Orbital analysis of oxo and peroxo dicopper complexes via quantum chemical workflows in MoSGrid

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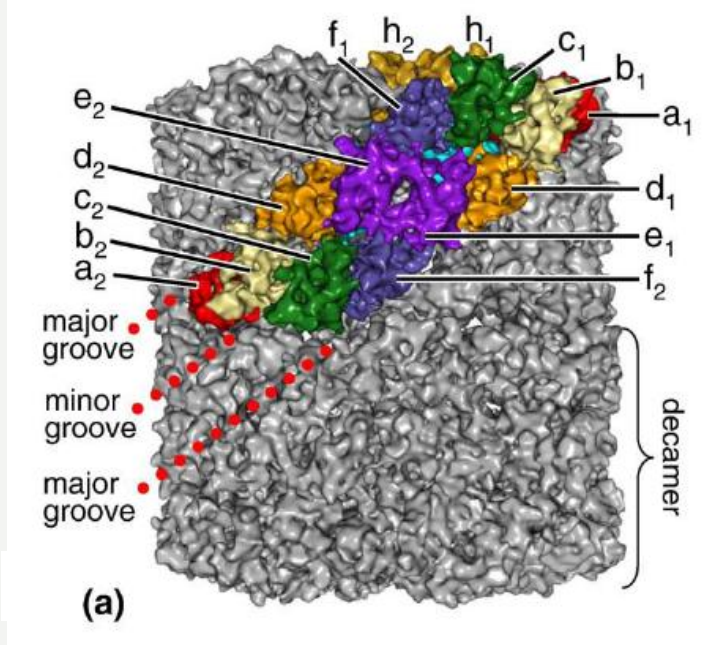
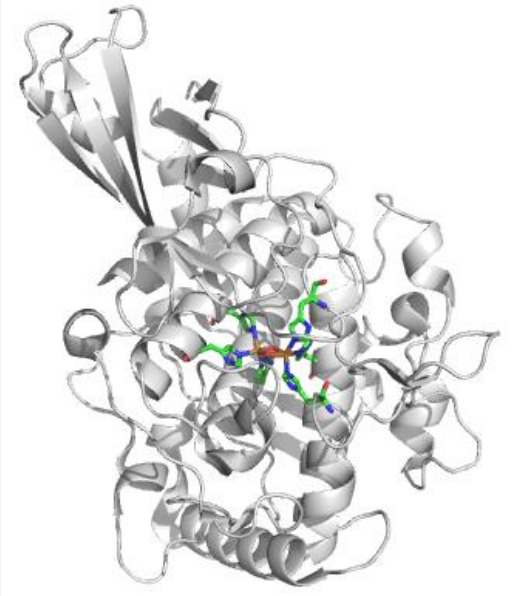
Copper protein: Hemocyanin

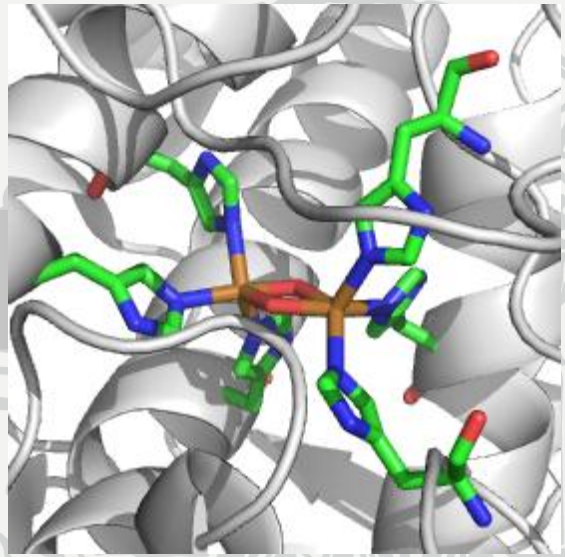
- Oxygen transport protein in arthropods and molluscs




- Oligomers of Decamers



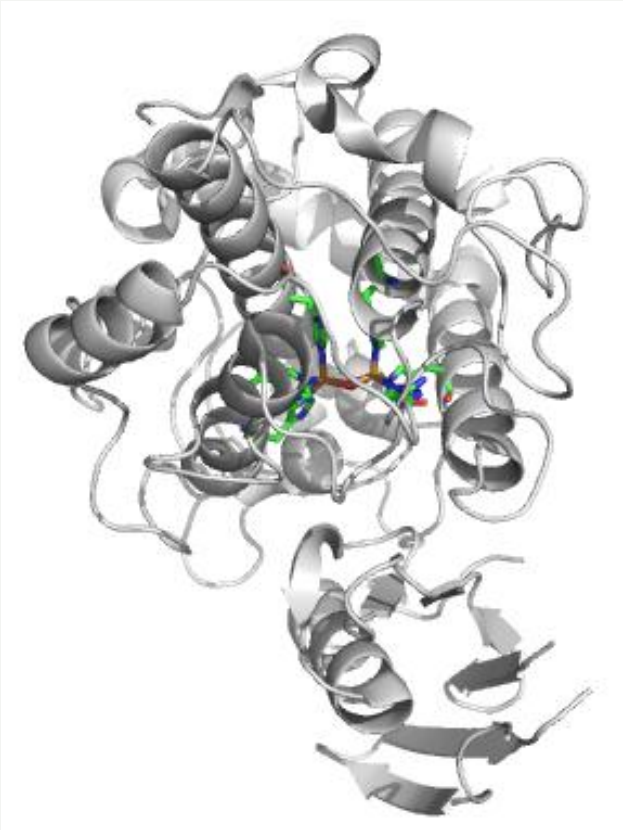


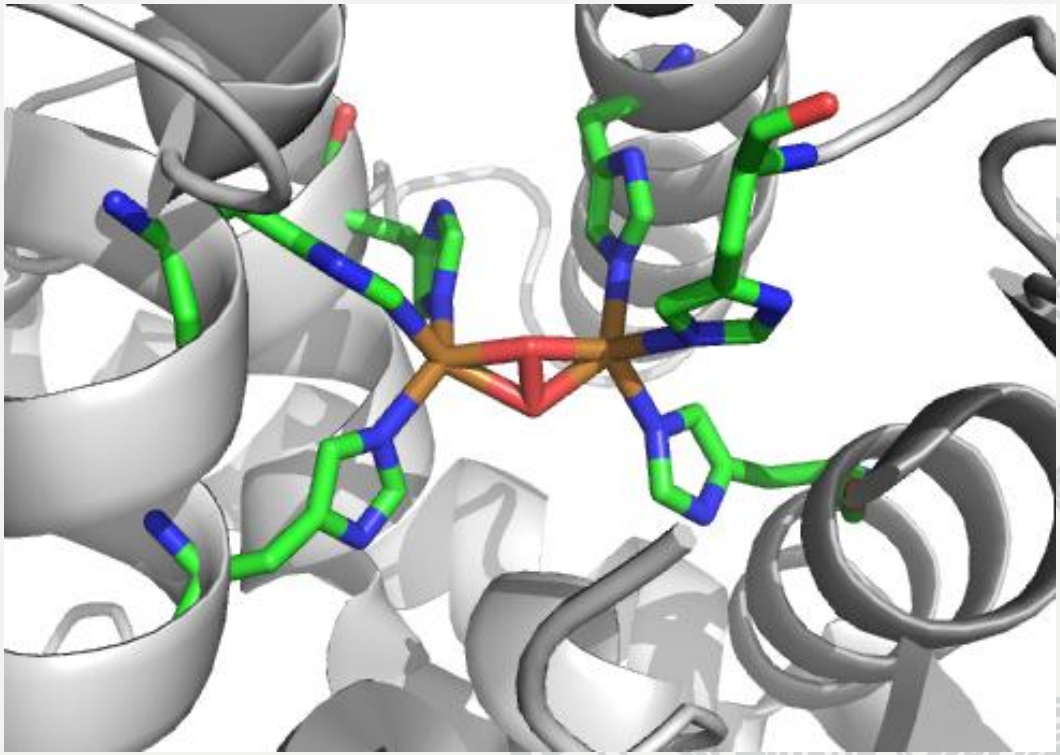


C. Gatsogiannis, J. Markl, *J. Mol. Biol.* **2009**, *385*, 963; K.E. van Holde et al., *J. Mol. Biol.* **1998**, *278*, 855.

Copper protein: Tyrosinase

- Oxidation of phenoles to quinones
- Involved in pigment accumulation (melanin) in skin, hair, feathers and in browning process of fruits.

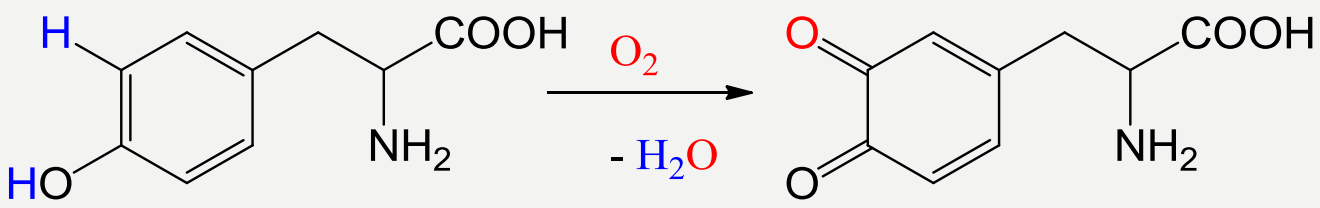




Y. Matoba et al., *J. Biol. Chem.* **2006**, *281*, 8981.

Function of Tyrosinase

- Function of Tyrosinase: Oxidation of phenoles to quinones (→ melanin biosynthesis)



tyrosine dopaquinone

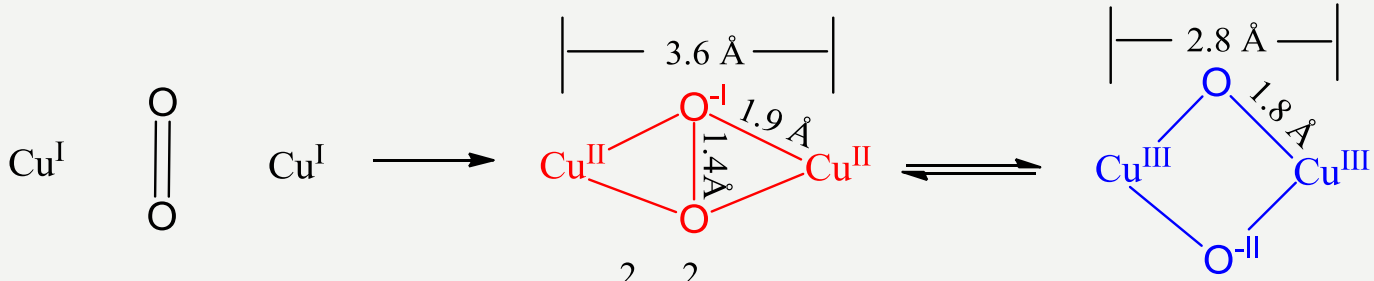
Goal:

For the development of green oxidation catalysts, the biological principle must be transferred to industrial needs!

„Learning from nature“

Oxygen activation by copper complexes

- Which Cu_2O_2 core hydroxylates in tyrosinase the tyrosine?



μ-η²-η²- peroxo
P core

Bis-μ-oxo
O core

UV/Vis-bands: 350 nm and 550 nm 300 nm and 400 nm

- In oxygen activating and transferring copper proteins only the μ-η²:η²-peroxo-dicopper(II) form was found.
- For a deeper understanding more orbital analyses are needed!
  → major challenge in computational chemistry

L.M. Mirica, X. Ottenwaelder, T.D.P. Stack, *Chem Rev.* **2004**, *104*, 1013

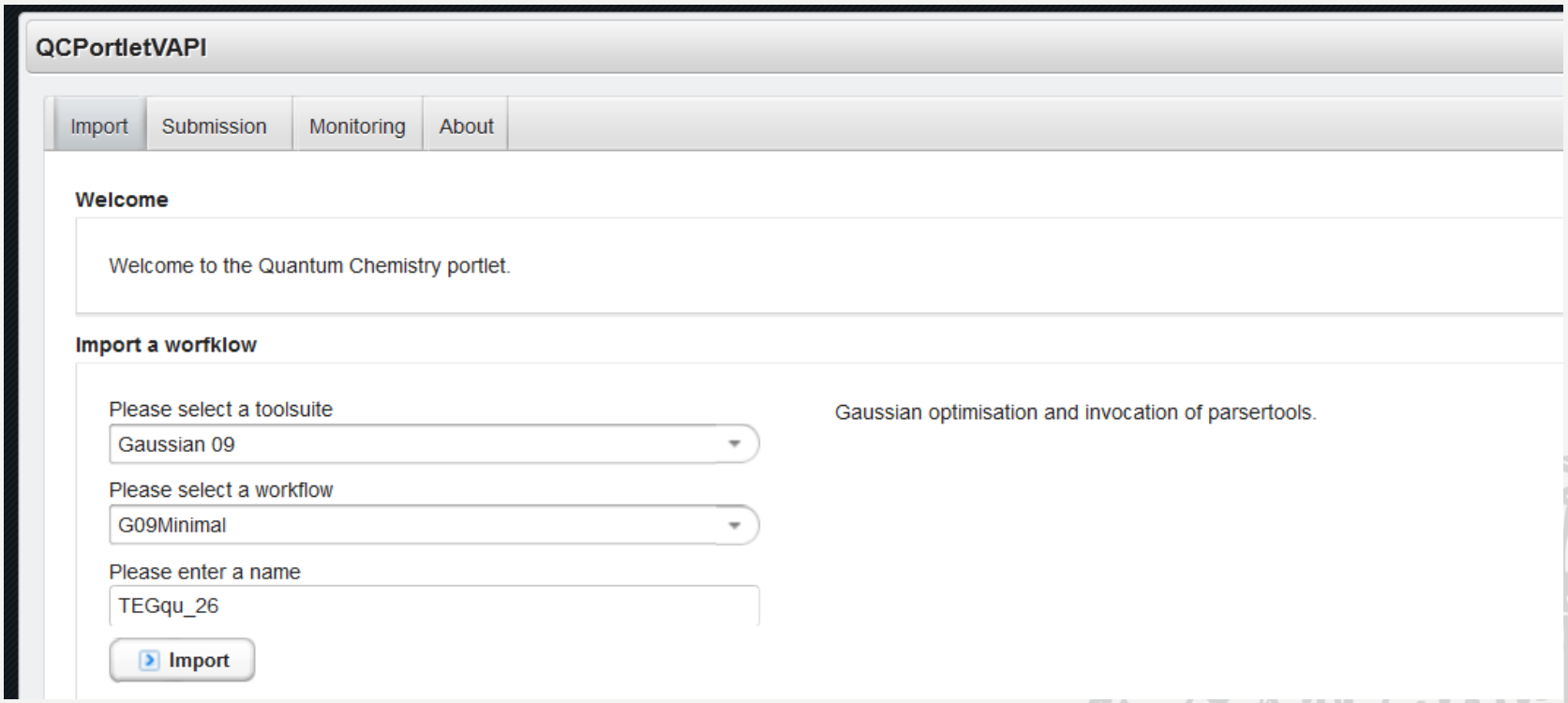
Job definition and analysis: time consuming process

Solution: user-friendly portal like MoSGrid

A chemist with a quantum chemical problem and ONE job definition

A chemist with a complex quantum chemical problem and HUNDREDS of job definitions

The QC Portlet @ MoSGrid.de



- Specialised interface for quantum chemistry software (Gaussian, Turbomole)
- Basic Gaussian workflows
- Easy Generation or Uploading of Input Files

Orbital Analysis Workflow

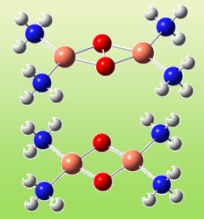
User Data

Portal

Grid Resource

„Simulation Recipes“:
Optimisation
Basis set
Functional

Oxo and peroxo complexes



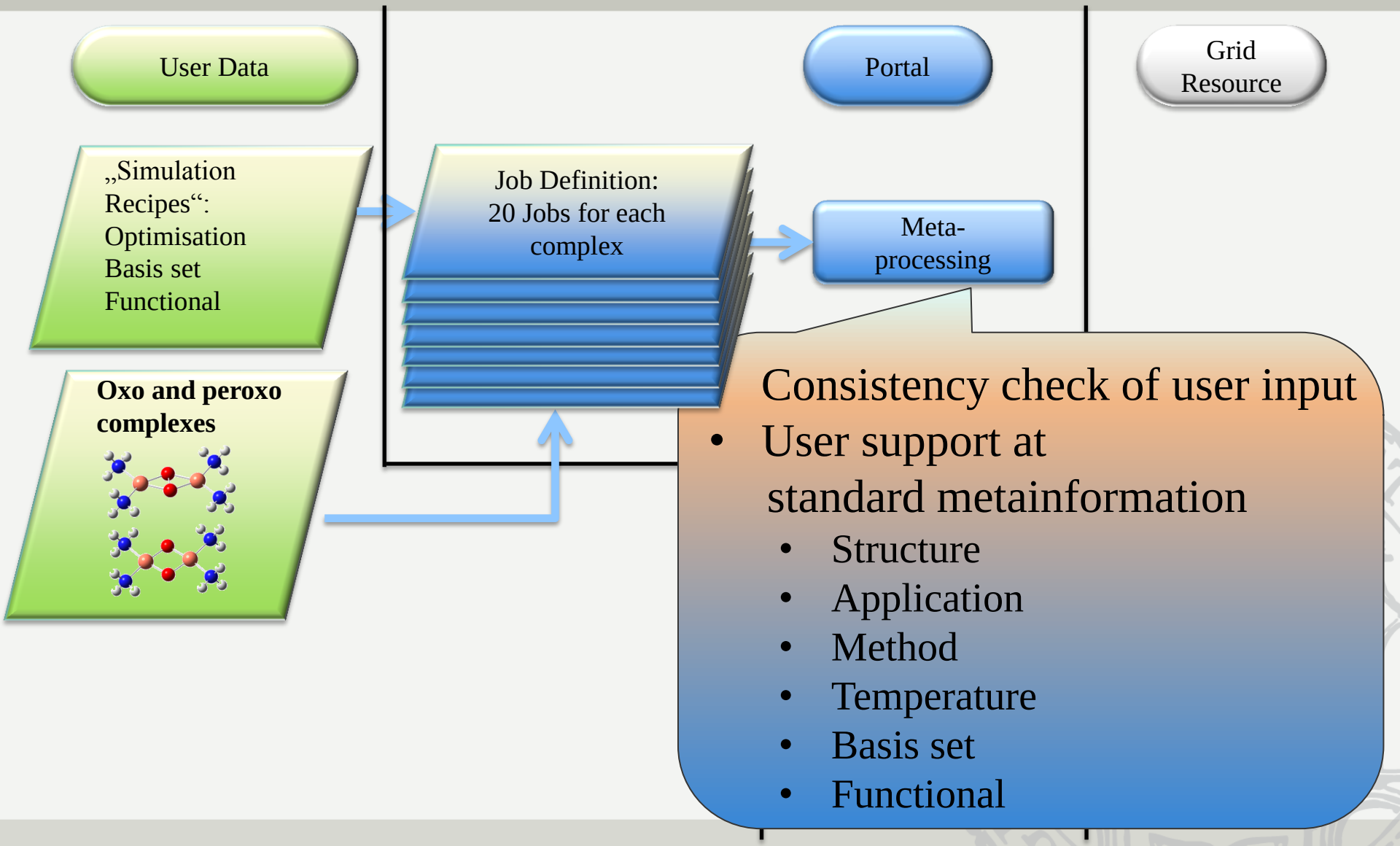
Job Definition:
20 Jobs for each complex

Molecular Structure
- Upload
- Data Repositories

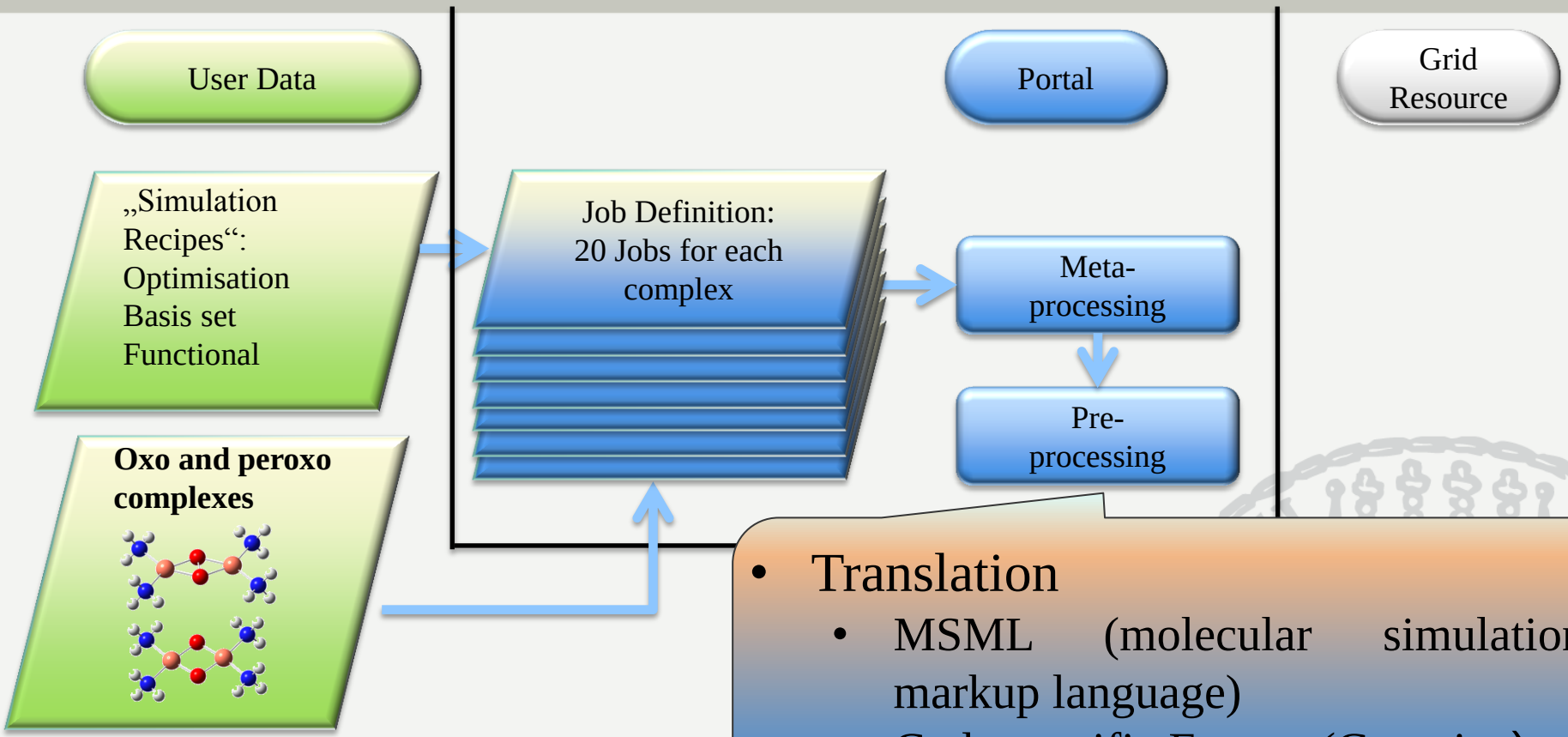
Workflow
- Generation
- Use of Recipes

The orbital analysis can be mapped to a multi-step workflow which consists of the following tasks.

Orbital Analysis Workflow

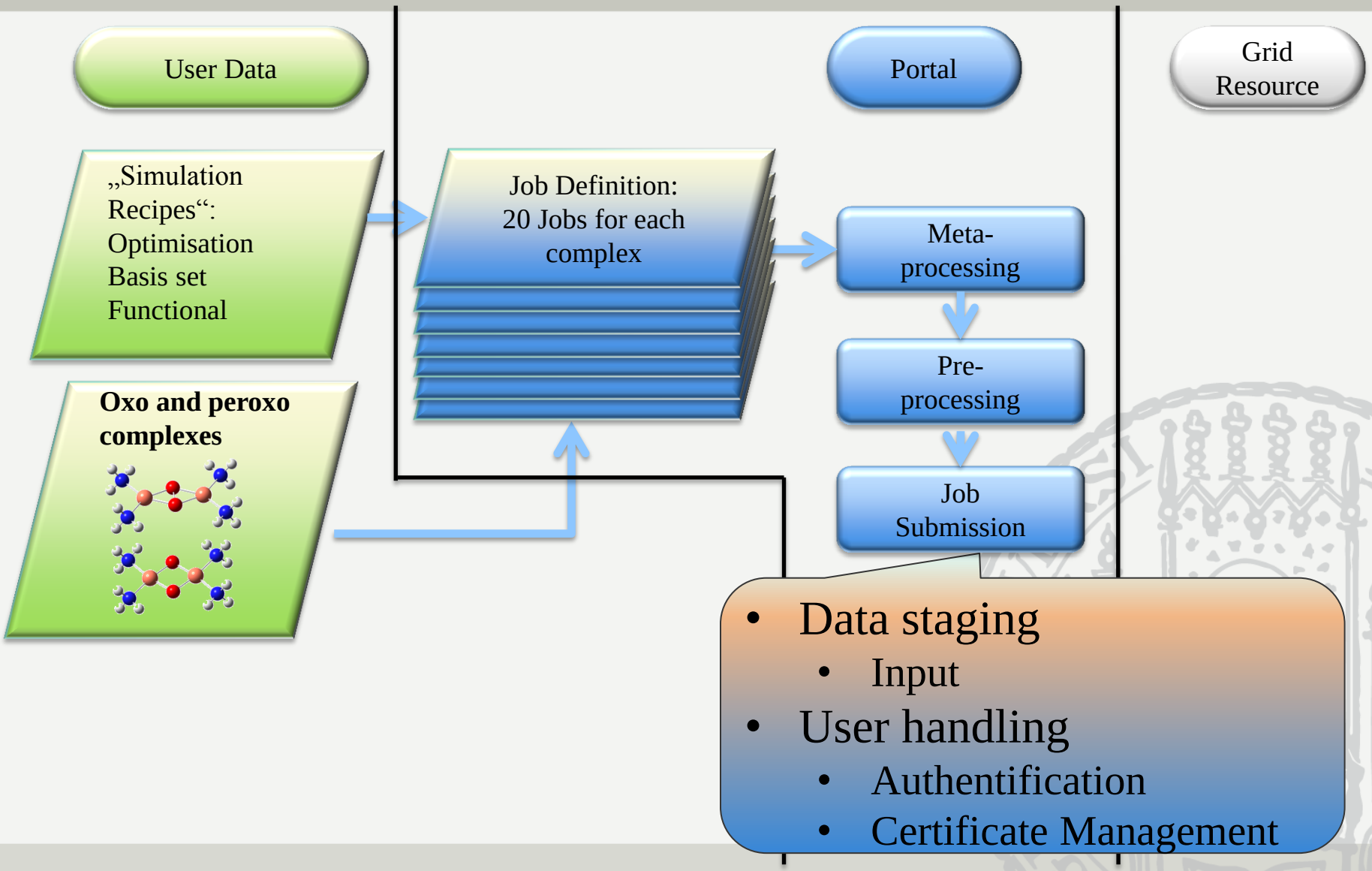


Orbital Analysis Workflow

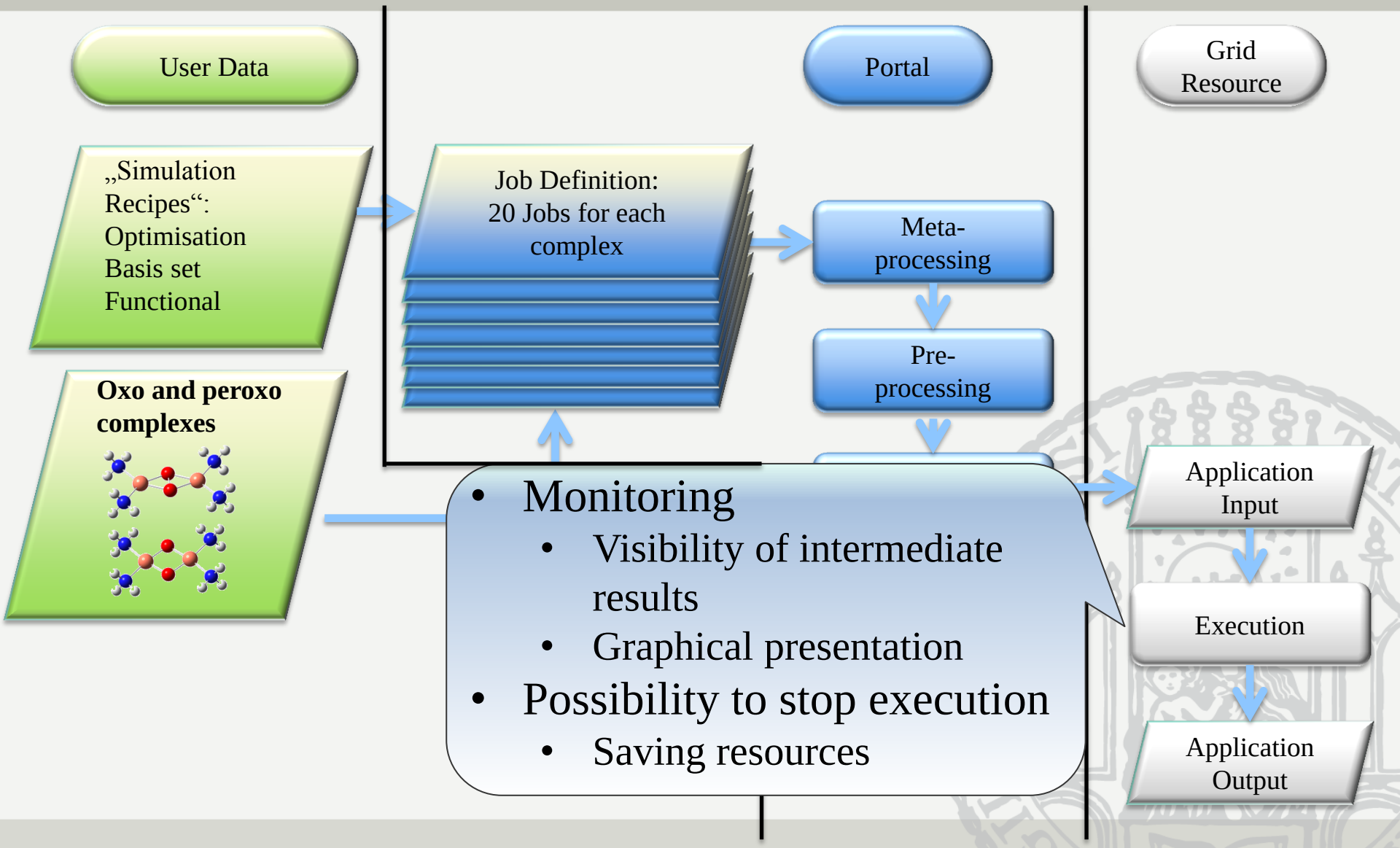


- Translation
  - MSML (molecular simulations markup language)
  - Code specific Format (Gaussian)

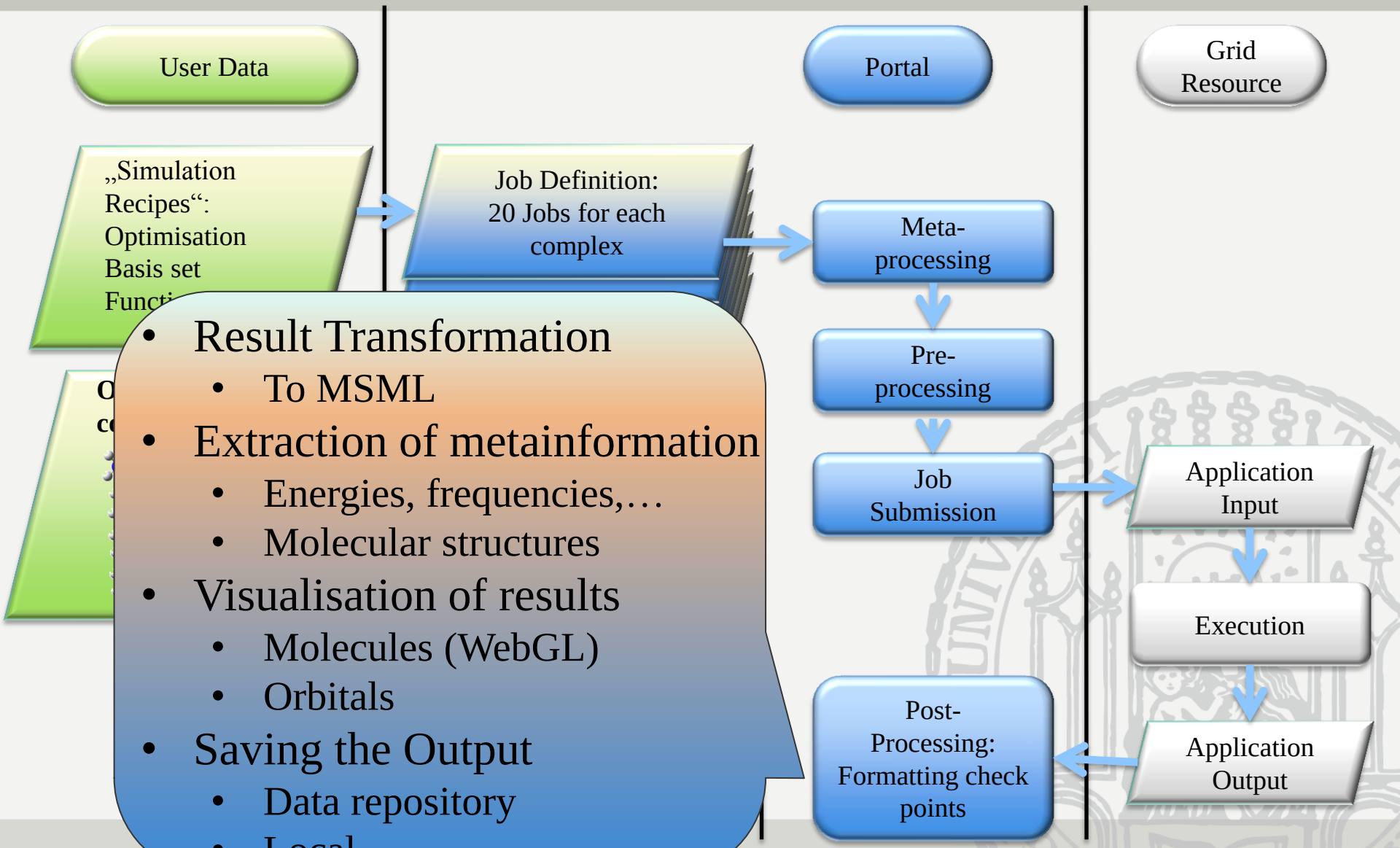
Orbital Analysis Workflow



Orbital Analysis Workflow

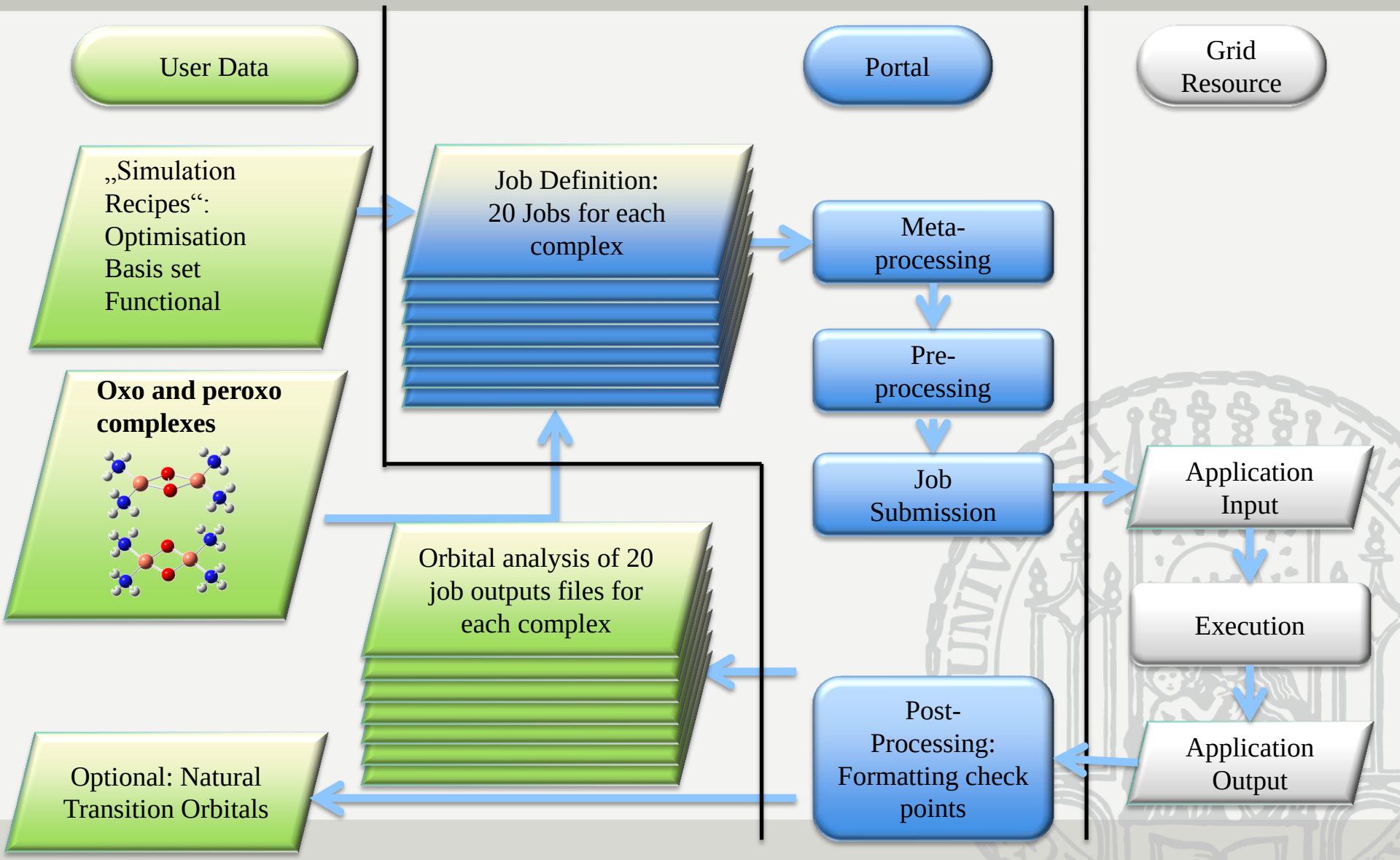


Orbital Analysis Workflow

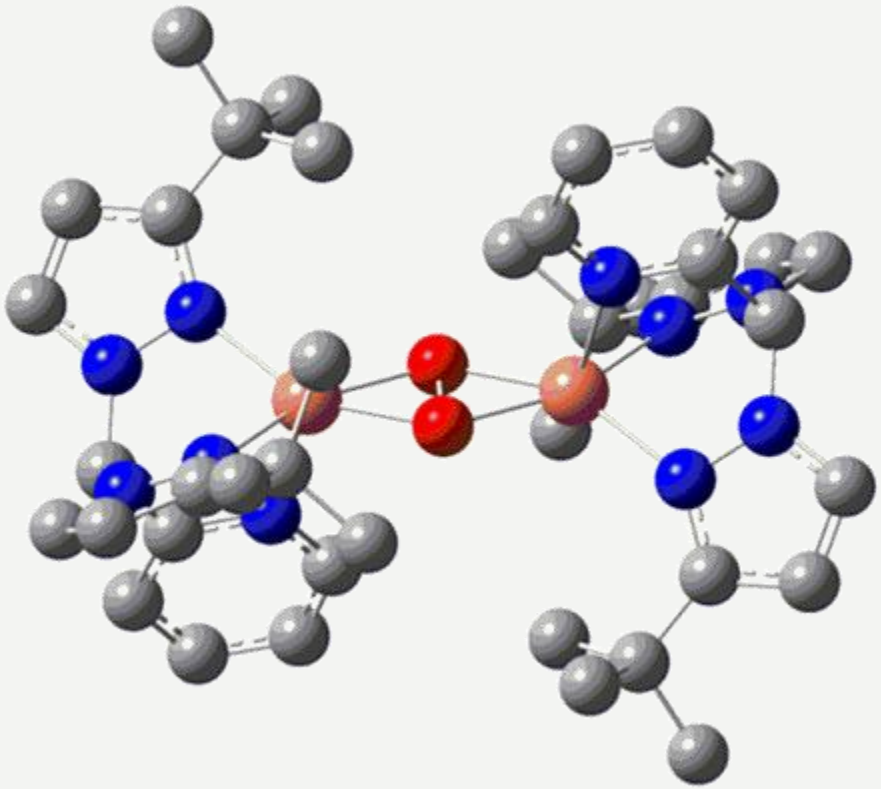


- Result Transformation
  - To MSML
- Extraction of metainformation
  - Energies, frequencies,…
  - Molecular structures
- Visualisation of results
  - Molecules (WebGL)
  - Orbitals
- Saving the Output
  - Data repository
  - Local

Orbital Analysis Workflow



μ-η^2:η^2-Peroxo-dicopper(II) species $[(HC(3tBupz)_2(py))_2Cu_2O_2][SbF_6]_2$



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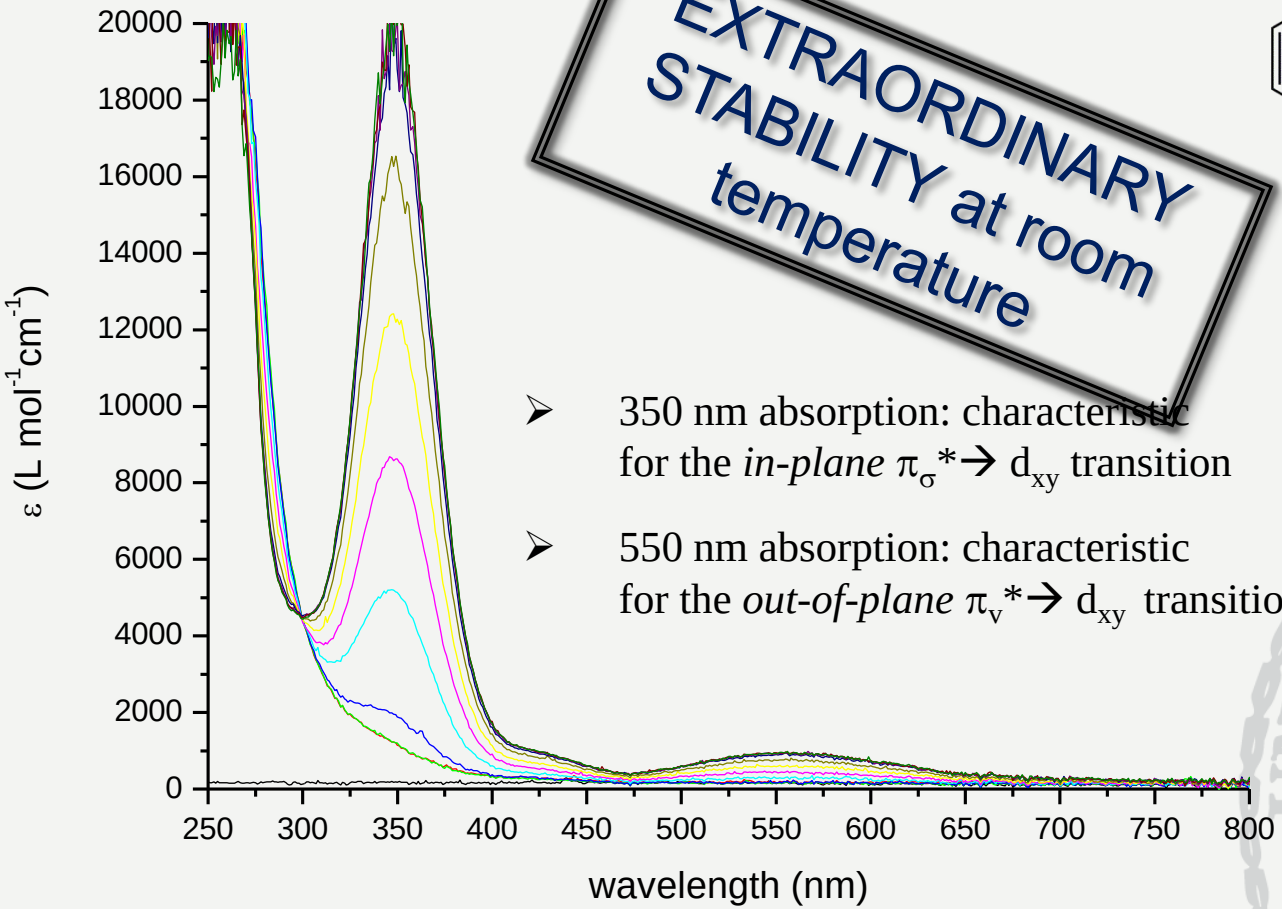
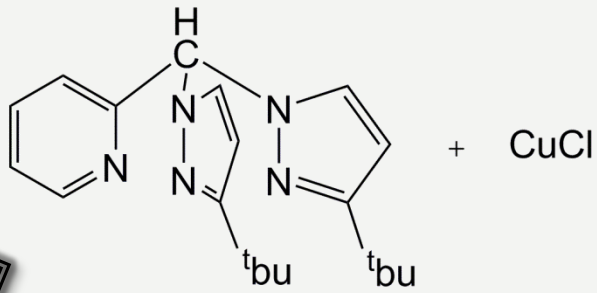
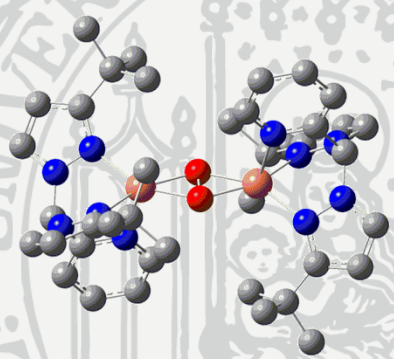


EXTRAORDINARY STABILITY at room temperature

- 350 nm absorption: characteristic for the *in-plane* $\pi_\sigma^* \rightarrow d_{xy}$ transition
- 550 nm absorption: characteristic for the *out-of-plane* $\pi_v^* \rightarrow d_{xy}$ transition



1. $AgSbF_6$, - AgCl
2. - 80°C
   + O_2



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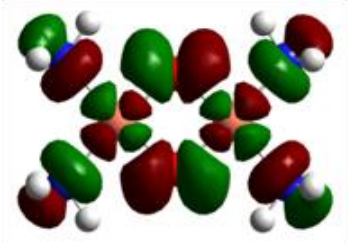
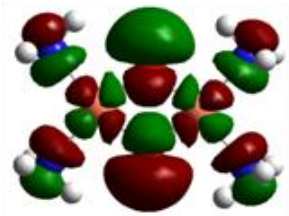
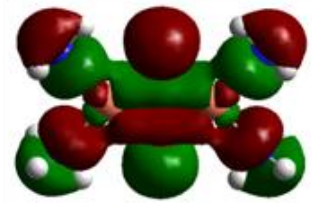
Molecular orbitals of the frontier orbitals of the small model systems: the oxo-core



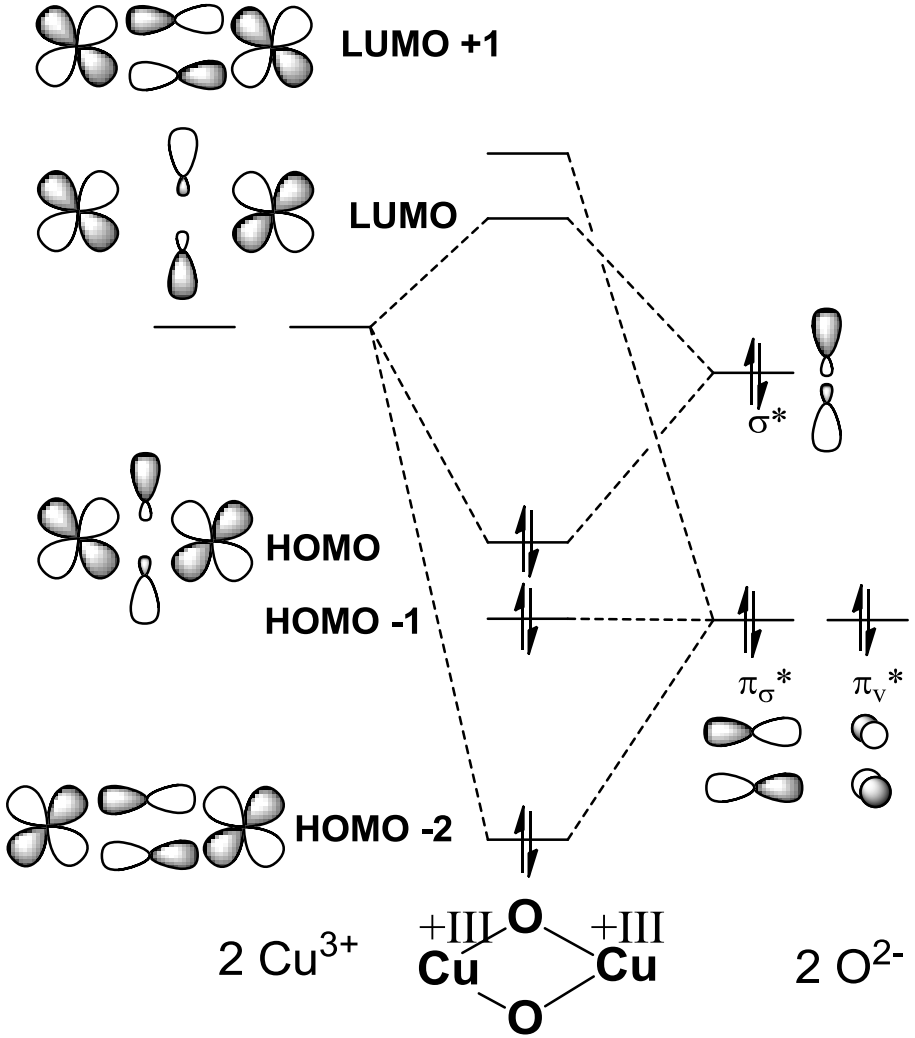
LUMO+1

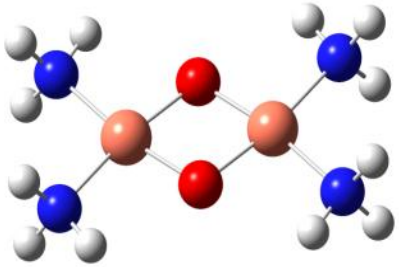


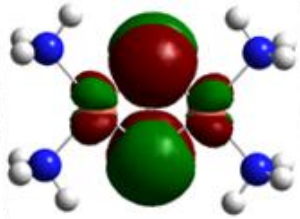
LUMO



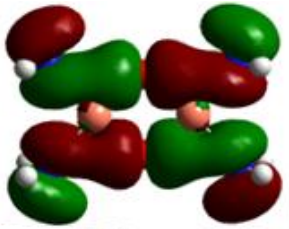
HOMO





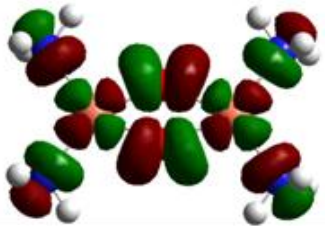


HOMO-1

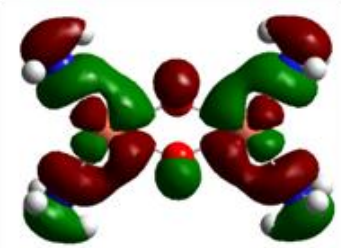


HOMO-2

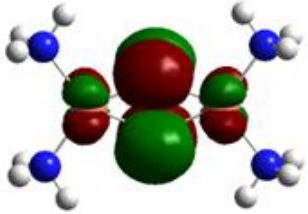
Molecular orbitals of the frontier orbitals of the small model systems: the peroxo-core



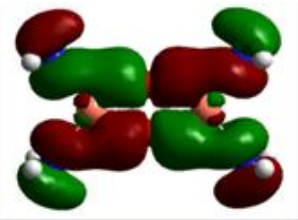
LUMO



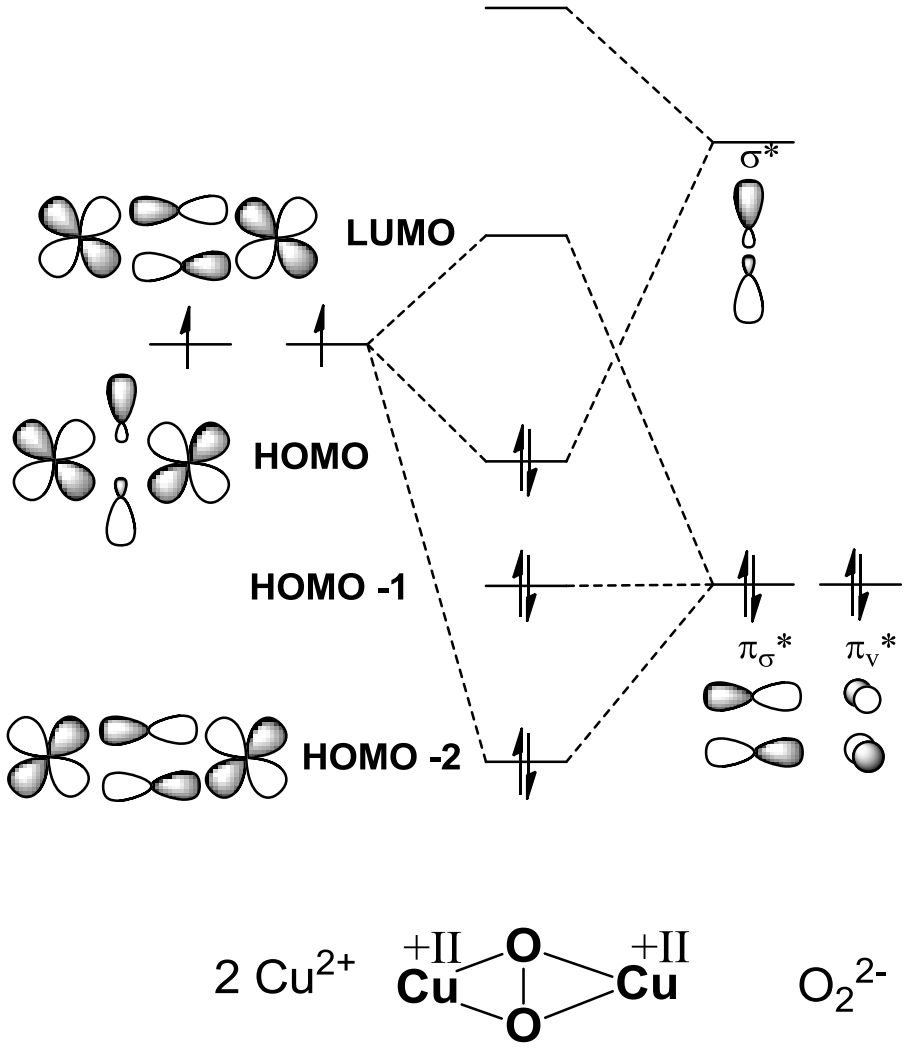
HOMO

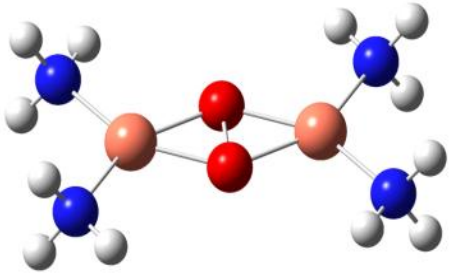


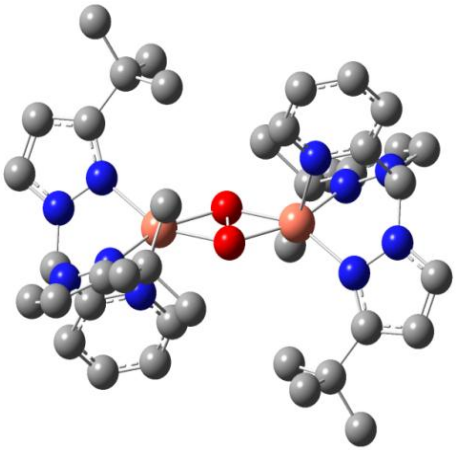
HOMO-1



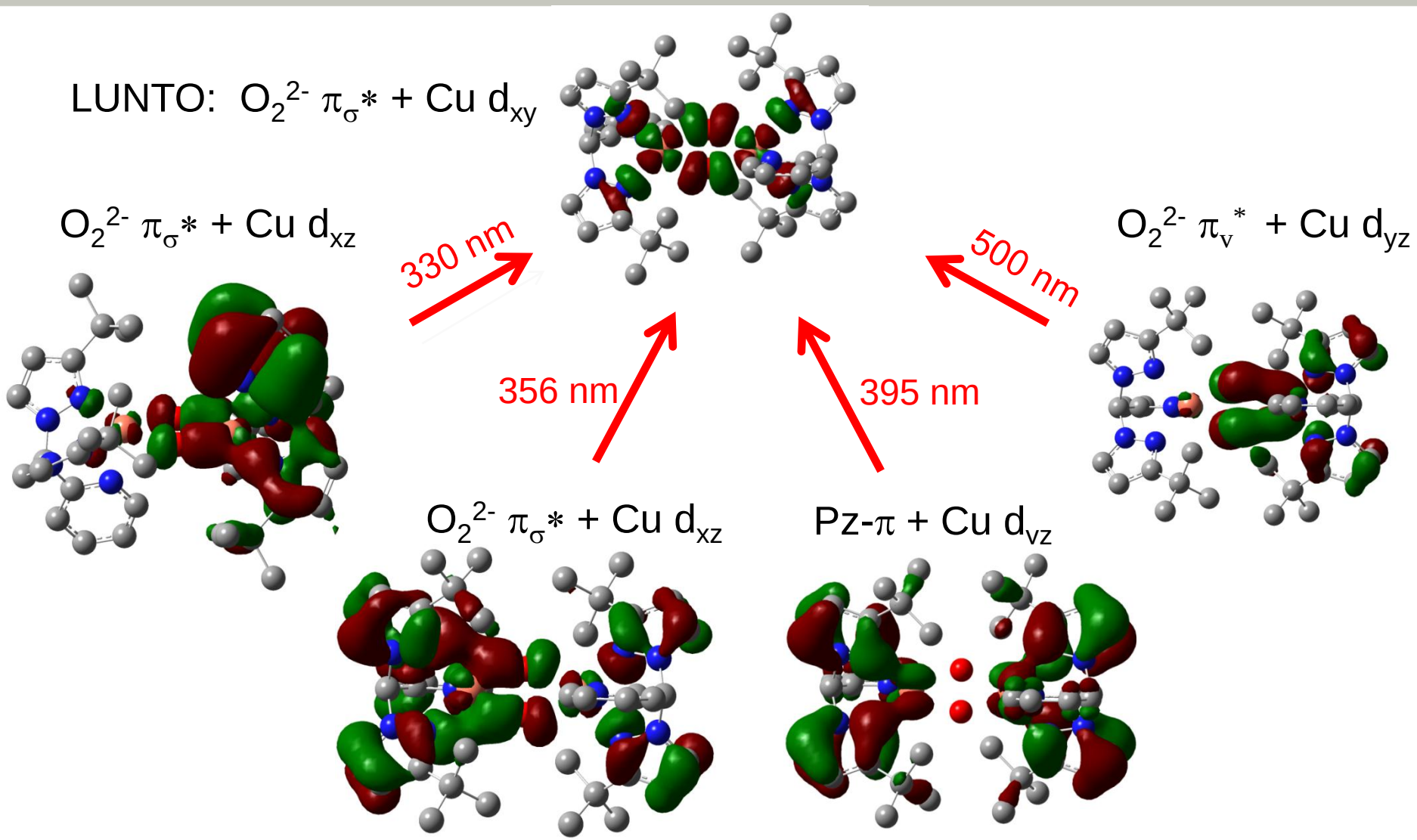
HOMO-2







Natural transitions orbitals (NTOs) of the "real life" system



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Conclusion

- MoSGrid: user-friendly portal for molecular simulations
- Use of workflows saves researcher´s time!
- Small model systems – „real-life“ system: difference between the frontier orbitals
- Significant ligand influence

Outlook

- More workflows, e.g. meta-workflows for combination of orbital analyses and spectroscopic workflows
- Easier access to computational analyses

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