

4th Winter School of Computational Chemistry
Sharif University of Technology

Exercise Manual



Geometry Optimization, and Frequency Calculation
Potential Energy Surface

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Geometry Optimization, and Frequency Calculation

Geometry optimizations

On your desktop, open Avogadro, select **Build, Insert, Fragment**, and choose the molecule. Click **Insert** on the molecule to add a fragment. Then close the window.

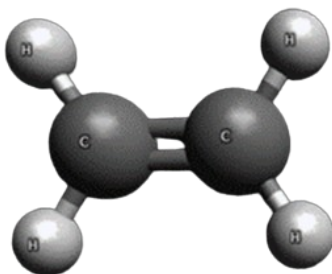
After choosing the fragment, again select **Build** and then **Cartesian Editor** to see the Cartesian coordinate of a molecule.

Now you can copy the coordinates on your **input file**.

Open any Text Editor you have, Notepad, notepad++, ...and save the file with “.inp” extension.

On your notepad file write the method and basis set and paste the coordinate from Avogadro. Then save the file with the “.inp” extension. (basename.inp)

```
! B3LYP Def2-SVP Opt
* xyz 0 1
H      1.1610300000      0.0660680000      1.0238850000
C      0.6578960000     -0.0044590000      0.0639790000
H      1.3351900000     -0.0830130000     -0.7814260000
C     -0.6578350000      0.0044580000     -0.0638470000
H     -1.3354850000      0.0830070000      0.7812720000
H     -1.1607960000     -0.0660610000     -1.0238630000
*
```



On your desktop, right-click to open a terminal and enter the path of the input file, or go to the folder where orca is located and enter the following command by opening cmd:

```
orca basename.inp > basename.out
```

Wait for the job to finish (<1 minute) and open `basename.out` in the related folder

To make sure that the run is done correctly, check the statement `****ORCA TERMINATED NORMALLY****` at the end of the output file.

Generating and Visualizing Molecular Orbital

In this step, we use the new geometry obtained in the optimization run and create a new input file to generate molecular orbitals.

```
! B3LYP def2-SVP

%output
  print[p_mos] 1
  print[p_basis] 2
end

* xyz 0 1
H    1.14763538032723      0.06787867944812      1.04401871500948
C    0.66349268258141     -0.00443412366993      0.06448921374936
H    1.32609585559607     -0.08470073189697     -0.80365926899303
C   -0.66349297051130      0.00443446347416     -0.06448407909659
H   -1.32610760697121      0.08470054881831      0.80365397958594
H   -1.14762334102220     -0.06787883617369     -1.04401856025516
*
```

After generating the input file, run it with the following command on your cmd.

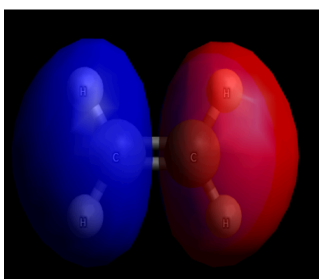
```
orca Ethylene_MOs.inp > Ethylene_MOs.out
```

To visualize Molecular Orbitals, open the output file with Avogadro.

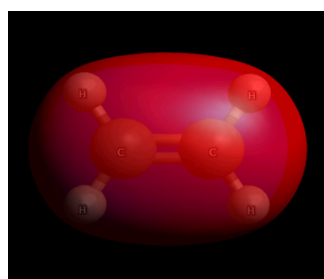
```
-----
ORBITAL ENERGIES
-----
```

```
NO    OCC          E (Eh)          E (eV)
```

0	2.0000	-10.187066	-277.2041
1	2.0000	-10.186376	-277.1854
2	2.0000	-0.747885	-20.3510
3	2.0000	-0.568728	-15.4759
4	2.0000	-0.463263	-12.6060
5	2.0000	-0.417991	-11.3741
6	2.0000	-0.351485	-9.5644
7	2.0000	-0.272541	-7.4162
8	0.0000	0.008706	0.2369
9	0.0000	0.085368	2.3230
10	0.0000	0.104727	2.8498
11	0.0000	0.116508	3.1703
12	0.0000	0.187303	5.0968
13	0.0000	0.327592	8.9142
14	0.0000	0.398945	10.8558
15	0.0000	0.434031	11.8106



LUMO



HOMO

Another way to view molecular orbitals is to use the IboView program. You can download it easily here. (<http://www.iboview.org/index.html>)

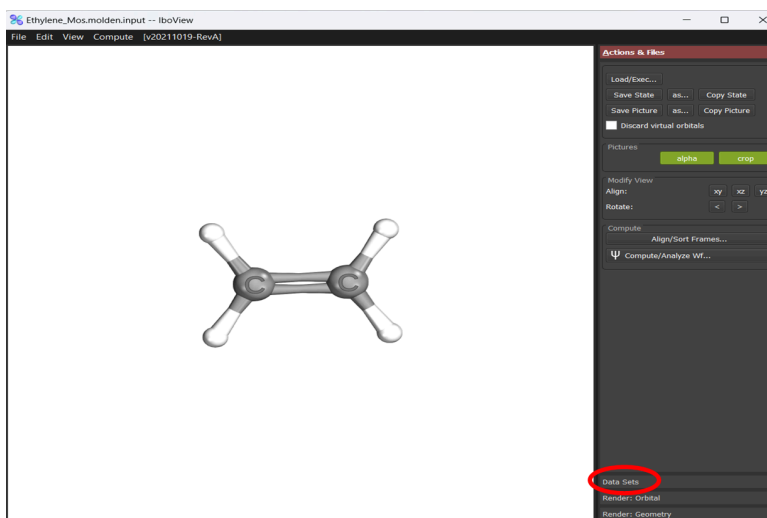
From your last calculation on Ethylene_MOs, go to the MOs folder and write the following command on cmd to generate the molden file:

```
orca_2mkl Ethylene_Mos -molden
```

This command makes the **Ethylene_Mos.molden.input** file on your folder.

Lastly, visualize the molden file with iboView software.

Now drag the Ethylene_MOs.molden.input to iboView software and click on **Data Sets**



To visualize the HOMO, LUMO, and another orbital, double-click on them to see it.
Be careful! In Orca, the number of orbitals starts from 0, but in IboView starts from 1.

In addition to HOMO and LUMO orbitals, other orbitals such as HOMO-1 and LUMO+1, etc. can be seen along with their energies.

Vibrational Frequency

In this step, to calculate the frequency of the ethylene molecule, we use the geometry obtained in the optimization step and perform the run using the “Freq” keyword.

```
! B3LYP def2-SVP Freq
* xyz 0 1
H      1.14763538032723      0.06787867944812      1.04401871500948
C      0.66349268258141     -0.00443412366993      0.06448921374936
H      1.32609585559607     -0.08470073189697     -0.80365926899303
C     -0.66349297051130      0.00443446347416     -0.06448407909659
H     -1.32610760697121      0.08470054881831      0.80365397958594
H     -1.14762334102220     -0.06787883617369     -1.04401856025516
*
```

When the input file is ready, run the frequency calculation with the previous command on your cmd.

orca Ethylene_Freq.inp > Ethylene_Freq.out

After the frequency run is finished, a “.hess” file is created in which the Hessian matrix, vibrational frequencies, and other things are printed. For the Ethylene molecule, the Hessian matrix is 18 × 18:

1.0998914565E-01	8.4248643389E-03	1.1936777570E-01	2.5682342318E-04	6.3817551171E-05
8.4252109177E-03	2.5458529375E-02	2.0259934369E-02	1.2501794297E-02	-8.7829223131E-04
1.1936813731E-01	2.0259074654E-02	2.9542958972E-01	-8.7829119530E-04	1.6938826914E-03
-1.0628103169E-01	-7.8824156633E-03	-1.0983572034E-01	3.5574550200E-04	1.5711348706E-03
-7.4971913624E-03	-3.7718773022E-02	-1.8616541020E-02	5.9814280313E-03	-3.8672256748E-04
-1.0522790055E-01	-1.8688519716E-02	-2.8566931132E-01	6.9200834075E-05	1.4467981507E-03
8.8184932786E-03	-1.0035949944E-03	-1.1185097967E-02	-1.4511358524E-04	3.0634342206E-05
1.1788467141E-03	2.4609581274E-03	-1.1729612049E-03	-8.6933461999E-03	8.0307078300E-04
1.5644329508E-02	-1.5735127911E-03	-1.4008439119E-02	8.0222207376E-04	1.1871138410E-03
-9.1742131674E-03	3.5571206712E-04	1.5712472733E-03	-7.8824464280E-03	-1.0983464984E-01
-2.2007829810E-03	5.9814146721E-03	-3.8668202738E-04	-3.7718495575E-02	-1.8616932468E-02
-2.9862195317E-02	6.9167493460E-05	1.4470819967E-03	-1.8688884953E-02	-2.8567352703E-01
1.4225786877E-03	-1.4512718696E-04	3.0582056654E-05	-1.0035291736E-03	-1.1184840825E-02
-1.4605769928E-04	-8.6932458703E-03	8.0303930560E-04	2.4609941568E-03	-1.1729441844E-03
2.7370726017E-05	8.0222503021E-04	1.1870314000E-03	-1.5735278867E-03	-1.4008279163E-02
-4.7775825619E-03	2.5681215290E-04	6.3791106666E-05	8.4247570687E-03	1.1936624598E-01
2.5682087949E-04	1.2501794365E-02	-8.7829171901E-04	2.5458302578E-02	2.0260304115E-02
6.3801758564E-05	-8.7829156121E-04	1.6938825630E-03	2.0259444585E-02	2.9543384506E-01

18 x 18

Also, you can check the vibrational frequency in “.hess” file:

```
$vibrational_frequencies
18
 0      0.000000
 1      0.000000
 2      0.000000
 3      0.000000
 4      0.000000
 5      0.000000
 6      822.848401
 7      963.665261
 8      970.621779
 9     1058.064878
10     1220.518021
11     1358.373672
12     1442.789529
13     1697.622040
14     3120.310476
15     3137.442553
16     3207.756935
17     3230.464167
```

The first few frequencies are always zero, for they correspond to the **rotational** and **translational** modes.

Vibrational modes:

3N-5 for a linear molecule

3N-6 for non-linear molecule

The “orca_mapspc” program (part of the ORCA package) can be used to create spectra from an ORCA spectroscopy calculation. The program creates simple text files containing energies and intensities that can then be plotted using any plotting program (e.g. GnuPlot, Origin, Excel, ...).

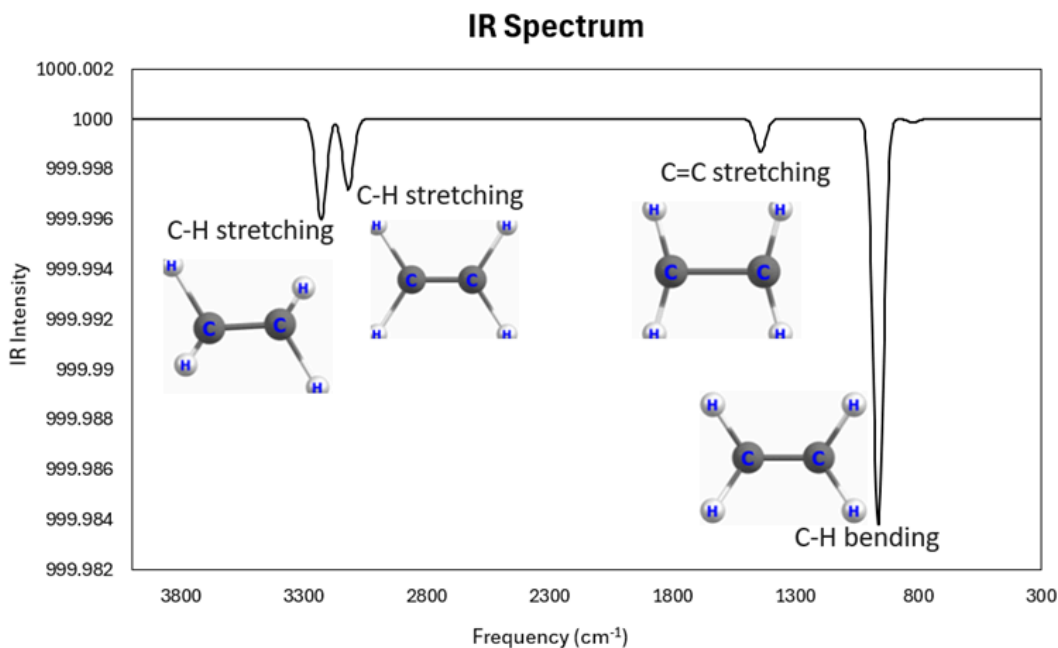
```
D:\orca_5_0_1>orca_mapspc Ethylene_Freq.out IR -x0300 -x14000
Mode is IR
stopping import!
Last line read:
Number of peaks      ...      12
Start wavenumber [cm-1] ...      300
Stop wavenumber [cm-1] ...     4000
Peak FWHM [cm-1]    ...      50
Number of points     ...     1024
```

This creates two files.

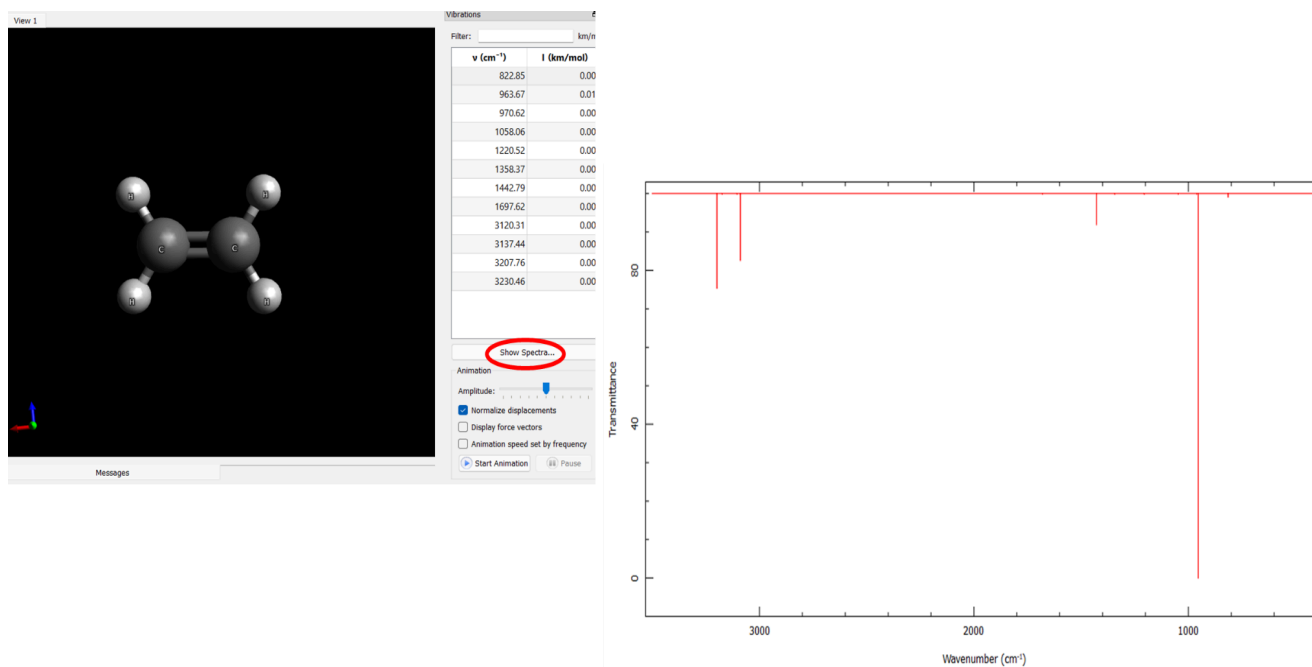


Plotting an IR spectrum in the region 300-4000 cm^{-1} using default broadening:

You can copy the data from Ethylene_Freq.out.ir.dat in Excel to see the IR Spectrum



Also, we can get the IR spectrum by opening the **output** file of **frequency** in Avogadro and clicking **Show Spectra**:



If you want to run vibrational frequency with symmetry, just write the keyword “Usesym” in the input file.

```
! B3LYP def2-SVP Freq Usesym
* xyz 0 1
H      1.242719034      0.000000000      0.931267514
C      0.666634020      0.000000000      0.000000000
H      1.242719034      0.000000000     -0.931267514
C     -0.666634020      0.000000000      0.000000000
H     -1.242719034      0.000000000      0.931267514
H     -1.242719034      0.000000000     -0.931267514
*
```

Finally, to run the “Anharmonic Vibrational Frequency” make this input file, and after running it check the difference between harmonic and anharmonic frequency.

```
! B3LYP def2-SVP ExtremeSCF Freq
!VPT2 # second-order vibrational perturbation theory
```

```

%vpt2
  VPT2          On
  AnharmDisp    0.05  #anharmonic displacement factor
  HessianCutoff 1e-12 # cut-off for Hessian matrix elements
  PrintLevel    4     # VPT2 print level [1, 2, 3, 4]
  MinimiseOrcaPrint True
end

%method
  Z_Tol 1e-14  #The CP-SCF equations should be converged to at least 10-12
end

* xyz 0 1
O   0.0000000000000000  0.06256176106279  0.06256176106280
H   0.0000000000000000 -0.06185639479702  0.99929463373422
H   0.0000000000000000  0.99929463373424 -0.06185639479703
*

```

Fundamental transitions [1/cm]

Mode	w	v	Diff
0	1547.788	1482.523	-65.265
1	4080.758	3909.913	-170.845
2	4191.698	4016.170	-175.528

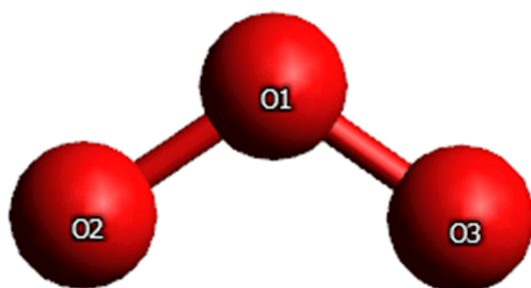
Potential Energy Surface

Intro

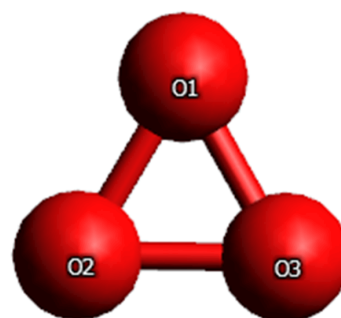
The Born-Oppenheimer (BO) approximation is a widely used approximation in molecular physics and quantum chemistry. It is based on the assumption that the motion of atomic nuclei and electrons in a molecule can be separated. The approximation neglects the kinetic energy of the atomic nuclei when describing the electrons in a molecule. The BO approximation leads to the concept of potential energy surfaces (PES), which are effective potentials for the electronic states on which the nuclei can move. These PES are also known as adiabatic potential energy surfaces. The PES is a function of the nuclear coordinates and describes the energy of the molecule as a function of the positions of the nuclei. The Born-Oppenheimer approximation is valid when the distances separating particles are not unusually small, and the kinetic energy of the nuclei is much larger than the electronic energy.

O₃ Molecule

The O₃ molecule, with a low degree of freedom, serves as a good example for exploring potential energy surfaces. It exhibits two structural isomers: the ozone molecule, considered the more stable form, and iso-ozone. These structures are connected by a transition state, although this exercise does not involve finding it.

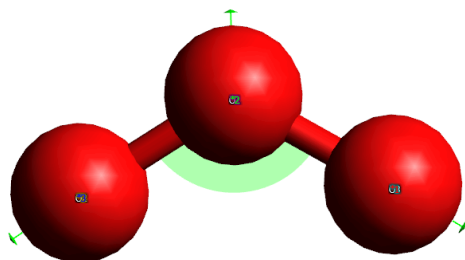


a) Ozone



b) Iso-ozone

Here, you will learn how to explore the potential energy surface of the O₃ structure concerning the O-O bond distance and O-O-O angle, with experimental values of 1.2717 Å and 116.78°, respectively.



Step 1 - Creating the input

Create a new folder named "ozone" Open your preferred text editor, write the following input into a new file, and save it in the "ozone" folder with the name "o3.inp":

```
# Two dimensional PES of O3 structure
!PAL2 # Number of CPUs
!HF 3-21G # Method and Basis Set
!LargePrint PrintBasis # Visualisation Options

%scf
  MaxIter 2000 # Maximum number of iterations
end

%paras
  R = 1.0, 2.0, 21 # O-O bond distance
  Theta = 50, 160, 21 # O-O-O angle
end

* int 0 1 # Coordinate system, charge, and multiplicity
O 0 0 0 0 0
O 1 0 0 {R} 0
O 1 2 0 {R} {Theta} 0
*
```

In this input, within the main block starting with the "!" symbol, three sections are defined. These sections cover the number of processors, the method, and the basis set. The "PAL{N}" keyword specifies the number of CPUs for the job, where "N" is an integer (e.g., PAL2 for two CPUs). Since the focus is solely on learning to explore the potential energy surface, we won't go beyond the Hartree-Fock calculation. A small and simple Pople basis set, 3-21G, is used for the calculation, where "HF" defines the computational method. In the third section of the main block, "LargePrint" and "PrintBasis" options are utilised to visualise the molecular orbital without additional processing, using the Avogadro program.

We define two sub-blocks in this job. The first one is "scf" where we increase the maximum number of iterations using the "MaxIter" option. It's important to note that there is no equal sign in front of "MaxIter" in the input. The next sub-block is "paras," which allows us to scan the two-dimensional potential energy surface (PES) of O₃ by defining two parameters: "R" for the O-O bond distance and "Theta" for the O-O-O angle. "R" includes 21 bond distances between 0.8 Å to 2.0 Å, while "Theta" is defined with 21 angles between 45° to 160°. When defining parameters, the first variable is the starting point, the second is the ending point, and the third is the number of steps. Alternatively, you could provide a list of numbers using brackets. It's worth mentioning that when defining a parameter using a list, you should not use the equal sign.

```
%paras
  R = 1.0, 2.0, 3
end
%paras
  R [1.0 , 1.5, 2.0]
end
```

Finally, we should define the coordinates of the system. The two O-O bonds, having the same value and changing together with the O-O-O angle, constitute the two dimensions of the potential energy surface (PES). It's important to note that the dimension for visualizing the surface is three, as we need to consider the energy dimension along with bond distance and angle.

Step 2 - Running the job

To run your job, open your terminal. On Linux, press Ctrl+Alt+T together; on Windows, press Win+R, type "cmd" and press enter. MacOS users can search for the terminal app. First, navigate to your input directory (the "ozone" folder you created for your O₃ input file) using the "cd" command in all terminals. For instance, if you've stored your "ozone" folder at "C:\Users\Nima\Desktop\ozone" navigate to it using this command:

```
cd C:\Users\Nima\Desktop\ozone
```

Next, you should call ORCA using its full installation path to run parallel jobs. For example, if I installed ORCA in the "C:\orca504" directory, after ORCA's full path, provide the job's input name, followed by the ">" symbol and its output name. Look at the sample command below to run the O₃ job:

```
C:\orca504\orca o3.inp > o3.out
```

Now, you have to wait until the job is done. It may take more than 30 minutes for the job to finish, so please do not interrupt the run. While the job is running, you can check your calculation by looking up the output file. After running the job, you should see the "o3.out" file in your "ozone" directory.

Step 3 - Analysing the output

When the job is done, in the "ozone" directory, there should be plenty of files. Most of them are "gbw" files containing information regarding the calculation at each point of the scan. Along with these files, you should see these files too:

o3.densities, o3.gbw, o3.inp, o3.out, o3.prop, o3.trjact.dat, o3.trjscf.scf, o3_property.txt.

Open the "o3.out" file. First, you should see the ORCA logo and contributions. After scrolling down, you will see the input that you provided for the program:

```
=====
                                INPUT FILE
=====
NAME = O3.inp
| 1> !PAL4
| 2> !HF 3-21G
| 3> !LargePrint PrintBasis
| 4>
| 5> %scf
| 6> MaxIter      2000
| 7> end
| 8>
| 9> %paras
|10> R = 1.0, 2.0, 21
|11> Theta = 50, 160, 21
|12> end
|13>
|14> * int 0 1
|15> 0 0 0 0      0      0
|16> 0 1 0 0      {R}      0
|17> 0 1 2 0      {R}      {Theta} 0
|18> *
|19>
|20>                      ****END OF INPUT****
=====
```

Next, you can see the information regarding the "Parameter Scan Calculation." At the end of this section, you can find the total number of points for energy calculations. These points will ultimately form our potential energy surface (PES).

```
*****
* Parameter Scan Calculation *
*****

Trajectory settings:
  -> SCF surface will be mapped

There are 2 parameter(s) to be scanned
      R: range= 1.00000000 .. 2.00000000 steps= 21
```

```
THETA: range= 50.00000000 .. 160.00000000 steps= 21
There will be 441 energy evaluations
```

By scrolling down, you will see ORCA printing out information about energy calculation at different points. It first provides information about the parameter values in the energy calculation. For example, in the first point, the O-O bond distance is 1.0 Å, and the O-O-O angle is 50°. Next, in two different coordinate systems and two different units, it prints the geometry of the system:

```
*****
                                TRAJECTORY STEP 1
      R : 1.00000000
    THETA : 50.00000000
*****

-----
CARTESIAN COORDINATES (ANGSTROEM)
-----
O      0.000000    0.000000    0.000000
O      1.000000    0.000000    0.000000
O      0.642788    0.766044    0.000000

-----
CARTESIAN COORDINATES (A.U.)
-----
NO LB   ZA   FRAG   MASS           X           Y           Z
  0 O    8.0000  0   15.999    0.000000    0.000000    0.000000
  1 O    8.0000  0   15.999    1.889726    0.000000    0.000000
  2 O    8.0000  0   15.999    1.214693    1.447614    0.000000

-----
INTERNAL COORDINATES (ANGSTROEM)
-----
O      0  0  0    0.000000000000    0.00000000    0.00000000
O      1  0  0    1.000000000000    0.00000000    0.00000000
O      1  2  0    1.000000000000    50.00000000    0.00000000

-----
INTERNAL COORDINATES (A.U.)
-----
O      0  0  0    0.000000000000    0.00000000    0.00000000
O      1  0  0    1.889726133921    0.00000000    0.00000000
O      1  2  0    1.889726133921    50.00000000    0.00000000
```

The basis set information comes next:

```
-----
BASIS SET INFORMATION
-----
```

There are 1 groups of distinct atoms

```
Group 1 Type O : 6s3p contracted to 3s2p pattern {321/21}
```


The SCF calculation starts right after the integral section. In this part, the output provides you with data regarding all aspects of the SCF cycle. Each SCF cycle ends with an output like this:

```

-----
!           ITERATION           14           !
-----
Total Energy      :      -221.506779452259 Eh
Energy Change    :           0.000119555022 Eh
MAX-DP           :           0.000673825481
RMS-DP           :           0.000084280653
Orbital gradient :           0.000429429178
Orbital Rotation :           0.000323667919
Actual Damping   :           0.0000

===> SHARK/Fock/General/Sym: HFTyp=1 DoJ=1 DoX=1 facj= 2.000 facx=-0.500 NFock=1
NumOp=1 NMat=1 RangeSep=0 GeneralContraction=0 PGCOpt=-1
-> L=0 0 0 0:      0.000 sec done=      231 (= 84.6%) skipped=      42
-> L=1 0 0 0:      0.000 sec done=      596 (= 94.6%) skipped=      34
-> L=1 0 1 0:      0.000 sec done=      378 (=100.0%) skipped=       0
-> L=1 1 0 0:      0.000 sec done=      256 (= 94.8%) skipped=      14
-> L=1 1 1 0:      0.001 sec done=      324 (=100.0%) skipped=       0
-> L=1 1 1 1:      0.000 sec done=       66 (=100.0%) skipped=       0
-> RHF LowL loop time =      0.002 sec
->Total SHARK integral loop time =      0.000 sec
->Total LIBINT loop time =      0.000 sec
      **** Energy Check signals convergence ****
      ***Rediagonalizing the Fockian in SOSCF/NRSCF***

      *****
      *                               *
      *                SUCCESS                *
      *                SCF CONVERGED AFTER 15 CYCLES                *
      *                               *
      *****

```

Here you can find details about the SCF calculation:

```

-----
TOTAL SCF ENERGY
-----

Total Energy      :      -221.50678000 Eh      -6027.50592 eV

Components:
Nuclear Repulsion :      107.80316100 Eh      2933.47315 eV
Electronic Energy  :     -329.30994100 Eh     -8960.97906 eV
One Electron Energy:     -514.80196165 Eh    -14008.47355 eV
Two Electron Energy:      185.49202065 Eh      5047.49449 eV

Virial components:
Potential Energy   :     -451.71619565 Eh     -12291.82259 eV
Kinetic Energy     :      230.20941566 Eh      6264.31667 eV
Virial Ratio       :           1.96219687

```

Scrolling down, you find orbital energies, which are valuable pieces of information:

```

-----
ORBITAL ENERGIES
-----

NO   OCC      E (Eh)      E (eV)
 0   2.0000   -20.648031   -561.8615
 1   2.0000   -20.641177   -561.6750
 2   2.0000   -20.622278   -561.1607
 .   . . . .   . . . . .   . . . . .
 .   . . . .   . . . . .   . . . . .
 .   . . . .   . . . . .   . . . . .

-----
MOLECULAR ORBITALS
-----

              0          1          2          3          4          5
-20.64803 -20.64118 -20.62228 -2.68060 -1.53573 -1.29393
 2.00000  2.00000  2.00000  2.00000  2.00000  2.00000
-----
00  1s    -0.019276  0.000027 -0.982954 -0.114780  0.166709  0.000002
00  2s    -0.005745  0.000006 -0.100836  0.148580 -0.166350 -0.000002

```

```

00  1pz      0.000000 -0.000000 -0.000000 -0.000000 -0.000000  0.000000
..  ...      .....
..  ...      .....
..  ...      .....

```

After this, you can find valuable information about the population analysis of the job, and the calculation for the next point in the PES will be started. When the calculation has been done for all trajectories without a problem, you can find information regarding the surface you calculated:

```

          **** TRAJECTORY DONE ***

          SUMMARY OF THE CALCULATED SURFACE

-----
TRAJECTORY RESULTS
-----

Column   1: R
Column   2: THETA

The Calculated Surface using the 'Actual Energy'
 1.00000000  50.00000000 -221.50678000
 1.00000000  55.50000000 -221.85973753
 1.00000000  61.00000000 -222.06051304
 .....
 .....
 .....

The Calculated Surface using the SCF energy
 1.00000000  50.00000000 -221.50678000
 1.00000000  55.50000000 -221.85973753
 1.00000000  61.00000000 -222.06051304
 .....
 .....
 .....

```

At the end you should see the timing of the job:

```

Timings for individual modules:

Sum of individual times      ...      331.513 sec (=  5.525 min)
GTO integral calculation     ...      86.611 sec (=  1.444 min)  26.1 %
SCF iterations               ...      244.903 sec (=  4.082 min)  73.9 %
          ****ORCA TERMINATED NORMALLY****
TOTAL RUN TIME: 0 days 0 hours 7 minutes 43 seconds 394 msec

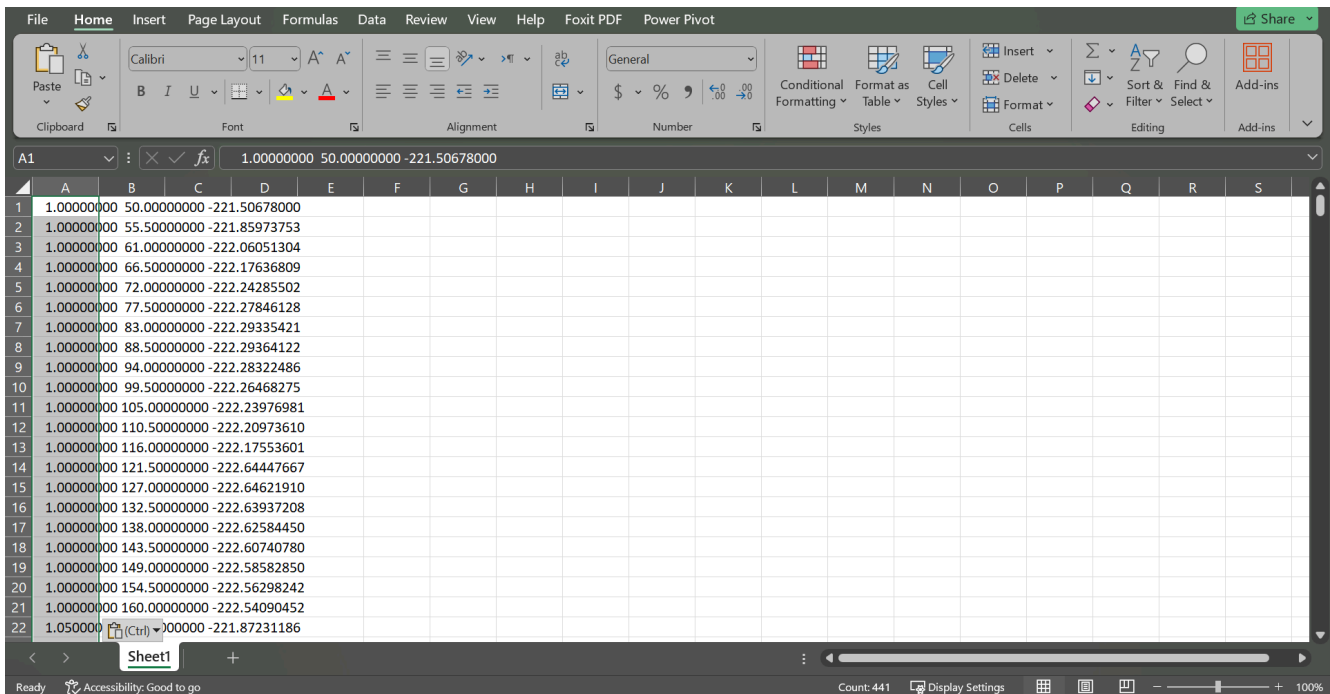
```

Step 4 - Plotting the surface

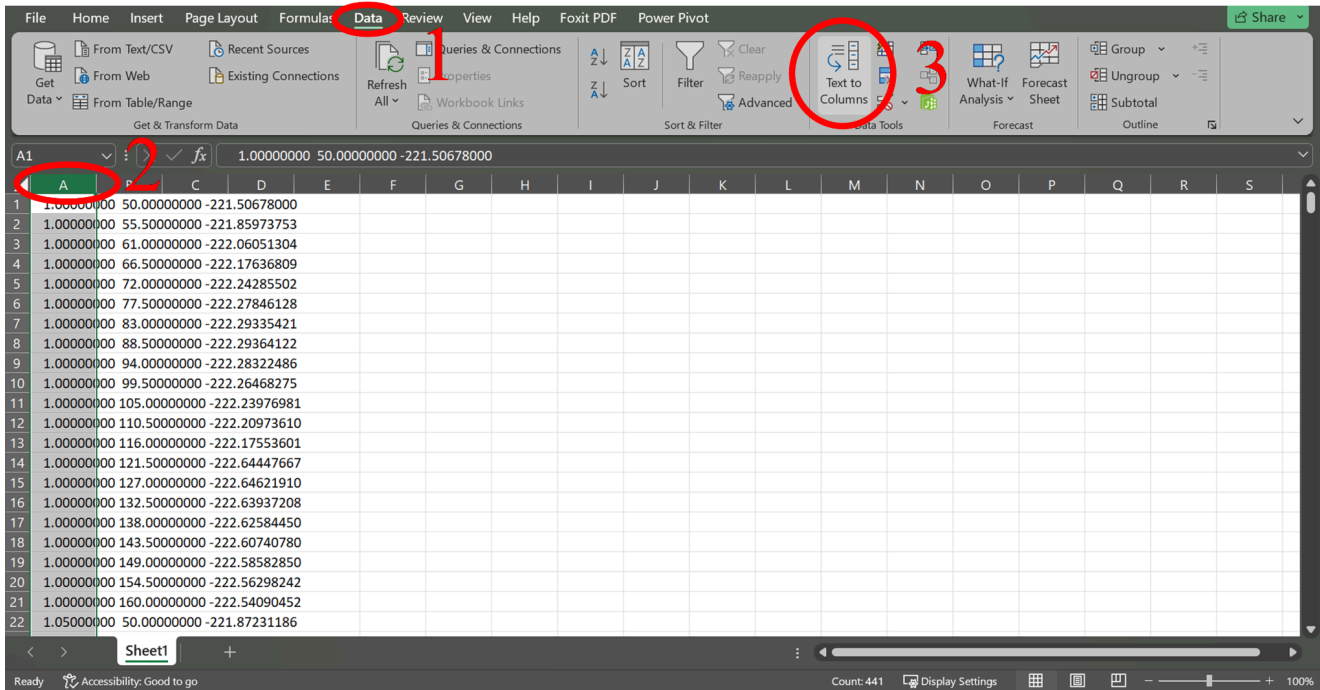
To plot the 3D surface, we offer two options here: one is plotting with Microsoft Excel, and the other is using Python.

Microsoft Excel

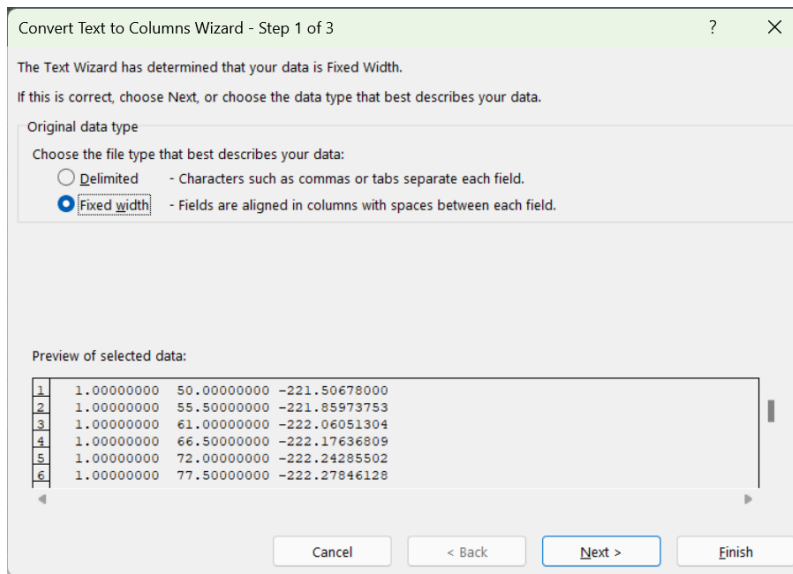
1. Open the output file and copy the data from “The Calculated Surface using the 'Actual Energy””.
2. Open Microsoft Excel and create a “Blank workbook”.
3. Paste the data into cell “A1”:



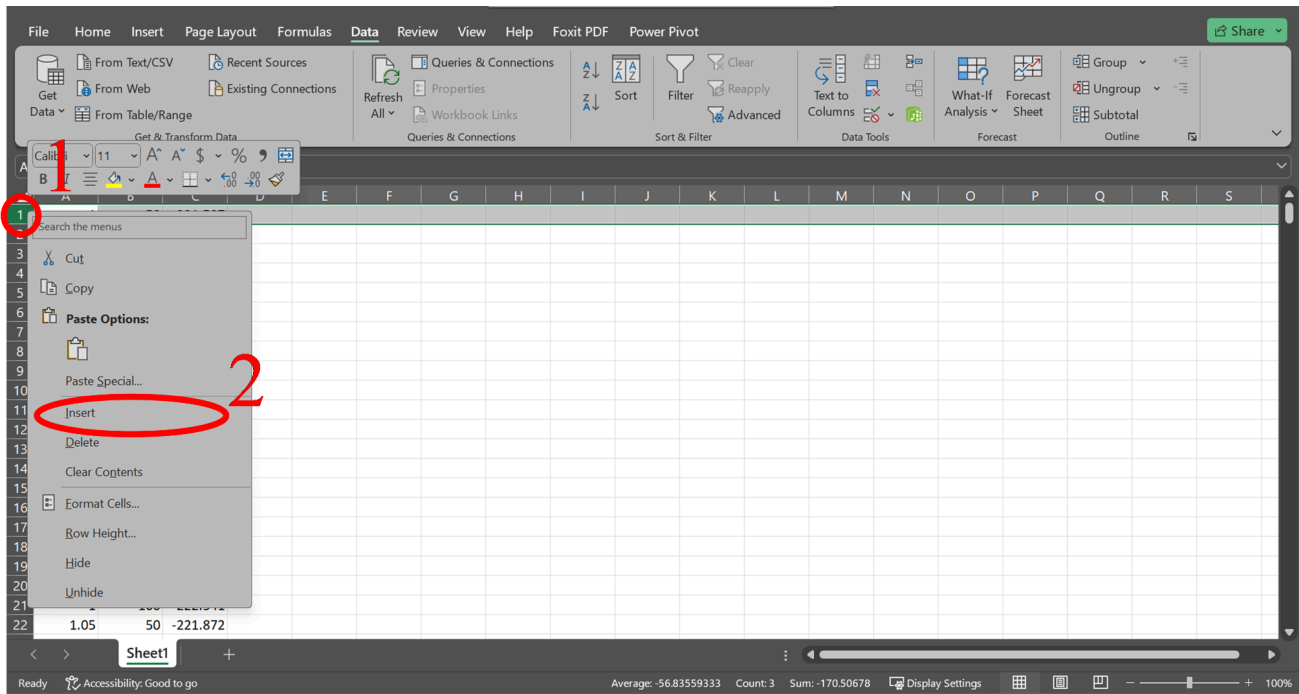
4. Go to the “Data” tab, select “A” column, and select “Text to Column” option:



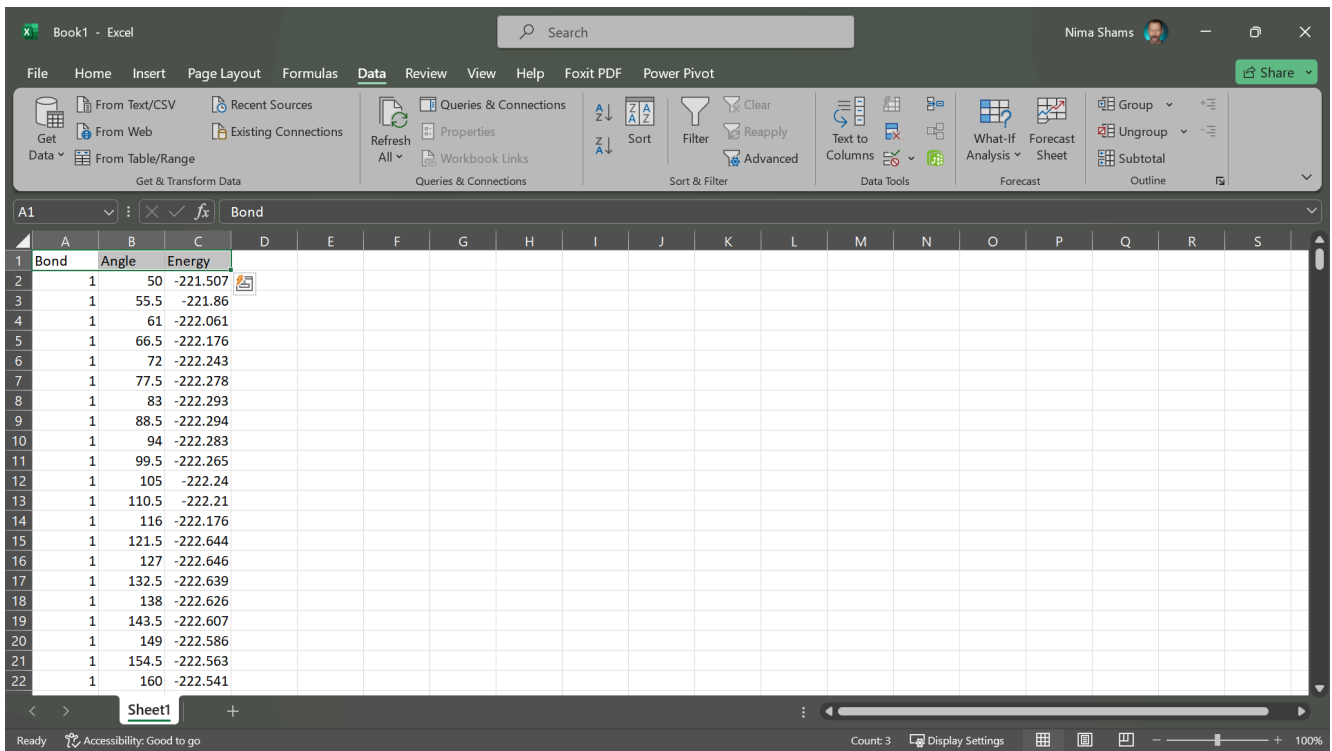
5. Select “Fixed width” option and click on “Finish”:



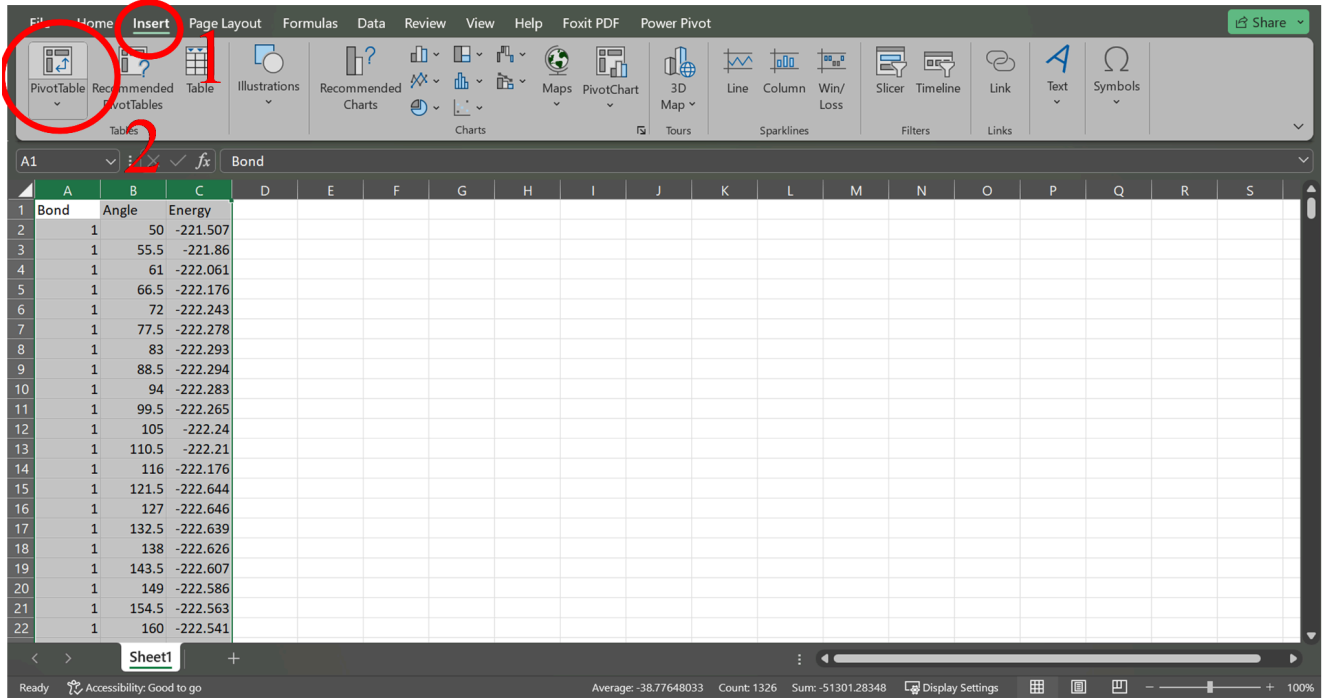
6. Next you must see your data in three separated columns. Right click on the row number one and click on insert:



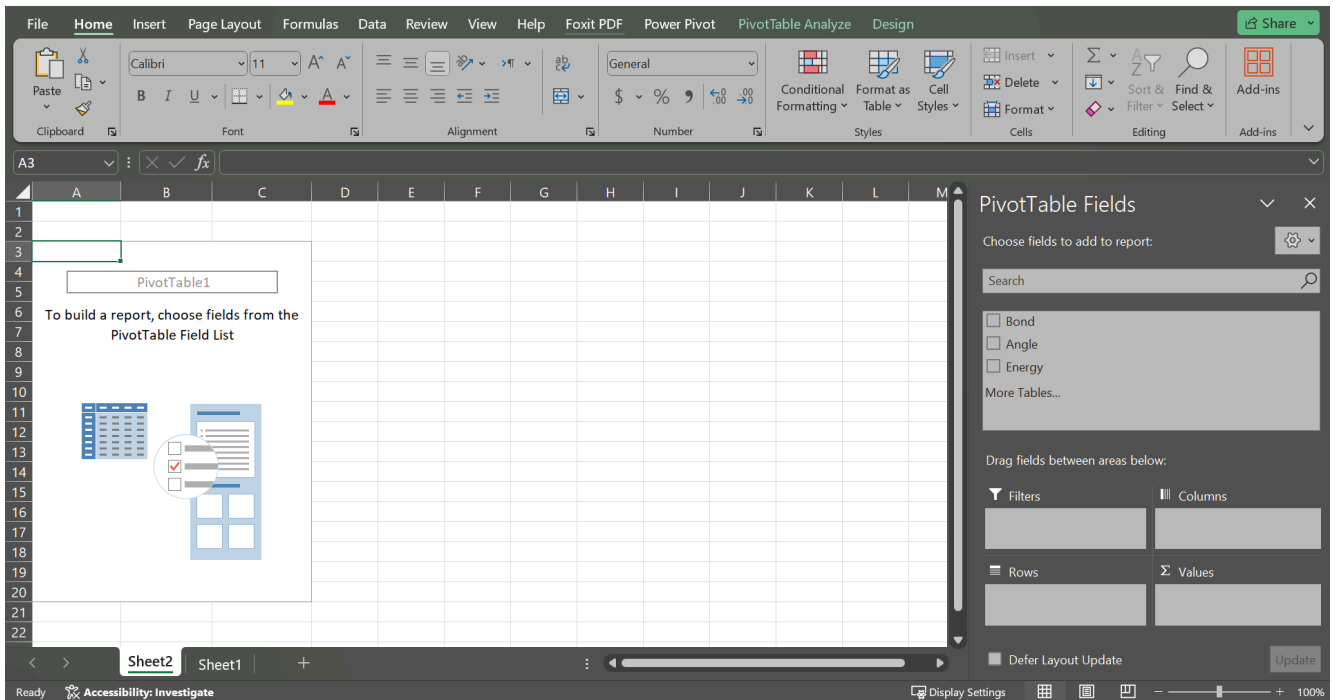
7. Name three first columns Bond, Angle, and Energy:



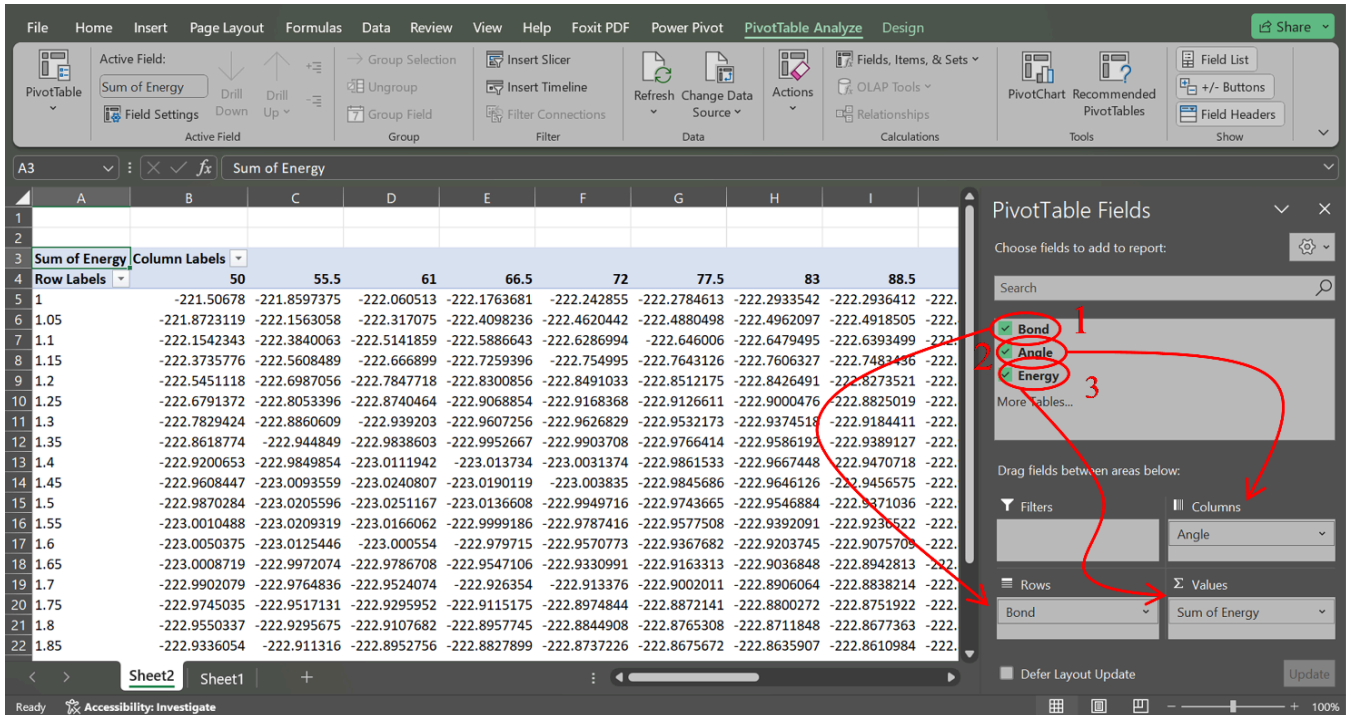
8. Go to the “Insert” tab, select three defined column and click on “PivotTable” Option:



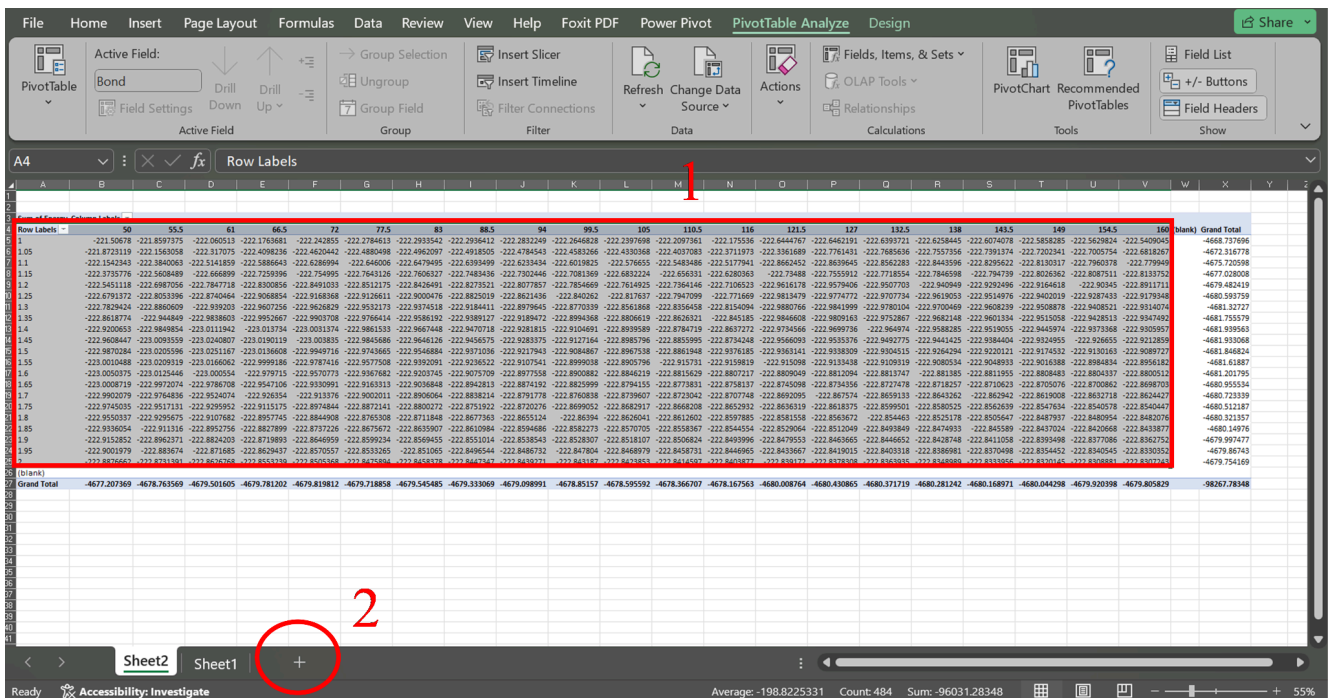
9. Click on “OK”, now you should see a page like this:



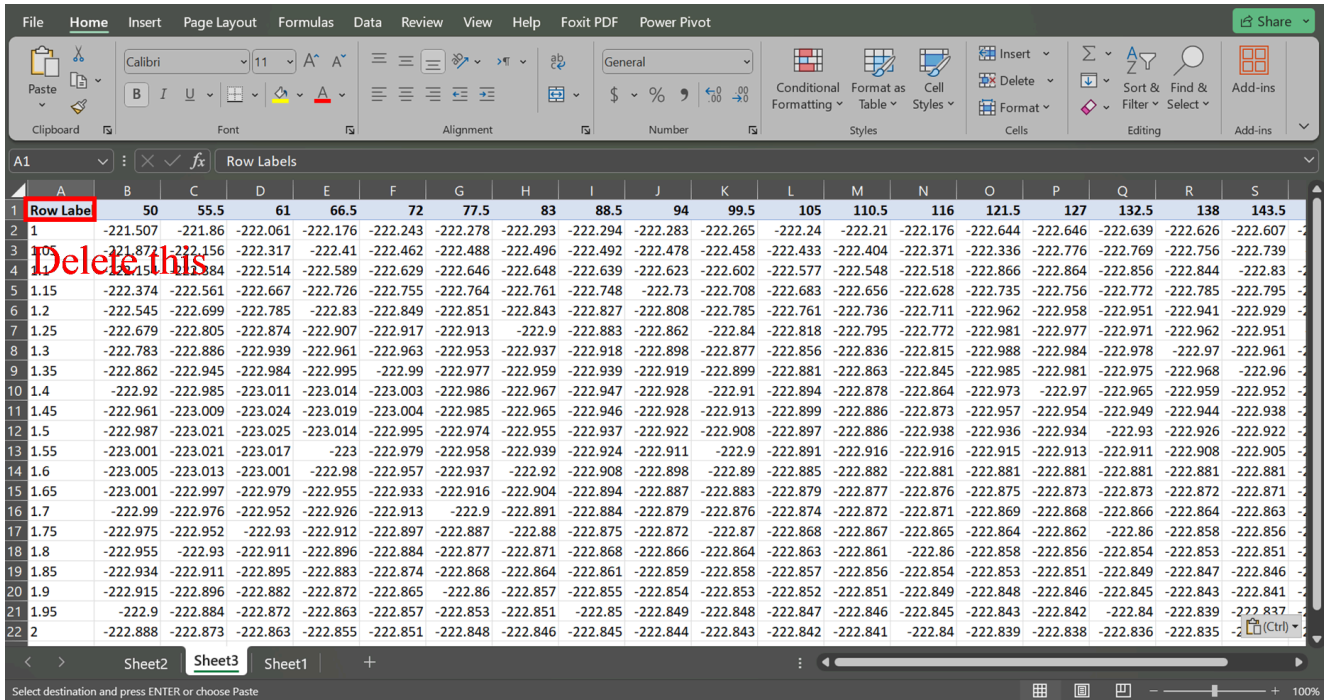
10. Now drag the “Bond” to the “Rows”, “Angle” to the “Columns”, and “Energy” to “Values” like the picture. You will get a table where two parameters are shown in the rows and columns and their corresponding energy value is present in the table:



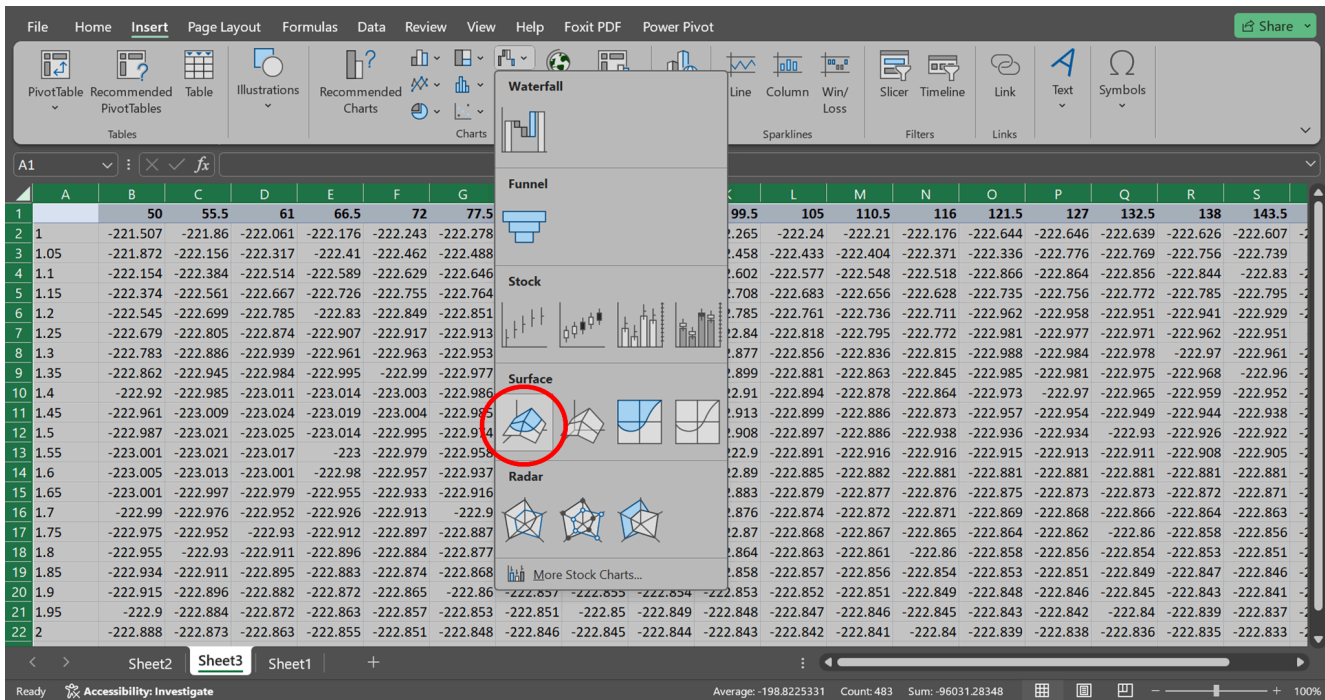
11. Select the table like picture below, copy it, and create a new sheet:



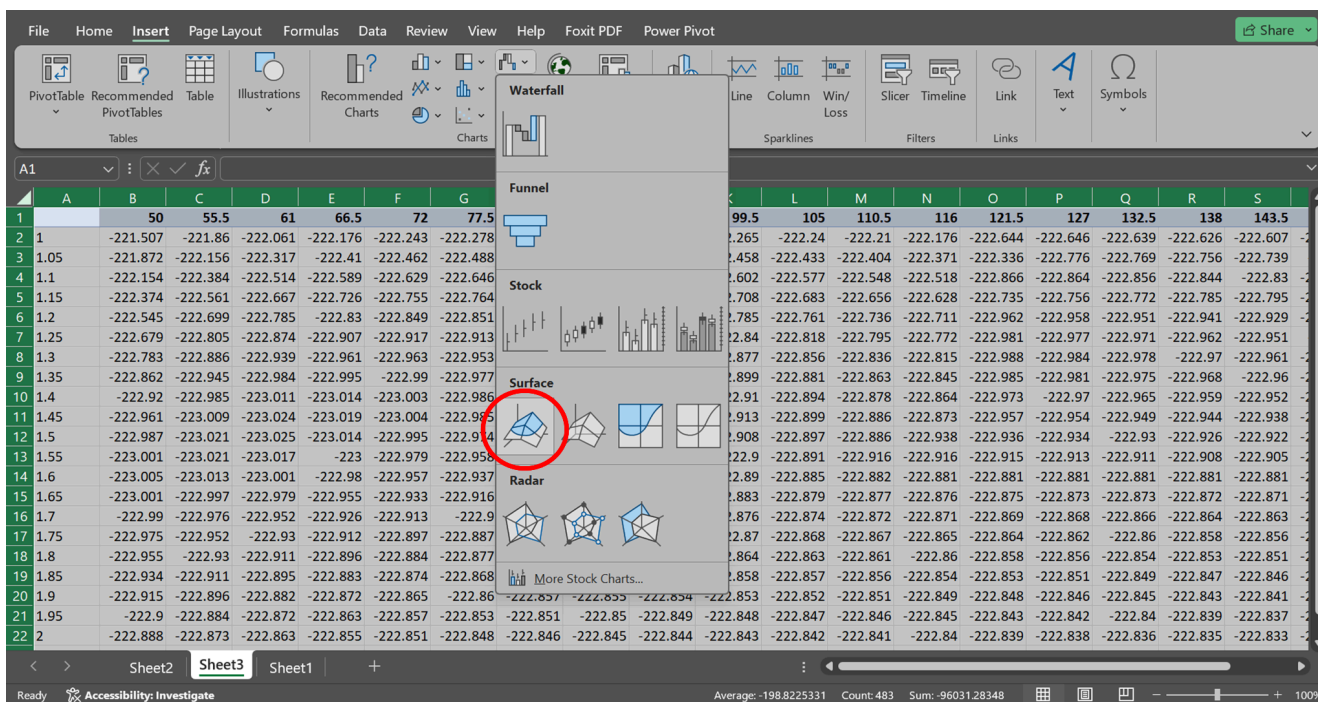
12. In the new sheet paste the table in the “A1” cell. Then select the cell that includes “Row Labels” and delete it by pressing the “delete” key on your keyboard:



13. Go to the “Insert” tab and click on the box between the “A” column and “1” row. Now from the “Chart” section select “Insert Waterfall, Funnel, Stock, Surface, or Radar Chart” option:

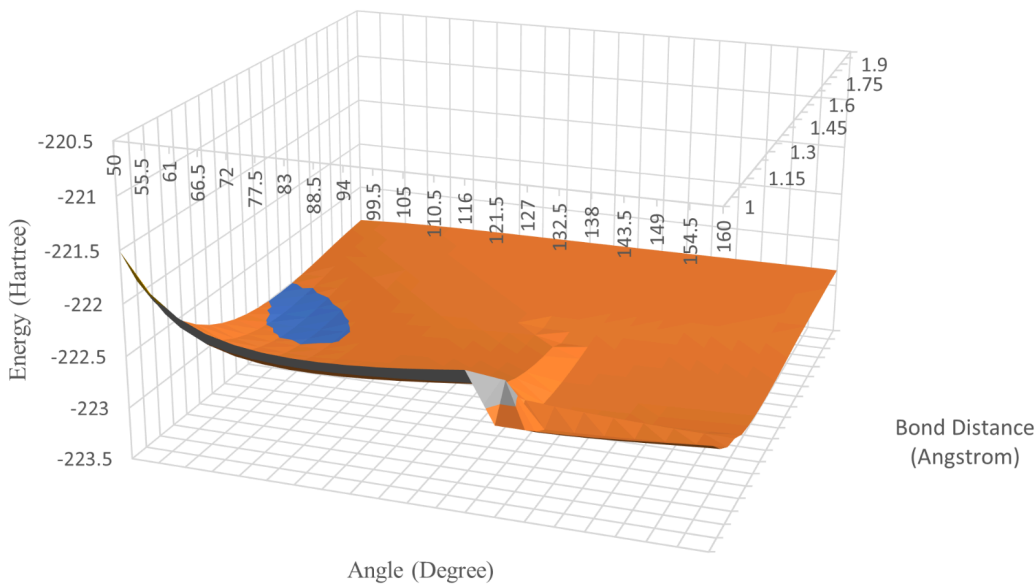


14. From the drop down menu select 3-D Surface:

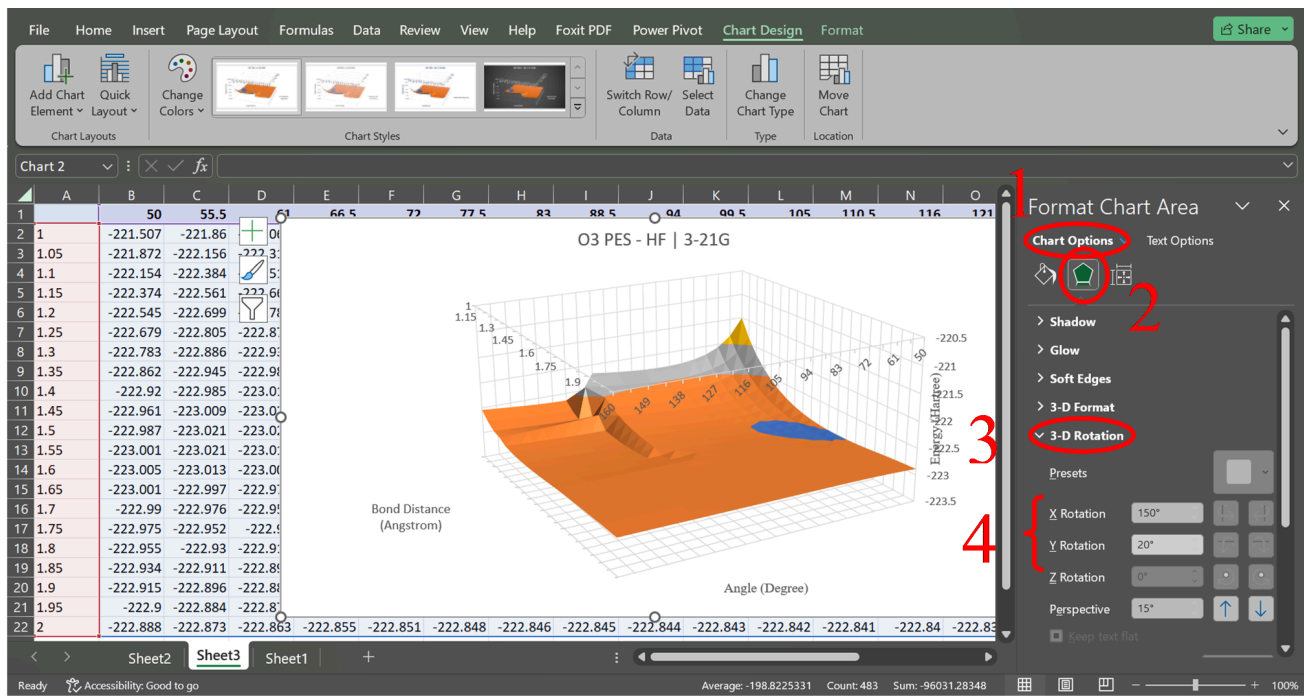


15. Now you should have a chart similar to the one below:

O3 PES - HF | 3-21G



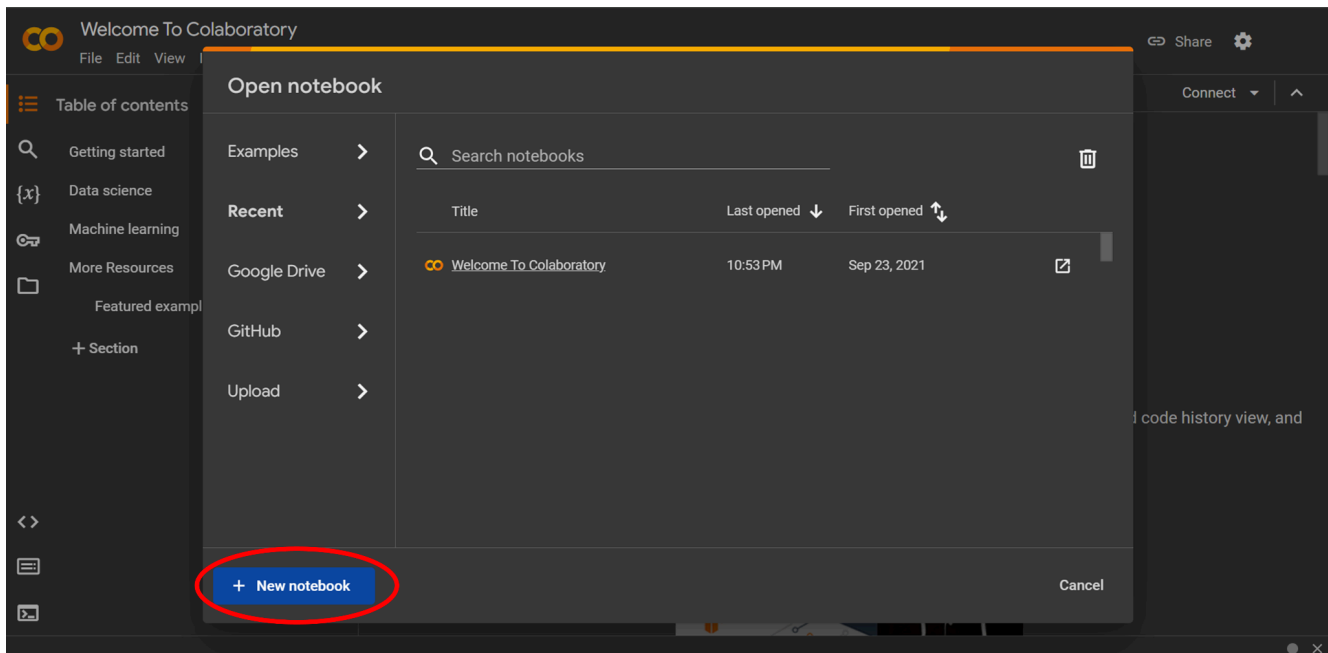
16. You can modify your chart elements using “Add Chart Element” button. You can rotate the surface by doing right-click on the chart and select “Format Chart Area”, in “Chart Option > Effects”, under 3-D rotation section you can change your view:



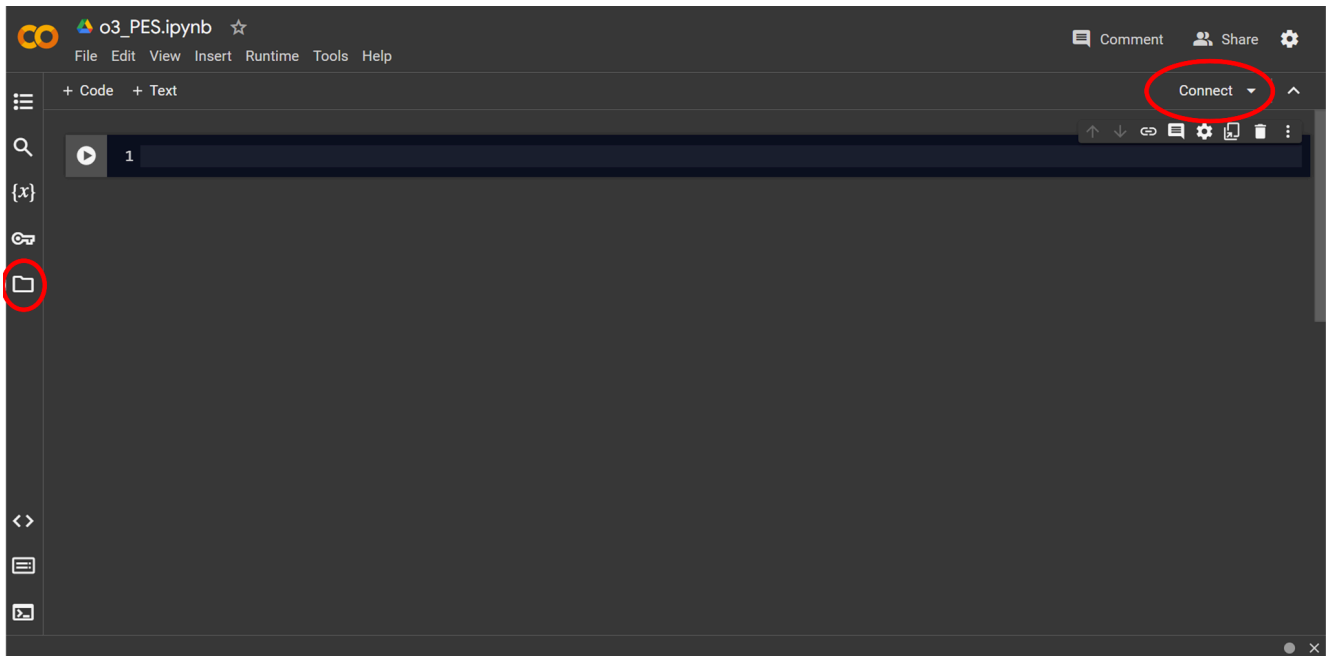
Python

The python version of plotting is just going to a python environment, read your output file, and get the surface plot. Here we use “Google Colaboratory ” which is an online interactive Python notebook. If you have python on your system, all you need is to have the “Numpy”, “Pandas”, and “Plotly” libraries installed on your machine.

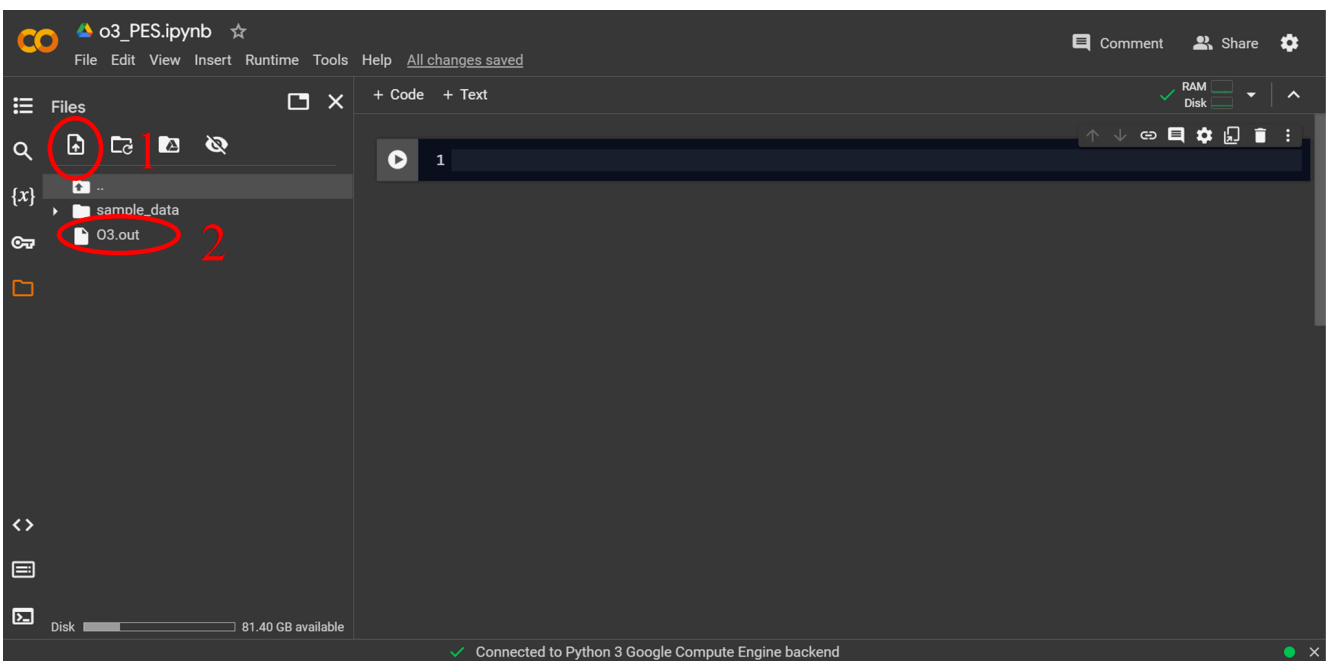
1. Go to [Google Colaboratory](https://colab.research.google.com/) website, sign in and create a new notebook:



2. Click on the “Connect” button, and then open your file explorer from the left-side toolbar:



3. Using the upload button, upload the “o3.out” file. Make sure the upload finishes completely and you can see the “o3.out” file in your file manager:



4. Now copy the following Python code and paste it into the cell, then click on play button:

```

# Importing Libraries
import numpy as np
import pandas as pd
import plotly.graph_objects as go
import re
from io import StringIO

# The directory of output file
out_path = 'O3.out'

# Reading the file
with open(out_path, 'r') as f:
    out = f.read()

# Creating a pattern to find the scan data
regex = r"The Calculated Surface using the 'Actual Energy'\s(?:\s+\d+\.\d+\s+\d+\.\d+\s+\d+\s+?\d+\.\d+\s+)"

# Finding matches
matches = re.findall(regex, out)
matches = '\n'.join(matches[0].split('\n')[1:])

# Loading and processing data
data = np.loadtxt(StringIO(matches))
df = pd.DataFrame(data, columns=['R', 'A', 'E'], dtype=float)

sorted_df = df.sort_values(by='E')

# Print information about minimums
mins1 = sorted_df[sorted_df['A'] > 100].iloc[:10,:]
print(f'10 min energies around 100 - 120 degrees:\n{mins1}\n')

mins2 = sorted_df[sorted_df['A'] < 100].iloc[:10,:]
print(f'10 min energies around 50 - 70 degrees:\n{mins2}\n')

# Surface plotting

X = df['R'].unique()
Y = df['A'].unique()
Z = df.pivot_table(columns='R', index='A', values='E').values

data= go.Surface(x=X,
                 y=Y,
                 z=Z,
                 contours = {"x": {"show": True, "size": 0.05, "color":"white"},
                             "y": {"show": True, "size": 0.05, "color":"white"}},)

fig = go.Figure(data)

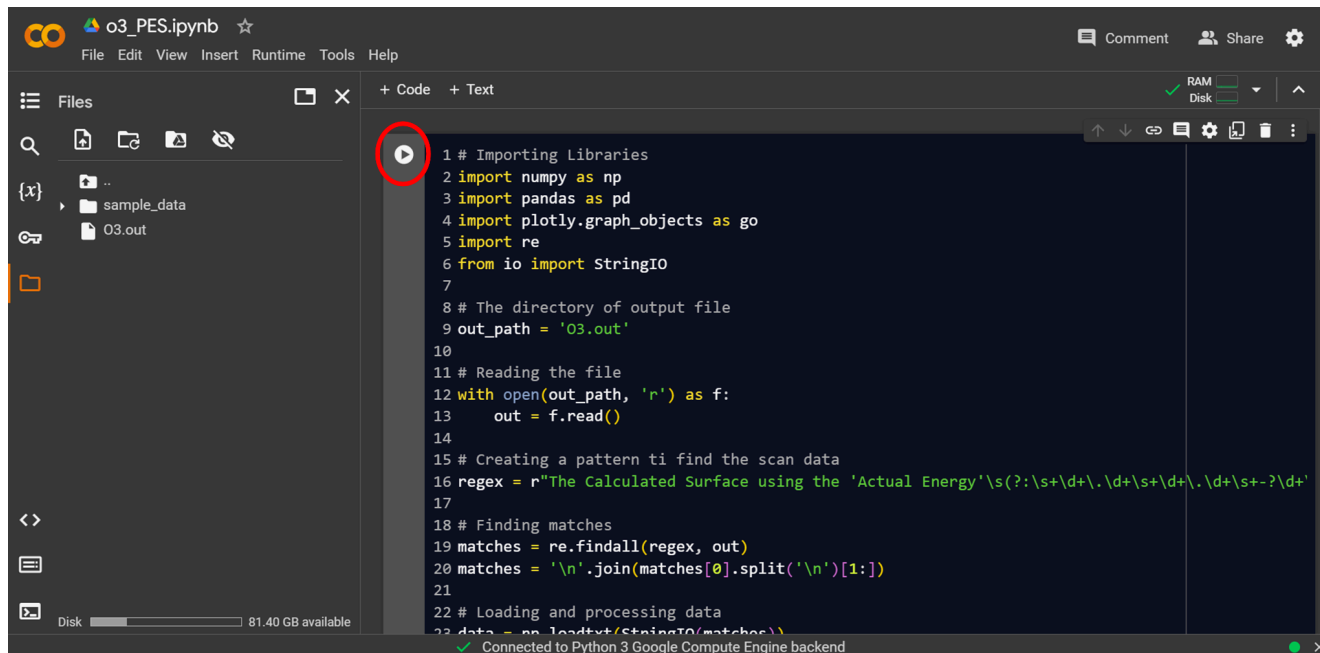
fig.update_traces(contours_z=dict(show=True, usecolormap=True,
                                 highlightcolor="limegreen", project_z=True))

fig.update_layout(title='O3 PES - HF | 3-21G',
                  scene = {"xaxis": {"nticks": 10}, "yaxis": {"nticks": 10}, "zaxis":
{"nticks": 5},
                  "xaxis_title" : "O-O Bond Length (Angstrom)",
                  "yaxis_title" : "O-O-O Angle (Degree)",
                  "zaxis_title" : "Energy (Hartree)",
                  "aspectratio": {"x": 1, "y": 1, "z": 1}})

fig.show()

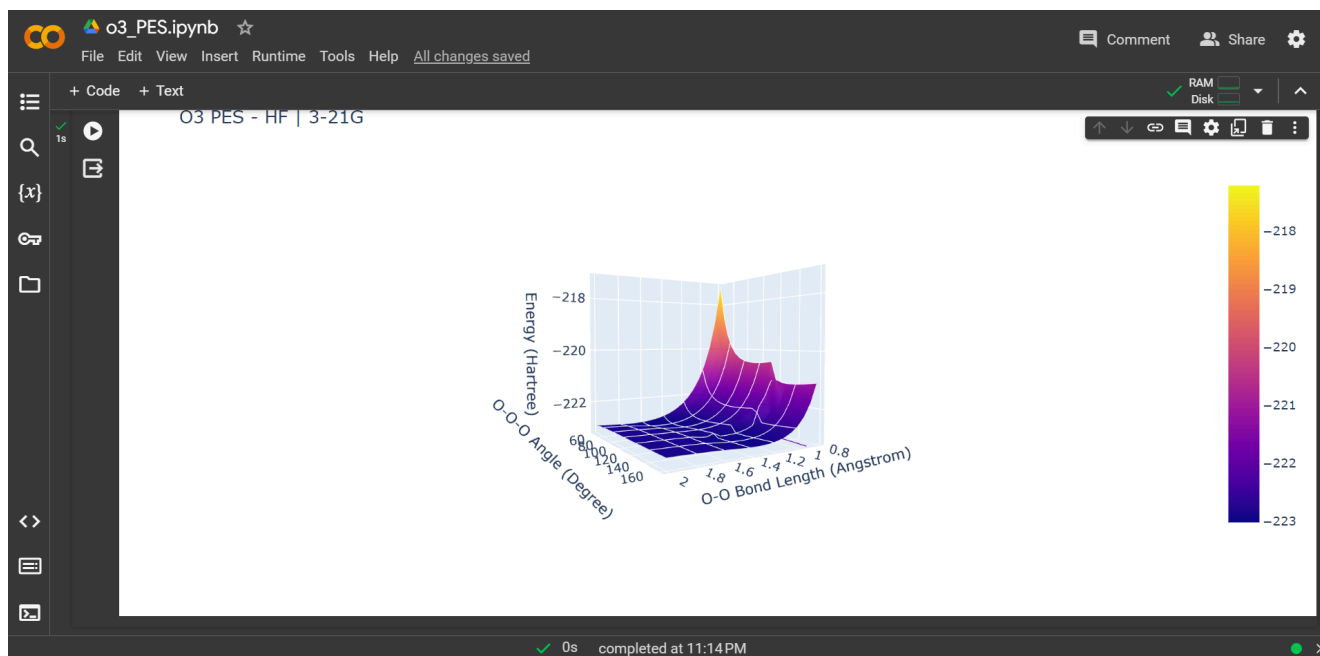
```

Like the picture below:



```
1 # Importing Libraries
2 import numpy as np
3 import pandas as pd
4 import plotly.graph_objects as go
5 import re
6 from io import StringIO
7
8 # The directory of output file
9 out_path = 'O3.out'
10
11 # Reading the file
12 with open(out_path, 'r') as f:
13     out = f.read()
14
15 # Creating a pattern to find the scan data
16 regex = r"The Calculated Surface using the 'Actual Energy'\s(?:\s+\d+\.\d+\s+\d+\.\d+\s+)-?\d+"
17
18 # Finding matches
19 matches = re.findall(regex, out)
20 matches = '\n'.join(matches[0].split('\n')[1:])
21
22 # Loading and processing data
23 data = np.loadtxt(StringIO(matches))
```

Now you can see interactive PES of O₃ molecule:



C2H4 Molecule

Rigid Scan:

Run the following input:

```

! PBE Opt 6-31G AUTOAUX NormalPrint RijCosX TightSCF

%PAL NPROCS 4 END

%scf
  MaxIter 200
  #CNVDIIS 1
  CNVSOSCF 1
end

%output
  print[p_mos] true
  print[p_basis] 5
end

%geom Scan
  B 0 1 = 2, 0.8, 25
  end
  invertConstraints true
end

* xyz 0 1
  C   -2.15132745530608   -0.27856333272197   -0.00000000267306
  C   -0.80797254523934   -0.27856333340366   -0.00000000200138
  H   -2.73123729815909    0.02124697449207   -0.87971351420847
  H   -2.73123728426517   -0.57837364121745    0.87971351556187
  H   -0.22806270325592    0.02124697540171   -0.87971351350182
  H   -0.22806271377440   -0.57837364255070    0.87971351682286
*

```

Relaxed Scan:

Run the following input:

```

! PBE Opt 6-31G AUTOAUX NormalPrint RijCosX TightSCF

%PAL NPROCS 4 END

%scf
  MaxIter 200
  #CNVDIIS 1
  CNVSOSCF 1
end

```

```

%output
  print[p_mos] true
  print[p_basis] 5
end

%geom Scan
  B 0 1 = 2, 0.8, 25
  end
end

* xyz 0 1
C   -2.15132745530608   -0.27856333272197   -0.00000000267306
C   -0.80797254523934   -0.27856333340366   -0.00000000200138
H   -2.73123729815909    0.02124697449207    -0.87971351420847
H   -2.73123728426517   -0.57837364121745    0.87971351556187
H   -0.22806270325592    0.02124697540171    -0.87971351350182
H   -0.22806271377440   -0.57837364255070    0.87971351682286
*

```