

HRTEM and STEM Image Simulation

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

Quantitative simulation?

- ▶ Problems.
- ▶ Perfect microscopes.
- ▶ Aberrations.

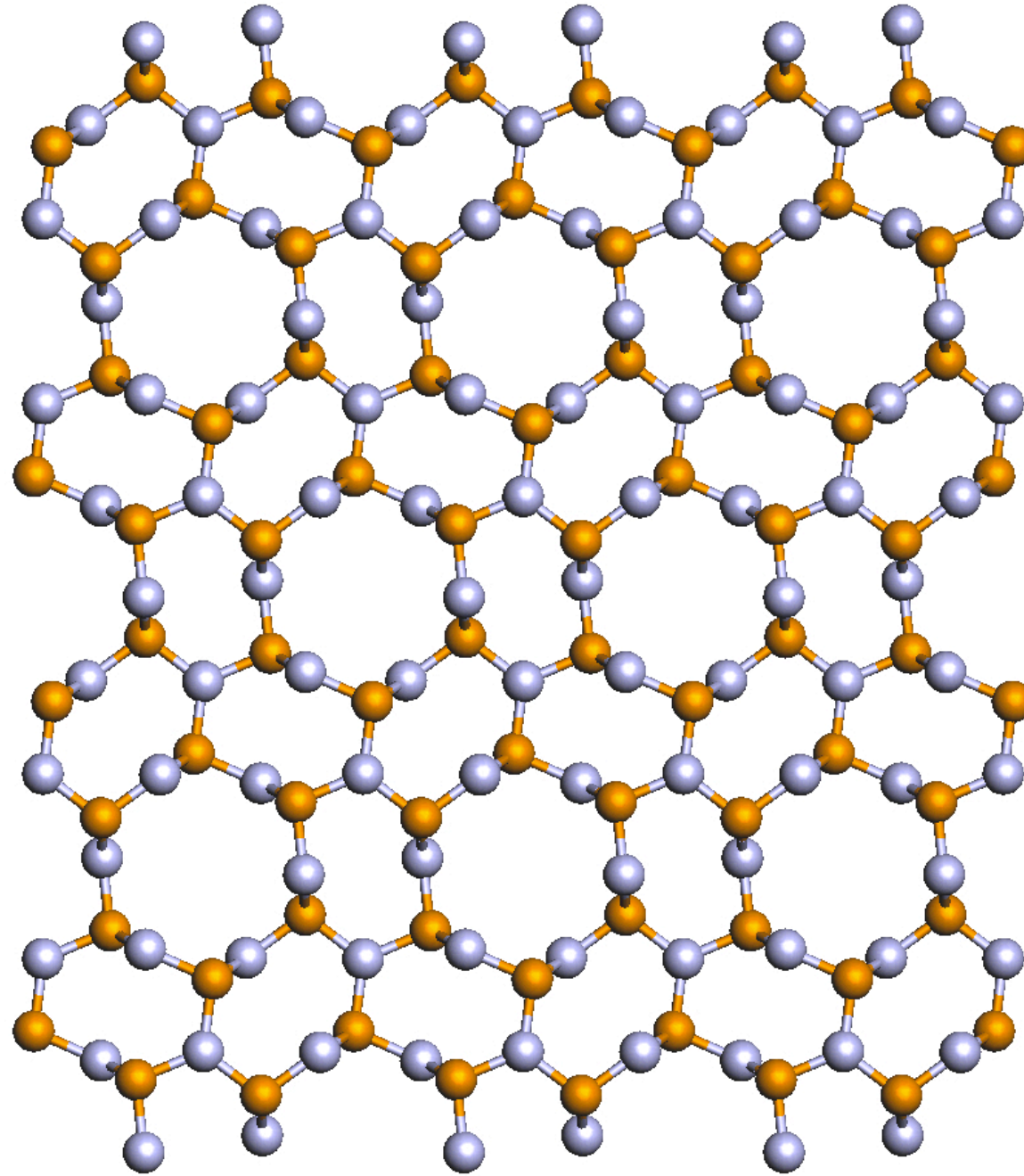
Why HRTEM image simulation?

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

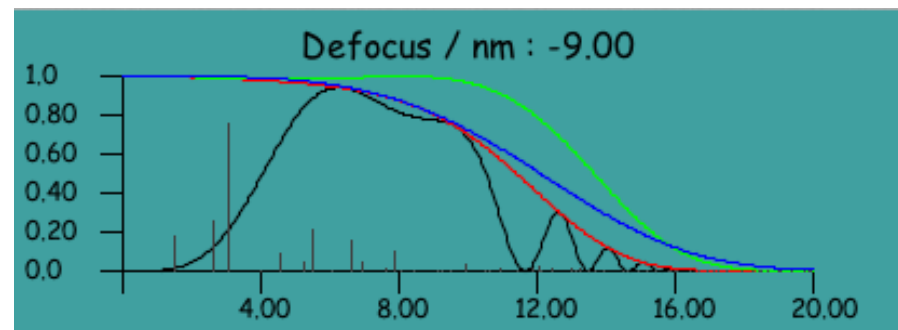
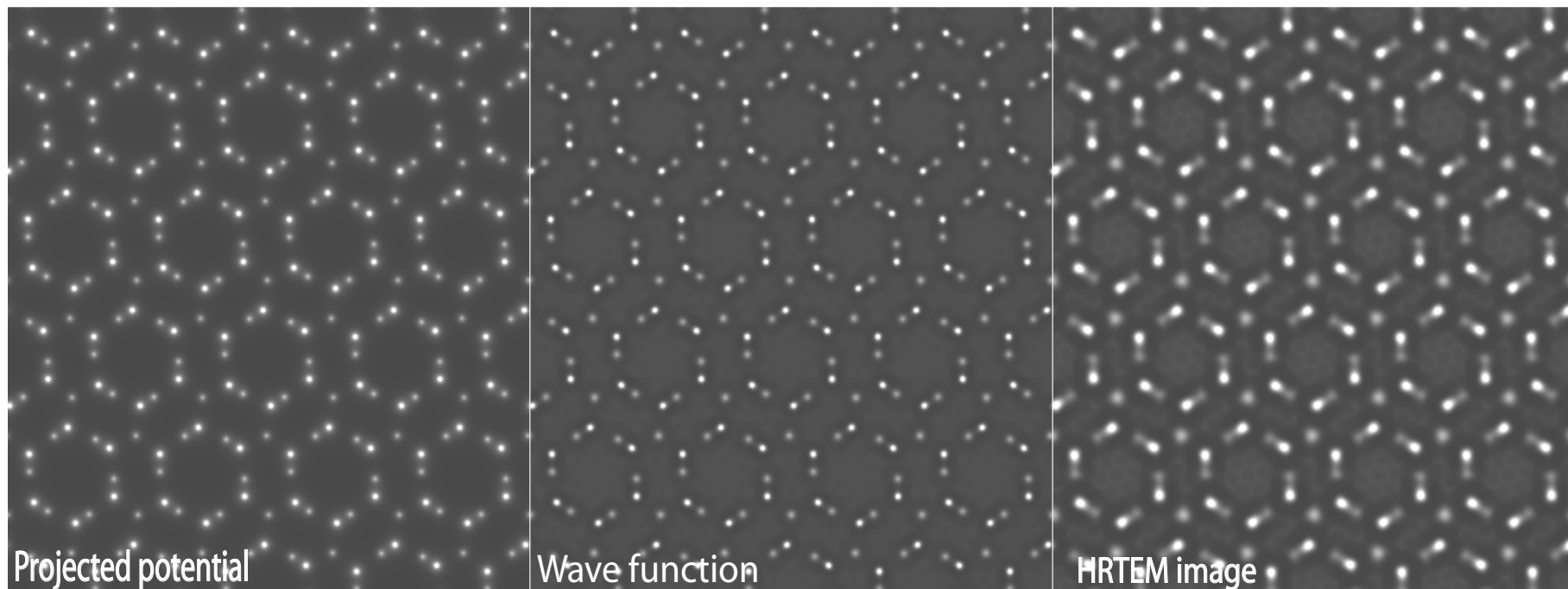
- ▶ Specimen structure..
- ▶ Chemical composition.
- ▶ Functional properties.
- ▶ ...

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

For example **object defocus** affects strongly HRTEM images.

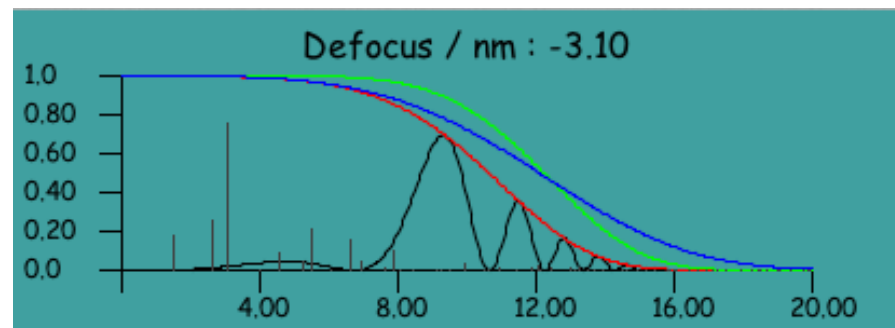
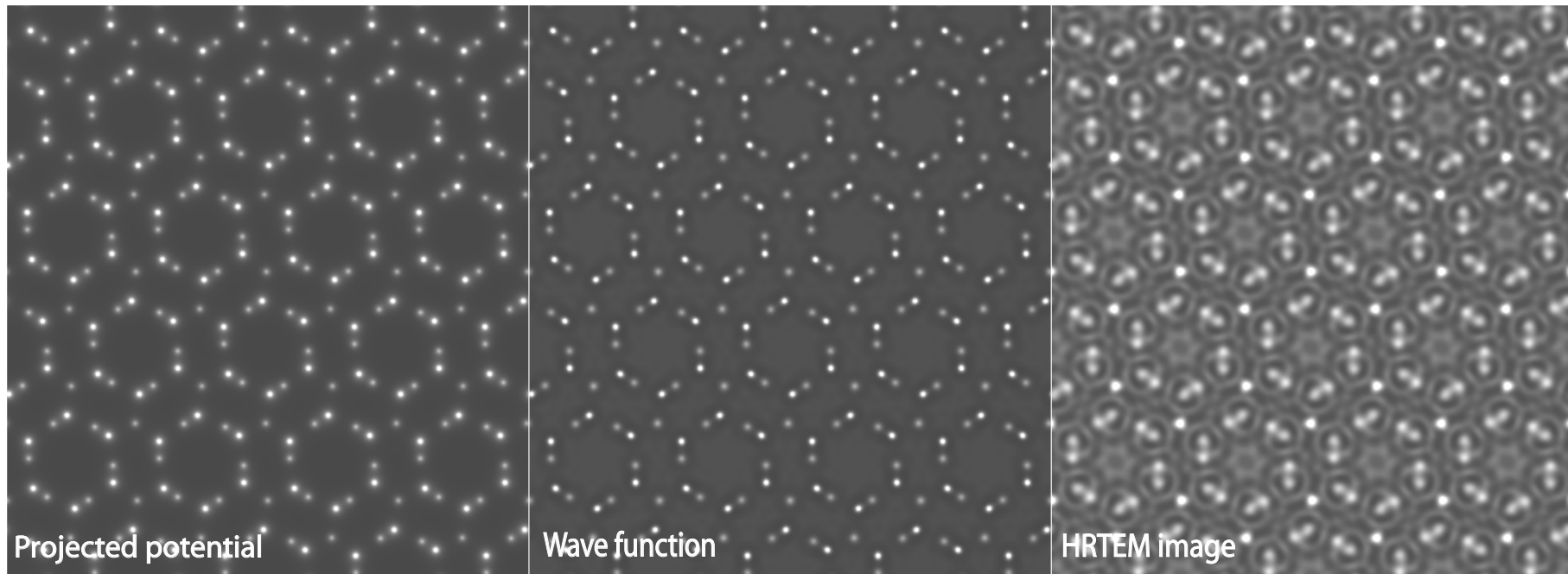


Images: Si_3N_4 P 63: [001], 10 nm thick, -9 nm defocus



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?

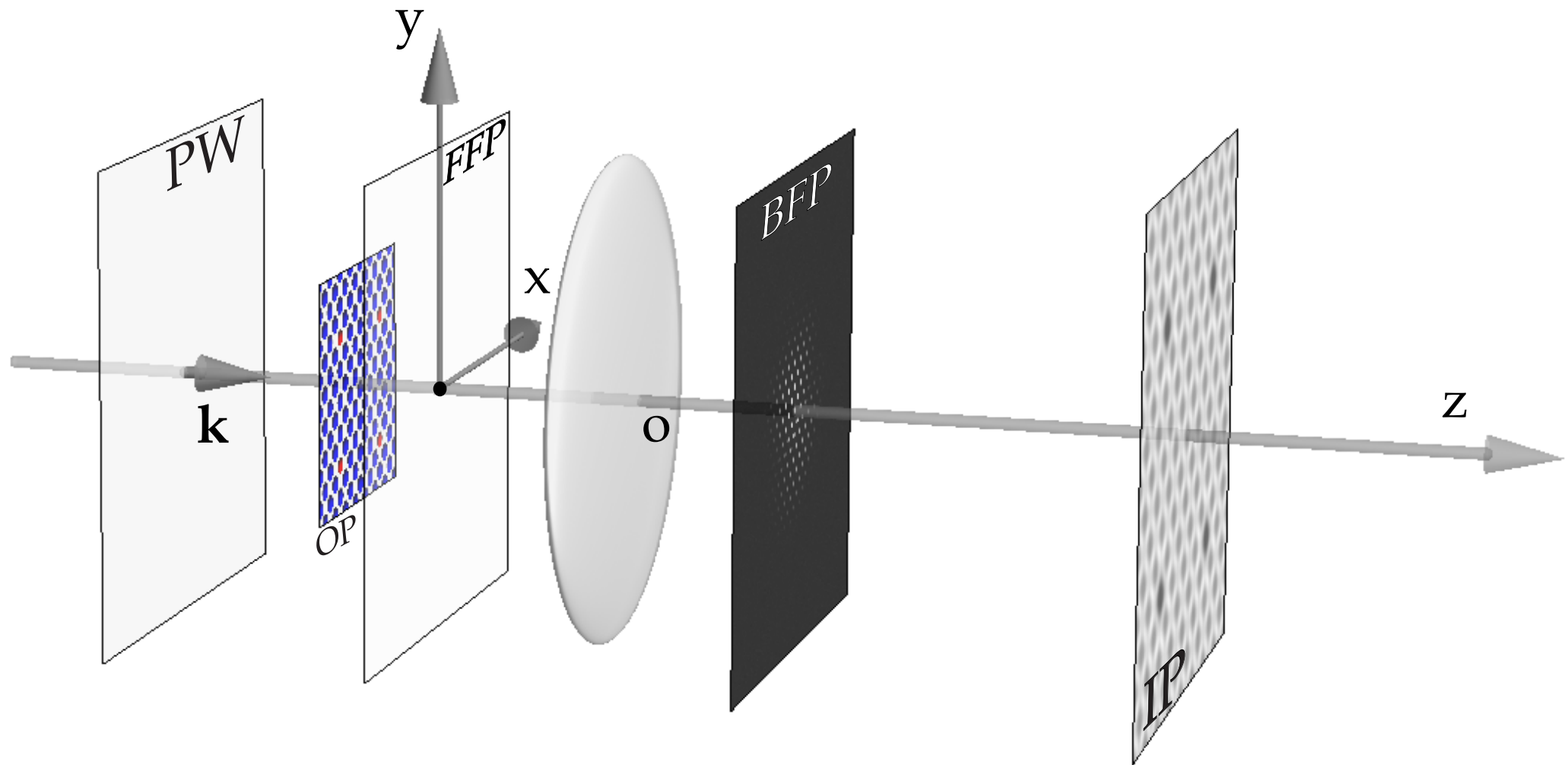
Formation of Electron Microscopy diffraction/images involves complex physical processes.

Approximations and models of these physical processes

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

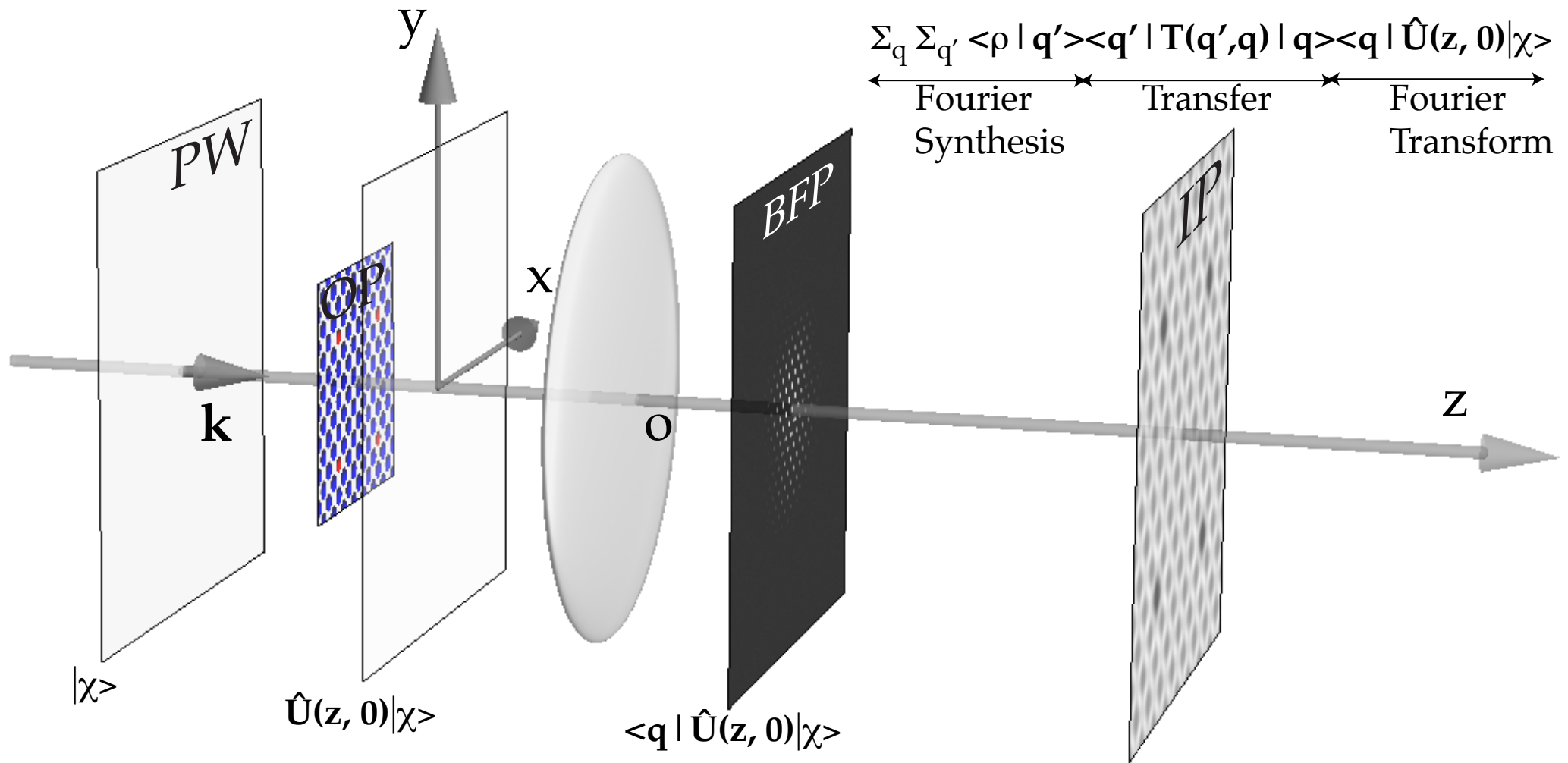
Needed: crystallography, optics, quantum mechanics, ... and computer programming.

TEM (very) simplified model



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

Image formation modeling (HRTEM)



$|\chi\rangle \implies$ incident wave function

$$|\Psi_i\rangle = \underbrace{\sum_{q'} \langle \rho | q' \rangle}_{\text{Fourier synthesis}} \underbrace{\sum_q \langle q' | T(q', q) | q \rangle}_{\text{Objective lens transfer}} \underbrace{\langle q | U(z, 0) | \chi \rangle}_{\text{Fourier transform}}$$

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

- ▶ The electron beam properties.
 - ▶ Convergence.
 - ▶ Source size.
 - ▶ Coherence (spatial and temporal).
- ▶ The specimen properties¹.
- ▶ How is the incident electron 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/Rb2W09/Rb2W09.html>

- ▶ 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 calculations².

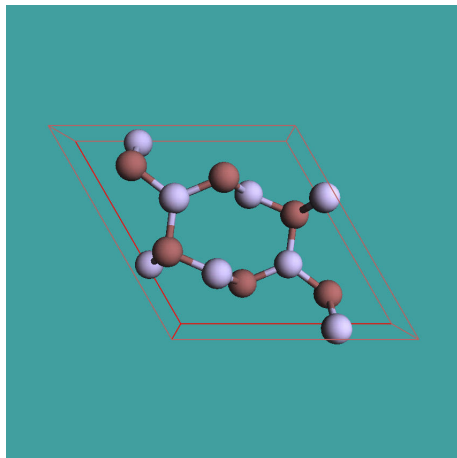


Figure: Si_3N_4 hexagonal lattice.

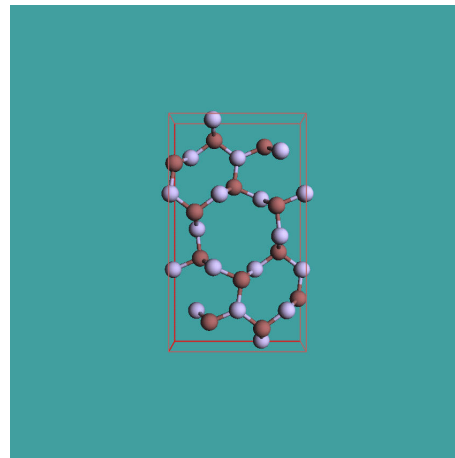


Figure: Si_3N_4 orthorhombic lattice.

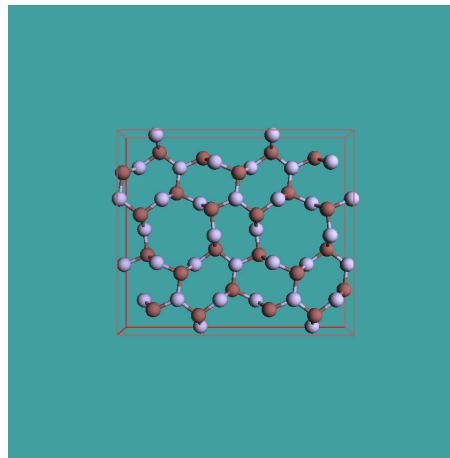


Figure: Si_3N_4 orthorhombic lattice x 2.

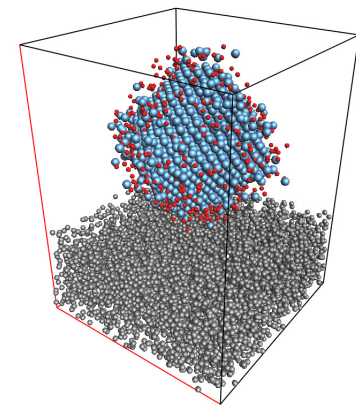


Figure: Pt catalyst on amorphous carbon film (9600 atoms).

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

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

Atomic scattering amplitude

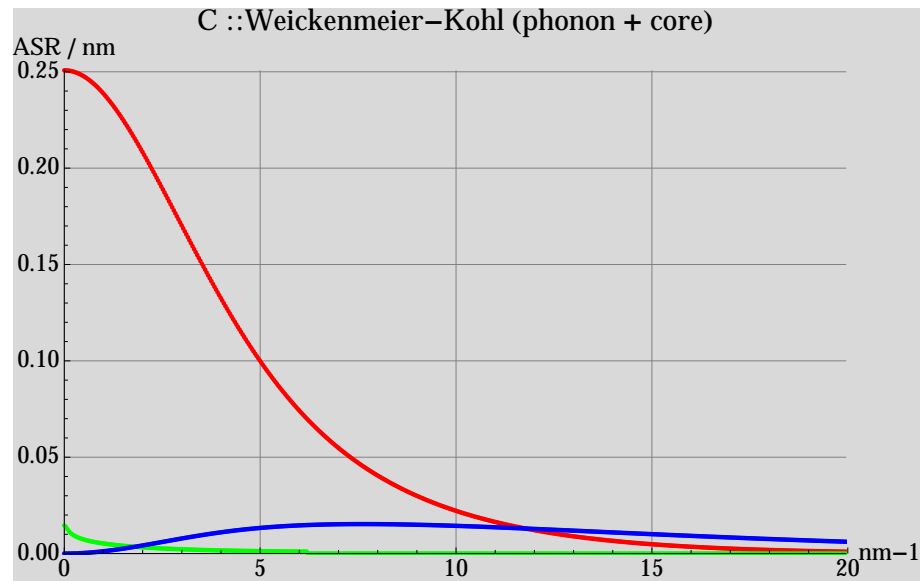


Figure: Carbon. Red: real part, green: imaginary part, blue: thermal diffuse scattering.

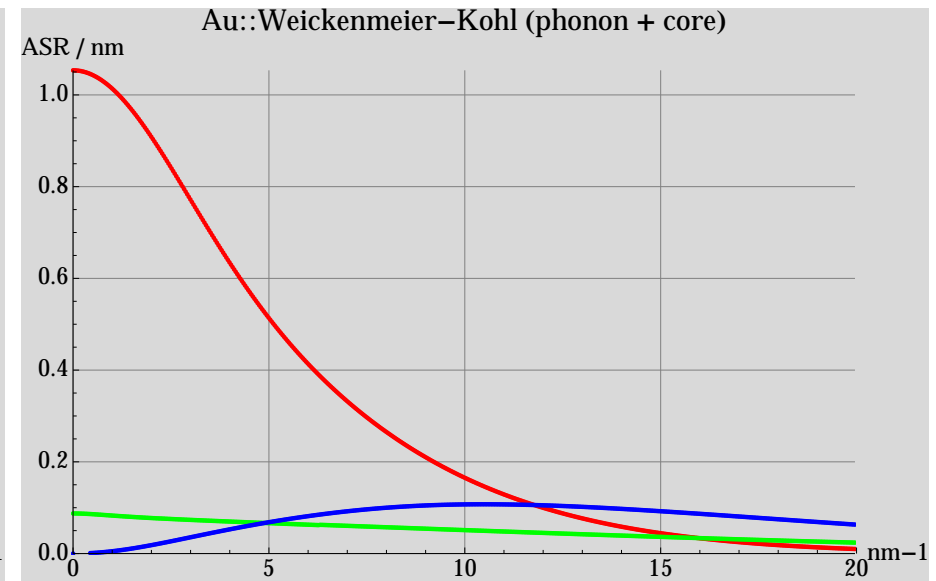


Figure: Gold. Red: real part, green: imaginary part, blue: thermal diffuse scattering.

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.

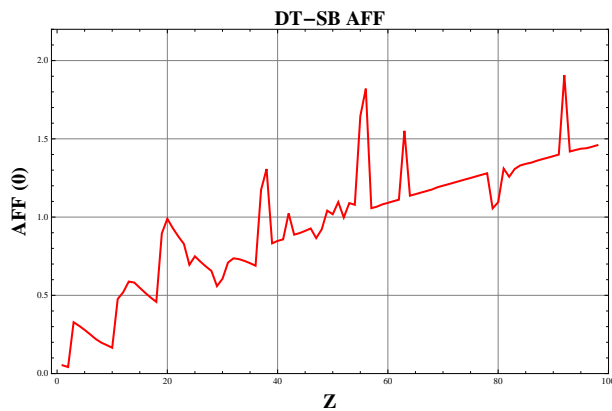


Figure: Doyle-Turner or Smith-Burger.

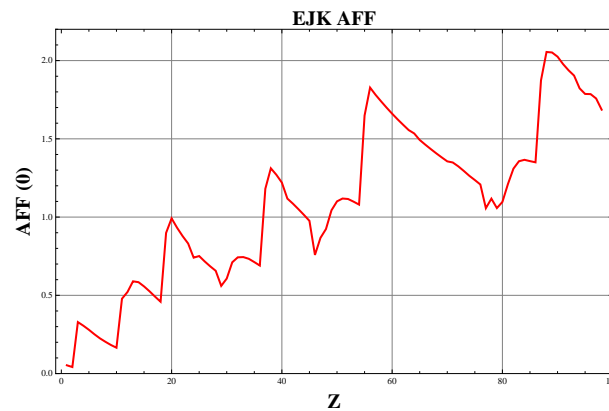


Figure: E. J. Kirkland.

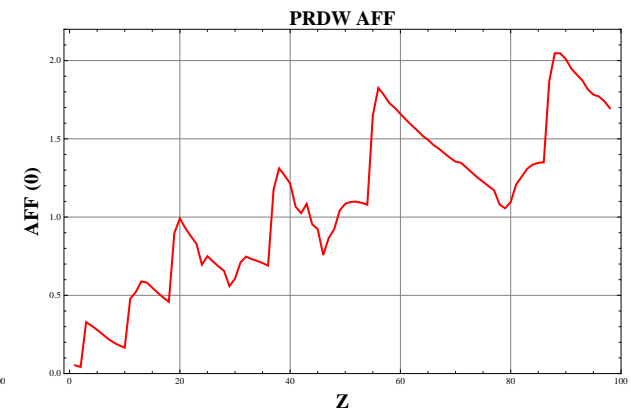


Figure: Peng-Ren-Dudarev-Whelan.

A extremely useful *ASA* tabulation including phonon and core loss absorption is due to Weickenmeier-Kohl³.

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

Crystal structure are defined by:

1. $a, b, c, \alpha, \beta, \gamma$ lattice parameters.
2. Space-group or symmetry operators.
3. Atoms positions (Symbol, x, y, z with $0 \leq (x, y, z) < 1$)

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

Useful servers:

www.minsocam.org

www.crystallography.net

www.cryst.ehu.es

ICSD & AMS: data bases for crystal structures

Available CIF files

- Triiron tetraoxide
- Iron oxide (0.93/1)
- Iron oxide
- Iron(III) oxide - alpha
- Iron(III) oxide - alpha
- Iron(III) oxide - alpha
- Iron(III) oxide - alpha
- Iron(III) oxide - alpha
- Iron(III) oxide - alpha
- Iron oxide (2.93/4)
- Iron oxide (2.95/4)
- Iron oxide (2.94/4)
- Iron oxide (2.95/4)
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- Iron oxide (2.96/4)
- Iron oxide (2.94/4)
- Iron oxide (2.95/4)
- Iron(III) oxide - alpha
- Iron oxide (21.34/32) - gamma
- Iron(III) oxide - alpha
- Iron(III) oxide - alpha
- Iron diiron(III) oxide
- Iron(III) oxide - alpha
- Iron oxide (.92/1)
- Iron oxide (.93/1)
- Iron oxide (.89/1)
- Iron oxide (.91/1)
- Iron oxide (.91/1)
- Iron oxide (0.95/1)
- Iron(III) oxide - alpha
- Iron oxide
- Triiron tetraoxide
- Iron oxide (0.93/1)
- Iron(III) oxide - alpha
- Iron(III) oxide - alpha
- Iron(III) oxide - alpha
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- Iron oxide (2.95/4)
- Iron(III) oxide - alpha
- Iron oxide (21.34/32) - gamma
- Iron(III) oxide - alpha
- Iron(III) oxide - alpha
- Iron oxide (.92/1)
- Iron oxide (.92/1)
- Iron oxide (.88/1)
- Iron oxide (.9/1)
- Iron oxide (.92/1)
- Iron oxide (.92/1)
- Iron oxide (0.95/1)
- Iron oxide (0.95/1)
- Diiron(III) oxide - alpha

Fe (O) at : (0.375, 0.375, 0.875)

ICSD_82237 : [0, 0, 1]

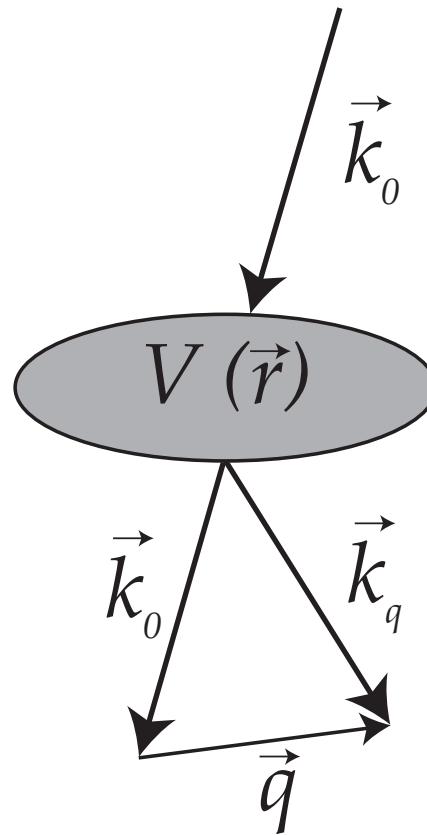
Projections

- [0, 0, 1]
- [1, 0, 0]
- [0, 1, 0]

Cancel Select

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 transferred by the solid⁴.

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

⁴Magnetic and spin effects are ignored.

With energy conservation and momentum transfer ($\vec{s}_g = 0$), i.e. elastic scattering:

$$|\vec{k}_i + \vec{g}| = |\vec{k}_g|$$

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

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

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

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

\implies Bragg law:

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

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

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

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. $s_{hkl} = \frac{\sin(\theta_B)}{\lambda} = \frac{1}{2d_{hkl}}$.

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

Simple cubic: (hkl) no condition.

1 atom at $(0, 0, 0)$.

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

Body centered cubic: $(hkl) : h + k + l = 2n$

2 atoms at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

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

Face centered cubic: (hkl) all even or odd.

4 atoms at $(0, 0, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$

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

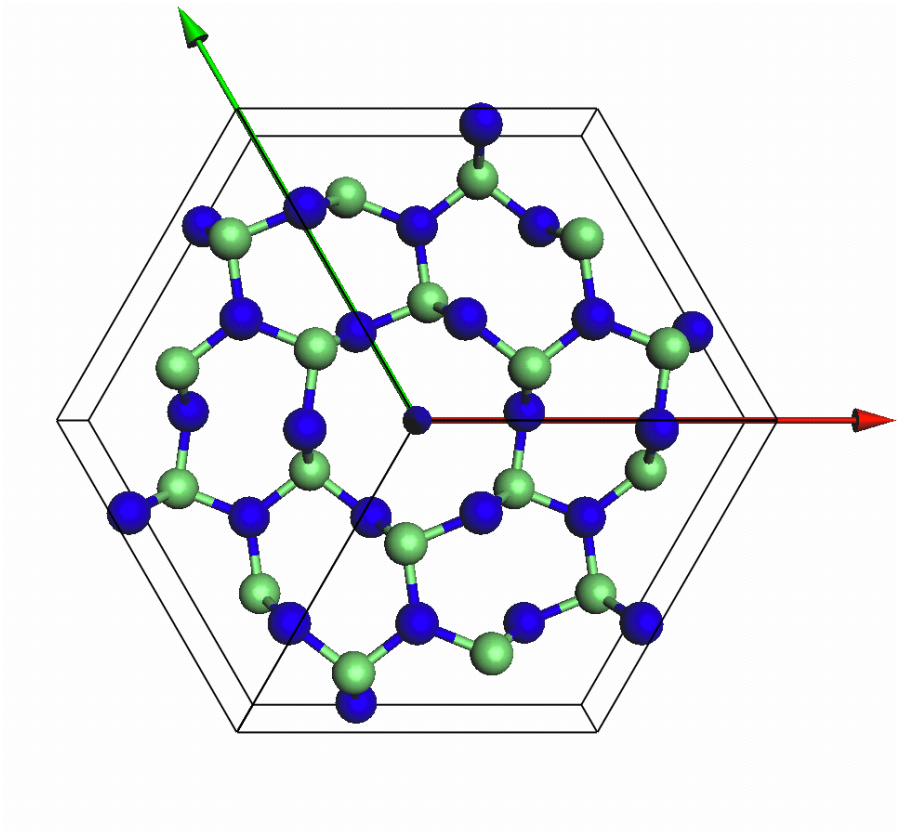


Figure: Model (Ge_3N_4).

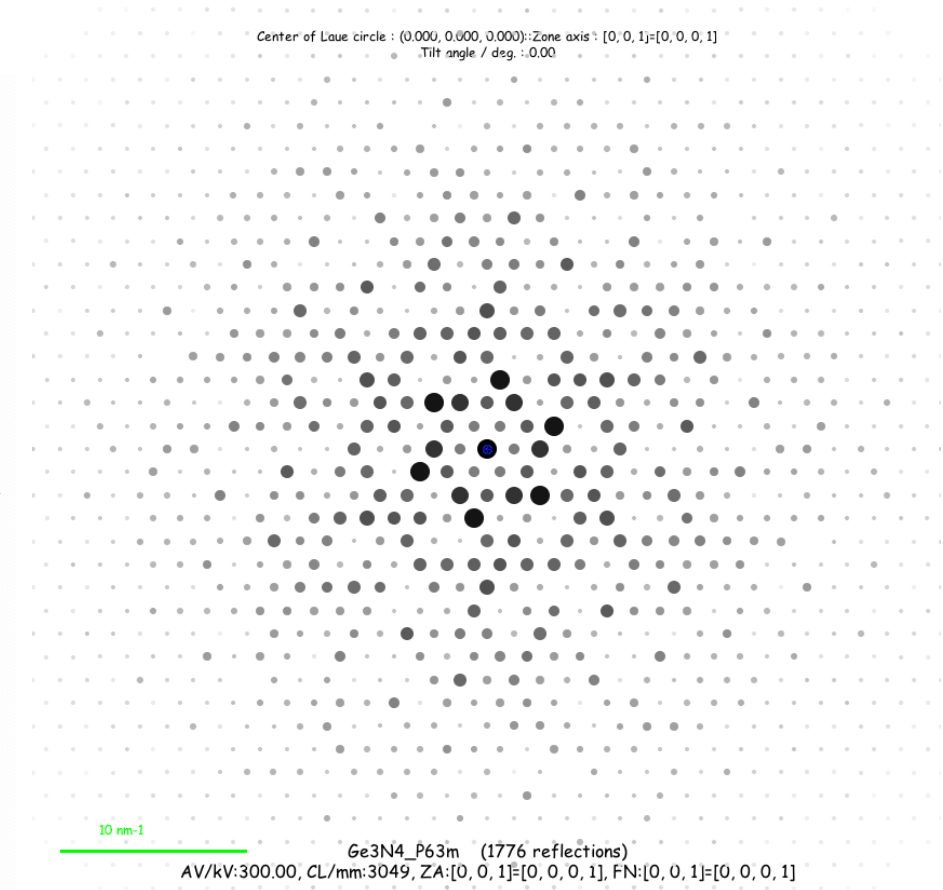


Figure: Kinematical diffraction Ge_3N_4 , [001].

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

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

Including inelastic scattering more complicated and computer intensive.

Gratias & Portier: small angle & elastic scattering approximations

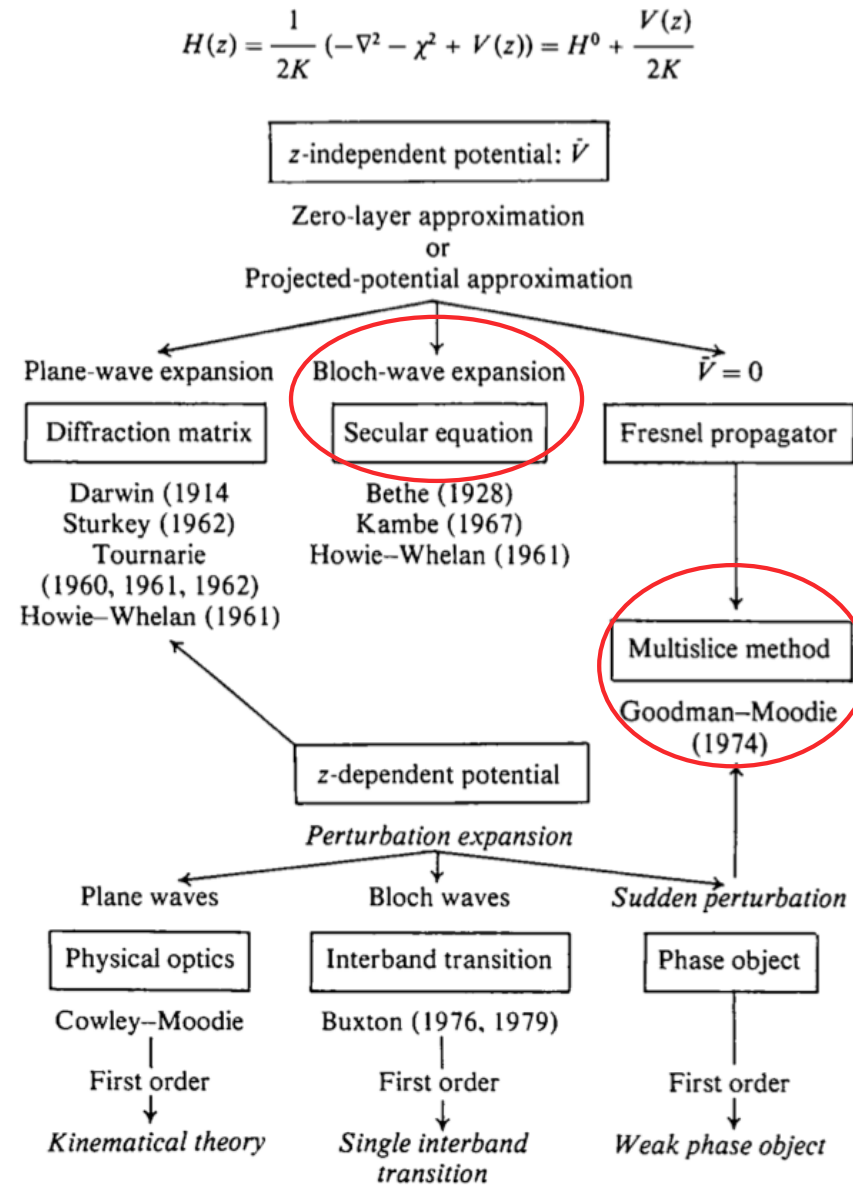


Figure: From Gratias and Portier⁵

⁵D. 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:

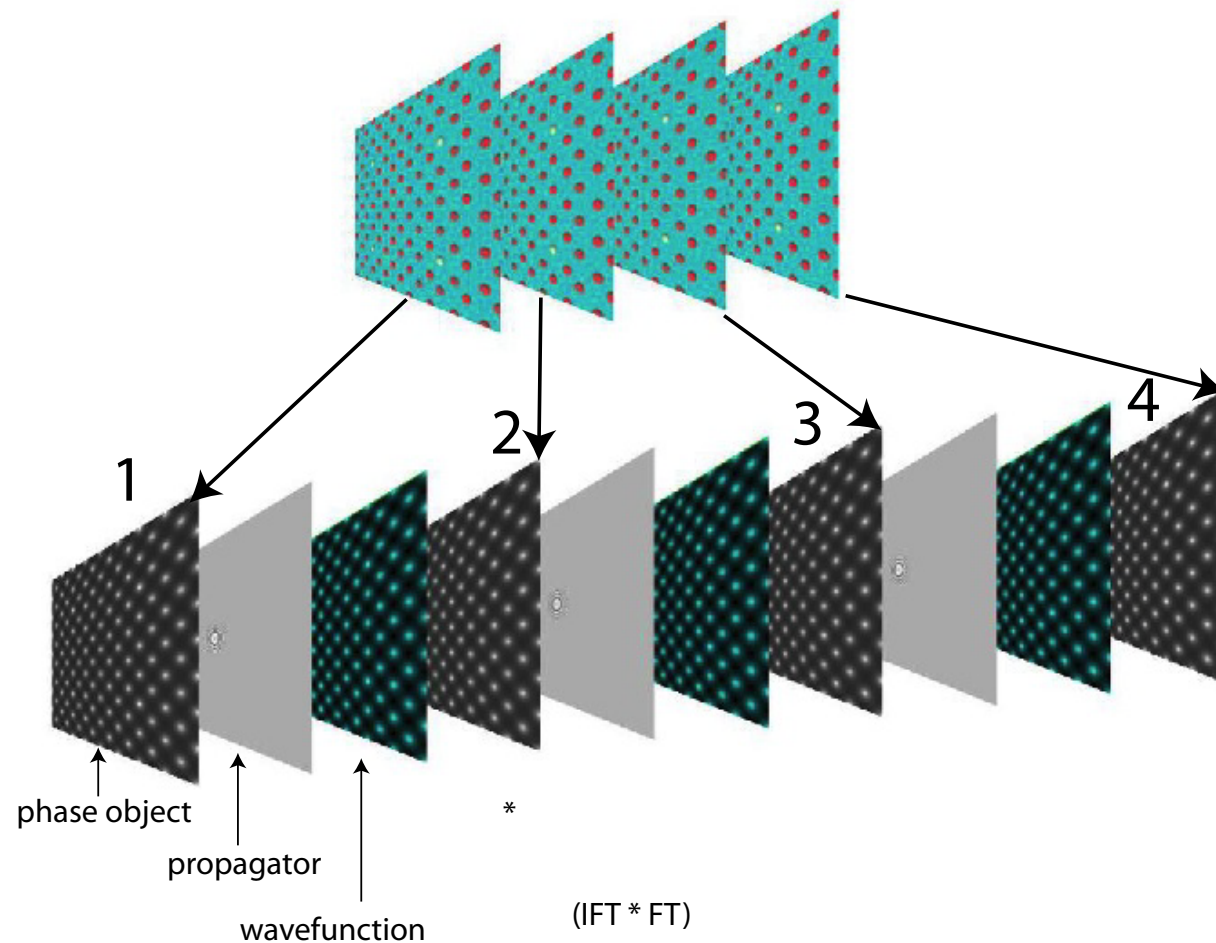
- ▶ The multislice approximation⁶.
- ▶ The Bloch-wave method⁷.

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.

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

⁷H. 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 wavelength⁸.

$$\Psi(i + 1) = [\Psi(i)PO(i)] \otimes FP_{i \rightarrow i+1}$$

⁸<file:///localhost/Applications/jemsMacOSX/html/PtOct/a.html>

Can simulate:

- ▶ Perfects crystals.
- ▶ Defects under the periodic continuation assumption ⁹.

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<file:///localhost/Applications/jemsMacOSX/html/PtOct/b.html>

¹⁰K. Ishizuka, Acta Cryst. A33 (1977) 740-749.

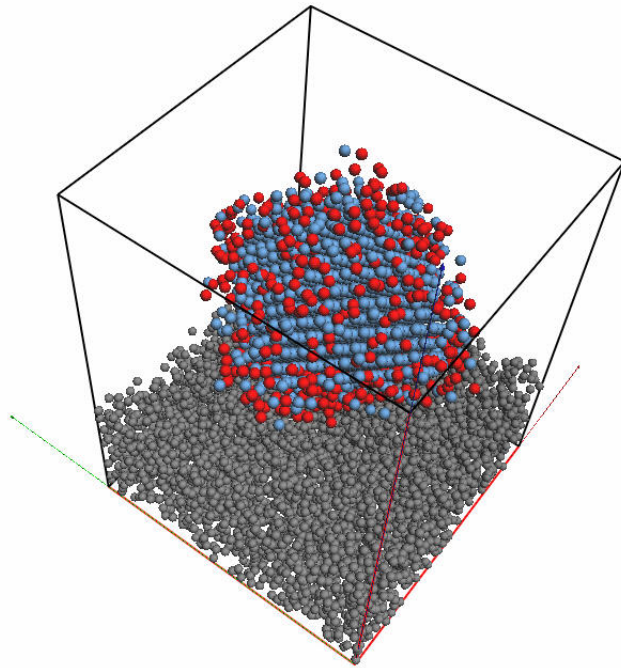


Figure: Model (one unit cell).

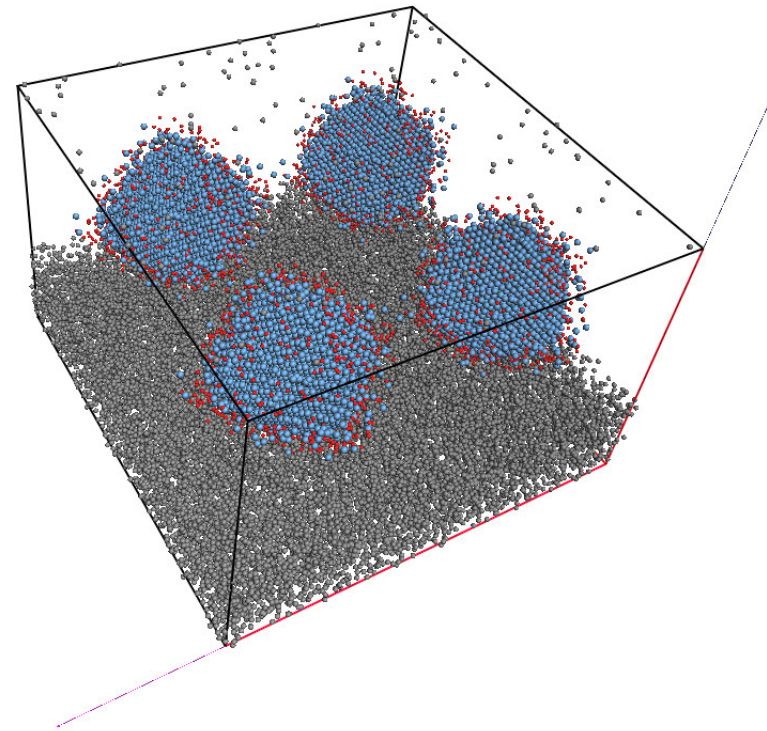
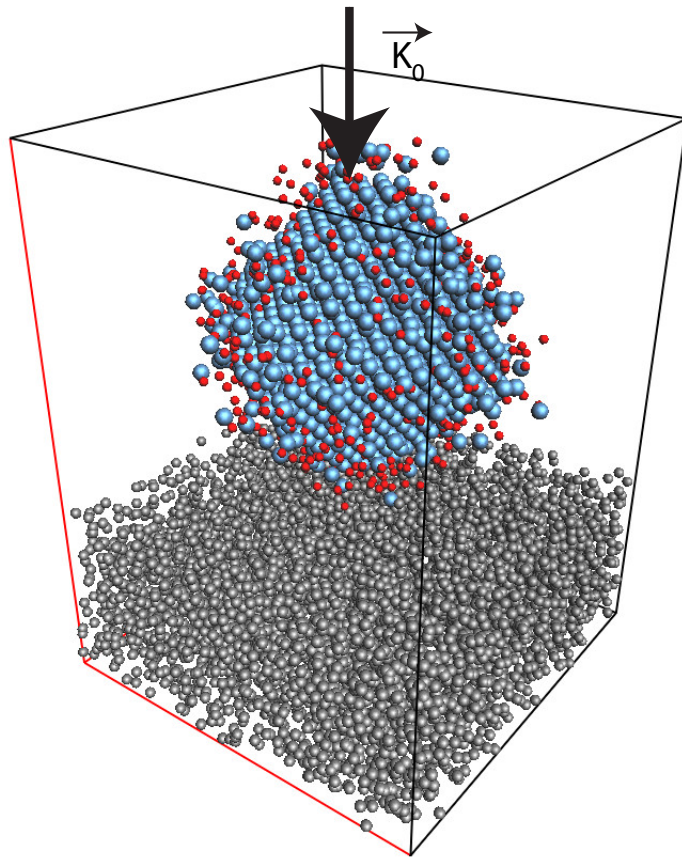


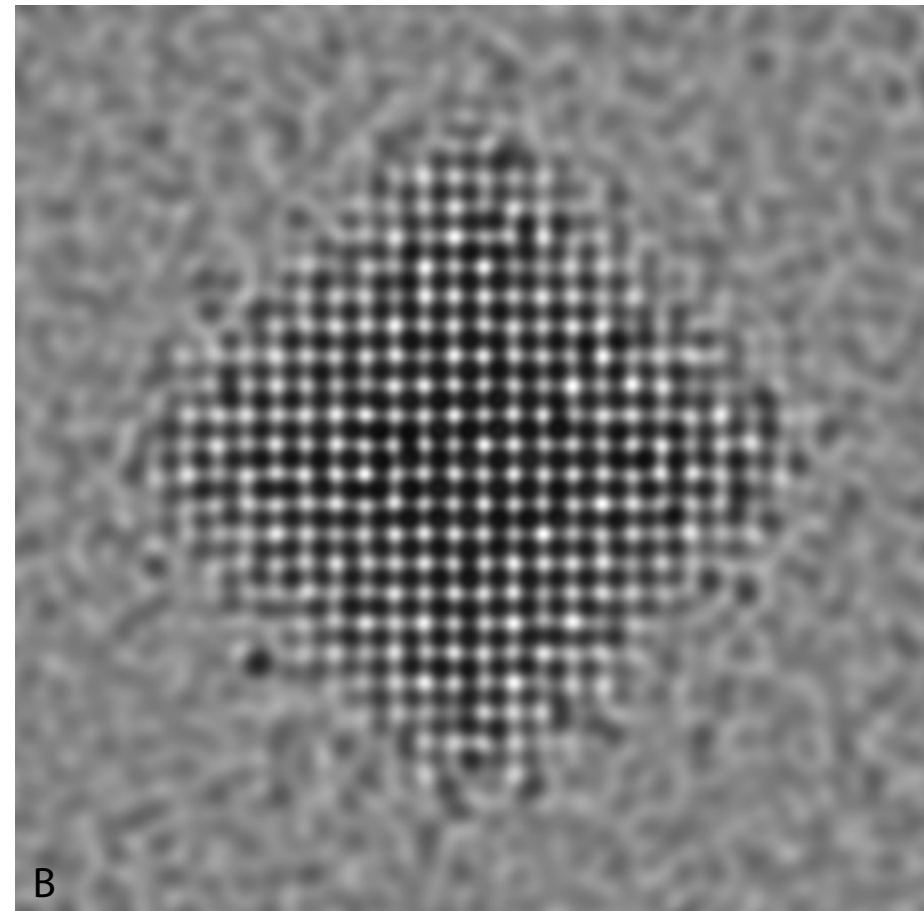
Figure: Model with periodic continuation (2 x 2 unit cells).

¹¹A.J. Skarnulis, Thesis, Arizona State University 1975.

Example multislice: Pt catalyst



A



B

A: catalyst model (9500 atoms)¹². B: HREM image (Jeol 400kV).

Bloch wave method: z-independent potential

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

$$\hat{H} = \sum_j \gamma_j |j\rangle \langle j|$$

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

$$\hat{U}(z, 0) = e^{-i\hat{H}z} = \sum_j e^{-i\gamma_j z} |j\rangle \langle j|$$

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

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

$$\phi_q(z) = \langle q | \hat{U}(z, 0) | 0 \rangle = \sum_j e^{-i\gamma_j z} \langle q | j \rangle \langle j | 0 \rangle$$

$$c_0^{*j} = \langle j | 0 \rangle \quad \text{and} \quad c_q^j = \langle q | j \rangle$$

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

Simulation of:

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

Works best for small lattice parameters crystals¹³.

¹³Some more details in Appendix1.

CBED: ZnTe [110]

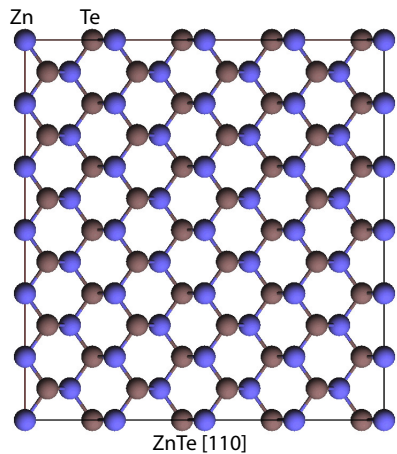


Figure: ZnTe [110].

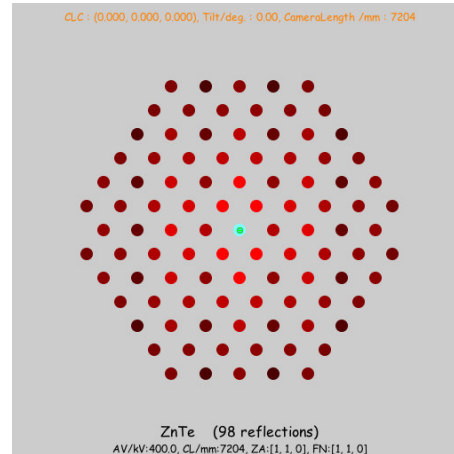


Figure: Reflections (1 + 49), $|\chi| \geq 0$.

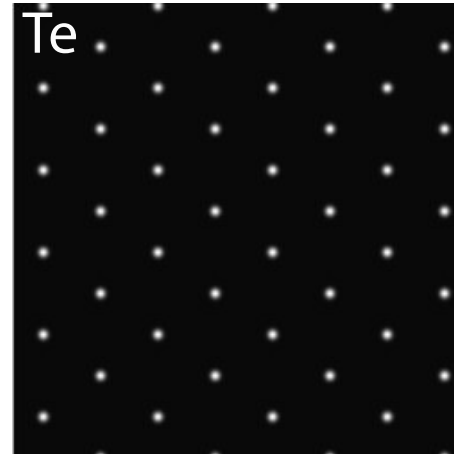


Figure: Bloch-wave 1 (Te 1s).

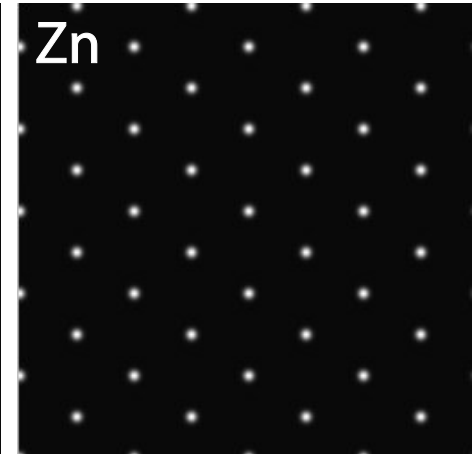


Figure: Bloch-wave 2 (Zn 1s).

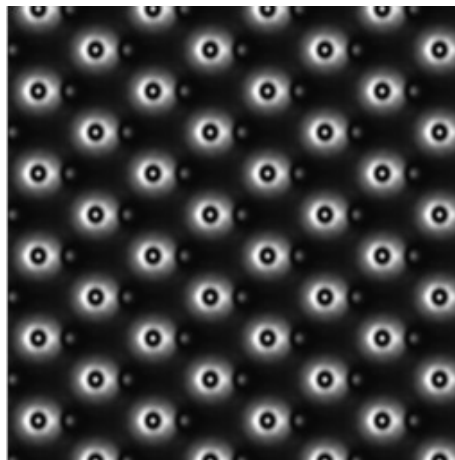


Figure: Bloch-wave 5 (Te-Zn).

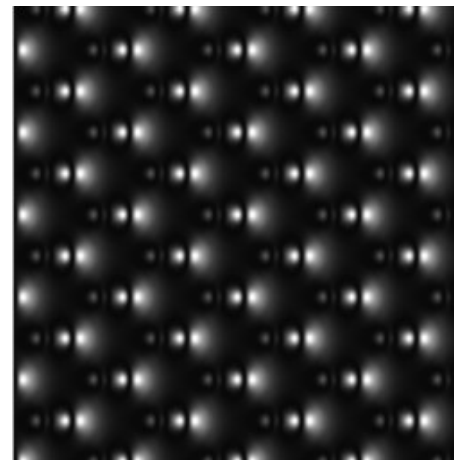


Figure: Bloch-wave 7 (Te-Zn).

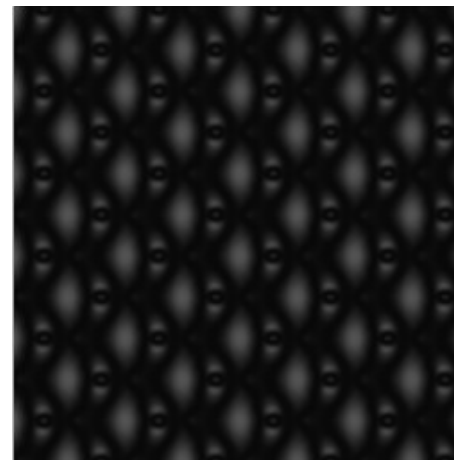


Figure: Bloch-wave 8 (Te-Zn).

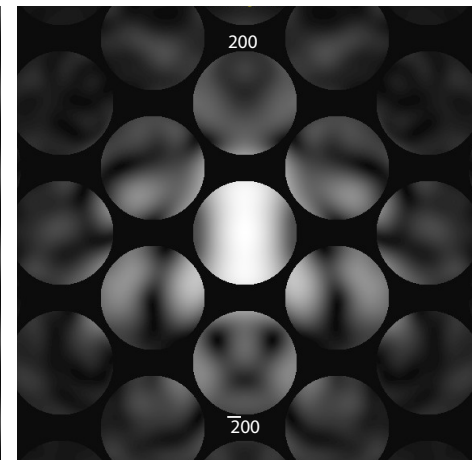
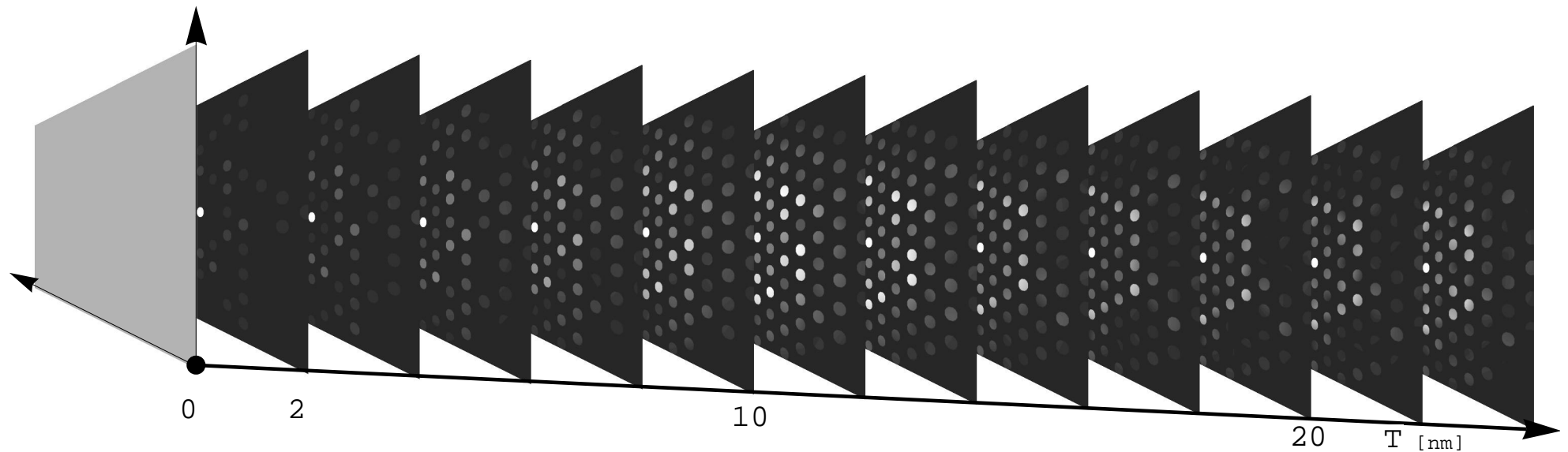


Figure: CBED (ZnTe polarity).



In BFP diffraction pattern depends specimen thickness.

Goodness of dynamical diffraction theories?

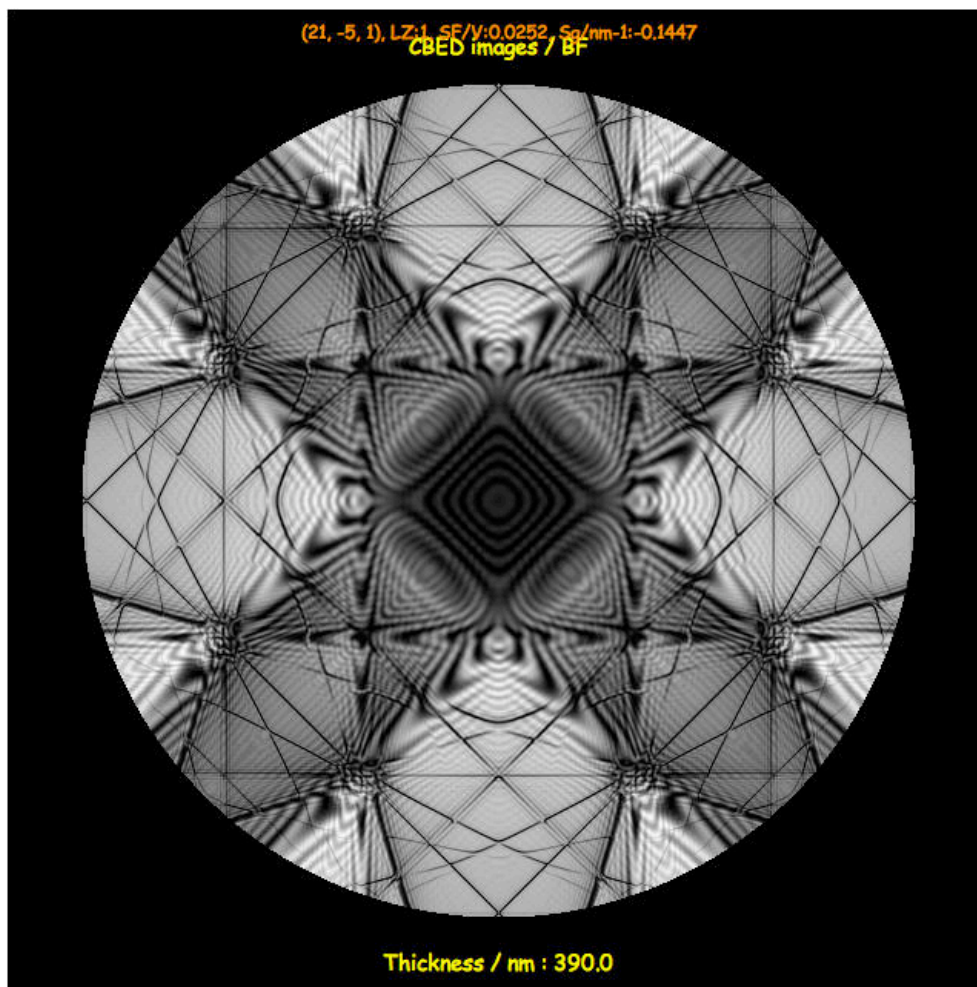


Figure: LACBED Si [001]: simulation.

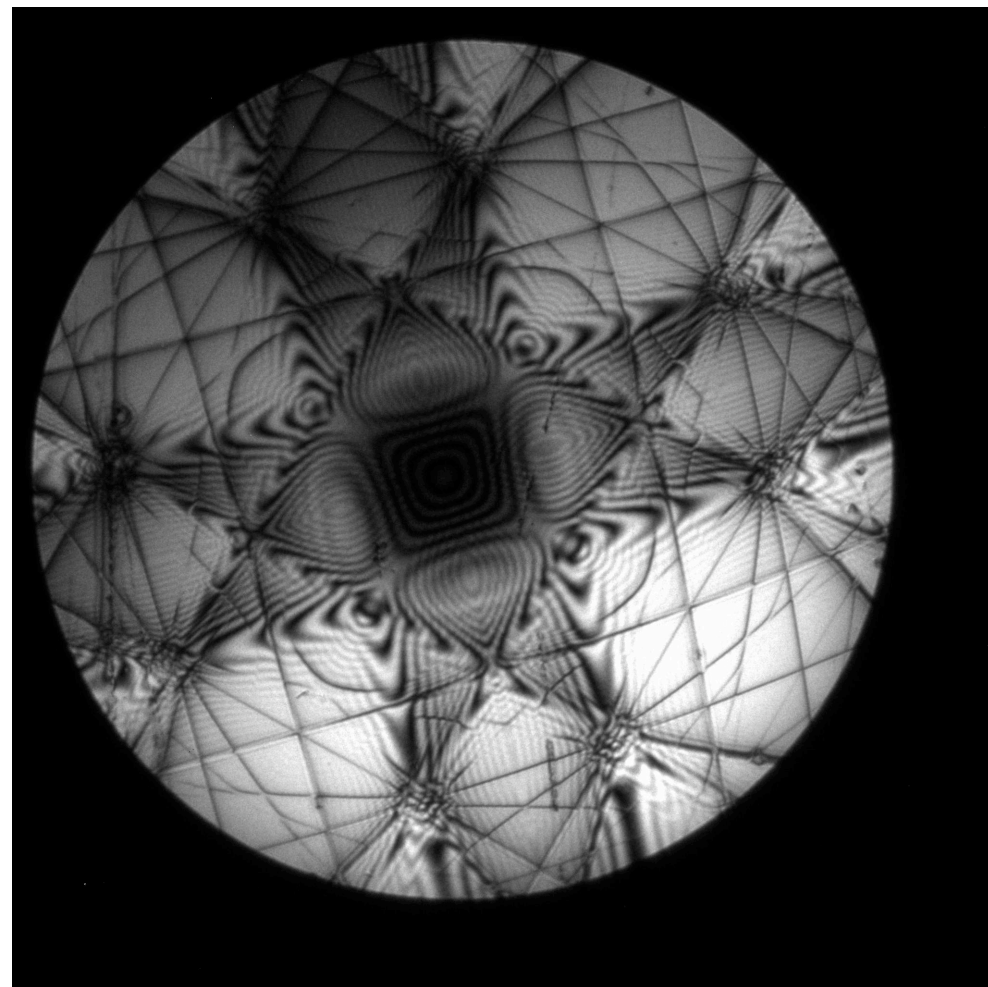


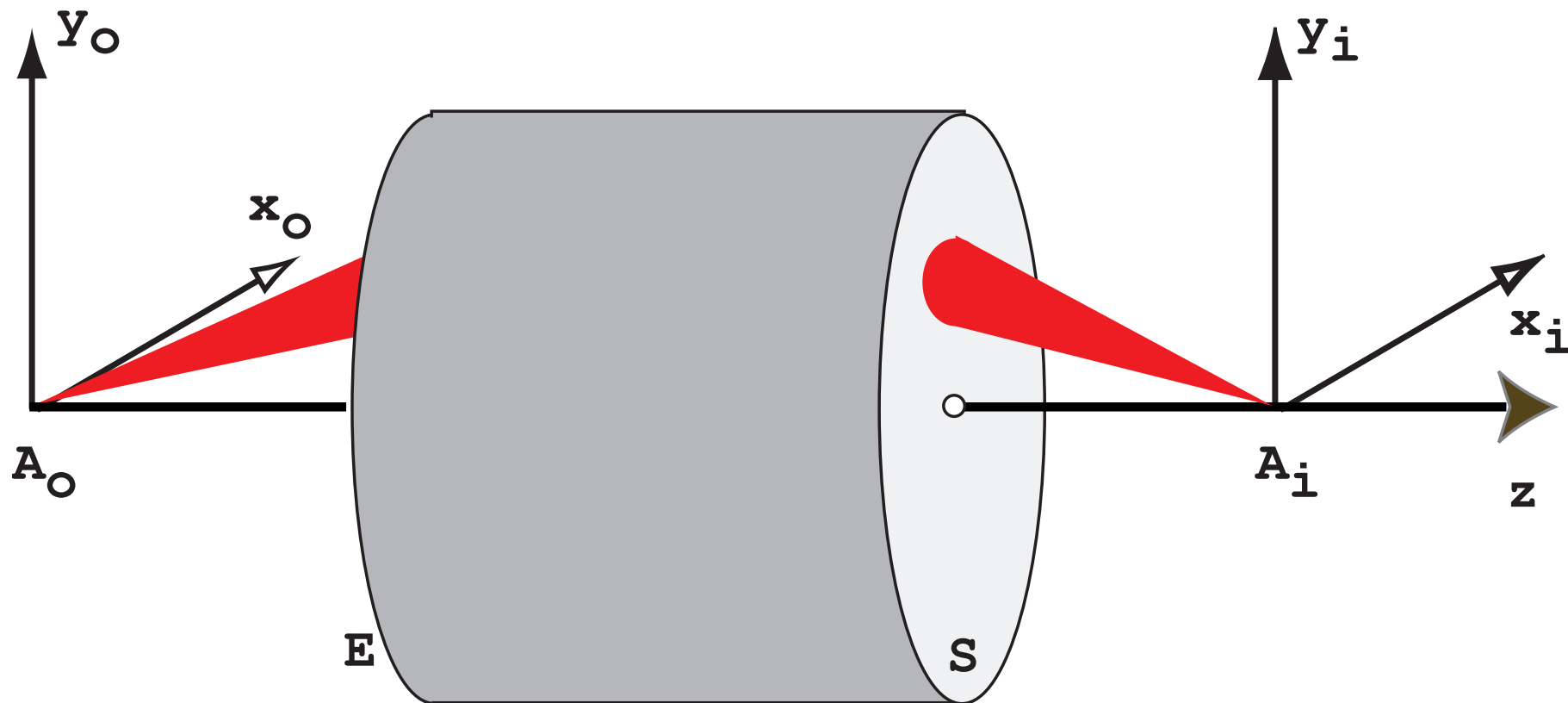
Figure: LACBED Si [001]: experimental (Web site EM centre - Monash university, J. Etheridge).

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

Image formation

- ▶ Abbe image formation.
- ▶ Transfer function.
- ▶ Perfect thin lens.
- ▶ Aberrations.

Optical system



An optical system produces the **image** A_i of a **point source** object A_o . A_o and A_i are said to be conjugate. A_i is **not** a point since any optical system is diffraction limited. This limitation is introduced by the entrance and exit pupils of the optical system.

Some light rays emitted by object point A_o do not reach the image at point A_i .

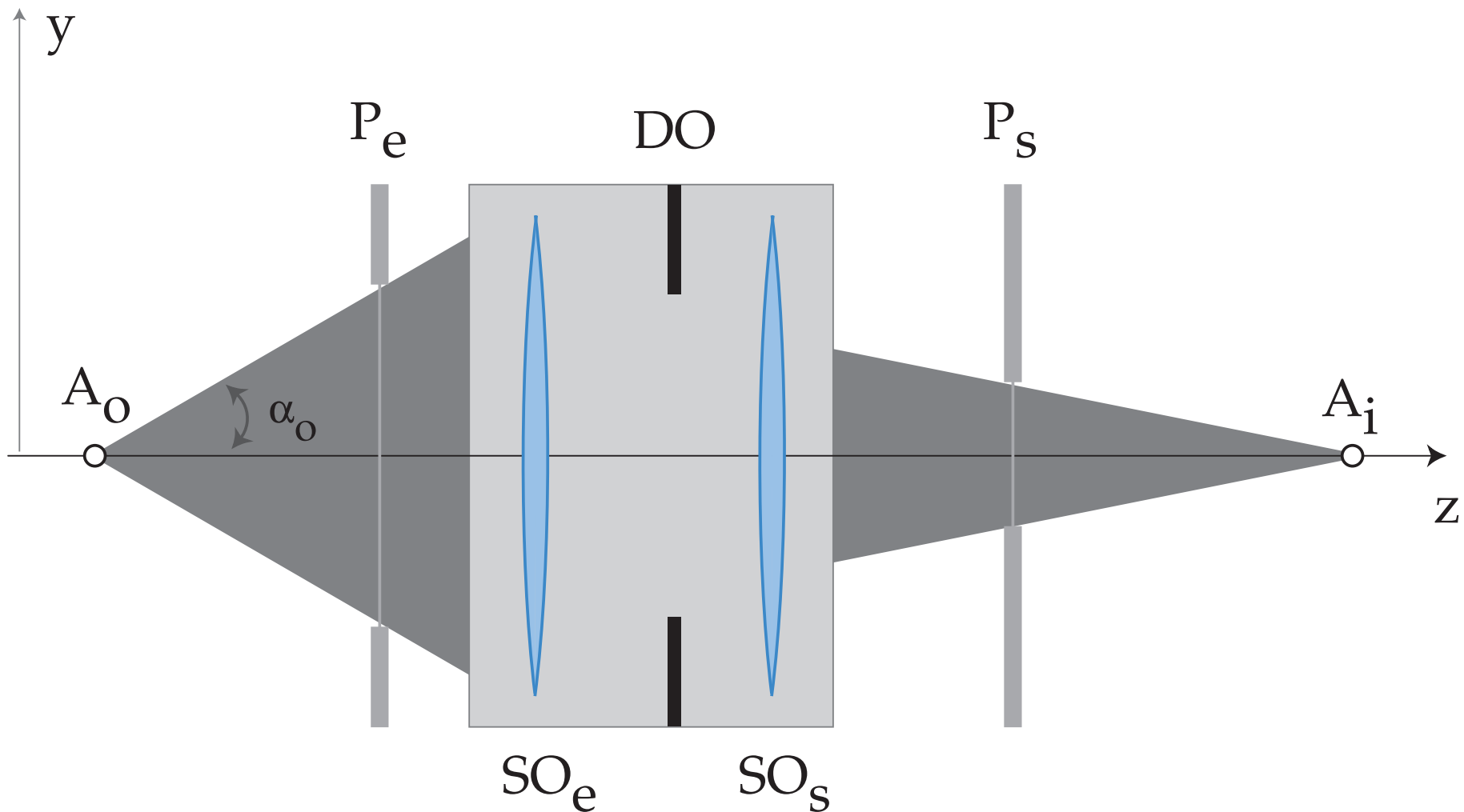
Position of A_i \longrightarrow intersection of the reference light ray (non deviated) and the image plane.

The image of a point source is a **spot** whose shape and intensity depend of the quality of the optical system.

Two types of aberrations:

1. **Monochromatic.**
2. Chromatic (λ dependent).

Pupils



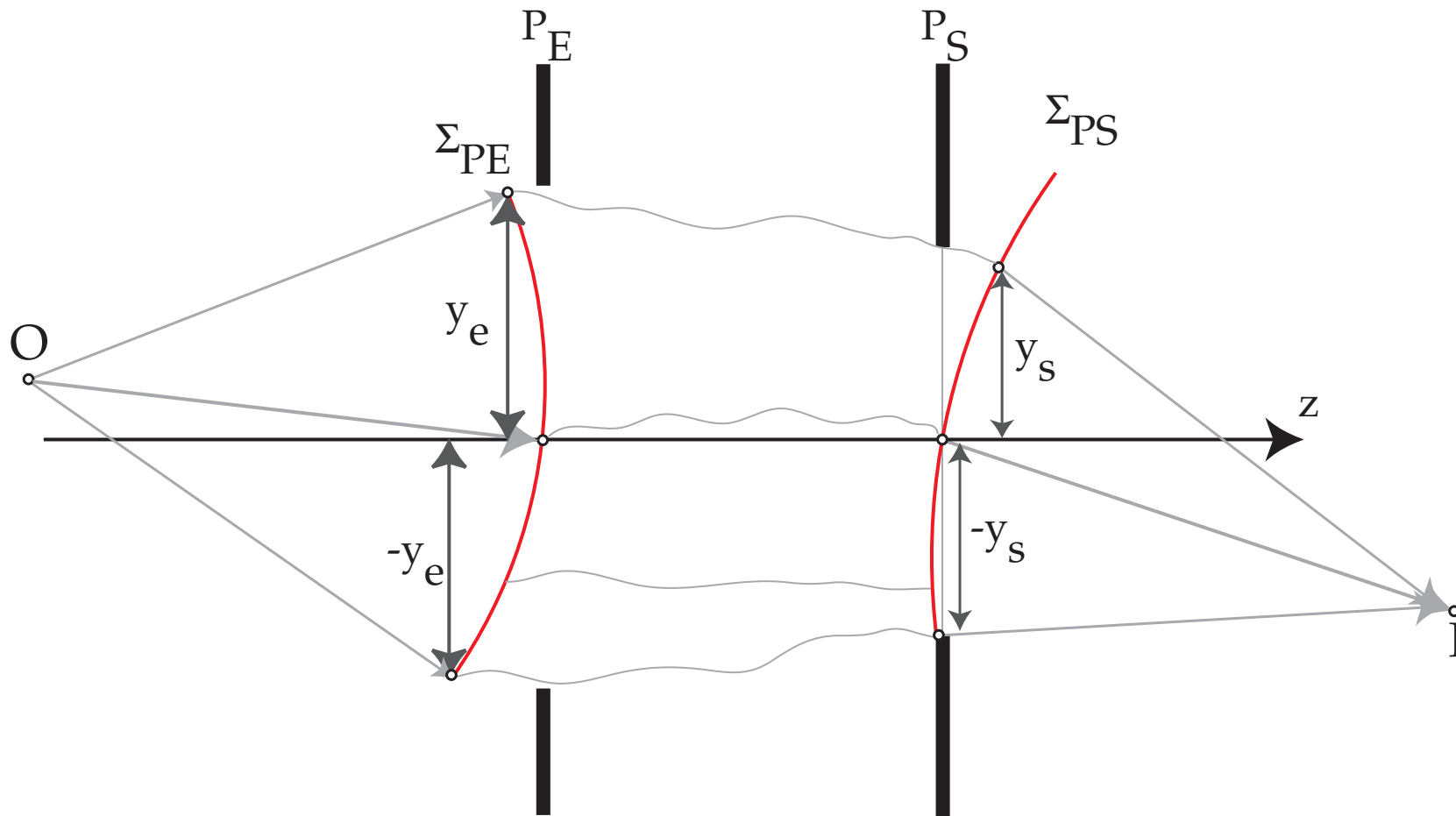
Any optical system can be characterised by an entrance pupil P_e and an exit pupil P_s . The pupils are the image of the opening aperture DO by the entrance and exit optical subsystems SO_e and SO_s . What are P_e and P_s for a thin lens?

In order to evaluate the monochromatic aberrations one must define a function characteristic of the optical system.

This function will depend on:

1. The selected reference planes.
2. The optical path followed by the light ray.

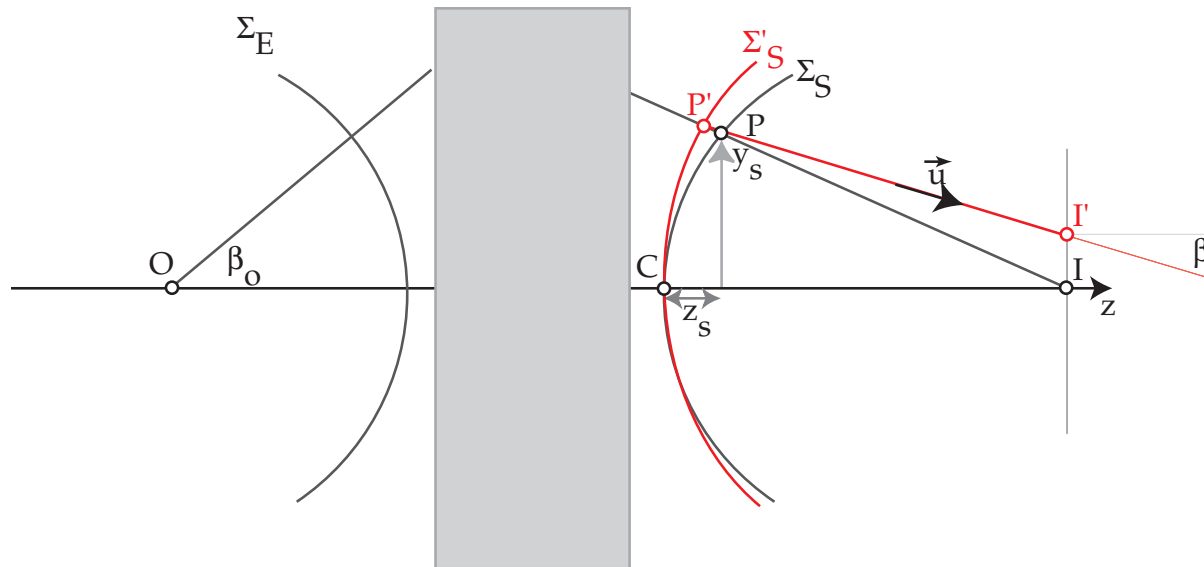
Optical Path Length: OPL



- ▶ **Before** P_E the reference wavefront Σ_{PE} is spherical (point source at O).
- ▶ **After** P_S the reference wavefront Σ_{PS} is spherical (converges towards I).

For a perfect optical system, both the entrance Σ_{PE} and exit Σ_{PS} wavefronts are spherical. The **O**ptical **P**ath **L**ength from O to I is independent of the path.

Optical Path Difference (OPD): aberrations



In the presence of aberrations the wavefront Σ'_S is no more spherical. The **O**ptical **P**ath **D**ifference (distance between the deformed Σ'_S and spherical wavefront Σ_S) introduces a **phase shift** $\delta\phi$. With P' close to $P = (x_s, y_s)$ on reference sphere Σ_S , the OPD at $P' =$ (i.e. OPL from P' to P) is given by (Fermat principle):

$$W(x_s, y_s) = n_i \overline{P'P}$$

n_i refractive index of the medium \longrightarrow phase shift:

$$\delta\phi = e^{2\pi i \frac{W(x_s, y_s)}{\lambda}}$$

Transverse geometric aberrations: $\vec{\epsilon}$

The transverse geometric aberrations are proportional to $\frac{d}{d\theta}$ wavefront aberrations¹⁴:

$$\epsilon_x = -\frac{f \partial W}{n_i \partial x_s}$$
$$\epsilon_y = -\frac{f \partial W}{n_i \partial y_s}$$

f focal length.

The OPD's introduced by all the aberrations of the imaging system are collected in a function $\chi(\vec{u})$ and the phase shift is¹⁵:

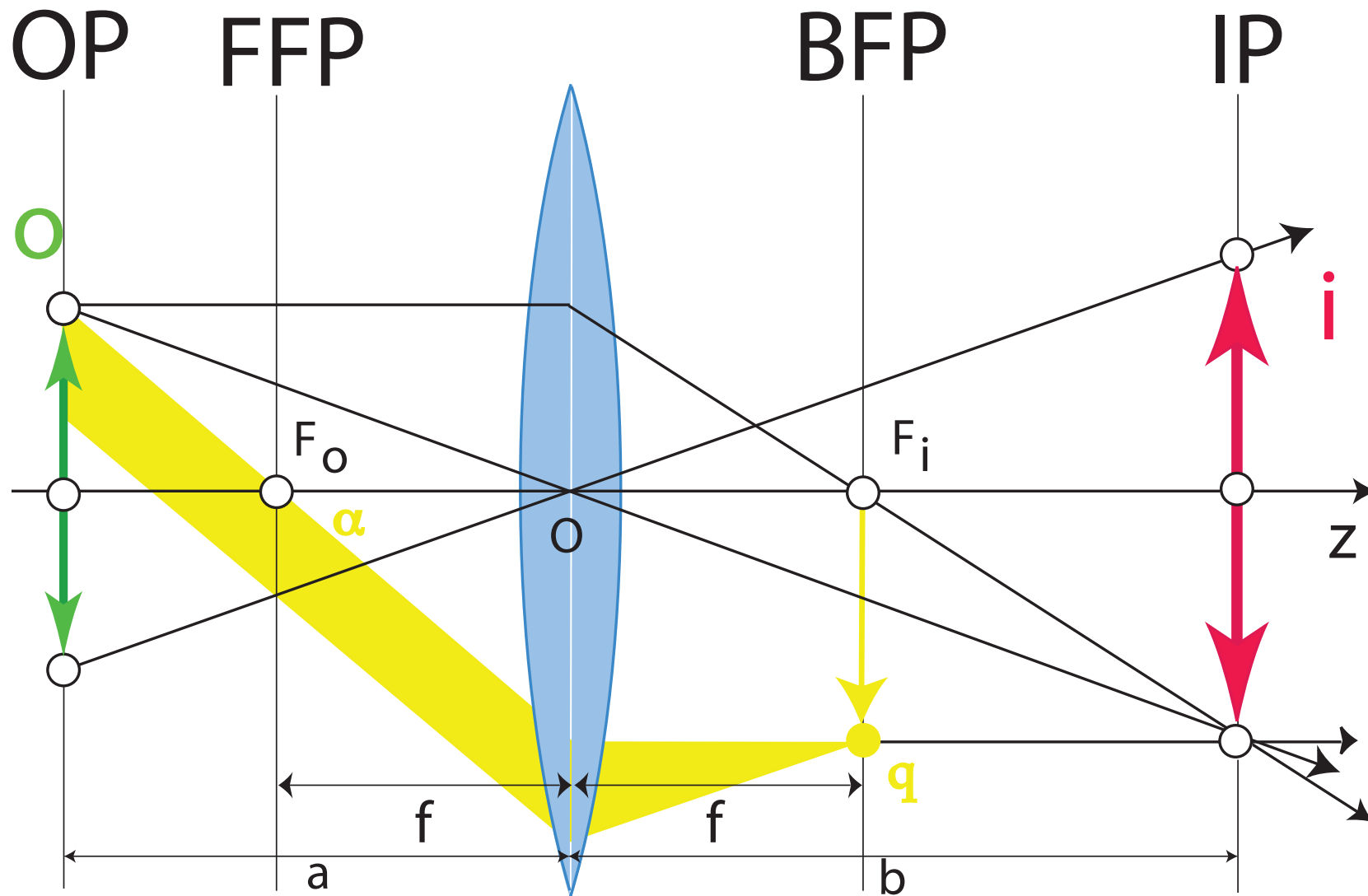
$$\tilde{T}(\vec{u}) = e^{i\chi(\vec{u})}$$

$\tilde{T}(\vec{u})$ has been first employed by Abbe in his description of image formation (1866).

¹⁴ $P(x_s, y_s)$ on the spherical reference wavefront can be characterised by the radial angle θ .

¹⁵The angle θ corresponds (through Bragg law) to a spatial frequency \vec{u} , i.e. a distance in the back focal plane.

Paraxial optics: principal rays



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

Microscope modelling: Abbe image formation theory

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

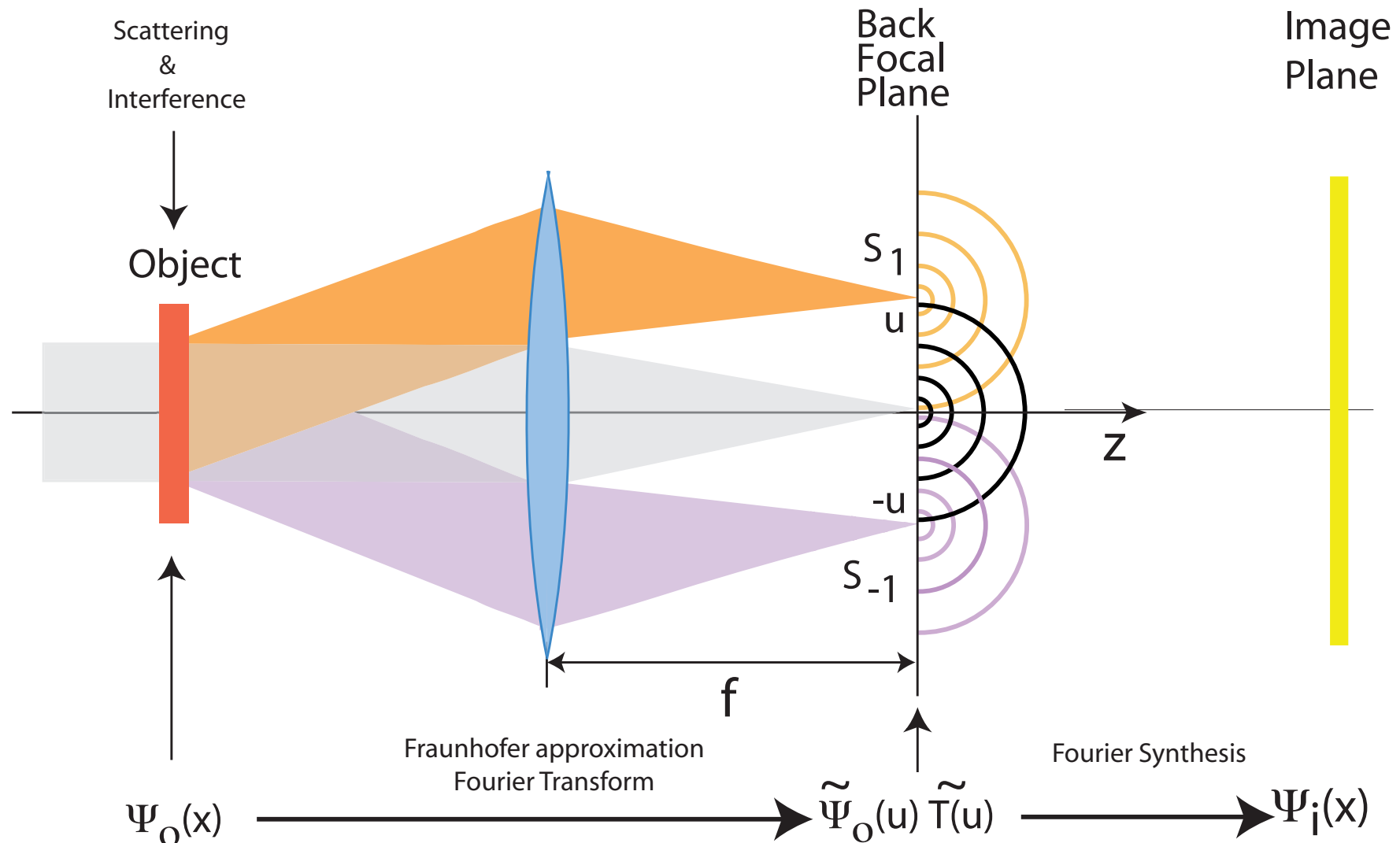


Image forming system has 2 properties (**Abbe theory**):

- ▶ Linear.
- ▶ Space invariant.

Coherence of illumination:

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

Partial coherence (always the case): $\tilde{T}(q', q)$: transmission cross-coefficients
 \implies is approximated by a transfer function $\tilde{T}(\vec{u})$ and several envelope functions
(attenuation of a range of spatial frequencies)..

Two cases:

→ **TEM** ($\tilde{T}(\vec{u})$: **T**ransfer **F**unction):

$$\tilde{\Psi}_i(\vec{u}) = \tilde{\Psi}_o(\vec{u}) \tilde{T}(\vec{u})$$

$$\Psi_i(\vec{x}) = \int \tilde{\Psi}_o(\vec{u}) \tilde{T}(\vec{u}) e^{2\pi i \vec{u} \cdot \vec{x}} d\vec{u}$$

→ **STEM** ($\widetilde{OTF}(\vec{u}) = \tilde{T}(\vec{u}) \otimes \tilde{T}(-\vec{u})$: **O**ptical **T**ransfer **F**unction):

$$I(\vec{x}) = \langle \Psi_i(\vec{x}; t) \Psi_i^*(\vec{x}; t) \rangle$$

$$\Psi_i(\vec{x}; t) = \Psi_o(\vec{x}; t) \otimes T(\vec{x})$$

$$I(\vec{x}) = \langle [\Psi_o(\vec{x}; t) \otimes T(\vec{x})] [\Psi_o^*(\vec{x}; t) \otimes T^*(\vec{x})] \rangle \quad (\otimes \text{ convolution.})$$

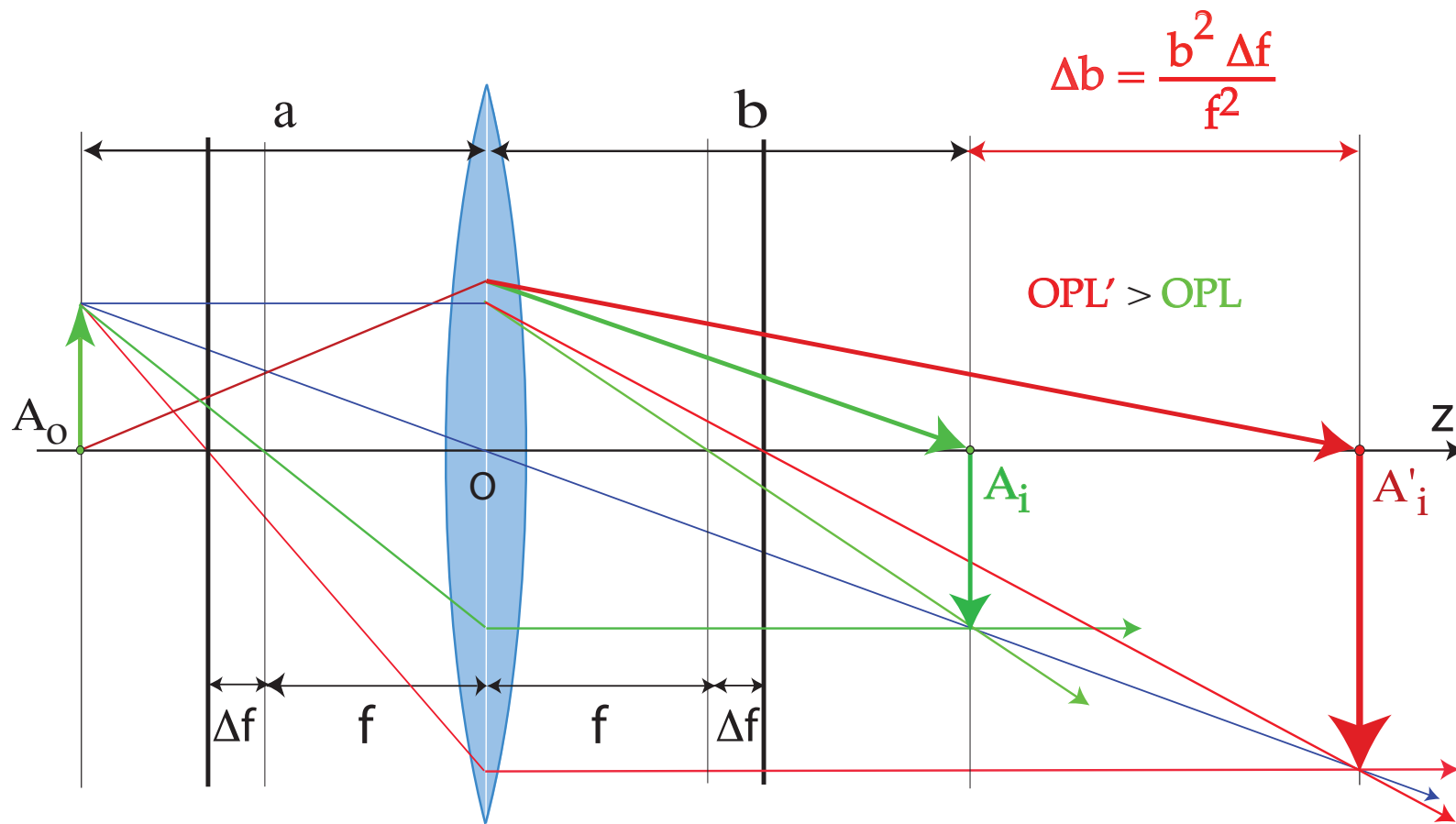
$$I(\vec{x}) = [T(\vec{x}) T^*(\vec{x})] \otimes \langle \Psi_o(\vec{x}; t) \Psi_o^*(\vec{x}; t) \rangle \quad (T(\vec{x}) \text{ is time independent.})$$

$$\langle \Psi_o(\vec{x}; t) \Psi_o^*(\vec{x}; t) \rangle = |\Psi_o(\vec{x})|^2 \quad (\text{complete spatial incoherence})$$

$$I(\vec{x}) = |\Psi_o(\vec{x})|^2 \otimes [T(\vec{x}) T^*(\vec{x})]$$

$$I(\vec{x}) = I_o(\vec{x}) \otimes OTF(\vec{x})$$

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:

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

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

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

Where:

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

Wavefront aberrations to 6th order (cartesian coordinates)

$$\{z, \pi (u^2 + v^2) \lambda\} \text{ (defocus)}$$

$$\{W(1, 1), 2\pi(u \cos(\phi(1, 1)) + v \sin(\phi(1, 1)))\}$$

$$\{W(2, 2), \pi\lambda((u - v)(u + v) \cos(2\phi(2, 2)) + 2uv \sin(2\phi(2, 2)))\}$$

$$\{W(3, 1), \frac{2}{3}\pi (u^2 + v^2) \lambda^2 (u \cos(\phi(3, 1)) + v \sin(\phi(3, 1)))\}$$

$$\{W(3, 3), \frac{2}{3}\pi\lambda^2 (u (u^2 - 3v^2) \cos(3\phi(3, 3)) - v (v^2 - 3u^2) \sin(3\phi(3, 3)))\}$$

$$\left\{ W(4, 0), \frac{1}{2}\pi (u^2 + v^2)^2 \lambda^3 \right\} \text{ (3rd order spherical aberration or } C_3)$$

$$\{W(4, 2), \frac{1}{2}\pi (u^2 + v^2) \lambda^3 ((u - v)(u + v) \cos(2\phi(4, 2)) + 2uv \sin(2\phi(4, 2)))\}$$

$$\{W(4, 4), \frac{1}{2}\pi\lambda^3 ((u^4 - 6v^2u^2 + v^4) \cos(4\phi(4, 4)) + 4u(u - v)v(u + v) \sin(4\phi(4, 4)))\}$$

$$\left\{ W(5, 1), \frac{2}{5}\pi (u^2 + v^2)^2 \lambda^4 (u \cos(\phi(5, 1)) + v \sin(\phi(5, 1))) \right\}$$

$$\{W(5, 3), \frac{2}{5}\pi (u^2 + v^2) \lambda^4 (u (u^2 - 3v^2) \cos(3\phi(5, 3)) - v (v^2 - 3u^2) \sin(3\phi(5, 3)))\}$$

$$\{W(5, 5), \frac{2}{5}\pi\lambda^4 (u (u^4 - 10v^2u^2 + 5v^4) \cos(5\phi(5, 5)) + v (5u^4 - 10v^2u^2 + v^4) \sin(5\phi(5, 5)))\}$$

$$\left\{ W(6, 0), \frac{1}{3}\pi (u^2 + v^2)^3 \lambda^5 \right\} \text{ (5th order spherical aberration or } C_5)$$

$$\left\{ W(6, 2), \frac{1}{3}\pi (u^2 + v^2)^2 \lambda^5 ((u - v)(u + v) \cos(2\phi(6, 2)) + 2uv \sin(2\phi(6, 2))) \right\}$$

$$\left\{ W(6, 4), \frac{1}{3}\pi\lambda^5 ((u^6 - 5v^2u^4 - 5v^4u^2 + v^6) \cos(4\phi(6, 4)) + 4uv (u^4 - v^4) \sin(4\phi(6, 4))) \right\}$$

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

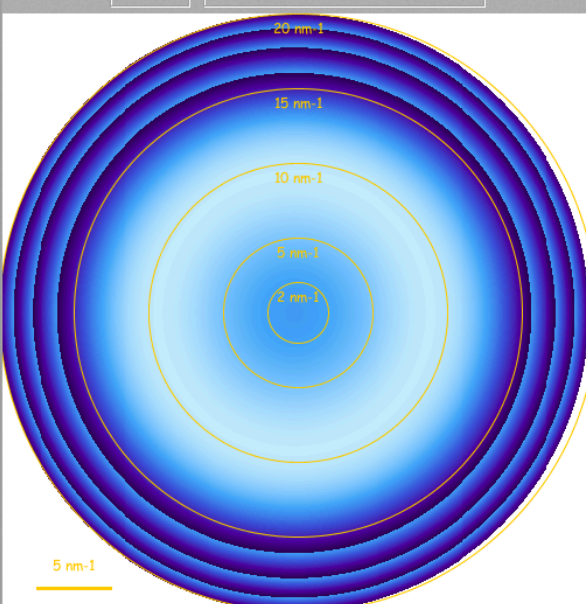
jems describes wavefront aberrations to order 8.

Transfer Function::Microscope::Titan 80-300 | FEI Titan 80-300 Cs corrected | 300.0

Gamma

Aberrations CTF profile CTF Diffractogram OTF

LUT Color Phase jumps 2π π π/2 π/4 π/6



Transfer function controls

Aberrations Coherence Defocus Drift & Noise Microscope Shift & tilt Order 0 Order 1 Order 2 Order 3

0th order 1st order 2nd order 3rd order

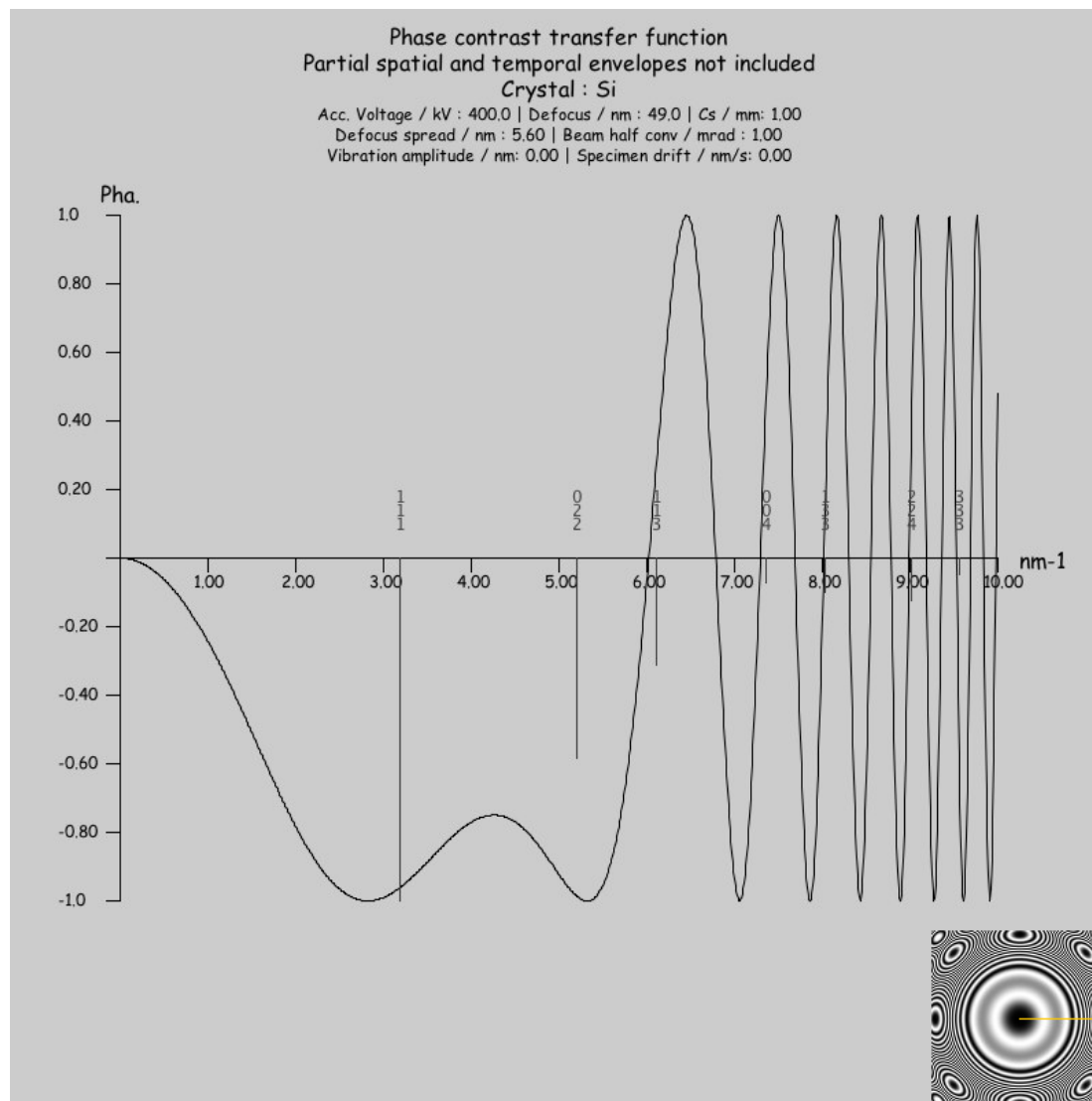
Amplitude

W00: Cc

C_c (Cc W_{00}) [mm]	2.0	
C_{01} (I W_{11}) [nm]	0.0	0.0
C_{10} (Z W_{20}) [nm]	-9.4	
C_{12} (A ₁ W_{22}) [nm]	0.0	0.0
C_{21} (3B ₂ W_{31}) [nm]	0.0	0.0
C_{23} (A ₂ W_{33}) [nm]	0.0	0.0
C_{30} (C ₃ W_{40}) [mm]	-0.03	
C_{32} (4S ₃ W_{42}) [μm]	0.0	0.0
C_{34} (A ₃ W_{44}) [μm]	0.0	0.0
C_{41} (5B ₄ W_{51}) [μm]	0.0	0.0
C_{43} (5D ₄ W_{53}) [μm]	0.0	0.0
C_{45} (A ₄ W_{55}) [μm]	0.0	0.0
C_{50} (C ₅ W_{60}) [mm]	5.0	
C_{52} (6S ₅ W_{62}) [mm]	0.0	0.0
C_{54} (6R ₅ W_{64}) [mm]	0.0	0.0
C_{56} (A ₅ W_{66}) [mm]	0.0	0.0
C_{61} (7B ₆ W_{71}) [mm]	0.0	0.0
C_{63} (7D ₆ W_{73}) [mm]	0.0	0.0
C_{65} (7F ₆ W_{75}) [mm]	0.0	0.0
C_{67} (A ₆ W_{77}) [mm]	0.0	0.0
C_{70} (C ₇ W_{80}) [m]	0.0	
C_{72} (8S ₇ W_{82}) [m]	0.0	0.0
C_{74} (8R ₇ W_{84}) [m]	0.0	0.0
C_{76} (8G ₇ W_{86}) [m]	0.0	0.0
C_{78} (A ₇ W_{88}) [m]	0.0	0.0

Reset Formula

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.

In the **W**eak **P**hase **O**bject **A**pproximation 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)

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

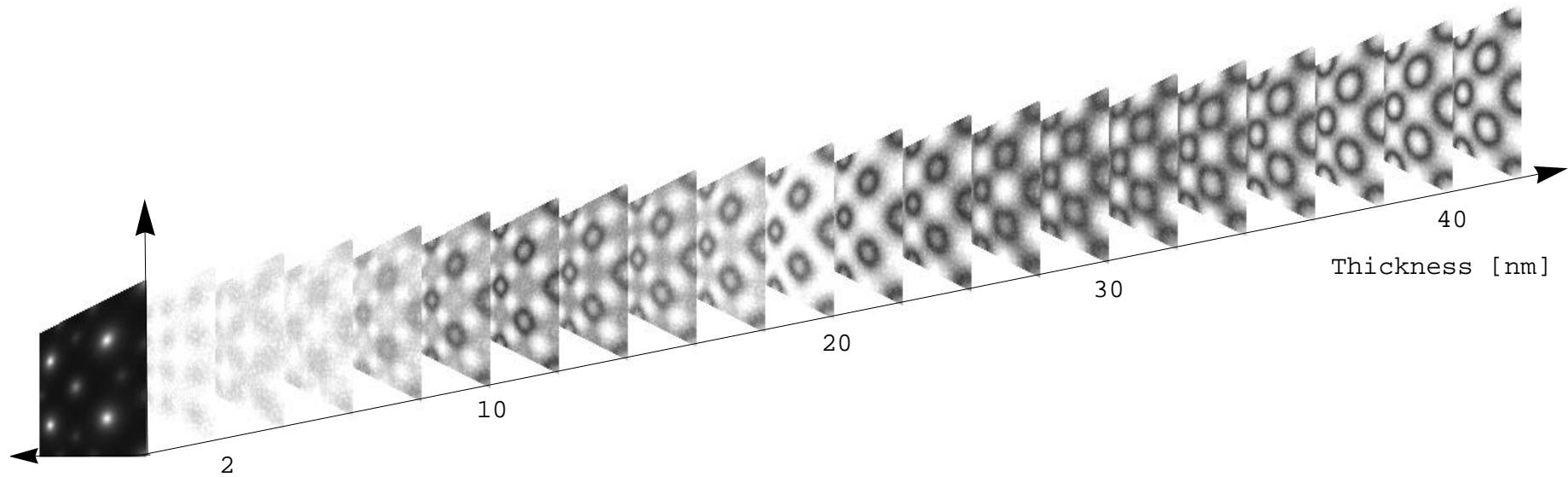
Where:

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

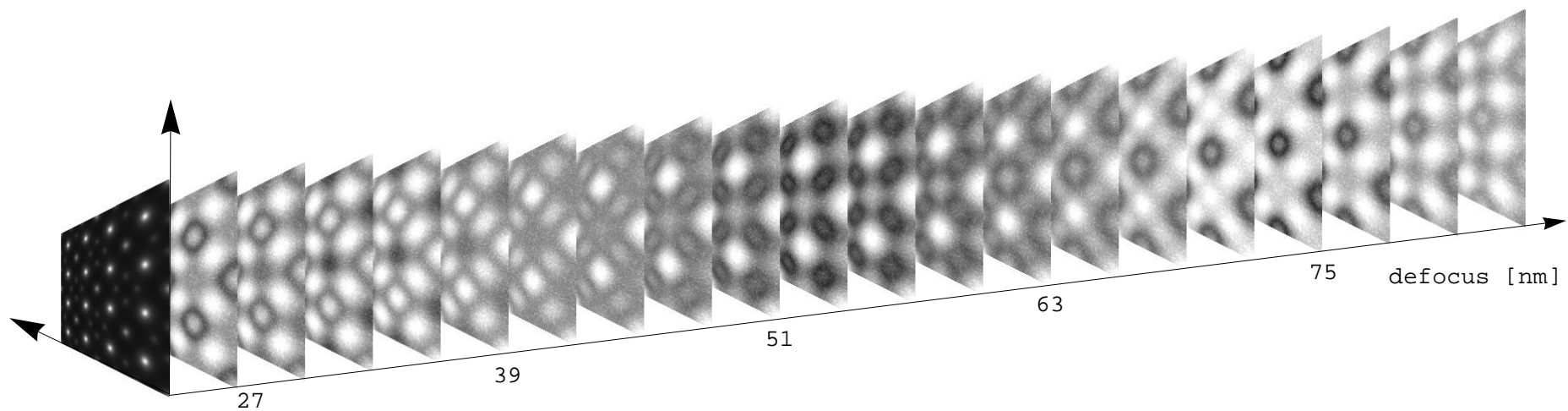
σ : electron matter interaction constant

HRTEM image depends on specimen thickness and object defocus

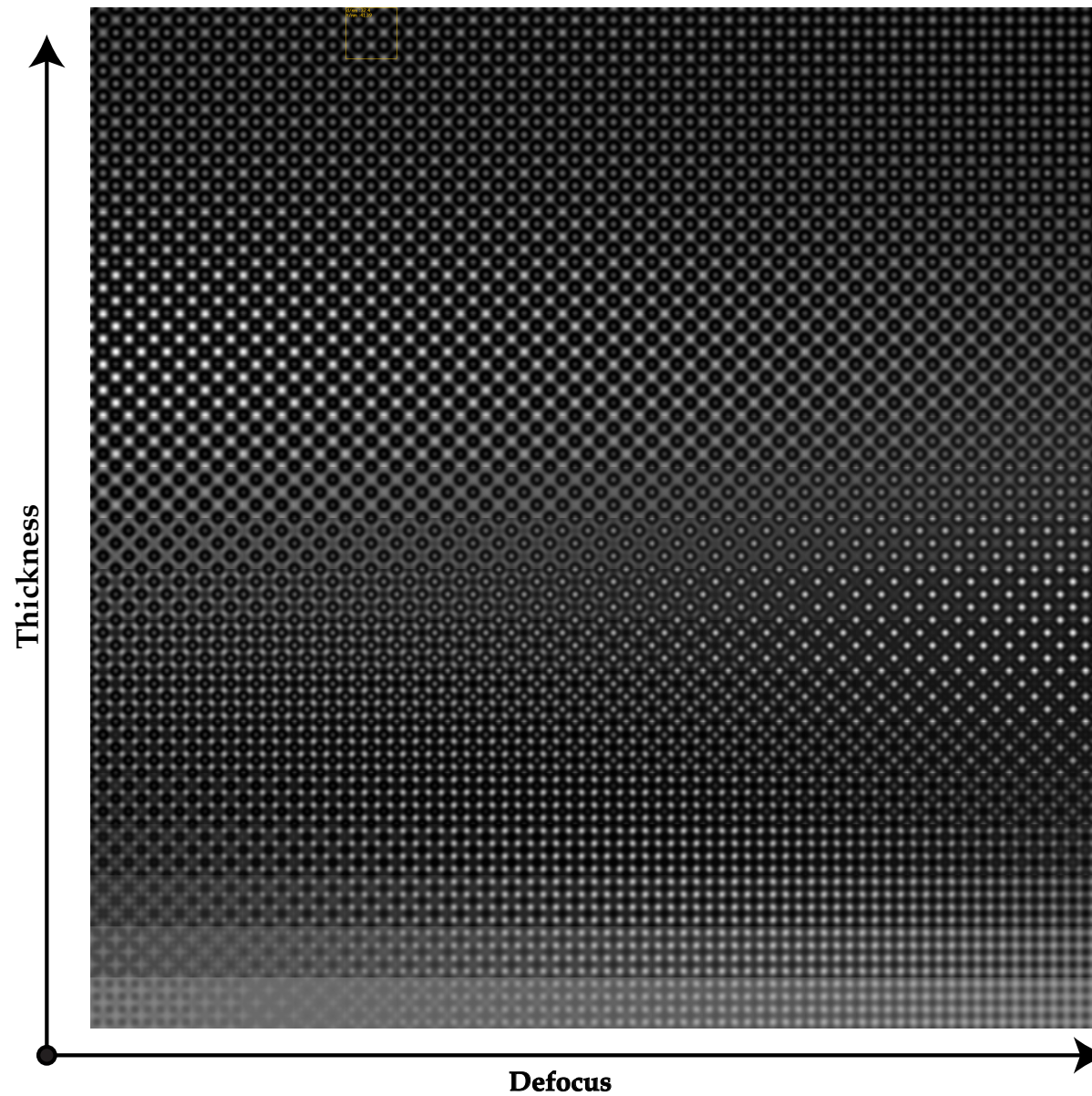
Thickness series



Defocus series



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



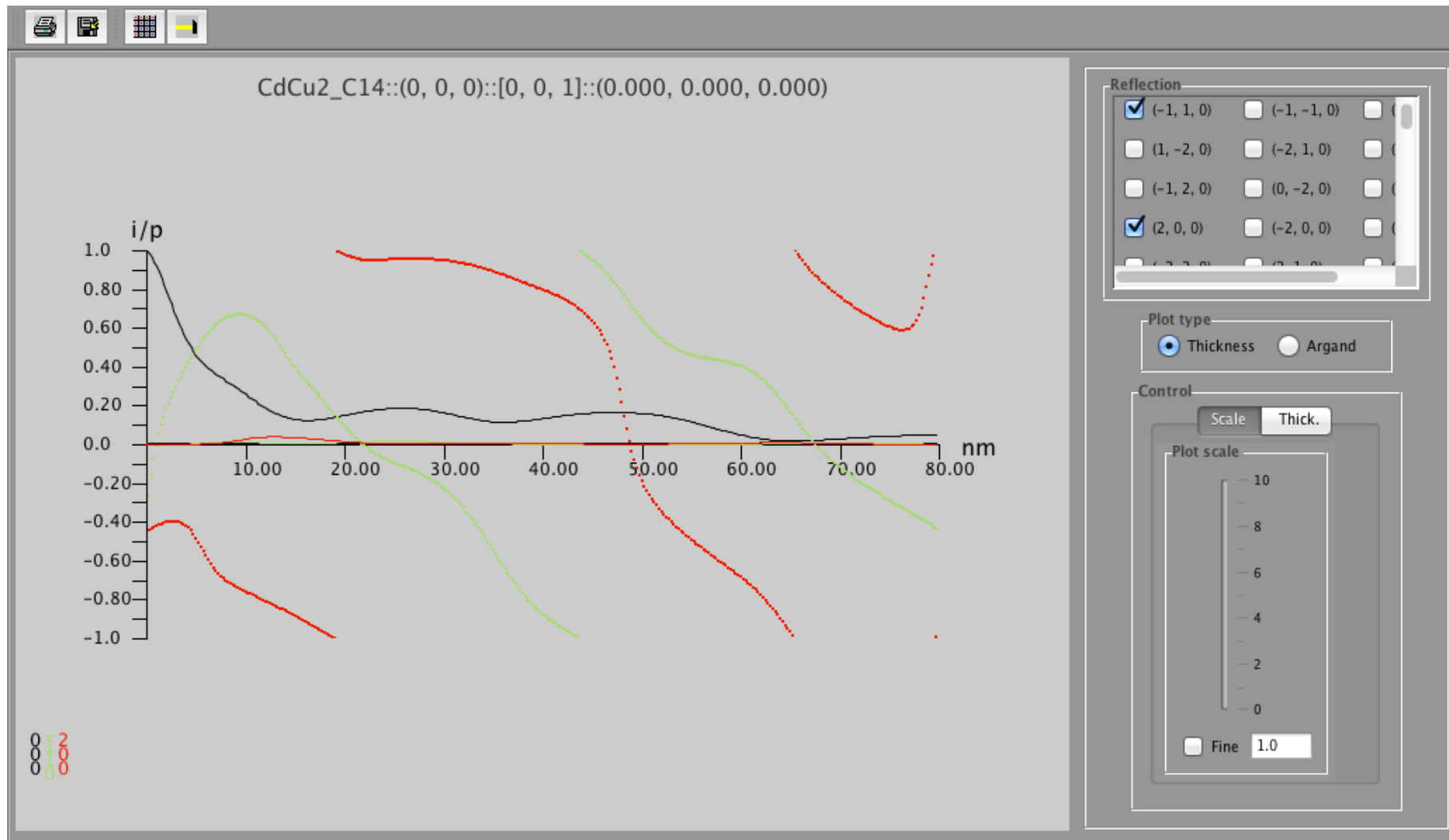
HREM map does not include the Modulation Transfer Function (MTF) of the detector.

Problems

- ▶ 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 noise¹⁶, ...
- ▶ ...

¹⁶S. 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.

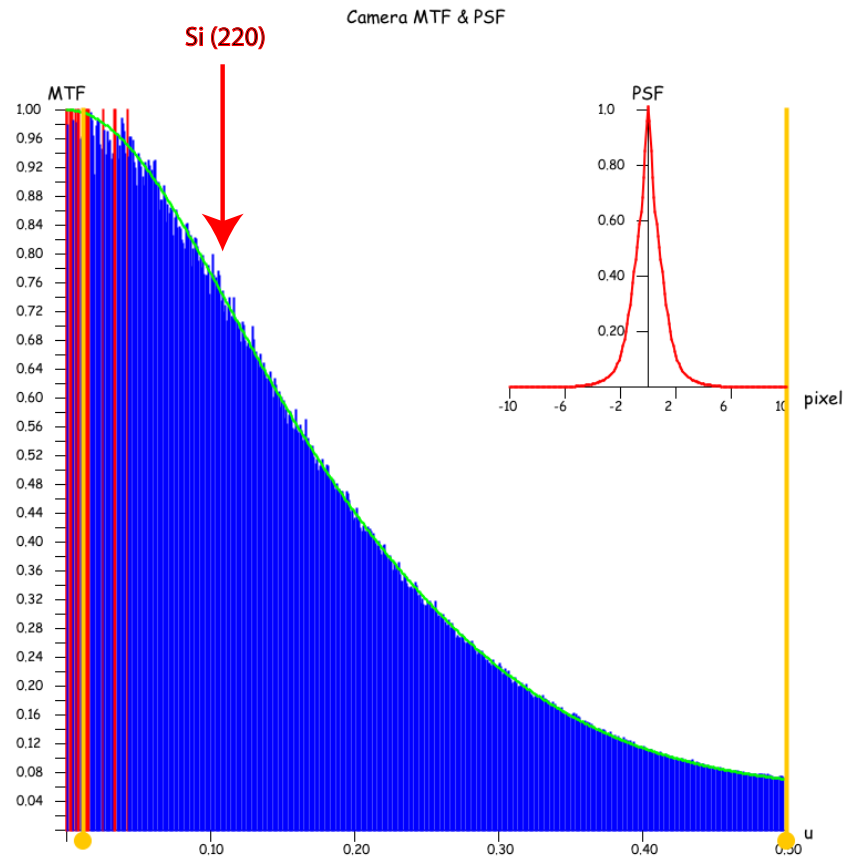


Figure: At high magnification Si (220) planes imaged with high contrast.

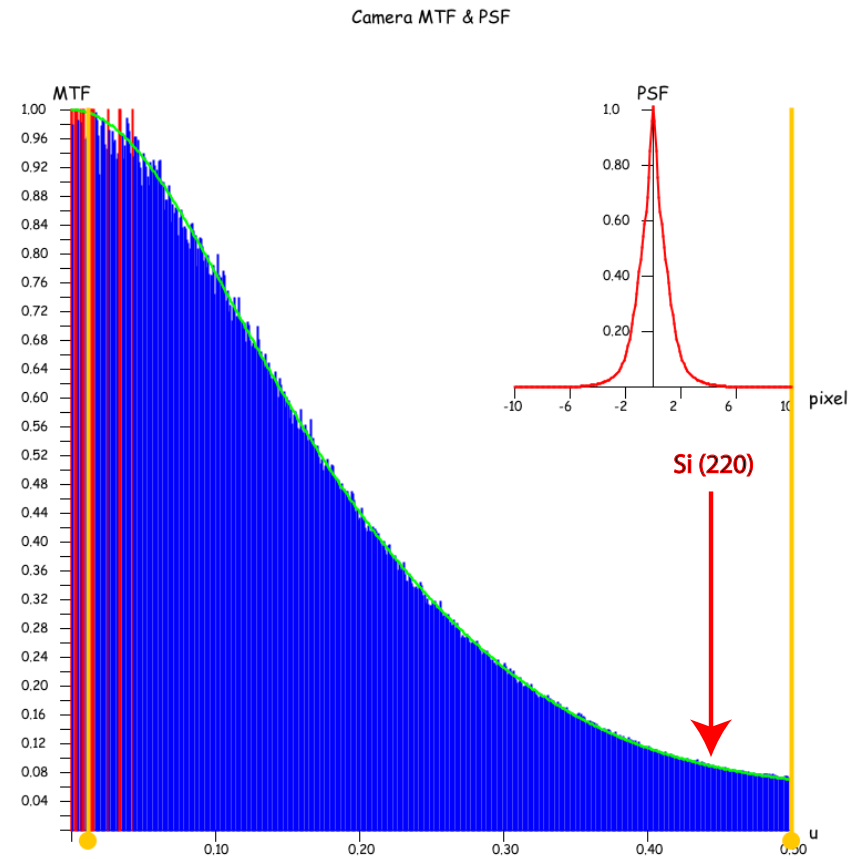


Figure: At low magnification Si (220) planes imaged with low contrast.

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

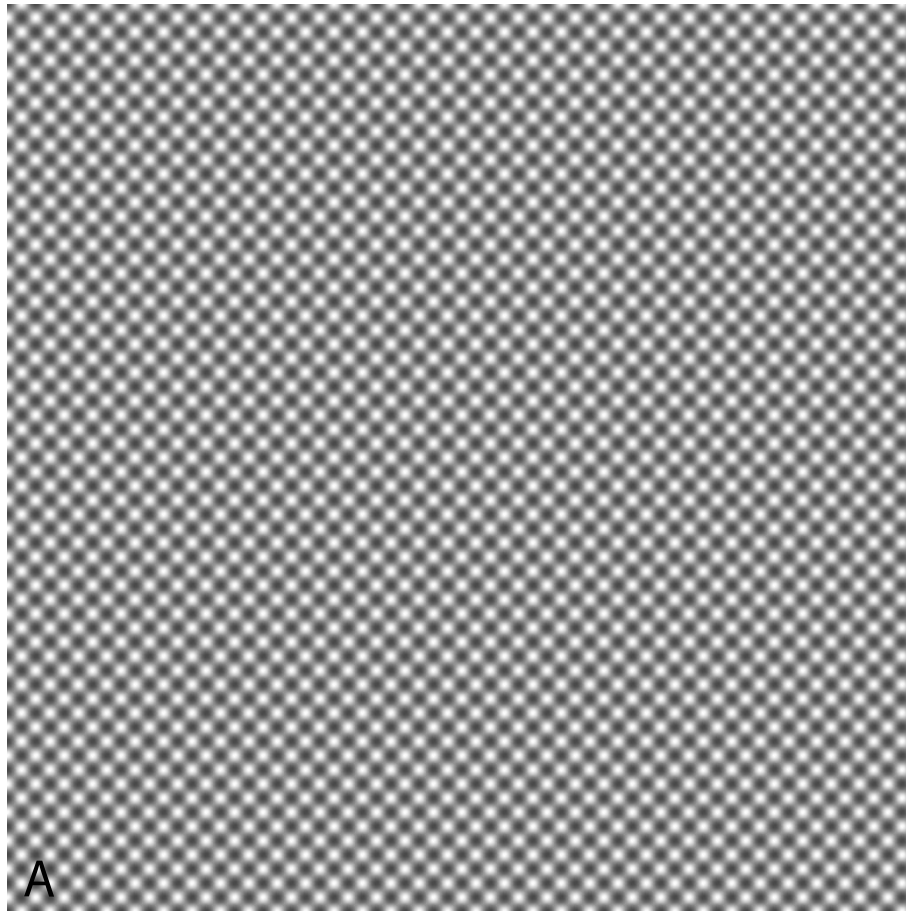


Figure: A: Si [001] simulation.

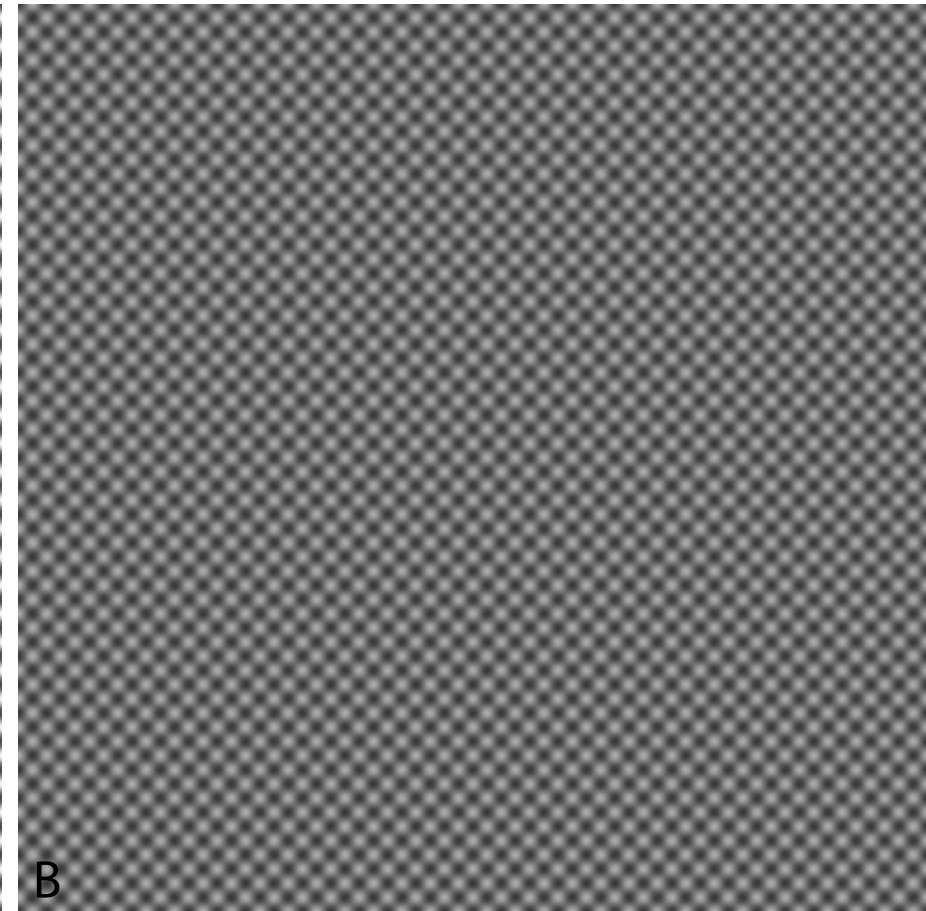


Figure: B: Si [001], simulation + CCD MTF.

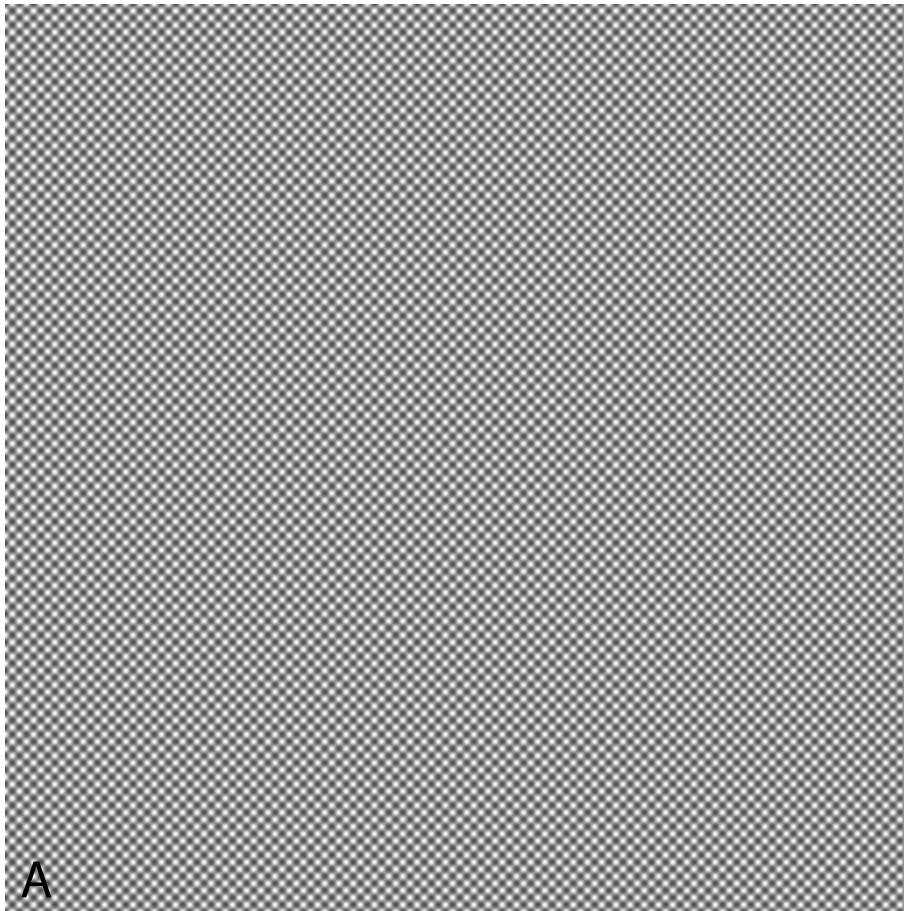


Figure: A: Si [001] simulation.

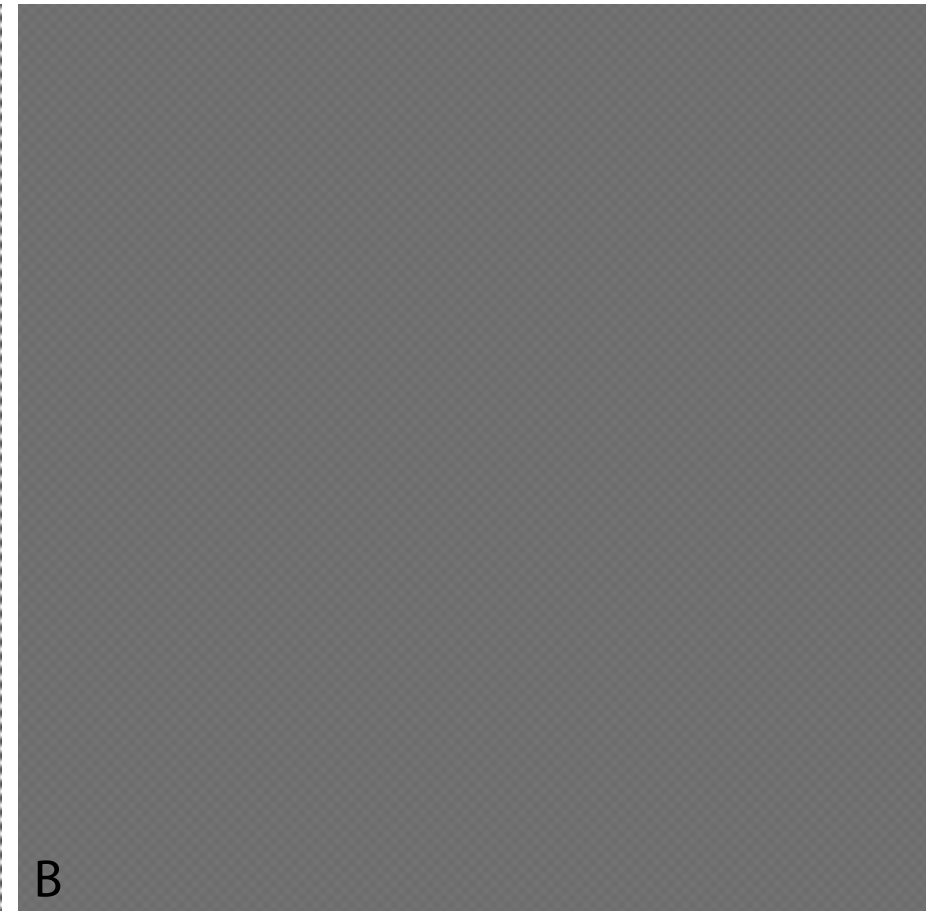


Figure: B: Si [001], simulation + CCD MTF.

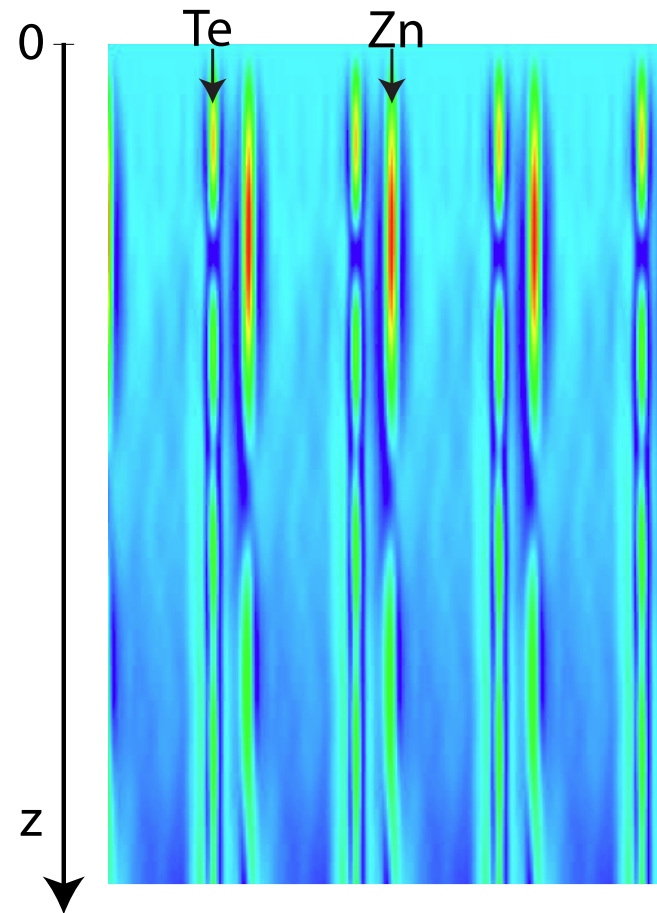
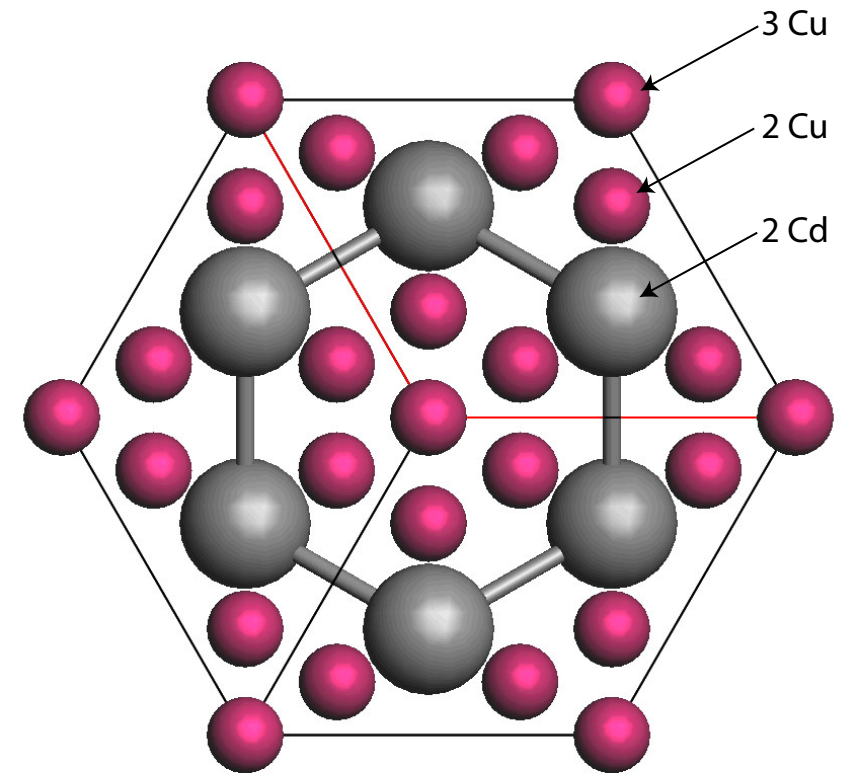
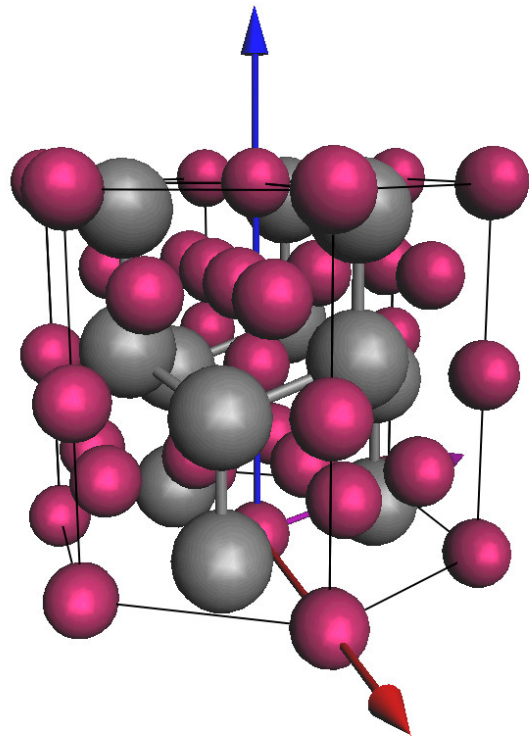


Figure: ZnTe [110] wave function intensity.

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?

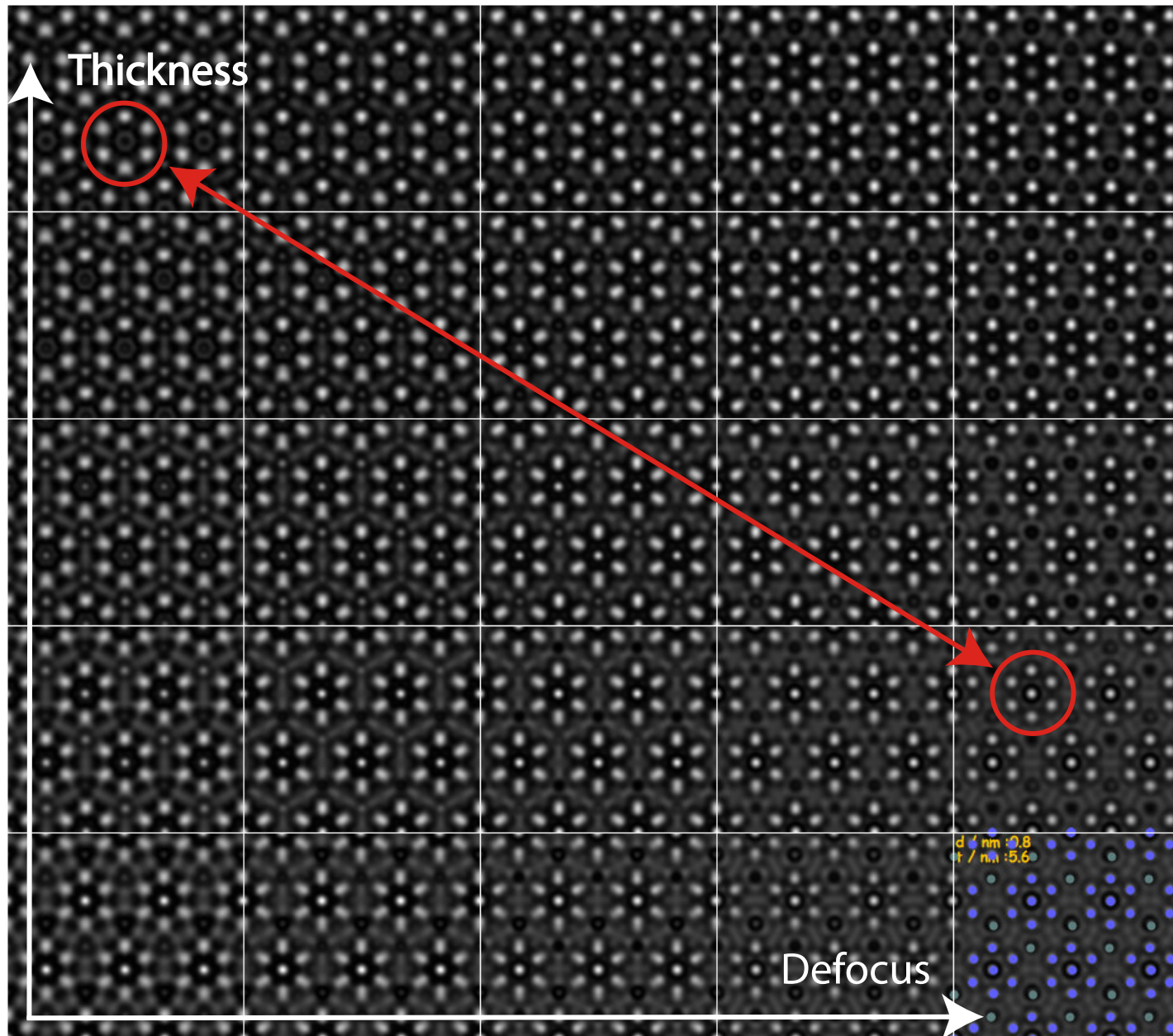
Example: CdCu_2 , visibility of the 3 Cu atomic columns.



HRTEM image simulation conditions

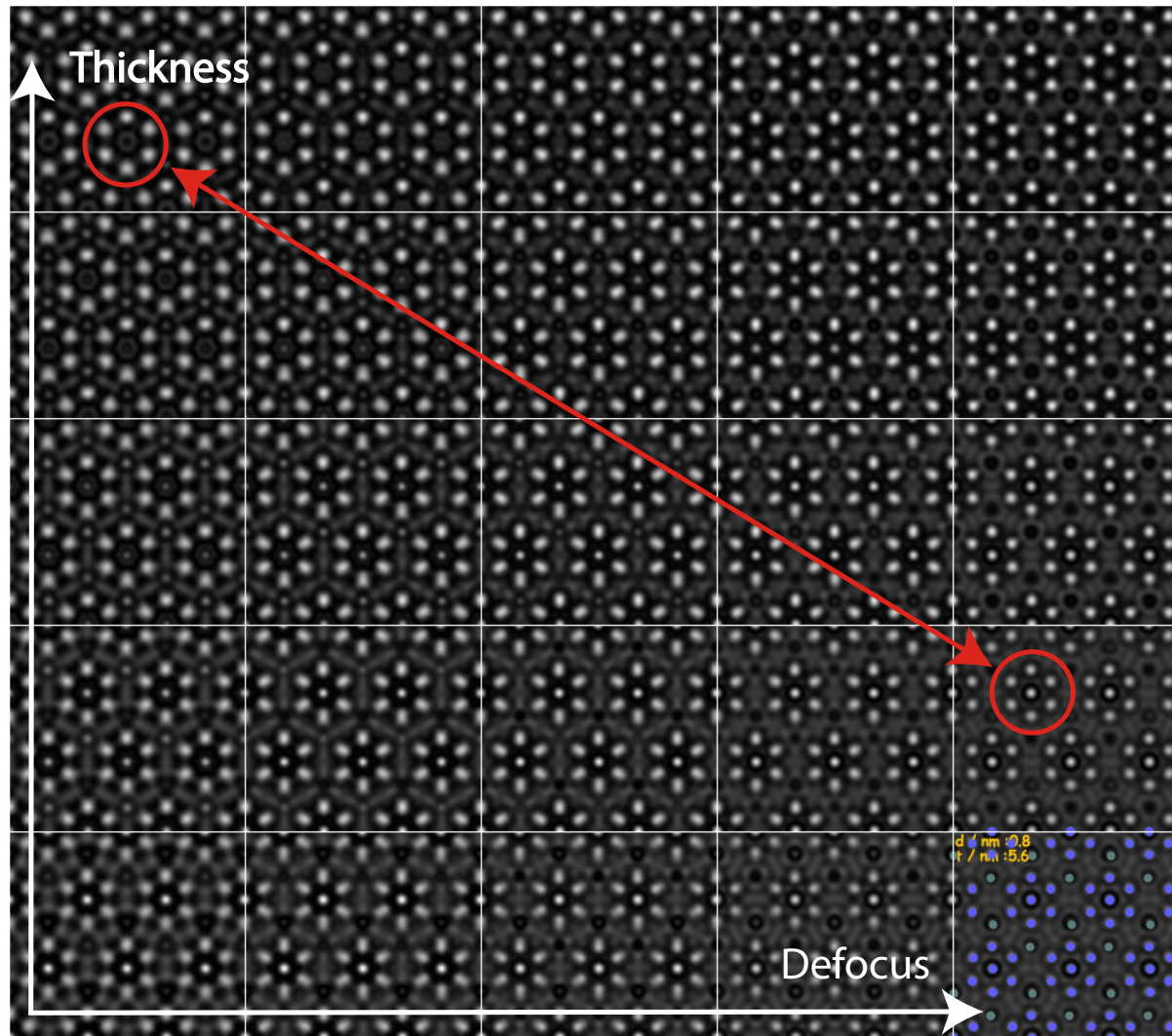
Acc. [kV]	C_s [mm]	C_5 [mm]	C_c [mm]	ΔE [eV]	Z [nm]	Δz [nm]
300	-0.008	30	0.5	0.6	-4.9	1
300	-0.008	30	0.1	0.2	-2.0	1

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



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 (≤ 10 nm) will allow **faithful** imaging of crystal projected potential.

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...

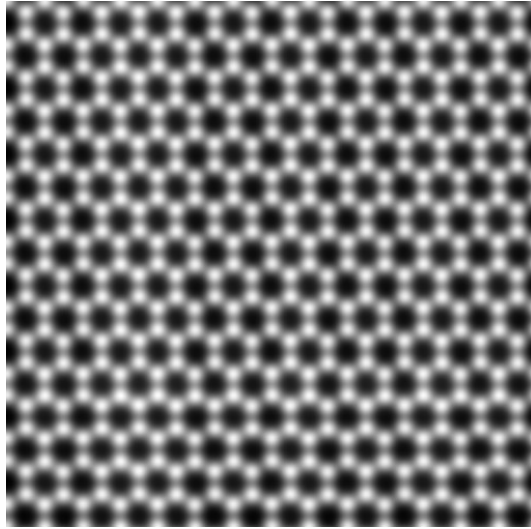


Figure: Proj. pot. approx.

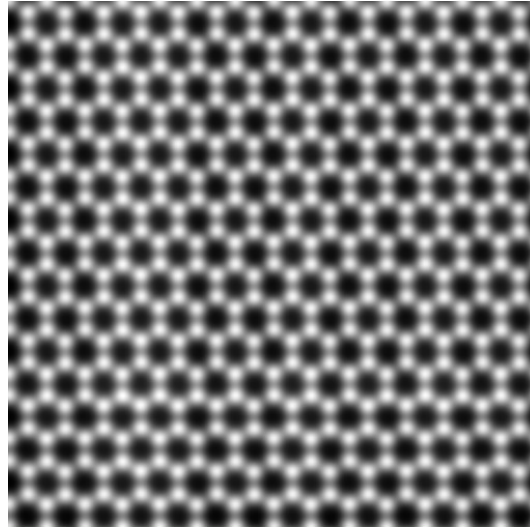


Figure: Channeling calculation.

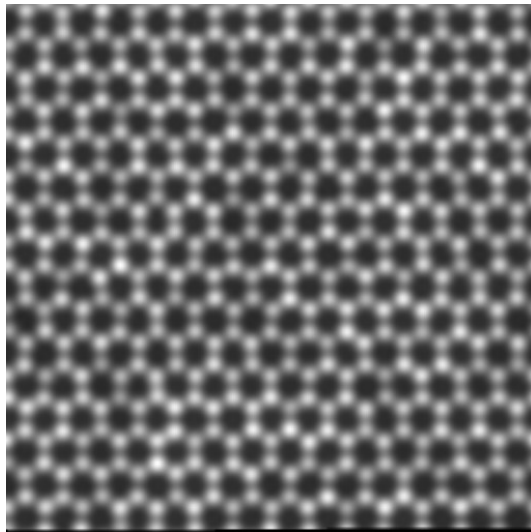


Figure: Frozen lattice 5 conf.

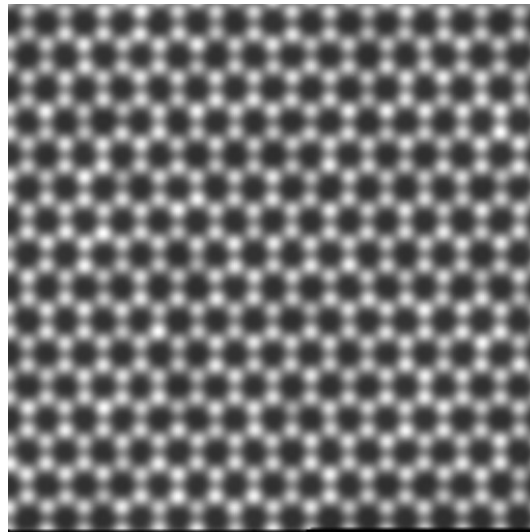


Figure: Frozen lattice 10 conf.

HRSTEM - HRTEM comparison: graphene with add atoms

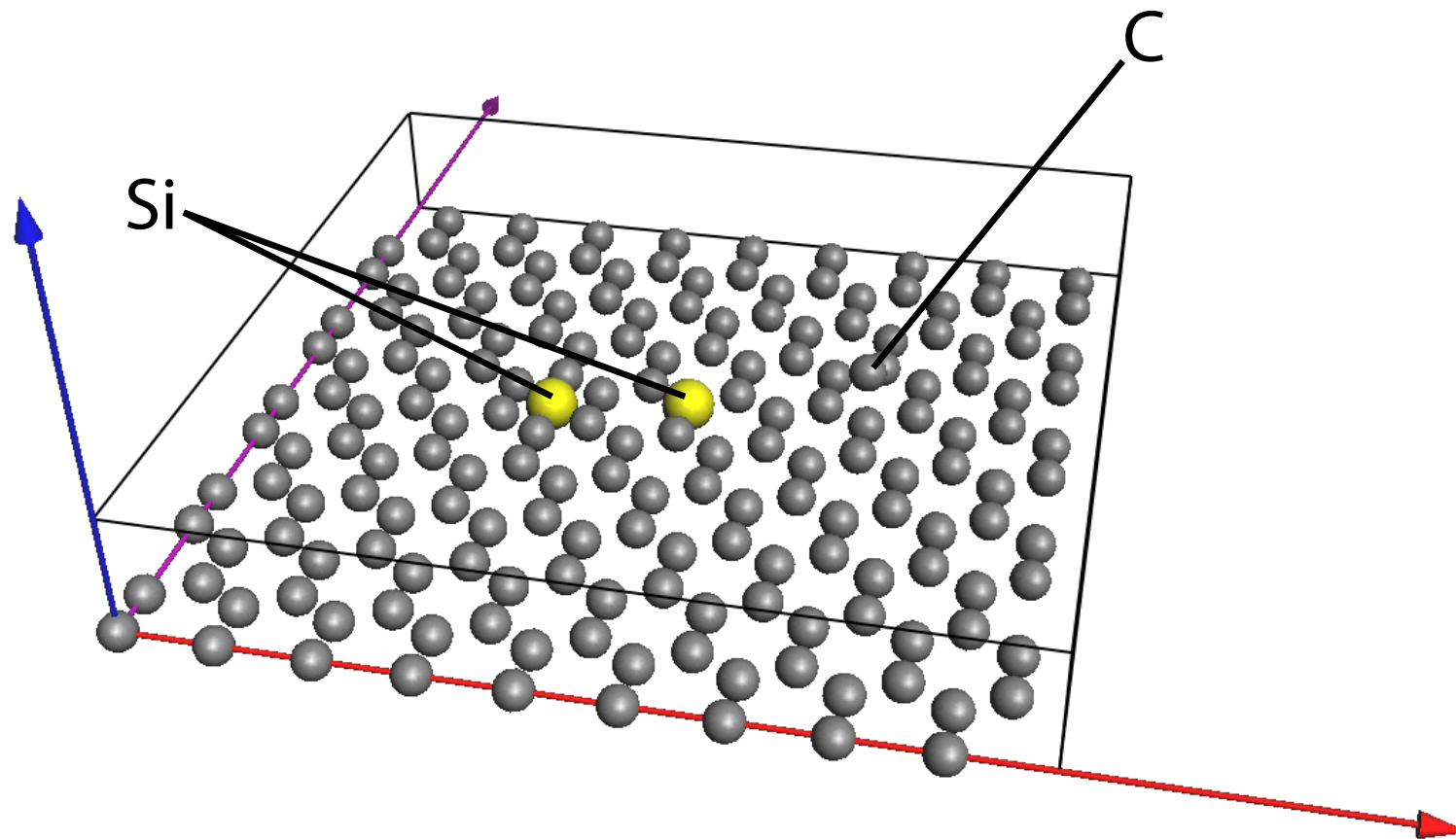


Figure: Graphene with Si in 6 C ring, Si substitutional and 2 C column.

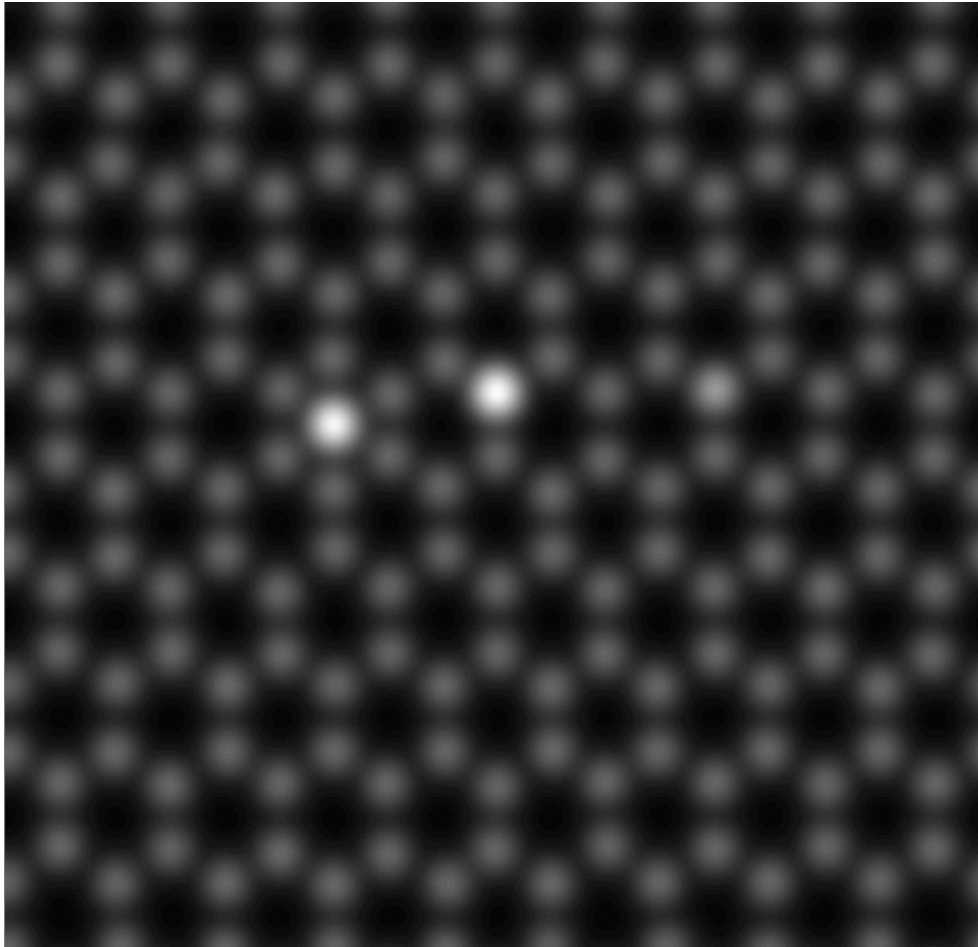


Figure: Frozen lattice (~ 400 s).



Figure: Channeling (~ 2 s).

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

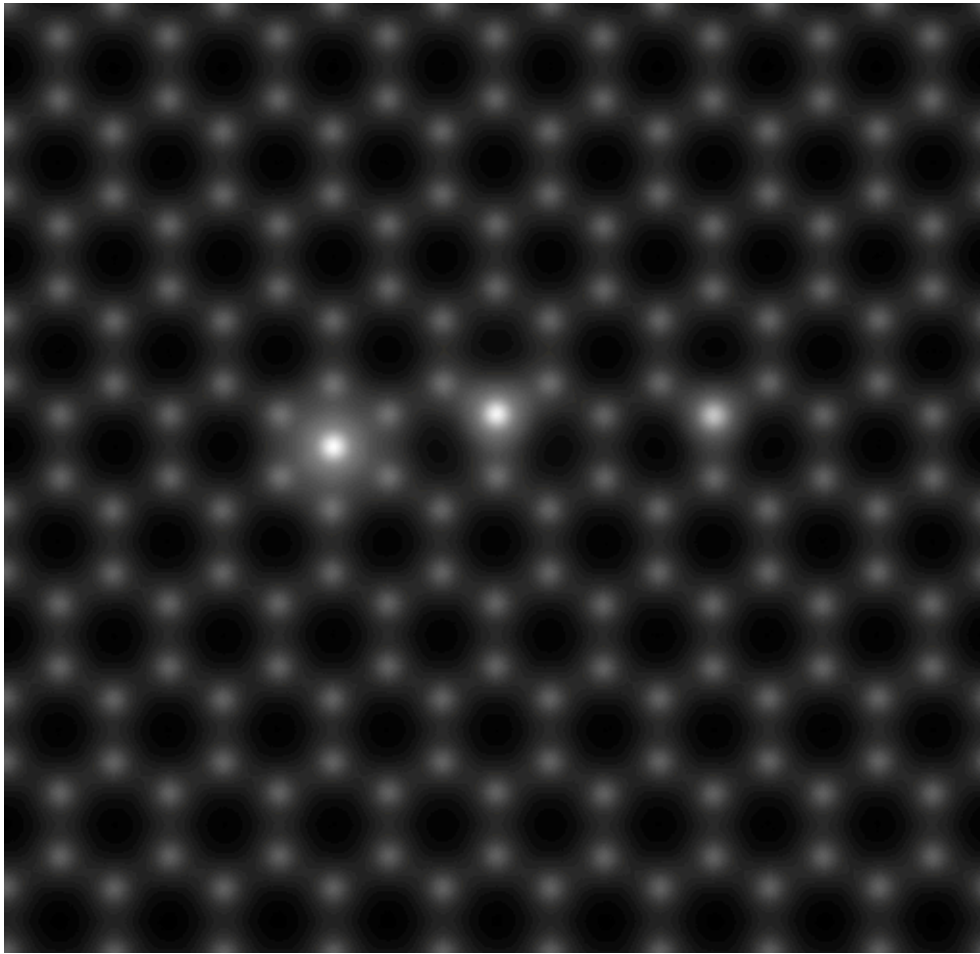


Figure: Weak phase object app., $C_c = 0.5\text{mm}$

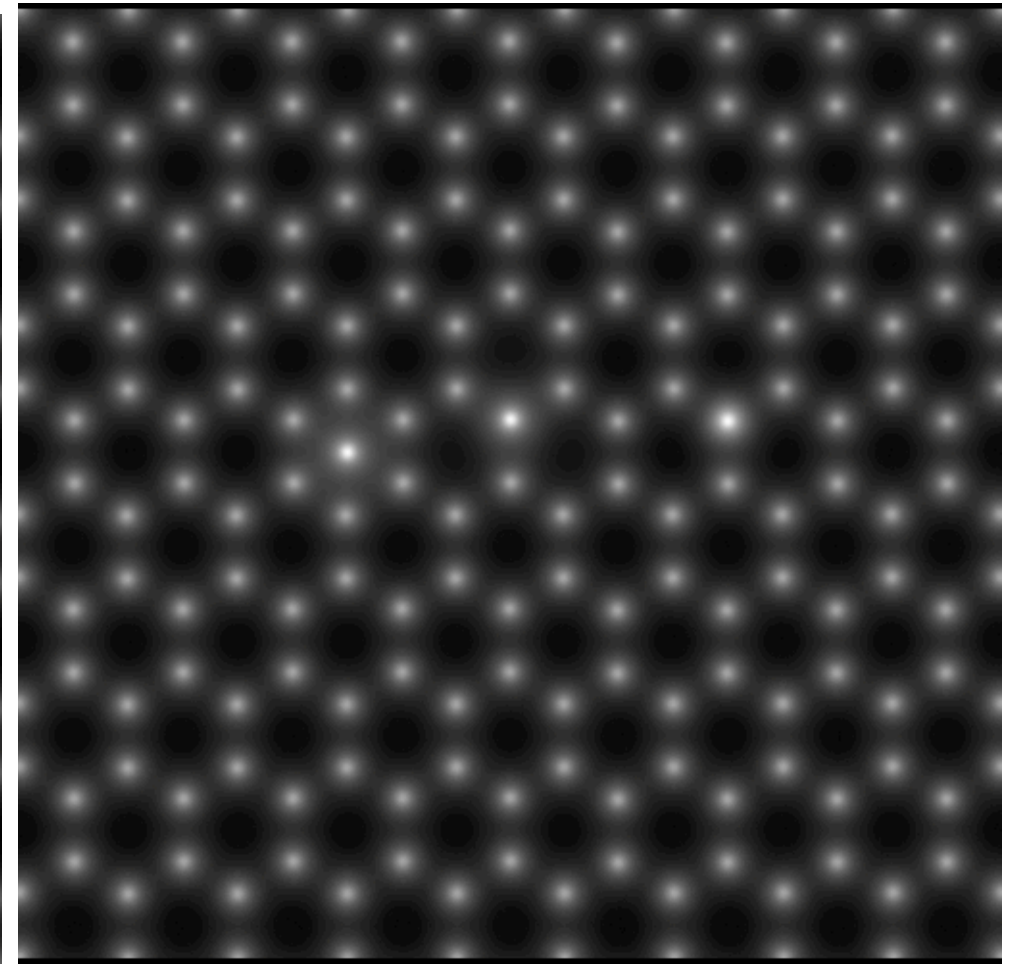


Figure: Multislice, $C_s = -0.033\text{mm}$, $C_c = 0$, no thermal magnetic noise.

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

Image simulation necessary for quantitative work¹⁷.

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

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

¹⁷K. 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.

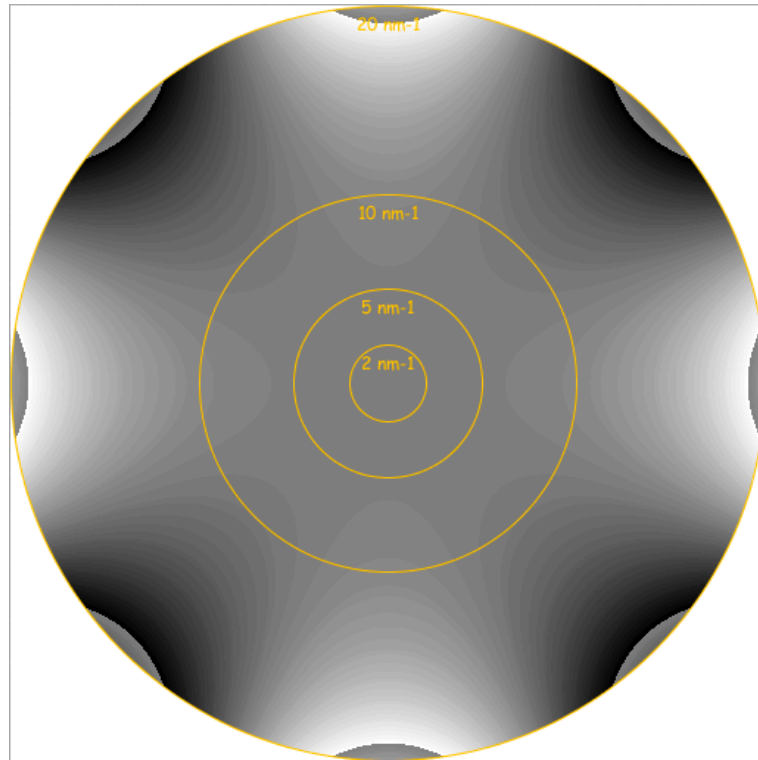


Figure: Aberration figure of $C_{34}(0.5\mu\text{m})$, phase jump at $\frac{\pi}{4}$.

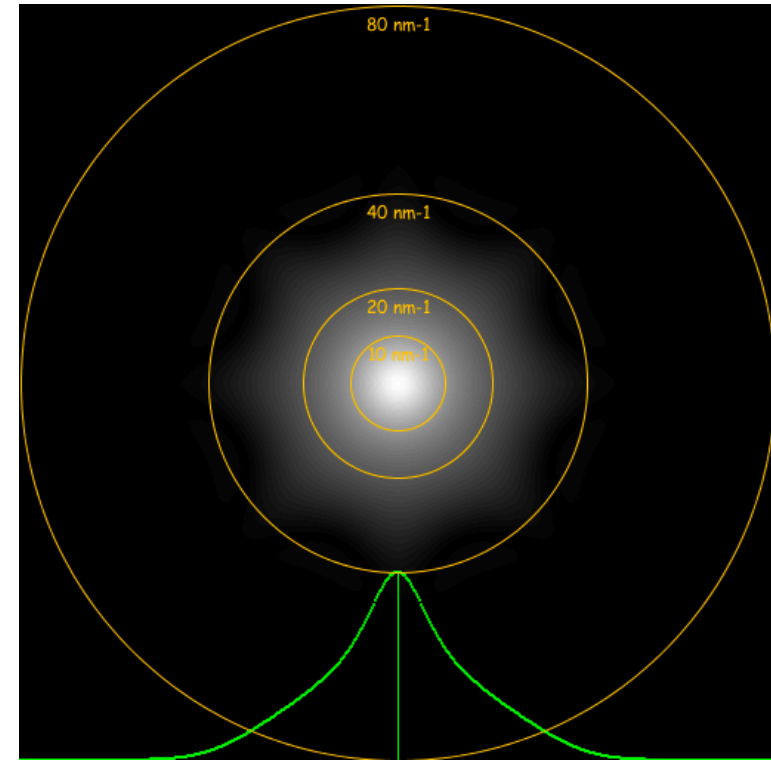


Figure: Optical Transfer Function.

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

HAADF: graphene

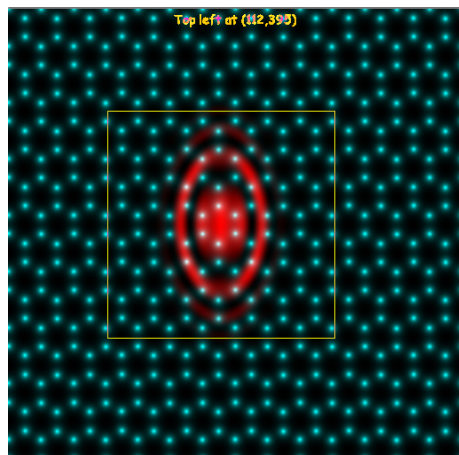


Figure: Probe affected by 2 fold astigmatism.

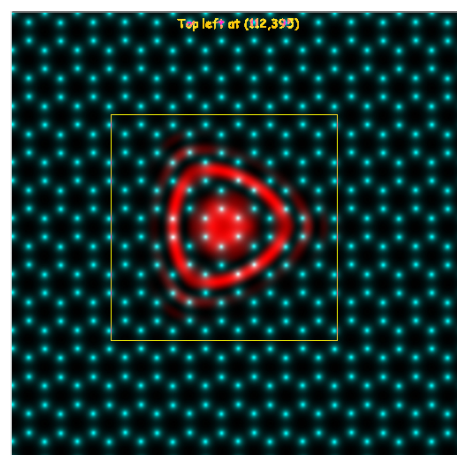


Figure: Probe affected by 3 fold astigmatism.

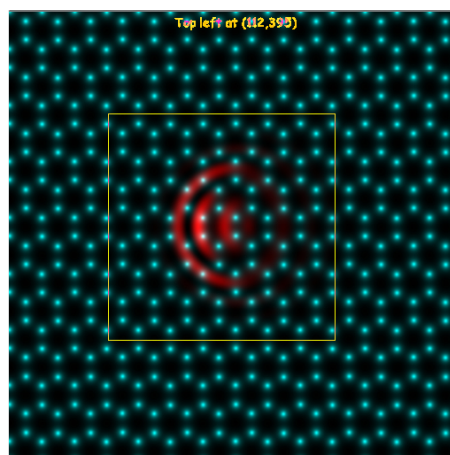


Figure: Probe affected by coma.

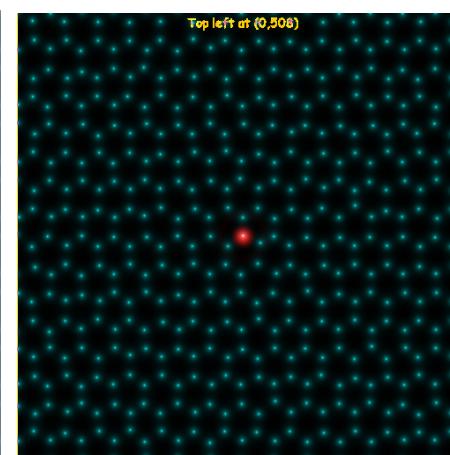


Figure: Corrected probe (best defocus).

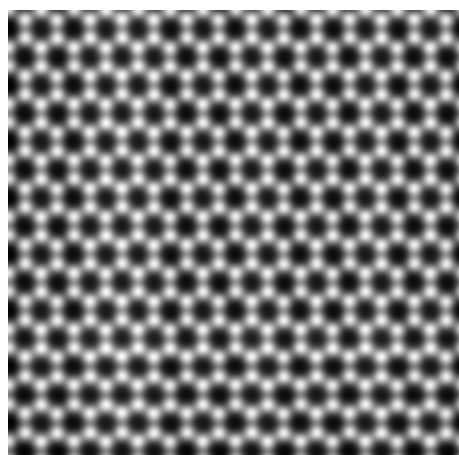


Figure: HAADF projected potential approximation.

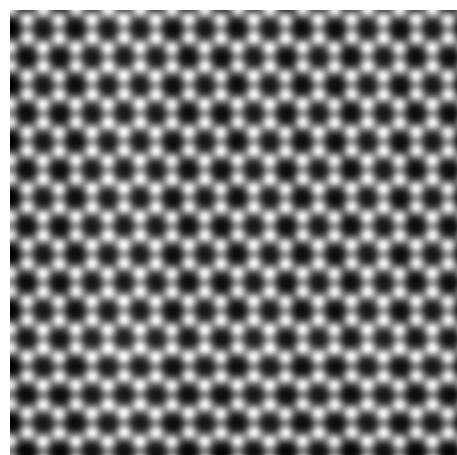


Figure: HAADF multislice calculation (simple).

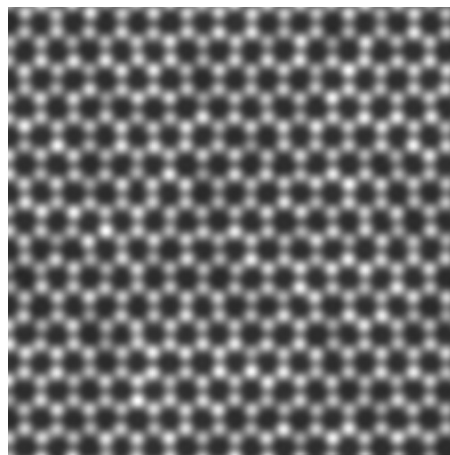


Figure: Frozen phonons 5 configurations.

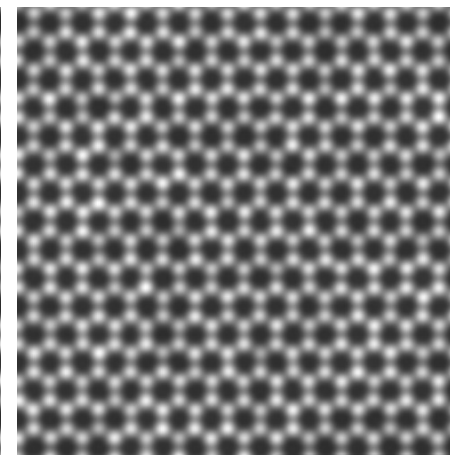


Figure: Frozen phonons 10 configurations.

Appendix 1: 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 eE is the **Schrödinger** equation ([?]):

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

With a change of notation its is written as:

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

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 $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is written as: $\Delta_\rho + \frac{\partial^2}{\partial z^2}$. As a result, $[\Delta + \dots]e^{2\pi i k_z z}\Psi(\rho; z)$ is given by: $[\Delta_\rho + \frac{\partial^2}{\partial z^2} + \dots]e^{2\pi i k_z z}\Psi(\rho; z)$.

Performing the z-differentiation:

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

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

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

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

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

Rearranging the last equation:

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

Fundamental equation

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

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**:

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

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

- ▶ 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 $10 - 20 \text{ V}$.
- ▶ **Electron backscattering** is neglected, the electrons 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:

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

where:

$$H = -\frac{1}{4\pi k_z} [\Delta_\rho + 4\pi^2 \chi^2 + 4\pi^2 V(\rho; z)] = H_0 + \frac{4\pi^2 V(\rho; z)}{4\pi k_z}$$

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

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

Causal evolution operator

$U(z, 0)$: **unitary operator** (the norm of $|\Psi\rangle$ is conserved), in general not directly integrable \implies **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 [?]:

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

$H(\rho; z)$ 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 its potential term (**phase object**).

Three approximations are available in jems:

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