

# Chemical Crystallography and Structural Chemistry

VO 270063-1

Lecture N° 9 — 22<sup>th</sup> June 2023

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## Course Schedule

2 <sup>nd</sup>	March	Lecture N <sup>o</sup> 1	9 <sup>th</sup>	March	Lecture N <sup>o</sup> 2
16 <sup>th</sup>	March	Lecture N <sup>o</sup> 3	23 <sup>th</sup>	March	Exercise N <sup>o</sup> 1
30 <sup>st</sup>	March	Lecture N <sup>o</sup> 4	20 <sup>th</sup>	April	Lecture N <sup>o</sup> 5
27 <sup>th</sup>	April	Exercise N <sup>o</sup> 2	4 <sup>th</sup>	May	Lecture N <sup>o</sup> 6
11 <sup>th</sup>	May	Lecture N <sup>o</sup> 7	25 <sup>th</sup>	May	Exercise N <sup>o</sup> 3
1 <sup>st</sup>	June	<b>no lecture</b>	15 <sup>th</sup>	June	Lecture N <sup>o</sup> 8
22 <sup>nd</sup>	June	Lecture N <sup>o</sup> 9	29 <sup>th</sup>	June	Exercise N <sup>o</sup> 4

Exercise N<sup>o</sup> 4: Hands-on at the X-ray Centre, Lab 2E45/2E46, at 10:15am.

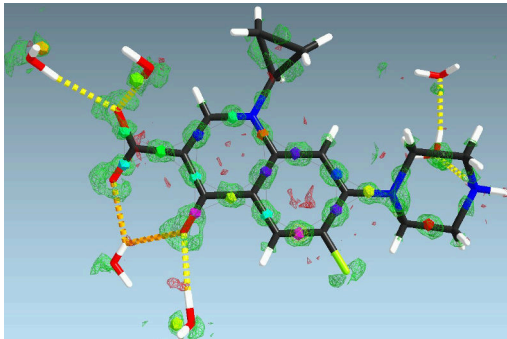
## Previous Lecture

- Electron crystallography
- Applications of electron crystallography
- Examples

# 1 Ultra-high resolution: limits of the IAM and charge density refinement

## Data better than model

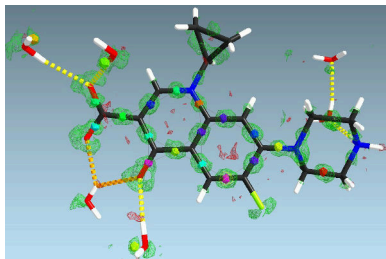
- X-rays interact with electron (cloud)
- Independent atom model (IAM) centres electron cloud about the nucleus
- Particularly strong deviation in hydrogen (single electron)



## Unspherical valence electrons

The IAM assumes spherical atoms. Sufficient up to  $\approx 0.7 \text{ \AA}$  resolution.

Provides 3D-structure: atom positions, chirality



Structure of Ciprofloxacin, *J. Holstein et al., Cryst. Eng. Comm. 2012 (14), pp. 2520–2531 (0.43 \AA)*

Ciprofloxacin at  $0.43 \text{ \AA}$ : data “better” than model:

- IAM: does not model valence electrons
- dipole moments at terminal atoms  $O$ ,  $F$

## X-ray crystallography beyond the IAM

- Ultra-high resolution provides insight into the chemical bond
- Residual density with “Independent Atom Model”
- necessary: different model to describe chemistry
- This will provide more information than “just” the structure

## Starting point

The equation

$$\begin{aligned} F(hkl) &= \int \rho(x, y, z) e^{2\pi i(\vec{h} \cdot \vec{x})} d^3x \\ &= FT(\rho(x, y, z)) \end{aligned}$$

remains valid — definition of the structure factor

- Context with experiment:  $I(hkl) = |F(hkl)|^2$
- So far with IAM:  $\rho(x, y, z)$  calculated from form factors  $f_i(\theta, \lambda)$  and ADPs  $U_{ij}$ .
- Extending the IAM description of  $\rho(x, y, z)$  of the unit cell at better precision.



## Requirements to the extended model

- Fourier transformation should be computable (fast)
- should make chemical sense
- limited number of parameters

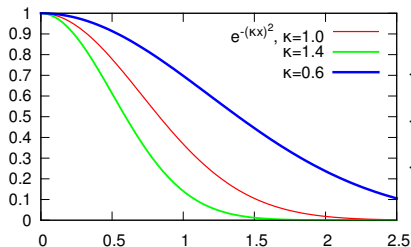
## Models for the description of $\rho(x, y, z)$

1. spherical atoms with  $\kappa$ -Formalism (predecessor of the multipole model; Coulson 1961)
2. Hirshfeld-Formalism (1976):  $\cos^n$  summation
3. multipole model (MPM) with spherical harmonics (Hansen & Coppens 1978)
4. Invariom model (B. Dittrich *et al.*, 2004)

## The $\kappa$ -Formalism - Coulson 1961

- Idea: exchange of valence electrons
- still spherically symmetric like IAM

$$\rho_{\text{atom}}(r) = \rho_{\text{core}}(r) + P_{\nu} \kappa^3 \rho_{\text{valence}}(\kappa r)$$



- $P_{\nu}$  population of the valence shell
- $\kappa < 1$  expansion of valence shell
- $\kappa > 1$  contraction of valence shell

- cf. Brown & Spackman, "A Model Study of the  $\kappa$ -Refinement Procedure for Fitting Valence Electron Densities", Acta Cryst. **A47** (1991), S. 21–29

## Hirshfeld refinement

describes the deformation of electron density for every atom with cosine functions with dependence on bond direction

$$\Delta\rho_i(n, \vec{k}) = \sum_{n, \vec{k}} N_n r_i^n e^{-\alpha_i r_i} \cos^n \theta_{i, \vec{k}}$$

- $n$ : 0, ..., 4
- $\alpha_i$ : shape parameter per atom
- $N_n$ : normalisation constant
- $\theta_{i, \vec{k}}$ : angle between  $\vec{r}_i$  and  $\vec{k}$ , bond direction
- up to 35 parameters per atom

(Hirshfeld, Hope, "An X-ray Determination of the Charge Deformation Density of 2-Cyanoguanidine", Acta Cryst **B36** (1980), 406–415)

## Multipole model — Hansen & Coppens, 1978

$$\rho_{\text{atom}}(x, y, z) = p_c \rho_{\text{core}}(r) + p_v \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum_{l=0}^{l_{\text{max}}} \kappa'^3 R_l(\kappa' r) \sum_{m=-l}^l p_{lm} d_{lm}(\theta, \phi)$$

$$d_{lm} = \begin{cases} N'_{lm} P_l^m(\cos \theta) \cos(m\phi) & m \geq 0 \\ N'_{lm} P_l^m(\cos \theta) \sin(m\phi) & m < 0 \end{cases}$$

$$P_l^m(x) = \left( \sqrt{1-x^2} \right)^m \left( \frac{d}{dx} \right)^{l+m} \frac{1}{2^l l!} (x^2 - 1)^l$$

- $p_c, p_v, p_{lm}$ : populations
- $R_l(\kappa' r)$  description of  $s$ -shell electron in transition metals.
- $P_l^m(x)$ : “associated Legendre polynomials”
- closely related to spherical harmonics

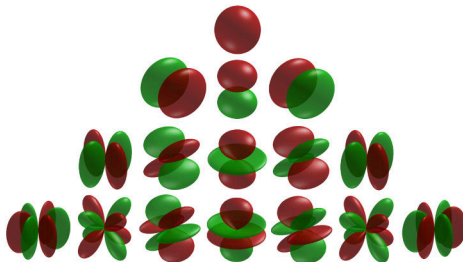
$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) e^{im\phi}$$

## Visualisation of spherical harmonics

- electrostatic potential of  $2^l$  point charges with total charge =  $0e$ .
- arbitrarily complex charge distribution

→ deformation of  $\rho_{\text{atom}}$

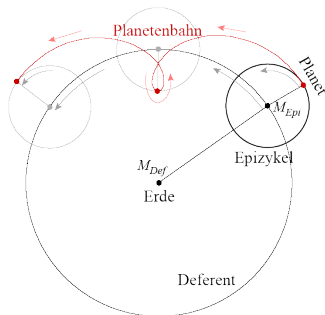
- favourable properties for certain differential equations like Maxwell equations, Schroedinger equation



[http://en.wikipedia.org/wiki/Spherical\\_harmonics](http://en.wikipedia.org/wiki/Spherical_harmonics)

## Number of parameters in MPM

- parameter = number to match model with data
- chemical interpretation depends on refined parameter values
- too many parameters: overfitting, uncertainty of correctness of the model



[http://de.wikipedia.org/wiki/Geozentrisches\\_Weltbild](http://de.wikipedia.org/wiki/Geozentrisches_Weltbild), according to Ptolemy

## Number of parameters in MPM

$$\rho_{\text{atom}}(x, y, z) = p_c \rho_{\text{core}}(r) + p_\nu \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum_{l=0}^{l_{\text{max}}} \kappa'^3 R_l(\kappa' r) \sum_{m=-l}^l p_{lm} d_{lm}(\theta, \phi)$$

1.  $\rho_{\text{core}}$ :  $x, y, z, U_{ij}, p_c$ :  $\geq 10$  parameters
2.  $\rho_{\text{valence}}$ :  $\kappa, p_\nu$
3. MPM parameters increase quickly with  $l_{\text{max}}$ :  $(l_{\text{max}}+1) \times \kappa' + \sum_{l=1}^{l_{\text{max}}} 2(l+1) \times N'_{lm}, p_{lm}$

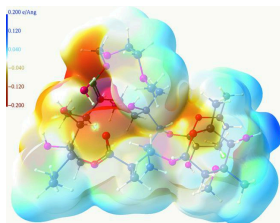
multipole model in crystallography usually uses  $l_{\text{max}} = 3$  or  $l_{\text{max}} = 4$

up to 35 parameters per atom, compared with 9 for the IAM  
ultra-high resolution required



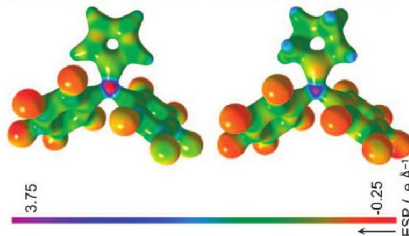
## MPM: electrostatic potential of molecules

Combination of the electron distribution with positively charged nuclei directly results in the Coulomb potential of the unit cell



ESP of Roxithromycin

J. Holstein *et al.*, Acta Cryst. B66 (2010)  
568ff



ESP of  $(C_6F_5)_2BNC_4H_4$  and  
 $(C_6F_5)_2BNC_4H_8$

U. Flierler *et al.*, Chem. – Eur. J. (2009),  
Vol. 15, 4595–4601

## QTAIM – “Quantum Theory of Atoms in Molecules”

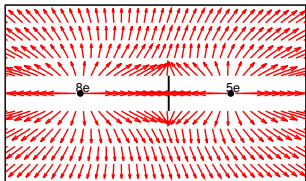
- Richard Bader ( $\approx$  1960)
- Definition of **atom** and **bond** in solid state materials
- Atom: peak of electron density
- Bond: connecting line (vertex)

## Chemical interpretation: QTAIM



[http://commons.wikimedia.org/wiki/File:Fuscherkarkopf-\\_Sinwelleck.JPG](http://commons.wikimedia.org/wiki/File:Fuscherkarkopf-_Sinwelleck.JPG)

## bond critical points — *bcp*



field lines between two charges

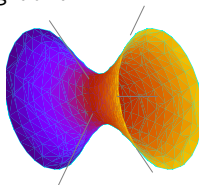
- electron cloud = negative charge
- attracted by nuclei
- between two atoms: cancellation

## bond critical points — *bcp*

According to “quantum theory of atoms in molecules” (QTAIM): two atoms are chemically bound if there is a (3,-1)-critical point (“bind critical point”) on their common (charge) surface

**bond critical point position** ( $x_c, y_c, z_c$ ):

1.  $\nabla\rho(x_c, y_c, z_c) = 0$  — cancellation of field lines
2. Hesse matrix  $H(\rho(x_c, y_c, z_c)) = \left( \frac{\partial^2 \rho(x_c, y_c, z_c)}{\partial x_i \partial x_j} \right)$  with
  - two negative eigenvalues: decreasing  $\rho$  perpendicular to bond
  - one positive eigenvalue: increasing  $\rho$  along bond



<http://en.wikipedia.org/wiki/Hyperboloid>

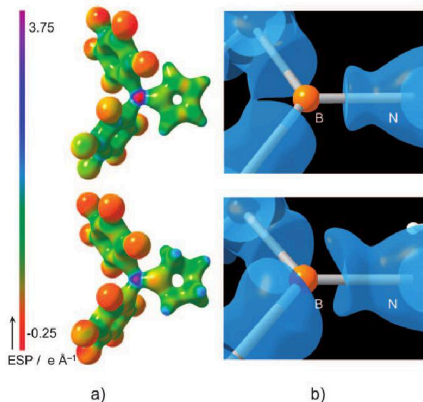
## The Laplace surface

- Surface presentation of

$$\begin{aligned}\nabla^2\rho(x, y, z) &= \frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} + \frac{\partial^2\rho}{\partial z^2} \\ &= \text{trace}(H(\rho(x, y, z)))\end{aligned}$$

- $\nabla^2\rho(x, y, z) < 0e\text{\AA}^{-5}$  electron concentration, characteristic for **covalent bond**
- $\nabla^2\rho(x, y, z) > 0e\text{\AA}^{-5}$  electron sink, indicates an **ionic bond**

## The Laplace surface



- $\nabla^2\rho(x, y, z)$  for
  - $(C_6F_5)_2BNC_4H_4$  and
  - $(C_6F_5)_2BNC_4H_8$

- Plotting of

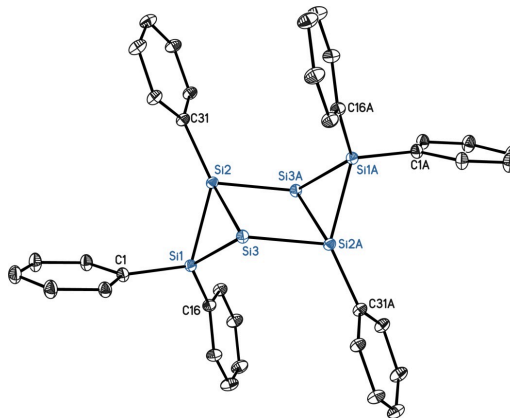
$$\nabla^2\rho(x, y, z) = 0e\text{Å}^{-5}$$

- reactive surface (of the Boron):  
Location of change of sign of the  
“Laplacian”

U. Flierler *et al.*, Chem.–Eur. J. (2009), Vol.  
15, 4595–4601

## Example Hexasilabenzene [1]

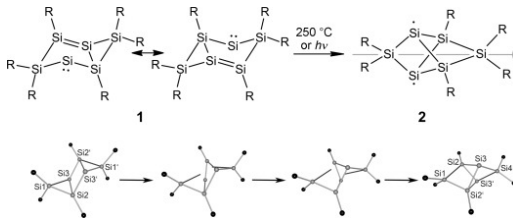
(PhD thesis Dr Daniel Kratzert, Prof. Stalke (Uni Göttingen))





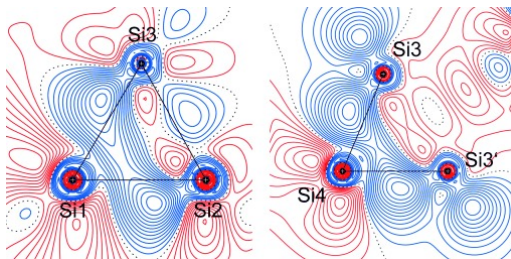
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(PhD thesis Dr Daniel Kratzert, Prof. Stalke (Uni Göttingen))



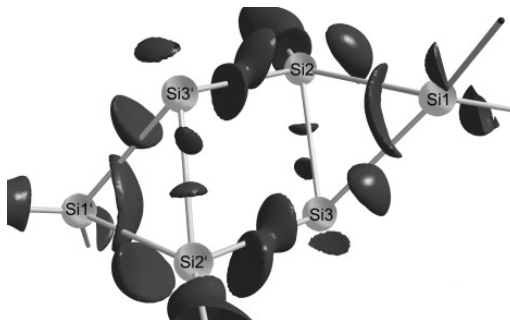
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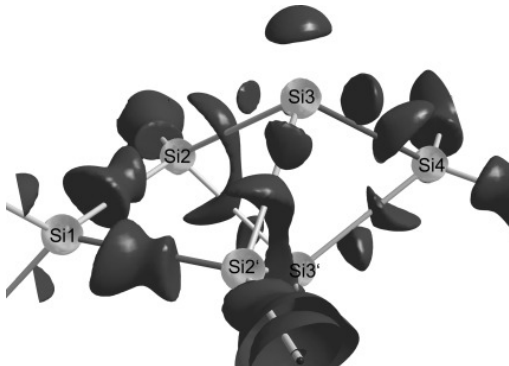
(PhD thesis Dr Daniel Kratzert, Prof. Stalke (Uni Göttingen))



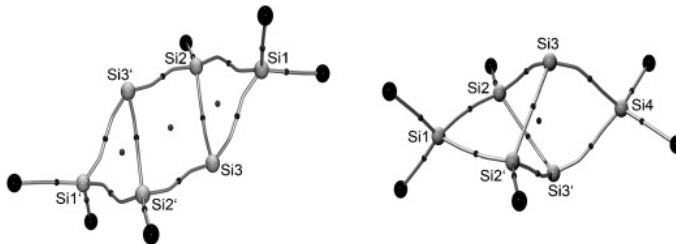
- No interaction for the through-space interaction between Si3 and Si3'
- Si1-Si2-Si3 triangle typical example of strained ring systems with bent bonds

## Example Hexasilabenzene [1]

(PhD thesis Dr Daniel Kratzert, Prof. Stalke (Uni Göttingen))



## Example Hexasilabenzene [1]



- actual bonds and connectivity for hexasilabenzene
- bonds are not straight lines

## References

- [1] Daniel Kratzert et al. 'An Experimental Charge Density Study of Two Isomers of Hexasilabenzene'. In: *Angew. Chem., Int. Ed.* 52 (2013), pp. 4478–4482. DOI: 10.1002/anie.201209906.