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FZU Institute of Physics of the Czech Academy of Sciences

Charge density analysis from 3D ED data

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the inadequate START....

The most common methods to determine the crystal structures resort on a simple model, where the crystal is seen as an assembly of non-interacting atoms and the corresponding electronic distribution is described as a collection of spherically symmetric atomic electron densities, centered on the coordinates of the corresponding nuclei.

"Independent Atom Model" (IAM)

In routine structure determination, the refined parameters are the atomic fractional coordinates and the mean square displacements of nuclei, around their equilibrium positions, due to thermal vibrations.

- **Chemically inconsistent**
- **For isolated atoms**
- **The refined positional and thermal atomic parameters are biased by the non-modelled aspherical distribution of the valence ED**

So what now?

Multipolar Atom Model

$$\rho_{atom}(\vec{r}) = \rho_{core}(|\vec{r}|) + \kappa^3 P_{val}\rho_{val}(\kappa|\vec{r}|) + \sum_{l=0}^{l_{max}} \kappa'^3 R_l(\kappa'|\vec{r}|) \sum_{m=-l}^{+l} P_{lm} Y_{lm}(\theta, \varphi)$$

Atomic electron density

Spherical deformation of valence electrons

Aspherical deformation of valence electrons

Transferable Aspherical Atom Model (TAAM)

The values of electron density parameters obtained from multipolar refinements are almost identical for atoms in a similar chemical environment (Brock et al., 1991). Therefore, a number of **databanks are developed** for different types of so-called transferable aspherical atoms (pseudoatoms) and the databanks are applied to create an electron density model called the Transferable Aspherical Atom Model (TAAM)

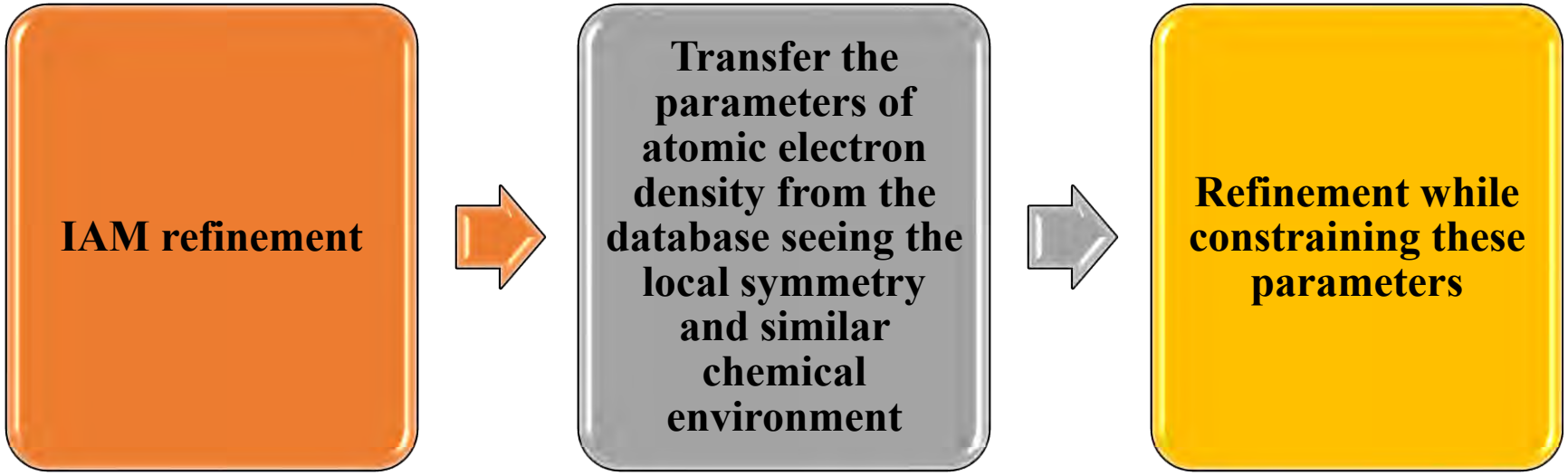
Some of the common databases used

- **ELMAM2** (Zarychta et al., 2007; Domagała et al., 2012; Nassour et al., 2017)
- **Invariom** (Dittrich et al., 2004, 2005, 2006, 2013)
- **MATTS/UBDB** (Volkov et al., 2007; Dominiak et al., 2007; Jarzembska & Dominiak, 2012; Kumar et al., 2019)

- **Improves the X—H bond lengths which becomes comparable to corresponding averaged neutron lengths.**
- **Refinement parameters and R-factors are improved.**
- **Anisotropic refinements of hydrogen-atom displacements are possible**
- **Chemically more consistent**

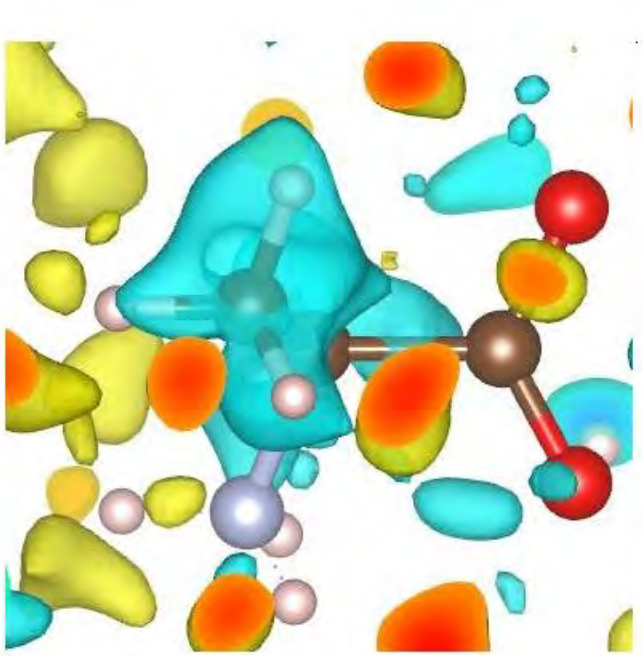
TAAM

Refinement strategy used



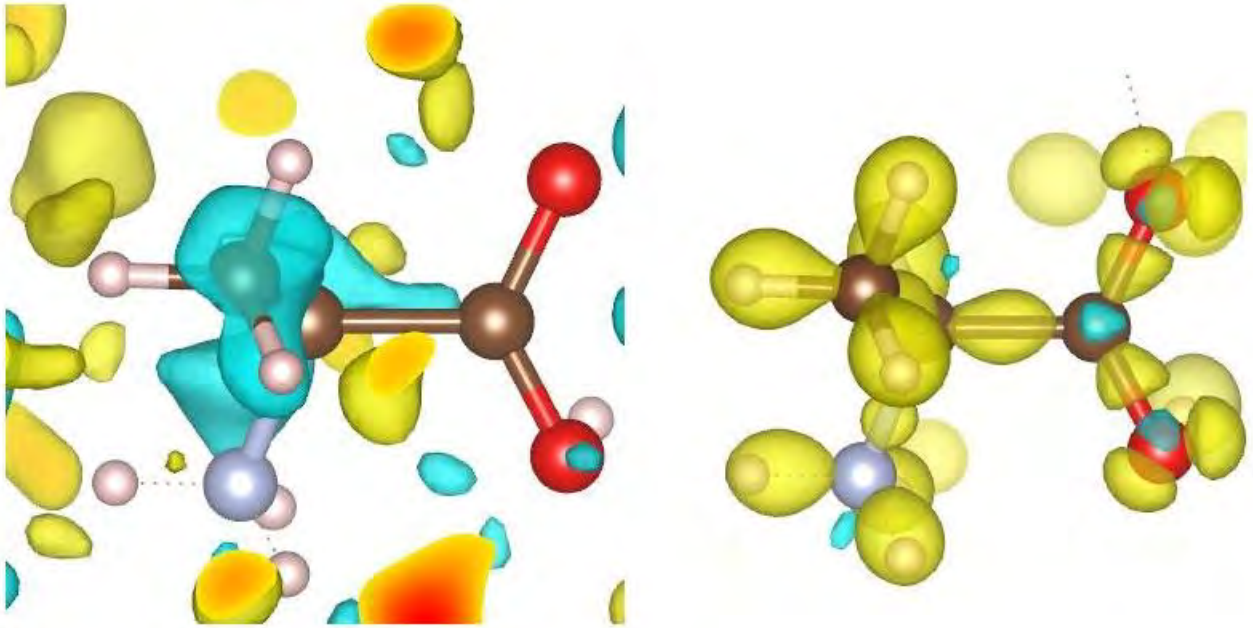
L-alanine

IAM



Robs: 10.19
Rall: 10.19

TAAM



Robs: 9.38
Rall: 9.38

Resolution: 1.4 Å^{-1}

Multipole refinement

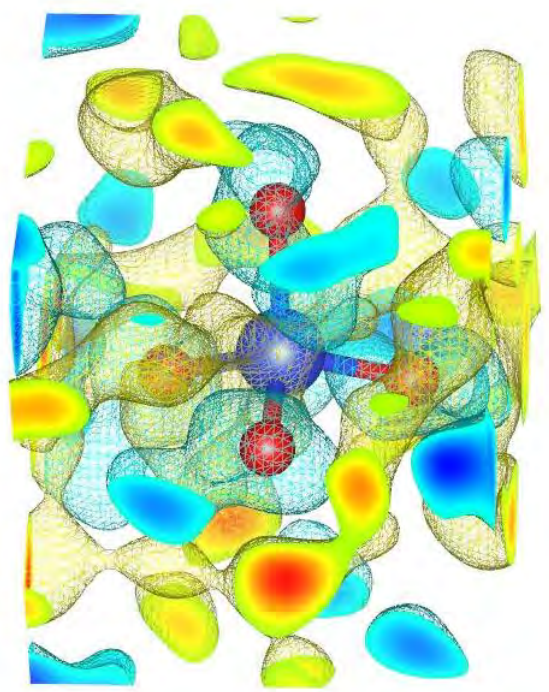
$$\rho_{atom}(\vec{r}) = \rho_{core}(|\vec{r}|) + \kappa^3 P_{val}\rho_{val}(\kappa|\vec{r}|) + \sum_{l=0}^{l_{max}} \kappa'^3 R_l(\kappa'|\vec{r}|) \sum_{m=-l}^{+l} P_{lm} Y_{lm}(\theta, \varphi)$$

Kappa refinement

Multipole refinement

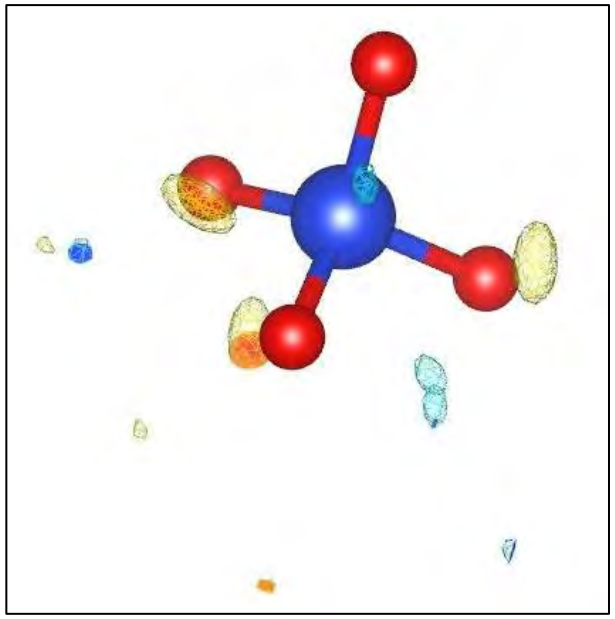
Quartz

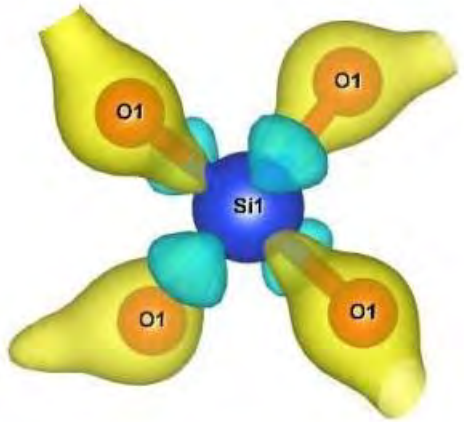
IAM



Robs: 3.71
Rall: 4.59

Multipole refinement



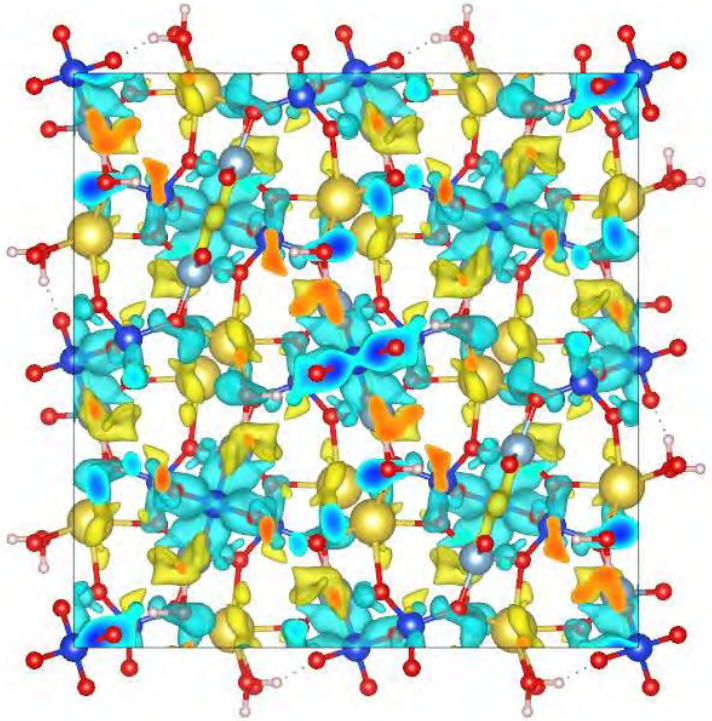


Robs: 3.08
Rall: 3.98

Resolution: 2.5 Å^{-1}

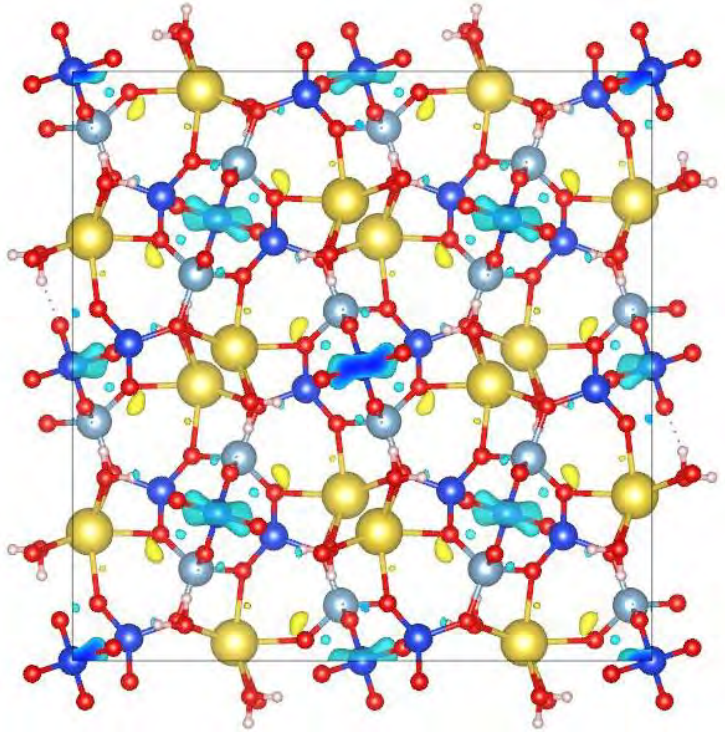
Natrolite

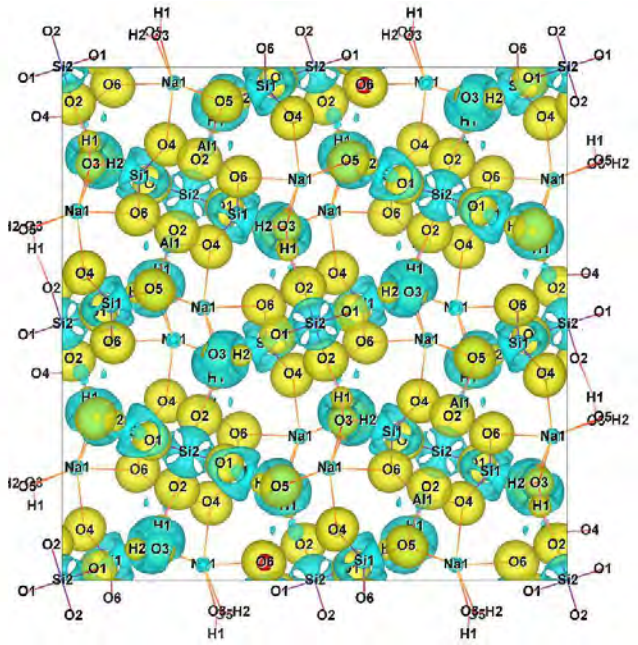
IAM



Robs: 5.86
Rall: 6.04

Kappa refinement



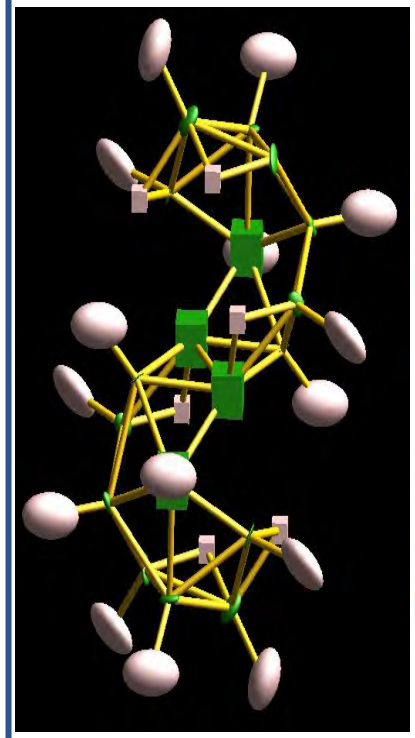


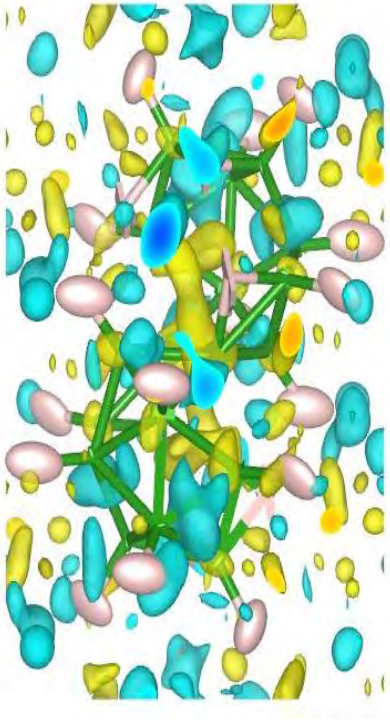
Robs: 5.29
Rall: 5.48

Resolution: 2.0 Å^{-1}

Borane

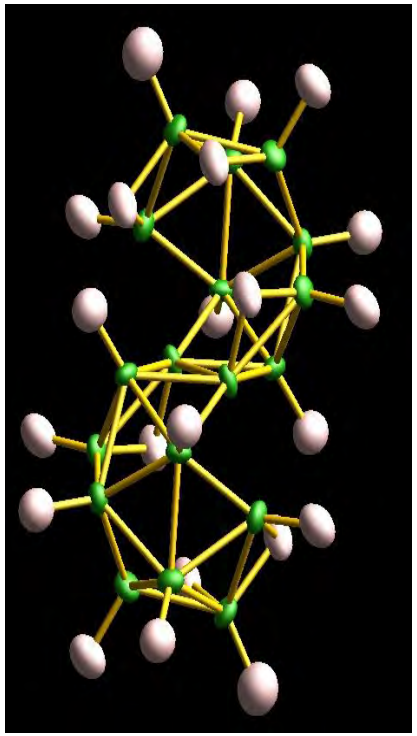
IAM

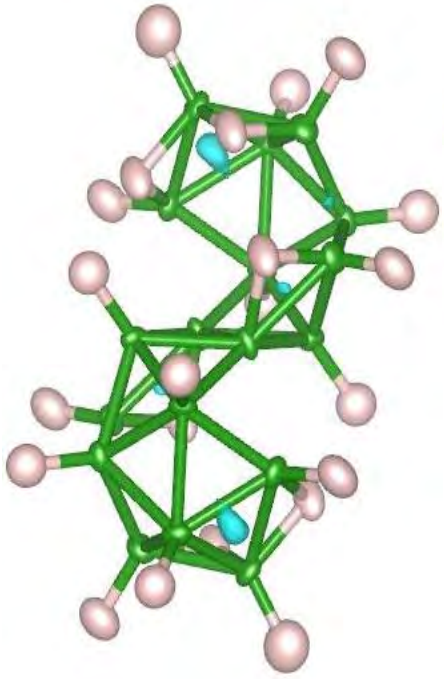


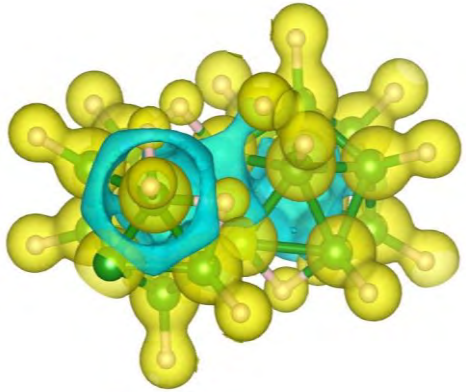


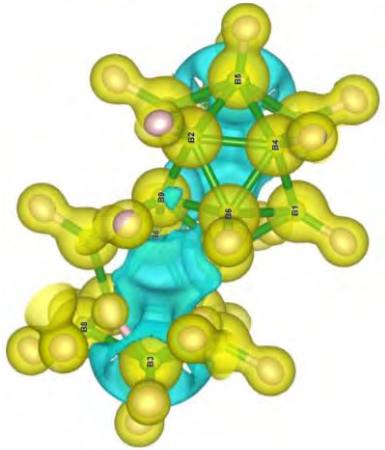
Robs: 6.03
wRall: 6.74

Kappa refinement









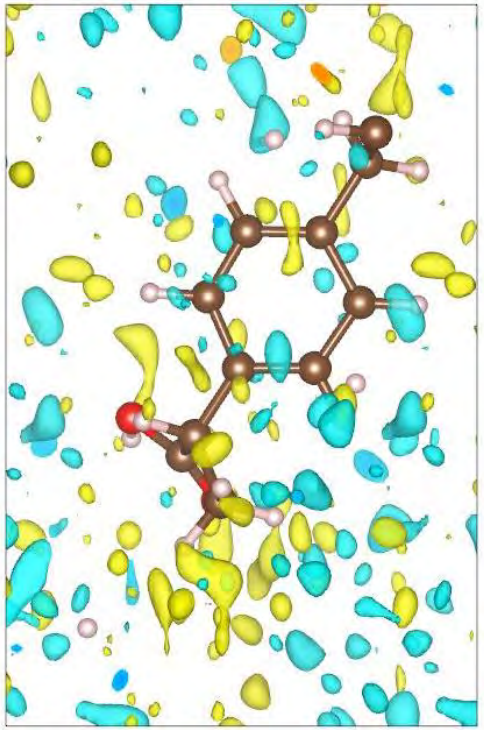
Robs: 4.62
wRall: 5.35

Resolution: 1.25 Å^{-1}


Challenges
Time consuming & complex
Need really good data: High completeness, good resolution, etc

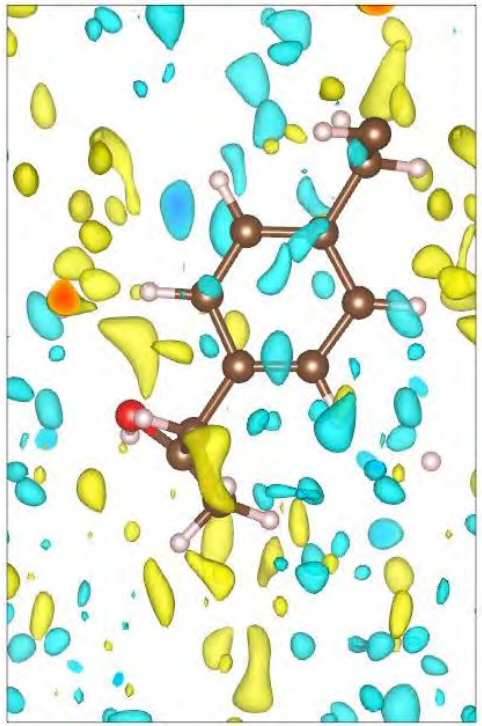
Ibuprofen

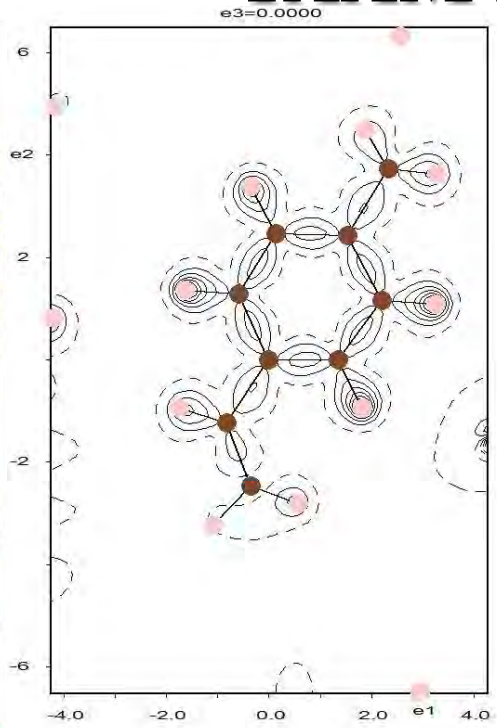
IAM

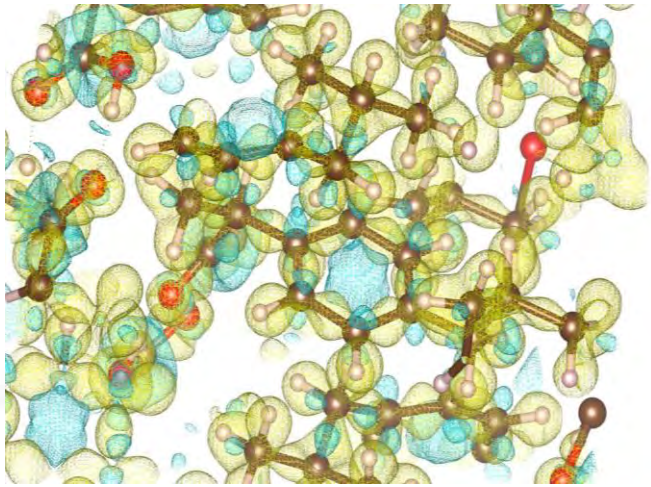


Robs: 8.99
wRall: 9.84

TAAM refinement





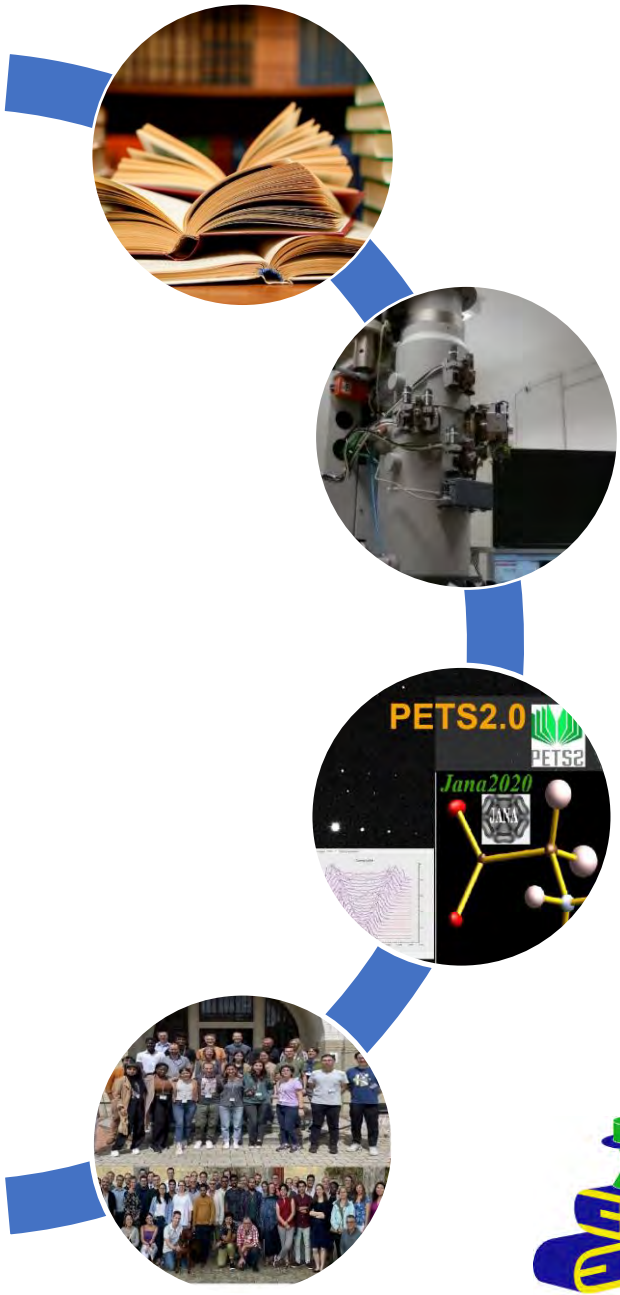


Robs: 9.28
wRall: 10.09

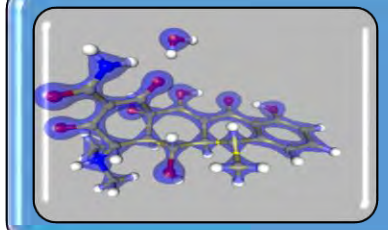
Resolution: 1.0 Å^{-1}

Conclusion & Status of the Project- The Present

- The current refinement models do not represent the bound state and the typical features of chemical bonding.
- I have been using a refinement strategies known as kappa refinement and multipole refinement on samples like L-alanine, natrolite, quartz, borane, etc to study the charge transfer from cations to anions.
- We have observed a good improvement in the R factors and in the quality of the refinements
- But the strategy requires good data (with high resolution, good completeness, etc) and high computing power.



What's next? : The Future



More data analysis and charge density studies

- Charge density refinement using the multipole refinement method
- Performing DFT calculations to theoretically obtain multipole parameters to perform TAAM and multipole refinements on inorganic and organic samples.

PhD studies in Charles University.

- Doctoral study Programme: Physics of Condensed Matter and Material research

Secondments

- IIT: M. Gemmi (charge density study in organic materials);
- Tescan: D. van der Wal (FIB sample preparation);
- SU: Cheuk-Wai Tai (ePDF on disordered systems)
- IUCr: B. McMahon (syntax of CIF files)

Results Dissemination

THANK YOU