Electron diffraction & HRTEM Image Simulation

Ecole Nord Africaine et workshop en Microscopie Electronique

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TEM diffraction/image simulation

- Why?
- How?
  - Methods.
  - Applications.

Quantitative simulation?

- Problems.
- Perfect microscopes.

Why diffraction/image simulation?

Example: HR(S)TEM Si_3N_4 P 63: [001]

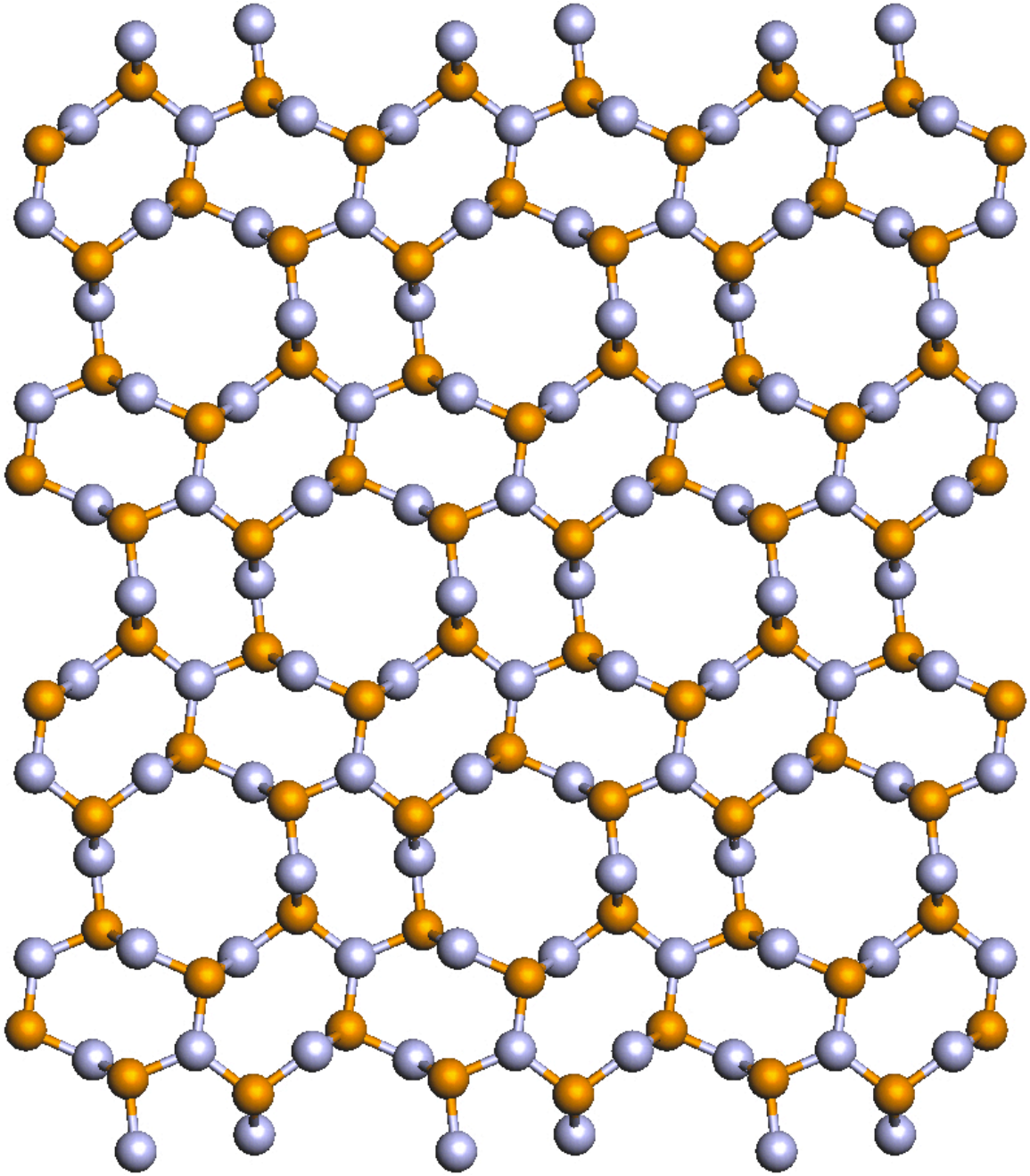
HR(S)TEM $\Longrightarrow$ to acquire knowledge on observed material (oriented in particular [uvw] directions):

- Specimen structure..
- Chemical composition.
- Functional properties.
- ...

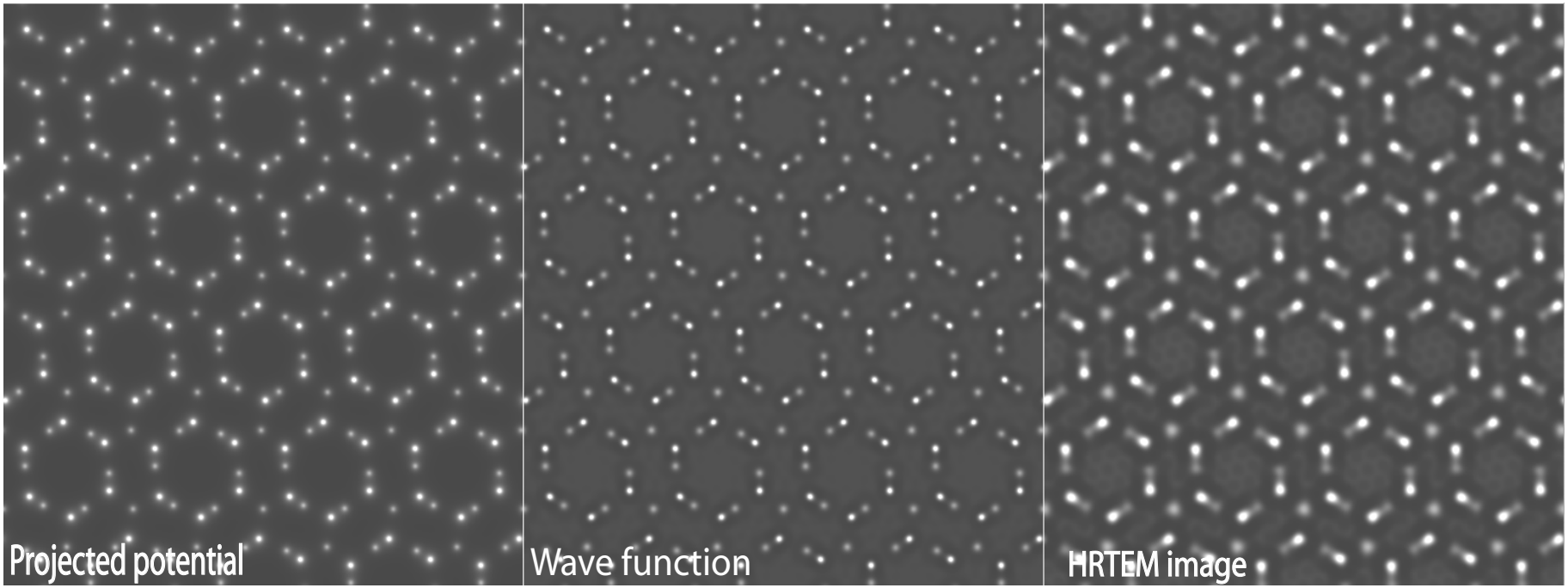
But HR(S)TEM images depend of several adjustable microscope parameters.

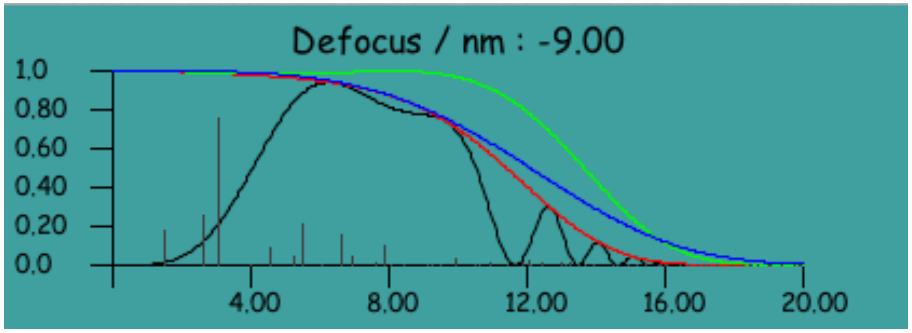
For example object defocus affects strongly HRTEM images.

Structure: Si_3N_4 P 63: [001]



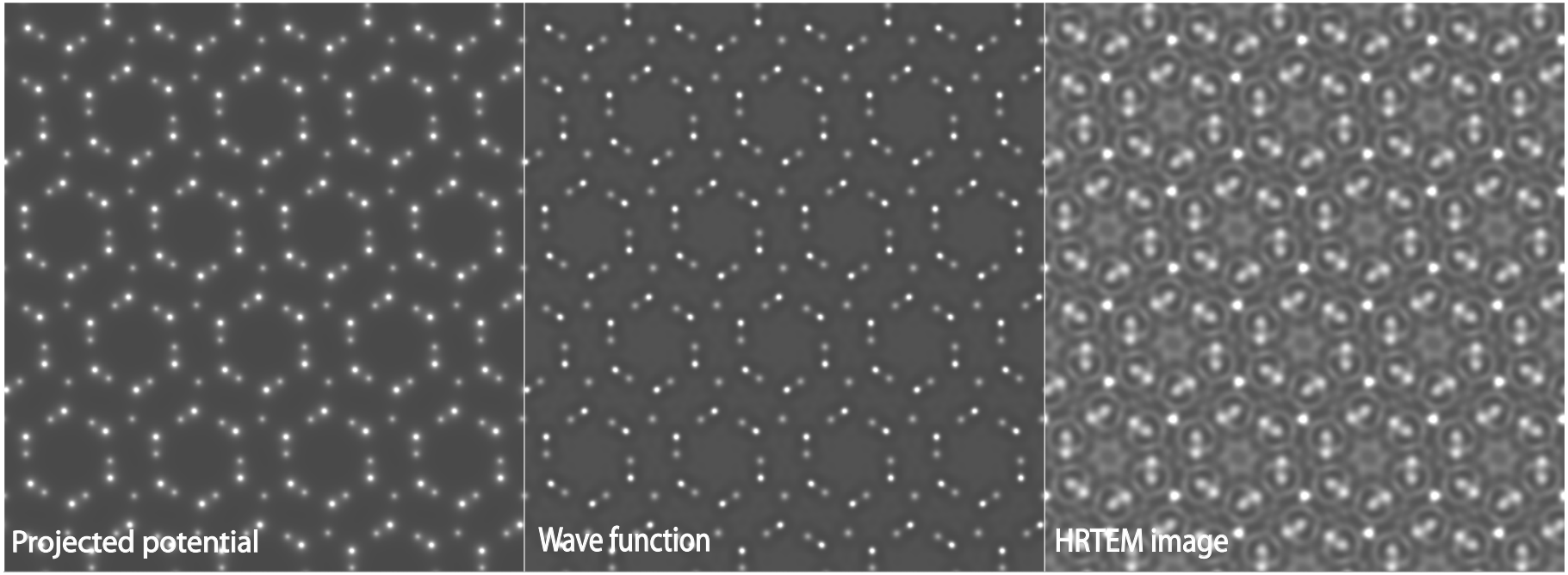
Images: Si_3N_4 P 63: [001], 10 nm thick, -9 nm defocus

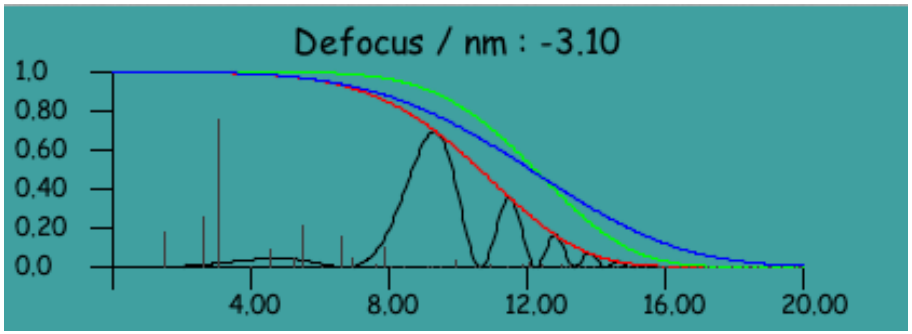




Imaging parameters: Titan 80-300 (300 kV), C_s -0.033 mm

Si_3N_4 P 63: [001], 10 nm thick, -3 nm defocus





Imaging parameters: Titan 80-300 (300 kV), C_s -0.033 mm

How to do diffraction/image simulation?

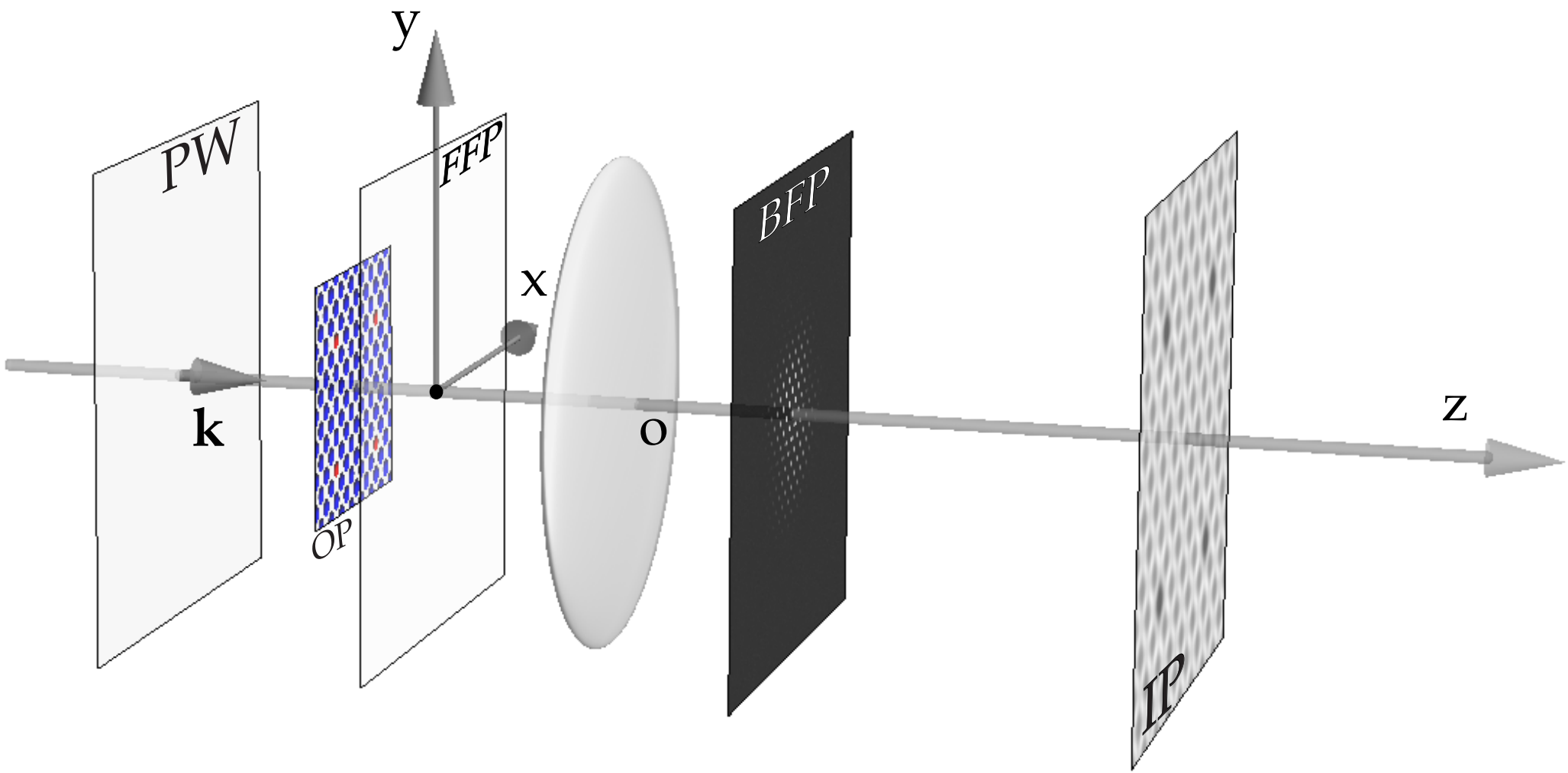
Formation of Electron Microscopy diffraction/images involves complex physical processes.

Approximations and models of these physical processes

are required in order to perform computer simulations. Models are based on electron scattering, diffraction, optics, ...

Needed: crystallography, optics, quantum mechanics, ... and computer programming.

TEM (very) simplified model



Modeling steps: Incident wave (PW), crystal (OP), electron-matter interaction, Fraunhofer approximation, image formation (Abbe theory), ...

Image formation modeling (HRTEM)

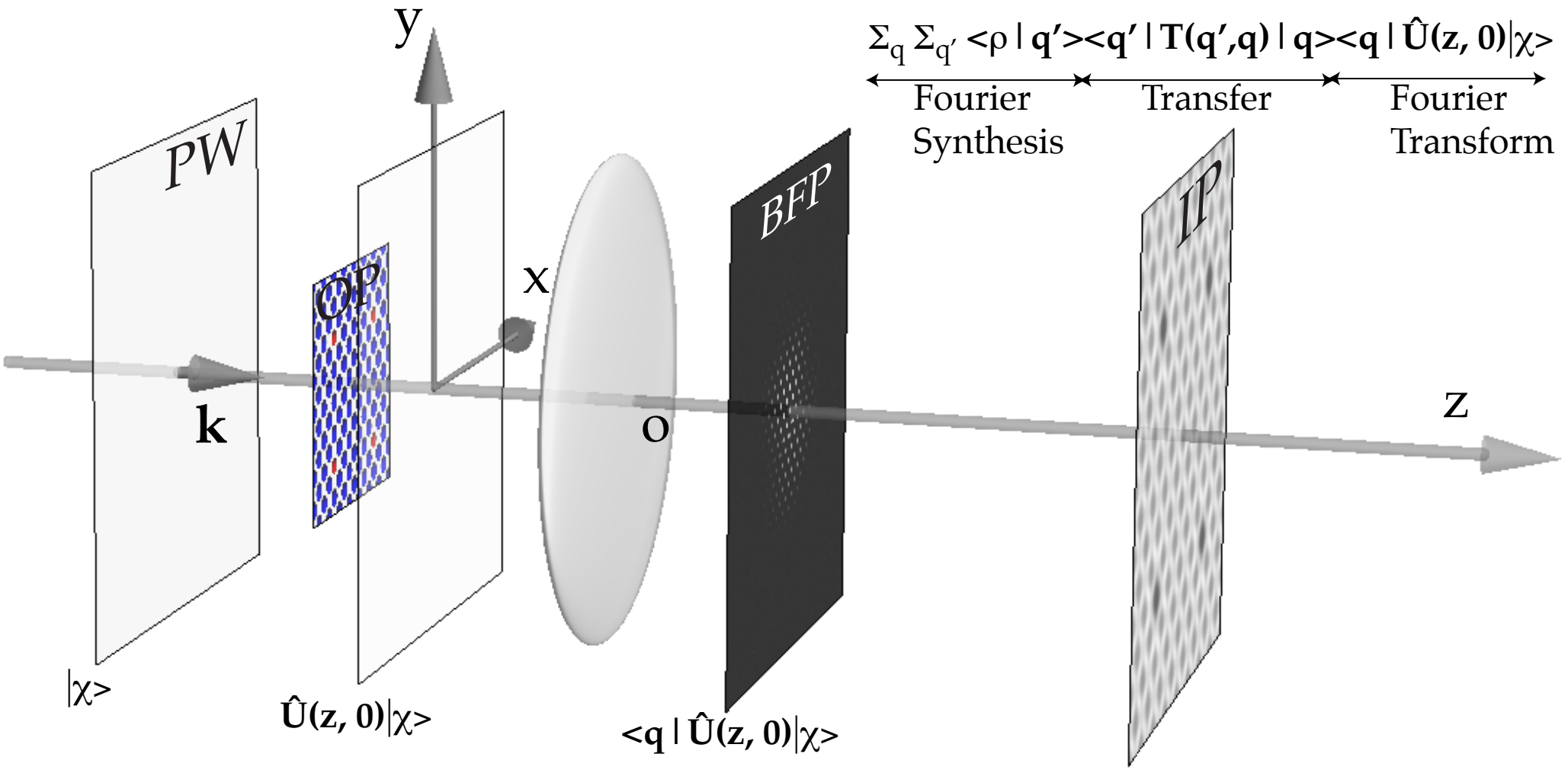


Image wave function: $|\Psi_i>$

$$|\chi> \implies \text{incident wave function}$$

$$|\Psi_i> = \underbrace{\sum^{q'} <\rho|q'>}_{\text{Fourier synthesis}} \underbrace{\sum^{q} <q'|T(q',q)|q>}_{\text{Objective lens transfer}} \underbrace{<q|U(z,0)|\chi>}_{\text{Fourier transform}}$$

Modeling steps

Prior to perform any calculation the following items (from the electron source to the detector) must characterized and modeled:

- The electron beam properties.
- The specimen properties[1].
- How is the incident electrons beam scattered by the specimen?
- How does the microscope transfer the scattered electron beam?
- How do we measure the properties of the scattered electron beam (diffraction, image, hologram)?
- What are the properties of the detection system?

[1] file://localhost/Applications/jemsMacOSX/html/Rb2WO9/Rb2WO9.html

Modeling steps

- Object.
- Scattering & diffraction.
- Image formation:
  - HRTEM.
  - HRSTEM.
- Image acquisition.

Modeling the object

Evolution operator U (z, 0) defines the object properties

1. Amorphous material or crystalline material.
2. Thin or thick.
3. Orientation (high or low symmetry [uvw]).

You might have to transform the unit cell in order to perform dynamical calculations[2].

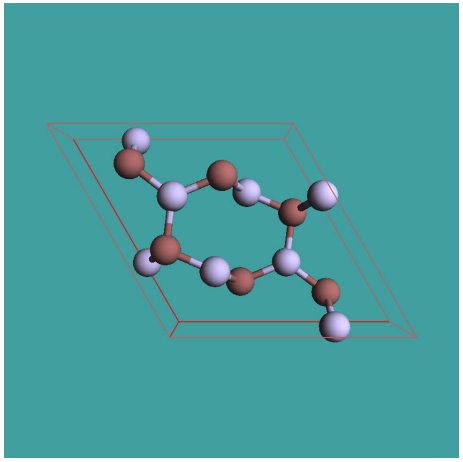


Figure: Si_3N_4 hexagonal lattice.

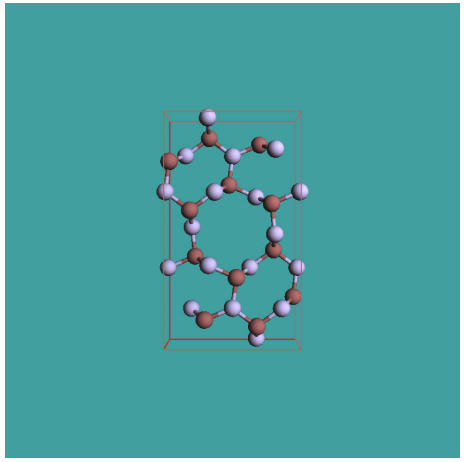


Figure: Si_3N_4 orthorhombic lattice.

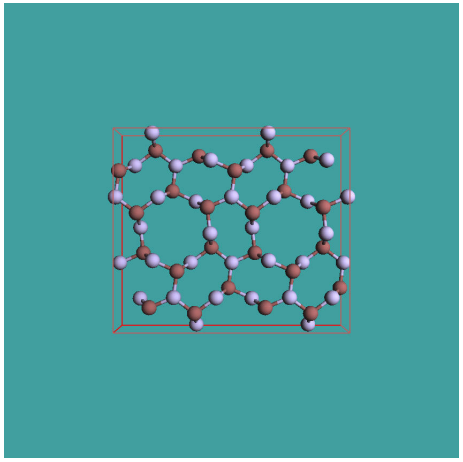


Figure: Si_3N_4 orthorhombic lattice x 2.

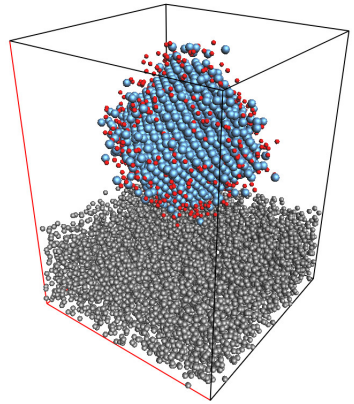


Figure: Pt catalyst on amorphous carbone film (9600 atoms).

Any model is considered a periodic unit cell independent of its complexity.

[2] See International Tables for Crystallography (1992) Vol. 1, Chapter 5.

Atomic scattering amplitude

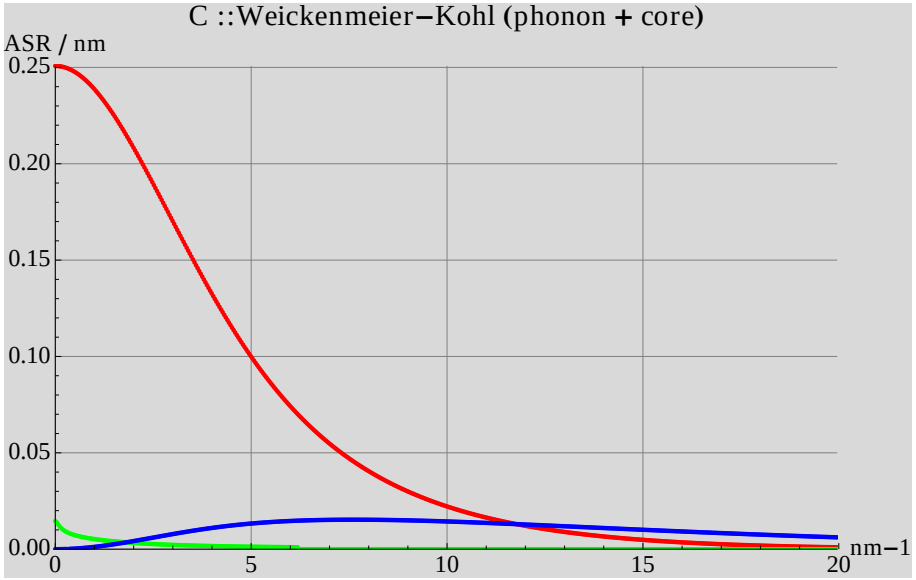


Figure: Carbon. Red: real part, green: imaginary part, blue: thermal diffuse scattering.

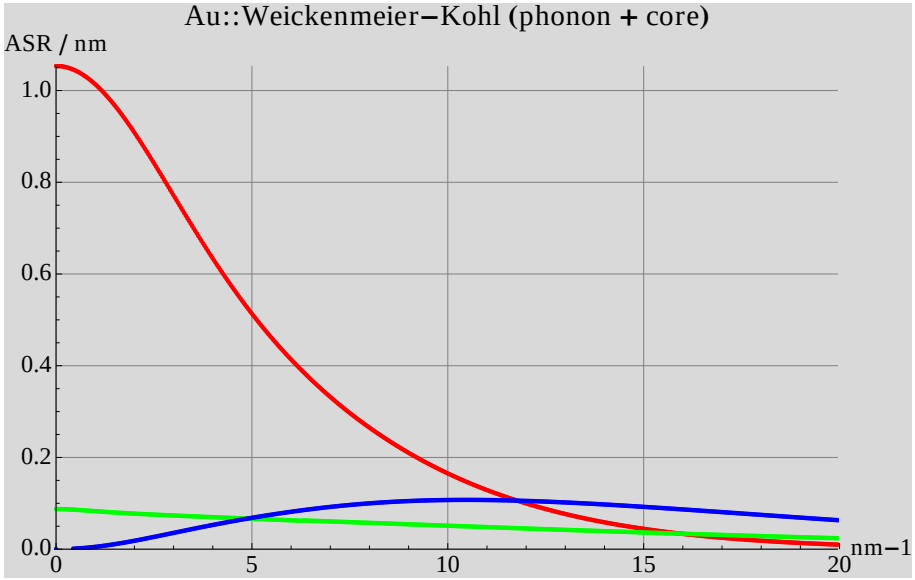


Figure: Gold. Red: real part, green: imaginary part, blue: thermal diffuse scattering.

The TDS (Thermal Diffuse Scattering) at large s ($=\sin(\theta)$) scales as $\approx Z^{1.7}$. It explains HAADF (High Angle Annular Dark Field) atomic column contrast.

Atomic form factors

Atomic form factors have been tabulated by many authors:

1. Doyle-Turner and Smith-Burge.
2. E.J. Kirkland.
3. Peng-Ren-Dudarev-Whelan.
4. ...

Take care ASA of heavy atoms aren't always tabulated properly.

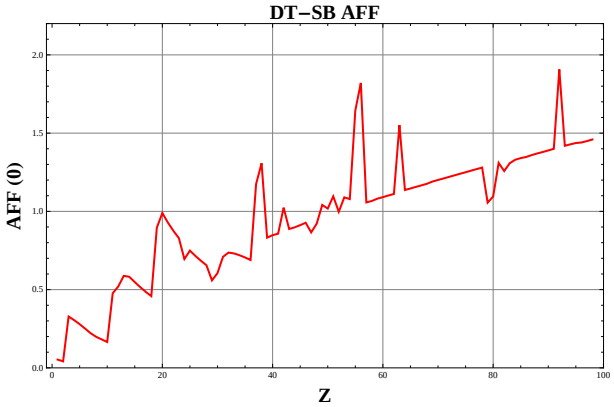


Figure: Doyle-Turner or Smith-Burger.

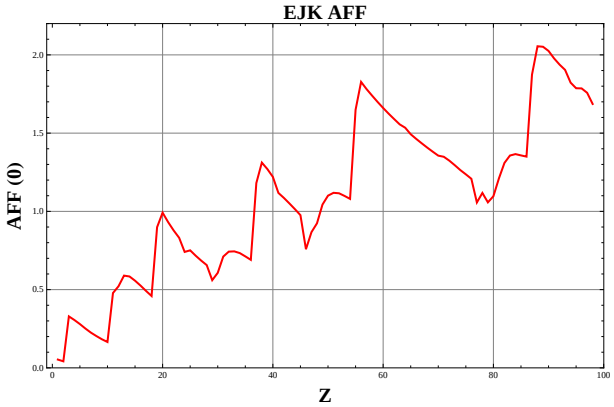


Figure: E. J. Kirkland.

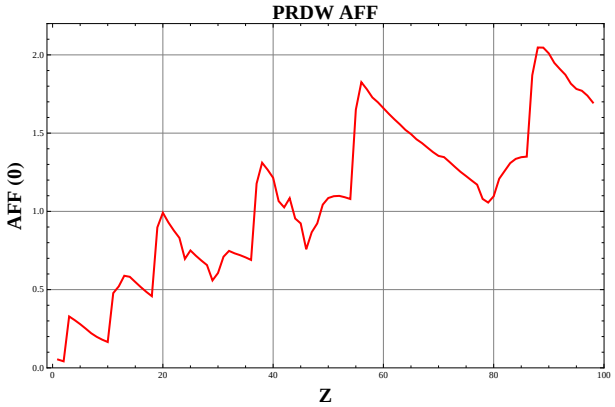


Figure: Peng-Ren-Dudarev-Whelan.

A extremely useful ASA tabulation including phonon and core loss absorption is due to Weickenmeier-Kohl[3].

[3] A. Weickenmeier, H. Kohl, Acta Cryst. A 47 (1991) 590.

Atomic form factors

Crystal structure are defined by:

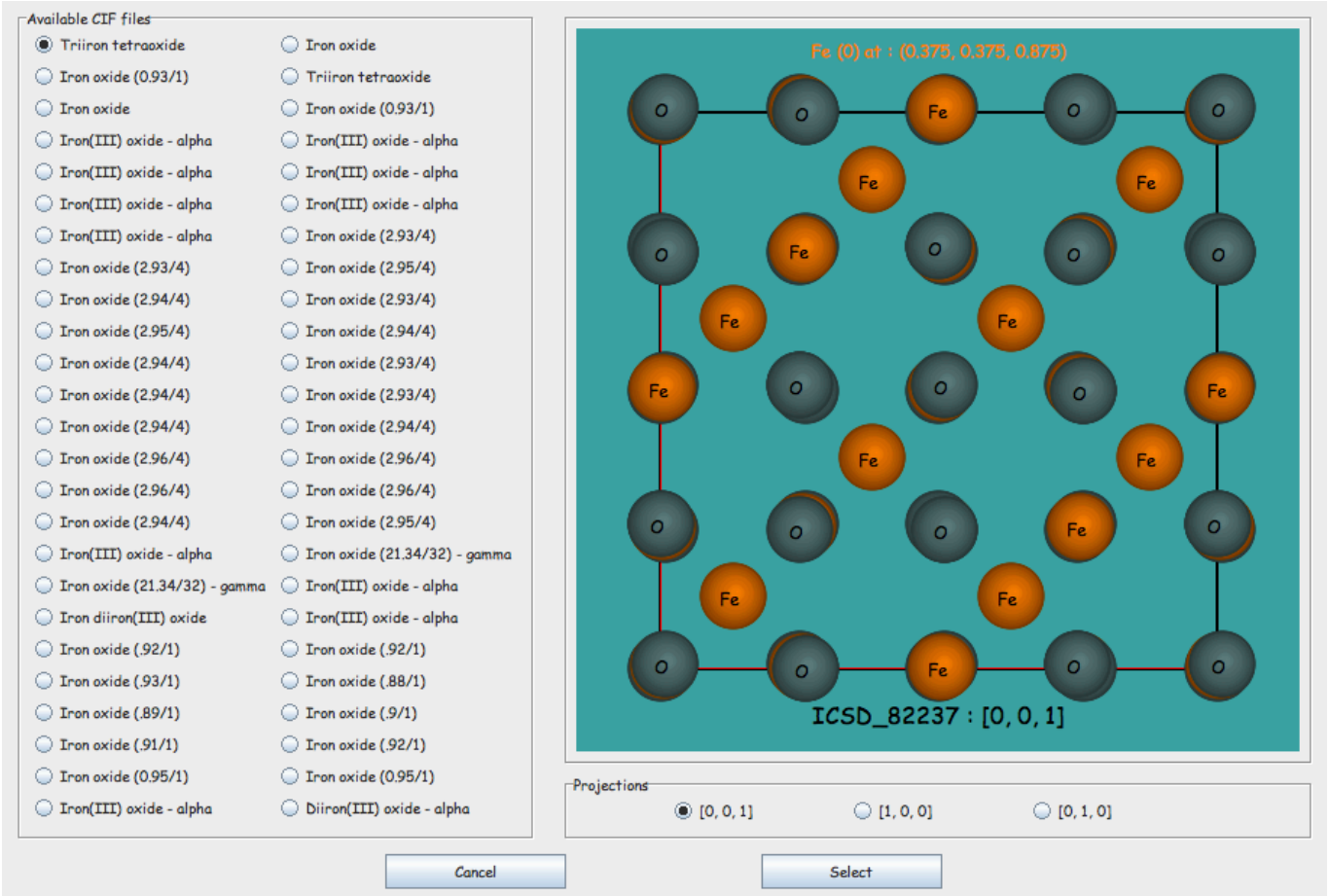
1. a, b, c, α, β, γ lattice parameters.
2. Space-group or symmetry operators.
3. Atoms positions (Symbol, x, y, z with $0 \leqq (x, y, z) \lneq 1$)

$> 10^5$ crystal structures provided by data bases (ICSD, Min. Soc. Ame., Cryst. Open Database)

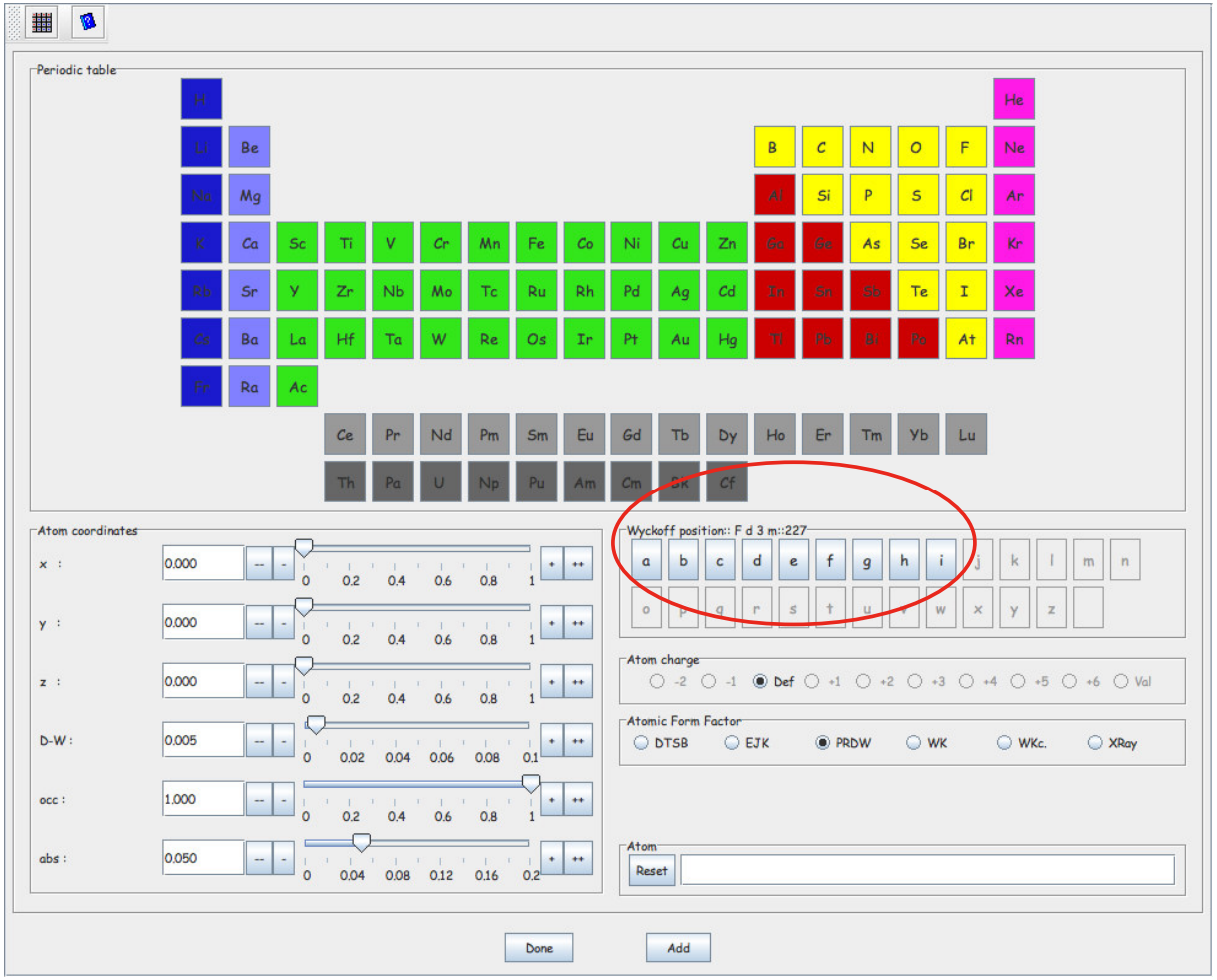
Useful severs:

www.minsocam.org
www.crystallography.net
www.cryst.ehu.es

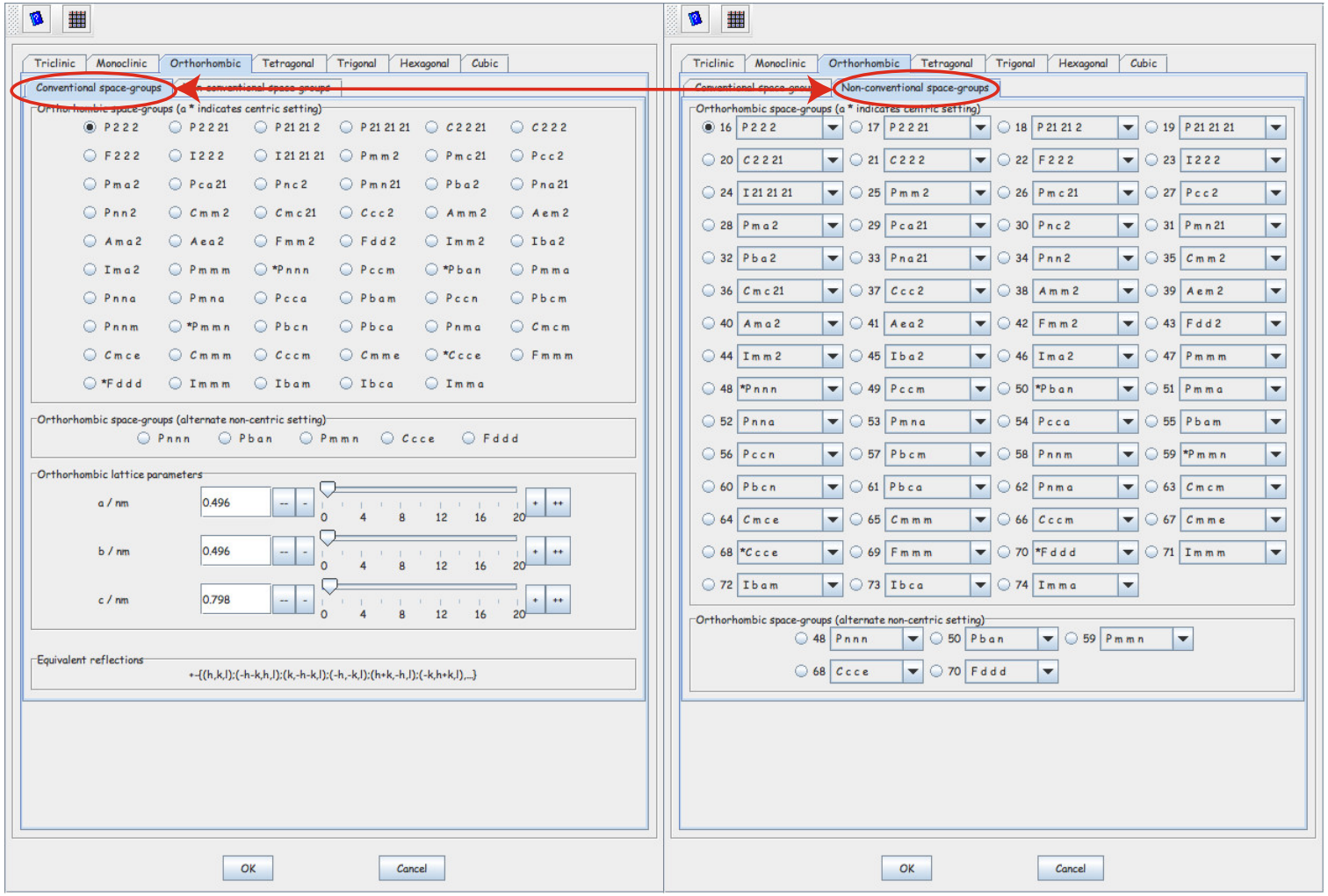
ICSD & AMS: data bases for crystal structures



Atom editor

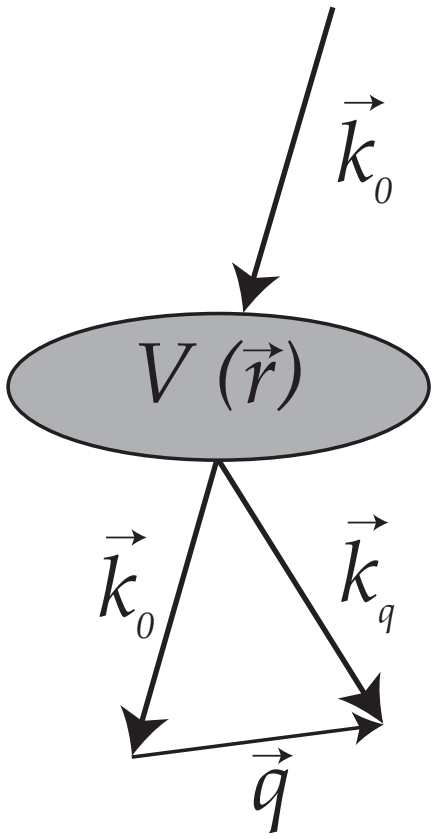

Periodic table
Atom coordinates
x :
y :
z :
D-W :
occ :
abs :
0.000
0.005
1.000
0.050
Wyckoff position:: F d 3 m::227
Atom charge
Def
Atomic Form Factor
DTSB
EJK
PRDW
WK
WKc.
XRay
Atom
Reset
Done
Add

Space-group selector



Scattering & diffraction

Scattering: electron-matter interaction



An incident electron of wave vector $\vec{k}_0$ interacts with a solid of scalar potential $V(\vec{r})$. The wave vector of the scattered electron is $\vec{k}_q = \vec{k}_0 + \vec{q}$ where $\vec{q}$ is the momentum transfered by the solid[4].

$$\text{Elastic scattering} \longrightarrow ||\vec{k}_q|| = ||\vec{k}_0||.$$

[4] Magnetic and spin effects are ignored.

X-Ray diffraction: Bragg law

With energy conservation and momentum transfer ($\vec{s_g} = 0$):

$$|\vec{k_i} + \vec{g}| = |\vec{k_g}|$$

$$k_i^2 + 2 \times k_i \times g \times \cos(\vec{k_i}, \vec{g}) + g^2 = k_g^2$$

$$2k_i \times \cos(\vec{k_i}, \vec{g}) = -g$$

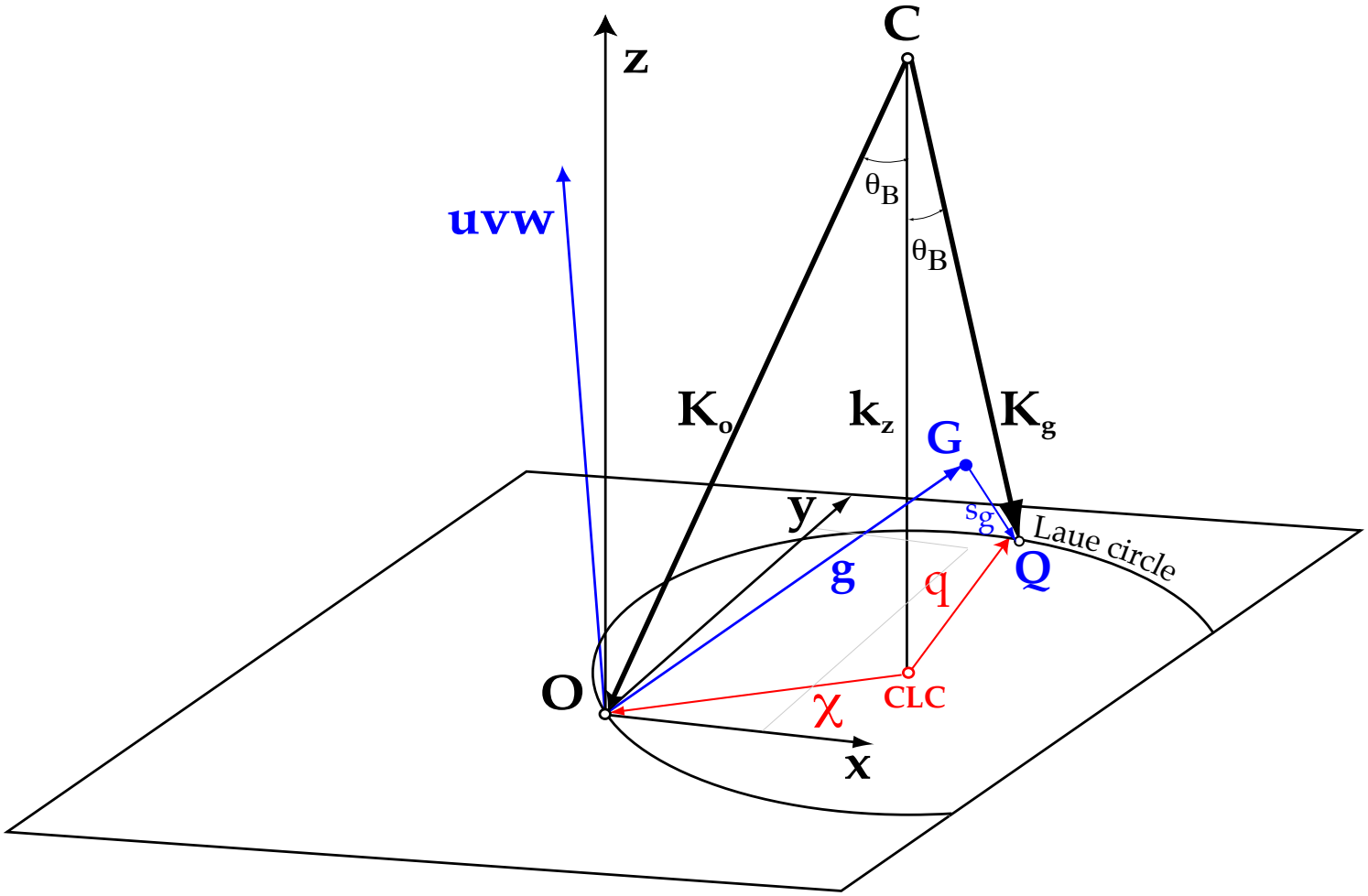
$$2k_i \times \cos(90^o - \theta_B) = -g$$

$$\frac{2}{\lambda} \times \sin(\theta_B) = g = \frac{1}{d_g}$$

$\Longrightarrow$ Bragg law:

$$2 \times d_{hkl} \times \sin(\theta_B) = \lambda$$

Diffraction geometry



Center of the Ewald sphere (C) and Center of the Laue Circle (CLC), projection of C onto the zero order Laue zone. All reflections on the circle of radius χ are at exact Bragg condition. Notice that the Bragg angles are pretty small (of the order a few ^{o}) and that consequently the small angle approximation is quite good.

Structure factors

The structure factor gives the scattering *strength* of (h,k,l) planes.

$$F_{hkl} = \sum_{i=atomes} f_i(s_{hkl}) e^{(2\pi\imath(hx_i+ky_i+lz_i))}$$

where:

1. $f_i(s_{hkl})$ is the atomic scattering amplitude.
2. (x_i, y_i, z_i) are the fractional coordinates of atom i $(0 \leq x_i < 1)$.
3. $s_{hkl} = \frac{sin(\theta_B)}{\lambda} = \frac{1}{2d_{hkl}}$.

Crystal symmetries: extinction rules + kinematical diffraction

In general all reflections allowed by the Bravais lattice are visible:

Simple cubic: (hkl) no condition.
1 atom at (0, 0, 0).

$$\Longrightarrow F_{hkl} = f_i(s_{hkl})$$

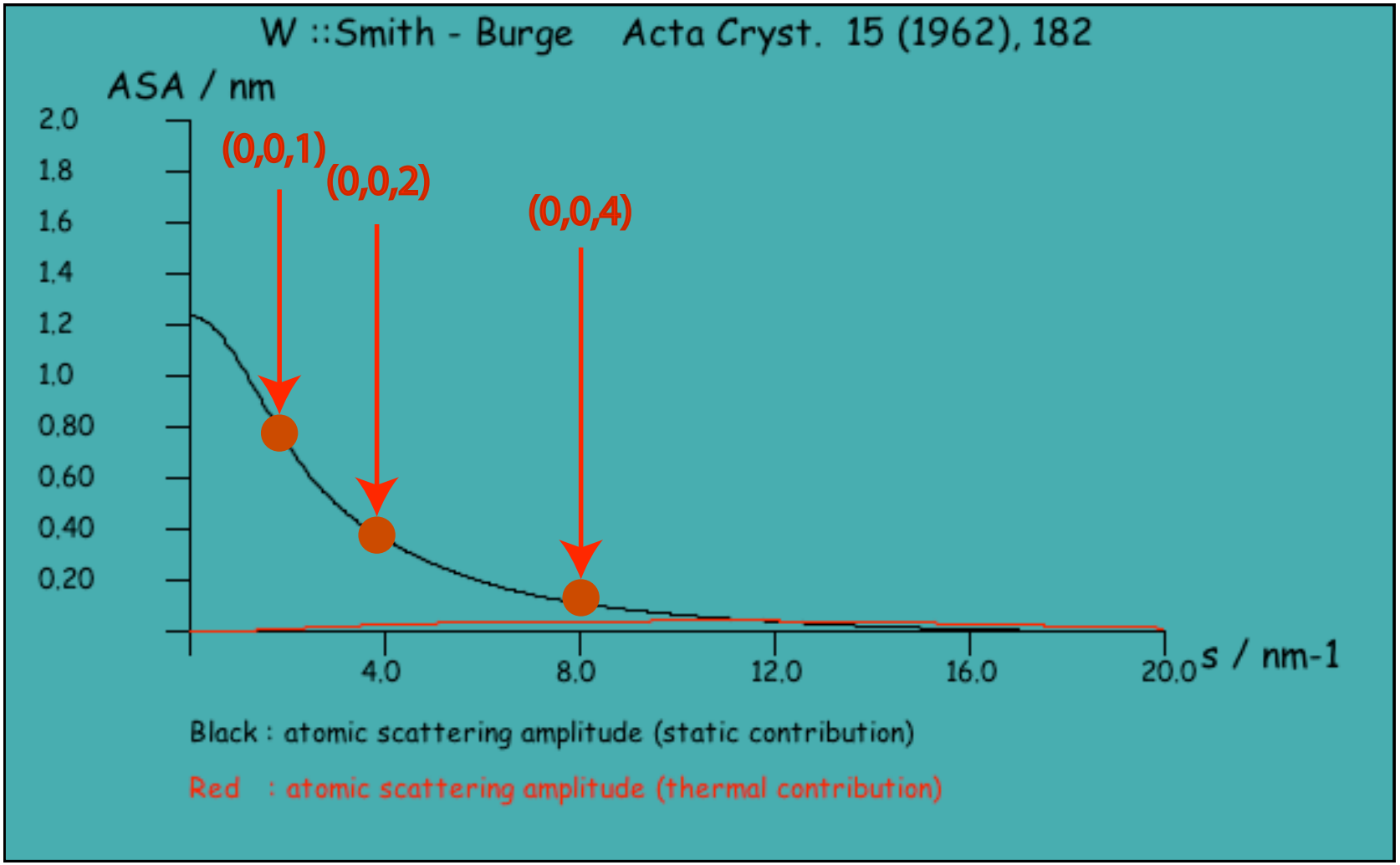
Body centered cubic: $(hkl) : h + k + l = 2n$
2 atoms at (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

$$\Longrightarrow F_{hkl} = f_i(s_{hkl}) \left[1 + e^{\pi\imath(h+k+l)}\right]$$

Face centered cubic: (hkl) all even or odd.
4 atoms at $(0,0,0)$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$

$$\Longrightarrow F_{hkl} = f_i(s_{hkl}) \left[1 + e^{\pi\imath(h+k)} + e^{\pi\imath(h+l)} + e^{\pi\imath(k+l)}\right]$$

Atomic scattering amplitude



Dynamical diffraction: $< q|U(z,0)|\chi >$

$< q|U(z,0)|\chi > \implies$ Fourier transform of object wavefunction

Dynamical scattering (many approaches under small angle approximation and elastic scattering).

Gratias & Portier: small angle & elastic scattering approximations

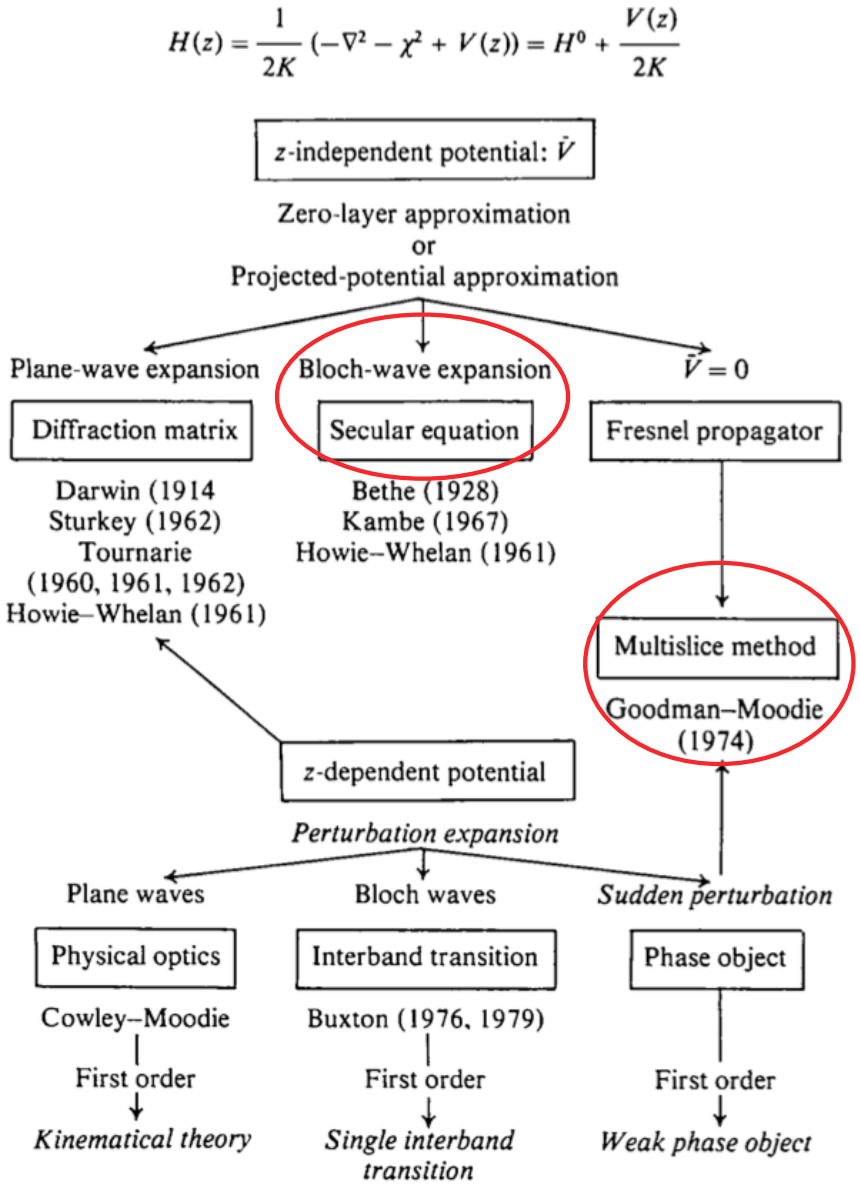


Figure: From Gratias and Portier [5]

[5] D. Gratias and R. Portier, Acta Cryst. **A39** (1983) 576.

The two most employed calculation methods

All approximations are numerically equivalent, but perform best in particular cases.

We will consider only 2 approximations:

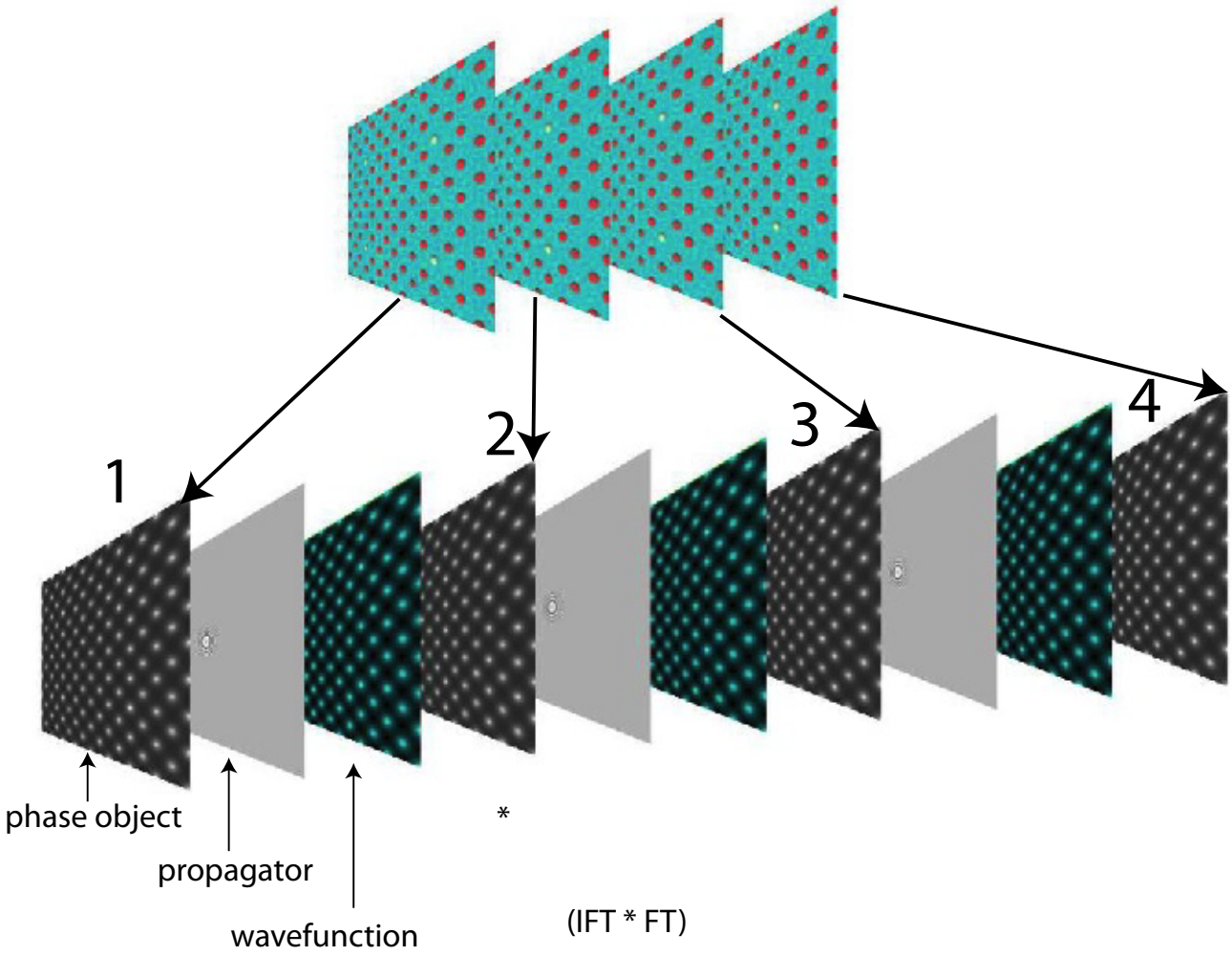
- The multislice approximation[6].
- The Bloch-wave method[7].

The multislice method performs best when simulating crystalline or amorphous solids of large unit cell or containing defects while the Bloch-wave method is adapted to the calculation of crystalline solids of small unit cell and in any [uvw] orientation. The Bloch-wave method has also several advantages (speed, ease of use) for simulating CBED, LACBED or PED patterns and for polarity and chirality determination.

[6] J. Cowley and A.F. Moodie, Proc. Phys. Soc. B70 (1957) 486, 497 and 505.

[7] H. A. Bethe, Ann. Phys. 87 (1928), 55.

Multislice method



The solid is sliced into thin sub-slices. The incident wave-function is transferred by the first slice (diffraction) and propagated to the next one. The propagation is done within the Fresnel approximation, the distance between the slices being 20 - 50 times the wavelength[8].

[8] file://localhost/Applications/jemsMacOSX/html/PtOct/a.html

Multislice algorithm[9]

Can simulate:

- Perfects crystals.
- Defects under the periodic continuation assumption.

2 steps:

- Diffractor: transfer by a slice $\Rightarrow$ multiplication by phase object function ($POF(\vec{\rho})$).
- Propagator: propagation between slices $\Rightarrow$ convolution by the Fresnel propagator (is nowadays performed by a FFT followed by a multiplication and an inverse FFT (FT^{-1}, multiplication, FFT)).

[9] K. Ishizuka, Acta Cryst. A33 (1977) 740-749.

Multislice: periodic continuation[10]

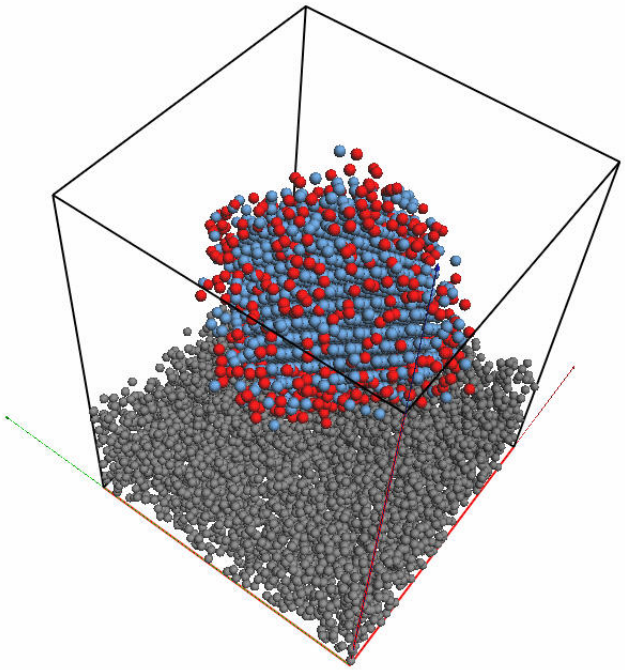


Figure: Model (one unit cell).

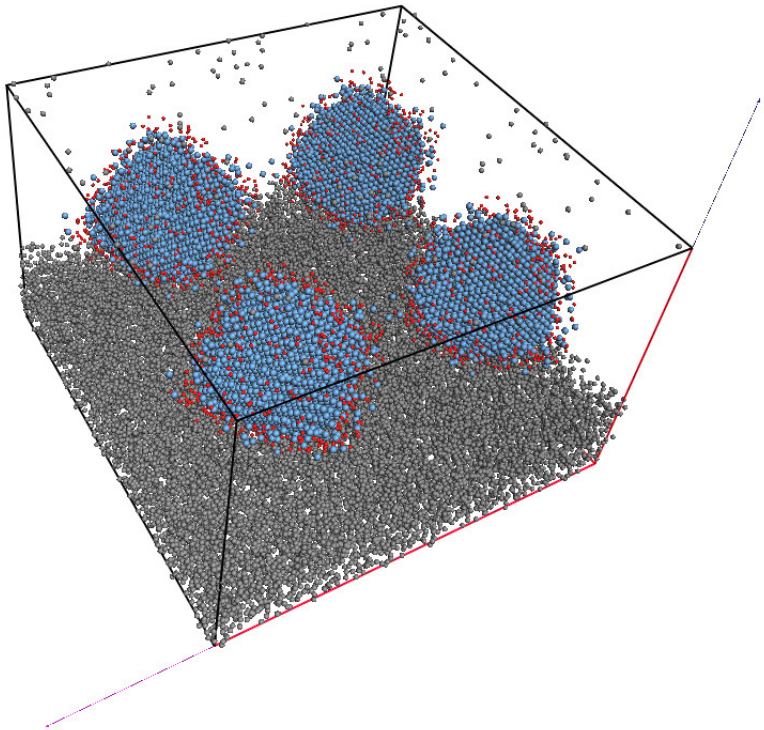
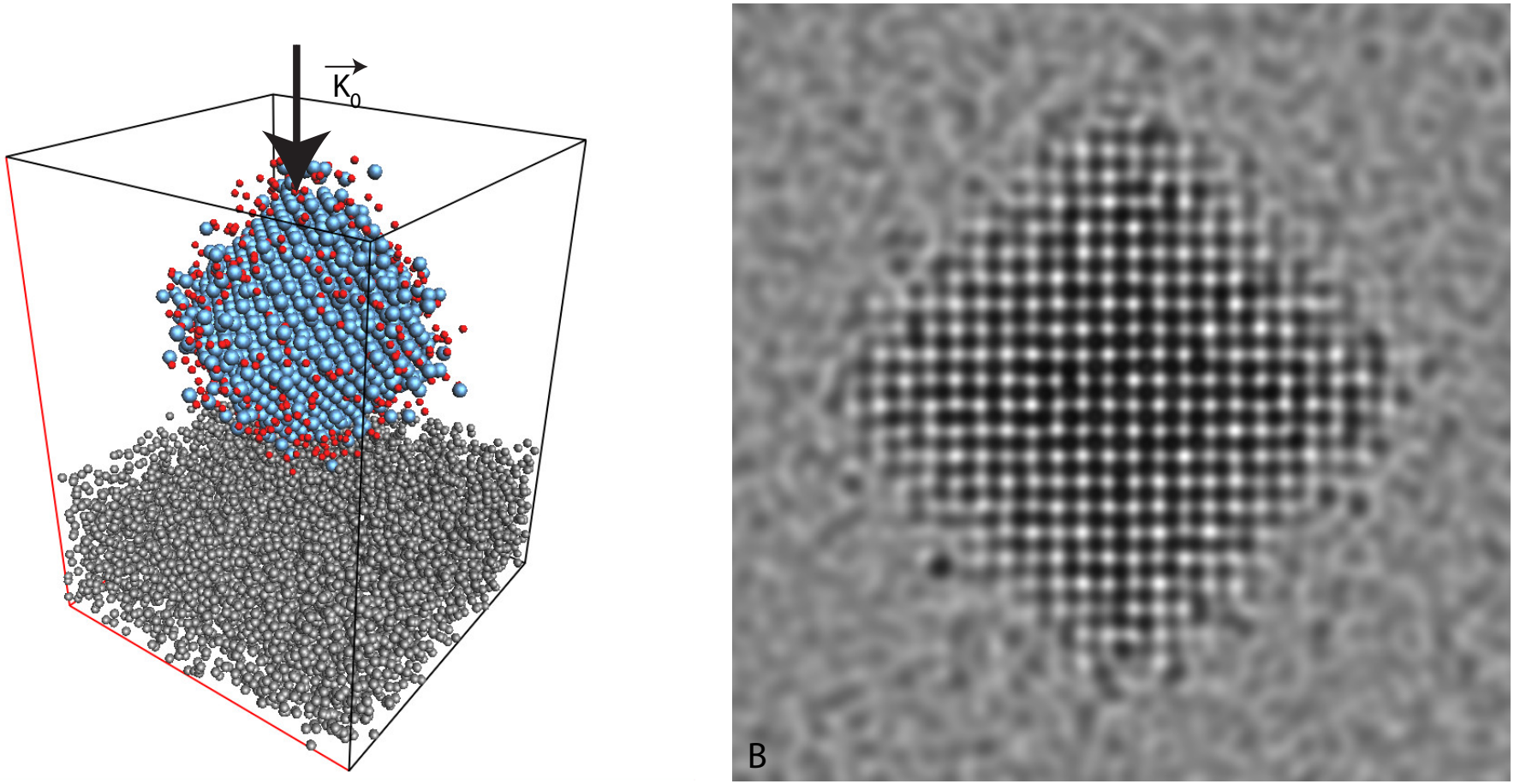


Figure: Model with periodic continuation (2 x 2 unit cells).

[10] A.J. Skarnulis, Thesis, Arizona State University 1975.

Example multislice: Pt catalyst



A: catalyst model (9500 atoms)[11]*. B: HREM image (Jeol 400kV).*

[11] file://localhost/Applications/jemsMacOSX/html/pot3D/pot3D.html

Bloch wave method: z-independent potential

When the scattering potential is periodic, the eigenstates $|j>$ of the propagating electrons are Bloch waves. The hamiltonian of the system is projected on the eigenstates $|j>$ with eigenvalues γ_j (*"anpassung"* parameter).

$$\widehat{H} = \sum_j \gamma_j |j><j|$$

The evolution operator is then given by (since $V = V(\vec{\rho})$):

$$\widehat{U}(z,0) = e^{-i\widehat{H}z} = \sum_j e^{-i\gamma_j z}|j><j|$$

The wave-function at z developed on plane waves basis $|q>$:

$$\Psi(z) = \sum_q \phi_q(z)|q>$$

$$\phi_q(z) =< q|\widehat{U}(z,0)|0>= \sum_j e^{-i\gamma_j z} < q|j><j|0>$$

$$c_0^{*j} =< j|0> \text{ and } c_q^j =< q|j>$$

where in usual notation c_0^{*j} and c_q^j are the Bloch-wave excitations (component of the initial state $|0>$ on $|j>$) and coefficients (component of reflection $|q>$ on $|j>$) respectively.

Bloch wave method: applications

Simulation of:

- SAED (kinematical and dynamical).
- CBED (polarity).
- LACBED (specimen thickness, symmetry).
- PED (Precession Electron Diffraction).
- HRTEM.

Works best for small lattice parameters crystals.

CBED: ZnTe [110]

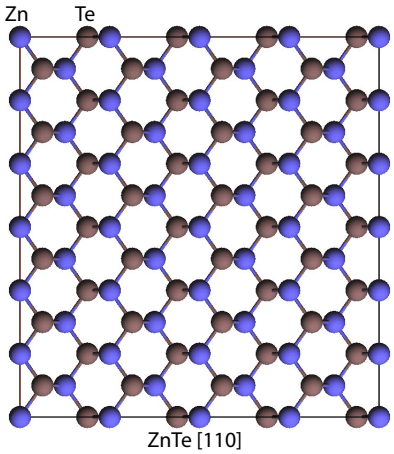


Figure: ZnTe [110].

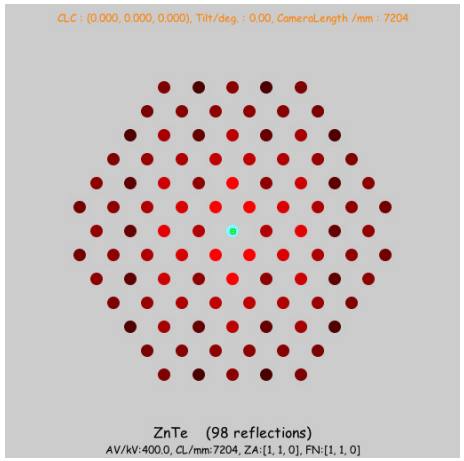


Figure: Reflections (1 + 49), $|\chi >= 0$.

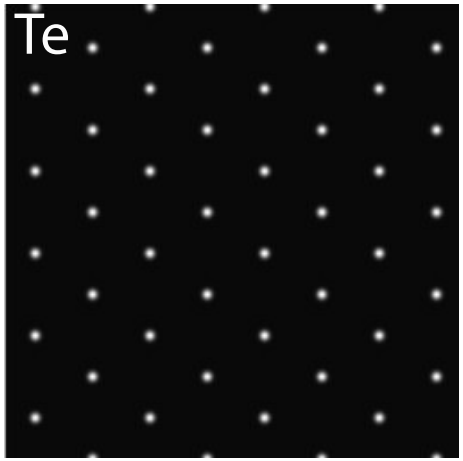


Figure: Bloch-wave 1 (Te 1s).

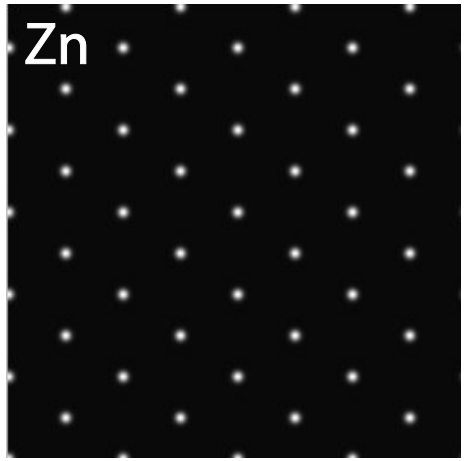


Figure: Bloch-wave 2 (Zn 1s).

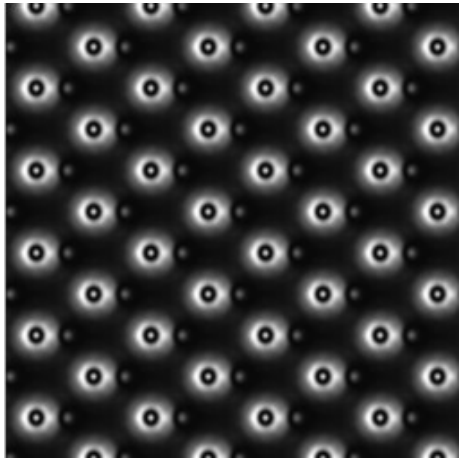


Figure: Bloch-wave 5 (Te-Zn).

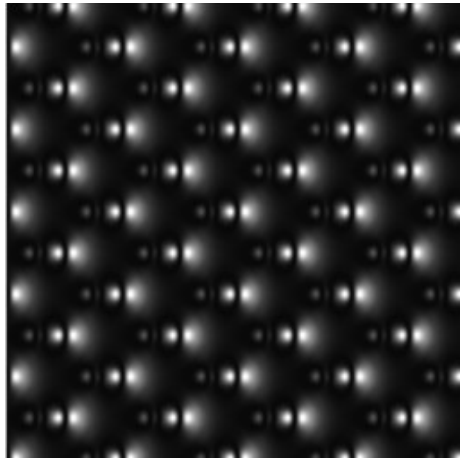


Figure: Bloch-wave 7 (Te-Zn).

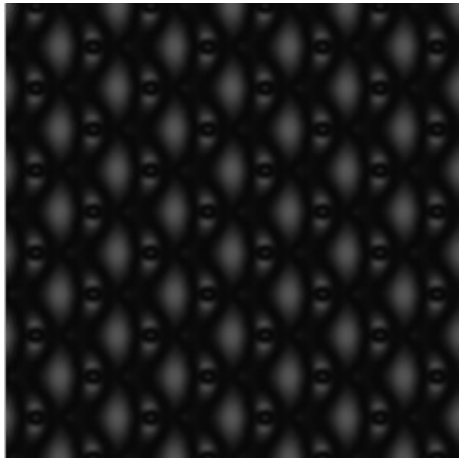


Figure: Bloch-wave 8 (Te-Zn).

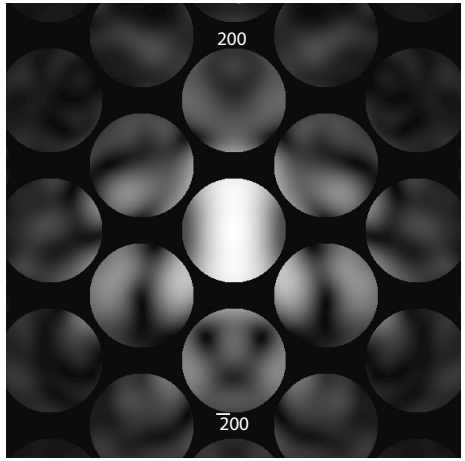
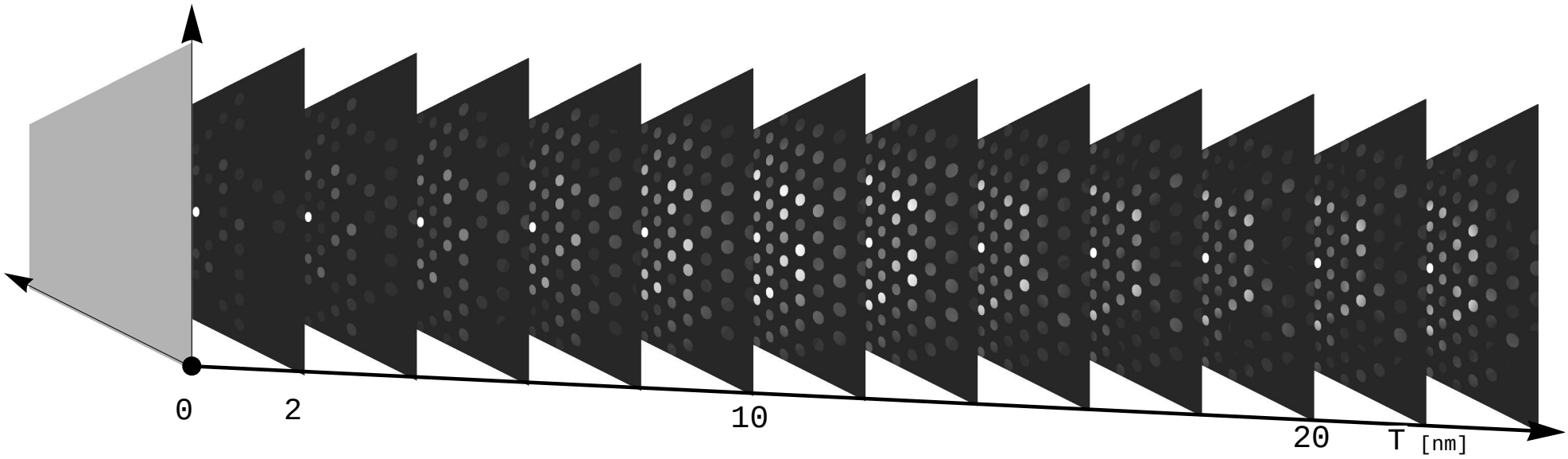


Figure: CBED (ZnTe polarity).

SAED: Diffraction pattern & specimen thickness



In BFP diffraction pattern depends specimen thickness.

Goodness of dynamical diffraction theories?

LACBED: Si [001]

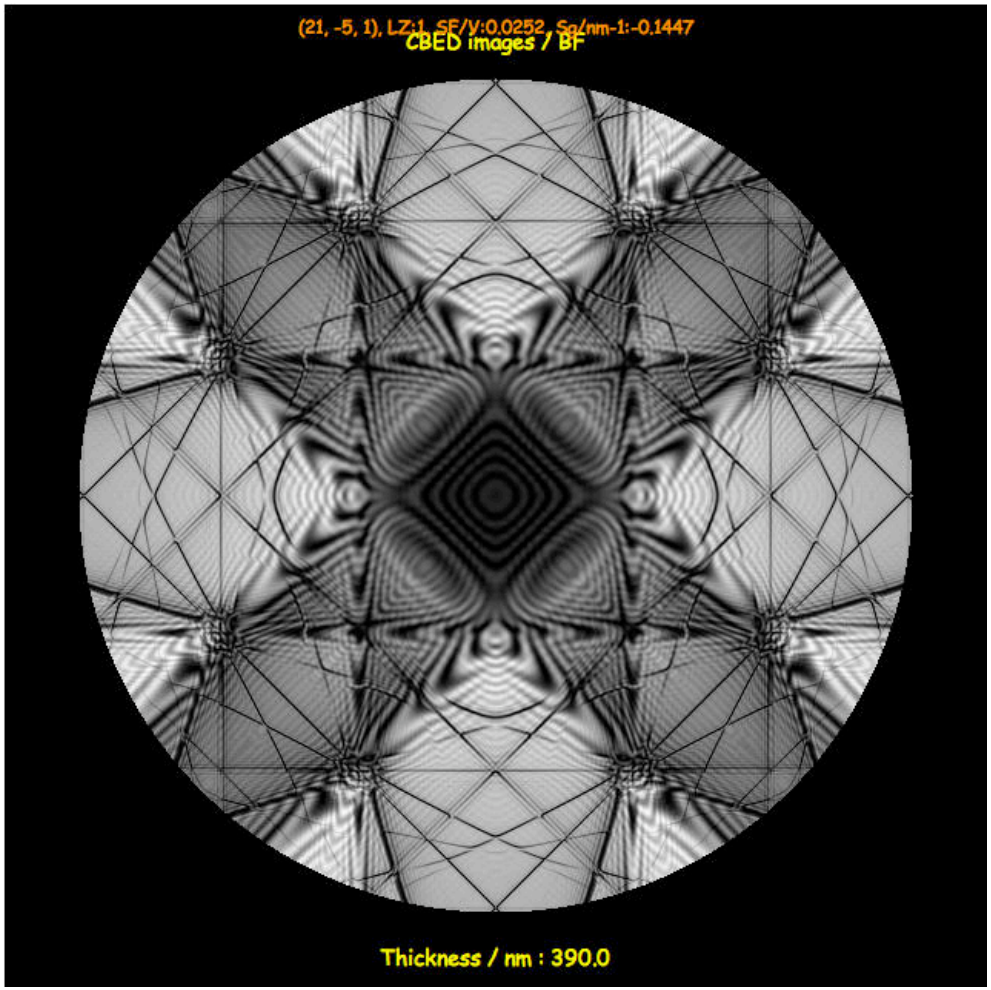


Figure: LACBED Si [001]: simulation.

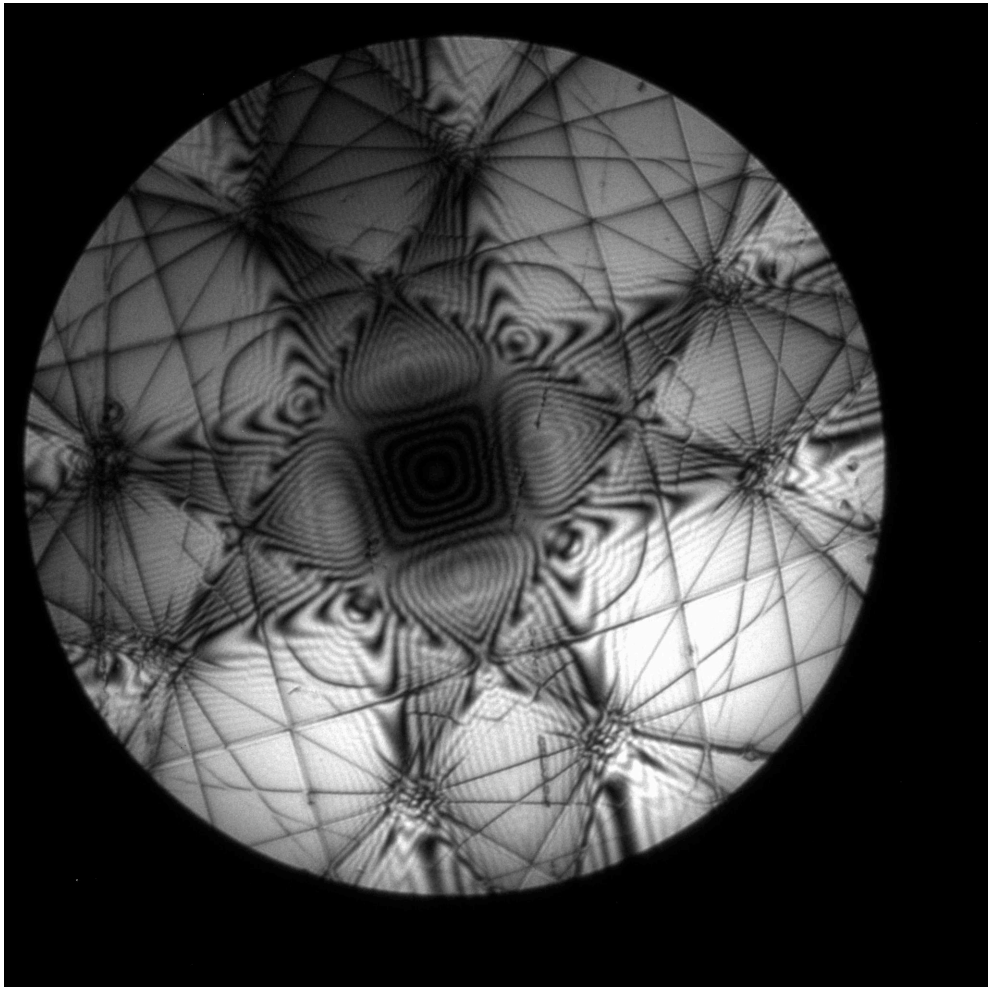


Figure: LACBED Si [001]: experimental (Web site EM centre - Monash university, J. Etheridge).

Note that the experimental LACBED pattern is blurred (inelastic scattering and/or MTF of CCD camera?).

Electron diffraction: precession

Electron crystallography $\Longrightarrow$ precession electron diffraction (Spinning Star).

Questions:

1. Are dynamical effects important?

Electron diffraction: precession

Electron crystallography $\Longrightarrow$ precession electron diffraction (Spinning Star).

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2. Can we interpret the measured intensities as:

Electron diffraction: precession

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   - kinematical?

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Electron crystallography $\Longrightarrow$ precession electron diffraction (Spinning Star).

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   - 2-beams dynamical?

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Questions:

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   - 2-beams dynamical?
   - n-beams dynamical?

Electron diffraction: precession

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Questions:

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   - kinematical?
   - 2-beams dynamical?
   - n-beams dynamical?
3. Best precession angle?

Electron diffraction: precession

Electron crystallography $\Longrightarrow$ precession electron diffraction (Spinning Star).

Questions:

1. Are dynamical effects important?
2. Can we interpret the measured intensities as:
   - kinematical?
   - 2-beams dynamical?
   - n-beams dynamical?
3. Best precession angle?
4. Maximum crystal thickness?

PED: $CdCu_2[001]$

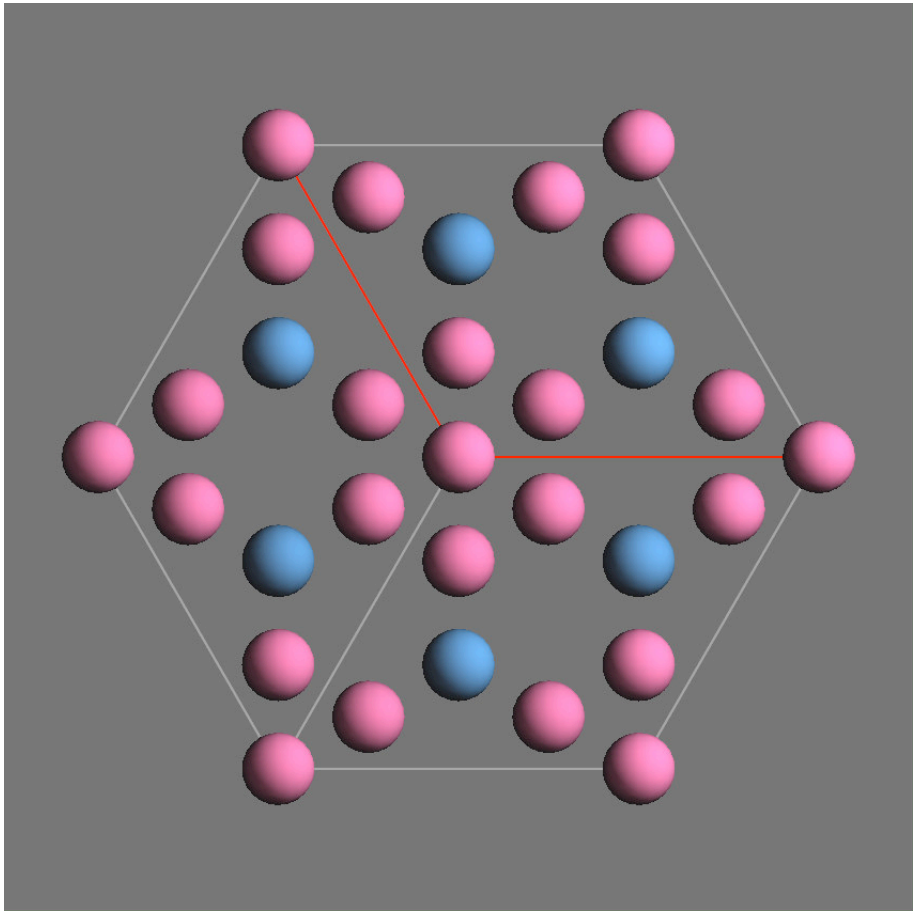


Figure: *Structure projection* $CdCu_2$

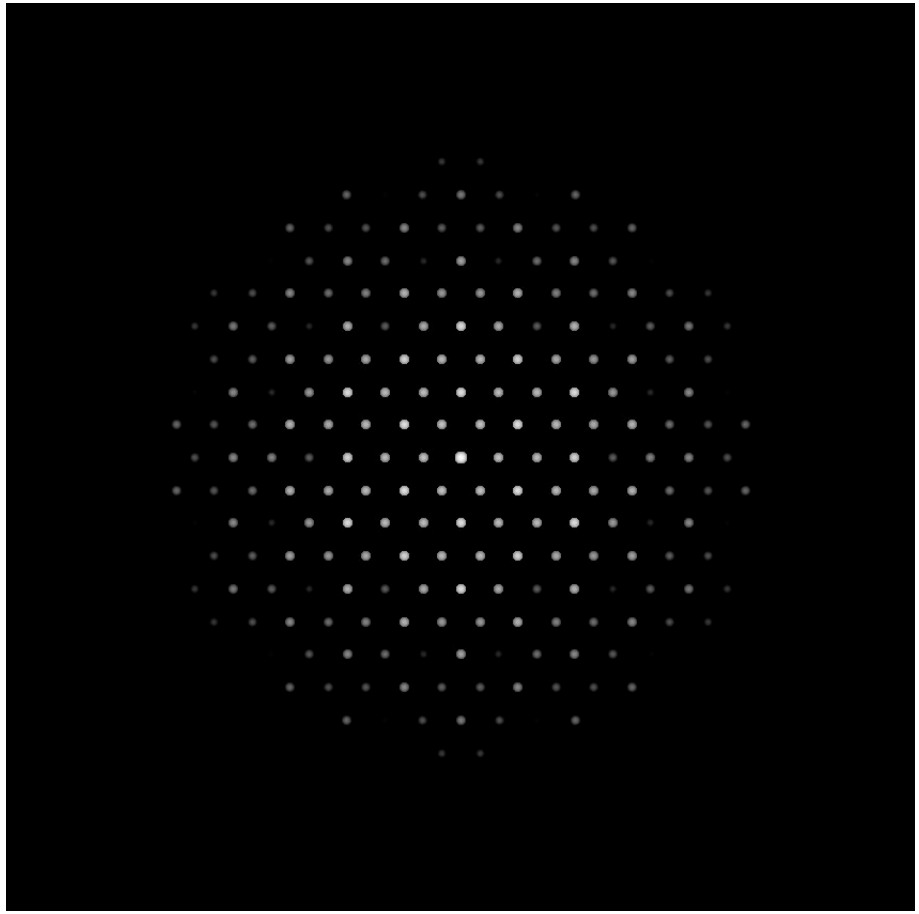


Figure: *Dynamical SAED pattern (5 nm)*

$CdCu_2[001]$: *precession*

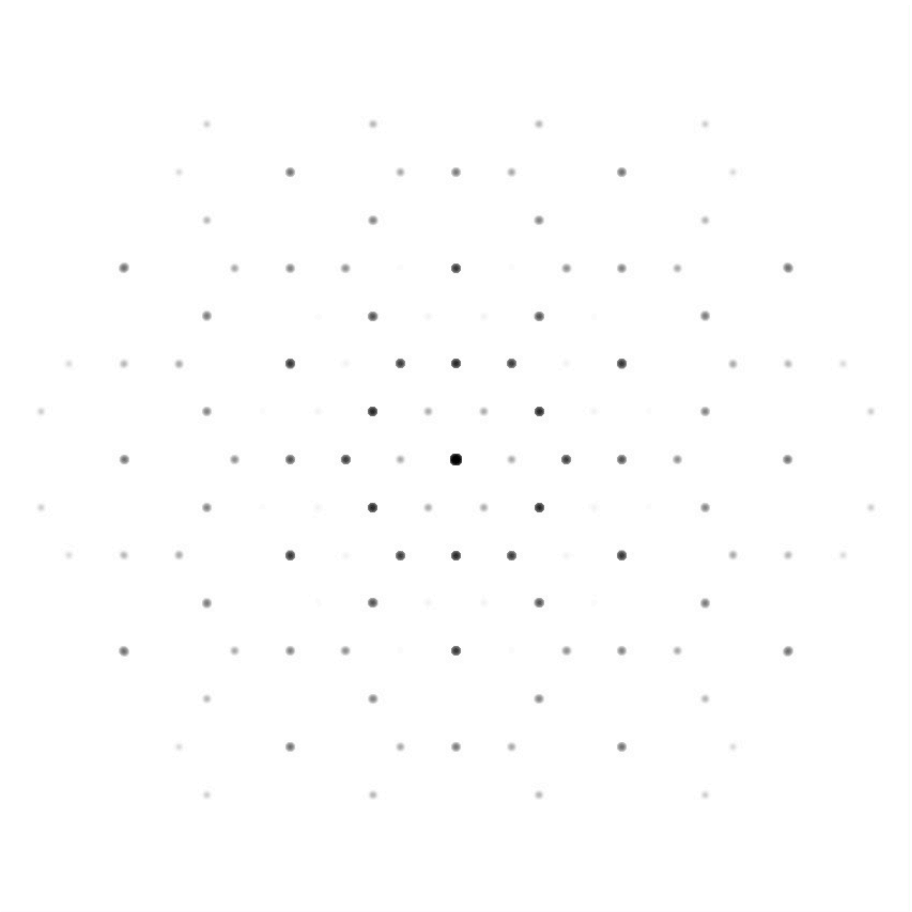


Figure: $CdCu_2$ *kinematical SAED pattern.*

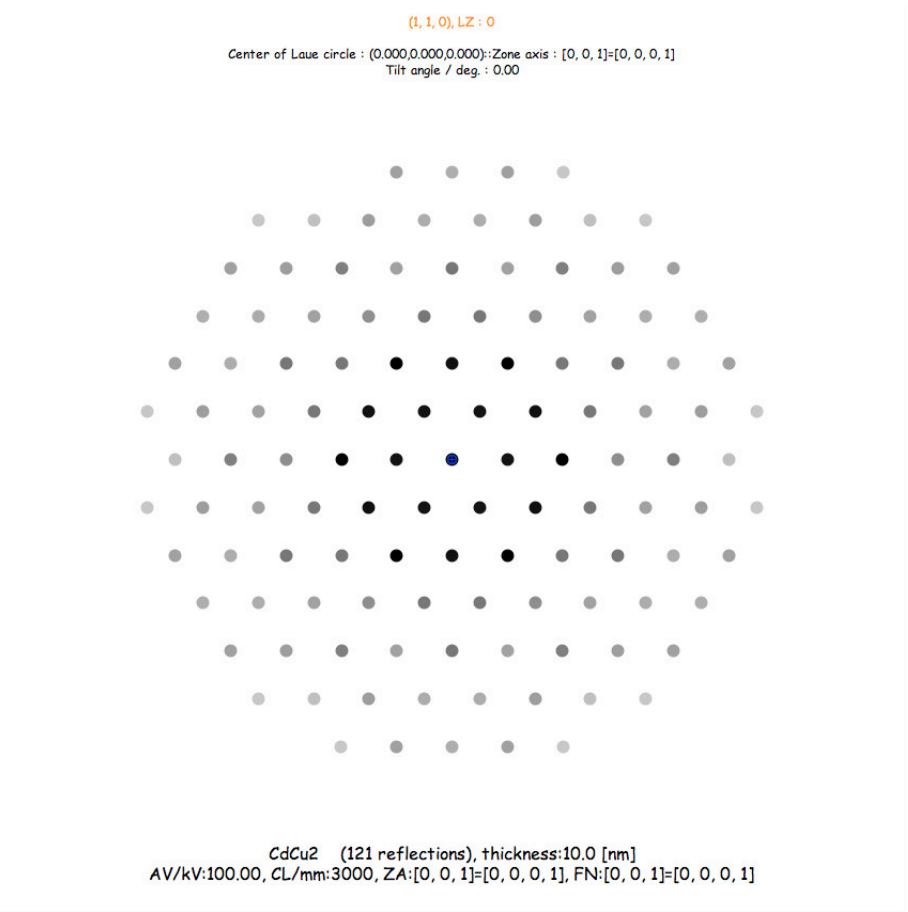


Figure: $CdCu_2$ *dynamical SAED pattern (5 nm)*

$CdCu_2[001]$ – ZAP

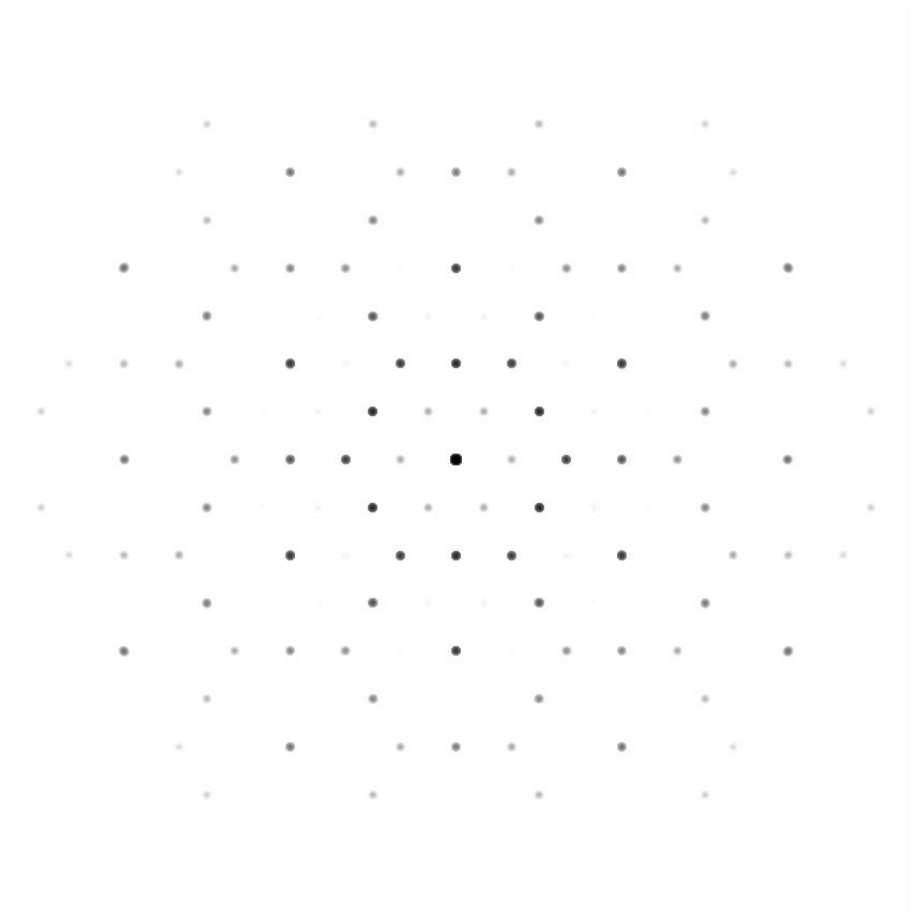


Figure: *Kinematical.*

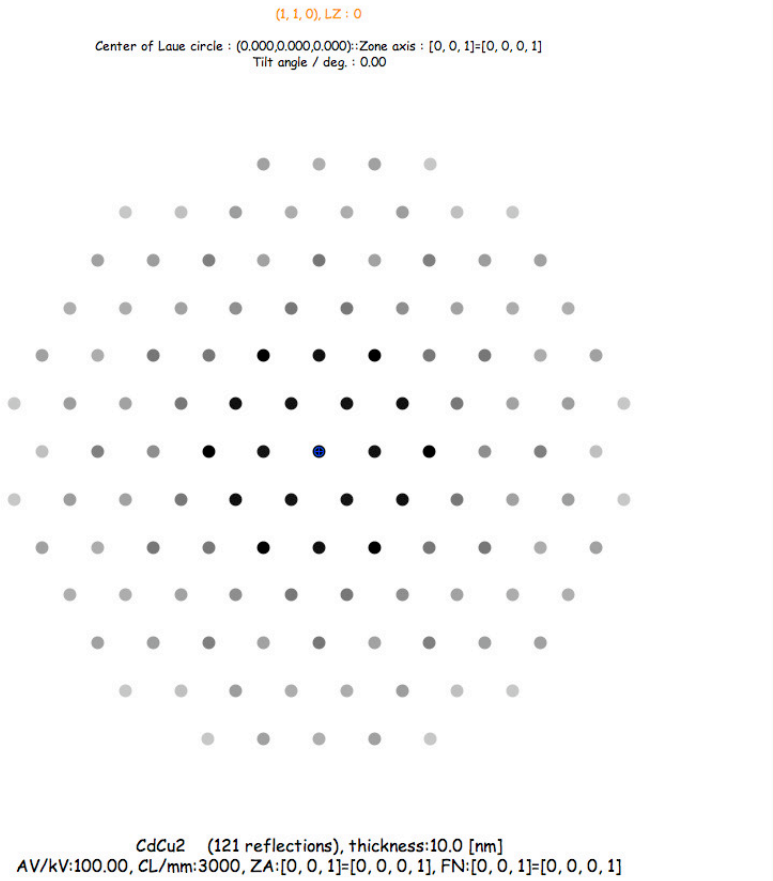


Figure: *Dynamical (121 - beams).*

$CdCu_2[001]$ — precession 3^o

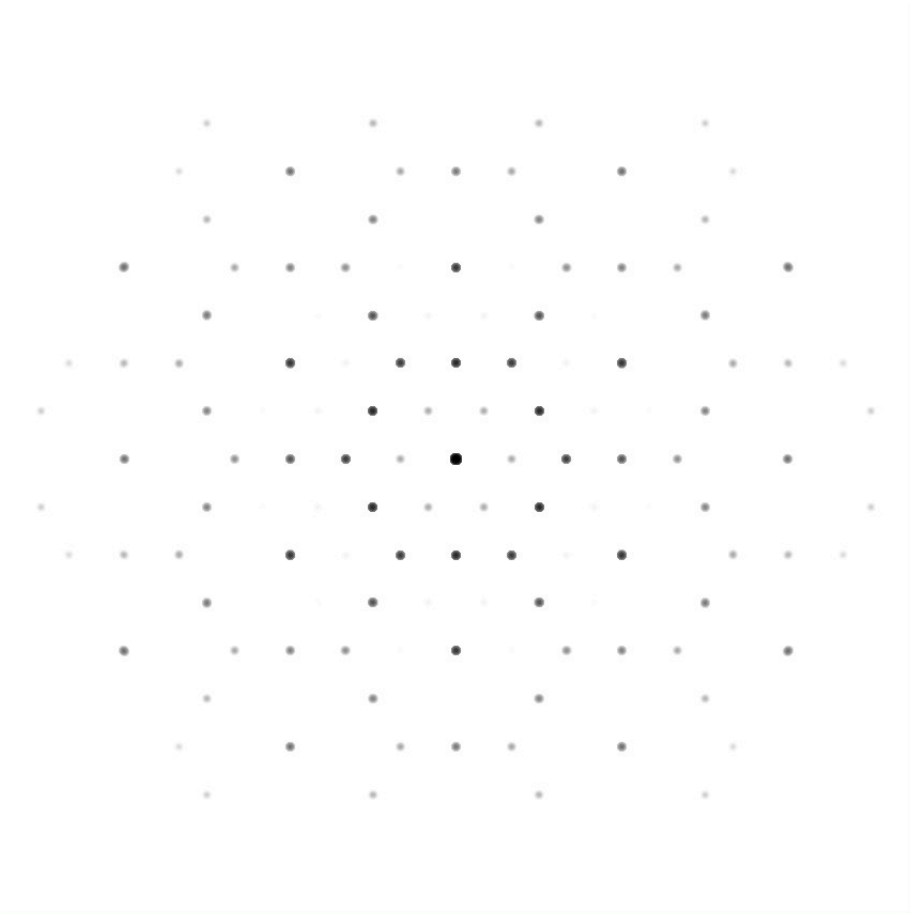


Figure: *Kinematical.*

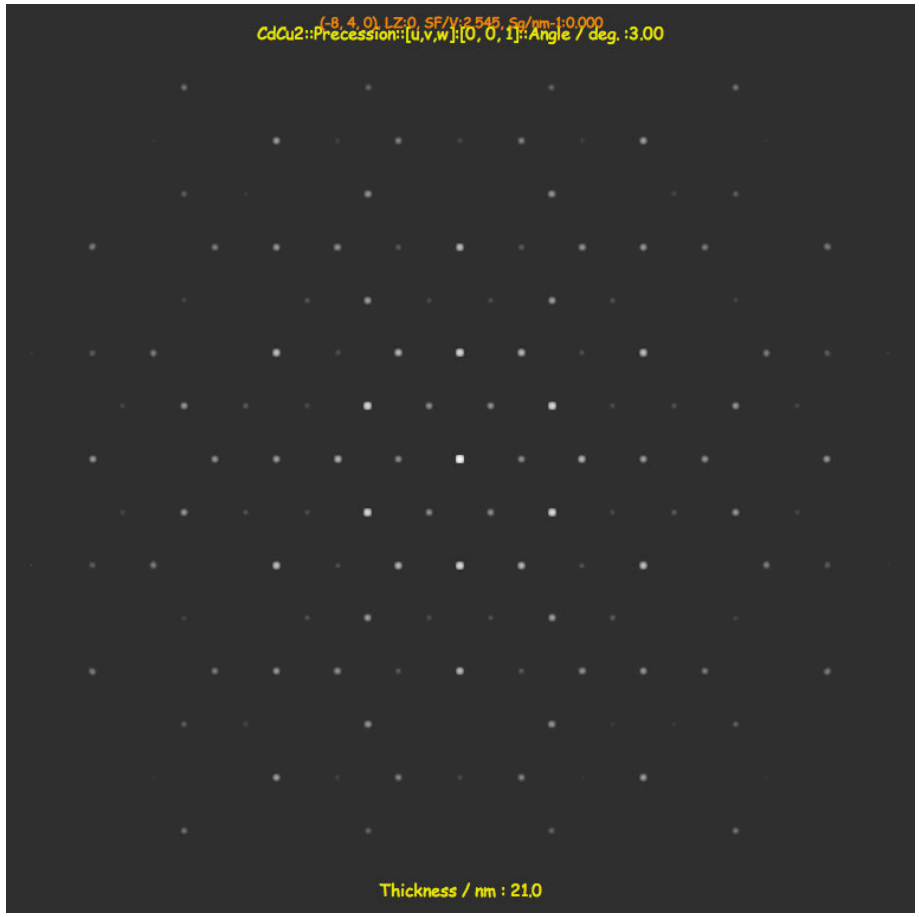
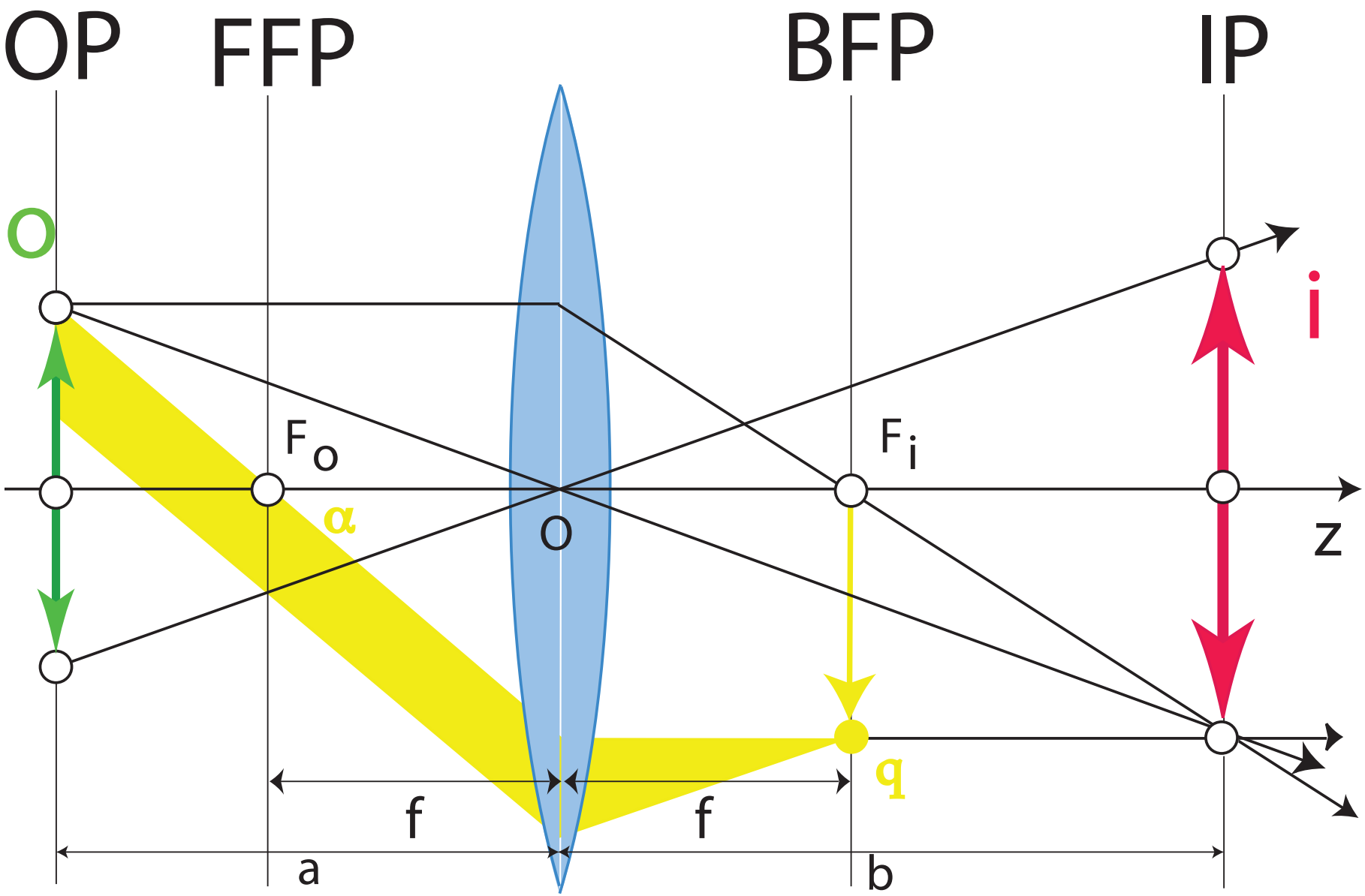


Figure: *Dynamical (121 - beams).*

At first sight kinematical approximation looks sufficient (detailed values are available).

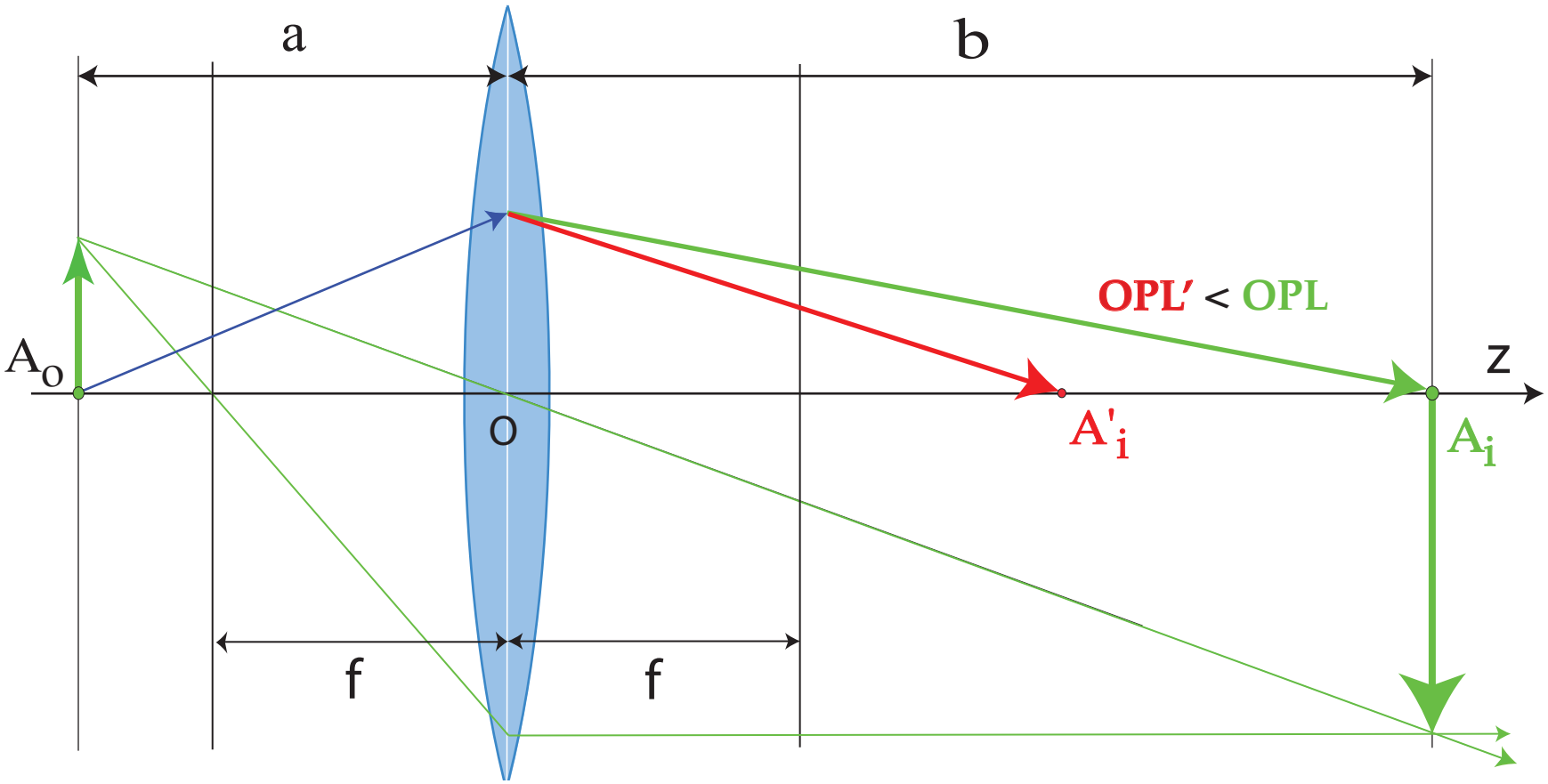
Image formation

Paraxial optics: perfect thin lens



Principal rays of paraxial optics. Reflection (plane wave) making an angle α, where $\alpha = 2\theta_B$, corresponds to spatial frequency q.

Optical Path Length: spherical aberration

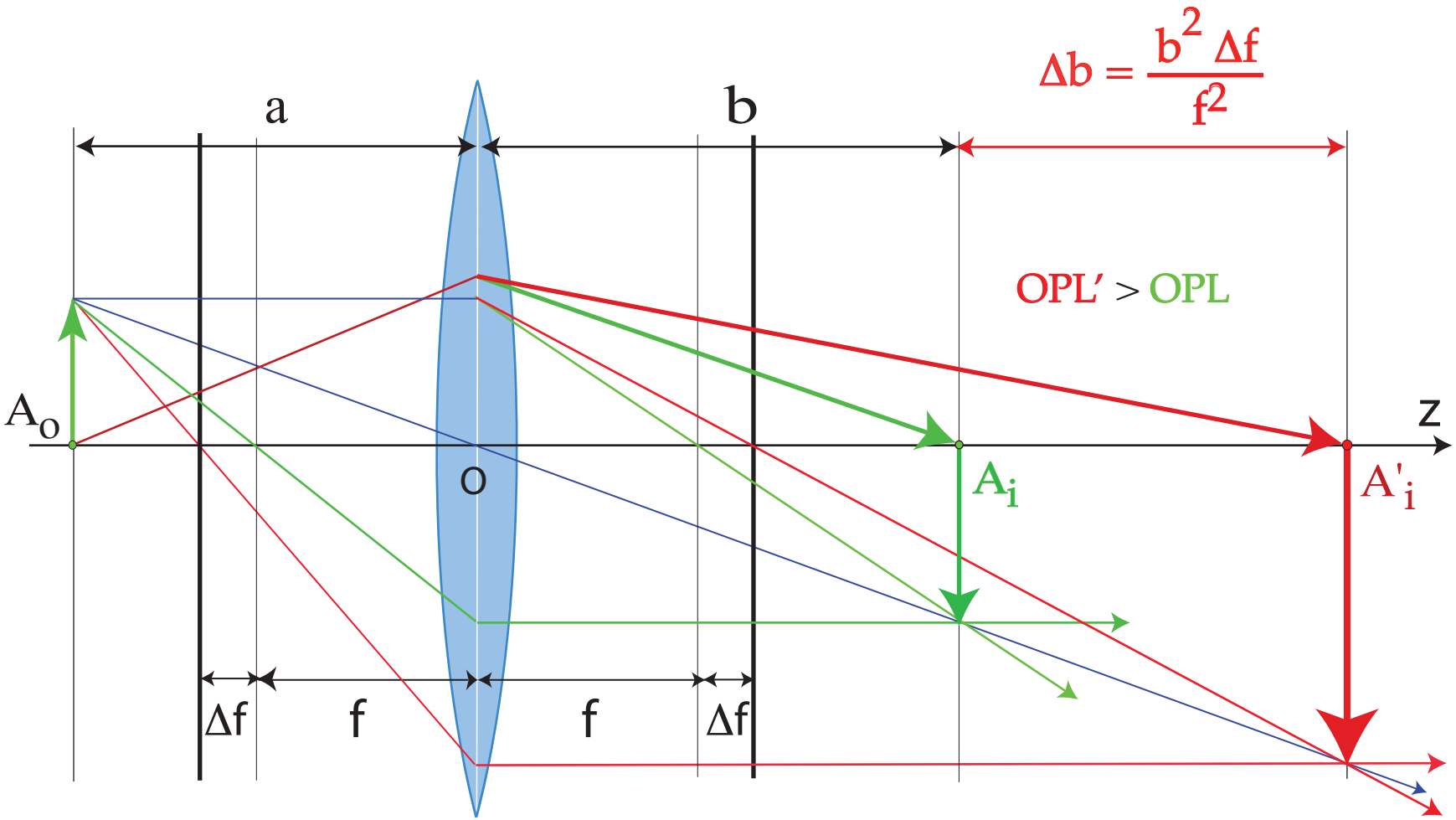


In presence of spherical aberration, the optical path length (OPL') form A_o to A'_i is smaller than OPL from A_o to A_i. The wavefront at A'_i is out-of-phase by[12]:

$$e^{-2\pi i \frac{C_s \lambda^3 (\vec{q}\cdot\vec{q})^2}{4}}$$

[12]With our plane wave choice.

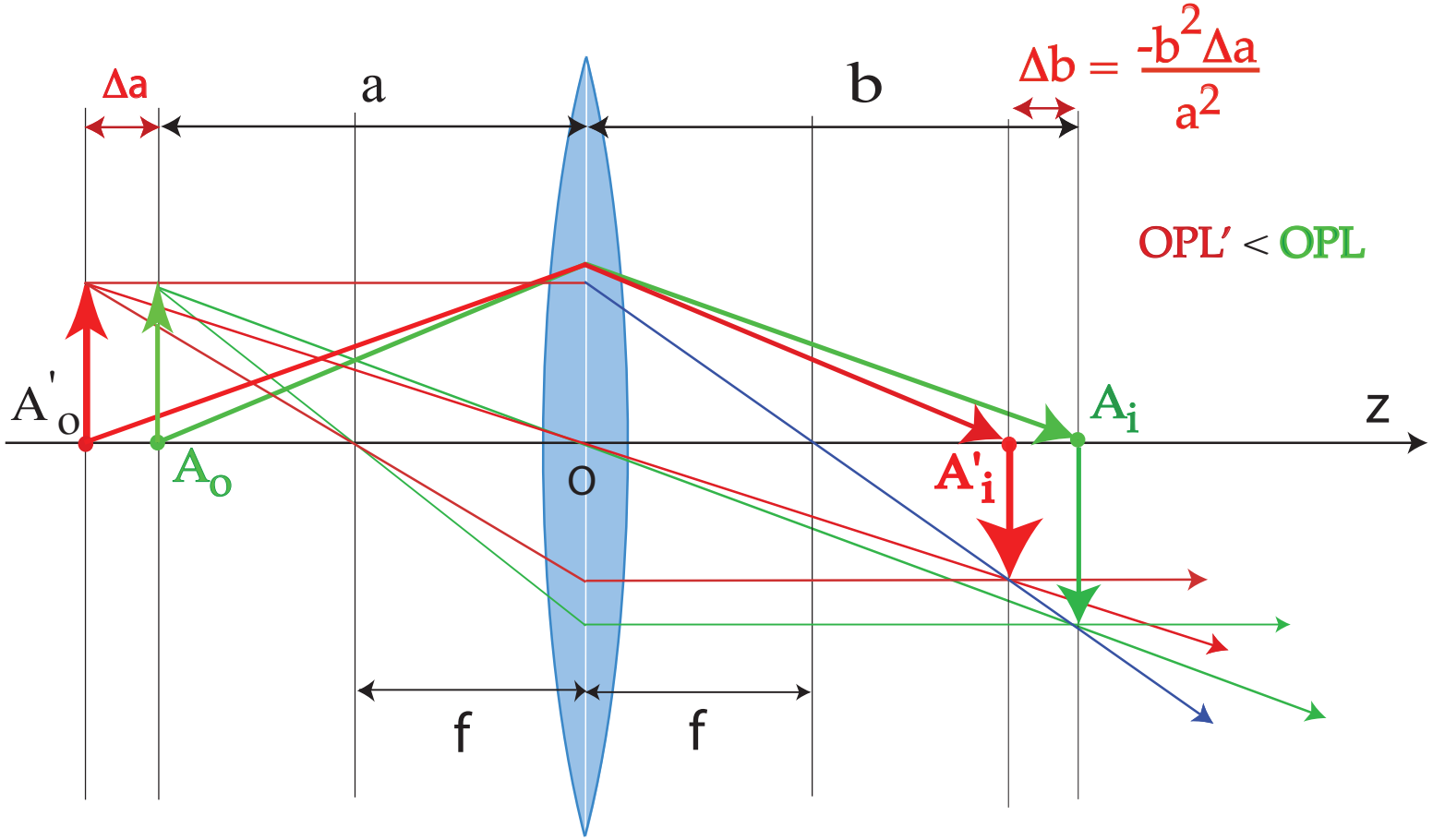
Optical Path Length: underfocus



Underfocus weakens the objective lens, i.e. increases f. As a consequence the OPL from A_o to A'_i is larger:

$$e^{2\pi i \frac{\Delta f \lambda (\vec{q}\cdot\vec{q})}{2}}$$

Optical Path Length: eccentricity



On the contrary keeping f constant and moving the object by Δa decreases the OPL.

Transfer by objective lens: $< q' | T(q', q) | q >$

Image forming system has 2 properties (Abbe theory):

- Linear.
- Space invariant.

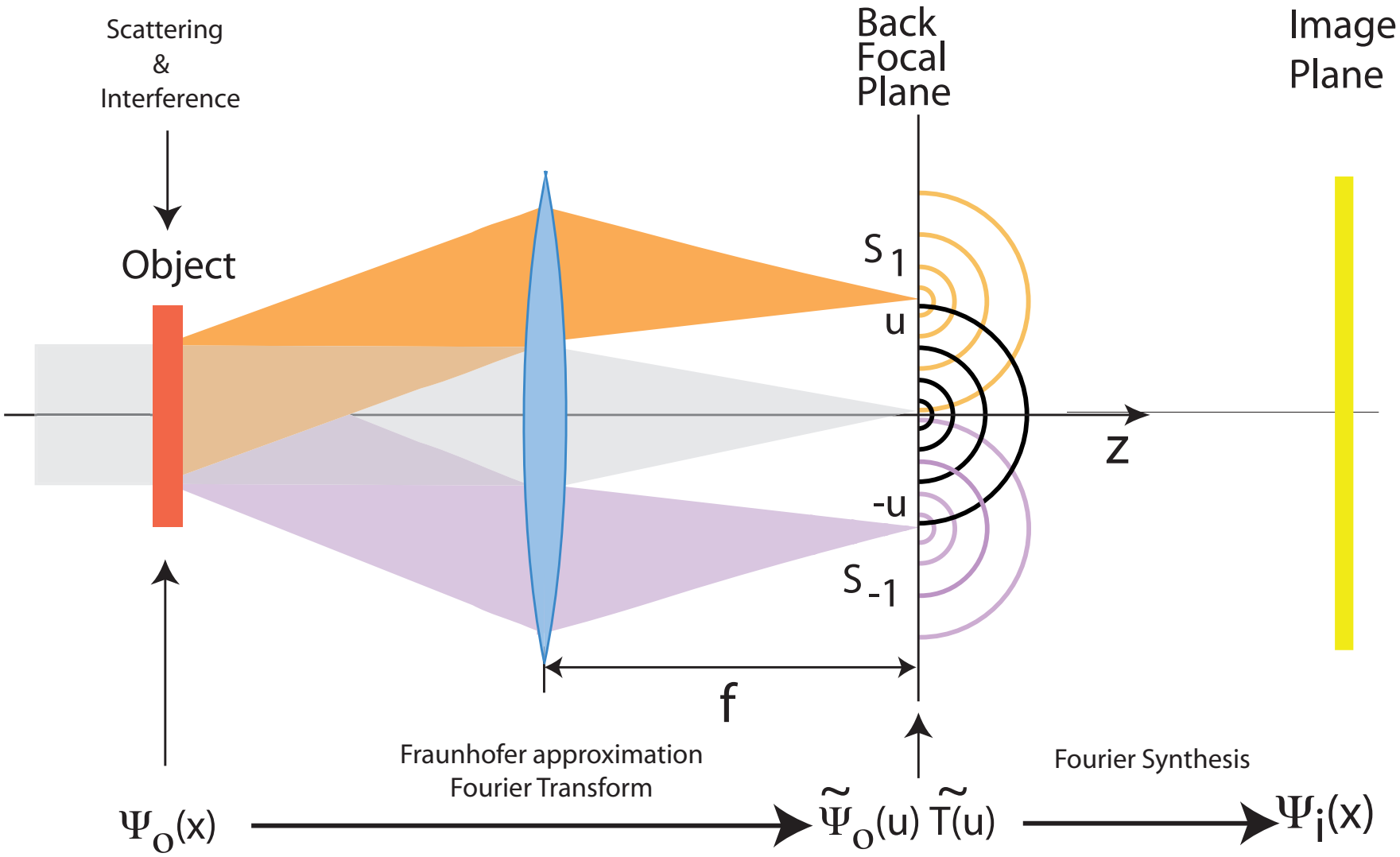
Coherence of illumination:

- Source size (spatial coherence).
- Energy spread (temporal coherence).

HRTEM: T (q', q) : transmission cross-coefficients $\Longrightarrow$ approximation by envelope functions.

Microscope modeling: Abbe image formation theory

Objective lens is modeled as a thin lens that brings Fraunhofer diffraction pattern at finite distance (i.e. in its Back Focal Plane).



Transfer function $T(\vec{q})$

$$T(\vec{q}) = e^{\chi(\vec{q})} = \cos(\chi(\vec{q})) + i \underbrace{\sin(\chi(\vec{q}))}_{\text{Contrast transfer function}}$$

$$\chi(\vec{q}) = \pi \left[W_{20}\, \lambda\, \vec{q}.\vec{q} + W_{40} \frac{\lambda^3 (\vec{q}.\vec{q})^2}{2} + ... \right]$$

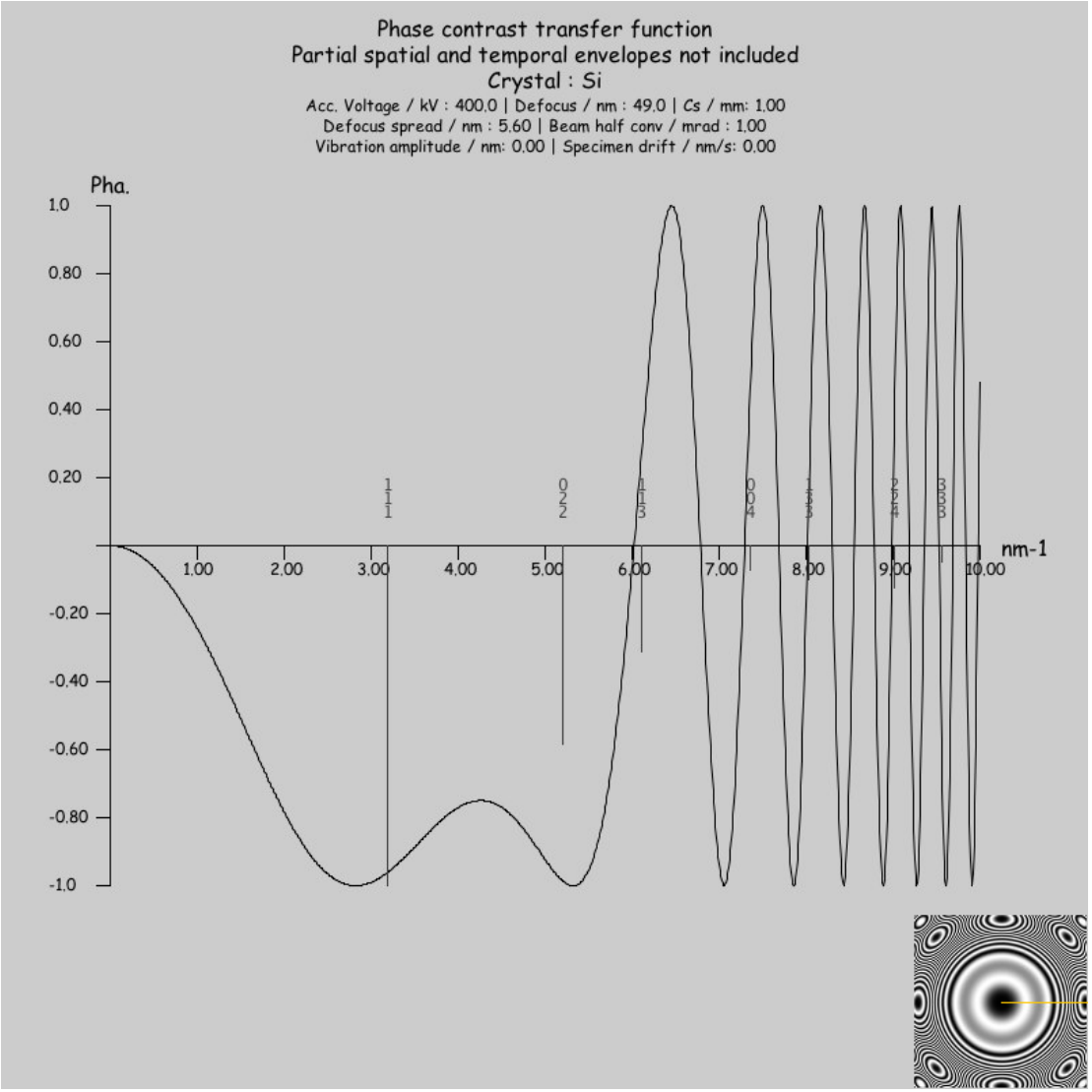
Where:

- W_{20} : defocus (z)
- W_{40}: spherical aberration (C_s)

Wavefront aberrations to 6^{th} order (cartesian coordinates)

$\{z, \pi\left(u^2+v^2\right)\lambda\}$ (*defocus*)
$\{W(1,1), 2\pi(u\cos(\phi(1,1))+v\sin(\phi(1,1)))\}$
$\{W(2,2), \pi\lambda((u-v)(u+v)\cos(2\phi(2,2))+2uv\sin(2\phi(2,2)))\}$
$\left\{W(3,1), \frac{2}{3}\pi\left(u^2+v^2\right)\lambda^2(u\cos(\phi(3,1))+v\sin(\phi(3,1)))\right\}$
$\left\{W(3,3), \frac{2}{3}\pi\lambda^2\left(u\left(u^2-3v^2\right)\cos(3\phi(3,3))-v\left(v^2-3u^2\right)\sin(3\phi(3,3))\right)\right\}$
$\left\{W(4,0), \frac{1}{2}\pi\left(u^2+v^2\right)^2\lambda^3\right\}$ (*spherical aberration*)
$\left\{W(4,2), \frac{1}{2}\pi\left(u^2+v^2\right)\lambda^3((u-v)(u+v)\cos(2\phi(4,2))+2uv\sin(2\phi(4,2)))\right\}$
$\left\{W(4,4), \frac{1}{2}\pi\lambda^3\left(\left(u^4-6v^2u^2+v^4\right)\cos(4\phi(4,4))+4u(u-v)v(u+v)\sin(4\phi(4,4))\right)\right\}$
$\left\{W(5,1), \frac{2}{5}\pi\left(u^2+v^2\right)^2\lambda^4(u\cos(\phi(5,1))+v\sin(\phi(5,1)))\right\}$
$\left\{W(5,3), \frac{2}{5}\pi\left(u^2+v^2\right)\lambda^4\left(u\left(u^2-3v^2\right)\cos(3\phi(5,3))-v\left(v^2-3u^2\right)\sin(3\phi(5,3))\right)\right\}$
$\left\{W(5,5), \frac{2}{5}\pi\lambda^4\left(u\left(u^4-10v^2u^2+5v^4\right)\cos(5\phi(5,5))+v\left(5u^4-10v^2u^2+v^4\right)\sin(5\phi(5,5))\right)\right\}$
$\left\{W(6,0), \frac{1}{3}\pi\left(u^2+v^2\right)^3\lambda^5\right\}$
$\left\{W(6,2), \frac{1}{3}\pi\left(u^2+v^2\right)^2\lambda^5((u-v)(u+v)\cos(2\phi(6,2))+2uv\sin(2\phi(6,2)))\right\}$
$\left\{W(6,4), \frac{1}{3}\pi\lambda^5\left(\left(u^6-5v^2u^4-5v^4u^2+v^6\right)\cos(4\phi(6,4))+4uv\left(u^4-v^4\right)\sin(4\phi(6,4))\right)\right\}$
$\left\{W(6,6), \frac{1}{3}\pi\lambda^5\left(\left(u^6-15v^2u^4+15v^4u^2-v^6\right)\cos(6\phi(6,6))+2uv\left(3u^4-10v^2u^2+3v^4\right)\sin(6\phi(6,6))\right)\right\}$

Contrast transfer function: $\sin(\chi(\vec{q}))$



The transfer function of the objective lens in the absence of lens current and accelerating voltage fluctuations (Scherzer defocus). The (111) and (022) reflections of Si are phase shifted by $-\frac{\pi}{2} \rightarrow$ black atomic columns.

HRTEM image intensity: WPOA

In the Weak Phase Object Approximation under optimum transfer conditions the image intensity $I(\vec{x})$ is:

- positive C_s (black atomic columns)

$$I(\vec{x}) \sim 1 - 2\sigma V_p(\vec{x})$$

- negative C_s (white atomic columns)

$$I(\vec{x}) \sim \sigma V_p(\vec{x})$$

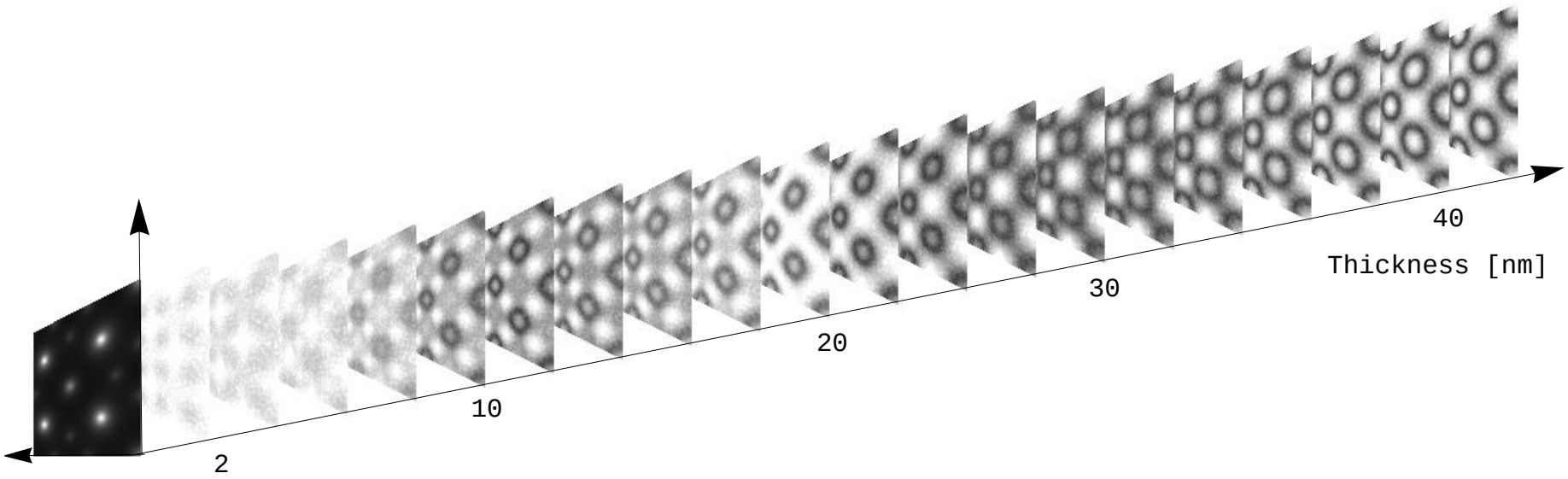
Where:

$$V_p(\vec{x}) : \text{projected potential}$$

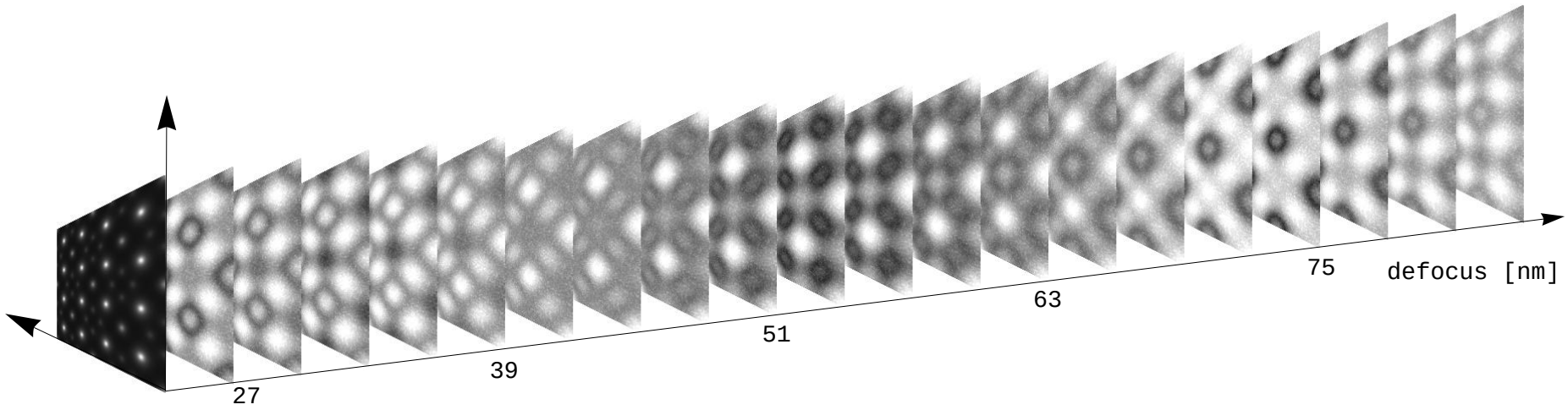
$$\sigma : \text{electron matter interaction constant}$$

HRTEM image depends on specimen thickness and object defocus

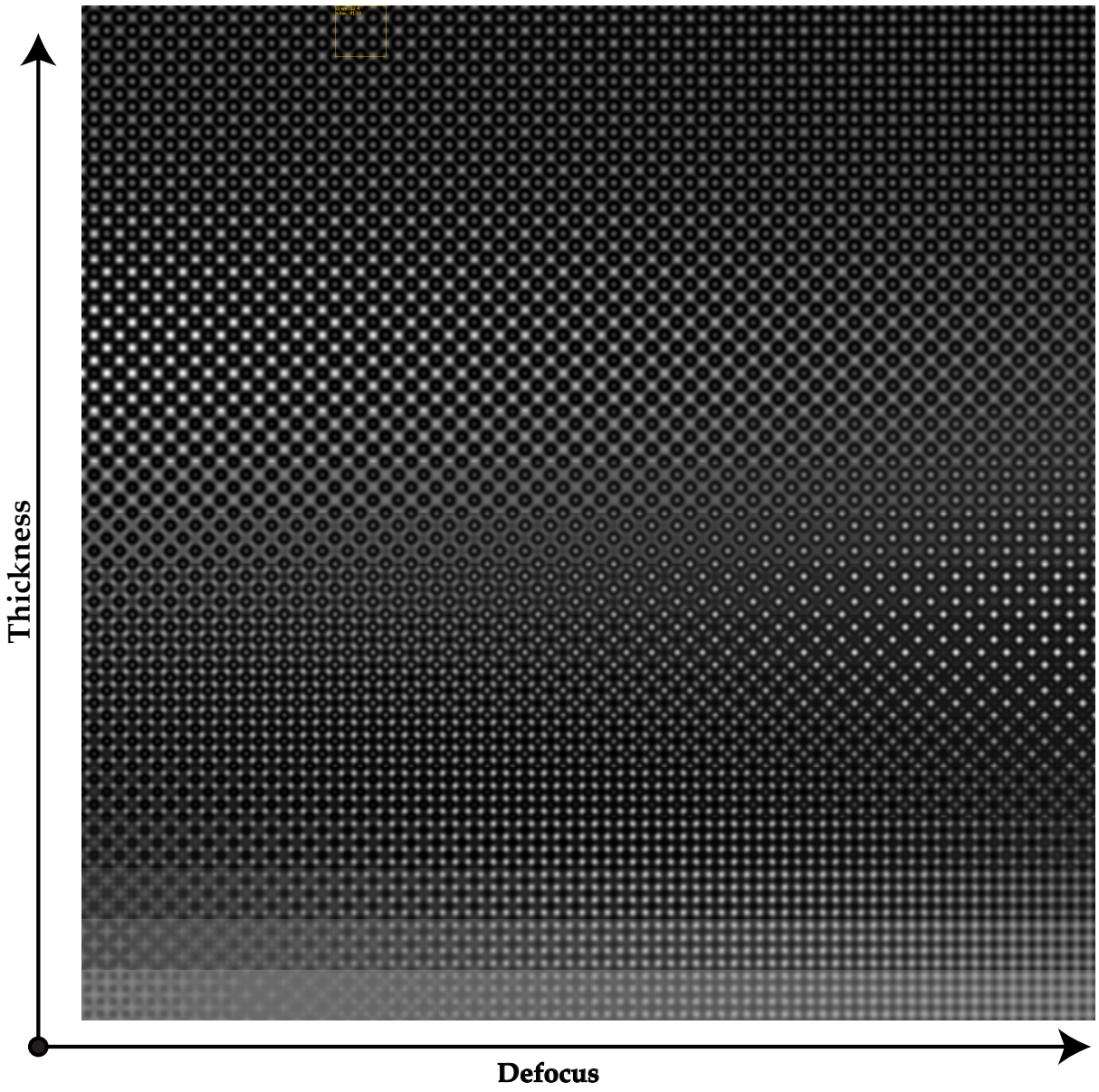
Thickness series



Defocus series



Si [001] images map: contrast dependence of defocus & thickness



HREM map does not include the Modulation Transfer Function (MTF) of the detector.

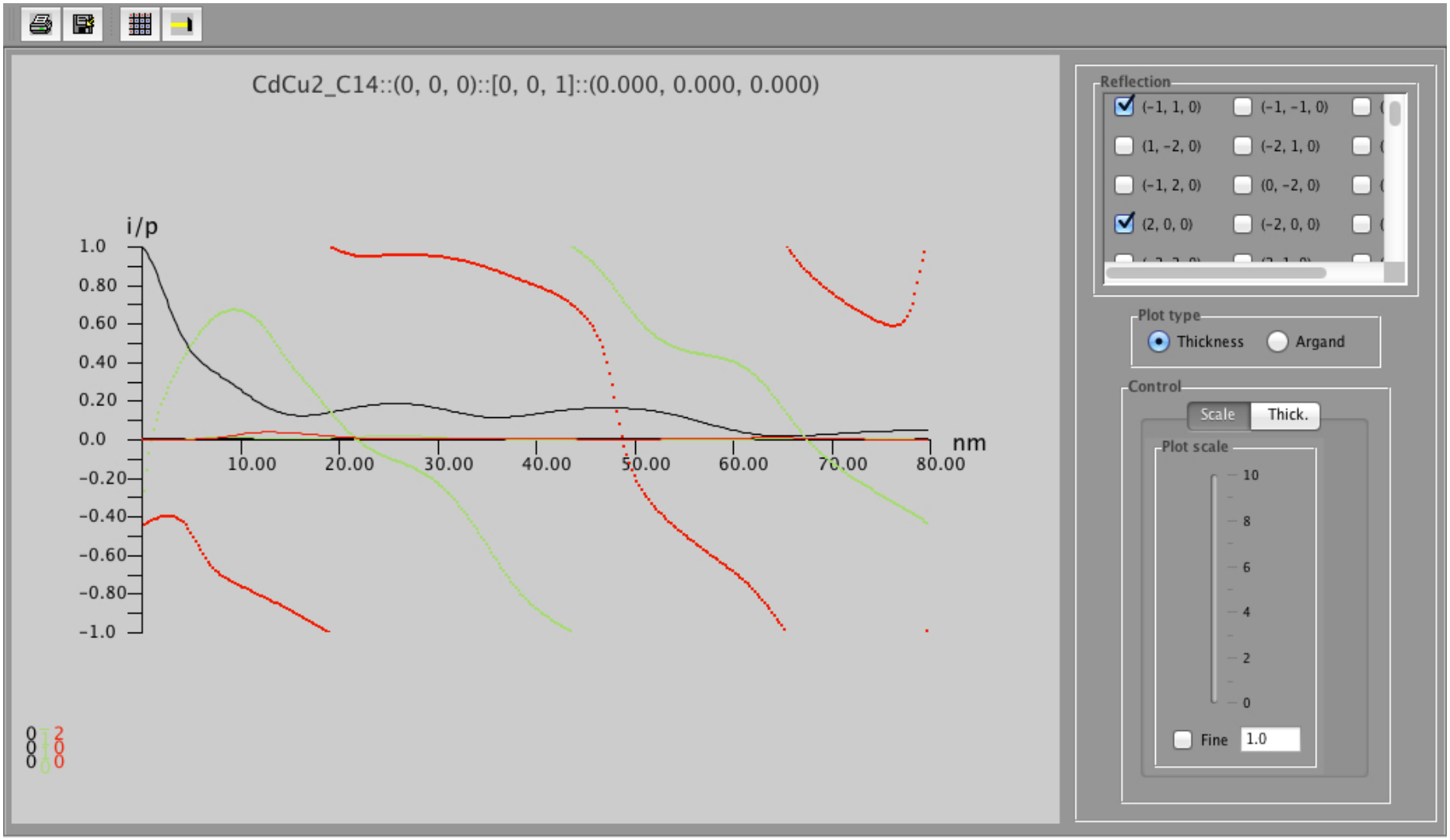
Problems

Problems...

- Object
  - → Atomic scattering amplitude below 50 kV?
  - → Potential by DFT calculation?
  - ...
- HRTEM → Phase of diffracted beams evolves with specimen thickness.
- HRTEM → MTF of image acquisition system (Stobbs factor?).
- HRTEM / HRSTEM → Electron channeling depends on atomic column content.
- HRTEM / HRSTEM → Aberrations of optical system.
- HRTEM → Inelastic scattering (J.M. Cowley, E.J. Kirkland, D. van Dyck, A. Rosenaurer, K. Ishizuka, Z.L. Wang, H. Rose, H. Mueller, L. Allen, ...).
- HRTEM / HRSTEM → Drift, vibration, Johnson-Nyquist noise[13], ...
- ...

[13] S. Uhlemann, H. Mueller, P. Hartel, J. Zach & M. Haider, Phys. Rev. Lett. **111** (2013) 046101.

HRTEM problem: amplitude and phase of diffracted beams



Note that phase of diffracted beam is $\frac{\pi}{2}$ out-of-phase with respect to transmitted beam.

HRTEM problem: CCD MTF (Gatan MSC 1K x 1K, 24 μm)

To make quantitative comparison with experimental HRTEM images the MTF of the detector must be introduced in the simulation.

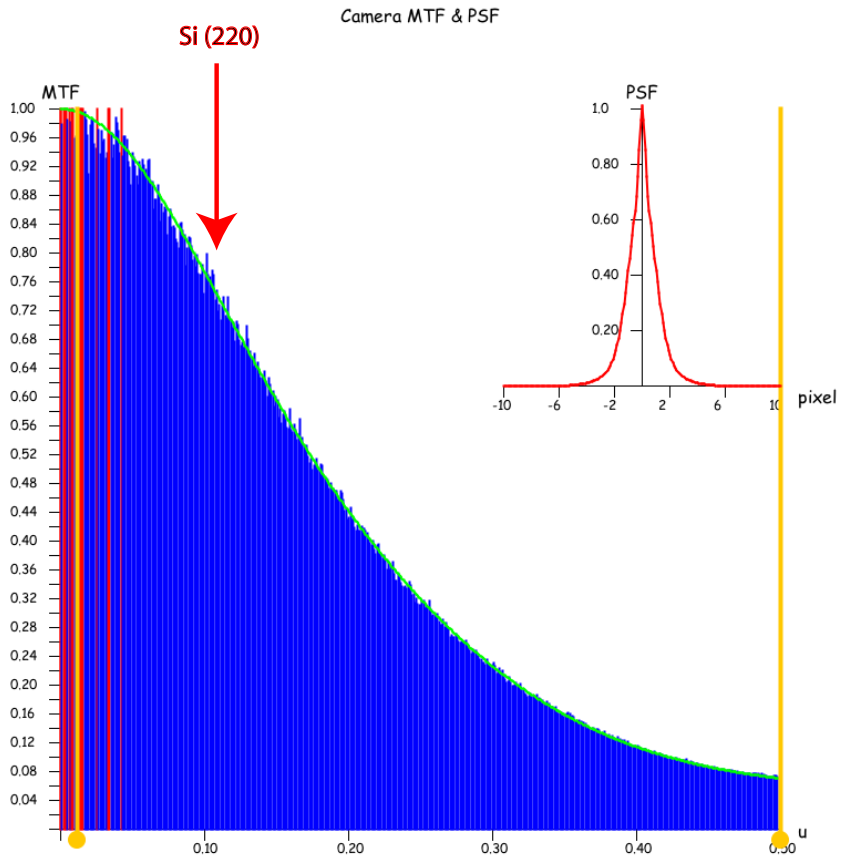


Figure: At high magnification Si (220) planes imaged with high contrast.

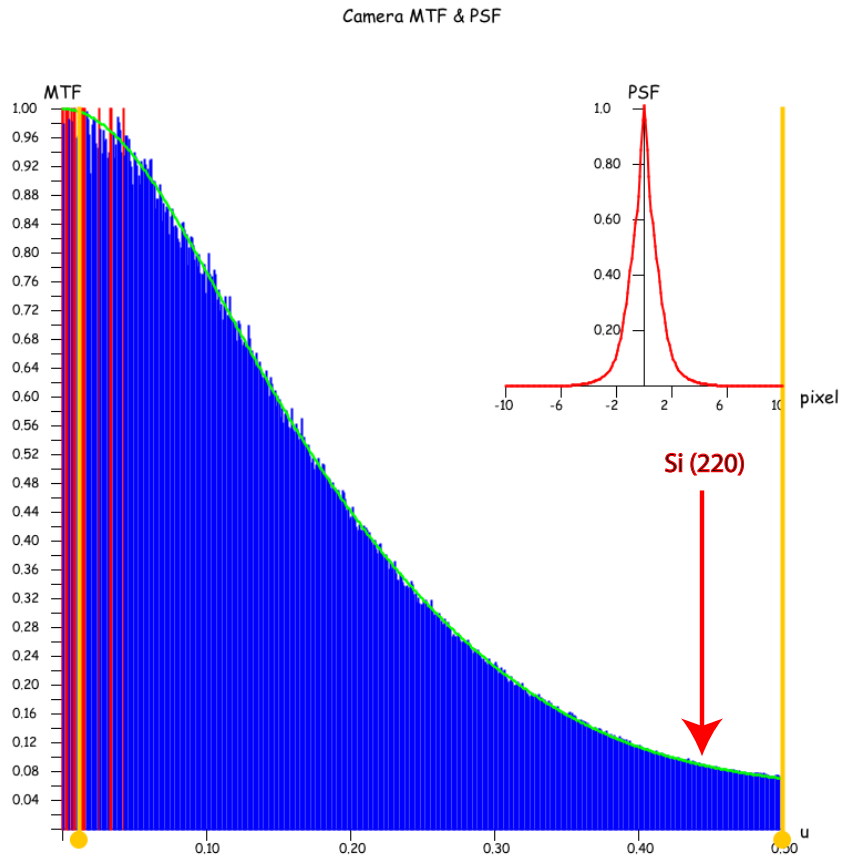


Figure: At low magnification Si (220) planes imaged with low contrast.

For quantitative comparison always use highest possible magnification (or include CCD MTF in simulations)!

CCD MTF: high magnification (900 kx)

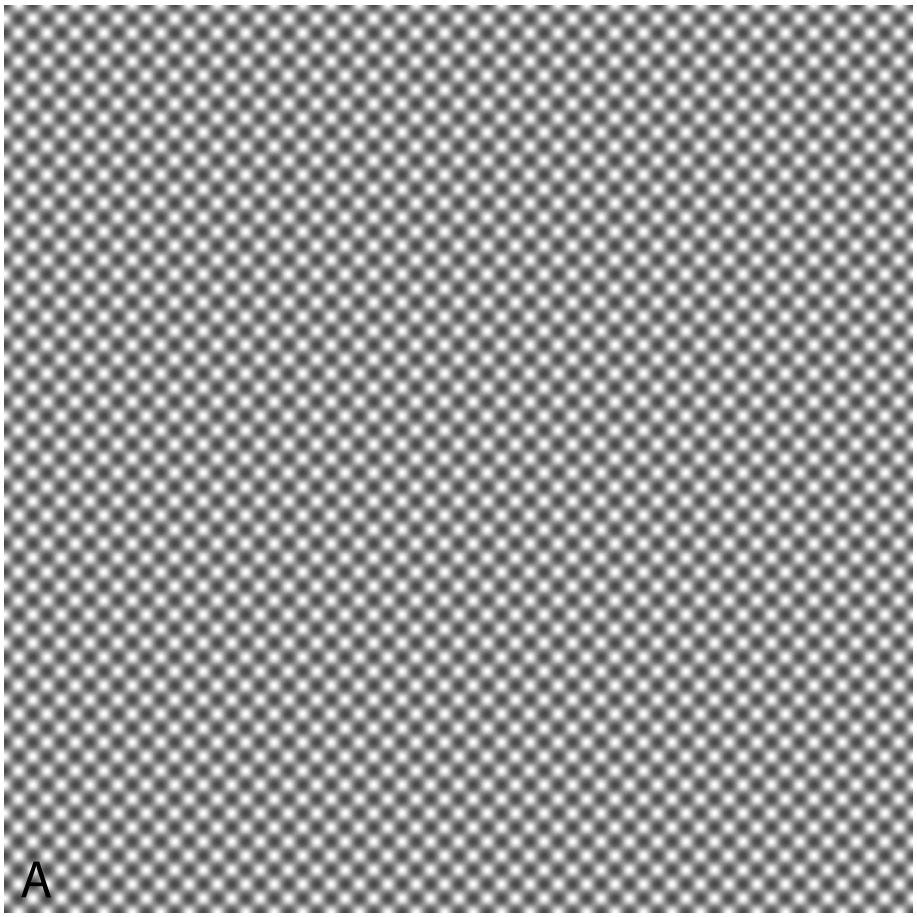


Figure: A: Si [001] simulation.

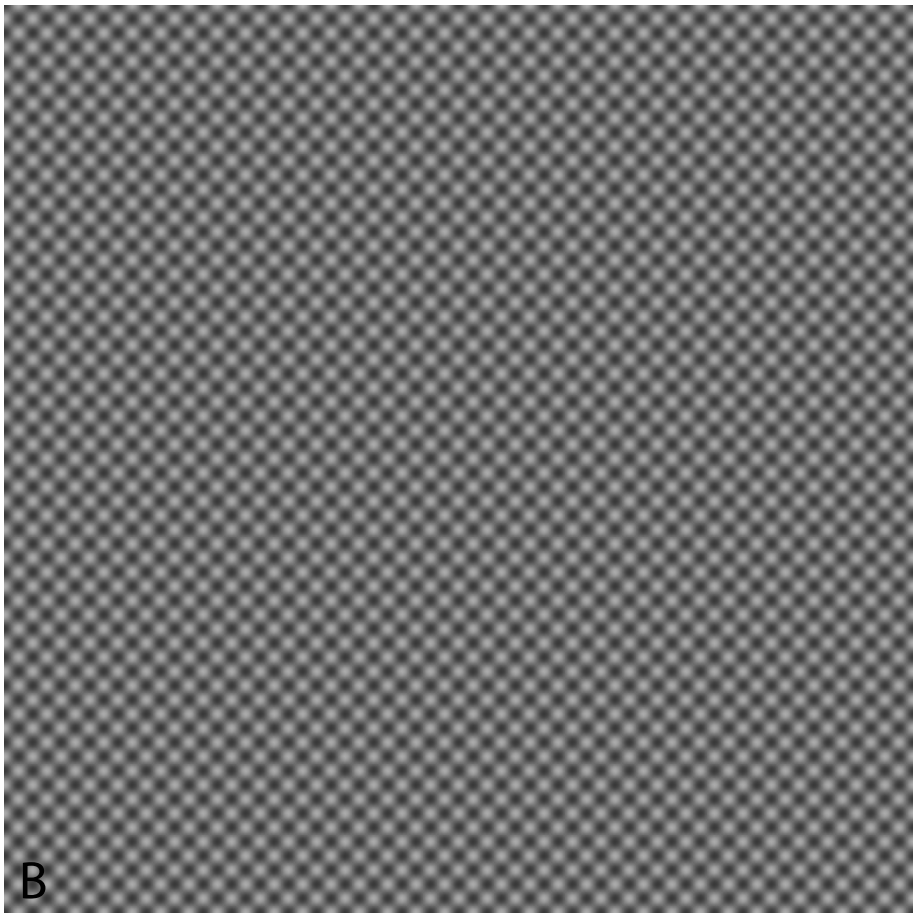


Figure: B: Si [001], simulation + CCD MTF.

CCD MTF: low magnification (225 kx)

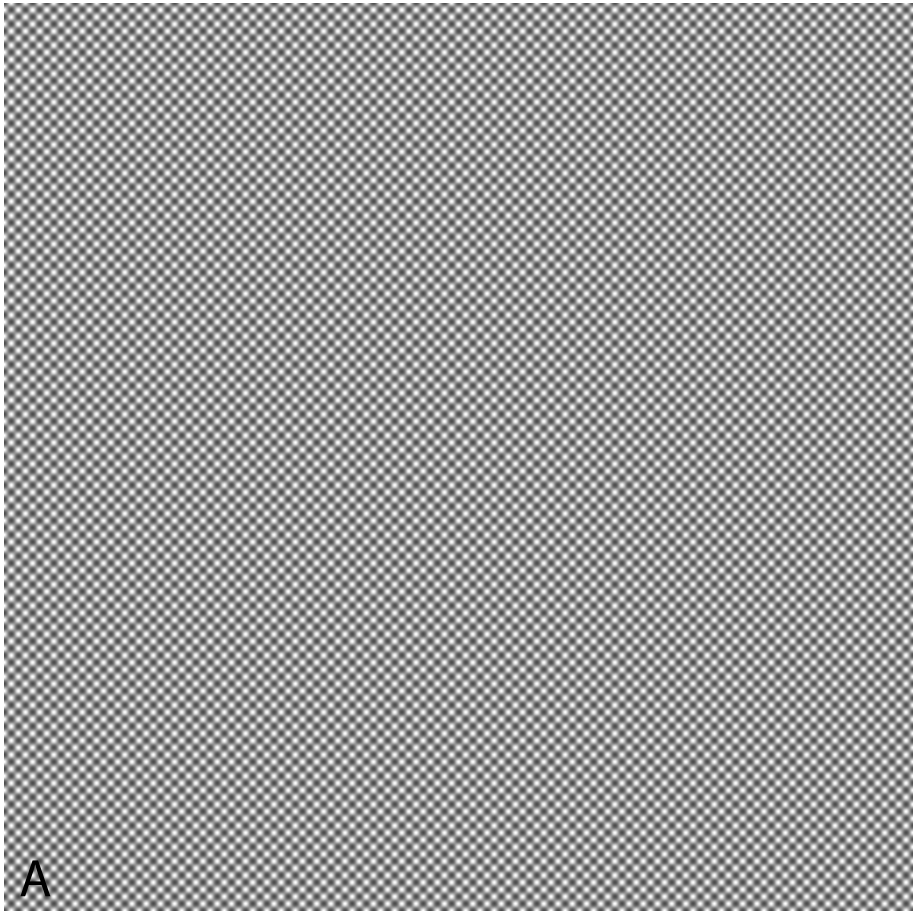


Figure: A: Si [001] simulation.

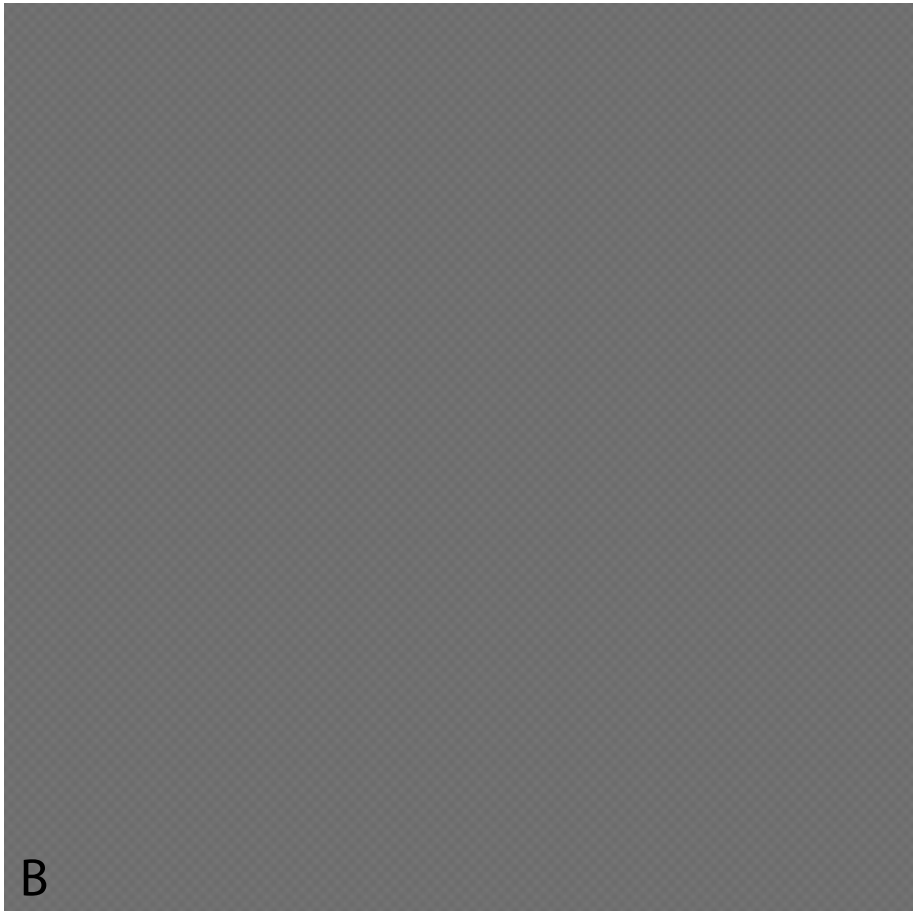


Figure: B: Si [001], simulation + CCD MTF.

HRTEM / HRSTEM problem: electron channeling (ZnTe [110])

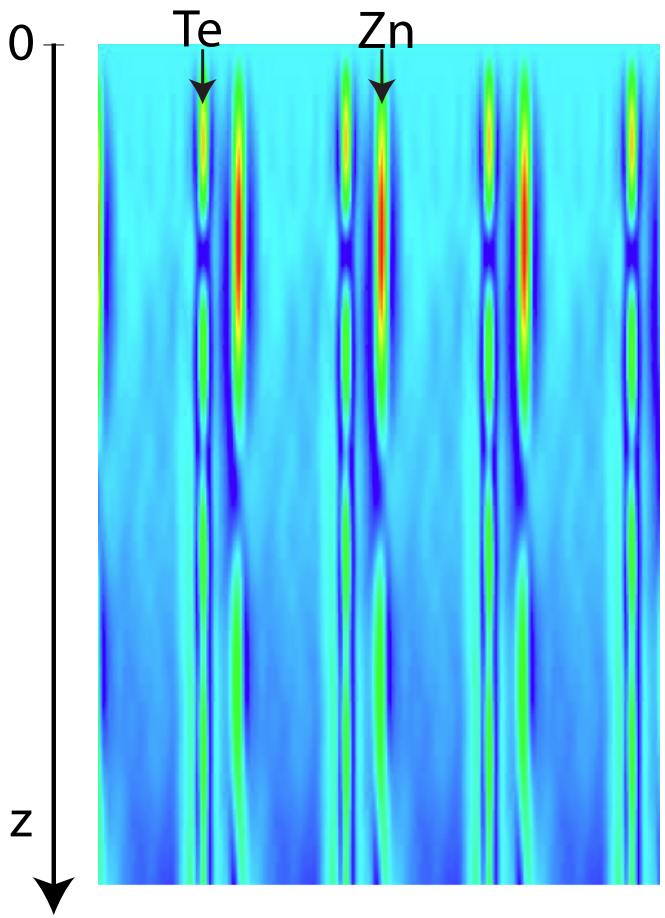
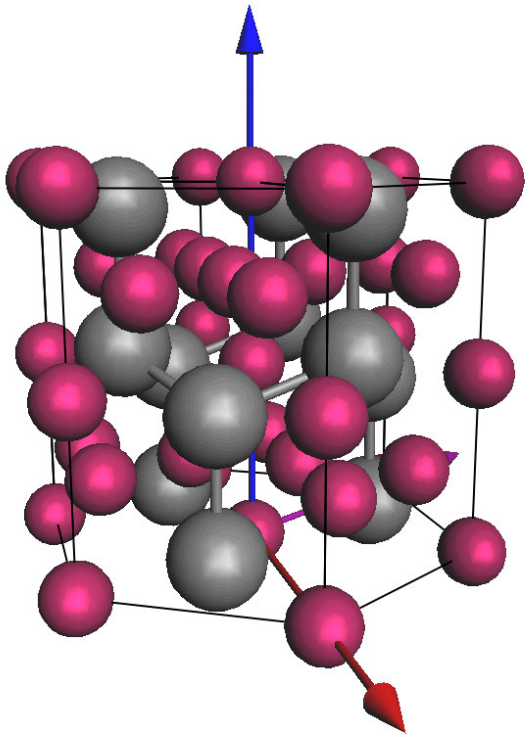


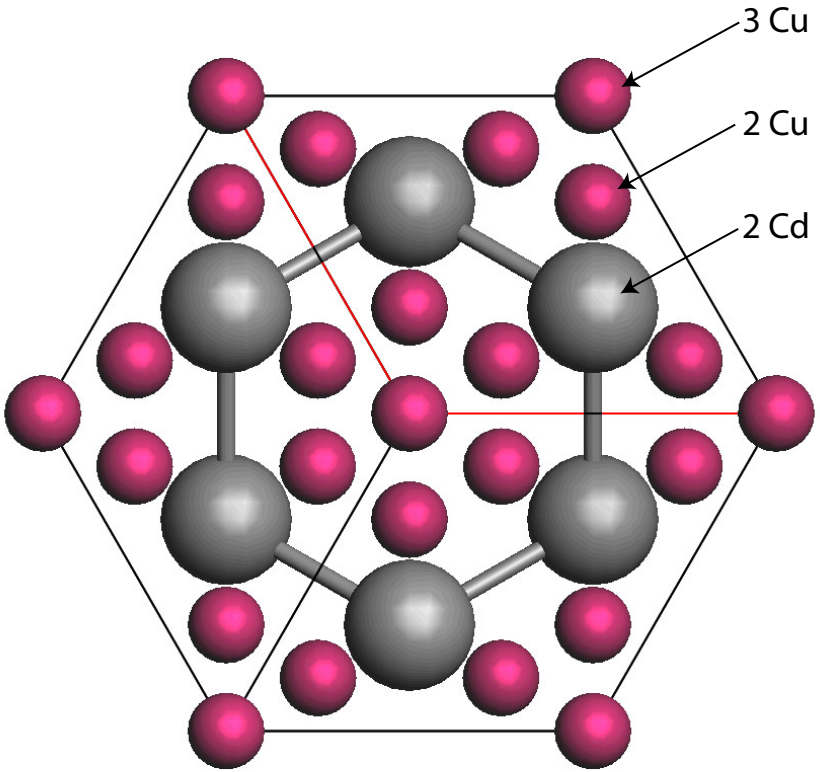
Figure: ZnTe [110] wave function intensity.

Channeling explains several features of HRTEM and STEM images (i.e. appearance / disappearance of contrast of impurities).

Does C_s and C_c correction solves all imaging problems?

Example: CdCu_2, visibility of the 3 Cu atomic columns.



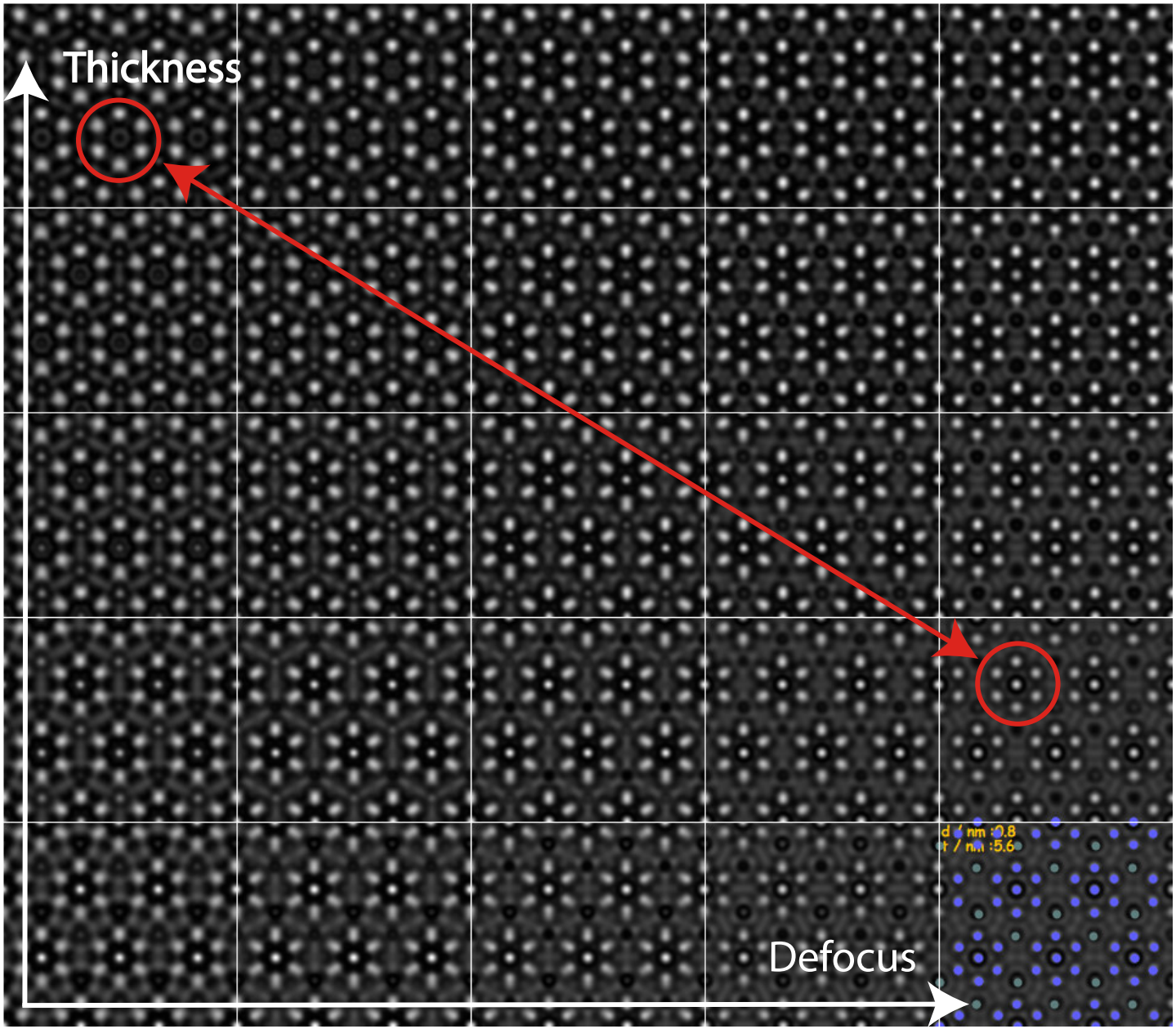


HRTEM image simulation conditions

Acc. [kV]	$C_s[mm]$	$C_5[mm]$	$C_c[mm]$	$\Delta E[eV]$	Z [nm]	$\Delta z[nm]$
300	-0.008	30	0.5	0.6	-4.9	1
300	-0.008	30	0.1	0.2	-2.0	1

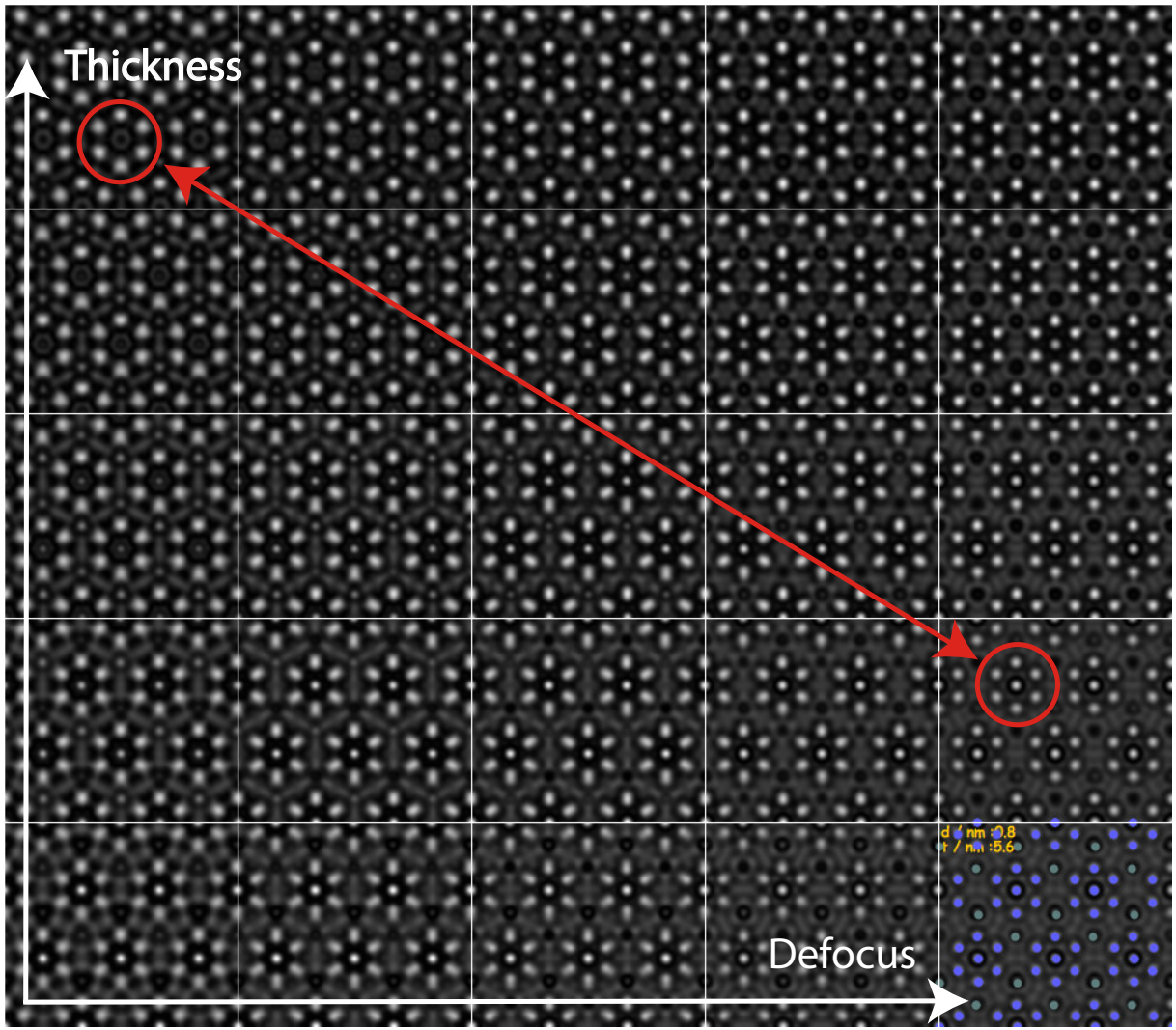
Dynamical scattering effects are not affected by C_s and/or C_c corrected TEM!

$CdCu_2[001]$: imaging parameters set 1



Visibility of 3 Cu atomic columns depends on specimen thickness and defocus.

$CdCu_2[001]$: imaging parameters set 2



Improving C_c and ΔE does not affect the visibility of 3 the Cu atomic columns. It depends on specimen thickness (and defocus indeed). Visibility of the 3 Cu atomic columns is always affected by dynamical scattering. Only extremely thin specimen ($\leq$ 10 nm) will allow faithful imaging of crystal projected potential.

STEM HAADF imaging

High Angle Annular Dark Field (HAADF): inelastically scattered electrons.

When simulation is necessary how to simulate images?

Numerous approximations:

- Simple projected + convolution with probe intensity: no channeling effect (Weak Object Approximation).
- Multislice calculation: channeling + inelastic scattering (absorption potential) + convolution with probe intensity.
- Frozen lattice (phonon) approximation: atoms of super-cell displaced out of equilibrium position, probe scanned on imaged area, intensity collected by annular detector.
- Pennycook, Nellist, Ishizuka, Shiojiri, Allen, Wang, Rosenauer, van Dyck, ...

Except the first 2 methods, simulation time expensive (luxury?). Approximations (necessity) may suffice...

HAADF: graphene

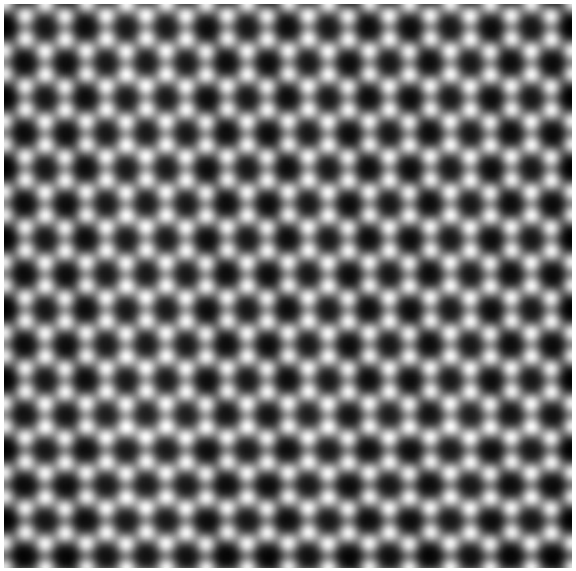


Figure: Proj. pot. approx.

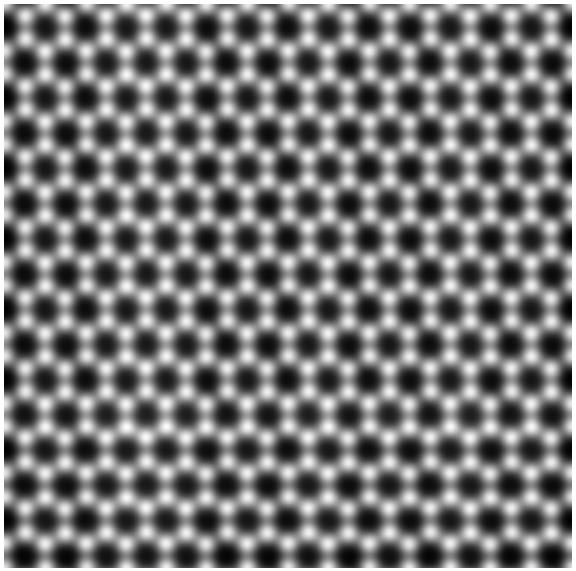


Figure: Channeling calculation.

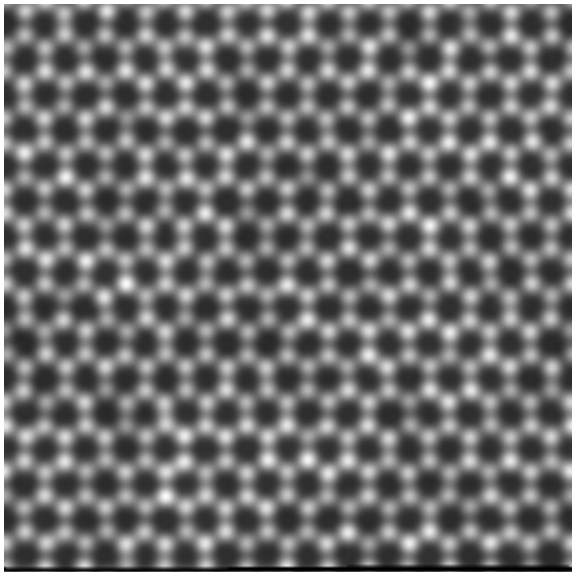


Figure: Frozen lattice 5 conf.

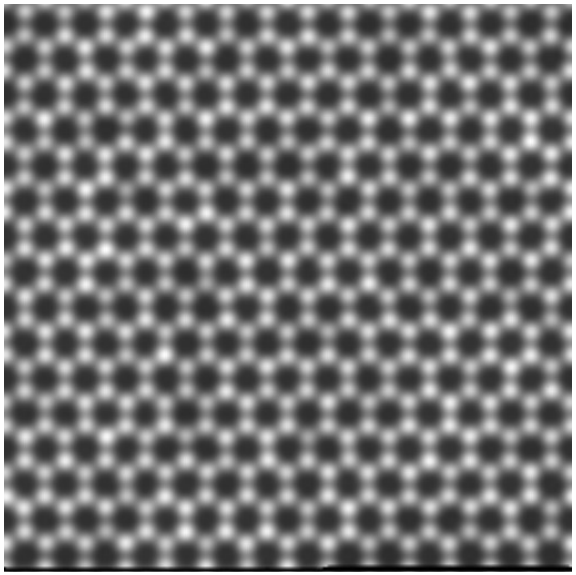


Figure: Frozen lattice 10 conf.

HRSTEM - HRTEM comparison: graphene with add atoms

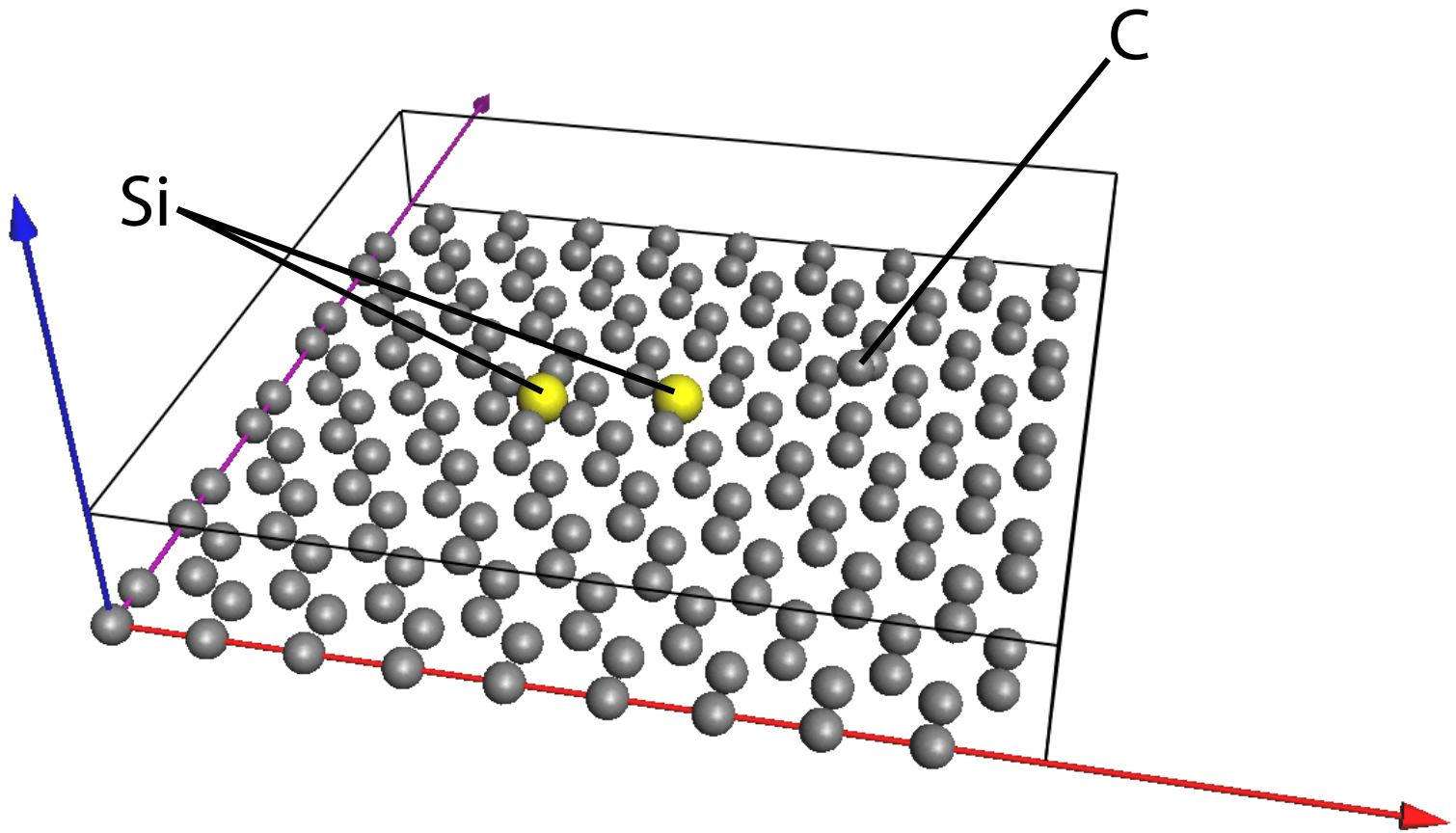


Figure: Graphene with Si in 6 C ring, Si substitutional and 2 C column.

Graphene HAADF (100 kV, 70 -150 mrad)

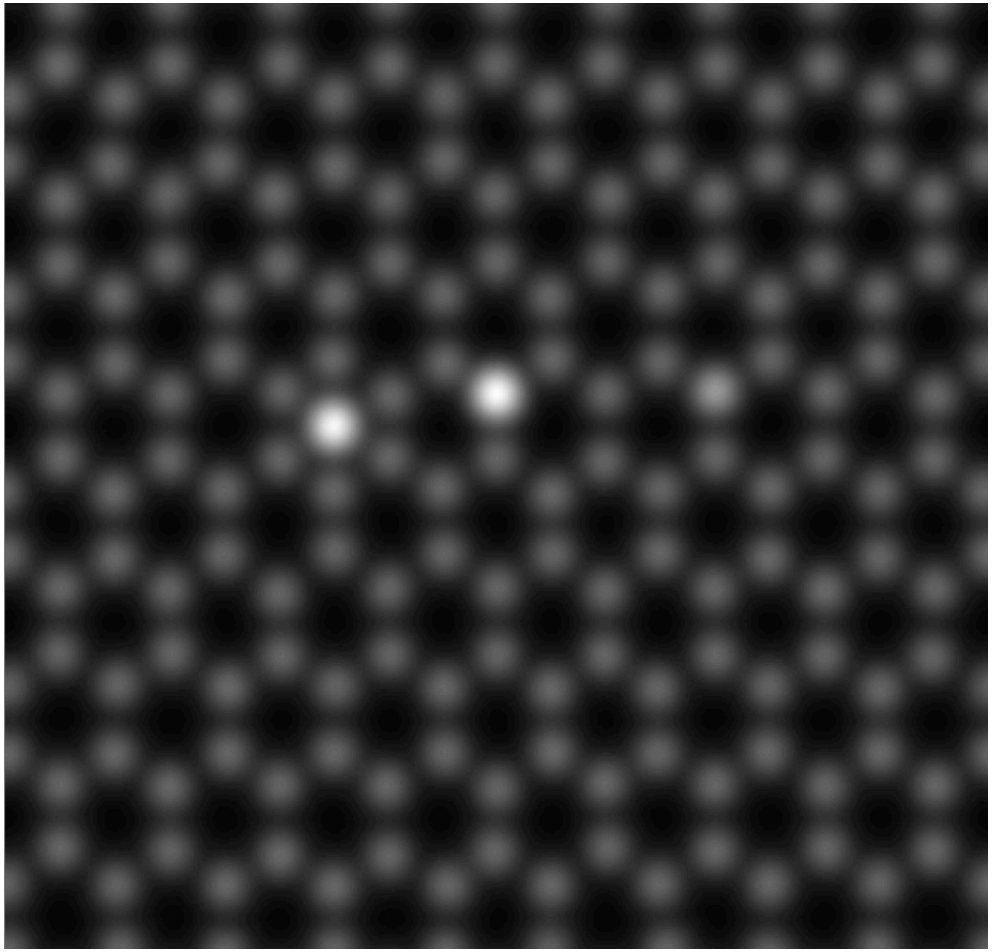


Figure: Frozen lattice (∼400 s).

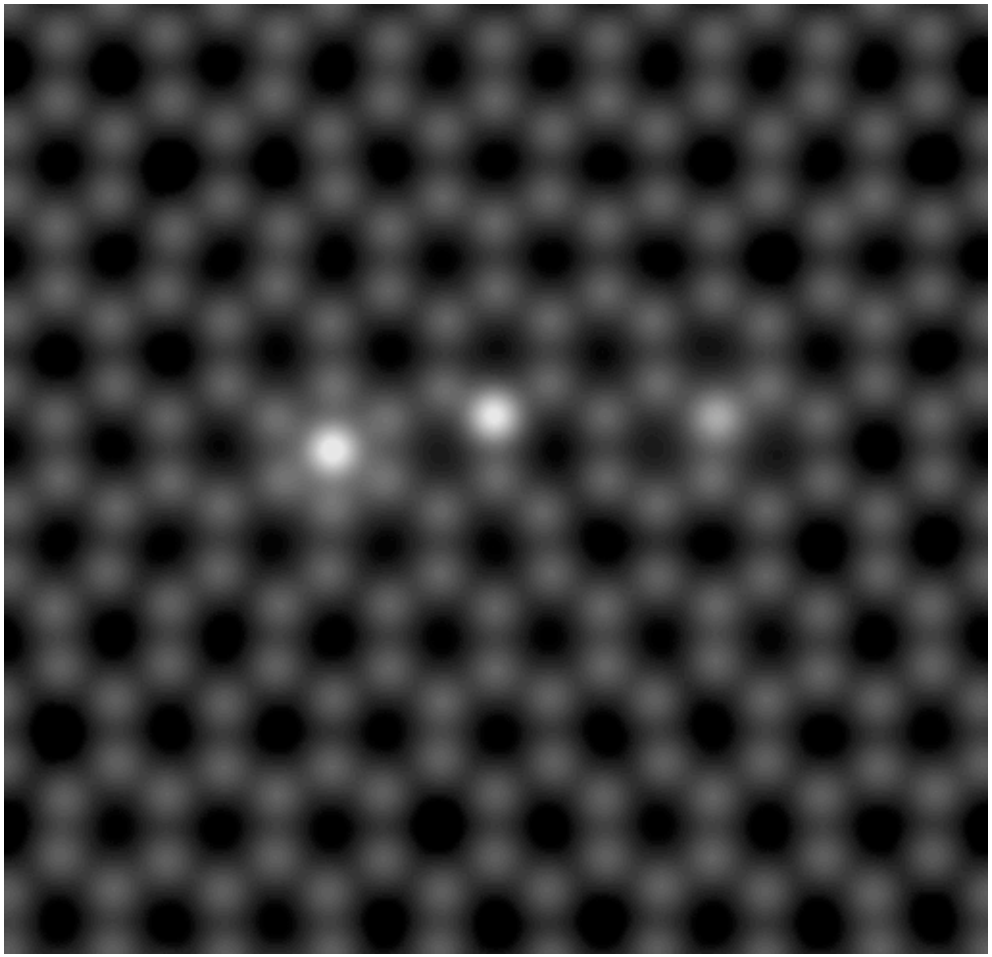


Figure: Channeling (∼2 s).

One Si shows more contrast than 2 C atoms (i $\sim Z^2$) : 14^2 compared to $\sim 2 \times 6^2$.

Graphene HRTEM (100 kV, $C_s - 0.033mm$)

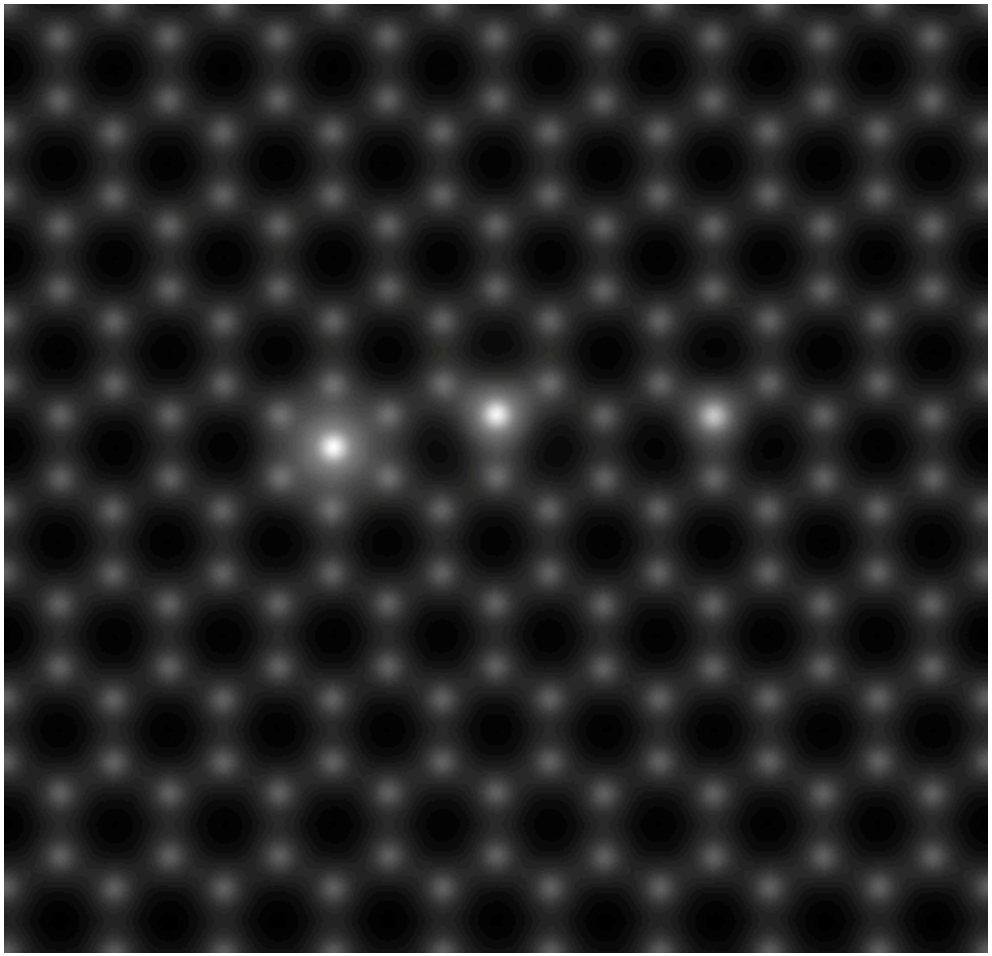


Figure: Weak phase object app., $C_c = 0.5mm$

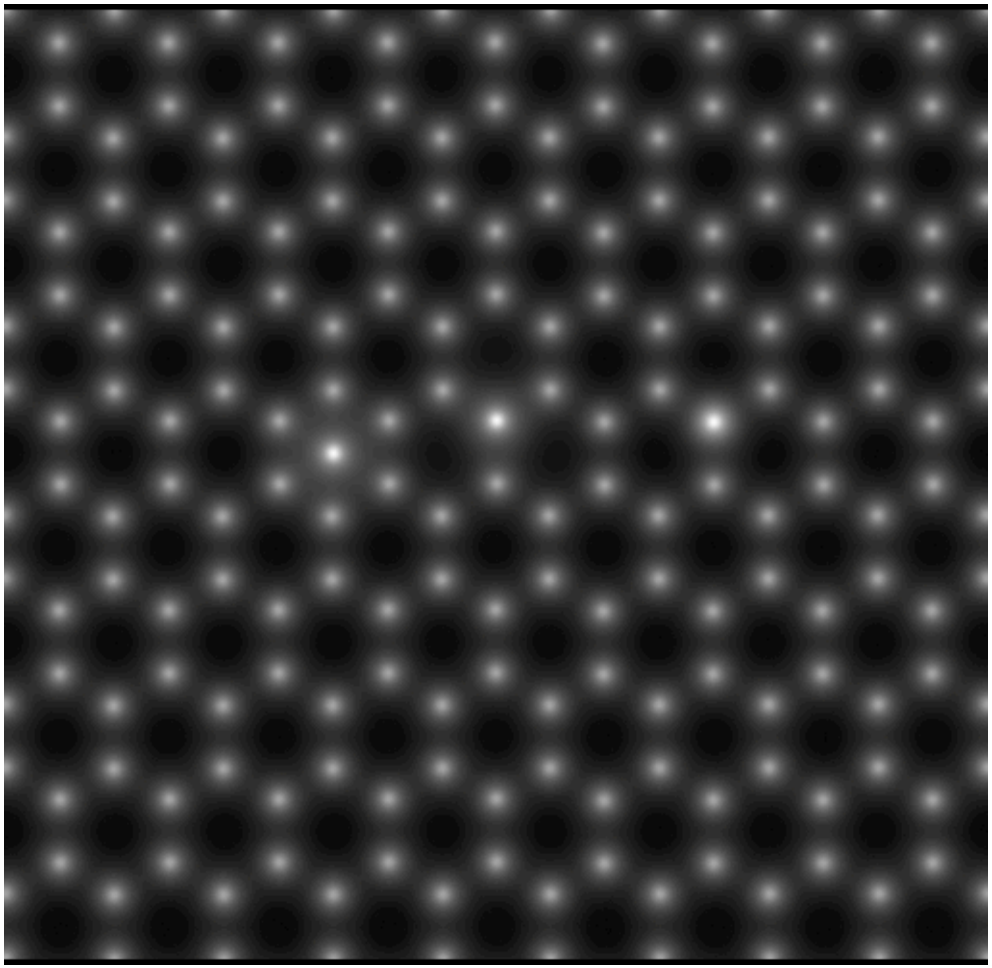


Figure: Multislice, $C_s = -0.033mm$, $C_c = 0$, no thermal magnetic noise.

HRTEM does not display the strong contrast difference between one Si and two C as given by HAADF.

Quantitative HR(S)TEM

No doubt that image simulation necessary for quantitative work[14].

- Exit wave function recovery using focal series reconstruction.
- Transport of intensity equation.

But... can also be used for teaching or planing HRTEM/HRSTEM observations.

[14] K. W. Urban, Science **321** (2008) 506.

HRTEM / HRSTEM problem: aberrations of optical system

Reaching 0.05 nm resolution sets very strong conditions on aberrations correction.

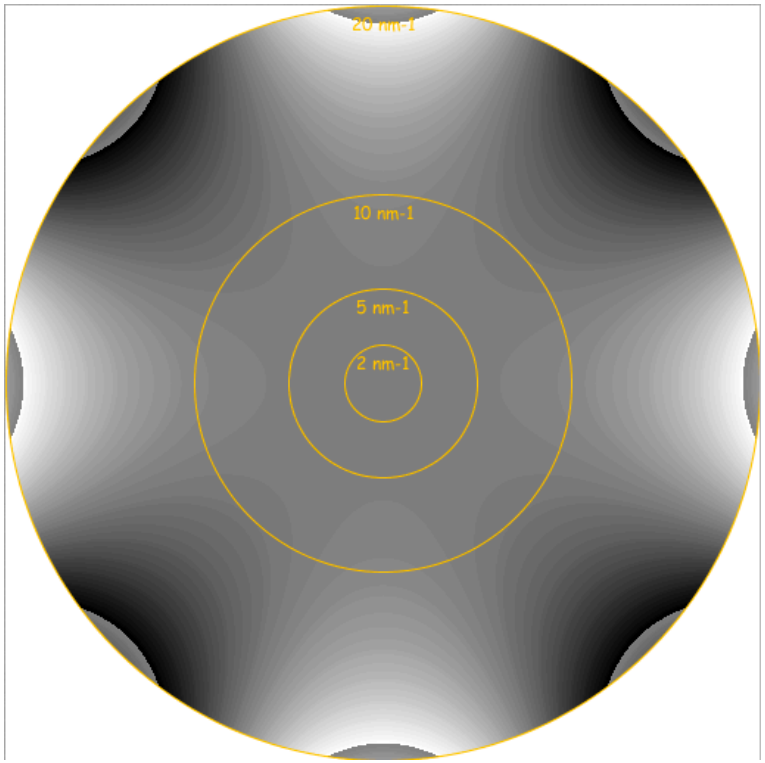


Figure: Aberration figure of $C_{34}(0.5\mu\text{m})$, phase jump at $\frac{\pi}{4}$.

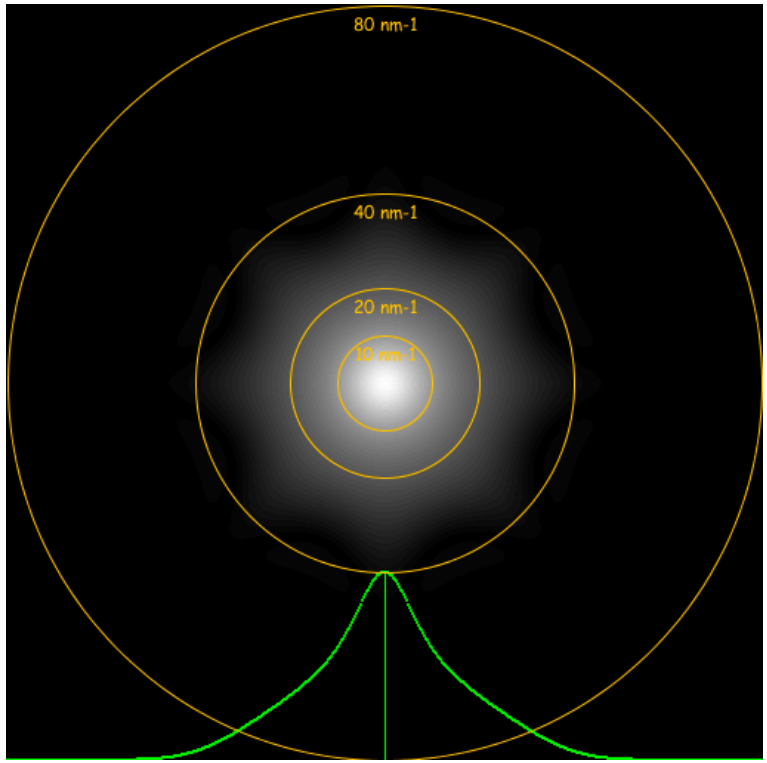


Figure: Optical Transfer Function.

Note that Optical Transfer Function (HRSTEM) transfers higher spatial frequencies than Ccoherent Transfer Function (HRTEM).

To conclude...

$\rightarrow$ Let's look at perfect microscopes!

Dynamical theory of elastic scattering of high energy electron

We aim to understand in details multiple elastic scattering of electrons by crystals.

- High energy electron (eE).
- Periodic interaction potential $V(\vec{r})$.
- Time independent flux of incident electrons.

The fundamental equation of electron elastic scattering by a potential $V_v\,[Volt]$(positive inside a crystal) in the approximation of a stationary flux of electrons of a given energy $e\,E$ is the Schrödinger equation ([**?**]):

$$\triangle\Phi(\vec{r}) + \frac{2me}{\hbar^2}[E + V_v(\vec{r})]\Phi(\vec{r}) = 0$$

With a change of notation its is written as:

$$[\triangle + 4\pi^2 K_i^2]\ \Phi(\vec{r}) = -4\pi^2 V_v(\vec{r})\ \Phi(\vec{r})$$

Where the wavevector $|\vec{K}_i|$ of the incident electrons is given by:

$$|K_i| = \frac{\sqrt{2meE}}{h}$$

and

$$m = \gamma\ m_0$$

Schrödinger equation

The Laplacian $\triangle = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is written as: $\triangle_\rho + \frac{\partial^2}{\partial z^2}$. As a result, $[\triangle + ...]e^{2\pi\imath k_z z}\Psi(\rho; z)$ is given by: $[\triangle_\rho + \frac{\partial^2}{\partial z^2} + ...]e^{2\pi\imath k_z z}\Psi(\rho; z)$.
Performing the z-differentiation:

$$\frac{\partial^2}{\partial z^2}e^{2\pi\imath k_z z}\Psi(\rho; z) = e^{2\pi\imath k_z z}[-4\pi^2 k_z^2 + 4\pi\imath k_z\frac{\partial}{\partial z} + \frac{\partial^2}{\partial z^2}]\Psi(\rho; z)$$

Inserting the last expression and dropping the term $e^{2\pi\imath k_z z}$:

$$[\triangle_\rho + 4\pi^2(K_i^2 - k_z^2 + V(\rho; z)) + 4\pi\imath k_z\frac{\partial}{\partial z} + \frac{\partial^2}{\partial z^2}]\Psi(\rho; z) = 0$$

Since $K_i^2 = k_z^2 + \chi^2$:

$$[\triangle_\rho + 4\pi^2\chi^2 + 4\pi^2 V(\rho; z) + 4\pi\imath k_z\frac{\partial}{\partial z} + \frac{\partial^2}{\partial z^2}]\Psi(\rho; z) = 0$$

Rearranging the last equation:

$$\imath\frac{\partial\Psi(\rho; z)}{\partial z} = -\frac{1}{4\pi k_z}[\triangle_\rho + 4\pi^2\chi^2 + 4\pi^2 V(\rho; z) + \frac{\partial^2}{\partial z^2}]\Psi(\rho; z)$$

Fundamental equation

$$\imath\frac{\partial\Psi(\rho;z)}{\partial z} = -\frac{1}{4\pi k_z}[\triangle_\rho + 4\pi^2\chi^2 + 4\pi^2 V(\rho;z) + \frac{\partial^2}{\partial z^2}]\Psi(\rho;z)$$

The term $|\frac{\partial^2\Psi(\rho;z)}{\partial z^2}|$ being much smaller than $|k_z\frac{\partial\Psi(\rho;z)}{\partial z}|$ we drop it (this is equivalent to neglect backscattering).

Fundamental equation of elastic scattering of high energy mono-kinetic electrons with a potential within the approximation of small angle scattering:

$$\imath\frac{\partial}{\partial z}\Psi(\rho;z) = -\frac{1}{4\pi k_z}[\triangle_\rho + 4\pi^2\chi^2 + 4\pi^2 V(\rho;z)]\Psi(\rho;z)$$

Time dependent Schrödinger equation $\Longrightarrow$ solution by many methods of quantum mechanics!

Remarks

- The approximations of the fundamental equation are equivalent to assume that the scattering potential is small compared to the accelerating potential and that k_z varies only slightly with z. It is in fact a quite good approximation, since the mean crystal potential is of the order of $10 - 20\ V$.
- Electron backscattering is neglected, the electron are moving forwards.
- The fundamental equation is actually equivalent to a 2-dimensional Schrödinger equation ($\rho = \{x, y\}$) where z plays the role of time. The system evolution is causal, from the past to the future.

Fundamental equation in Hamiltonian form:

$$\imath \frac{\partial}{\partial z} \Psi = H\ \psi$$

where:

$$H = -\frac{1}{4\pi k_z}[\triangle_\rho + 4\pi^2\chi^2 + 4\pi^2 V(\rho; z)] = H_o + \frac{4\pi^2 V(\rho; z)}{4\pi k_z}$$

A fundamental postulate of quantum mechanics ([**?**, **?**]) says that the evolution operator obeys the equation:

$$\imath \frac{\partial}{\partial z} U(z, 0) = H(\rho; z)\ U(z, 0)$$

Causal evolution operator

$U(z,0)$: unitary operator (the norm of $|\Psi>$ is conserved), in general not directly integrable $\Longrightarrow$ approximations.

$U(z,0)$ can be directly integrated only when $H(\rho;z)$ and $\frac{\partial}{\partial z}H(\rho;z)$ commute. In that case the general solution is [**?**]:

$$U(z,0) = e^{-\imath \int_0^z H(\tau)\, d\tau}$$

$H(\rho;z)$ and $\frac{\partial}{\partial z}H(\rho;z)$ commute when:

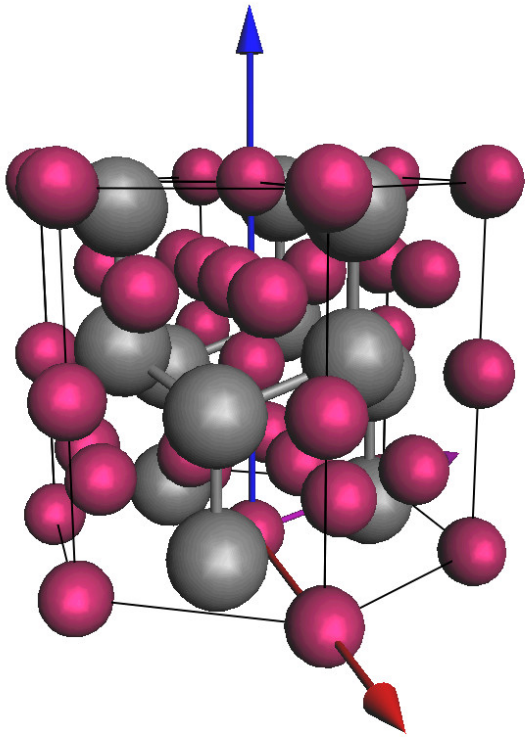
- $V(\rho;z)$ does not depend on z, i.e. $V(\rho;z) = V(\rho)$(perfect crystal).
- $V(\rho;z)$ can be neglected (free space propagation).
- $H(\rho;z)$ is approximated by it potential term (phase object).

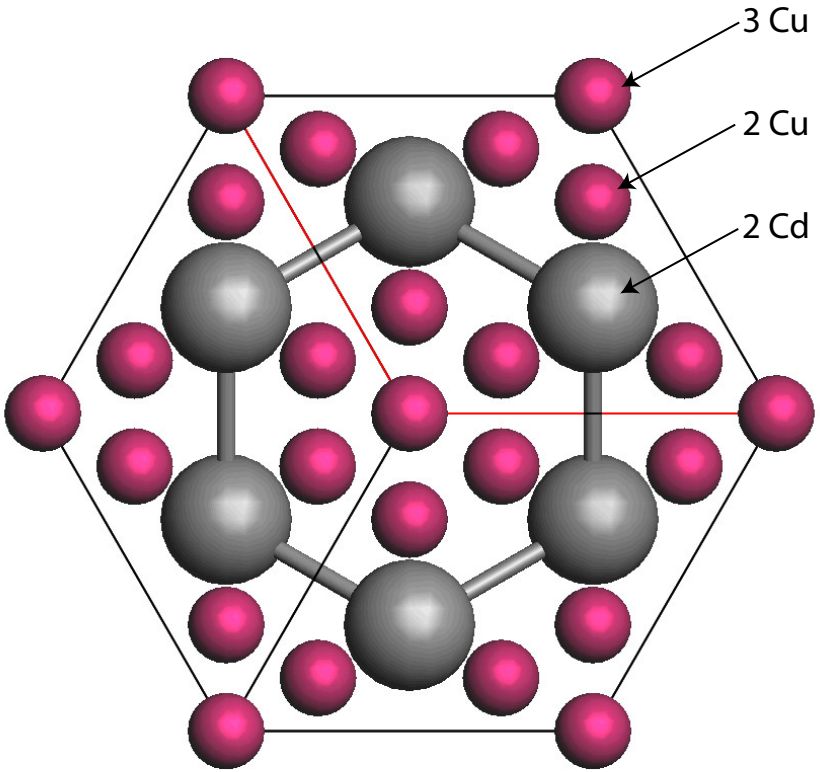
Three approximations are available in jems:

- Multislice method.
- Bloch wave method.
- Howie-Whelan column approximation.

Future of HRTEM simulation with the C_s and C_c corrections?

Example: CdCu_2, visibility of the 3 Cu atomic columns.



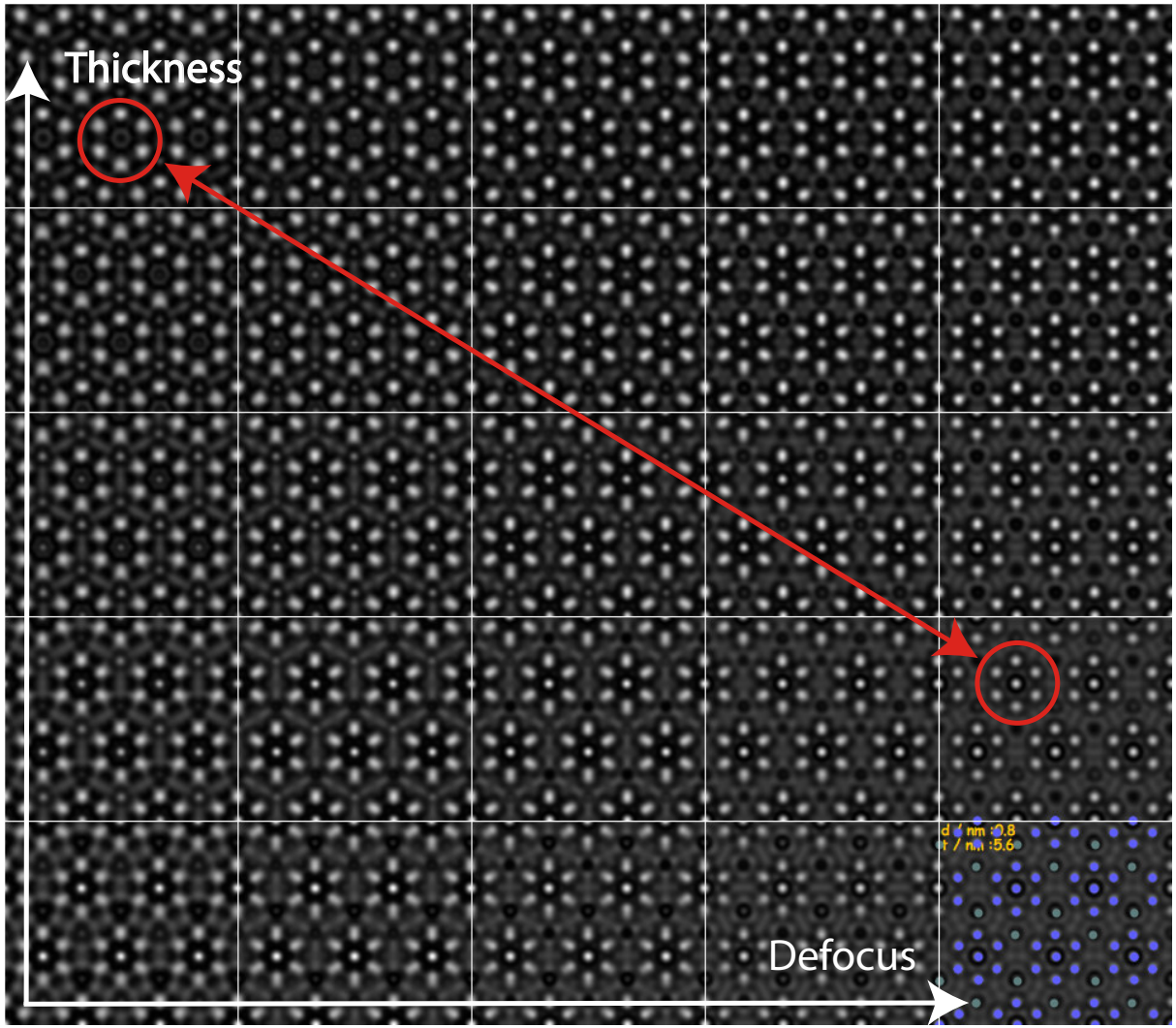


HRTEM image simulation conditions

Acc. [kV]	$C_s[mm]$	$C_5[mm]$	$C_c[mm]$	$\Delta E[eV]$	Z [nm]	$\Delta z[nm]$
300	-0.008	30	0.5	0.6	-4.9	1
300	-0.008	30	0.1	0.2	-2.0	1

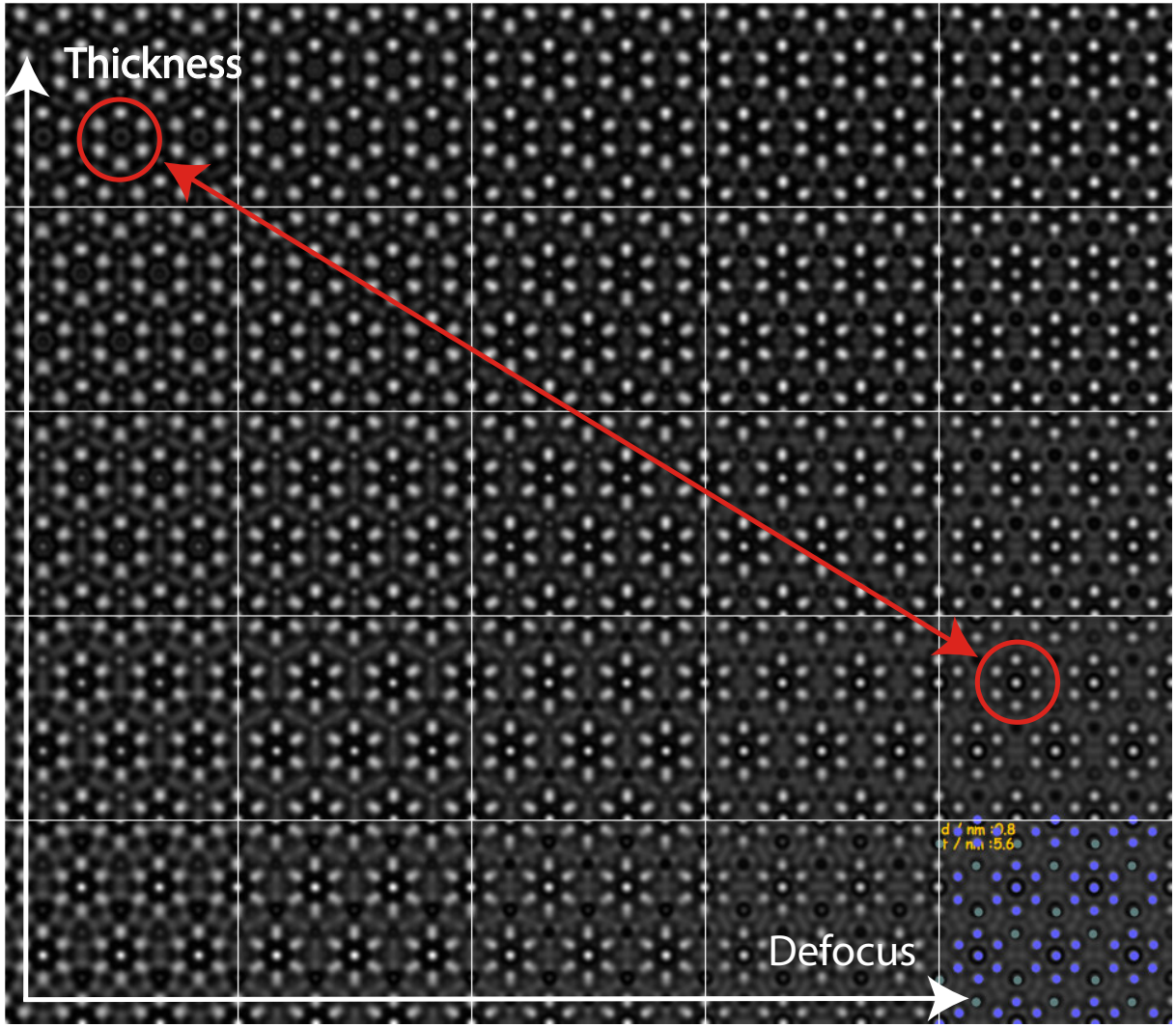
Dynamical scattering effects are not affected by C_s and/or C_c corrected TEM!

$CdCu_2[001]$: imaging parameters set 1



Visibility of 3 Cu atomic columns depends on specimen thickness and defocus.

$CdCu_2[001]$: imaging parameters set 2



Improving C_c and ΔE does not affect the visibility of 3 the Cu atomic columns depends on specimen thickness and defocus.

Visibility of the 3 Cu atomic columns is affected dynamical scattering (1 MeV C_s and C_c TEM).

STEM image simulation

High Angle Annular Dark Field (HAADF): inelastically scattered electrons. How to simulate images?

Various approximations:

- Simple projected + convolution with probe intensity: no channeling effect (WPOA).
- Multislice calculation: channeling + inelastic scattering (absorption potential) + convolution with probe intensity.
- Frozen phonons approximation: atoms of super-cell displaced out of equilibrium position[15], probe scanned on imaged area, intensity collected by annular detector.
- Ishizuka: ...
- Shiojiri:...
- ....

Except the first 2 methods, simulation time expensive. Approximations may suffice...

[15] file://localhost/Applications/jemsMacOSX/html/graphene/ap.html

HAADF: graphene

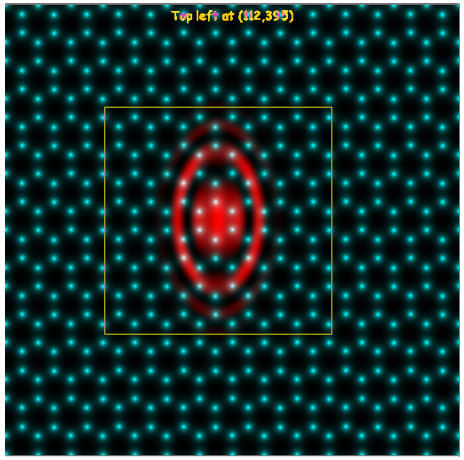


Figure: Probe affected by 2 fold astigmatism.

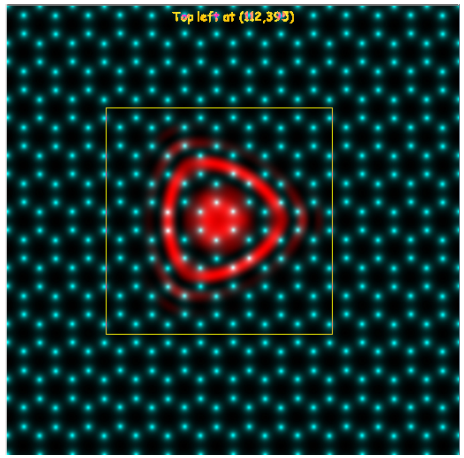


Figure: Probe affected by 3 fold astigmatism.

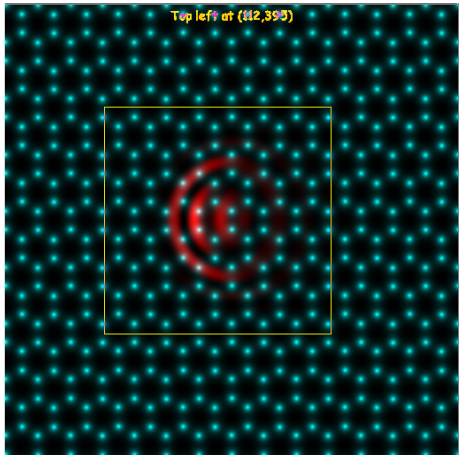


Figure: Probe affected by coma.

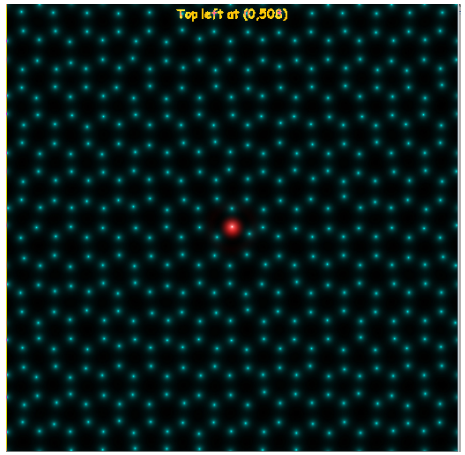


Figure: Corrected probe (best defocus).

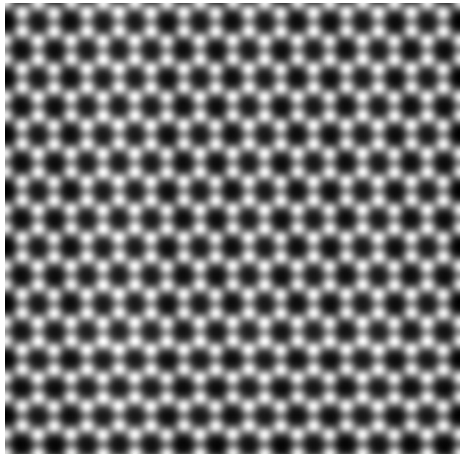


Figure: HAADF projected potential approximation.

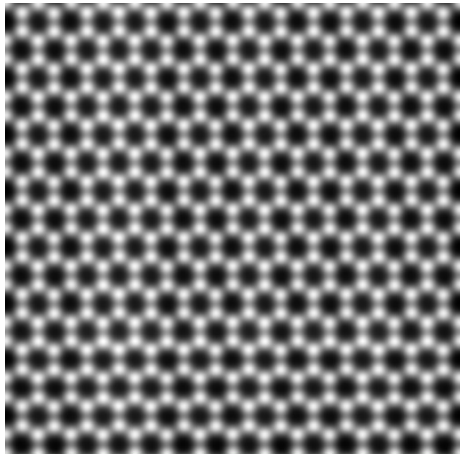


Figure: HAADF multislice calculation (simple).

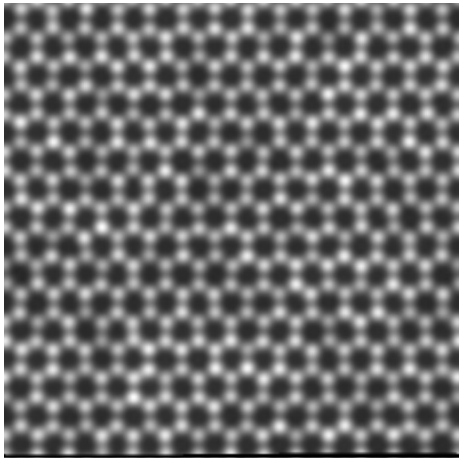


Figure: Frozen phonons 5 configurations.

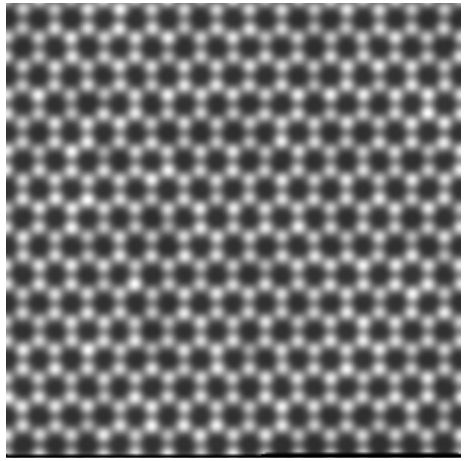


Figure: Frozen phonons 10 configurations.

Thanks you for attention!

My gratitude to:

- All my collaborators!