Molecular Modeling using WebMO

for Physical Chemistry (1) Course

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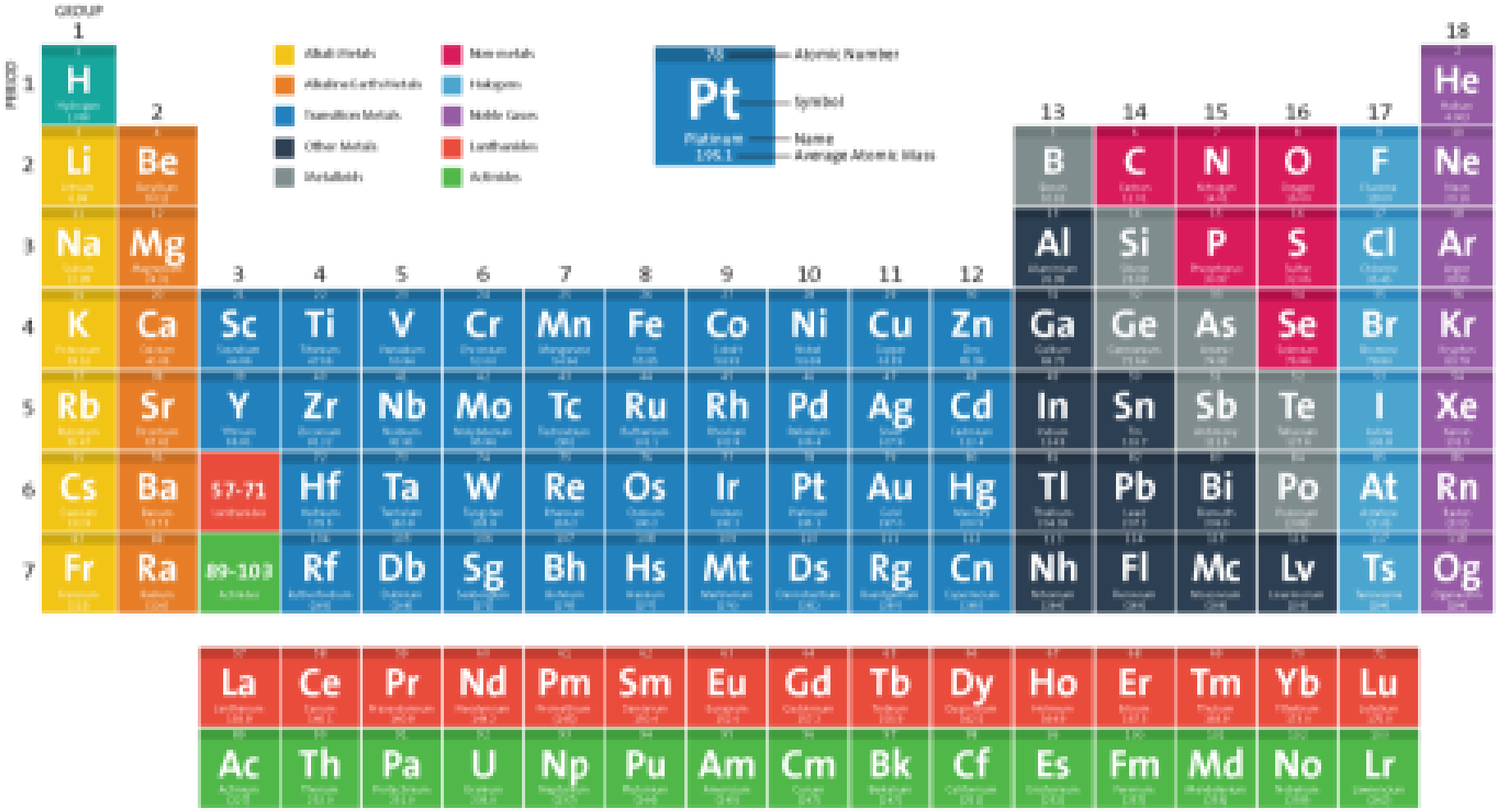
ACS Chemistry for Life®

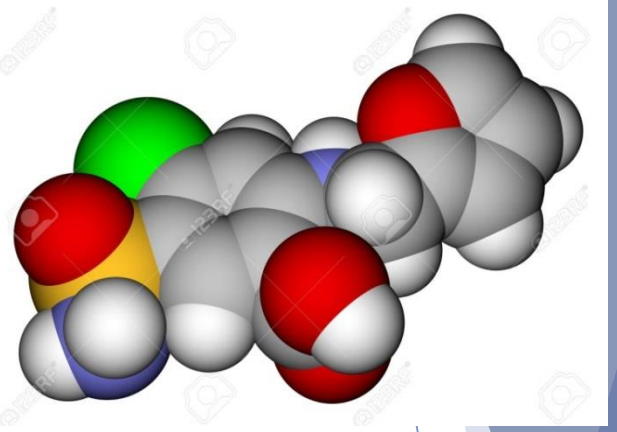
PERIODIC TABLE OF ELEMENTS



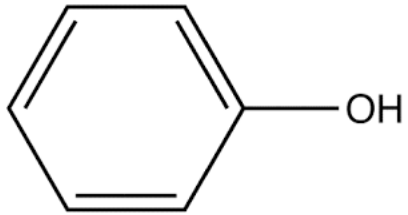
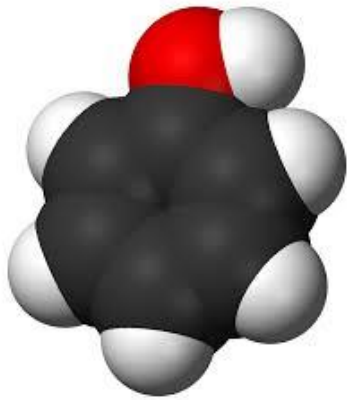
American Chemical Society

www.acs.org/outreach

Molecular Modeling



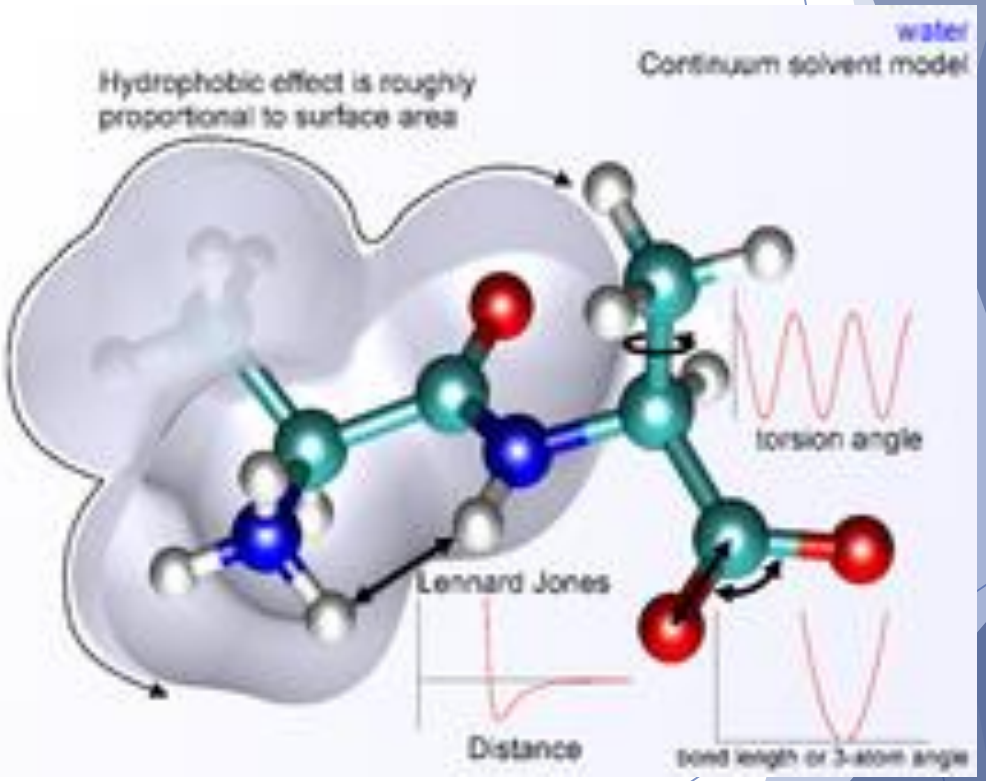
- Model What ?
  Structure → Properties → Chemistry

- C_6H_6O →  → 

- 3-D structures →

Thermodynamics, Electron Density, Spectroscopy,
Molecular Interaction, Chemical Reactions

Molecular Modeling needs a force field

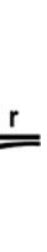


Molecular Mechanics Force Field

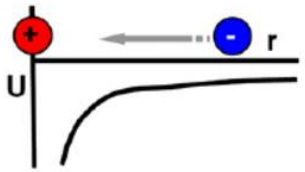
(MMFF, Functional Form + Parameter Sets)

- Total energy is the sum of the functional forms：

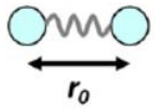
$$U = \sum_{i<j}\sum 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$



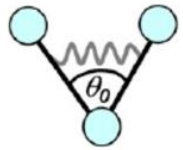
$$+\sum_{i<j}\sum\frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$



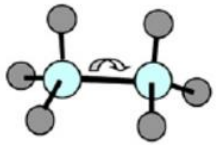
$$+\sum_{bonds}\frac{1}{2}k_b(r-r_0)^2$$



$$+\sum_{angles}\frac{1}{2}k_a(\theta-\theta_0)^2$$



$$+\sum_{torsions}k_\phi[1+\cos(n\phi-\delta)]$$



Parameters are from experimental data or quantum chemical calculation

Commonly used Force Fields:

AMBER

CHARMM

UFF

MMFF

MM2, MM3, MM4

VSEPR

no electrons, bonds do not break!

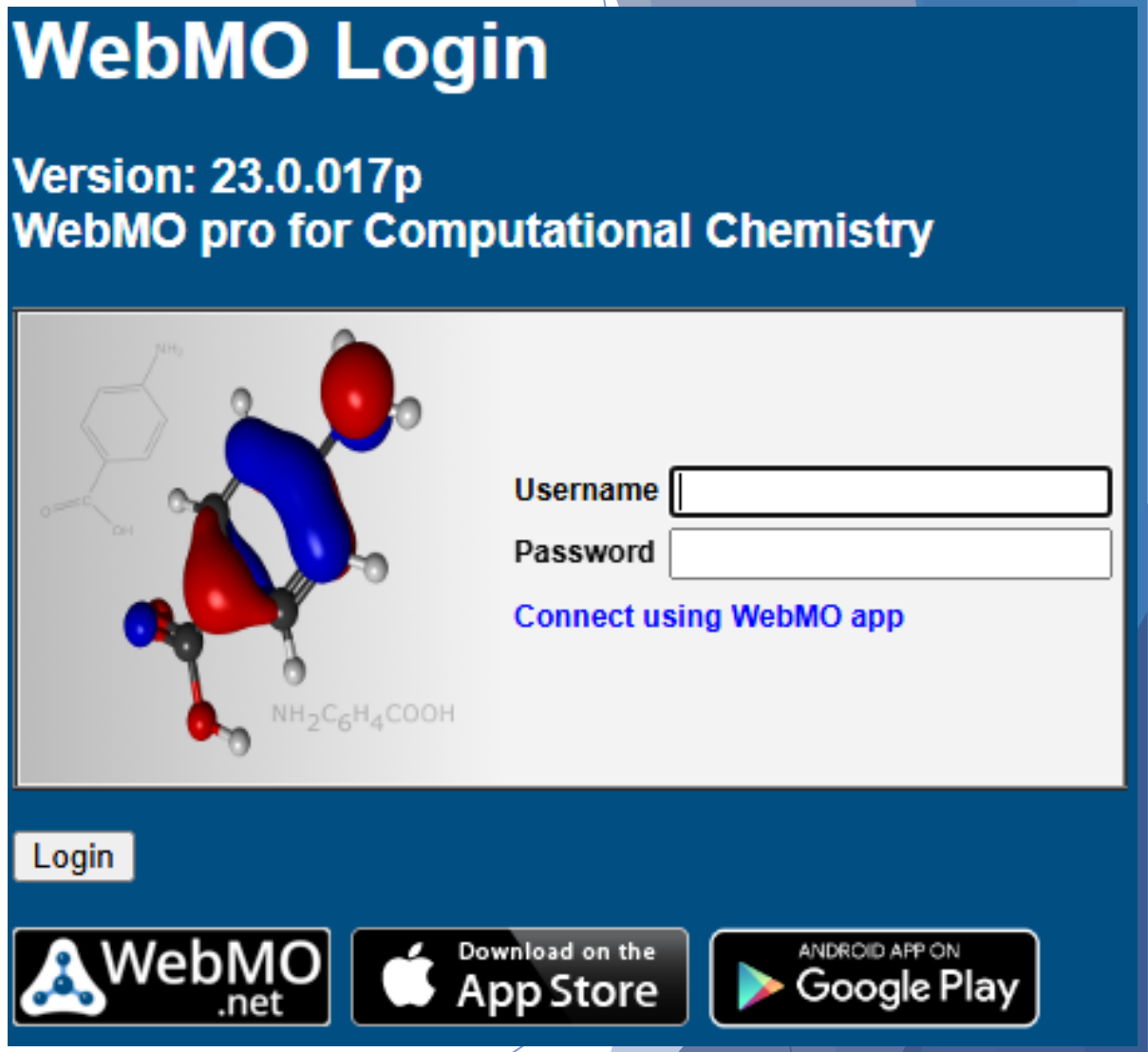
Quantum Chemistry: HF, MP2, DFT, Semiempirical: PM3, AM1

How to Login WebMO?

Connect to WebMO Page from your Web Browser

Find the username and passwd the TA provided

Enter the account info. to login

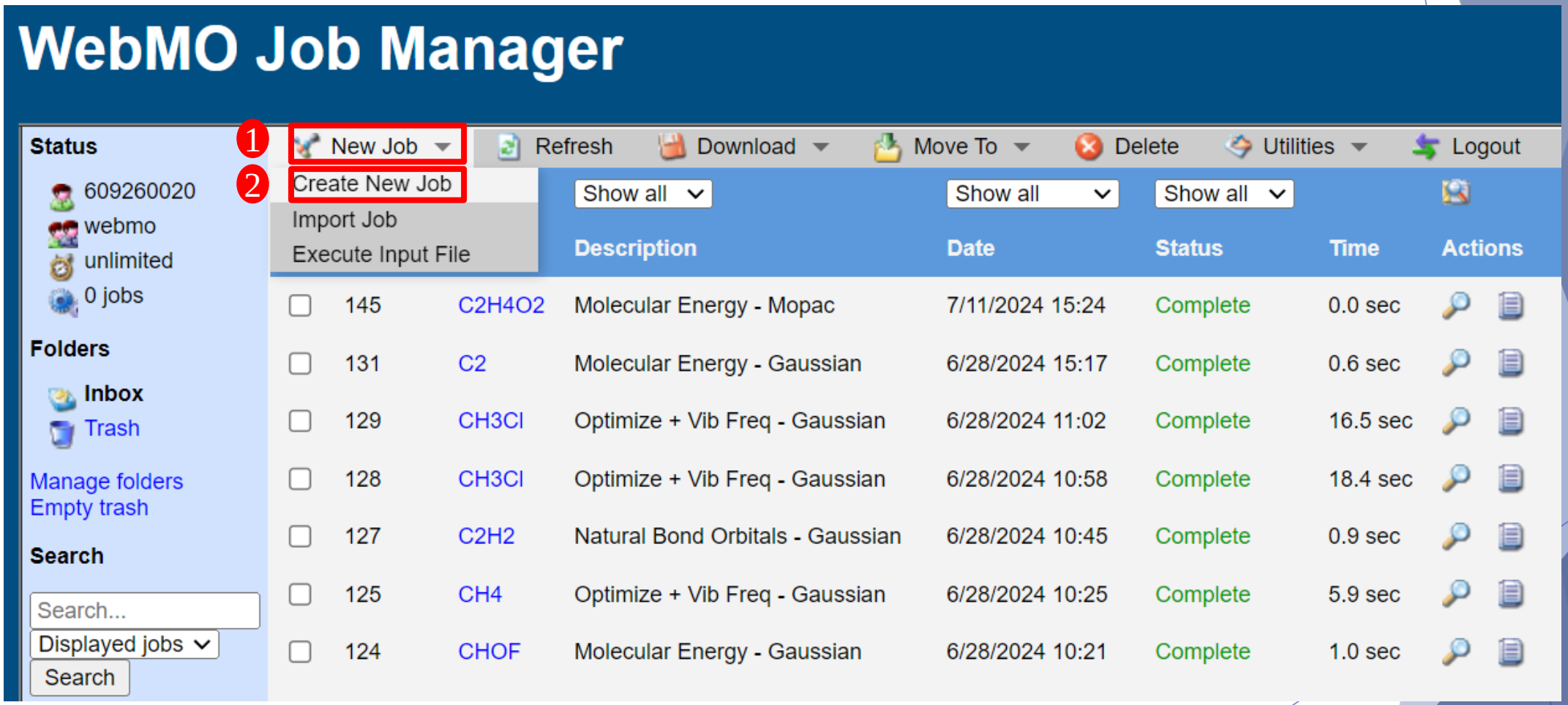


WebMO

http://apollo.chem.ccu.edu.tw/~WebMO/cgi-bin/webmo_pro/login.cgi

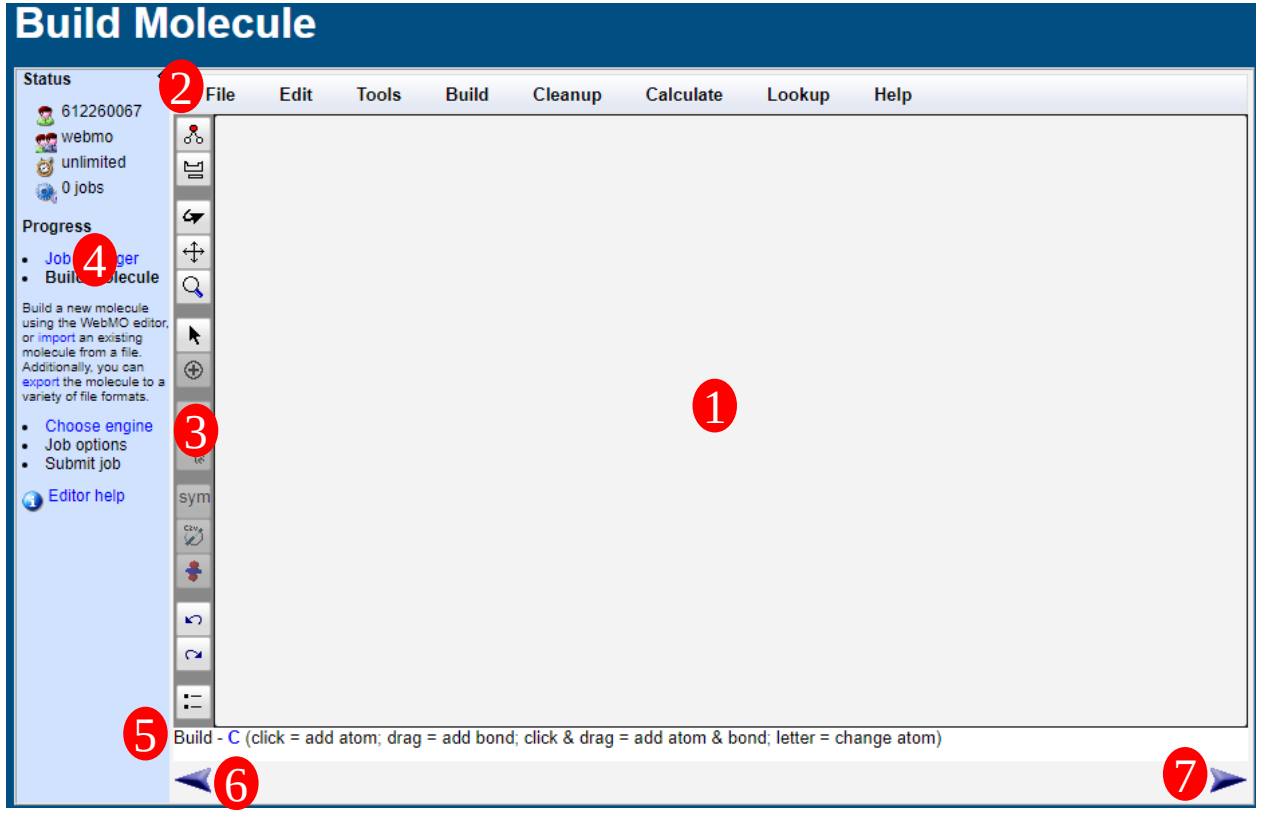
Job manager

After you log in, you see the Job Manager page listing all the job you have submitted.



Press「New job」and then「Create new job 」to open「 Build molecule 」page

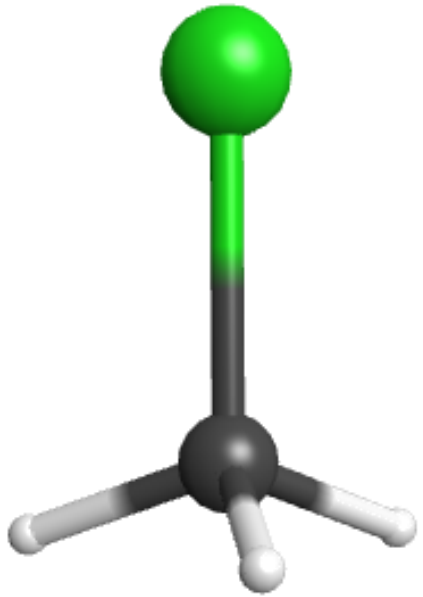
Build Molecule



1. Molecular Editor Window
2. Function Menu
3. Tool Bar
4. Progress
5. Current Mode
6. Previous Step
7. Next Step

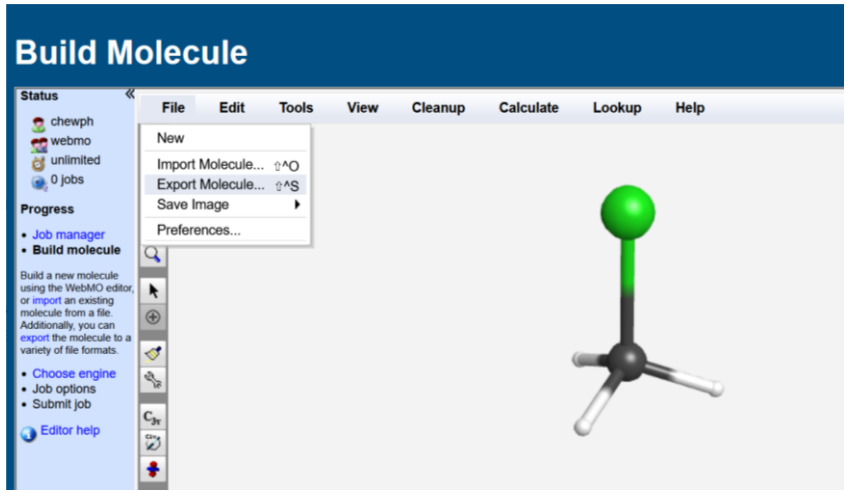
Build Molecule

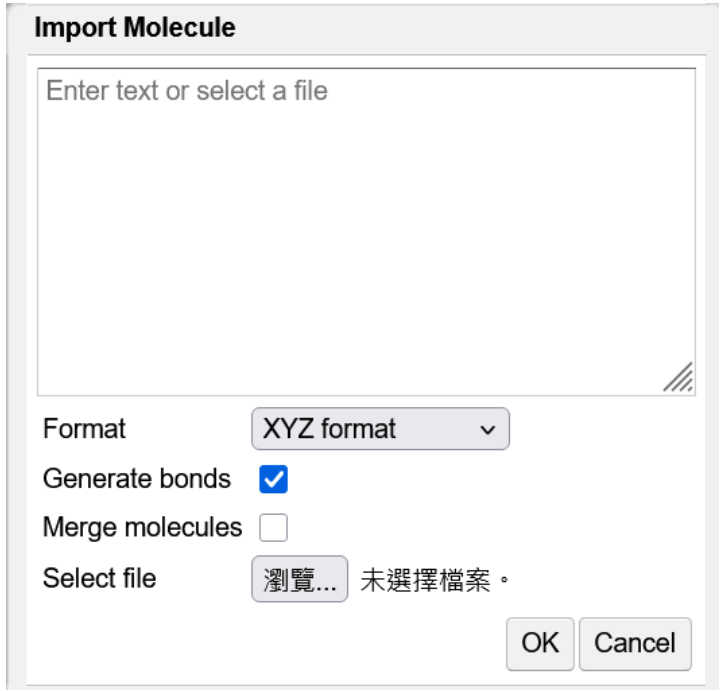
Chloromethane Molecule (CH_3Cl)：



1. Click in the window to insert the C atom
2. Click Build → Other to select Cl and pull it out from C to generate C-Cl
3. Choose Cleanup  or 

Save Molecule



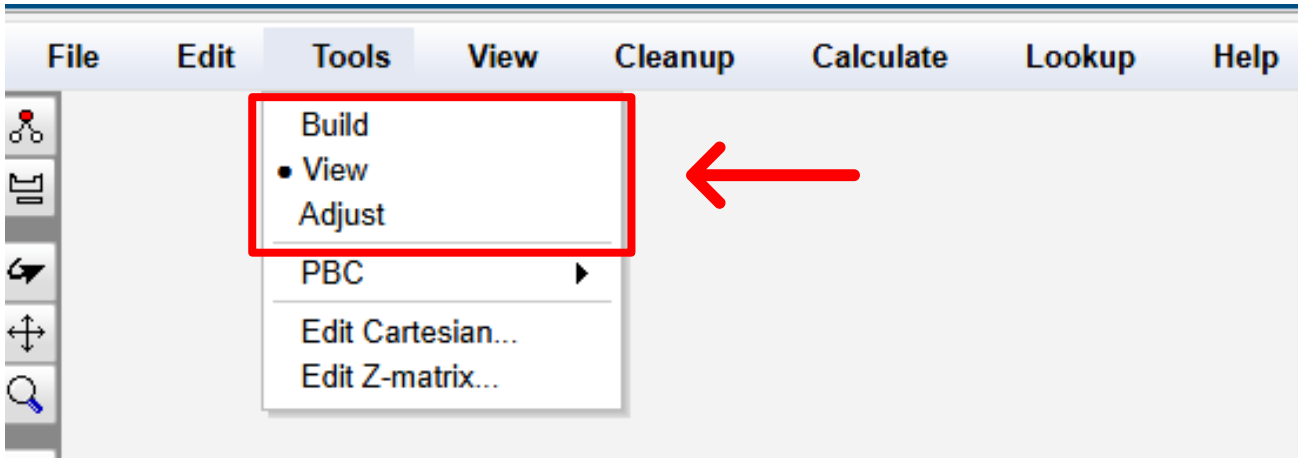


Click File → Export Molecule → XYZ format → OK

You may want to rename it.

You can Import the molecule later on.

Build Molecule - Tools



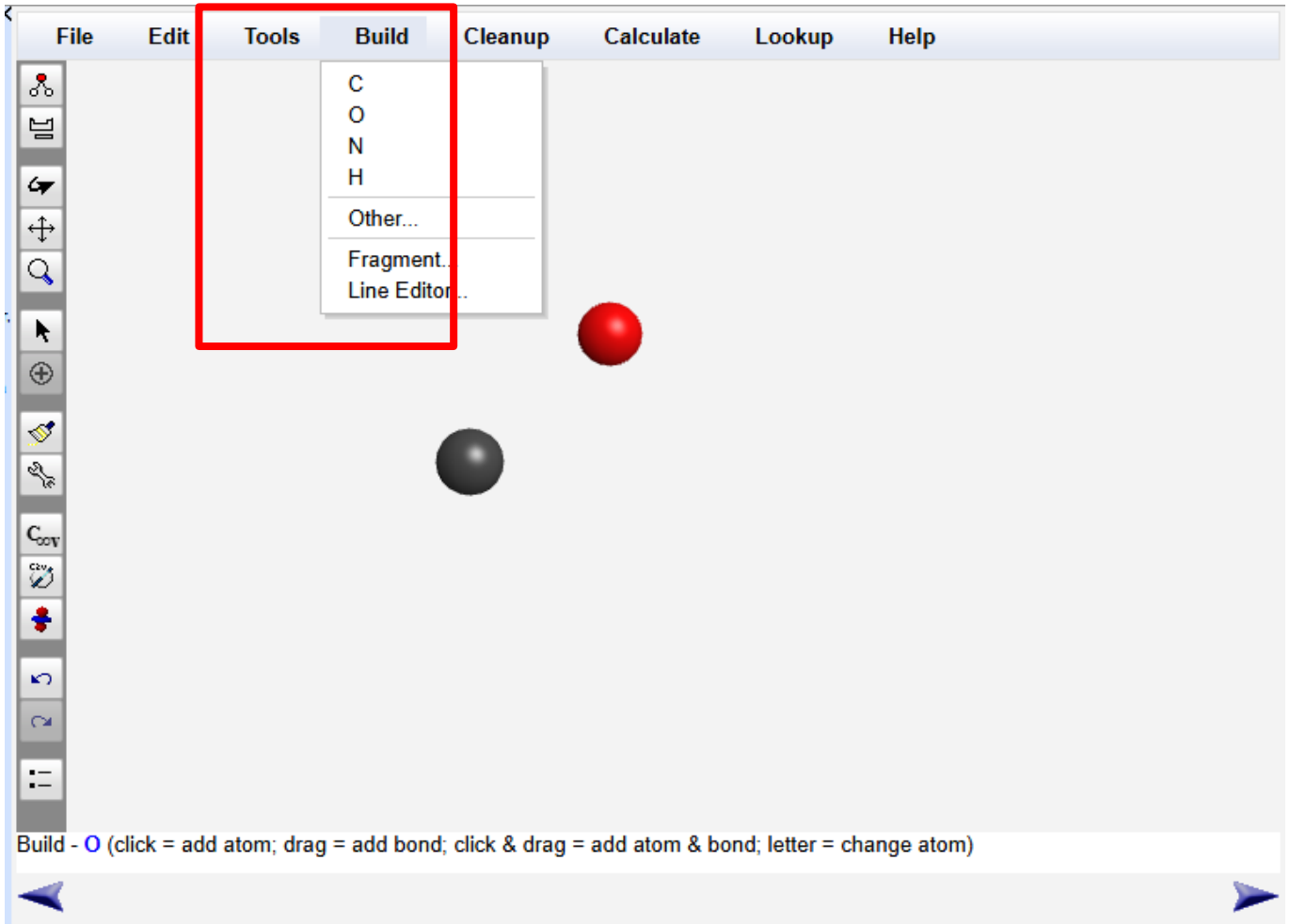
Build：Add new atoms

View：Rotate, translate, or scale molecules

Adjust：Change the key length, key angle, or dihedral angle

Build

After selecting Build, the right side of Tools in the upper toolbar will change to Build. Click Build to build atoms. To select other atoms, click Periodic Table. 



View

- Rotate

X、Y axis : Mouse dragging

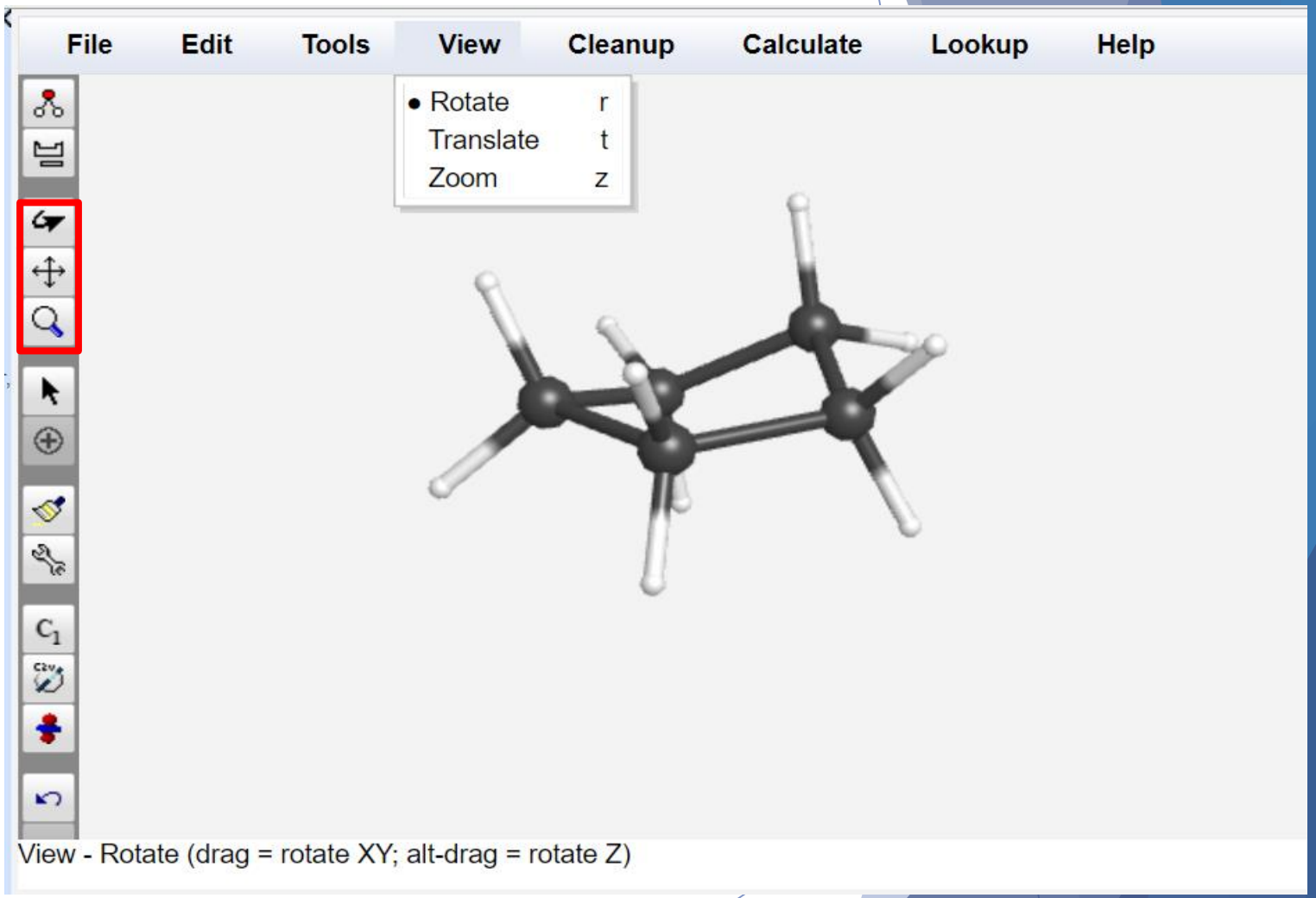
Z axis : Alt+Mouse dragging

- Translate

Mouse dragging

- Zoom

Mouse dragging

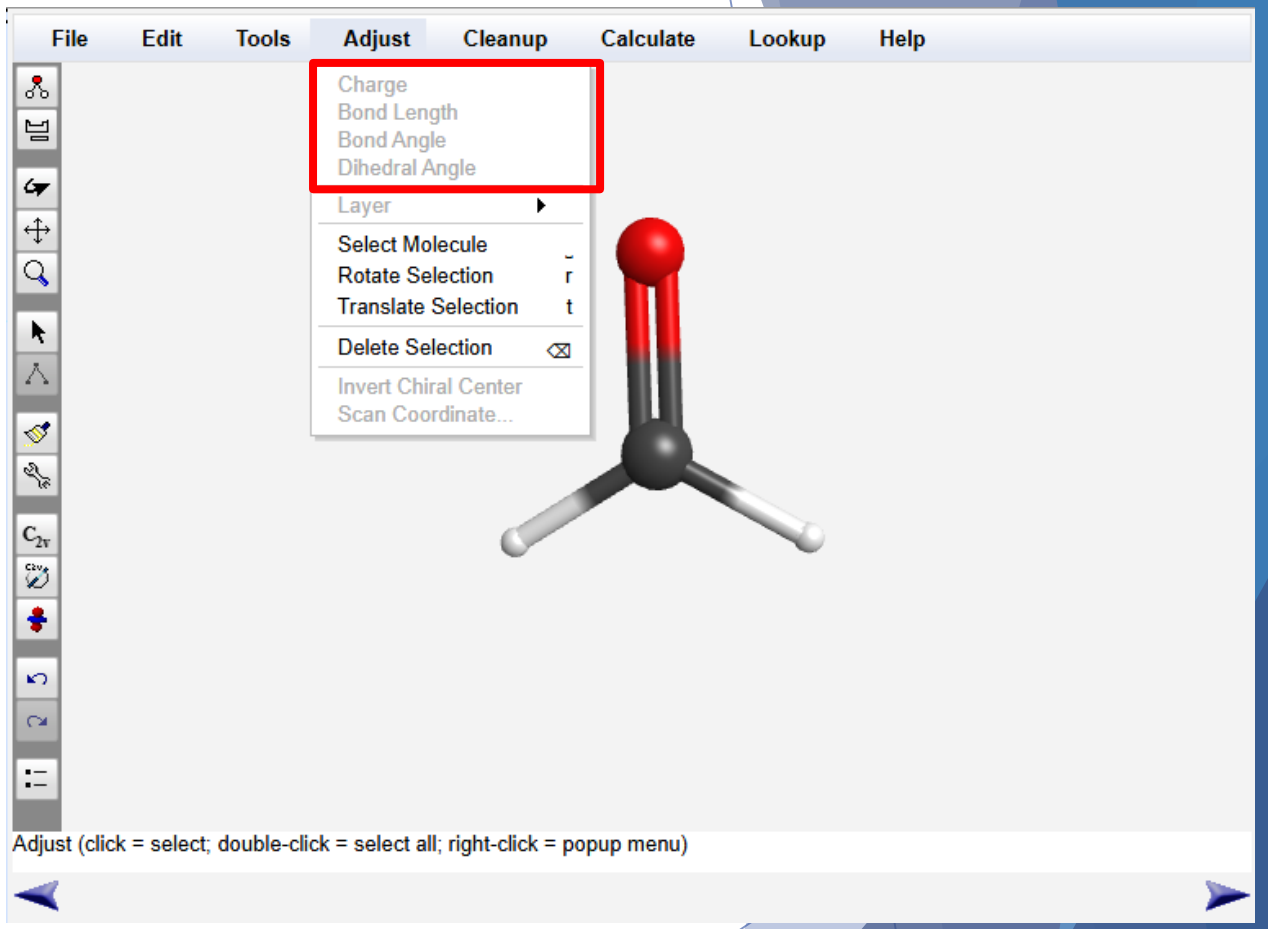


Adjust

1. Bond length ：Set the bond length of the two atoms

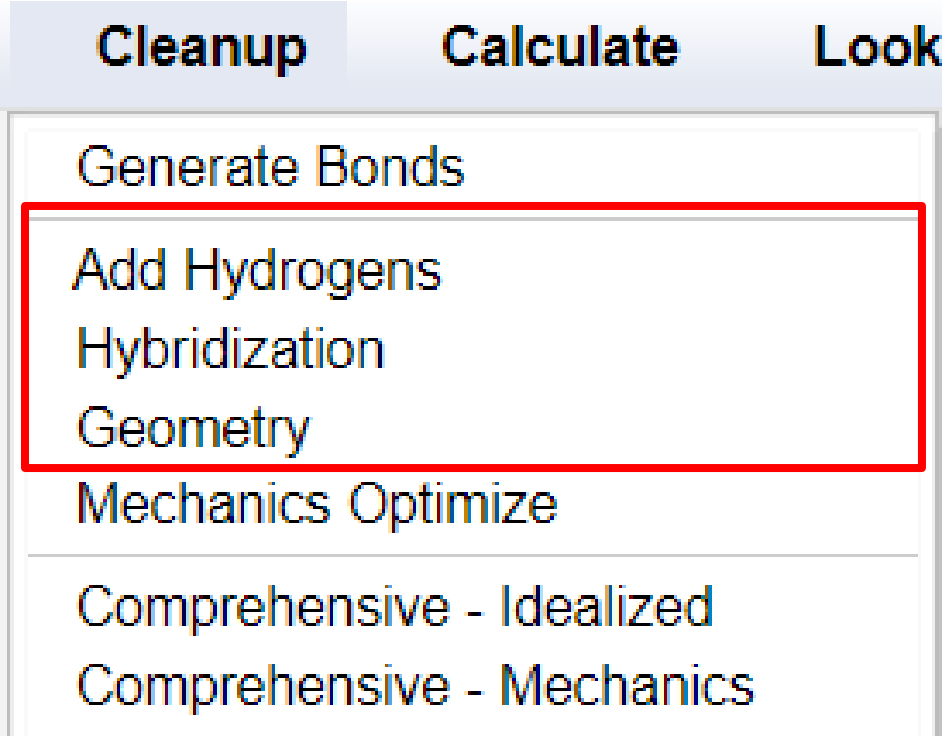
2. Bond angle ：Sets the bond angle between the three atoms

3. Dihedral angle ：Set the dihedral angle of the four atoms



When the icon  is clicked, the atom can be selected

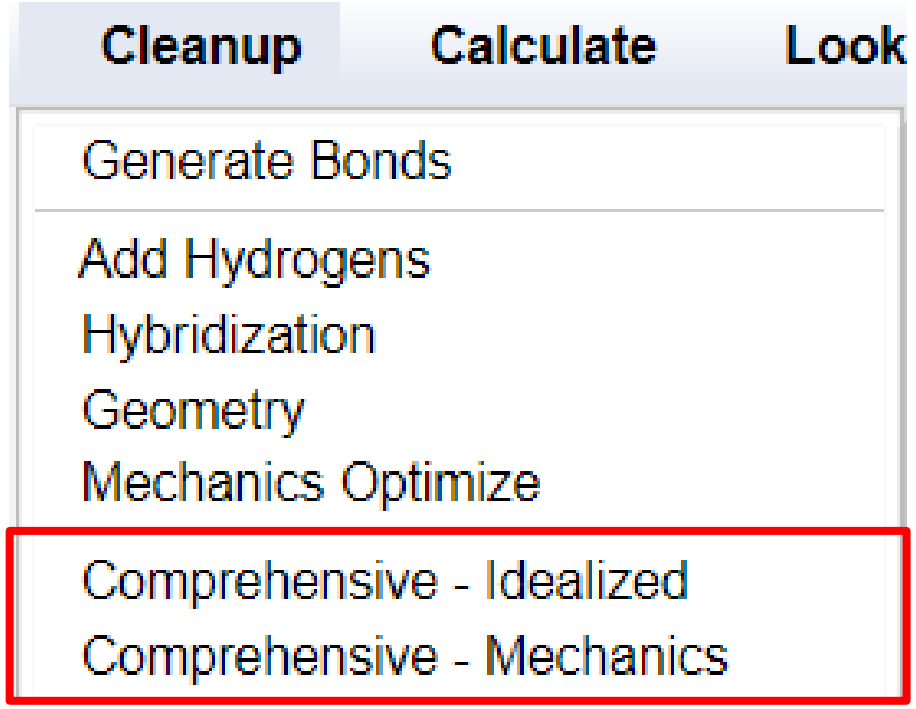
Cleanup



1. Add Hydrogen
2. Hybridization
3. Geometry

The above steps need to be completed in order

Cleanup



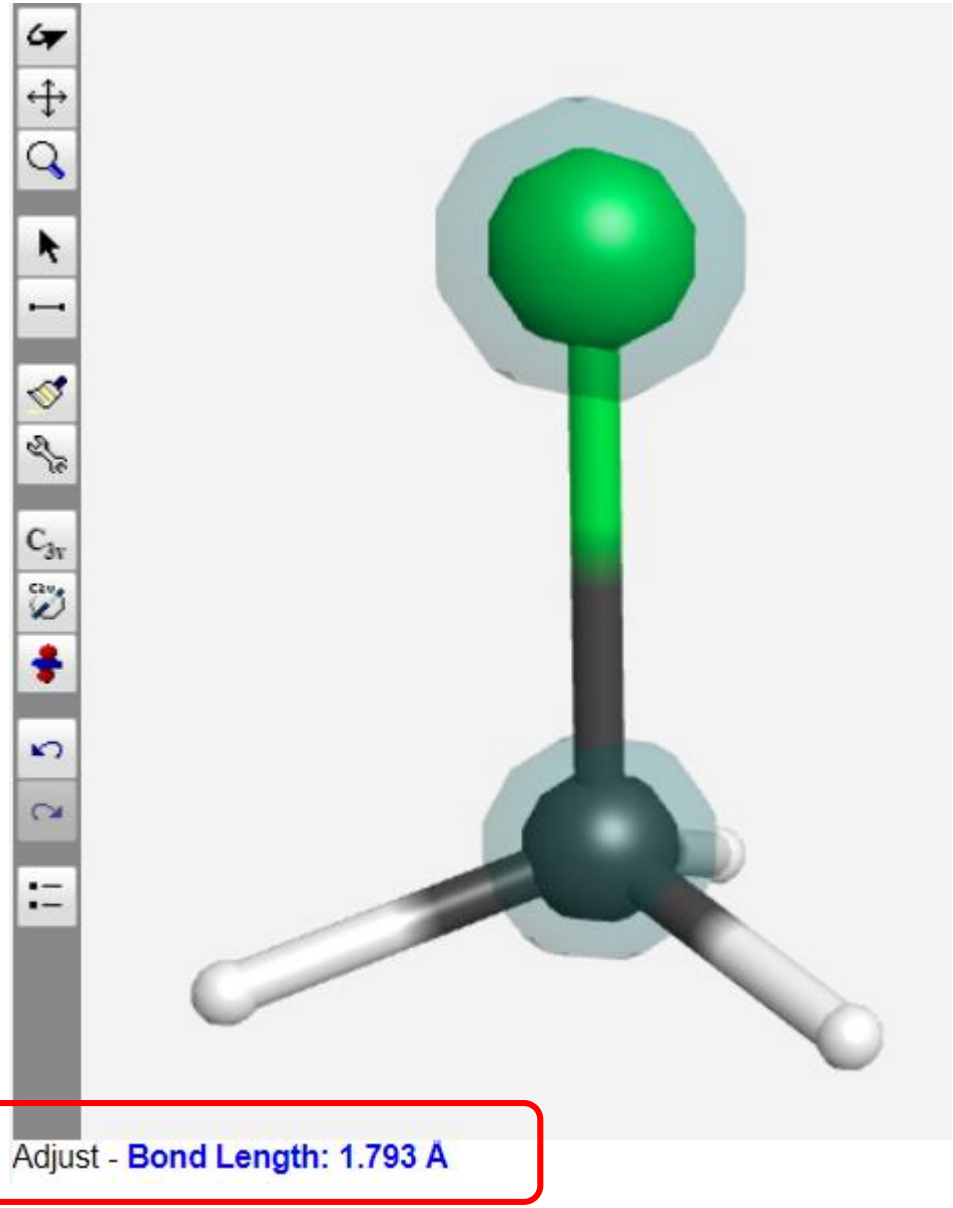
1. Comprehensive – Idealized
   Conform to VSEPR

2. Comprehensive – Mechanics
   Use Molecular Mechanics Force Fields (MMFF)
   Do not consider the effect of e-commerce

Comprehensive Cleanup using Idealized Geometry

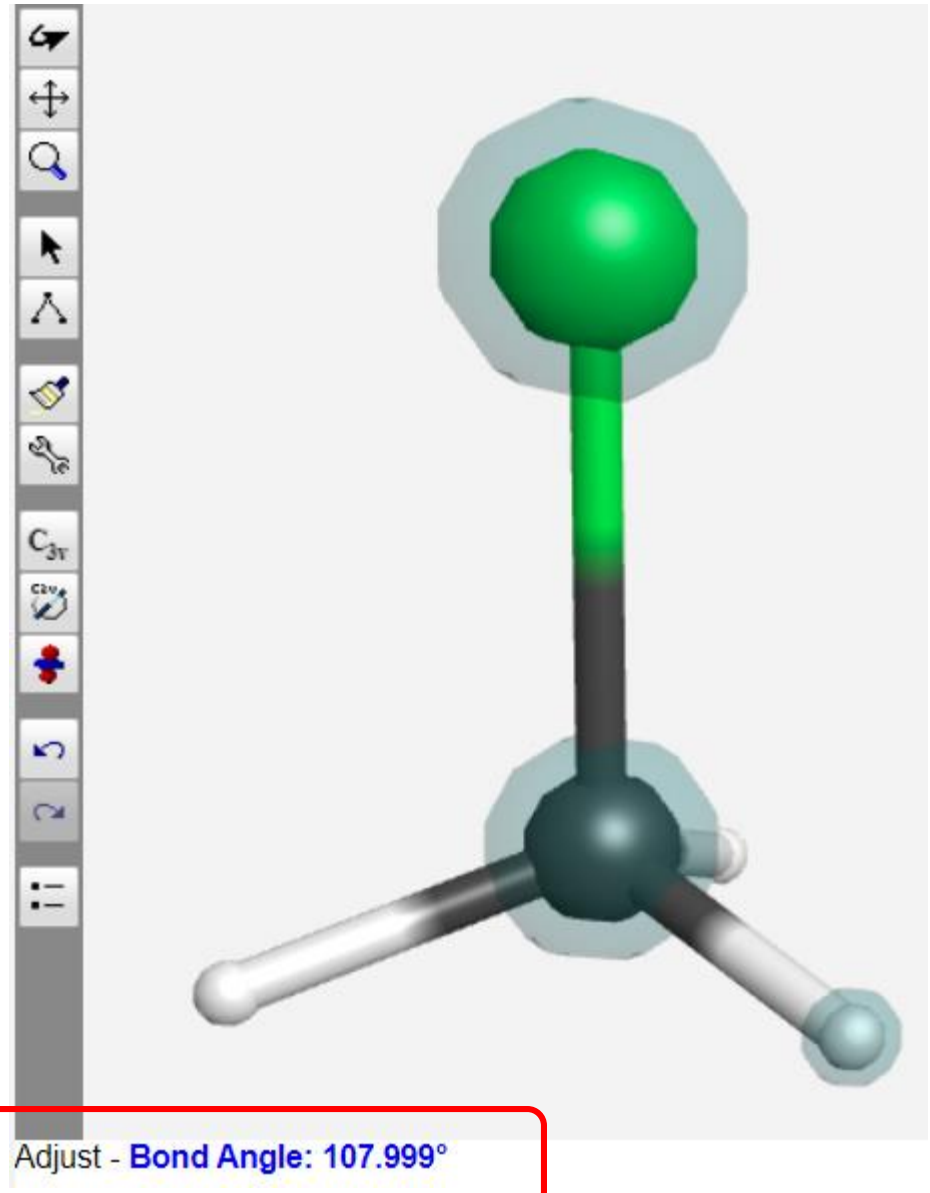
Comprehensive Cleanup using Mechanics

Measure Bond Length



Click on the two atoms you want to measure the length of the bond

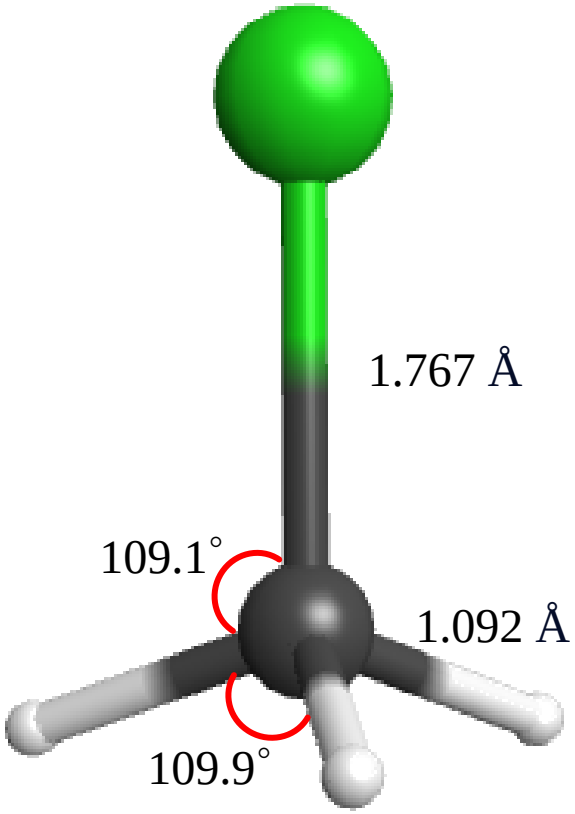
Measure Bond Angle



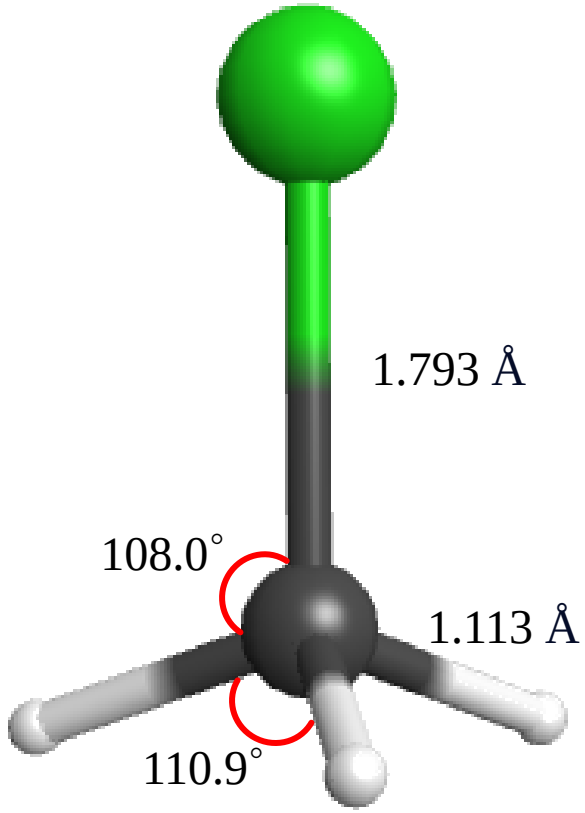
Click on the three atoms you want to measure the bond angle

Compare with Experimental Structure

CH_3Cl experimental value：

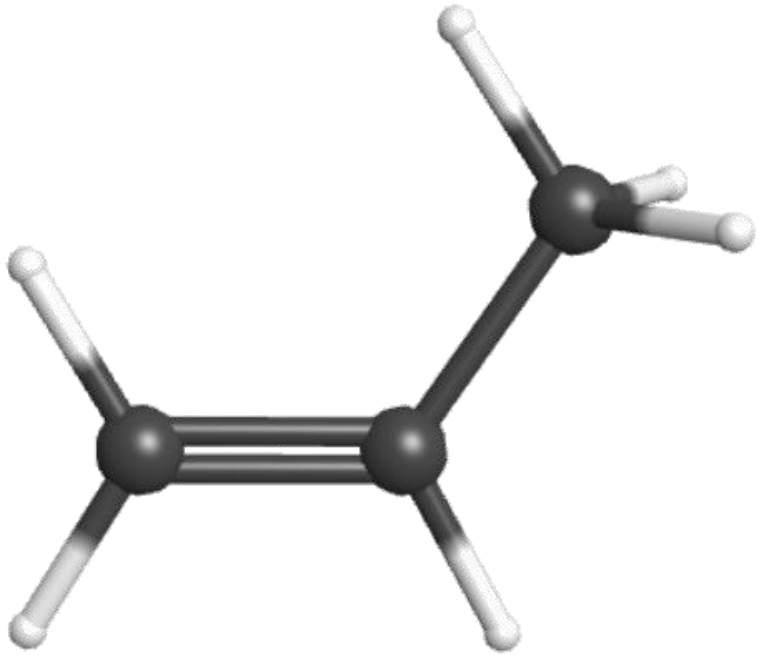


Optimized structure by MMFF：



Build Molecule

Propylene(C_3H_6)：

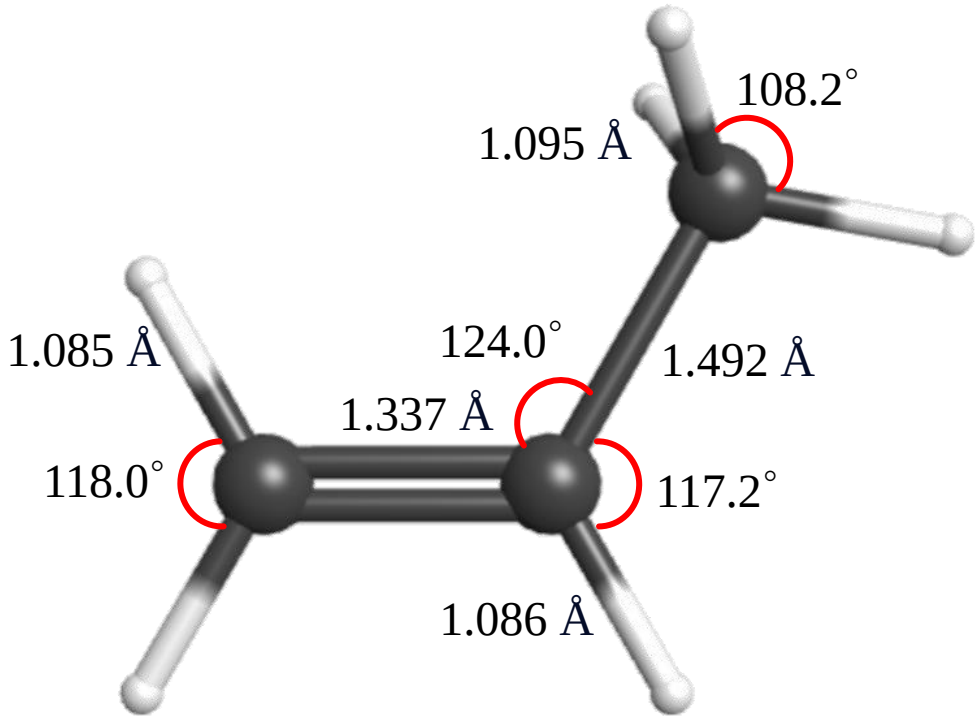


1. Click in the window to insert a C atom, pull outward along C twice to create C=C, and pull the other way form a new C-C

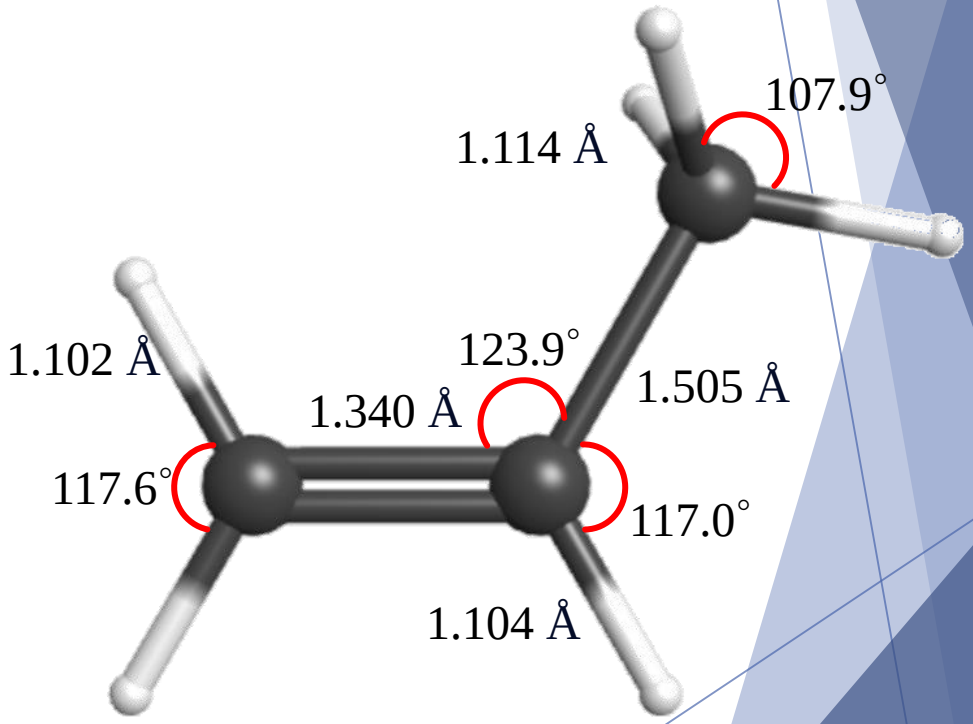
2. Choosing Cleanup  allows for initial structural optimization

Compare with Experimental Structure

C_3H_6 experimental value ：

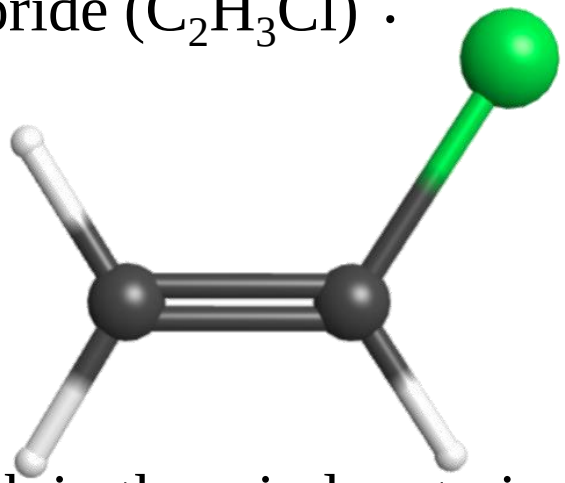


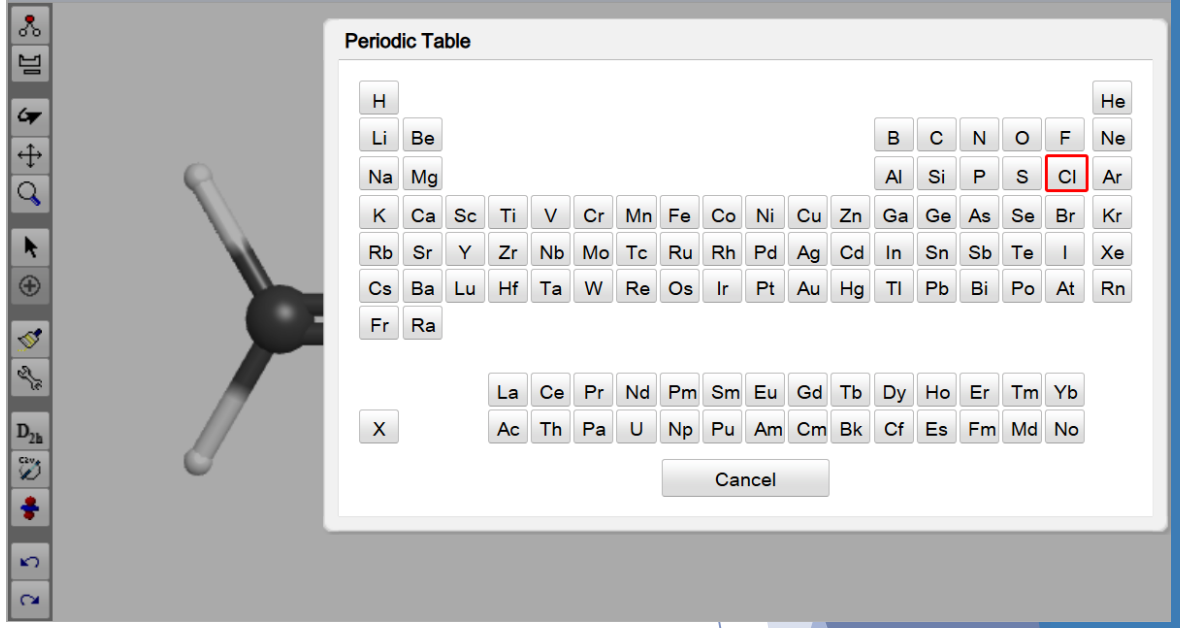
MMFF Optimized structure ：



Build Molecule-Replace Atom

Vinyl chloride (C_2H_3Cl)：

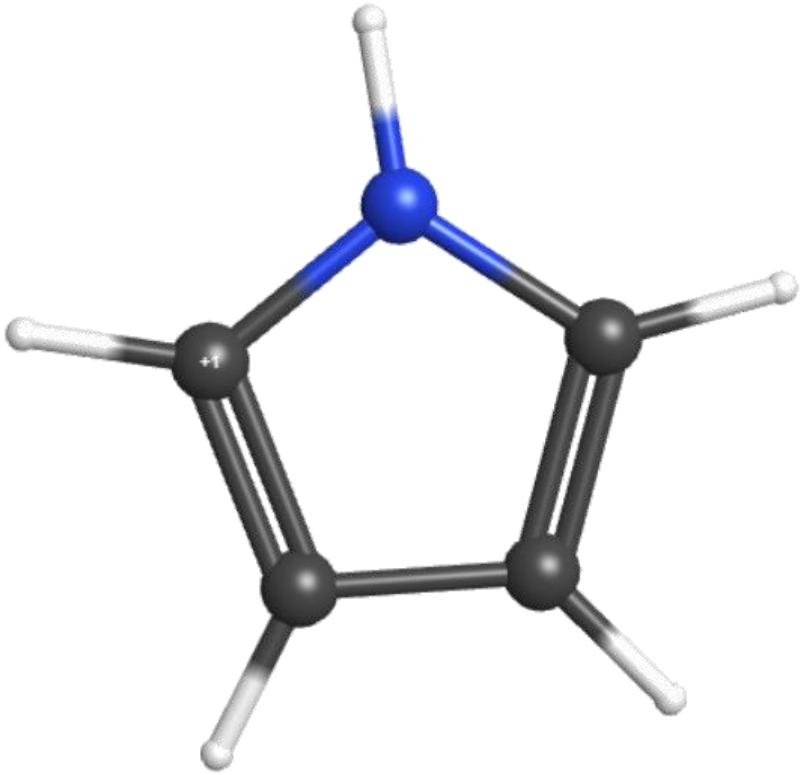




1. Click in the window to insert the C atom, and pull it out along C to produce C-C. Pull it again to form a double bond.
2. Choose Cleanup 
3. Replace one of the hydrogen atoms with chlorine. Click the button  select chlorine, then click on the hydrogen atom you want to replace.
4. Cleanup again

Build Molecule

Pyrrole：

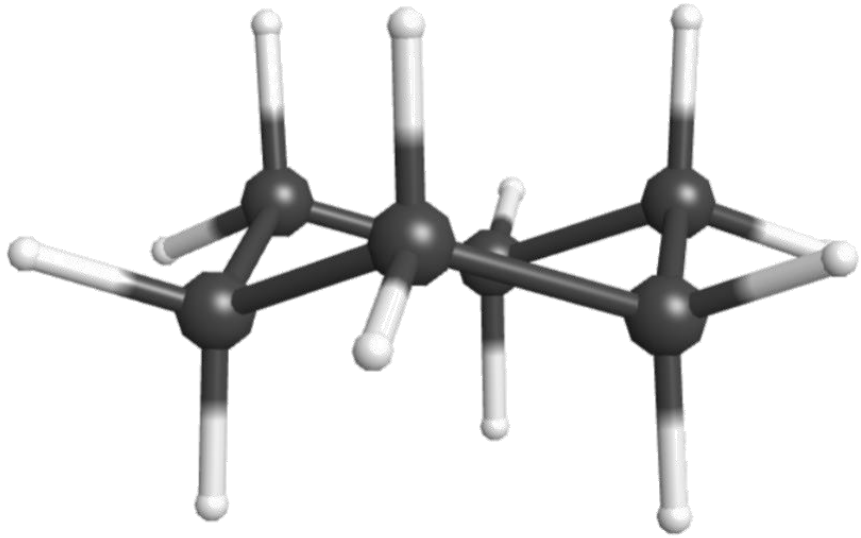


1. Press once in the window to insert the C atom, and C pulls outward to produce C-C, forming a five-member ring. When the double bond is pulled, replace the middle C by N

2. Choosing Cleanup 

Build Molecule

Cyclohexane (C_6H_{12})：

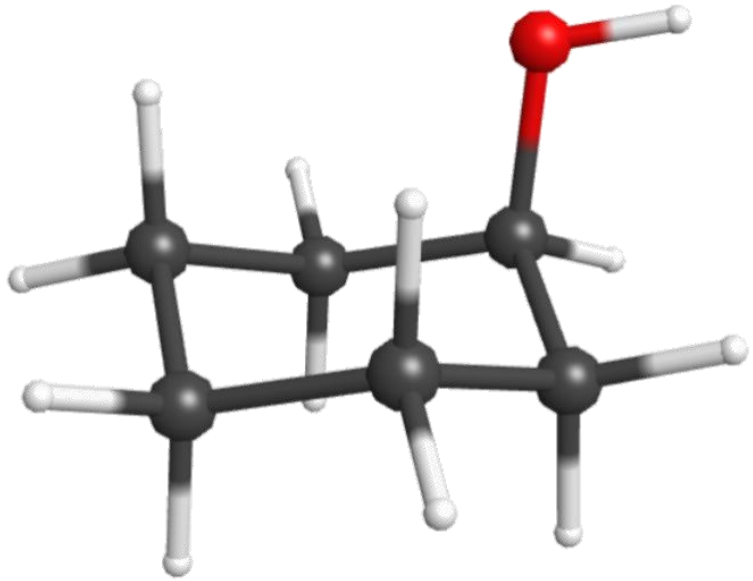


1. Click in the window to insert the C atom. Pull from C to form new C-C bonds, repeat and close the ring to form cyclohexane.

2. Choose Cleanup  to optimize the molecule with MMFF.

Build Molecule

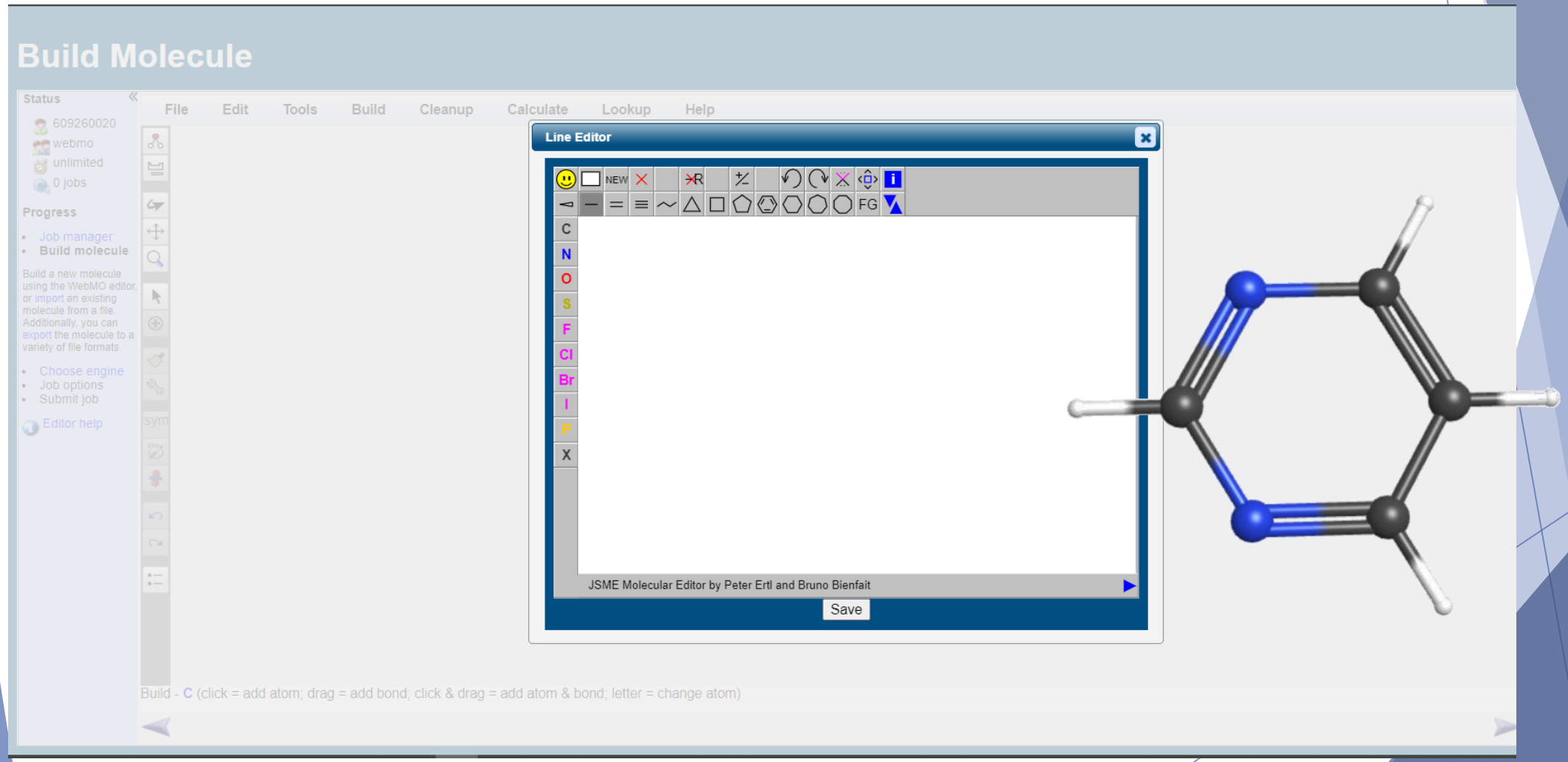
Cyclohexanol ：



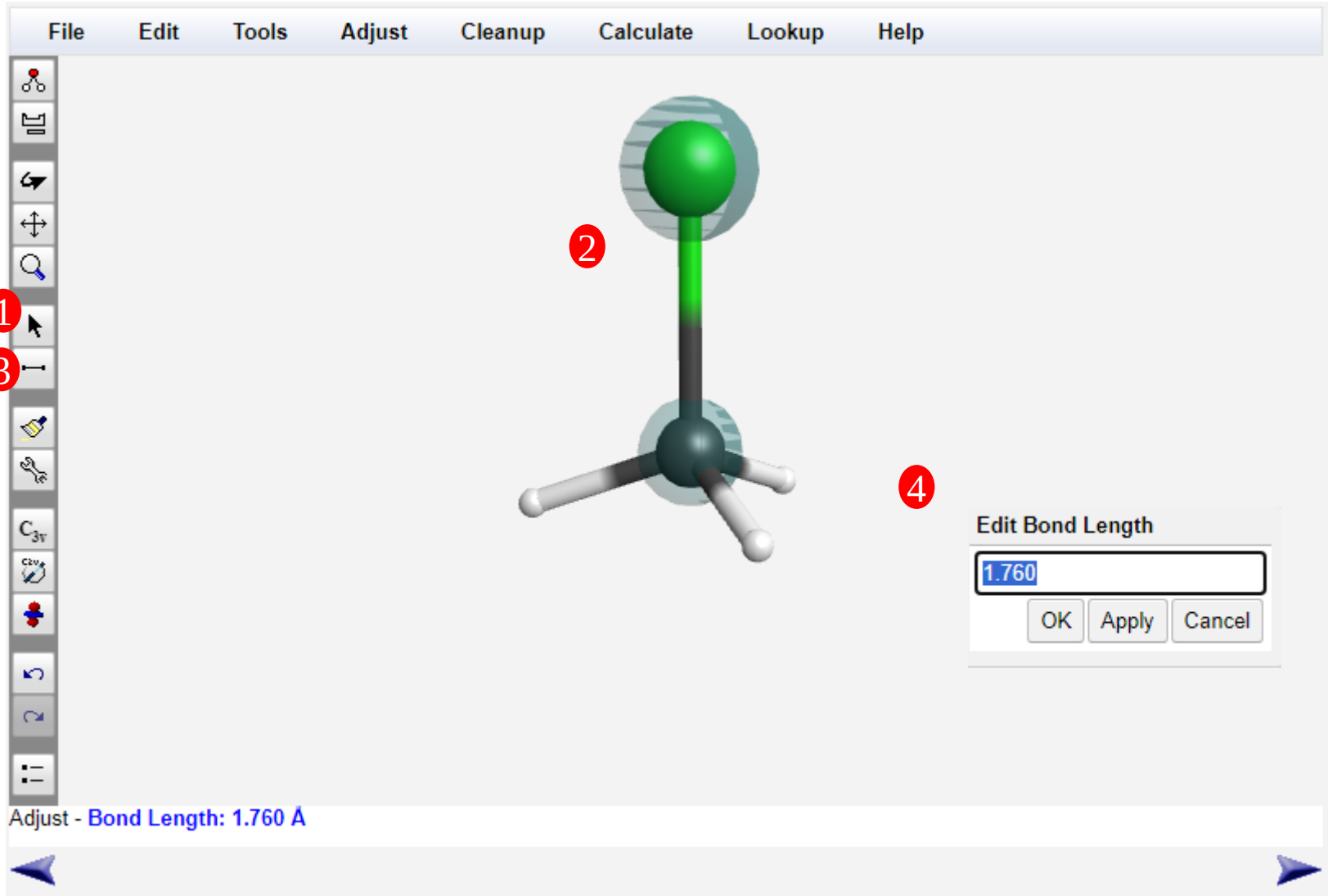
1. Press once in the window to insert the C atom, and drag the C atom in the C atom to insert the C atom to form a six-membered ring
2. Choosing Cleanup 
3. Swap one H for O
4. Choose Cleanup

Build Molecule-Line Editor

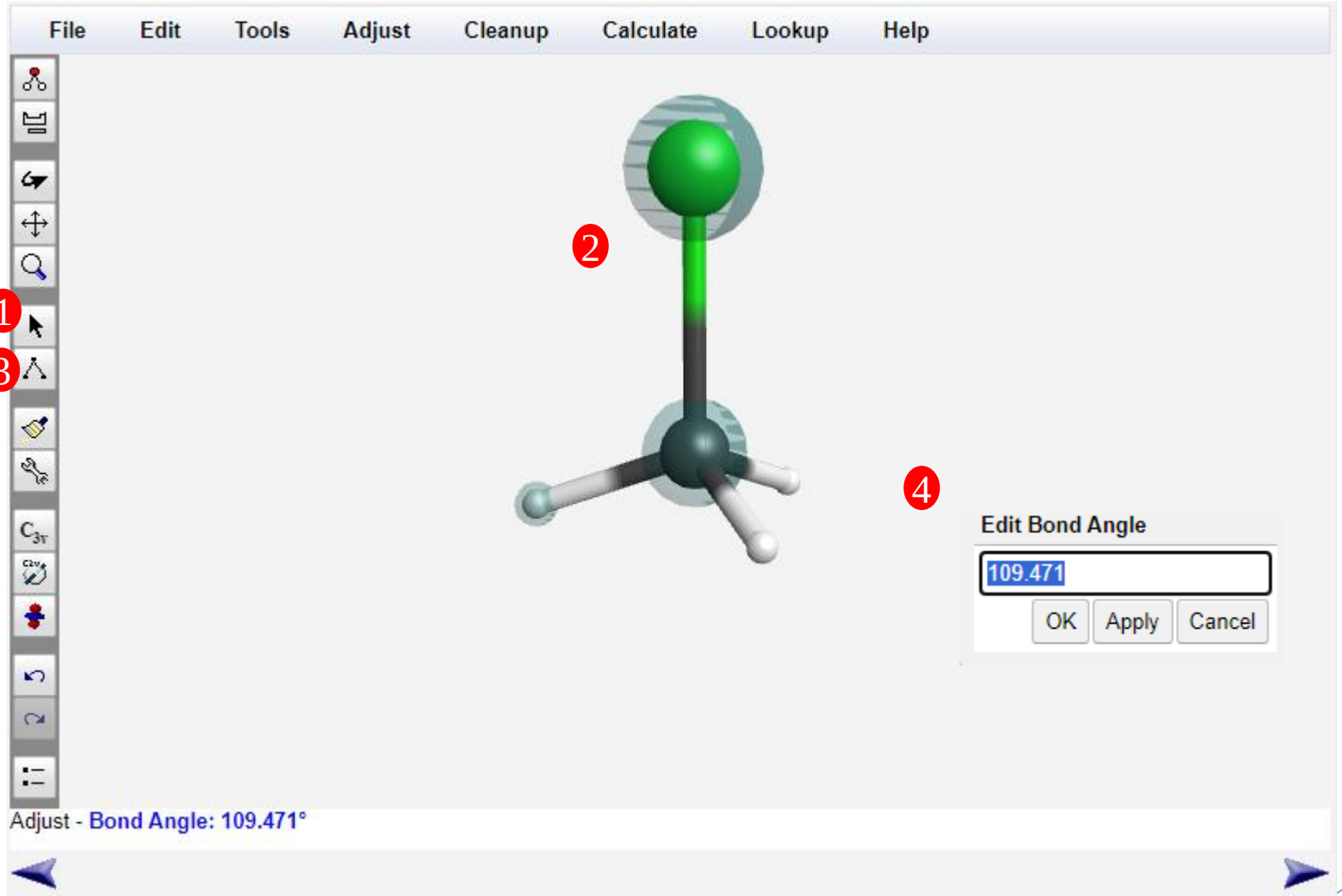
Create Pyrimidine using 2D Line Editor



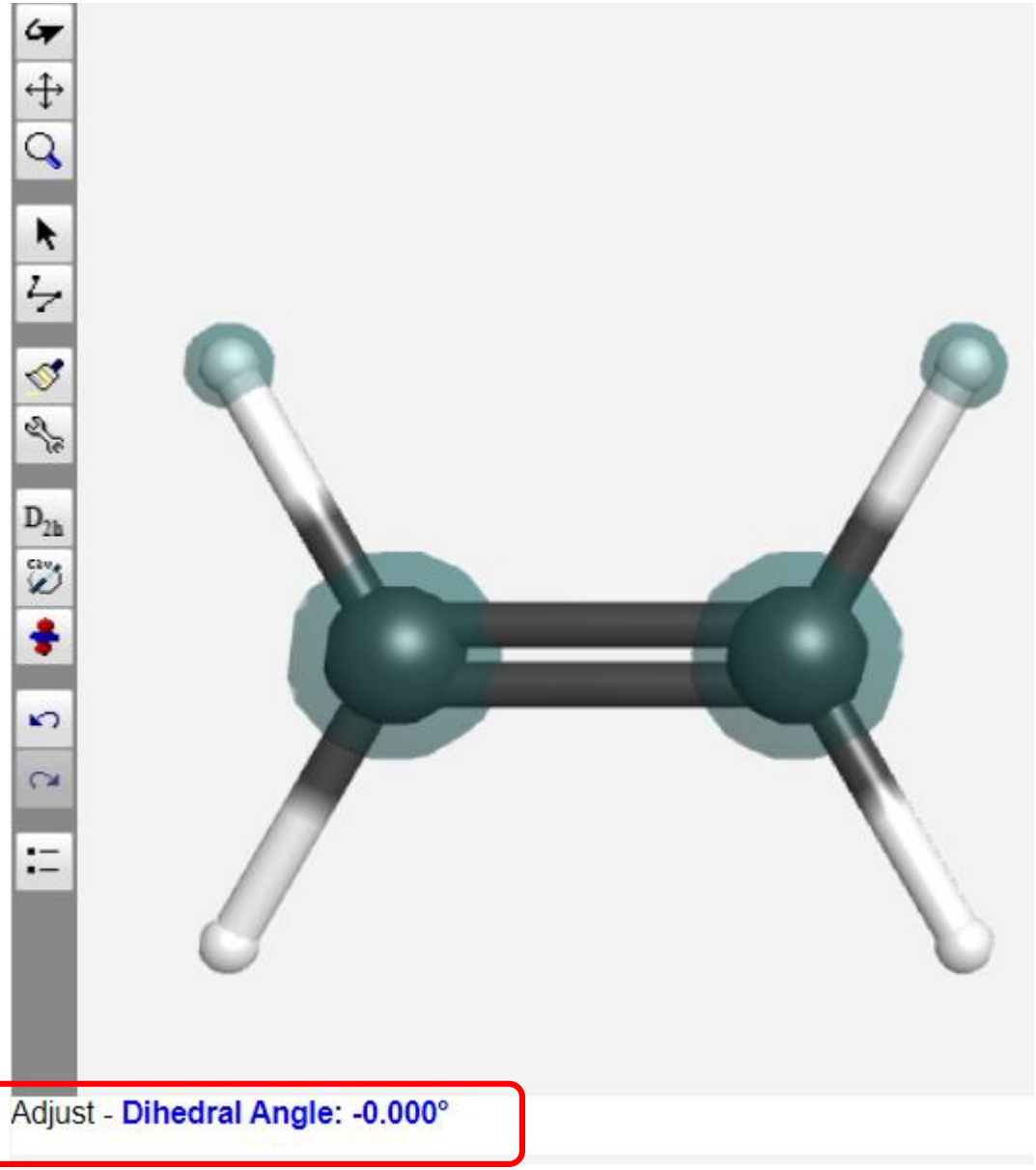
Edit Bond Length



Edit Bond Angle

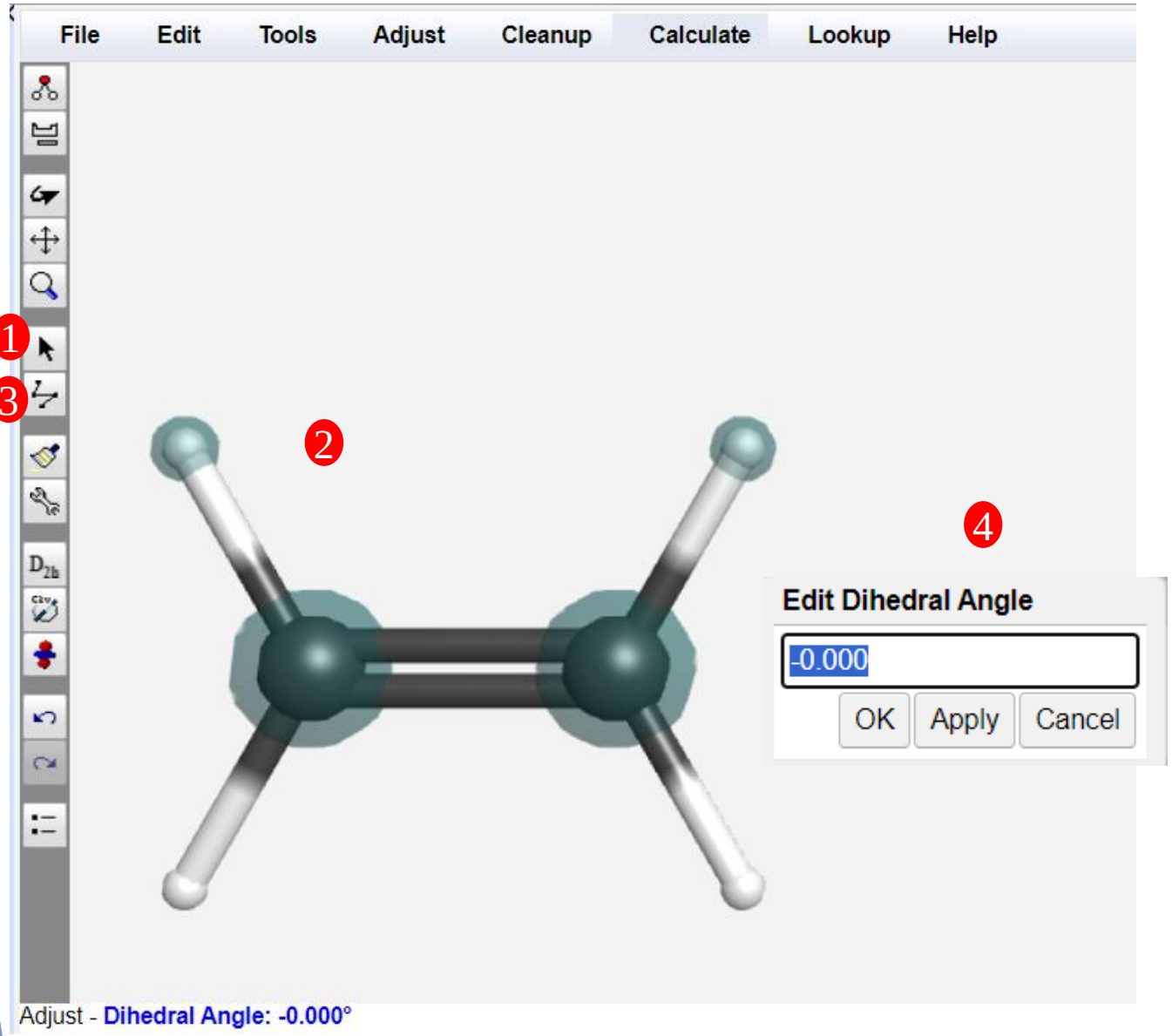


Measure Dihedral Angle

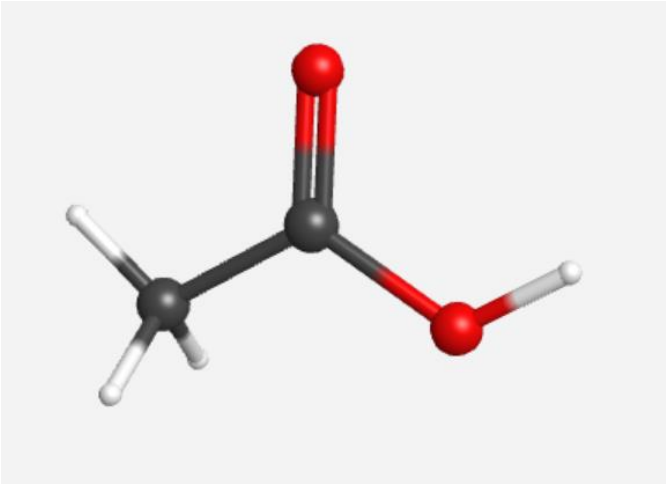


Click on the four atoms you want to measure the dihedral angle

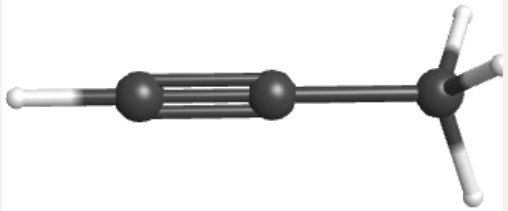
Edit Dihedral Angle



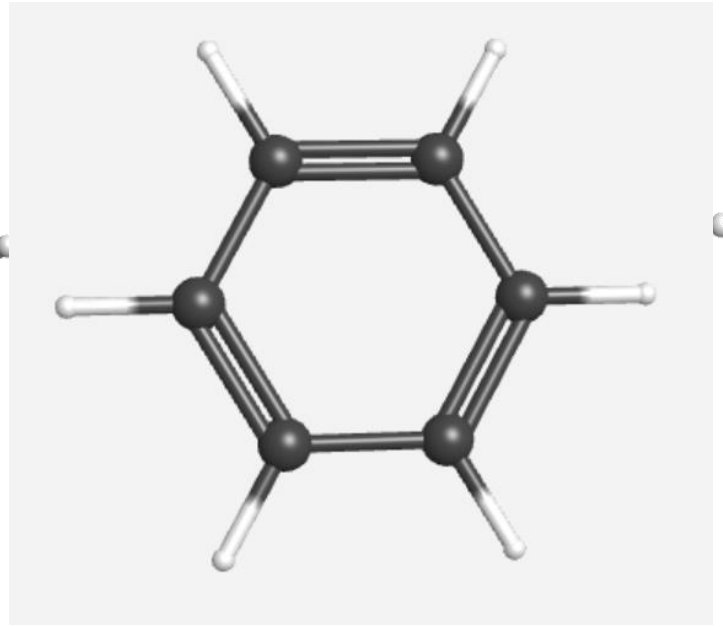
Exercise

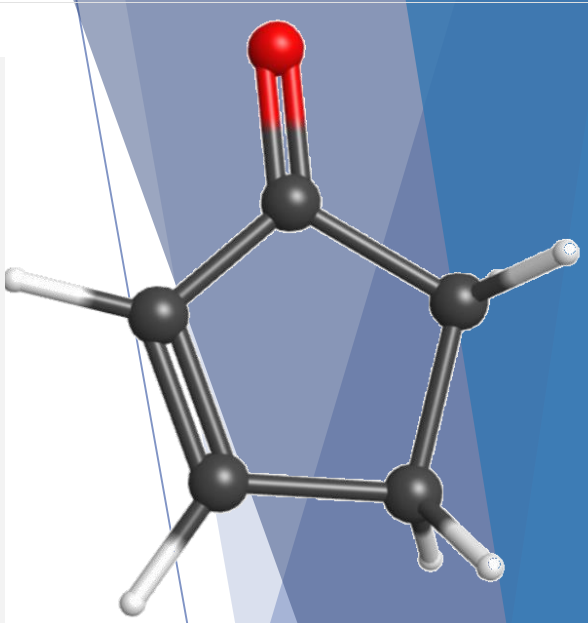


Acetic acid

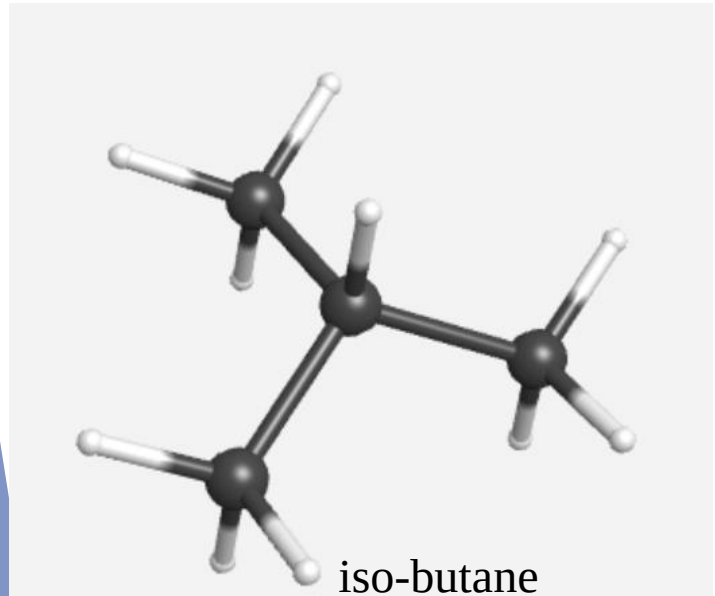


Propyne

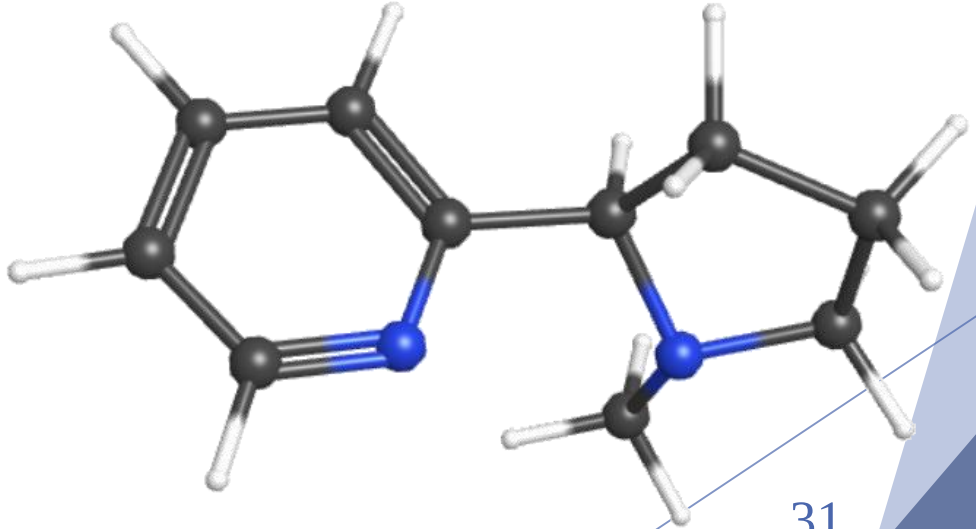




Cyclopentenone



iso-butane

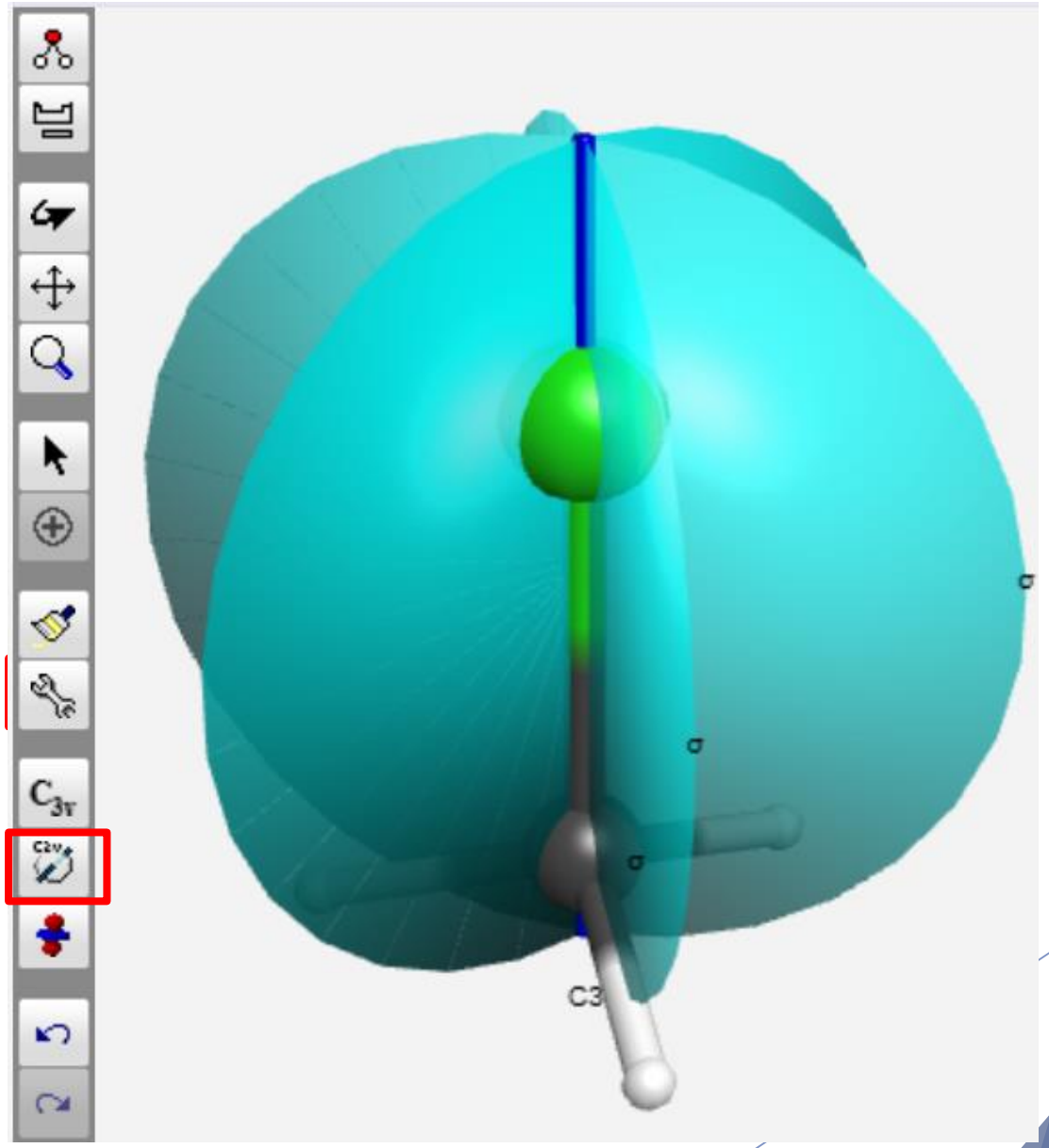


Nicotine

Point Group and Symmetry Elements

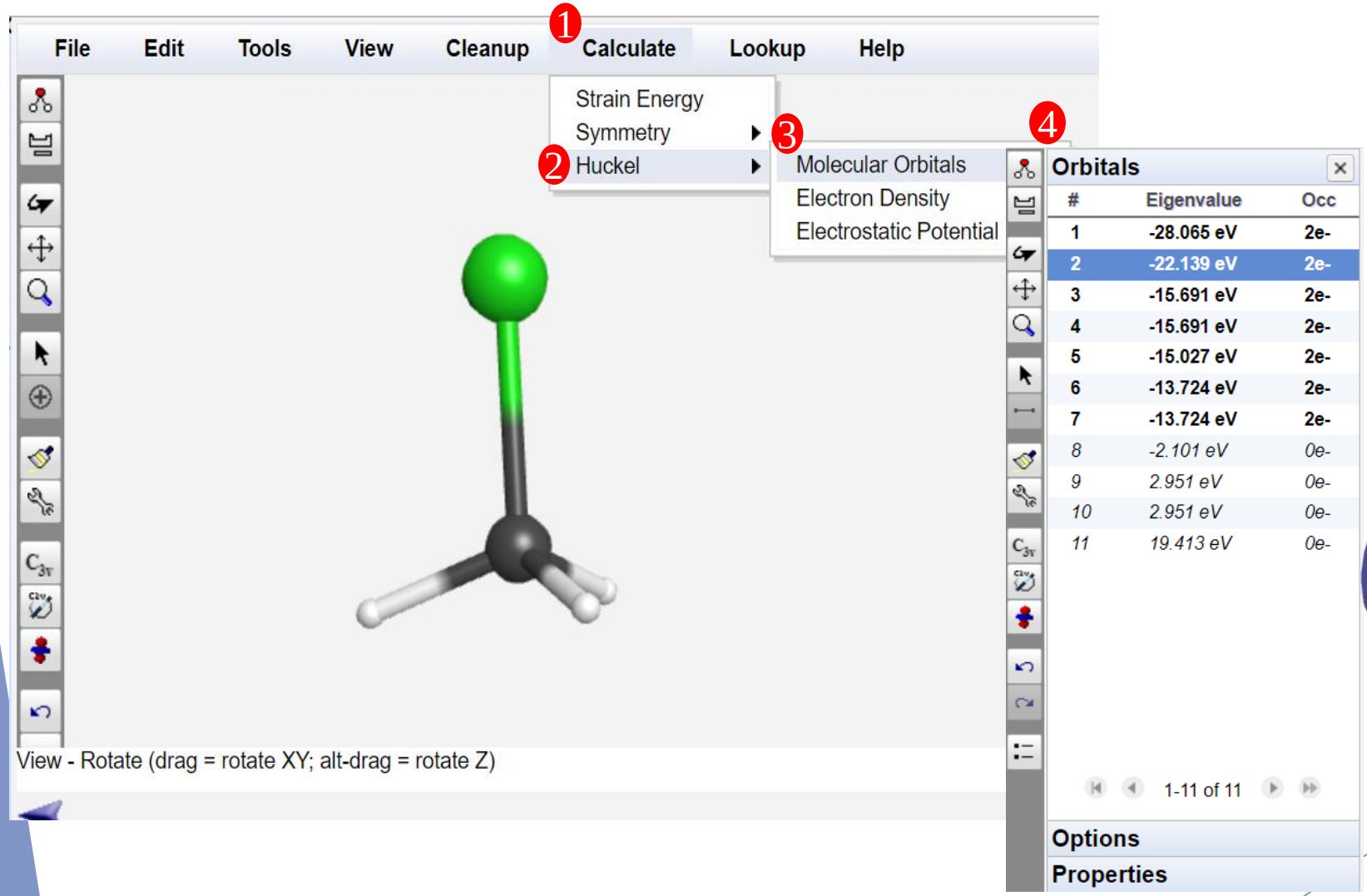
Molecular symmetry can be obtained on the side

Symmetry elements can be show by click the button 

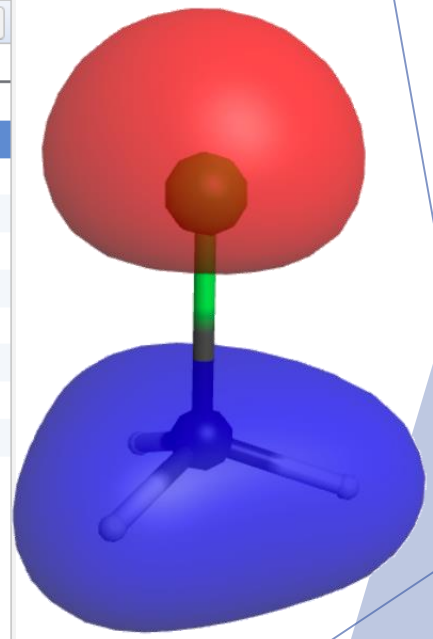


Hückel Orbital

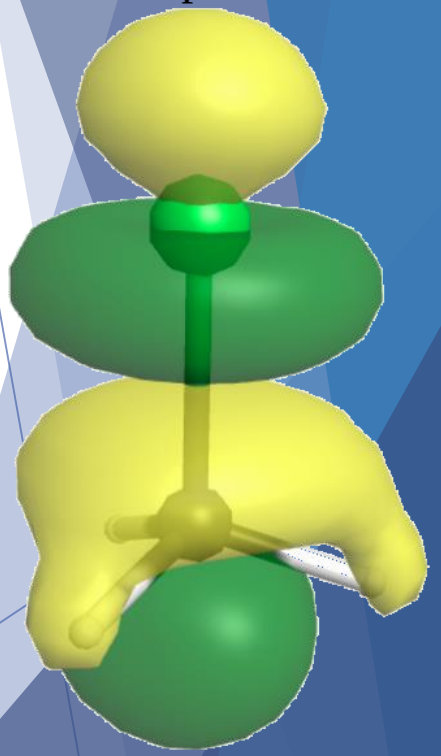
Select Calculate → Hückel → Molecular Orbitals in the left toolbar.
You can select the orbital of the molecule, which is Frontier Molecular Orbital



Occupied orbitals

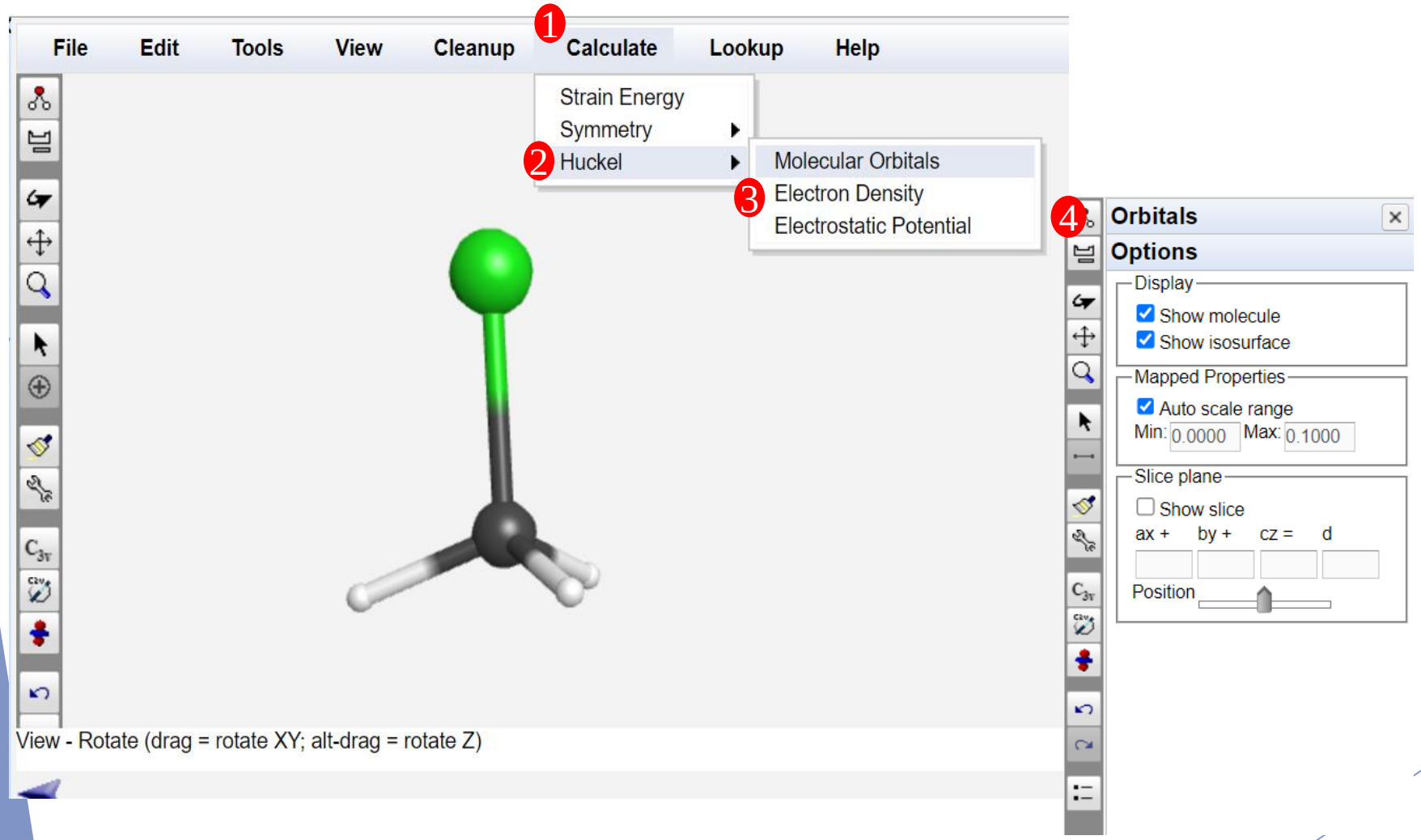


Unoccupied orbitals

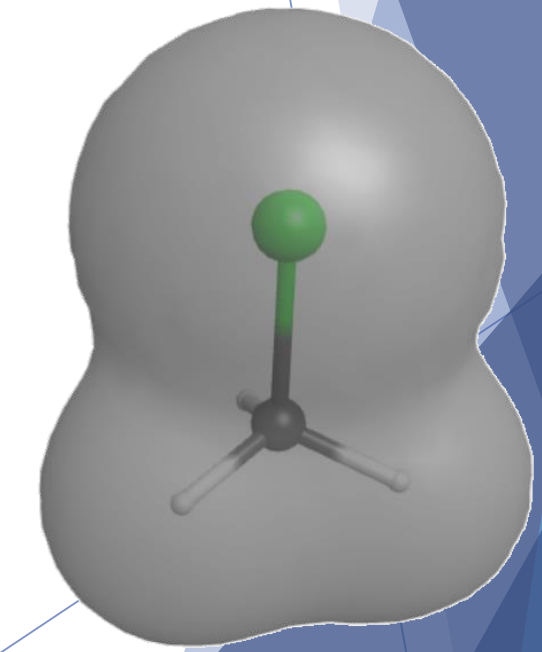


Hückel Calculation

Select Calculate → Hückel → Molecular Orbitals in the left toolbar.

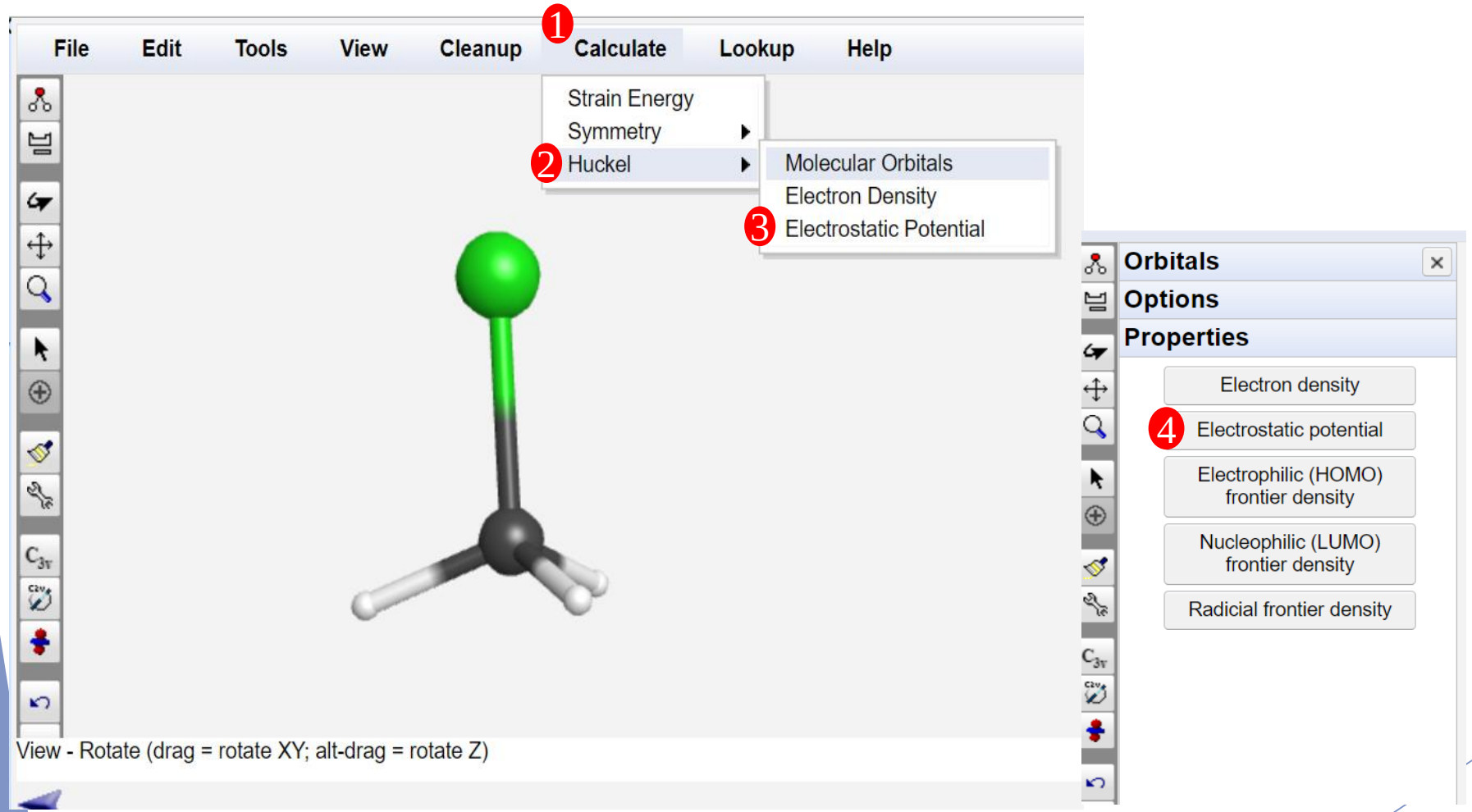


Electron density

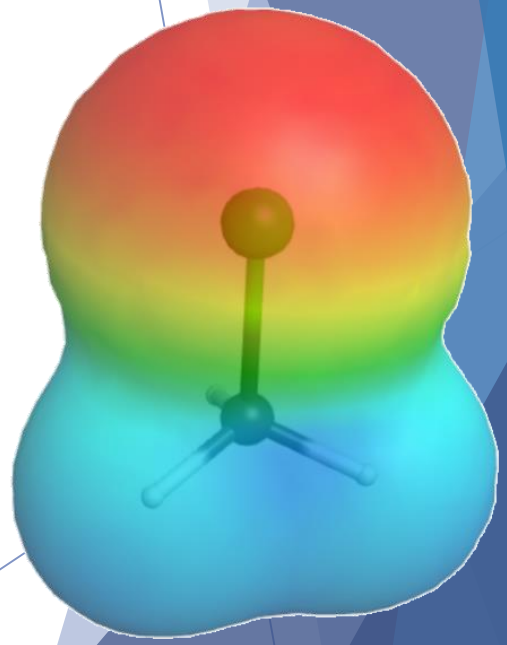


Hückel Calculation

Select Calculate → Hückel → Electrostatic Potential

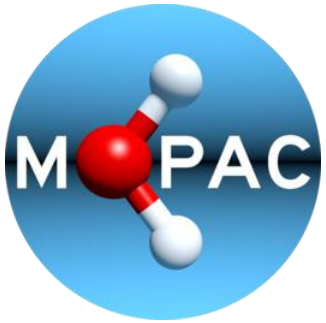


Electrostatic potential



Quantum chemical calculations

Advanced - Introduction to Computational Methods in Quantum Chemistry



Molecular Orbital PACkage (MOPAC)

1. MOPAC is a free software with a semi-empirical approach, which can be used directly in WebMO. Commonly used theoretical methods include: AM1, PM3, etc

2. The semi-empirical method, which is fast to calculate, can calculate structural optimization, vibration frequency analysis, and contains a wave function to generate atomic charge and electron density distributions. In order to obtain more accurate values than the experimental values, further quantum chemistry methods are needed in the textbooks of physical and chemical experiments.

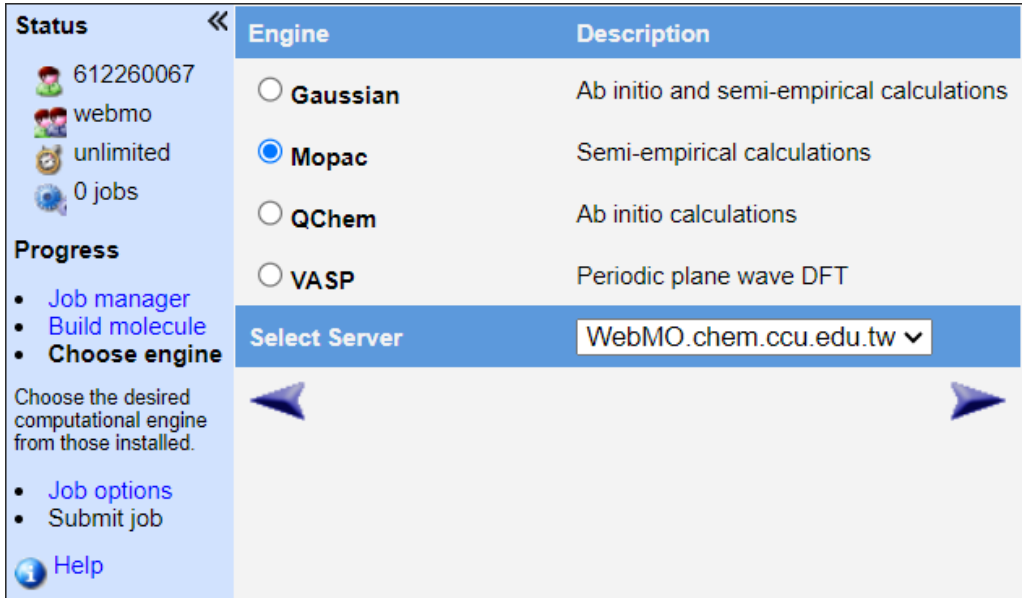
3. It does not take into account electron-related effects, cannot change the substrate function and theoretical methods, and has low accuracy

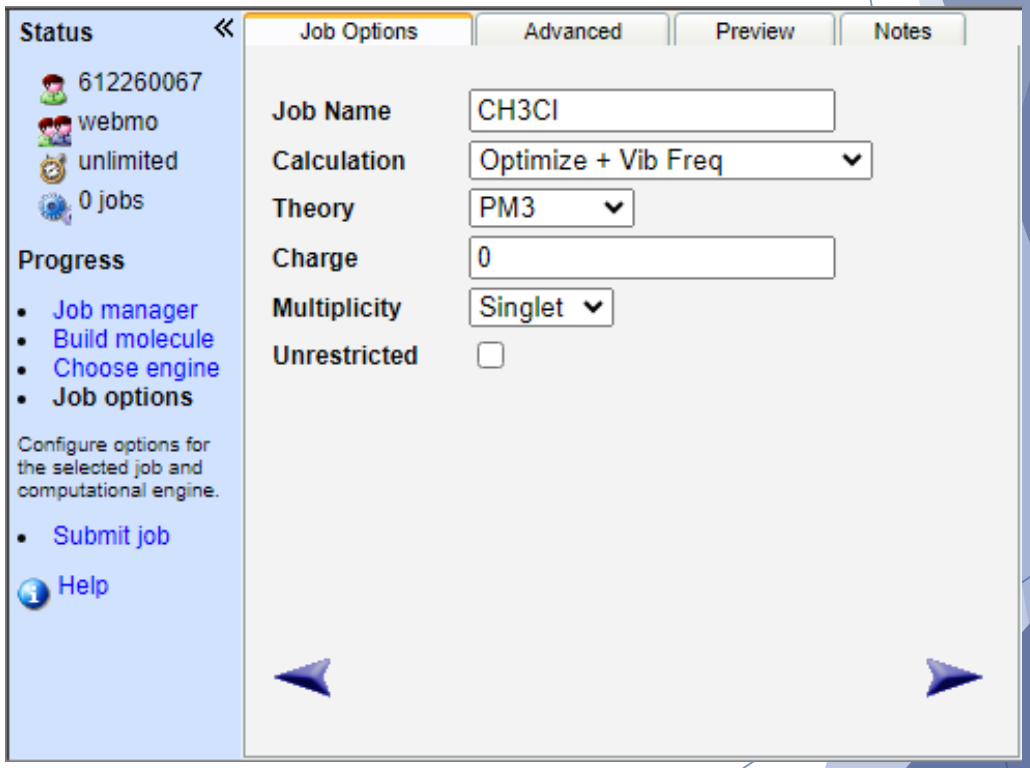
References:https://en.wikipedia.org/wiki/MOPAC

Quantum chemical calculations

The MMFF method used above does not consider the effects of electrons, and the methods of quantum chemistry are used to account for electron-related effects.

Mopac Engine Theory : PM3



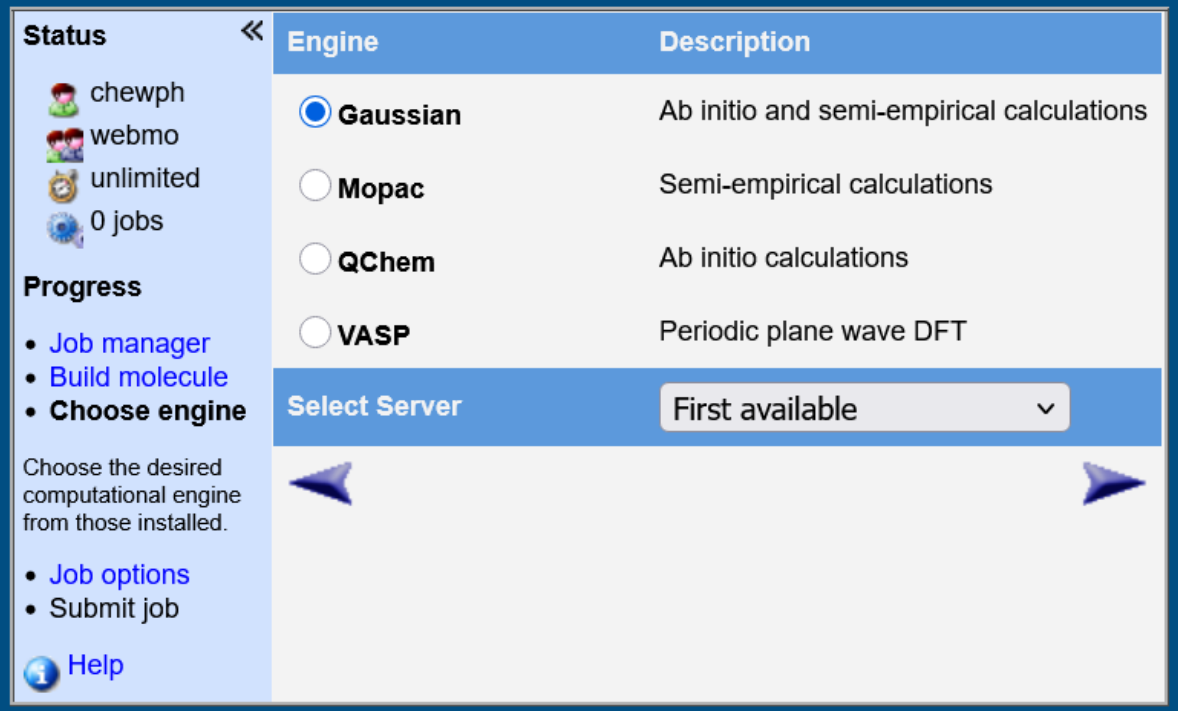


Single-point calculation of energy(SP)

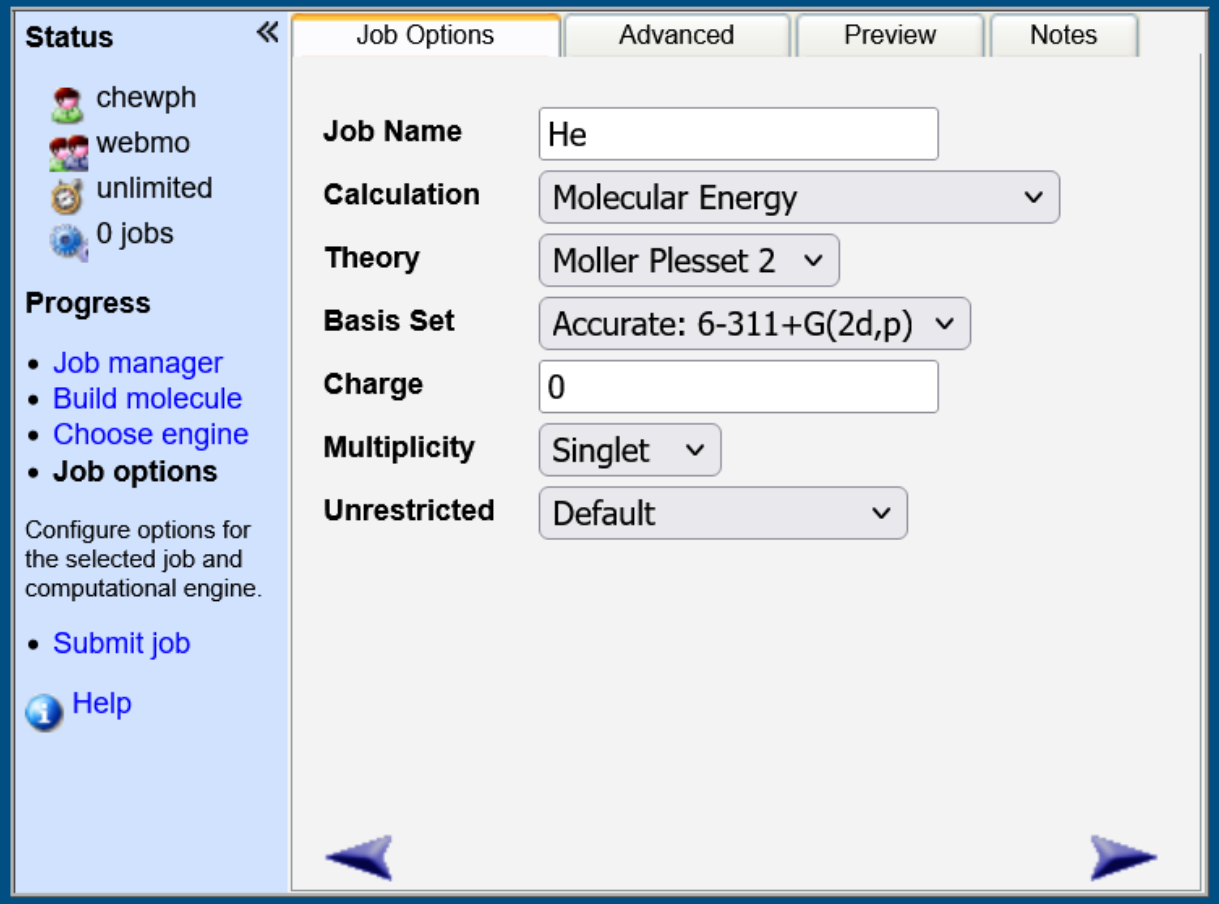
Gaussian Program

- Developed by John Pople's Group (Carnegie-Mellon University) in 1970s
- Using *Gaussian*-type atomic orbitals
- Originally deposited in Quantum Chemistry Program Exchange (Gaussian 80, QCPE) ，1987 Gaussian Inc.
- John Pople (1925-2004) and Walter Kohn won 1998 Nobel Prize in Chemistry
- Gaussian is the most powerful and widely used quantum chemical program，the newest version is Gaussian 16, Rev. C01

Choose Computational Engine



Configure Gaussian Job Options



Single-point calculation of energy (SP)

Use Gaussian Engine
Theory : MP2

- Calculate the electron affinity of fluorine atom
  $F + e^- \rightarrow F^-$ (expt: 78.4 kcal/mol)

- Calculate the first ionization energy of helium atom
  $He \rightarrow He^+ + e^-$ (expt: 567.0 kcal/mol)

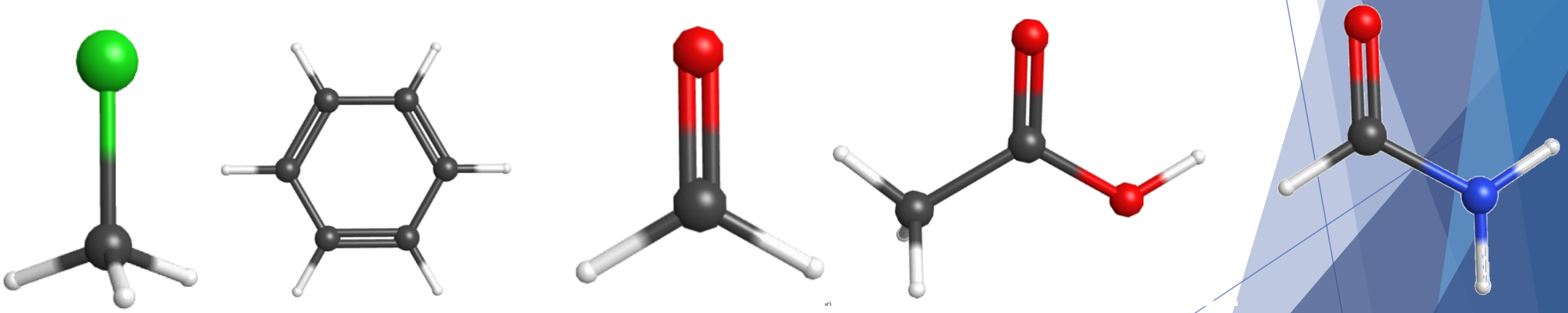
Structural Optimization Calculations (OPT)

Structural Optimization Calculations (OPT)

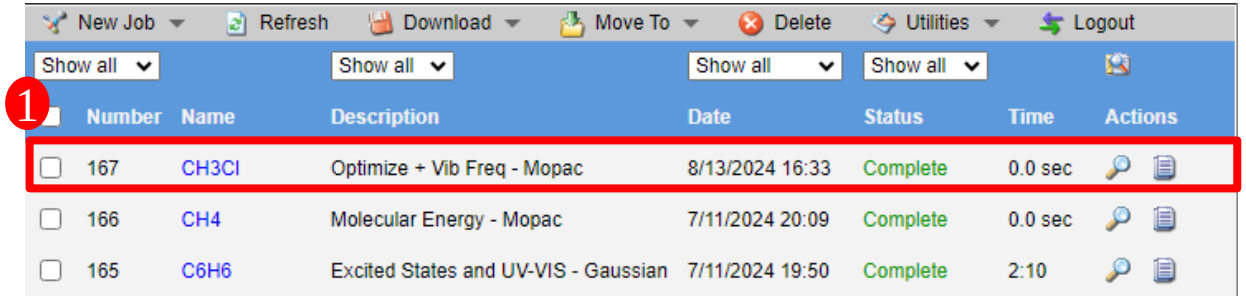
Use Mopac Engine

- Calculate the bond lengths (Theory : PM3)

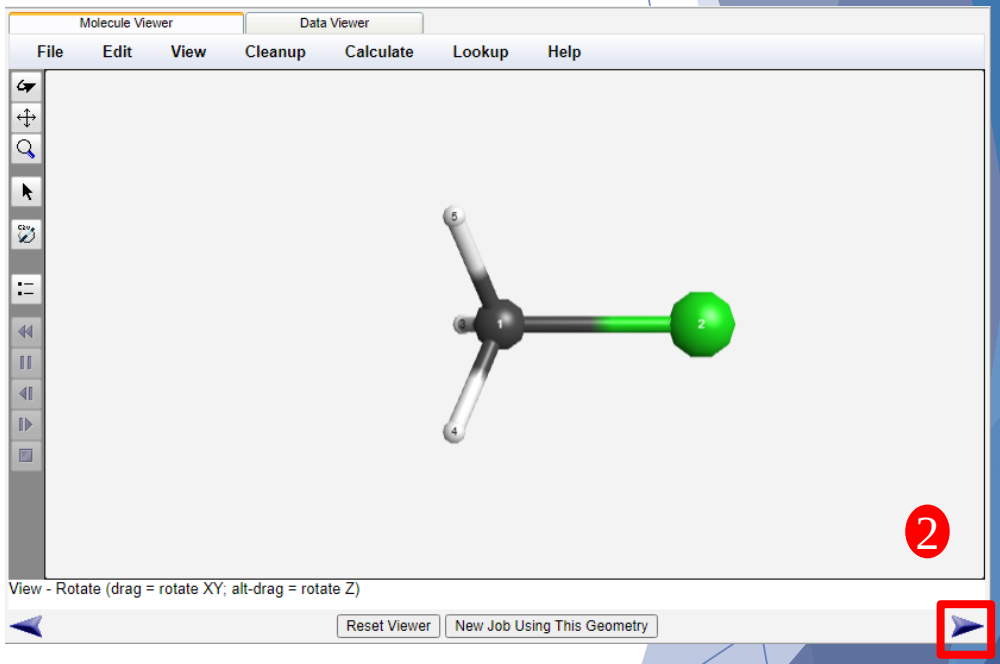
CH_3Cl、C_6H_6 、HCHO、CH_3COOH、CH_3ON



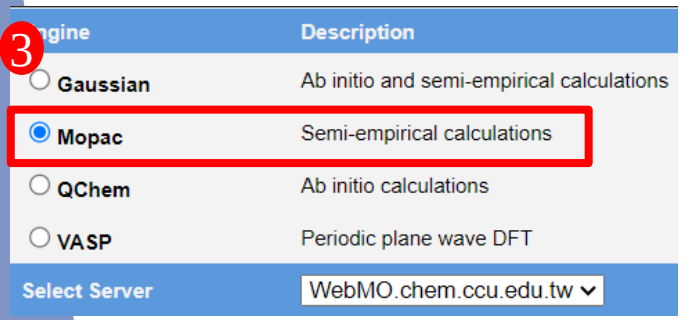
振動頻率計算 (FREQ)

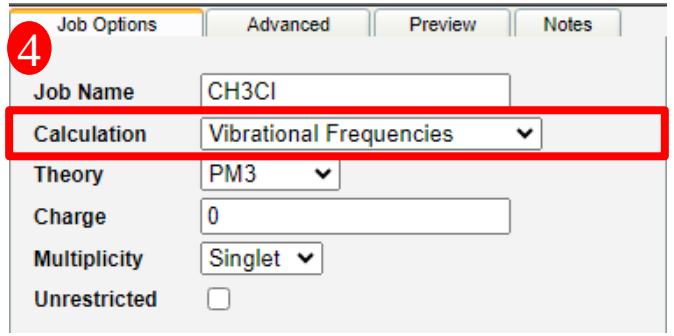


Find the calculated optimal structure and click on it



Clicking on the arrow in the bottom right corner will take you to the editing page again





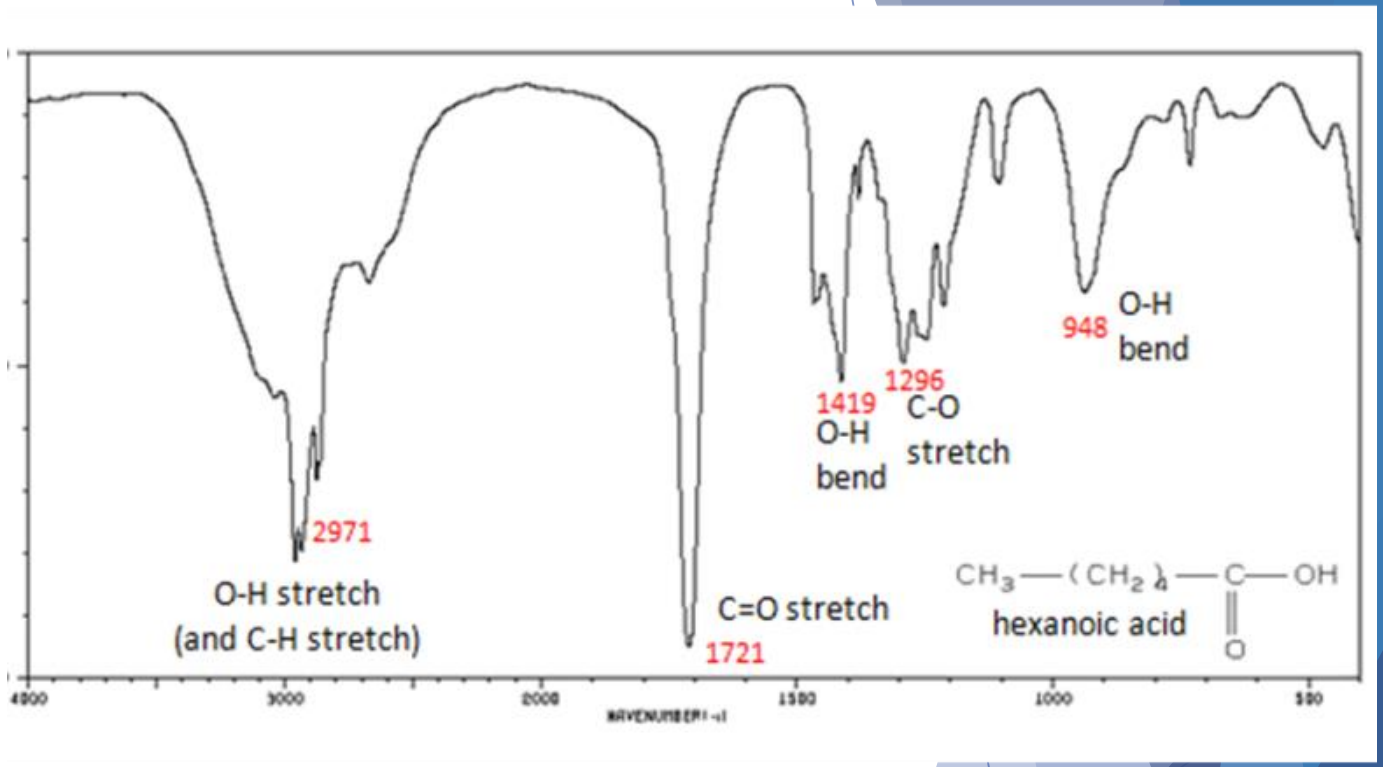
Select Mopac for Engine and Vibrational Frequencies for Calculation

IR Spectrum Simulation

IR Spectrum Calculation

Confirmed as the lowest point of energy
The optimized structure may not be the lowest point of energy

Simulate or predict IR spectra
It can be compared with experimental spectra to confirm unknowns
Understand the atomic motion corresponding to the vibrational spectrum



Note:
The same method must be used for structural optimization
It is very time-consuming, and it is better to use a theory that has an analytical quadratic differentiation

Calculated Quantities

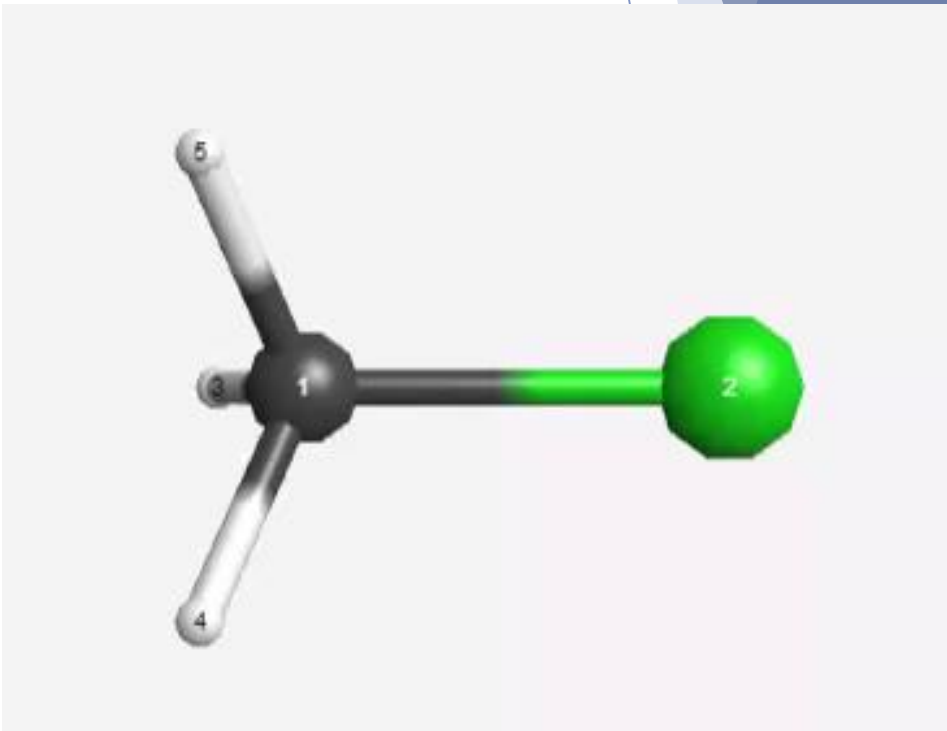
After the calculation is completed, a new output file will be generated on the main page, at this time, you can click 🔎 to find Vibrational Modes, and click on the right to be the vibrational mode at that frequency. 🎞

Vibrational Modes

Show all

Mode	Symmetry	Frequency (cm^{-1})	IR Intensity	Actions
1	-	676.64601	0.9770	🔎 🎞
2	-	1007.50927	0.0154	🔎 🎞
3	-	1007.77389	0.0155	🔎 🎞
4	-	1345.54450	0.4992	🔎 🎞
5	-	1384.04669	0.0757	🔎 🎞
6	-	1384.06214	0.0755	🔎 🎞
7	-	3123.13694	0.1081	🔎 🎞
8	-	3123.68714	0.1082	🔎 🎞
9	-	3194.22843	0.0585	🔎 🎞

Frequency Scale Factor	1
Normal Mode Amplitude	1.0
Animation Speed	50
IR Spectrum	🔎
Peak Width (cm^{-1})	40

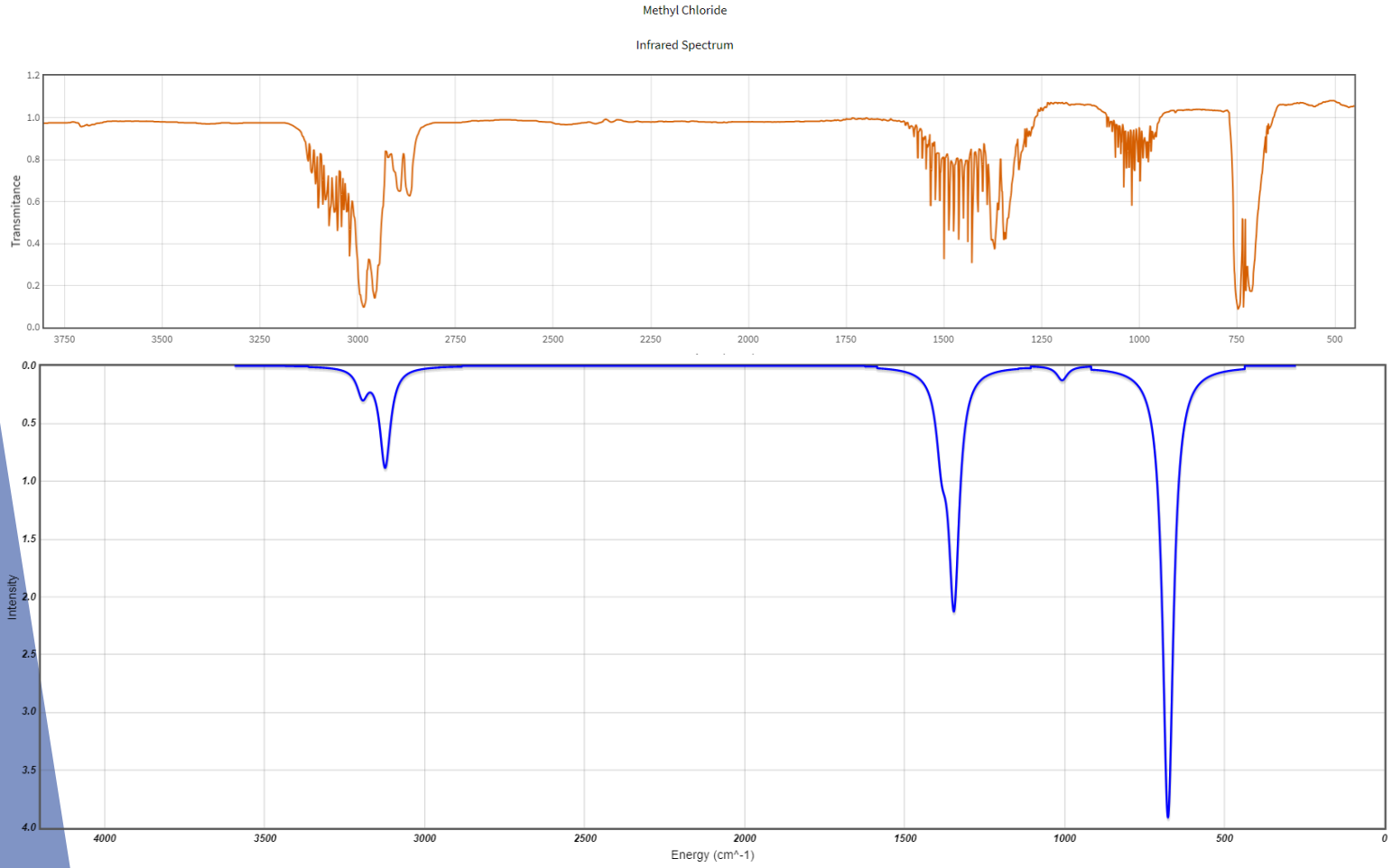


You can view the IR spectrum

Exercise

The IR spectra of CH3Cl were simulated and compared with experiments

Theory:PM3

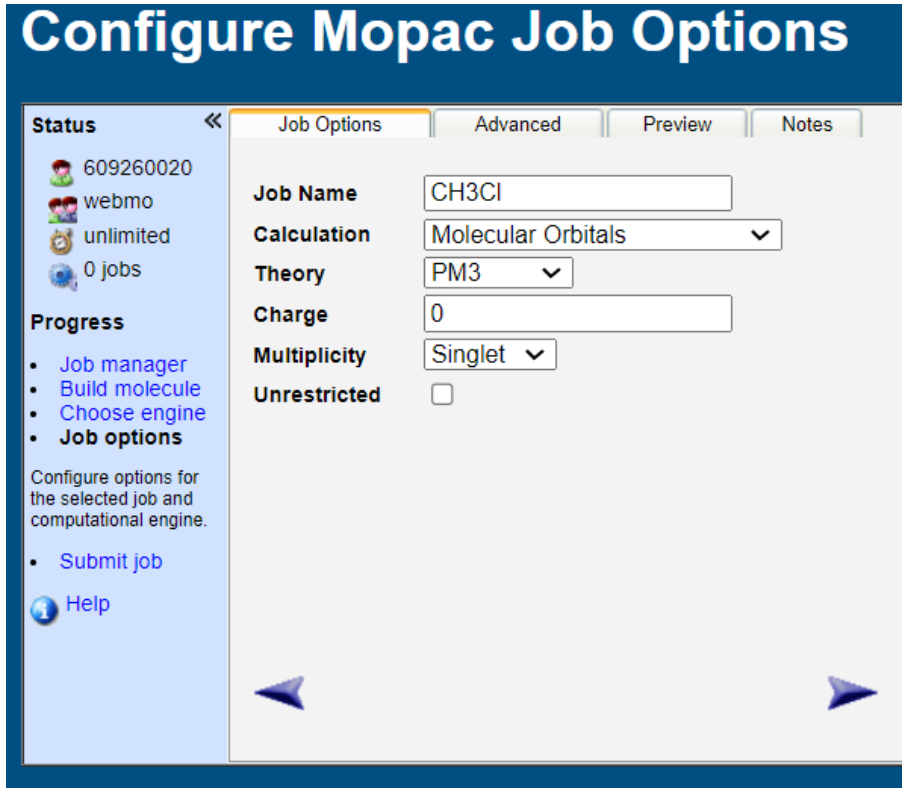


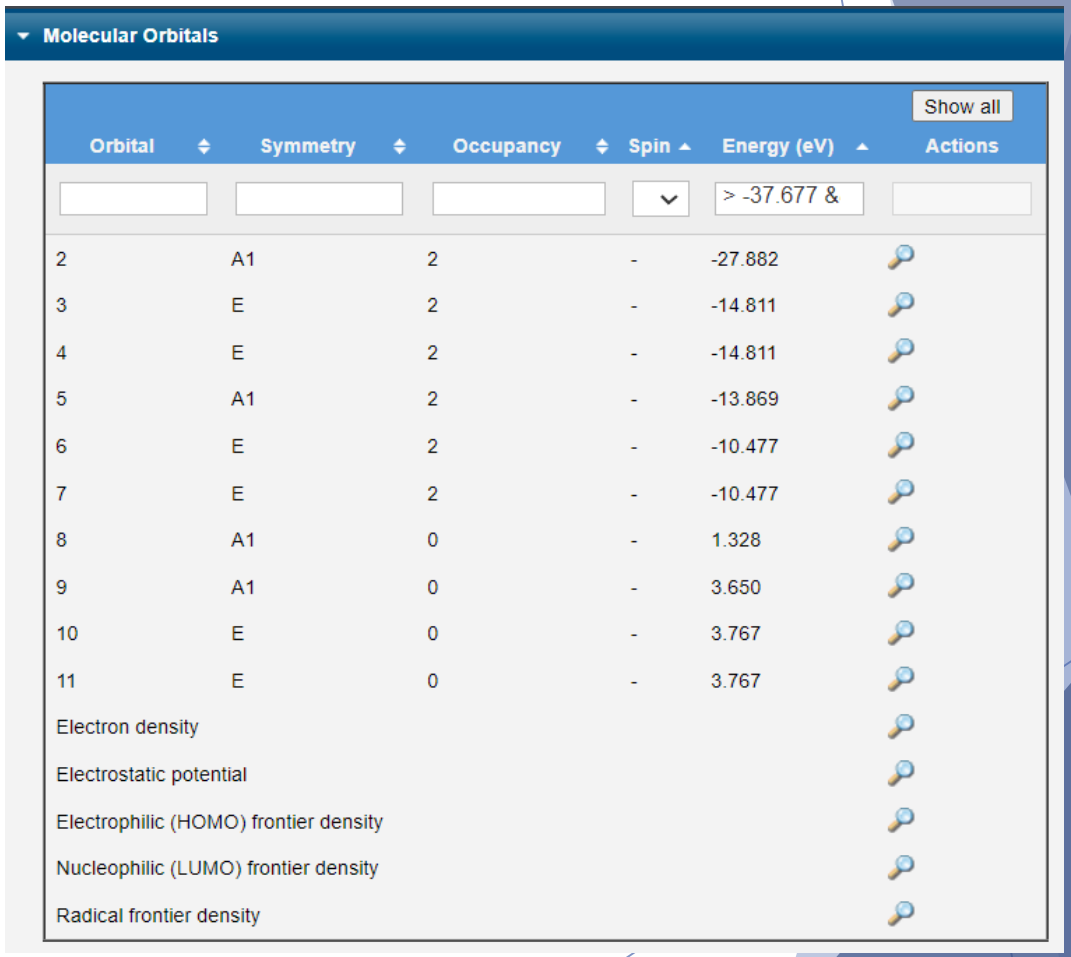
There are 3*5 – 6= 9 vibration frequencies,

They are:676, 1007, 1007, 1345, 1384, 1384, 3123, 3123, 3194 cm^{-1}

Molecular Orbital

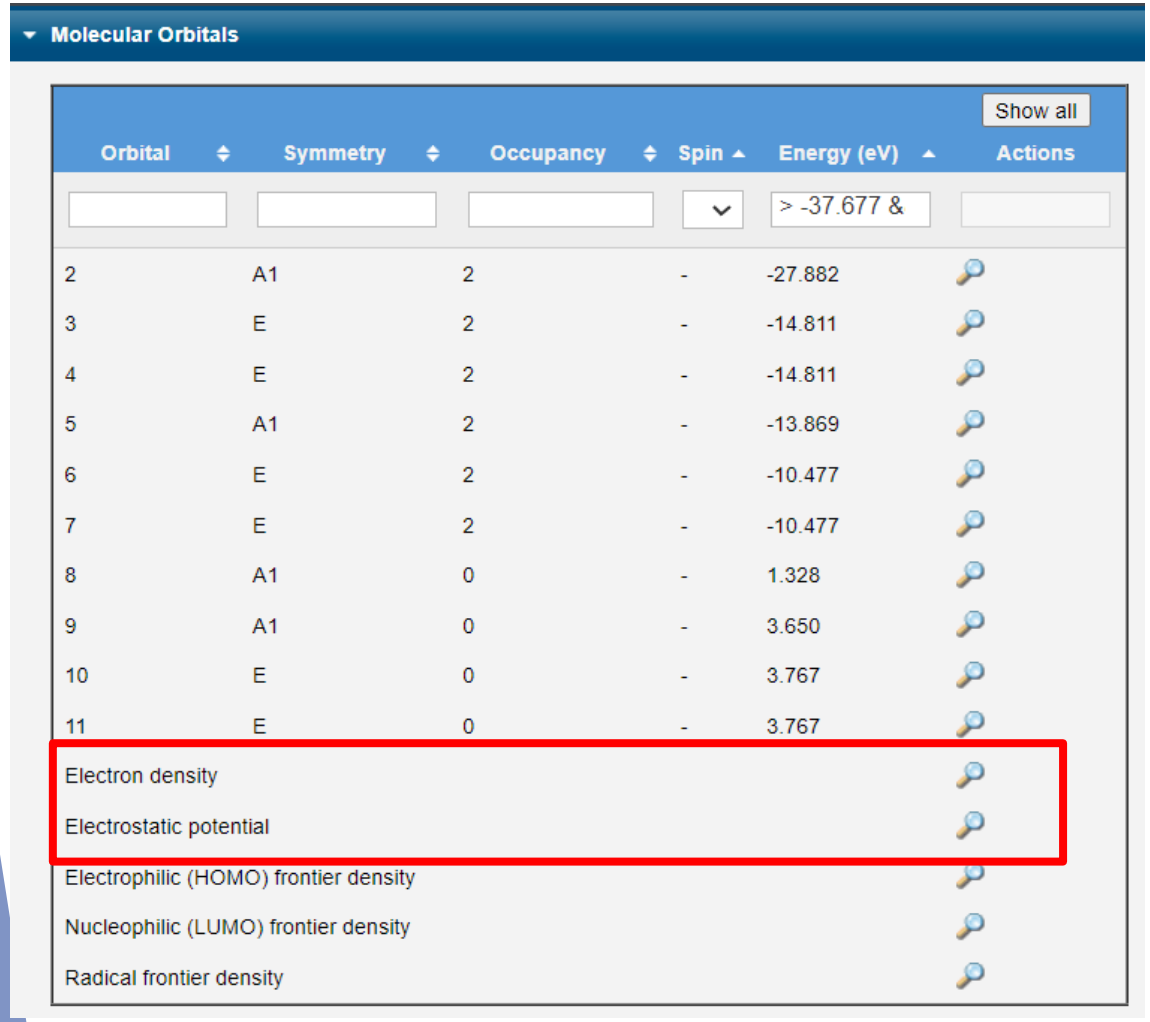
Select the structure to be calculated → Molecular Orbitals using PM3

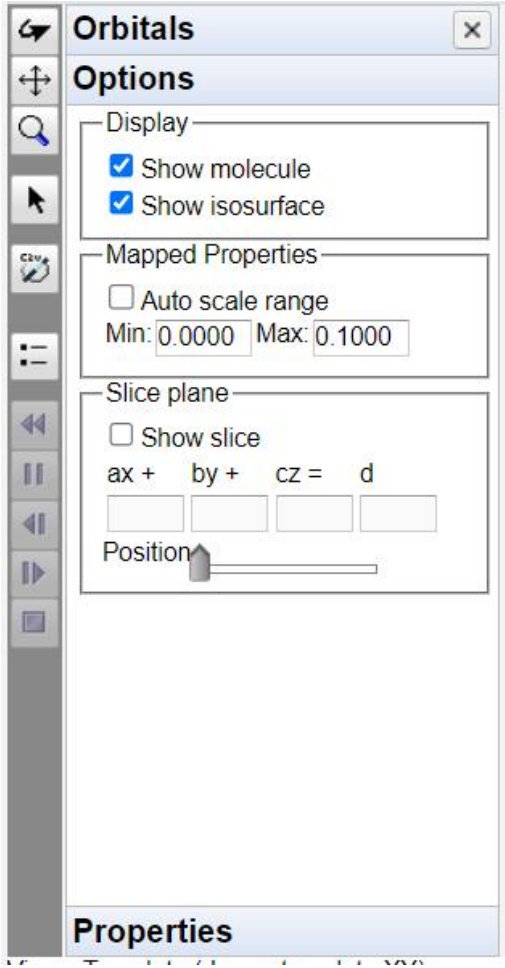


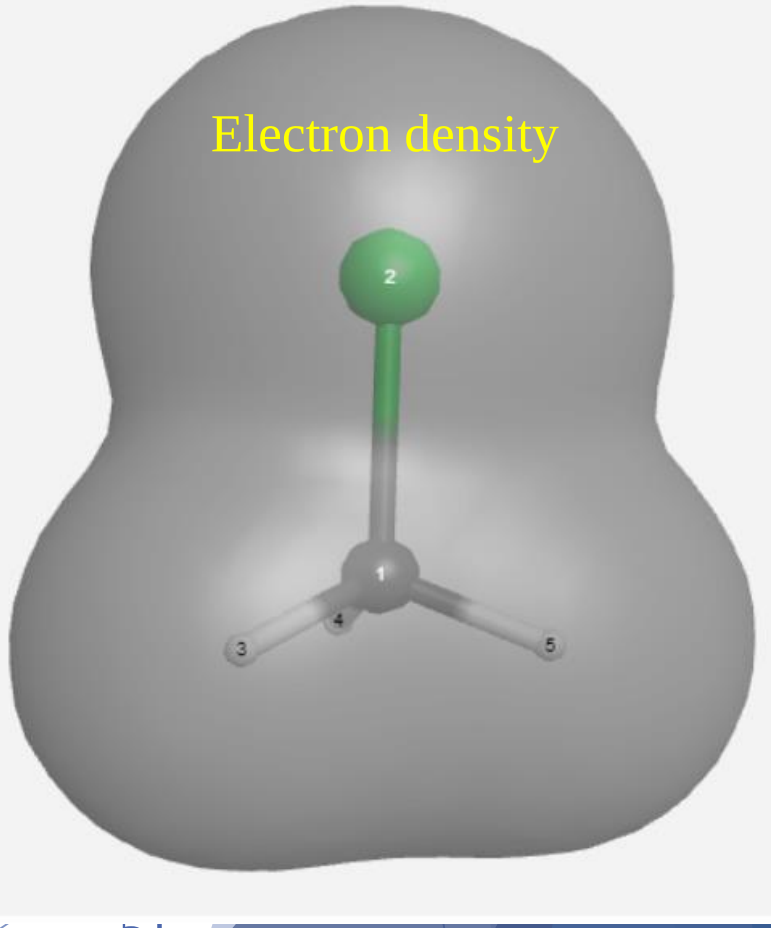


Molecular Orbital

Once the calculation is complete, a new output file will be generated, at which point you can click 🔎 to find Molecular Orbital

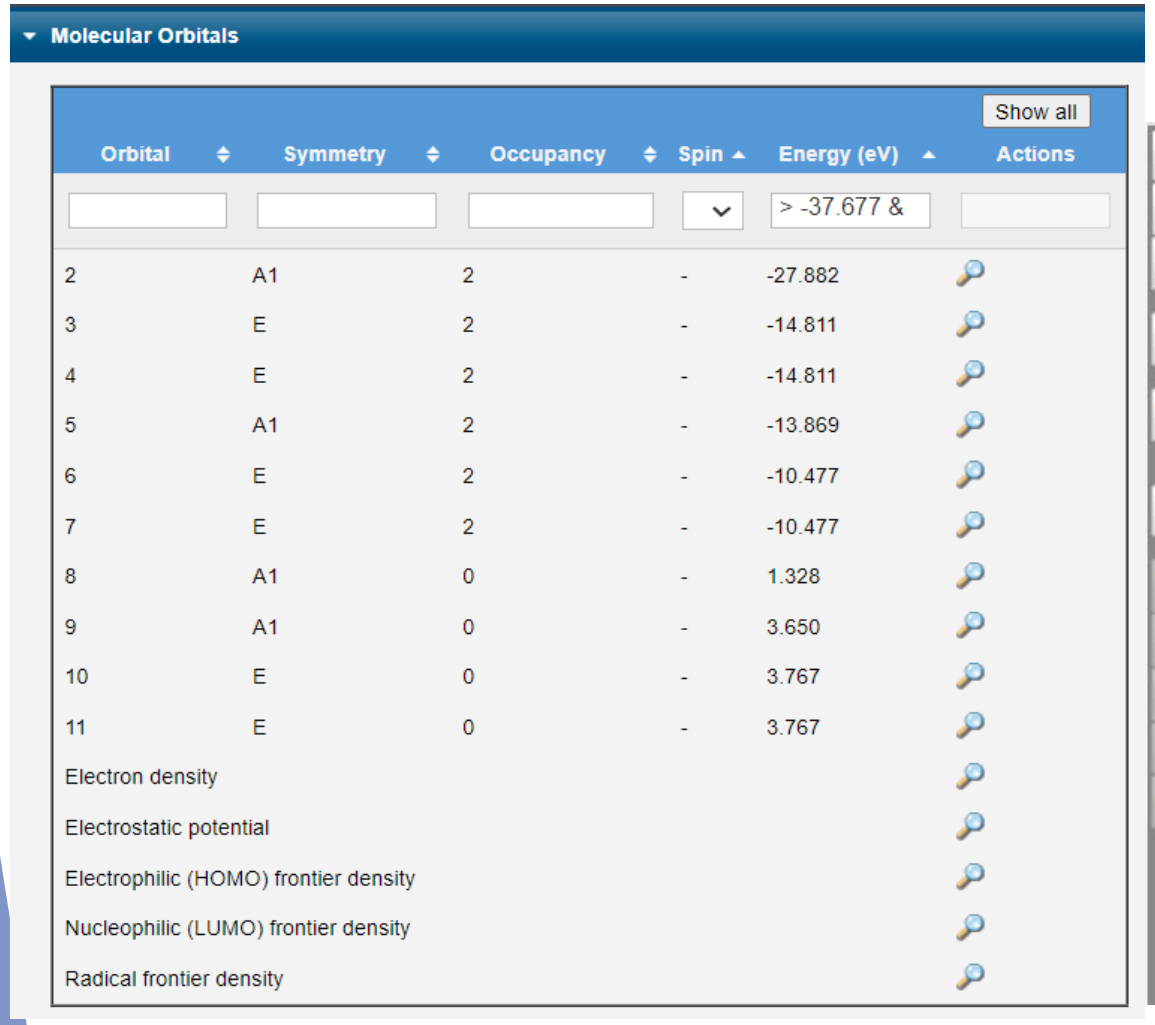


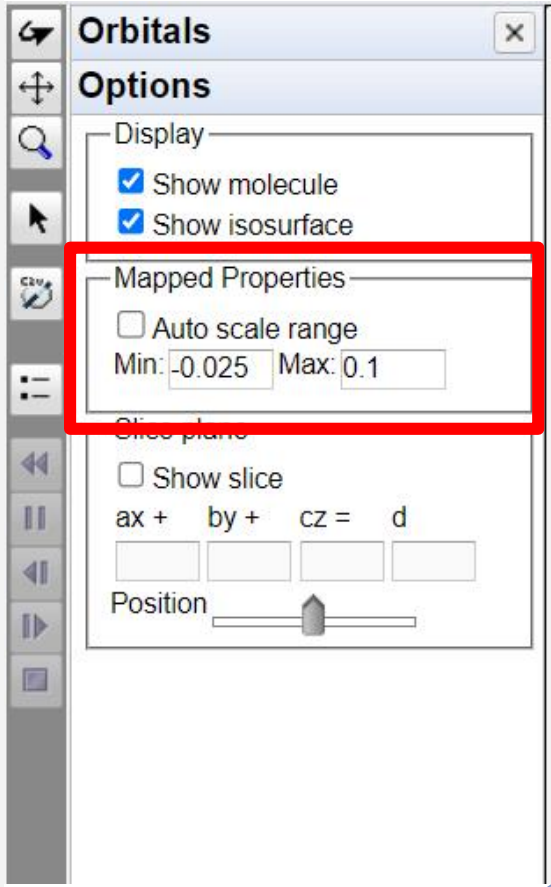


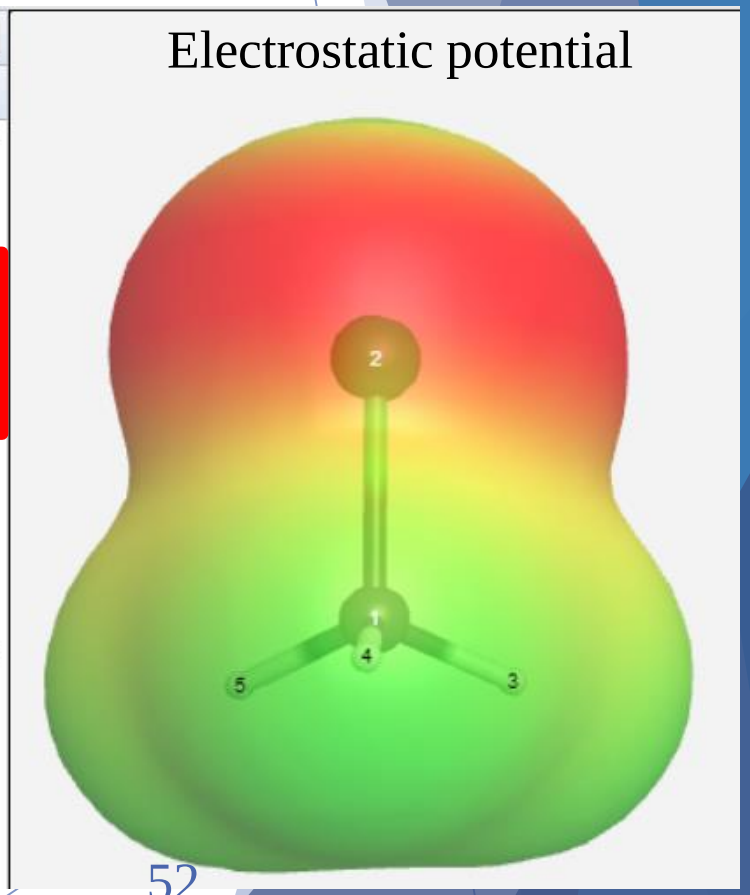


Molecular Orbital

Once the calculation is complete, a new output file will be generated, at which point you can click 🔎 to find Molecular Orbital

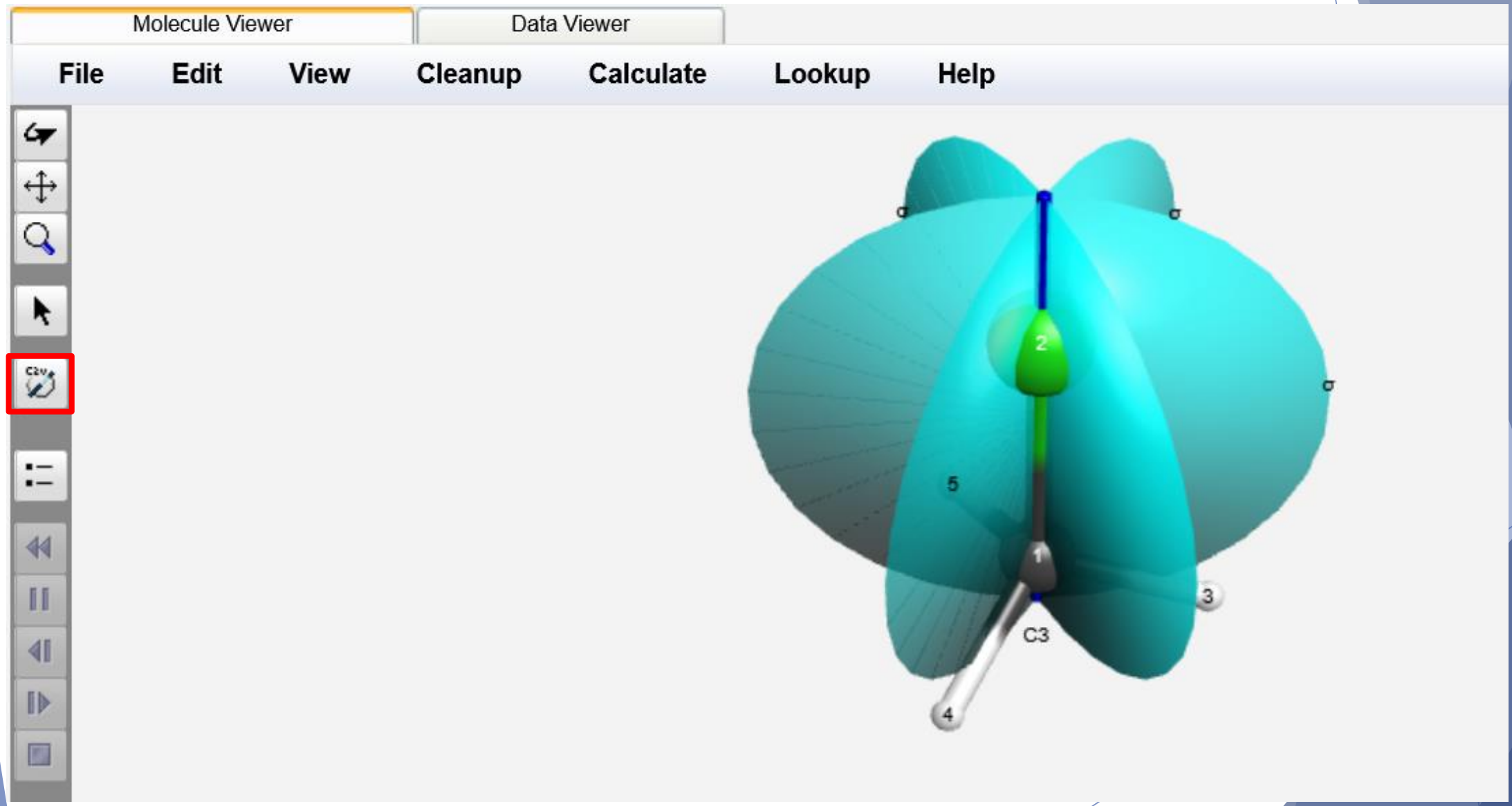






Auto scale range. Don't choose the color is only available after adjusting the range

View the Symmetry Elements



Calculated Quantities

Scroll down to find it

- Overview
- Partial Charges
- Bond Order

Calculated Quantities

Collapse all

Quantity	Value
Job History	170
Route	PM3 BONDS CHARGE=0 SINGLET PRECISE GNORM=0.0
Method	
Symmetry	C3V
PM3 Heat of Formation	-14.68088 kcal/mol
Dipole Moment	1.377 Debye
Server	WebMO.chem.ccu.edu.tw (0)
CPU time	0.003 sec

Partial Charges

Atom	Symbol	Charge
1	C	-0.0856
2	H	0.0498
3	H	0.0498
4	H	0.0498
5	Cl	-0.0638

Bond Order

Atom	Symbol	1 C	2 H	3 H	4 H	5 Cl
1	C	4.214255				
2	H	0.988231	0.902879			
3	H	0.988232	0.001003	0.902881		
4	H	0.988231	0.001003	0.001003	0.902881	
5	Cl	0.992272	0.007283	0.007283	0.007284	13.113455

Overview

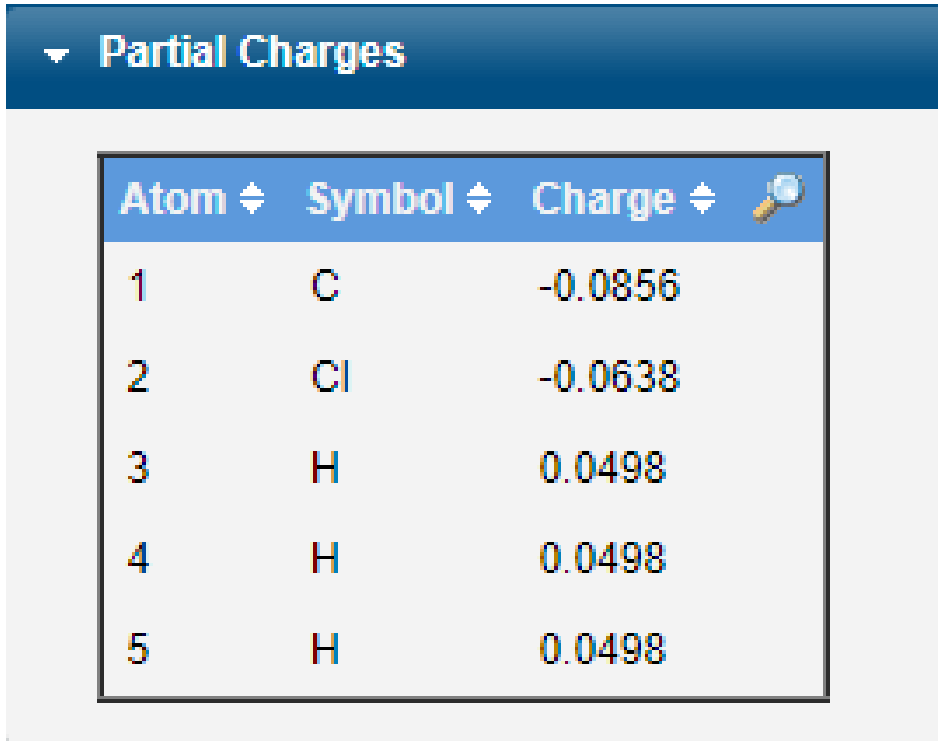
Describe the parameters of the calculation input, including the method used, the number of charges, the multiple states, as well as the symmetry of the molecule, the heat of generation, and the dipole moment

Overview

Quantity	Value
Route	PM3 BONDS CHARGE=0 SINGLET PRECISE GNORM=0.0
Method	
Symmetry	C3V
PM3 Heat of Formation	-14.68089 kcal/mol
Dipole Moment	1.377 Debye
Server	WebMO.chem.ccu.edu.tw (0)
CPU time	0.003 sec

Partial Charges

It can know the charge of each atom in the molecule, and understand the ability of atoms in the molecule to pull electrons or donate electrons



Bond Order

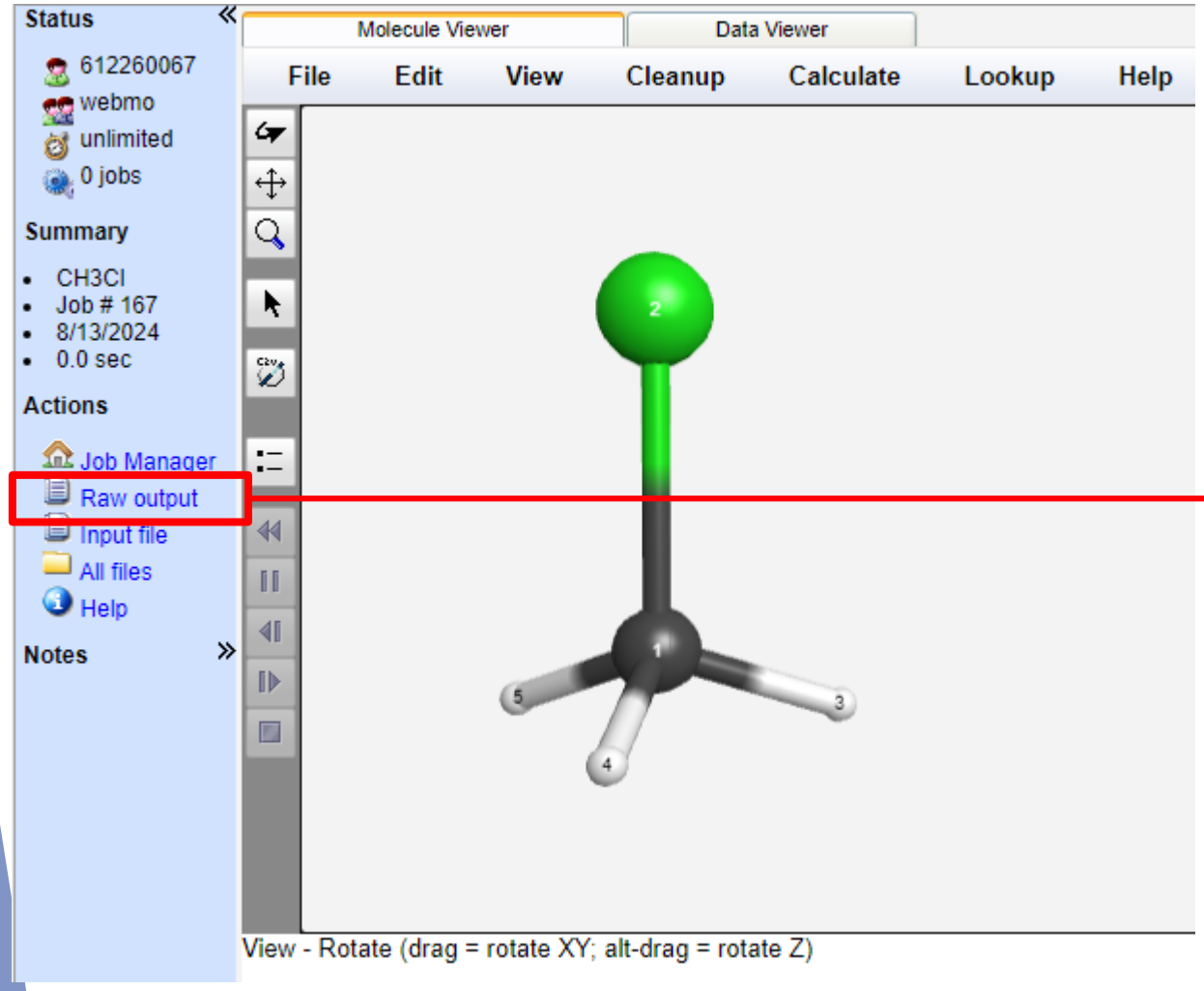
The bonding of the individual atoms

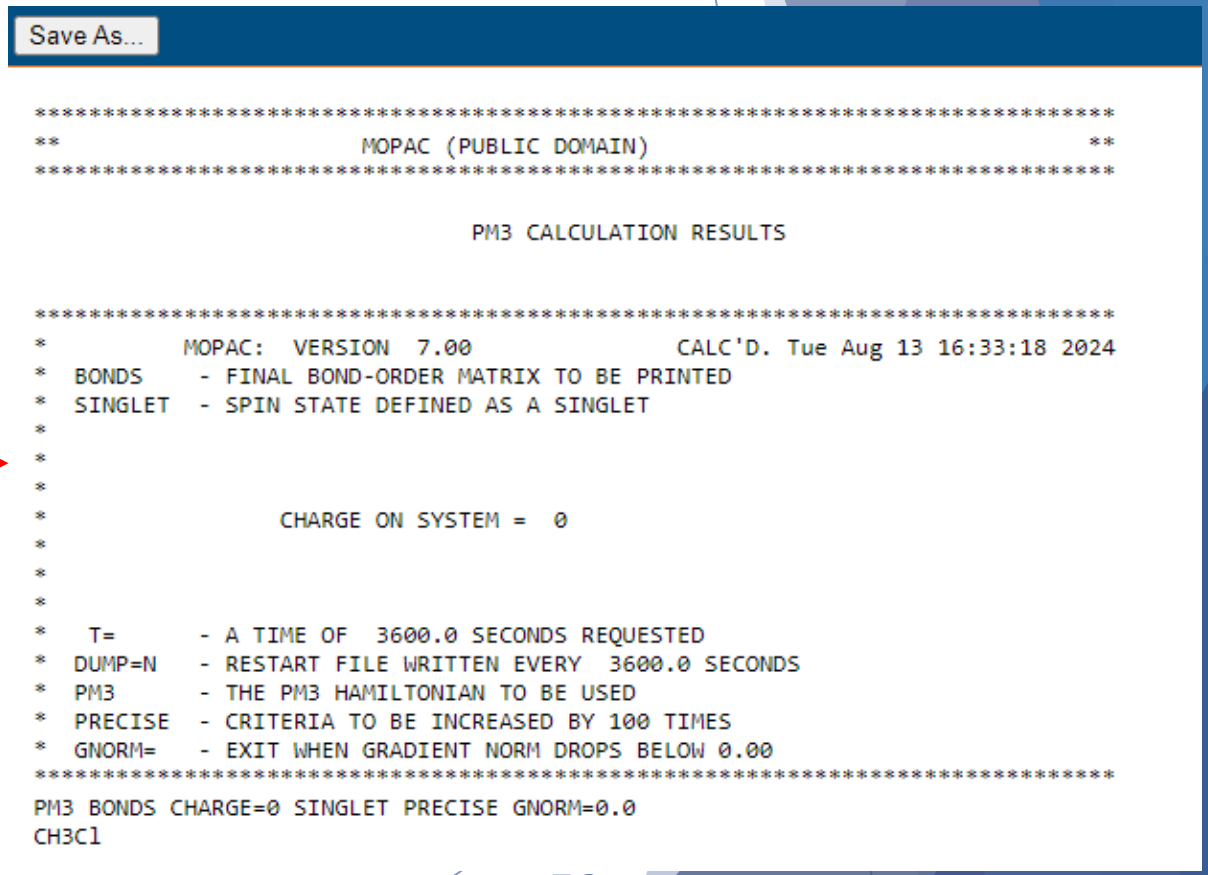
Bond Order

Atom	Symbol	1 C	2 Cl	3 H	4 H	5 H
1	C	4.214258				
2	Cl	0.992271	13.113457			
3	H	0.988231	0.007284	0.902880		
4	H	0.988231	0.007283	0.001003	0.902879	
5	H	0.988231	0.007283	0.001003	0.001003	0.902880

Raw output

If you want to know more about the molecular structure, you can click on Raw output on the left to view the full output file





Contributions of Translation and Rotation to Thermodynamic Functions

(Ideal Gas, Rigid Molecule, Classical Limit)

Equipartition Theorem

Each quadratic degree of freedom contributes

$$\frac{1}{2}\,k_B T$$

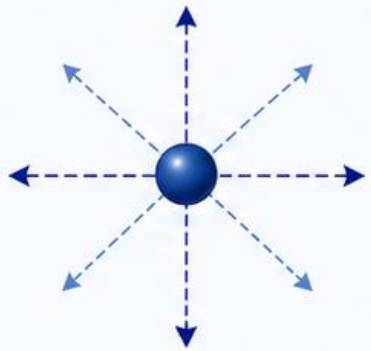
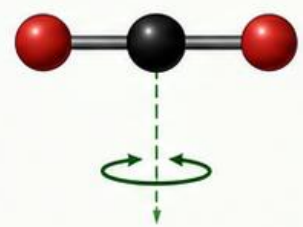
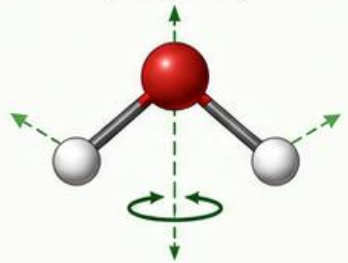
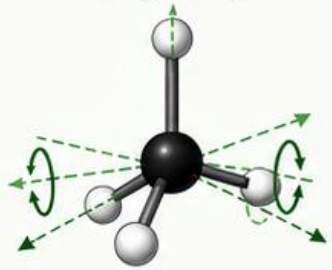
to the internal energy.

U	Internal energy
H	Enthalpy
S	Entropy
R	Gas constant
T	Temperature
k_B	Boltzmann constant
N	Number of molecules

For an ideal gas:

$$H = U + pV = U + nRT$$

(where $n = N/N_A$)

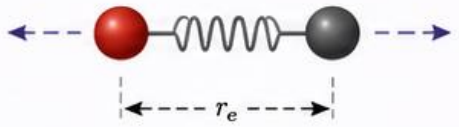
	TRANSLATION Motion of the center of mass	ROTATION Rotation about molecular axes		
		Linear Molecule (e.g., CO_2)	**Nonlinear Planar Molecule** (e.g., H_2O)	**Nonlinear 3D Molecule** (e.g., CH_4)
				
	3 translational degrees of freedom $(f_{trans} = 3)$	2 rotational degrees of freedom $(f_{rot} = 2)$	3 rotational degrees of freedom $(f_{rot} = 3)$	3 rotational degrees of freedom $(f_{rot} = 3)$
U	$U_{trans} = \frac{3}{2}\,Nk_BT = \frac{3}{2}\,nRT$	$U_{rot} = \frac{2}{2}\,Nk_BT = Nk_BT = nRT$	$U_{rot} = \frac{3}{2}\,Nk_BT = \frac{3}{2}\,nRT$	$U_{rot} = \frac{3}{2}\,Nk_BT = \frac{3}{2}\,nRT$
H	$H_{trans} = U_{trans} + nRT = \frac{5}{2}\,nRT$	$H_{rot} = U_{rot} + nRT = 2\,nRT$	$H_{rot} = U_{rot} + nRT = \frac{5}{2}\,nRT$	$H_{rot} = U_{rot} + nRT = \frac{5}{2}\,nRT$
S	$S_{trans} = Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right]$	$S_{rot} = Nk_B\left[\ln\left(\frac{8\pi^2 I k_B T}{\sigma h^2}\right) + 1\right]$	$S_{rot} = Nk_B\left[\ln\left(\frac{\sqrt{\pi}(I_A I_B)^{1/2}(k_B T)^{3/2}}{\sigma h^3}\right) + \frac{3}{2}\right]$	$S_{rot} = Nk_B\left[\ln\left(\frac{\sqrt{\pi}(I_A I_B I_C)^{1/2}(k_B T)^{3/2}}{\sigma h^3}\right) + \frac{3}{2}\right]$

m = molecular mass; I, I_A, I_B, I_C = moments of inertia; σ = symmetry number; h = Planck constant; k_B = Boltzmann constant

Vibrational Contributions to Thermodynamic Functions and Calculation of the Gibbs Free Energy

1. VIBRATIONAL MOTION

Harmonic Oscillator Model



Each normal mode of vibration behaves as an independent quantum harmonic oscillator with frequency ν_i.

Total Number of Vibrational Modes

- Nonlinear molecule: $f = 3N - 6$ (no. of atoms $= N$)
- Linear molecule: $f = 3N - 5$

Symbols

h	Planck constant
c	Speed of light
k_B	Boltzmann constant
T	Temperature
N	Number of molecules
$\tilde{\nu}_i = \nu_i / c$	Wavenumber (cm^{-1}) of mode i
$n_{v_i} = \frac{1}{e^{\frac{h\nu_i}{k_B T}} - 1}$	Mean vibrational quantum number

★ **Quantum treatment is essential.**
Vibrational motion is quantized; classical equipartition (e.g., $\frac{1}{2} k_B T$ per quadratic degree) is not valid for vibrations.

2. THERMODYNAMIC FUNCTIONS FOR ONE VIBRATIONAL MODE i (HARMONIC OSCILLATOR)

Function	Expression (per molecule)	Explanation
Internal energy $U_{\text{vib},i}$	$U_{\text{vib},i} = h\nu_i \left(n_{v_i} + \frac{1}{2}\right) = \frac{h\nu_i}{2} + \frac{h\nu_i}{e^{h\nu_i/(k_B T)} - 1}$	Zero-point energy $\frac{1}{2} h\nu_i$ plus thermal excitation.
Enthalpy $H_{\text{vib},i}$	$H_{\text{vib},i} = U_{\text{vib},i} + pV = U_{\text{vib},i} + k_B T$	For an ideal gas, $pV = k_B T$ per molecule.
Entropy $S_{\text{vib},i}$	$S_{\text{vib},i} = k_B \left[\frac{h\nu_i/(k_B T)}{e^{h\nu_i/(k_B T)} - 1} - \ln\left(1 - e^{-\frac{h\nu_i}{k_B T}}\right) \right] = k_B \left[(n_{v_i} + 1)\ln(n_{v_i} + 1) - n_{v_i} \ln n_{v_i} \right]$ (both forms are equivalent)	Increases with T as more vibrational states become populated.

3. TOTAL VIBRATIONAL CONTRIBUTIONS (ALL f VIBRATIONAL MODES)

$$U_{\text{vib}} = \sum_{i=1}^{f} U_{\text{vib},i} \qquad H_{\text{vib}} = \sum_{i=1}^{f} H_{\text{vib},i} = U_{\text{vib}} + f k_B T \qquad S_{\text{vib}} = \sum_{i=1}^{f} S_{\text{vib},i}$$

4. LIMITING BEHAVIOR (ONE MODE i)

Low temperature $\left(T \ll \frac{h\nu_i}{k_B}\right)$

- $n_{v_i} \approx 0$
- $U_{\text{vib},i} \approx \frac{h\nu_i}{2}$ (zero-point energy only)
- $H_{\text{vib},i} \approx \frac{h\nu_i}{2} + k_B T$
- $S_{\text{vib},i} \approx k_B \frac{h\nu_i}{k_B T} e^{-\frac{h\nu_i}{k_B T}} \to 0$

High temperature $\left(T \gg \frac{h\nu_i}{k_B}\right)$

- $n_{v_i} \approx \frac{k_B T}{h\nu_i}$
- $U_{\text{vib},i} \approx k_B T$ (equipartition: $\frac{1}{2} k_B T$ kinetic + $\frac{1}{2} k_B T$ potential)
- $H_{\text{vib},i} \approx 2\, k_B T$
- $S_{\text{vib},i} \approx k_B \left[1 + \ln\left(\frac{k_B T}{h\nu_i}\right)\right]$

At high T, each vibrational mode contributes
$U_{\text{vib},i} \to k_B T$, $H_{\text{vib},i} \to 2\, k_B T$, $S_{\text{vib},i} \to k_B \left[1 + \ln\left(\frac{k_B T}{h\nu_i}\right)\right]$.

5. GIBBS FREE ENERGY

Definition

$$G = H - TS$$

For an ideal gas (per molecule)

$$G = U + pV - TS = H - TS$$

Total Gibbs Free Energy (including all motions)

$$G = G_{\text{trans}} + G_{\text{rot}} + G_{\text{vib}}$$

with

$$G_x = H_x - TS_x \qquad x = trans, rot, vib$$

For N molecules

$$G_{\text{tot}} = NG$$
(or $G_{\text{tot}} = n_{\text{mol}}\, G$ in moles)

Example: CO_2 at 298.15 K, 1 atm

1. Compute U, H, S contributions from translation, rotation (linear), and the 4 vibrational modes.
2. Obtain $G = H - TS$.
3. Compare relative stabilities:
   $\Delta G = G_{\text{products}} - G_{\text{reactants}}$

CO_2 vibrational frequencies (cm^{-1}):
667 (bend, doubly degenerate),
1388 (symmetric stretch),
2349 (asymmetric stretch)

Linear molecule

Useful Relations

$pV = N k_B T$ (ideal gas) | $\sum_{i=1}^{f} 1 = f$ (number of vibrational modes) | $G = H - TS$ (natural variables: T, p) | $\Delta G = \Delta H - T\,\Delta S$ (spontaneous if $\Delta G < 0$)

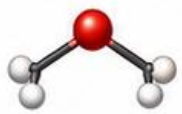
Notes: (i) Formulas assume the harmonic oscillator and ideal gas. (ii) Anharmonicity and mode coupling can cause deviations, especially at high T.

Reaction Thermodynamics and Equilibrium Constants from Computational Chemistry

How to obtain ΔU°, ΔH°, ΔS°, ΔG°, and K from molecular calculations

1. Compute thermodynamic functions for each species

Geometry optimization → Frequency calculation → Thermodynamic analysis



For each species i, computational chemistry gives U_i°, H_i°, S_i°, G_i° at **temperature** T and **standard state**.

$$H_i^\circ = E_{\mathrm{elec},i} + ZPE_i + H_{\mathrm{thermal},i} \qquad G_i^\circ = H_i^\circ - T\,S_i^\circ$$

Thermal contributions from molecular motions and electronics:

$$U_i^\circ = U_{\mathrm{trans}} + U_{\mathrm{rot}} + U_{\mathrm{vib}} + U_{\mathrm{elec}}$$

$$S_i^\circ = S_{\mathrm{trans}} + S_{\mathrm{rot}} + S_{\mathrm{vib}} + S_{\mathrm{elec}}$$

- Translation
- Rotation
- Vibration
- Electronic

Use the same temperature and standard state for all species.

2. Obtain reaction thermodynamic functions

General reaction:

$$\sum_i \nu_i X_i = 0$$

Products have positive ν_i; reactants have negative ν_i.

For any thermodynamic function $X = U, H, S, \text{ or } G$:

$$\Delta X^\circ_{\mathrm{rxn}} = \sum_i \nu_i X_i^\circ$$

- $\Delta U^\circ = \sum_i \nu_i U_i^\circ$
- $\Delta H^\circ = \sum_i \nu_i H_i^\circ$
- $\Delta S^\circ = \sum_i \nu_i S_i^\circ$
- $\Delta G^\circ = \sum_i \nu_i G_i^\circ = \Delta H^\circ - T\Delta S^\circ$

These values are usually reported per mole of reaction.

3. Convert ΔG° into the equilibrium constant

$$\Delta G^\circ = -RT \ln K \qquad K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$

K is dimensionless when defined with standard states.

Intuitive interpretation

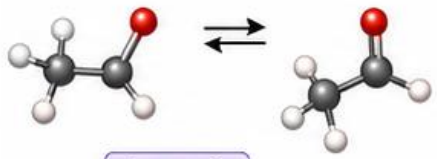
If $\Delta G^\circ < 0$	→	$K > 1$ (products favored)
If $\Delta G^\circ > 0$	→	$K < 1$ (reactants favored)

Typical standard states:

1 bar for ideal gases

1 M for solutes

4. Example A: Unimolecular reaction

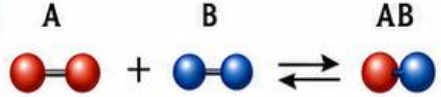


$\Delta n = 0$

- $\Delta H^\circ = H_B^\circ - H_A^\circ$
- $\Delta S^\circ = S_B^\circ - S_A^\circ$
- $\Delta G^\circ = G_B^\circ - G_A^\circ$
- $K = \exp\left[-\frac{G_B^\circ - G_A^\circ}{RT}\right]$

- Because the number of molecules does not change, translational entropy often changes only modestly.
- Equilibrium mainly reflects the balance between relative energies and molecular entropies of *A* and *B*.

5. Example B: Bimolecular reaction



$\Delta n = -1$

- $\Delta H^\circ = H_{AB}^\circ - H_A^\circ - H_B^\circ$
- $\Delta S^\circ = S_{AB}^\circ - S_A^\circ - S_B^\circ$
- $\Delta G^\circ = G_{AB}^\circ - G_A^\circ - G_B^\circ$
- $K = \exp\left[-\frac{G_{AB}^\circ - G_A^\circ - G_B^\circ}{RT}\right]$

- Two molecules combine into one, so translational entropy usually decreases strongly.
- *A favorable ΔH° is often needed to overcome the entropy penalty.*

6. Practical workflow

Optimize each reactant, product, and intermediate →

Run frequency calculations →

Extract U°, H°, S°, G° for every species →

$\sum$ Combine by stoichiometric coefficients →

Calculate ΔG° and then K

For reaction comparisons, *always use the same level of theory and the same standard-state convention.*

Calculating Thermodynamic Functions of CH_4 with M06-2X/6-31+G(d,p) in WebMO (Gaussian 16)

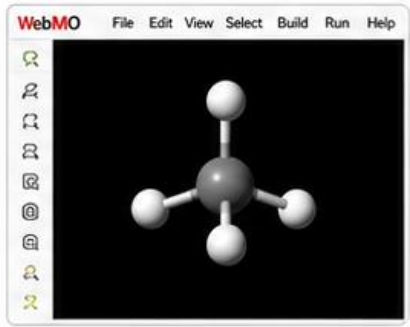
Goal: Obtain internal energy U, enthalpy H, Gibbs free energy G, entropy S, and heat capacity C_v for methane (CH_4) at 298.15 K and 1 atm. **Engine:** Gaussian 16 via WebMO

1 Go to WebMO

- Open https://www.webmo.net
- Log in (free account)

2 Build CH_4

- Click "Create" → "Molecule"
- Build methane (tetrahedral)
- Click "Save" (e.g., name: CH_4)



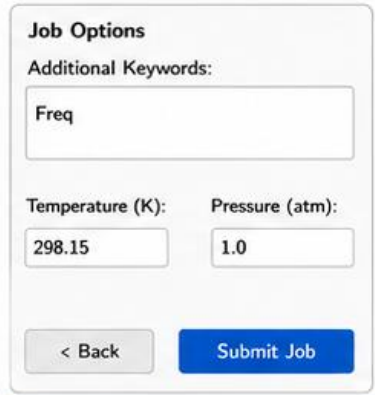
CH_4 C_1 (T_d) symmetry)

3 Set Up Calculation

- Click "Run" → "Gaussian"
- Choose "Gaussian 16"

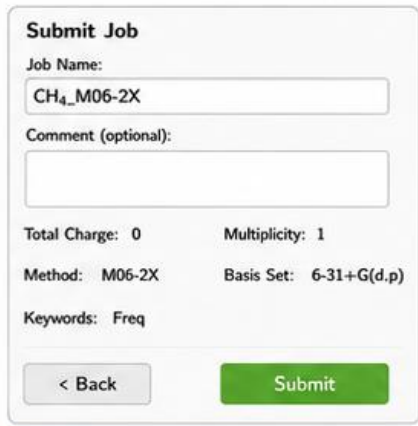
4 Job Options

- In "Additional Keywords", add Freq
- This ensures frequencies and thermochemistry are computed.



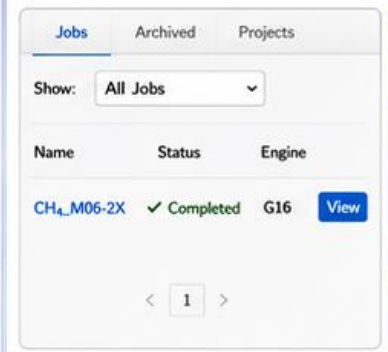
5 Submit Job

- Give the job a name (e.g., CH_4_M06-2X)
- Click "Submit"



6 Monitor Progress

- Go to "Jobs" to monitor status.
- When finished, click "View" to see results.



7 Results: Thermochemistry (from Frequency Calculation)

- In the result page, go to: **Results → Thermochemistry**
- WebMO (Gaussian 16) will report thermodynamic functions at the specified T and P.

Thermochemistry (Ideal Gas, 298.15 K, 1.000 atm)		
Zero-point correction (ZPE)	0.027328	Hartree
Thermal correction to Energy (U)	0.042770	Hartree
Thermal correction to Enthalpy (H)	0.043714	Hartree
Thermal correction to Gibbs Free Energy (G)	0.005492	Hartree
Sum of electronic and zero-point Energies	−40.190742	Hartree
Sum of electronic and thermal Energies (U)	−40.175301	Hartree
Sum of electronic and thermal Enthalpies (H)	−40.174356	Hartree
Sum of electronic and thermal Free Energies (G)	−40.212578	Hartree
Entropy (S)	0.186000	cal/(mol·K)
Heat Capacity (C_v)	9.918	cal/(mol·K)

8 Convert to Common Units (per mole)

- Conversion factor: 1 Hartree = 627.5095 kcal/mol

Quantity	Hartree	Formula	kcal/mol	Units
U	−40.175301	× 627.5095	−25,209.96	kcal/mol
H	−40.174356	× 627.5095	−25,209.37	kcal/mol
G	−40.212578	× 627.5095	−25,233.32	kcal/mol
S	0.186000	(no conversion)	116.64	cal/(mol·K)
C_v	9.918	(no conversion)	9.918	cal/(mol·K)

Values above are for $T = 298.15$ K and $P = 1$ atm.
(Numbers shown are illustrative; your results may differ slightly.)

9 Where to Find in WebMO

After job completion:

Information	WebMO Menu Path
Optimized geometry	Results → Summary
Vibrational frequencies	Results → Vibrational Freq.
Thermochemistry (U, H, G, S, C_v)	Results → Thermochemistry
Full Gaussian output	Results → Gaussian Output

Notes

- Frequency calculation is required to obtain thermodynamic functions.
- The results correspond to the ideal gas, rigid rotor, harmonic oscillator approximation (as implemented in Gaussian).
- You can change temperature and pressure in Step 4 (Job Options) and resubmit to obtain values at other conditions.

Summary of Workflow

Chemical System

- Molecule: Methane (CH_4)

Level of Theory

- Functional: M06-2X
- Basis Set: 6-31+G(d,p)

Software

- WebMO
- Engine: Gaussian 16

Reaction Thermochemistry from Quantum Chemistry

Example: Hydrogen Abstraction by OH Radical

$$OH + CH_4 \longrightarrow H_2O + CH_3$$

- **Method:** M06-2X/6-31+G(d,p)
- **Software:** WebMO (Gaussian 16)

1 Perform Four Calculations

Use the same workflow in WebMO for each species.

Species	Method
CH_4	M06-2X/6-31+G(d,p)
OH	M06-2X/6-31+G(d,p)
H_2O	M06-2X/6-31+G(d,p)
CH_3	M06-2X/6-31+G(d,p)

Workflow

Optimize Geometry → Frequency Calculation → Thermochemistry → U, H, G, S

CH_4

(T_d symmetry)

OH

($^2\Pi$)

H_2O

(C_{2v} symmetry)

CH_3

(planar, $^2A''$)

Note: CH_3 is a planar radical with C_{3v} symmetry ($^2A''$).

2 Obtain Thermochemical Functions

From WebMO:

Results → Thermochemistry

Record the following quantities for each species at 298.15 K, 1 atm.

Quantity	Meaning
U	Internal energy (thermal + electronic)
H	Enthalpy
G	Gibbs free energy
S	Entropy
C_v	Heat capacity at constant volume

(Units: Hartree in WebMO; convert using

1 Hartree = 627.5095 kcal/mol)

3 Calculate Reaction Quantities

For a reaction: $a\,A + b\,B \longrightarrow c\,C + d\,D$

$$\Delta U = \sum U_{\text{products}} - \sum U_{\text{reactants}}$$

$$\Delta H = \sum H_{\text{products}} - \sum H_{\text{reactants}}$$

$$\Delta G = \sum G_{\text{products}} - \sum G_{\text{reactants}}$$

$$\Delta S = \sum S_{\text{products}} - \sum S_{\text{reactants}}$$

For this reaction:

$$OH + CH_4 \longrightarrow H_2O + CH_3$$

Example for ΔH:

$$\Delta H = H(H_2O) + H(CH_3) - H(OH) - H(CH_4)$$

Compute ΔU, ΔH, ΔG, ΔS at 298.15 K and 1 atm.

4 Experimental Values from NIST (298.15 K, 1 atm, Gas Phase)

NIST WebBook: Standard Enthalpies of Formation, $\Delta_f H^\circ_{298}$ (kJ/mol)

Species	$\Delta_f H^\circ_{298}$ (kJ/mol)	NIST WebBook Link*
CH_4 (g)	−74.6	C-00074
OH (g)	+39.0	C-00037
H_2O (g)	−241.8	C-00001
CH_3 (g)	+146.7	C-01323

* https://webbook.nist.gov/chemistry/

Compute reaction enthalpy from formation enthalpies:

$$\begin{aligned}\Delta H^\circ_{298} &= \sum \Delta_f H^\circ_{298}\ (\text{products}) - \sum \Delta_f H^\circ_{298}\ (\text{reactants}) \\ &= [\Delta_f H^\circ(H_2O) + \Delta_f H^\circ(CH_3)] - [\Delta_f H^\circ(OH) + \Delta_f H^\circ(CH_4)] \\ &= [(-241.8) + (+146.7)] - [(+39.0) + (-74.6)] \\ &= -59.5\ \text{kJ/mol}\end{aligned}$$

Experimental $\Delta H^\circ_{298} = -59.5$ kJ/mol

(Accepted value from NIST)

5 Compare Calculation with Experiment

Typical M06-2X/6-31+G(d,p) Result (from Gaussian/WebMO)

$\Delta H_{\text{calc}} \approx -55$ to -65 kJ/mol

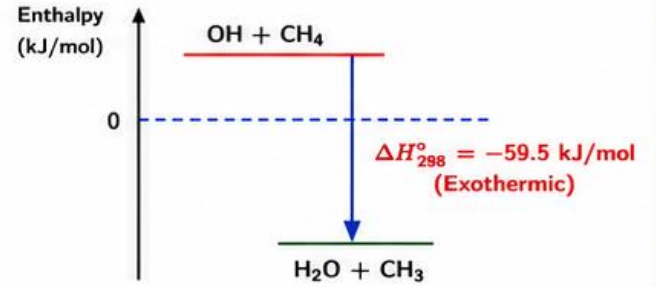
(depnding on basis set and details)

Compare with Experiment

Error = $\Delta H_{\text{calc}} - \Delta H_{\text{exp}}$

(ideally close to zero)

Reaction Energy Diagram (Enthalpy)



Why is this reaction important in the troposphere?

This hydrogen abstraction reaction by the OH radical is one of the most important removal pathways for methane (CH_4), a major greenhouse gas. It initiates a chain of reactions that ultimately converts CH_4 to CO_2 and H_2O, thereby helping to cleanse the atmosphere and control the lifetime of methane. Accurate thermochemistry is essential for modeling atmospheric chemistry.

Summary of Procedure

1. Build Molecules (OH, CH_4, H_2O, CH_3)
2. Optimize Geometry
3. Frequency Calculation
4. Thermochemistry (298.15 K, 1 atm) Obtain U, H, G, S
5. Compute ΔU, ΔH, ΔG, ΔS for reaction
6. Compare with NIST Experiment

Key Point: Quantum chemistry provides thermodynamic functions for individual molecules. By combining reactants and products, ΔU, ΔH, ΔG, and ΔS can be obtained and directly compared with experiment. This is the foundation of computational thermochemistry.

Transition-State Search and Reaction Kinetics

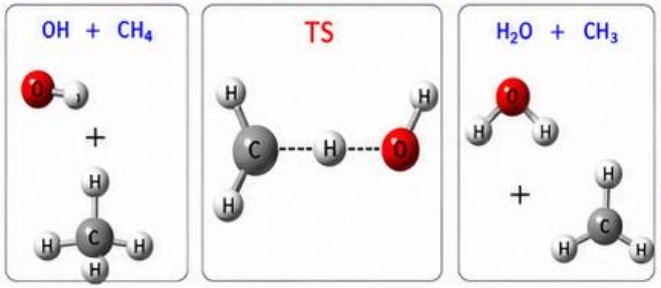
Example: $OH + CH_4 \longrightarrow H_2O + CH_3$

Method: M06-2X/6-31+G(d,p)
Software: Gaussian 16

1 Why Do We Need a Transition State?

Reaction thermodynamics tells us the reaction is exothermic.

$\Delta H^\circ_{298} = -11.75$ kcal/mol



A reaction must pass through a high-energy configuration (transition state, TS) before products can form.

The TS shows the O atom abstracting H from CH_4 (breaking C–H, forming O–H).

2 Transition-State Optimization in Gaussian

Build an initial TS guess
↓
Opt=TS (transition-state optimization)
↓
Frequency calculation
↓
One imaginary frequency
↓
Verified transition state

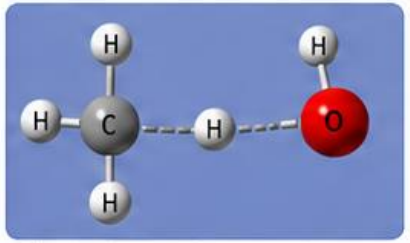
Recommended route section:

```
# M06-2X/6-31+G(d,p)
Opt=(TS,CalcFC)
Freq
```

3 How Do We Know It Is a TS?

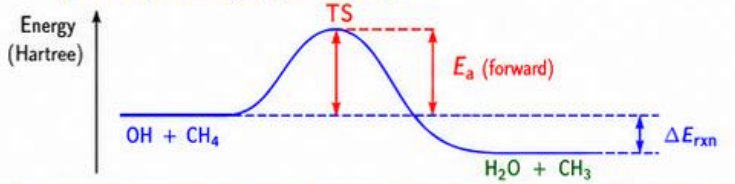
The frequency calculation shows exactly one imaginary frequency.

Imaginary frequency:
$\nu_i = -1038.6\ cm^{-1}$



The imaginary mode corresponds to hydrogen transfer: breaking the C–H bond while forming the O–H bond. The O atom abstracts H.

4 Energies Along the Reaction Coordinate (M06-2X/6-31+G(d,p), 298.15 K)



Species	E_{ele} (Hartree)	U (Hartree)	H (Hartree)	G (Hartree)
OH	−75.701751	−75.690774	−75.689829	−75.710062
CH_4	−40.487945	−40.439999	−40.438955	−40.460084
Reactants (R = OH + CH_4)	−116.189695	−116.130673	−116.128784	−116.170146
TS	−116.180323	−116.124155	−116.123210	−116.154330
H_2O	−76.394984	−76.370536	−76.369592	−76.391664
CH_3	−39.811897	−39.778861	−39.777916	−39.800135
Products (P = H_2O + CH_3)	−116.206881	−116.149397	−116.147508	−116.191799

ΔE_{rxn}	= $E_P - E_R$ =	−0.017186	Hartree	=	−10.78	kcal/mol
ΔU_{rxn}	=	−0.018724	Hartree	=	−11.75	kcal/mol
ΔH_{rxn}	=	−0.018724	Hartree	=	−11.75	kcal/mol
ΔG_{rxn}	=	−0.021653	Hartree	=	−13.59	kcal/mol

5 Barrier Heights (298.15 K)

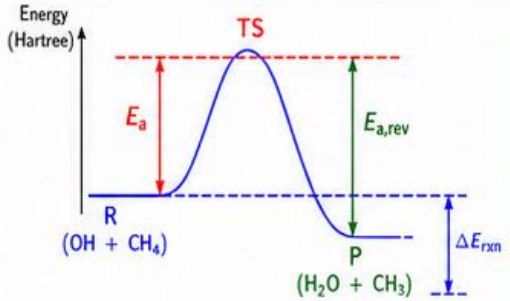
Electronic forward barrier:
$E_a = E_{TS} - E_R$
$= 0.009372$ Hartree $= 5.88$ kcal/mol

Thermal forward barrier ($\Delta H^\ddagger$):
$H_{TS} - H_R = 0.005574$ Hartree $= 3.50$ kcal/mol

Gibbs activation free energy:
$\Delta G^\ddagger = G_{TS} - G_R = 0.015816$ Hartree $= 9.92$ kcal/mol

Reverse electronic barrier:
$E_{TS} - E_P = 0.026558$ Hartree $= 16.67$ kcal/mol

1 Hartree = 627.5095 kcal/mol



6 From Transition State to Rate Constant

Transition-State Theory (TST):

$$k(T) = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right)$$

with $\Delta G^\ddagger = G_{TS} - G_{reactants}$

- Frequency calculations provide thermal and entropic corrections.
- Larger $\Delta G^\ddagger$ (or E_a) → slower reaction.
- Smaller $\Delta G^\ddagger$ (or E_a) → faster reaction.
- These quantities are the starting point for kinetic modeling; tunneling corrections can be added for more advanced treatments.

7 Atmospheric Importance

$OH + CH_4 \rightarrow H_2O + CH_3$ is one of the most important reactions in the troposphere because it removes the greenhouse gas methane.

$OH + CH_4 \longrightarrow H_2O + CH_3$

- Removes ~90% of methane in the troposphere.
- Controls the atmospheric lifetime of CH_4 (~10 years).
- Initiates oxidation of methane to CO_2 and H_2O.
- Important for climate modeling.

8 TST Rate Constant at 298.15 K and Comparison with Experiment

Eyring / TST equation:
$$k(T) = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right)$$

Gibbs free-energy barrier (298.15 K):
$\Delta G^\ddagger(298.15\ K) = 0.015816$ Hartree
$= 9.92$ kcal mol^{-1}

Bimolecular TST rate constant (298.15 K):
$k_{TST}(298.15\ K) = 1.34 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}

Experiment at 298 K:
$k_{exp}(298\ K) \approx 6.3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

Comparison:
TST / experiment ≈ 2.1
(about a factor of 2 larger than experiment)

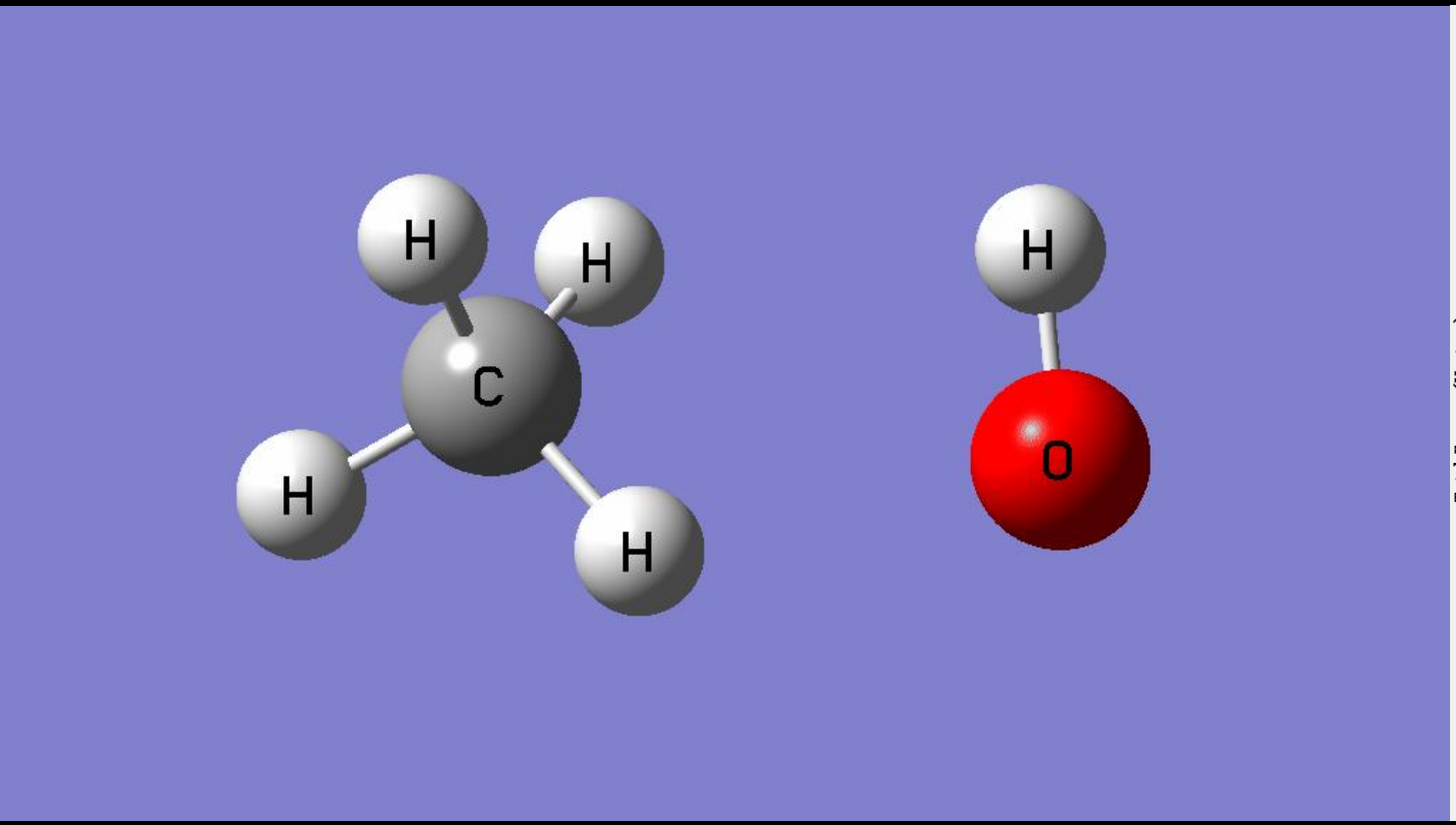
Teaching takeaway: The computed free-energy barrier can be converted into a predicted reaction rate and directly compared with experiment.

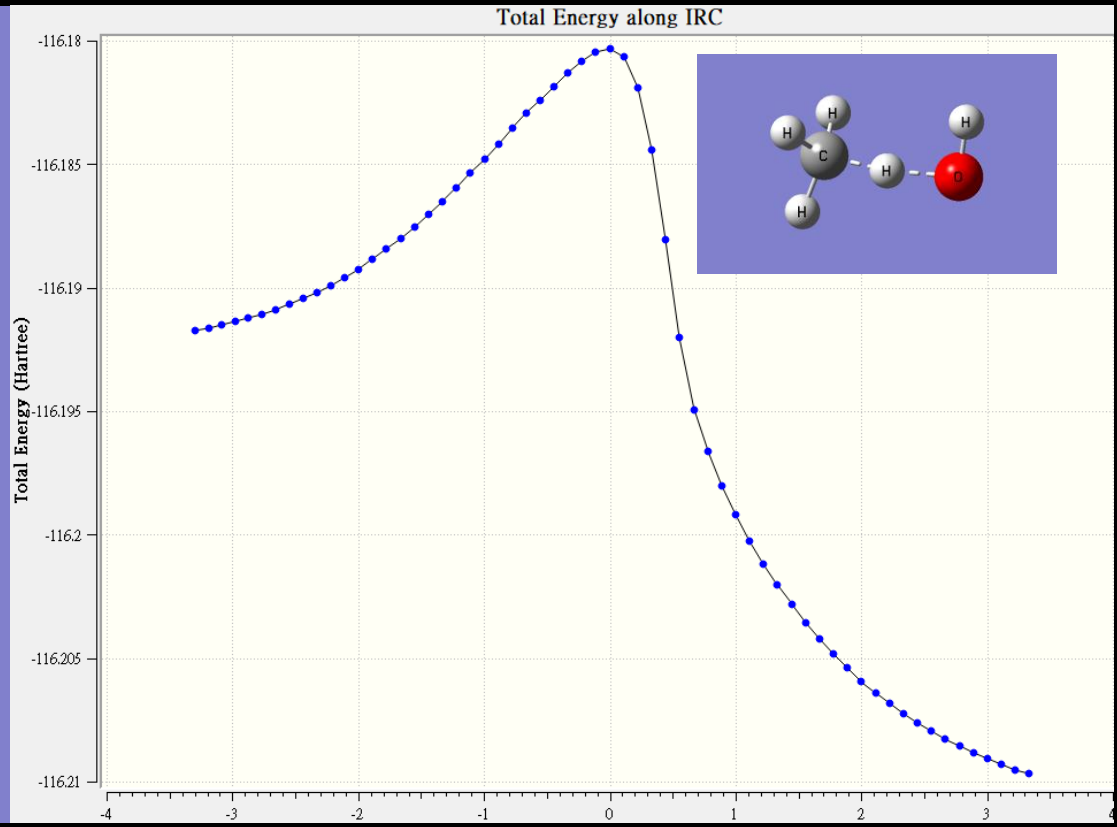
9 From Quantum Chemistry to Atmospheric Impact

Geometry optimization & TS search → Frequency calculation → Barrier height ($\Delta G^\ddagger$, E_a) → Rate constant $k(T)$ → Methane lifetime in the atmosphere

Key Message: Quantum chemistry provides the structures and energies of reactants, transition states, and products. From these, we obtain reaction energies and barrier heights, which can then be used to estimate rate constants and model atmospheric chemistry.

Reaction path of $OH + CH_4 \rightarrow H_2O + CH_3$

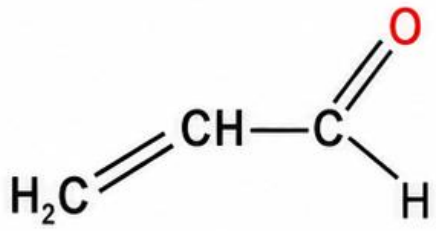




TD-DFT UV-Vis Spectrum of Acrolein: Procedure and Result Analysis

Example for undergraduate physical chemistry using WebMO

1. Build and optimize the molecule



acrolein

- Build CH_2=CH–CHO in WebMO
- Run geometry optimization
- Recommended method: B3LYP/6-31+G(d,p)
- Run frequency calculation to confirm a true minimum

Check: no imaginary frequencies

2. Run the TD-DFT calculation

WebMO / Computational workflow

Geometry optimization (Ground state)

↓

TD-DFT excited states (Calculation of transitions)

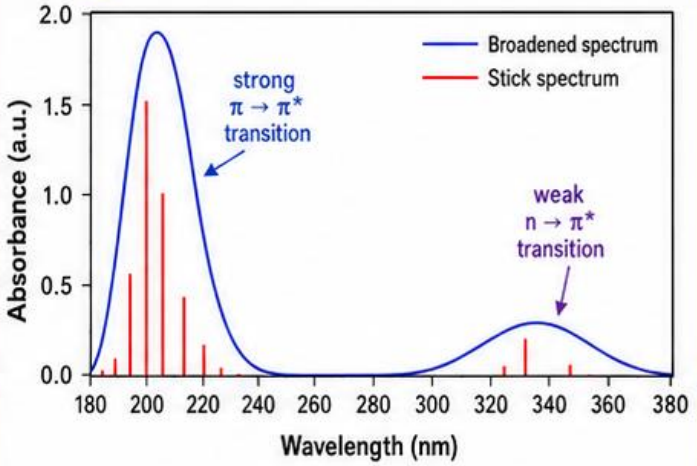
↓

UV-Vis spectrum (Simulated)

- TD-B3LYP/6-31+G(d,p)
- Request about 10 excited states
- Use the optimized ground-state geometry

Output gives excitation energy, wavelength, oscillator strength, and orbital contributions.

3. Simulated UV-Vis results

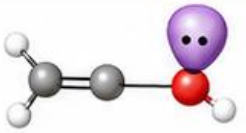


State	Transition	λ (approx.)	*f*	Intensity
S_1 (lowest singlet)	n → π*	300–350 nm	small ($\sim10^{-3}$–10^{-2})	weak
Higher singlet state(s)	π → π*	200–230 nm	larger ($\sim10^{-1}$–1)	strong

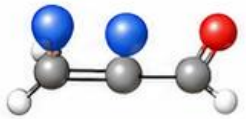
Values are approximate and illustrative.

4. How to analyze the results

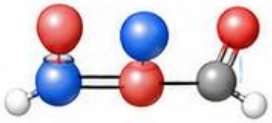
n orbital = lone pair on O



π orbital = conjugated C=C–C=O bonding orbital



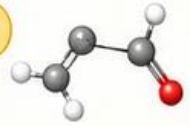
π* orbital = antibonding orbital

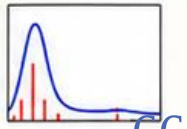
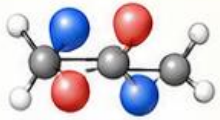


- The lowest-energy transition is often n → π* and has low oscillator strength.
- The stronger absorption usually comes from a π → π* excitation.
- Conjugation lowers the excitation energy compared with isolated C=C or C=O groups.
- Compare calculated wavelengths and intensities with experiment qualitatively.

***Important lesson:** the lowest-energy transition is not always the most intense.*

Recommended classroom workflow

1.  Optimize geometry
2.  Verify minimum by frequency analysis
3. 

Run TD-DFT excited states
4.  Plot UV-Vis spectrum
5.  Assign transitions using orbitals and oscillator strengths

Thank You for Your Participation

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