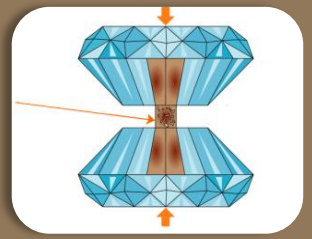
TOPOLOGICAL STUDY OF CHEMICAL BONDS UNDER PRESSURE:

Hydrogen as a model case

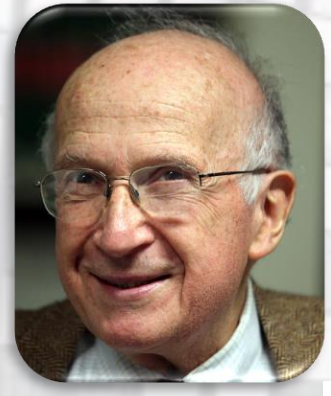


Vanessa Labet

Paris, FRANCE

UPMC SORBONNE UNIVERSITÉS cnrs SORBONNE UNIVERSITÉS

Neil
ASHCROFT



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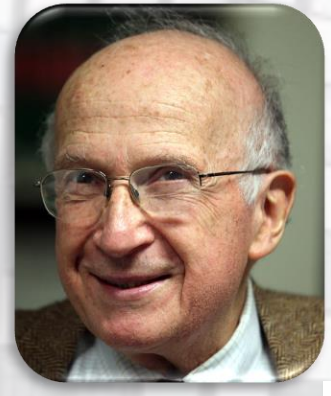
HOFFMANN

Cornell Univ.

Postdoc 2009-2011

Neil ASHCROFT



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Vanessa RIFFET

Julia CONTRERAS -GARCIA

Outline

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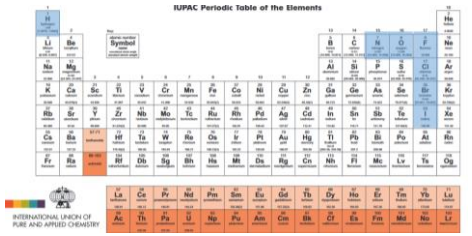

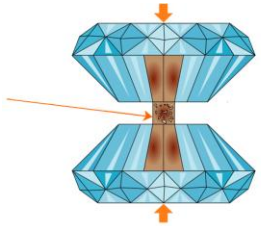

2. Solid Hydrogen under pressure : focus on the H---H distances (intra + intermolecular) - *Cornell*

3. Study of a non periodic model for solid H under pressure : topological tools (NCI + ELF)

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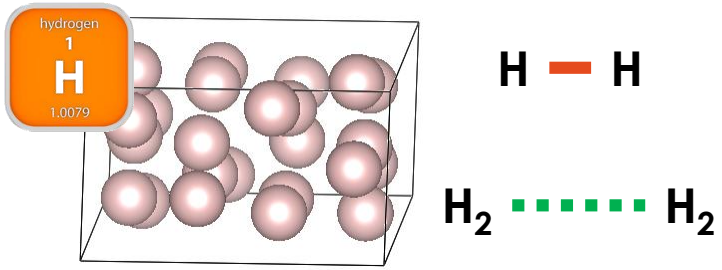

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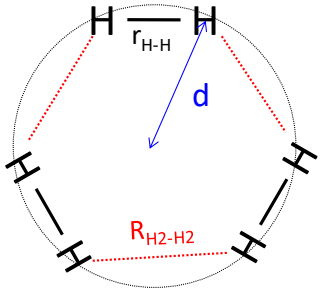

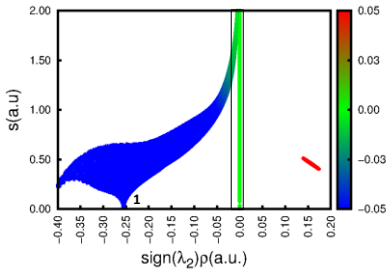

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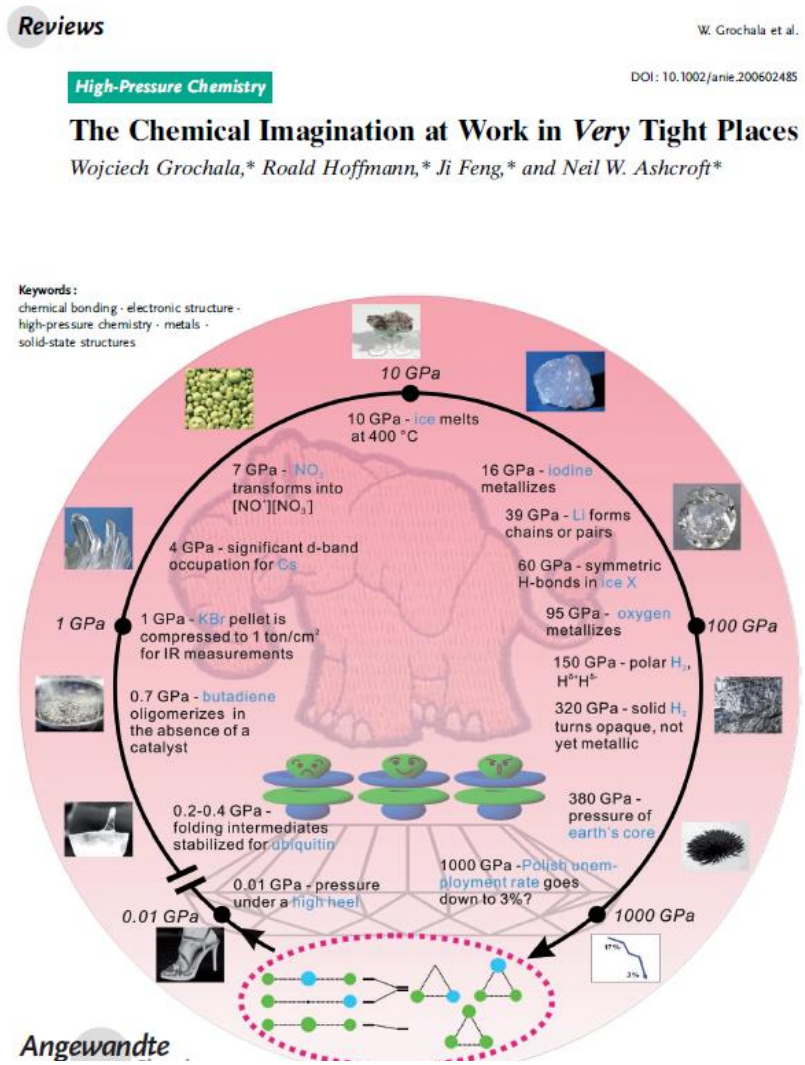


Grochala et al. Angew. Chem. Int. Ed. 2007, 46, 3620-3642

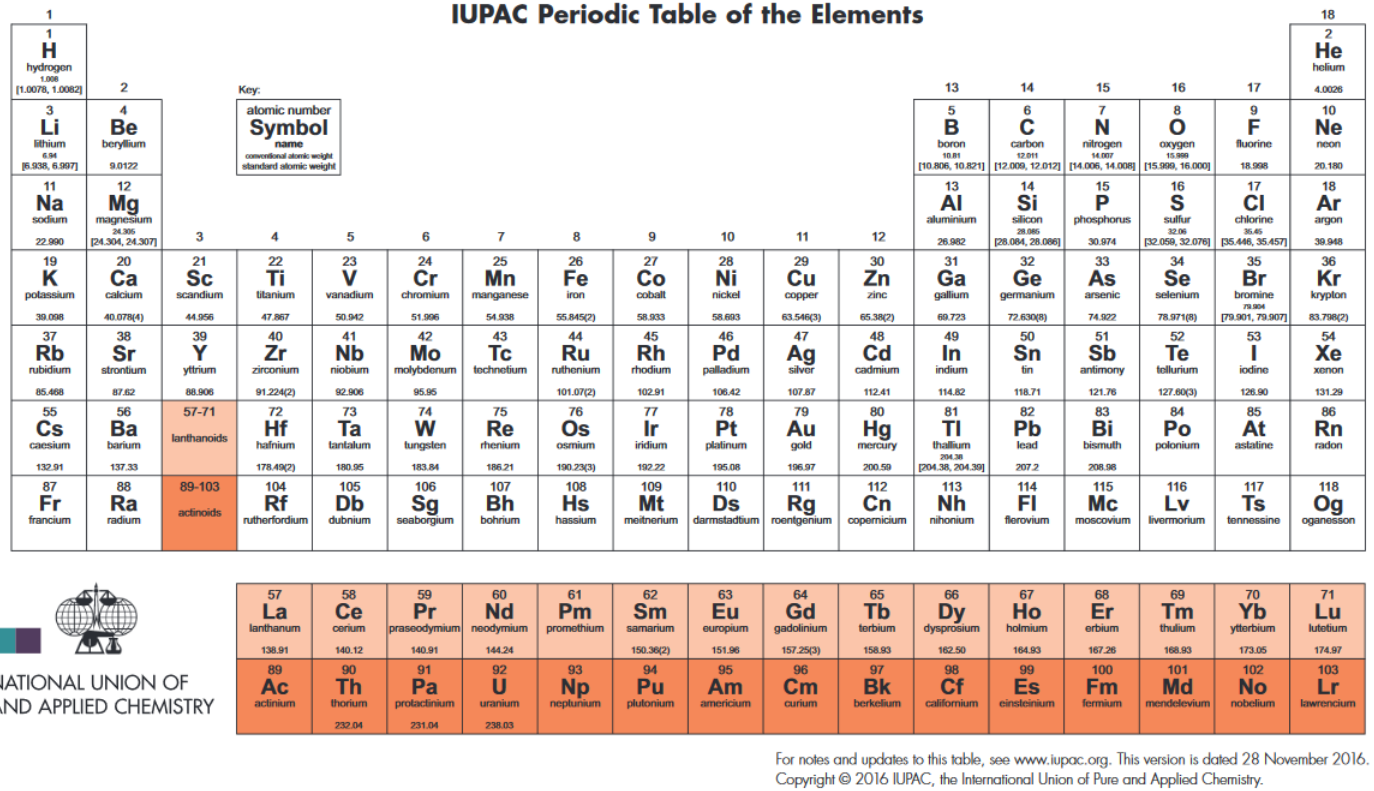
Molecular solids under Pressure :

$T = 0K$ Enthalpy $H = E + pV$

Finding ways of decreasing volume V

1. Squeezing the « van der Waals space »
2. Increasing coordination numbers
3. Shortening bonds
4. Electrons moving off their atoms

Context



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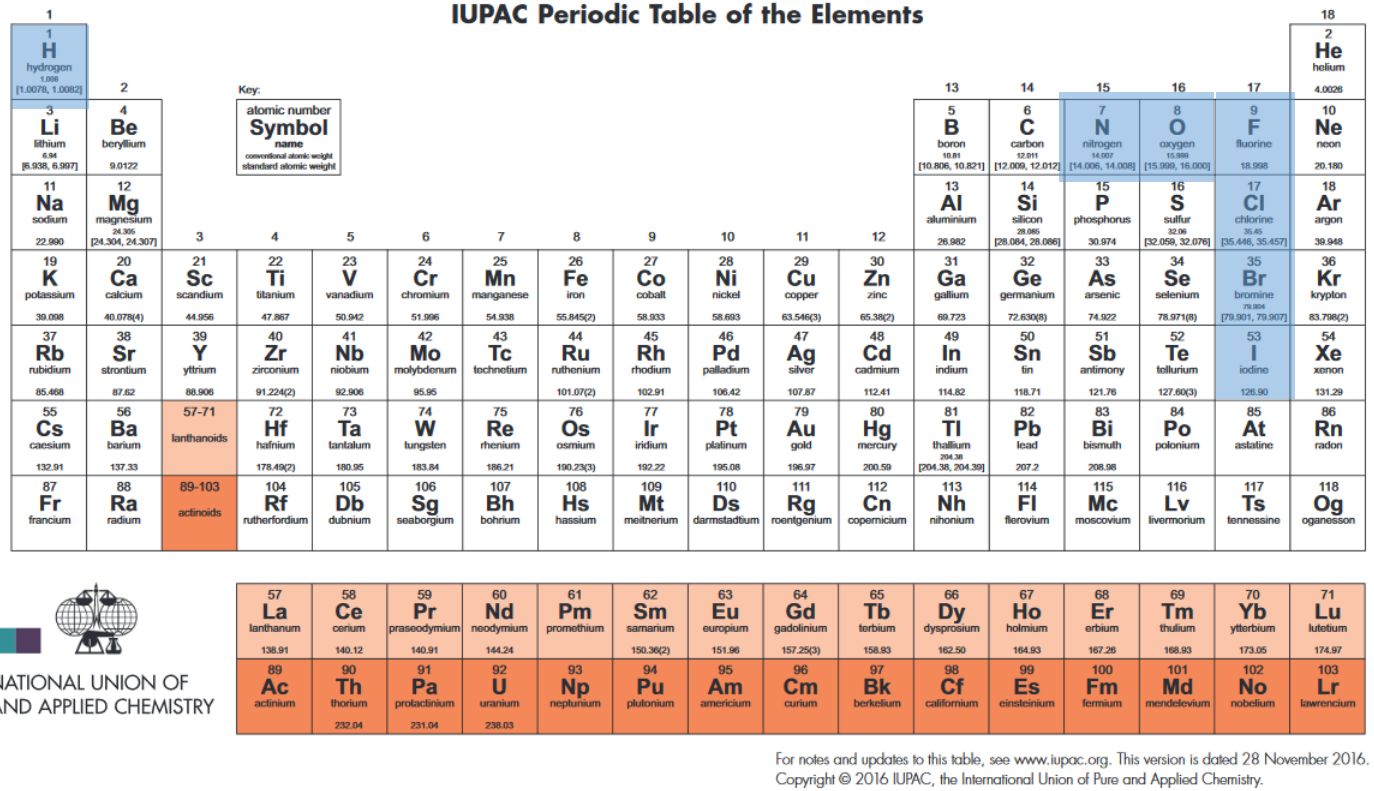

IUPAC Periodic Table of the Elements

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3 Li lithium 6.94 [6.938, 6.997]	4 Be beryllium 9.0122											5 B boron 10.81 [10.806, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999 [15.999, 16.000]	9 F fluorine 18.998	10 Ne neon 20.180
11 Na sodium 22.990	12 Mg magnesium 24.305 [24.304, 24.307]	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 26.982	14 Si silicon 28.085 [28.084, 28.086]	15 P phosphorus 30.974	16 S sulfur 32.06 [32.059, 32.076]	17 Cl chlorine 35.45 [35.446, 35.457]	18 Ar argon 39.948
19 K potassium 39.098	20 Ca calcium 40.078(4)	21 Sc scandium 44.956	22 Ti titanium 47.867	23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845(2)	27 Co cobalt 58.933	28 Ni nickel 58.693	29 Cu copper 63.546(3)	30 Zn zinc 65.38(2)	31 Ga gallium 69.723	32 Ge germanium 72.630(8)	33 As arsenic 74.922	34 Se selenium 78.971(8)	35 Br bromine 79.904 [79.901, 79.907]	36 Kr krypton 83.798(2)
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87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganesson

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89 Ac actinium	90 Th thorium 232.04	91 Pa protactinium 231.04	92 U uranium 238.03	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

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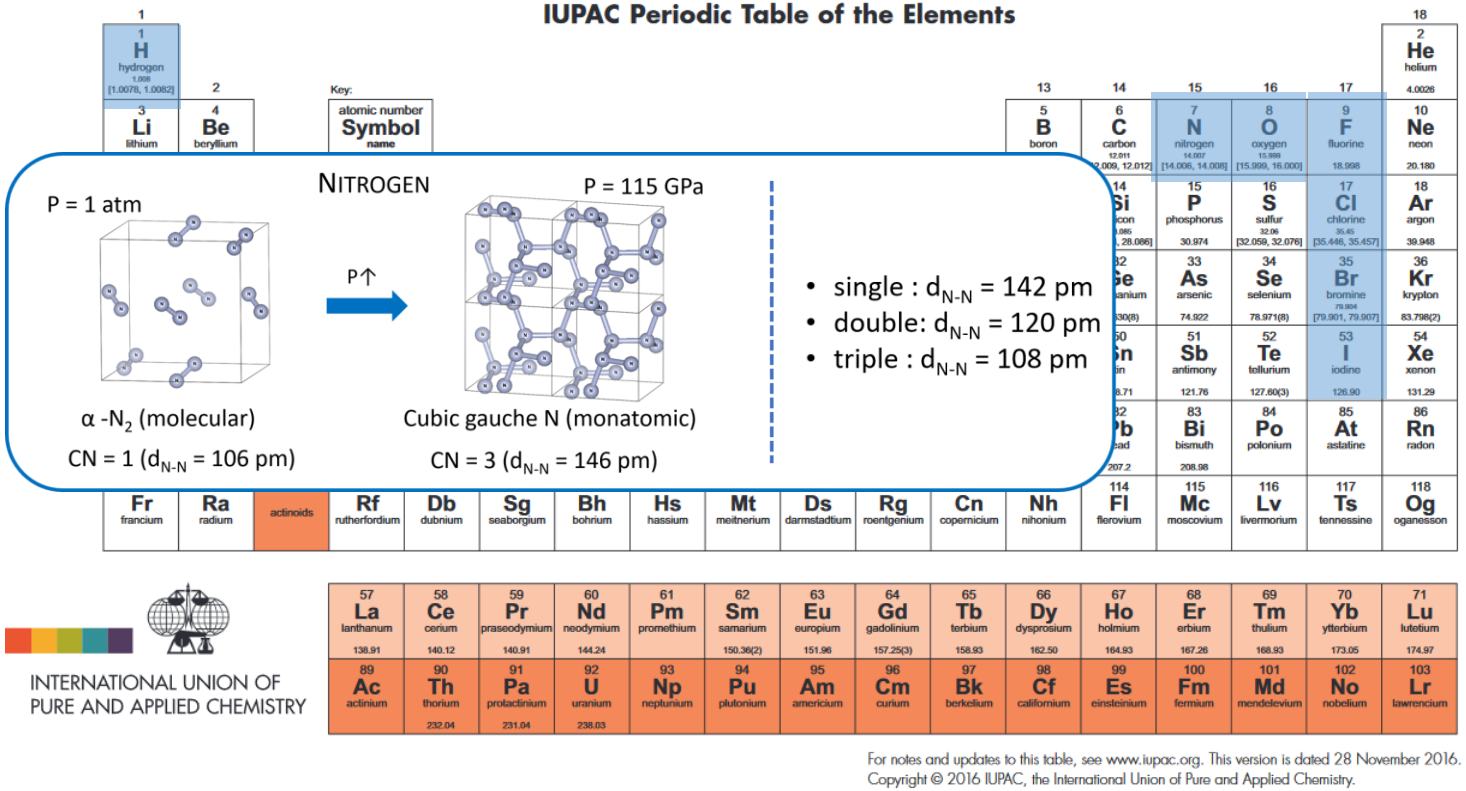

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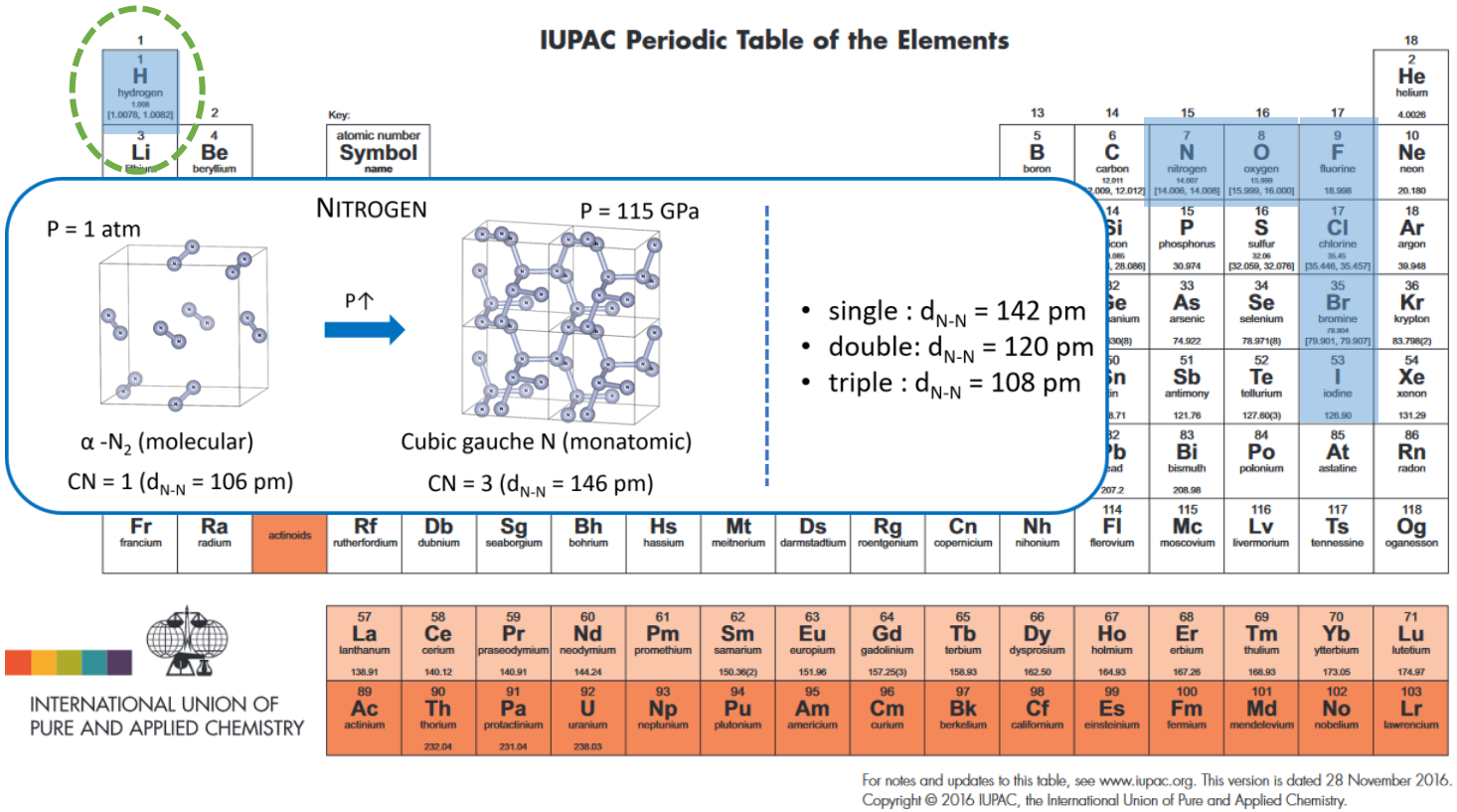

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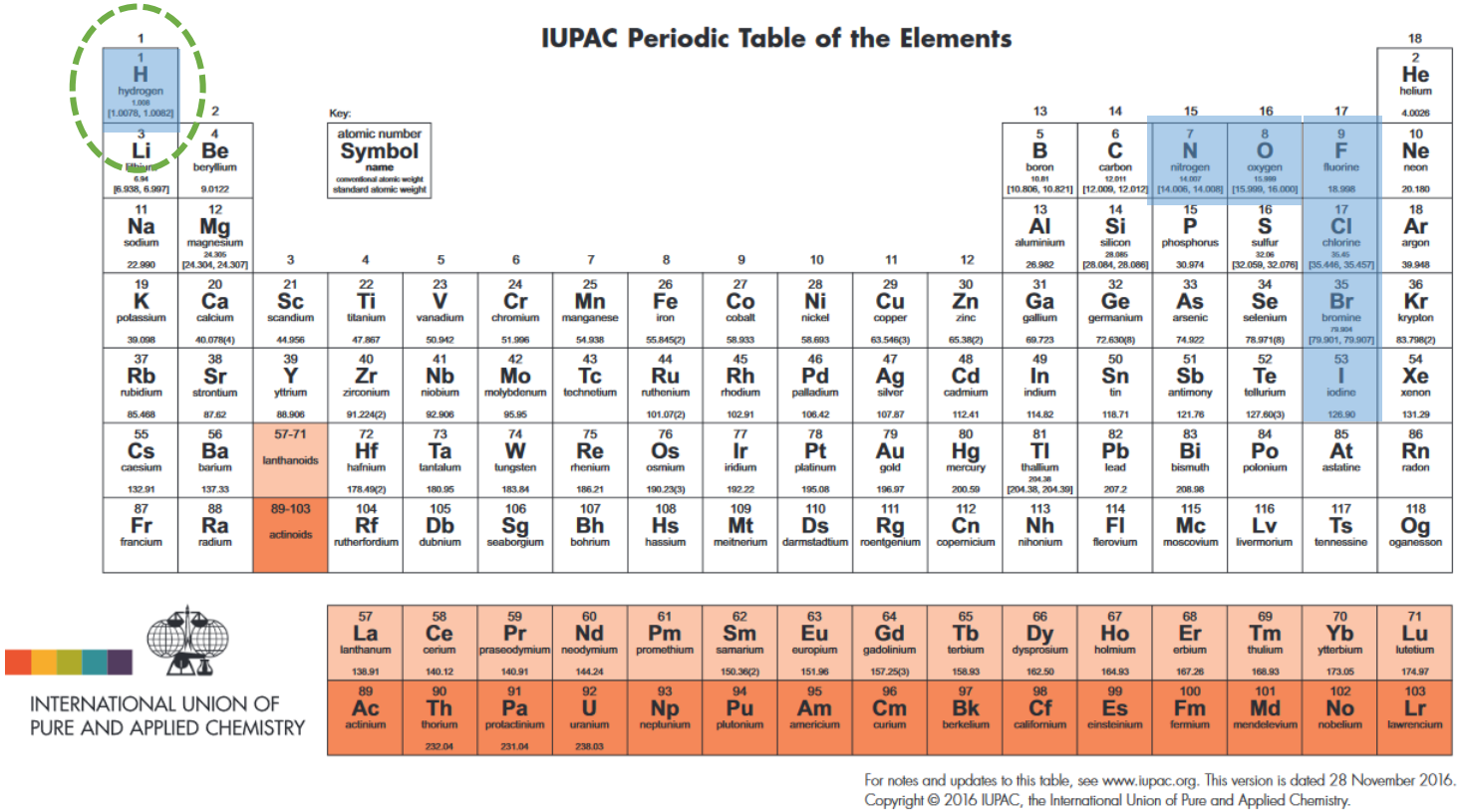

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Same behavior expected
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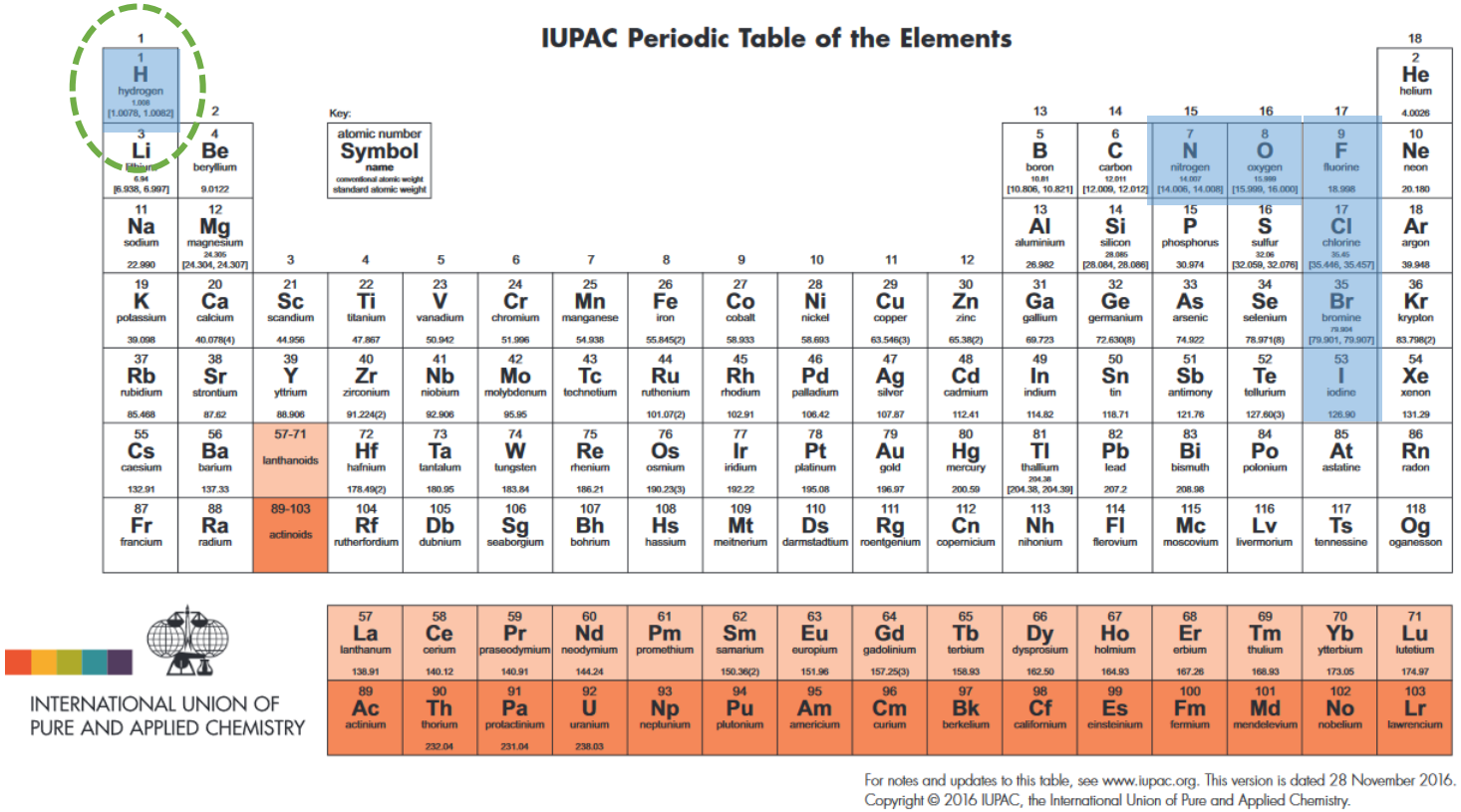

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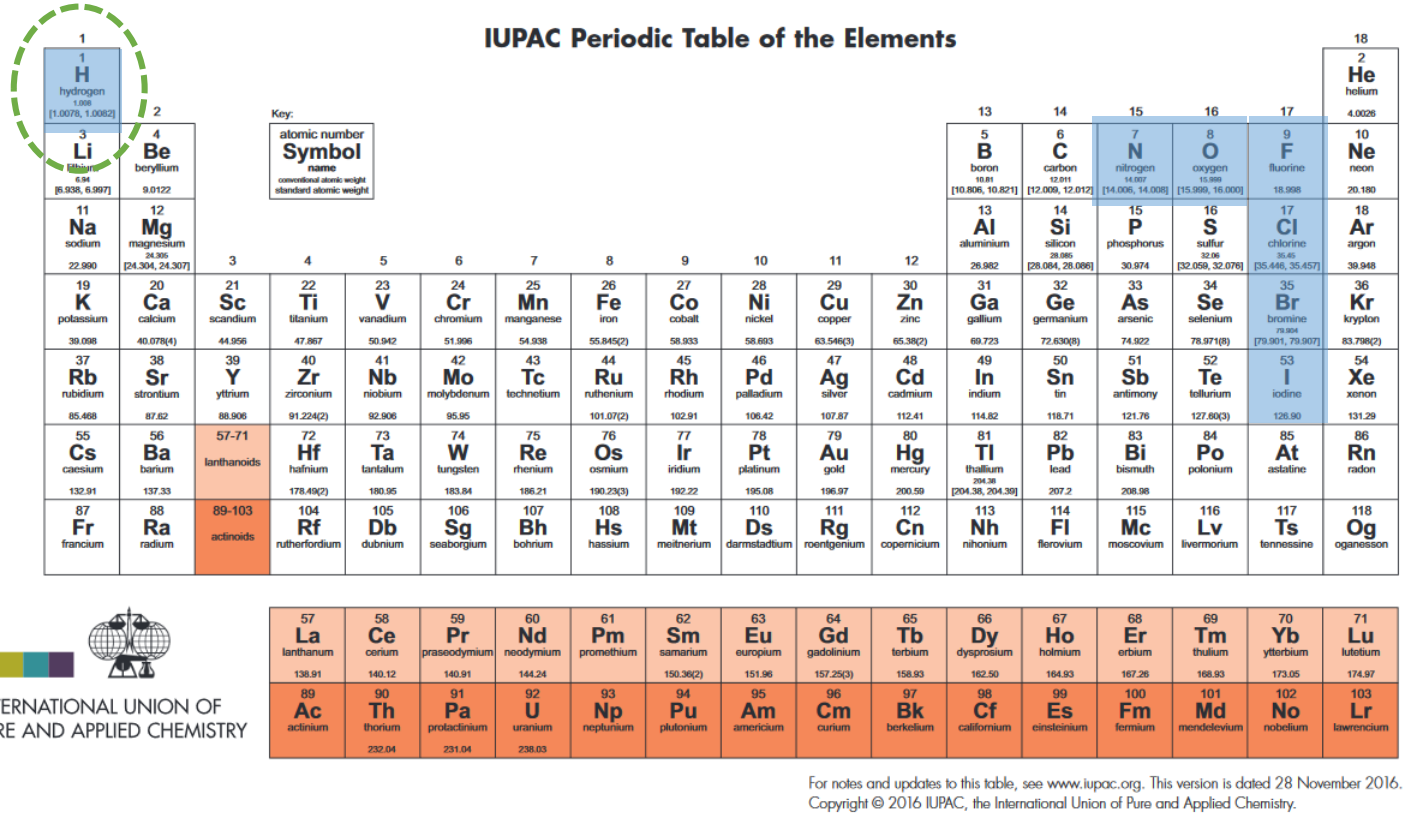

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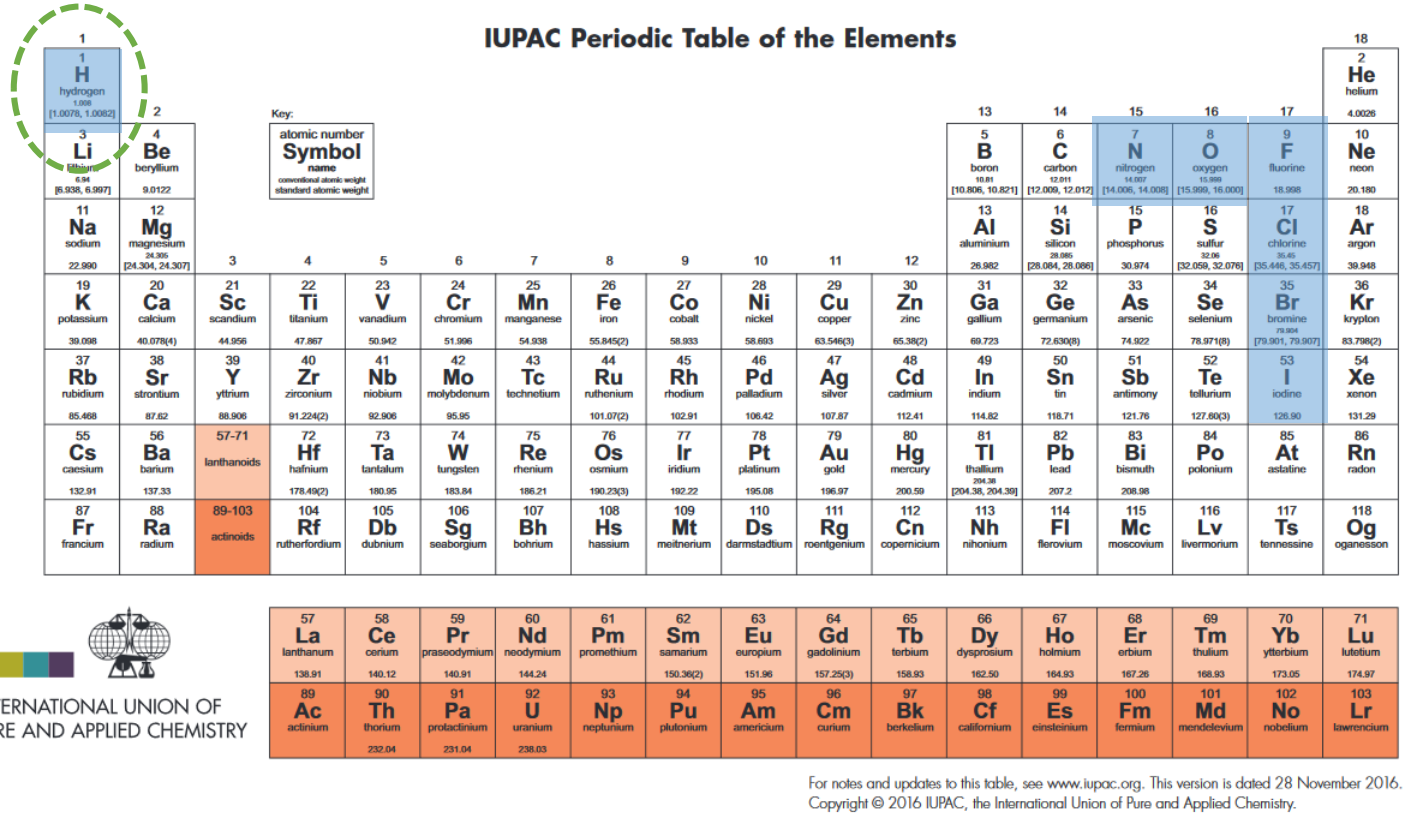

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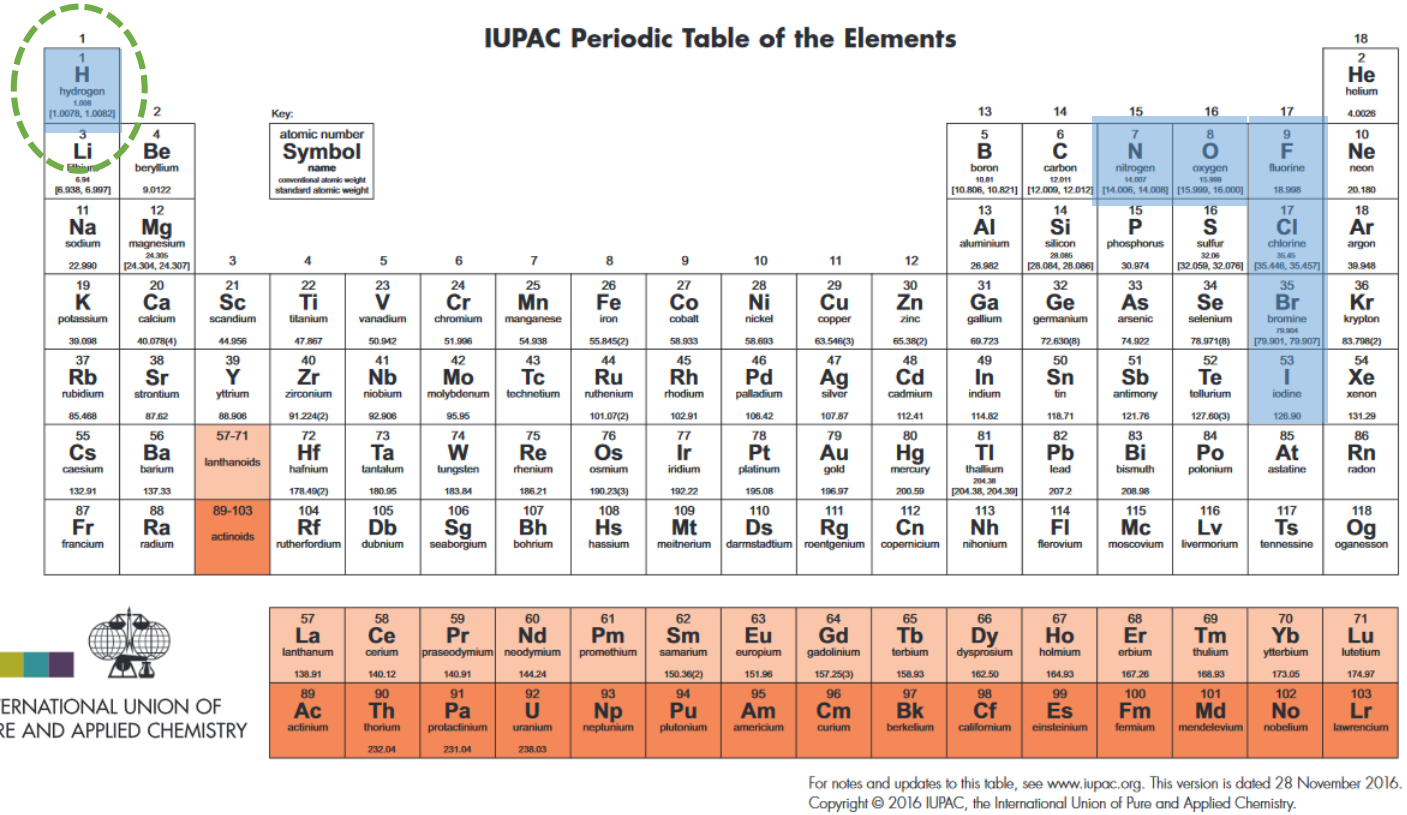

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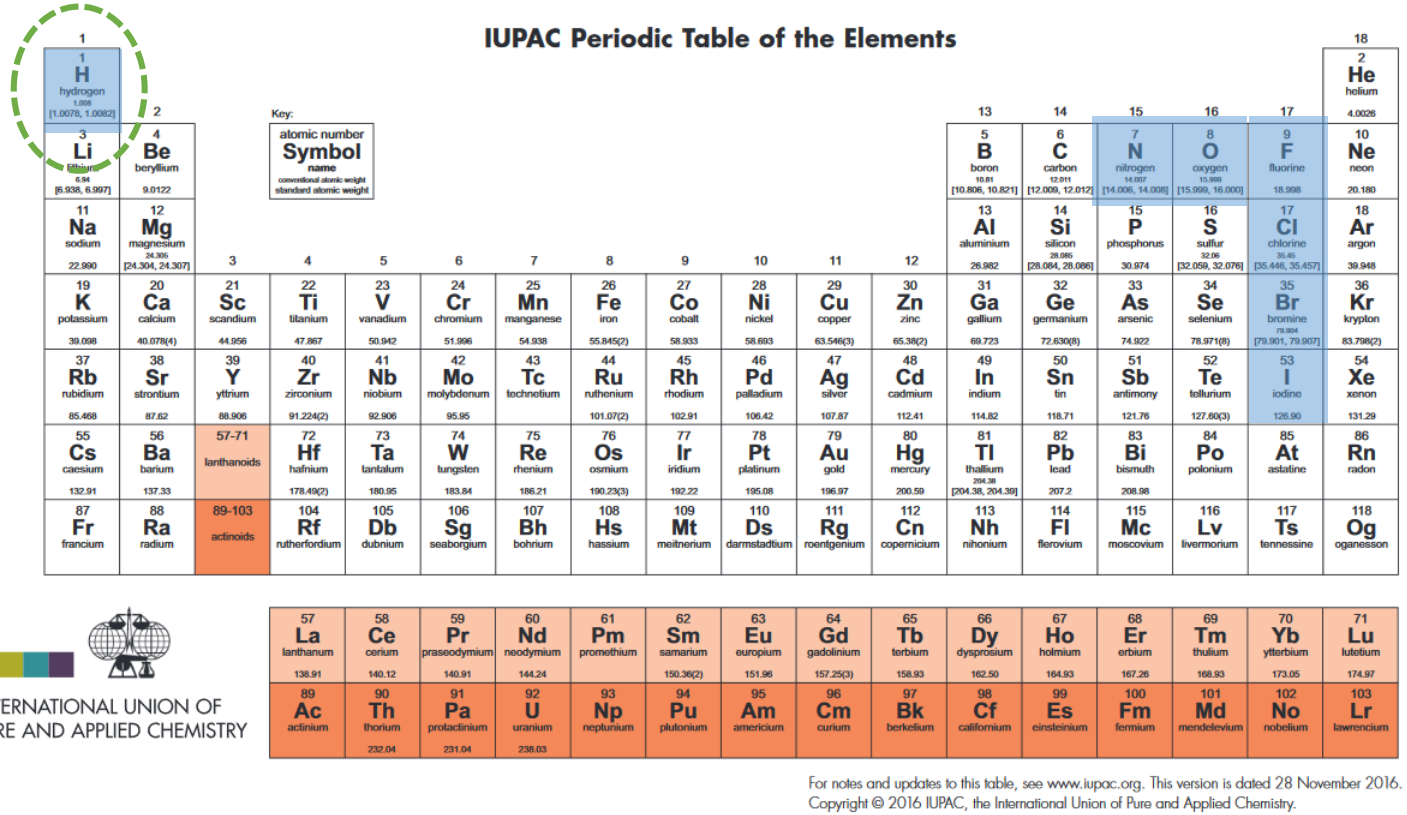

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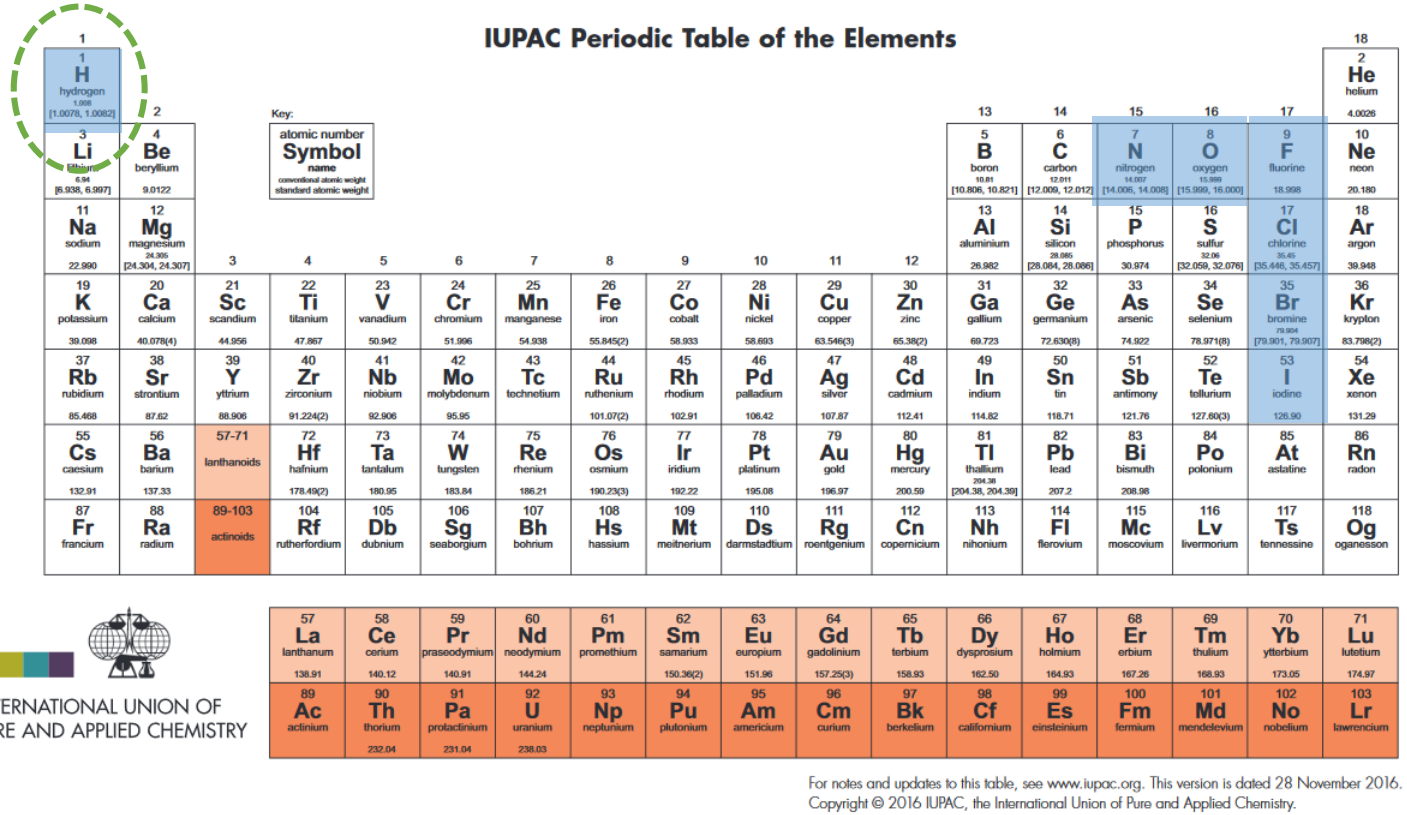

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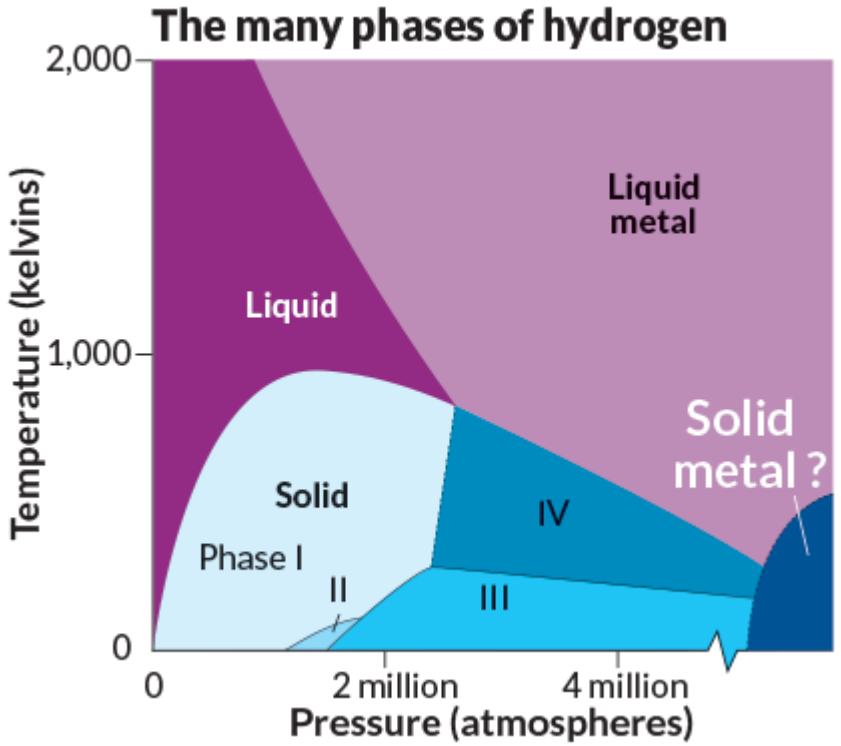
Holly Grail of physics

Dense solid hydrogen - Summary



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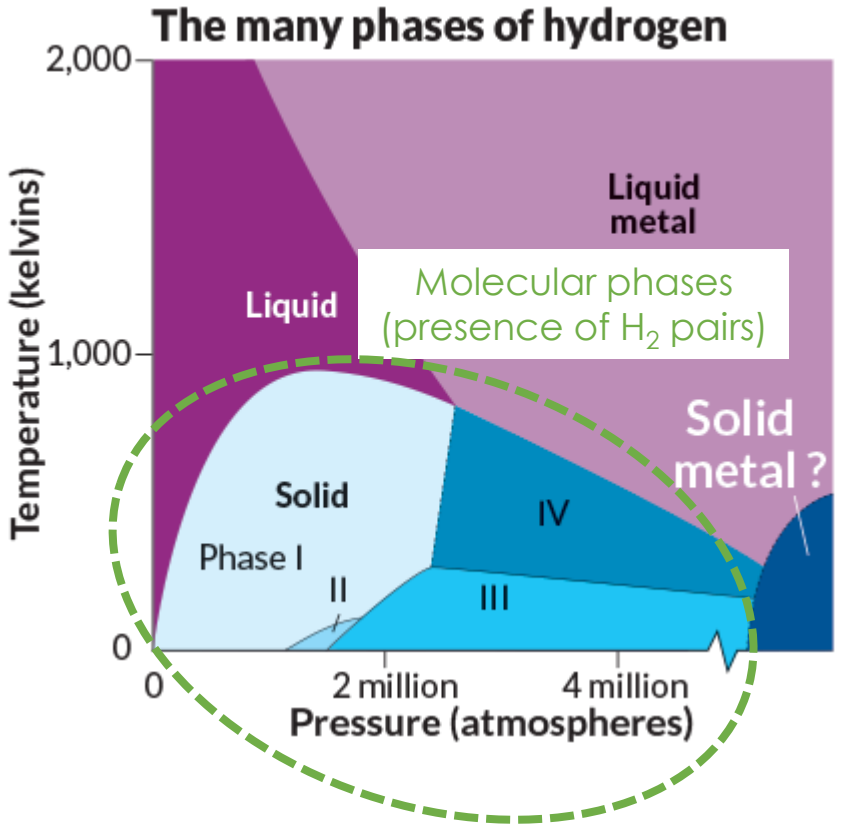

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  - I : H_2 freely rotating
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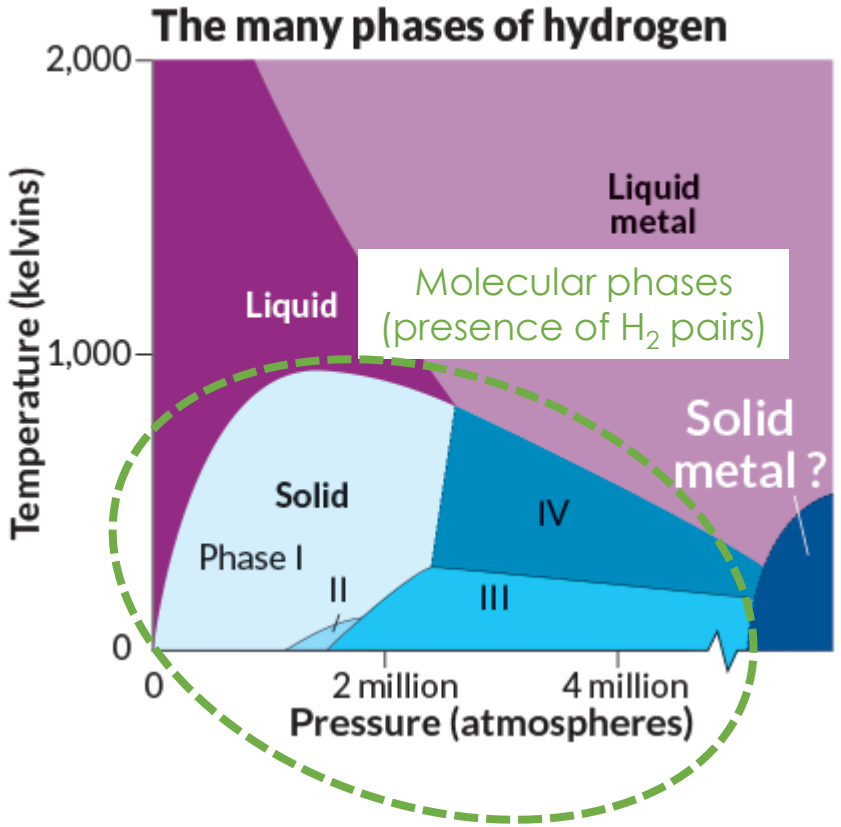

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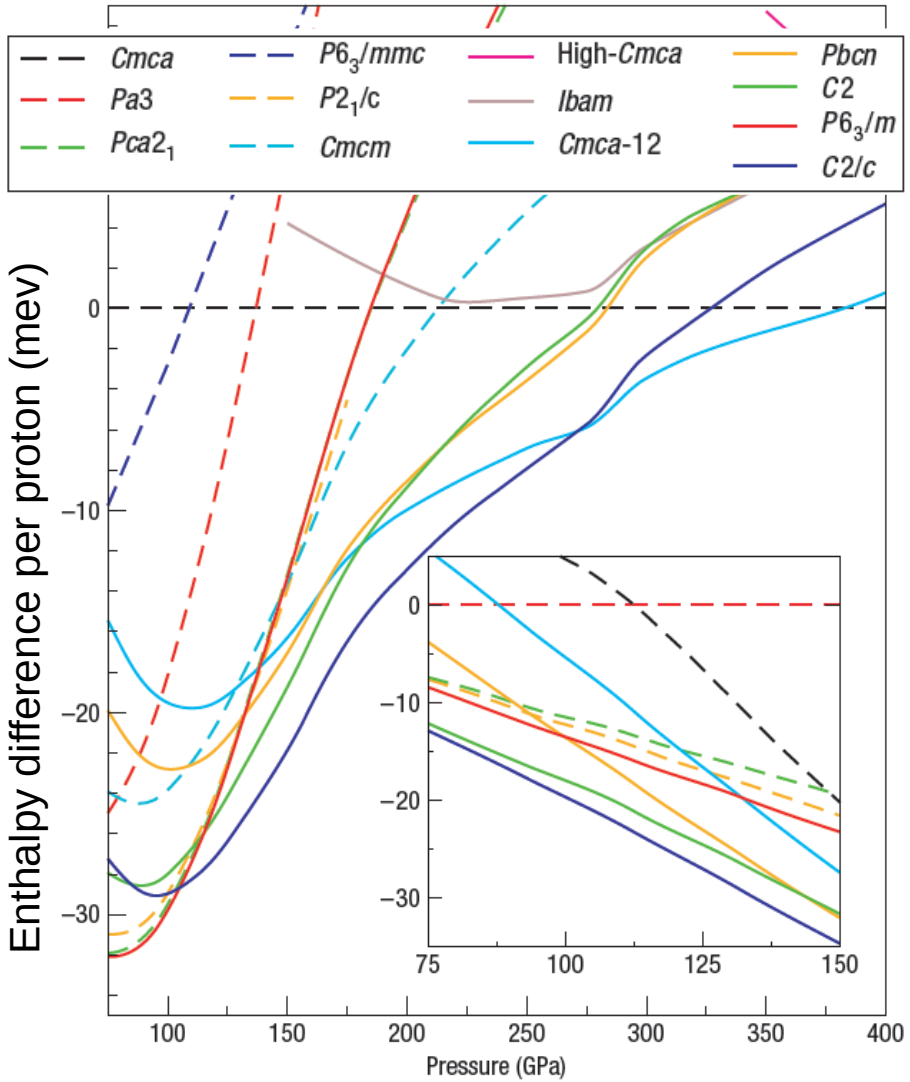

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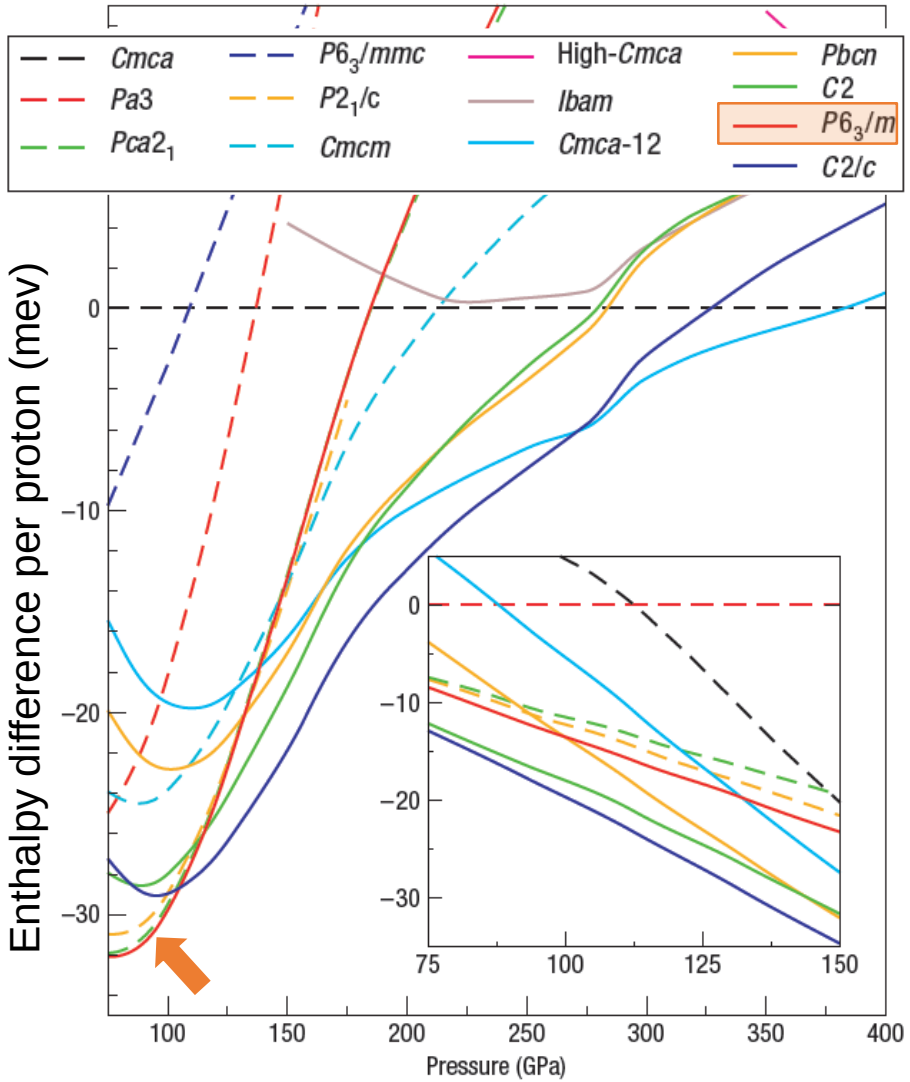

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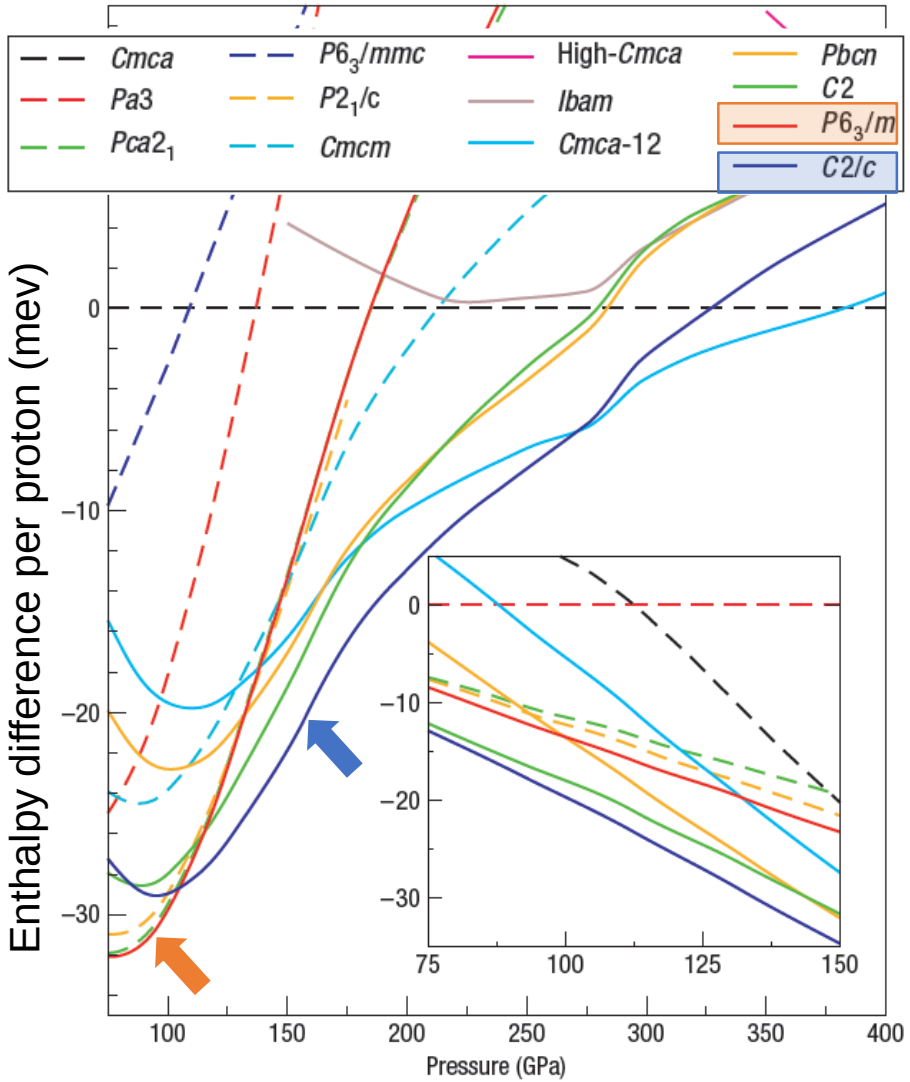

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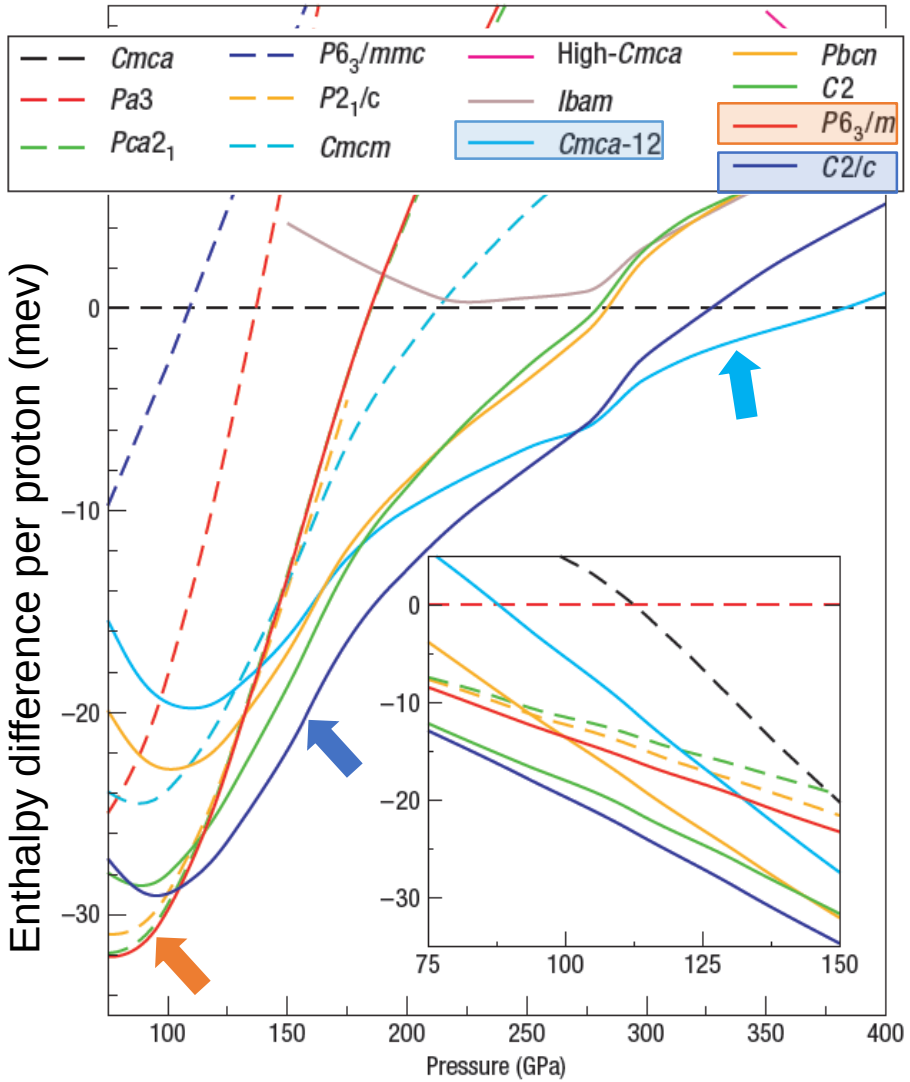

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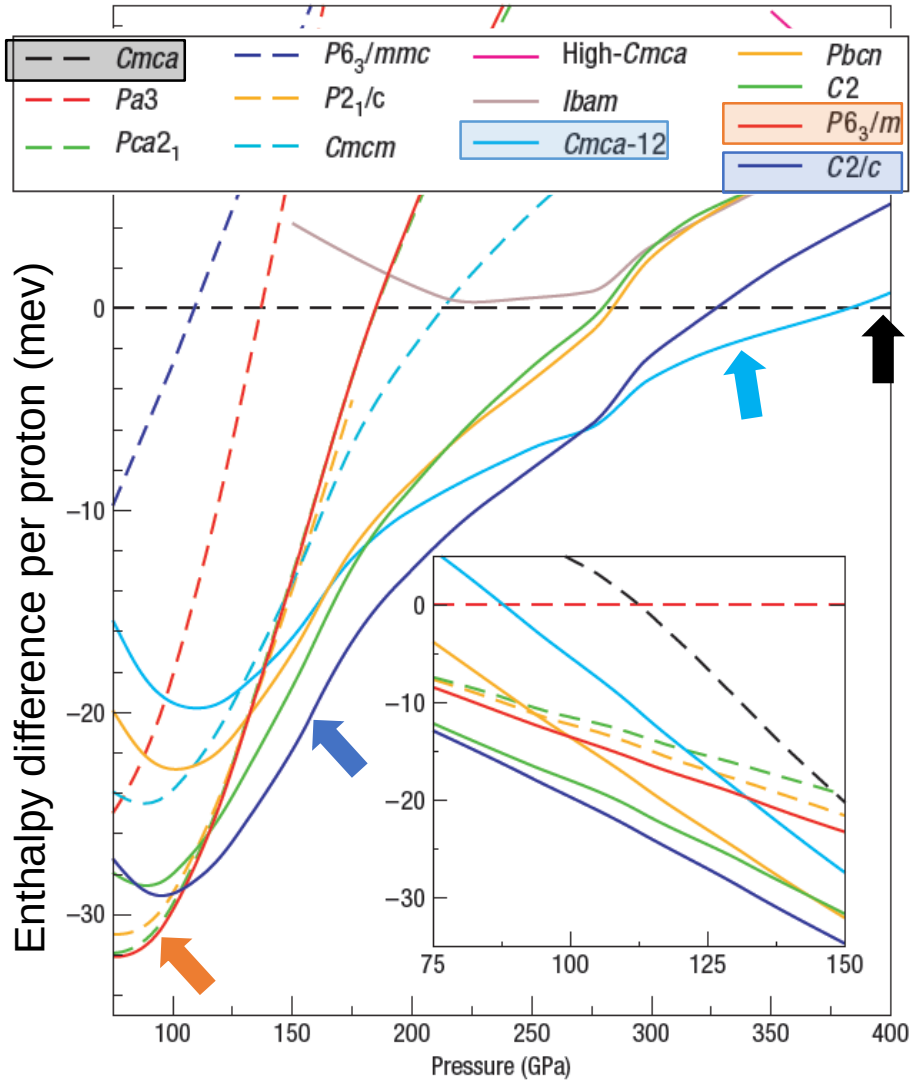

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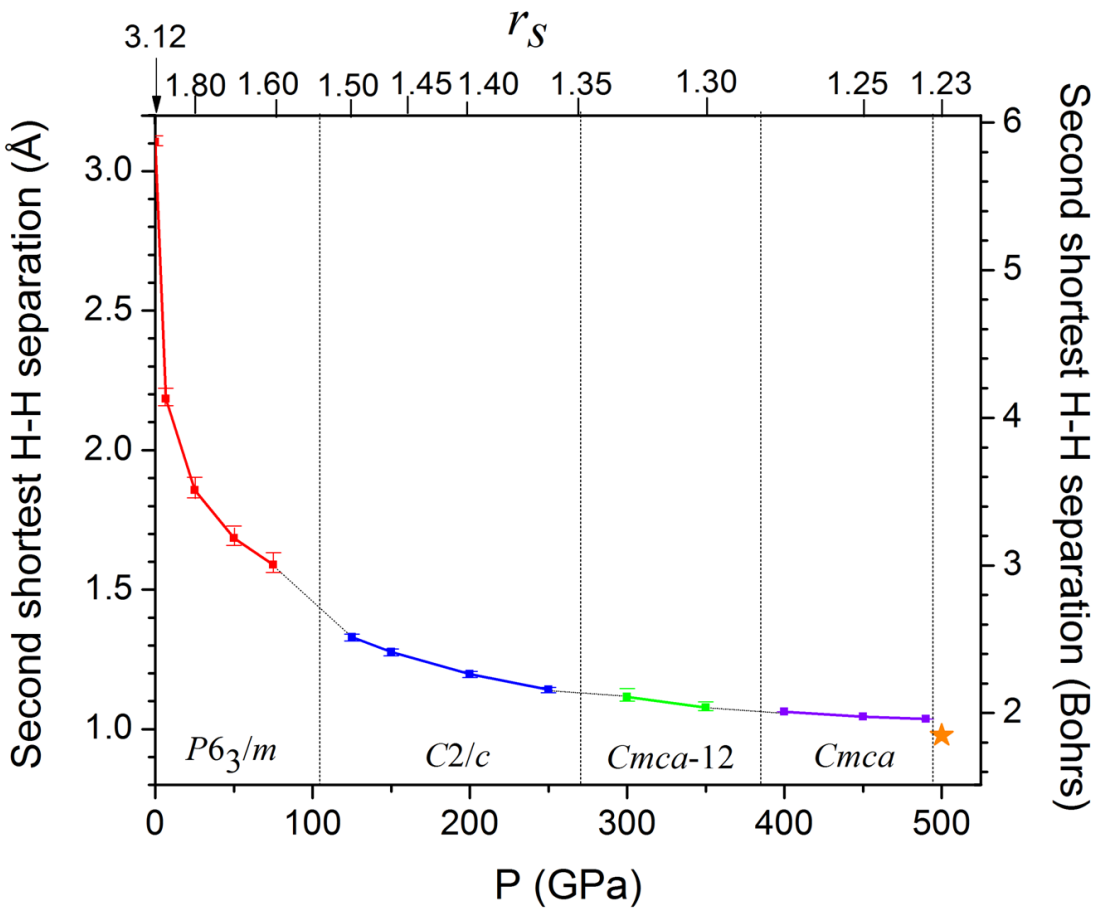
- Use of numerical simulation coupled to evolurionary algorithms to propose structural models
  - Many structures very close in enthalpy
  - Interactions responsible for the coesion are essentially the same
  - Essentially the same response to P ↗

C. J. Pickard and R. J. Needs, Nature Physics, 2007, 3, 473

Inter- and intramolecular H-H separations

Intermolecular



Labet, Gonzalez-Morelos, Hoffmann, Ashcorft, JCP, 136, 074501 (2012)

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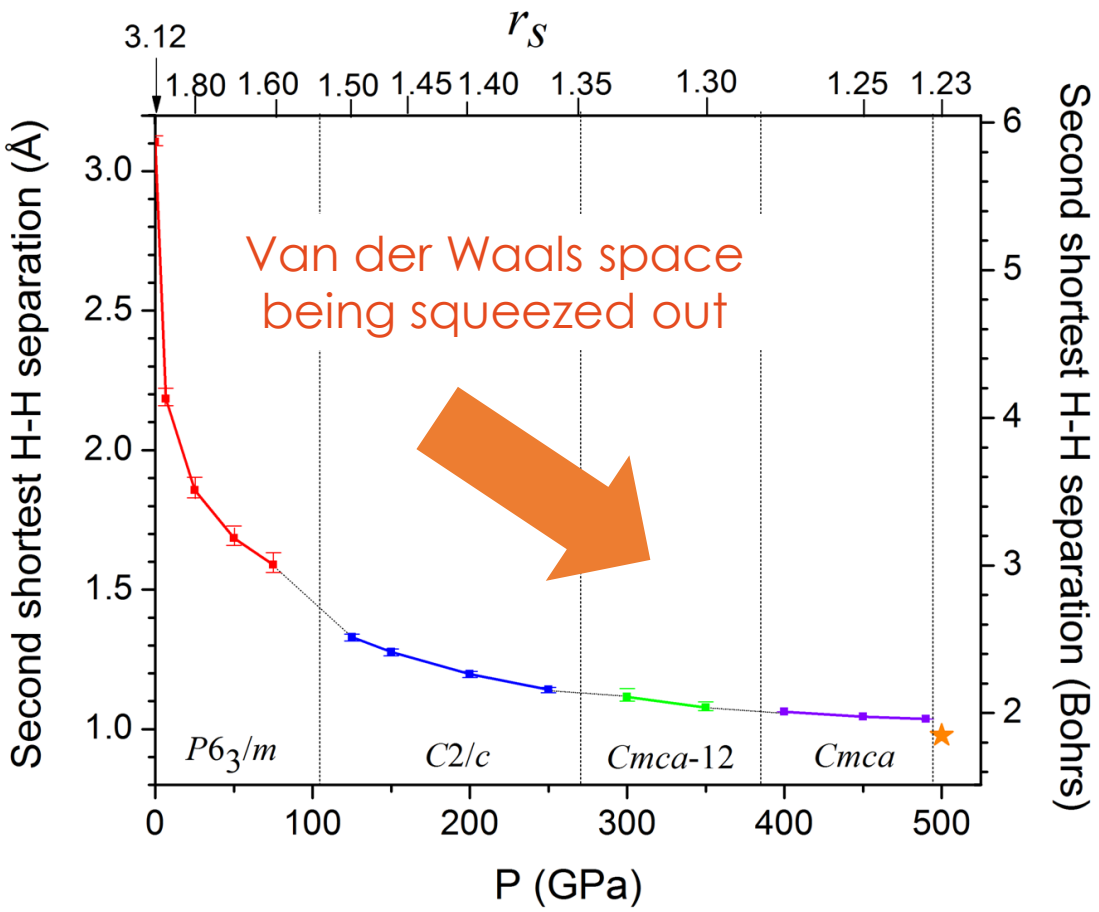

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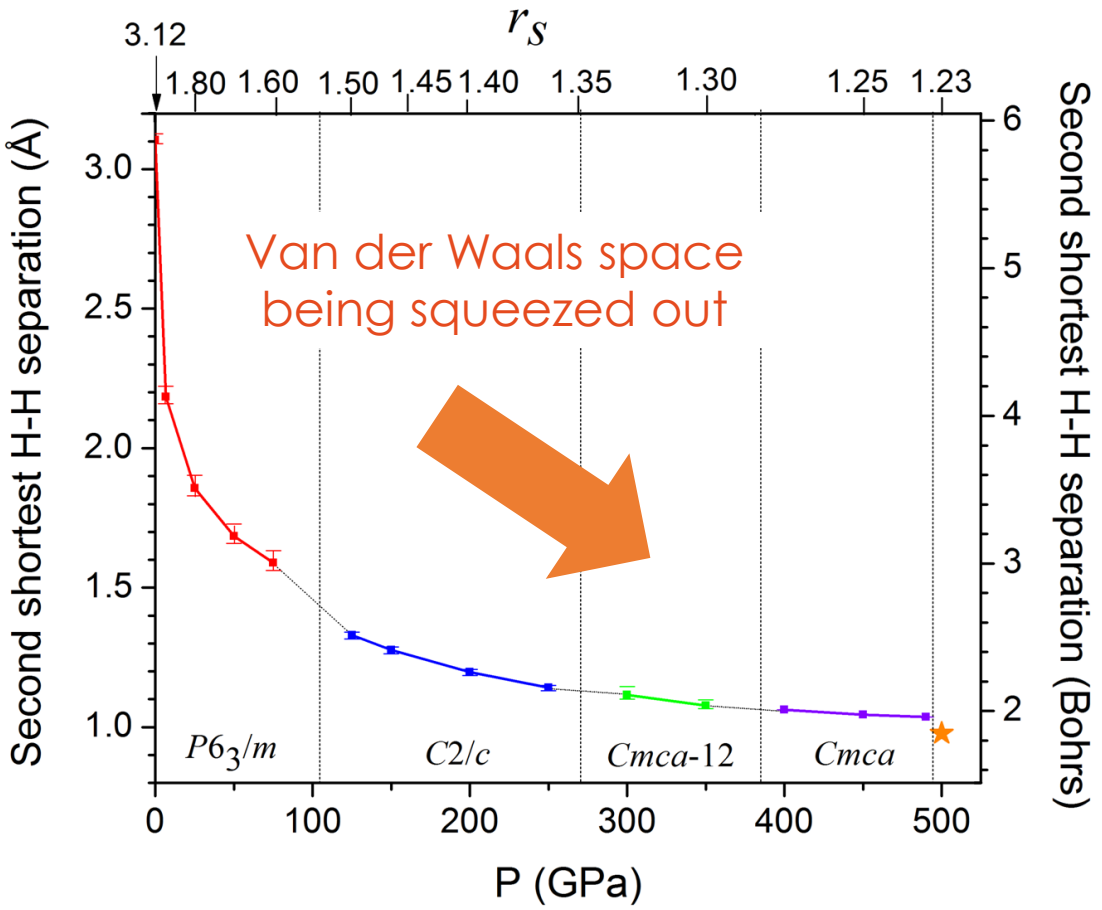
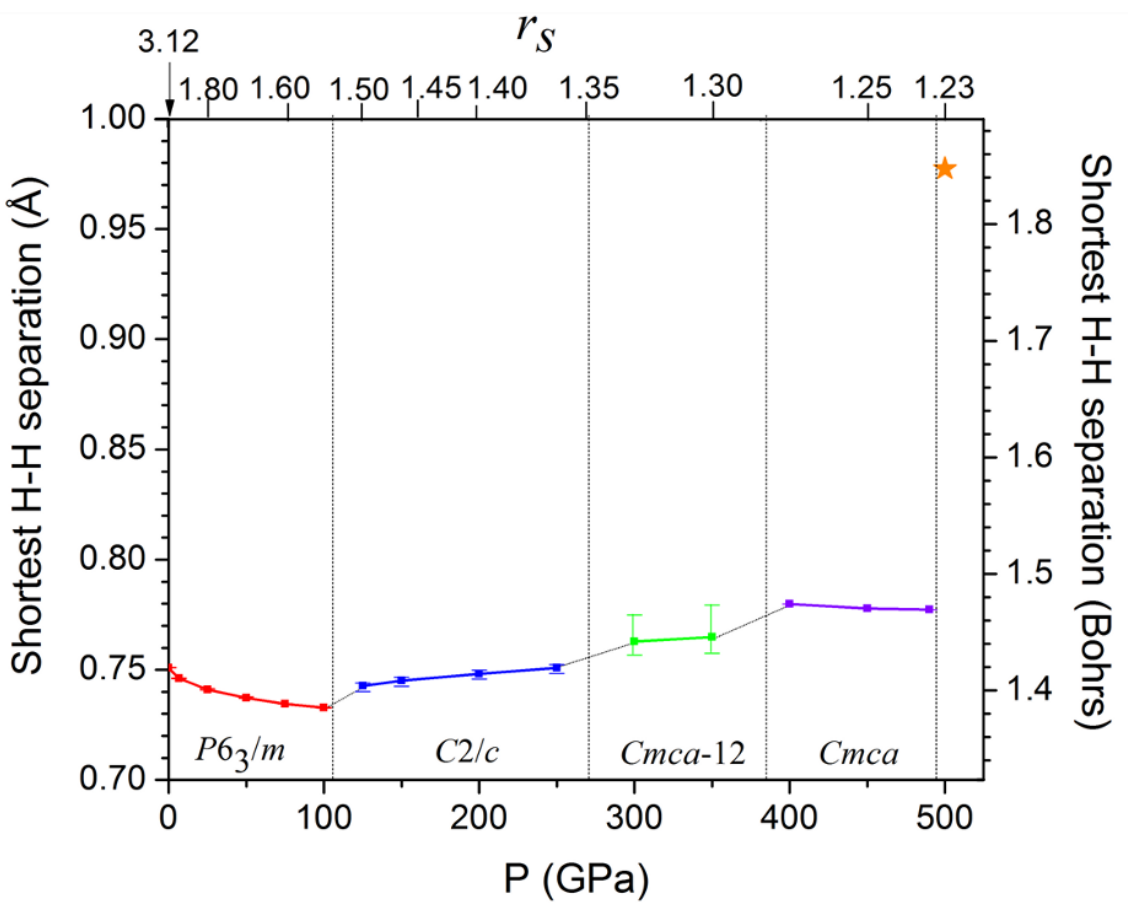


Intramolecular



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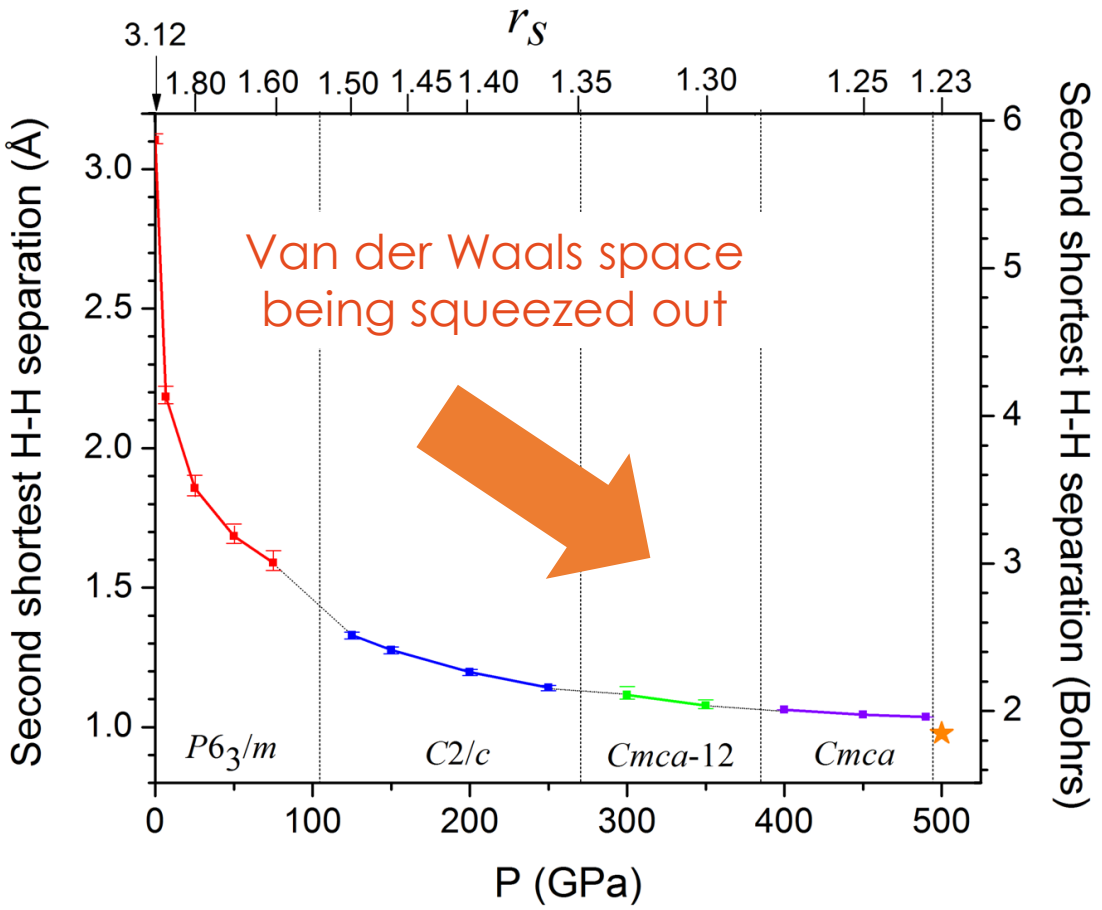

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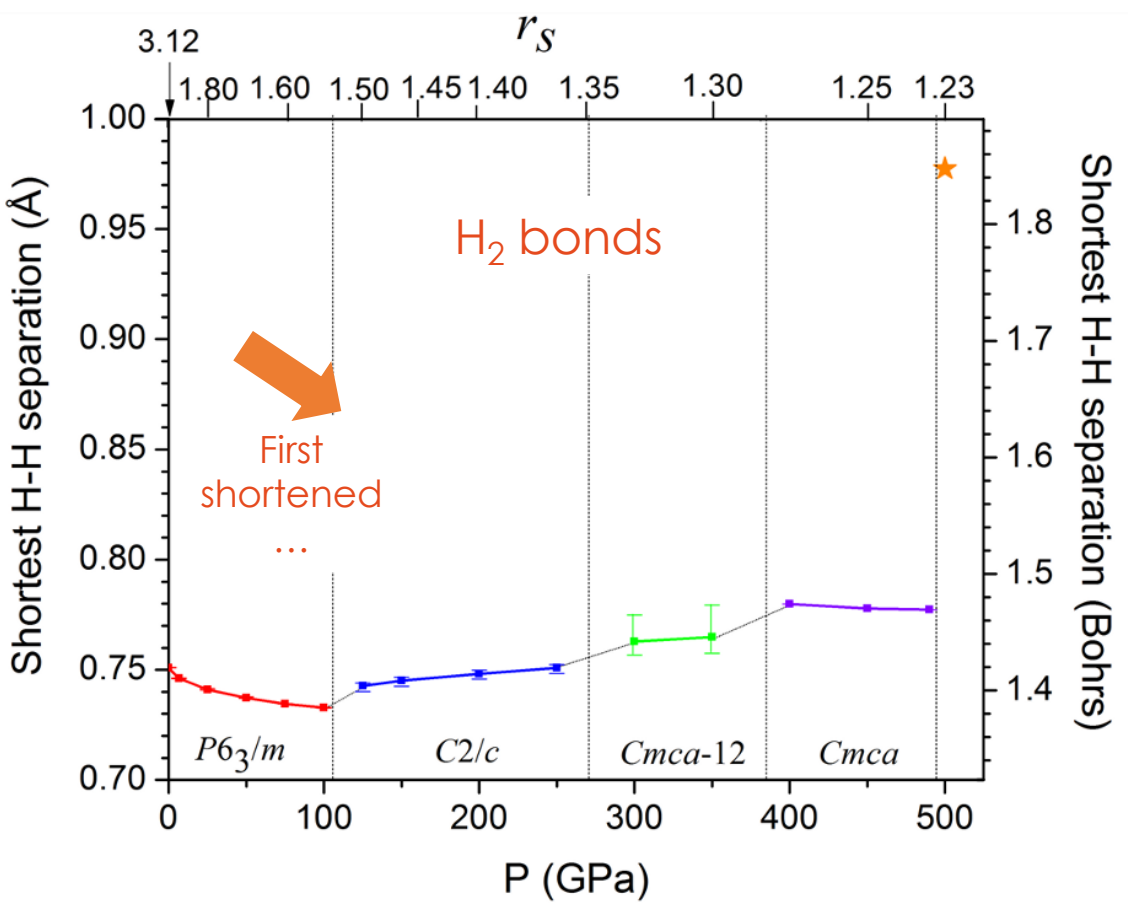

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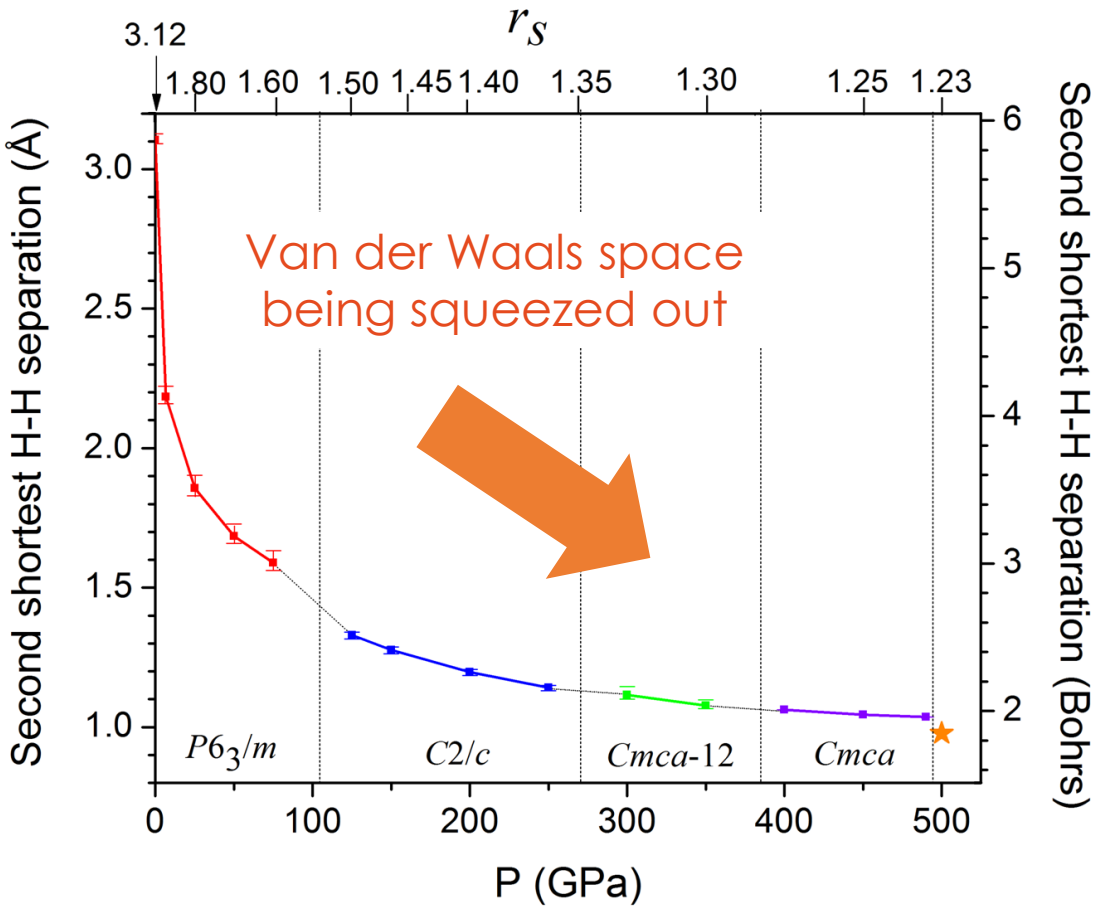
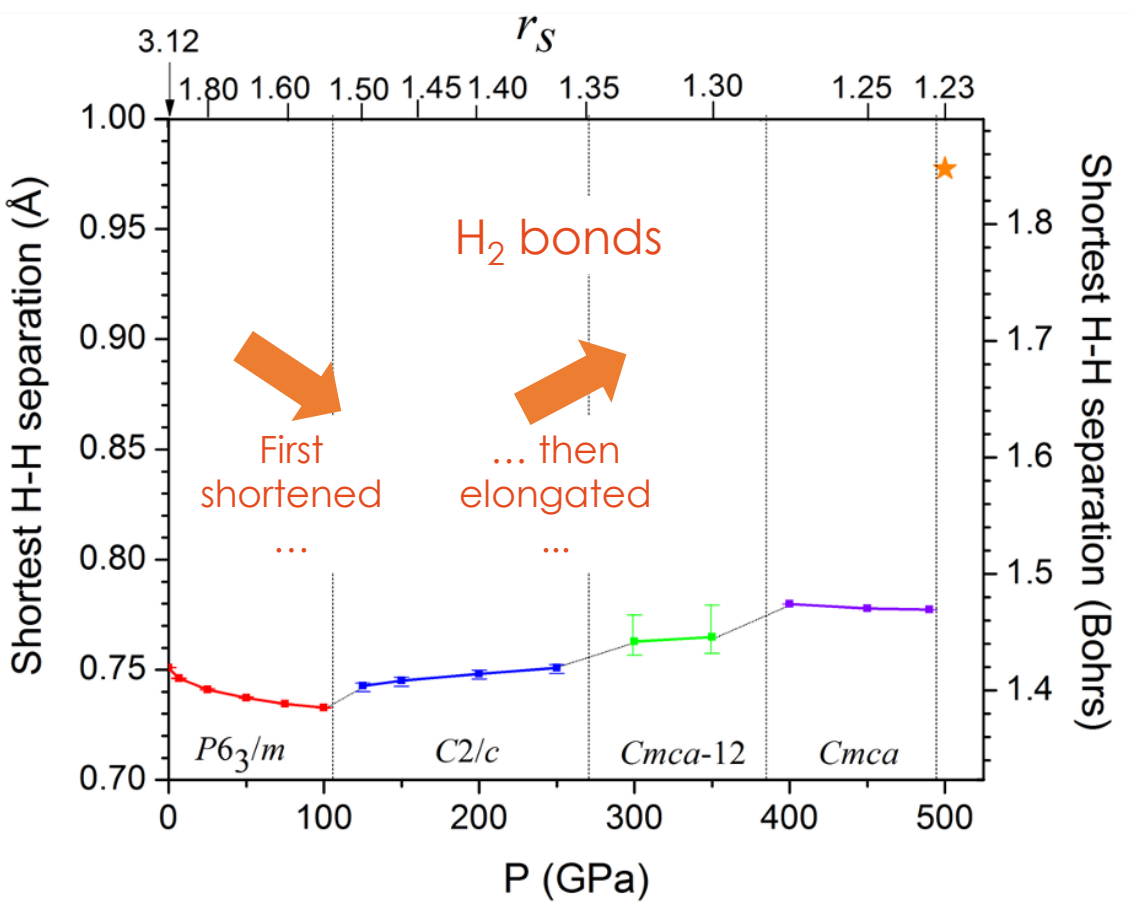


Intramolecular



Labet, Gonzalez-Morelos, Hoffmann, Ashcorft, JCP, 136, 074501 (2012)

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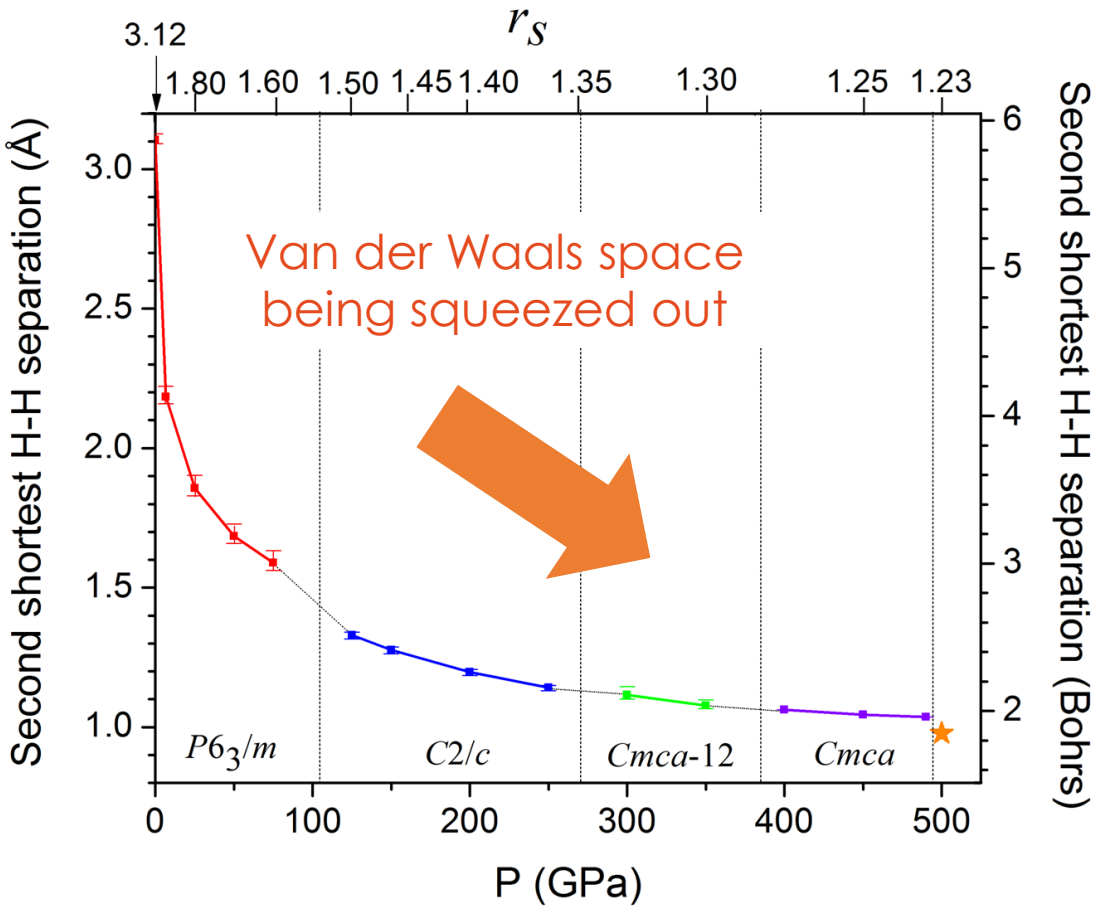
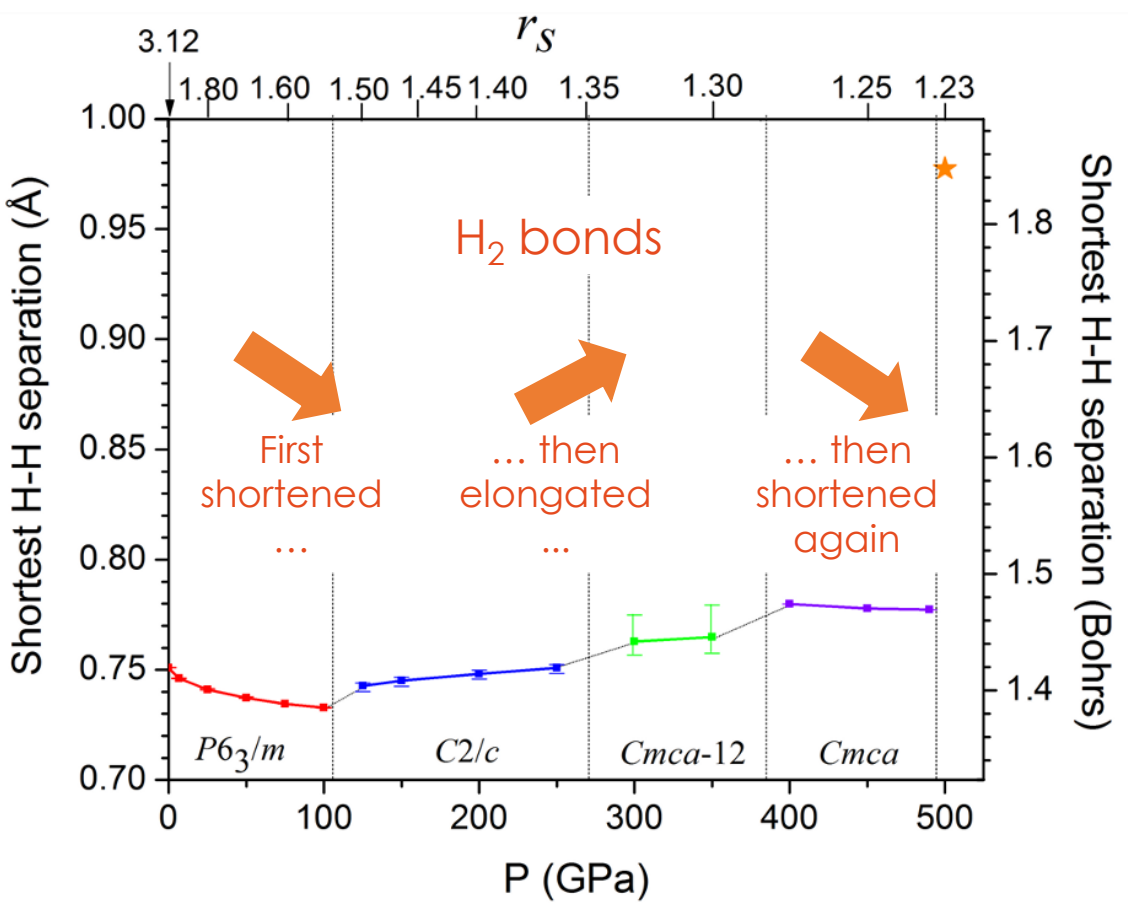


Intramolecular



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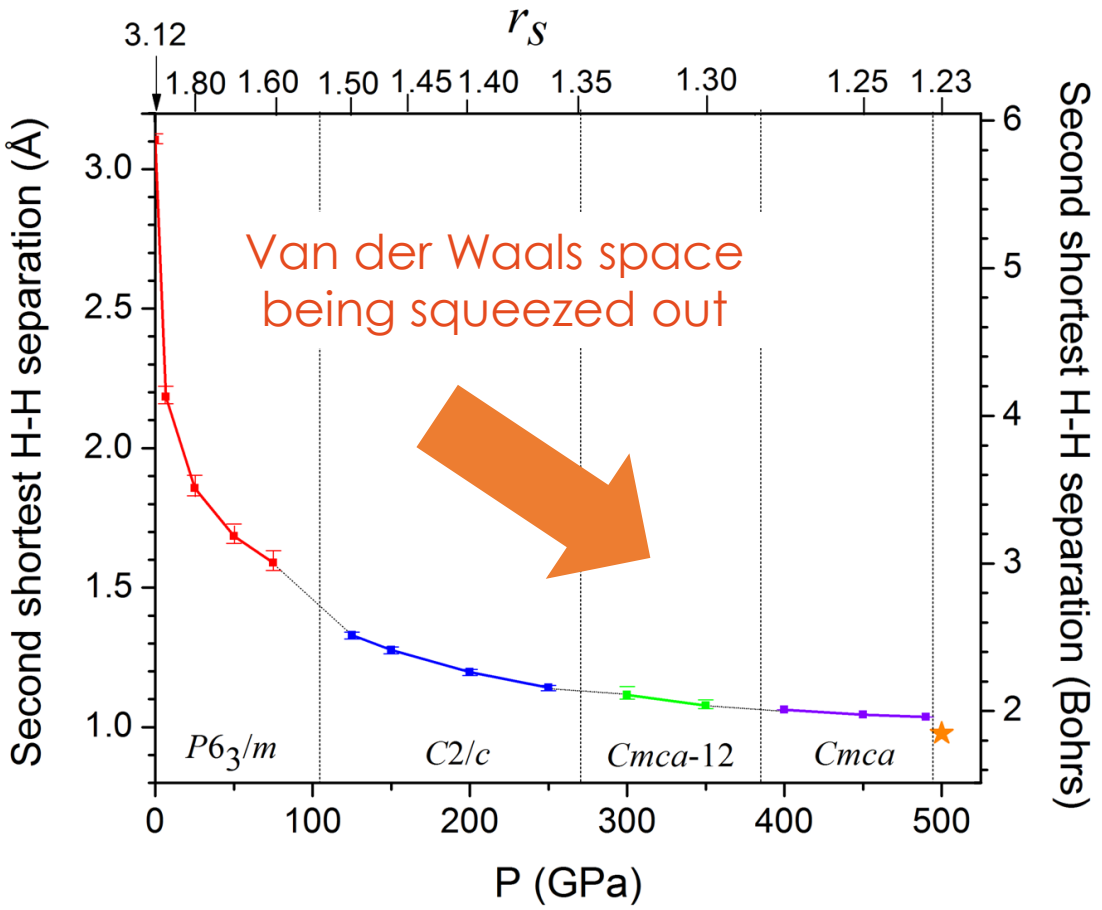

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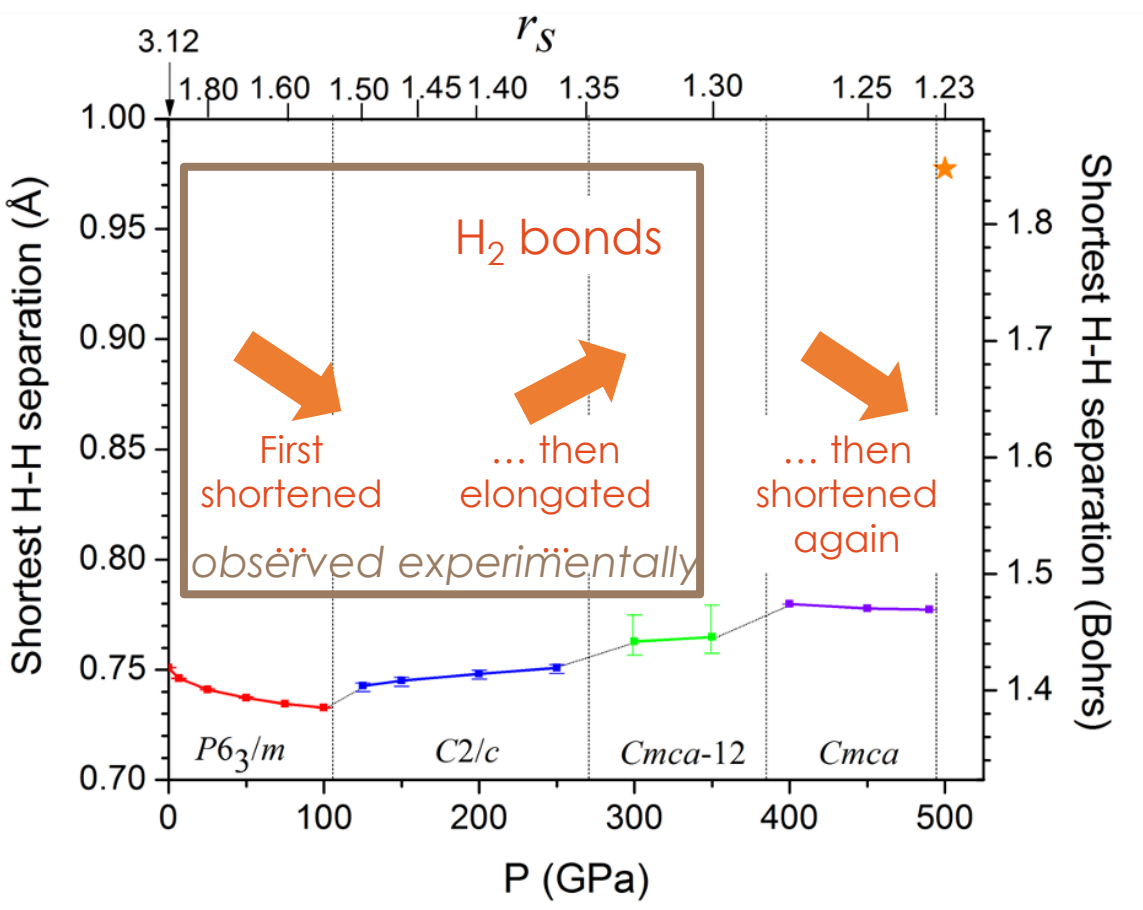
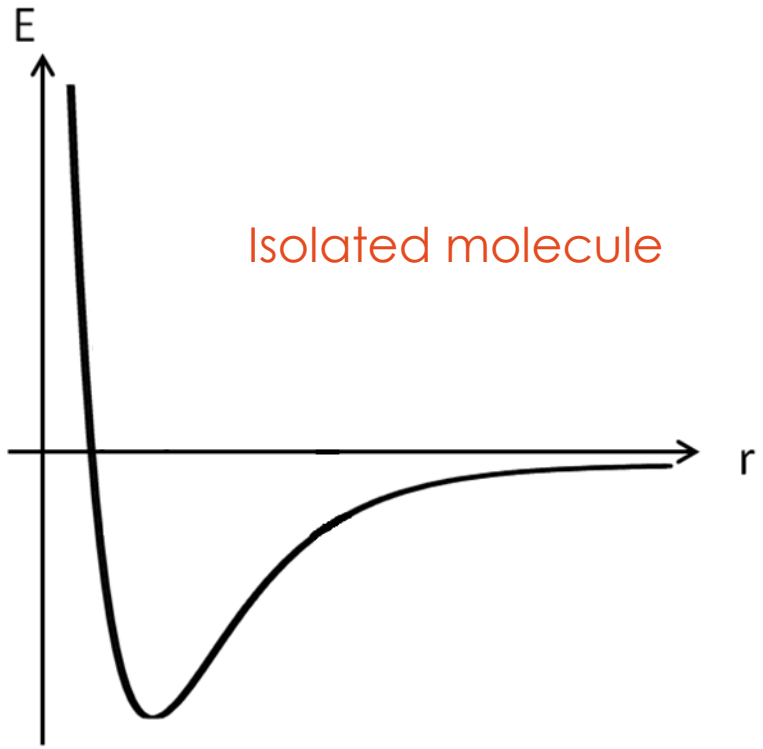


2 competing effects influencing the H_2 bond length

Bond shortening - The physical wall

Diatomic molecule

Potential Energy Curve

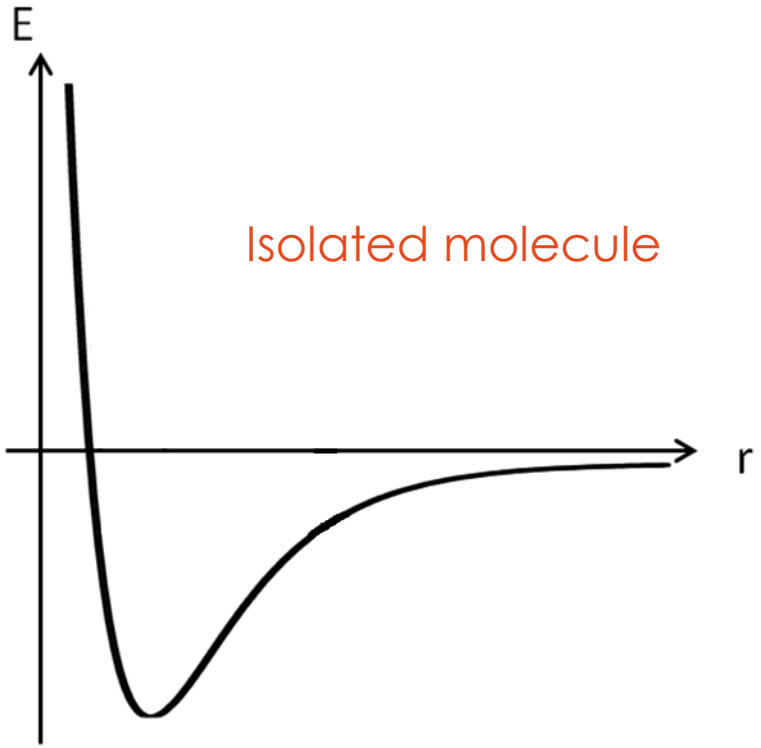


Isolated molecule

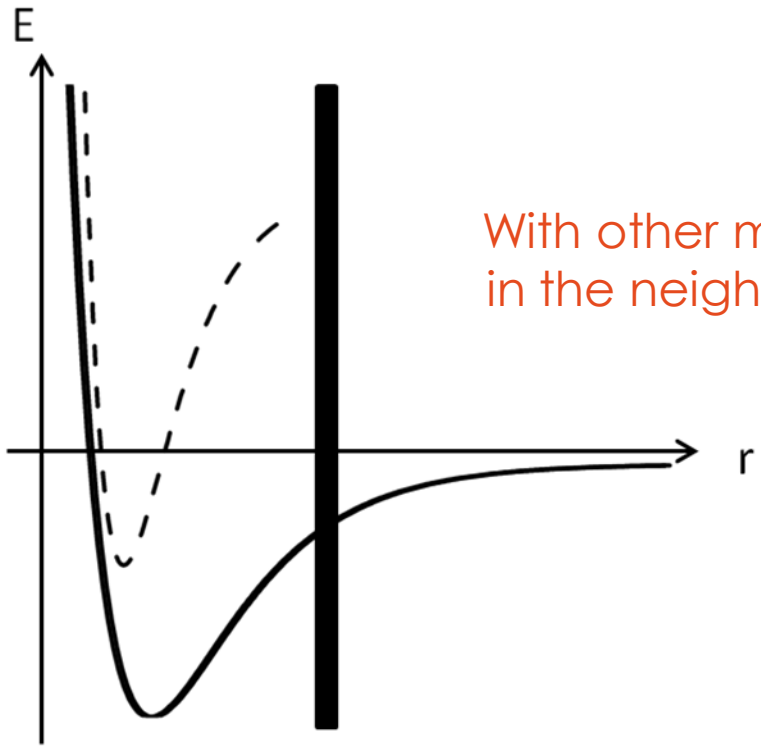
Bond shortening - The physical wall

Diatomic molecule

Potential Energy Curve

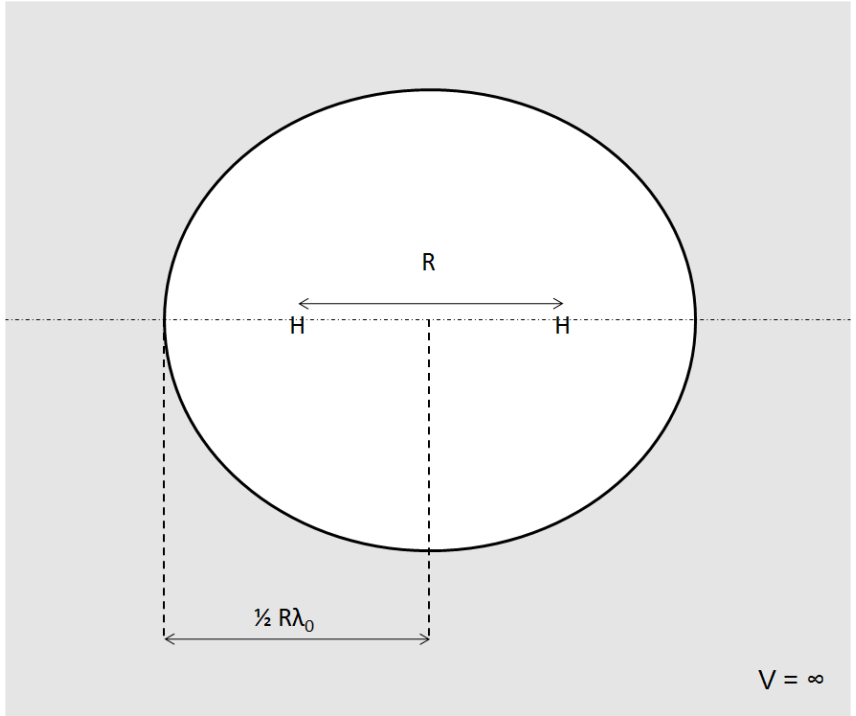


Isolated molecule



With other molecules
in the neighborhood

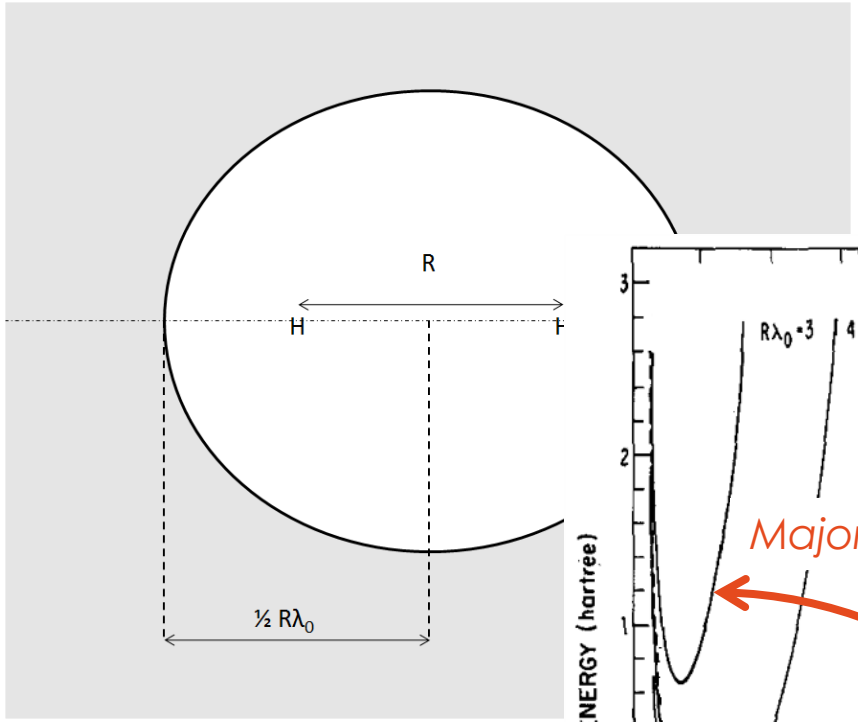
Bond shortening - The physical wall



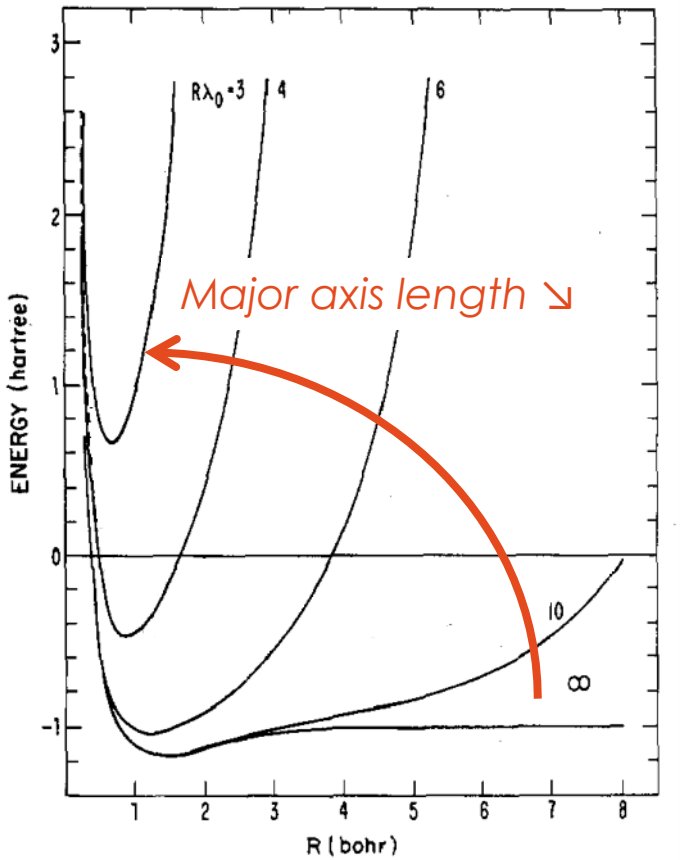
H_2 molecule in a spheroidal box

LeSar & Herschbach, J. Phys. Chem 85, 2798 (1981)

Bond shortening - The physical wall



H_2 molecule in a spheroidal box



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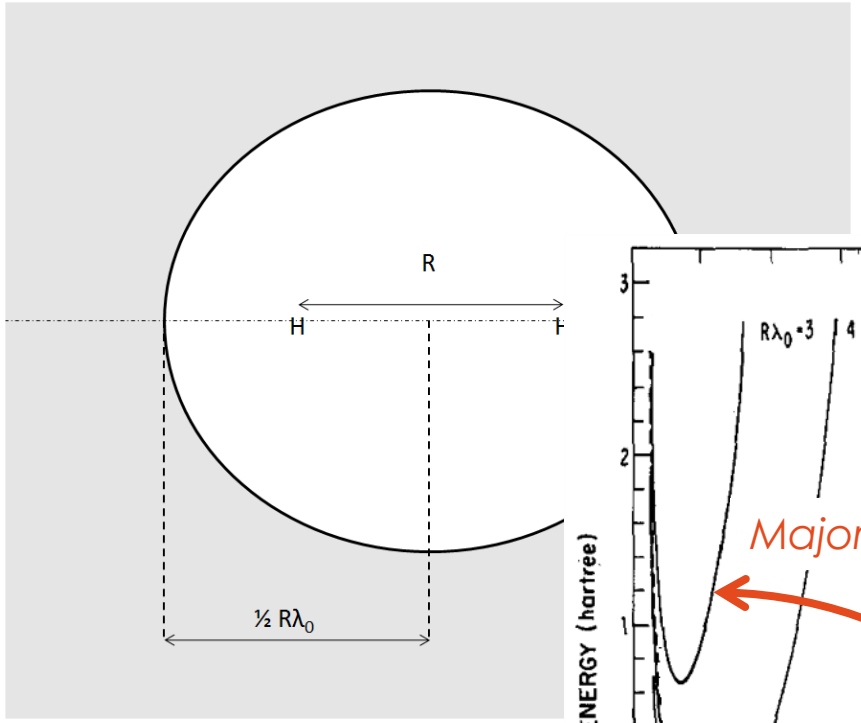

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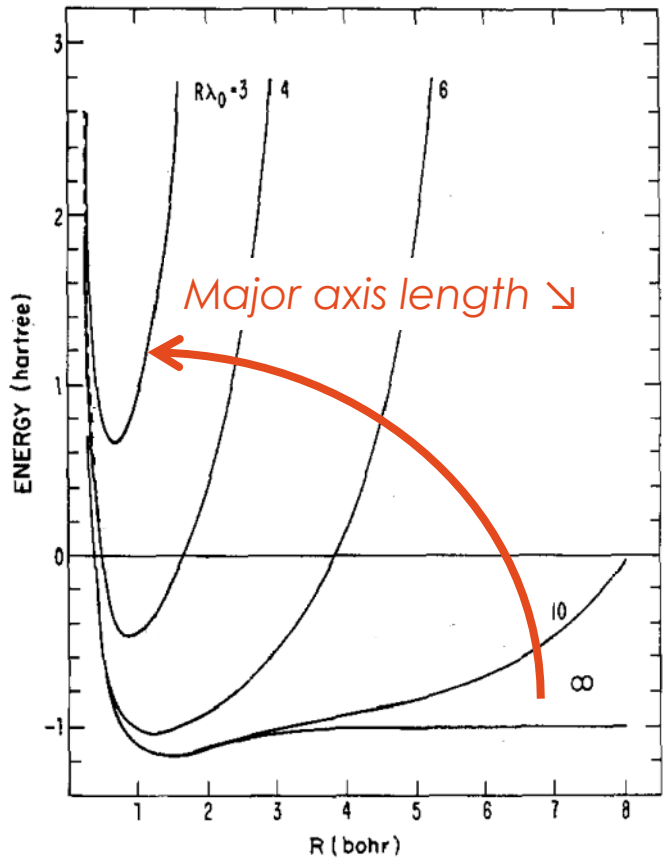

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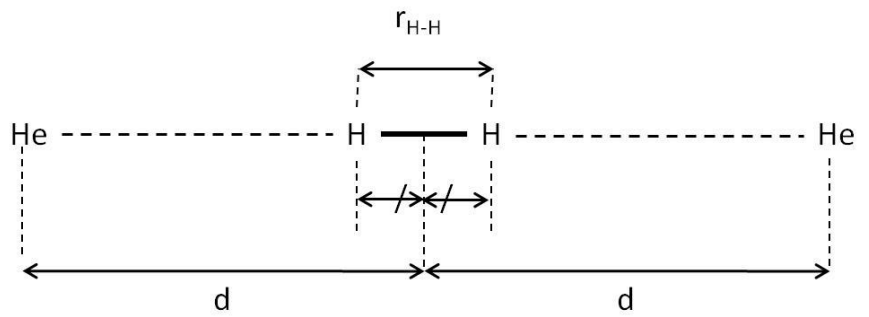
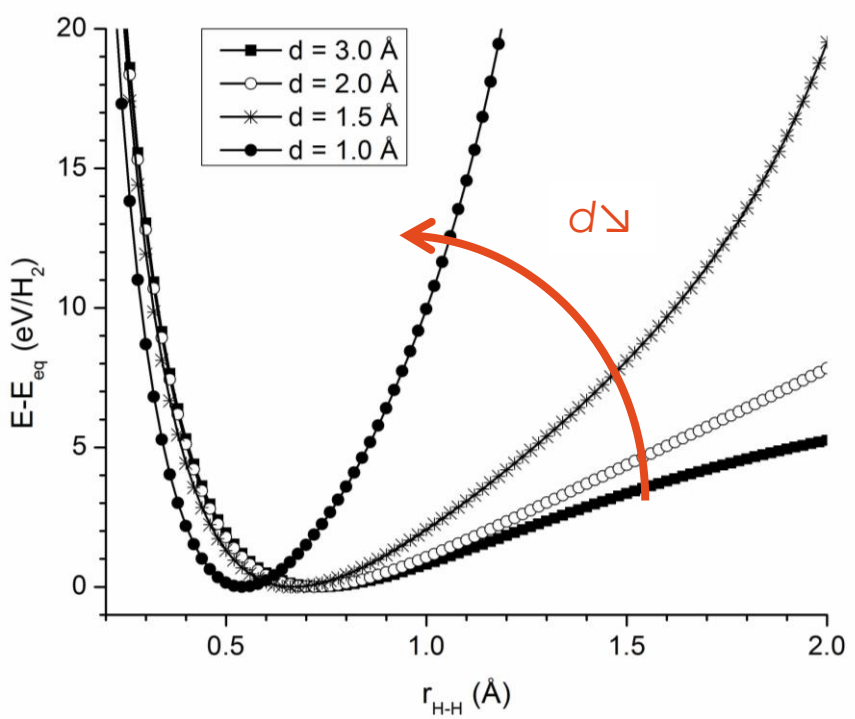
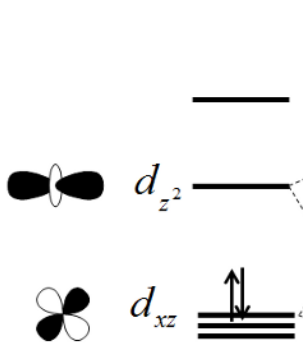


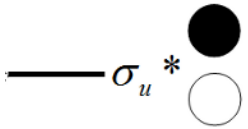
H_2 molecule between 2 He atoms

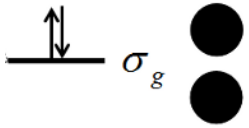


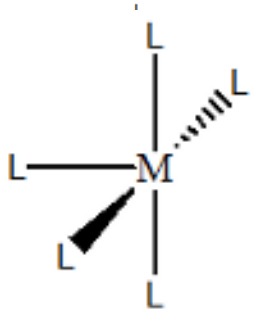
Labet, Hoffmann, Ashcorft, JCP, 136, 074502 (2012)

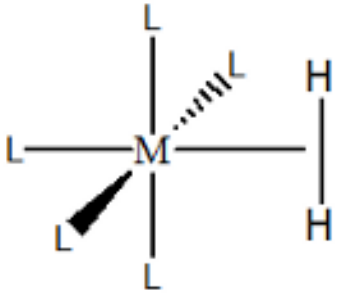
Bond lengthening – Orbital mixing

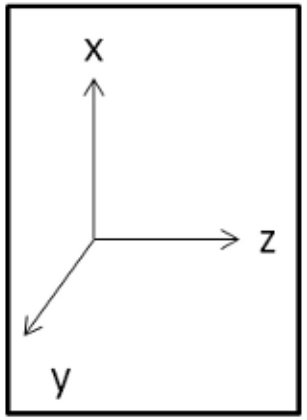












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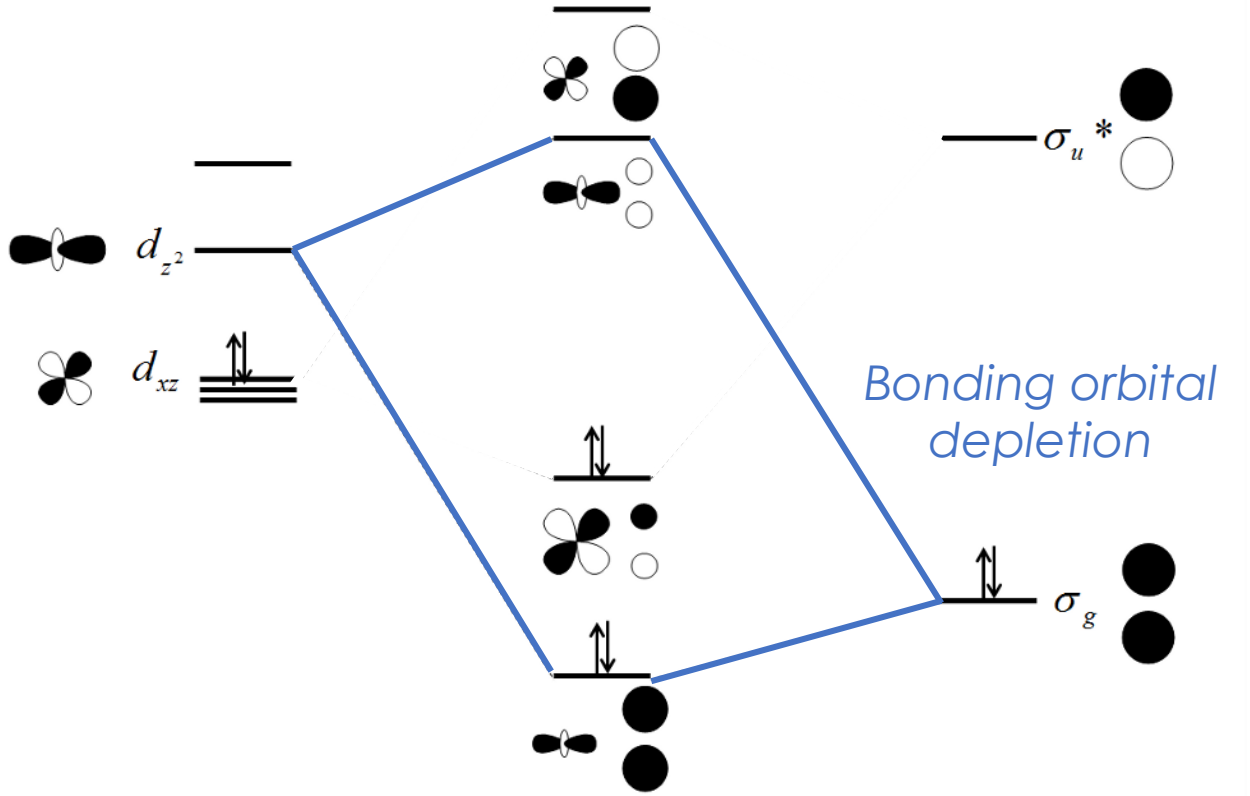

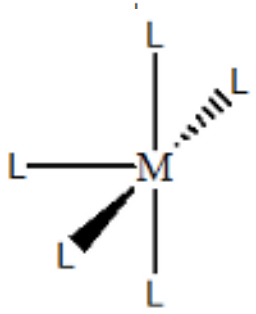

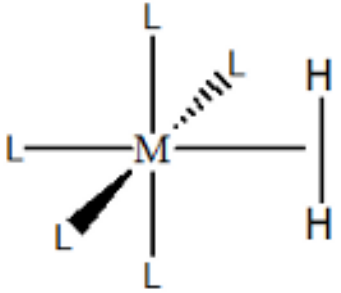

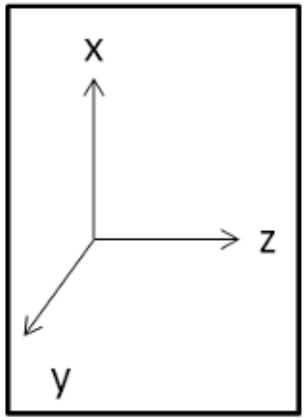

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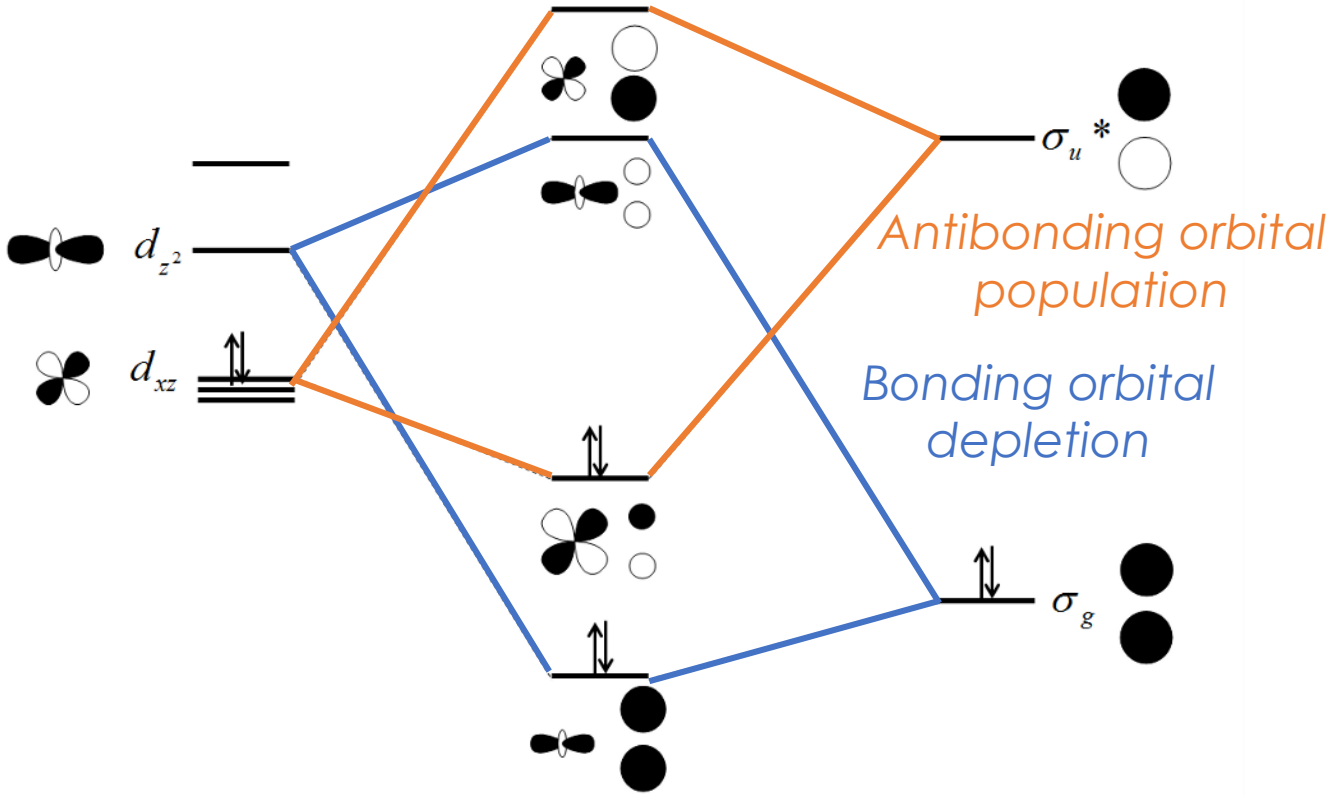

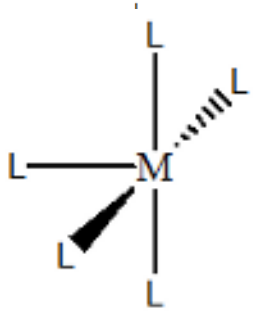

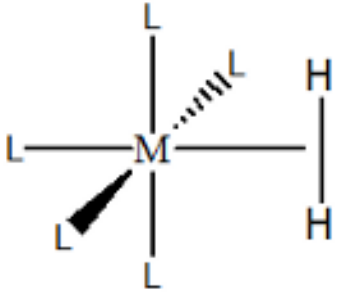

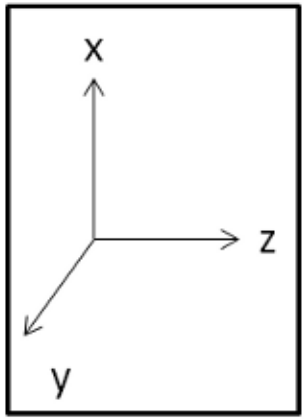

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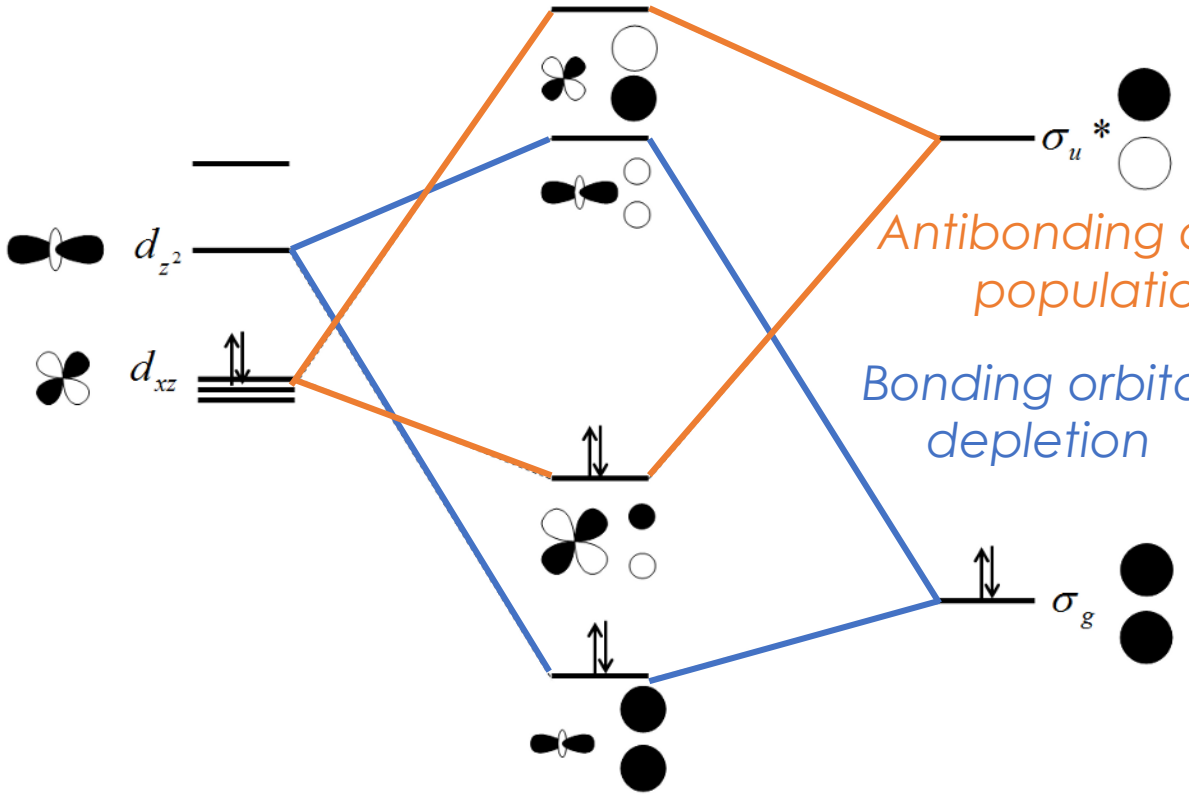


Kubas complexes

Antibonding orbital population

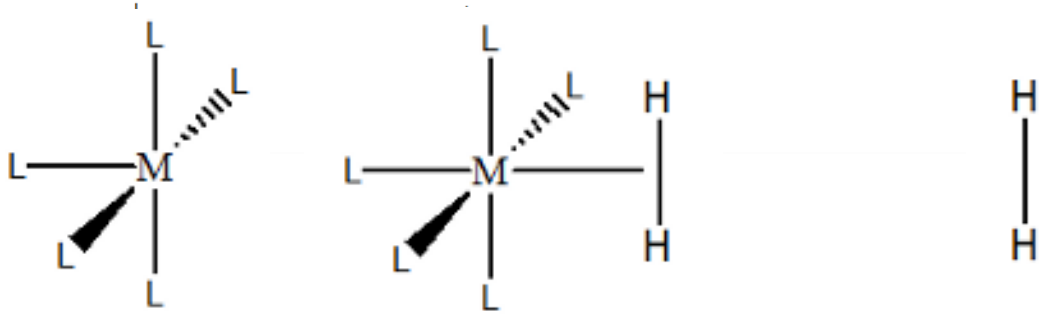
Bonding orbital depletion

electron transfer from σ_g to σ_U*

via the ML_n fragment

↓

H-H bond elongation



Bond lengthening – Orbital mixing

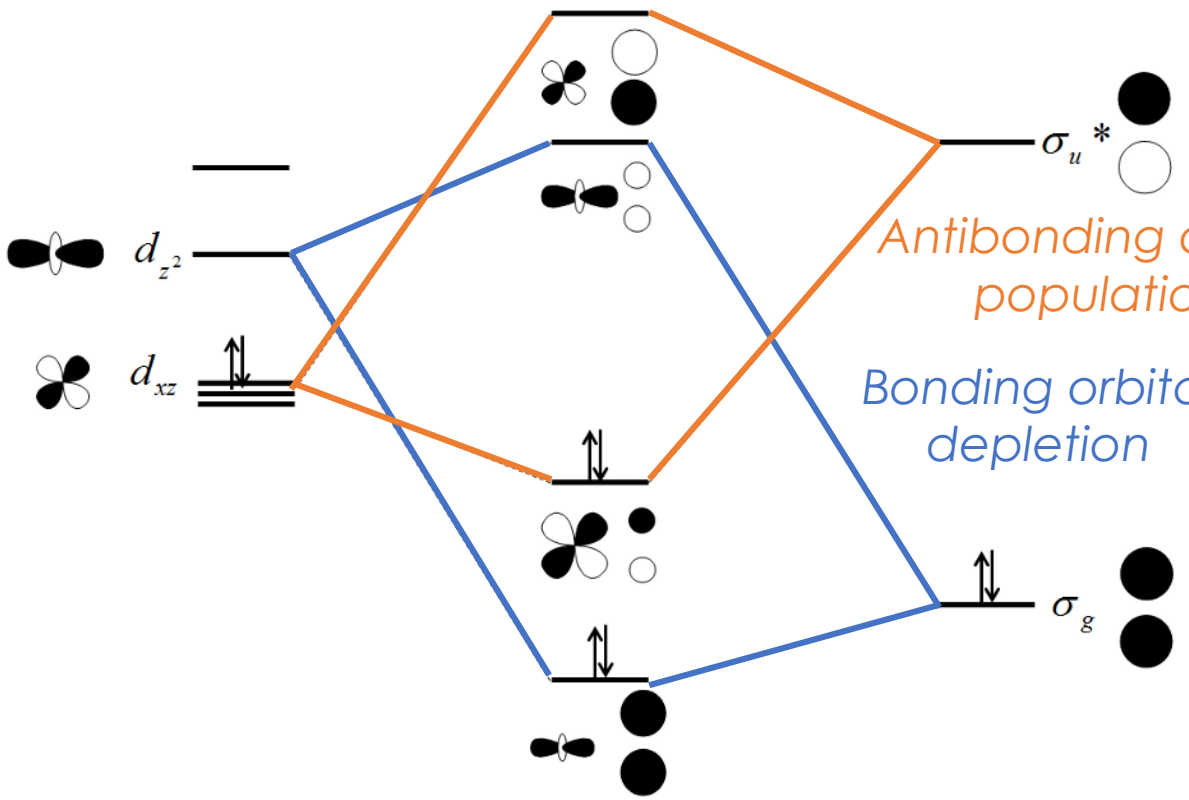
Solid H under Pressure

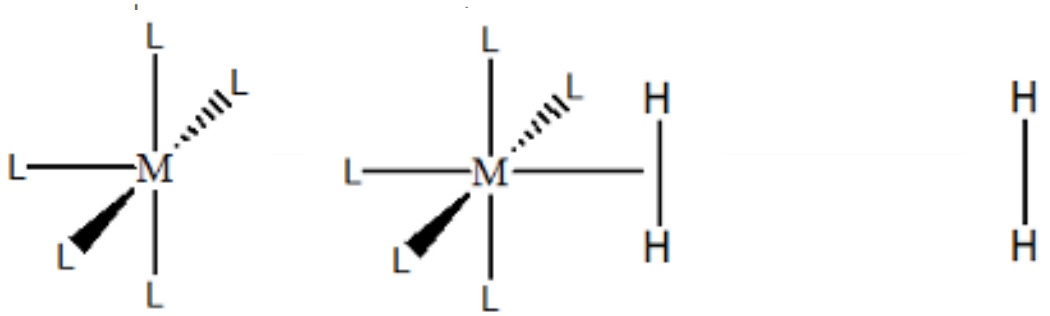
electron transfer from σ_g to σ_u*

via other H_2 mol. coming closer and closer

↓

H-H bond elongation





Kubas complexes

electron transfer from σ_g to σ_u*

via the ML_n fragment

↓

H-H bond elongation

Intermediate summary

As P increases

H-H intramolecular bonds

First strengthen and shorten …

« Physical wall »

… then weaken and elongate

Orbital mixing

Intermediate summary

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What about strengthening and weakening ?

Badger's rule
(bond strength related to bond length)

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Intermediate summary

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Shortening and elongation observed numerically on periodic structural models for dense solid H

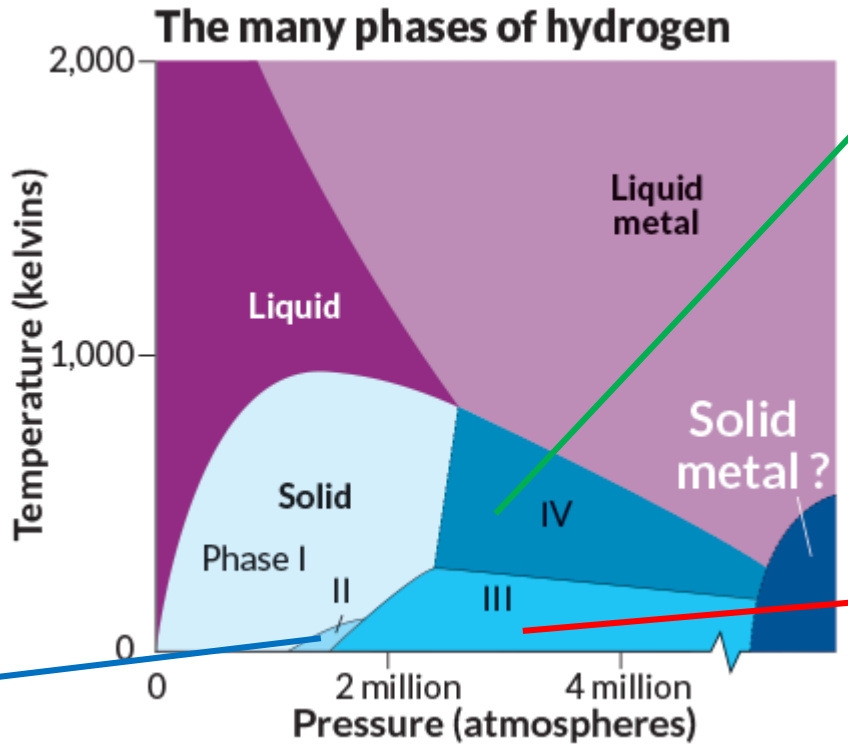
What about strengthening and weakening ?

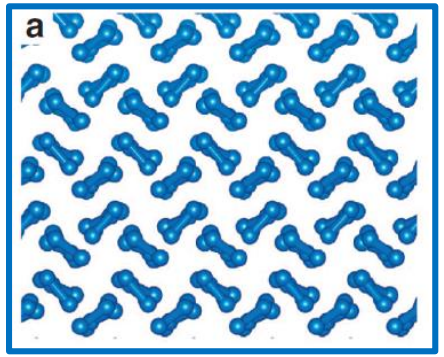
Badger's rule
(bond strength related to bond length)

Use of topological tools

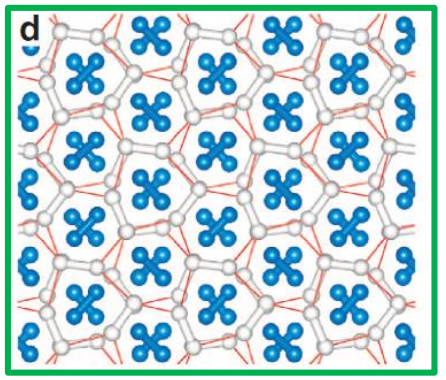
Relevance of a cluster model ?
(easier to manipulate)

Which structural model for solid H2 under pressure ?

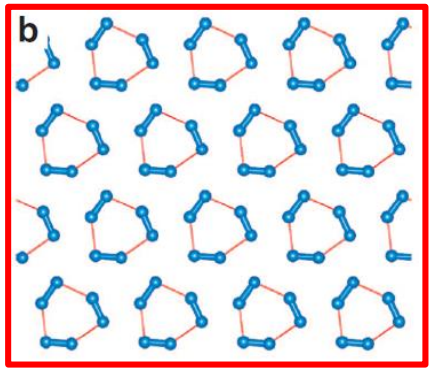




$P2_1/c$-24 models phase II



Pc-48 models phase IV

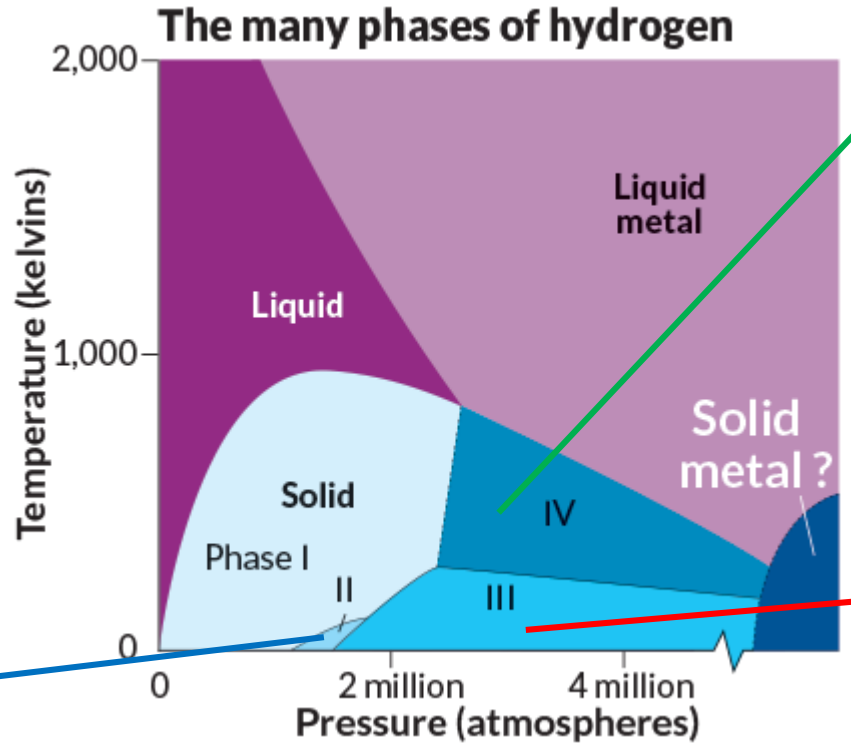


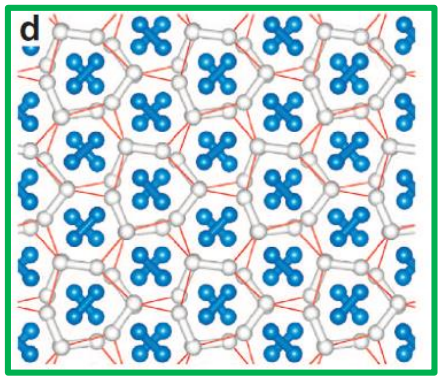
C2/c-24 models phase III

Drummond et al., Nature Communications 6, 7794 (2015)

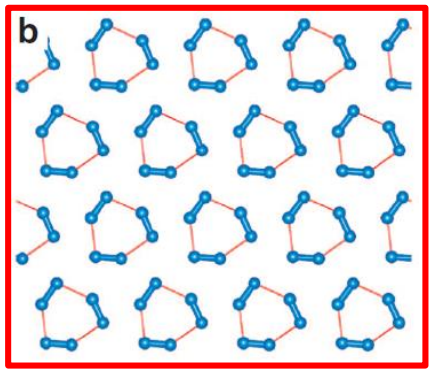
Which structural model for solid H2 under pressure ?

Distorted graphenelike layers

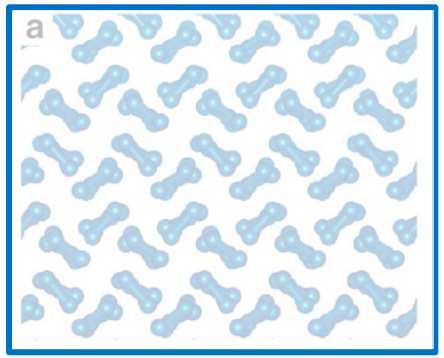




Pc-48 models phase IV



C2/c-24 models phase III



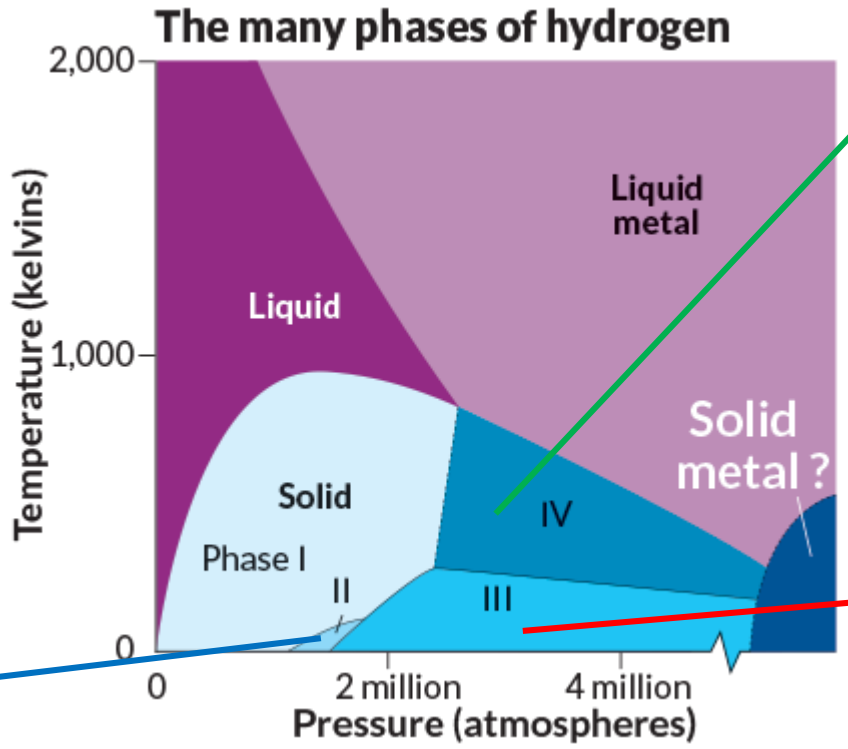
$P2_1/c$-24 models phase II

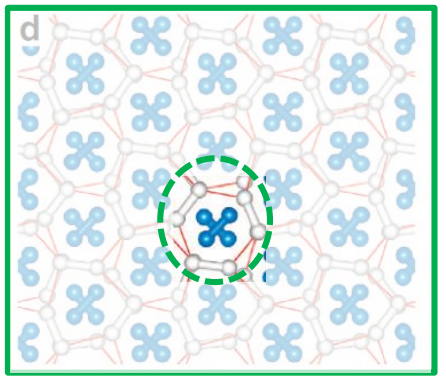
Drummond et al., Nature Communications 6, 7794 (2015)

The « 3 H_2 » motif

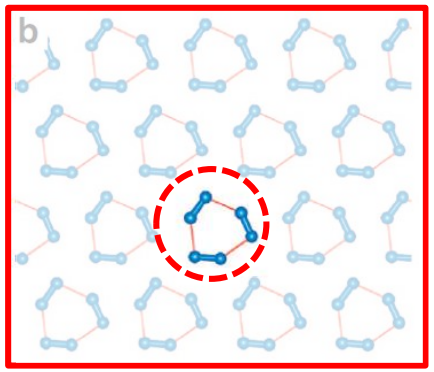
Distorted graphenelike layers

3 H_2 motif

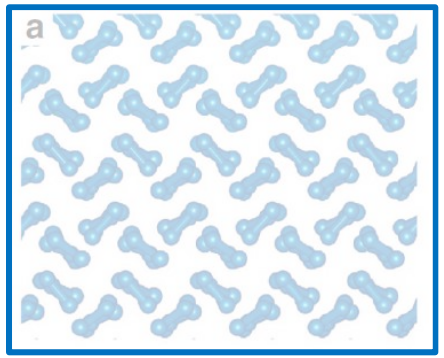




Pc-48 models phase IV



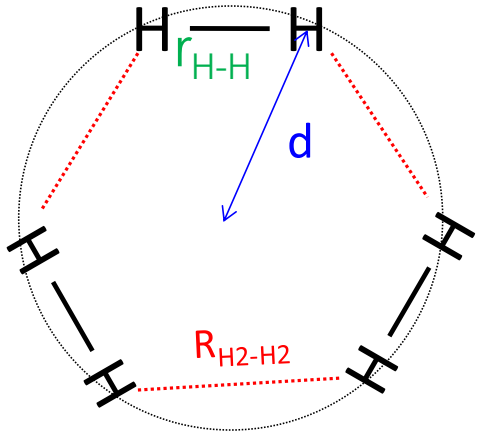
C2/c-24 models phase III



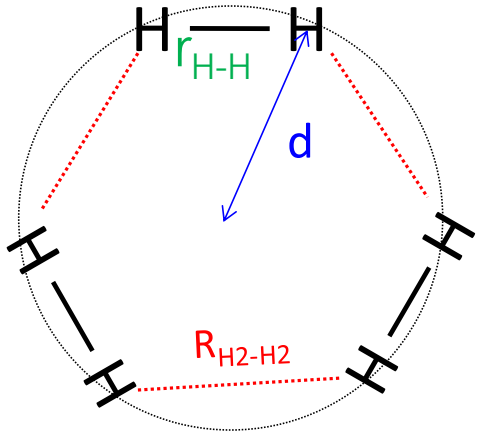
$P2_1/c$-24 models phase II

Drummond et al., Nature Communications 6, 7794 (2015)

Non-periodic model

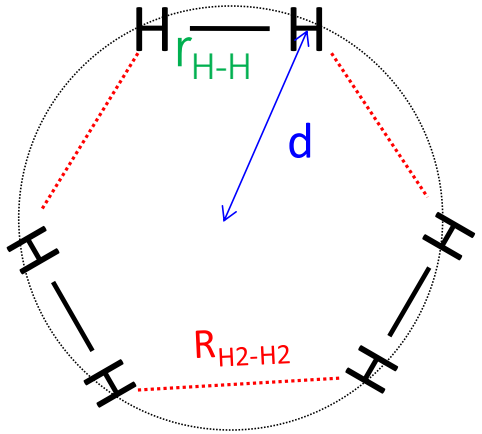


Non-periodic model



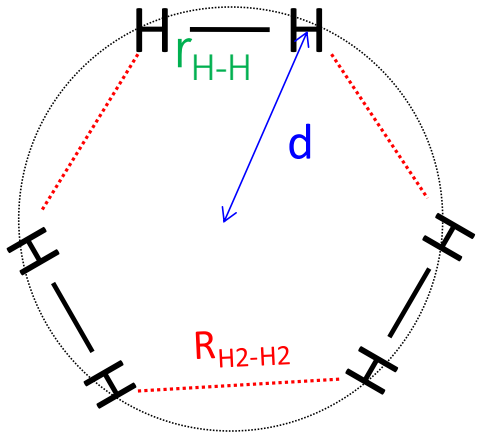
- 6 protons constrained to be on a ring of radius d

Non-periodic model



- 6 protons constrained to be on a ring of radius d
- D_{3h} symmetry imposed
  ➔ 1 degree of freedom to optimize (r_{H-H}, R_{H2-H2})

Non-periodic model



- 6 protons constrained to be on a ring of radius d
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- d ↘to model P ↗

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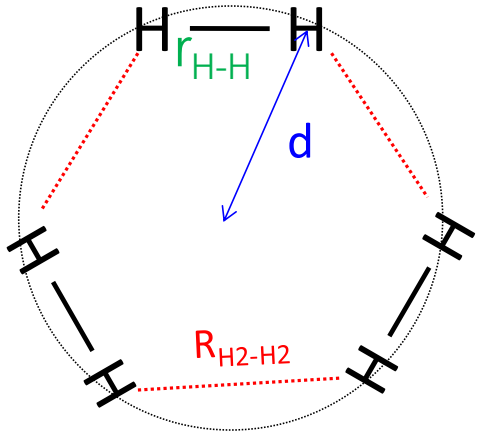

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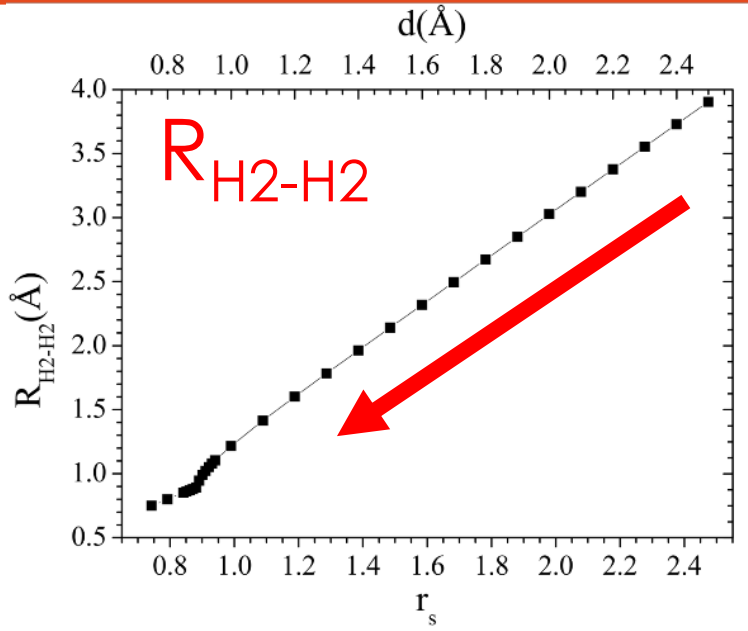
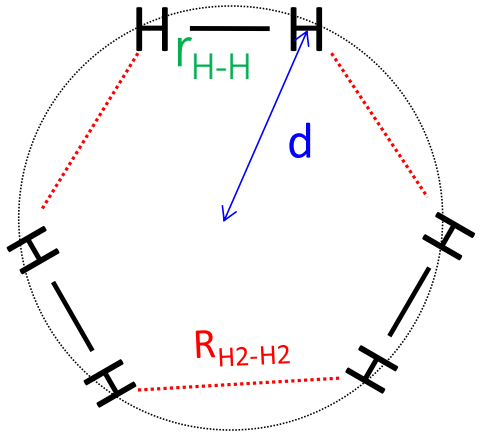


van der Waals space squeezed out

Non-periodic model



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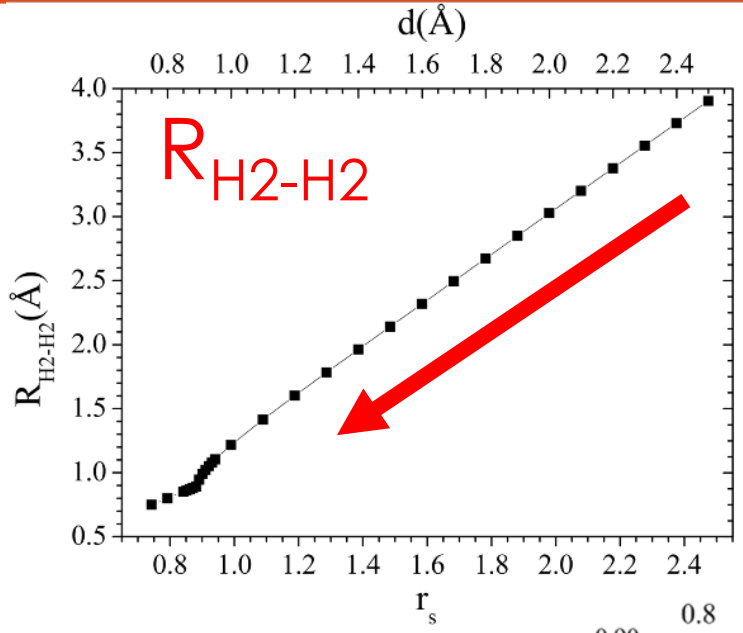
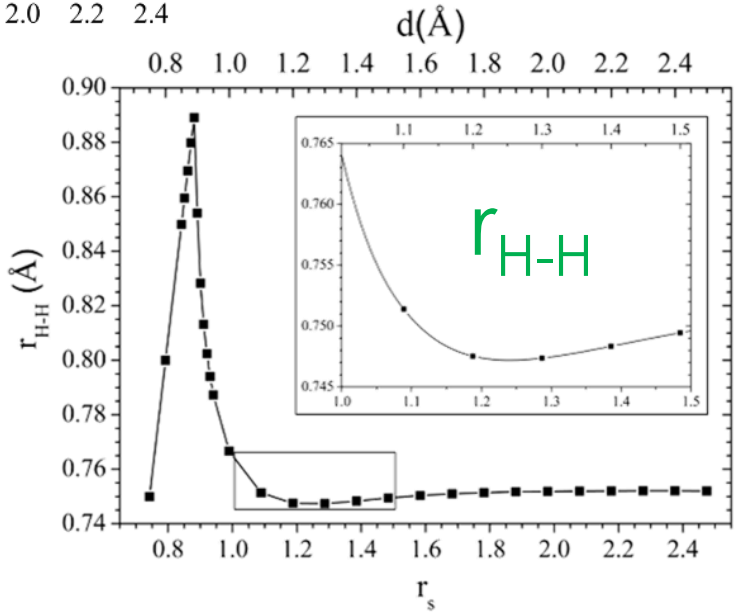


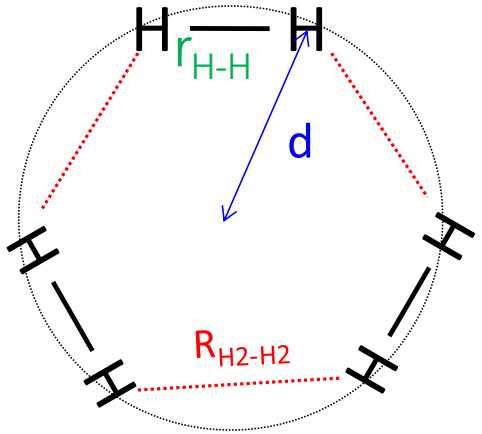
van der Waals space squeezed out

Reproduction of the non monotonous behavior of the H_2 bond length

P↗ (or d ↘)
r_{H-H} ↘ then ↗ then ↘



Non-periodic model



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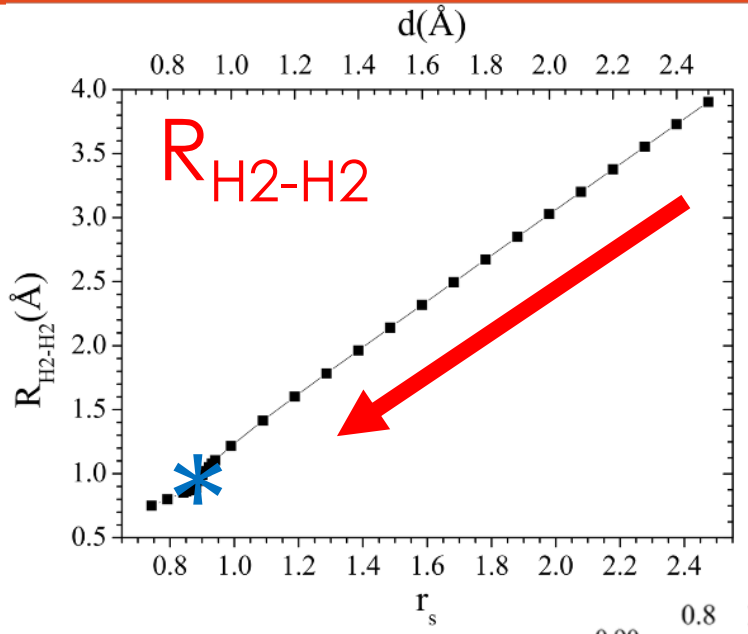

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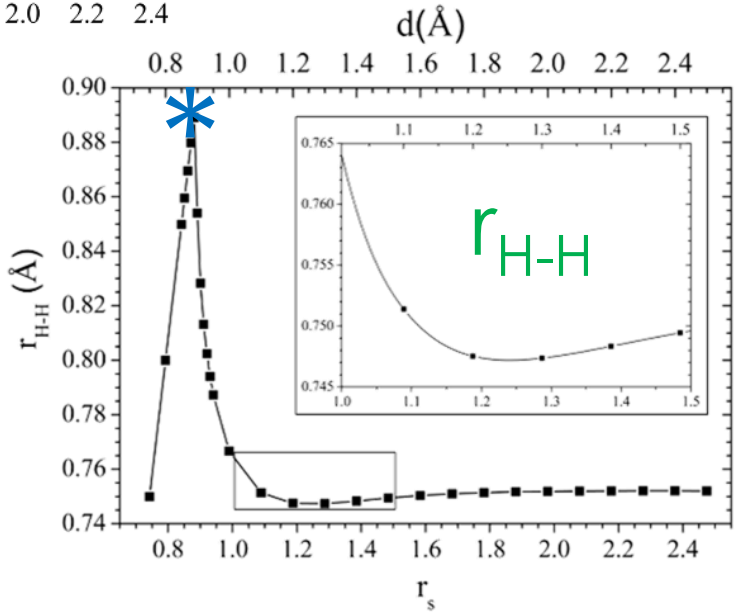

NCI index

Plotting $s = f(\rho)$

$$s = \frac{1}{C_S}\frac{|\nabla\rho|}{\rho^{4/3}}$$

Reduced gradient density

E. R. Johnson et al., J. Am. Chem. Soc., 2010, 132, 6498.

NCI index

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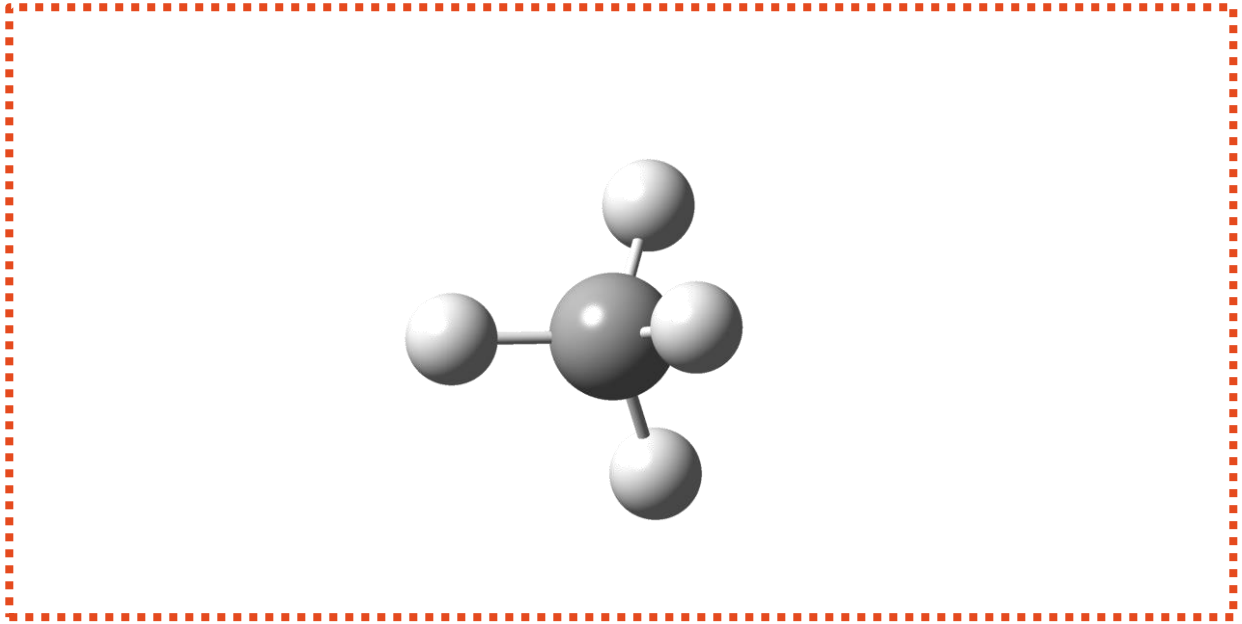

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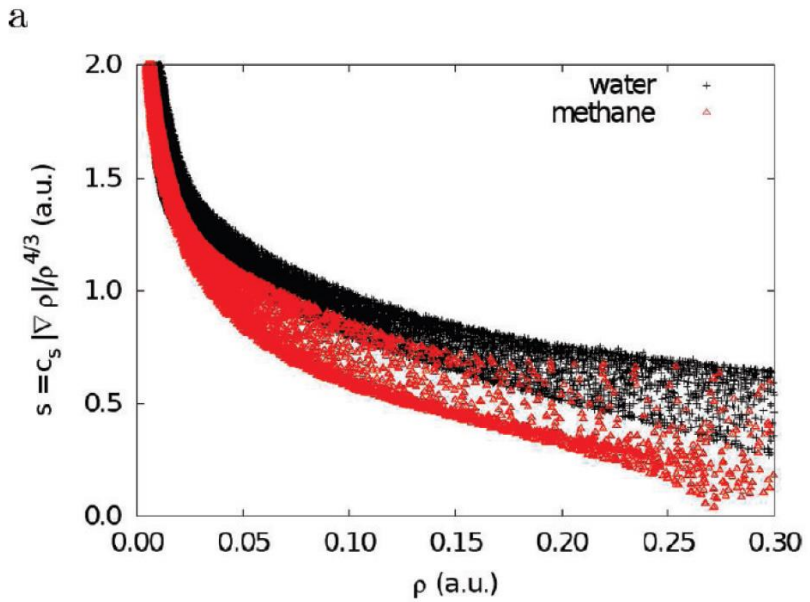

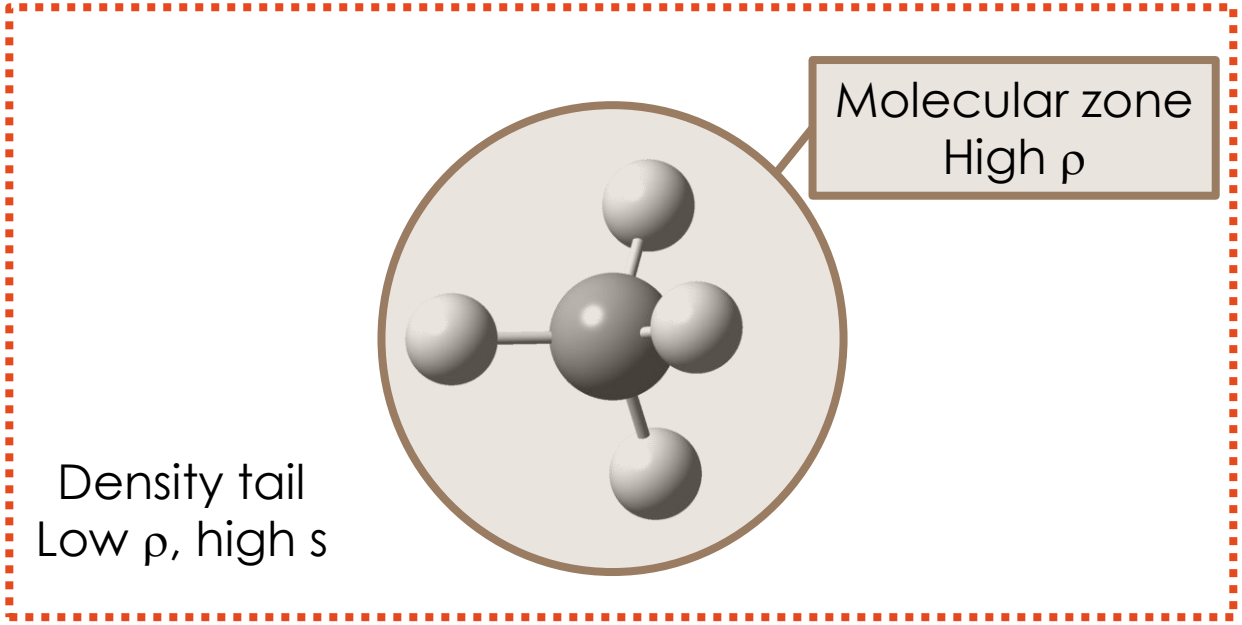

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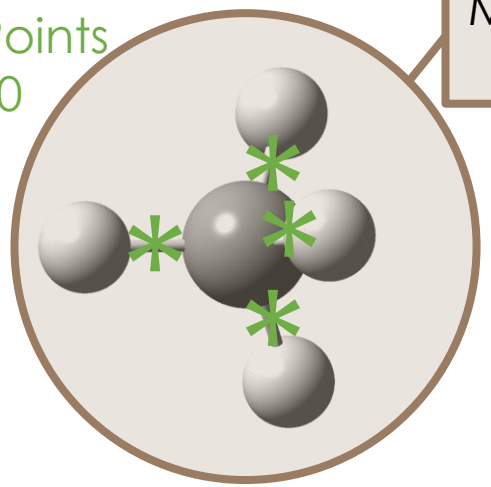
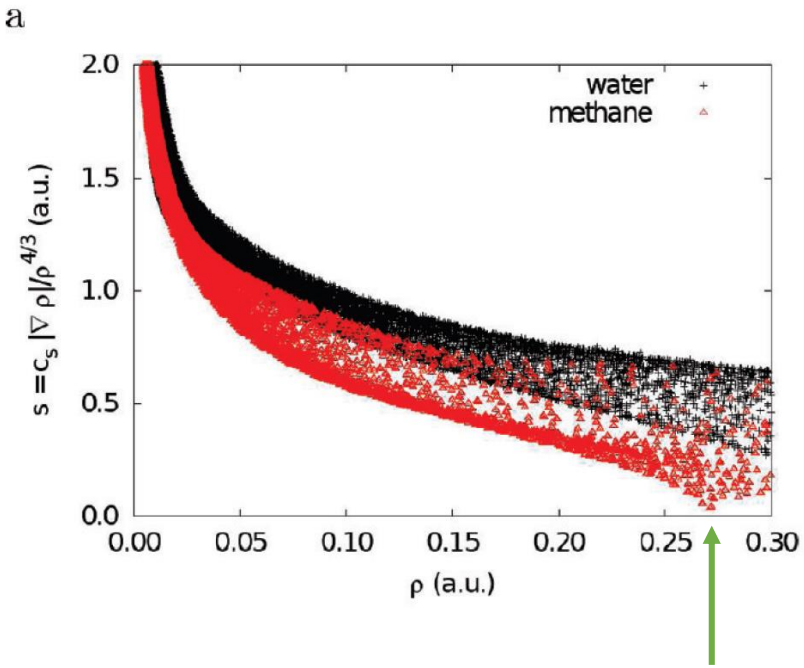
Reduced gradient density

QTAIM
Bond Critical Points
High ρ, s = 0



Molecular zone
High ρ

Density tail
Low ρ, high s



C-H BCPs

E. R. Johnson et al., J. Am. Chem. Soc., 2010, 132, 6498.

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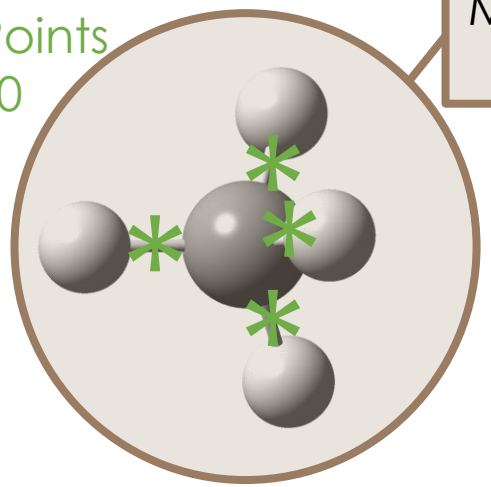

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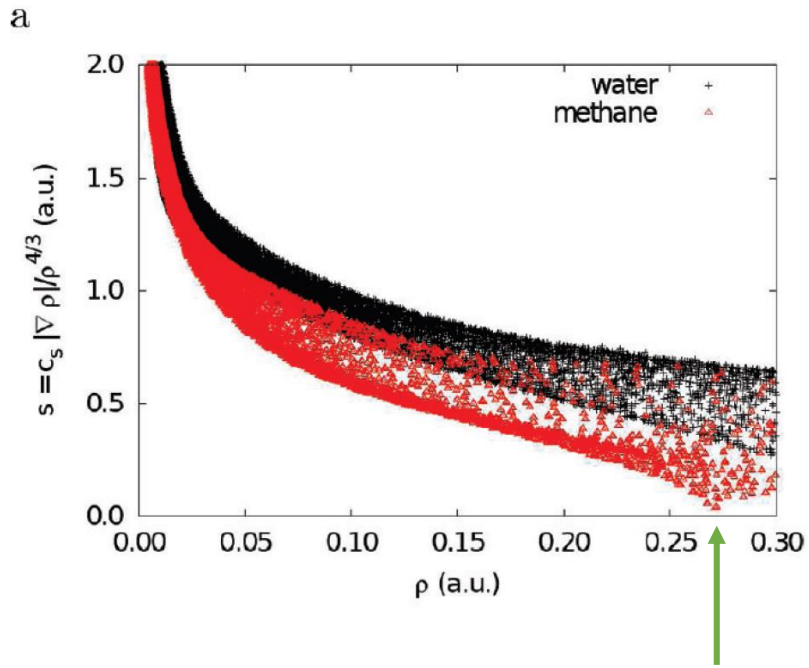

C-H BCPs

Reveals the presence of
intramolecular interactions

E. R. Johnson et al., J. Am. Chem. Soc., 2010, 132, 6498.

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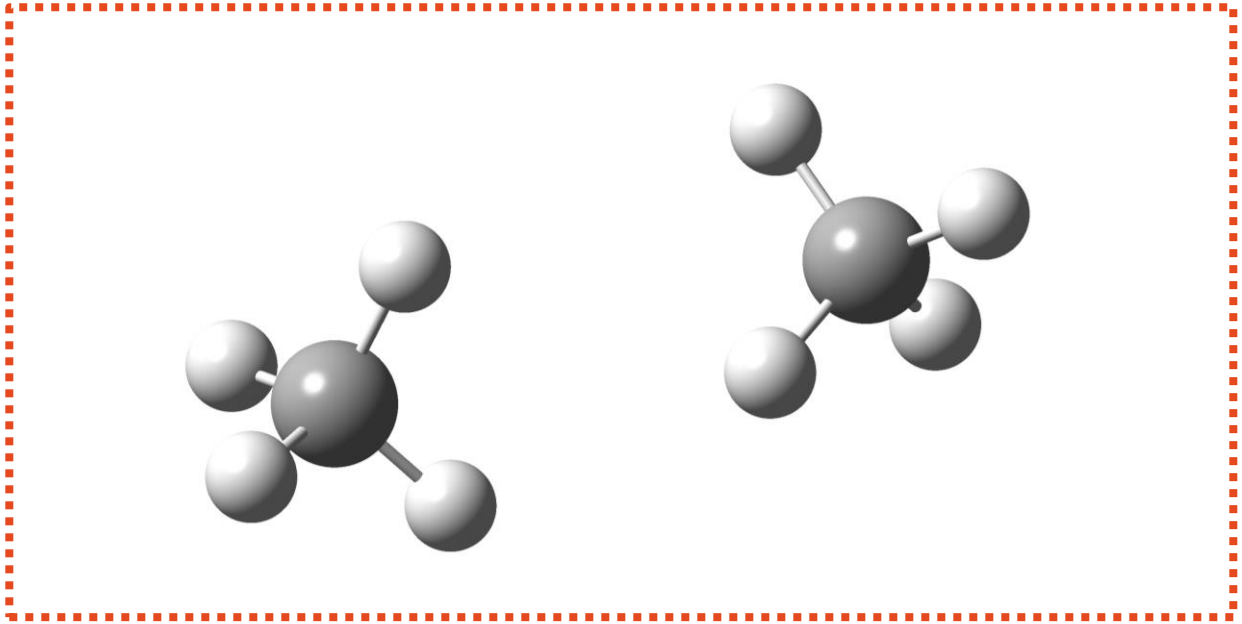

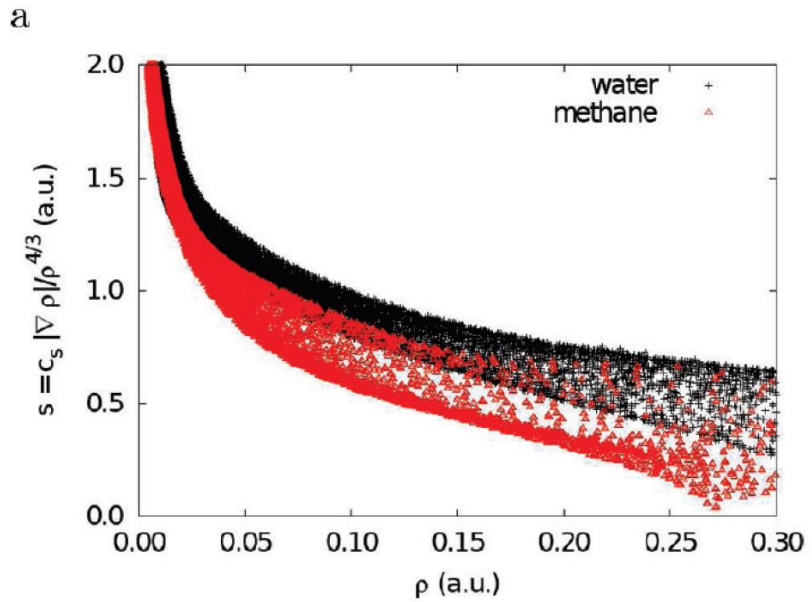

E. R. Johnson et al., J. Am. Chem. Soc., 2010, 132, 6498.

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Plotting $s = f(\rho)$

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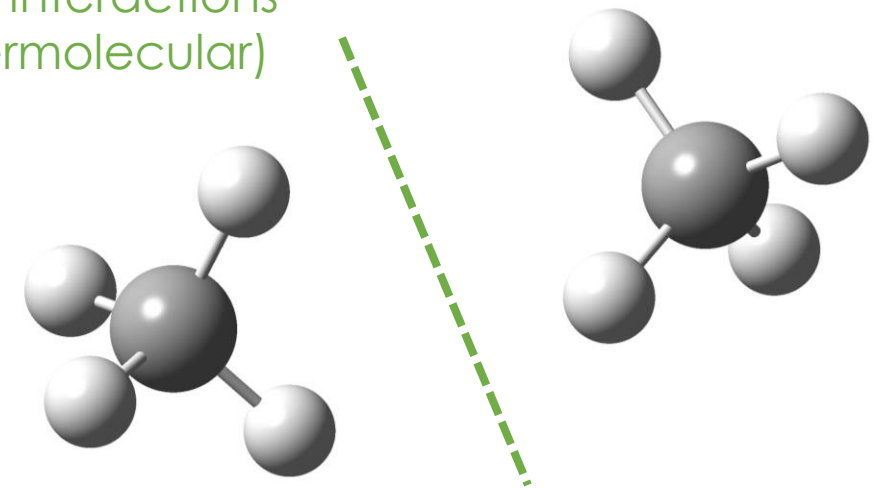
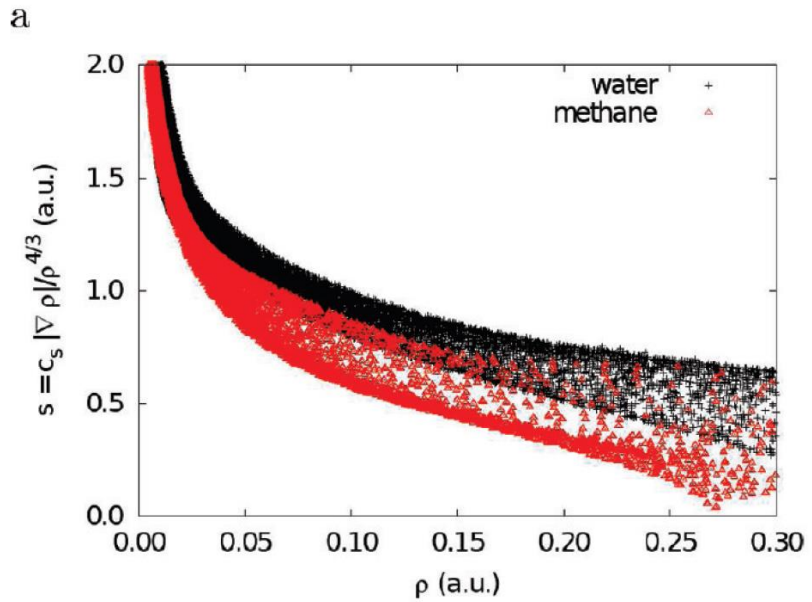
Reduced gradient density

vdW interactions
(intermolecular)





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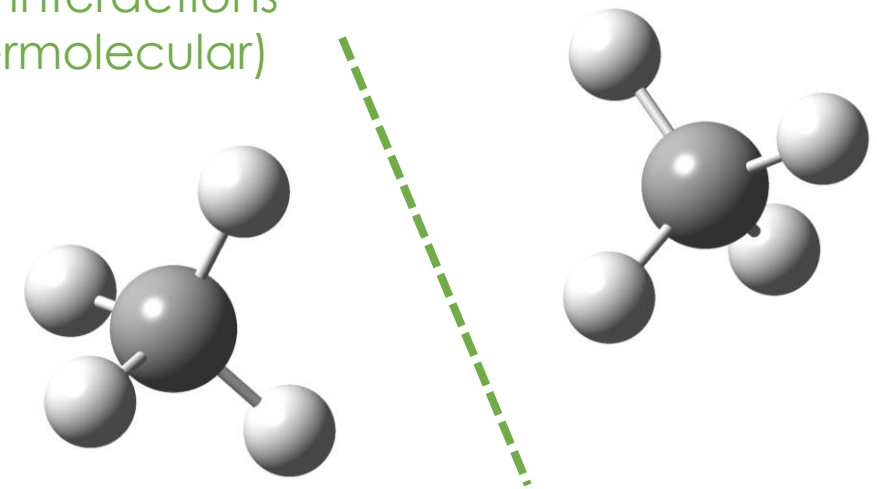

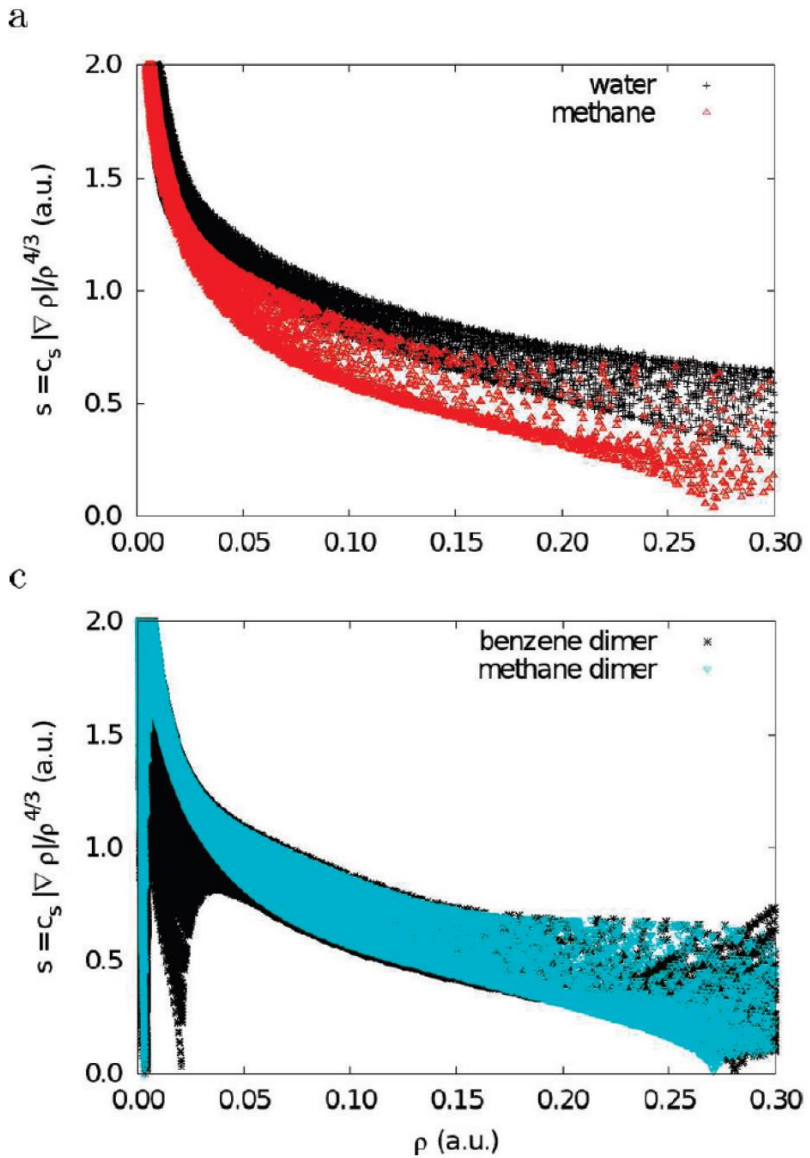

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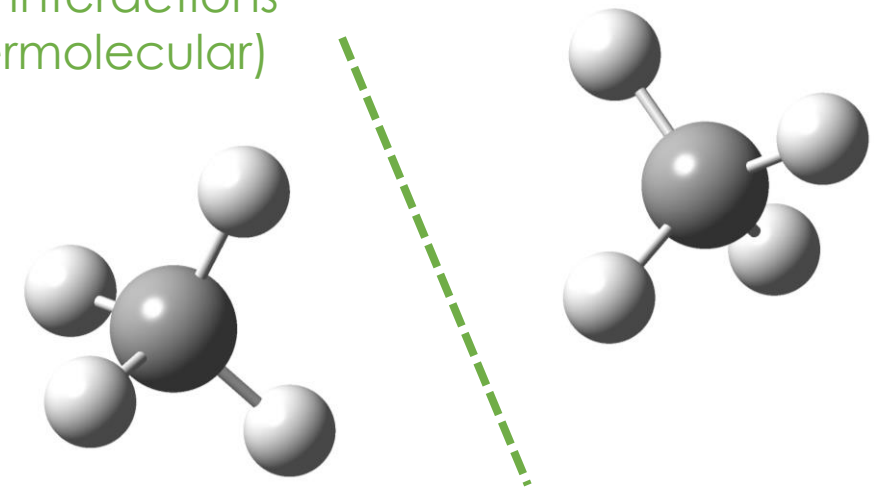
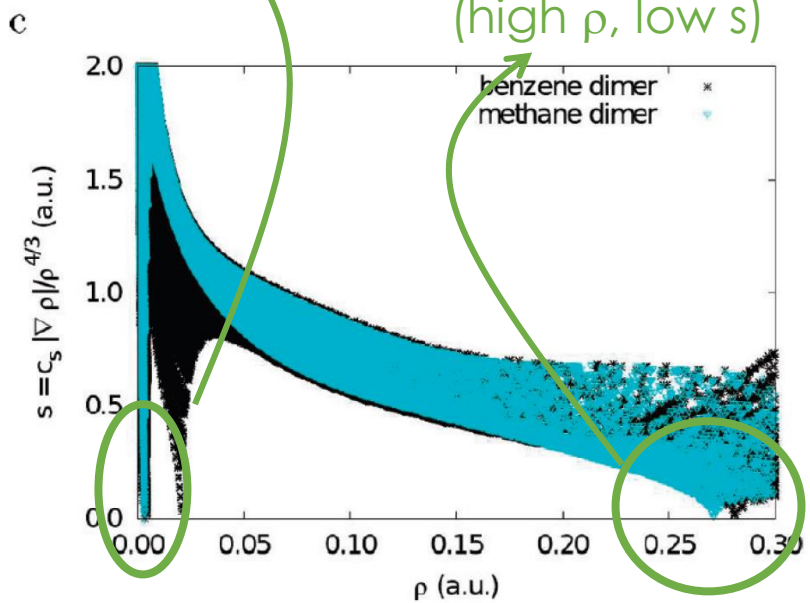


Intermolecular
Interactions
(low ρ, low s)

Intramolecular
Interactions
(high ρ, low s)



E. R. Johnson et al., J. Am. Chem. Soc., 2010, 132, 6498.

NCI index

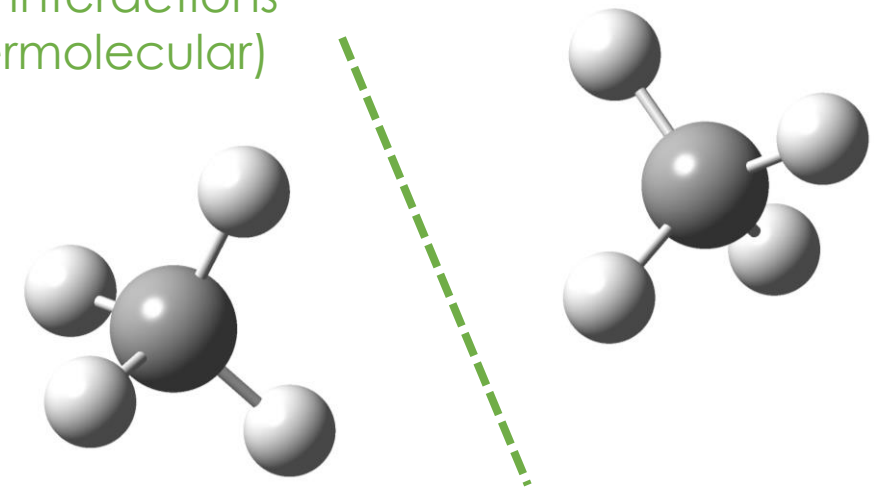
Plotting $s = f(\rho)$

Spikes ρ ↔ interaction strength

$$s = \frac{1}{C_S}\frac{|\nabla\rho|}{\rho^{4/3}}$$

Reduced gradient density

vdW interactions
(intermolecular)



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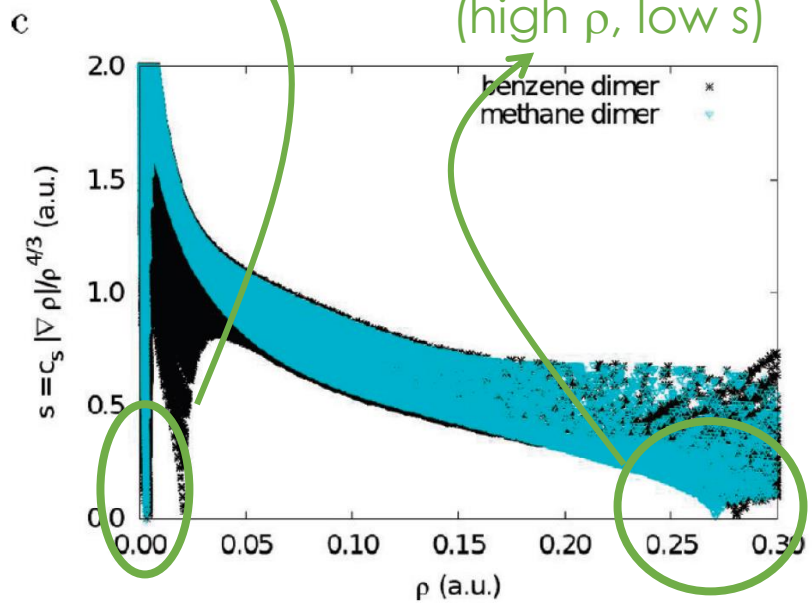

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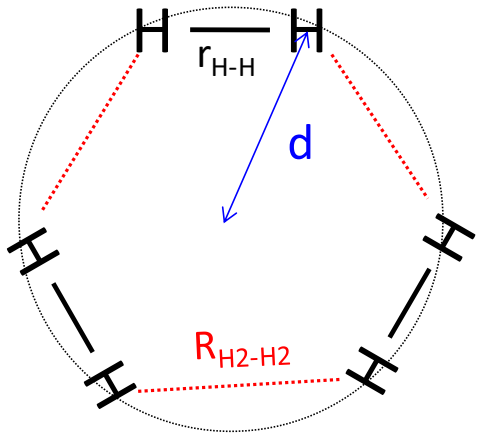
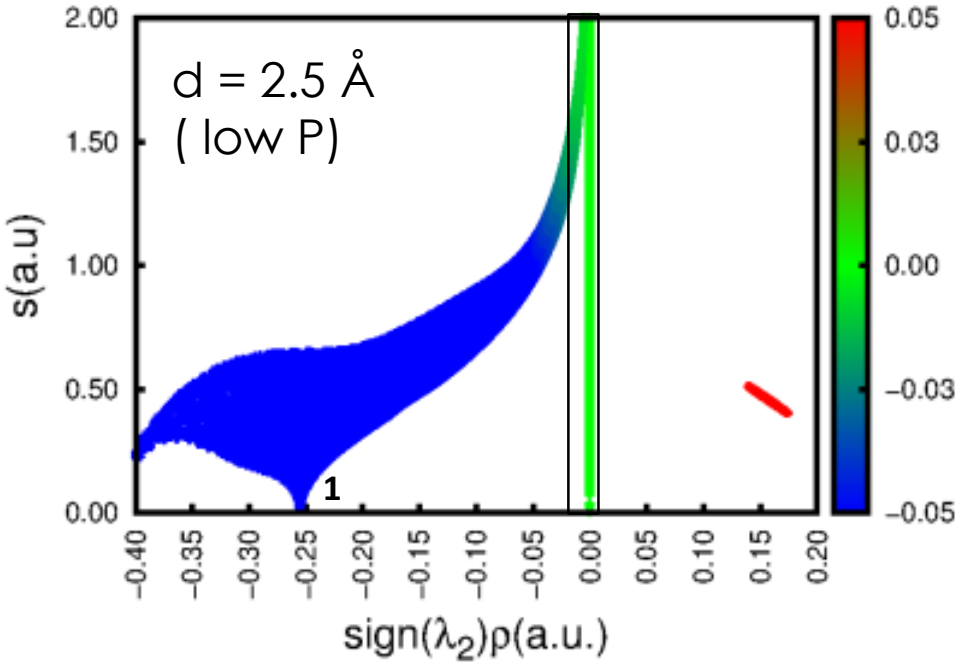
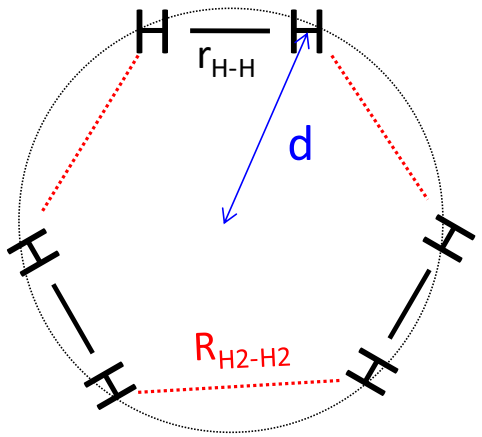
NCI index – inventaire of the interactions

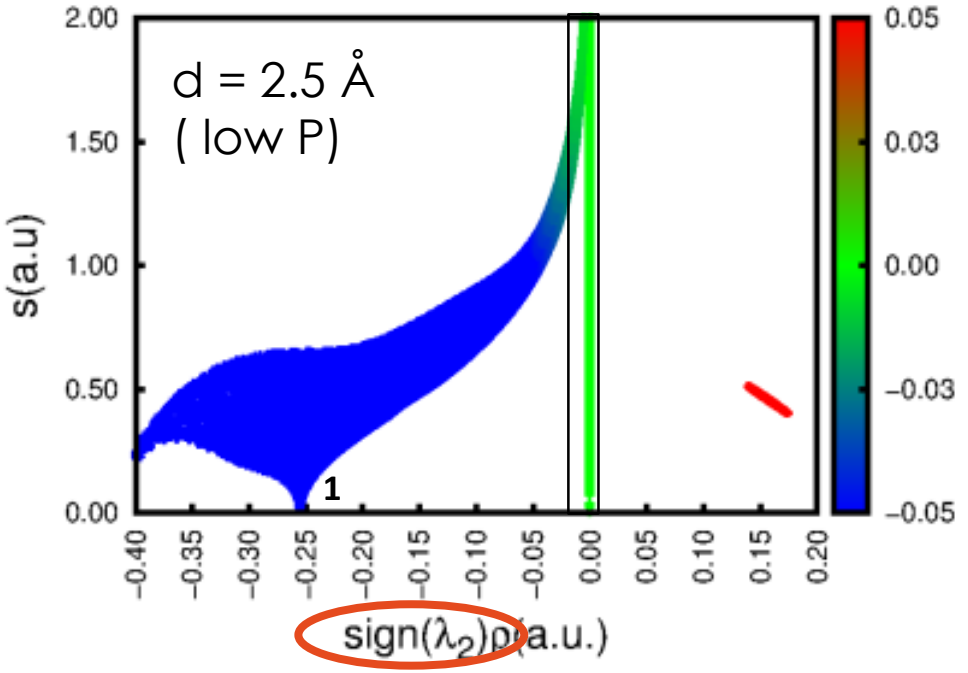




Riffet, Labet, Contreras-Garcia, PCCP, accepted

NCI index – inventaire of the interactions

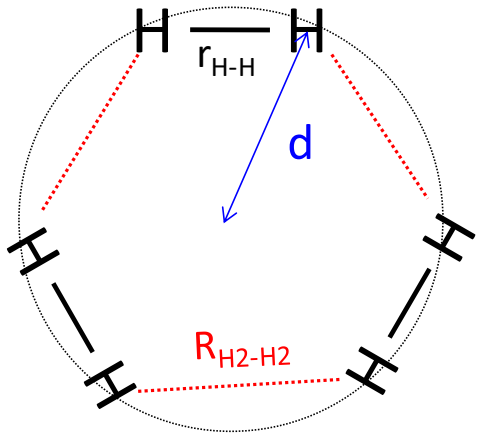


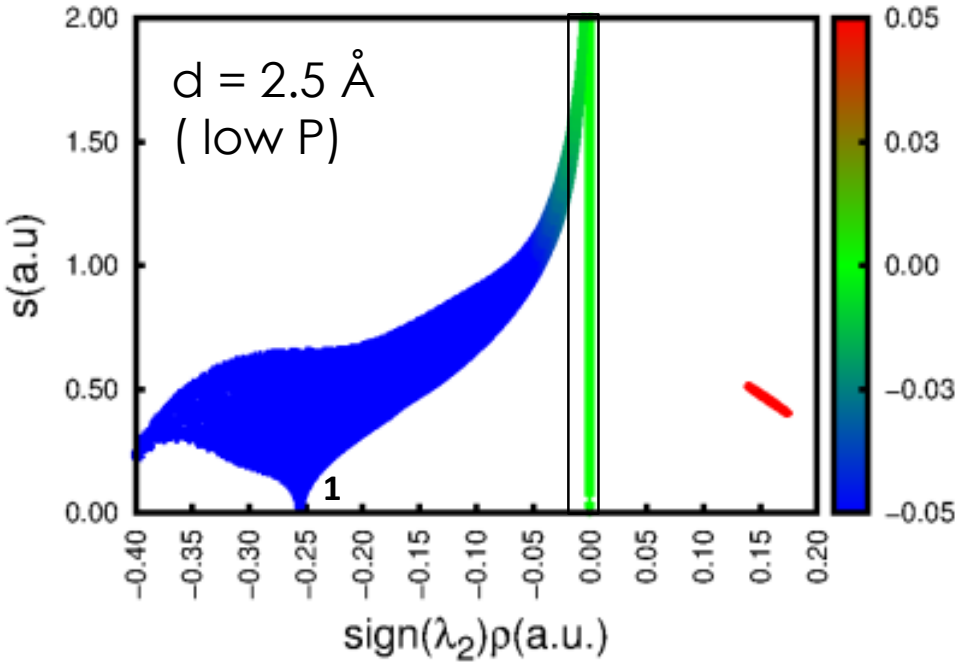


λ_2 : eigenvalue of the ρ Hessian matrix
($\lambda_1 < \lambda_2 < \lambda_3$)

Riffet, Labet, Contreras-Garcia, PCCP, accepted

NCI index – inventaire of the interactions





λ_2 : eigenvalue of the ρ Hessian matrix
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$\lambda_2 < 0$: attractive interaction
$\lambda_2 > 0$: repulsive interaction

Riffet, Labet, Contreras-Garcia, PCCP, accepted

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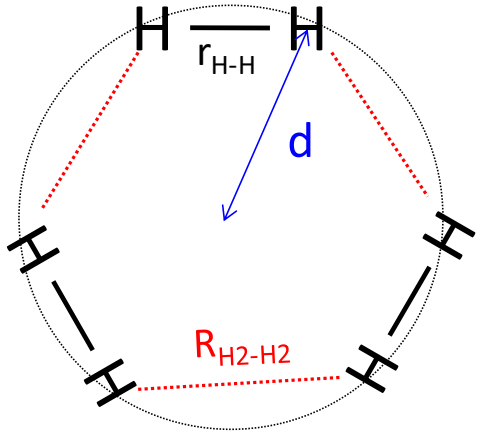

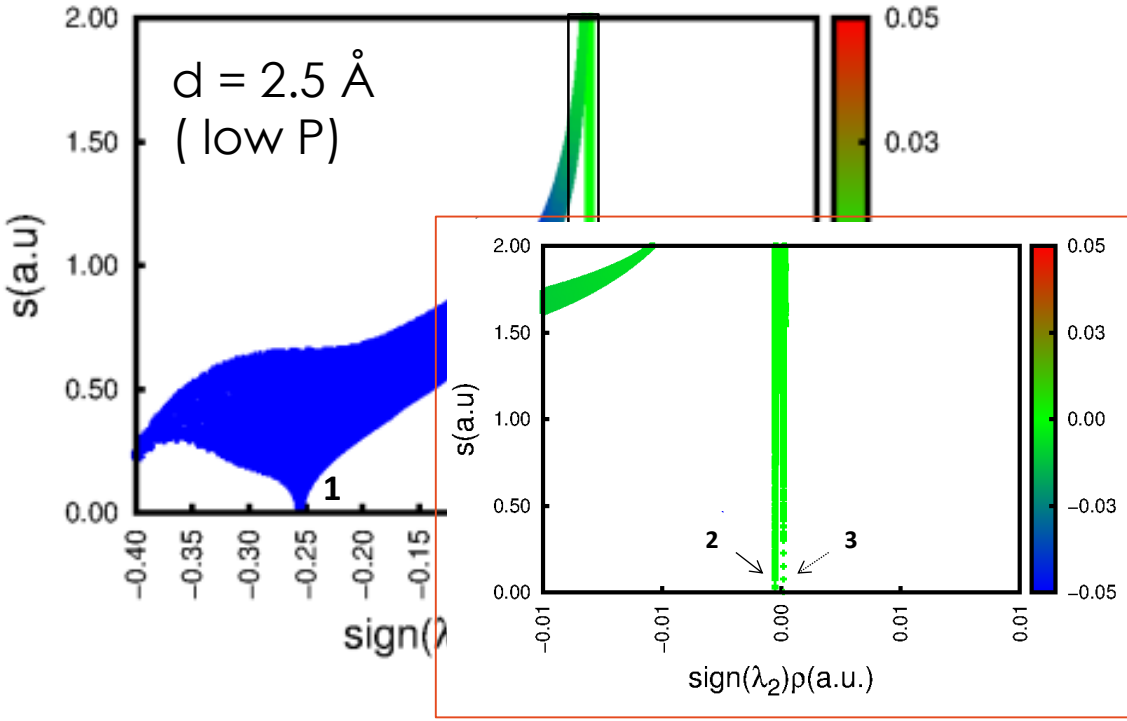

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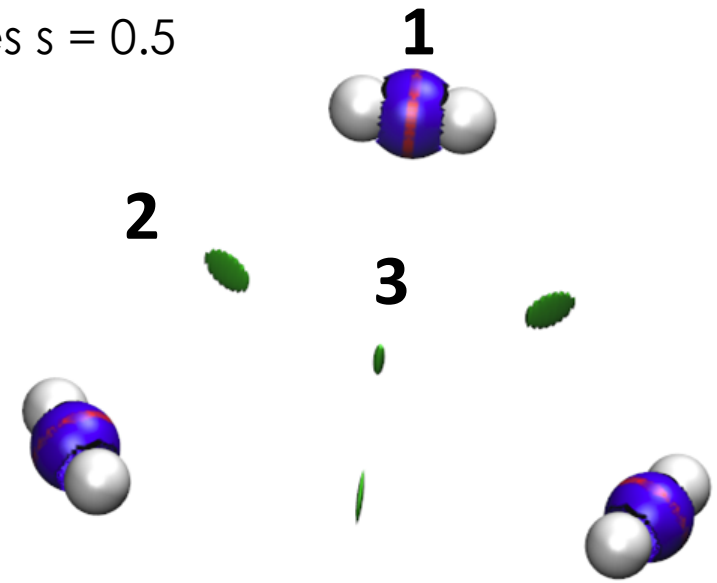
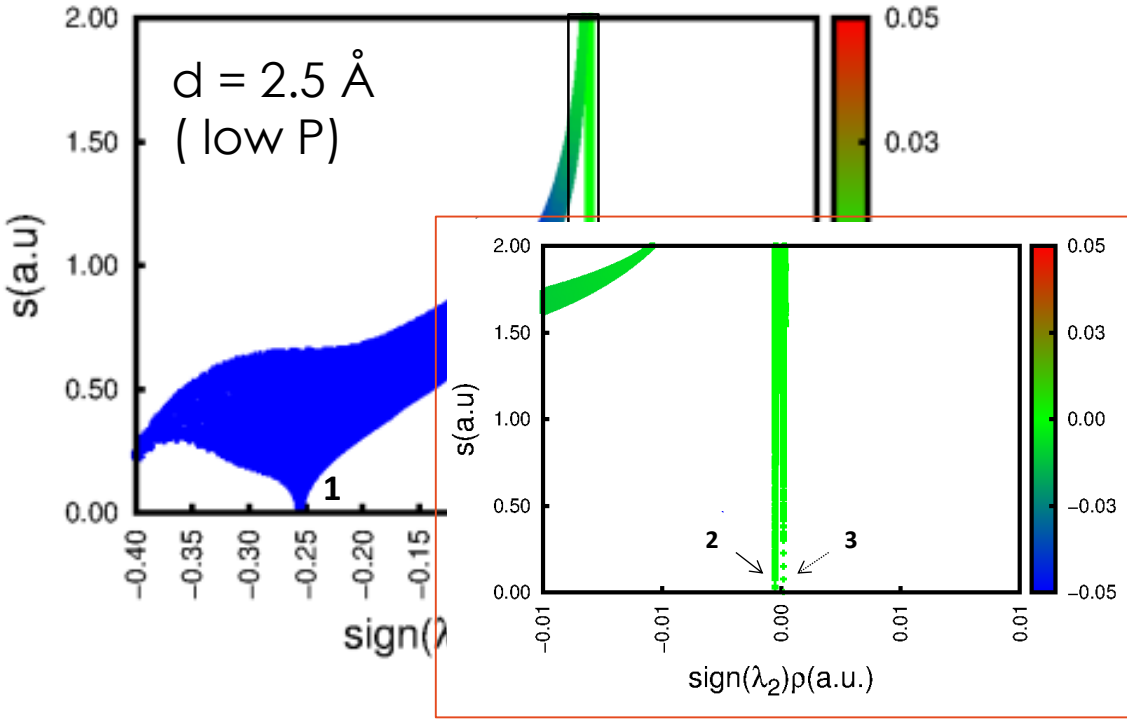
Riffet, Labet, Contreras-Garcia, PCCP, accepted

NCI index – inventaire of the interactions

Isosurfaces s = 0.5



1. H-H intramolecular covalent bonds
2. Attractive intermolecular interaction (vdW)
3. Repulsive intermolecular interaction



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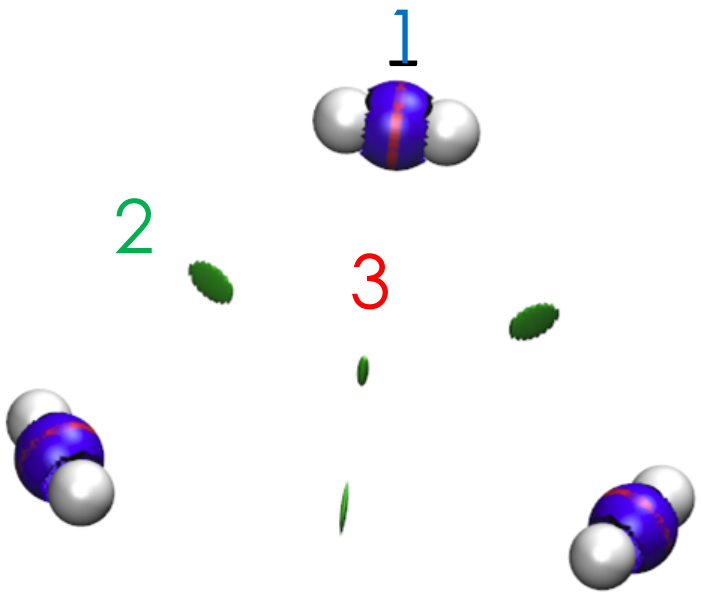
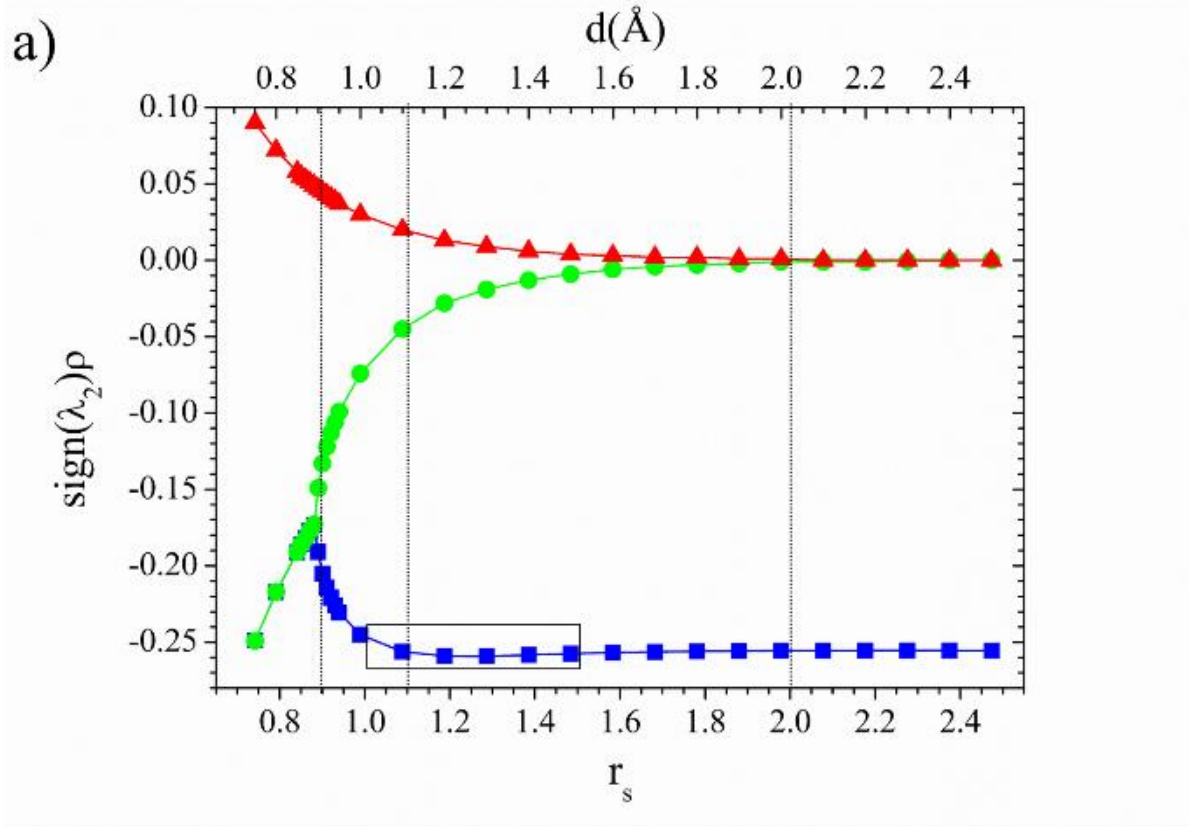
Riffet, Labet, Contreras-Garcia, PCCP, accepted

NCI index – evolution with pressure

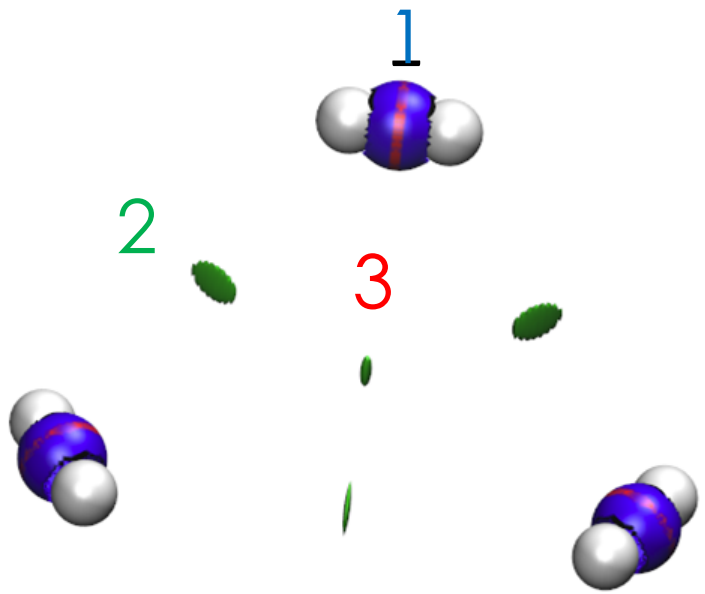




d ↘ ; P↗

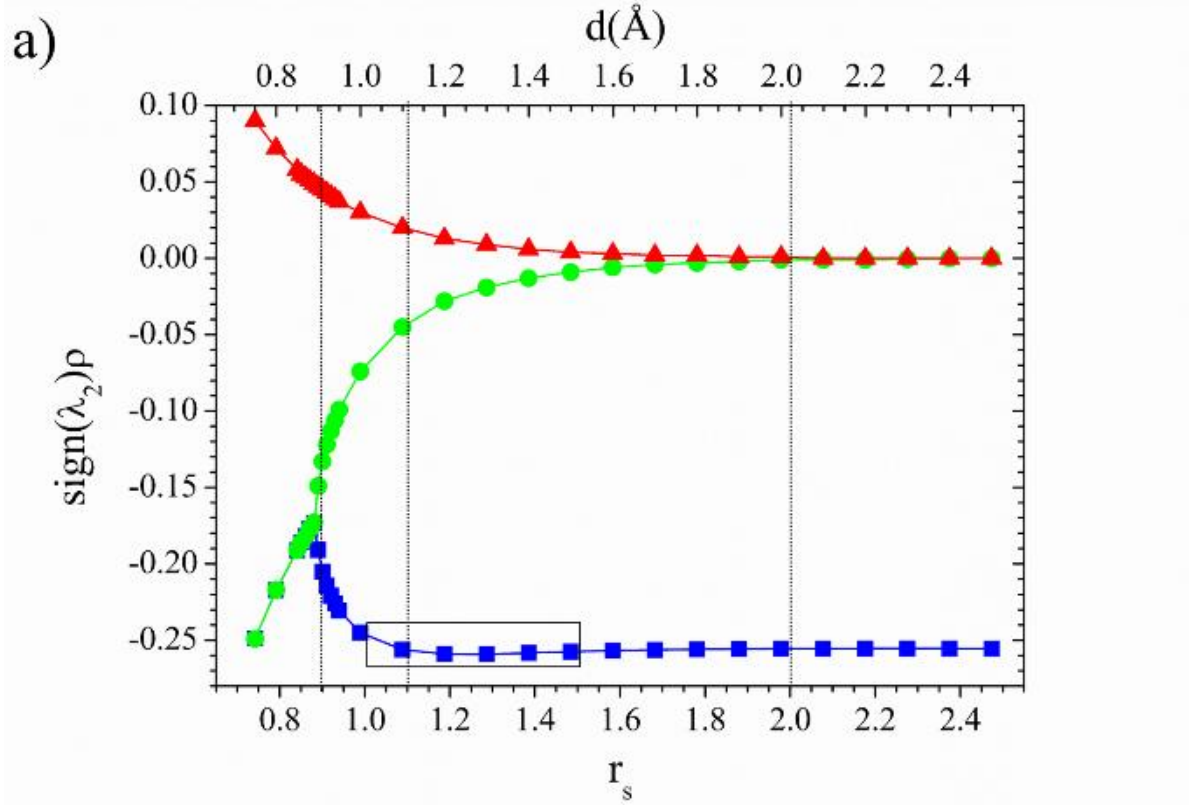
Riffet, Labet, Contreras-Garcia, PCCP, accepted

NCI index – evolution with pressure



As d ↘ (models P ↗)

- Intermolecular interactions strengthen (both attractive and repulsive)



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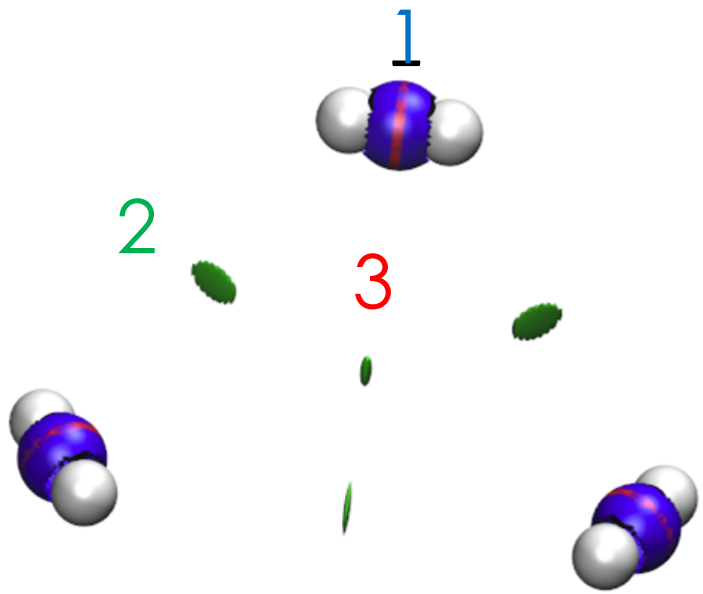

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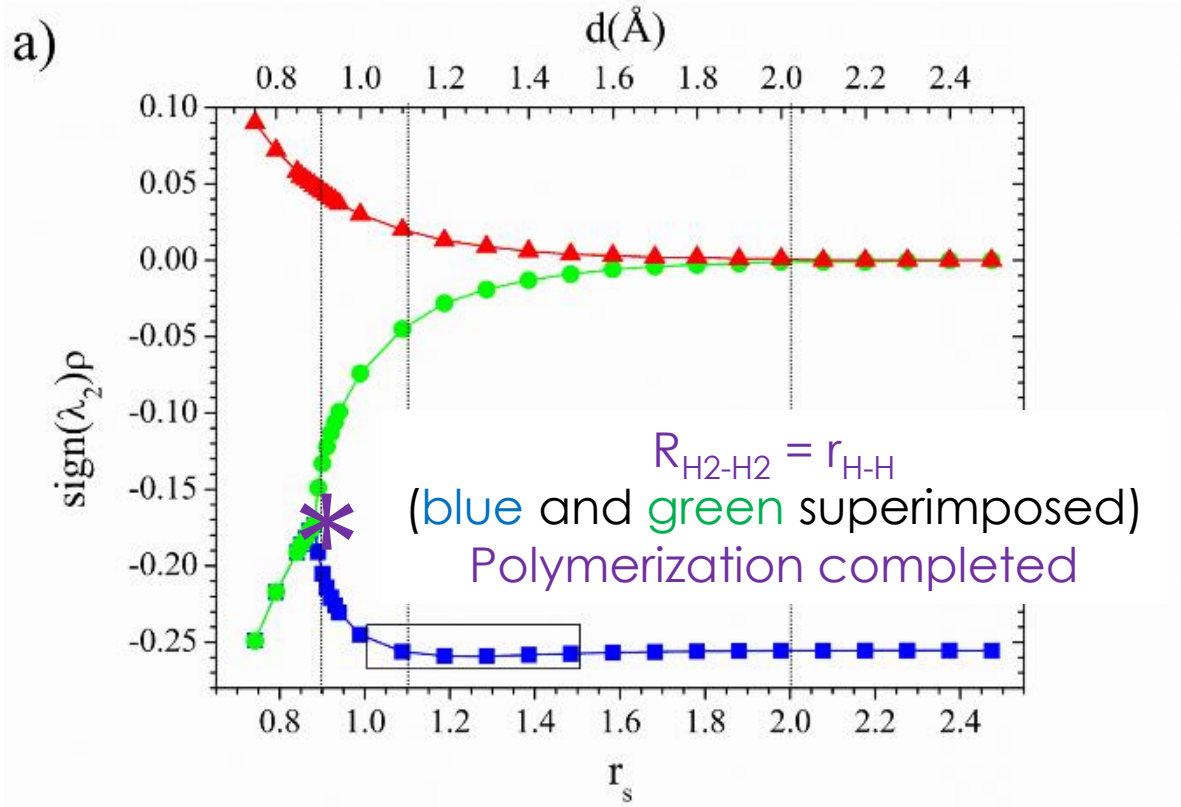

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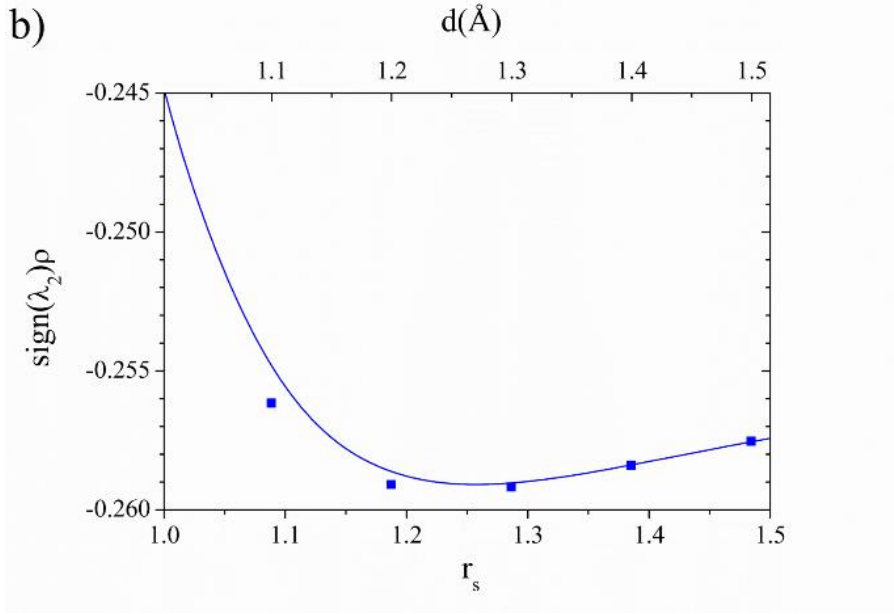
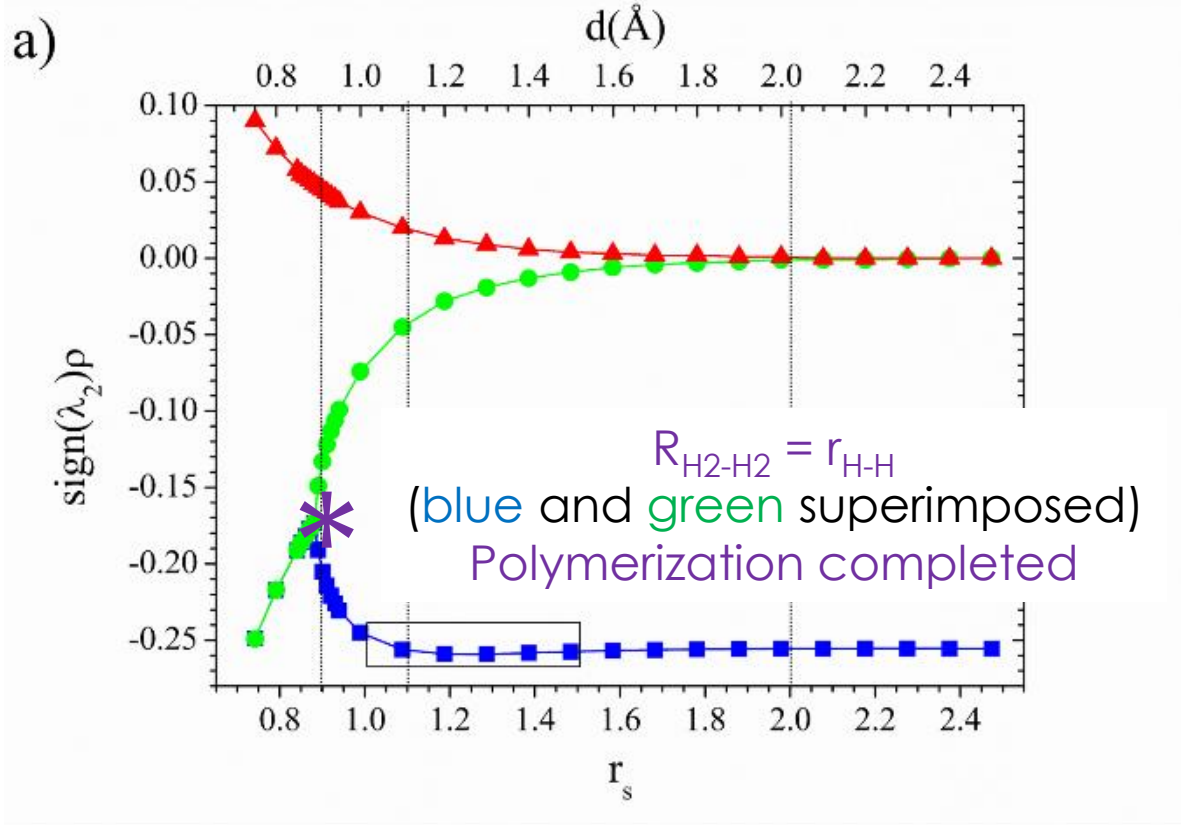
NCI index – evolution with pressure





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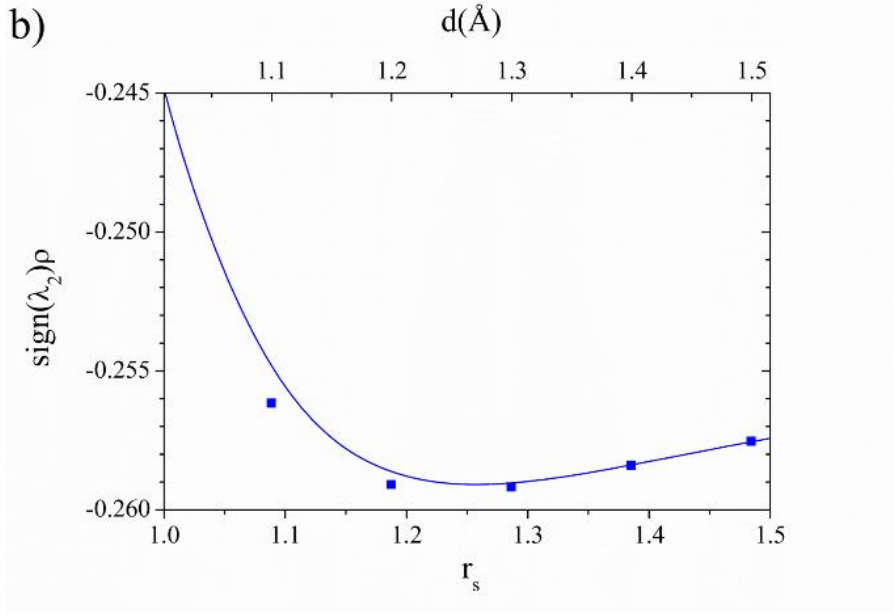

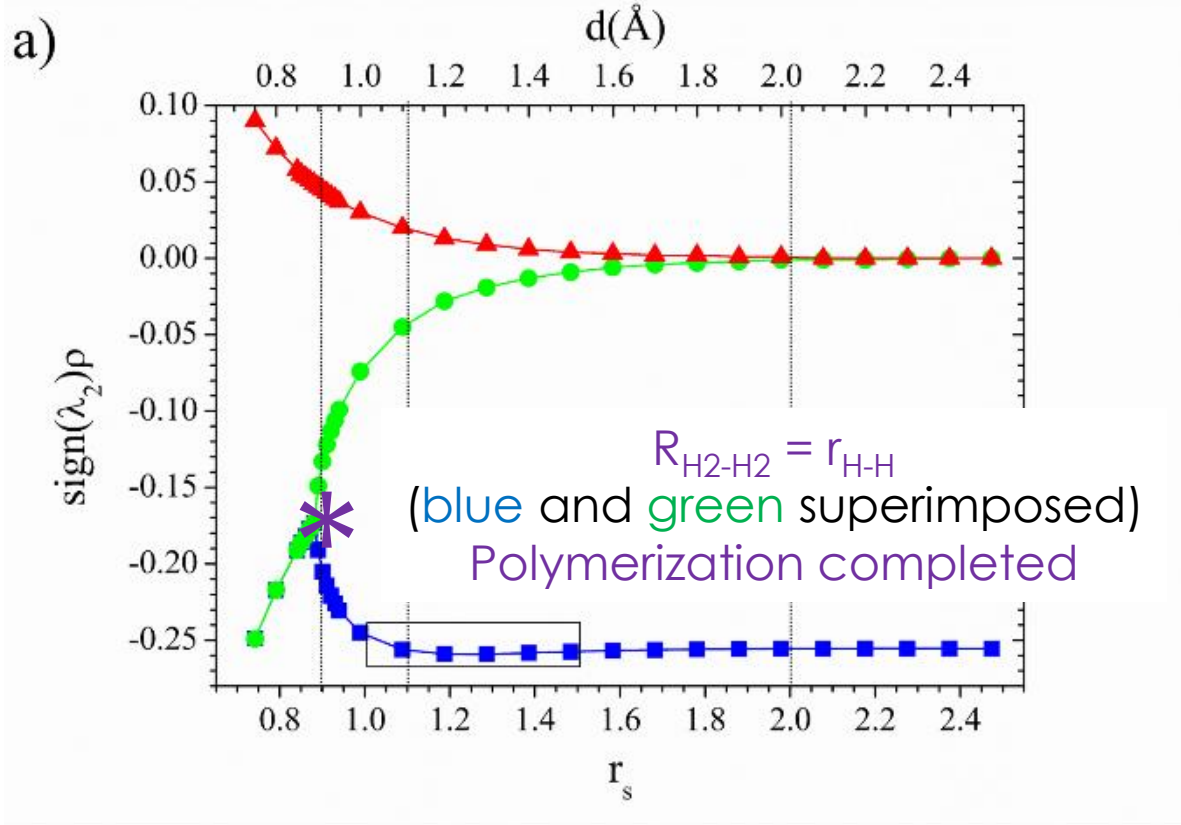

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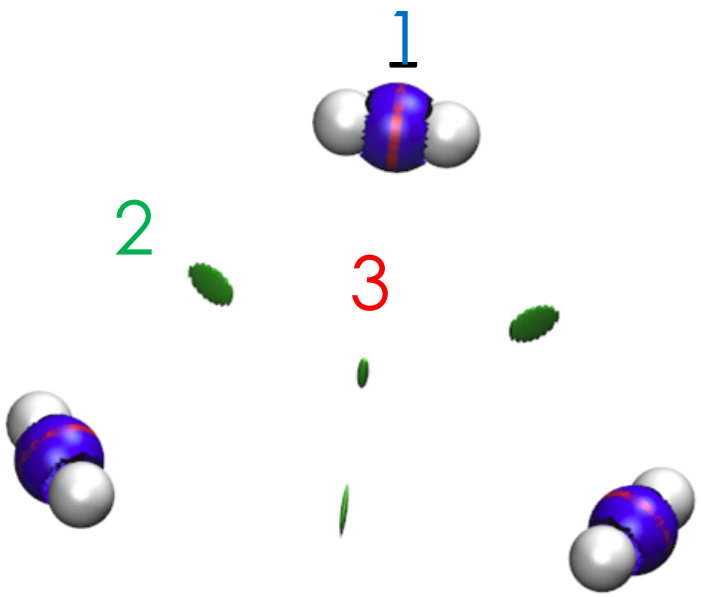
d ↘ ; P↗

Badger's rule !

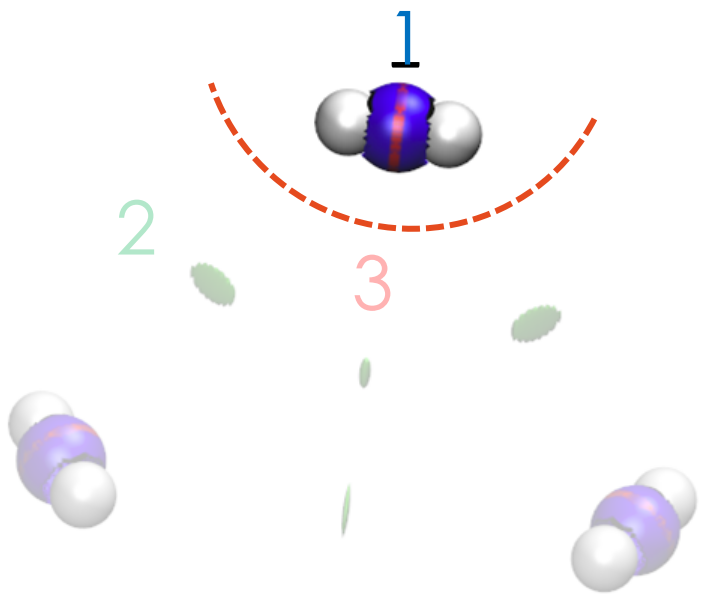
Comparison with an H_2 adapted in length

At a given d,
comparison of the electronic distribution

H_2 of the interacting system



H_2 of the interacting system
Isolated from its neighbors



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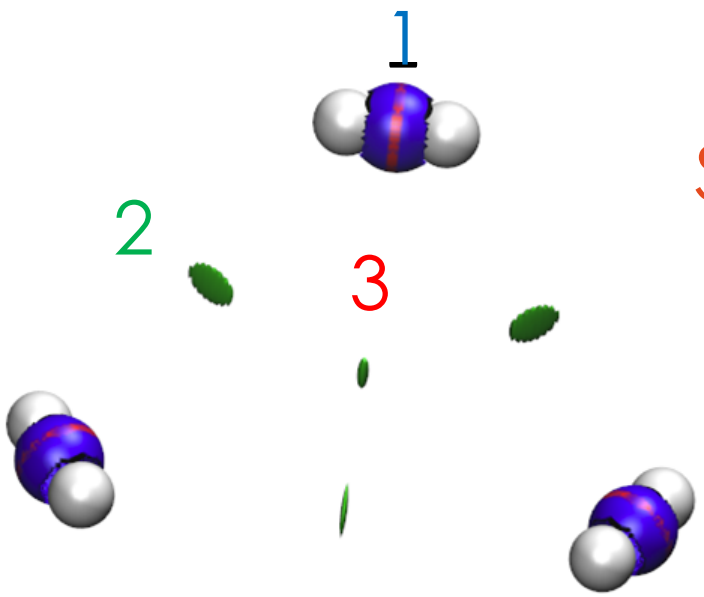
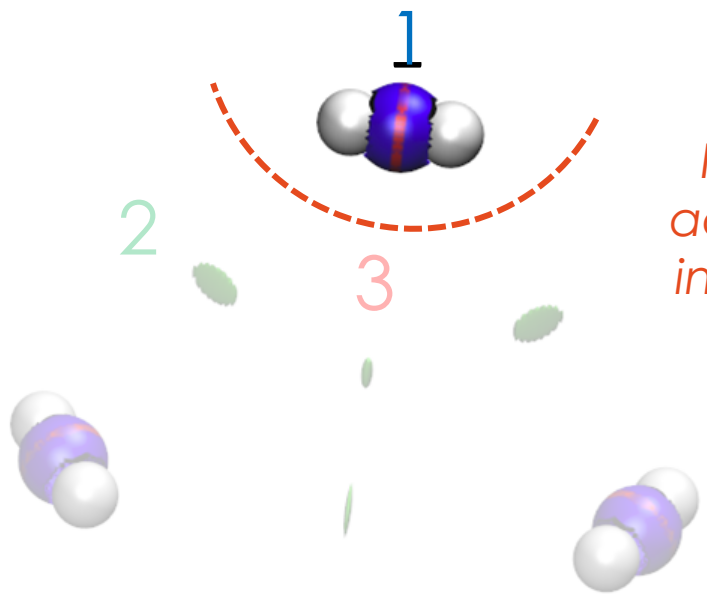


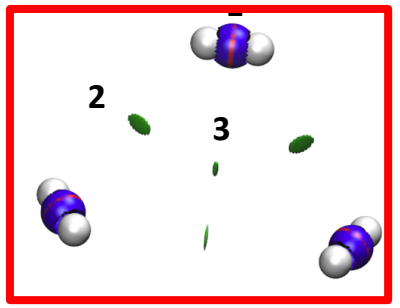
Same bond length !

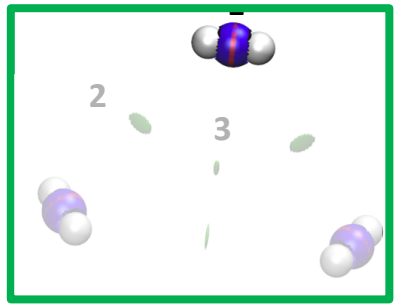
H_2 of the interacting system
Isolated from its neighbors

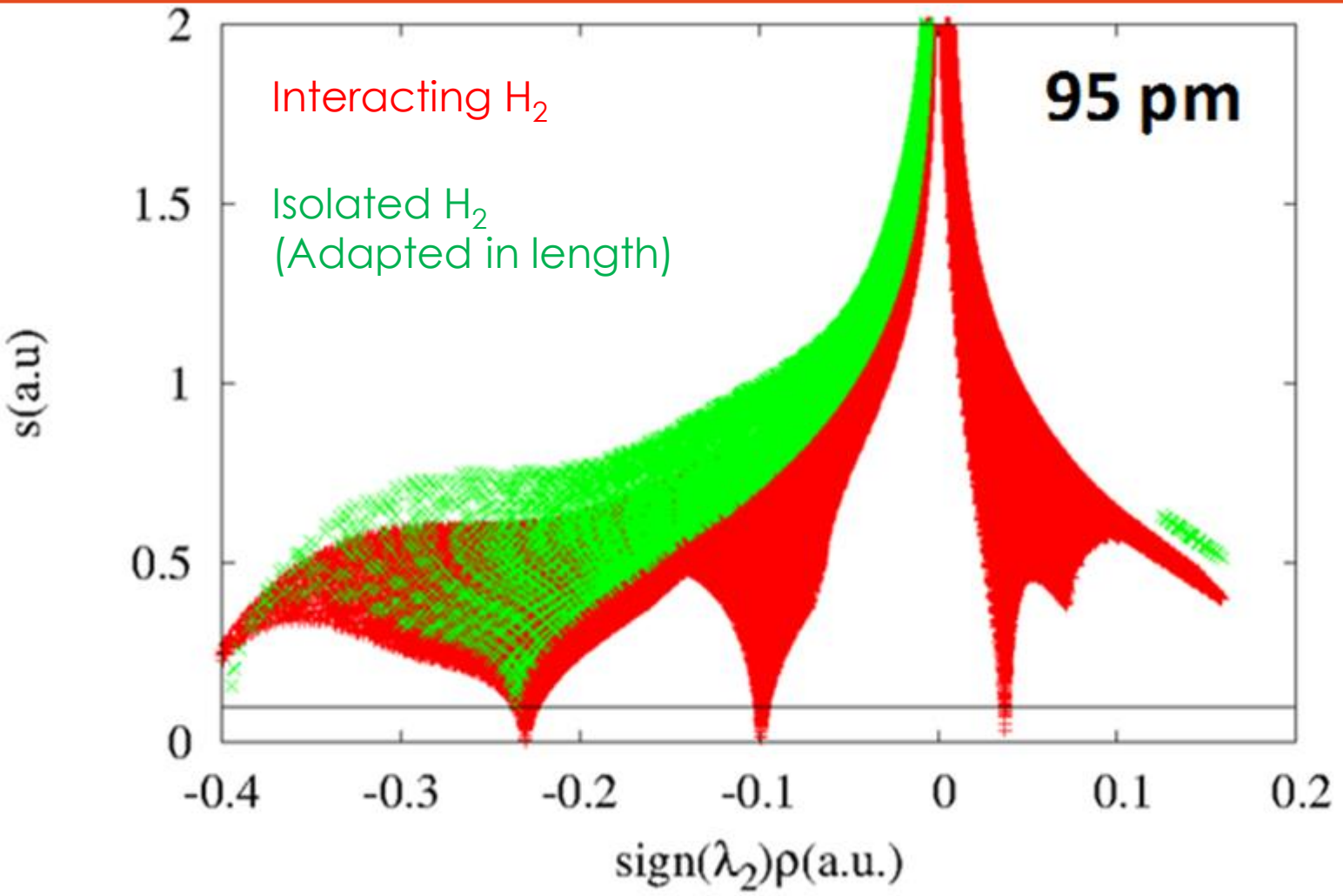


H_2 mol adapted in length

Comparison with an H_2 adapted in length







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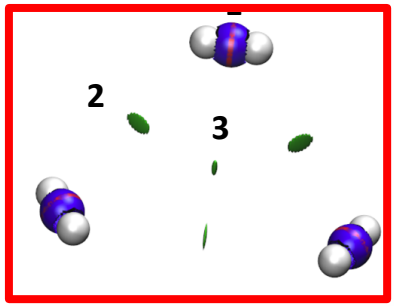
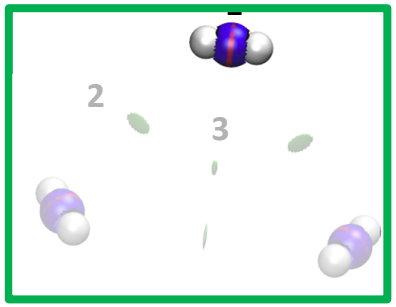
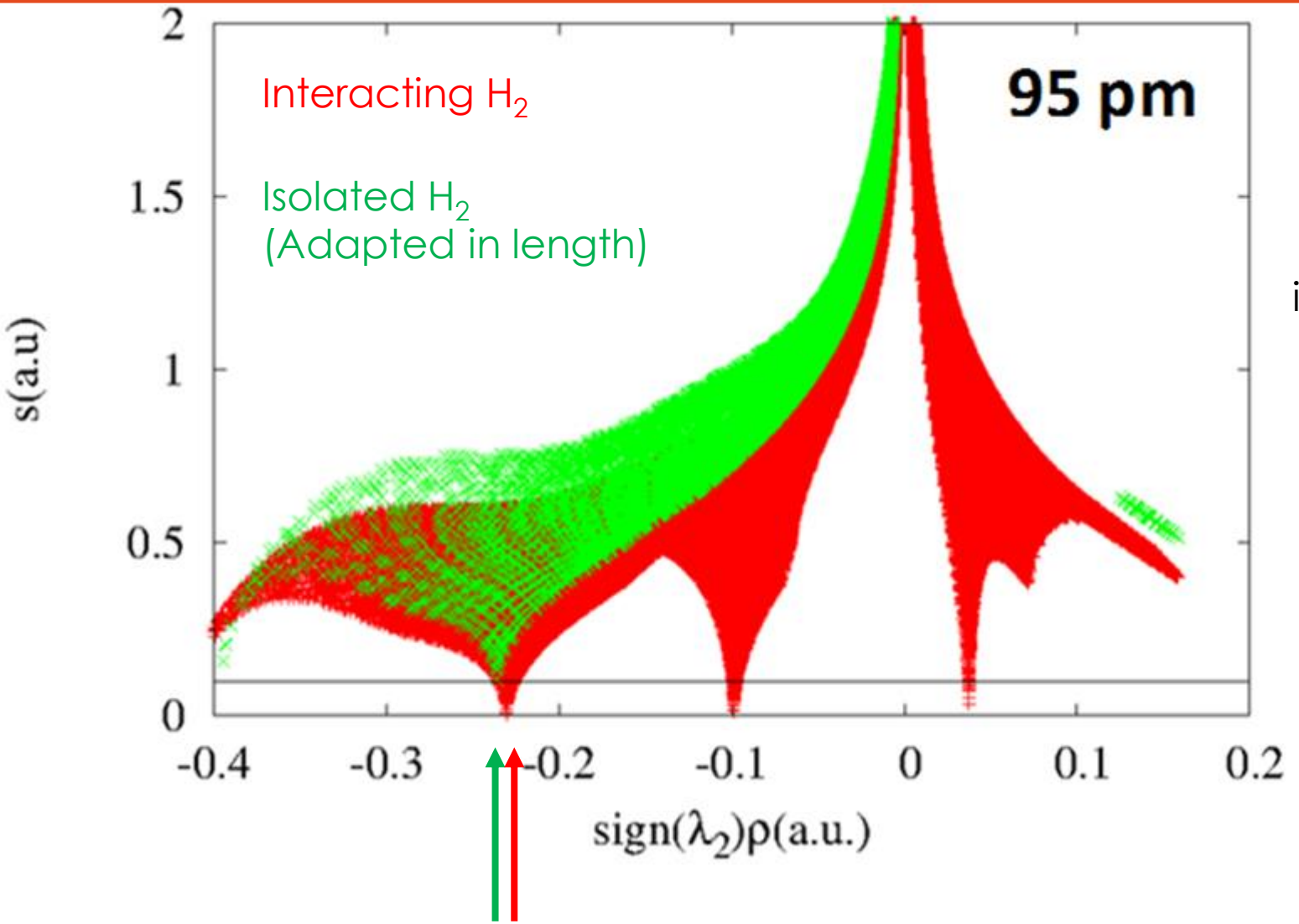
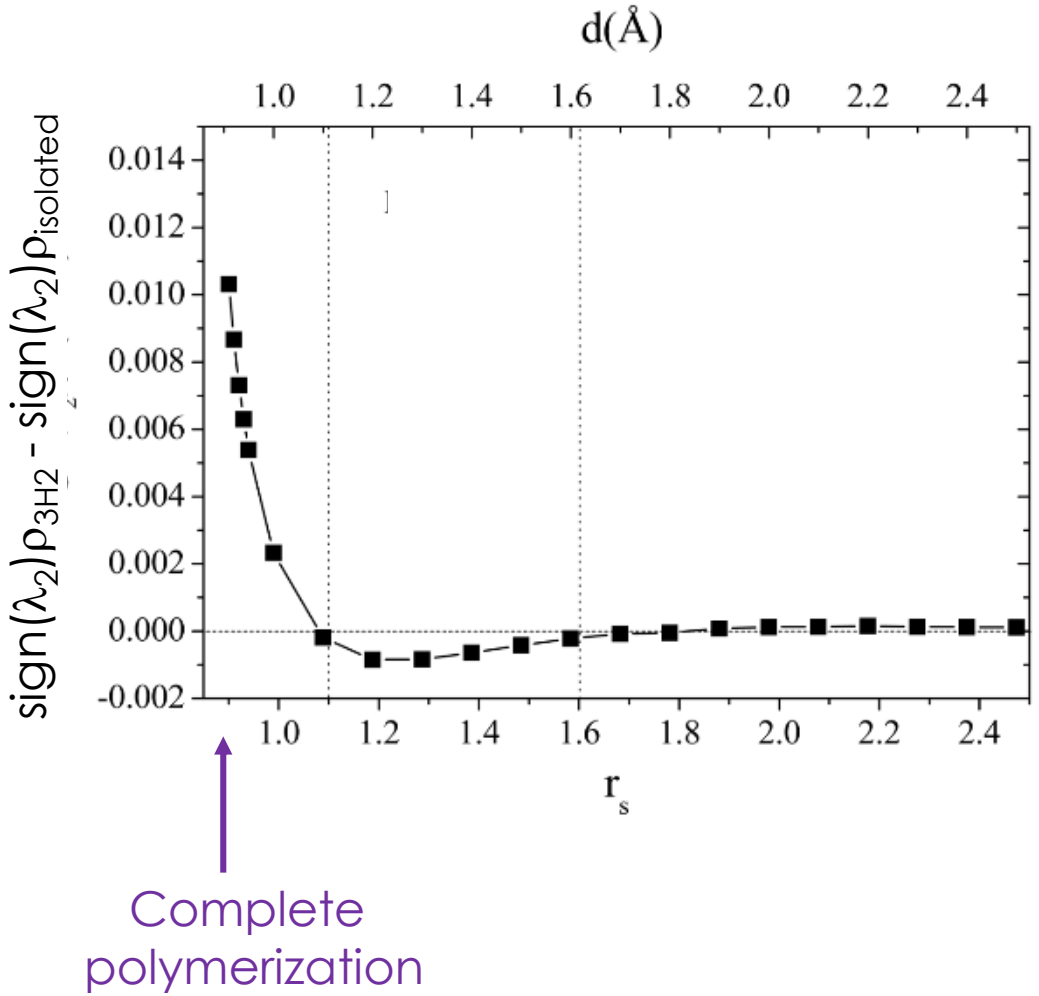






Small shift
in the density
of the
intramolecular spikes

Before complete polymerization



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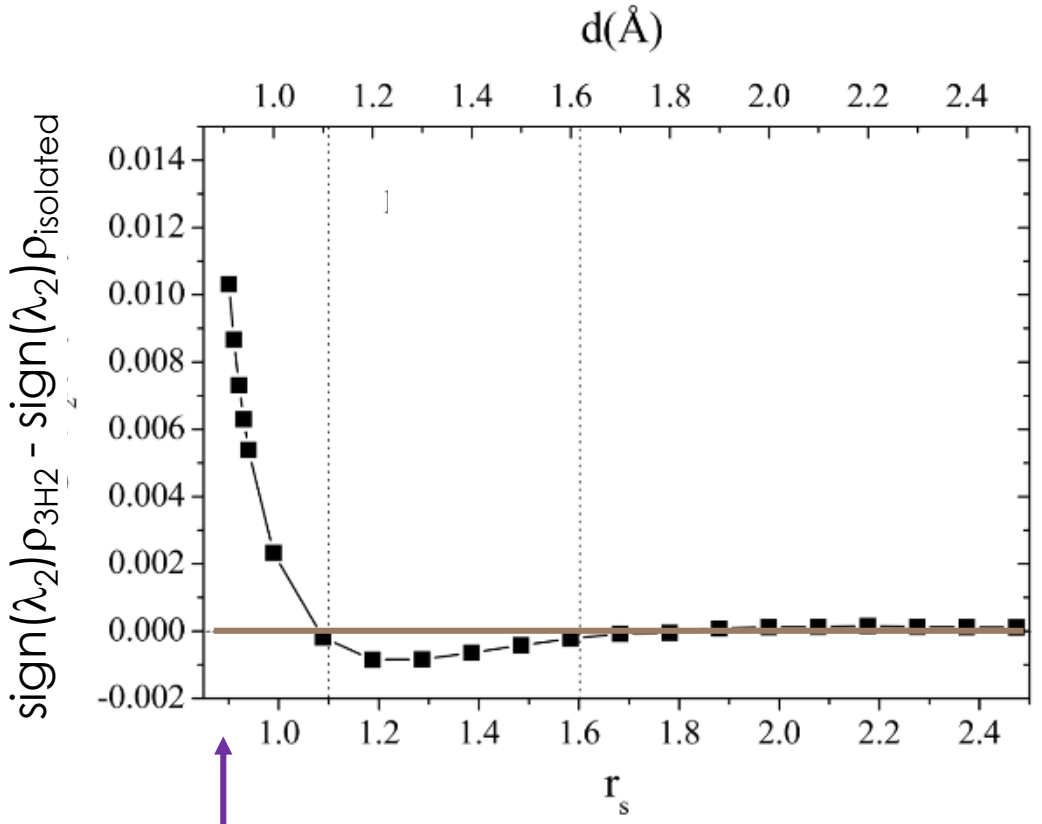

$\rho_{BCP,3H2} < \rho_{BCP,isolated}$

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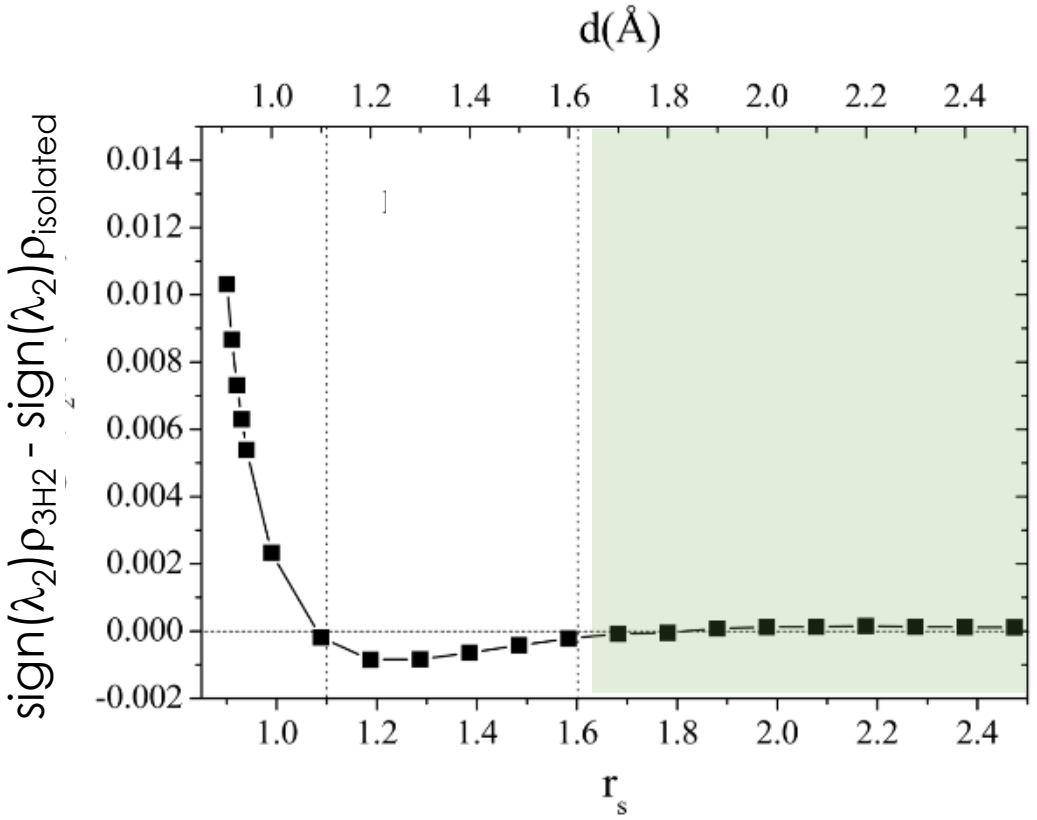
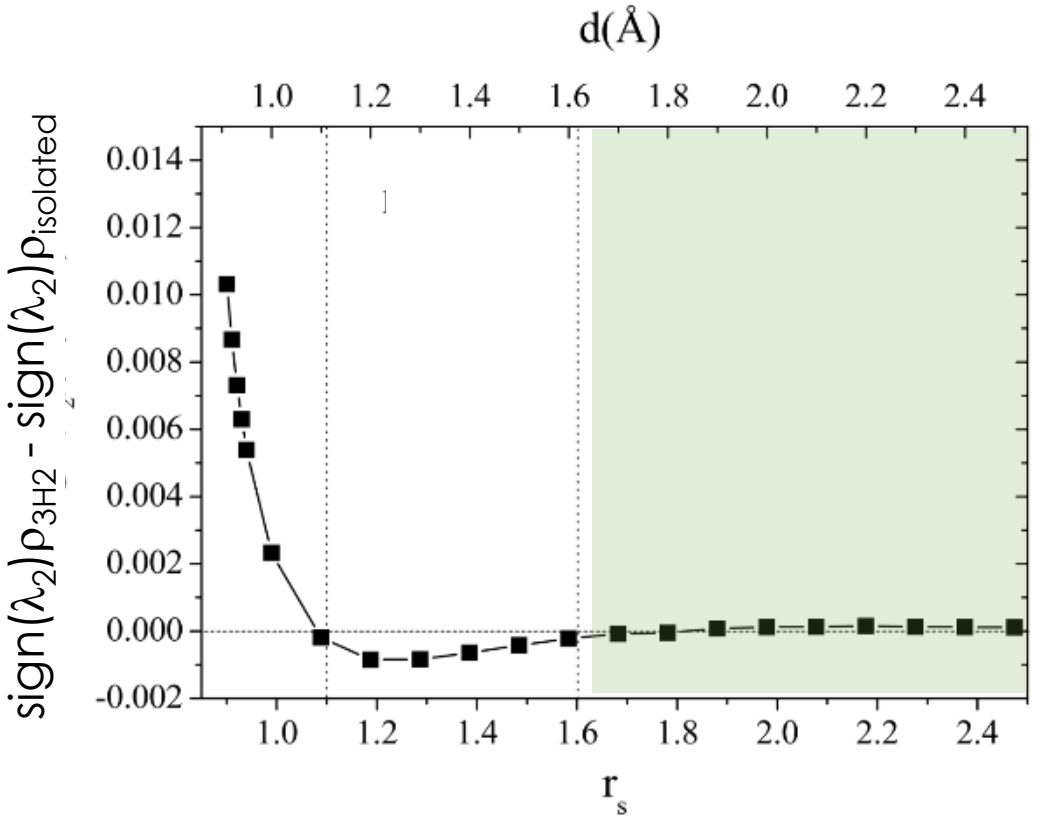
Complete polymerization

3 regimes



ρ organizes like
in an isolated molecule
having the same length

3 regimes



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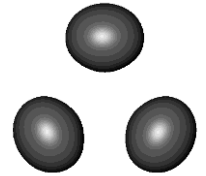
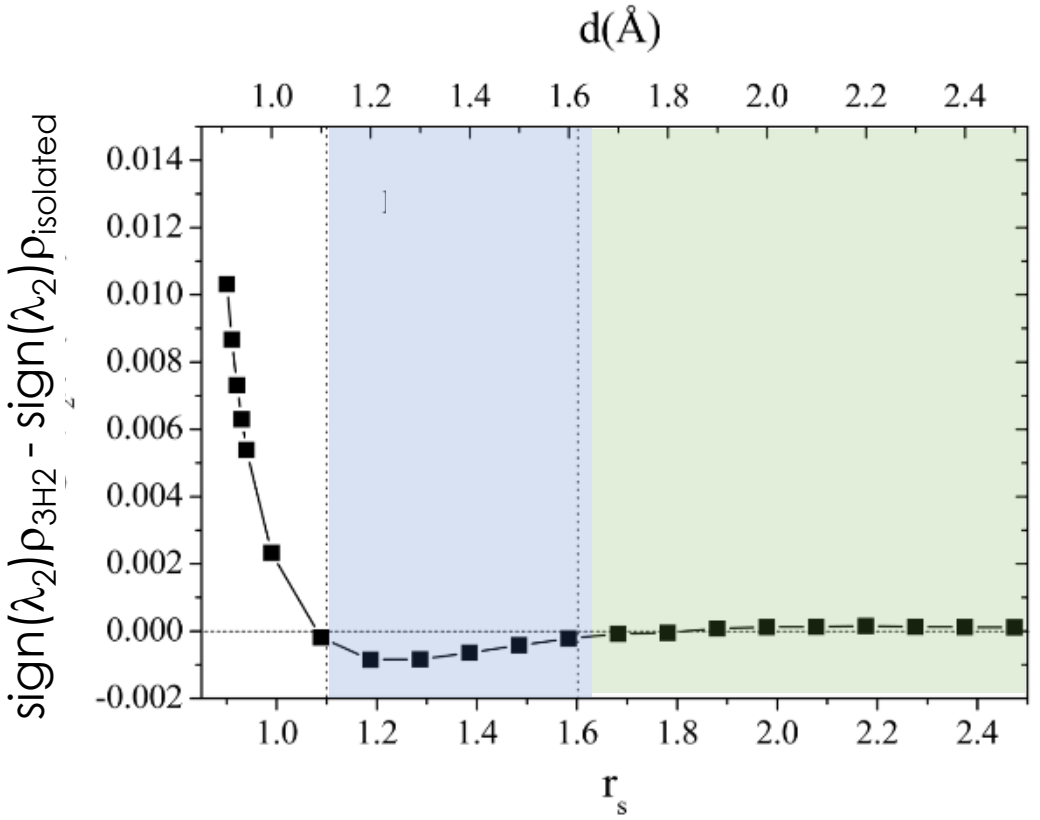


Prolate shape

ELF (0.95)

3 regimes



H_2 shorter than a normal mol.

ρ_{BCP} higher than in a « shortened » H_2 mol.

ρ reorganization: inter → intra

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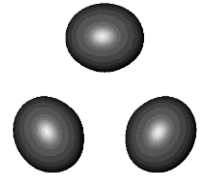

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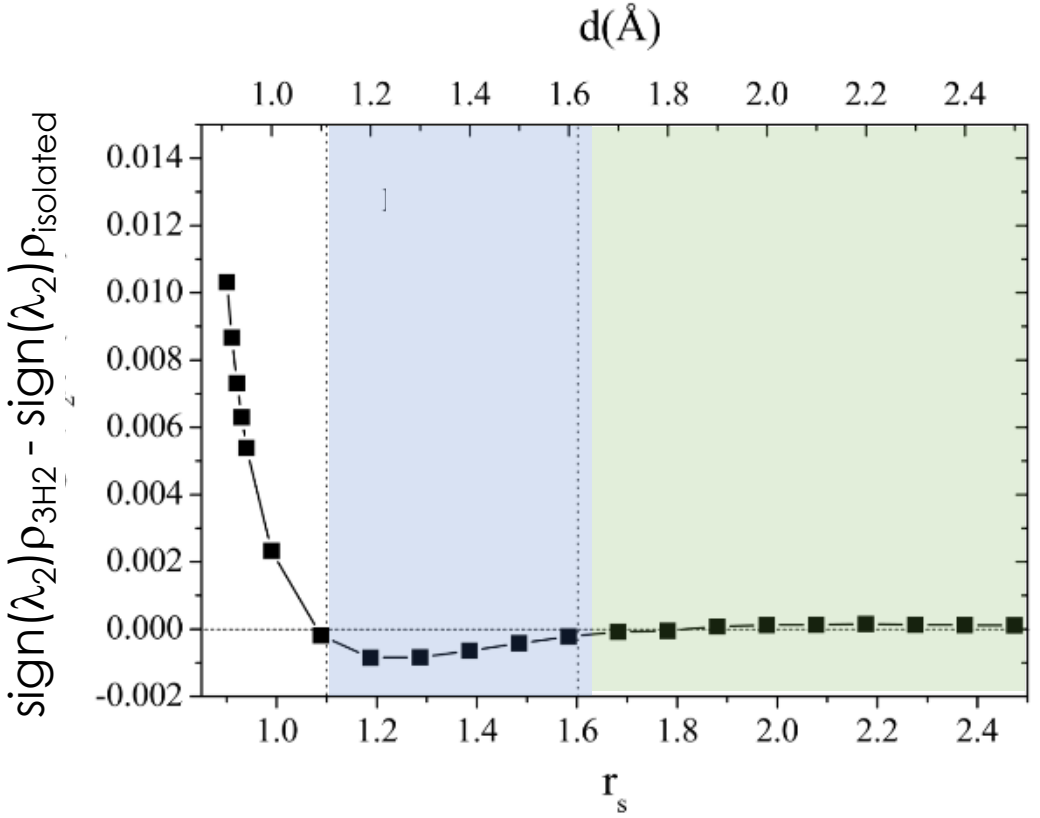

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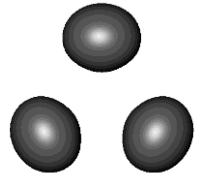

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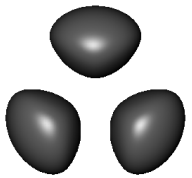

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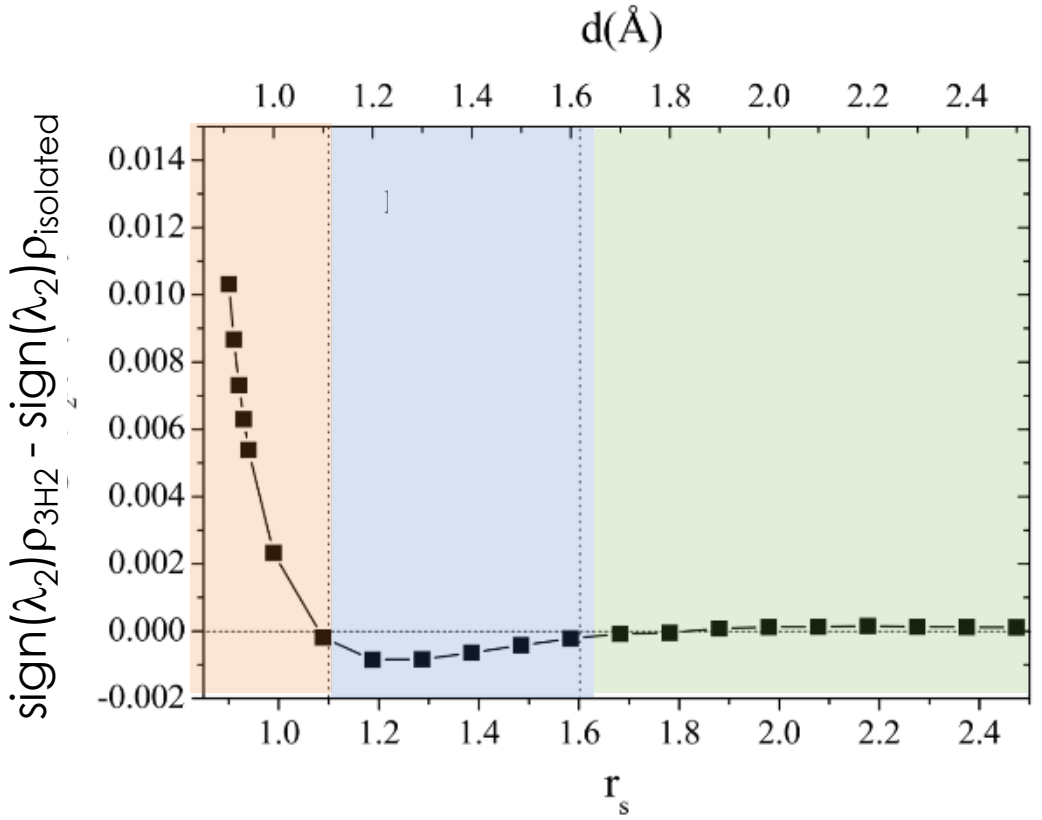

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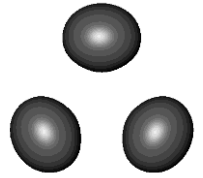

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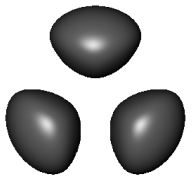

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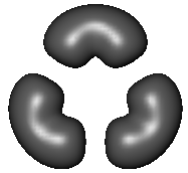

ELF (0.95)

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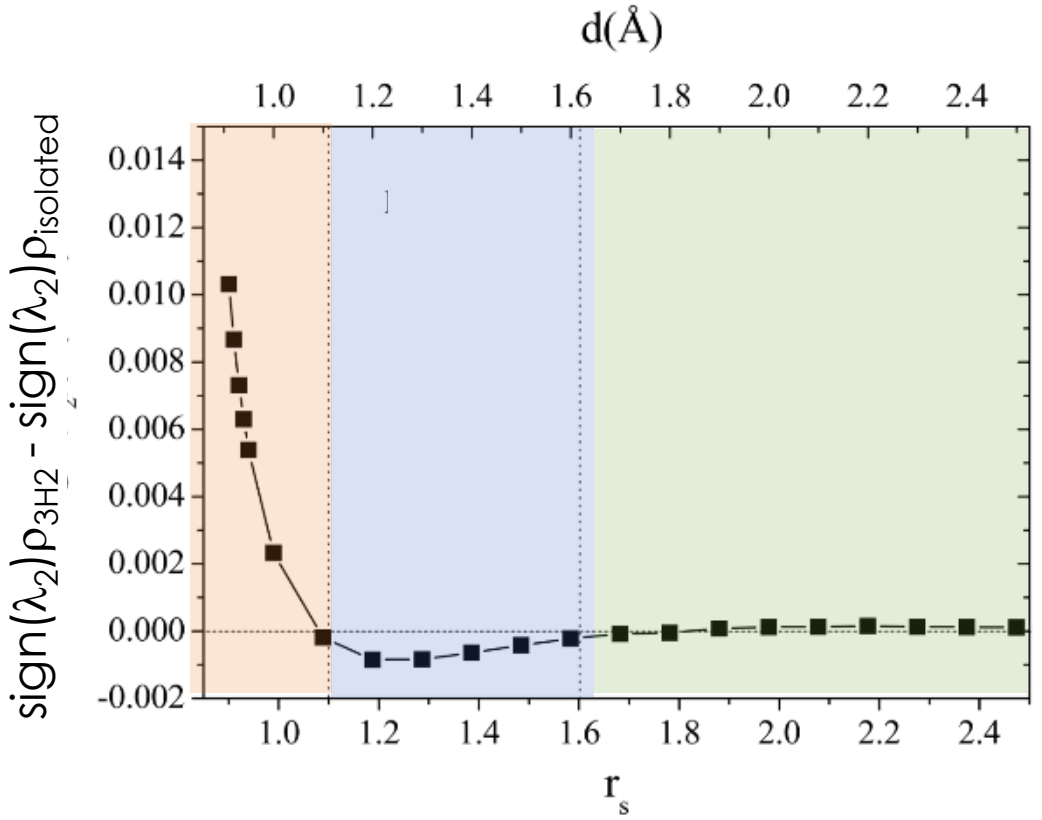

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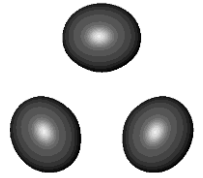

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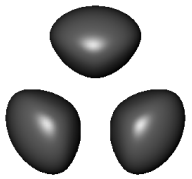

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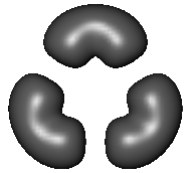

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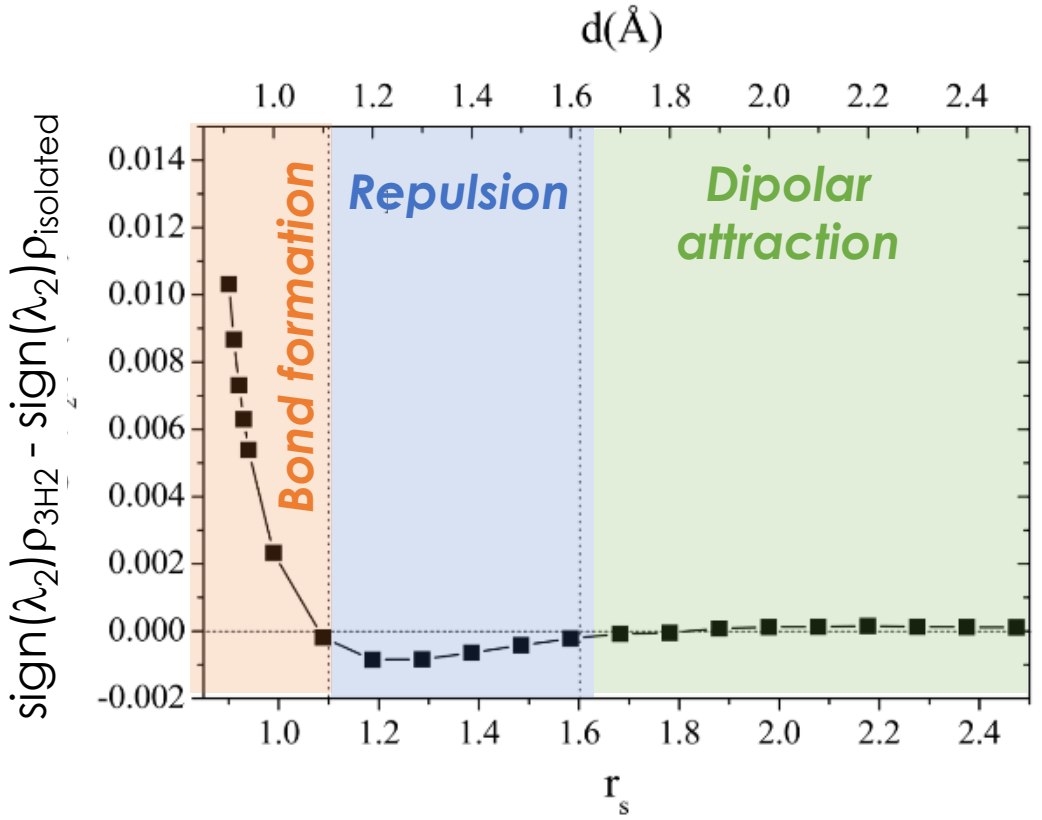

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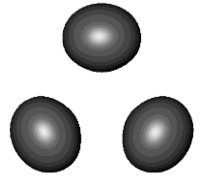

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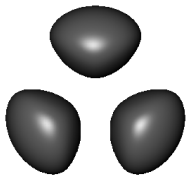

Deformation to avoid intermol. regions

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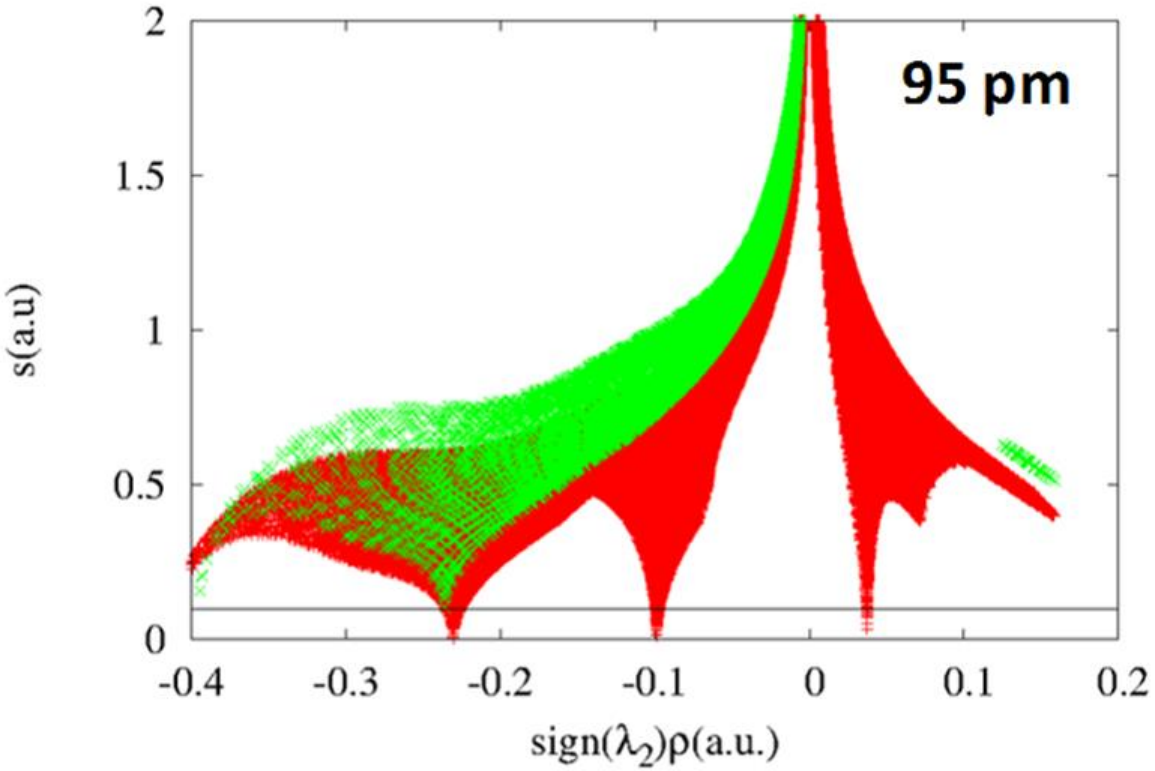
Volume of interaction



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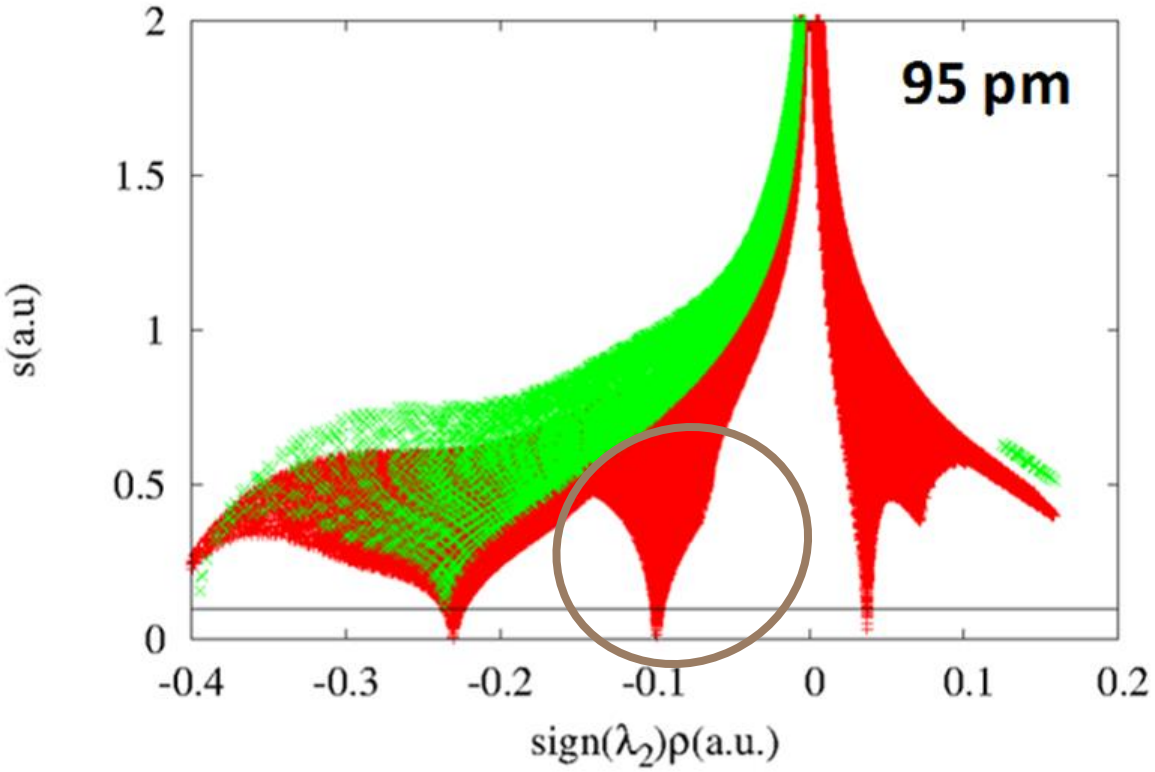
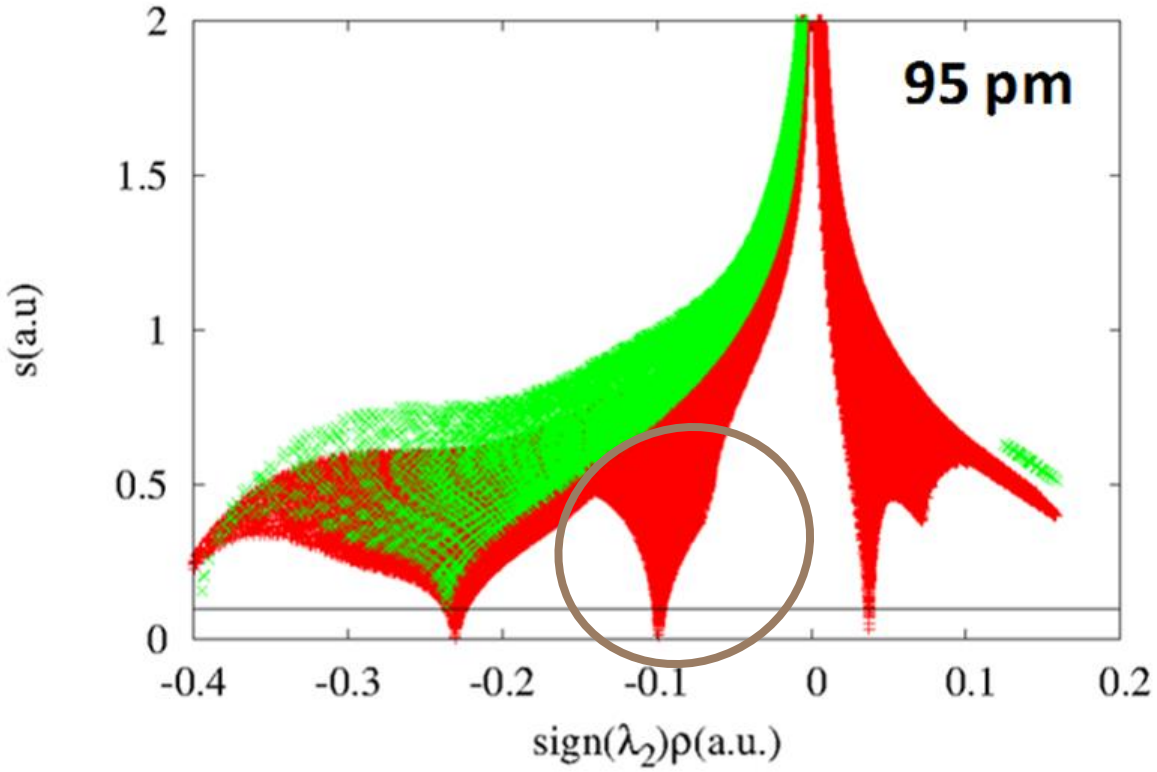


Localizing these points in the 3D space allows defining the volume of interaction.

Volume of interaction



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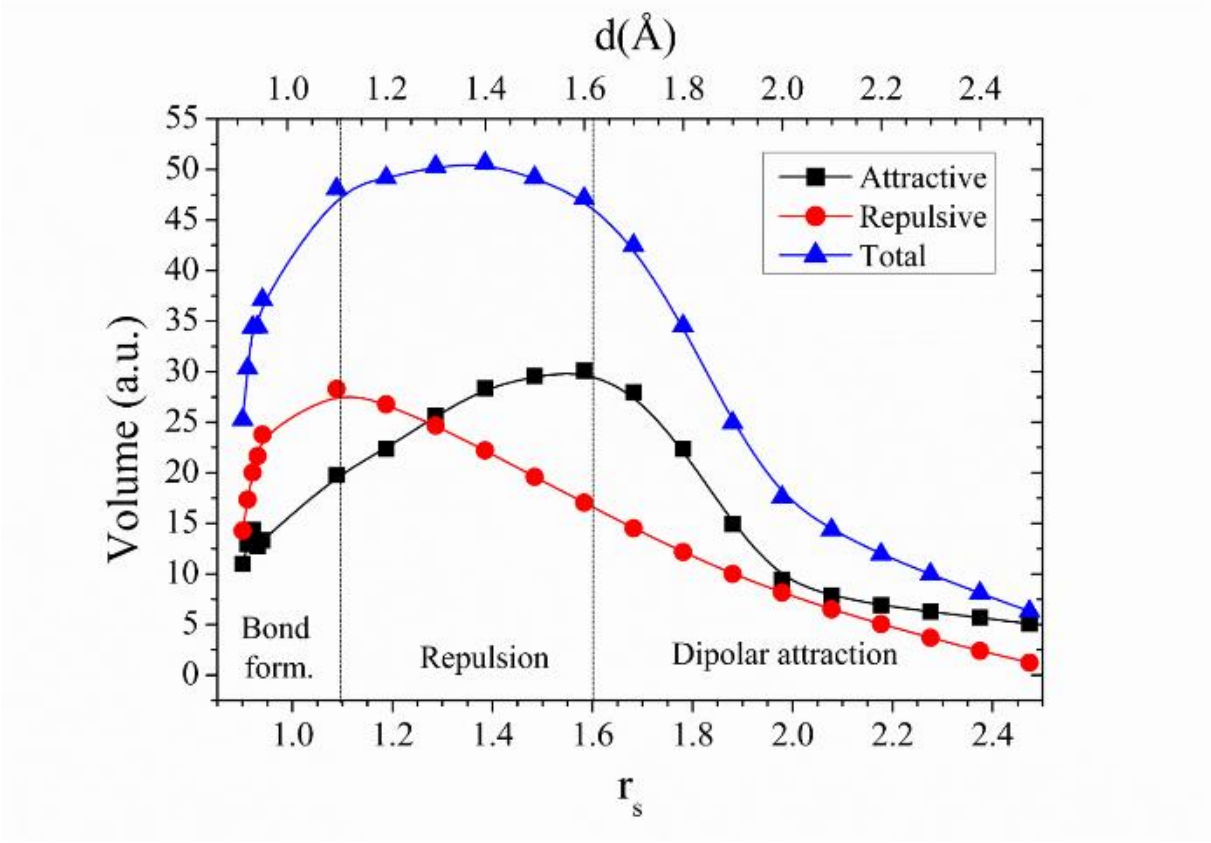

The global volume of interaction behaves like in a chemical reaction (maximum at the TS)

Summary

Analysis of H-H distances :

- Coexistence of 2 phenomena having opposite effects on the H_2 bond length
  - Physical wall (H-H bonds shorter and stiffer)
  - Orbital mixing (H-H bonds longer and weaker)

Topological tools

As H_2 molecules are coming closer and closer

- Bond length adaptation + Electronic distribution adaptation
- 3 successive regimes: dipolar attraction, repulsion, bond formation

- Relevance of a very simple non periodic model to capture the essence of the P-induced phnomenon

After squeezing hydrogen in numerical experiments …

… experiencing squeezed time