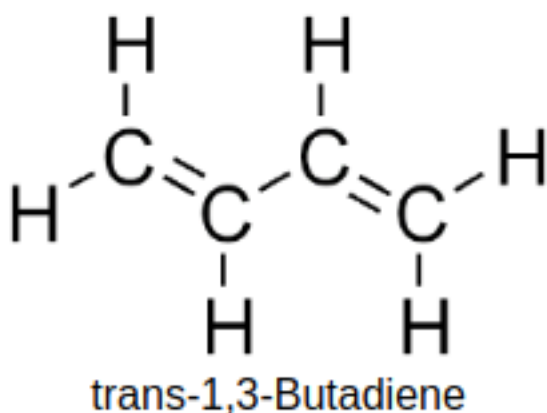


HW

Hückel theory

- The molecular orbitals are linear combination of atomic orbitals
- Standard approximation of Hückel theory
 - $H_{ii} - ES_{ii} = \alpha$
 - $H_{ij} - ES_{ij} = \beta$, When $i = j \pm 1$
 - $H_{ij} - ES_{ij} = 0$, Others
- Calculate the delocalize energy

Example 1,3-Butadiene



1. Linear combination of molecular orbitals $|\psi_i\rangle = \sum_j^4 c_{ij} |p_i\rangle$ $|\psi_i\rangle = c_{i1}|p_1\rangle + c_{i2}|p_2\rangle + c_{i3}|p_3\rangle + c_{i4}|p_4\rangle$

2. For solving the i^{th} molecular orbital $|\psi_i\rangle$ need to solve

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & H_{23} - ES_{23} & H_{24} - ES_{24} \\ H_{13} - ES_{13} & H_{23} - ES_{23} & H_{33} - ES_{33} & H_{34} - ES_{34} \\ H_{14} - ES_{14} & H_{24} - ES_{24} & H_{34} - ES_{34} & H_{44} - ES_{44} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0$$

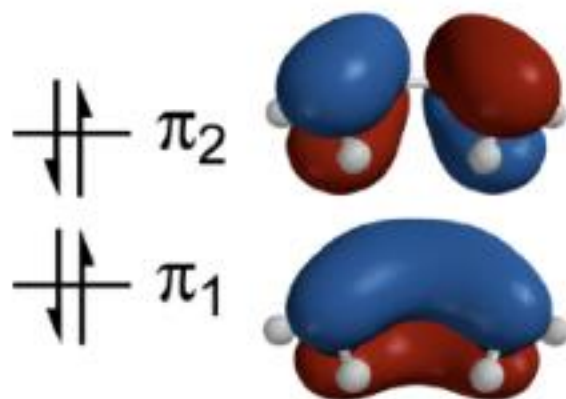
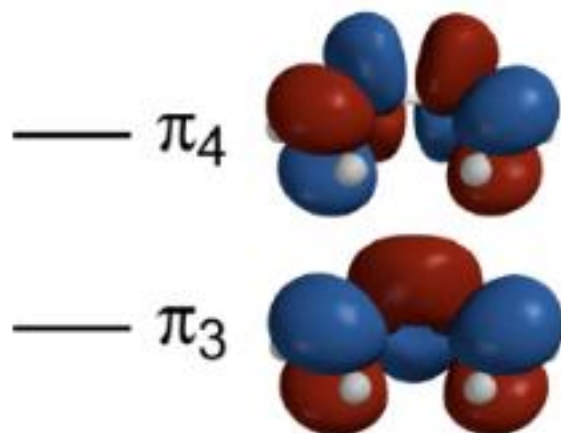
3. By standard approximation of Hückel theory the matrix become

$$\begin{bmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0$$

4. If c_1, c_2, c_3, c_4 is not trivial then the determinant is 0. E is the eigenvalue

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

5. Simplify by divided by β and $x = \frac{\alpha-E}{\beta}$ then $\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$
6. Solve the equation $x^4 - 3x^2 + 1 = 0$ $x^2 = \frac{3 \pm \sqrt{5}}{2}$
7. Derive the E_1, E_2, E_3, E_4 $E_1 = \alpha + 1.618\beta$ $E_2 = \alpha + 0.618\beta$ $E_3 = \alpha - 0.618\beta$ $E_4 = \alpha - 1.618\beta$
8. The electron configuration and shape (by HF/6-31G*)



9. Calculate the energy of molecular orbitals
 $E_{\pi}(\text{butadiene}) = 2 \times E_1 + 2 \times E_2 + 0 \times E_3 + 0 \times E_4$
 $= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$
 $= 4\alpha + 4.472\beta$

10. Compare the energy of butadiene with two ethylene

- The **delocalization energy** is about $0.48\beta = -35 \text{ kJ/mol}$
- The delocalization can stabilize the molecular

$$\begin{aligned} E_{\pi}(\text{butadiene}) &= 2 \times E_{\pi}(\text{ethylene}) \\ &= 2 \times 2(\alpha + \beta) \\ &= 4\alpha + 4\beta \end{aligned}$$

3-node

(b) $\psi_{\pi} = c_1 \phi_{pz,1} + c_2 \phi_{pz,2} + c_3 \phi_{pz,3} + c_4 \phi_{pz,4} + c_5 \phi_{pz,5} + c_6 \phi_{pz,6}$

(c)
$$H = \begin{bmatrix} \alpha & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha \end{bmatrix}$$

(d)
$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

$-4\beta^6 + 9\beta^4(\alpha-E)^2 - 6\beta^2(\alpha-E)^4 + (\alpha-E)^6 = 0$, let $E = \alpha + x\beta$ let x

$-4 + 9x^2 - 6x^4 + x^6 = 0$, let $u = x^2$, $u^3 = x^6$

$\Rightarrow -4 + 9u - 6u^2 + u^3 = 0$

$(u-1)(u-4) = 0$

$u = 1, 4 \Rightarrow x = \pm 1, \pm 2, \pm 1$

$\Rightarrow E = \alpha + \beta, \alpha - \beta, \alpha + 2\beta, \alpha - 2\beta$

(b) The wavefunction of the π MOs (ψ_{π}) of benzene

$$\psi_{\pi} = c_1 \phi_{pz,1} + c_2 \phi_{pz,2} + c_3 \phi_{pz,3} + c_4 \phi_{pz,4} + c_5 \phi_{pz,5} + c_6 \phi_{pz,6}$$

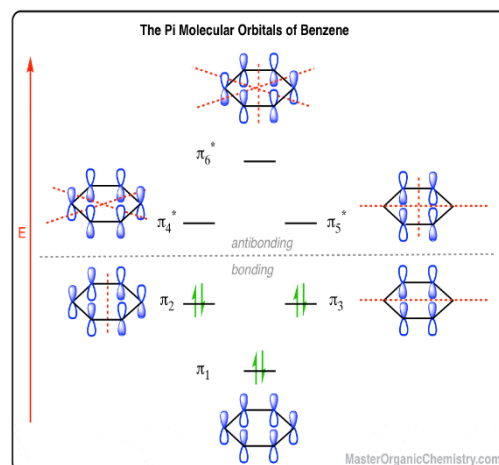
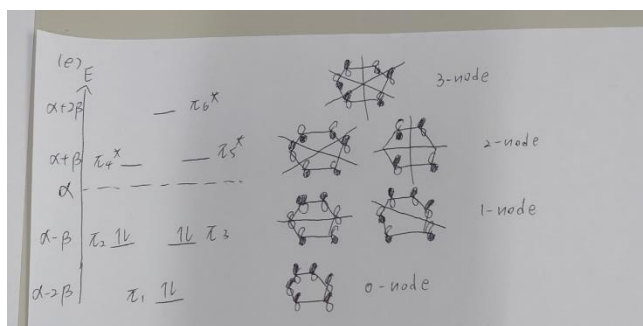
(c) The Hamiltonian matrix for benzene

$$\begin{bmatrix} \alpha & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha \end{bmatrix}$$

(d)

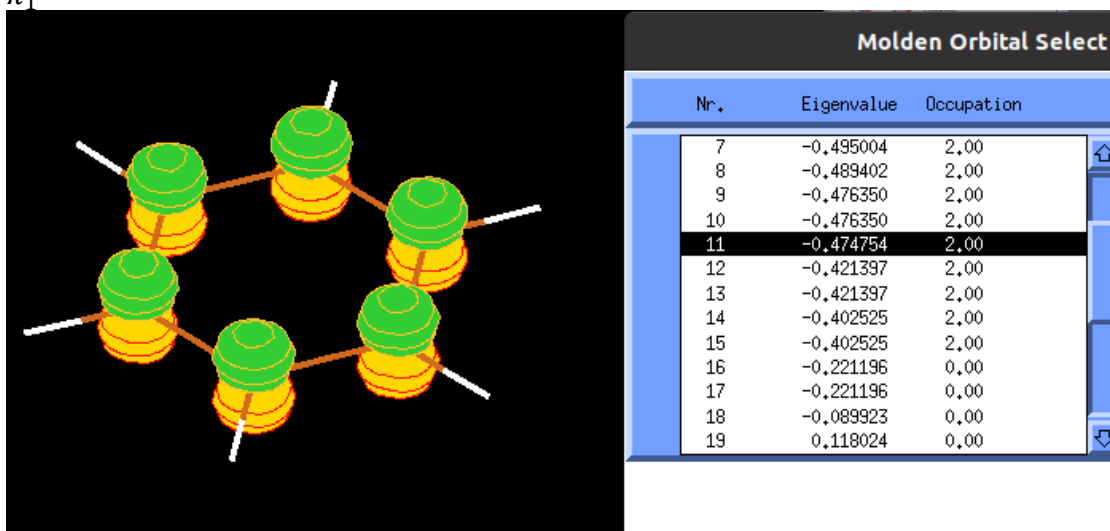
$$E = \alpha + \beta, \alpha - \beta, \alpha + 2\beta, \alpha - 2\beta, \alpha + \beta, \alpha - \beta$$

(e)

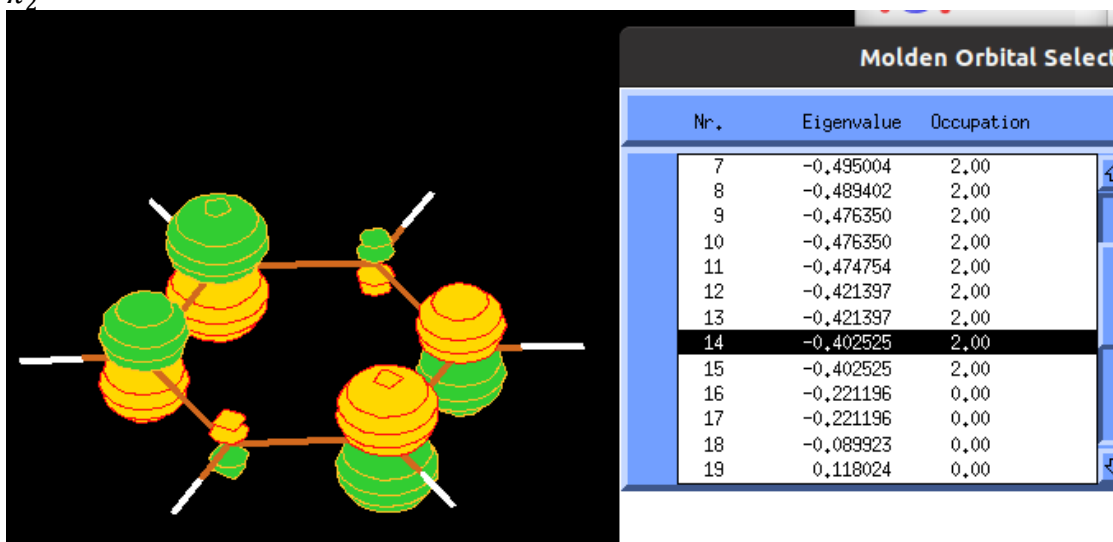


(f)

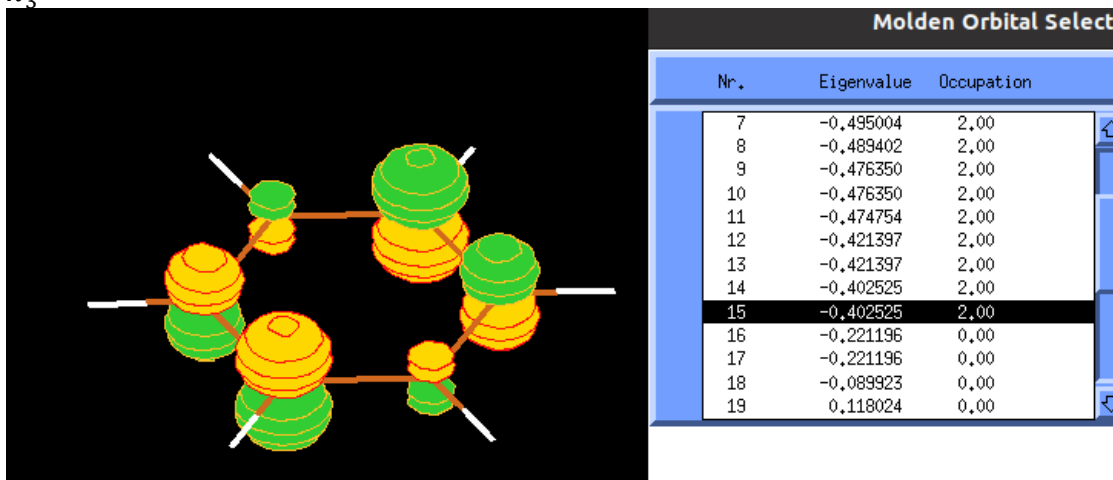
- π_1



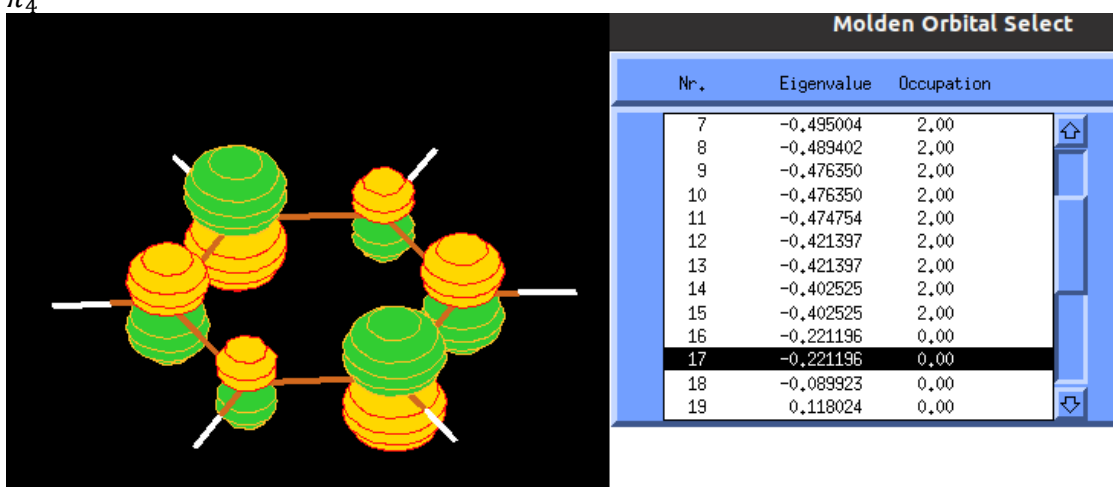
- π_2



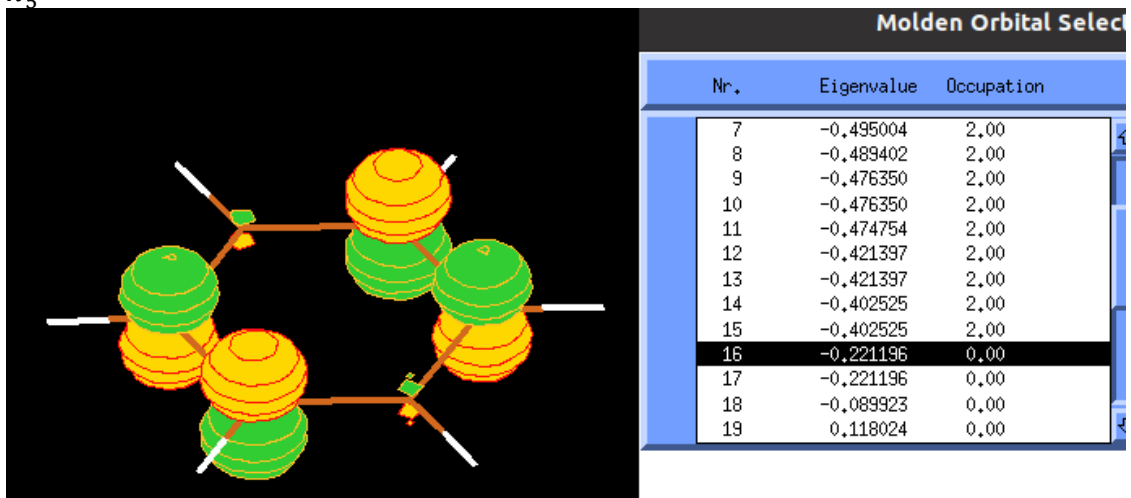
- π_3



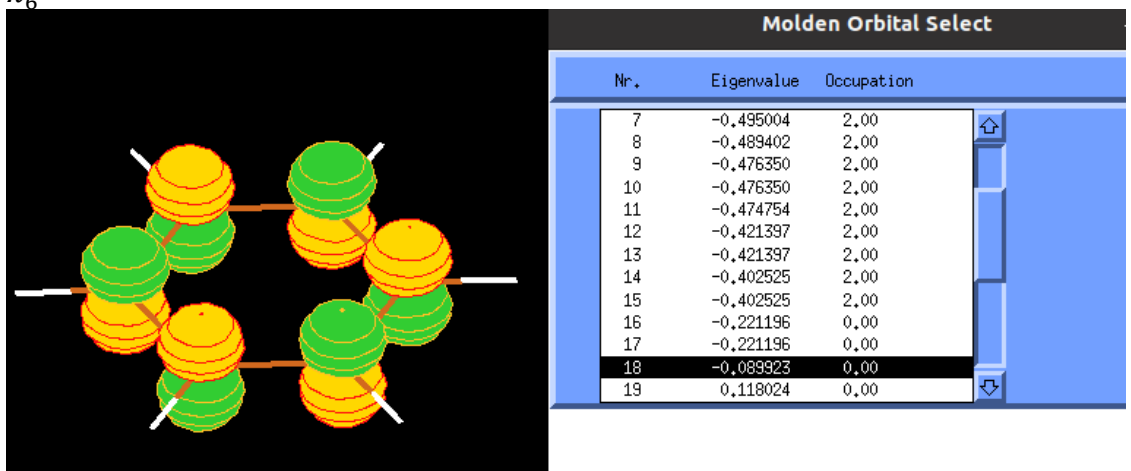
- π_4^*



- π_5^*



- π_6^*



- $E2-E1 \neq E6-E5$
 - $E1 = -0.474754$
 - $E2 = -0.402525$
 - $E3 = -0.402525$
 - $E4 = -0.221196$
 - $E5 = -0.221196$
 - $E6 = -0.089923$

2.

generate files and directory

```
for dir in aN nN aA nN;do mkdir $dir ; cp naphthalene.xyz $dir;done
```

aA xtb

- parameter
 - charge: -1

- unpair-electrons: 1
- -opt
- -molden
- command
`xtb -c -1 -u 1 --opt --molden naphthalene.xyz > xtb.out`
- Energy:
 - $E = -25.638035481112 \text{ Eh}$
 - LUMO = -0.033169

nN xtb

- parameter
 - charge: 0
 - unpair-electrons: 0
 - -opt
 - -molden
- command
`xtb -c 0 -u 0 --opt --molden xtbopt.xyz > xtb.out`
- Energy:
 - $E = -25.474386099963 \text{ Eh}$
 - LUMO = -0.257933

aN xtb

The aN is the anion with the ground state geometry - Use nN naphthalene_opt.xyz(ground state geometry) - parameter - charge: -1 - unpair-electrons: 1 - -molden - command

`xtb -c -1 -u 1 --molden xtbopt.xyz > xtb.out`

- Energy
 - $E = -25.633869367054 \text{ Eh}$
 - LUMO = -0.035127

Conclude

	E(hartree)	LUMO
nN	-25.474386099963	-0.257933
aA	-25.638035481112	-0.033169
aN	-25.633869367054	-0.035127

- $EA_{\text{vertical}} = -0.1595 \text{ Eh} = -4.3402183 \text{ eV}$
- $EA_{\text{adiabatic}} = -0.163649381 \text{ Eh} = -4.45312877 \text{ eV}$
- $EA(\text{exp}) = -0.200 \pm 0.050 \text{ eV}$

1 Eh = 27.2114 eV

HOMO, LUMO and their difference for oligothiophene

Structure bulid

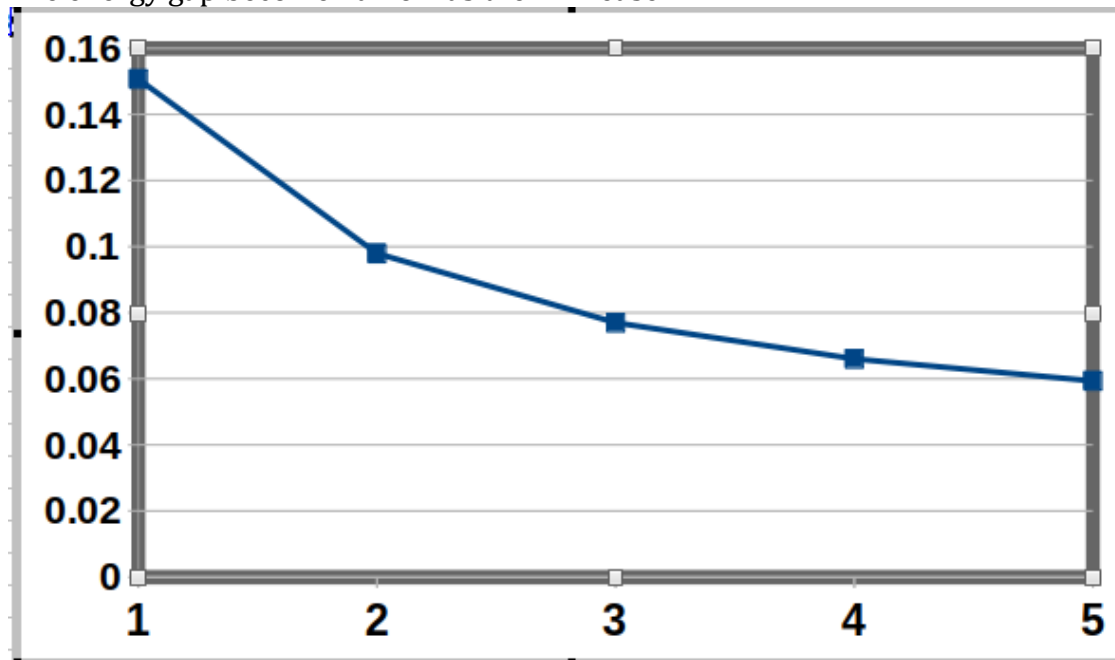
1. Draw the structure by the following html
http://www.cheminfo.org/flavor/malaria/Utilities/SMILES_generator__checker/index.html
2. Output the structure by SMILES
3. Use Avogadro to optimize the structure
4. Output with the file.xyz

HOMO,LUMO

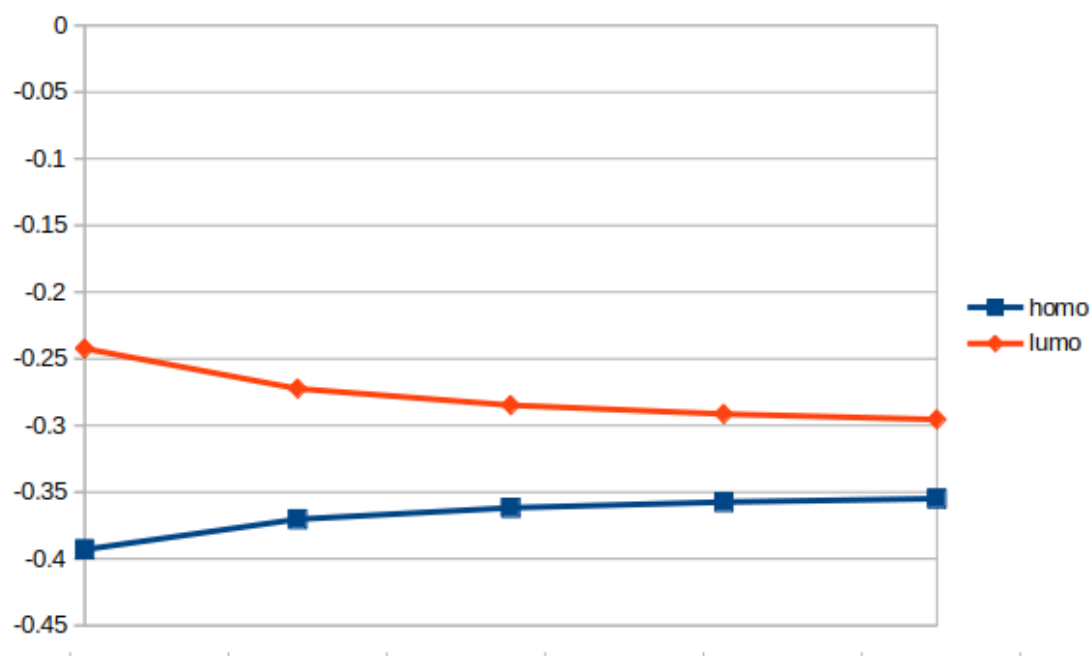
- Search HOMO,LUMO
`grep "Occu" -B 2 molden.input`

n	1	2	3	4	5
HOMO	-0.39302	-0.370329	-0.361751	-0.357424	-0.354870
LUMO	-0.24234	-0.272395	-0.284796	-0.291401	-0.295524
Gap	0.15068	0.097933	0.076967	0.066022	0.05934

- The energy gap become narrow as the n increase

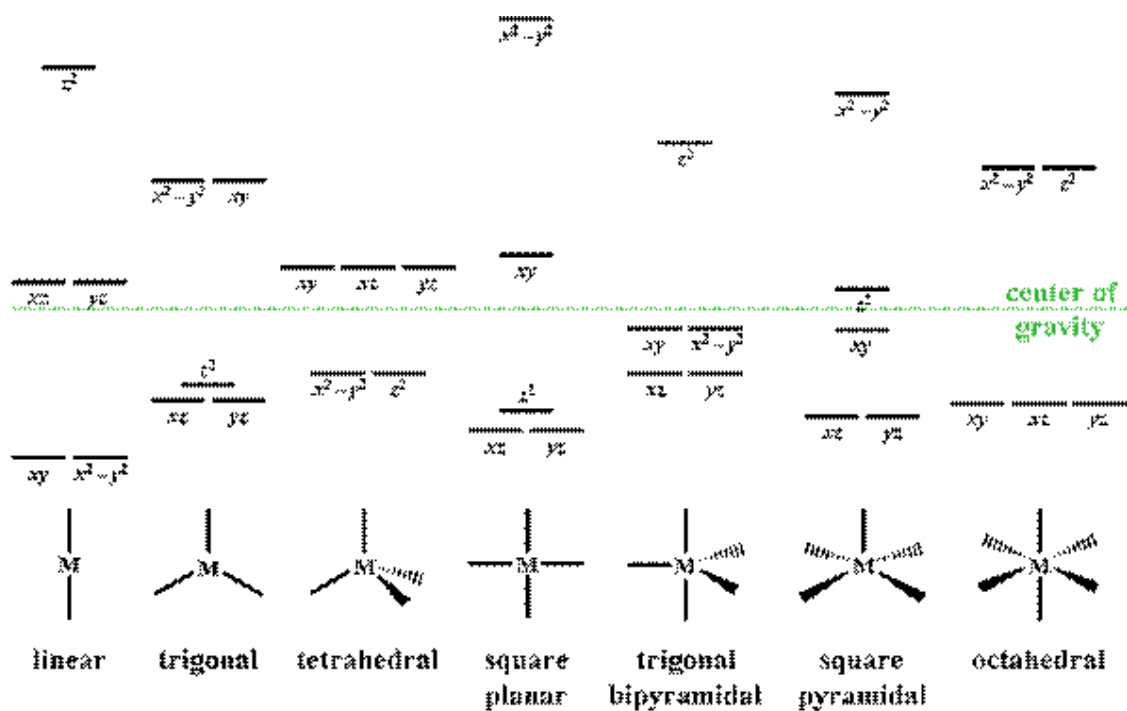


- The homo increase and lumo decrease as the n increase

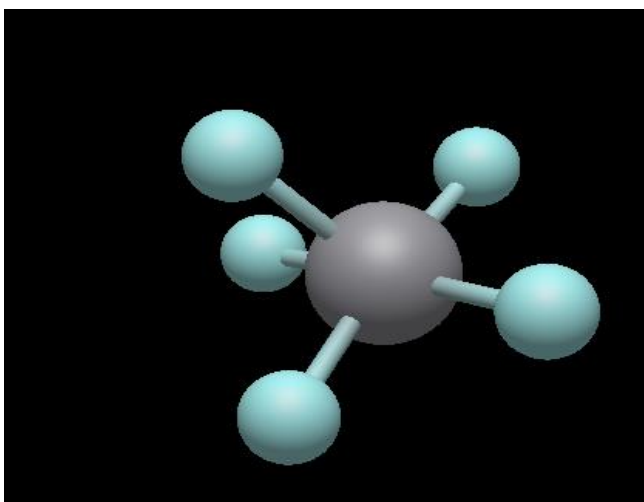


MOs for VF_5

Splitting field

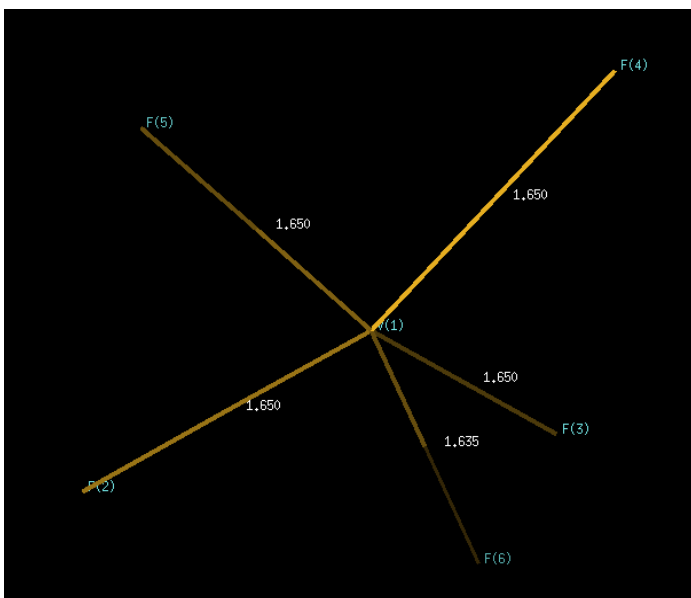


square pyramidal



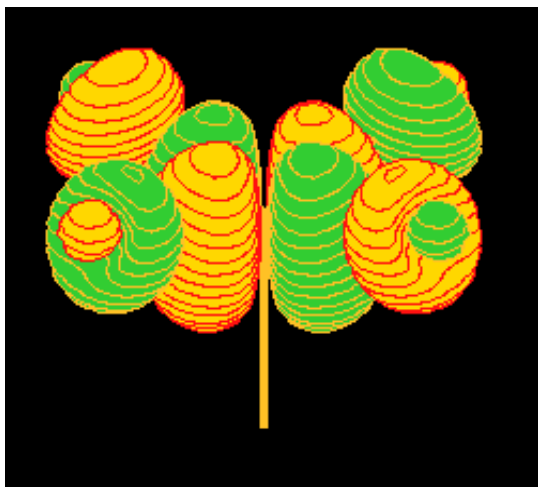
- Energy : -25.830963344050 Eh

bond length



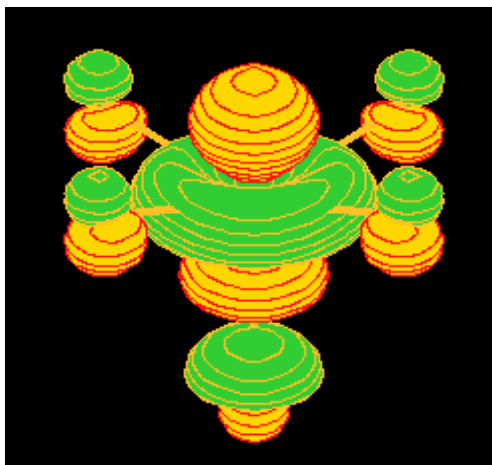
(c)

- $25d_{x^2-y^2}$



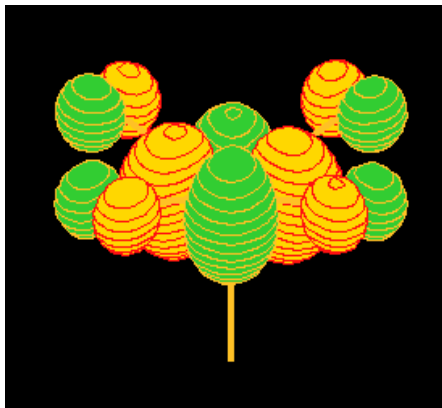
•

- $24d_{z^2}$



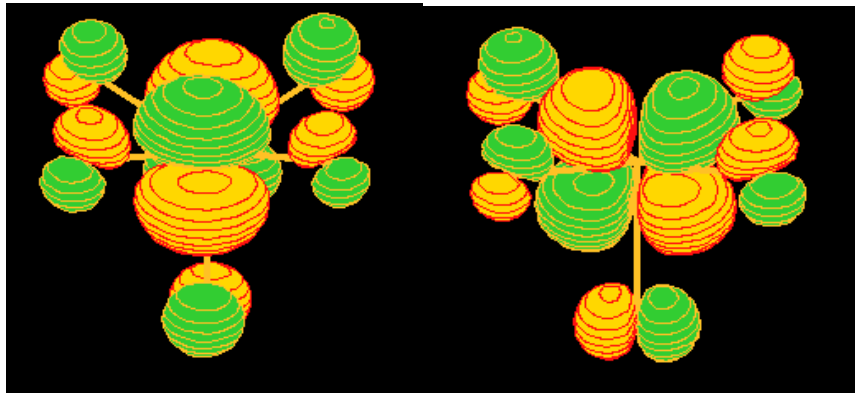
•

- $23d_{xy}$



•

- $22d_{xz}, 21d_{yz}$

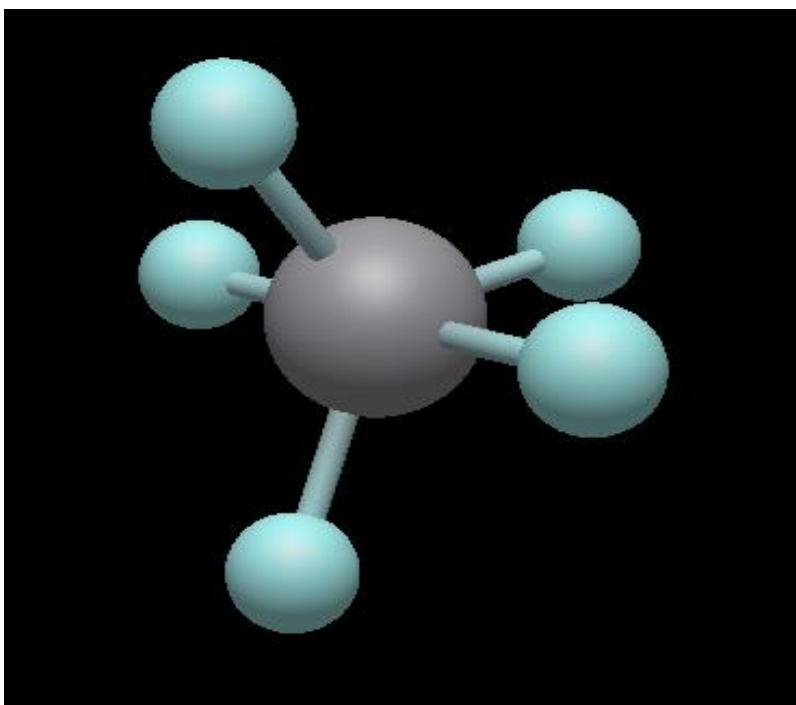


-
- E:

Molden Orbital Select		
Nr.	Eigenvalue	Occupation
16	-0.572693	2.00
17	-0.563997	2.00
18	-0.561667	2.00
19	-0.561636	2.00
20	-0.555149	2.00
21	-0.417597	0.00
22	-0.417564	0.00
23	-0.417255	0.00
24	-0.346189	0.00
25	-0.022611	0.00
26	0.370289	0.00
27	0.485351	0.00
28	0.485745	0.00

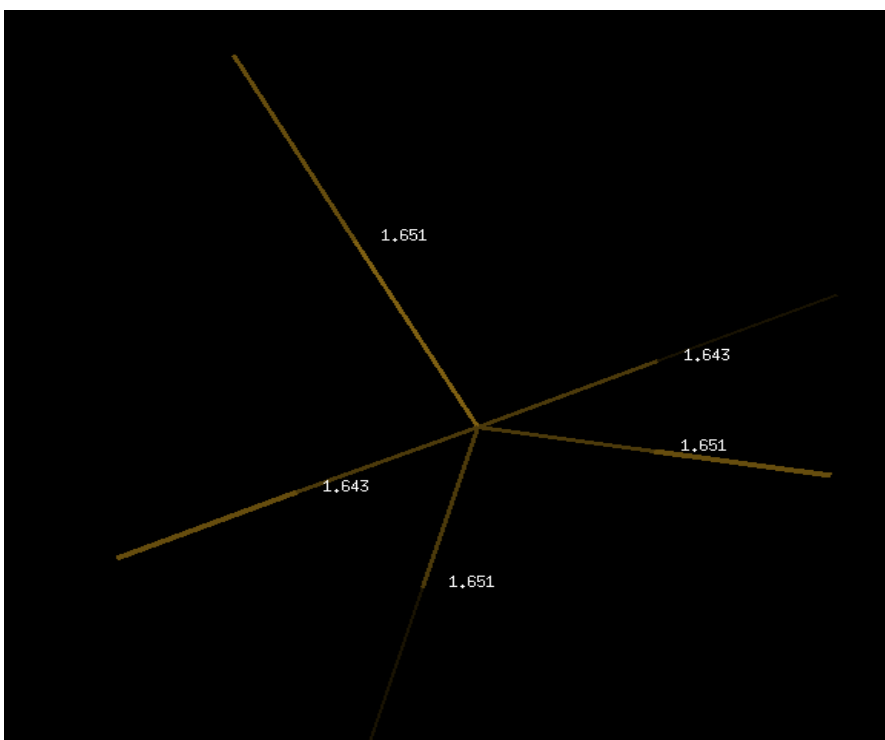
-

trigonal bipyramidal



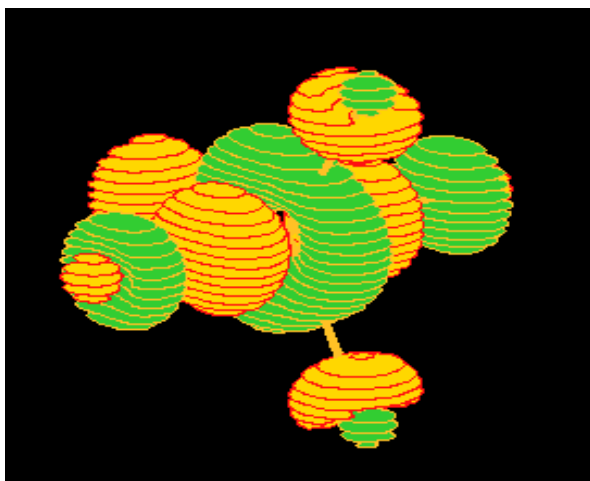
- Energy : -25.835167715651 Eh

bond length

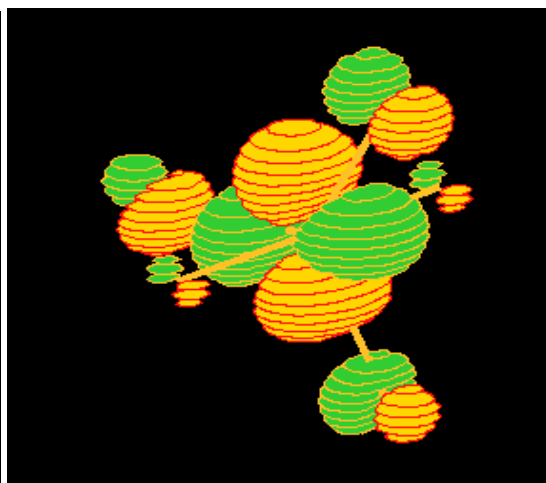
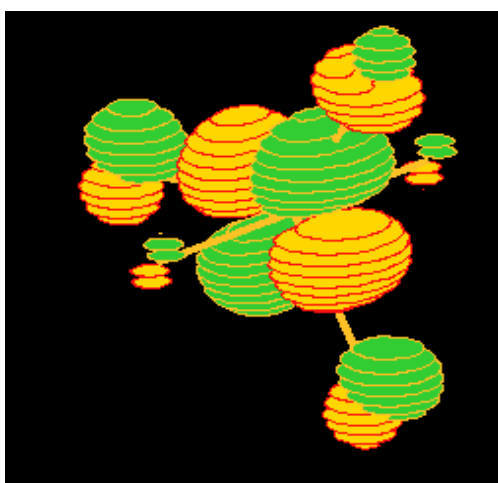


(c)

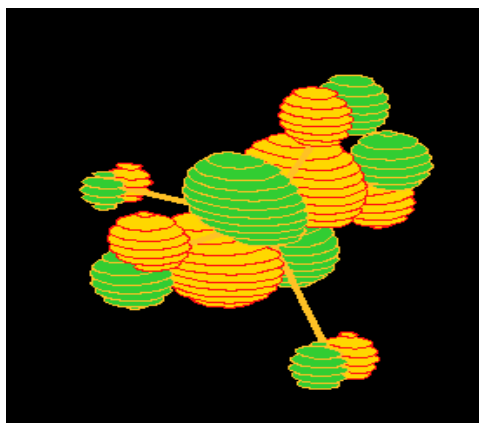
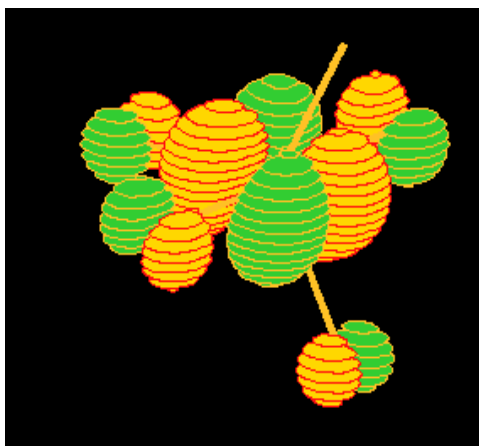
- $25d_{z^2}$



-
- $24 d_{xy}, 23 d_{x^2-y^2}$



-
- $22 d_{xz}, 21 d_{yz}$



- E

Nr.	Eigenvalue	Occupation
17	-0.566645	2.00
18	-0.564275	2.00
19	-0.563893	2.00
20	-0.563884	2.00
21	-0.423404	0.00
22	-0.423398	0.00
23	-0.370851	0.00
24	-0.370847	0.00
25	-0.059249	0.00
26	0.432751	0.00
27	0.432756	0.00
28	0.491821	0.00
29	0.609983	0.00

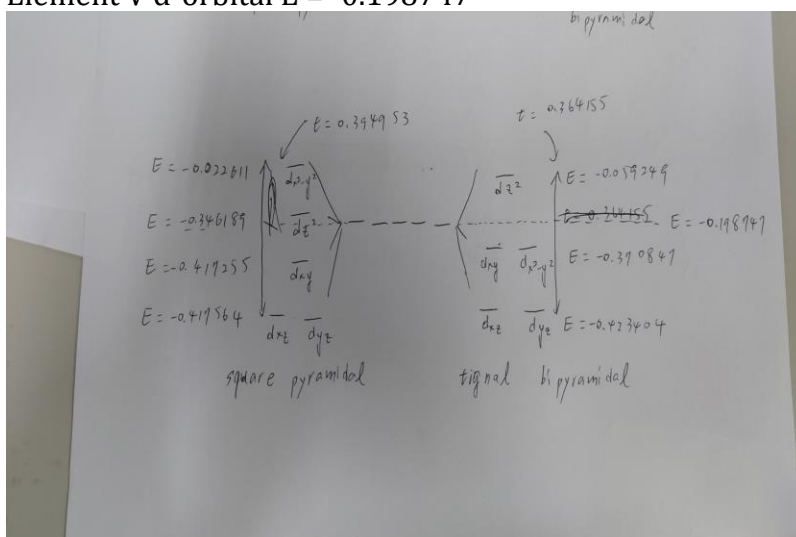
bond angle

(b)

- The square pyramidal is more stable

(d)

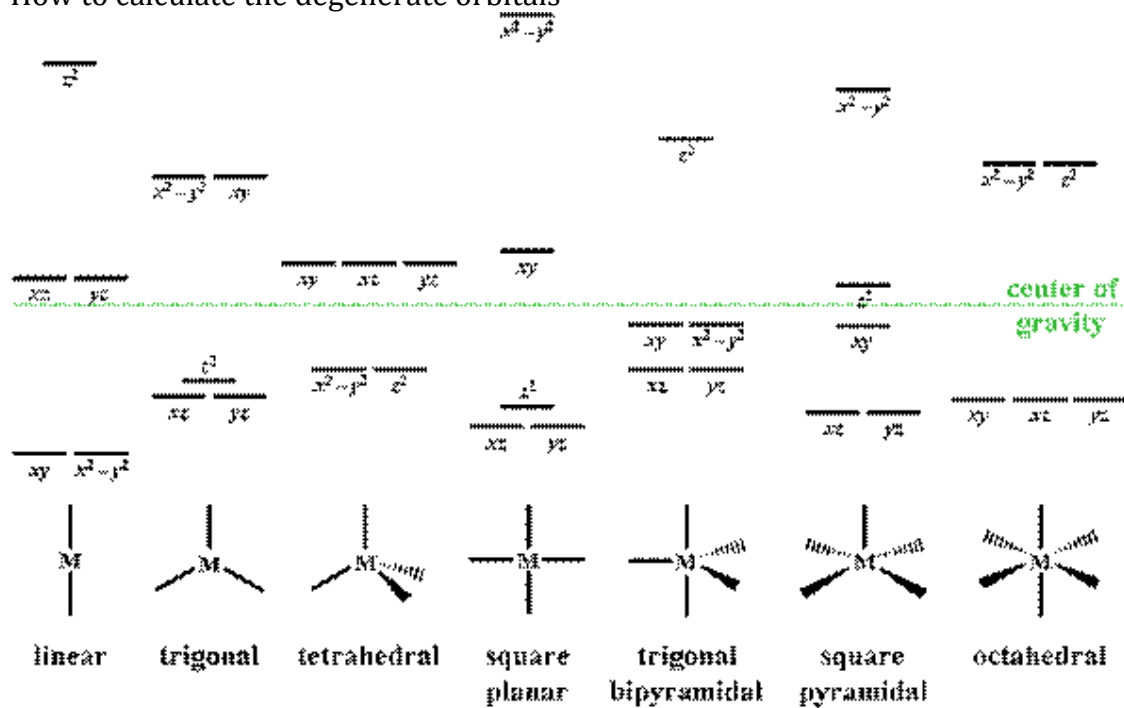
- Element V d-orbital E = -0.198747



Questions

1. The molecular orbitals have like d orbital but in low orbital

2. How to calculate the degenerate orbitals



repository

<https://github.com/pumachu/2022-xTB-summer-school>