



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

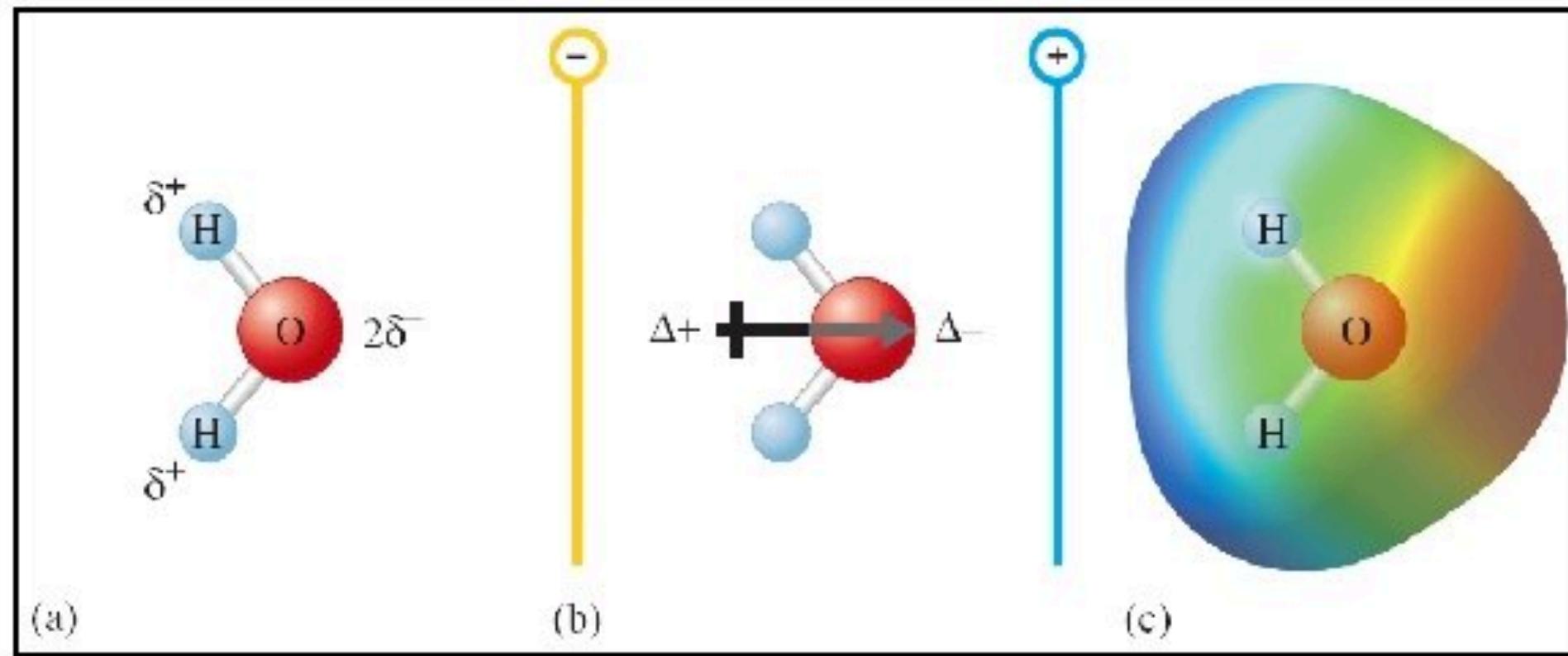
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Department of Chemical Engineering,
National Tsing Hua University, Taiwan

Week 3. Electrostatic Potential & Intermolecular Interactions

What is electrostatic potential?

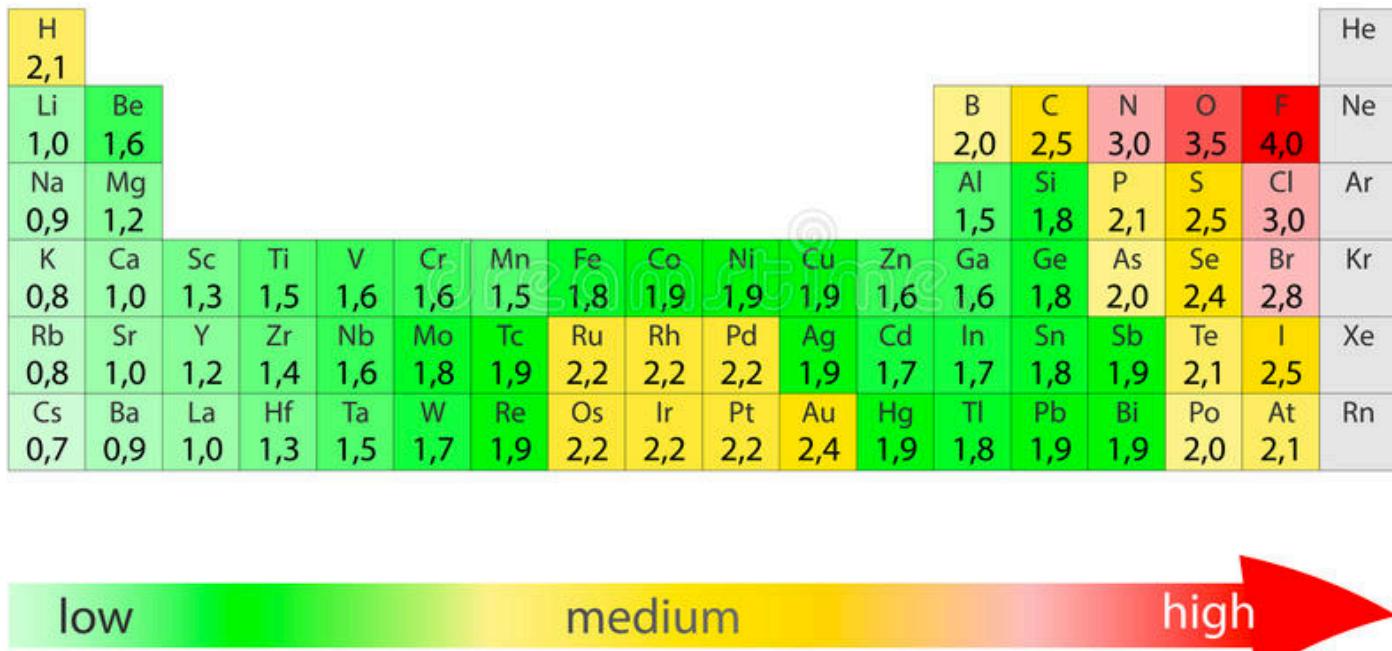
- Measures the 3D charge distribution.
 - Include contributions from nucleus (+) and electrons (-)
 - Measured by putting a positive “test charge”
- Why is it important?
 - Polarity of molecules (electronegativity)
 - Intermolecular interactions
 - Reactivity

Examples: electrostatic potential map of H₂O



Electronegativity

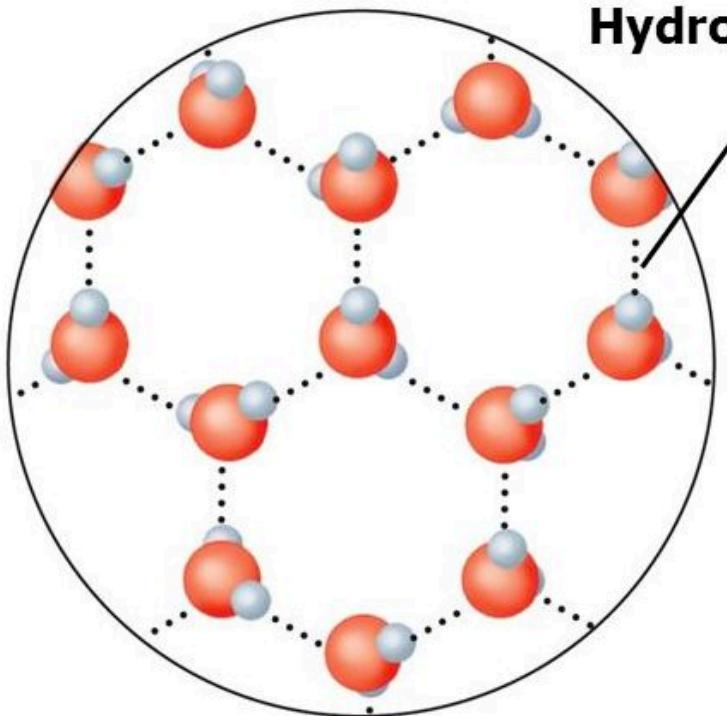
ELECTRONEGATIVITY



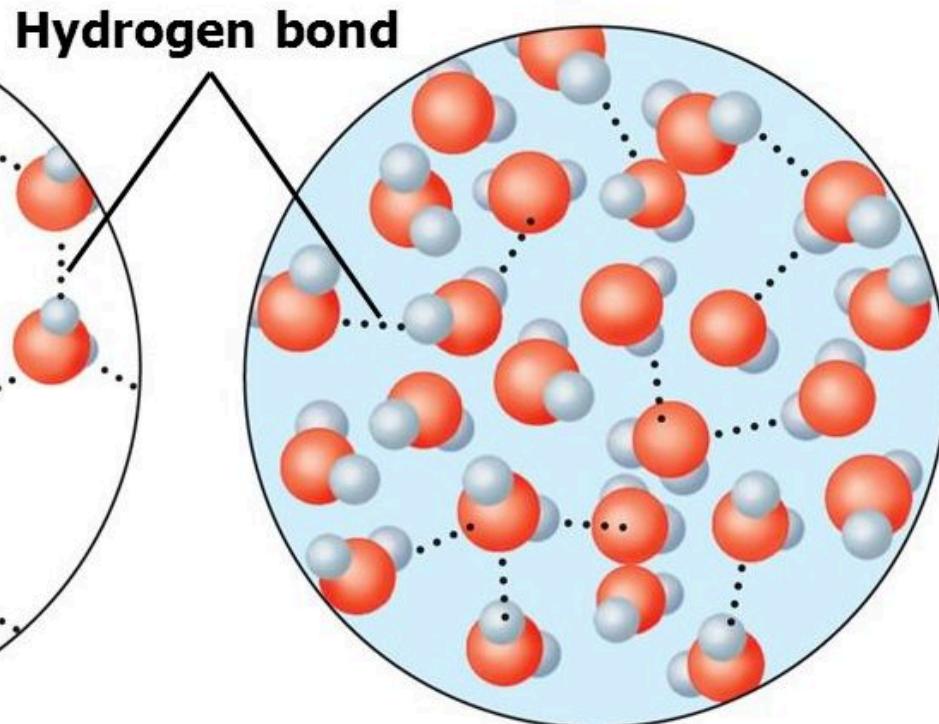
- Tendency to attract e⁻
 - Different versions exist
 - Pauling (difference)
$$|\chi_A - \chi_B| = \sqrt{E_d(AB) - \frac{E_d(AA) + E_d(BB)}{2}}$$
 - Mulliken (absolute)
$$\chi = \frac{IE + EA}{2} = -\mu$$
 - Allred–Rochow (absolute)

$$\chi = 3590 \frac{Z_{eff}}{r_{cov}^2} + 0.744$$

Hydrogen bond: water vs ice molecular packing



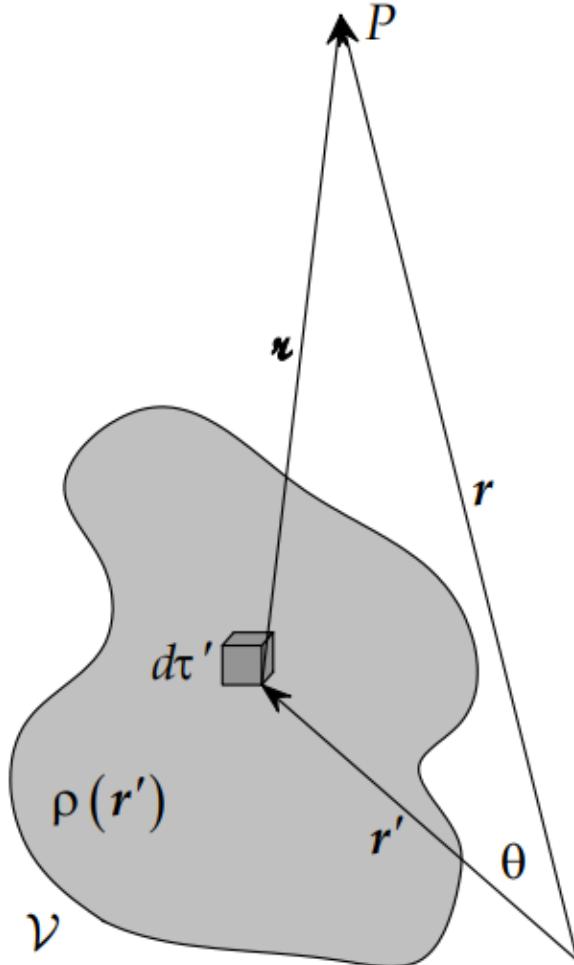
**Ice
Hydrogen bonds
are stable**



**Liquid water
Hydrogen bonds
constantly break and re-form**

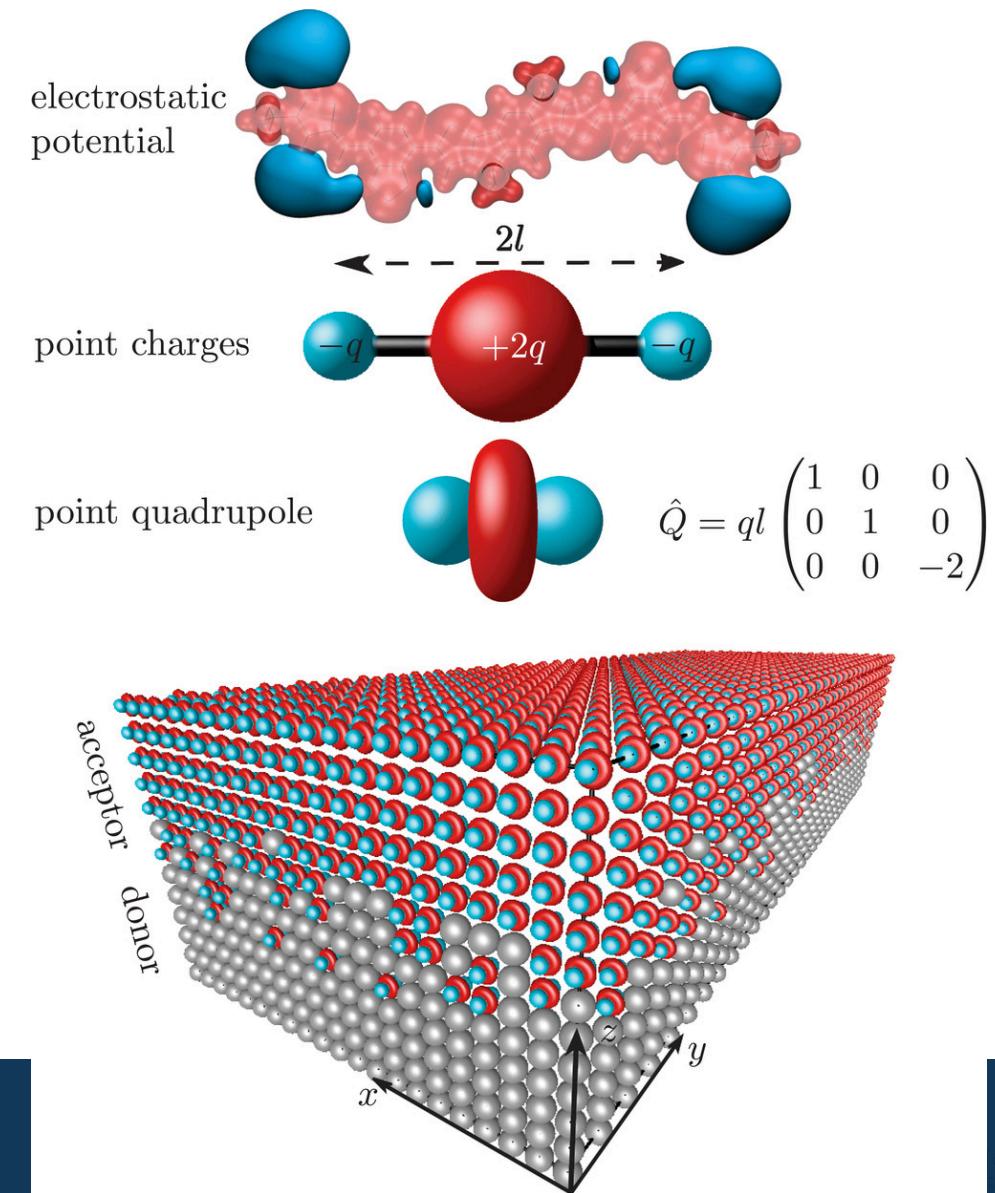
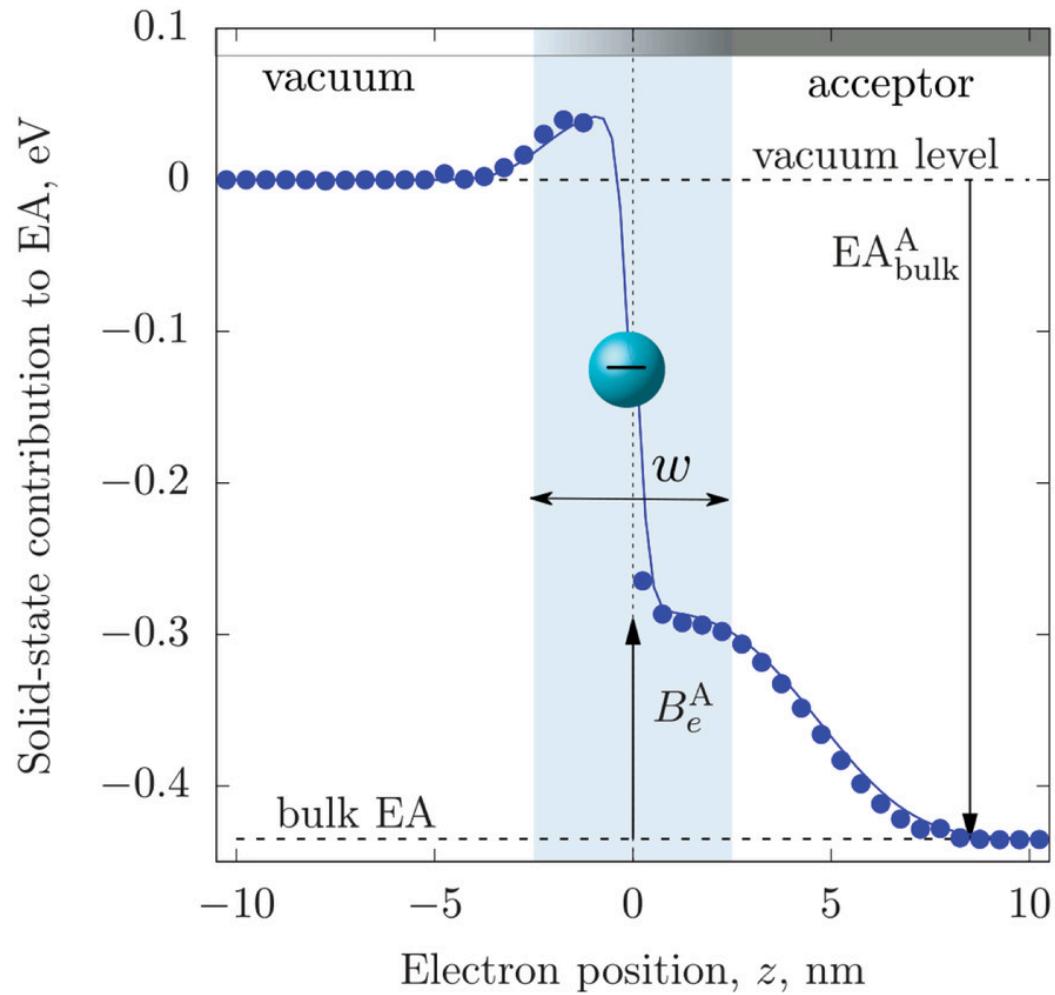
Any water molecule forms
H-bonds with 4 neighbor
water molecules in ice

Multipole expansion



- We want to know the electrostatic potential at point P due to a charge distribution $\rho(r')$
 - $V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'^3$
 - Exact but gives no simple but clear intuition
- Multipole expansion!
 - $V(\mathbf{r}) = V_{mono}(\mathbf{r}) + V_{dip}(\mathbf{r}) + V_{quad}(\mathbf{r}) + \dots$
 - $\frac{1}{|\mathbf{r}-\mathbf{r}'|} = 1 - \frac{\hat{\mathbf{r}} \cdot \mathbf{r}'}{r} + \frac{1}{2r^2} [r'^2 - 3(\hat{\mathbf{r}} \cdot \mathbf{r}')^2] + O(\frac{r'}{r})^3$

Examples: effect of quadrupole moment



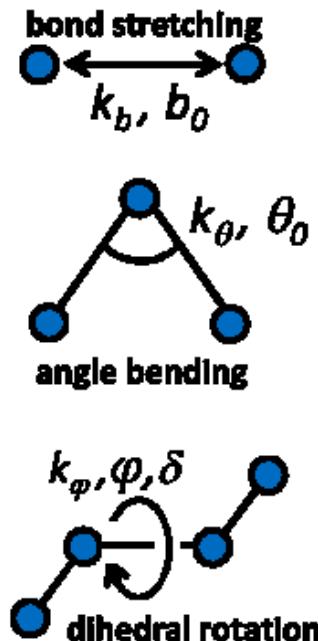
(All-atom) forcefield approaches

Describe interactions between atoms (objects) using mathematical functions.

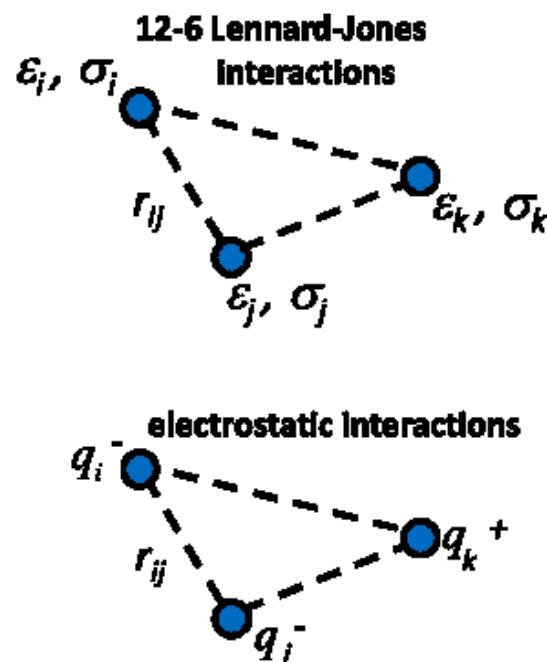
Force Field Equation

$$PE = \sum k_b (b - b_o)^2 + \sum_{\text{angle}} k_\theta (\theta - \theta_o)^2 + \sum_{\text{dihed}} k_\phi [1 + \cos(n\phi - \delta)] + \sum_{L-J} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{\text{Coulomb}} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

Bonded Terms



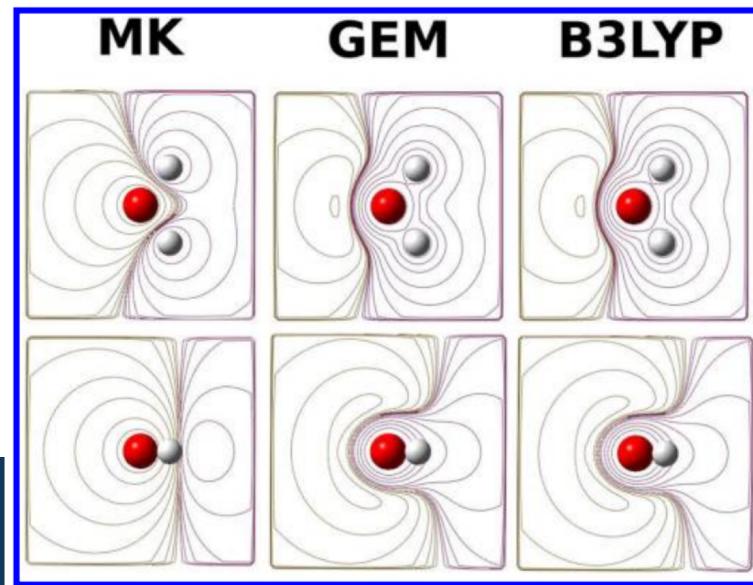
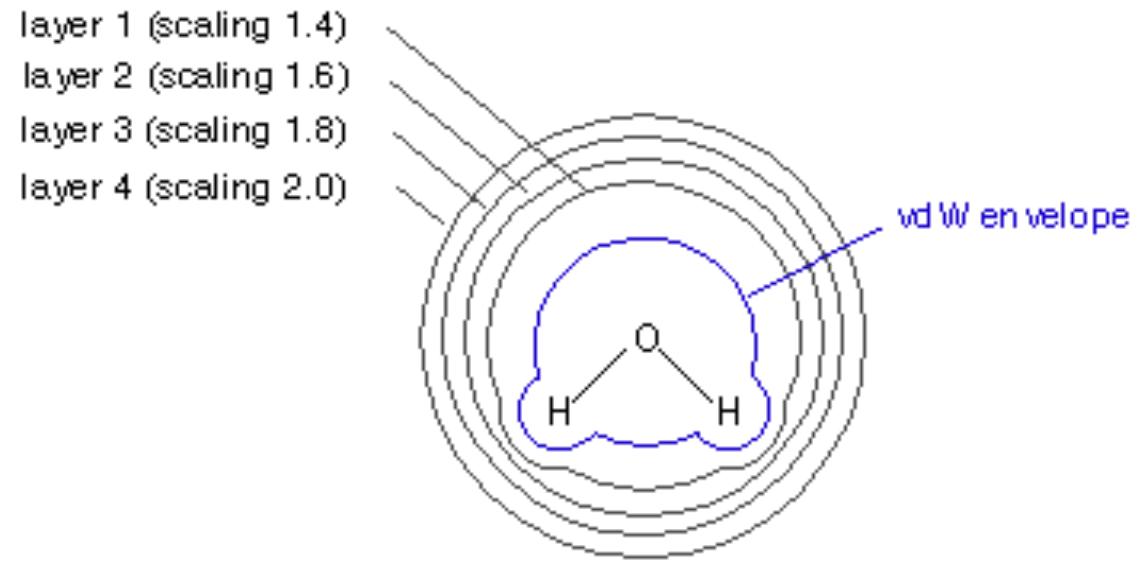
Nonbonded Terms



- Bonded and nonbonded
- **Harmonic** approximations
 - Bond breaking?
- Pair interactions
 - Lennard-Jones
 - Point charges

Forcefield: Merz-Singh-Kollman charge

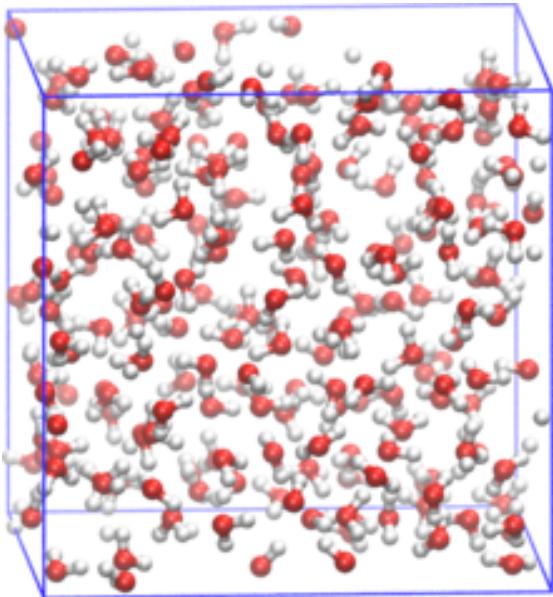
- Reproduce electrostatic potential using atomic point charges
 - **NOT** multipole expansion
 - Fast -> suitable for MD simulations
- Pros and cons
 - Weak basis-set dependent (vs Mulliken charge)
 - Unable to capture higher order multipole effects



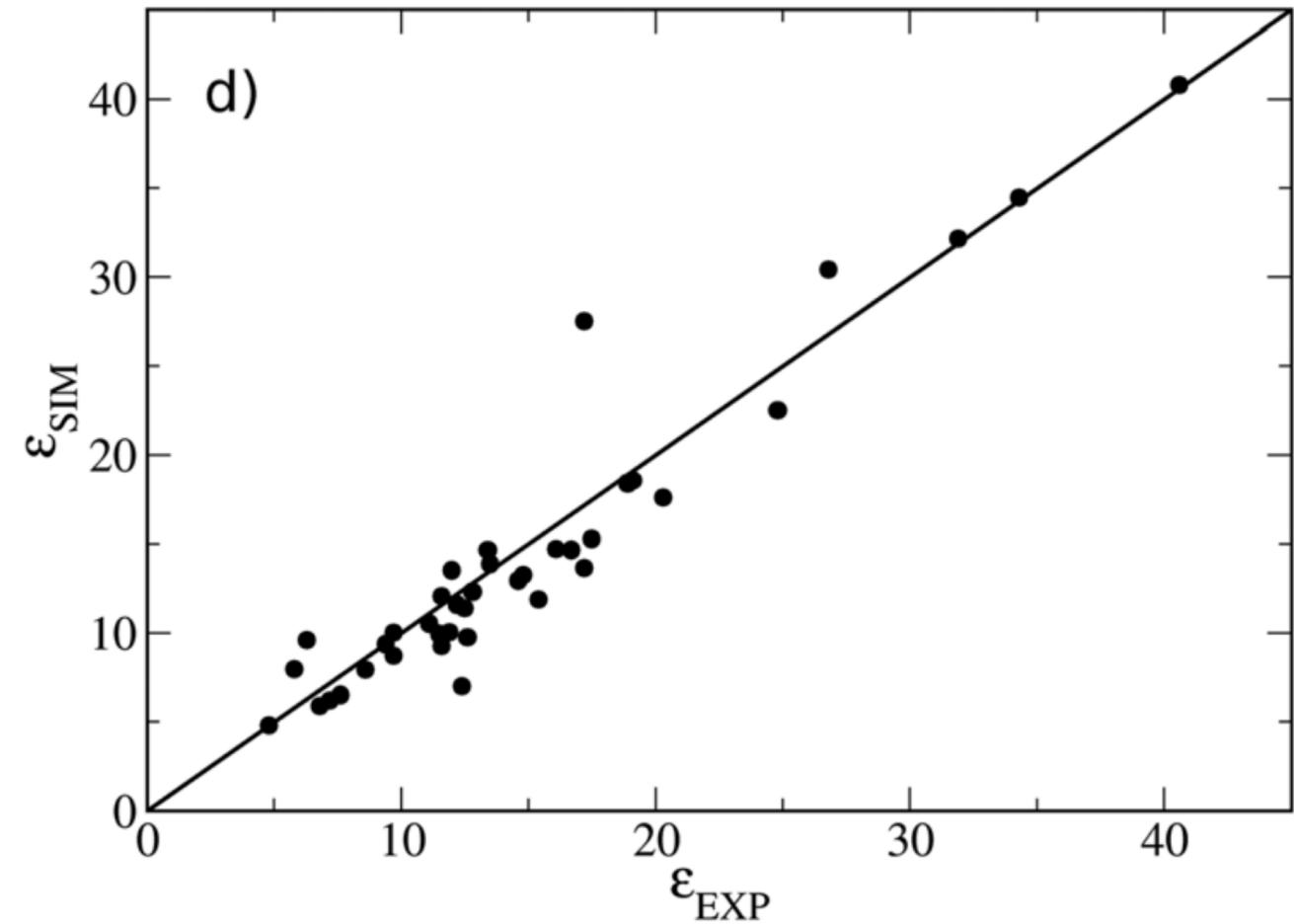
Examples: dielectric constant

dipole fluctuation formula

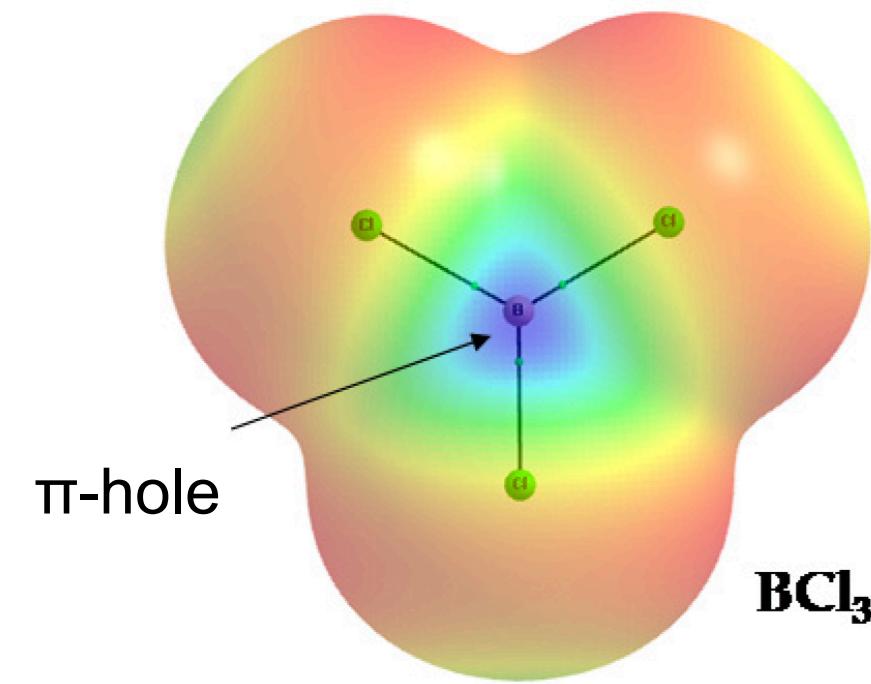
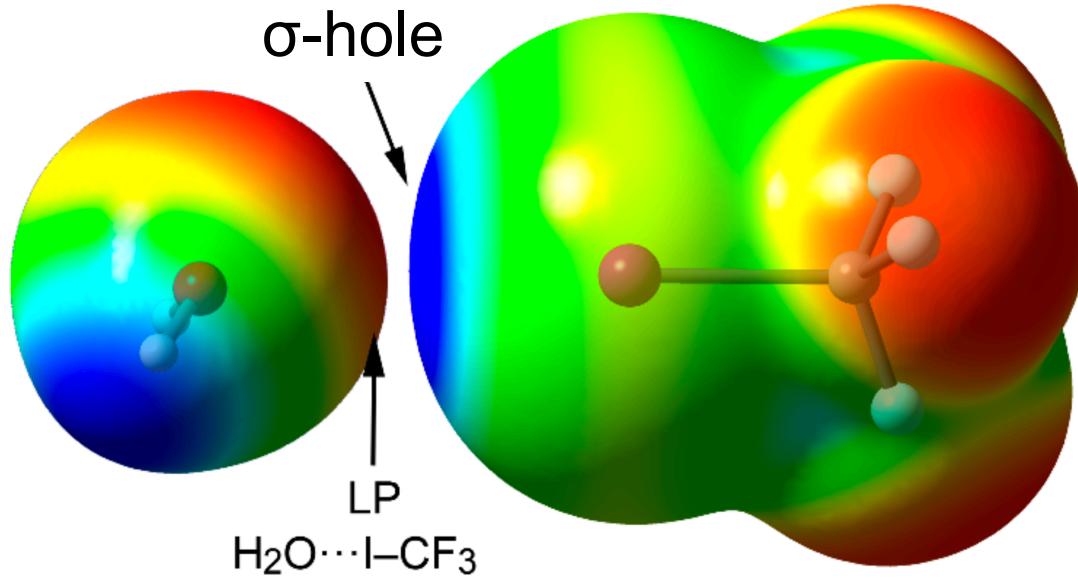
$$\varepsilon_r = \varepsilon_\infty + \frac{\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2}{3\varepsilon_0 k_B T \langle V \rangle}$$



dipole of the
whole system



Examples: σ -hole in halogen and chalcogen bonds



Can be utilized for molecular design in various applications!

Hands-on: electronic structure and molecular properties

Learning Goal

- Learn how to plot electrostatic potential map.
- Calculate the binding energy vs distance plot for benzene dimers.
- Understand the xTB output and extract molecular dipole and quadrupole from it.
- Compare the intermolecular interactions obtained from xTB with the approximation using multipole-multipole interactions

Visualize electrostatic potential map of benzene

Inputs and output of this exercise

The outputs of this exercise were uploaded on Github repository

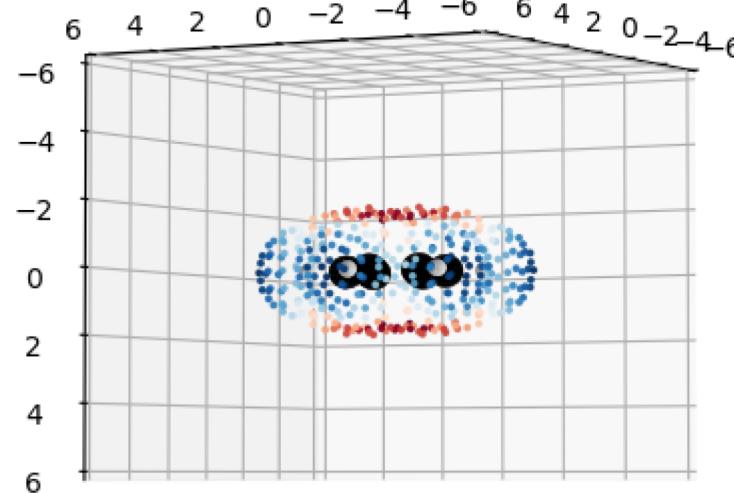
- W3/01_ESP

Step-by-step operation

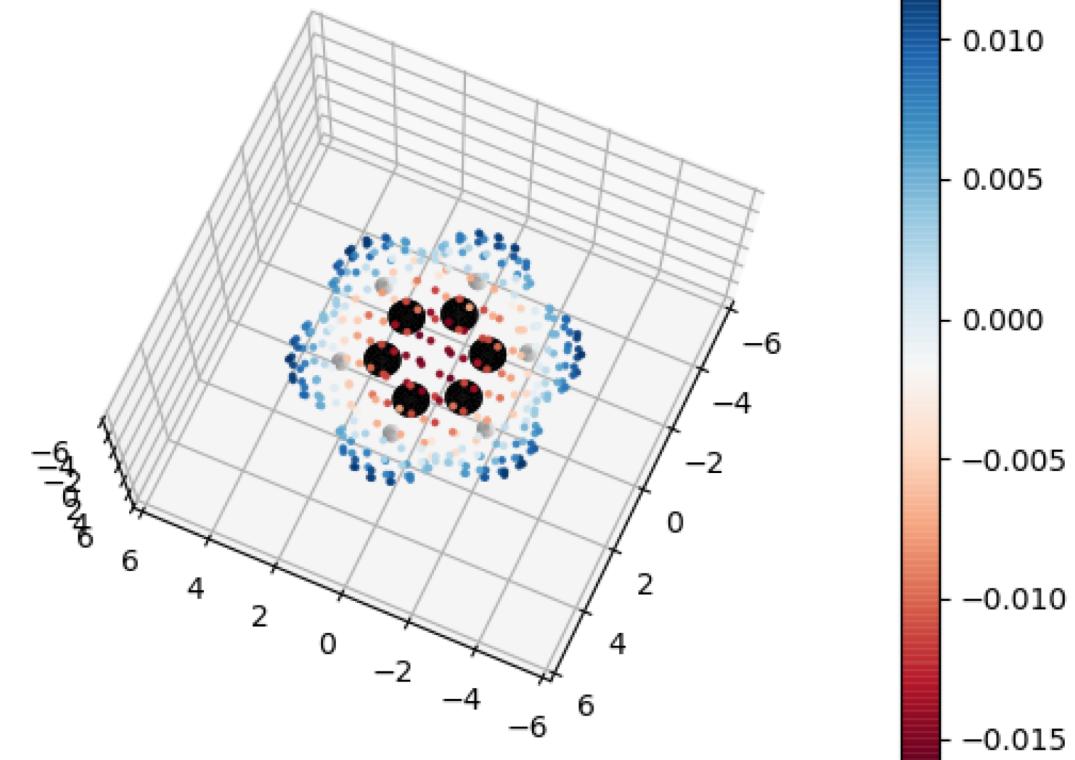
- Create a folder called W3
 - mkdir W3
- Enter the folder
 - cd W3
- Create a folder under W3
 - mkdir 01_ESP
 - cd 01_ESP
- Copy the running script
 - cp yourpath/W3/01_ESP/opt_xtb.sh .
- Copy the H₂ input structure
 - cp yourpath/W3/01_ESP/input.xyz .
- Modify the last line of the script
 - vi opt_xtb.sh Create a esp.dat
 for ESP visualization
 - xtb -c 0 -u 0 input.xyz -opt normal **--esp** > xtb.out
- Run it!
 - bash opt_xtb.sh

Electrostatic potential map of benzene

Results (electrostatic potential)



python plot_esp.py

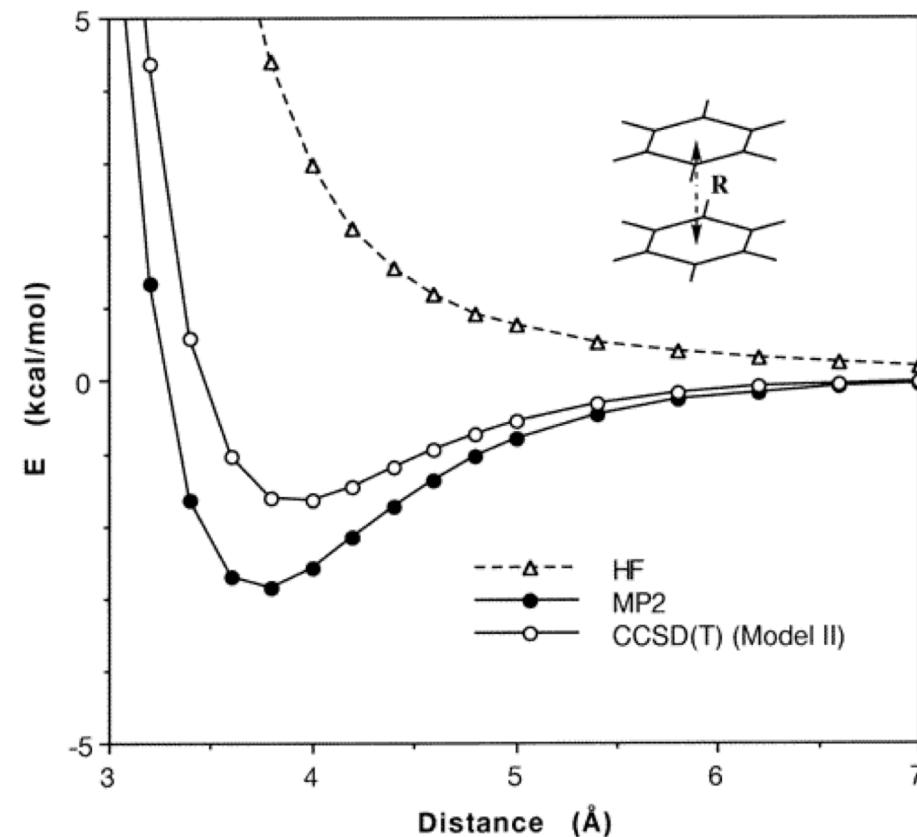


Calculate intermolecular interactions between parallel-stacked benzenes

Inputs and output of this exercise

The outputs of this exercise were uploaded on Github repository

- W3/02_Eb



Step-by-step operation

- Enter the folder
 - cd W3
- Create a folder under W3
 - mkdir 02_Eb
 - cd 02_Eb
- Copy the bash script for creating a series of folders
 - cp yourpath/W3/02_Eb/create.sh .
 - cp yourpath/W3/02_Eb/xtb.sh .
 - cp yourpath/W3/02_Eb/xtbopt.xyz .
- Copy the python scripts
 - cp yourpath/W3/02_Eb/prin_axis.py .
 - cp yourpath/W3/02_Eb/rotate.py .
 - cp yourpath/W3/02_Eb/gen_dimer.py .
 - cp yourpath/W3/02_Eb/plot_Eb.py .

Calculate the principal axis of benzene

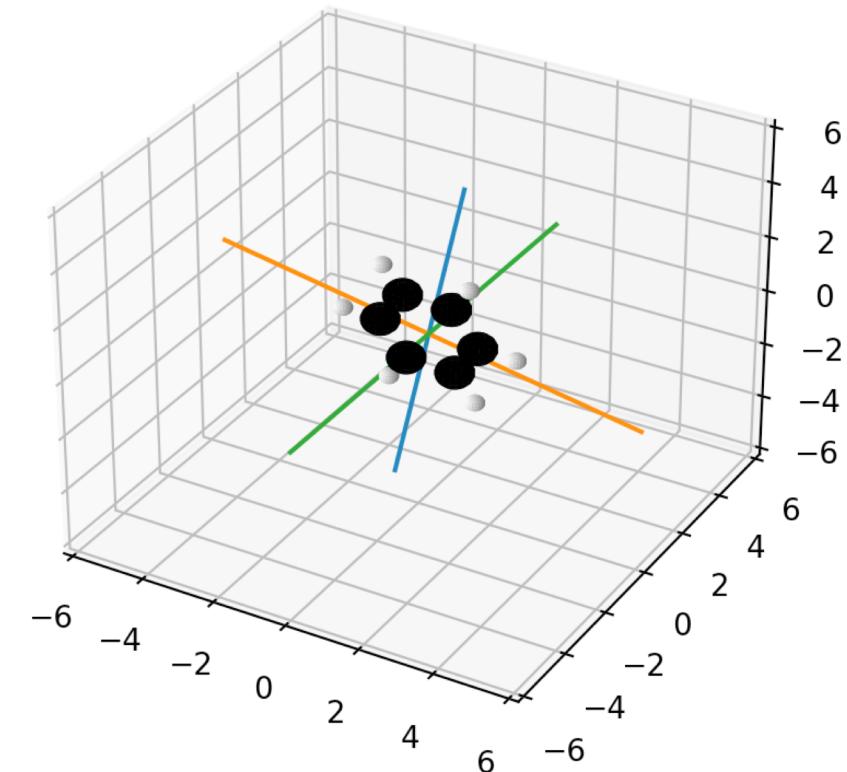
vi prin_axis.py

```
import numpy as np
from ase.io import read, write
from ase.build import rotate
from mpl_toolkits.mplot3d import Axes3D
import matplotlib.pyplot as plt

# A function to draw the atoms as spheres
def drawSphere(xCenter, yCenter, zCenter, r):
    #draw sphere
    u, v = np.mgrid[0:2*np.pi:20j, 0:np.pi:10j]
    x = np.cos(u)*np.sin(v)
    y = np.sin(u)*np.sin(v)
    z = np.cos(v)
    #shift and scale sphere
    x = r*x + xCenter
    y = r*y + yCenter
    z = r*z + zCenter
    return (x,y,z)

# Read the xyz as ASE Atom object
xyz = read('xtbopt.xyz')
```

python prin_axis.py xtbopt.xyz



Align the short axis with z-axis

vi rotate.py

```
import numpy as np
from ase.io import read, write
from ase.build import rotate
from mpl_toolkits.mplot3d import Axes3D
import matplotlib.pyplot as plt

# Read the xyz as Atom object in ASE
xyz = read('xtbopt.xyz')

# Get the moment of inertia of the compound
I = xyz.get_moments_of_inertia(vectors=True)

# Get the center of mass before translation
COM = xyz.get_center_of_mass()
print('Original center of mass: ', COM)

# Get the center of mass after translation COM to (0,0)
xyz.translate(-COM)
COM = xyz.get_center_of_mass()
print('Center of mass after translation: ', COM)

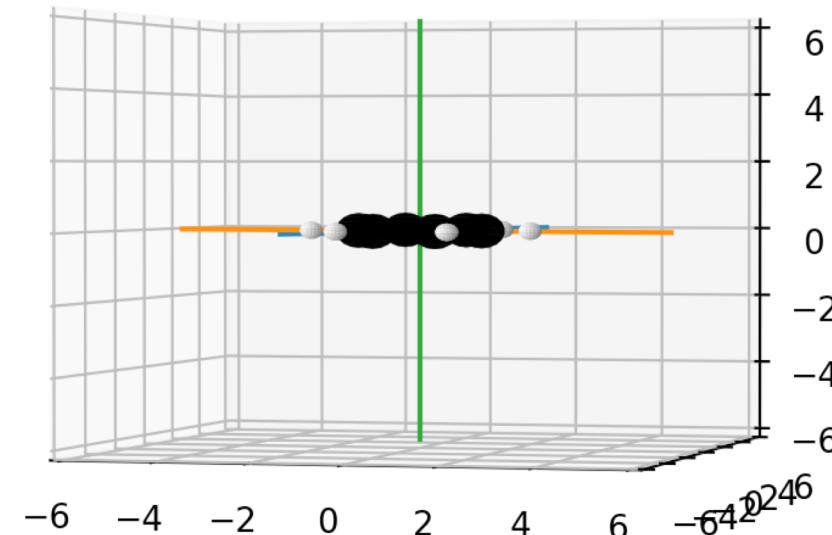
# Align the shortest molecular axis to z-axis
xyz.rotate(I[1][2], 'z', 'COM', rotate_cell=False)

# Write out the final structure as new.xyz
xyz.write('aligned_z.xyz')
```

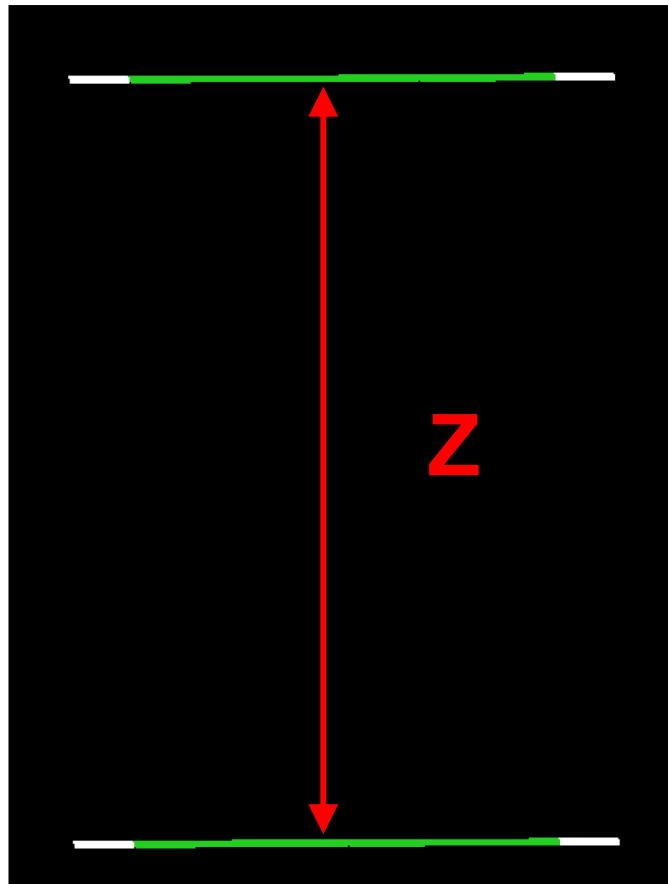
python rotate.py

```
[(base) linkunhande-MacBook-Pro:W3 pumachu$ python rotate.py
Original center of mass: [1.27040680e-01 2.79476642e-01 2.04572689e-07]
Center of mass after translation: [-4.69399082e-17 -7.93681201e-17 7.38568198e-17]
```

python prin_axis.py aligned_z.xyz



Create benzene dimer with different Z

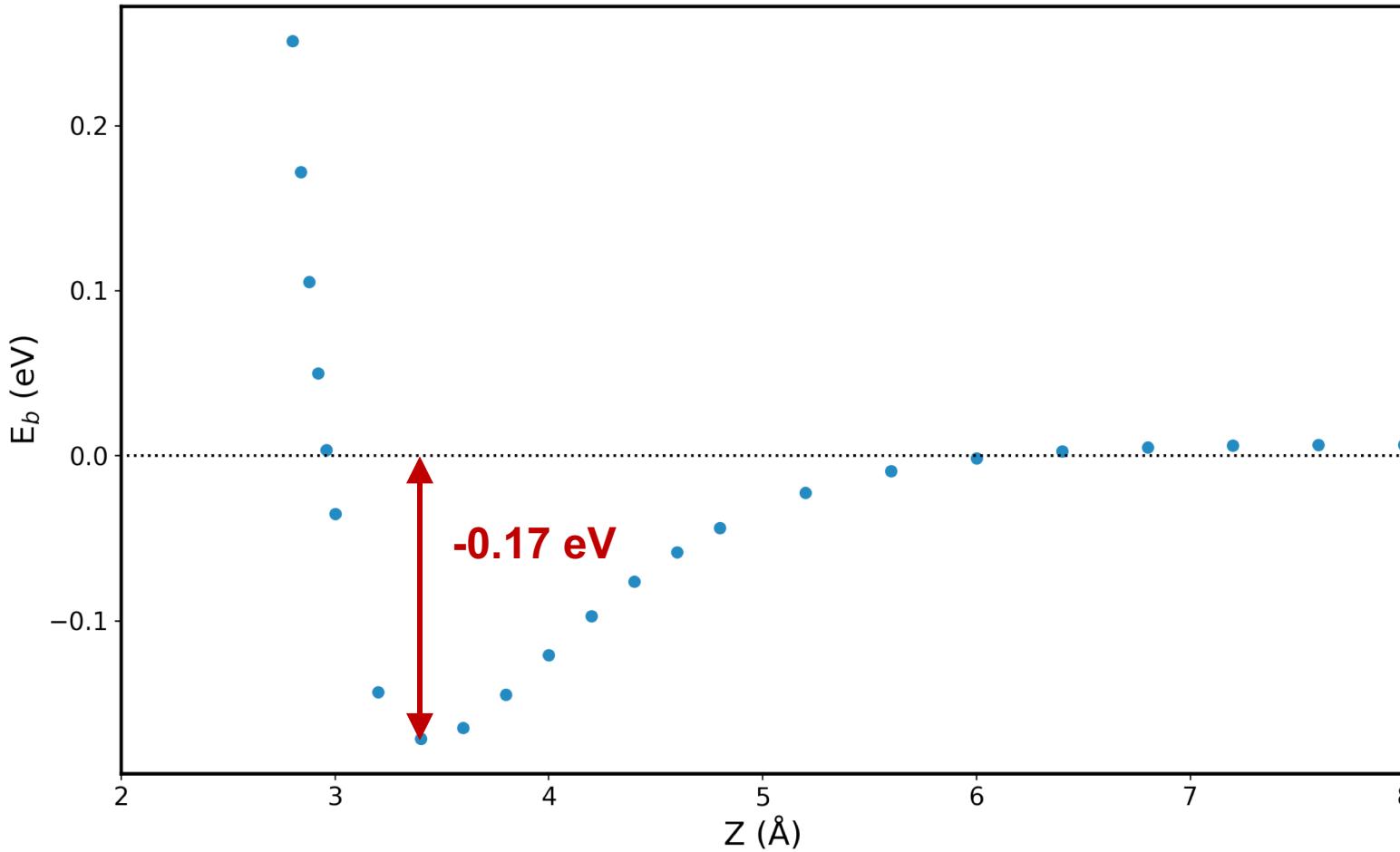


Create a binding energy plot similar to what we did in HW1 for H₂

$$E_b(Z) = E_{dimer}(Z) - 2 * E_{monomer}$$

- Create a series of folders with inputs and run
 - bash create.sh
- Copy the bash script for creating a series of folders
 - cp yourpath/W3/02_Eb/create.sh .
 - cp yourpath/W3/02_Eb/xtb.sh .
 - cp yourpath/W3/02_Eb/xtbopt.xyz .

Binding energy of parallel-stacked benzene



python plot_Eb.py

With aug-6-311G* basis set:

MP2: -0.11 eV

CCSD(T): -0.04 eV

Approximate intermolecular interactions using multipole-multipole interactions

Inputs and output of this exercise

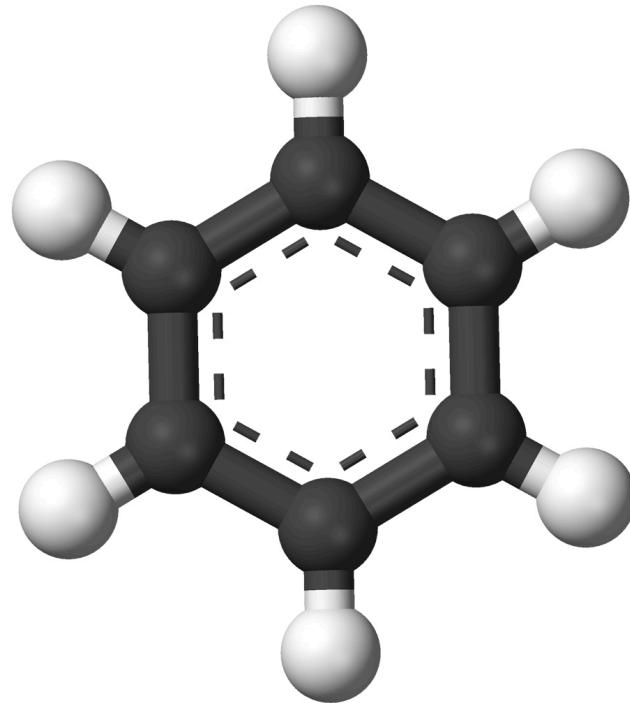
The outputs of this exercise were uploaded on Github repository

- W3/03_Q-Q

Step-by-step operation

- Enter the folder
 - cd W3
- Create a folder under W3
 - mkdir 03_Q-Q
 - cd 03_Q-Q
- Copy the python scripts
 - cp yourpath/W3/03_Q-Q/plot_QQ.py .

Multipoles of benzene



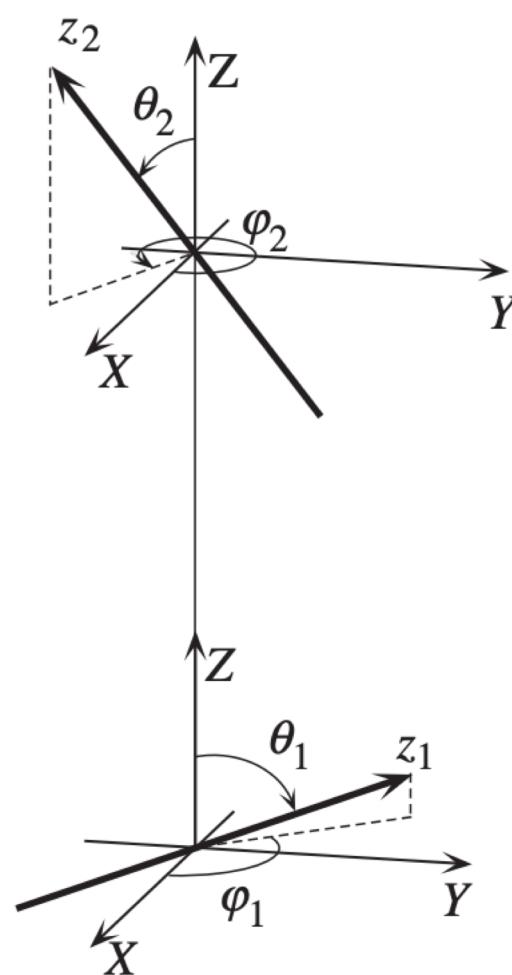
D_{6h} symmetry

- Check the dipole and quadrupole of benzene
 - vi W3/02_Eb/monomer/xtb.out

molecular dipole:					
	x	y	z	tot (Debye)	
q only:	0.000	0.000	-0.000		
full:	0.000	0.000	-0.000	0.000	
molecular quadrupole (traceless):					
	xx	xy	yy	xz	yz
q only:	0.640	0.000	0.640	0.000	-0.000
q+dip:	2.669	-0.000	2.669	0.000	-0.000
full:	1.334	-0.000	1.334	0.000	-0.000
				zz	
				-1.280	
				-5.338	
				-2.669	

- zero dipole moment due to inversion symmetry
- 1.334, 1.334 and -2.669 for Q_{xx} , Q_{yy} and Q_{zz}

Quadrupole-quadrupole interaction energy



$$U_{QQ} = \frac{Q^A Q^B}{4\pi\epsilon_0 R^5} \frac{3}{4} [1 - 5\cos^2\theta_A - 5\cos^2\theta_B - 15\cos^2\theta_A \cos^2\theta_B + 2(4\cos\theta_A \cos\theta_B - \sin\theta_A \sin\theta_B \cos\varphi)^2]$$

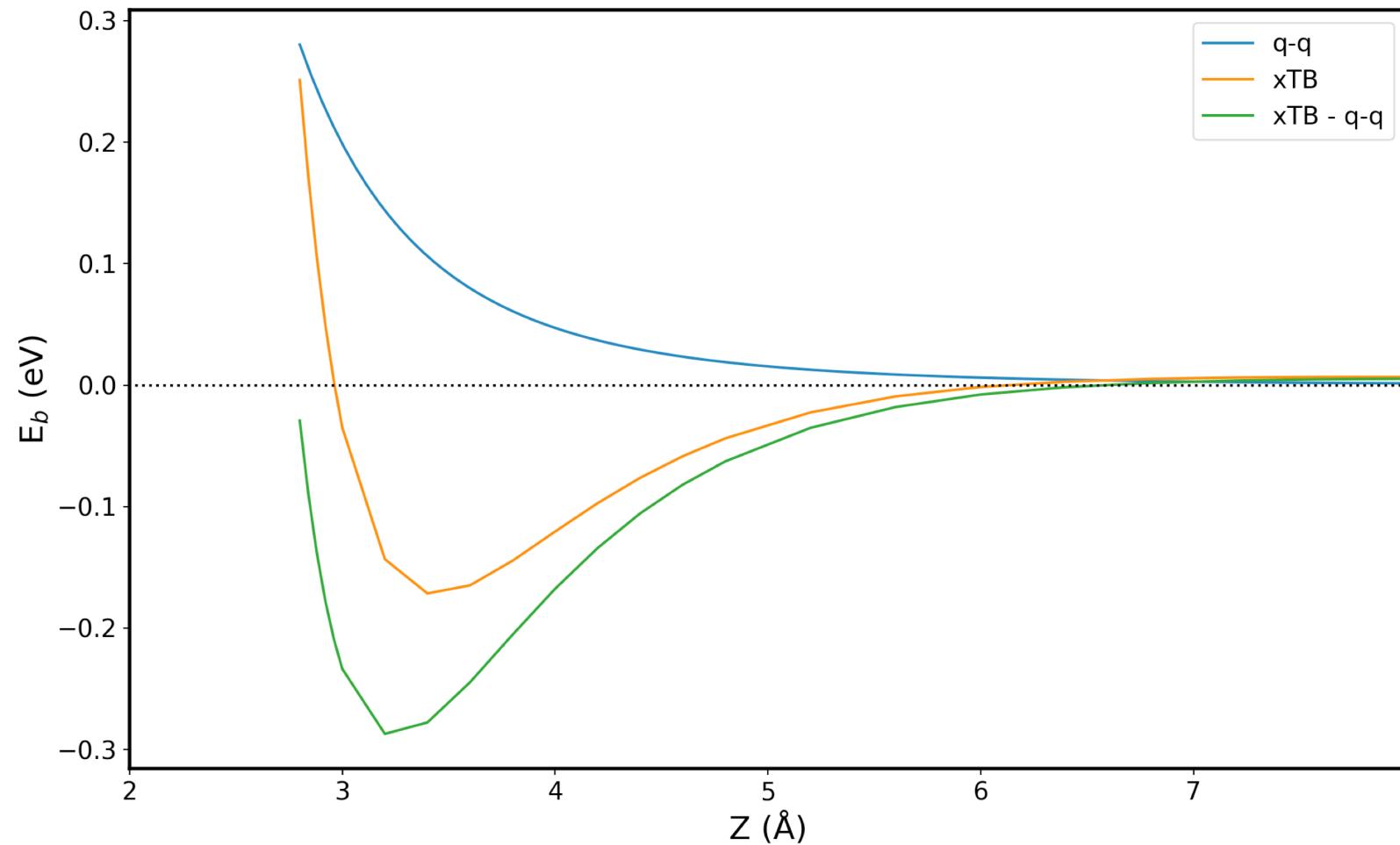
Q^A and Q^B are the Q_{zz} of molecule A and B (note: this is only true for linear or highly-symmetrical molecules and when the molecular axis is aligned with z-axis ->

$$Q_{xx} = Q_{yy} = -2Q_{zz}; \text{ off-diagonal terms} = 0)$$

$$U_{QQ} = \frac{Q^A Q^B}{4\pi\epsilon_0 R^5} 6 \text{ for parallel-stacked}$$

+6

Comparison between xTB and q-q



python plot_QQ.py

- Can not describe by electrostatic only (R^{-5})!
 - Polarization
 - Dispersion (R^{-6})
 - Pauli exclusion (R^{-12})

Readings

- Molecular interactions
 - The Theory of Intermolecular Forces, 2nd Ed., Anthony Stone