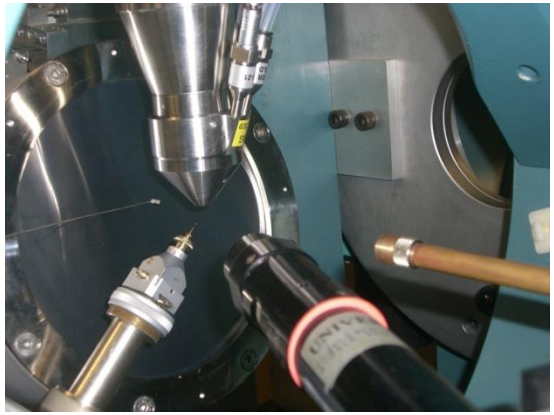
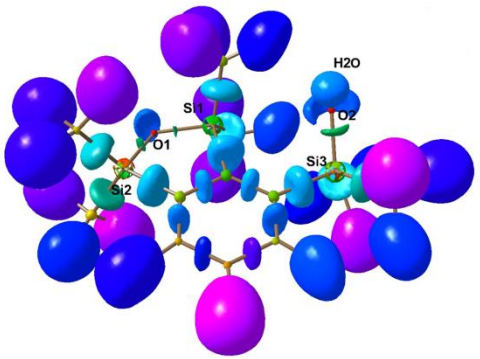
Quantum Crystallography



+ $|\Psi(r,t)|^2$ =

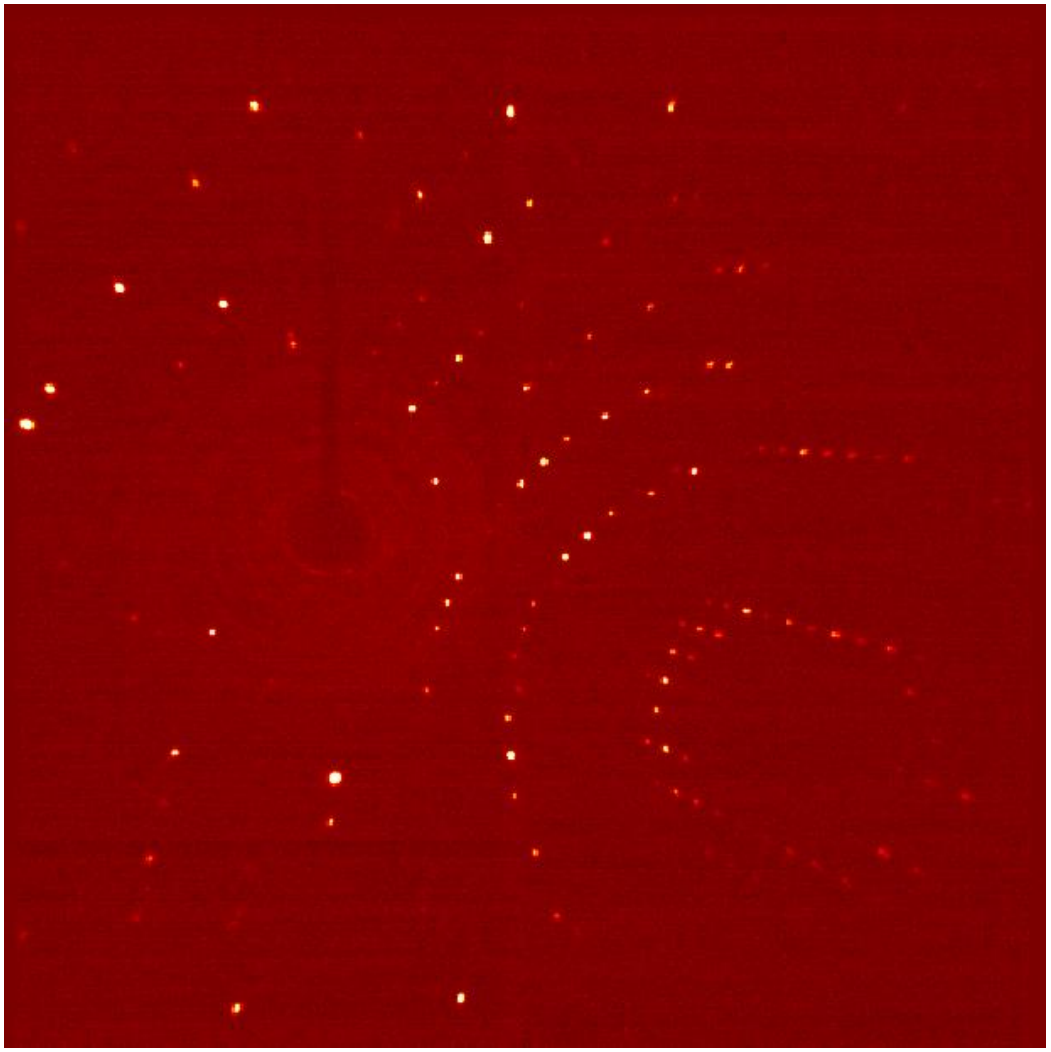


PD Dr. Simon Grabowsky

University of Bern

Switzerland

Single-crystal X-ray diffraction



$$I(\vec{h}) \sim \left| F(\vec{h}) \right|^2$$

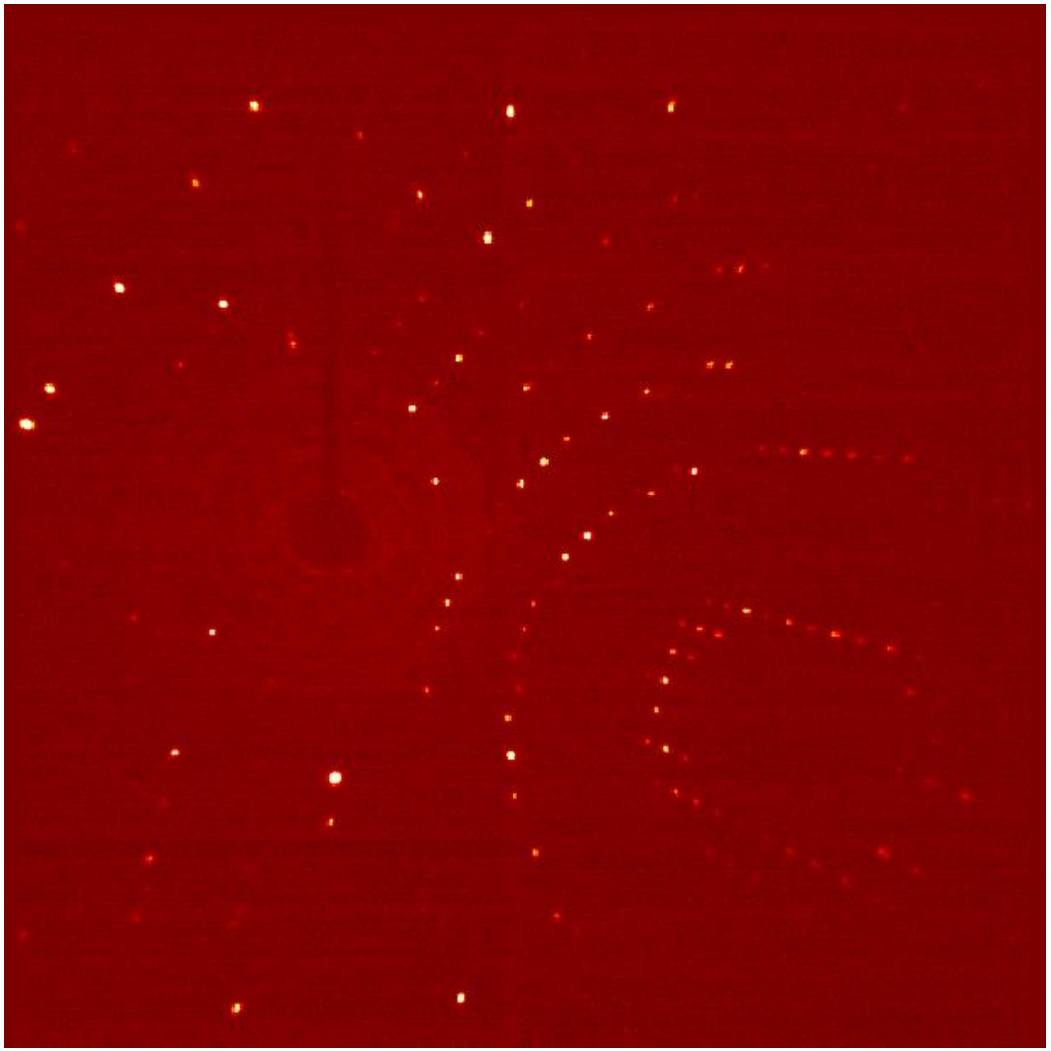
$$F(\vec{h}) = \int_V \rho(\vec{r}) \cdot e^{2\pi i \vec{h}\vec{r}} \, dV$$

phase problem → necessity of a model

$$F(\vec{h}) = \sum_{j=1}^{N} f_j \cdot e^{2\pi i \vec{h}\vec{r}_j}$$

f_j … atomic form factor

Single-crystal X-ray diffraction



$$I(\vec{h}) \sim \left|F(\vec{h})\right|^2$$

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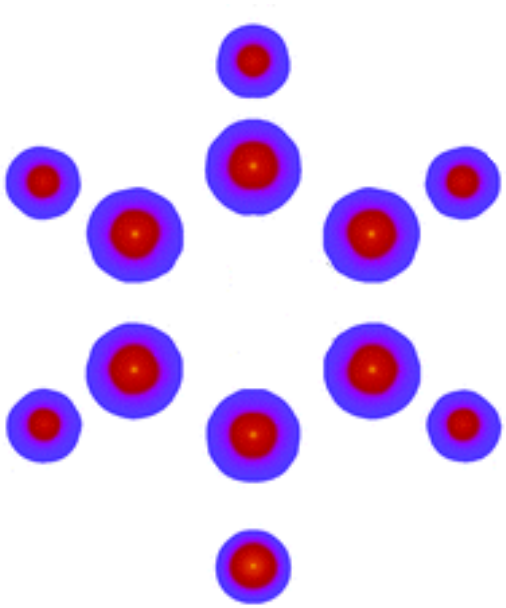
phase problem → necessity of a model

$$F(\vec{h}) = \sum_{j=1}^{N} f_j \cdot e^{2\pi i \vec{h}\vec{r}_j}$$

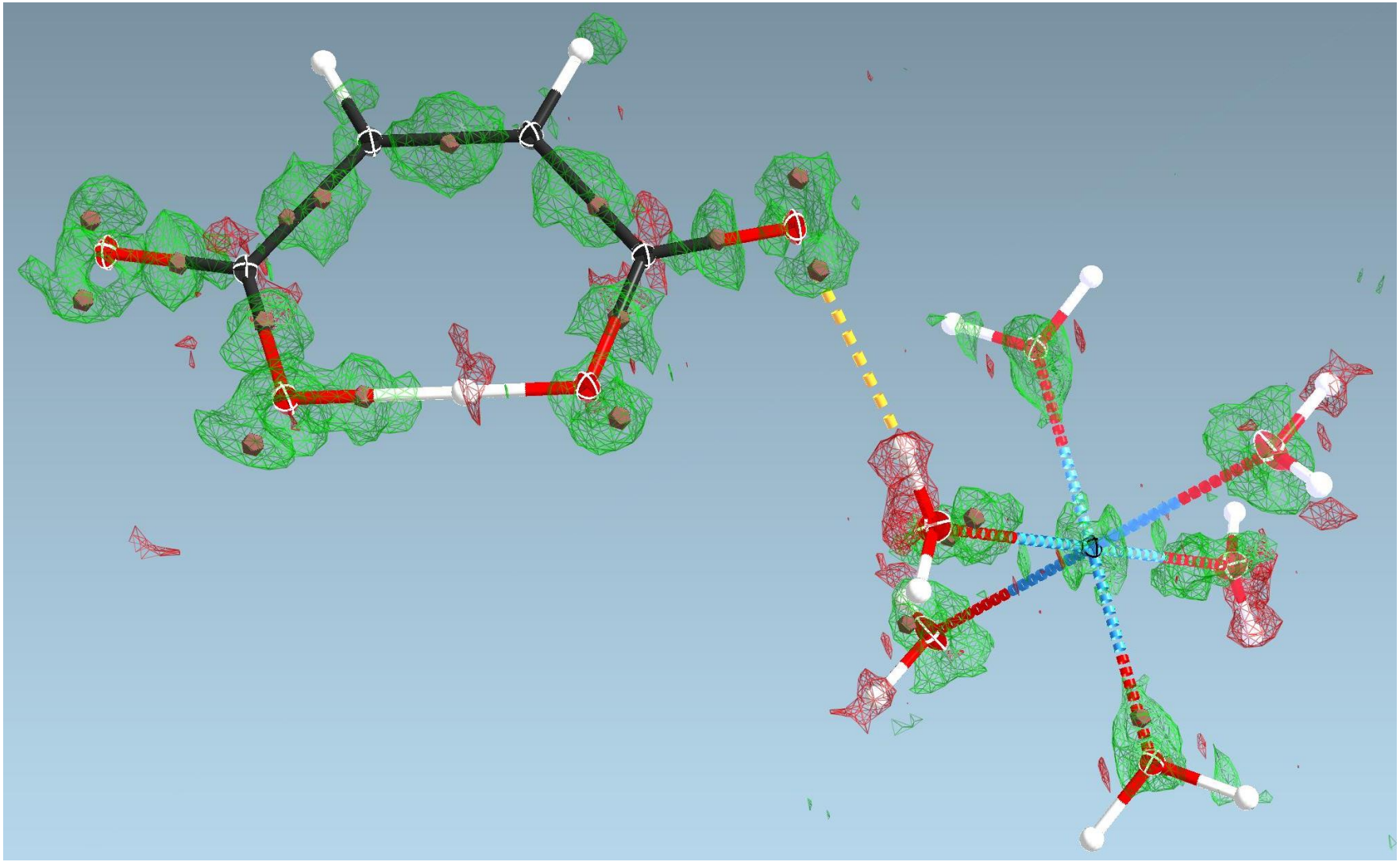
f_j … **atomic form factor**

Spherical model



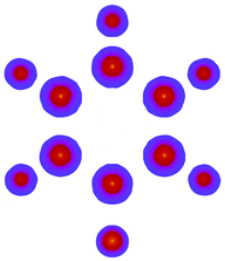
IAM = Independent Atom Model

Spherical model



Residual electron density

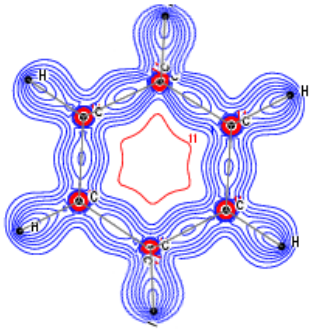
Non-spherical models



IAM
(spherical model)

non-spherical model

Multipole-based techniques

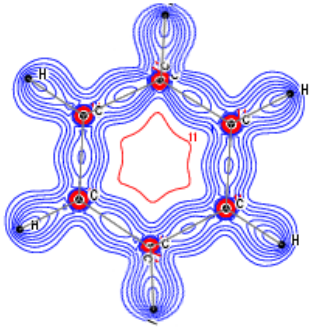


non-spherical model

Maximum entropy methods

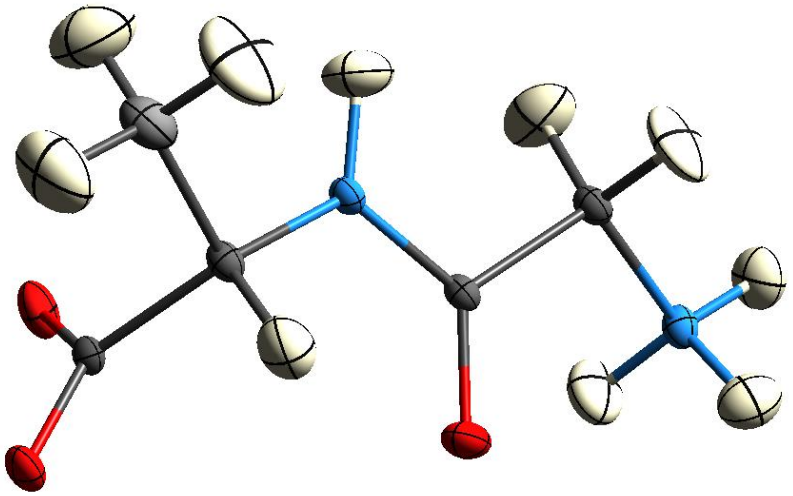
non-spherical model

Wavefunction-based techniques



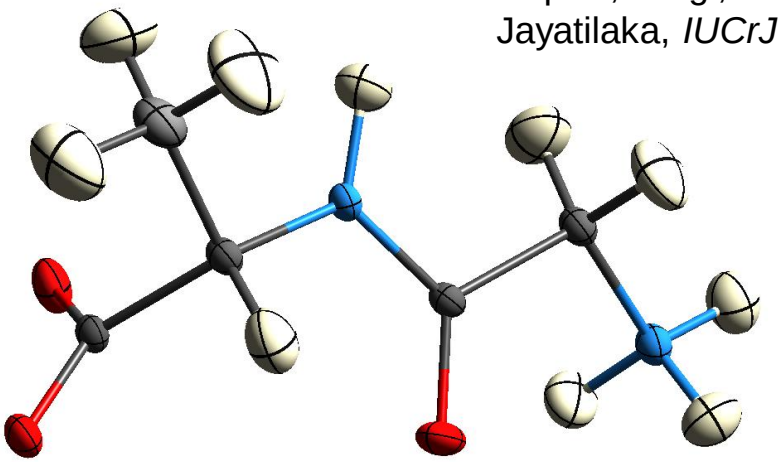
Prospects of Quantum Crystallography

- Accurate and precise structure determination, including hydrogen-atom positions and ADPs



X-ray data,
QCr treatment

Capelli, Bürgi, Dittrich, Grabowsky, Jayatilaka, *IUCrJ* **2014**, *1*, 361

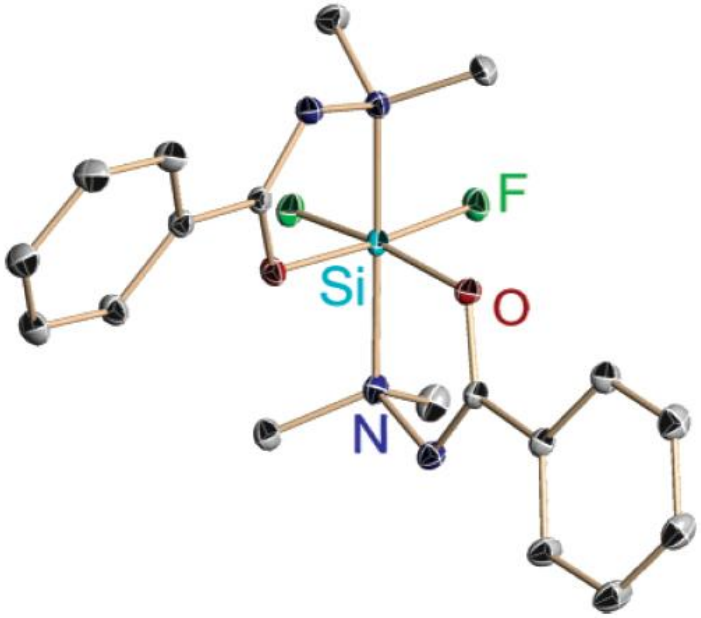


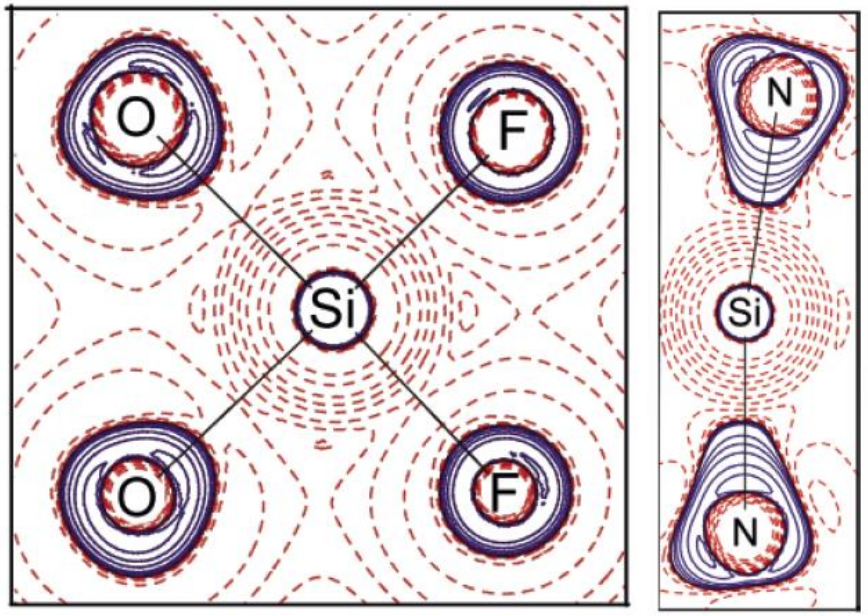
Neutron data

Prospects of Quantum Crystallography

- Electron density and chemical bonding

N. Kocher, D. Stalke et al., *J. Am. Chem. Soc.* 2004, *126*, 5563



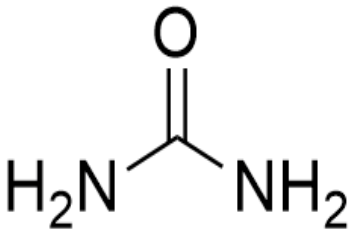


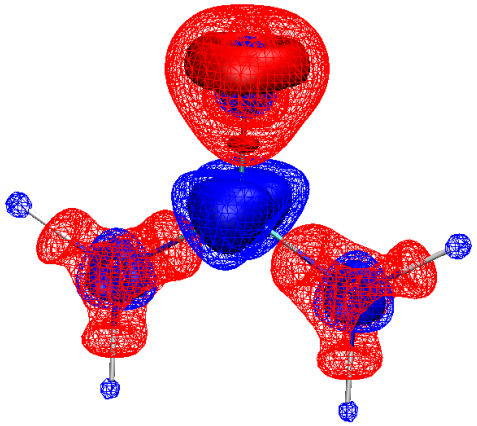
„…we conclude that the silicon atom in **1** definitely is not hypervalent.”

Prospects of Quantum Crystallography

- Measuring electron correlation

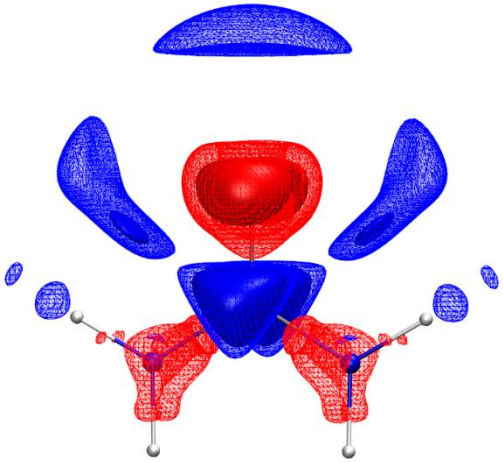
urea





Difference
Electron Densities:

Electron Correlation
from the experiment



Difference
Exchange-Correlation Potential:

Electron Correlation
from the experiment

Genoni et al., *IUCrJ* **2017**, *4*, 136

Prospects of Quantum Crystallography

- Measuring polarization

P. Macchi et al.,
J. Appl. Cryst.
2014, *47*, 1452

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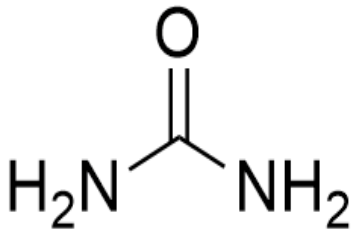
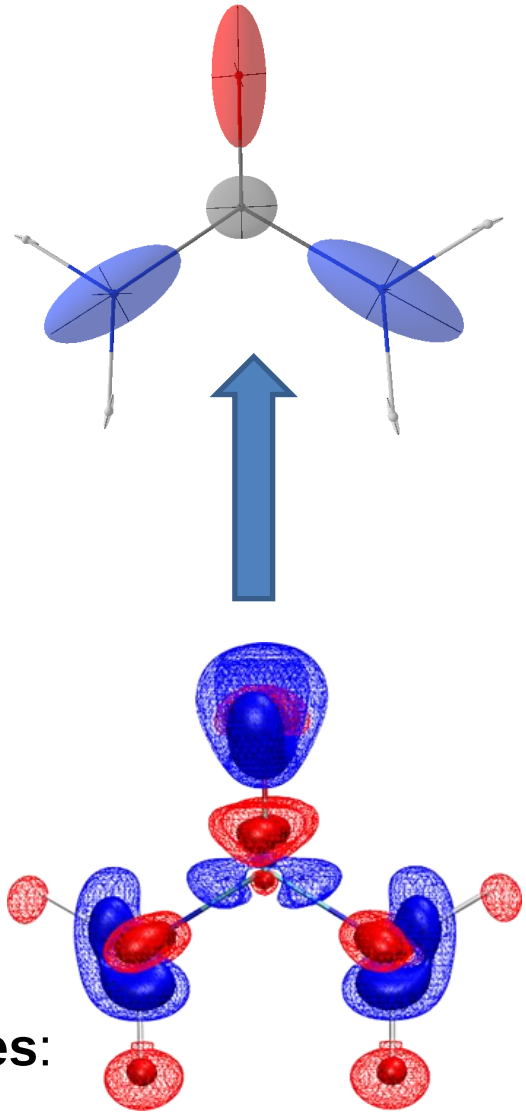




Difference
Electron Densities:

Atomic properties:
- Atomic polarizability tensors

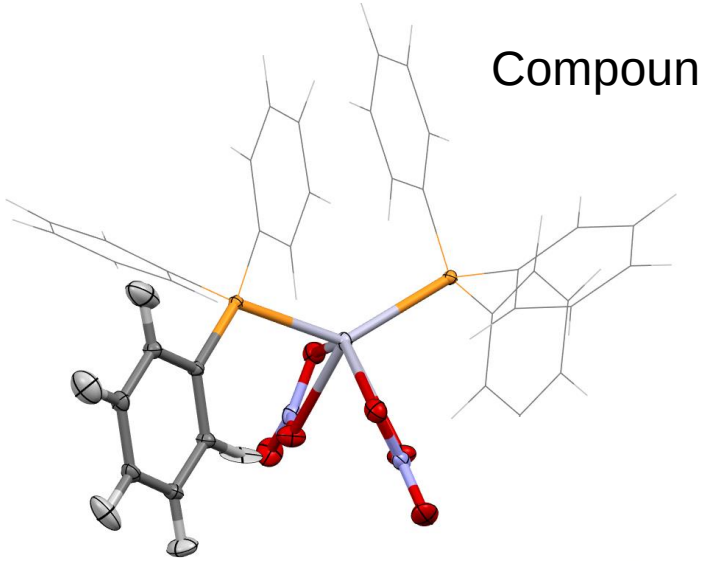
Molecular properties:
- Molecular or fragment polarizability tensors
- Molecular refractive index

Crystal properties:
- Crystal susceptibility
- Crystal dielectric constant
- Crystal refractive index

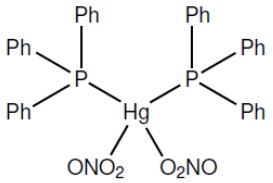
Polarization
from the experiment
→ Optical properties, Reactivity

Prospects of Quantum Crystallography

- Core deformation and relativistic effects

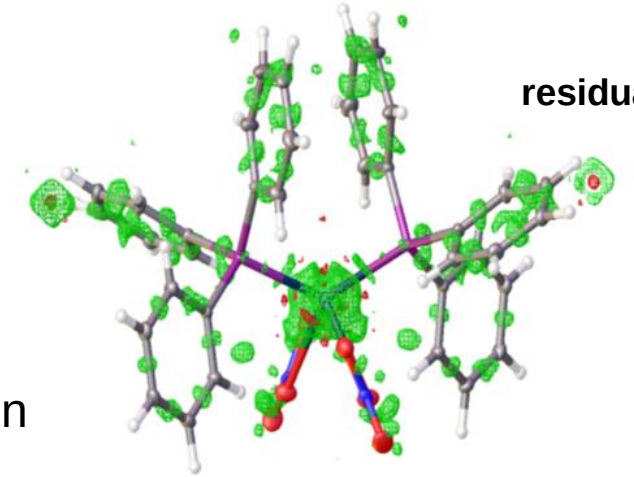


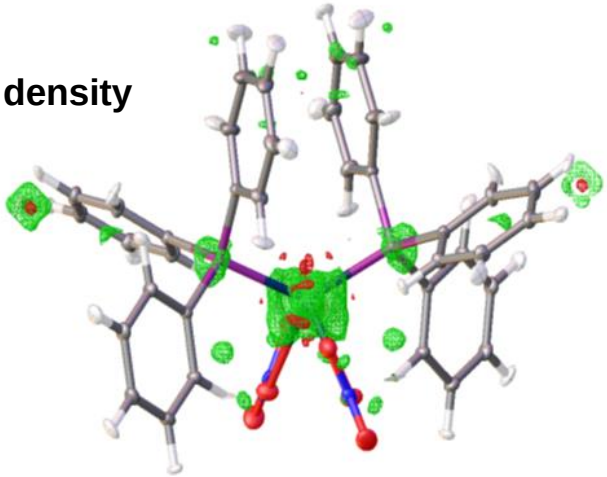
Compounds with **heavy elements**



$Hg(PPh_3)_2(NO_3)_2$

residual density





Problems:

- Absorption
- Anomalous dispersion
- Radiation damage

S. J. Coles et al.,
IUCrJ **2019**, *6*, 703

before QCr,
$\Delta\rho_{max}$=3.8 eÅ^{-3}

after QCr,
$\Delta\rho_{max}$=1.4 eÅ^{-3}

Requirements for quantum crystallography measurements

- Best possible quality (importance of low order data)
- 100% complete and highly redundant (> 20 times)
- Very high resolution (d = 0.5 Å and better)
- Temperatures < 100 K

Krzysztof’s part

Non-spherical models: theoretical raw data

NoSpherA2 = non-spherical atoms in Olex2

Chemical Science

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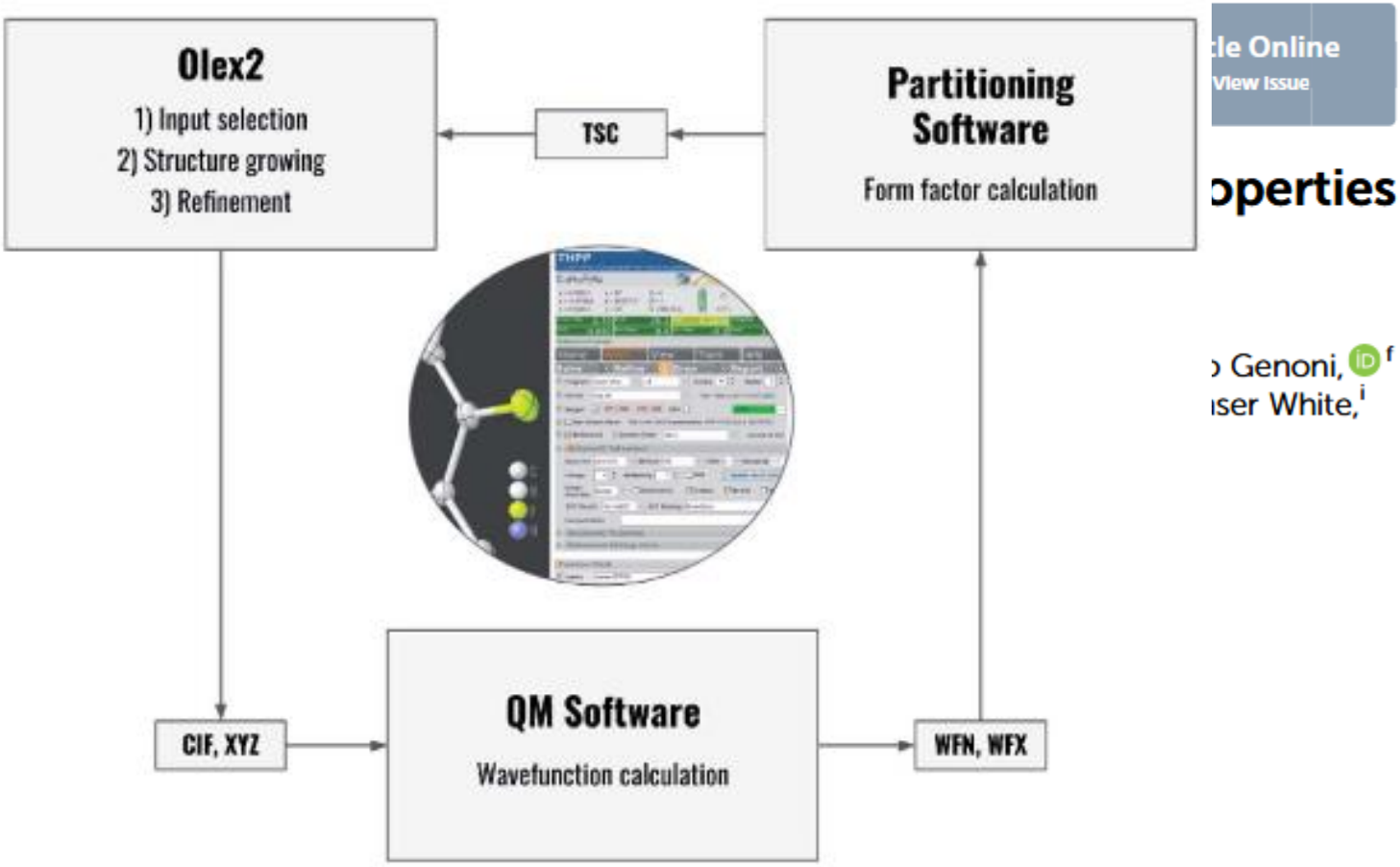

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Genoni,
ser White,

TITLE: *optional title of the structure*

SYMM: `expanded' *or list of symmetries*[1]

AD: TRUE or FALSE (anomalous dispersion)

SCATTERERS: *space-separated list of all atoms*

[ANYTHING]: *colon must be present*

DATA: (denotes the end of the header)

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h_2	k_2	l_2	$f_1(h_2, k_2, l_2)$	$f_2(h_2, k_2, l_2)$	...	$f_n(h_2, k_2, l_2)$
⋮	⋮	⋮	⋮	⋮	⋮	⋮
h_n	k_n	l_n	$f_1(h_n, k_n, l_n)$	$f_2(h_n, k_n, l_n)$	...	$f_n(h_n, k_n, l_n)$

nitron_ACN_Mo_absorption.tsc - Notepad

File Edit Format View Help

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Every structure determination is always based on two sources of raw data:

- Measured structure factors/ intensity data
- Calculated atomic form factors

→ Both types of raw data should be considered when we talk about publishing/ depositing raw data