Enlighten Chemical Interactions Using Real Space Theories of Chemical Bond

Current Topics in Theoretical Chemistry School – Trujillo, Peru
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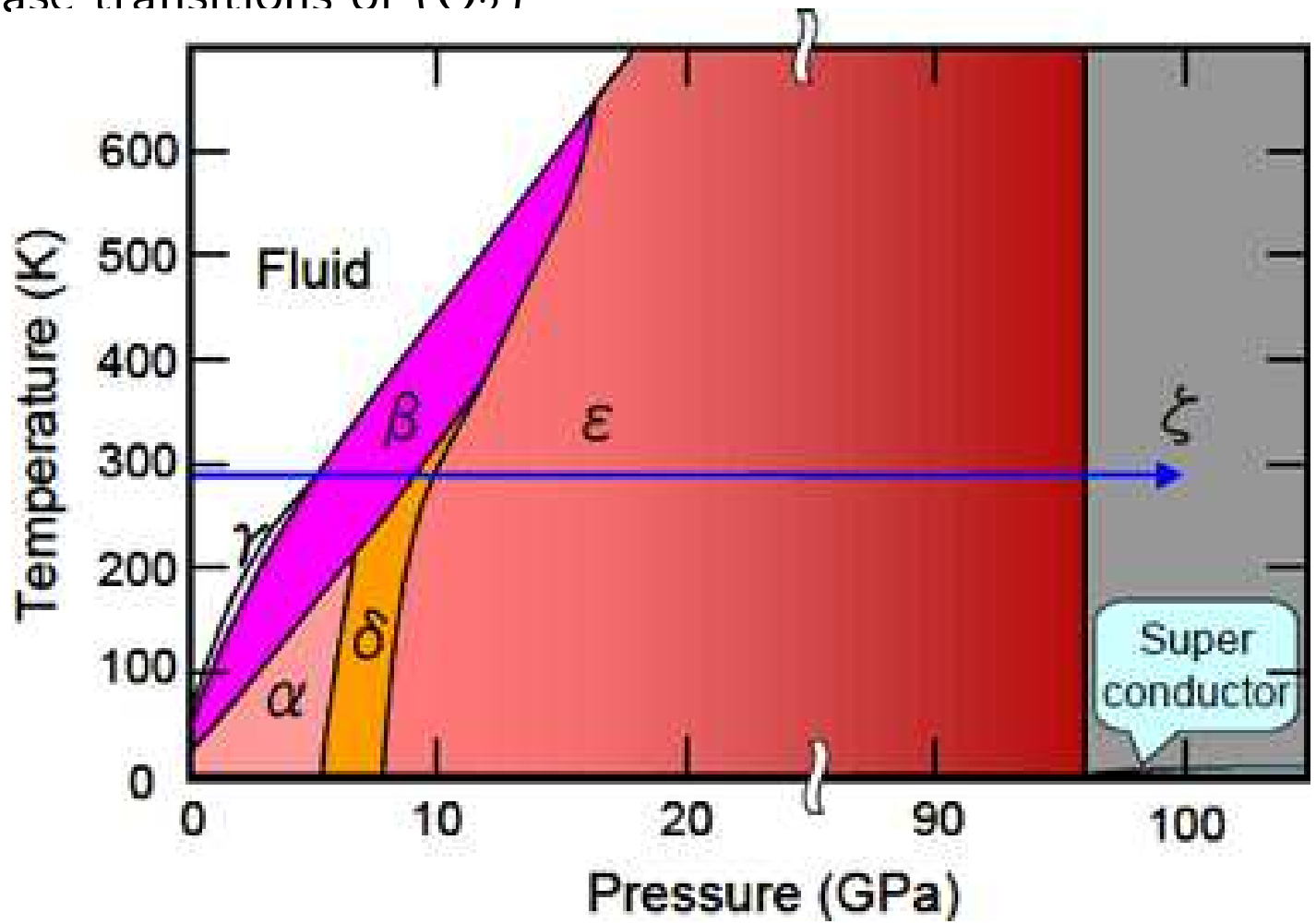
24-25 Sept 2016

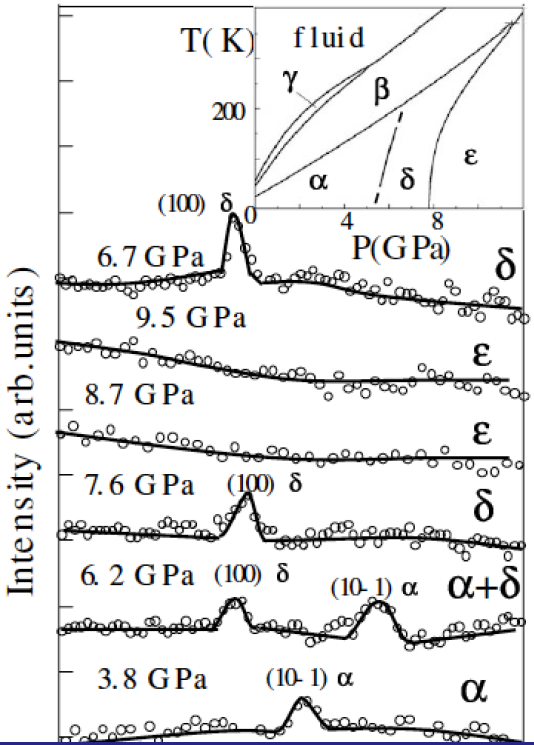
Outline

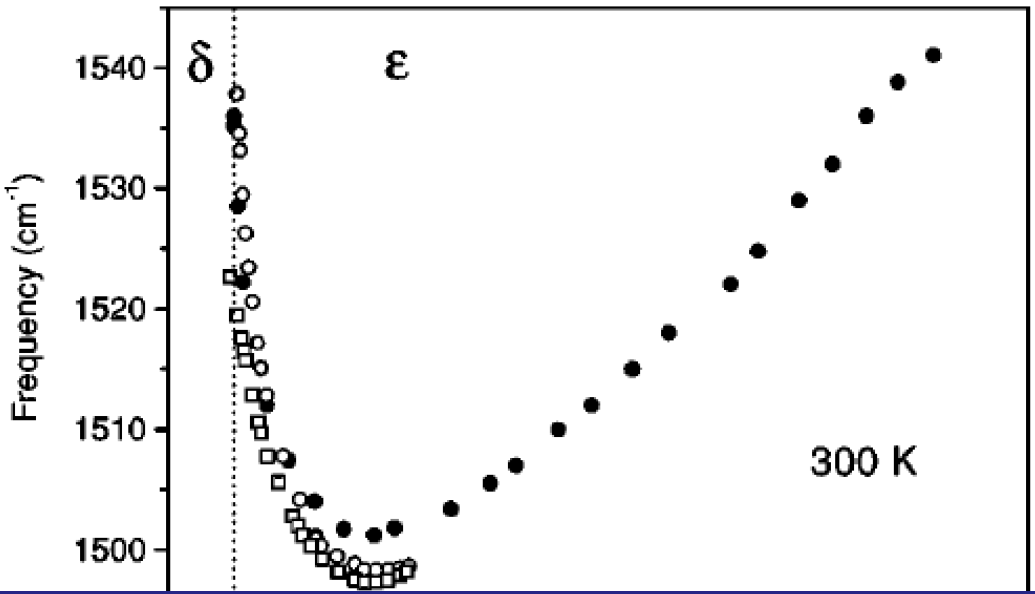
- Phase transitions of (O_2)



1GPa = 1×10^4 atm

- Changes in physical properties along the compression process
  - Magnetic and volume collapse (*Goncharenko, Phys. Rev. Lett. 2005, 94, 1*)
  - Peculiar spectroscopic behavior (*Gorelli, et al., H. Phys. Rev. B. 2001. 63, 104110*)





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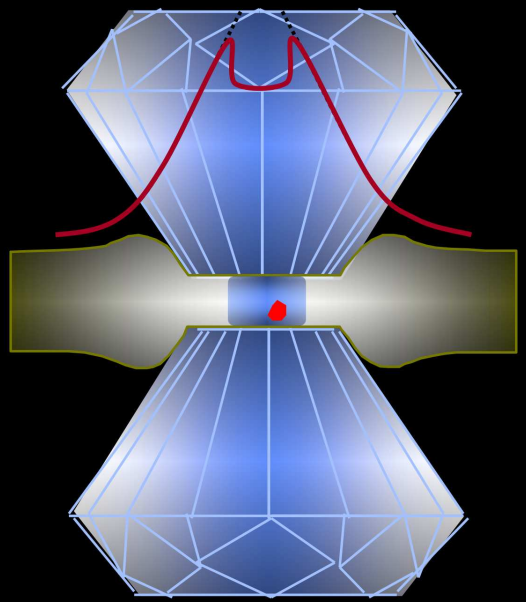
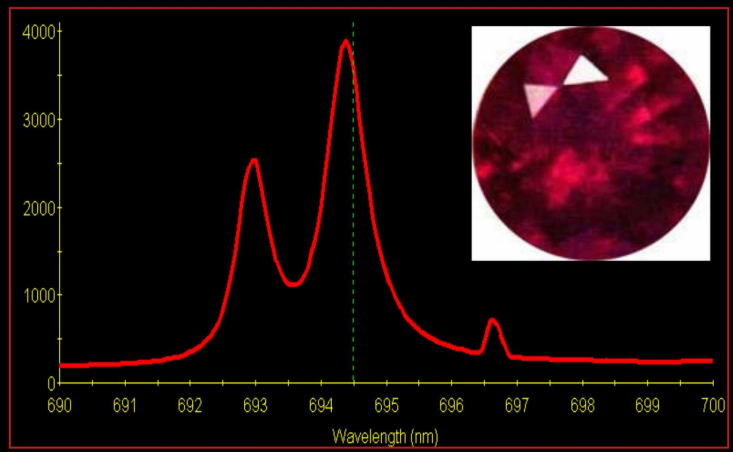
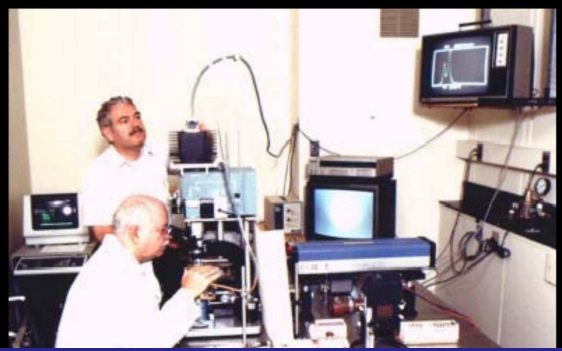
Escala de presión-luminiscencia del Rubí

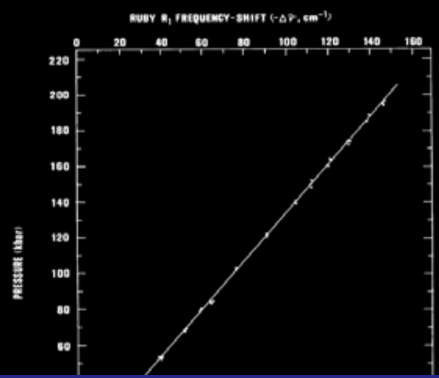


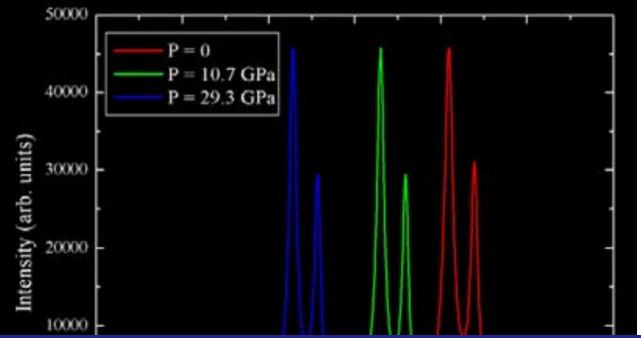


$\Delta\lambda/\Delta P = 0.365$ A kbar^{-1}

$\Delta\lambda/\Delta P = -0.753$ cm^{-1} kbar^{-1}

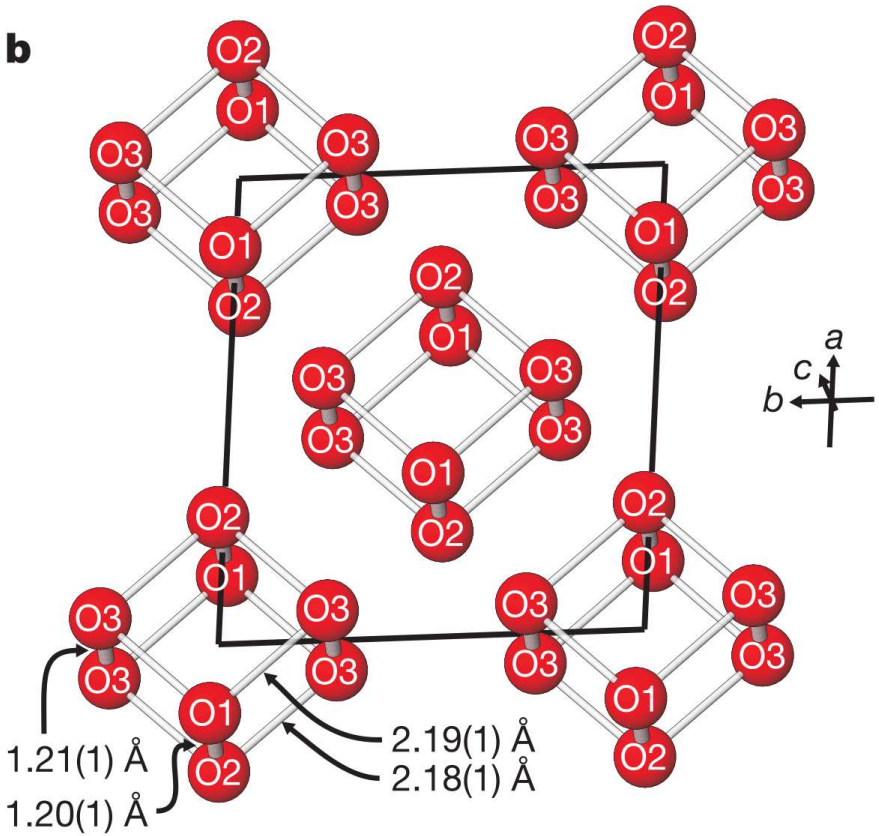






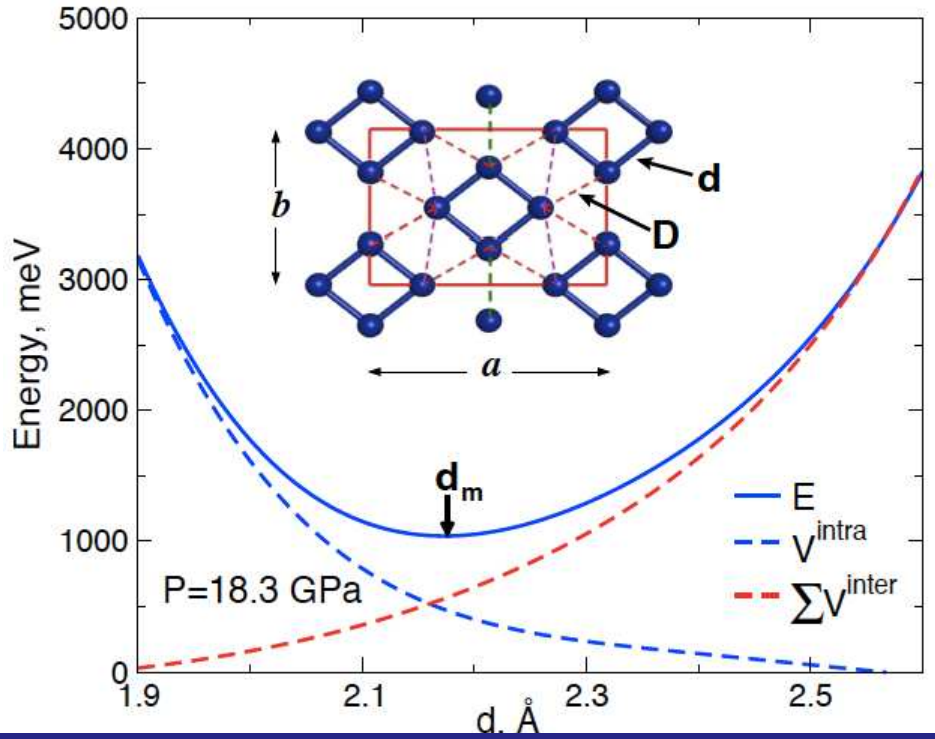
The solid, $(O_2)_4$ unit

- The structure for the ϵ-(O_2) was solved in 2006



Lundegaard, et al. *Nature* 2006 **443**, 201.
Fujihisa, et al. *Phys. Rev. Lett.* 2006 **97**, 085503.

- The experimental geometry of ϵ phase was reproduced using high correlated methodologies. RCCSD(T)/CASPT2 for $(O_2)_4$ plus a pair potential for neighbor O_2 molecules
$\mathrm{E(d)} = V^{intra}(d) + \frac{1}{2}\sum_{ij} V_{ij}^{inter}(r_{ij})$



Can we extract information about chemical bonding directly from Quantum Mechanics?

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- Wavefunction $\Psi(\vec{\chi}, t)$.
- **Operators**, $\hat{\mathscr{H}} = \hat{T} + \hat{V}$
- **Observables**, E .
- Electron density, $\rho(\vec{r}) = |\Psi|^2$
- Pair Density , $\rho_2(\vec{r}_1, \vec{r}_2)$
- La ecuación estacionaria de Schrodinger.

$$\hat{\mathscr{H}}\psi(\vec{\chi}) = E\psi(\vec{\chi}) \tag{1}$$

- There are not $\hat{\mathscr{O}}$ related with chemical bond, delocalisation, aromaticity, reactivity, etc.

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  - $E^A_{\text{self}} = T^A + V^{AA}_{en} + V^{AA}_{ee}$, self energy of an atom.

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  - Writing $\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho^{xc}_2(\mathbf{r})$,
    $E^{AB}_{\text{int}} = V^{AB}_{\text{cl}} + V^{AB}_{xc}$, interaction between atoms, where
    $V^{AB}_{\text{cl}} = \int_A \int_B \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} + V^{AB}_{en} + V^{AB}_{ne} + V^{AB}_{nn}$
    y $V^{AB}_{\text{xc}} = \int_A \int_B \frac{\rho^{xc}_2(\mathbf{r})}{r_{12}}$

Blanco, et al., J. Chem. Theory Comput., 2005 **1**,1096.

- V_{cl}^{AB} measures the ionic contribution of a interaction.

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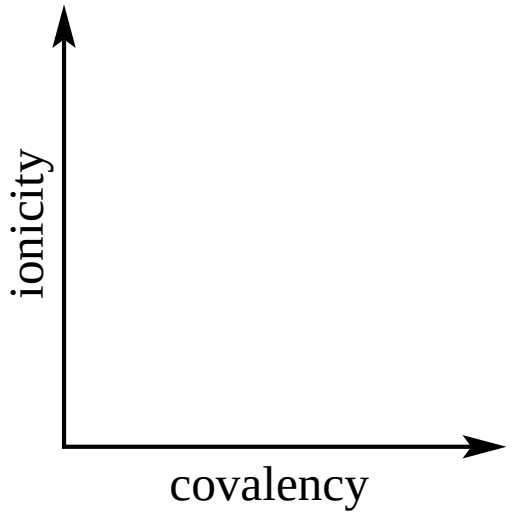

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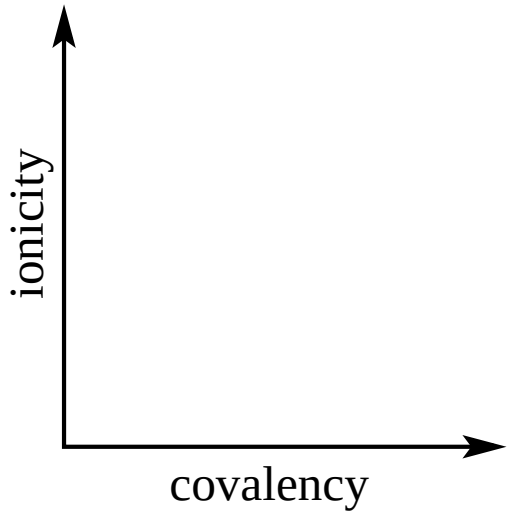

- A $\Re^3$ partition defined by the 3N-dimensional domain D
- $\Omega_k(\cup_{k=1}^{m}\Omega_k = R^3)$

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- In a integer distribution of electrons, $(S) = n_1, n_2, \cdots, n_m$, the probability to find n_1 electrons in Ω_1, n_2 in $\Omega_2, \cdots$ y n_m in Ω_m is defined by:

$$p(S) = \frac{N!}{n_1!...n_m!}\int_D |\psi|^2 dr_1 \cdots dr_N,$$

$$\sum_s p(S) = 1$$

- S is named as a real space resonance structure (RSRS)

Francisco et al. J. Chem. Phys. 2007, 126, 094102.

Computational details:

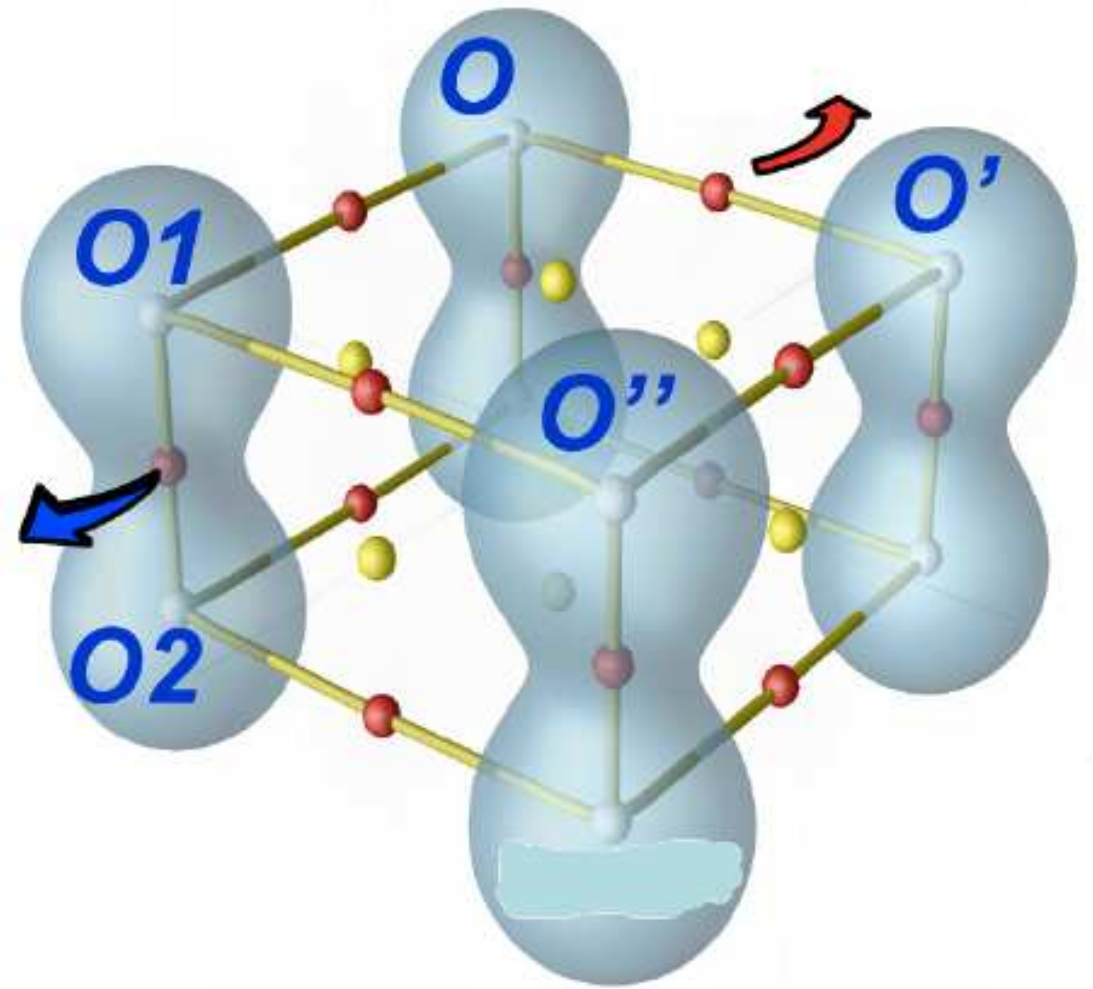
$(O_2)_4$ singlet state, CAS[8,8]//aug-cc-pVQZ

The reaction coordinate is the d_m defined by Bartolomei et al.

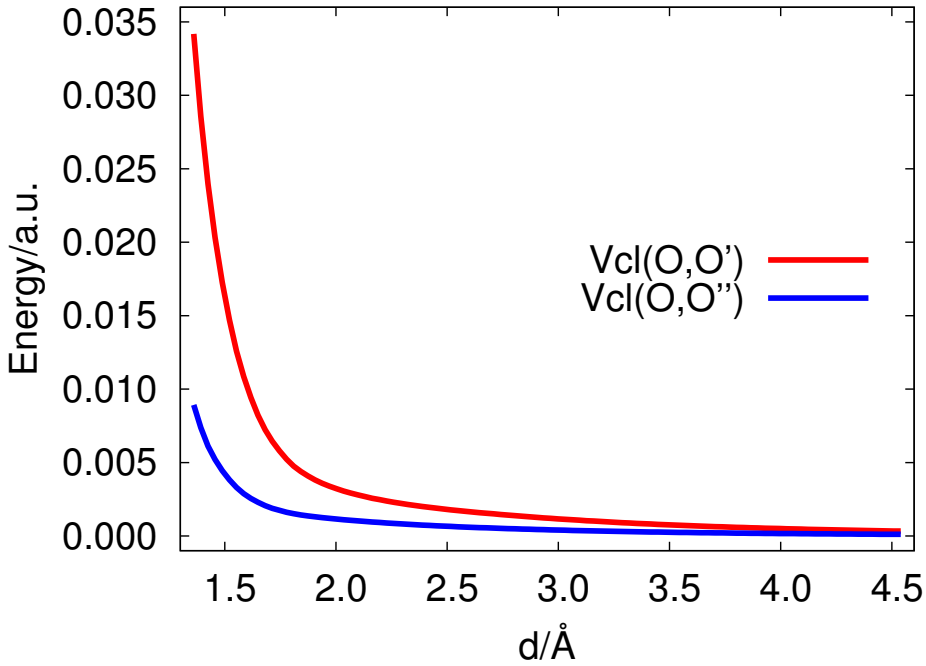
IQA partition was done using the PROMOLDEN code

EDF calculations where done with the EDF code

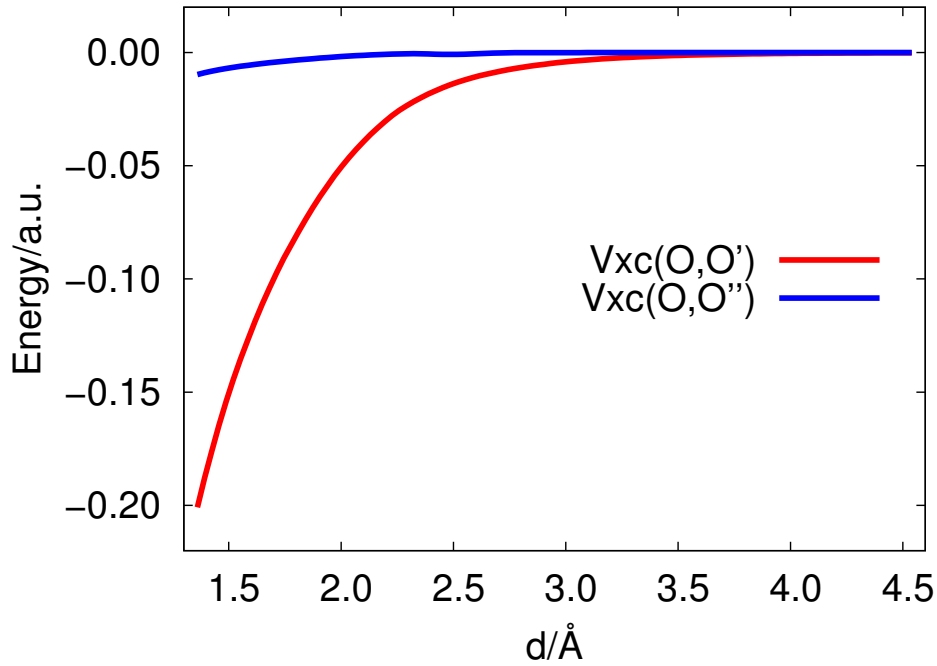
AIM partition of $\Re^3$.


O
O'
O1
O''
O2

V_{cl} inter-monomer

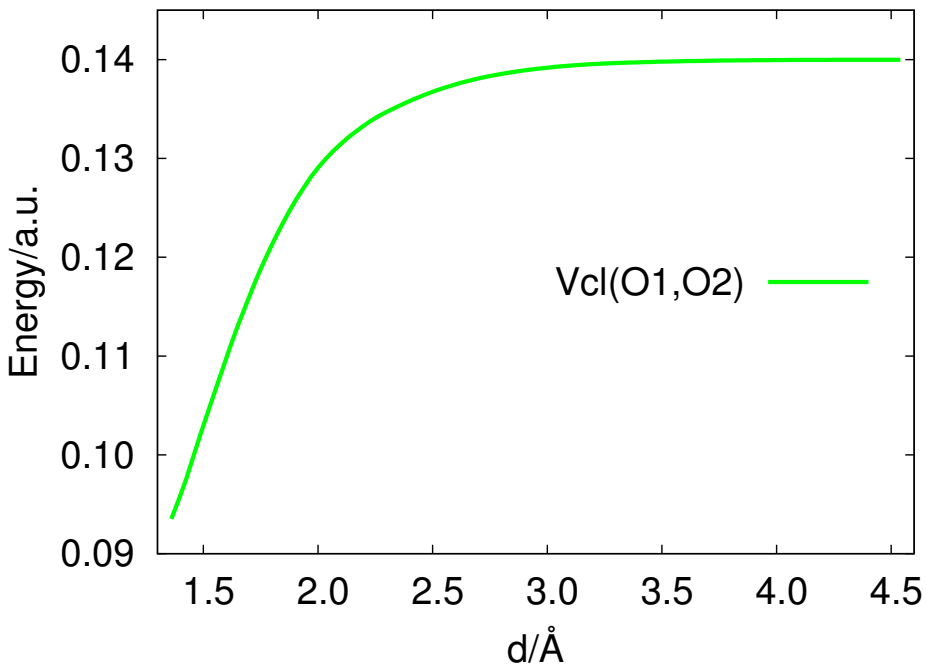


V_{xc} inter-monomer

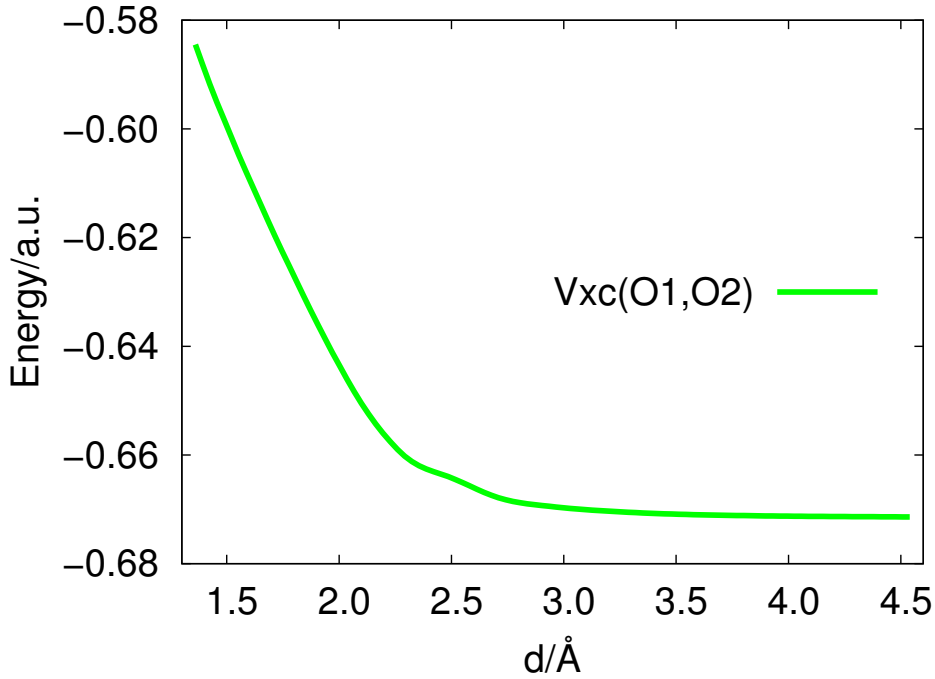


Garcia-Revilla, et al., J. Chem. Theory Comput. 2013, 9, 2179-2188

V_{cl} intra-monomer

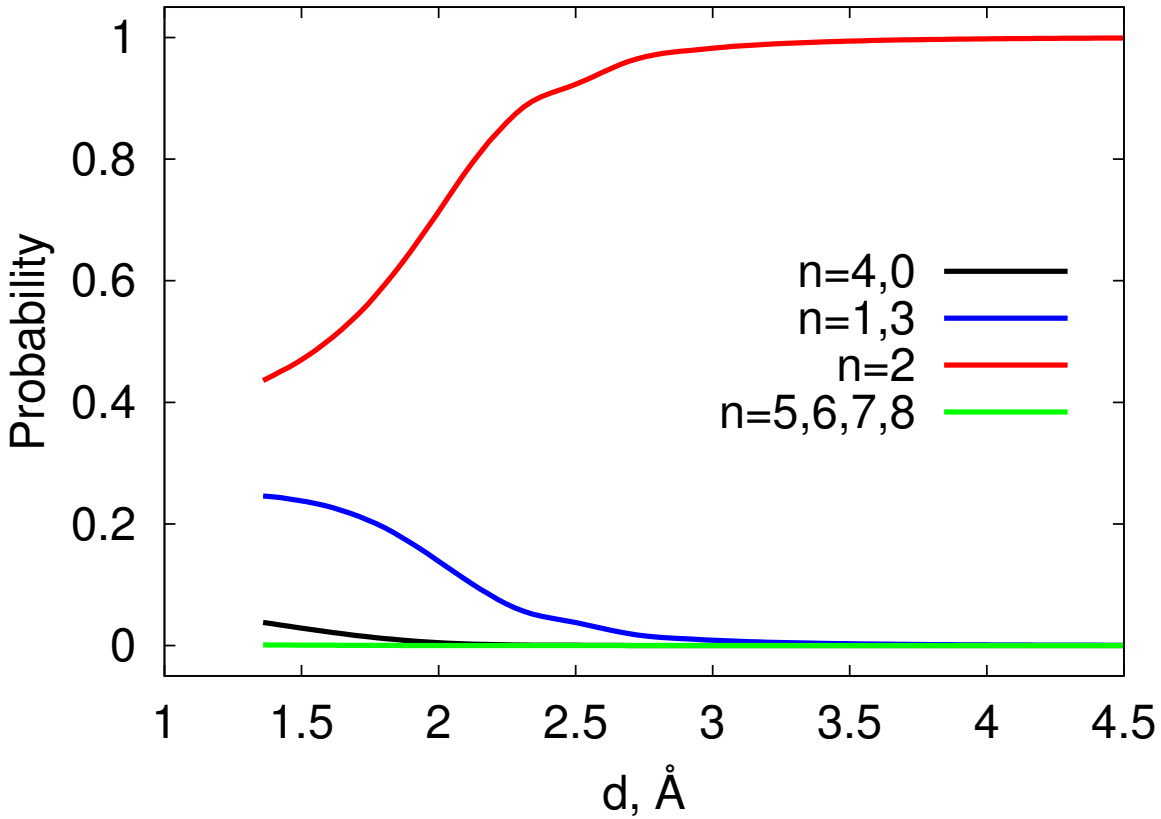


V_{xc} intra-monomer



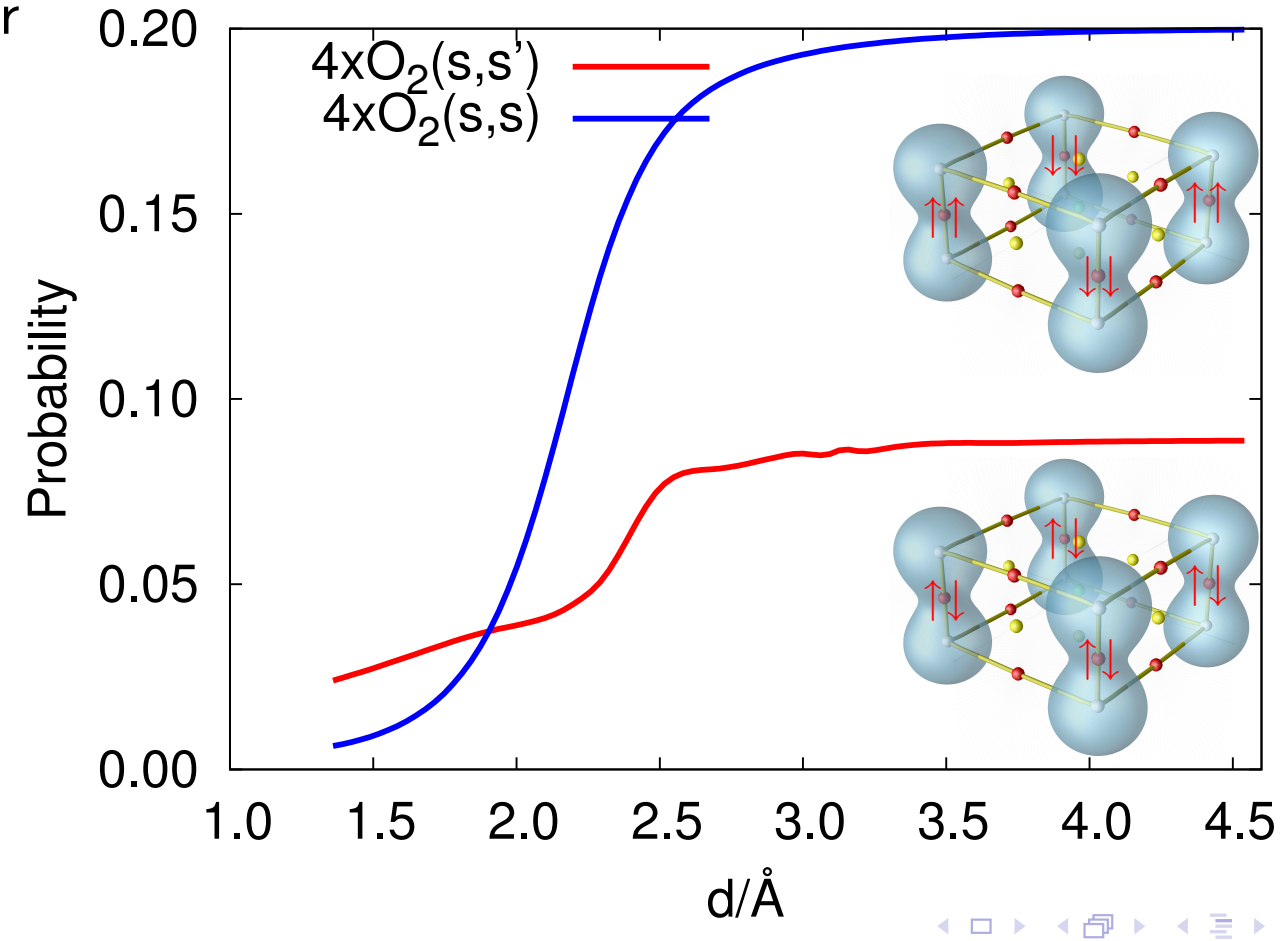
Garcia-Revilla, et al., J. Chem. Theory Comput. 2013, 9, 2179-2188

Spinless EDFs for the probability of finding a number n of active electrons in one oxygen molecule



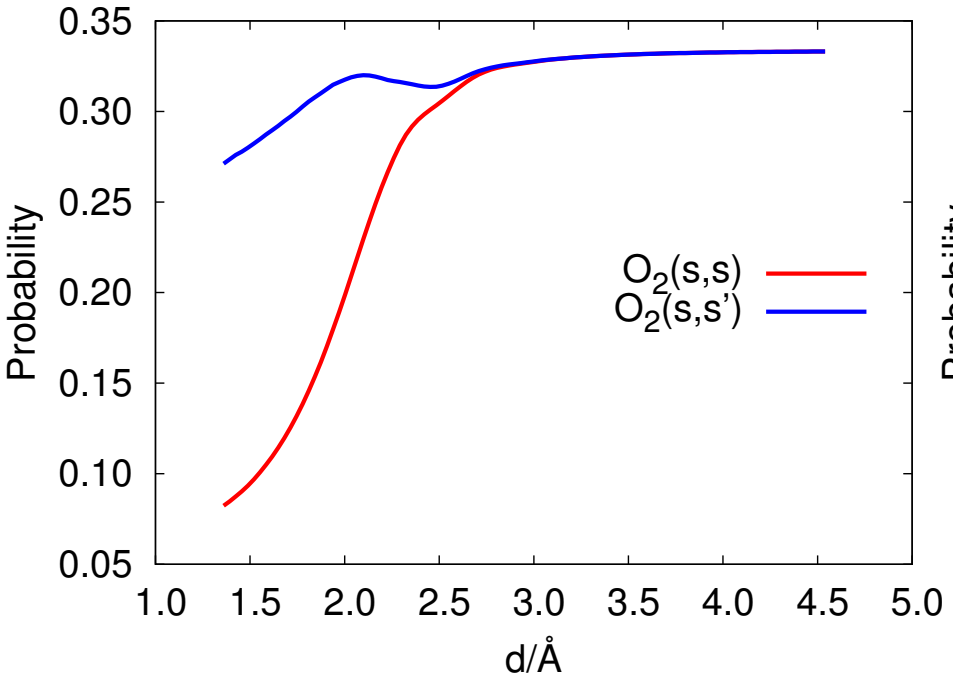
García Revilla, et al., J. Chem. Theory Comput. 2013, 9, 2170-2188

EDF probabilities for a spin arrangement in the molecular oxygen tetramer

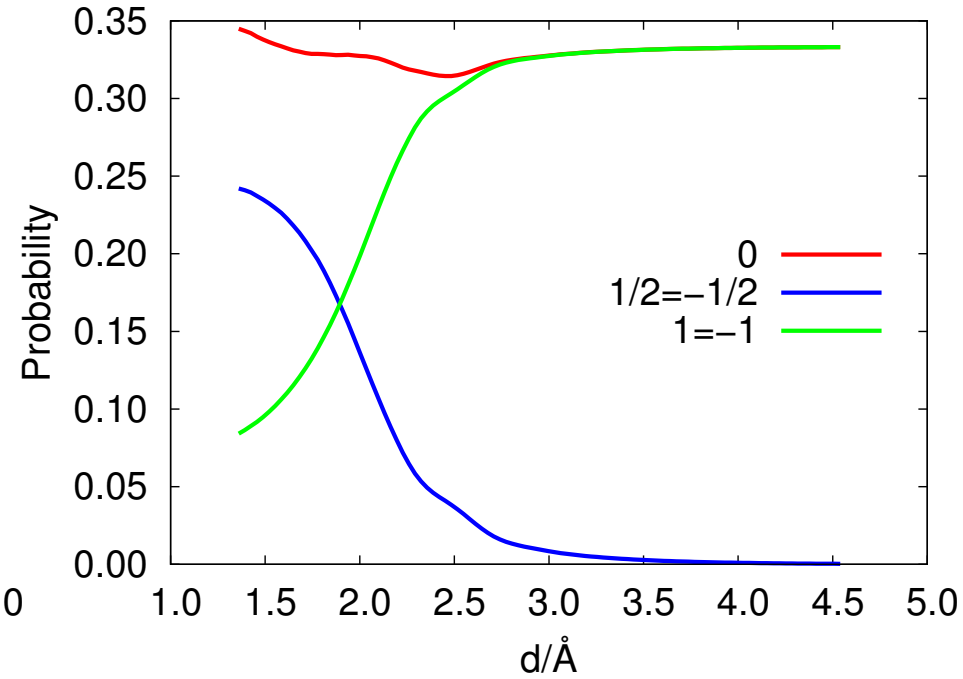


EDF probabilities for a given oxygen molecule within the molecular oxygen tetramer

S, single molecule



Ms, single molecule



Garcia-Revilla, et al., J. Chem. Theory Comput. 2013, 9, 2179-2188

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- Along the compression process the intermolecular bonding is built up from a simultaneous weakening of the intramolecular bond.
- EDF reveals the changes in spin structure along the compression process of $(O_2)_4$.
- EDF evidences a pairing of the electron spins at short distances in $(O_2)_4$ in agreement with the experimental behavior.

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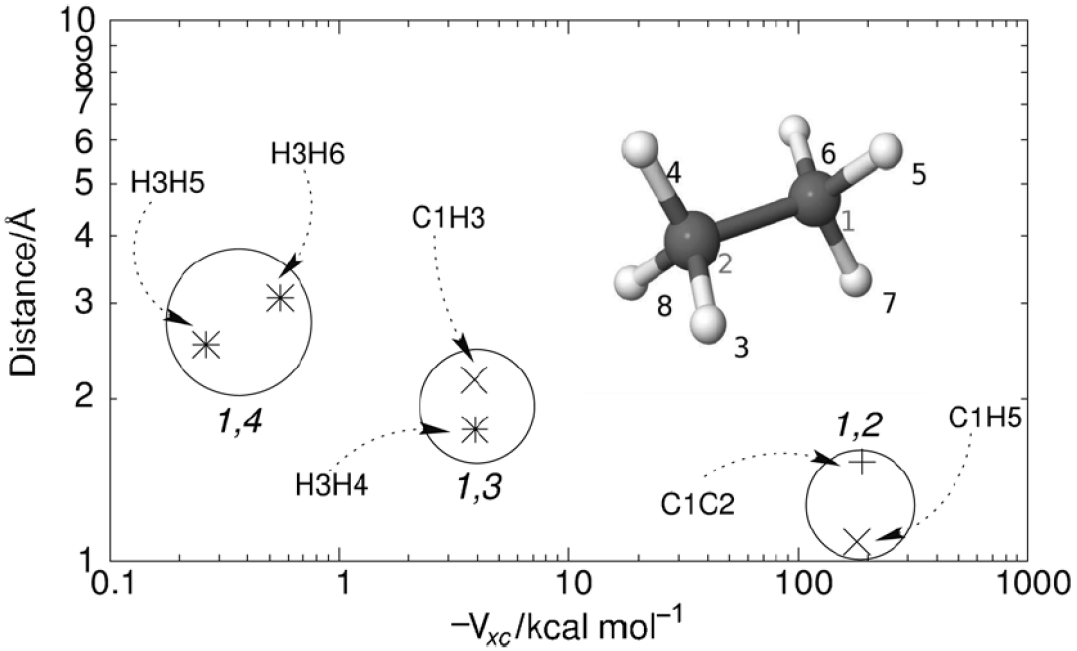
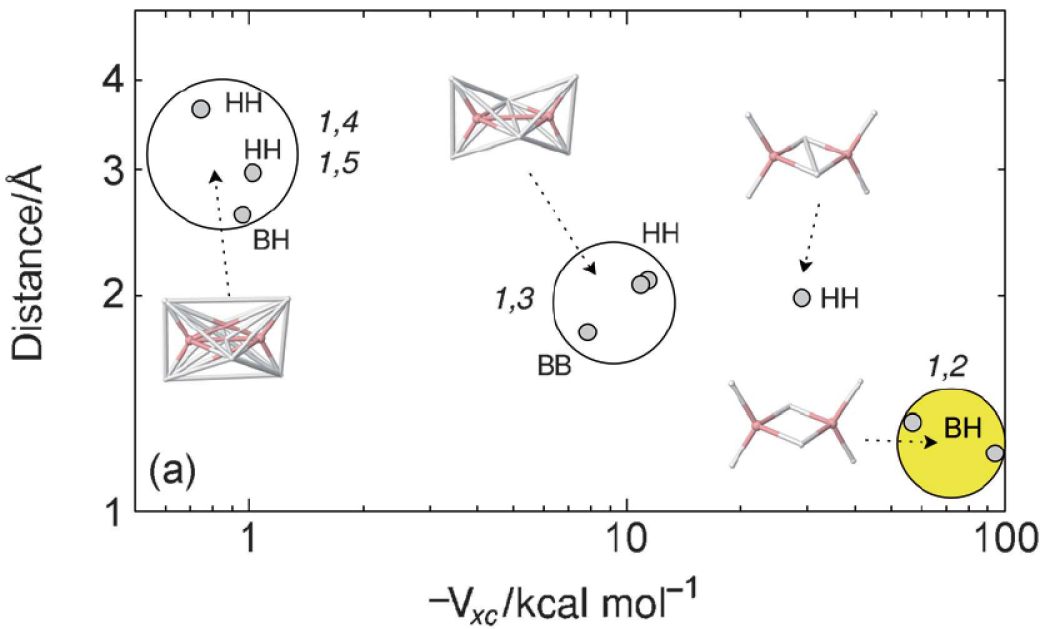
Beyond the topology of $\rho(r)$ of QTAIM, IQA can be sued to draw molecular graphs from energy partitioning.

- A simple example, V_{xc} can be used to differentiate between different chemical interactions in ethane.



3 clusters can be found: (C-C,vicinal C-H), non vicinal C-H. and non vicinal H-H

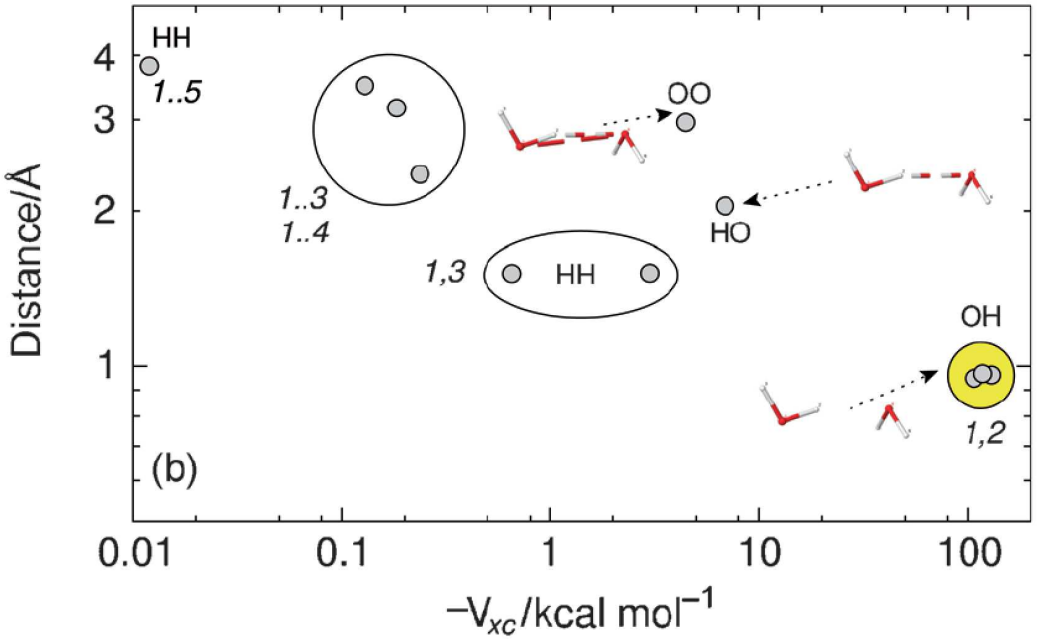
- Diborane interactions:



level of theory HF//6-311G(d,p)

clusters differentiate inteactions, observe molecular graphs

- Water dimer interactions:



clusters differentiate inteactions, observe molecular graphs

level of theory CAS[6, 5]//6-311G(d,p)

Conclusions$(O_2)_4$

- Vxc is useful to draw molecular graphs with physical and chemical insight

Thank you!