



國立清華大學

化學工程學系

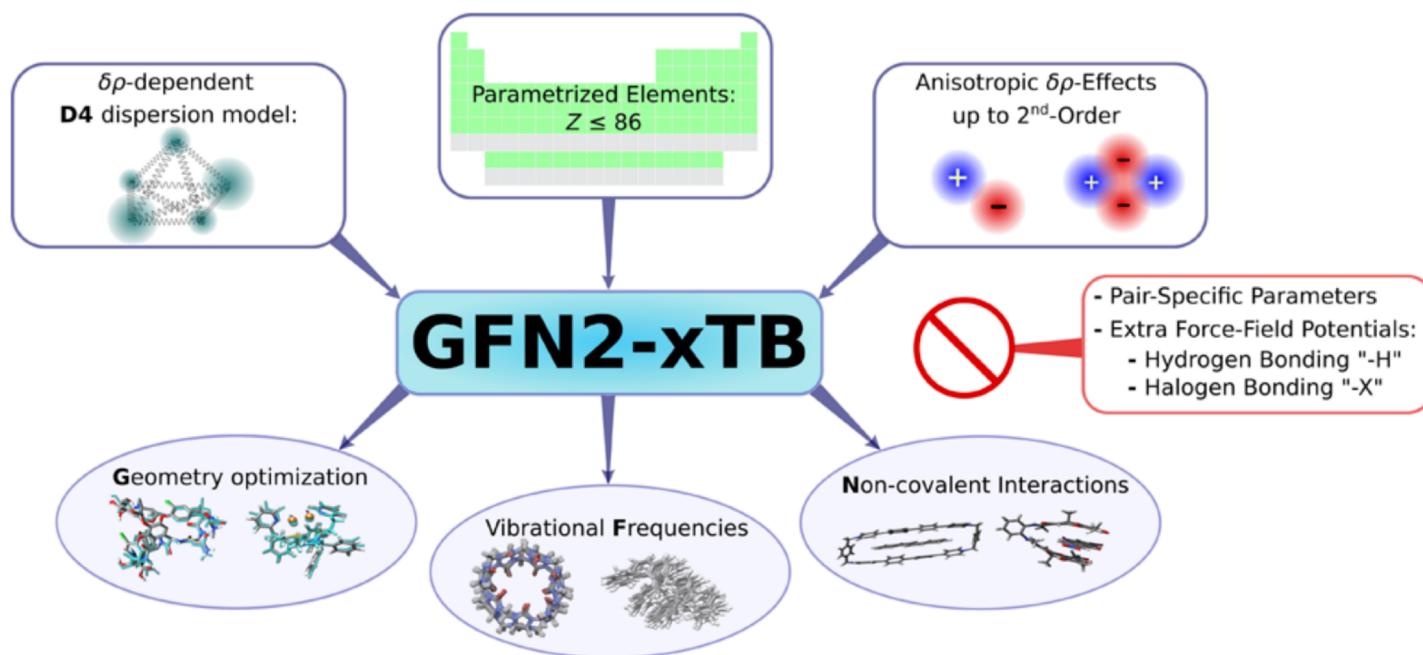
National Tsing Hua University  
Department of Chemical Engineering

# 2022 Summer School

## Electronic Structure Calculations Using GFN2-xTB

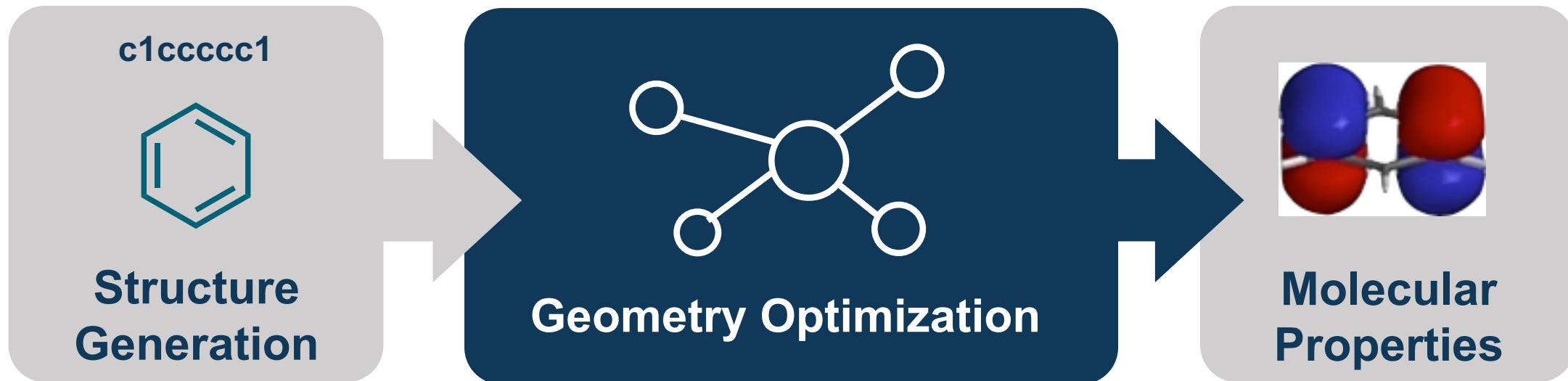
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National Tsing Hua University, Taiwan

# What is xTB?



- Electronic structure method
- Semiempirical
  - Parameters
  - Element-specific
- DFTB3 variants
  - Expand energy up to the 3<sup>rd</sup> order wrt  $\rho_0$
- Fast
  - Geometry optimization

# Common workflow in computational chemistry



Avogadro,  
Chemdraw,  
Openbabel,

...

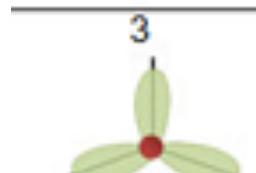
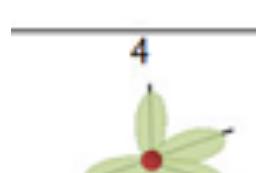
DFT, WF-based method,  
semiempirical, forcefield...

Electronic structure  
method needed

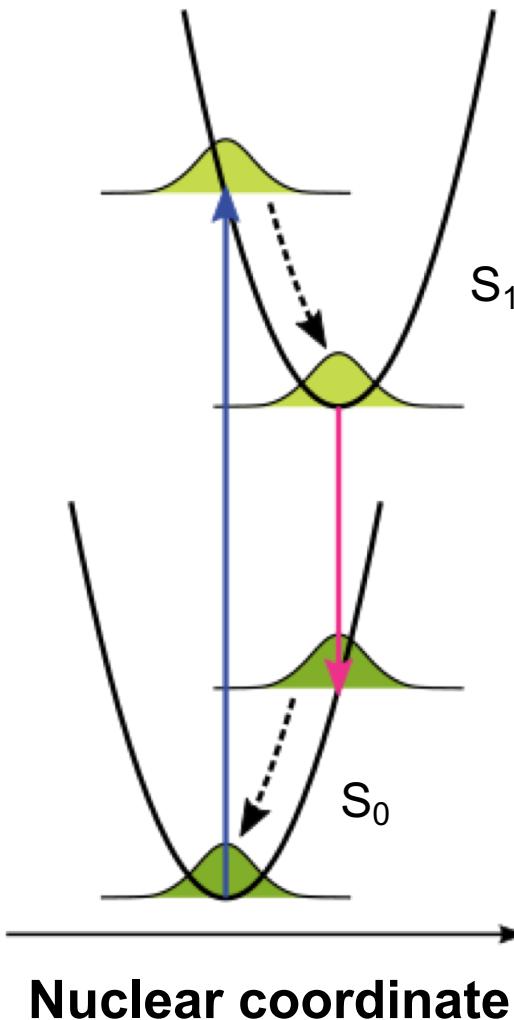
# **Week 1. Geometry Optimization**

# What is molecular geometry?

- 3D structure or arrangement of atoms in a molecule
- Why is it important?
  - Electronic structure depends on the geometry
  - Properties depend on the electronic structure
- What is the most representative geometry?
  - VSEPR
  - The one with the lowest energy

Number of Electron Dense Areas	Electron-Pair Geometry	No Lone Pairs
2	Linear	
3	Trigonal planar	
4	Tetrahedral	

# Examples – absorption and relaxation processes



- The molecular geometries are different in  $S_1$  and  $S_0$  minimum. (**? shift**)
- Absorption-relaxation process
  - The molecule is mostly in its minimum at ground state  $S_0$ .
  - Light absorption triggers the electron to occupy higher state  $S_0 \rightarrow S_1$ . This process is so fast that the molecular keeps its ground state geometry. (**? Principle**)
  - Vibrational relaxation to the minimum of  $S_1$ .
  - Emission of a photon and  $S_1 \rightarrow S_0$ . (geometry fixed)
  - Vibrational relaxation to the minimum of  $S_0$ .

# Potential energy surface

Under **Born-Oppenheimer approximation**:

$$\Psi(\mathbf{r}, \mathbf{R}) = \varphi_e(\mathbf{r}; \mathbf{R}) \varphi_N(\mathbf{R})$$

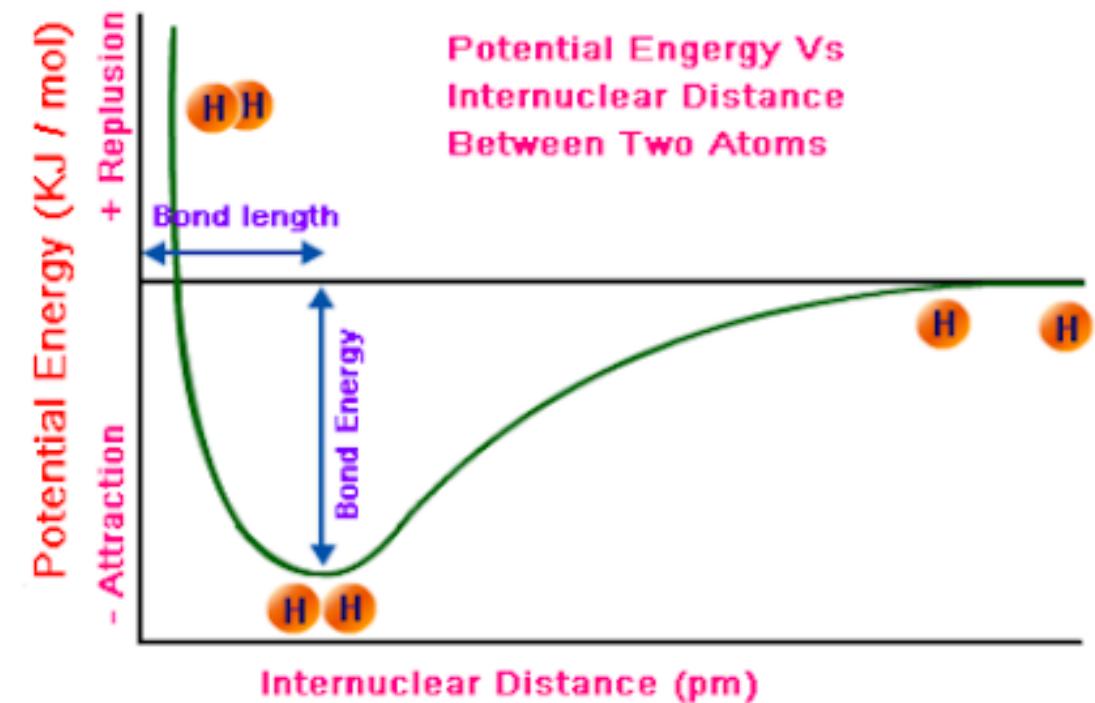
$$\hat{H}_{el}\varphi_e(\mathbf{r}; \mathbf{R}) = E_{el}\varphi_e(\mathbf{r}; \mathbf{R})$$

$$\{\hat{T}_N + E_{el} + \hat{V}_{NN}\}\varphi_N(\mathbf{R}) = E_{tot}\varphi_N(\mathbf{R})$$

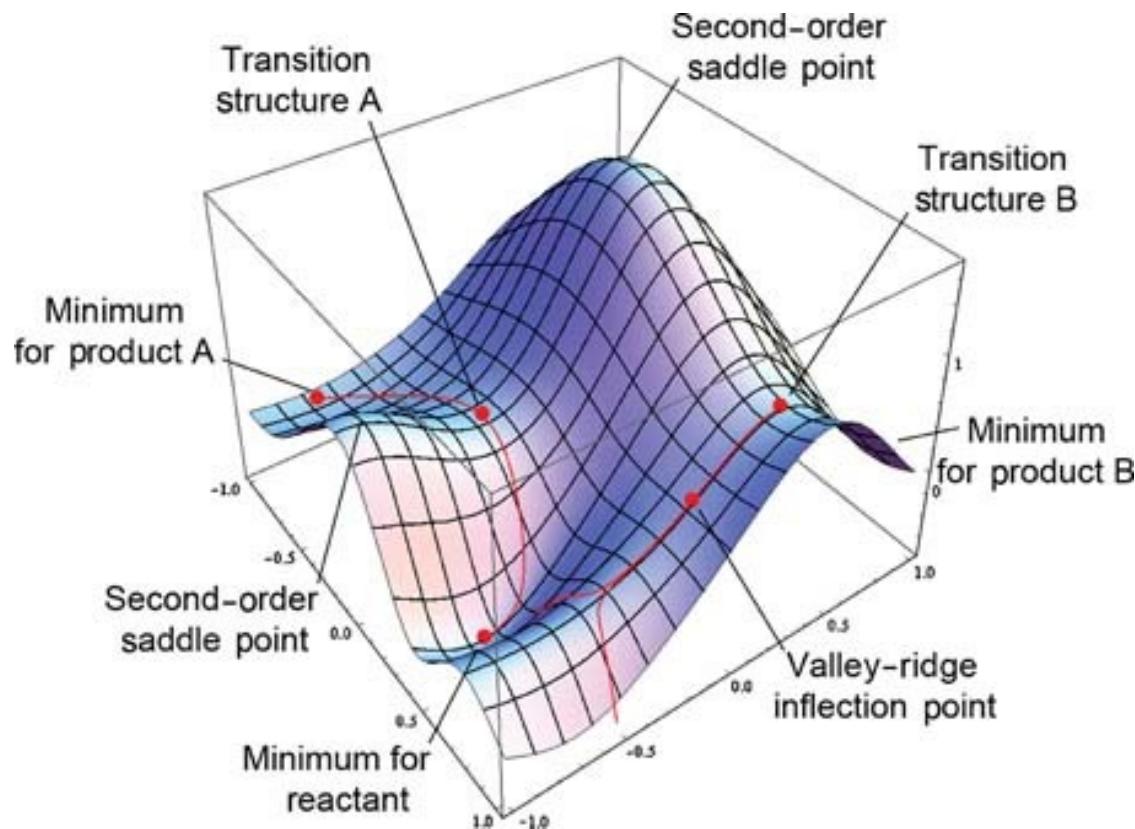
This means that for each nuclear coordinate  $\mathbf{R}$ , we can compute its associate potential energy.

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R})$$

Schrödinger equation

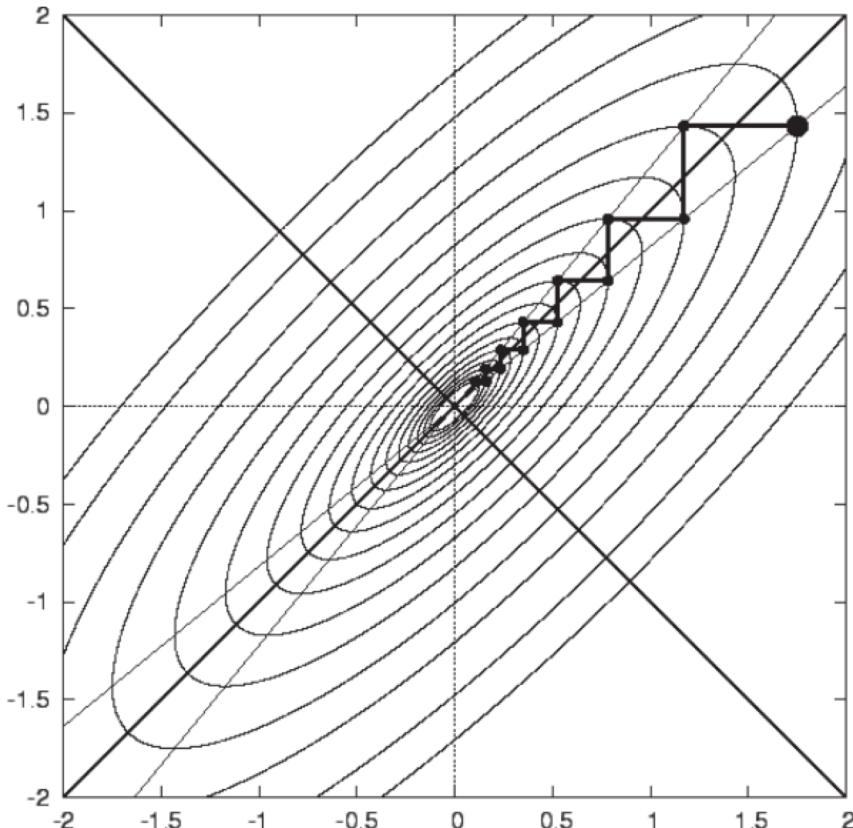


# Geometry optimization: what and why?



- Ground state minimum
  - Geometry with lowest energy in ground state
  - Most stable and representative
- Statistical mechanics
  - Boltzmann factor  $P_l = \frac{\exp(-\epsilon_l/k_B T)}{\sum_l \exp(-\epsilon_l/k_B T)}$
- Several local minimum
  - **Conformational isomers (examples?)**

# Geometry optimization: how?



Characteristic zig-zagging pattern produced by the basic gradient descent method.

- Optimization problem
  - Finding global minimum
  - But often, we stuck at local ones
- Algorithms
  - **Steepest descent, conjugate gradients, BFGS**
- Overcome local minimum
  - **Simulated annealing**

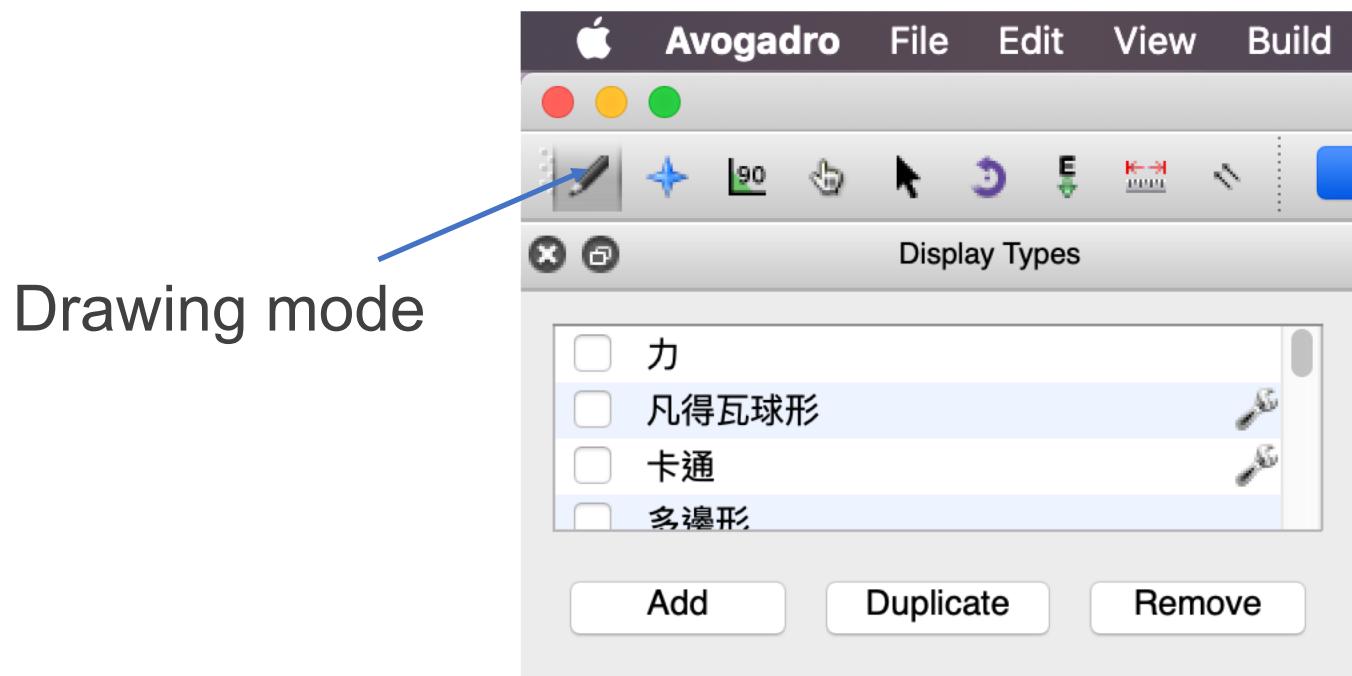
# Hands-on: optimization of benzene molecule

## Learning Goal

- Generate initial molecular geometry of benzene using Avogadro.
- Preoptimize the geometry using the force-field approach.
- Perform geometry optimization using xTB.
- Visualize the initial and final molecular geometry.
- Understand the output of xTB.

# Generate initial structure using Avogadro

By drawing

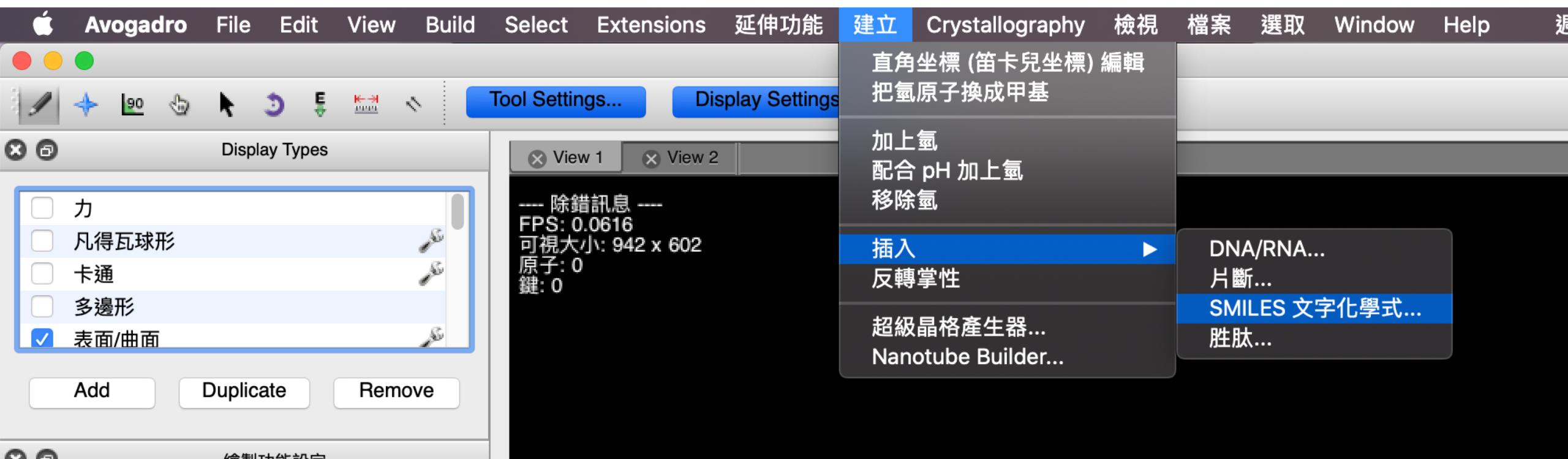


Other function?

# Generate initial structure using Avogadro

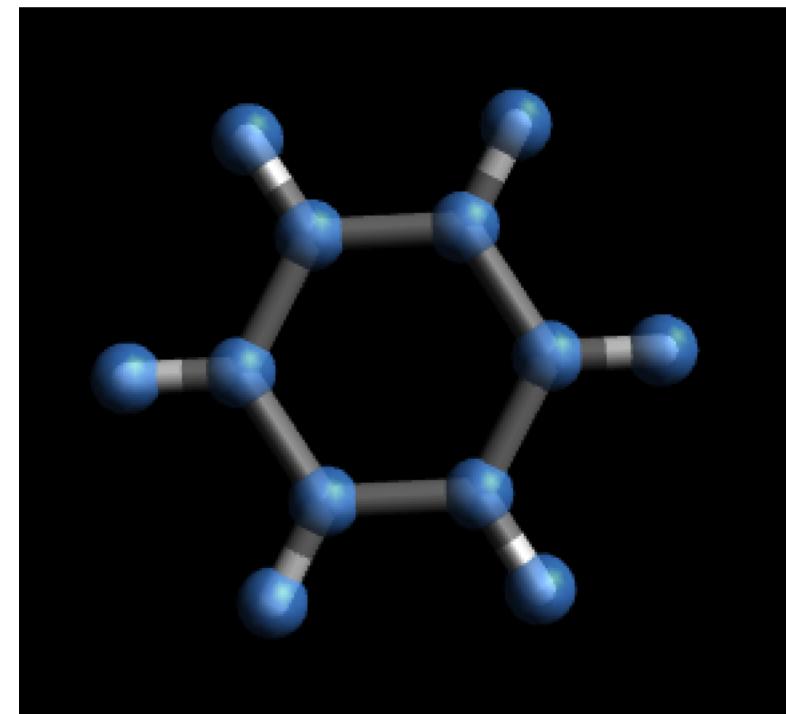
## Generate initial structure with SMILES

Try c1ccccc1

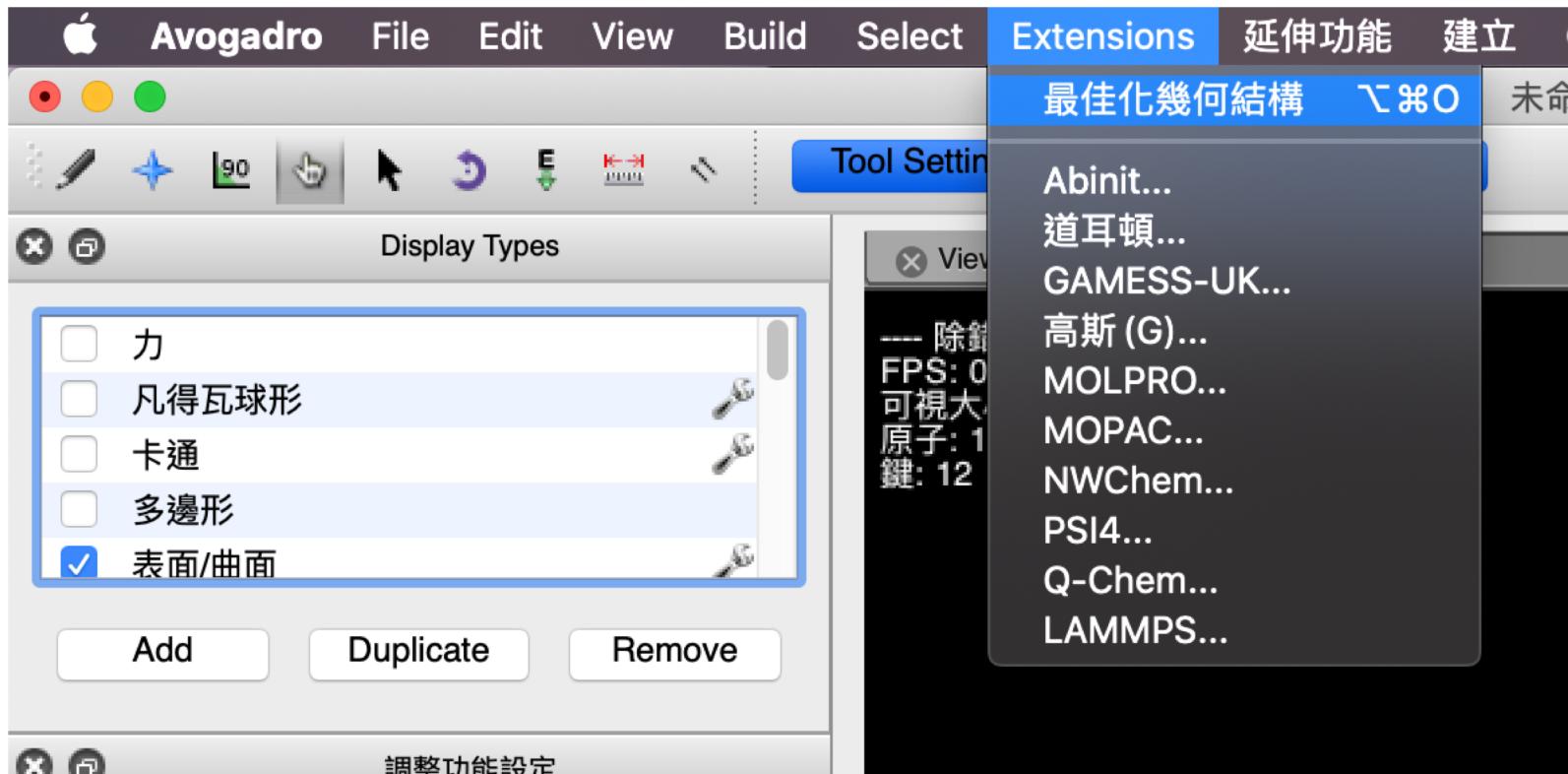


# Generate initial structure using Avogadro

## Generate initial structure with SMILES

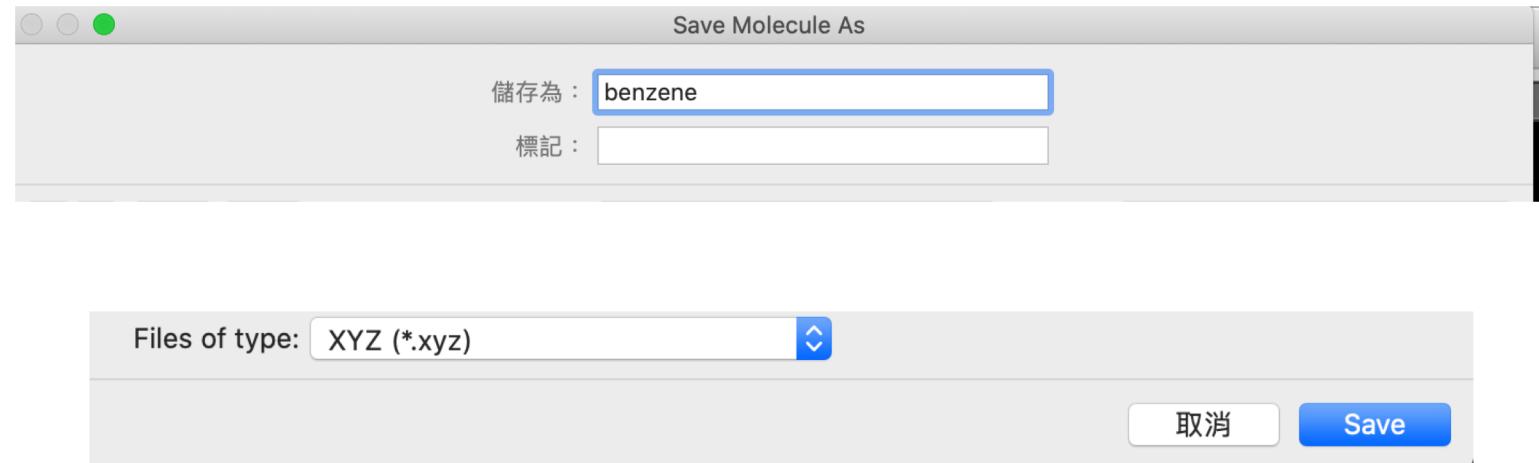
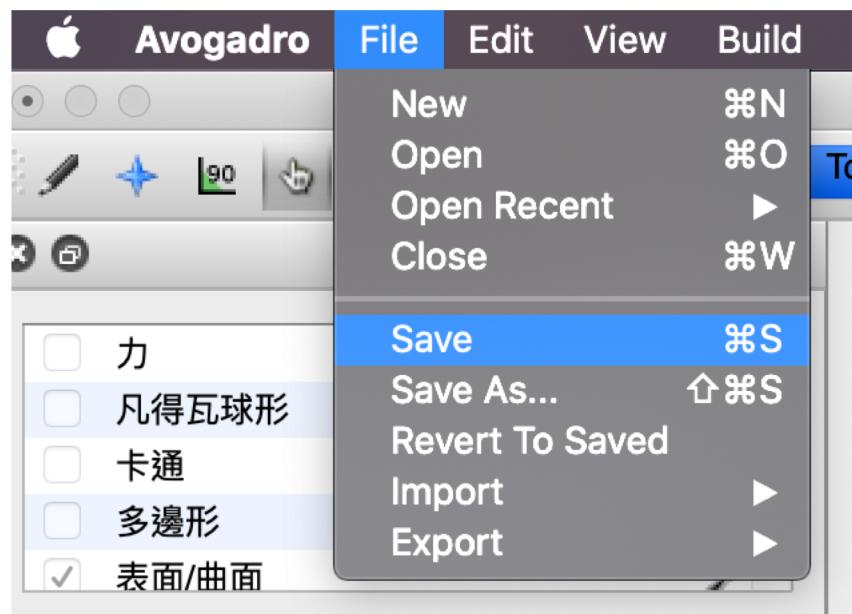


# Preoptimization using FF



What force field it uses? How is it defined?

# Save the structure as .xyz format



# Commands in Linux terminal mode

- List the files in the current folder
  - ls (欸摟欸摟, 不是哀哀)
- Show the absolute path of the current folder
  - pwd
- Create a folder
  - mkdir(空格)*name\_of\_the\_folder*
- Enter the folder
  - cd(空格)*name\_of\_the\_folder*
- Go to the parent directory of the current folder (回上一層)
  - cd(空格)..

# Commands in Linux terminal mode

- Copy a file from folder A to folder B
  - cp(空格)*absolute\_path\_A/file\_name*(空格)*absolute\_path\_B*
- Open the file with vi editor (像是用記事本打開檔案)
  - vi(空格)*file\_name*
- Remove a file (be careful!!!!)
  - rm(空格)*file\_name*
- Remove a folder (be careful!!!!)
  - rm(空格)-r(空格)*folder\_name*
- Copy a file from folder A to the current folder
  - cp(空格)*absolute\_path\_A/file\_name*(空格).

# Commands in Linux terminal mode

- When you open a file with vi editor
  - 鍵盤輸入小寫的i, 不用按enter, 就會進入編輯模式(INSERT mode)
  - 此時可以打字, 就像在記事本輸入文字一樣
  - 當你想要離開, 但不想儲存已作的變更, 輸入:q!
  - 如想儲存, 輸入:wq
  - 還有很多很多功能, 搜尋vi Editor Cheat Sheet
  - 我們接下來會利用vi創建xTB的input, 以及檢視xTB的output, 所以一定要熟練他。

# How to run xTB?

- Create a folder called benzene
  - mkdir W1
- Enter the folder
  - cd W1
- Copy the running script
  - cp path\_2\_the\_script .
- Copy the .xyz file
  - cp path\_2\_the\_xyz .
- Export the xtb bin folder path
  - vi ~/.bashrc
  - Add a line: export  
PATH="path\_2\_the\_bin:\$PATH"

# How to run xTB?

- Running the script

- First check the script
    - vi opt\_xtb.sh
    - Memory setting and number of cpus
    - Correct input xyz name?
    - Running it in the background
      - nohup bash opt\_xtb.sh &

```
export OMP_STACKSIZE=4G
ulimit -s unlimited
export OMP_NUM_THREADS=8,1
export MKL_NUM_THREADS=8

xtb -c 0 -u 0 input.xyz --opt normal --molden --esp --pop > xtb.out
```

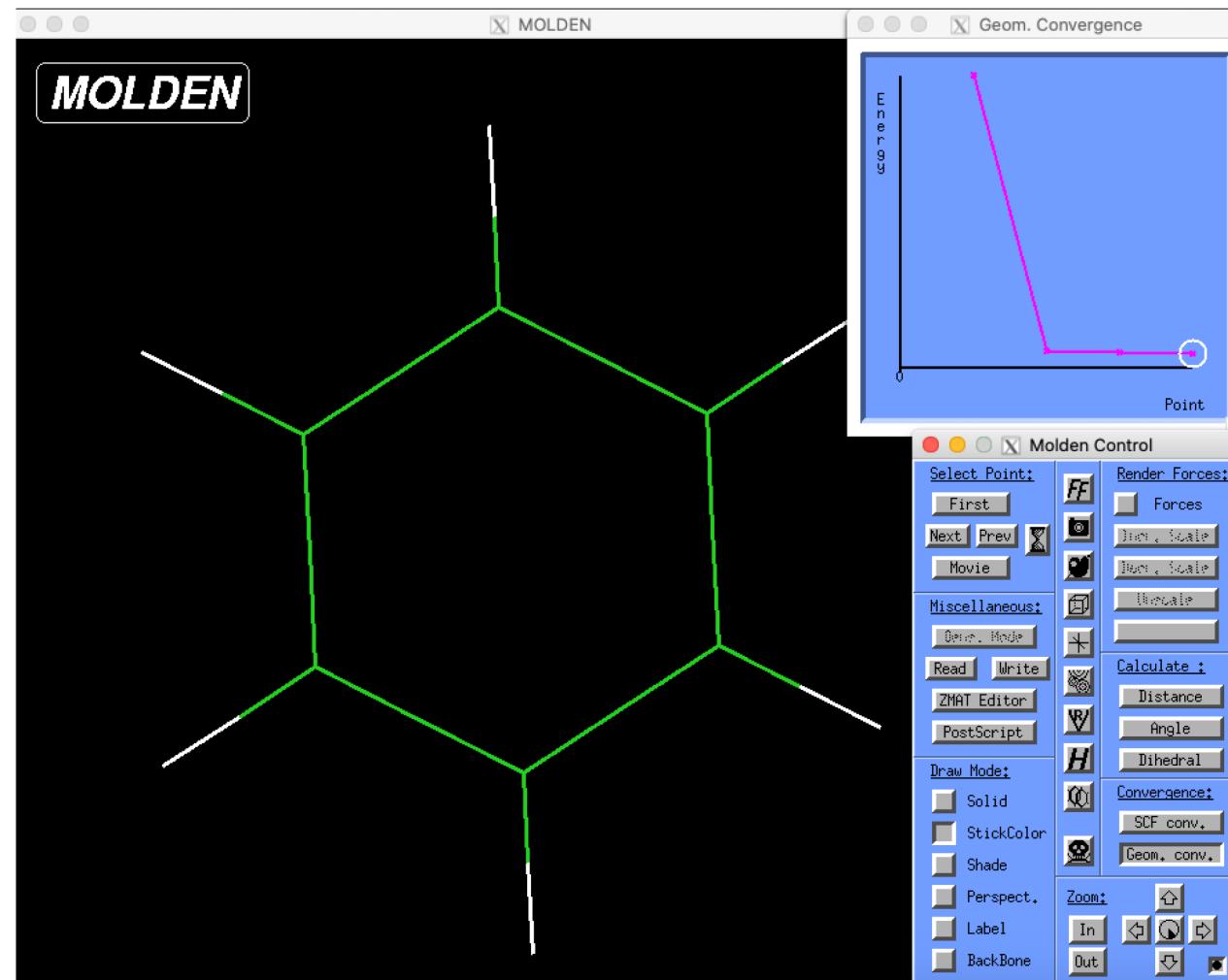
number of unpaired electrons:  
Close-shell (singlet) = 0  
doublet = 1, triplet = 2,...

charge state of the molecule:  
Neutral = 0  
+1 Cation = +1  
-1 Anion = -1...

# Visualization using molden

## Results (xtbopt.log)

Movie of the trajectory  
during optimization.



3 steps in total

# Visualization using molden

## Results (xtb.out)

```
..... CYCLE 1 ...
1 -16.1773247 -0.161773E+02 0.166E-05 4.83 0.0 T
2 -16.1773247 -0.376588E-12 0.104E-05 4.83 2779.2 T
3 -16.1773247 -0.294875E-12 0.614E-06 4.83 4705.1 T
SCC iter. ... 0 min, 0.001 sec
gradient ... 0 min, 0.001 sec
* total energy : -15.8788435 Eh change -0.6741363E-09 Eh
gradient norm : 0.0191628 Eh/α predicted 0.0000000E+00 (-100.00%)
displ. norm : 0.0799401 α lambda -0.1412047E-02
maximum displ.: 0.0796274 α in ANC's #16, #24, #17, ...
..... CYCLE 2 ...
1 -16.1944478 -0.161944E+02 0.483E-02 4.92 0.0 T
2 -16.1944479 -0.120098E-06 0.295E-02 4.92 1.0 T
3 -16.1944479 -0.468465E-07 0.165E-03 4.92 17.5 T
4 -16.1944479 -0.135188E-08 0.625E-04 4.92 46.2 T
SCC iter. ... 0 min, 0.001 sec
gradient ... 0 min, 0.001 sec
* total energy : -15.8796311 Eh change -0.7875903E-03 Eh
gradient norm : 0.0019070 Eh/α predicted -0.7105352E-03 ( -9.78%)
displ. norm : 0.0151193 α lambda -0.1920350E-04
maximum displ.: 0.0151187 α in ANC's #16, #24, #17, ...
```

nuclear cycle

electronic cycle

total energy of the current step

norm of the gradient

size of the displacement

the largest element of the displacement vector

# Total energy

- The potential energy of the molecule at a given molecular geometry.
  - No nuclear kinetic energy  $\rightarrow$  0 K!

```
:::::::::::::::::::  
:: SUMMARY ::  
:::::::::::  
:: total energy -15.879640657009 Eh ::  
:: gradient norm 0.000043906528 Eh/a0 ::  
:: HOMO-LUMO gap 4.934244420570 eV ::  
:::::::::::  
:: SCC energy -16.196547785192 Eh ::  
:: -> isotropic ES 0.000791496535 Eh ::  
:: -> anisotropic ES 0.002517684630 Eh ::  
:: -> anisotropic XC 0.012388859324 Eh ::  
:: -> dispersion -0.008019530469 Eh ::  
:: repulsion energy 0.316900344000 Eh ::  
:: add. restraining 0.000000000000 Eh ::  
:::::::::::
```

# Coordination number

## Results

# (xtb.out)

coordination number			Dispersion C6		
#	Z	covCN	q	C6AA	$\alpha(0)$
1	6 C	2.920	-0.029	28.718	8.788
2	6 C	2.920	-0.029	28.718	8.788
3	6 C	2.920	-0.029	28.718	8.788
4	6 C	2.920	-0.029	28.718	8.788
5	6 C	2.920	-0.029	28.718	8.788
6	6 C	2.920	-0.029	28.718	8.788
7	1 H	0.926	0.029	2.604	2.524
8	1 H	0.926	0.029	2.604	2.524
9	1 H	0.926	0.029	2.604	2.524
10	1 H	0.926	0.029	2.604	2.524
11	1 H	0.926	0.029	2.604	2.524
12	1 H	0.926	0.029	2.604	2.524

# atomic partial charges

## atomic polarizability

# Wiberg bond order

## Results (wbo)

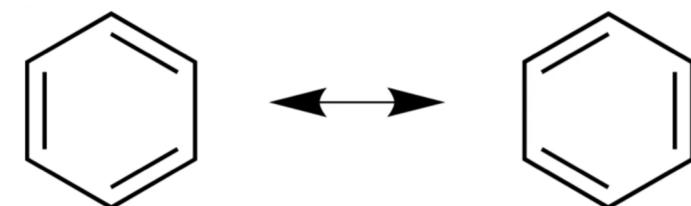
2	1	1.44125328643880
3	2	1.44125339618724
4	3	1.44125333597055
5	4	1.44125345619253
6	1	1.44125353233466
6	5	1.44125323528169
7	1	0.971586995180207
8	2	0.971587024481716
9	3	0.971587023253386
10	4	0.971587015783432
11	5	0.971587014780909
12	6	0.971587001350755

C-C: ~1.5; C-H: ~1

## Wiberg bond order

$$W_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}^2$$

Summation is over atomic orbitals  $\mu$  on atom A and atomic orbitals  $\nu$  on atom B, and  $P_{\mu\nu}$  is the corresponding **density matrix element**.



# Readings

- Geometry optimization
  - Molecular geometry optimization, Dr. Ilya Kuprov
  - Chapter 5 / Molecular modelling: principles and applications, Andrew R. Leach
- Empirical force field
  - Chapter 4 / Molecular modelling: principles and applications, Andrew R. Leach
- Born Oppenheimer approximation
  - Chapter 8 / Molecular Quantum Mechanics 5<sup>th</sup> Ed., Peter Atkins