Benoît BRAÏDA

The Maximum Probability Domains method

Workshop on Topological Approaches to Intermolecular Interactions, 26-28 June 2013, Paris

Laboratoire de Chimie Théorique

Université Pierre et Marie Curie - Sorbonne universités

Schedule

- 09:00/09:30 : The MPD method (BB)
- 16:30/17:30 : The MPD program / Training (MM)

Real space regions interpretative methods

Method	*Function*	*Regions*
AIM	$\rho(r)$	Atomic regions
ELF	ELF(r)	ELF basins
MPD	$p_\nu(\Omega)$	Domains of max. probability (Ω)

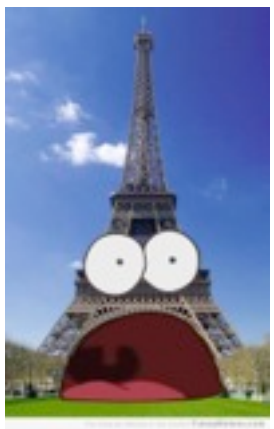
- Ancestor of MPD : Daudel's loges theory

MPD history

- Selected references :
  - Savin A (**2002**) In: Sen KD (ed) Reviews of modern quantum chemistry: a celebration of the 252 contributions of Robert G. Parr. World Scientific, Singapore, p43
  - Cancès E, Keriven R, Lodier F, Savin A (**2004**) Theor Chem Acc 111, 373
  - Scemama A, Caffarel M, Savin A (**2007**) J Comp Chem 28, 442
  - Causa M, Savin A Z. Anorg. Allg. Chem. **2011**, 637 / Causa M, Savin A J. Phys. Chem. A **2011**, 115, 13139
  - Mafra Lopez Jr. O, Braïda B, Causa M, Savin A in Progress in Theoretical Chemistry and Physics vol 22, p173 ed Hoggan, Springer UK, London (**2011**)

MPD connexion

Paris



Andreas Savin, Benoît BRAÏDA
Pascal Frey, Simona B. Savescu
MPD program (molecules)

Oviedo

Ángel Martín Pendás
Marcos Menendez

Napoli

Mauro Causa'
MPD program (solids)

Ghent

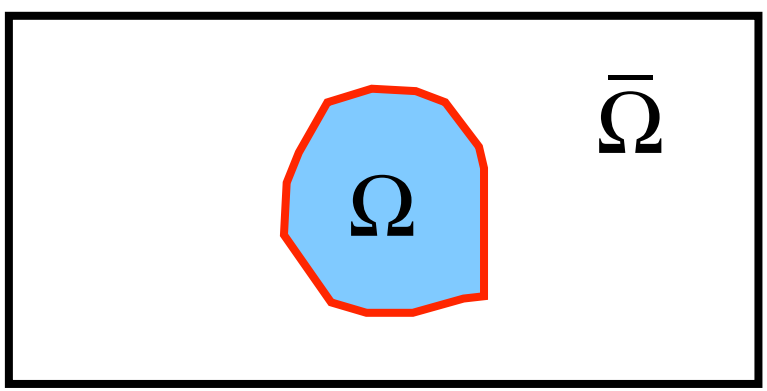
Patrick Bultinck
Guillaume Acke

Basics

1) The probability function :

Probability to find *v and only v* electrons in a given region of space Ω :

$$p_v(\Omega) = \binom{N}{v} \int_{\Omega} dx_1 .. dx_v \int_{\bar{\Omega}} dx_{v+1} .. dx_N |\psi|^2$$



Basics

1) The probability function :

Probability to find ν *and only* ν electrons in a given region of space Ω :

$$p_\nu(\Omega) = \binom{N}{\nu} \int_\Omega dx_1 .. dx_\nu \int_{\bar{\Omega}} dx_{\nu+1} .. dx_N |\psi|^2$$

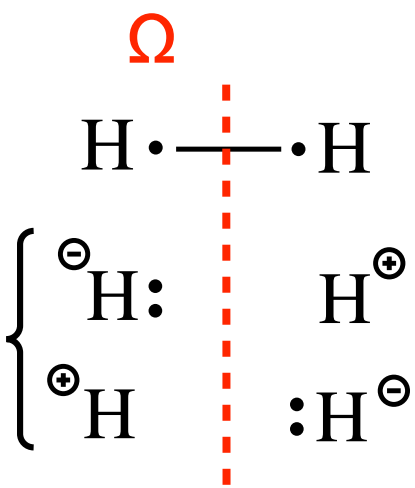
Rem : $$p_1(\Omega) \neq \int_\Omega \rho(x_1) dx_1 = N \int_\Omega dx_1 \int_{R^3} dx_2 .. dx_N |\psi|^2 = <\nu>_\Omega$$

We rather have : $$<\nu>_\Omega = \sum_{\nu=0}^{N} \nu \, p_\nu(\Omega)$$

Basics

1) The probability function :

Example : dihydrogen molecule - large interactomic distance :



	$p_1(\Omega)$	$p_0(\Omega) = p_2(\Omega)$	$\langle v \rangle$
Ground (covalent) state :	1.	0.	1.
Excited ionic state :	0.	0.5	1.

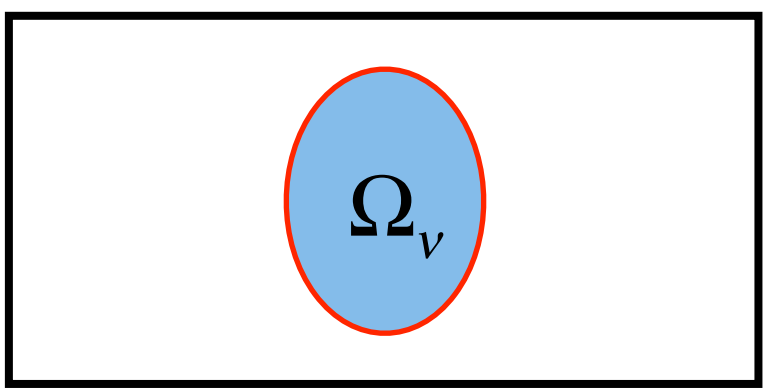
➡ Probabilities contain more informations than populations

Basics

2) MPD / Definition :

A **M**aximum **P**robability **D**omain (**MPD**) is a region of space *locally* maximizing $p_\nu(\Omega)$:

$$\Omega_\nu = \max_{\Omega} p_\nu(\Omega)$$

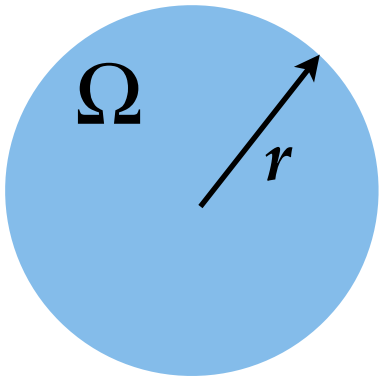


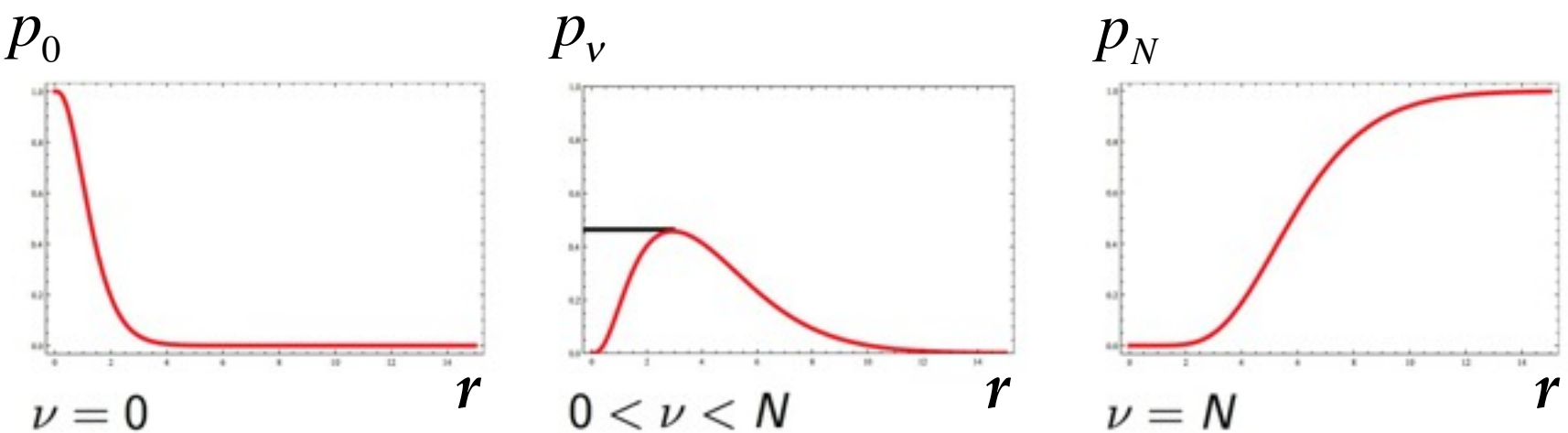
Basics

2) MPD / existence :

Example : atom case (N e^-),

atomic-centered spherical domain :





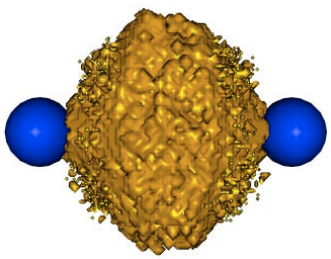
➡ For any ν, at least one Ω_ν always exists

Basics

2) MPD / Optimization (in a nutshell) :

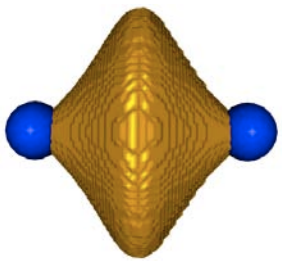
Guess domain

Ω



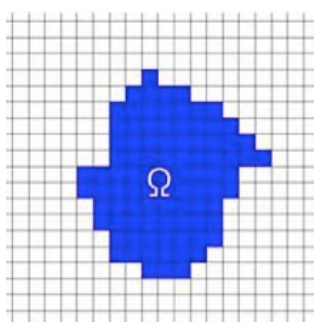
Optimisation

$\max_{\Omega} p_v(\Omega)$

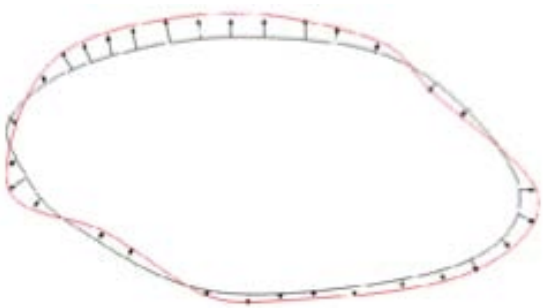


MPD

Ω_v



Acceptation/Rejection (0)

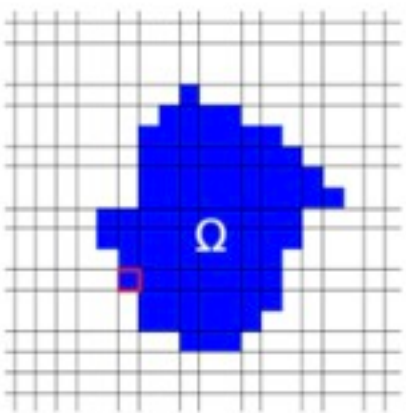


Shape derivatives (1)

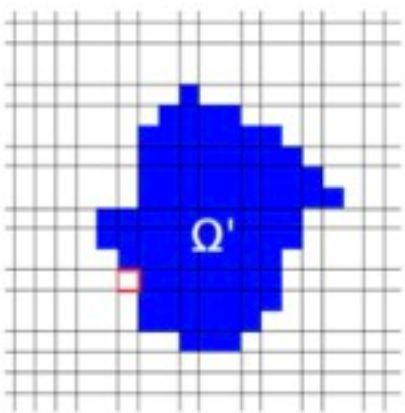
Basics

2) MPD / Optimization (in a nutshell) :

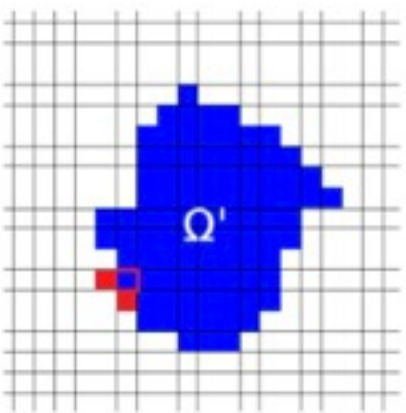
Acceptation/rejection algorithm (0) :



Random element selection of the surface



$p_\nu(\Omega') > p_\nu(\Omega) \Longrightarrow$ OK



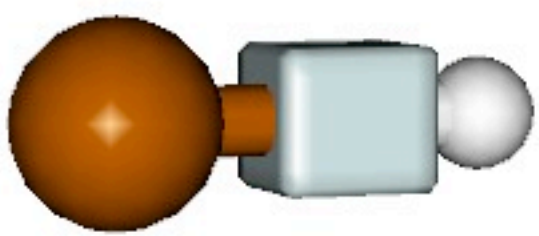
$p_\nu(\Omega') > p_\nu(\Omega) \Longrightarrow$ OK

➡ Single domain optimization only

Basics

2) MPD / Optimization (example) :

Searching a Ω_2 domain in the Li—H molecule :



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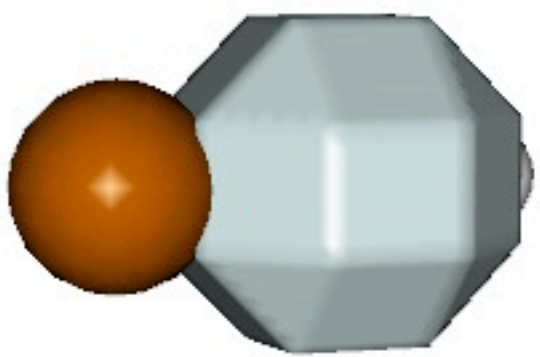

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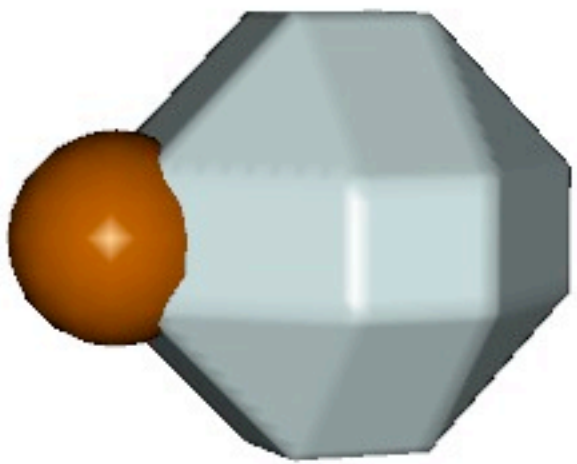

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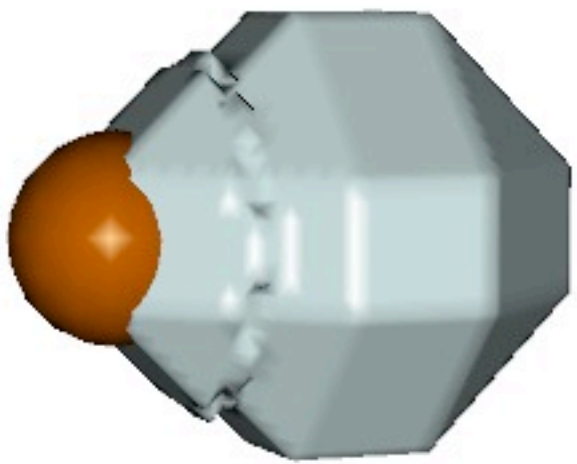

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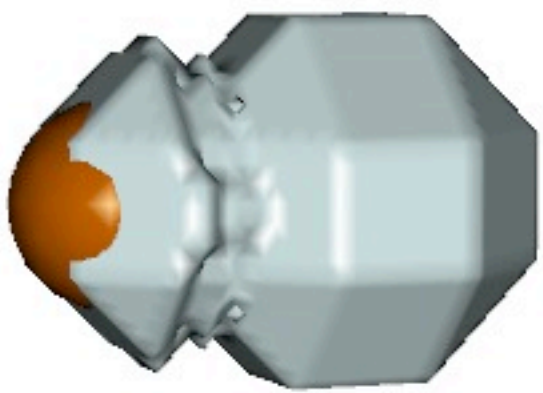

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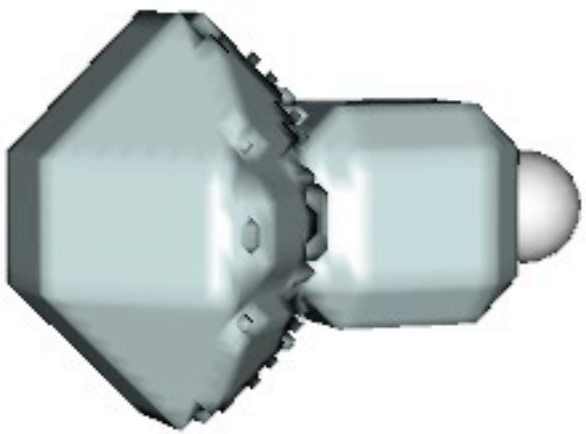

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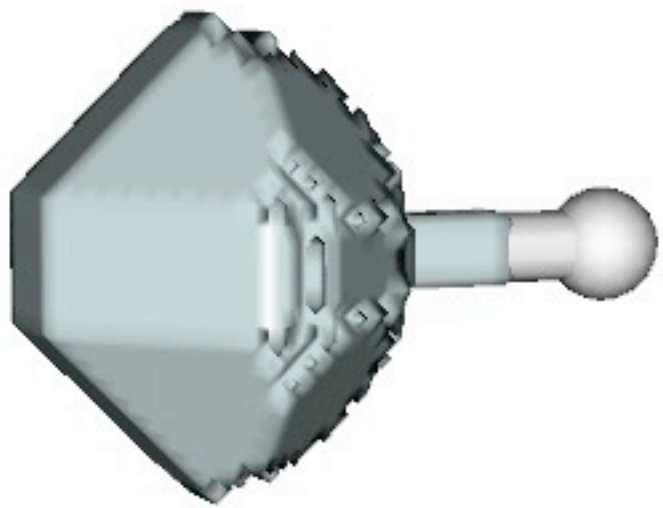

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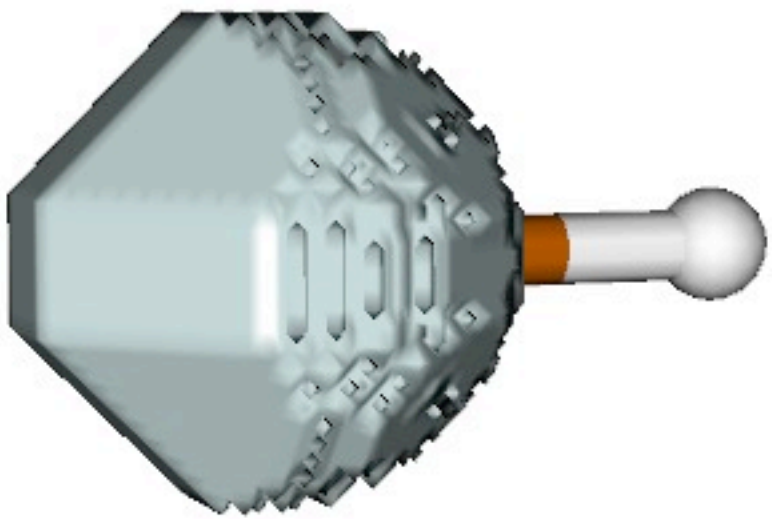

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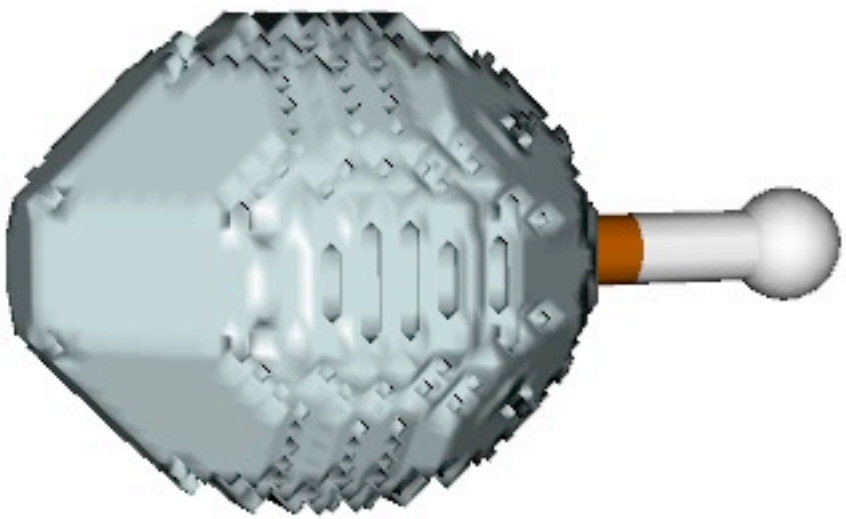

Basics

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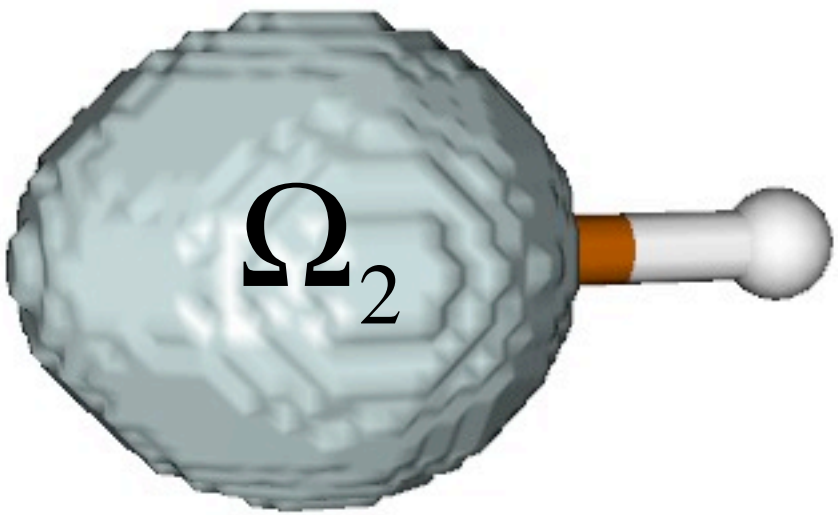
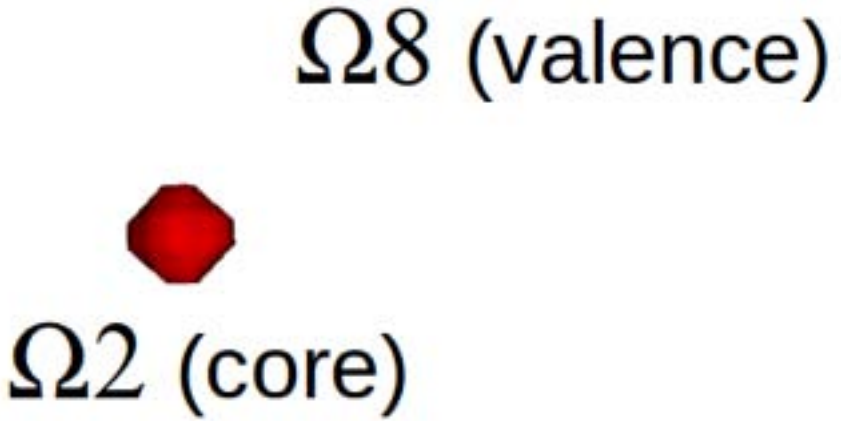


$\bar{\Omega}_2$

Examples and properties

- Ne atom ($10e^-$) :

$$p_2(\Omega) = \binom{10}{2} \int_{\Omega} dx_1 dx_2 \int_{\bar{\Omega}} dx_3 .. dx_{10} |\psi|^2 = \binom{8}{2} \int_{\Omega} dx_9 dx_{10} \int_{\bar{\Omega}} dx_1 .. dx_8 |\psi|^2 = p_8(\bar{\Omega})$$



➡ MPDs always provide a partition of space in two parts

Examples and properties

- Ne atom ($10e^-$) :

$$p_2(\Omega) = \binom{10}{2} \int_{\Omega} dx_1 dx_2 \int_{\overline{\Omega}} dx_3 .. dx_{10} |\psi|^2$$

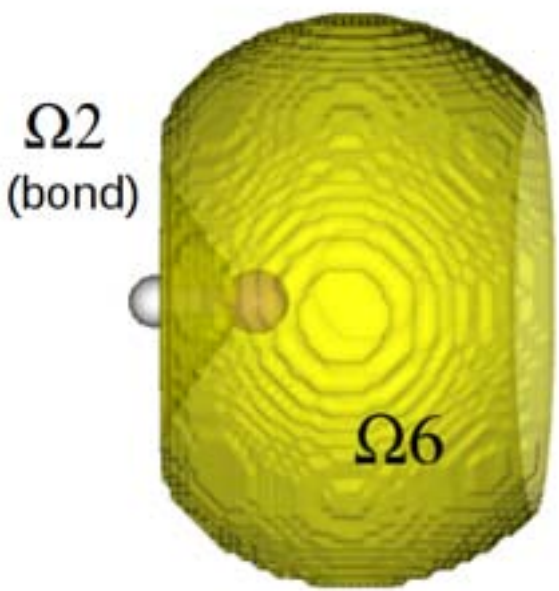
➡ Multiple «chemical» solutions may exist (core/valence pairs)

➡ Multiple solutions due to symmetry may exists

Examples and properties

- H–F molecule with pseudo ($8e^-$) :

$$p_2(\Omega) = \begin{pmatrix} 8 \\ 2 \end{pmatrix} \int_{\Omega} dx_1 dx_2 \int_{\bar{\Omega}} dx_3 .. dx_{10} |\psi|^2 = p_6(\bar{\Omega})$$



Examples and properties

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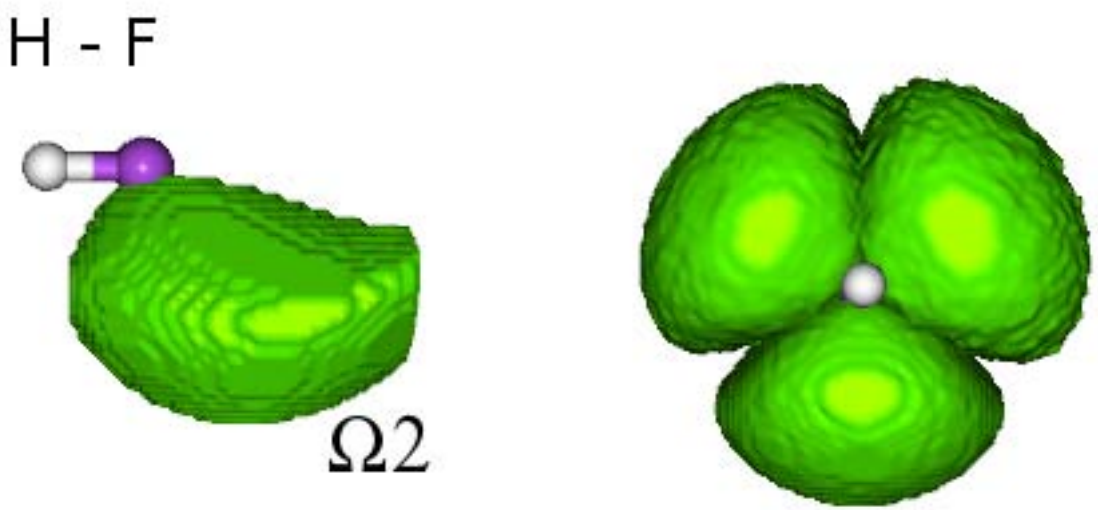
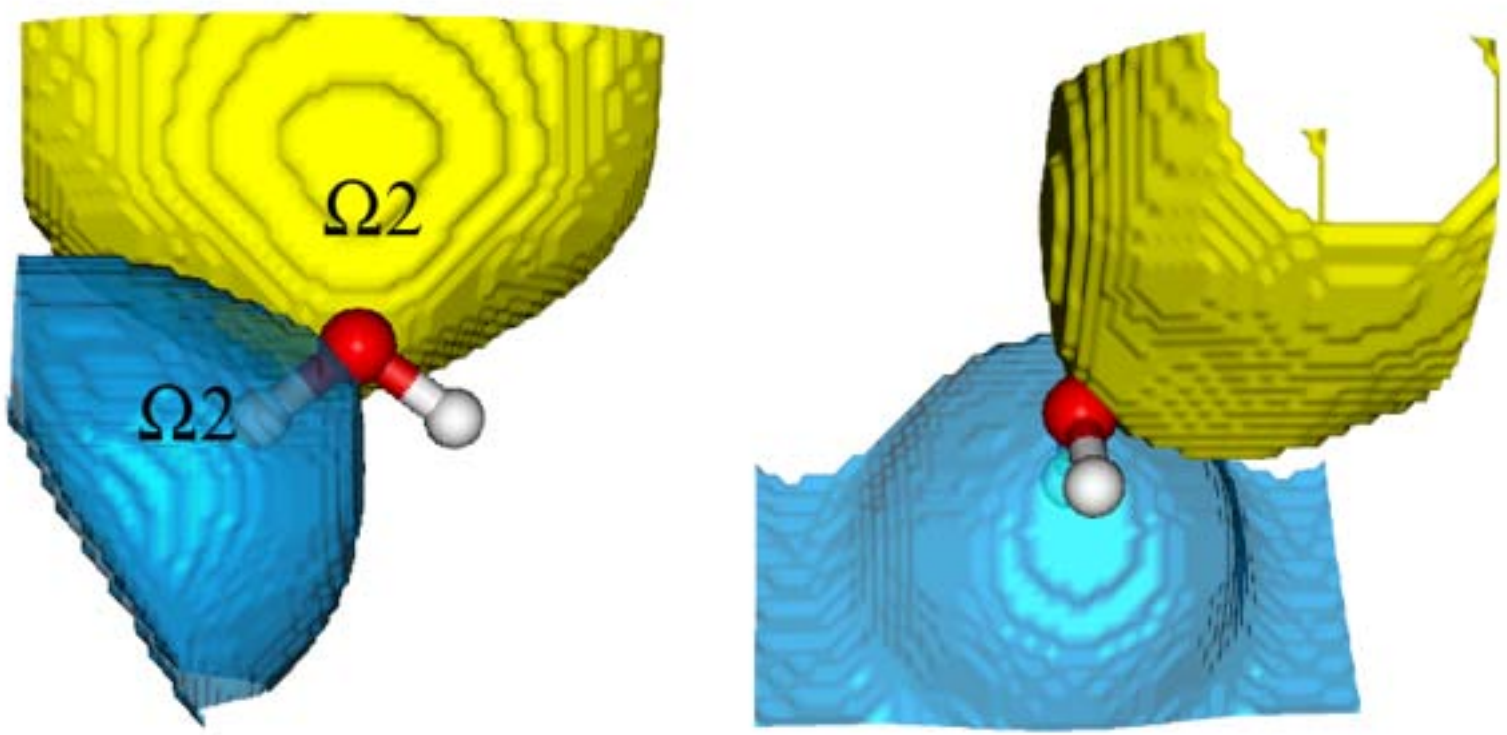


➡ MPD allows different viewpoints (Ω_ν search for any ν)

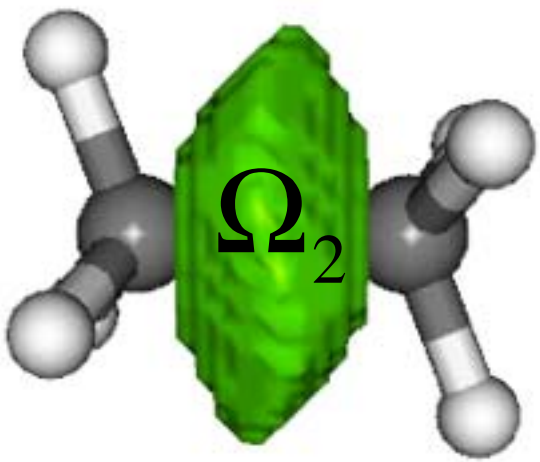
Examples and properties

- Water molecule :



Examples and properties

- Ethane :

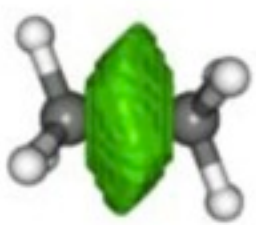


$$p_2 = 0.402$$
$$\langle \nu \rangle_\Omega = 1.965$$
$$\text{Vol.}(\Omega) = 19.050$$

➡ Population is close to ν even if it is p_ν which is optimized

Examples and properties

- MPD vs. ELF / Ethane :



$p_2(\Omega)$

$$p_2 = 0.402$$
$$\langle \nu \rangle_{\Omega} = 1.965$$
$$\text{Vol.}(\Omega) = 19.050$$

ELF C-C basin

$$p_2 = 0.40$$
$$\langle \nu \rangle_{\text{basin}} = 1.82$$
$$\text{Vol.}(\text{basin}) = 17.66$$

➡ ELF basins may be good approximations of MPDs

Examples and properties

- MPD vs. ELF / Dinitrogen :

$p_6(\Omega)$

$$p_6 = 0.307$$
$$\langle \nu \rangle_{\Omega} = 5.989$$
$$\text{Vol.}(\Omega) = 611.842$$

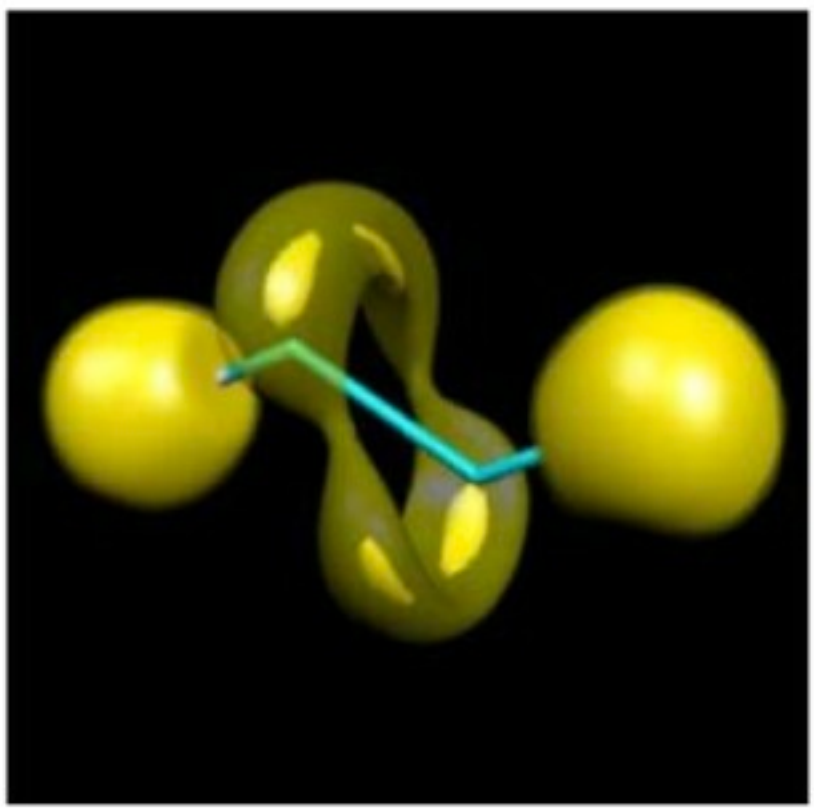
ELF N-N basin

$$p_6 = 0.04$$
$$\langle \nu \rangle_{\text{basin}} = 3.41$$
$$\text{Vol.}(\text{basin}) = 40.66$$

➡ ELF basins may also be poor approximations of MPDs !

Examples and properties

- MPD vs. ELF / Bent Si_2H_2 :

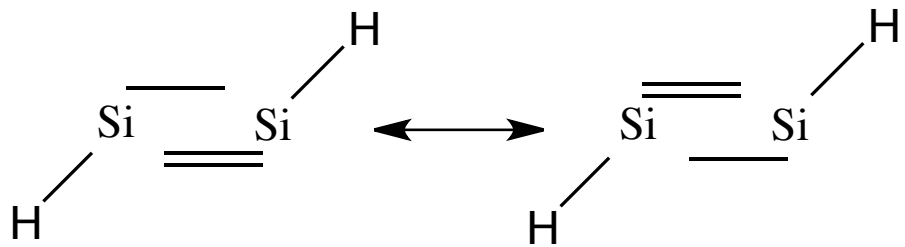


ELF isosurfaces

Four ELF maxima (???...)

Examples and properties

- MPD vs. ELF / Bent Si_2H_2 :

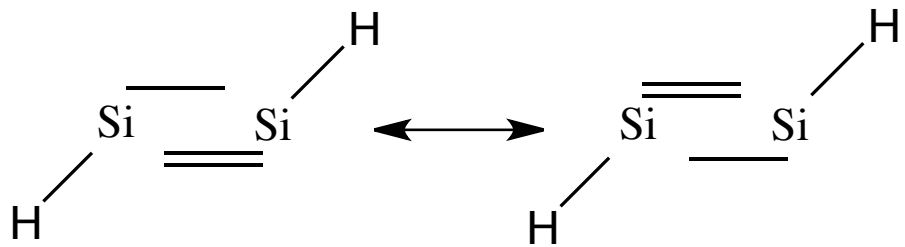


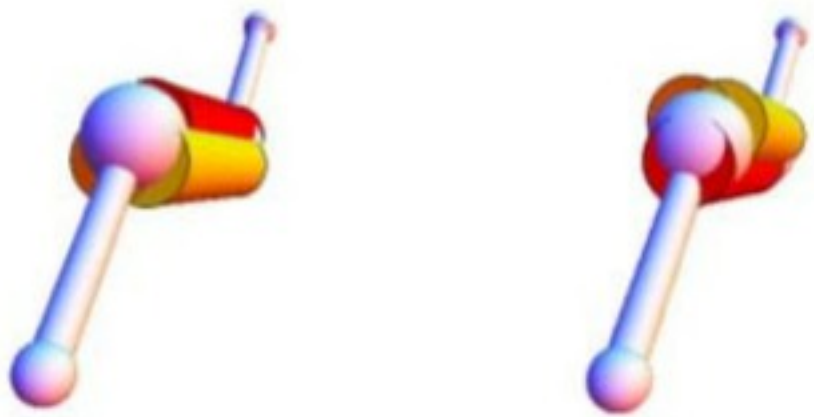
MPDs: Three (shifted) banana bonds

A. Scemama et al., *J. Comp. Chem* 28, 442 (**2007**)

Examples and properties

- MPD vs. ELF / Bent Si_2H_2 :



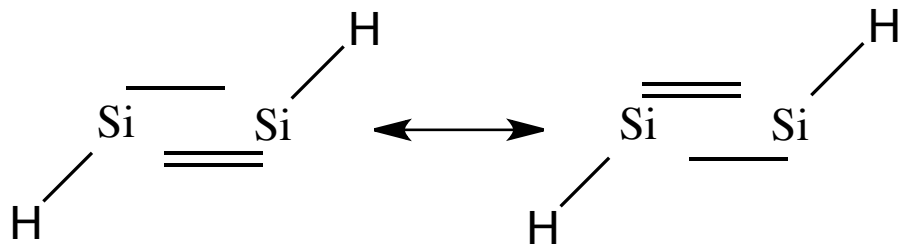


MPDs: Two equivalents triples of banana bonds

A. Scemama et al., *J. Comp. Chem* 28, 442 (**2007**)

Examples and properties

- MPD vs. ELF / Bent Si_2H_2 :



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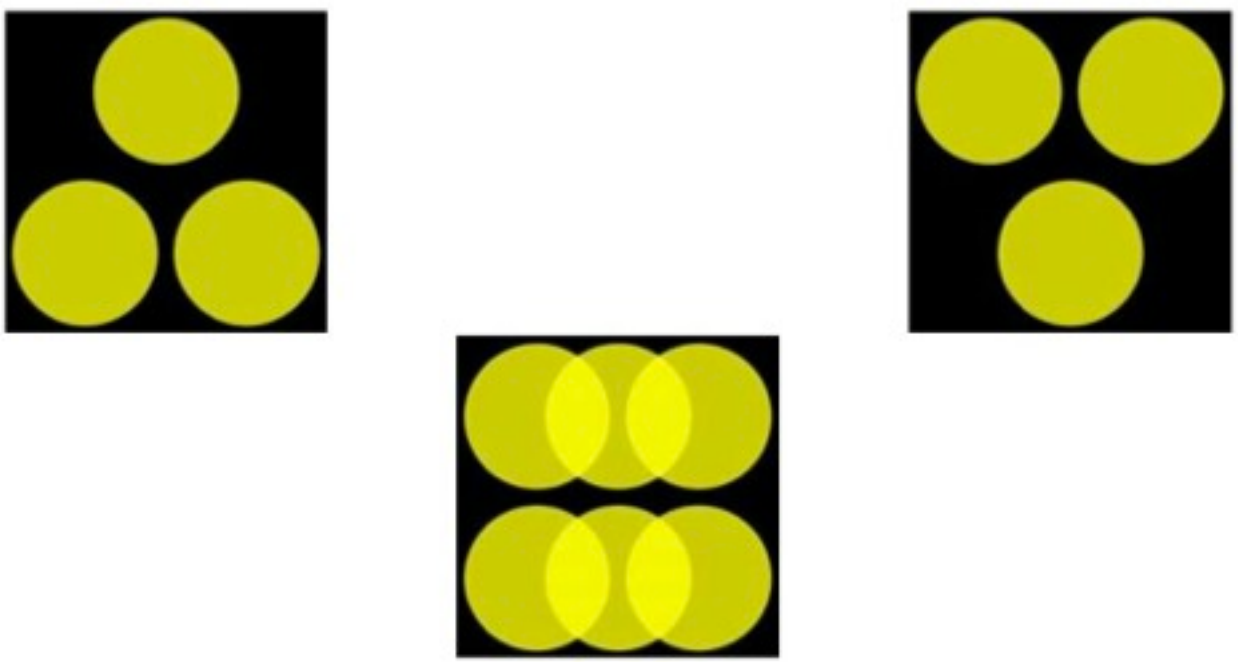
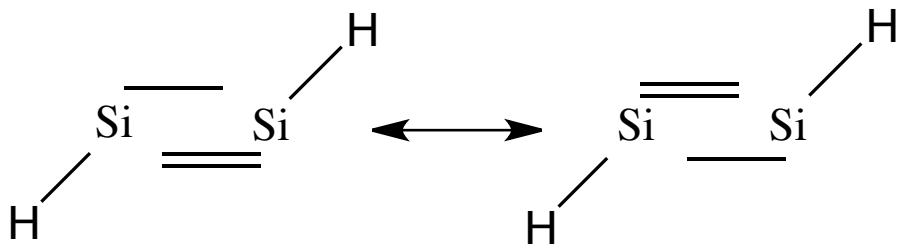


Examples and properties

- MPD vs. ELF / Bent Si_2H_2 :



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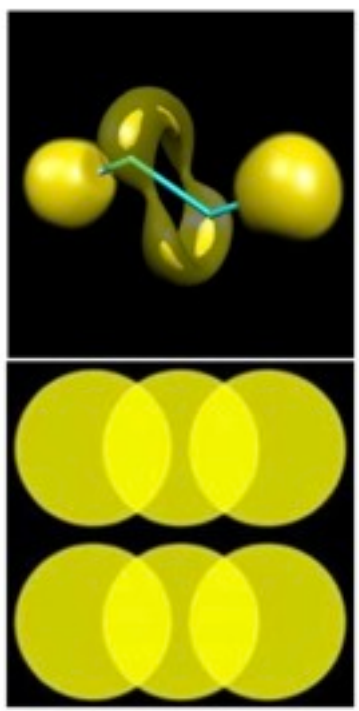

Perspectives

- **Algorithms developments** (adaptative mesh, level sets,...)

- **Conceptual developments** (compute physical quantities into MPDs, volume-related definition of hardness,...)

- **Applications** (hypervalency,...)