Data processing and interpretation of momentum-dependent Electron Energy-Loss Spectroscopy spectra

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15th June 2021

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Abstract

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Contents

1 Introduction

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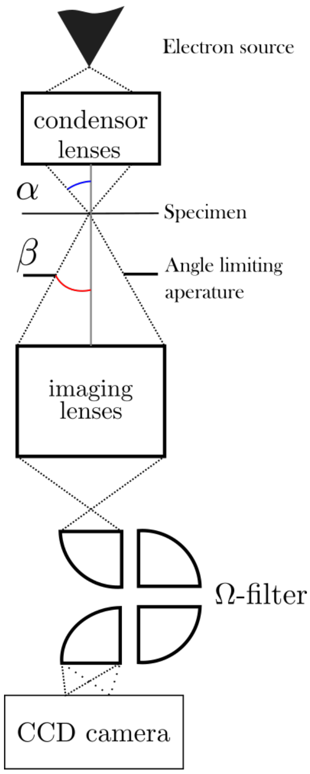

Figure 1: TEM

2 Theory

2.1 The Transmission electron microscope

The Transmission electron microscope (TEM) is a microscope that far exceeds the capabilities of a normal light microscope. Both types of microscope use a series of lenses to magnify the image of a specimen. A normal light microscope can amplify an image up to about $1500\times$ and is limited by the diffraction limit. Assuming an average wavelength of $550nm$ for green light a high-end microscope is limited to resolving features $100nm$ apart. This limit is too low for looking at atomic structures. [1]
An electron microscope circumvents this limit by using electrons, not light, to probe the specimen. Electrons when accelerated have a smaller wavelength than light thus allowing for images with resolved features as small as $0.05nm$. [2] The TEM works by releasing electrons from an electron source and accelerating them to an energy typically expressed in kilo-electronvolt. After being accelerated the electrons pass multiple electromagnetic lenses and a condenser aperture to shape the beam before it 'illuminates' the specimen as illustrated in 1. The beam incident on the sample is limited to a illumination semi-angle α which is inversely proportional to the resolution, but limiting α decreases the amount of electrons incident on the specimen and thus a frame needs more time for a decent exposure. After having interacted with the specimen the beam is again limited by an aperture, this aperture sets the collection semi-angle β which controls the limit of scattering angles allowed into the imaging lenses. After the beam is conditioned by the imaging lenses it passes trough four electromagnetic prisms which make up an energy filter called an Ω-filter named after the shape it needs to have to keep the TEM stack aligned with the CCD-camera to limit aberrations. The Ω-filter is used for energy filtered TEM images discussed in section 2.3.1.
Two types of images can be made with the TEM, a normal image which shows the magnified sample and a diffraction pattern image which can be made by placing the capture device in the focal point of the lens and filter system. A diffraction mode image shows the diffraction peaks that are characteristic of the sample and yields information on the reciprocal lattice of the sample.

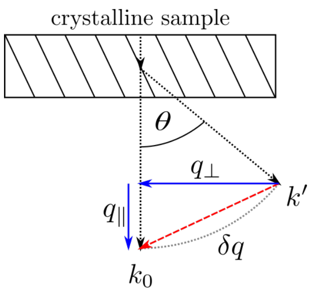

Figure 2: The elastic scattering k' of an electron over an angle θ due to the interaction with a crystalline sample.

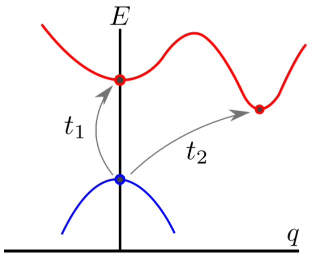

Figure 3: The band structure of the crystalline sample in fig. 2 showing both a direct bandgap t_1 and an indirect bandgap t_2.

2.2 Electron scattering theory

In a TEM setup electrons are essentially shot through a sample in which the electrons can either simply pass through or scatter, in the latter scenario there are two possibilities, electrons can scatter elastically or inelastically. Scattering is a result of the interaction between the sampling electrons from the TEM source and the charges particles in the specimen.
When scattering elastically the electrons interact with a nucleus of the specimen whose mass is many times greater than that of the sampling electron, resulting in a small and usually unmeasurable energy transfer. In a crystalline specimen electrons can only be scattered at certain angles due to the crystal structure creating a diffraction pattern of bright spots. In cases of large scattering angles the electron does transfer a significant amount of energy and can even reverse direction, this energy transfer can permanently displace atoms in the crystal structure causing a defect.
When the sampling electron interacts with an electron in the specimen's crystal lattice inelastic occurs due tot the similarity in mass between the two electrons. The energy transfer of this interaction ranges from a few electronvolts up to multiple hundreds of electronvolts. Inelastic scattering not only results in an energy transfer but also in a momentum transfer as shown in figure 2, the k'-vector shows a scattered electron that deviates from the not scattered electron vector k_0. The total momentum transfer is the sum of the perpendicular momentum transfer $q_\perp$ proportional to the scattering angle θ and the momentum transfer parallel to the undisturbed path due to an energy transfer from the sampling electron to the sample. This parallel momentum transfer is thus proportional to the energy loss of the electron. Figure 3 shows the band structure of the crystalline sample of which the electrons scatter. In this figure two bands are shown, both bands can be occupied by electrons of certain energies, to excite an electron from the blue band to the red band an electron needs either energy (path t_1) or energy and momentum (path 2). The needed energy and momentum are transferred from an incident sampling electron in the inelastic interaction. By measuring the energy and momentum of a scattered electron it is possible to piece together all the combinations of energy and momenta transfer possible and thus find the band structure of the sample.

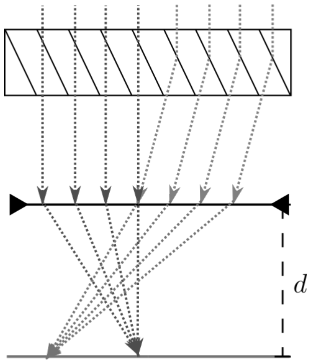

Figure 4: scat

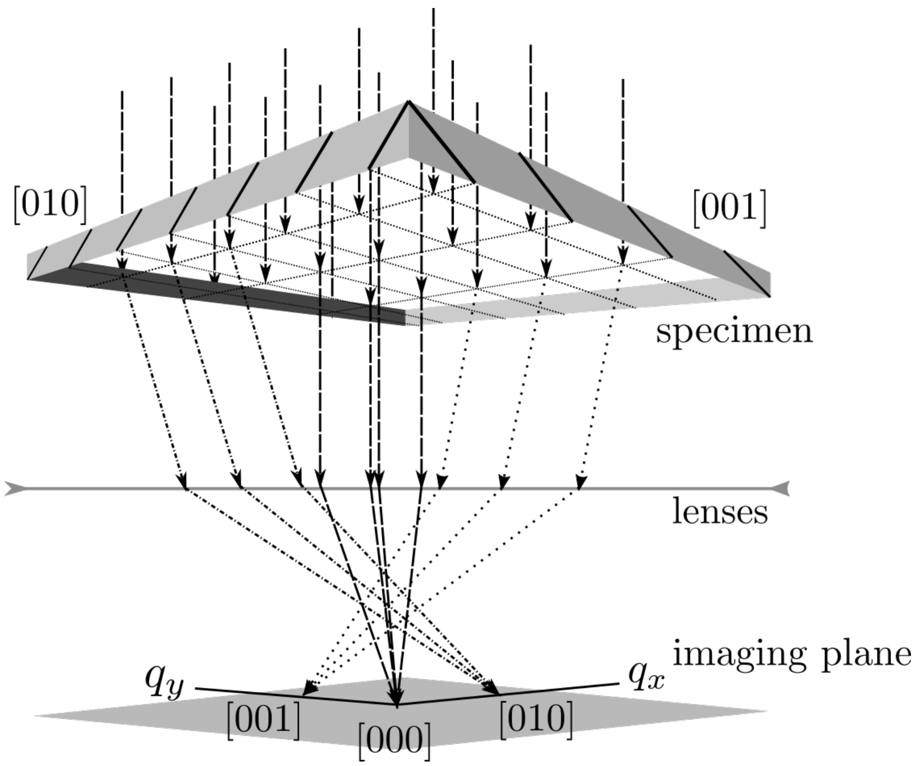

Figure 5: scat

2.3 Momentum resolved electron energy-loss spectroscopy

2.3.1 Energy filtered transmission electron microscope

2.4 Physical relevance of MREELS data

[3] [4] [5]

3 Experimental Method

3.1 Data format

3.2 Data correction techniques

3.3 Removing/altering values

3.3.1 zero-loss peak substraction

3.3.2 Batson correction

3.4 Data processing techniques

3.4.1 Integration techniques

3.4.2 Slicing techniques

3.5 Data extraction techniques

4 Results

4.1 Comparing integration techniques

4.2 Comparing Batson correction

4.3 Interesting features from data

5 Discussion

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6 Conclusion

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References

[1] E. G. van Putten, D. Akbulut, J. Bertolotti, W. L. Vos, A. Lagendijk, and A. P. Mosk, “Scattering lens resolves sub-100 nm structures with visible light,” *Phys. Rev. Lett.*, vol. 106, p. 193905, May 2011.

[2] C. Kisielowski, B. Freitag, M. Bischoff, H. van Lin, S. Lazar, G. Knippels, P. Tiemeijer, M. van der Stam, S. von Harrach, M. Stekelenburg, and et al., “Detection of single atoms and buried defects in three dimensions by aberration-corrected electron microscope with 0.5-Å information limit,” *Microscopy and Microanalysis*, vol. 14, no. 5, p. 469477, 2008.

[3] E. Gaufrès, F. Fossard, V. Gosselin, L. Sponza, F. Ducastelle, Z. Li, S. G. Louie, R. Martel, M. Côté, and A. Loiseau, “Momentum-resolved dielectric response of free-standing mono-, bi-, and trilayer black phosphorus,” *Nano Letters*, vol. 19, no. 11, pp. 8303–8310, 2019. PMID: 31603690.

[4] P. Shekhar, M. Malac, V. Gaind, N. Dalili, A. Meldrum, and Z. Jacob, “Momentum-resolved electron energy loss spectroscopy for mapping the photonic density of states,” *ACS Photonics*, vol. 4, no. 4, pp. 1009–1014, 2017.

[5] M. K. Kinyanjui, G. Benner, G. Pavia, F. Boucher, H.-U. Habermeier, B. Keimer, and U. Kaiser, “Spatially and momentum resolved energy electron loss spectra from an ultra-thin prnio3 layer,” *Applied Physics Letters*, vol. 106, no. 20, p. 203102, 2015.

Appendix

Placeholder and code block test

Python

The python code used to calculate the ellipse axes is displayed below.

```python
def ellipse_calc(x,y):
    # replace nans by average
    x_ = np.where(np.isnan(x), np.nanmean(x), x)
    y_ = np.where(np.isnan(y), np.nanmean(y), y)

    # Calculate variance and covariance
    var_x = np.sum((x_-np.mean(x_))**2)/(len(x)+1)
    var_y = np.sum((y_-np.mean(y_))**2)/(len(y)+1)
    cov = np.sum((x_-np.mean(x_))*(y_-np.mean(y_))/(len(x_)+1))

    cov_matrix = np.asarray([[var_x, cov],[cov,var_y]])
    evals,evecs = linalg.eig(cov_matrix)
    evecs_ = evals*evecs
    #plt.plot(x,y, linestyle='none',marker='x',zorder=1)
    #plt.quiver(np.nanmean(x),np.nanmean(y),-evecs_[1,:],-evecs_[0,:],
    zorder=2, units='xy', scale=1, width=1e-8, headwidth=4)


    a = np.max(evals)
    b = np.min(evals)
    print(a)
    print(b)
    index_a = np.where(evals == a)[0]
    theta = np.arctan(evecs[0,index_a]/evecs[1,index_a])
    print('theta =', theta)
    return a,b,theta
```

Literature Study

2008 - Electron energy-loss spectroscopy in the Transmission Electron Microscope (TEM)

Information in the paper includes:

1. **The workings of an TEM**
   The transmission electron microscope works by accelerating electrons and shooting them through a material, this results in electrons with different velocities which will be separated into a spectrum by a magnetic prism. This spectrum then falls upon a detector.

2. **The physics of an Electron Energy-Loss Spectrum**
   The aforementioned spectrum is a superimposed spectrum of smaller spectrums which are the result of different interactions between the sample and the shot electrons.

   The paper continuously talks about a "differential cross section" expressed by σ which is a measure of probability for scattering to occur.

   Elastic Scattering
   This type of scattering transforms energy from the shot electron to the sample, its angular distribution is quite narrow. The scattering angle is a result of how close the shot electron passes the nucleus of an atom. These angles are discretised and called Bragg angles, (I assume this relates quite closely to the studied material for Solid State Physics were this was due to the repeating lattice). The scattering angles can be widened due to extra phonon scattering but these energies are to low to be measured in a TEM-EELS system. Probability is given by $d\sigma/d\Omega$ where Ω is the absolute angle.

   Inelastic Scattering
   Coulomb interaction gives rise to this type of scattering. Due to the similarity in mass (probably talking about effective masses m^*) between the projectile (shot electron) and target (electron bound to sample) the energy loss of the shot electron is quite large, $1...10^2 eV$. Probability is given by $d^2\sigma/d\Omega dE$.

   Plasmon excitation
   A phenomenon that arises because outer-shell electrons are weakly bound to the atoms but enjoy a strong interaction by electrostatic forces and thus form an energy band. When a high energy electron travels trough a material at a speed higher then the Fermi-speed in that material the electron pushes away the surrounding electrons which leaves a relatively positive wake behind, this creates a net force decelerating the speeding electron. *Interesting*.

   The energy loss is a result of plasmon-loss event which are related to the mean free path of an electron. This quantity can be used to estimate the thickness of the material (Here).

   Surface plasmons and radiation loss
   Before the electrons even reach the specimen they polarise its entire surface, in case of a conducting sample longitudinal charge-density waves can be observed. The frequency of these waves is a direct result from the permittivity of the sample thus knowing the loss in energy of an electron due to this effect yields information about the sample permittivity.

Single-electron excitation and fine structure
In addition to the previously stated effect a incident shot electron can also excite a single electron into a higher energy state, these can be observed by fine-structure peaks that occur at energies above and below the plasmon peak, resulting in a more jagged profile. Between the 0-10eV range.

Core-electron excitation
Electrons located in the inner shells of a atom have high binding energies ($10^2...10^3 eV$) whose ionisation gives rise to the **ionisation edges** in the ELS. Since these edges are different for every atom they can be used to determine which materials are present in a sample.

Core-Loss fine structure
Depends on the density of states

3. **Applications and Limitations of TEM-EELS**
Thickness measurement
The spectrum can be used to provide a per pixel thickness of the material

Electron properties
The spectrum can provide information of the bandgap of semiconductors and insulator.

Plasmon spectroscopy
The plasmon energy is related to many mechanical properties of the material

Elemental analysis
Because each ionisation edge occurs at an energy loss that is characteristic of a particular element, EELS can identify elements in a material.

Spatial resolution
EELS provides a spatial resolution of about 0.2nm when compensating for aberrations, to go beyond this point room sized specialised set-up are needed

Magnetic measurments
Using a spin-polarised electron source the local magnetic properties of a material can be mapped.

Damage
Shooting electrons at a sample damages it with doses needed for a certain degree of damage differing per material. Resembles the radiation dose calculations from HS.

2012 - Angular momentum resolved EELS by energy filtered nanobeam diffraction

Information in this paper:

Using a Ω-filter, a filter which allows the filtering of electron energies, the team behind the paper was able to select one data cube and its angular resolved vectors. This resulted in data that was more complete than data gotten with the aperture shift method. The new method also preserves parallel illumination of the sample while creating a 3D data cube resolved in diffraction angle. All this comes at a cost of a loss in energy resolution but increases momentum resolution.
This technique overcomes the issue of convolution between EELS spectra and area-selecting apertures.

2015 - Spatially and momentum resolved energy electron loss spectra from an ultra-thin $PrNiO_3$ layer.

Information in this paper:

The paper start of by stating that MREELS (Momentum resolved electron energy-loss spectroscopy) is capable of determining dispersions and thus can image bandgaps, bonding anisotropy, as well as indirect and dipole-forbidden excitations (excitations that are only allowed in higher-order approximations at low rates).
The momentum loss is determined by a scattering process similar to X-ray diffraction. By selecting a certain angle a MREELS set-up is capable of determining energy loss ΔE and momentum transfer $||\vec{q}||$. The obtainable spatial resolution is determined by the angle of convergence of the electron beam, lens aberrations and the diameter of the selecting aperture.

2017 - Momentum-resolved electron energy loss spectroscopy for mapping the photonic density of states.

Information in this paper:

This paper informs about using momentum resolved electron energy-loss spectroscopy (q-EELS) to probe the momentum resolved photonic density of states (q-PDOS).
When probing a material that has no translational invariance along the electron path there is a distinction between q-EELS and q-PDOS. q-EELS has a loss function produced by an inductive field produced by a moving charge whereas the loss function of q-PDOS is the result of an oscillating electric dipole. This difference presents itself in momentum and position space. In momentum space we see different relations between the energy-loss-function and the transferred electron-momentum into the material.

2019 - Momentum-resolved dielectric response of free-standing mono-, bi-, and trilayer black phosphorus.

Information in this paper:

The team of researches was able to determine the bandgap- and binding- energy as well as the dielectric function for single, double and triple layer black phosphor. They reported on a small deviation which they believed came from screening from there different method of imaging without a substrate. They used a similar filtered set-up as previous papers so they probably used MR-EELS to determine the optical properties, but this is **just a guess**. The effect of quantum confinement for small layer numbers on excitonic properties vanishes when there is strong screening from the environment.
They did use MR-EELS to probe the dielectric response of ultrathin BP with electrons in the $10 - 40eV$ range as well as the dispersion (so also the DOS? applying q-PDOS).

2014 - π-Plasmon Dispersion in Free-Standing Graphene by Momentum-Resolved Electron Energy-Loss Spectroscopy

Information in this paper:

In this paper the authors are able to study the dispersive characteristics of the bound π-electrons due to the lattice absorbing either energy, momentum or both from the electron beam. Thus exciting these electrons. The difference in energy and momentum is unique and corresponds to the dispersion.

2013 - Angular Resolved low loss EELS for Materials Characterisations

Information in this paper

EELS in TEM in the low loss region charts the "loss function" and gives information about the optical properties and the electron structure. Angular resolved EELS gives further information.

Instrumentation

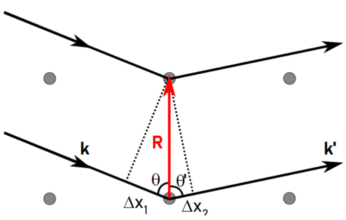
Sample preparation

4 Theory

4.1 Electron Scattering, Shooting electrons at a specimen makes them fly in all kinds of directions. Relevant for my project are the **Elastically** and **Inelastically** scattered electrons. The interaction between the electron beam and the specimen is due to coulomb interaction, the probability of scattering is proportional to the scattering cross-section σ as seen earlier in 2008.

- **Elastic scattering** is a deviation from the straight path of an electron. Multiple electrons since they also behave as waves will produce bright interference spots.
- **Inelastic scattering** is when an incident electron looses energy while interacting with the specimen. The momentum transfer depends on the energy loss, which can be due to plasmon excitation (paper above) , inter-band or core-loss interaction or scattering angle. These losses lead to the EELS-spectrum

  The distinction arises from the fact that the system considered is the single probe electron and the specimen. Phonon losses are in the range of meV which makes them undetectable by EELS
- **Diffraction,** A diffraction pattern is made up of bright spots on a less intense background. It is directly related to the crystallographic structure of the specimen. The spots are the result of constructive interference. A spot is indexed by (hkl) which are the miller indices, all electrons that scatter in the same direction? contribute to a single bright spot (as in picture below but not sure).



4.2 Electron energy-loss spectroscopy The EELS spectrum shows how many electrons scattered with a certain energy loss, it can be interpreted as a scattering amount per scattering energy lost. Notable features of EELS spectra are:

- The **Zero-Loss Peak**: for thin specimen this is the most intense peak. It corresponds to electrons that haven't lost energy due to elastic scattering. Its width comes from a number of phenomena that mess with the electron energy before or after interacting with the specimen. The ZLP can be approximated as a gaussian or Lorentzian with long trailing edges that might obscure other features in the spectrum.
- **Small Peaks**: Small peaks correspond to plasmon excitations (collective oscillations of the free electron gas), inter-band transitions and transitions from the valence band to an unoccupied state in the transition band. This peaks are in the low-loss region with $\delta E \approx eV$
- **Sharp or smooth edges**: These edges correspond to electrons which interact with core shell electrons of the atoms. These edges are at the binding energies of core electrons to the atom

nucleus, measuring this results in chemical analysis of the specimen. A deeper analysis allows for information of the electronic structure to be recorded.

4.3 Angular resolved EELS, a special technique where also the scattering angle of the electrons is taken into consideration. Doing this yields the possibility of retrieving information about the scattering probability as a function of electron excitation frequency and momentum. $\partial^2 P/\partial\omega\partial\Omega(\omega,\vec{q})$. This function is in itself proportional to the dielectric function. An advantage of EELS is that the momentum transfer $\vec{q}$ and the energy loss δE may be tuned independently.

4.4 Energy Filtered TEM (EFTEM), When a energy filter such as an Ω-filter is placed in the TEM column it is possible to acquire data using only electrons of specific energy by filtering out the rest. If multiple "images" are taken at different electron energies (slices) it becomes possible to construct a 3D data cube called an "EFTEM stack". It is then possible to produce EELS spectra by examining the same pixels across slices. This allows the analysis of plasmon peaks. The advantage of this technique is the better spatial resolution in each slice and if a diffraction pattern is acquired the technique allows for good angular resolution.

A **problem** is that the data stacks might need to be realigned. (This reminds me of the "Optical Tweezers" research project where I was tasked with rewriting MATLAB code into Python. This code needed to be able to very accurately (sub-pixel) find the centre of a bead trapped in a optical trap. This code could be repurposed for aligning these subpixel centres.) For better solutions need to check reference 68, schaffer et al.

https://s3-us-west-2.amazonaws.com/secure.notion-static.com/db2cc90c-3ec2-4f22-a6fd-7699ae93d398/1-s2.0-S0304399104001652-main.pdf

5 Data extraction

This week

- Studied and summarised several papers relating to several TEM-techniques such as spatially and momentum resolved EELS.

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- Looked at the use of EELS to determine the plasmon dispersion in graphene, the photonic dispersion and dielectric function of various materials.

This week

- Studied and summarised several papers relating to several TEM-techniques such as spatially and momentum resolved EELS.
- Looked at the use of EELS to determine the plasmon dispersion in graphene, the photonic dispersion and dielectric function of various materials.
- Looked at the structure of the data generated by the TEM and the post processing needed to "clean" the data.

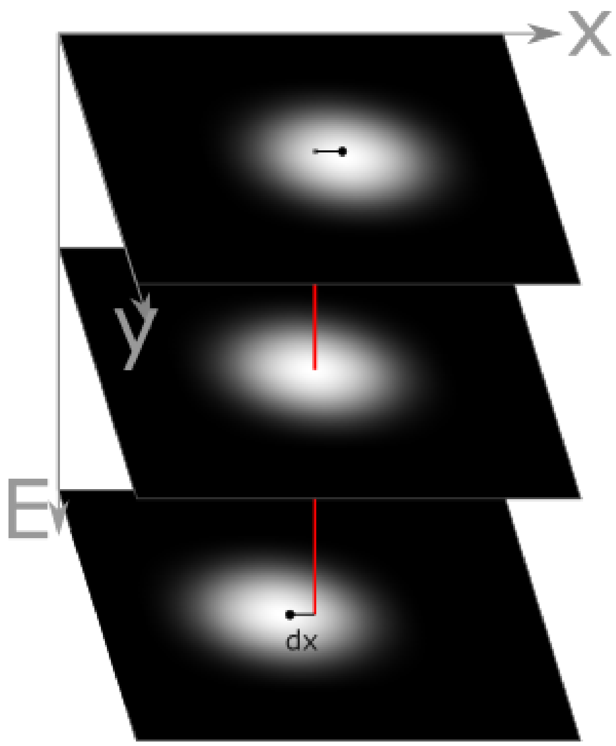
Next week

- Try to import the data generated by the TEM into Python as some sort of usable object.

Next week

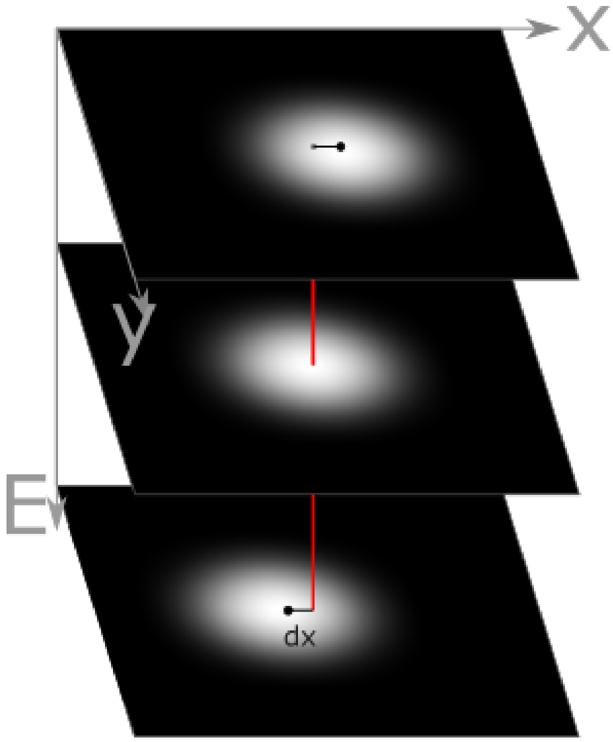
- Try to import the data generated by the TEM into Python as some sort of usable object.
- "Clean" the data by correcting for drift of the sample and errors in the data as in this paper. [1]

Data Processing



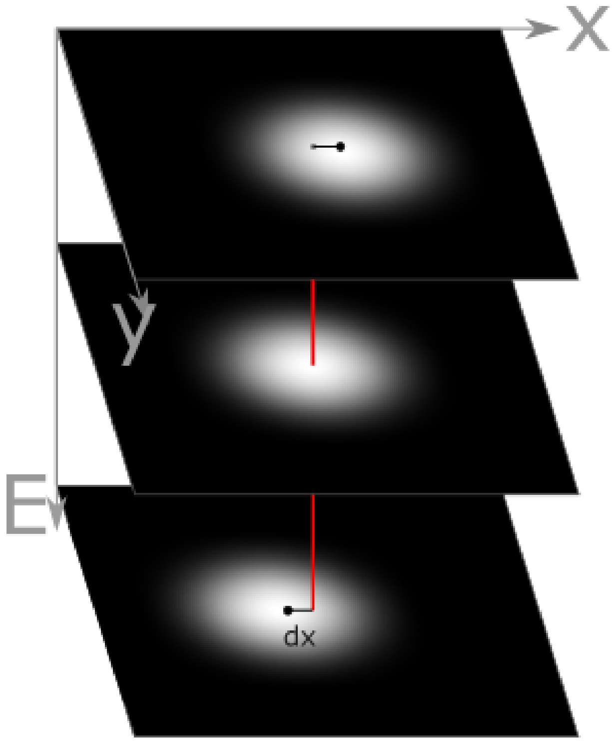
- Process the file and convert it to a python object.

Data Processing



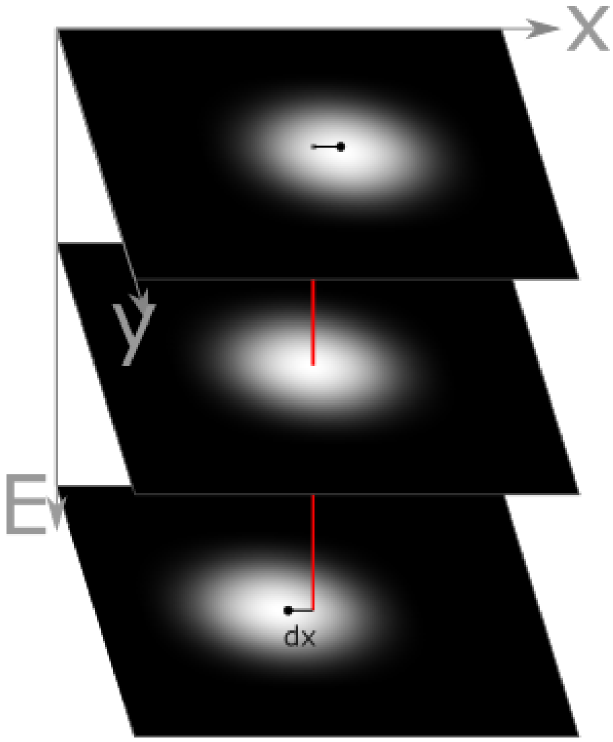
- Process the file and convert it to a python object.
- Remove any small bright pixels from unknown sources.

Data Processing



- Process the file and convert it to a python object.
- Remove any small bright pixels from unknown sources.
- Realign the slices that were shifted in between measurements.

Data Processing



- Process the file and convert it to a python object.
- Remove any small bright pixels from unknown sources.
- Realign the slices that were shifted in between measurements.
- Try to get some useful data.

References

S. Schneider, "Angular resolved low loss eels for materials characterization," 2013.