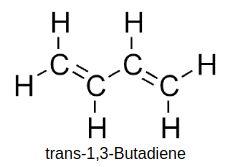
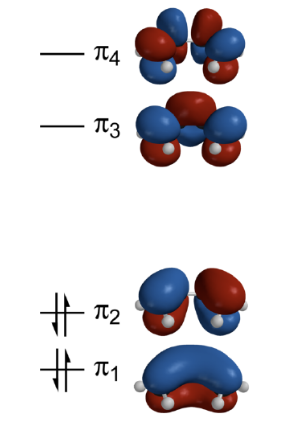
## HW

### Hückel theory

* The molecular orbitals are linear combination of atomic orbitals
* Standard approximation of Hückel theory
  + , When
  + , Others
* Calculate the delocalize energy

#### Example 1,3-Butadiene

 1. Linear combination of molecular orbitals

1. For solving the ith molecular orbital need to solve
2. By standard approximation of [Hückel theory](#Hückel-theory) the matrix become
3. If c1,c2,c3,c4 is not trivial then the determinant is 0. E is the eigunvalue
4. Simplfy by divided by and then
5. Solve the equation
6. Derive the E1, E2, E3, E4
7. The electron configeration and shape(by HF/6-31G\* ) 
8. Calculate the energy of molecular orbitals
9. Compare the energy of butadiene with two ethylene

* The **delocalization energy** is about 0.48 = -35 kJ/mol
* 一張含有 文字, 白板 的圖片

  自動產生的描述The delocalization can stable the molecular

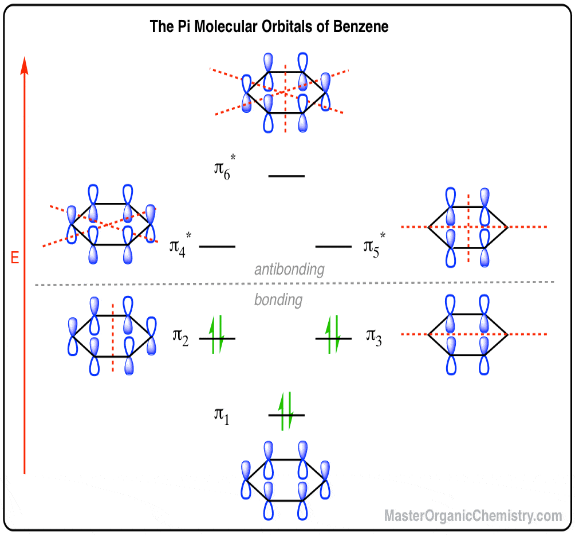
#### (b) The wavefunction of the π MOs () of benezne

#### (c) The Hamiltonian matrix for benezene

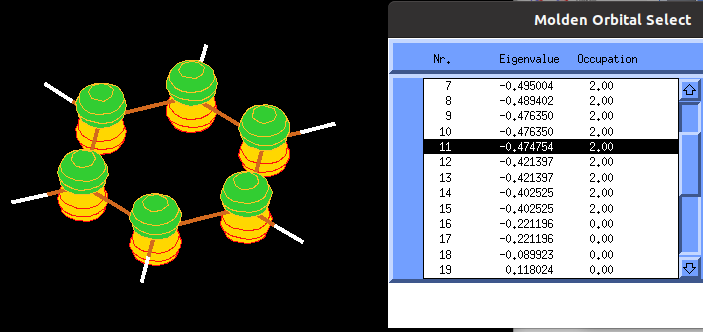
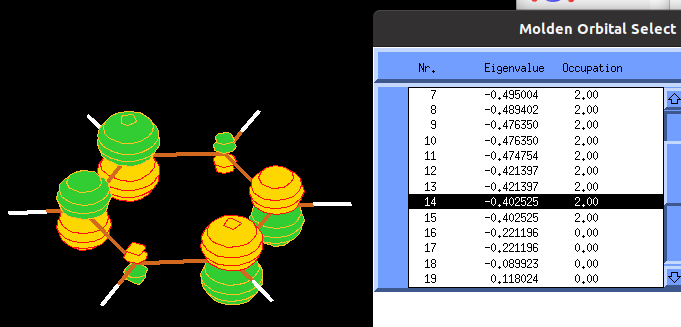
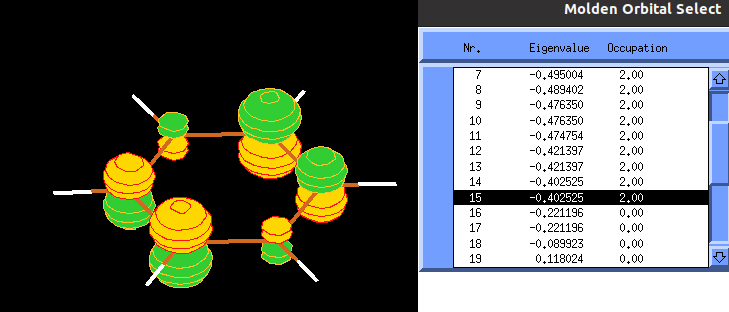
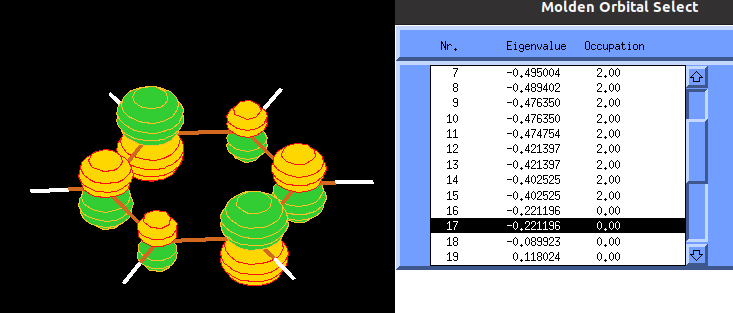
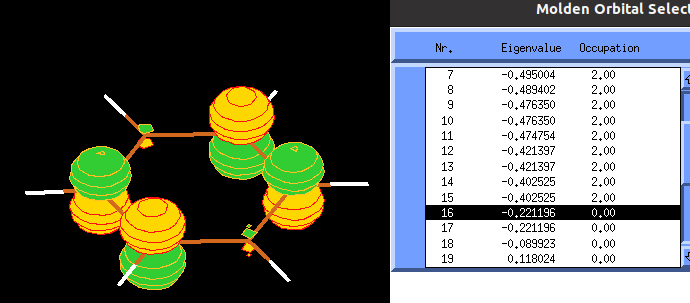
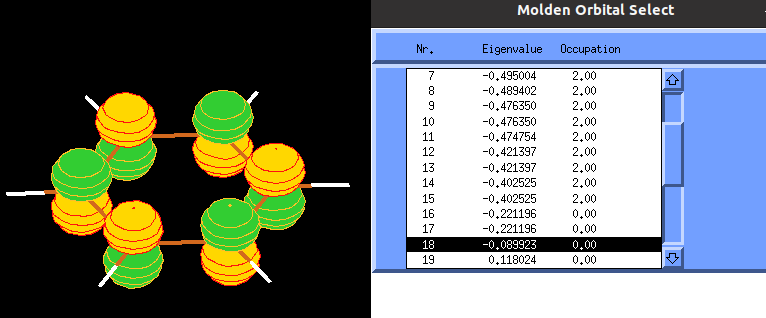
#### 一張含有 文字, 白板 的圖片 自動產生的描述(d)

E =

(e)



#### (f)

* 
* 
* 
* \* 
* \* 
* \* 
* E2-E1 ≠ 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 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 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 Eh
  + LUMO = -0.035127

#### Conclude

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

* EAvertical = −0.1595 Eh = −4.3402183 eV
* EAadiabatic = −0.163649381 Eh = −4.45312877 eV
* EA(exp) = -0.200 ± 0.050 eV

1 Eh = 27.2114 eV

### HOMO, LUMO and their difference for oligothiophene

#### Structure bulid

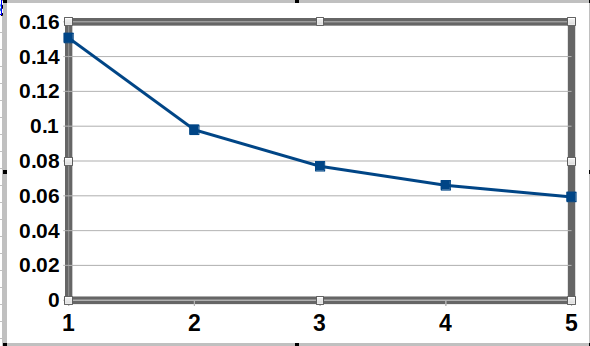
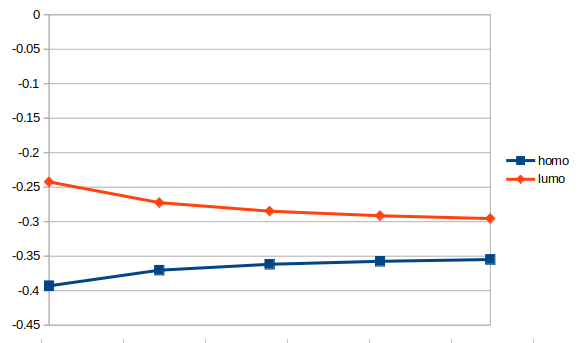
1. Draw the structure by the following html http://www.cheminfo.org/flavor/malaria/Utilities/SMILES\_generator\_\_\_checker/index.html
2. Output the structure by SMILES
3. Use Avogadro to optimize the structure
4. Output with the file.xyz

#### HOMO,LUMO

* Search HOMO,LUMO

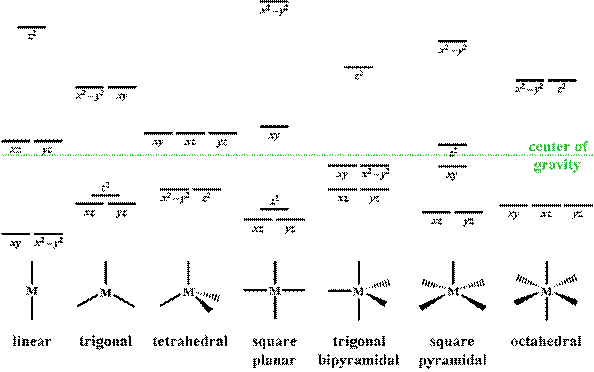
grep "Occu" -B 2 molden.input

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| 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 |

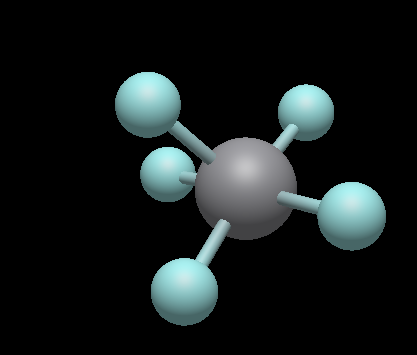
* The energy gap become narrow as the n inrease 
* The homo increase and lumo decrease as the n increase 

### MOs for VF5

#### Splitting field

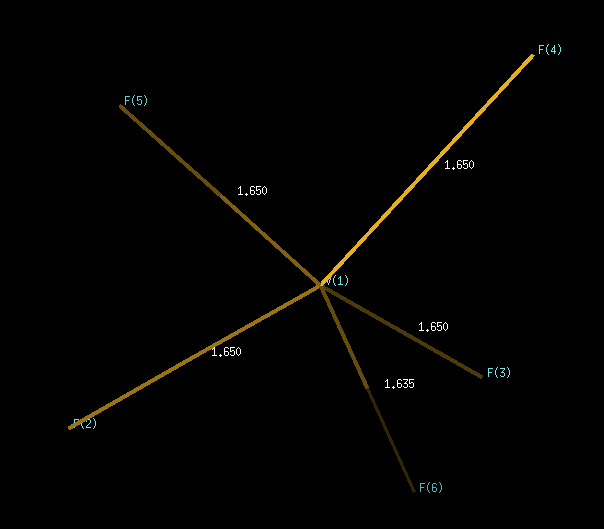


#### square pyramidal

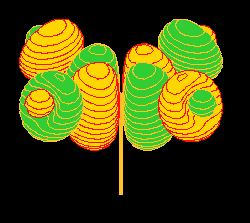
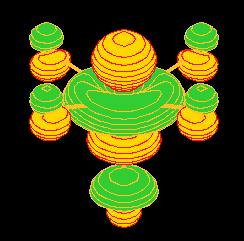
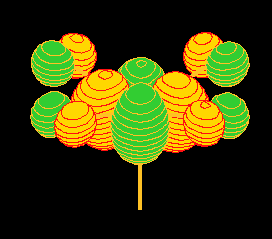


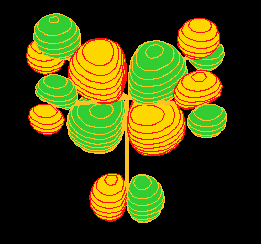
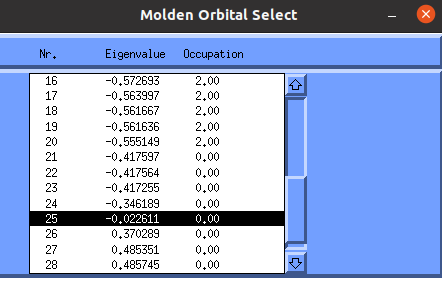
* Energy : -25.830963344050 Eh

##### bond length

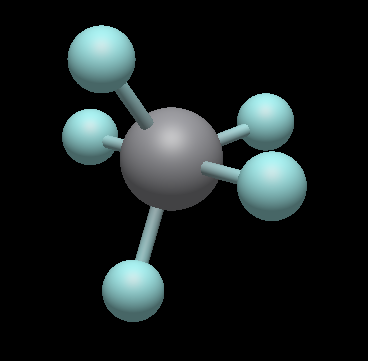


##### (c)

* 
* 24
* 
* 23dxy
* 
* 22dxz,21dyz
* 一張含有 汽球, 向量圖形, 交通號誌 的圖片

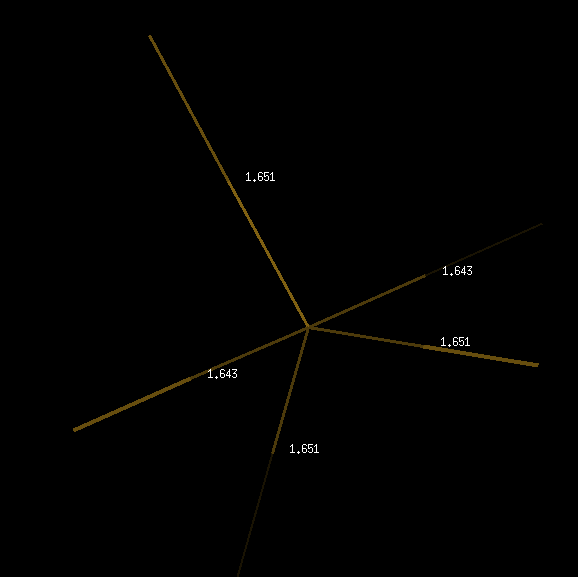
  自動產生的描述
* E :
* 

#### trigonal bipyramidal

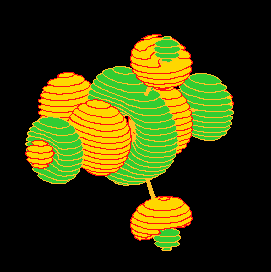
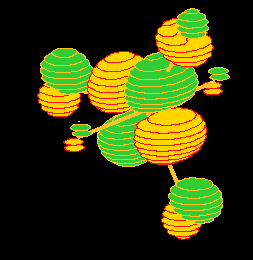
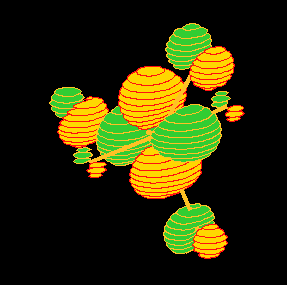
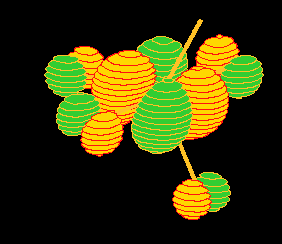
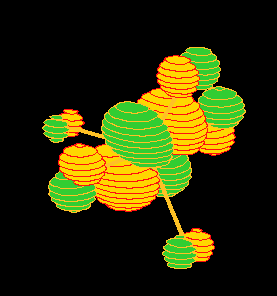


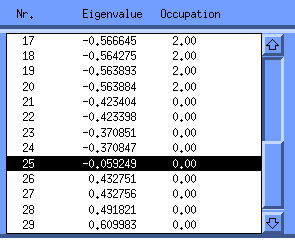
* Energy : -25.835167715651 Eh

##### bond length



##### (c)

* 25
* 
* 24 dxy,23
*  
* 22 dxz, 21 dyz
*  
* E

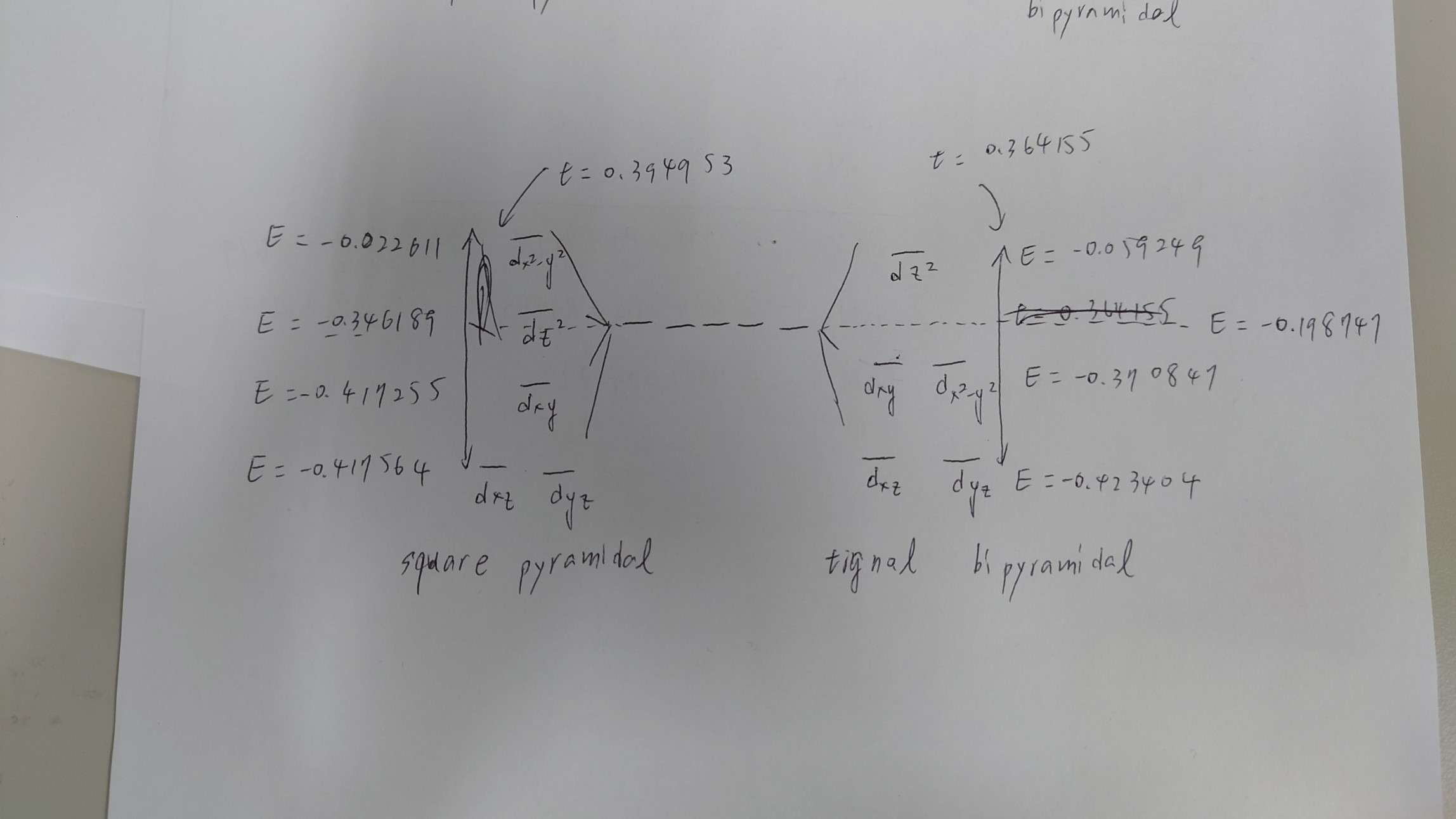


##### bond angle

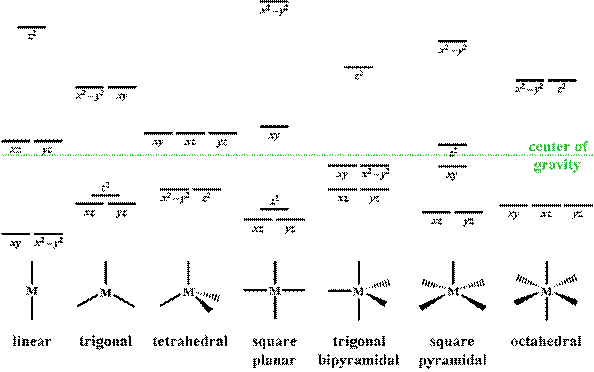
#### (b)

* The sqare 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