IUPAC Hydrogen Bonding Workshop, Pisa 2005

Comparing the topological properties of the experimentally determined EDD obtained by X-ray and neutron diffraction to the theoretically calculated values for hydrogen bonding and other intra- and inter-molecular interactions

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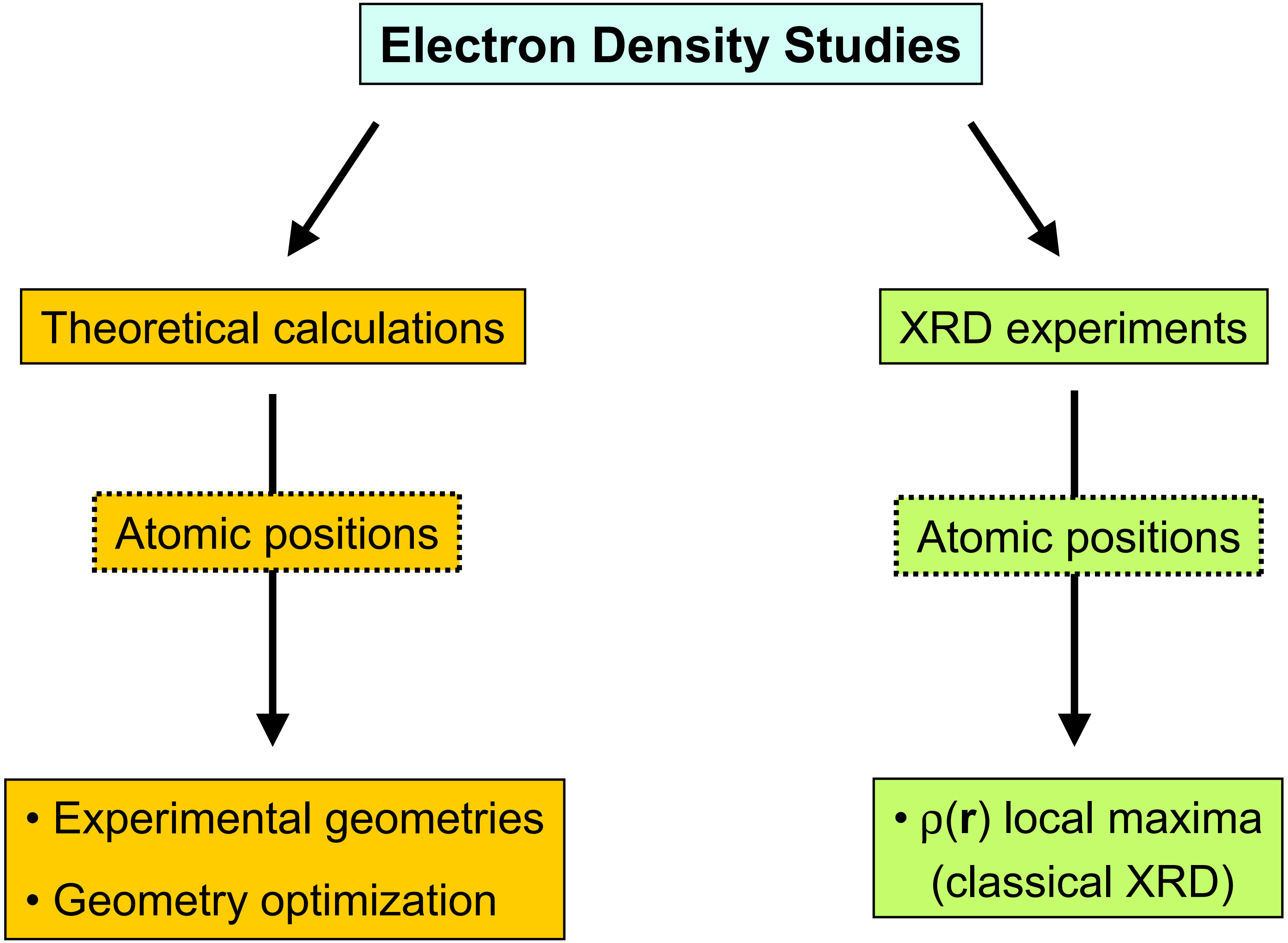
Introduction



Electron Density Studies

Theoretical calculations

Atomic positions

- Experimental geometries
- Geometry optimization

XRD experiments

Atomic positions

- $\rho(\mathbf{r})$ local maxima (classical XRD)

Introduction

Atomic positions experimentally determined

What you see … that's what you get ….

XRD experiment

↓

Interaction : photons ⟷ e^-'s

↓

Crystalline $\rho(\mathbf{r})$

But …. Why $\rho(\mathbf{r})$ leads to atomic positions ?

Introduction

Atomic positions experimentally determined

Hypothesis : $\rho(\mathbf{r})$ exhibits local maxima at nuclei….

$\rho(\mathbf{r})$ local maxima

↓

Nuclei positions

↓

Atomic positions

But …. Is the hypothesis true ?

Introduction

Atomic positions experimentally determined

The hypothesis is true for all elements …. except H !

H-atom : Only one e^- involved in the X-H chemical bond

$\rho_H(\mathbf{r})$ local maximum displaced from H-nucleus

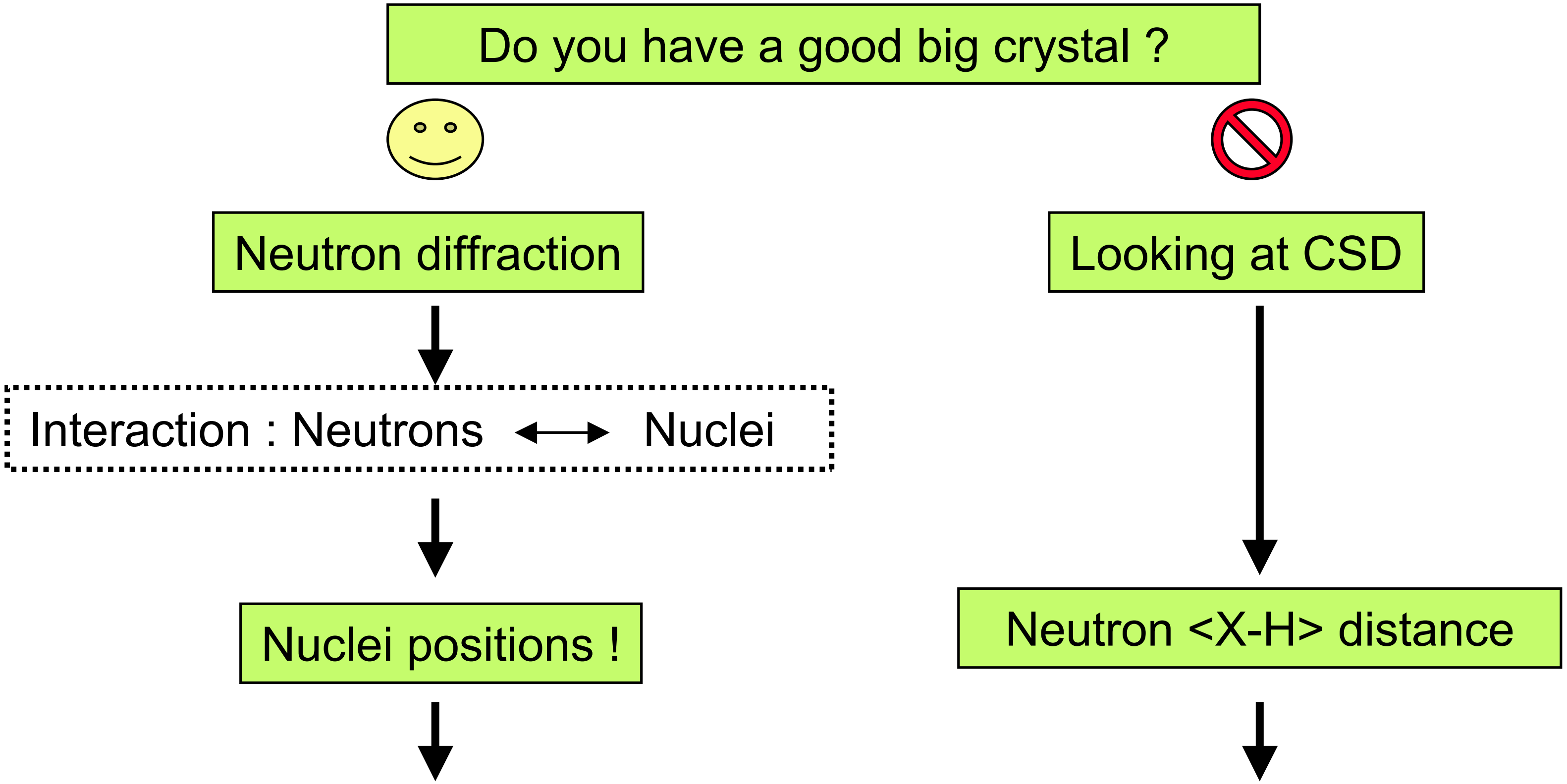
XRD : X-H distance systematically too short !

Hydrogen bonding interactions …. What can we do ?

Introduction

Experimental electron density studies

H’s positions and hydrogen bonding interactions



Do you have a good big crystal ?

Neutron diffraction

Interaction : Neutrons ⟷ Nuclei

Nuclei positions !

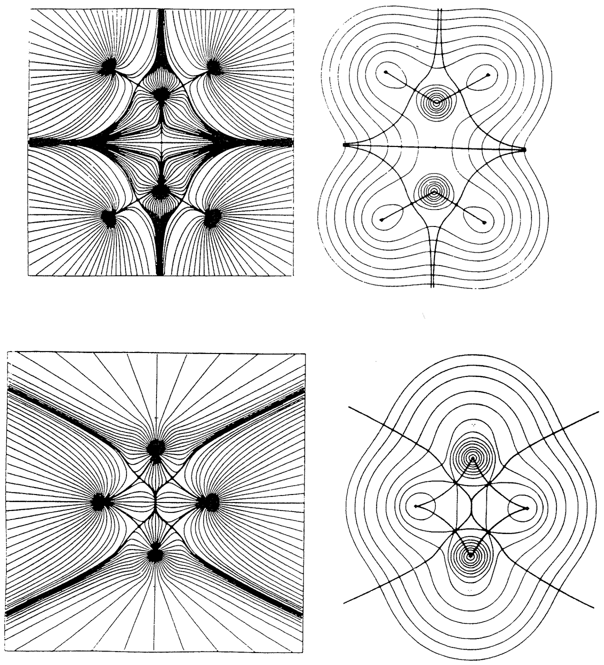
Looking at CSD

Neutron <X-H> distance

… Including neutron information in $\rho_{mod}(r)$

Introduction

The topological analysis of ρ(**r**) : What for ?



$\nabla\rho(\boldsymbol{r})$ $\rho(\boldsymbol{r})$

R.F.W. Bader
“Atoms in Molecules- A Quantum Theory”(1990)

Space partition

↓

$$\nabla\rho(\boldsymbol{r})\cdot\boldsymbol{n}(\boldsymbol{r})=0,\forall\boldsymbol{r}\in S(\boldsymbol{r})$$

↓

S(***r***) and atomic basins

↓

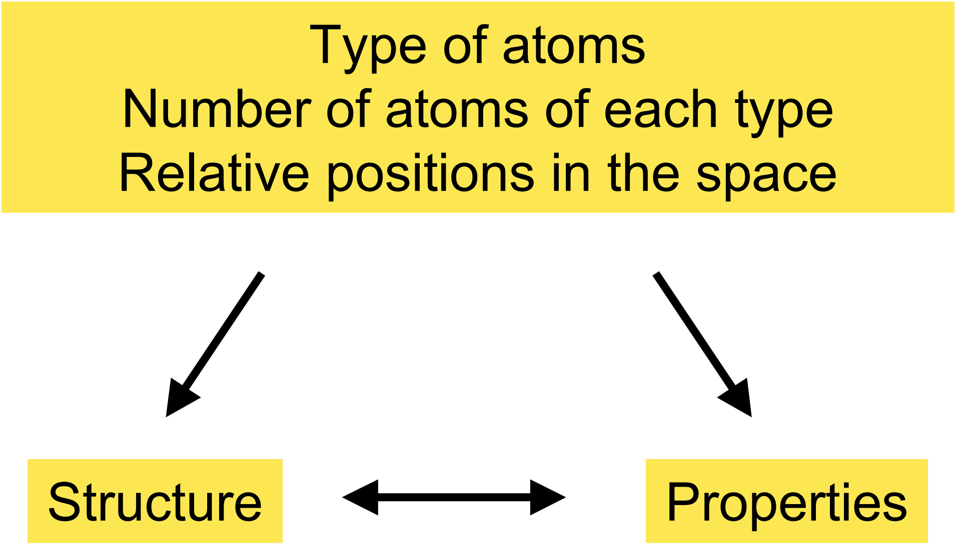
Integrated atomic properties
Local properties at *S*(***r***)

Along the bond direction, saddle distribution at $S(\boldsymbol{r} = \boldsymbol{r}_{\mathrm{BCP}})$:

ρ, $\nabla^2\rho$, λ_i (i = 1,2,3), G, V, H ⟷ **Interatomic Interactions**

Introduction

The chemical system



Type of atoms
Number of atoms of each type
Relative positions in the space

Structure

Properties

Changing one leads to a new set of
interatomic interactions
… and to new structure and properties

Introduction

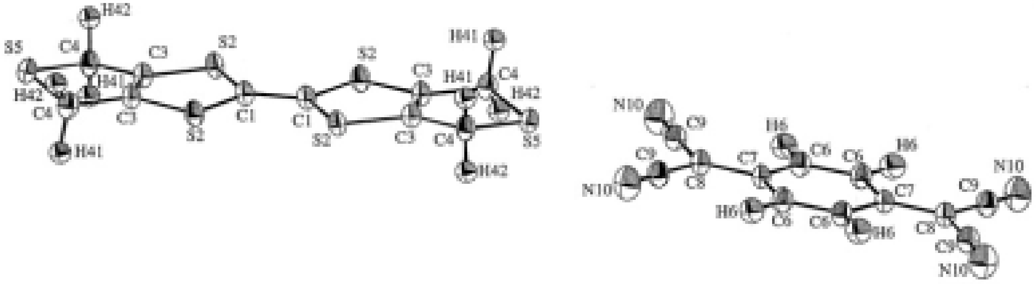
Electron properties at interatomic surfaces

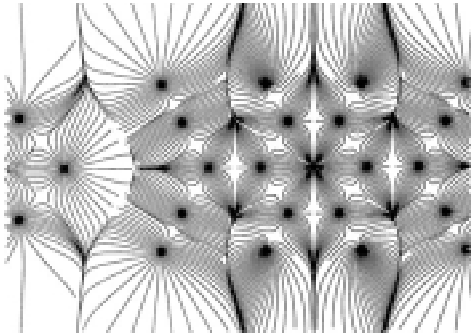
=

Boundary conditions related to chemical structure ?

Topological properties of ρ(r) at BCP’s, reflecting …

… System properties ?





ORTEP view : BTDMTTF···TCNQ interaction

$\nabla\rho(\mathbf{r})$: BTDMTTF···TCNQ interaction

Phys. Rev. B, **1997**, 56, 1820-1833.

Understanding the behaviours of ρ(r) properties at BCP's

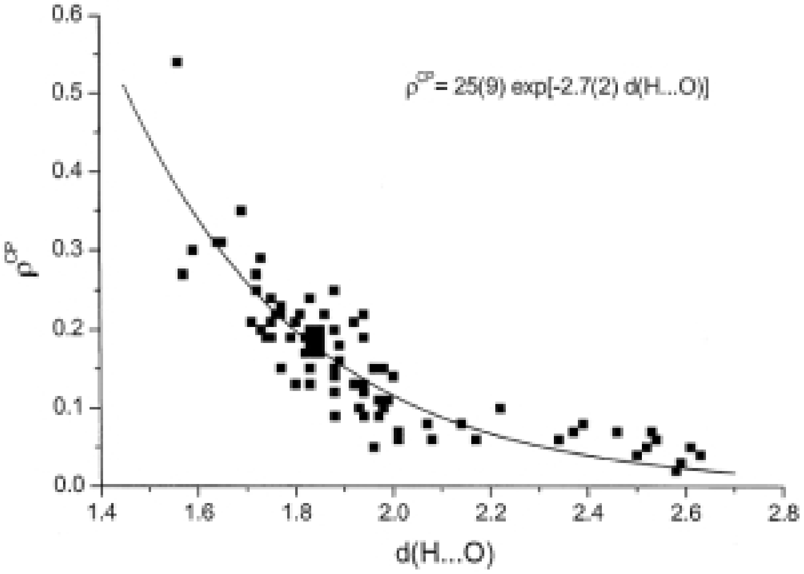
Experimental data set : 83 X-H…O (X = C, N, O)
CS - interactions : 1.54 < d(H…O) < 2.65 Å

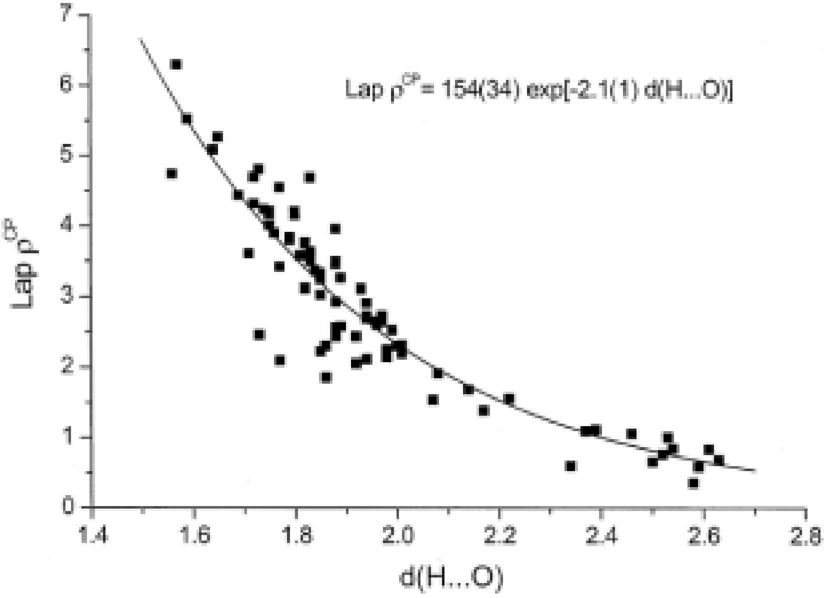
The shorter the internuclear distance, the stronger the interaction :

Electron clouds recover much better each other → $\rho^{CP}\uparrow$

CS interaction : The price to pay → $\nabla^2 \rho^{CP} \uparrow$

Exponential functions : Good fittings



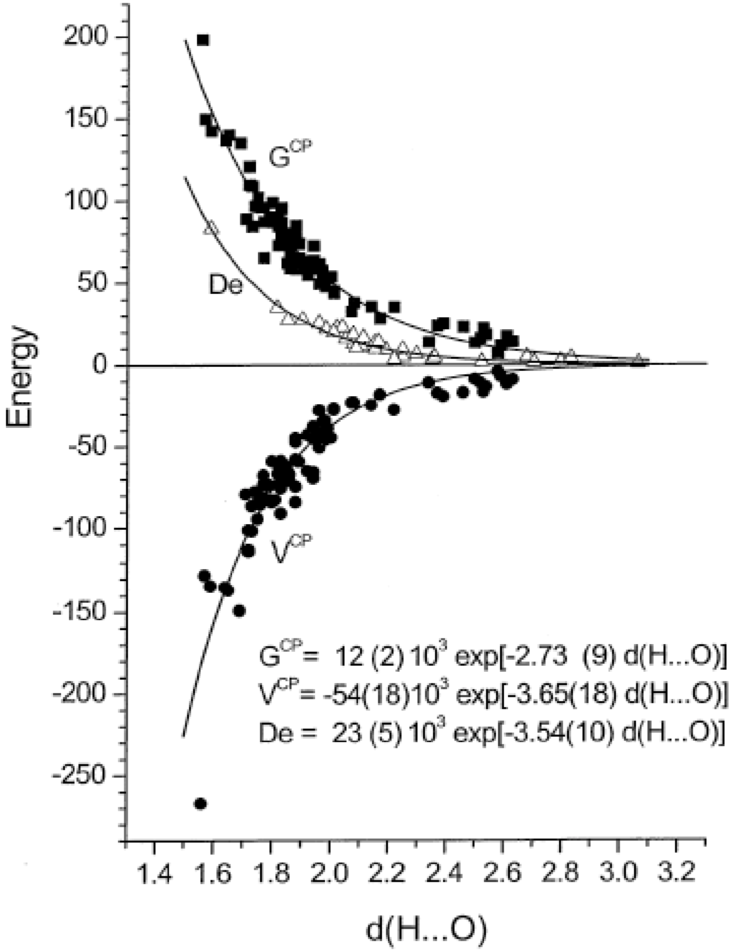


Acta Cryst. **1999**, B55, 563-572.

Understanding the behaviours of ρ(r) properties at BCP's

Abramov's functional : $G_{CP} = \frac{3}{10}\left(3\pi^2\right)^{2/3}\rho_{CP}^{5/3} + \frac{1}{6}\nabla^2\rho_{CP}$

Virial theorem (local form) at r_{BCP} : $2G_{CP} + V_{CP} = \frac{1}{4}\nabla^2\rho_{CP}$



For d(H…O) ↓ : G^{CP} ↑ and $|V^{CP}|$ ↑

$|V^{CP}|$ and G^{CP} interpretations :

Energy densities → Pressures

$|V^{CP}|$ ↑ ↔ ρ^{CP} ↑

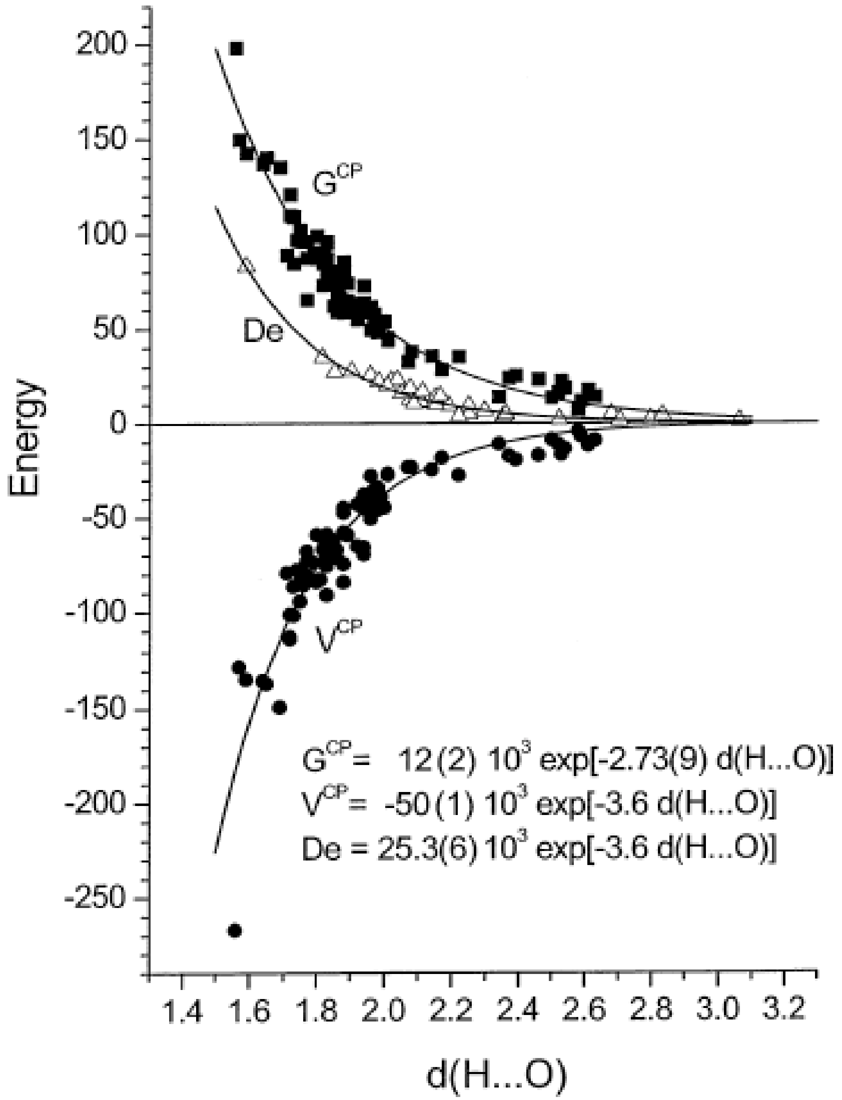
G^{CP} ↑ ↔ $\nabla^2 \rho^{CP}$ ↑ … when ρ^{CP} ↑

Exponential fittings for G^{CP}, V^{CP} …

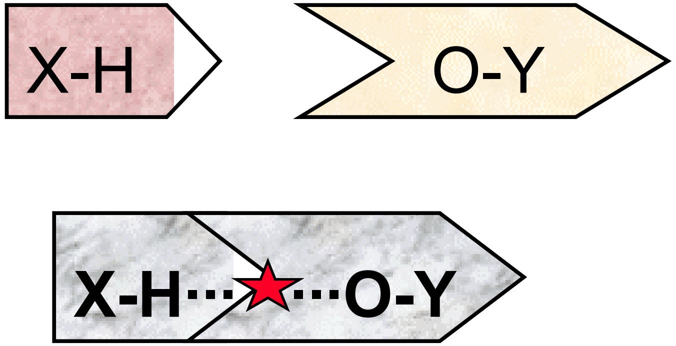
… and De (theoretical data) (?!)

Chem. Phys. Lett. **1998**, 285, 170-173.

From local BCP quantities to system properties



Chem. Phys. Lett. **1998**, 285, 170-173.



- De = E(X-H…O-Y) - E(X-H) - E(O-Y)

De = System property

V^{CP} = Local quantity

De ≈ -1/2 V^{CP}

V^{CP} reflects De …

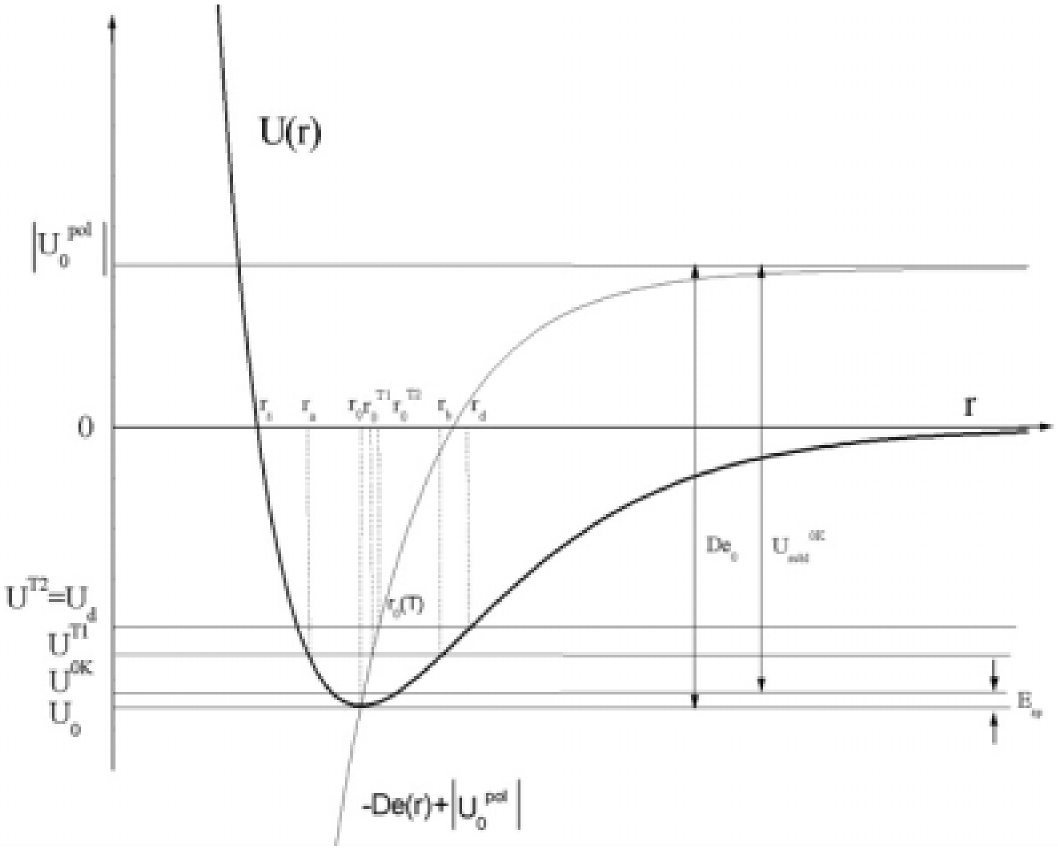
… as a ★ boundary condition

From local BCP quantities to system properties

$H^{CP} = G^{CP} + V^{CP} = 12000 \exp(-2.73r) - 50000 \exp(-3.6r)$

Following De ≈ 1/2 V^{CP} …. Interaction potential U $\longleftrightarrow$ H^{CP} ?

Model : $\boxed{\mathbf{U = -\zeta \cdot H^{CP}}}$



J. Chem. Phys. **2000**, 113, 5686-5694.

$dU/dr = 0$: $r_0 = 1.958$ Å

$(d^2U/dr^2)_{r = r0} = k$: $\zeta = f(k)$

Ice VIII (Raman data)

$k = 22.7$ N/m :

$\zeta = 0.982\ a_0^3$

$U_0 = -13.6$ kJ/mol

From local BCP quantities to system properties

1.- Checking U and De = 1/2 V^{CP} against energetic properties (kJ/mol)

Polarization energy	$U_0 + De_0$	Ice VIII$_{exp}$ (Theor.)
	8.1	5.9 / 9.0
Sublimation energy (0 K)	De_0	Ice (Exp.)
	21.7	28.0
Lattice energy	De_0	Ice VIII (Theor.)
$r_0^{10K,exp}$ = 1.910 Å	25.8	23.5
$r_0^{minimised}$ = 1.928 Å	24.2	22.1 / 24.3
Molecular binding energy	$-De_0 + U^{pol}_0$	Ice VIII$_{exp}$ (Theor.)
$r_0^{10K,exp}$ (Ignoring relaxation)	-17.7	-19.5
Molecular binding energy	De_0	Ice Ih$_{theo}$ (Theor.)
$r_0^{antiferroelectric}$ = 1. 813 Å	36.6	33.0
$r_0^{ferroelectric}$ = 1. 878 Å	29.0	29.9

2.- Checking against the linear expansion coefficient ($\alpha_{Ice} = 5 \cdot 10^{-5}\ K^{-1}$)

Assuming r_0^{0K} = 1.958 Å :	Our model	α_{Ice}
Expected r_0^{273K} *value*	1.989 Å	1.985 Å

J. Chem. Phys. **2000**, 113, 5686-5694.

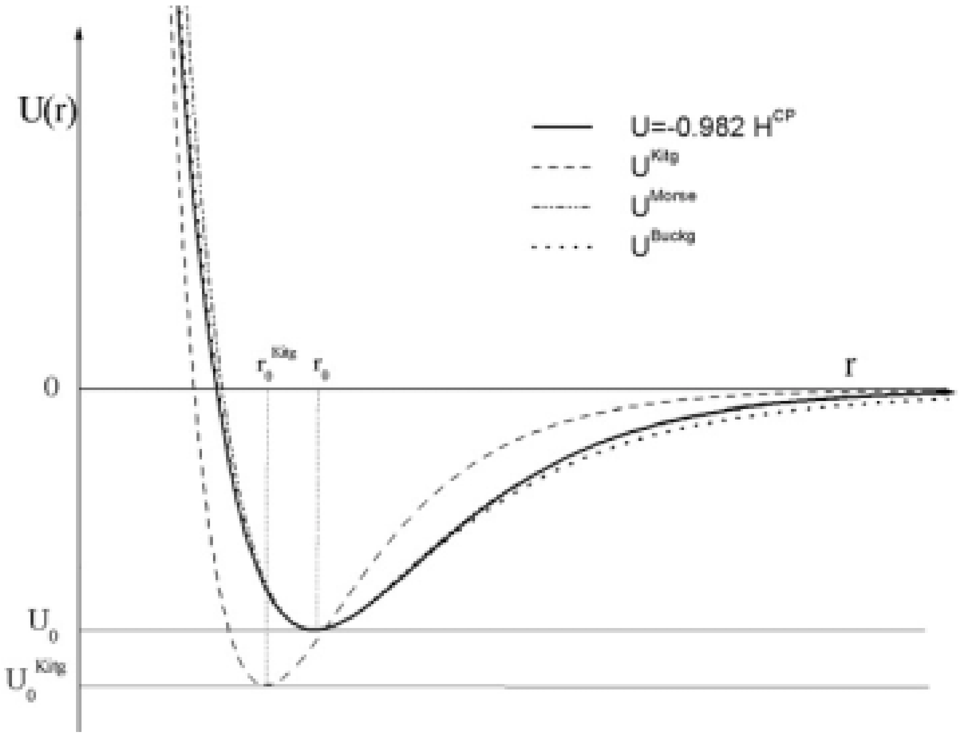
Local BCP quantities and modelling

3.- Comparing interaction potentials to $U = -\zeta \cdot H^{CP}$

$U^{Morse} = U_0 \cdot [1 - \exp(-\alpha \cdot (r - r_0))] - U_0$ (Spectroscopy)

$U^{Buckingham} = -A \cdot r_{ij}^{-6} + B \cdot \exp(-\alpha \cdot r_{ij})$ (Atom-atom potential method)

$U = -0.982 \cdot H^{CP} = 49100 \exp(-3.6 \cdot r) - 11800 \exp(-2.73 \cdot r)$



Kitaigorodsky (60's) : $U^{Kitg} = U^{Morse}$

(U_0 = 16.7 kJ/mol, α = 3 Å^{-1}, r_0 = 1.80 Å)

If U^{Buckg}, U^{Morse} and $U = -0.982 \cdot H^{CP}$ are constrained to:

U_0 = -13.6 kJ/mol
r_0 = 1.958 Å
k = 22.7 N/m

Perfect matching…

… in the full range of distances (?!)

J. Chem. Phys. **2000**, 113, 5686-5694.

Beyond H…O closed-shell interactions

Experimental data set : 83 X-H…O (X = C, N, O)
CS - interactions
1.54 < d(H…O) < 2.65 Å

What about systems exhibiting d(H…O) < 1.54 Å ?

Experimental examples present a short range of internuclear distances !

We need :

a) X-A…B-Y systems permitting a continuous analysis from weak to strong interactions

b) Theoretical calculations

Beyond H…O closed-shell interactions

Theoretical calculations and data sets

- The isolated H…F pairwise interaction :

  6-311++G** basis set/ GAMES and GAUSSIAN98
  NBO and CASSCF methods
  Topological and MO analyses
  0.80 Å < d(H…F) < 2.50 Å

- 79 X-H…F-Y complexes (n, + and -) :

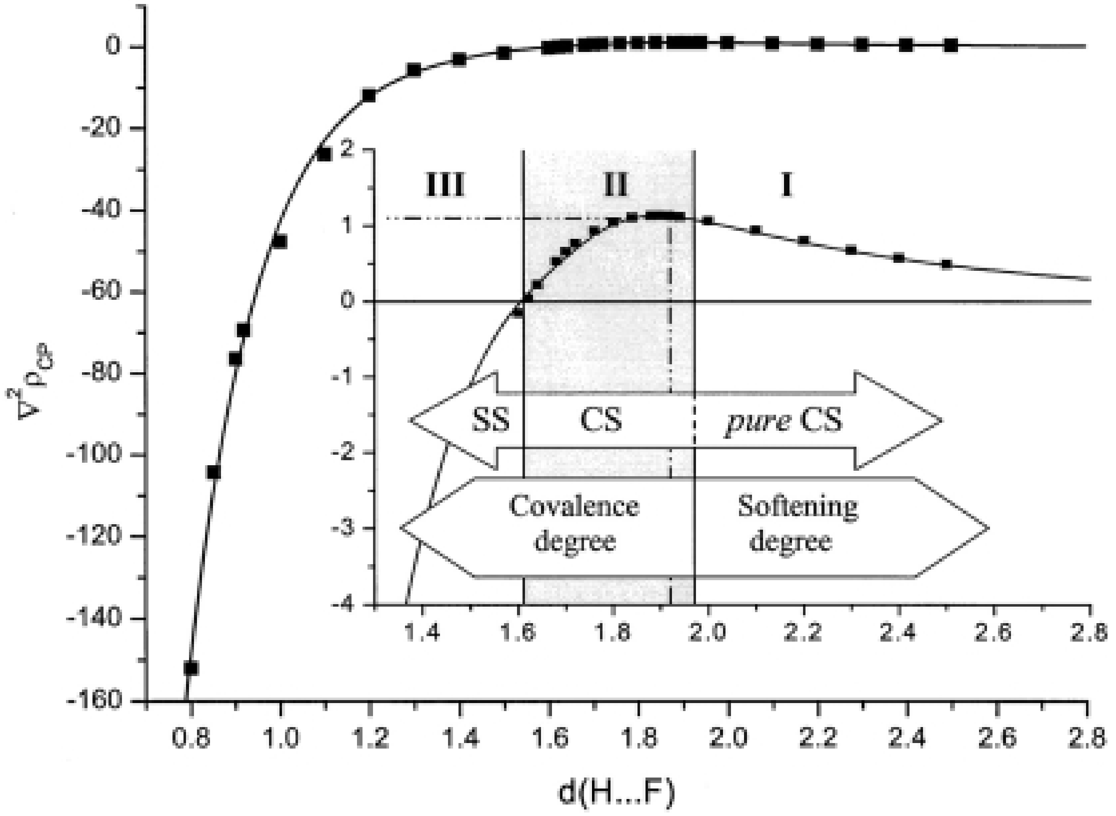
  6-311++G** basis set/ GAUSSIAN98
  Optimised geometries at MP2 perturbation method
  $[F\ldots H\ldots F]^-$ and FH…FH complexes partially optimised
  0.92 Å < d(H…F) < 2.80 Å

J. Chem. Phys. **2002**, 117, 5529-5542.

The isolated H…F pairwise interaction

Fitting : two unweighted exponentials linked by a join function

Typical behaviour of $\nabla^2 \rho_{CP}$ characterised by three geometries :
$\mathbf{d_{cov}} \approx 1.96$ Å, $\mathbf{d_{max}} \approx 1.90$ Å and $\mathbf{d_0} \approx 1.62$ Å.



J. Chem. Phys. **2002**, 117, 5529-5542.

Regions I, II and III

Continuous transit

CS ⟷ SS

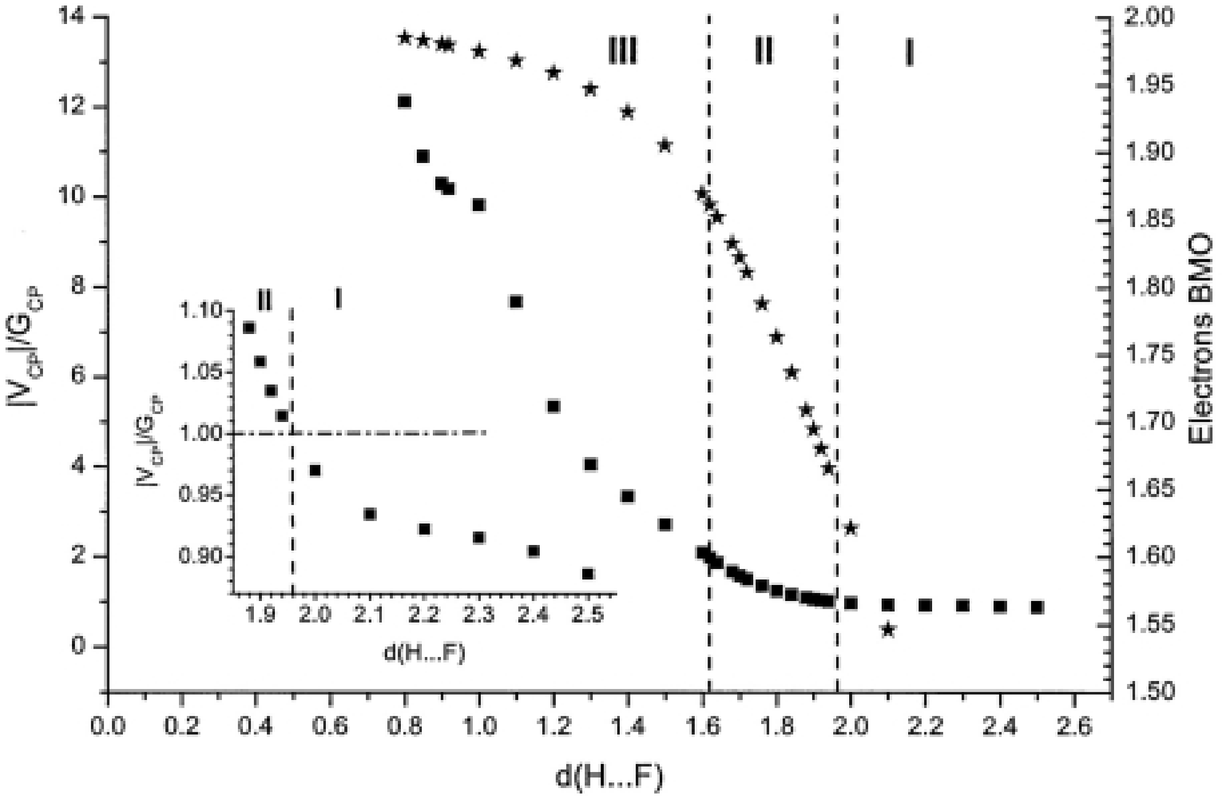
($\nabla^2 \rho_{CP} > 0$) ($\nabla^2 \rho_{CP} < 0$)

…but…

Region I ≠ Region II !

$\mathbf{d_{cov}}$ **?**

The isolated H…F pairwise interaction



Region I ($d > d_{cov}$) : CS

$|V_{CP}|/G_{CP} < 1$ ($H_{CP} > 0$)

- At d ≈ 2.1 Å :

BMO affords convergence Behaviour $|V_{CP}|/G_{CP} \neq$

- **At $d_{cov} \approx 1.96$ Å :**

$|V_{CP}|/G_{CP} = 1$
$\nabla^2 \rho_{CP} \neq$ exp

Region II ($d_0 < d < d_{cov}$) : CS

$2 > |V_{CP}|/G_{CP} > 1$ ($H_{CP} < 0$)

BMO filling (75 to 93 %)

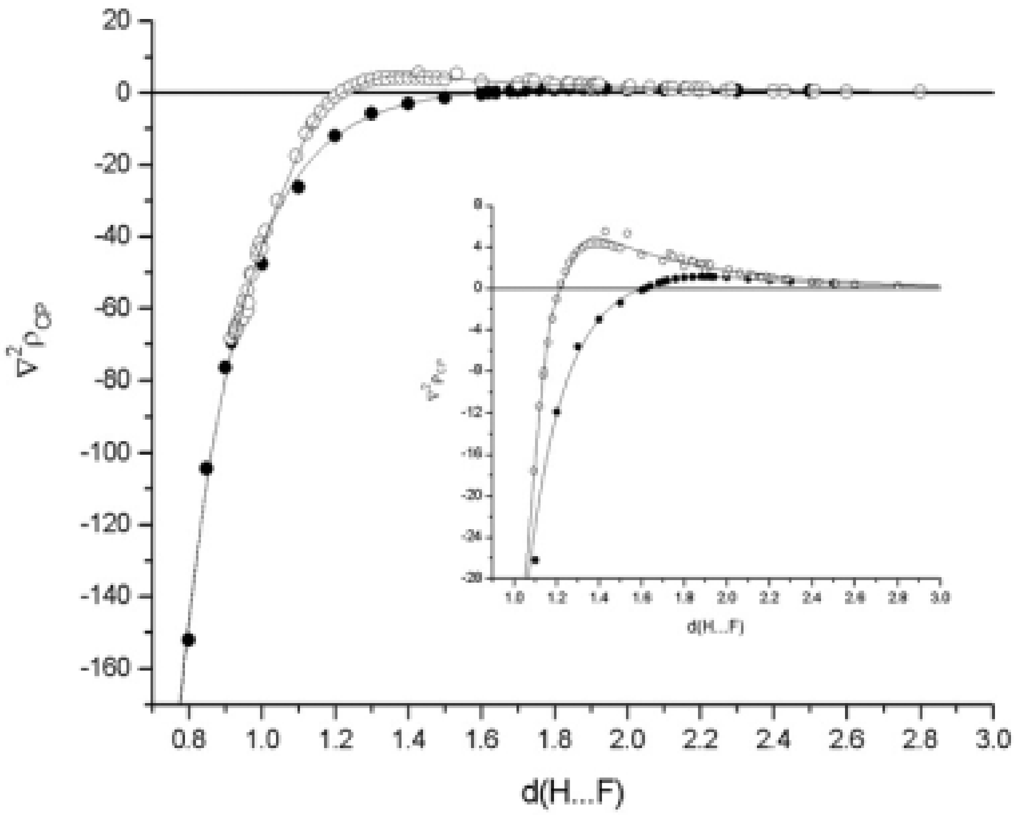
Region III ($d < d_0$) : SS

$|V_{CP}|/G_{CP} > 2$ ($H_{CP} < 0$)

BMO filling (93 to 100 %)

d_{cov} is the geometry related to a Covalence Degree

The H…F interaction and the 79 X-H…F-Y complexes



Regions I and III :

Similar $\nabla^2 \rho_{CP}$ behaviours / values

Region II :

Similar $\nabla^2 \rho_{CP}$ behaviours, but…

…shift of values and
…shift of characteristic distances :

	d_{cov}	d_{max}	d_0
H…F	1.96	1.90	1.62
H-X…F-Y	1.39	1.35	1.20

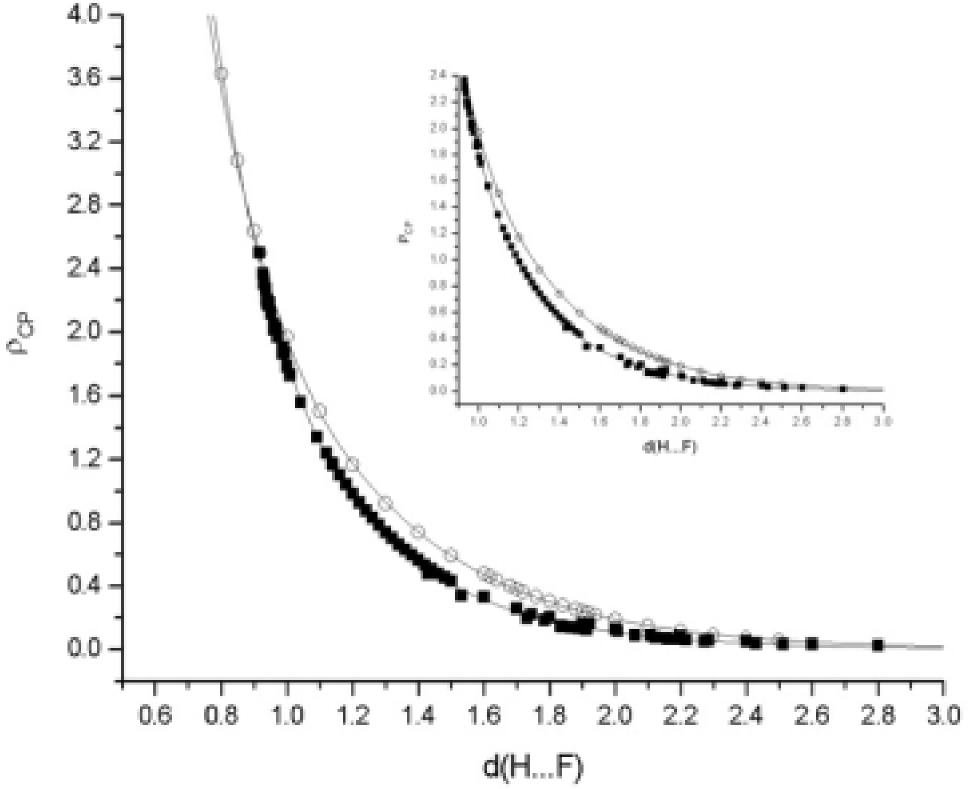
The X-H…F-Y data set : $d_{cov}(+) < d_{cov}(n) < d_{cov}(-) < d_{cov}[F…H…F]^-$

… and similar classifications for d_{max} and d_0.

The H…F interaction and the 79 X-H…F-Y complexes

The greater the ρ_{CP} magnitude the stronger the interaction

One exponential fits well ρ_{CP} *vs*. d(H…F) data, but…
… the log-linear plot indicates two exponential functionalities



In regions I and III :

Similar ρ_{CP} behaviours/values

In region II :

Only slightly different ρ_{CP} values

ρ_{CP}(H…F) > ρ_{CP} (X-H…F-Y)

Characterising differences between systems : **$\nabla^2 \rho_{CP}$ more sensitive than ρ_{CP}**

The H…F interaction and the 79 X-H…F-Y complexes

V_{CP} in regions I and III :
Similar behaviours/values

V_{CP} in region II :
$|V_{CP}$ (X-H…F-Y)$|$ > $|V_{CP}$ (H…F)$|$

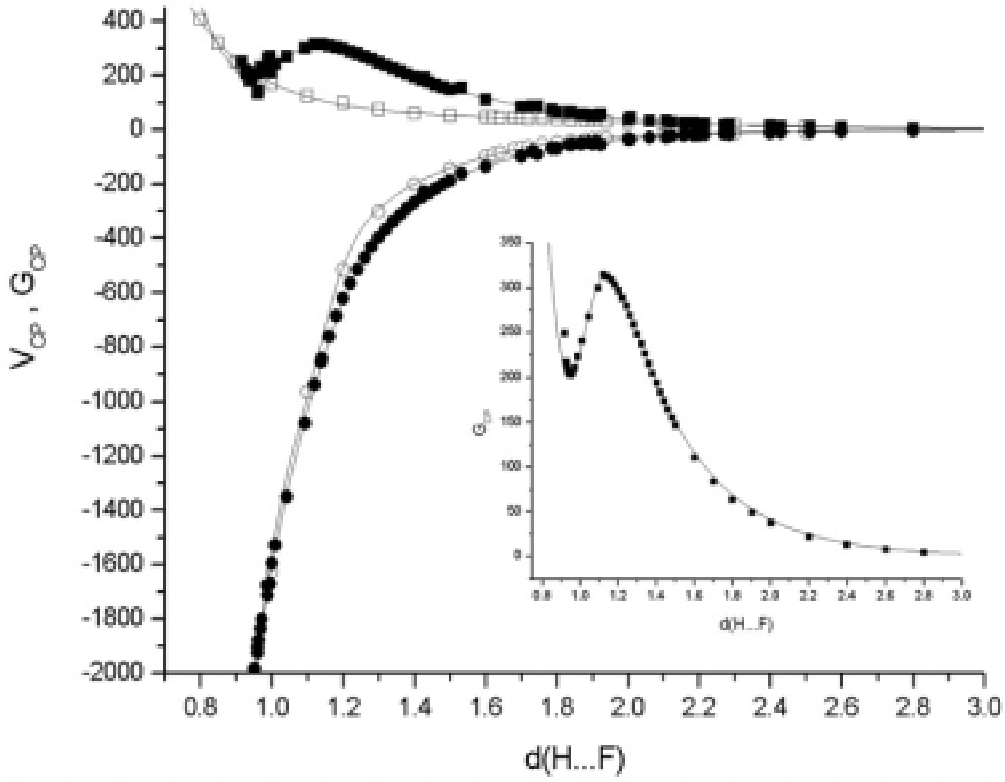
G_{CP} in region III :
Similar behaviours/values

G_{CP} in regions II and I :
G_{CP}(X-H…F-Y) > G_{CP} (H…F)

Comparing both data sets :

Quite different behaviours !

G_{CP} is more sensitive than V_{CP}



What's G_{CP} indicating ?

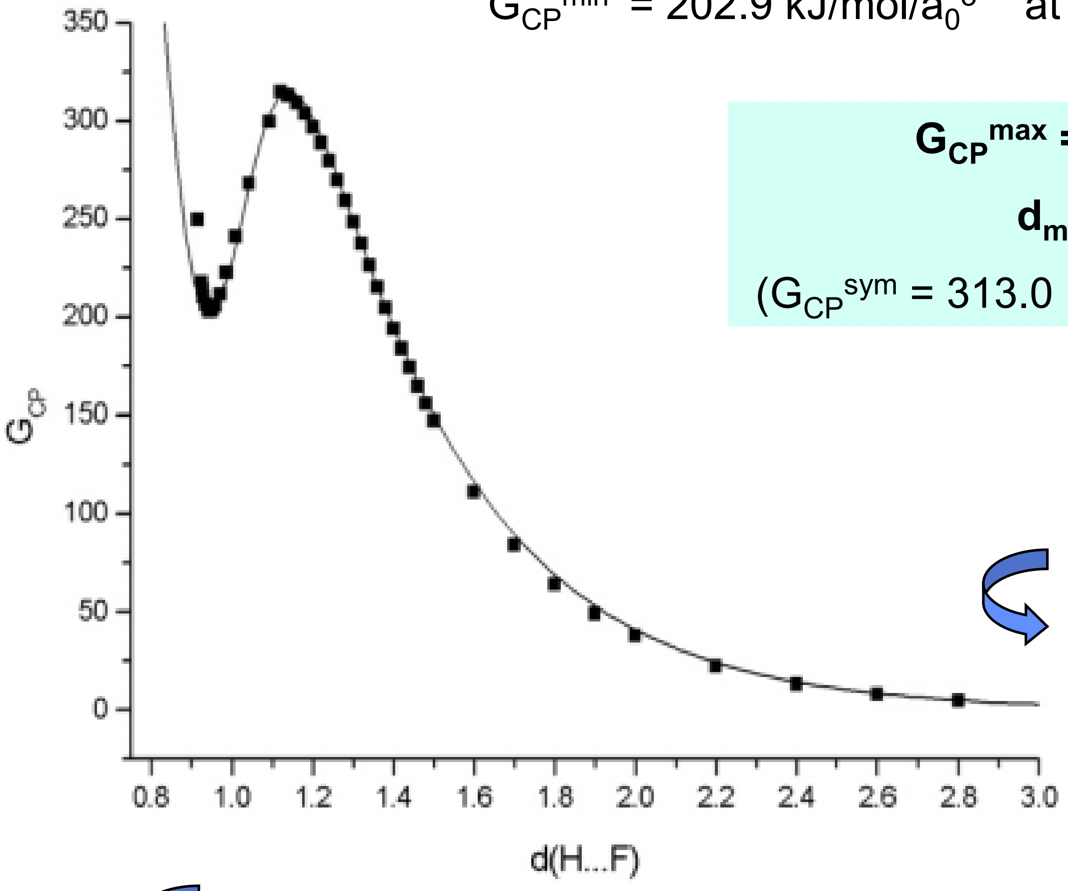
… selecting $[F…H…F]^-$ data

G_{CP} : A useful descriptor for HB systems

Data involving $[F\ldots H\ldots F]^-$ complexes showing local max. and min. :

$G_{CP}^{max} = 314.7$ kJ/mol/a_0^3 at $d_{max} = 1.120$ Å

$G_{CP}^{min} = 202.9$ kJ/mol/a_0^3 at $d_{min} = 0.946$ Å



G_{CP}^{max} = Max. e^- mobility at CP

$d_{max} \approx d_{sym} = 1.138$ Å

($G_{CP}^{sym} = 313.0$ kJ/mol/a_0^3 , $\nabla^2 \rho_{CP}^{sym} = -8.4$ eÅ^{-5})

G_{CP}^{min} = Min. e^- mobility at CP

$d_{min} = d_{H\text{-}F} = 0.9462$ Å

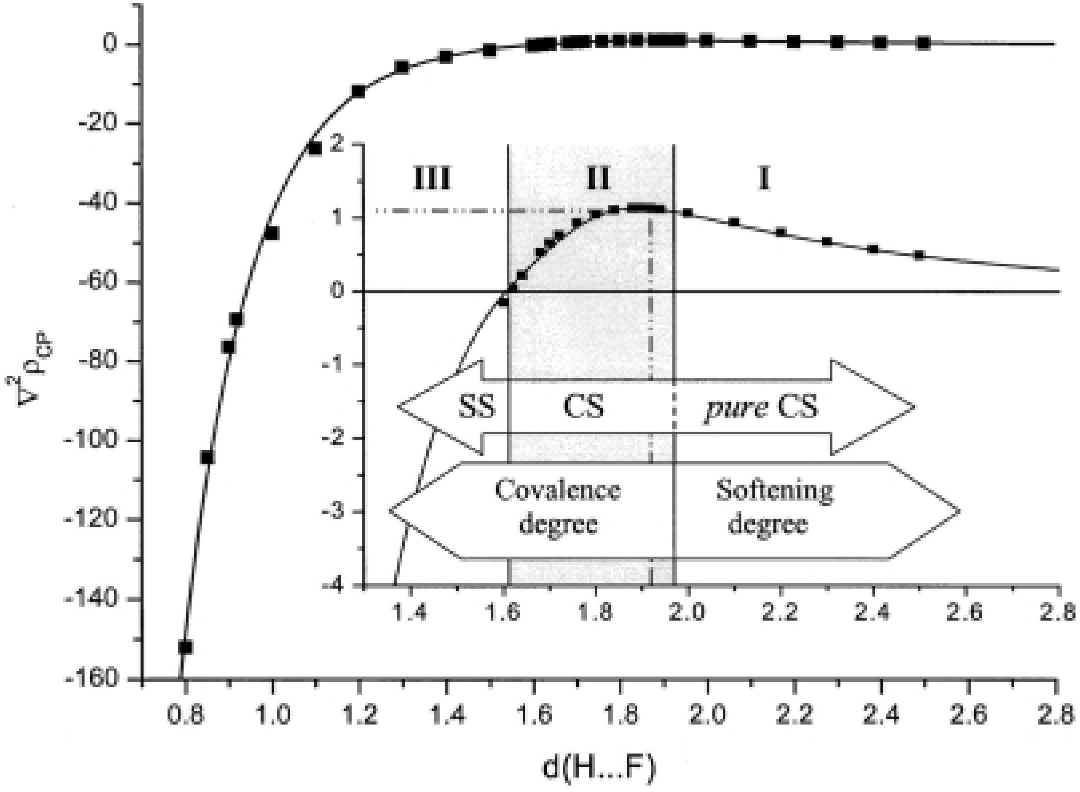
d_{max} = proton transfer geometry

d_{min} = eq. geom. (covalent bond)

RAHB : $d_{eq} < d_{transf} < d_0 < d_{cov}$ and $\nabla^2 \rho_{CP}$, G_{CP} good descriptors !

What about BCP quantities and system properties ?

Based on d_{cov}, the Bond Degree parameter : B.D. = H_{CP}/ρ_{CP}



B.D. interpretation :

Total energy / e^-

Total pressure / ρ

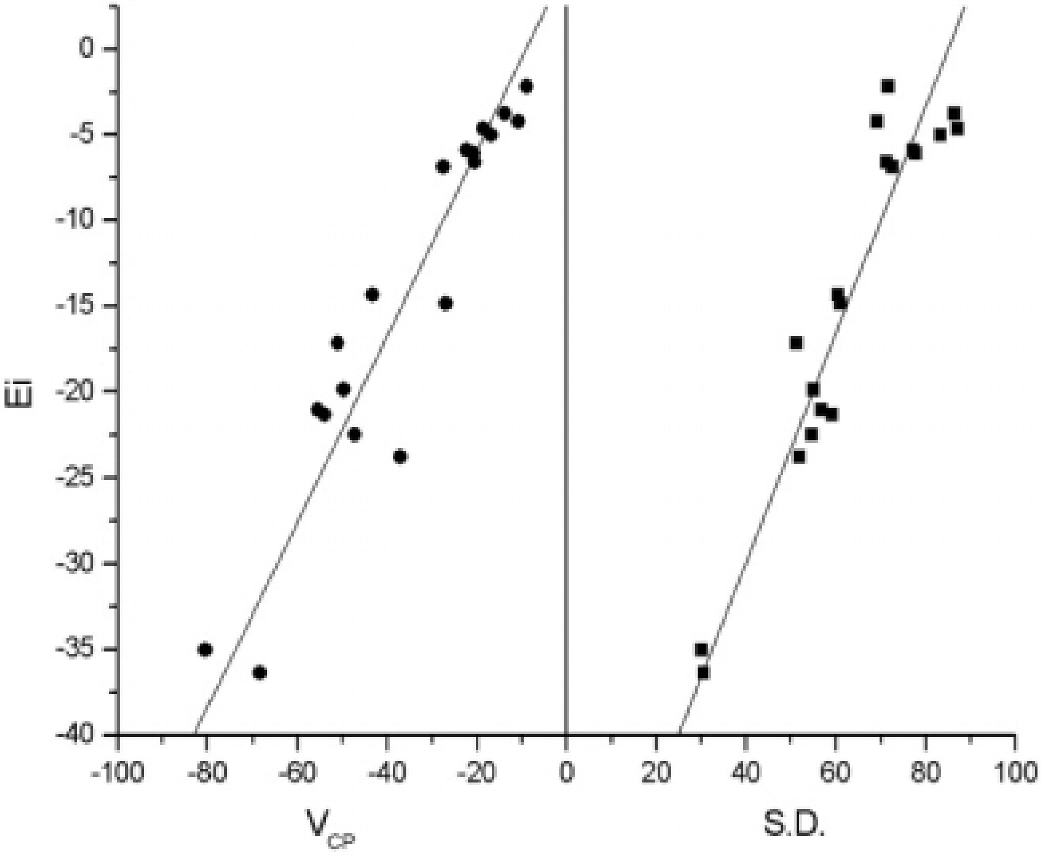
At d_{cov}, BMO building :

If $H_{CP} < 0$: B.D. = C.D.

If $H_{CP} > 0$: B.D. = S.D.

What about BCP quantities and X-H…F-Y properties ?

Neutral X-H…F-Y complexes involving *pure* CS interactions



$Ei = 3(2) + 0.48(4) \cdot V_{CP}$ $Ei = -53(3) + 0.61(5) \cdot S.D.$

Ei vs. V_{CP}

If $Ei = 3(2) + 0.48(4) \cdot V_{CP}$
If $Ei = 0.42(2) \cdot V_{CP}$

≈ 0.5 estimated for H…O

Ei vs. S.D.(H_{CP}/ρ_{CP}) : narrow distribution

↓

Useful for experimental Ei estimations ?

Yes, comparing both of them

Conclusions

» Chemical information is reflected by the form of atoms interact to each other

» Interatomic surfaces …. resulting from interatomic interactions

System properties should be summarized at these surfaces…

… where the information is coded.

Thanks to

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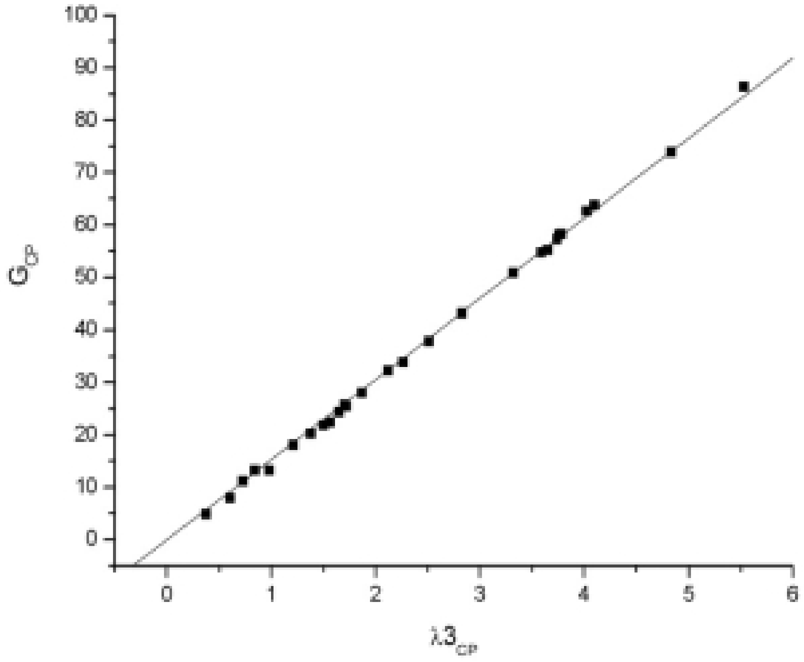
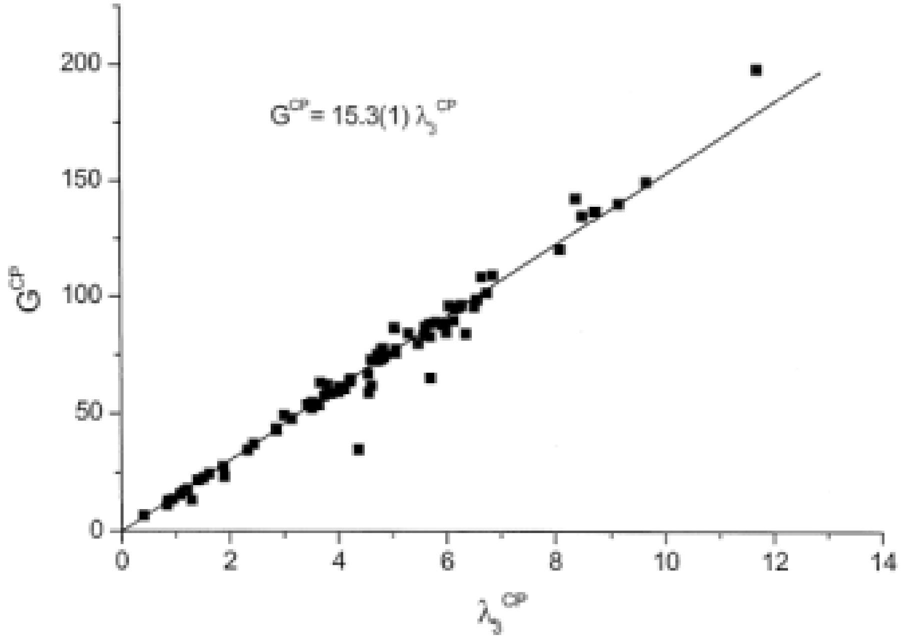
Roger Guilard	L.I.M.S.A.G. - Dijon Université de Bourgogne (France)

Comparing X-H…F-Y and X-H…O *pure* CS interactions





Theoretical X-H…F-Y data

$G_{CP} = 15.31(6) \cdot \lambda 3_{CP}$

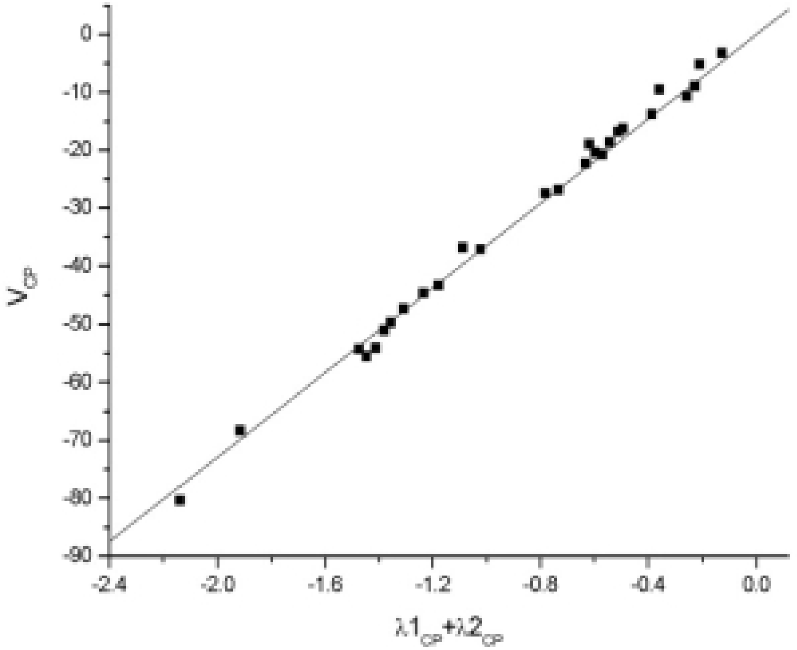
J. Chem. Phys. **2002**, 117, 5529-5542.

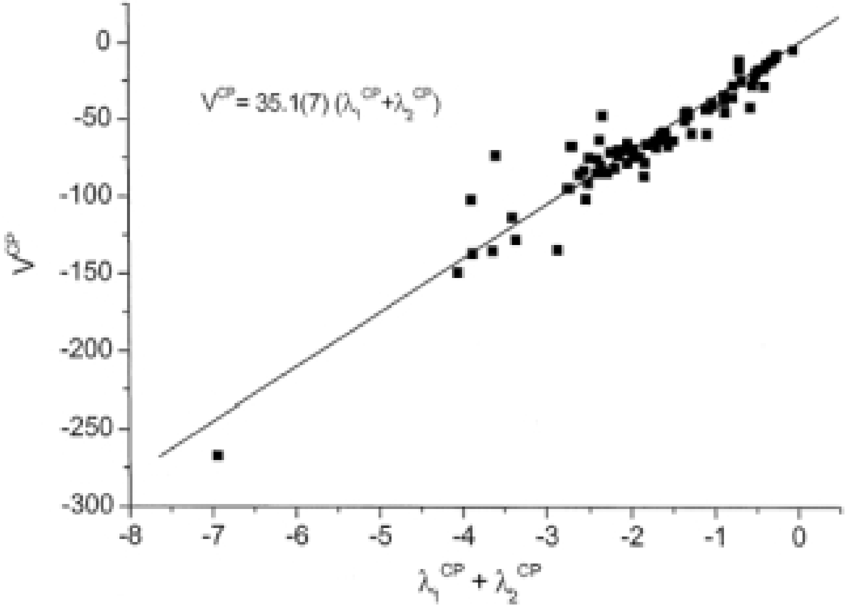
Experimental X-H…O data

$G_{CP} = 15.3(1) \cdot \lambda 3_{CP}$

Chem. Phys. Lett. **1999**, 300, 745-748.

Comparing X-H…F-Y and X-H…O *pure* CS interactions





Theoretical X-H…F-Y data

$V_{CP} = 36.4(3)\cdot(\lambda1_{CP} + \lambda2_{CP})$

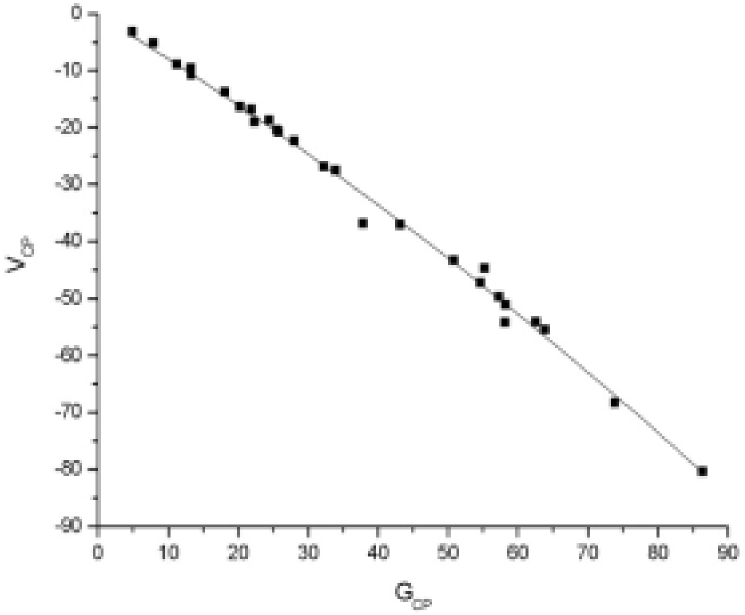
J. Chem. Phys. **2002**, 117, 5529-5542.

Experimental X-H…O data

$V_{CP} = 35.1(7)\cdot(\lambda1_{CP} + \lambda2_{CP})$

Chem. Phys. Lett. **1999**, 300, 745-748.

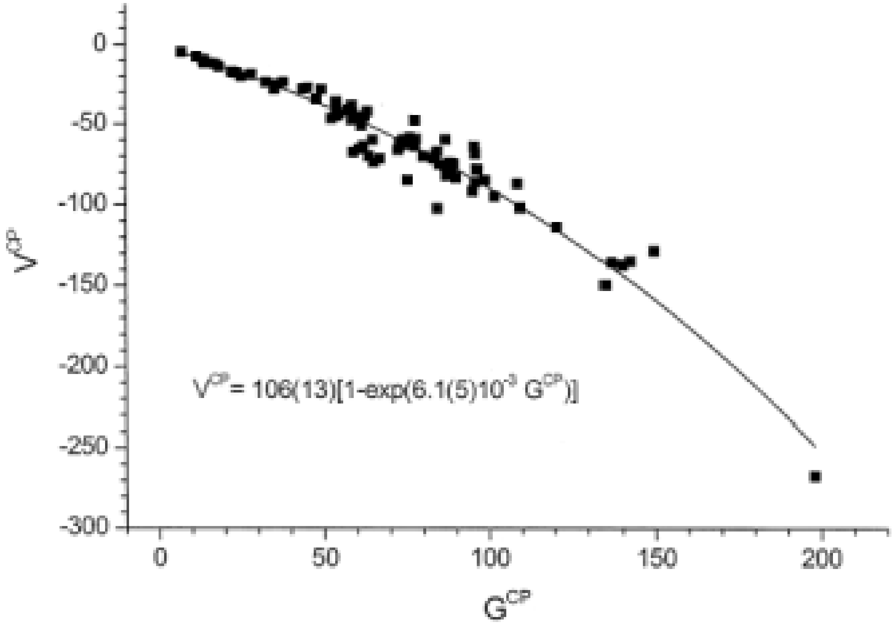
Comparing X-H…F-Y and X-H…O *pure* CS interactions



Theoretical X-H…F-Y data

$$V_{CP} = 158(34) \cdot [1 - \exp(4.8(9) \cdot 10^{-3} \cdot G_{CP}]$$

J. Chem. Phys. **2002**, 117, 5529-5542.

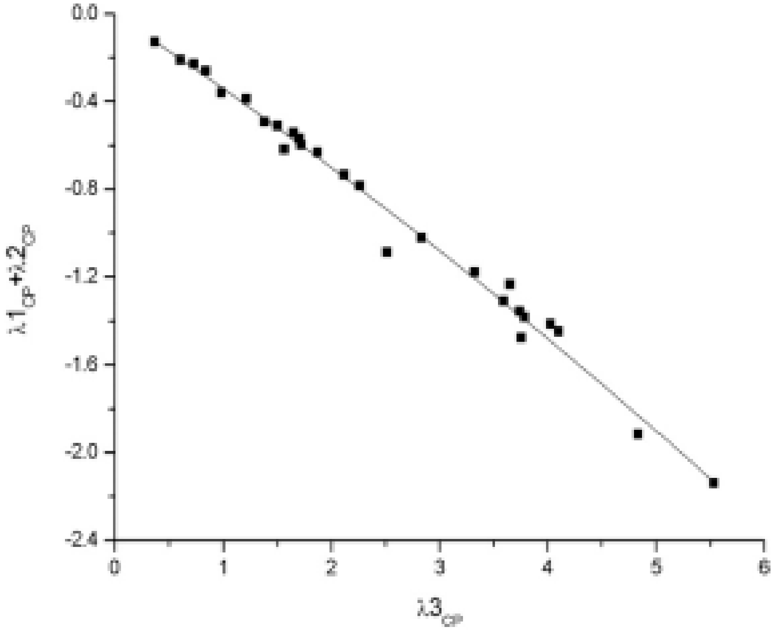


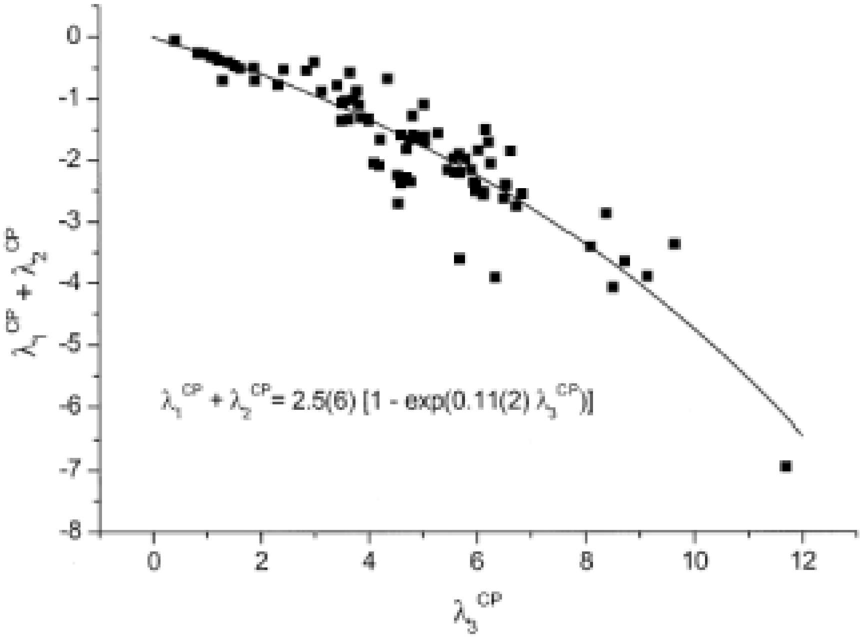
Experimental X-H…O data

$$V_{CP} = 106(13) \cdot [1 - \exp(6.1(5) \cdot 10^{-3} \cdot G_{CP}]$$

Chem. Phys. Lett. **1999**, 300, 745-748.

Comparing X-H…F-Y and X-H…O *pure* CS interactions





Theoretical X-H…F-Y data

Experimental X-H…O data

$$\lambda1_{CP}+\lambda2_{CP} = 5(2)\cdot[1-\exp(0.06(2)\cdot\lambda3_{CP}]$$

$$\lambda1_{CP}+\lambda2_{CP} = 2.5(6)\cdot[1-\exp(0.11(2)\cdot\lambda3_{CP}]$$

J. Chem. Phys. **2002**, 117, 5529-5542.

Chem. Phys. Lett. **1999**, 300, 745-748.

Comparing X-H…F-Y and X-H…O *pure* CS interactions

For *pure* CS interactions ($H_{CP} > 0$)…

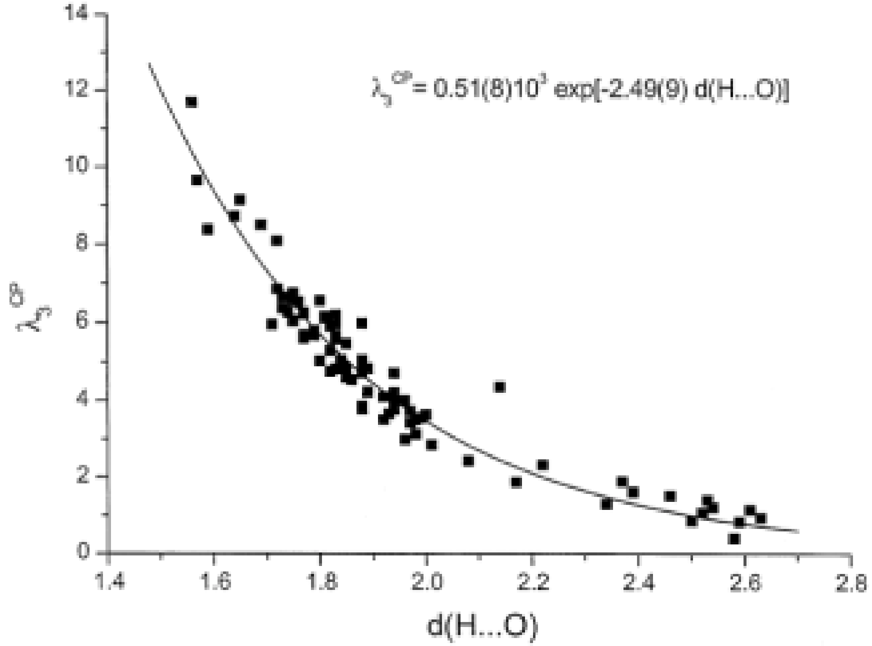
…Universal relationships between topological and energetic properties at BCP's ?

If yes …

… last equations could be used for the modelling of experimental $\rho(r)$ (soft interactions)

In particular, $\lambda 3_{CP}$ dependences !

Acta Cryst. **1999**, B55, 563-572.



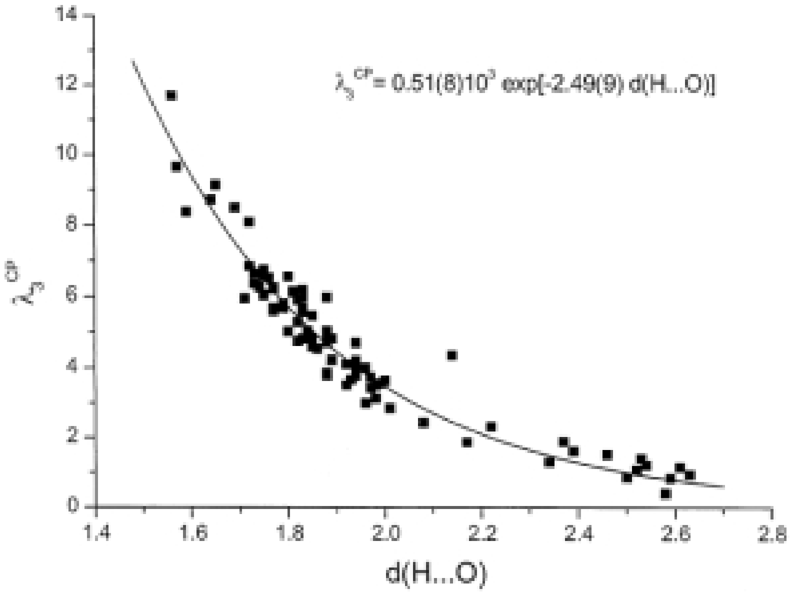
Understanding the behaviours of $\rho(r)$ properties at BCP's

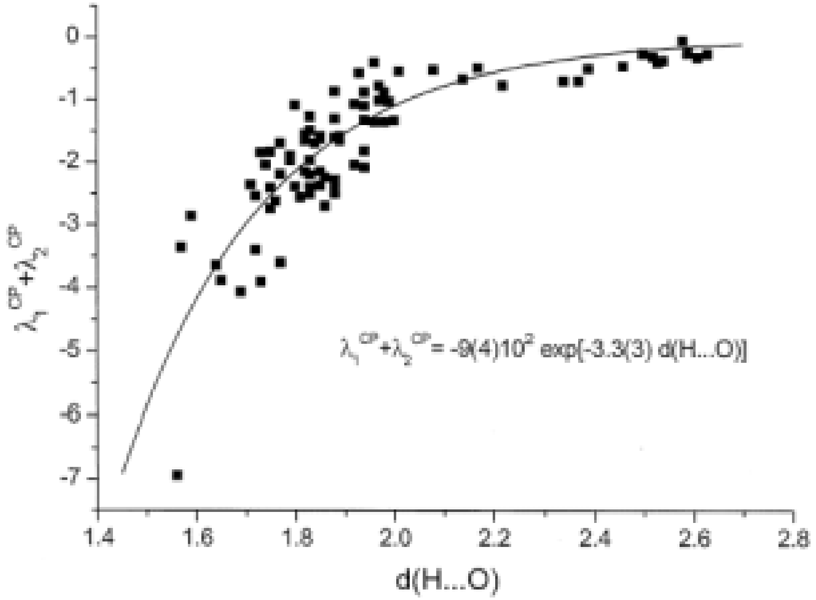
83 X-H…O (X = C, N, O) CS - interactions

$1.54 < d(H…O) < 2.65$ Å

The curvatures at CP : exponential functionalities

The *cleanest* experimental behaviour : λ_3^{CP} *vs*. d(H…O))

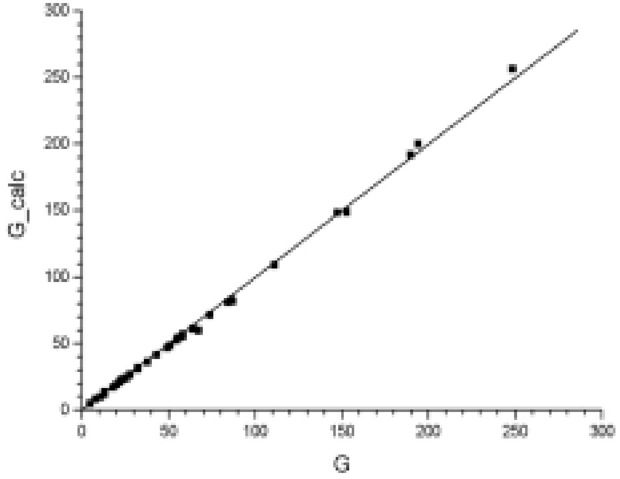


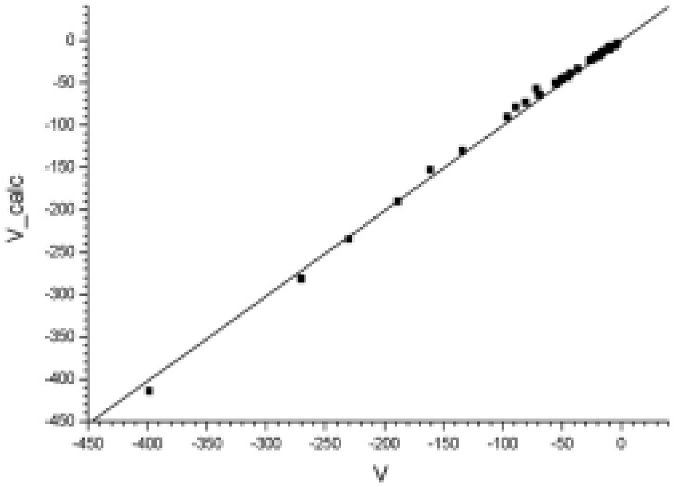


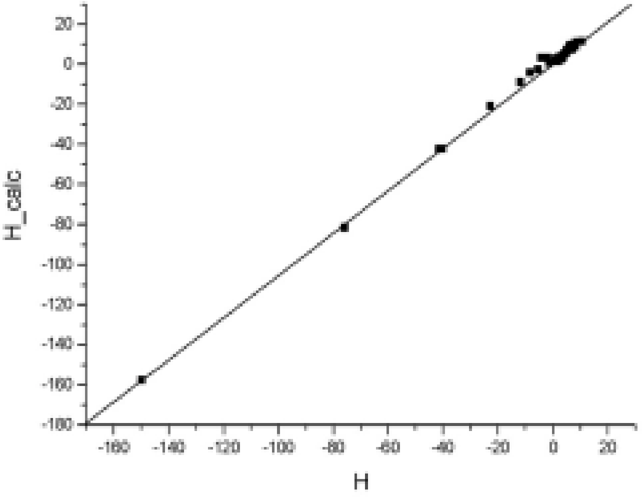
Acta Cryst. **1999**, B55, 563-572.

About the evaluation of the local energies at BCP's

37 X-H…F-Y closed-shell interactions ($\nabla^2\rho^{CP} > 0$)







G_{calc} = 0.998(6)·G (R^2 = 0.999), <ΔG/G> ~ 4 %

V_{calc} = 1.006(9)·V (R^2 = 0.999), <ΔV/V> ~ 9 %

H_{calc} = 1.05(1)·H (R^2 = 0.999), <ΔH/H> ~ 43 %

Chem. Phys. Lett. **2001**, 336, 457-461.

Introduction

Experimental electron density studies

The $\rho_{mul}(\mathbf{r})$ multipolar model

$$\rho_{mul}(\boldsymbol{r}) = \sum_{i=1}^{Nat} \rho_i(\boldsymbol{r})$$

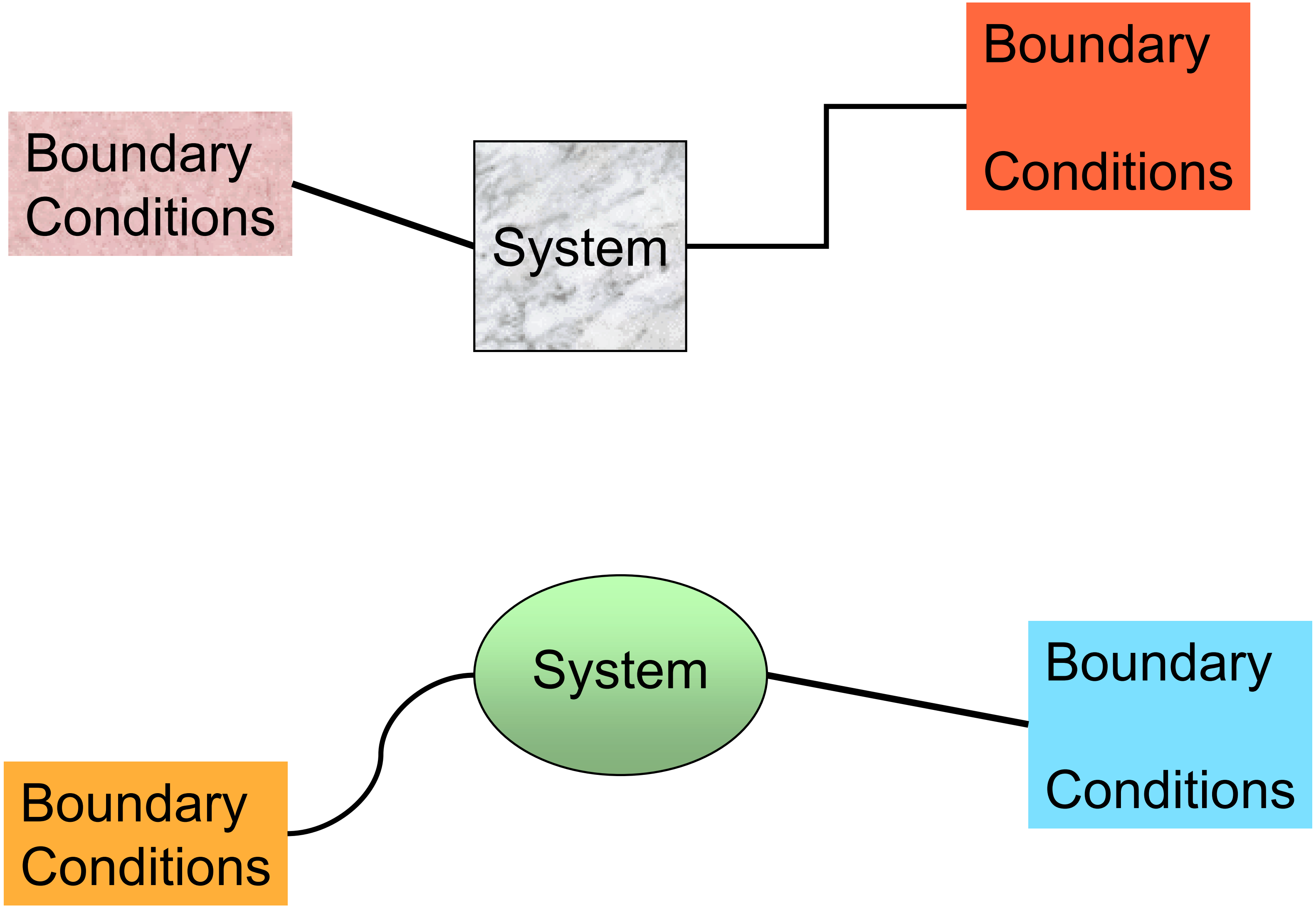
$$\rho_i(\boldsymbol{r}) = \rho_{core}(r) + P_{val}\kappa^3\rho_{val}(\kappa r) + \sum_{l=0}^{l\max}\sum_{m=0}^{l} \kappa'^3 R_{nl}(\kappa' r) P_{l\pm m} y_{l\pm m}(\theta,\varphi)$$

$\rho_{core}(r)$: unperturbed spherical distribution

$P_{val}\kappa^3\, \rho_{core}(\kappa r)$: perturbed spherical valence distribution

$\sum\sum \kappa'^3 R_{nl}(\kappa' r) P_{l\pm m}\, y_{l\pm m}(\theta,\varphi)$: perturbed no-spherical valence distribution

Introduction



Boundary Conditions

System

Boundary Conditions

System

Boundary Conditions

Boundary Conditions