Single crystal diffraction

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Acknowledgements

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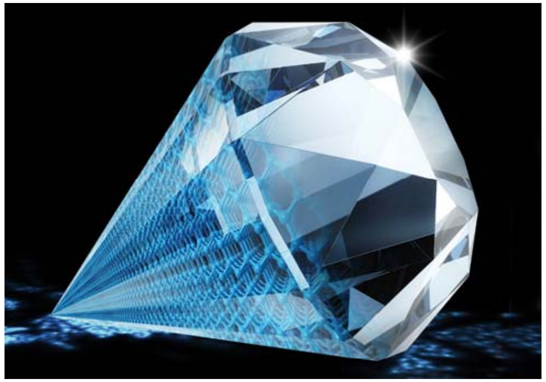
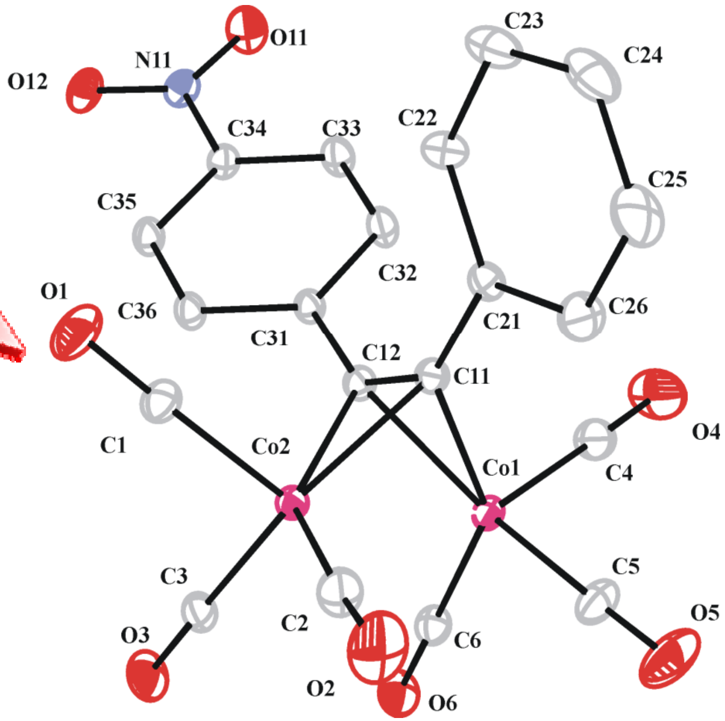
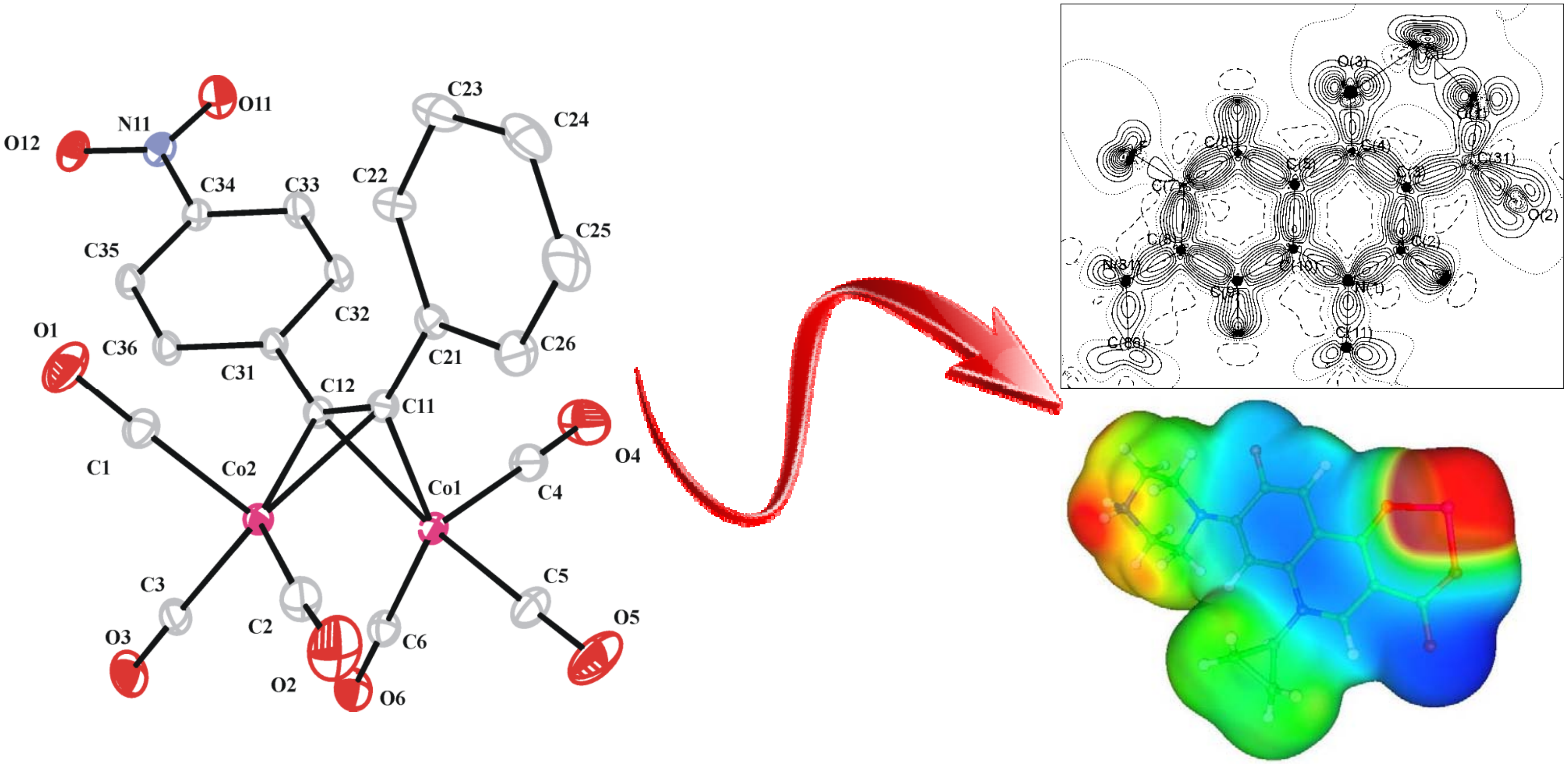
The ambition of this talk…





... to understand the steps involved in this process..

The ambition of this talk…



... and as a bonus also these steps..

Overview of the presentation

Part One

- **Understanding of single crystals – and why they are so important in science**
- **Taking crystallography a step further – Extension of the IAM**
- **Experimental requirements & challenges**
- **Synchrotron radiation – why?**

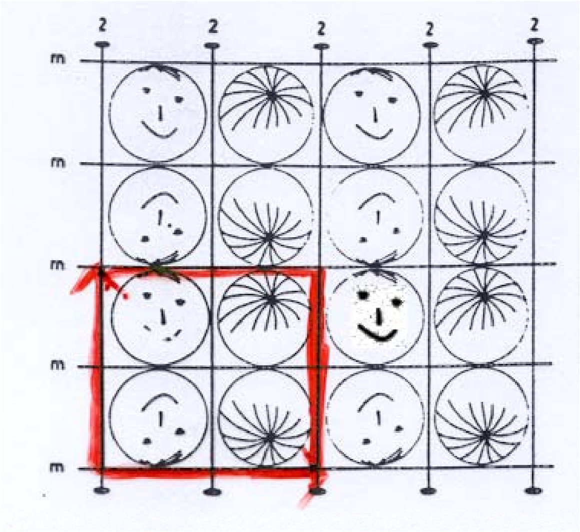
Part Two

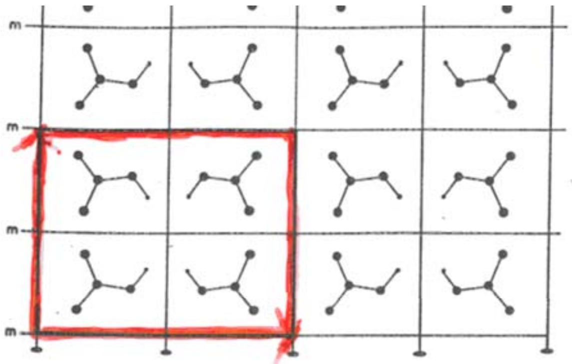
- **Time for some examples**

Single crystals

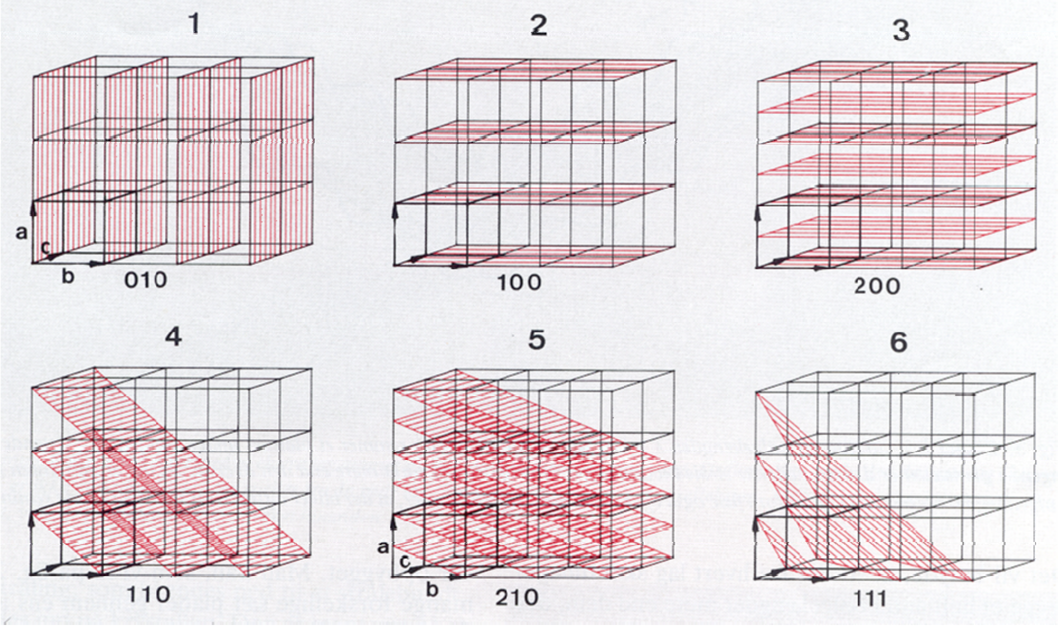
What is inside a single-crystal?

Definition: *“An arrangement of molecules or atoms, which is periodic in 3D”*



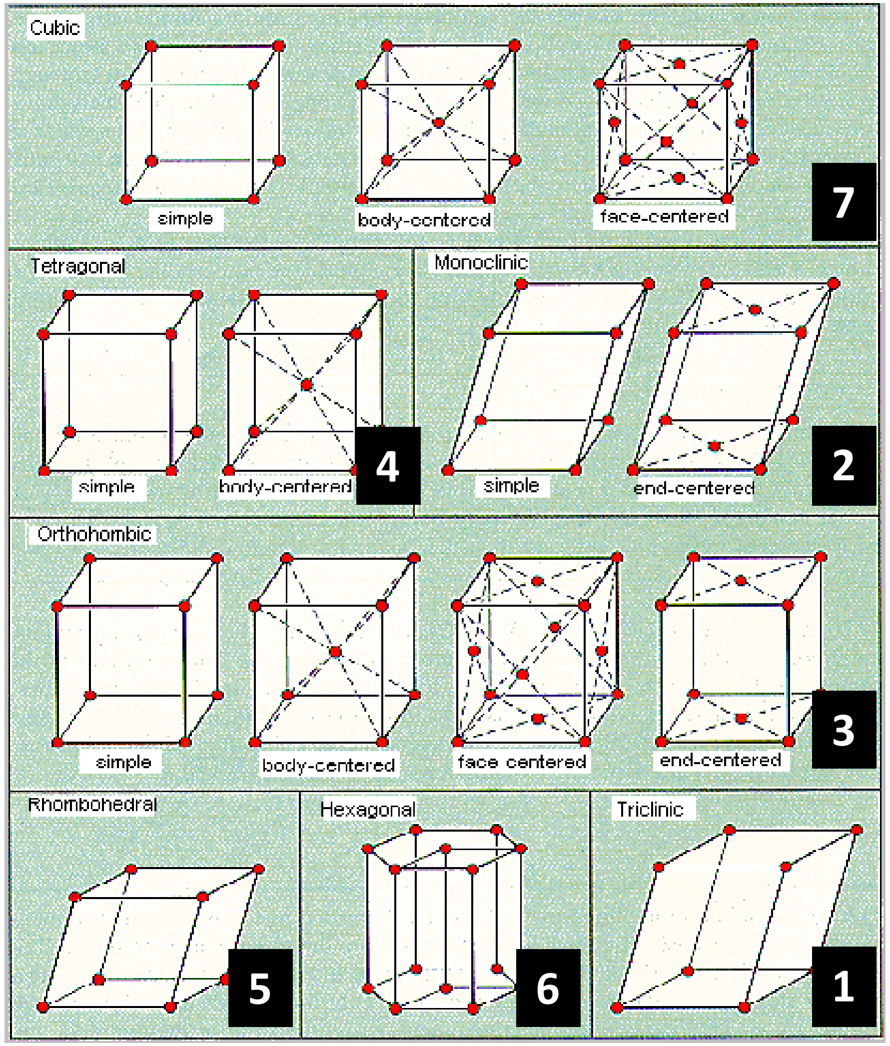


Crystal planes are named using Miller indices (reciprocal of the crossing with the axes)



Unit cell denotes a coordinate system

The building block – the unit cell



Low symmetry

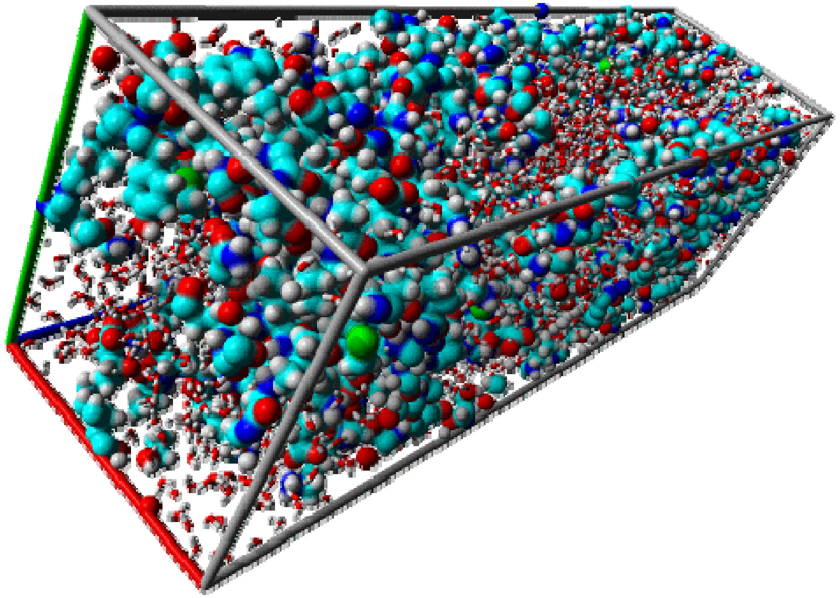
↓

High symmetry

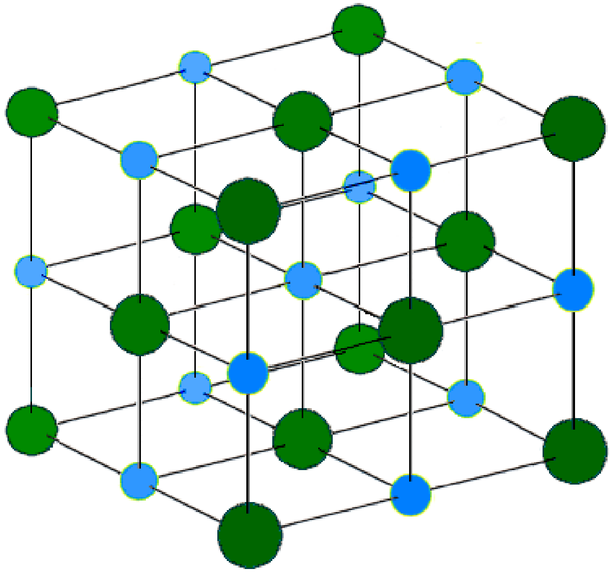
1. ***Triclinic*** *($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90$)*
2. ***Monoclinic*** *($a \neq b \neq c$, $\alpha \neq \gamma \neq 90$, $\beta = 90$)*
3. ***Orthorhombic*** *($a \neq b \neq c$, $\alpha = \beta = \gamma = 90$)*
4. ***Tetragonal*** *($a = b \neq c$, $\alpha = \beta = \gamma = 90$)*
5. ***Rhombohedral*** *($a = b = c$, $\alpha = \beta = \gamma$)*
6. ***Hexagonal*** *($a = b \neq c$, $\alpha = \beta = 90$, $\gamma = 120$)*
7. ***Cubic*** *($a = b = c$, $\alpha = \beta = \gamma = 90$)*

Atomic parameters

The atomic coordinates are refered to the three basis vectors of the unit cell: **a, b, c,** and are called *x,y,z.*

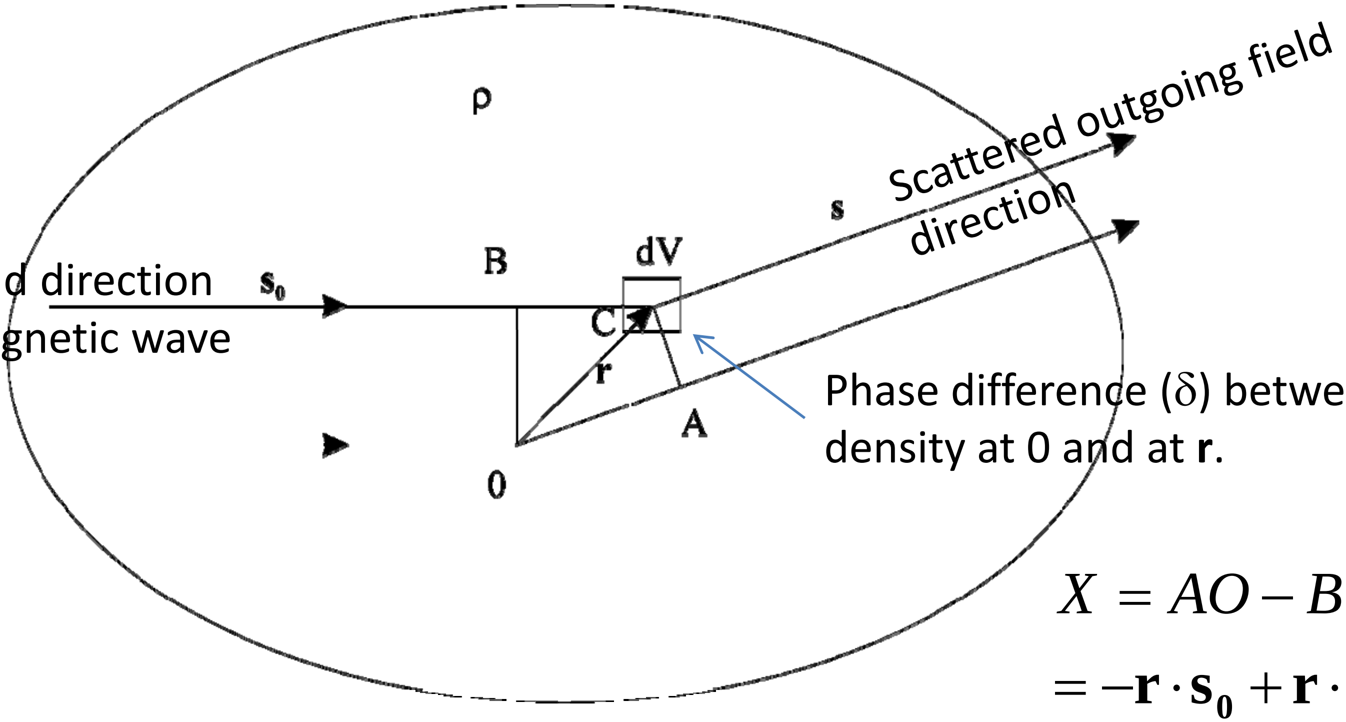


Complicated



Simple

Scattering from a material unit



Incoming field direction of electromagnetic wave

Scattered outgoing field direction

Phase difference (δ) between density at 0 and at **r**.

$$X = AO - BC$$

$$= -\mathbf{r}\cdot\mathbf{s}_0 + \mathbf{r}\cdot\mathbf{s}$$

$$\delta = \frac{2\pi}{\lambda}\mathbf{r}\cdot\left(\mathbf{s} - \mathbf{s}_0\right)$$

$$= 2\pi\mathbf{r}\cdot\mathbf{r}^*$$

$$\left|\mathbf{r}^*\right| = 2\sin\theta/\lambda$$

Interference patterns arise due to the spatial separation of scattering centers.

Scattering from a material unit

The observer sees a wave:

$$F(\mathbf{r}^*) = \sum_{j=1}^{N} A_j \exp(2\pi i \mathbf{r} \cdot \mathbf{r}^*)$$

Scattering from an atom:

$$f(\mathbf{r}^*) = \int_V \rho(\mathbf{r}) \exp\left(2\pi i \mathbf{r} \cdot \mathbf{r}^*\right) d\mathbf{r}$$

$$f(\mathbf{r}^*) = T\left[\rho(\mathbf{r})\right]$$

In other words, the scattering from an atom is the ***Fourier transform of the atomic electron density***

Scattering from a molecule

ASSUMPTION: Chemical bonding does not exist!

The molecular density is a simple sum of non-interacting atomic densities, ie the

Independent Atom Model (IAM).

$$\rho_{mol}(\mathrm{r}) = \sum_{atoms} \rho_j(\mathrm{r} - \mathrm{r_j})$$

Scattering amplitude

$$= \sum_{j=1}^{N} \left(\int_V \rho_j\left(\mathrm{r} - \mathrm{r_j}\right) \exp\left(2\pi i \mathrm{r} \cdot \mathrm{r}^*\right) d\mathrm{r} \right)$$

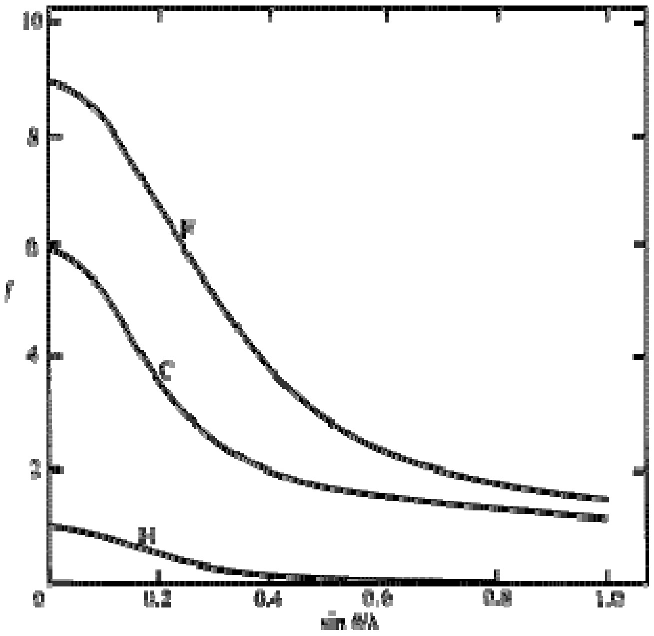
Continuous function

$$= \sum_{j=1}^{N} f_j\left(\mathrm{r}^*\right) \exp\left(2\pi i \mathrm{r}_j \cdot \mathrm{r}^*\right)$$

Atomic scattering factor

$$f_{atom}\left(\mathrm{r}^*\right)=\int_V \rho\left(\mathrm{R}\right)\exp\left(2\pi i\mathrm{R}\cdot\mathrm{r}^*\right)d\mathrm{R}$$

$$f_{atom}\left(0\right)=\int_V \rho\left(\mathrm{R}\right)d\mathrm{R} = Z$$



Now we need single crystals!

$$\sum_{j=1}^{N} f_j\left(\mathrm{r}^*\right)\exp\left(2\pi i \mathrm{r}_j \cdot \mathrm{r}^*\right)$$

Scattered radiation amplitude = convolution of unit cell density and Fourier transform of lattice function

Infinite 3D lattice: $$L(\mathbf{r}) = \sum_{n=-\infty}^{+\infty} \delta\left(\mathbf{r} - n\mathbf{r}\right)$$

$$F(\mathbf{r}^*) = F_M(\mathbf{r}^*)\frac{1}{V}\sum_{h,k,l=-\infty}^{+\infty} \delta\left(\mathbf{r}^* - \mathbf{r}_H^*\right)$$

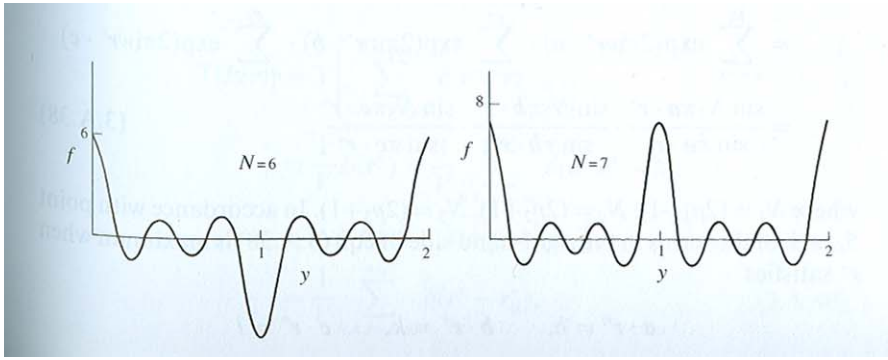


Fig. 3.A.5
The function $f(y) = \sin N\pi y / \sin \pi y$ for $N = 6, 7$.

Reciprocal lattice

1. Only diffracted waves at certain directions where: $r^* = r^*_H$ (**Bragg reflections**)
2. The crystal can be considered an “amplifier” of the signal (**Interference**)
3. The directions of scattering are given by the reciprocal lattice

Summarized in the Laue equations: $\mathbf{a}\cdot\mathbf{r}^* = h; \mathbf{b}\cdot\mathbf{r}^* = k; \mathbf{c}\cdot\mathbf{r}^* = l$

Scattering only takes place in certain directions: $\mathbf{r}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* = \mathbf{H}$

This is the reciprocal lattice!

The structure factor

The crystallographic structure factor is the amplitude of scattering from the unit cell, ie. the Fourier transform of the unit cell electron density, and it is given by:

$$F(\mathbf{H}) = \sum_j f_j \exp\left(2\pi i \mathbf{H}\cdot\mathbf{r}_j\right) * T_j$$

!!!! This is the basis of all crystallography !!!!!

The structure factor

The structure factor can be written in different ways, emphasizing certain characteristics of it:

“Normal”

$$F(\mathbf{H}) = \sum_{j}^{N} f_j \exp\left(2\pi i \mathbf{H}\cdot\mathbf{r}_j\right)$$

Complex no

$$F(\mathbf{H}) = \sum_{j}^{N} f_j \exp\left(2\pi i \mathbf{H}\cdot\mathbf{r}_j\right) = A_{\mathbf{H}} + iB_{\mathbf{H}}$$

$$A_{\mathbf{H}} = \sum_{j}^{N} f_j \cos\left(2\pi \mathbf{H}\cdot\mathbf{r}_j\right) \quad B_{\mathbf{H}} = \sum_{j}^{N} f_j \sin\left(2\pi \mathbf{H}\cdot\mathbf{r}_j\right)$$

$$F_{hkl} = \sum_{j}^{N} f_j \exp\left(2\pi i\left(hx_j + ky_j + lz_j\right)\right)$$

Phase

$$F\left(\mathbf{H}\right) = \left|F\left(\mathbf{H}\right)\right| \exp\left(i\varphi_{\mathbf{H}}\right), \varphi_{\mathbf{H}} = \arctan\left(\frac{B_{\mathbf{H}}}{A_{\mathbf{H}}}\right)$$

Historical background

Basic structure factor: $F(\mathbf{H}) = \sum_{i=1}^{nat} f_i(\mathbf{H}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_i) T_i$

$$f(\mathbf{S}) = \int \rho_{at}(\mathbf{r}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) d\mathbf{r}$$

Born-Oppenheimer approximation

$$\rho_{free}(\mathbf{r}) = \int \rho(\mathbf{r} - \mathbf{u}) p(\mathbf{u}) d\mathbf{u} = \rho_{static}(\mathbf{u}) \otimes p(\mathbf{u})$$

$$f_{atom}(\mathbf{r}^*) = f_{static}(\mathbf{r}^*) q(\mathbf{r}^*)$$

In theory, X-ray scattering gives info about the *FULL* electron distribution!

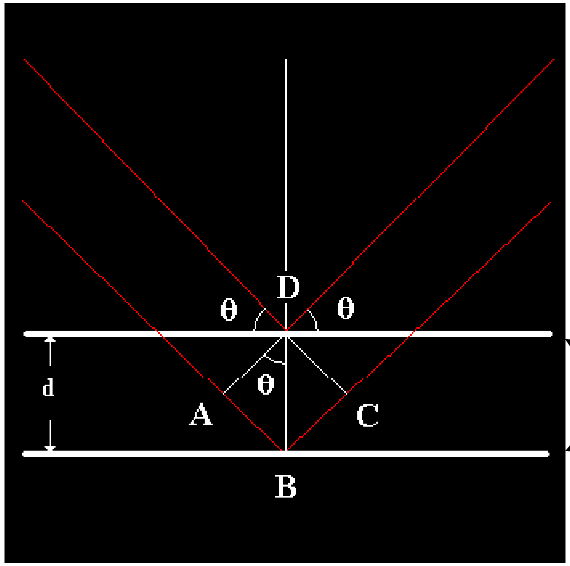
Braggs Lov

X-ray diffraction "sees" and interacts with the electrons.

To have diffraction in certain directions we require a large degree of constructive interference:

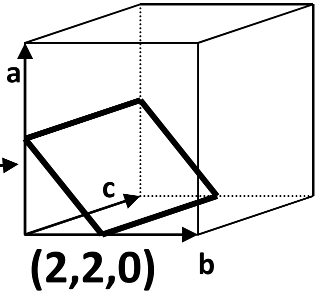
THEREFORE SINGLE-CRYSTALS!

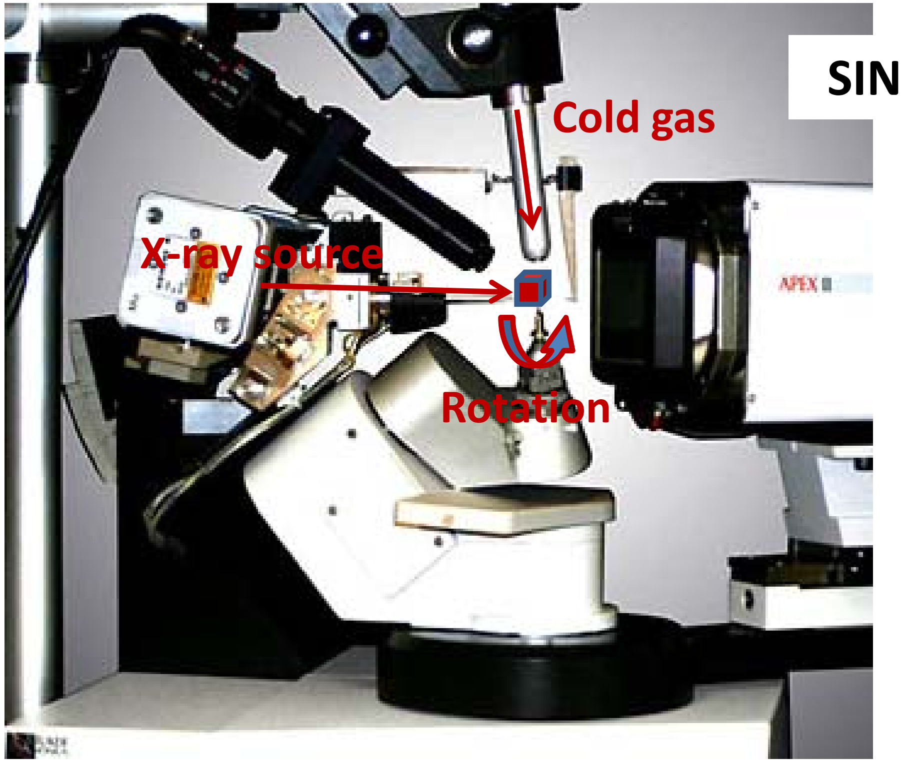
Ewald sphere



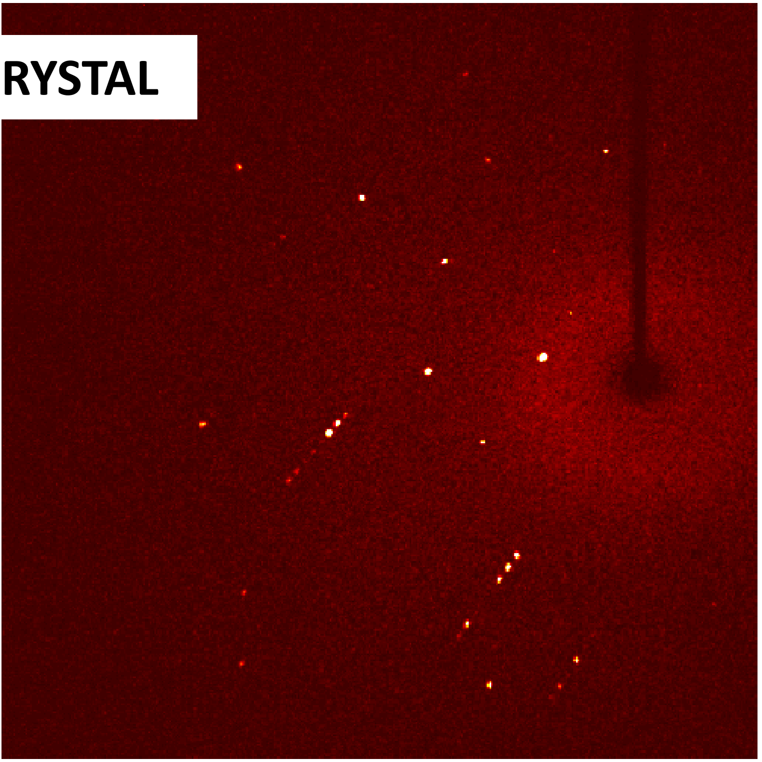
$$2d_H \sin\theta = \lambda$$

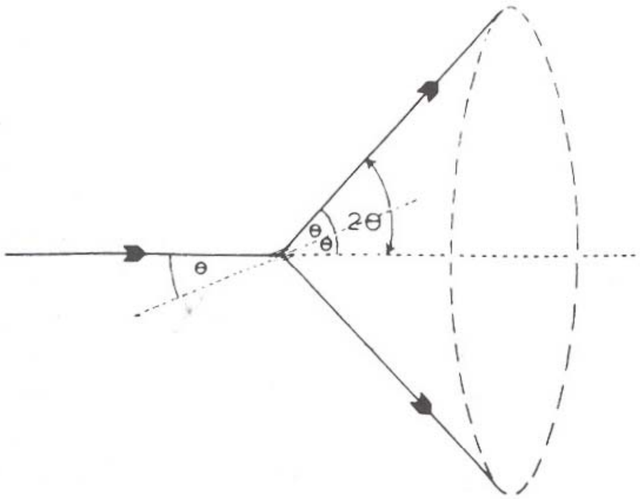
Lattice planes



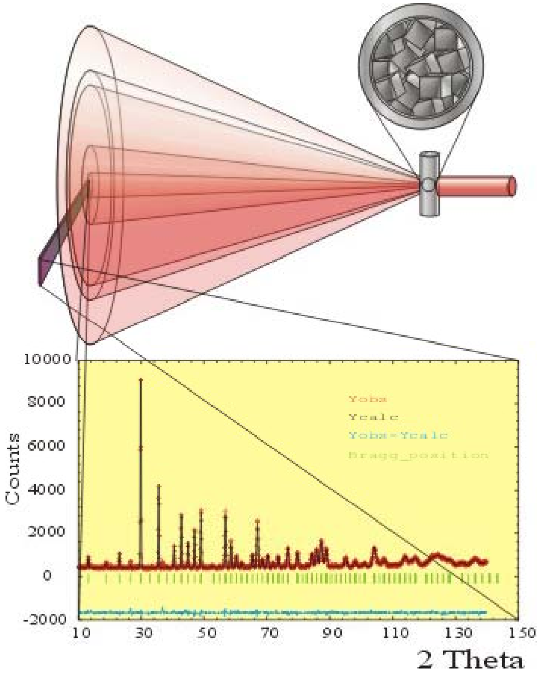


SINGLE CRYSTAL





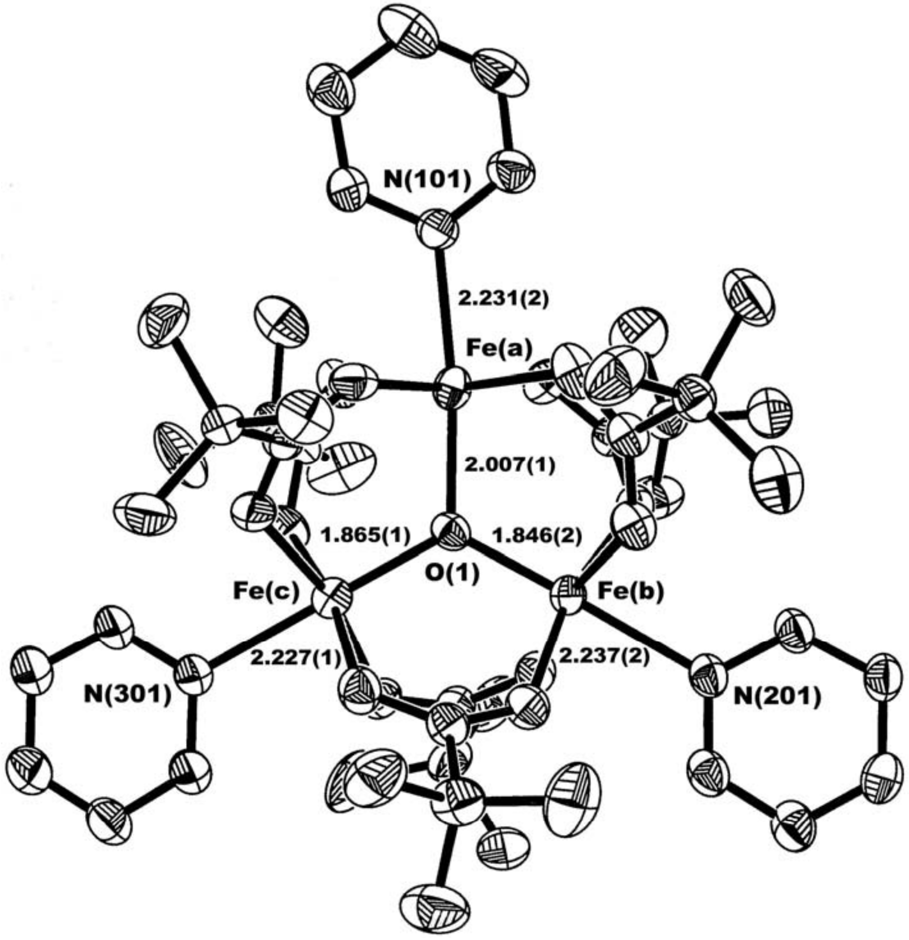
POWDER



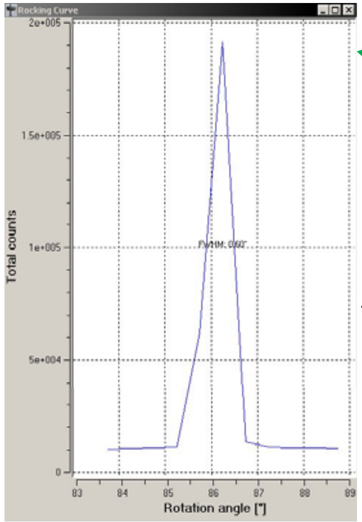
Normal structure determination (IAM)

”Result” of a crystallographic structure determination is the usual ORTEP-drawing which shows the **NUCLEAR PROBABILITY DENSITY FUNCTION**

The IAM model is only concerned with the core electrons/nuclear density. It works surprisingly well!



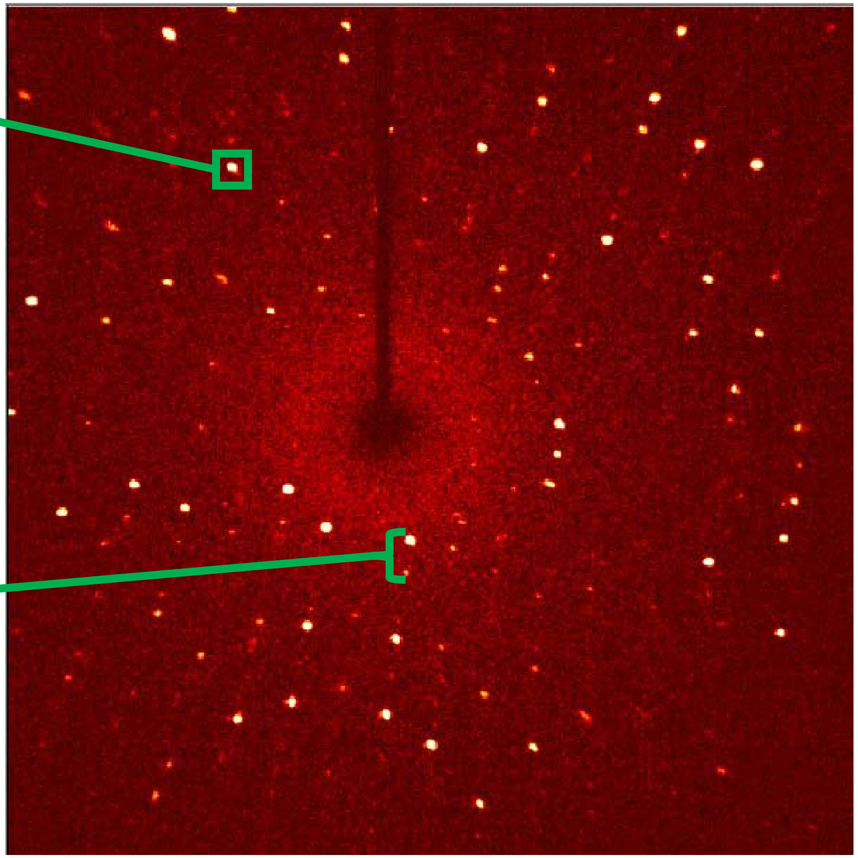
Interpretation of data



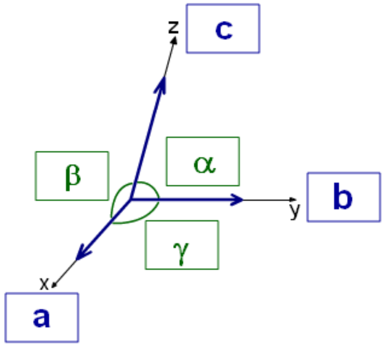
Reflections are observed over many frames

→**Integration:**

Reveals the content of the unit cell



Characteristic distance: Gives the dimensions of the unit cell



Problem almost solved ☺

$$I(\mathbf{H}) \propto |F(\mathbf{H})|^2$$

Intensities are measured using X-ray detectors ☺

$$F(\mathrm{H}) = \sum_{j}^{atomer} f_j \exp\left(2\pi i \mathrm{H}\cdot \mathrm{r}_j\right) = \overset{\text{Measured}}{\boxed{|F(\mathrm{H})|}}\,\overset{\text{Unknown!}}{\boxed{\exp(i\varphi)}}$$

Crystallographic PHASE PROBLEM!!!

Solution devised by Karle and Hauptman in 1985 – Nobel prize!

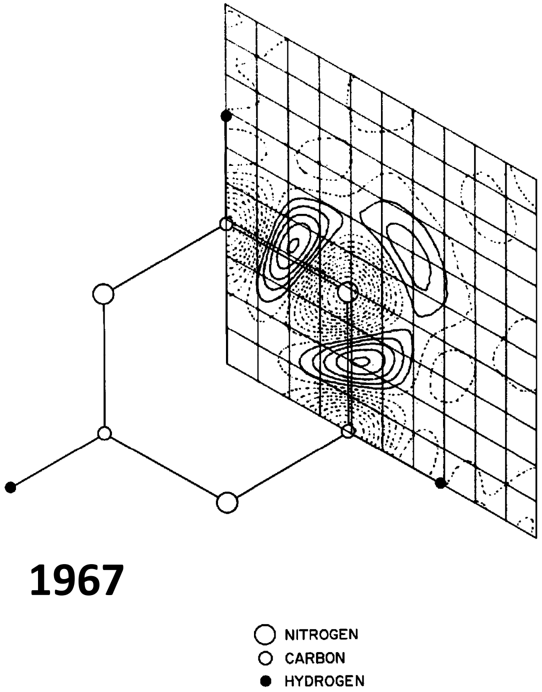
Short version: direct methods use probabilities of sets of structure factors – built in to software and automated – black box

$$\rho_{uc}(r) = \frac{1}{V_c}\sum F(\mathrm{H})\exp(-2\pi i \mathrm{H}\cdot \mathrm{r})$$

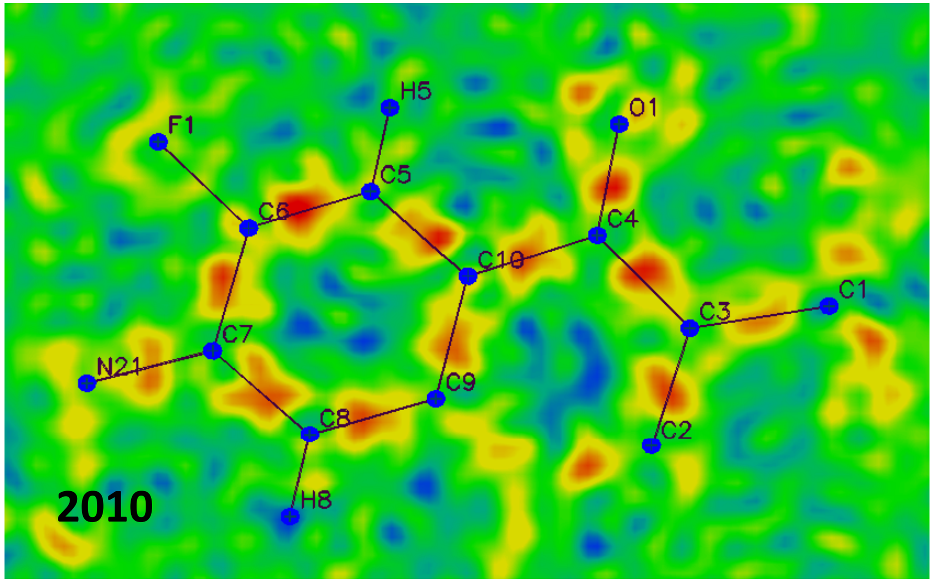
The electron density reveals ALL about the structure – we want to know this!

The IAM model

Difference Fourier maps: $\Delta\rho(\mathbf{r}) = \frac{1}{V_{uc}} \sum_{\mathbf{H}} \left(\frac{\mathbf{F}_{obs}(\mathbf{H})}{k} - \mathbf{F}_{calc}(\mathbf{H}) \right) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r})$



1967



2010

Can we quantify this additional information?
YES

Expanding the atomic model

Stewart (1969): Derives Generalized scattering factors from orbital products.
Suggests that the effects are significant enough to be measured.

Hansen-Coppens (1978): Builds on the work by Stewart, but uses a modified version where the angular part of the density functions are based on spherical harmonic functions :

ρ *= core + valence + deformation (bonding, lone pair etc)*

$$\rho(\mathbf{r}) = P_c \rho_c + P_v \rho_v(\kappa r)\kappa^3 + \sum_{l=0}^{l_{\max}} R_l(\kappa' r)\kappa'^3 \sum_{m=0}^{l} P_{lm\pm} d_{lm\pm}(\theta, \phi)$$

Characteristics of spherical harmonics

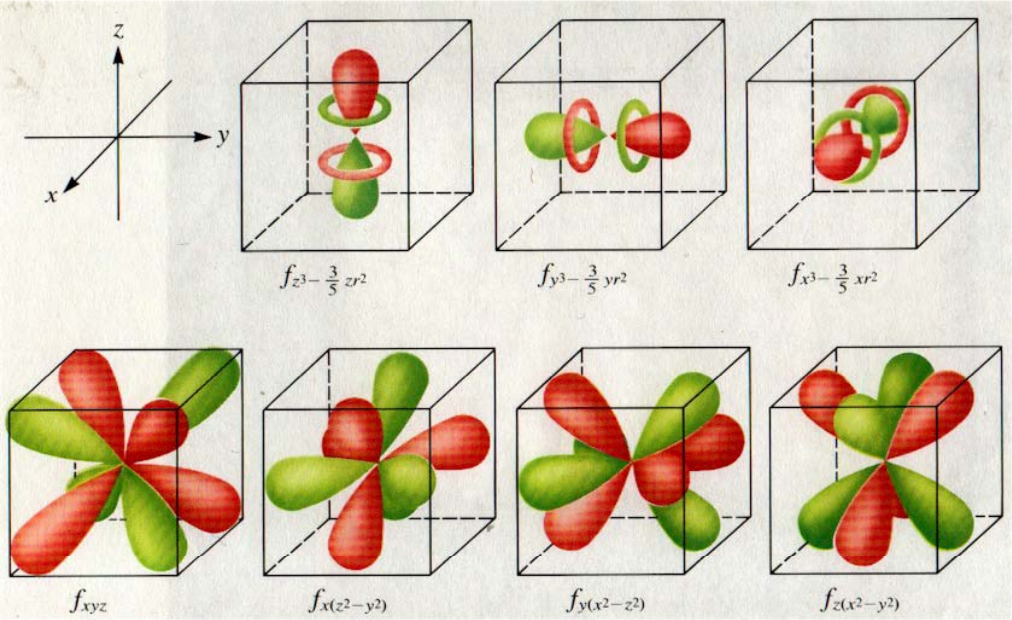
Hansen-Coppens structure factor:

$$F(\mathbf{H})=\sum_{i=1}^{nat} f_i(\mathbf{H})\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_i)T_i \rightarrow$$

$$F(\mathbf{H})=\sum_{i}\left(P_c f_{c,i}+P_v f_{v,i}(\mathbf{H}/\kappa)\kappa^3+4\pi\sum_{l=0}^{l_{\max}}\sum_{m=0,l}P_{lm\pm}i^l\langle j_l(H/\kappa')\rangle d_{lm\pm}(\beta,\gamma)\right)\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_i)T_i$$

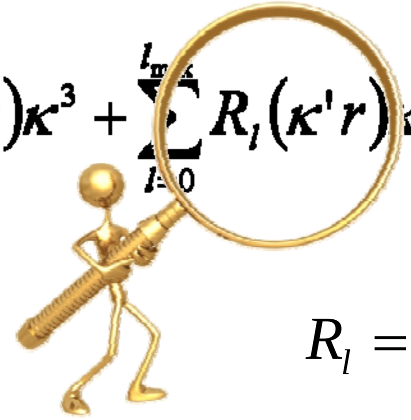
Ex. f-orbitalic functions (octopoles):

Charge is **<u>moved</u>** from red to green if the multipole is populated in the lsq.



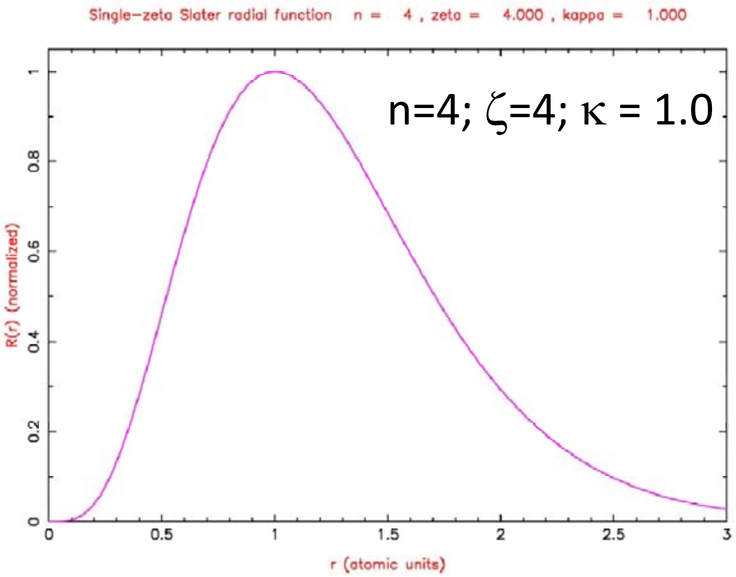
The radial function

$$\rho(\mathbf{r}) = P_c\rho_c + P_v\rho_v(\kappa r)\kappa^3 + \sum_{l=0}^{l_{max}} R_l(\kappa' r)\kappa'^3 \sum_{m=0}^{l} P_{lm\pm} d_{lm\pm}(\theta,\phi)$$



Nodeless, normalized, density functions:

$$R_l = \kappa'^3 \frac{\zeta^{n_l+3}}{(n_l+2)!} (\kappa' r)^{n_l} \exp(-\kappa' \zeta_l r)$$



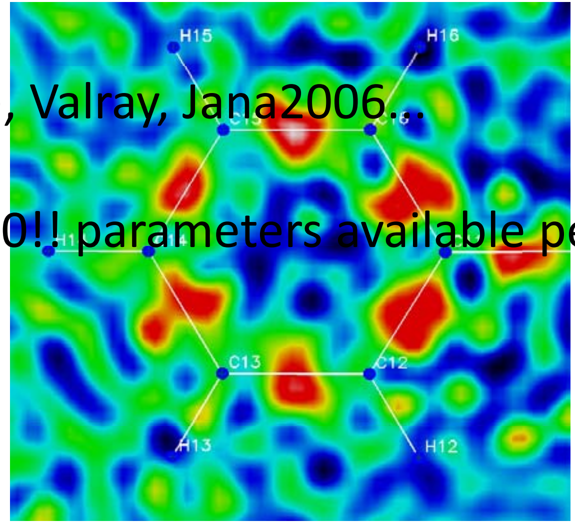
Refinement approach

A general entry to charge density modeling

- As always, complete an IAM structure determination (SHELX or other)
- Study the Fourier difference maps from the above – do they show excess bonding density or other characteristic trends? If yes, the option is there.

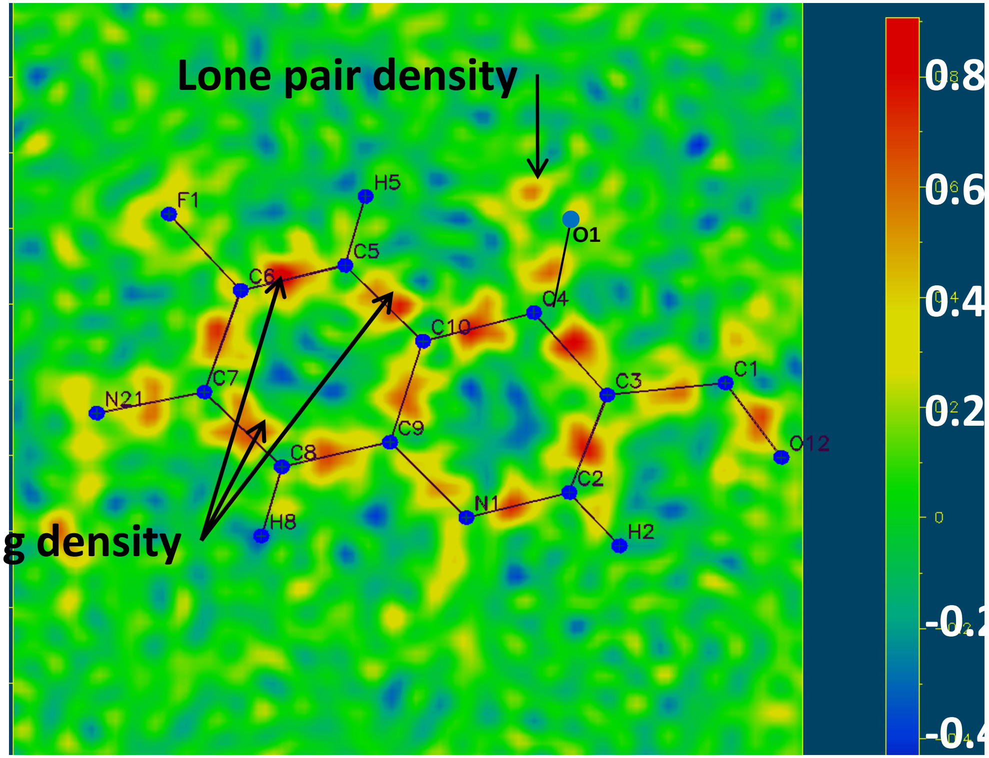
- Specialised software is required: XD (WinXD), Valray, Jana2006...

- 3(xyz)+6(U's)+1(κ)+25(anharm)+25(P_{lm}'s) = 60!! parameters available per atom



Any improvement of the fit?

IAM model: $\Delta F = (F(obs)-F(calc))$

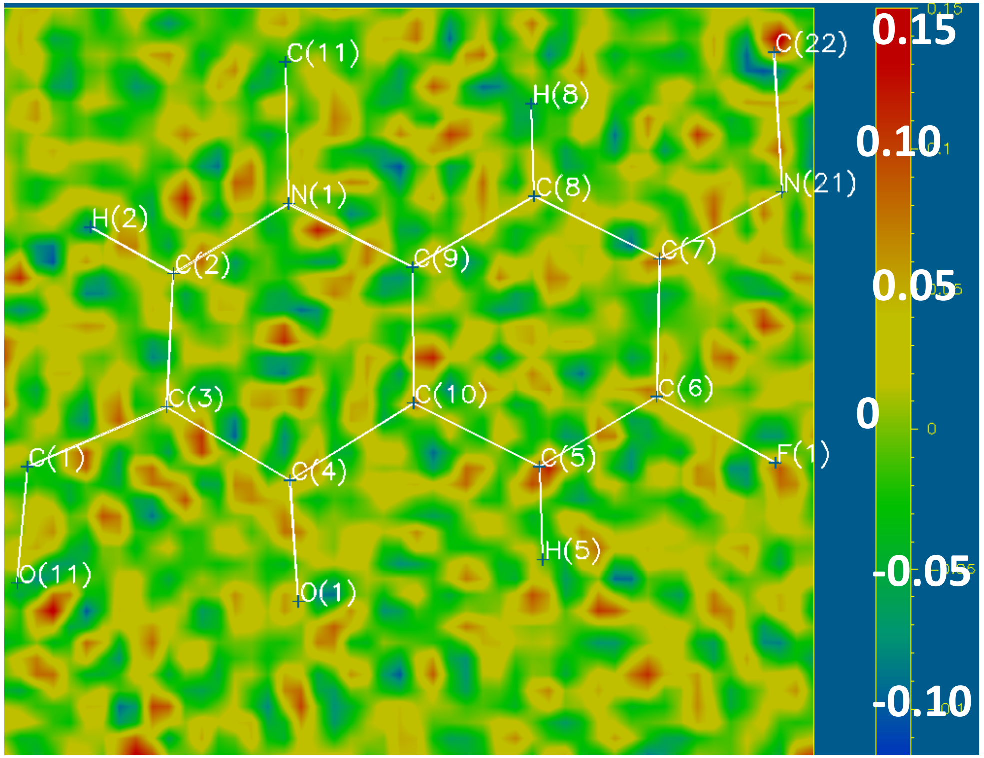


Lone pair density

Bonding density

Improvement

Multipole model: ΔF = (F(obs)-F(calc))



How suitable is your compound?

The suitability factor

The structure factors gives information on the FULL electronic distribution, while chemical bonding is primarily due to changes in the valence electrons!
The relative core scattering intensity per unit volume determines the suitability of the crystal for charge density determination:

$$S = \frac{V}{\sum_{i}^{u.c.} n_{core,i}^{2}}$$

Examples:

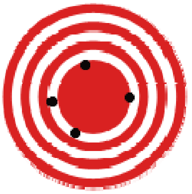
Formamide	4.7
Tetracyanoethylene	3.7
Co-dimer	0.35
S_8	0.26
Th-complex	0.07

The ideal way to charge density data

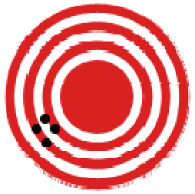
The ideal experiment has the following ingredients

- Significant diffraction to high-angle ($(\sin(\theta)/\lambda)_{max} > 1.0$ Å^{-1})
- Spherical or face-indexed crystal
- Very low temperature (liquid He-flow or closed-cycle cryostat)
- High incoming intensity, eg. synchrotron X-ray source with high brilliance
- Neutron data for H-parameters (position and anisotropic adp)
- High accuracy as well as high precision (as in low R(int) from Sortav etc.)

low precision
high
accuracy →



high
precision low
accuracy →



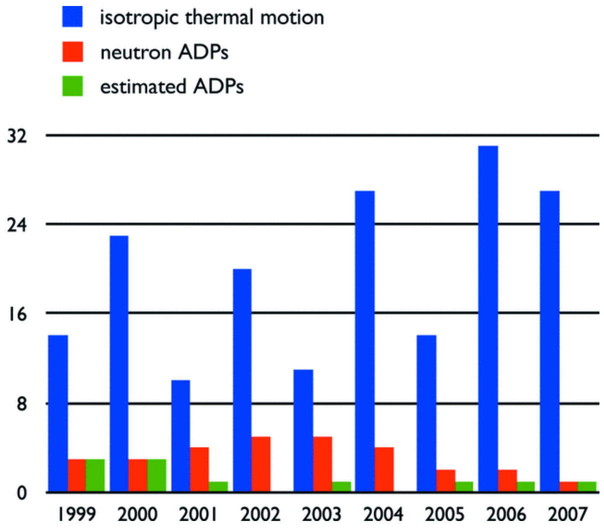
How can we determine what we have?

- Comparison with theoretical calculations
- Comparison of data from different sources and using different equipment, detectors...

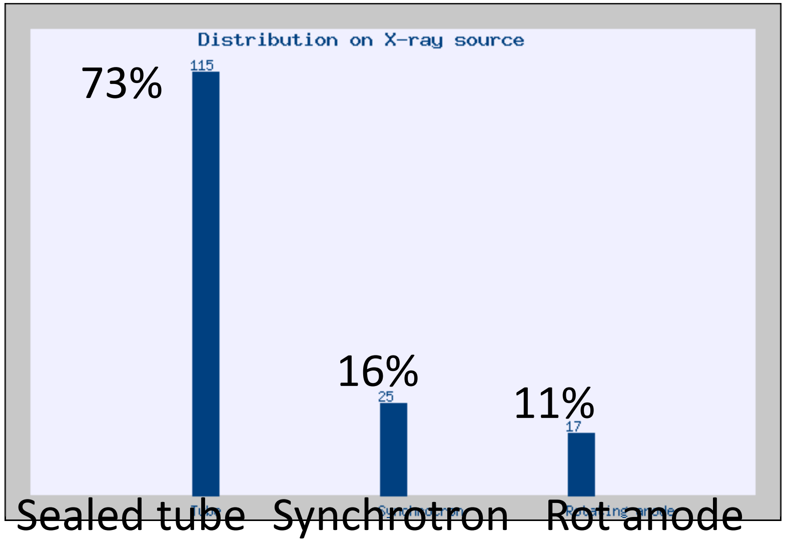
The actual way to charge density data

Are all CD studies following this route? Some numerical facts:

Maximum sin(θ)/λ > 1.0 Å^{-1}:	93% (recently, this is easier to achieve)
Using He-cooling:	30% (expensive & problematic)
Using synchrotron or rotating anode:	27% (beam time limitations & problematic)
Combined with neutron data:	~10% (large crystals necessary – SNS??)

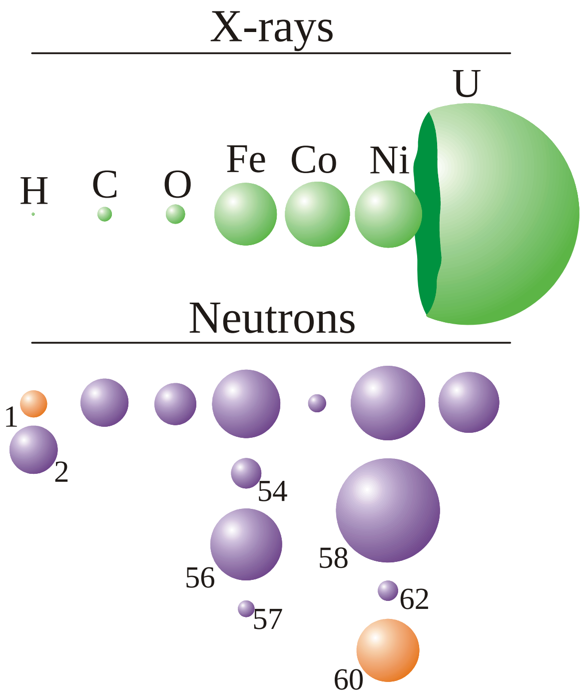


Spackman *et al., Acta Cryst.* **2008**, A**64**, 465-475



The hydrogen problem

…no reasonable estimate of the charge-density parameters can be obtained without an adequate description of thermal motion.‘ (Koritszansky & Coppens, 2001)

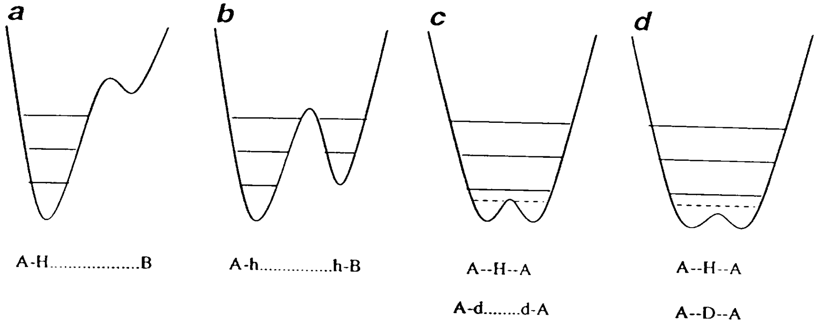


Hydrogen characteristics:

Very weak scatterer

No core electrons => asphericity shift

Potential Energy Surface

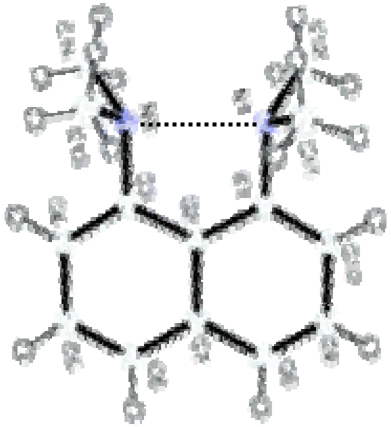


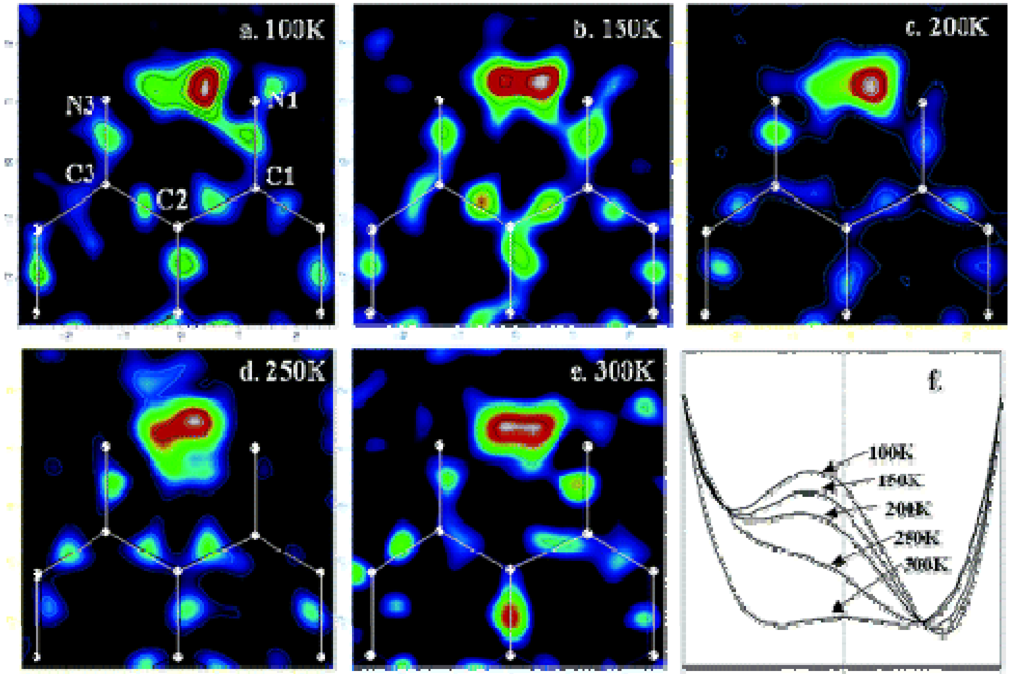
WEAK STRONG

Strong hydrogen bonds have partial covalency

Hydrogen dynamics

- Accurate multi-temperature X-ray studies combined with difference Fourier methods may illustrate the proton movement, i.e. reveal details of the potential energy surface

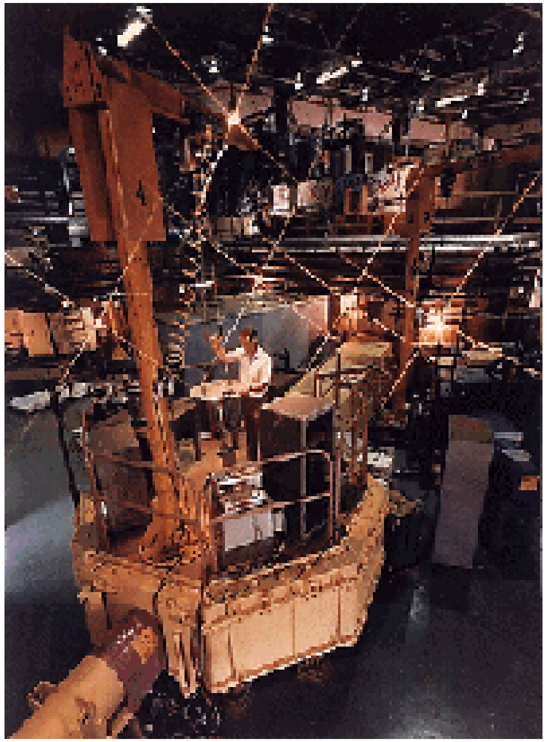




A. Parkin, K. Wozniak, C. C. Wilson *Cryst. Grow. Des.* **2007**, *7*, 1393. Reproduced courtesy of Andrew Parkin, University of Glasgow.

Combining neutrons with X-rays

- Grow LARGE crystals (volume > 1 mm^3)
- Preferably use very low T (~15 K) – matching for X and N
- From N exp: refine X and U_{ij} values for ALL atoms.
- From X exp: refine an IAM with U_{ij} for heavy atoms.



IPNS

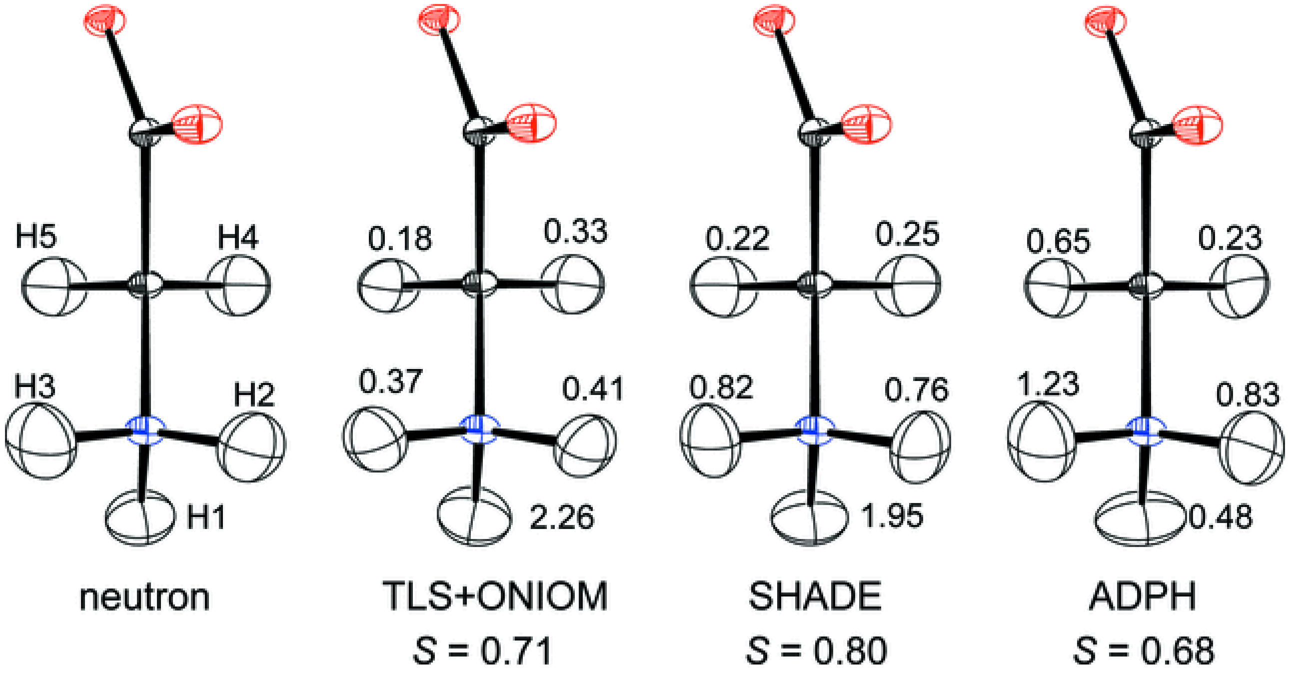
Combining neutrons with X-rays

- A scaling of U_{ij} between X and N is necessary: **program UIJXN** by Robert Blessing
  $U_{ij}(X) = k*U_{ij}(N) + \Delta U_{ij}$
- Ap
- How well should X and N compare – some benchmark numbers:

Compound	**Temp**	**# HA**	$\langle\Delta U\rangle$	$\langle U_{ii,X}/U_{ii,N}\rangle$
OxHy complex	10	15	0.00076(45)	0.97(21)
Cu(OH2)6(SO4)2(NH4)2	9	10	0.00031 (23)	0.97 (7)
Ni(NO2)2(NH3)4	9	5	0.00018 (27)	0.96 (5)
Catalytic triade	28	50	0.00091 (80)	1.01 (2)
KHC2O4	11	7	0.00030 (3)	0.99 (1)
MoO(O2)(HMPA)(dipic)	28	27	0.00134 (40)	1.32 (1)
_-Glycine	23	5	0.00083 (86)	0.80 (11)
1-Methyluracil	21	9	0.00021 (24)	1.03 (8)
l-Alanine	23	6	0.00176 (165)	0.62 (5)
2-Methyl-4-nitroaniline	10	11	0.00150 (139)	1.28 (21)
MBADNP	20	21	0.00223 (189)	1.81 (26)
Acetamide	23	4	0.00273 (190)	1.62 (15)
Co(OD2)6SO4	25	12	0.00094 (72)	1.17 (28)
Xylitol	122	10	0.00113 (103)	1.23 (10)
Adenosine	100	19	0.00124 (109)	0.83 (4)
Nit(SMe)Ph	114	19	0.00186 (127)	1.16 (9)
Alloxan	123	7	0.00049 (39)	1.02 (5)
Beryllium metal	298	1	0.00008 (7)	1.00 (3)

What can we do without neutron data ☹

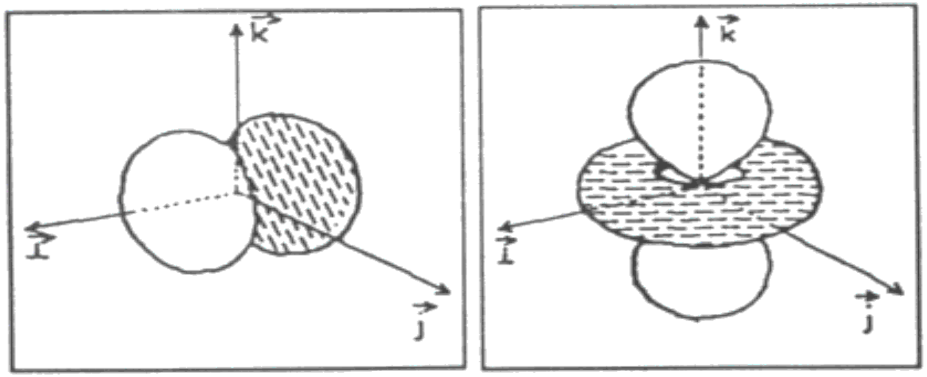
$$U_{tot}(H) = \underset{\substack{\uparrow \\ \text{atomic} \\ \text{vibrations}}}{U_{int}} + \underset{\substack{\nwarrow \\ \text{Rigid body} \\ \text{motion}}}{U_{ext}}$$



Madsen, A. Ø., Spackman, M. *et al*:
J. Appl. Crystallogr. **2006**, *39*, 757-758 & *Acta Cryst.* **2008**, A**64**, 465-475

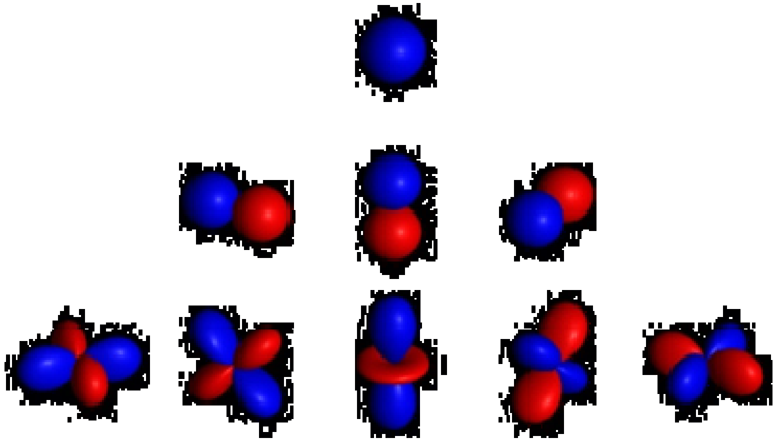
Hydrogen multipoles?

Isotropic U(H): only bond directed multipoles



Hydrogen multipoles?

Anisotropic U(H): all dipoles and quadropoles



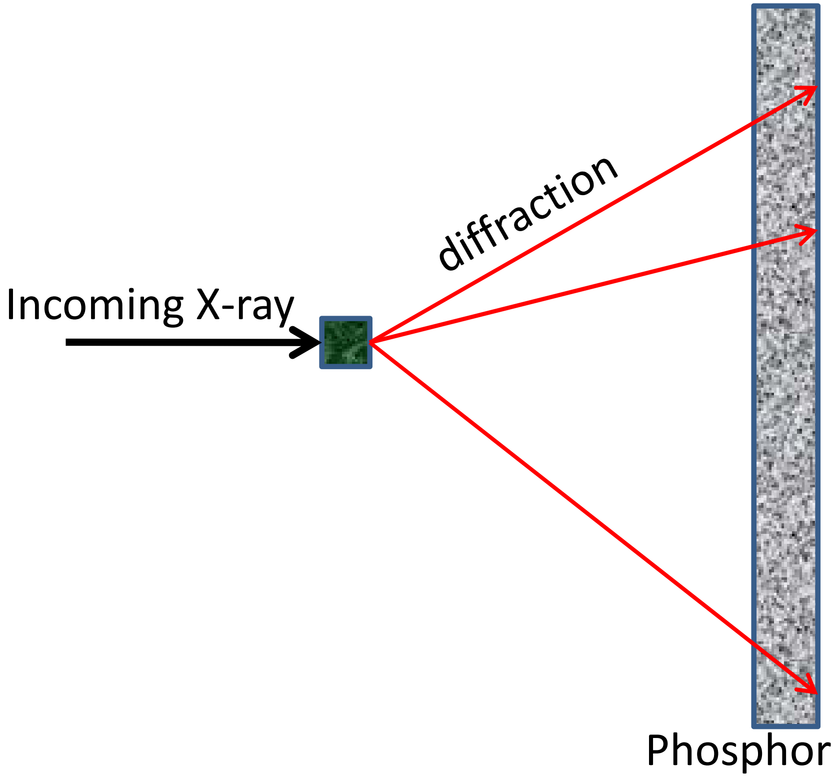
l=0

l=1

l=2

Synchrotron issues

Oblique incidence correction



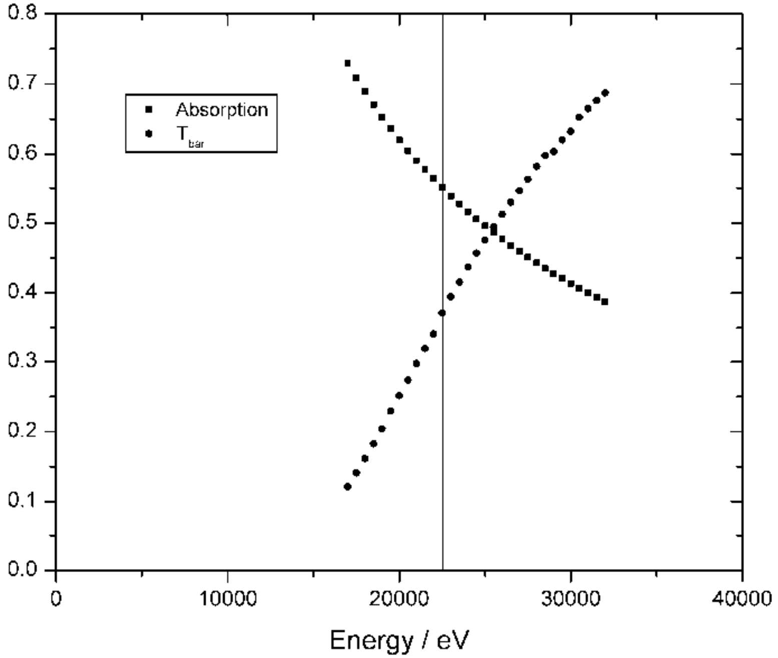
Path length (L) through phosphor depends on incidence angle, α

$$I \propto L$$

Oblique incidence correction

Incomplete absorption in the phosphor creates an incidence angle dependent correction. The used approach is adopted from work by Wu *et al* (1) in correction of APS data using this expression:

$$\frac{I_{corr}}{I_{meas}} = \frac{1-T}{1-\exp\left(\frac{\ln(T)}{\cos\alpha}\right)}$$

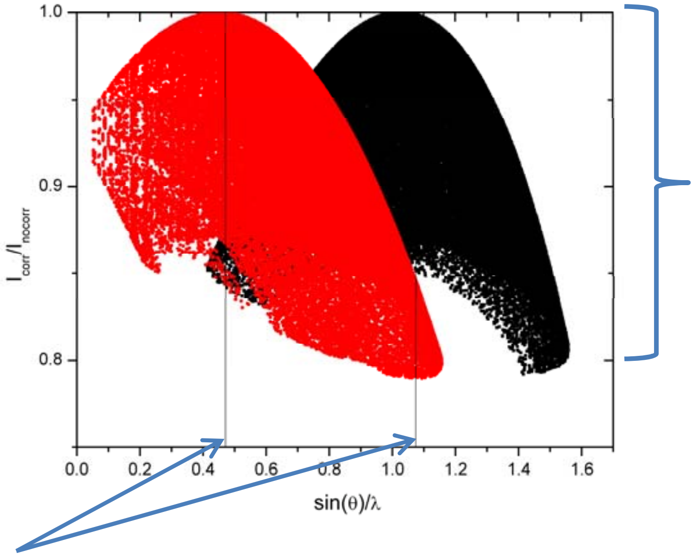


G. Wu, B. L. Rodrigues, P. Coppens, *J. Appl. Cryst.* **2002**, *35*, 356.

The absorption was measured as a function of wavelength on a sample piece of phosphor. This is used to obtain T_{bar} values for the the correction

Oblique incidence correction

The effect of the oblique incidence is very significant. Two series of data collected to high scattering angle.



Relative correction up to 20%!!

Perpendicular incidence

Oblique correction now in SADABS

The recurrent use of the oblique program has led the developers at Bruker to incorporate this into their software, despite the use of a flood field correction that should take care of the problem.

$$\frac{I_{corr}}{I_{meas}} = \frac{1-T}{1-\exp\left(\frac{\ln(T)}{\cos\alpha}\right)} \Leftrightarrow \frac{I_{corr}}{I_{meas}} = \frac{f}{1-(1-f)^{1/\cos\alpha}}$$

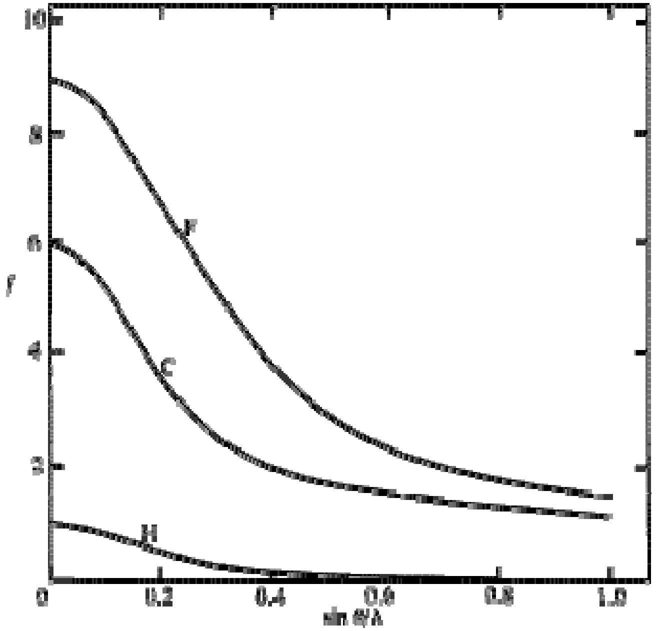
f = 1 - T = detector efficiency

Refinement details

A rough guide to charge density modeling

- Initiate with a refinement of the positional and thermal parameters using the high-angle data, typically maintaining a cut-off of at least 0.8 Å^{-1}.

Scattering factor functions



http://xrayweb.chem.ou.edu/notes/crystallography.html#scatter

Refinement details

A rough guide to charge density modeling

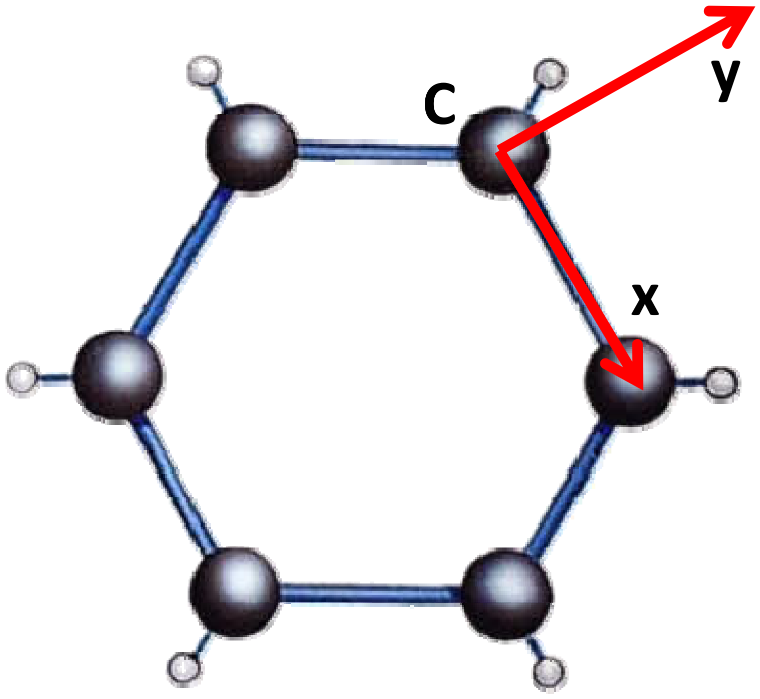
- Initiate with a refinement of the positional and thermal parameters using the high-angle data, typically maintaining a cut-off of at least 0.8 $Å^{-1}$.
- Fix these parameters. Now start with a κ-refinement of κ and P_v.
- Make clever local coordinate systems & find any possible non-crystallographic symmetry elements to introduce constraints on the choice of refinable P_{lm}'s.

Local coordinate system

Choose for each atom two neighbours to define the LCS.

If, for instance, a mirror plane is ⊥ z, then selection rules apply:

1	any	all (*l,m,±)*
1	any	(2 l,m, ±)
2	2‖z	*(l,2μ, ±)*
m	m⊥z	*(l,l-2μ, ±)*
2/m	2‖z, m⊥z	(2 l,2μ, ±)
222	2‖z, 2‖y	(2 l,2μ,+), (2l+1,2μ,–)
mm2	2‖z, m⊥y	*(l,2μ,+)*
mmm	m⊥z, m⊥y	(2l,2μ, +)



Refinement details

A rough guide to charge density modeling

- Initiate with a refinement of the positional and thermal parameters using the high-angle data, typically maintaining a cut-off of at least 0.8 $Å^{-1}$.
- Fix these parameters. Now start with a κ-refinement of κ and P_v.
- Make clever local coordinate systems & find any possible non-crystallographic symmetry elements to introduce constraints on the choice of refinable P_{lm}'s.
- Introduce the multipoles in a sequence of refinement steps and examine the parameters for significance.
- Eventually include also κ', although this may not converge or give large deviations from unity $\rightarrow$ KRMM

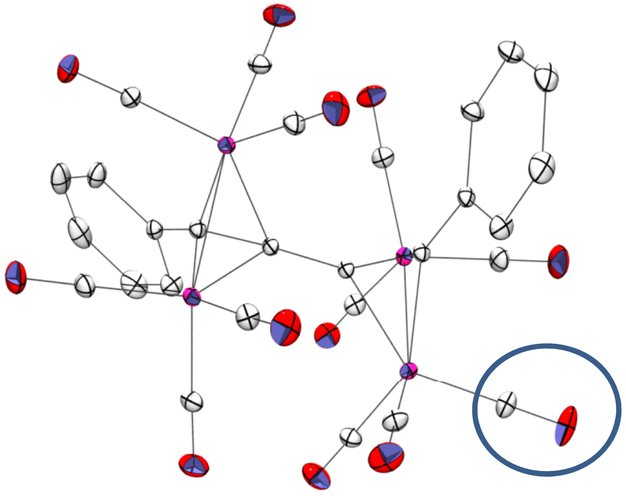
Multipole model bias (KRMM)

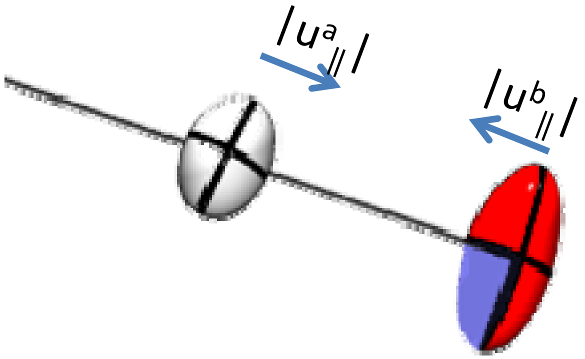
$$\rho(\mathbf{r}) = P_c\rho_c + P_v\rho_v(\kappa r)\kappa^3 + \sum_{l=0}^{l_{\max}} R_l(\kappa' r)\kappa'^3 \sum_{m=0}^{l} P_{lm\pm} d_{lm\pm}(\theta,\phi)$$

- Multipole model introduces a bias, due to limited flexibility of the radial function.
- Solution could be more sophisticated model – several sets of multipole functions, but this is not feasible in most cases!
- Kappa restricted multipole model (KRMM) method:
    - Large spread of experimental values of κ’ for similar atoms
    - Based on tabulated values of κ’ from MM of theoretical structure factors
    - Direct import of these leads to improved and more stable fits

Validating the (final) model

- Hirshfeld rigid bond test



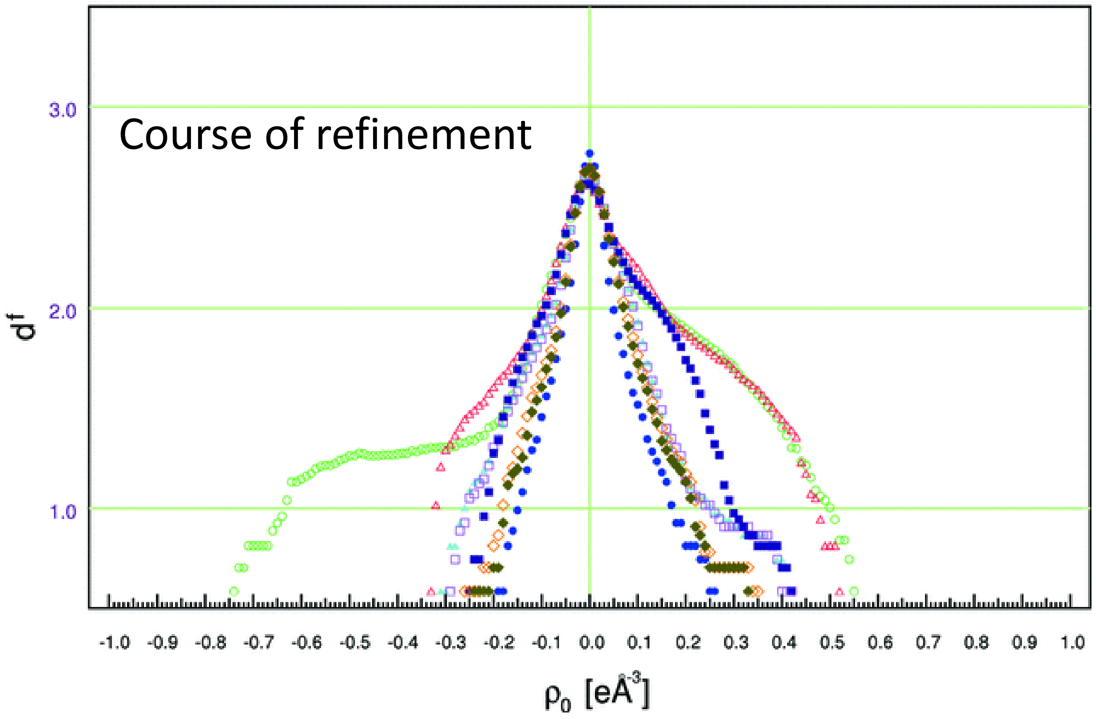


$|u^a_{\parallel}| - |u^b_{\parallel}| \sim 0$ ($<10^{-3}$ Å^2)

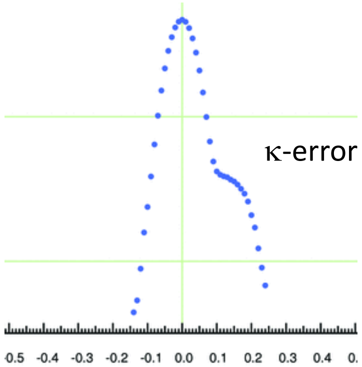
Hirshfeld, F. L. *Acta Crystallogr. Sect A.* **1976**, *32*, 239-244.

Validating the (final) model

- Analysis of the residual density in the unit cell – *program jnk2RDA*



A number of systematic errors were introduced and their fingerprint in the fractal distribution plot was clarified.



Meindl, K.; Henn, J. *Acta Crystallogr. Sect A.* **2008**, *64*, 404-418.

Validating the (final) model

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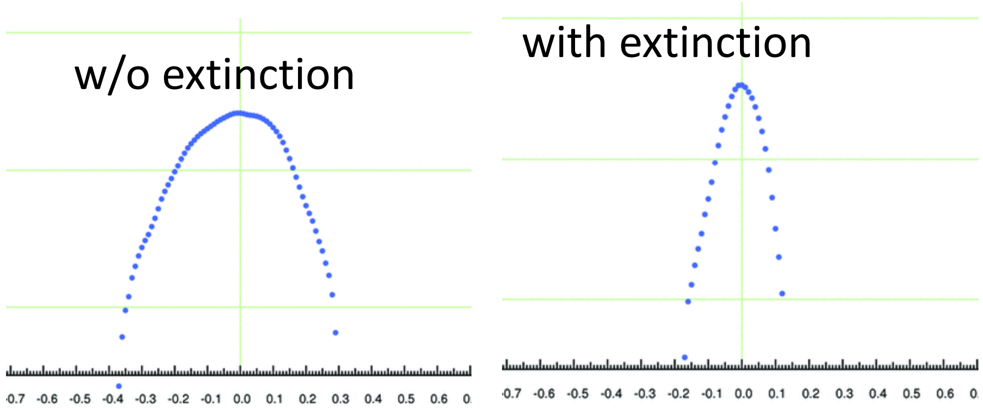
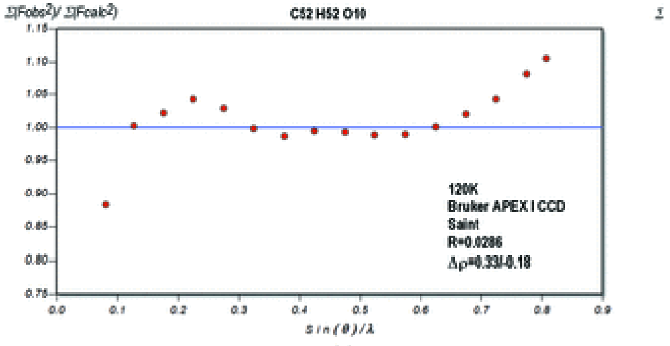


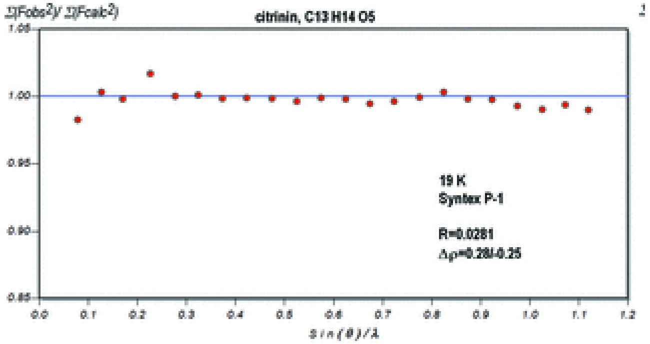
Meindl, K.; Henn, J. *Acta Crystallogr. Sect A.* **2008**, *64*, 404-418.

Validating the (final) model

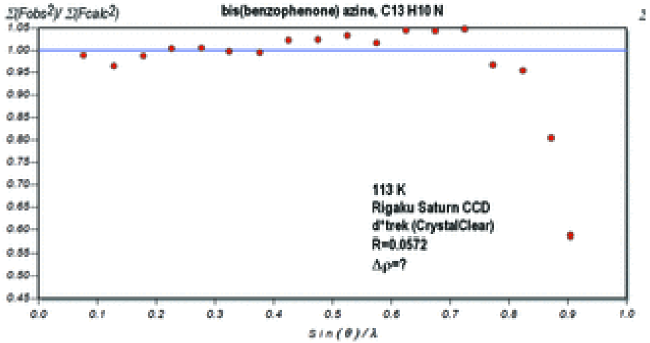
- Shell like behaviour of $\sum F_{obs}^{2} / \sum F_{calc}^{2}$



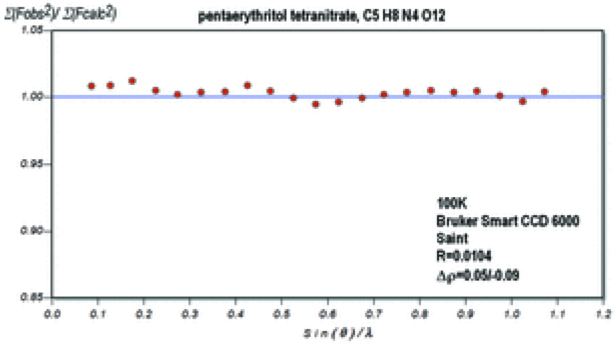
(*a*)



(*a*)



(*c*)



(*c*)

Zhurov, V. V.; Zhurova, E. A.; Pinkerton A. A. *J. Appl. Crystallogr.* **2008**, *41*, 340-349.

Is it worth the effort?

☐ An analytical expression for the total electron density distribution! From this we can get the following properties:

1. Outer electronic moments: dipole moments, quadrupole moments etc
2. d-orbital populations for metal atoms
3. Electric field gradients on the nuclear position – correlate with measured quadrupole splitting energy from Mossbauer spectroscopy
4. Estimates of the crystal lattice energy
5. Better U-values!!!

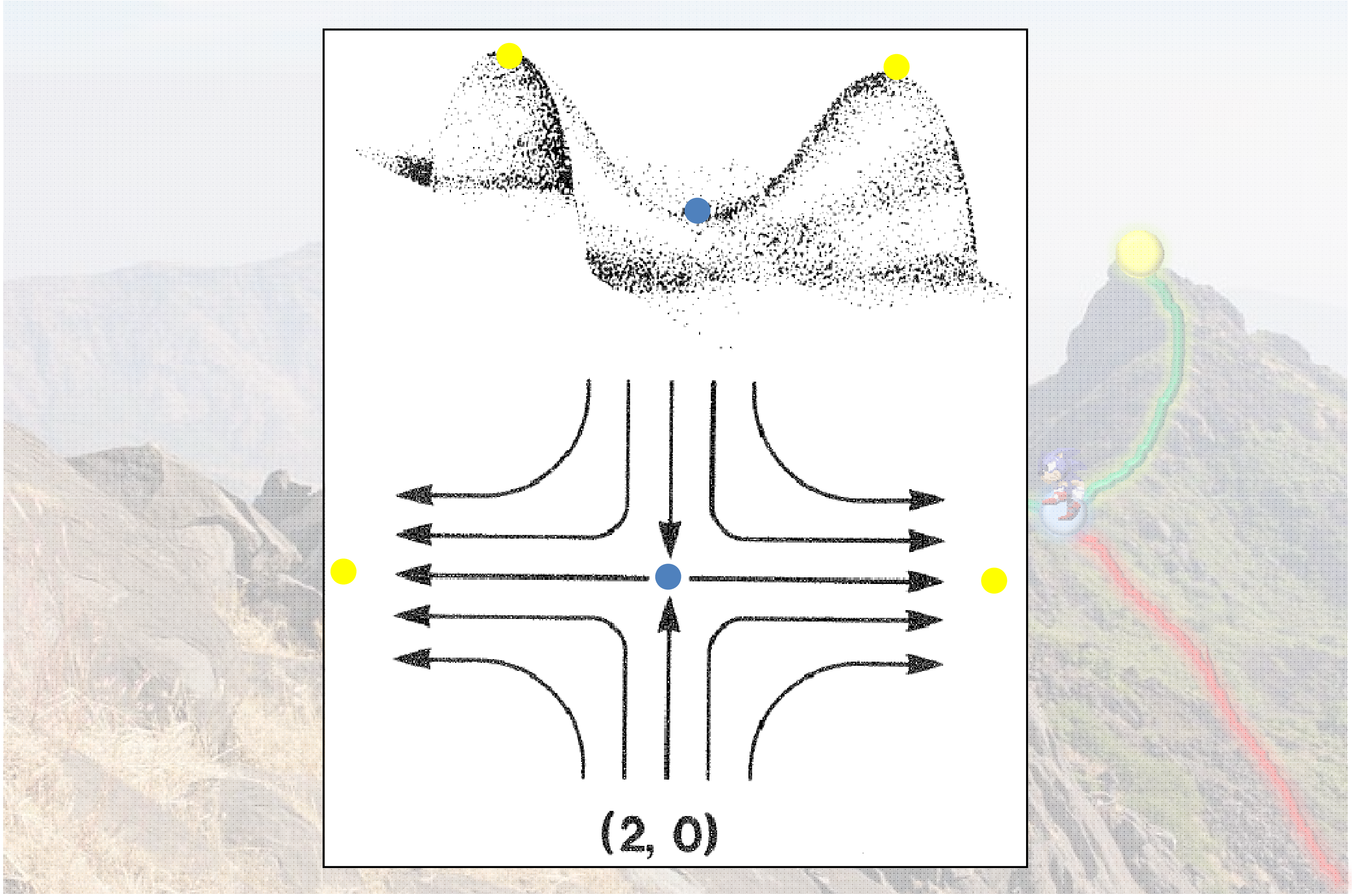
QTAIM analysis!!

QTAIM analysis of the electron density

The fundamental improvement is that the experimental electron density is now described analytically and can thus be analysed using the Atoms in Molecules theory by Richard Bader:

- ✓ Zero-flux surface $\nabla\rho(\mathbf{r})\cdot\mathbf{n} = 0$ separates atomic basin which all contain one and only one nuclei.
- ✓ Critical points where $\nabla\rho=0$.
- ✓ At the critical points, there are four possibilities for the algebraic sum of λ_i:
  -3, -1, +1 or +3 corresponding to a nuclei, a bond, a ring, and a cage.
- ✓ Atomic properties can be calculated by integration over the atomic basin, for instance the atomic charge: $q(\Omega) = N(\Omega) - Z = \int_\Omega \rho(r)\,d\tau$ and volume: $V(\Omega) = \int_\Omega d\tau$

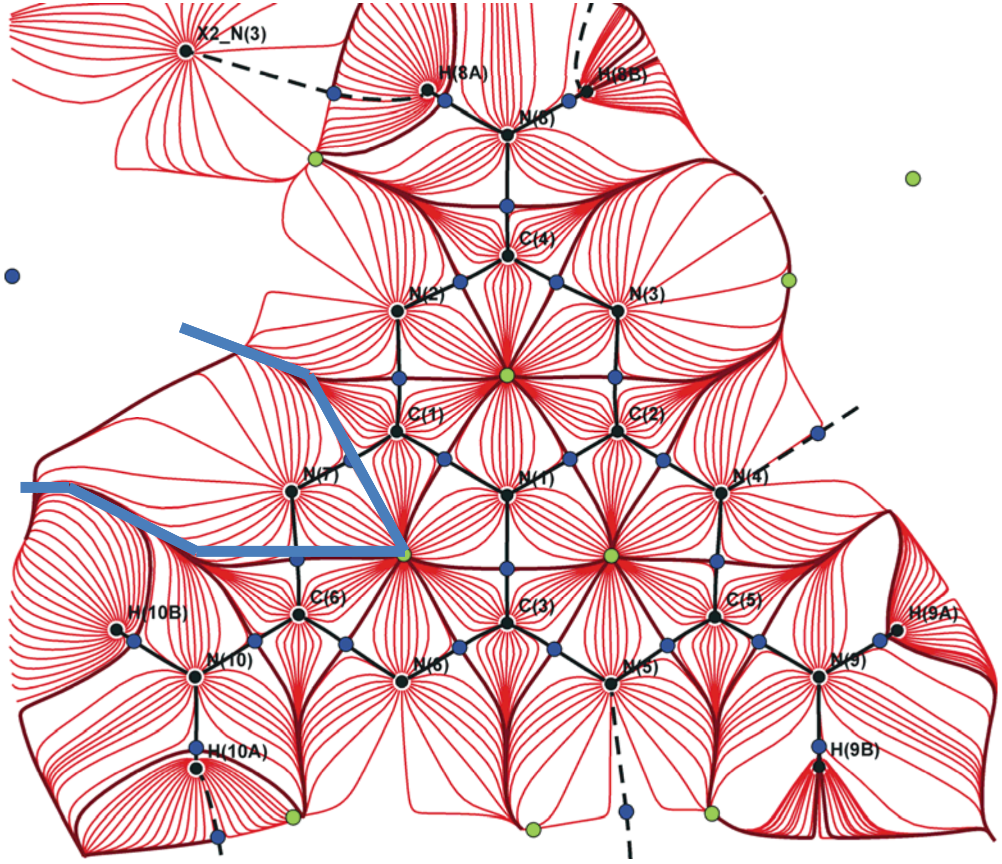
All these quantities can be compared to theoretical values!
Difficult to calculate for network structures, heavy atom molecules etc.



R. F. W. Bader; Atoms In Molecules, Cleardon Press, Oxford 1990

Atoms in Molecules partioning

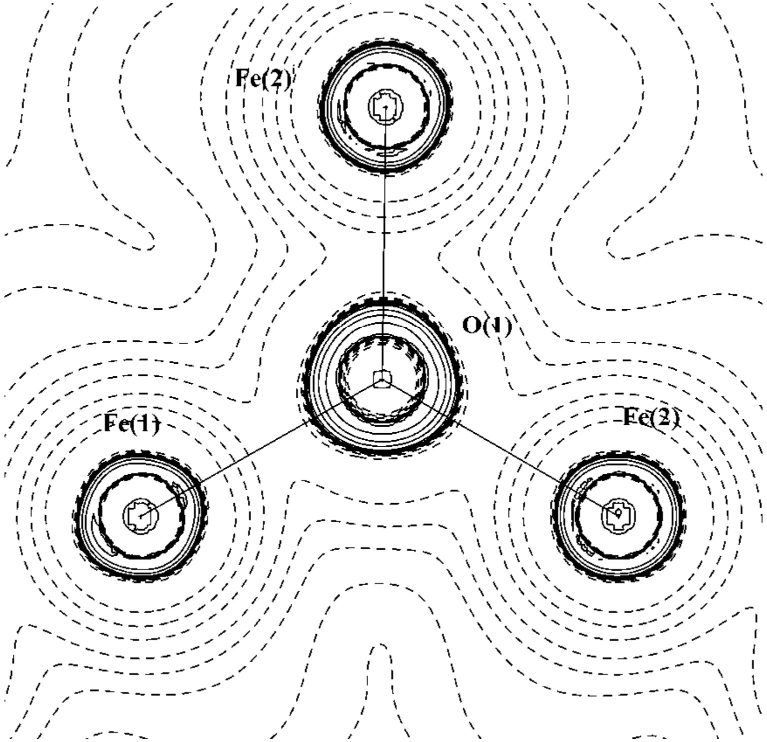
In 2D



Characterization of chemical interactions

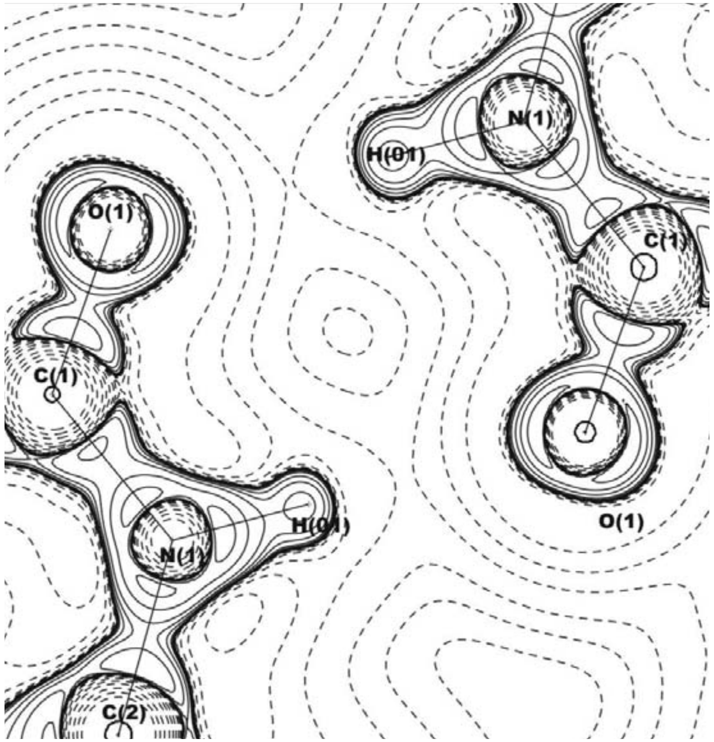
Charge depletion
$\nabla^2\rho(r) > 0$

Ionic bonds



Charge accumulation
$\nabla^2\rho(r) < 0$

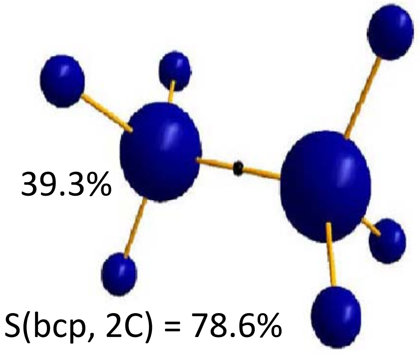
Covalent bonds



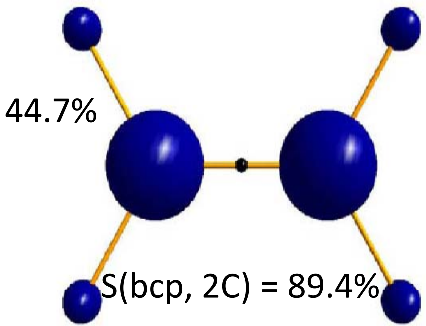
Source function

$$\rho(\mathbf{r}) = \int_{\mathbf{V}} -\frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}\nabla^2\rho(\mathbf{r}')d\mathbf{r}'$$

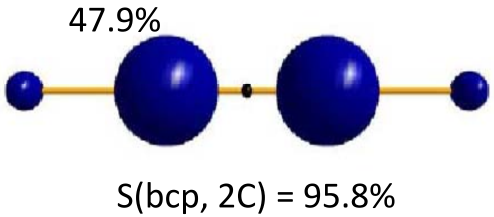
$$= \sum_{\Omega}\int_{\Omega} -\frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}\nabla^2\rho(\mathbf{r}')d\mathbf{r}' \equiv \sum_{\Omega} S(\mathbf{r},\Omega)$$



Ethane



Ethylene



Acetylene

Bader, R.F.W., Gatti, C. (1998), Chem. Phys. Lett. 287, 233-238.
C. Gatti in "The Quantum Theory of Atoms in Molecules: from Solid State to DNA and Drug Design", C. Matta and R. Boyd (Eds.), Wiley-VCH.

Energy densities

- Energy densities can be estimated from the topological analysis using the expression by Abramov:

$$G(\mathrm{r}_{bcp}) = \frac{3}{10}\left(3\pi^2\right)^{2/3}\rho(\mathrm{r}_{bcp})^{5/3} + \frac{1}{6}\nabla^2\rho(\mathrm{r}_{bcp})$$

- Based on results from neutron diffraction studies and the local virial theorem, Espinosa proposed a formula to derive the dissociation energy of a HB:

$$V(\mathbf{r}_{bcp}) = \frac{\hbar}{4m}\nabla^2\rho(\mathbf{r}_{bcp}) - 2G(\mathbf{r}_{bcp})$$

$$\mathbf{E}_{\mathbf{HB}} = 0.5 * V(\mathbf{r}_{bcp})$$

Abramov, Yu. A. *Acta Cryst.* **1997**, **A***53*, 264.
Espinosa, E. et al., *Chem. Phys. Lett.* **1998**, *285,* 170.

Bond classifications

- A classification based on these properties was suggested:

LL atoms	$\rho(r_{bcp})$	$\nabla^2\rho(r_{bcp})$	$G(r_{bcp})/\rho(r_{bcp})$	$H(r_{bcp})$
Open shell (C-C)	Large	Negative	<1	Negative
Polar bonds (C-O)	Large	?	>1	Negative
Closed shell (HB)	Small	Positive	>1	Positive
HH atoms	$\rho(r_{bcp})$	$\nabla^2\rho(r_{bcp})$	$G(r_{bcp})/\rho(r_{bcp})$	$H(r_{bcp})$
Shared	Small	~0	<1	Negative
Donor acceptor	Small	Positive	~1	Negative

Macchi, P. *et al* JACS, **1998**, *120*, 13429.

Conclusions

Take-home message

- The experimental charge density method can give otherwise unattainable information on a wide variety of chemically interesting compounds
- Synchrotron data can be imperative
- A whole new array of properties are available through the use of QTAIM
- Very low temperature is strongly recommended
- Charge density modeling is ”just” advanced structure refinement – but it requires extreme care in data acquisition and data analysis