T02. Basic Quantum Chemistry Calculations in ORCA

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Introduction of ORCA

ORCA is a quantum chemistry software developed by Frank Neese in Max Planck Institute.

It is a free software (but not the open-source) for non-profit purpose

The name “ORCA” is not an acronym, and purely derives from Frank Neese’s personal experience.

Downloading ORCA

You can download ORCA from its official page,
https://orcaforum.kofo.mpg.de/app.php/portal
by making the account and going to the Downloads page.

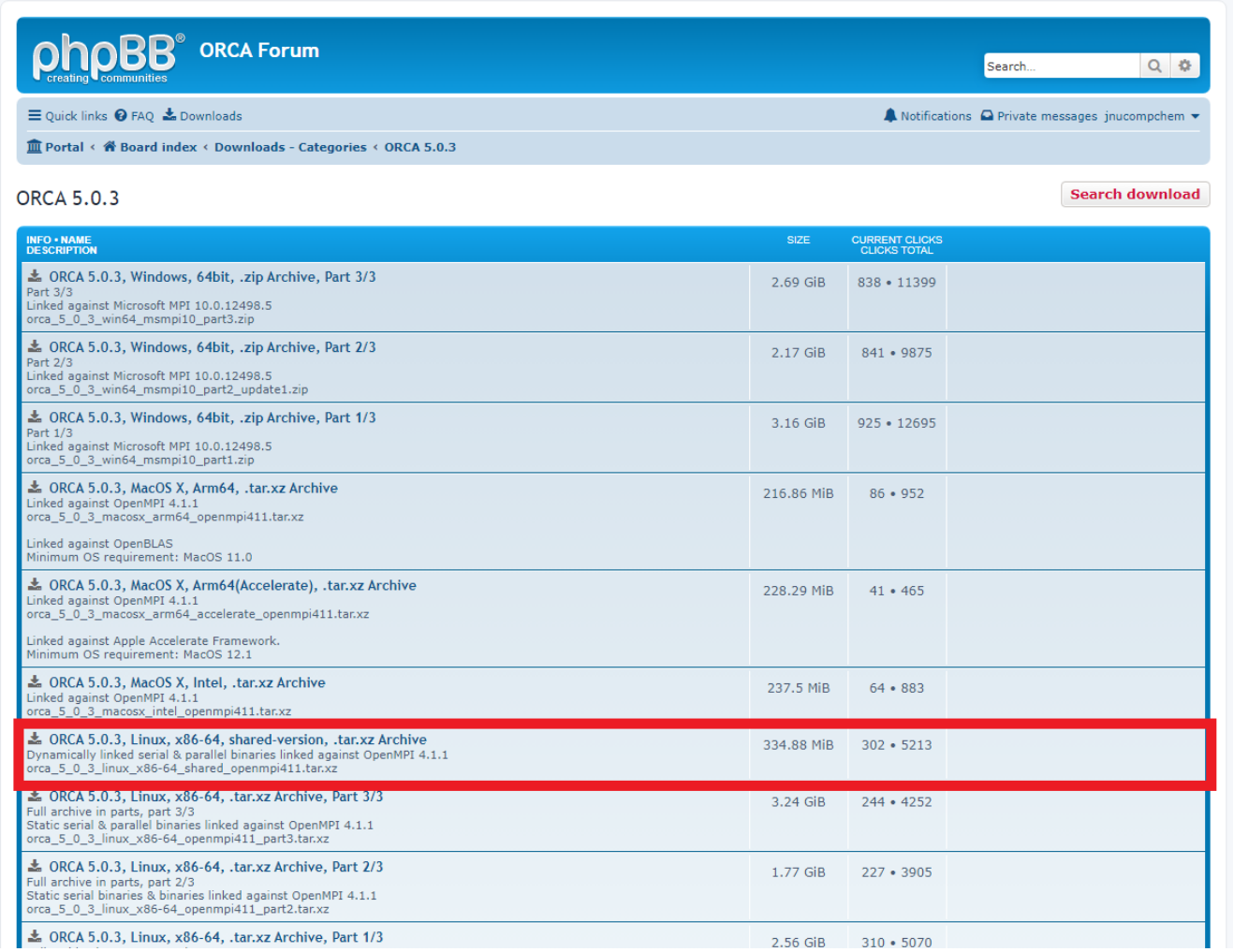
Downloading ORCA

ORCA supports Windows, MacOS and Linux.

In this lecture, you will use the Linux version already installed in the server.

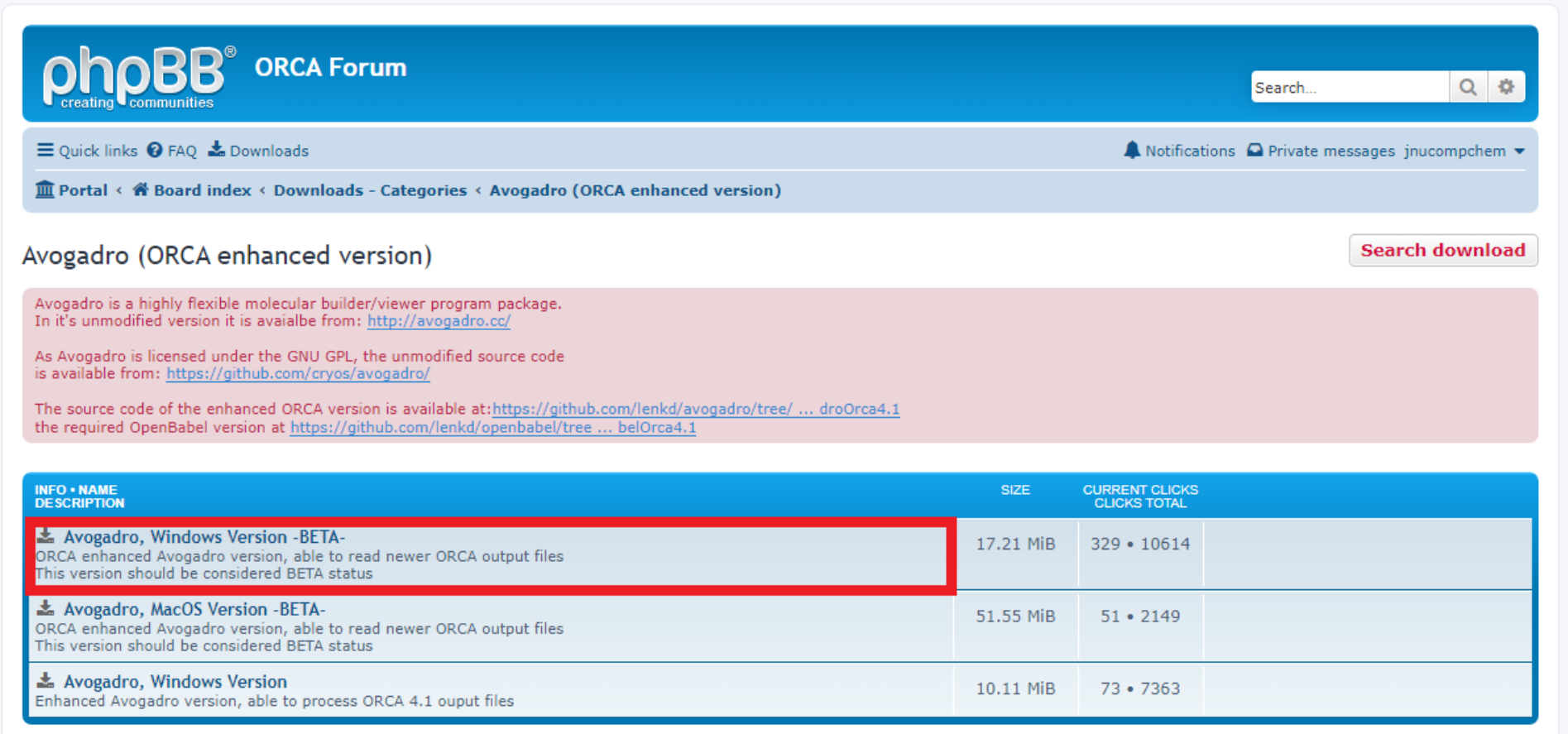
However, you can practice on your own by using the Windows version.

(or Linux version if you can install wsl in your laptop)

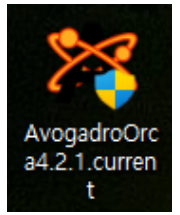


Avogadro

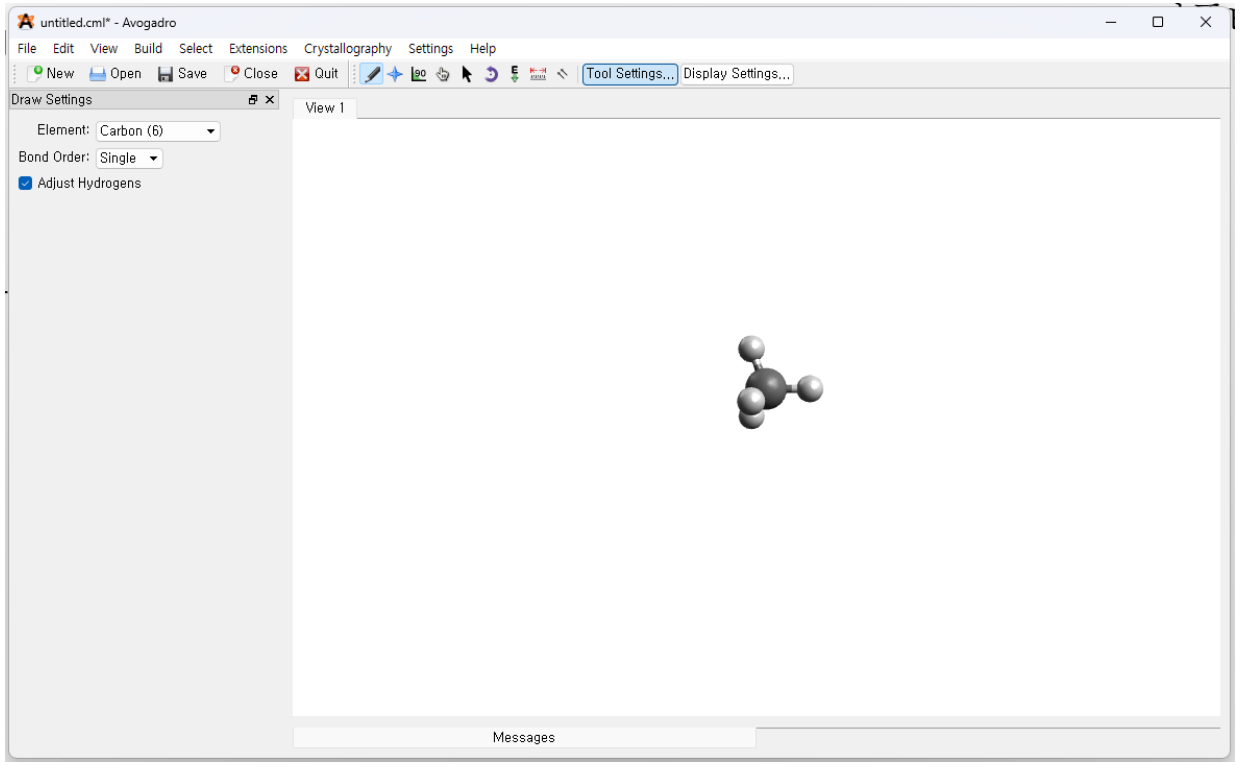
The program is provided in the ORCA homepage, but let us just download the install file from the e-class.



Avogadro

You can install Avogadro in your laptop by clicking 

After the installation, you can click the empty space to draw a methane:

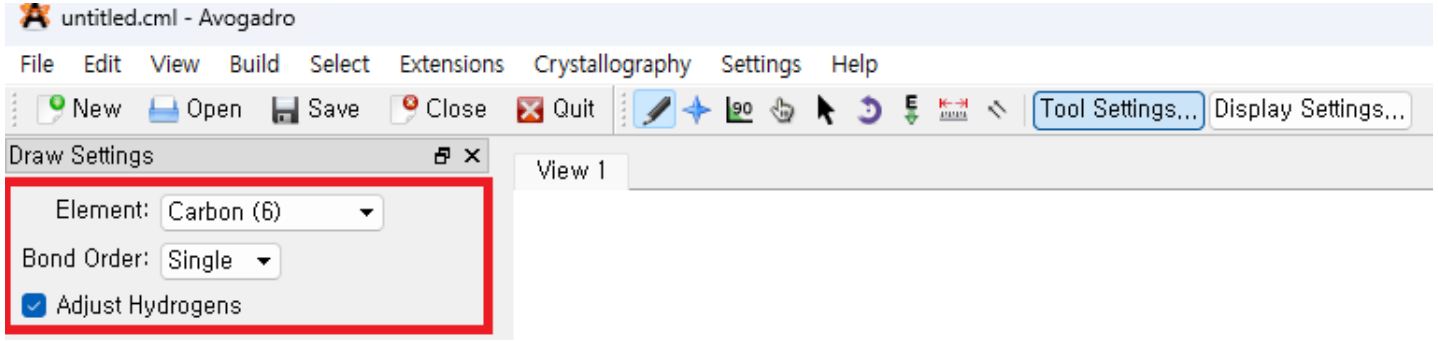


Avogadro

The icons in the topmost menu bar let us switch between modes.

The default mode is the “draw” mode 

You can place (erase) an atom by clicking the left (right) button.

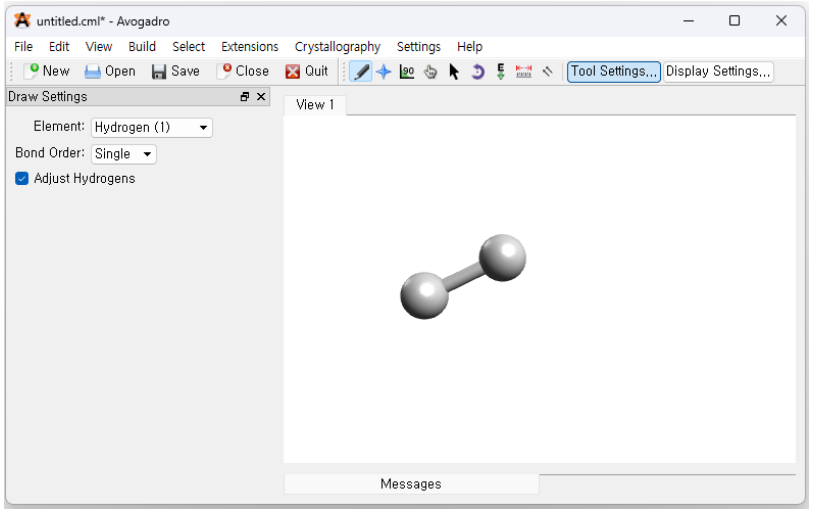


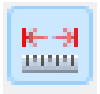
The options for the drawing can be controlled at the left.

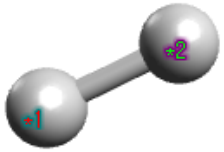
If the “Adjust Hydrogens” is checked, the program will try to automatically attach hydrogen based on the molecular structure.

Calculation on the Hydrogen Molecule

Let us draw a hydrogen molecule.



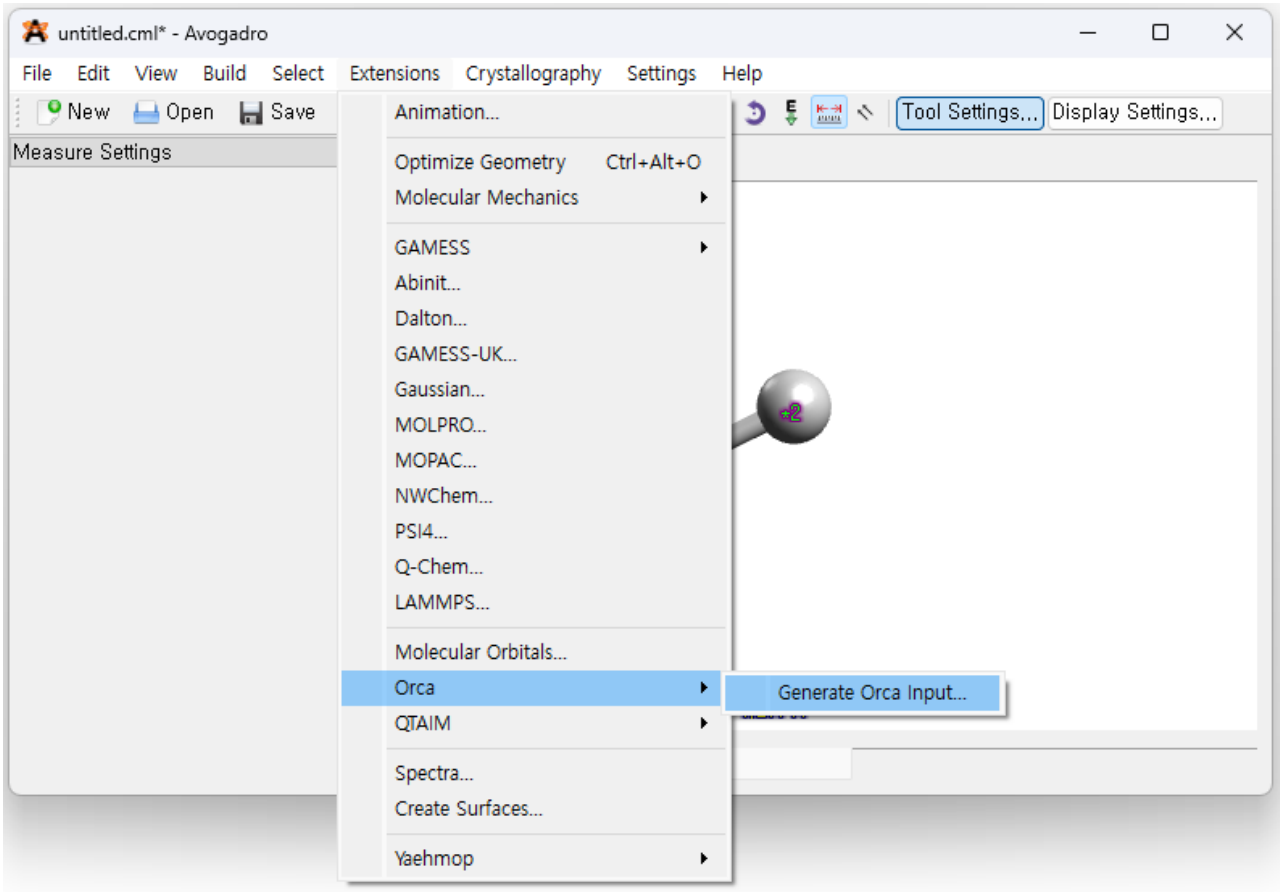
The H-H bond length can be displayed by clicking  button and consecutively clicking the two hydrogen atoms.



Distance(s): 1.211 Å

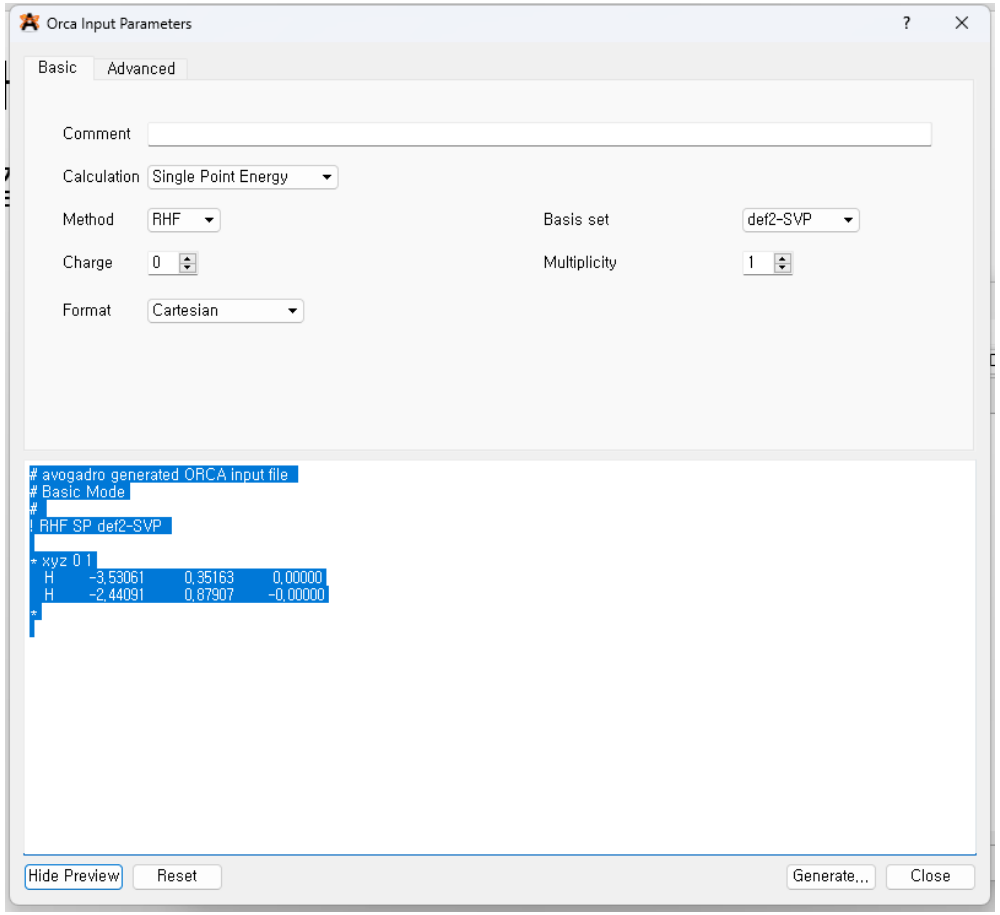
Calculation on the Hydrogen Molecule

We can use Avogadro to automatically generate an ORCA input file by clicking Extensions → Orca → Generate Orca input.



Calculation on the Hydrogen Molecule

Copy the whole text from the message box below.



Calculation on the Hydrogen Molecule

Type vi h2.in (the name is not important, but I suggest it ends with .in) to open an empty document and paste the copied text.

Do not forget to enter the write mode before pasting.

```
# avogadro generated ORCA input file
# Basic Mode
#
! RHF SP def2-SVP

* xyz 0 1
   H       -3.53061        0.35163        0.00000
   H       -2.44091        0.87907       -0.00000
*
```

Save the input and quit to the command line.

Type orca h2.in and press enter to run the calculation.

```
Sum of individual times         ...        0.426 sec (=   0.007 min)
GTO integral calculation        ...        0.047 sec (=   0.001 min)  11.1 %
SCF iterations                  ...        0.379 sec (=   0.006 min)  88.9 %
                          ****ORCA TERMINATED NORMALLY****
TOTAL RUN TIME: 0 days 0 hours 0 minutes 0 seconds 536 msec
DESKTOP-8RK1H7H:~/qchem/scratch>
```

Calculation on the Hydrogen Molecule

You can redirect the message from the program to a file by using >.

Type orca h2.in > h2.out to save the messages in h2.out.

Open h2.out and type /SCF ITER in the command mode to jump to the SCF calculation.

```
--------------
SCF ITERATIONS
--------------
ITER       Energy         Delta-E        Max-DP      RMS-DP      [F,P]     Damp
               ***  Starting incremental Fock matrix formation  ***
                      *** Initiating the SOSCF procedure ***
                      *** Re-Reading the Fockian ***
                      *** Removing any level shift ***
ITER      Energy       Delta-E        Grad      Rot      Max-DP    RMS-DP
  0     -1.05879461  -1.0587946095  0.000001  0.000001  0.000000  0.000000
              *** Restarting incremental Fock matrix formation ***
                **** Energy Check signals convergence ****
              ***Rediagonalizing the Fockian in SOSCF/NRSCF***

              ***************************************************
              *                    SUCCESS                      *
              *           SCF CONVERGED AFTER   1 CYCLES        *
              ***************************************************
```

The SCF calculation converges to the answer in just a single step.

The time increases with the complexity of the molecule.

Calculation on the Hydrogen Molecule

Type /SINGLE POINT in the command mode, and one finds

```
-------------------------   --------------------
FINAL SINGLE POINT ENERGY         -1.058794609541
-------------------------   --------------------
```

The term “single point energy” means the energy evaluated at a fixed structure of a molecule

The energy is conventionally written in Hartree (1 Ha = 2625.5 kJ mol^{-1})

You can also find the information about the dipole moment a little below

```
-------------
DIPOLE MOMENT
-------------
                                X           Y           Z
Electronic contribution:     -0.00000    -0.00000     0.00000
Nuclear contribution   :      0.00000    -0.00000     0.00000
                            -----------------------------------
Total Dipole Moment    :     -0.00000    -0.00000     0.00000
                            -----------------------------------
Magnitude (a.u.)       :      0.00000
Magnitude (Debye)      :      0.00000
```

The Structure of the Input File

```
# avogadro generated ORCA input file
# Basic Mode
#
! RHF SP def2-SVP

* xyz 0 1
   H        -3.53061         0.35163         0.00000
   H        -2.44091         0.87907        -0.00000
*
```

Comment
(ignored by the program)

Computation option

Molecular information

RHF: Restricted Hartree-Fock (the easiest SCF calculation)

SP: Single point

def2-SVP: basis function

xyz 0 1: Cartesian coordinates, charge neutral, spin singlet

Geometry Optimization

If you can calculate the energy of a molecule, you can also obtain information about the direction of movement which lowers the energy.

If you keep pushing the nuclei in such direction, you will eventually be able to reach a point where the energy is not lowered any more.

Such a point is called the local minimum of the energy.

To perform optimization, you replace SP by OPT in your input file.

```
# avogadro generated ORCA input file
# Basic Mode
#
! RHF OPT def2-SVP

* xyz 0 1
   H       -3.53061        0.35163        0.00000
   H       -2.44091        0.87907       -0.00000
*
```

Geometry Optimization

Let us perform the optimization by copying h2.in to h2_opt.in and replacing SP with OPT.

Start the calculation by typing orca h2_opt.in > h2_opt.out.

The messages will be saved in h2_opt.out.

The energy change at every optimization step can be monitored by typing grep “SINGLE POINT” h2_opt.out.

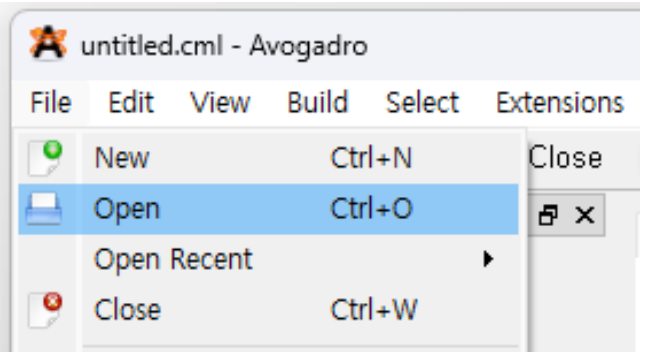
```
DESKTOP-8RK1H7H:~/qchem/scratch> grep "SINGLE POINT" h2_opt.out
FINAL SINGLE POINT ENERGY        -1.058794609538
FINAL SINGLE POINT ENERGY        -1.090425885683
FINAL SINGLE POINT ENERGY        -1.117358204211
FINAL SINGLE POINT ENERGY        -1.128812527745
FINAL SINGLE POINT ENERGY        -1.128899043794
FINAL SINGLE POINT ENERGY        -1.128928523520
FINAL SINGLE POINT ENERGY        -1.128928568542
DESKTOP-8RK1H7H:~/qchem/scratch>
```

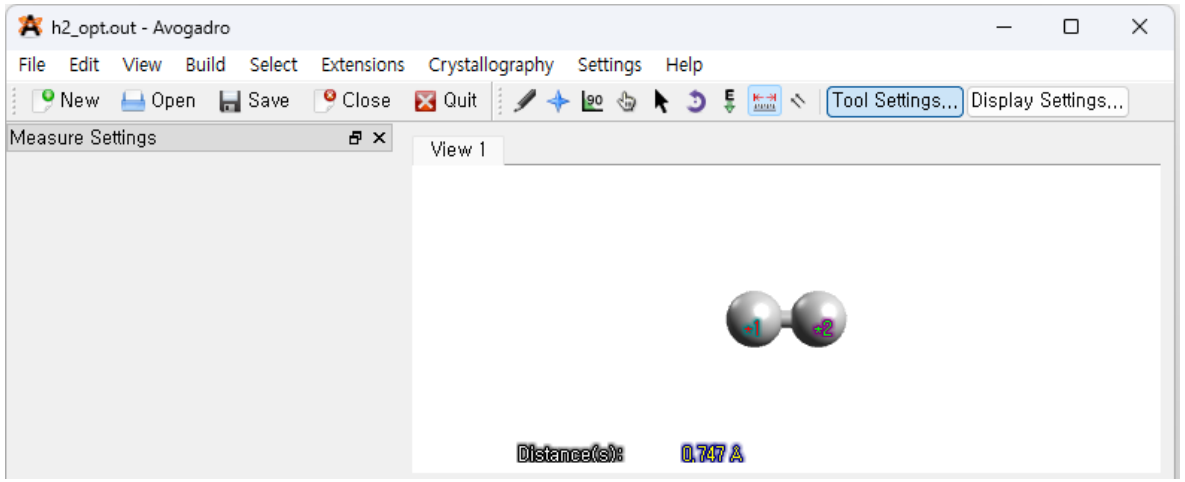
Geometry Optimization

The output file can be downloaded to the personal laptop and opened with Avogadro.

scp -rp -P XXXX <ID>@168.131.XXX.XXX:~/h2_opt.out .
scp -rp -P XXXX <ID>@168.131.XXX.XXX:~/h2_opt_trj.xyz .

You can open h2_opt.out and measure the bond length of the optimized geometry.

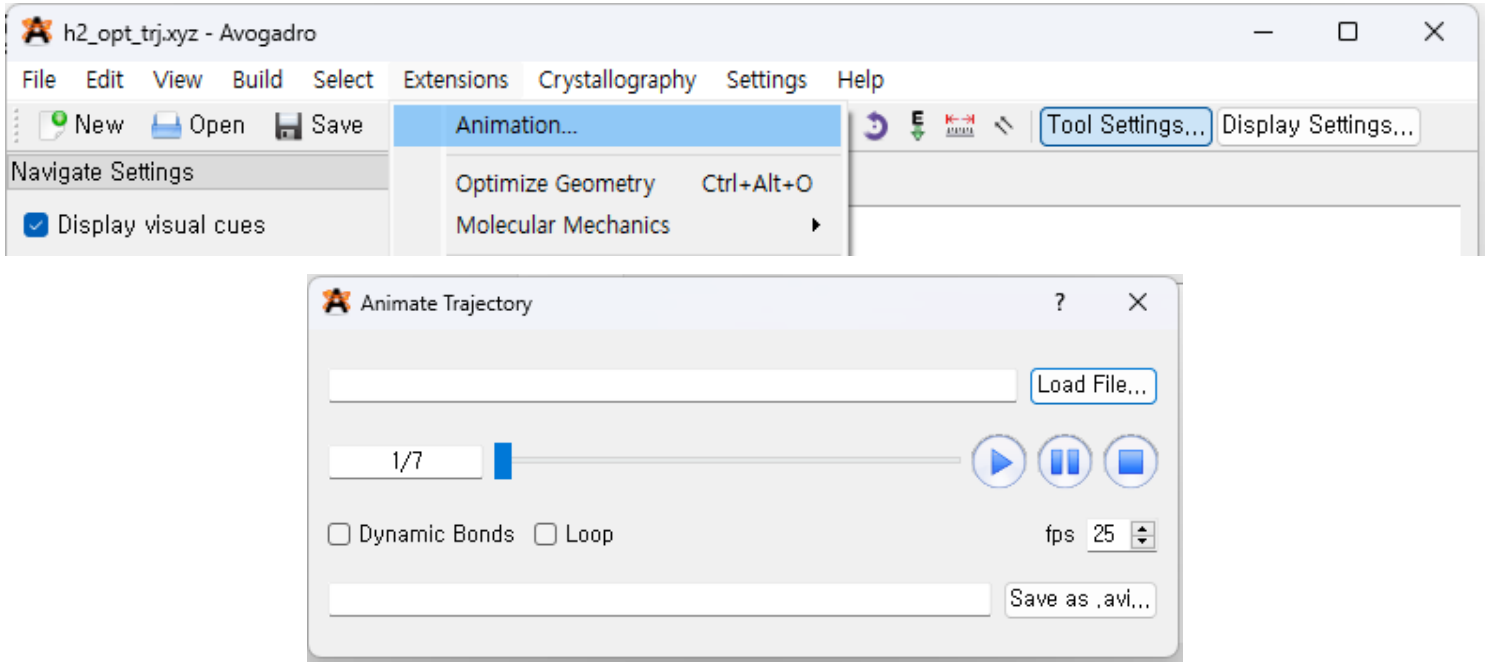




Geometry Optimization

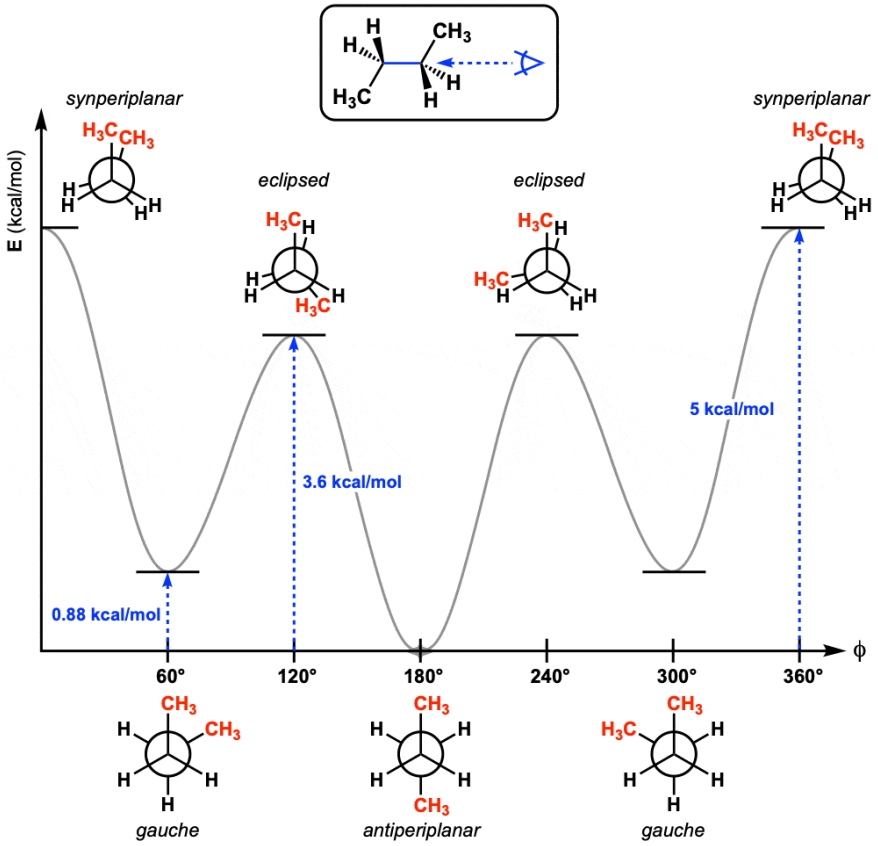
The automatically generated h2_opt_trj.xyz stores the geometry of the molecule at every optimization step.

To visualize the optimization process, open the file and go to Extensions → Animation.



Geometry Optimization

One must be always aware that the local minimum is not always the structure with the lowest energy (global minimum).



Consider the following diagram showing the rotation of the C-C bond of n-butane.

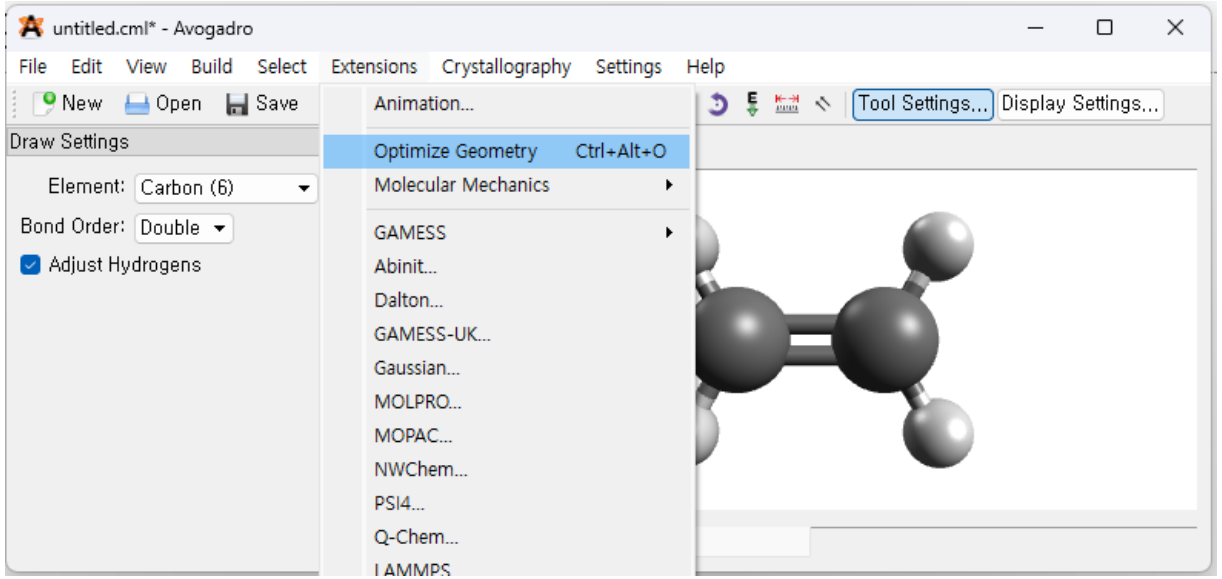
Starting at 150˚will lead to antiperiplanar form, which is the global minimum.

However, starting at 90˚will lead to the gauche form, which is not the lowest in energy.

Geometry Optimization for Ethylene

For large molecules, it is efficient to optimize the structure in Avogadro before using ORCA.

Avogadro performs optimization based on molecular mechanics, which is crude but much quicker compared to quantum chemistry.



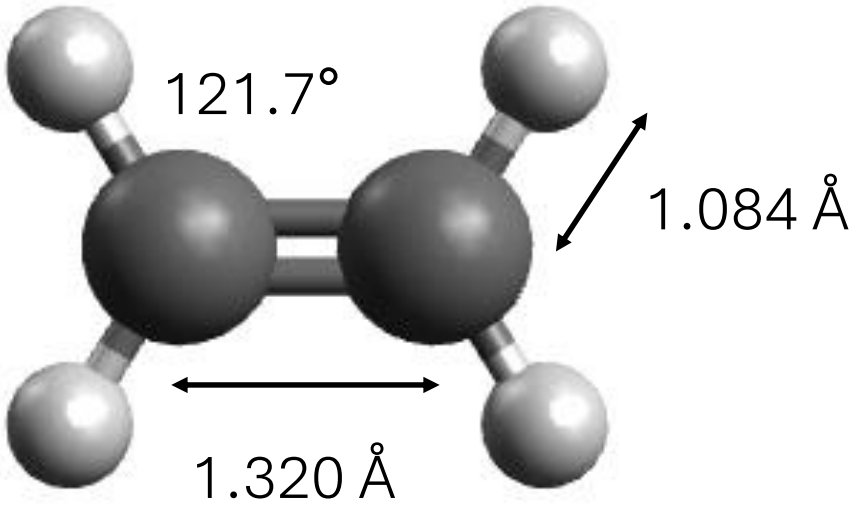
Hence, it can provide a good initial structure that is close to the final optimum.

Geometry Optimization for Ethylene

Make the input file eth.in and change the calculation option to OPT.

Perform the calculation by orca eth.in > eth.out.

Download the output file to the laptop and measure the bond lengths and angles.



Visualizing Molecular Orbital

Copy eth.in to eth_orb.in to create a new input

To copy the coordinate, open eth.xyz by using vi and place the cursor at the line 3 where the coordinate section begins

In the command mode, press shift+v and you will see ---VISUAL LINE--- at the bottom left of the screen

```
6
Coordinates from ORCA-job eth
  C   -3.240989547204400      -0.100656436607110       0.000000239150620
  C   -1.922477161339280      -0.036463605248740      -0.000000309039290
  H   -3.843171869480410       0.549722605175150       0.623624230248030
  H   -3.777145728686290      -0.806456444205320      -0.623623231301510
  H   -1.386321087452420       0.669336426682850       0.623623238797740
  H   -1.320294605837200      -0.686842545796840      -0.623624167855590
```

Select all 6 lines and press y to copy the text

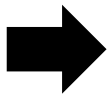
You will see the message “6 lines yanked” at the bottom left

Visualizing Molecular Orbital

Do not exit the editor, and type :e eth_orb.in to open the input file we created before.

Put the cursor at where we want to paste the copy the text and press p.

```
* xyz 0 1
   C       -3.24884       -0.10104        0.00000
   C       -1.91463       -0.03608        0.00000
   H       -3.84136        0.55579        0.62911
   H       -3.77476       -0.81232       -0.62911
   H       -1.38871        0.67520        0.62911
   H       -1.32210       -0.69291       -0.62911
*
```



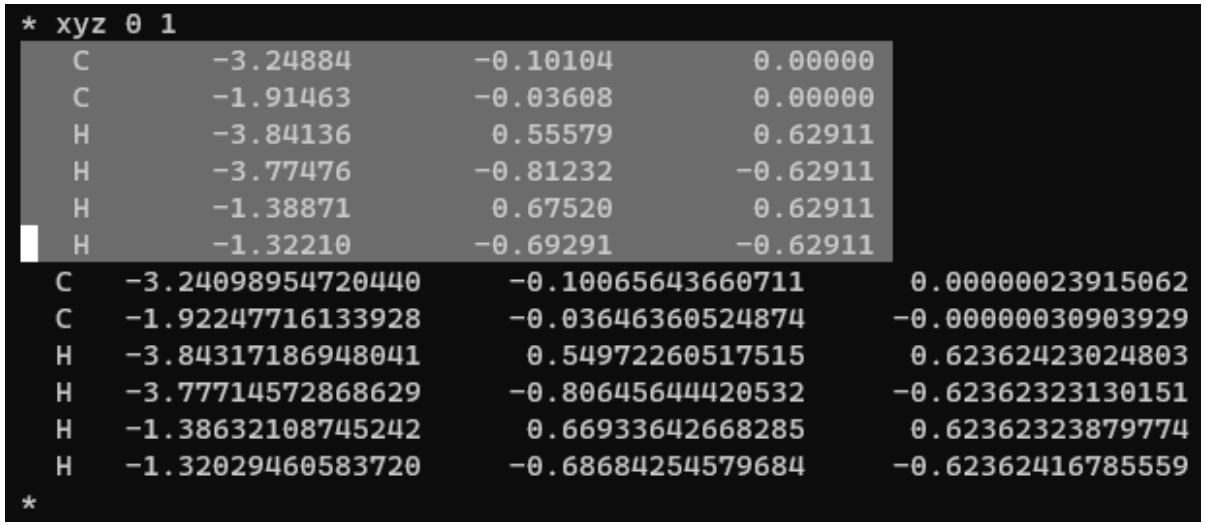
```
* xyz 0 1
   C       -3.24884       -0.10104        0.00000
   C       -1.91463       -0.03608        0.00000
   H       -3.84136        0.55579        0.62911
   H       -3.77476       -0.81232       -0.62911
   H       -1.38871        0.67520        0.62911
   H       -1.32210       -0.69291       -0.62911
   C   -3.24098954720440    -0.10065643660711     0.00000023915062
   C   -1.92247716133928    -0.03646360524874    -0.00000030903929
   H   -3.84317186948041     0.54972260517515     0.62362423024803
   H   -3.77714572868629    -0.80645644420532    -0.62362323130151
   H   -1.38632108745242     0.66933642668285     0.62362323879774
   H   -1.32029460583720    -0.68684254579684    -0.62362416785559
*
```

Keep in mind that we can always use u to undo the changes

Visualizing Molecular Orbital

We now need to erase the old coordinates

Again, we can use the visual line, but this time we press d to cut the text



The deleted text is still in the memory of the editor, and you can paste it anywhere you want before it is overwritten.

Visualizing Molecular Orbital

To print the orbital information, we change the calculation option to

RHF SP def2-SVP PRINTBASIS LARGEPRINT

```
! RHF SP def2-SVP PRINTBASIS LARGEPRINT

* xyz 0 1
  C    -3.240989547204400     -0.100656436607110      0.000000239150620
  C    -1.922477161339280     -0.036463605248740     -0.000000309039290
  H    -3.843171869480410      0.549722605175150      0.623624230248030
  H    -3.777145728686290     -0.806456444205320     -0.623623231301510
  H    -1.386321087452420      0.669336426682850      0.623623238797740
  H    -1.320294605837200     -0.686842545796840     -0.623624167855590
*
```

Run the calculation and store the output in eth_orb.out.

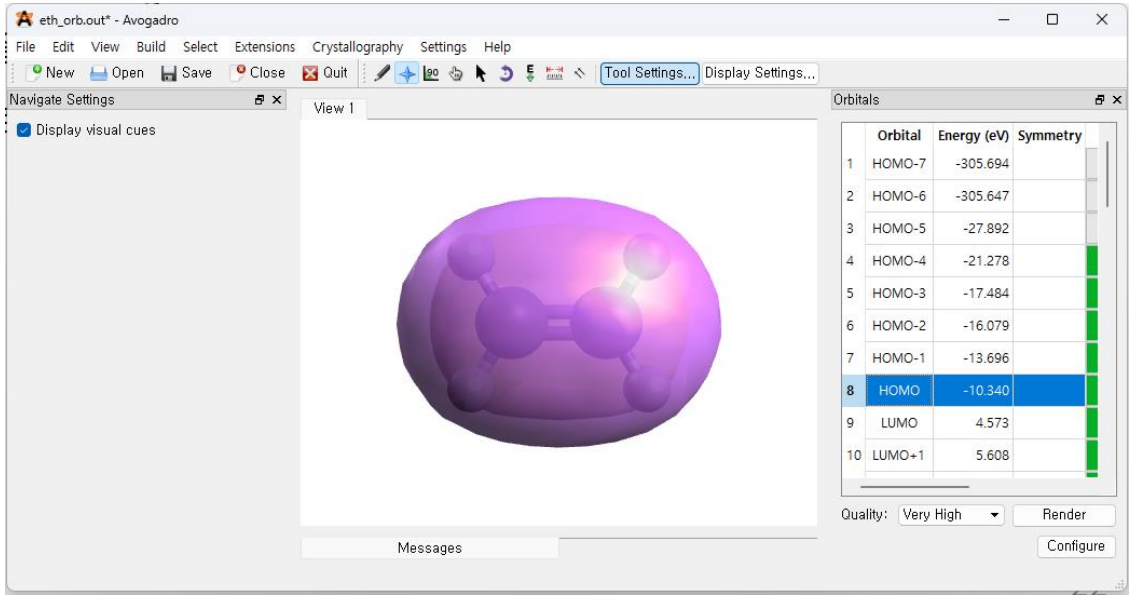
orca eth_orb.in > eth_orb.out

Download the output file to the laptop.

Visualizing Molecular Orbital

Opening eth_orb.out in Avogadro shows an additional menu that allow us to select the orbital to visualize.

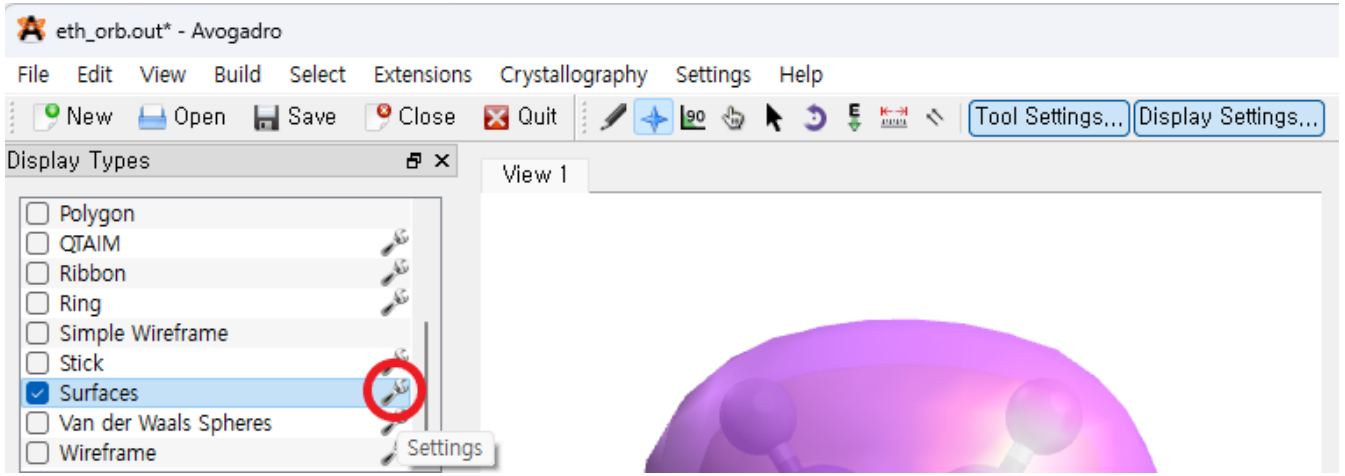
Normally 10 orbitals near HOMO and LUMO are loaded.

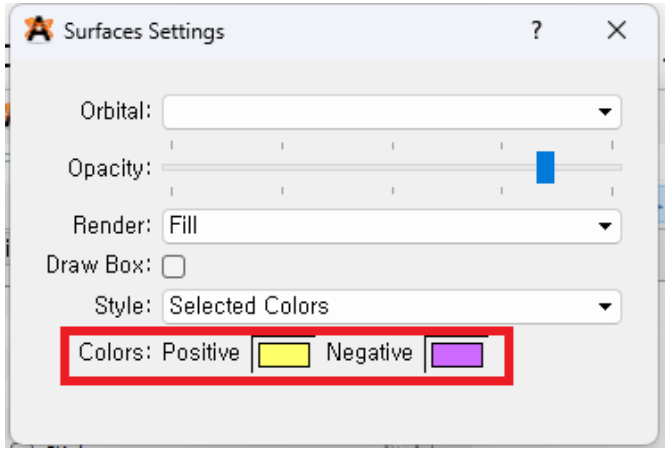


The sign of the orbital amplitude is represented with two different colors.

Visualizing Molecular Orbital

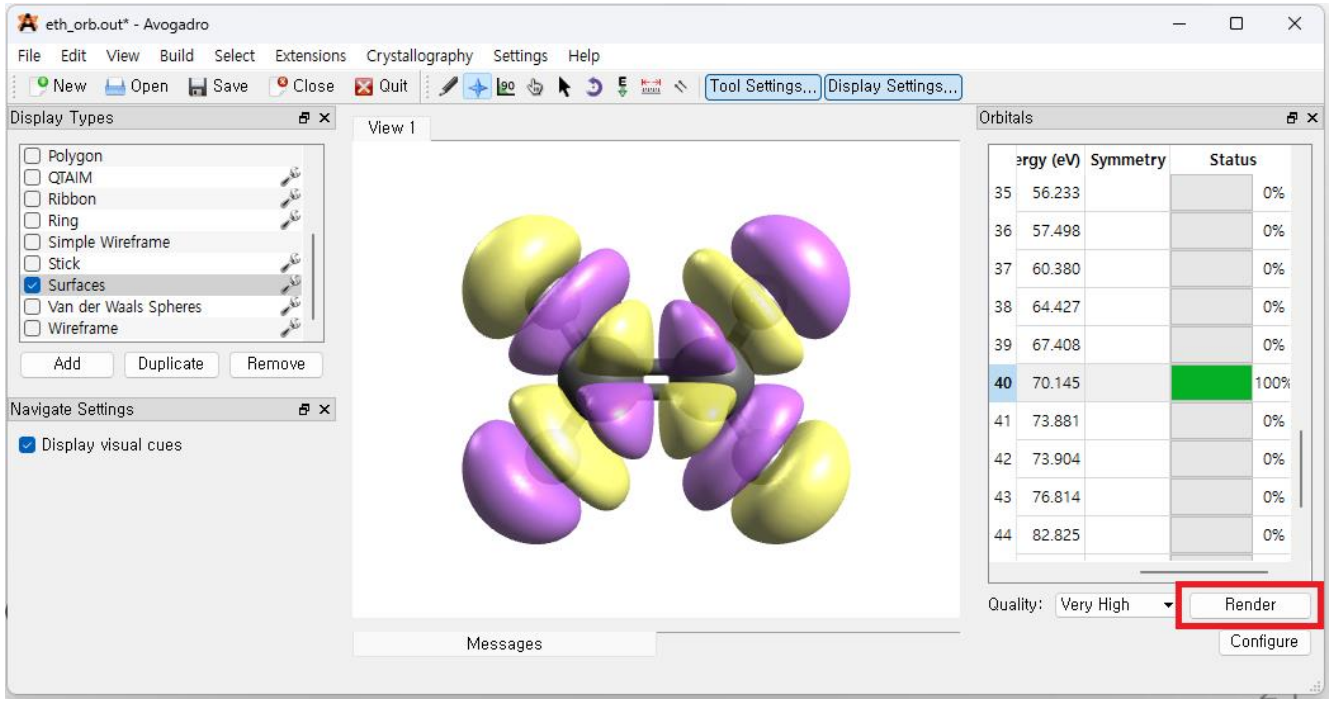
You can change the color of the orbitals in Display Settings → Surfaces.





Visualizing Molecular Orbital

If you want to see other orbitals that are not loaded by default, select it and click “Render.”



Keep in mind that LUMO orbitals become more inaccurate when the energy is increased.