Design of Local Filters for the Deconvolution of Electron Energy Loss Spectrum

David Brie, Christian Heinrich

DESIGN OF LOCAL FILTERS FOR THE DECONVOLUTION OF ELECTRON ENERGY LOSS SPECTRUM

David Brie

CRAN - UMR 7039
Faculté des sciences B.P. 239
54506 Vandœuvre-lès-Nancy, France

Christian Heinrich

LSIIT - UMR 7005
Pôle API Bd Sébastien Brant BP 10413
67412 Illkirch, France

ABSTRACT

This article proposes a new approach to the deconvolution of Electron Energy Loss Spectra, used for material characterization. This approach is based on local filters with varying bandwidth, adapted to the local (non-stationary) characteristics of the signal to restore. The local filter synthesis is achieved by means of three parameters determined by optimizing a compound criterion. The effectiveness of this approach is shown on an example.

1. INTRODUCTION

The Electron Energy Loss Spectroscopy (EELS) is a technique used to characterize material. It can provide information about the chemical composition, the crystallographic structure and the electronic properties of the studied specimen. When used in Transmission Electron Microscope, this information may be directly obtained if the sample is thin as compared to the mean free path for inelastic scattering. When the thickness of the sample increases, multiple scattering phenomena occur, resulting in a self convolution process which highly complicates the spectra interpretation. Deconvolution is used to remove this multiple scattering as well as the distorsion introduced by the instrument itself.

The classical approaches to EELS deconvolution [1, 2] can be interpreted in terms of linear invariant low-pass filtering and, consequently, they can be efficiently implemented. But they suffer one major shortcoming which results from they global (isotropic) character of the low-pass filter. Such a global filter will act is the same way on the signal, whatever the local (non stationary) characteristics of the signal are, while it appears intuitively sound to adapt the filter to these local characteristics. Basically, the filter bandwidth should be greater in the dynamical parts of the signal and smaller in its non dynamical parts. This is such an approach that we are developing now.

2. MODELLING OF THE DIRECT PROBLEM

2.1. The EELS Spectrum

A typical Electron Energy Loss Spectrum may be decomposed into 3 parts:
– zero loss peak (Instrument response): The most intense peak centered on 0 is representative of the electrons which are transmitted without suffering any measurable energy loss, that are those which can be regarded as being un-scattered;
– low-loss Region (LL): The low-loss region is typically located between 0 and 100 eV. This region is representative of inelastic scattering with outer-shell (valence) electrons;
– core-loss Region (CL): At high energy loss ($> 100eV$) the electron intensity decreases according to some fairly high power of energy loss. Superimposed on this smoothly decreasing signal are ionisation edges which represent inner-shell excitation.

From a signal processing point of view, the ionisation edges are the most challenging, because they are composed of abrupt edges on which are superimposed peaks of variable amplitude and width (see figure 2).

2.2. Model of the EELS Spectrum

Let $Z(E)$ be the zero-loss peak with intensity $I_0 = \int Z(E)dE$ where E represents the energy loss. Assuming independent scattering events, the model of the EELS spectrum, noted $J(E)$, is given by [1]:

$$J(E) = Z(E) \star \left\{ \delta(E) + \frac{S(E)}{I_0} + \frac{S(E) \star S(E)}{2!\, I_0^2} + \frac{S(E) \star S(E) \star S(E)}{3!\, I_0^3} + ... \right\}, \quad (1)$$

where $S(E)$ represents the single scattering signal which has to be estimated. Defining $j(\omega), s(\omega), z(\omega)$ as the Fourier transforms of $J(E), S(E), Z(E)$, the Fourier transform of equation 1 is

$$j(\omega) = z(\omega) \exp\left(\frac{s(\omega)}{I_0}\right). \quad (2)$$

Due to the properties of the self-convolution, the EELS spectrum in the core loss regions may be well approximated by [1]

$$J_{CL}(E) \simeq J_{LL}(E) \star S_{CL}(E), \tag{3}$$

where $J_{CL}(E)$ et $S_{CL}(E)$ represent the EELS and single scattering signals in the high energy loss region. $J_{LL}(E)$ corresponds to the EELS signal in the low loss region.

3. CLASSICAL APPROACHES TO EELS DECONVOLUTION

Because EELS deconvolution is an ill posed problem, classical approaches use low-pass filters to regularize the inverse filter (least square) solution [1, 2]. For core loss region spectra, the use of model (3) leads to the solution :

$$S_{CL}(E) = \mathcal{F}^{-1}\left\{h(\omega)\frac{j_{CL}(\omega)}{j_{LL}(\omega)}\right\}. \tag{4}$$

For low loss region spectra, the use of model (2), results in the following regularized solution :

$$\frac{S(E)}{I_0} = \mathcal{F}^{-1}\left\{h(\omega)\log\left(\frac{j(\omega)}{z(\omega)}\right)\right\}. \tag{5}$$

An alternative solution is given by [2] :

$$\frac{S(E)}{I_0} = \mathcal{F}^{-1}\left\{\log\left(1 + h(\omega)\frac{j(\omega) - z(\omega)}{z(\omega)}\right)\right\}. \tag{6}$$

The point is that, for all cases, the low pass filter $h(\omega)$ should be chosen to manage at best the tradeoff between resolution and noise amplification.

4. A LOCAL FILTERING APPROACH TO EELS DECONVOLUTION

In fact, such a low passed filtering approach suffers one major shortcoming which results from its global (isotropic or shift invariant) character. The basic idea of the proposed approach is to adapt the filter to the local characteristics of the signal which has to be restored. Basically, the filter bandwidth should be greater in the dynamical parts of the signal and smaller in its non dynamical parts. This leads us to consider local filters instead of global filter. Intuitively, this point of view may be linked to the one consisting in introducing hidden variable in Bayesian approaches (see for exemple [3, 4])

4.1. Local Filters

A local filter is characterized by its impulse response $H(E, E')$, representing the response of the filter at energy loss E to a Dirac impulse centered on E'. Knowing this impulse response, the response to an arbitrary excitation $X(E)$ is given by the generalized input/output relationship:

$$Y(E) = \int H(E, E - E')X(E')dE'. \tag{7}$$

We also defined the local frequency response of the filter as :

$$h(E, \omega) = \underset{E' \to \omega}{\mathcal{F}}\{H(E, E')\} = \int H(E, E')\mathrm{e}^{-j\omega E'}dE', \tag{8}$$

from which we get :

$$\begin{aligned} Y(E) &= \iint h(E, \omega)\ X(E')\ \mathrm{e}^{j\omega(E-E')}\ d\omega\ dE' \\ &= \int h(E, \omega)\ x(\omega)\ \mathrm{e}^{j\omega E}\ d\omega. \end{aligned} \tag{9}$$

4.2. EELS Deconvolution by Local Filtering

Let $S(E)$ be the signal restored by local filtering. For core loss region spectra, the counter part of equation (4) is given by:

$$S_{CL}(E) = \int h(E, \omega)\ \frac{j_{CL}(\omega)}{j_{LL}(\omega)}\ \mathrm{e}^{j\omega E}\ d\omega. \tag{10}$$

For low energy loss spectra, the counter part of equation (5) is:

$$\frac{S(E)}{I_0} = \int h(E, \omega)\ \log\left(\frac{j(\omega)}{z(\omega)}\right)\mathrm{e}^{j\omega E}\ d\omega, \tag{11}$$

while that of equation (6) is:

$$\frac{S(E)}{I_0} = \int\ \log\left(1 + h(E, \omega)\frac{j(\omega) - z(\omega)}{z(\omega)}\right)\mathrm{e}^{j\omega E}\ d\omega. \tag{12}$$

5. DESIGN OF LOCAL FILTERS TO EELS DECONVOLUTION

5.1. Method

For the design of the local filter, we use a non-stationary point of view by defining the local filter as a low-pass filter with varying bandwidth. Basically, we aim at designing a local filter having a local (intantaneous) bandwidth adapted to the bandwidth of the signal to restore. As a specific example, we consider a gaussian local filter :

$$h(E, \omega) = \exp\left(-\frac{\omega^2}{2\Omega(E)}\right). \tag{13}$$

In this framework, the design of the local filter comes down to the problem of estimating the bandwidth $\Omega(E')$. For this problem the proposed solution is as follows :

Initial estimation of the signal to restore: this initial estimated signal, noted $S^0(E)$ is obtained by a global low-passed filtering (equations 4, 5 or 6).

Estimation of $\Omega(E')$: the quantity $\left|\frac{d}{dE}S^0(E)\right|^2$ is proportional to the local (instantaneous) bandwidth of the signal

$S_0(E)$ and, thus, it can be interpreted as a very imperfect estimator of the local bandwidth of the signal to restore. To compensate these imperfections, we propose to estimate the local filter bandwidth as:

$$\Omega(E) = \alpha \left(1 + \beta \left| \frac{d}{dE} S^0(E) \right|^2 \right)^{\gamma}, \qquad (14)$$

where α, β and γ are design parameters that enable to adjust at best the shape of $\Omega(E)$. The local filter as well as the restored signal are then functions of these parameters, noted respectively $h_{\alpha,\beta,\gamma}(E',\omega)$ and $S_{\alpha,\beta,\gamma}(E)$.

Optimal values of α, β and γ: As mentioned before, α, β and γ are design parameters that have to be chosen to adjust at best the shape of $\Omega(E)$. In that respect, we consider the criterion :

$$\mathcal{C}\left\{S_{\alpha,\beta,\gamma}(E)\right\} = \mathcal{Q}\left\{S_{\alpha,\beta,\gamma}(E)\right\} + \lambda \mathcal{R}\left\{S_{\alpha,\beta,\gamma}(E)\right\}. \qquad (15)$$

The optimal values of α, β and γ and consequently the optimal estimation of $S(E)$ is given by :

$$\hat{S}_{\alpha,\beta,\gamma}(E) = \underset{\alpha,\beta,\gamma}{\operatorname{argmin}}\, \mathcal{C}\left\{S_{\alpha,\beta,\gamma}(E)\right\}. \qquad (16)$$

5.2. Criterion Design

The criterion $\mathcal{C}\left\{S_{\alpha,\beta,\gamma}(E)\right\}$ is a compound criterion, the relative weight of each terms being adjusted by the value of λ:
- the first term of the criterion $\mathcal{Q}\left\{S_{\alpha,\beta,\gamma}(E)\right\}$ is a data fitting measure :

$$\mathcal{Q}\left\{(S_{\alpha,\beta,\gamma}(E)\right\} = \int \left| J(E) - J_{\alpha,\beta,\gamma}(E) \right|^2 dE, \qquad (17)$$

where $J_{\alpha,\beta,\gamma}(E)$ corresponds to the EELS spectrum estimating according equations (1) or (3) with $S(E) = S_{\alpha,\beta,\gamma}(E)$;
- the second term $\mathcal{R}\left\{S_{\alpha,\beta,\gamma}(E)\right\}$ is a regularization term:

$$\mathcal{R}\left\{S_{\alpha,\beta,\gamma}(E)\right\} = \int \Psi\left(\left|\mathcal{D}S_{\alpha,\beta,\gamma}(E)\right|\right) dE. \qquad (18)$$

The choice of both regularization function $\Psi(\cdot)$ and differential operator $\mathcal{D}$ should be made according to the available *a priori* knowledge on the signal to restore. In general the differential operator is of the form $\mathcal{D} = \frac{d^n}{dE^n}$. The derivative order depends on the signal to restore. Basically, a n-order derivative operator is suited to the reconstruction of a signal with a null n-order derivative (first order derivative for a constant signal, second order derivative for a constant drift signal, ...).

Let us consider now the choice of the regularization function $\Psi(\cdot)$. The regularization function assigns a cost to every value of the n-order signal derivative and thus should have some general properties. To be specific, we now restrict our attention to edge preserving reconstruction of signal, that is the restoration of piecewise constant signal for which we follow the approach of [5]. For that case, the relevant differential operator is the first-order derivative. The classical choice in regularized least squares deconvolution is the quadratic function $\Psi(t) = t^2$. But despite its computational advantage (the criterion $\mathcal{C}$ being quadratic, the restored signal is a a linear estimate), this quadratic function is ill suited to edge preserving reconstruction. Firstly, large value of the gradient will be heavily penalized and thus deters the reconstruction of sharp edges. Secondly, the slow growth of $\Psi(t) = t^2$ around 0, favors the small variations of the signal to restore. Thus, an edge preserving regularization function should :
– weakly penalize large values of the signal gradient to favor the reconstruction of sharp edges;
– have a derivative large enough around $t = 0$ to favor flat segments.

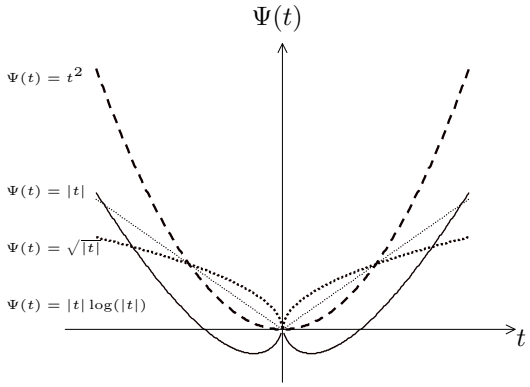

Fig. 1: different regularization functions.

In that respect, among the different regularization functions of figure 1, this is the function $\Psi(t) = \sqrt{|t|}$ which is better suited to edge preserving signal reconstruction. Note that the function $\Psi(t) = |t|\log(|t|)$ which corresponds to maximum entropy restoration is ill suited to that problem first because its minimum is not in $t = 0$ and also because large gradients will be heavily penalized.

5.3. Criterion Minimization

To find the optimal values of α, β and γ according to (16), we need a criterion minimization algorithm. We were not able to calculate an explicit expression of the criterion gradient; thus, we focuss our attention to algorithm that do not need this gradient. A possible method is given by the Nelder and Mead algorithm [6] which, due to the small number of parameters (three), has a reasonable computational burden. However, this algorithm does not guarantee the criterion minimum to be reached. In that respect, the Nelder-Mead algorithm is not optimal. Other optimization algorithms may be used as well but we don't have paid further attention to that point.

One may also consider a faster approach to minimize the criterion based on the following heuristic procedure : instead of considering the minimization over the entire set of local filters $h_{\alpha,\beta,\gamma}(E',\omega)$, we only consider local filters having an average bandwidth equal to Ω_0. The values of β and γ being fixed, one can evaluate α as :

$$\alpha = \Omega_0 \left[\frac{1}{\Delta E} \int_{\Delta E} \left(1 + \beta \left| \frac{d}{dE'} S^0(E') \right|^2 \right)^{\gamma} dE \right]^{-1} \quad (19)$$

where ΔE corresponds to the energy loss range of the signal considered. Ω_0 is estimated as the linear invariant gaussian filter bandwidth which minimizes the criterion (15). Adopting such an approach yields a smaller computational burden because only the two parameters β and γ are yet to be estimated. Again, we still cannot guarantee the criterion minimum to be reached.

6. EXPERIMENTAL RESULTS

The results that are presented, have been obtained on EELS spectra coming from a pure nickel sample of thickness $\frac{t}{\mu} = 1.4$ (t is the sample thickness and μ is the mean free path). The signal considered (see figure 2, curve 1) shows the Nickel ionization edges L_1 (1010 eV), L_2 (872 eV) and L_3 (854 eV). Due to the sample thickness, the multiple scattering contributions are quite important : attenuation of the L_2 edge, increase of the mean value after 880 eV, L_1 edge quite invisible. The curve 2 of figure 2 shows the deconvoluted EELS spectrum obtained by the Egerton method. This approach enables to remove the multiple scattering effects and makes the L_2 edge more visible. But the resolution increase is very weak. In addition, some residual fluctuations still remain in the non dynamical parts of the signal, in particular in the L_1 edge region, making the signal interpretation difficult. The curves 3 and 4 show the deconvoluted spectrum obtained by the proposed local filtering approach for different values of λ in criterion (15) ($\lambda = 20$ for curve 3, $\lambda = 10$ for curve 4). In both cases, the regularization function is $\Psi(t) = \sqrt{|t|}$. It appears the local filtering approach yields simultaneously a greater dynamical resolution and smaller residual fluctuations. In particular the L_1 edge is more easily seen. Comparing curves 3 and 4 shows that increasing the value of λ results in a more important smoothing. This is in agreement with theory.

7. CONCLUSION

In this paper, the design of local filters for EELS deconvolution has been addressed. The proposed approach uses a non-stationary point of view in the sense that the local filter is designed to have a variable bandwidth adapted to the signal to restore. In fact, it appears that the local filter design is nothing but the estimation of the optimal bandwidth of the local filter. For that we propose a method transforming this problem into the determination of three design parameters that minimize a criterion. This criterion is a compound criterion consisting in a data fitting measure and a regularization term which can account for *a priori* knowledge. The effectiveness of the proposed approach is shown on a pure nickel EELS spectrum corresponding to the L_1, L_2 and L_3 ionisation edges.

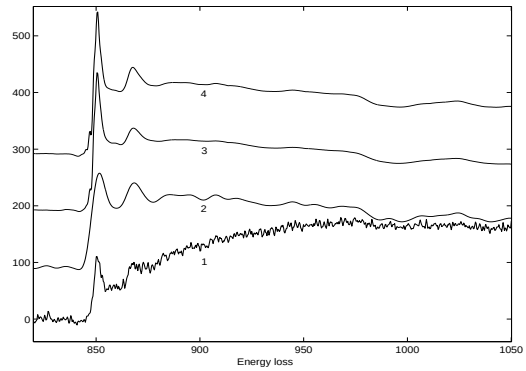

Fig. 2: An example of EELS deconvolution. To improve the readability of the figure the different curves are shifted with a constant value. Curve 1 corresponds to the EELS spectrum, curve 2 to the deconvoluted spectrum obtained by the Egerton method. Curves 3 and 4 correspond to the deconvoluted spectrum obtained by the proposed approach for different values of the regularization parameter λ.

8. REFERENCES

[1] R. F. Egerton, *Electron Energy Loss Spectroscopy in the Electron Microscope*, Plenum Press, 1986.

[2] D. Brie, N. Bozzolo, and P. Wahlbring, "Déconvolution des spectres de perte d'énergie des électrons," in *Actes du 17ème colloque GRETSI*, pp. 1165–1168. 1999.

[3] G. Demoment and J. Idier, "Chapitre iii : Approche bayésienne pour la résolution des problèmes inverses en imagerie," in *ARAGO, OFTA*, vol. 22, pp. 59–77. TEC & DOC édition, 1999.

[4] S. Geman and D. Geman, "Stochastic relaxation, gibbs distributions and the bayesian retoration of images," *IEEE Trans. on Pattern Analysis ans Machine Intelligence*, vol. 7, pp. 721–741, 1984.

[5] D. Geman and G. Reynolds, "Constrained restoration and the recovery of discontinuities," *IEEE Trans. on Pattern Analysis ans Machine Intelligence*, vol. 14, pp. 367–383, 1992.

[6] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical recipes in C*, Cambridge University Press, 1992.