



國立清華大學

化學工程學系

National Tsing Hua University
Department of Chemical Engineering

2022 Summer School

Electronic Structure Calculations Using GFN2-xTB

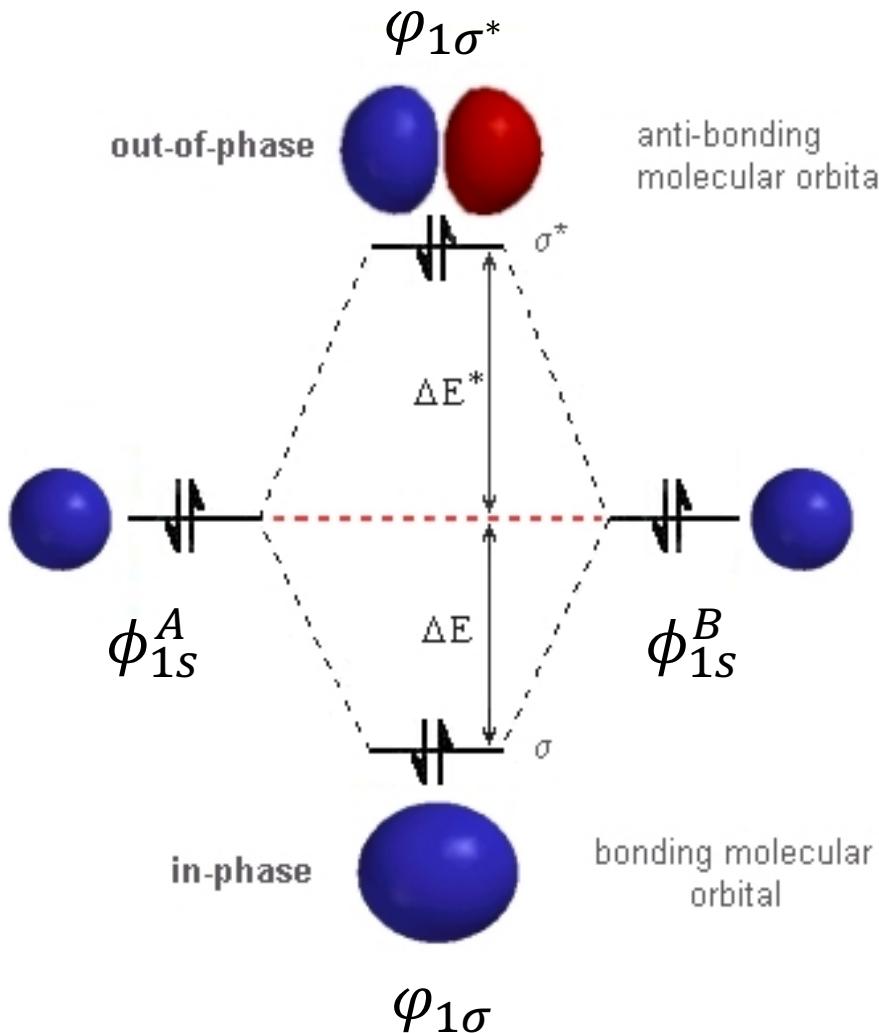
Prof. Kun-Han Lin (林昆翰助理教授)
Department of Chemical Engineering,
National Tsing Hua University, Taiwan

Week 2. Electronic Structure and Molecular Properties

What is electronic structure?

- The probability distribution of electron in the system.
 - The molecular orbitals
 - And the associated energies (energy levels of MOs)
 - The band structure and the density of states (crystals)
- Why is it important?
 - It determines the molecular properties
 - Explains the chemistry

Examples: why He_2 is not stable



Linear Combination of Atomic Orbitals (LCAO)

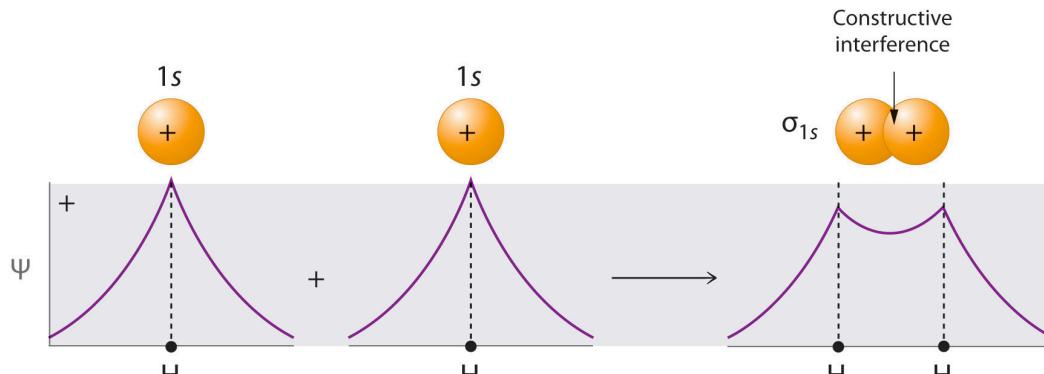
$$\varphi_{1\sigma} = \frac{1}{\sqrt{2(1+S)}} [\phi_{1s}^A + \phi_{1s}^B]$$

constructive interference

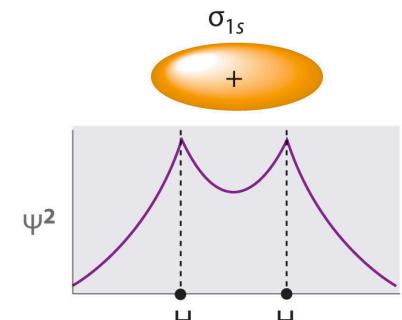
$$\varphi_{1\sigma^*} = \frac{1}{\sqrt{2(1-S)}} [\phi_{1s}^A - \phi_{1s}^B]$$

destructive interference

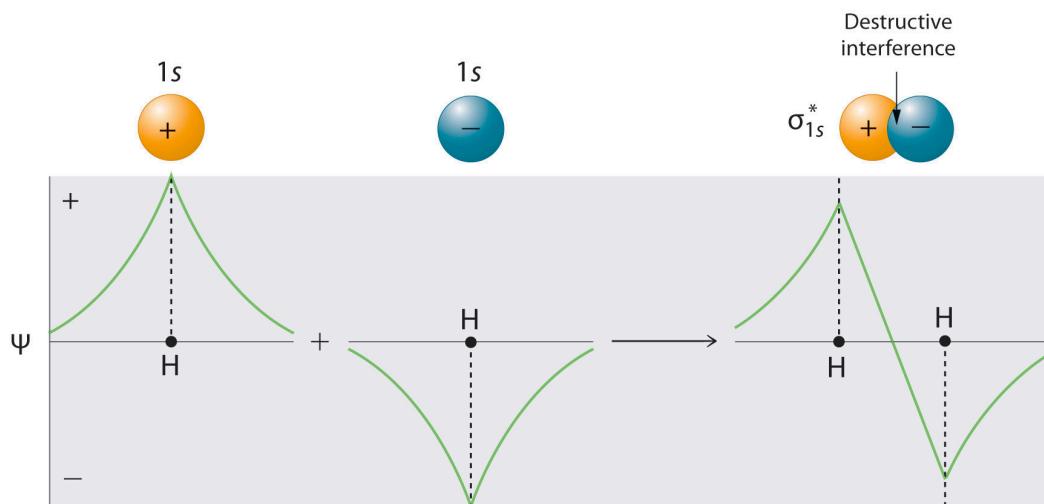
Bonding and anti-bonding orbitals



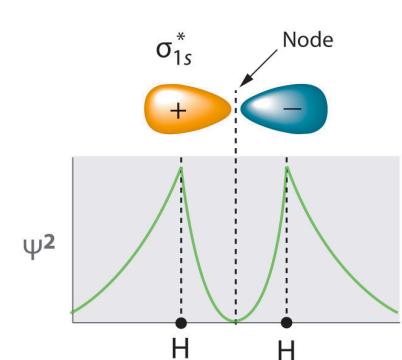
(a) Wave functions combined for σ_{1s}



(b) Bonding probability density



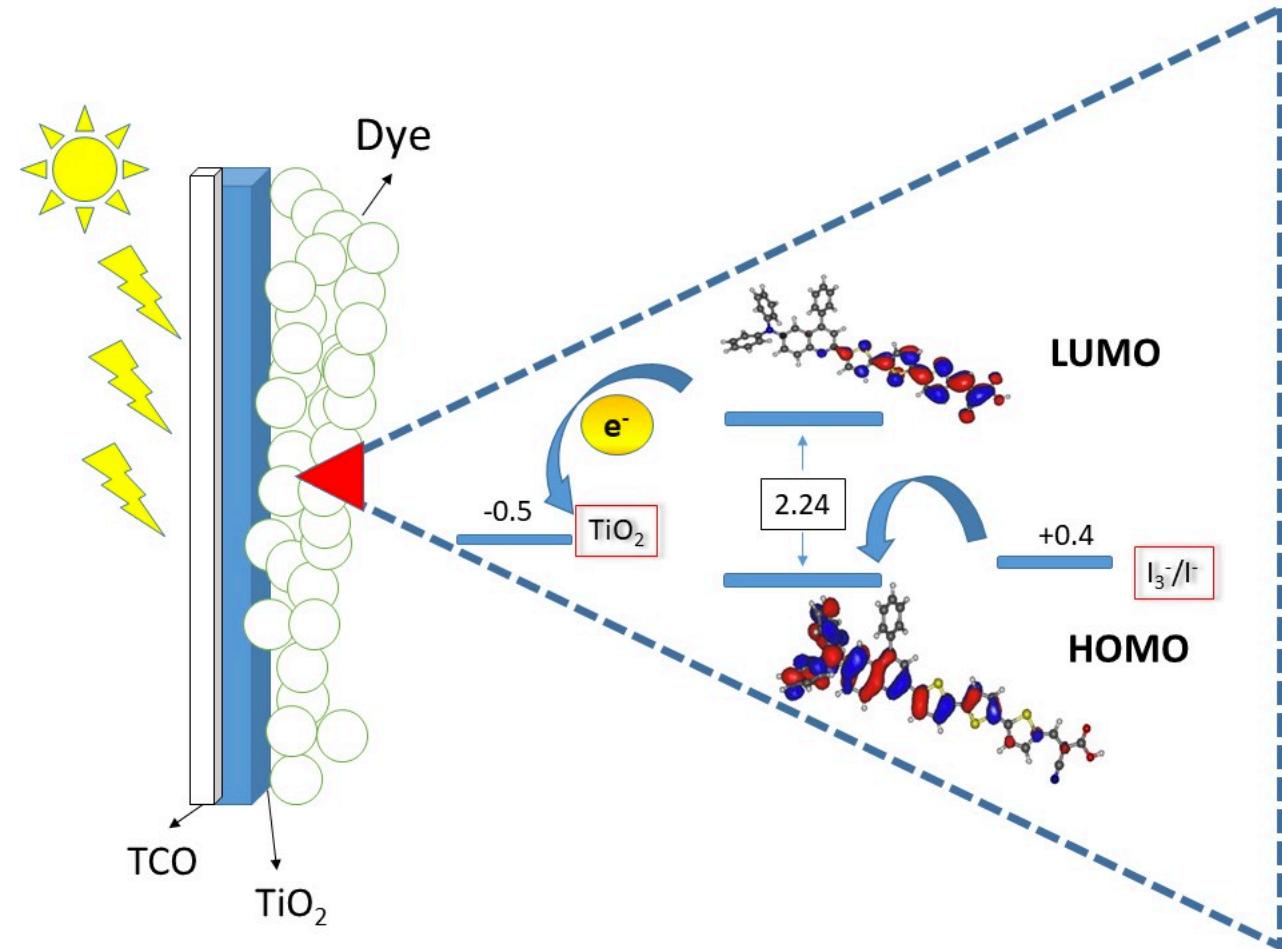
(c) Wave functions combined for σ_{1s}^*

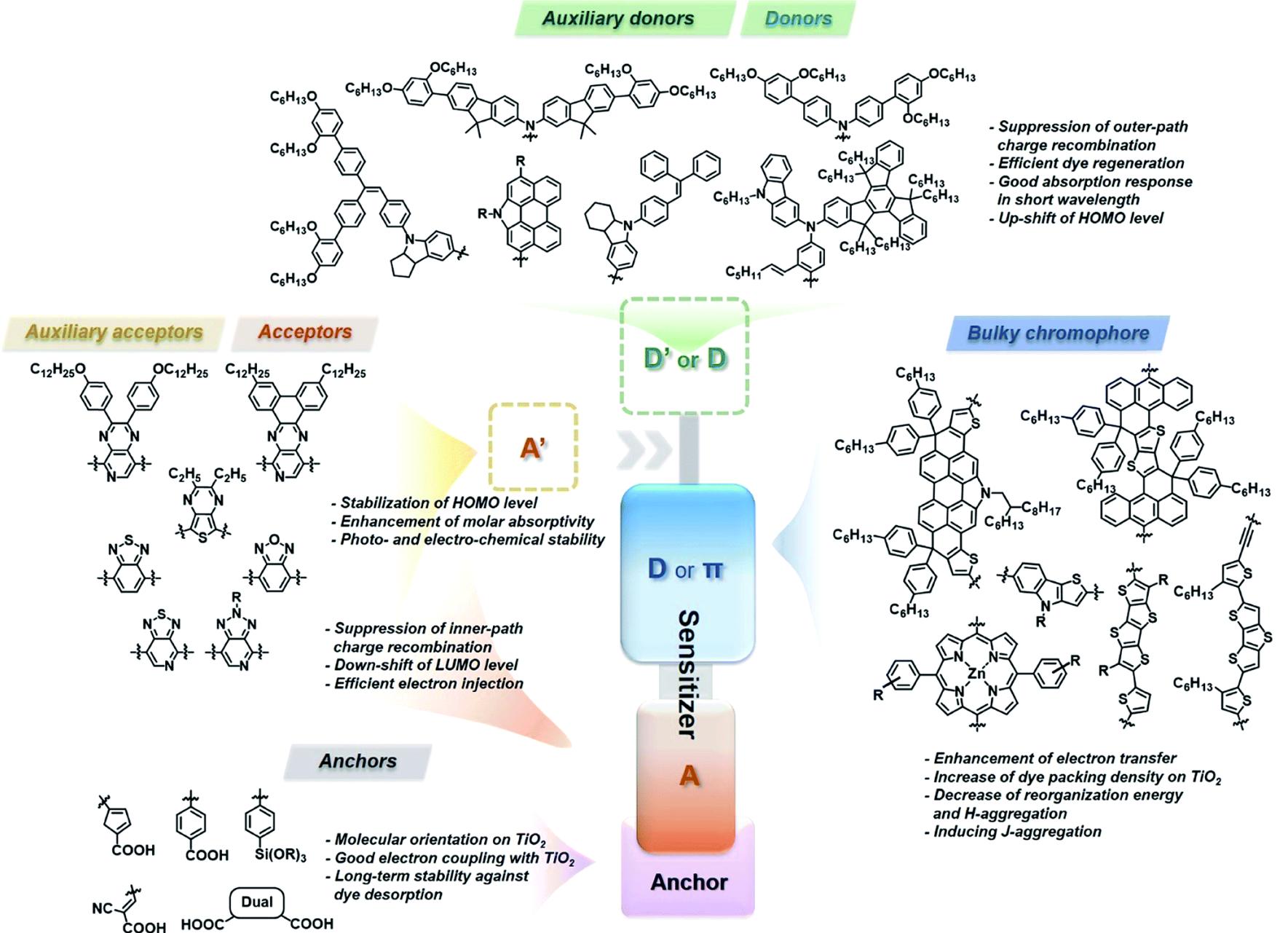


(d) Antibonding probability density

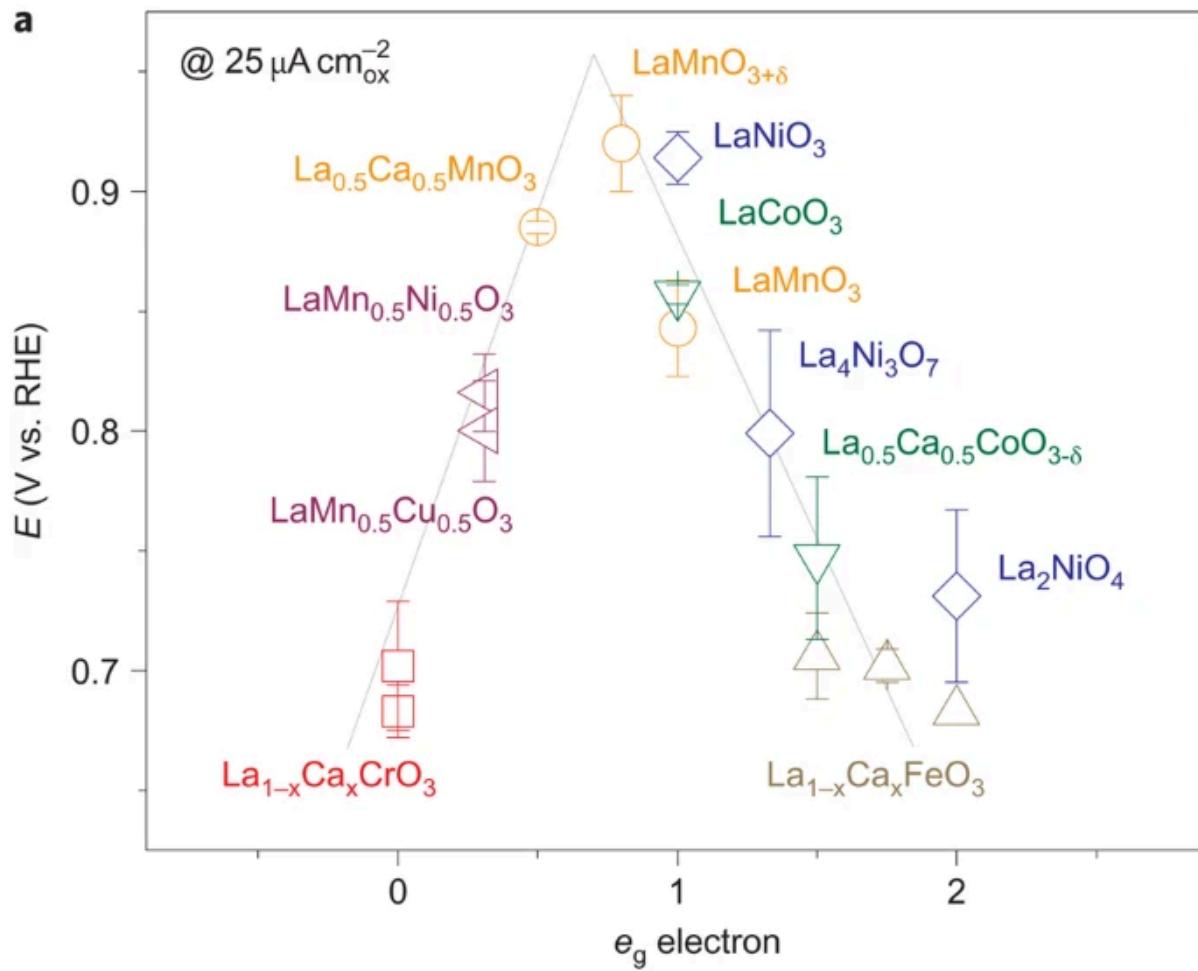
Examples: HOMO, LUMO and HOMO-LUMO gap

- MO energy matters!
 - Otherwise electron/hole separation won't occur
 - If HOMO-LUMO gap too large, no absorption
- MO distribution matters!
 - Less likely to recombine
 - Easier to transfer

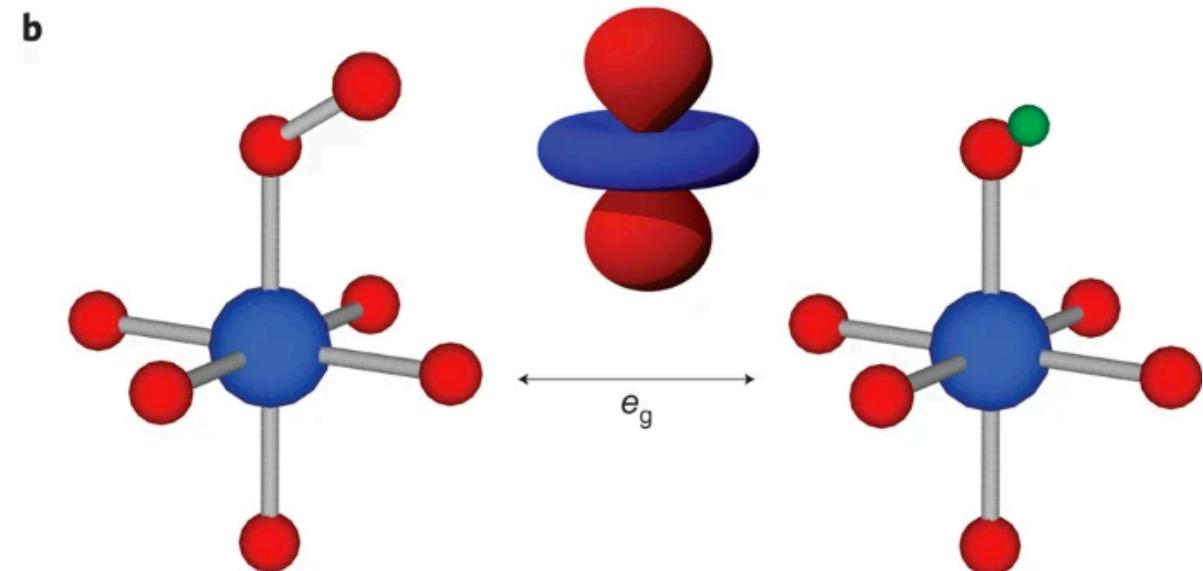




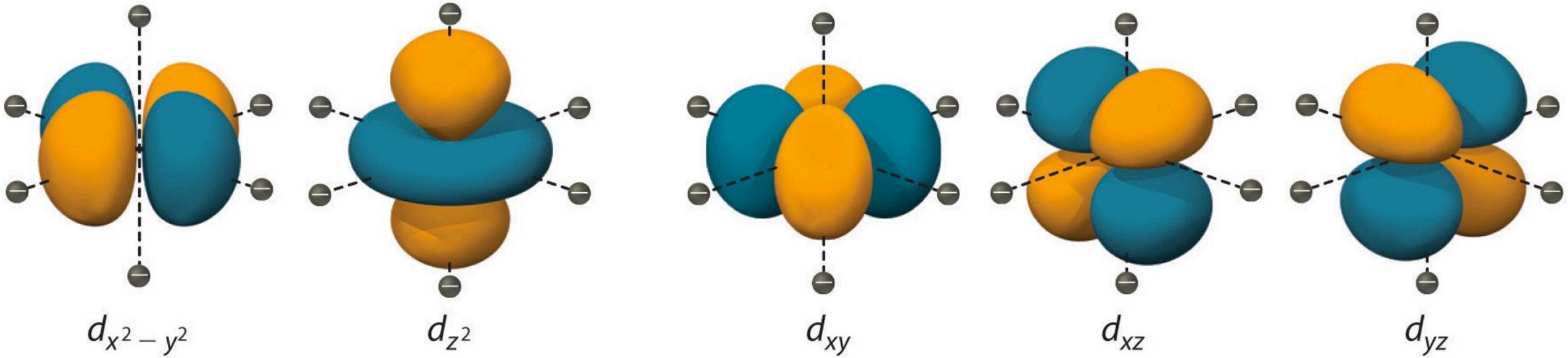
Examples: ORR activity vs e_g electron



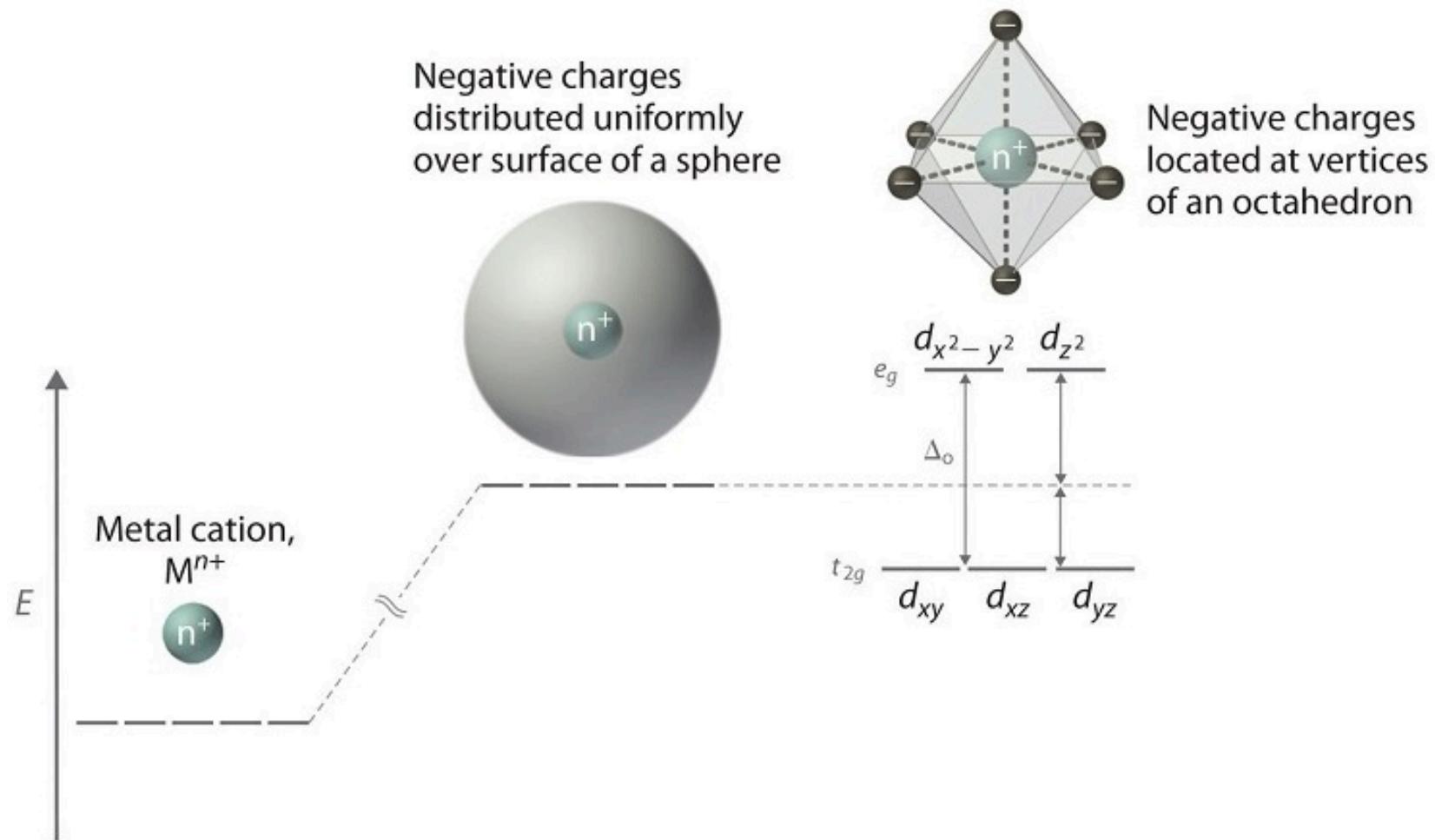
- Volcano plot! (Sabatier principle)
 - Bind "just right!"



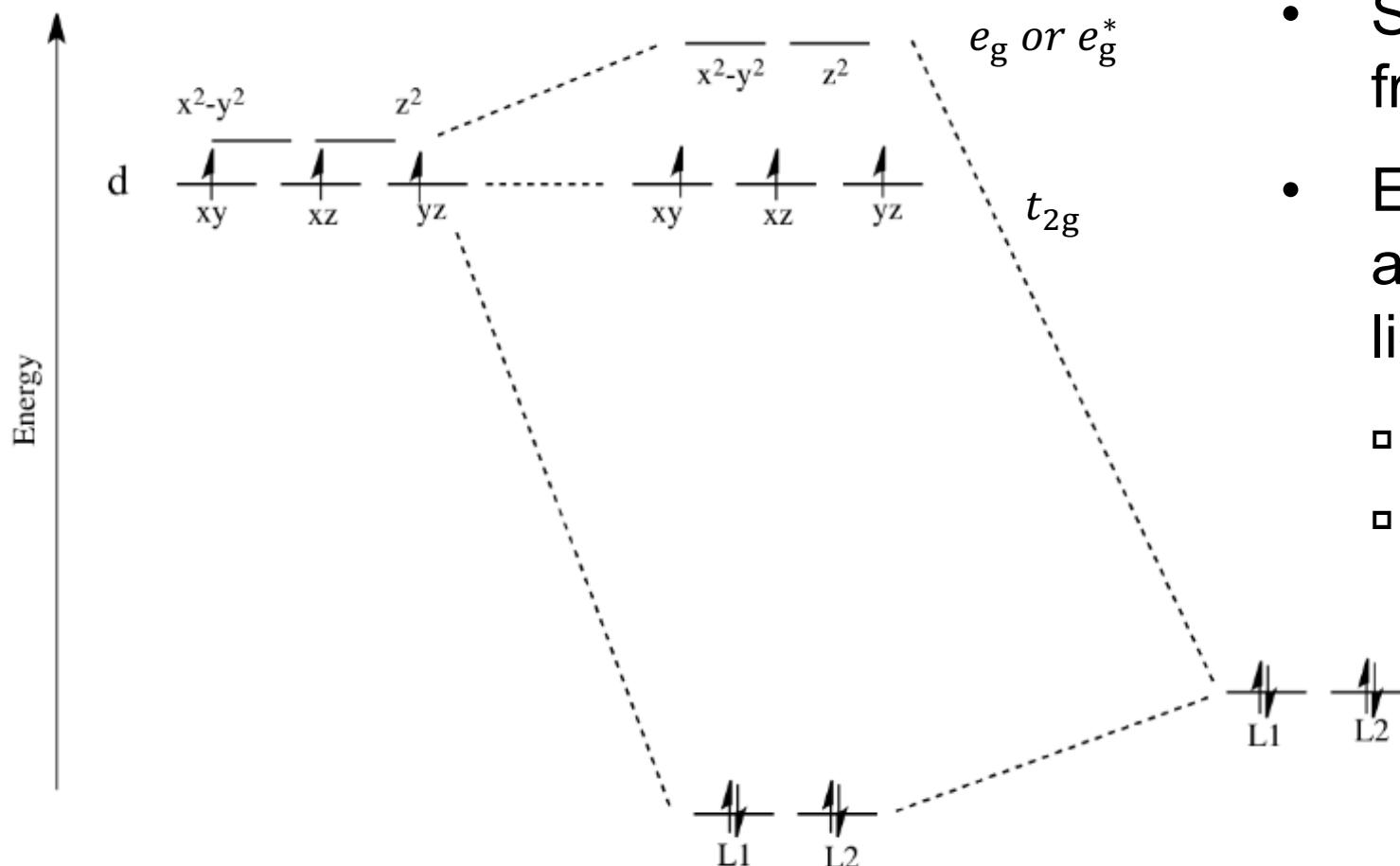
d orbitals of transition metals



Crystal field theory: octahedral



Ligand field theory: octahedral



- Simplified version: s and p orbitals from metals may also contribute.
- Energy of d orbitals from metals are usually much higher vs p from ligands.
 - Anti-bonding from metal mostly (e_g)
 - More electron in e_g , weaker in M-L bond.

Hands-on: electronic structure and molecular properties

Learning Goal

- Visualize molecular orbitals (MOs) of several examples.
- Visualize the bonding and antibonding MOs of H_2 .
- Compare MOs of metal complexes from xtb to that predicted from CFT and LFT.
- Compute ionization energy (IE) and HOMO level. Explain their differences.

Visualize MOs of the H₂ molecule

Inputs and output of this exercise

The outputs of this exercise were uploaded on Github repository

- H₂ at optimized geometry
 - W2/01_H2/opt
- H₂ where 2 H atoms are far from each other
 - W2/01_H2/far
- Isolated H
 - W2/01_H2/H

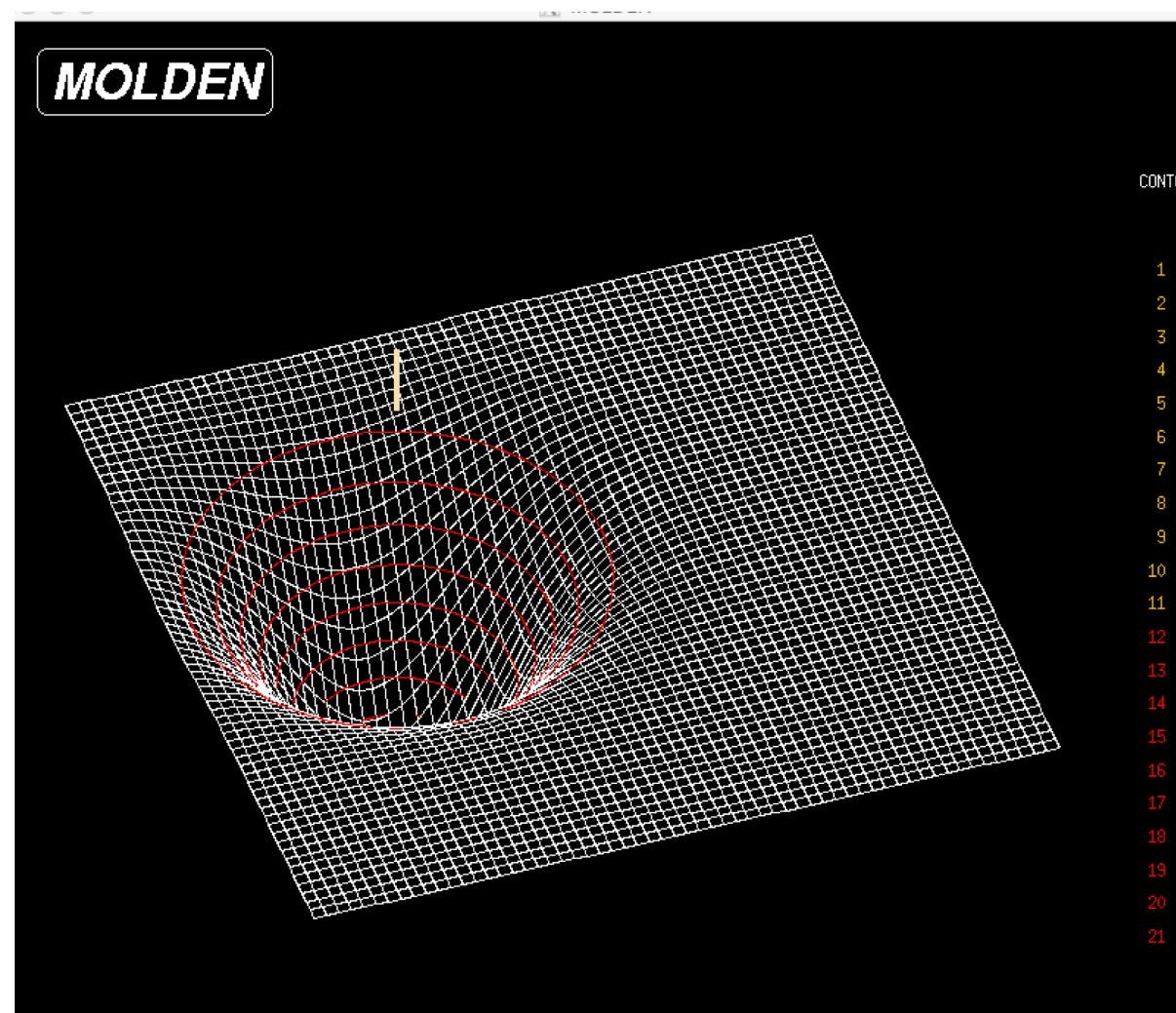
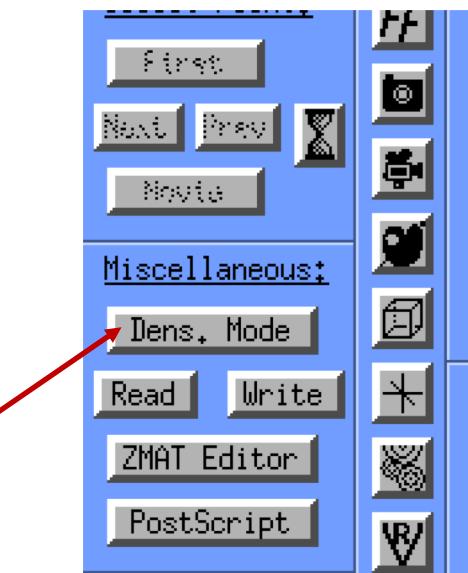
Step-by-step operation

- Create a folder called W2
 - mkdir W2
- Enter the folder
 - cd W2
- Create a folder under W2
 - mkdir 01_H2
 - cd 01_H2
- Copy the running script
 - cp yourpath/W2/01_H2/opt/opt_xtb.sh .
- Copy the H₂ input structure
 - cp yourpath/W2/01_H2/opt/input.xyz .
- Modify the last line of the script
 - vi opt_xtb.sh
 - xtb -c 0 -u 0 input.xyz -opt normal **--molden** > xtb.out
- Run it!
 - bash opt_xtb.sh

Create a molden.input
for MO visualization

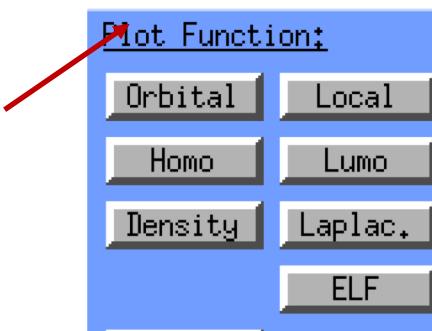
Visualize MOs of the H₂ molecule

- Open molden.input using molden
 - molden molden.input
- Click “Dens. Mode”
 - This is to switch to density mode



Visualize MOs of the H₂ molecule

- Click “Orbital”
 - Two MOs in total for H₂.
 - This is basis-set-size dependent!
 - One fully occupied; the other empty.
 - Click the first MO



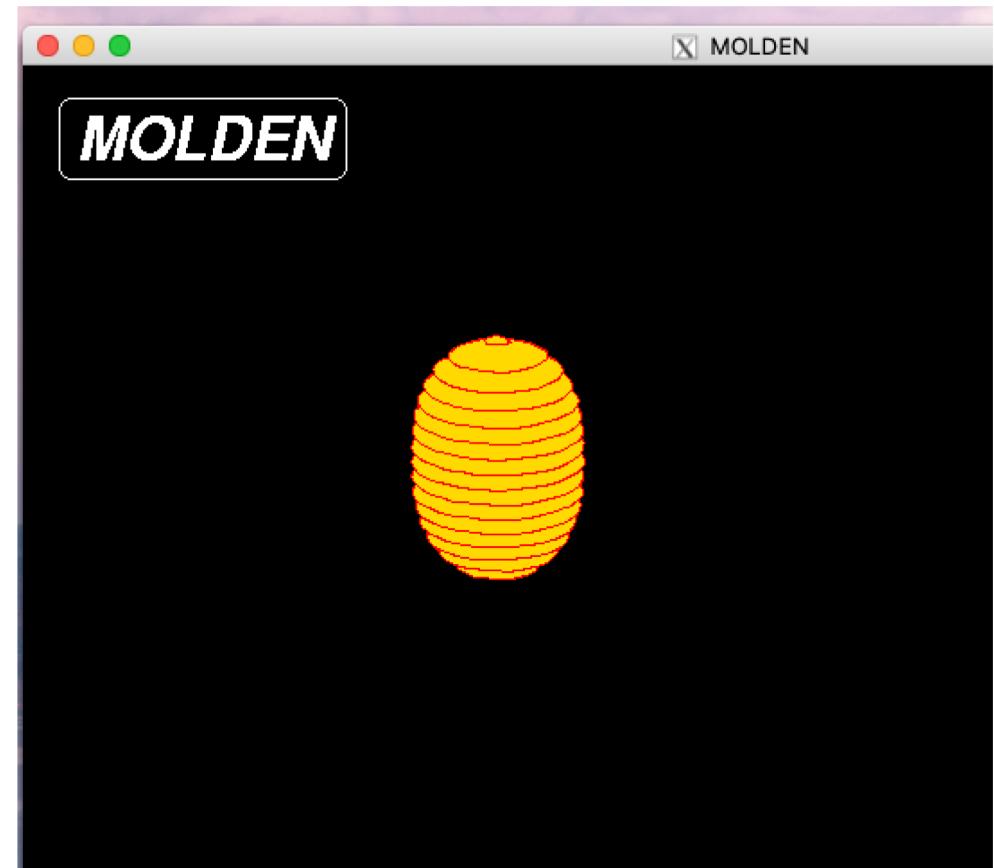
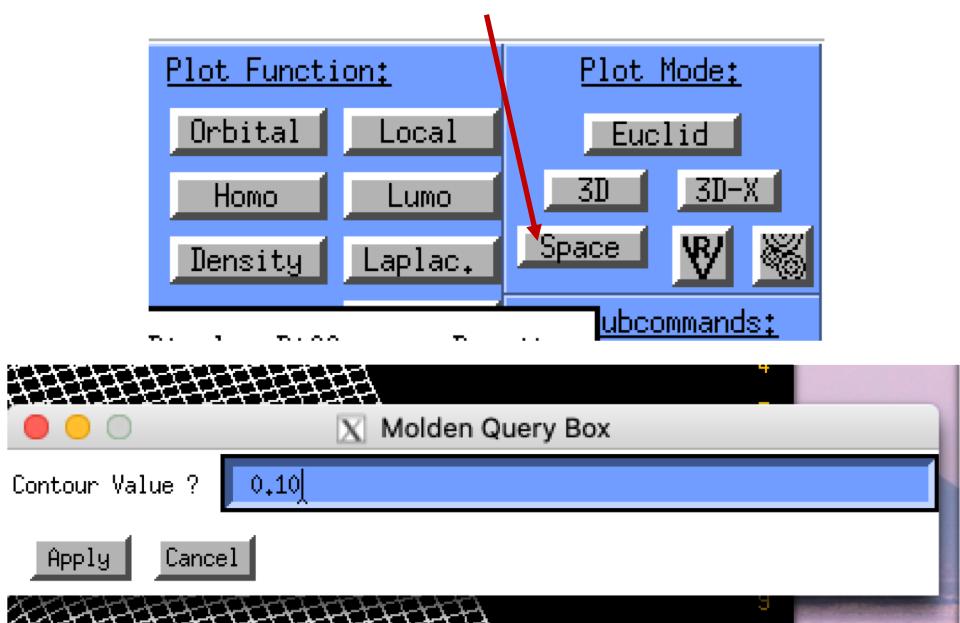
Energy of the MO

of electrons filled in

Nr.	Eigenvalue	Occupation
1	-0.464661	2.00
2	0.126257	0.00

Visualize MOs of the H₂ molecule

- Close the Orbital Select Window
- Click “Space”
 - Enter 0.1 for contour value

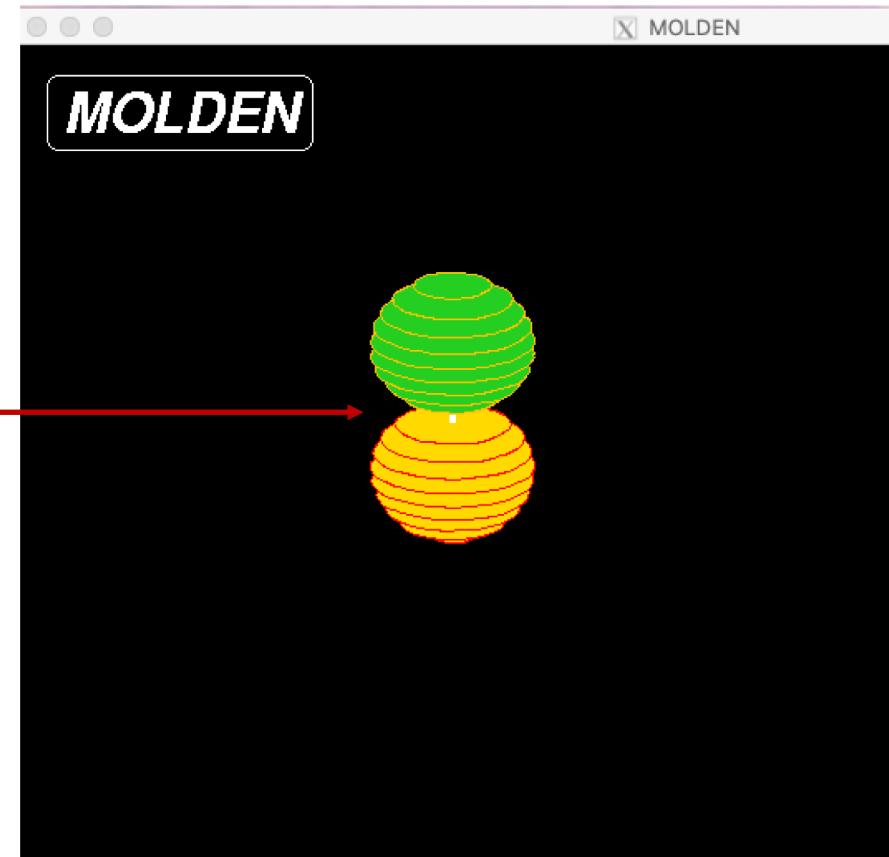


$\varphi_{1\sigma}$

Visualize MOs of the H₂ molecule

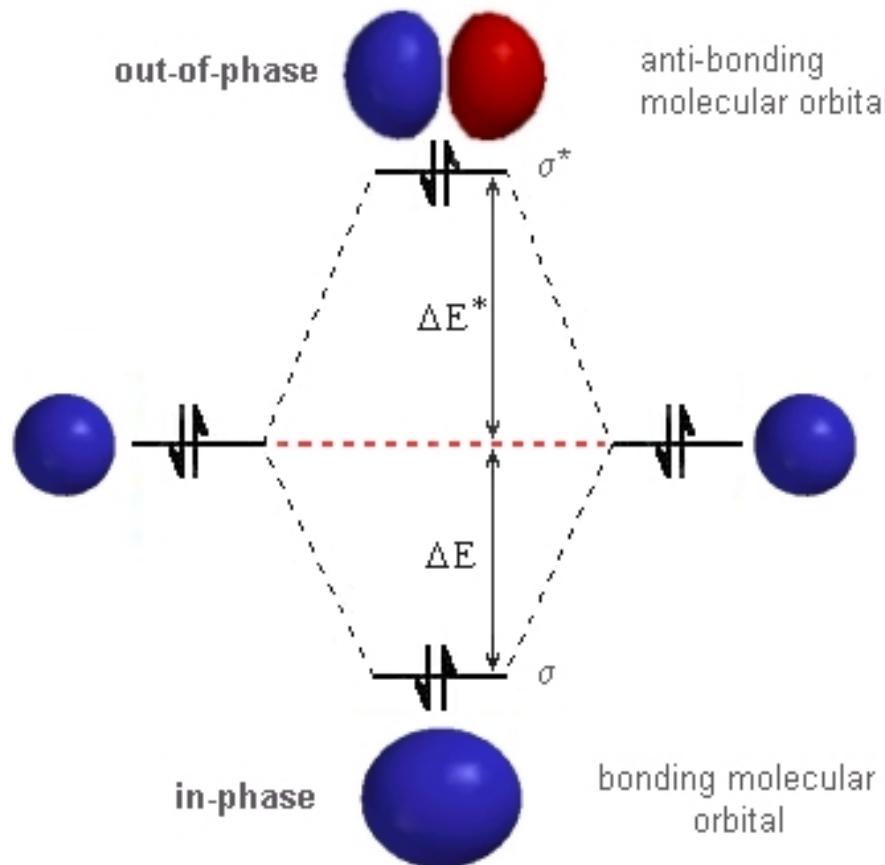
- Click “Orbital” again and select the 2nd MO.

-
Nodal plane
+
→



$$\varphi_{1\sigma^*}$$

MO diagram of the H₂ molecule



Energy difference between $\varphi_{1\sigma}$ and $\varphi_{1\sigma^*}$

Nr.	Eigenvalue	Occupation
1	-0.464661	2.00
2	0.126257	0.00

$$0.126257 - (-0.464661) = 0.590918 \text{ Hartree}$$

$$1 \text{ Hartree} = 27.2114 \text{ eV}$$

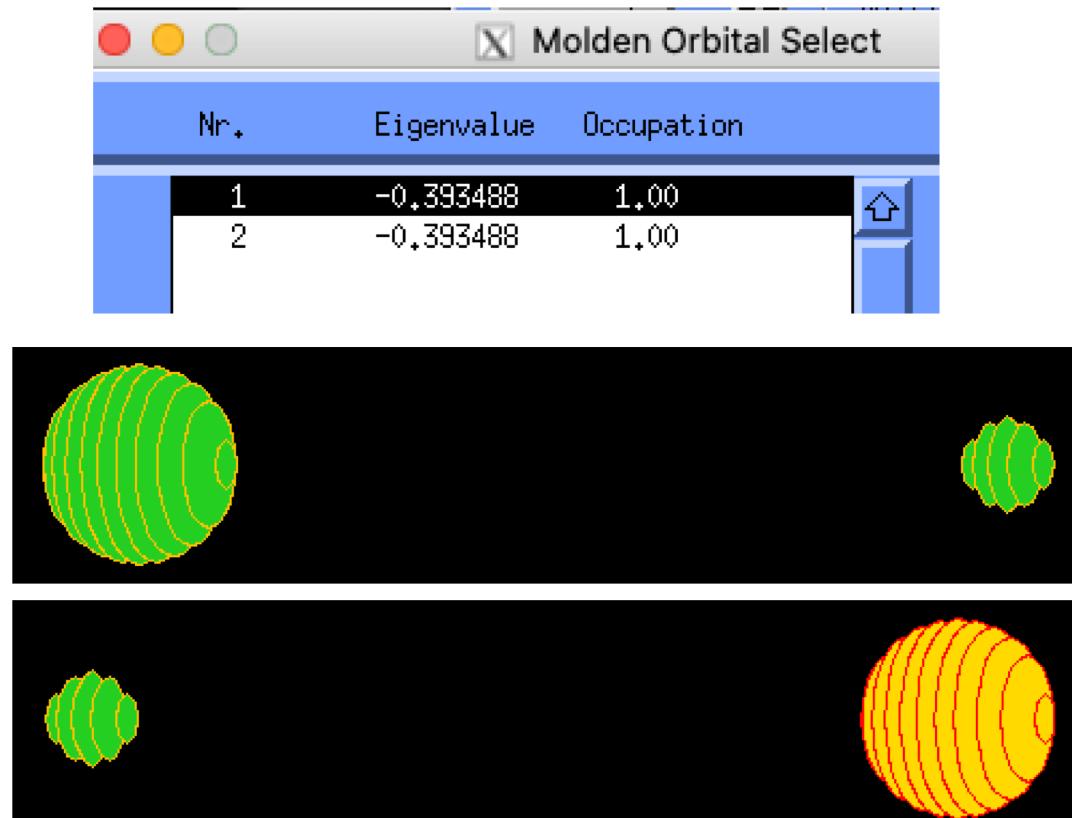
$$0.590918 \text{ Hartree} \approx 16 \text{ eV}$$

This is super huge!

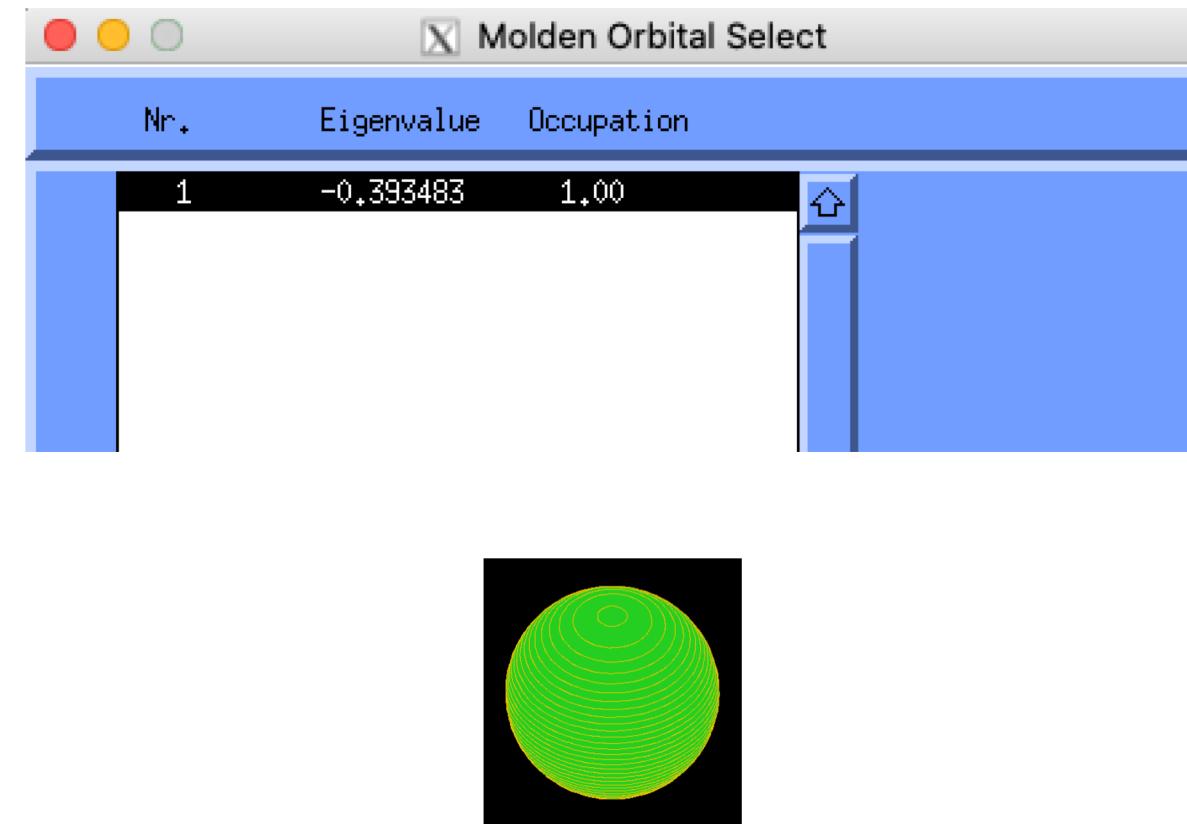
17.84 eV using DFT (ω B97XD/def2-TZVP)

Increase H...H distance, what do you see?

H₂ with 6.93 Å H...H distance



Isolated H



Nearly degenerate MO level -> nearly non-interacting

Visualize MOs of the TiCl_4 metal complex

Inputs and output of this exercise

The outputs of this exercise were uploaded on Github repository

- W2/02_TiCl4

Step-by-step operation

- Enter the folder
 - cd W2
- Create a folder under W2
 - mkdir 02_TiCl4
 - cd 02_TiCl4
- Copy the running script
 - cp yourpath/W2/02_TiCl4/opt_xtb.sh .
- Copy the TiCl₄ input structure
 - cp yourpath/W2/02_TiCl4/input.xyz .
- Modify the last line of the script
 - vi opt_xtb.sh Create a molden.input for MO visualization
 - xtb -c 0 -u 0 input.xyz -opt normal **--molden** > xtb.out
- Run it!
 - bash opt_xtb.sh

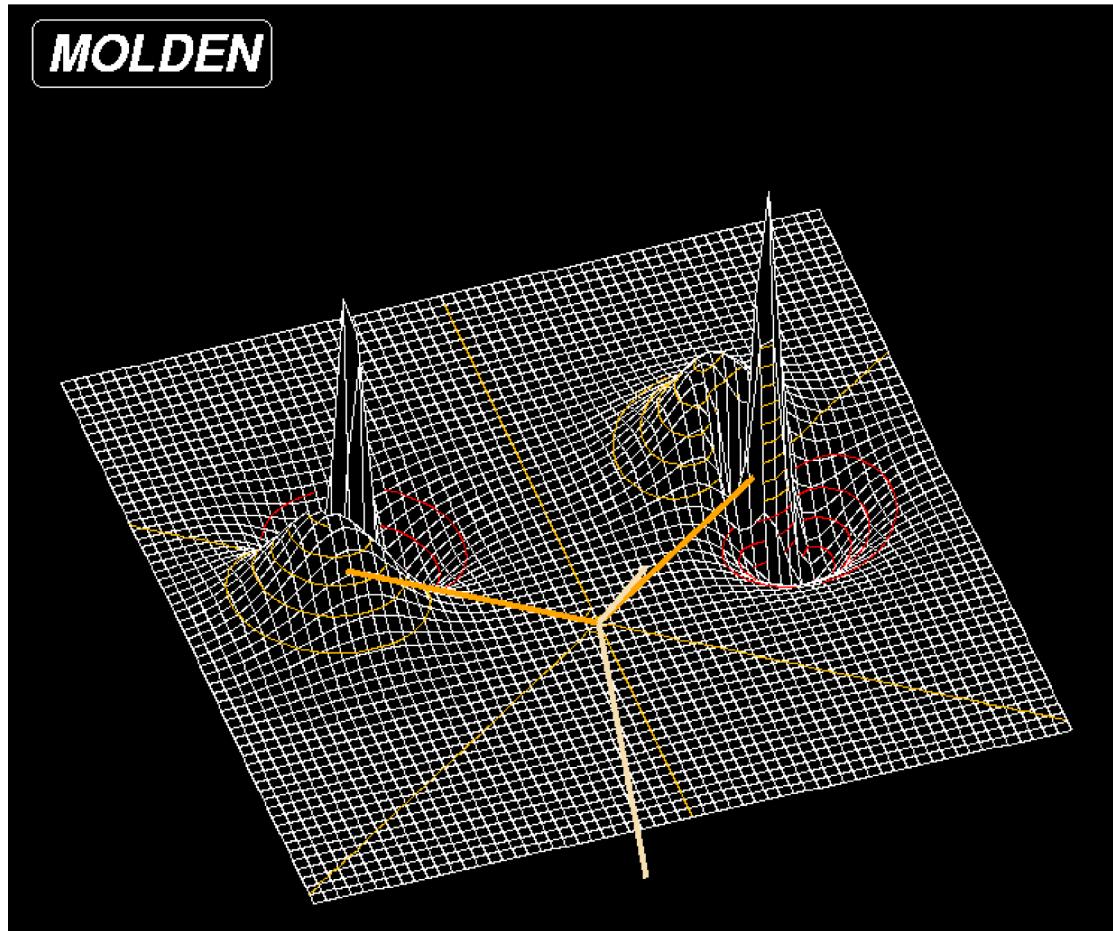
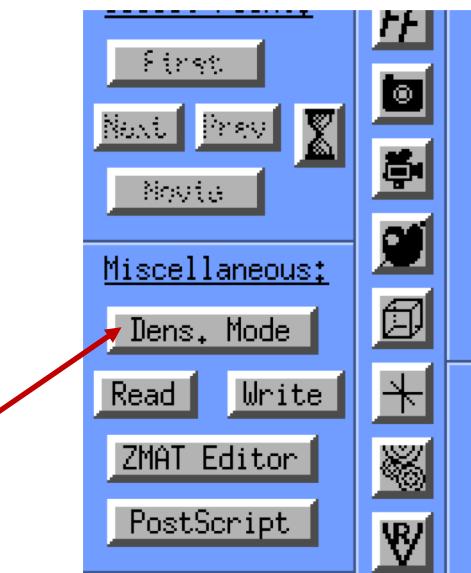
Visualize geometry of TiCl_4

- Open molden.input using molden
 - molden molden.input
- Inspect the structure
 - What is its shape?
 - What is the Ti-Cl bond length?
 - Cl-Ti-Cl angle?



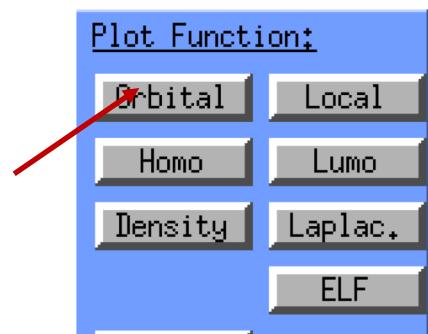
Visualize MOs of TiCl_4

- Click “Dens. Mode”
 - This is to switch to density mode



Visualize MOs of TiCl_4

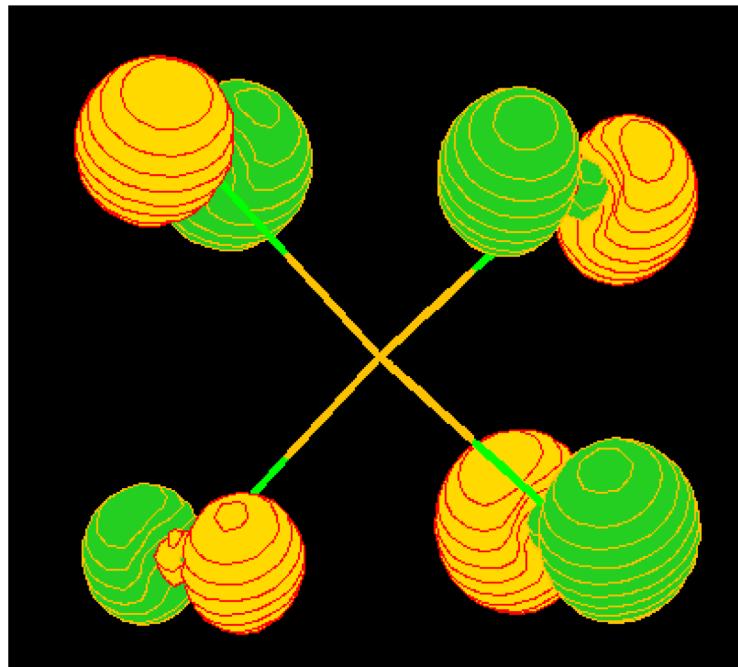
- Click “Orbital”
 - 45 MOs in total for TiCl_4 .
 - How many are occupied?
 - 14,15 and 16 are degenerate
 - 17 and 18 are degenerate
 - 19, 20 and 21 are degenerate



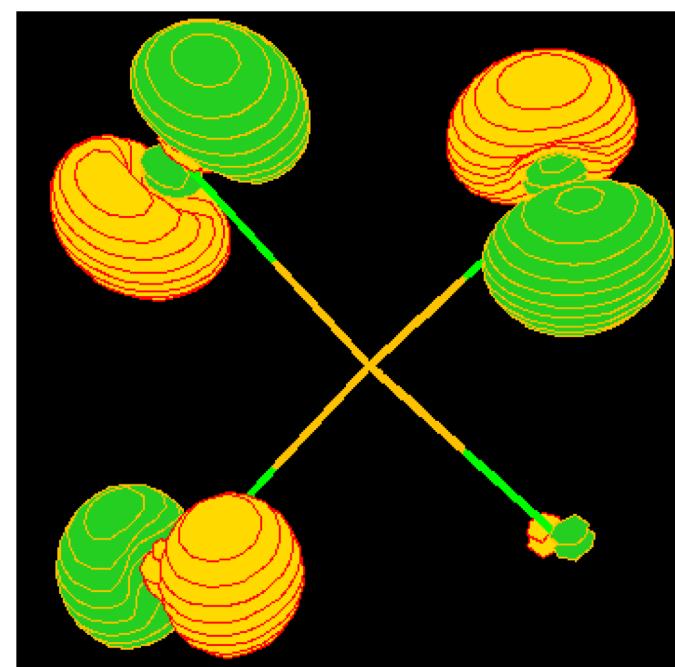
Nr.	Eigenvalue	Occupation	
13	-0.471923	2.00	
14	-0.461711	2.00	
15	-0.461711	2.00	
16	-0.461711	2.00	
17	-0.351612	0.00	
18	-0.351612	0.00	
19	-0.316599	0.00	
20	-0.316599	0.00	
21	-0.316599	0.00	
22	-0.018668	0.00	
--	

Visualize 14, 15 and 16

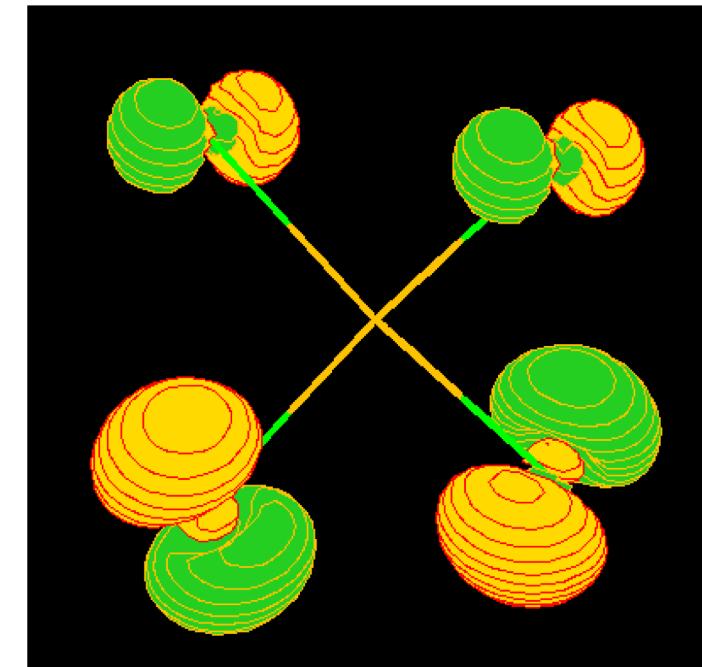
14



15



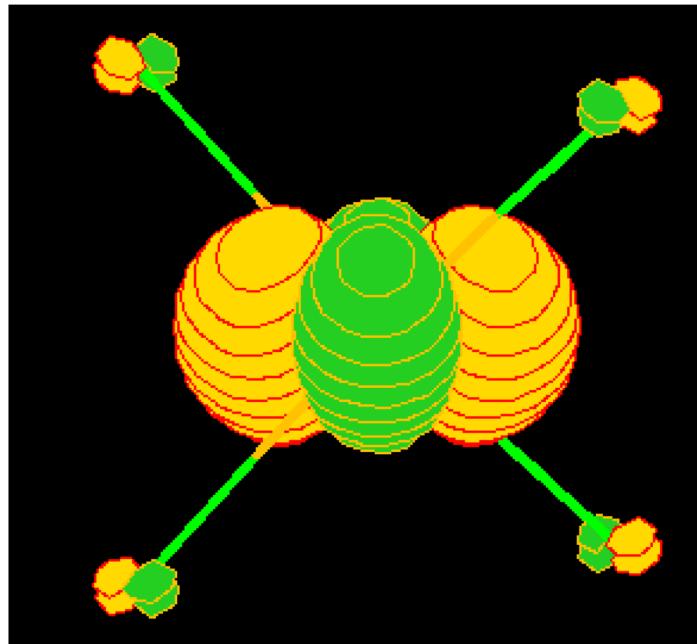
16



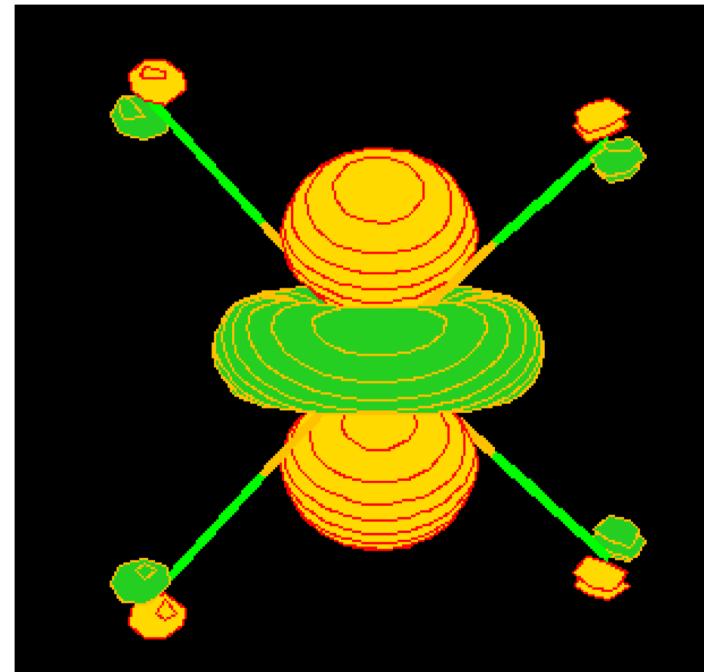
Linear combination of p orbitals from Cl ligands

Visualize 17 and 18

17 $d_{x^2-y^2}$



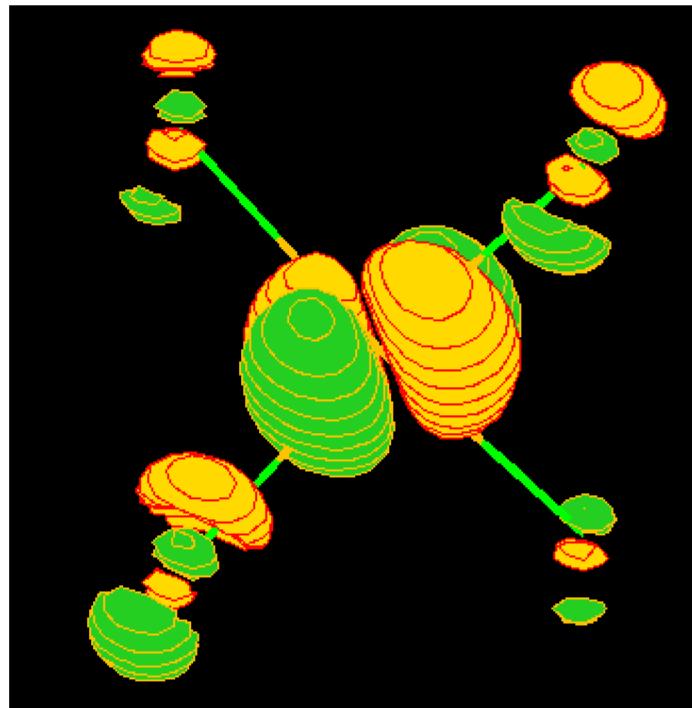
18 d_{z^2}



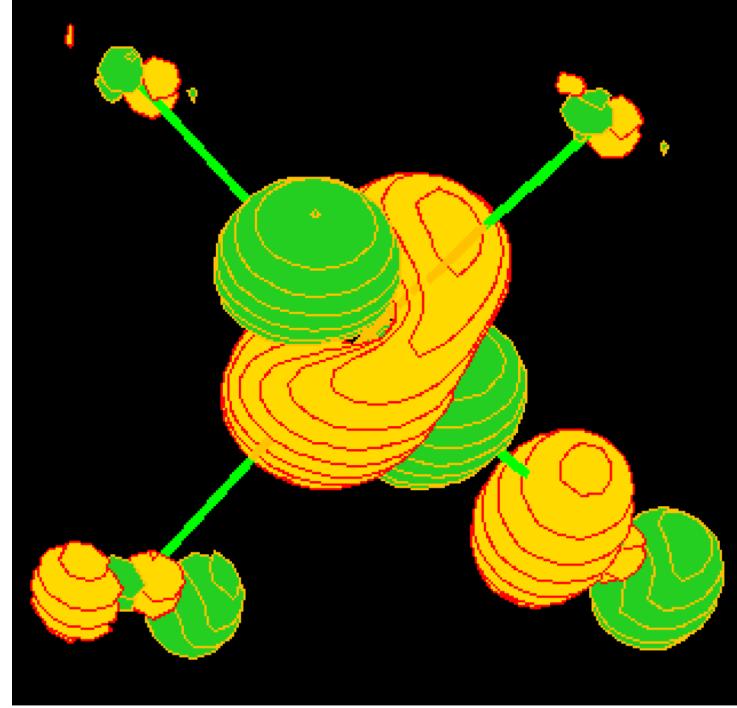
Mainly from d orbital of Ti

Visualize 19, 20 and 21

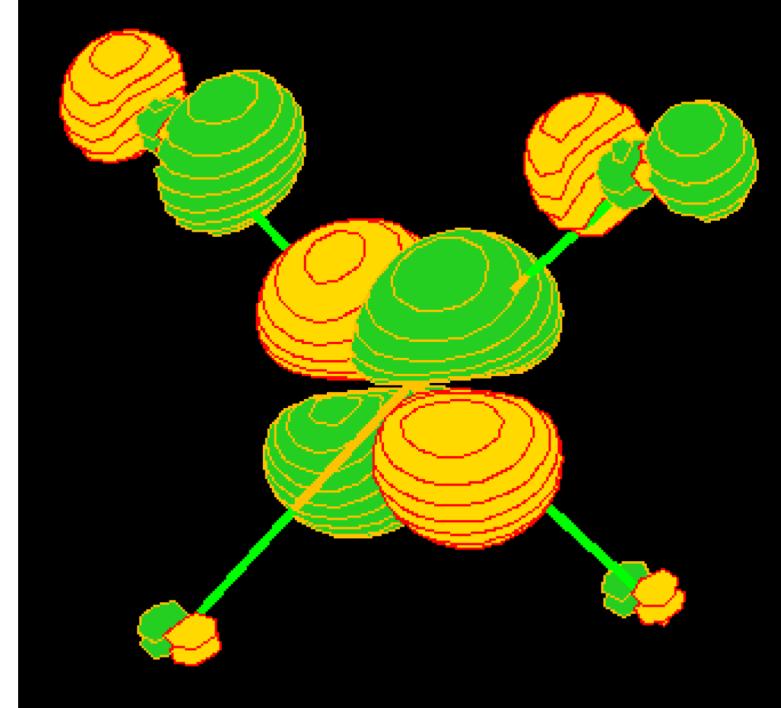
19 d_{xz}



20 d_{xy}

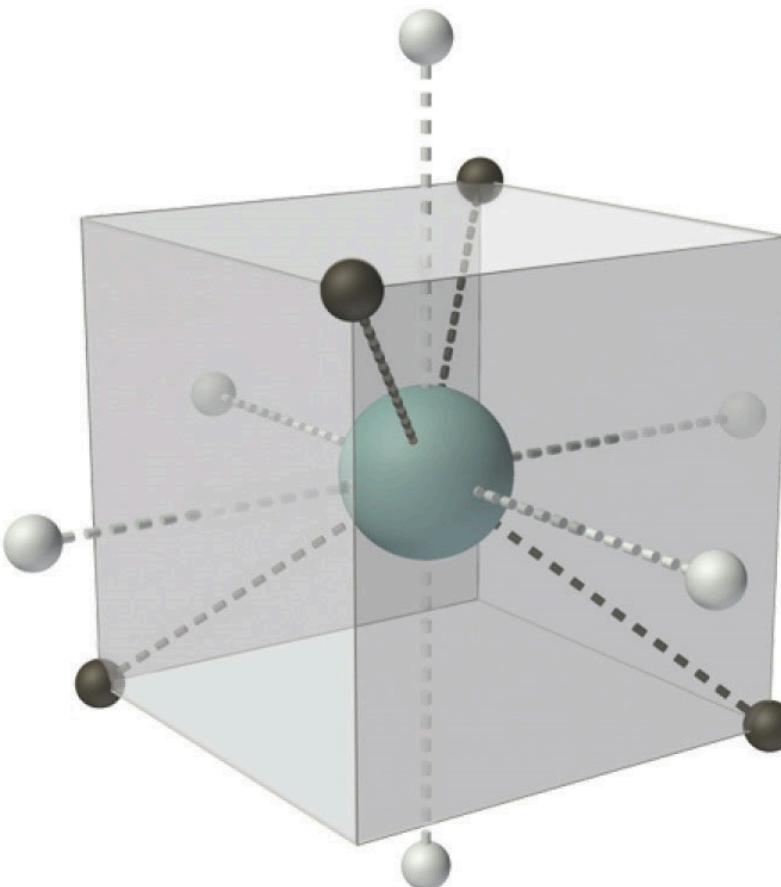


21 d_{yz}

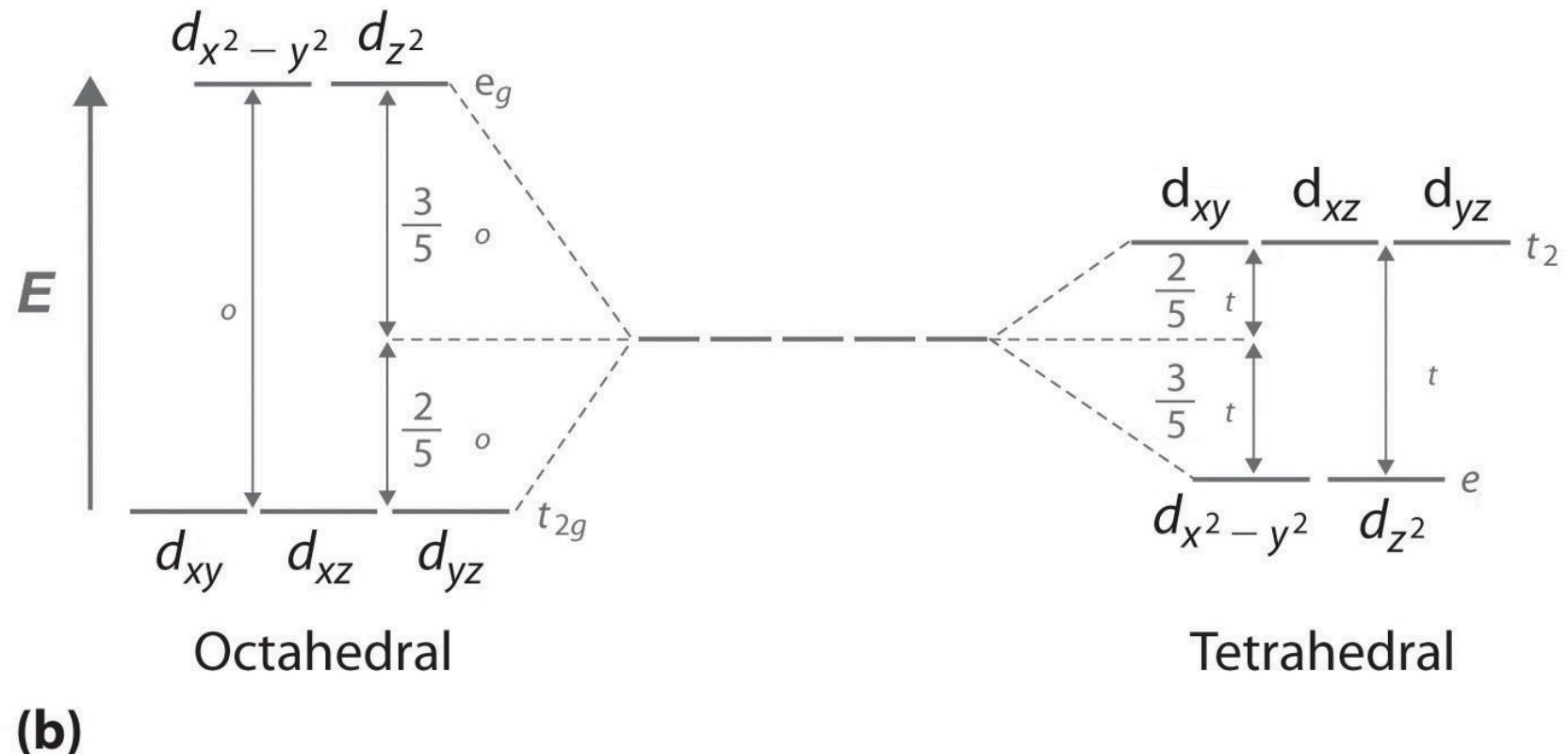


Mainly from d orbital of Ti

Tetrahedral complex predicted from CFT



How large is the splitting t from xtb output?



Calculate IE of benzene

Inputs and output of this exercise

The outputs of this exercise were uploaded on Github repository

- Optimize neutral benzene
 - W2/03_benzene/nN
- Optimize cationic benzene
 - W2/03_benzene/cC
- Calculate energy of cationic benzene at neutral benzene geometry
 - W2/03_benzene/cN

nN

neutral charge state

Neutral geometry

Step-by-step operation-nN

- Enter the folder
 - cd W2
- Create a folder under W2
 - mkdir 03_benzene
 - cd 03_benzene
- Create a folder under 03_benzene
 - mkdir nN
 - cd nN
- Copy the running script
 - cp yourpath/W2/03_benzene/nN/opt_xtb.sh .
- Copy the benzene input structure
 - cp yourpath/W2/03_benzene/nN/input.xyz .
- Run it!
 - bash opt_xtb.sh

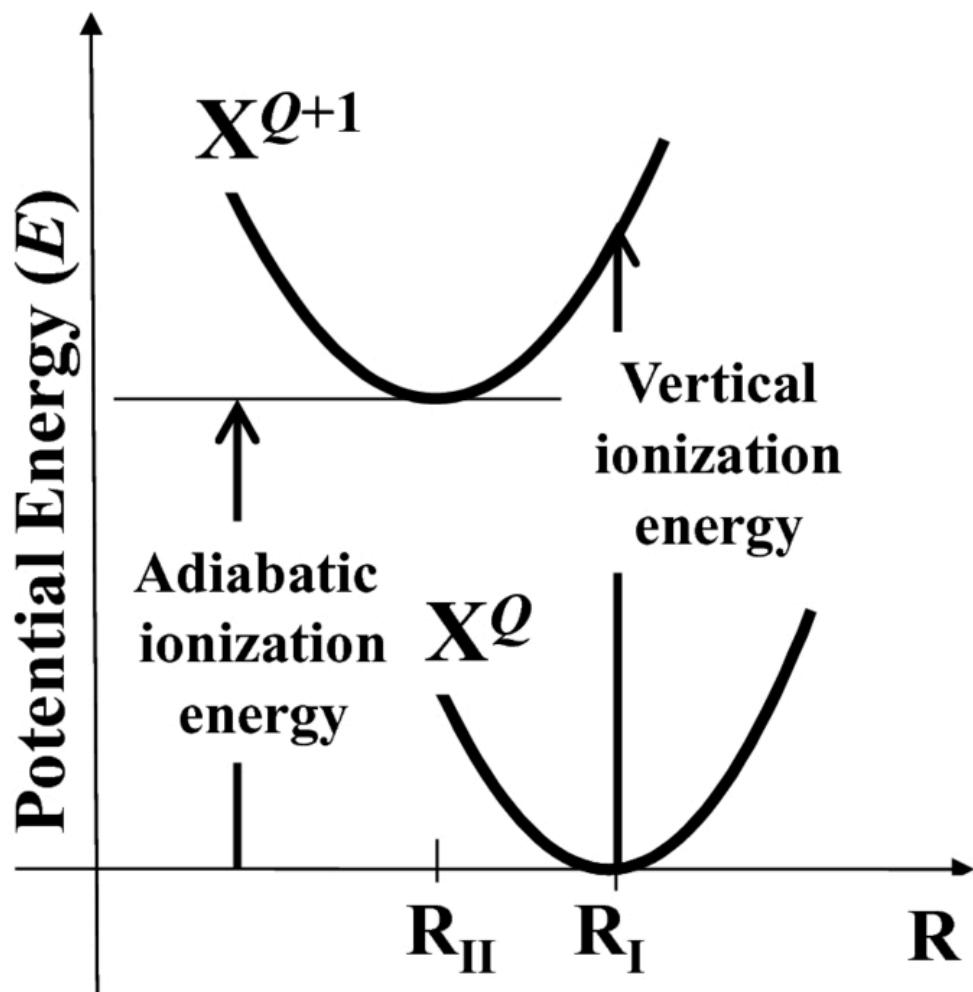
Step-by-step operation-cC

- Enter the folder
 - cd W2
- Create and enter cC
 - cd 03_benzene
 - mkdir cC
 - cd cC
- Copy the running script
 - cp yourpath/W2/03_benzene/cC/opt_xtb.sh .
- Copy the benzene input structure
 - cp yourpath/W2/03_benzene/cC/input.xyz .
- Run it!
 - bash opt_xtb.sh

Step-by-step operation-cN

- Enter the folder
 - cd W2
- Create and enter cN
 - cd 03_benzene
 - mkdir cN
 - cd cN
- Copy the running script
 - cp yourpath/W2/03_benzene/cN/opt_xtb.sh .
- Copy the benzene input structure
 - cp yourpath/W2/03_benzene/cN/input.xyz .
- Run it!
 - bash opt_xtb.sh

Adiabatic and vertical IE



nN

TOTAL ENERGY	-15.879640657009 Eh
GRADIENT NORM	0.00043905286 Eh/ α
HOMO-LUMO GAP	4.934244423848 eV

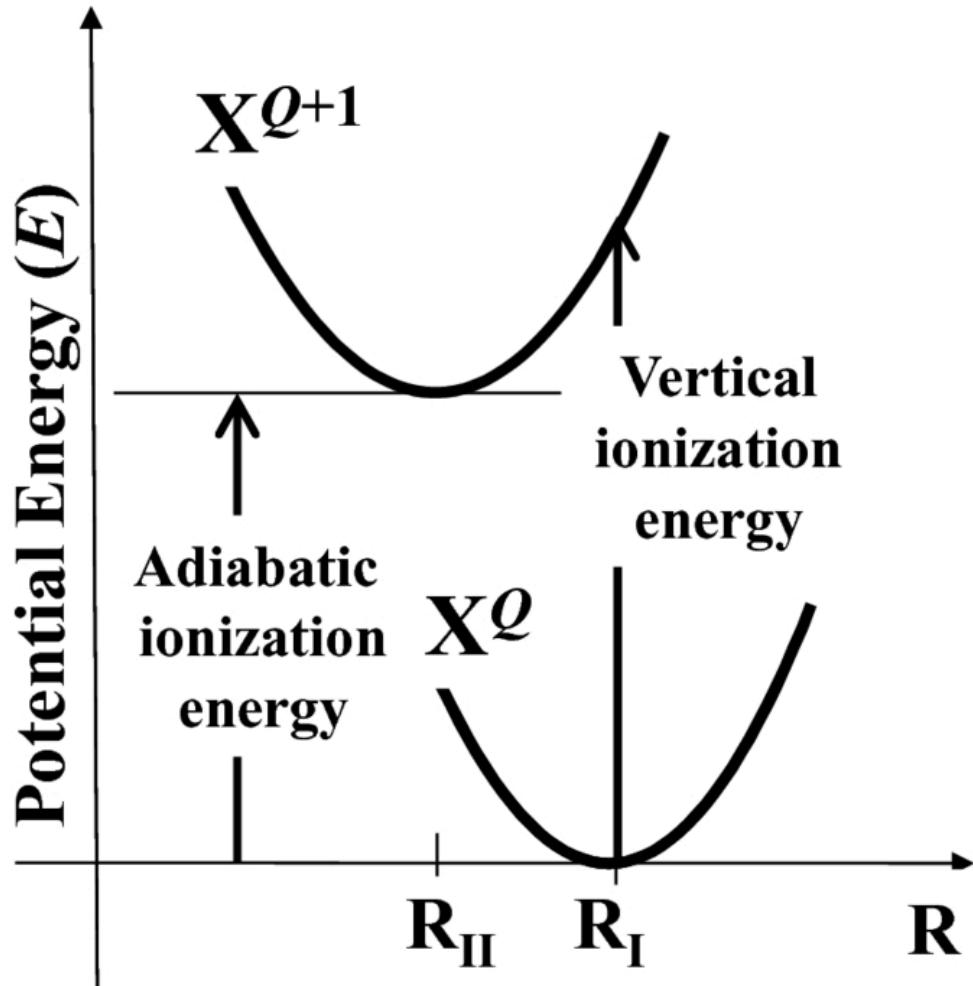
cC

TOTAL ENERGY	-15.358208434260 Eh
GRADIENT NORM	0.000327175694 Eh/ α
HOMO-LUMO GAP	4.842740511729 eV

cN

TOTAL ENERGY	-15.357234835766 Eh
GRADIENT NORM	0.022515866055 Eh/ α
HOMO-LUMO GAP	4.999113471826 eV

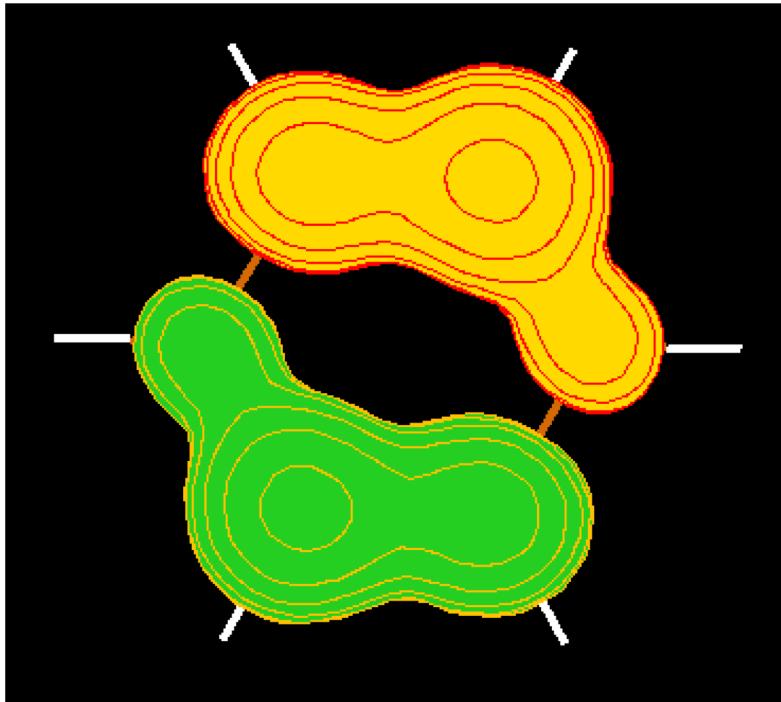
Adiabatic and vertical IE



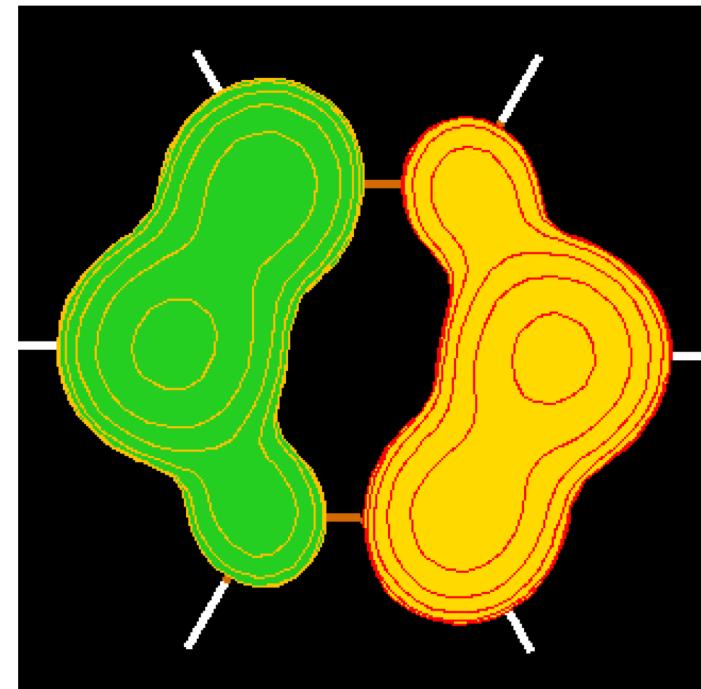
- Vertical IE
 - $E_{cN} - E_{nN} = 14.22 \text{ eV}$
- Adiabatic IE
 - $E_{cc} - E_{nN} = 14.19 \text{ eV}$
- Difference
 - $E_{cN} - E_{cc} = 0.03 \text{ eV}$
 - Nuclear relaxation energy
- Exp. value
 - 9.25 eV*

* Kimura, Katsumata, et al., 1981 in NIST

Degenerate HOMO & HOMO-1 of benzene



HOMO-1

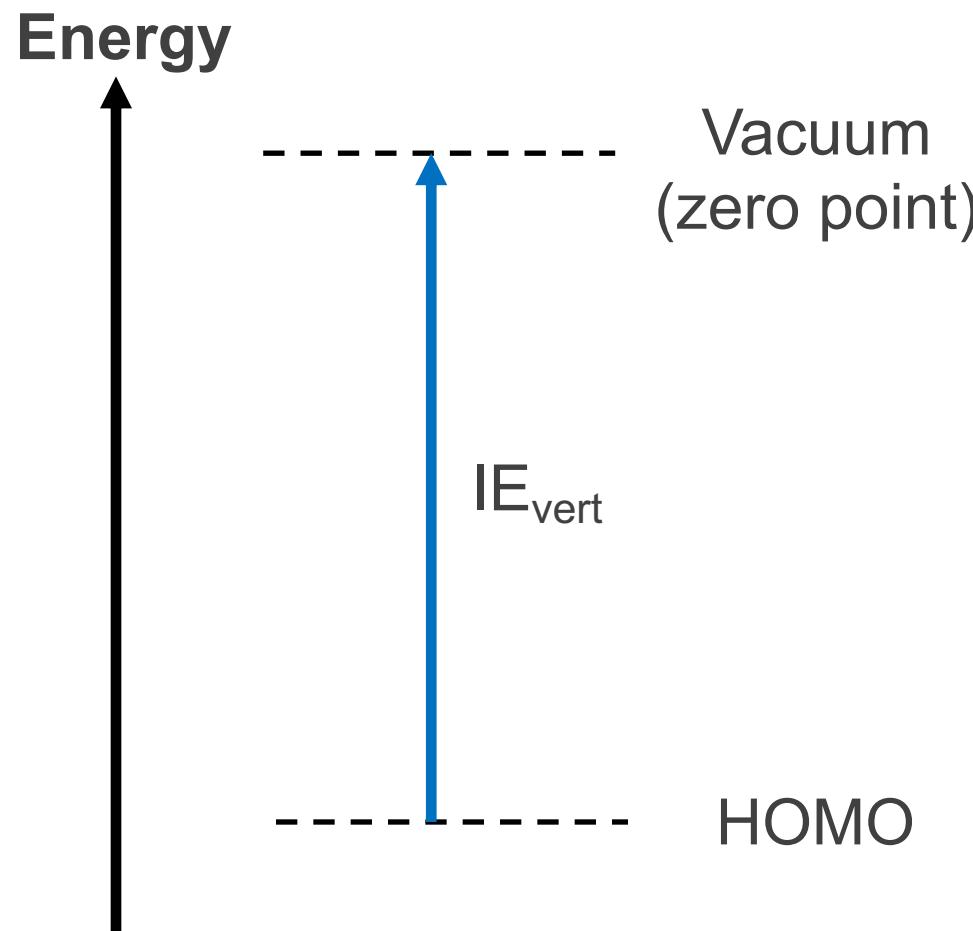


HOMO

Nr.	Eigenvalue	Occupation
9	-0.476350	2.00
10	-0.476350	2.00
11	-0.474755	2.00
12	-0.421397	2.00
13	-0.421397	2.00
14	-0.402526	2.00
15	-0.402526	2.00
16	-0.221196	0.00
17	-0.221195	0.00
18	-0.089922	0.00
19	0.118018	0.00
...	^ 4.7774 ^	^ ^ ^

$$-0.402526 * 27.2114 = 10.95 \text{ eV}$$

Koopmans' (and Janak's) theorem



Koopmans' theorem states that in closed-shell Hartree–Fock theory (HF), the first IE of a molecular system is equal to the negative of (HOMO).

14.19 eV vs 10.95 eV

Huge difference! What may be the reason?

Readings

- Molecular orbital theory
 - Chapter 8 / Molecular Quantum Mechanics 5th Ed., Peter Atkins
- CFT and LFT
 - Crystal Field Theory - Chemistry LibreTexts
 - Introduction to Ligand Field Theory (Octahedral complexes) - Chemistry LibreTexts