winmostar tutorial

GAMESS Chemical Reaction Analysis (Heat of Formation and Activation Energy)

V11.5.6

5 February 2024 X-Ability Co., Ltd.

About This Manual

- This manual is a tutorial demonstrating use cases for Winmostar V11.
- For those using Winmostar V11 for the first time, please consult Beginner's Guide.
- For those who wish to explore the details of each feature, please refer to Winmostar User Manual.
- Those who wish to practice the contents of this manual are encouraged to attend a training session.
  - Winmostar Introductory Training Session:This guide only introduces the operation methods of the Basic Tutorial.
  - Winmostar Basic Training Session:We will cover the theoretical background, explanations on interpreting results, operational methods of the Basic Tutorial, and procedures for some tutorials beyond the basic level.
  - Individual Training Session:You can freely customize the training content according to your preferences.
- If you are unable to proceed with the operations as outlined in this manual, please first consult Frequently asked questions.
- If your issue is not resolved through the Frequently Asked Questions, for the purpose of information accumulation and management, please contact us using Contact page. Attach files generated at the time of the issue and provide steps to reproduce the problem.
-

Overview

Calculate the heat of formation and activation energy for the following two chemical reactions at the B3LYP/6-31G* level.

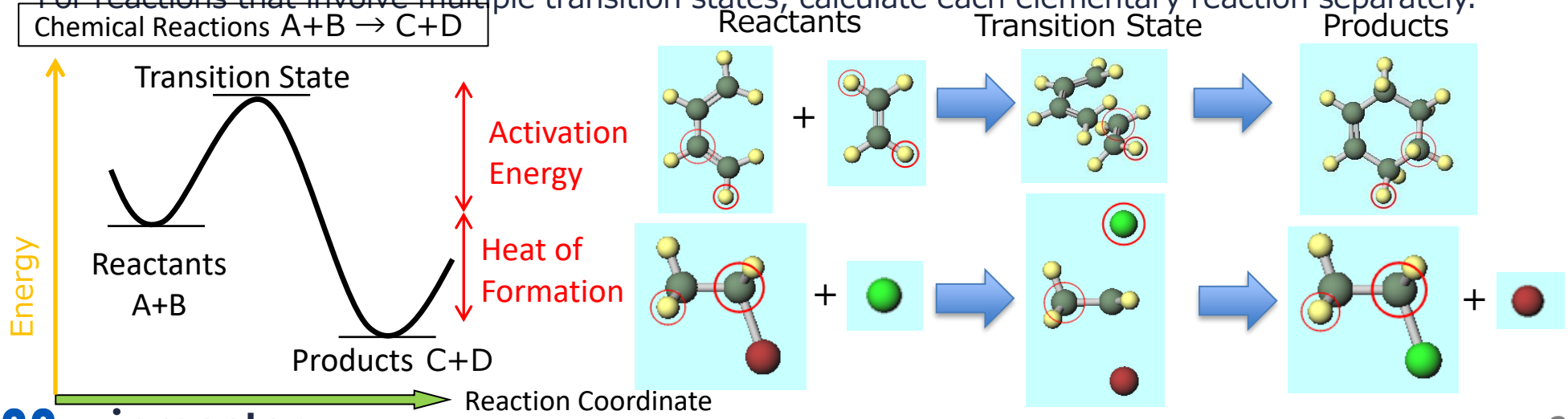
A. For cases where the transition state structure can be somewhat predicted:
Vacuum Diels-Alder reaction of butadiene and ethylene. ($C_4H_6 + C_2H_4 \rightarrow C_6H_{10}$)

B. For cases where the initial structure of the transition state is calculated by another method:
S_N2 reaction of bromoethane and Cl- ion in DMSO solution ($CH_3CH_2Br + Cl^- \rightarrow CH_3CH_2Cl + Br^-$)

Note:

・The initial structure for the transition state calculation of the S_N2 reaction will use the results from MOPAC transition state calculations. Please complete the content of MOPAC (Transition State and IRC) tutorial beforehand.

・For reactions that involve multiple transition states, calculate each elementary reaction separately.

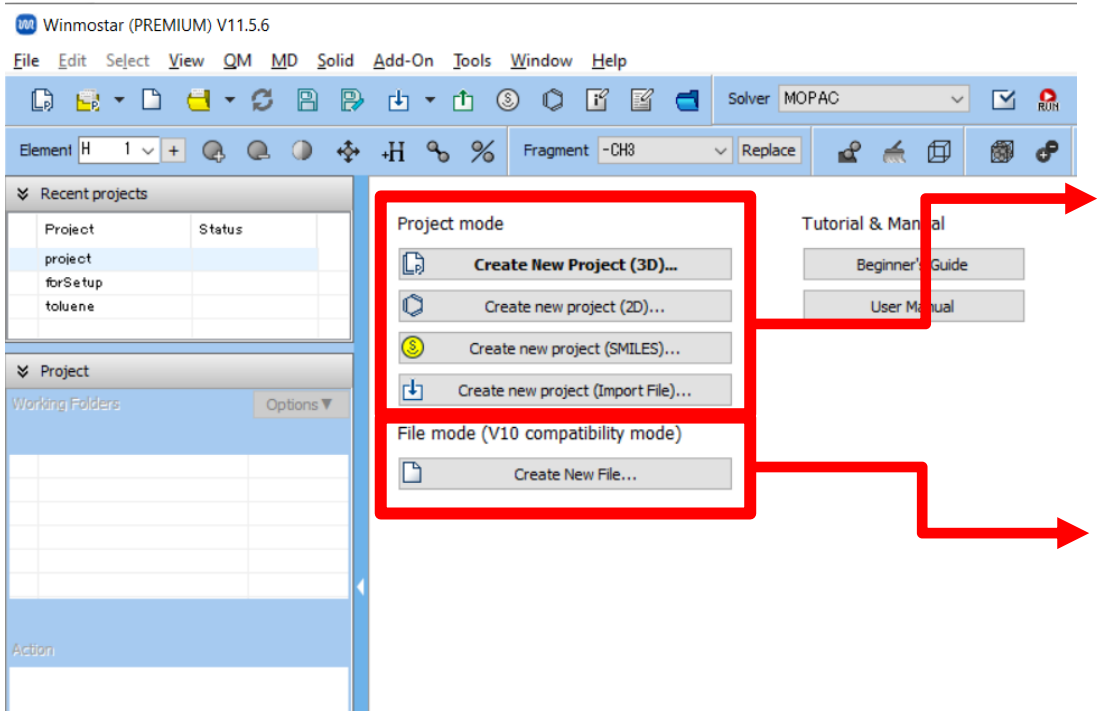


Preference of Operating Environment

- For GAMESS:
  - Please install GAMESS according to GAMESS Installation Manual available at https://winmostar.com/en/manual_en/installation/GAMESS_install_manual_en_win.pdf

Operating Modes of Winmostar V11

V11 offers two operating modes: **Project Mode** and **File Mode**.
This manual focuses on operations in Project Mode.
For operations in File Mode, please refer to tutorial for version 10.



Project Mode **New Features in V11**

Users can manage jobs without having to manage individual files.
We generally recommend using this mode.

File Mode

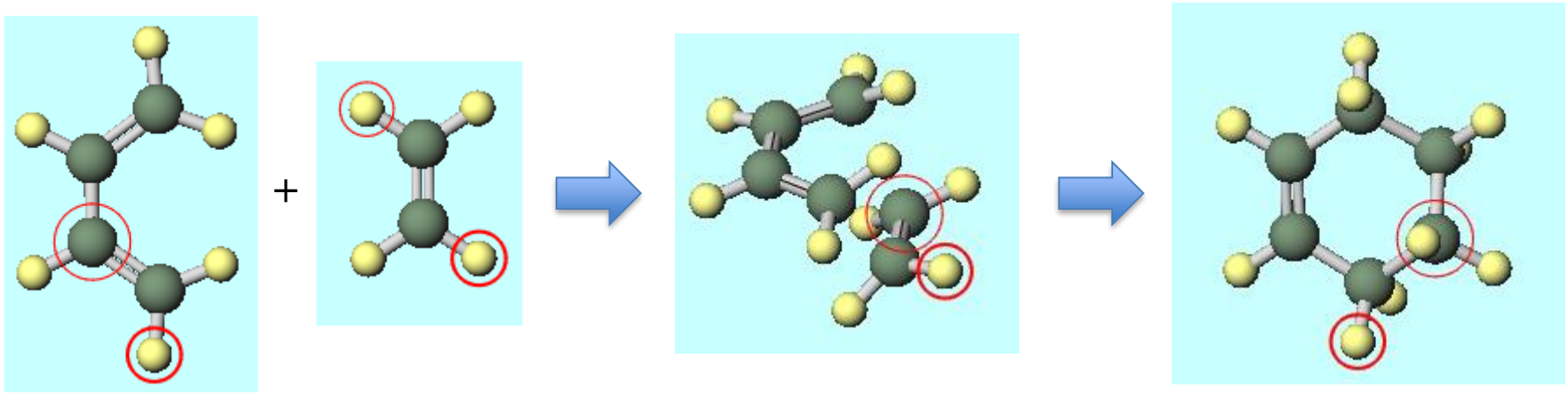
Users explicitly create and manage individual files.
The operational procedure is the same as from V10 and earlier versions.

When creating a continuation job in File Mode or versions before V10, you must display the final structure of the original job each time. In Project Mode, this final structure is automatically inherited.

A. Diels-Alder Reaction between Butadiene and Ethylene

A. Calculation Procedure

Perform structure optimization calculations for the reactants (C_4H_6、 C_2H_4), the product (C_6H_{10}), and the transition state, and determine their respective energies. From the summation and subtraction of these energies, calculate the heat of formation and the activation energy for this reaction.

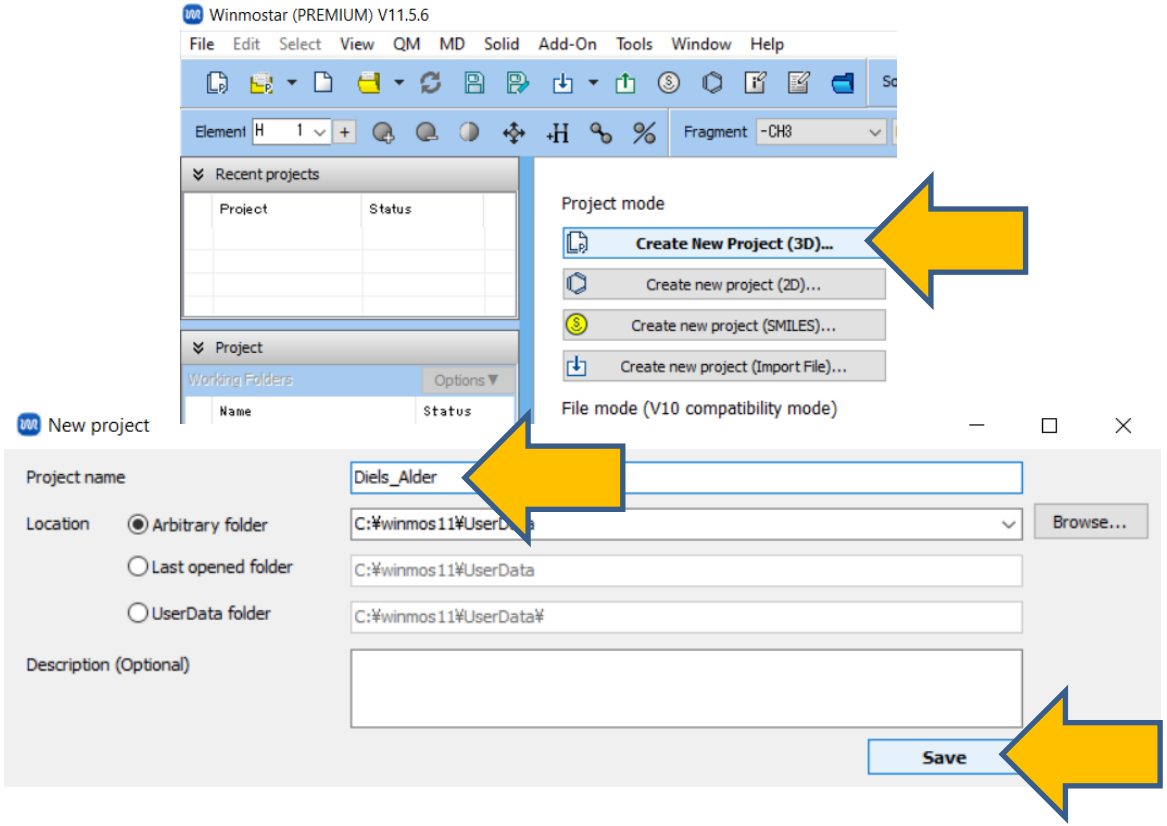


A. Calculation Procedure

For basic operation methods, please refer to GAMESS Foundation Tutorial.

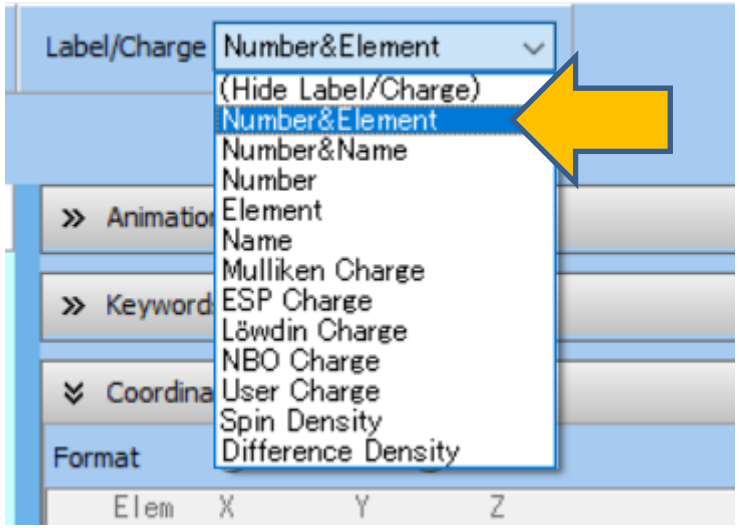
A. Launch Winmostar and click **Create New Project (3D)**. If Winmostar is already running, first click **File | Close**.

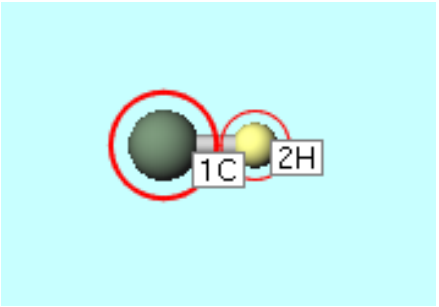
B. Enter 'Diels_Alder' for **Project name** and click **Save**.



B. Structure Optimization Calculation (Butadiene)

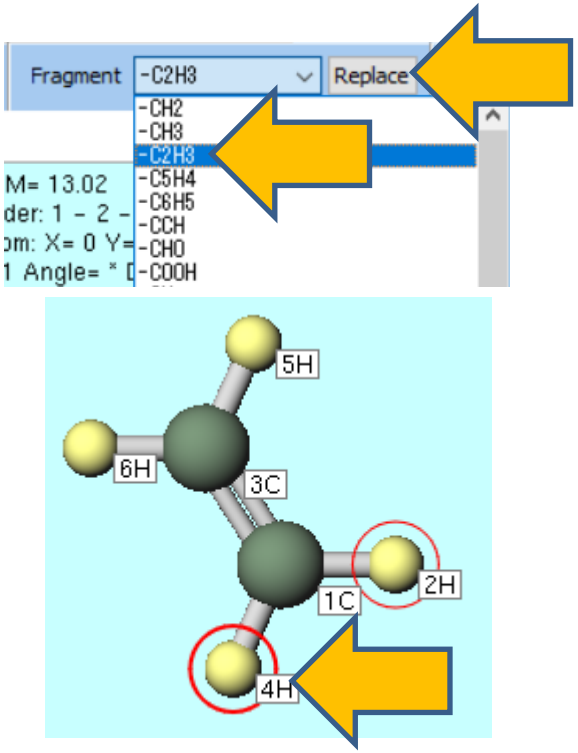
From **Label/Charge** menu at the top right of Main Window, select **Number & Element** to display the names of each atom in Viewport.

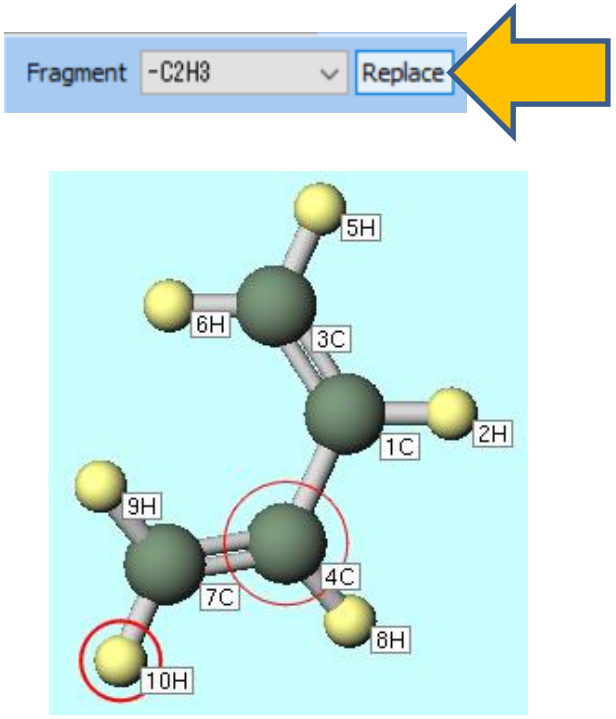




B. Structure Optimization Calculation (Butadiene)

A. Select –**C2H3** from **Fragment** at the top of Main Window and click **Replace** once.
B. Click on **4H** atom (yellow) so it is marked with a thick red circle, then click **Replace** again to create cis-butadiene.



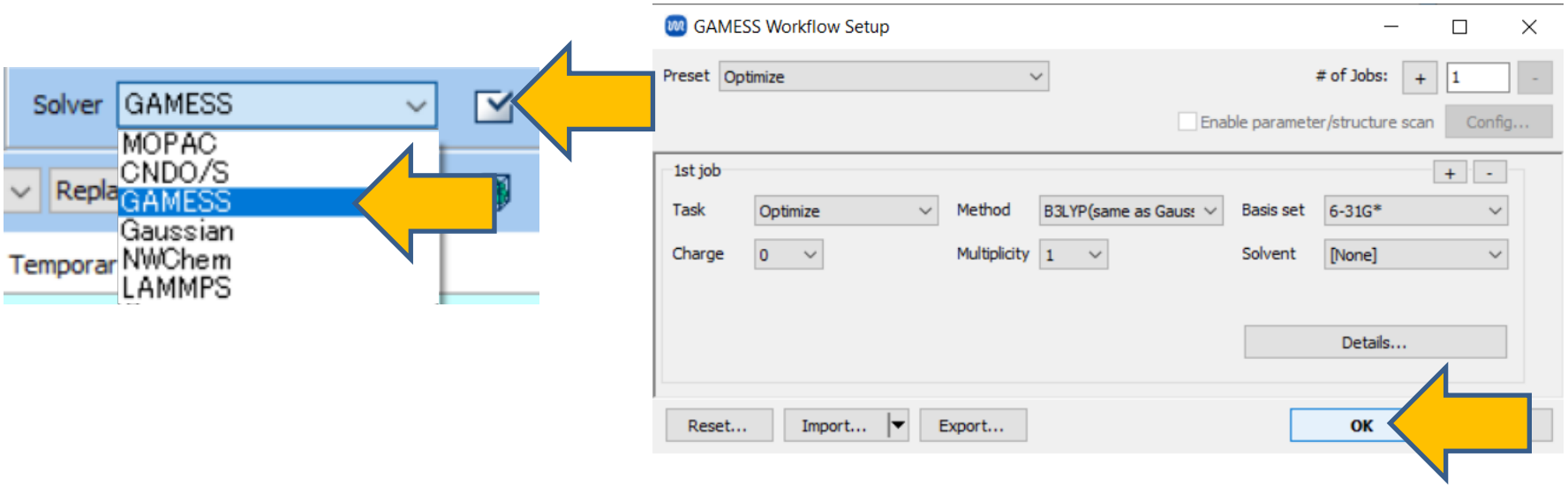


B. Structure Optimization Calculation (Butadiene)

A. Select **GAMESS** from **Solver** and click **Workflow Setup**.
B. In **GAMESS Workflow Setup** window, click **OK**.

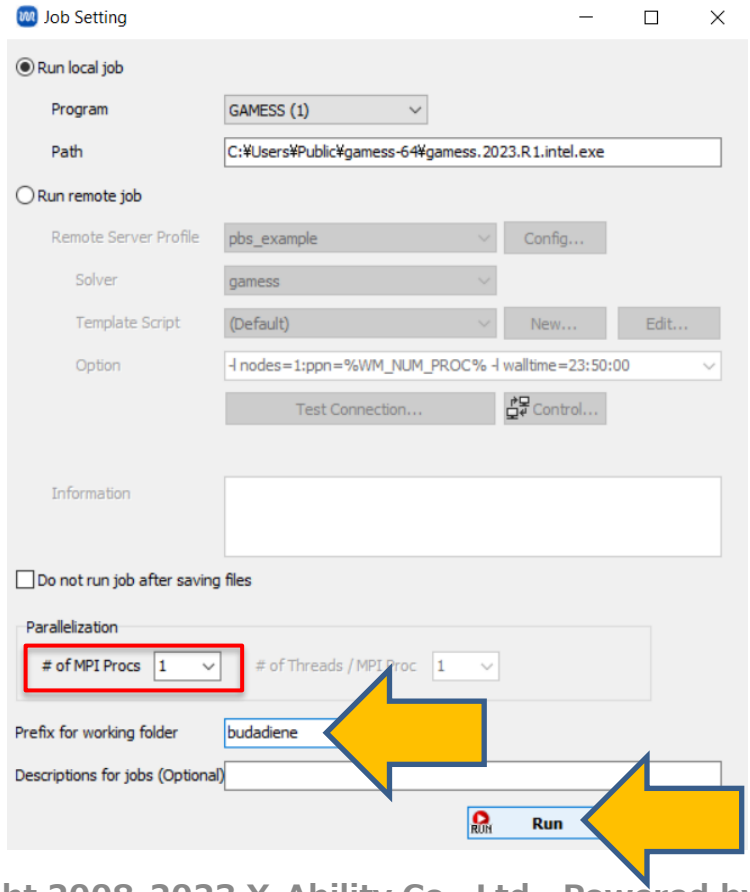
・ By default, the structure optimization is carried out at the B3LYP/6-31G* level.
・ If you want to reduce computational accuracy to finish calculations more quickly, change Basis set to STO-3G.

If you switch to STO-3G, it is necessary to run not only butadiene but all molecules in this Diels-Alder reaction at the STO-3G level.



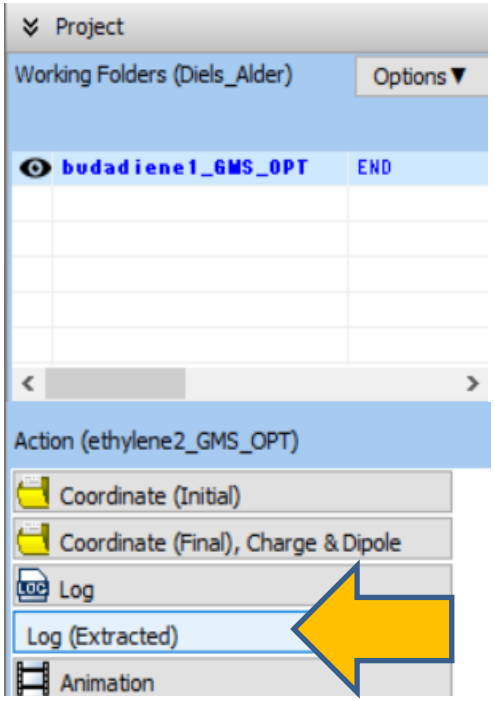
B. Structure Optimization Calculation (Butadiene)

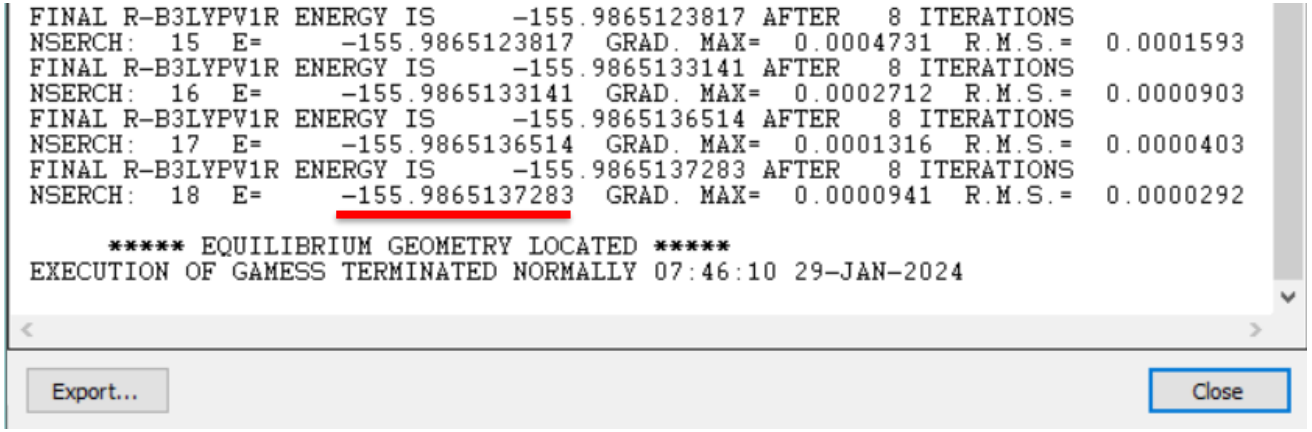
A. Change **Prefix for working folder name** to 'butadiene'.
B. Set # of MPI Procs according to the number of cores on your computer. When running on a remote machine, also configure settings such as the profile.
C. Click **Run**.



B. Structure Optimization Calculation (Butadiene)

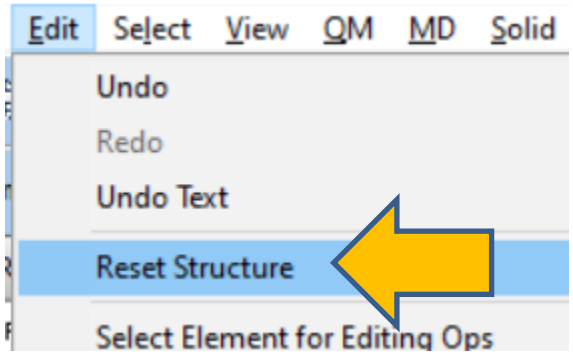
A. After the calculation is complete and the status of the working folder changes to **END** or **END(-)**, click **Log (Extracted)** in Action.
B. In **Extracted Log** window, copy the number after E= at the end of the last NSERCH line into Excel or a similar program. This value (-155.98651 Hartree) represents the energy of butadiene in its stable structure.
C. Close **Extracted Log** window.

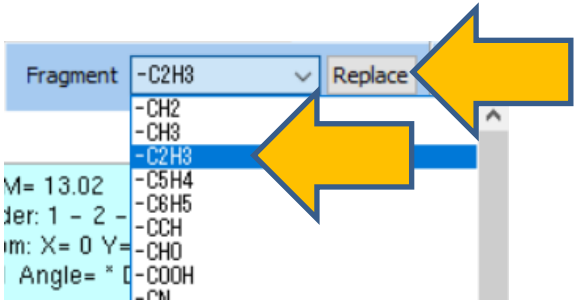


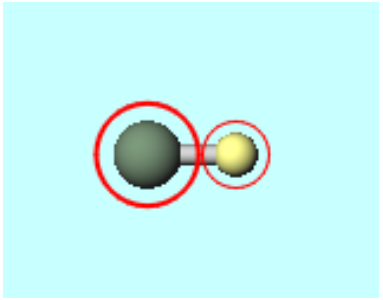


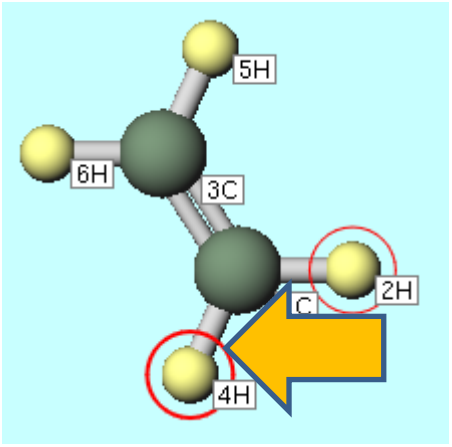
C. Structure Optimization Calculation (Ethylene)

A. Click **Edit | Reset Structure** to revert to the initial C-H state.
B. Select **-C2H3** from **Fragment** at the top of Main Window, then click **Replace** once to create Ethylene.





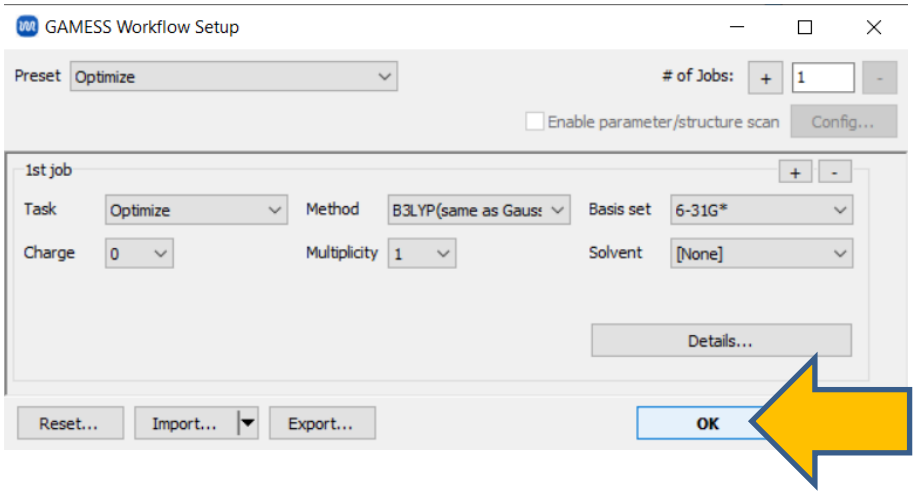


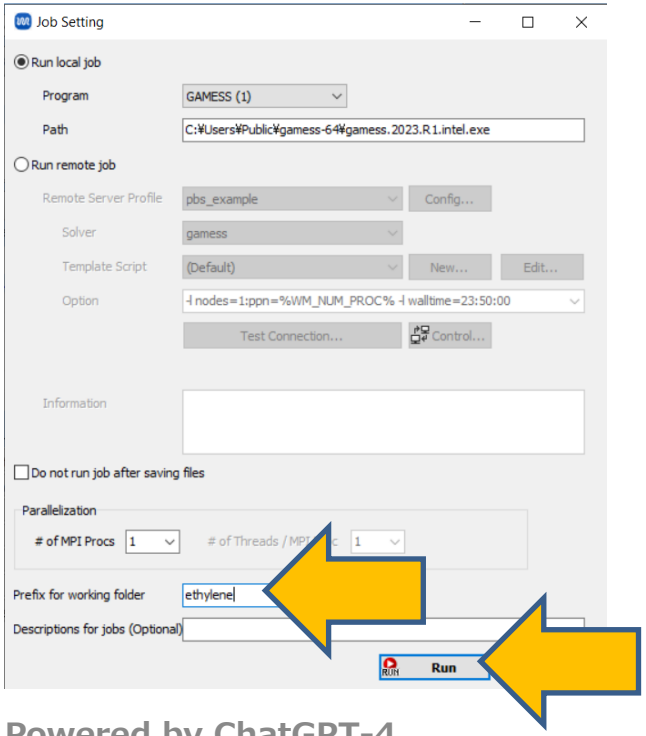


C. Structure Optimization Calculation (Ethylene)

A. Click (**Workflow Setup**).
B. If 'Do you want to continue from previous run?' appears, click **No**.
C. In **GAMESS Workflow Setup** window, click **OK**.
D. In **Job Setting** window, change **Prefix for working folder name** to 'ethylene' and click **Run**.

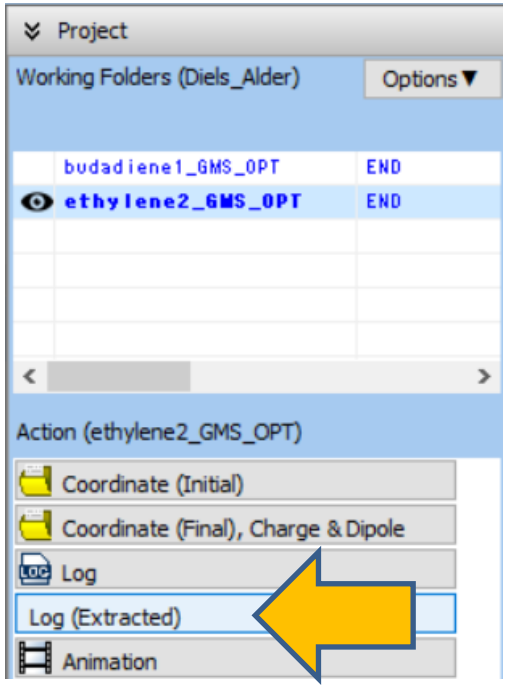
・ If you want to reduce the calculation accuracy to finish the calculation faster, change Basis set to STO-3G.

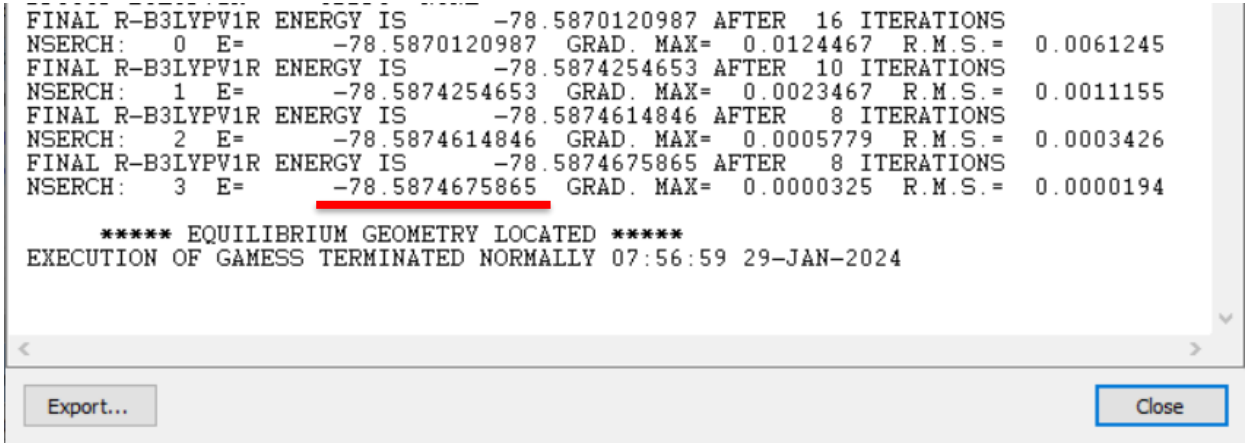




C. Structure Optimization Calculation (Ethylene)

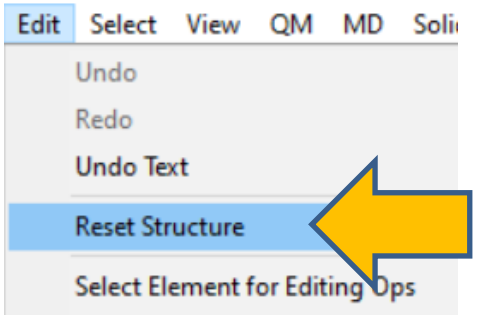
A. After the calculation is complete and the status of the working folder changes to **END** or **END(-)**, click **Log (Extracted)** in Action.
B. In **Extracted Log** window, copy the number after E= at the end of the last NSERCH line into Excel or a similar program. This value (-78.58746 Hartree) represents the energy of Ethylene in its stable structure.
C. Close **Extracted Log** window.

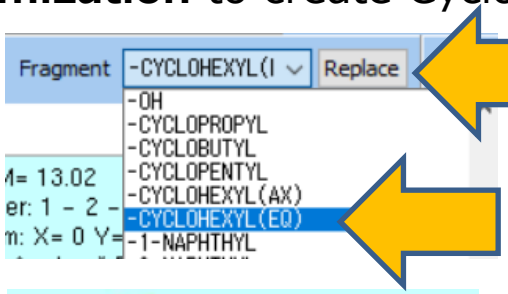


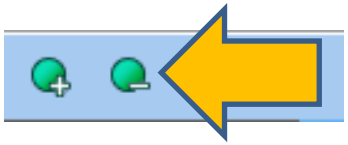


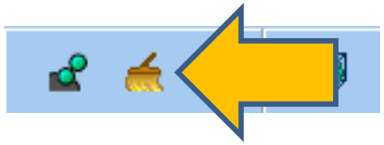
D. Structure Optimization Calculation (Cyclohexene)

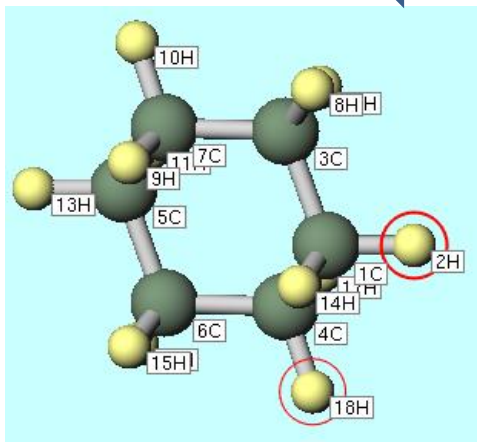
A. Click **Edit | Reset Structure**.
B. Select **-CYCLOHEXYL(EQ)** from **Fragment** at the top of Main Window, then click **Replace** once.
C. Click sequentially on the atoms **13H** and **15H** (yellow), and then click **Delete Atom** twice.
D. Click **Quick Optimization** to create Cyclohexene.

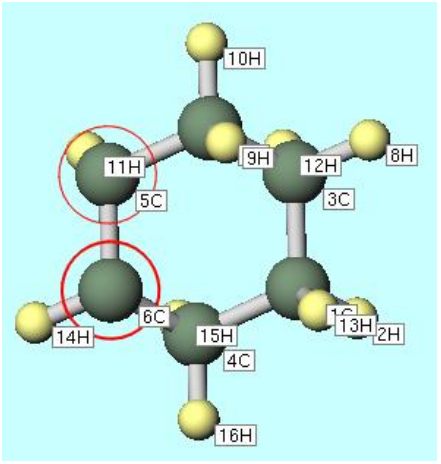


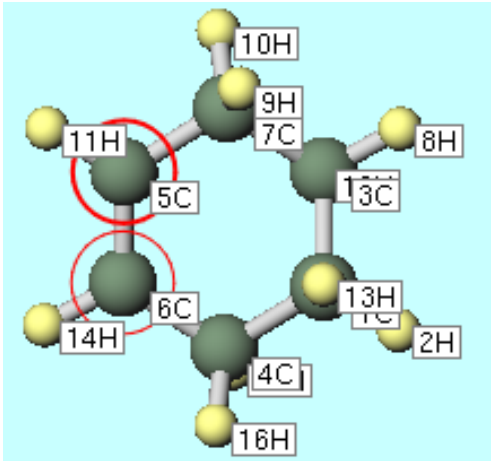








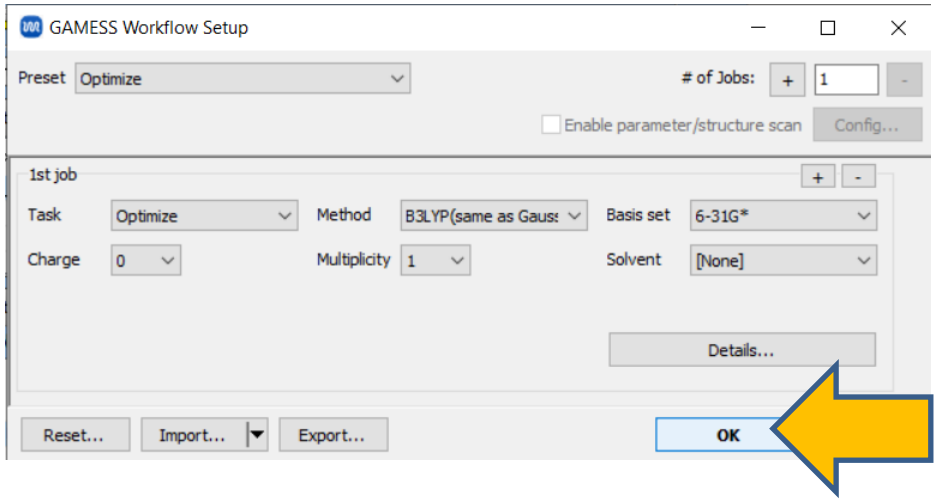


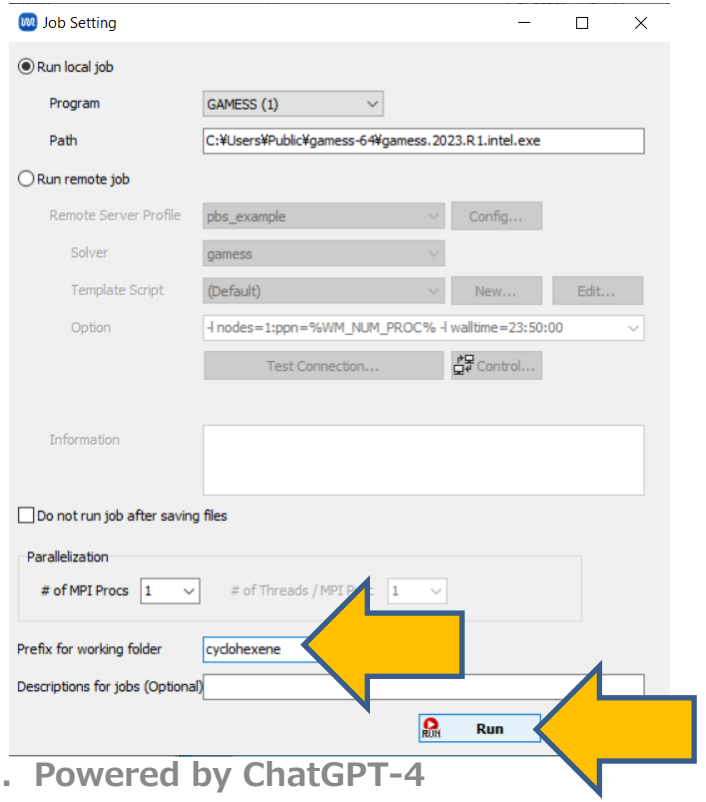


D. Structure Optimization Calculation (Cyclohexene)

A. Click (**Workflow Setup**) .
B. If 'Do you want to continue from previous run?' appears, click **No**.
C. In **GAMESS Workflow Setup** window, click **OK**.
D. In **Job Setting** window, change **Prefix for working folder name** to 'cyclohexene' and click **Run**.

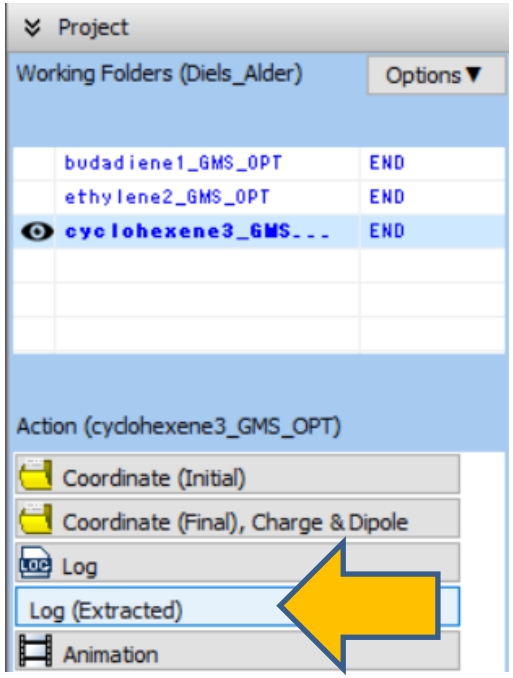
・ If you want to reduce the calculation accuracy to finish the calculation faster, change Basis set to STO-3G.

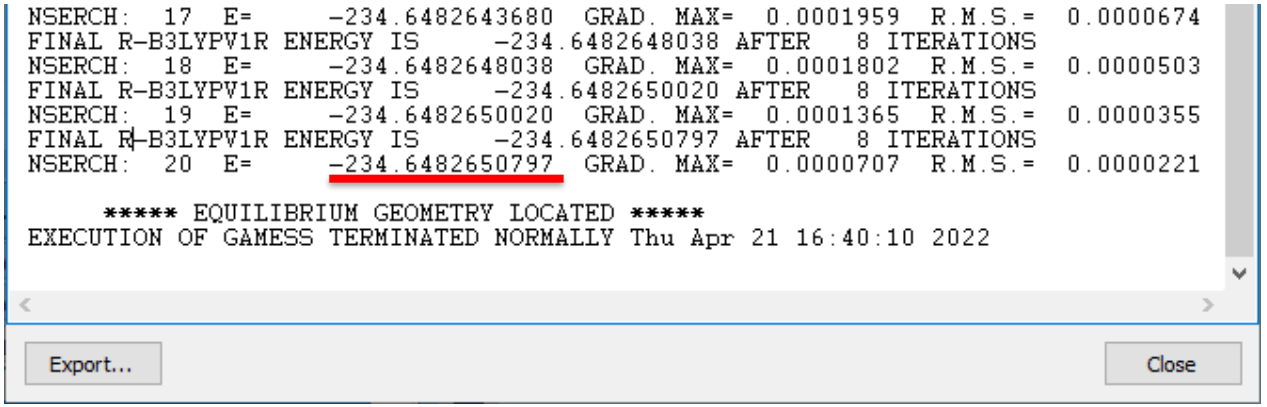




D. Structure Optimization Calculation (Cyclohexene)

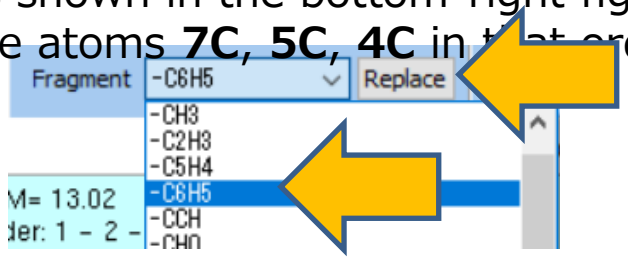
A. After the calculation is complete and the status of the working folder changes to **END** or **END(-)**, click **Log (Extracted)** in Action.
B. In **Extracted Log** window, copy the number after E= at the end of the last NSERCH line into Excel or a similar program. This value (-234.64826 Hartree) represents the energy of Ethylene in its stable structure.
C. Close **Extracted Log** window.

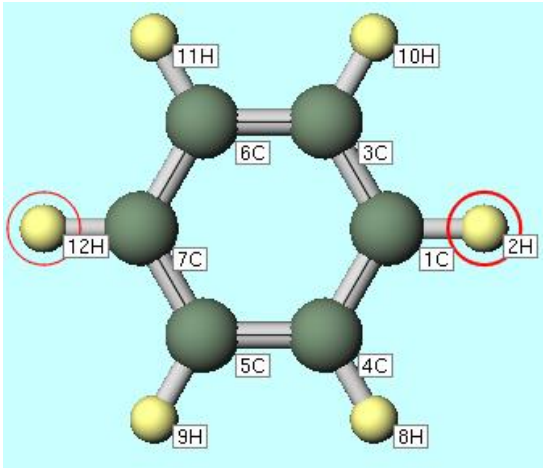


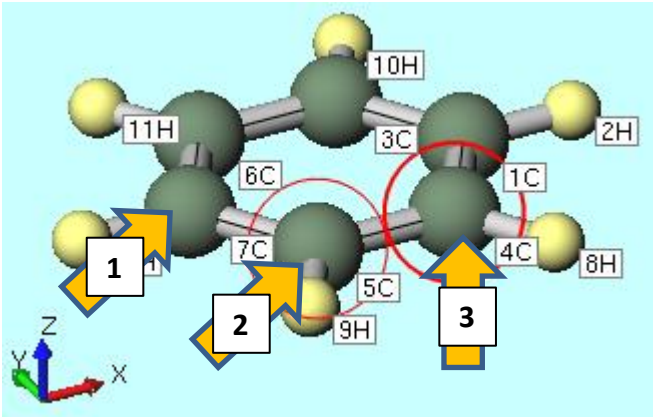


E. Transition State (TS) Structure Optimization Calculation

A. Click **Edit | Reset Structure**.
B. Select **-C6H5** from **Fragment** at the top of Main Window, then click **Replace** once to create Benzene.
C. Rotate the molecule by clicking and dragging near the molecule (light blue) until it aligns as shown in the bottom-right figure.
D. Click on the atoms **7C**, **5C**, **4C** in that order.

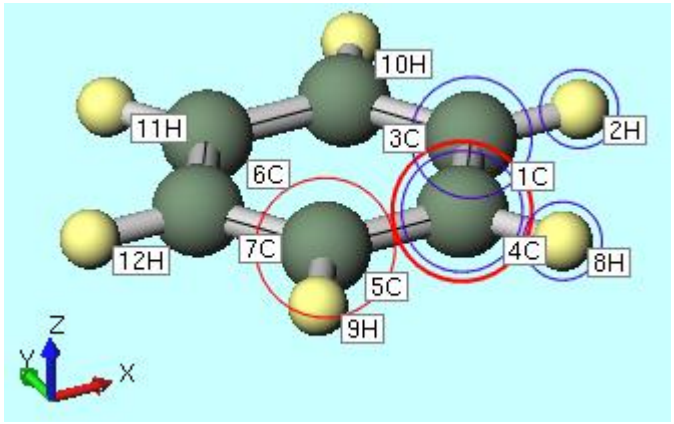


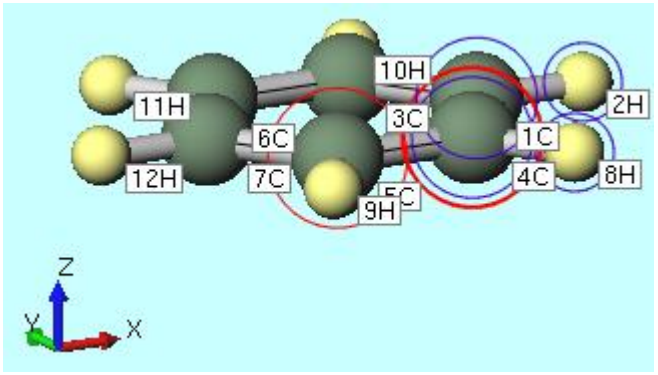


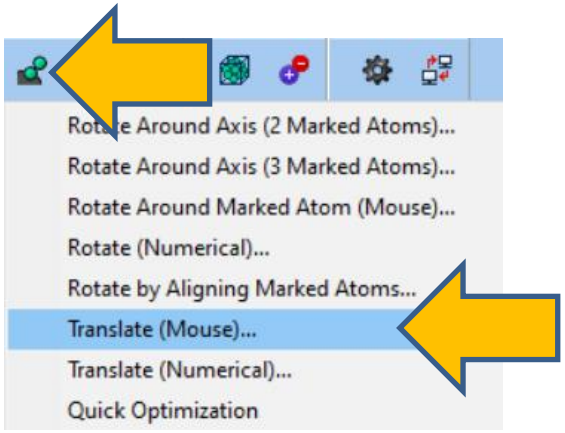


E. Transition State (TS) Structure Optimization Calculation

A. Press and hold **Ctrl** and click on the atoms **1C**, **2H**, **4C**, and **8H** to select them as a group, indicated by blue circles.
B. Rotate the molecule by clicking and dragging near the molecule to align it as shown in the central figure.
C. Click **Modify Selected Group** and select **Translate (Mouse)**.

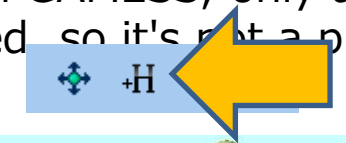


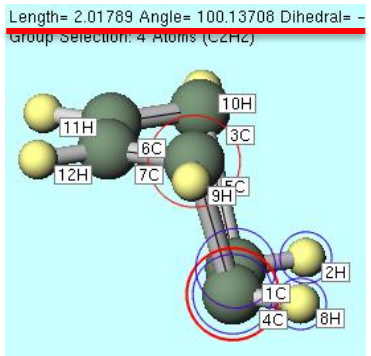


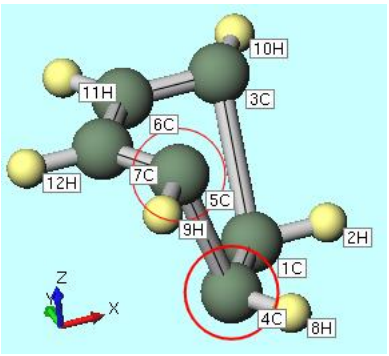


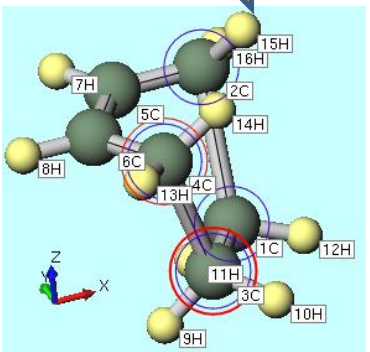
E. Transition State (TS) Structure Optimization Calculation

A. Consider the overlap of π orbitals between two molecules in the Diels-Alder reaction and position the carbon skeletons of butadiene and ethylene accordingly. Drag the screen to move the C_2H_2 part until the Length is approximately 2.0 Å and the Angle is about 100°, as shown in the lower-left figure. Since the goal is to create an initial structure for the transition state, the values do not need to be matched precisely.
B. Click near the molecule once to deselect the group selection (blue circles), then click and drag near the molecule again to rotate it as shown in the central lower figure.
C. While holding **Ctrl**, click on atoms **1C**, **3C**, **4C**, and **5C** to select them as a group (blue circles), and then click **Add Hydrogen to Marked Atom** once. This completes the initial structure for the transition state calculation. In GAMESS, only atomic coordinates are used, and bond information is not utilized, so it's not a problem if a bond remains between C_4H_6 and C_2H_4.



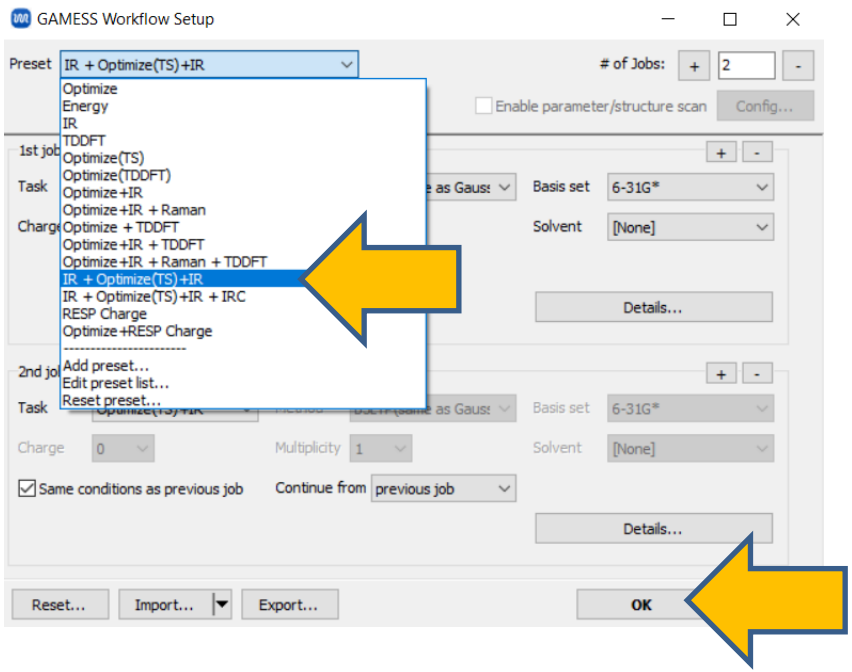


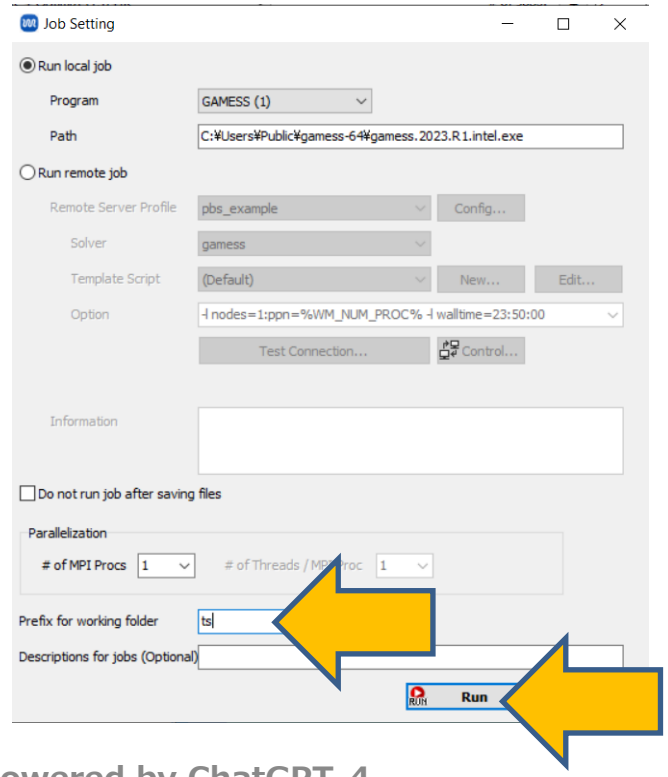




E. Transition State (TS) Structure Optimization Calculation

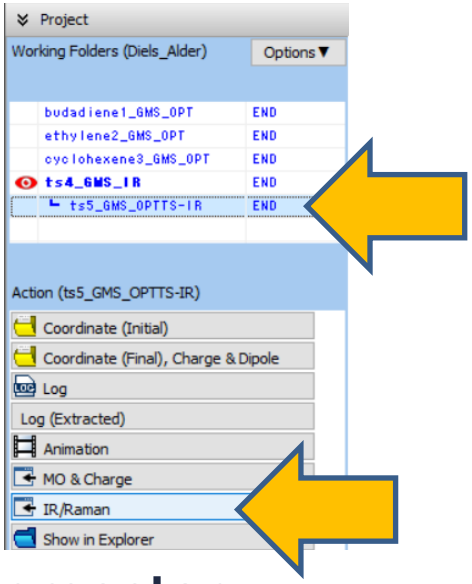
A. Click  (**Workflow Setup**) .
B. If 'Do you want to continue from previous run?' appears, click **No**.
C. In **GAMESS Workflow Setup** window, change **Preset** to **IR + Optimize(TS) + IR**.
D. In **Job Setting** window, change **Prefix for working folder name** to 'ts' and click **Run**.
・ If you want to reduce the calculation accuracy to finish the calculation faster, change Basis set to STO-3G.

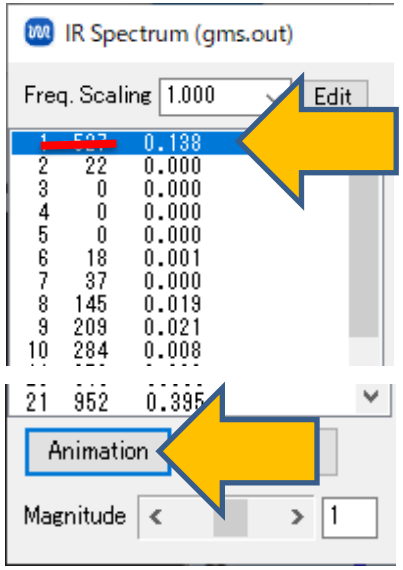


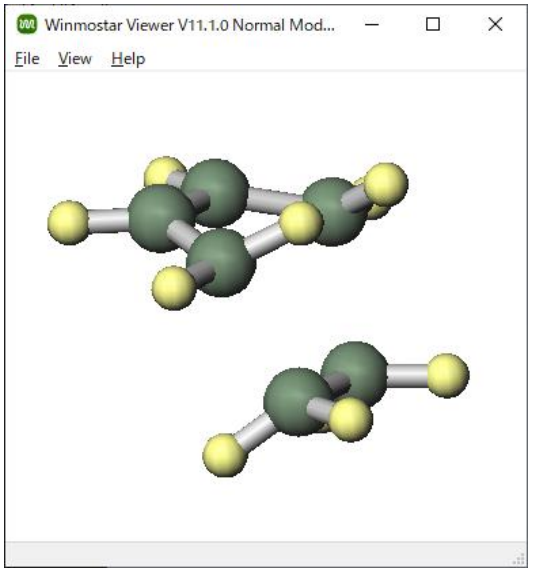


E. Transition State (TS) Structure Optimization Calculation

A. After the calculation is completed and the status of the work folder changes to **END** or **END(-)**, click on the folder 'ts5_GMS_OPTTS-IR' in Working folders, and then click **IR/Raman** in Action.
B. In **IR Spectrum** window, if there is only one negative value (appearing as negative but actually an imaginary value) in the list of vibration frequencies at the top left, it signifies that the transition state structure has been obtained.
C. After clicking on the first peak, click **Animation**. If the vibration between the carbons of butadiene and ethylene is displayed, it indicates that the desired transition state has been achieved.

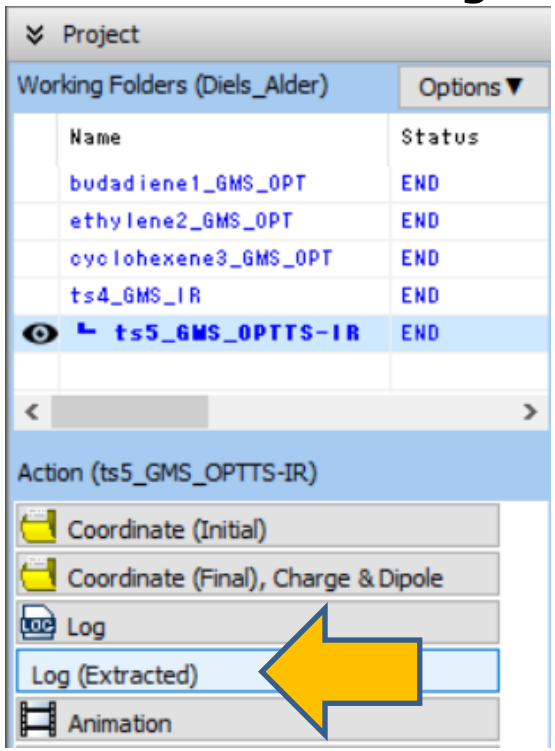


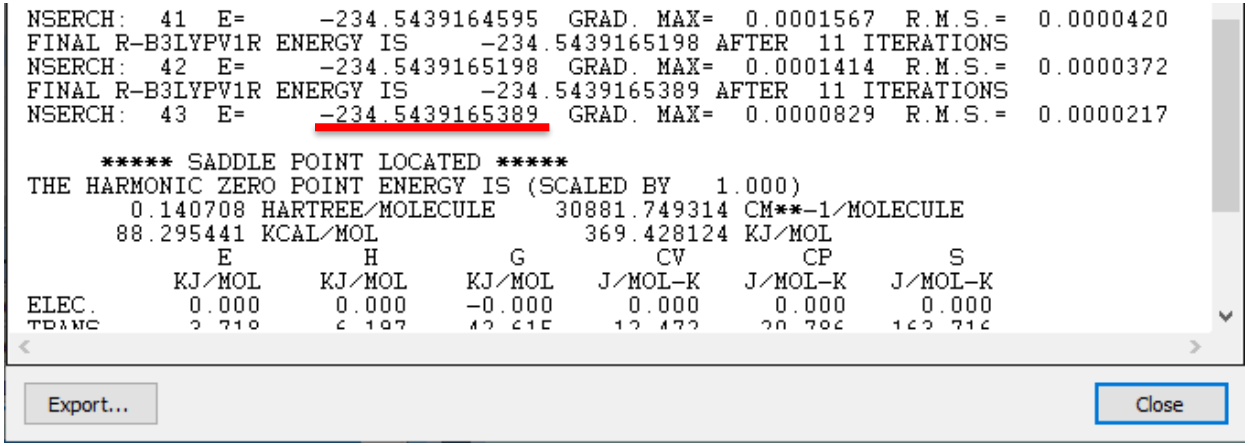




E. Transition State (TS) Structure Optimization Calculation

A. Click **Log (Extracted)** in Action.
B. In **Extracted Log** window, copy the number after E= at the end of the last NSERCH line into Excel or a similar program. This value (-234.54391 Hartree) represents the energy of Ethylene in its stable structure.
C. Close **Extracted Log** window.





F. Reaction Energy Calculation

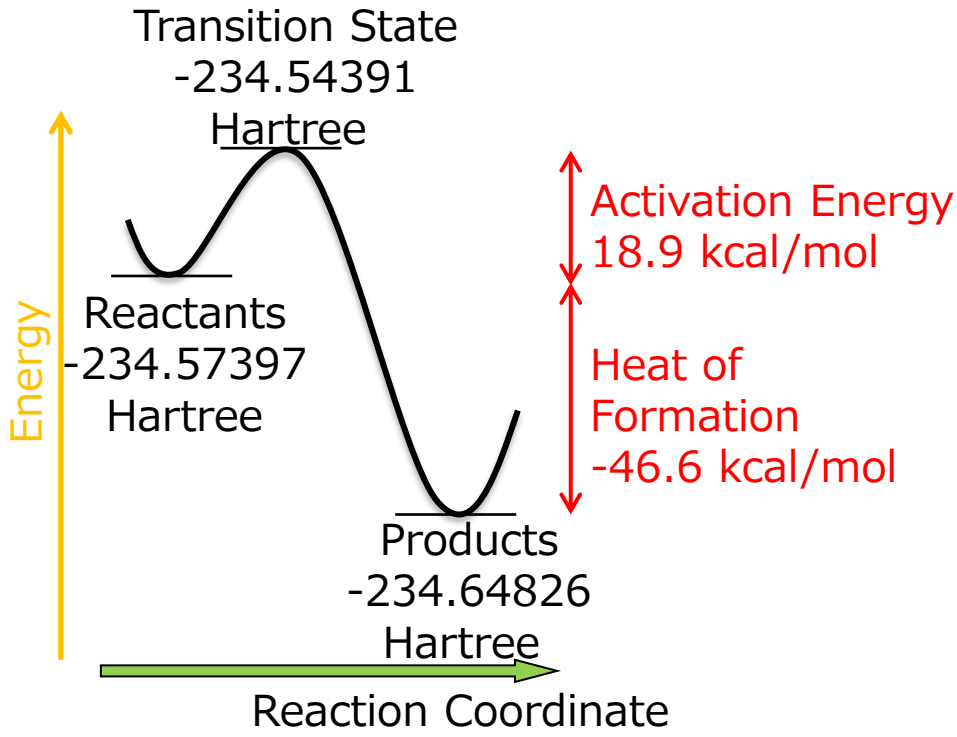
The calculation is performed as follows.

(Heat of Reaction) = (Energy of Products) - (Energy of Reactants)

(Activation Energy) = (Energy of Transition State) – (Energy of Reactants)

This reaction is exothermic by 46.6 kcal/mol, and the activation energy required to overcome the transition state is 18.9 kcal/mol.

	Energy
Reactants	-155.98651 + (-78.58746) = -234.57397 Hartree
Transition State	-234.54391 Hartree
Products	-234.64826 Hartree
Heat of Formation	-234.64826 – (-234.57397) = -0.07429 Hartree = -46.6 kcal/mol
Activation Energy	-234.54391 – (-234.57397) = 0.03006 Hartree = 18.9 kcal/mol

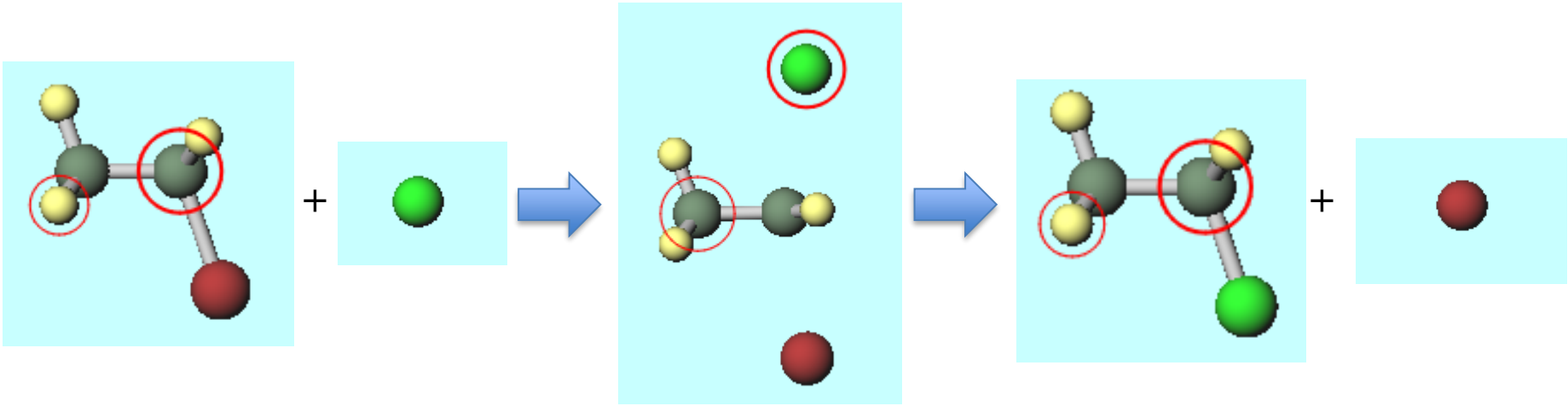


B. SN2 Reaction of Bromoethane with Cl- Ion

A. Calculation Procedure

Perform structure optimization calculations for the reactants (CH_3CH_2Br、Cl^-), products (CH_3CH_2Cl、Br^-), and the transition state in DMSO solution, a non-protic polar solvent, using the PCM method. The energies obtained from these calculations are used to compute the heat of reaction and activation energy for the reaction.
Note:

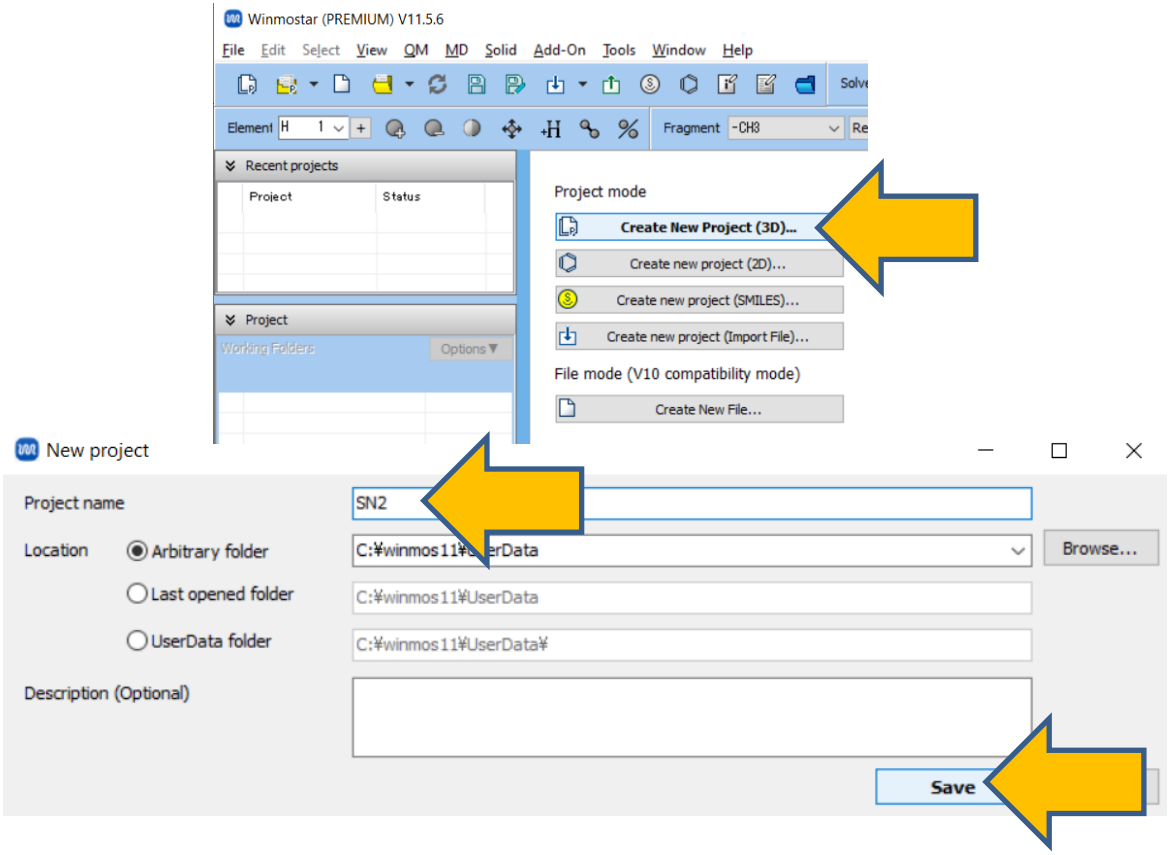
- The initial structure for the transition state calculation should utilize results from MOPAC calculations. Therefore, it's necessary to complete MOPAC (Transition State & IRC Calculation) tutorial in advance.



A. Calculation Procedure

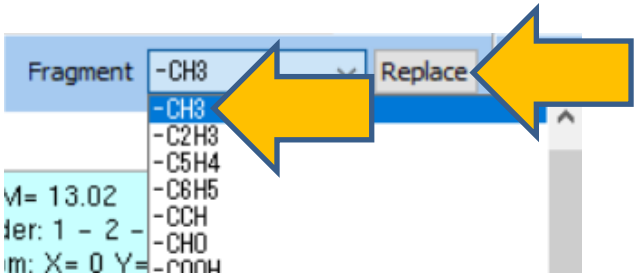
A. Launch Winmostar and click **Create New Project (3D)**. If Winmostar is already running, first click **File | Close**.

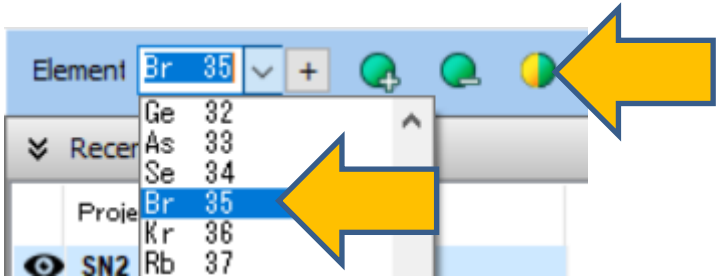
B. Enter 'SN2' for **Project name** and click **Save**.

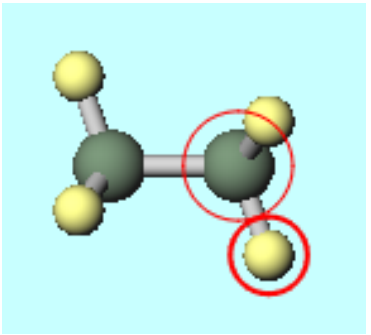


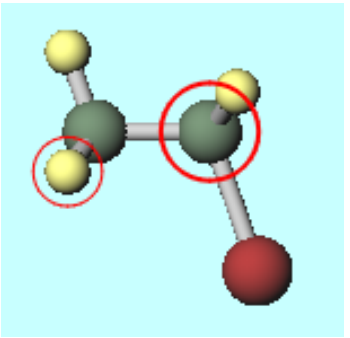
B. Structural Optimization Calculation (Bromethane)

A. Select **-CH3** from **Fragment** at the top of Main Window and click **Replace** twice to create ethane.
B. With the **H** atom (yellow) marked with a thick red circle, select **Br 35** from **Element for editing operations** at the top of Main Window.
C. Click **Change Element** to create bromoethane.







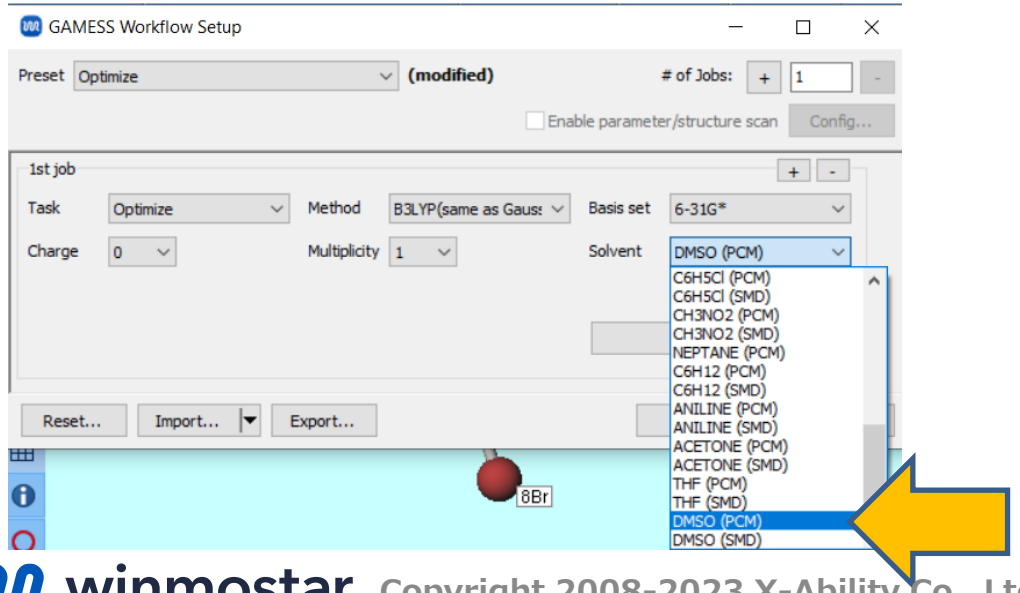


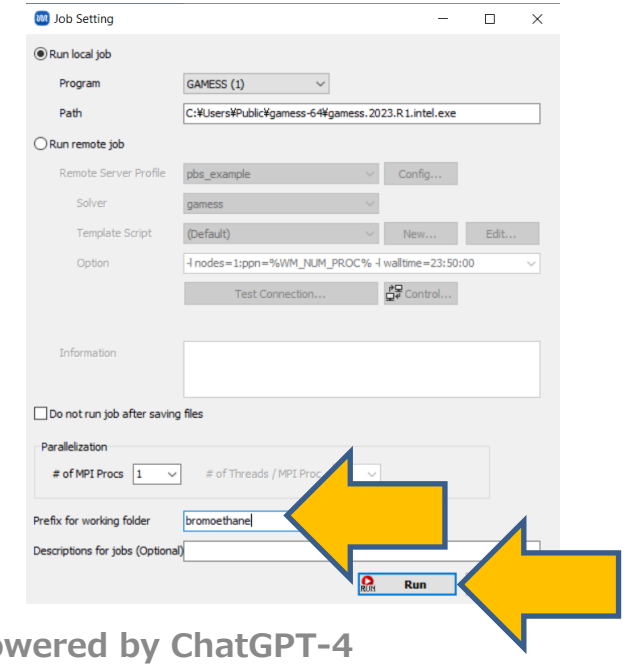
B. Structural Optimization Calculation (Bromethane)

A. Click (**Workflow Setup**).
B. In **GAMESS Workflow Setup** window, change **Solvent** to **DMSO (PCM)** and click **OK**.
C. In **Job Setting** window, **Prefix for working folder name** to "bromoethane" and click **Run**.

・If you want to finish the calculation faster by reducing the calculation accuracy, change Basis set to STO-3G.

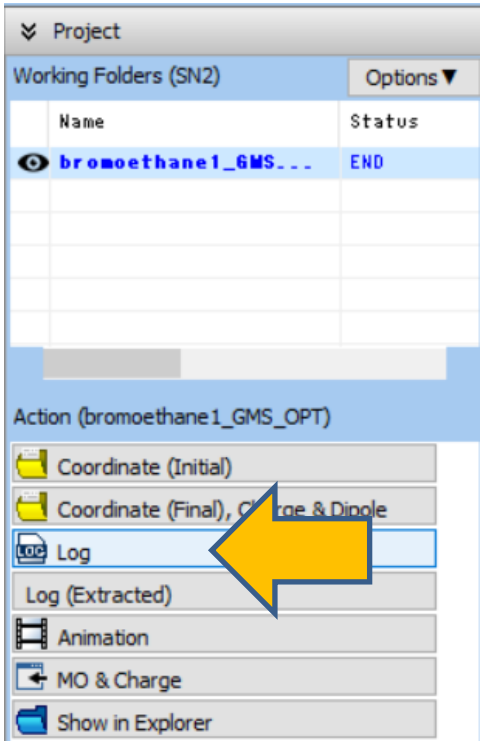
If you change to STO-3G, it's necessary to perform all the molecules involved in this SN2 reaction at STO-3G as well.





B. Structural Optimization Calculation (Bromethane)

A. After the calculation has finished and the status of the working folder changes to **END** or **END(-)**, click **Log** in Action.
B. Copy the value from the line "TOTAL FREE ENERGY IN SOLVENT" found near the end of the displayed log into Excel or similar.



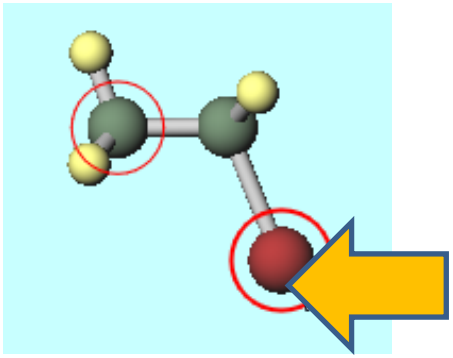
gms.out - Notepad

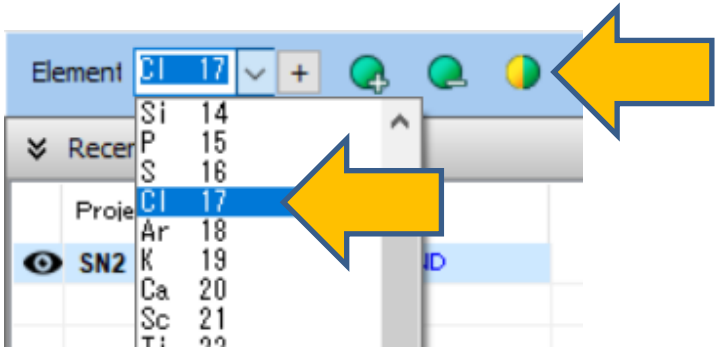
File Edit Format View Help

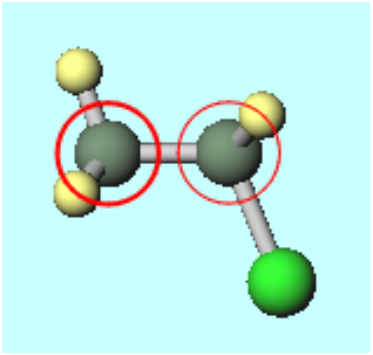
```
 ......END OF GEOMETRY SEARCH......
 STEP CPU TIME =     0.00 TOTAL CPU TIME =         47.3 (      0.8 MIN)
 TOTAL WALL CLOCK TIME=         48.1 SECONDS, CPU UTILIZATION IS    98.33%


            ------------------------------------------------
            -------   RESULTS OF PCM CALCULATION   -------
            ------------------------------------------------


 FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI>       =    -2653.1165817056 A.U.
 INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI>       =    -2653.1119221002 A.U.
 DELTA INTERNAL ENERGY =  <D-PSI| H(0) |D-PSI>       =        0.0000000000 A.U.
 ELECTROSTATIC INTERACTION                           =       -0.0046596054 A.U.
 PIEROTTI CAVITATION ENERGY                          =        0.0000000000 A.U.
 DISPERSION FREE ENERGY                              =        0.0000000000 A.U.
 REPULSION FREE ENERGY                               =        0.0000000000 A.U.
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP)   =       -0.0046596054 A.U.
 TOTAL FREE ENERGY IN SOLVENT                        =    -2653.1165817056 A.U.
```

C. Structural Optimization Calculation (Chloroethane)

A. Click **Br** atom of bromoethane to mark it with a thick red circle.
B. From **Element for editing operations** at the top of Main Window, select **Cl 17**.
C. Click **Change Element** to create chloroethane.



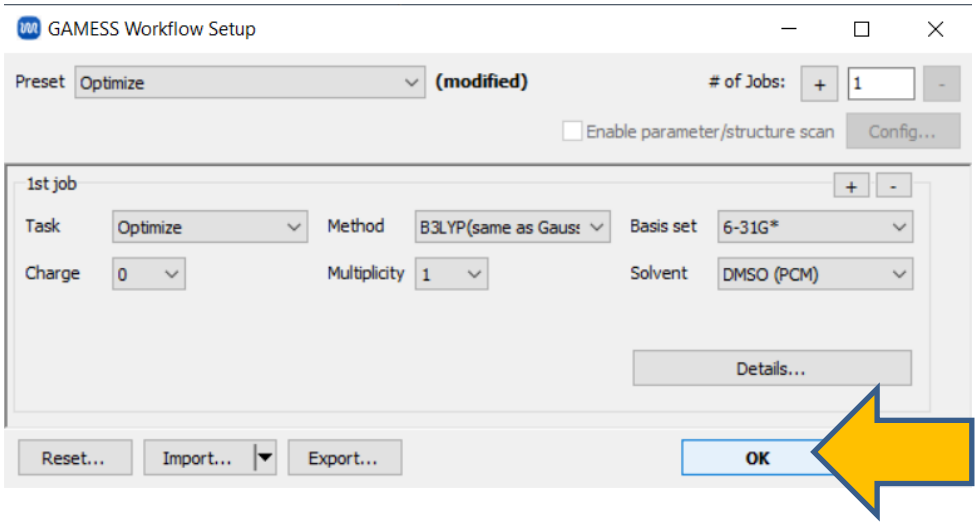


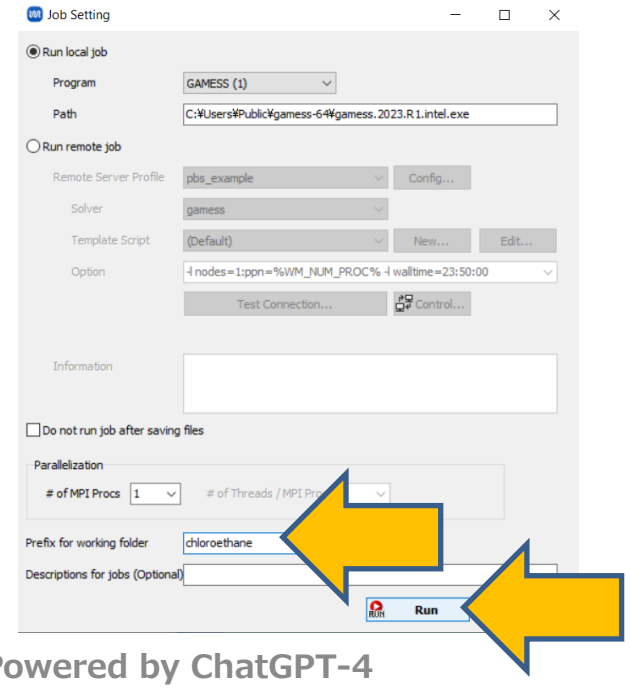


C. Structural Optimization Calculation (Chloroethane)

A. Click (**Workflow Setup**).
B. If 'Do you want to continue from previous run?' appears, click **No**.
C. In **GAMESS Workflow Setup** window, with **Solvent** set to **DMSO(PCM)**, click **OK**.
D. In **Job setting** window, change **Prefix for working folder name** to "chloroethane" and click Run.

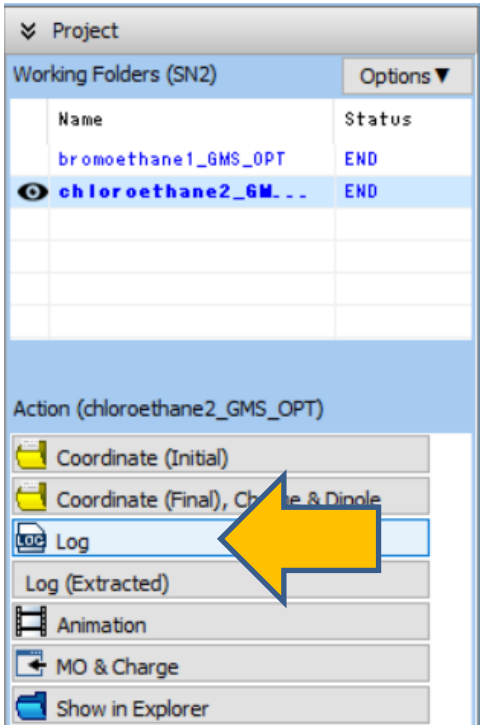
・If you want to speed up the calculation by reducing the calculation accuracy, change Basis set to STO-3G.

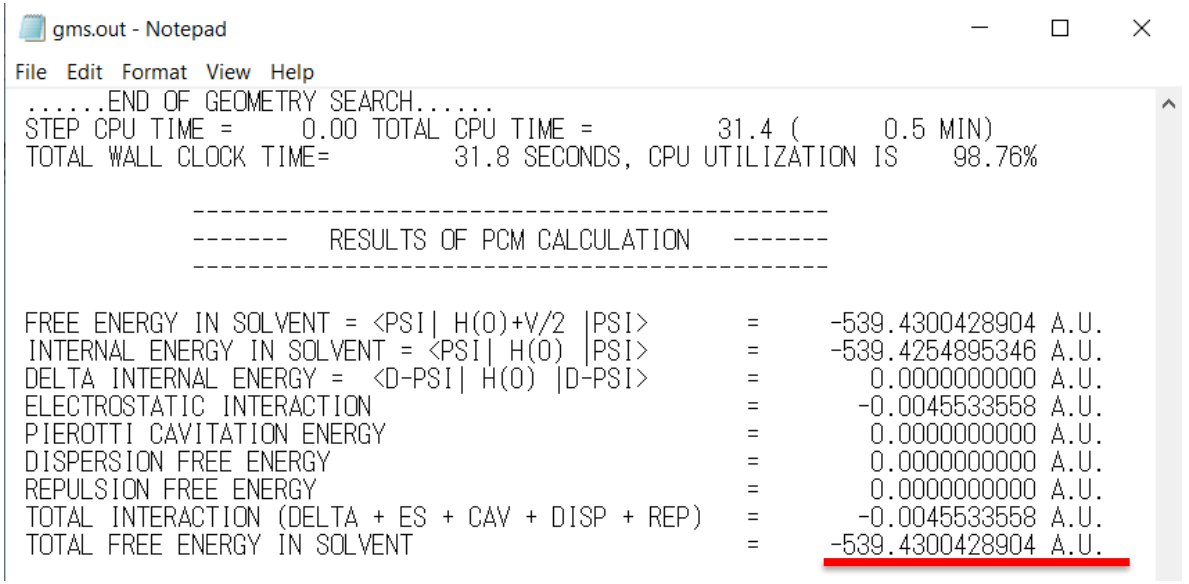




C. Structural Optimization Calculation (Chloroethane)

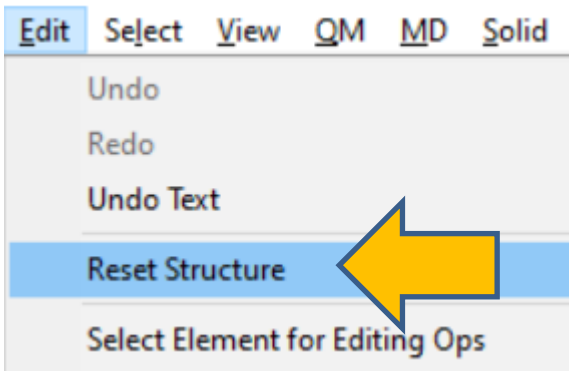
A. After the calculation has finished and the status of the working folder changes to **END** or **END(-)**, click **Log** in Action.
B. Copy the value from the line "TOTAL FREE ENERGY IN SOLVENT" found near the end of the displayed log into Excel or similar.

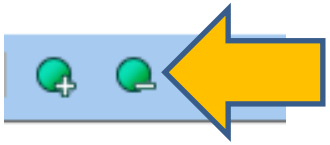


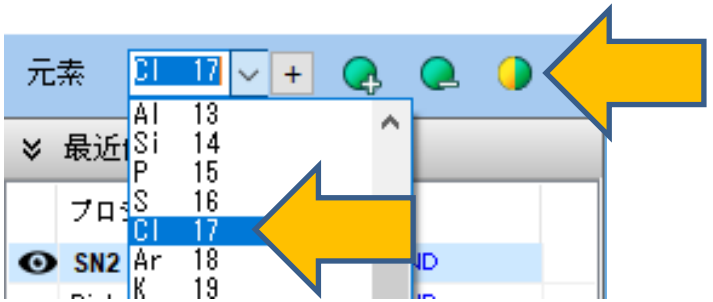


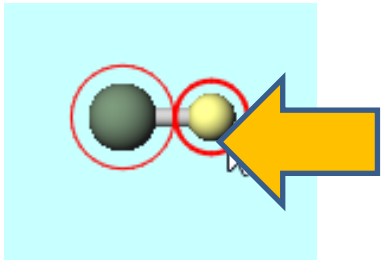
D. Energy Calculation (Cl Ion)

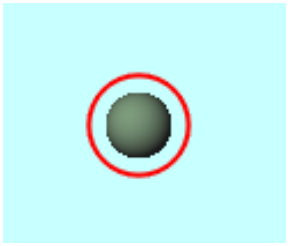
A. Click **Edit | Reset Structure**.
B. Click on the right **H** atom (yellow) to mark it with a thick red circle, then click **Delete Atom** to leave only the **C** atom.
C. From **Element for editing operations** at the top of Main Window, select **Cl 17**.
D. Click **Change Element** to change it to a **Cl** atom.

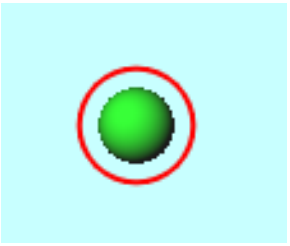








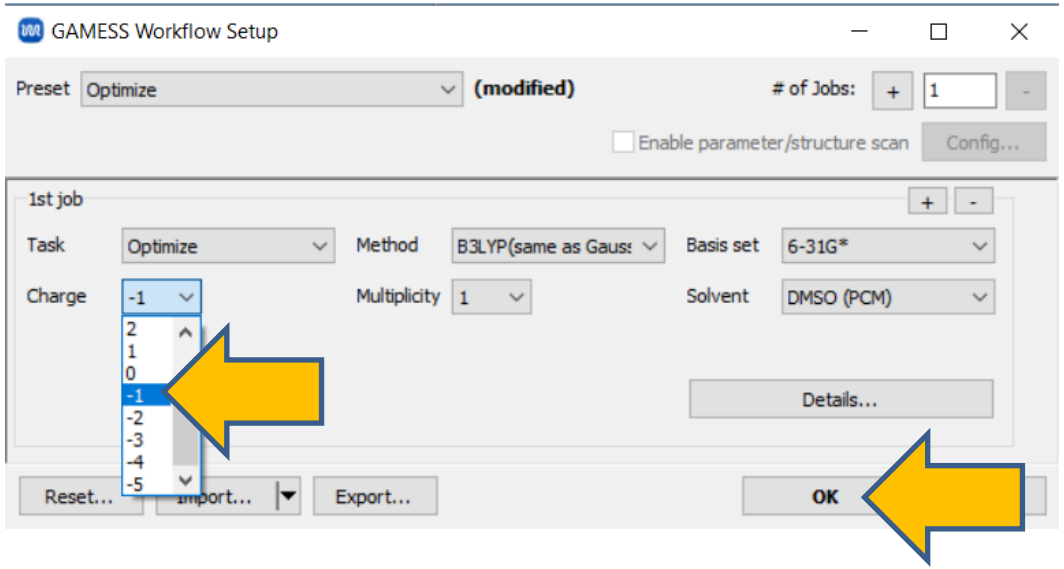


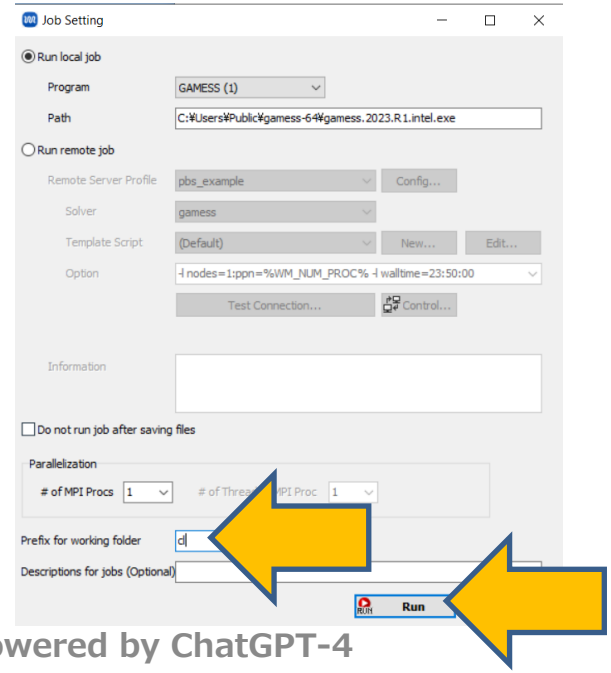


D. Energy Calculation (Cl Ion)

A. Click (**Workflow Setup**).
B. If 'Do you want to continue from previous run?' appears, click **No**.
C. In **GAMESS Workflow Setup** window, with **Solvent** set to **DMSO(PCM)** and **Charge** set to **−1**, and then click **OK**.
D. In **Job setting** window, change **Prefix for working folder name** to "cl" and click **Run**.

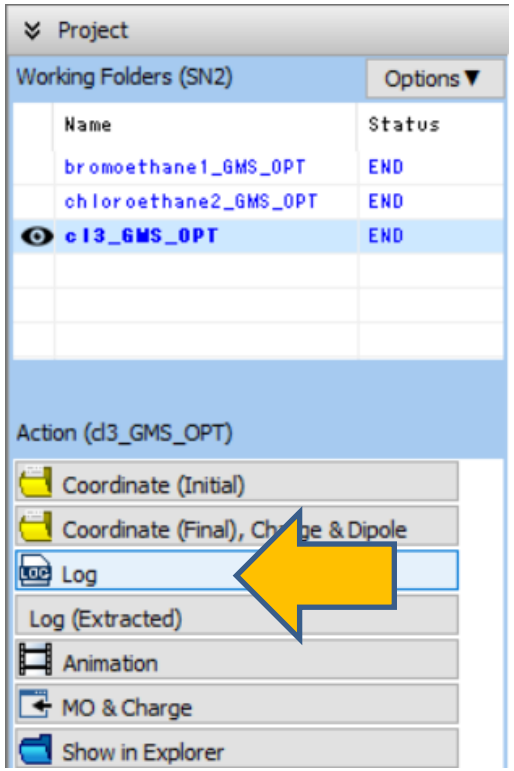
・If you want to speed up the calculation by reducing the calculation accuracy, change Basis set to STO-3G.

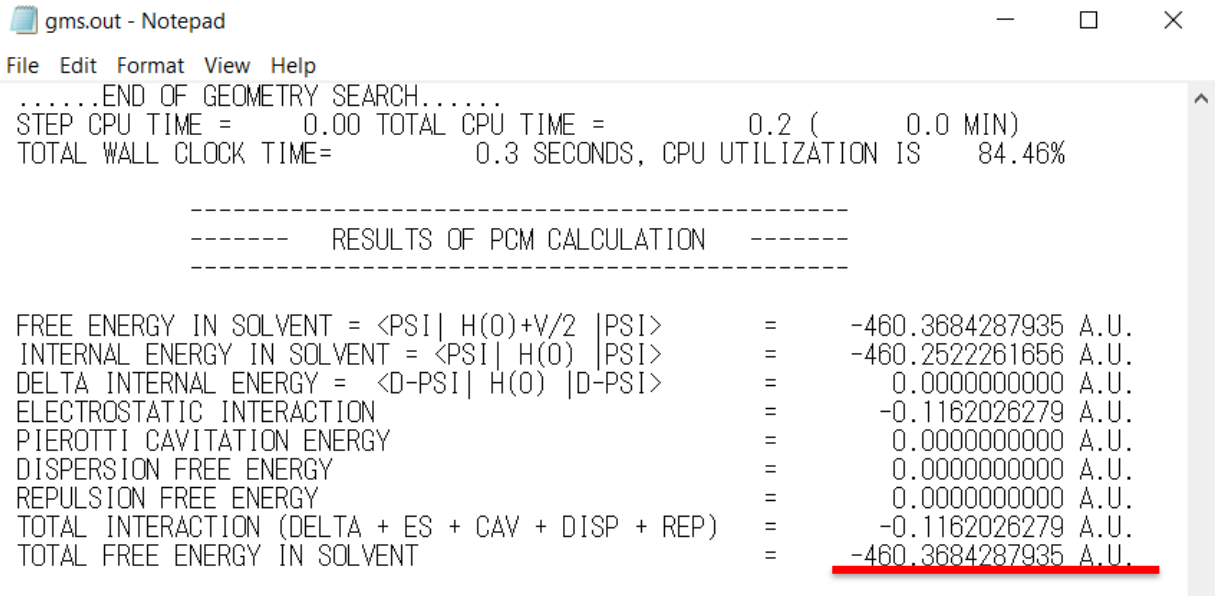




D. Energy Calculation (Cl Ion)

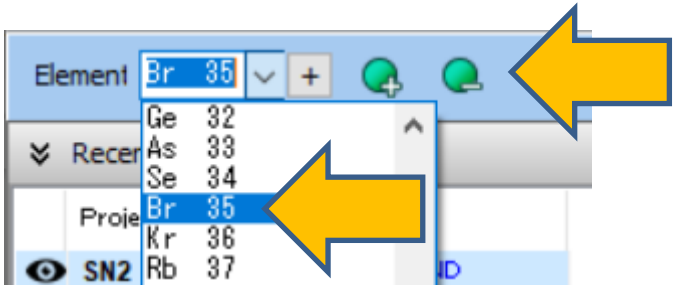
A. After the calculation has finished and the status of the working folder changes to **END** or **END(-)**, click **Log** in Action.
B. Copy the value from the line "TOTAL FREE ENERGY IN SOLVENT" found near the end of the displayed log into Excel or similar.

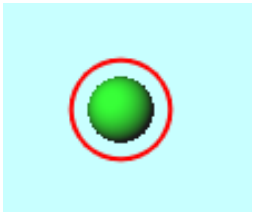


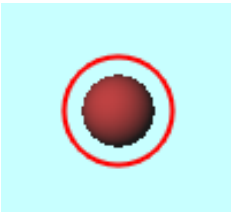


E. Energy Calculation (Br Ion)

A. With **Cl** atom displayed, select **Br 35** from **Element for editing operations** at the top of Main Window.
B. Click **Change Element** to change it to a **Br** atom.

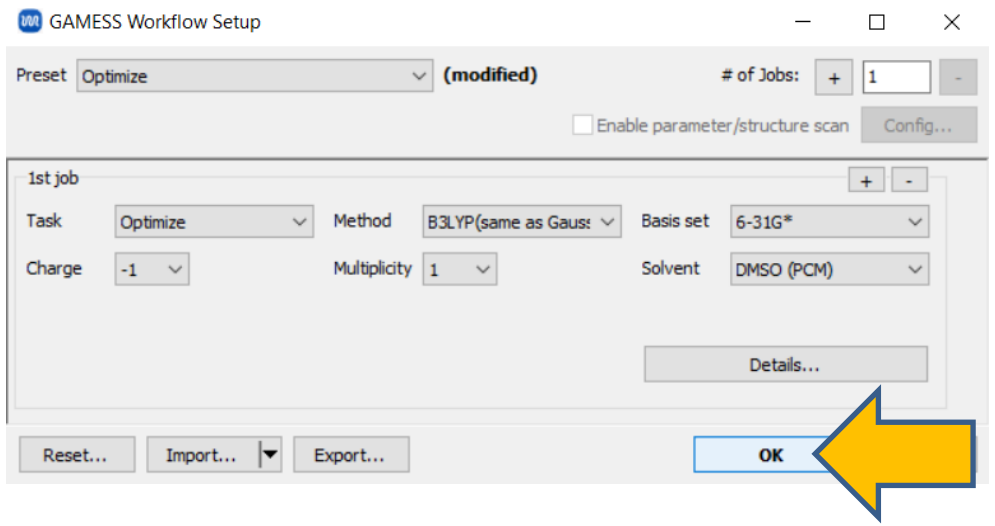


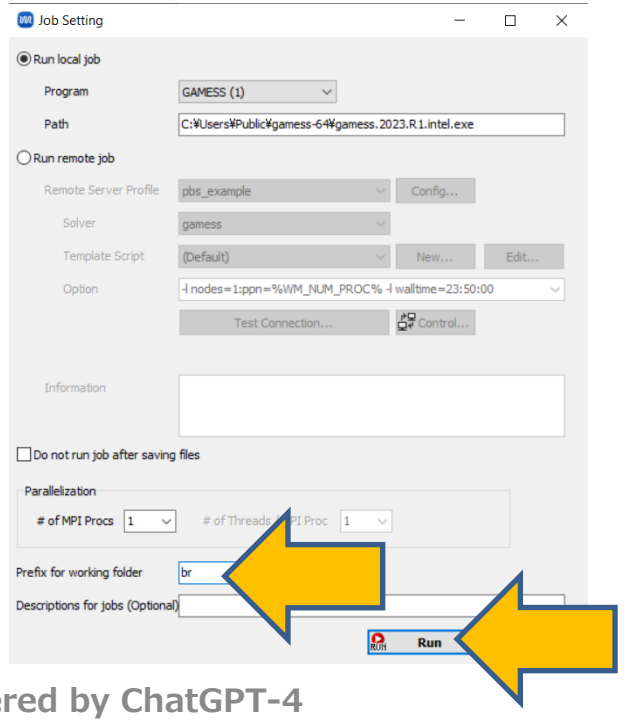




E. Energy Calculation (Br Ion)

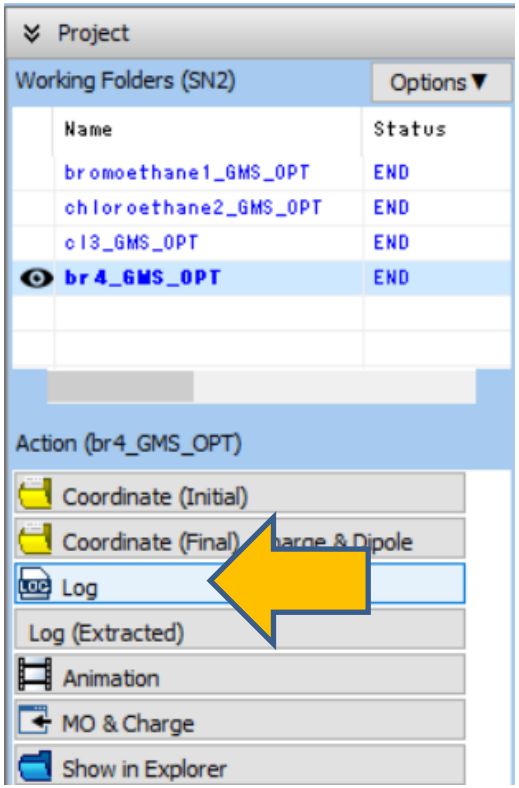
A. Click (**Workflow Setup**).
B. If 'Do you want to continue from previous run?' appears, click **No**.
C. In **GAMESS Workflow Setup** window, with **Solvent** set to **DMSO(PCM)** and **Charge** set to **−1**, and then click **OK**.
D. In **Job setting** window, change **Prefix for working folder name** to "br" and click **Run**.
・If you want to speed up the calculation by reducing the calculation accuracy, change Basis set to STO-3G.

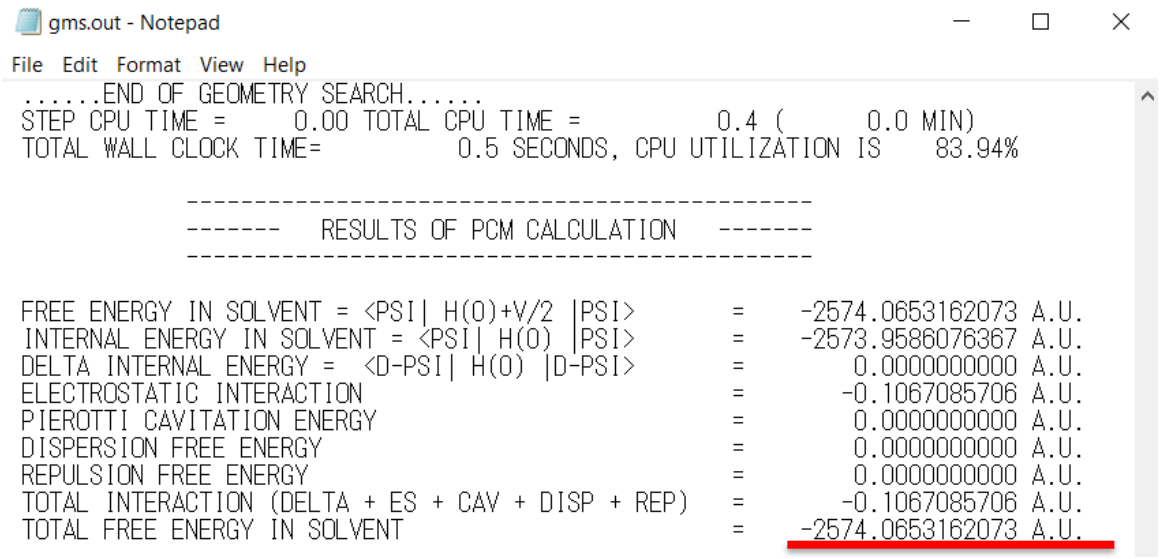




E. Energy Calculation (Br Ion)

A. After the calculation has finished and the status of the working folder changes to **END** or **END(-)**, click **Log** in Action.
B. Copy the value from the line "TOTAL FREE ENERGY IN SOLVENT" found near the end of the displayed log into Excel or similar.

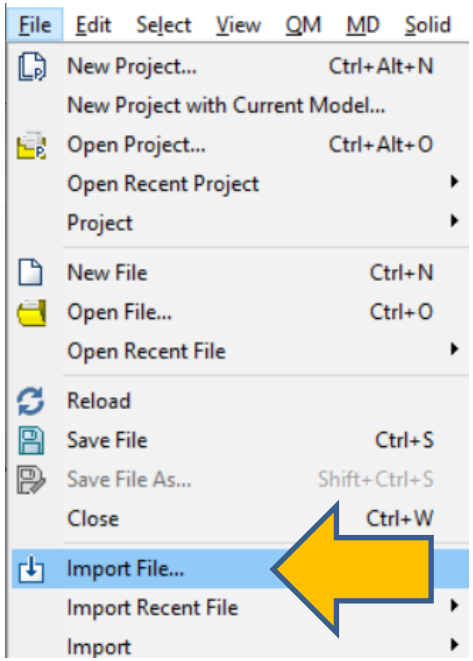


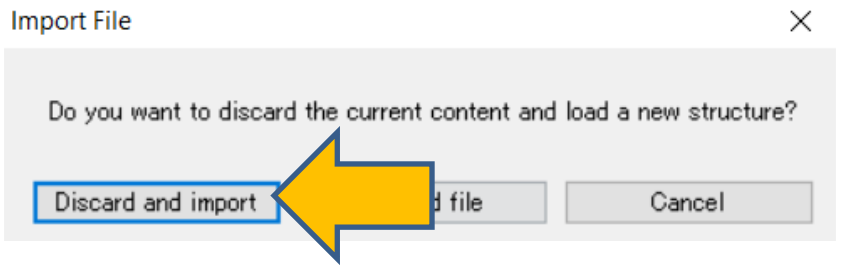


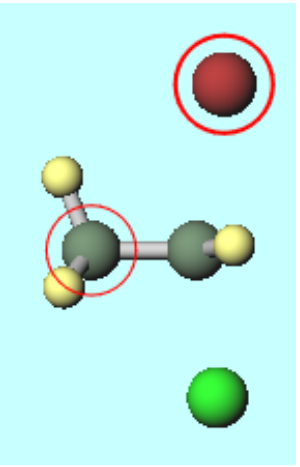
F. Transition State (TS) Structure Optimization Calculation

Assuming MOPAC (Transition State & IRC) tutorial has already been completed.

A. Select **File | Import File**.
B. Enter "ts.arc" (the file name of the transition state calculation result from MOPAC (Transition State & IRC) tutorial) and click **Open**.
C. If prompted with "Do you want to dixcard the current content ana load a new structure?", click **Discard and Import**.



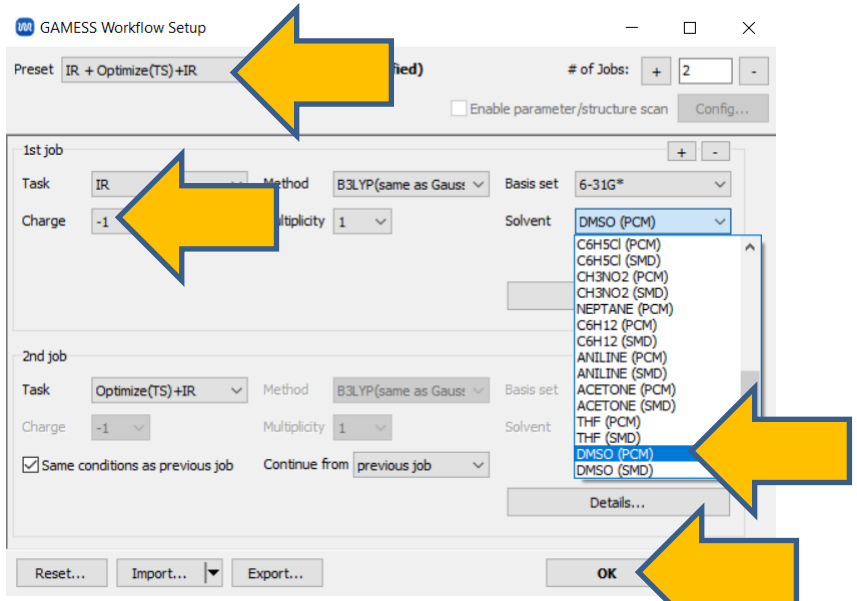


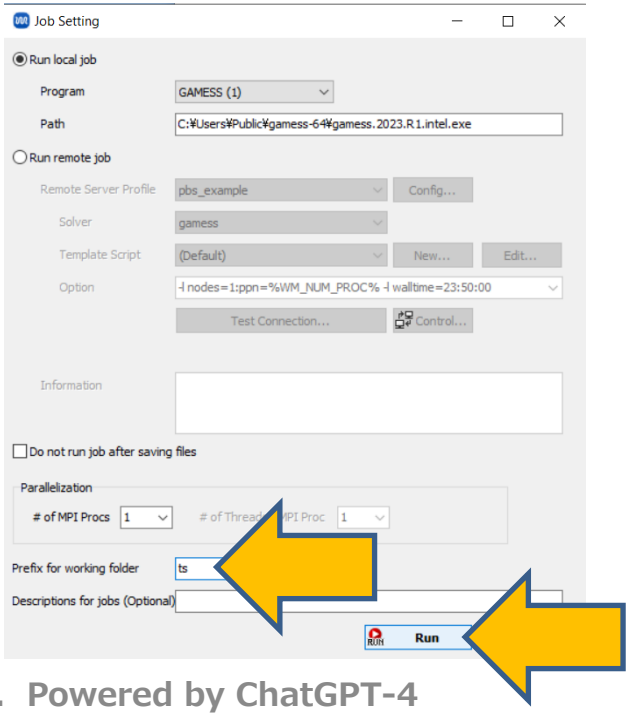


F. Transition State (TS) Structure Optimization Calculation

A. Click  (**Workflow Setup**).
B. If 'Do you want to continue from previous run?' appears, click **No**.
C. In **GAMESS Workflow Setup** window, change **Preset** to **IR + Optimize(TS)+IR**. Change **Charge** to **-1** and **Solvent** to **DMSO(PCM)** in **1st job** , then click **OK**.
D. In **Job Setup** window, change **Prefix for working folder name** to "ts" and click **Run**.

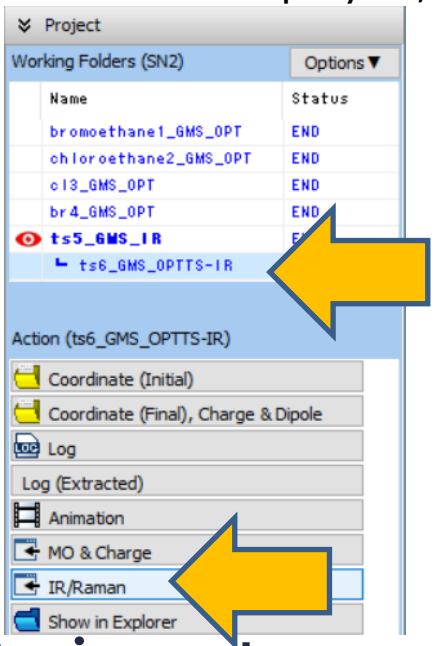
・If you wish to reduce the calculation accuracy for a quicker completion, change Basis set to STO-3G.

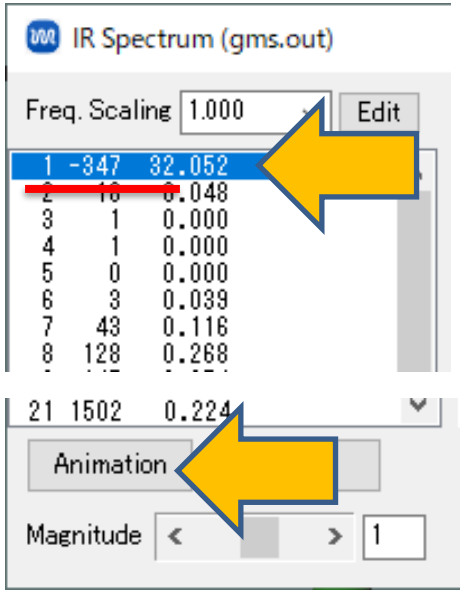


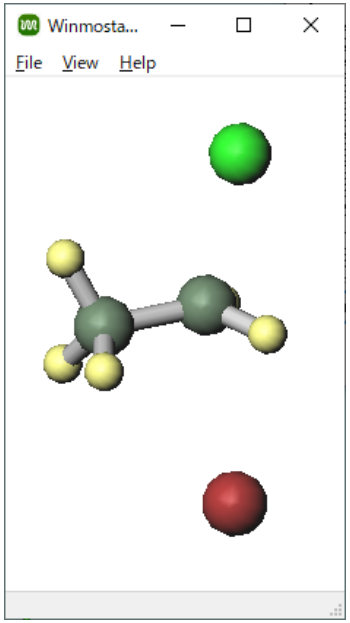


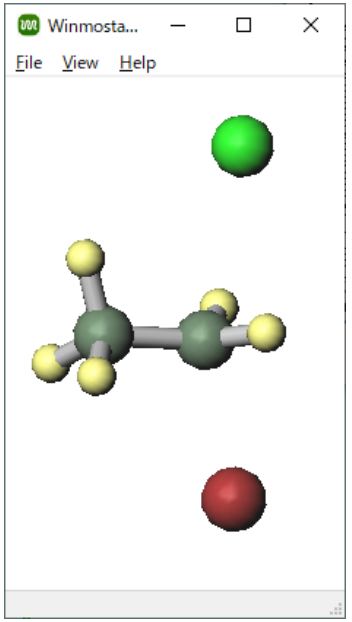
F. Transition State (TS) Structure Optimization Calculation

A. After the calculation ends and the status of the working folder changes to **END** or **END(-)**, click on the "ts6_GMS_OPTTS-IR" folder in Working Folders, then click **IR/Raman** in Action.
B. If there is only one negative value (shown as a negative value, but technically an imaginary value) in the list of vibrational frequencies at the top left of **IR Spectrum** window, it means that the transition state structure has been obtained.
C. Click on the first peak and then click **Animation**. If the vibration between Cl^-,Br^-, and carbon is displayed, it means the desired transition state has been achieved.



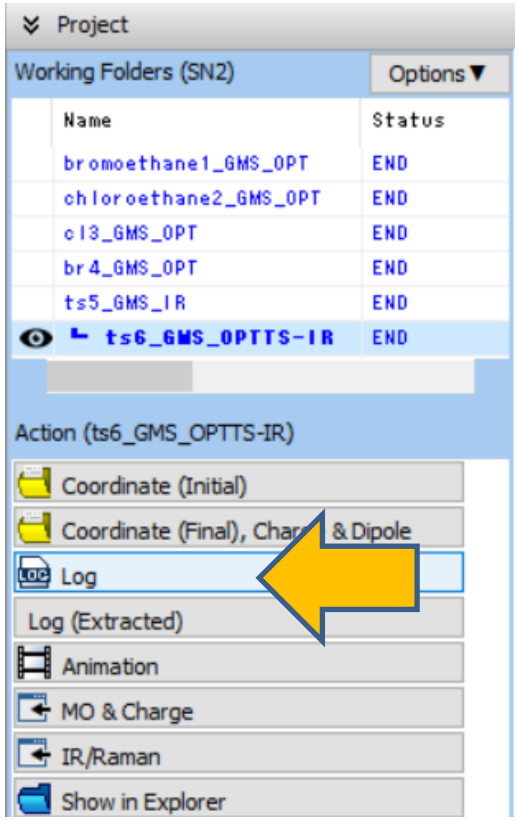


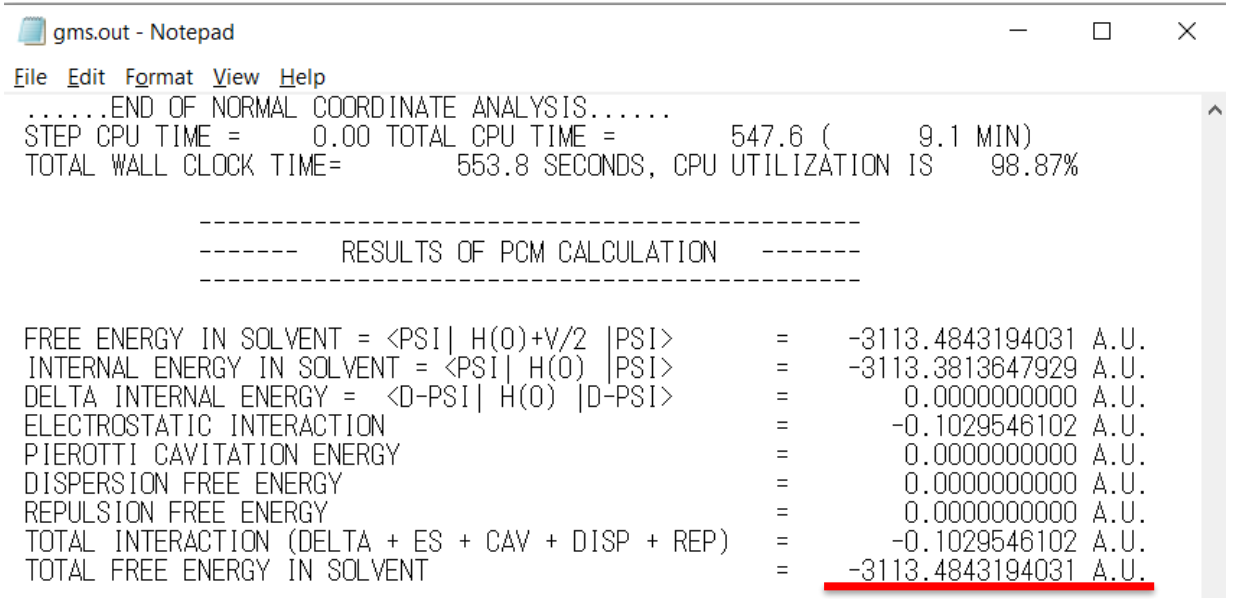




F. Transition State (TS) Structure Optimization Calculation

A. Copy the value from the line "TOTAL FREE ENERGY IN SOLVENT" written towards the end of the displayed log into Excel or similar software.





G. Reaction Energy Calculation

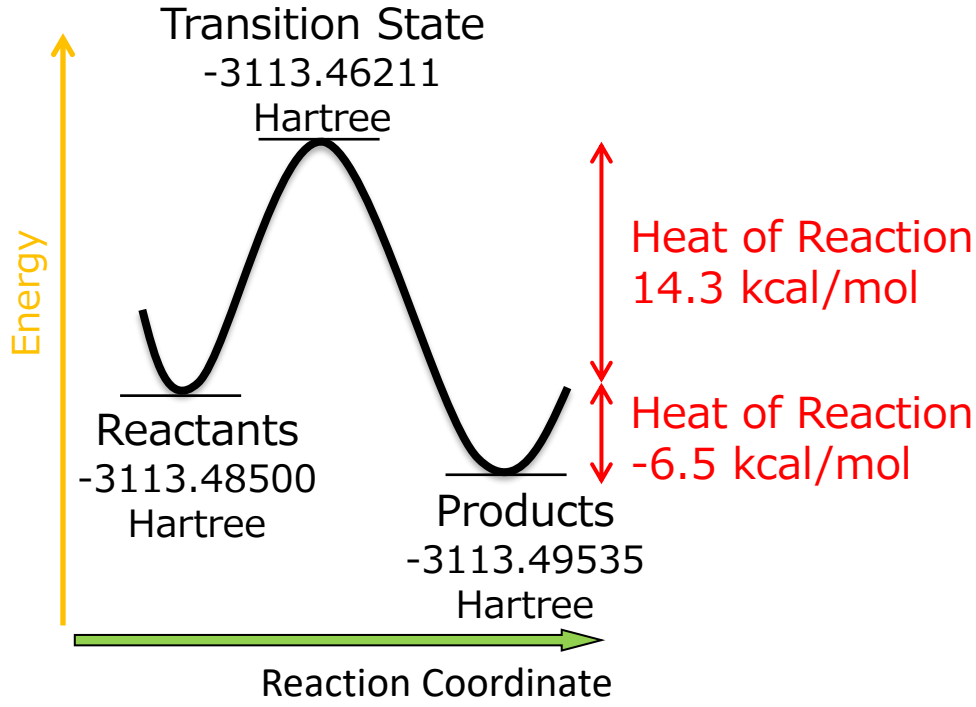
The heat of reaction is calculated as follows:

Heat of Reaction = Energy of Products - Energy of Reactants

Activation Energy = Energy of Transition State - Energy of Reactants

This reaction is exothermic by 6.5 kcal/mol, and the activation energy required to surpass the transition state is 14.3 kcal/mol.

	エネルギー
Reactants	-2653.11658 + (-460.36842) = -3113.48500 Hartree
Transition State	-3113.46211 Hartree
Products	-539.43004 + (-2574.06531) = -3113.49535 Hartree
Heat of Reaction	-3113.49535 – (-3113.48500) = -0.01035 Hartree = -6.5 kcal/mol
Activation Energy	-3113.46211– (-3113.48500) = 0.02286 Hartree =14.3 kcal/mol



G. Reaction Energy Calculation

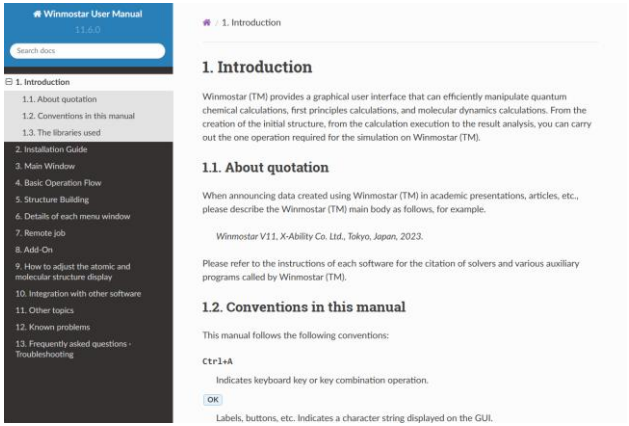
For reference, we summarize the comparison of the heat of reaction and activation energy in DMSO solution and in vacuum. The energy values in vacuum were calculated by setting **Solvent** to **[None]** in **GAMESS Workflow Setup** window.

The heat of reaction differs by about 6 kcal/mol between DMSO solution and vacuum, but the trend is the same. On the other hand, the sign of the activation energy is reversed, with the transition state being more stable than the reactants in vacuum. Comparing the energy of each molecule, the atoms with a charge of -1, Cl- and Br-, are significantly stabilized in solution, but the stabilization in solution for the transition state, which has an overall charge of -1, is smaller compared to Cl- and Br-. For reactions involving molecules with a significant charge imbalance, solvent effects can be important.

	溶液中	真空中
Reactants	-2653.11658 + (-460.36842) = -3113.48500 Hartree	-2653.1127 + (-460.2522) = -3113.3649 Hartree
Transition State	-3113.46211 Hartree	-3113.3782 Hartree
Products	-539.43004 + (-2574.06531) = -3113.49535 Hartree	-539.4263 +(-2573.9586) = -3113.3849 Hartree
Heat of Reaction	-3113.49535 – (-3113.48500) = -0.01035 Hartree = -6.5 kcal/mol	-3113.3849 – (-3113.3649) = -0.0200 Hartree = -12.6 kcal/mol
Activation Energy	-3113.46211– (-3113.48500) = 0.02286 Hartree = 14.3 kcal/mol	-3113.3782 – (-3113.3649) = -0.0133 Hartree = -8.3 kcal/mol

Finally

- For detailed information on each feature, please refer to Winmostar User Manual.



Winmostar User Manual

Scenes from Winmostar Training Session

- If you wish to practice the contents of this guide, please consider attending Winmostar Introductory Training Session, Winmostar Basic Training Session, or Individual Training Session. (See page 2 for details.)
- If you are unable to proceed as instructed in this guide, please first consult Frequently asked questions.
- If FAQs do not resolve your issue, for the purposes of information accumulation and management, please contact us through Contact page, detailing the steps to reproduce the issue and attaching any generated files at that time.