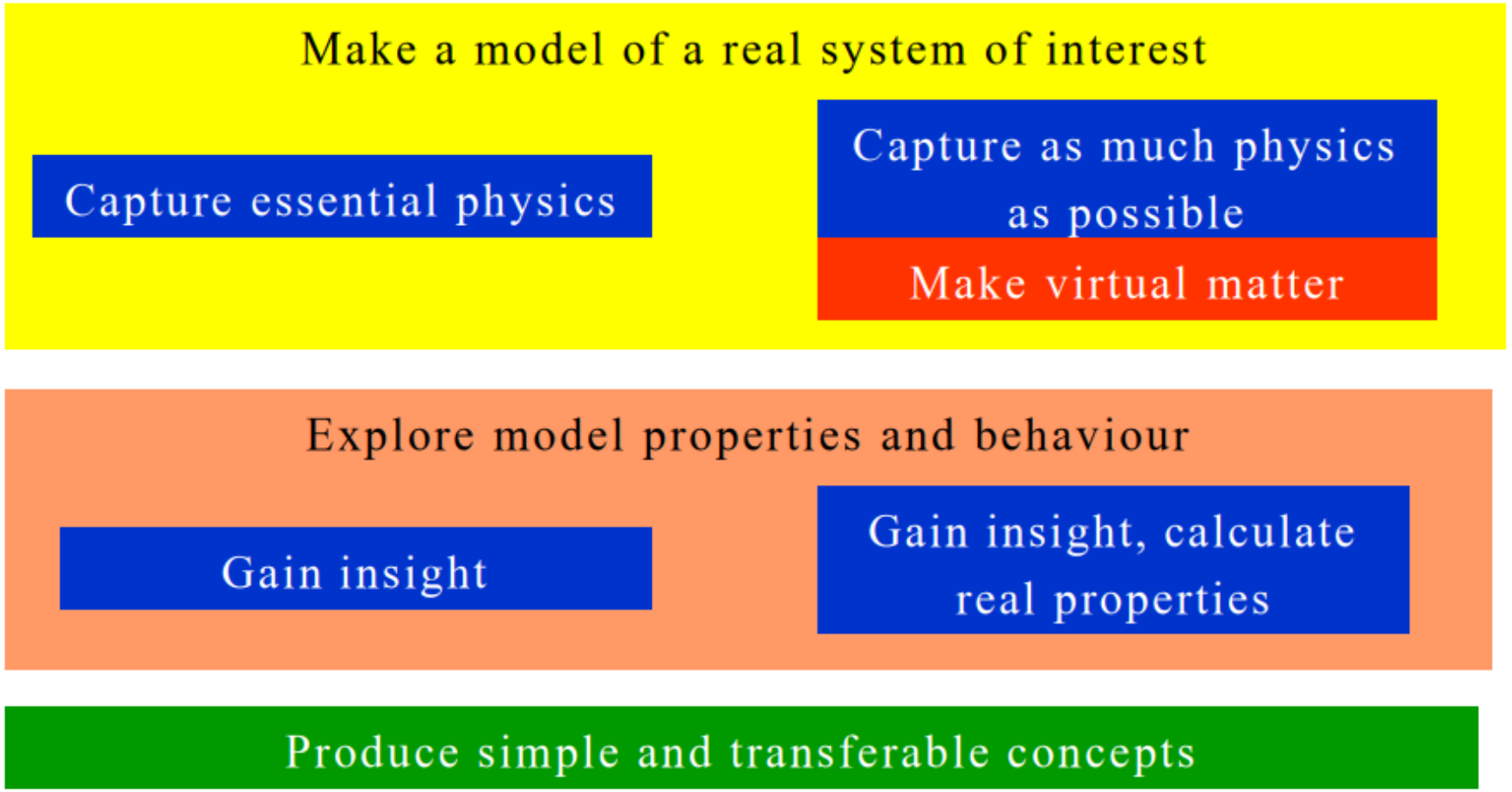
Single Point Calculation
Electronic Properties Analysis

Atomistic Modelling
first-principles simulation



Atomistic Modelling
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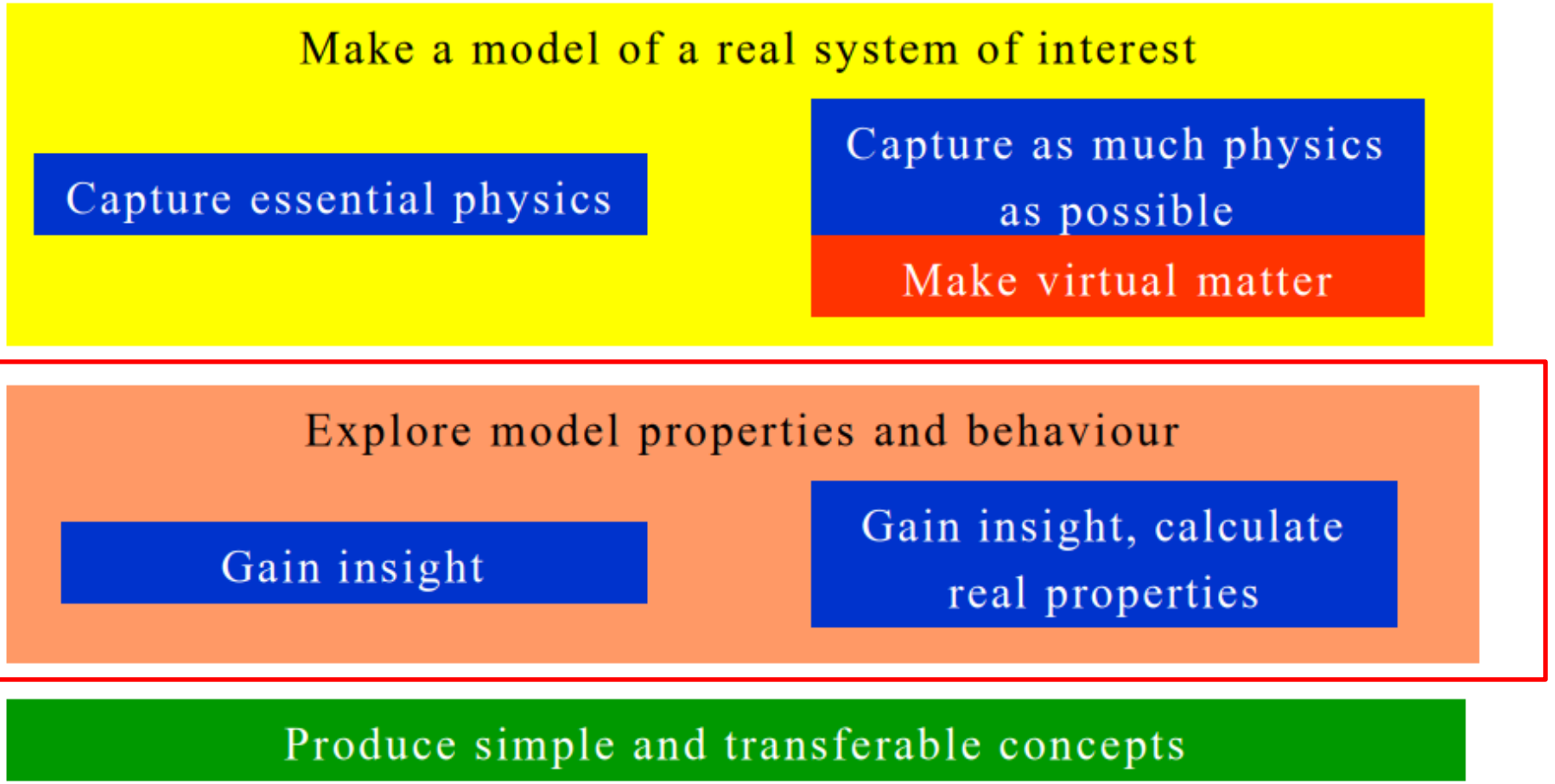


Starting from a model

- We build a trial model
- We optimize the atomic positions (and lattice constants for periodic systems)
- We perform a single-point calculation on the optimized structure

From the optimized structures → the destination properties

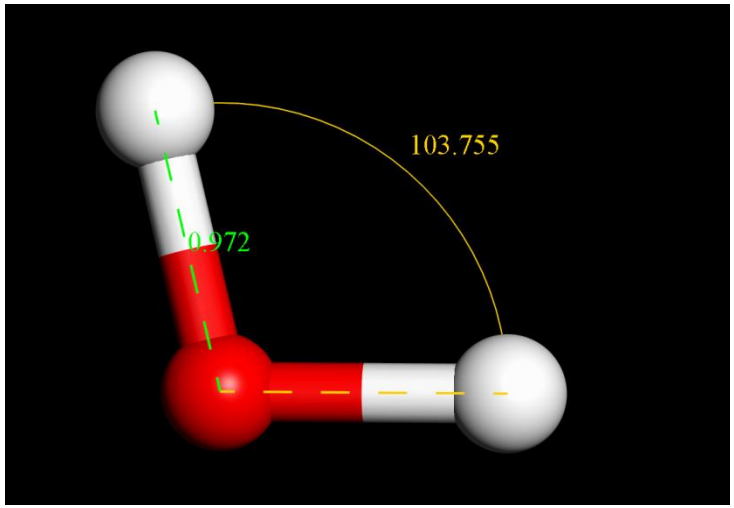
- What kinds of properties?

The first thing: Energy

- Schrödinger Equation: $H\psi = E\psi$
- Energy is a direct physical quantity, we obtained in calculaitons

Simple calculation with water molecule

H2O.xyz



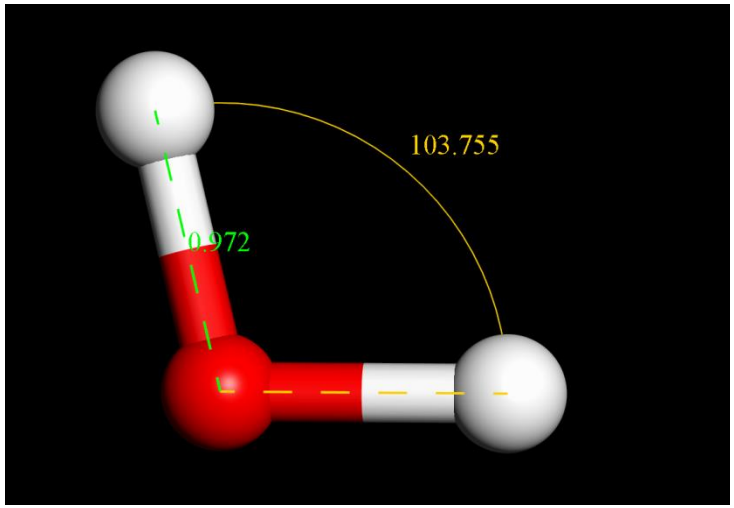
HOH: 103.8 Degree
OH: 0.972 A

```
# Task parameters
Calculate                   energy
Symmetry                    off
Max_memory                  2048
File_usage                  smart

# Electronic parameters
Spin_polarization           restricted
Charge                      0
Basis                       dnp
Pseudopotential             none
Functional                  rpbe
Aux_density                 octupole
Integration_grid            fine
Occupation                  fermi
Cutoff_Global               5.0000 angstrom
Scf_density_convergence     1.0000e-006
Scf_charge_mixing           2.0000e-001
Scf_iterations              50
Scf_diis                    6 pulay
```

Simple calculation with water molecule

H2O.xyz



Energy components:

Sum of atomic energies = -76.0906476Ha
-2070.533 eV

Kinetic = -0.1247817Ha

Electrostatic = -0.5419030Ha

Exchange-correlation = 0.1581831Ha

Spin polarization = 0.1368447Ha

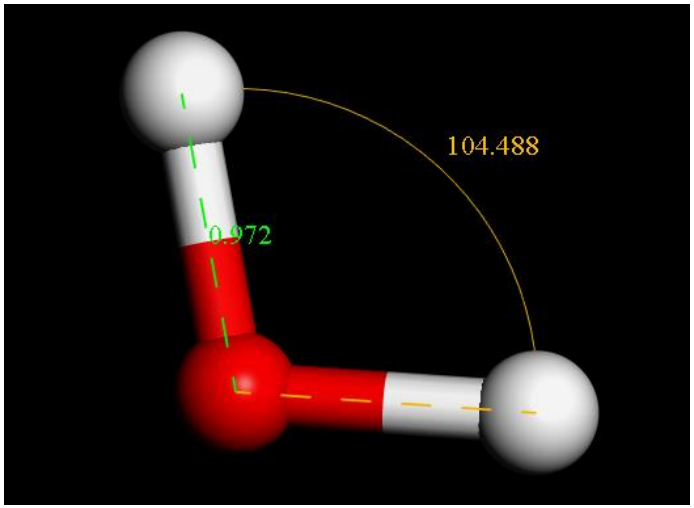
HOH: 103.8 Degree

OH: 0.972 A

What is meaning of total energy?

If we use different softwares

H2O.xyz



- With VASP :
  cut off energy =600,
  energy convergence threshold = 10^{-7} eV

- Energy :
  Energy of H_2O molecule = -14.226 eV

HOH: 104.5 Degree
OH: 0.972 A

What is the meaningful result about energy?

The value of total energy depends on the methods, including the basis set, functional, cutoff, k-points, pseudopotential …

Most time: useless to discuss with total energy!

1. The energies changes for same systems with different states

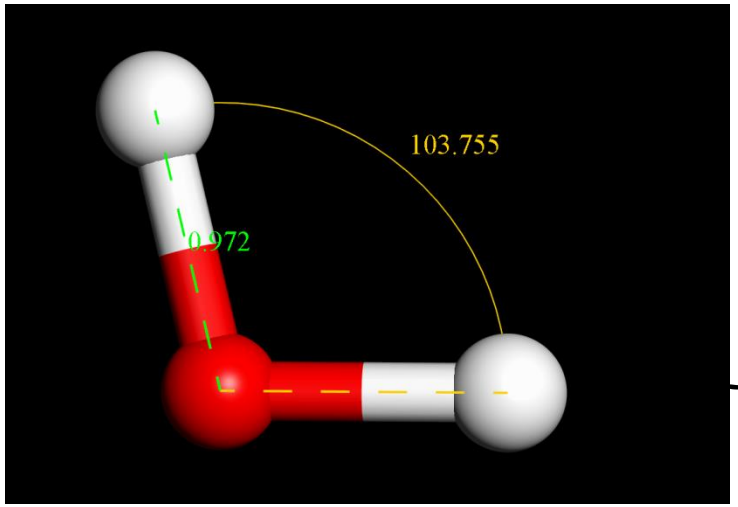
   reaction heat, energy barrier, relative stability .. .. ..

2. The binding energy or cohesive energy … …

   The bonding energies, relative stability .. .. ..

Let's look again on the water molecule

$$E_{binding} = E_{total} - Sum(E_{atom})$$



binding energy
-0.3716570Ha
-10.11330eV
-233.223kcal/mol

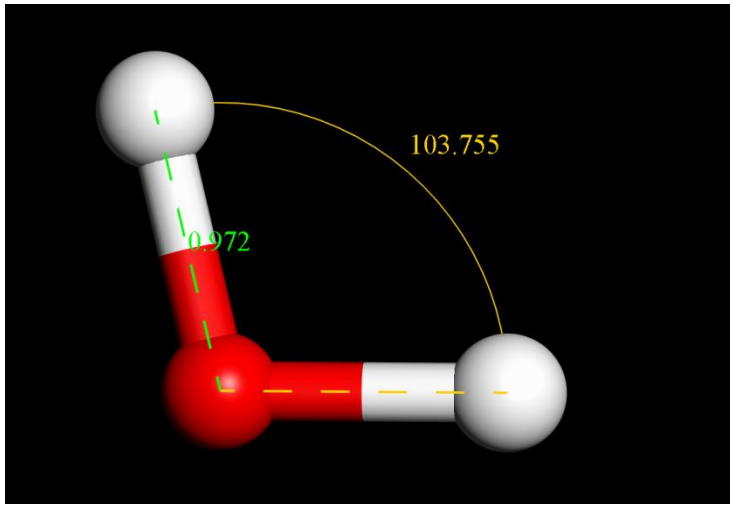
Thus, O-H bond energy 10.11330/2=5.05665 eV

Energy of O atom = -1.909 eV
Energy of H atom = -1.117 eV

$E_{binding} = E_{total} - E_{O\text{-}atom} - 2*E_{H\text{-}atom}$
= -10.083 eV/molecule

If we start from H_2 and O_2 molecule

$$E_{react} = E_{total}(H_2O) - E_{total}(H_2) - \tfrac{1}{2}E_{total}(O_2)$$



$$H_2 + \tfrac{1}{2}\,O_2 = H_2O$$

$E(H_2O)$ = -76.0906476Ha
$E(H_2)$ = -1.1786201 Ha
$E(O_2)$ = -150.3526624 Ha

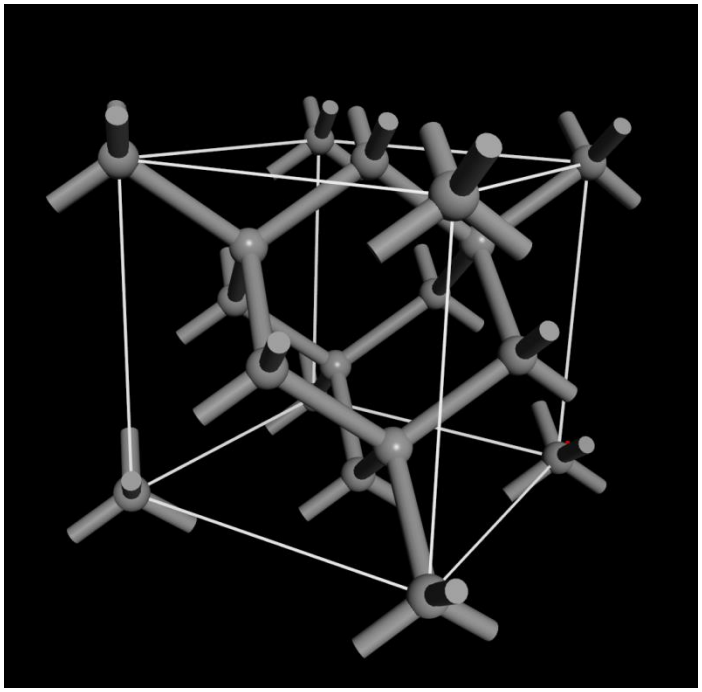
Reaction Energy: - 0.2643037 Ha
- 7.1921 eV

Exothermic process

$\Delta G = E - TS$, we could calculate the free energy

For periodic system

For example: diamond



Cohesive Energy

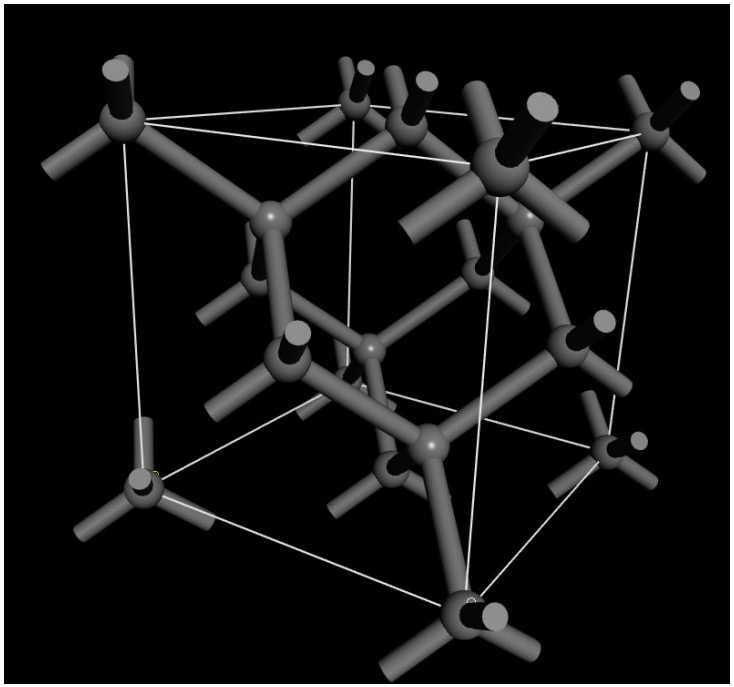
$E=(E_{total}-n \times E_{atom})/n$

n is the number of atom in cell

$E_{cohesive}$ = -0.2696834 Ha
= -7.3384 eV

If we use different softwares

diamond.xyz



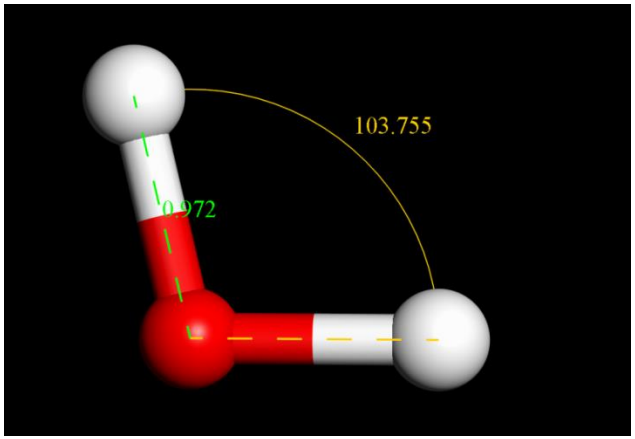
Bond angle: 109.471 Degree
C-C: 1.547 A

- With VASP :
  cut off energy =600,
  energy convergence threshold = 10^{-7} eV

- Energy :
  Energy of H_2O molecule = -18.191 eV
  Energy of C atom = -1.371 eV

$E_{binding} = (E_{total} - E_{C\text{-}atom}*2)/2$
$= -7.725$ eV/atom

Energy Level & Occupation



Energy of Highest Occupied Molecular Orbital: -0.25579Ha -6.960eV
Energy of Lowest Unoccupied Molecular Orbital: -0.00006Ha -0.002eV

HOMO is orbital number 5
LUMO is orbital number 6

state	eigenvalue (au)	(ev)	occupation
1 + 1 a	-18.769995	-510.758	2.000
2 + 2 a	-0.923184	-25.121	2.000
3 + 3 a	-0.474958	-12.924	2.000
4 + 4 a	-0.335762	-9.137	2.000
5 + 5 a	-0.255792	-6.960	2.000
6 + 6 a	-0.000063	-0.002	0.000
7 + 7 a	0.084485	2.299	0.000
8 + 8 a	0.472357	12.853	0.000
9 + 9 a	0.517305	14.077	0.000
10 + 10 a	0.534581	14.547	0.000
11 + 11 a	0.588682	16.019	0.000
12 + 12 a	0.729882	19.861	0.000
13 + 13 a	0.996960	27.129	0.000
14 + 14 a	1.093356	29.752	0.000
15 + 15 a	1.184304	32.227	0.000
16 + 16 a	1.226036	33.362	0.000
17 + 17 a	1.879578	51.146	0.000
18 + 18 a	2.001477	54.463	0.000
19 + 19 a	2.142533	58.301	0.000
20 + 20 a	2.390558	65.050	0.000
21 + 21 a	2.421420	65.890	0.000
22 + 22 a	2.769555	75.363	0.000
23 + 23 a	3.171791	86.309	0.000
24 + 24 a	3.606781	98.146	0.000

HOMO-LUMO Gap 6.958 eV

Closed shell system

Density of States Analysis
Partial and Local Density of States

Displaying the molecule orbital spectrum with DOS

The degeneracy of orbitals is then indicated by the height of the functions: delta functions

$$D_d(\mathrm{E})=\sum_i \delta(E - E_i)$$

The DOS results in a better match with experimental data obtained from methods like UPS and XPS. Two common ways of doing is are Gaussian and Lorentzian broadening.

Gaussian broadening $$D_g(E) = \sum_{i=1}^{N} exp\left(-\frac{E - E_i}{\sigma}\right)$$

Lorentzian broadening $$D_l(E) = \sum_{i=1}^{N} \frac{\sigma}{(E - E_i)^2 + \sigma^2}$$

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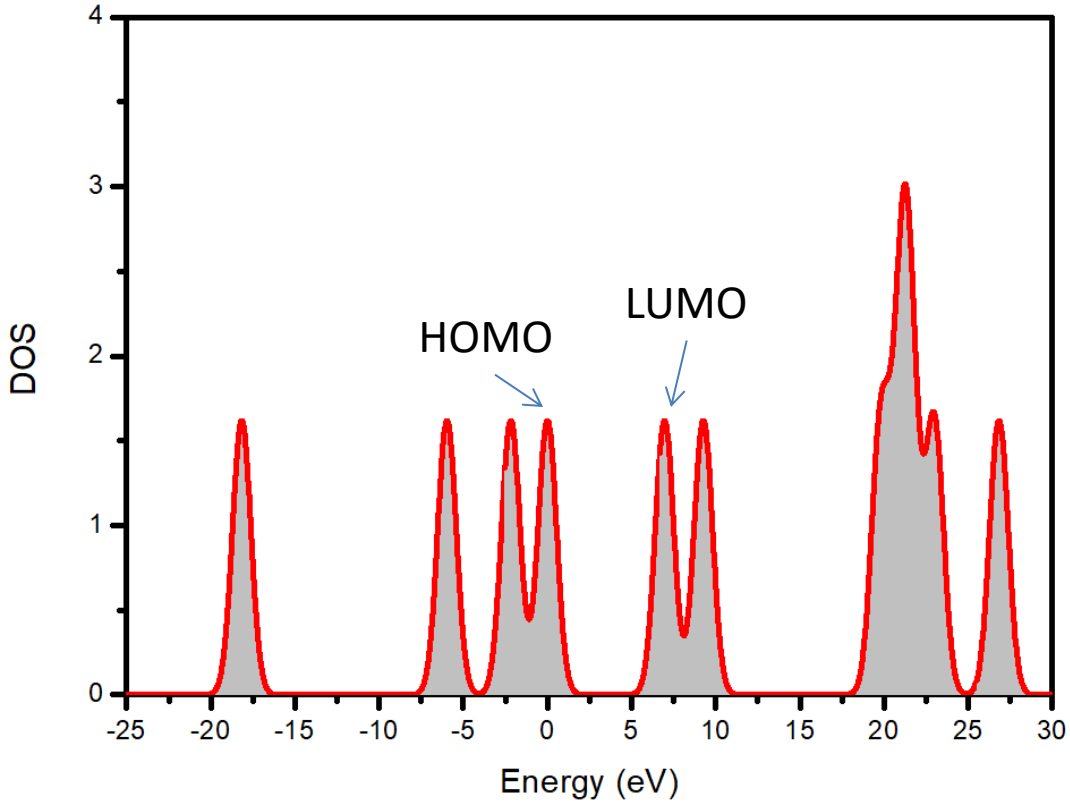
Density of States Analysis
Partial and Local Density of States



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Density of States Analysis
Partial and Local Density of States

Partial DOS or local DOS

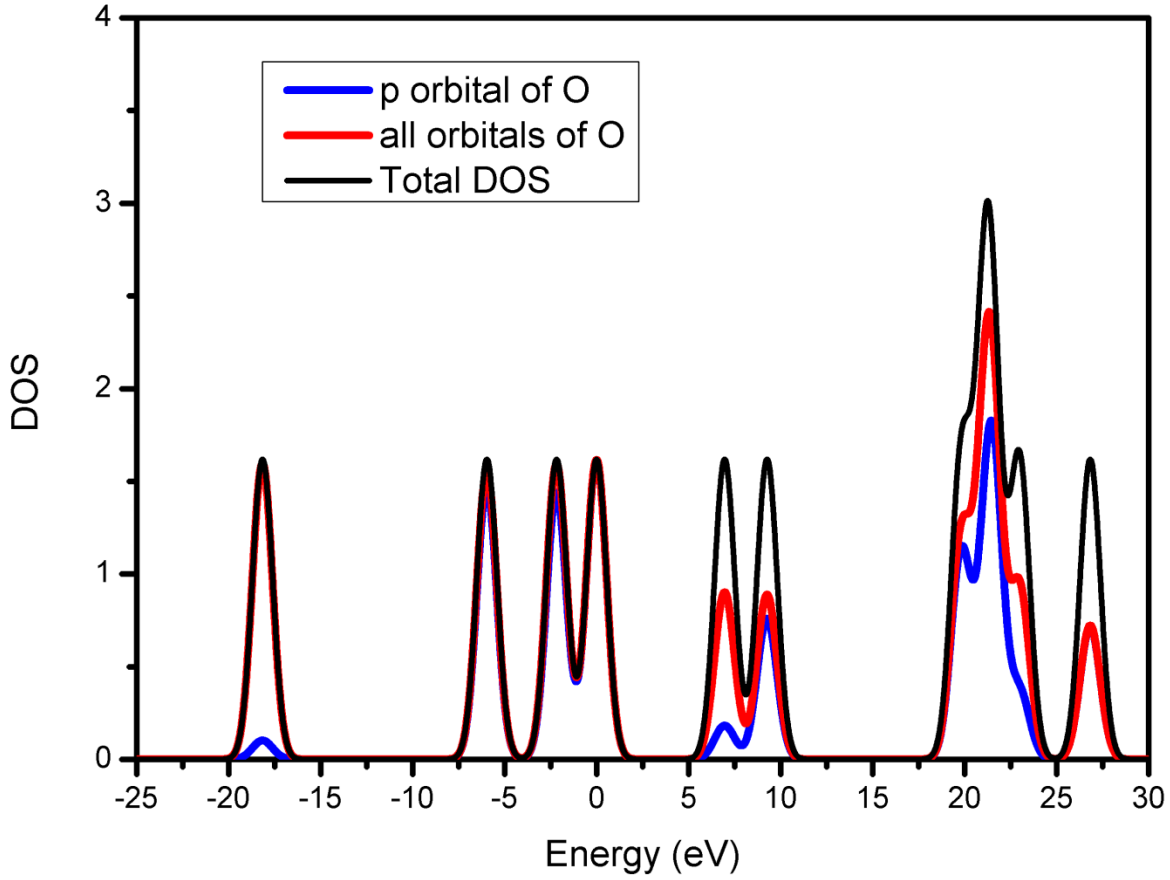
the contribution of a particular orbital or group of orbitals to the molecular orbital spectrum

Simply, project the atomic wavefunction onto the molecular orbitals

$$D_j(E) = \sum_{i=1}^{N} \langle \varphi_j | \psi_i \rangle \delta(E - E_i) n_i$$

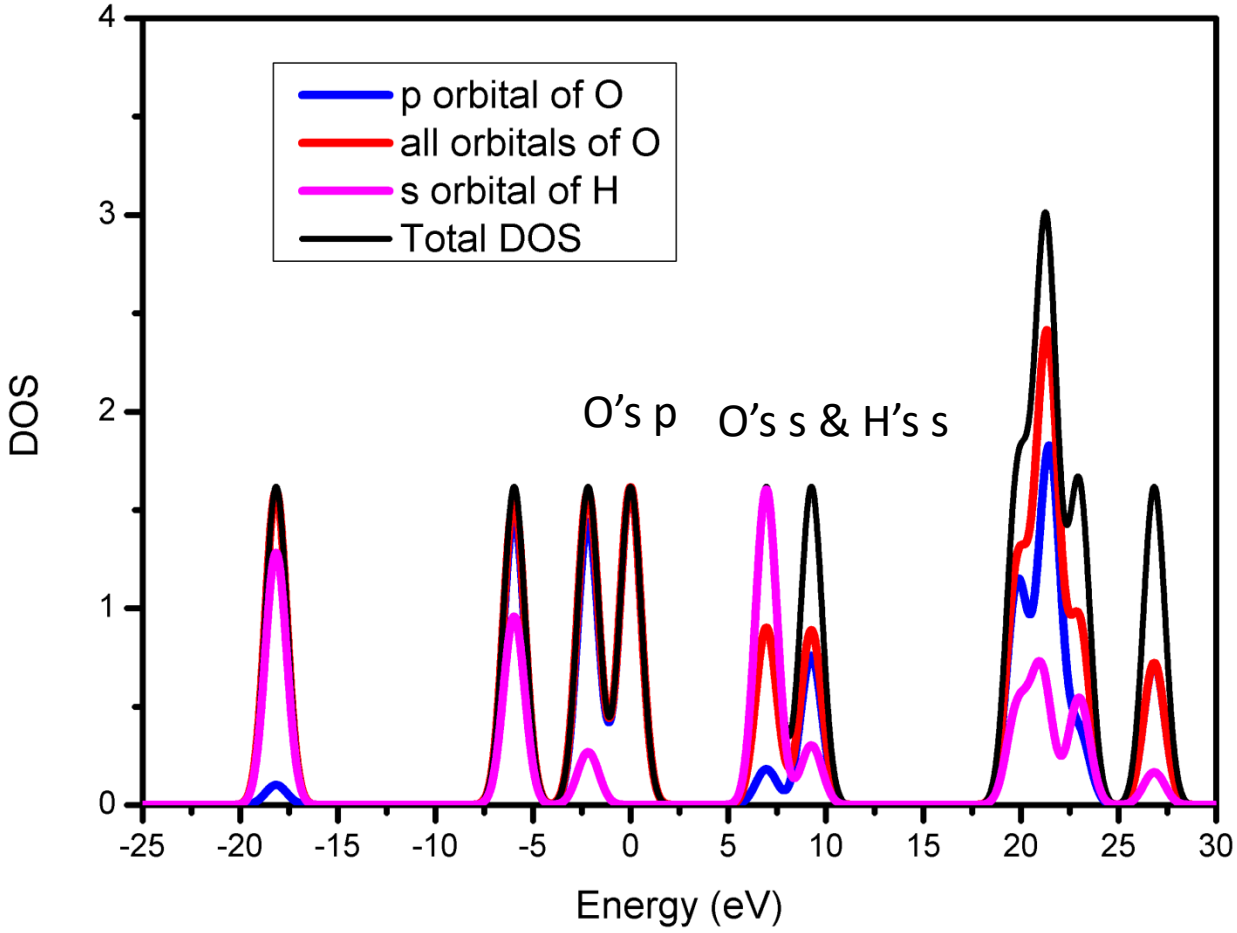
Density of States Analysis
Partial and Local Density of States

Water molecule: contribution of O

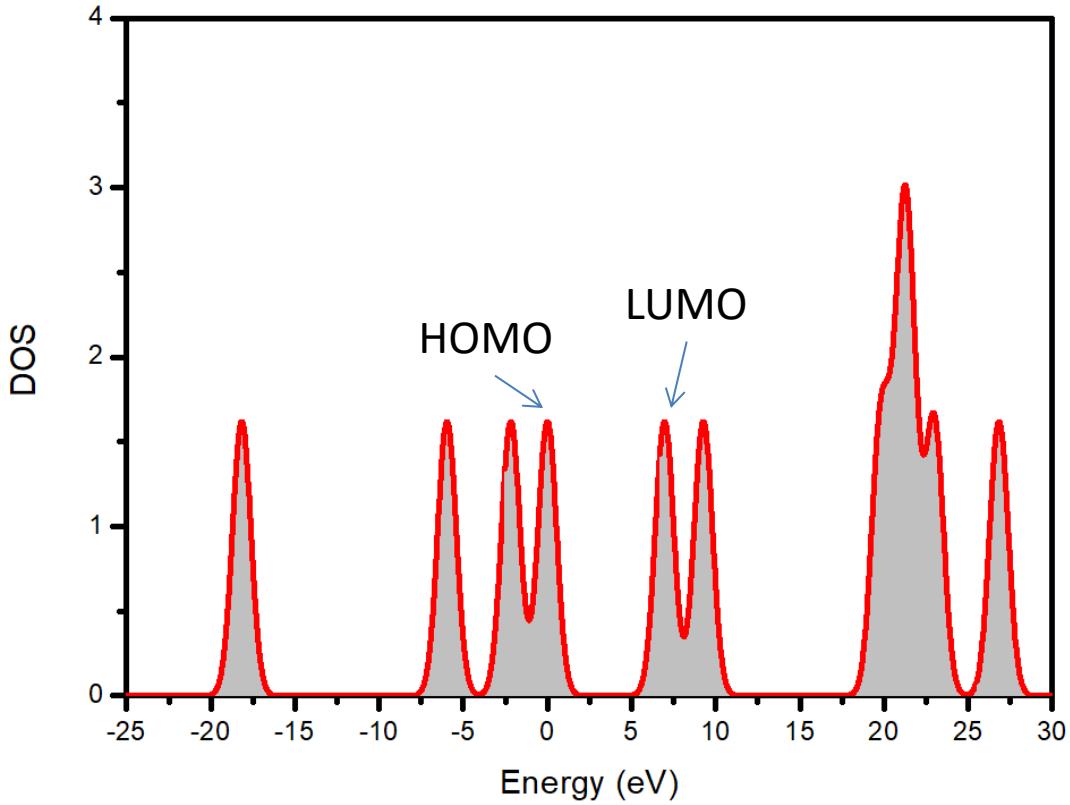


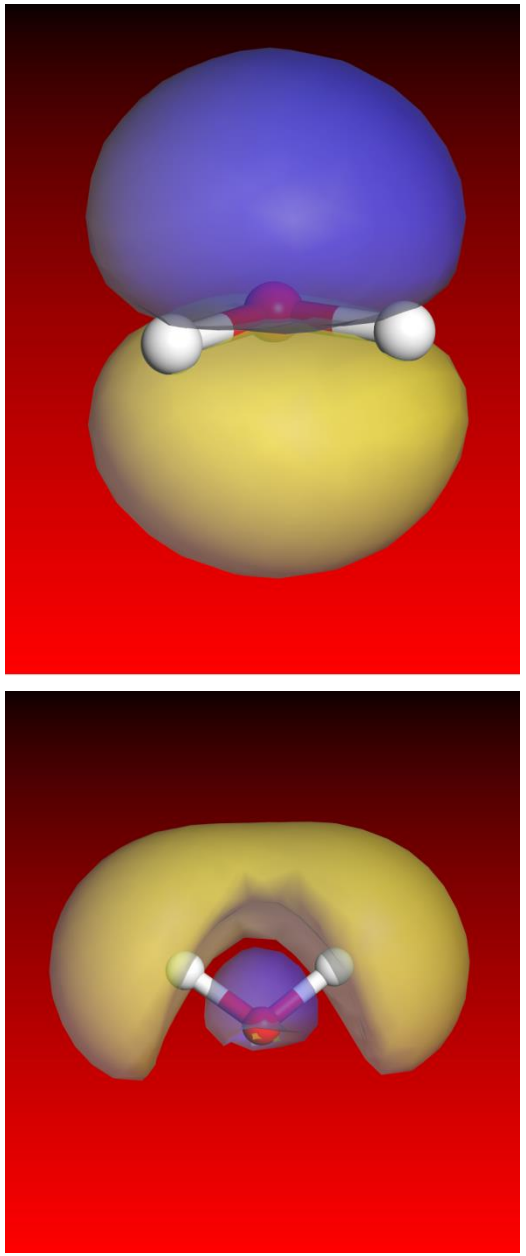
Density of States Analysis
Partial and Local Density of States

Water molecule: contribution of H and O

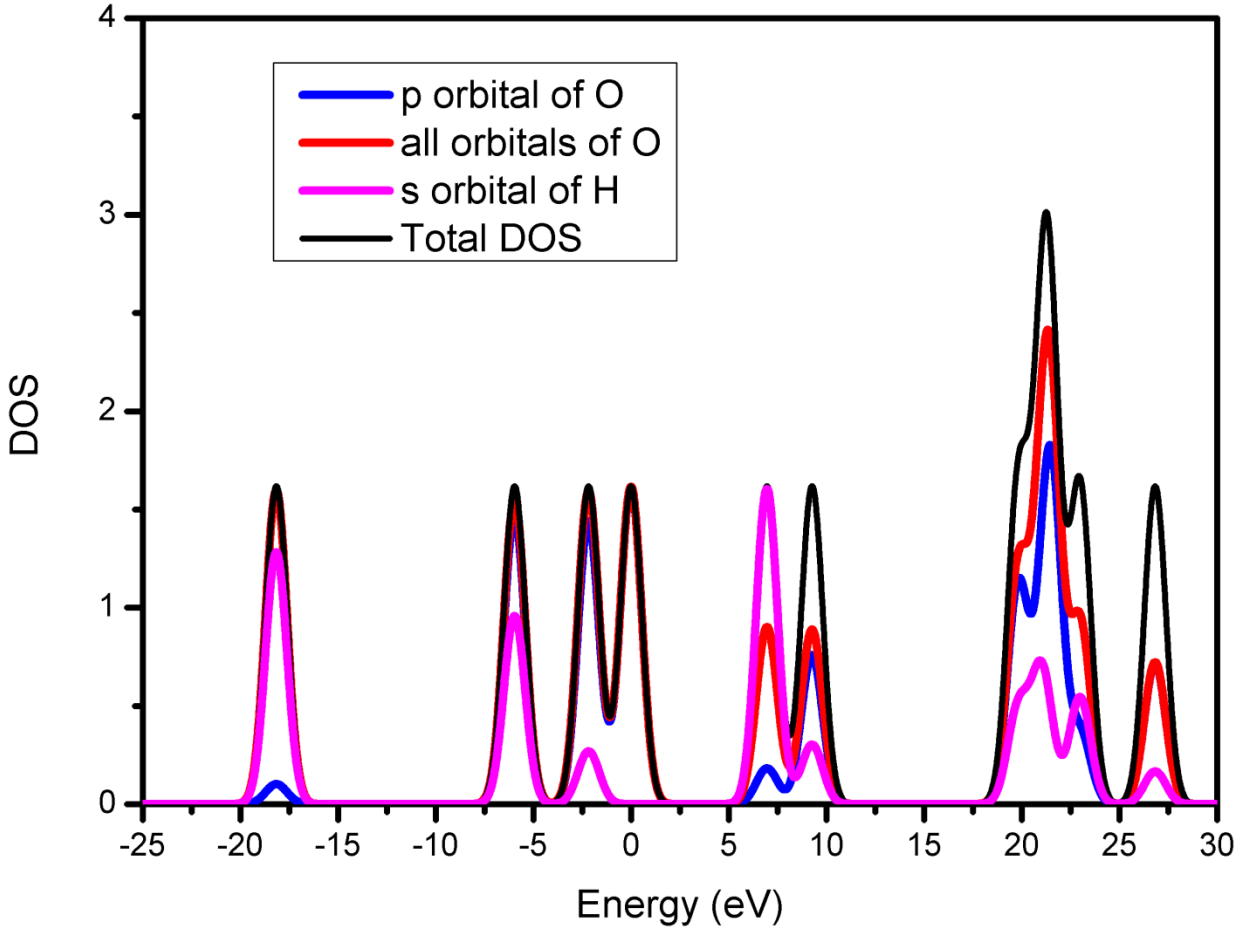


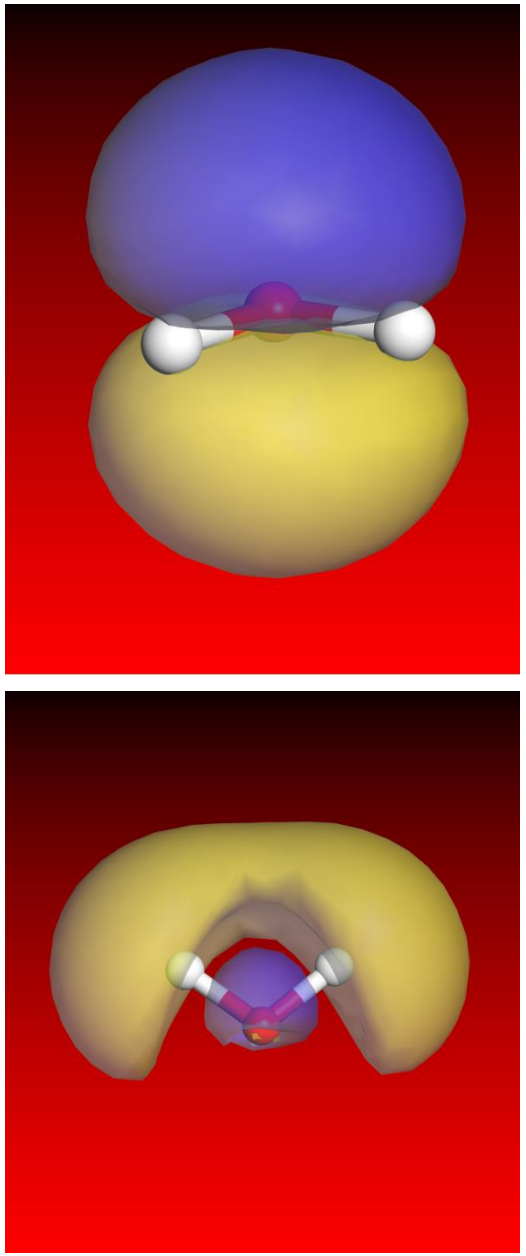
Wave function





Wave function

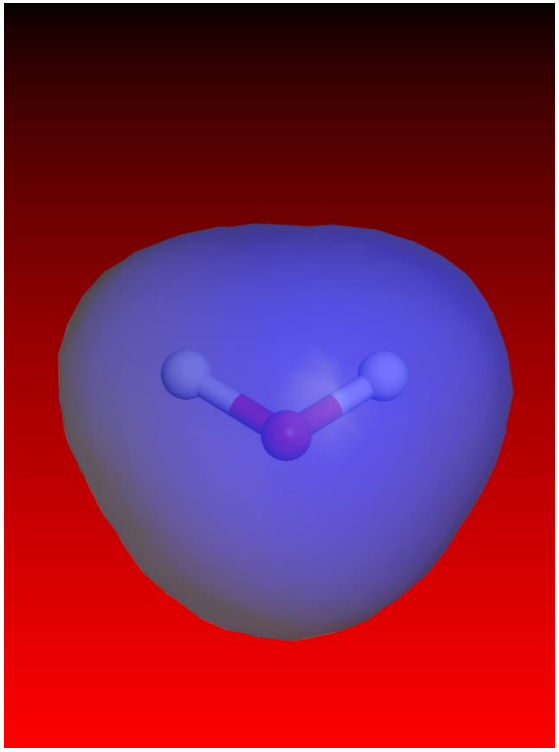


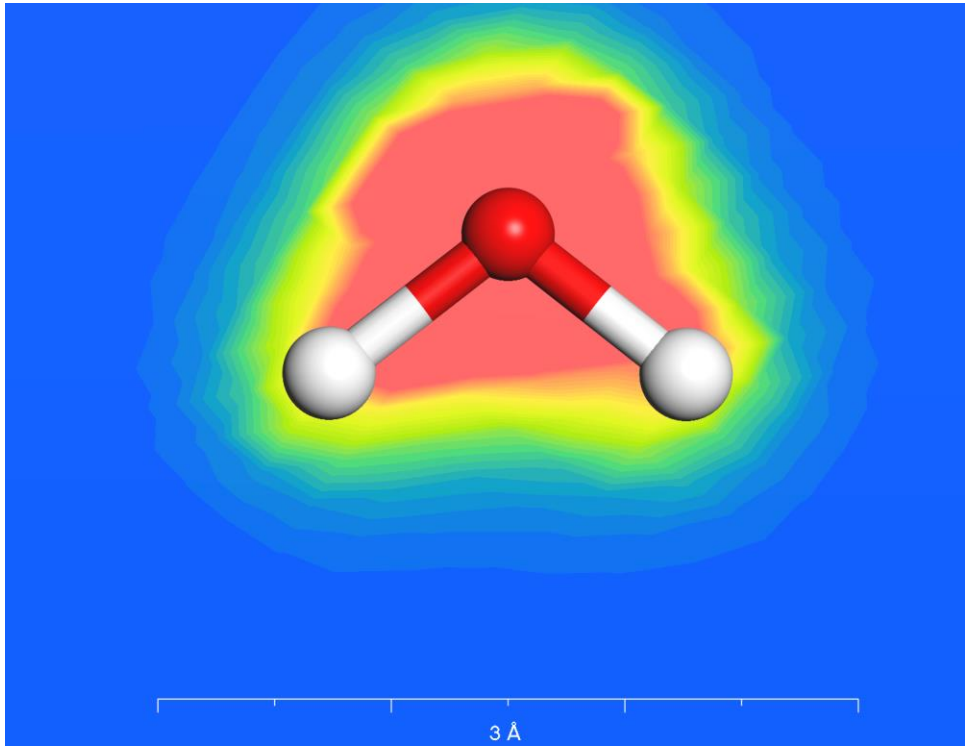


From Wavefunction to Charge Density

$$\rho = \sum_{i=1}^{occ} |\psi_i|^2$$

Total charge density

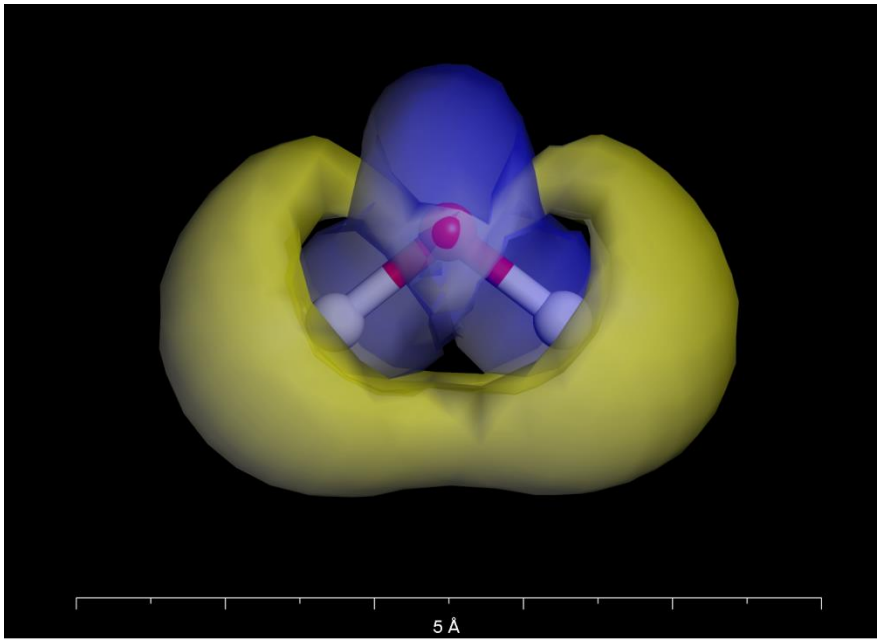


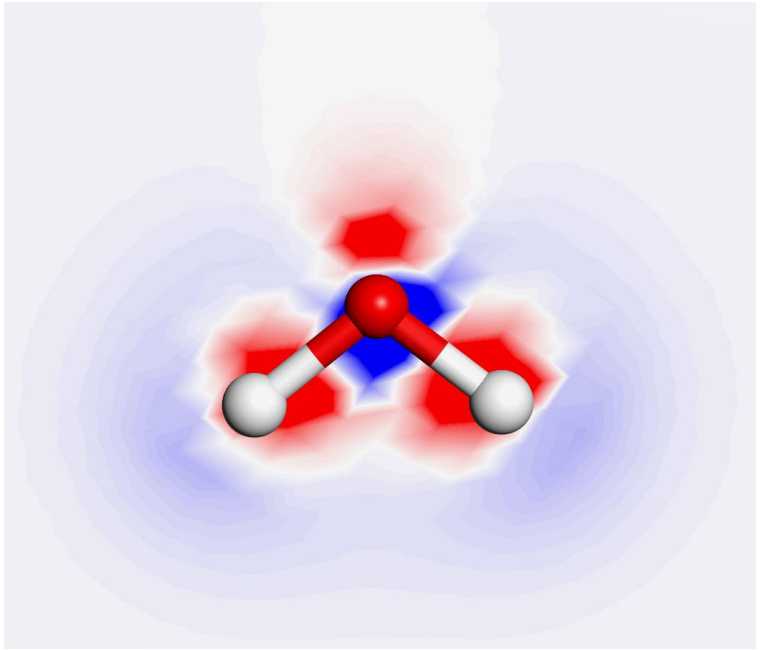


Deformation charge density

$$\rho = \sum_{i=1}^{occ} |\psi_i|^2$$

$$\rho_{deform} = \rho_{total} - \sum_{i} \rho_{atom}$$



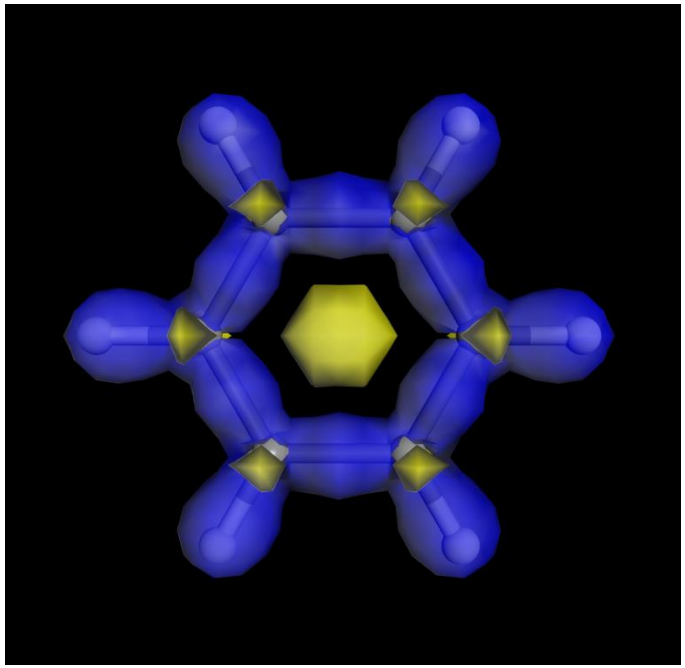


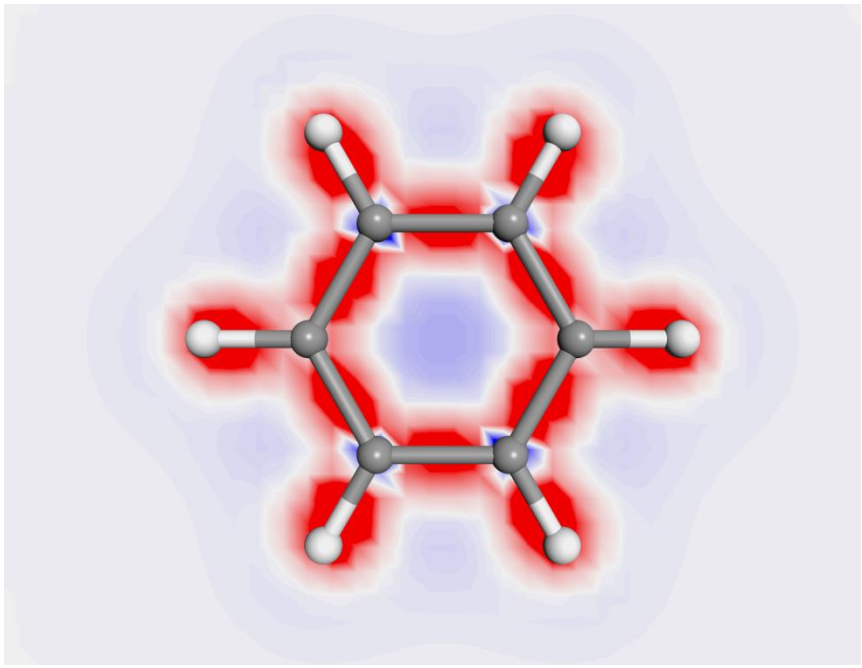
Ionic covalent bonding

Deformation charge density

$$\rho = \sum_{i=1}^{occ} |\psi_i|^2$$

$$\rho_{deform} = \rho_{total} - \sum_{i} \rho_{atom}$$





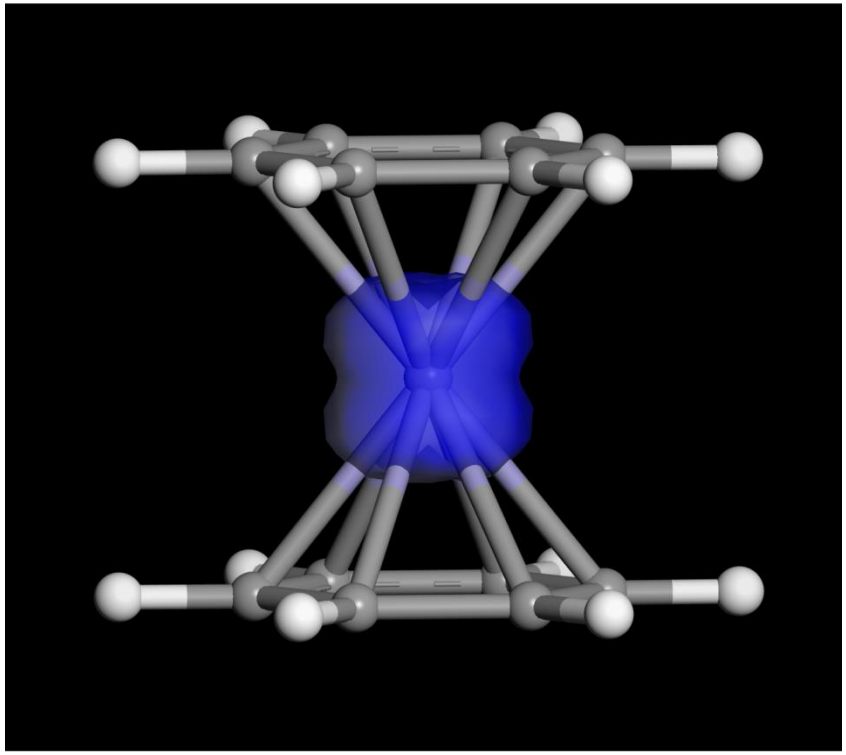
Covalent bonding

$$\rho = \sum_{i=1}^{occ} |\psi_i|^2$$

Spin charge density

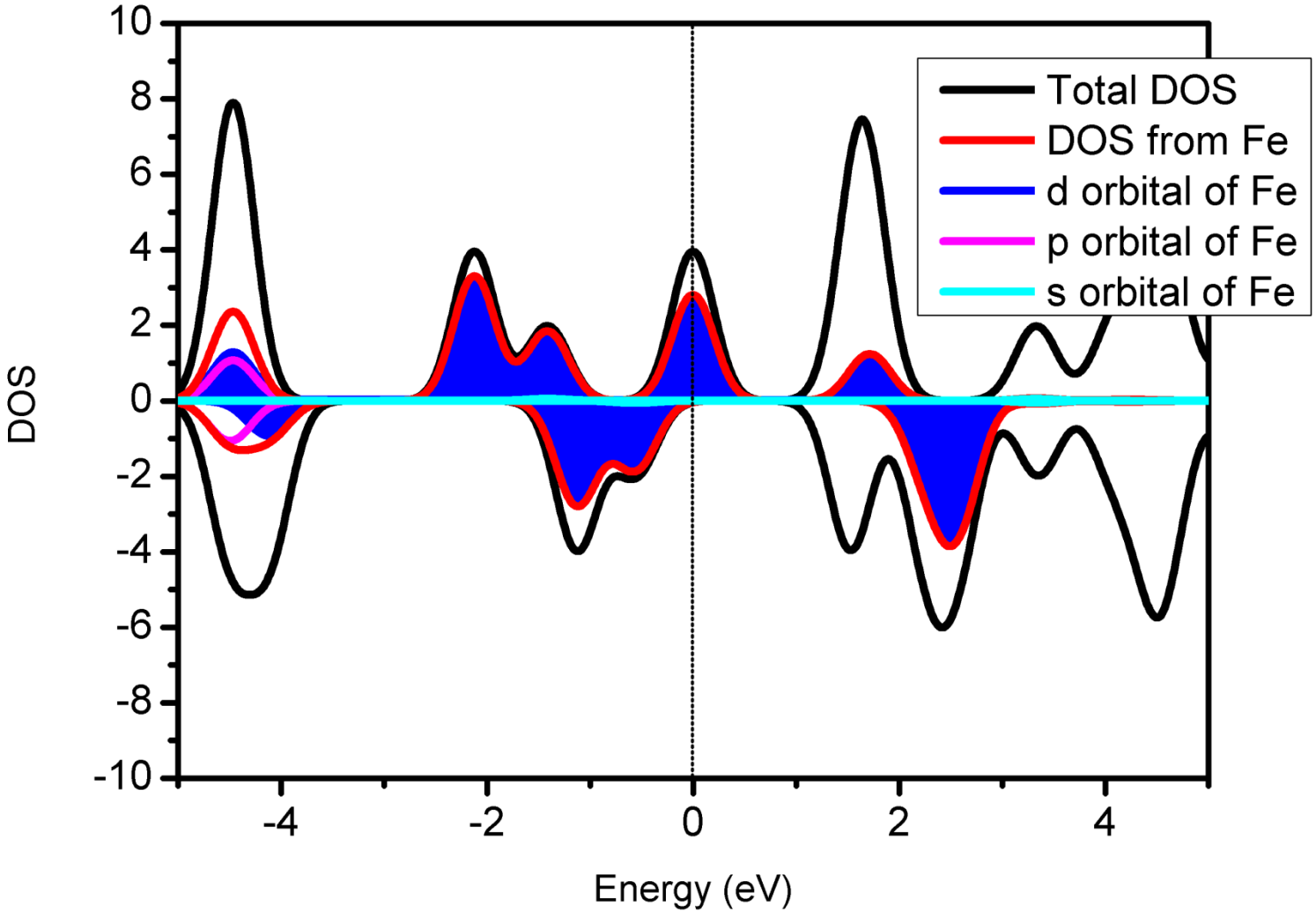
$$\rho_{spin} = \rho_{up} - \rho_{down}$$

Molecular magnet $Fe(C_5H_5)_2$



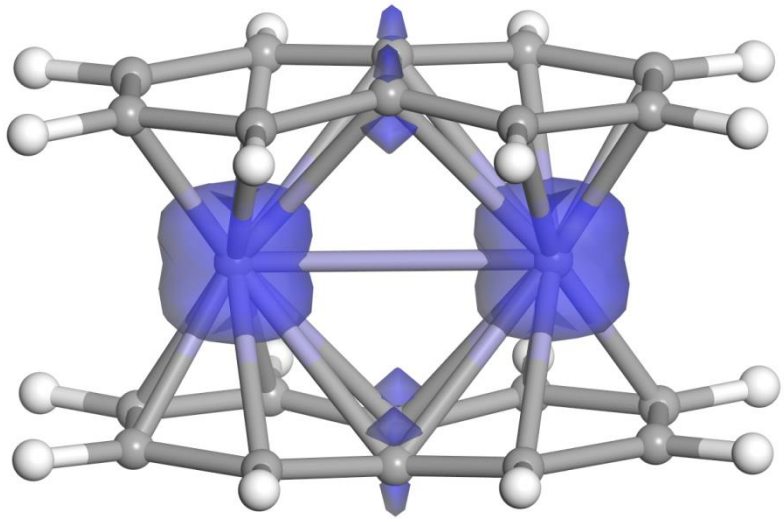
Understand the origin of Magnetism

Molecular magnet $Fe(C_6H_6)_2$



FM or AFM coupling

Molecular magnet $Fe_2(C_{10}H_{10})_2$



Population of Charge

Define a density matrix

$$P_{\mu v} = \sum_i C_{i\mu} C_{iv}$$

The trace of matrix P and the overlap S is equal to the total number of electrons

$$N = Tr\ PS = \sum_{\mu} (PS)_{\mu}$$

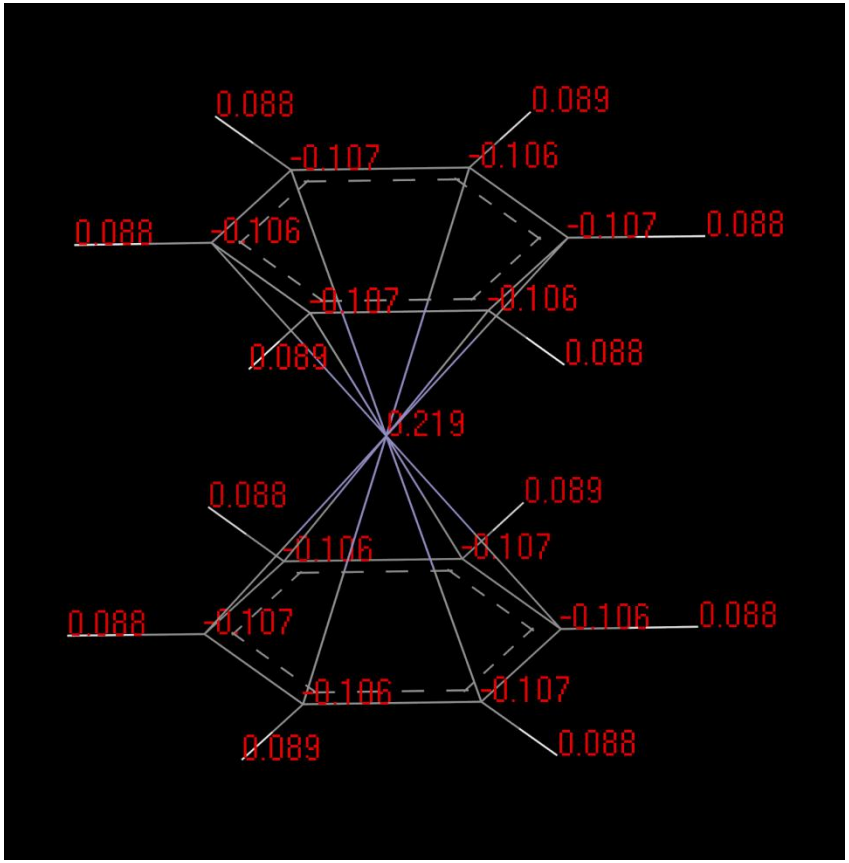
$(PS)_{AB}$ associate the electrons on the A-B bond : Muilliken population analysis

The net charge on atom A

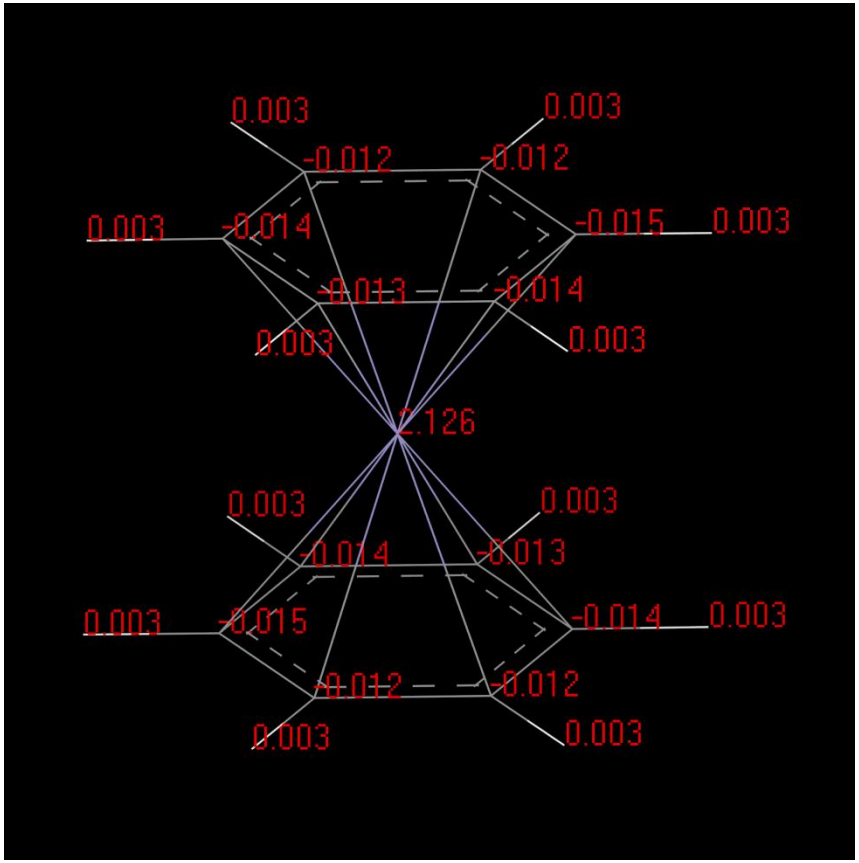
$$q_A = Z_A - \sum_{\mu \in A} (PS)_{\mu\mu}$$

Population of Charge, local magnetic moment

Charge

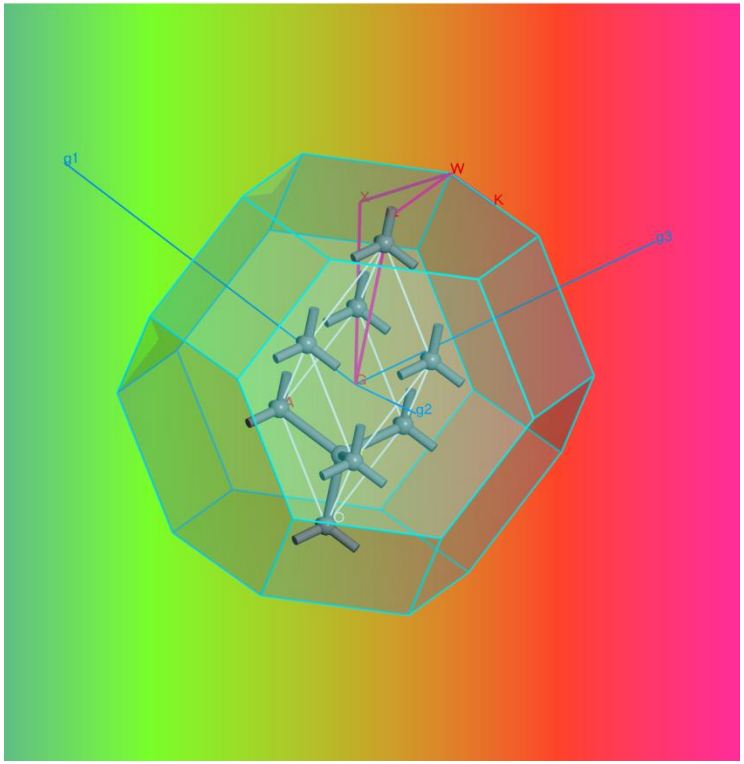


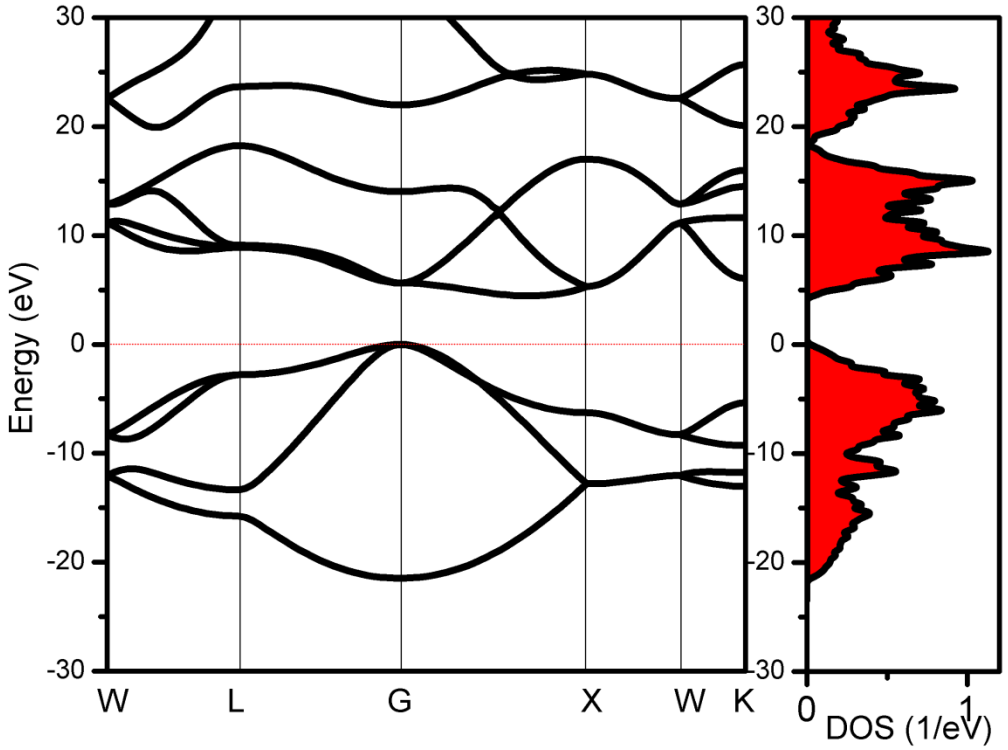
Local magnetic moment



Same things for Periodic System

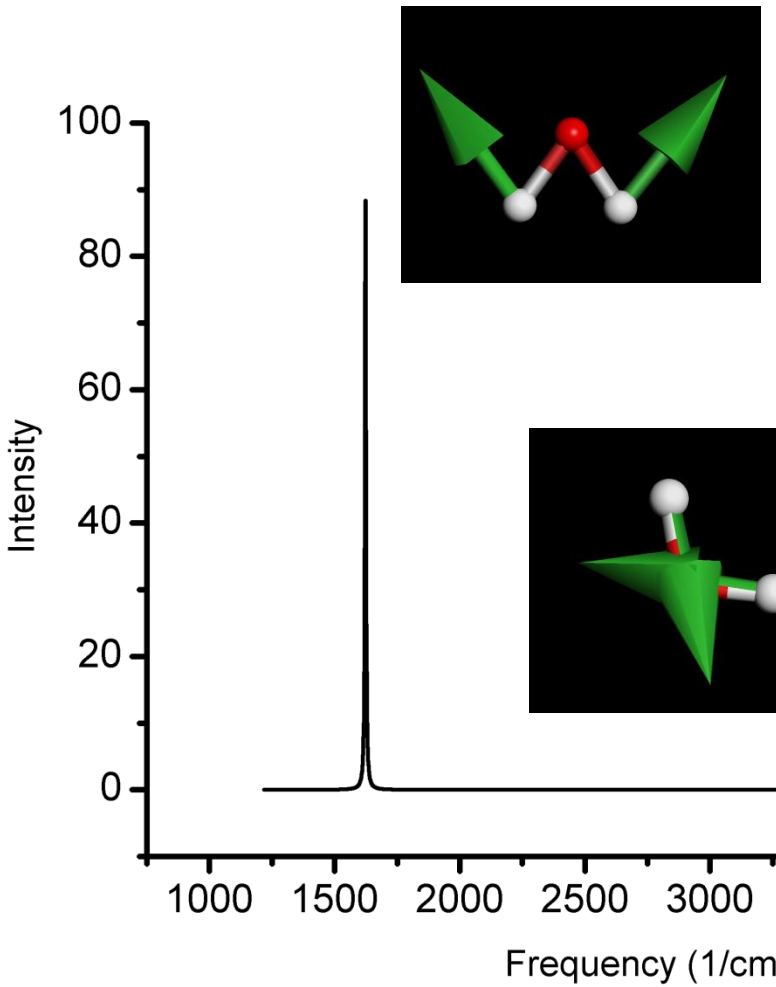
Different from discrete energy level, we have band structures with dispersion

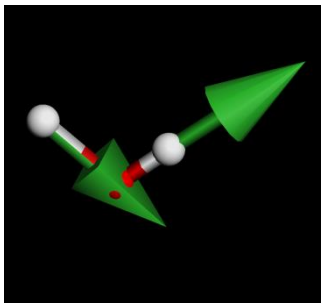




Vibration Information

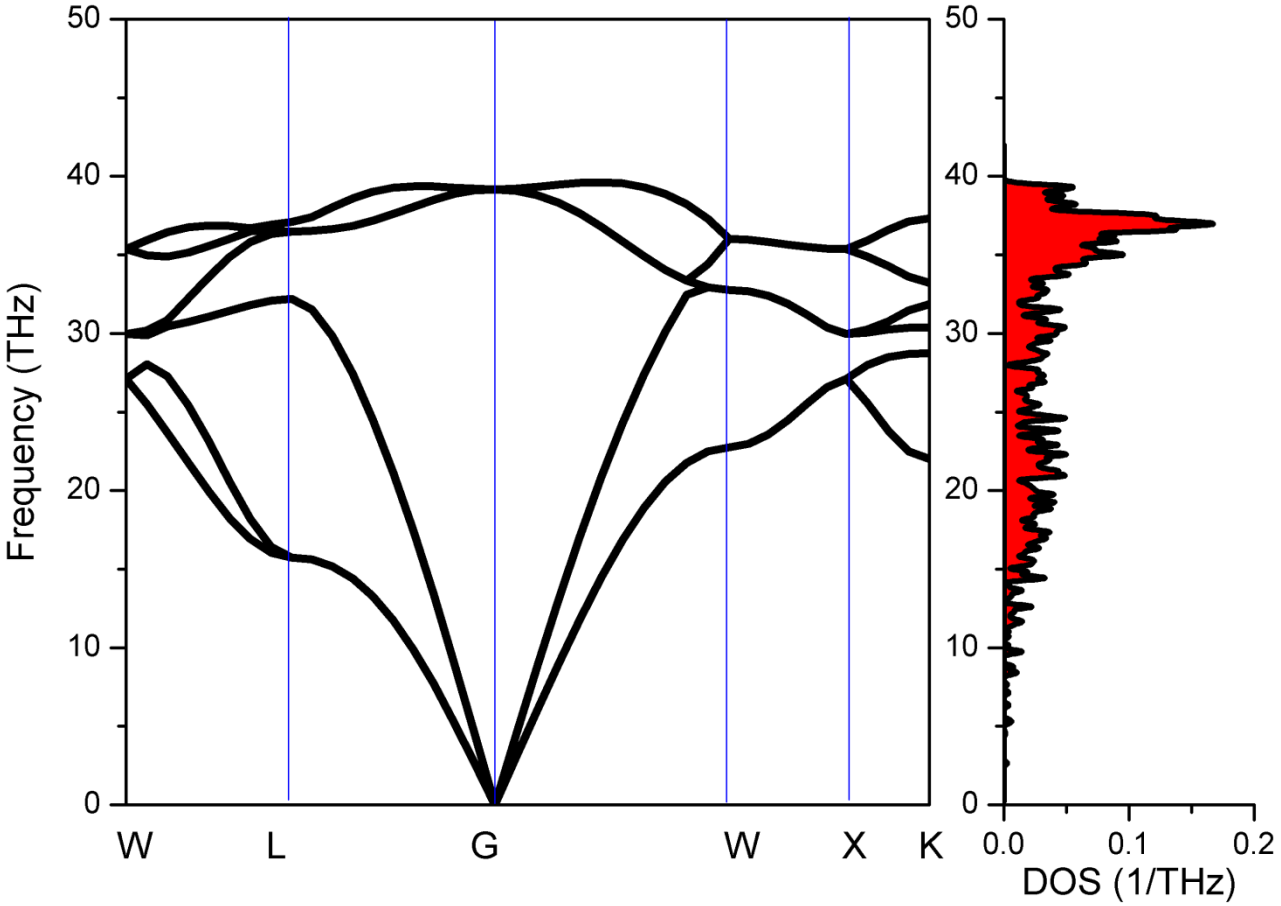
Important for determine : Raman, thermodynamic properties, transition state



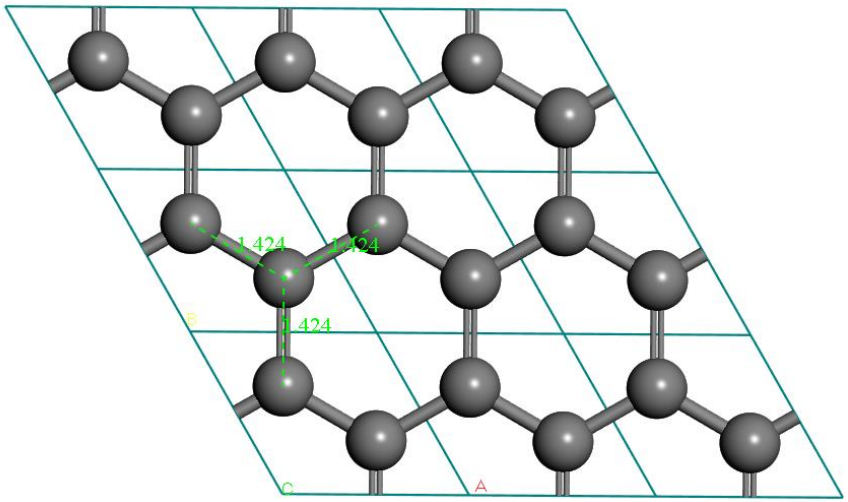


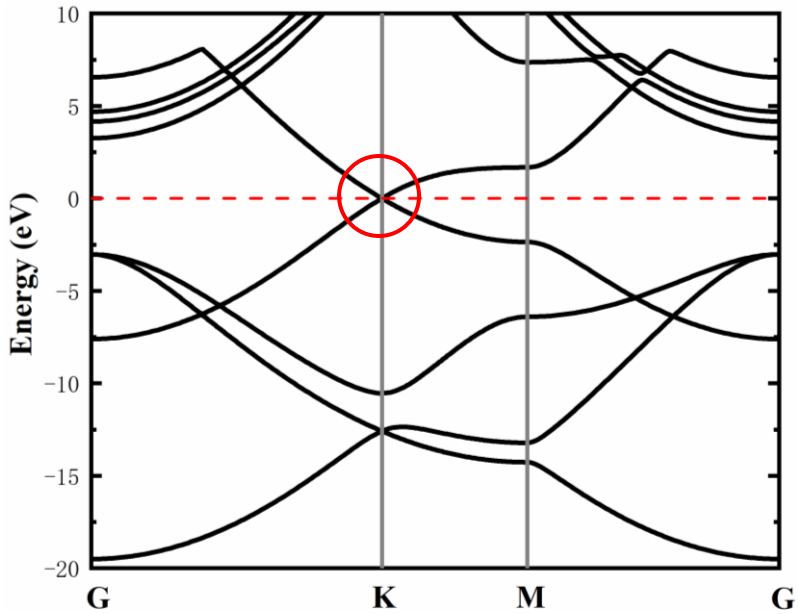
Frequency (1/cm)	Intensity (km/mol)
1622.81	88.36
3751.52	12.74
3869.59	69.93

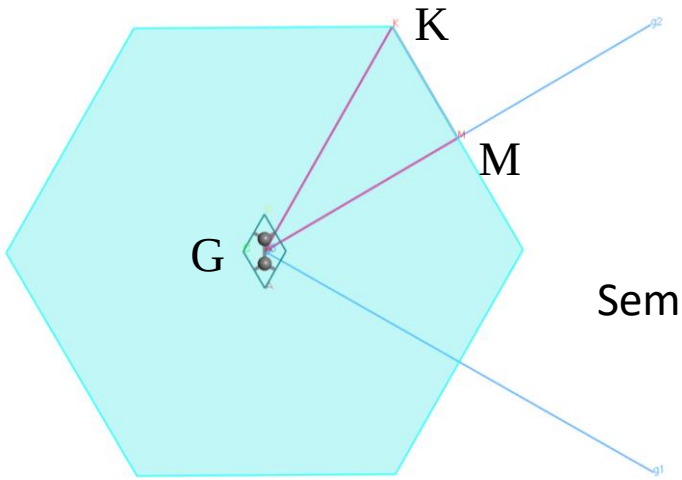
For periodic system: Phonon Spectrum



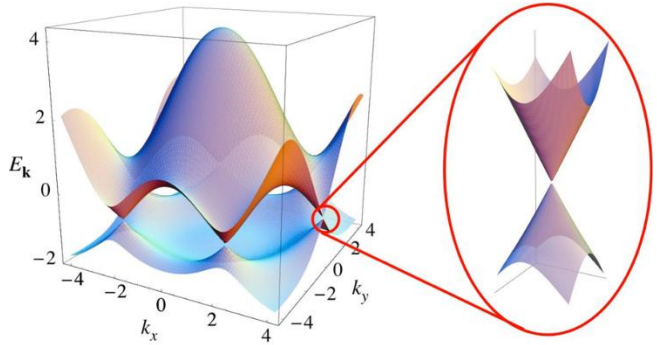
Same things for Periodic System





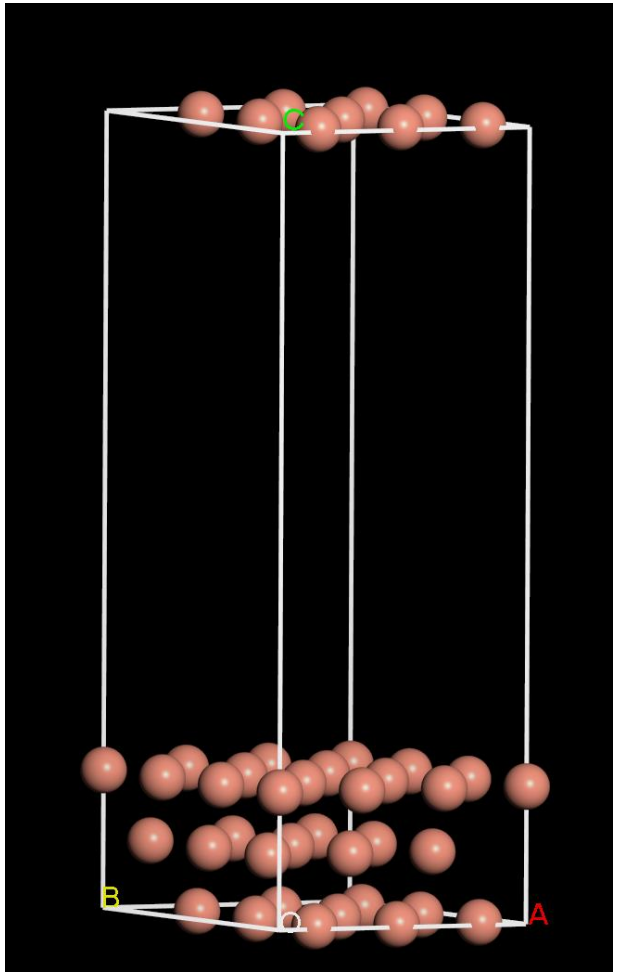


Semimetal !



http://exciting-code.org/carbon-graphene-from-the-ground-state-to-excitations

Potential calculation for working function



Potential calculation for working function

Potential profile