# Monte Carlo and Density Functional Theory Simulation of Electron Energy Loss Spectra

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### Abstract

The scope of this thesis is the study of electron transportation and electron energy loss spectra using Monte Carlo and density functional theory calculations. In the first part, the electron transportations in the bulk materials and thin solid films were studied using Monte Carlo simulations based on the optical data model. The optical data model gives the benefit of the calculations of the backscattering and transmission coefficients from very low (about 100 eV) to high (about 500 keV) beam energies. The simulation results for backscattering and transmission coefficients are in good agreement with the available experimental data. Based on the Monte Carlo simulation results a new relation between backscattering and transmission coefficients of thin solid films was suggested enabling the estimation of one coefficient by having the other coefficient. A universal form for the signal-to-background ratio and the signal-to-noise ratio versus thickness divided by the inelastic mean free path was observed by Monte Carlo simulations in agreement with the available theoretical models. In addition, a simple equation was suggested for the estimation of the optimum thickness for the highest amount of signal-to-noise ratio. The equation implies that by having the value of one optimum thickness at a given beam energy the optimum thicknesses at other beam energies can be estimated.

In the second part of the thesis, the fine structure of energy-loss near-edge structure (ELNES) obtained by the density functional theory calculations was introduced to the Monte Carlo simulations of the electron energy loss spectra. Density functional theory calculations successfully predicted the shape of energy-loss near-edge in comparison with the experimental measurements. Based on the suggested approach, the fine structure of an ionization edge can be introduced to the optical oscillator strength instead of the X-ray photoelectric data. X-ray photoelectric data does not contain the solid state effects and is appropriate for single atoms only. As a result of this approach, the total X-ray absorption

coefficient can be calculated including the fine structure of inner-shell ionization edges. Using the Monte Carlo simulations with the new optical oscillator strength containing the fine structure of ionization edges, effect of different parameters of background removal for the ionization edges was studied. Monte Carlo simulations provided the optimum values for the optimization of the signal-tobackground ratio calculations.

In the third part of thesis, effect of temperature and pressure on the lowloss region of energy loss function were investigated. The energy loss function is in the direct relationship with the optical oscillator strength; hence it is important to study the parameters affecting the energy loss function. The density functional theory calculations were performed based on the change in the lattice parameter variation of solids with temperature and pressure. The results of density functional theory calculations are in the good agreement with the experimental temperature dependency of plasmon energy of aluminum. In addition, a new model for the temperature and pressure dependency of the plasmon energy of solids was suggested by combination of the free electron model and the pseudo-spinodal equation of state. The results of suggested model are in good agreement with the results of density function theory calculations. As well, the departure from the free electron behavior at high pressures was confirmed from the results of density functional theory calculations.

### Résumé

Cette thèse étudie le transport d'électrons et les spectres de perte d'énergie en utilisant la méthode de Monte Carlo et de la méthode de la densité fonctionnelle des atomes. Dans la première partie, les transports d'électrons dans les matériaux massifs et des films minces ont été étudiées à l'aide de simulations de Monte Carlo basées sur le modèle de données optiques. Le modèle de données optique donne l'avantage des calculs des coefficients de rétrodiffusion et de transmission de très faible (environ 100 eV) à très élevé (environ 500 keV) des énergies de faisceau. Les résultats de la simulation pour les coefficients de rétrodiffusion et de transmission et sont en bon accord avec les données expérimentales disponibles. Sur la base des résultats de simulation de Monte Carlo, une nouvelle relation entre les coefficients de rétrodiffusion et de transmission de films minces a été proposée. Elle permet l'estimation d'un coefficient par un. Une équation universelle pour le rapport signal-bruit de fond et le rapport signal-sur-bruit par rapport au l'épaisseur divisé par libre parcours moven inélastique a été observé par simulations de Monte Carlo, en accord avec les modèles théoriques disponibles. De plus, une simple équation a été suggérée pour l'estimation de l'épaisseur optimale de la plus grande quantité de rapport signal sur bruit. L'équation implique qu'en ayant la valeur d'une épaisseur optimale à une énergie de faisceau donné, les épaisseurs optimales à d'autres énergies de faisceau peuvent être estimées.

Dans la deuxième partie de la thèse, la structure fine de la structure de perte d'énergie quasi-bord obtenu par les calculs de la densité fonctionnelle des atomes a été introduite pour les simulations de Monte Carlo des spectres de perte d'énergie des électrons. La densité fonctionnelle des atomes prédit avec succès la forme de perte d'énergie quasi-bord en comparaison avec les mesures expérimentales. Basé sur l'approche proposée, la structure fine d'un bord d'ionisation peut être introduite dans la force d'oscillateur optique à la place de la radiographie des données photoélectriques. Ces données photoélectrique ne contiennent pas les effets de l'état solide et sont appropriées pour les atomes isolés seulement. En conséquence de cette approche, le coefficient d'absorption totale de rayons X peut être calculé y compris la structure fine des bords d'ionisation. En utilisant les simulations de Monte Carlo avec la nouvelle force d'oscillateur optique contenant la structure fine des bords d'ionisation, l'effet de différents paramètres de suppression du fond pour les bords d'ionisation a été étudiée.

Dans la troisième partie de la thèse, ont été étudiés les effets de la température et de la pression sur la région à faible perte de la fonction de perte d'énergie. La fonction de perte d'énergie est dans la relation directe avec la force d'oscillateur optique; par conséquent, il est important d'étudier les paramètres affectant la fonction de perte d'énergie. Les calculs de la densité fonctionnelle des atomes ont été réalisés sur la base du changement dans le paramètre de maille variant dans les solides avec la température et la pression. Les résultats de la densité fonctionnelle des atomes sont en bon accord avec la dépendance expérimentale de la température sur l'énergie du plasmon de l'aluminium. En outre, un nouveau modèle de la dépendance de l'énergie des plasmon selon la température et la pression a été suggéré par la combinaison du modèle d'électrons libres et de l'équation d'état pseudo-spinodale. Les résultats de modèle proposé sont en bon accord avec les résultats des calculs de la densité fonctionnelle des atomes. En outre, le départ du comportement des électrons libres à haute pression a été confirmée par les résultats des calculs de densité théorie de la fonctionnelle.

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## **Contributions of Author and Co-Authors of Published Works Presented in This Thesis**

1. **M. Attarian Shandiz**, F.Salvat, R. Gauvin, Detailed Monte Carlo simulation of electron transport and electron energy loss spectra, to be submitted to: Ultramicroscopy (Chapter 3).

2. **M. Attarian Shandiz**, M.J.-F. Guinel, M. Ahmadi, R. Gauvin, Monte Carlo simulations of the fine structures of the electron energy-loss spectra, to be submitted to: Ultramicroscopy (Chapter 4)

3. **M. Attarian Shandiz**, R. Gauvin, Density functional and theoretical study of the temperature and pressure dependency of the plasmon energy of solids, Journal of Applied Physics, 116 (2014) 163501 (Chapter 5).

4. M. J-F Guinel, N. Brodusch, G. Sha, **M. Attarian Shandiz**, H. Demers, M. Trudeau, J. Boselli, S. P. Ringer, R. Gauvin, Microscopy and Microanalysis of Complex Nanosized Strengthening Precipitates in New Generation Commercial Al-Cu-Li Alloys, J. Microscopy, 225 (2014) p. 128.

(The thesis includes the papers 1-3.)

In all the papers included in this thesis, the author has conducted all the Monte Carlo simulations and density functional theory calculations, performed analysis and modeling as well as prepared the manuscript drafts. All the manuscripts were co-authored by Prof. Raynald Gauvin, who supervised the research projects. The code provided by Prof. Francesc Salvat from University of Barcelona was adopted to perform Monte Carlo simulations. The experimental

electron energy loss spectra in chapter 4 were collected by Maxime Guinel and Majid Ahmadi from University of Puerto Rico.

The accuracy of the above statements is attested by the student's supervisor. Prof. Raynald Gauvin

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### **Chapter 1. Introduction**

Electron energy loss spectroscopy (EELS) is the technique to measure the amount of energy loss in an inelastic scattering event, when electrons pass through the material [1]. Transmission electron microscopy (TEM) is the appropriate microscope for EELS since in order to have the projection image, electrons should transport in the material [2]. Because of the improved aberration corrections and the usage of modern electron guns, high spatial and energy resolution at the angstrom and sub electron volt level can be achieved in new TEMs and EELS detectors [3, 4]. This improvement of EELS technique has dramatically enriched our knowledge on the electronic structure and composition of materials. EELS has been successfully used for the measurement of electronic structure [5], optical properties [6-8], density and thickness of thin film specimens [9-11] as well as plasmon mapping [12-14].

In addition to giving information on the electronic structure of the material, the main characteristic of electron energy loss (EEL) spectra is ionization edges [15]. In fact, ionization edges can determine the type of the element with high energy resolution in comparison to other technique, e.g. energy dispersive X-ray (EDX). However, the main difficulty of quantitative analysis in compassion to EDX technique is the large amount of the background signal in EELS [16].

The quantitative analysis can be performed in EELS using the intensity under each ionization edge as a criterion for the amounts of the elements in the material [17]. Although, some errors can occur in quantitative analysis using experimental EEL spectra. The reason for these inaccuracies result from the instrumental factors such as the detector noise and the inaccuracy in the removal of the background signal [15]. The specimens should also be thin enough and their preparation is time consuming and not applicable for all materials, so the optimum thickness should be determined before start of experiments. In addition, in many practical situations, changing experimental parameters such as specimen thickness and collection semi-angle of detector to collect the scattered electrons is not easy. All of these emphasize on the importance of computer simulation of EEL spectra to overcome the aforementioned limitations.

The Monte Carlo technique has been used successfully for simulation of the electron scattering in the scanning and the transmission electron microscope for simulation of EDX X-ray spectra [18]. On the other hand, limited number of research has been performed for Monte Carlo simulation of the EEL spectra [19-22]. Indeed, the Bethe equation is the basis for the calculation of the mean energy loss of electrons in the electron microscope [18]. Nevertheless, since there are not enough numbers of signal counts for the validation of the Bethe equation, it cannot be used to describe low energy interactions in the scanning electron microscope (SEM) and high energy electron scattering in the TEM. For the above range of energy interactions, an optical data model is suitable. Optical data models are established upon building a Bethe surface to calculate the inelastic differential cross section [23]. In fact, the inelastic differential cross section has a direct relationship with the generalized oscillator strength (GOS) concept [24]. The GOS can be calculated analytically only for the atomic hydrogen and the free electron gas [25]. Consequently, the concept of optical oscillator strength (OOS) has been developed due to this difficulty.

The OOS is related to the calculation of energy loss function (ELF) [26-28]. As a result, the OOS can be obtained by measuring of some optical properties. The experimental OOS data are available for a limited number of materials and a limited range of energy loss. In addition, the complete OOS can only be obtained by combining a variety of data range from different techniques and specimens [23]. Hence, simulation methods can be a good substitution to overcome the limitation of acquiring the experimental OOS data. In this research, the ELF will be obtained from *ab initio* methods to calculate OOS as an input for the Monte Carlo simulation of whole EEL spectra (low and high energy loss) based on the optical data model. Introducing the *ab initio* calculation into the OOS can lead to improvement of the Bethe surface and consequently a better model for the quantitative analysis of EEL spectra. Generally, the available simulations of EEL spectra are based on *ab initio* calculations. They are nonetheless limited to energy-loss near-edge structure (ELNES). Band structure methods based on the density functional theory (DFT) compute the electron density and the ELNES can be derived as a result of calculations [29-31]. So the predicted ELNES does not include the background signal originating from multiple inelastic scatterings in the experimental EELS. Hence to simulate the effect of multiple scattering on the shape of ELNES other methods should be considered. In this research, the ELNES obtained by DFT calculations is introduced into the Monte Carlo simulation of electron energy loss (EEL) spectra to study effect of multiple inelastic scatterings by increasing thickness on the ELNES.

Low-loss region of the EEL spectra is an important part of experimental EELS and the OOS in the optical data models. Temperature [32] and pressure can change [33] the EEL spectra, the energy loss function and accordingly the plasmon energy of solids. As well, the plasmon energy variations can be used for the measurement of many other physical and mechanical properties [34]. Hence, the study of the effect of temperature and pressure in the low-loss EEL spectra is important for better understanding of the influence of the effect of the variation of physical and mechanical conditions on the EEL spectra.

This thesis comprises 7 chapters: subsequent to this introduction, a brief literature review of EELS, optical data models, Monte Carlo simulation and DFT calculations of the solid state properties as well as the effect of temperature and pressure on the low-loss EEL spectra are explained in chapter 2. Chapter 3 includes the calculation of the backscattering and transmission coefficients as well of the universal forms of signal-to-background and signal-to-noise ratio of ionization edges in the EEL spectra. In chapter 4, the fine structure of ionization edges obtained by DFT calculations is introduced to the Monte Carlo simulation of EEL spectra. Accordingly, the effect of different parameters of background removal on the signal-to-noise ratio calculation of inner-shell ionization edges is investigated. In chapter 5, the temperature and pressure dependency of plasmon

energy of solids are modeled by combination of the free electron model and the equation of state based on the pseudo-spinodal approach. In addition, the effect of pressure and temperature on the energy loss function and the plasmon energy are studied by DFT calculations based on the variation of volume and the lattice parameters. Lastly, chapter 6 and 7 summarize the main results of the thesis and expresses the original contributions to knowledge as well as suggestions for the future work.

### **Chapter 2. Literature Survey**

#### 2.1. EELS instrumentation

The foundation of EELS is based on measuring the amount of energy-loss by an incident electron beam that interacts with a specimen. For this reason, the electron beam should have sufficient amount of energy to be able to pass through the prepared specimen as a thin film. EELS operates in the typical energy range of TEM, i.e. the initial energy of electron beam is about 100-300 keV [2]. There is an aperture to improve the energy resolution by prohibition of the entrance of the high-angle scattered electrons into the spectrometer [2]. After the entrance of electrons to the spectrometer, the amount of energy loss is determined and stored to generate the EEL spectra. Figure 2-1 shows the schematic demonstration of the significant parameters affecting the EEL spectra.



Figure 2-1. Schematic illustration of the parameters affecting the collection of EEL spectra including the beam energy  $(E_0)$ , the collection semi-angle  $(\beta)$  and the thickness of specimen (t) based on the concept from Ref. [1].



Figure 2-2. Schematic illustration of the position and components of a parallel EELS detector from Ref. [35].

EELS detectors (spectrometers) are used to record the amount of energy loss in the inelastic scattering of electrons with material. A magnetic-prism is the main component of EELS detectors. In the magnetic field of prism, electrons progress in a circular orbit where the radius of curvature can be calculated by the following equation [1]:

$$R = \frac{\gamma m_0}{eB} v \tag{2-1}$$

where  $\gamma = (1 - (v/c)^2)^{1/2}$  is the relativistic factor, *B* is the magnetic field,  $m_0$ , *e* and *v* are the rest mass, charge and the velocity of electrons, respectively. Also, *c* is the speed of light. According to equation (2-1), electrons that have lost energy in the inelastic scatterings have a lower speed and consequently smaller *R* leads to a larger deflection angle when they leave the magnetic field of prism [1]. Based on this fact, the energy loss of electrons can be calculated and recorded to collect the experimental EEL spectra. A magnetic-prism in a parallel EELS

detector provides the advantage of easy alignment in a TEM, adequate energy resolution to differentiate all the elements in the periodic table and working in the typical energy range of commercial TEMs [35]. Figure 2-2 illustrates the schematic diagram regarding the position of specimen and the magnetic-prism of parallel collection EELS detector.

#### 2.2. Introduction to EEL spectra

Scattering of electrons in materials can be divided into two types: elastic and inelastic. In the elastic scattering, electrons do not lose energy and instead they only change their direction [36]. These electrons can be identified as the highest intensity in the spectra namely the zero-loss peak (shown in figure 2-3). On the other hand, electrons can lose their energy and change their direction in inelastic scattering. In fact, the inelastic scattering is the consequence of excitation of inner-shell, valance or conduction electrons. A typical EEL spectra of carbon nanotube filled with manganese is shown in figure 2-3.



Figure 2-3. EEL spectra of a carbon nanotube filled with manganese. The main characteristics of EEL spectra can be seen including the zero-loss, plasmon peak and the ionization edges from Ref. [12].

The energy loss region is habitually divided into low-loss (up to 50eV) and high-loss regions [36]. The low-loss region contains two distinct features. The first feature is zero-loss peak from elastically scattered electrons in which it has the highest intensity in the EEL spectra. As well, the zero-loss peak has a typical width of about 0.2-2 eV, and originates from the energy distribution of electrons produced by the electron gun [2]. The second feature of low-loss region is the plasmon energy ( $E_p$ ) resulted from collective excitation of valence (weakly bond) electrons defined as [1]:

$$E_p = \hbar \sqrt{\frac{ne^2}{\varepsilon_0 m}}$$
(2-2)

where  $\hbar$ , m, e,  $\varepsilon_0$  and n are reduced Planck's constant, the effective mass of electron, the electron charge, the dielectric permittivity of vacuum and the density of free (valence) electrons, respectively. Hence, by changing the valence electron density with variation of the composition and electronic structure, plasmon energy will change [37]. As a result, the low-loss region can be used as a fingerprint of the materials to identify the type of the compounds and the electron bonds [35]. In figure 2-4, low-loss region of graphite, amorphous-carbon (a-C) and graphene oxide (GO) is presented from Ref. [38]. In this figure, the change in the shape of the low-loss region for different compounds and different type of bonds can be easily seen.

As another example, the low-loss region can be used for the detection of different bond configurations of carbon in polymers [39]. The low-loss data of polystyrene (PS) and polyvinylpyrrolidone (PVP) collected by Ritsko and Bigelow [40] is shown in figure 2-5. In this figure, at about 4.75eV in PVP, an additional small peak can be seen. This peak is resulted from the nitrogen on the atomic ring in PVP and generates an irregularity in the delocalized wave function in comparison with that in PS [39].



Figure 2-4. The low-loss region of EEL spectra of graphite, amorphous-carbon (a-C) and graphene oxide (GO) presenting differences in the intensity versus energy loss for different structures of carbon from Ref. [38].



Figure 2-5. Low-loss spectra of PVP (polyvinylpyrrolidone) and polystyrene (PS) from Ref. [40].

The characteristic of the high-loss (core-loss) region is the presence of sharp ionization edges caused from the breaking the bonds of inner-shell electrons [37, 39]. The intensity fluctuation above the ionization edges is called the fine structure. The fine structure can be divided in two categories of energy-loss near-edge structure (ELNES) and extended energy-loss fine structure (EXELFS) [35].

ELNES is the intensity fluctuations around the edge. EXELFS is the intensity oscillations bigger than 50eV and after the ionization edge due to the diffraction effects [35]. In figure 2-6, the schematic characteristic shape of an ionization edge is shown.



Figure 2-6. The schematic shape of an inner-shell ionization edge. a) The ELNES, b) The EXELFS from Ref. [35].

The ELNES structure changes by changing the type of the bonds and variation of the coordination number of atoms [39]. In figure 2-7, the change in the ELNES of carbon [41] and hematite [42] for their different structures is presented. From this figure, the applicability of ELNES to determine different structures can be inferred. Compared to the EXELFS, the ELNES contains more signals and is much easier to measure. Hence, ELNES is more common to use

[35]. Ultimately, modern EELS detectors have provided the capability of the investigation of difference in atomic bonds due to vacancies [43] and impurities [44].



Figure 2-7. Differences between ELNES of a) the carbon K-edge in graphite and diamond from Ref. [41] b) Fe L<sub>2,3</sub> edges from two different forms of Fe<sub>2</sub>O<sub>3</sub> from Ref. [42].

#### 2.3. Background removal from EEL spectra

The area below the core-loss region is proportional to the amounts of the element in the material and can be used for quantitative analysis [15, 37]. In an inelastic collision, the electron will lose some of its energy, and may contribute to the other inelastic scattering called plural scattering or background signal [35, 45]. According to Leapman [39], the pre- and after edge background signal can be originated from: 1) the detector noise 2) single or multiple scatterings of valence electrons 3) single or multiple scatterings of core excitations with less energy than the ionization edge. All these type of background signal can mask the useful

signal for the elemental analysis and practical quantification. Hence, the development of methods to remove the background signal  $(I_b)$  and determine the amount of useful signal from the core excitations of the edge  $(I_K)$  is vital for the EELS microanalysis [46-49].



Figure 2-8. Schematic diagram demonstrating the parameters for the extrapolation of the background by power-law from Ref. [46]. In the figure, E and J represent the amount of energy loss and intensity, respectively.

The power-law is the major method [46, 47] for the estimation of the background using a certain window range ( $\Delta$ ) for the integration over the ionization edge and a fitting range ( $\Gamma$ ) before starting point of the edge as depicted in figure 2-8.  $I_b$  and  $I_K$  can be determined based on the values of  $\Delta$  and  $\Gamma$  for a certain collected EEL spectra. Nevertheless, the mathematical methods usually used for the removal of the background are not accurate. Egerton [46] has suggested the following equation to compute the signal-to-noise ratio (SNR) including the uncertainties of the parameters affecting the background signal:

$$SNR = \frac{I_K}{\sqrt{I_K + hI_b}}$$
(2-3)

where *h* is calculated by:

$$h = 1 + \frac{\operatorname{var}(I_b)}{I_b} \tag{2-4}$$

 $var(I_b)$  is the variance of  $I_b$  and is dependent on the coefficients (a and b) of the fitted line by power-law to the background signal in the logarithmic scale by this equation [46]:

$$\operatorname{var}(I_b) = (\partial I_b / \partial a)^2 \operatorname{var}(a) + (\partial I_b / \partial b)^2 \operatorname{var}(b)$$
(2-5)

Because variations of  $\Delta$  and  $\Gamma$  lead to the variations of var $(I_b)$  and  $I_b$  in equation (2-4); hence the value of h depends also on  $\Delta$  and  $\Gamma$ . To increase the amount of SNR, the value of h should be reduced. The value of  $\Delta$  and  $\Gamma$  can affect significantly the SNR, as illustrated in figure 2-9. Generally, increasing  $\Gamma$ leads to the smaller values of h and consequently bigger SNR [46]. Also, increasing  $\Delta$  increases h.

Generally, the available methods for calculations of SNR does not include the fine structure of edges and utilize simplified models for the differential cross sections. However, the proper values for  $\Delta$  and  $\Gamma$  depend on many parameters such as the energy of ionization edge, the presence of other ionization edges at the vicinity of the edge, the beam energy, collection semi-angle and the thickness of specimen. Monte Carlo simulations due to the ability to utilize accurate differential cross sections as well as including the fine structure of ionization edges can provide more precise calculation of SNR.

The signal-to-background ratio (SBR) is another useful factor for the estimation of the useful amount of signal from a core excitation [50-52] is calculated using  $I_b$  and  $I_K$  as follows:

$$SBR = \frac{I_K - I_B}{I_B} \tag{2-6}$$

The difference between SBR and SNR should be considered for the estimation of useful amount of signal from ionization edges. For example, SBR decreases continuously by increasing the thickness of specimen [39]; however SNR reaches a maximum value at a certain thickness. More details regarding the effect of

different parameters for the background removal on SNR and SBR can be found in chapter 4.



Figure 2-9. Illustration of effect of fitting and integration range on the SNR and *h* at different amount of ionization edge energies from Ref. [46].

#### 2.4. Monte Carlo (MC) simulations for electron scattering

MC simulation is based on random sampling to explain the behavior of stochastic phenomena [53]. Electron scattering in solids have a random nature. For example, when electrons scatter due to a collision, they may change their path to any direction. Accordingly, MC simulation is an effective method for the modeling of electron scattering [54]. It is important to emphasize that many practical cases cannot be described by analytical methods and MC simulation may be the only viable solution in particular for complex geometries [18]. Due to the stochastic nature of MC technique, it includes the statistical uncertainties [55]. Hence, the statistical number of interactions should be large enough to reduce these uncertainties [56].

The main advantage of MC technique for the electron scattering is the possibility of applying accurate differential cross section [57]. Hence, the accuracy of MC simulation is dependent on the suitable models of differential cross section. With the increasing speed of computers, simulation time is not the main concern of MC technique and instead the main concern is being focused on better scattering models [56]. Each available elastic and inelastic differential cross section model is applicable for a special range of energy. As a result, for each range of energy, an appropriate model should be used.

The MC method has been successfully used for electron beam interactions that lead to secondary electrons, backscattered electrons, characteristic X-rays and bremsstrahlung radiation [54]. Casino [58] and Win X-ray [18] were developed by Gauvin and co-workers for the MC simulation of electron trajectory for electron beam interactions using slowing down approximation based on [18]:

$$E_{j+1} = E_j + \frac{dE}{dS}L_j \tag{2-7}$$

where dE/dS is the rate of energy loss at the  $E_j$  and  $L_j$  is the distance between two collisions.  $E_{j+1}$  indicates the amount of energy loss at the next inelastic scattering. In these simulations, the Bethe equation is the basis for mean energy loss calculation (dE/dS) of the electron scatterings as follows [18]:

$$\frac{dE}{dS} = -7.85 \times 10^4 \frac{\rho}{E_j} \sum_{i=1}^n \frac{c_i Z_i}{A_i} \ln\left(\frac{1.166E_j}{J_i^*}\right)$$
(2-8)

where  $\rho$ ,  $A_i$  and  $c_i$  are the specimen mass density, total atomic weight and the weight fraction of element *i*, respectively.  $J_i^*$  is the modified mean ionization potential element *i* as proposed by Joy and Luo [59]. Equation (2-8) is valid due to of the presence of enough signal (scattering collisions). However, for the low energy interactions (less than 1 keV) in the SEM and high energy interactions in the TEM, the Bethe equation is not applicable and suitable models should be utilized. Optical data models have been developed for the latter interactions [60] and will be discussed in the next section.

The elastic and inelastic differential cross sections are necessary to be calculated for the MC simulations. In figure 2-10, the flowchart for the MC simulation process is illustrated based on Ref. [61]. First the initial position of electron is determined. After calculation of differential cross sections, all other dependent quantities such as total mean free path ( $\lambda_T$ ) at a certain trajectory by energy of *E* are calculated. The path length between each trajectory can be calculated as below [24]:

$$L = -\lambda_T \ln(R_1) \tag{2-9}$$

where  $R_1$  is a random number uniformly distributed. Subsequently, mean free path, the next position and direction of electron are calculated. If the traveled distance in the perpendicular direction to the plane of entrance (Lz) is less than the thickness (t) of specimen, the next step is to determine that the interaction of electron is elastic or inelastic. If  $R_2 \cdot \sigma_T < \sigma_{in}$  the interaction is considered inelastic and otherwise is elastic scattering, where  $R_2$  is a random number uniformly distributed [24].  $\sigma_{in}$ ,  $\sigma_{el}$  and  $\sigma_T$  are the inelastic, the elastic and the total differential cross sections, respectively. For the elastic interaction, the polar scattering angle ( $\theta$ ) and for the inelastic interaction polar scattering angle as well as the amount of energy loss (W) are sampled according to their probability distribution function. The base of sampling methods can be found in Ref. [61] with much more details. Afterward, the azimuthal scattering angle ( $\phi$ ) will be selected randomly from 0 to  $2\pi$ . Based on the sampled  $\theta$  and  $\phi$ , the new direction of electron will be determined and this process continues until the electron is transmitted or absorbed [24]. The total amount of energy loss for each electron is stored and can be plotted as the EEL spectra.



Figure 2-10. Flowchart of Monte Carlo simulation of electron scattering in a specimen with thickness *t*. *N* and  $n_t$  are the total number of transmitted electrons and the number of atoms per unit volume, respectively.

#### 2.5. Optical data models

### 2.5.1. Introduction to optical data models

A number of optical data models have been proposed to compute the inelastic differential cross section. Optical oscillator strength (OOS) from experimental
data or calculations is extended into non-zero momentum transfer region by an extension algorithm in the optical data models. The extended OOS to the non-zero momentum transfer zone is called the generalized oscillator strength (GOS). The GOS is in direct relation with the inelastic differential cross section, and will be the heart of EEL spectra simulations [60].

According to Fernandez-Varea et al [23], the work of Tung et al [62] can be considered as the first major attempt in development of the optical data models by combination of the local plasma approximation and the homogeneous freeelectron gas model from the Lindhard theory [63]. Afterward, Ashley [64] developed one-mode approximation for simplification the calculations. The next major progress was presented by Penn [65] by suggesting the medium as the mixture of homogenous electron gas [60]. Later, Ashley [66] simplified the Penn model to improve speed of calculations [60]. Ashley and Penn's models have been used by other researchers extensively since their inception [67, 68]. The results of these two models are very similar for small value of momentum transfer, while the Ashley's model noticeably simplifying and reducing the calculations time [60].

The extension algorithms based on the free electron gas theory are more suitable to model excitations of weakly bound electrons and do not offer valuable results for inner-shell ionizations [23]. In fact, a proper extension algorithm for inner-shell ionization has been presented by Mayol and Salvat [69]. All of these models are basically non-relativistic and are only valid for moderate range of energies (< 50 keV) [60]. A more advanced version of two-modes model considering full relativistic equation as well as Fermi density effect has been presented by Fernandez-Varea et al [60]. In this research, a general overview of the optical data model is introduced. This model is the basis of MC simulation for the electron transport in this thesis.

## 2.5.2. Basis of optical data models

In an inelastic collision of an electron having the kinetic energy E and the momentum  $\mathbf{p}$  ( $\mathbf{p} = \hbar \mathbf{k}$  where  $\mathbf{k}$  is the wave vector) with the specimen, the momentum of scattered electron changes to  $\mathbf{p}'$ . Hence, the momentum transfer ( $\mathbf{q}$ ) is  $\mathbf{q} = \mathbf{p} - \mathbf{p}'$ . The kinematics of this inelastic scattering is illustrated in figure 2-11. The new kinetic energy of scattered electron is E' = E - W, where W is the energy transfer (loss) in the collision. The scattering angle,  $\theta$ , can be calculated using this equation:  $q^2 = p^2 + p'^2 - 2pp'\cos\theta$  [60].



Figure 2-11. Kinematics of inelastic scattering based on the concept in Ref. [60].

The differential cross sections determine the probability for an specific type of scattering with a certain energy loss. Based on the first order perturbation theory, the inelastic differential cross section of an electron or a positron with the kinetic energy E in the nonrelativistic form can be written as [70, 71]:

$$\frac{d^2\sigma_{in}}{dQdW} = \frac{\pi e^4}{E} \frac{1}{WQ} \frac{df(Q,W)}{dW}$$
(2-10)

where Q is called the "recoil energy" defined as [60]:

$$Q(Q+2m_ec^2) = (cq)^2$$
(2-11)

where  $m_e$  and c are the rest mass of electron and the speed of light in vacuum, respectively. In non-relativistic form Q can be calculated as  $Q = 2E - W - 2\sqrt{E(E - W)} \cos\theta$  [23]. The quantity df(Q,W)/dW is the GOS. The GOS can be described as the "effective number of electrons in the target that participate in an inelastic interaction" [55] in a specified energy and momentum transfer.

The GOS can also be described with the following equation that is based on the Born approximation [26]:

$$GOS(Q,W) = \frac{df(Q,W)}{dW} = \frac{W}{Q} \left| \left\langle \Psi \left| \sum_{j=1}^{Z} \exp(iq.r_j / \hbar) \right| \Psi_0 \right\rangle \right|^2$$
(2-12)

where  $\Psi_0$  and  $\Psi$  are the ground state and excited state atomic (or molecular) wave functions, respectively. The summation is performed over the number of electrons in the target (Z). The analytic solution of equation (2-12) is merely known for atomic hydrogen and for the free-electron gas [26]. For any other system, the GOS should be calculated by numerical integration of the wave functions. The GOS represents a surface over the (Q,W) or (q,W) plane, known as the Bethe surface [60]. In figure 2-12 the Bethe surface for the ionization of the hydrogen atom is shown.



Figure 2-12. The GOS for ionization of the hydrogen atom in the ground state.  $U_i = 13.6$  eV is the ionization energy from Ref. [60].

There is a useful relation between the GOS and the dielectric energy loss function,  $\text{Im}(-1/\varepsilon(Q,W))$ , for a condensed media which is the foundation to reduce the complexity of calculations [24, 26]:

$$\frac{df(Q,W)}{dW} = \frac{2W}{\pi E_p^2} Z \operatorname{Im}(\frac{-1}{\varepsilon(Q,W)})$$
(2-13)

where  $\varepsilon(Q,W)$  is the complex dielectric function of material and  $E_p$  is the plasmon energy of an homogonous electron gas and Z is the number of electrons per atom or molecule.

Calculations of total inelastic differential cross section need to perform double integration over the (Q,W) plane. This numerical task is difficult, time consuming and as a result not appropriate for the MC simulations [26]. The optical data models have been proposed to overcome the calculation difficulties of GOS from the first principles. The starting point of these models is to rewrite the GOS as [24]:

$$\frac{df(Q,W)}{dW} = \int_0^\infty \left[\frac{df(W')}{dW'}\right] F(W';Q,W)dW'$$
(2-14)

where F(W';Q,W) is an extension algorithm that extrapolates the OOS ( df(W)/dW) to the non-zero momentum transfer region and W' is the resonance energy. Figure 2-13 shows the schematic illustration of building Bethe surface by means of the OOS and the extension algorithm.

In the optical limit (Q = 0), the GOS reduces to the OOS i.e. df(W)/dW = df(0,W)/dW. Figure 2-14 shows experimental OOS data for aluminum and copper. The inner- shell excitations appear as sharp edges for both elements. For Al, the sharp peak about  $W \approx 15 eV$  is the plasmon excitation. On the other hand, the plasmon peak for Cu has a complex structure and a definitive value cannot be attributed. All these variations originate from the different electronic structure of the elements.



Figure 2-13 . Schematic illustration of building Bethe surface using OOS and extension algorithm.



Figure 2-14. The OOSs for Al (continuous curve) and Cu (dashed curve) from Ref. [26]. The Kand L-shell edges of both elements are shown in the figure.

For excitations of weakly bound and inner-shell electrons, proper extension algorithms are needed separately [24]. Indeed, the extension algorithm for excitation of weakly bound electrons is the two-modes model, and is a suitable approximation of the Lindhard theory [60]. For the excitation of inner-shell electrons, models based on the free electron gas are not appropriate and  $\delta$ -oscillator presented by Liljequist [72] are more suitable. The  $\delta$ -oscillator model considers contribution of both distant and close collisions of the electrons [60].

#### 2.5.3. Extension algorithms

It is complicated to calculate the GOS of atoms in solids from first principles and in practice GOS can be estimated by appropriate models [56]. The optical data models extend OOSs obtained from theoretical calculations or experimental measurements using appropriate extension algorithms to estimate the GOS for Q > 0 [56].

## 2.5.4. Excitation of weakly bound electrons

The outer, weakly bound, electrons of an atom can be assumed as free ones for the explanation of their inelastic excitations reasonably. The Lindhard theory of the homogeneous free-electron gas [63] hence has an central role in the most suggested optical data models so far. The following two-modes model [23] is used as a suitable approximation to the Lindhard free-electron gas GOS [26] to simplify the calculations as given by:

$$F_T(W';Q,W) = [1 - g(Q)]\delta(W - W_r(Q)) + g(Q)\delta(W - Q)$$
(2-15)

where  $\delta(x)$  is the Dirac delta function ( $\delta(x) = 0$  if  $x \neq 0$  and  $\delta(x) = \infty$  if x = 0,

with  $\int_{-\infty}^{\infty} \delta(x) dx = 1$ ). The concept of the model is illustrated in figure 2-15a. There are two excitation modes inside a small region of Q. The first term (mode) with strength (1-g(Q)) indicates the plasmon excitations with the dispersion relation  $W_r(Q)$  and the second term with strength g(Q) stands for electron-hole excitations [26]. For small values of Q, g(Q) leads to zero and accordingly the strength of the plasmon branch is one for Q = 0. The form of the functions g(Q) and  $W_r(Q)$  can be determined by the fact that the results of the two-modes model should be in agreement with those of the Lindhard theory strictly [23, 26].

#### 2.5.5. Excitation of inner-shell electrons

The ionization of inner shell electrons cannot be described well by models based on the free-electron gas [26]. The  $\delta$ -oscillator model suggested by Liljequist [72] is more suitable for the inner-shell ionizations as a one-electron GOS:

$$F_{\delta}(W',Q,W) = \delta(W-W')\Theta(W'-Q) + \delta(W-Q)\Theta(Q-W')$$
(2-16)

where  $\Theta$  is the unit step function ( $\Theta(x) = 0$  if x < 0 and  $\Theta(x) = 1$  if x > 0). In this extension algorithm (figure 2-15b), the first term describes the contribution from distant collisions (i.e. dipole transitions in the optical limit  $Q \rightarrow 0$ ), while the second term originates from the close collisions (i.e. the Bethe ridge) [23, 26].



Figure 2-15. Extension algorithms: (a) two-modes model and (b)  $\delta$ -oscillator from Ref. [26].

Details of the extension algorithms employed in the optical data models in this research can be found in chapter 3.

## 2.5.6. OOS from EEL spectra

The maximum effective collection semi-angle of EELS detectors ( $\theta_{max}$ ) is very small (about a few milli radians). In addition, the initial kinetic energy of incident electrons is much bigger than the observed energy loss. In such a condition ( $\theta_{max} \ll 1$ ,  $W \ll E$ ), the EEL spectra can be considered in a single collision and the total cross section can be written as [23]:

$$\left[\frac{d\sigma}{dW}\right]_{\theta < \theta_{\max}} = \int_{\mathcal{Q}(\theta=0)}^{\mathcal{Q}(\theta=\theta_{\max})} \frac{d^2\sigma}{dQdW} dQ \approx \frac{\pi e^4}{E} \frac{1}{W} \frac{df(W)}{dW} \ln\left[1 + \left(\frac{2E\theta_{\max}}{W}\right)^2\right]$$
(2-17)



Figure 2-16. EEL spectra of Cu (E = 60 keV,  $\theta_{max} = 0.1rad$ ), calculated by means of equation (2-17) (full curve) [23], and obtained from experimental data (dashed line) [73]. The figure is from Ref. [23].

According to equation (2-17), the df(W)/dW (OOS) is the most important input parameter of calculation; hence the accurate model for the OOS is necessary for

the MC simulations. Small-angle EEL spectra for Cu computed based on equation (2-17) from ref. [23] is shown in figure 2-16. As can be seen, a good agreement between the simulation results based on equation (2-17) and experimental data at low-loss region is depicted, confirming the accuracy of the applied optical data model.

#### 2.6. Energy loss function (ELF)

The most important characteristic of optical data model is that differential cross section can be computed by the OOS. The OOS can be obtained experimentally by measuring EEL spectra using equation (2-17) or it can be calculated by having optical constants. Unfortunately, experimental OOS is available for a limited number of materials. As well, available experimental OOS are acquired by joining a variety of measured optical [74-76] and X-ray photoelectric data [77-80] from different specimens and instruments [60]. Hence, obtaining a suitable method to determine the OOS has a great importance. The OOS should satisfies the Bethe sum rule as [55]:

$$\int_0^\infty \frac{df(W)}{dW} dW = Z \tag{2-18}$$

The Bethe sum rule can be used for the normalization of the final OOS obtained from different sources.

Based on equation (2-13), when  $Q \rightarrow 0$  (optical limit), the GOS will turn to OOS [26]:

$$\frac{df(W)}{dW} = \frac{2W}{\pi E_p^2} Z \operatorname{Im}(\frac{-1}{\varepsilon(W)})$$
(2-19)

where  $\varepsilon(W)$  is the dielectric function in the optical limit and can be written as:  $\varepsilon(W) = \varepsilon(Q = 0, W) = \varepsilon_1 + i\varepsilon_2 = (n + i\kappa)^2$ (2-20)

where *n* is the refractive index and  $\kappa$  is the extinction coefficient [9]. Both *n* and  $\kappa$  depend on the frequency of field ( $\omega$  ( $= W / \hbar$ )).  $\varepsilon_1$  and  $\varepsilon_2$  are the real and

imaginary parts of dielectric function.  $\text{Im}(-1/\varepsilon(W))$  is called the energy loss function (ELF) and is given by [1]:

$$\operatorname{Im}(-1/\varepsilon) = \varepsilon_2 / (\varepsilon_1^2 + \varepsilon_2^2) \tag{2-21}$$

In accordance with equation (2-19), the OOS will be obtained by having the ELF. ELF can be obtained also from *ab initio* methods. In *ab initio* calculations, by having electron densities, optical matrix elements can be determined and then the imaginary part of the dielectric function,  $\varepsilon_2$ , can be computed [4]. Consequently, Kramers–Kronig transformation must be applied to obtain  $\varepsilon_1$  [81, 82]:

$$\operatorname{Re}\left[\frac{1}{\varepsilon(W)}\right] = 1 - \frac{2}{\pi} P \int_0^\infty \operatorname{Im}\left[\frac{-1}{\varepsilon(W)}\right] \frac{W'}{W'^2 - W^2} dW'$$
(2-22)

where *P* indicates the Cauchy principle part of the integral. The details of *ab initio* calculation of ELF can be found in chapter 5.

#### 2.7. Energy-loss near-edge structure (ELNES) calculation

Inelastic differential cross section based on the first Born approximation [83, 84] for an isotropic material can be written as:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \left[\frac{4\gamma^2}{a_0^2 q^4}\right] \frac{k_f}{k_f} \sum_{i,f} \left| \left\langle f \left| e^{i \vec{q} \cdot \vec{r}} \right| i \right\rangle \right|^2 \delta(E - E_f + E_i)$$
(2-23)

where  $\Omega$  is the solid angle of scattering. To derive equation (2-23), it is assumed that the incoming and the outgoing fast electrons are plane waves with wave vectors,  $\vec{k_i}$  and  $\vec{k_f}$ . q is the momentum transfer equals to  $\vec{q} = \vec{k_i} - \vec{k_f}$ ,  $a_0$  is the Bohr radius, E is the energy loss and  $\gamma$  is the relativistic factor. Since the momentum transfer (q) is small compared to the incident energy, the low-qexcitations are dominant and as a result  $e^{i\vec{q}\cdot\vec{r}}$  can be estimated by the  $q \cdot r$ operator (based on Taylor expansion) [85].  $|i\rangle$  is the initial (ground) state of the target electron and  $|f\rangle$  indicates the free state occupied by the target electron in the final state (conduction band) [83]. A core hole will be produced that changes electron density in the transition of excited electron to the final state [84].

## 2.8. ab initio method for EELS

Accurate calculation of the electron density in the material is the basis of reliable ELF and ELNES calculations. As explained before, recent progress in EELS instrumentation has provided high energy resolution that enables us to compare the experimental results with the simulated spectra. Calculations of the properties of solids can be performed by the classical approach or quantum mechanical calculations based on the *ab initio* methods. On the contrary to the classical approach, *ab initio* methods do not need to have any prior experimental knowledge of the studied system [86]. Hence, *ab initio* methods can study the unusual or unexplained behavior of materials [87].

Two main *ab initio* methodologies are extensively used currently for ELNES and ELF calculations. The first method is band structure (BS) and the second one is based on real space multiple scattering theory [3]. Both methods use the density functional theory (DFT) to calculate properties of electronic structure [85]. The BS method relies on the crystallinity of structure and is formulated in the reciprocal space [84]. Hence, the BS method is suitable for periodic structures in crystalline form. Multiple scattering (MS) method is formulated in the real space and does not need any assumption of symmetry. In fact, compared to the BS method, the MS is more appropriate for aperiodic systems such as defects, interfaces, vacancies and impurities [85]. The main advantage of the BS method is the calculation of many physical properties based on electron density calculation in the material [87]. Electron density calculations leads to consistent interpretation of the essential solid state properties such as band structure diagrams, optical properties and density of states [88]. Consequently, from the results of the BS method, ELNES and ELF can be calculated. It should be noticed that the BS methods are generally appropriate for the ground state properties and the results for the excited states should be interpreted carefully [29]. However, ELNES and

low-loss spectra calculations by the BS method have been used successfully in many studies. Generally, the BS methods are much more common compared to the MS method and produce more accurate results [89]. Even though, the MS method has enough accuracy to compare the simulation results with the experimental data [3].

#### **2.8.1.** Density functional theory (DFT)

Density functional theory is the established method for the *ab initio* calculations of the properties of materials based on the estimation of the electronic density by solving the Schrödinger equations for a quantum mechanical manybody problem [86-88]. In a quantum many-body problem, *N* nuclei interact with *ZN* electrons, where *Z* is the atomic number of material. The total Hamiltonian of this system includes the kinetic energy of electrons and nuclei, Coulomb interaction between electrons-electrons ( $E_{ee}$ ), nuclei-electrons ( $E_{Ne}$ ) and nucleinuclei ( $E_{NN}$ ) [90]. The many-body particle in quantum mechanics is a complicated problem, so some simplifications are necessary to solve the problem.

Mass of the nucleus is much bigger than the mass of electron; hence the nuclei are considered static based on Born-Oppenheimer approximation [90]. Therefore, the many-body problem reduces to *NZ* interacting electrons which are in the potential of nuclei. The Born-Oppenheimer approximation leads to the simplification of the Hamiltonian of the quantum mechanical many body particles [90].

Hohenberg and Kohn [91] proved that the ground electron density ( $\rho$ ) uniquely determines the total energy ( $E_{tot}$ ) of the quantum mechanical many-body particle system at the ground state. Hence,  $E_{tot}$  can be expressed as the result of the summation of following terms [87]:

$$E_{tot}(\rho) = T_s(\rho) + E_{ee}(\rho) + E_{Ne}(\rho) + E_{NN}$$
(2-24)

where  $T_s$  is the kinetic energy of the non-interacting particles. In fact, the Hohenberg-Kohn theory concludes that the ground state density distinctively

defines the external potential  $(V_{ext})$  [92]. Based on the Hohenberg-Kohn theory, Kohn and Sham [93] derived a set of equations to calculate the electronic density by DFT. According to the Kohn-Sham theory, the variation of the total energy of the system provides a series of effective one-particle Schrödinger equations [92, 94]:

$$\left(-\frac{\hbar^2}{2m_e}\vec{\nabla}_i^2 + V_{eff}(\mathbf{r})\right)\phi_i = \mathbf{\varepsilon}_i\,\phi_i \tag{2-25}$$

where  $(-\hbar^2/2m_e)\vec{\nabla}_i^2 + V_{eff}(\mathbf{r})$  is the Kohn-Sham Hamiltonian of the system (  $\hat{H}_{KS}$ ). Also,  $\boldsymbol{\varepsilon}_i$  is a Lagrange multiplier guaranteeing normalization [94].  $V_{eff}(\mathbf{r})$  is the effective one-electron potential defined by [92, 94]:

$$V_{eff}(\mathbf{r}) = \int \frac{\rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'} + V_{xc} + V_{ext}$$
(2-26)

where  $V_{xc}$  is the exchange-correlation potential.  $V_{xc}$  is related to the exchange-correlation energy as follows [94]:

$$V_{xc} = \delta E_{xc}[\rho] / \delta \rho \tag{2-27}$$

Having the results of Eq. (2-25), the ground state electron density can be obtained as:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \phi_i(\mathbf{r}) * \phi_i(\mathbf{r})$$
(2-28)

The Kohn-Sham equations (from (2-25) to (2-28)) provides a practical way to calculate ground state electron density. The major estimation for solving the Kohn-Sham equations is the exchange-correlation potential. The simplest approach for the exchange-correlation potential is the local density approximation (LDA). LDA has the propensity of the over binding and leads to too small lattice constants [86]. The generalized gradient approximation (GGA) improves LDA by addition of gradient term of the electron density [95]. Besides, new forms of exchange-correlation potentials for the materials with complex electronic structure such as modified Becke-Johnson exchange potential [96-99] should be

chosen for the reliable electronic density calculations. Hence, one of the major steps for accurate DFT calculations is the choice and development of appropriate exchange-correlation potentials.

## 2.8.2. Linearized augmented plane waves (LAPW) method

There are many methods to solve the Kohn-Sham equations numerically. However, the linearized augmented plane waves (LAPW) is one of the most accurate and recognized methods for the solution of Kohn-Sham equations. In the LAPW, space will be divided into two regions [87]. The first region is atomic spheres that should not overlap and the second region is the interstitial space between atomic spheres. Wave functions initiate from atomic spheres expand to the interstitial spaces as plane waves [100]. Figure 2-17 illustrates the two different regions of calculations.



Figure 2-17. Schematic illustration of atomic sphere and interstitial regions based on the concept from Ref. [87].

Inside the atomic sphere with radius  $R_t$ , the basis function,  $\phi$ , can be calculated by [101]:

$$\phi(\boldsymbol{k}_{n},\boldsymbol{r}) = \sum_{l,m} [A_{lm}(\boldsymbol{k}_{n})u_{l}(\boldsymbol{r},E_{l}) + B_{lm}(\boldsymbol{k}_{n}) \left(\frac{\partial u_{l}}{\partial E}(\boldsymbol{r},E)\right)_{E_{l}}]Y_{lm}(\hat{\boldsymbol{r}})$$
(2-29)

where  $\mathbf{k}_n$  is the reciprocal lattice vector,  $u_l$  is the standard solution of the radial Schrödinger equation for the spherical part of the potential at energy of  $E_l$  and  $Y_{lm}(\hat{\mathbf{r}})$  is the spherical harmonics.  $A_{lm}$  and  $B_{lm}$  are calculated by obliging that the basis function at the edge of sphere be equal to the value of basis function at the interstitial region. The values of  $E_l$  in the energy bands can be calculated by the following boundary condition [101]:

$$\begin{cases} \left(\frac{\partial u_l}{\partial r}(r,E)\right)_{R_l,E_l} = 0\\ u_l(R_l,E_l) = 0 \end{cases}$$
(2-30)

In the interstitial region, the basis function is a plane wave [87]:

$$\phi(\mathbf{k}_n, \mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{k}_n \cdot \mathbf{r})$$
(2-31)

where  $\Omega$  is the volume of unit cell. At this region, the solution of Kohn-Sham equations can be obtained using the linear combination of basis functions [87]:

$$\psi_{k} = \sum_{n} c_{n} \phi(\boldsymbol{k}_{n} \cdot \boldsymbol{r})$$
(2-32)

where the coefficients,  $c_n$ , are calculated using the Rayleigh-Ritz variational principle [101]. The convergence of the solutions are examined by a cutoff parameter:  $R_{MT} \times K_{max}$ , where  $R_{MT}$  is the smallest atomic sphere radius in the unit cell and  $K_{max}$  is the magnitude of the largest k vector [100].

The augmented plane waves (APW) are combined with local orbitals (lo) called APW+lo method [102] with the following form [87]:

$$\phi_{lm}^{LO} = [A_{lm}u_l(r, E_{1,l}) + B_{lm}\dot{u}_l(r, E_{1,l}) + C_{lm}u_l(r, E_{2,l})]Y_{lm}(\hat{r})$$
(2-33)

where  $\dot{u}_l(r, E_{1,l}) = \partial u_l(r, E) / \partial E \Big|_{E=E_{1,l}}$  is the derivation of  $u_l$  at  $E_{1,l}$ . APW+lo method is used for inside the atomic spheres where the essential l-orbitals are hard to converge in the LAPW method or for the atoms with small atomic sphere [87].

#### 2.8.3. WIEN2K program

WIEN2k [100] is one of the most recognized DFT codes for the calculations of the electronic density of crystalline structures. Currently, more than 2000 groups in the world use the code for the solid state calculations of the properties of materials. WIEN2k program was chosen to perform density functional theory calculation in this research.

WIEN2k utilizes the LAPW method to calculate electron density [86]. A successful calculation by WIEN2k program includes two major steps [100]: 1) an initial electron density will be calculated according to the parameters of simulation. 2) an iterative process is necessary to calculate the final electron density. This iterative process is called the self consistent field (scf) calculations. In the iterative process, the electron density from the previous step will be used as the basis of next step. The electron density in each step will be calculated by solving the Schrödinger equations using Kohn-Sham theory [101]. The process will be continued to reach a convergence point depending on the desired accuracy.

The major steps for the calculation of the electron density at the ground state in WIEN2k [100] are presented in figure 2-18 as a flowchart. Based on the manual of program [100] the major steps can be described as: First, the distance of nearest neighbors are calculated by NN program. NN also ensures that atomic spheres are not overlapping. SGROUP determines the space group of the crystal structure and SYMMETRY program applies the operations for the symmetry based on the applied space group. LSTART estimates atomic electron densities and the atomic potentials for the start of self consistent calculations. KGEN prepares the k-mesh for the calculations in the irreducible Brillouin zone (IBZ). DSTART calculates the first crystalline charge densities based on the results of LSTART by superposition of atomic densities.



Figure 2-18. The flowchart representing the major steeps for the calculation of the electron densities at ground state in WIEN2k based on the manual of program [100].

Subsequent to preparation of the initial electron densities and potentials as well as the necessary input files, the self consistent calculations begin. LAPW0 calculates the total potential by the summation of the Cloumb ( $V_C$ ) and the exchange-correlation potentials ( $V_{xc}$ ). Valence bands are calculated by LAPW1 program by generation of the eigenvectors and eigenvalues.

LAPW2 expands the calculations of the valence charge density for all the occupied states and k-meshes. The core states are calculated by LCORE program. Finally, MIXER computes the total density by combination of all the calculated densities of the core, semi-core and the valence densities. The calculations can be considered convergent if the difference between particular parameter such as the total charge or the total energy is less than a certain value.

Sequentially, many physical properties of crystal can be obtained by having the electron density distributions. The calculation of the optical properties such as ELF is performed by OPTIC program [103, 104] and ELNES by TELNES program [84].



Figure 2-19. Comparison of experimental carbon *K*-edge in graphite (continues line) with the calculated ELNES (dashed line) based on WIEN2k program from Ref. [116].

The accuracy of WIEN2k code has been confirmed by the comparison with many measurements of optical properties [105-109] and comparison with the shape of collected ELNES experimentally [110-116]. As shown in figure 2-19, a good agreement between experimental and simulation results from WIEN2k [44] can be seen, especially on the shape of carbon K-edge ELNES.

## 2.9. Effect of temperature and pressure on the low-energy loss spectra

Temperature and pressure can affect many physical and mechanical properties of materials. The variation of temperature [32] and pressure [33] can change the valence electron density and plasmon energy; hence it can be expected that the related properties to the electronic structure change also. The measurement of plasmon energy has been related to the study of many other physical and mechanical properties [34, 117-120]. Hence, the study of low-loss region of EEL can provide a method to investigate effect of temperature and pressure on electronic density related properties.

Generally, the majority of EEL spectra are acquired at the ambient pressure and temperature. However, there is a shortage of experimental measurements regarding the effect of temperature and pressure on the energy loss spectra. Effect of temperature on the energy loss can be studied by EELS [32]. Although effect of pressure should be investigated by other techniques, since at high pressures electron scattering happens and degrades the useful signal. Inelastic X-ray scattering (IXS) has been developed in recent years for the investigation of pressure effect on the low energy loss region [121]. Also, IXS has the benefit of not suffering from multiple scattering at high momentum transfers [121].

Study of effect of temperature on the electron energy spectra was started by Watanabe [122]. Nevertheless, the energy resolution of the detectors was not enough to conclude a meaningful trend in his experimental data [123]. By improvement of the energy resolution of detectors, the decrease in the plasmon energy by temperature was confirmed by several researchers [32, 123-128]. Abe and co-workers [123] performed accurate measurement of the plasmon energy as the prominent feature of the low-energy loss spectra and concluded that aluminum follows the free electron model by the expansion of the lattice parameter. However, they suggested the plasmon energy reduction of silver by variation of temperature cannot completely be explained by the free electron model because of interband transitions [125]. High energy resolution EELS detectors has provided the reliable data collection for the effect of temperature in

pure elements and alloys in the solid or liquid forms [126]. Figure 2-20 represents the experimental measurement of low-energy loss spectra of aluminum by EELS in both solid and liquid phases. In recent years, the decrease in the surface plasmon energy for some materials has been also confirmed [127, 128]. However, there is a shortage of *ab initio* calculations for the understanding of the plasmon energy variation by temperature in solids.



Figure 2-20. a) EEL spectra of Al at different temperatures acquired throughout cooling. b) Plasmon energy measurement of solid and liquid Al at different temperatures from Ref. [126].

The experimental measurement of the variation of low-energy loss at different pressures is more recent in comparison to the study of temperature due to the recent developments of IXS technique for the study of the effect of high pressures. The experimental measurements of low-energy loss spectra has been performed for a limited number of elements [33, 121, 129-131] and there is a scarcity of data for materials with more complex structure.



Figure 2-21. a) Variation of IXS spectra at different pressures for the energy transfer spectra of Na at the fixed momentum transfer of  $q = 5nm^{-1}$ . b) Plasmon energy variations of Na as the function of pressure and momentum transfer variations from Ref. [129].

Experimental measurements confirmed the increase in the plasmon energy because of the increase in the valence electron density for sodium as depicted in figure 2-21. However, at high pressures the crystal structure reforms to more stable forms [132] and the continues increase has been reported to a decrease in the plasmon energy for Na at 105 GPa [131]. This a new and challenging field of research and more experimental and theoretical models as well as *ab initio* calculations are necessary to be performed. Furthermore, there is a lack of study of the effect of pressure and temperature on the plasmon energy at the same time.

In chapter 5 by combination of free electron model and a pesudo-spinodal equation of states [133-135], the effect of temperate and pressure will be studied on the plasmon energy variations.

## 2.10. References

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# **Chapter 3. Detailed Monte Carlo simulation of electron transport and electron energy loss spectra**

In this chapter, the optical model used for the Monte Carlo simulation of electron transportation and electron energy loss spectra is described. In addition, the details regarding the procedure of Monte Carlo simulation as well as the optical oscillator strength (OOS) preparation are explained. The backscattering and transmission coefficients of electrons with kinetic energies between 0.1 and 500keV of in the bulk and the thin solid film specimens are calculated by Monte Carlo simulations and compared with the experimental measurements. Also, the electron energy loss spectra of various elemental thin solid films are simulated at different beam energies and thicknesses. A simple model is introduced to calculate the optimum thickness for the maximum signal-to-noise ratio of thin solid films. This chapter –with the same title- and co-authored by Francesc Salvat and Raynald Gauvin has been submitted to Ultramicroscopy.

# Abstract

A computer program for detailed Monte Carlo simulation of the transport of electrons with kinetic energies in the range between about 0.1 and about 500keV in bulk materials and in thin solid films is presented. Elastic scattering is described from differential cross sections calculated by the program ELSEPA using the relativistic (Dirac) partial-wave expansion method with different models of the scattering potential. Inelastic interactions are simulated from an optical-data model based on an empirical optical oscillator strength that combines optical functions of the solid with atomic photoelectric data. The generalized oscillator strength is built from the adopted optical oscillator strength by using an extension algorithm derived from Lindhard's dielectric function for a free-electron gas. It is shown that simulated backscattering fractions of electron beams from bulk (semiinfinite) specimens are in good agreement with experimental data for beam energies from 0.1 keV up to about 500 keV. Simulations also yield transmitted and backscattered fractions of electron beams on thin solid films that agree closely with measurements for different film thicknesses and incidence angles. Simulated most probable deflection angles and depth-dose distributions also agree satisfactorily with measurements. Finally, electron energy loss spectra of several elemental solids are simulated and the effects of the beam energy and the foil thickness on the signal to background and signal to noise ratios are investigated.
# 3.1. Introduction

The reliability of Mont Carlo (MC) simulation of multiple electron interactions is primarily determined by the accuracy of the adopted differential cross-section (DCS) models. A wide variety MC models have been used in studies aimed at describing various aspects of the interaction of electron beams with solid specimens, including backscattering, secondary electron emission, X-ray emission and bremsstrahlung photon emission [1]. The MC programs Casino [2] and Win X-ray [3] were developed by Gauvin and co-workers to simulate electron trajectories in scanning electron microscopy (SEM). In these programs, as well as in other programs used in SEM, electron energy losses are described using the continuous-slowing-down approximation (i.e., by means of the average energyloss obtained from the Bethe stopping power formula), which is though to be sufficient when the number of inelastic interactions along each electron trajectory is large. However, for the lower energies (< 1 keV) used in SEM and for the highenergy beams in transmission-electron microscopy (TEM), energy straggling is important and one should rely on detailed simulation schemes, where individual inelastic collisions are simulated from the corresponding DCSs. A convenient framework for describing inelastic interactions is provided by the so-called optical-data models (ODM) [4, 5].

Various MC programs [6, 7, 8] with detailed simulation of inelastic collisions using different ODMs have been developed. The theoretical assumptions underlying an ODM are equivalent to the first-order plane-wave Born approximation, in which the DCS is expressed as the product of kinematical factors and the generalized oscillator strength (GOS). The basic ingredient of an ODM is the optical oscillator strength (OOS), that is, the GOS for null momentum transfer. Typically, the OOS is built from optical data (refractive index and extinction coefficient) obtained from experiments or from density functional theory calculations, which are usually available only for relatively small energy transfers, complemented with calculated or experimental photoelectric cross sections for higher energy transfers. While optical data provide a realistic

description of low-energy excitations of conduction and valence electrons, photoelectric cross sections usually give the most reliable approximation available for excitations of inner electron shells. The GOS for finite momentum transfers is obtained from the adopted OOS by means of a suitable extension algorithm. In the present work, we follow Fernández-Varea et al.[4], and adopt an extension algorithm that combines an analytical approximation to the one-electron DCS of the free-electron gas, the "two-modes model", for excitations of valence and conduction electrons with the "delta-oscillator model" for excitations of inner shells.

We have developed a generic MC program that performs detailed MC simulations of electrons in a homogeneous specimen of a given thickness. The structure of the program and the adopted sampling methods are similar to those of the program LEEPS [8]. However, the considered interactions models are more flexible, and faster and more robust algorithms are used. This program allows the simulation of electron transport in solids of arbitrary composition in a wide range, from about 0.1 keV to about 500 keV. In Section 3.2 we give an overview of the considered interaction models and sampling methods. The information and models utilized to assemble the OOS of a material are described in Section 3.3. Section 3.4 gives a brief description of our MC simulation code. Results from simulations of electron backscattering and transmission are compared to available experimental data from various sources in Section 3.5, where we also analyze the effects of the beam energy and the foil thickness on the signal to background and signal to noise ratios in electron-energy-loss (EEL) spectra. Finally some concluding remarks are made in Section 3.6.

## **3.2. Interaction models**

In the energy range of interest, the dominant interactions of electrons in solids are elastic collisions and inelastic interactions. Bremsstrahlung emission, which has a continuous energy-loss spectrum and contributes less than  $\sim 1.5$  % to the stopping power of 500 keV electrons, will be disregarded. Elastic collisions

may cause relatively large deflections of the electron trajectories, with negligible energy loss. Inelastic interactions induce electronic excitations of the medium, and involve both a loss of energy and a deflection of the projectile electron.

To cover the energy range of interest, we must use relativistic kinematics. We recall that the kinetic energy E and the momentum p of an electron are related by

$$(cp)^2 = E(E + 2m_e c^2),$$
 (3-1)

where  $m_e$  is the electron mass and c is the speed of light in vacuum. Moreover,

$$E = (\gamma - 1)m_e c^2$$
 and  $\mathbf{p} = \beta \gamma m_e c \hat{\mathbf{v}}$ , (3-2)

where

$$\beta = \frac{v}{c} = \sqrt{\frac{E(E + 2m_e c^2)}{(E + m_e c^2)^2}}$$
(3-3)

is the velocity v of the electron in units of c, and

$$\gamma = \sqrt{\frac{1}{1 - \beta^2}} = \frac{E + m_e c^2}{m_e c^2}$$
(3-4)

is the total energy in units of the electron rest energy.

#### 3.2.1. Elastic scattering

Elastic events are characterized by a DCS depending only on the cosine of the polar scattering angle  $\theta$ ,  $d\sigma_{\rm el}/d(\cos\theta)$ . The DCSs adopted in the simulations were generated by using the computer program ELSEPA [9, 10]. This program computes elastic DCSs by the relativistic (Dirac) partial-wave expansion method, which accounts for spin and relativistic effects in a consistent way [11]. In its default mode, the scattering potential considered in ELSEPA is the sum the electrostatic potential of the neutral atom (with the electron density obtained from Dirac-Hartree-Fock self-consistent atomic structure calculations) and the local exchange potential of Furness and MacCarthy [12]. ELSEPA allows slightly more elaborated potential models, which include a polarization term (accounting for the effect of the atomic dipole polarizability) and an absorptive complex potential (which accounts for the depopulation of the elastic channel due to inelastic collisions). Moreover, the effect of atomic aggregation can be accounted for approximately by using a muffin-tin model potential [9].

The DCSs adopted in the simulations were generated using the ELSEPA default (static plus exchange) potential. In the case of scattering by neutral free atoms, this approach yields DCSs in good agreement with available experimental data for electrons with kinetic energy E higher than about 1 keV [11, 13]. In the case of compounds and mixtures, the "molecular" DCS is obtained as the incoherent sum of the DCSs of the atoms in a molecule. That is, we disregard aggregation effects and coherent scattering effects, which are expected to be negligible for electrons with energies larger than about 1 keV.

Our simulation program reads a table of DCSs for a dense logarithmic grid of energies E, with 15 points per decade, and a non-uniform grid of 606 polar scattering angles. The DCS for arbitrary energies is calculated by natural cubic spline interpolation, in both E and  $\theta$ , of the input table. The quantities employed in the simulation of elastic events are the mean free path,  $\lambda_{el}$ , and the probability distribution function,  $p(\cos \theta)$ , of the angular deflection in each event. The mean free path is given by

$$\lambda_{\rm el} = \frac{1}{\mathcal{N}\sigma_{\rm el}}\,,\tag{3-5}$$

where  $\mathcal{N}$  is the number of molecules per unit volume and

$$\sigma_{\rm el} = \int_{-1}^{1} \frac{\mathrm{d}\sigma_{\rm el}}{\mathrm{d}\cos\theta} \,\mathrm{d}(\cos\theta) \tag{3-6}$$

is the total elastic cross section. The angular distribution is

$$p_{\rm el}(\cos\theta) = \frac{1}{\sigma_{\rm el}} \frac{d\sigma_{\rm el}}{d\cos\theta}$$
(3-7)

The random sampling of  $cos(\theta)$  is performed by using the RITA algorithm (rational inverse transform with aliasing, see Ref. [14]), which combines an adaptive rational interpolation of the inverse cumulative function with Walker's aliasing method. This sampling algorithm is extremely fast and accurate; interpolation errors are less than about  $10^{-4}$ , and are usually masked by statistical uncertainties. An initialization routine precalculates tables of sampling parameters for a dense logarithmic grid of energies  $E_i$ , which are stored in memory. In principle, the angular distribution at the current energy E is obtained by linear interpolation in  $\ln(E)$ . That is, if  $E_i \leq E < E_{i+1}$ , we set

$$p_{\rm el}(E;\cos\theta) = \pi_i \, p_{\rm el}(E_i;\cos\theta) + \pi_{i+1} \, p_{\rm el}(E_{i+1};\cos\theta) \tag{3-8a}$$

with

$$\pi_i = \frac{\ln E_{i+1} - \ln E}{\ln E_{i+1} - \ln E_i} \quad \text{and} \quad \pi_{i+1} = \frac{\ln E - \ln E_i}{\ln E_{i+1} - \ln E_i}.$$
(3-8b)

However, there is no need of actually performing the interpolation, because we can sample  $cos(\theta)$  only for the energies  $E_i$  of the grid. The trick is to regard the interpolated distribution as an statistical mixture of the distributions at  $E_i$  and  $E_{i+1}$ , with interpolation weights  $\pi_i$  and  $\pi_{i+1}$ , which are positive and add to unity. Consequently, the random sampling of  $cos(\theta)$  can be performed by using the composition method, as follows: 1) sample a random index k, which can take the values i or i + 1 with point probabilities  $\pi_i$  and  $\pi_{i+1}$ , and 2) sample  $cos(\theta)$  from the distribution  $p_{el}(E_k; \cos \theta)$  by using the RITA algorithm.

## **3.2.2. Inelastic scattering**

As inelastic interactions play a central role in the determination of EEL spectra, the DCSs utilized in the simulations will be presented in some detail. For electrons with kinetic energy less than about 500 keV we can use a semi-relativistic form of the plane-wave (first) Born approximation [8]. Since we are mostly interested on the effect of inelastic interactions on the projectile, we consider the doubly-differential cross section (DDCS) depending on the energy transfer W and the polar scattering angle  $\theta$ . Each interaction alters the energy E and the momentum  $\mathbf{p}$  of the projectile; the corresponding values after the interaction are

$$E' = E - W$$
 and  $\mathbf{p}' = \mathbf{p} - \mathbf{q}$ , (3-9)

where q is the momentum transfer. Note that

$$p' = c^{-1}\sqrt{(E - W)(E - W + 2m_e c^2)}$$
(3-10)

and

$$q^2 = p^2 + p'^2 - 2pp'\cos\theta.$$
(3-11)

Instead of the scattering angle, it is more convenient to express the DDCS in terms of the recoil energy Q defined by [5, 15]

$$Q(Q+2m_ec^2) = (cq)^2.$$
(3-12)

The DDCS derived from the Born approximation can be expressed as [16]

$$\frac{d\sigma_{\rm in}^2}{dQ\,dW} = \frac{2\pi e^4}{m_e v^2} \frac{1}{WQ} \frac{df(Q,W)}{dW},$$
(3-13)

where e is the electron charge, v is the velocity of the projectile, and df(Q,W)/dW is the generalized oscillator strength (GOS). This DCS has the form

of the non-relativistic DCS [16]; the main relativistic effects are accounted for through the use of the relativistic velocity,  $v = \beta c$  in equation (3-13), and of relativistic kinematics. It should be noted that equation (3-13) accounts only for the instantaneous Coulomb interaction, the so-called longitudinal interaction. We are disregarding the contribution from the transverse interactions (exchange of virtual photons between the projectile and the electrons in the medium), which has a small effect for electrons with energies less than about 500 keV, and can be neglected for the purposes of the present study.

In the optical limit  $(Q \rightarrow 0)$ , the GOS reduces to the optical oscillator strength (OOS), df(W)/dW, which is proportional to the photoelectric cross section of photons of energy W, calculated within the dipole approximation,

$$\frac{df(W)}{dW} \equiv \frac{df(Q,W)}{dW} = \frac{m_e c}{2\pi^2 e^2 \hbar} \,\sigma_{\rm ph}(W)\,. \tag{3-14}$$

The GOS satisfies the Bethe sum rule [16]

$$\int_0^\infty \frac{df(Q,W)}{dW} \, dW = Z_{\rm m} \qquad \forall Q, \tag{3-15}$$

where  $Z_{\rm m}$  is the total number of electrons in a molecule.

For a given energy loss W, the allowed values of the recoil energy lie in the interval  $(Q_-, Q_+)$ , with endpoints given by equations (3-11) and (3-12) with  $\cos \theta = +1$  and -1, respectively. That is,

$$Q_{\pm} = \sqrt{\left[c(p \pm p')\right]^2 + m_e^2 c^4} - m_e c^2.$$
(3-16)

When  $W \ll E$ , the lowest allowed recoil energy can be calculated from the approximate relation (see, e.g., Ref. [5])

$$Q_{-}(Q_{-} + 2m_ec^2) = W^2/\beta^2$$
(3-17)

The precise value of  $Q_+$ , which is always larger than W, is quite irrelevant, because the GOS vanishes for  $Q \gtrsim W$ . The energy-loss DCS is obtained by integrating over the kinematically allowed values of the recoil energy,

$$\frac{d\sigma_{\rm in}}{dW} \equiv \int_{Q_-}^{Q_+} \frac{d^2\sigma_{\rm in}}{dW\,dQ}\,dQ,\tag{3-18}$$

The mean free path  $\lambda_{in}$  in for inelastic collisions is

$$\lambda_{\rm in} = \frac{1}{\mathcal{N}\sigma_{\rm in}}\,,\tag{3-19}$$

where  $\mathcal{N}$  is the number of atoms or molecules per unit volume, and

$$\sigma_{\rm in} = \int_0^{W_{\rm max}} \frac{d\sigma_{\rm in}}{dW} \, dW \tag{3-20}$$

is the total cross section for inelastic interactions. The quantity  $W_{max}$  is the maximum energy loss in an interaction which, considering the projectile and the active target electron as distinguishable, is equal to *E*. The stopping power, i.e., the average energy loss per unit volume, is given by

$$S_{\rm in} = \mathcal{N} \int_0^{W_{\rm max}} W \, \frac{d\sigma_{\rm in}}{dW} \, dW, \tag{3-21}$$

where the integral defines the stopping cross section.

Alternatively, the slowing down of electrons caused by inelastic interactions can be described by using the semi-classical dielectric formalism [5, 15, 17], that is, by considering the specimen as an isotropic dielectric material and by assuming a linear response to external electromagnetic fields. Under these assumptions, the medium is characterized by a complex dielectric function  $\epsilon(k, w)$ , which depends on the angular frequency  $\omega$  and the wavenumber k of electromagnetic disturbances. The passage of fast charged particle originates an induced electromagnetic field which exerts a stopping force on the projectile. The explicit calculation of this force (see, e.g., Ref. [17]) leads to an expression that is strictly equivalent to the right-hand side of equation (3-21) if one makes the identification

$$\frac{df(Q,W)}{dW} \equiv W(1+Q/m_e c^2) \frac{2Z}{\pi \Omega_p^2} \operatorname{Im}\left(\frac{-1}{\epsilon(k,\omega)}\right).$$
(3-22)

where  $\epsilon(k, w)$  is the value of the dielectric function at  $k = q/\hbar$  and  $\omega = W/\hbar$ , and  $\Omega_p$  is the plasma resonance energy of a homogeneous free-electron gas with the electron density of the medium,

$$\Omega_{\rm p} = \sqrt{4\pi \mathcal{N} Z_{\rm m} \hbar^2 e^2 / m_e}.$$
(3-23)

Note that the OOS and the optical dielectric function,  $\epsilon(\omega) \equiv \epsilon(0, \omega)$ , are related by

$$\frac{df(W)}{dW} \equiv W \frac{2Z}{\pi \Omega_{\rm p}^2} \operatorname{Im}\left(\frac{-1}{\epsilon(\omega)}\right).$$
(3-24)

The optical dielectric function determines the refractive index  $n(\omega)$  and the extinction coefficient  $\kappa(\omega)$  of the material, which are defined by the equality  $n(\omega) + i\kappa(\omega) = \sqrt{\epsilon(\omega)}$ , where the branch of the square root is the one yielding a non-negative n.

The GOS can be expressed as the sum of contributions from the various atomic electron subshells. Subshells with binding energy larger than about 75 eV are considered as inner subshells. As the orbitals of these subshells are only weakly affected by the presence of neighboring atoms, their GOSs can be approximated by those of free atoms calculated, e.g., by using self-consistent Dirac-Hartree-Fock-Slater atomic electron orbitals [18]. However, the calculation of GOS of outer subshells, with smaller binding energy, and of valence and conduction electrons is not always possible with current theoretical and computational methods, and one must rely on approximate semi-empirical models. The most elaborate GOSs available are provided by the so-called optical-data models, in which the GOS is constructed from an experimental, semi-empirical or calculated OOS, from which the GOS for Q > 0 is generated by

means of physically motivated extension algorithms, usually based on the response of a free-electron gas (FEG). Our procedure for building OOS is described in detail in Section 3.3 below.

To set a plausible extension algorithm, it is convenient to consider the GOS of a FEG, as obtained from Lindhard's dielectric function. This dielectric function is given by a closed analytical expression, and accounts for both plasmon and electron-hole excitations. The resulting GOS, however, it is too complicated for simulation purposes. To ease the calculations, Fernández-Varea et al. [19] proposed the following simple approximation to the GOS per electron of a FEG,

$$F_{\rm TM}(W_{\rm p};Q,W) = (1 - f_{\rm p}(Q))\,\delta(W - W_{\rm r}(Q)) + f_{\rm p}(Q)\,\delta(W - Q),\tag{3-25a}$$

where  $W_p$  is the plasma-resonance energy of the FEG,  $\delta(x)$  is the Dirac delta distribution,

$$f_{\rm p}(Q) = \min\left\{1, \frac{AQ^3}{W_{\rm p}^2(W_{\rm p}+Q)}\right\}, \qquad W_{\rm r}(Q) = W_{\rm p} + BQ,$$
 (3-25b)

and the parameters A and B are given by

$$A = \begin{cases} 2/3, & \text{if } w \le 0.62 \text{ eV}, \\ 0.9069 + 0.3577 w^2 - 1.565 w^3 + 1.478 w^4 - 0.4524 w^5, \\ & \text{if } w > 0.62 \text{ eV}, \end{cases}$$
(3-25c)

and

$$B = 0.2598 + (0.3532/w) \tag{3-25d}$$

with  $w = (W/eV)^{-1/3}$ . In spite of its simplicity, this approximation keeps the essential physics of Lindhard's theory. The two terms (modes) in expression (3-25a) describe, respectively, plasmon excitation and electron-hole excitations. The plasmon line is defined by the dispersion relation  $W = W_r(Q)$ , which agrees closely with Lindhard's theory at small Q, and electron-hole excitations are localized on the line W = Q of the (Q, W) plane (Bethe ridge), which corresponds

to binary collisions with free electrons at rest. While plasmon excitation occurs only for recoil energies less than a cutoff value  $Q_c$  (the lowest Q for which  $f_p(Q) = 0$ ), electron-hole excitations are possible for arbitrary energy transfers, from 0 to E. The main difference between the approximation (equation 3-25a) and the actual (Lindhard) GOS of the FEG is the neglect of the finite width of Lindhard's electron-hole continuum, i.e., the Bethe ridge is collapsed into a zerowidth resonance. The parameters A and B were determined so as to ensure that the inelastic mean free path and the stopping power calculated from the GOS (equation 3-25) practically coincide with those obtained from the Lindhard dielectric function [19].

Evidently, the GOS (equation 3-25) satisfies the Bethe sum rule (for one target electron),

$$\int_0^\infty F_{\rm TM}(W_{\rm p}; Q, W) \, dW = 1 \qquad \forall Q,$$
(3-26)

and reduces to the form  $\delta(W - W_p)$  of a sharp resonance at Q = 0. Our opticaldata model utilizes the "two-modes model" (equation 3-25) as extension algorithm for excitations of valence and conduction electrons. That is, the GOS for these excitations is approximated in the form

$$\frac{df(Q,W)}{dW} = \int_0^\infty \left[\frac{df(W')}{dW'}\right]_{\exp} F_{\rm TM}(W';Q,W) \, dW',\tag{3-27}$$

where  $[df(W)/dW]_{exp}$  is the experimental OOS. That is, the GOS is expressed as an admixture of FEGs of different plasma energies, weighted so as to reproduce the experimental OOS. Evidently, this GOS reduces to the adopted OOS at Q = 0.

The two-modes model (as well as the "exact" Lindhard GOS of the FEG) is not appropriate for modeling excitations of electrons in inner subshells. The reason is that ionization of an inner subshell occurs only when the energy transfer is larger than the corresponding binding energy, whereas the two-modes model allows arbitrarily small energy transfers. Following Fernández-Varea et al. [8], for inner-shell excitations we use a simpler extension algorithm, the so-called delta oscillator, defined by

$$F_{\delta}(W';Q,W) \equiv \delta(W-W')\Theta(W'-Q) + \delta(W-Q)\Theta(Q-W'), \qquad (3-28)$$

where  $\Theta(x)$  is the unit step function (= 1 if x < 0, = 0 otherwise). The two terms in this expression represent resonant distant interactions and binary close collisions, respectively. Note that the delta oscillator only allows energy transfers larger than the resonance energy, and satisfies the one-electron sum rule (equation 3-26).

Because we normally do not have the OOS decomposed into contributions from different inner subshells and bands, we shall use the two-modes model for W' less than a fixed switch energy  $W_s$ , and the delta oscillator for resonance energies above  $W_s$ . In the calculations we take the switch energy equal to the lowest ionization energy of electron subshells which is larger than about 75 eV, because low-Q excitations with  $W \lesssim W_s$  do have a small-Q component with plasmon-like (collective) character. That is, we set

$$\frac{\mathrm{d}f(Q,W)}{\mathrm{d}W} = \int_{0}^{W_{\mathrm{s}}} \left[ \frac{\mathrm{d}f(W')}{\mathrm{d}W'} \right]_{\mathrm{exp}} F_{\mathrm{TM}}(W';Q,W) \,\mathrm{d}W' 
+ \int_{W_{\mathrm{s}}}^{\infty} \left[ \frac{\mathrm{d}f(W')}{\mathrm{d}W'} \right]_{\mathrm{exp}} F_{\delta}(W';Q,W) \,\mathrm{d}W',$$
(3-29)

Evidently, if the OOS satisfies the Thomas-Reiche-Kuhn sum rule

$$\int_0^\infty \left[\frac{df(W)}{dW}\right]_{\exp} dW = Z_{\rm m},\tag{3-30}$$

the Bethe sum rule (equation 3-15) is automatically satisfied.

It is convenient to write the DDCS in the form

$$\frac{d\sigma_{\rm in}^2}{dQ\,dW} = \int_0^\infty \left[\frac{df(W')}{dW'}\right]_{\rm exp} \frac{d\sigma^2(W')}{dQ\,dW}\,dW' \tag{3-31}$$

with

$$\frac{d\sigma^2(W')}{dQ\,dW} = \frac{2\pi e^4}{m_e v^2} \frac{1}{WQ} F_{\text{TM},\delta}(W';Q,W) \,. \tag{3-32}$$

The latter quantity can be regarded as the DDCS for excitation of a "one-electron oscillator" with resonance energy W', represented by the GOS of either the twomodes model or the delta-oscillator, as prescribed by the adopted switch energy.

The plane-wave Born approximation does not account for exchange effects, which result from the indistinguishability of the projectile and the active target electron in the material. For low-Q excitations, these effects can be described by means of the modified Ochkur approximation [19, 20], which introduces a simple factor into the DDCS. The corrected DDCS for excitations of a one-electron oscillator with resonance energy E

$$\frac{d\sigma^2(W')}{dQ\,dW} = \frac{2\pi e^4}{m_e v^2} \frac{1}{WQ\,(1+Q/2c^2)} C_{\rm ex} \, F_{{\rm TM},\delta}(W';Q,W) \tag{3-33}$$

with

$$C_{\rm ex} = 1 + \left(\frac{Q}{E+D-W}\right)^2 - \frac{Q}{E+D-W},$$
 (3-34)

where the first term accounts for direct interactions, the second term represents exchange collisions (in which the projectile and target electrons exchange places) and the third terms results from interference of the wave functions of the two emerging electrons. The prescription (equation (3-34)) differs from the original Ochkur correction by the presence of the energy D, which is interpreted as the effective binding energy of the target electron in its initial state. This energy is set equal to the resonance energy W' for delta oscillators, and equal to zero for the two-modes model because conduction and valence electrons have null or small binding energies. We apply the Ochkur correction only to interactions with Q smaller than the onset of the Bethe ridge. These are, in the case of the two-modes model, electron-hole interactions with Q less than the plasmon cutoff  $Q_c$ , and, in the case of the delta oscillator, resonant distant interactions. For plasmon excitation, we set  $C_{\text{ex}} = 1$ , because these interactions do not involve the ejection of a secondary electron. Interactions on the Bethe ridge are represented as binary collisions with free electrons at rest. The "exact" energy-loss DCS (within the plane-wave Born approximation, and including transverse interactions) for these collisions is given by the modified Møller formula [5, 21],

$$\frac{d\sigma_{\rm M}}{dW} = \frac{2\pi e^4}{m_e v^2} \frac{1}{W^2} \left[ 1 + \left(\frac{W}{E+D-W}\right)^2 - \frac{(1-a)W}{E+D-W} + \frac{aW^2}{(E+D)^2} \right]$$
(3-35a)

where

$$a = \left(\frac{E}{E+c^2}\right)^2. \tag{3-35b}$$

We set D = W' for delta oscillators and D = 0 for the two-modes model. Accordingly, the exchange factor for interactions on the Bethe ridge is

$$C_{\rm ex} = 1 + \left(\frac{W}{E+D-W}\right)^2 - \frac{(1-a)W}{E+D-W} + \frac{aW^2}{(E+D)^2}.$$
(3-35c)

The introduction of the exchange correction requires the redefinition of the maximum allowed energy loss  $W_{max}$ . Because of the indistinguishability of the projectile and the struck electron after the collision, we are free to consider the "primary" electron as being the fastest of the two. Since they have kinetic energies E - W and W - D, the maximum allowed energy loss occurs in the situation where the final energies of the two electrons are equal. That is,

$$W_{\max} = \frac{1}{2}(E+D).$$
 (3-36)

It should be noted that this does not imply neglecting interactions with larger energy transfers (where the "projectile" emerges with less energy than the stuck electron), because these interactions are represented by the second terms in expressions (3-34) and (3-35c); the final terms arise from interference between the wave functions of the two electrons and from relativistic corrections.

The advantage of using simple extension algorithms is that most of the calculations, including the random sampling of W and  $cos(\theta)$  in inelastic interactions, can be performed easily. Details of the numerical calculations and sampling methods are given in Ref. [5], and references therein. The simulation is simplified by considering the resonance energy of the active oscillator, W', as a random variable with the following probability distribution function,

$$p_{\rm in}(W') = \left[\frac{df(W')}{dW'}\right]_{\rm exp} \frac{\sigma_{\rm TM,\delta}(W')}{\sigma_{\rm in}}, \qquad (3-37)$$

where

$$\sigma_{\text{TM},\delta}(W') = \int_0^{W_{\text{max}}} dW \int_{Q_-}^{Q_+} dQ \, \frac{d\sigma^2(W')}{dQ \, dW} \,, \tag{3-38}$$

is the total cross section for excitations of the active oscillator. In our simulation program the cumulative distribution of W'

$$\mathcal{P}(E;W') \equiv \int_0^{W'} p_{\rm in}(W'') \, dW'', \tag{3-39}$$

is precalculated for a dense grid of energies  $E_i$  and stored in memory. The cumulative distribution for a given energy is defined by linear interpolation in  $\ln(E)$ ,

$$\mathcal{P}_{\rm in}(E;W') = \pi_i \,\mathcal{P}_{\rm in}(E_i;W') + \pi_{i+1} \,\mathcal{P}_{\rm in}(E_{i+1};W')\,. \tag{3-40}$$

With the aid of the interpolation by weight method [cf. equation (3-8)], W' is effectively sampled only for the energies  $E_i$  in the grid, by using the inverse

transform method. Finally, the values of W and Q are sampled from the (normalized) DDCS of the active oscillator using analytical formulas.

The polar deflection of the projectile is given by equations (3-11) and (3-12),

$$\cos\theta = \frac{(cp)^2 + (cp')^2 - Q(Q + 2m_ec^2)}{2c^2pp'}.$$
(3-41)

Inelastic interactions may result in the emission of secondary electrons. The initial energy of a secondary electron is equal to  $E - E_B$ , where  $E_B$  is the binding energy of the target electron in its initial level (0 for conduction electrons). Because a partition of the OOS into contributions from the various subshells is not generally available, we replace  $E_B$  by the effective binding energy D of the active oscillator, which is set equal to 0 for the two-modes model and equal to the resonance energy W' for delta oscillators. When the energy transfer is larger than D, we consider that a secondary electron is released with kinetic energy W - D. The polar angle of the initial direction of the secondary electron,  $\theta_r$ , is set equal to that of the momentum transfer q. Squaring the identity  $\mathbf{p}' = \mathbf{p} - \mathbf{q}$  we obtain

$$\cos \theta_{\mathbf{r}} = \frac{p^2 + q^2 - p'^2}{2pq}$$
$$= \frac{E(E + 2m_e c^2) + Q(Q + 2m_e c^2) - (E - W)(E - W + 2m_e c^2)}{2\sqrt{E(E + 2m_e c^2)} Q(Q + 2m_e c^2)}$$
(3-42)

# 3.3. Building the OOS

Traditionally, the OOSs employed in optical-data models were obtained by combining available experimental optical information (refractive index, extinction coefficient) on the material with inner-shell photoelectric cross sections of free atoms. The most authoritative source of measured optical information are the three volumes of the Handbook of Optical Constants of Solids [22, 23, 24], which provide optical dielectric functions for photon energies in the long-wavelength

range, up to some keV, for metals, semiconductors and insulators. Subshell photoelectric cross sections, calculated from the independent-electron approximation, with the Dirac-Hartree-Fock-Slater self- consistent potentials, are available from various databases and publications [14, 25, 26, 27]. The OOSs of the materials Be, Al, Si, Cu, and Au employed in the present simulations were generated in this way.

While for energy transfers larger than about 100 eV, the OOS can be reasonable approximated from X-ray photoelectric data, experimental optical information available for lower energy transfers is quite scarce and for a limited number of materials. Moreover, experimental OOSs are typically inferred from a variety of measured data, acquired from different specimens, using different techniques and instruments, and affected by different sources of uncertainty (see, e.g., Ref. [22]). When accurate optical functions are not available, dielectric functions can be calculated numerically with modern density functional theory codes. Additionally, OOSs can be derived from electron energy-loss measurements.

# **3.3.1. OOS from density-functional theory**

The OOS of simple solids between the infrared and soft X-ray frequencies can be calculated by using the method described by Werner et al. [28]. The program optic of Ambrosch-Draxl and Sofo [29] calculates dielectric functions within the random-phase approximation from electronic wave functions computed by the wien2k code [30, 31], which solves the Kohn-Sham equations by using the linearized augmented plane-wave method. We have used this approach to compute the low-energy OOS of P and NiO employed in our simulations. In the wien2k calculation for P we used the exchange-correlation potential given by the generalized gradient approximation of Perdew et al. [32]. In the case of NiO, which exhibits a strongly correlated behavior [33], we used the modified Becke-

Johnson exchange potential [33, 34] and local density approximation as the correlation potential. Modified Becke-Johnson exchange potential provides a more accurate description of the band gap in semiconductors and strongly correlated systems [33].

### 3.3.2. OOS from EEL spectra

The OOS can also be inferred from EEL spectra measurements on thin specimens where single-scattering prevails, i.e., specimens with thickness t much smaller than the mean free path  $\lambda_{in}$  in which, for energies higher than 100 keV, is larger than about 100 nm (see, e.g. Ref. [5]). The collected spectrum corresponds to electrons that have undergone inelastic interactions with scattering angle less than the effective collection semi-angle  $\theta_{max}$  of the experimental setup. Typically,  $\theta_{max}$  is small (a few degrees) and the initial kinetic energy is much larger than the observed energy losses. Under these circumstances ( $\theta_{max} \ll 1$ ,  $W \ll E$ ), the relevant interactions involve small recoil energies ( $Q \ll 2m_ec^2$ ) in the interval between the kinematical minimum (for  $\theta = 0$ ),

$$Q_{-} \simeq \frac{(p-p')^2}{2m_e},$$
 (3-43)

and the value  $Q(\theta_{\max})$  corresponding to the maximum deflection of the detected electrons,

$$Q(\theta_{\max}) \simeq \frac{(p-p')^2}{2m_e} + \frac{pp'}{m_e} (1 - \cos\theta_{\max}) \simeq Q_- + \frac{E(E+2m_ec^2)}{m_ec^2} 2\sin^2(\theta_{\max}/2).$$
(3-44)

The measured energy-loss spectrum is then given by

$$I(W) = I_0 \mathcal{E}_{\mathrm{d}} t \mathcal{N} \left[ \frac{d\sigma}{dW} \right]_{\theta < \theta_{\mathrm{max}}}, \qquad (3-45)$$

where  $I_0$  is the number of incident electrons,  $\mathcal{E}_d$  is the efficiency of the detector, and the last factor is the restricted energy-loss DCS,

$$\left[\frac{d\sigma}{dW}\right]_{\theta<\theta_{\max}} = \int_{Q_-}^{Q(\theta_{\max})} \frac{d^2\sigma}{dQdW} \, dQ \simeq \frac{2\pi e^4}{m_e v^2} \frac{1}{W} \frac{df(W)}{dW} \ln\left[\frac{Q(\theta_{\max})}{Q_-}\right].$$

Introducing the approximation [see equation (3-17)],

$$Q_{-} \simeq \frac{W^2}{2m_e c^2 \beta^2},$$

we have

$$\left[\frac{d\sigma}{dW}\right]_{\theta<\theta_{\max}} \simeq \frac{2\pi e^4}{m_e v^2} \frac{1}{W} \frac{df(W)}{dW} \ln\left[1 + \left(\frac{E+2m_e c^2}{E+m_e c^2} \frac{2E}{W}\right)^2 \sin^2(\theta_{\max}/2)\right], \quad (3-46)$$

This result shows explicitly that the small-angle energy spectrum is determined primarily by the OOS, i.e., it is essentially independent of the adopted extension algorithms. The OOS can thus be derived from the EEL spectrum, except possibly an instrumental constant which may eventually be obtained by invoking the Bethe sum rule.

# 3.4. Monte Carlo simulation

The input information for simulation in a given material reduces to the table of elastic DCSs generated by ELSEPA and a table of values of the OOS covering the relevant range of excitation energies. The energies of the OOS table are sufficiently spaced to ensure that log-log linear interpolation of the OOS does not introduce any significant distortions. The OOS used in our simulations were built by combining experimental optical data or results from density-functional theory calculations with X-ray photoelectric data. The only additional parameter is the switch energy,  $(W_s)$ , which determines the interval where each extension algorithm (two-modes model or delta oscillator) applies.

The generation of random electron trajectories is performed by the conventional detailed (event by event) simulation method. The DCSs, and other relevant quantities derived from them, depend on the kinetic energy E of the transported electron. The total cross section is

$$\sigma_{\rm T} = \sigma_{\rm el} + \sigma_{\rm in} \,, \tag{3-47}$$

The total mean free path, defined by

$$\lambda_{\rm T} = \left(\mathcal{N}\sigma_{\rm T}\right)^{-1}\,,\tag{3-48}$$

gives the interaction probability per unit path length. The probability density of the path length s to the next interaction is

$$p(s) = \frac{1}{\lambda_{\rm T}} \exp(-s/\lambda_{\rm T}). \tag{3-49}$$

Consider an electron starting its motion from a point  $\mathbf{r}$  with energy E and direction specified by the unit vector  $\hat{\mathbf{d}}$ . The length s of the free flight to the next interaction is generated using the sampling formula

$$s = -\lambda_{\rm T} \ln(\xi), \tag{3-50}$$

where  $\xi$  is a random number uniformly distributed between 0 and 1. The electron is moved to its new position,  $\mathbf{r} + s\hat{\mathbf{d}}$ . The kind of interaction, elastic or inelastic, that occurs there is selected randomly according to the respective point probabilities,  $p_{\text{el}} = \sigma_{\text{el}}/\sigma_{\text{T}}$  and  $p_{\text{in}} = \sigma_{\text{in}}/\sigma_{\text{T}}$ . If the interaction is elastic, the polar deflection  $\cos \theta$  is sampled from the probability distribution (equation 3-7) using the numerical algorithms described in Section 3.2.1. If the interaction is inelastic, random values of the energy loss W and the angular deflection  $\cos \theta$  are generated by using the strategy sketched in Section 3.2.2. In both cases, the azimuthal scattering angle  $\phi$  is sampled uniformly in the interval  $(0, \pi)$ . The values  $\cos \theta$  and  $\phi$  determine the direction  $\hat{\mathbf{d}}$  of the electron after the interaction. In inelastic events the energy of the electron is reduced and, when a secondary electron is released, its initial position, direction and energy are stored in memory. The simulation proceeds by iterating these operations, until the electron leaves the specimen or its energy becomes smaller than a selected absorption (cutoff) energy. After completing the trajectory of an electron, the program loads the last electron in the secondary stack and tracks it. The simulation of the shower induced by a primary electron ends when the stack is empty.

## 3.5. Results and Discussions

The simulation results presented below were generated from independent runs of our MC code. Transported electrons were assumed to be absorbed in the material when their kinetic energy became less than 50 eV. The number of simulated electron showers in each run was larger than 1 million, so that the statistical uncertainties of the results are generally less than one percent, and the corresponding error bars are less than the size of symbols in the plots.

### 3.5.1. Backscattered and transmitted fractions

Figure 3-1 displays backscattering coefficients,  $\eta_B$ , of electron beams impinging normally on thick specimens of Be, Al, Cu and Au, with energies from 0.1 keV to 400 keV. Simulation results are seen to be in reasonable agreement with experimental data from the database compiled by Joy [35]. Unfortunately, experimental uncertainties are quite large, as revealed by the spread of data from different authors.



Figure 3-1. Backscattering coefficient  $\eta_B$  of electron beams impinging normally on thick specimens of Be, Al, Cu and Au, as a function of the beam energy. Dashed lines represent results from present MC simulations; symbols are experimental data from the database compiled by Joy [35].



Figure 3-1. Continued

Figure 3-2 illustrates the dependence of the backscattering coefficient on the atomic number Z of the specimen, for electron beams of 5 keV and 41 keV at normal incidence. Simulation results are seen to be in close agreement with experimental measurements by Hunger and Kuchler [36]. The increase of the backscattering coefficient with Z results from the prevalence of elastic scattering against inelastic interactions.



Figure 3-2. Variation of the backscattering coefficient with the atomic number for electron beams with initial energies of  $E_0 = 5$  and 41 keV impinging normally on elemental samples. The lines are results from present simulations. Symbols represent experimental data from [36].

Backscattering and transmission coefficients of electron beams of various energies impinging normally on thin films of Al and Au are displayed in figure 3-3 as functions of the film thickness. Results from our simulations are compared with data measured by Reimer and Seidel [37]. Agreement between simulated and measured transmission coefficients is satisfactory. However, simulated backscattering coefficients are systematically lower than measurements. This difference is partially due to the retarding electric fields in the experimental arrangement, which cause low-energy transmitted electrons to be deflected back and cross the film.



Figure 3-3. Backscattering and transmission coefficients,  $\eta_B$  and  $\eta_T$  of electron beams with energy  $E_0$  impinging normally on Al and Au thin films, as functions of the film thickness. Lines are results from present simulations. Symbols represent the experimental data from Ref. [37].  $\Box$ ,  $E_0 = 9.3 \text{ keV}; \circ, E_0 = 17.3 \text{ keV}; \Delta, E_0 = 25.2 \text{ keV}; \triangleright, E_0 = 41.5 \text{ keV}; \delta, E_0 = 102 \text{ keV}.$ 



Figure 3-3. Continued.

 $\eta_B$  can be assumed as a function of  $\eta_T$  by  $\eta_B = a\eta_T^b + c$ . Since  $\lim_{\eta_T \to 0} \eta_B = \eta_{B,max}$  and  $\lim_{\eta_T \to 1} \eta_B = 0$ , it can be concluded that  $c = -a = \eta_{B,max}$ . Hence, the relation between  $\eta_B$  and  $\eta_T$  can be simplified as:

$$\eta_B/\eta_{B,max} = (1 - \eta_T^b) \tag{3-51}$$

where  $\eta_{B,max}$  is the maximum  $\eta_B$  at the range of beam energies. Therefore by calculation of the constants *b* and  $\eta_{B,max}$  for a thin solid film,  $\eta_B$  can be obtained

just by having  $\eta_T$ . Figure 3-4 presents  $\eta_B$  as a function of  $\eta_T$  based on the results of MC simulations for Al and Au at different beam energies and thicknesses as illustrated in figure 3-3. The fitted values of constants *a*, *b*, and *c* are depicted in figure 3-4. As it can be seen for both Al and Au, the absolute values of *a* and *c* are approximately equal confirming the applicability of equation (3-51).



Figure 3-4. Transmission coefficient,  $\eta_T$ , versus backscattering coefficient,  $\eta_B$ , of electron beams at different energies impinging normally on Al and Au thin films. Lines are results of data interpolation and symbols represent the results of MC simulations as represented in figure 3-3.

In addition, the variation of  $\eta_B$  versus  $\eta_T$  in figure 3-4 can be explained by the fact that the range of backscattered electrons is about 1/3 of the total range of internal electrons. So, the backscattering coefficient saturates at a smaller thickness than the thickness for transmission coefficient.

Figure 3-5 shows the variation of the backscattering and transmission coefficients with the angle of incidence of 30-keV-electron beams in thin films of Al and Au. Our simulation results agree closely with experimental measurements by Neubert and Rogaschewski [38].



Figure 3-5. Backscattering and transmission coefficients of 30 keV electron beams impinging on thin Al and Au films as functions of the angle of incidence. Solid lines are results from the present simulations, symbols represent experimental data from Neubert and Rogaschewski [38]. The numerals at the end of each data set indicates the film thickness in  $\mu g/cm^2$ .



Figure 3-5. Continued.

# 3.5.2. Energy and angular distributions

Let us now analyze the energy and angular distributions of transmitted electrons. In figure 3-6 we compare energy distributions of electrons, with initial energies  $E_0 = 15$  keV and 20 keV and at normal incidence, transmitted through Al films of various thicknesses. Our simulation results are seen to be in reasonable agreement with measurements in Refs. [39, 40]. Because of the increase in the

number of inelastic events, when the film thickness increases the probability of high energy transmitted electrons decreases and the maximum value of  $d\eta_T/d(E/E_0)$  shifts towards lower values of  $E/E_0$ .



Figure 3-6. Energy distributions of electrons from beams with initial energies of  $E_0 = 15$  and 20 keV at normal incidence transmitted through Al films of various thicknesses. Continuous lines are results from our MC simulations and dashed lines represent experimental data from Refs. [39, 40].

Figure 3-7 shows simulated angular distributions  $2\pi sin(\theta)N(\theta)$  (i.e., probability per unit deflection angle) for electrons transmitted through Au thin films from beams of 5 and 20 keV at normal incidence. When film thickness increases, the most probable angle increases and the distribution becomes more symmetrical. This trend is in agreement with measurements by Cosslett and Thomas [41]. This feature is demonstrated in figure 3-8 where we compare the most probable deflection angles,  $\theta_m$ , for electrons transmitted through thin films of Al, Cu and Au obtained from our simulations with experimental data of Cosslett and Thomas [41]. It is seen that the saturation value of  $\theta_m$  is quite independent of the atomic number.



Figure 3-7. Simulated angular distribution of electrons transmitted through Au films of the indicated thicknesses, for beams with initial energies of 5 and 20 keV and normal incidence.



Figure 3-8. Most probable deflection angle  $\theta_m$  of electrons energies transmitted through films of Al (>), Cu ( $\circ$ ) and Au ( $\Box$ ), for different beam energies, as a function of the film thickness t. The lines are results from the present simulations (solid, dash and dash-dot lines are for Al, Cu and Au, respectively); symbols represent experimental data from Ref. [41].



Figure 3-9. Depth-dose distribution of electron beams at normal incidence and with the indicated energies in Si. Continuous lines represent results from the present simulations. Symbols are experimental data from Ref. [42].

The depth-dose distribution (i.e., deposited energy per unit depth) results from the combined effect of elastic scattering and energy loss. It therefore represents a demanding test to the interaction models adopted in simulation. Figure 3-9 compares normalized depth-dose distributions measured by Werner et al [42] for electrons of various energies in Si, at normal incidence, with results from our simulations. A good agreement between our MC simulation results and the experimental measurements can be seen.

#### 3.5.3. Electron energy-loss spectra

We now turn to the simulation of electron energy-loss (EEL) spectra. Specifically, we consider a converging beam with probe-illumination angle of 2 mrad centered on the normal to the target, and simulate the energy distribution of electrons that are transmitted with deflections less than the collection angle of the detector, which we set equal to 10 mrad. Figure 3-10 displays simulated EEL spectra of 200 keV electrons in Al and P films of different thicknesses. All the EEL spectra are normalized to one incident electron. The spectra clearly show the occurrence of multiple plasmon excitations, as well as ionizations of the  $L_3$  subshell. Both the number of plasmon excitations and the intensity of the background increase with the foil thickness.



Figure 3-10. Simulated EEL spectra for 200 keV electrons in a) Al and b) P films of the indicated thickness. The scale of the vertical axis is logarithmic.

Figure 3-11 shows the signal (peak) to background ratio (SBR) of the L<sub>3</sub> ionization edge for Al, Si and P for various beam energies as a function of the film thickness in units of the mean free path for inelastic collisions. As the film thickness increases, the SBR decreases, because low-energy excitations are much more probable than high-energy excitations. This can be explained by the fact that the inelastic differential cross section at low-energy loss excitations has a higher probability in comparison to the high-energy energy loss excitations of the ionization edges. The nearly exponential decrease of the SBR with  $t/\lambda_{in}$  is in agreement with the theoretical analysis by Leapman [43].



Figure 3-11. Simulated signal-to-background ratio (SBR) of the L<sub>3</sub> edge for a) Al, b) Si, and c) P at different beam energies as a function of film thickness.



Figure 3-12. Simulated signal-to-noise ratio (SNR) of the  $L_3$  edge for a) Al, b) Si, and c) P at different beam energies as a function of film thickness.

Another quantity of interest is the signal-to-noise ratio (SNR), defined by [44]:

$$SNR = \frac{I_E - I_B}{\sqrt{I_B}} \tag{3-52}$$

where  $I_E$  and  $I_B$  are, respectively, the signal and background intensities at the ionization edge. Figure 3-12 shows the SNR at the L<sub>3</sub> edge of Al, Si, and P, for various beam energies as a function of film thickness. The definition of the SNR in equation (3-52) is based on the assumption of Poisson counting statistics [44]. The SNR-vs.-thickness curves present a broad maximum, corresponding to the optimal thickness  $t_m$  for recording the EEL spectrum. For thicker films, the background intensity increases, and the edge signal becomes weaker [45].



Figure 3-13. Optimum thickness as a function of the beam energy, calculated from the Leapman formula, equation (3-54), for Al and Si.

The results in figure 3-12 indicate that the reduced optimum thickness,  $t_m/\lambda_{in}$  in , stays essentially constant with the beam energy. This implies that, given the optimum thickness  $t_m(E_1)$  at a certain energy  $E_1$ , the simple formula
$$t_m(E_2) \simeq t_m(E_1) \frac{\lambda_{in}(E_2)}{\lambda_{in}(E_1)} , \qquad (3-53)$$

can be used to estimate the optimum thickness for any other energy. The values from this formula do not differ much the approximation suggested by Leapman [43],

$$t_m = \frac{\lambda_{in}\lambda_e}{2\lambda_{in} + \lambda_e} , \qquad (3-54)$$

Figure 3-13 shows the  $t_m$  values predicted by this formula, with the mean free paths corresponding to the interaction models used in the simulations, for Al and Si and energies between 50 keV and 300 keV. Indeed, the values so obtained agree with those inferred from simulation (see figure 3-12).



Figure 3-14. Simulated EEL spectra of NiO from films with the indicated thicknesses, and SBRs for the O K and Ni L edges as functions of the film thickness t. Experimental data are from Huber et al [46]. The scale of the vertical axis for simulated EEL spectra of NiO is logarithmic.

Finally, figure 3-14 displays the results from simulations of EEL spectra of 200 keV electrons in NiO and the corresponding SBRs for the O K edge and Ni L edge, for various film thicknesses. The probe illumination and collection angles used in the simulations were 9 and 18 mrad, respectively. Calculated SBRs are in

close agreement with values derived (from spectral areas) from measurements by Huber et al [46].

#### **3.6.** Conclusions

We have presented a generic MC algorithm for detailed simulation of electron transport in bulk specimens and foils. The adopted interaction models can be adapted to describe electron transport in arbitrary materials. The DCSs for elastic scattering were calculated using the relativistic partial-wave code ELSEPA [9], which allows considering different scattering potentials. The OOS, which completely determines the DCS for inelastic collision, can be assembled by combining atomic photo absorption cross sections with low-energy optical oscillator strengths obtained either from experimental optical data or from density-functional theory calculations. Comparison of simulation results with a variety of experimental measurements shows that our MC code provides a realistic description of the penetration and energy loss of electrons in solids, within the considered energy range. As an application, we have considered the practical use of the code in EEL spectroscopy.

#### 3.7. Acknowledgements

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# 3.8. References

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# Chapter 4. Monte Carlo simulations of the fine structures of the electron energy-loss spectra

In the previous chapter, the accuracy of the applied optical data model in Monte Carlo simulations for the calculations associated with the electron transportation and the electron energy loss was verified. Also, it was described that optical oscillator strength (OOS) of the ionization edges are built using the X-ray photoelectric data. However, the X-ray photoelectric data does not contain the fine structure of core-loss excitations. Hence in this chapter, the fine structure of electron energy-loss near edge structure (ELNES) obtained by density functional theory calculations is introduced to the OOS. Using the new OOS, effect of beam energy and thickness of specimens on the ELNES of various ionization edges are studied by Monte Carlo simulations. In addition, effect of the fitting range for the background removal from ionization edges and the integration range under the edges were investigated to obtain the maximum signal-to-noise ratio. This chapter –with the same title- and co-authored by Maxime J.-F. Guinel, Majid Ahmadi and Raynald Gauvin has been submitted to Ultramicroscopy.

#### Abstract

A new approach is suggested to introduce the fine structure of core-loss excitations into the electron energy loss spectra of ionization edges by MC simulations based on an optical oscillator model. The optical oscillator strength is refined using the calculated electron energy-loss near-edge structure (ELNES) by density functional theory calculations. The suggested approach can predict effect of multiple scattering and thickness on the fine structure of ionization edges. In addition, the effects of the fitting range for the background removal and the integration range on the signal-to-noise ratio of ionization edges are investigated.

## 4.1. Introduction

Transmission electron microscopes and electron energy loss (EEL) spectrometers have seen their performances dramatically improved over the past decade and it is now possible to record spectra with a resolution approaching  $\sim$  0.1 eV [1]. Hence, the fine structures of ionization edges and electron energy-loss near-edge structure (ELNES) now can be studied with a high level of accuracy. These fine structures originate from the interaction of the incident beam of electrons with the inner shell electrons and can reveal the nature of the electronic structure of atomic bonds in materials [2]. ELNES can provide tremendous information about the chemistry such as type of the atomic coordination and the nature of the bonds [3]. However, the high intensity of the background signal (strongly dependent on the thickness of specimen) complicates greatly the qualitative and quantitative analyses. Therefore, it is important to study the effects of the background signal on the total useful amount of signal from atomic excitations for the accurate quantitative analysis in EEL spectroscopy.

Commonly, the calculations of EEL spectra are based on the first principle methods using density functional theory (DFT) calculations [2-7]. However, first principle methods put the emphasis on the simulation of the shape and the fine structure of ionization edges, not the estimation of the background signal. Various methods have been developed for the synthesis of EEL spectra [8-11]. However, it is possible to create an all-inclusive method using both DFT calculations for the shape of ELNES and Monte Carlo (MC) simulations for the synthesis of EEL spectra yielding a reasonable estimation of the background signal.

Combination of MC methods and DFT calculations can provide the important benefit of the study of the accurate shape of ELNES as well as the geometry of the specimen. DFT calculations offer the accurate prediction of the shapes of ELNES by means of suitable exchange and correlation potentials [12], whereas, MC simulations have the benefit of considering the thickness and the experimental conditions [13]. In this study, the ELNES of different edges of some selected materials are studied by combination of band structure calculations of

ELNES derived from DFT calculations and MC simulation of EEL spectra. By synthesis of EEL spectra, the effect of different parameters for the collection of EEL spectra and the background removal of the inner-shell ionization edges are studied.

#### 4.2. The model

For the reliable MC simulation of EEL spectra, accurate models for inelastic differential cross sections are essential. Optical data models have been used as effective methods for the calculation of inelastic differential cross section in MC simulations [14-20]. The main input for optical data models is the optical oscillator strength (OOS) [17]. Then, using proper extension algorithms, OOS is extended to the momentum transfer space [18]. OOS contains two parts: the first is low-loss excitations generally related to the electron interactions with the valance electrons, and the second is related to the core-loss excitations of atoms [19]. The data for the low-loss part of OOS can be obtained using existing experimental optical data or DFT calculations of energy loss function (ELF). To calculate the OOS for the ionization of core-loss excitations, generally X-ray photoelectric absorption data are used [20]. However, X-ray photoelectric absorption data does not give the fine structure of ionization edges that depends on the configuration of the various atoms in the solid. Hence, by using DFT calculations the fine structure is introduced to the OOS and the new OSSs are used for MC simulation of EEL spectra.

The shape and intensity of ionization edges in DFT calculations are determined based on the band structure calculation of double differential scattering cross-section for inelastic interaction [3]. In a band structure method based on the Born approximation, the double differential cross section for the inelastic scattering electrons of anisotropic materials can be calculated using [21]:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E}(E, \boldsymbol{q}) = \frac{4\gamma^2}{a_0^2} \frac{1}{(q^2 - q_z^2 (v/c)^2)^2} \frac{k_f}{k_i} \times \sum_{i, f} \left| \left\langle f \left| e^{i \boldsymbol{q}, \boldsymbol{r}} (1 - \frac{\boldsymbol{\vec{p}} \, \boldsymbol{\vec{v}}_{\theta}}{mc^2}) \right| i \right\rangle \right|^2 \delta(E - E_f + E_i) \quad (4-1)$$

where  $\vec{q} = \vec{k}_i - \vec{k}_f$  is the momentum transfer from initial to the final plane waves, *m* is the electron mass,  $a_0$  is the Bohr radius and  $\gamma = \sqrt{1 - (v/c)^2}$  is the relativistic factor, where *v* and *c* are the speed of electron and light respectively.  $q_z$  is defined by  $q_z = E/(v_0\hbar)$  where  $\hbar$  is the reduced Planck constant. Also,  $\vec{p}$ is the momentum operator,  $\vec{v}_0$  is the velocity of incoming electron, *E* is the energy loss,  $E_i$  and  $E_f$  are the initial and final energy of the closed system, respectively. The first Born approximation considers that both incoming and outgoing fast electrons are plane waves [4]. Using self-consistent calculations of the electron density by DFT calculations equation (4-1) can be calculated [5]. The integration is performed over the dipole region of scattering which means that the exponential part of equation (4-1) can be simplified to  $e^{iq \cdot r} \approx 1 + i q \cdot r$ .

The integration of inelastic differential cross section should be performed over the certain convergence semi-angle of beam ( $\alpha$ ) and the collection semi-angle ( $\beta$ ) as following [22]:

$$\frac{d\sigma}{dE}(E) = \int_{\alpha,\beta} dq \,\frac{\partial^2 \sigma}{\partial \Omega \partial E}(E,q) \tag{4-2}$$

where  $d\sigma / dE$  is called the energy transfer cross section [23], and it can be considered equivalent of the EEL spectra assuming the single scattering is the major inelastic contribution [17]. Equation (4-1) and equation (4-2) describe the main theory for the band structure calculations of ELNES based on the DFT calculations.

In the experimental collection of EEL spectra, if the multiple scattering is insignificant, the energy transfer cross section can be considered proportional to the single scattering intensity of the inner-shell edge  $(J_k(\beta, \Delta))$  [1]:

$$J_k(\beta, \Delta) = N I_0 \frac{d\sigma}{dE}$$
(4-3)

where  $I_0$  is the total zero loss intensity and N is the number of atoms per unit of volume. Here,  $\Delta$  indicates the integration range from the start of ionization

energy of edge ( $E_c$ ). By the integration over certain range of energy in equation (4-2) and equation (4-3), the inelastic cross section can be calculated over the specified collection semi-angle and integration window ( $\Delta$ ):

$$\sigma_k(\beta, \Delta) = \int_{E_k}^{E_k + \Delta} \frac{d\sigma}{dE} dE$$
(4-4)

 $\sigma_k(\beta, \Delta)$  is the partial cross section of inner-shell ionization edge [24] and can be used for the quantitative analysis. For the  $\beta$  smaller than the Bethe ridge angle (  $\theta_r \approx (E/E_0)^{1/2}$ , where  $E_0$  is the beam energy [25]) and for a sufficiently large integration window,  $\sigma_k(\beta, \Delta)$  was calculated by Egerton [24] as:

$$\sigma_k(\beta) \cong 4\pi a_0^2 (R/T) (R/\overline{E}) f_k \ln\left[1 + (\beta/\overline{\theta})^2\right]$$
(4-5)

where *R* is the Rydberg energy  $(R = \hbar^2 / (2m_0a_0^2)), T = m_0v^2/2$  is the effective incident energy  $f_k$  is the dipole oscillator strength of the inner-shell and  $\overline{\theta} = \overline{E} / (2\gamma T)$ .  $\overline{E}$  is calculated using [1]:

$$\overline{E} = \int_{0}^{E_{0}} E\left(\frac{d\sigma}{dE}\right) dE / \int_{0}^{E_{0}} \left(\frac{d\sigma}{dE}\right) dE$$
(4-6)

Equation (4-5) is based on the scattering in the dipole region i.e.  $(qa_0) < 1$  [1]; hence, the range of validity of equation should be considered. Based on equation (4-5), the dipole oscillator strength and inelastic cross section of inner-shell ionization edge are proportional. Hence, the partial inelastic cross section can be considered proportional to the optical oscillator strength i.e.  $d\sigma / dE \propto df_k / dE$ .

Generally, to build OOS the data from low-loss and high-loss regions are combined. For the core-loss excitation, the X-ray photoelectric absorption cross sections data ( $\sigma_{ph}$ ) are calculated by [20, 26]:

$$\frac{df}{dE} = \frac{mc}{2\pi^2 e^2 \hbar} \sigma_{ph}(E) \tag{4-7}$$

Equation (4-7) is generally valid for energies approximately bigger than 100 eV [20]; hence the limitations of this approach and its accuracy should be considered. However, X-ray photoelectric data does not contain the fine structure of core-loss excitations. To include the fine structure from DFT calculations of EEL spectra into the OOS after building OOS using low-loss and X-ray photoelectric data, the normalization factor,  $\kappa$ , is introduced as follows:

$$\kappa = \left(\int_{E_k}^{E_k + \Delta E} \left[ d\sigma(E) / dE \right]_{\text{DFT}} \right) / \left(\int_{E_k}^{E_k + \Delta E} \left[ \left( df(E) / dE \right)_e - \left( df(E) / dE \right)_b \right]_{\text{X-ray}} dE \right)$$
(4-8)

where indexes *e* and *b* refer to the intensity from edge and from the background, respectively. Here the background in the OOS from X-ray data refers to the tails of the previous ionization edges or the OOS at energies less than  $E_k$ . For the region  $E_k$  to  $E_k + \Delta$ , the calculated EEL spectra is multiplied by the constant  $\kappa$  and is replaced into the original OOS from X-ray photoelectric data. The background is estimated by line  $(df_k / dE)_b$  and is added to the final OOS. Figure 4-1 shows the schematic illustration for the calculated EEL spectra by DFT calculations does not include the background related data and generally the intensity starts from zero, so the background removal is not necessary to be included in the numerator of equation (4-8) ( $[d\sigma(E)/dE]_{DFT}$ ).

To build OOS for the low-loss region, the relation between OOS and the energy loss function  $(\text{Im}(-1/\varepsilon(E)) \text{ can be used } [27]:$ 

$$\frac{df(E)}{dE} = \frac{2E}{\pi E_p^2} Z \operatorname{Im}(\frac{-1}{\varepsilon(E)})$$
(4-9)

where  $\varepsilon(E)$  is the dielectric function in the optical limit, and  $E_p$  is the plasmon energy. By combining OOS from DFT calculations from equation (4-9) and OOS from X-ray photoelectric cross sections [28] by equation (4-7), consecutively the fine structure of ionization edges was introduced using equation (4-8). The final OOS should obey the Bethe sum rule as given by [27]:

$$\int_0^\infty \frac{df(E)}{dE} dW = Z \tag{4-10}$$

where Z is the number of electrons per atom or molecule. Hence the total OOS will be normalized by equation (4-10).



Figure 4-1. Schematic illustration of the parameters for the of calculation of the normalization factor ( $\kappa$ ) in equation (4-8).

#### 4.3. DFT calculations of ELNES

DFT calculations were performed with full potential linear augmented plane wave (FLAPW) approach using WIEN2k code [29-31]. AlN, GaN, InN and NiO were selected to study the ELNES by MC simulations where AlN, GaN and InN are the group III semiconductors and NiO is a oxide with strongly correlated behavior [32]. Hence, proper exchange-correlation potentials for the accurate DFT calculations are essential. For the calculations, modified Becke-Johnson (mBJ) was used as exchange potential and local density approximation (LDA) as the correlation potential. The combination of modified Becke-Johnson and local density approximation is called mBJLDA. Modified Becke- Johnson potential has been developed recently for the accurate calculation of band gap in the semiconductors and insulators [33, 34]. It also has been used successfully for the strongly correlated systems such as NiO [34].

The crystal structure of AlN, GaN and InN for calculations was considered hexagonal (wurtzite structure) and for NiO the antiferromagnetic unit cell was used [32]. For AlN, GaN and InN, 10000 k-points in the first Brillouin zone corresponding to a 26x26x14 meshes in the reduced Brillouin zone and for NiO 4000 k-points equal to 15x15x15 meshes in the first Brillouin zone were used. For V<sub>2</sub>O<sub>5</sub> 2000k (equal to 6x19x16 in the first Brillouin zone) was selected. The values for the number of k-points are dependent on the type of system; however, calculations should converge by increasing the number of k-points. The value of spherical harmonic expansion has been set to 10. The calculations were considered as convergent when the charge density difference between the input and output electron density was less than 0.001e Also,  $R_{MT} \times K_{max} = 7$  is assumed, where  $R_{MT}$  is the smallest atomic sphere radius in the unit cell and  $K_{max}$  is the magnitude of the largest k vector. After running self-consistent calculations, the ELNES for different ionization edges of AlN, GaN, InN and NiO were calculated.

#### 4.4. Results and Discussion

According to the suggested approach in the model section, the fine structures were introduced into the OOS at the specific ionization edges. After having the OOS, the modified LEEPS (low-energy electron and positron simulation) code [18] was adapted to perform simulations of EEL spectra for both plasmon and inner-shell excitations. The comprehensive details of MC simulation program and the applied optical data model can be found in Ref. [35]. The number of simulated electron showers in each run was larger than one billion to reduce the statistical uncertainties of the results to less than one percent. For all the MC simulations of EEL spectra for AlN, GaN and InN, the probe illumination angle ( $\alpha$ ) and collection semi-angle ( $\beta$ ) were 5 and 10 mrad, respectively. For NiO,  $\alpha$  and  $\beta$  were set to 9 and 18 mrad, respectively. Also, for all the signal-tonoise calculations the spectrum acquisition time ( $t_a$ ) and the probe current ( $I_p$ ) were set to 1 s (second) and 0.1 nA, respectively.

The samples of NiO and V<sub>2</sub>O<sub>5</sub> were examined using a high resolution transmission electron microscope (HRTEM, JEOL JEM-2200FS, operated at 200kV and  $\beta$ =36 mrad) by placing the materials onto support transmission electron microscope (TEM) grids. EEL spectra were recorded using the *incolumn* energy filter.

Figure 4-2 shows the density of states (DOS) of AlN and NiO calculated by different exchange-correlations. Figure 4-2a shows the DOS for AlN calculated by LDA and mBJLDA methods. The band gap of AlN is about 6.13 eV [36] and LDA method predicts the band gap 4.3 eV and mBJLDA predicts its value about 5.7 eV. As it can be seen the modified Becke-Johnson exchange potential improves the prediction of band gap. Modified Becke-Johnson exchange potential in comparison to other methods has the significant advantage of accurate calculation of band gap without adjusting of any free parameter [12].

Using mBJ also improves the accuracy of calculations for NiO noticeably. Figure 4-2b presents the calculated DOS by generalized gradient approximation (GGA) [37] as well as mBJLDA method. Both LDA and GGA are very common methods for DFT calculations as exchange and correlation potentials. NiO has a band gap of 4.3 eV [38]. GGA method gives the value of bang gap energy about 0.9 eV and mBJLDA about 4.1eV. Here, again using modified Becke-Johnson exchange potential shows a clear improvement in comparison to GGA approach. The calculations of DOS and the band gap for AlN and NiO by different exchange and correlation potentials proves the importance of the proper potentials for the accuracy of the results of DFT calculations.



Figure 4-2. Density of states for a) AlN using LDA and mBJLDA and (b) DOS for NiO using GGA and mBJLDA exchange-correlation potential. In the plots the energy is above the Fermi level.



Figure 4-3. Comparison between the fine structures of a) N K and b) Al K edges in AlN form the DFT calculations and the experimental measurement from [40].

Figure 4-3 shows the ELNES for Al and N K edges in AlN. Different exchange and correlation potentials were used to simulate the shape of ELNES. For N K edge, using of just LDA without core hole does not give acceptable results. Even using mBJLDA approach without considering core-hole effect does not improve the calculated ELNES. However, using a super cell by size of 2x2x1

with a core hole improves the accuracy significantly. Because of using super-cell the number of k-points was reduced to 1000 to save the calculation time. For Al K edge the same trend as N K edge can be observed; nevertheless, it is less sensitive to adding of a core hole. Experimental data for ELNES are extracted from the EELS database [39] using the work by Serin et al [40].

Figure 4-4 shows the simulated shape of O K and Ni  $L_{2-3}$  edges by DFT calculations using mBJLDA approach for NiO. The power law was used for the background removal from the original spectrum of NiO. No core hole was considered for the DFT calculation of EEL spectra of NiO, because it does not have much effect on the shape of spectra in this case [30]. According to the study by Mauchamp et al [41], a core hole always affect any core-level spectroscopy experiment; however its effect is not always evident. For example for transition metal oxides, the core-hole effect for the O K edge is negligible because the first vacant states in the conduction band have the major role on the transition metal [41].

In figure 4-5, the experimental and DFT calculations of ELNES for V L<sub>2-3</sub> and O K edges of V<sub>2</sub>O<sub>5</sub> are compared. Because V L<sub>2-3</sub> and O K edges are very close in the EEL spectra, the edge separation should be performed. The edge deconvolution was performed using Frat program for Fourier ratio deconvolution proposed by Egerton [1]. DFT calculations of ELNES for V<sub>2</sub>O<sub>5</sub> were performed using GGA for the exchange and correlation potentials. Using GGA for V<sub>2</sub>O<sub>5</sub> had led to good agreement for the ELNES in other studies [42] and this can be related to the fact that V<sub>2</sub>O<sub>5</sub> is not a strongly correlated system nor a semiconductor. The crystal structure of V<sub>2</sub>O<sub>5</sub> is orthorhombic (P<sub>mmn</sub>); hence the anisotropy of ELNES in different directions is expected. However, Su et al [42] calculated that at the collection semi-angles more than ~10 mrads, the anisotropy of the ELNES for O K edges in V<sub>2</sub>O<sub>5</sub> will be averaged out and the ELNES is not dependent on the direction of beam to the zone axis.



Figure 4-4. Comparison between the fine structures of a) O K and b) Ni L<sub>2-3</sub> edges from the DFT calculations and the experimental measurements.



Figure 4-5. a) EEL spectra recorded from V<sub>2</sub>O<sub>5</sub> where the V L<sub>2-3</sub> and O K edges are visible. Comparison between the fine structures of b) V L<sub>2-3</sub> and c) O K edges from the DFT calculations and the experimental measurements.

Recently, Achkar et al [43, 44] suggested a method to measure the total (absolute) value of x-ray absorption coefficient using angle dependent inverse partial fluorescence yield (IPFY). Achkar et al [43] showed that the total X-ray absorption coefficient is directly proportional to the angle dependence of IPFY. Hence, they could measure the X-ray absorption coefficient with the fine structure originating from the solid states effects. Hence, the X-ray absorption

coefficient measured by Achkar et al [44] were compared with our calculated OOS using DFT calculations of ELNES in figure 4-6.

Figure 4-6 shows the comparison of our total X-ray absorption coefficient of Ni  $L_{2-3}$  in NiO with the measurements of Achkar et al [44]. Equation (4-8) can be used for the calculation of X-ray absorption coefficient since the OOS is proportional to the X-ray photoelectric data. Generally, our calculations are in agreement with the measurements and confirm the presence of the sharp peak at Ni  $L_{2-3}$ . Nevertheless, the differences between our calculations and the measurements can be seen as a consequence of the difference in the nature of methods. Also, broadening of the ELNES can change the intensity of calculated X-ray absorption coefficient which should be considered. It should be mentioned that Chantler et al's data [45] are the results of calculations for a single atom and hence the data do not include band structure effects leading to the fine structure of the ionization edges. As a result, the Chantler et al's data for the X-ray photoelectric absorption cross sections are limited to the ionization edges and the resolution cannot be defined for them similar to the experimental measurements.



Figure 4-6. Comparison of the total linear X-ray absorption coefficient (μ) of Ni L<sub>2-3</sub> in NiO by our calculations with the measurements by Achkar et al [44] and Chantler et al [45]. The measured μ by Achkar et al [44] has been scaled via a non-arbitrary scaling factor.

To investigate the accuracy of the obtained OOSs for the calculations of measurable scattering parameters, the mean free path of electrons in GaN is compared with experimental data and our calculations in figure 4-7. A good agreement between our calculations and the experimental data by Krawczyk et al. [46] and their results calculated by the predictive formula of TPP-2M by Tanamma et al [47, 48] can be observed.



Figure 4-7. Inelastic mean free path (IMFP) of incident electrons in GaN using the obtained OOS and its comparison with the experimental data [46] and the results from predictive formula of TPP-2M.

Figure 4-8 shows the effect of thickness on the simulated fine structure of O K and Ni  $L_{2-3}$  edge in NiO . As expected by increasing the thickness more background is introduced to the fine structure and the jump ratio decreases. The jump ratio is the maximum intensity to the minimum intensity at the ionization edge. As it can be seen in figure 4-8, the simulated EEL spectra using just X-ray photo-electric data does not contain any fine structure. Figure 4-9 presents the MC simulations of the fine structure of N K edge in a) AlN, b) GaN and c) InN at different thicknesses (50, 100 and 200nm). Similar to figure 4-8, the increase of background and decrease of signal to background can be observed.



Figure 4-8. MC simulations of the fine structures for the a) O K and b) Ni L<sub>2-3</sub> edges in NiO for thicknesses of 25, 75 and 150nm with  $t_a = 1$  s,  $I_p = 1$  nA and  $E_0 = 200$  keV. The scale of the vertical axis is logarithmic.

Signal-to-noise ratio (SNR) can be a good indicator for the useful amount of signal for the practical quantitative analysis of inner-shell ionization edges. Egerton [49] suggested the following equation for the calculation of SNR:

$$SNR = \frac{I_k}{(I_k + hI_b)^{1/2}}$$
(4-11)

where  $I_k$  and  $I_b$  are the core-loss and the background intensity of the ionization edges determined over a range of integration. Also, h is defined by:

$$h = \frac{I_b + \operatorname{var}(I_b)}{I_b} \tag{4-12}$$

*h* indicates the background dependency of  $I_k$  originating from the extrapolation and fitting errors [49]. Variation of noise can change var( $I_b$ ) and consequently *h*. So, the effect of noise can be considered in the calculations of SNR.

Figure 4-10 shows the schematic illustration of the different parameters used for estimating the background and edge intensity.  $\Delta$  and  $\Gamma$  are the widths of integration region and the background fitting range of the inner-shell edge, respectively. SNR can be noticeably affected by the choice of  $\Delta$  and  $\Gamma$ .



Figure 4-9. MC simulations of the fine structure for the N K edge in a) AlN, b) GaN and c) InN for different thicknesses (50, 100 and 200nm) with  $t_a=1$  s,  $I_p=1$  nA and  $E_0=200$  keV. The scale of the vertical axis is logarithmic.

Figure 4-11 shows the effects of  $\Delta$  and  $\Gamma$  on *h* and SNR for N K edge in AlN at 100 nm thickness and  $E_0 = 200$  keV using MC simulations. Increasing  $\Gamma$ decreases *h* and increases SNR at the same value of integration width, because by choosing bigger values of  $\Gamma$  a better estimation of  $I_b$  can be obtained. However, after a certain amount of  $\Gamma$ , the SNR does not change much meaning a proper estimate of background signal has been obtained. Both  $I_b$  and  $I_k$  increase by increasing  $\Delta$ ; therefore, h and SNR increase simultaneously. However, the favorable quantity that should be maximized is SNR. So,  $\Delta$  and  $\Gamma$  should be selected in a proper range to lead the highest amount of SNR. It should be mentioned that the appropriate values for  $\Delta$  and  $\Gamma$  rely on some other factors such as the existence of other ionization edges at the proximity of the edge, the initial beam energy, the thickness of specimen and collection semi-angle. MC simulations can provide a proper understanding for the effect of these parameters as a result of the their capacity to employ precise differential cross sections. Consequently, the proper optimum conditions for achievement of highest SNR can be computed.



Figure 4-10. Schematic illustration of the parameters for background removal from an ionization edge based on the concept from Ref [49].



Figure 4-11. Effect of a)  $\Gamma$  and b)  $\Delta$  on *h* and SNR for N K edge in AlN with thickness of 100nm and  $E_0=200$  keV.

Effect of thickness of specimen (*t*) and  $\Gamma$  on the signal-to-background ratio (SBR) of N K edge in AlN, GaN and InN are presented in figure 4-12 using MC simulations. SBR decreases by increasing the thickness of specimen because the background signal continuously increases. Increase of  $\Gamma$  also decreases the SBR for N K edge in AlN and GaN indicating that using big values of  $\Gamma$  increases the background ratio and can limit the amount of useful signal.



Figure 4-12. Effects of specimen's thickness (*t*) and  $\Gamma$  on the-signal-to-background ratio (SBR) for the N K edge in AlN, GaN and InN at 200 keV.  $\Delta$  was considered 45.5 eV.

Effect of the initial beam energy  $(E_0)$  and  $\Gamma$  on SNR and the optimum thickness for the maximum amount of SNR  $(t_m)$  for N K edge in AlN at different thicknesses are presented in figure 4-13 using MC simulations. At  $\Gamma$ =50eV, *h* and SNR fluctuate and a certain maximum for SNR cannot be seen. Hence, the variation of *h* by thickness is considerable. Generally, increasing  $\Gamma$  provides more energy intervals leading to the smaller variance of background signal for specimens with thickness close to  $t_m$ . Consequently, by increasing the fitting range to 150 eV, the fluctuations vanish and a smooth curve for h and SNR can be observed. So, for the calculation of  $t_m$  the proper value of fitting range for the background removal should be used. In addition, increasing the beam energy increases SNR which is in agreement with the experimental EEL spectroscopy; although its effect on h varies at different thicknesses. Besides, the increase of beam energy increases the mean free path of inelastic scattering; hence the thickness for the maximum SNR ( $t_m$ ) increases.



Figure 4-13. Effects of beam energy ( $\Box$ ,  $E_0 = 50 \text{ keV}$ ;  $\circ$ ,  $E_0 = 100 \text{ keV}$ ;  $\Delta$ ,  $E_0 = 200 \text{ keV}$ ) and  $\Gamma$  on the SNR for the N K edge in AlN by variation of thickness.  $\Delta$  was considered 50 eV.

Figure 4-14 illustrates the effect of specimen's thickness and the fitting range of background removal on SNR of N K edge in AlN, GaN and InN by MC simulations. Similar to the results in figure 4-13, the fluctuation of h at low values of  $\Gamma$  can be seen.  $t_m$  depends on the value of  $\Gamma$  specially for N K in AlN.



Figure 4-14. Effects of  $\Gamma$  on the SNR for the N K edge in AlN, GaN and InN by variation of specimen's thickness.  $\Delta$  was considered 45.5 eV and  $E_0=200$  keV.

In general, increase of  $\Gamma$  increases the SNR ; however for thicker specimens (t > 100nm) larger value of  $\Gamma$  decreases SNR for AlN and GaN. The vicinity of In M<sub>4</sub> and M<sub>5</sub> edges to the N K edge in InN can be the reason for to some extent visible differences for the effect of  $\Gamma$  on h and SNR in comparison with AlN and GaN. Here, it can be seen that h and SNR depend strongly on the extrapolated value of  $I_b$ . Hence, to achieve a more objective value for the detectability limit the jump ratio (ratio of maximum to minimum intensity at the ionization edge) can be used. However, jump ratio continuously decreases by increasing thickness similar to the trend for the thickness dependency of SBR presented in figure 4-12. Therefore, jump ratio calculation cannot provide the optimum thickness for the highest amount of SNR . More details regarding the jump ratio calculations can be found in Ref. [35].



Figure 4-15. The fine structures of N K edge at 200 keV in AlN, GaN and InN for three collection semi-angles (5, 15 and 30 mrad) with  $\alpha$ = 5 mrad,  $t_a$ =1 s and  $I_p$  = 1 nA.

Figure 4-15 demonstrates the MC simulations of the fine structure of N K edge in a) AlN, b) GaN and c) InN at different collection semi-angels for the aperture of EELS detector. Increase of collection semi-angel increases the amount of signal, because more signal can be collected by using larger aperture. However, the higher amount of signal does not necessarily mean higher amount of core-loss signal. Increase of collection semi-angle adds up the background signal noticeably

[1]; for this reason the proper size of aperture should also be selected. It should be mentioned that for the anisotropic materials the direction of the incident beam with the crystal axis of the specimen should be considered at angles less than the magic angle [50]. For this reason, large enough  $\beta$  should be used for DFT calculation to cancel the shape dependency of ELNES on the collection angle.

## 4.5. Conclusions

An approach was proposed to introduce the fine structure of ELNES from DFT calculations into the optical oscillator strength from the X-ray photoelectric cross sections. Using the refined optical oscillator strength, ELNES for the N K edge in AlN, GaN and InN as well as O K and Ni L<sub>2-3</sub> edges in NiO were simulated by MC simulations. Effect of beam energy, thickness of specimen and collection semi-angle were investigated on the N K edge in AlN, GaN and InN. It was found that h (=1+var( $I_b$ )/ $I_b$ ) is strongly dependent on the aforementioned parameters; hence the proper values for the optimal SNR should be chosen. In addition, MC simulations provided the optimum thickness as well as proper fitting range for the background removal and integration range of ionization edge to maximize SNR for N K edge in AlN, GaN and InN.

# 4.6. Acknowledgements

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# 4.7. References

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# Chapter 5. Density functional and theoretical study of the temperature and pressure dependency of the plasmon energy of solids

In the chapters 3 and 4, effect of beam energy and thickness of specimens as well as the parameters for the background removal from the ionization edges at the high energy loss region of EEL spectra were investigated. However, the low energy loss region of the EEL spectra containing the plasmon excitations provides many useful information regarding the electronic structure of materials. Both temperature and pressure can change the plasmon energy because of the consequent change of the valence electron density in the material. Hence, the influence of temperature and pressure should be considered on the EEL spectra. In this chapter, the effect of temperature and pressure on the plasmon energy of materials are studied by density function theory calculations of energy loss function. In addition, a model is suggested for the variation of plasmon energy by temperature and pressure via the combination of free electron model and the pseudo-spinodal equation of state. This chapter –with the same title- and coauthored by Raynald Gauvin has been published in the Journal of Applied Physics 116 (2014) 163501.

# Abstract

The temperature and pressure dependency of the volume plasmon energy of solids were investigated by density functional theory calculations. The volume change of crystal is the major factor responsible for the variation of valence electron density and plasmon energy in the free electron model. Hence, to introduce the effect of temperature and pressure for the density functional theory calculations of plasmon energy, the temperature and pressure dependency of lattice parameter was used. Also, by combination of the free electron model and the equation of state based on the pseudo-spinodal approach, the temperature and pressure dependency of the plasmon energy was modeled. The suggested model is in good agreement with the results of density functional theory calculations and available experimental data for elements with the free electron behavior.

#### 5.1. Introduction

Plasmon excitations, originating from the collective oscillations of the valence electrons in reply to an applied electric field, are the main feature of low-loss electron energy loss spectroscopy (EELS) [1, 2]. Plasmon energy, the energy corresponding to the distinctive frequency of excitation, is related to the density of valence electrons and hence it can be representative of electronic structure of material [1-3]. There are many studies relating the plasmon energy measurement to the direct measurement of other physical and mechanical properties [3-6]. For example the strain of lattice structure can be directly related to the plasmon energy variations [4]. Also, the mechanical properties such as Young modules have been measured in a direct relationship with plasmon energy [5, 6]. Hence, understanding the effect of physical and thermodynamical parameters on the plasmon energy measurement can be beneficial for the study of many other electronic structure-related properties of materials.

Various experiments have shown the change of plasmon energy by the variation of applied temperature and pressure on a material. Experimental measurements [7-13] confirm that by increasing of temperature the plasmon energy decreases. Also at higher pressures, the higher values of plasmon energy have been reported by different experiments and simulations [14, 15]. The main reason for the plasmon energy variations by temperature and pressure can be explained by the change in the valence electron density by change in the volume of system [9]. Because the change in the plasmon energy loss detectors, the effect of temperature should be considered in the theoretical models and for the accurate explanation of experimental data. Furthermore, at high pressures the new electronic structures lead to a significant difference in optical and physical properties which plasmon energy can be a good indicator for the measurement of these variations.

Since an equation of state (EOS) can describe the relation between temperature, pressure and volume, a proper EOS can predict the valence electron density variation. An analytical model based on the combination of free electron model with the pseudo-spinodal approach for the equation of state suggested by Baonza et al [16-18] is presented to study effect of temperature and pressure on the plasmon energy variations. The advantage of using EOS is the study of effect of temperature and pressure on the plasmon energy variations at the same time. There is a lack of studies regarding of the application of an EOS for the study of plasmon variations versus the temperature and pressure. Hence, the current study can be helpful to investigate the applicability of a simple volumetric model based on a free electron model for different materials.

In addition to the analytical model, the density functional theory (DFT) calculations were performed for the investigation of temperature and pressure dependence of plasmon energy. Similar to the analytical model, DFT calculations are performed based on the variation of the volume of system. The volume variation by temperature has been used successfully in other studies for the prediction of mechanical properties using DFT calculations. Wang et al [19] used DFT calculations to predict elastic modulus variations by temperature for solids considering the fact that the variation in the elastic modulus is mostly controlled by the change in the volume of solid. The results of DFT calculations are compared with the suggested model and available experimental data.

#### 5.2. The model

For the modeling of the temperature and pressure dependency of plasmon energy, the free electron model can be used. Based on the Drude model for the valence electron excitations of free electrons, plasmon energy ( $E_p$ ) of a material can be expressed according to equation (5-1) [1]:

$$E_p = \hbar \omega_p = \hbar \sqrt{\frac{ne^2}{\varepsilon_0 m}}$$
(5-1)

where  $\hbar$ , n, m, e and  $\varepsilon_0$  are reduced Planck's constant, the density of free electrons, the effective mass of electron , the electron charge and the dielectric permittivity of vacuum, respectively. Also  $\omega_p$  is the frequency of plasmon excitation in the material. Density of free electrons, n, can be defined as n = N/V, where N is the total number of free electrons and V is the volume [13]. The total number of free electrons corresponding to the number of valence electrons can be considered independent of temperature (T) in metals [20, 21]. Assuming the independency of the number of valence electron by pressure (P) at two different states of  $(T_1, P_1)$  and  $(T_2, P_2)$  between electron density and volume of crystal we can obtain the relation:  $N = n(T_1, P_1)V(T_1, P_1) = n(T_2, P_2)V(T_2, P_2)$ . So, the temperature and pressure dependency of plasmon energy can be directly related to the volume changes by temperature and pressure as below:

$$\frac{E_p(T_2, P_2)}{E_p(T_1, P_1)} = \sqrt{\frac{V(T_1, P_1)}{V(T_2, P_2)}}$$
(5-2)

Hence, by having the variation of volume of solid versus the temperature and pressure, the dependency of plasmon energy to the temperature and pressure can be obtained.

The relationship among temperature, volume, pressure and other thermodynamic variables of solids can be described by the equation of state (EOS) [22]. An EOS model relies on the inter-atomic interactions in the system; hence it can offer a test for the reliability of the applied solid state models [18]. Many models have been suggested for the EOS of solids; however a simple EOS which can be valid for a wide range of temperature and pressure is hard to achieve [17]. The EOS suggested by Banoza et al [16-18] based on pseudo-spinodal approach provides an accurate EOS for a wide range of temperature and pressure for the solids. The idea of spinodal corresponds to the limit of metastability of the one phase state in the two phase region [23] and a pseudo-spinodal approach means an approach similar to the spinodal concept. Banzona et al [16-18] proved the existence of a simple universal isothermal EOS valid for all condensed materials including solids with the following equation:

$$V(P) = V_{sp} \exp\{[-\kappa^*/(1-\beta)][P-P_{sp}]^{(1-\beta)}\}$$
(5-3)

where  $V_{sp}$  and  $P_{sp}$  are the volume and pressure along a certain pseudo-spinodal curve, respectively.  $\kappa^*$  and  $\beta$  describe the pressure behavior of isothermal compressibility.  $\beta$  is a universal constant which here is 0.85. In contrast to the other universal EOSs, the pseudo-spinodal EOS in the isothermal form can be simply rearranged to show the pressure as an explicit function of volume [18]. Banoza et al also included thermal effect in their EOS model using the Einstein model [17].

Based on the recent works by Banoza et al [18], Ronggang et al [22] derived the EOS including the correction for the zero-pressure condition. Hence, Ronggang et al [22] presented the volumetric form of thermal Banoza EOS as follows:

$$\ln(V_0 / V) = \left[B'_0(\beta^{-1} - 1)\right]^{-1} \times \left(Q^{1-\beta} - 1\right)$$
(5-4)

$$Q(T,P) = 1 + \frac{B'_0 P}{\beta B_0} - \frac{3B'_0 \gamma_0^G N_t k_B \Theta_E}{\beta B_0 V_0 (e^{\Theta_E/T} - 1)}$$
(5-5)

where  $V_0$ ,  $B_0$ ,  $B_0'$  and  $\gamma_0^G$  are molar volume, isothermal bulk modulus, pressure derivative of isothermal bulk modulus and Grüneisen parameter at the zero temperature and pressure, respectively. Also, P,  $\Theta_E$ ,  $k_B$  and  $N_t$  are the pressure of system, the Einstein temperature, the Boltzmann constant and the number of particles respectively.

The volume of solid can be calculated at any temperature and pressure using equation (5-4) and equation (5-5); hence equation (5-2) can be directly obtained for the temperature and pressure dependency of plasmon energy as following:

$$\frac{E_{p}(T_{2}, P_{2})}{E_{p}(T_{1}, P_{1})} = \exp\left(\frac{1}{2} \frac{\left(Q(T_{2}, P_{2})^{1-\beta} - Q_{1}(T_{1}, P_{1})^{1-\beta}\right)}{B_{0}^{'}(\beta^{-1} - 1)}\right)$$
(5-6)

Equation (5-6) provides the variation of plasmon energy by change in the temperature and pressure from the reference temperature and pressure of  $(T_1, P_1)$  to any other temperature and pressure of  $(T_2, P_2)$ . The reference temperature can be chosen equal to zero temperature; however because of the limitation in the achievement of zero temperate for the experimental purposes higher temperatures is more favorable as the reference temperature.

#### 5.3. Density functional theory calculations

In this study, DFT calculations were performed with full potential linear augmented plane wave (FLAPW) method using WIEN2k code [24, 25]. For exchange-correlation potential, generalized gradient approximation (GGA) by Perdew et al [26] was used.  $R_{MT} \times K_{max}$  was assumed 8, where  $R_{MT}$  is the smallest atomic sphere radius in the unit cell and  $K_{max}$  is the magnitude of the largest k vector. 100,000 k-points in the first Brillouin zone for calculations were used. The value of spherical harmonic expansion has been set to 10. The calculations were considered as convergent when the charge density difference between the input and output electron density was less than 0.0001*e*. Optical properties were calculated by the code using random phase approximation (RPA) based on the work of Ambrosch-Draxl and Sofo [27]. The imaginary part of the interband dielectric function ( $e^{inter}$ ) is calculated according to the below equation [28]:

Im 
$$\in^{\text{inter}} (\omega) = \frac{1}{\pi} \left( \frac{\hbar e}{m \omega} \right)^2 \sum_{n,n',\mathbf{k}} \int_{\mathbf{k}} \left| p_{n',n,\mathbf{k}} \right|^2 \left( f(\varepsilon_n, \mathbf{k}) - f(\varepsilon_{n'}, \mathbf{k}) \right) \delta(\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}} - \omega) d^3 k$$
  
(5-7)

where  $p_{n',n,k}$  is the momentum matrix element between bands n and n' at the specific k point.  $n \neq n'$  corresponds to the interband transitions and n = n' is for the intraband transitions.  $\omega$  and k are the frequency of oscillator and the crystal wave vector, respectively. Also f is the occupation number of single particle with the eigenvalue of  $\varepsilon$ . The real part of  $\in^{inter}$  can be calculated by Kramers-Kronig transformation. The intraband part of dielectric function is calculated by Drude-like shape function as following [27, 28]:

$$\epsilon^{\text{intra}}(\omega) = 1 - \frac{\omega_{pl}^2}{\omega^2 + \Gamma^2} + i \frac{\Gamma \omega_{pl}^2}{\omega(\omega^2 + \Gamma^2)}$$
(5-8)

where  $\Gamma$  is the lifetime broadening and  $\omega_{pl}$  is the plasma frequency of free electrons [28]:

$$\omega_{pl}^{2} = \frac{1}{\pi} \left(\frac{\hbar e}{m}\right)^{2} \sum_{n} \int_{k} \left|p_{n,n,k}\right|^{2} \delta(\varepsilon_{n,k} - \varepsilon_{F}) d^{3}k$$
(5-9)

The final dielectric function is the result of summation of the interband and intraband dielectric functions. The value of lifetime broadening for the intraband contribution was set to 0.2 eV. Also for the interband contributions, the amount of Lorentzian broadening was considered 0.1 eV. It should be mentioned in this chapter  $\Gamma$  is the lifetime broadening and in chapter 4  $\Gamma$  indicates the background fitting range.

#### 5.4. Results and Discussions

In this section first, the results on the temperature dependency of plasmon energy is investigated. Figure 5-1 shows the density of states (DOS) of aluminum at different lattice parameters which corresponds to 10 and 773K temperatures. Our calculations are in very good agreement with calculations performed by Kresch et al [29]. The lattice parameters measured by Kresch et al [29, 30] using inelastic neutron scattering measurements were used for our DFT calculations. For the lattice parameters not provided by the experiments, the interpolation of data was used in the range of available experimental data.



Figure 5-1. Density of states of aluminum at different temperatures obtained by DFT calculations.  $E_F$  is the Fermi energy. The dots are the results from Kresch et al [29].

Figure 5-2a shows the calculated energy loss function (ELF) of Al by DFT calculations for some selected temperatures. Similar to the calculations of DOS, the same approach of change in the lattice parameter has been applied. As it can be seen, the volume plasmon energy decreases by increasing the temperature resembling the experiments [9]. The increase in the ELF at energy losses less than plasmon energy (e.g. 14 eV) by increasing temperature can be explained based on the simple equation originating from the free electron model as below [1]:

$$\operatorname{Im}\left[\frac{-1}{\in(E)}\right] = \frac{E(\Delta E_{pl})E_{p}^{2}}{(E^{2} - E_{p}^{2})^{2} + (E\Delta E_{pl})^{2}}$$
(5-10)

where  $\Delta E_{pl} = \hbar/\tau$  is the full width at half-maximum (FWHM) and  $\tau$  is the relaxation time. Since the polynomial order of plasmon energy in the denominator is 4 in comparison with 2 in the numerator, by increasing temperature and so decreasing the value of plasmon energy the ELF increases. In addition, according to our DFT calculations  $\Delta E_{pl}$  decreases by increasing temperature leading to the further increase of ELF.

In figure 5-2b, the calculated plasmon energy by DFT calculations for Al are compared with the present model based on equation (5-6). For the calculations in equation (5-6),  $T_0$  was 10K as the starting point and  $E_p(T_0)$  is the corresponding value from DFT calculations. The good agreement between DFT calculations and free electron based model (equation (5-6)) can be seen.



Figure 5-2. a) Energy loss function (ELF) of Al as a function of temperature calculated by DFT calculations. b) Comparison between the temperature dependency of plasmon energy for Al calculated by DFT calculations (dots) and the predictions by equation (5-6) (solid line).



Figure 5-3. a) Comparison between the experimental data by Abe et al [9] (dots) and the results from equation (5-6) (solid line) for the temperature dependency of plasmon energy of Al. b) Comparison between experimental data by Abe et al [9] and Moorthy and Howe [11] and DFT calculations for Al.  $\Delta E_p$  is the difference between the plasmon energy at a given temperature and the plasmon energy at 24°C.

In figure 5-3a, the temperature dependency of plasmon energy of Al measured by Abe et al [9] and its comparison with equation (5-6) is presented. Equation (5-6) can predict the temperature dependency of plasmon energy with a good agreement with experiments. This verifies that using the EOS not only can be proper for the predictions in the variation of thermodynamics state of solids by temperature and pressure but also it can be applied for the temperature variation of plasmon energy successfully. For the calculations,  $T_0$  was 98K as the starting point and  $E_p(T_0)$  was the corresponding value from the experiment.

Figure 5-3b shows the comparison between experimental results by Abe et al [9] and Moorthy and Howe [11] and our DFT calculations for  $\Delta E_p = E_p(T) - E_p(24^\circ C)$ . Since different methods predict different values of plasmon energy, the difference of  $E_p$  and a reference point ( $E_p(24^\circ C)$ ) was used for the comparison. Here also, our DFT calculations show a good agreement with the experimental measurements confirming the applicability of the suggested approach of using volume change to predict the variations of plasmon energy by the temperature in DFT calculations. Also, this consequence corroborates that variation of volume is the main factor affecting the variation of plasmon energy by the temperature for Al because of its free electron behavior.

Figure 5-4 shows the results of DFT calculations for the variations of ELF around the plasmon energy for a) Li, b) Na and c) Cs for some selected temperatures. Similar to the previous figures for Al, each temperature corresponds to a certain lattice parameter. The lattice parameters are extracted from the available experimental data or the results of calculations. The lattice parameter for Li was extracted from calculations by Taravillo et al [18]. For Na and Cs the data were extracted from experimental work of Anderson and Swenson [31, 32]. The available data for Na and Cs were in the molar volume at the certain temperature. It should be mentioned that Barrett [33] reported the coexistence of close-packed hexagonal structure along with the body-centered cubic structure in high vacuum at the temperatures below 36K and 78K for Na and Li, respectively.



For our DFT calculations, only the body-centered cubic structures were considered.

Figure 5-4. The results of DFT calculation for ELF of a) Li b) Na and c) Cs at different temperatures.



Figure 5-5. Comparison between the temperature dependency of plasmon energy for a) Li b) Na and c) Cs calculated by DFT calculations (dots) and the predictions by equation (5-6) (solid line).



Figure 5-5. (Continued)

Figure 5-5 presents the comparison between the plasmon energy calculated by the DFT calculations with the results from equation (5-6). All the values for the parameters in equation (5-6) are from the calculations by Ronggang et al [22]. For Li, Na and Cs a general good agreement between DFT calculations and the model can be seen. This means that free electron model can be applied

with success for the temperature dependency of these elements. In fact temperature variation below the melting point leads to the small volume changes of these solids; hence the departure from the free electron model will not be significant for them. It should be emphasized that the current model is based on just volume variations of solids by temperature and a more accurate model could consider the other factors such as electron–phonon interactions [13, 34-36]. However based on our results, the volume expansion has the major effect on the plasmon energy variation of the elements with free electron behavior. Moreover, using free electron model for materials with strong interband transition such as Ag can lead to inaccurate results for the prediction of the change in plasmon energy by temperature [10].

It should be mentioned that generally the experimental measurements of plasmon energy variations by the temperature are performed by the EELS [9-12]. However, the limitations of EELS should also be considered at high pressures and high momentum transfers. At high momentum transfers, multiple scatterings control the spectra [37]; hence the amount of useful signal decreases rapidly. Moreover, because the electron beam should be at low pressures to avoid the electron scatterings [14]. For these reasons, the inelastic X-ray spectroscopy (IXS) has an obvious advantage because of capability of working at high pressures as well as not suffering from multiple scattering at high momentum transfers for the plasmon energy measurements [37].

After studying the temperature effect on the plasmon energy, the pressure dependency of plasmon energy is investigated. Figure 5-6 shows contour plots of difference in valence electron density at (100) plane in Al at different ratios of the reduced volume of unit cell (V) at higher pressures to the volume of unit cell at ambient pressure ( $V_0$ ). As shown in figure 5-6, the area with high density of valence electrons extends from the area around the atom to a much broader area on the crystal plane by increasing the pressure. The type of four fold symmetry in the plane does not change; however the shape of difference in valence electron density presents a dramatic change. This vast difference in the valence electron



density by increasing pressure can cause the high amount of variation in the optical properties.

Figure 5-6. Contour plots of difference in valence electron density ( $\Delta n$ ) in (1 0 0) plane of Al for a) V/V<sub>0</sub>=1, b) V/V<sub>0</sub>=0.8 c) V/V<sub>0</sub>=0.7 and d) V/V<sub>0</sub>=0.6. The plots were generated by Xcrysden [38] software.

Figure 5-7 demonstrates the effect of pressure on some selected elements for a) Li, b) Na, c) Al and d) Zn at xx and e) Zn at zz directions. The different pressures correspond to different volumes of unit cells. In figure 5-7, the five different pressures from zero to the higher values correspond to  $V/V_0=1$ , 0.9, 0.8, 0.7 and 0.6, respectively. Based on the values of V and V<sub>0</sub> the amount of pressures was calculated using equation (5-4) and equation (5-5). For the calculation of pressure, the effect of temperature was ignored since the thermal contribution at room temperature on the total pressure is negligible in comparison with the volume changes from the high amount of pressure. The crystal structure and the lattice parameters at  $V/V_0=1$  for the DFT calculations were considered equal to the values in the ambient temperature and pressure corresponding to the values from Ref. [39].



Figure 5-7. The energy loss function of a) Li, b) Na, c) Al, d) Zn at xx and e) Zn at zz direction at different unit cell volumes. The lines with blue, red, green, gray and black color correspond to  $V/V_0=1$ ,  $V/V_0=0.9$ ,  $V/V_0=0.8$ ,  $V/V_0=0.7$  and  $V/V_0=0.6$ , respectively.



Figure 5-7. (Continued)



Figure 5-7. (Continued)

As it can be seen in figure 5-7, for all the elements the value of plasmon energy increases by increasing the pressure. Also, the ELF at the plasmon energy region decreases which can be explained by equation (5-10). Furthermore, it can be observed the full width at maximum-half ( $\Delta E_{pl}$ ) increases based on the results of DFT calculation. Hence the increase of  $\Delta E_{pl}$  leads to the decrease of ELF since the order of  $\Delta E_{pl}$  is higher in the denominator. Lao et al [15] confirmed a strong pressure dependency for the plasmon line width. The increase of plasmon line width by increasing pressure can be explained by the decrease of plasmon lifetime because of the electron-hole excitations [15]. Increasing pressure dramatically changes the shape of ELF for lithium. A second sharp peak before the plasmon energy emerges as the pressure increases which can be related to the so-called zone boundary collective state (ZBCS) [40]. ZBCS is very anisotropic and in polycrystalline structure disappear [37]. The predication of the additional peak is in agreement with the DFT calculations by Rodriguez-Prieto et al [40]. The main plasmon peak corresponds with the free-electron-like plasmon and the additional peak emerges from the anisotropic flattening of bands in the band structure and

the related electronic localization of Li at high pressures [40]. Generally, increasing of pressure increases the s to p orbital mixing and changes eventually the electronic band structure dramatically [40].

For the other elements in figure 5-7, the additional peak was not observed at the range of reduced volume of unit cell; however for Zn the general shape of ELF changes dramatically and the maximum value of ELF at V/V<sub>0</sub>=0.7 and 0.8 shifts from the first major peak to the second peak in the ELF. However, for our calculations of the plasmon energy the placement of the original peak has been considered. As well, at pressures higher than 105 GPa the crystal structure of Na turns into CI16 structure [41] which has lower symmetry in comparison to the bcc and fcc structure and the plasmon energy starts to drop. It should be mentioned that it was assumed there is no change in the crystal structures in the range of reduction in the volume of unit cells of crystal structures. The reason for this approach is for the sake of comparison with the original crystal structure and using the same parameters in equation (5-6). However for some of the elements used for the calculations, the crystal structure in the ambient pressure would be unstable at high pressures [42].

Figure 5-8 shows the comparison of the results of DFT calculations of plasmon energy with the predication of free electron model based on equation (5-1) (dashed lines) for Li, Na, Mg, Al, Si, Ca and Zn. For the anisotropic elements of Mg and Zn the average plasmon energy in the xx and zz directions has been used. Generally, the volume model (equation (5-1)) predicts the variation of plasmon energy by the volume of unit cell in good agreement with the results of DFT calculation. However, it is clear by increasing the pressure the accuracy of equation (5-1) decreases for the estimation of increase in the plasmon energy which means more deviation from the free electron model behavior.



Figure 5-8. Comparison of the results of DFT calculations with the volume model (equation (5-1)) for Li, Na, Al, Si, Ca and Zn at different unit cell volumes. The continuous lines represent the DFT calculation and the dashed lines correspond to the volume model.

The deviation from free electron model can be contributed to the different factors. In a nearly free electron metal, there is a weak interaction between the cores and the conduction electrons [15]. The reason for this weak interaction is ion cores occupy a very small fraction of the total volume of solid [43]. However, by increasing pressure the ratio of volume of cores to the total atomic volume increases and so the interaction between the ions (core) and the valence electrons increases [43]. For example for alkaline metals, high pressures increase the hybridization of the valence (s) orbitals which leads to the more deviation from

the free electron model [43]. Also, the core polarization has negligible effect on the improvement of free electron model at high pressures according to Lao et al [15].



Figure 5-9. Plasmon energy variation by temperature and pressure according to equation (5-6) for Na and Al.  $(T_0, P_0)$  indicates the values of temperate and pressure at their zero value.

Figure 5-9 presents the effect of temperature and pressure at the same time on the plasmon energy variations using equation (5-6) for Al and Na. It can be observed the outcome of pressure is much more apparent on the plasmon energy variation because it can alter the volume of unit cell in the much broader range.

## 5.5. Conclusion

DFT calculations successfully predicted the effect of temperature and pressure on the volume plasmon energy using the temperature and pressure dependency of the lattice parameters. Our suggested model derived from the combination of free electron model and the EOS based on the pseudo-spinodal approach can predict the pressure and temperature dependency of plasmon energy. The model is in good agreement with experimental and DFT results for the temperature dependency of plasmon energy of Al and DFT calculations for Li, Na and Cs. Also, the pressure dependency of plasmon energy can be estimated by the model. However, by increasing the pressure the deviation from the simple free electron model was observed.

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## **Chapter 6. Conclusions and contributions to original knowledge**

# 6.1. Conclusions

Based on the obtained results in the thesis, the main conclusions can be summarized as below:

- 1- Monte Carlo simulations based on the optical data model can be used for the prediction of the backscattering and transmission coefficients of electrons in the bulk and the thin solid film specimens from very low ( $\sim 0.1$  kev) to high ( $\sim 500$  keV) energies.
- 2- The ratio of the optimum thickness for the highest amount of signal-to-noise ratio of the inner-shell ionization edges  $(t_m)$  to the inelastic mean free path  $(\lambda_{in})$ can be considered constant in a specific range of energy, approximately. This estimation can be used for the calculation of  $t_m$  at different beam energies for the electron energy loss spectroscopy.
- 3- A simple equation between the backscattering and transmission coefficients of thin solid films can be obtained based on the results of Monte Carlo simulations.
- 4- The fine structure of the energy-loss near-edge structure (ELNES) of ionization edges can be introduced into the Monte Carlo simulation of electron energy loss spectra using density functional theory calculations. Consequently, the effect of thickness, collection semi-angle, beam energy and different parameters of the background removal can be investigated on the fine structure of ionization edges by Monte Carlo simulations.
- 5- Density functional theory calculations can be used for the improvement of optical oscillator strength (OOS) calculations in the low and high energy loss regions of electron energy loss spectra.

- 6- The volume variation of the lattice parameter by the temperature can be used in the density functional theory calculations for the study of effect of temperature on the plasmon energy of elements with the free electron behavior.
- 7- Combination of pseudo-spinodal approach for the equation of states of solids and the free electron model successfully predicts the effect of temperature and pressure on the plasmon energy of elements with the free electron behavior.
- 8- Density functional theory calculations confirm the departure from the free electron model at very high pressures in the prediction of plasmon energy.

# 6.2. Contributions to original knowledge

The main contributions to the original knowledge are summarized as follows:

- 1- Electron energy transportations and electron energy loss spectra were studied by combination of density functional theory with Monte Carlo simulations. Monte Carlo simulations based on the optical data model can successfully predict the backscattering and transmission coefficients of thin solid films and bulk specimens.
- 2- Effect of different parameters of experimental electron energy loss spectra such as thickness, beam energy and collection semi-angle on the signal and the background of inner shell ionizations were investigated using Monte Carlo simulations based on a optical data model.
- 3- A new equation for the calculation of optimum thickness for the highest amount of signal-to-noise ratio of the inner-shell ionization edges was suggested. The equation suggests by measuring or computing one optimum thickness for the maximum signal-to-noise ratio at a certain beam energy, the optimum thickness can be estimated for any other energy in a specific range of energy.
- 4- A new equation and concept for the relation between electron backscattering and transmission coefficients of thin solid films were introduced. The equation

suggests that by measuring backscattering or transmission coefficient, the other coefficient can be calculated.

- 5- Fine structure of ionization edges was introduced into the Monte Carlo simulations of the energy-loss near-edge structure (ELNES) using density function theory calculations with a new approach. As a consequence of the approach, signal-to-noise ratio can be computed including the effect the of fine structure of ionization edges. Also, this will lead to improved quantification schemes for elemental composition.
- 6- Effect of different parameters of background removal on the signal-to-noise ratio and the signal-to-background ratio of the inner-shell ionization edges were studied using Monte Carlo simulation of the ELNES. Monte Carlo simulations can successfully predict the effect of different parameters of background removal on the signal-to-background ratio.
- 7- Effect of temperature on the low-loss energy loss function and the plasmon energy were investigated using density functional theory calculations based on the volume variation of the lattice parameter by the temperature. The results of density functional theory calculations are in good agreement with the available experimental measurements for aluminum confirming the applicability of the suggested approach.
- 8- By combination of free electron model with pseudo-spinodal approach for the equation of states of solids, a new equation was suggested to study effect of temperature and pressure on the plasmon energy. The model can successfully predict the variation in the experimental measurements for the temperature dependency of aluminum. Also, the results of density functional theory calculations are in agreement with the suggested model.
- 9- Effect of pressure on the low-loss energy loss function and the plasmon energy of various elements were studied using density functional theory calculations. Departure from the free electron model behavior at very high pressures was confirmed by comparison of the results of density functional theory and the prediction of the free electron model.

# **Chapter 7. Future work**

- 1- Monte Carlo simulations can be used for the complex geometries. Hence, the application of the optical data models for the different geometries can be investigated in the future works.
- 2- For very thin specimens, the surface energy loss can add the surface plasmon excitations into the electron energy loss spectra. Hence, the surface energy loss can be introduced into the optical data models to study effect of variation of thickness on the electron energy loss spectra.
- 3- The study of probability of the generation of secondary electrons is important in electron microscopy. As a new application of improved optical data model using the solid state effects in this research, the probability of the secondary electron generation can be investigated by Monte Carlo simulations leading to simulation of secondary electron images
- 4- Electron-phonon interactions can be considered in the model introduced in chapter 5 for the study of the effect of temperature on the variations of plasmon energy. For the semiconductors, effect of temperature and pressure on the density of conduction and valence electrons as well as the variation of band gap can be considered for the improvement of the suggested model.