

Computational modelling using WebMO

(<http://www.webmo.net/>)

This assignment show you how to use the WebMO computational modelling web interface. WebMO is a browser-based tool that provides a simple user interface for computational chemistry programs (e.g. Gaussian). WebMO makes it easy to create the complicated text-based input files needed to run simulations. Thus, with just a little practice, you can run simulations and use them to help you understand chemistry.

- Useful links:
 - WebMO help manual: <https://www.webmo.net/link/help/>
 - Quick video tutorials: <https://www.youtube.com/user/WebMOLLC>
 - Intro, Login - <https://youtu.be/9M15aO3exxY>
 - Building a molecule - https://youtu.be/_YHpr4lAyQw
 - Geometry Optimization 1 - <https://youtu.be/qouStq8M-ig>
 - Geometry Optimization 2 - <https://youtu.be/IBOpOygd2rs>

At UBC, we have dedicated web resources for WebMO that are already linked to the appropriate computer systems. To access the UBC WebMO interface follow the given series of steps:

1. Login to UBC Canvas : <https://canvas.ubc.ca> using your login information
2. Click on CHEM 218
3. Find and click on “Abacus”

During this assignment we will be using the B3LYP functional and 6-31G(d) basis set for **all** calculations. These parameters will be specified in the “Configure Gaussian Job Option” window as shown in Fig. 1.

Calculation, Charge, and Multiplicity will be specified depending on the task. The Job name

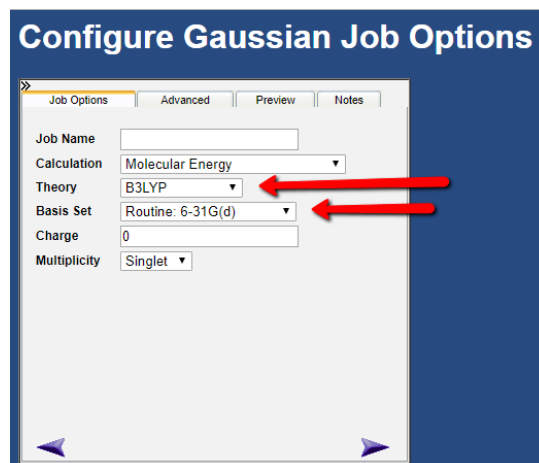
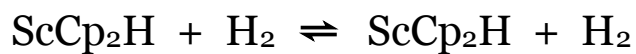


Figure 1 – “Configure Gaussian Job Options” window showing theory and basis set as required in this assignment

will be suggested, but you can choose any name.

CHEM 218:
Modelling mechanism of the reaction:
 $\text{ScCp}_2\text{H} + \text{H}_2$
using WebMO and Gaussian.



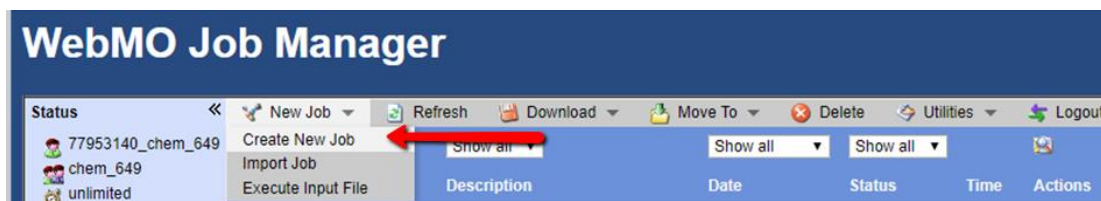
For this exercise, we will be using WebMO to explore mechanism of the σ -bond metathesis reaction of the ScCp_2H complex with H_2 .

By the end of this assignment you will be able to:

- Build a molecule in WebMO and optimize it's structure
- Optimize the geometry of given reactants and products
- Recognize and optimize a transition state of a given reaction
- Calculate vibrational frequencies
- Calculate energetics of a given reaction

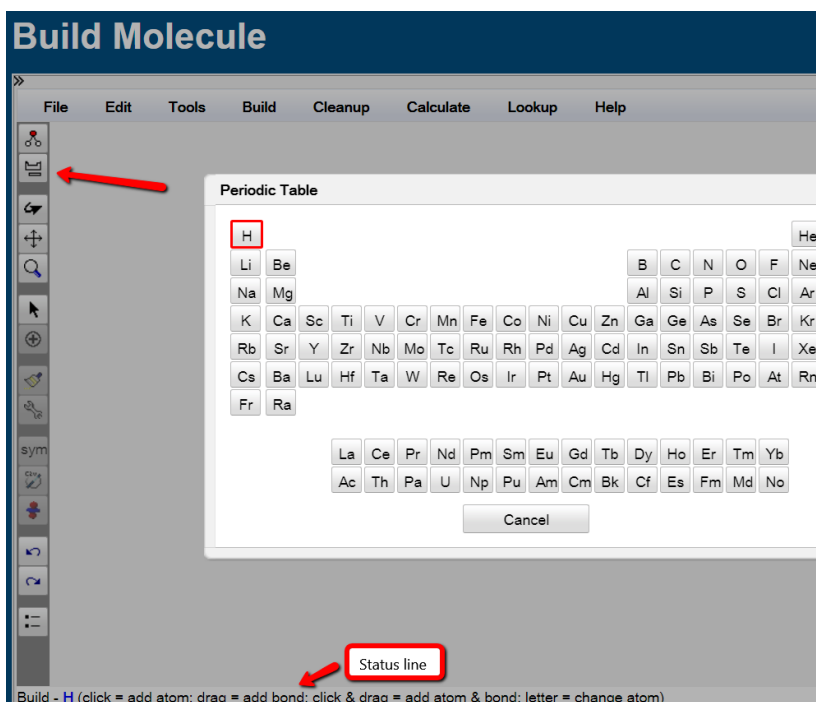
Step 1. Build an H₂ molecule

- 1.1. Click “New Job” on the top left of the WebMO Job Manager page.
- 1.2. Click “Create New Job” from the drop down menu.








You are now in the “Build Molecule” page.

- 1.3. Click on the “Periodic Table’ icon  and select H.



Notice WebMO editor status bar at the bottom of the page. This bar indicates the current atom: hydrogen. The status bar also shows what operations are permitted currently.

- 1.4. To add an atom, simply click anywhere in the editor window having selected H in 1.3.
- 1.5. To add a bond and a second atom, click on an existing atom and drag the pointer to a new location.
- 1.6. To check the bond length, first click on the adjust icon 

- 1.7. Click on the atoms at either end of the bond.
- 1.8. A new button will appear to the left , allowing you to read and change the bond length. Try to guess the H-H bond length.
- 1.9. Click on the “Adjust Bond Length” icon  and insert a value.
- 1.10. Use the “Cleanup” tool: Comprehensive-Idealized  or Comprehensive-Mechanics  to adjust the bond length to a reasonable value.

Clean up tool terminology:

Idealized geometry sets all bond lengths to average values (based on the sum of atomic radii and then scaled for bond order) and all bond angles to ideal VSEPR values (based on the hybridization of the central atom in the angle).

Mechanics geometry uses an extended MM2 force field to adjust the bond lengths, bond angles, and dihedral angles (based on a simple algorithm to minimize strain energy).

For more information see:


<https://www.webmo.net/link/help/Cleanup.html>

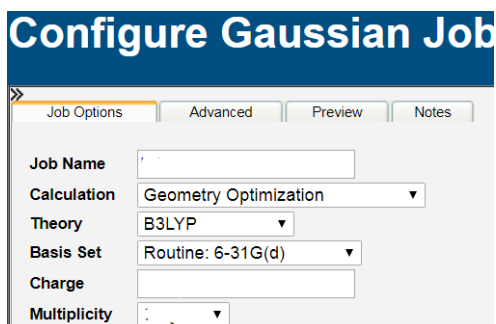
- 1.11. Apply the Cleanup tool and check the bond length.

The comprehensive cleanup tool may also be used to add hydrogen atoms and idealize all bond lengths (and angles in the case there is an angle).

- 1.12. Check the value of the H-H bond length after using a “Cleanup” tool. The resulting structure of a molecule after using a clean-up tool is often a good guess for the starting geometry for a geometry optimization calculation.

Step 2. Geometry optimization of H₂ molecule


- 2.1. Click on the right button arrow  to continue. You should now see the “Configure Gaussian Job Options” window.
- 2.2. To optimize the molecular geometry, we will need to configure the Gaussian Job Options according to the following specifications:

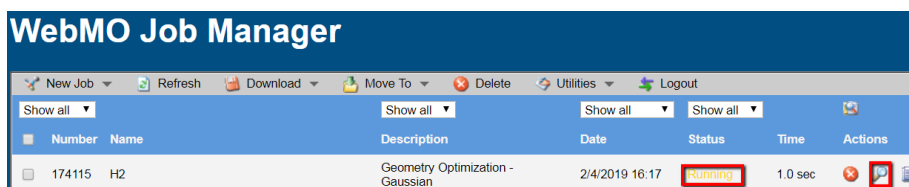



Job Name: H2 optimization
Calculation: Geometry optimization
Theory: B3LYP
Basis Set: Routine: 6-31G(d)
Charge: 0
Multiplicity: Singlet


For more information on “Configure Gaussian Job Options” see:

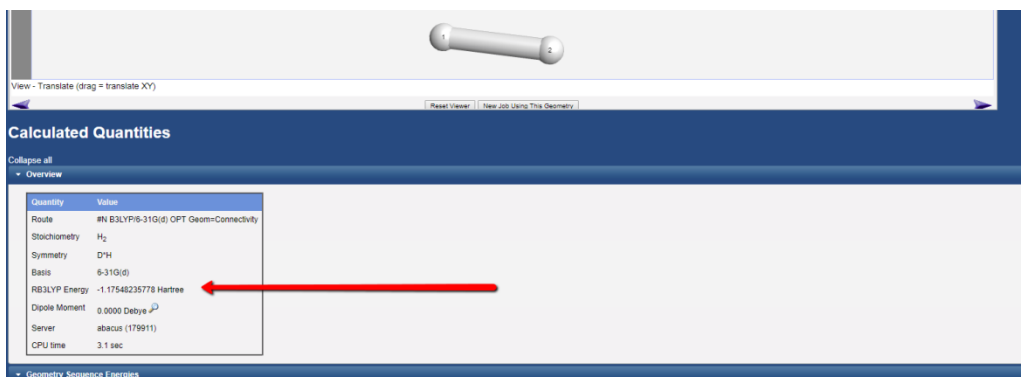
<https://www.webmo.net/link/help/JobOptions.html>

- 2.3. Click Continue (the bottom-right arrow ) to submit the calculation to the Gaussian server calculation queue.
“Job Manager” windows should show this job under the status “Running”. This window can be refreshed and no work will be lost.



Number	Name	Description	Date	Status	Time	Actions
174115	H2	Geometry Optimization - Gaussian	2/4/2019 16:17	Running	1.0 sec	


- 2.4. When the job status changes to ‘complete’, click on the ‘view job’ icon  to view the result of the calculations. The molecule should now be in view again.
- 2.5. Scroll down in order to see the Calculated Quantities. The calculated energy of the molecule should be: RB3LYP Energy = -1.1754824 Hartree.




Quantity	Value
Route	#N B3LYP/6-31G(d) OPT Geom=Connectivity
Stoichiometry	H ₂
Symmetry	D [∞] H
Basis	6-31G(d)
RB3LYP Energy	-1.17548235778 Hartree
Dipole Moment	0.0000 Debye
Server	abacus (179911)
CPU time	3.1 sec

Step 3. Calculate vibrational frequencies:

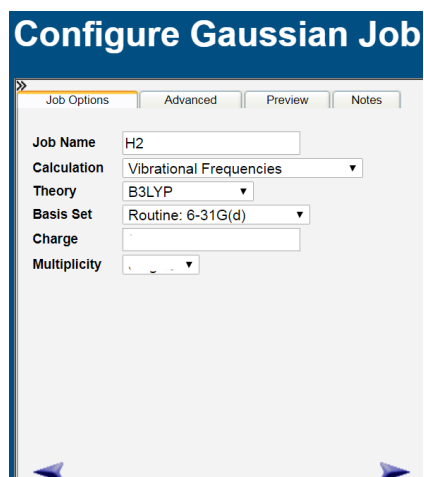
In order to calculate Vibrational Frequencies we must always start from an optimized structure.

3.1. A new job may be started using the final geometry of the any completed job (Geometry Optimization) by going to the “View Job” window (clicking on  in the Job Manager as we did in 2.4).

3.2. Click on “New Job Using This Geometry”

3.3. Click on Continue  to go to “Configure Gaussian Job Options”.

In order to calculate Vibrational Frequencies, we will need to configure the Gaussian Job Options according to these specifications below:



Configure Gaussian Job

Job Options | Advanced | Preview | Notes

Job Name: H2

Calculation: Vibrational Frequencies

Theory: B3LYP

Basis Set: Routine: 6-31G(d)

Charge:

Multiplicity: Singlet

Job Name: H2 Vib Freq

Calculation: Vibrational Frequencies

Theory: B3LYP

Basis Set: Routine: 6-31G(d)

Charge: 0

Multiplicity: Singlet

One of the reasons we calculate vibrational frequencies is to obtain various thermodynamic quantities at a given temperature and pressure (standard condition by default) such as: Enthalpy, Gibbs Free Energy, Entropy etc.

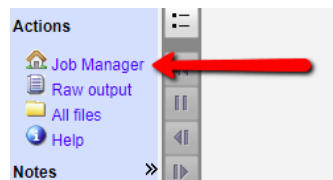
3.4. Click on Continue  to submit the calculation to Gaussian.

3.5. When the job is completed, look for the calculated thermodynamic quantities for H₂ (scroll down). This information you will need later to answer a few of the questions at the end of this tutorial.

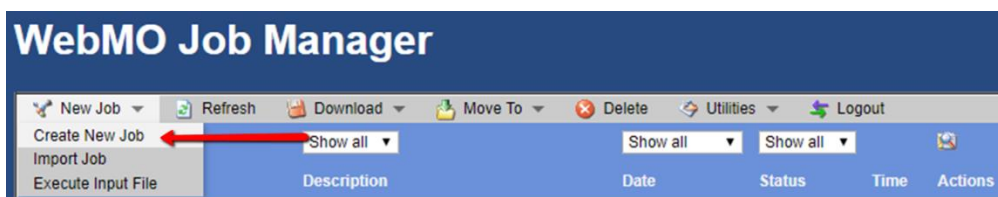
Step 4. Import a molecule to WebMO

Rather than designing a molecule from scratch; we will import an existing ScCp₂H molecule to WebMO.

- 4.1. Go back to the “Job Manager” page by clicking it on the left hand side of the screen.

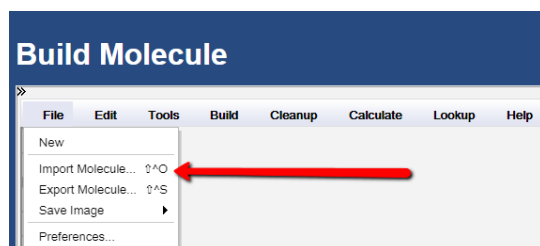


- 4.2. Click “New Job” on the top left of the WebMO Job Manager page.
- 4.3. Click “Create New Job” from the drop down menu.

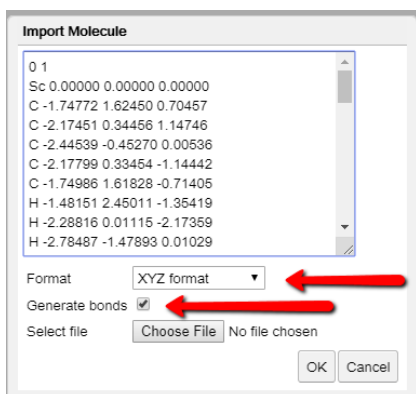


You are now in the “Build Molecule” page.

- 4.4. From the top menu, choose “File” and select “Import Molecule”.



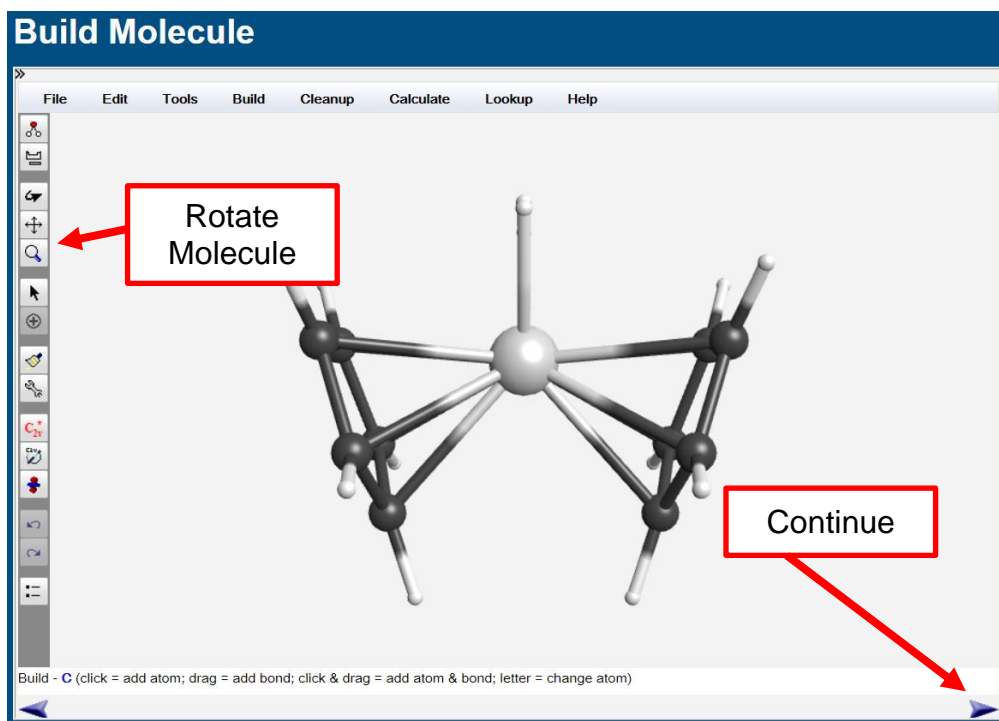
- 4.5. In the new window, paste the XYZ coordinates of the ScCp₂H reactant (these are provided in Appendix A part 1 at the end of this document).
- 4.6. Select Format as “XYZ format” and check the “Generate Bonds” option.



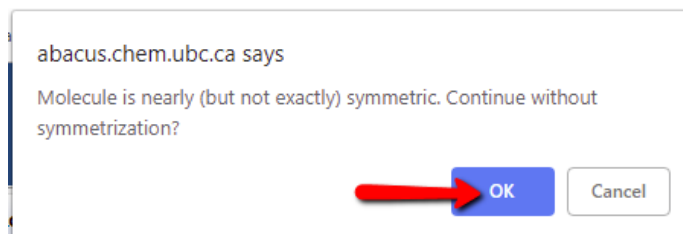
The first line (0 1) corresponds to charge and multiplicity while the lines following (e.g- Sc 0.00000 0.00000 0.00000) correspond to the name of the element and its xyz coordinates. The coordinates are of optimised structure for ScCp₂H, calculated using DFT methods with the B3LYP functional and 6-31g(d) basis set.

4.7. Click OK. You should now see the ScCp₂H complex.

At this point you can view the molecule, rotate it, and have a look at bond lengths and angles. It is important that you do not change the molecule. If you do change it at this point, you will need to re-import and start again.



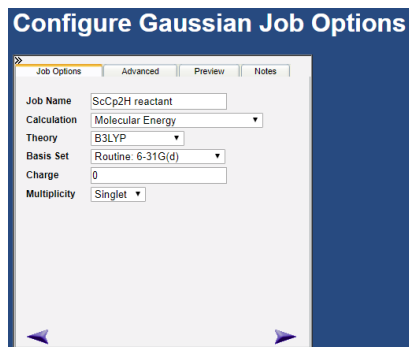
4.8. Click on the right bottom arrow to continue. A pop up screen might show warning about symmetry, but if it does just press OK.




You should now see the “Configure Gaussian Job Options” window.

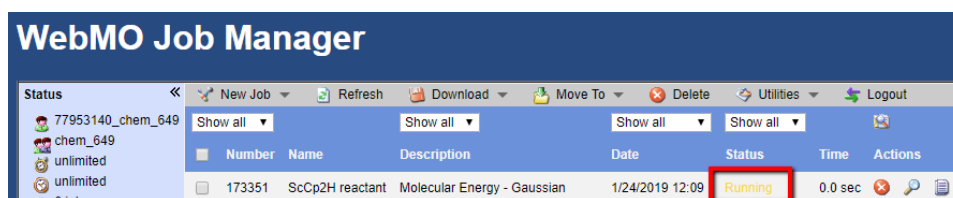
Step 5. Calculate Molecular Energy

- 5.1. To calculate the molecular energy, we will need to configure the Gaussian Job Options according to the following specifications:

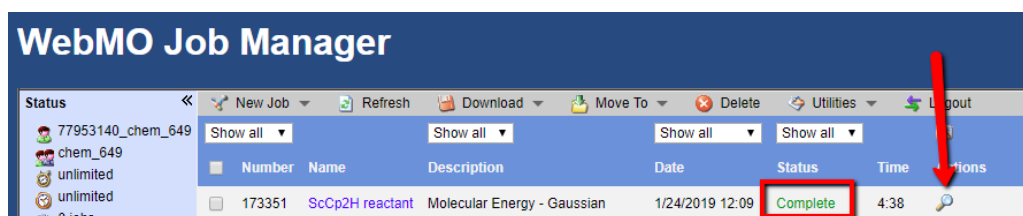


Job Name: ScCp2H reactant
Calculation: Molecular Energy
Theory: B3LYP
Basis Set: Routine: 6-31G(d)
Charge: 0
Multiplicity: Singlet

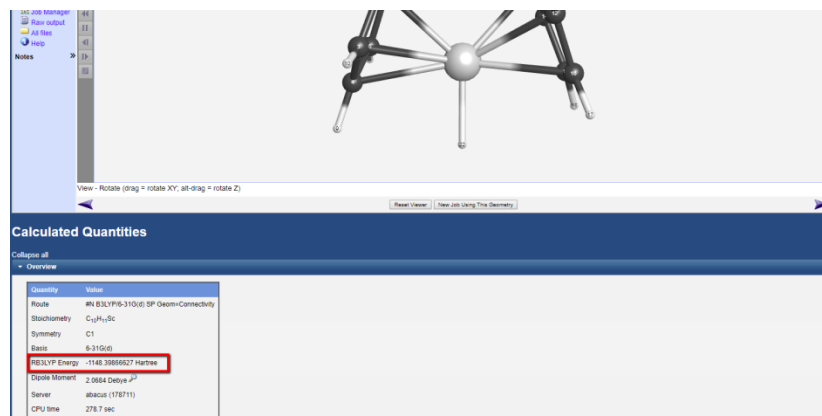
- 5.2. Click the continue button  to submit the calculation to the Gaussian server calculation queue.
- 5.3. The “Job Manager” window should show this job under the status “Running”. This might take up to 10 min so you can continue to the next task (Step 6) and return here after the job is completed. This window can be refreshed and no work will be lost.



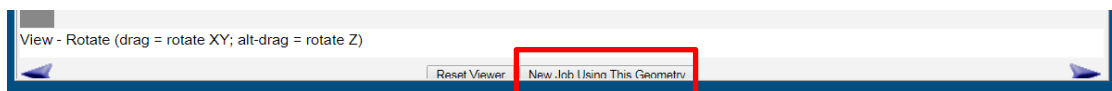
- 5.4. When the job status changes to ‘complete’, click on the ‘view job’ icon to view the result of the calculations.




- 5.5. The molecule should be in view again. Scroll down in order to see the Calculated Quantities. The calculated energy of the molecule should be:
RB3LYP Energy = -1148.398943 Hartree.





- 5.6. In order to continue working on this molecule click 'New Job Using This Geometry'.

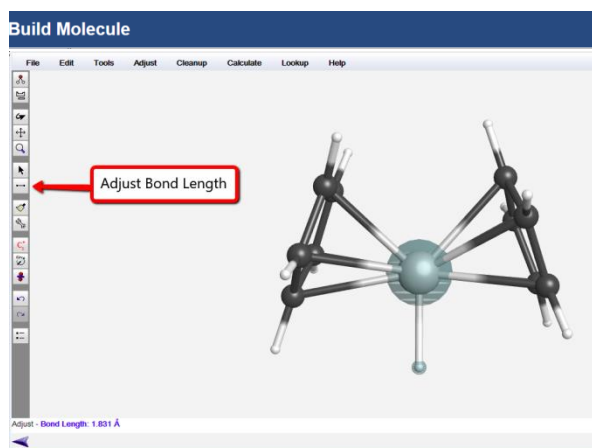



- 5.7. You can go back to using a saved geometry by clicking the "Job Manager" and selecting an older job.
- 5.8. Click "view" 
- 5.9. Next click "New Job Using This Geometry".

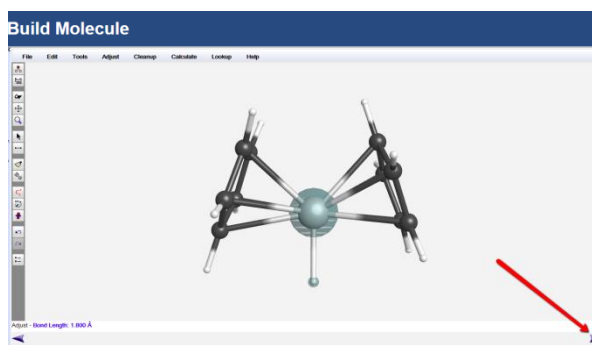
Step 6. Distort the structure of the molecule and re-optimize the geometry

At this point we will introduce a small change to the geometry of the molecule in order to try to re-optimize the structure.

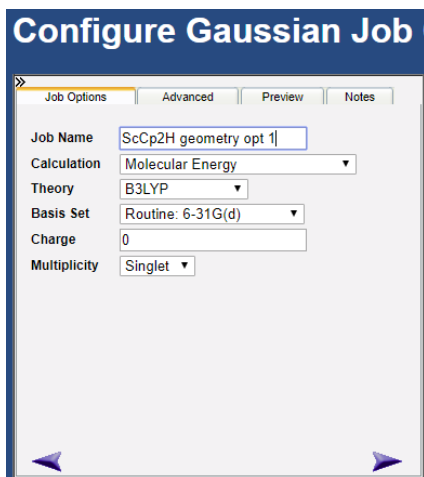
- 6.1. Start from an optimized molecular structure. You can use the imported molecule you used in step 4.
- 6.2. Click on the adjust icon 
- 6.3. Make a small distortion to the Sc-H bond length by clicking the H and the Sc atoms. A new button will appear to the left , allowing you to read and change the bond length. You can also see the bond length in the status bar at the bottom of the screen.
- 6.4. Change the bond length from 1.831 Å to 1.800 Å.



- 6.5. Click on the bottom-right arrow  to submit a job using this distorted structure.





- 6.6. In order to run Geometry Optimization, we will need to configure the Gaussian Job Options according to these specifications:



Job Name: ScCp2H geometry opt 1
Calculation: Geometry Optimization
Theory: B3LYP
Basis Set: Routine: 6-31G(d)
Charge: 0
Multiplicity: Singlet

- 6.7. Follow the rest of the job submitting steps as described in 2.2 - 2.5.
- 6.8. Check if the energy of the current molecule is equal to the reactant before we introduced the distortion. What does that indicate about the Geometry Optimization process? Was it a success?
- 6.9. Repeat this distortion process, this time apply a bigger distortion (for example, elongate or shorten bond Sc-H by 0.35 Å). Depending on the distortion applied, this calculation may run for up to 10-30 minutes or even longer.

If the results of the geometry optimization calculation give a structure with a higher energy than the optimized structure, then the optimization failed and Gaussian was not able to optimize the structure to the minimum energy of the molecule. Apply a smaller distortion and try again.

- 6.10. In order to see the optimization process, click on the “animate” icon  to see changes in geometry during the optimization steps.
- 6.11. Click the “view”  icon to see how the energy changed during the optimization steps.

Collapse all

Overview

Quantity	Value
Job History	173351
Route	#N B3LYP/6-31G(d) OPT Geom=Connectivity
Stoichiometry	C ₁₀ H ₁₁ Sc
Symmetry	C1
Basis	6-31G(d)
RB3LYP Energy	-1148.39866654 Hartree
Dipole Moment	2.0671 Debye
Server	abacu
CPU time	1186.7

View Animate

Geometry Sequence Energies

Step	Energy
0	-1148.39106777
1	-1148.39839059
2	-1148.39866334
3	-1148.39866576
4	-1148.39866654

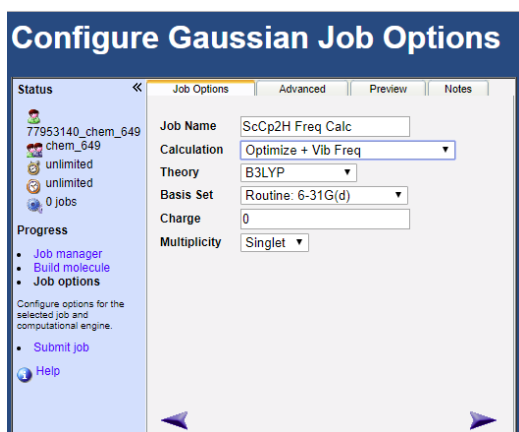
Animation speed: 5

Loop: None

Step 7. Calculate vibrational frequencies:

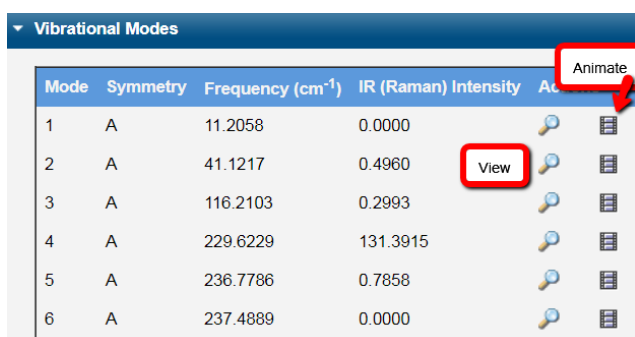
To check whether the final geometry is in fact the true minima, you will need to calculate the vibrational frequencies. Remember you must use an optimized structure.

- 7.1. Click on “Job Manager”.
- 7.2. Choose a job that resulted in an optimized structure. If you don't have one, choose the imported reactant from section 4.
- 7.3. In order to calculate vibrational frequencies, we will need to configure the Gaussian Job Options according to these specifications:



Job Name: ScCp2H Freq Calc
Calculation: Optimize + Vib Freq
Theory: B3LYP
Basis Set: Routine: 6-31G(d)
Charge: 0
Multiplicity: Singlet

- 7.4. Follow the rest of the job submitting steps as described in 2.2 - 2.5.
- 7.5. When the job is completed, look in Calculated Quantities for the Vibrational Modes. If all of the frequencies are positive numbers then the system is confirmed to be at a stationary point at the local (or global) energy minimum. One imaginary frequency (big negative value, bigger than 100 cm^{-1}) indicates a transition state.

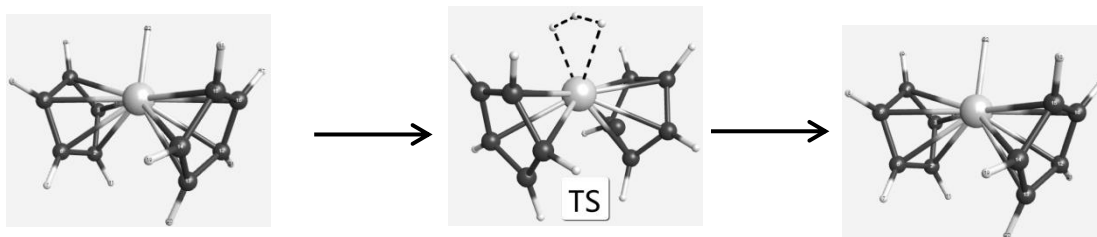


Mode	Symmetry	Frequency (cm^{-1})	IR (Raman) Intensity	View	Animate
1	A	11.2058	0.0000		
2	A	41.1217	0.4960		
3	A	116.2103	0.2993		
4	A	229.6229	131.3915		
5	A	236.7786	0.7858		
6	A	237.4889	0.0000		

Vibrational calculations can also help obtain thermodynamic quantities at standard conditions (e.g., enthalpy, Gibbs free energy, heat capacity).

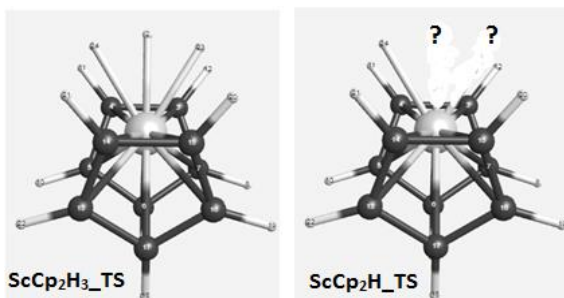
Step 8. Create a transition state of the reaction: $\text{ScCp}_2\text{H} + \text{H}_2$

The mechanism of the $\text{ScCp}_2\text{H} + \text{H}_2$ reaction involves a four-member transition state.



Modelling the transition state of a 23-atom molecule can be a bit tricky and time consuming. In order to speed up this process, a partial TS structure is provided for this exercise.

- 8.1. Import the partial TS ($\text{ScCp}_2\text{H_TS}$) to WebMO according to the procedure in section 4. Coordinates are given in Appendix A part 2.
- 8.2. Find the bond length of Sc-H and compare it to the Sc-H bond length in the original reactant molecule (section 4). What is the difference between them?
- 8.3. Attach 2 hydrogen atoms to the Sc atom to create the complete transition state molecule. Follow the Build instructions given in Step 1.

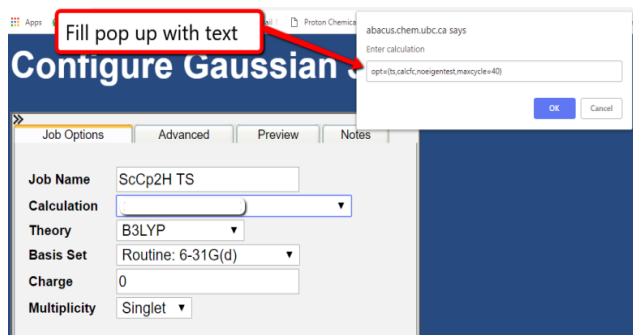


The task is to put back these hydrogens to the structure to create the molecule on the left.

- 8.4. Before you can optimize the structure, make sure the angles and bond lengths are between these ranges:
 - The bond length Sc-H(middle) is between $1.85 \text{ \AA} - 2.10 \text{ \AA}$
 - The bond length Sc-H(side) is between $1.85 \text{ \AA} - 2.10 \text{ \AA}$
 - The angle H(side)-Sc-H(side) is between $58^\circ - 62^\circ$

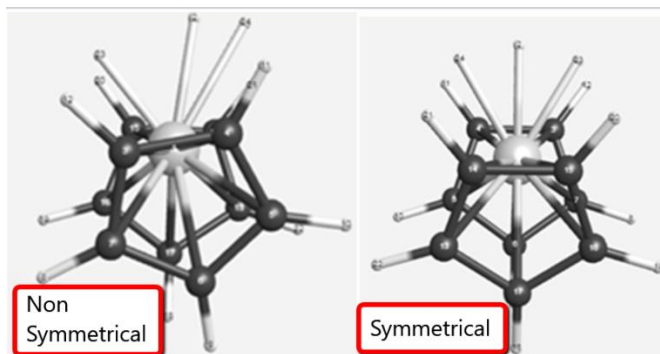
* To see the correct angle, you must click the atoms in order. This means that the atom in the center of the angle you are examining should be clicked second.

- 8.5. In order to optimize the transition state structure, we will need to configure the Gaussian Job Options according to these specifications (pop up should appear when choosing 'Other'):



Job Name: ScCp2H TS
Calculation: Other
opt=(ts,calcfc,noeigentest,maxcycle=20)
Theory: B3LYP
Basis Set: Routine: 6-31G(d)
Charge: 0
Multiplicity: Singlet

















- 8.6. Follow the rest of the job submitting steps as described in 2.2-2.5. This job is expected to take 1-2 hours, but the exact time depends on the input structure submitted for calculation. The closer the input is to the optimized structure, the shorter the calculation.
- 8.7. Monitor the progress of the calculation every hour to see if the calculation was completed.
- 8.8. When completed, assess the calculated structure. The structure should be symmetric and resemble the one in the image below. If it is not, the calculation probably failed to optimize the structure and should be restarted with different bond lengths and angles.




















Notice the distance between the central H and the ones beside it. Is this distance symmetrical or not.


- 8.9. In case the structure seems symmetrical, we need to confirm it is indeed the transition state by vibrational frequency calculations., if one of the frequencies is

imaginary (printed as negative value) then the system is confirmed to be at a transition state (a saddle point). As indicated before in step 7.5 all positive value would indicate a stable intermediate (a local minimum).

Vibrational Modes					
Mode	Symmetry	Frequency (cm ⁻¹)	IR (Raman) Intensity	Actions	
1	A	<u>-873.4781</u>	785.9621		
2	A	25.4073	0.0000		
3	A	59.2679	0.1761		
4	A	135.3047	0.0624		
5	A	214.5294	18.5370		
6	A	241.6484	0.9034		
7	A	249.7653	0.0000		
8	A	252.0373	1.4669		

- 8.10. Repeat Step 7 to calculate vibrational frequencies.
- 8.11. Assess if you indeed have the Transition State. If you are not, restart section 5. To do this, adjust the Bond length and order to be a bit different, but still in the provided range.
- 8.12. Press the “Animate” button  next to the imaginary frequency. This will show you the vibrational mode that corresponds to breaking and forming of the bond.

Vibrational Modes					
Mode	Symmetry	Frequency (cm ⁻¹)	IR (Raman) Intensity	Actions	
1	A	<u>-873.4781</u>	785.9621		
2	A	25.4073	0.0000		
3	A	59.2679	0.1761		
4	A	135.3047	0.0624		
5	A	214.5294	18.5370		
6	A	241.6484	0.9034		
7	A	249.7653	0.0000		
8	A	252.0373	1.4669		

 Click here to animate the vibration mode

Questions:

1. How many steps did Gaussian require to re-optimize the structure after you distorted the reactant molecule?
2. What values of bond length and angle did you find that were able to optimize to a transition state?
3. From the obtained data calculate the energies of the reaction (E_a , ΔE , G_a , ΔG ,)

Appendix A: XYZ Files

1. ScCp₂H reactant:

O 1

Sc 0.00000 0.00000 0.00000

C -1.75628 -1.61717 -0.70934

C -2.17796 -0.33328 -1.14586

C -2.44349 0.46025 0.00005

C -2.17793 -0.33336 1.14589

C -1.75626 -1.61722 0.70927

H -1.49397 -2.45411 1.34514

H -2.28530 -0.01429 2.17672

H -2.77927 1.48770 0.00009

H -2.28536 -0.01413 -2.17666

H -1.49401 -2.45402 -1.34528

C 1.75626 -1.61722 -0.70927

C 1.75628 -1.61717 0.70935

C 2.17796 -0.33328 1.14586

C 2.44349 0.46025 -0.00005

C 2.17793 -0.33337 -1.14589

H 2.28530 -0.01430 -2.17672

H 2.77927 1.48770 -0.00009

H 2.28535 -0.01413 2.17666

H 1.49400 -2.45401 1.34529

H 1.49397 -2.45412 -1.34513

H -0.00000 1.83005 -0.00001

2. ScCp₂H partial Transition State:

O 1

Sc 0.00000 0.00000 0.00000

C 2.36569 0.21249 0.70973

C 2.36573 0.21259 -0.70958

C 1.92263 -1.06487 -1.14771

C 1.66013 -1.85549 -0.00009

C 1.92256 -1.06503 1.14766

H 1.82039 -1.38469 2.17842

H 1.32217 -2.88396 -0.00017

H 1.82052 -1.38439 -2.17852

H 2.66411 1.03597 -1.34555

H 2.66403 1.03578 1.34584

C -1.92257 -1.06500 -1.14767

C -2.36569 0.21251 -0.70970

C -2.36572 0.21257 0.70961

C -1.92262 -1.06491 1.14770

C -1.66013 -1.85549 0.00006

H -1.32217 -2.88396 0.00010

H -1.82049 -1.38445 2.17850

H -2.66409 1.03593 1.34561

H -2.66405 1.03582 -1.34578

H -1.82041 -1.38463 -2.17844

H 0.00000 1.68939 -0.98953

3. ScCp₂H₂ partial Transition State:

O 1

Sc 0.00000 0.00000 0.00000

C 2.36565 0.21276 0.70965

C 2.36565 0.21277 -0.70965

C 1.92266 -1.06478 -1.14768

C 1.66019 -1.85535 -0.00000

C 1.92266 -1.06479 1.14768

H 1.82051 -1.38439 2.17845

H 1.32229 -2.88384 -0.00000

H 1.82051 -1.38438 -2.17846

H 2.66389 1.03614 -1.34570

H 2.66389 1.03613 1.34570

C -1.92266 -1.06478 -1.14768

C -2.36565 0.21276 -0.70965

C -2.36565 0.21277 0.70965

C -1.92266 -1.06478 1.14768

C -1.66019 -1.85535 0.00000

H -1.32229 -2.88384 0.00000

H -1.82051 -1.38438 2.17846

H -2.66389 1.03614 1.34570

H -2.66389 1.03613 -1.34570

H -1.82051 -1.38439 -2.17846

H 0.00000 1.68960 0.99037

H 0.00000 1.68960 -0.99036