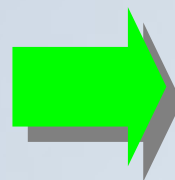
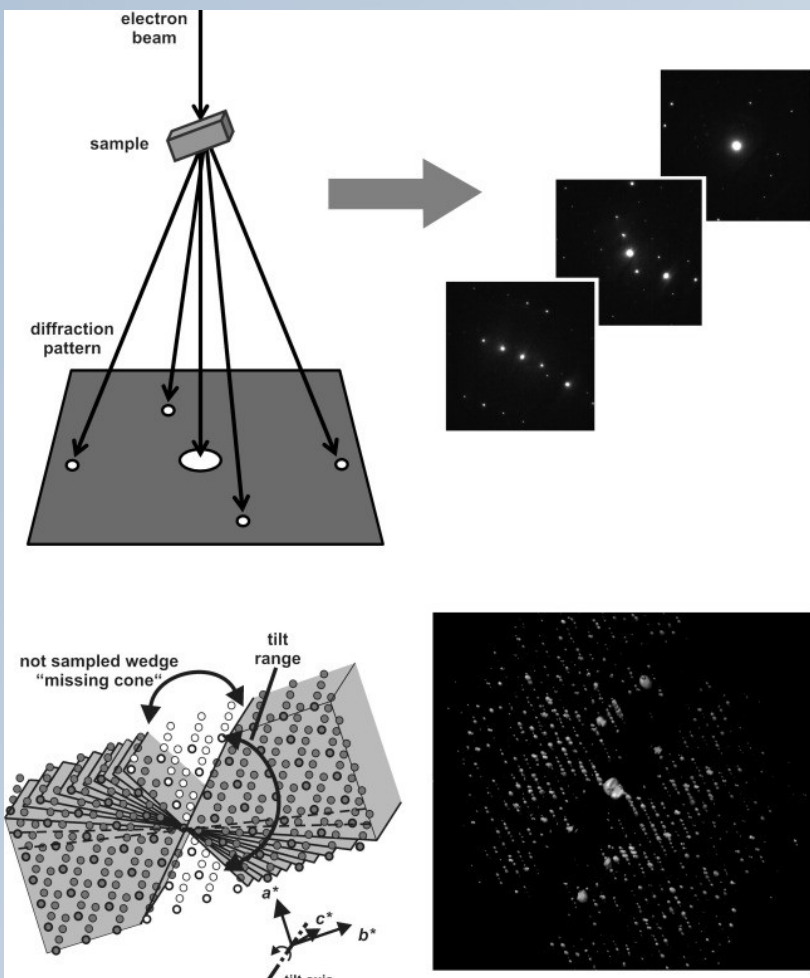


Phase Problem, Direct methods

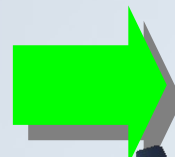
Corrado Cuocci

Institute of Crystallography — National Research Council (CNR), Bari, Italy

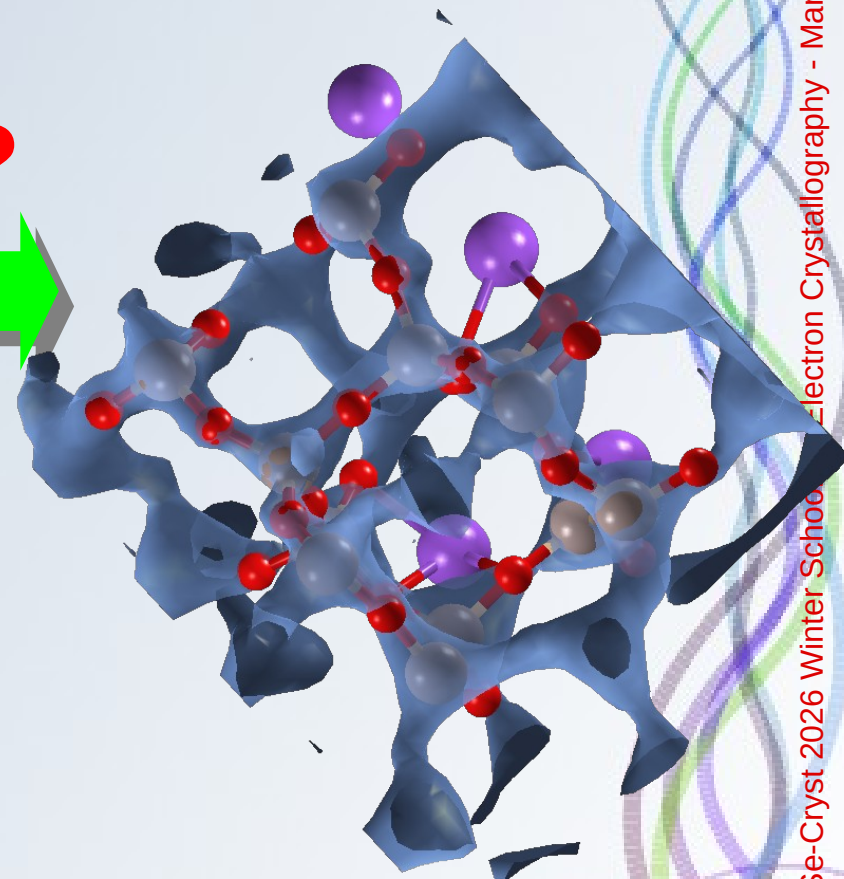
The Phase Problem



I_h



?



Mugnaioli, E., Kolb, U. (2014). MICROPOROUS AND MESOPOROUS MATERIALS, 189, 107-114

Structure Factor

$$F_{\mathbf{h}} = \sum_{j=1}^n f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j)$$

n is the total number of atoms in the unit cell

f_j is the atomic scattering factor

$$\mathbf{h} \cdot \mathbf{r}_j = \begin{pmatrix} h & k & l \end{pmatrix} \times \begin{pmatrix} x_j \\ y_j \\ z_j \end{pmatrix} = hx_j + ky_j + lz_j$$

$$F_{\mathbf{h}} = \sum_{j=1}^n f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

$$F_{\mathbf{h}} = \sum_{j=1}^n O_j t_j(s) f_j(s) \exp[2\pi i(hx_j + ky_j + lz_j)]$$

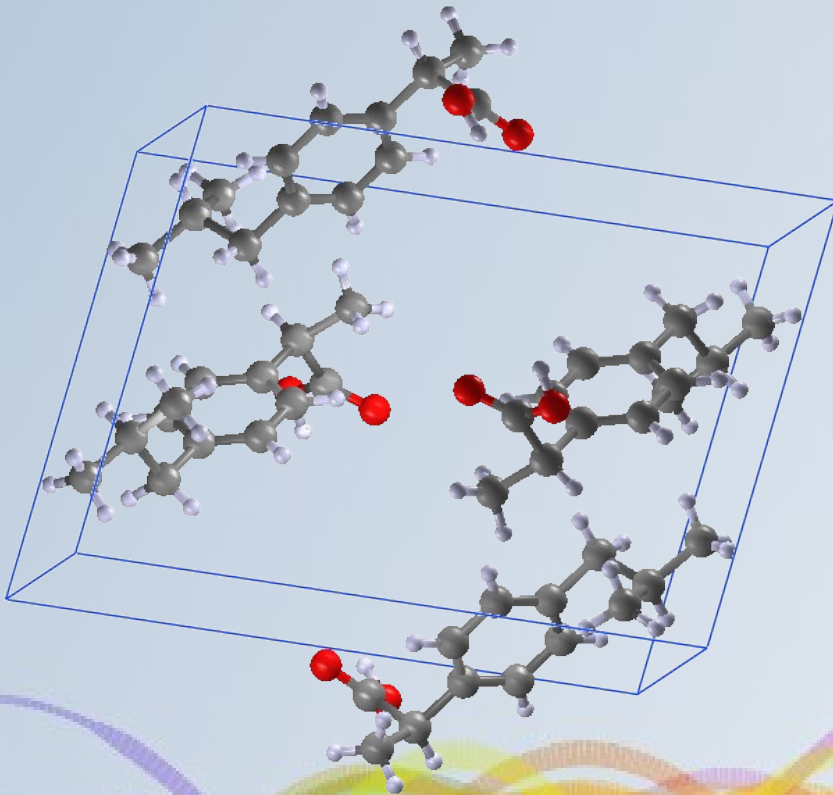
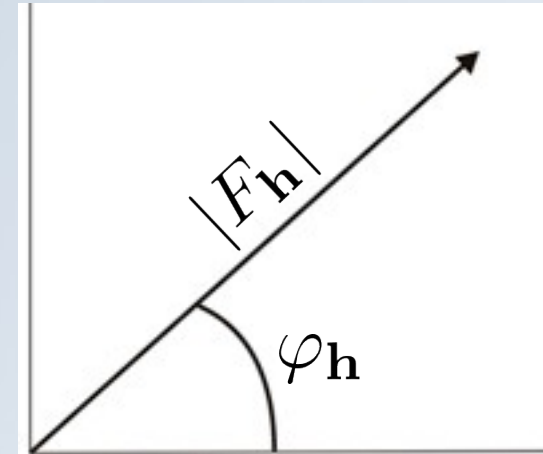
t_j is the temperature factor (atomic displacement parameters)

O_j is the occupation factor

s is $\sin \theta_{\mathbf{h}} / \lambda$

Phase Angle

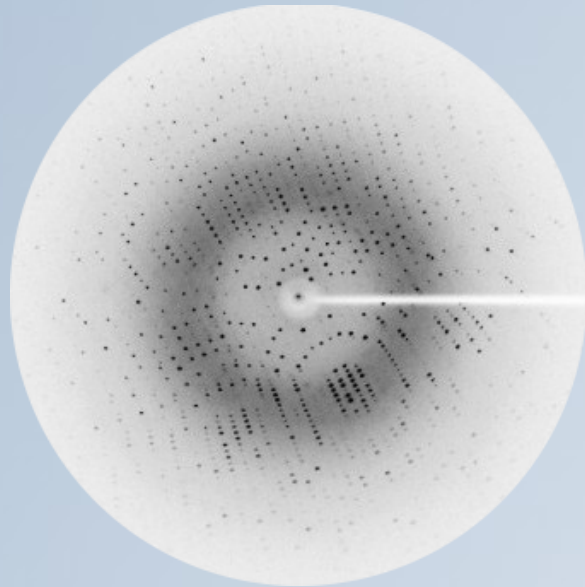
$$F_{\mathbf{h}} = |F_{\mathbf{h}}| \exp(i\varphi_{\mathbf{h}})$$



$F_{\mathbf{h}}$

Fourier Transform

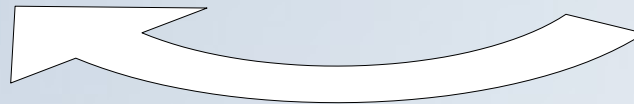
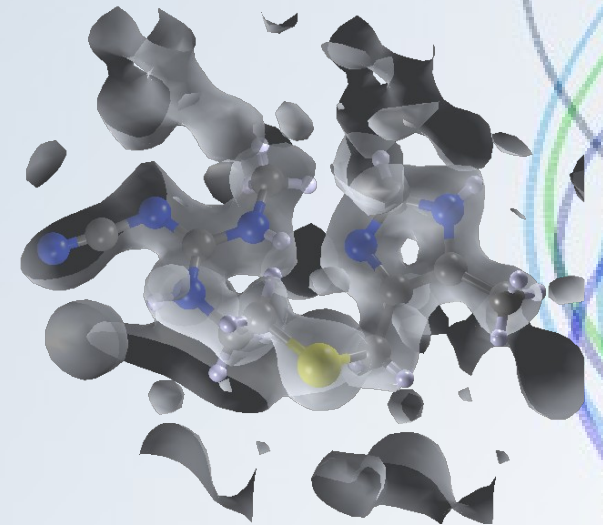
Reciprocal space



FT^{-1}



Direct space



FT

$$F(\mathbf{h}) = FT [\varrho(\mathbf{r})]$$

$$\varrho(\mathbf{r}) = FT^{-1} [F(\mathbf{h})]$$

$$F(\mathbf{h}) = \int_V \varrho(\mathbf{r}) \exp[2\pi i(\mathbf{h} \cdot \mathbf{r})] d\mathbf{r}$$

$$\varrho(\mathbf{r}) = \int_{V^*} F(\mathbf{h}) \exp[-2\pi i(\mathbf{h} \cdot \mathbf{r})] d\mathbf{h}$$

The electron-density equation

$$F_{\mathbf{h}} \xrightarrow{FT^{-1}} \rho(\mathbf{r})$$

$$\rho(\mathbf{r}) = FT^{-1} [F_{\mathbf{h}}] = \frac{1}{V_{cell}} \sum_{\mathbf{h}} F_{\mathbf{h}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r})$$

$$\rho(x, y, z) = \frac{1}{V_{cell}} \sum_h \sum_k \sum_l F_{hkl} \exp[-2\pi i(hx + ky + lz)]$$

$$F_{hkl} = |F_{hkl}| \exp(i\varphi_{hkl}) = |F_{hkl}| (\cos \varphi_{hkl} + i \sin \varphi_{hkl})$$

$$\rho(x, y, z) = \frac{1}{V_{cell}} \sum_h \sum_k \sum_l |F_{hkl}| \cos[2\pi(hx + ky + lz) - \varphi_{hkl}]$$

Phase Problem

$$\rho(x, y, z) = \frac{1}{V_{cell}} \sum_h \sum_k \sum_l |F_{hkl}| \cos [2\pi(hx + ky + lz) - \varphi_{hkl}]$$

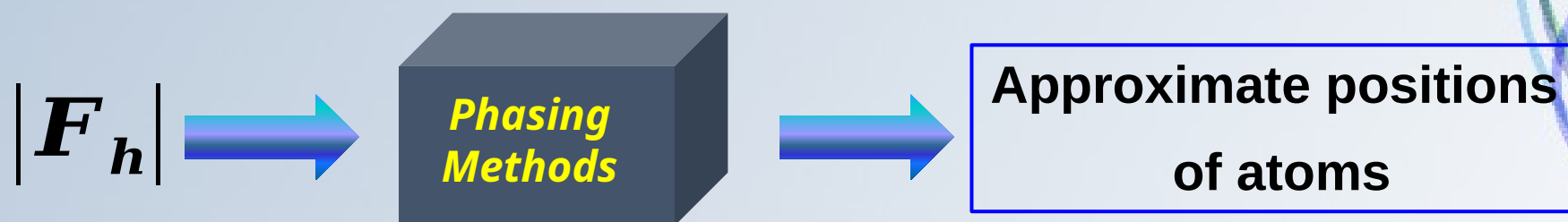
$$I_{hkl} = C |F_{hkl}|^2$$

Phase



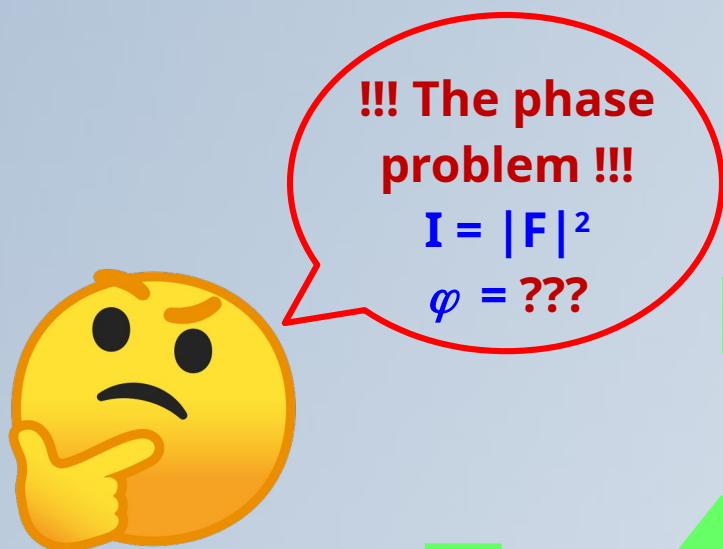
Phase Problem

Accurate structure determination requires both the amplitudes and phases of the structure factors. This difficulty is known as the **phase problem**, as the phase information is missing from diffraction data.



Phases must be estimated and refined using appropriate **phasing methods**.

Phasing Methods



Traditional approaches:

- direct methods
- Patterson methods

Direct space methods

Alternative expressions: real space, global optimization, global search

Other methods:

- charge flipping
- molecular replacement

Direct Methods: the Theoretical Basis

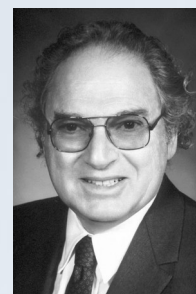
Direct Methods emerged in 1948, achieving full theoretical and practical maturity by the 1970s.

Key points in DM development include

- Sayre's equation (1952)
- Structure invariants by Hauptman and Karle (1953)
- Cochran's three-phase probability distribution (1955)
- Hauptman and Karle's **tangent formula** (1956)

Automated direct methods software

- MULTAN (Main, 1980)
- SIMPEL (Schenk, 1988)
- SHELX-76 (Sheldrick, 1976)
- SIR (Giacovazzo, 1982)



Herbert A. Hauptman



Jerome Karle

DM practically solved the phase problem for small molecules, earning H. Hauptman and J. Karle the 1985 **Nobel Prize in Chemistry**.

Constraints on the electron density

Discrete atoms (atomicity)

$$F_{\mathbf{h}} \xrightarrow{FT^{-1}} \rho(\mathbf{r})$$

$$E_{\mathbf{h}} \xrightarrow{FT^{-1}} \text{point-atom structure}$$

$$|E_{\mathbf{h}}|^2 = \frac{|F_{\mathbf{h}}|^2}{\langle |F_{\mathbf{h}}|^2 \rangle} \quad \langle |F_{\mathbf{h}}|^2 \rangle = \epsilon_{\mathbf{h}} \sum_{i=1}^N f_i^2$$

Non-negative electron density (positivity)

$$\rho(\mathbf{r}) > 0$$

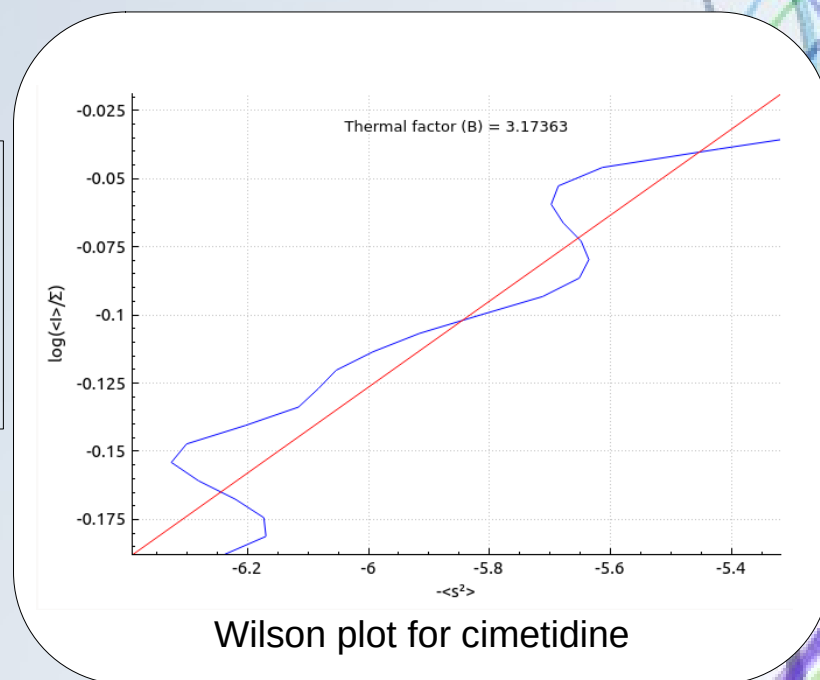
A Typical Direct Methods Procedure

Scaling and normalization of the structure factors $F_h \rightarrow E_h$

$$|F_h|_{obs}^2 = K |F_h|^2 = K |F_h^0|^2 \exp(-2Bs^2)$$

$$\ln \left(\frac{\langle |F_h|_{obs}^2 \rangle_s}{\sum_s^0} \right) = \ln K - 2B \langle s^2 \rangle$$

$$\sum_s^0 = \sum_{j=1}^N (f_j^0)^2 \quad s = \sin(\theta)/\lambda$$



$$|E_h|^2 = \frac{|F_h|_{obs}^2}{\langle |F_h|_{obs}^2 \rangle} = \frac{|F_h|_{obs}^2}{K \exp(-2Bs^2) \epsilon_h \sum_{j=1}^N (f_j^0)^2}$$

Normalized Structure Factors

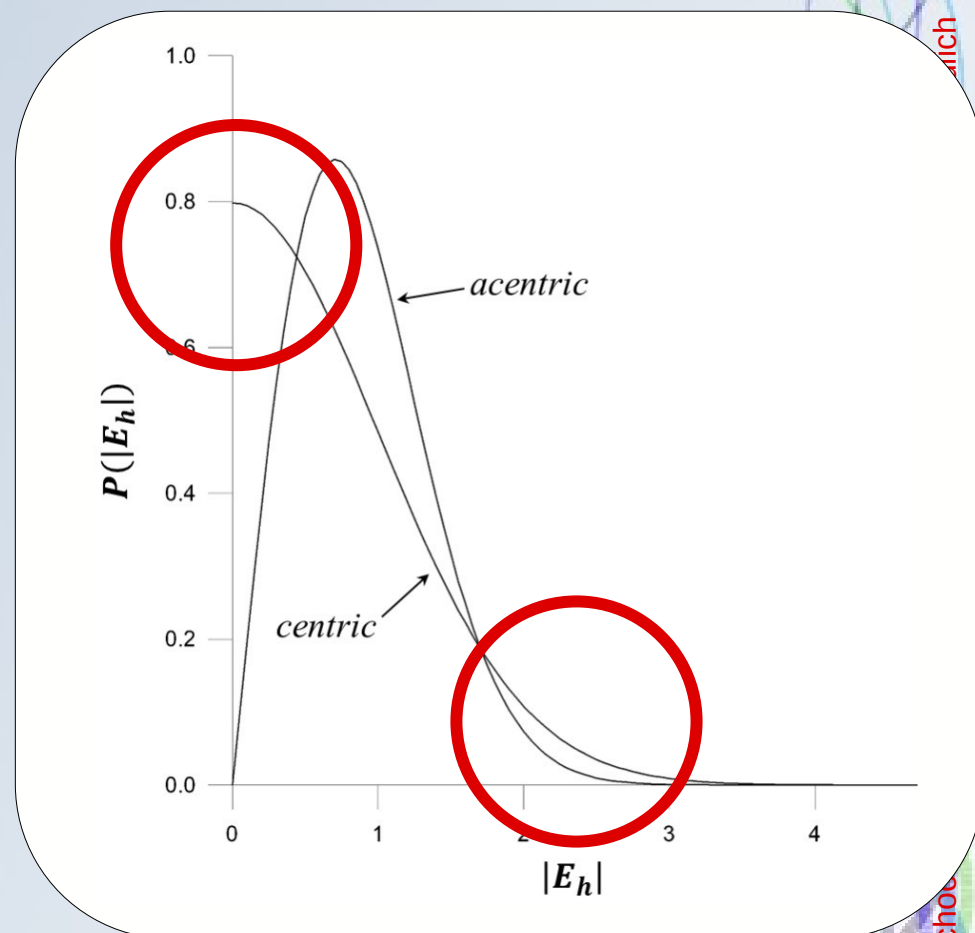
Centric structures

$$P_1(|E|) = \sqrt{\frac{2}{\pi}} \exp(-|E|^2 / 2)$$

Acentric structures

$$P_1(|E|) = 2 |E| \exp(-|E|^2)$$

Normalization helps to reveal underlying symmetry (i.e. inversion centre) in the data.



Comparison of theoretical and experimental distribution functions.

| | exp. data | acentric | centric | hypercentric | a. c. h. |
|-------------------|-----------|----------|---------|--------------|----------|
| mod (E) | 0.865 | 0.886 | 0.798 | 0.718 | * |
| E**2 | 1.000 | 1.000 | 1.000 | 1.000 | |
| E**3 | 1.419 | 1.329 | 1.596 | 1.916 | * |
| E**4 | 2.364 | 2.000 | 3.000 | 4.500 | * |
| E**5 | 4.497 | 3.323 | 6.383 | 12.260 | * |
| E**6 | 9.593 | 6.000 | 15.000 | 37.500 | * |
| mod (E**2-1) | 0.805 | 0.736 | 0.968 | 1.145 | * |
| (E**2-1)**2 | 1.364 | 1.000 | 2.000 | 3.500 | * |
| (E**2-1)**3 | 4.501 | 2.000 | 8.000 | 26.000 | * |
| (mod (E**2-1))**3 | 4.974 | 2.415 | 8.691 | 26.903 | * |

Structure Invariant Definition

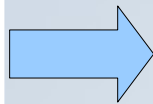
$$F_{\mathbf{h}} = |F_{\mathbf{h}}| \exp(i\varphi_{\mathbf{h}}) = \sum_{j=1}^n f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j)$$

The origin is moved by a general vector \mathbf{r}_0

$$F_{\mathbf{h}} \longrightarrow F'_{\mathbf{h}}$$

$$\begin{aligned} F'_{\mathbf{h}} &= |F'_{\mathbf{h}}| \exp(i\varphi'_{\mathbf{h}}) = \sum_{j=1}^n f_j \exp[2\pi i \mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_0)] \\ &= \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_0) \sum_{j=1}^n f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) \\ &= \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_0) F_{\mathbf{h}} \end{aligned}$$

Shifting the origin by a vector \mathbf{r}_0



$$\begin{aligned} |F'_{\mathbf{h}}| &= |F_{\mathbf{h}}| \\ \varphi'_{\mathbf{h}} &= \varphi_{\mathbf{h}} - 2\pi i \mathbf{h} \cdot \mathbf{r}_0 \end{aligned}$$

$|F_{\mathbf{h}}|$ is a structure-invariant quantity, i.e. independent of the choice of origin, whereas $\varphi_{\mathbf{h}}$ is not.

Structure Invariant Definition

A structure invariant is a product of structure factors whose phase is independent of the choice of origin.

The most general structure invariant is represented by the product:

$$F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h}_m} = |F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h}_m}| \exp[i(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \dots + \varphi_{\mathbf{h}_m})]$$

when

$$\mathbf{h}_1 + \mathbf{h}_1 + \dots + \mathbf{h}_m = 0$$

Every structure invariant must satisfy the condition that the sum of the Miller indices equals **ZERO**

Triplet invariants:

$$F_{\mathbf{h}} F_{\mathbf{k}} F_{-\mathbf{h}-\mathbf{k}} = |F_{\mathbf{h}} F_{\mathbf{k}} F_{-\mathbf{h}-\mathbf{k}}| \exp[i(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{-\mathbf{h}-\mathbf{k}})]$$

Quartet invariants:

$$F_{\mathbf{h}} F_{\mathbf{k}} F_{\mathbf{l}} F_{-\mathbf{h}-\mathbf{k}-\mathbf{l}} = |F_{\mathbf{h}} F_{\mathbf{k}} F_{\mathbf{l}} F_{-\mathbf{h}-\mathbf{k}-\mathbf{l}}| \exp[i(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{-\mathbf{h}-\mathbf{k}-\mathbf{l}})]$$

Probability methods

$$\Phi_{\mathbf{hk}} = \varphi_{\mathbf{h}} + \varphi_{-\mathbf{k}} + \varphi_{\mathbf{k}-\mathbf{h}}$$

$$|F_{\mathbf{h}}| = |F_{-\mathbf{h}}| \longrightarrow I_{\mathbf{h}} = I_{-\mathbf{h}} \quad \text{Friedel's law}$$

$$\varphi_{\mathbf{h}} = -\varphi_{-\mathbf{h}}$$

$$\Phi_{\mathbf{hk}} = \varphi_{\mathbf{h}} + \varphi_{-\mathbf{k}} + \varphi_{\mathbf{k}-\mathbf{h}} = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}}$$

The probability formulae for triplet invariants derived by Cochran:

$$P(\Phi_{\mathbf{hk}}) = \frac{1}{2\pi I_0 G_{\mathbf{hk}}} \exp(G_{\mathbf{hk}} \cos(\Phi_{\mathbf{hk}}))$$

Equal atoms: $G_{\mathbf{hk}} = \frac{2}{\sqrt{N}} |E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}|$

$$\sigma_n = \sum_{j=1}^N Z_j^n$$

Non-equal atoms: $G_{\mathbf{hk}} = 2\sigma_3 \sigma_2^{-3/2} |E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}|$

I_0 is the modified Bessel function of zero order

Z is the atomic number

Probability methods

$P(\Phi_{\mathbf{hk}})$ is a so-called **von Mises distribution**

$$G_{\mathbf{hk}} = \frac{2}{\sqrt{N}} |E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}|$$

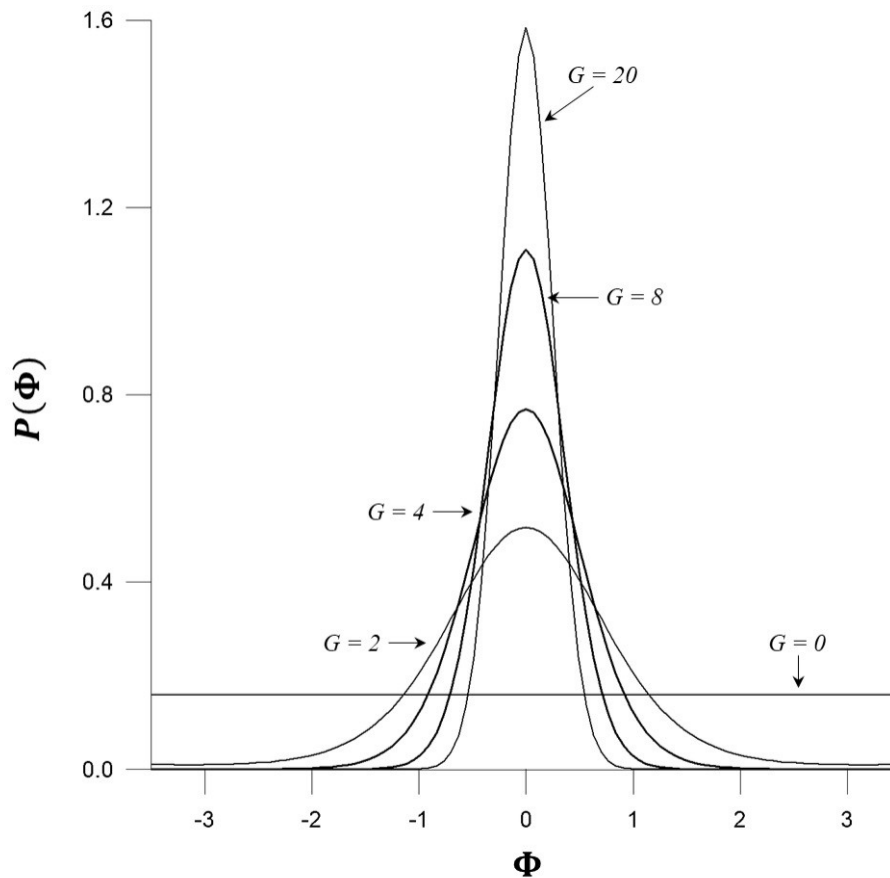
$$\Phi_{\mathbf{hk}} = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}} \approx 0$$

\approx indicates 'is distributed about'

$$\varphi_{\mathbf{h}} \approx \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}$$

Which shows that if the phases of two structure factors are known then the phase of the third one may be estimated.

Probability distributions based on Cochran's formula for different values of the parameter G



Structure Factor Phase Estimate (the Tangent Formula)

If more than one pair of phases

$$\varphi_j \approx \varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j} \quad j=1,2,\dots,r$$

are known, all defining the same phase $\varphi_{\mathbf{h}}$ through triplet relations

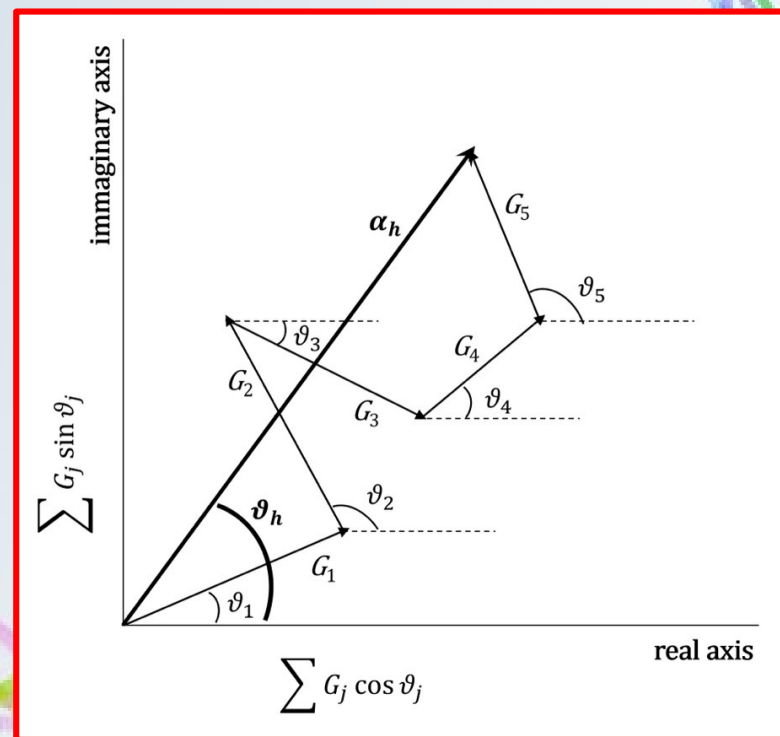
$$\tan \varphi_{\mathbf{h}} \approx \frac{\sum_j^r G_j \sin(\varphi_j)}{\sum_j^r G_j \cos(\varphi_j)} = \frac{A_{\mathbf{h}}}{B_{\mathbf{h}}}$$

$$G_j = G_{\mathbf{h}\mathbf{k}_j}$$

gives the most probable value of $\varphi_{\mathbf{h}}$.

$$\alpha_{\mathbf{h}} = \sqrt{A_{\mathbf{h}}^2 + B_{\mathbf{h}}^2} \quad \text{reliability parameter}$$

Graphical representation of the tangent formula: is visualized in the Argand plane as the resultant of the sum of five complex vectors $G_j \exp(i\vartheta_j)$.



A Typical Direct Methods Procedure

Scaling and normalization of the structure factors $\mathbf{F}_h \rightarrow \mathbf{E}_h$

Triplet and negative quartet invariants are found among the reflections with largest \mathbf{E}_h

$$\varphi_j \approx \varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j}$$
$$\tan \varphi_{\mathbf{h}} \approx \frac{\sum_j^r G_j \sin(\varphi_j)}{\sum_j G_j \cos(\varphi_j)}$$

Random phases assignment

Phase Extension

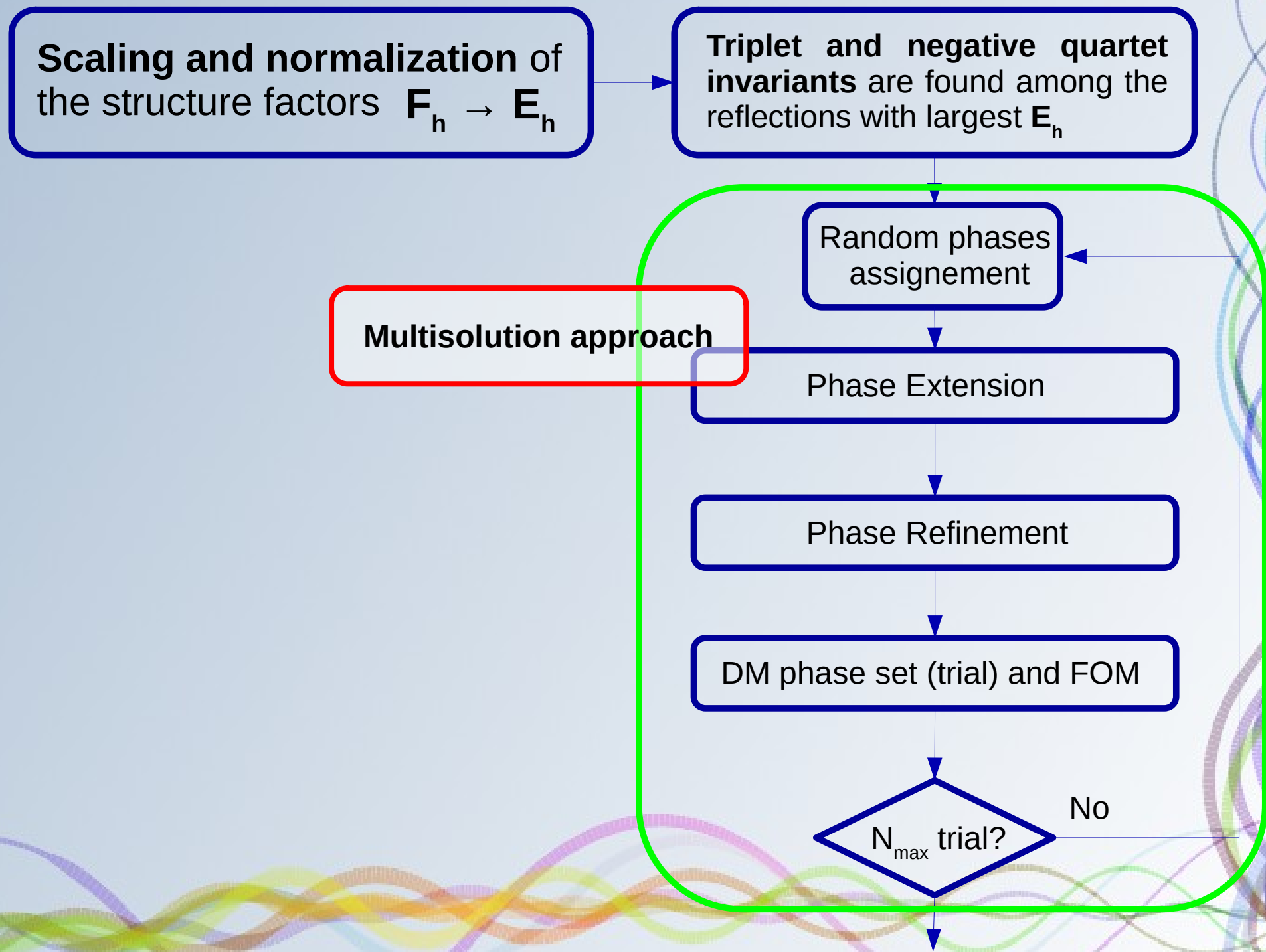
Phase Refinement

DM phase set (trial) and FOM

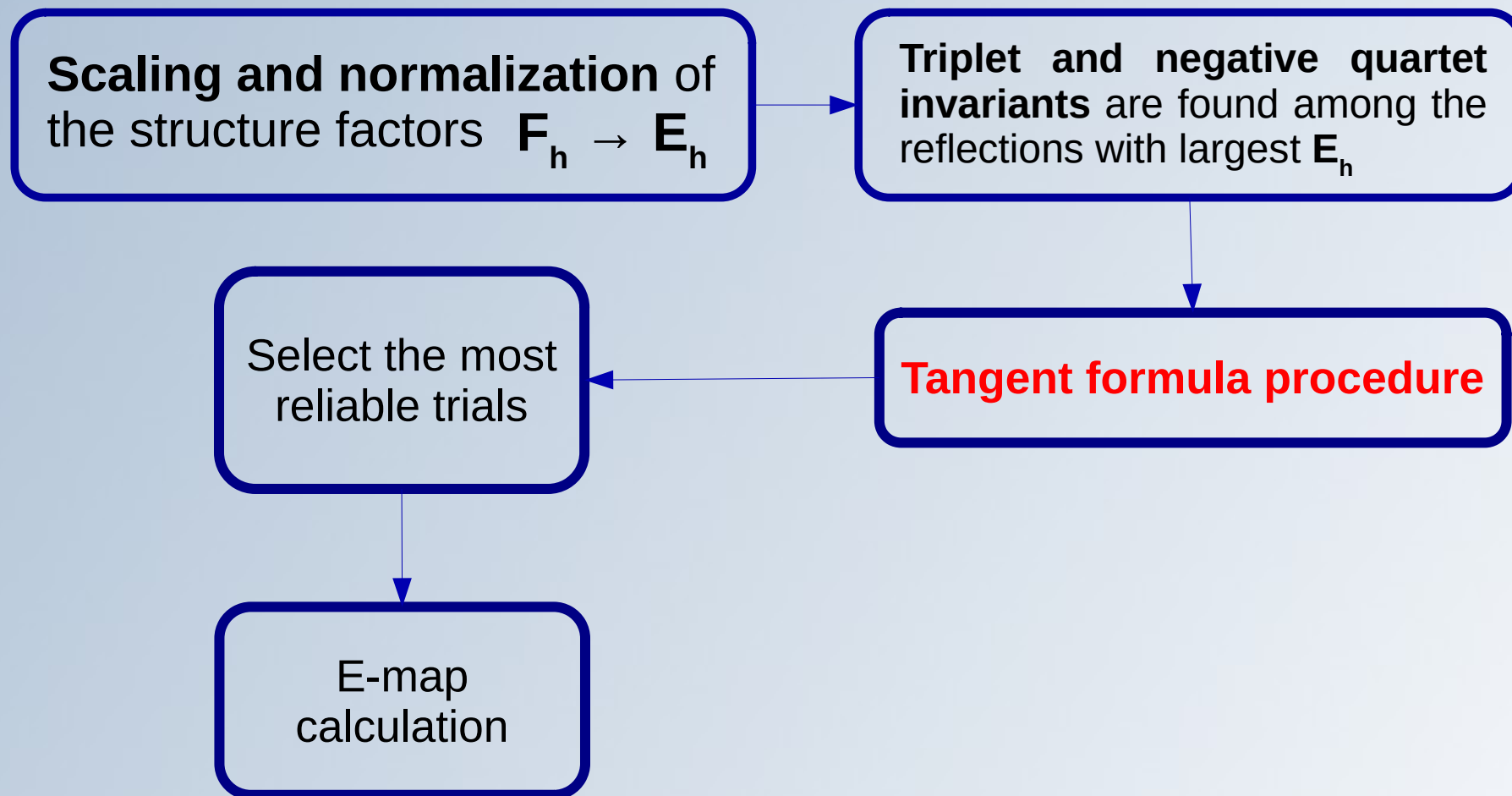
N_{\max} trial?

No

A Typical Direct Methods Procedure

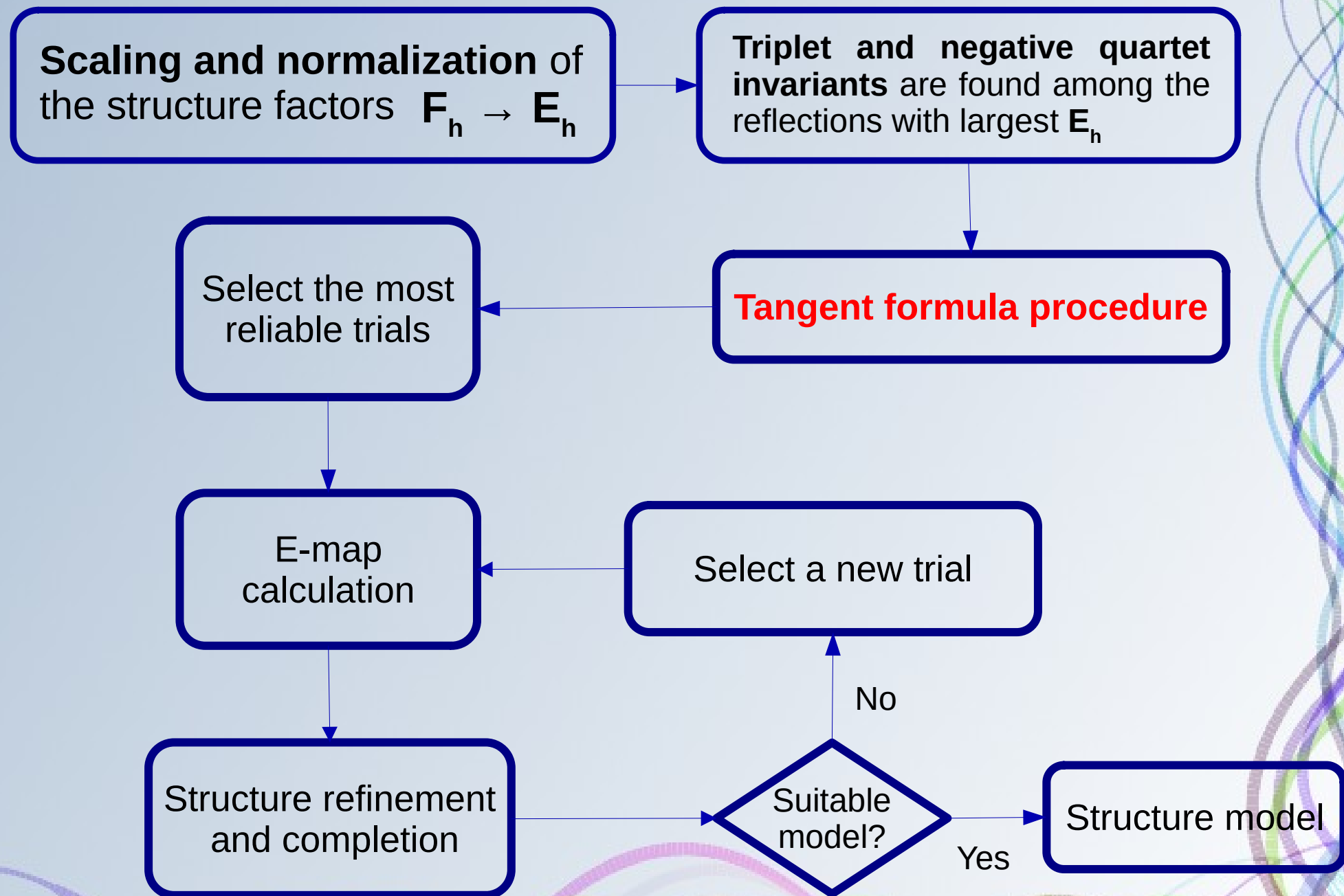


A Typical Direct Methods Procedure



$$\rho(\mathbf{r}) = FT^{-1}[w_{\mathbf{h}}E_{\mathbf{h}}] = \frac{1}{V_{cell}} \sum_{\mathbf{h}} w_{\mathbf{h}} |E_{\mathbf{h}}| \exp(i\varphi_h) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r})$$

A Typical Direct Methods Procedure



Completing and refining the structure

Errors in the model: missing atoms, position errors, errors in the thermal parameters

A Fourier series having as coefficients $F_{\mathbf{h}}^c$

$$\rho_c(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} F_{\mathbf{h}}^c \exp(-2\pi i \mathbf{h} \cdot \mathbf{r})$$

Positions of the atoms of the given model

A Fourier series having as coefficients $F_{\mathbf{h}}^o = |F_{\mathbf{h}}^o| \exp(i\varphi_{\text{true}})$

$$\rho_o(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} F_{\mathbf{h}}^o \exp(-2\pi i \mathbf{h} \cdot \mathbf{r})$$

The true structure

$$\Delta\rho(\mathbf{r}) = \rho_o(\mathbf{r}) - \rho_c(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} (F_{\mathbf{h}}^o - F_{\mathbf{h}}^c) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r})$$

How much the initial model deviates from the real structure

Completing and refining the structure

Difference Fourier synthesis method

$$\Delta\rho(\mathbf{r}) = \rho_o(\mathbf{r}) - \rho_c(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} (F_{\mathbf{h}}^o - F_{\mathbf{h}}^c) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r})$$

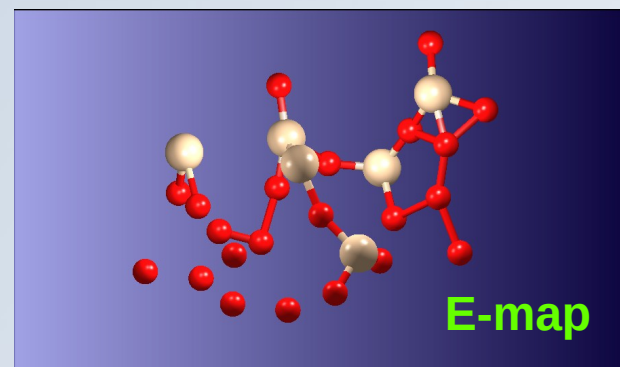
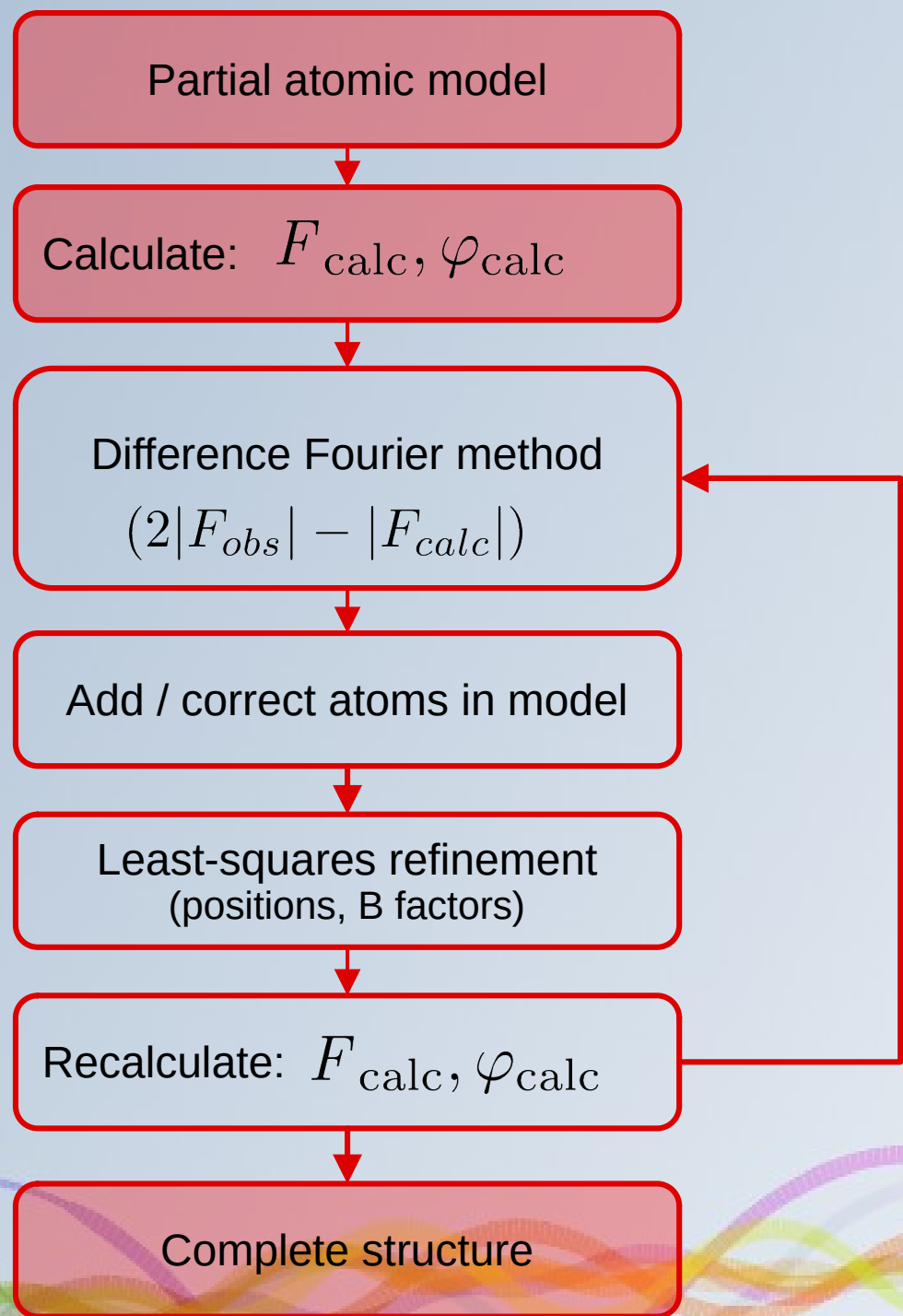
φ_{true} are unknown

$\varphi_{\text{true}} \approx \varphi_{\mathbf{h}}^c$

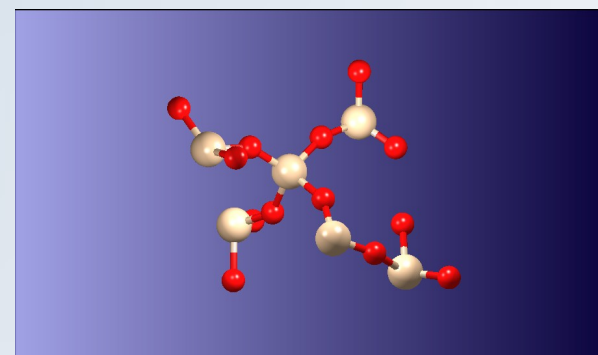
$$\Delta\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} (|F_{\mathbf{h}}^o| - |F_{\mathbf{h}}^c|) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r} + i\varphi_{\mathbf{h}}^c)$$

$$\rho_{\text{best}}(\mathbf{r}) = \frac{1}{V} \sum_{|\mathbf{h}|} (2|F_{\mathbf{h}}^o| - |F_{\mathbf{h}}^c|) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r} + i\varphi_{\mathbf{h}}^c)$$

Completion of the Crystal Structure and Preliminary Refinement



**Kinematical
Model
Refinement**



Least-squares method

Functions to minimize:

$$M = \sum_{\mathbf{h}} w_{\mathbf{h}} (|F_{\mathbf{h}}^o| - |F_{\mathbf{h}}^c|)^2 \quad M' = \sum_{\mathbf{h}} w'_{\mathbf{h}} (|F_{\mathbf{h}}^o|^2 - |F_{\mathbf{h}}^c|^2)^2$$

Residual Factors (R-factors):

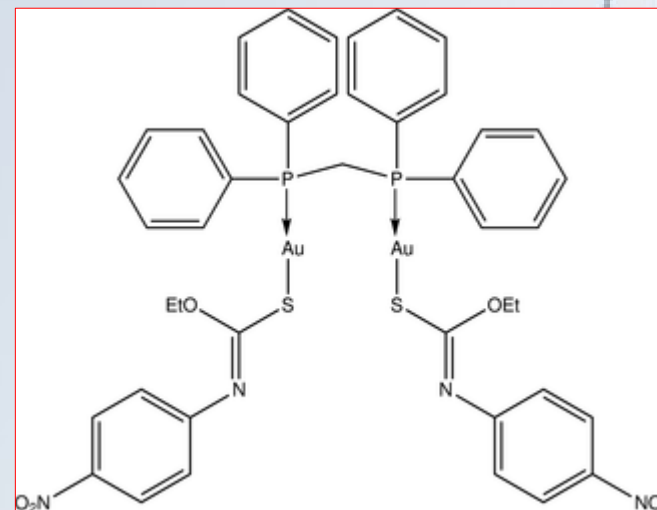
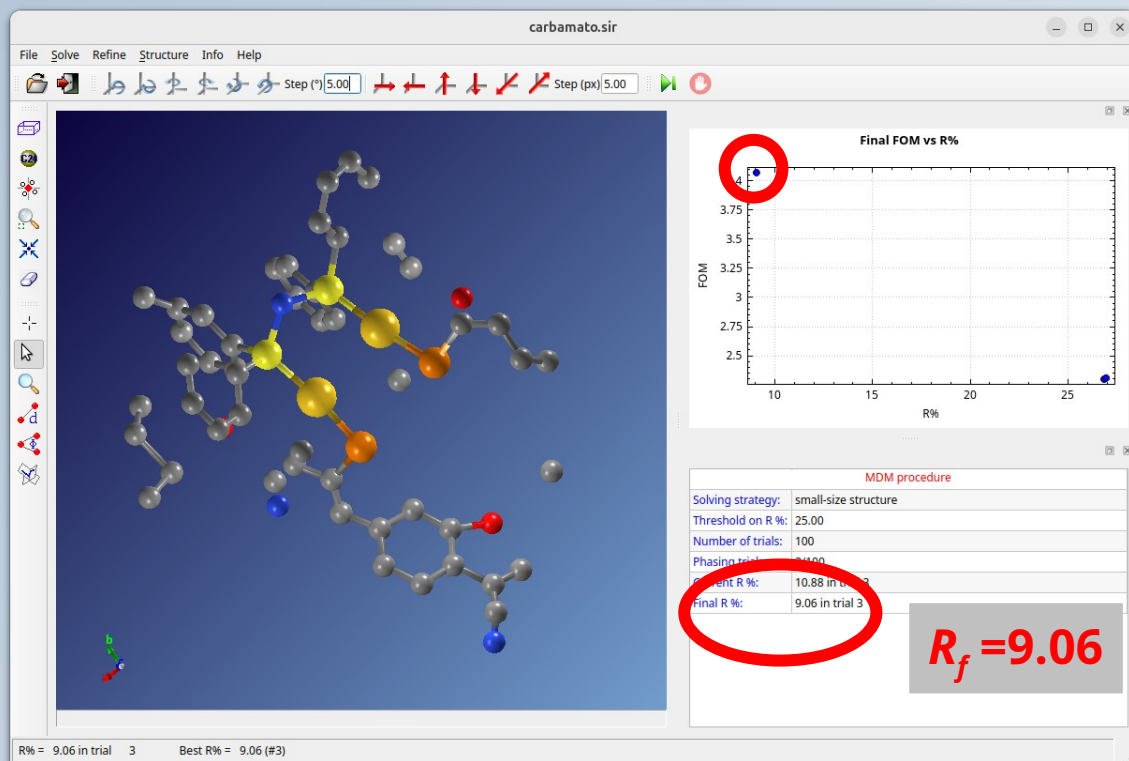
$$wR_f = \left[\frac{\sum_{\mathbf{h}} w_{\mathbf{h}} (|F_{\mathbf{h}}^o| - |F_{\mathbf{h}}^c|)^2}{\sum_{\mathbf{h}} w_{\mathbf{h}} |F_{\mathbf{h}}^o|^2} \right]^{1/2}$$

$$R_f = \frac{\sum_{\mathbf{h}} ||F_{\mathbf{h}}^o| - |F_{\mathbf{h}}^c||}{\sum_{\mathbf{h}} |F_{\mathbf{h}}^o|}$$

$$S = \left[\frac{\sum_{\mathbf{h}} w_{\mathbf{h}} (|F_{\mathbf{h}}^o| - |F_{\mathbf{h}}^c|)^2}{N_R - N_P} \right]^{1/2}$$

Correct Solution Identification

For X-ray data, the correct solution is marked by an outstanding value of the FOM ($R_f \ll 25\%$).



This is not always true for Electron Diffraction data.
The lowest value of R_f does not necessary indicate the best solution.

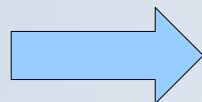
Main Parameters in Phasing Process

Data Resolution

When data resolution is around 1 Å or better, phase determination can normally be obtained *ab initio* by direct methods

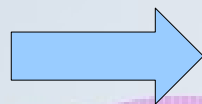
Data Completeness

>70–80% completeness



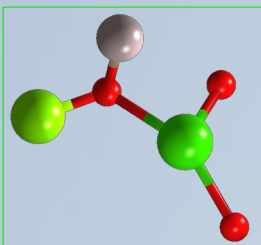
Structure solution is often feasible

<60% completeness

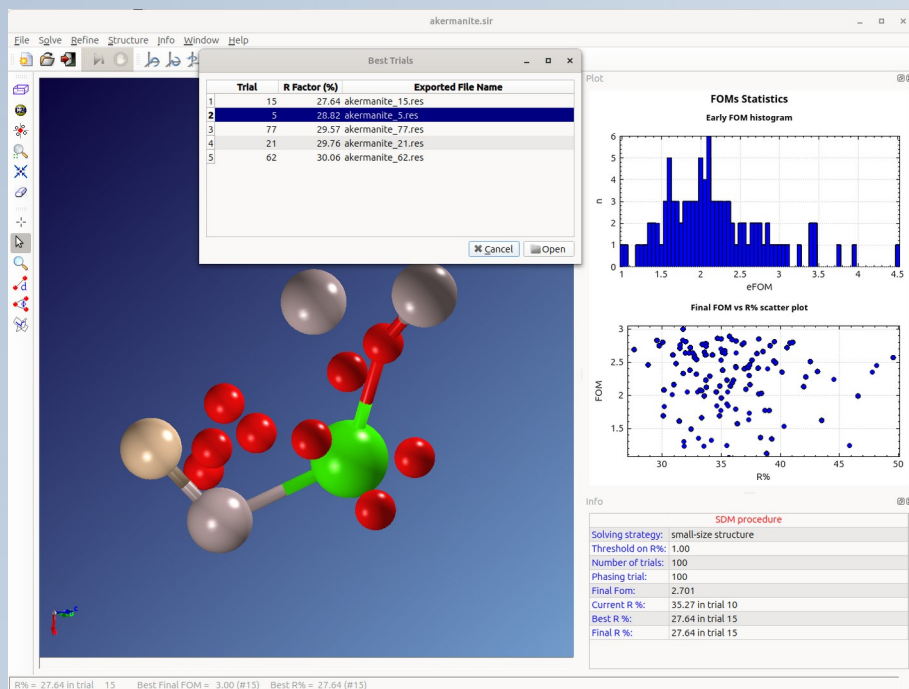


Solution becomes difficult or unstable, depending also on resolution and data quality

Main Parameters in Phasing Process: Data Completeness



Akermanite* PED Data



Data up to 0.4 Å
Completeness ≈ 23%

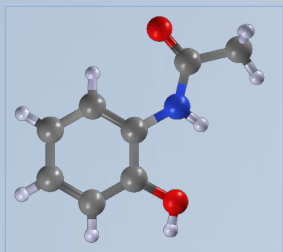
Distribution of reflections up to 0.40 Å.

| Angstrom resolution | No. of expected | No. of observed | No. of missing | % of completeness |
|---------------------|-----------------|-----------------|----------------|-------------------|
| up to 10.0 | 0 | 0 | 0 | 0 |
| 10.0 - 8.0 | 0 | 0 | 0 | 0 |
| 8.0 - 6.0 | 0 | 0 | 0 | 0 |
| 6.0 - 5.0 | 2 | 2 | 0 | 100 |
| 5.0 - 4.0 | 1 | 1 | 0 | 100 |
| 4.0 - 3.0 | 4 | 3 | 1 | 75 |
| 3.0 - 2.5 | 3 | 3 | 0 | 100 |
| 2.5 - 2.0 | 9 | 6 | 3 | 67 |
| 2.0 - 1.8 | 7 | 4 | 3 | 57 |
| 1.8 - 1.6 | 9 | 4 | 5 | 44 |
| 1.6 - 1.4 | 14 | 9 | 5 | 64 |
| 1.4 - 1.3 | 9 | 4 | 5 | 44 |
| 1.3 - 1.2 | 16 | 8 | 8 | 50 |
| 1.2 - 1.1 | 16 | 8 | 8 | 50 |
| 1.1 - 1.0 | 26 | 14 | 12 | 54 |
| 1.0 - 0.9 | 41 | 17 | 24 | 41 |
| 0.9 - 0.8 | 58 | 22 | 36 | 38 |
| 0.8 - 0.7 | 94 | 35 | 59 | 37 |
| 0.7 - 0.6 | 166 | 53 | 113 | 32 |
| 0.6 - 0.5 | 309 | 83 | 226 | 27 |
| 0.5 - 0.4 | 661 | 63 | 598 | 10 |
| All | 1445 | 339 | 1106 | 23 |

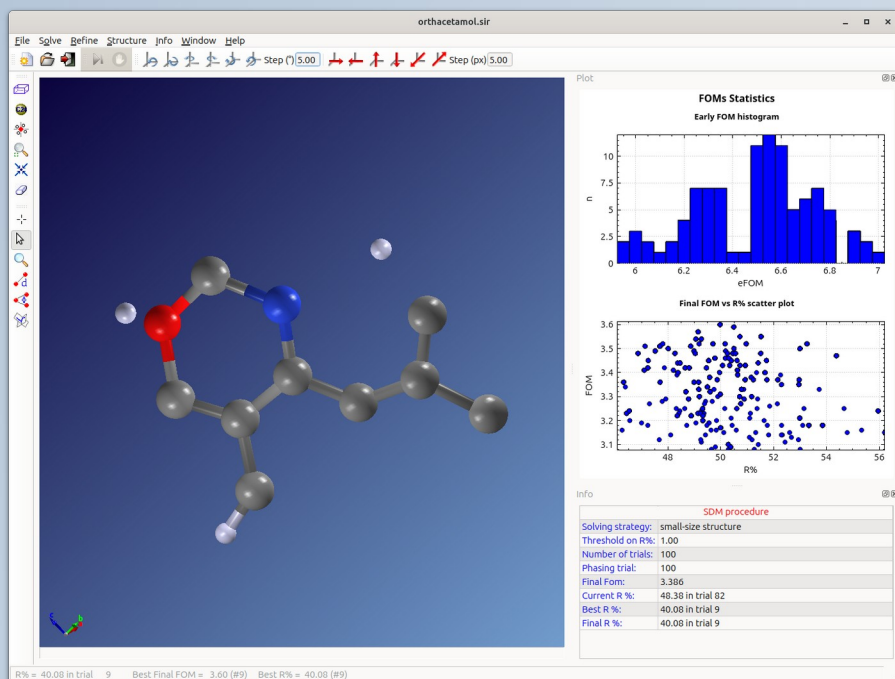
% of completeness up to 0.40 Å. resolution = 23.46

*Gemmi et al., Amer. Miner. 92, 408 (2007)

Main Parameters in Phasing Process: Data Completeness



Orthocetamol* STEM-3DED Data



Data up to 0.78 Å
Completeness ≈ 80%

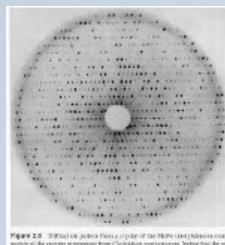
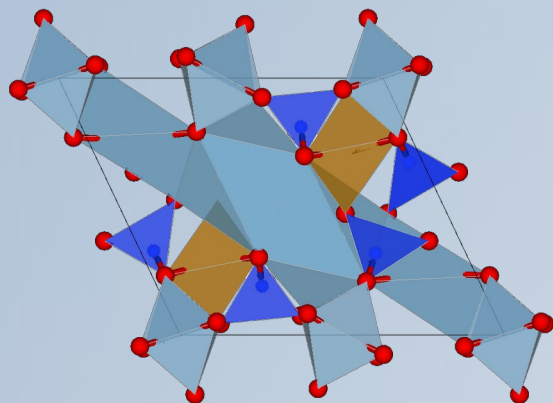
Distribution of reflections up to 0.78 Ang.

| Angstrom resolution | No. of expected | No. of observed | No. of missing | % of completeness |
|---------------------|-----------------|-----------------|----------------|-------------------|
| up to 10.0 | 0 | 0 | 0 | 0 |
| 10.0 - 8.0 | 0 | 0 | 0 | 0 |
| 8.0 - 6.0 | 4 | 4 | 0 | 100 |
| 6.0 - 5.0 | 4 | 2 | 2 | 50 |
| 5.0 - 4.0 | 4 | 3 | 1 | 75 |
| 4.0 - 3.0 | 17 | 17 | 0 | 100 |
| 3.0 - 2.5 | 20 | 14 | 6 | 70 |
| 2.5 - 2.0 | 47 | 42 | 5 | 89 |
| 2.0 - 1.8 | 33 | 26 | 7 | 79 |
| 1.8 - 1.6 | 66 | 56 | 10 | 85 |
| 1.6 - 1.4 | 88 | 70 | 18 | 80 |
| 1.4 - 1.3 | 68 | 58 | 10 | 85 |
| 1.3 - 1.2 | 95 | 78 | 17 | 82 |
| 1.2 - 1.1 | 140 | 115 | 25 | 82 |
| 1.1 - 1.0 | 186 | 161 | 25 | 87 |
| 1.0 - 0.9 | 291 | 243 | 48 | 84 |
| 0.9 - 0.8 | 443 | 364 | 79 | 82 |
| 0.8 - 0.7 | 101 | 31 | 70 | 31 |
| All | 1607 | 1284 | 323 | 80 |

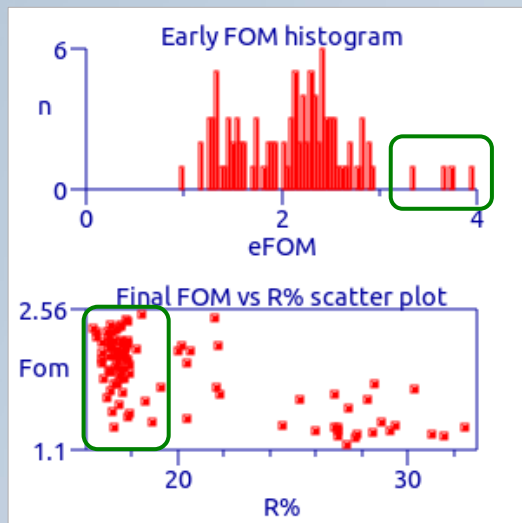
% of completeness up to 0.78 Ang. resolution = 79.90

*Andrusenko et al., Angew. Chem. Int. Ed. 2019, 58, 10919–10922

Structure Solution of the complex silicate $\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{13}$ by Direct Methods



Cell: 8.86 5.62 10.11 **90 115.3 90**
Space Group: **$P2_1/m$**



Res: 0.77 $R_{\text{int}} = 14.27\%$

| Angstrom | Number | Rint |
|------------|--------|--------|
| up to 10.0 | 0 | ---- |
| 10.0 - 8.0 | 1 | 3.00% |
| 8.0 - 6.0 | 0 | ---- |
| 6.0 - 5.0 | 1 | 16.79% |
| 5.0 - 4.0 | 5 | 5.59% |
| 4.0 - 3.0 | 10 | 7.61% |
| 3.0 - 2.5 | 13 | 7.17% |
| 2.5 - 2.0 | 31 | 10.02% |
| 2.0 - 1.8 | 22 | 12.12% |
| 1.8 - 1.6 | 37 | 11.39% |
| 1.6 - 1.4 | 51 | 11.64% |
| 1.4 - 1.3 | 37 | 13.76% |
| 1.3 - 1.2 | 69 | 14.29% |
| 1.2 - 1.1 | 74 | 15.48% |
| 1.1 - 1.0 | 114 | 14.44% |
| 1.0 - 0.9 | 165 | 16.38% |
| 0.9 - 0.8 | 257 | 16.25% |
| 0.8 - 0.7 | 116 | 16.60% |
| All | 1003 | 14.27% |

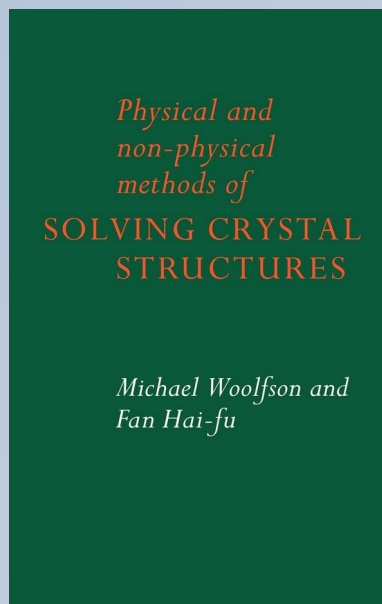
| Distribution of reflections up to 0.77 Ang. | | | | |
|---|-----------------|-----------------|----------------|-------------------|
| Angstrom resolution | No. of expected | No. of observed | No. of missing | % of completeness |
| up to 10.0 | 0 | 0 | 0 | 0 |
| 10.0 - 8.0 | 2 | 1 | 1 | 50 |
| 8.0 - 6.0 | 1 | 0 | 1 | 0 |
| 6.0 - 5.0 | 1 | 1 | 0 | 100 |
| 5.0 - 4.0 | 7 | 5 | 2 | 71 |
| 4.0 - 3.0 | 12 | 10 | 2 | 83 |
| 3.0 - 2.5 | 17 | 13 | 4 | 76 |
| 2.5 - 2.0 | 36 | 31 | 5 | 86 |
| 2.0 - 1.8 | 24 | 22 | 2 | 92 |
| 1.8 - 1.6 | 45 | 39 | 6 | 87 |
| 1.6 - 1.4 | 62 | 51 | 11 | 82 |
| 1.4 - 1.3 | 41 | 38 | 3 | 93 |
| 1.3 - 1.2 | 79 | 69 | 10 | 87 |
| 1.2 - 1.1 | 83 | 76 | 7 | 92 |
| 1.1 - 1.0 | 130 | 118 | 12 | 91 |
| 1.0 - 0.9 | 188 | 167 | 21 | 89 |
| 0.9 - 0.8 | 295 | 265 | 30 | 90 |
| 0.8 - 0.7 | 133 | 118 | 15 | 89 |
| All | 1156 | 1024 | 132 | 89 |

% of completeness up to 0.77 Ang. resolution = 88.58

The merging residual value:

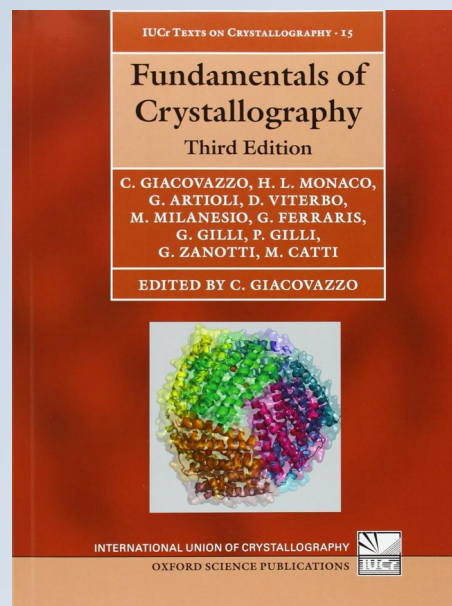
$$R_{\text{int}} = \frac{\sum |F_o^2 - \langle F_o^2 \rangle|}{\sum F_o^2}$$

Recommended Reading on Direct Methods



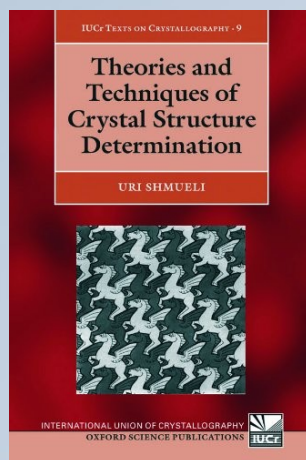
Physical and Non-Physical Methods of Solving Crystal Structures 1st Edition

by Michael M. Woolfson, Fan Hai-Fu



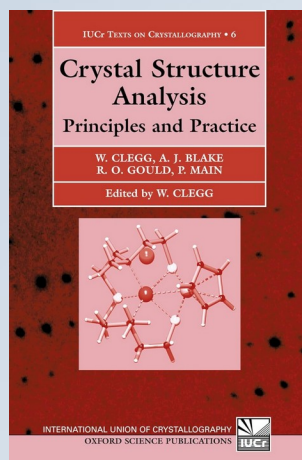
Fundamentals of Crystallography (International Union of Crystallography Texts on Crystallography) 3rd Edition

by Carmelo Giacovazzo, Hugo Luis Monaco, Gilberto Artioli, Davide Viterbo, & 6 more



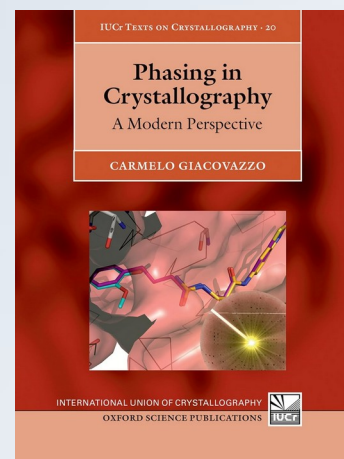
Theories and Techniques of Crystal Structure Determination

by Uri Shmueli



Crystal Structure Analysis: Principles and Practice

by Peter Main, Clegg William, Alexander J. Blake, Robert O. Gould



Phasing in Crystallography: A Modern Perspective

by Carmelo Giacovazzo

Thank you for your kind attention

Contact, software download and info

<http://www.ba.ic.cnr.it/softwareic/sir/>

Acknowledgements

G. Cascarano, B. Carrozzini

Thank you for your kind attention