HRTEM and STEM Image Simulation
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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: $|\Psi_i >$

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

$|\Psi_i > = \sum_{q'} <\rho|q'> \sum_q <q'|T(q',q)|q> <q|U(z,0)|\chi>$

Assuming that the potential is $z$ independent, the evolution operator $U(z,0)$ depends on the Hamiltonian $H(\vec{\rho}, z)$ of the system "crystal + incident electron" (where $\vec{\rho}$ are the $(x, y)$ coordinates in a plane perpendicular to the optical axis $O_z$ of the microscope):

$$U(z, 0) = \exp^{-i \int_0^z H(\vec{\rho}, z) dz}$$

The main problem of high-energy electron diffraction and imaging is to determine $U(z, 0)$. 
Prior to perform any calculation the following items (from the electron source to the detector) must characterized and modeled:

- The electron beam properties.
  - Convergence.
  - Source size.
  - Coherence (spatial and temporal).
- The specimen properties.
- 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?
Modelling steps

- **Object:**
  - crystal structure.
  - crystal orientation.
  - crystal shape.

- **Scattering & Diffraction:**
  - incident wave-function.
  - evolution operator.
  - exit wave-function.

- **Image Formation:**
  - HRTEM: Transfer Function (TF) or Transmission Cross Coefficients (TCC).
  - HRSTEM: Optical Transfer Function (OTF).

- **Image acquisition:**
  - characterisation of the Modulation Transfer Function (MTF) of the detector.
Modelling the object
Evolution operator $U(z, 0)$ depends on 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\(^1\).

$Si_3N_4$ hexagonal lattice.

$Si_3N_4$ orthorhombic lattice.

$Si_3N_4$ orthorhombic lattice x 2.

Pt catalyst on amorphous carbone film (9600 atoms).

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


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.
4. ...

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

A extremely useful ASA tabulation including phonon and core loss absorption is due to Weickenmeier-Kohl\(^2\).

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 ≤ (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
Scattering & diffraction
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 solid$^3$. 

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

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$^3$Magnetic and spin effects are ignored.
With energy conservation and momentum transfer ($\vec{s}_g = 0$), i.e. elastic scattering:

\[
|\vec{k}_i + \vec{g}| = |\vec{k}_g|
\]

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

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

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

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

\[\Rightarrow\] Bragg law:

\[
2 \times d_{hkl} \times \sin(\theta_B) = \lambda
\]
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 $\chi$ are at exact Bragg condition. Notice that the Bragg angles are pretty small (of the order a few $^\circ$) and that consequently the small angle approximation is quite good.
Structure factors

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

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

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 \((0,0,0)\).
\[
\Rightarrow F_{hkl} = f_i(s_{hkl})
\]

**Body centered cubic**: \((hkl)\) : \(h + k + l = 2n\)
2 atoms at \((0,0,0)\) and \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\).
\[
\Rightarrow F_{hkl} = f_i(s_{hkl}) \left[ 1 + e^{\pi i(h+k+l)} \right]
\]

**Face centered cubic**: \((hkl)\) all even or odd.
4 atoms at \((0,0,0)\), \((0,\frac{1}{2}, \frac{1}{2})\), \((\frac{1}{2}, 0, \frac{1}{2})\), \((\frac{1}{2}, \frac{1}{2}, 0)\)
\[
\Rightarrow F_{hkl} = f_i(s_{hkl}) \left[ 1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)} \right]
\]
Kinematical diffraction: $\langle q|U(z,0)|\chi\rangle$

Figure: Model ($\text{Ge}_3\text{N}_4$).

Figure: Kinematical diffraction $\text{Ge}_3\text{N}_4$, [001].
Dynamical diffraction: $\langle q | U(z, 0) | \chi \rangle$

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

Dynamical scattering (many approaches under small angle approximation and elastic scattering).
Including inelastic scattering more complicated and computer intensive.
From Gratias and Portier\textsuperscript{4}.

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\(^5\).
▶ The Bloch-wave method\(^6\).

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.

\(^6\)H. A. Bethe, Ann. Phys. 87 (1928), 55.
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.

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

2 steps:

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

For improved multislice calculations \( O(z^2) \) the wave-function is propagated over \( z/2 \), then multiplied by the phase-object function of the slice and finally propagated again over \( z/2 \). Slices do not need to have equal thicknesses.

Work best to simulate:

▶ Perfects crystals of large unit cell parameters\(^7\).
▶ Defects under the periodic continuation assumption\(^8\).

Is also used for:

▶ ADF image simulation in the "Frozen Lattice" approximation\(^9\).

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\(^9\)E.J. Kirkland, Advanced Computing in Electron microscopy.
Multislice: periodic continuation

In order to avoid "aliasing problems" during the multislice iterations the phase-object function and the propagator function must be sampled properly and also be "band-limited".

One unit cell model.  Periodic continuation model (2 x 2 unit cells).
Example multislice: Pt catalyst

A: catalyst model (9500 atoms)

B: HREM image (Jeol 400kV).

This simulation was performed with a phase-object function sampled on a 1024 x 1024 grid.
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 $\gamma_j$ ("anpassung" parameter).

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

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

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

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

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

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

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

where in usual notation $c_{0j}^*$ 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.10

Simulation of:

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

Works best for small lattice parameters crystals\textsuperscript{11}.

\textsuperscript{11}Some more details in Appendix 1.
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?**
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?).
Image formation

- Abbe image formation.
- Transfer function.
- Perfect thin lens.
- Aberrations.
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.
Aberrations of optical systems: how to define them

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

Position of \( A_i \rightarrow \) 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 (\( \lambda \) dependent).
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 $\Sigma_{PE}$ is spherical (point source at O).
- After $P_S$ the reference wavefront $\Sigma_{PS}$ is spherical (converges towards I).

For a perfect optical system, both the entrance $\Sigma_{PE}$ and exit $\Sigma_{PS}$ wavefronts are spherical. The Optical Path Length form O to I is independent of the path.
In the presence of aberrations the wavefront $\Sigma'_S$ is no more spherical. The Optical Path Difference (distance between the deformed $\Sigma'_S$ and spherical wavefront $\Sigma_S$) introduces a phase shift $\delta \phi$. With $P'$ close to $P = (x_s, y_s)$ on reference sphere $\Sigma_s$, 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 $\rightarrow$ 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 aberrations$^{12}$:

\[
    \epsilon_x = -\frac{f}{n_i} \frac{\partial W}{\partial x_s}, \\
    \epsilon_y = -\frac{f}{n_i} \frac{\partial W}{\partial y_s}
\]

$f$ 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 is$^{13}$:

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

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

$^{12}$ $P(x_s, y_s)$ on the spherical reference wavefront can be characterised by the radial angle $\theta$.

$^{13}$ The angle $\theta$ corresponds (through Bragg law) to a spatial frequency $\vec{u}$, i.e. a distance in the back focal plane.
Principal rays of paraxial optics. Reflection (plane wave) making an angle $\alpha$, 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).
Transfer by objective lens: $\langle q' | \tilde{T}(q', q) | q \rangle$

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 is approximated by a transfer function $\tilde{T}(\vec{u})$ and several envelope functions (attenuation of a range of spatial frequencies).
Two cases:

→ **TEM** ($\tilde{T}(\vec{u})$: Transfer Function):

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

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

→ **STEM** ($\tilde{OTF}(\vec{u})$: Optical Transfer Function):

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

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

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

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

$$\langle \Psi_o(\vec{x}; t) \Psi_o^*(\vec{x}; t) \rangle = |\Psi_o(\vec{x})|^2$$

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

$$I(\vec{x}) = I_o(\vec{x}) \otimes OTF(\vec{x})$$
Underfocus weakens the objective lens, i.e. increases f. As a consequence the OPL from $A_o$ to $A'_i$ is larger:

$$e^{2\pi i \frac{\Delta f \lambda (\vec{a} \cdot \vec{q})}{z}}$$
Transfer function $T(\vec{q})$

\[
T(\vec{q}) = e^{i\chi(\vec{q})} = \cos(\chi(\vec{q})) + i \sin(\chi(\vec{q}))
\]

Contrast transfer function

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

Where:

- $W_{20}$: defocus ($z$)
- $W_{40}$: spherical aberration ($C_s$)
Wave-front aberrations to $6^{th}$ order (cartesian coordinates)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

jems describes wave-front aberrations to order 8.
Wave-front aberrations to order 8
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 **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:

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

$\sigma$ : 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 / HRSTEM** → **Drift, vibration, Johnson-Nyquist noise**
- ...

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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.
Channeling explains several features of HRTEM and STEM images (i.e. appearance / disappearance of contrast of impurities).
Does $C_s$ and $C_c$ correction solve all imaging problems?

Example: Cd$_2$Cu$_2$, visibility of the 3 Cu atomic columns.

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

<table>
<thead>
<tr>
<th>HRTEM image simulation conditions</th>
</tr>
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<tbody>
<tr>
<td>Acc. [kV]</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>300</td>
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<tr>
<td>300</td>
</tr>
</tbody>
</table>
Visibility of 3 Cu atomic columns depends on specimen thickness and defocus.
Improving $C_c$ and $\Delta E$ does not affect the visibility of 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.
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)

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

**Figure**: Frozen lattice ($\sim 400$ s).

**Figure**: Channeling ($\sim 2$ s).
Graphene HRTEM (100 kV, $C_s - 0.033mm$)

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

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

Figure: Multislice, $C_s = -0.033mm$, $C_c = 0$, no thermal magnetic noise.
Quantitative HR(S)TEM

Image simulation necessary for quantitative work\textsuperscript{15}.

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

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

HRTEM / HRSTEM problem: aberrations of optical system

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

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

Note that Optical Transfer Function (HRSTEM) transfers higher spatial frequencies than Coherent Transfer Function (HRTEM).
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 $V_v\ [\text{Volt}]$ (positive inside a crystal) in the approximation of a stationary flux of electrons of a given energy $e \ E$ is the Schrödinger equation:\(^{16}\)

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

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:

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

and

$$m = \gamma \ m_0$$

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, $[\Delta + ...] e^{2\pi ik_z z} \Psi(\rho; z)$ is given by: $[\Delta \rho + \frac{\partial^2}{\partial z^2} + ...] e^{2\pi ik_z z} \Psi(\rho; z)$.

Performing the $z$-differentiation:

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

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

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

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

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

Rearranging the last equation:

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

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

Time dependent Schrödinger equation $\implies$ 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:

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

where:

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

A fundamental postulate of quantum mechanics$^{17}$ 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 $|\Psi>$ 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.

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