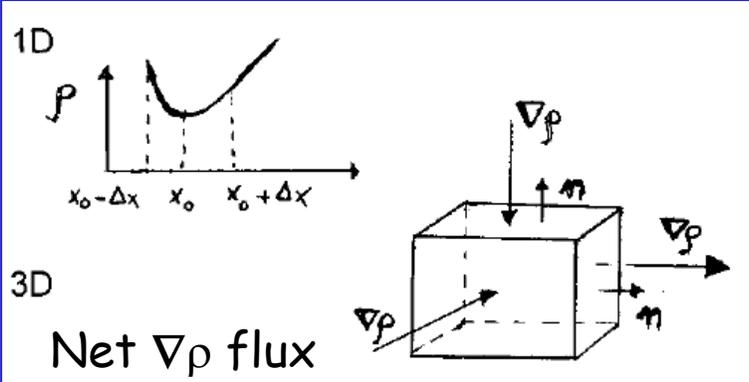
# The Laplacian of the electron density, $\nabla^2\rho$

$$\nabla\cdot\nabla\rho=\nabla^2\rho= \Sigma_i\lambda_i = \Sigma(\partial^2\rho/\partial x^2_{ii}), \; i=1\text{-}3$$
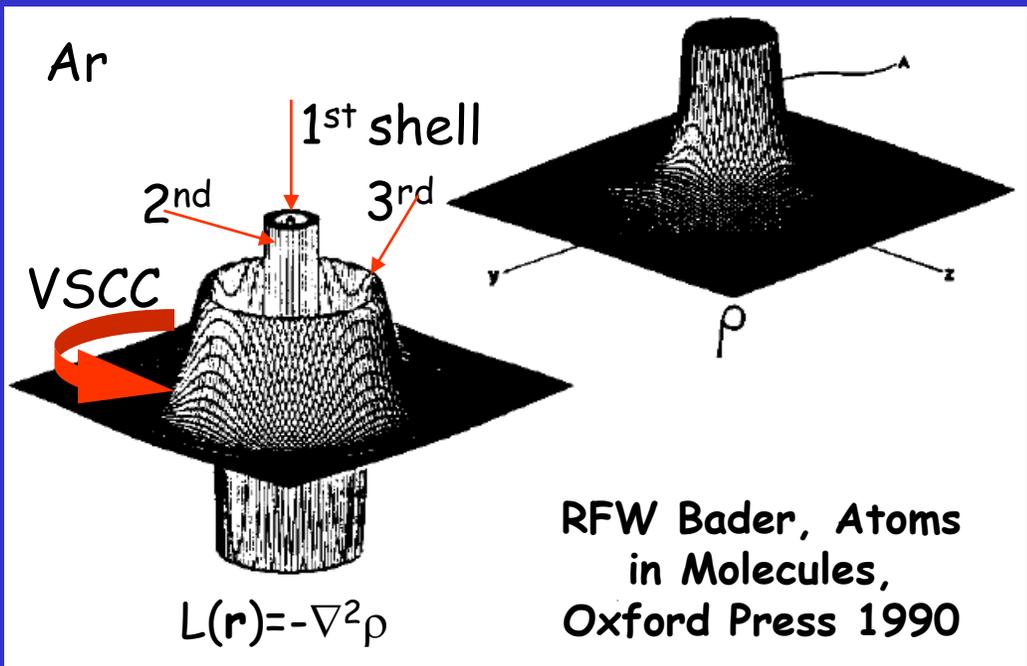
a positive (negative) second derivative at $x$ indicates that the ED is on average lower (higher) in $x$ than it is in a symmetrical neighborhood of $x$.

The ED is depleted (concentrated) at $x$.



Ar

1st shell

2nd    3rd

VSCC

$L(\mathbf{r})=-\nabla^2\rho$

$\rho$

**RFW Bader, Atoms in Molecules, Oxford Press 1990**

1D

3D

Net $\nabla\rho$ flux

CC regions : a net $\nabla\rho$ flux enters the region
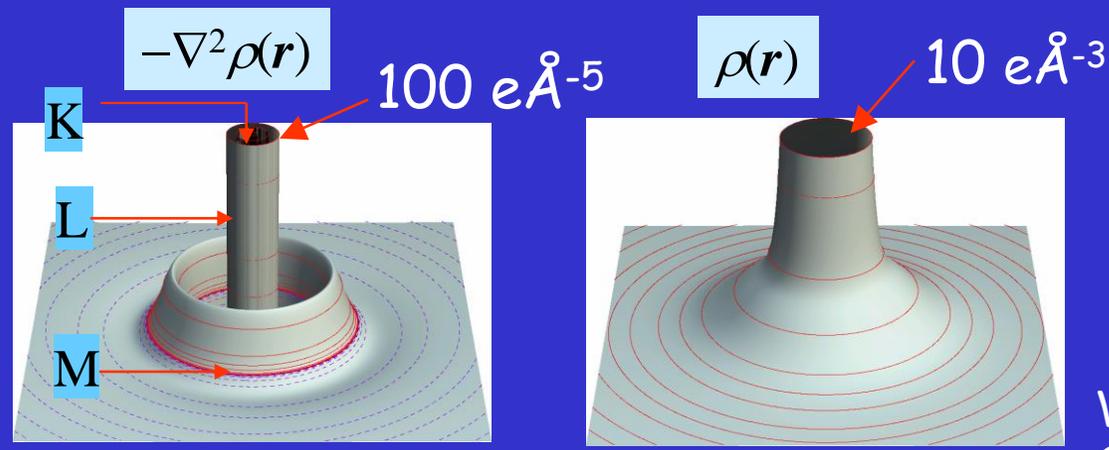
CD regions : a net $\nabla\rho$ flux leaves  the region

■ $\nabla^2\rho>0$   electron density is depleted at $\mathbf{r}$

■ $\nabla^2\rho<0$  electron density is concentrated at $\mathbf{r}$

Through the Divergence theorem

$$\int_V\nabla^2\rho(\mathbf{r})\, d\tau = \int_V\nabla\bullet\nabla\rho(\mathbf{r})\, d\tau$$

$$= \oint_{S(\Omega)}^{u} \nabla\rho\bullet\mathbf{n}(\mathbf{r}_s)dS$$

# The Laplacian as a Magnification Glass for the Shell Structure of Atoms

$\rho(r)$

argon atom

10

0

0          (1.59 Å)

$-\nabla^2\rho(r)$

100

0

K · L       M

-100

0                (1.59 Å)
~ 3 au

Quantum shell   M

$-\nabla^2\rho(r)$         100 eÅ⁻⁵

K
L
M

$\rho(r)$        10 eÅ⁻³
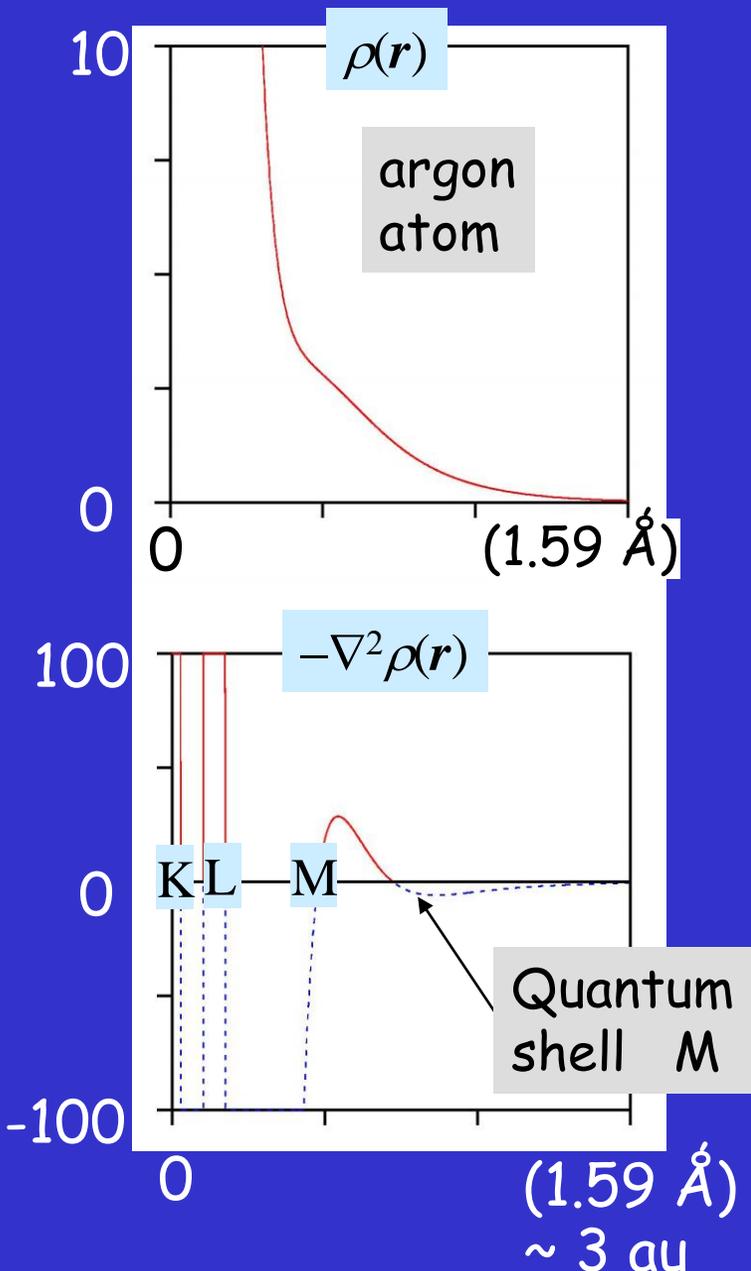
relief maps
contour maps

$-\nabla^2 r(r) > 0$
region of charge concentration (CC)

Wolfgang Scherer, private communication
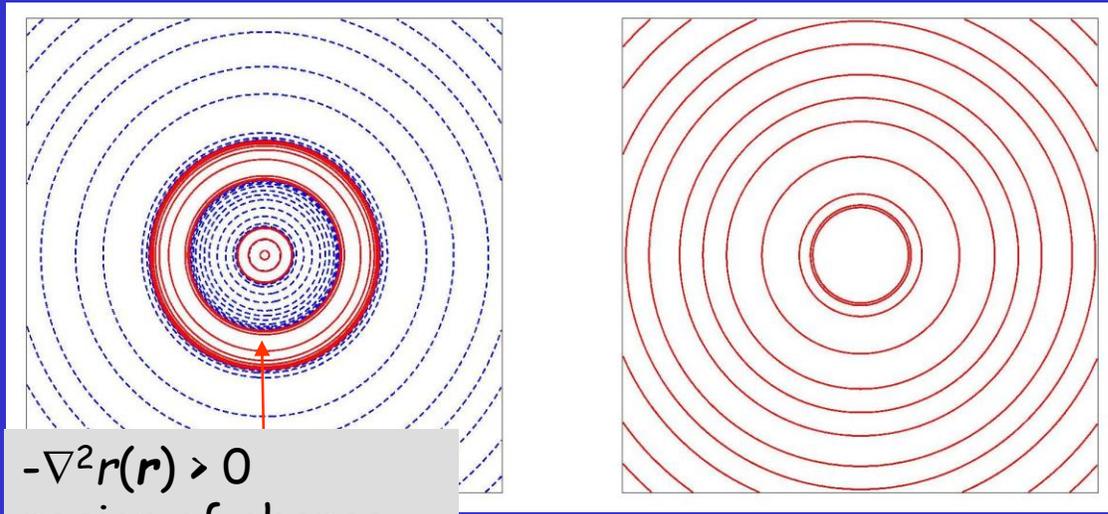
Level of approximation:
B3LYP/6-311++G(2d,2p)

The 1:1 correspondence of the $\nabla^2\rho$ distribution with the shell structure of isolated atoms is lost for all the d-block elements

Sagar et al., J. Chem. Phys. 88, 4367 (1988); Shi et al. J. Chem. Phys. 88, 4375 (1988)
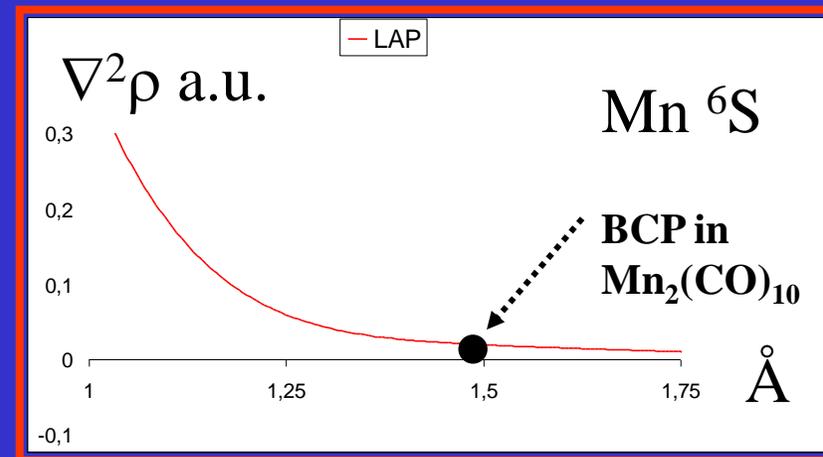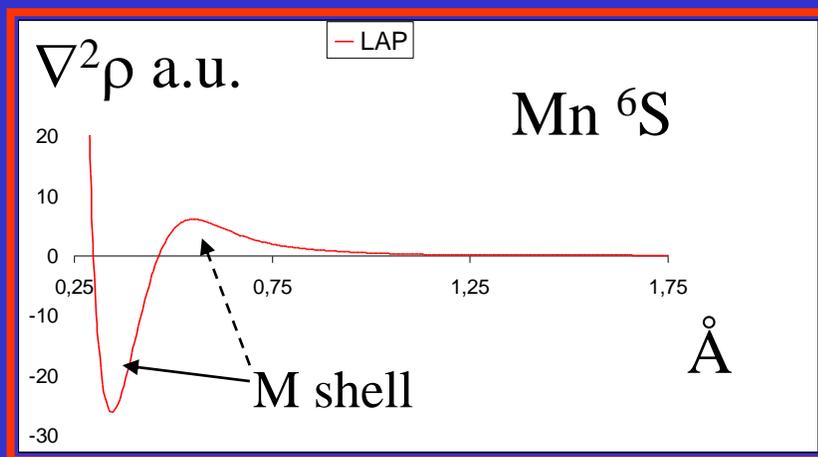


Shell M (3s,3p,3d) : $0.298 \text{ Å} \leq r \leq 0.463 \text{ Å}$ VSCC

$0.463 \text{ Å} \leq r$ to $\infty$ VSCD

From Sc to Ge, the N shell becomes indistinguishable from the M shell and the corresponding regions of CC and CD are missing
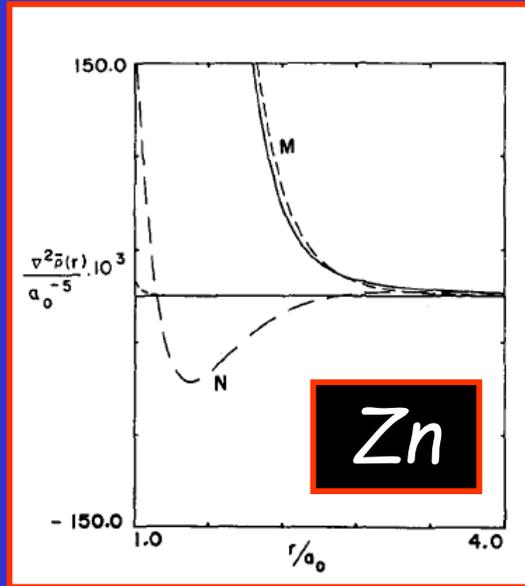
From Sc to Ge, the N shell becomes indistinguishable from the M shell

Zn: M-shell and N-shell contributions

M-shell CD overweights N-shell CC

M and N shells separate again from As up to Kr, but the sign of the Laplacian at the outermost minimum is found to be positive, rather than negative as for the other minima.
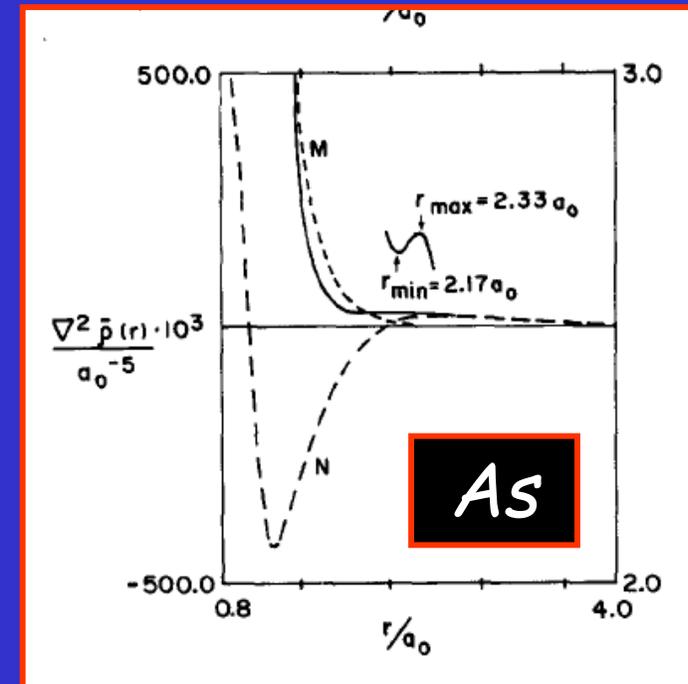


Similar trends were observed for the successive rows, with five being the number of maximum distinguishable shells

Warning for bonding classification schemes in terms of the sign of the $\nabla^2\rho$

VSCC maxima of $-\nabla^2\rho$ (au)

Te
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^4$

Shell-L   Shell-M   Shell-N

Shell-N and -O are not resolved, only 3 rather than 4 maxima for shells with n=2-5

TABLE I. Radii of minima in the Laplacian of the charge density of the spherical atoms Li–Xe.[a]

| Atom | | $r_2$ | $r_3$ | | Atom | | $r_2$ | $r_3$ | $r_4$ | | Atom | | $r_2$ | $r_3$ | $r_4$ | $r_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2.494 | | | | | 0.226 | 0.981 | 4.938 | | | | 0.106 | 0.381 | 1.376 | 5.516 |
| Li | $^2S$ | 0.002 | | | K | $^2S$ | 1115 | 2.219 | $-3.1E-5$ | | Rb | $^2S$ | 49 977 | 435.2 | 0.152 | $-3.5E-5$ |
| | | 1.594 | | | | | 0.213 | 0.898 | 3.773 | | | | 0.103 | 0.367 | 1.278 | 4.369 |
| Be | $^1S$ | 0.027 | | | Ca | $^1S$ | 1544 | 3.818 | $-1.2E-4$ | | Sr | $^1S$ | 58 191 | 541.4 | 0.275 | $-2.0E-4$ |
| | | 1.188 | | | | | 0.201 | 0.834 | | | | | 0.100 | 0.354 | 1.204 | |
| B | $^2P$ | 0.141 | | | Sc | $^2D$ | 2067 | 5.804 | | | Y | $^2D$ | 67 246 | 653.7 | 0.517 | |
| | | 0.942 | | | | | 0.190 | 0.779 | | | | | 0.098 | 0.342 | 1.140 | |
| C | $^3P$ | 0.506 | | | Ti | $^3F$ | 2712 | 8.478 | | | Zr | $^3F$ | 77 430 | 788.6 | 0.879 | |
| | | 0.776 | | | | | 0.181 | 0.731 | | | | | 0.095 | 0.331 | 1.082 | |
| N | $^4S$ | 1.447 | | | V | $^4F$ | 3507 | 12.05 | | | Nb | $^4F$ | 88 851 | 943.2 | 1.438 | |
| | | 0.658 | | | | | 0.172 | 0.691 | | | | | 0.092 | 0.320 | 1.031 | |
| O | $^3P$ | 3.480 | | | Cr | $^5D$ | 4433 | 15.84 | | | Mo | $^5D$ | 101 420 | 1116 | 2.277 | |
| | | 0.569 | | | | | 0.165 | 0.652 | | | | | 0.090 | 0.310 | 0.984 | |
| F | $^2P$ | 7.592 | | | Mn | $^6S$ | 5614 | 22.71 | | | Tc | $^6S$ | 115 450 | 1320 | 3.450 | |
| | | 0.500 | | | | | 0.158 | 0.618 | | | | | 0.088 | 0.301 | 0.940 | |
| Ne | $^1S$ | 15.29 | | | Fe | $^5D$ | 6993 | 30.39 | | | Ru | $^5D$ | 131 010 | 1551 | 4.976 | |
| | | 0.442 | 3.436 | | | | 0.151 | 0.587 | | | | | 0.086 | 0.292 | 0.901 | |
| Na | $^2S$ | 29.99 | $1.5E-4$ | | Co | $^4F$ | 8648 | 39.84 | | | Rh | $^4F$ | 148 210 | 1807 | 7.074 | |
| | | 0.396 | 2.549 | | | | 0.145 | 0.559 | | | | | 0.084 | 0.284 | 0.865 | |
| Mg | $^1S$ | 55.61 | 0.002 | | Ni | $^3F$ | 10 554 | 51.67 | | | Pd | $^3F$ | 167 080 | 2092 | 9.772 | |
| | | 0.359 | 2.081 | | | | 0.140 | 0.535 | | | | | 0.082 | 0.276 | 0.830 | |
| Al | $^2P$ | 96.15 | 0.009 | | Cu | $^2S$ | 12 705 | 63.72 | | | Ag | $^2D$ | 187 700 | 2413 | 13.22 | |
| | | 0.327 | 1.760 | | | | 0.134 | 0.510 | | | | | 0.080 | 0.269 | 0.802 | |
| Si | $^3P$ | 157.4 | 0.038 | | Zn | $^1S$ | 15 398 | 83.76 | | | Cd | $^1S$ | 210 880 | 2691 | 17.66 | |
| | | 0.301 | 1.522 | | | | 0.130 | 0.487 | | | | | 0.078 | 0.261 | 0.770 | |
| P | $^4S$ | 247.4 | 0.115 | | Ga | $^2P$ | 18 494 | 109.0 | | | In | $^2P$ | 236 010 | 3186 | 23.23 | |
| | | 0.278 | 1.341 | | | | 0.125 | 0.466 | | | | | 0.076 | 0.254 | 0.740 | |
| S | $^3P$ | 375.3 | 0.273 | | Ge | $^3P$ | 22 126 | 140.2 | 2.175 | | Sn | $^3P$ | 263 580 | 3662 | 30.14 | |
| | | 0.258 | 1.198 | | | | 0.121 | 0.446 | 1.833 | | | | 0.075 | 0.248 | 0.713 | |
| Cl | $^2P$ | 553.3 | 0.592 | | As | $^4S$ | 26 303 | 179.7 | $-0.026$ | | Sb | $^4S$ | 293 890 | 4186 | 38.66 | |
| | | 0.241 | 1.080 | | | | 0.117 | 0.427 | 1.833 | | | | 0.073 | 0.242 | 0.688 | |
| Ar | $^1S$ | 794.7 | 1.196 | | Se | $^3P$ | 31 124 | 226.9 | $-0.025$ | | Te | $^3P$ | 327 020 | 4779 | 48.91 | |
| | | | | | | | 0.113 | 0.410 | 1.652 | | | | 0.072 | 0.236 | 0.665 | 2.228 |
| | | | | | Br | $^2P$ | 36 615 | 288.3 | $-0.010$ | | I | $^2P$ | 363 180 | 5446 | 61.10 | $-0.037$ |
| | | | | | | | 0.110 | 0.394 | 1.503 | | | | 0.070 | 0.230 | 0.643 | 2.000 |
| | | | | | Kr | $^1S$ | 42 961 | 361.4 | $-0.052$ | | Xe | $^1S$ | 402 520 | 6184 | 76.09 | $-0.037$ |

[a] Each radius, $r_i$, is followed by the negative value of the Laplacian of the charge density at a radial distance $r_i$. All values are in atomic units.
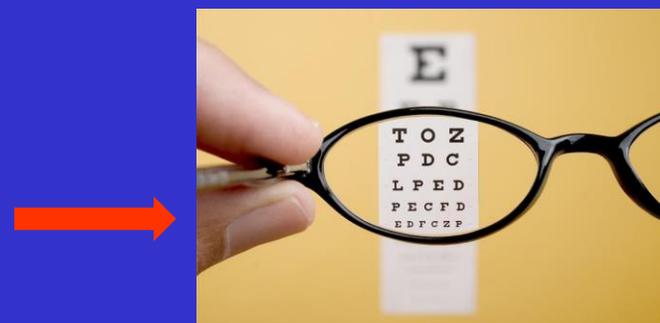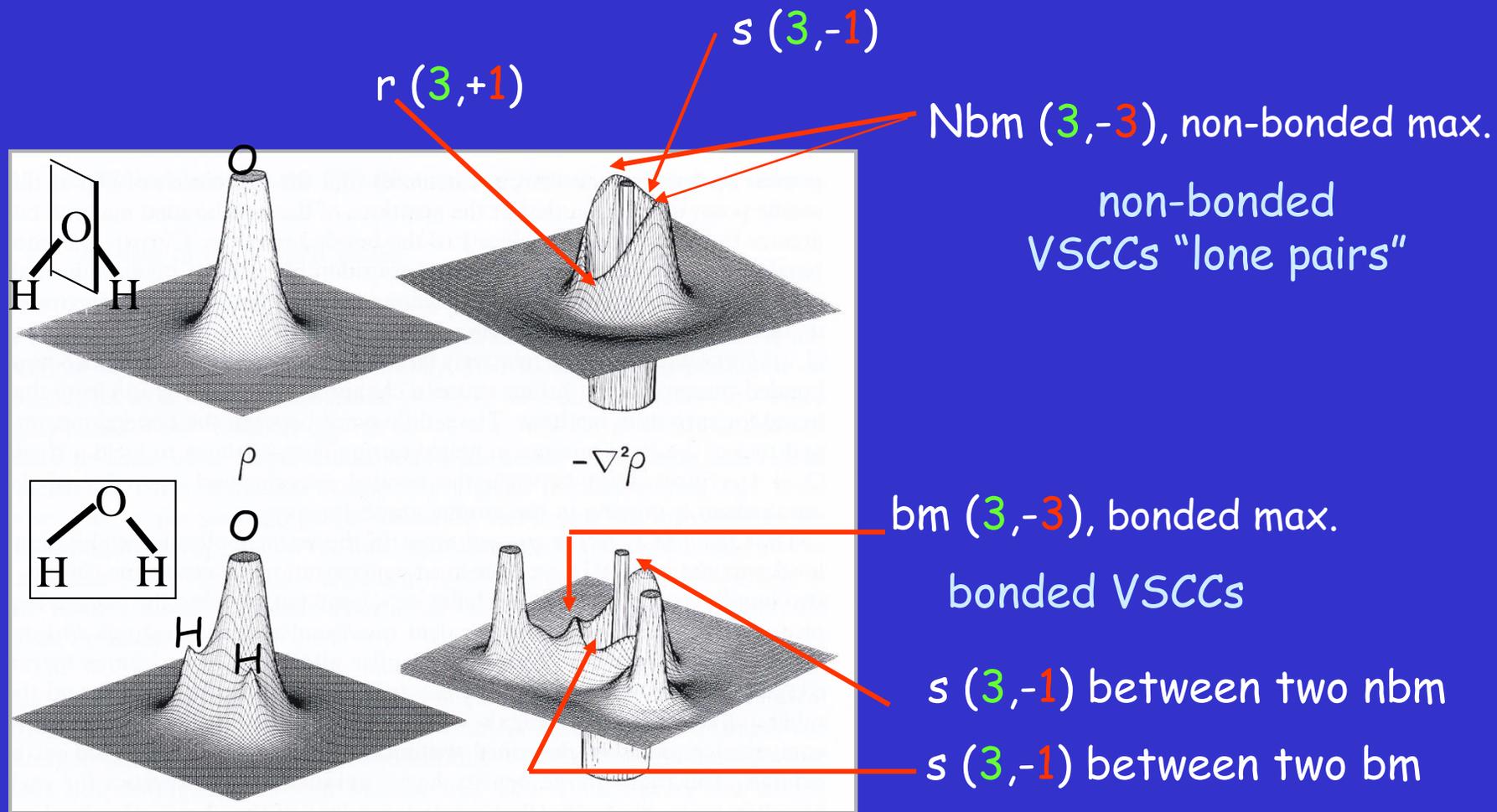
| R, au | | 0.073 | 0.242 | 0.688 |
|---|---|---|---|---|
| Te | $^3P$ | 327 020 | 4779 | 48.91 |

$-\nabla^2\rho$ (au)   Shell-L   Shell-M   Shell-N

∇²ρ and the Lewis Electron Pair Model

s (3,-1)

r (3,+1)

Nbm (3,-3), non-bonded max.

non-bonded
VSCCs "lone pairs"

bm (3,-3), bonded max.

bonded VSCCs

s (3,-1) between two nbm

s (3,-1) between two bm

R. F. W. Bader et al. *J. Am. Chem. Soc.* **1984**, *106*, 1594.

$$\nabla\rho = 0 \longleftarrow \text{CPs} \longrightarrow \nabla(\nabla^2\rho) = 0$$

**Charge Density Analysis of Actinide Compounds from the Quantum Theory of Atoms in Molecules and Crystals**

Alessandro Cossard, Jacques K. Desmarais, Silvia Casassa, Carlo Gatti, and Alessandro Erba*

Read Online

## Need to be very careful !!

The VSCC for n=7 is not visible both for the isolated U atom $\nabla^2\rho$ profile and for the $UF_6^-$ compound as the negative $\nabla^2\rho$ due to n=7 concentration region is overcompensated by positive $\nabla^2\rho$ contributions due to the depletion regions of the innermost shells
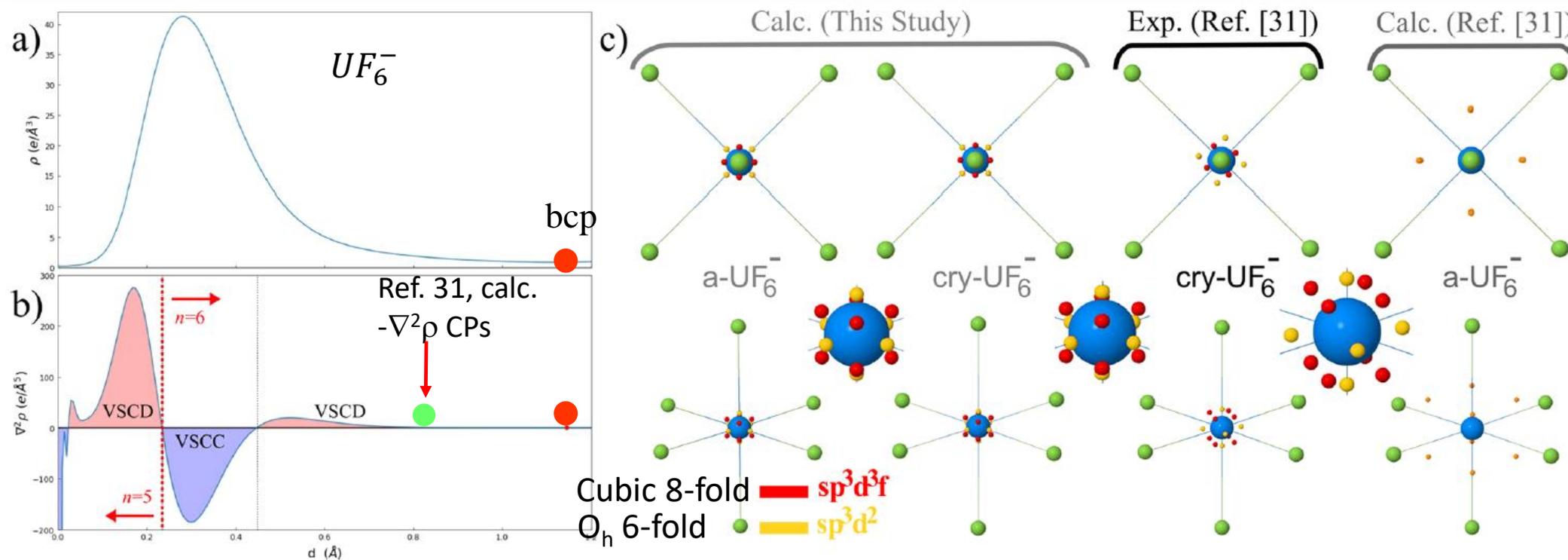
$UF_6^-$

bcp

Ref. 31, calc. $-\nabla^2\rho$ CPs

Cubic 8-fold $\quad$ $sp^3d^3f$
$O_h$ 6-fold $\quad$ $sp^3d^2$

Calc. (This Study) $\qquad$ Exp. (Ref. [31]) $\qquad$ Calc. (Ref. [31])

a-$UF_6^-$ $\qquad$ cry-$UF_6^-$ $\qquad$ cry-$UF_6^-$ $\qquad$ a-$UF_6^-$

**Figure 3.** Topology of the Laplacian $\nabla^2\rho(\mathbf{r})$ of the electron density of $UF_6^-$: (a) electron density profile along the U−$F_e$ bond (the red circle denotes the location of the bond critical point); (b) Laplacian profile along the U−$F_e$ bond (the dashed red vertical line separates the $n = 5$ from the $n = 6$ valence radial region); (c) spatial distribution of the VSCC critical points (3, +3) of the Laplacian around the U atom in present calculations, in the experiments, and in previous calculations. A zoomed-in view in the vicinity of the U atom is also provided for the first three data sets (i.e., for present calculations and previous experiments).

# Bond classification

P. Macchi

Macchi, P., Proserpio, D. M., Sironi, A. , J. Am. Chem. Soc. 120 (1998) 13429
Macchi, P.; Sironi, A.: Coordination Chem. Rev. 238–239 (2003) 383.

The classification[d] based on the atomic valence shell and on both the local (*bcp*) and integral properties

| | $\varrho_b$ | $\nabla^2\varrho_b$ | $G_b/\varrho_b$ | $H_b/\varrho_b$ | $\delta(A,B)$ | $\oint_{AB} \varrho(\mathbf{r}_s)\, dr_s$ |
|---|---|---|---|---|---|---|
| *Bonds between light atoms* | | | | | | |
| Open-shell (covalent bonds); e.g. C−C, C−H, B−B | Large | ≪0 | <1 | ≪0 | ~ Formal bond order | Large |
| Intermediate interactions (polar bonds, donor-acceptor bonds; e.g. C−O, $H_3B$−CO | Large | any value | ≥ 1 | ≪0 | < Formal bond order | Large |
| Closed-shell (ionic bonds, HBs, van der Waals interactions; e.g. LiF, H...O, Ne...Ne | Small | >0 | ≥ 1 | > 0 | ~ 0 | Small |
| *Bonds between heavy atoms* | | | | | | |
| Open-shell (e.g. Co−Co) | Small | ~0 | <1 | < 0 | Formal bond order (unless bond delocalisation occurs) | Medium/large |
| Donor acceptor (e.g. Co−As) | Small | >0 | ~1 | <0 | < Formal bond order | Medium/large |

General and detailed discussion on several bond classification schemes

Gatti, C. , *Chemical bonding in crystals: new directions*, (2005) Z. Kristallogr. 220, 399-457

**Chemical bond nature vs BCP properties in solids**

### Shared interactions

| SYSTEM | BOND | $R_e$ (Å) | $\rho_b$ | $\nabla^2\rho_b$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $|\lambda_{12}|/\lambda_3$ |
|---|---|---|---|---|---|---|---|---|
| UREA | C-O | 1.261 | 0.38 | -0.3 | -1.0 | -1.0 | 1.8 | 0.6 |
| | C-N | 1.345 | 0.35 | -1.2 | -0.9 | -0.8 | 0.5 | 1.6 |
| | N-H | 1.009 | 0.34 | -2.0 | -1.5 | -1.4 | 0.9 | 1.6 |
| DIAMOND | C-C | 1.545 | 0.26 | -0.9 | -0.5 | -0.5 | 0.2 | 2.5 |

### Not shared closed-shell interactions

| SYSTEM | BOND | $R_e$ (Å) | $\rho_b$ *10 | $\nabla^2\rho_b$ *10 | $\lambda_1$ *10 | $\lambda_2$ *10 | $\lambda_3$ *10 | $|\lambda_{12}|/\lambda_3$ |
|---|---|---|---|---|---|---|---|---|
| **Dative interactions** | | | | | | | | |
| LCOB[a] | Co-N | 1.966 | 0.92 | 5.4 | -0.7 | -0.6 | 6.7 | 0.1 |
| | Li-O | 2.030 | 0.21 | 2.0 | -0.4 | -0.4 | 2.8 | 0.2 |
| **Hydrogen bonds** | | | | | | | | |
| UREA | NH...O | 2.058 | 0.19 | 0.8 | -0.3 | -0.2 | 1.3 | 0.2 |
| IceVIII | OH...O | 2.080 | 0.18 | 0.6 | -0.2 | -0.2 | 1.0 | 0.2 |
| LCOB[a] | CH...O | 2.528 | 0.06 | 0.4 | -0.1 | -0.1 | 0.5 | 0.1 |

(a) Lithium Bis (tetramethylammonium)Hexanitrocobaltate (III)

### Ionic (or not shared) interactions

| SYSTEM | BOND | $R_e$ (Å) | $\rho_b$ *10 | $\nabla^2\rho_b$ *10 | $\lambda_1$ *10 | $\lambda_2$ *10 | $\lambda_3$ *10 | $|\lambda_{12}|/\lambda_3$ |
|---|---|---|---|---|---|---|---|---|
| Li oxide | Li-O | 1.980 | 0.29 | 2.2 | -0.5 | -0.5 | 3.1 | 0.2 |
| K oxide | K-O | 2.789 | 0.18 | 0.8 | -0.1 | -0.1 | 1.0 | 0.1 |
| Li-H | Li-H | 2.042 | 0.13 | 0.7 | -0.1 | -0.1 | 1.0 | 0.1 |
| Li-H | H-H | 4.083 | 0.09 | 0.1 | -0.1 | -0.0 | 0.2 | 0.2 |

### Metals

| SYSTEM | BOND | $R_e$ (Å) | $\rho_b$ *100 | $\nabla^2\rho_b$ *100 | $\lambda_1$ *100 | $\lambda_2$ *100 | $\lambda_3$ *100 | $|\lambda_{12}|/\lambda_3$ |
|---|---|---|---|---|---|---|---|---|
| Li, bcc | | 3.040 | 0.81 | 0.6 | -0.1 | -0.1 | 0.8 | 0.1 |

$\rho_b$, $\nabla^2\rho_b$, $\lambda_{1-3}$ of closed shell interactions are generally one or two order of magnitude smaller than for shared interactions

$|\lambda_{1,2}|/\lambda_3 \approx 1$ shared interactions

$|\lambda_{1,2}|/\lambda_3 \approx 0.1$ closed-shell int.
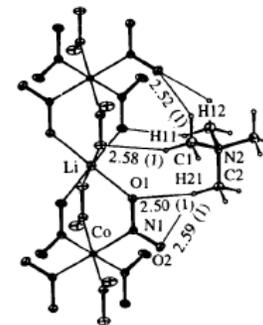
*Acta Cryst.* (1996). **B52**, 471–478

Theoretical and Experimental (113 K) Electron-Density Study of Lithium Bis(tetramethylammonium) Hexanitrocobaltate(III)

## Some general warning about chemical bonding characterization

❑ Use of too precise rules to characterize a specific bonding interaction may be dangerous and should be always done *cum grano salis*, especially if these rules are given in terms of typical intervals for the values of properties at BCP, like $\rho_b$, $\nabla^2\rho_b$, $G_b$, $V_b$, and $H_b$.

❑ Regardless of the nature of bonding (ionic, covalent, metallic, charge-shift, etc.), the numerical values of any bond property for a given A–B pair are very much related to the principal quantum number of the A and B valence shell electrons and to their difference from A to B

❑ By keeping in mind this fact, bond properties, especially for 'heavy atoms,' that is, from the first-transition element row on, are often more properly understood if compared with those predicted by the IAM model. Or even better, and, whenever possible, with those predicted by the fragment model – the sum of electron densities of not-interacting fragments, that is, of a model system where the bond under study is not yet formed

See
B. Silvi*, R.J. Gillespie*, C. Gatti*, **Electron Density analysis**, J. Reedijk and K. Poeppelmeier, Eds, in *Comprehensive Inorganic Chemistry* II vol. 9, Elsevier 2013

# General discussion on several bond classification schemes: Gatti, C. , Chemical bonding in crystals: new directions, (2005) Z. Kristallogr. 220, 399-457, special issue on *Computational Crystallography*, edited by A.R. Oganov

Chemical bonding in crystals: new directions        409

**Table 4.** Classification of atomic interactions.

The dichotomous classification[a] based on the sign of $\nabla^2\varrho_b$

| Property | Shared shell, $\nabla^2\varrho_b < 0$ Covalent and polar bonds | Closed-shell, $\nabla^2\varrho_b > 0$ Ionic, H-bonds and vdW molecules |
|---|---|---|
| $\lambda_1$ | $\lambda_{1,2}$ dominant; $\|\lambda_{1,2}\|/\|\lambda_3\| > 1$ | $\lambda_3$ dominant; $\|\lambda_{1,2}\|/\lambda_3 \ll 1$ |
| VSCC[b] | The VSCCs of the two atoms form one continous region of charge concentration | $\nabla^2\varrho > 0$ over the entire interaction region. The spatial display of $\nabla^2\varrho$ is mostly atomic-like |
| $\varrho_b$ | Large | Small |
| Energy lowering | By accumulating $\varrho$ in the interatomic region | Regions of dominant $V(\mathbf{r})$ are separately localized within the boundaries of interacting atoms |
| Energy components | $2G_b < \|V_b\|; G_b/\varrho_b < 1; G_{b\|} \ll G_{b\perp}; H_b < 0$ | $2G_b > \|V_b\|; G_b/\varrho_b > 1, G_b \gg G_{b\perp}; H_b$ any value |

*Bond polarity is increasing* ------- →

← ------- *Bond covalency is increasing*

The classification[c] based on the adimensional $\|V_b\|/G_b < 1$ ratio

| Shared shell (SS) | Transit region, incipient covalent bond formation | Closed-shell (CS) |
|---|---|---|
| $\|V_b\|/G_b > 2$ | $1 < \|V_b\|/G_b < 2$ | $\|V_b\|/G_b < 1$ |
| $H_b < 0; \nabla^2\varrho_b < 0$ Bond degree (BD) = $H_b/\varrho_b \equiv$ Covalence degree (CD) | $H_b < 0; \nabla^2\varrho_b > 0$ BD $\equiv$ CD | $H_b > 0; \nabla^2\varrho_b > 0$ BD $\equiv$ Softness degree (SD) |
| BD large and negative | BD negative and smaller in magnitude than for SS interactions | SD positive and large |
| The larger is \|BD\| the more covalent is the bond | BD Approaching zero at the boundary with CS region | The larger is SD the weaker and closed-shell in nature is the bond |

The classification[d] based on the atomic valence shell and on both the local (*bcp*) and integral properties

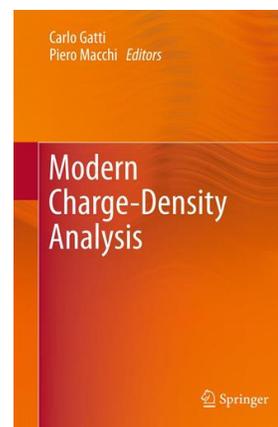| | $\varrho_b$ | $\nabla^2\varrho_b$ | $G_b/\varrho_b$ | $H_b/\varrho_b$ | $\delta(A,B)$ | $\oint_{AB} \varrho(\mathbf{r}_s)\,d\mathbf{r}_s$ |
|---|---|---|---|---|---|---|
| *Bonds between light atoms* | | | | | | |
| Open-shell (covalent bonds); e.g. C−C, C−H, B−B | Large | $\ll 0$ | $< 1$ | $\ll 0$ | ~ Formal bond order | Large |
| Intermediate interactions (polar bonds, donor-acceptor bonds; e.g. C−O, $H_3B$−CO | Large | any value | $\geq 1$ | $\ll 0$ | < Formal bond order | Large |
| Closed-shell (ionic bonds, HBs, van der Waals interactions; e.g. LiF, H...O, Ne...Ne | Small | $> 0$ | $\geq 1$ | $> 0$ | ~ 0 | Small |
| *Bonds between heavy atoms* | | | | | | |
| Open-shell (e.g. Co−Co) | Small | ~ 0 | $< 1$ | $< 0$ | Formal bond order (unless bond delocalisation occurs) | Medium/large |
| Donor acceptor (e.g. Co−As) | Small | $> 0$ | $\sim 1$ | $< 0$ | < Formal bond order | Medium/large |

a: according to Ref. [90].
b: VSCC is the Valence Shell Charge Concentration, that is the valence region of the isolated atom where the Laplacian is negative [13]
c: according to Ref. [93]
d: according to Ref. [109]; the lower part of this Table is an adaptation of Table 5 and Table 4 of Ref. [109] and Ref. [97], respectively. Ref. [109] defines as heavy atoms the atoms having more than three atomic shells, i.e. from K atom onwards.
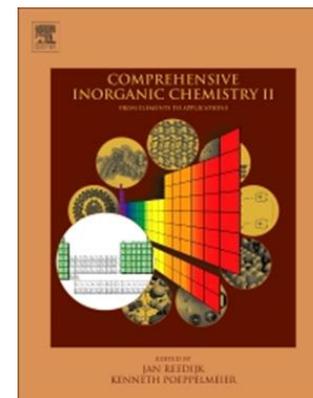
COMPREHENSIVE INORGANIC CHEMISTRY II
EDITED BY JAN REEDIJK KENNETH POEPPELMEIER

B. Silvi*, R.J. Gillespie*, C. Gatti*, **Electron Density analysis**, J. Reedijk and K. Poeppelmeier, Eds, in *Comprehensive Inorganic Chemistry* II vol. 9, Elsevier 2013

Carlo Gatti Piero Macchi *Editors*
Modern Charge-Density Analysis
Springer
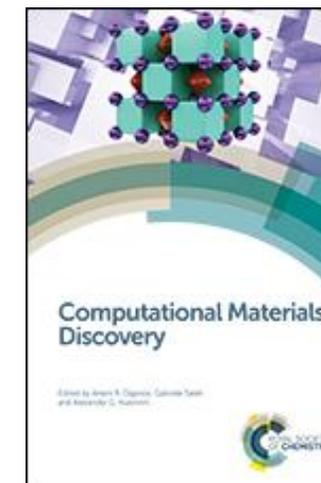
C. Gatti and P. Macchi, Eds, Springer 2012

Computational Materials Discovery

G. Saleh, D. Ceresoli, G. Macetti and C. Gatti*, **Chapter 5: Chemical Bonding Investigations for Materials**, in *Computational Materials Discovery*, A.R. Oganov, G. Saleh, A.G. Kvashnin Eds., RSC 2019
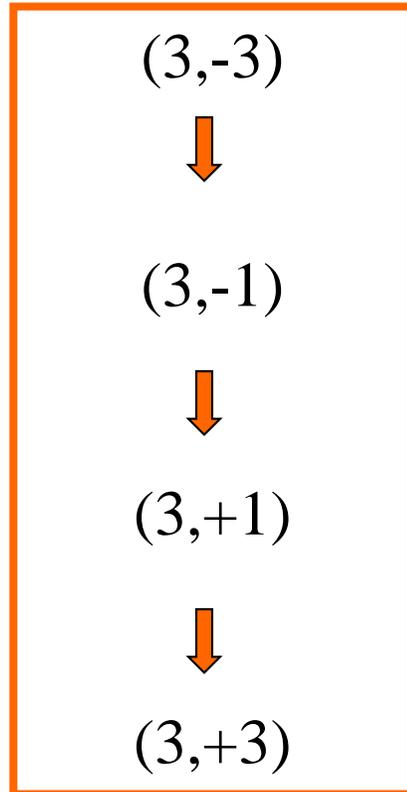
C. Roetti

Crystal graph – retrieving intermolcular interactions in the crystal

✓ How important are packing effects on intramolecular bonds?

✓ Does the packing have different impact on the different atoms/chemical groups present in the molecule?

✓ How large is the enhancement of the molecular dipole on crystallization?

✓ How can each oxygen atom in the urea crystal be involved in four OH...O hydrogen bonds (HBs)?

(3,-3)

⬇

(3,-1)

⬇

(3,+1)

⬇

(3,+3)

⬅ Sequence of the chainlike search strategy for locating CPs

At each search stage, an EF step specific for the kind of CP searched for is adopted.

# Fully-automated and chain-like CP searches

1. Search of **(3,-3)** associated to **nuclear maxima**, starting from the nuclear position of each of the unique atoms of the unit cell

2. Search of all **(3,-1)** unique **bcps** associated to the unique bonded atom pairs within the cluster. Search started from internuclear axis midpoint

3. **Non-nuclear (3,-3) attractors**, if any, are recovered at this stage by determining the nature of the termini of the atomic lines (**bond paths)** associated to the unique (3,-1) CPs found

4. Search of unique **(3,+1) rcps** by considering all unique nuclear triplets having at least 2 of their 3 atoms bonded to each other and CM (Center of Mass) not too differently distant from each of the 3 nuclei. CP search started from CM (mass =1 assigned to each nucleus)

5. Search of unique **(3,+3) cage** CPs between all pairs of ring CPs

A grid-search for CPs in a given portion of the cell

| Constraint | Constraint type |
|---|---|
| 1 | $X \leq ay$ |
| 2 | $X \leq (a+y)/2$ |
| 3 | $Y \leq ax$ |
| 4 | $Y \leq \min [a - x, (a + x)/2]$ |
| 5 | $Y \leq \min (x, a - x)$ |
| 6 | $Y \leq \min (2x, a - x)$ |
| 7 | $Y \leq a - x$ |
| 8 | $z \leq ay$ |
| 9 | $z \leq a + y$ |
| 10 | $z \leq \min (y, a - x)$ |

$\Rightarrow$    xmin    xmax   xinc

$\Rightarrow$    ymin     ymax   yinc

$\Rightarrow$    zmin    zmax    zinc

        all in fractionary units

▮ Warning: the grid search is very costly if the whole asymmetric unit is explored.

▮ The CP search algorithm can be chosen (EF or NR). NR is strongly recommended here, because the starting point of the CP search is moved slightly and smoothly during the search on a grid. On top of this, the general interest is in locating all CPs in the asymmetric unit, rather than one peculiar type of CP

▮ Space group constraints among x,y,z fractional coordinates may be exploited

Why?

$$n - b + r - c = 0$$

For a closed domain
Morse Relation

| n | (3,-3) nuclei or NNA |
|---|---|
| b | (3,-1) bcps |
| r | (3,+1) rcps |
| c | (3,+3) ccps |

Grid search in the asymmetric unit may be the only way to fulfill Morse's relationship

Fulfilment of the relationship implies a compatible CP set, not necessarily the complete set of CPs within the cell !

# Fulfillment of Morse relationship in urea crystal

w    m

| | | | |
|---|---|---|---|
| c | 2 | (3,-3) | C |
| c | 2 | (3,-3) | O |
| e | 4 | (3,-3) | N |
| e | 4 | (3,-3) | H' |
| e | 4 | (3,-3) | H" |

w, Wyckoff positions

m, multiplicity

| | | | |
|---|---|---|---|
| c | 2 | (3,+1) | ring |
| e | 4 | (3,+1) | ring |
| e | 4 | (3,+1) | ring |
| f | 8 | (3,+1) | ring |
| f | 8 | (3,+1) | ring |

| | | | |
|---|---|---|---|
| c | 2 | (3,-1) | C-O |
| e | 4 | (3,-1) | C-N |
| e | 4 | (3,-1) | N-H' |
| e | 4 | (3,-1) | N-H" |
| e | 4 | (3,-1) | O…H' |
| e | 4 | (3,-1) | O…H" |
| d | 4 | (3,-1) | N…N, 4.3 Å |
| f | 8 | (3,-1) | N…N, 3.4 Å |

| | | | |
|---|---|---|---|
| e | 4 | (3,+3) | cage |
| a | 2 | (3,+3) | cage |
| b | 2 | (3,+3) | cage |

$n - b + r - c = 0$

$16 - 26 + 18 - 8 = 0$

Gatti et al. JCP, 101,10686 (1994)

$16 - 34 + 26 - 8 = 0$

# The complete bond network in urea crystal



N-H...O

1.99 Å

2.06 Å

N...N, 3.4 Å

N...N, 4.3 Å

# Crystal field effects on the topological properties of the electron density in molecular crystals: The case of urea

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# Deformation and interaction density and changes in bcp properties of urea

all in au

$\varepsilon = (\lambda_1 / \lambda_2) - 1$

| X-Y | $\rho$ | $\nabla^2 \rho$ | $\lambda_3$ | $\varepsilon$ |
|---|---|---|---|---|
| C-O | 0.374 | -0.550 | 1.409 | 0.038 |
| | 0.384 | -0.666 | 1.239 | 0.125 |
| | 0.384 | -0.666 | 1.229 | 0.125 |
| | 0.299 | 0.118 | 0.974 | 0.038 |
| C-N | 0.342 | -0.952 | 0.721 | 0.143 |
| | 0.334 | -0.825 | 0.817 | 0.097 |
| | 0.334 | -0.825 | 0.817 | 0.097 |
| | 0.262 | -0.099 | 0.627 | 0.044 |
| N-H | 0.347 | -2.003 | 0.874 | 0.052 |
| | 0.346 | -1.735 | 0.945 | 0.070 |
| | 0.346 | -1.735 | 0.945 | 0.070 |
| | 0.234 | -0.271 | 1.240 | 0.006 |
| O...H'N $d_{O...H} =$ 1.992 | 0.023 | 0.081 | 0.143 | 0.024 |
| | 0.021 | 0.092 | 0.147 | 0.003 |
| | 0.030 | 0.088 | 0.164 | 0.059 |
| O...H"N $d_{O...H} =$ 2.058 | 0.019 | 0.080 | 0.130 | 0.034 |
| | 0.019 | 0.086 | 0.136 | 0.006 |
| | 0.026 | 0.083 | 0.145 | 0.045 |

$\rho_{CRYSTAL}$

Interaction density

$\Sigma \rho_{MOLECULES}$

$\rho_{MOLECULE}$

Deform. density

Mol. Deform. density

$\Sigma \rho_{ATOMS}$ (procrystal)

| Property | Shared shell, $\nabla^2\rho_b < 0$ Covalent and polar bonds | Closed-shell, $\nabla^2\rho_b > 0$ Ionic, H- bonds and vdW molecules |
|---|---|---|
| $\lambda_I$ | $\lambda_{1,2}$ dominant ; $|\lambda_{1,2}|/|\lambda_3| > 1$ | $\lambda_3$ dominant; $|\lambda_{1,2}|/|\lambda_3| << 1$ |
| VSCC | The VSCCs of the two atoms form one continuous region of CC | $\nabla^2\rho > 0$ over the entire interaction region. The spatial display of $\nabla^2\rho$ is mostly atomic-like |
| $\rho_b$ | Large | Small |
| Energy Lowering | By accumulating $\rho$ in the interatomic region | Regions of dominant $V(r)$ are separately localized within the boundaries of interacting atoms |
| Energy components | $2G_b < |V_b|$; $G_b/\rho_b < 1$; $G_{b||} << G_{b\perp}$; $H_b < 0$ | $2G_b > |V_b|$ ; $G_b/\rho_b > 1$, $G_{b||} >> G_{b\perp}$; $H_b$ any value |

Electron sharing is decreasing (ond polarity increasing)

Electron sharing (covalency) is increasing (and polarity decreasing)

# Interaction density and changes in BCP properties of urea



CG molecule           OG molecule

Bulk - molecule

10% increase/decrease
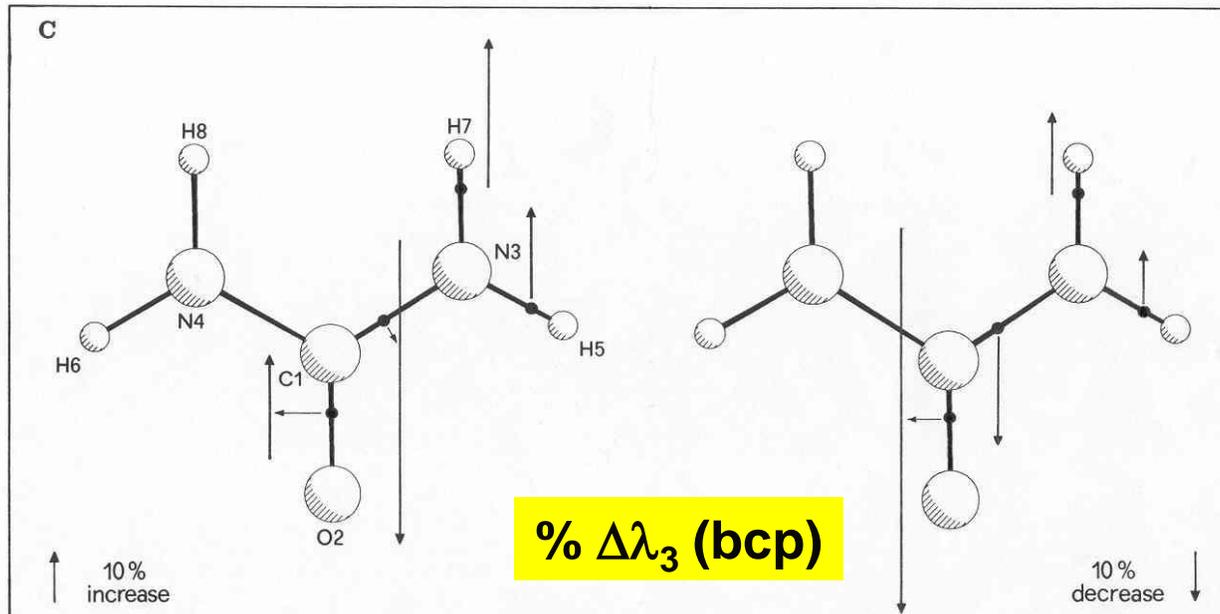
% $\Delta\lambda_3$ (bcp)

+0.05 increase/decrease

$\Delta\varepsilon$ (bcp)
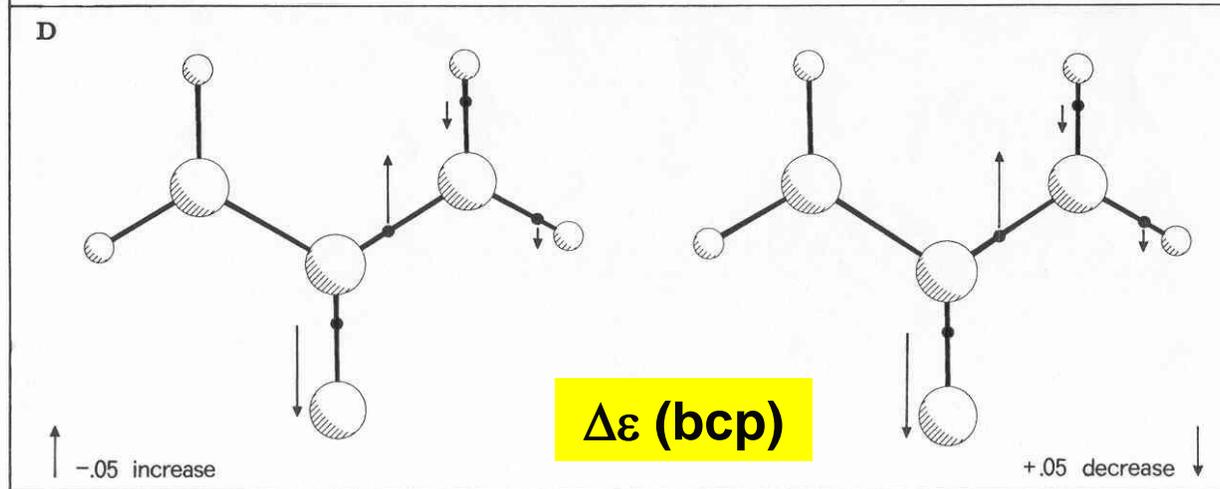
C=O, N-H become **more ionic**; C-N **more covalent**

## Bulk -molecule

## Bulk - dimer

% $\Delta\lambda_3$ (bcp)

$\leftarrow - - - \rightarrow$

% $\Delta\rho$ (bcp)

$\leftarrow \longrightarrow$

## Crystal field effects on the topological properties of the electron density in molecular crystals: The case of urea

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$$\mu = \mu_{el} + \mu_{nuc} = \Sigma_\Omega [ -\int_\Omega r\rho(r)d\tau + X_\Omega Z_\Omega ]$$

$$r = r_\Omega + X_\Omega \quad ; q_\Omega = Z_\Omega - \int_\Omega dr\rho(r) = Z_\Omega - N_\Omega$$

$$\mu = \Sigma_\Omega [-\int_\Omega r_\Omega \rho(r)d\tau + X_\Omega(Z_\Omega - \int_\Omega \rho(r) d\tau]$$

$$\mu = \Sigma_\Omega [M_\Omega + X_\Omega q_\Omega] = \mu_{AP} + \mu_{CT}$$
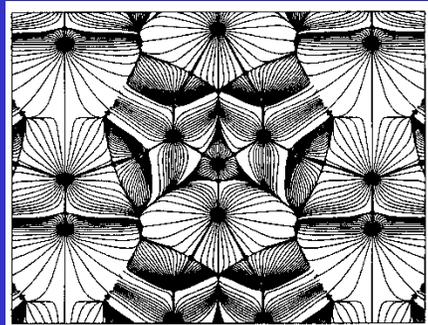
Both sums are origin independent (if $\Sigma q_\Omega = 0$)

For $\mu_{AP}$ also each term in the $\Sigma$ is origin independent

## Enhancement of molecular dipole moment of urea in the bulk

■ The non-interacting molecules and the crystal periodic RHF densities look very much alike despite the 37% |μ| enhancement in the crystal
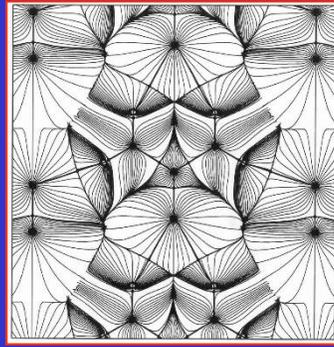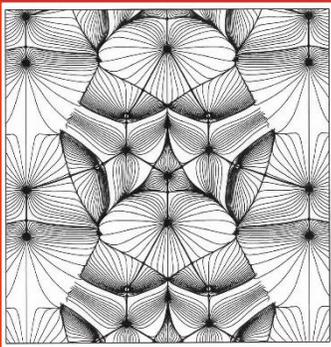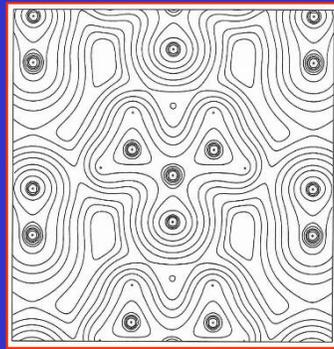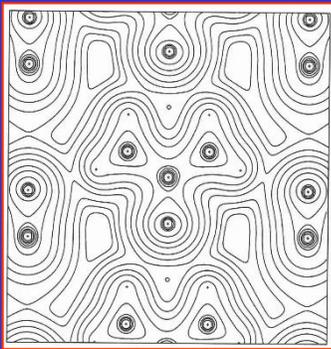
Non interacting molecules

Crystal
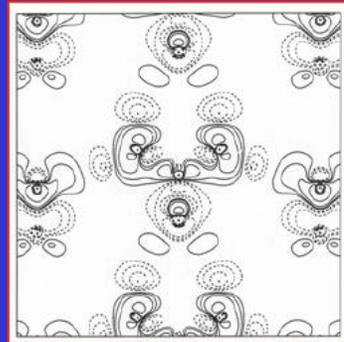
Inter. density , Highest contour level ±2·10⁻³ au

■ |μ| values are very sensitive to the atomic boundaries location and to the atomic ED distribution changes

| Contribution | OG Mol. | CG Mol | Crystal |
|---|---|---|---|
| $\mu_A$,($\Delta|\mu_A|$%) | 0.71 | 0.54 | 0.45 (-16.7) |
| $\mu_{CT}$,($\Delta|\mu_{CT}|$%) | -2.52 | -2.56 | -3.22 (+25.8) |
| $\mu$ , ($\Delta|\mu|$%) | -1.81 | -2.01 | -2.77 (+37.1) |

Gatti et al, JCP 101, 10686 (1994)
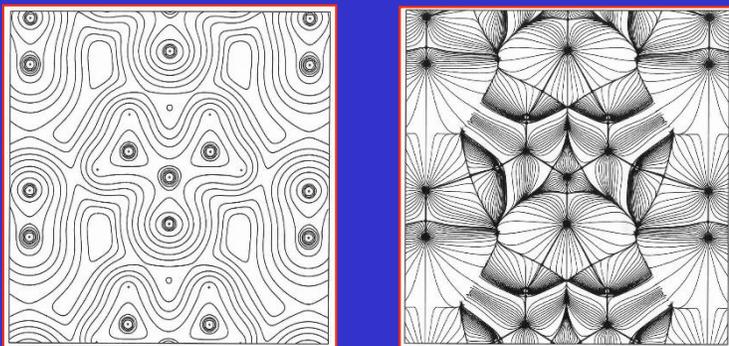
Crystal

**Clearly the result of a more polarized molecule in the bulk**

All the heavy atoms gain
electrons at the expense
of the H's in the bulk

Following  HB formation there is
a net flux of 0.067 e⁻ from the
amino-group  hydrogen donor to
the carbonyl acceptor.

| $\Omega$ | Mol (CG) | Crystal | |
|---|---|---|---|
| | $N(\Omega)$ | $N(\Omega)$ | $\Delta N(\Omega)$ |
| C | 3.512 | 3.545 | +0.032 |
| O | 9.383 | 9.476 | +0.092 |
| N | 8.481 | 8.568 | +0.087 |
| H' | 0.508 | 0.454 | -0.053 |
| H'' | 0.565 | 0.465 | -0.100 |
| CO | 12.895 | 13.021 | +0.126 |
| $NH_2$ | 9.554 | 9.487 | -0.067 |

Gatti et al, JCP 101, 10686 (1994)

# Crystal field effects on the topological properties of the electron density in molecular crystals: The case of urea

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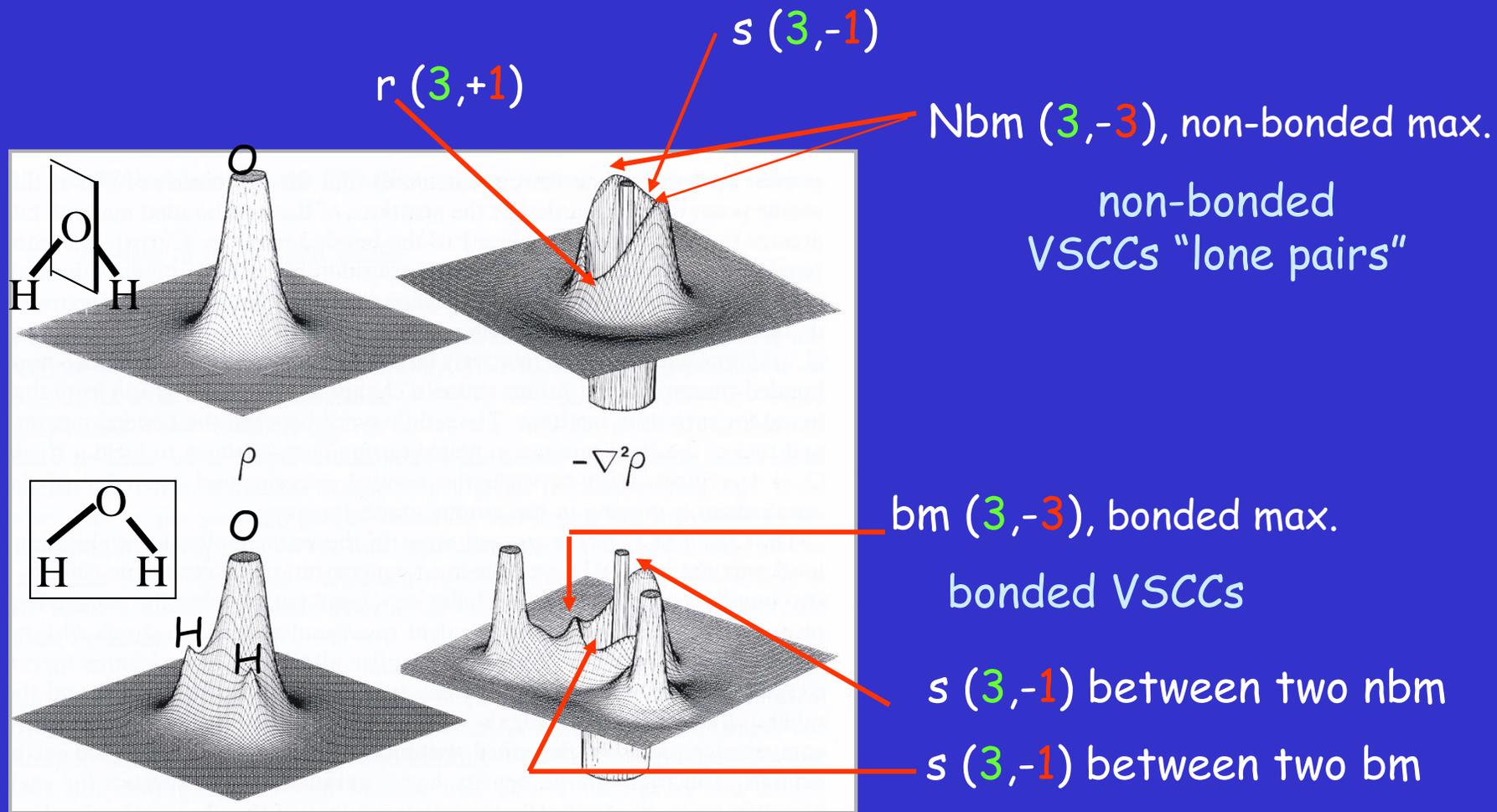
C. Roetti
*Gruppo di Chimica Teorica, Università di Torino, via Giuria 5, I-10125 Torino, Italy*

- ✓ How important are packing effects on intramolecular bonds?

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- ✓ How does the global molecular volume contraction observed in the solid result from the individual atomic volume change on crystallization?

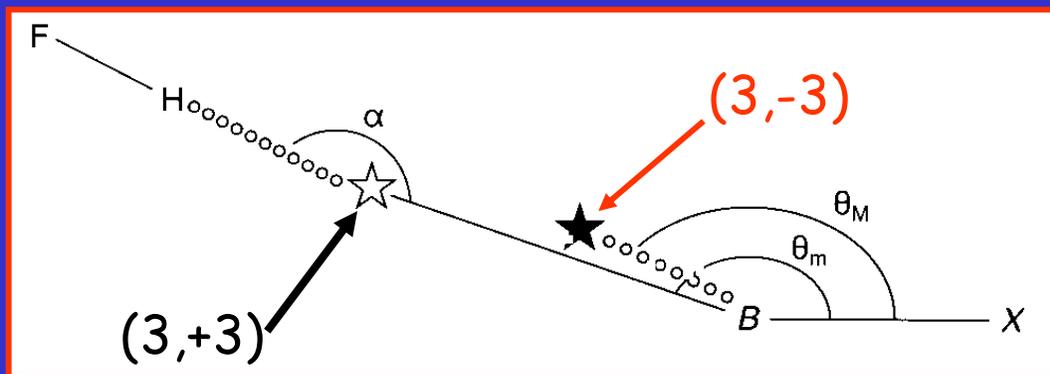# $\nabla^2\rho$ and the Lewis Electron Pair Model

s (3,-1)

r (3,+1)

Nbm (3,-3), non-bonded max.

non-bonded
VSCCs "lone pairs"



$\rho$

$-\nabla^2\rho$

bm (3,-3), bonded max.

bonded VSCCs

s (3,-1) between two nbm

s (3,-1) between two bm

R. F. W. Bader et al. *J. Am. Chem. Soc.* **1984**, *106*, 1594.

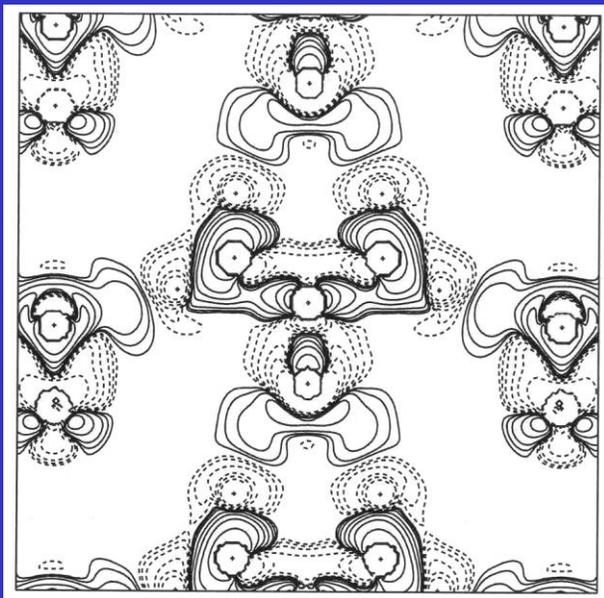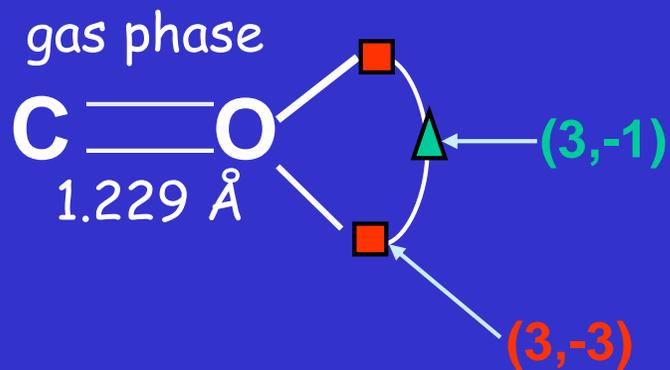$$\nabla\rho = 0 \longleftarrow CPs \longrightarrow \nabla(\nabla^2\rho) = 0$$

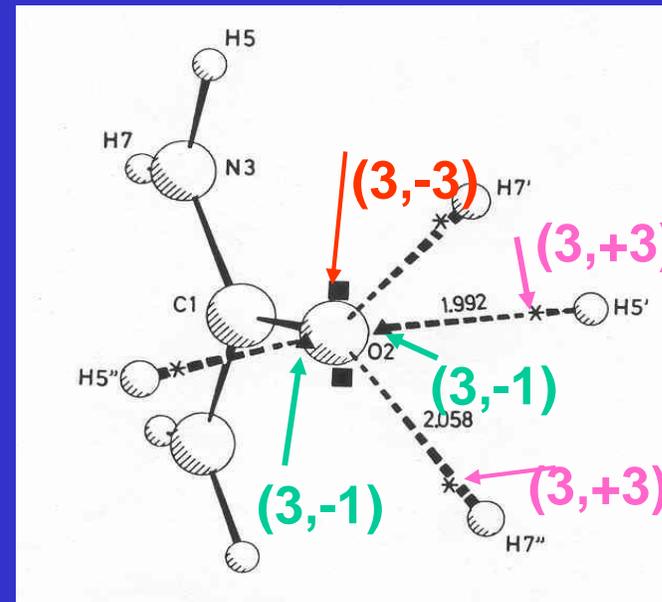● HBs may be seen in terms of a generalized Lewis acid and base interaction



● Generally the approach of the acidic hydrogen to the base will be such as to align the (3,+3) minimum in the VSCC of the H with the most suitable (3,-3) Base maximum

gas phase

$C = O$

1.229 Å

(3,-1)

(3,-3)

crystal

$C = O$

1.261 Å

(3,-1)

$-(\nabla^2\rho_{crystal} - \nabla^2\rho_{molecule})$

Gatti et al. , JCP 101, 10686 (1994)

$\nabla^2\rho_{crystal}$

(3,-3)

(3,+3)

(3,-1)

(3,-1)

(3,+3)

# Crystal field effects on the topological properties of the electron density in molecular crystals: The case of urea

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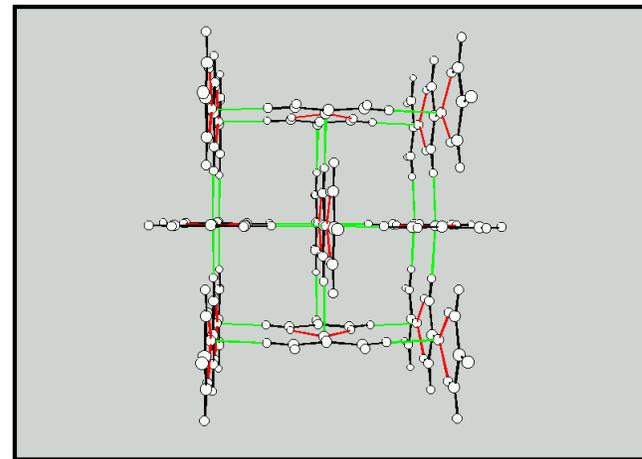
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JCP 101 , 10686-10696 (1994)

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## Atomic volumes

$$V(\Omega) = \int_\Omega d\tau \qquad\qquad \sum_{\Omega \text{ of all cell}} V(\Omega) = V_{cell}$$

Generally infinite in the molecular case; always finite in the crystalline case

Normally the atomic volume is however defined as the region of space enclosed by the intersection of the atomic zero-flux surface and a particular envelope of $\rho$

$$V_{0.001}(\Omega) \equiv V1 = \int_{\Omega^*} d\tau ; \qquad \Omega^*: \forall \mathbf{r} \in \Omega \text{ where } \rho \geq 0.001 \text{ au}$$

$V_{0.001}$ yields molecular sizes in agreement with those determined from the analysis of the kinetic theory data for gas-phase molecules (van der Waals volumes)

$$V_{0.002}(\Omega) \equiv V2 = \int_{\Omega^{**}} d\tau ; \qquad \Omega^{**}: \forall \mathbf{r} \in \Omega \text{ where } \rho \geq 0.002 \text{ au}$$

$V_{0.002}$ yields molecular sizes compatible with the closer packing found in the solid state

| $\Omega$ | Molecule (CG) | | Crystal | | |
|---|---|---|---|---|---|
| | V1 | V2 | V1 | V2 | $V_{tot}$ |
| C | 19.9 | 18.5 | 21.0 | 19.1 | 21.2 |
| O | 132.2 | 111.1 | 115.6 | 104.6 | 124.3 |
| N | 117.9 | 101.4 | 120.2 | 107.5 | 135.0 |
| H' | 24.6 | 18.8 | 16.8 | 15.3 | 17.7 |
| H" | 27.4 | 20.8 | 18.2 | 16.3 | 18.7 |
| CO | 152.1 | 129.6 | 136.6 | 123.7 | 145.5 |
| $NH_2$ | 170.0 | 140.9 | 155.2 | 139.1 | 171.4 |
| Molec | 492.2 | 411.5 | 447.0 | 401.8 | 488.2 |
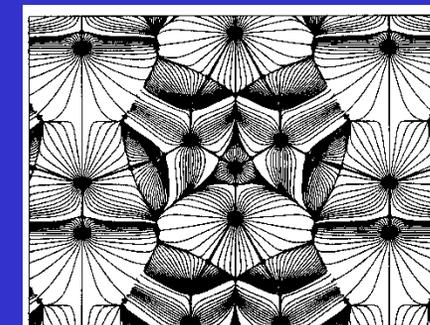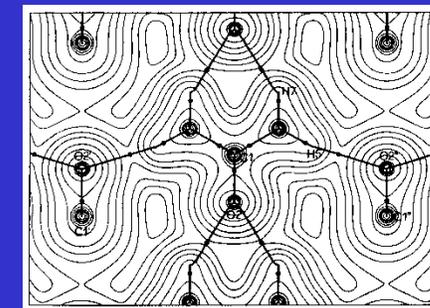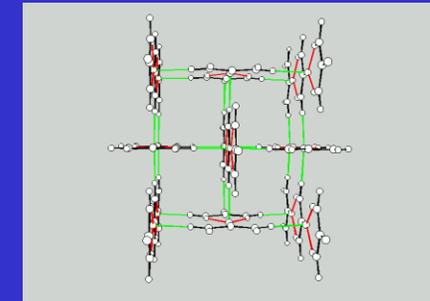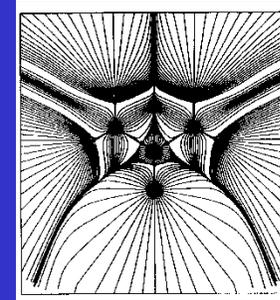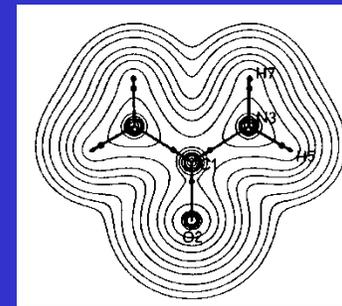










As a reaction of molecules to the intermolecular exch. forces:

✓ V1 –10% ; V2 –2% ; $V_{tot, cry} \approx$ V1, gas phase

✓ V2 is $\approx$ 90% and 83% of V1 in the bulk and gas phase: the molecular density dies off more rapidly in the bulk

✓ the reported trends do not apply to single $\Omega$, but they do to the functional groups CO and NH2

✓ Contraction of mol. volume in crystal arises primarily from contraction of the $\Omega$'s directly involved in H-bonds

O : $\Delta V_2$ = -6%, $\Delta V_1$ = -13%;  H'(H") : $\Delta V_2$ = -19(-28)%

Giovanna Bruno [1] ⓘ, Giovanni Macetti [2] ⓘ, Leonardo Lo Presti [1] ⓘ and Carlo Gatti [3,4,*] ⓘ

- ❑ Few studies have appeared on $s(\mathbf{r})$ thus far despite its role in Spin DFT Functional theory and it being the basic observable for describing and understanding magnetic phenomena

- ❑ A systematic full topological analysis of this function is lacking, in seemingly contrast to the blossoming in the last 20 years of many studies on the topological features of other scalar fields of chemical interest.

- ❑ Filling this gap, we may unveil that kind of information hidden in the $s(\mathbf{r})$ distribution which only its topology can disclose.
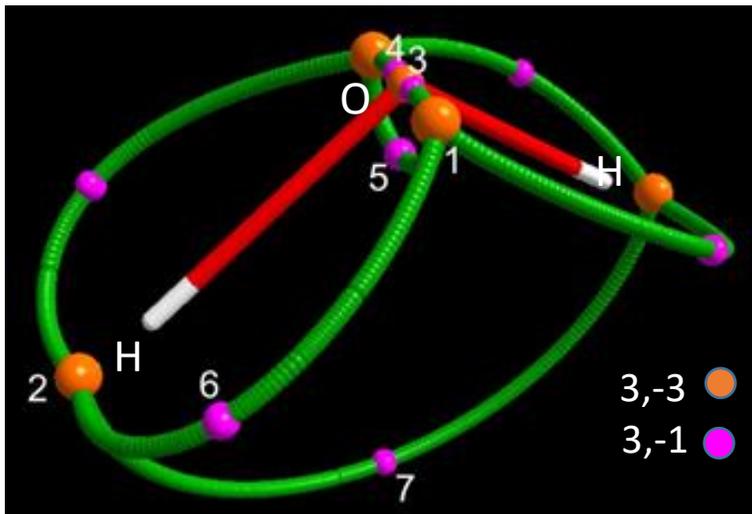
*s(r)* **Critical points (CPs)**

$$\nabla s(\boldsymbol{r}_{CP}) = \nabla\big(\rho_\alpha(\boldsymbol{r}_{CP}) - \rho_\beta(\boldsymbol{r}_{CP})\big) = 0 \ \rightarrow \ \nabla\rho_\alpha(\boldsymbol{r}_{CP}) \equiv \nabla\rho_\beta(\boldsymbol{r}_{CP})$$

This condition is opposite to that for ρ(**r**) at CP : $\nabla\rho_\alpha(\boldsymbol{r}_{CP}) \equiv -\nabla\rho_\beta(\boldsymbol{r}_{CP})$). This latter, in the case of a non-spin-polarized system is also more stringent as both derivatives need to be equal to zero.

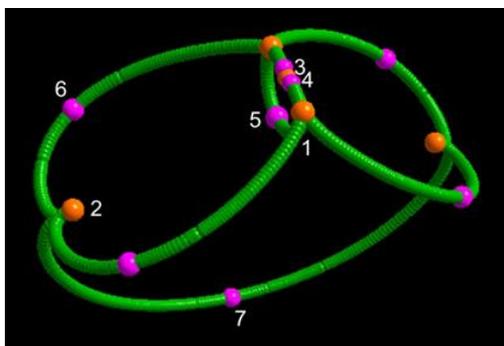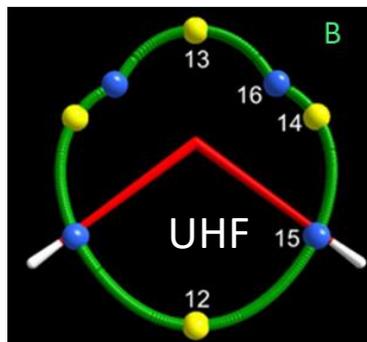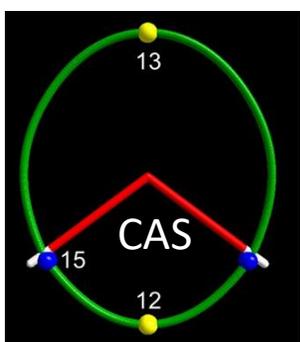*s*(**r**) CPs will clearly differ in number and location relative to those of ρ(**r**)

H$_2$O in the $^3B_1$ state

$s$ spin graph ($\alpha$-$\alpha$ maxima joining paths) and molecular graph (CAS)

3,-3 ⬤ (orange)
3,-1 ⬤ (magenta)



$s$ spin graph of only $s_{mag}$ (CAS)



CAS



UHF

$s$ spin graph ($\beta$-$\beta$ maxima joining paths)

3,-3 ⬤ (blue)
3,-1 ⬤ (yellow)   $-s(\mathbf{r})$

- ❑ $s$ topology is richer and less trivial than that of $\rho(\mathbf{r})$, **25 CPs vs 5, 15 vs 3** unique CPs (CAS level).

- ❑ $s(\mathbf{r})$, differently from $\rho(\mathbf{r})$ and likewise ESP or $\nabla^2\rho(\mathbf{r})$ exhibits either positive ($s_+$) or negative ($s_-$) local values. The only constraint on $s$ is that $\int_{R^3} s(\mathbf{r}) = n_\alpha$ (number of the excess $\alpha$-electrons)

- ❑ The possibility of negative values for a scalar has an impact on the total number and kind of its CPs. The scalar is topologically analysed by separating regions where it is >0 from those where it is <0 and by treating each of them as a distinct system.

- ❑ $s_+$ topology is (almost) stable with the method, while $s_-$ is largely method dependent (or absent by nature, ROHF)

- ❑ Each $s(\mathbf{r})$ may be decomposed into a *magnetic* (due to the fully unpaired $\alpha$-electron density, SONOs) and a *relaxation* part (due to *t*he remaining $\alpha$- and $\beta$-electrons density). The magnetic part is "stable" and resembles $s_+$ while the relaxation part is rather method dependent

- ❑ $n_{-3} - n_{-1} + n_{+1} - n_{+3} = n_+ - n_-$ ($n_+$ and $n_-$ number of asymptotic minima and maxima) If the $s_-$ regions are **fully embedded** in $s_+$ regions, $n_-$ will be equal to 0 and the CPs of the whole $s(\mathbf{r})$ fulfils $n_{-3} - n_{-1} + n_{+1} - n_{+3} = 1$ as $\rho(\mathbf{r})$ (Poincaré-Hopf relationship)

- ❑ The collection of $\alpha$-$\alpha$ maxima (or $\beta$-$\beta$ maxima) joining paths is a *molecular spin graph.* A spin-polarised system has as many $\alpha$-$\alpha$ and $\beta$-$\beta$ *molecular spin graphs* as is the number of its $s_+$ and $s_-$ separate regions. $\alpha$-$\alpha$ ($\beta$-$\beta$) maxima joining paths link maximally $\alpha$- ($\beta$-)polarized centers

SONO₁    SONO₂

CAS

UHF

$\rho(\mathbf{r})$    $s(\mathbf{r})$    $\rho_{A_1}(\mathbf{r}) \equiv s_{A_1}(\mathbf{r})$    $\rho_{B_1}(\mathbf{r}) \equiv s_{B_1}(\mathbf{r})$

$s_+$
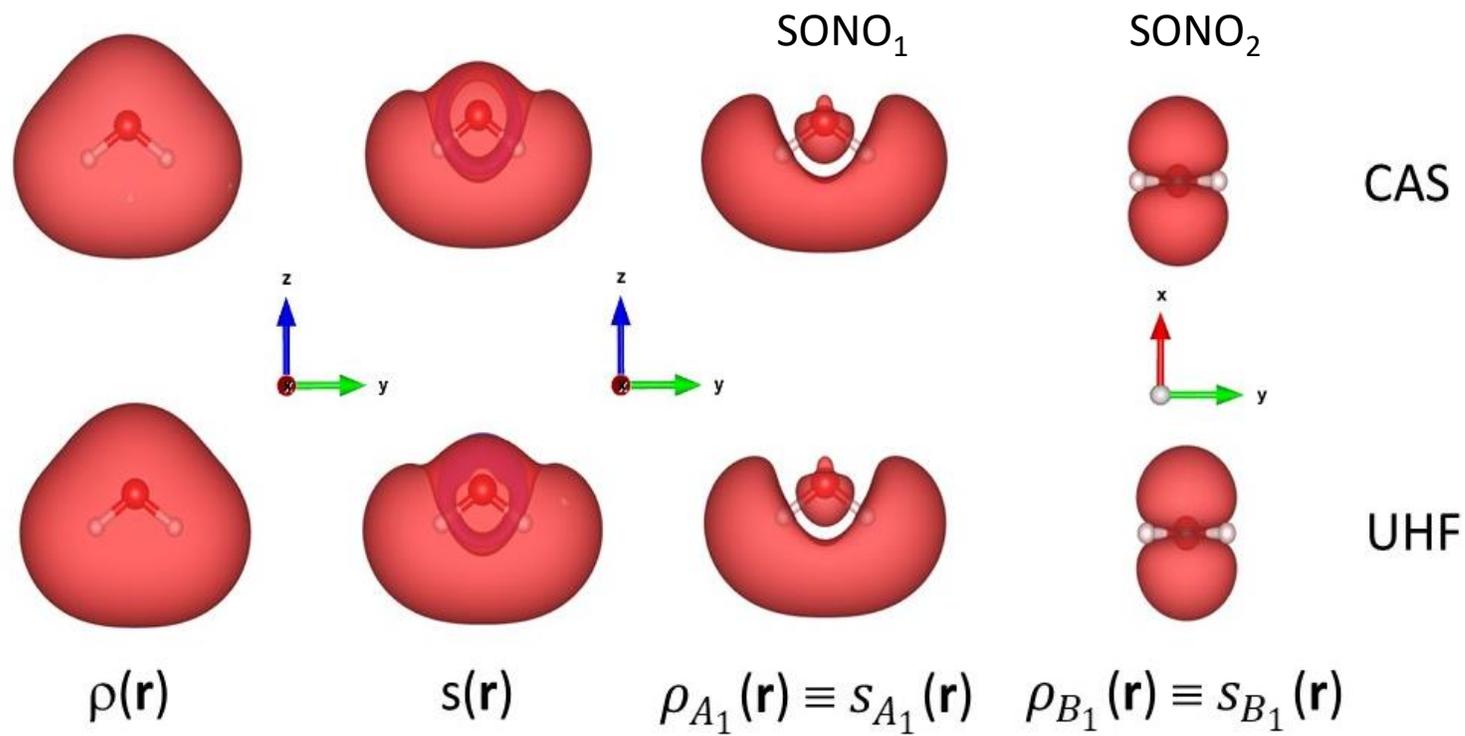
$s_-$

$s_-$
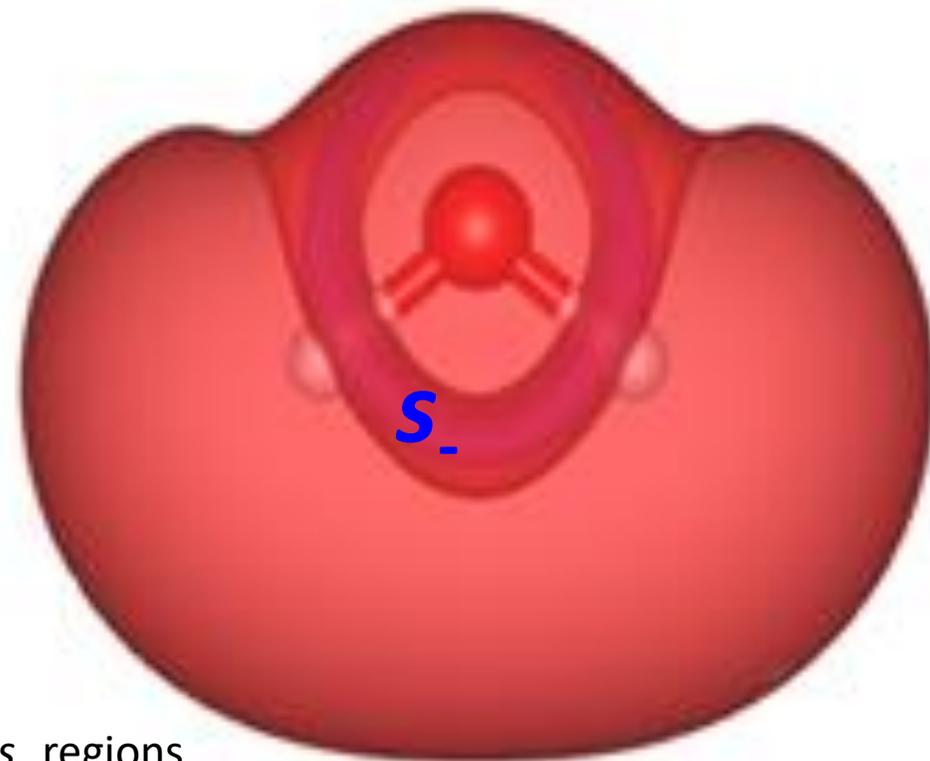
For $^3B_1$ $H_2O$ the $s_-$ regions are **fully embedded** in $s_+$ regions
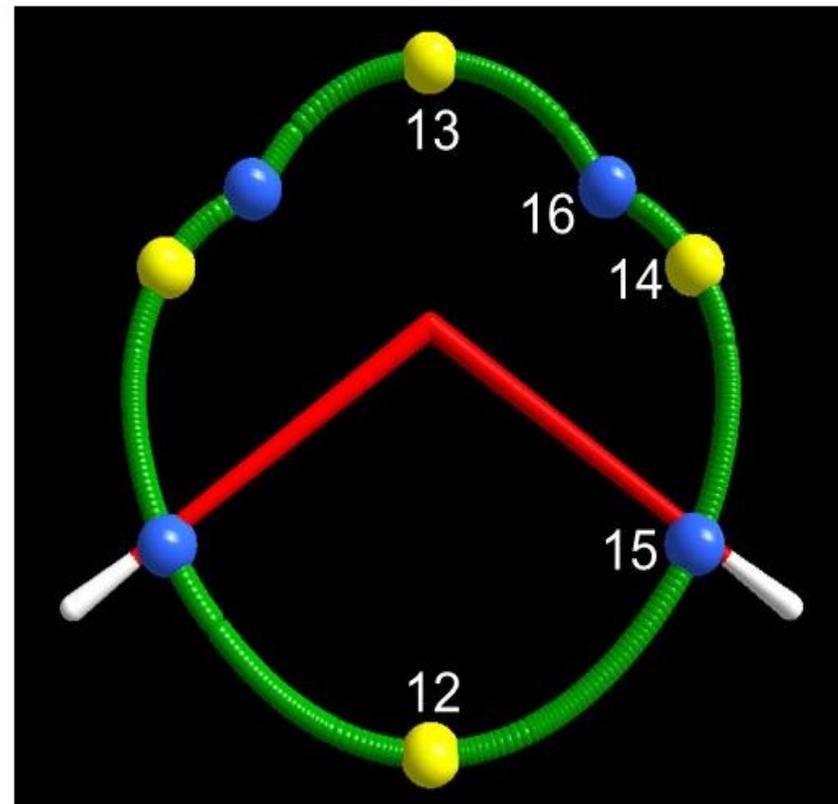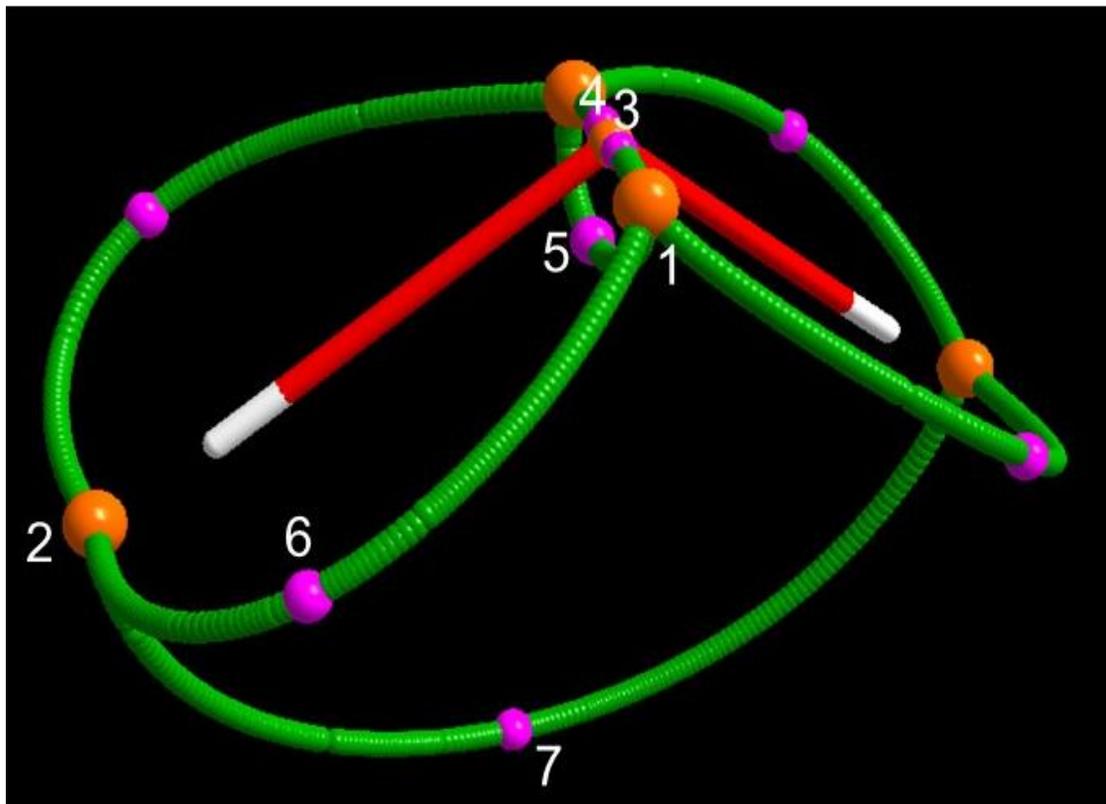
Two kinds of structures are associated with a spin-polarized molecule:

❑ *Molecular graph* structure (defined through $\nabla\rho$ and the collection of bond paths)

        +

❑ *Spin graph* magnetic structure (defined through $\nabla s$ and composed in general by at least two independent spin graphs, related to spin-density maxima and minima)
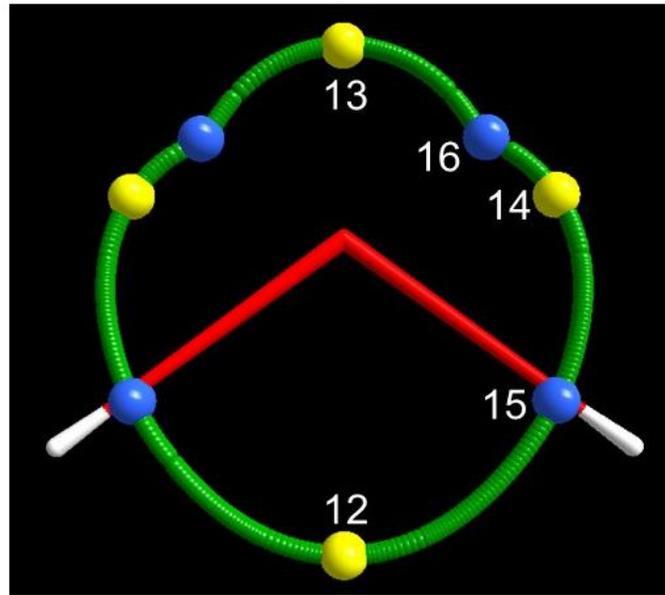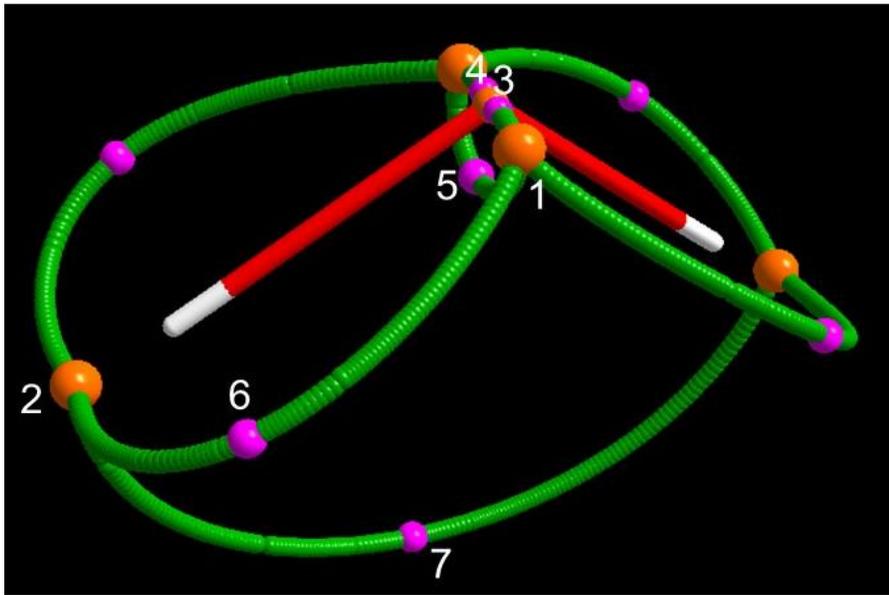
☐ The spin structure of the $^3B_1$ $H_2O$ molecule is more complex than its total electron structure, but both concur to a complete description of the molecule. It is like observing the same molecule by wearing two different pairs of lenses.

☐ One of these pairs is working in summation of the α- and β-densities, while the other in subtraction of the same densities.

The spin density structure does not have a direct connection between O and H nuclei as in the molecular graph. Yet, it exhibits a direct link between the maxima located nearby the H nuclei. The two O-H linkages of the conventional structure of $H_2O$ are replaced in the spin graph by 4 much longer linkages between maxima associated with the unpaired electrons of the O atom, lying quite far apart from the nucleus and the maxima close to the H nuclei. In addition, there are 3 more gradient paths, all contained within the O atomic basin

❑ The four kind of CPS may be further classified in 18 different types depending on relative concentration/depletion of the $\alpha$ and $\beta$ densities at CP

| CP(r,s) | $-\nabla^2 s$ | Type | $-\nabla^2\rho_\alpha$ | $-\nabla^2\rho_\beta$ | Constraint |
|---|---|---|---|---|---|
| (3, −3), max | > 0 | 1 | > 0 | > 0 | $-\nabla^2\rho_\alpha > -\nabla^2\rho_\beta$ |
| | > 0 | 2 | > 0 | < 0 | None |
| | > 0 | 3 | < 0 | < 0 | $|-\nabla^2\rho_\alpha| < |-\nabla^2\rho_\beta|$ |
| | | | | | |
| (3, −1), 1st order SP | > 0 | 1 | > 0 | > 0 | $-\nabla^2\rho_\alpha > -\nabla^2\rho_\beta$ |
| | > 0 | 2 | > 0 | < 0 | None |
| | > 0 | 3 | < 0 | < 0 | $|-\nabla^2\rho_\alpha| < |-\nabla^2\rho_\beta|$ |
| | < 0 | 4 | > 0 | > 0 | $-\nabla^2\rho_\alpha < -\nabla^2\rho_\beta$ |
| | < 0 | 5 | < 0 | > 0 | None |
| | < 0 | 6 | < 0 | < 0 | $|-\nabla^2\rho_\alpha| > |-\nabla^2\rho_\beta|$ |
| (3, +1), 2nd order SP | Same as for (3, −1) | | | | |
| (3, +3), min | < 0 | 1 | > 0 | > 0 | $-\nabla^2\rho_\alpha < -\nabla^2\rho_\beta$ |
| | < 0 | 2 | < 0 | > 0 | None |
| | < 0 | 3 | < 0 | < 0 | $|-\nabla^2\rho_\alpha| > |-\nabla^2\rho_\beta|$ |

3

6

6

3

18 in total

# Electron Spin density (3,-3) and (3,-1) CPs in the H₂O ³B₁ state

Title: Electron Spin density (3,-3) and (3,-1) CPs in the H$_2$O $^3$B$_1$ state

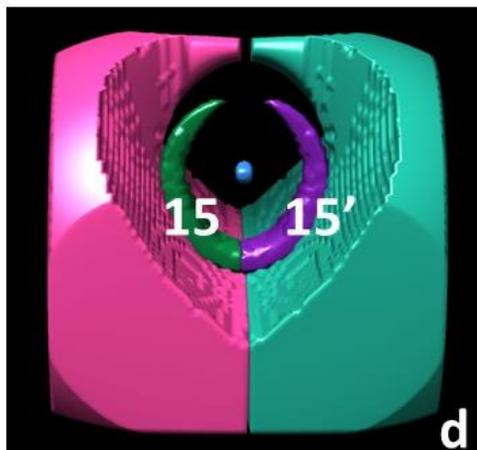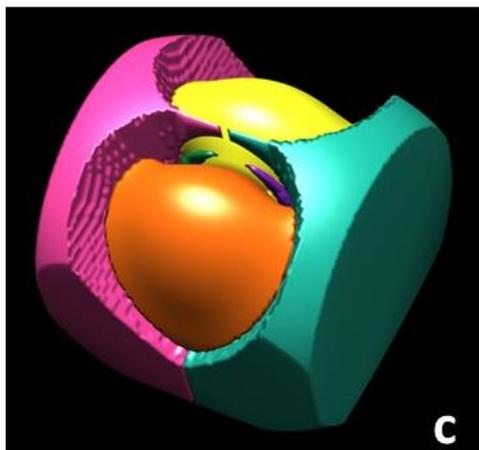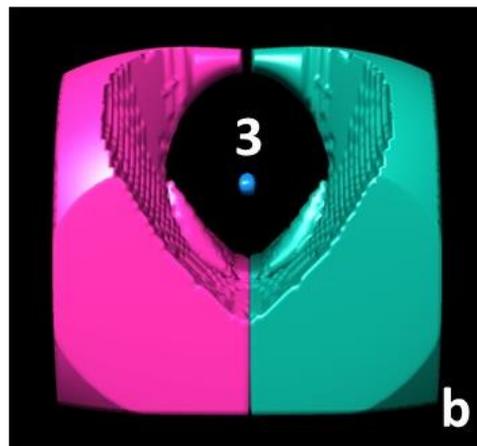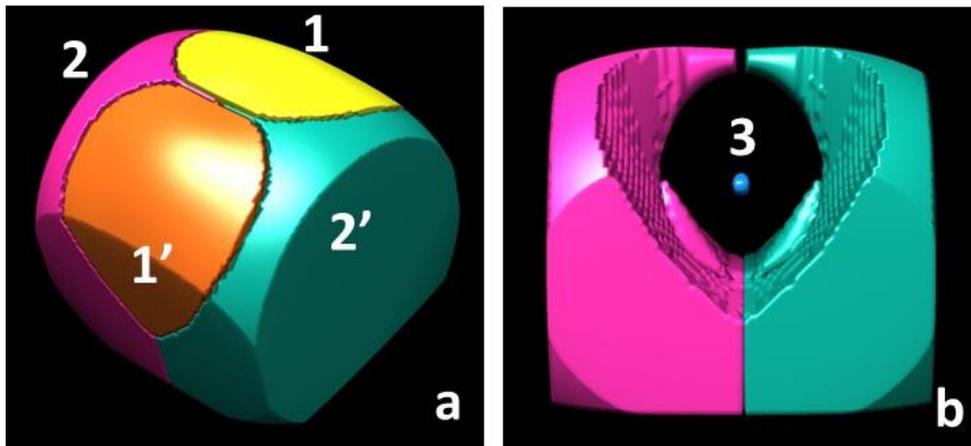| N | M | WFN | Type | s | $s_{mag}$ | $\rho$ | $\nabla\rho_\alpha \equiv \nabla\rho_\beta$ | $\nabla^2 s$ | $\nabla^2\rho_\alpha$ | $\nabla^2\rho_\beta$ | SPI($r_c$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | ROHF | 3 | 0.603 | 0.603 | 1.938 | 8.715 | −26.978 | 81.209 | 108.186 | 1.269 |
|   | 2 | UHF | 3 | 0.613 | 0.607 | 1.816 | 7.714 | −25.944 | 71.334 | 97.278 | 1.346 |
|   | 2 | CAS | 3 | 0.617 | 0.615 | 1.820 | 7.681 | −25.670 | 71.105 | 96.775 | 1.351 |
|   |   |   |   |   |   |   |   |   |   |   |   |
| 2 | 2 | ROHF | 1 | 0.018 | 0.018 | 0.263 | 0.341 | −0.697 | −5.517 | −4.821 | 0.765 |
|   | 2 | UHF | 2 | 0.015 | 0.016 | 0.090 | 0.123 | −0.119 | −0.091 | 0.028 | 0.923 |
|   | 2 | CAS | 3 | 0.012 | 0.014 | 0.072 | 0.096 | −0.082 | 0.003 | 0.086 | 0.936 |
|   |   |   |   |   |   |   |   |   |   |   |   |
| 3 | 1 | ROHF | 1 | 0.683 | 0.683 | 295.534 | 557.768 | $-5.6 \times 10^3$ | $-1.2 \times 10^6$ | $-1.2 \times 10^6$ | 0.670 |
|   | 1 | UHF | 1 | 0.840 | 0.706 | 295.432 | 587.366 | $-6.7 \times 10^3$ | $-1.2 \times 10^6$ | $-1.2 \times 10^6$ | 0.670 |
|   | 1 | CAS | 1 | 1.262 | 0.725 | 295.814 | 408.328 | $-10.1 \times 10^3$ | $-1.2 \times 10^6$ | $-1.2 \times 10^6$ | 0.672 |
| 4 | 2 | ROHF | 1 | 0.367 | 0.367 | 82.250 | 648.694 | −45.534 | $-4.85 \times 10^3$ | $-4.80 \times 10^3$ | 0.673 |
|   | 2 | UHF | 1 | 0.415 | 0.380 | 64.569 | 503.389 | −47.064 | $-1.91 \times 10^3$ | $-1.86 \times 10^3$ | 0.675 |
|   | 2 | CAS | 1 | 0.474 | 0.417 | 41.885 | 323.092 | −45.172 | −66.122 | −20.950 | 0.682 |
|   |   |   |   |   |   |   |   |   |   |   |   |
| 5 | 1 | ROHF | 6 | 0.094 | 0.094 | 1.265 | 1.691 | 2.051 | 8.785 | 6.734 | 0.773 |
|   | 1 | UHF | 6 | 0.130 | 0.100 | 1.308 | 1.921 | 1.206 | 11.013 | 9.807 | 0.813 |
|   | 1 | CAS | 6 | 0.147 | 0.102 | 1.327 | 2.032 | 0.850 | 11.728 | 10.877 | 0.833 |
|   |   |   |   |   |   |   |   |   |   |   |   |
| 6 | 4 | ROHF | 6 | 0.006 | 0.006 | 0.085 | 0.098 | 0.023 | 0.099 | 0.077 | 0.744 |
|   | 4 | UHF | 6 | 0.005 | 0.006 | 0.048 | 0.057 | 0.013 | 0.086 | 0.073 | 0.819 |
|   | 4 | CAS | 6 | 0.004 | 0.005 | 0.039 | 0.047 | 0.010 | 0.076 | 0.066 | 0.826 |
|   |   |   |   |   |   |   |   |   |   |   |   |
| 7 | 1 | ROHF | 3 | 0.003 | 0.003 | 0.006 | 0.003 | −0.002 | 0.003 | 0.006 | 2.455 |
|   | 1 | UHF | 3 | 0.003 | 0.004 | 0.006 | 0.003 | −0.003 | 0.003 | 0.005 | 2.575 |
|   | 1 | CAS | 3 | 0.003 | 0.003 | 0.006 | 0.003 | −0.003 | 0.002 | 0.005 | 2.581 |
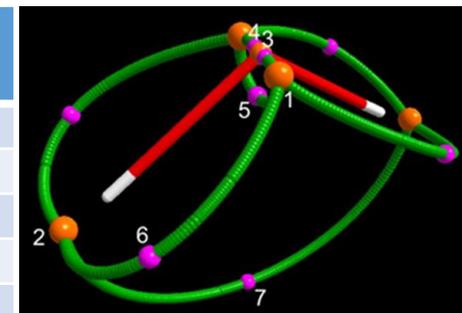


$$\text{SPI}(\mathbf{r}) = \frac{\rho_\alpha(\mathbf{r})/\rho\beta(\mathbf{r})]}{N_\alpha/N\beta}$$

**S**pin **P**olarization **I**ndex

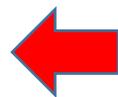SPI $\equiv$ 1 if local polarization is = to the average

> 1 higher; < 1 lower

No polarization
$1/ (N_\alpha/N\beta)$
(0.667 for H$_2$O $^3$B$_1$ state)

Basins bounded by local Zero-Flux Surfaces (ZFS) of $\nabla s$

May contain points with either $s(r)>0$ and $s(r)<0$
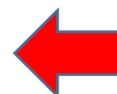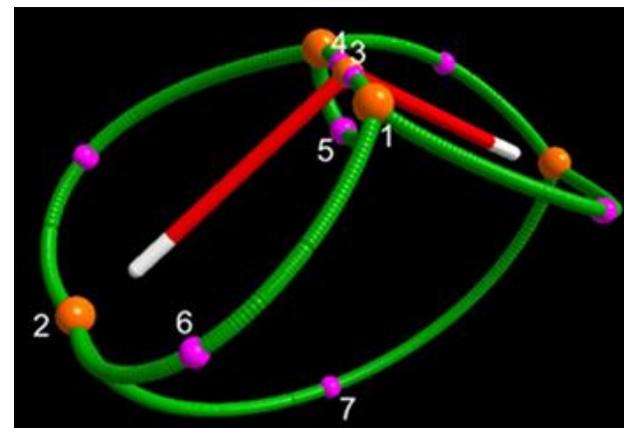The $\nabla s$ ZFS basins are not "quantum" object, so other basins are worth of being considered

$^3B_1$ H$_2$O CAS spin-density basins

Basins labelled by their enclosed (3, −3) spin maximum or, for basin 15, by its enclosed (3, +3) spin minimum

Each basin retains the same colour in all panels

Basins bounded by $s = 0$ isosurfaces ($s_+$ and $s_-$ basins)

They contains only positive ($s_+$) or only negative ($s_-$) $s$ points. This disjoint, exhaustive and alternative $R^3$ space partition, separates molecular regions in terms of their α- or β-density dominance. The sum of population of $s_-$ basins yields a quantitative measure of the spin counter-polarization effect, enabling to judge the quality of the wf model ($\Sigma = 0$ for ROHF)

Panels **b** (**d**) differ from panels **a** (**c**) for the removal of basins 1 and 1'. The small, embedded basin 3 around the O nucleus is disclosed
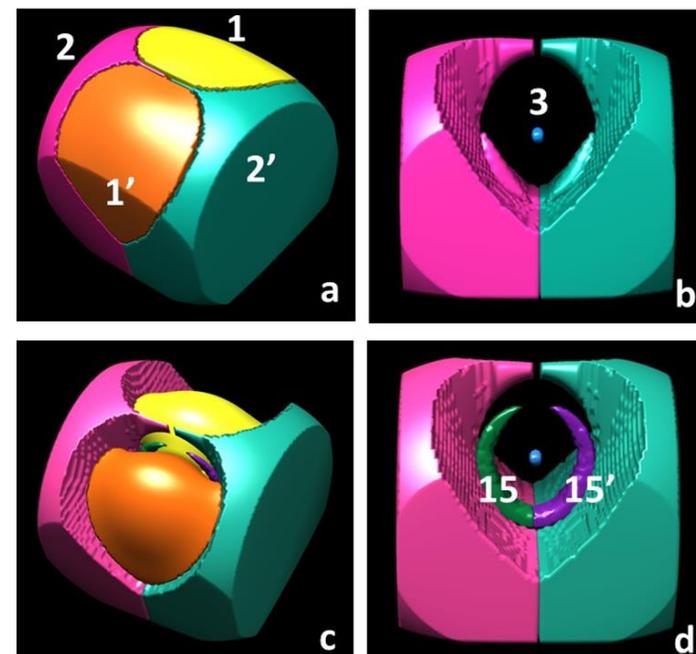
$$\mathrm{SPI}_\Omega = \frac{N_{\alpha,\Omega}/N_{\beta,\Omega}}{N_\alpha/N_\beta}$$

Basin SPI : Same meaning as the local SPI, but referred to the whole basin

$$\bar{s}_\Omega = SP_\Omega/V1_\Omega$$

$\bar{s}_\Omega$ is an absolute measure of the basin average α-electron excess.

| $\Omega$ | M | WFN | $N_\Omega$ | $SP_\Omega$ | $SP_{mag,\Omega}$ | $SPI_\Omega$ | $V1_\Omega$ | $V2_\Omega$ | $\bar{s}_\Omega$ |
|---|---|---|---|---|---|---|---|---|---|
| ∇ρ ZFS boundaries |
| O | 1 | ROHF | 8.867 | 1.409 | = | 0.919 | 180.6 | 127.4 | 0.008 |
|  | 1 | UHF | 8.856 | 1.417 | 1.409 | 0.921 | 179.2 | 126.8 | 0.008 |
|  | 1 | CAS | 8.743 | 1.406 | 1.387 | 0.922 | 173.3 | 122.5 | 0.008 |
| H | 2 | ROHF | 0.565 | 0.294 | = | 2.113 | 71.8 | 39.8 | 0.004 |
|  | 2 | UHF | 0.571 | 0.290 | 0.295 | 2.046 | 72.2 | 40.3 | 0.004 |
|  | 2 | CAS | 0.628 | 0.296 | 0.306 | 1.856 | 76.9 | 42.6 | 0.004 |
| ∇s ZFS boundaries |
| $\Omega_1$ | 2 | ROHF | 3.469 | 0.587 | = | 0.938 | 53.9 | 42.0 | 0.011 |
|  | 2 | UHF | 3.740 | 0.597 | 0.591 | 0.920 | 52.1 | 40.9 | 0.011 |
|  | 2 | CAS | 3.620 | 0.604 | 0.595 | 0.934 | 52.4 | 40.9 | 0.012 |
| $\Omega_2$ | 2 | ROHF | 0.901 | 0.409 | = | 1.773 | 108.3 | 61.4 | 0.004 |
|  | 2 | UHF | 0.907 | 0.402 | 0.407 | 1.727 | 109.8 | 62.7 | 0.004 |
|  | 2 | CAS | 0.913 | 0.394 | 0.403 | 1.676 | 111.2 | 63.0 | 0.004 |
| $\Omega_3$ | 1 | ROHF | 1.231 | 0.006 | = | 0.673 | 0.04 | 0.04 | 0.174 |
|  | 1 | UHF | 0.699 | 0.003 | 0.002 | 0.672 | 0.01 | 0.01 | 0.196 |
|  | 1 | CAS | 0.935 | 0.005 | 0.002 | 0.674 | 0.02 | 0.02 | 0.231 |
| s = 0 isovalue surface boundaries |
| $\Omega_1$ | 2 | UHF | 3.574 | 0.598 | 0.587 | 0.935 | 50.9 | 39.7 | 0.012 |
|  | 2 | CAS | 3.509 | 0.606 | 0.589 | 0.945 | 51.6 | 40.2 | 0.012 |
| $\Omega_2$ | 2 | UHF | 0.836 | 0.403 | 0.409 | 1.906 | 109.4 | 62.3 | 0.004 |
|  | 2 | CAS | 0.821 | 0.395 | 0.407 | 1.901 | 110.6 | 62.3 | 0.004 |
| $\Omega_3$ | 1 | UHF | 0.640 | 0.002 | 0.002 | 0.671 | 0.01 | 0.01 | 0.210 |
|  | 1 | CAS | 0.916 | 0.005 | 0.004 | 0.674 | 0.02 | 0.02 | 0.237 |
| $\Omega_{15}$ | 2 | UHF | 0.173 | −0.002 | 0.002 | 0.653 | 1.02 | 1.02 | −0.002 |
|  | 2 | CAS | 0.212 | −0.003 | 0.003 | 0.650 | 1.45 | 1.45 | −0.002 |
| $\Omega_{16}$ | 2 | UHF | 0.097 | −0.000 | 0.001 | 0.660 | 0.68 | 0.68 | −0.001 |

| $\Omega$ | M | WFN | $N_\Omega$ | $SP_\Omega$ | $SP_{mag,\Omega}$ | $SPI_\Omega$ | $V1_\Omega$ | $V2_\Omega$ | $\bar{s}_\Omega$ |
|---|---|---|---|---|---|---|---|---|---|
| $\nabla\rho$ ZFS boundaries |||||||||
| O | 1 | ROHF | 8.867 | 1.409 | = | 0.919 | 180.6 | 127.4 | 0.008 |
|  | 1 | UHF | 8.856 | 1.417 | 1.409 | 0.921 | 179.2 | 126.8 | 0.008 |
|  | 1 | CAS | 8.743 | 1.406 | 1.387 | 0.922 | 173.3 | 122.5 | 0.008 |
| H | 2 | ROHF | 0.565 | 0.294 | = | 2.113 | 71.8 | 39.8 | 0.004 |
|  | 2 | UHF | 0.571 | 0.290 | 0.295 | 2.046 | 72.2 | 40.3 | 0.004 |
|  | 2 | CAS | 0.628 | 0.296 | 0.306 | 1.856 | 76.9 | 42.6 | 0.004 |
| $\nabla s$ ZFS boundaries |||||||||
| $\Omega_1$ | 2 | ROHF | 3.469 | 0.587 | = | 0.938 | 53.9 | 42.0 | 0.011 |
|  | 2 | UHF | 3.740 | 0.597 | 0.591 | 0.920 | 52.1 | 40.9 | 0.011 |
|  | 2 | CAS | 3.620 | 0.604 | 0.595 | 0.934 | 52.4 | 40.9 | 0.012 |
| $\Omega_2$ | 2 | ROHF | 0.901 | 0.409 | = | 1.773 | 108.3 | 61.4 | 0.004 |
|  | 2 | UHF | 0.907 | 0.402 | 0.407 | 1.727 | 109.8 | 62.7 | 0.004 |
|  | 2 | CAS | 0.913 | 0.394 | 0.403 | 1.676 | 111.2 | 63.0 | 0.004 |
| $\Omega_3$ | 1 | ROHF | 1.231 | 0.006 | = | 0.673 | 0.04 | 0.04 | 0.174 |
|  | 1 | UHF | 0.699 | 0.003 | 0.002 | 0.672 | 0.01 | 0.01 | 0.196 |
|  | 1 | CAS | 0.935 | 0.005 | 0.002 | 0.674 | 0.02 | 0.02 | 0.231 |
| s = 0 isovalue surface boundaries |||||||||
| $\Omega_1$ | 2 | UHF | 3.574 | 0.598 | 0.587 | 0.935 | 50.9 | 39.7 | 0.012 |
|  | 2 | CAS | 3.509 | 0.606 | 0.589 | 0.945 | 51.6 | 40.2 | 0.012 |
| $\Omega_2$ | 2 | UHF | 0.836 | 0.403 | 0.409 | 1.906 | 109.4 | 62.3 | 0.004 |
|  | 2 | CAS | 0.821 | 0.395 | 0.407 | 1.901 | 110.6 | 62.3 | 0.004 |
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|  | 1 | CAS | 0.916 | 0.005 | 0.004 | 0.674 | 0.02 | 0.02 | 0.237 |
| $\Omega_{15}$ | 2 | UHF | 0.173 | −0.002 | 0.002 | 0.653 | 1.02 | 1.02 | −0.002 |
|  | 2 | CAS | 0.212 | −0.003 | 0.003 | 0.650 | 1.45 | 1.45 | −0.002 |
| $\Omega_{16}$ | 2 | UHF | 0.097 | −0.000 | 0.001 | 0.660 | 0.68 | 0.68 | −0.001 |

- ❑ The electron and ($\alpha$-$\beta$) spin population of all s_ basins sum up to 0.424 and −0.006 $e^-$ at the CAS level and to 0.540 and −0.004 $e^-$ at the UHF level.

- ❑ About 6% of the valence electrons in the molecule are included in these basins.

- ❑ The spin populations of these basins are dominated by the relaxation component, $SP_{mag,\Omega}$ being, by nature, positive.

- ❑ The spin polarization index $SPI_\Omega$ needs to be smaller than 2/3, but it is just below this value (about 0.65), marginally different from the $\rho_\alpha = \rho_\beta$ reference value (2/3)

- ❑ $N_\Omega$ and $SP_\Omega$ values, sizes and other properties of the s_ basins collectively highlight the relevance of going beyond ROHF restriction

## Preliminary Conclusions

❑ Novel notions, such as *spin graphs*, spin *basins* and spin *valence*, and novel descriptors, such as the local/integral *Spin Polarization Indices* (SPI) or the *basin average spin density*

❑ Two kinds of structures associated with a spin-polarized molecule (the usual one and the magnetic structure consisting of at least two spin graphs

❑ Local and nonlocal s(**r**) descriptors help to explain real–space magnetic structure and to single out those features that are largely model dependent

❑ Spin-density topology discloses a wealth of chemically and physically meaningful information. Most of the introduced spin-density descriptors do not require the explicit knowledge of the system's wavefunction, being therefore amenable to experimental investigation of the s(**r**) observable

❑ Pioneering studies based on combined X-ray and neutron structure factors are already available; in the next future, it is foreseeable that a combination of accurate neutron detectors and more intense sources will disclose more and more reliable and precise experimental spin-density distributions in crystalline materials

❑ The topological toolbox helps to gains insights into yet unexplored aspects of complex magnetic structures

❑ Stereospecific recognition of chiral molecules is an important issue in various aspects of life sciences and chemistry including analytical separation sciences



enantioselective molecular recognition adapted to liquid phase separation

$K_1$ adsorption / desorption

$K_2$ adsorption / desorption

stationary phase — chiral selector (enantiopure)

enantiomer 1

stationary phase

diastereomeric complex less stable (enantiomer 1 first eluted)
$\Delta G_1 = - RT \ln K_1$

$$\Delta\Delta G = \Delta G_2 - \Delta G_1$$
$$\Delta\Delta G = - RT \ln(K_2/K_1) = - RT \ln\alpha$$
$$\alpha \text{ separation factor} = K_2/K_1$$

diastereomeric complex more stable (enantiomer 2 second eluted)
$\Delta G_2 = - RT \ln K_2$

chiral stationary phase (CSP)

enantiomer 2

chiral analyte (selectand)

solvated environment (mobile phase)

attractive and/or repulsive noncovalent interactions dependent on chiral selector, chiral analyte and mobile phase underlie complex formation

❑ The basis of analytical enantioseparations is the formation of transient diastereomeric complexes  driven by **hydrogen bonds or ionic, ion-dipole, dipole-dipole, van der Waals as well as π-π interactions**

# Halogen and chalcogen bonds

❑ XB can drive enantioseparations in HPLC environment. XB is profiled as a chemo-, regio-, site- and stereoselective interaction which is active in HPLC environment *besides* other known interactions based on the complementarity between selector and selectand

❑ Chalcogen bonds (ChB) were also found to act as stereoselective secondary interactions for HPLC enantioseparations



**halogen bond**

**X = Cl, Br, I**

MEP

**chalcogen bond**

**Ch = S, Se, Te**

**A = Lewis base (O, N, S, halogen, $\pi$-donor, anion); Y = EWG**
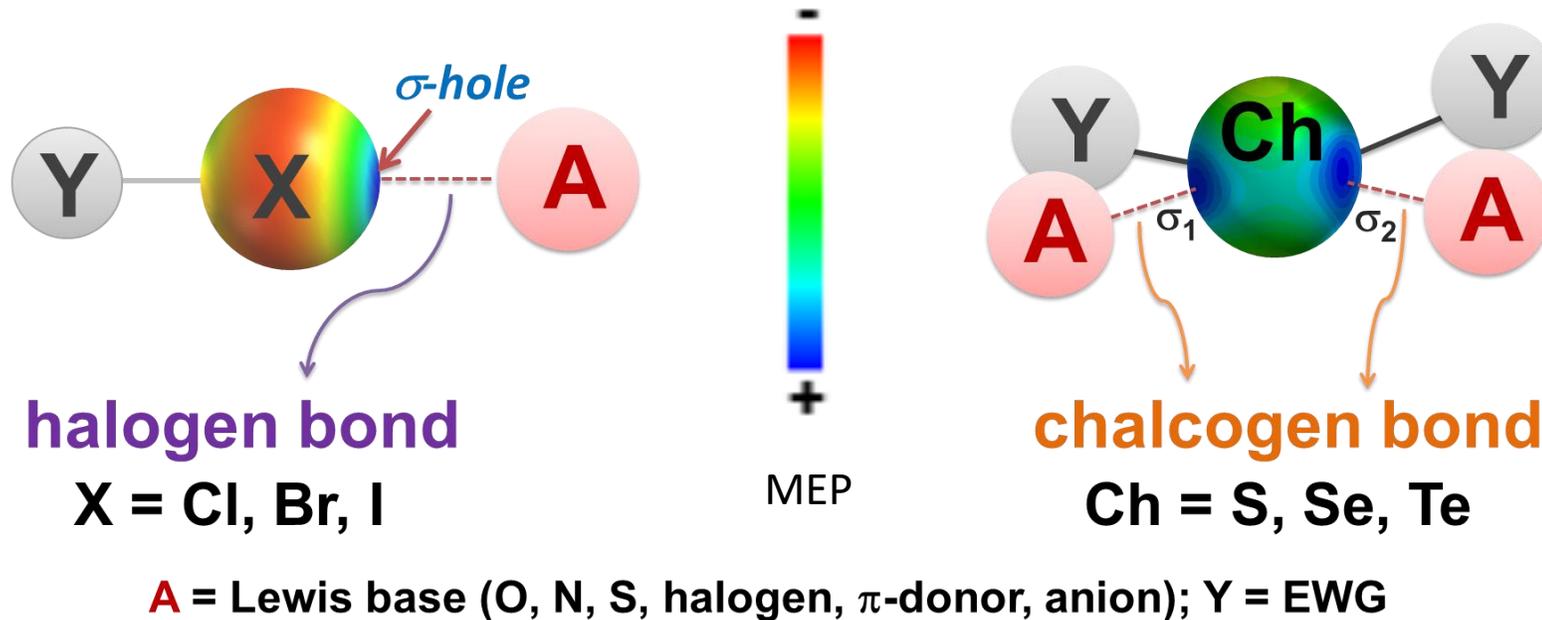
ChB: $\sigma$-hole based NCI between a Lewis base and an electrophilic element of group VI, which behaves as a Lewis acid

# Selectand and selector examples

selectand

selector

**chiral analytes**

(EP legend: - ▬▬▬▬ +)
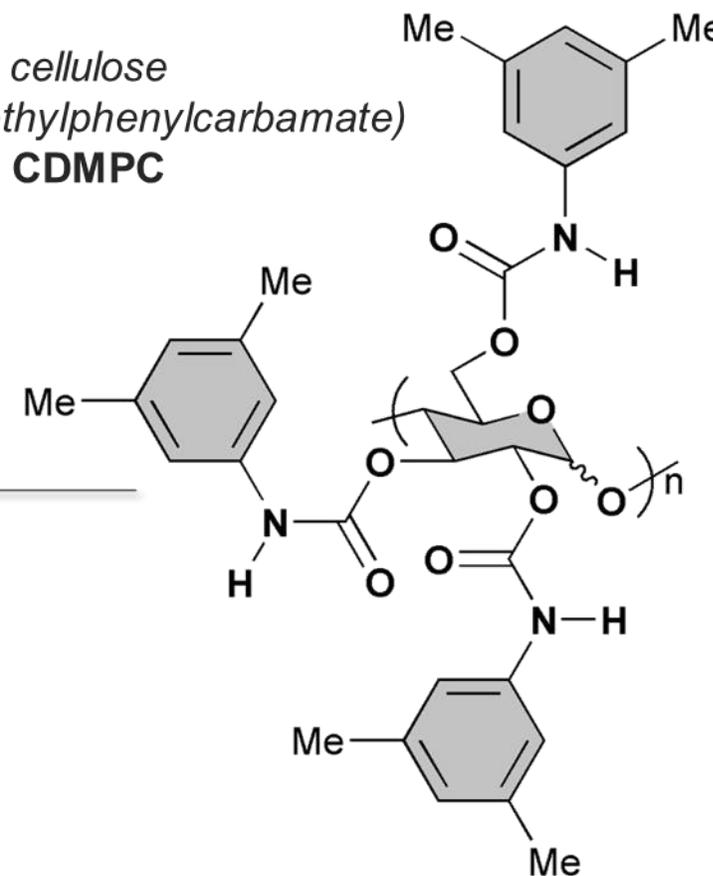
**chiral stationary phase**
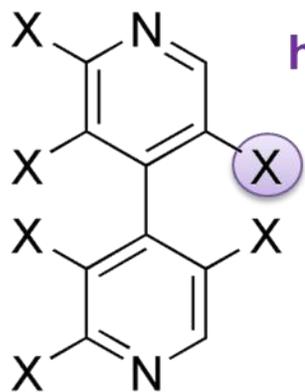
**halogen bond donors**
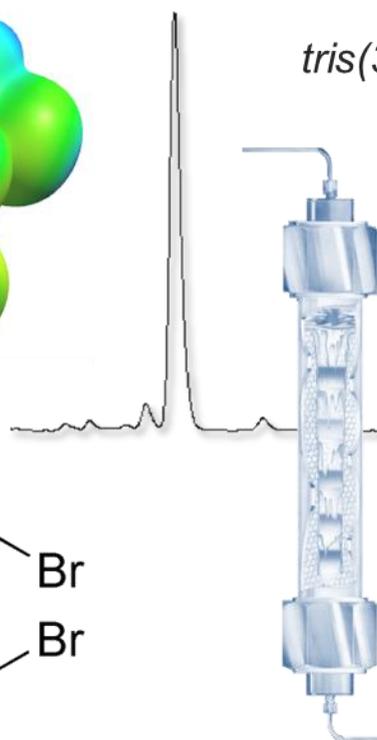
*electrostatic potential surface (EPS), X = I*

*cellulose tris(3,5-dimethylphenylcarbamate)* **CDMPC**
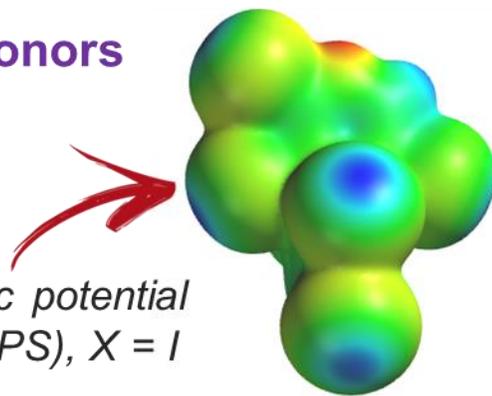
**chalcogen bond donors**
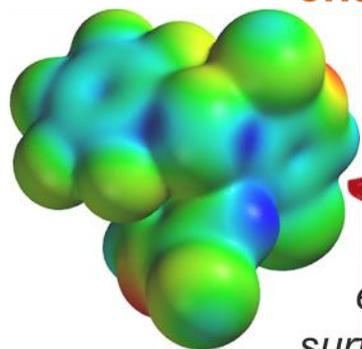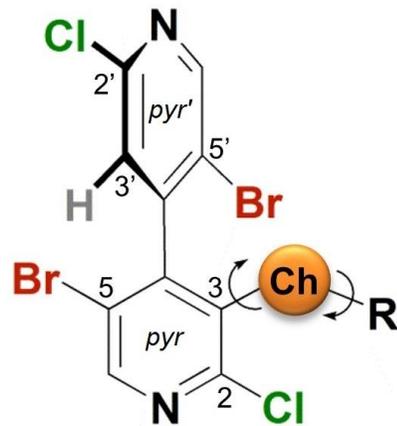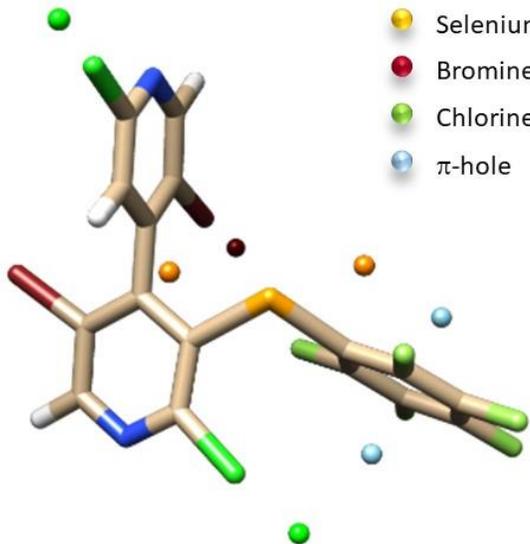
*electrostatic potential surface (EPS), R = SeC₆F₅*

X- or Ch- substituted atropoisomeric 4,4'-bipyridines as σ-donors

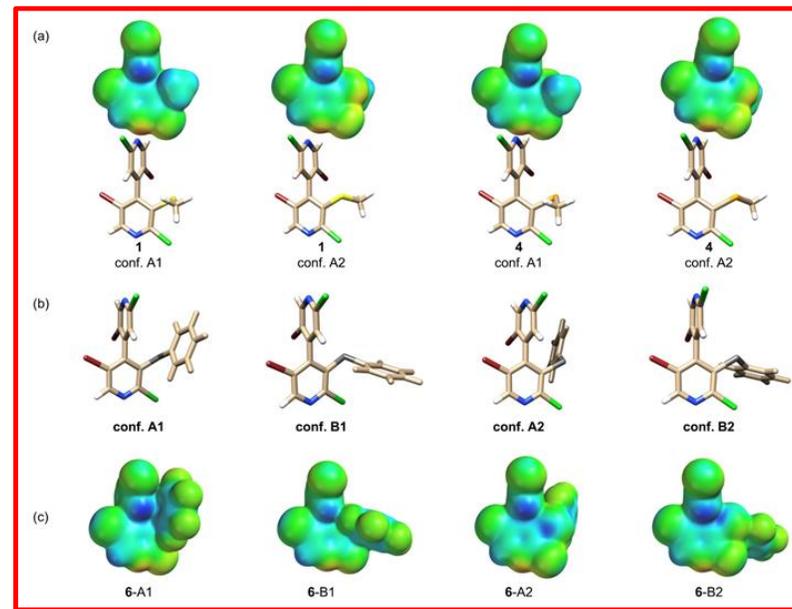Cellulose-based polymers as XB acceptors

# σ- and π-hole magnitude variability



Selenium σ-hole
Bromine σ-hole
Chlorine σ-hole
π-hole

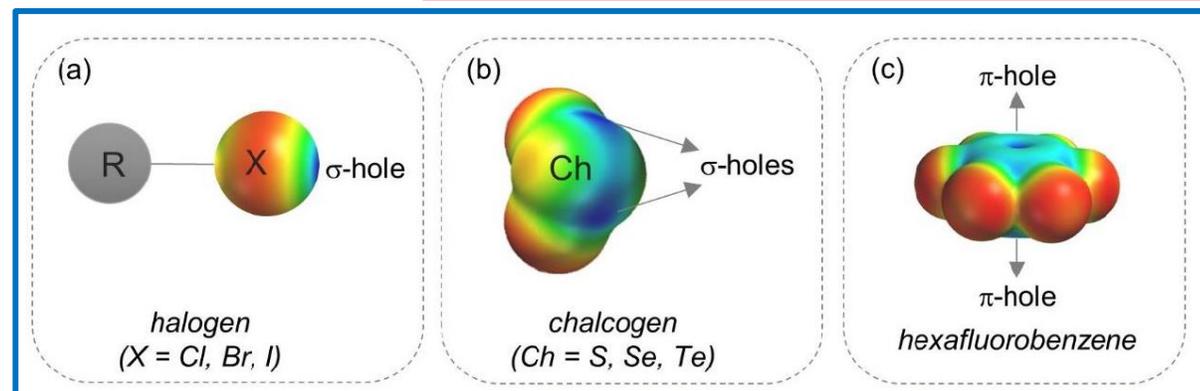Substitution pattern
1: Ch = S, R = Me
2: Ch = S, R = Ph
3: Ch = S, R = $C_6F_5$
4: Ch = Se, R = Me
5: Ch = Se, R = Ph
6: Ch = Se, R = $C_6F_5$

$V(r)$ Extrema on the 0.002 au ED isosurface

| Hole | $V_{min} \leftrightarrow V_{max}$, au | $\Delta V$, au |
|------|------|------|
| σ-hole $C_{pyr}$-Ch | $0.027 \leftrightarrow 0.059$ | 0.032 |
| σ-hole $C_R$-Ch | $0.017 \leftrightarrow 0.061$ | 0.044 |
| π-holes | $-0.015 \leftrightarrow 0.054$ | 0.069 |

(a) halogen (X = Cl, Br, I)
(b) chalcogen (Ch = S, Se, Te)
(c) hexafluorobenzene

❑ How can we interpret these dramatic changes in the σ/π hole V values?

❑ Can we find a tool enabling us to design changes in the σ- and π-hole regions aimed at affecting their potential involvement in noncovalent interactions in a desired way?

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❑ σ- and π-hole regions are important in molecular recognition processes (e.g. in HPLC enantiomeric separation)

❑ Hole regions may be revealed through V. *However* V(r) is a function of the whole molecular electron/nuclear distribution

**QUESTION : Which group/moiety is/are responsible of ΔV due to chemical/conformational changes?**

$$V(\mathbf{r}) = V_{elec}(\mathbf{r}) + V_{nuc}(\mathbf{r}) = \left[ -\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \sum_A \frac{Z_A}{|\mathbf{r}-\mathbf{R}_A|} \right] = \sum_\Omega \left[ -\int_\Omega \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{Z_\Omega}{|\mathbf{r}-\mathbf{R}_\Omega|} \right] =$$

Ω, Bader's atomic or atomic group basin

$$= \sum_\Omega [V_{elec}(\mathbf{r},\Omega) + V_{nuc}(\mathbf{r},\Omega)] = \sum_\Omega V(\mathbf{r},\Omega)$$ ⟹ *V*(**r**,Ω) ≡ *SF*(**r**, Ω) to *V*(**r**)

$\nabla\rho$
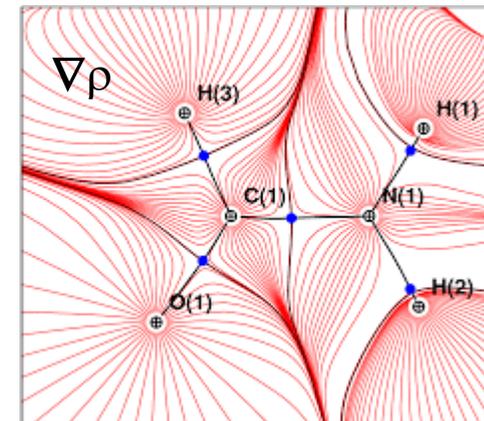
∇ρ·**n** = 0 ∀ **r**$_s$∈ *S* where *S* are the bounding surfaces of quantum atoms Ω

$$\rho(\mathbf{r}) = \int_{all\ space} LS(\mathbf{r},\mathbf{r}')\cdot d\mathbf{r}' = \sum_\Omega \int_\Omega LS(\mathbf{r},\mathbf{r}')\cdot d\mathbf{r}' \equiv \sum_\Omega SF(\mathbf{r},\Omega)$$

$$LS(\mathbf{r},\mathbf{r}') = -\frac{(1/4\pi)}{|\mathbf{r}-\mathbf{r}'|}\nabla^2\rho(\mathbf{r}')$$ For *V*, ∇²*V* (**r**) = ρ(**r**), Poisson equation

Source Function approach to chemistry, Bader RFW and Gatti C, *Chem. Phys. Lett*. 287, 233 (1998)

$\nabla^2\rho$

CAUSE

EFFECT

$\rho$

**ANSWER : Rigorous V decomposition in group/moiety contributions enables to get insights on group/atomic contributions to V(r) and enables efficient molecular design**
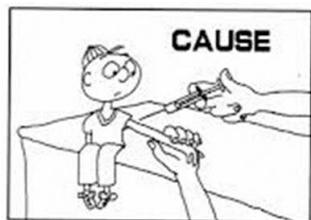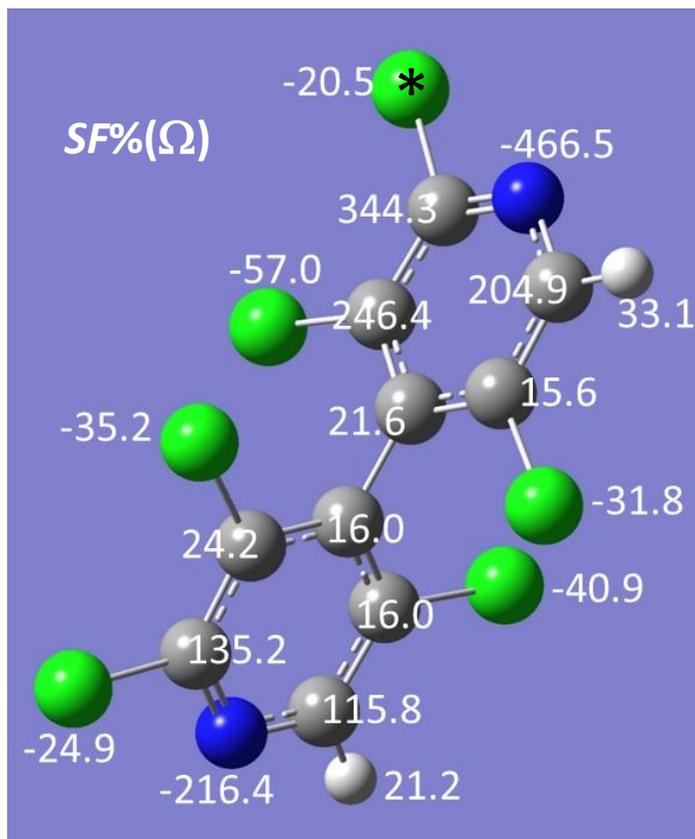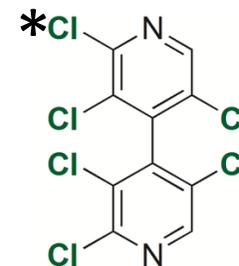
# A useful tool or just a nightmare?

**SF% decomposition of EP σ-hole close to Cl***

$$V(\mathbf{r}) = V_{elec}(\mathbf{r}) + V_{nuc}(\mathbf{r}) = \left[ -\int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \right] = \sum_\Omega \left[ -\int_\Omega \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{Z_\Omega}{|\mathbf{r} - \mathbf{R}_\Omega|} \right]$$





Two problems:

1) $V_{elec}$ and $V_{nuc}$ have different sign and on the 0.002 au ρ isosurface their sum, i.e. $V$, is very small and typically 4 order of magnitude smaller in magnitude than either $V_{elec}$ or $V_{nuc}$

2) The individual Ω give *SF%* contributions that are either positive or negative and of the same order of magnitude as the value of *V* itself

Apparently a nightmare….

# The suite of developed SW codes and the solution

**GAUSSIAN-XX**

.wfn file

**MULTIWFN**
module enabling quantitative analyses of molecular surfaces

$V(\mathbf{r})$ σ-hole maxima on the 0.002 au ED isosurface

**VEXTLOC**
associate EP extrema to Ω's. Select those of interest for the SF EP analysis

❑ **Multiwfn** T. Lu, F. Chen, J.Comp. Chem. 33, (2012) 580-592

❑ **Quantitative Analysis of Molecular Surfaces** based on improved Marching Tetrahedra algorithm, T. Lu, F. Chen, J. Mol. Graph. Model., 38 (2012) 314

❑ **Other codes**, except Gaussian-XX, **are home made** (C. Gatti)

**ANASFR_EP_ED**
Check accuracy of SF reconstructions Extract and combine $SF_V(r,\Omega)$ and $SF_\rho(r,\Omega)$ values in SF group contributions

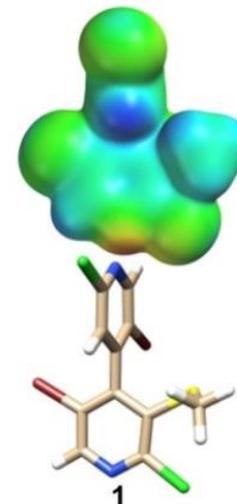$V(\mathbf{r},\Omega) \equiv SF_V(\mathbf{r},\Omega)$ and $SF_\rho(\mathbf{r},\Omega)$ values
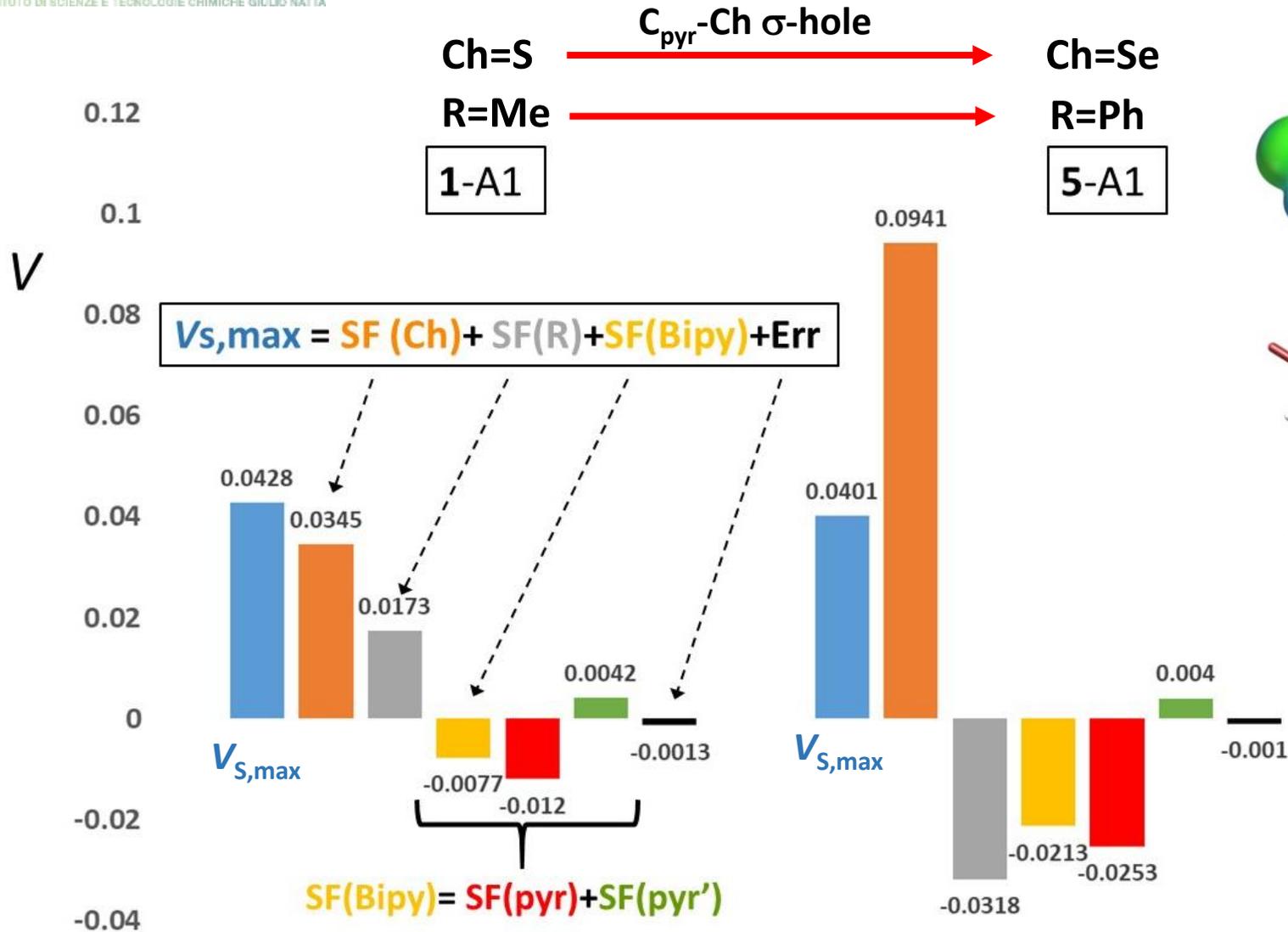
$V(\mathbf{r})$ values +{$\mathbf{r}$} *rps* SF analysis of $V(\mathbf{r})$

**SF_ESI code**
$V(\mathbf{r})$ and $\rho(\mathbf{r})$ SF reconstructions

SCITEC
ISTITUTO DI SCIENZE E TECNOLOGIE CHIMICHE GIULIO NATTA

# Example I



$C_{pyr}$-Ch σ-hole

Ch=S → Ch=Se

R=Me → R=Ph

**1**-A1    **5**-A1

$V_{s,max}$ = SF (Ch)+ SF(R)+SF(Bipy)+Err

$V_{S,max}$

0.0428  0.0345  0.0173  0.0042  -0.0013
-0.0077  -0.012

SF(Bipy)= SF(pyr)+SF(pyr')

$V_{S,max}$

0.0401  0.0941  0.004  -0.001
-0.0213  -0.0253  -0.0318

A1 conformer

Substitution pattern
**1**: Ch = S, R = Me
**2**: Ch = S, R = Ph
**3**: Ch = S, R = $C_6F_5$
**4**: Ch = Se, R = Me
**5**: Ch = Se, R = Ph
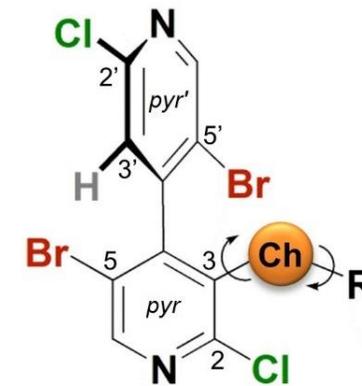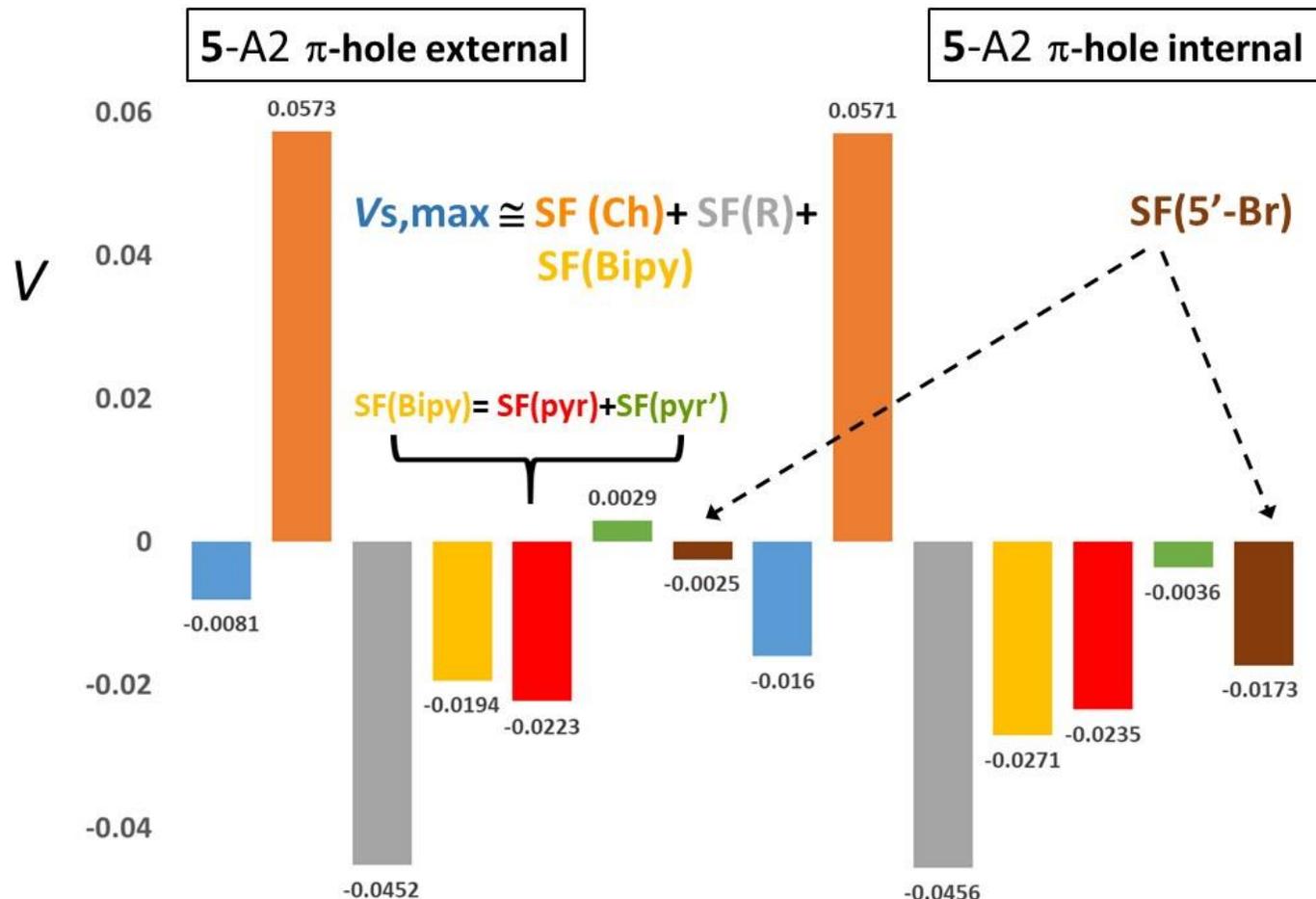**6**: Ch = Se, R = $C_6F_5$

*molecules*  25, 4409 (2020)

Article
Factors Impacting σ- and π-Hole Regions as Revealed by the Electrostatic Potential and Its Source Function Reconstruction: The Case of 4,4′-Bipyridine Derivatives
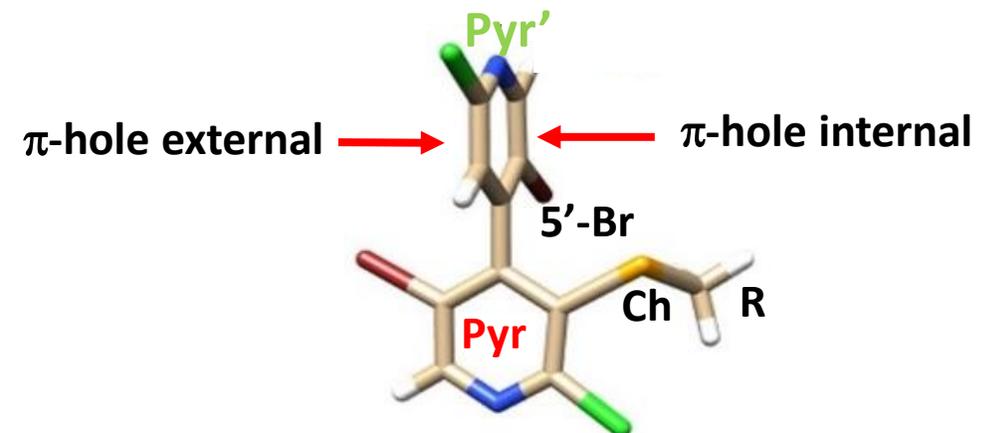
Similar $V_{S,max}$ (1-A1→ 5-A1) $C_{pyr}$-Se σ-hole values, yet the roles of the Ch, R and Bipy moieties are strikingly different
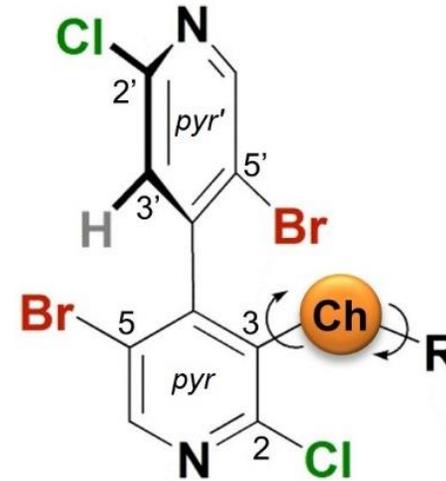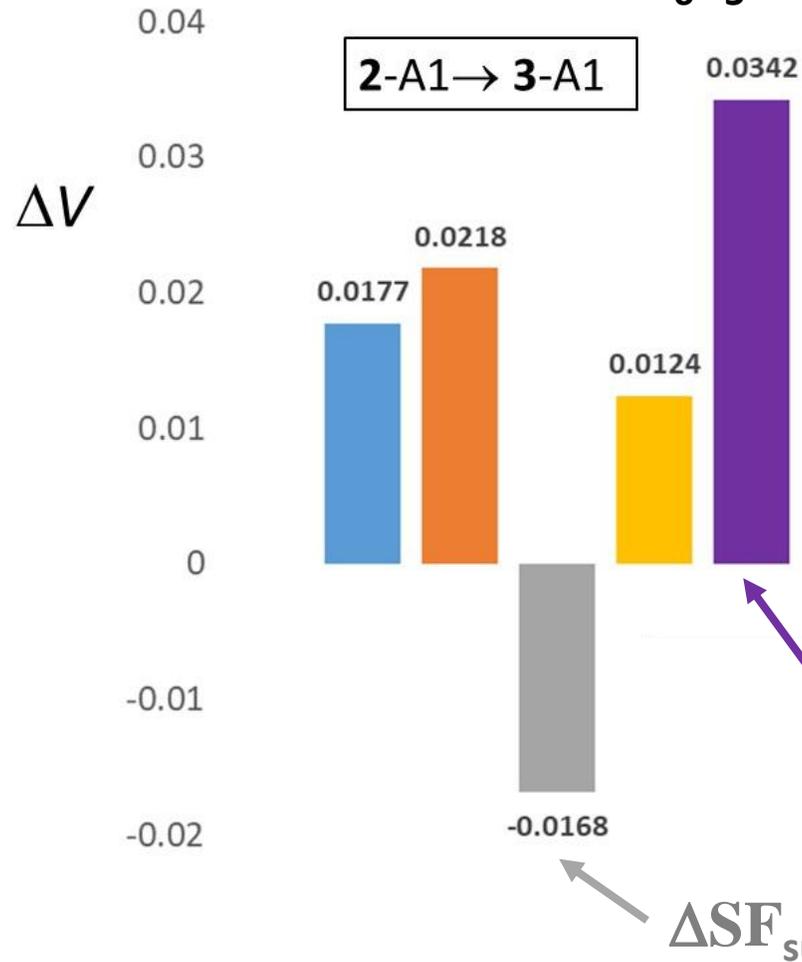
# Example II



SF (Ch) and SF(R) are almost equal for the two holes, while SF(Bipy) is the responsible for the internal $\pi$-hole $V_{S,max}$ of 5-A2 being twice as negative because of the different sign SF contribution from its pyr', hosting the 5'-Br atom. This atom points its p-cloud towards the phenyl ring internal p-hole making this hole negative rather than positive

# Example III

**C$_R$-S σ-hole**

**R=Ph** ⟶ **R=C$_6$F$_5$**



Substitution pattern
1: Ch = S, R = Me
2: Ch = S, R = Ph
3: Ch = S, R = C$_6$F$_5$
4: Ch = Se, R = Me
5: Ch = Se, R = Ph
6: Ch = Se, R = C$_6$F$_5$

$$\Delta V\text{s,max} = \Delta SF\,(Ch) + \Delta SF(R) + \Delta SF(Bipy)$$

$$\Delta V_{S,max}\,(\mathbf{2}\text{-A1}\rightarrow\mathbf{3}\text{-A1}) \cong \Delta SF_{substitution} + \Delta SF_{rearrangement}$$

$$\Delta SF_{rearrangement}\,(\mathbf{2}\text{-A1}\rightarrow\mathbf{3}\text{-A1}) = \Delta SF\,(Ch) + \Delta SF(Bipy)$$

Chart ($\Delta V$), **2**-A1→ **3**-A1:
- 0.0177
- 0.0218
- -0.0168 ($\Delta SF_{substitution}$)
- 0.0124
- 0.0342 ($\Delta SF_{rearrangement}$)

# Example IV

**C$_R$-S σ-hole**

$$\Delta V_{S,max} \cong \Delta SF_{substitution} + \Delta SF_{rearrangement}$$

$$\boxed{\textbf{2-B1} \rightarrow \textbf{2-A2}}$$

$$\Delta Vs,max(\textbf{2-B1} \rightarrow \textbf{2-A2}) \equiv \Delta SF_{rearrangement}$$
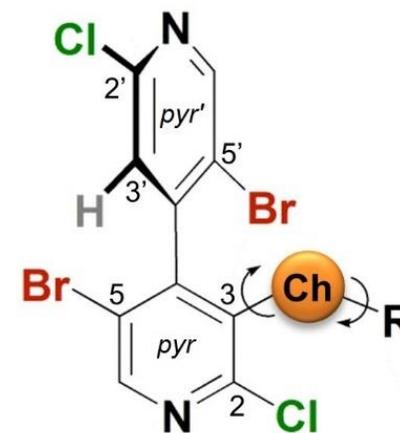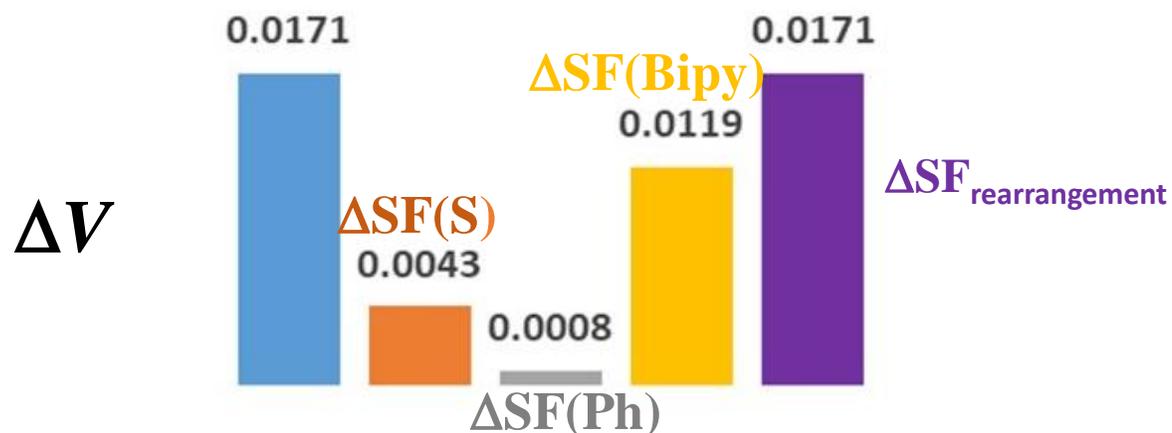


*Substitution pattern*
1: Ch = S, R = Me
2: Ch = S, R = Ph
3: Ch = S, R = C$_6$F$_5$
4: Ch = Se, R = Me
5: Ch = Se, R = Ph
6: Ch = Se, R = C$_6$F$_5$

$\Delta V$

0.0171  ΔSF(S) 0.0043  0.0008 ΔSF(Ph)  ΔSF(Bipy) 0.0119  0.0171 ΔSF$_{rearrangement}$



conf. B1          conf. A2
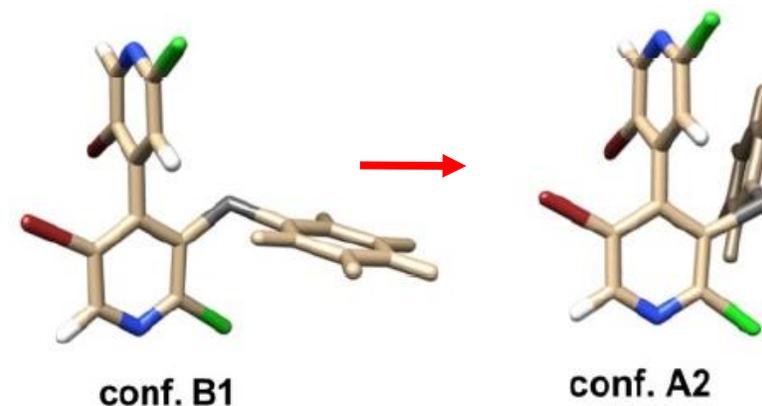
The molecular transformations of examples III and IV yield quite similar $V_{S,max}$ variations, yet the roles of the Ch, R and Bipy moieties in producing such similar changes strikingly differ. It is shown that **a change of molecular conformation only may be as effective as a chemical substitution in its impact on the $V_{S,max}$ value.**

# Example V



$C_{pyr}$-Se σ-hole
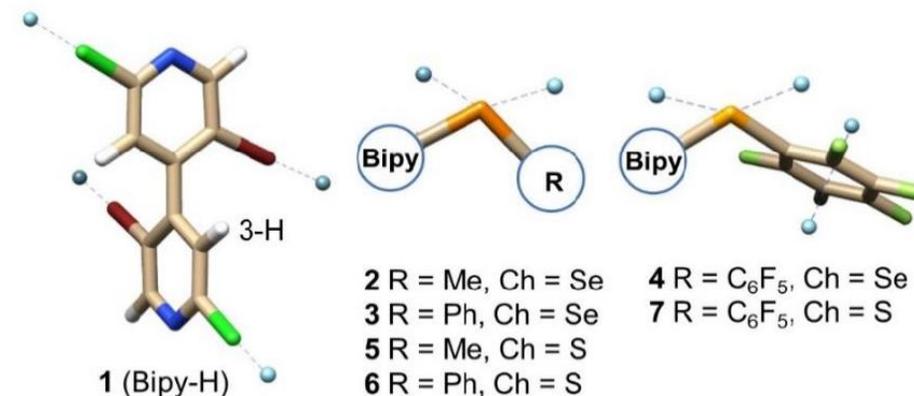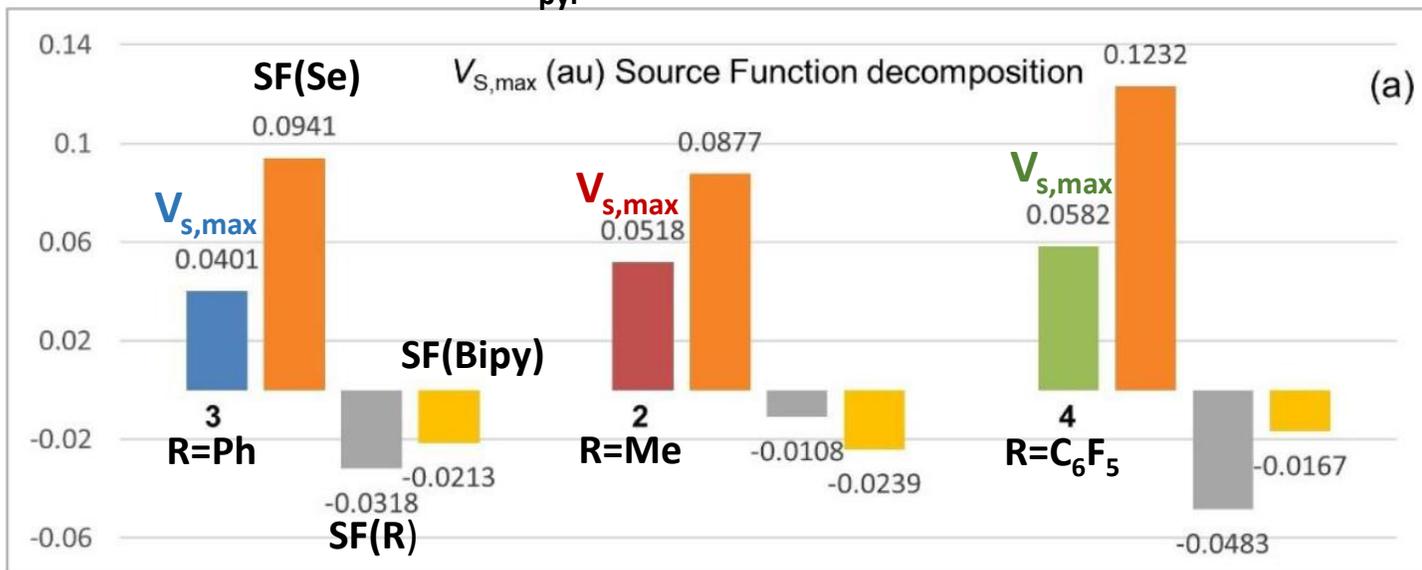
$V_{S,max}$ (au) = SF(Ch)+SF(Bipy)+SF(R)

Thanks to

all (mentioned + photos!) coauthors

DNRF for funding through  CMC
Center for Materials Crystallography


Danmarks Grundforskningsfond
Danish National Research Foundation

...to all of you for
your attention

# Phase Change Materials (PCMs)

**Table 1 Crucial properties of phase-change alloys**

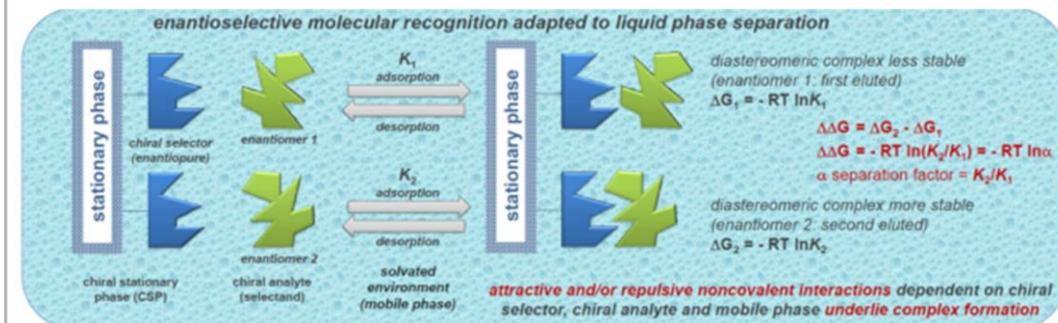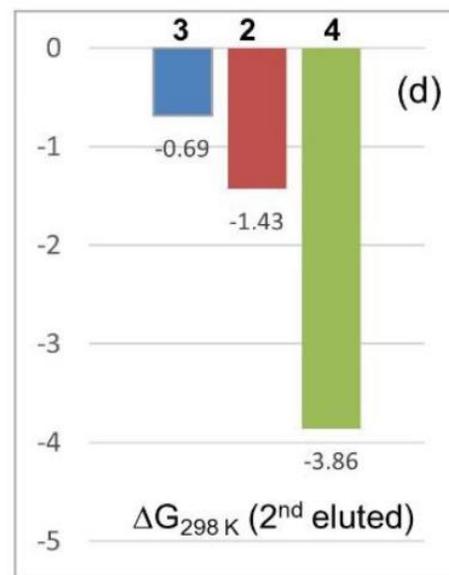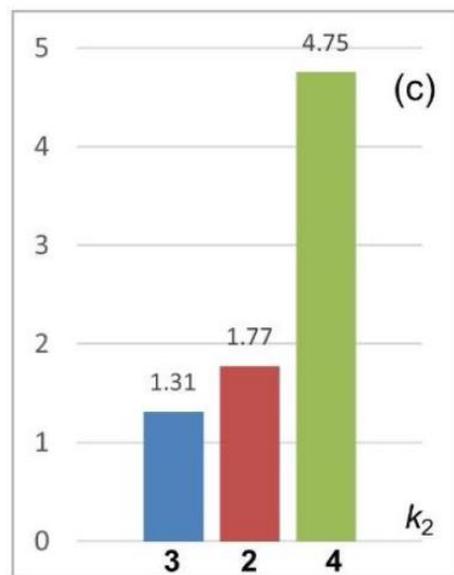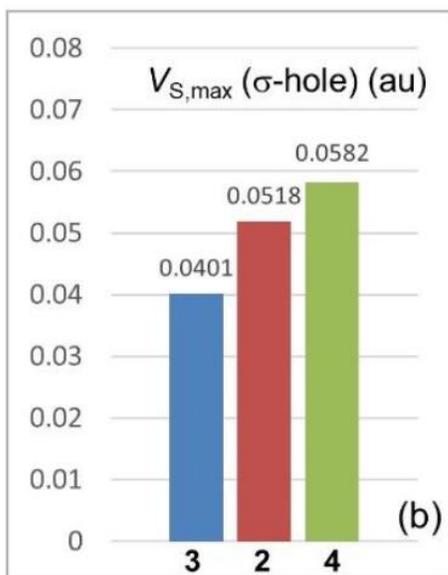| Required property of PC material | Specification |
|---|---|
| High-speed phase transition | Induced by nanosecond laser or voltage pulse |
| Long thermal stability of amorphous state | At least several decades at room temperature |
| Large optical change between the two states (for rewriteable optical storage) | Considerable difference in refractive index or absorption coefficient |
| Large resistance change between the states (for non-volatile electronic storage) | Natural consequence of the transformation from amorphous to crystalline state |
| Large cycle number of reversible transitions | More than 100,000 cycles with stable composition |
| High chemical stability | High water-resistivity |

❑ Can be rapidly and reversibly switched between the amorphous (AS) and the crystalline state (CS). **Yet** this transition is accompanied by a *pronounced change* of **optical** and **electronic** properties

❑ Though their transformation occurs through very fast melt, quench and anneal cycles, the 2 states are extremely long lived at ambient T: they do represent 2 stable and competing structural/bonding alternatives

❑ Their portfolio of properties is very appealing for **memory applications** and **photonics**

❑ PCMs have been successfully employed in : a) rewriteable optical data storage (DVD, Blue Ray, HD Digital Versatile Disks) b) fast, yet nonvolatile electronic memories (**PCM, PCME, PRAM, PCRAM, OUM)**. Their pronounced optical contrast is also utilized in nanophotonic applications and has been discussed as a means to realize ultrafast optical switches
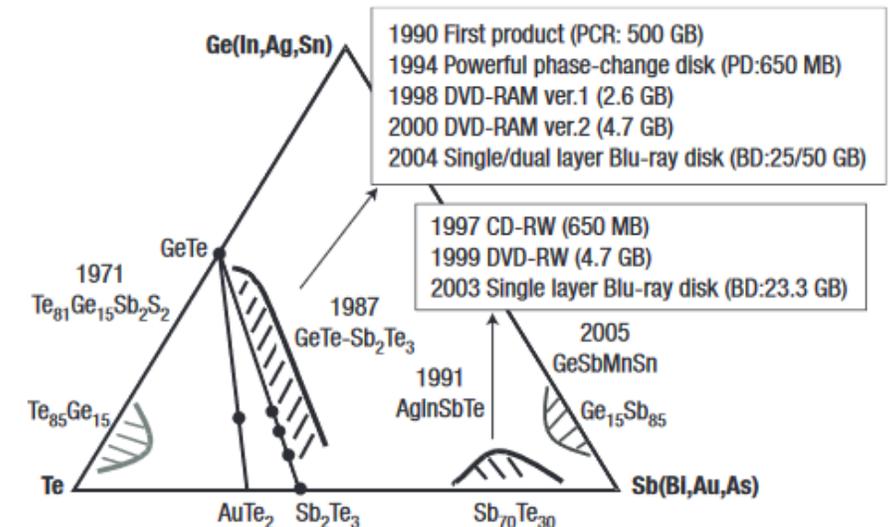


**Figure 2** Ternary phase diagram depicting different phase-change alloys, their year of discovery as a phase-change alloy and their use in different optical storage products.

# Upon transition to CS....

## Special *fingerprints* of PCM crystalline phases

Zhu, M., Cojocaru-Mirédin, O., Mio, A. M., Keutgen, J., Küpers, M., Yu, Y., Cho, J. Y., Dronskowski, R., Wuttig, M., *Adv. Mater.* 2018, 30, 1706735.

These findings imply that the *bonding* mechanism in crystalline PCMs differs substantially from conventional bonding mechanisms such as metallic, ionic, and covalent bonding....

- ❑ Unusually high coordination number (Zintl-Klemm 8-$N$ rule no longer fulfilled

- ❑ Electronic polarizability rises sharply ➡ Extraordinary large optical dielectric constant

- ❑ Chemical bond polarizability increases ➡ unusually high Born effective charges

- ❑ Almost metal-like conductivity

- ❑ Vibrational properties are largely affected, with unusual phonon softening Huge mode-specific Grüneisen parameter for transverse optical phonons

- ❑ Unusual bond breaking mechanism in laser-assisted atom probe tomography

*Really a* novel *bonding* mechanism besides those already established?

*Metavalent* bonding?

## Upon transition to CS....

## Special *fingerprints* of PCM crystalline phases

GS Static view of bonding (1*e* and 2*e* distributions)

*or*

Property view of bonding as a specific reaction to an external stimulus?

❑ Unusually high coordination number (Zintl-Klemm 8-*N* rule no longer fulfilled)

*Geometry*

❑ Electronic polarizability rises sharply ➡ Extraordinary large optical dielectric constant

*Response properties (involve excited states)*

❑ Chemical bond polarizability increases ➡ unusually high Born effective charges

❑ Almost metal-like conductivity

❑ Vibrational properties are largely affected, with unusual phonon softening Huge mode-specific Grüneisen parameter for transverse optical phonons

❑ Unusual bond breaking mechanism in laser-assisted atom probe tomography

*Response property to an external, very large, destroying stimulus*
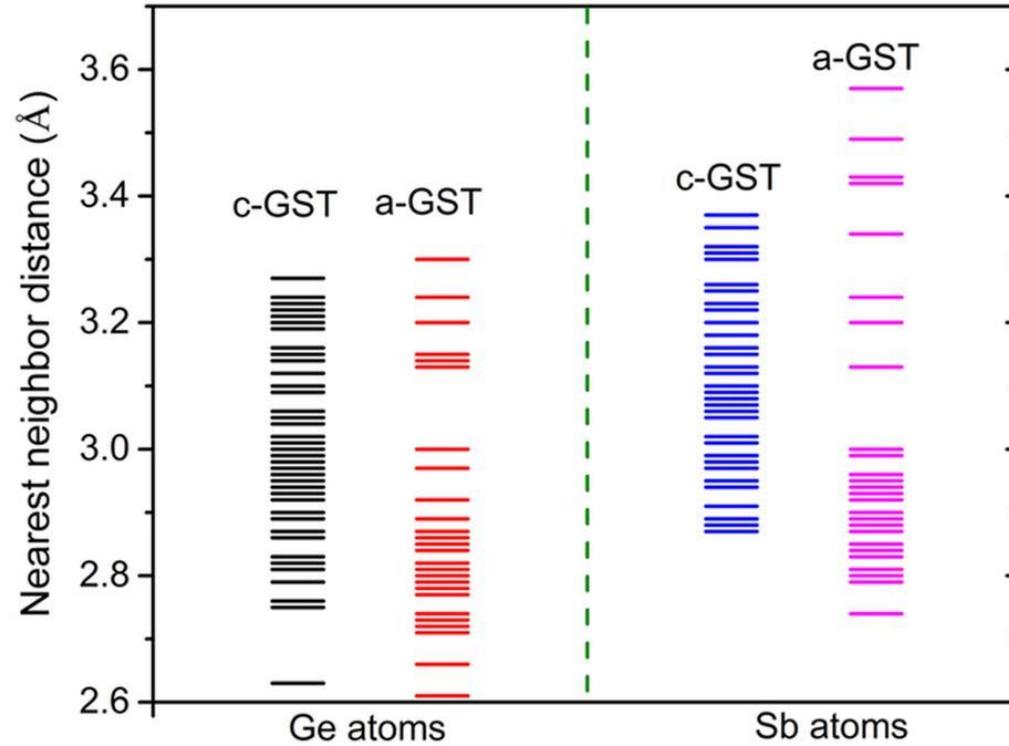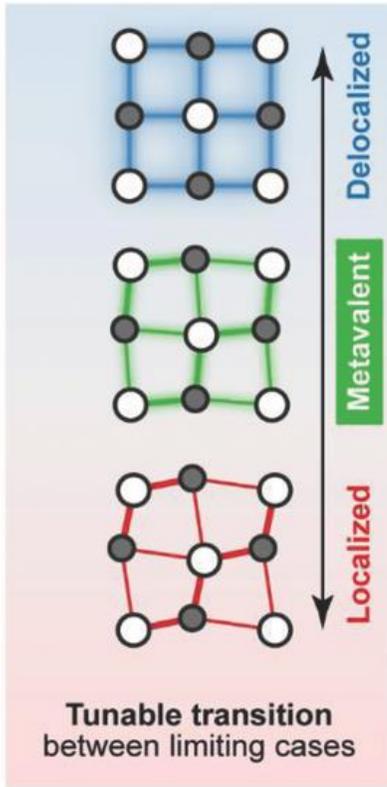
$Ge_2Sb_2Te_5$ (GST)
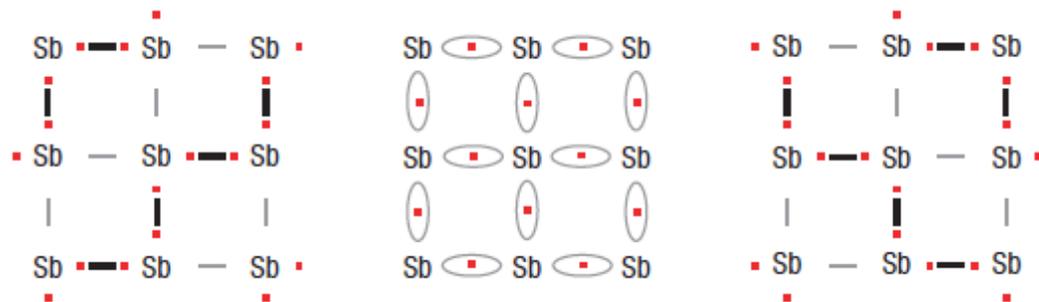
c-GST slighltly distorted cubic, 1c-2e, more delocalized

a-GST short and long nnb distances, 2c-2e more localized. Closer to 8-N ZK rule

## Localization and delocalization indices should give an unbiased answer

$$\rho_2(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}\left[\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2)\right]$$

CrossMark

### Domain overlap matrices from plane-wave-based methods of electronic structure calculation

Pavlo Golub[1] and Alexey I. Baranov[1,2,a)]
[1]*Department of Chemistry and Food Chemistry, Technical University of Dresden, Bergstrasse 66, 01062 Dresden, Germany*
[2]*Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Strasse, 40, 01187 Dresden, Germany*

$$\text{LI(A)} = \lambda(A) = \int_A\int_A \rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

Half N. of *e* pairs fully localised in *A*

$$\text{DI(A,B)} = \delta(A,B) = 2\cdot\int_A\int_B \rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

N. of *e* pairs shared between A and B

Plane waves are one of the most popular and efficient basis sets for electronic structure calculations of solids; however, their delocalized nature makes it difficult to employ for them classical orbital-based methods of chemical bonding analysis. The quantum chemical topology approach, introducing chemical concepts via partitioning of real space into chemically meaningful domains, has no difficulties with plane-wave-based basis sets. Many popular tools employed within this approach, for instance delocalization indices, need overlap integrals over these domains—the elements of the so called domain overlap matrices. This article reports an efficient algorithm for evaluation of domain overlap matrix elements for plane-wave-based calculations as well as evaluation of its implementation for one of the most popular projector augmented wave (PAW) methods on the small set of simple and complex solids. The stability of the obtained results with respect to PAW calculation parameters has been investigated, and the comparison of the results with the results from other calculation methods has also been made. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4964760]

$$\sum_A\left[\lambda(A) + \frac{1}{2}\sum_{B\neq A}\delta(A,B)\right] = N$$

For HF (and SD wfs ansatz)

$$\rho_{2,xc}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{i,j=1}^{M=N/2}2\left[\phi_i(\mathbf{r}_2)\phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\right]$$

$$\lambda(\Omega_1) = 2\cdot\sum_{i,j=1}^{M=N/2}\int_{\Omega_1}\int_{\Omega_1}\phi_i(\mathbf{r}_2)\phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = 2\cdot\sum_{i,j=1}^{M=N/2}\left(S_{ij}^{\Omega_1}\right)^2$$

$$\delta(\Omega_1,\Omega_2) = 4\cdot\sum_{i,j=1}^{M=N/2}\int_{\Omega_1}\int_{\Omega_2}\phi_i(\mathbf{r}_2)\phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = 4\cdot\sum_{i,j=1}^{M=N/2}S_{ij}^{\Omega_1}S_{ij}^{\Omega_2}$$

### Domain-averaged Fermi-hole analysis for solids

Alexey I. Baranov,[1,a)] Robert Ponec,[2] and Miroslav Kohout[1]
[1]*Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Strasse 40, 01187 Dresden, Germany*
[2]*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic v.v.i., Rozvojová 135, 165 02 Prague 6, Czech Republic*

JCTC Journal of Chemical Theory and Computation — Article

Cite This: *J. Chem. Theory Comput.* 2018, 14, 4699–4710 — pubs.acs.org/JCTC

JCTC **14**, 4699 (2018)

$$S_{ij}^{\Omega_k} = \int_{\Omega_k}\phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)d\mathbf{r}_1$$

DOM

### Quantitative Electron Delocalization in Solids from Maximally Localized Wannier Functions

A. Otero-de-la-Roza,*,[†] Ángel Martín Pendás,[†] and Erin R. Johnson[‡]

[†]*Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33006 Oviedo, Spain*
[‡]*Department of Chemistry, Dalhousie University, 6274 Coburg Road, Halifax, Nova Scotia, Canada B3H 4R2*

**DOM from plane wave calculations**

Augmented Plane Wave (APW) or Projector Augmented wave (PAW) methods:

❑ Interstitial region (IR)

   +

❑ Non overlapping atomic or muffin-tin (MT) spheres

$$\tilde{\psi}_{j\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{j\vec{k}}(\vec{G}) e^{\iota(\vec{k}+\vec{G})\vec{r}}$$

IR : Bloch states with band index j and k-vector $\vec{k}$, expanded in PWs

$\Sigma$ over the reciprocal lattice vectors $\vec{G}$

$$S_{j\vec{k};j'\vec{k}'}(\Omega) = \int d\vec{r}\,\tilde{\psi}^*_{j\vec{k}}(\vec{r})\,w^{\Omega}(\vec{r})\,\chi_{IR}(\vec{r})\,\tilde{\psi}_{j'\vec{k}'}(\vec{r})$$

$$+ \sum_{a} \int d\vec{r}\,\psi^{a*}_{j\vec{k}}(\vec{r})\,w^{\Omega}(\vec{r})\,\psi^{a}_{j'\vec{k}'}(\vec{r}).$$

IR PW contribution
$\chi(IR)=1$ in IR and 0 elsewhere

Atomic spheres contribution

**Domain overlap matrices from plane-wave-based methods of electronic structure calculation**

Pavlo Golub[1] and Alexey I. Baranov[1,2,a]
[1]Department of Chemistry and Food Chemistry, Technical University of Dresden, Bergstrasse 66, 01062 Dresden, Germany
[2]Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Strasse, 40, 01187 Dresden, Germany

**M. Kohout, Program Dgrid-4.7, Radebeul, 2012**

DOM calculation implemented for the PAW method as a general purpose module of the program DGRID interfaced to the output of the ABINIT code. DOM evaluated for QTAIM basins

# A Quantum-Mechanical Map for Bonding and Properties in Solids

Jean-Yves Raty, Mathias Schumacher, Pavlo Golub, Volker L. Deringer, Carlo Gatti, and Matthias Wuttig*

❑ Combine the quantum mechanically based (1$e$ and 2$e$ distributions) and the property-based perspective to derive a holistic view of bonding in solids

❑ Do "metavalent" solids exhibit special DI and LI features, besides their 5 "fingerprints properties" ?

For conductivity and coordination numbers, "metavalent" solids are located between the covalent and metallic regimes

They are, however, distinctly different from both because they show

a) anomalously large response properties
b) a unique APT (Atom Probe Tomography) bond-breaking mechanism not observed in either covalent or metallic solids

Definition based on a set of observable properties has led to a revision of "resonant" bonding model, previously widely used to describe bonding in PCMs. **Response** properties of PCMs are fundamentally different from those of resonantly bonded benzene and graphite

|  | Structure |
| --- | --- |

**Elements:**

| | |
| --- | --- |
| Al | $Fm\bar{3}m$ |
| Ag | $Fm\bar{3}m$ |
| $Sn^{\alpha}$ | $Fd\bar{3}m$ |
| Pb | $Fm\bar{3}m$ |
| Si | $Fd\bar{3}m$ |
| Ge | $Fd\bar{3}m$ |
| Na | $Im\bar{3}m$ |
| Mg | $P6_3/mmc$ |
| Ca* | $P6_3/mmc$ |
| $C^{diamond}$ | $Fd\bar{3}m$ |
| $C^{graphite}$ | $P6_3/mmc$ |

**Intermetallics:**

| | |
| --- | --- |
| NiAl | $Pm\bar{3}m$ |
| TiAl | $P4/mmm$ |

**IIIA-VA compounds:**

| | |
| --- | --- |
| AlN | $P6_3mc$ |
| AlP | $F\bar{4}3m$ |
| AlAs | $F\bar{4}3m$ |
| AlSb | $F\bar{4}3m$ |
| AlBi | $F\bar{4}3m$ |
| GaN | $P6_3mc$ |
| GaP | $F\bar{4}3m$ |
| GaAs | $F\bar{4}3m$ |
| GaSb | $F\bar{4}3m$ |
| InN* | $F\bar{4}3m$ |
| InP | $F\bar{4}3m$ |
| InAs | $F\bar{4}3m$ |
| InSb | $F\bar{4}3m$ |

**IA-VIIA compounds:**

| | |
| --- | --- |
| NaCl | $Fm\bar{3}m$ |
| NaF | $Fm\bar{3}m$ |
| KF | $Fm\bar{3}m$ |
| KCl | $Fm\bar{3}m$ |
| KBr | $Fm\bar{3}m$ |
| KI | $Fm\bar{3}m$ |
| RbCl | $Fm\bar{3}m$ |
| RbBr | $Fm\bar{3}m$ |
| $RbBr^{Pm\bar{3}m*}$ | $Pm\bar{3}m$ |
| CsF | $Fm\bar{3}m$ |
| $CsF^{Pm\bar{3}m*}$ | $Pm\bar{3}m$ |

**Ternary compounds:**

| | |
| --- | --- |
| $AgBiSe_2$ | |
| $AgBiTe_2$ | |
| $AgSbTe_2$ | |

**IIA-VIA compounds:**

| | |
| --- | --- |
| BeO | $P6_3mc$ |
| BeS | $F\bar{4}3m$ |
| BeSe | $F\bar{4}3m$ |
| BeTe | $F\bar{4}3m$ |
| MgO | $Fm\bar{3}m$ |
| MgS | $Fm\bar{3}m$ |
| MgSe* | $F\bar{4}3m$ |
| MgTe | $F\bar{4}3m$ |
| CaO | $Fm\bar{3}m$ |
| CaS | $Fm\bar{3}m$ |
| CaSe | $Fm\bar{3}m$ |
| CaTe | $Fm\bar{3}m$ |
| SrO | $Fm\bar{3}m$ |
| SrS | $Fm\bar{3}m$ |
| SrSe | $Fm\bar{3}m$ |
| SrTe | $Fm\bar{3}m$ |
| BaS | $Fm\bar{3}m$ |
| BaSe | $Fm\bar{3}m$ |
| BaTe | $Fm\bar{3}m$ |

**IIB-VIA compounds:**

| | |
| --- | --- |
| ZnO* | $F\bar{4}3m$ |
| ZnS | $F\bar{4}3m$ |
| $ZnS^{Wurtzite*}$ | $P6_3mc$ |
| ZnSe | $F\bar{4}3m$ |
| ZnTe | $F\bar{4}3m$ |
| CdS | $F\bar{4}3m$ |
| CdSe | $F\bar{4}3m$ |
| CdTe | $F\bar{4}3m$ |
| HgS | $F\bar{4}3m$ |
| HgSe | $F\bar{4}3m$ |
| HgTe | $F\bar{4}3m$ |

**IVA-VIA compounds:**

| | |
| --- | --- |
| GeSe | $Pnma$ |
| $GeTe^{220u*}$ | $R3m$, dist. |
| $GeTe^{221u*}$ | $R3m$, dist. |
| $GeTe^{224u*}$ | $R3m$, dist. |
| $GeTe^{227u*}$ | $R3m$, dist. |
| $GeTe^{ortho*}$ | $Pnma$ |
| $GeTe^{230u*}$ | $R3m$, dist. |
| $GeTe^{233u*}$ | $R3m$, dist. |
| $GeTe^{R3m}$ | $R3m$ |
| $GeTe^{239u*}$ | $R3m$, dist. |
| $GeTe^{242u*}$ | $R3m$, dist. |
| $GeTe^{245u*}$ | $R3m$, dist. |
| $GeTe^{cub*}$ | $Fm\bar{3}m$ |
| SnO | $P4/nmm$ |
| SnS | $Pnma$ |
| SnSe | $Pnma$ |
| SnTe | $R3m$, dist. |
| $SnTe^{cub*}$ | $Fm\bar{3}m$ |
| PbO | $P4/nmm$ |
| $PbSe^{u2300*}$ | $R3m$, dist. |
| $PbSe^{u2400*}$ | $R3m$, dist. |
| $PbSe^{u2440*}$ | $R3m$, dist. |
| $PbSe^{u2464*}$ | $R3m$, dist. |
| $PbSe^{u2482*}$ | $R3m$, dist. |
| PbSe | $Fm\bar{3}m$ |
| $PbTe^{u2300*}$ | $R3m$, dist. |
| $PbTe^{u2400*}$ | $R3m$, dist. |
| $PbTe^{u2440*}$ | $R3m$, dist. |
| $PbTe^{u2464*}$ | $R3m$, dist. |
| $PbTe^{u2482*}$ | $R3m$, dist. |
| PbTe | $Fm\bar{3}m$ |

11 elemental phases
74 binary phases of main-group elements
11 binary phases of IIB transition metals
 2 Intermetallics
3 Ternary phases
+ metastable phases of PCM

\* indicates metastable phases; the label "dist." signifies gradual Peierls distortions

# 2D map of bonding in materials
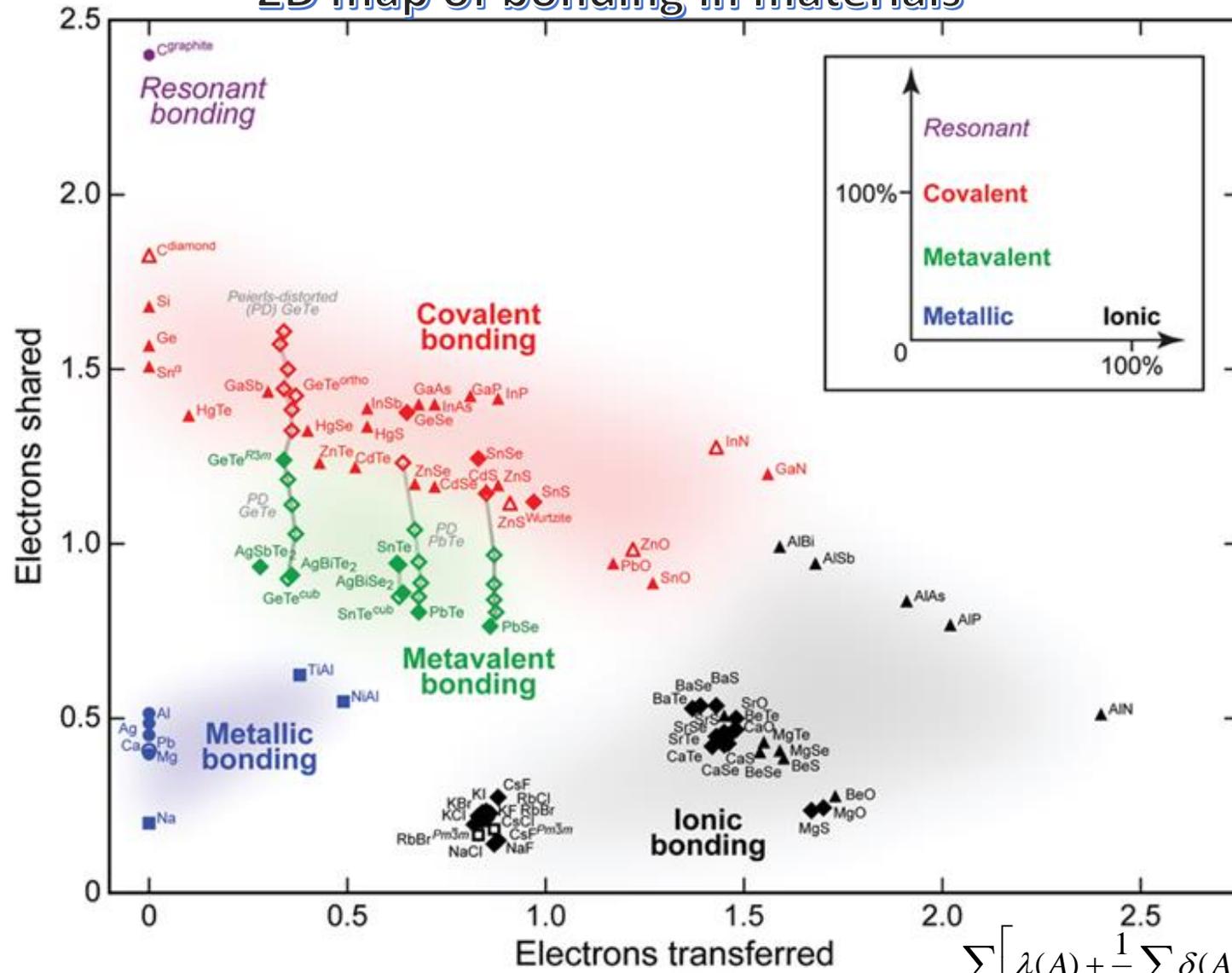
Legend:
- △ sp³ tetrahedrally bonded solids
- ◇ Distorted and ideal rocksalt types (octahedrally coordinated)
- ☐ Body-centered
- ○ Closed-packed metal structures

**Filled symbols**: thermodynamically stable phases (T=0)

**Open symbols**: metastable phases

**GeTe, SnTe,PbTe,PbSe** : additional structural intermediates along the Peierls distortion coordinate (gray line, as guide for the eye)

Archetypes of ionic, covalent, and metallic bonding lie in distinctly different, physically meaningful regions

$$\sum_A \left[ \lambda(A) + \frac{1}{2} \sum_{B \neq A} \delta(A,B) \right] = N$$

➡ Explains departure from perfect covalency with increasing polarity
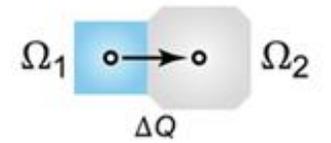
Central region of the map which lies between the 3 archetypical mechanisms, without belonging to one of them, and is populated by materials as well

# van Arkel–Ketelaar triangles
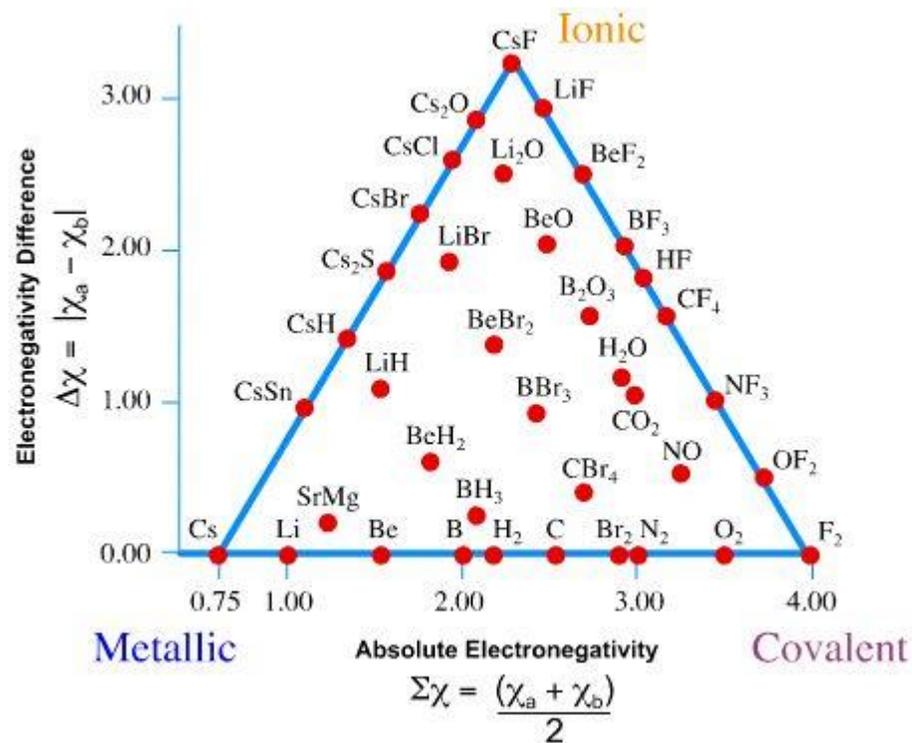


Arkel, A. E. V. *Molecules and Crystals in Inorganic Chemistry*; Interscience: New York, 1956.
Ketelaar, J. A. A. *Chemical Constitution: An Introduction to the Theory of Chemical Bond*, 2nd ed.; Elsevier: New York, 1958.

# J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

## Distinguishing Bonds

Martin Rahm* and Roald Hoffmann

# J|A|C|S
ARTICLES
Published on Web 11/13/2002

**A Classification of Covalent, Ionic, and Metallic Solids Based on the Electron Density**

P. Mori-Sanchez, A. Martin Pendas, V. Luana,
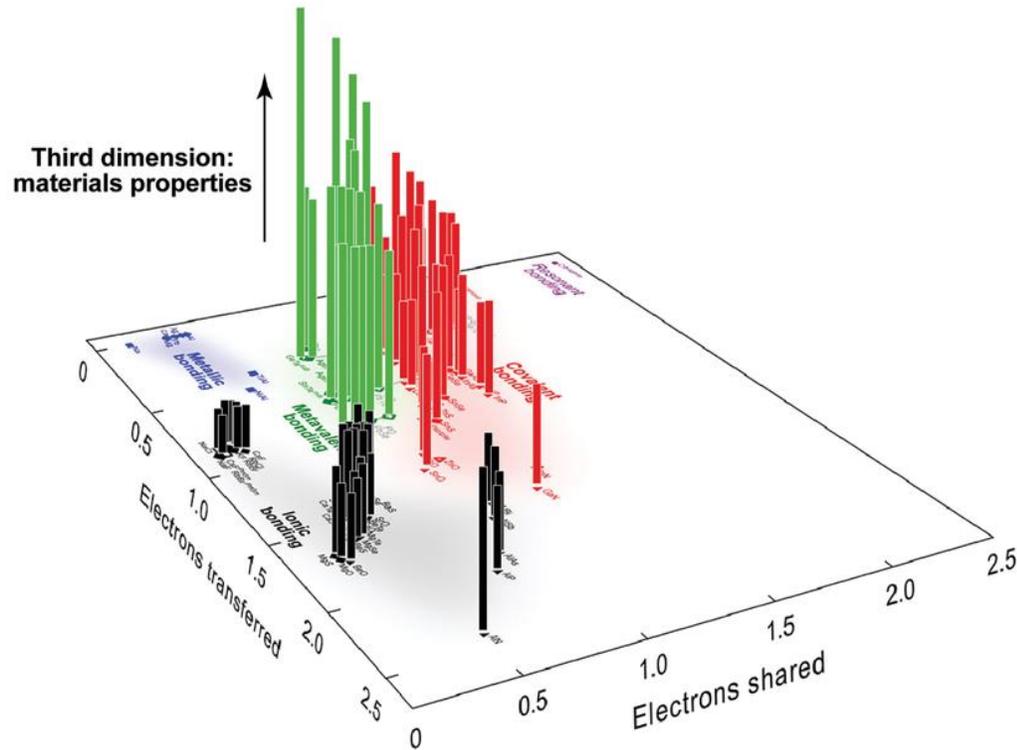*J. Am. Chem. Soc.* **124**, 14721 (2002)

The 3 indices, flatness, CT, and molecularity, easily obtained from the ED give rise to a classification in close resemblance to the classical van Arkel-Ketelaar diagrams
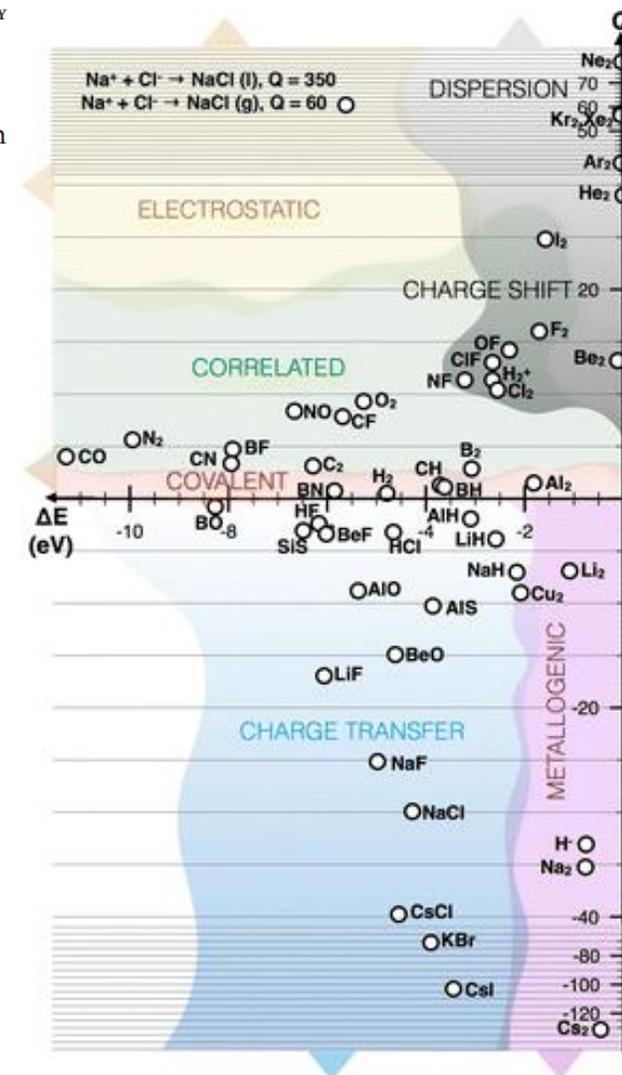


The *Q*-scale plotted against the bond dissociation energy $\Delta E$ in a range of diatomics reveals familiar groups of chemical interactions

- ❑ Missing aspect: a rigorous link between a compound's location in the 2D map and its physical properties (as relevant for applications)
- ❑ Such a link would make it possible not only to classify bonding in materials, but to exploit the quantitative bonding information for materials design.

# A Quantum-Mechanical Map for Bonding and Properties in Solids

**a** Third dimension: materials properties

**b** Born effective charges (bond polarizability) $|Z^*|$

**c** Optical dielectric constants (optical identifier) $\varepsilon_\infty$

**d** Grüneisen parameters (anharmonicity identifier) $|\gamma_{TO}|$ "

3D maps defining design rules for materials with desired properties

The base plane is defined as in the 2D map

Extending this map in the third dimension three response properties are quantified:
(b) Born effective charges, Z* (averaged over atoms)
(c) optical dielectric constants, $\varepsilon_\infty$
(d) absolute transverse optical (TO) mode Grüneisen parameters, $|\gamma_{TO}|$ for binary compounds
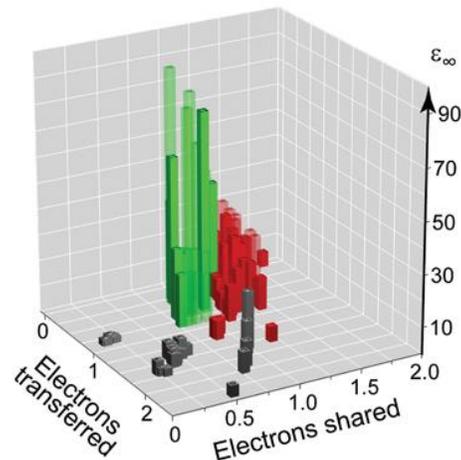
Ionic materials (**Black**), Covalent (**red**) Metavalent (**green**) ( structural intermediates as semitransparent bars)

"Metavalent" bonding is characterized by unusually high values of all three indicators (**green bars**).
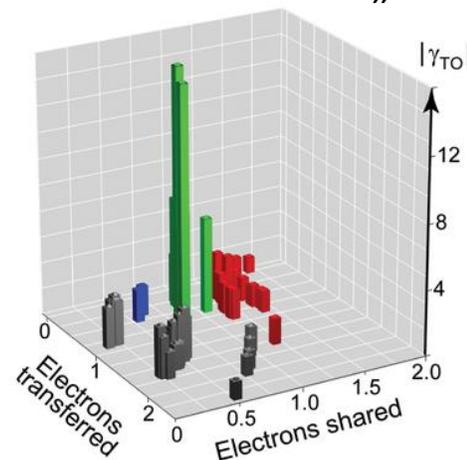
H-bonds may have vdW, ionic, covalent contributions with weights depending from D to A distance. However their properties (e.g OH stretching frequency) vary smoothly with $R_{DA}$

"Metavalent" bonding is not intermediate, in terms of properties, between covalent and metallic bonding

**a** Third dimension: materials properties

Metallic bonding — Metavalent bonding — Covalent bonding — Resonant bonding — Ionic bonding

Electrons transferred (0, 0.5, 1.0, 1.5, 2.0, 2.5)
Electrons shared (0, 0.5, 1.0, 1.5, 2.0, 2.5)

**b** Born effective charges (bond polarizability) $|Z^*|$
Electrons transferred — Electrons shared

**c** Optical dielectric constants (optical identifier) $\varepsilon_\infty$
Electrons transferred — Electrons shared

**d** Grüneisen parameters (anharmonicity identifier) $|\gamma_{TO}|$
Electrons transferred — Electrons shared

The 3D map suggests a blueprint to tailor the properties of a MVB material.

Bonding in chalcogenides was suggested to be closely interwoven with a lattice instability, leading to large Gruneisen parameters (S. Lee et al. *Nat. Comm. 5,* 3525, 2014)

Our 3D plot (d) shows that this anomaly is uniquely linked to MVB. More specifically, to the border between MVB and metallic bonding
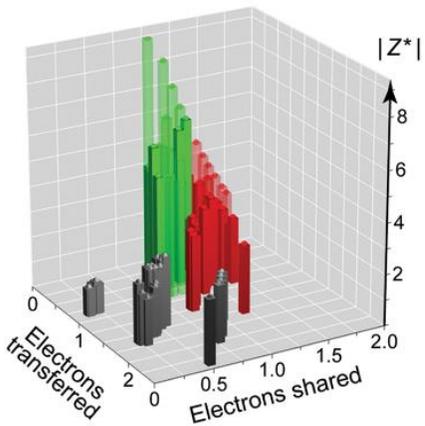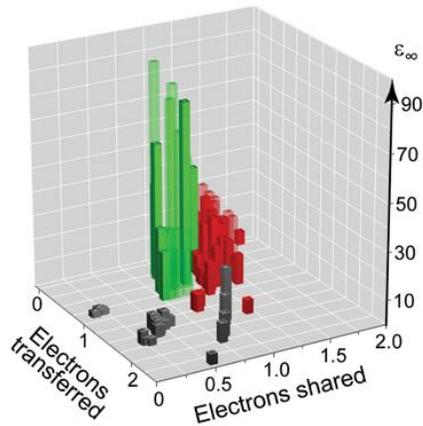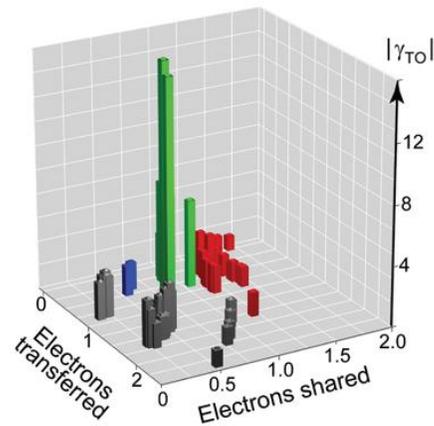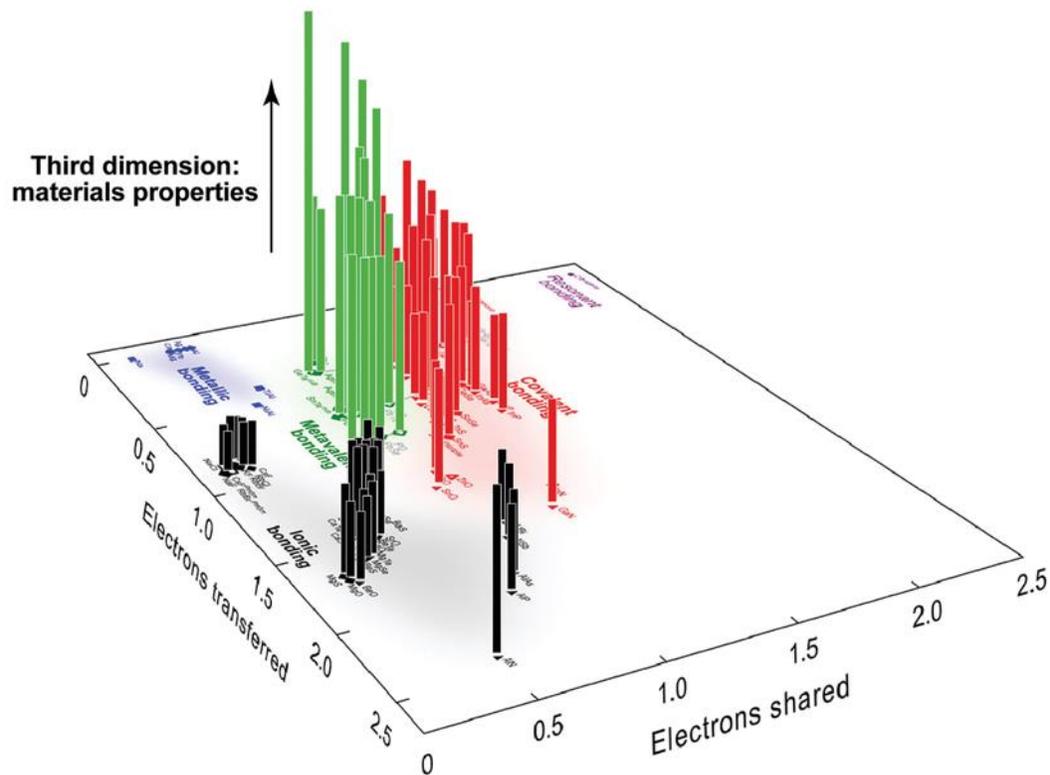
Search for thermoelectric good candidates

Move on the 2D map to MVB materials that border on metals, at around ≈0.8 e (0.4 e pair) shared

M. Cagnoni, D. Fuhren, M. Wuttig
Adv. Mater. 2018, 30, 1801787

**a** Third dimension: materials properties

Metallic bonding · Metavalent bonding · Covalent bonding · Resonant bonding · Ionic bonding

Electrons transferred · Electrons shared

**b** Born effective charges (bond polarizability) — $|Z^*|$

Electrons transferred · Electrons shared

**c** Optical dielectric constants (optical identifier) — $\varepsilon_\infty$

Electrons transferred · Electrons shared

**d** Grüneisen parameters (anharmonicity identifier) — $|\gamma_{TO}|$

Electrons transferred · Electrons shared

My view: No special need to introduce a new bonding type

But recognize that specific *electron-deficient* covalent bonds may lead to a rapid change and anomalously large values for (three) independent response properties.
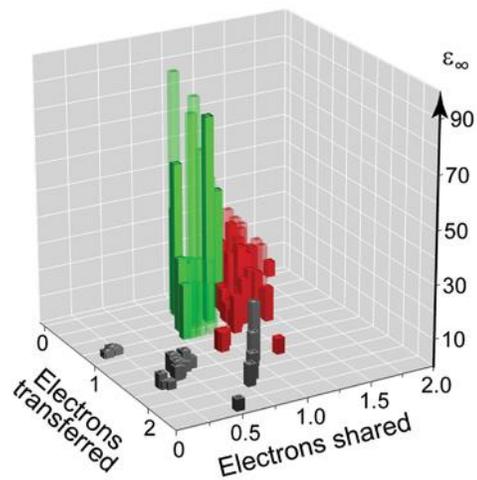
So the question again is what we mean for bonding…

And the message is : look at bonding also upon an external stimulus…

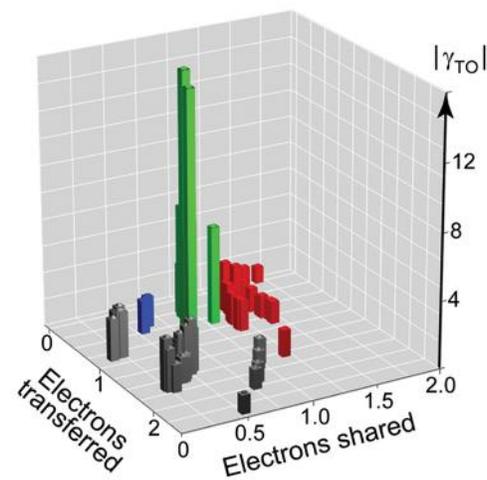MVB reveals itself only when a dynamic picture of bonding and of its properties is probed and exploited.
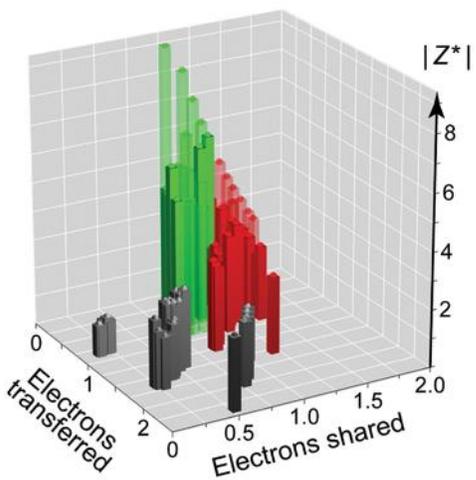
# Spatially resolved characterization of electron localization and delocalization in molecules: Extending the Kohn-Resta approach

Andrey A. Astakhov | Vladimir G. Tsirelson

A study on the electron organization of many-electron systems in the context of *linear response theory*

It highlights the *profound connection* between the variances of the local electron position and momentum operators and the optical conductivity tensor, hence between **electron localization/delocalization in position and momentum space and the observed spectroscopic and conductivity properties**.

Our study seem to emphasizes the dramatic role such connections may play in a peculiar case of bonding, namely, MVB
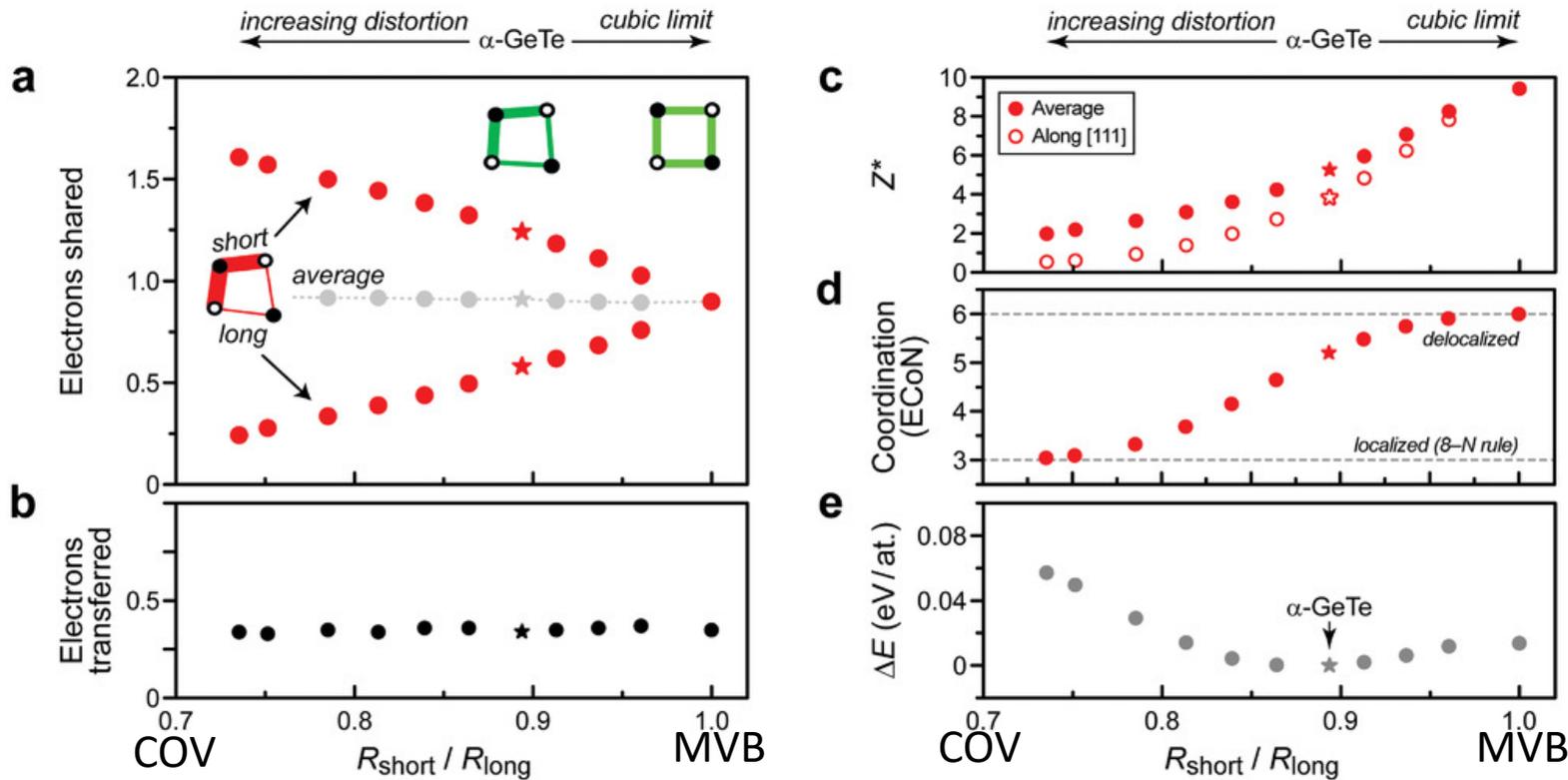
Tsirelson's study shows that electron localization and delocalization phenomena in atoms and molecules can be probed by external electric field.

The approach provides new electronic descriptors distinguishing and quantifying chemical bonds of different types.

# More insights in the property changes upon Peierls distortion

Many of them crystallize in the rocksalt type with ideal $O_h$ coordination of atoms but some, prominently GeTe, show a small distortion, 3 shorter and 3 longer bonds (referred to as a Peierls distortion, PD)

The progressive PD induces a redistribution of electrons between short and long GeTE bonds which become (**a**) respectively stronger and weaker, but the *average* amount of electrons shared is almost invariant (**b**)
(**c**) $Z^*$, a measurable indicator for the onset of MVB ( ● average; ○ projected along [111] where the effect of distortion is >)
(**d**) ECon, quantifies the gradual departure from the 8-N rule
(**e**) the energy cost associated with the distortion relative to GeTe (very small overall)

# More insights in the property changes upon Peierls distortion
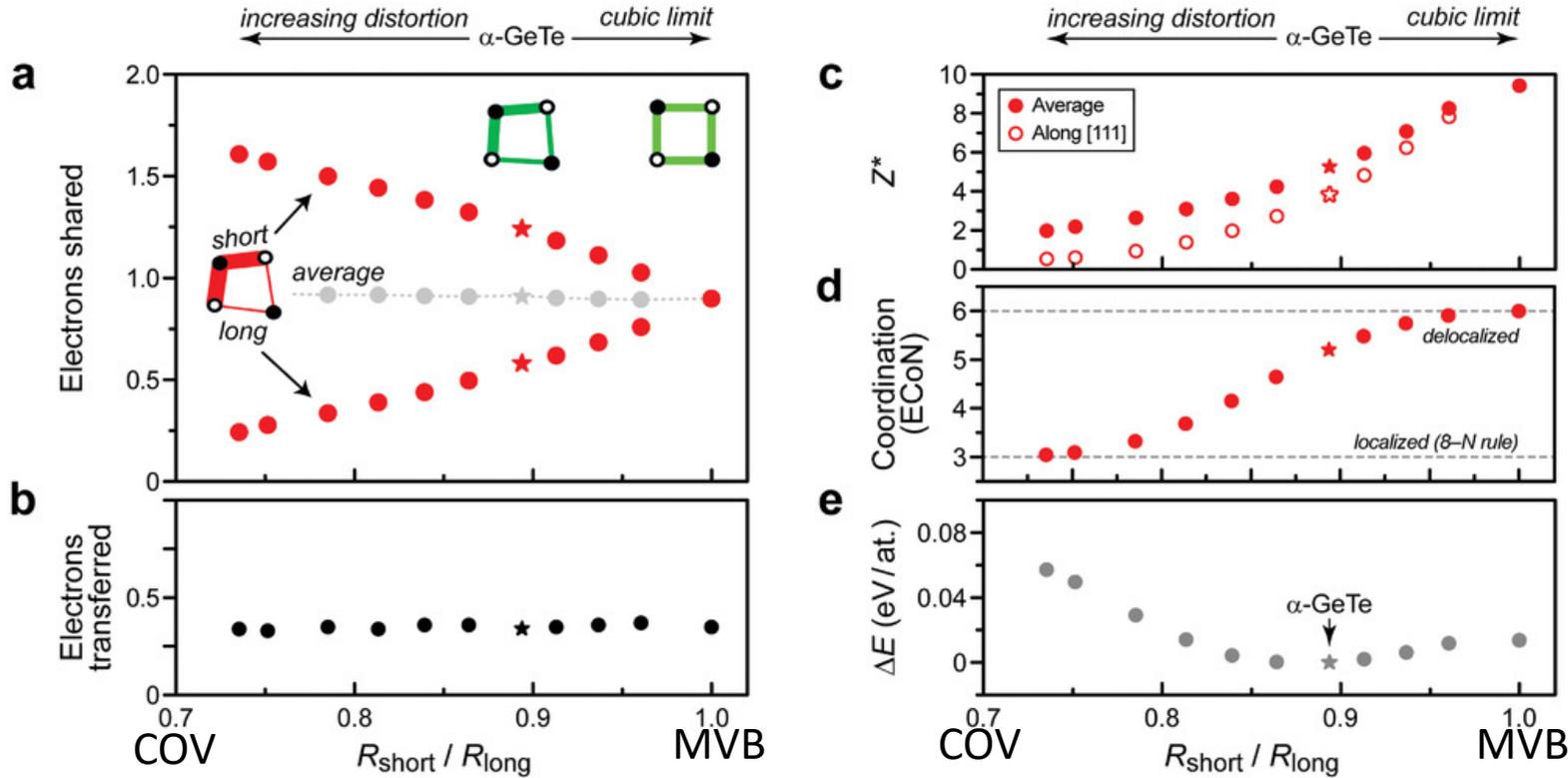


In the amorphous phases of PCMs the PD becomes extremely large and directionally blurred. Anomalous properties are lost, thus creating the electronic and optical property contrast exploited in device applications

Trends in the figures suggest a route toward the design of properties and thereby of "tailored" MVB materials if one achieves control over the PD. This could be done by strain, alloying, creating defects, or nanostructuring (moving along the horizontal axis in the Figure and modifying the ECoN), and this directly allows to tune the properties.

A Quantum-Mechanical Map for Bonding and Properties in Solids

It opens up a conceptually new avenue for materials design:
1) search for desired properties in a 3D space
2) map this back onto the 2D plane of bonding, navigating structural and composition spaces and identifying highly promising target materials.

# Thermoelectric Performance of IV–VI Compounds with Octahedral-Like Coordination: A Chemical-Bonding Perspective

*Matteo Cagnoni, Daniel Führen, and Matthias Wuttig\**
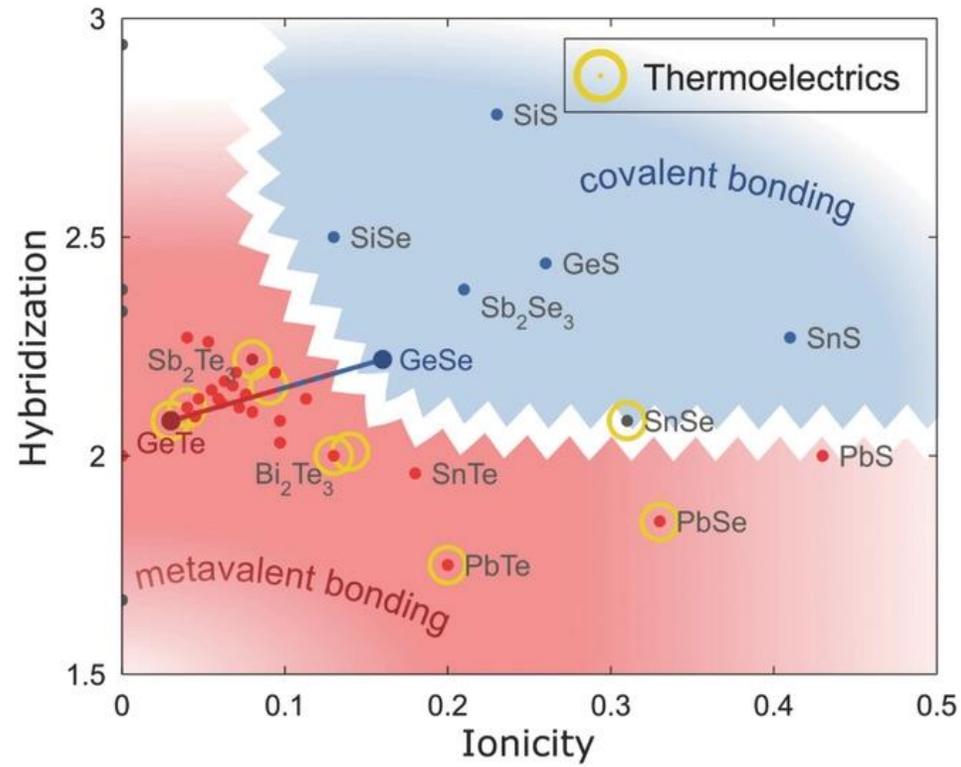
Moving along the $GeTe_{1-x}Se_x$ pseudo-binary line
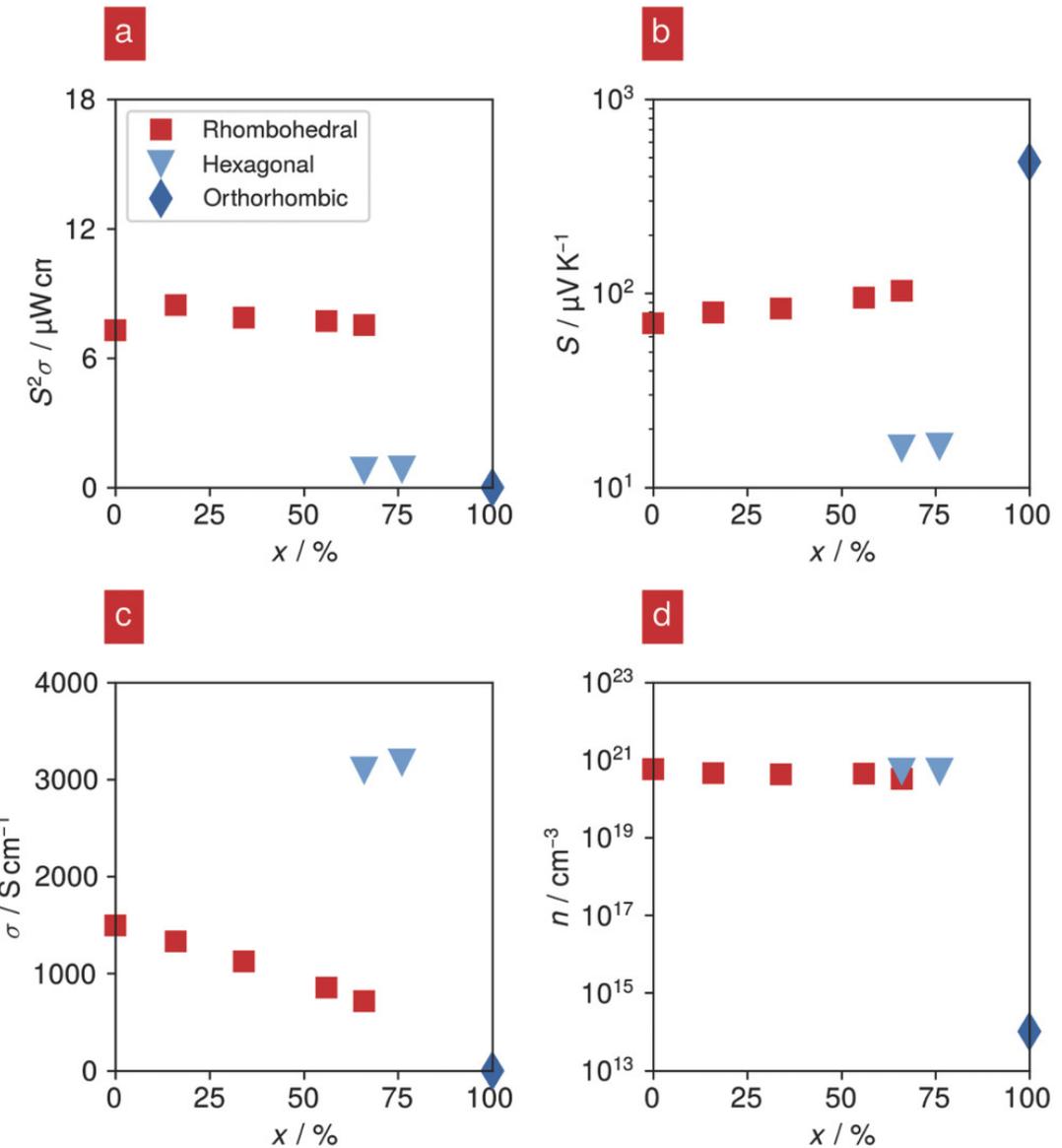


Electronic transport properties in crystalline $GeSe_xTe_{1-x}$ alloys

From Chemistry World

**FUNCTIONAL MATERIALS**

# A functional materials map

Brent Grocholski

Chemical bonding is important for understanding and designing new functional materials. In two papers, Wuttig *et al.* and Raty *et al.* propose a bonding type they term "metavalent." Metavalent materials lie between covalently and metallically bound ones but are distinctly different from both. Several of the compounds that plot in the metavalent field have unique and important physical properties that make for good thermoelectric, phase-change, and other functional materials. The new bonding category potentially provides a guide for the development of interesting new materials.

*Adv. Mater.* 10.1002/adma.201803777, 10.1002/adma.201806280 (2018).

NEWS

# Bonding rethink called for as new metavalent bond proposed

BY PHILIP BALL | 19 DECEMBER 2018

One of the most basic facts that chemistry students learn is the distinct types of chemical bond in solid-state materials: covalent, ionic and metallic, as well as curiosities such as hydrogen bonding. But if a proposal in two recent papers holds up, they will soon need to be taught about another class: the metavalent bond.

Would we have been *reported* if the term *metavalent* had not been used and a new bonding type had not been claimed?

Thanks:

Mathias Schumcher

Pavlo Golub

Volker L. Deringer

Matthias Wuttig

Jean-Yves Raty

RWTH, Physics Dept, Aachen, Germany

Dept. of Physics of Solids Interfaces and Nanostructures Université de Liège, Belgium

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…and to all of you for your attention and patience…