

# How to solve a structure?

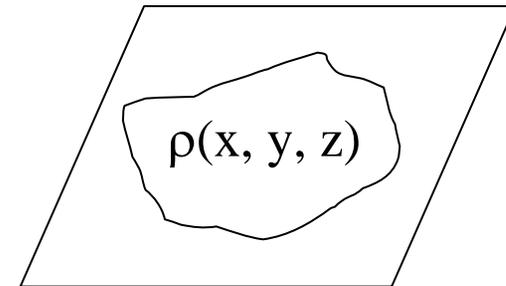


- Guess, then refine
  - Will always give something, but if the guess is wrong GIGO
- Use Patterson function
  - Difficult for complicated structures (in a moment)
- Get an image
  - STM is hard to interpret
  - HREM, can be ambiguous
- Use DFT
  - If the original guess is wrong, GIGO
  - Functionals can be inaccurate for TMO's
- Try something else?

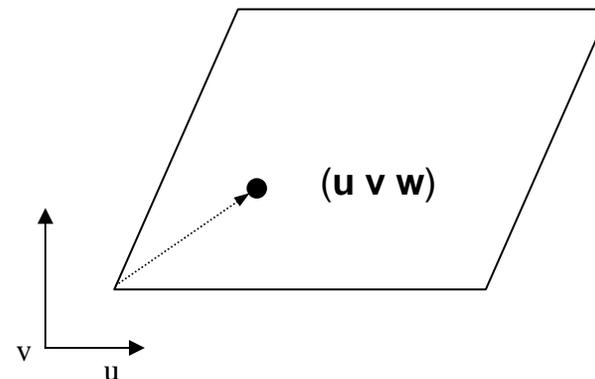
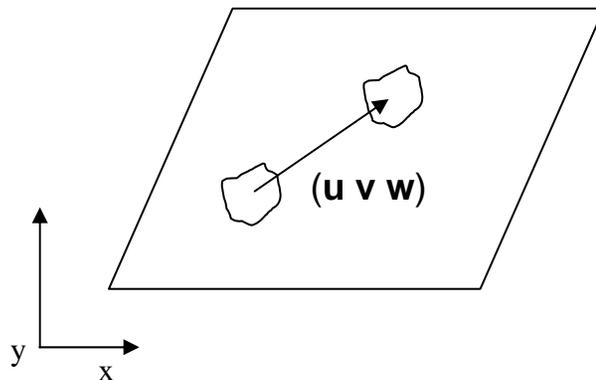
# Patterson Function I (FT of Diffraction Pattern)



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



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

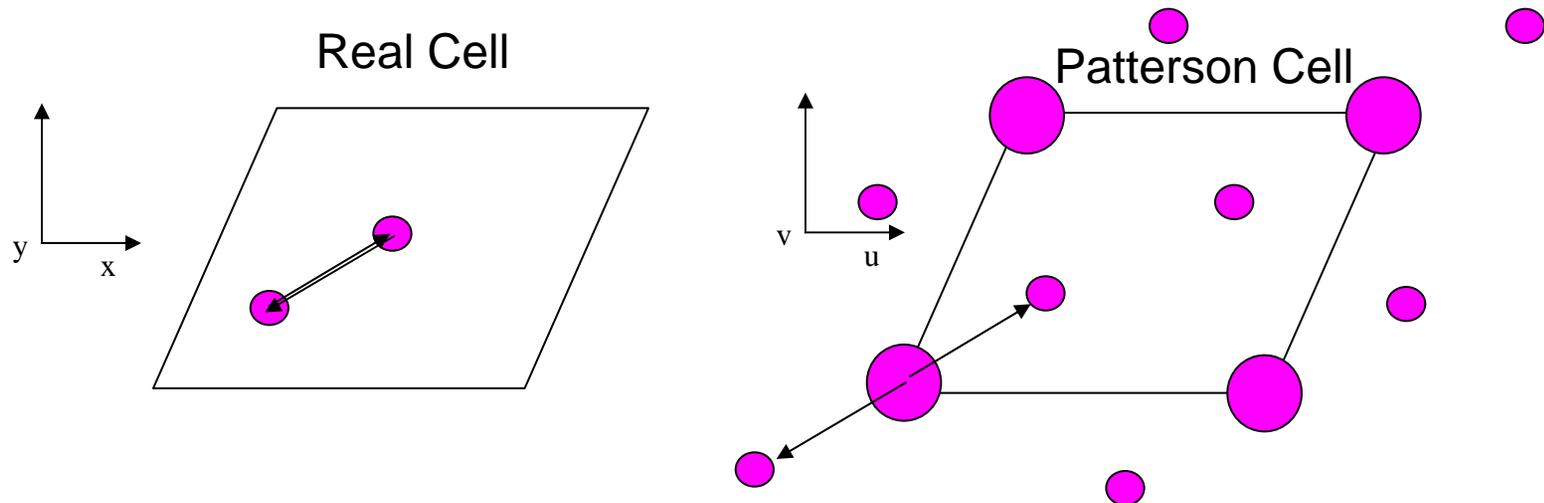


# Patterson Function II



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

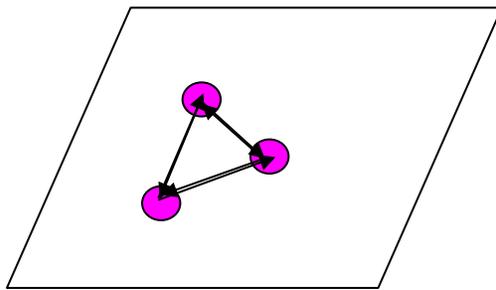
Patterson map will contain points corresponding to vectors between atoms in the real cell



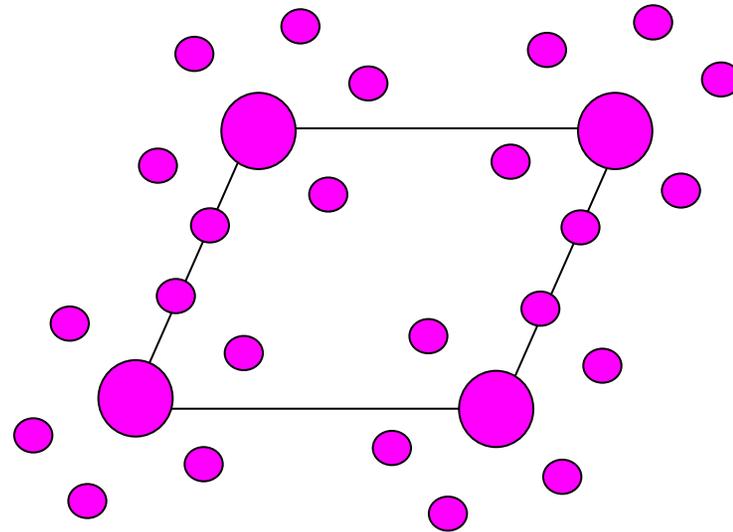
# Patterson Function III



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)  $\rightarrow$  gets complicated!

# Basics



- We know the amplitudes
- We want to find the phases
- Problem is insolvable without additional information – constraints
- Use an iterative approach

# Diffraction Phase Problem



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

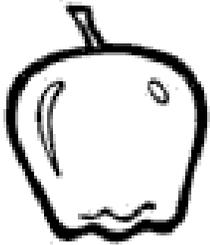
Measured diffraction intensities

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

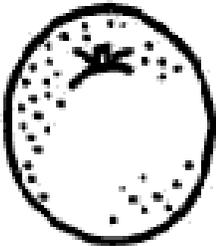
Unmeasured

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

# Phase: Apples & Oranges



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



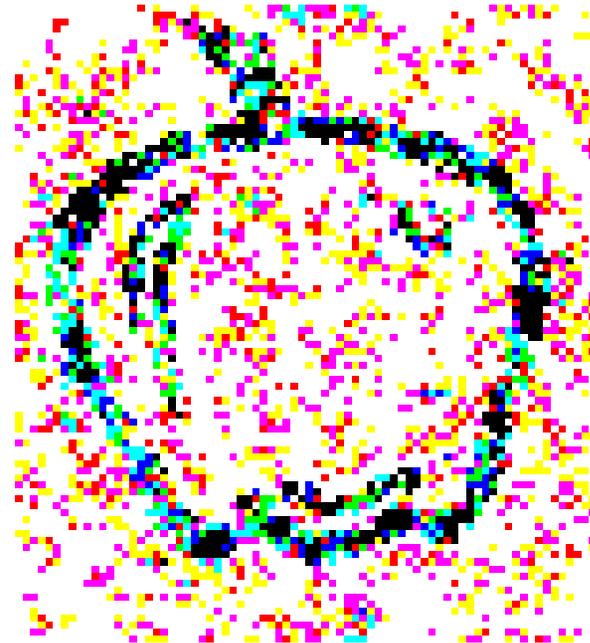
$$\text{FT} \rightarrow A_o \exp(-i \phi_o)$$

+

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

Phase of Apple + Amplitude of Orange = ?

# Phase of Apple = Apple



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

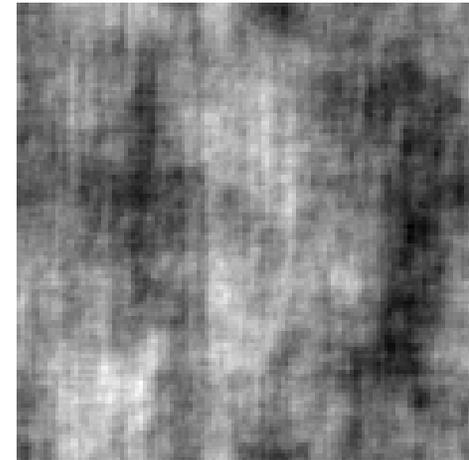
Phase is more important than amplitude

# The importance of phase information



Suzy

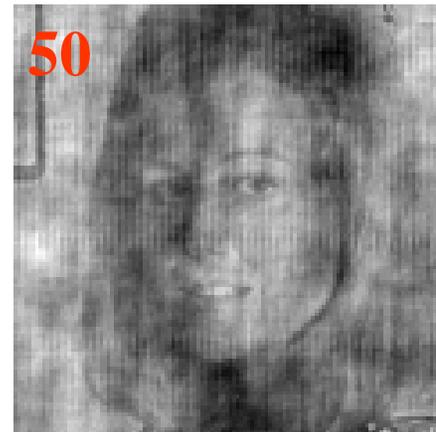
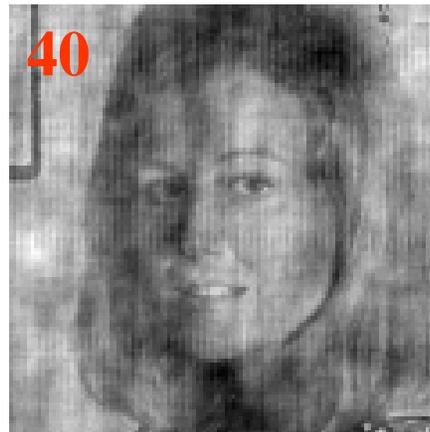
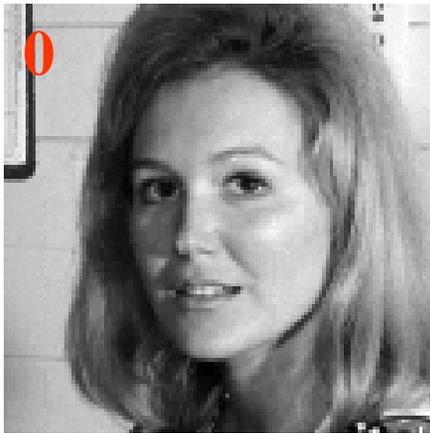
Correct Modulus  
Random Phases



Correct Phase  
Random Modulus

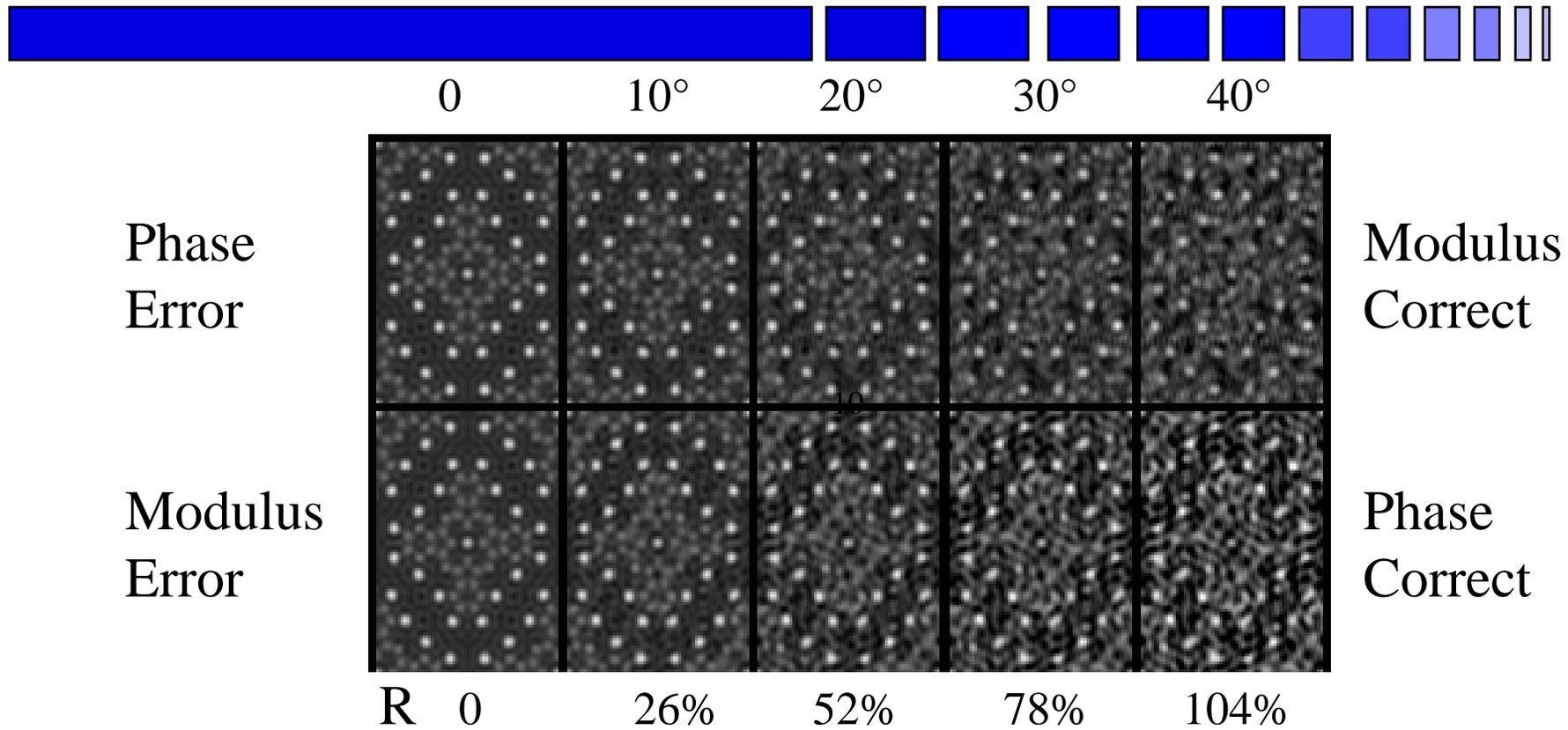


# Role of error in phases (degrees)



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

# Phase and Modulus Errors

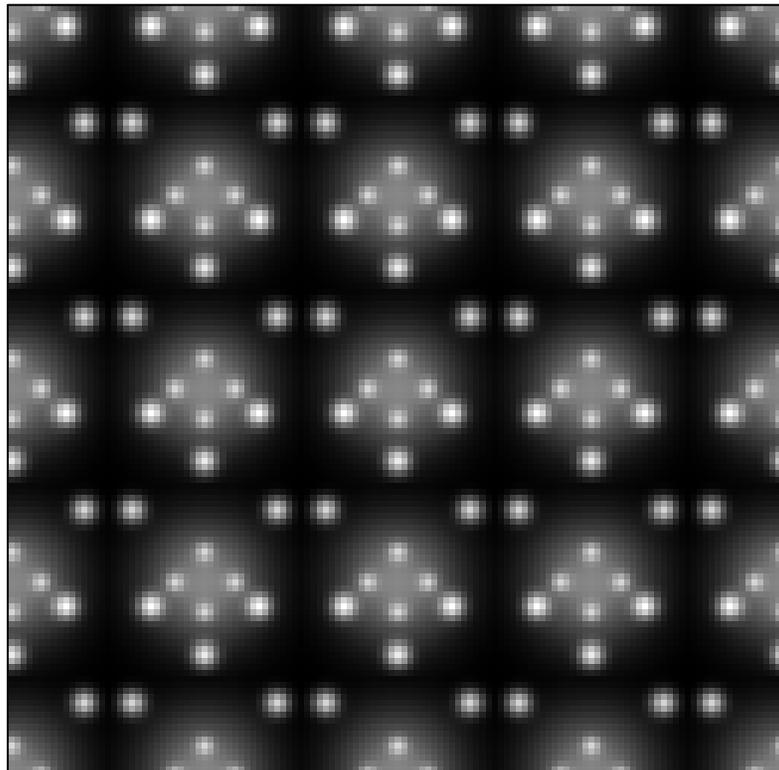


We only need **approximately correct** phases  
We can **tolerate** modulus errors

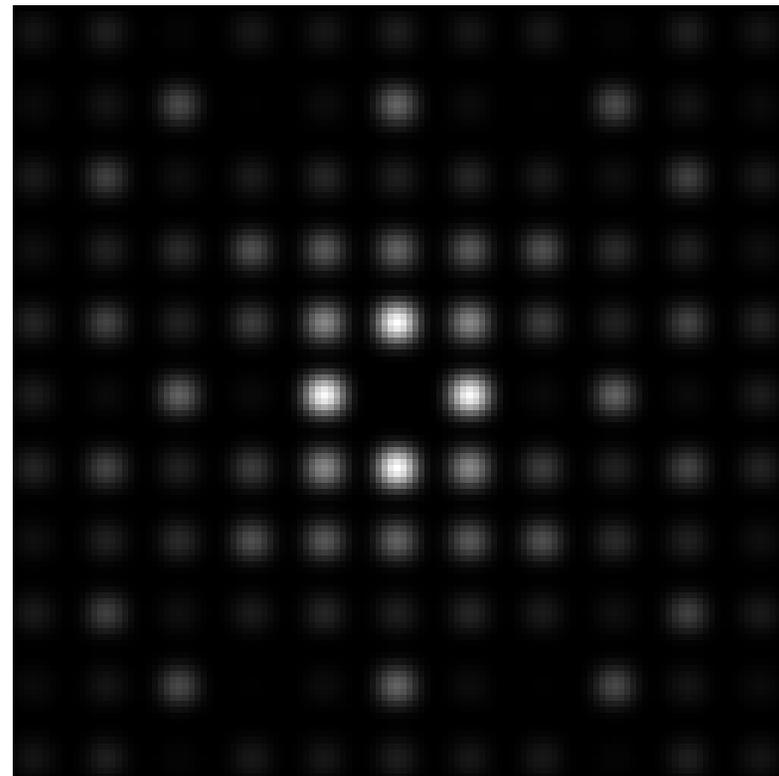
**Demonstration: how resolution works in reciprocal space: If we can add beams at large distance from center of patterns *with the correct phase*, we can reconstruct the structure with very high definition:**



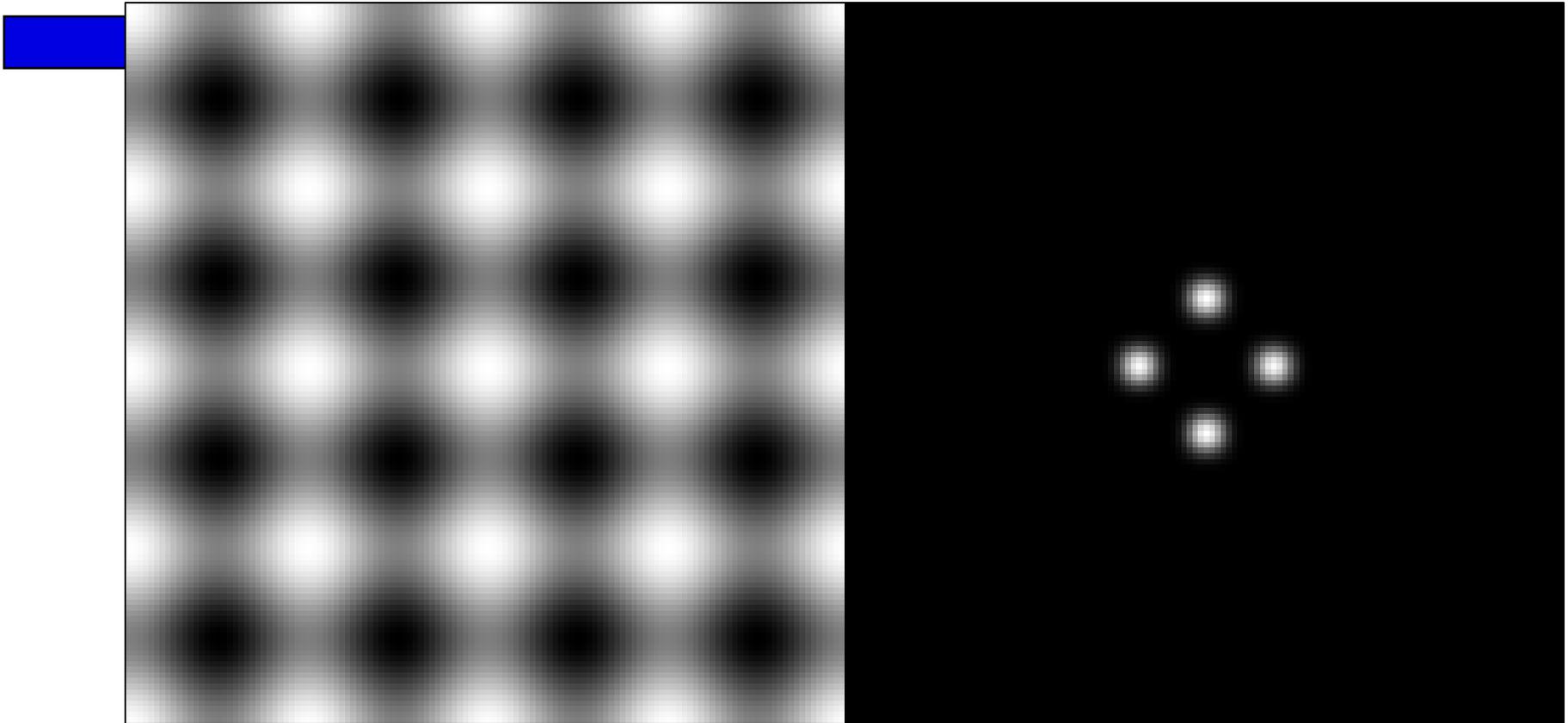
Example: simple test structure  
of repeated molecule



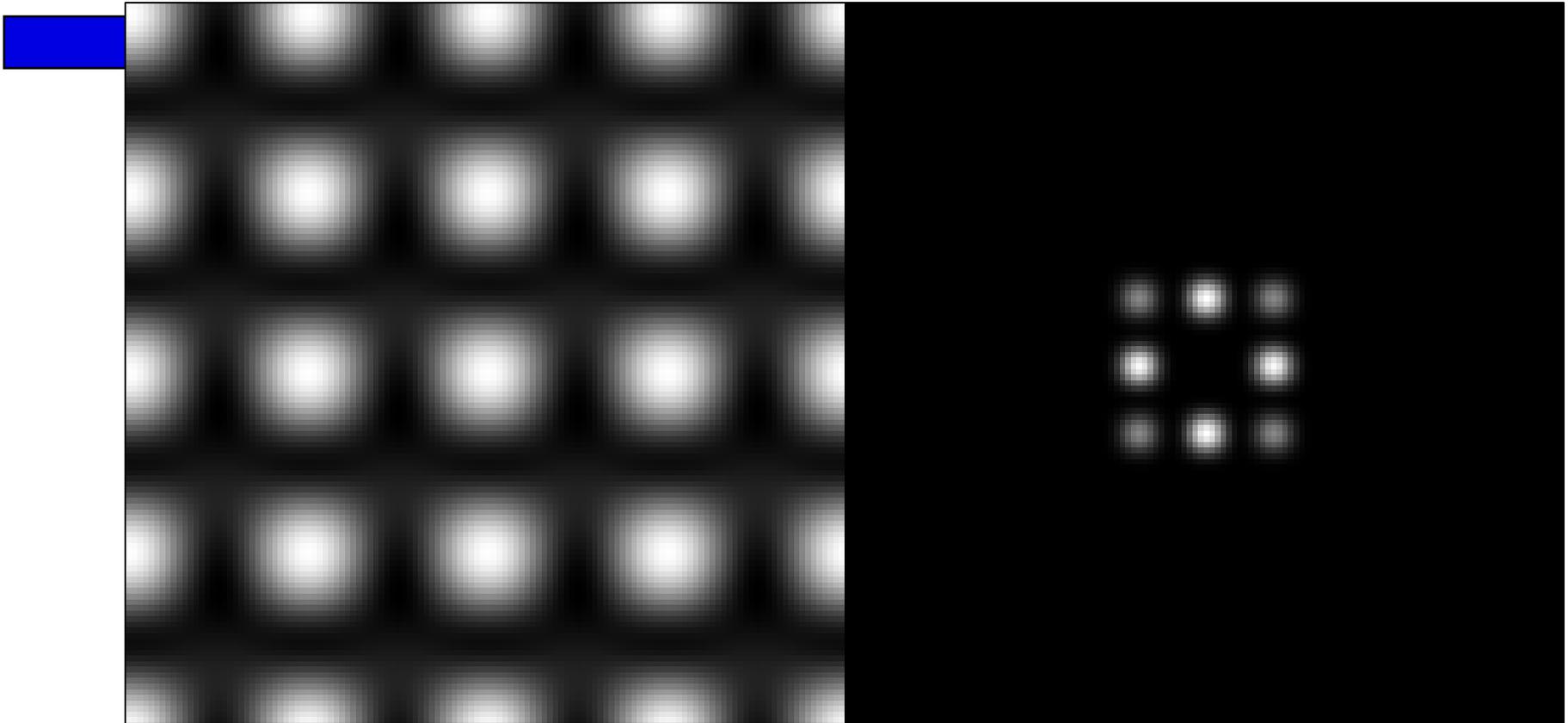
Computed diffraction pattern of  
structure at left.



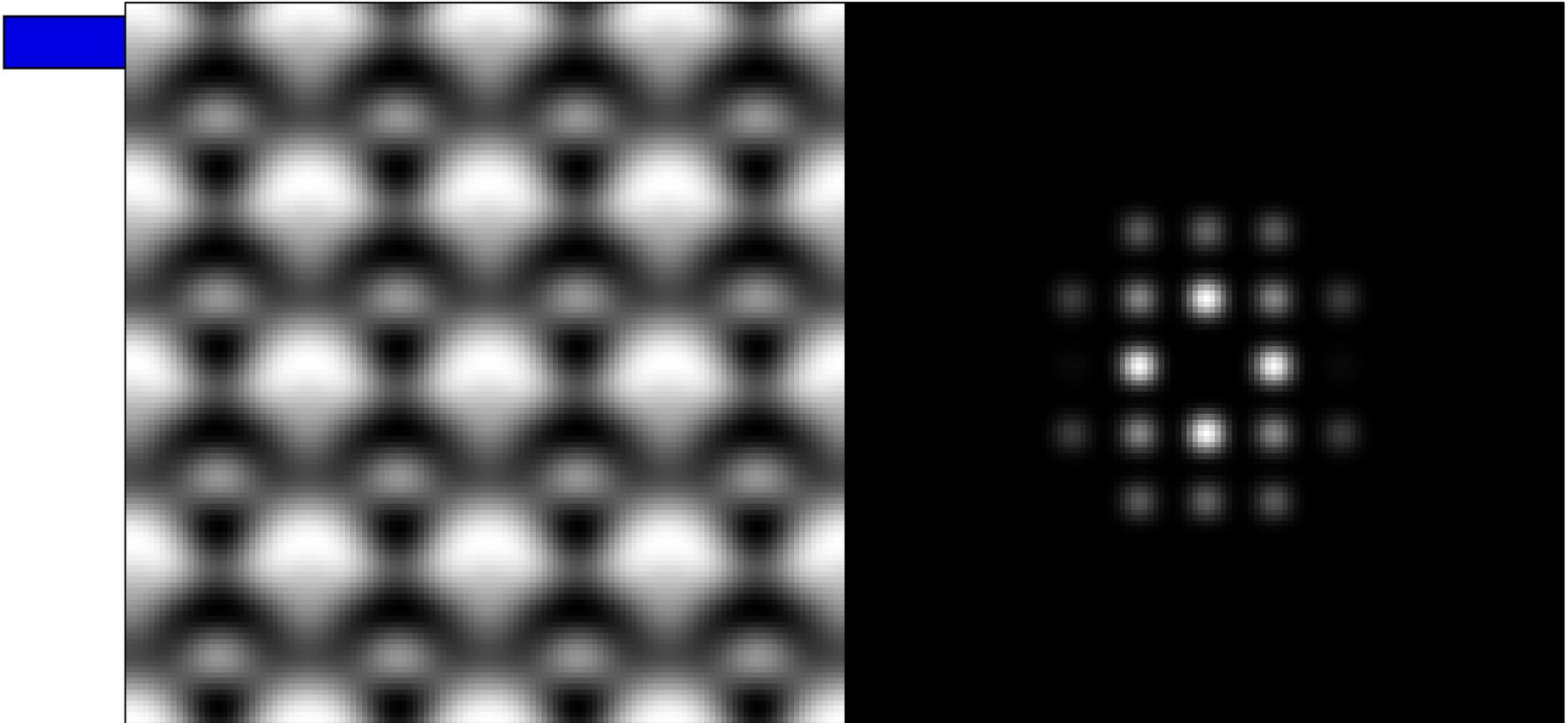
# Low Resolution ...



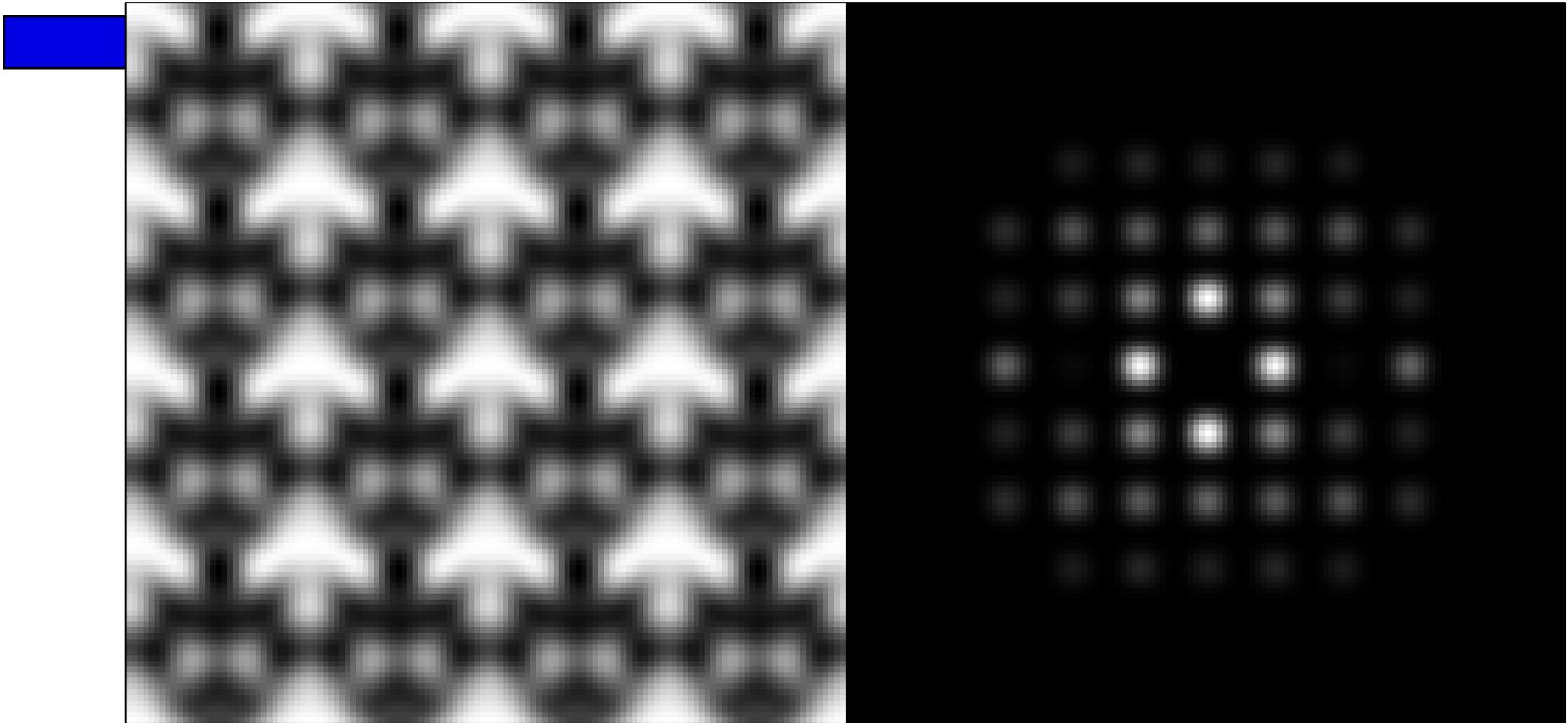
# Higher resolution ...



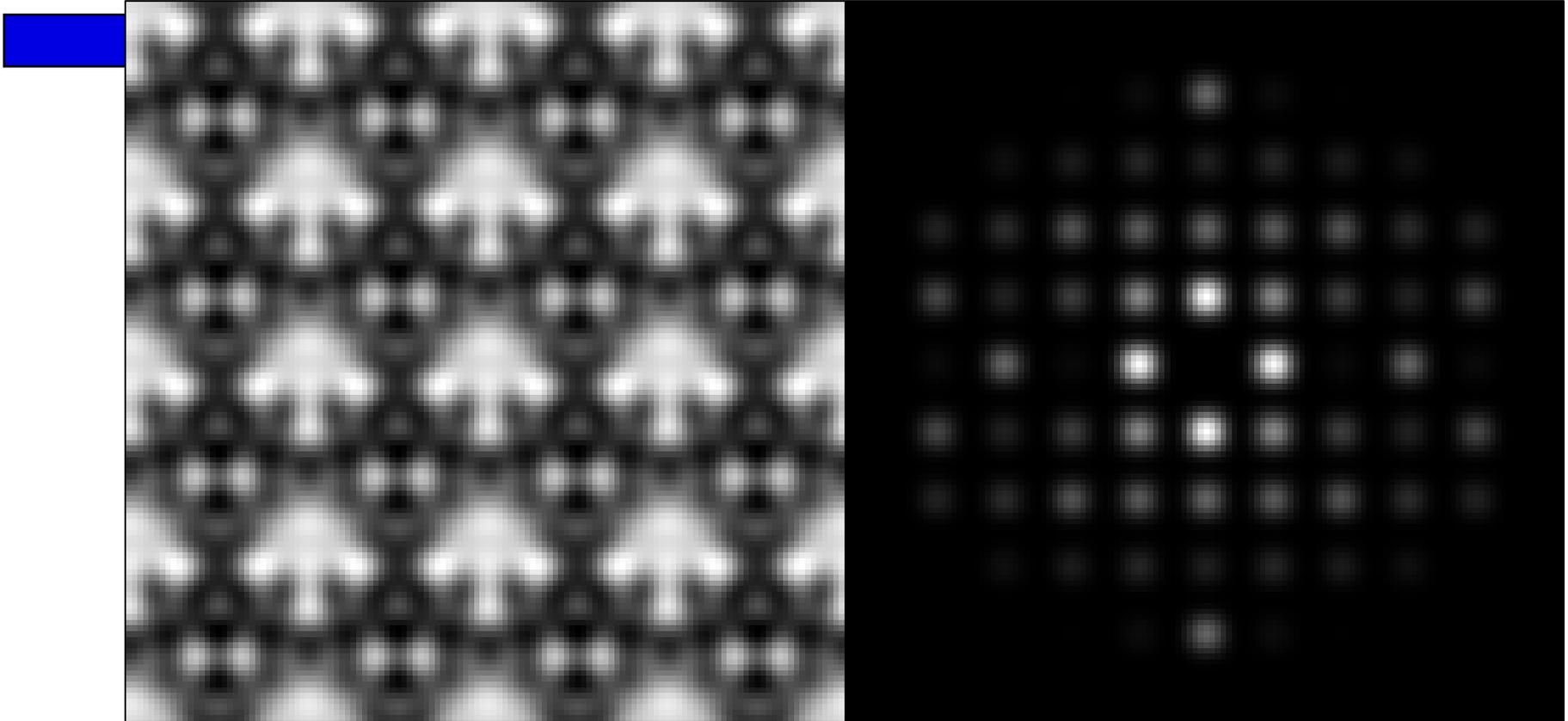
# Higher resolution ...



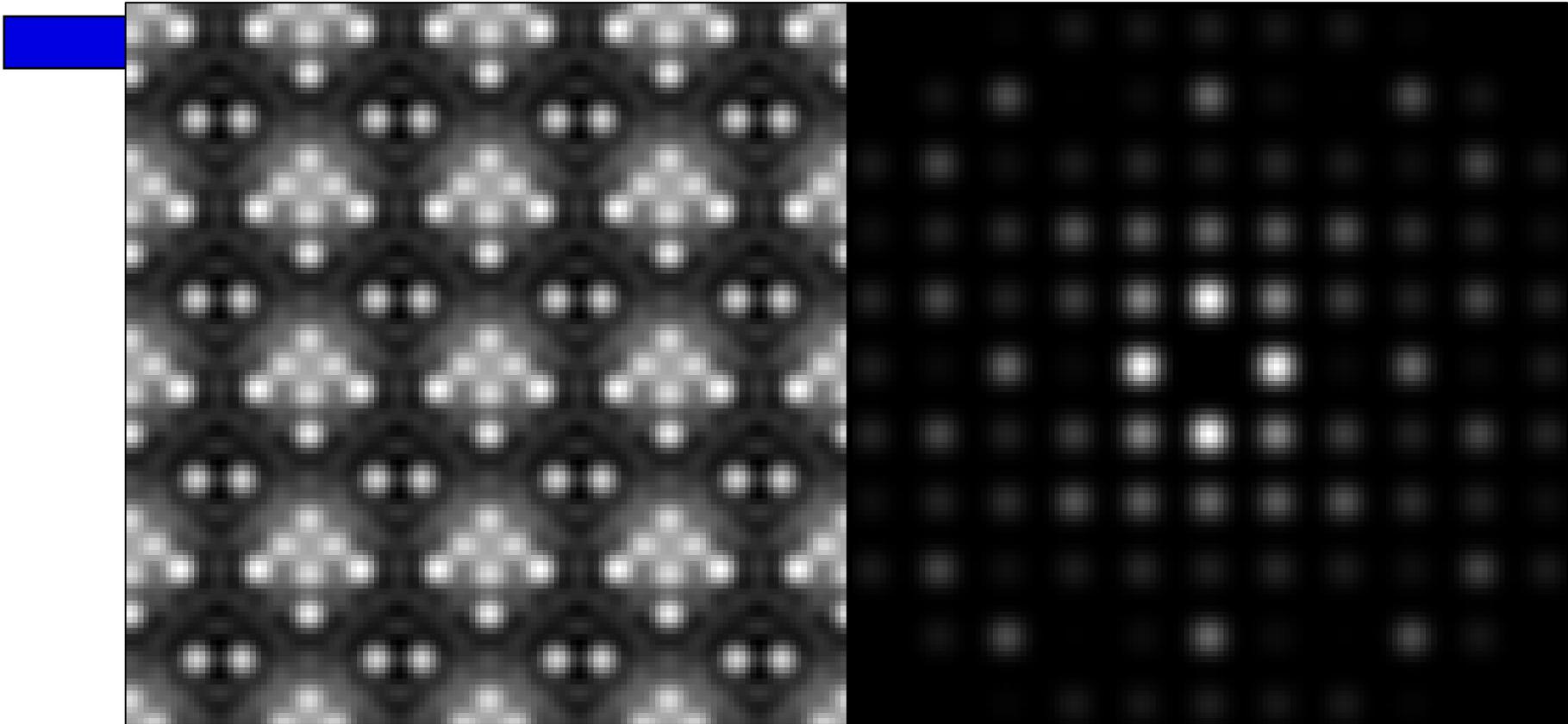
# Higher resolution ...



# Higher resolution ...

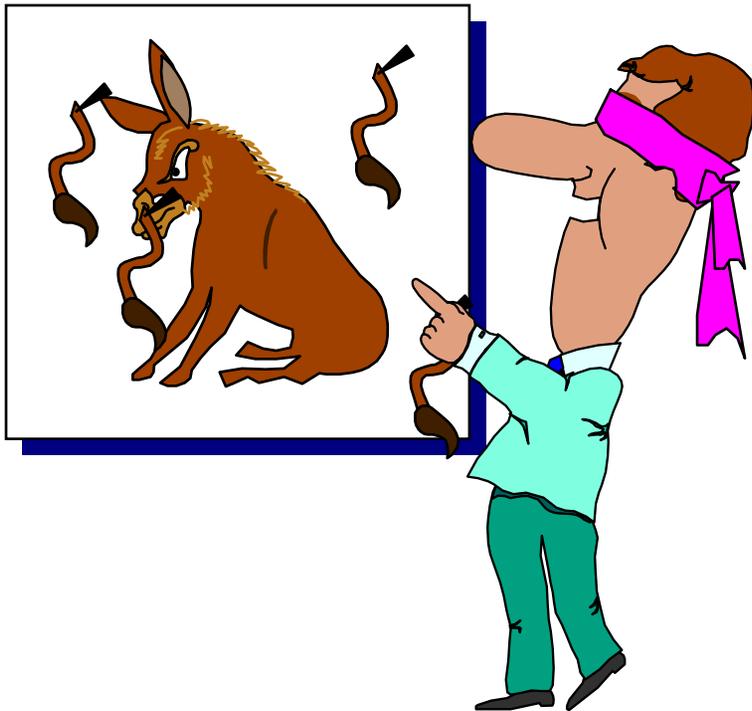


This is the goal of direct methods. Given measurement of amplitudes, obtain phases using educated guesswork. As illustrated, good phases give accurate representation of structure.



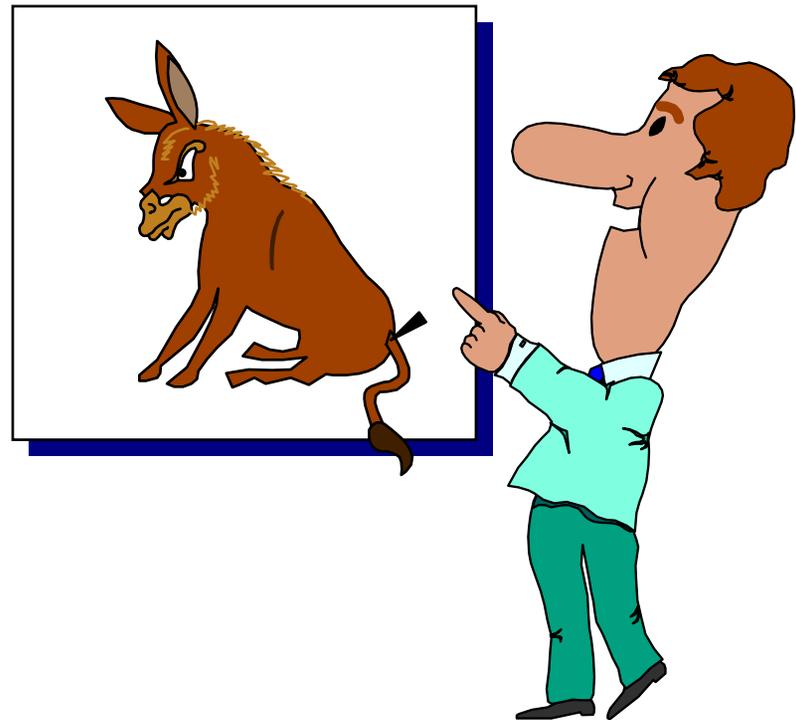
# Direct Methods vs. Indirect Methods

Indirect Methods:  
“Trial and Error”



Direct Methods:

Using available information  
to find solutions



# Implementation

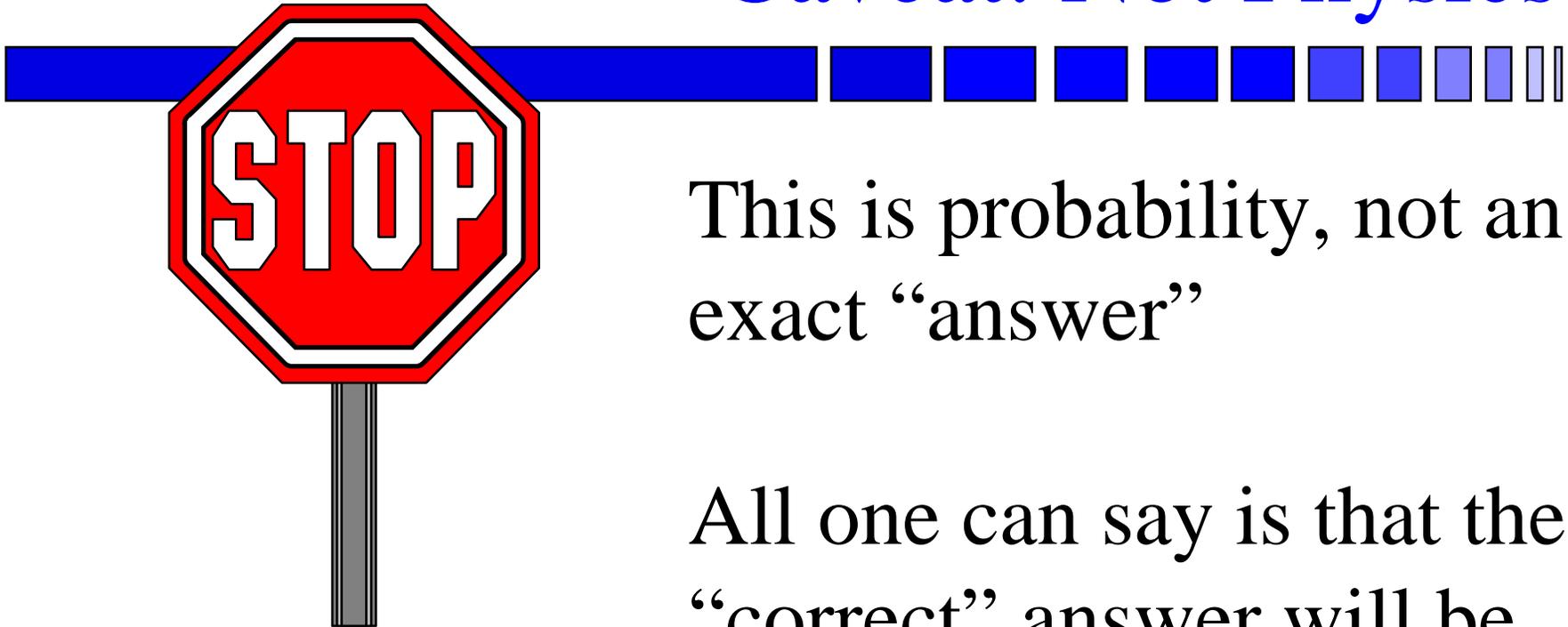
*Infinite Number of Possible  
Arrangements of  
Atoms*

*Direct Methods*

*Finite*

R,  $\chi^2$ , structure,  
DFT and chemistry

## Caveat: Not Physics



This is probability, not an exact “answer”

All one can say is that the “correct” answer will be among those that are found



## 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

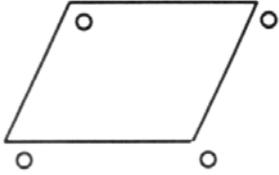
# Symmetry



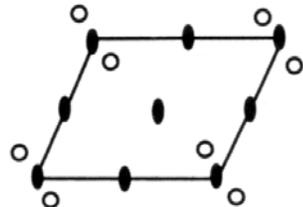
- Has to be determined *a-priori*
  - CBED
  - HREM (maybe)
  - Spot Pattern (can be tricky)



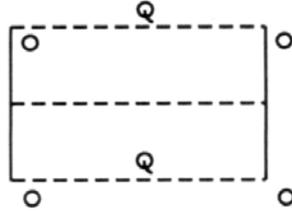
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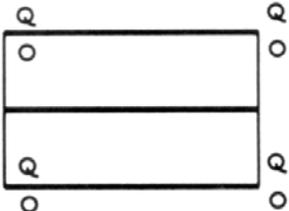
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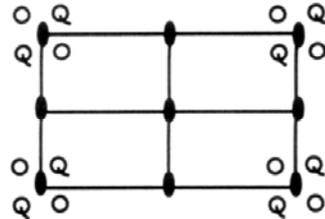
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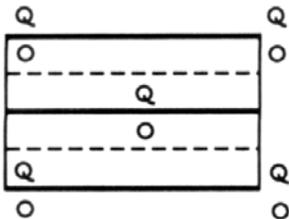
pm



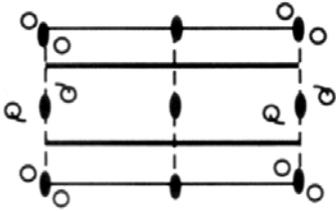
pmm



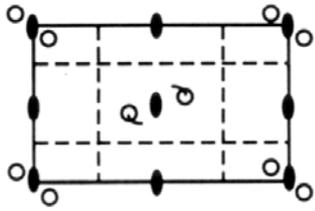
cm



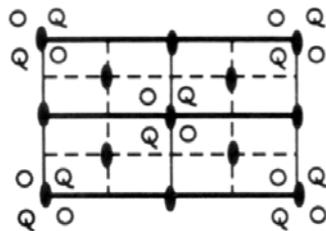
pmg



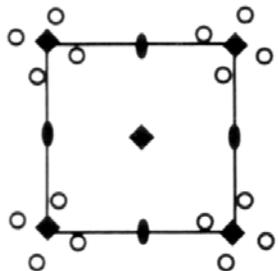
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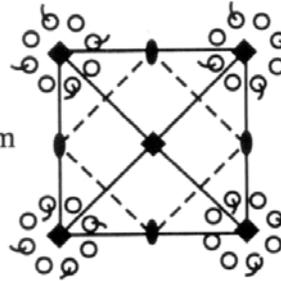
cmm



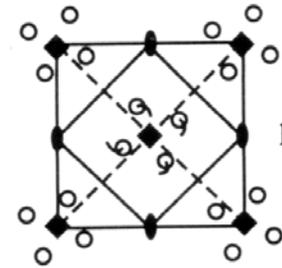
p4



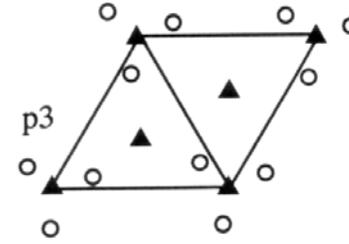
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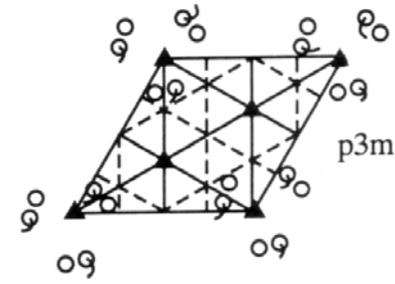
p4g



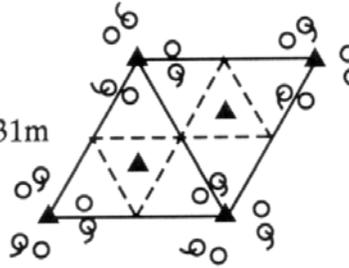
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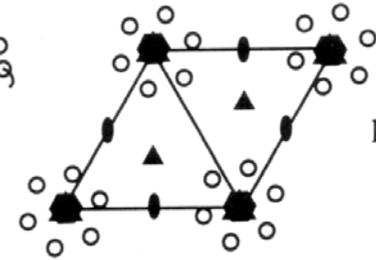
p3m1



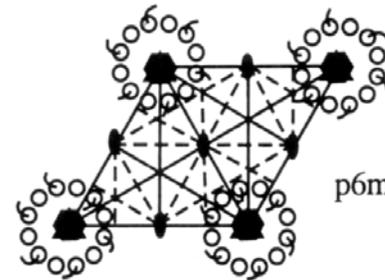
p31m

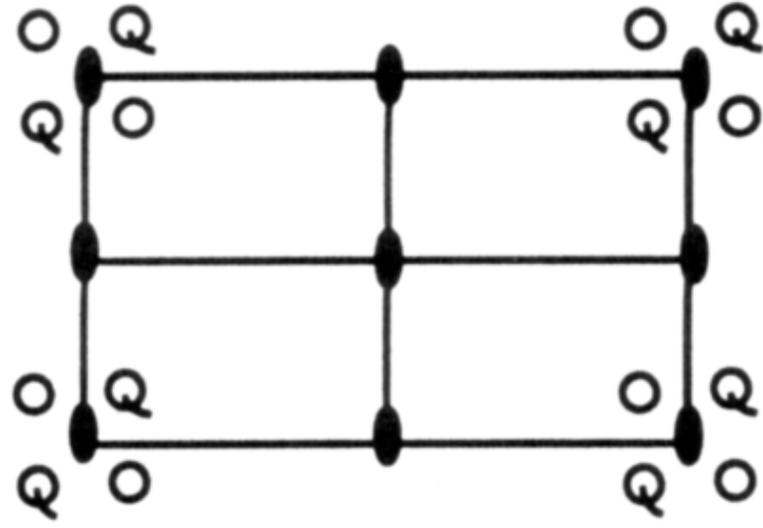


p6

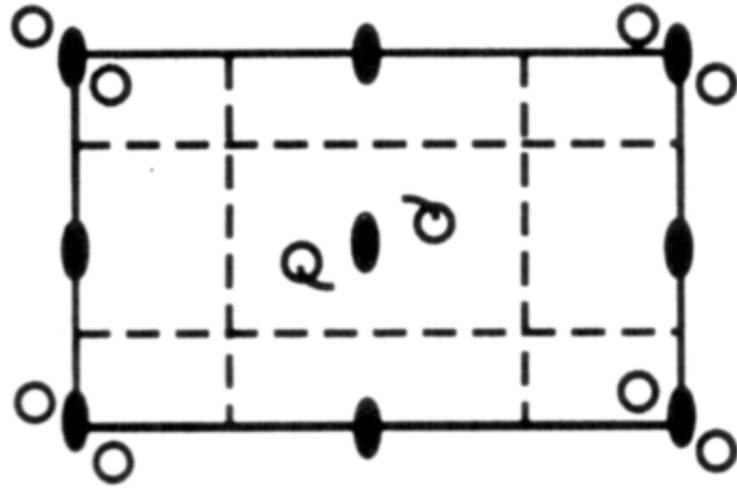
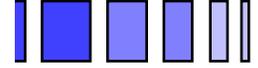


p6m





pmm



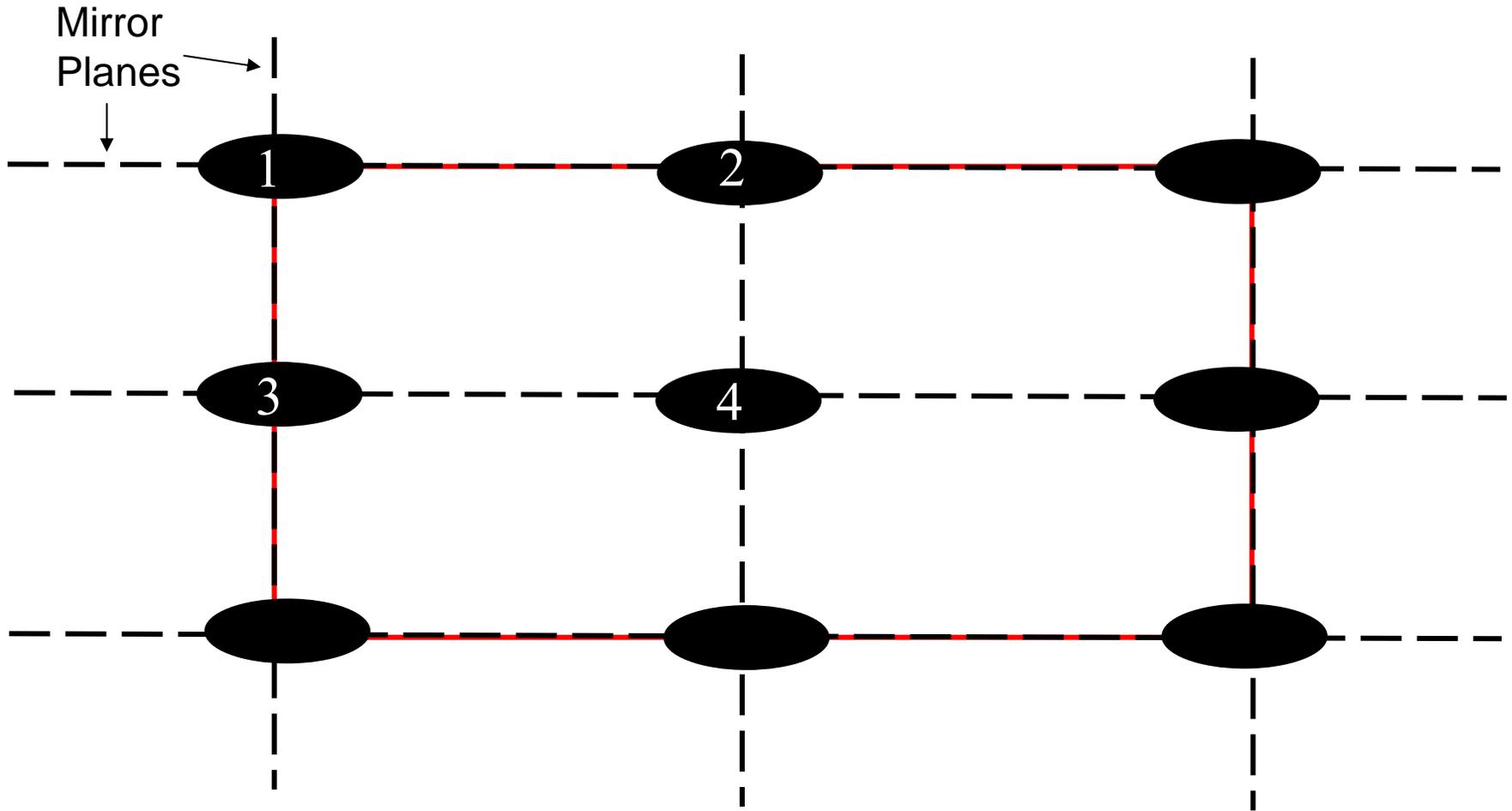
pgg

# First Step: Origin Definition

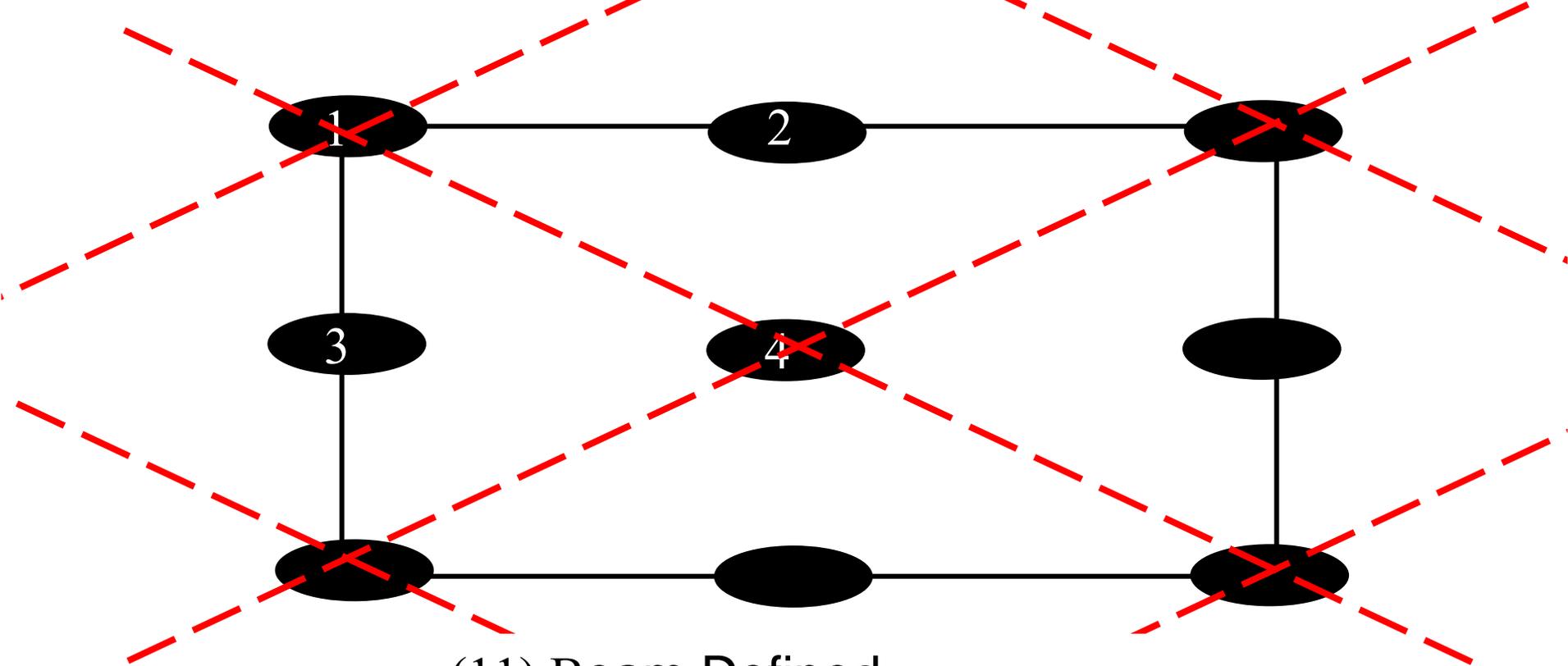


- Not all phases are unknown
  - Translating the crystal has no physical significance
  - Can therefore fix an origin for the crystal – equivalent to fixing certain reflections
  - Relevant for crystallographic phase (not absolute phase of wavefunction which is not important)

# Origin Definition c2mm

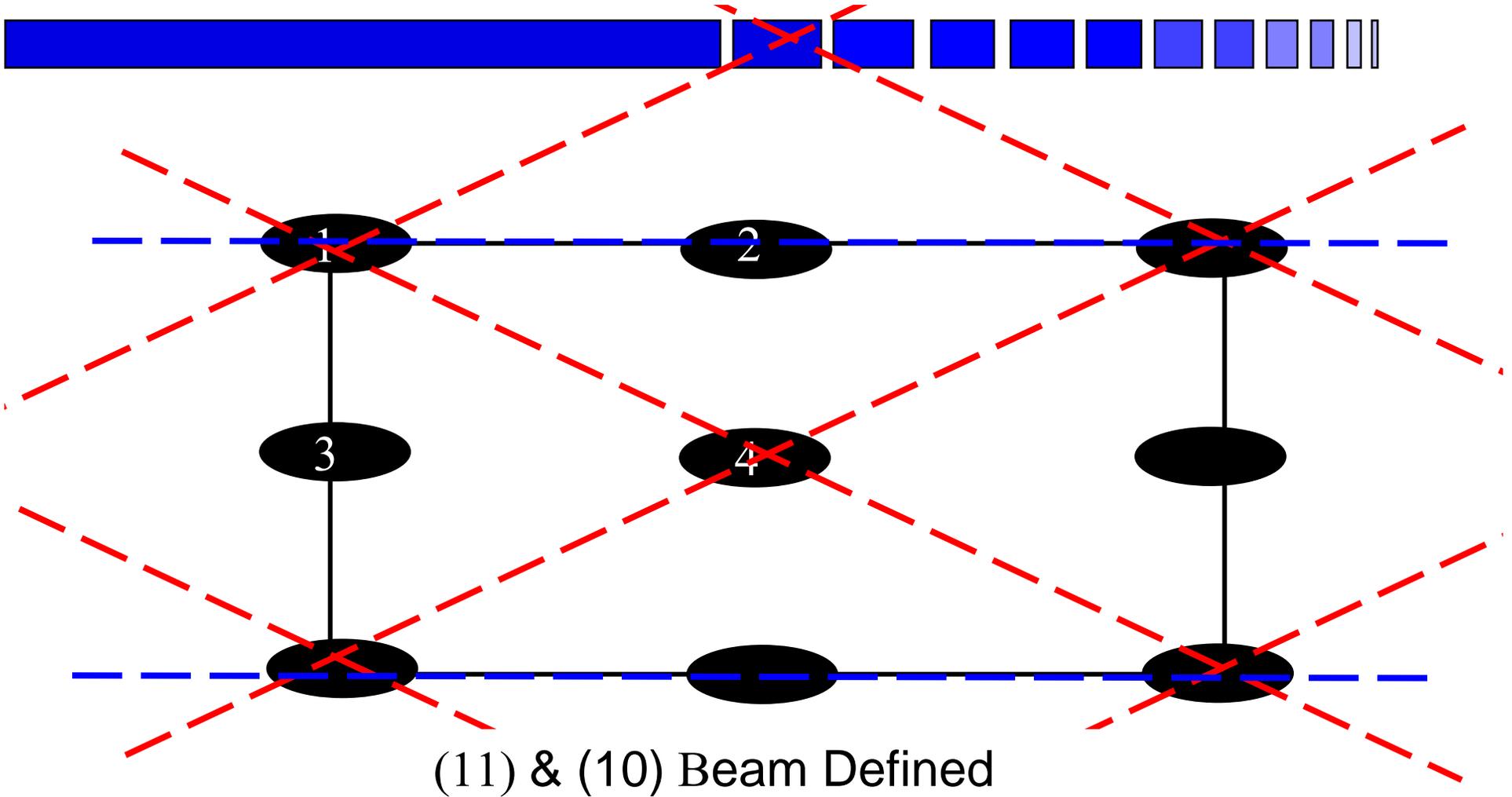


# Origin Definition c2mm



(11) Beam Defined

# Origin Definition c2mm



# Next Steps: Basic Ideas

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

- Simple case, Unitary Sayre Equation, 1 type

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

- Divide by N, #atoms & f(k), atomic scattering factors

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

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

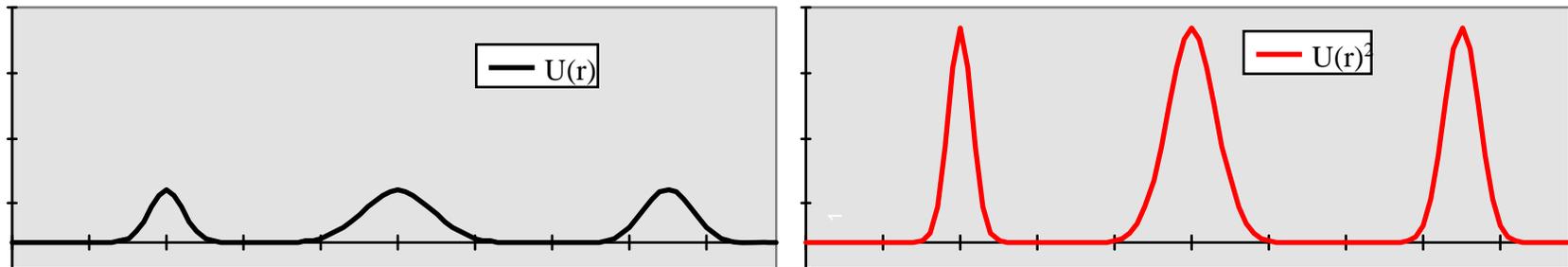
↙ Constraint

# 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 ( $\Sigma_2$ ): 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 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



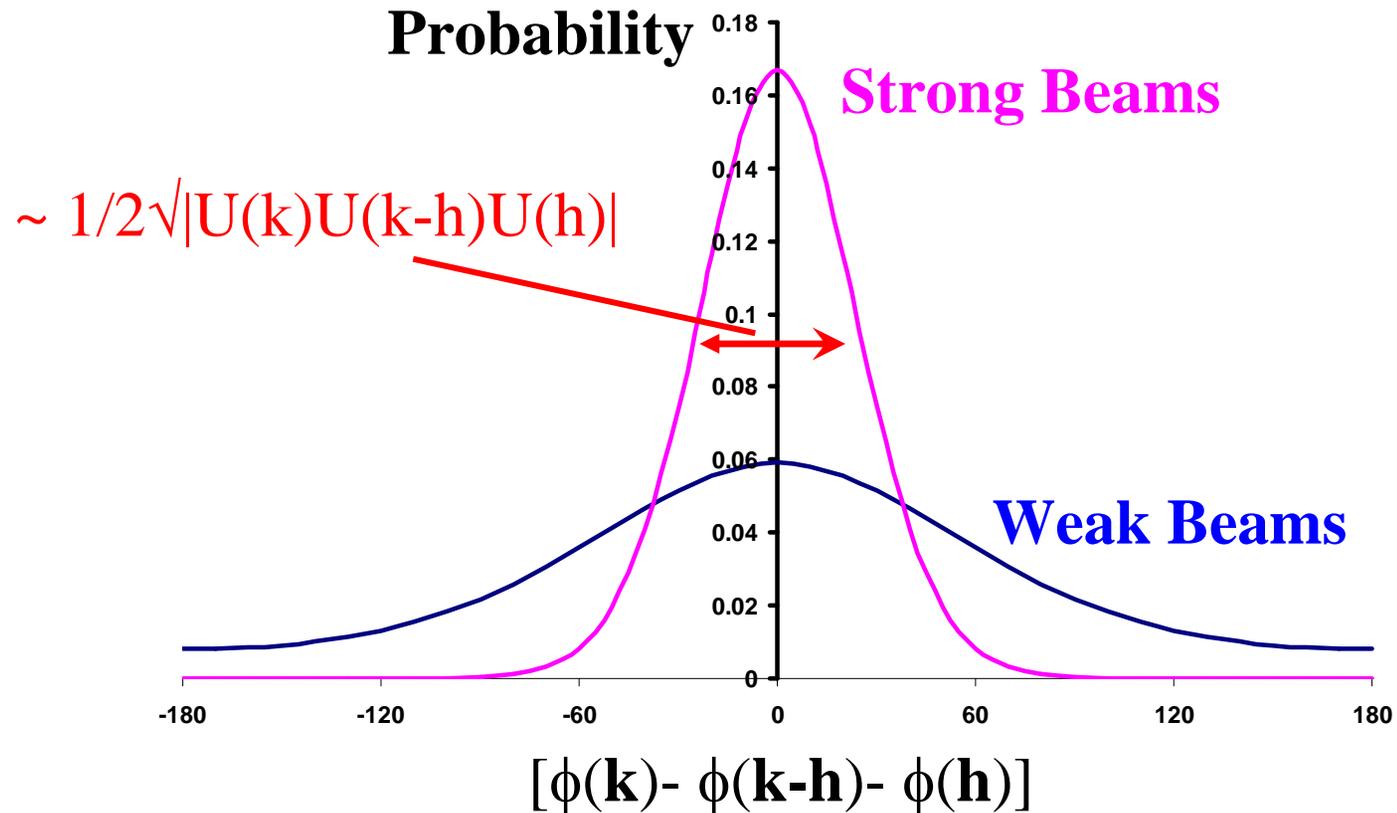
- Consider next

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

# Cochran Distribution: III

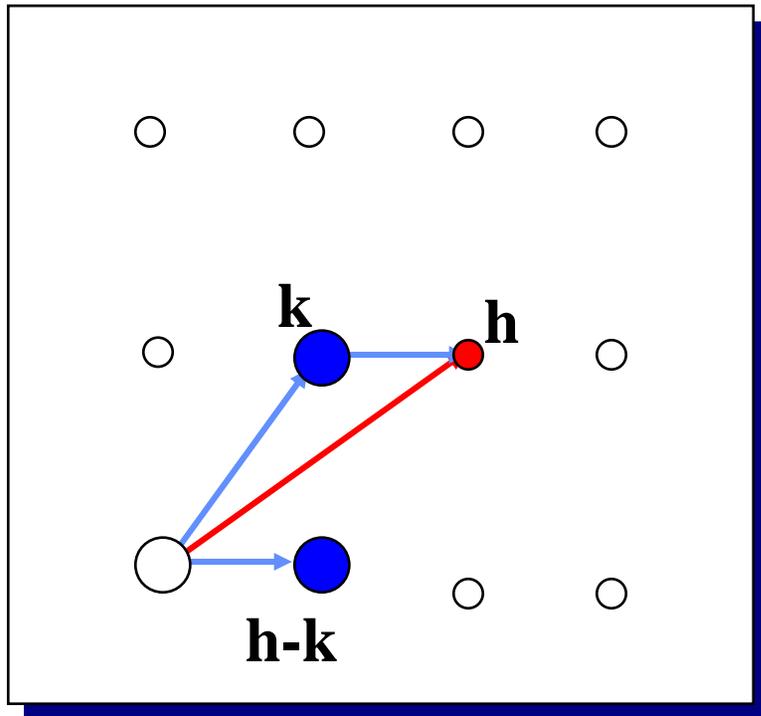
- We have a distribution of values. The Central Limit theorem: all distributions tend towards Gaussian. Hence a probability:
- $P(U(\mathbf{k}) - NU(\mathbf{k-h})U(\mathbf{h}))$   
 $\sim C \exp(-|U(\mathbf{k}) - NU(\mathbf{k-h})U(\mathbf{h})|^2)$   
 $\sim C \exp(2|U(\mathbf{k})U(\mathbf{k-h})U(\mathbf{h})|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

# $\Sigma_2$ Triplet



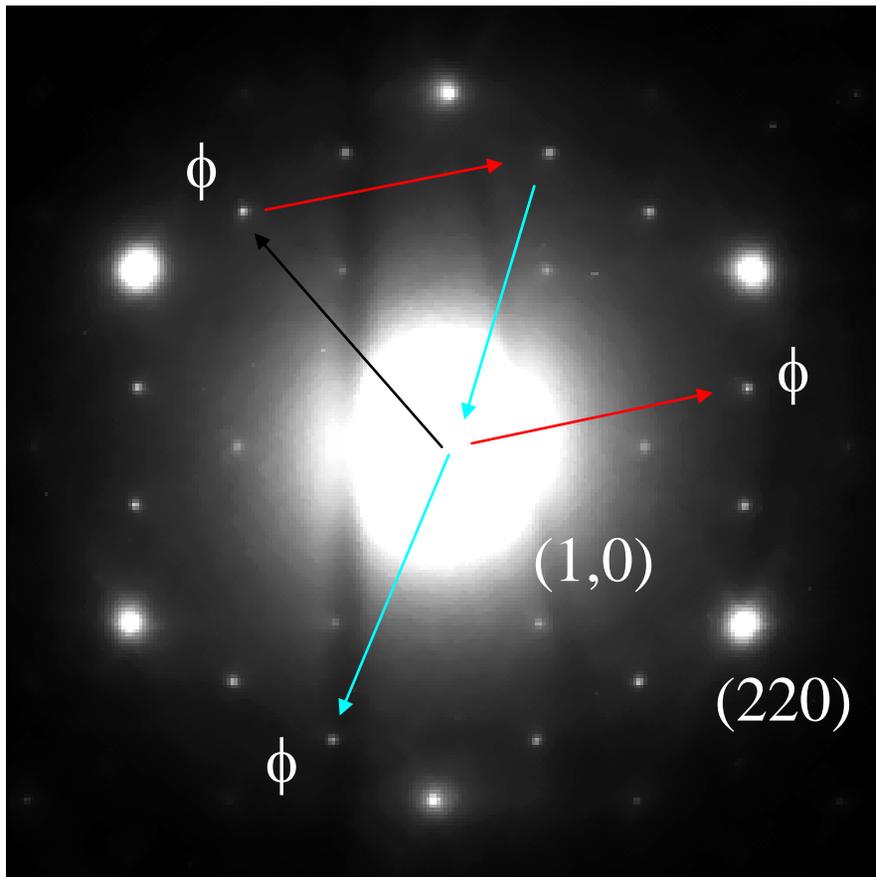
For reflections  $\mathbf{h-k}$ ,  $\mathbf{k}$  and  $\mathbf{h}$ :

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

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

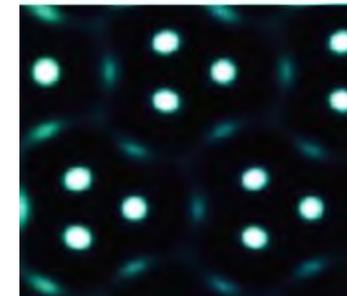
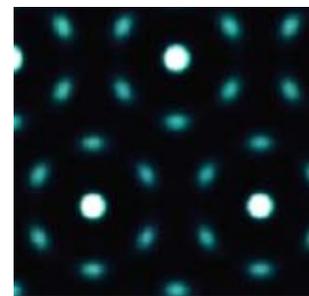
-  = known structure amplitude and phase
-  = known structure amplitude and unknown phase

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

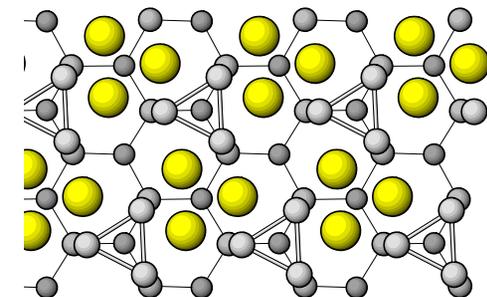


Only one strong reflection

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



Other information  
3 Au



# Inequalities

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

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

$\sum a_i b_i = U(k)$

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

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

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

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

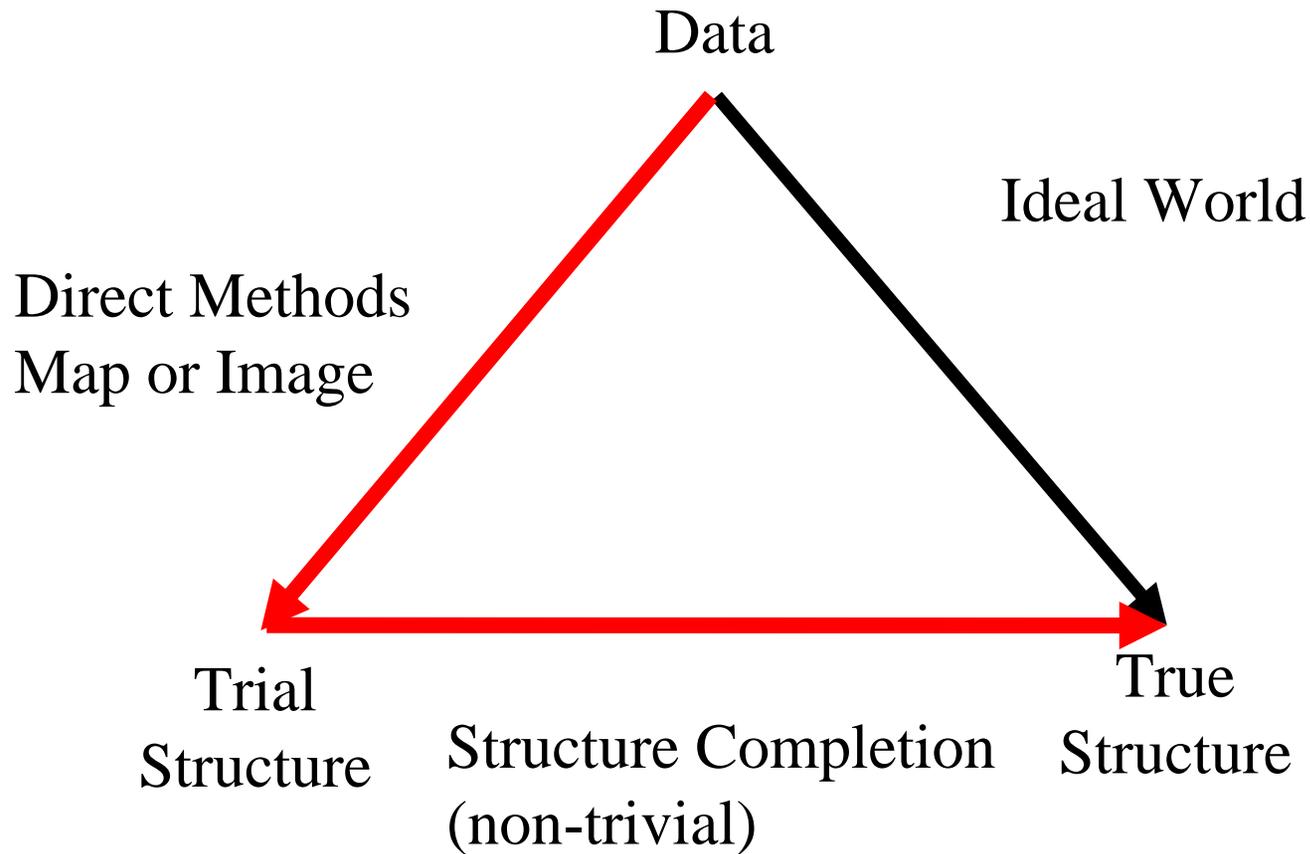
# Last step - Refinement



- 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  $I_{\text{calc}}$  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

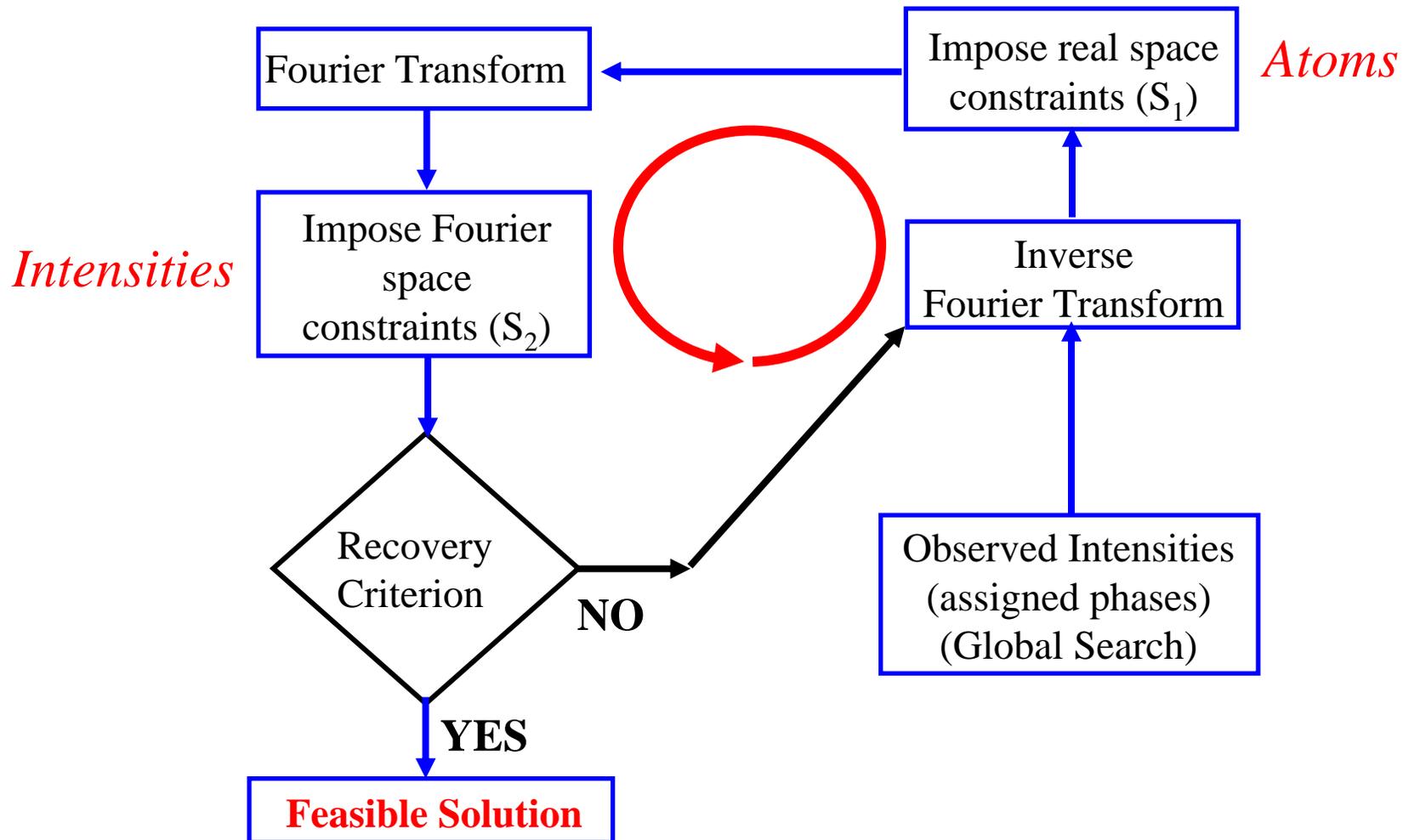


1. Initial  $\rho(\mathbf{r})$
2. Project onto “Real Space Constraint”  $\rho^2(\mathbf{r})$
3. FFT
4. Project amplitudes onto Observed
5. FFT

# 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  $\theta$
  - $\exp(i\theta) = \exp(i\theta')$ ;  $\text{Tan}(\theta) = \text{Tan}(\theta')$
  - Replace old  $\theta$  by new one

# Algorithm Overview (Gerschberg-Saxton)



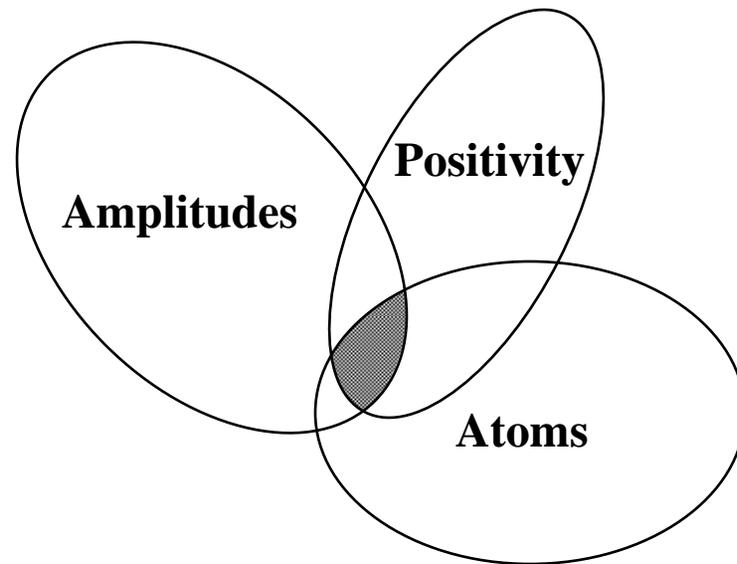
# More: 1970's Mathematics

- 
- 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

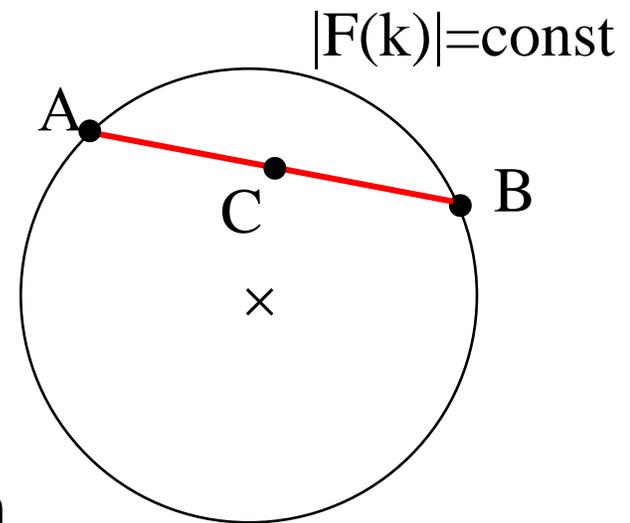
- A set is convex if any point between two members is also a member
  - If all the sets are convex, problem has one solution
  - If they are not, there may be more than one local minimum

- Amplitude measurements

**do not** form a convex set

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

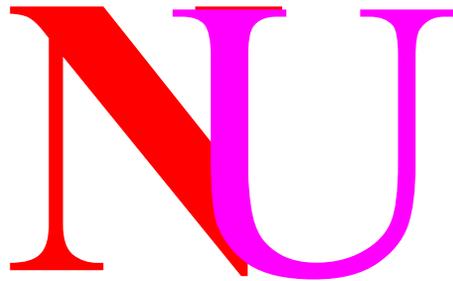
- Unsolved mathematical problem



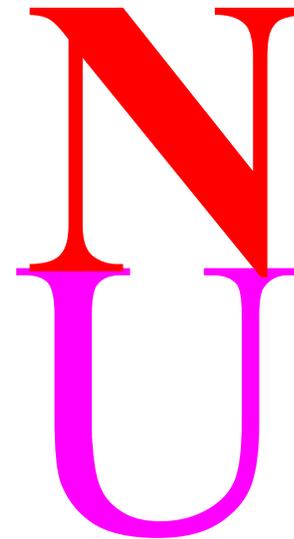
# Multiple non-convex constraints



Consider the two sets “N” and “U”



Overall Convex



Overall Non-Convex

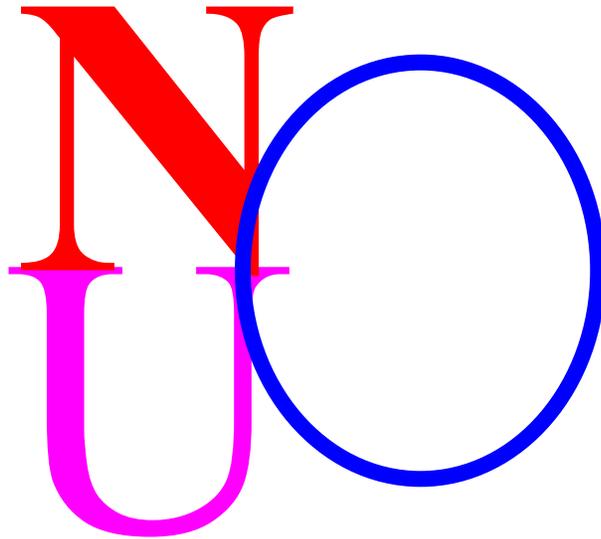
# Crystallographic methodology



## Overall Unique

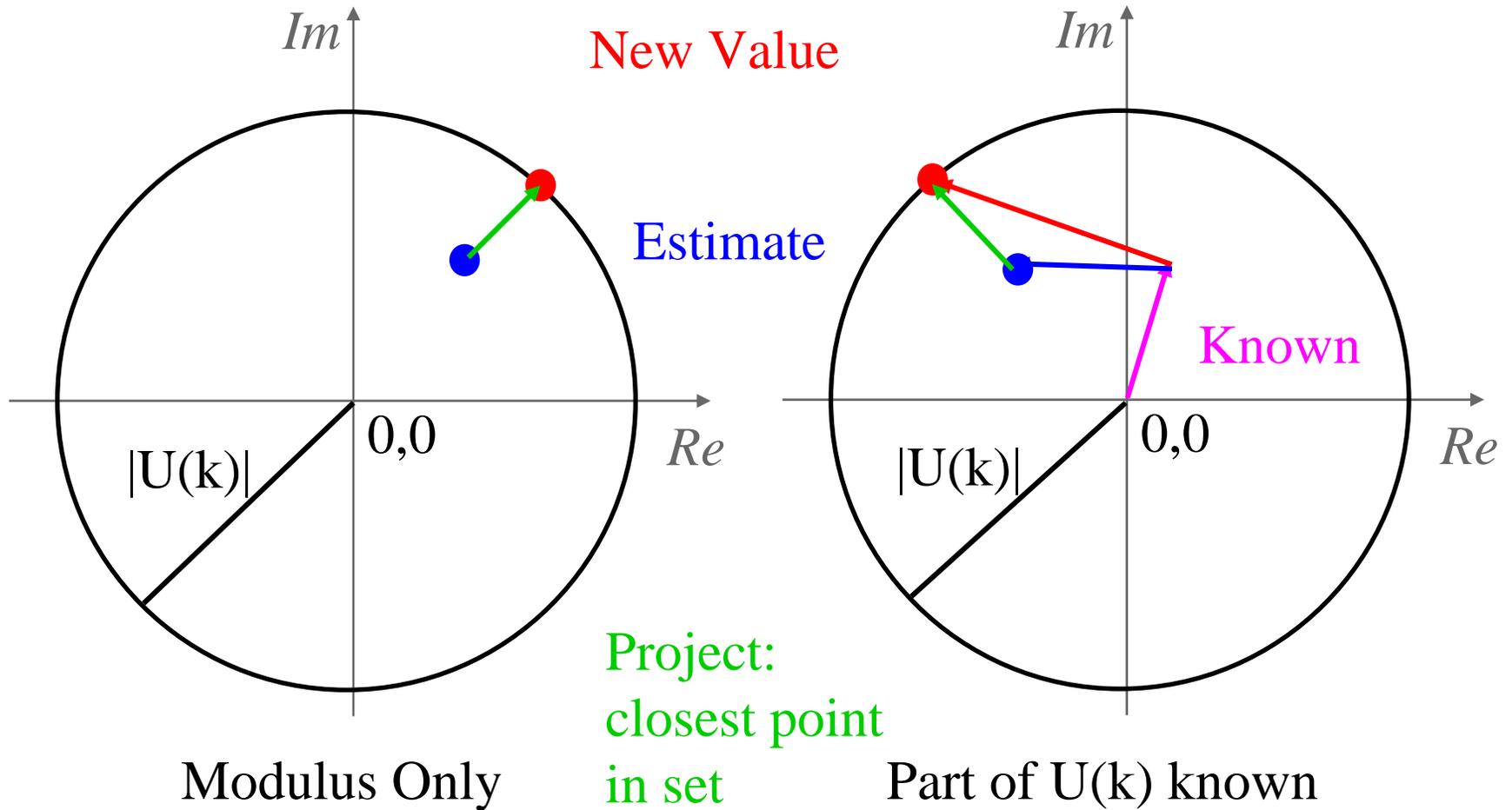
Addition of additional convex constraints tends to give a unique solution

Structure Completion:  
add additional constraints as the phases become known



Overall Non-Convex

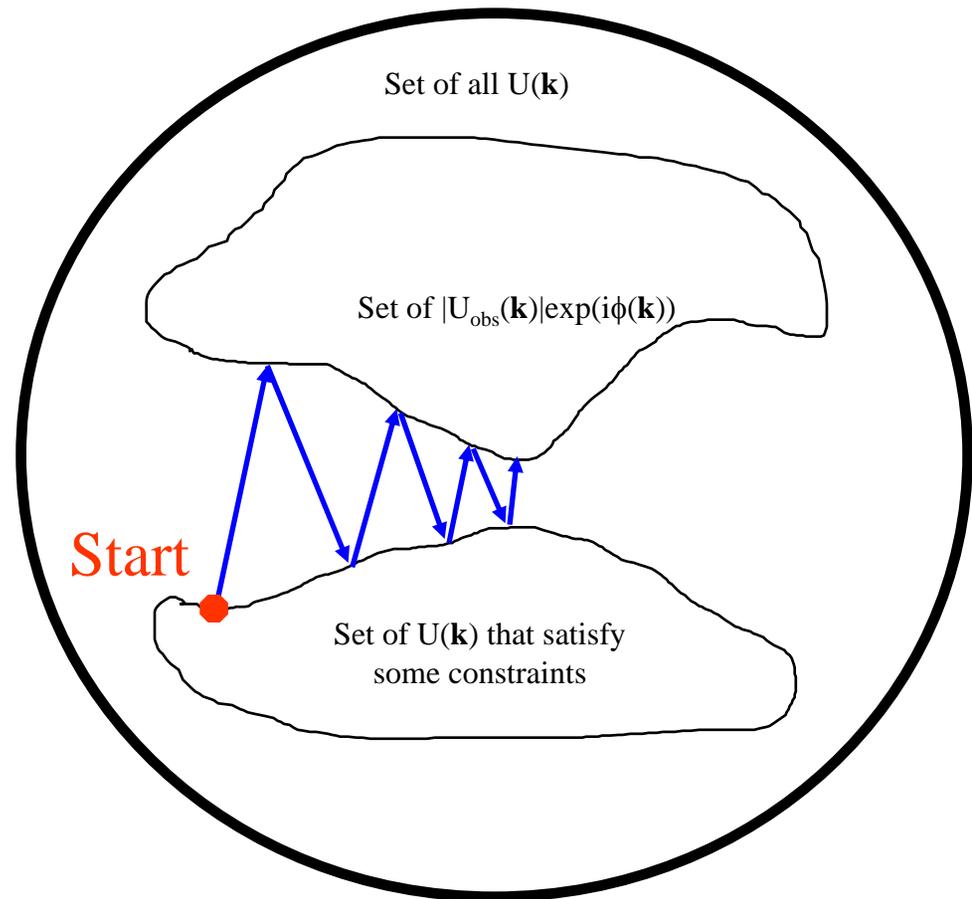
# Orthogonal Projections



# Successive Projections

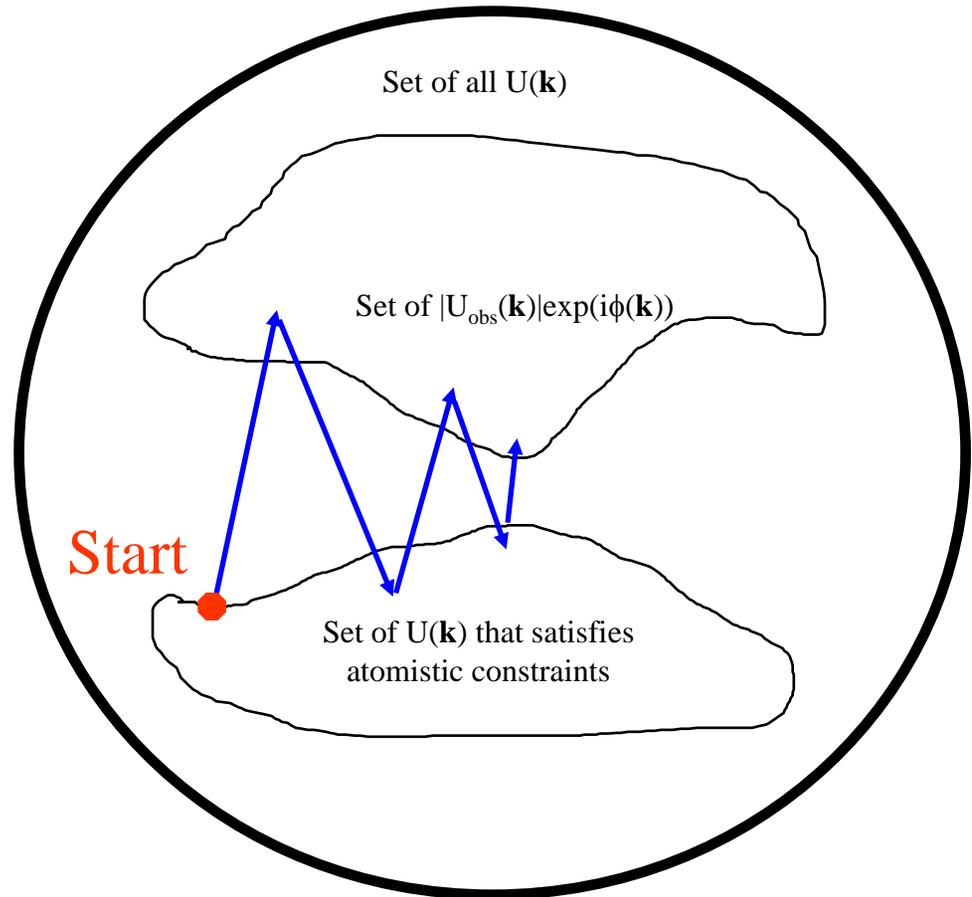


- Iterate between projections
- Other variants possible (see Combettes, *Advances in Imaging and Electron Physics* **95**, 155-270, 1996)



# Over-relaxed Projections

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



# Classic Direct Methods

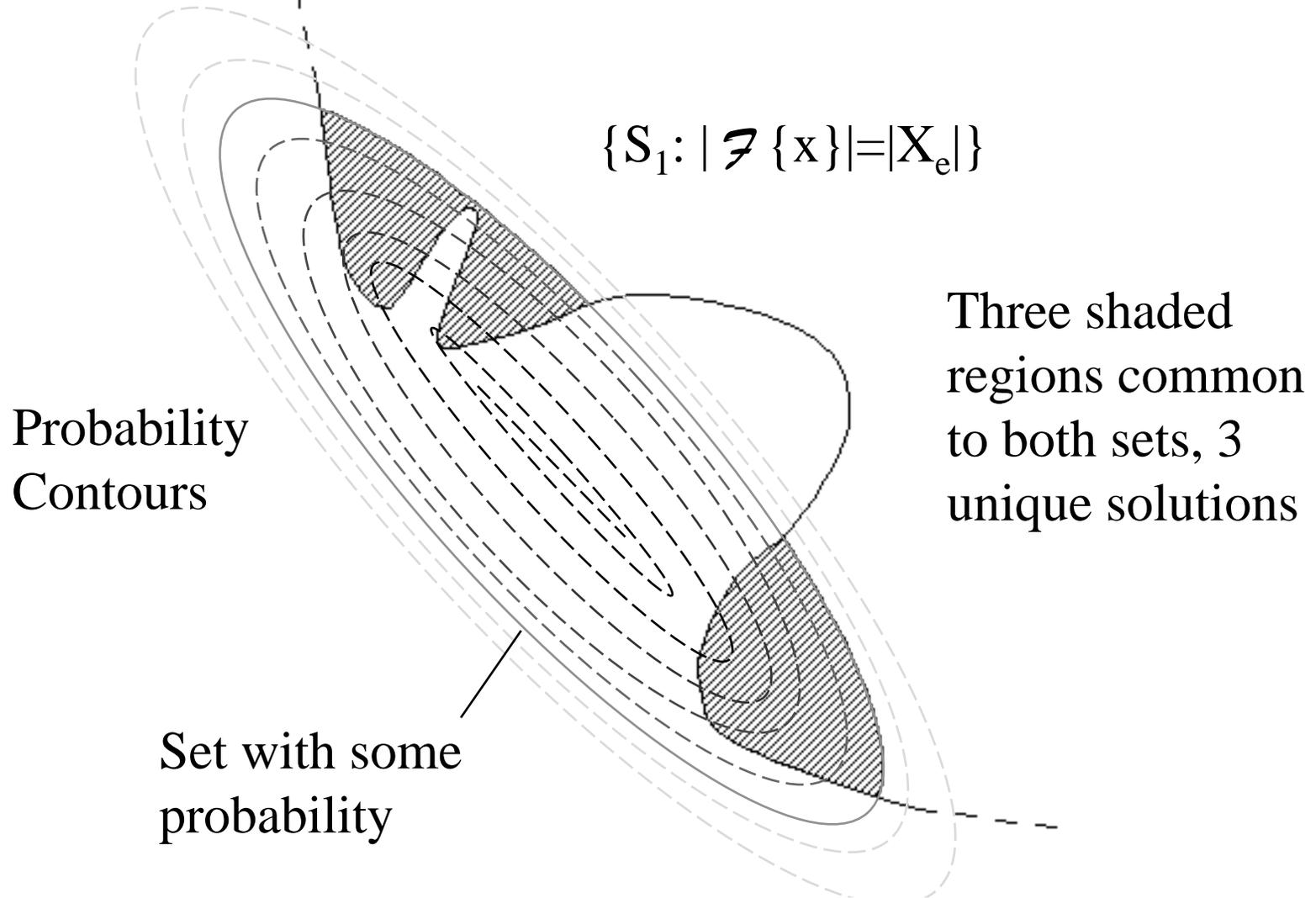
- Consider as an iteration

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

- Note the similarities

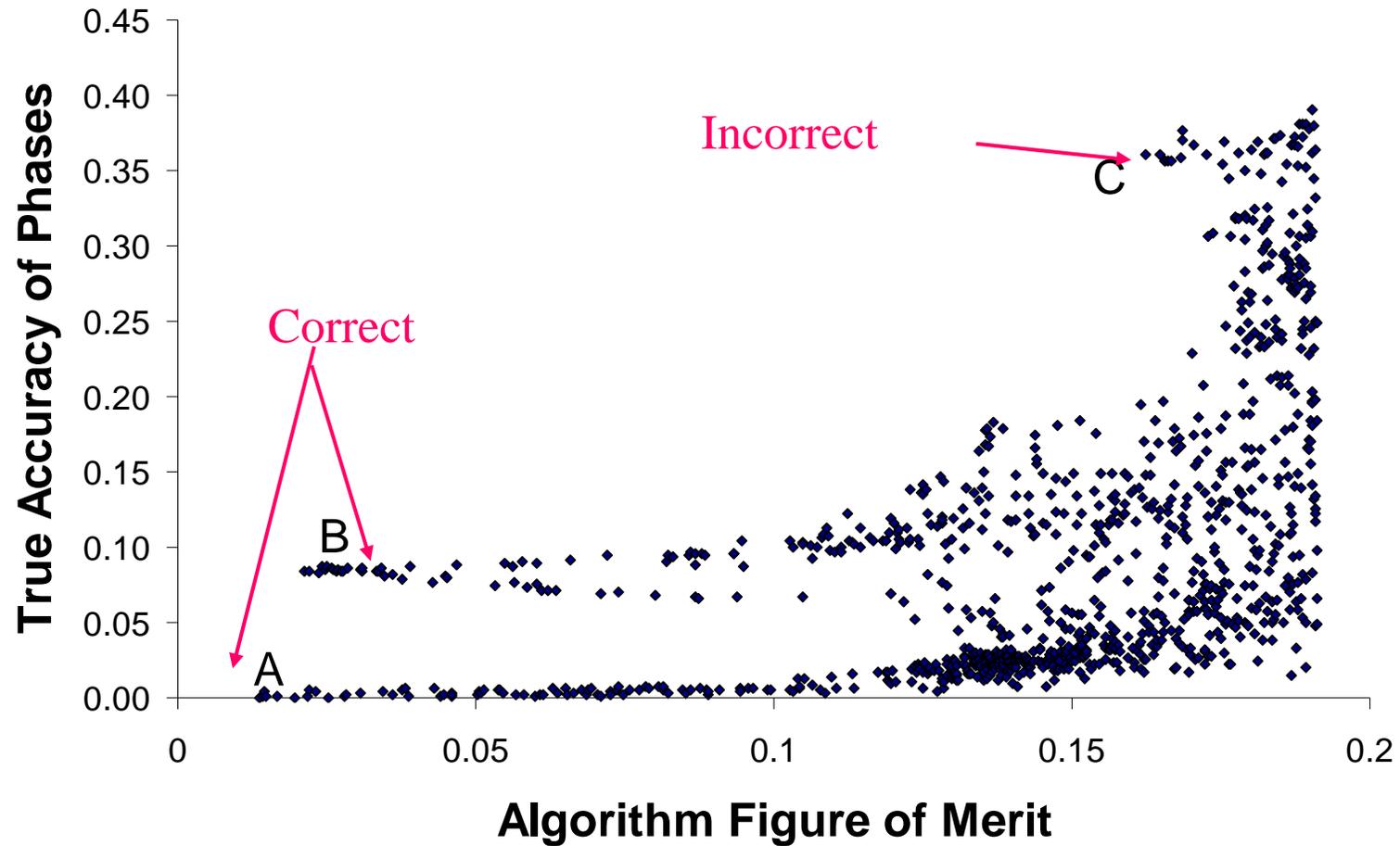
- Tangent Formula  $\equiv$  Orthogonal Projection
- Real space operator, effectively an eigenfunction (fixed point) method

# 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

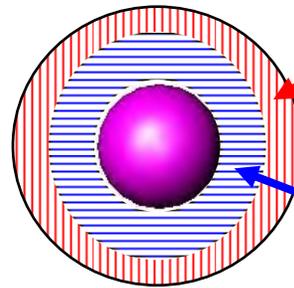
Non-Convex

Positivity (weak)	Presence of Atoms
Atoms at given positions	Bond Lengths
Least bias (MaxEnt)	Interference $A(\mathbf{k})= B(\mathbf{k})+\text{Known}(\mathbf{k}) ^2$
Intensities & errors $\equiv \chi^2$	Anti-bumping
Statistics (e.g. $\Sigma_2$ )	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,  $|F(k)|$
- We know part of the structure,

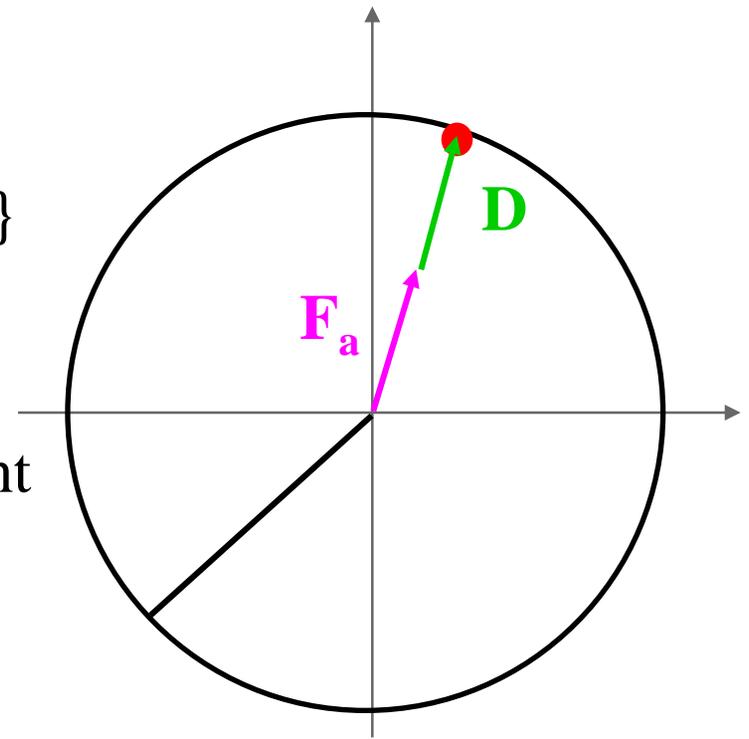
$$F_a(k) = |F_a(k)|\exp(i\phi_a(k))$$

- Project onto known moduli

$$D(k) = \exp(i\phi_a(k))\{|F(k)_{\text{obs}}| - |F_a(k)|\}$$

Conventional Fourier Difference  
Map

- Other methods (SIM wts) equivalent to further projections.

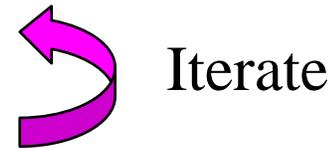


# Operators as projections

- 
- 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  $O(x) \equiv \alpha x^2$ ;  $\alpha$  = 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

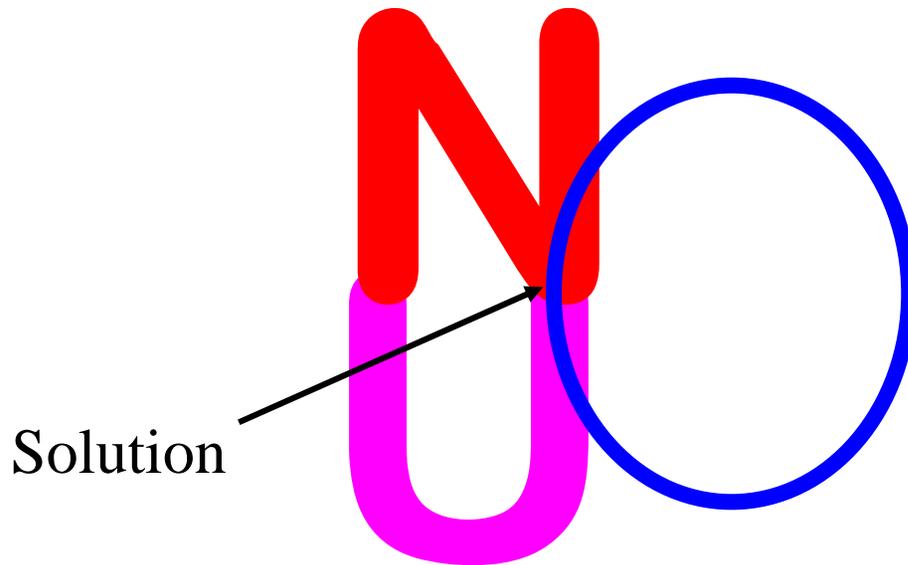


- Explanation (pseudo-mathematical) of why structure completion strategies can solve, uniquely, problems when the initial maps are not so good

# Structure Completion



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



Solution

Overall Convex

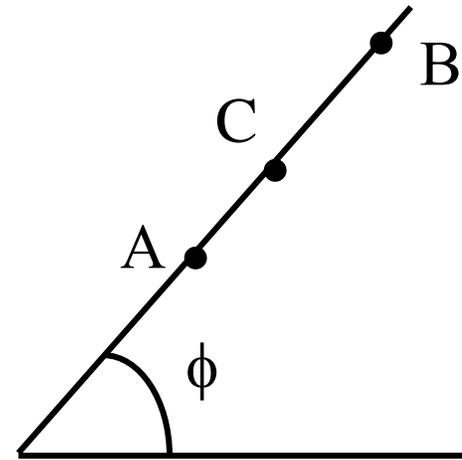
- Add a third set “O”
- Addition of additional constraints tends to give a unique solution
- Structure Completion: add additional constraints as the atoms become known

# IV Convex Set for unmeasured

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

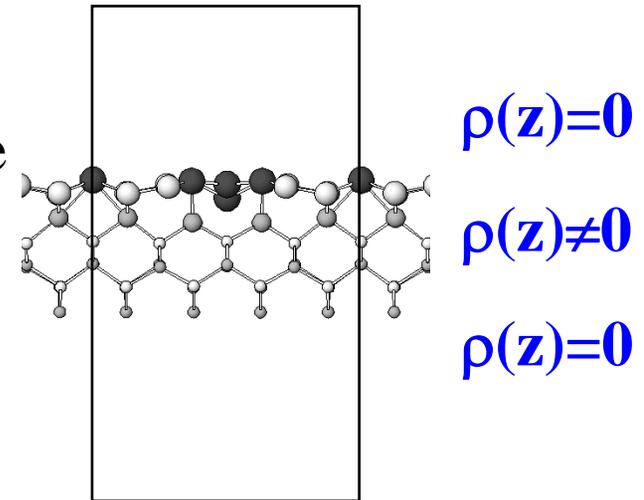


- Phase of  $U(h,k,l)$  can be estimated from other reflections
- Set of  $U(h,k,l)$  with a given phase is **convex**
- Hence  $|U(h,k,l)|$  is well specified and can be (approximately) recovered
- Remember, phase is more important than amplitude



# Support Constraint

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



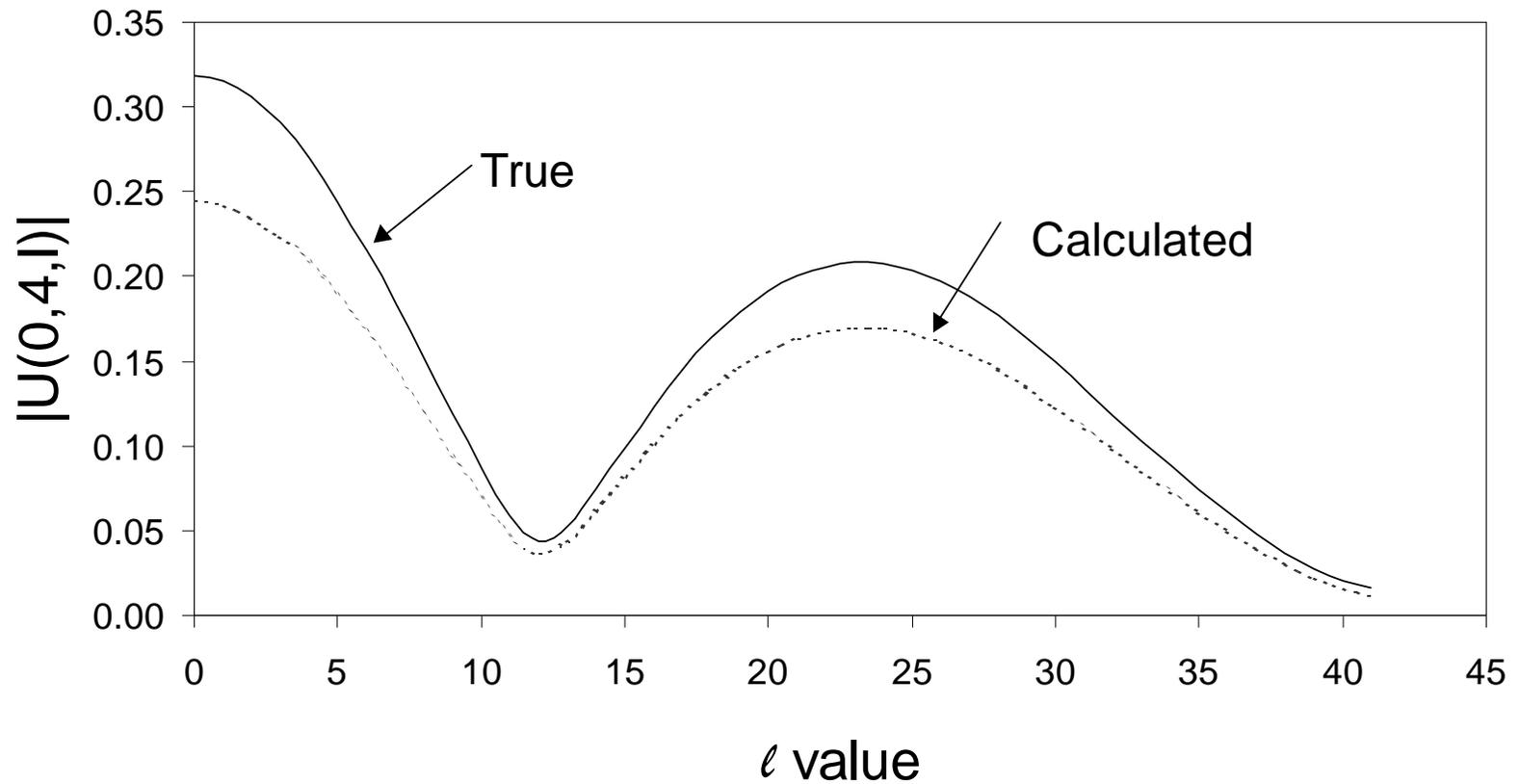
PRB 60, 2771 (1999)

<sup>1</sup>Biharmonic expansion of strain field, SS 294, 324 (1993)

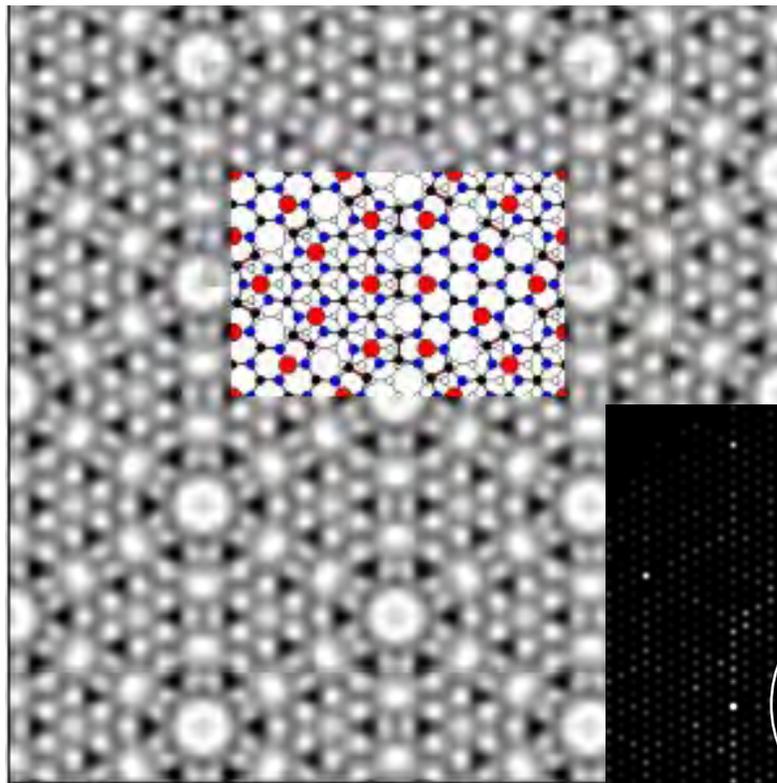
# Unmeasured Reflections



Recovery of Unmeasured Reflections

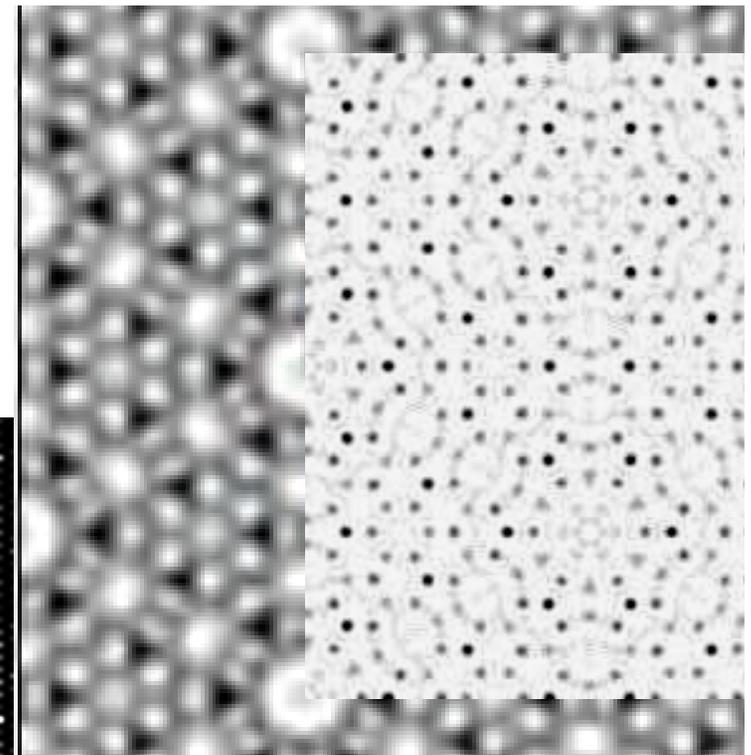
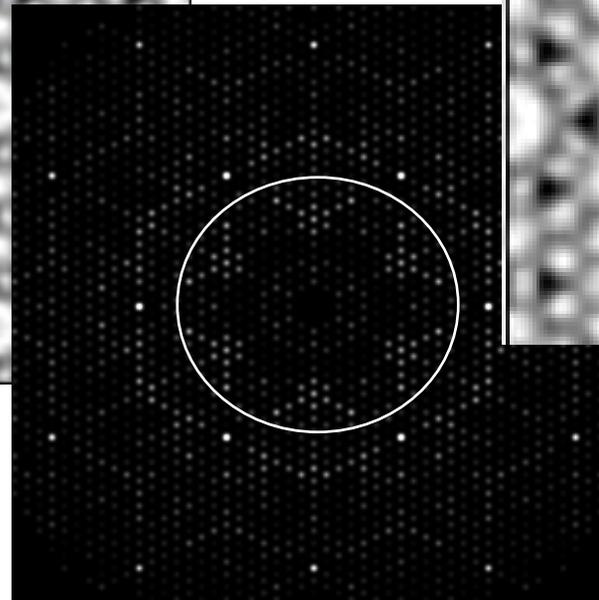


# Restoration and Extension



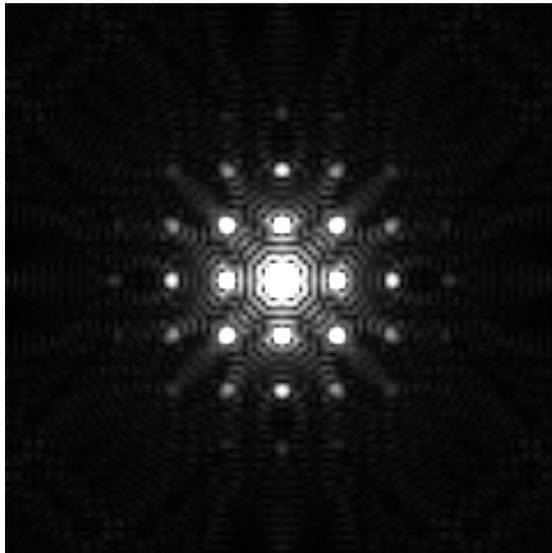
0.3nm Image

+DP



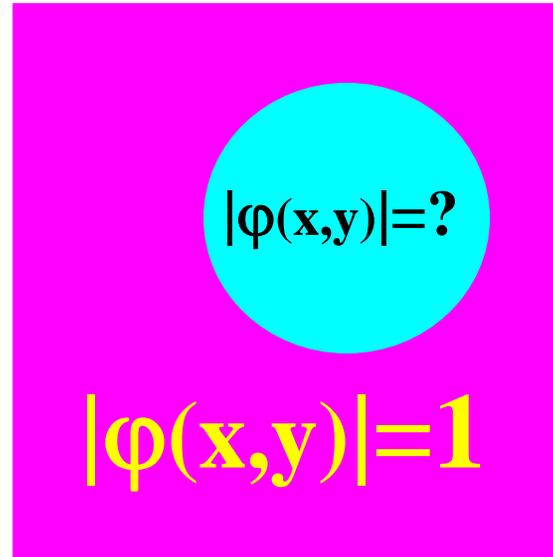
0.05nm Image

# Example V: Diffractive Imaging



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

+



Convex Support  
Constraint

= ?

# Example V: Diffractive imaging

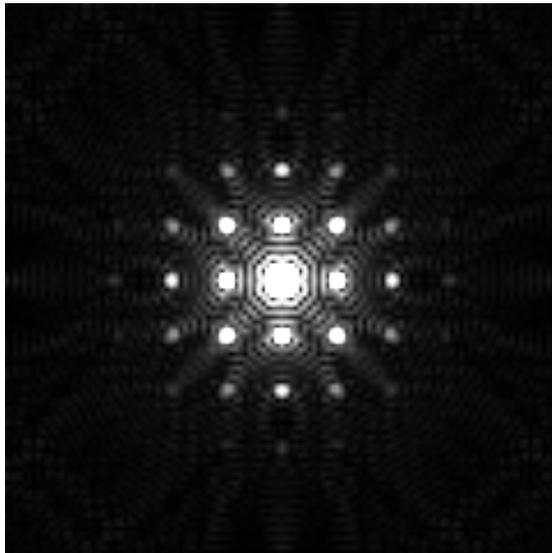


- Constraint: part of real-space  $x$  is zero
- Convex constraint
- Iteration
  - $x = 0$ , part of map
  - $|\mathbf{X}| = |\mathbf{X}_{\text{observed}}|$



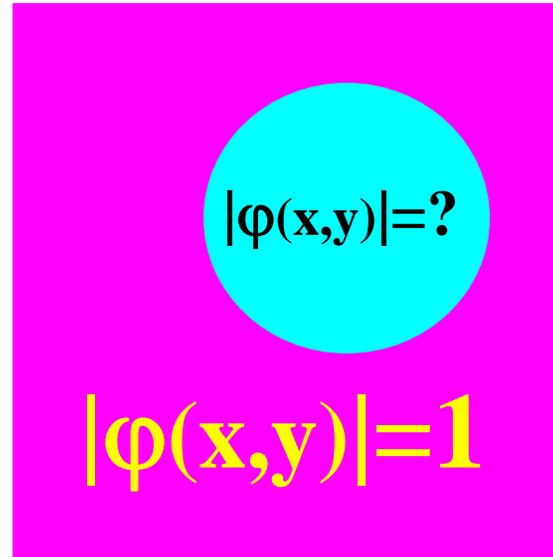
Iterate

# Example V: Diffractive Imaging



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

+



Convex Support  
Constraint

= ?

# Example V: Diffractive imaging

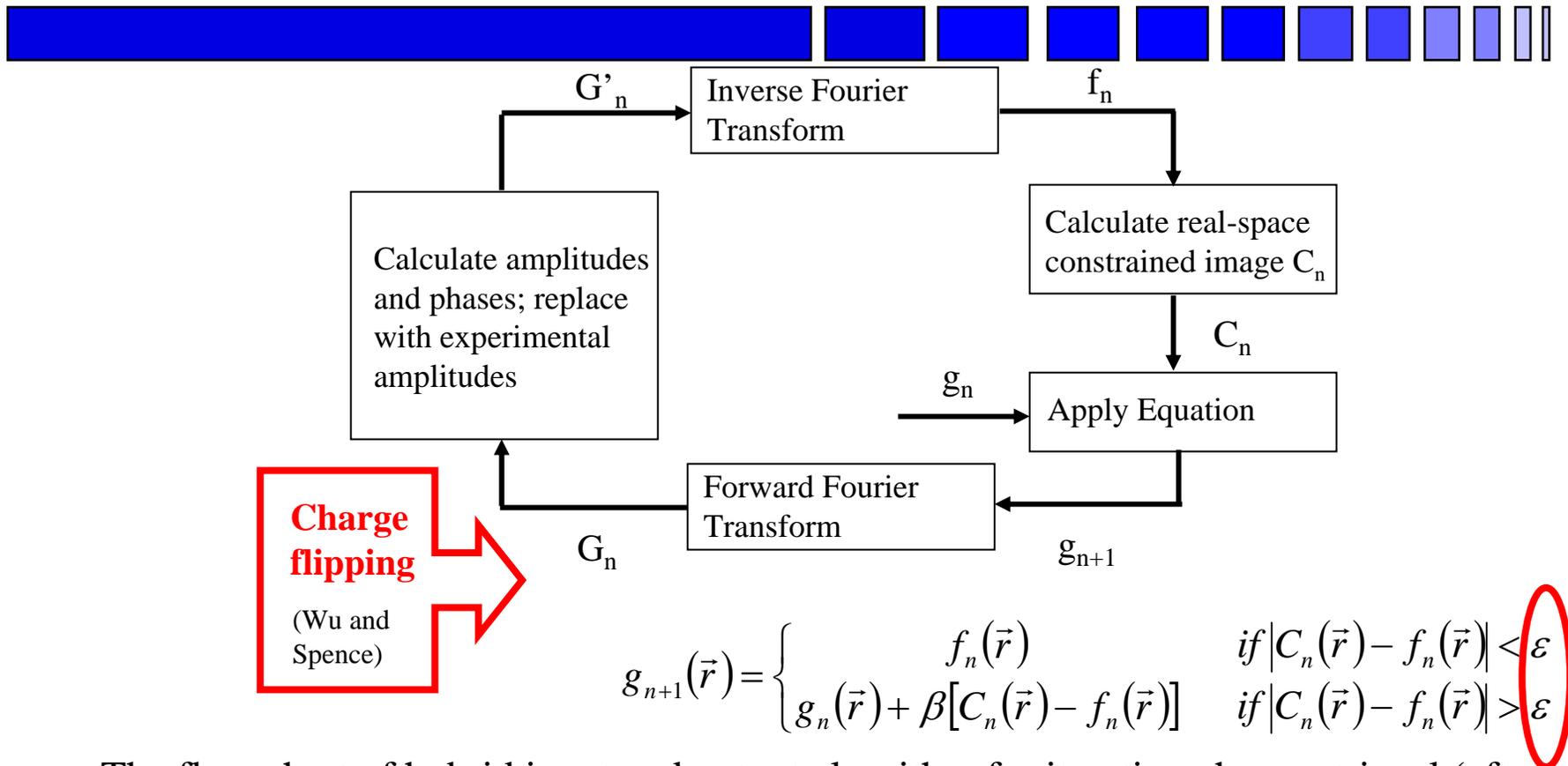


- Constraint: part of real-space  $x$  is zero
- Convex constraint
- Iteration
  - $x = 0$ , part of map
  - $|\mathbf{X}| = |\mathbf{X}_{\text{observed}}|$



Iterate

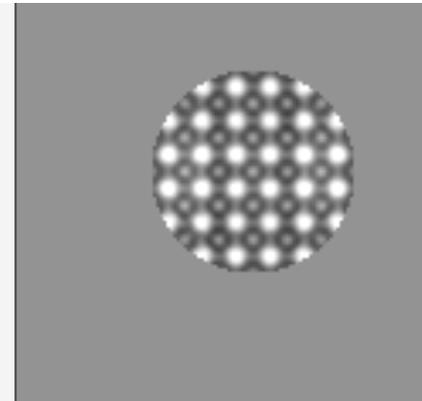
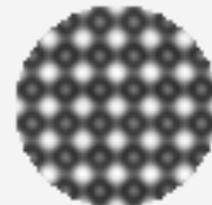
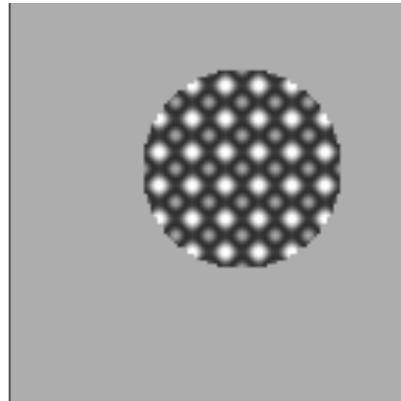
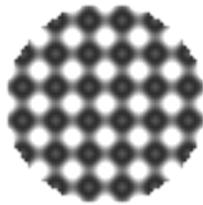
# The Algorithm



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



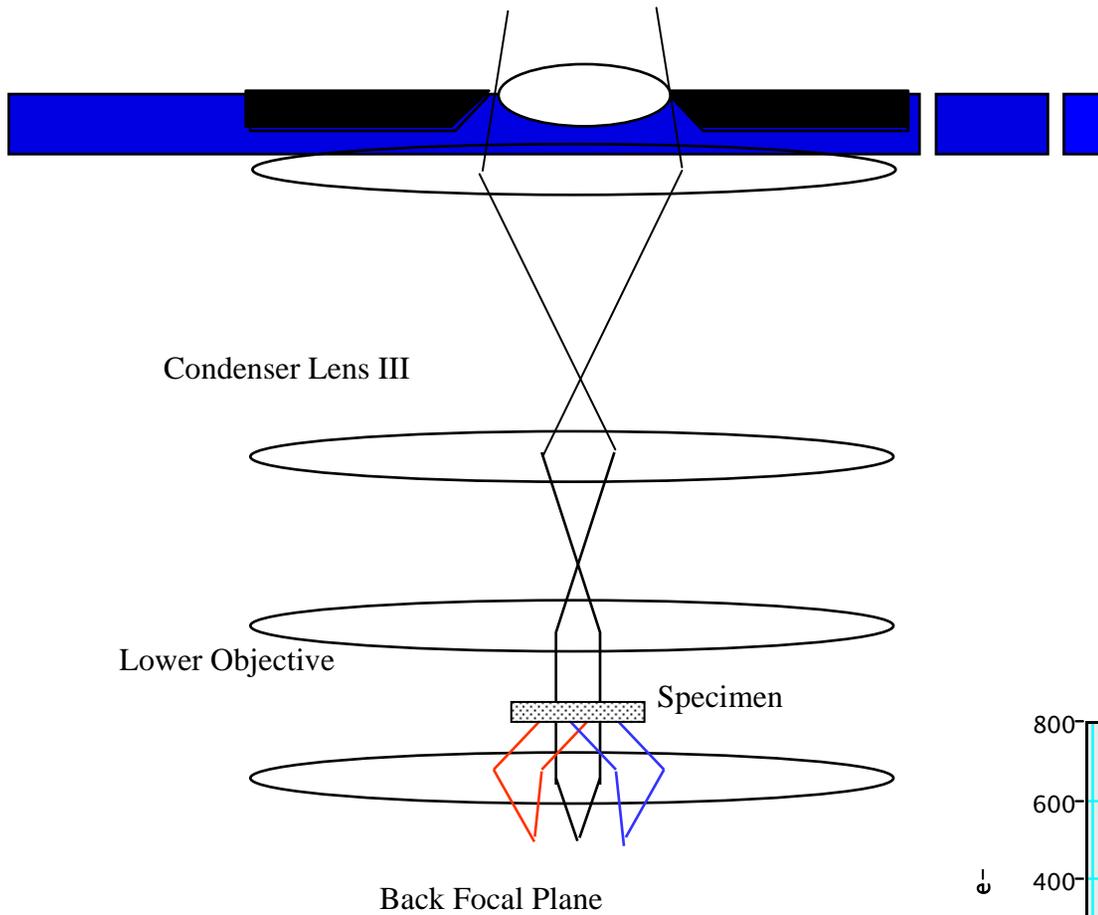
# Phase Recovery for a Small Particle



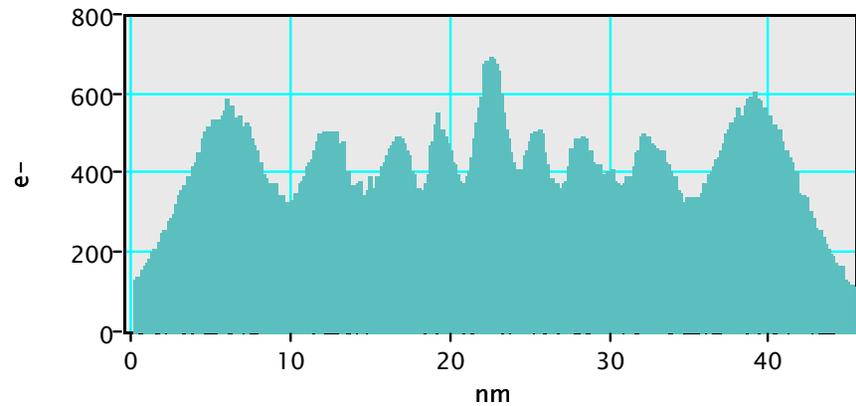
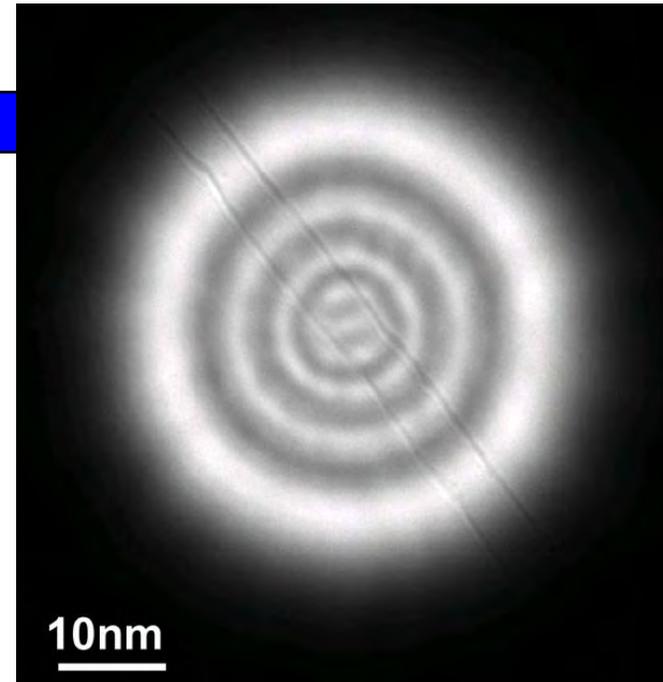
True real space exit wave for small particle model

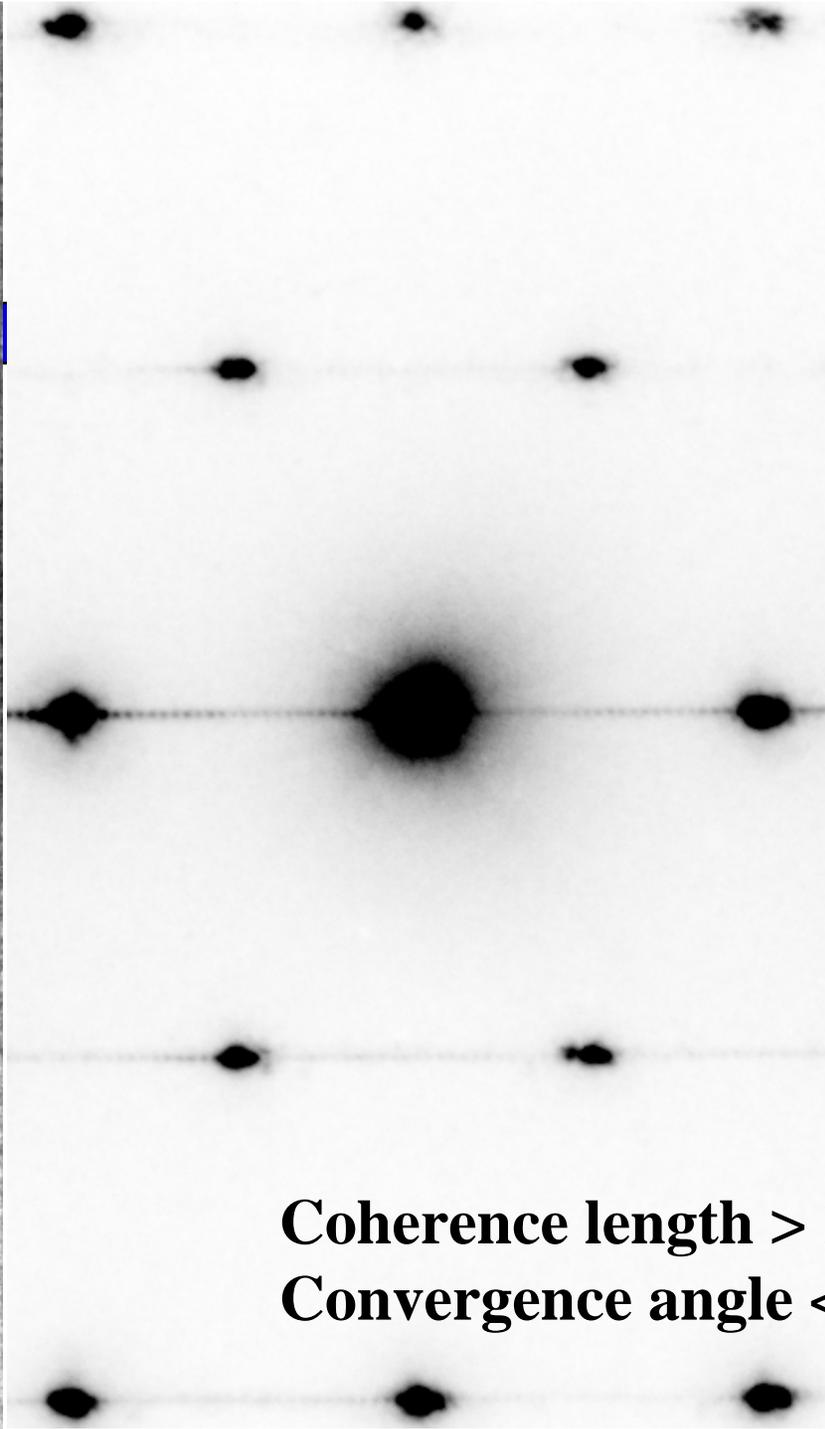
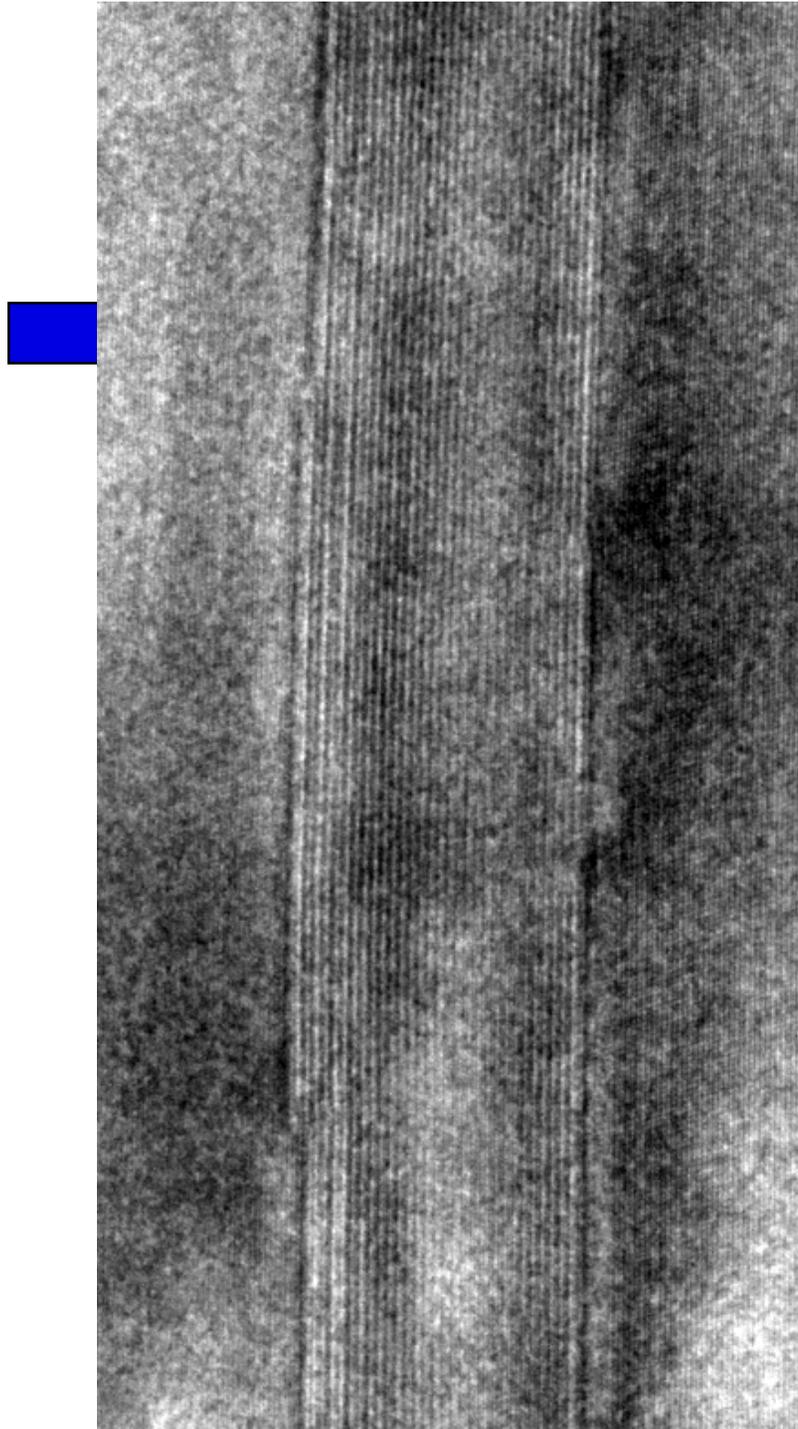
Reconstructed exit wave after 3000 iterations

# Electron Nanoprobe formation



10  $\mu\text{m}$  aperture  $\rightarrow$  50 nm beam  
 $M = 1/200$





**Coherence length  $> 15$  nm**  
**Convergence angle  $< 0.2$  mrad**

# Coherent X-ray Diffraction

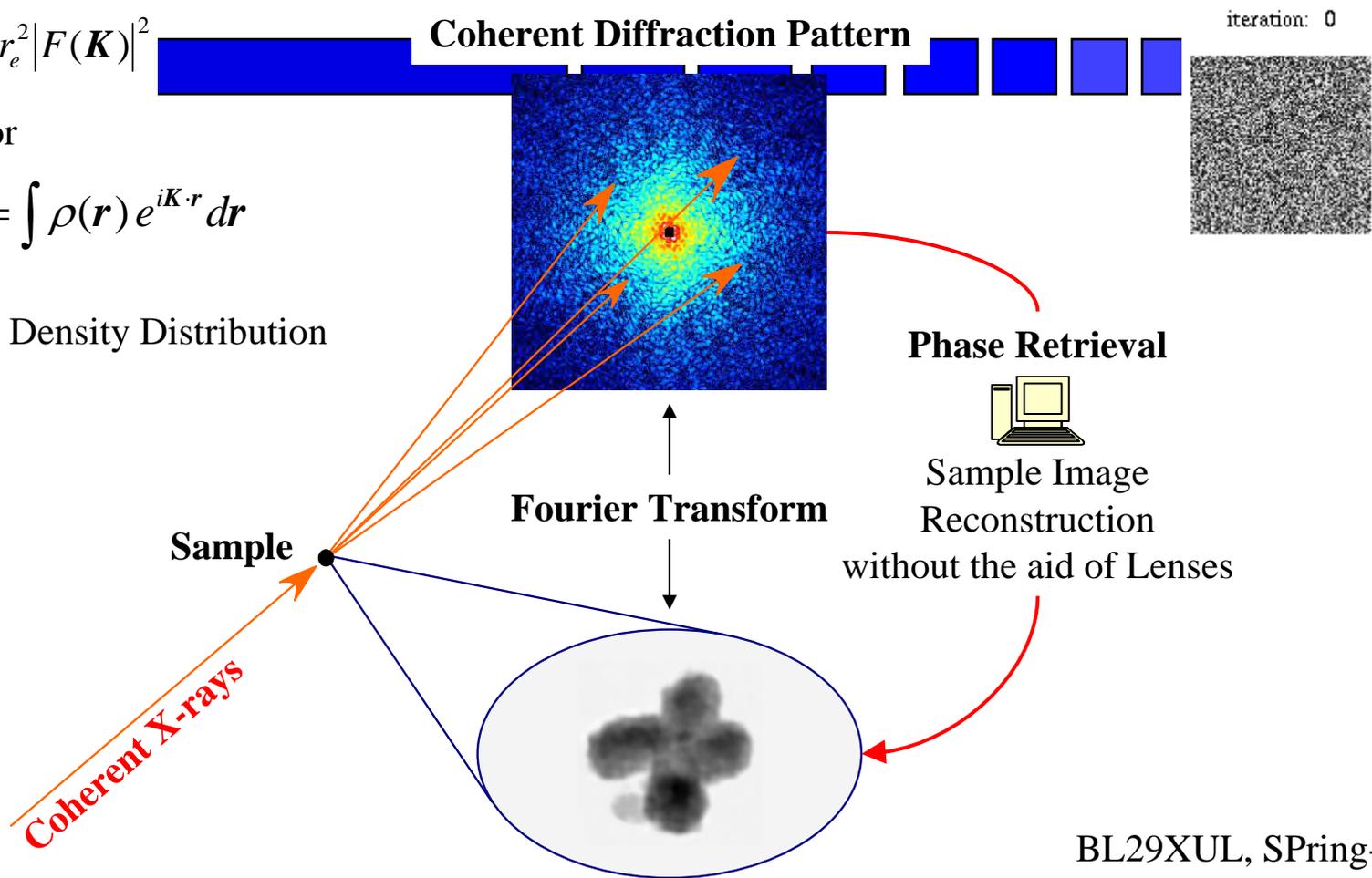
Differential Cross Section

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

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**

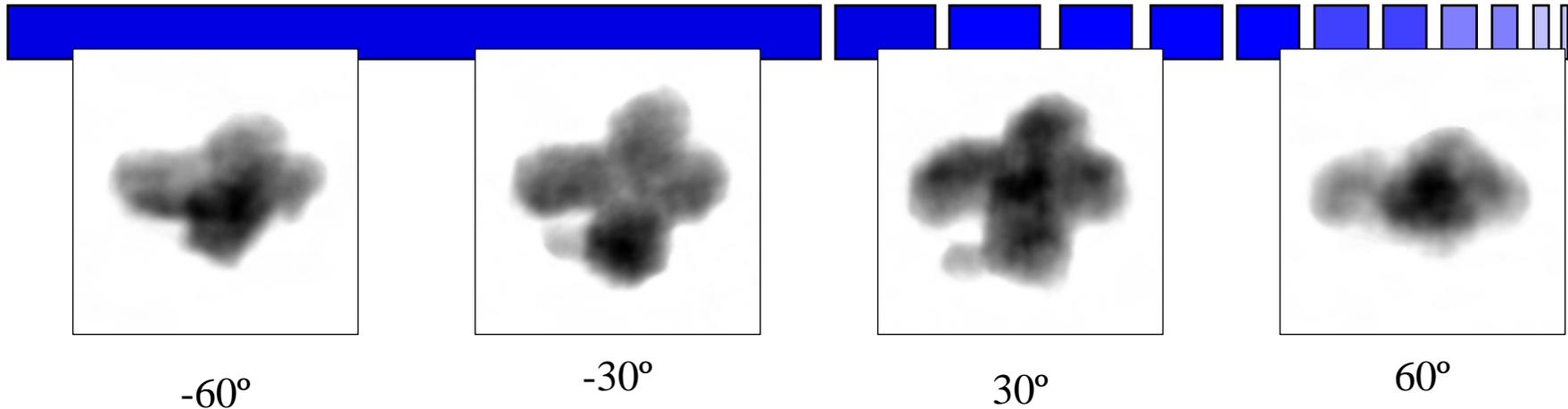
BL29XUL, SPring-8

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

# From 2D to 3D

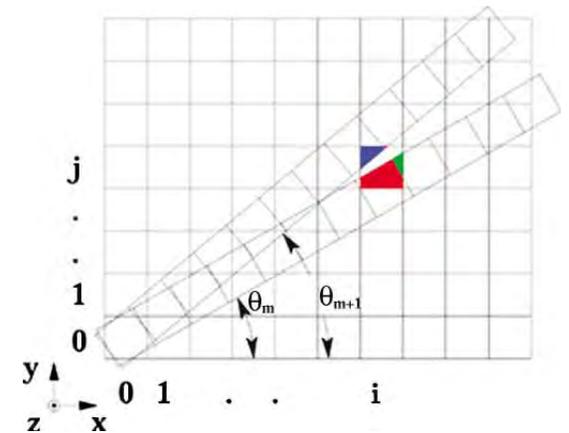
## Coherent diffraction measurement at 38 incident angles

from  $-70^\circ$  to  $70^\circ$  at  $2.5^\circ$  intervals at the minimum



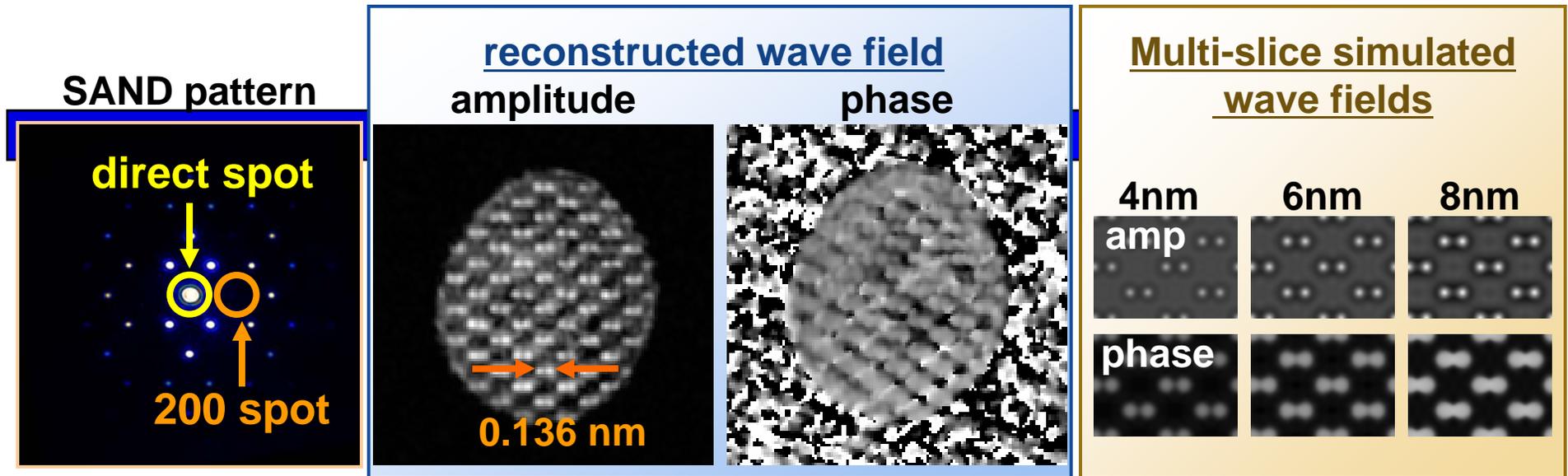
exposure time at each incident angle: 2700 s

- **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**