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

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TUDelft

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Abstract

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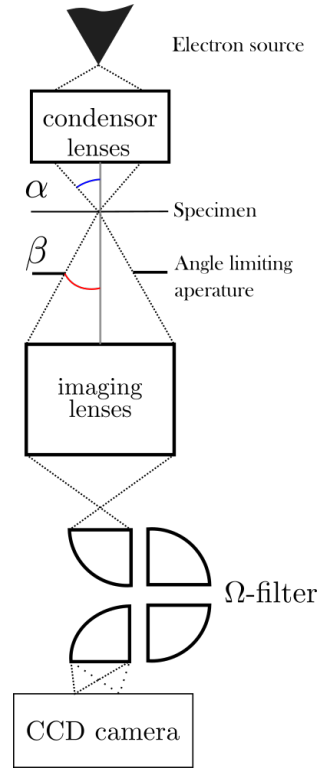
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1 Introduction

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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. [3]
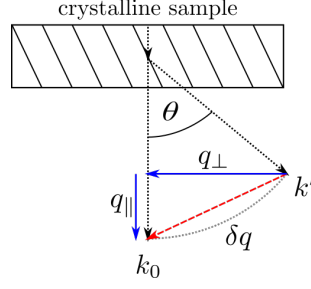
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Figure 2: The elastic scattering k' of an electron over an angle θ due to the interaction with a crystalline sample.

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 t_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.

Another form of inelastic scattering is plasmon excitation. Since the outer-shell electrons of an atom are only weakly bound to the nucleus due to screening effects but are coupled together by electrostatic interaction. These delocalised electrons form an energy band similar to that shown in figure 3. When a fast-moving sampling electron is shot through the sample all nearby outer-shell electrons are displaced. If the sampling electron's velocity exceeds the fermi speed the displacement of outer-shell electrons creates an oscillating ripple creating waves of alternating positive and negative electric charge, this is known as a plasmon wake.

2.3 Momentum resolved electron energy-loss spectroscopy

Momentum resolved electron energy-loss spectroscopy hereafter abbreviated as MREELS is a TEM imaging technique in which the imaging plane of the CCD camera is placed in the focal point of the imaging lenses and energy filter. This allows the camera to take a diffraction mode image in which the diffraction pattern of the scattering electrons is shown. This is illustrated in figure 4. In this figure the crystalline sample is shown as the box with the slanted lines that represent the Miller planes of the crystal structure. As shown in the figure all electrons that scatter of of the same family of Miller planes get focused on the same region on the imaging sensor, electrons that do not scatter also get focused in one spot at the centre of the diffraction pattern. A diffraction mode image does not image normal space but instead shows reciprocal
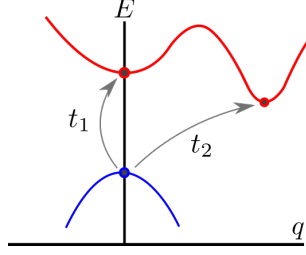
Figure 3: The band structure of the crystalline sample in fig. 2 showing both a direct bandgap t_1 and an indirect bandgap t_2.
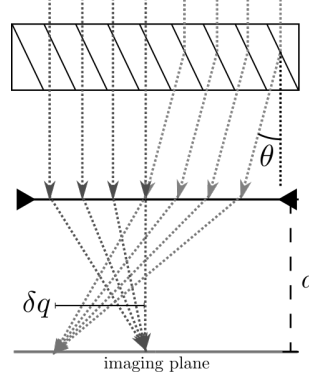

Figure 4: scat

space which is also the reason this type of image is useful. In a normal image one would attribute lengths to the axes of an image but in a diffraction mode image the separation of features is given by a momentum difference. The separation of the light and dark grey arrows on the imaging plane in figure 4 is thus equal to the difference in perpendicular momentum transfer between scattering electrons (light grey) and electrons that do not scatter (dark grey). Since the momentum transfer for the electrons that do not scatter is zero the momentum transfer for scattering of a certain family of planes can be determined.

2.3.1 Energy filtered transmission electron microscope

An energy filtered transmission electron microscope is a microscope with an energy filter placed in the optical column of the TEM. Energy filtering is accomplished by the use of electromagnetic prisms such as those shown in figure 6. These prisms just like ordinary prism disperse the electrons with different wavelengths proportional to electron energy. By sliding a slit into the cone of dispersed electrons it is possible to choose a finite range of electron energies to image. The EFTEM setup can be used in conjunction with the MREELS imaging technique to gather information on both the momentum transfer of the electron (via MREELS) and the energy loss associated (via EFTEM) with that momentum transfer.

2.4 Physical relevance of (MR)EELS data

As hinted at in section 2.3, the combination of both energy and momentum information allows for the reconstruction of the band structure of the specimen. This information can be used to determine the density of states of the specimen [4] [3]. EELS spectra can also be used to determine the electronic properties of the specimen, the bandgap of a semiconductor and the dielectric function, as well as mechanical properties [3]. Different signature peaks in the EELS data can be used to determine the elemental makeup of the specimen [3].
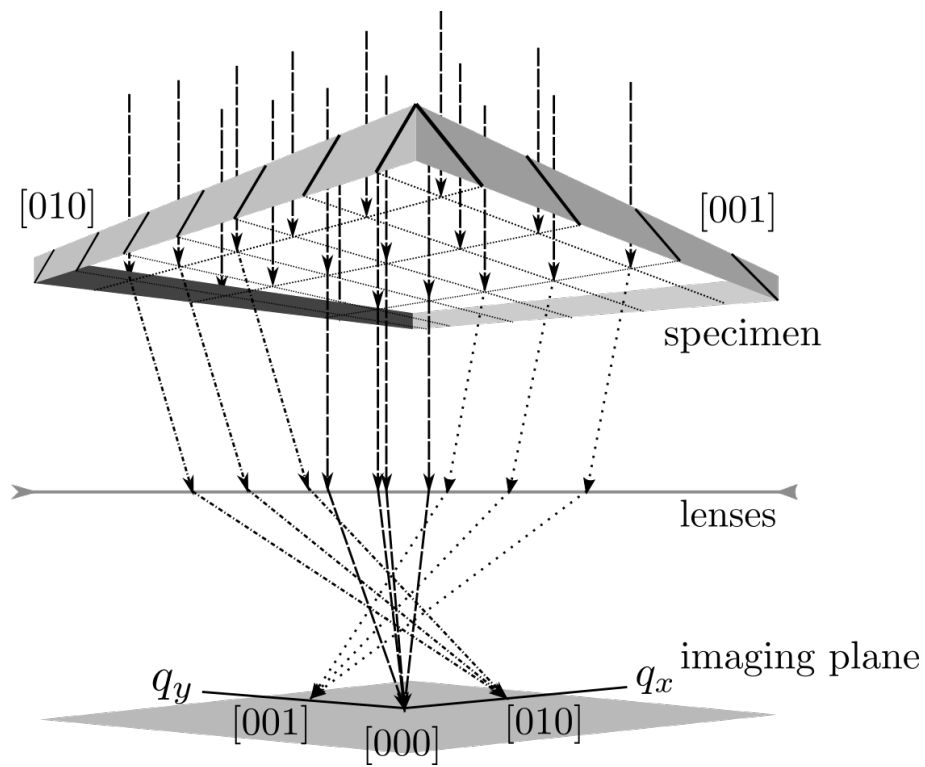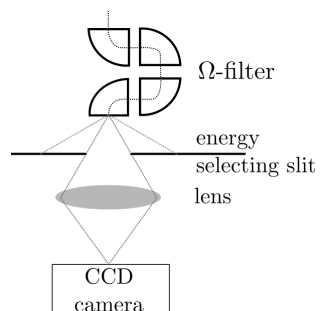
Figure 5: scat

Figure 6: A Ω-spectrometer spreading the electrons based on their energy and a slit selecting energies to focus on the CCD camera.

3 Experimental Method

3.1 Data format

For this work a specimen of γ-InSe was imaged using the momentum resolved electron energy loss technique in an energy filtered transmission electron microscope. The file was supplied with aligned zero-loss peaks in Gatan's *.dm4* format which had to be converted to a python object for further data processing in python, for the conversion from Gatan's proprietary file to a python object the excellent ncempy package [5] was used.

The measurement data is gathered by taking energy filtered diffraction images, meaning that there is a diffraction mode image for a large range of energy losses. All these images are stacked corresponding to the correspond energy value, resulting in a EFTEM image stack as illustrated in figure **??**. In the illustrated cube the horizontal planes are diffraction mode images associated with an energy loss ΔE, these energy slices have their own momentum axes that are not necessarily aligned with the whole stack. After alignment the individual pixels in the EFTEM stack can be fully expressed by four values, three coordinates: q_x, q_y, ΔE and one scattering intensity I.

Once the EFTEM stack is aligned it is possible to start extracting sets of values in meaningful ways. One way is to take a single column from the top of the stack to the bottom, doing this results in a 1D-array of values for a set position in momentum space and varying energy-loss, this is called an electron energy loss spectrum. An example of such a spectrum is illustrated in figure **??**. Another way is to extract multiple of these columns such that their total momentum increases, doing this yields a energy-momentum map as pictured in figure **??**.

3.2 Data correction techniques

3.2.1 Removing/altering values

Before any meaningful results can be extracted from the EFTEM stack it is important to first correct the data. This process starts by removing all the values corresponding to negative energy losses, these values are a result of the microscope software aligning the slices such that the zero-loss peak is at an energy loss of $0eV$. It does this by shifting slices up or down to match them to their true energy loss, slices corresponding to negative energy losses are duplicates of slices at positive energy losses.
After removing the negative energy loss slices the negative intensity values are raised by the minimum amount needed to make all values positive. This means that all values of the entire stack are raised by the absolute value of the most negative intensity. Doing this changes the performance of further techniques for the better.

3.2.2 zero-loss peak subtraction

3.2.3 Batson correction

3.3 Data processing techniques

3.3.1 Integration techniques

3.3.2 Slicing techniques

3.4 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] R. F. Egerton, "Electron energy-loss spectroscopy in the TEM," *Reports on Progress in Physics*, vol. 72, p. 016502, dec 2008.

[4] 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.

[5] P. Ercius, P. Gonzalo, T. Schoonjans, fniekiel, tcpekin, and koschie, "ncempy." The last three authors are github usernames.

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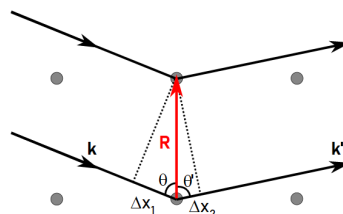
4.2 Electron energy-loss spectroscopy The EELS spectrum shows how many electrons scattered with a certain energy loss, it can be interpreted as a scattering amount per scattering energy lost. Notable features of EELS spectra are:

- 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-7699 ae93d398/1-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.
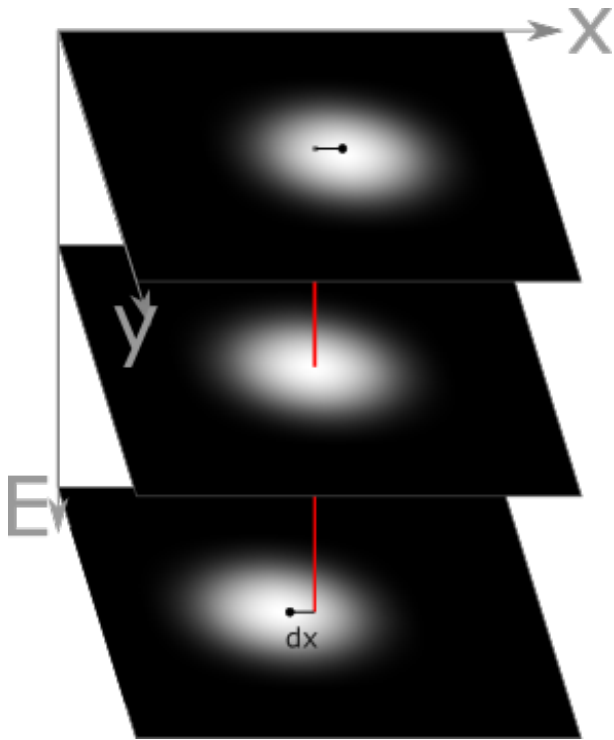
Next week

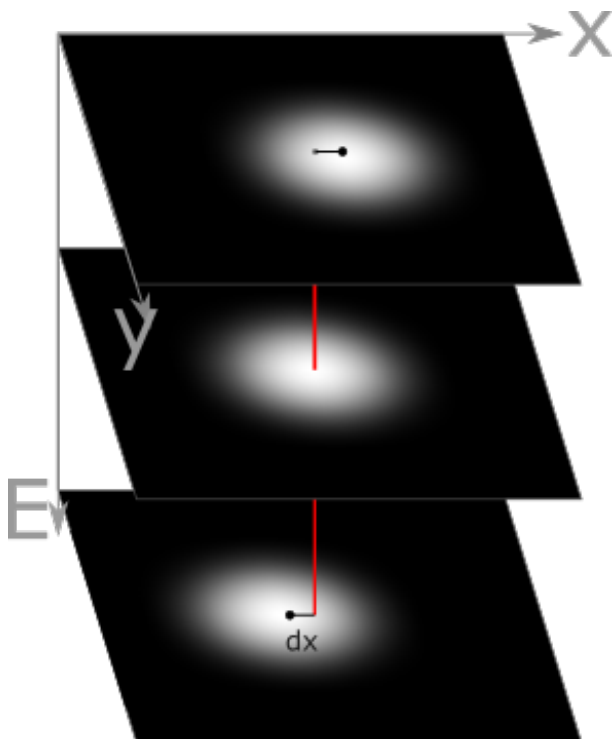- ▶ Try to import the data generated by the TEM into Python as some sort of usable object.

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]
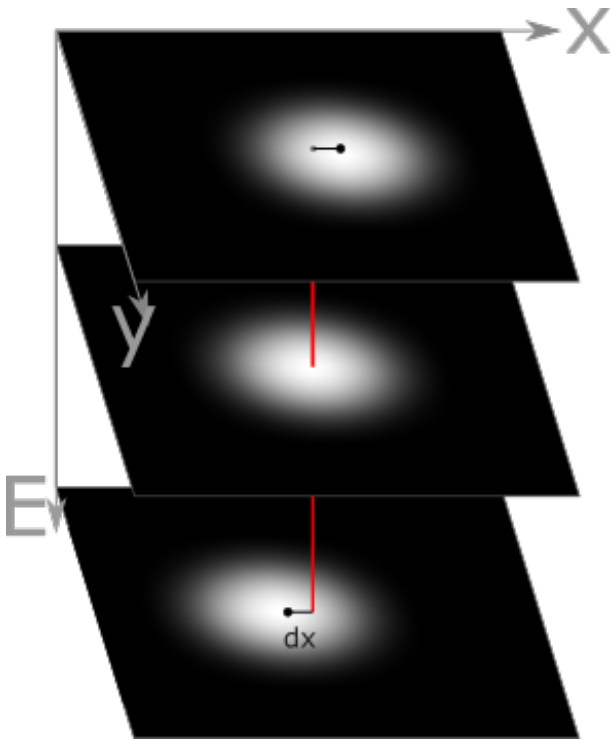
Data Processing

▶ Process the file and convert it to a python object.
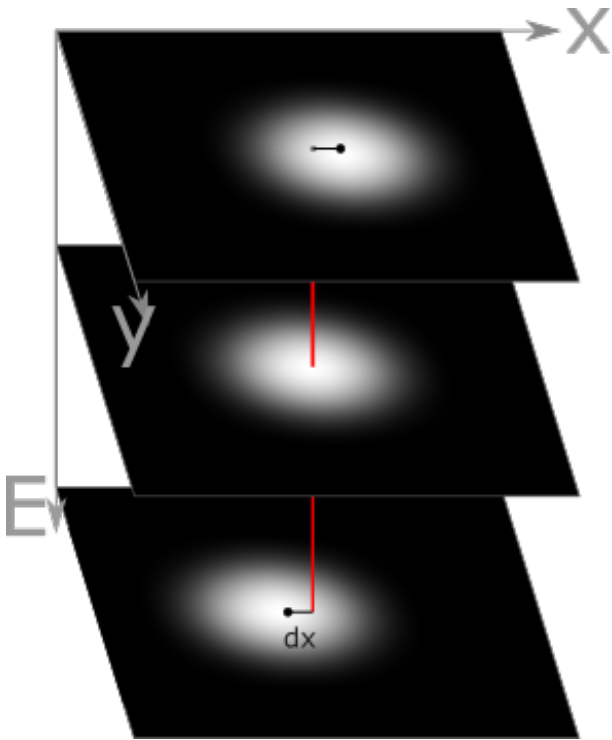
Data Processing

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