Aalto University
School of Chemical
Engineering

Advanced Exercises in Quantum Chemistry

CSC Spring School on Computational Chemistry 2024

Antti Karttunen

2024-04-18

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 ($B_3N_3H_6$)
  - Can be completed even on a local workstation/laptop

- **Tutorial 2:** Excited states of indigo dye ($C_{16}H_{10}N_2O_2$)
  - We will use Puhti supercomputer

- **Tutorial 3:** Organometallic Au(I) complex $(AuC_2Ph)_2PPh_2C_2C_6H_4C_2PPh_2$
  - 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

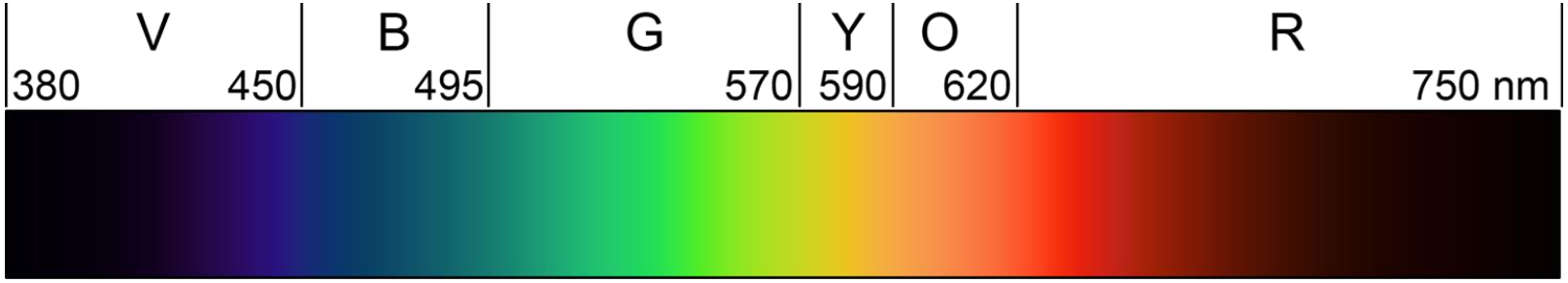


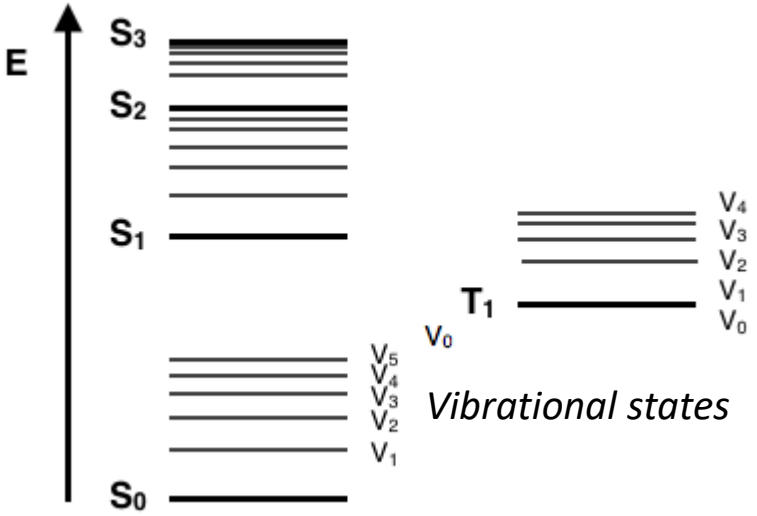
Figure: Wikimedia Commons (Public Domain)

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

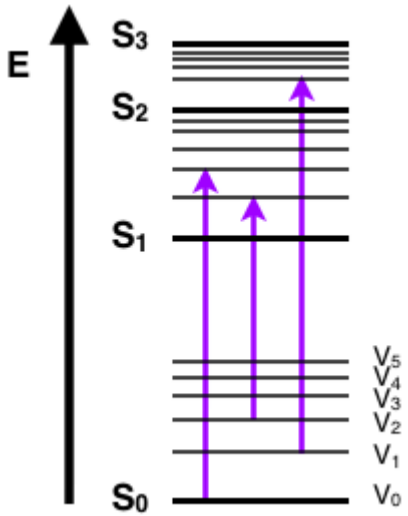
https://en.wikipedia.org/wiki/Visible_spectrum

Jablonski diagrams (1/3)

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

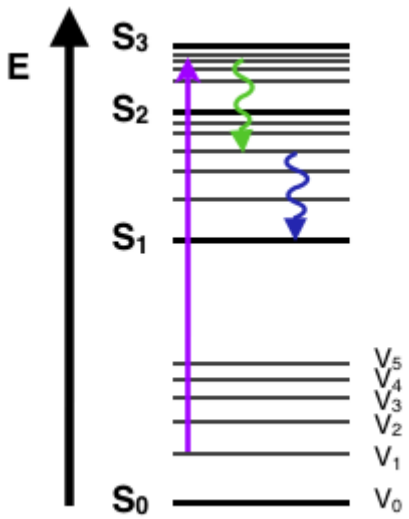


Foundation of a typical Jablonski Diagram

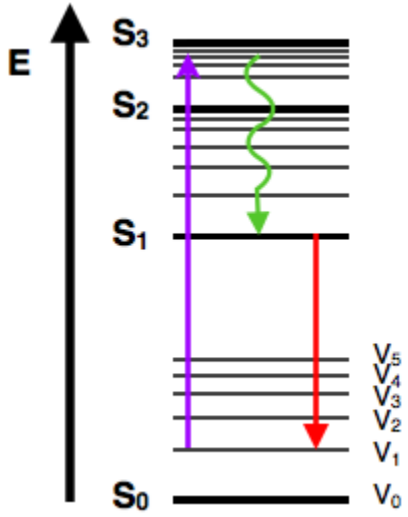


Three possible absorption transitions represented.
These can be measured by **UV/Vis** spectroscopy. **The tutorial focuses on this kind of transitions**.

Jablonski diagrams (2/3)

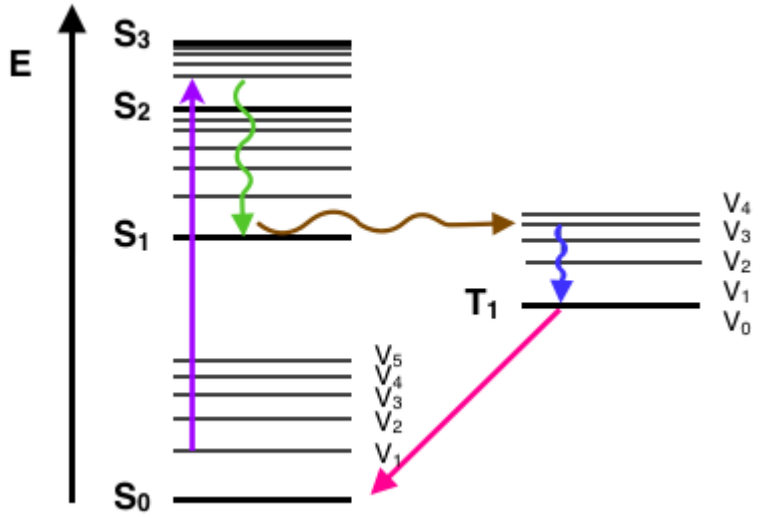


Possible scenario with absorption, internal conversion, and vibrational relaxation *processes shown.*



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.

Source: chem.libretexts.org (CC BY)

Timescales

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

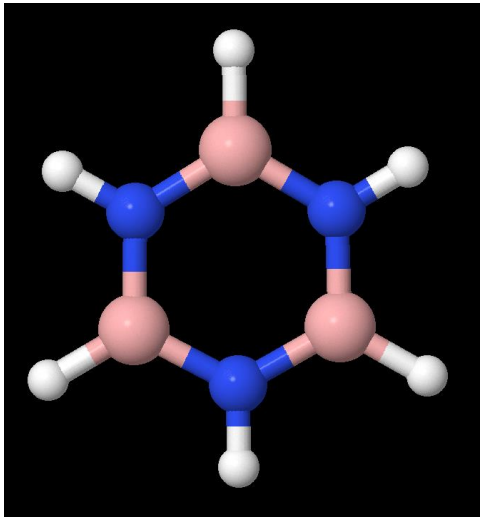
Transition	Timescale	Radiative Process?
Internal Conversion	10^{-14} - 10^{-11} s	no
Vibrational Relaxation	10^{-14} - 10^{-11} s	no
Absorption	10^{-15} s	yes
Phosphorescence	10^{-4} - 10^{-1} s	yes
Intersystem Crossing	10^{-8} - 10^{-3} s	no
Fluorescence	10^{-9} - 10^{-7} s	yes

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

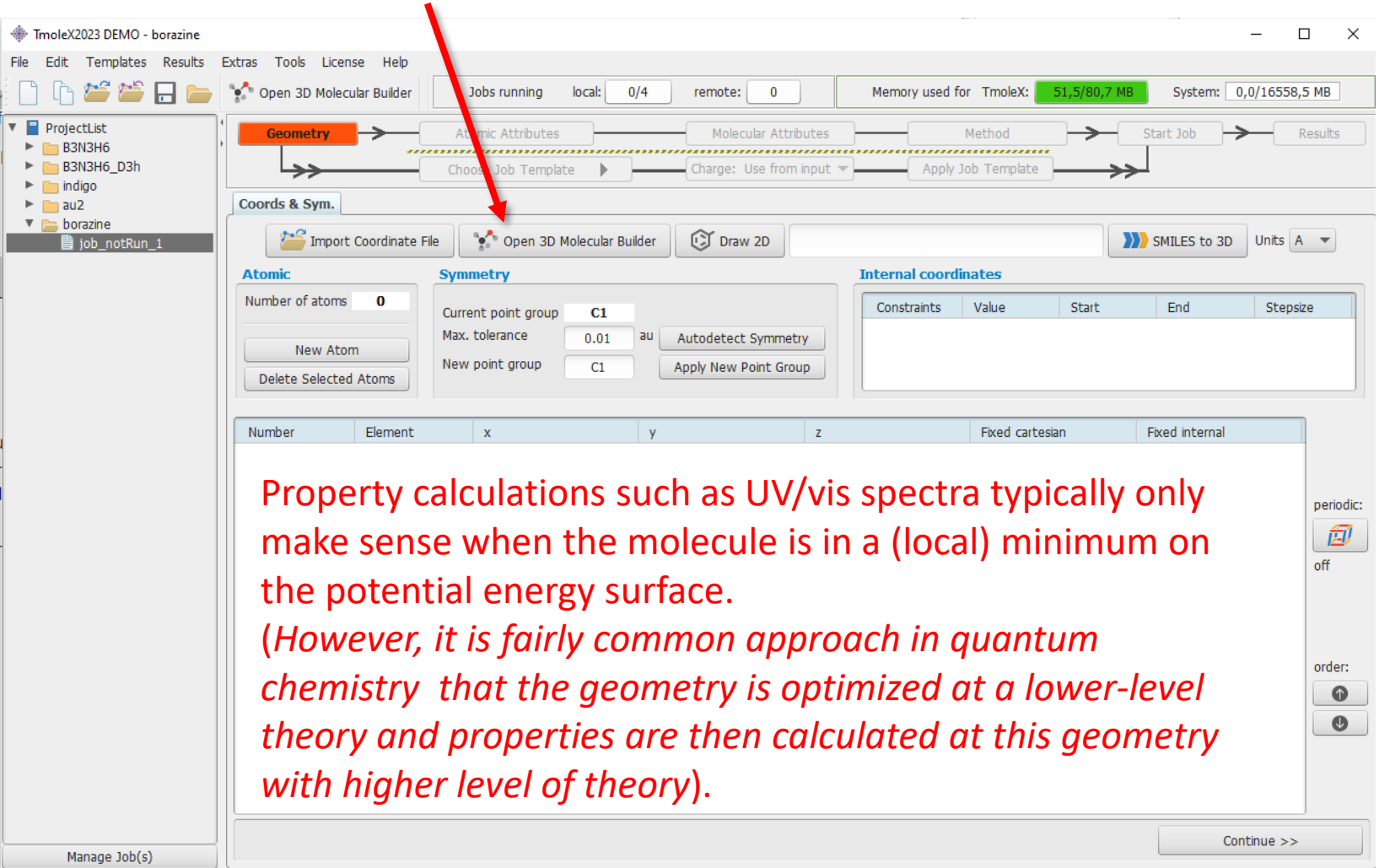
- TmoleX is a graphical user interface to create, run, and analyze TURBOMOLE calculations.

- 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)

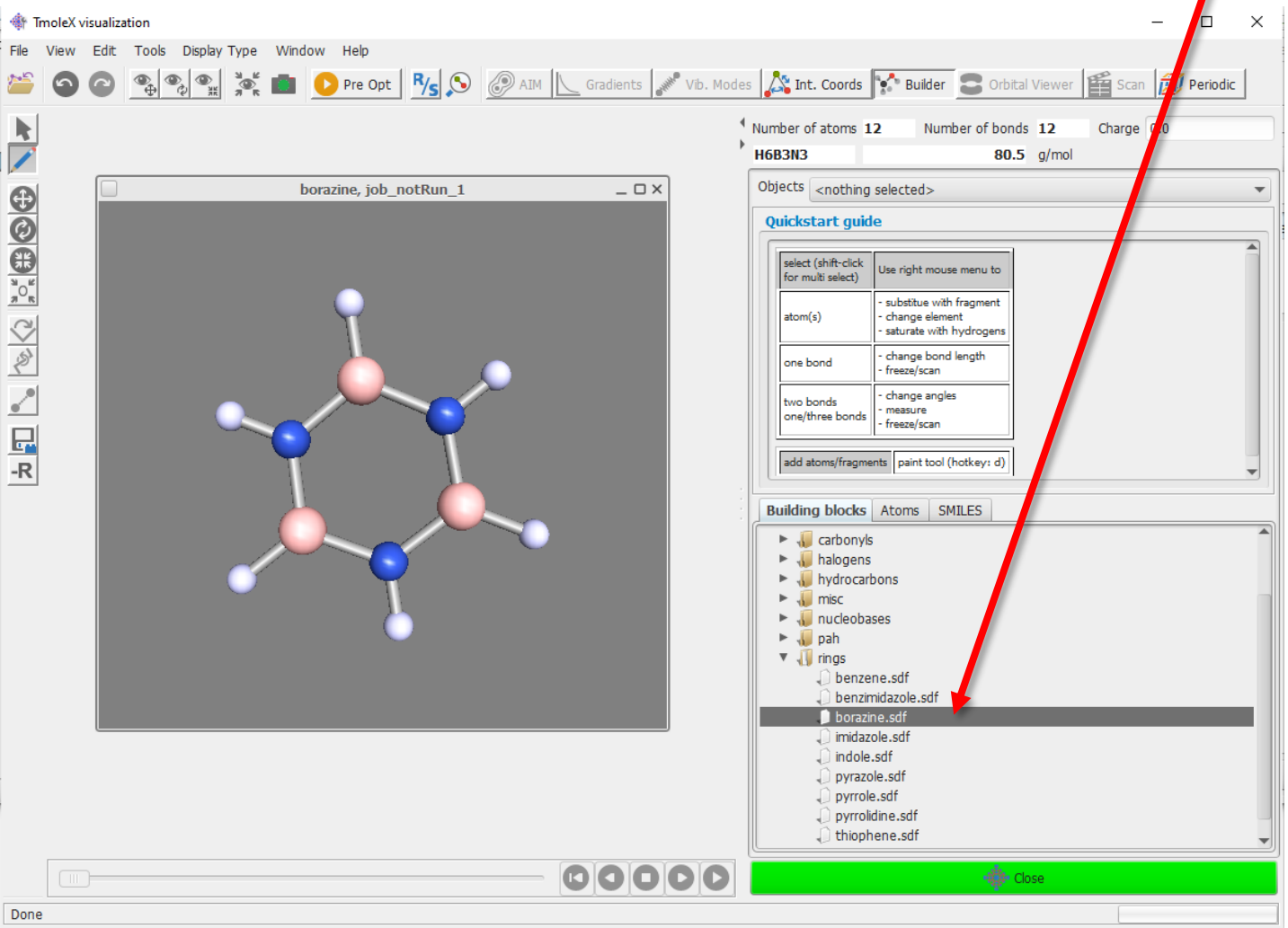
We need to optimize the molecular structure of borazine in the electronic ground state before we can proceed to study the excited states. Start a new project **borazine** in TmoleX and open the 3D Molecular Builder:



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*).

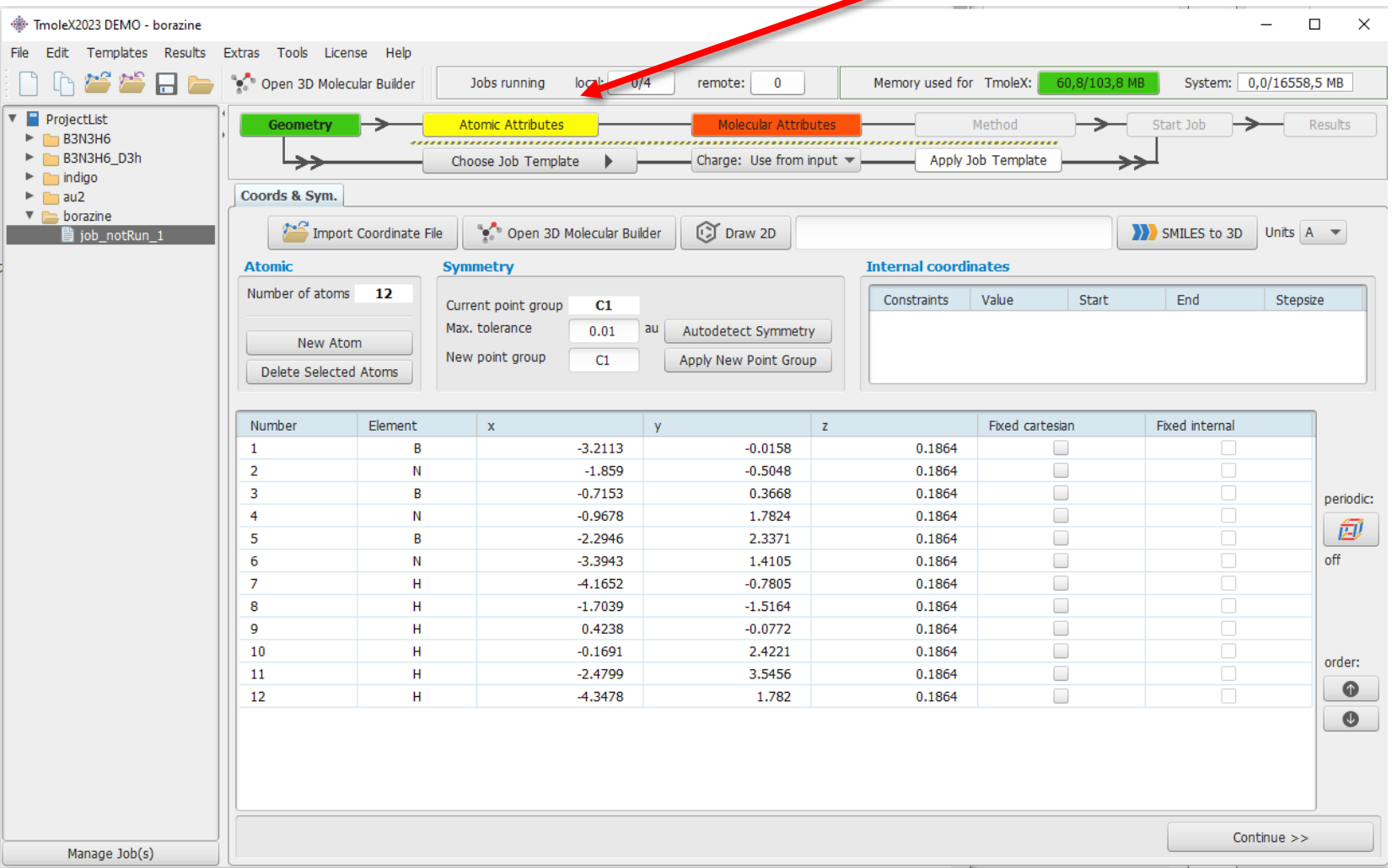
Geometry optimization (2)

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**).



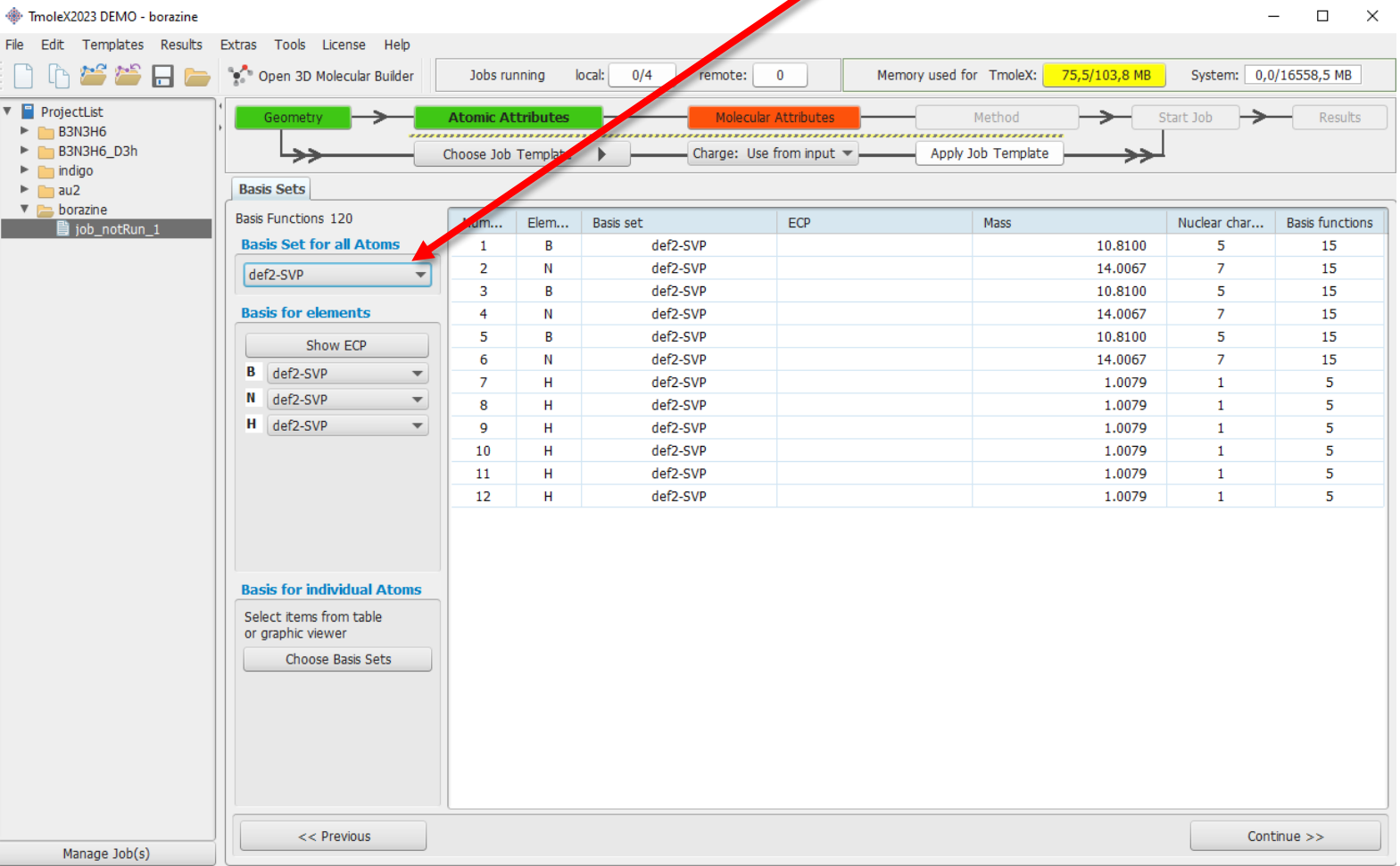
Geometry optimization (3)

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



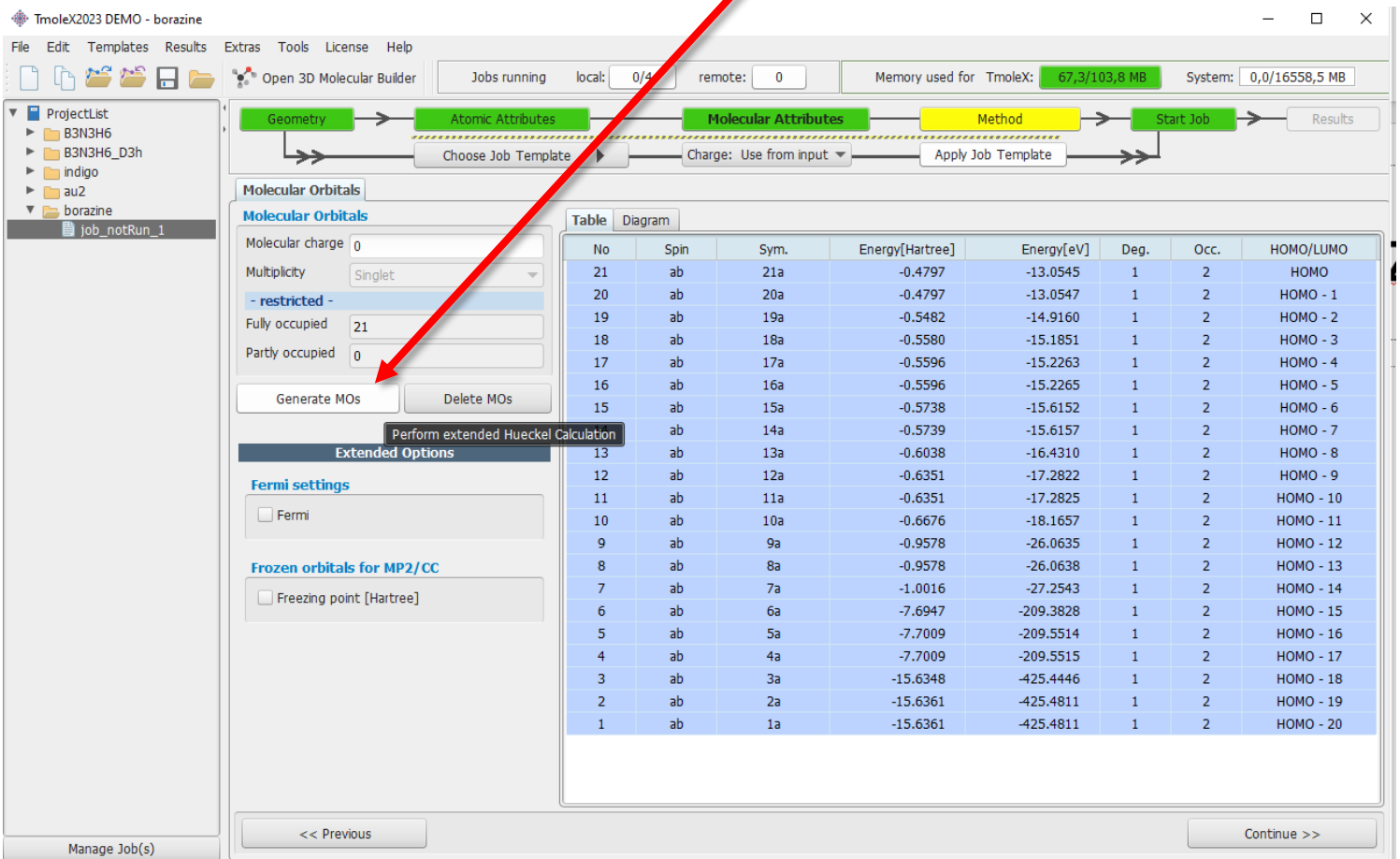
Geometry optimization (4)

Let’s first run the calculations with a small basis set. Choose def2-SVP basis set for all atoms.
Proceed to Molecular Attributes.



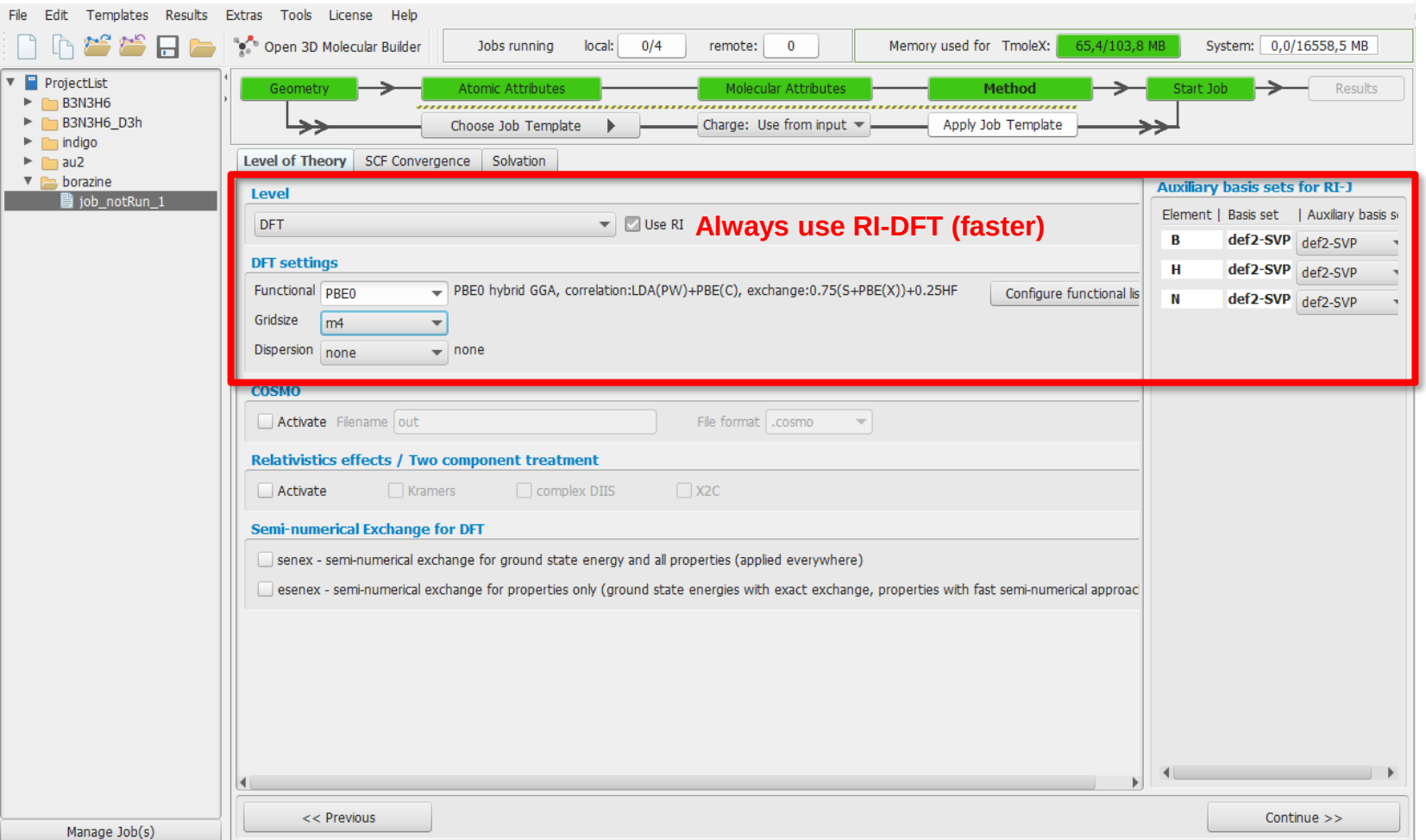
Geometry optimization (5)

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



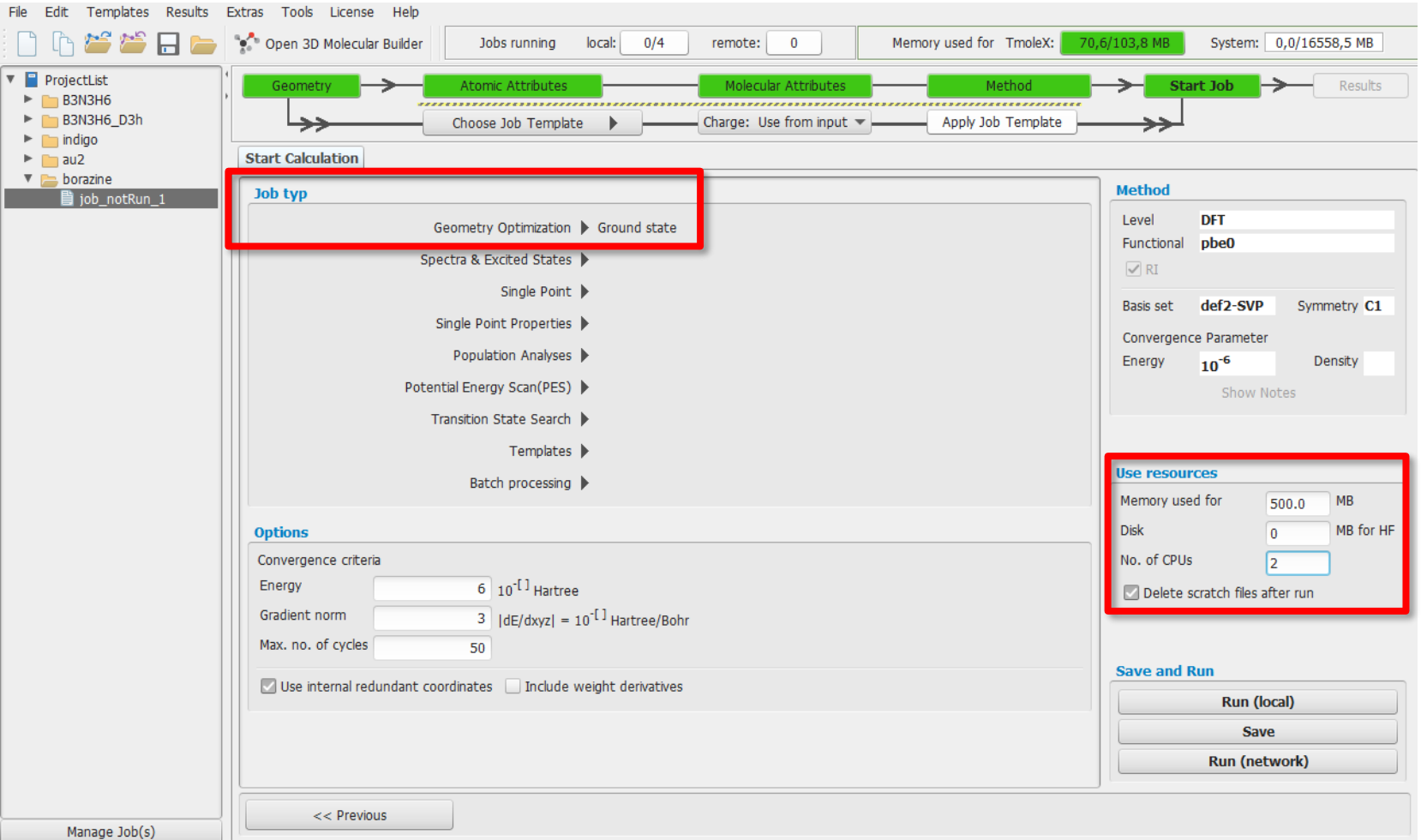
Geometry optimization (6)

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.



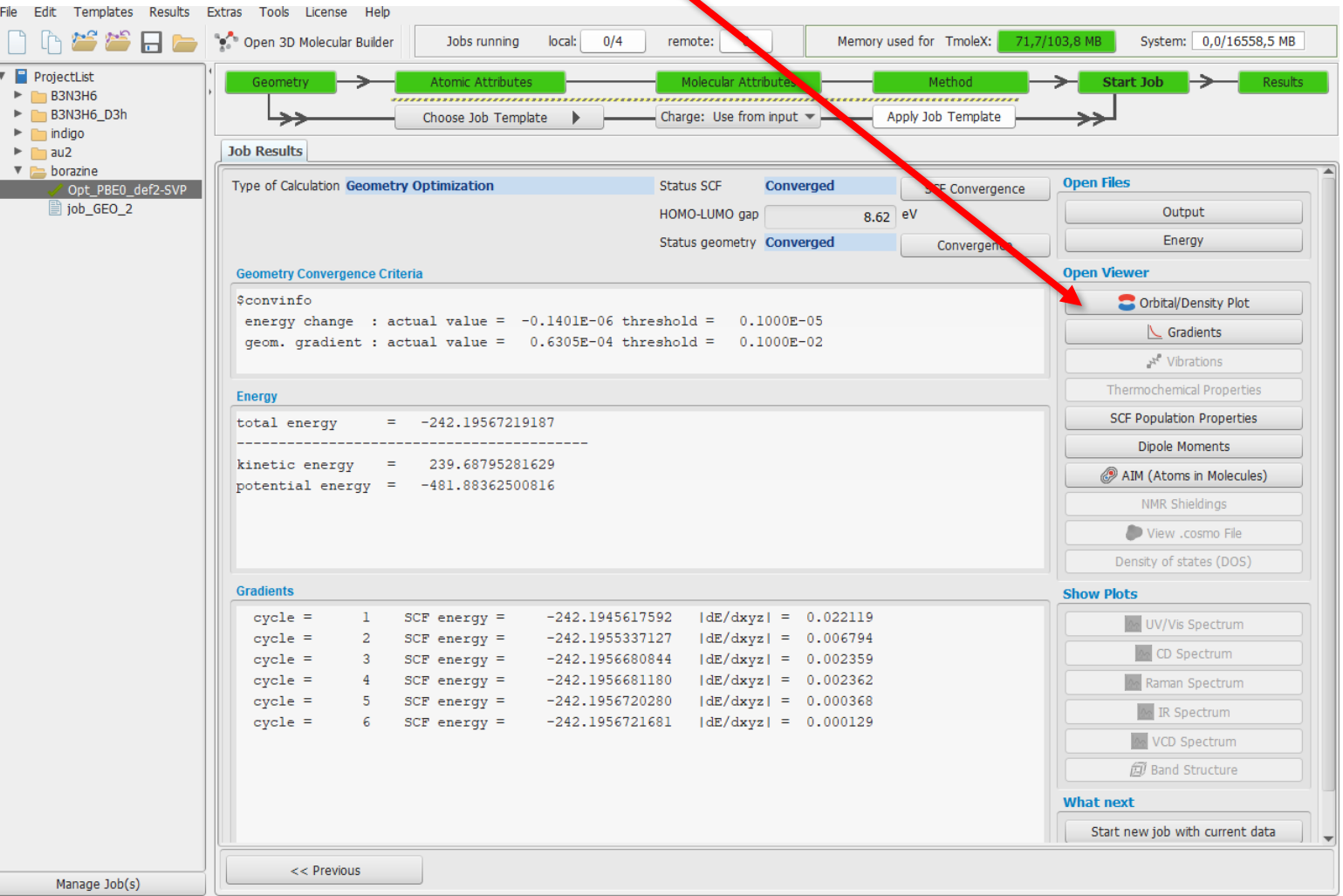
Geometry optimization (7)

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*.



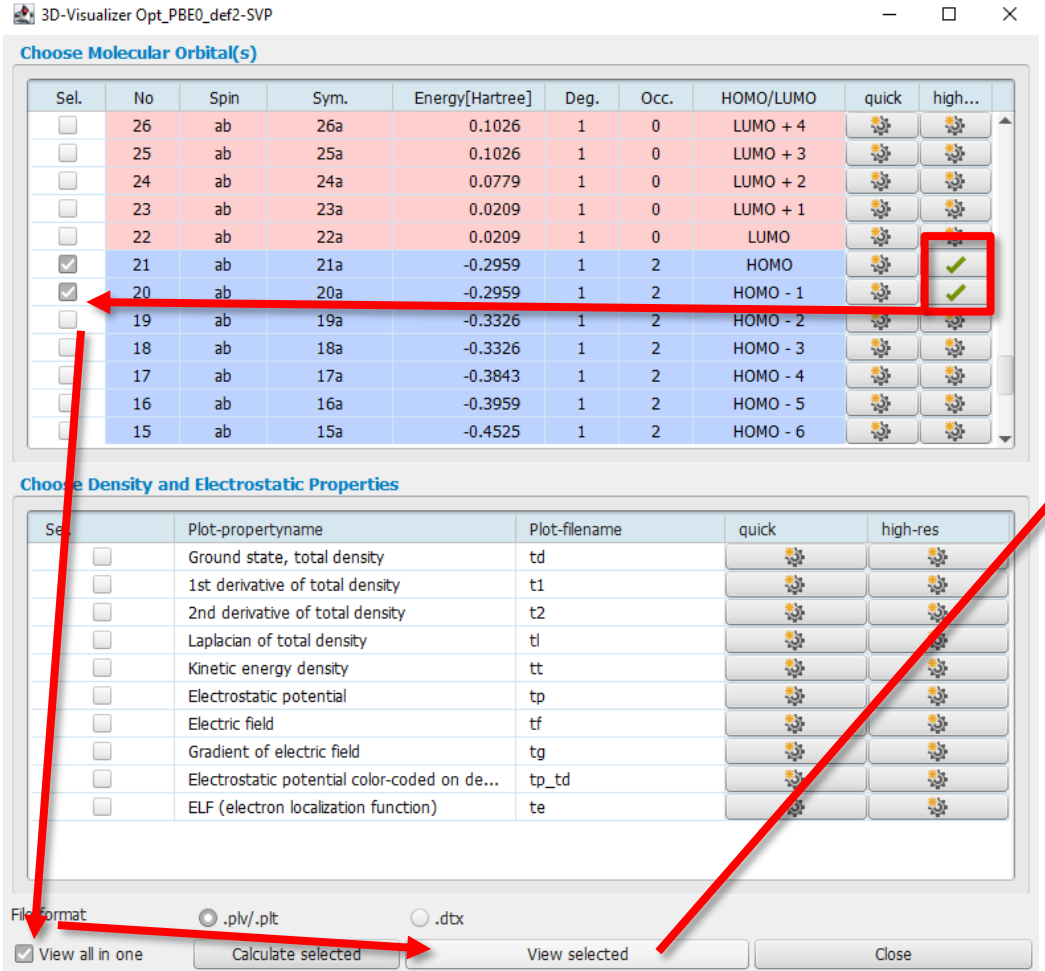
Geometry optimization (8)

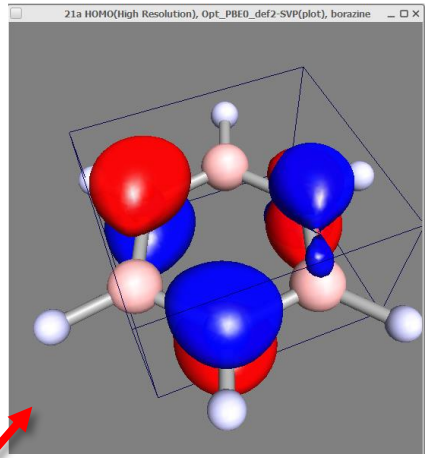
The optimization job will finish quickly (here it took six steps, that is, six energy + gradient evaluations). You can see how the geometry changed from **Gradients**. Next, proceed to Orbital/Density Plot



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.

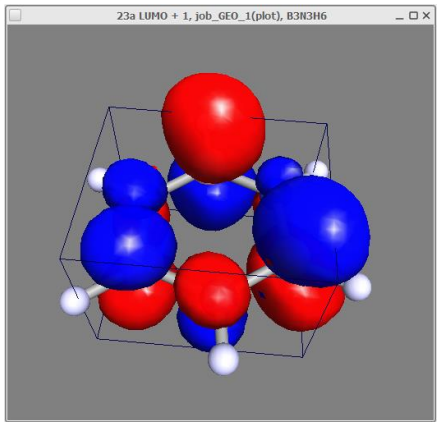




HOMO and HOMO-1.

Isosurface +/-

Isovalue 0.08 a.u.



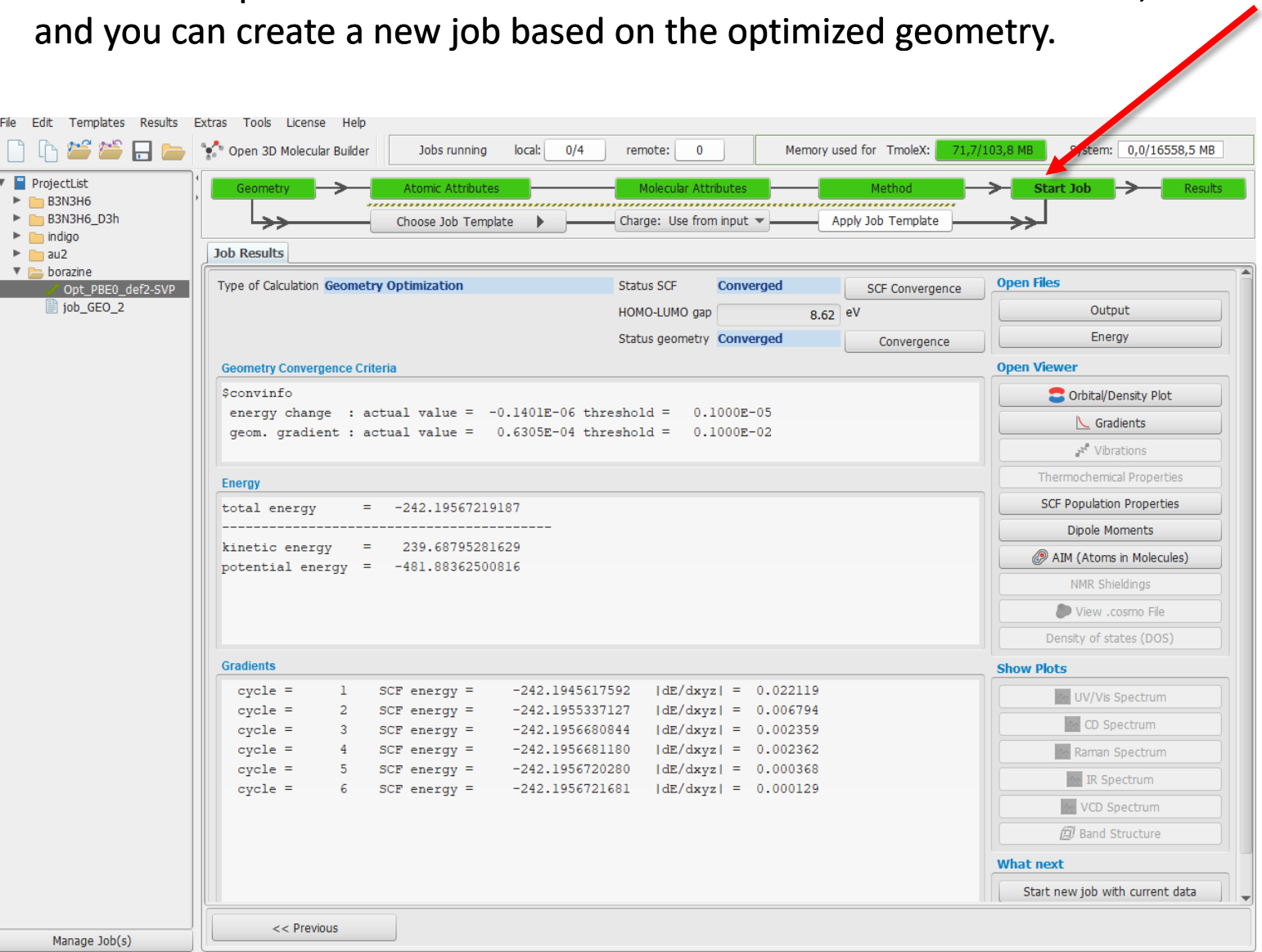
LUMO and LUMO-1.

Isosurface +/-

Isovalue 0.08 a.u.

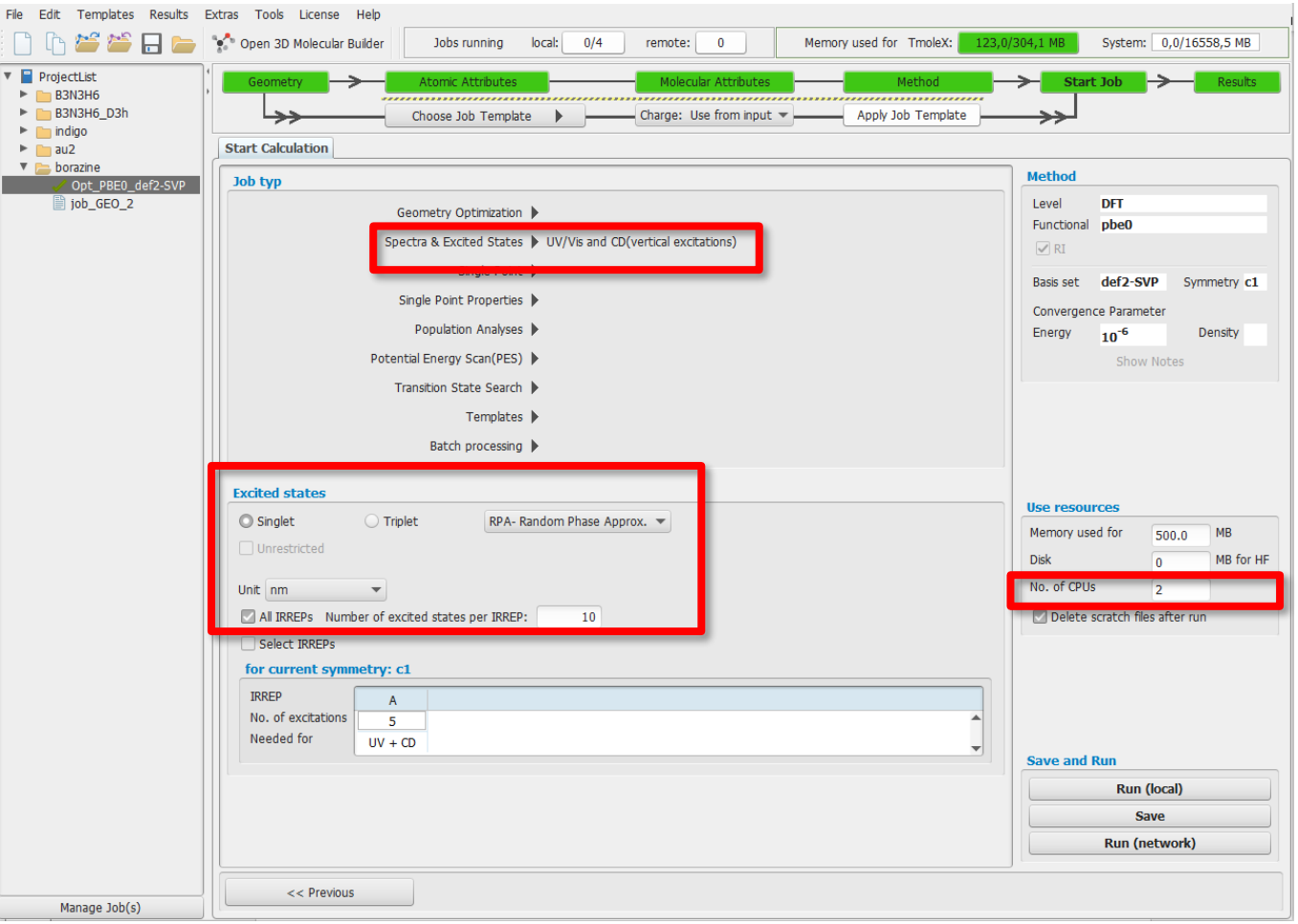
Excited states (1)

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.



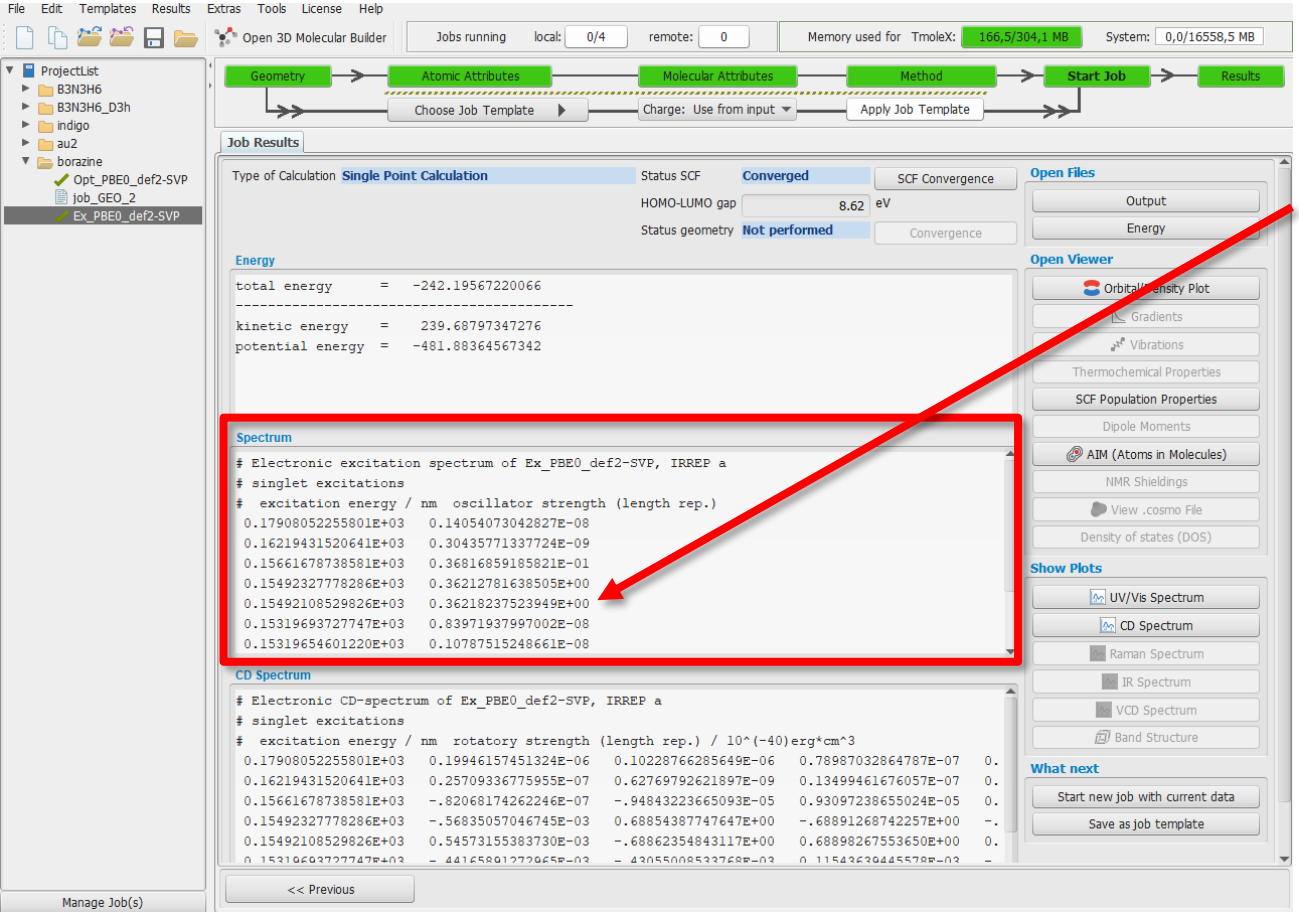
Excited states (2)

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.



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)



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.|^2*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!

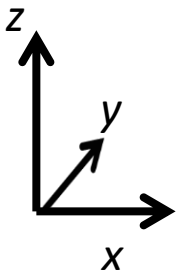
The role of molecular symmetry

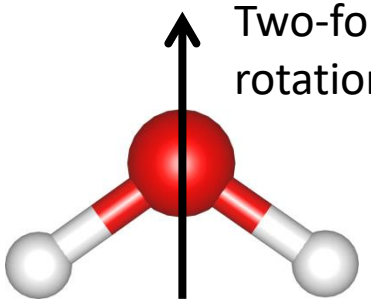
- Molecular symmetry plays a key role in molecular spectroscopies.
- If the molecule has some symmetry, its excited state properties can often be understood better when the symmetry is taken into account.
- Let's study the excited states of borazine again, but this time taking symmetry into account.
- 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	σ
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

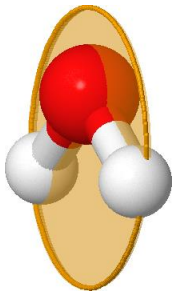




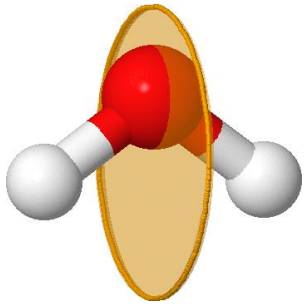
Two-fold proper rotation axis C_2

H_2O (point group C_{2v})

Mirror plane σ_{yz}



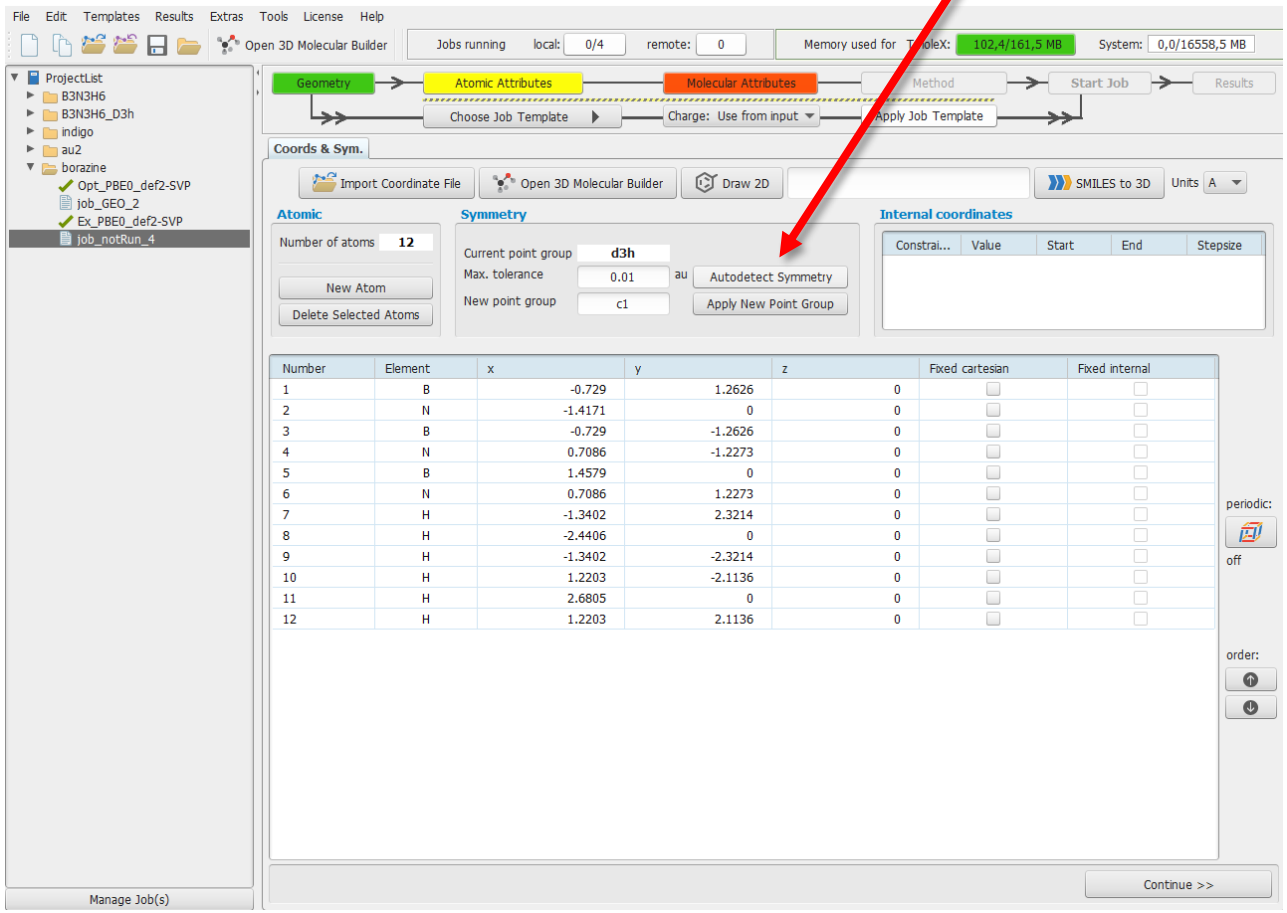
Mirror plane σ_{xz}



Figures: AJK

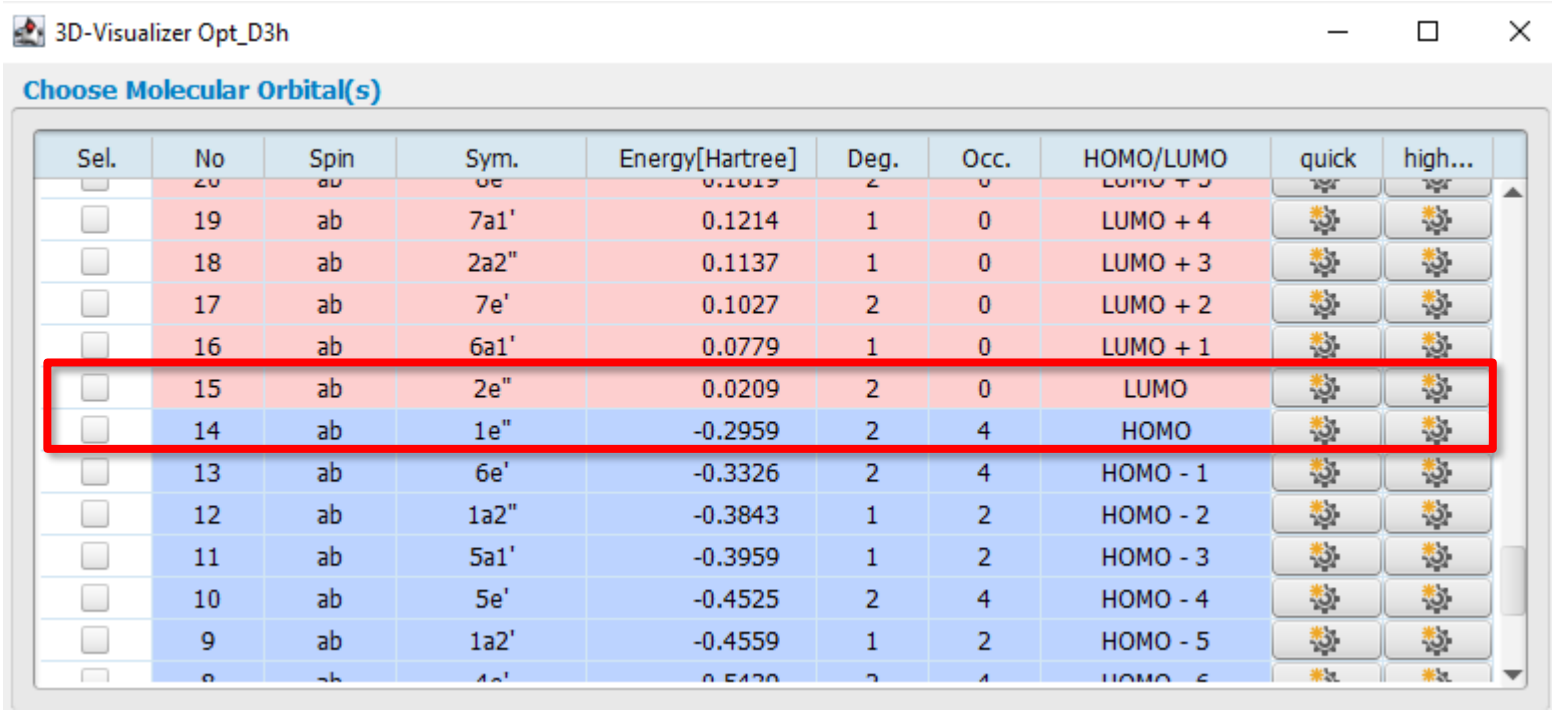
Applying point group symmetry

- 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



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)

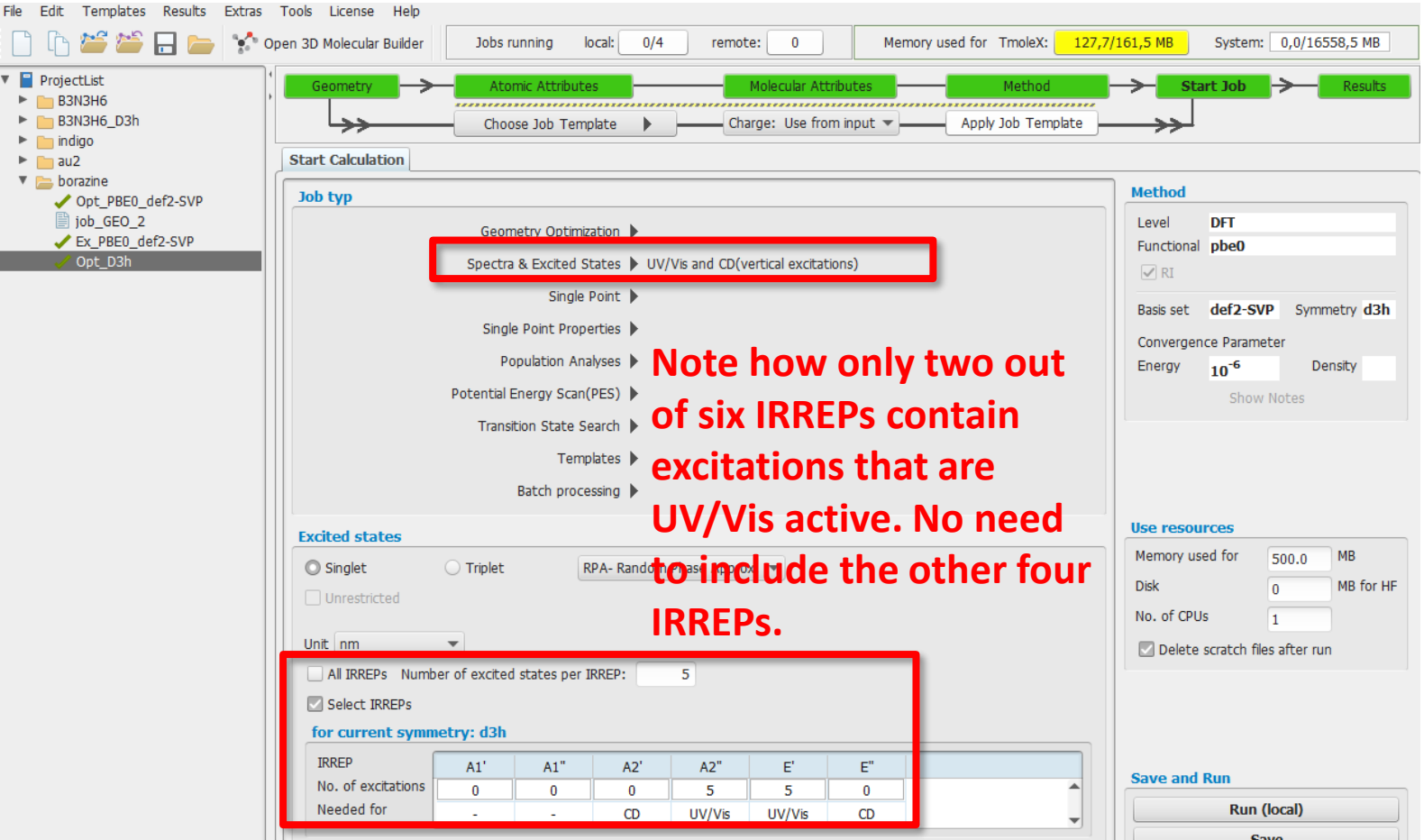


Sel.	No	Spin	Sym.	Energy[Hartree]	Deg.	Occ.	HOMO/LUMO	quick	high...
	19	ab	7a1'	0.1214	1	0	LUMO + 4		
	18	ab	2a2"	0.1137	1	0	LUMO + 3		
	17	ab	7e'	0.1027	2	0	LUMO + 2		
	16	ab	6a1'	0.0779	1	0	LUMO + 1		
	15	ab	2e"	0.0209	2	0	LUMO		
	14	ab	1e"	-0.2959	2	4	HOMO		
	13	ab	6e'	-0.3326	2	4	HOMO - 1		
	12	ab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

Excited states with symmetry (1)

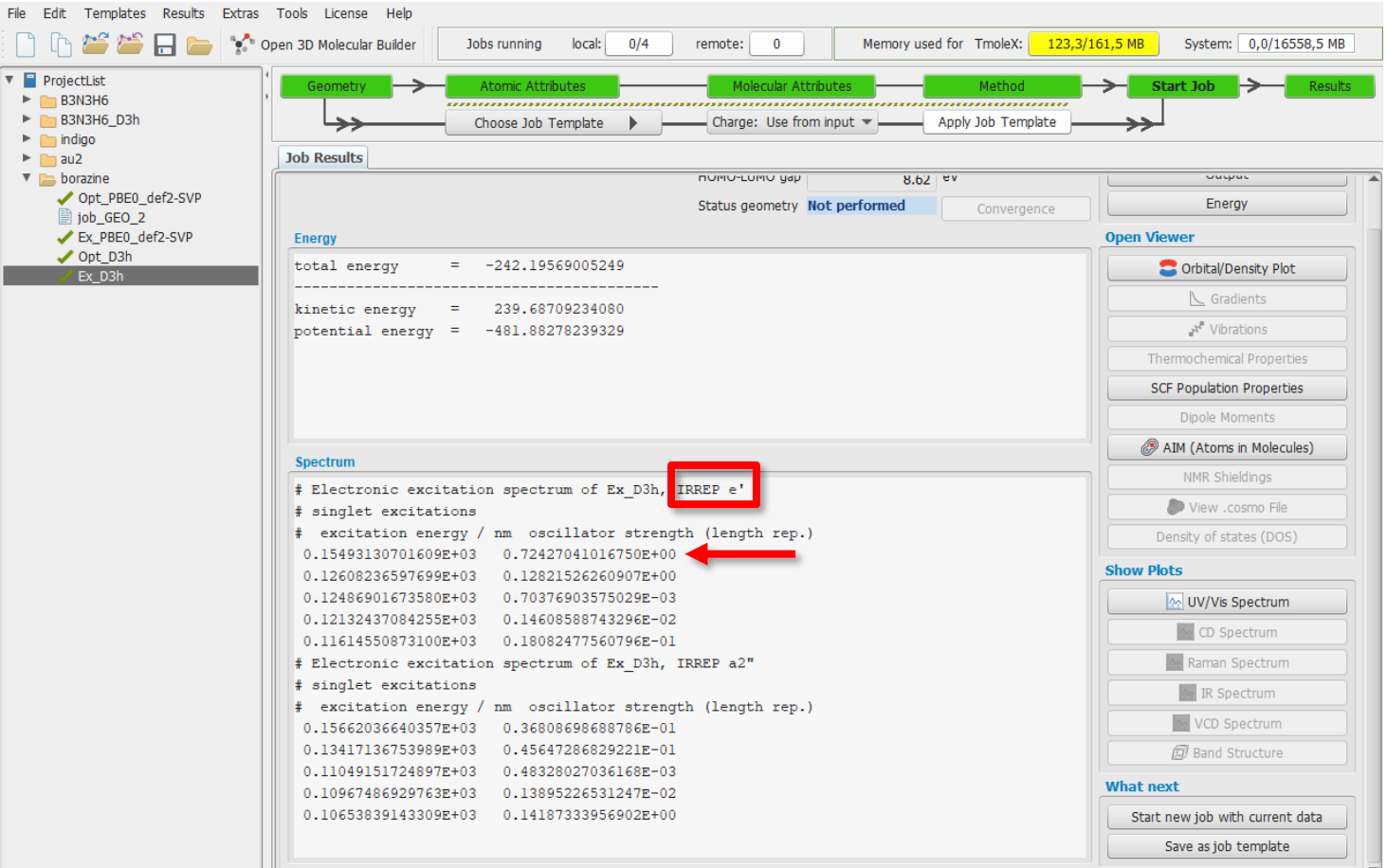
Now we can proceed to excited state calculation. In the **Results** menu, click **Start Job** to create a new job based on the optimized geometry.

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.



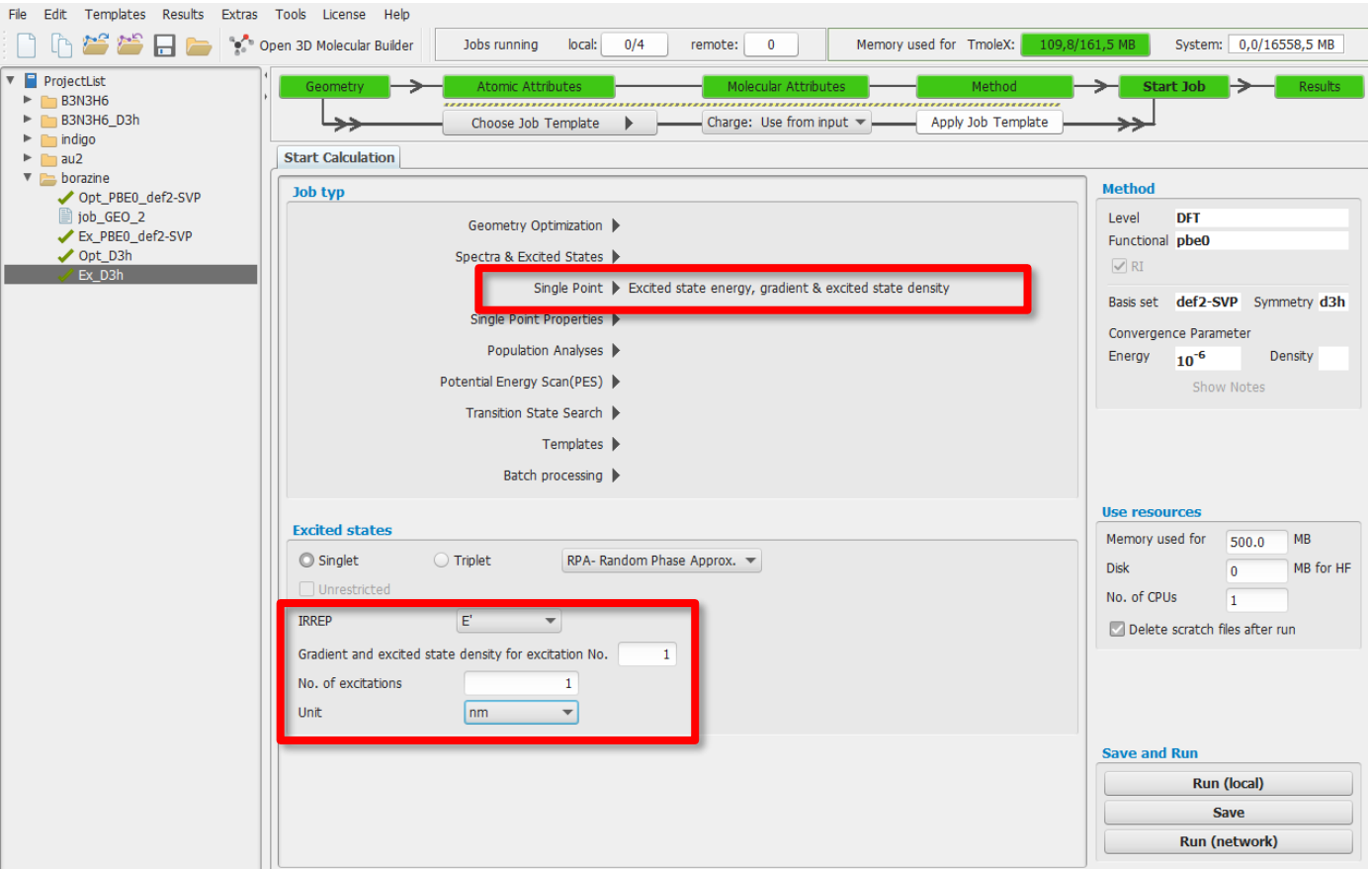
Excited states with symmetry (2)

- 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**.



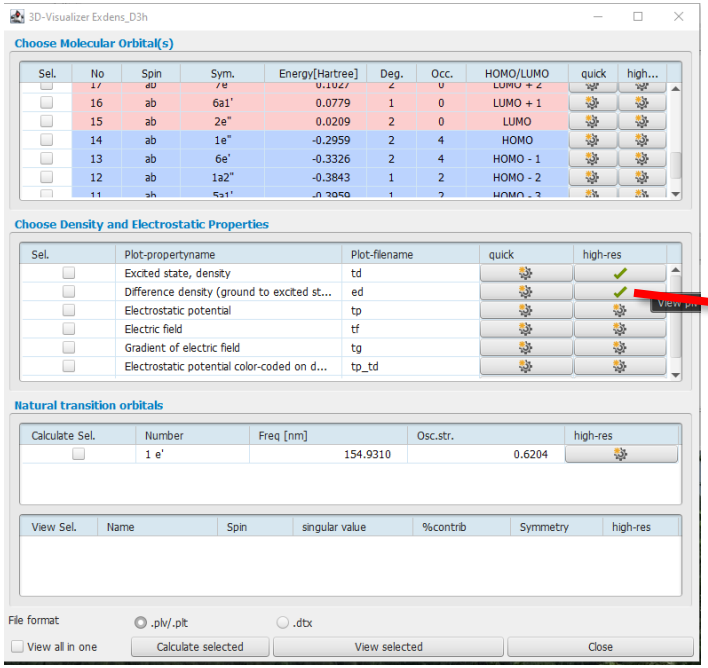
Excited state difference density (1)

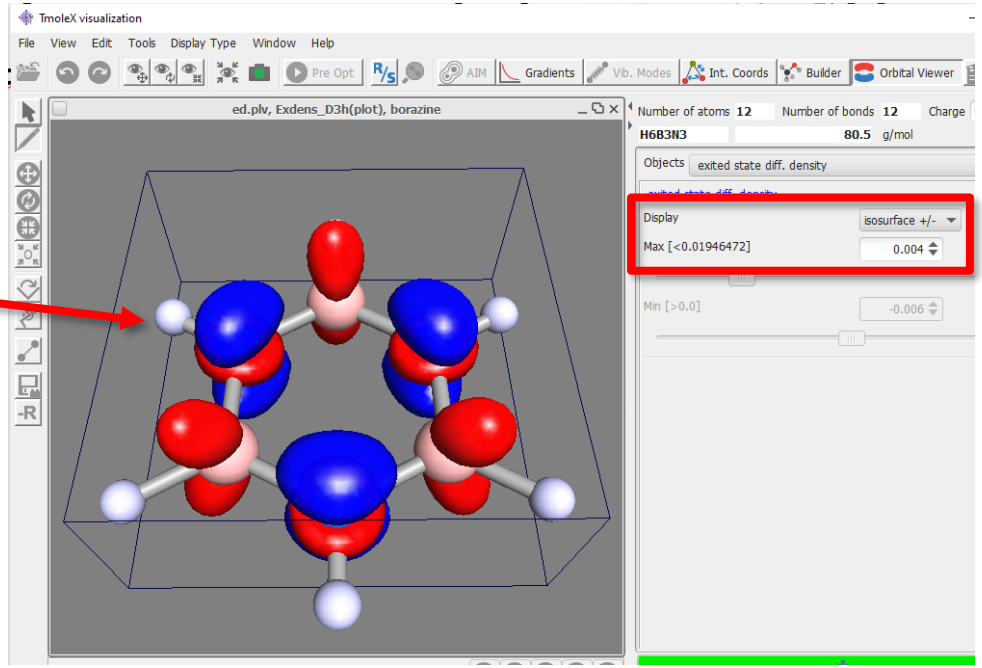
Choose **Excited state energy, gradient & excited state density** as the job type.
Pay attention on the settings in the **Excited states** block: we will only calculate the electron density for one state: the state with the largest osc. strength (IRREP e', state 1).
Run the calculation. TmoleX will first calculate the total electron density of the ground state and then total electron density of the excited state.



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^{-}/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.





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.

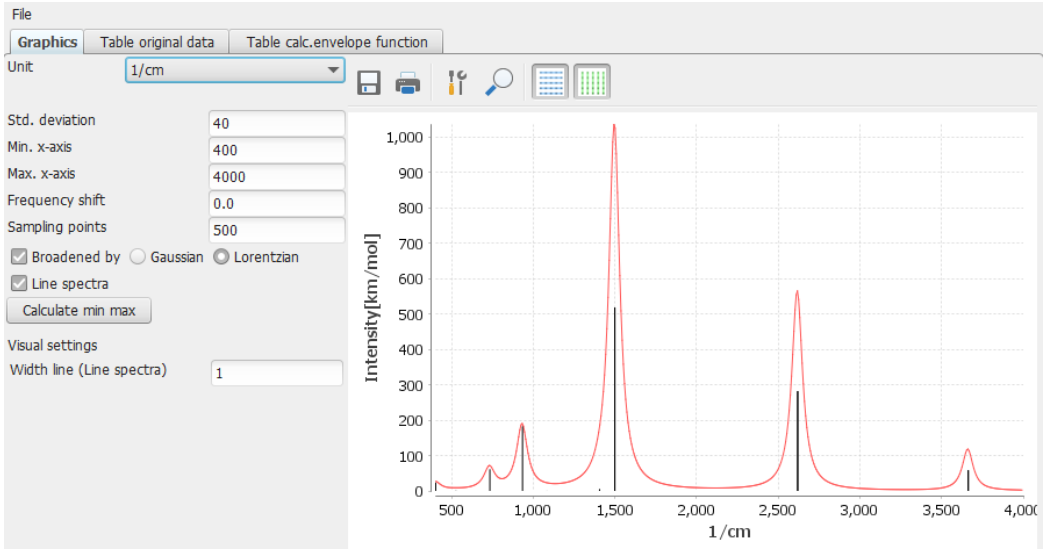
- Start a new project from File -> New Project.
- Build the borazine molecule. Use point group symmetry.
- This time, choose the larger def2-TZVP basis set for all atoms. Use PBE0 method (and gridsize m4).
- Optimize the geometry.
- Run a UV/Vis calculation. Does the result improve in comparison to the 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 boratzine, based on DFT-PBE0/def2-TZVP harmonic frequencies.

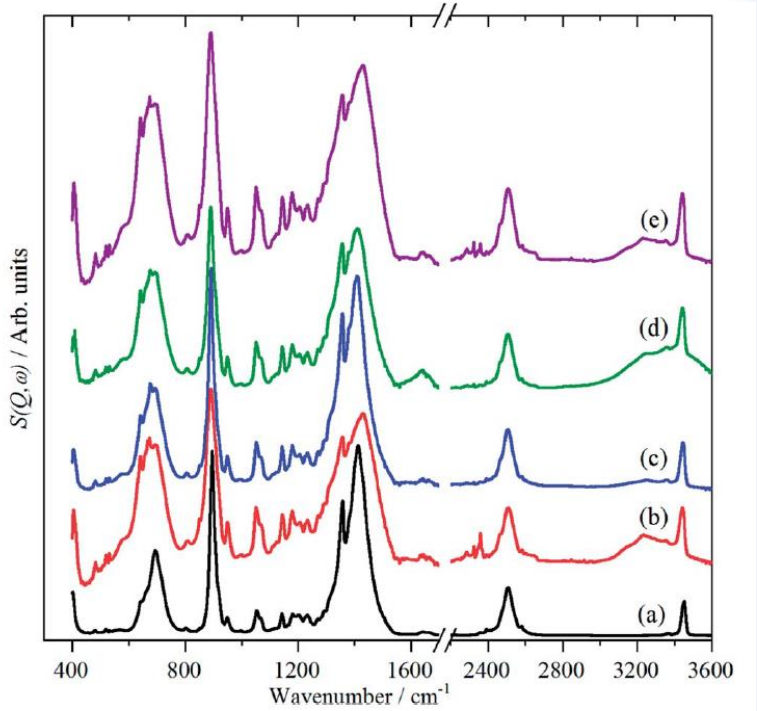


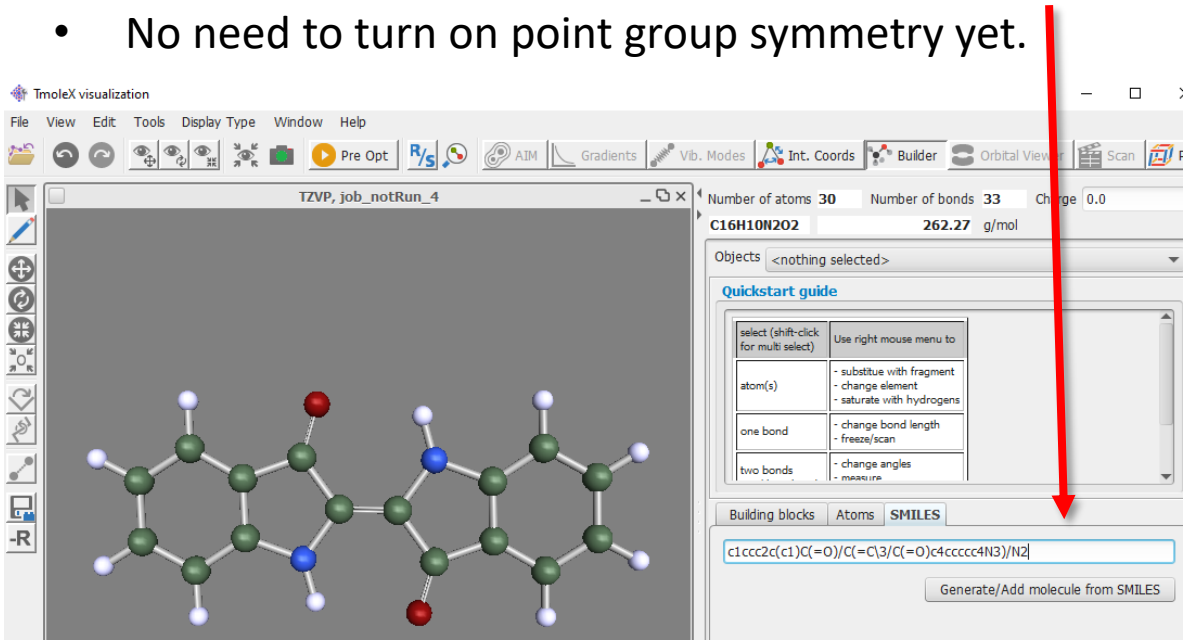
Fig. 3 Vibrational temperature infrared spectra of borazine. (a) liquid at 298 K, solid at: (b) 258 K, (c) 213 K, (d) 160 K and (e) 105 K. The broad features at 1650 and 3300 cm^{-1} are due to ice.

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

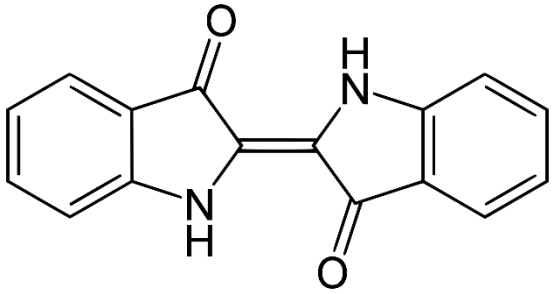
Tutorial 2

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)c4ccccc4N3)/N2
- Use the SMILES string to generate the structure.
- No need to turn on point group symmetry yet.



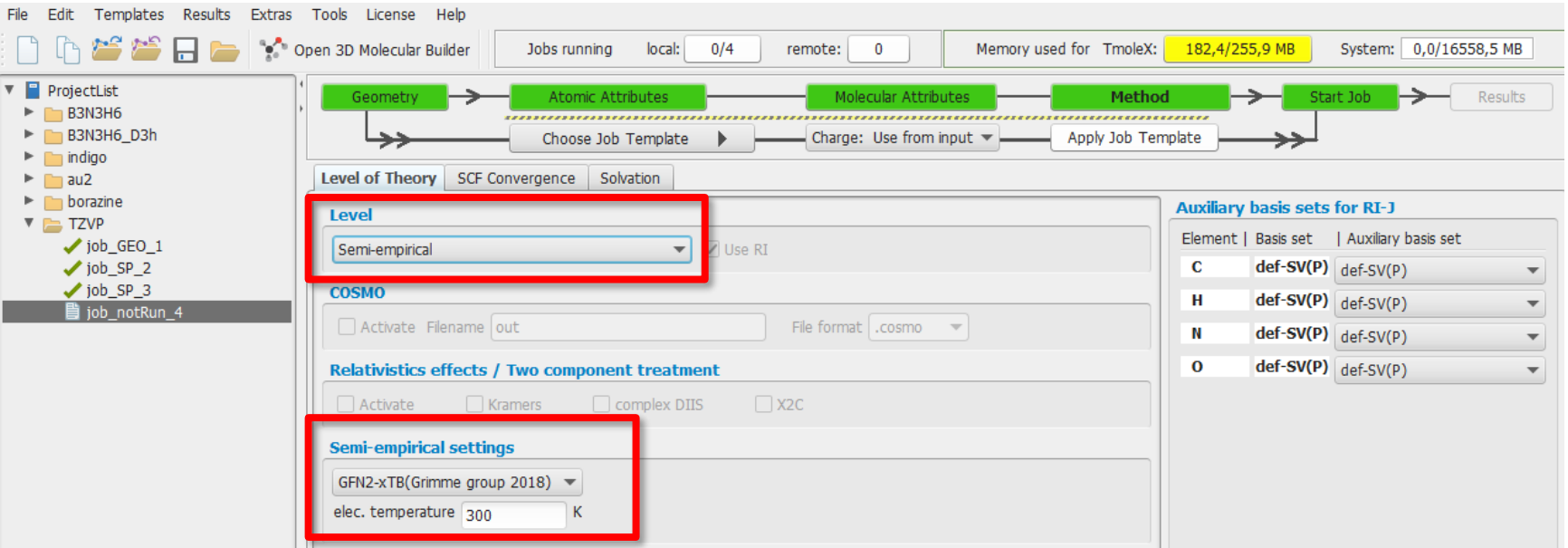
Extract of Indigo plant applied to paper. Figure from Wikimedia Commons. License: Public Domain.



Molecular structure of indigo dye. Figure from Wikimedia Commons. License: Public Domain.

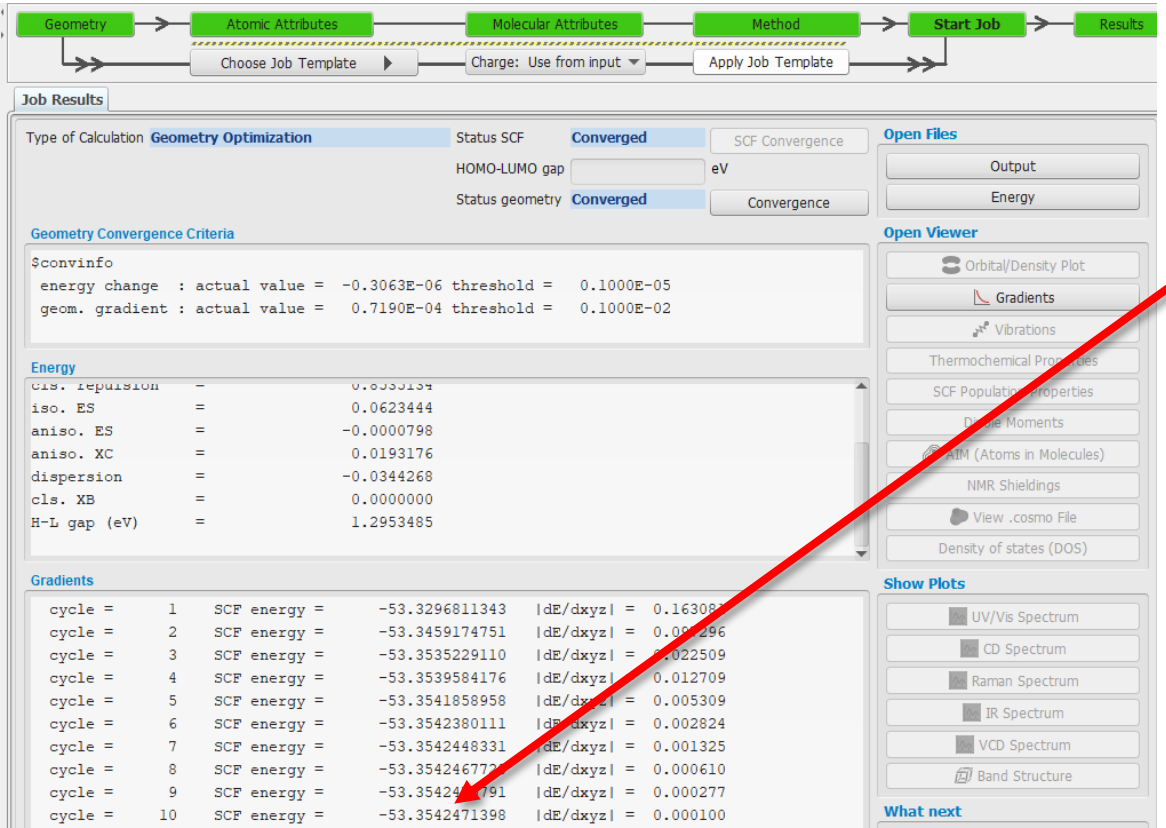
Pre-optimization with GFN2-xTB (1)

- 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).



Pre-optimization with GFN2-xTB (2)

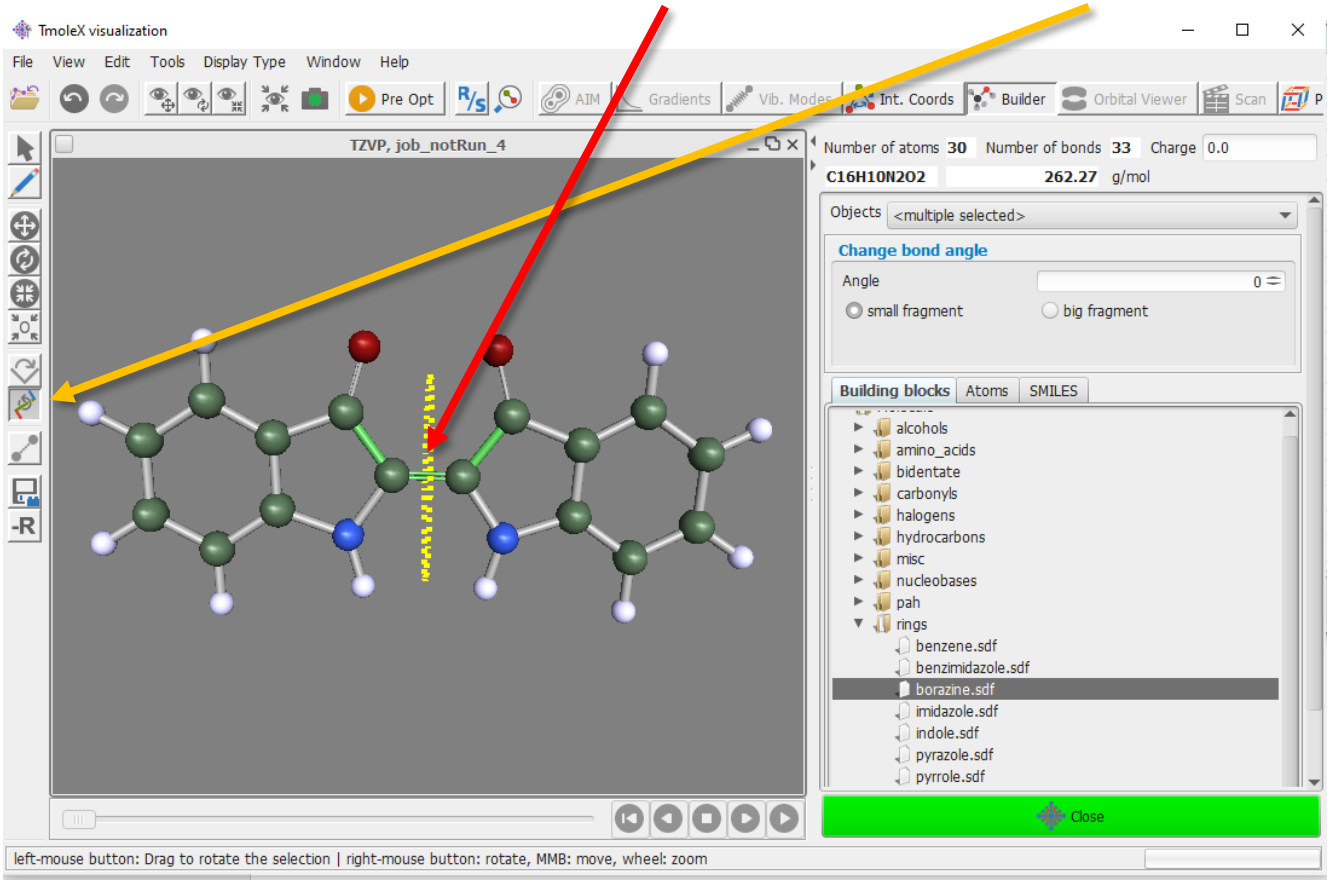
- It would be faster to run the pre-optimization on the local computer, but the demo version does not allow it.
- Run the pre-optimization remotely on Puhti.
  - Instructions on the last two slides.
- The job will finish in less than 10 seconds, but TmoleX waits a minute before retrieving the results.



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°

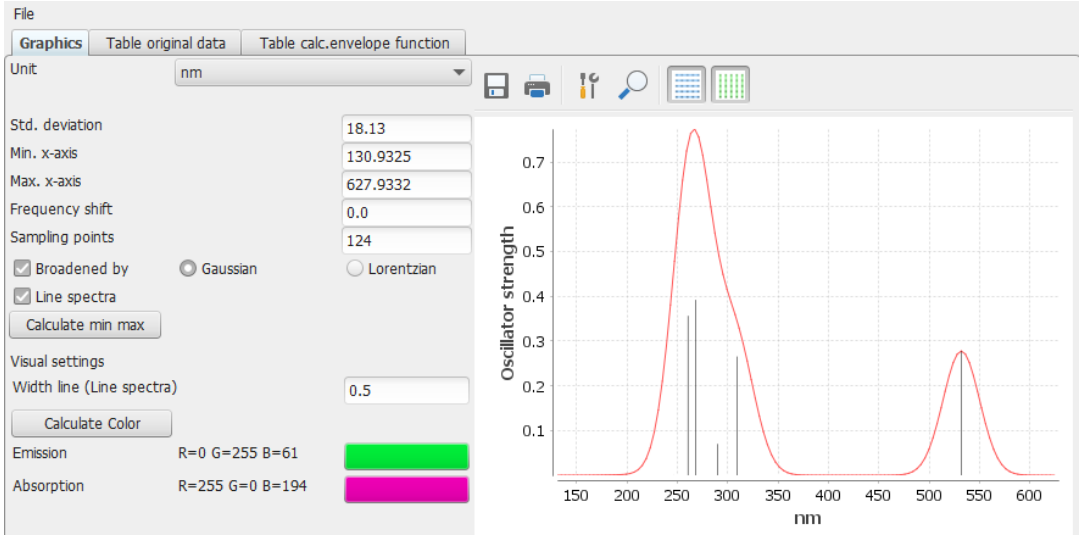


Energy comparison of the isomers

- 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!

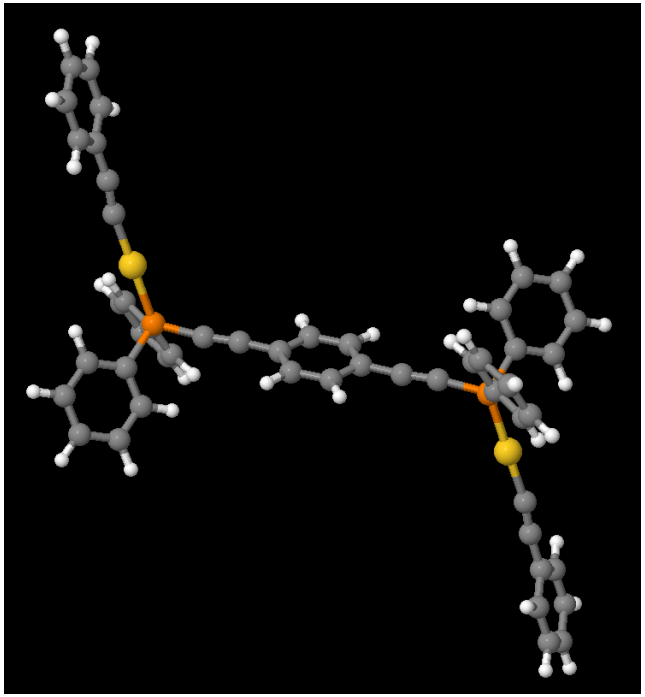
- What else did you learn?

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 PPh_2-C_2-$(C_6H_4)_n$-C_2-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 -> S_1 and S_0 -> 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)

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

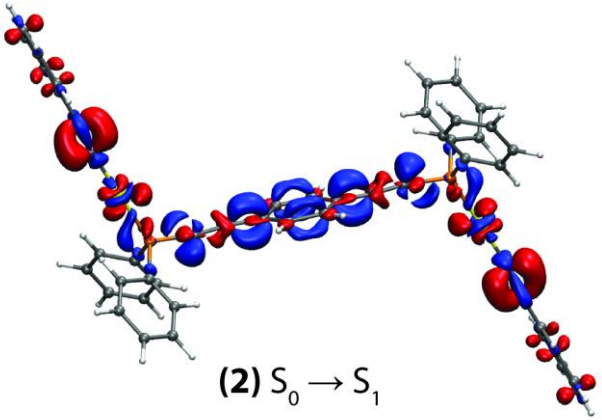
[a] Wavelengths in nm, oscillator strengths given in parentheses.

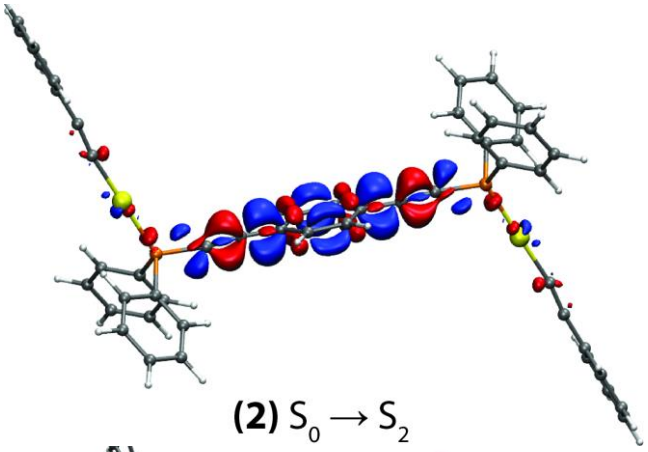
Tutorial 3 with CAM-B3LYP

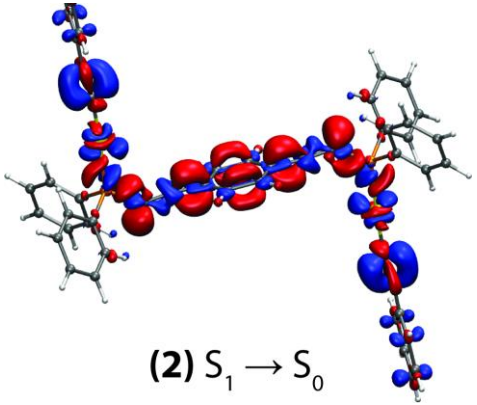
- Repeat the UV/Vis spectrum calculation with long-range corrected CAM-B3LYP functional (you can use PBE0 geometry).
- Long-range corrected functionals can manage better charge-transfer (CT) excitations, which are challenging for TD-DFT.
- CT excitations are delocalized over large distances. Such excitations 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.

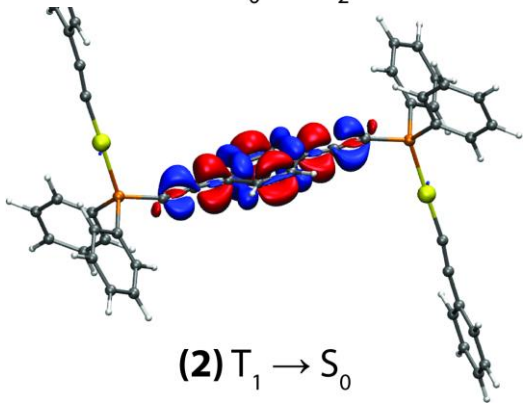
Excited state difference densities at CC2/TZVP level of theory

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 -> S_1 excitation (localized / delocalized).





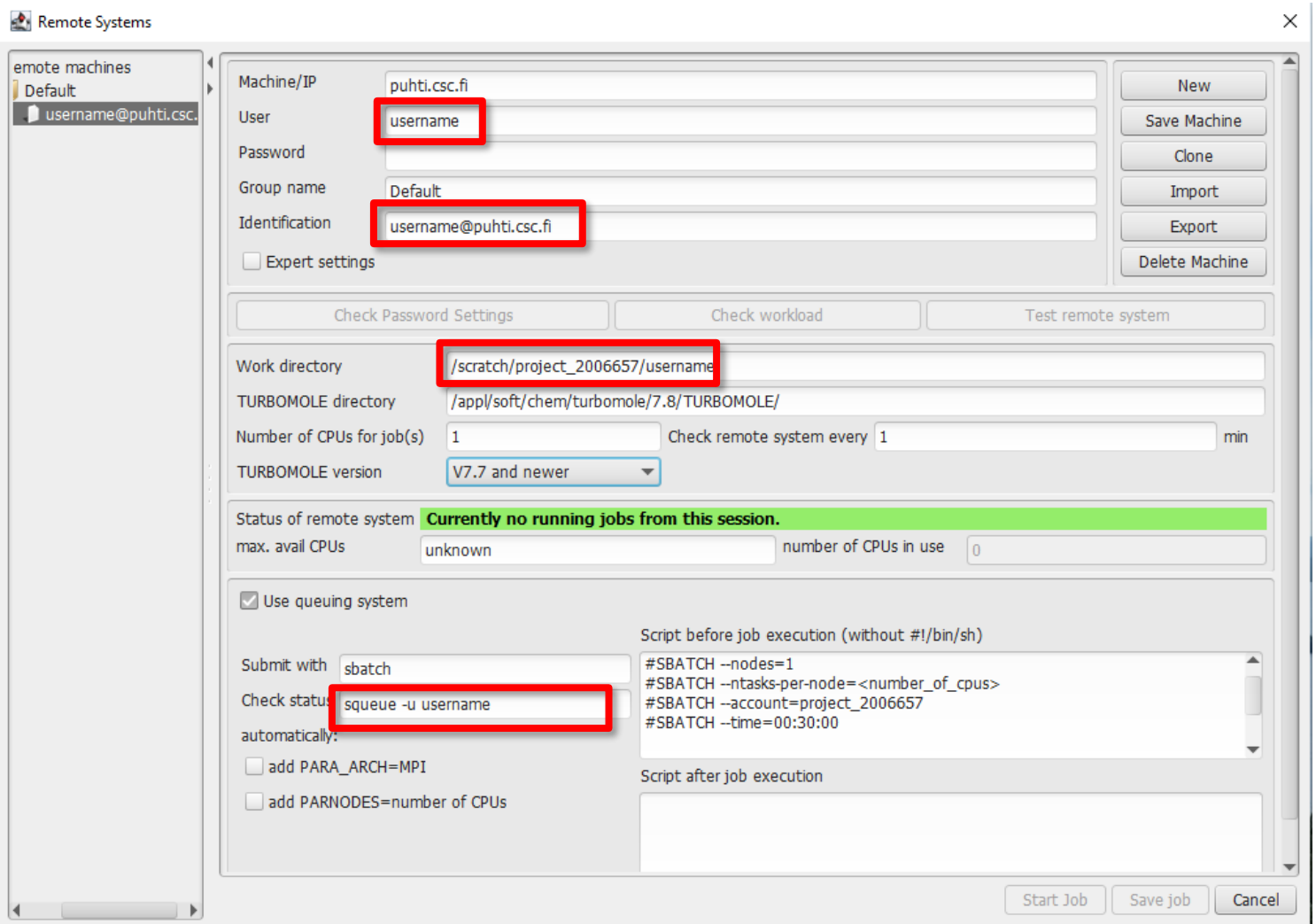




Settings for running jobs remotely on Puhti

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*.



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
```