

ORCA Computational Chemistry Lab

Getting Started with Quantum Chemical Calculations

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Geometry Optimization and Frequency

1. Geometry Optimization (Opt)

- **Goal:** Find the "equilibrium" structure.
- Atoms move to reach the lowest energy state (local minimum).
- Like a ball rolling to the bottom of a valley.

2. Frequency Calculation (Freq)

- **Goal:** Verify the minimum and get spectra.
- Checks the "curvature" of the valley.
- Provides: IR/Raman spectra and Gibbs Free Energy (G).

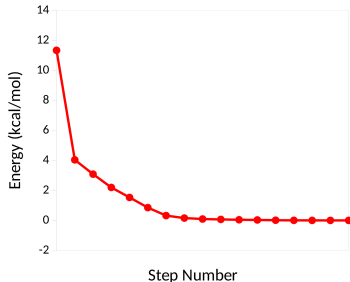


Figure: Energy changing in a geometry optimization

Intrinsic Reaction Coordinate (IRC) Calculation

The Reaction: $A + B \rightarrow C$

- How do reactants transform into products?
- Must pass through a transition state (TS).
- IRC maps the entire pathway.

What is an IRC Calculation?

- **Goal:** Trace the minimum energy path from TS to reactants and products.
- Follows the reaction coordinate "downhill" in both directions.

What you get:

- Confirmation that TS connects correct reactants/products
- Energy profile along reaction path
- Structural changes during reaction

Using Nano Text Editor

Nano is a command-line text editor for creating and editing files.

Basic Commands:

- Open/create a file: `nano filename`
- Save: `Ctrl + O` (it will prompt you for a name, press Enter)
- Exit: `Ctrl + X`
- Cut line: `Ctrl + K` (Delete an entire line)

Tip: All commands are shown at the bottom of the nano window.
The `^` symbol means “Ctrl”.

Input Files Needed for ORCA

To run an ORCA calculation, you need:

1 Starting Geometry (.xyz)

- Contains: initial molecular coordinates
- Built in Avogadro 2, saved as XYZ format
- Example: `molecule.xyz`

2 ORCA Input File (.inp)

- Contains: method, basis set, job type, molecular geometry
- Example: `molecule.inp`

3 SLURM Batch Script (.sh)

- Tells the C1 cluster how to run your job
- Specifies: time limit, memory, number of processors
- Example: `submit_orca.sh`

Making a Molecule in Avogadro 2

Avogadro 2 is a molecular editor for building 3D structures.

Steps:

- 1 Open Avogadro 2: avogadro (or from Applications menu)
- 2 Build your molecule:
 - Select “Draw Tool” (pencil icon)
 - Click to add atoms (default: Carbon)
 - Change element: Right-click on atom or use Element dropdown
 - Draw bonds: Click and drag between atoms
- 3 Optimize geometry:
 - Extensions → Optimize Geometry
 - This gives a reasonable starting structure
- 4 Save coordinates:
 - File → Save As (Mac/Linux)/Export(Windows) → Choose **XYZ format**
 - Name it: e.g. molecule.xyz

Writing an ORCA Input File

Basic ORCA input structure (using external XYZ file):

```
1 # Comment line describing your calculation
2 ! B3LYP pc-0 TightSCF Opt Freq
3
4 * xyzfile 0 1 structure.xyz
```

Key components:

- ! line: Method (B3LYP), basis set (pc-0), job type (Opt), convergence (TightSCF)
- * xyzfile: Directs ORCA to read an external coordinate file
- 0 1: Charge (0) and multiplicity (1 = singlet)
- structure.xyz: The name of your geometry file (must be in the same folder)

Note: The shown method ensures your .xyz file is consistent with what you made in Avogadro 2, you can also copy-paste coordinates directly into the .inp file.

Writing a SLURM Batch Script

Create a file called `submit_orca.sh` (using nano):

```
1 #!/bin/bash
2 #SBATCH --job-name=HY_pc0      (Name it anything)
3 #SBATCH --time=01:00:00       (DD:HH:MM)
4 #SBATCH --mem-per-cpu=4000     (4000MB = 4GB)
5
6 module load orca/6.0.0
7
8 orca HY.inp                    (Tells the cluster to run orca on your .inp file)
```

Submit your job: (On command line)

```
1 sbatch submit_orca.sh
```

Check job status: `squeue -u $USER` (Use your WatIAM id)

Complete Workflow Summary

- 1 **Build molecule** in Avogadro 2 → Save as `.xyz`
- 2 **Create ORCA input** using nano:
 - `nano molecule.inp`
 - Add method, basis set, job type, geometry
- 3 **Create SLURM script:**
 - `nano submit_orca.sh`
 - Set resources and load ORCA module
- 4 **Submit job:** `sbatch submit_orca.sh`
- 5 **Check results** in output file: `molecule.out`

Today's Exercise: Learning from a "Bad" Calculation

Strategy: Run ONE calculation with small basis set, compare to converged results

Workflow:

- 1 Build HY and PY molecules in Avogadro 2
- 2 Create ORCA input files with pc-0 basis set
- 3 Run YOUR calculations

Learning Goals:

- Experience computational workflow hands-on
- See dramatically wrong predictions from small basis sets
- Compare to experimental literature values

Running Opt + Freq in ORCA

To run both sequentially, simply add both keywords to the ! line.

Input File Structure (HY.inp)

```
1 ! B3LYP pc-0 Opt Freq TightSCF
2
3 * xyzfile 0 1 HY.xyz
```

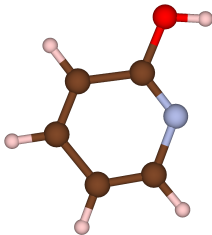
What happens during the run?

- 1 ORCA moves atoms until the forces are near zero (**Opt**).
- 2 Once stable, it computes the vibrations (**Freq**) on that specific geometry.
- 3 **Crucial:** If the Opt fails, the Freq will likely give incorrect results

The Two Tautomers

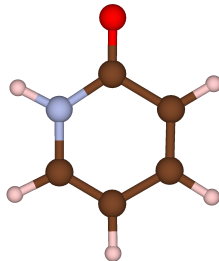
2-Hydroxypyridine (HY)

- Enol form
- O-H group
- Aromatic N



2-Pyridone (PY)

- Keto form
- C=O group
- N-H group



The Question: Which form is more stable?

Step 1: Build Molecules in Avogadro 2

Launch Avogadro 2 on your local computer Build HY (2-Hydroxypyridine):

- 1 Draw Tool → Draw benzene ring
- 2 Click on one C → Change to N (periodic table button)
- 3 Click on C next to N → Draw O
- 4 Click on O → Add H
- 5 Add H to remaining carbons
- 6 Extensions → Optimize Geometry (Force Field: UFF)

Save coordinates:

- File → Save As → HY.xyz

Build PY the same way:

- Start with pyridine ring (N in ring)
- Make C=O double bond (next to N)
- Add H to N
- Optimize and save as PY.xyz

Step 2: Transfer XYZ Files to Cluster

From your local computer, upload to cluster:

```
scp HY.xyz $USER@c1cluster:~/Lab_BasisSet/HY/  
scp PY.xyz $USER@c1cluster:~/Lab_BasisSet/HY/
```

Or: Copy-paste method

- 1 Open HY.xyz in a text editor locally
- 2 Copy the coordinates
- 3 SSH to cluster
- 4 Create file with nano and paste

Verify files are there:

```
ssh c1cluster  
cd ~/Lab_BasisSet/HY  
ls -l
```

Step 3: Create ORCA Input File for HY

Check your XYZ file exists:

```
ls HY.xyz
```

Create ORCA input file:

```
nano HY.inp
```

Input file contents:

```
! B3LYP pc-0 TightOPT
! Opt Freq
xyzfile 0 1 HY.xyz
```

Notes:

- xyzfile tells ORCA to read coordinates from HY.xyz
- Format: xyzfile charge multiplicity filename
- Must have both HY.inp and HY.xyz in same directory

Save: Ctrl+O, then Ctrl+X

Step 4: Create ORCA Input File for PY

Check your XYZ file exists:

```
ls PY.xyz
```

Create ORCA input file:

```
nano PY.inp
```

Input file contents:

```
! B3LYP pc-0 TightOPT
! Opt Freq
xyzfile 0 1 PY.xyz
```

Save: Ctrl+O, then Ctrl+X

Step 5: Submit Your Calculations

Create submission script for HY:

```
nano HY_run.sh
```

Script contents:

```
#!/bin/bash
#SBATCH --job-name=HY_pc0
#SBATCH --time=01:00:00
#SBATCH --mem-per-cpu=4000

module load orca/6.0.0
orca HY.inp
```

Repeat for PY Submit both jobs:

```
sbatch HY_run.sh
sbatch PY_run.sh
```

Monitor progress:

```
squeue -u $USER          # Check job status
tail -f HY.out           # Watch output (Ctrl+C to exit)
```

Step 6: Check Your Results

Are your calculations done?

```
grep "ORCA TERMINATED NORMALLY" *.out
```

Extract YOUR final energies:

```
grep "FINAL SINGLE POINT ENERGY" *.out
```

Compare to reference:

- Reference HY: -323.456 Eh
- Reference PY: -323.466 Eh

If values don't match:

- Check geometry and basis set input
- Ask TA for help

Step 6: Analyze Results and Fill Table

Extract final energies from output files:

```
grep "FINAL SINGLE POINT ENERGY" HY.out  
grep "FINAL SINGLE POINT ENERGY" PY.out
```

Example calculation:

HY energy: HY Eh

PY energy: PY Eh

$E = E(\text{PY})_{\text{Eh}} - E(\text{HY})_{\text{Eh}}$

Convert to kJ/mol: $1\text{Eh} \sim 2625.5\text{kJ/mol}$

Fill in table in handout with pc-0 results:

- Energy difference (kJ/mol)

Step 8: Extract Bond Lengths

ORCA creates optimized geometry as .xyz file:

```
ls *.xyz
```

```
# Should see: HY_pc0.xyz  PY_pc0.xyz
```

Download to your computer:

```
# From your local computer:
```

```
scp c1cluster:~/Lab_BasisSet/HY/*.xyz ./
```

Open in Avogadro 2:

- 1 Open Avogadro 2
- 2 File → Open → Select HY_pc0.xyz
- 3 Use Measure Tool
- 4 Click on O atom, then H atom
- 5 Bond length displays at bottom
- 6 Record: O-H = _____ Å

Summary of steps

Building:

- Avogadro 2 → Draw molecule → Save as .xyz

Transfer:

- `scp file.xyz c1cluster: /Lab_BasisSet/HY/`

Setup:

- `export PATH=/scic/app/cpu/orca/6.0.0:$PATH`
- `nano HY_pc0.inp` - Create input
- Paste coordinates from .xyz (skip first 2 lines)

Running:

- `orca HY_pc0.inp > HY_pc0.out &`
- `tail -f HY_pc0.out` - Monitor

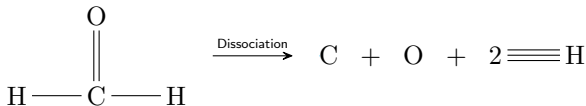
Extracting:

- `grep "FINAL SINGLE POINT ENERGY" HY_pc0.out`
- Download .xyz files and open in Avogadro 2 for bond lengths

Part 2

Transition State Calculations

Formaldehyde Molecular Dissociation



Energy calculations:

$$E_{\text{dissociation}} = (E_{\text{C}} + E_{\text{O}} + 2E_{\text{H}}) - E_{\text{H}_2\text{CO}}$$

Exploring the Reaction: $\text{CO} + \text{H}_2 \rightarrow \text{COH}_2$

The Reaction Energy Surface

- Chemical reactions occur on complex energy surfaces
- **Multiple minima** exist:
 - Reactants: $\text{CO} + \text{H}_2$
 - Product: COH_2 (formaldehyde)
 - Separated atoms: $\text{C} + \text{O} + 2\text{H}$
- Separated by **transition states** (saddle points)

Our Strategy

- Find the transition state structure
- Map the reaction pathway (IRC)
- Calculate activation energies
- Understand how molecules transform

Considering Molecular Dissociation

Why Consider Dissociation?

- Provides a reference energy
- $\text{COH}_2 \rightarrow \text{C} + \text{O} + 2\text{H}$ is the "ultimate" high-energy limit
- Helps understand bond strengths
- Validates our calculations

What We Need:

- Energy of individual atoms: **C, O, H**
- Energy of molecules: **CO, H₂, COH₂**
- All energies must be **zero-point corrected**

Zero-Point Energy (ZPE):

- Even at 0 K, molecules vibrate
- Atoms have no vibrational ZPE
- Must add ZPE from frequency calculations
- $E_{\text{corrected}} = E_{\text{SCF}} + \text{ZPE}$

Energy Comparisons Required Calculations:

- 1 Single-point energies for C, O, H (atoms)
- 2 Opt + Freq for CO
- 3 Opt + Freq for H₂
- 4 Opt + Freq for COH₂

Required Energies for the Analysis

What We Need to Calculate:

1. Reactants & Products:

- **CO:** Opt + Freq $\rightarrow E_{\text{CO}} + \text{ZPE}$
- **H2:** Opt + Freq $\rightarrow E_{\text{H}_2} + \text{ZPE}$
- **COH2:** Opt + Freq $\rightarrow E_{\text{H}_2\text{CO}} + \text{ZPE}$

2. Transition State:

- TS Optimization $\rightarrow E_{\text{TS}}^{\text{SCF}}$
- Frequency calculation $\rightarrow \text{ZPE}_{\text{TS}}$
- IRC calculation \rightarrow verify connectivity

3. Activation Energy:

- Forward: $E_a^f = (E_{\text{TS}} + \text{ZPE}_{\text{TS}}) - (E_{\text{CO}} + E_{\text{H}_2} + \text{ZPE})$
- Reverse: $E_a^r = (E_{\text{TS}} + \text{ZPE}_{\text{TS}}) - (E_{\text{H}_2\text{CO}} + \text{ZPE})$

Why HF/STO-3G Level?

Method: Hartree-Fock (HF)

- **Simplest** ab initio method
- No electron correlation included
- Fast and stable convergence

Basis Set: STO-3G

- **Minimal basis set**
- 1s for H, 1s/2s/2p for C,O
- Very small - very fast!
- Suitable for educational purposes

Trade-offs:

- Not chemically accurate
- Overestimates barriers
- Demonstrates the methodology
- Correct qualitative behavior

For This Lab:

Purpose

We use HF/STO-3G to:

- Learn the *procedure*
- Understand the *workflow*
- Complete calculations *quickly*

*In research, you would use
B3LYP/TZVP or better.*

Three Calculations for TS Energy

Step 1: TS Optimization

- Uses different optimization algorithm
- Yields SCF energy: E_{TS}^{SCF}
- **Not** a minimum - it's a maximum along reaction coordinate

Step 2: Frequency Calculation

- Calculate vibrational modes
- Extract Zero-Point Energy (ZPE)
- **Must have exactly 1 imaginary frequency**
- Confirms structure is a TS

Step 3: IRC Calculation

- Traces path from TS downhill
- Goes in both directions
- Validates that we found the TS

ORCA Input Examples

1. TS Optimization:

```
1 ! RHF STO-3G TightSCF
2 ! OptTS
3 * xyzfile 0 1 COH2.xyz
```

2. Frequency:

```
1 ! RHF STO-3G NumFreq
2 * xyzfile 0 1 ts_optimized.xyz
```

3. IRC:

```
1 ! RHF STO-3G IRC
2 * xyzfile 0 1 ts_optimized.xyz
```

How to Optimize a Transition State

The Challenge:

- Normal optimization finds minima
- TS is a *saddle point* - max in one direction
- Need a good initial guess!

Our Strategy for $\text{CO} + \text{H}_2 \rightarrow \text{COH}_2$:

1. Start with product (COH_2)

- Optimize COH_2 normally first

2. Distort toward TS:

- **Detach one H** from the carbon
- Stretch C-H bond (e.g., $1.1 \text{ \AA} \rightarrow 1.8 \text{ \AA}$)
- **Increase O-C-H angle** (e.g., $120^\circ \rightarrow 150^\circ$)

3. This creates a structure between reactants and products that has a higher energy than both. A good starting point for OptTS

Steps for IRC Calculation

Prerequisites:

- Must have an optimized TS
- Must have run Freq (confirms 1 imaginary mode)
- TS geometry saved as .xyz file

ORCA IRC Input:

```
1 ! RHF STO-3G IRC TightSCF
2
3 * xyzfile 0 1 ts_optimized.xyz
```

What ORCA does:

- 1 Starts at TS geometry
- 2 Follows gradient "downhill" forwards then backwards
- 3 Saves trajectory points to .xyz

Key ORCA Keywords

Keyword	Purpose
IRC	Run IRC calculation
TightSCF	Tight convergence
xyzfile	Read geometry

Important Notes:

Critical!

- IRC reads the Hessian from the Freq calculation
- Must use *same* level of theory as TS opt
- Use same charge and multiplicity
- ORCA automatically uses the imaginary mode

Output files:



Verifying the TS: Frequency Calculation

Why Run Frequency on TS?

- **Confirms it's a true TS**
- Provides Zero-Point Energy (ZPE)
- Shows the reaction coordinate

What to Look For:

1. Exactly ONE imaginary frequency

- Shown as negative value
- If 0 imaginary: it's not a TS

2. Check the imaginary mode:

- Should show bond breaking/forming
- Visualize in Avogadro2

3. Extract ZPE:

- Found in output file
- Used to correct E_{TS} :
$$E_{TS}^{corrected} = E^{SCF} + ZPE$$

ORCA Frequency Input

```
1 ! RHF STO-3G NumFreq TightSCF
2
3 * xyzfile 0 1 ts_optimized.xyz
```

Example Output:

```
1 VIBRATIONAL FREQUENCIES
2 -----
3 0: -824.55 cm***-1 <- IMAGINARY because negative
4 1: 156.32 cm***-1
5 2: 487.91 cm***-1
6 3: 652.18 cm***-1
7 ...
8
9 Zero point energy: 0.01234 Eh
```


Predicting Activation Energies

Definition:

- **Activation energy (E_a):** Energy barrier from reactants to TS
- Determines reaction rate
- Higher E_a = slower reaction

Forward Activation Energy:

$$E_a^{\text{forward}} = E_{\text{TS}} - E_{\text{reactants}}$$

- $E_{\text{TS}} = E_{\text{TS}}^{\text{SCF}} + \text{ZPE}_{\text{TS}}$
- $E_{\text{reactants}} = E_{\text{CO}} + E_{\text{H}_2} + \text{ZPE}_{\text{CO}} + \text{ZPE}_{\text{H}_2}$

Relationship:

$$E_a^{\text{forward}} - E_a^{\text{reverse}} = \Delta E_{\text{rxn}}$$

Units: Convert to kcal/mol or kJ/mol

$$1 \text{ Hartree} = 627.51 \text{ kcal/mol}$$

Reverse Activation Energy:

$$E_a^{\text{reverse}} = E_{\text{TS}} - E_{\text{products}}$$

Bonus 1: Complete Convergence Study

Extend Your Analysis

Part A: Basis Set Convergence

- Run calculations with **pc-1, pc-2, pc-3**
- Same molecules (HY and PY)
- Same method: B3LYP + TightOPT + Freq
- Compare how ΔE changes with basis set size

Create a convergence plot:

- X-axis: Basis set (pc-0 to pc-3)
- Y-axis: ΔE (kJ/mol)
- Add horizontal line at experimental value

Part B: IR Spectra Comparison

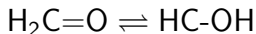
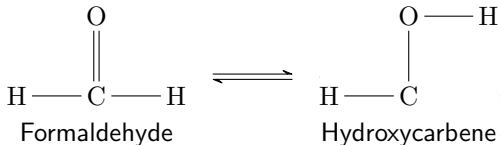
Using Avogadro:

- 1 Open HY.out in Avogadro
- 2 Extensions → Vibrations → View
- 3 Note frequencies of:
 - O-H stretch
 - C=O stretch
 - Ring modes
- 4 Repeat for PY.out
- 5 Compare: N-H vs. O-H region

How do the spectra reflect structural differences? Can you identify the tautomeric forms by IR alone?

Bonus Challenge 2: 1,2-Hydrogen Shift in Formaldehyde

The Reaction:



Tasks:

- 1 Find TS for H-shift
- 2 Run frequency (verify 1 imaginary)
- 3 Calculate activation barrier
- 4 Run IRC to confirm pathway

Building TS in Avogadro:

- 1 Start with H_2CO
- 2 Move one H halfway between C and O
- 3 Distance: C-H $\sim 1.4 \text{ \AA}$, O-H $\sim 1.3 \text{ \AA}$
- 4 Adjust C-O-H angle $\sim 100^\circ$
- 5 Save as `ts_guess.xyz`