



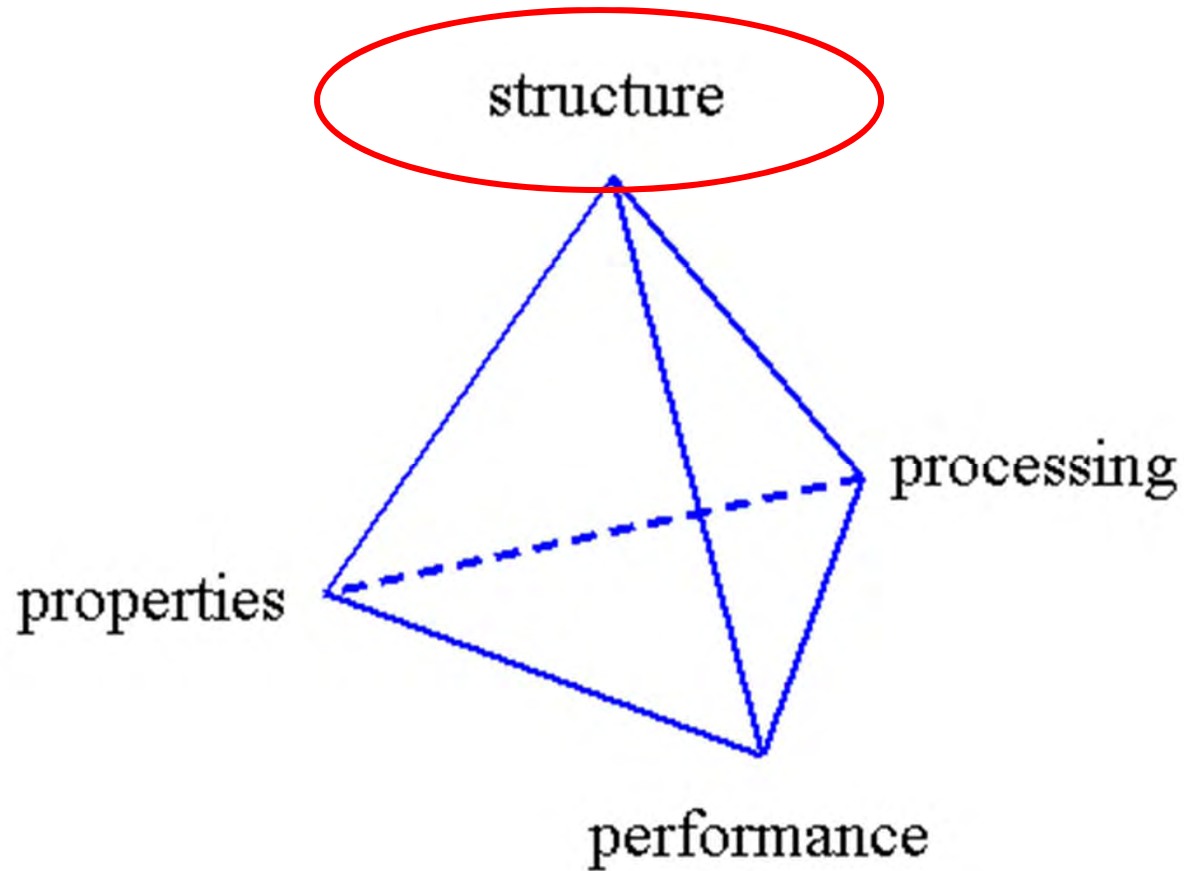
The Phase Problem for Electrons

L. D. Marks


Northwestern University

465 Version, 2013

What is the science?



Why determine the structure?

- 
- To finish my PhD
 - To get/keep my job
 - Because structure *coupled* with other science really matters – but only when coupled
 - Follow the science, not the electron

How to solve a structure?



- Guess, then refine
 - Will always give something, but if the guess is wrong GIGO
- Use Patterson function
 - Difficult for complicated structures (more to come)
- Use DFT
 - If the original guess is wrong, GIGO
 - Functionals are inaccurate for most oxides (energies wrong)
- Get an image
 - STM is hard to interpret
 - HREM, can be ambiguous (more to come)
- Get a Diffraction Pattern
 - Incomplete information (more to come)

Four basic elements are required to solve a recovery problem



1. A data formation model

Imaging/Diffraction/Measurement

2. A priori information

The presence of atoms or similar

3. A recovery criterion:

A numerical test of Goodness-of-Fit

4. A solution method.

Mathematical details

Four basic elements are required to solve a recovery problem



1. A data formation model

Imaging/Diffraction/Measurement

Kinematical Theory/Linear Imaging

Single Weak Scattering + Ewald Sphere

Qualitatively correct; Quantitatively inaccurate

Bragg's Law

Single Scattering + Zero Excitation Error

Worse than Kinematical Theory (it is different)

Dynamical Theory/Non-Linear Imaging

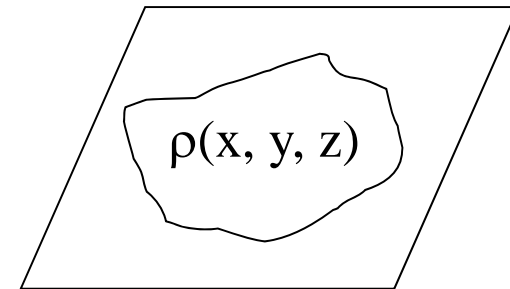
Quantitatively correct, to the accuracy of the electrostatic potential (exact in principle)

Warning: Errors in the model introduce systematic errors in the recovery which of course can lead to GIGO

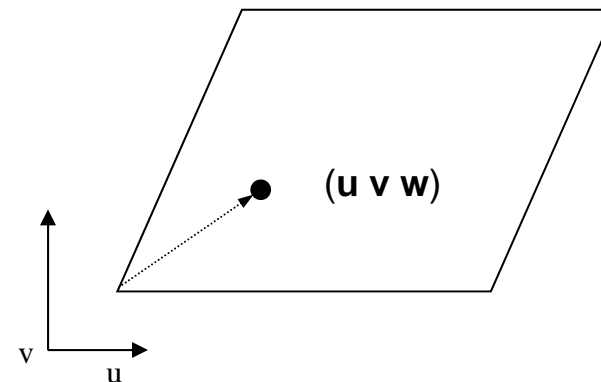
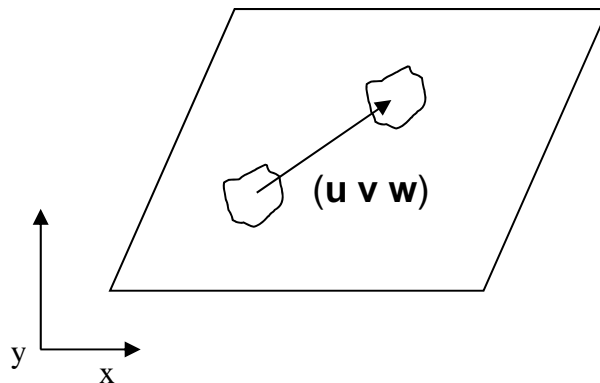
Patterson Function I (FT of Diffraction Pattern)



$$P(uvw) = \frac{1}{V} \sum_{hkl} I(hkl) e^{-2\pi i(hu+lv+kz)}$$



$$P(\vec{u}) = \int \rho(\vec{r}) \rho(\vec{r} + \vec{u}) d^3 \vec{r}$$

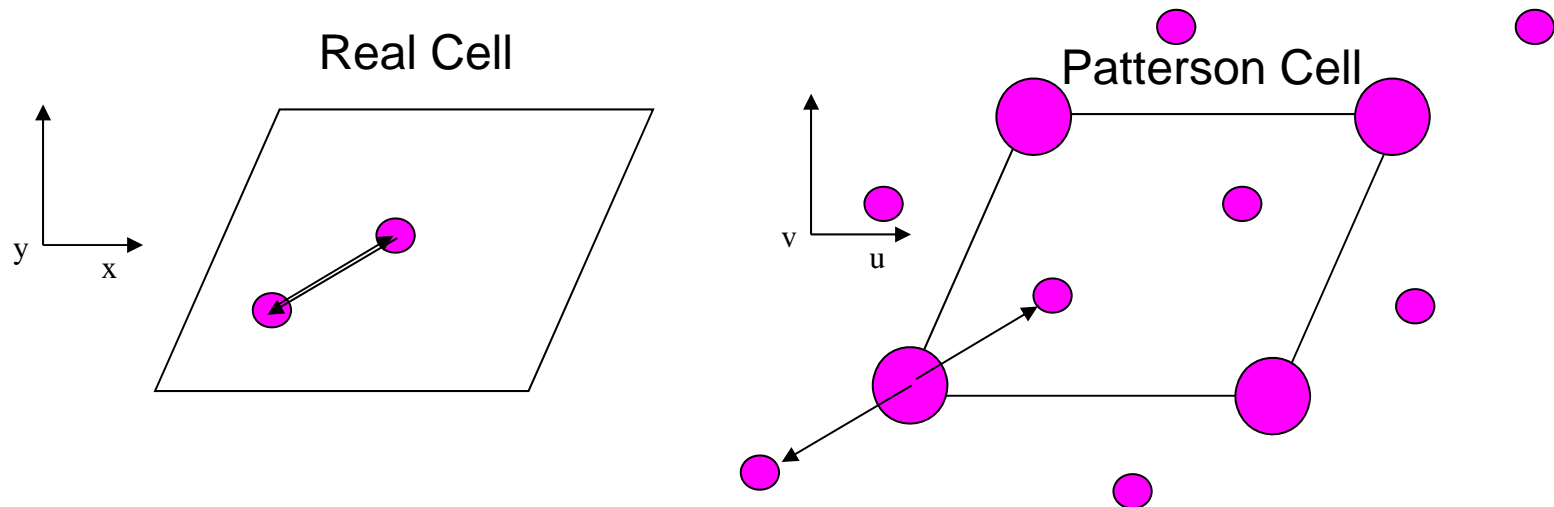


Patterson Function II



Solids normally contain well-separated atoms, and majority of scattering is near the core -- peaked

Patterson map will contain points corresponding to vectors between atoms in the real cell

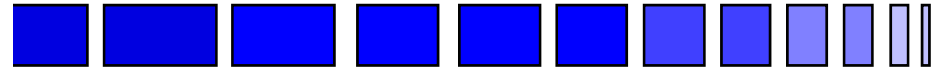


$$P(uvw) = \frac{1}{V} \sum_{hkl} I(hkl) e^{-2\pi i(hu+lv+kw)}$$

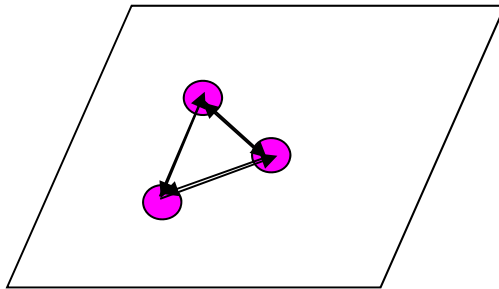
Patterson Function



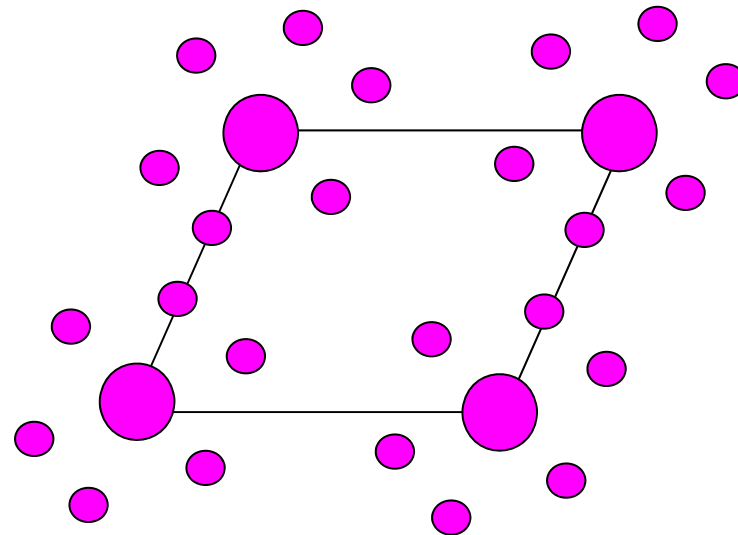
$$P(\vec{u}) = \int \rho(\vec{r}) \rho(\vec{r} + \vec{u}) d^3\vec{r}$$



Real Cell

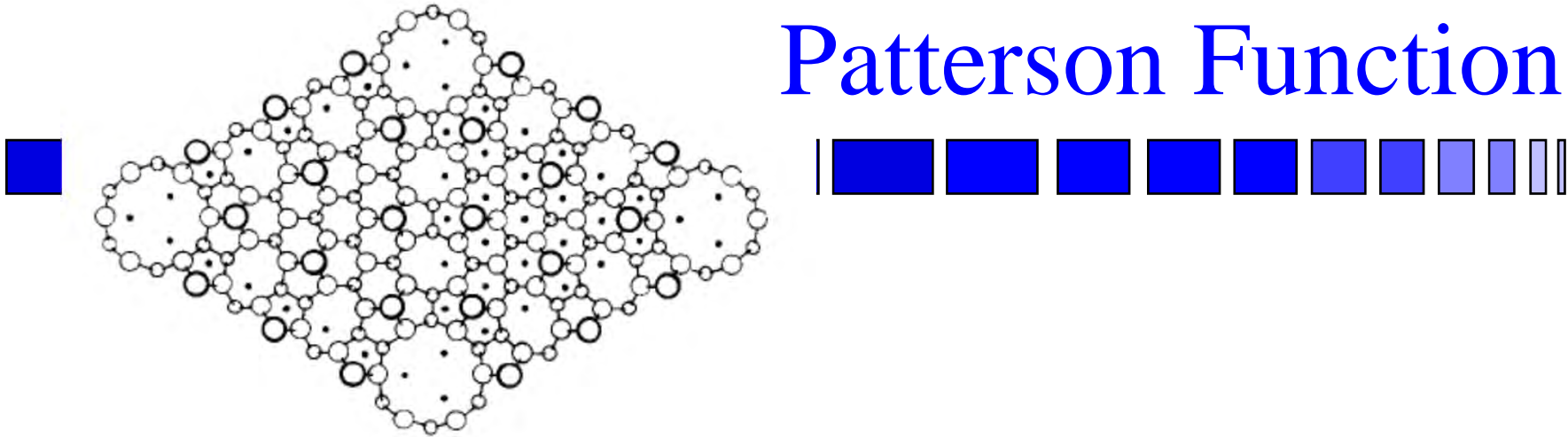


Patterson Cell



- 1) Patterson is symmetric about origin (centrosymmetry)
- 2) Can see pattern of real cell in Patterson cell repeated N times
- 3) Contains $N(N-1)$ peaks (not counting origin) → gets complicated!

Patterson Function



Structural analysis of Si(111)-7×7 by UHV-transmission electron diffraction and microscopy

K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi


Department of Physics, Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo 152, Japan

(Received 5 October 1984; accepted 13 December 1984)

Structural analysis of the surface reconstructions investigated by ultrahigh vacuum (UHV) transmission electron microscopy (TEM) and diffraction (TED) is shown. By TED intensity analysis a new structural model of Si(111)-7×7 is derived. The model basically consists of 12 adatoms arranged locally in the 2×2 structure, nine dimers on the sides of the triangular subunits of the 7×7 unit cell and a stacking fault layer. UHV-HREM of Si (111)-7×7 surface is commented.

J Vac Sci Technol A3, 1502 (1986) > 1800 Citations

The Phase Problem

- 
- We have an exit wave from the sample
 - $\psi(\mathbf{r})$ wave in real space = $a(\mathbf{r})\exp(-i\phi(\mathbf{r}))$
 - $\Psi(\mathbf{u}) = \int \exp(-2\pi i \mathbf{u} \cdot \mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} = A(\mathbf{u})\exp(-i\phi(\mathbf{u}))$
 - Observables
 - $I(\mathbf{r}) = \langle |\psi(\mathbf{r})|^2 \rangle = \langle a(\mathbf{r})^2 \rangle$ Real Space Image
 - $I(\mathbf{u}) = \langle |\Psi(\mathbf{u})|^2 \rangle = \langle A(\mathbf{u})^2 \rangle$ Diffraction Pattern
 - Note: “ $\langle \rangle$ ” is average over incoherent aberrations and other statistical terms

Diffraction Phase Problem



$$\text{Surface} \equiv \rho(\vec{\mathbf{r}}) \xrightarrow{\text{FFT}} \mathbf{F}(\vec{\mathbf{h}}) = |\mathbf{F}(\vec{\mathbf{h}})| \exp[2\pi i \Phi(\vec{\mathbf{h}})]$$

Measured diffraction intensities

$$|\mathbf{F}(\vec{\mathbf{h}})| = [I(\vec{\mathbf{h}})]^{1/2}$$

Unmeasured

An equal opportunity problem – true for x-ray and electron diffraction

Phase: Apples & Oranges



$$\text{FT} \rightarrow A_a \exp(-i \phi_a)$$



$$\text{FT} \rightarrow A_o \exp(-i \phi_o)$$

+

$$A_o \exp(-i \phi_a) \rightarrow \text{IFT} \rightarrow \begin{cases} \text{Oranle ?} \\ \text{Appge ?} \end{cases}$$

Phase of Apple + Amplitude of Orange = ?

Phase of Apple = Apple



$$\text{FT}^{-1} \{ A_o \exp(-i \phi_a) \} \Rightarrow \text{Apple}$$

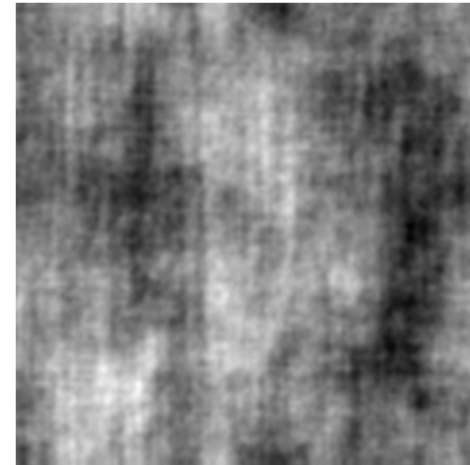
Phase is more important than amplitude

The importance of phase information



Suzy

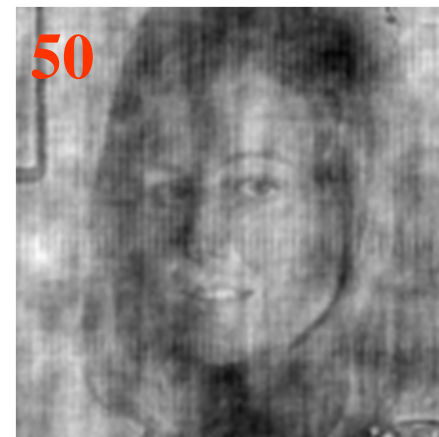
Correct Modulus
Random Phases



Correct Phase
Random Modulus

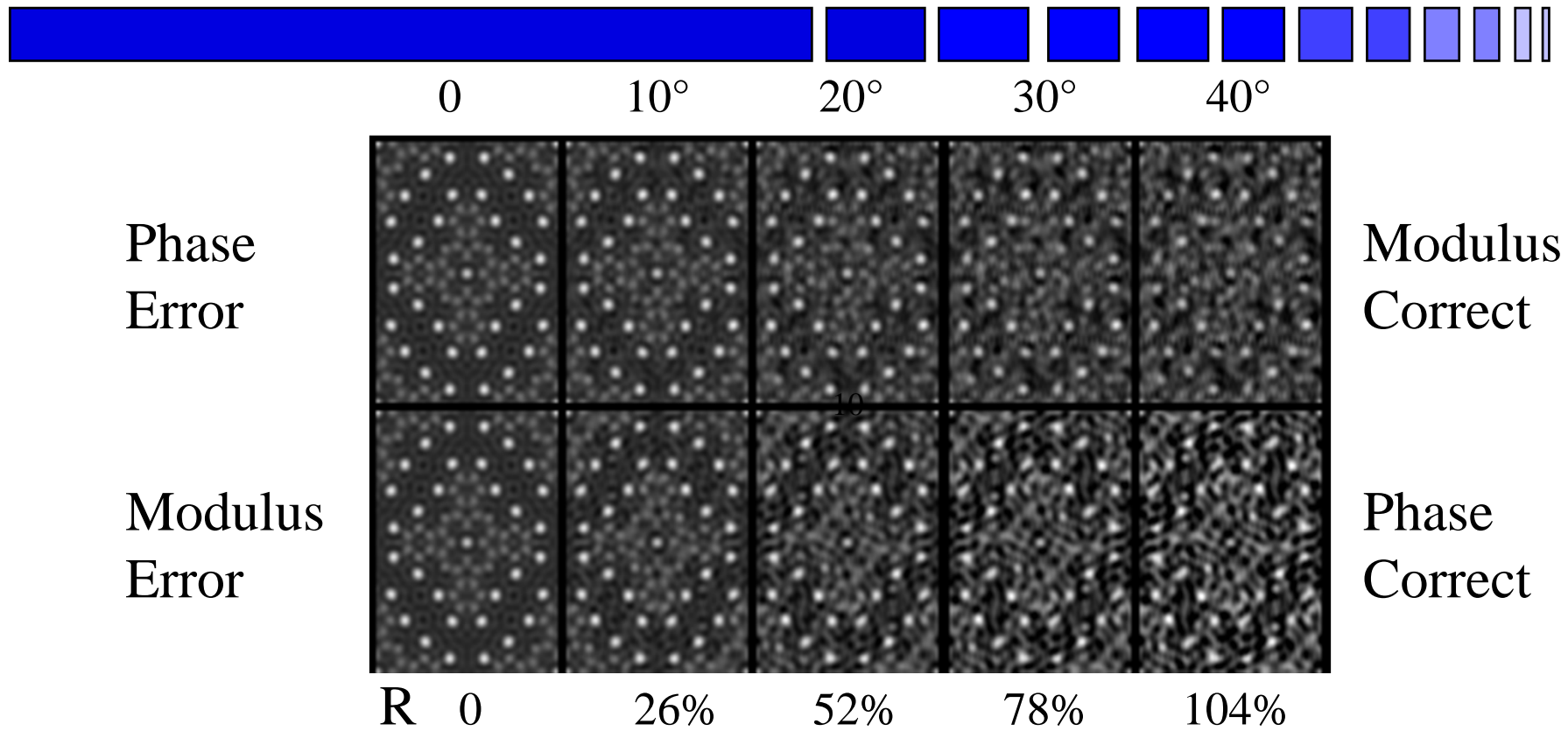


Role of error in phases (degrees)



We would like to find the phases exactly, but we don't have to

Phase and Modulus Errors



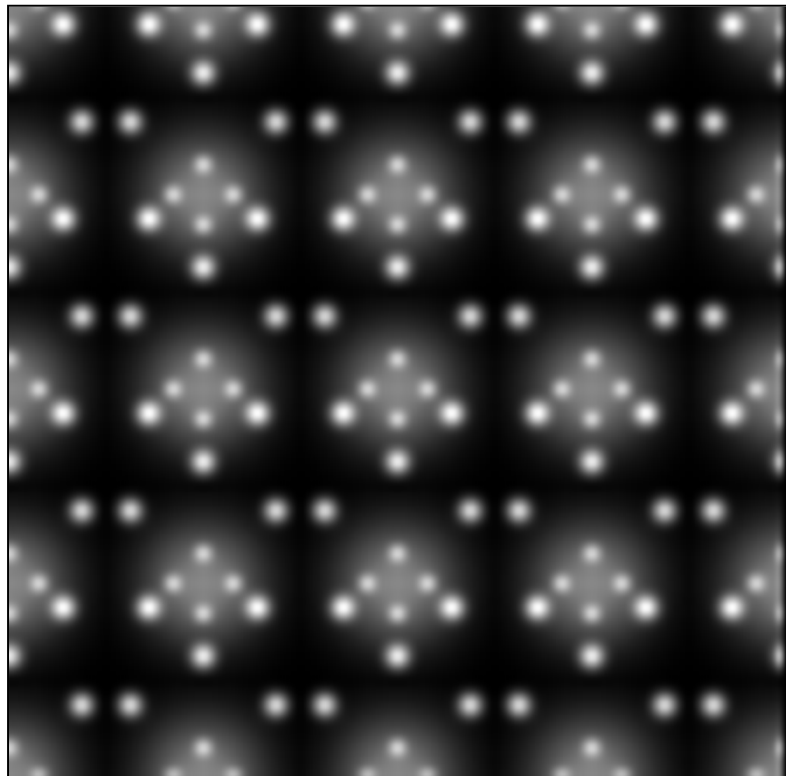
We only need **approximately correct** phases

We can **tolerate** modulus errors

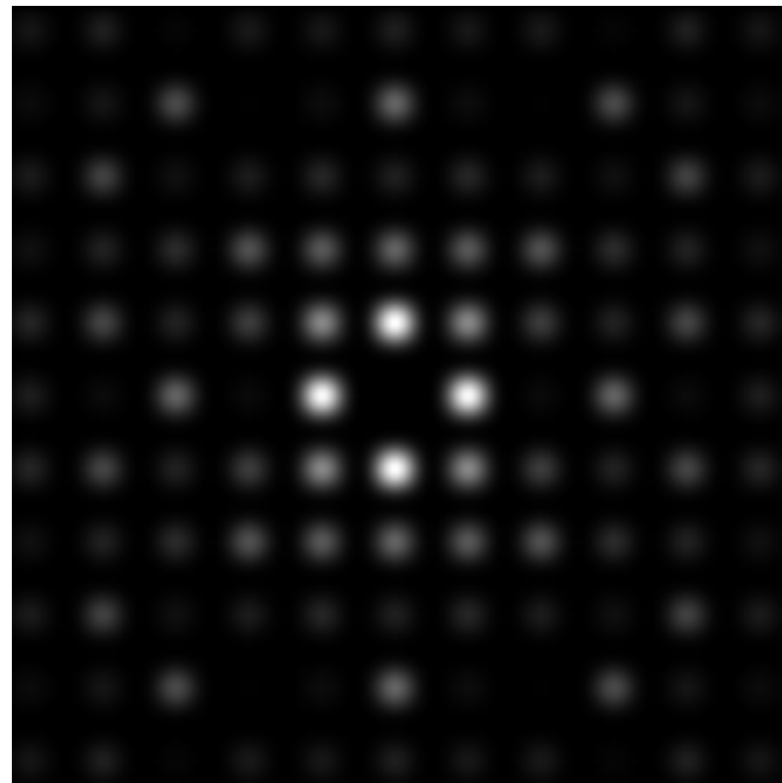
Demonstration: how resolution works in reciprocal space: If we can add beams at large distance from center of patterns *with the correct phase*, we can reconstruct the structure with very high definition:



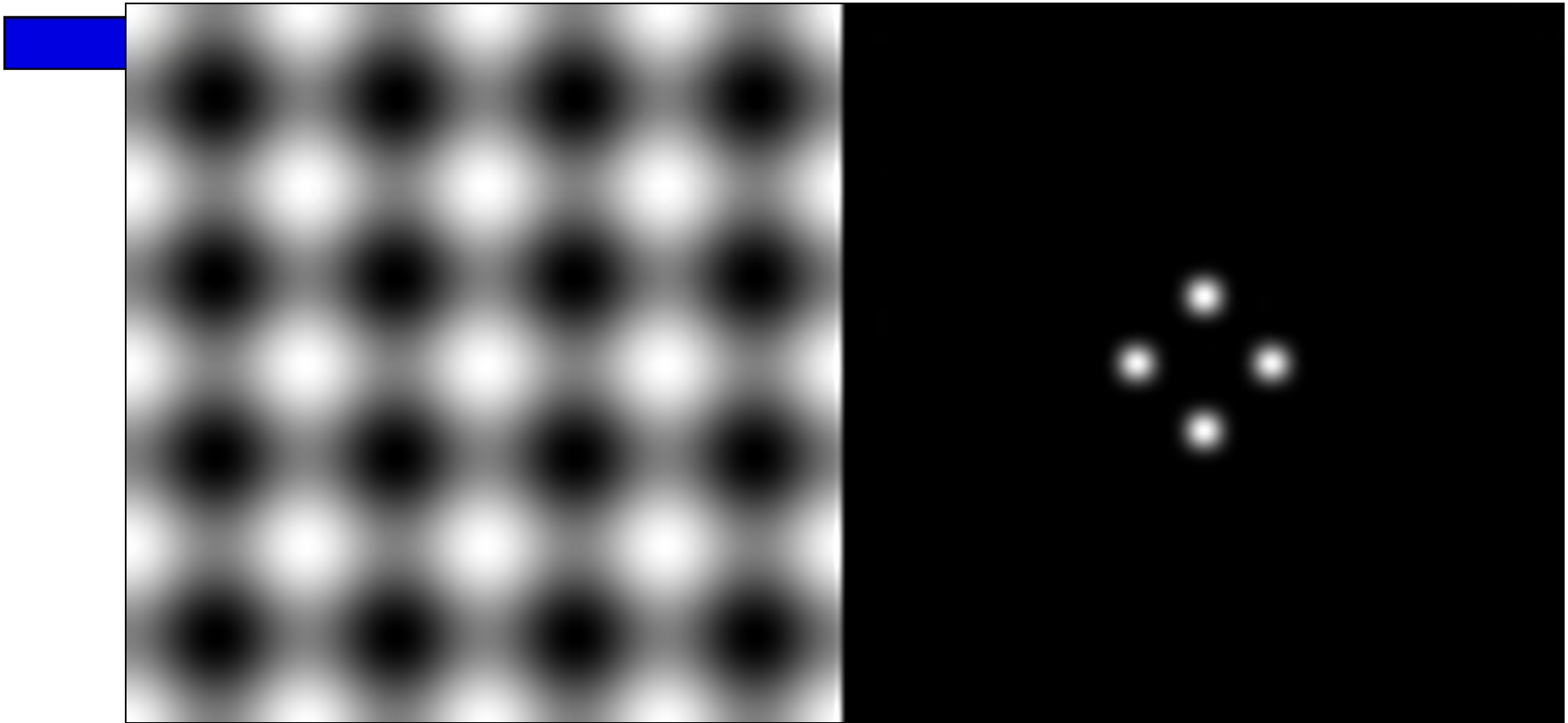
Example: simple test structure of repeated molecule



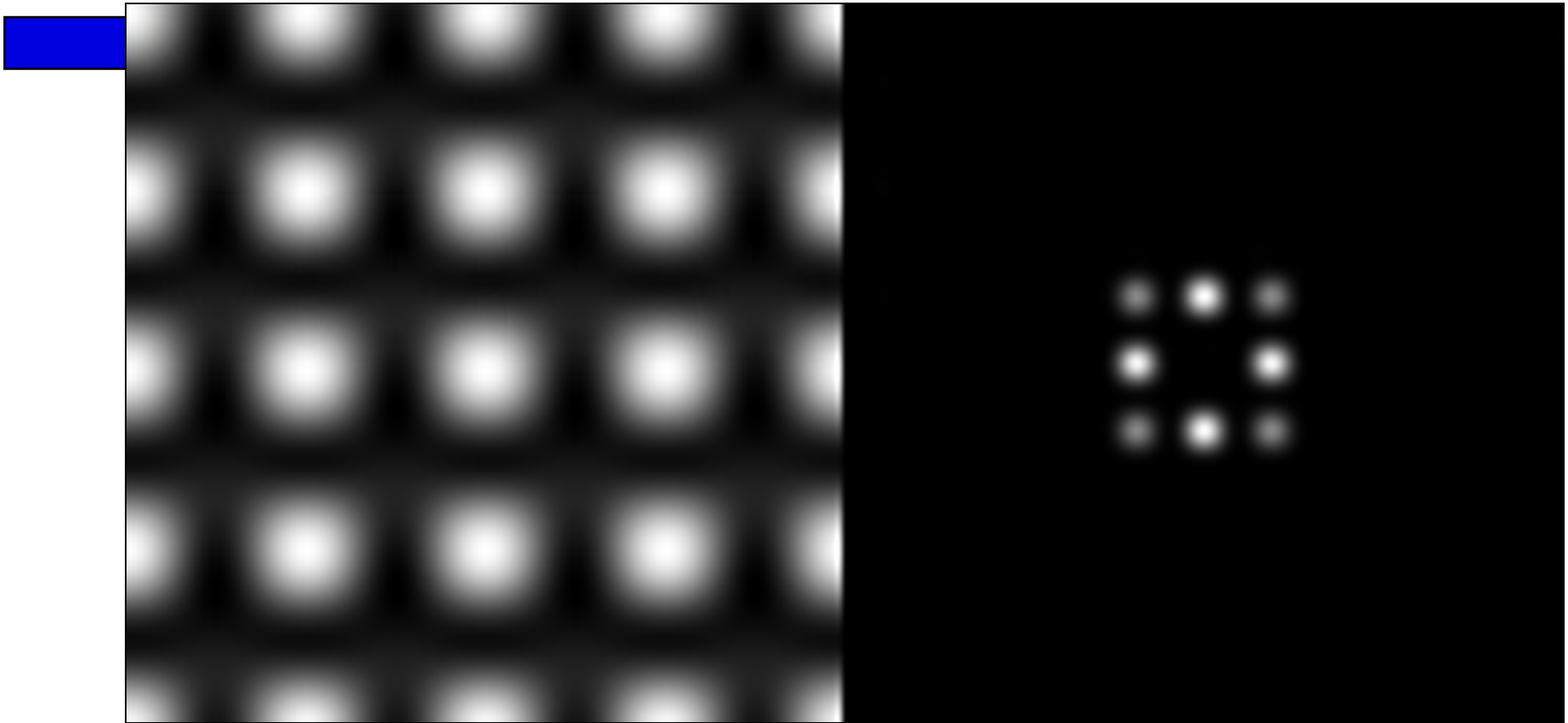
Computed diffraction pattern of structure at left.



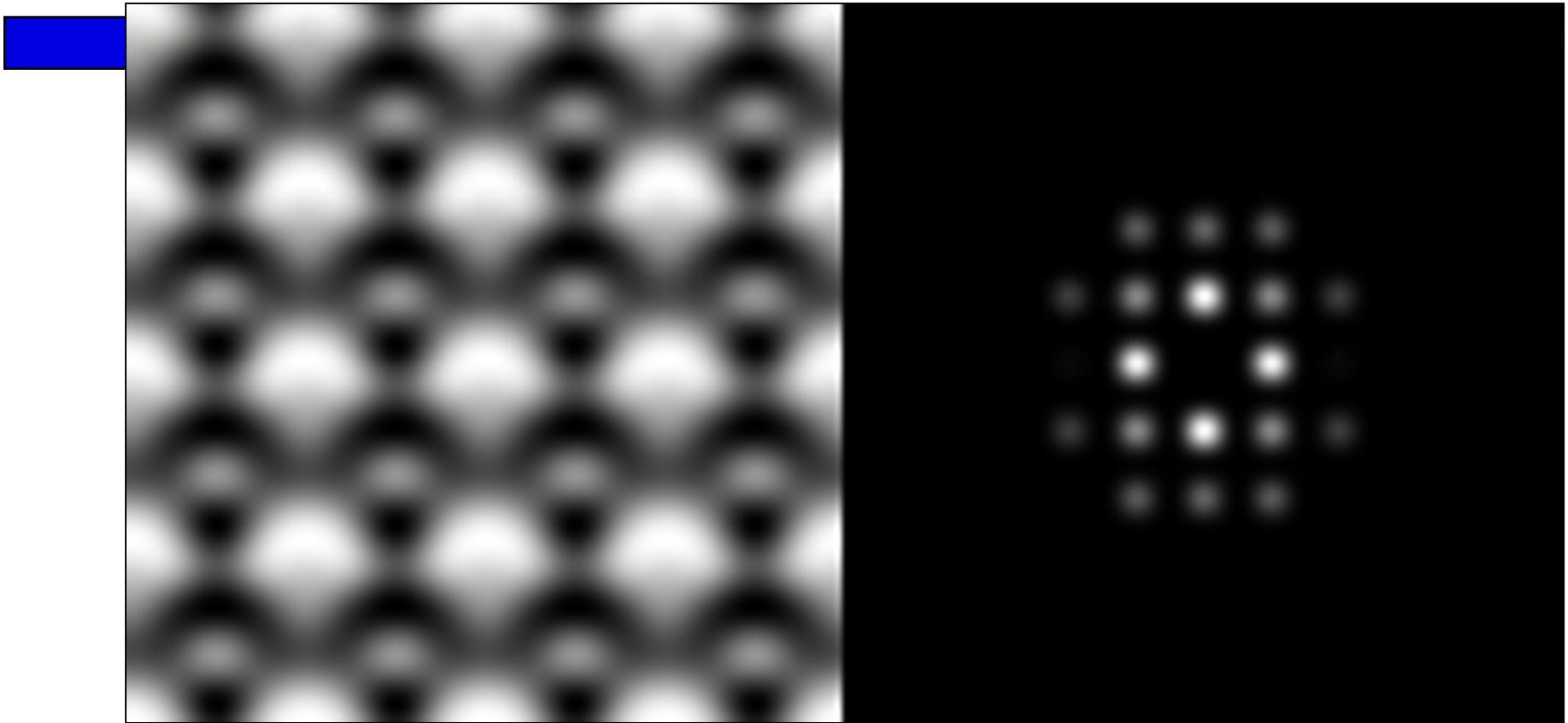
Low Resolution ...



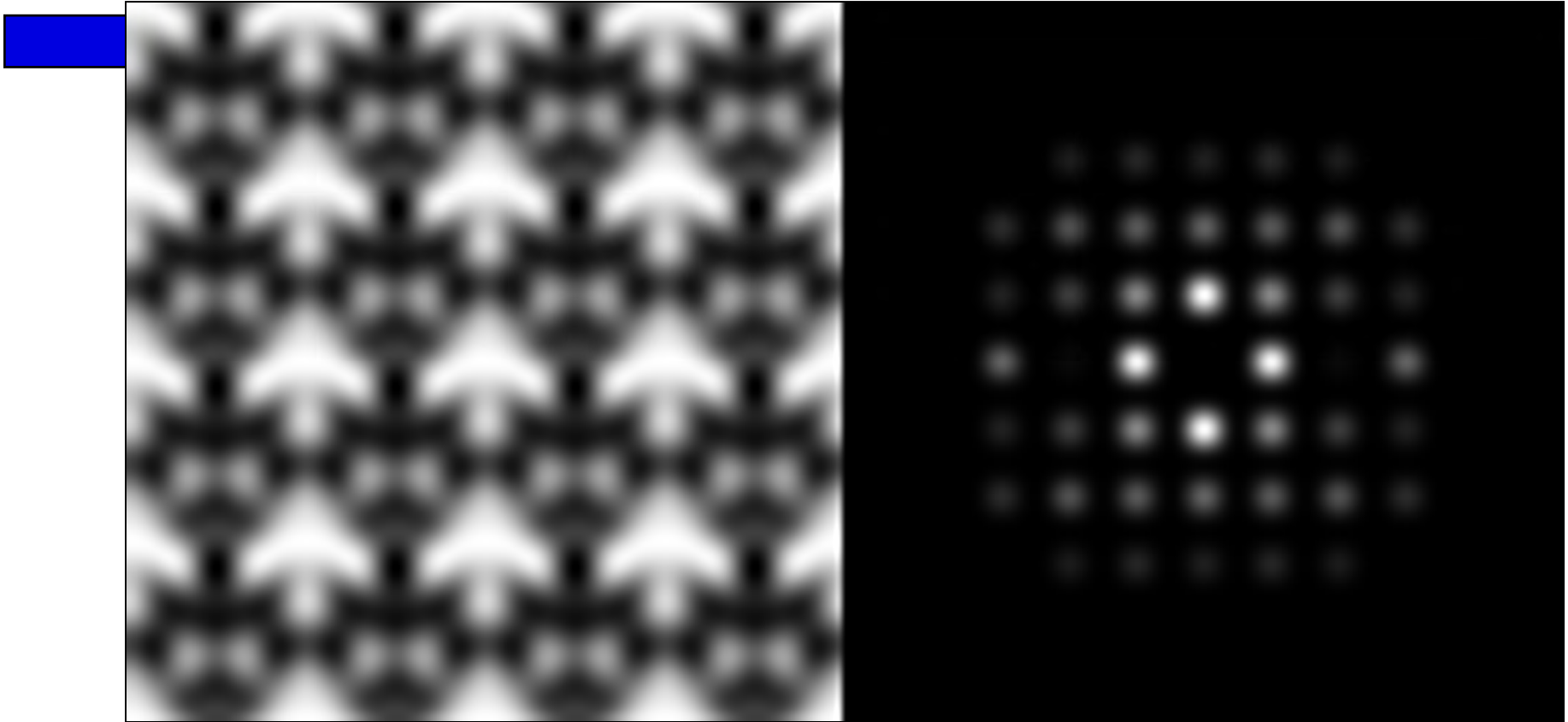
Higher resolution ...



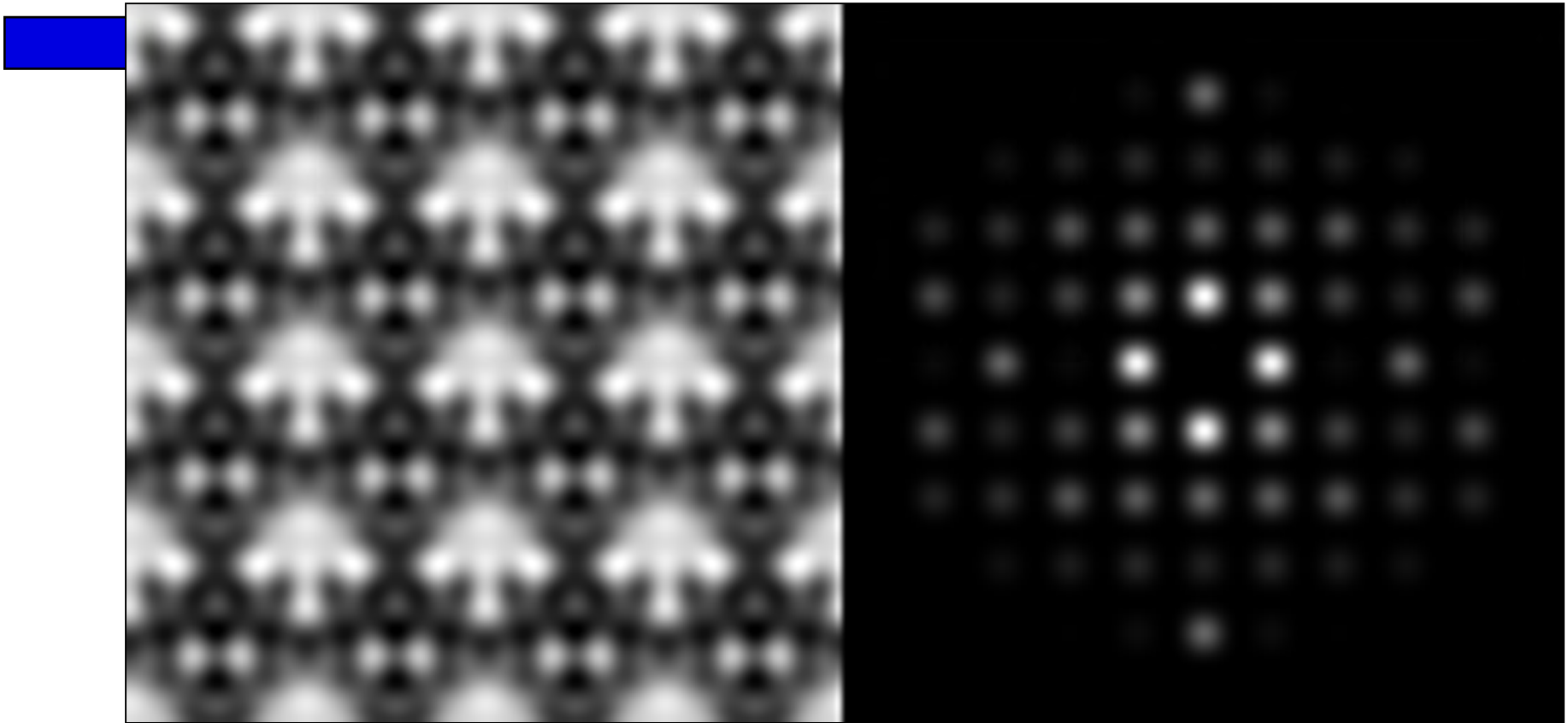
Higher resolution ...



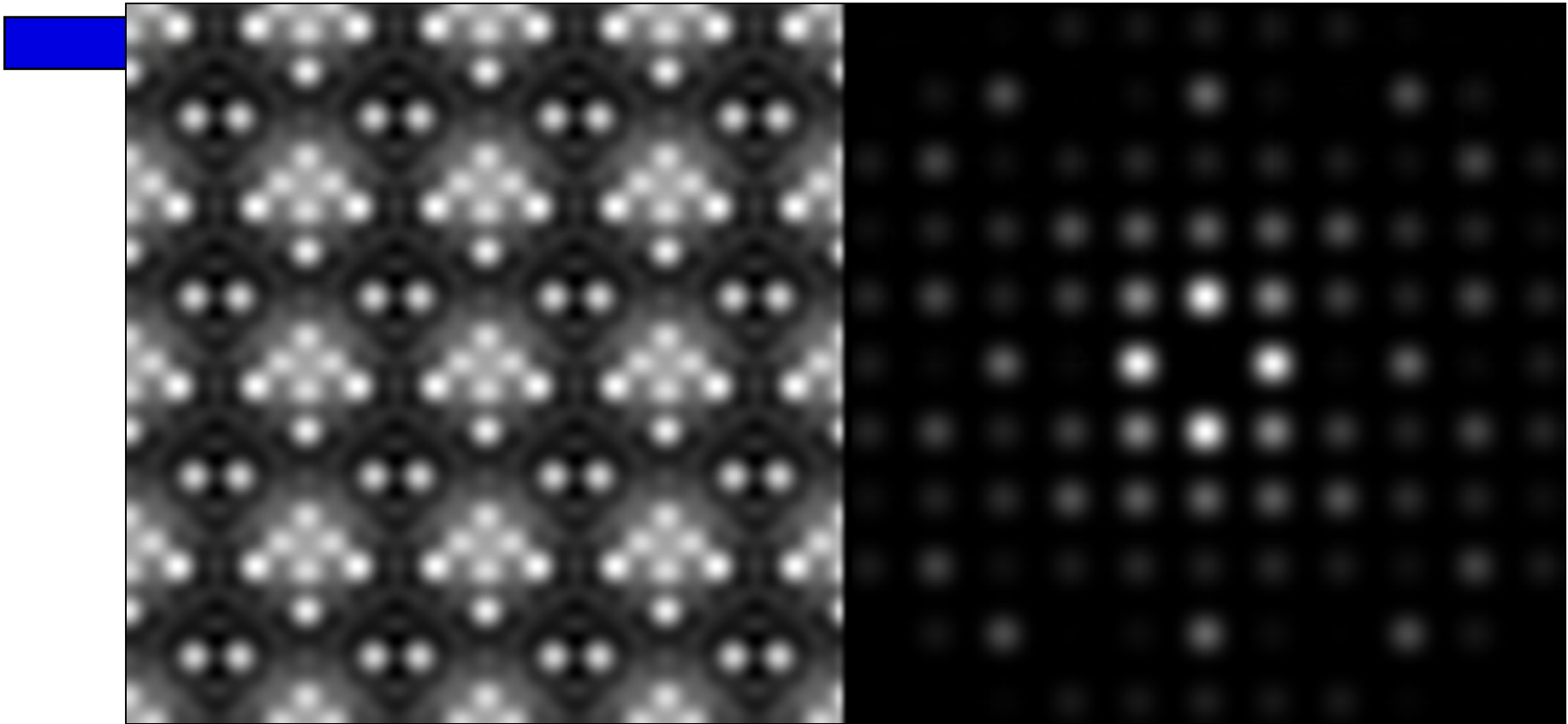
Higher resolution ...



Higher resolution ...



This is the goal of direct methods. Given measurement of amplitudes, obtain phases using educated guesswork. As illustrated, good phases give accurate representation of structure.



How do we overcome this



- Recover phase information from a series of images at different defocus.
 - Classic inversion problem which can be ill-conditioned
- Recover phase information for special cases where solution is exact (in principle)
- Recover approximate phase information using constraints (direct methods)

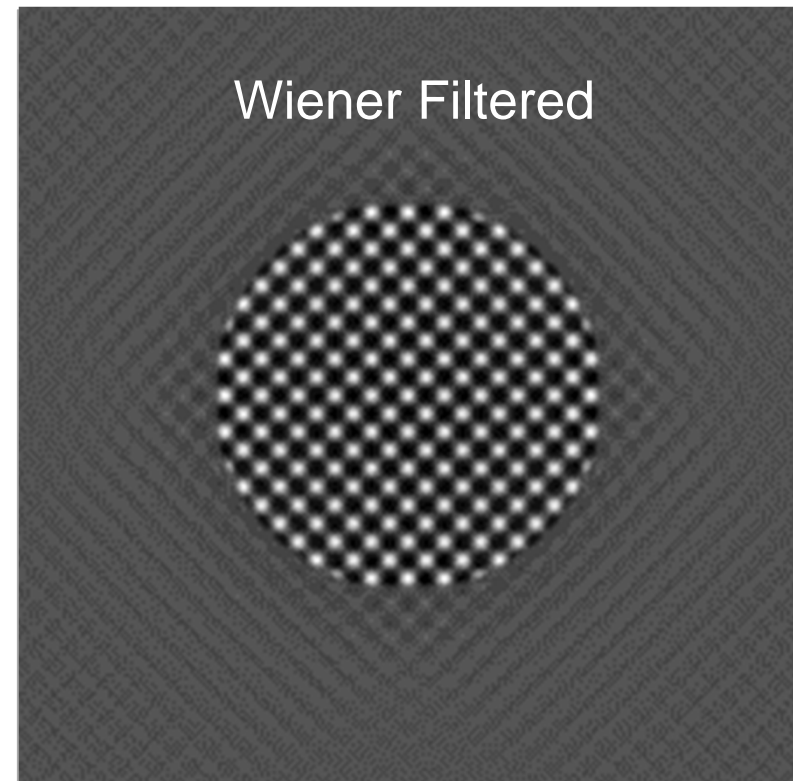
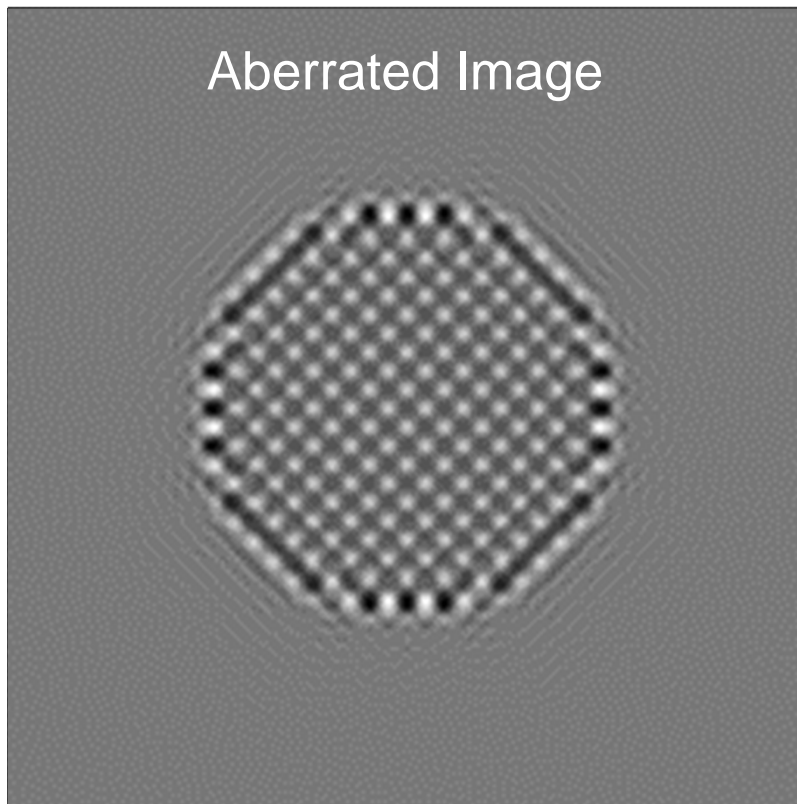
Inversion



- $I(r) \sim \int \Psi(u)T(u)\exp(2\pi iu.r)du + \text{noise}$
write $A(u)=\Psi(u)T(u)$
- The optimal filter (L2) $F(u)$ to apply is given by (Wiener, 1940)
$$F(u) = T^*(u)/\{|T(u)|^2+n(u)^2/S(u)^2\}$$

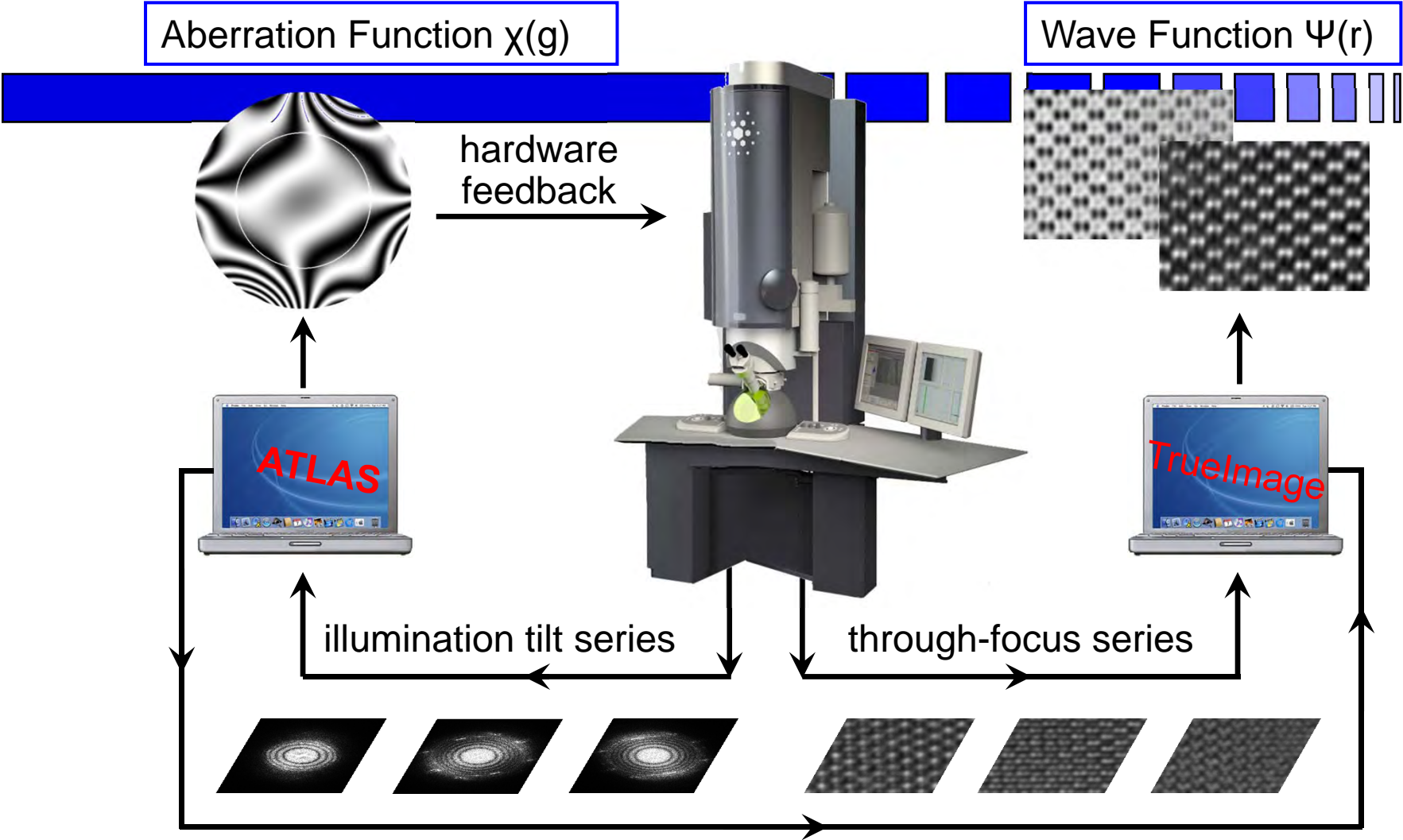
 $n(u)$ = spectral distribution of noise
 $S(u)$ = estimate of signal

Wiener Filtering

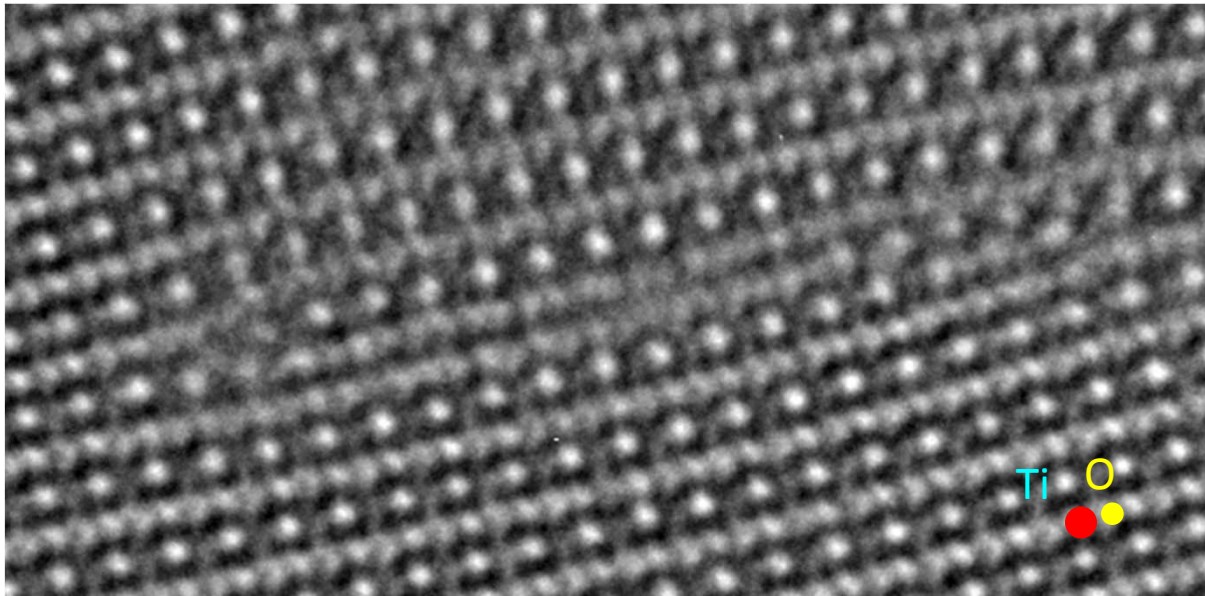


Simple Semper Example

Aberration control & reconstruction of electron wave function



ATLAS & Truelmage:: Stacking Faults in SrTiO₃ (110)



Z_{opt} micrograph

Titan 80-300

deficiencies:

shaded columns

inf. signal-to-noise ratio

spurious contrast peaks

[001]



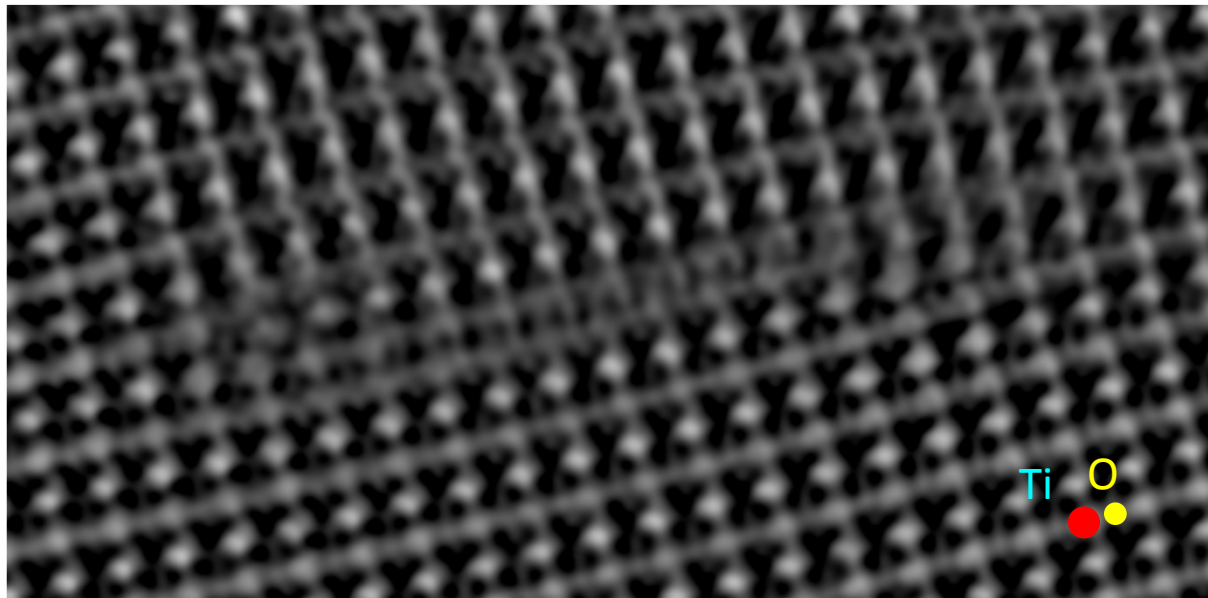
[1̄10]

1.38 Å

J. Barthel, PhD Thesis (2007)

Curtesy Rafal Dunin-Borkowski

ATLAS & TruelImage:: Stacking Faults in SrTiO₃ (110)



uncorrected phase image

Titan 80-300

deficiencies:

shaded columns

[001]



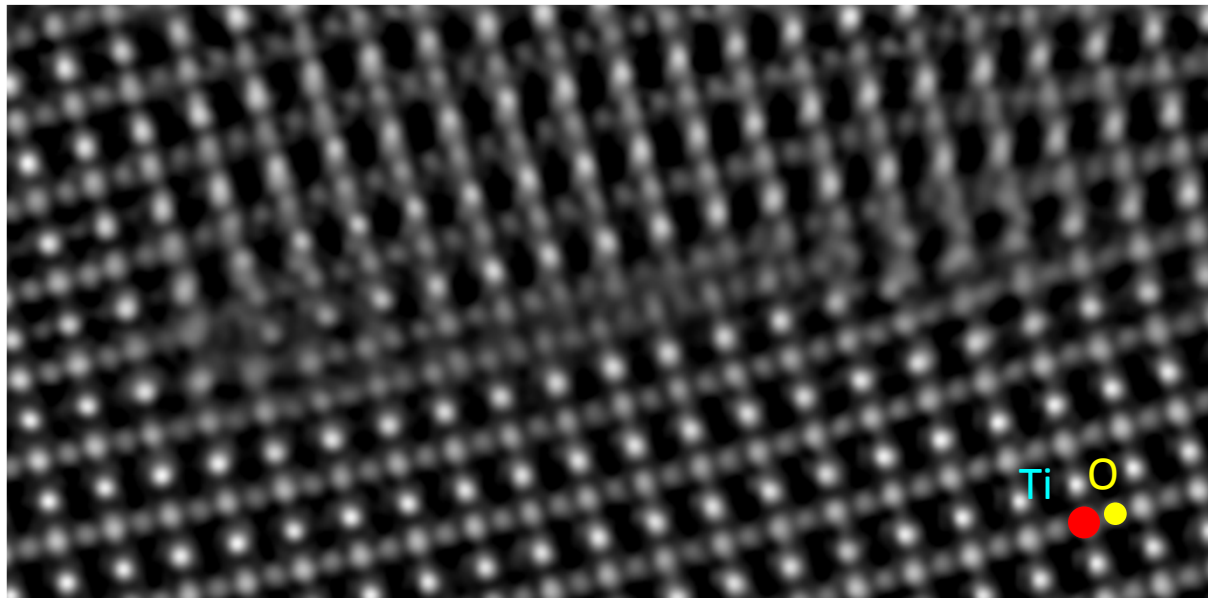
[1̄10]

1.38 Å

J. Barthel, PhD Thesis (2007)

Curtesy Rafal Dunin-Borkowski

ATLAS & TruelImage:: Stacking Faults in SrTiO₃ (110)



corrected phase image

Titan 80-300

deficiencies:

none

Ti O
1.38 Å

[001]
[1̄10]

J. Barthel, PhD Thesis (2007)

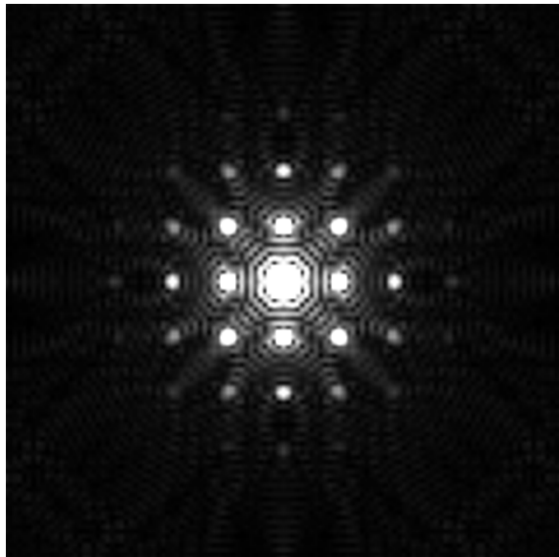
Curtesy Rafal Dunin-Borkowski

Exact Cases



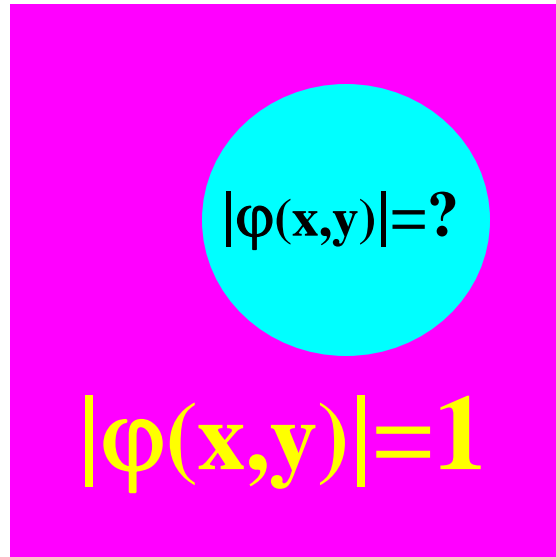
- Suppose we have N pixels, and $N/2$ are known to be zero (compact support)
- Wave is described by $N/2$ moduli, $N/2$ phases (for a real wave) in reciprocal space
- Unknowns – N ; measurements $N/2$; constraints $N/2$
- Problem is in principle fully solveable
(It can be shown to be unique in 2 or more dimensions, based upon the fundamental theorem of algebra)

Example: Diffractive Imaging



True diffraction pattern
for small particle model
(Non-Convex Constraint)

+



Convex Support
Constraint

= ?

Example: Diffractive imaging

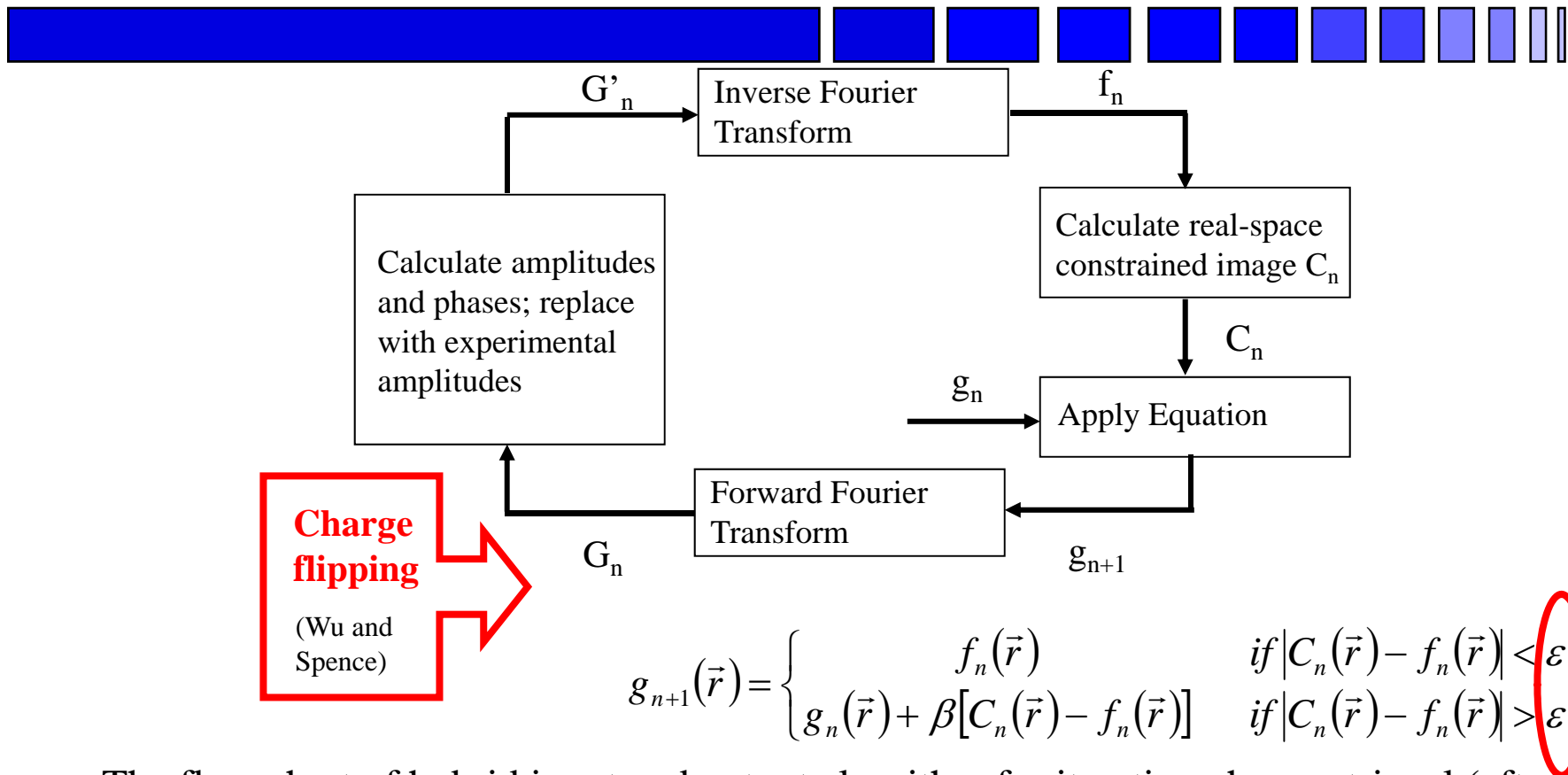


- Constraint: part of real-space x is zero
(Convex constraint)
- Iteration
 - $x = 0$, part of map
 - $|\mathbf{X}| = |\mathbf{X}_{\text{observed}}|$



Iterate

The Algorithm

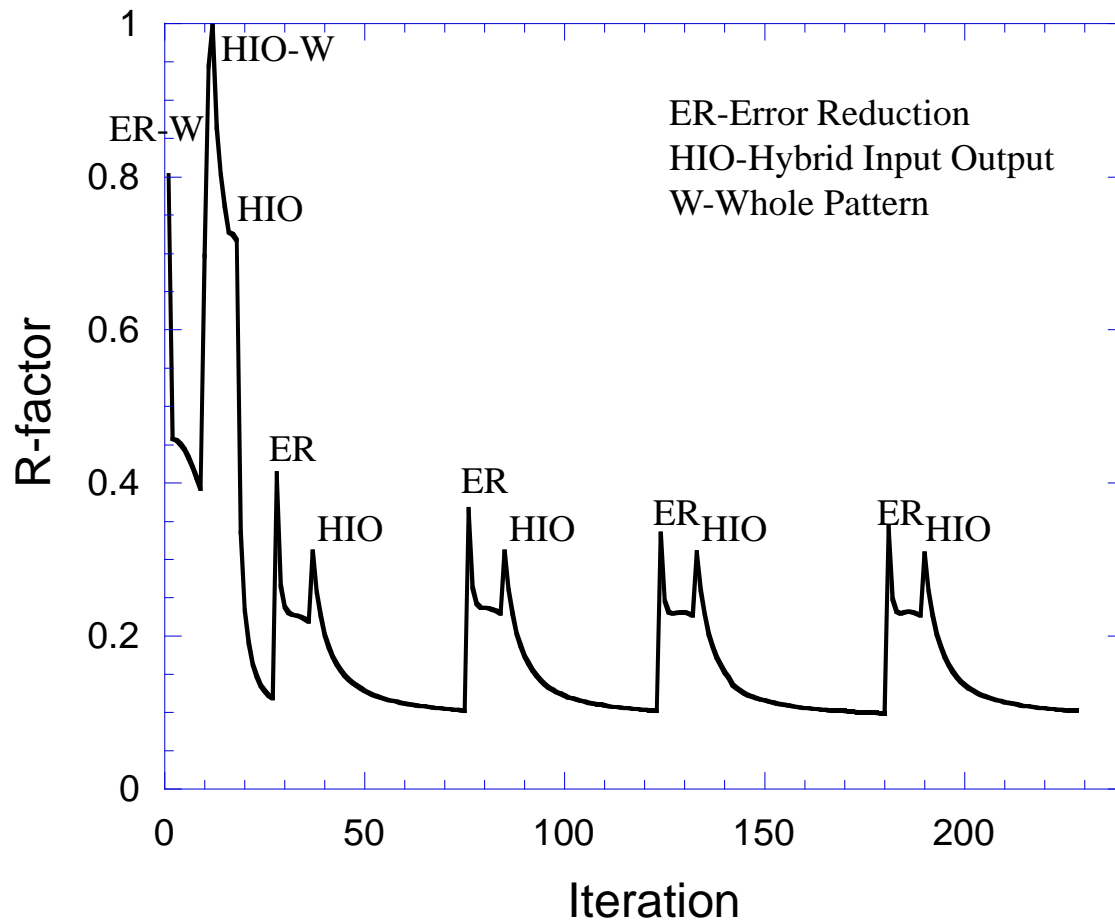


The flow chart of hybrid input and output algorithm for iterative phase retrieval (after Millane and Stroud, 1997).

Convergence and the Missing Central Beam



DW-4 Seed = 211

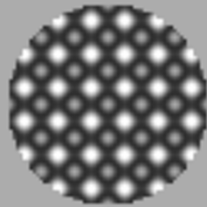
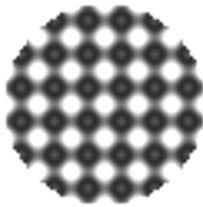
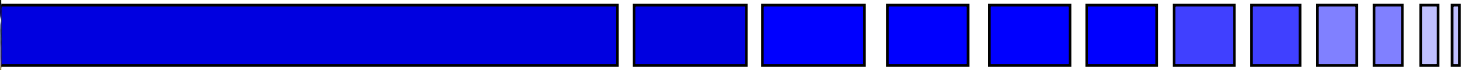


$$R = \frac{\sum \left| |F^{Exp}| - |F^R| \right|}{\sum |F^{Exp}|} 100\%$$

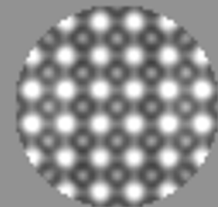
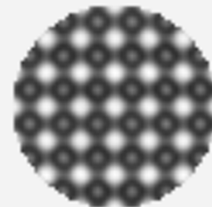
- Missing central beam from IP saturation
- Use low mag. TEM image
- Reconstruction start with the whole pattern
- Finish with as recorded diffraction pattern



Phase Recovery

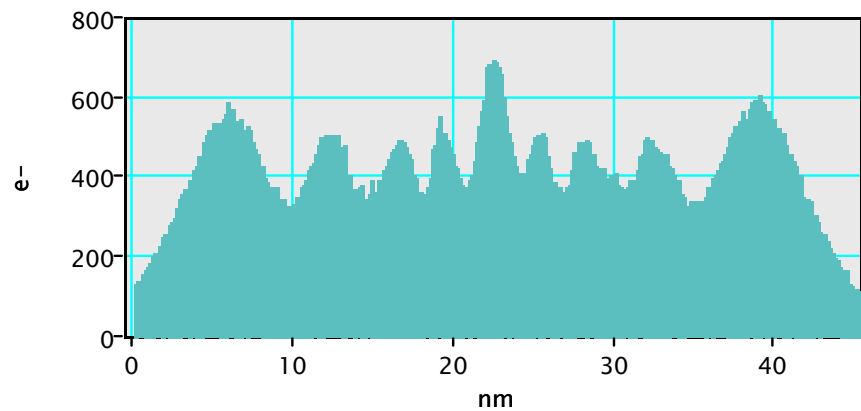
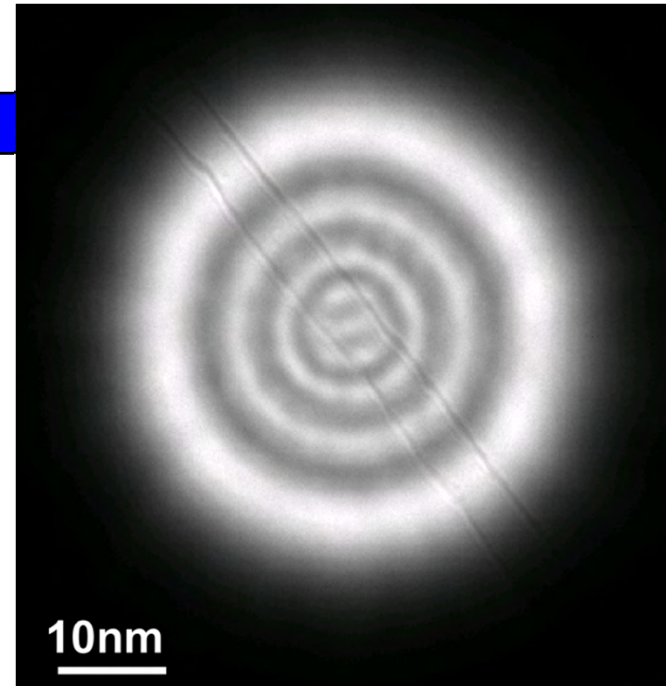
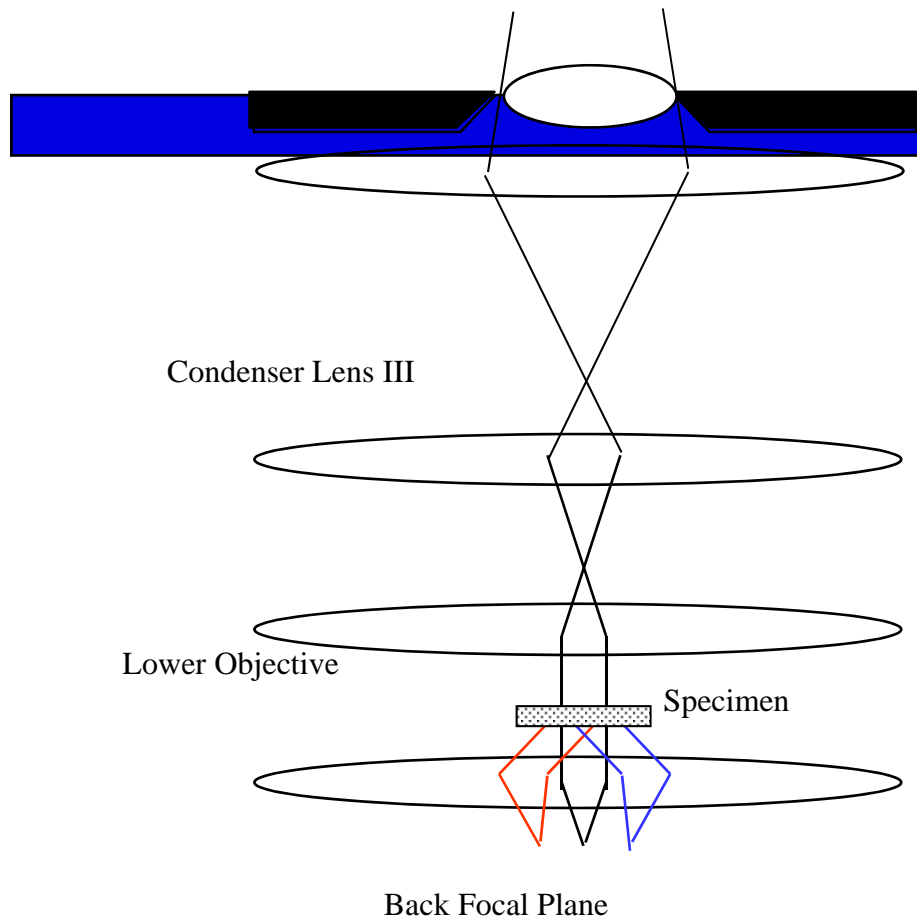


True real space exit wave for small particle model



Reconstructed exit wave after 3000 iterations

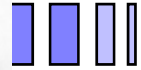
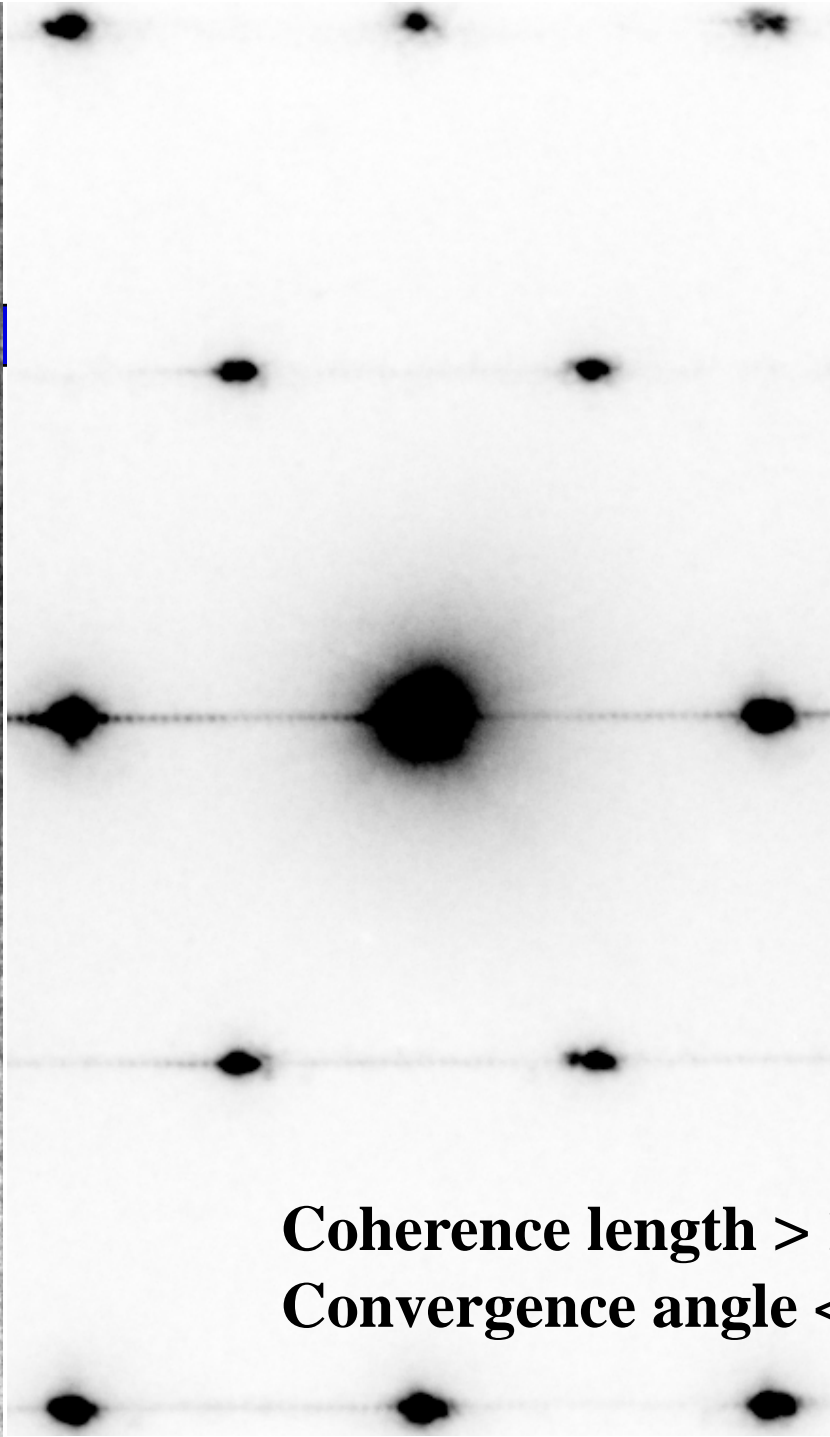
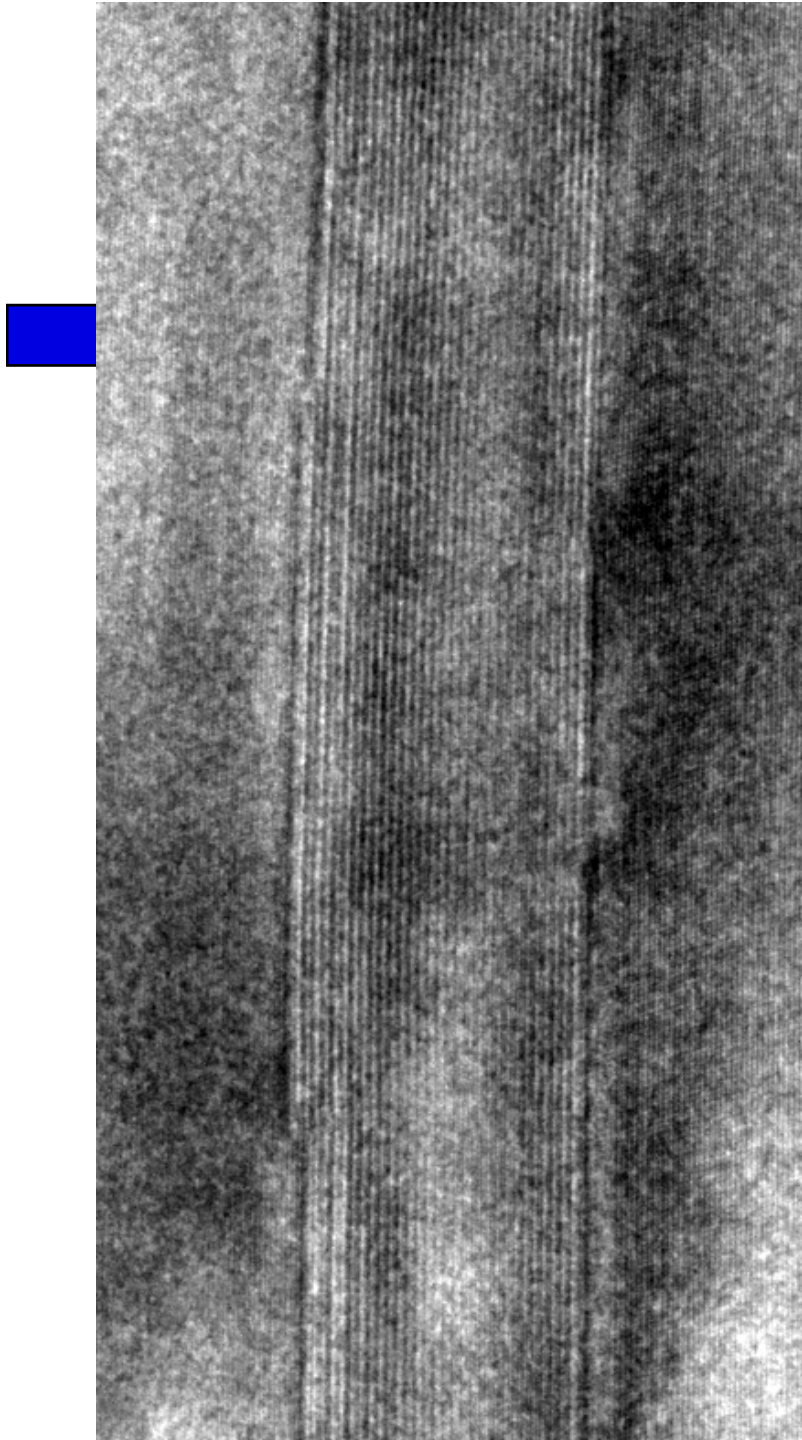
Electron Nanoprobe formation



10 μm aperture \rightarrow 50 nm beam

$M = 1/200$

JM Zuo et al, Science 300, 1419 (2003)



Coherence length > 15 nm
Convergence angle < 0.2 mrad

Coherent X-ray Diffraction

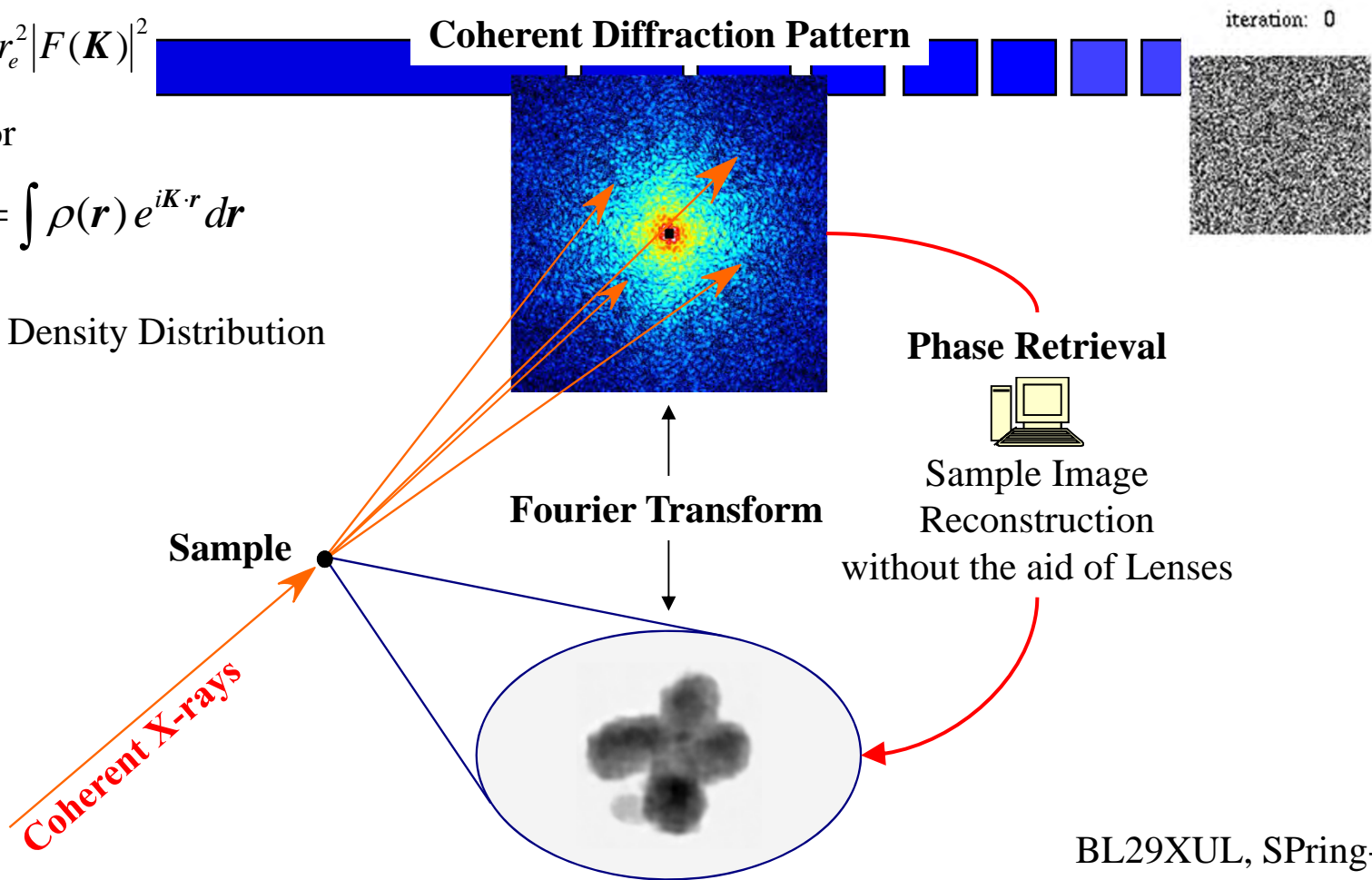
Differential Cross Section

$$\frac{d\sigma}{d\Omega} = Pr_e^2 |F(\mathbf{K})|^2$$

Structure Factor

$$F(\mathbf{K}) = \int \rho(\mathbf{r}) e^{i\mathbf{K}\cdot\mathbf{r}} d\mathbf{r}$$

$\rho(\mathbf{r})$: Electron Density Distribution



Unstained Human Chromosome

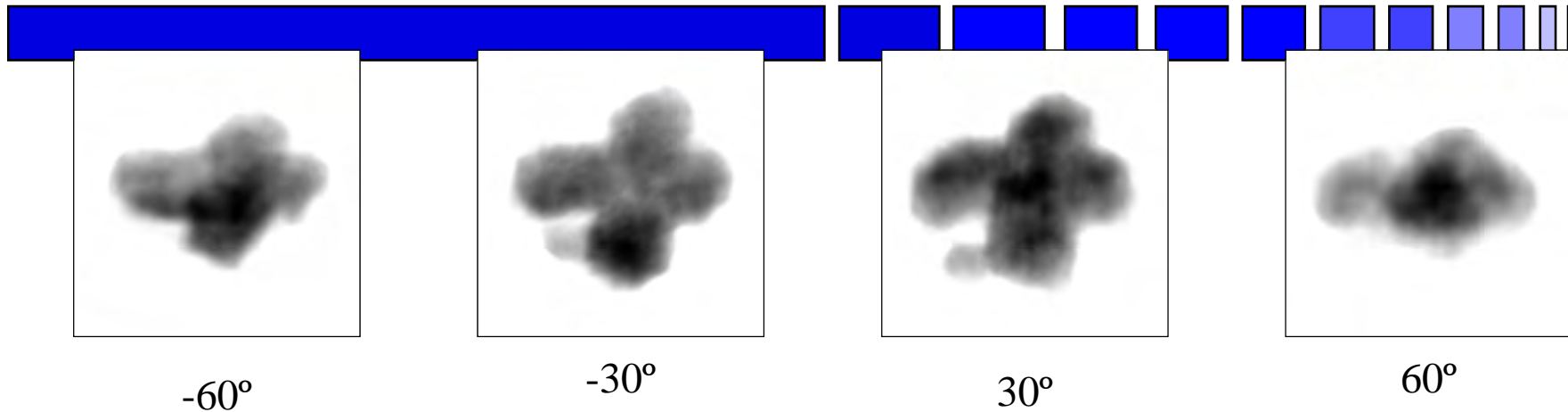
BL29XUL, SPring-8

Y. Nishino, Y. Takahashi, N. Imamoto, T. Ishikawa, and K. Maeshima, submitted (2008).

From 2D to 3D

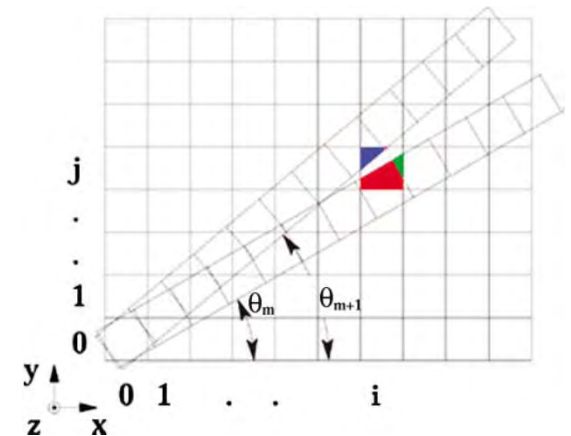
Coherent diffraction measurement at 38 incident angles

from -70° to 70° at 2.5° intervals at the minimum



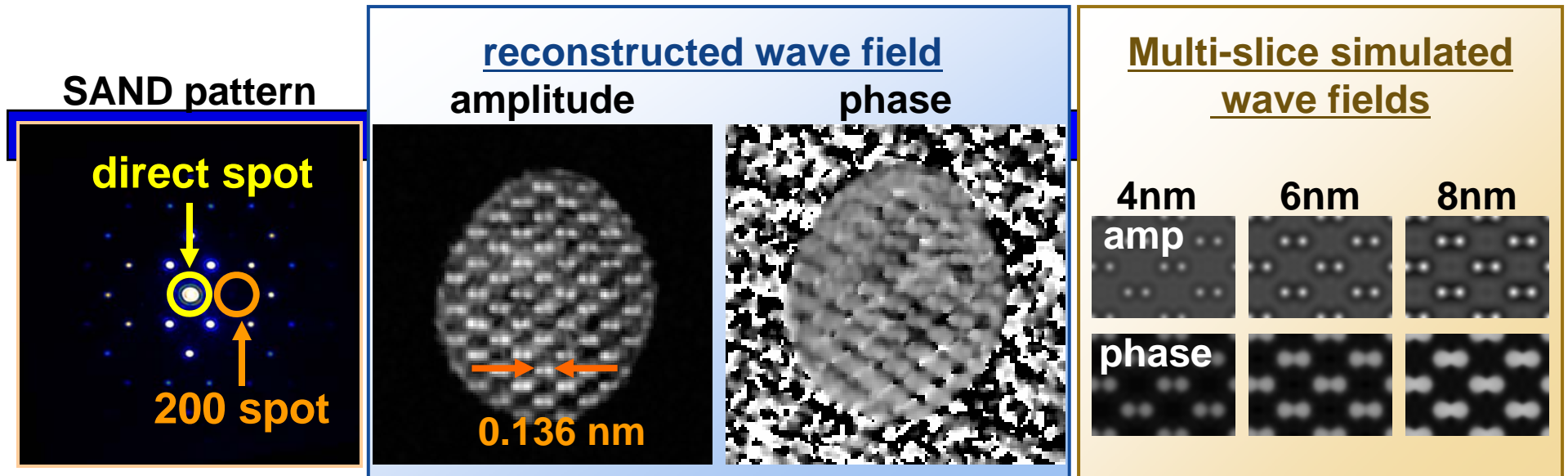
exposure time at each incident angle: 2700 s

- **normalize** the diffraction data by using the total number of electrons in the 2D reconstruction
- use **interpolation** to obtain diffraction intensity in each voxel
- image reconstruction using 3D Fourier transformation



J. Miao, T. Ishikawa, B. Johnson, E.H. Anderson, B. Lai & K.O. Hodgson, PRL **89**, 088303 (2002)

Reconstructed Si structure



- Intensity ratio of 200 and the direct spots → thickness : 4 ~ 8 nm

amplitude

- **Dumbbell structure with the separation of 0.136 nm is resolved clearly**
→ We succeeded in reconstructing dumbbell structure in silicon

phase

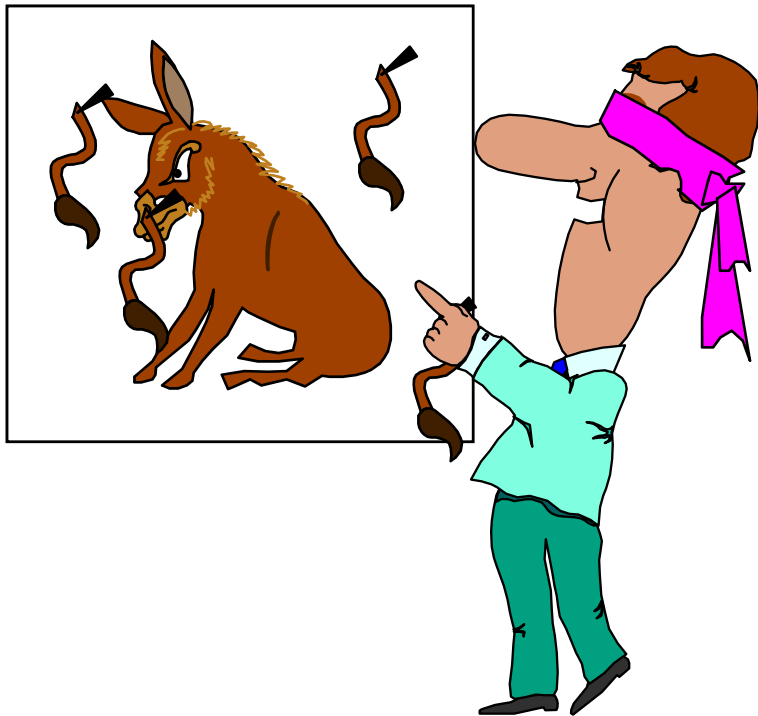
- Lattice fringes can be seen, but dumbbell structure is not reconstructed

**Nano structures can be reconstructed with atomic resolution
by electron diffractive imaging using SAND**

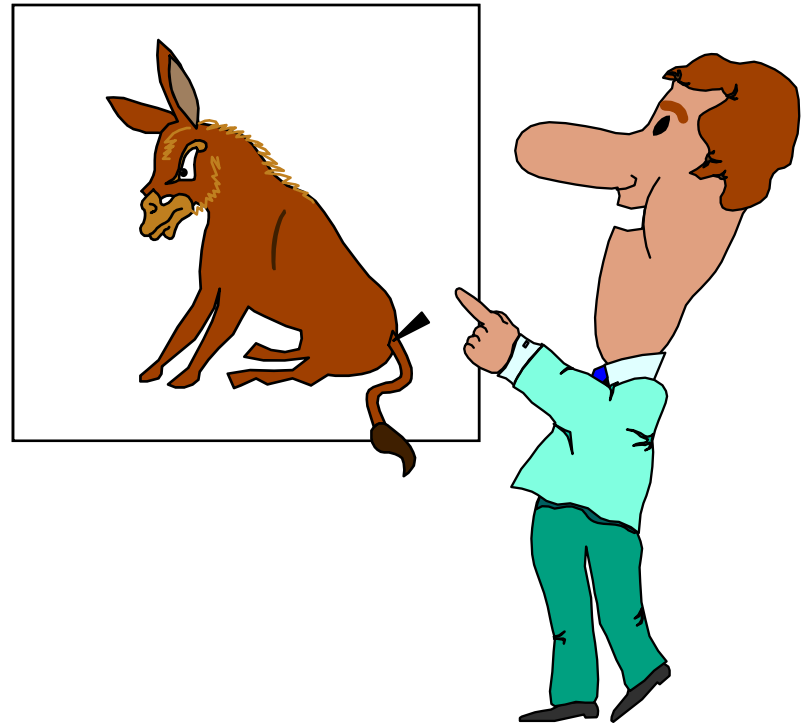
Direct Methods vs. Indirect Methods



Indirect Methods:
“Trial and Error”



Direct Methods:
Using available information
to find solutions



Implementation

*Infinite Number of Possible
Arrangements of
Atoms*

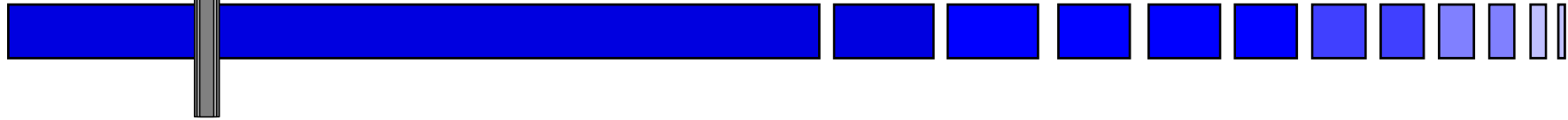
Direct Methods

Finite

R, χ^2 , structure,
DFT and chemistry



What do D.M. give us



- With the moon in the right quarter -- real space potential/charge density
- In other cases:
 - Atom positions may be wrong (0.1-0.2 Å)
 - Peak Heights may be wrong
 - Too many (or too few) atoms visible
- But... this is often (*not always*) enough to complete the structure

Chris Gimore

Additional Information Available



- Physical nature of experiment
 - Limited beam or object size
- Physical nature of scattering
 - Atomic scattering
- Statistics & Probability
 - Minimum Information/Bias = Maximum Entropy

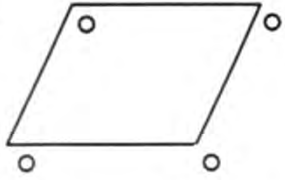
Symmetry



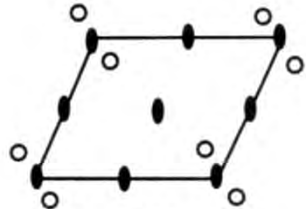
- Has to be determined *a-priori*
 - CBED
 - HREM (maybe)
 - Spot Pattern (can be tricky)



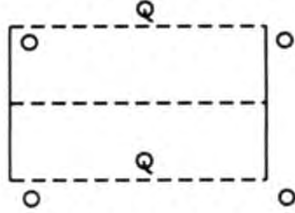
p1



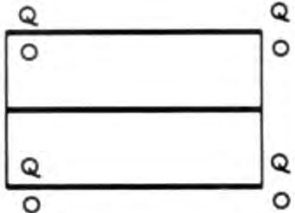
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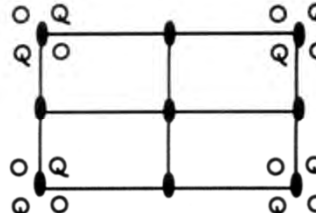
pg



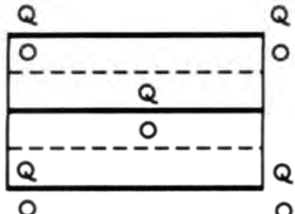
pm



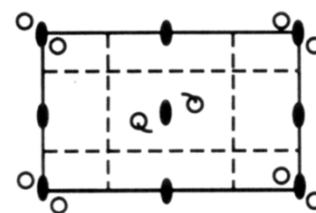
pmm



cm



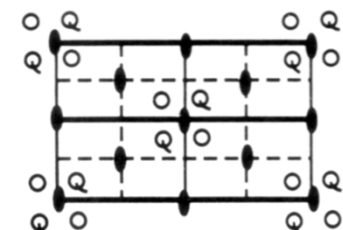
pgg



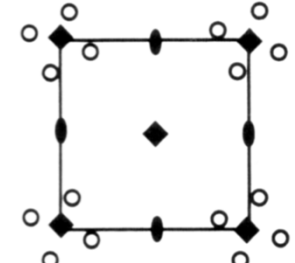
pmg



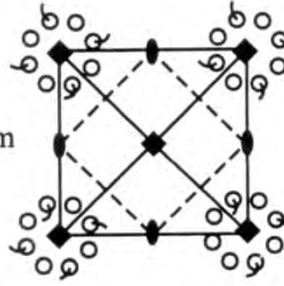
cmm



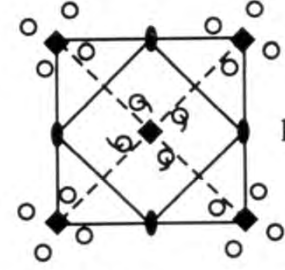
p4



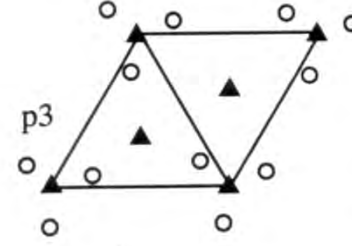
p4m



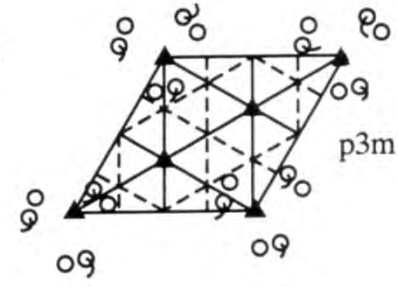
p4g



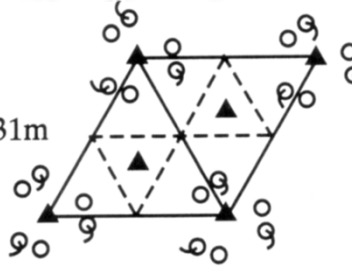
p3



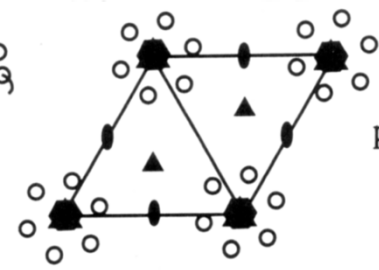
p3m1



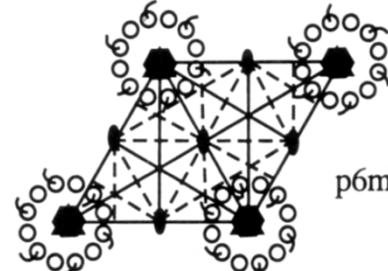
p31m

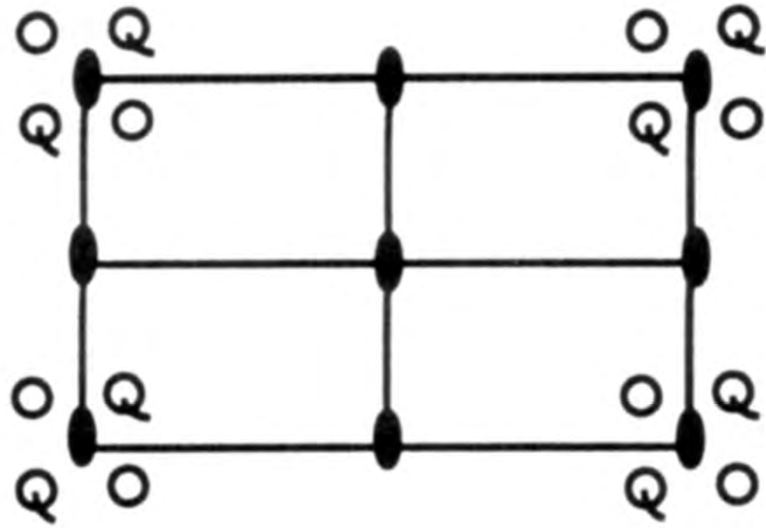


p6

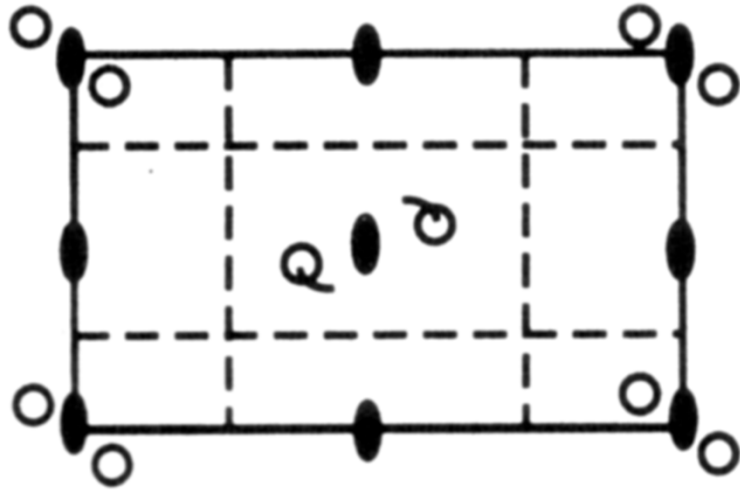


p6m





pmm



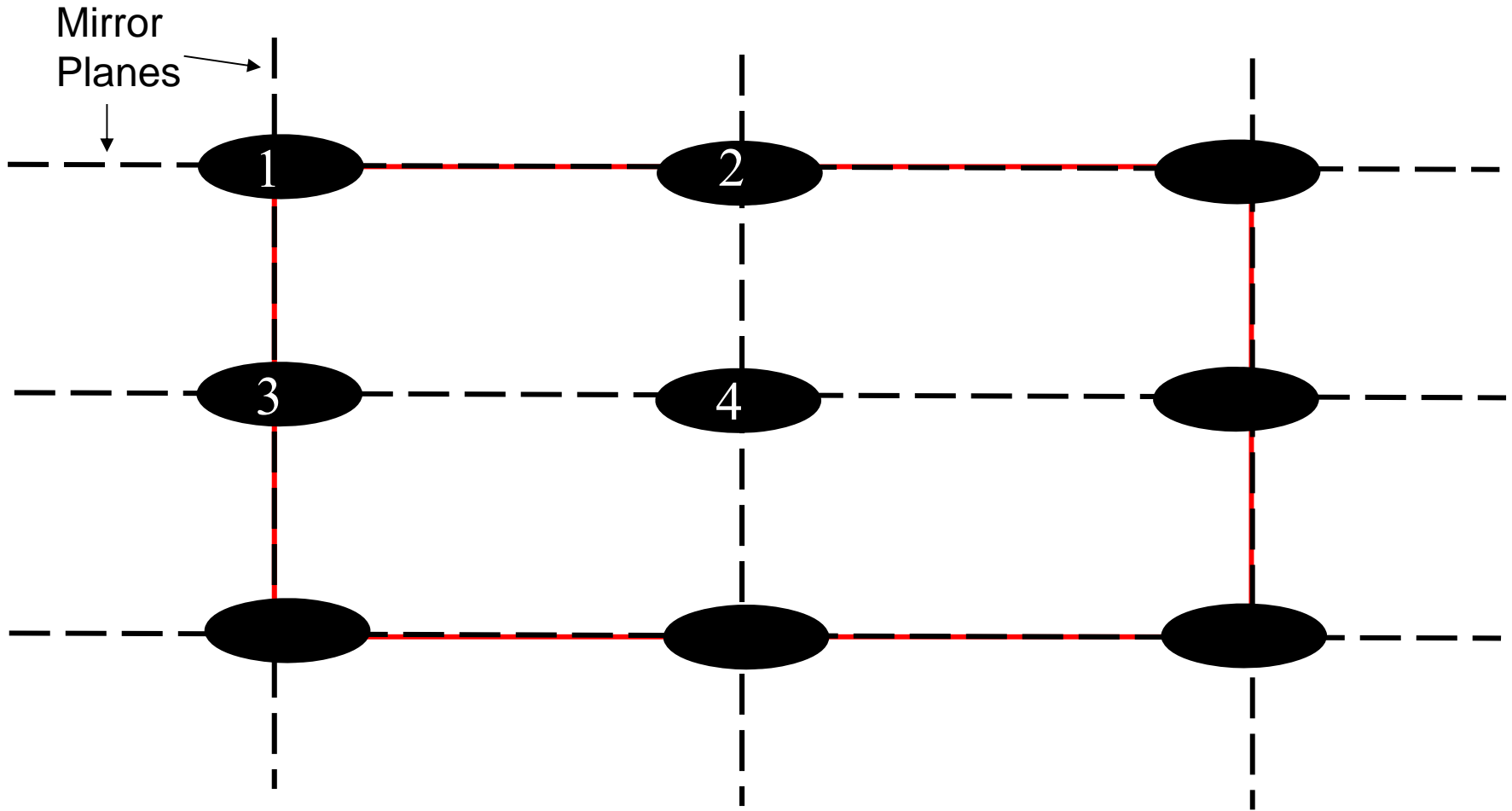
pgg

First Step: Origin Definition

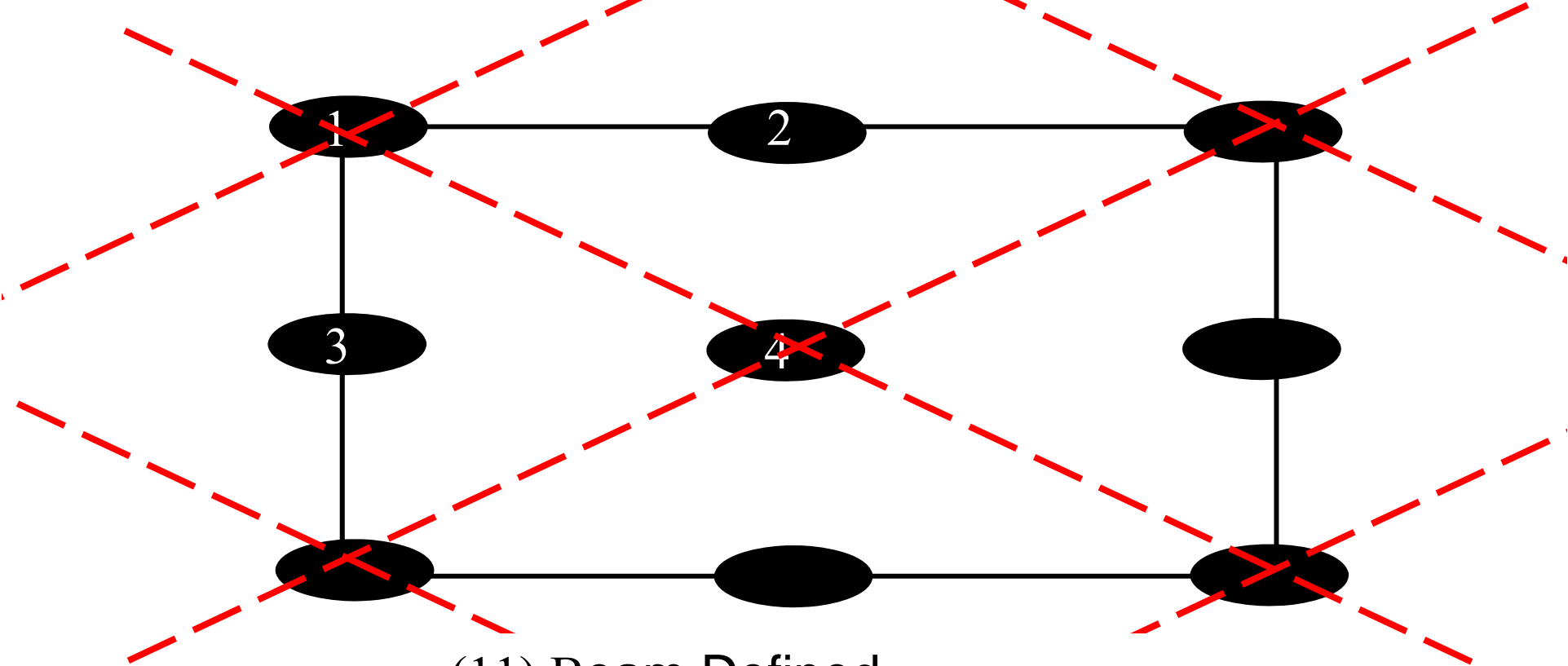


- Not all phases are unknown
 - Translating the crystal has no physical significance
 - Can therefore fix an origin for the crystal – equivalent to fixing certain reflections
 - Relevant for crystallographic phase (not absolute phase of wavefunction which is not important)

Origin Definition c2mm

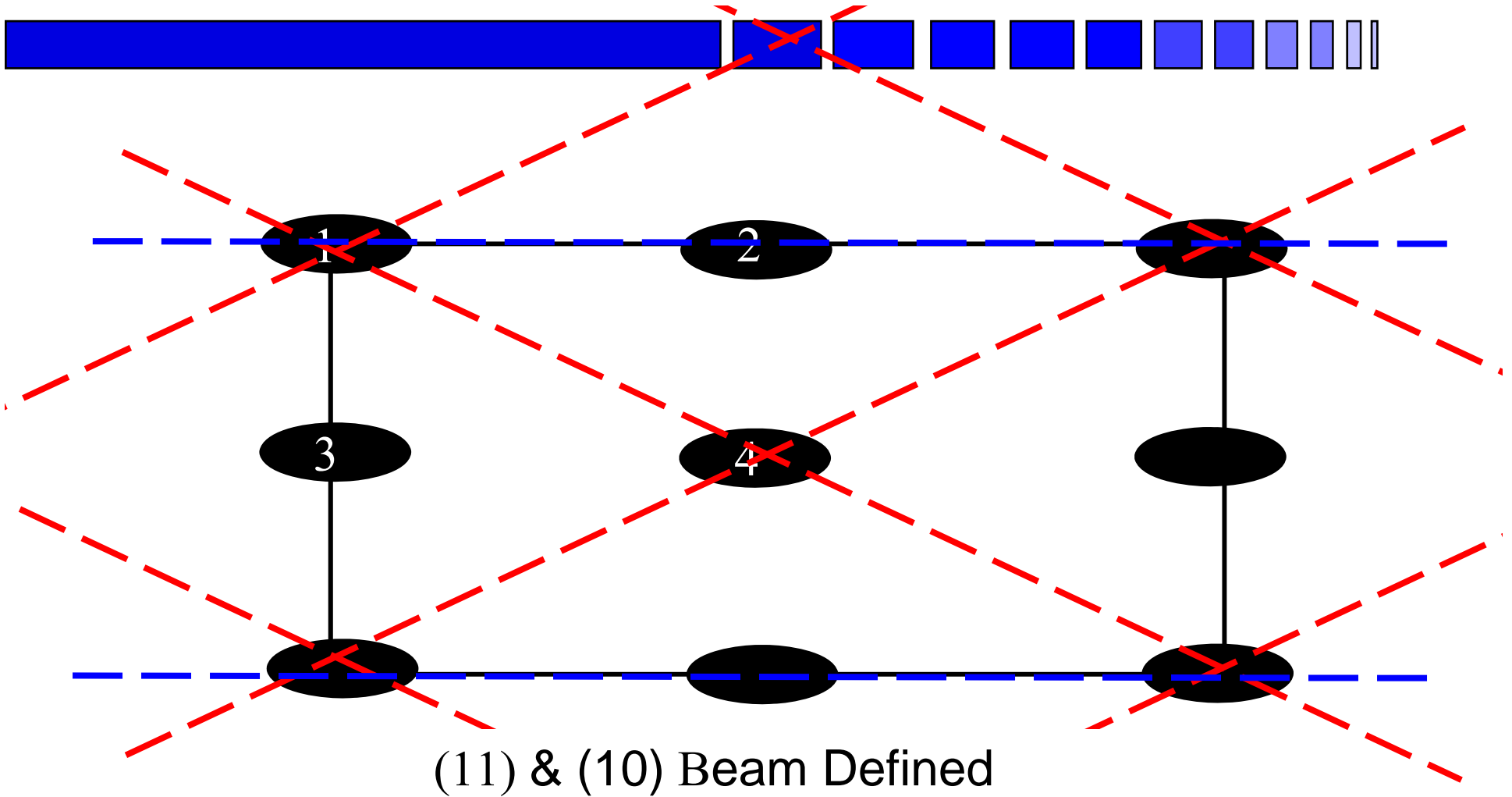


Origin Definition c2mm



(11) Beam Defined

Origin Definition c2mm



Basic Ideas

- There are certain relationships which range from exact to probably correct.

- Simple case, Unitary Sayre Equation, 1 type

$$F(k) = \sum_l f_l \exp(2\pi i k \cdot r_l)$$

- Divide by N, #atoms & f_l , atomic scattering factors

$$U(k) = 1/N \sum_l \exp(2\pi i k \cdot r_l); u(r) = 1/N \sum_l \delta(r - r_l)$$

$$u(r) = Nu(r)^2$$

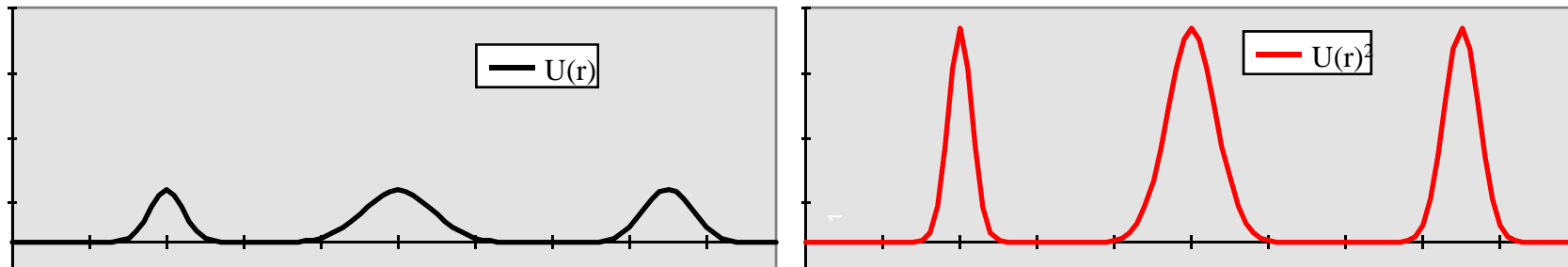
Constraint

Real/Reciprocal Space




$$U(\mathbf{h}) \approx \sum_{\mathbf{k}} U(\mathbf{k})U(\mathbf{h} - \mathbf{k})$$

$$U(\mathbf{r}) \approx U(\mathbf{r})^2$$



Reinforces strong (atom-like) features

Cochran Distribution (Σ_2): I

- 
- Definition: $U(k) = \left(\frac{1}{N}\right) \sum_m \exp(2\pi i k \cdot r_m)$
 - Consider the product

$$NU(k-h)U(h) = \left(\frac{1}{N}\right) \sum_m \exp(2\pi i k \cdot r_m) \sum_l \exp(2\pi i h \cdot (r_m - r_l))$$

- If the atoms are randomly distributed,

$$\left\langle \sum_l \exp(2\pi i h \cdot (r_m - r_l)) \right\rangle = 1$$

(exponential^l terms average to zero if $m \neq l$)

$$N \langle U(k-h)U(h) \rangle = \left(\frac{1}{N}\right) \sum_m \exp(2\pi i k \cdot r_m) = U(k)$$

Cochran Distribution: II



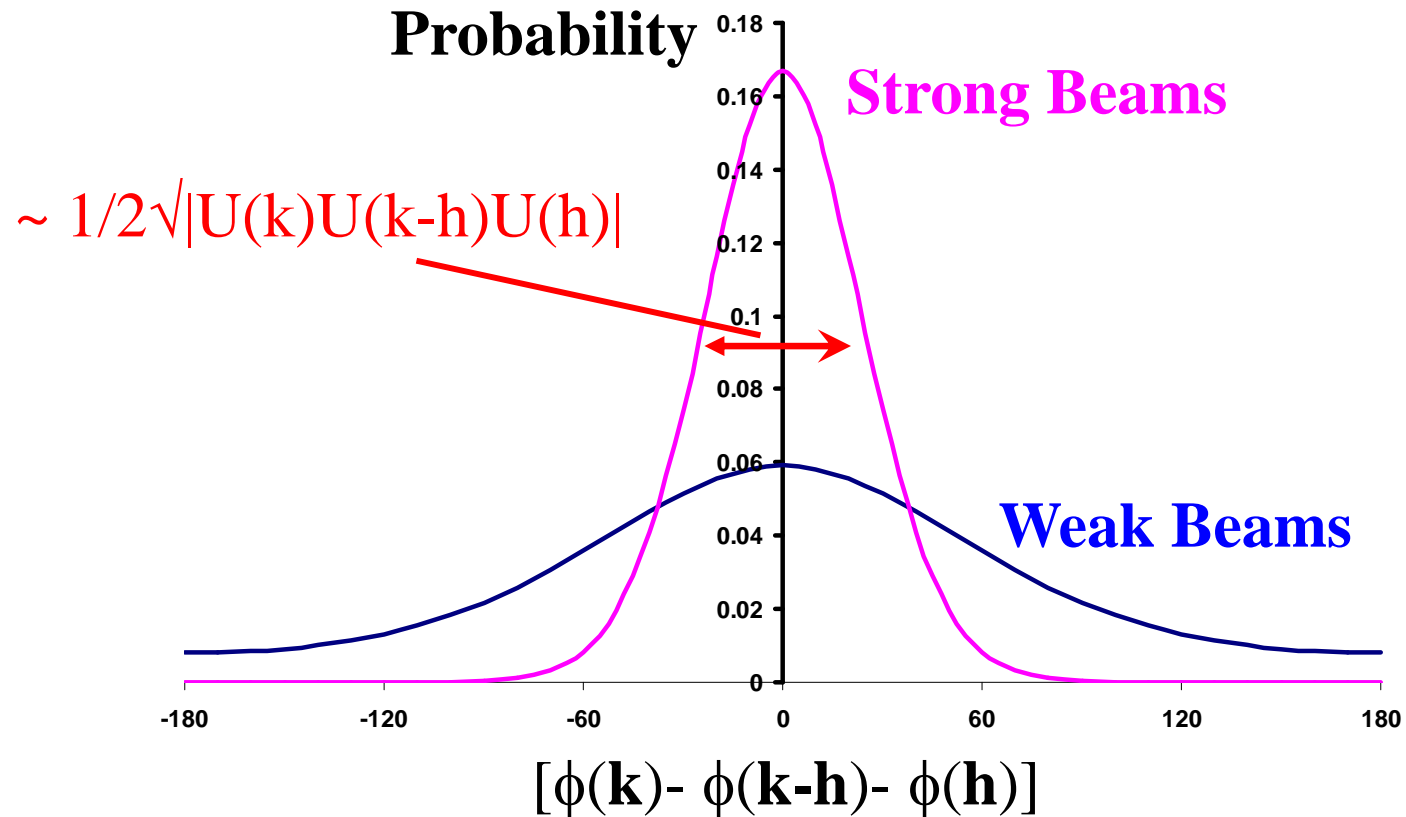
- Consider next

$$\begin{aligned}
 & |NU(k-h)U(h) - U(k)|^2 \quad \text{Average is zero} \\
 & = |U(k)|^2 + N^2|U(k-h)U(h)|^2 \quad \text{Known} \\
 & \quad - 2N|U(k)U(k-h)U(h)|\cos(\phi(k) - \phi(k-h) - \phi(h)) \\
 & \quad \quad \quad \uparrow \quad \quad \quad \uparrow \\
 & \quad \quad \text{Known} \quad \quad \quad \text{Average must be } 2n\pi
 \end{aligned}$$

Cochran Distribution: III

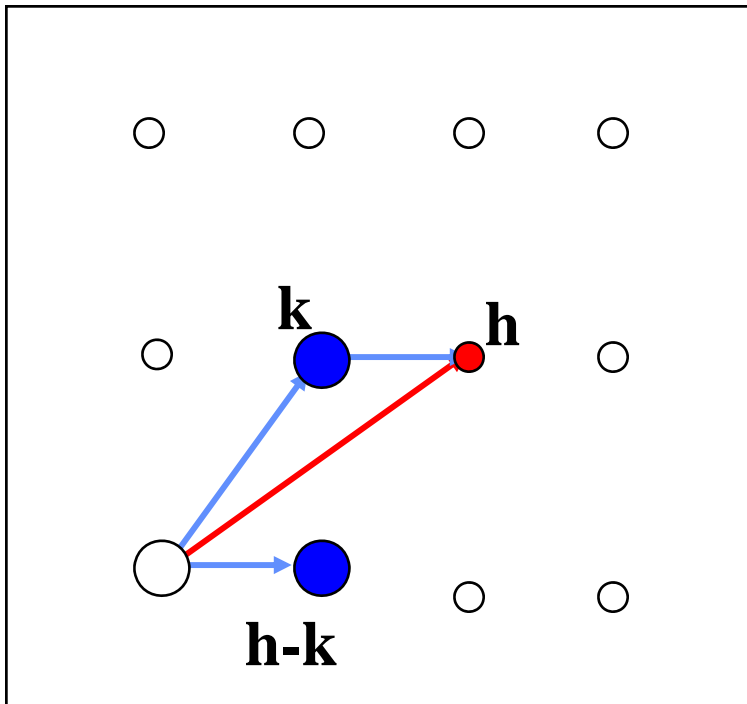
- We have a distribution of values. The Central Limit theorem: all distributions tend towards Gaussian. Hence a probability:
- $P(U(\mathbf{k}) - NU(\mathbf{k-h})U(\mathbf{h}))$
 - $\sim C \exp(-|U(\mathbf{k}) - NU(\mathbf{k-h})U(\mathbf{h})|^2)$
 - $\sim C \exp(2|U(\mathbf{k})U(\mathbf{k-h})U(\mathbf{h})| \cos[\phi(\mathbf{k}) - \phi(\mathbf{k-h}) - \phi(\mathbf{h})])$
- Compare to $\exp(-x^2/2\sigma^2)$
 - $\sigma^2 = 1/4|U(\mathbf{k})U(\mathbf{k-h})U(\mathbf{h})|$

Form of Distribution



Note: this is more statistics than the presence of atoms

Σ_2 Triplet



For reflections $\mathbf{h-k}$, \mathbf{k} and \mathbf{h} :

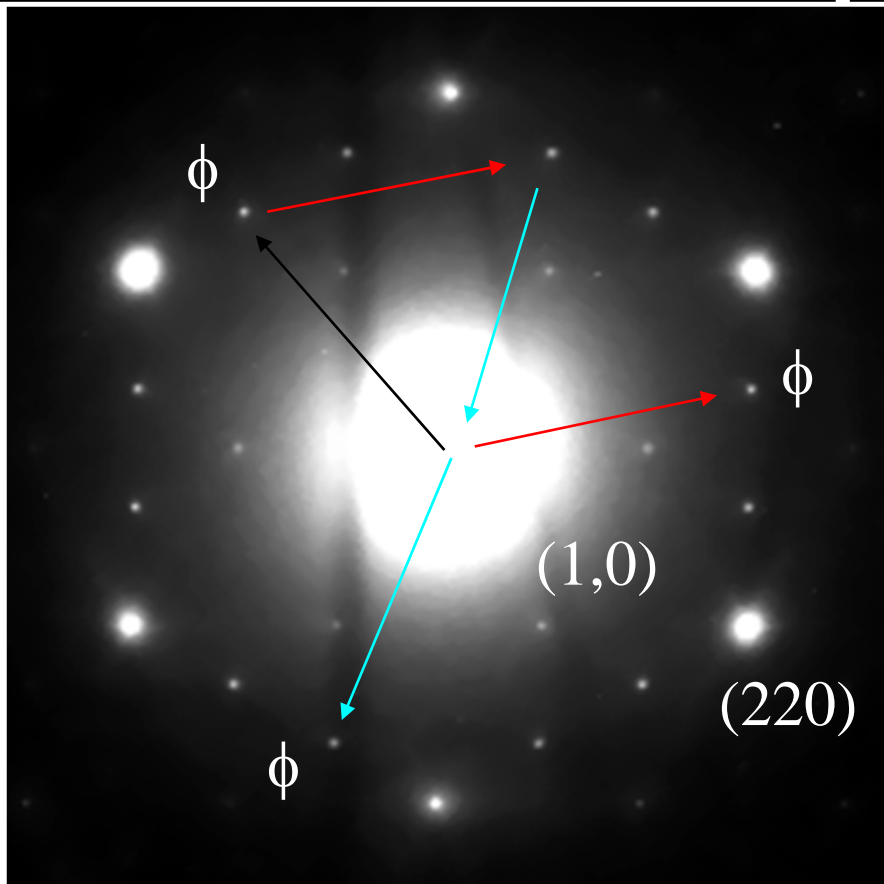
$$\phi(\mathbf{h}) \approx \phi(\mathbf{k}) + \phi(\mathbf{h-k})$$

W. Cochran (1955). Acta. Cryst. **8** 473-8.

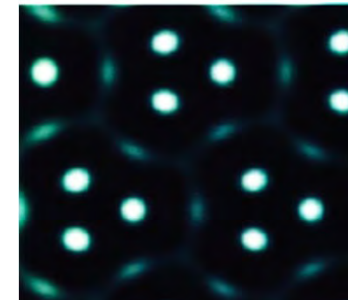
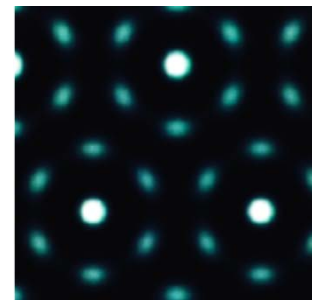
-  = known structure amplitude and phase
-  = known structure amplitude and unknown phase



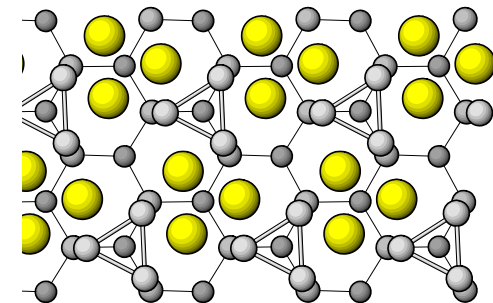
Example: Si(111) $\sqrt{3} \times \sqrt{3}$ Au



- $3\phi \sim 360n$ degrees
- $\phi=0, 120$ or 240
- $\phi=0$ has only 1 atom
- 120 or 240 have 3



Other information
3 Au



Only one strong reflection

L. D. Marks, et al, *Surf. Rev. Lett.* **4**, 1 (1997).

Inequalities

$$|\sum a_i b_i|^2 < \sum |a_i|^2 \sum |b_i|^2 \text{ (Triangle Inequality)}$$

$$a_i = 1/\sqrt{N} \cos(2\pi k r_i) ; b_i = 1/\sqrt{N}$$

$$\sum a_i b_i = U(k)$$

$$\sum |b_i|^2 = \sum 1/N = 1 \text{ for } N \text{ atoms}$$

$$\begin{aligned} \sum |a_i|^2 &= 1/N \sum \cos(2\pi k r_i)^2 \\ &= 1/2N \sum (1 + \cos(2\pi [2k] r_i)) \\ &= 1/2 + U(2k) \end{aligned}$$

$$\text{Hence } U^2(k) < 1/2 + U(2k)/2$$

If $U(k)$ is large – can set $U(2k)$

Quartets



- Phase relationships involving 4 terms for weak reflections
 - Positive and Negative
 - Very useful for x-ray diffraction
 - Rarely useful with TEM; dynamical effects can make weak reflections stronger than they should be

More subtle statistics



- Better statistics (Information Theory)
- Entropy of a distribution is more fundamental (as is Kullback-Liebler or relative entropy)
- Most probable distribution maximizes entropy

$$S = - \int u(r) \ln u(r) dr$$

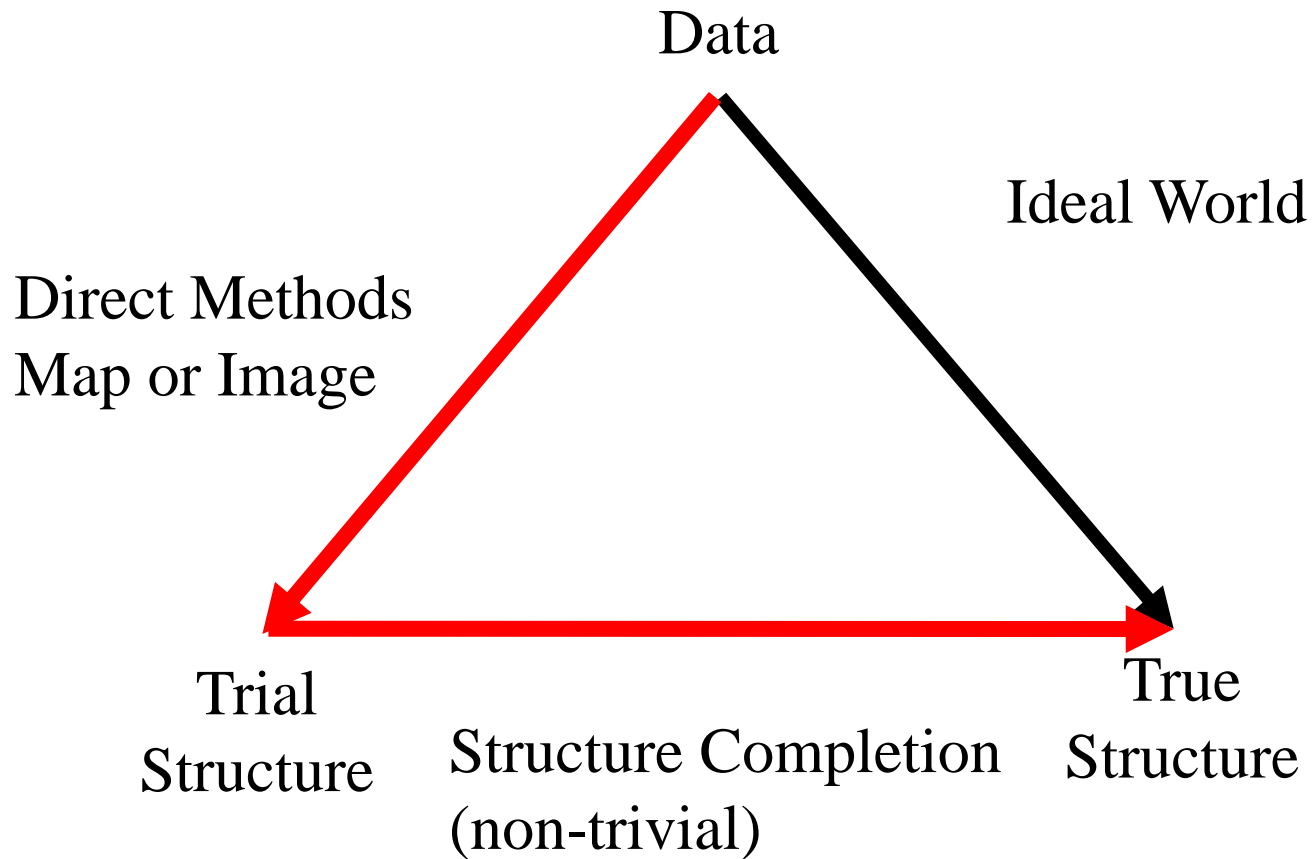
Last step - Refinement



- Fit atom positions via:
 - $R_n = \Sigma |I_{\text{calc}} - I_{\text{expt}}|^n / \Sigma I_{\text{expt}}^n$ (or $F_{\text{calc}}, F_{\text{expt}}$)
 - $\chi^n = \Sigma |I_{\text{calc}} - I_{\text{expt}}|^n / \sigma^n$
 - $n=1$ for Robust Estimation
- Should use dynamical I_{calc} for electrons
- $R_1 < 0.01$ for most x-ray structures, < 0.1 currently for TED.
- $R_1 \sim 0.5$ for random variables

Crystallographic Direct Methods

Structure Triangle



Implementation



1. Chose phases to define origin
2. Guess phases for some reflections
3. Generate from these phases for others and improved phases for initial set
4. Test consistency of predicted amplitudes and phases
5. Iterate, so long as consistency is improving

Note: permuting phases has lower dimensions than permuting atom positions

General Formalism as dual



1. Initial $\rho(\mathbf{r})$
2. Project onto “Real Space Constraint” $\rho^2(\mathbf{r})$
3. FFT
4. Project amplitudes onto Observed
5. FFT

In Reciprocal Space: Tangent Formula



- If $U(\mathbf{r}) = U(\mathbf{r})^2 = U'(\mathbf{r})$
- Important part is the phase
- $U(\mathbf{u}) = |U(\mathbf{u})|\exp(i\theta)$; we know $|U(\mathbf{u})|$ but not θ
- $\exp(i\theta) = \exp(i\theta')$; $\text{Tan}(\theta) = \text{Tan}(\theta')$
- Replace old θ by new one

Gerchberg-Saxton Algorithm



A Practical Algorithm for the Determination of Phase from Image and Diffraction Plane Pictures

By *R. W. Gerchberg* and *W. O. Saxton*

Cavendish Laboratory, Cambridge, England

Received 29 November 1971

Abstract

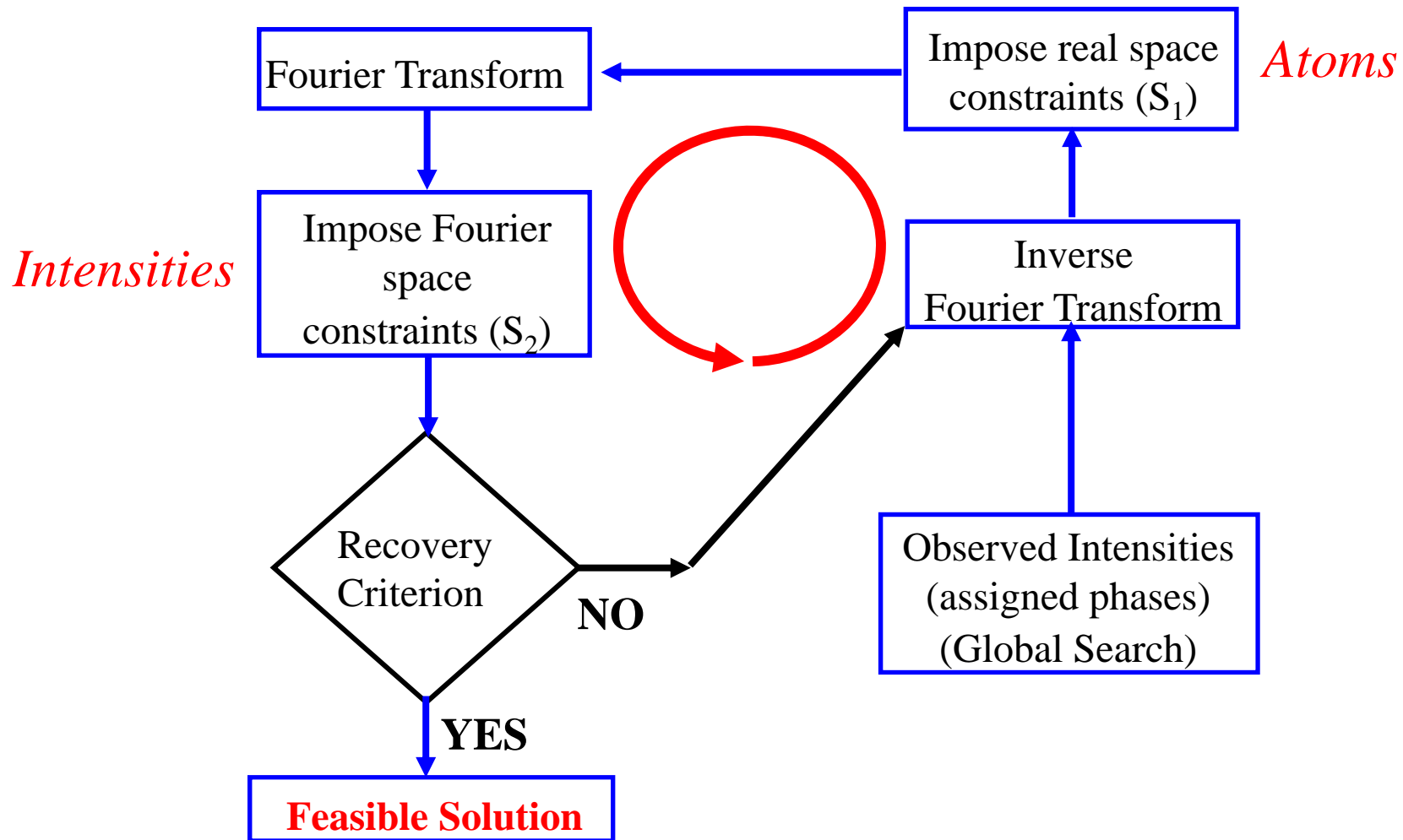
An algorithm is presented for the rapid solution of the phase of the complete wave function whose intensity in the diffraction and imaging planes of an imaging system are known. A proof is given showing that a defined error between the estimated function and the correct function must decrease as the algorithm iterates. The problem of uniqueness is discussed and results are presented demonstrating the power of the method.

Optik 35, 237 (1972)

Citations > 1500

Paper was rediscovered by Crystallographers in 1990's

Algorithm Overview (Gerschberg-Saxton)



More: 1970's Mathematics

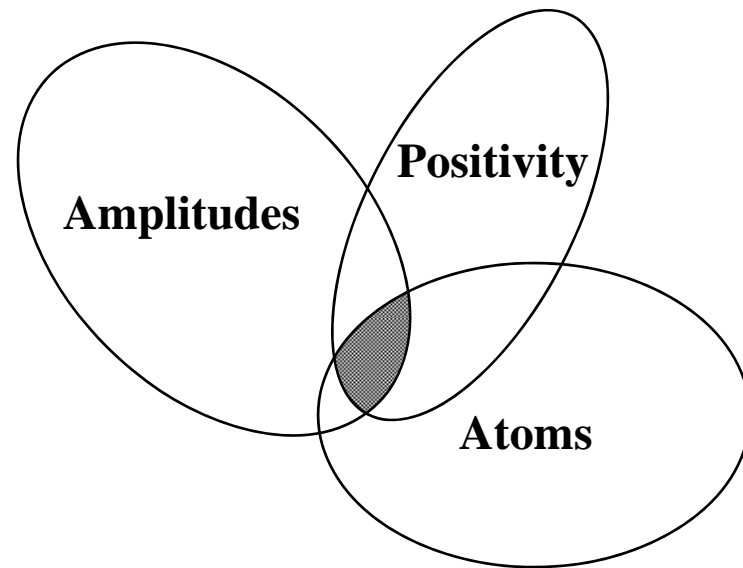


- C -- Some constraints (e.g. atomicity, probabilities of triplets)
- F -- Some function (e.g. a FOM)
- Minimize, e.g. Lagrangian

$$I = F + \lambda C$$

1990's Mathematics

- We have constraints (e.g. atomicity, amplitudes)
 - Treat as sets
- We are looking for the solution as intersection of several constraint sets



Acta Cryst A55, 601 (1999)

The \$64,000 question

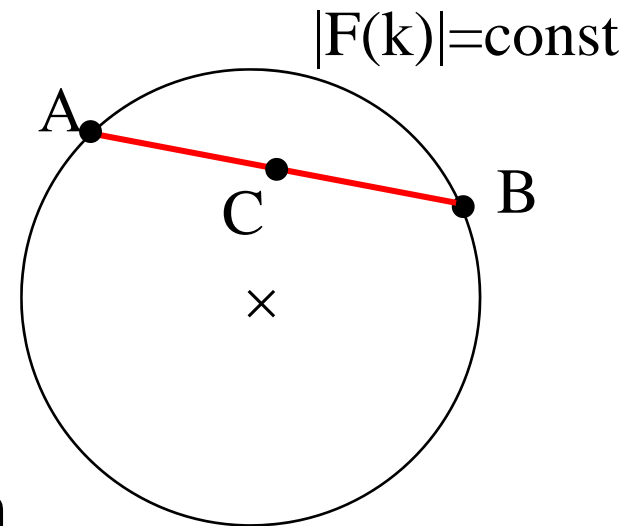
- A set is convex if any point between two members is also a member
 - If all the sets are convex, problem has one solution
 - If they are not, there may be more than one local minimum

- Amplitude measurements

do not form a convex set

- But...there still may only be one solution.

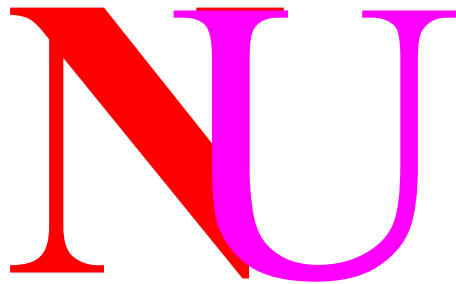
- Unsolved mathematical problem



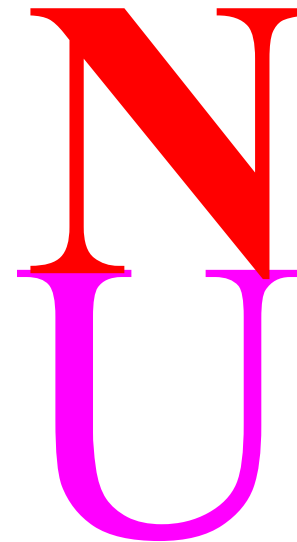
Multiple non-convex constraints



Consider the two sets “N” and “U”



Overall Convex



Overall Non-Convex

Crystallographic methodology



NO
UN

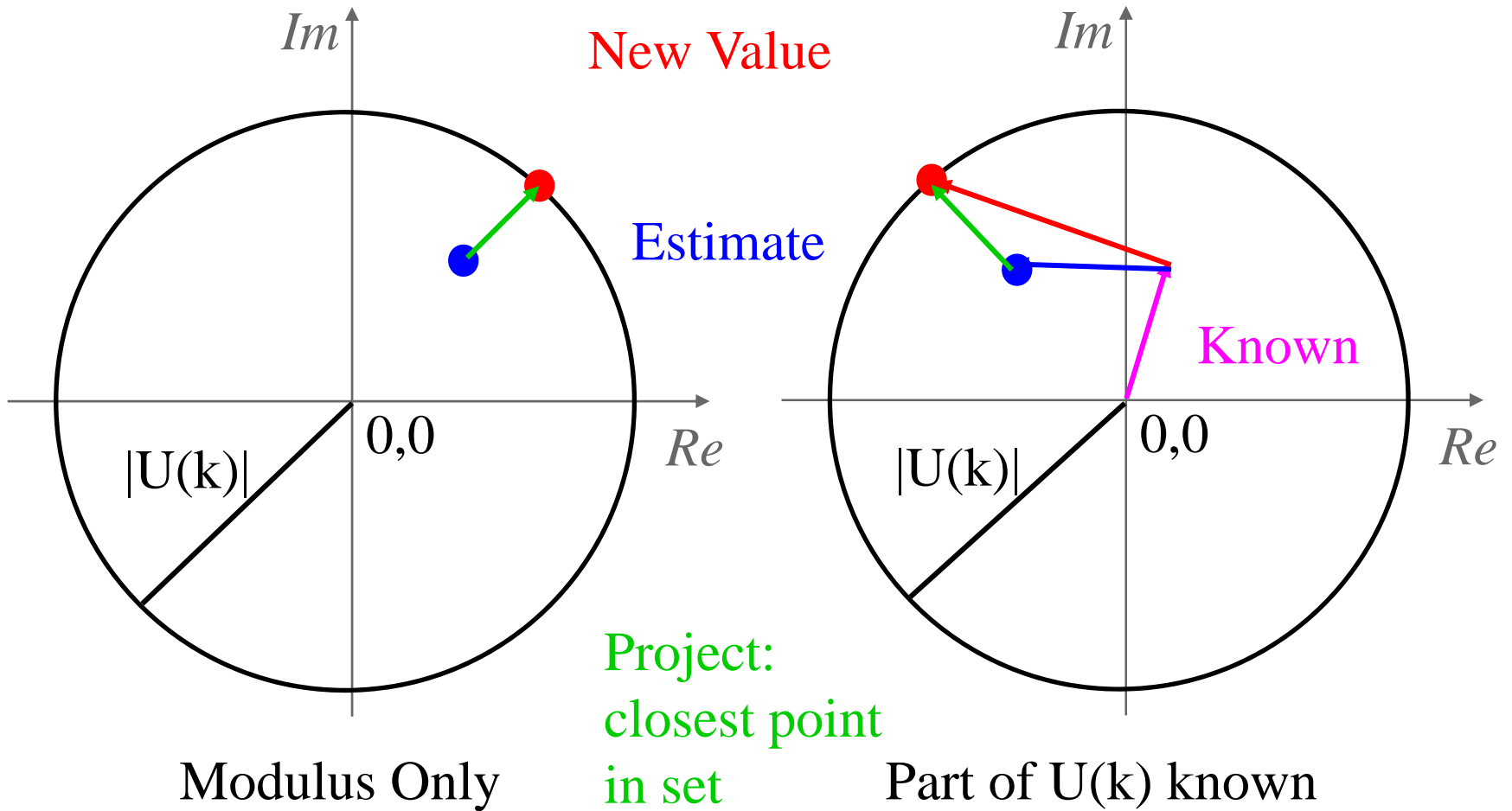
Overall Non-Convex

Overall Unique

Addition of additional convex constraints tends to give a unique solution

Structure Completion: add additional constraints as the phases become known

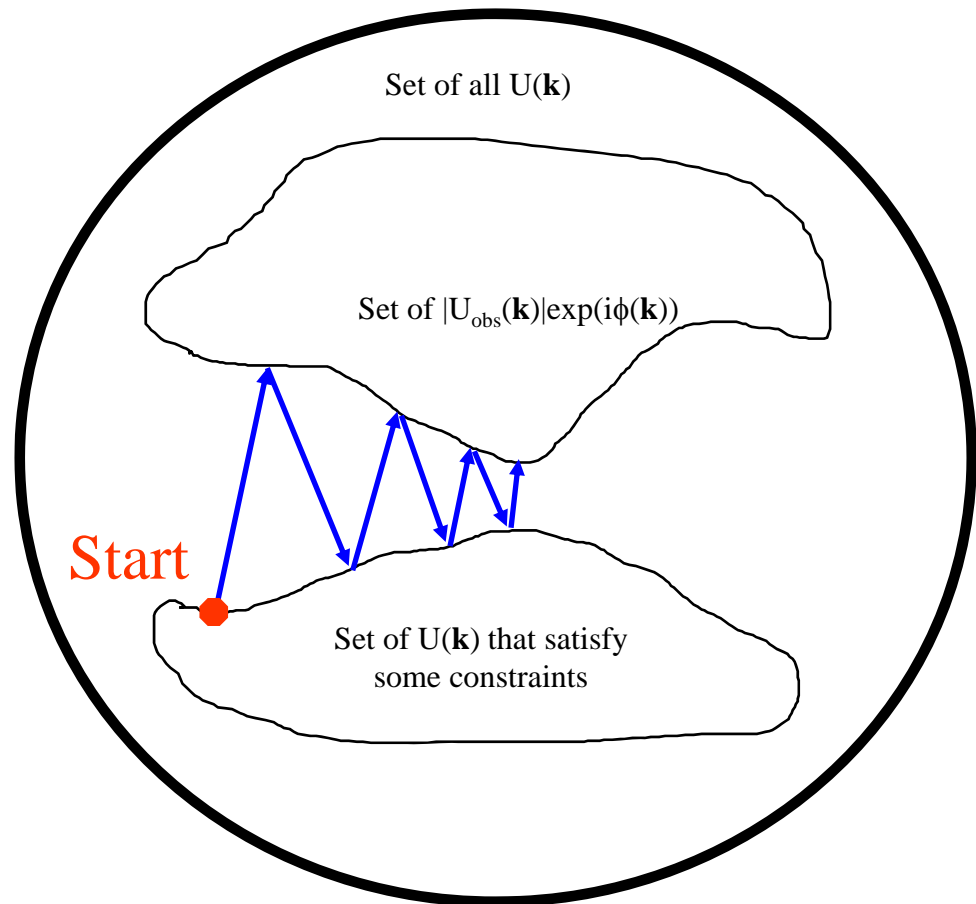
Orthogonal Projections



Successive Projections

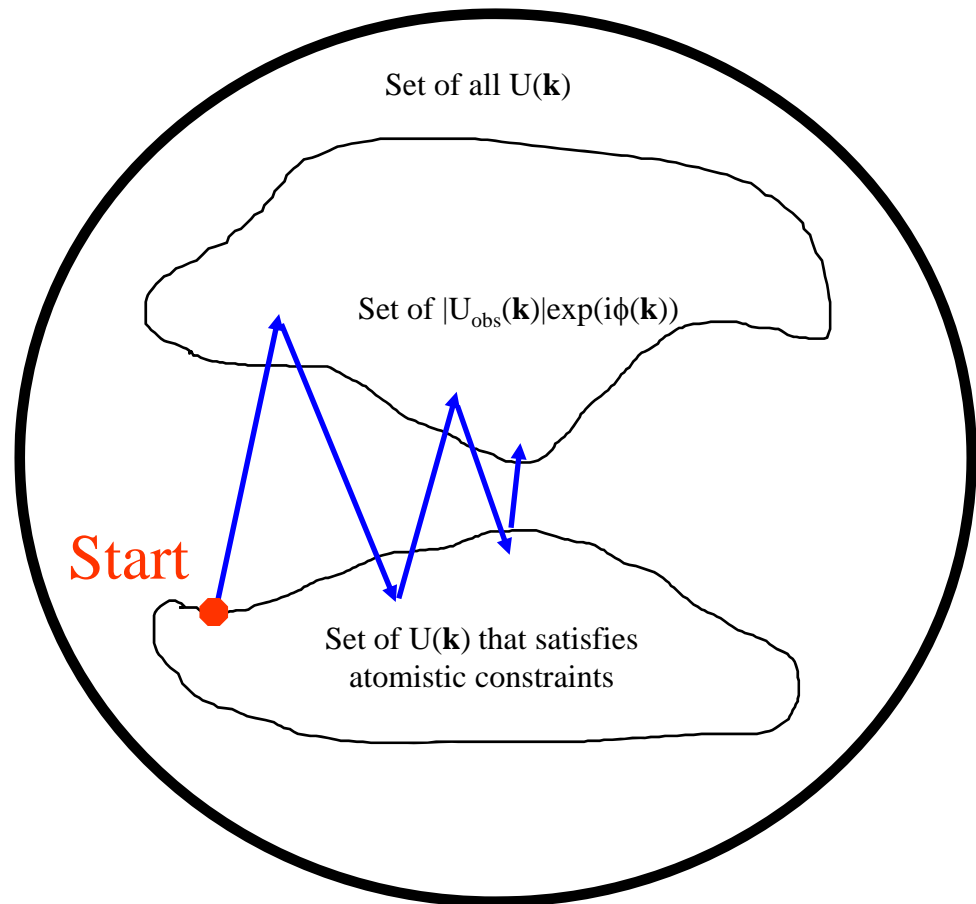
- Iterate between projections
- Other variants possible

Combettes, *Advances in Imaging and Electron Physics* **95**, 155, 1996
L. D. Marks, et al, *Acta Cryst A* **55**, 601, 1999



Over-relaxed Projections

- Iterate between projections
- Overshoot (deliberately)
- Converges faster
- Sometimes better solutions



Classic Direct Methods

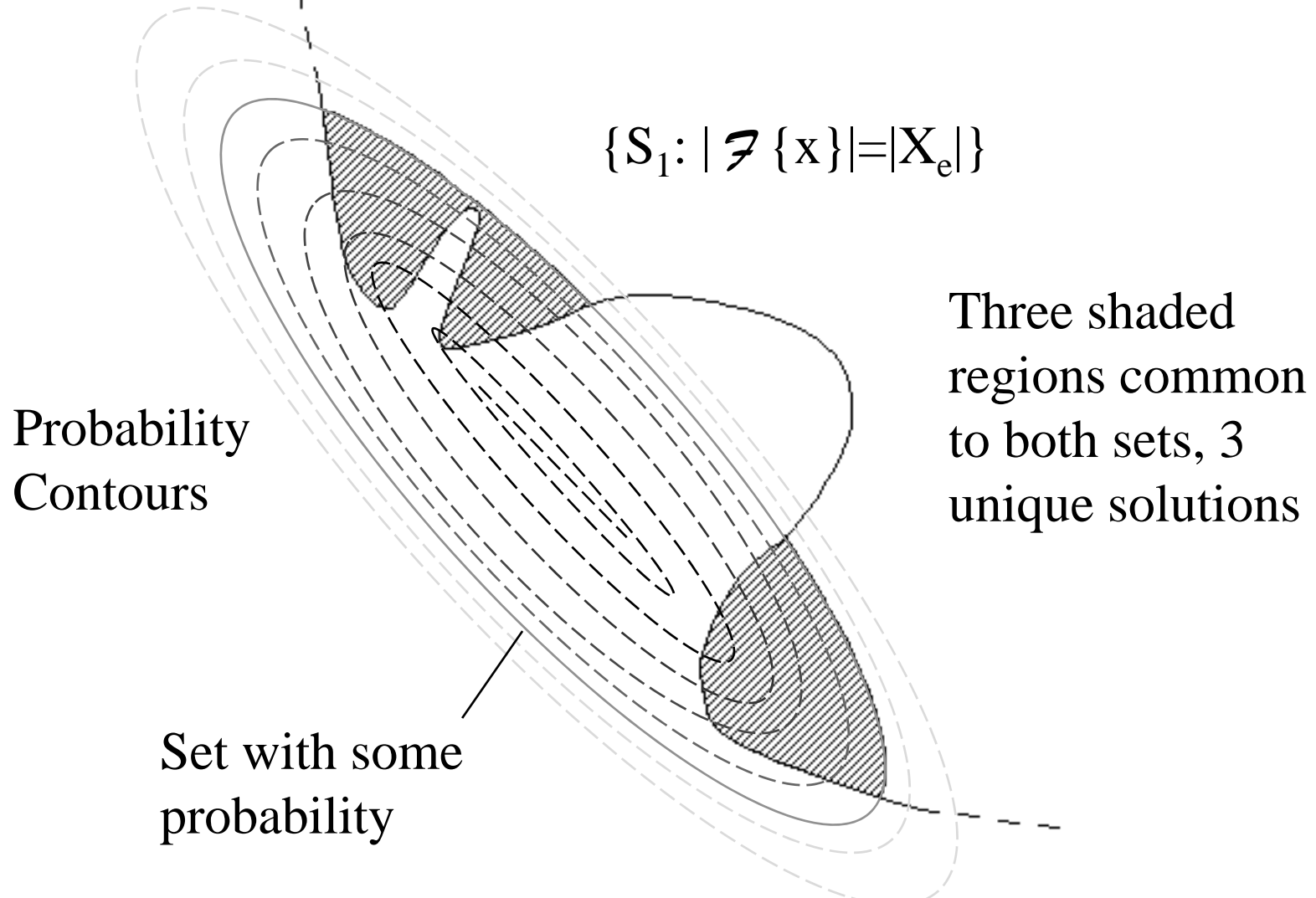
- Consider as an iteration

$$\begin{array}{ccc} U_n(\mathbf{k}) & \longrightarrow & u_n(\mathbf{r}) \\ \text{Constraint} \quad \uparrow & & \downarrow \quad \text{Constraint} \\ U'(\mathbf{k}) & \longleftarrow & u_n^2(\mathbf{k}) \end{array}$$

- Note the similarities

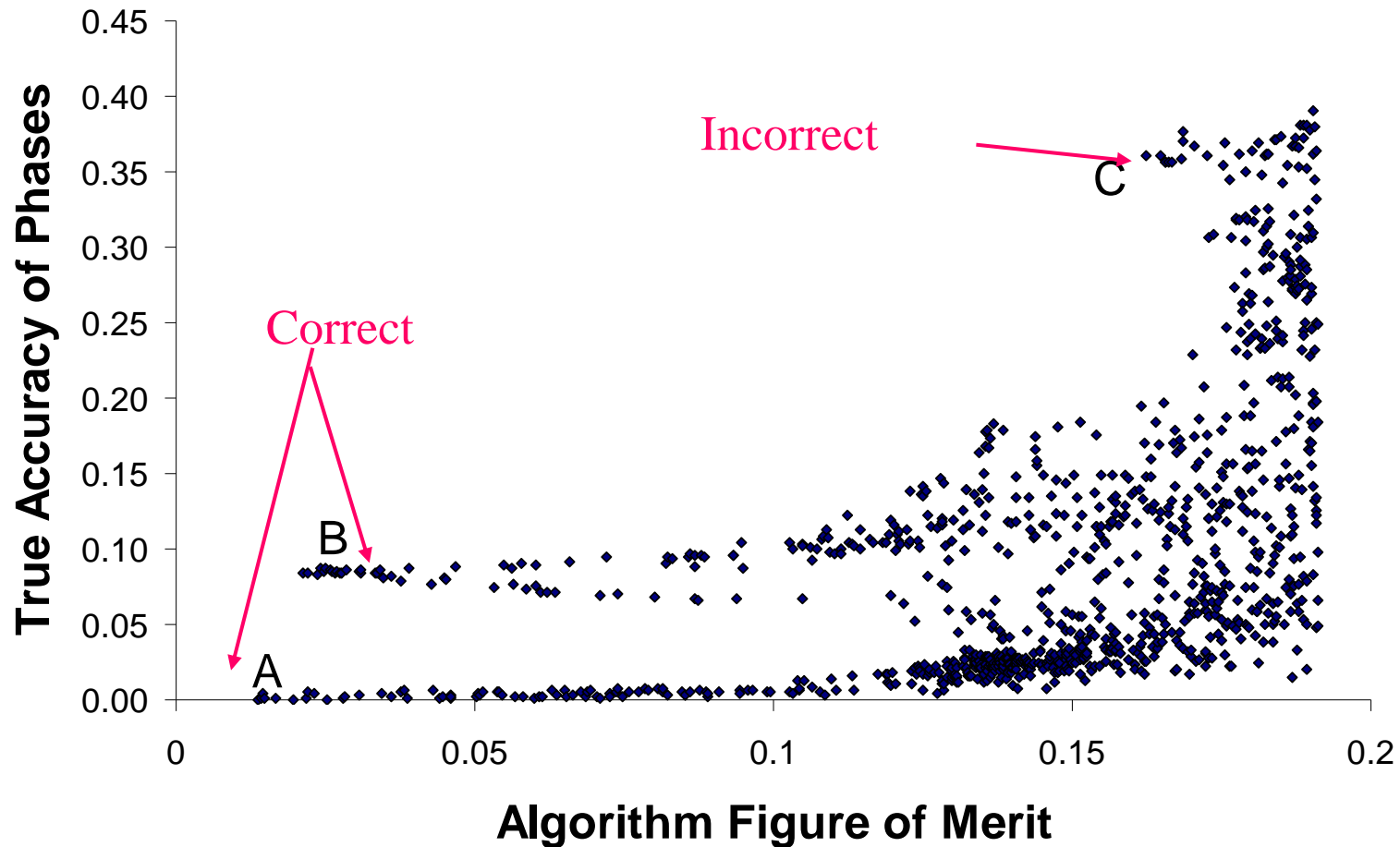
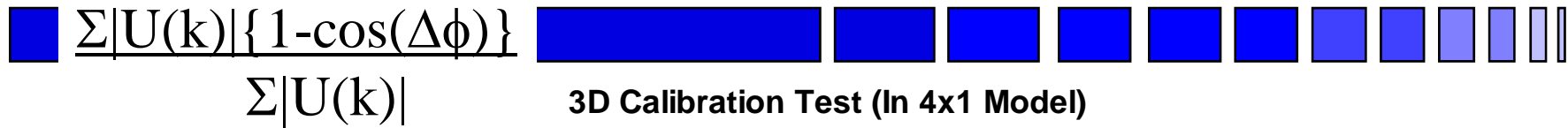
- Tangent Formula \equiv Orthogonal Projection
- Real space operator, effectively an eigenfunction (fixed point) method

Multiply-Connected Feasible Set



Typical results

$\Delta\phi$ = phase error



Types of Constraints



- Convex – highly convergent
 - Multiple convex constraints are unique
- Non-convex – weakly convergent
 - Multiple non-convex constraints may not be unique

More Constraints



Convex

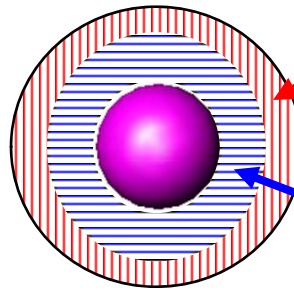
Non-Convex

Positivity (weak)	Presence of Atoms
Atoms at given positions	Bond Lengths
Least bias (MaxEnt)	Interference $A(k)= B(k)+Known(k) ^2$
Intensities & errors $\equiv \chi^2$	Anti-bumping
Statistics (e.g. Σ_2)	Bond angles
Support for gradient	
Symmetry	

Atomistic Constraints



$\rho(r)$ known
(convex if position
is known)



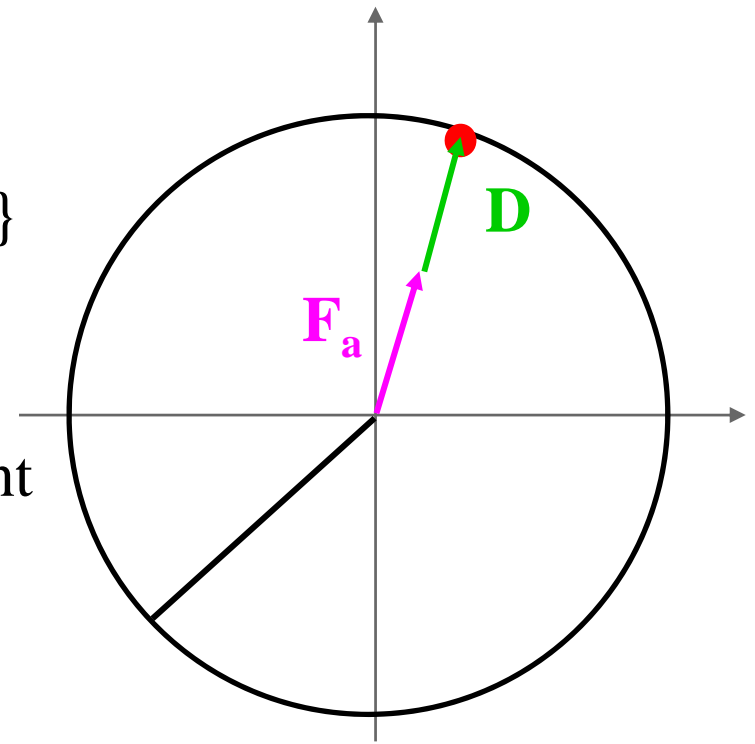
Bonding –
another atom

Bumping
 $\rho(r)=0$




Example I: Difference Map

- We know all the moduli, $|F(\mathbf{k})|$
- We know part of the structure,
 $F_a(\mathbf{k}) = |F_a(\mathbf{k})|\exp(i\phi_a(\mathbf{k}))$
- Project onto known moduli
 $D(\mathbf{k}) = \exp(i\phi_a(\mathbf{k}))\{|F(\mathbf{k})_{\text{obs}}| - |F_a(\mathbf{k})|\}$
Conventional Fourier Difference
Map
- Other methods (SIM wts) equivalent to further projections.

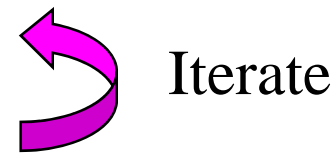


Operators as projections

- 
- Some operator O , apply to some current estimate (x in real space, X in reciprocal space)
 - Define a set for the cases where
$$\langle O(x) - x \rangle < \text{some number}$$
 - New estimate obtained by the iteration
$$x_{n+1} = O(x_n)$$
 - N.B., there are some important formal mathematical issues.....

Example II: Sayre Equation

- Use $O(x) \equiv \alpha x^2$; α = scaling term
- Couple with known moduli as second set
- Iteration
 - $x_{n+1} = O(x_n) = \alpha x_n^2$
 - $|X_{n+1}| = |X_{\text{observed}}|$
- This *is* the Sayre equation (and tangent formula)



Example III: Structure Completion

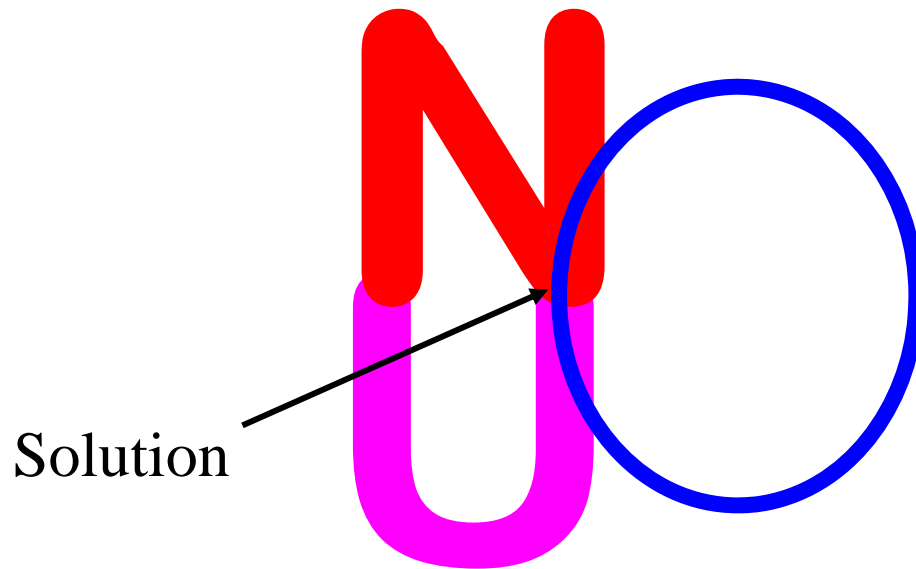


- Explanation (pseudo-mathematical) of why structure completion strategies can solve, uniquely, problems when the initial maps are not so good

Structure Completion



Consider the two non-convex sets “N” and “U”



Solution

Overall Convex

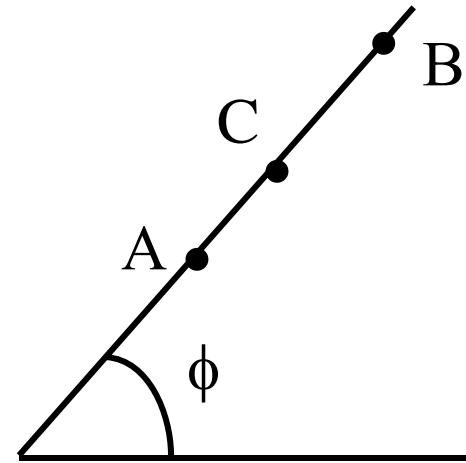
- Add a third set “O”
- Addition of additional constraints tends to give a unique solution
- Structure Completion: add additional constraints as the atoms become known

IV Convex Set for unmeasured

$$|U(h,k,l)|$$



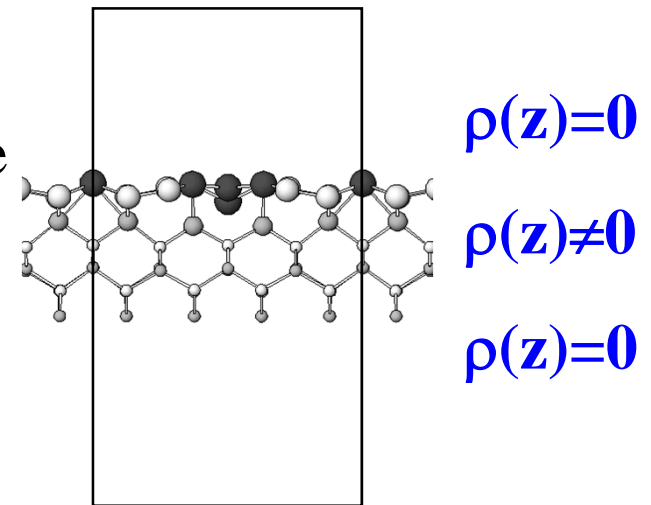
- Phase of $U(h,k,l)$ can be estimated from other reflections
- Set of $U(h,k,l)$ with a given phase is **convex**
- Hence $|U(h,k,l)|$ is well specified and can be (approximately) recovered
- Remember, phase is more important than amplitude



Support Constraint



- Displacements decay as $(\alpha+z)\exp(-qz)$ into bulk¹
- Real space constraint
 - $\rho(z)=\rho(z)w(z)$ $w(z)=1, -L<z<L$
 $=0, \text{ otherwise}$
- Convex constraint
- Has well documented properties



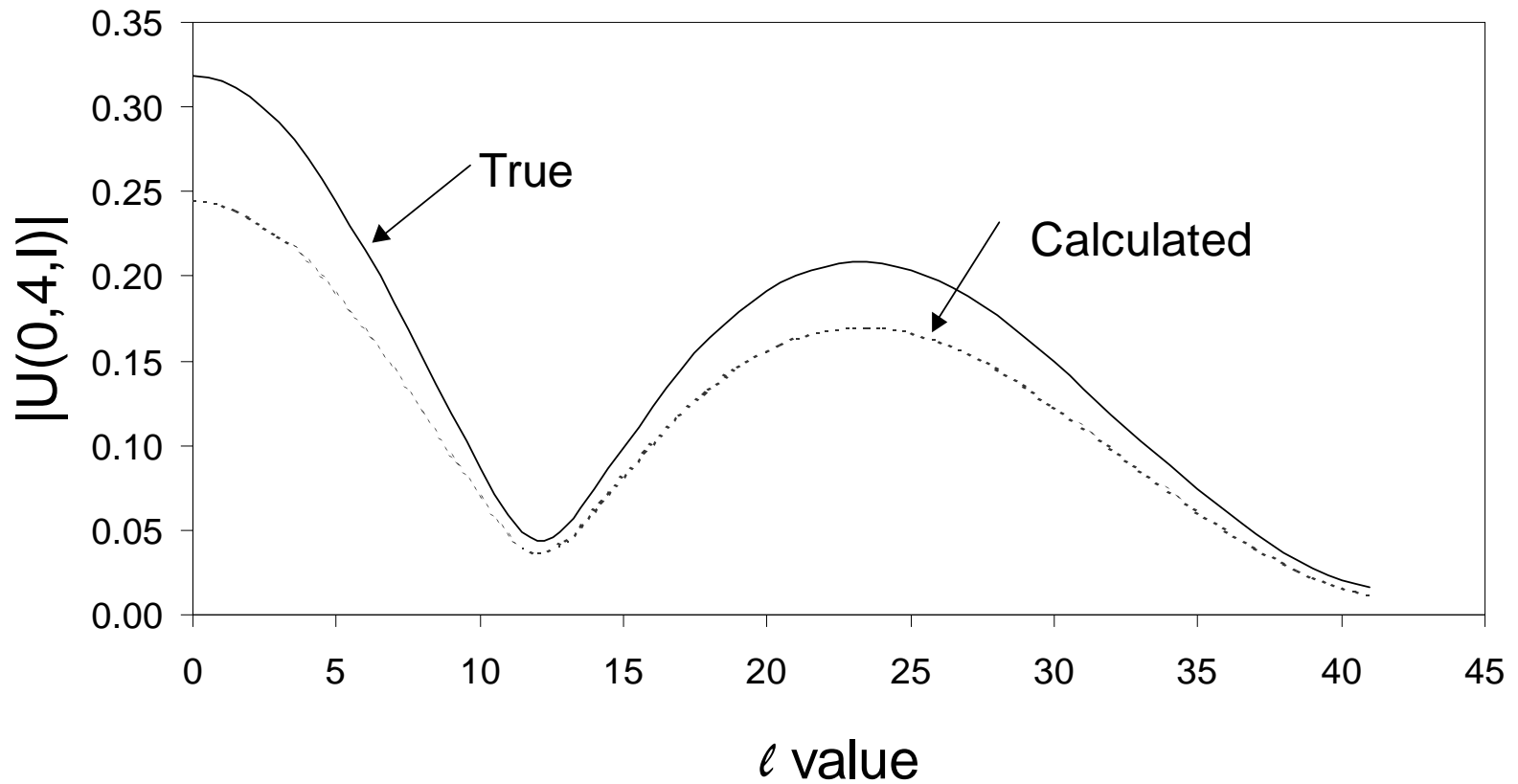
PRB 60, 2771 (1999)

¹Biharmonic expansion of strain field, SS 294, 324 (1993)

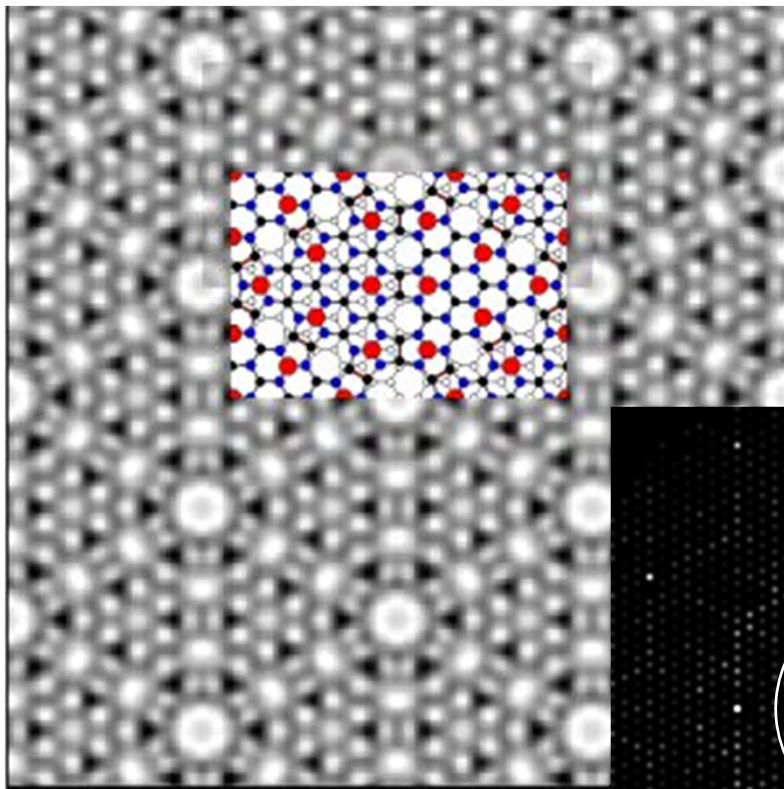
Unmeasured Reflections



Recovery of Unmeasured Reflections

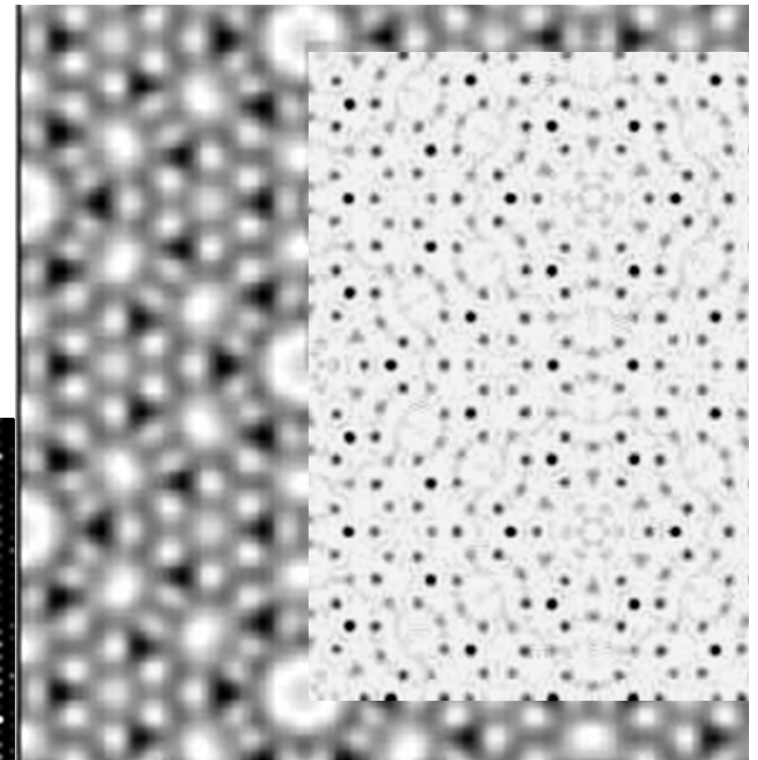
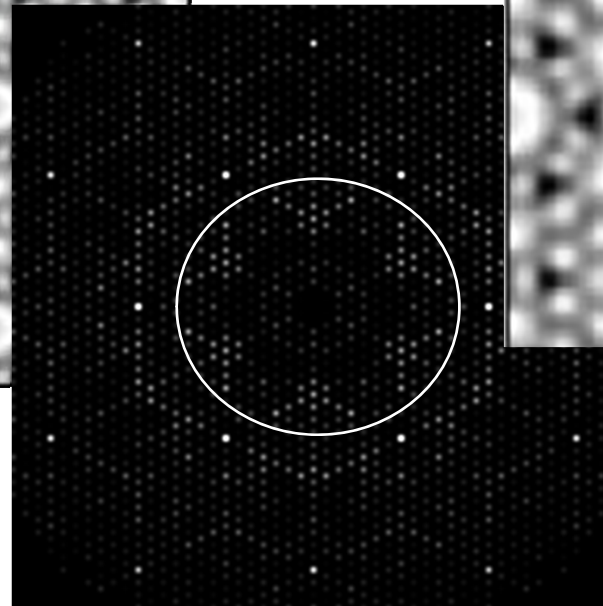


Restoration and Extension



0.3nm Image

+DP



0.05nm Image

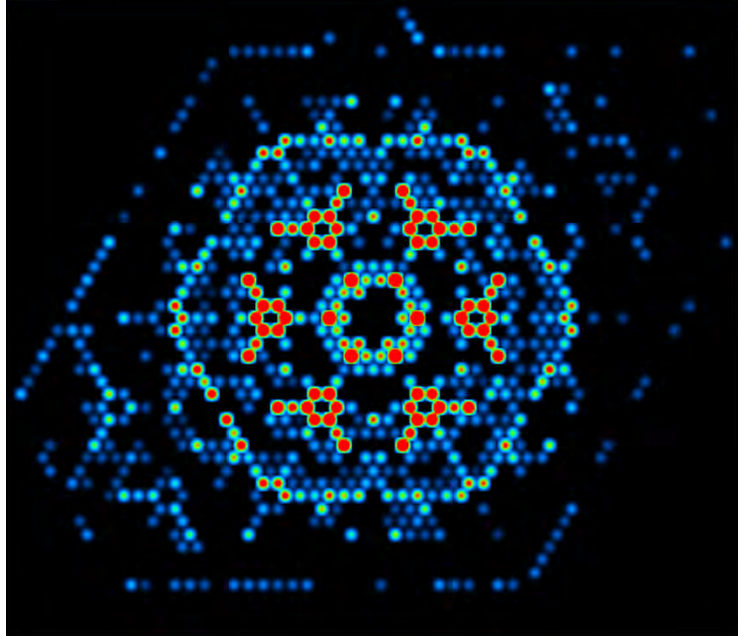
When does it work?



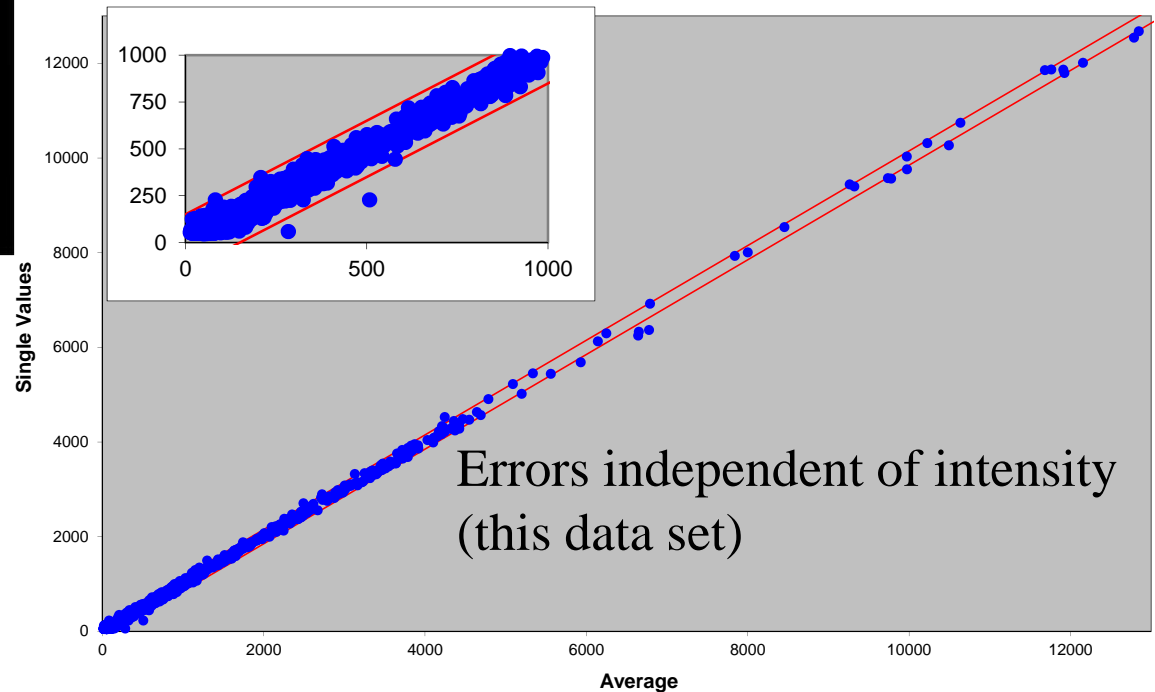
- Kinematical Diffraction (surfaces)
- 1s-Channelling
- Intensity ordering (PED)

L. D. Marks, W. Sinkler, Sufficient conditions for direct methods with swift electrons. *Microsc. Microanal.* **9**, 399 (2003).

TED: Si (111) 7x7



Method: Merge data for 6-20 different exposures to obtain accuracies of ~1% with statistical significance



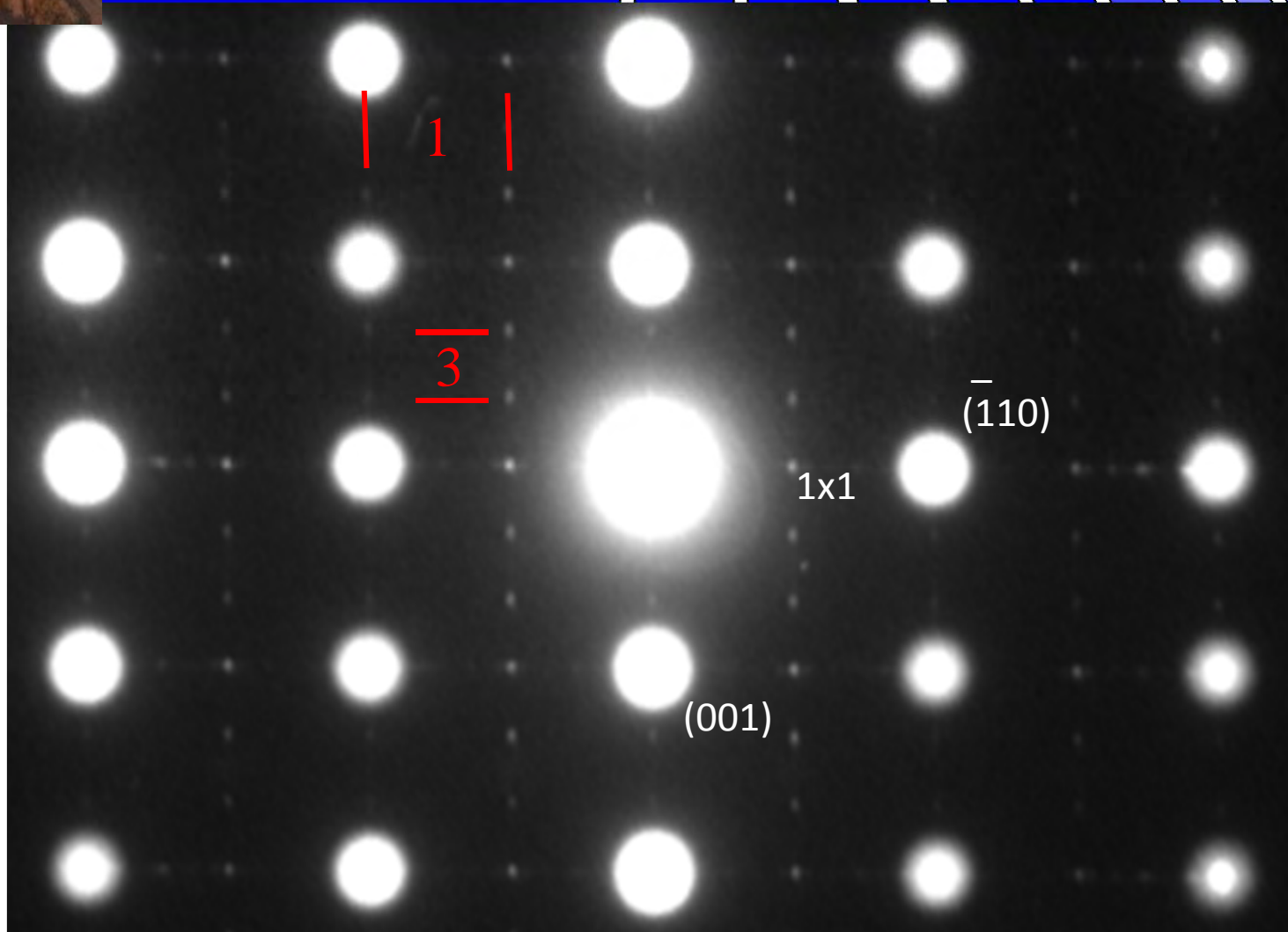
Cross-Correlation
Method

P. Xu, et al.

Ultramicroscopy **53**, 15
(1994).

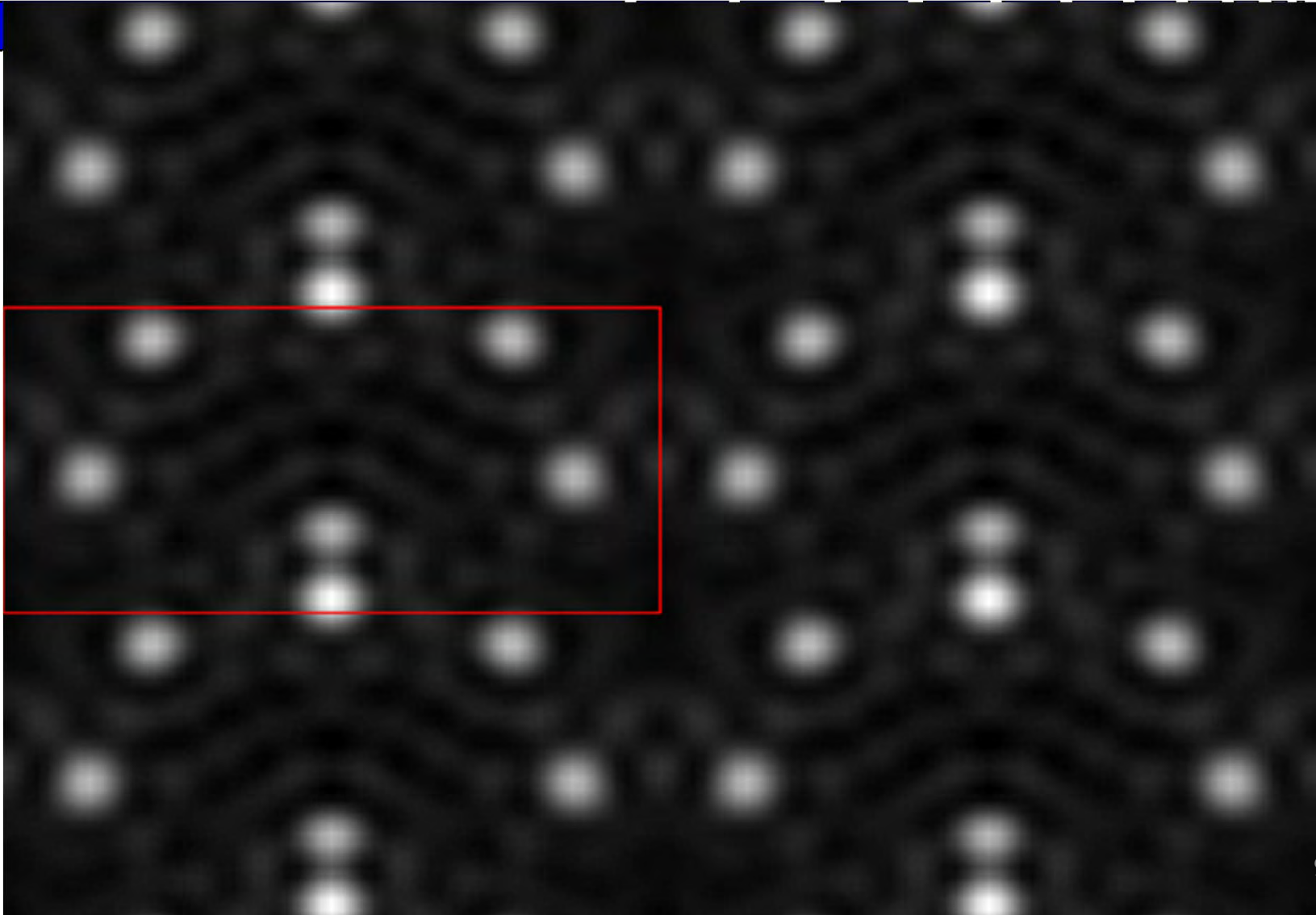


1000 °C in flowing O₂



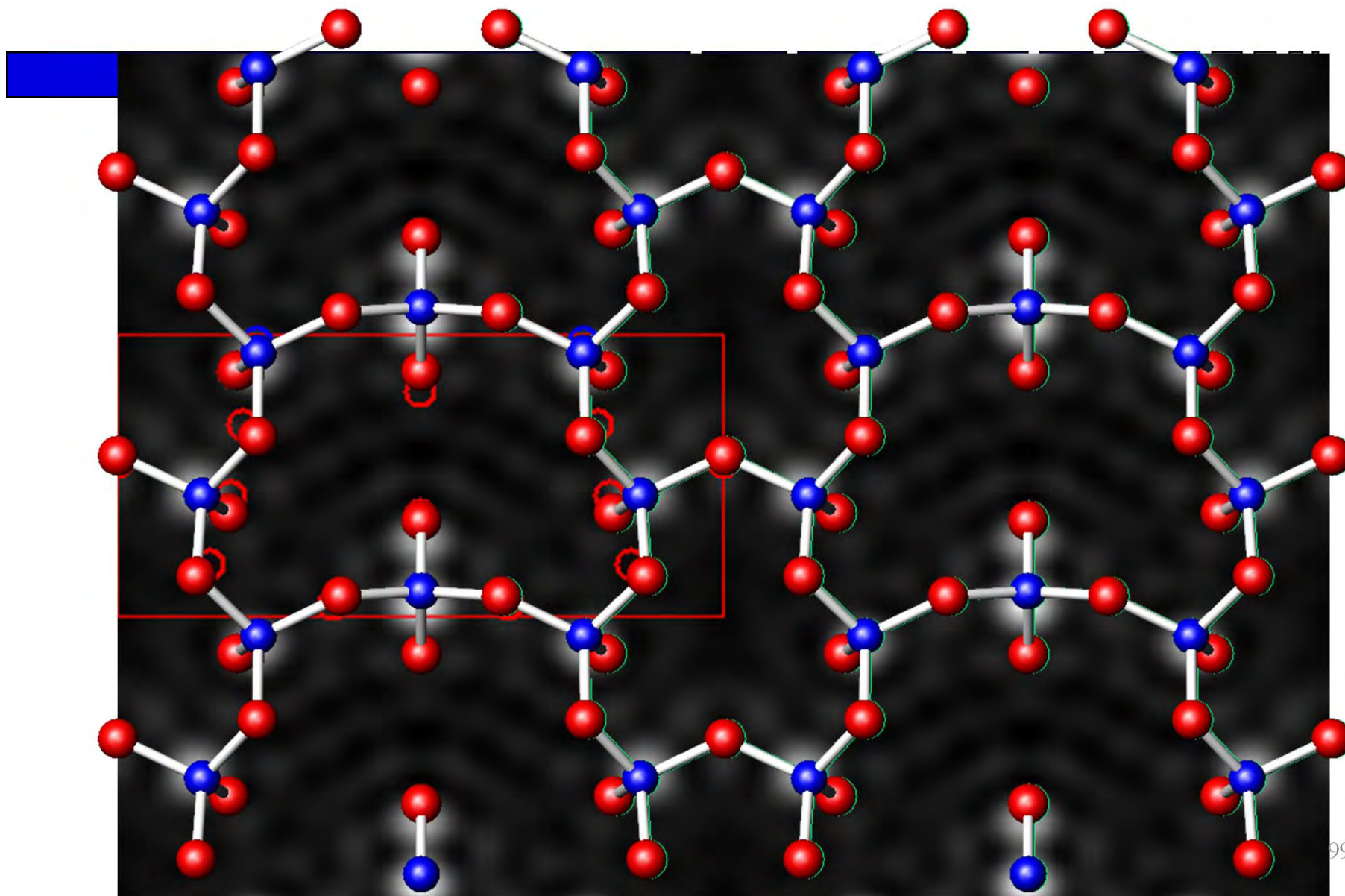


Direct Methods Solution





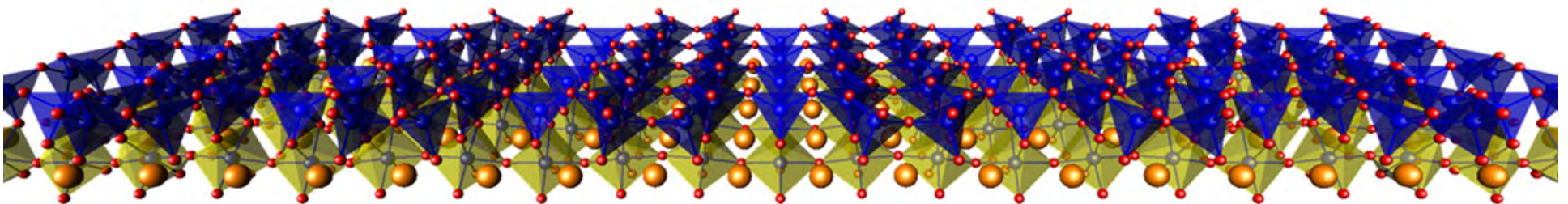
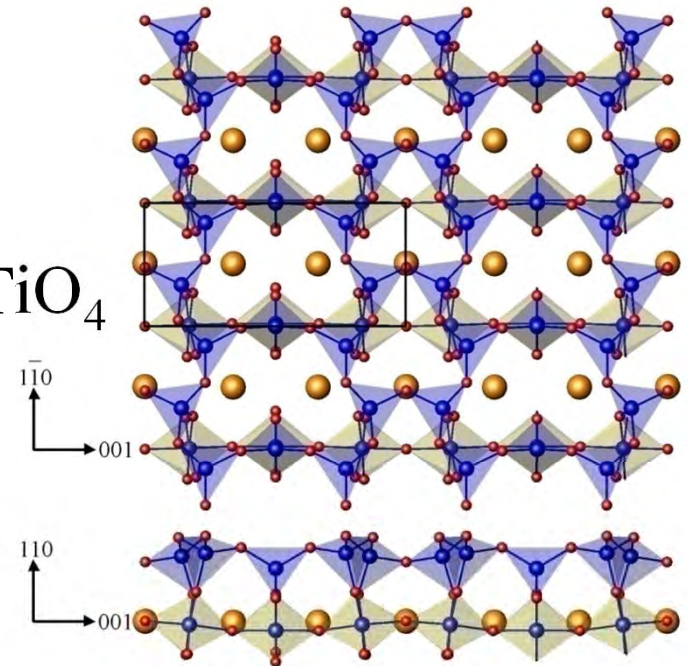
Atomic Positions Refined



SrTiO₃ (110) 3x1



- TiO₂ overall surface stoichiometry
 - Ti₅O₇ atop O₂ termination
 - Ti₅O₁₃ atop SrTiO termination
- Surface composed of corner sharing TiO₄ tetrahedra
 - Arranged in rings of 6 or 8 tetrahedra
 - 4 corner share with bulk octahedra
 - 1 edge shares with bulk octahedron



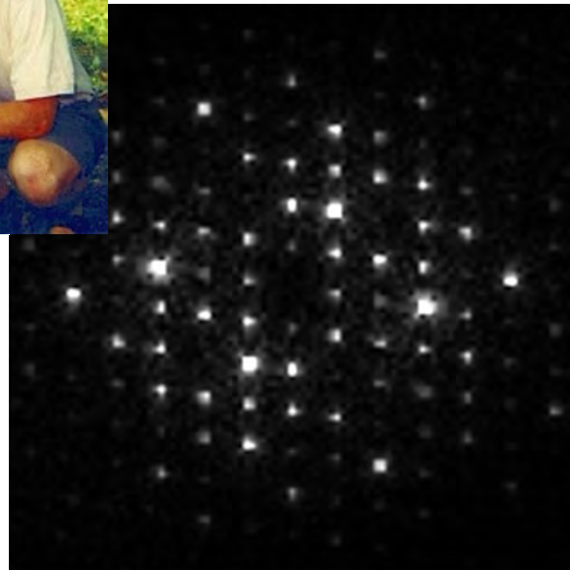
Blue polyhedra are surface polyhedra, gold are bulk octahedra, orange spheres Sr, blue spheres Ti, red spheres O

When does it work?

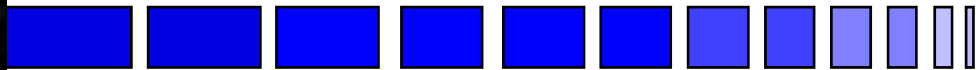


- Kinematical Diffraction (surfaces)
- **1s-Channelling**
- Intensity ordering (PED)

L. D. Marks, W. Sinkler, Sufficient conditions for direct methods with swift electrons. *Microsc. Microanal.* **9**, 399 (2003).

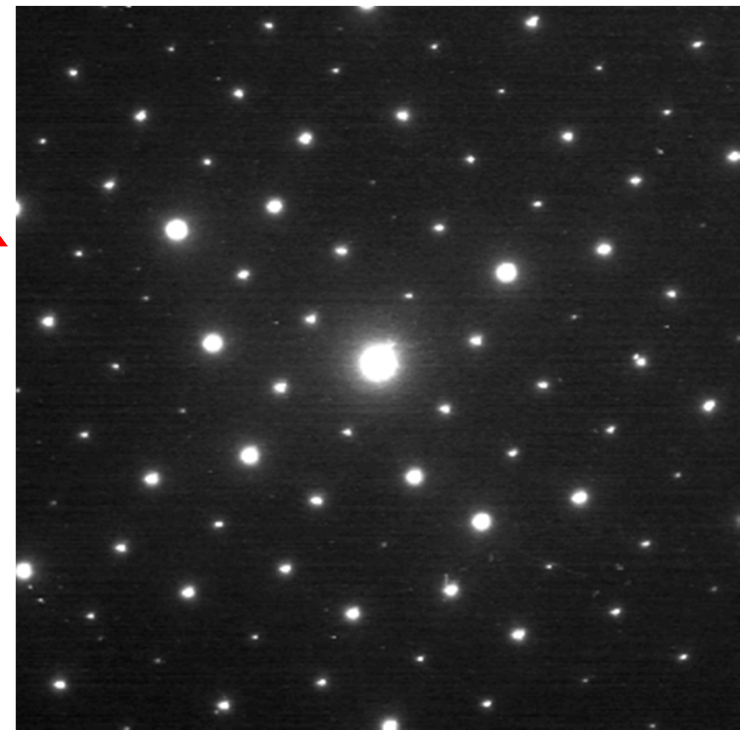


FFT

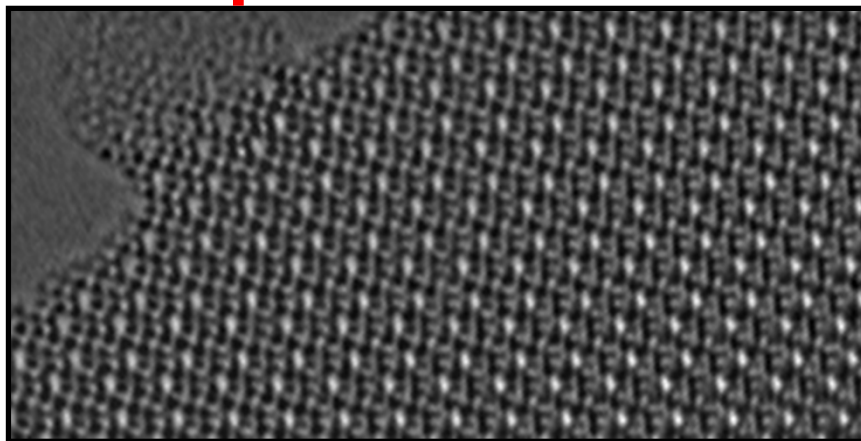


Method

Initial
Phases



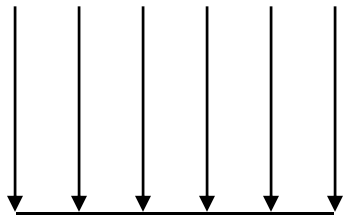
Nanoprobe
Diffraction Data



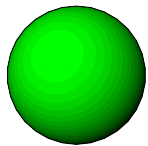
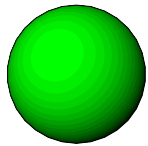
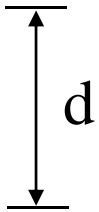
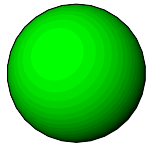
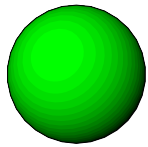
Conventional HREM Image

W. Sinkler et al. *Acta Crystallogr. Sect. A* **54**, 591 (1998)

Channeling Approximation



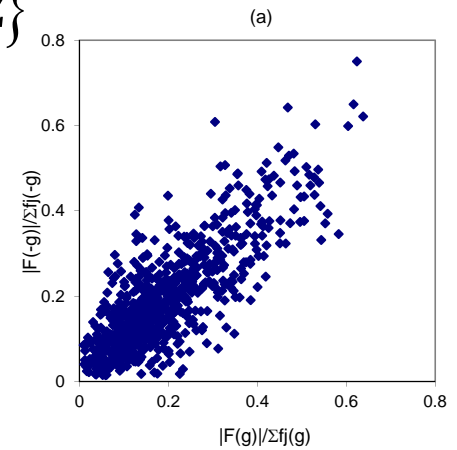
$$e^- \quad V(\mathbf{x}, \mathbf{y}) = \frac{1}{d} \int_{-\infty}^{\infty} V_0(\mathbf{r}) dz$$



$$\psi(\mathbf{r}, \mathbf{z}) = \sum_n C_n \Phi_n(\mathbf{r}) \exp\{-i\lambda_n \mathbf{z}\}$$

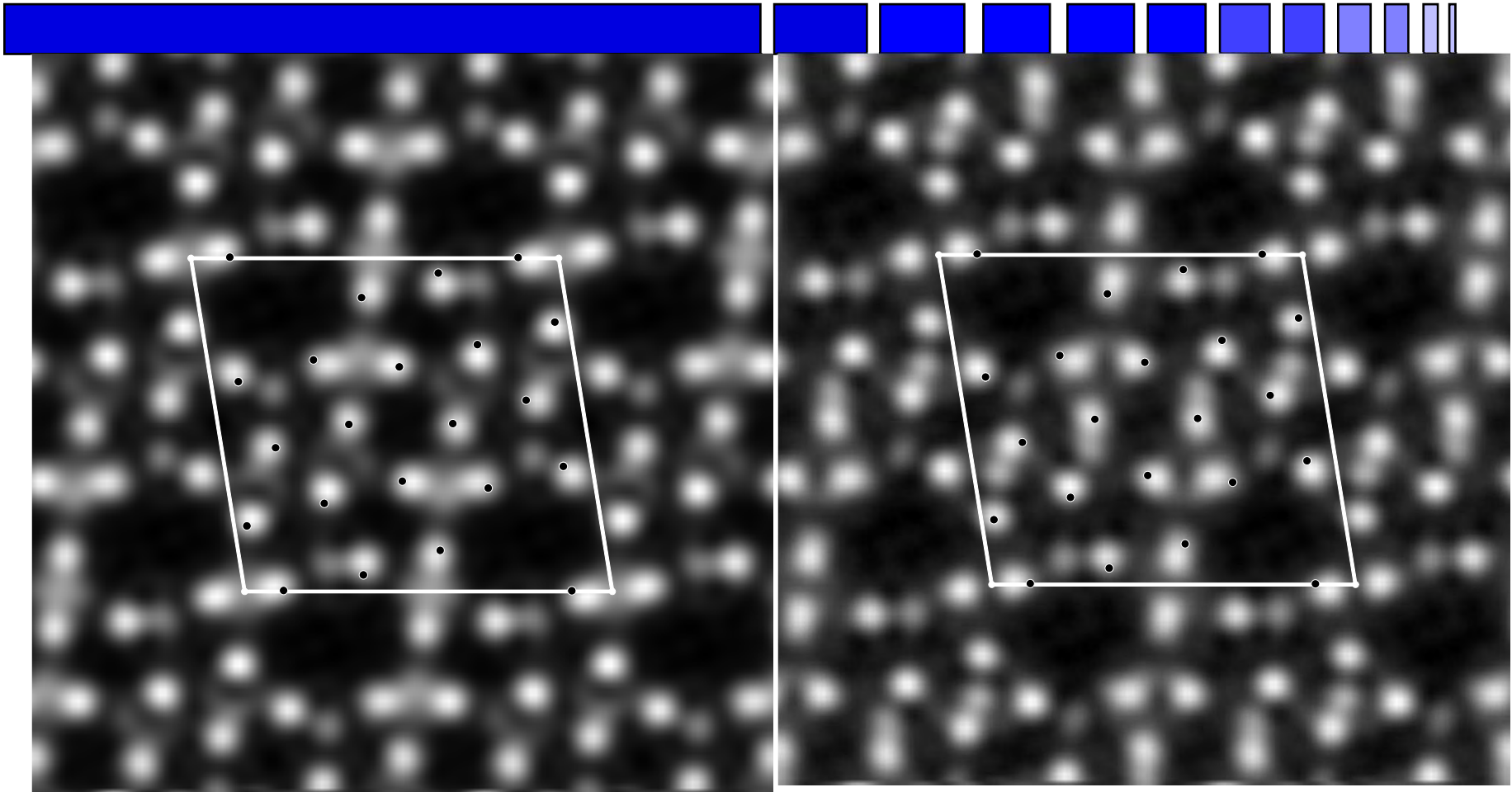
λ_n 2-D Eigenvalue

Σ_0 distribution is statistically kinematical



F. N. Chukhovskii, et al *Acta Cryst A* **57**, 231 (2001)

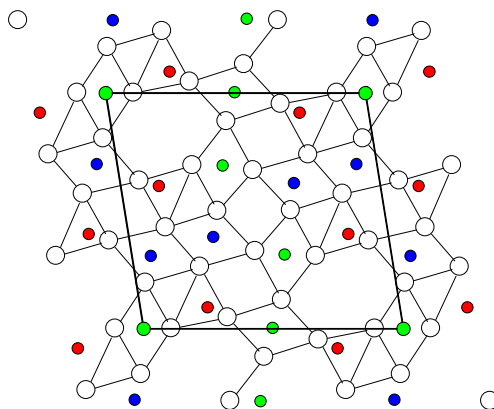
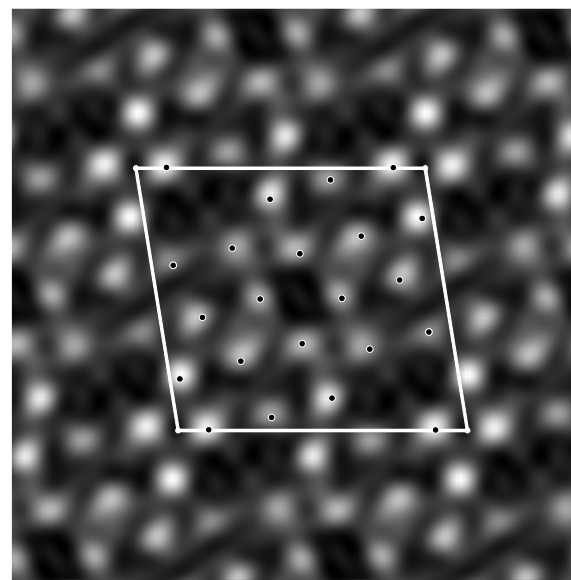
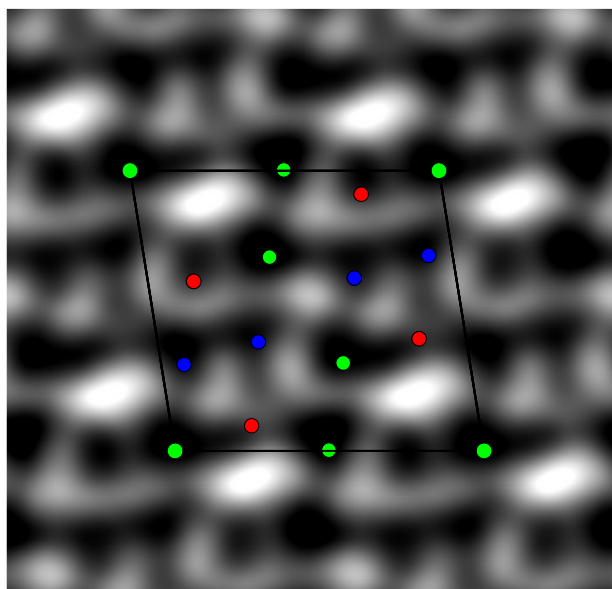
Calculated Wave



$|\psi(\mathbf{r})-1|$ at 113 Å thickness

$|\psi(\mathbf{r})-1|$ at 202 Å thickness

O sites in $(\text{Ga,In})_2\text{SnO}_5$ determined using direct phasing of TED data.



When does it work?



- Kinematical Diffraction (surfaces)
- 1s-Channelling (see also Chukhovskii and Van Dyck later)
- Intensity ordering (PED)

L. D. Marks, W. Sinkler, Sufficient conditions for direct methods with swift electrons. *Microsc. Microanal.* **9**, 399 (2003).

Precession Electron Diffraction

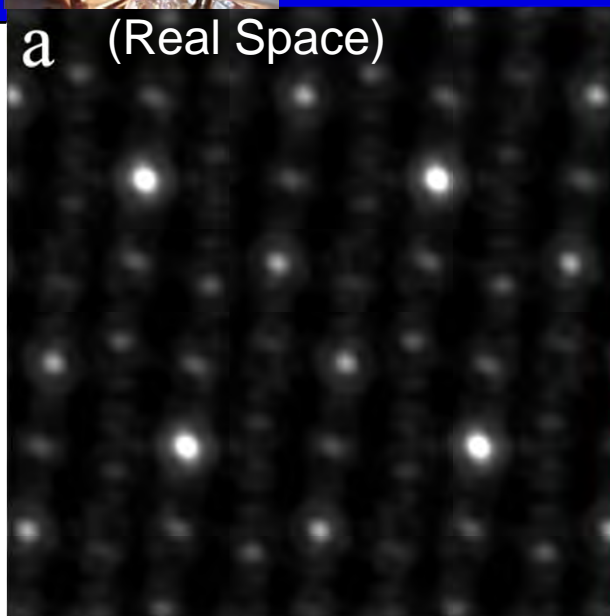


- Quasi-Kinematical Data
- Averaging over angle/phase (and thickness) dampens dynamical contributions
- Intensities are close to monatomic with structure factors (statistically)

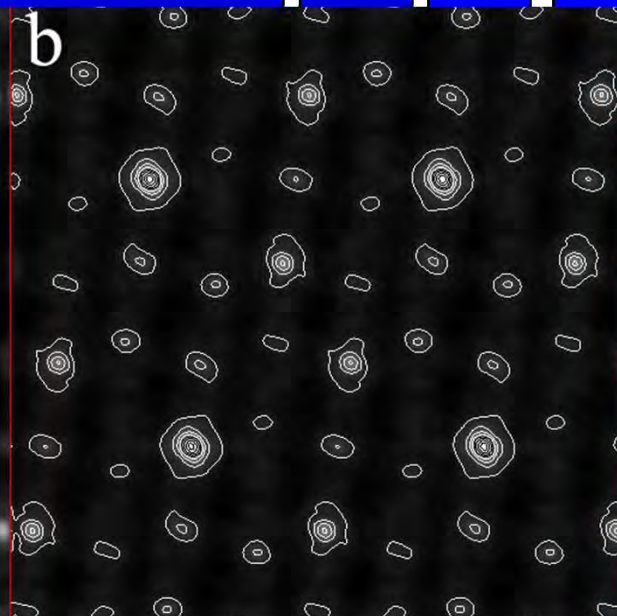


(Ga,In)₂SnO₄ precession data: Direct methods solution

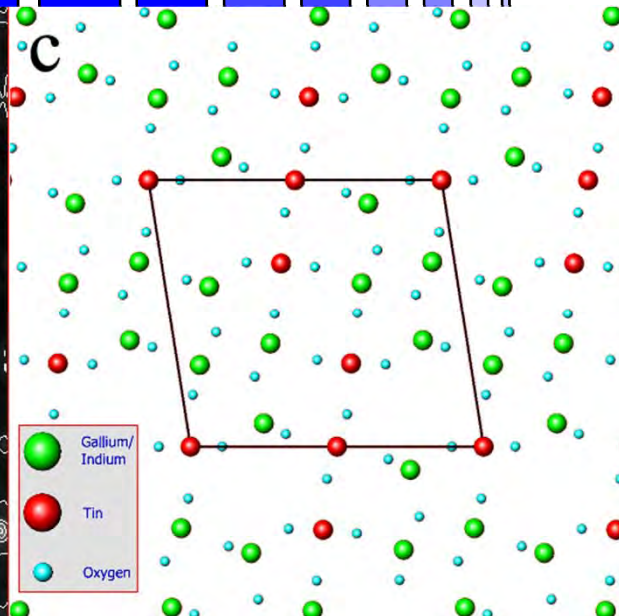
a (Real Space)



b



c



	ΔR (Å)
Sn1	0.00E+00
Sn2	0.00E+00
Sn3	6.55E-03
In/Ga1	5.17E-02
In/Ga2	2.37E-03
Ga1	6.85E-02
Ga2	1.22E-01


Displacement ($R_{\text{neutron}} - R_{\text{precession}}$):

$$\Delta R_{\text{mean}} < 4 \cdot 10^{-2} \text{ \AA}$$

(Sinkler, et al. J. Solid State Chem, 1998).

(Own, Sinkler, & Marks, submitted.)

Conclusion

- 
- The “Phase Problem” with electrons is no longer really a problem....assuming ideal data of course
 - Many technique work most of the time
 - Few techniques work all the time
 - Some unresolved issues (proper dynamical refinement)
 - Remember that we are solving an inversion problem, and these are susceptible to ill-conditioning

Four basic elements are required to solve a recovery problem



1. A data formation model

Imaging/Diffraction/Measurement

2. A priori information

The presence of atoms or similar

3. A recovery criterion:

A numerical test of Goodness-of-Fit

4. A solution method.

Mathematical details