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The Maximum Probability Domains method

Laboratoire de Chimie Théorique

Université Pierre et Marie Curie

Outline

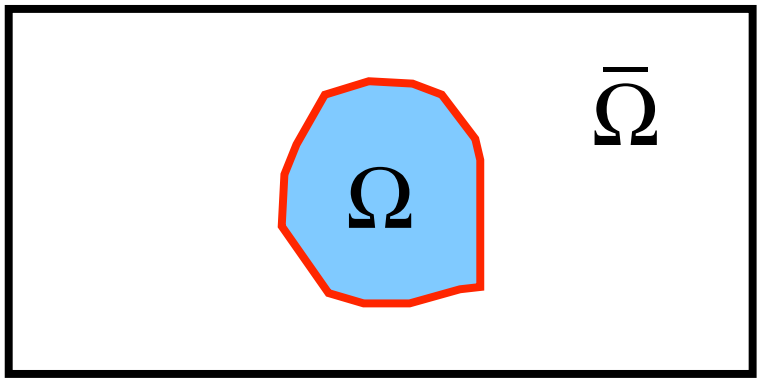
- Basics of MPDs
- Examples and properties
- Some applications

Basics

1) The probability function :

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

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



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

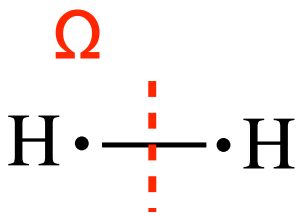
We rather have : $$<\nu>_\Omega = \sum_{\nu=0}^{N} \nu \, p_\nu(\Omega)$$

Basics

1) The probability function :

Example : dihydrogen molecule - infinite interactomic distance :

Ground (covalent) state :

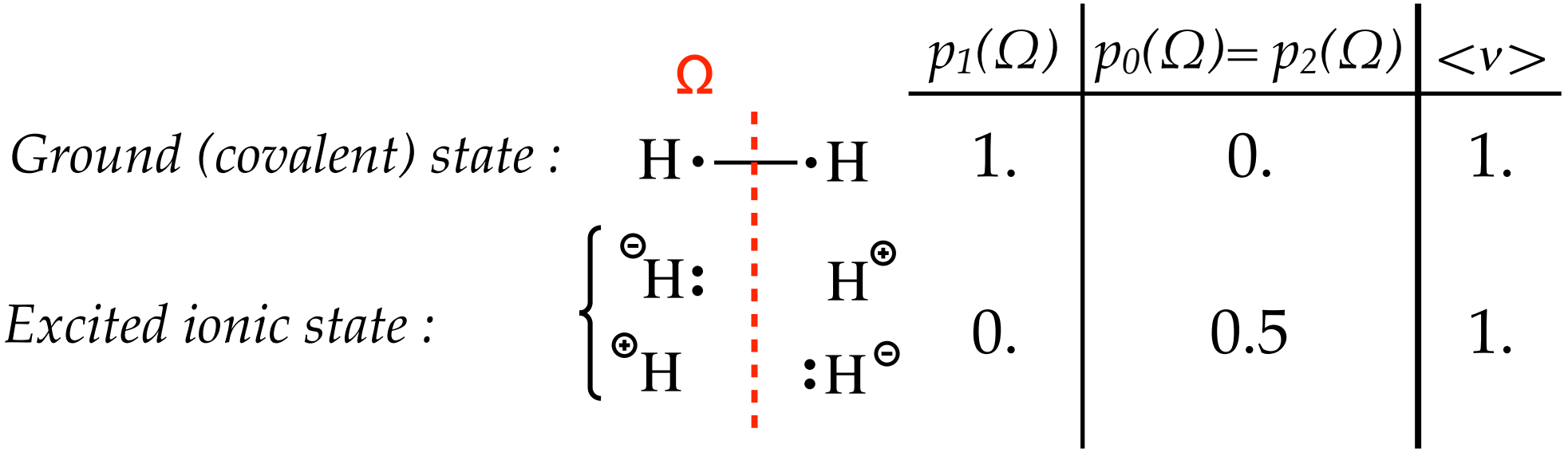


$p_1(\Omega)$	$p_0(\Omega) = p_2(\Omega)$	$\langle v \rangle$
1.	0.	1.

Basics

1) The probability function :

Example : dihydrogen molecule - infinite 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.

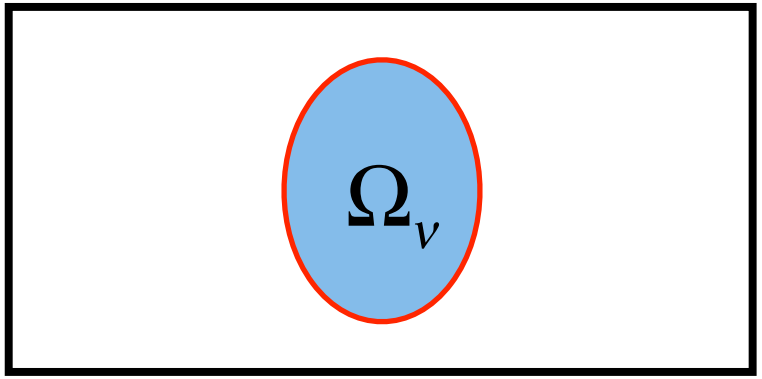
➡ **Probabilities contain more informations than populations**

Basics

2) MPD / Definition :

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

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

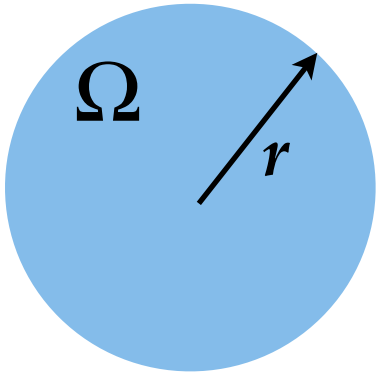


Basics

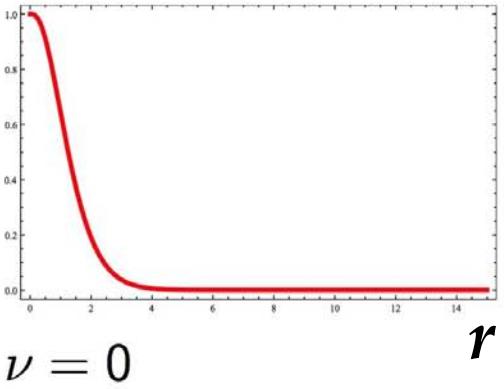
2) MPD / existence :

Example : atom case (N e^-),

atomic-centered spherical domain :

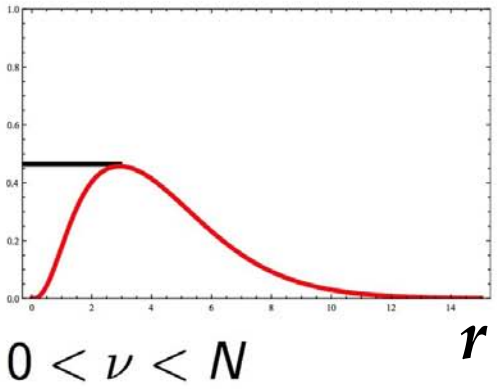


p_0



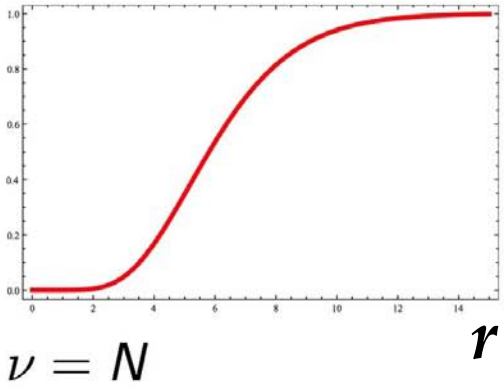
$\nu = 0$

p_ν



$0 < \nu < N$

p_N

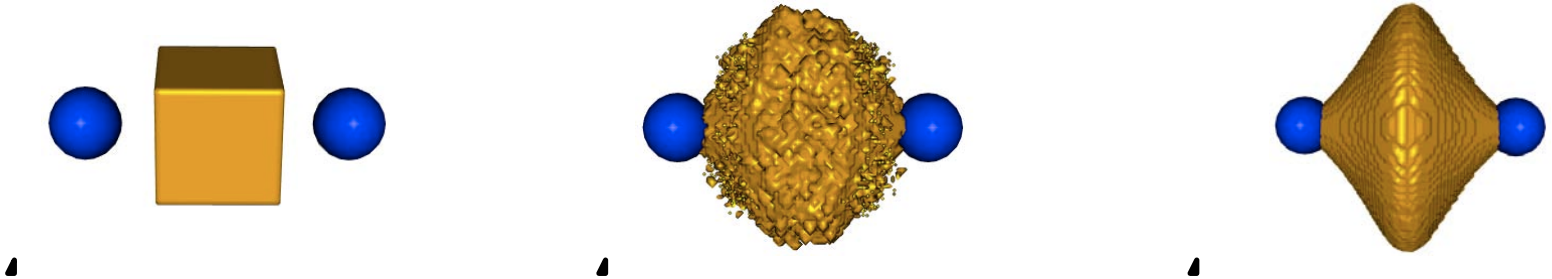


$\nu = N$

➡ For any ν, at least one Ω_ν always exists

Basics

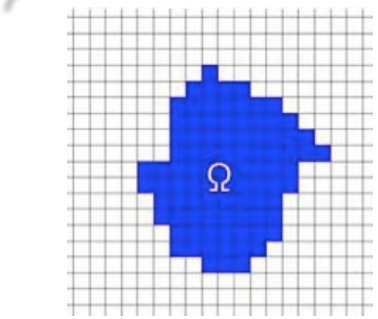
2) MPD / Optimization (in a nutshell) :



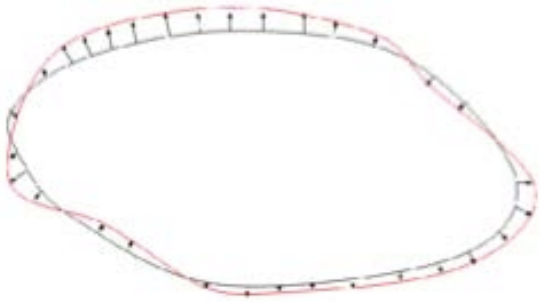
Guess domain
Ω

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

MPD
Ω_v



Acceptation/Rejection (0)

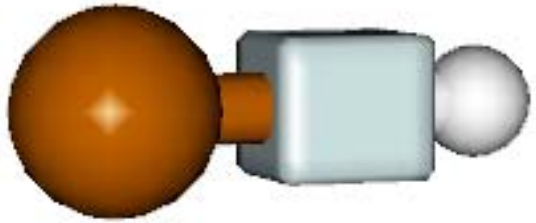


Shape derivatives (1)

Basics

2) MPD / Optimization (example) :

Searching a Ω_2 domain in the Li—H molecule :



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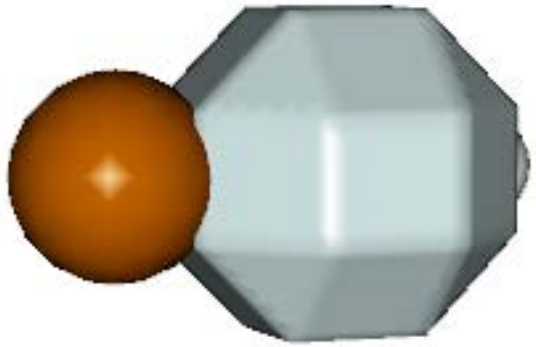

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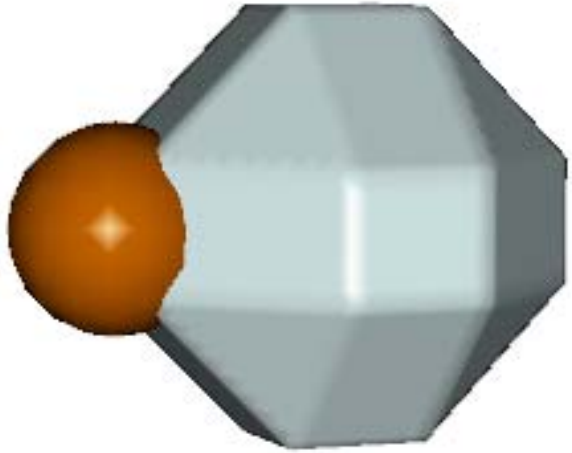

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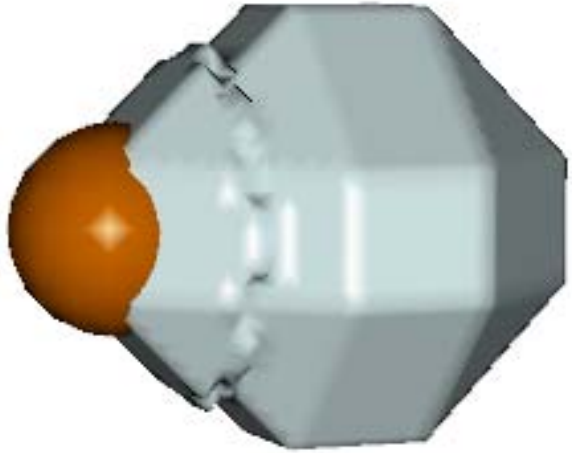

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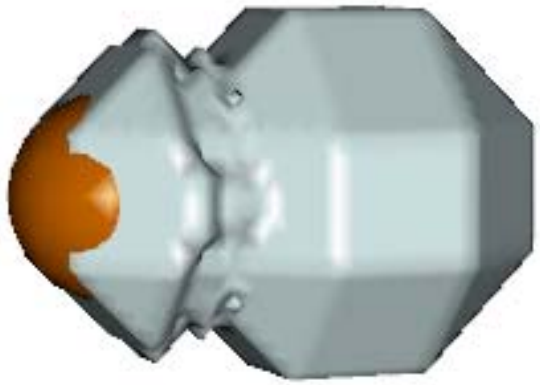

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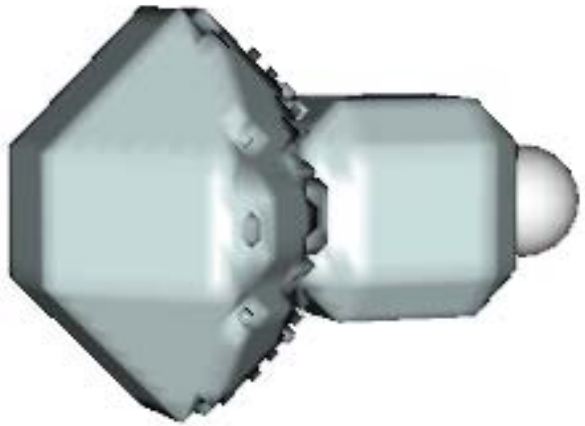

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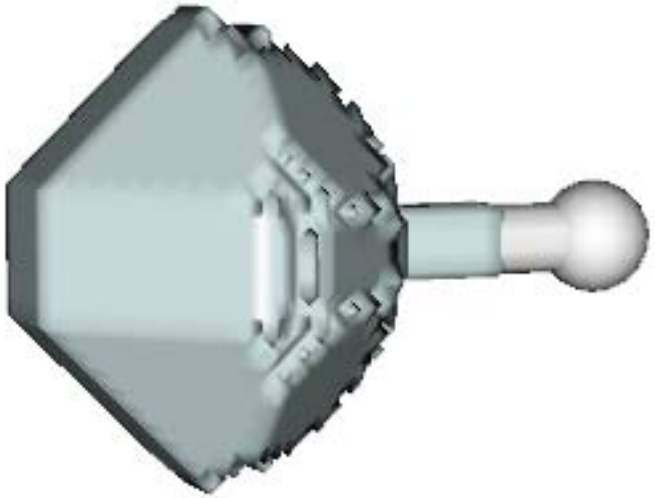

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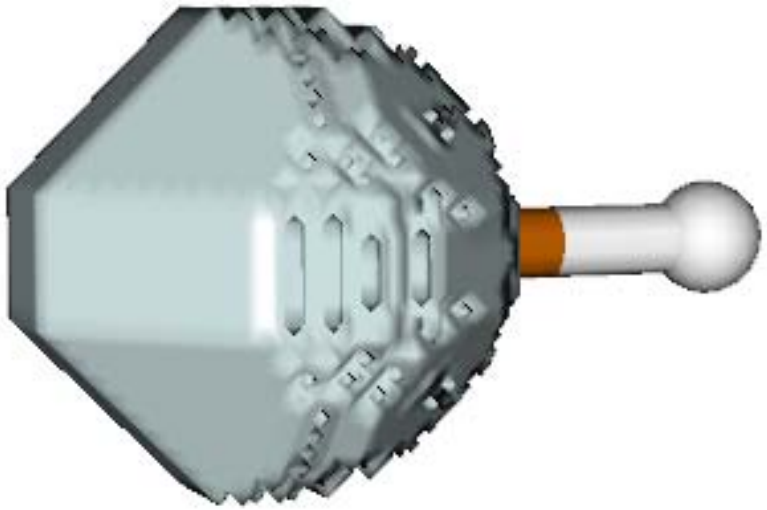

Basics

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Searching a Ω_2 domain in the Li—H molecule :

Basics

2) MPD / Optimization (example) :

Searching a Ω_2 domain in the Li—H molecule :

$\bar{\Omega}_2$

$$p_2(\Omega) = \binom{4}{2} \int_{\Omega} dx_1 dx_2 \int_{\bar{\Omega}} dx_3 dx_4 |\psi|^2 = \binom{4}{2} \int_{\bar{\Omega}} dx_1 dx_2 \int_{\Omega} dx_3 dx_4 |\psi|^2 = p_2(\bar{\Omega})$$

Basics

2) MPD / Optimization (example) :

Searching a Ω_2 domain in the Li—H molecule :

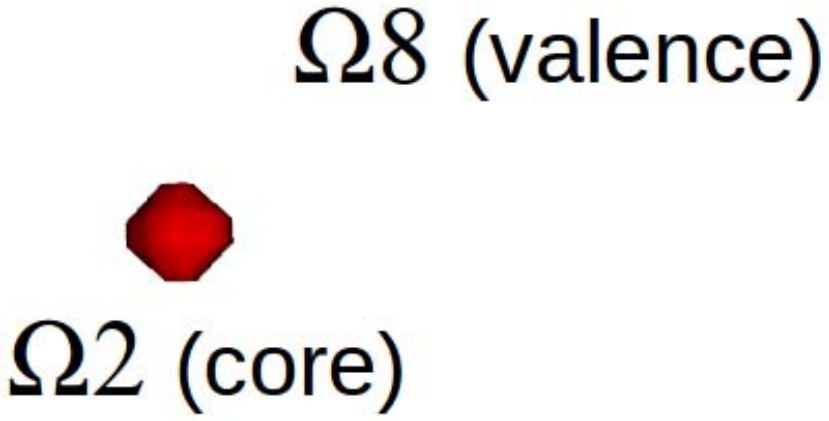
$\bar{\Omega}_2$

➡ MPDs always provide a partition of space in two parts

Examples and properties

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

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



➡ MPDs always provide a partition of space in two parts

Examples and properties

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

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

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

➡ Multiple solutions due to symmetry may exists

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

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

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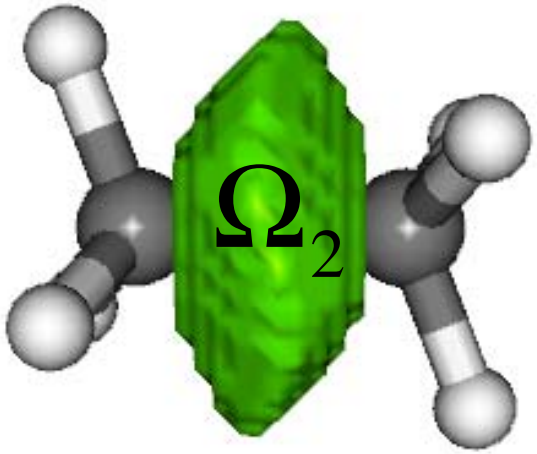
Examples and properties

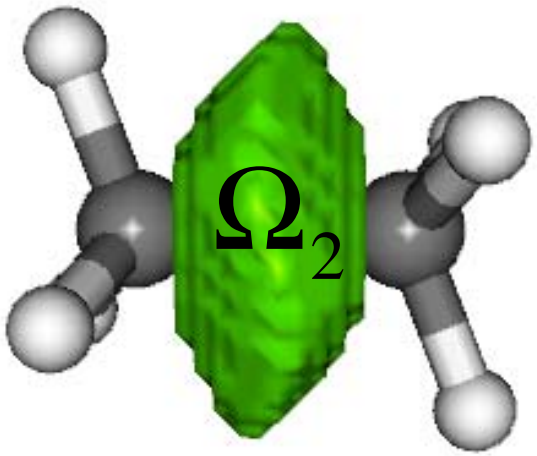
- Covalent bond in C_2H_6



➡ Prolate shape, extends **orthogonally** to the bond axis

Examples and properties

- Ethane :

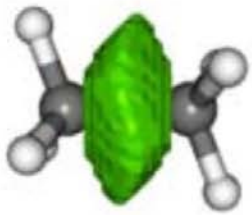


$$\mathbf{p_2} = \mathbf{0.402}$$
$$\langle \nu \rangle_{\Omega} = \mathbf{1.965}$$
$$\mathrm{Vol.}(\Omega) = \mathbf{19.050}$$

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

Examples and properties

- MPD vs. ELF / Ethane :



$p_2(\Omega)$

$\mathbf{p_2 = 0.402}$

$\langle \nu \rangle_{\Omega} = \mathbf{1.965}$

$\mathrm{Vol.}(\Omega) = \mathbf{19.050}$

ELF C-C basin

$\mathbf{p_2 = 0.40}$

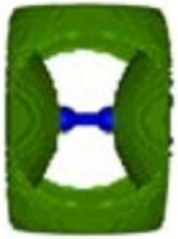
$\langle \nu \rangle_{\mathrm{basin}} = \mathbf{1.82}$

$\mathrm{Vol.(basin)} = \mathbf{17.66}$

➡ ELF basins may be good approximations of MPDs

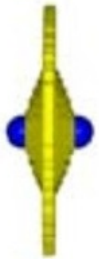
Examples and properties

- MPD vs. ELF / Dinitrogen :



$p_6(\Omega)$

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



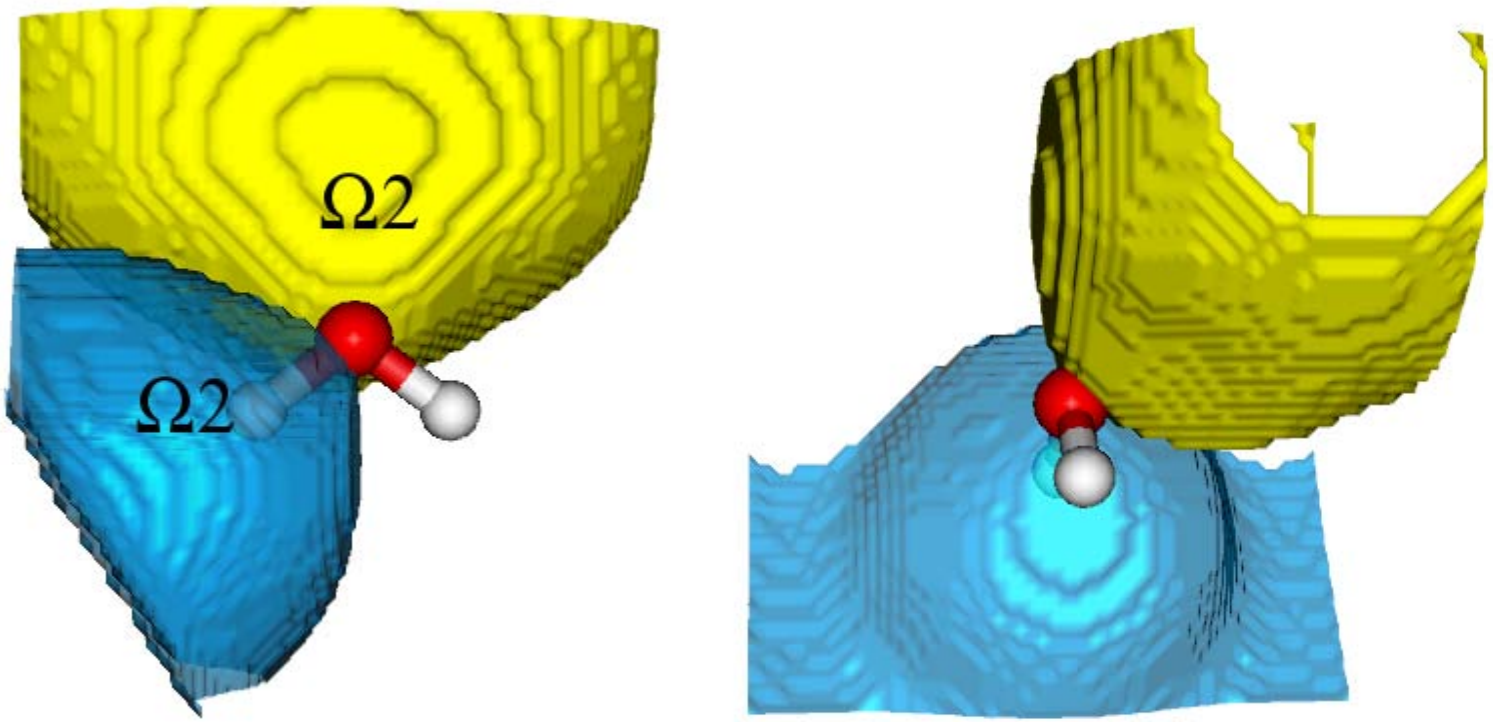
ELF N-N basin

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

➡ ELF basins may also be poor approximations of MPDs !

Examples and properties

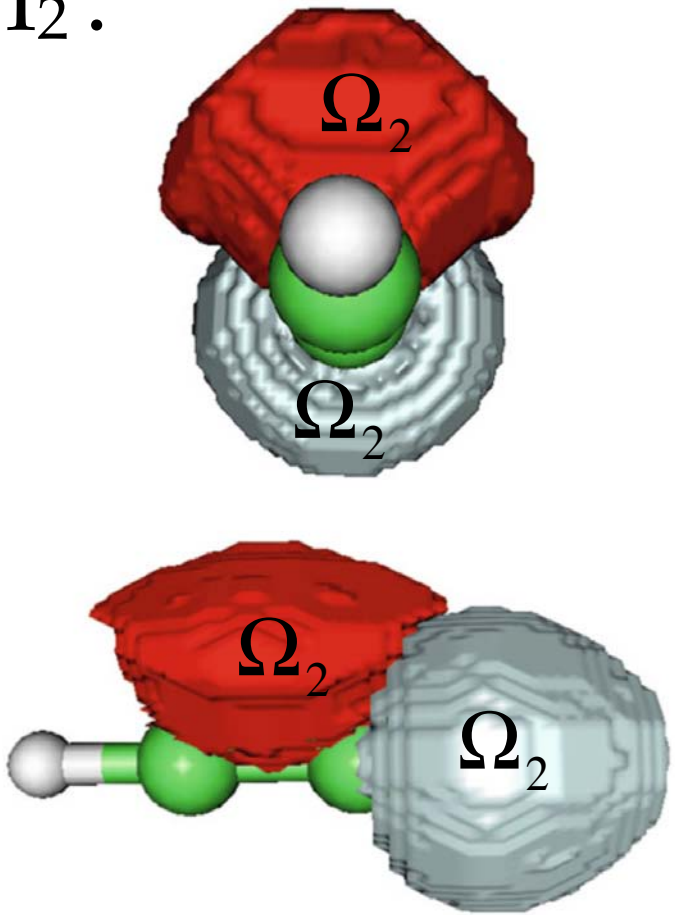
- Water molecule :



➡ Multiple solutions usually exist (chemically different)

Examples and properties

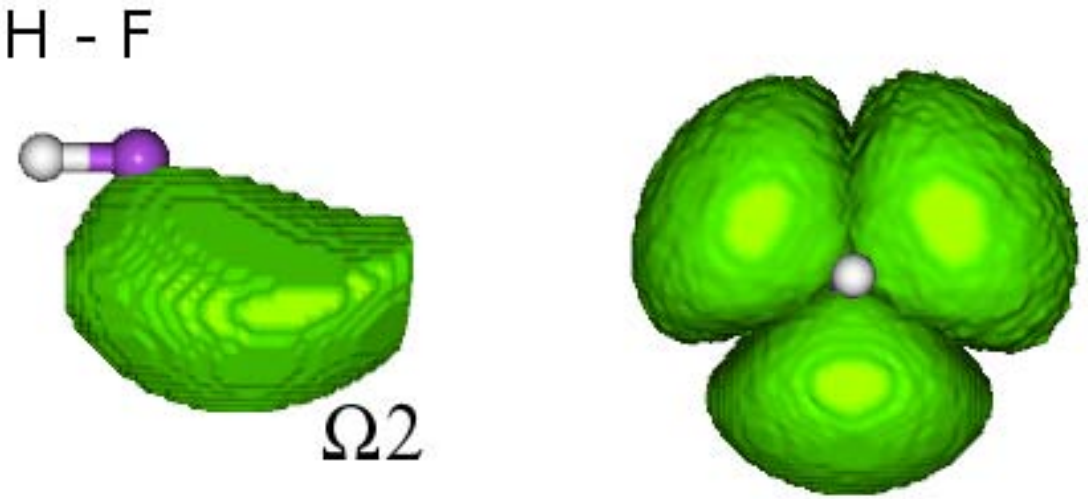
- C–C bond in C_2H_2 :



➡ C–C « banana bonds » domains are obtained for acetylene

Examples and properties

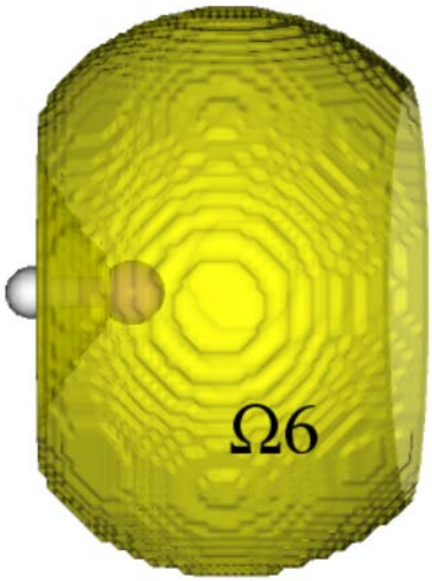
- Lone pairs in the H–F molecule ?

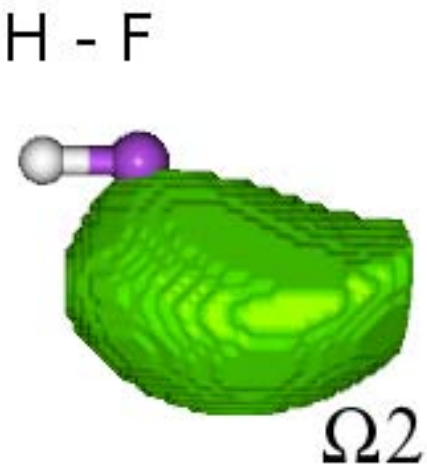


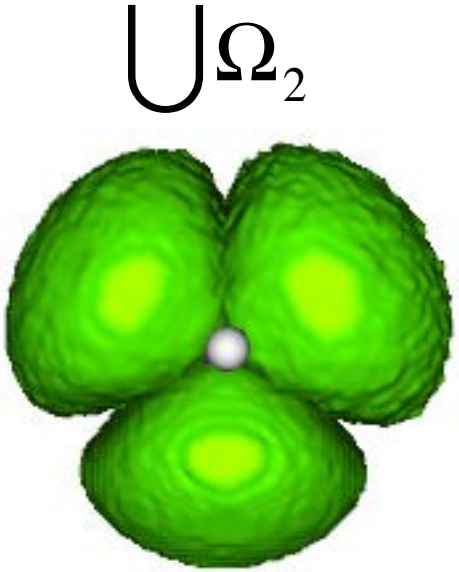
➡ Multiple solutions usually exist (by symmetry)

Examples and properties

- Lone pairs in the H–F molecule ?

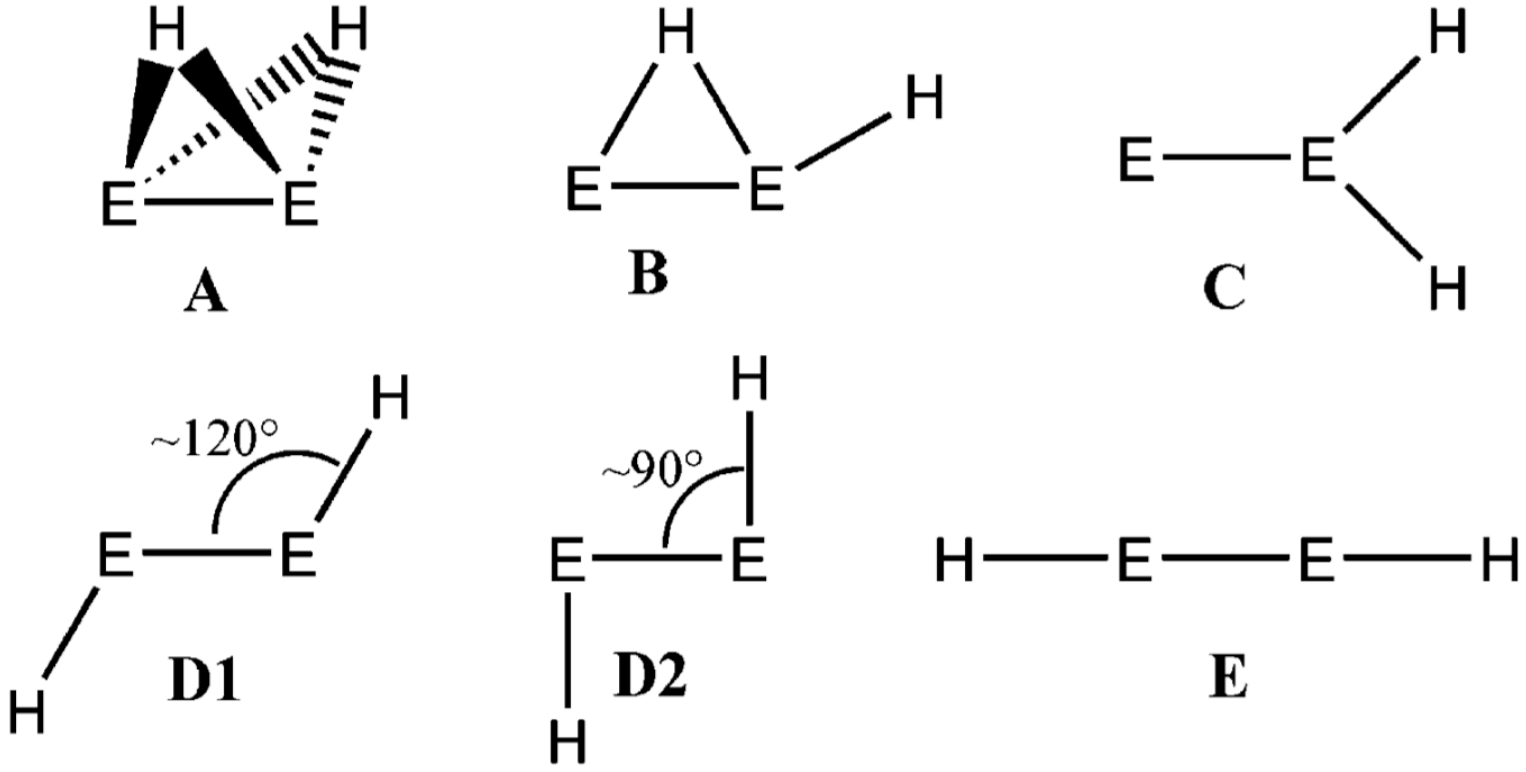






➡ MPD allows different viewpoints (Ω_ν search for any ν)

E_2H_2 (E=Si, Ge, Sn, Pb)



Lein, Krapp, Frenking, J. Am. Chem. Soc. 2005, 127, 6290

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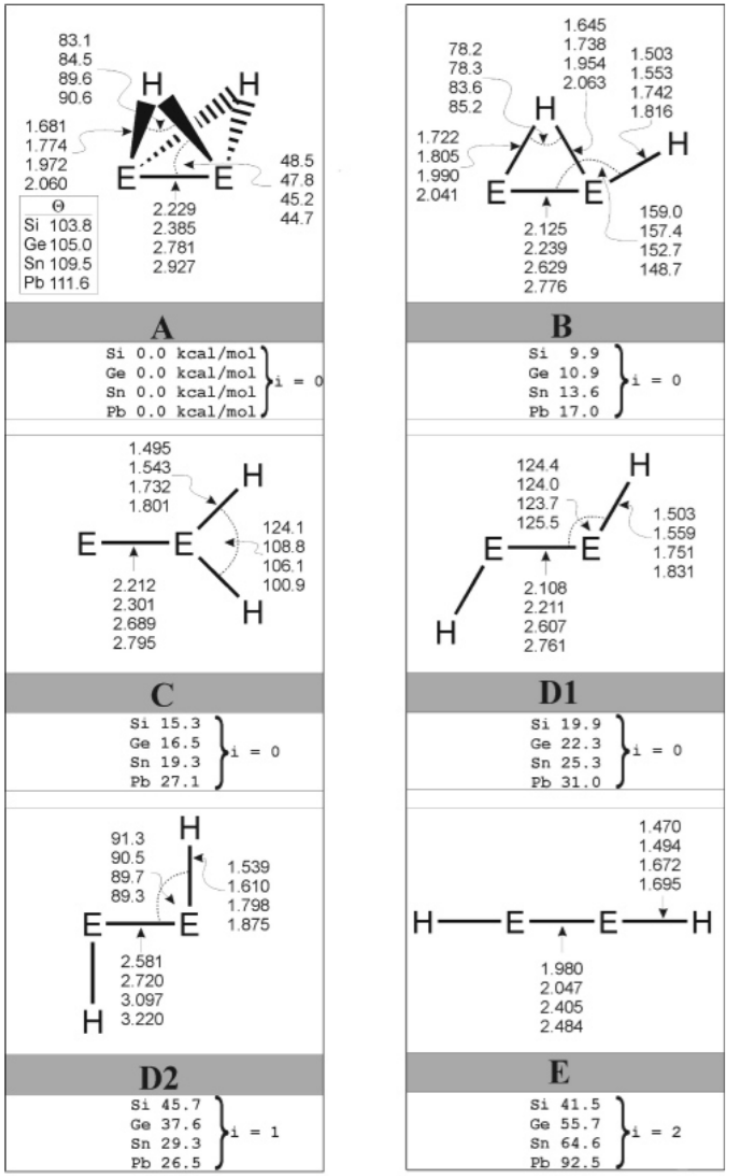

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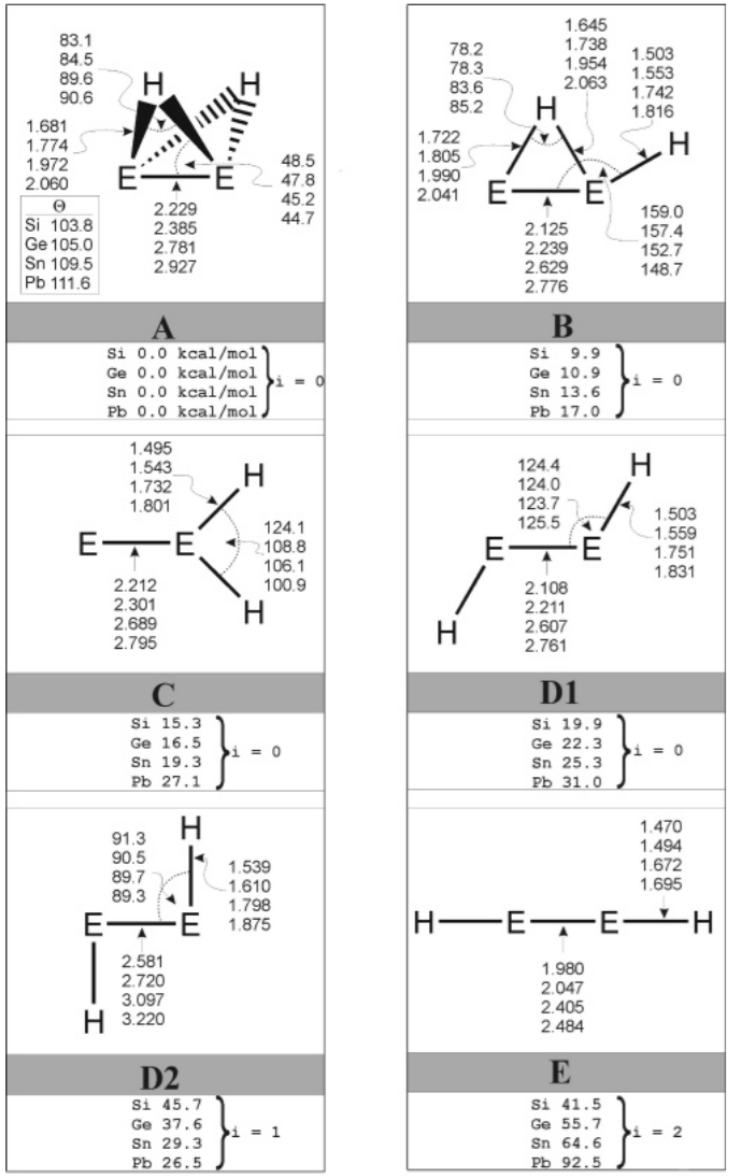

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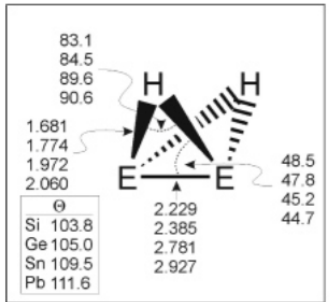
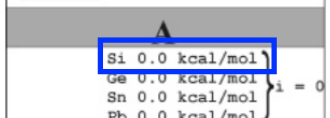
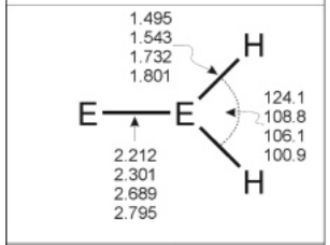
E_2H_2 (E=Si, Ge, Sn, Pb)

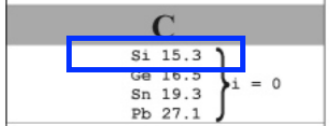
Absolute min.



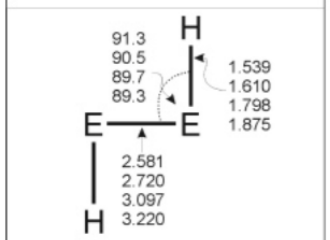


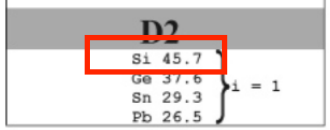
min. (3)

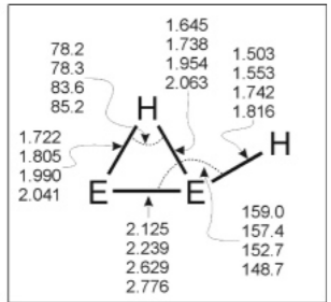




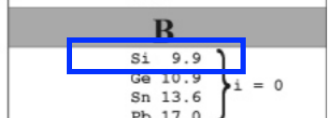
TS

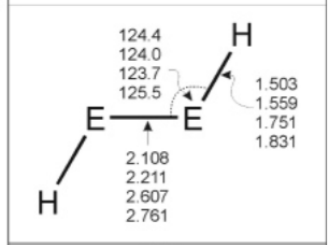




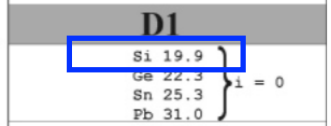


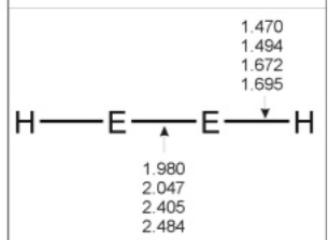
min. (2)



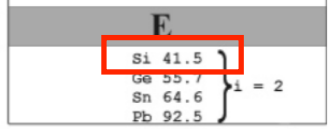


min. (4)





TS

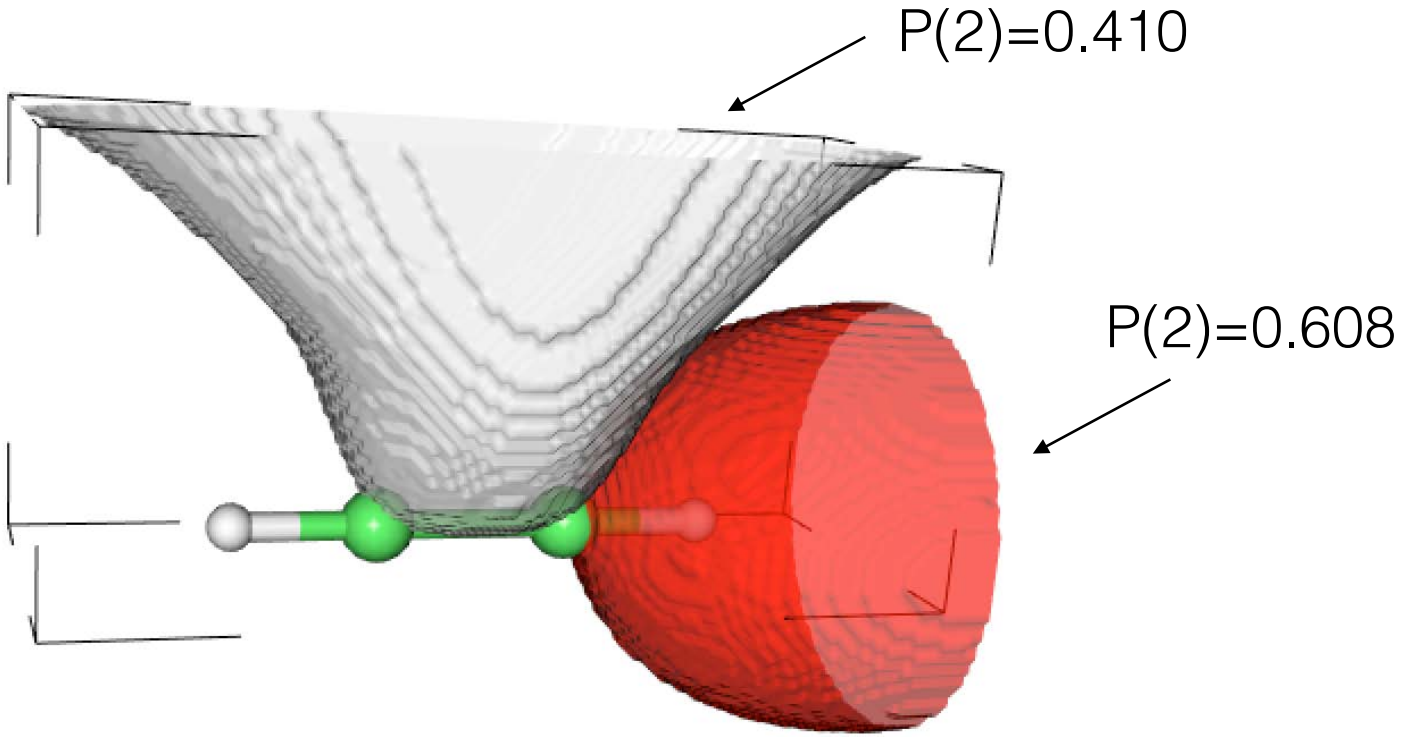


Lein, Krapp, Frenking, J. Am. Chem. Soc. 2005, 127, 6290

Si_2H_2

H—E—E—H

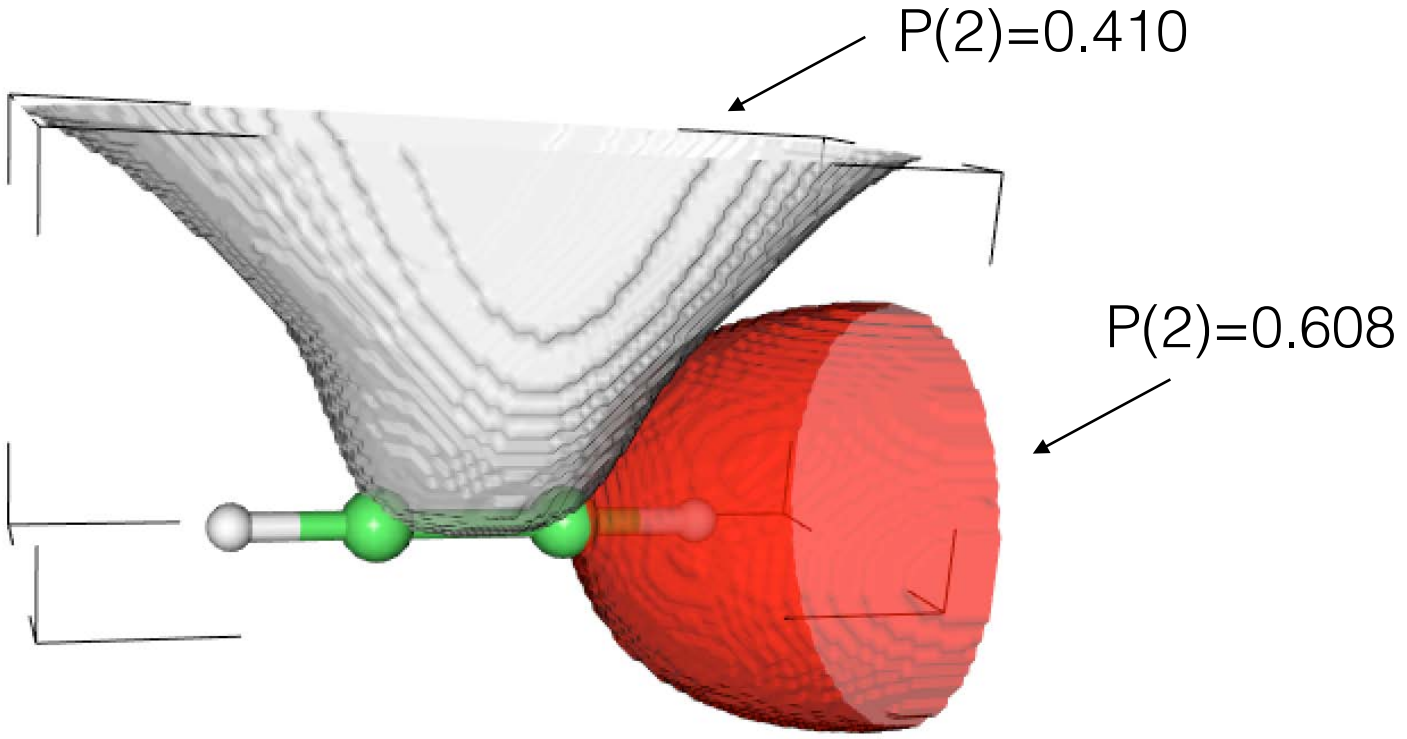
E

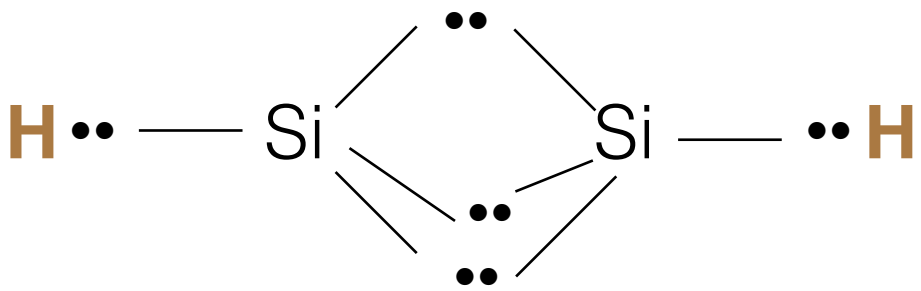


Si_2H_2

H—E—E—H

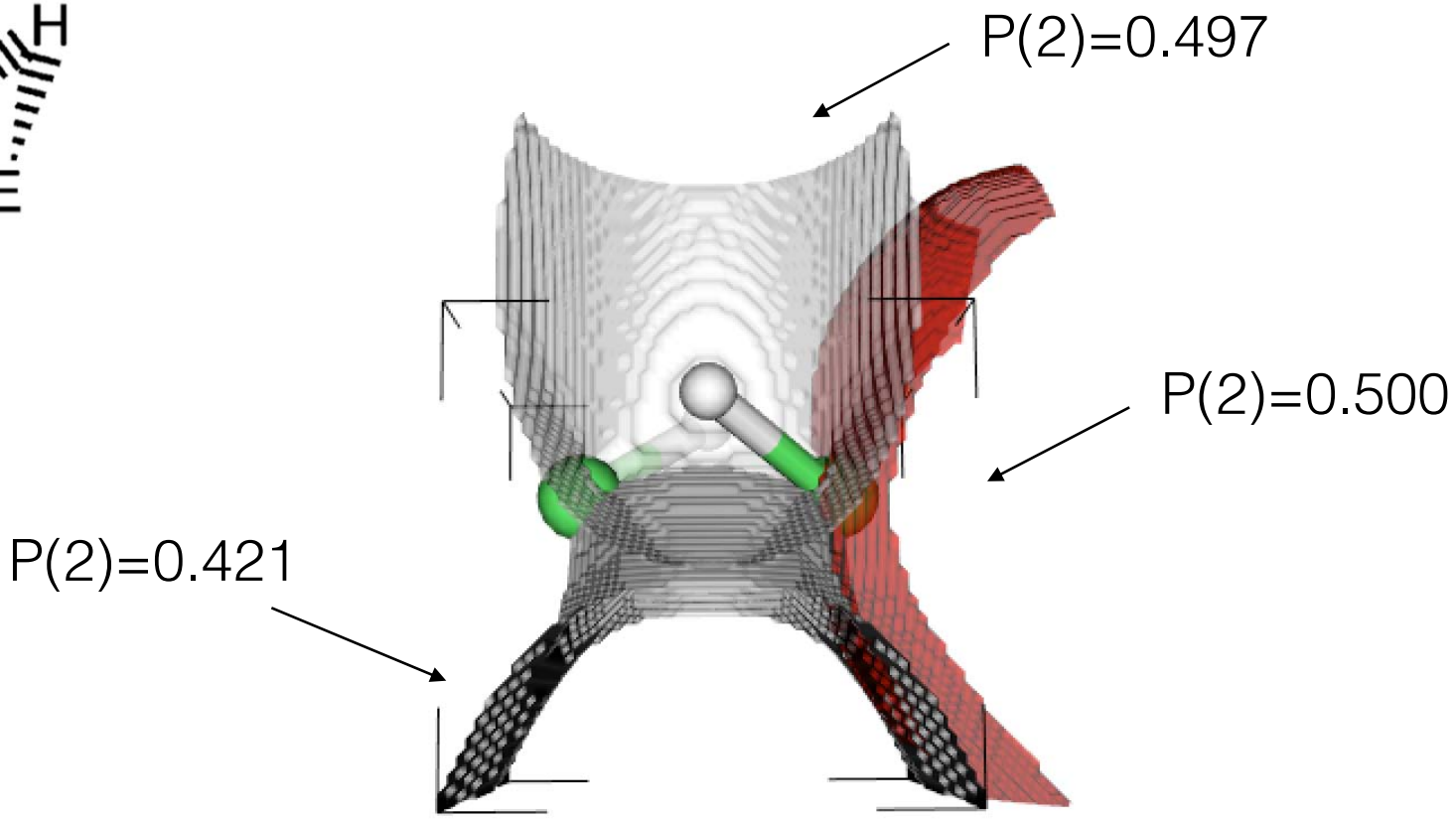
E





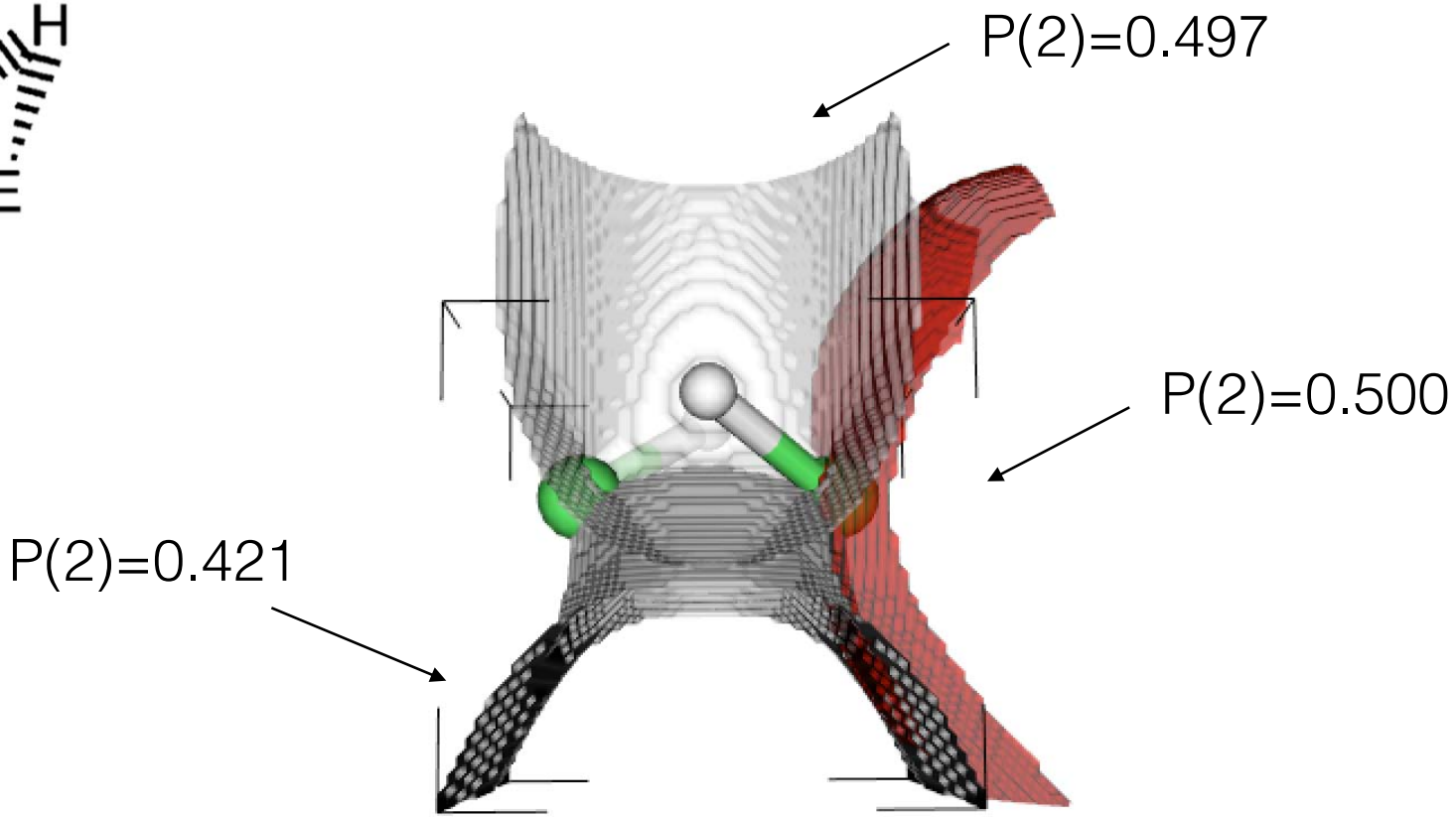
Si_2H_2

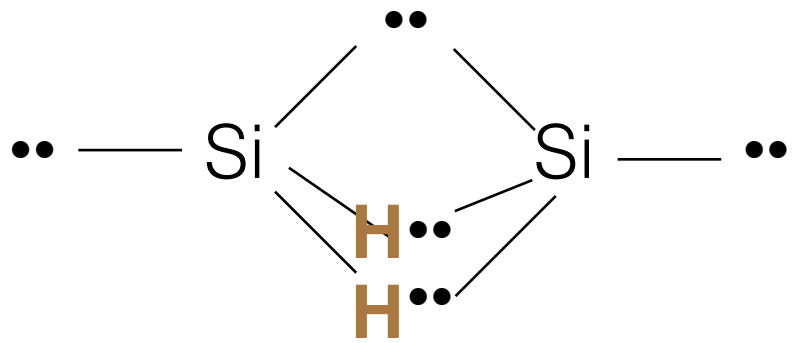
A



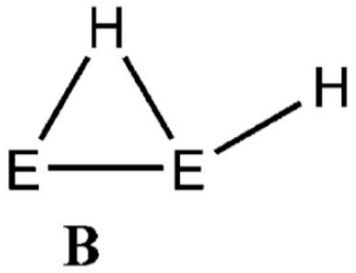
Si_2H_2

A

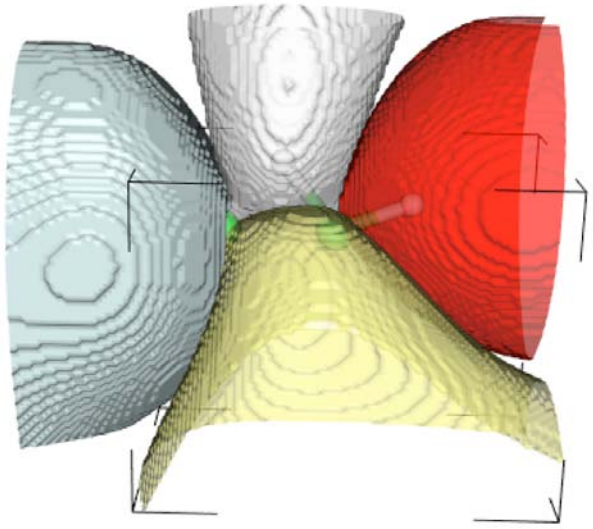




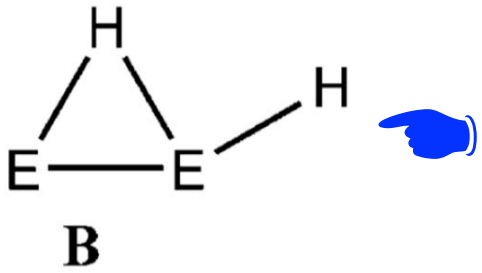
Si_2H_2

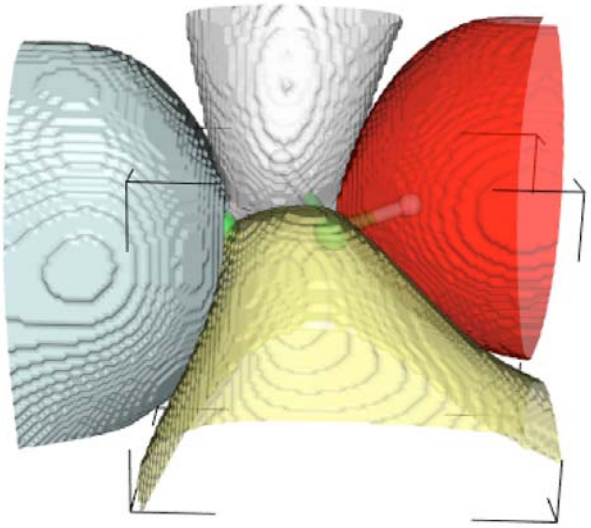


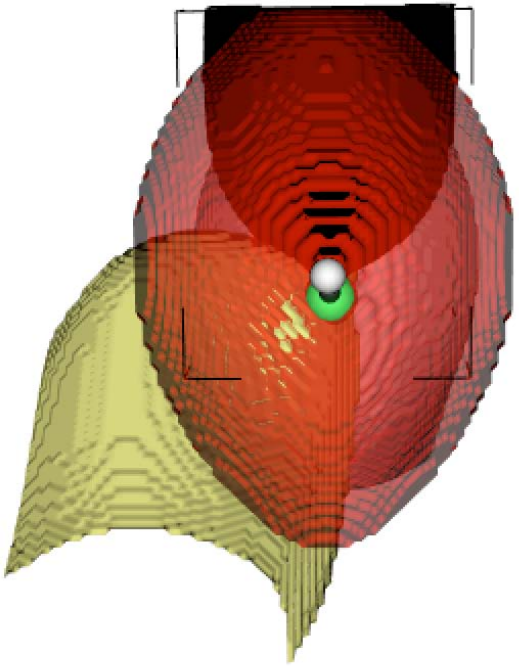
B



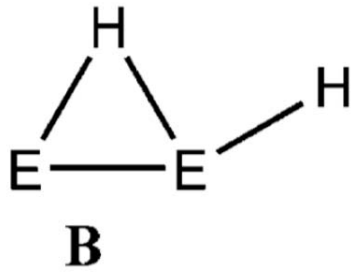
Si_2H_2







Si_2H_2



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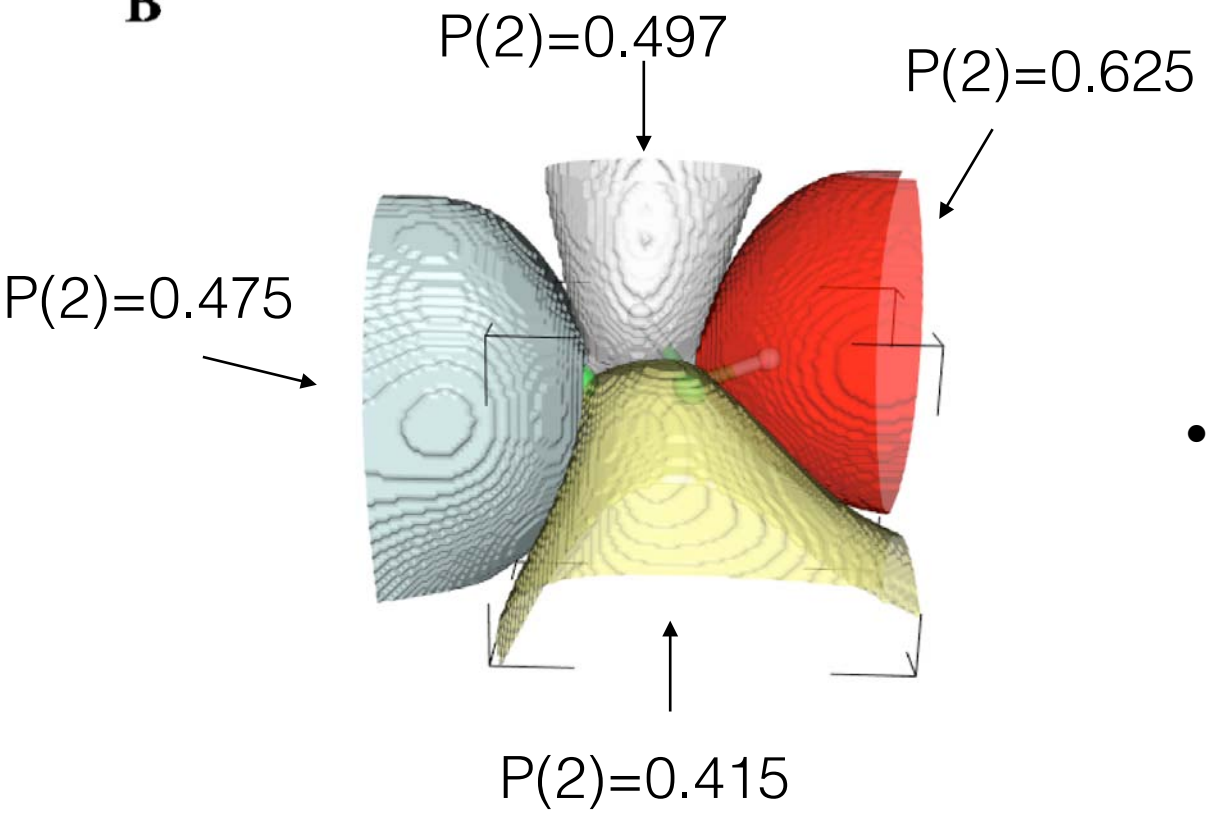
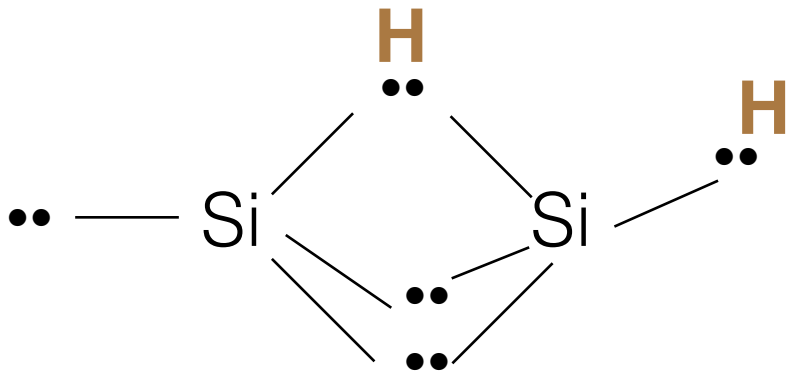
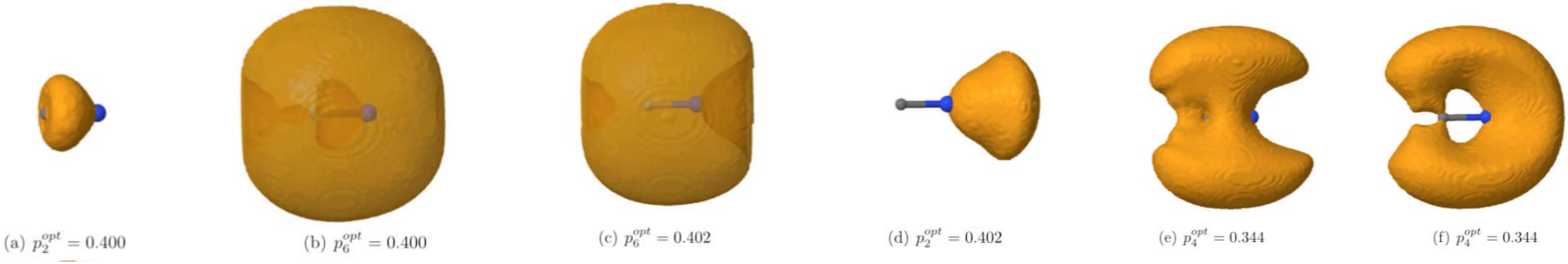


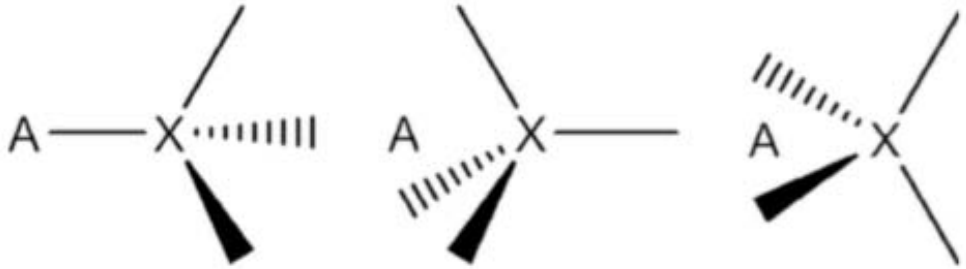


Ionic bond

LiCl :



(a) $p_2^{opt} = 0.400$ (b) $p_6^{opt} = 0.400$ (c) $p_6^{opt} = 0.402$ (d) $p_2^{opt} = 0.402$ (e) $p_4^{opt} = 0.344$ (f) $p_4^{opt} = 0.344$

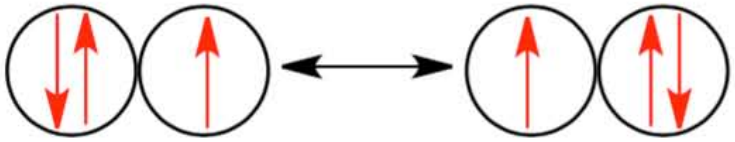


Scheme 3. Three different resonating structures for the pairs arrangements found in the LiX (X = F, Cl, Br, I) molecules.

M. Menéndez, A. Martín Pendás, B. Braïda, A. Savin *Comput. and Theor. Chem.*1053 (2015) 142–149

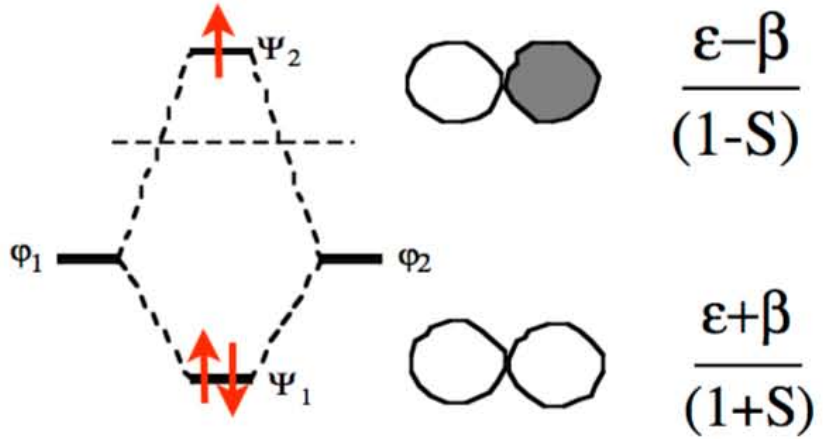
The 3e bond

VB description :



$$\Psi_{VB} = \left|a\bar{a}b\right| + \left|b\bar{b}a\right|$$

MO description :

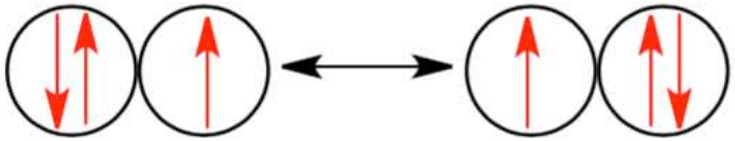


$$\Psi_{MO} = \left|\sigma\bar{\sigma}\sigma^{*}\right|$$

The 3e bond

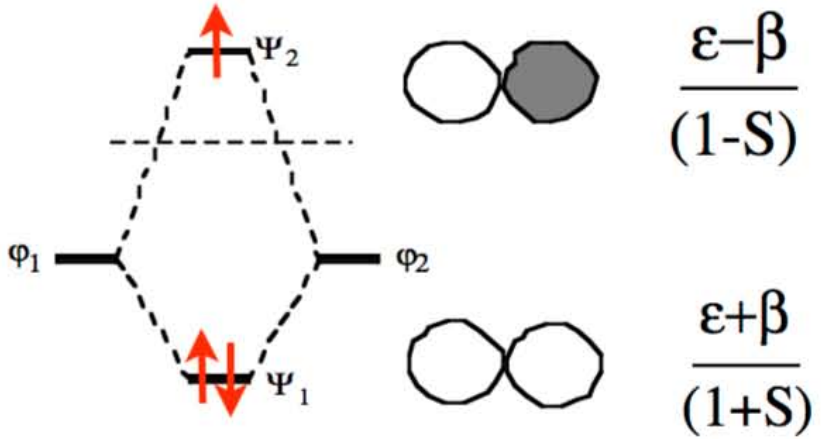
Prototypes : He_2^+, Ne_2^+, $HOOH^+$, $HSSH^-$, F_2^-, π bonds in O_2…

VB description :



$$\Psi_{VB} = |a\bar{a}b| + |b\bar{b}a|$$

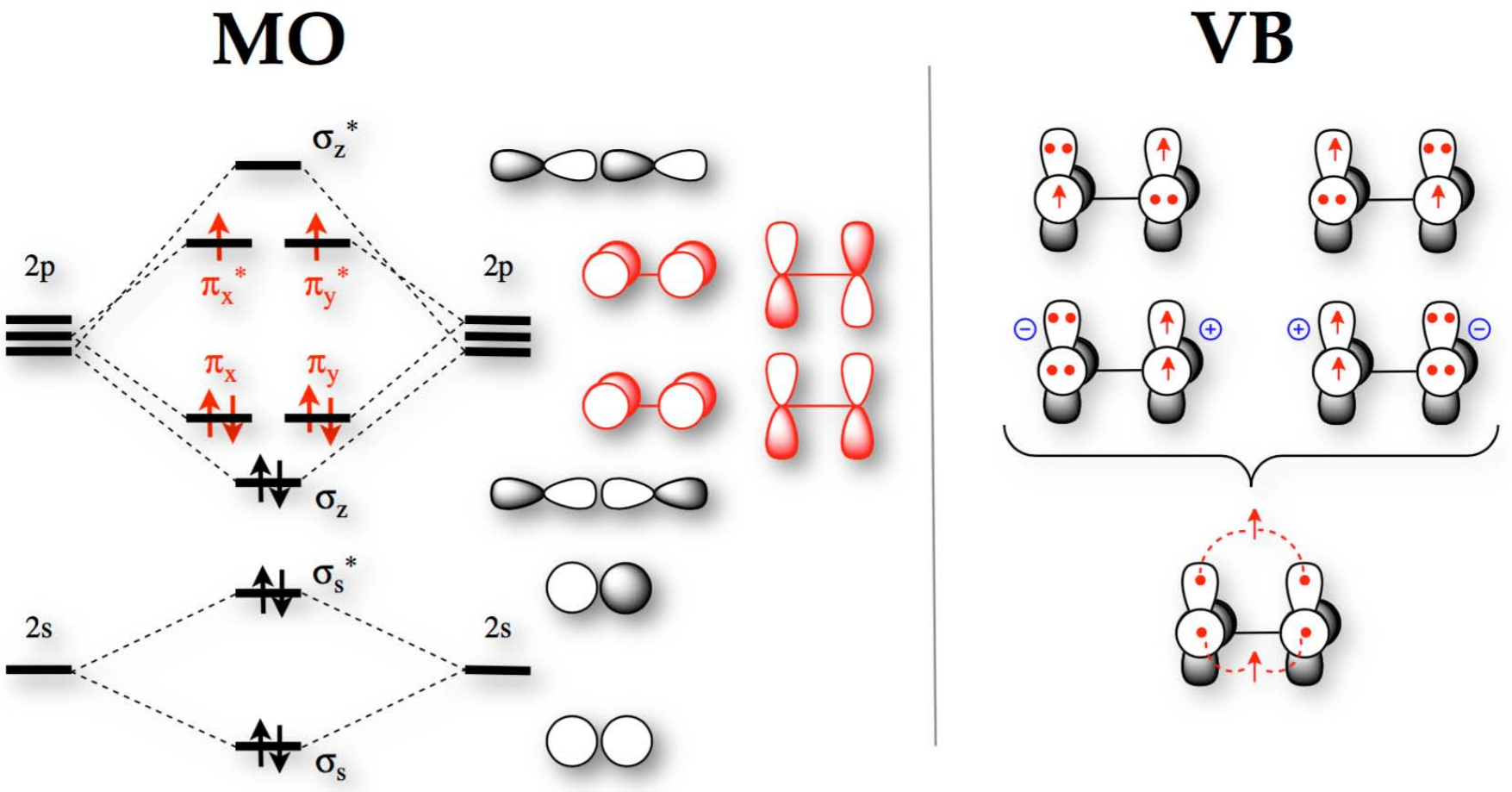
MO description :



$$\Psi_{MO} = |\sigma\bar{\sigma}\sigma^*|$$

The 3e bond

Dioxygen triplet ground state : two π-type 3e-bonds :



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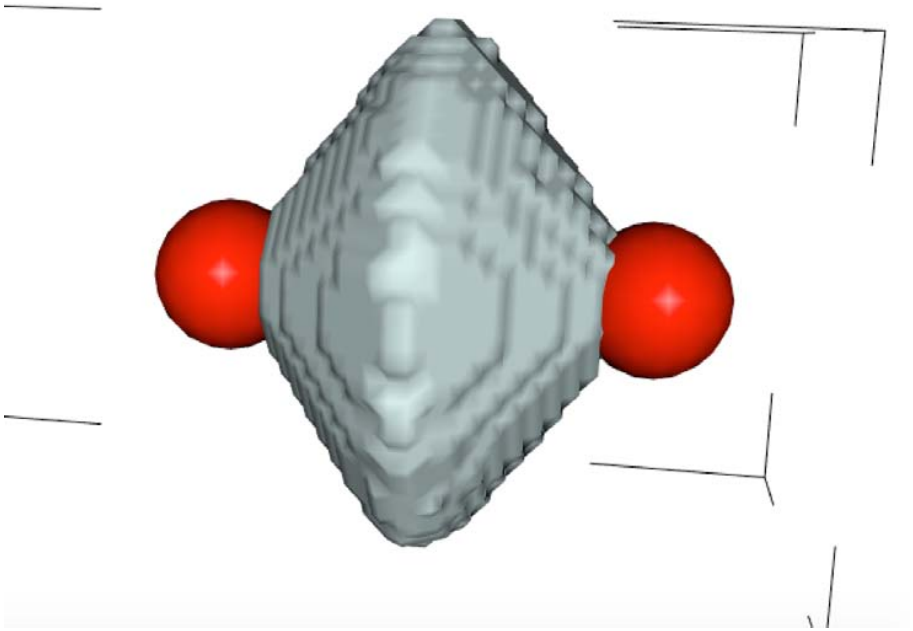
Prototypes : He_2^+, Ne_2^+, $HOOH^+$, $HSSH^-$, F_2^-, π bonds in O_2…

VB : $\mathbf{A}\uparrow\downarrow \;\; \uparrow\mathbf{B} \;\; \rightleftharpoons \;\; \mathbf{A}\uparrow \;\; \downarrow\uparrow\mathbf{B}$

Linnett : $\uparrow\mathbf{A}\downarrow\mathbf{B}\uparrow$

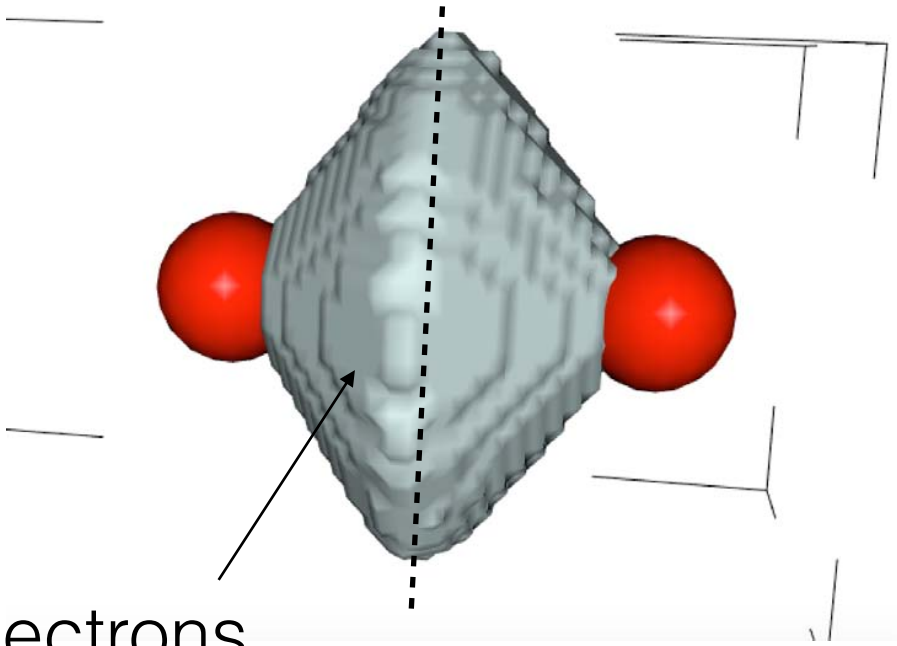
The 3e bond **in Ne_2^+**

$\Omega_{opt}(2\uparrow, 1\downarrow)$



The 3e bond in Ne_2^+

$\Omega_{opt}(\mathbf{2}\uparrow,\mathbf{1}\downarrow)$

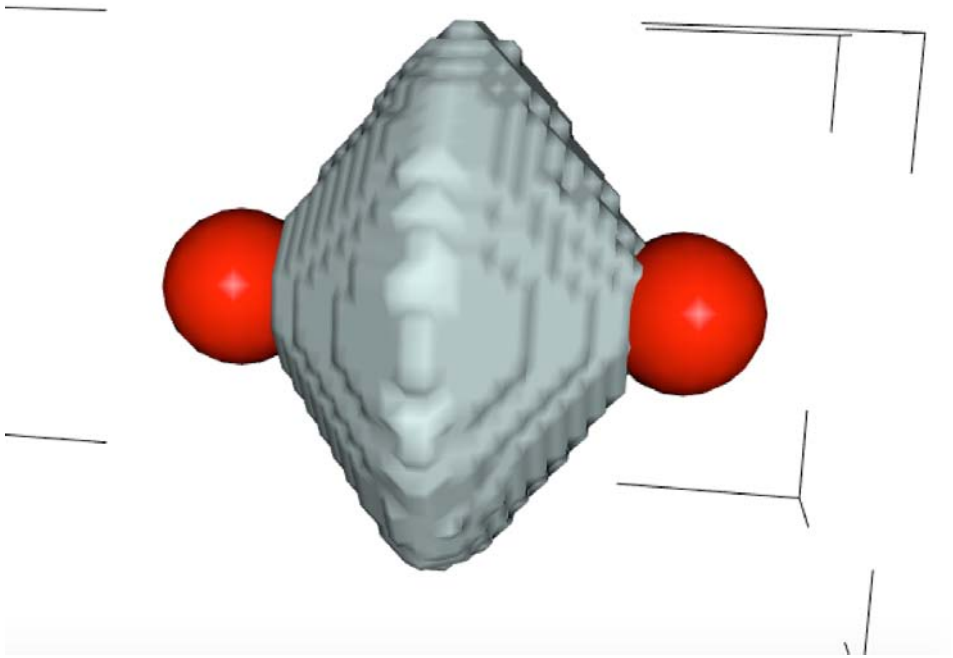


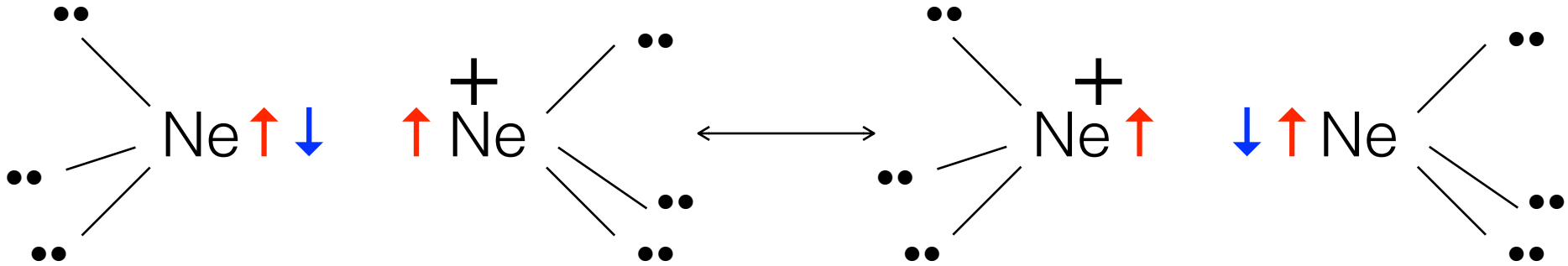
« 2 or 1 » electrons

<n>=1.5

P(**1**↑,**1**↓) + P(**1**↑,**0**↓)

The 3e bond in Ne_2^+





The 3e bond in Ne_2^+

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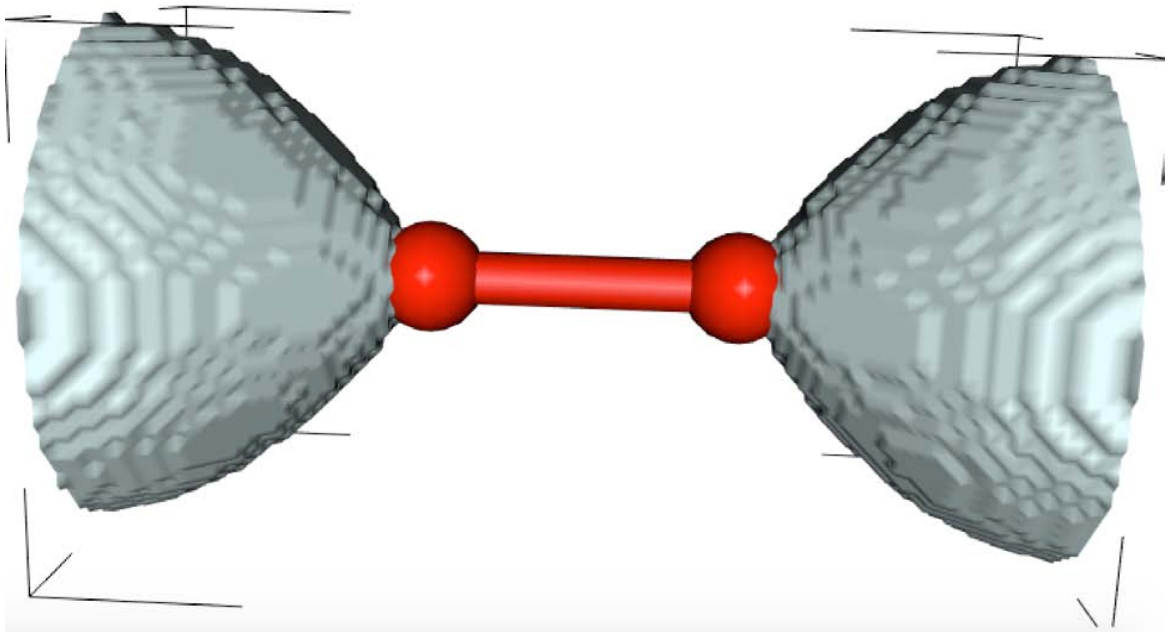
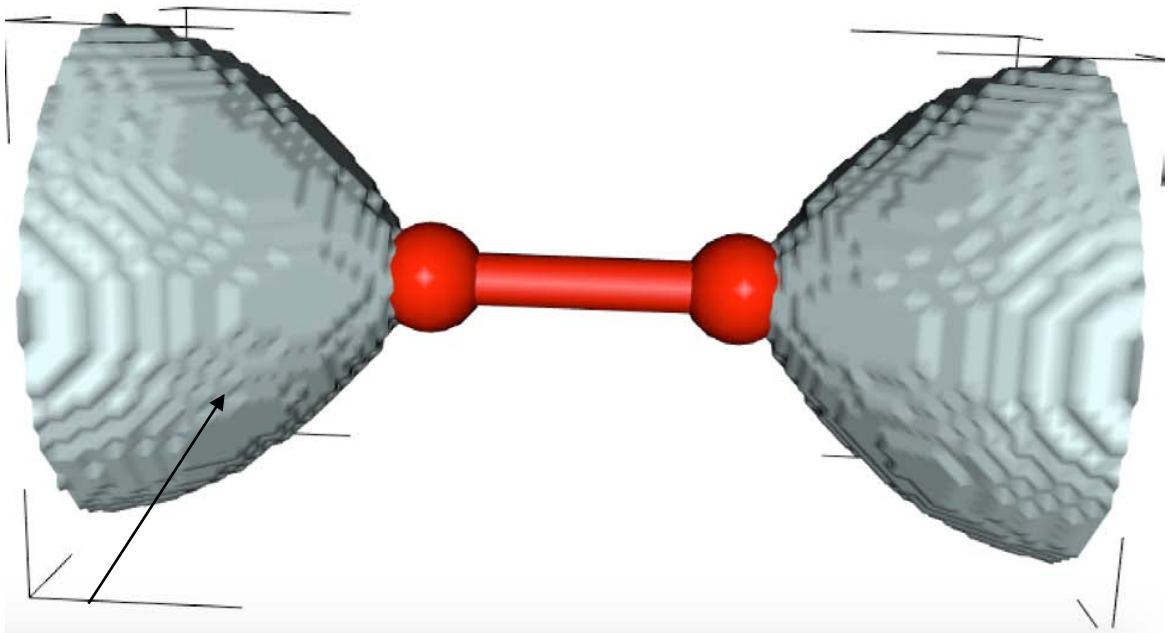


The 3e bond in Ne_2^+

$\Omega_{opt}(\mathbf{2}\uparrow,\mathbf{1}\downarrow)$



« 2 or 1 » electrons

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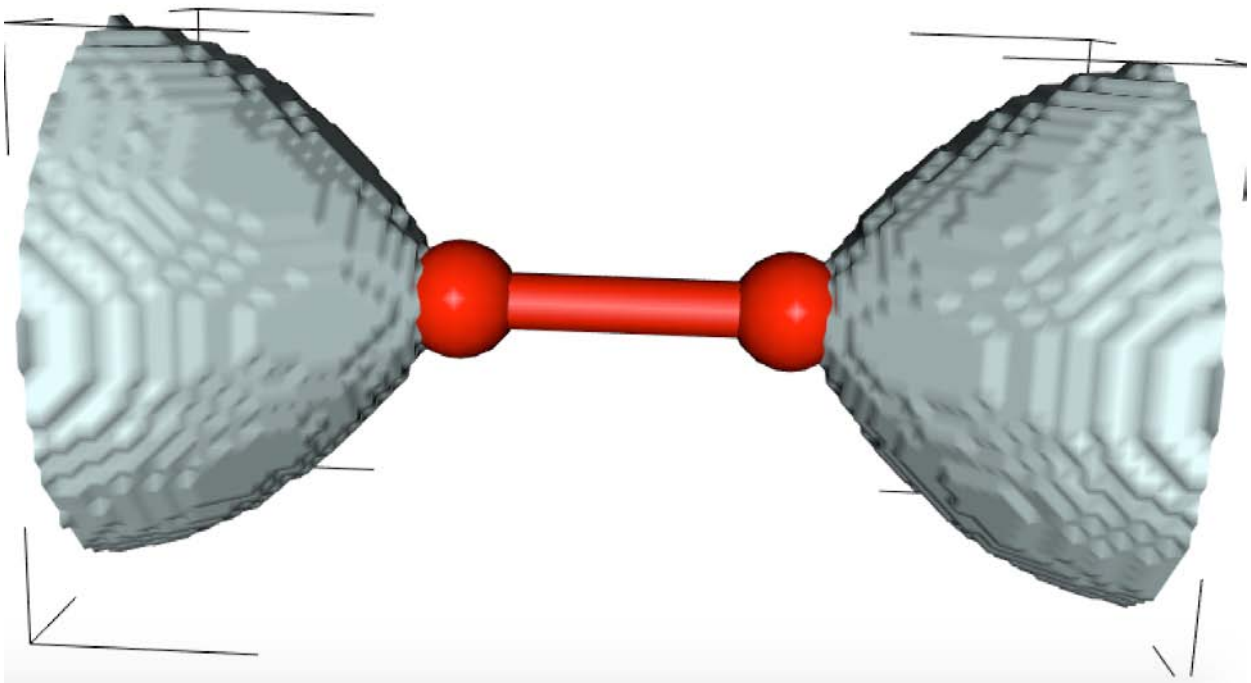
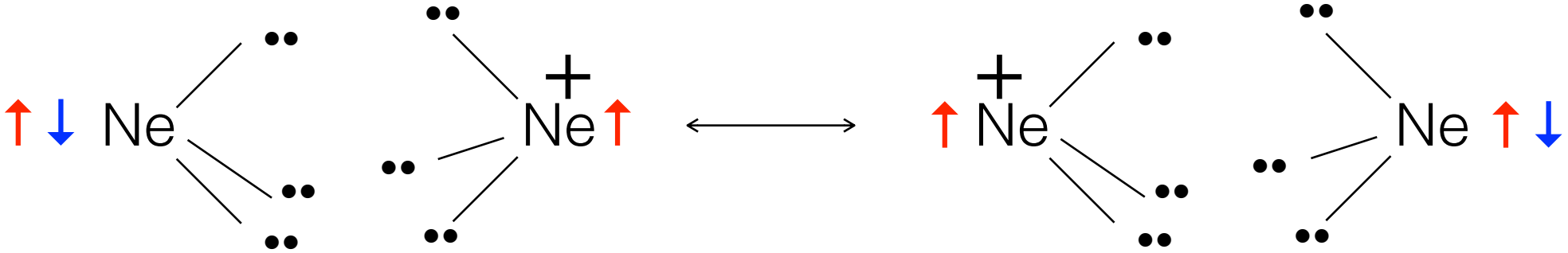
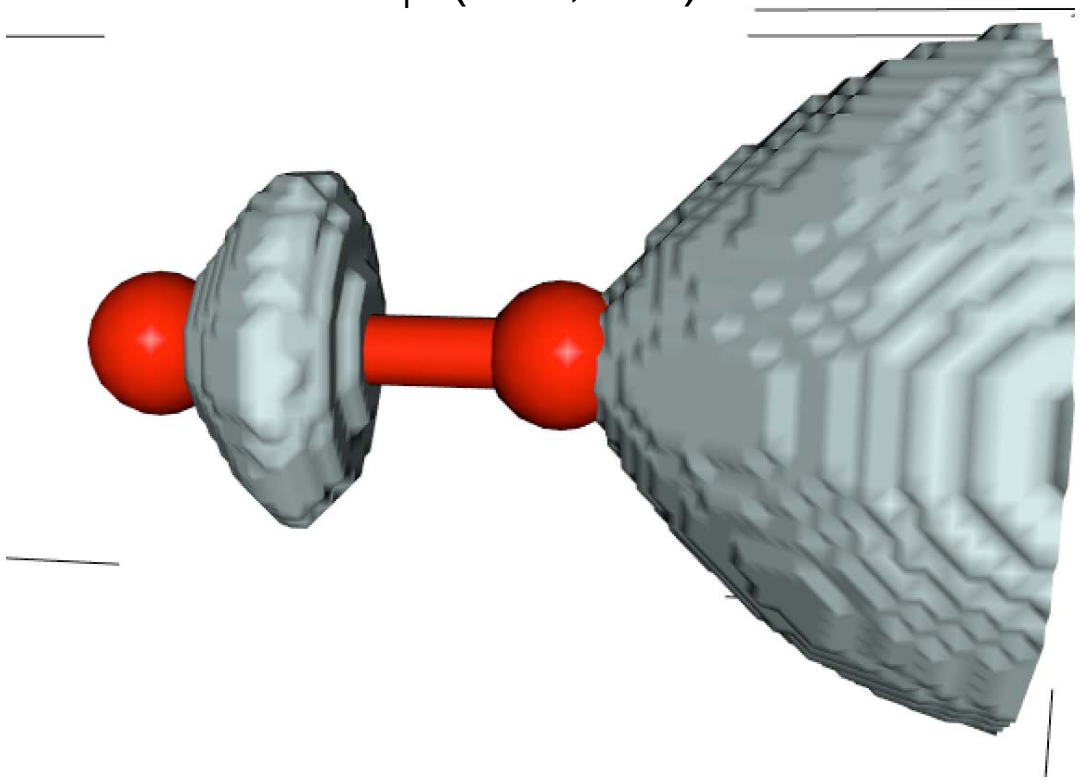
The 3e bond in Ne_2^+





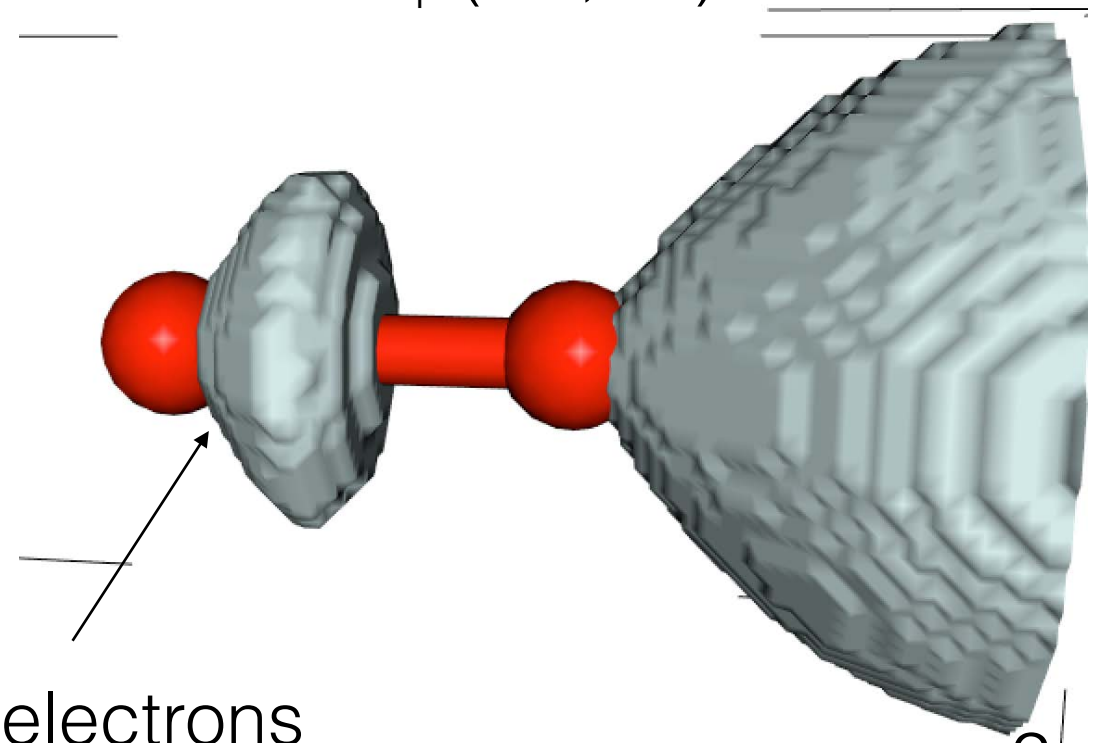
The 3e bond in Ne_2^+

$\Omega_{opt}(2\uparrow, 1\downarrow)$



The 3e bond in Ne_2^+

$\Omega_{opt}(2\uparrow,1\downarrow)$



« 2 or 1 » electrons

<n>=1.5

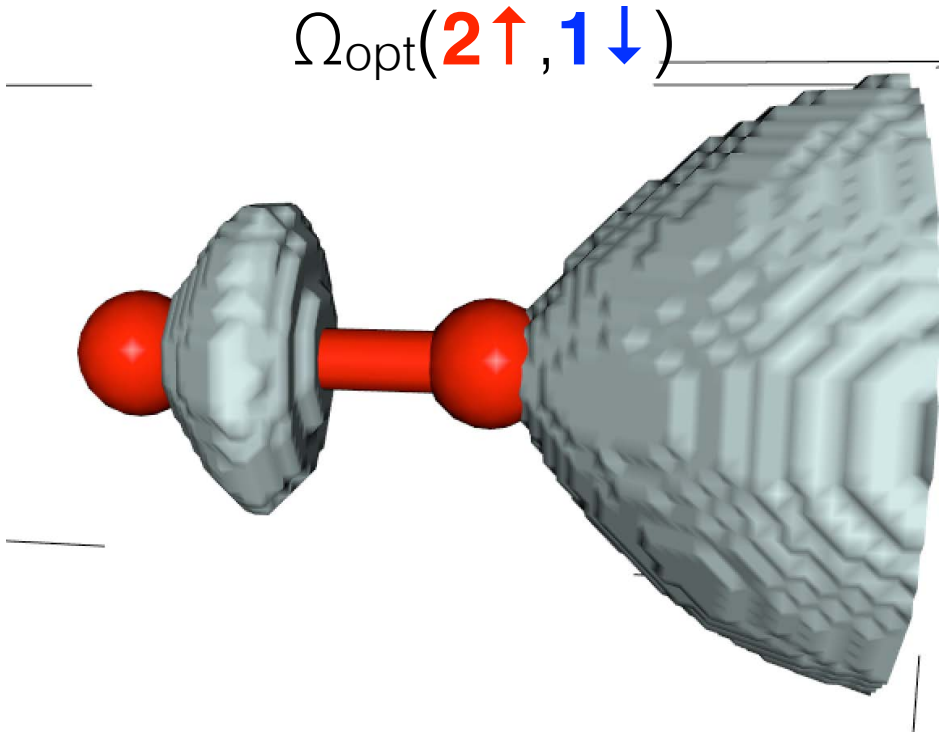
P(1↑,1↓) + P(1↑,0↓)

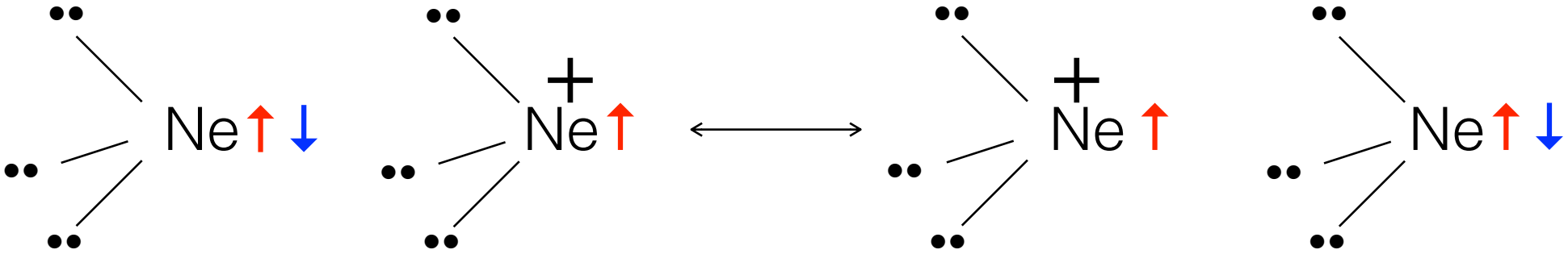
« 2 or 1 » electrons

<n>=1.5

P(1↑,1↓) + P(1↑,0↓)

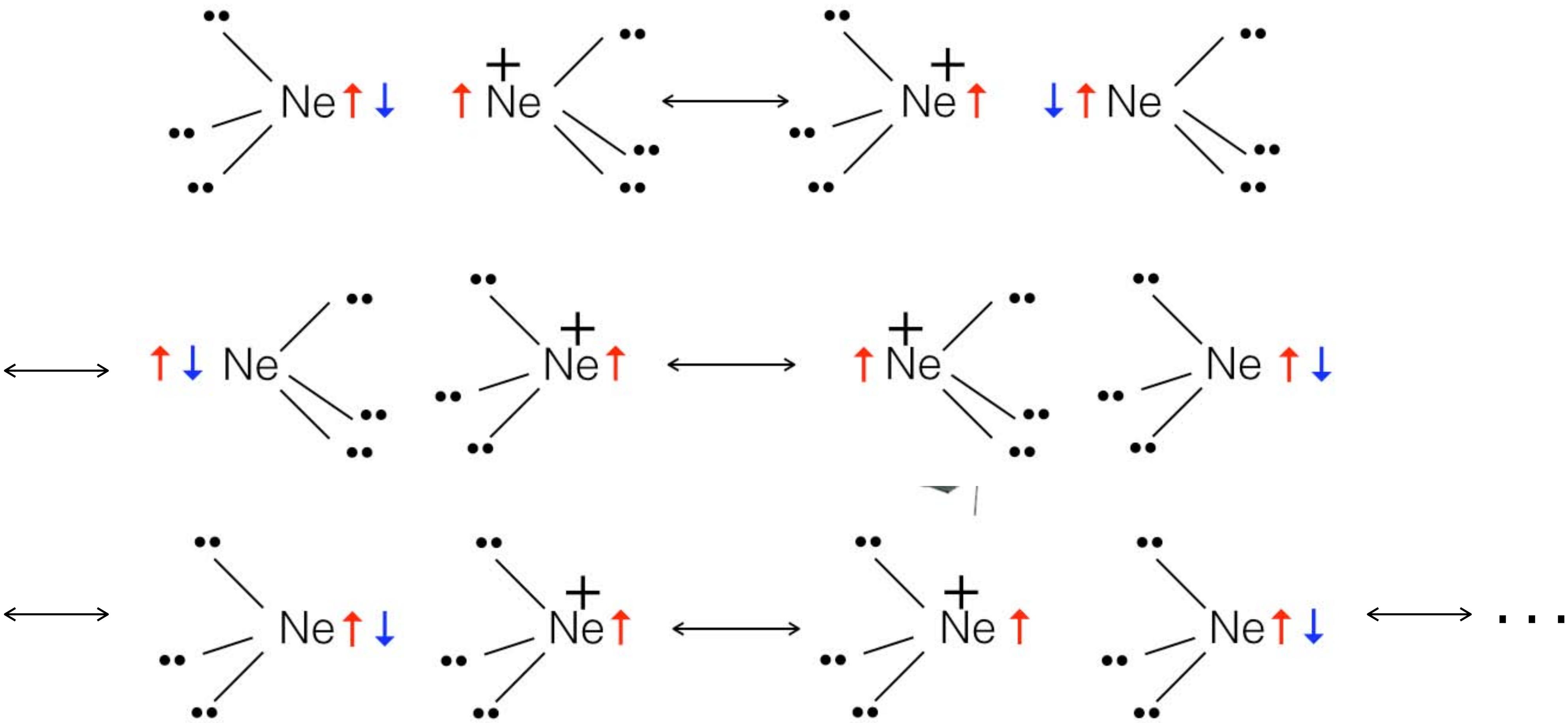
The 3e bond in Ne_2^+





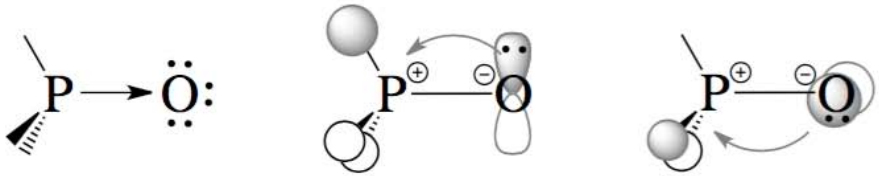
The 3e bond in Ne_2^+

- Conclusion:



4/4 Phosphonium oxydes and ylides X_3PO, X_3PCH_2

With: Marcos Menedez, Ángel Martín Pendás



Scheme 3: The "double-donation model": $\sigma + \pi$ backbonding model for P–O bonding.

(a) (b)

Scheme 4: (a) the σ + three backhanding model; (b) the three Ω bonds model.

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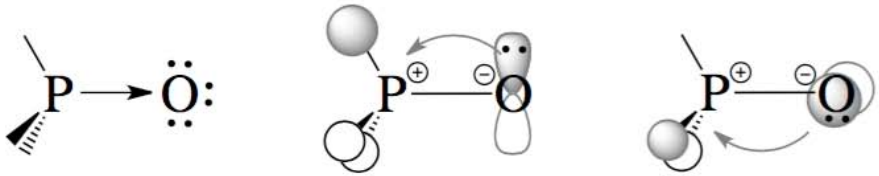

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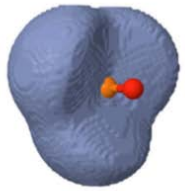
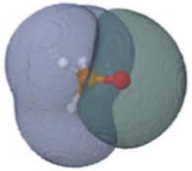
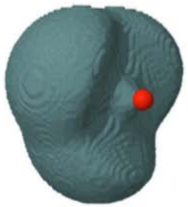
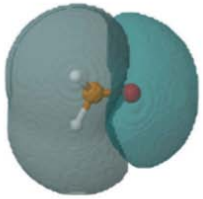
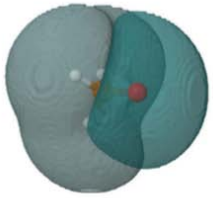
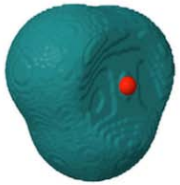
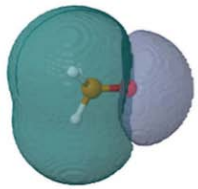
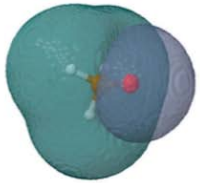




$\Omega_6(PH_3^{2+})/\Omega_8(O^{2-})$

$\Omega_8(PH_3)/\Omega_6(O)$

$\Omega_{10}(PH_3^{2-})/\Omega_4(O^{2+})$

	$P_{opt}(\nu)$	$\langle\nu\rangle$	$Var(\langle\nu\rangle)$
$\Omega_6(PH_3^{2+})$ / $\Omega_8(O^{2-})$	0.620	6.04 / 7.96	0.52
$\Omega_7(PH_3^{+})$ / $\Omega_7(O^{-})$	0.406	7.03 / 6.96	0.90
$\Omega_8(PH_3)$ / $\Omega_6(O)$	0.375	8.04 / 5.96	1.14
$\Omega_9(PH_3^{-})$ / $\Omega_5(O^{+})$	0.350	9.03 / 4.97	1.25
$\Omega_{10}(PH_3^{2-})$ / $\Omega_4(O^{2+})$	0.340	10.01 / 3.99	1.29

4/4 Phosphonium oxydes and ylides X_3PO, X_3PCH_2

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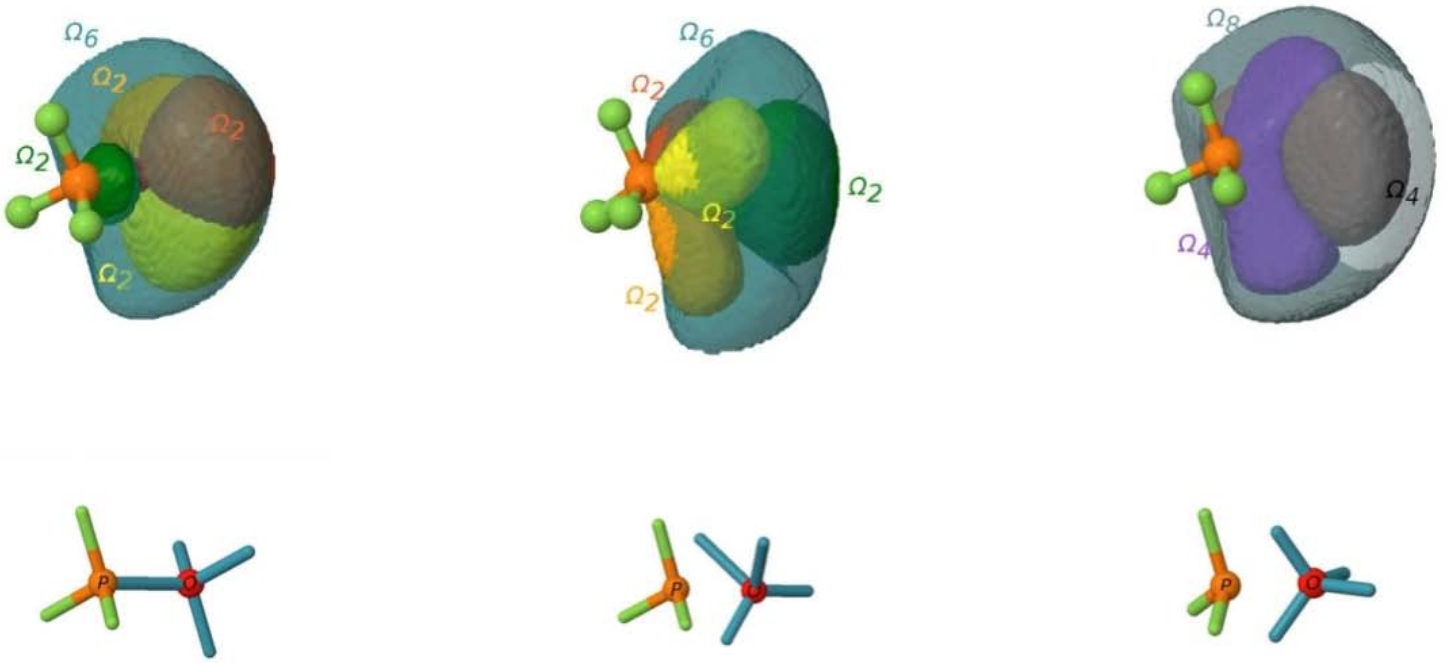

Phosphonium oxydes and ylides X_3PO, X_3PCH_2

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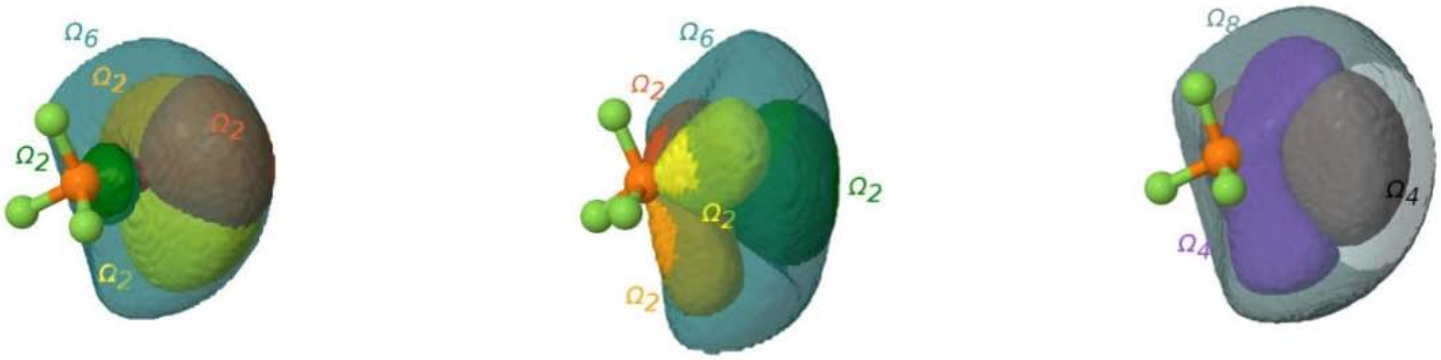

Domain	X	$P_{opt}(2)$	$\langle\nu\rangle$	$Var(\langle\nu\rangle)$
Ω_2(P-O axis)	H	0.387	1.97	1.06
	F	0.387	1.98	1.05
	CN	0.386	1.98	1.06
Ω_2(O side)	H	0.399	1.98	0.99
	F	0.404	1.98	0.98
	CN	0.400	1.97	0.99
Domain	X	$P_{opt}(6)$	$\langle\nu\rangle$	$Var(\langle\nu\rangle)$
Ω_6(O side)	H	0.375	5.96	1.14
	F	0.371	5.97	1.16
	CN	0.366	5.96	1.18
Ω_6(P-O axis)	H	0.351	6.00	1.31
	F	0.355	6.00	1.28
	CN	0.348	6.00	1.32
Domain	X	$P_{opt}(4)$	$\langle\nu\rangle$	$Var(\langle\nu\rangle)$
Ω_4(O side)	H	0.340	3.98	1.33
	F	0.341	3.99	1.32
	CN	0.339	3.98	1.32
Ω_4(P-O axis)	H			
	F	0.327	3.99	1.47
	CN			

4/4 Phosphonium oxydes and ylides X_3PO, X_3PCH_2

With: Marcos Menedez, Ángel Martín Pendás

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Scheme 5: The resonance description of phosphorus ylides.

4/4 Phosphonium oxydes and ylides X_3PO, X_3PCH_2

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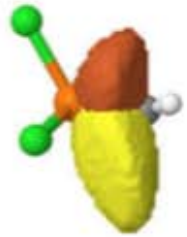
Scheme 5: The resonance description of phosphorus ylides.

H_3PCH_2

Cl_3PCH_2



F_3PCH_2

Conclusion

- MPDs: directly interpretable real-space domains.
- Visual information on the arrangement in electron in space.
- Direct understanding: in Si_2H_2 unveil the similarity of the electronic arrangements for very different geometries
- New views: dynamic view of ionic bonding

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