



Aalto University  
School of Chemical  
Engineering

# Advanced Exercises in Quantum Chemistry

CSC Spring School on Computational Chemistry 2024

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# Learning objectives and contents

- After the exercises, you will be able to:
  - Use TmoleX graphical user interface to run TURBOMOLE jobs on local computer and on Puhti supercomputer.
  - Use TURBOMOLE to study excited states of molecules with Time-Dependent Density Functional Theory (TD-DFT)
- **Tutorial 1:** Excited states of borazine ( $\text{B}_3\text{N}_3\text{H}_6$ )
  - Can be completed even on a local workstation/laptop
- **Tutorial 2:** Excited states of indigo dye ( $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ )
  - We will use Puhti supercomputer
- **Tutorial 3:** Organometallic Au(I) complex  $(\text{AuC}_2\text{Ph})_2\text{PPh}_2\text{C}_2\text{C}_6\text{H}_4\text{C}_2\text{PPh}_2$ 
  - We will use Puhti supercomputer

# Brief summary on excited states

# Excited states

- Photochemistry and photophysics of molecules and materials are highly active fields of research.
- Many important technologies such as light-emitting diodes and solar cells depend on the behavior of excited states.
- Excited states can be studied for example with Time-Dependent Density Functional Theory (TD-DFT). This is also the method primarily used in the present tutorial.
  - A review “Density functional methods for excited states: equilibrium structure and electronic spectra” from Furche and Rappoport is openly available at <https://escholarship.org/uc/item/7z63q82s>



Figure: [Wikimedia Commons](#) / PiccoloNamek (CC BY-SA)

# Electromagnetic spectrum visible to the human eye

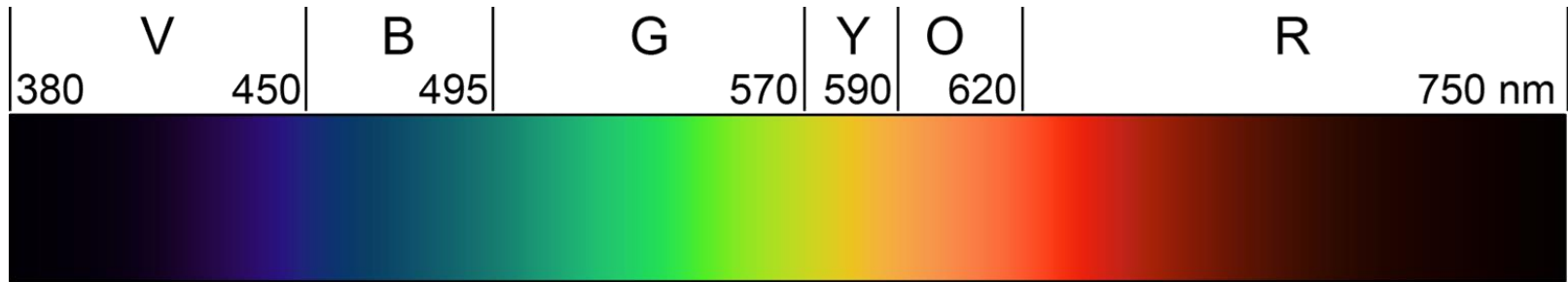







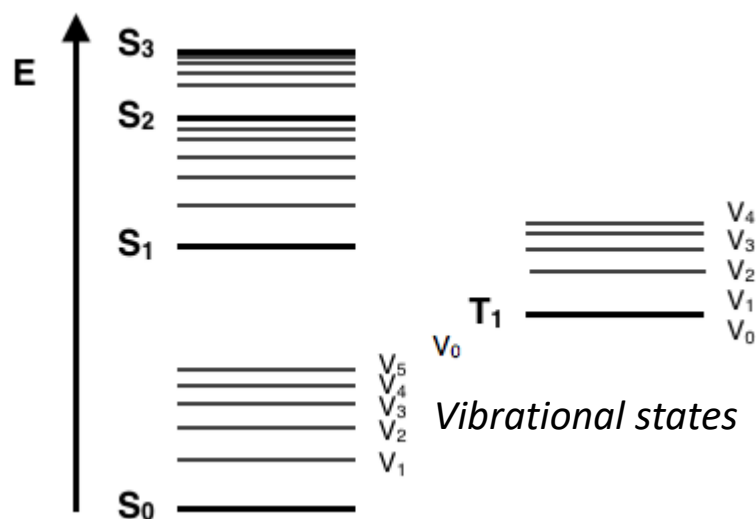


Figure: [Wikimedia Commons](#) (Public Domain)

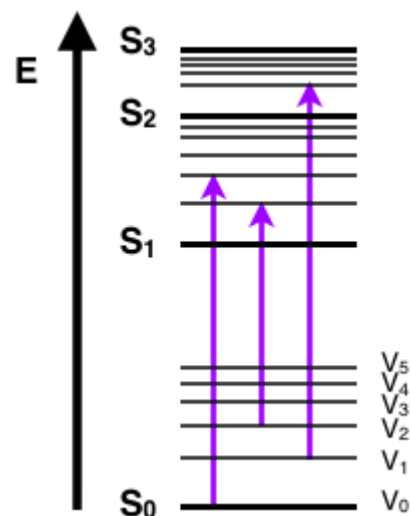
Color	Wavelength (nm)	Frequency (THz)	Photon energy (eV)
 <b>violet</b>	380–450	670–790	2.75–3.26
 <b>blue</b>	450–485	620–670	2.56–2.75
 <b>cyan</b>	485–500	600–620	2.48–2.56
 <b>green</b>	500–565	530–600	2.19–2.48
 <b>yellow</b>	565–590	510–530	2.10–2.19
 <b>orange</b>	590–625	480–510	1.98–2.10
 <b>red</b>	625–750	400–480	1.65–1.98

# Jablonski diagrams (1/3)

Excited states of molecules are typically schematically illustrated with Jablonski diagrams that show the electronic and vibrational excited states.



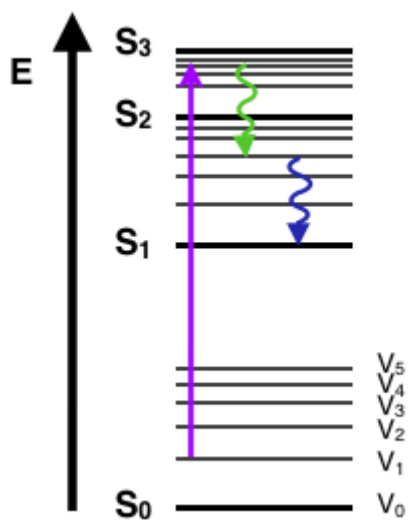
Foundation of a typical Jablonski  
Diagram



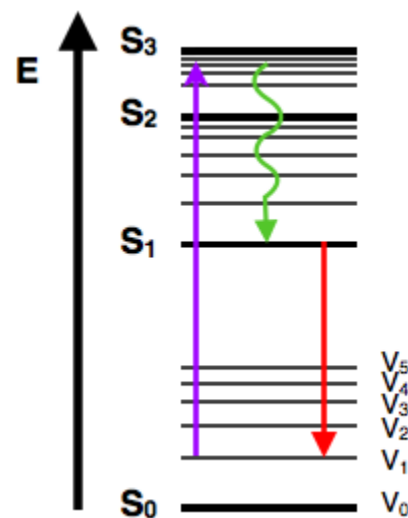
Three possible **absorption** transitions represented.

These can be measured by **UV/Vis** spectroscopy. **The tutorial focuses on this kind of transitions.**

# Jablonski diagrams (2/3)

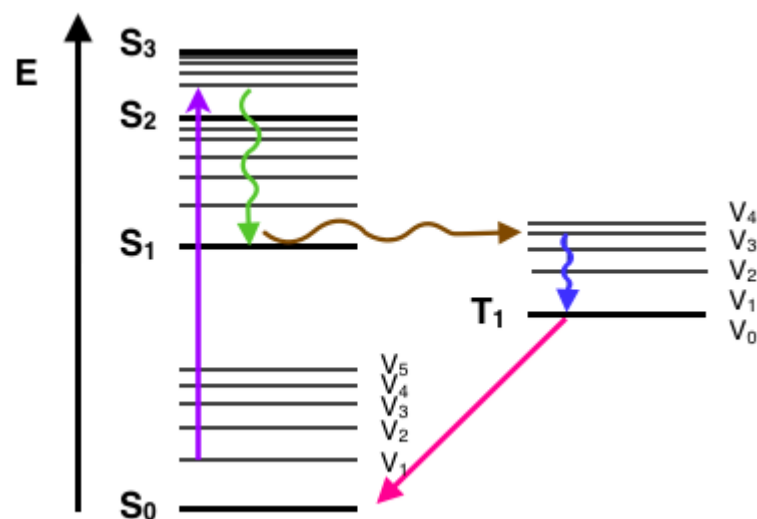


Possible scenario with **absorption**, **internal conversion**, and **vibrational relaxation** processes shown.



Possible scenario with **absorption**, **internal conversion** and **vibrational relaxation**, and **fluorescence** processes shown.

# Jablonski diagrams (3/3)



Possible scenario with **absorption**, **internal conversion**, **vibrational relaxation**, **intersystem crossing**, and **phosphorescence** processes shown.

# Timescales

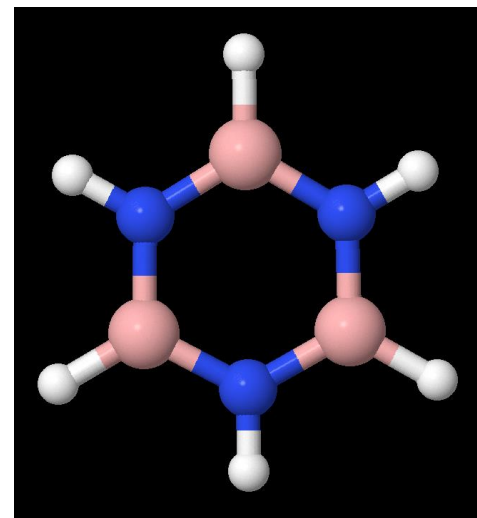
These are only for information. Our TD-DFT calculations are in reality time-independent.

Transition	Timescale	Radiative Process?
Internal Conversion	$10^{-14} - 10^{-11} \text{ s}$	no
Vibrational Relaxation	$10^{-14} - 10^{-11} \text{ s}$	no
Absorption	$10^{-15} \text{ s}$	yes
Phosphorescence	$10^{-4} - 10^{-1} \text{ s}$	yes
Intersystem Crossing	$10^{-8} - 10^{-3} \text{ s}$	no
Fluorescence	$10^{-9} - 10^{-7} \text{ s}$	yes

# Tutorial 1

# Tutorial 1: Borazine

- Borazine  $B_3N_3H_6$  is the inorganic analogue of benzene.
- Contents of this tutorial:
  - Basic use of TmoleX
  - Plotting molecular orbitals and excited state difference densities
  - Role of molecular symmetry
  - Basis set convergence
  - Comparisons between computational and experimental results



Borazine  $B_3N_3H_6$

# TmoleX

- TmoleX is a graphical user interface to create, run, and analyze TURBOMOLE calculations.
- On this course, there are three possible ways to use TmoleX:
  - Local computers in the training class at CSC
  - Your own laptop (see section “**Install your own TmoleX**” at <https://docs.csc.fi/apps/tmolex/>).
  - Puhti web interface (see section “Use via your browser” at <https://docs.csc.fi/apps/tmolex/>)
- You can now start TmoleX and begin the tutorial.

# Geometry optimization (1)

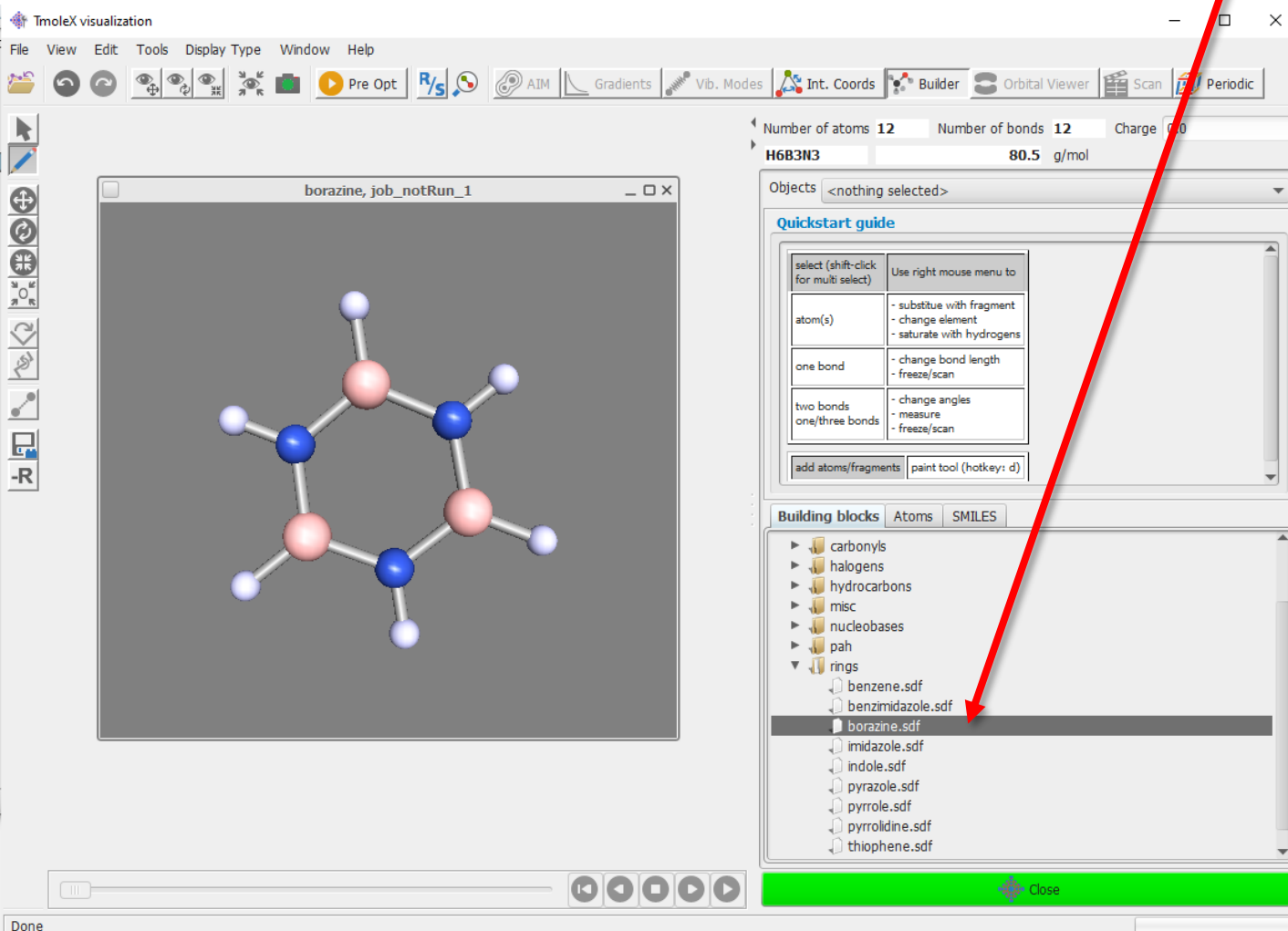
We need to optimize the molecular structure of borazine in the electronic ground state before we can proceed to study the excited states. Start a new project **borazine** in TmoleX and open the 3D Molecular Builder:

Property calculations such as UV/vis spectra typically only make sense when the molecule is in a (local) minimum on the potential energy surface.

*(However, it is fairly common approach in quantum chemistry that the geometry is optimized at a lower-level theory and properties are then calculated at this geometry with higher level of theory).*

# Geometry optimization (2)

The structure of borazine is readily available in the Building blocks library:  
Choose it, click the gray molecular window, and borazine appears.  
Return back to geometry menu by closing this window (**Close**).



# Geometry optimization (3)

The geometry menu is now ready and you can proceed to Atomic Attributes. Borazine is symmetric, but do not apply any symmetry yet!

The screenshot shows the TmoleX2023 DEMO - borazine interface. A red arrow points to the 'local: 0/4' status bar. The workflow is as follows:

```
graph LR
    Geometry --> AtomicAttributes[Atomic Attributes]
    AtomicAttributes --> MolecularAttributes[Molecular Attributes]
    MolecularAttributes --> Method
    Method --> StartJob[Start Job]
    StartJob --> Results
    AtomicAttributes --> ChooseJobTemplate[Choose Job Template]
    ChooseJobTemplate --> Charge[Charge: Use from input]
    Charge --> ApplyJobTemplate[Apply Job Template]
    ApplyJobTemplate --> StartJob
```

The 'Coords & Sym.' section contains the following controls:

- Import Coordinate File
- Open 3D Molecular Builder
- Draw 2D
- SMILES to 3D
- Units: A

The 'Atomic' section shows:

- Number of atoms: 12
- New Atom
- Delete Selected Atoms

The 'Symmetry' section shows:

- Current point group: C1
- Max. tolerance: 0.01 au
- Autodetect Symmetry
- New point group: C1
- Apply New Point Group

The 'Internal coordinates' section contains a table with the following data:

Constraints	Value	Start	End	Stepsize

The 'periodic' section shows:

- off

The 'order' section shows:

- ↑
- ↓

The 'Continue >>' button is at the bottom right.

Number	Element	x	y	z	Fixed cartesian	Fixed internal
1	B	-3.2113	-0.0158	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
2	N	-1.859	-0.5048	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
3	B	-0.7153	0.3668	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
4	N	-0.9678	1.7824	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
5	B	-2.2946	2.3371	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
6	N	-3.3943	1.4105	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
7	H	-4.1652	-0.7805	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
8	H	-1.7039	-1.5164	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
9	H	0.4238	-0.0772	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
10	H	-0.1691	2.4221	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
11	H	-2.4799	3.5456	0.1864	<input type="checkbox"/>	<input type="checkbox"/>
12	H	-4.3478	1.782	0.1864	<input type="checkbox"/>	<input type="checkbox"/>

# Geometry optimization (4)

Let's first run the calculations with a small basis set. Choose def2-SVP basis set for all atoms.

Proceed to Molecular Attributes.

TmoleX2023 DEMO - borazine

File Edit Templates Results Extras Tools License Help

Open 3D Molecular Builder

Jobs running local: 0/4 remote: 0

Memory used for TmoleX: 75,5/103,8 MB System: 0,0/16558,5 MB

Geometry → Atomic Attributes → Molecular Attributes → Method → Start Job → Results

Choose Job Template Charge: Use from input Apply Job Template

**Basis Sets**

Basis Functions 120

**Basis Set for all Atoms**

def2-SVP

**Basis for elements**

Show ECP

B def2-SVP

N def2-SVP

H def2-SVP

**Basis for individual Atoms**

Select items from table or graphic viewer

Choose Basis Sets

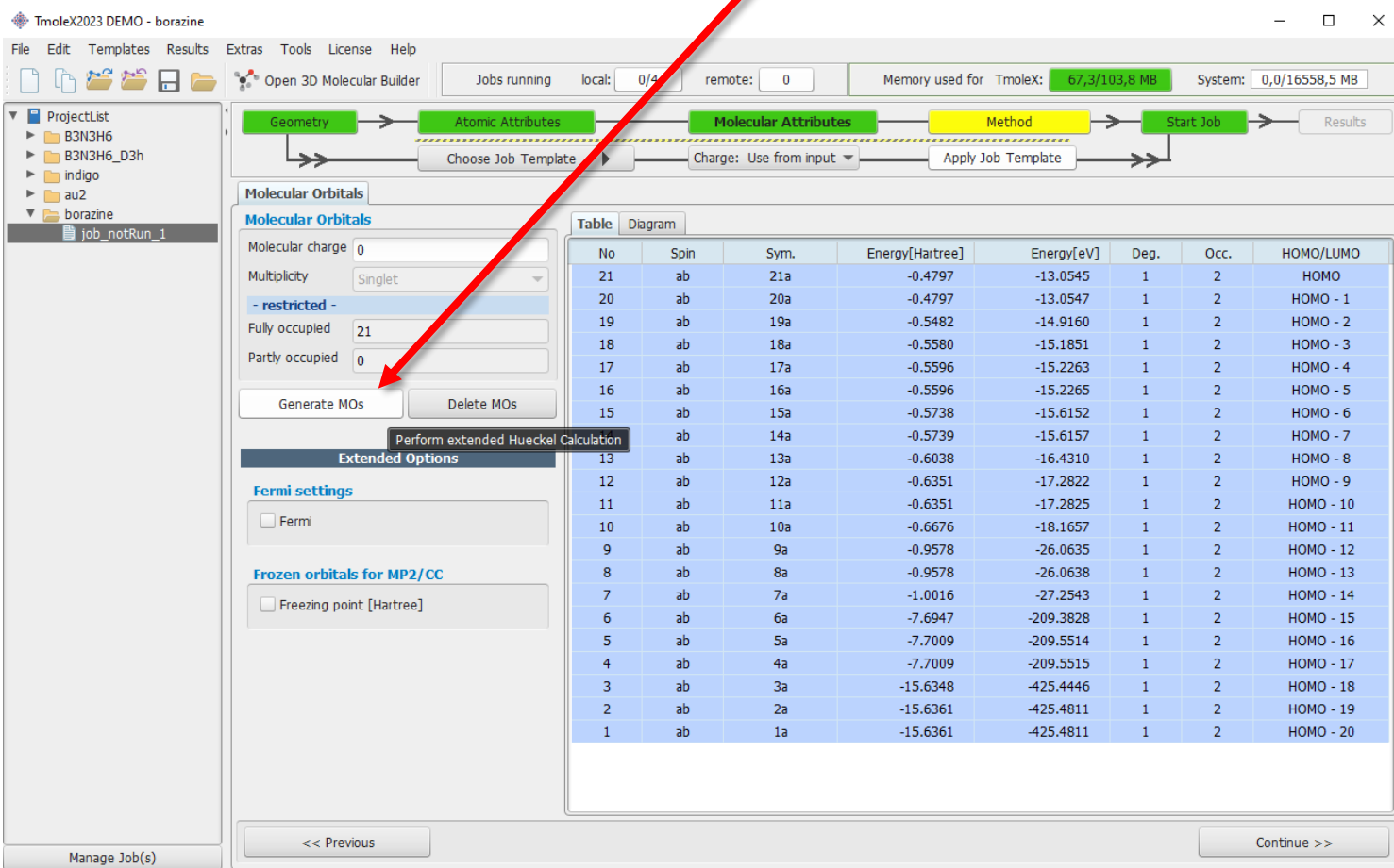
Num...	Elem...	Basis set	ECP	Mass	Nuclear char...	Basis functions
1	B	def2-SVP		10.8100	5	15
2	N	def2-SVP		14.0067	7	15
3	B	def2-SVP		10.8100	5	15
4	N	def2-SVP		14.0067	7	15
5	B	def2-SVP		10.8100	5	15
6	N	def2-SVP		14.0067	7	15
7	H	def2-SVP		1.0079	1	5
8	H	def2-SVP		1.0079	1	5
9	H	def2-SVP		1.0079	1	5
10	H	def2-SVP		1.0079	1	5
11	H	def2-SVP		1.0079	1	5
12	H	def2-SVP		1.0079	1	5

<< Previous

Continue >>

# Geometry optimization (5)

Generate initial guess of the molecular orbitals by clicking Generate MOs.  
The guess is based on semiempirical [Extended Hückel](#) method.  
Proceed to Method.



The screenshot shows the TmoleX2023 DEMO - borazine interface. The 'Molecular Orbitals' section is active, displaying a table of orbital data. A red arrow points to the 'Generate MOs' button. The 'Molecular Orbitals' table is shown below.

No	Spin	Sym.	Energy[Hartree]	Energy[eV]	Deg.	Occ.	HOMO/LUMO
21	ab	21a	-0.4797	-13.0545	1	2	HOMO
20	ab	20a	-0.4797	-13.0547	1	2	HOMO - 1
19	ab	19a	-0.5482	-14.9160	1	2	HOMO - 2
18	ab	18a	-0.5580	-15.1851	1	2	HOMO - 3
17	ab	17a	-0.5596	-15.2263	1	2	HOMO - 4
16	ab	16a	-0.5596	-15.2265	1	2	HOMO - 5
15	ab	15a	-0.5738	-15.6152	1	2	HOMO - 6
14	ab	14a	-0.5739	-15.6157	1	2	HOMO - 7
13	ab	13a	-0.6038	-16.4310	1	2	HOMO - 8
12	ab	12a	-0.6351	-17.2822	1	2	HOMO - 9
11	ab	11a	-0.6351	-17.2825	1	2	HOMO - 10
10	ab	10a	-0.6676	-18.1657	1	2	HOMO - 11
9	ab	9a	-0.9578	-26.0635	1	2	HOMO - 12
8	ab	8a	-0.9578	-26.0638	1	2	HOMO - 13
7	ab	7a	-1.0016	-27.2543	1	2	HOMO - 14
6	ab	6a	-7.6947	-209.3828	1	2	HOMO - 15
5	ab	5a	-7.7009	-209.5514	1	2	HOMO - 16
4	ab	4a	-7.7009	-209.5515	1	2	HOMO - 17
3	ab	3a	-15.6348	-425.4446	1	2	HOMO - 18
2	ab	2a	-15.6361	-425.4811	1	2	HOMO - 19
1	ab	1a	-15.6361	-425.4811	1	2	HOMO - 20

# Geometry optimization (6)

We use DFT. Choose **PBE0** exchange correlation functional and increase Gridsize to **m4** (I recommend to **always** increase it: default m3 is a bit too small integration grid for larger molecules and heavy atoms). *If you plan to compare the total energies of molecules to each other, all of them must be calculated with the same gridsize!* Proceed to Start Job.

File Edit Templates Results Extras Tools License Help

Open 3D Molecular Builder

Jobs running local: 0/4 remote: 0 Memory used for TmoleX: 65,4/103,8 MB System: 0,0/16558,5 MB

Geometry → Atomic Attributes → Molecular Attributes → Method → Start Job → Results

Choose Job Template Charge: Use from input Apply Job Template

Level of Theory SCF Convergence Solvation

**Level**

DFT ☒ Use RI **Always use RI-DFT (faster)**

**DFT settings**

Functional: PBE0 PBE0 hybrid GGA, correlation:LDA(PW)+PBE(C), exchange:0.75(S+PBE(X))+0.25HF Configure functional list

Gridsize: m4

Dispersion: none none

**Auxiliary basis sets for RI-J**

Element	Basis set	Auxiliary basis set
B	def2-SVP	def2-SVP
H	def2-SVP	def2-SVP
N	def2-SVP	def2-SVP

**COSMO**

☐ Activate Filename: out File format: .cosmo

**Relativistic effects / Two component treatment**

☐ Activate ☐ Kramers ☐ complex DIIS ☐ X2C

**Semi-numerical Exchange for DFT**

☐ senex - semi-numerical exchange for ground state energy and all properties (applied everywhere)

☐ esenex - semi-numerical exchange for properties only (ground state energies with exact exchange, properties with fast semi-numerical approach)

<< Previous Continue >>

# Geometry optimization (7)

The Job Type should be Geometry Optimization -> Ground state. You can run borazine on the local workstation/laptop. One or two CPUs is enough because this is a small system. Proceed to Run (local) (for Run (network): see guidelines in the end of the slideset). TMoleX then asks for job name, for example *Opt\_PBE0\_def2-SVP*.

The screenshot displays the TMoleX software interface. The top menu bar includes File, Edit, Templates, Results, Extras, Tools, License, and Help. Below the menu, a status bar shows 'Jobs running: local: 0/4, remote: 0' and 'Memory used for TmoleX: 70,6/103,8 MB, System: 0,0/16558,5 MB'. The main workflow is shown as a sequence of steps: Geometry, Atomic Attributes, Molecular Attributes, Method, Start Job, and Results. A 'Choose Job Template' button is located between Atomic Attributes and Molecular Attributes. The 'Start Calculation' section is highlighted with a red box, showing a tree view of job types. Under 'Geometry Optimization', 'Ground state' is selected. The 'Options' section is also visible, showing convergence criteria: Energy (6  $10^{-11}$  Hartree), Gradient norm (3  $|dE/dxyz| = 10^{-11}$  Hartree/Bohr), and Max. no. of cycles (50). The 'Use resources' section is highlighted with a red box, showing settings for Memory used for (500.0 MB), Disk (0 MB for HF), No. of CPUs (2), and a checked box for 'Delete scratch files after run'. The 'Method' section shows Level (DFT), Functional (pbe0), Basis set (def2-SVP), Symmetry (C1), and Convergence Parameter (Energy  $10^{-6}$ ). The 'Save and Run' section at the bottom right has buttons for 'Run (local)', 'Save', and 'Run (network)'.

File Edit Templates Results Extras Tools License Help

Open 3D Molecular Builder

Jobs running local: 0/4 remote: 0

Memory used for TmoleX: 70,6/103,8 MB System: 0,0/16558,5 MB

Geometry Atomic Attributes Molecular Attributes Method Start Job Results

Choose Job Template Charge: Use from input Apply Job Template

Start Calculation

Job typ

- Geometry Optimization ▶ Ground state
- Spectra & Excited States ▶
- Single Point ▶
- Single Point Properties ▶
- Population Analyses ▶
- Potential Energy Scan(PES) ▶
- Transition State Search ▶
- Templates ▶
- Batch processing ▶

Options

Convergence criteria

Energy 6  $10^{-11}$  Hartree

Gradient norm 3  $|dE/dxyz| = 10^{-11}$  Hartree/Bohr

Max. no. of cycles 50

☒ Use internal redundant coordinates ☐ Include weight derivatives

Method

Level DFT

Functional pbe0

☒ RI

Basis set def2-SVP Symmetry C1

Convergence Parameter

Energy  $10^{-6}$  Density

Show Notes

Use resources

Memory used for 500.0 MB

Disk 0 MB for HF

No. of CPUs 2

☒ Delete scratch files after run

Save and Run

Run (local)

Save

Run (network)

Manage Job(s)

<< Previous

# Geometry optimization (8)

The optimization job will finish quickly (here it took six steps, that is, six energy + gradient evaluations). You can see how the geometry changed from **Gradients**. Next, proceed to Orbital/Density Plot

The screenshot displays the Gaussian 09 software interface. The top menu bar includes File, Edit, Templates, Results, Extras, Tools, License, and Help. The main window is divided into several panels. On the left, the 'ProjectList' panel shows a tree view of files, including 'B3N3H6', 'B3N3H6\_D3h', 'indigo', 'au2', 'borazine', 'Opt\_PBE0\_def2-SVP', and 'job\_GEO\_2'. The central panel shows the 'Job Results' for a 'Geometry Optimization' job. The 'Status SCF' is 'Converged' and the 'Status geometry' is 'Converged'. The 'HOMO-LUMO gap' is 8.62 eV. The 'Geometry Convergence Criteria' section shows the following values:

Parameter	Actual Value	Threshold
energy change	-0.1401E-06	0.1000E-05
geom. gradient	0.6305E-04	0.1000E-02

The 'Energy' section shows the following values:

Energy Component	Value
total energy	-242.19567219187
kinetic energy	239.68795281629
potential energy	-481.88362500816

The 'Gradients' section shows the following values for each cycle:

Cycle	SCF energy	dE/dxyz
1	-242.1945617592	0.022119
2	-242.1955337127	0.006794
3	-242.1956680844	0.002359
4	-242.1956681180	0.002362
5	-242.1956720280	0.000368
6	-242.1956721681	0.000129

On the right side, the 'Open Viewer' panel contains buttons for 'Orbital/Density Plot', 'Gradients', 'Vibrations', 'Thermochemical Properties', 'SCF Population Properties', 'Dipole Moments', 'AIM (Atoms in Molecules)', 'NMR Shieldings', 'View .cosmo File', and 'Density of states (DOS)'. A red arrow points from the 'Gradients' button to the 'Orbital/Density Plot' button. The 'Show Plots' panel at the bottom right contains buttons for 'UV/Vis Spectrum', 'CD Spectrum', 'Raman Spectrum', 'IR Spectrum', 'VCD Spectrum', and 'Band Structure'. The 'What next' panel at the bottom contains a button for 'Start new job with current data'.

# Molecular orbitals

Notice how the two highest occupied orbitals (HOMO, HOMO-1) have exactly the same energy (they are *degenerate*). Same is true for the two lowest unoccupied orbitals (LUMO, LUMO+1). This is an indication that we could benefit from using molecular symmetry when investigating the electronic properties. You can visualize the orbitals by clicking the gear icons, selecting them, and choosing View selected. You can also view other orbitals if you like. Close after you are done.

3D-Visualizer Opt\_PBE0\_def2-SVP

Choose Molecular Orbital(s)

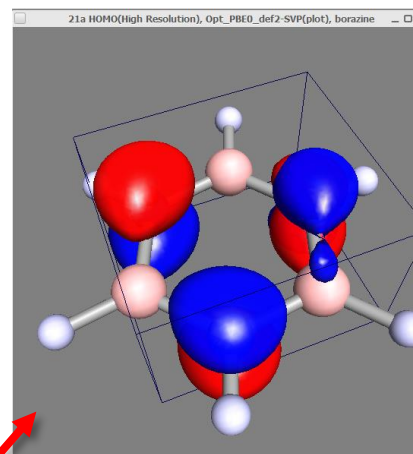
Sel.	No	Spin	Sym.	Energy[Hartree]	Deg.	Occ.	HOMO/LUMO	quick	high...
<input type="checkbox"/>	26	ab	26a	0.1026	1	0	LUMO + 4		
<input type="checkbox"/>	25	ab	25a	0.1026	1	0	LUMO + 3		
<input type="checkbox"/>	24	ab	24a	0.0779	1	0	LUMO + 2		
<input type="checkbox"/>	23	ab	23a	0.0209	1	0	LUMO + 1		
<input type="checkbox"/>	22	ab	22a	0.0209	1	0	LUMO		
<input checked="" type="checkbox"/>	21	ab	21a	-0.2959	1	2	HOMO		
<input checked="" type="checkbox"/>	20	ab	20a	-0.2959	1	2	HOMO - 1		
<input type="checkbox"/>	19	ab	19a	-0.3326	1	2	HOMO - 2		
<input type="checkbox"/>	18	ab	18a	-0.3326	1	2	HOMO - 3		
<input type="checkbox"/>	17	ab	17a	-0.3843	1	2	HOMO - 4		
<input type="checkbox"/>	16	ab	16a	-0.3959	1	2	HOMO - 5		
<input type="checkbox"/>	15	ab	15a	-0.4525	1	2	HOMO - 6		

Choose Density and Electrostatic Properties

Sel.	Plot-propertyname	Plot-filename	quick	high-res
<input type="checkbox"/>	Ground state, total density	td		
<input type="checkbox"/>	1st derivative of total density	t1		
<input type="checkbox"/>	2nd derivative of total density	t2		
<input type="checkbox"/>	Laplacian of total density	tl		
<input type="checkbox"/>	Kinetic energy density	tt		
<input type="checkbox"/>	Electrostatic potential	tp		
<input type="checkbox"/>	Electric field	tf		
<input type="checkbox"/>	Gradient of electric field	tg		
<input type="checkbox"/>	Electrostatic potential color-coded on de...	tp_td		
<input type="checkbox"/>	ELF (electron localization function)	te		

File format: ☒ .ply/.plt ☐ .dtx

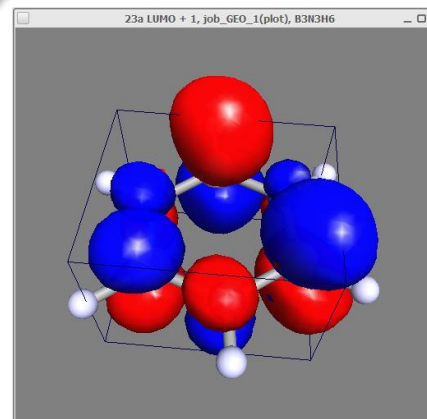
☒ View all in one



HOMO and  
HOMO-1.

Isosurface +/-

Isovalue 0.08  
a.u.



LUMO and  
LUMO-1.

Isosurface +/-

Isovalue 0.08  
a.u.

# Excited states (1)

Now we can proceed to excited state calculation. In the Results menu, click Start Job and you can create a new job based on the optimized geometry.

The screenshot shows the software interface with the 'Start Job' button highlighted by a red arrow. The interface displays the following information:

**Job Results**

Type of Calculation: **Geometry Optimization** | Status SCF: **Converged** | SCF Convergence: **Converged**

HOMO-LUMO gap: 8.62 eV

Status geometry: **Converged** | Convergence: **Converged**

**Geometry Convergence Criteria**

\$convinfo

energy change : actual value = -0.1401E-06 threshold = 0.1000E-05

geom. gradient : actual value = 0.6305E-04 threshold = 0.1000E-02

**Energy**

total energy = -242.19567219187

kinetic energy = 239.68795281629

potential energy = -481.88362500816

**Gradients**

cycle	SCF energy	dE/dxyz
1	-242.1945617592	0.022119
2	-242.1955337127	0.006794
3	-242.1956680844	0.002359
4	-242.1956681180	0.002362
5	-242.1956720280	0.000368
6	-242.1956721681	0.000129

**Open Files**

Output

Energy

**Open Viewer**

Orbital/Density Plot

Gradients

Vibrations

Thermochemical Properties

SCF Population Properties

Dipole Moments

AIM (Atoms in Molecules)

NMR Shieldings

View .cosmo File

Density of states (DOS)

**Show Plots**

UV/Vis Spectrum

CD Spectrum

Raman Spectrum

IR Spectrum

VCD Spectrum

Band Structure

**What next**

Start new job with current data

# Excited states (2)

Choose Spectra & Excited States -> UV/Vis and CD (vertical excitations).

Choose all IRREPs (default) and set number of excited states per IRREP to 10.

We will discuss IRREPs soon. Set CPUs to one or two and run the job.

The screenshot displays the Gaussian 09 graphical user interface. The top menu bar includes File, Edit, Templates, Results, Extras, Tools, License, and Help. Below the menu, a status bar shows 'Jobs running: local: 0/4, remote: 0', 'Memory used for TmoleX: 123,0/304,1 MB', and 'System: 0,0/16558,5 MB'. The main workflow area shows a sequence of steps: Geometry, Atomic Attributes, Molecular Attributes, Method, Start Job, and Results. The 'Start Calculation' button is highlighted. The 'Job type' section on the left lists various calculation types, with 'Spectra & Excited States' selected and highlighted by a red box. The 'Excited states' configuration panel is also highlighted by a red box, showing the following settings: 

- Geometry Optimization: Spectra & Excited States -> UV/Vis and CD(vertical excitations)
- Method: Level: DFT, Functional: pbe0, Basis set: def2-SVP, Symmetry: c1, Convergence Parameter: Energy: 10<sup>-6</sup>, Density: [blank]
- Use resources: Memory used for: 500.0 MB, Disk: 0 MB for HF, No. of CPUs: 2 (highlighted by a red box), Delete scratch files after run: [checked]
- Excited states: Singlet (selected), Triplet, RPA- Random Phase Approx., Unit: nm, All IRREPs (checked), Number of excited states per IRREP: 10
- for current symmetry: c1: IRREP: A, No. of excitations: 5, Needed for: UV + CD

 The bottom of the window shows a 'Manage Job(s)' button and a '<< Previous' button.

# Excited states (3)

The Spectrum textbox shows the calculated excitation energies (here wavelengths) and oscillator strengths (the larger the OS, the higher the probability of electronic absorption). You can click UV/Vis Spectrum to see a plotted spectrum, but it is not that exciting. There is a feature between 150 and 160 nm (UV regime)

ProjectList  
B3N3H6  
B3N3H6\_D3h  
indigo  
au2  
borazine  
Opt\_PBE0\_def2-SVP  
job\_GEO\_2  
Ex\_PBE0\_def2-SVP

Jobs running local: 0/4 remote: 0 Memory used for TmoleX: 166,5/304,1 MB System: 0,0/16558,5 MB

Geometry → Atomic Attributes → Molecular Attributes → Method → Start Job → Results

Choose Job Template Charge: Use from input Apply Job Template

Job Results

Type of Calculation **Single Point Calculation** Status SCF **Converged** SCF Convergence **Open Files**  
HOMO-LUMO gap 8.62 eV  
Status geometry **Not performed** Convergence

Energy

total energy = -242.19567220066  
kinetic energy = 239.68797347276  
potential energy = -481.88364567342

**Spectrum**

# Electronic excitation spectrum of Ex\_PBE0\_def2-SVP, IRREP a  
# singlet excitations  
# excitation energy / nm oscillator strength (length rep.)

0.17908052255801E+03	0.14054073042827E-08
0.16219431520641E+03	0.30435771337724E-09
0.15661678738581E+03	0.36816859185821E-01
0.15492327778286E+03	0.36212781638505E+00
0.15492108529826E+03	0.36218237523949E+00
0.15319693727747E+03	0.83971937997002E-08
0.15319654601220E+03	0.10787515248661E-08

**CD Spectrum**

# Electronic CD-spectrum of Ex\_PBE0\_def2-SVP, IRREP a  
# singlet excitations  
# excitation energy / nm rotatory strength (length rep.) / 10<sup>^(-40)</sup> erg\*cm<sup>3</sup>

0.17908052255801E+03	0.19946157451324E-06	0.10228766285649E-06	0.78987032864787E-07	0.
0.16219431520641E+03	0.25709336775955E-07	0.62769792621897E-09	0.13499461676057E-07	0.
0.15661678738581E+03	-.82068174262246E-07	-.94843223665093E-05	0.93097238655024E-05	0.
0.15492327778286E+03	-.56835057046745E-03	0.68854387747647E+00	-.68891268742257E+00	-.
0.15492108529826E+03	0.54573155383730E-03	-.68862354843117E+00	0.68898267553650E+00	0.
0.15319693727747E+03	-.44165891770655E-03	-.43055008532768E-03	0.11543639445578E-03	-.

Open Viewer

Orbital Density Plot  
Gradients  
Vibrations  
Thermochemical Properties  
SCF Population Properties  
Dipole Moments  
AIM (Atoms in Molecules)  
NMR Shieldings  
View .cosmo File  
Density of states (DOS)

Show Plots

UV/Vis Spectrum  
CD Spectrum  
Raman Spectrum  
IR Spectrum  
VCD Spectrum  
Band Structure

What next

Start new job with current data  
Save as job template

The excitation with largest oscillator strength appears to be degenerate (excitations 4 and 5). This again points into the role of symmetry

Open the full output file by clicking **Open files -> Output**

# Excited state calculation output

In the full output file of the escf module, TURBOMOLE lists all information for the calculated excited states after the header "I R R E P a"

Find the excitation 4 in the output. Here is a condensed version of the output for this vertical excitation.

Section "**Dominant contributions**" tells, which molecular orbitals are contributing to the transition.

Compare the numbers to the orbitals we viewed on the slide Molecular orbitals. You will notice that excitations from HOMO, HOMO-1 to LUMO, LUMO-1 are the dominant contributions. The degenerate excitation 5 is composed of the same contributions. By looking at the orbitals, we see that this excitation likely involves excitation from N to B atoms or vice versa.

4 singlet a excitation

Total energy: -241.9015673297261  
Excitation energy: 0.2941048421738530  
Excitation energy / eV: 8.003003375908039  
Excitation energy / nm: 154.9221438287858

Oscillator strength:  
velocity representation: 0.3102022277009974  
length representation: 0.3621383783631287

## Dominant contributions:

occ. orbital	energy / eV	virt. orbital	energy / eV	coeff.  <sup>2</sup> *100
20 a	-8.05	22 a	0.57	27.2
21 a	-8.05	23 a	0.57	27.2
20 a	-8.05	23 a	0.57	20.7
21 a	-8.05	22 a	0.57	20.7

It is not convenient to estimate the nature of electronic transitions by looking at the molecular orbitals only.

Here the situation is further complicated by the fact that we did not consider the molecular symmetry, even though the electronic structure suggests that excitations 4 and 5 seem identical.

Let's take molecular symmetry properly into account next!

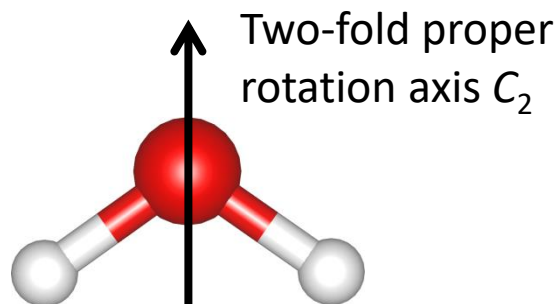
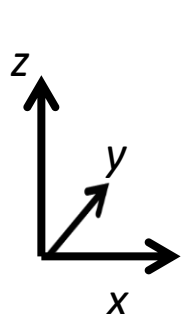
# The role of molecular symmetry

- Molecular symmetry plays a key role in molecular spectroscopies.
- If the molecule has some symmetry, its excited state properties can often be understood better when the symmetry is taken into account.
- Let's study the excited states of borazine again, but this time taking symmetry into account.
- The point group symmetry of the borazine molecule is  $D_{3h}$ .
  - If you are not familiar with point group symmetries, it is not critical for this tutorial.
  - An excellent resource for learning about point group symmetries is the Symmetry@Otterbein website: <https://symotter.org/>
- The next slide has a brief summary of point group symmetries

# Point group symmetry

- In point group symmetry operations, at least one point stays unchanged during the symmetry operation
  - If you close your eyes and your friend applies a symmetry operation to the molecule, the molecule will look the same when you open your eyes again.
- The **point group** of a molecule is based on the symmetry elements that are present.

Symmetry element	Symmetry operation	Schönflies symbol
Symmetry plane (mirror plane)	Reflection through plane	$\sigma$
Inversion	Every point $x,y,z$ translated to $-x,-y,-z$	$i$
Proper axis (rotation)	Rotation about axis by $360/n$ degrees	$C_n$
Improper axis (improper rotation)	Rotation by $360/n$ degrees followed by reflection through plane perpendicular to rotation axis	$S_n$

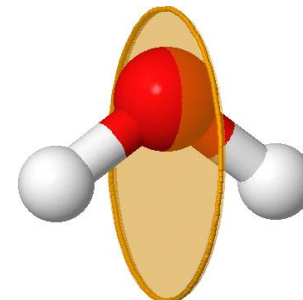


H<sub>2</sub>O (point group  $C_{2v}$ )

Mirror plane  $\sigma_{yz}$



Mirror plane  $\sigma_{xz}$



# Applying point group symmetry

- Open a completely new job from File -> New job.
- Build again the borazine molecule in the 3D Molecular Builder
- After building the molecule, click **Autodetect Symmetry**
- TMoleX will find the  $D_{3h}$  point group

The screenshot shows the TMoleX software interface. The 'Symmetry' section is active, displaying the 'Current point group' as  $d3h$ . A red arrow points to the 'Autodetect Symmetry' button. The 'Number of atoms' is 12. Below the symmetry section is a table of atom coordinates.

Number	Element	x	y	z	Fixed cartesian	Fixed internal
1	B	-0.729		1.2626	0	
2	N	-1.4171		0	0	
3	B	-0.729	-1.2626	0	0	
4	N	0.7086	-1.2273	0	0	
5	B	1.4579	0	0	0	
6	N	0.7086	1.2273	0	0	
7	H	-1.3402	2.3214	0	0	
8	H	-2.4406	0	0	0	
9	H	-1.3402	-2.3214	0	0	
10	H	1.2203	-2.1136	0	0	
11	H	2.6805	0	0	0	
12	H	1.2203	2.1136	0	0	

# Geometry optimization

- Build a complete input for geometry optimization of the  $D_{3h}$ -symmetric borazine.
- Use DFT-PBE0/def2-SVP level of theory, following the previous instructions (remember gridsize m4 for DFT).
- Run the optimization. Even one CPU is enough, the job will complete quickly.
- Open the Orbital/Density plot from the Results menu. Now the HOMO and LUMO orbitals with e'' symmetry are twofold degenerate.
- You can also visualize orbitals (this may fail on Windows computers due to " in the filename)

3D-Visualizer Opt\_D3h

Choose Molecular Orbital(s)

Sel.	No	Spin	Sym.	Energy[Hartree]	Deg.	Occ.	HOMO/LUMO	quick	high...
<input type="checkbox"/>	20	ab	8e'	0.1019	2	0	LUMO + 5		
<input type="checkbox"/>	19	ab	7a1'	0.1214	1	0	LUMO + 4		
<input type="checkbox"/>	18	ab	2a2''	0.1137	1	0	LUMO + 3		
<input type="checkbox"/>	17	ab	7e'	0.1027	2	0	LUMO + 2		
<input type="checkbox"/>	16	ab	6a1'	0.0779	1	0	LUMO + 1		
<input type="checkbox"/>	15	ab	2e''	0.0209	2	0	LUMO		
<input type="checkbox"/>	14	ab	1e''	-0.2959	2	4	HOMO		
<input type="checkbox"/>	13	ab	6e'	-0.3326	2	4	HOMO - 1		
<input type="checkbox"/>	12	ab	1a2''	-0.3843	1	2	HOMO - 2		
<input type="checkbox"/>	11	ab	5a1'	-0.3959	1	2	HOMO - 3		
<input type="checkbox"/>	10	ab	5e'	-0.4525	2	4	HOMO - 4		
<input type="checkbox"/>	9	ab	1a2'	-0.4559	1	2	HOMO - 5		
<input type="checkbox"/>	8	ab	4e'	-0.5120	2	4	HOMO - 6		

# Excited states with symmetry (1)

Now we can proceed to excited state calculation. In the **Results** menu, click **Start Job** to create a new job based on the optimized geometry.

Choose **UV/Vis** as the job type. Pay attention on the settings in the **Excited states** block. IRREP means irreducible representation. Each molecular orbital belongs to one IRREP and this determines the symmetry properties of the MO.

**Job type**

- Geometry Optimization ▶
- Spectra & Excited States ▶ UV/Vis and CD(vertical excitations)**
- Single Point ▶
- Single Point Properties ▶
- Population Analyses ▶
- Potential Energy Scan(PES) ▶
- Transition State Search ▶
- Templates ▶
- Batch processing ▶

**Excited states**

☒ Singlet ☐ Triplet RPA- Random phase approximation

☐ Unrestricted

Unit: nm

☐ All IRREPs Number of excited states per IRREP: 5

☒ Select IRREPs

for current symmetry: d3h

IRREP	A1'	A1''	A2'	A2''	E'	E''
No. of excitations	0	0	0	5	5	0
Needed for	-	-	CD	UV/Vis	UV/Vis	CD

**Method**

Level: **DFT**

Functional: **pbe0**

☒ RI

Basis set: **def2-SVP** Symmetry: **d3h**

Convergence Parameter

Energy: **10<sup>-6</sup>** Density:

Show Notes

**Use resources**

Memory used for: 500.0 MB

Disk: 0 MB for HF

No. of CPUs: 1

☒ Delete scratch files after run

**Save and Run**

Run (local)

# Excited states with symmetry (2)

- With  $D_{3h}$ -symmetry, the degeneracy of excitations is properly accounted for and the excitation with the largest oscillator strength is no longer "duplicated".
- Let's see next, how the excitation can be visualized with excited state difference density plots. Click again **Start Job**.

File Edit Templates Results Extras Tools License Help

Open 3D Molecular Builder

Jobs running local: 0/4 remote: 0 Memory used for TmoleX: 123,3/161,5 MB System: 0,0/16558,5 MB

Geometry → Atomic Attributes → Molecular Attributes → Method → Start Job → Results

Choose Job Template Charge: Use from input Apply Job Template

Job Results

HOMO-LUMO gap 8.62 eV  
Status geometry Not performed Convergence

Energy

total energy = -242.19569005249  
kinetic energy = 239.68709234080  
potential energy = -481.88278239329

Spectrum

# Electronic excitation spectrum of Ex\_D3h, IRREP e'  
# singlet excitations  
# excitation energy / nm oscillator strength (length rep.)  
0.15493130701609E+03 0.72427041016750E+00  
0.12608236597699E+03 0.12821526260907E+00  
0.12486901673580E+03 0.70376903575029E-03  
0.12132437084255E+03 0.14608588743296E-02  
0.11614550873100E+03 0.18082477560796E-01  
# Electronic excitation spectrum of Ex\_D3h, IRREP a2"  
# singlet excitations  
# excitation energy / nm oscillator strength (length rep.)  
0.15662036640357E+03 0.36808698688786E-01  
0.13417136753989E+03 0.45647286829221E-01  
0.11049151724897E+03 0.48328027036168E-03  
0.10967486929763E+03 0.13895226531247E-02  
0.10653839143309E+03 0.14187333956902E+00

Open Viewer

Orbital/Density Plot  
Gradients  
Vibrations  
Thermochemical Properties  
SCF Population Properties  
Dipole Moments  
AIM (Atoms in Molecules)  
NMR Shieldings  
View .cosmo File  
Density of states (DOS)

Show Plots

UV/Vis Spectrum  
CD Spectrum  
Raman Spectrum  
IR Spectrum  
VCD Spectrum  
Band Structure

What next

Start new job with current data  
Save as job template

# Excited state difference density (1)

Choose **Excited state energy, gradient & excited state density** as the job type.

Pay attention on the settings in the **Excited states** block: we will only calculate the electron density for one state: the state with the largest osc. strength (IRREP e', state 1).

Run the calculation. TmoleX will first calculate the total electron density of the ground state and then total electron density of the excited state.

The screenshot displays the TmoleX software interface. The top menu bar includes File, Edit, Templates, Results, Extras, Tools, License, and Help. Below the menu, a status bar shows 'Jobs running: local: 0/4, remote: 0' and 'Memory used for TmoleX: 109,8/161,5 MB, System: 0,0/16558,5 MB'. The main workspace is divided into several panels. On the left, a 'ProjectList' panel shows a tree structure of projects, with 'Ex\_D3h' selected. The central 'Job typ' panel lists various calculation types, with 'Single Point > Excited state energy, gradient & excited state density' highlighted by a red rectangle. Below this, the 'Excited states' panel is visible, featuring a 'Singlet' radio button, 'RPA- Random Phase Approx.' dropdown, and a red rectangle highlighting the 'IRREP' dropdown set to 'E'', 'Gradient and excited state density for excitation No.' set to '1', 'No. of excitations' set to '1', and 'Unit' set to 'nm'. On the right, the 'Method' panel shows 'Level: DFT', 'Functional: pbe0', 'Basis set: def2-SVP', and 'Symmetry: d3h'. The 'Use resources' panel at the bottom right shows 'Memory used for: 500.0 MB', 'Disk: 0 MB for HF', 'No. of CPUs: 1', and a checked box for 'Delete scratch files after run'. The 'Save and Run' panel at the bottom contains buttons for 'Run (local)', 'Save', and 'Run (network)'.

# Excited state difference density (2)

- In the Results menu, open the **Orbital/Density Plot** menu.
- TmoleX shows that the total electron density of the excited state (td) and the difference density to the ground state (ed) are available.
- Visualize the difference density by clicking the green tick mark.
- Use visualization mode isosurface +/- and isodensity 0.004 a.u. ( $e^-/\text{bohr}^3$ )
- In the red regions, electron density increases during the transition, in the blue regions it decreases. How would you describe the transition in your own words?
- Compare the difference density plot with the molecular orbitals studied previously.

3D-Visualizer Exdens\_D3h

Choose Molecular Orbital(s)

SEL	No	Spin	Sym.	Energy[Hartree]	Deg.	Occ.	HOMO/LUMO	quick	high...
<input type="checkbox"/>	17	ab	6a1'	0.1927	2	0	LUMO + 2		
<input type="checkbox"/>	16	ab	6a1'	0.0779	1	0	LUMO + 1		
<input type="checkbox"/>	15	ab	2e"	0.0209	2	0	LUMO		
<input type="checkbox"/>	14	ab	1e"	-0.2959	2	4	HOMO		
<input type="checkbox"/>	13	ab	6e"	-0.3326	2	4	HOMO - 1		
<input type="checkbox"/>	12	ab	1a2"	-0.3843	1	2	HOMO - 2		
<input type="checkbox"/>	11	ah	5a1'	-1.2050	1	2	HOMO - 3		

Choose Density and Electrostatic Properties

SEL	Plot-propertyname	Plot-filename	quick	high-res
<input type="checkbox"/>	Excited state, density	td		
<input type="checkbox"/>	Difference density (ground to excited st...	ed		
<input type="checkbox"/>	Electrostatic potential	tp		
<input type="checkbox"/>	Electric field	tf		
<input type="checkbox"/>	Gradient of electric field	tg		
<input type="checkbox"/>	Electrostatic potential color-coded on d...	tp_td		

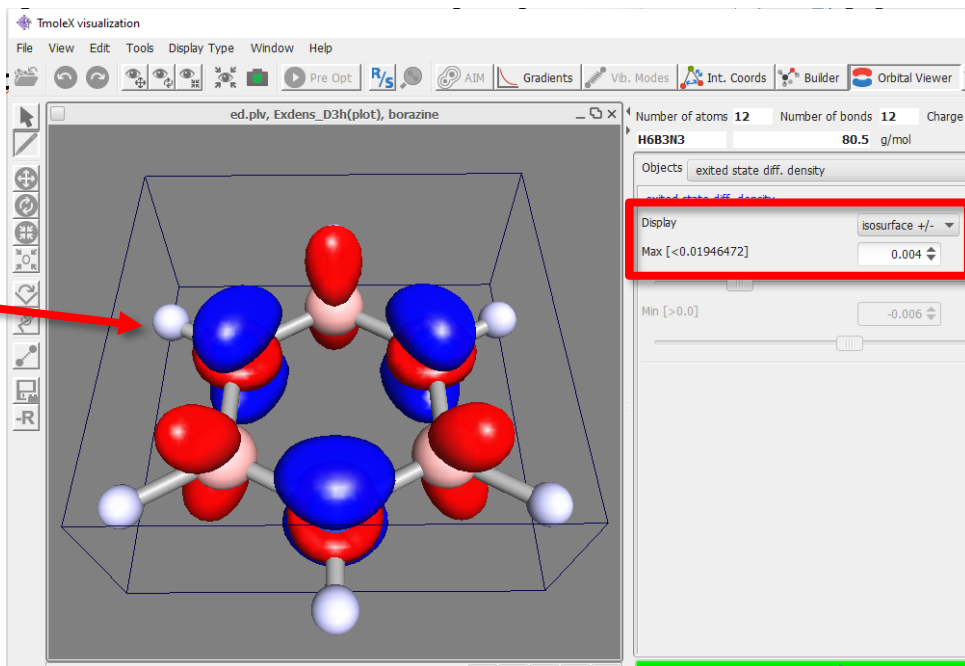
Natural transition orbitals

Calculate SEL	Number	Freq [nm]	Osc.str.	high-res
<input type="checkbox"/>	1 e'	154.9310	0.6204	

View SEL	Name	Spin	singular value	%contrib	Symmetry	high-res
----------	------	------	----------------	----------	----------	----------

File format: ☐ .plv/.plt ☐ .dtx

☐ View all in one



# Basis set effect

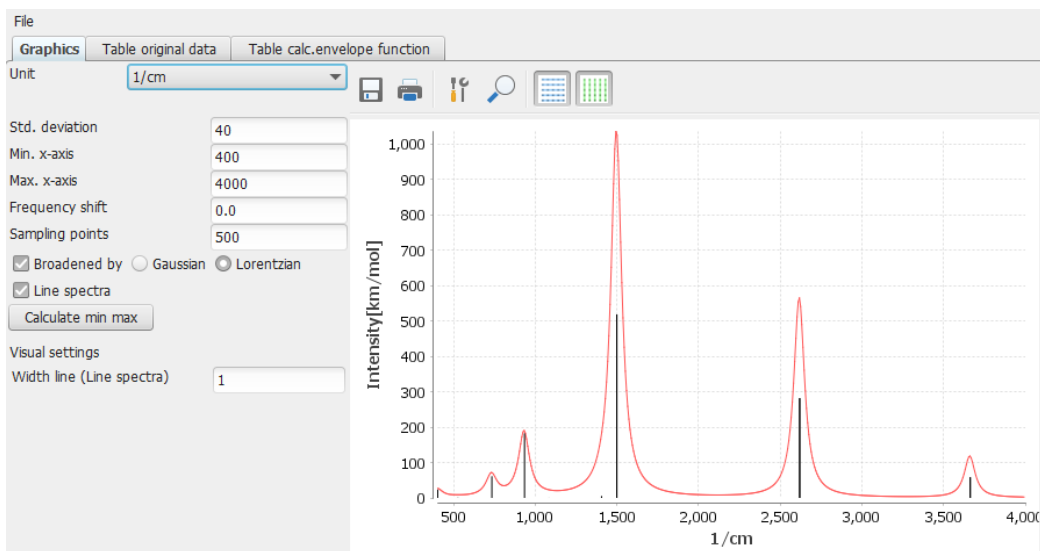
- In the case of borazine, an experimental vacuum UV-Vis study shows an absorption maximum at 165 nm (<https://doi.org/10.1063/1.1676802>).
  - For our DFT-PBE0/def2-SVP calculation, the absorption maximum was at 155 nm.
  - The difference between 165 nm and 155 nm is rather large (0.5 eV).
  - However, def2-SVP is a small basis set, and the results can be improved by increasing the basis set size.
- 
- Start a new project from File -> New Project.
  - Build the borazine molecule. Use point group symmetry.
  - This time, choose the larger def2-TZVP basis set for all atoms. Use PBE0 method (and gridsize m4).
  - Optimize the geometry.
  - Run a UV/Vis calculation. Does the result improve in comparison to the experiment? What is the difference to experiment in eV?

# Conclusions for borazine

- Molecular symmetry often helps to deal with excited states in a systematic way.
  - In larger molecules, it also speeds up calculations significantly.
  - Usually, it makes sense to utilize molecular symmetry, if it is present.
  - However, symmetry imposes constraints on the geometry of the molecule and you need to be sure how the **constraint may limit** the interpretation of the results (for example, by fixing the molecule into a certain conformer). Borazine is a rigid, flat molecule and using symmetry is perfectly fine.
- Excited state difference densities are a convenient and rigorous way to visualize electronic excitations.
- Larger basis set improved the agreement with the experiment.
  - However, this does not always work. Sometimes lower level of theory may benefit from cancellation of errors: the method, for example DFT, leads in error in one direction and too small basis set leads in error in another direction. As a result, the errors cancel out.
- What else did you learn?

# Borazine Bonus: IR spectrum

- We did not check after geometry optimizations that the structure is a true local minimum on the potential energy surface. This check should be part of production workflows.
- You can check the nature of the stationary point by running a vibrational frequency calculation for optimized geometry: Start Job -> IR and vibrational frequencies -> Run.
- Results -> IR Spectrum -> see settings below.
- Compare with spectrum (a) in the Fig. 3 (->).
- What factors can lead in differences between the calculated and experimental spectra?



IR spectrum of borazine, based on DFT-PBE0/def2-TZVP harmonic frequencies.

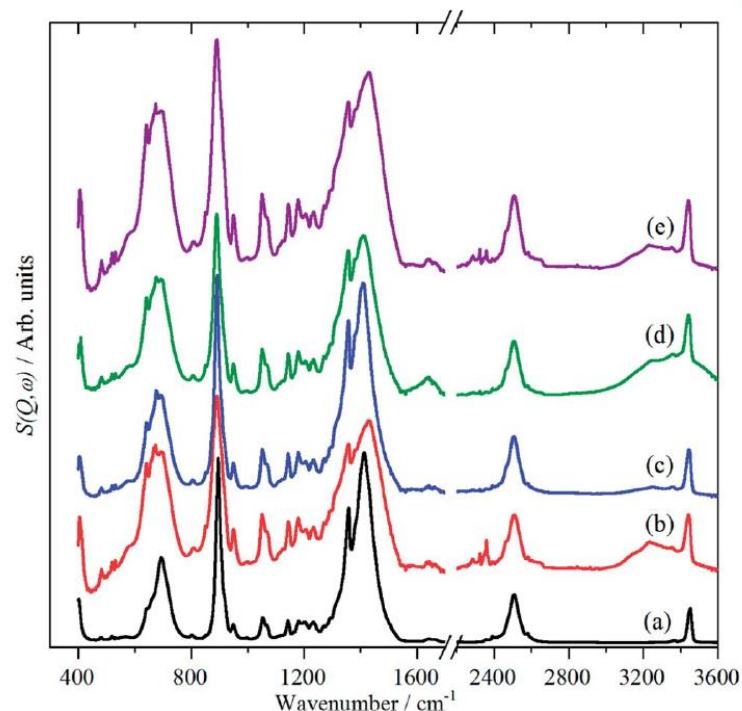


Fig. 3 Vibrational temperature infrared spectra of borazine. (a) liquid at 298 K, solid at: (b) 258 K, (c) 213 K, (d) 160 K and (e) 105 K. The broad features at 1650 and 3300 cm<sup>-1</sup> are due to ice.

Figure by Stewart Parker (License: CC BY)  
<https://doi.org/10.1039/C8RA04845B>

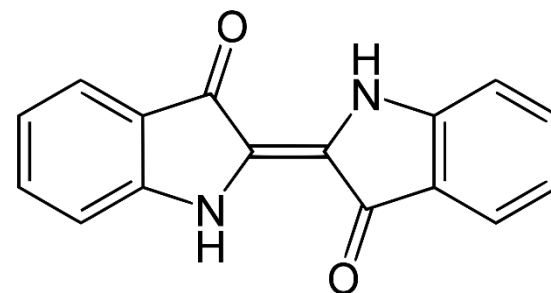
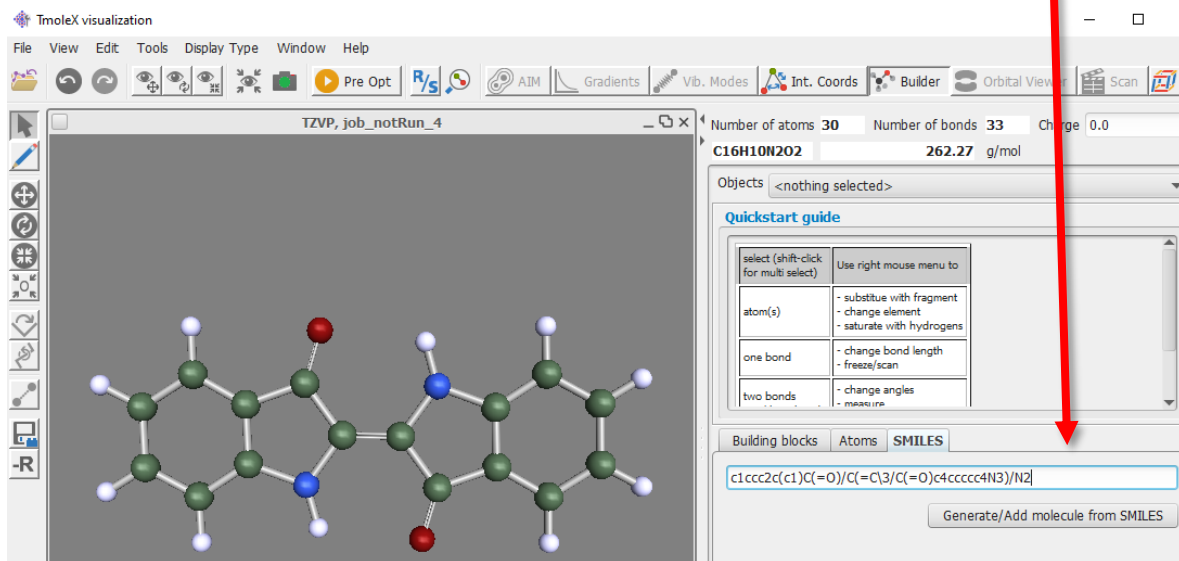
# Tutorial 2

# Tutorial 2: Indigo dye

- Indigo dye is used for example to produce blue jeans.
- Let's investigate the excited states of indigo dye.
- Open a new project called **indigo**.
- Open 3D Molecular Builder.
- Copy the [SMILES](#) of the molecule from [Wikipedia](#):  
c1ccc2c(c1)C(=O)/C(=C\3/C(=O)c4cccc4N3)/N2
- Use the SMILES string to generate the structure.
- No need to turn on point group symmetry yet.



Extract of Indigo plant applied to paper. Figure from [Wikimedia Commons](#). License: Public Domain.



Molecular structure of indigo dye. Figure from [Wikimedia Commons](#). License: Public Domain.

# Pre-optimization with GFN2-xTB (1)

- For larger molecules, it might be helpful to carry out a pre-optimization of the molecular structure with lower level of theory.
- Let's use GFN2-xTB extended semiempirical tight-binding model by Grimme and coworkers: <https://doi.org/10.1021/acs.jctc.8b01176>
  - “Primarily designed for the fast calculation of structures and noncovalent interaction energies for molecular systems with roughly 1000 atoms.”
- Choose any basis set in Atomic Attributes and initial guess in Molecular Attributes.
- In Method, choose Semi-empirical and GFN2-xTB (the method includes its own minimal basis set).

The screenshot shows the ORCA software interface. The 'Level of Theory' section has a dropdown menu set to 'Semi-empirical'. Below it, the 'Semi-empirical settings' section has a dropdown menu set to 'GFN2-xTB(Grimme group 2018)' and a text input for 'elec. temperature' set to 300 K. The 'Auxiliary basis sets for RI-J' section shows a table with elements C, H, N, and O, each with a 'Basis set' and an 'Auxiliary basis set' dropdown menu.

Element	Basis set	Auxiliary basis set
C	def-SV(P)	def-SV(P)
H	def-SV(P)	def-SV(P)
N	def-SV(P)	def-SV(P)
O	def-SV(P)	def-SV(P)

# Pre-optimization with GFN2-xTB (2)

- It would be faster to run the pre-optimization on the local computer, but the demo version does not allow it.
- Run the pre-optimization remotely on Puhti.
  - Instructions on the last two slides.
- The job will finish in less than 10 seconds, but TmoleX waits a minute before retrieving the results.

Geometry → Atomic Attributes → Molecular Attributes → Method → Start Job → Results

Choose Job Template | Charge: Use from input | Apply Job Template

Job Results

Type of Calculation: **Geometry Optimization** | Status SCF: **Converged** | SCF Convergence: **Converged** | HOMO-LUMO gap:  eV | Status geometry: **Converged** | Convergence:

Open Files

Output

Energy

Open Viewer

Orbital/Density Plot

Gradients

Vibrations

Thermochemical Properties

SCF Population Properties

Dipole Moments

GAUSS (Atoms in Molecules)

NMR Shieldings

View .cosmo File

Density of states (DOS)

Show Plots

UV/Vis Spectrum

CD Spectrum

Raman Spectrum

IR Spectrum

VCD Spectrum

Band Structure

What next

Geometry Convergence Criteria

\$convinfo

energy change : actual value = -0.3063E-06 threshold = 0.1000E-05

geom. gradient : actual value = 0.7190E-04 threshold = 0.1000E-02

Energy

cls. repulsion	=	0.6333134
iso. ES	=	0.0623444
aniso. ES	=	-0.0000798
aniso. XC	=	0.0193176
dispersion	=	-0.0344268
cls. XB	=	0.0000000
H-L gap (eV)	=	1.2953485

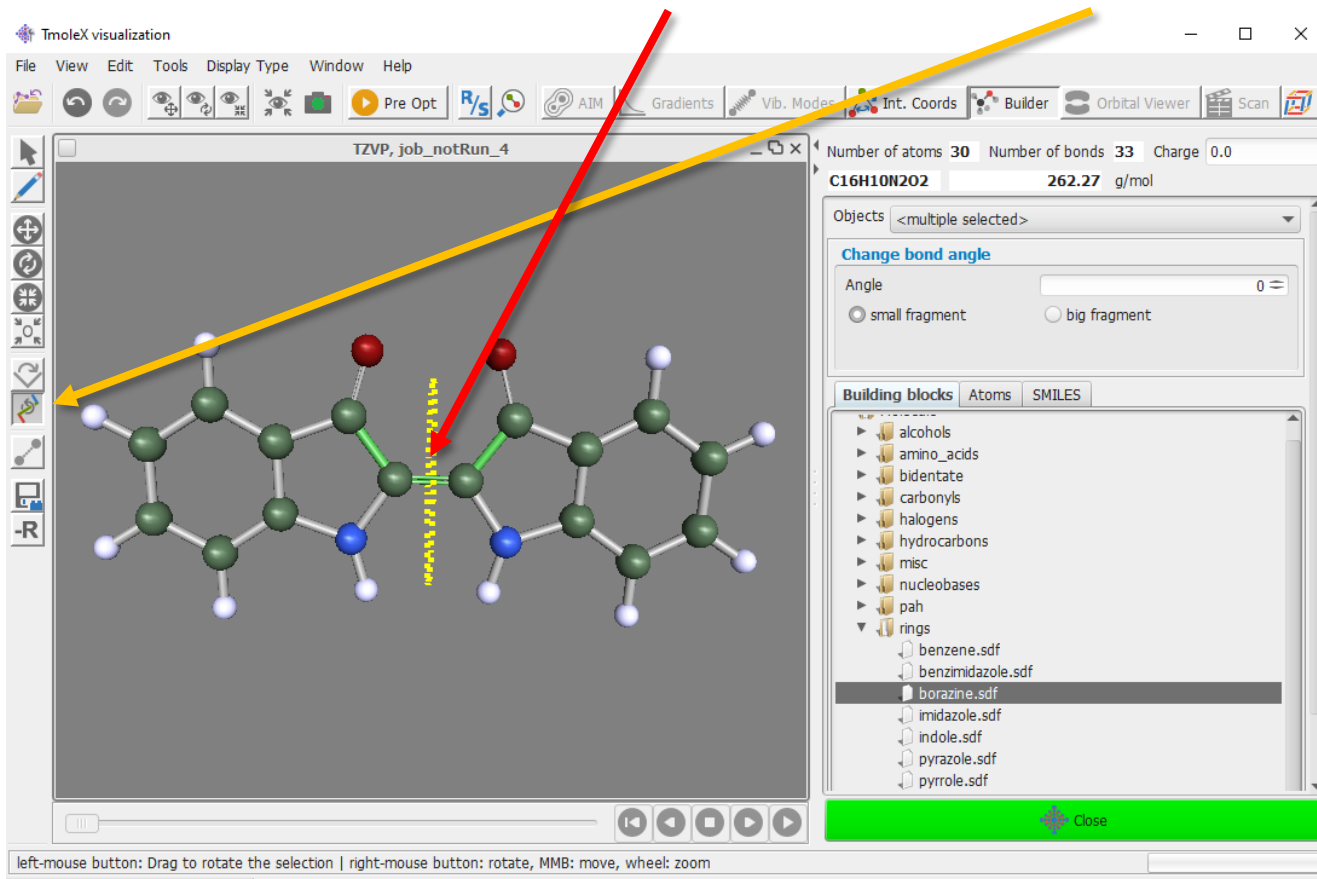
Gradients

cycle = 1	SCF energy =	-53.3296811343	dE/dxyz  =	0.16308
cycle = 2	SCF energy =	-53.3459174751	dE/dxyz  =	0.08296
cycle = 3	SCF energy =	-53.3535229110	dE/dxyz  =	0.022509
cycle = 4	SCF energy =	-53.3539584176	dE/dxyz  =	0.012709
cycle = 5	SCF energy =	-53.3541858958	dE/dxyz  =	0.005309
cycle = 6	SCF energy =	-53.3542380111	dE/dxyz  =	0.002824
cycle = 7	SCF energy =	-53.3542448331	dE/dxyz  =	0.001325
cycle = 8	SCF energy =	-53.354246772	dE/dxyz  =	0.000610
cycle = 9	SCF energy =	-53.3542471391	dE/dxyz  =	0.000277
cycle = 10	SCF energy =	-53.3542471398	dE/dxyz  =	0.000100

Take the total energy of the optimized structure from here and save it in Excel/Calc/Notepad

# Cis-isomer of indigo dye

- We pre-optimized the structure of *trans*-isomer of the indigo dye.
- Open a New job and build the *cis*-isomer of the same molecule (figure below).
- First, load the structure with SMILES.
- Click the double bond in the middle and use the **torsion tool** to rotate by 180°

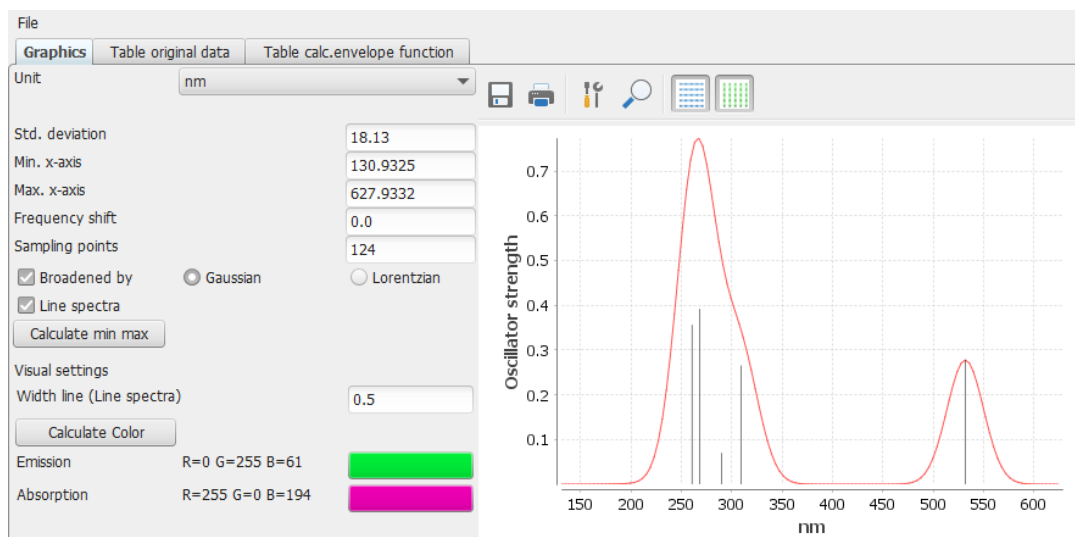


# Energy comparison of the isomers

- Pre-optimize also the *cis*-isomer of indigo with GFN2-xTB.
- Take the total energy of the optimized structure and compare it with the total energy of the *trans*-isomer. Which one is lower in energy (has more negative energy)? How much? The total energies are in Hartree units. 1 Hartree = 2625.5 kJ/mol.
- Next, open the pre-optimization job of the *trans*-isomer and create a new job based on the pre-optimized geometry.
  - Find point group symmetry for the molecule (should be  $C_{2h}$ )
  - Choose def2-TZVP basis set for all atoms.
  - Choose DFT-PBE0 as the method (remember gridsize m4)
  - Optimize the geometry. Use Puhti and **16 CPUs**.
  - Take the total energy of the optimized structure.
- Repeat for the *cis*-isomer.
  - Compare the total energies at the DFT-PBE0/def2-TZVP level of theory. How does the result compare with semi-empirical GFN2-xTB?

# UV/Vis spectrum of indigo

- The next task is to calculate the UV/Vis spectrum of the *trans*-isomer of indigo.
- Start a new job based on the DFT-PBE0/def2-TZVP optimized geometry ( $C_{2h}$ ).
- Choose UV/Vis spectrum calculation. Select IRREPs and include 5 excitations for IRREP **Au** and 5 excitations for IRREP **Bu**. Ag and Bg are inactive
- Run the calculation on Puhti, using **16 CPUs**.
- Go to Results menu and open UV/Vis spectrum.
- Click **Calculate Color**. The color for absorption is purple, not indigo. The lowest-energy (largest wavelength) excitation has too short wavelength.
- Experimentally, the absorption maximum is at 610 nm in dimethylformamide (DMF) solvent (<https://doi.org/10.1021/jp049076y>).



# Solvent effects

- Let's try to improve by including solvent effects with the COSMO solvent model.
- Start a new job based on the DFT-PBE0/def2-TZVP optimized geometry ( $C_{2h}$ ).
- In the Method menu, go to Solvation tab and activate COSMO.
  - Epsilon can be infinity and refractive index 1.33 (water).
- Choose UV/Vis spectrum calculation. Select IRREPs and include 5 excitations for IRREP **Au** and 5 excitations for IRREP **Bu**. Ag and Bg are inactive
- Run the calculation on Puhti, using **16 CPUs**.
- Go to Results menu and open UV/Vis spectrum. Calculate the absorption color again. Did the situation improve? What is the difference between the lowest-energy (largest wavelength) excitation and the experimental result in nm and in eV?
- Repeat the UV/Vis calculation one more time, but this time, switch on also **senex** and **esenex** on in Method menu. Seminumerical exchange speeds up the excited state calculation. How large is the speed-up? Do you see any significant loss in accuracy?

# Bonus tasks for indigo

- You can also visualize the excited state difference density for the lowest-energy excitation. How does the excitation look like?
- Run the UV/Vis spectrum calculation with 8 CPUs instead of 16. Is there a reasonable speedup when doubling the number of CPUs from 8 to 16?
- We did not include COSMO in the geometry optimization. It would be even more consistent strategy to have COSMO also in the geometry optimization before the excited state calculation. You can check whether this has a significant effect on the UV/Vis spectrum in this case.
- You can also try using COSMO parameters for [DMF solvent](#): epsilon 36.7 and refractive index 1.43. Does the agreement with the experiment show further improvement? (experimental study used DMF solvent)

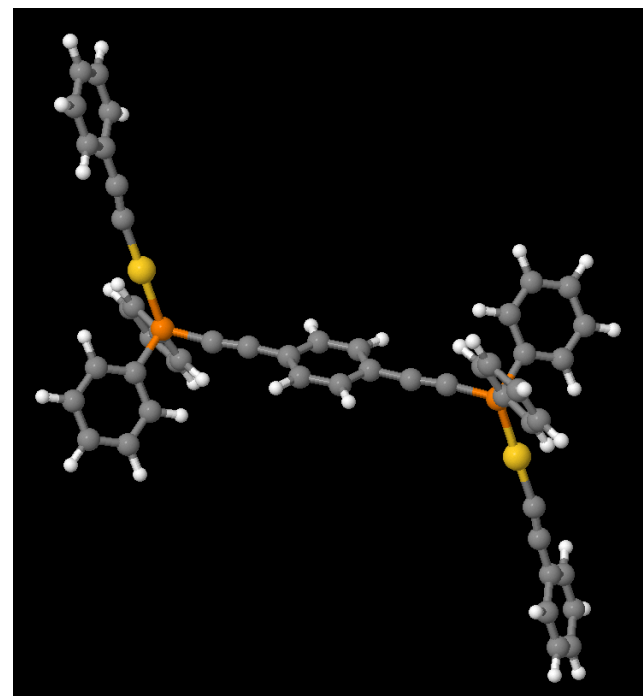
# Conclusions for indigo

- Solvent model improved the agreement with the experiment.
  - This is not always the case, but COSMO does often lead in better agreement with experimental solution-state spectra.
  - Often it is enough to use COSMO with default settings and not change the dielectric constant (epsilon) according to the solvent. You can of course also try changing the dielectric constant and refractive index according to the solvent.
- Seminumerical exchange can speed up excited state calculations significantly.
  - **Warning!** Do not compare total energies from senex calculations and "non-senex" calculations!
- What else did you learn?

# Tutorial 3

# Tutorial 3: Organometallic Au(I) complex

- The system in the last tutorial is photoactive bimetallic Au(I) complex.
- Structure in XYZ format available at <https://www.iki.fi/ankarttu/structures/au2.xyz>
- Complex **2** in publication "Synthesis, Characterization and Photophysical Properties of the  $\text{PPh}_2\text{-C}_2\text{-(C}_6\text{H}_4)_n\text{-C}_2\text{-PPh}_2$  Based Bimetallic Au(I) Complexes", Koshevoy, I. O.; Lin, C.-L.; Hsieh, C.-C.; Karttunen, A. J.; Haukka, M.; Pakkanen, T. A.; Chou, P.-T. *Dalton Trans.* **2012**, 41, 937–945.  
<http://doi.org/10.1039/C1DT11494H>



# Tutorial 3 with DFT-PBE0

- Download the XYZ file from <https://www.iki.fi/ankarttu/structures/au2.xyz>
- The molecule has  $C_{2h}$  point group symmetry, please use it.
- No need to preoptimize geometry with GFN2-xTB, this is a CC2/TZVP geometry.
- Optimize the geometry with **DFT-PBE0** method (**m4** grid). Use **def2-TZVP** basis set for non-hydrogen atoms and **def2-SVP** for H atoms to save some time.
- Use **senex** and **esenex**.
- Use **32 CPUs** on Puhti. Give 1000 MB of memory in the Start Job menu.
- After geometry optimization, run UV/Vis calculation. Use **senex** and **esenex**.
  - Select IRREPs: Au -> 2, Bu -> 2, Ag -> 0, Bg -> 0.
- Compare the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  excitation energies with the data in the table.

**Table 2** Computational photophysical results for the clusters **1–7** and the ligand **L3** (CC2/TZVP level of theory)

	$\lambda_{ab} S_0 \rightarrow S_1$ (nm)		$\lambda_{ab} S_0 \rightarrow S_2$ (nm)		$\lambda_{em} S_1 \rightarrow S_0$ (nm)		$\lambda_{em} T_1 \rightarrow S_0$ (nm)	
	Theor. <sup>a</sup>	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
<b>1</b>	310 (1.04)	302	266 (0.15)	286	387	394	392	455
<b>2</b>	306 (1.01)	312	274 (1.59)	294	397	370	518	517
<b>3</b>	311 (2.42)	315	293 (0.79)	299	363	370	550	570
<b>4</b>	325 (3.35)	325	295 (0.45)	285	378	394	564	591
<b>5</b>	325 (3.19)	325	—	—	377	392	565	593
<b>6</b>	324 (3.29)	325	—	—	376	393	565	595
<b>7</b>	333 (3.16)	327	247 (0.03)	277	386	394	569	593
<b>L3</b>	325 (3.03)	328	—	—	378	386	—	—

<sup>a</sup> Wavelengths in nm, oscillator strengths given in parentheses.

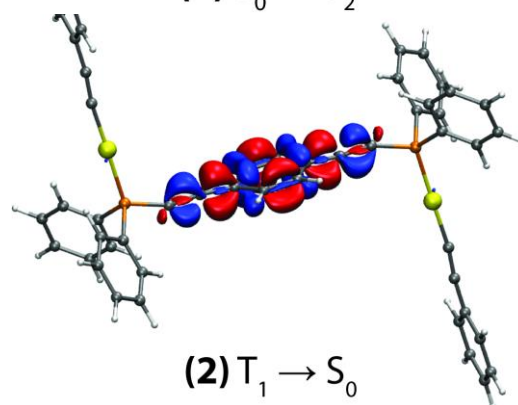
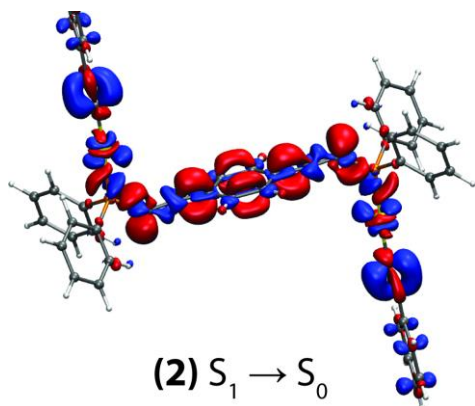
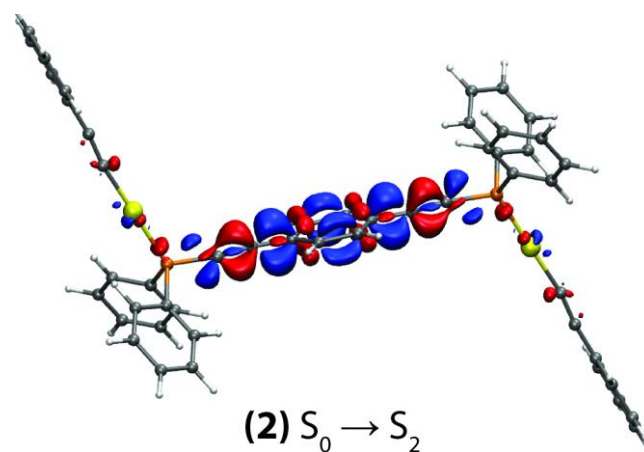
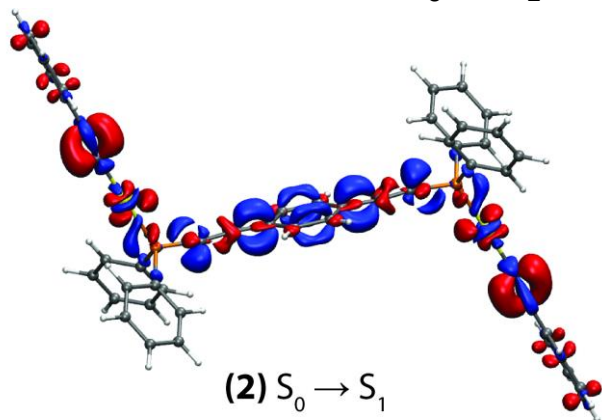
# Tutorial 3 with CAM-B3LYP

- Repeat the UV/Vis spectrum calculation with long-range corrected CAM-B3LYP functional (you can use PBE0 geometry).
- Long-range corrected functionals can manage better charge-transfer (CT) excitations, which are challenging for TD-DFT.
- CT excitations are delocalized over large distances. Such excitations are problematic for DFT-GGA and even hybrid functionals. Long-range corrected functionals work better for CT excitations.
  - See for example:
  - <https://doi.org/10.1021/ja039556n>
  - <https://doi.org/10.1021/cr0505627>
- Compare the CAM-B3LYP results with the PBE0 results. Which one agrees better with the experimental results in the table?
- You can then try to run excited state optimization for  $S_1$  and  $T_1$  states. This will give an estimate of the emission energies.

# Excited state difference densities at CC2/TZVP level of theory

Visualize the excited state difference densities and compare them to the CC2/TZVP results below. The isovalue is 0.002 a.u. Why did the long-range corrected CAM-B3LYP functional agree better with experiment compared to PBE functional?

Tip: look at the nature of the  $S_0 \rightarrow S_1$  excitation (localized / delocalized).



# Settings for running jobs remotely on Puhti

# Puhti settings (1)

Change *username* to your own CSC username everywhere. You can also set the number of CPUs here, but if you already set it in the Start Job menu, that setting will be used here. See the next slide for the contents in *Script before job execution*.

Remote Systems

emote machines  
Default  
username@puhti.csc.fi

Machine/IP: puhti.csc.fi  
User: username  
Password:   
Group name: Default  
Identification: username@puhti.csc.fi  
☐ Expert settings

New  
Save Machine  
Clone  
Import  
Export  
Delete Machine

Check Password Settings Check workload Test remote system

Work directory: /scratch/project\_2006657/username  
TURBOMOLE directory: /app/soft/chem/turbomole/7.8/TURBOMOLE/  
Number of CPUs for job(s): 1 Check remote system every 1 min  
TURBOMOLE version: V7.7 and newer

Status of remote system: **Currently no running jobs from this session.**  
max. avail CPUs: unknown number of CPUs in use: 0

☒ Use queuing system

Submit with: sbatch  
Check status: squeue -u username  
automatically:  
☐ add PARA\_ARCH=MPI  
☐ add PARNODES=number of CPUs

Script before job execution (without #!/bin/sh)  
#SBATCH --nodes=1  
#SBATCH --ntasks-per-node=<number\_of\_cpus>  
#SBATCH --account=project\_2006657  
#SBATCH --time=00:30:00

Script after job execution

Start Job Save job Cancel

# Puhti settings (2)

Script before job execution can be as follows. Adjust --time as necessary (format is hh:mm:ss). Here we use only OpenMP parallelization because it is efficient and technically robust. Many TURBOMOLE modules do also have MPI parallelization.

*TmoleX will fill in the part <number\_of\_cpus> based on your input.*

```
#!/bin/sh
#SBATCH --partition=small
#SBATCH --reservation=sscc_thu_small
#SBATCH --nodes=1
#SBATCH --ntasks-per-node=<number_of_cpus>
#SBATCH --account=project_2006657
#SBATCH --time=00:30:00

# Load TURBOMOLE and set OpenMP parallelization
ulimit -s unlimited
export PARA_ARCH="SMP"
export TM_PAR_OMP=on
export PARNODES=$SLURM_NTASKS
module load turbomole/7.8
export PATH="$${TURBODIR}/bin/`sysname`:${PATH}"

# Additional SLURM options
export SLURM_CPU_BIND=none
```