

IL PRESENTE MATERIALE È RISERVATO AL PERSONALE DELL'UNIVERSITÀ DI BOLOGNA E NON PUÒ ESSERE UTILIZZATO AI TERMINI DI LEGGE DA ALTRE PERSONE O PER FINI NON ISTITUZIONALI



# The X-ray characteristic line: different contributions in the framework of the Boltzmann transport equation

Jorge E. Fernández a,b

 <sup>a</sup> Laboratory of Montecuccolino-DIN, Alma Mater Studiorum University of Bologna, via dei Colli 16, 40136 Bologna, Italy
 <sup>b</sup> Alma Mater Studiorum Università di Bologna Representacion en la Republica Argentina, M. T. de Alvear 1149, Buenos Aires, Argentina



# Introduction

The emission of characteristic lines after x-ray excitation is usually explained as the consequence of two independent and consecutive physical processes:

- the photoelectric ionization produced by the incoming photons
- the successive spontaneous atomic relaxation.

However, the photoelectric effect is not the only ionization mechanism for the incoming photons:

- Compton ionization contributes not negligibly to the ionization of single shells, mainly L and M.
- Moreover, secondary electrons from both interactions, photoelectric and Compton, are also able to undergone ionization by means of the so called impact ionization.

Another mechanism of line modification is the so called self-enhancement produced by absorption of the tail of the Lorentzian distribution of the characteristic line.



## Introduction

All these effects concur to the formation of the characteristic lines giving a more precise picture which is specific of the single line and the element.

This work furnishes a review of these contributions and how they influence the formation of the line.

It is given a complete picture of the photon kernels describing the emission of characteristic x-rays comprising all these major and minor effects.

These kernels can then be followed along successive photon interactions in deterministic or Monte Carlo photon codes to describe the effect of the multiple scattering.



# Scheme of X-ray interaction mechanisms

#### The full description of the radiation field requires the modeling of coupled photon-electron transport





# Multiple scattering is usually described using the Boltzmann transport model

# The photon interactions are depicted with the interaction kernels $k_i$

$$\eta \frac{\partial}{\partial z} f(z, \vec{\omega}, E) = -\mu(E) f(z, \vec{\omega}, E)$$

$$+ \sum_{i}^{\text{all interactions}} \int_{0}^{\infty} \left( \int_{4\pi} \cup (z) k_{i} \left( \vec{\omega'}, E', \vec{\omega}, E \right) f\left( z, \vec{\omega'}, E' \right) d\omega' \right) dE'$$

$$+ S(z, \vec{\omega}, E)$$

Not all the radiative contributions involved in an X-ray transport process are considered by the Boltzmann model and by the used interaction kernels  $k_i$ 

# X-ray production mechanisms from coupling terms

The full description of the radiation field requires the modeling of coupled photon-electron transport





# MS is better described using the modified Boltzmann transport model

# The Boltzmann transport model has been recently modified to include the electron-photon contributions

 $\begin{aligned} \frac{\left[ \frac{n\partial}{\partial z} f^{\uparrow} p\left(z,\omega,E\right) = -\mu^{\uparrow} p\left(E\right) f^{\uparrow} p\left(z,\omega,E\right) + \sum i^{\uparrow} all \ photon}{interactions} \right] & \int 0^{\uparrow} \infty \left[ \left( \frac{A\pi}{\pi} \right) \left( \frac{z}{\omega} \right) k^{\downarrow} i^{\uparrow} p \rightarrow p\left(\omega^{\uparrow},E^{\uparrow},\omega,E\right) f^{\uparrow} p\left(z,\omega^{\uparrow},E^{\uparrow}\right) d\omega^{\uparrow} \right) d\omega^{\uparrow} \right] d\omega^{\uparrow} d\omega^{\uparrow} \\ \frac{E^{\uparrow}}{E^{\uparrow}} + \sum j^{\uparrow} all \ coupling \ terms \left[ \int 0^{\uparrow} \infty \left[ \left( \frac{A\pi}{\pi} \right) \left( \frac{z}{\omega} \right) k^{\downarrow} j^{\uparrow} e \rightarrow p\left(\omega^{\uparrow},E^{\uparrow},\omega,E\right) f^{\uparrow} p\left(z,\omega,E^{\uparrow},\omega,E\right) f^{\uparrow} p\left(z,\omega,E^{\uparrow},E^{\uparrow}\right) d\omega^{\uparrow} \right] d\omega^{\uparrow} d\omega^{\uparrow} d\omega^{\uparrow} \\ \frac{f^{\uparrow},E^{\uparrow}}{E^{\uparrow}} d\omega^{\uparrow} d\omega^{\uparrow} dE^{\uparrow} + S^{\uparrow} p\left(z,\omega,E\right) \end{aligned}$ 

### Major mechanism for producing XRF lines: photoelectric ionization





# Condition to fulfill in order to produce photoelectric effect





### Transport kernel for the emission of characteristic lines





# Minor contributions to the x-ray characteristic lines

### 1) Compton ionization

### 2) Inner shell impact ionization

### 3) Self-absorbtion of the Lorentzian tail

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Contribution of inner shell Compton ionization to the X-ray fluorescence line intensity  $\not\approx$ 



Jorge E. Fernández <sup>a,b,\*</sup>, Viviana Scot <sup>a</sup>, Eugenio Di Giulio <sup>a</sup>

<sup>a</sup> Laboratorio di Montecuccolino-DIN, Alma Mater Studiorum Università di Bologna, via dei Colli 16, 40136 Bologna, Italy

<sup>b</sup> Alma Mater Studiorum Università di Bologna Representacion en la Republica Argentina, M. T. de Alvear, 1149 Buenos Aires, Argentina



# Contribution from Compton ionization

Compton ionization is usually neglected because the total Compton cross section  $\sigma_C$  is much lower than the total photoelectric cross section  $\tau$  for low and mid range x-ray energies :  $\sigma_{C <<} \tau$ 

A proper comparison of the extent of Compton and photoelectric cross sections requires the comparison of **single shell cross sections** (instead of total cross sections) as a function of energy:

 $\sigma \downarrow Ci (E) \text{ vs } \tau \downarrow i (E)$ 



# Contribution from Compton ionization



The XRF emission due to Compton ionization may play a relevant role in terms of single shell contributions



### IA Compton cross section: Compton profiles

If the target consists of electrons with a distribution of momenta  $\rho(p)$ , the double differential cross section will be proportional to the projection  $\underline{I(p\downarrow z)} = \iint \uparrow \underline{m} \rho(p) dp \downarrow x$  $dp \downarrow y$  in a coordinate system in which the scattering vector defines the z-axis direction.

<u> $I(p\downarrow z)$ </u> is called the Compton profile. The constant of proportionality is the Klein-Nishina cross section. It is customary to define  $p\downarrow z /mc \approx Q/137$  with Q a dimensionless variable with tabulated values in the range [-100, 100].

 $\underline{Q=137 \ E-E \downarrow 0 + EE \downarrow 0 \ /mc^{2} \ (1-\cos\theta)/(E^{2}+E \downarrow 0 \ f^{2}-EE \downarrow 0 \ \cos\theta) f^{1}/2}$ 

For each shell, it is possible to express the maximum value of Q as a function of the incoming energy <u>*E*10</u> and the scattering angle (this is done by putting <u>*E*=*E*10 - *I*1*i*, <u>*I*1*i*</u>) being the binding energy of the shell):</u>

 $\frac{Q \downarrow iMAX = 137 \ E \downarrow 0 \ (E \downarrow 0 - I \downarrow i)/mc^{12} \ (1 - \cos\theta) - I \downarrow i / [(E \downarrow 0 - I \downarrow i)/2 + E \downarrow 0 \ f^{2} - 2(E \downarrow 0 - I \downarrow i) E \downarrow 0 \ \cos\theta ]f^{1}/2}{I \downarrow i )f^{2} + E \downarrow 0 \ f^{2} - 2(E \downarrow 0 - I \downarrow i) E \downarrow 0 \ \cos\theta ]f^{1}/2}$ 



### IA Compton cross section: Compton profiles



Tabulated values of the Compton profiles can be found in literature: Biggs et al, 1975. It is important to underline that these values are for free electrons. The decomposition of a Compton profile into the contribution of the various shells shows that inner shell electrons, more tightly bound, have larger momenta, ranging from 0 to large numerical values. For outer shells, the Compton profile is peaked for the 0 value.



# IA Compton cross section: single shell and total

By integrating the tabulated values of the Hartree-Fock Compton profiles in Biggs et al. 1975, it is possible to derive the **single shell** Compton cross section for each shell of the element:

 $\frac{\sigma \downarrow i \downarrow IA = \pi r \downarrow e^{\uparrow 2} n \downarrow i \int 0 \uparrow \pi m KN(E \downarrow 0, E \downarrow p, \theta) \int -\infty \uparrow Q \downarrow i MAX m}{J \downarrow i (Q) dQ \sin \theta d\theta}$ 

And the **total** Compton cross section is:

 $\frac{\sigma \downarrow IA = \pi r \downarrow e^{\uparrow 2} \sum_{i=1} f_{shell number} n \downarrow i \int 0 \uparrow \pi KN(E\downarrow 0, E\downarrow p, \theta) \int -\infty \uparrow Q \downarrow iMAX J \downarrow i (Q) dQ \sin \theta d\theta$ 

Here  $\frac{KN(E\downarrow0, E,\theta) = (E/E\downarrow0) 12 (E/E\downarrow0 + E\downarrow0/E - \sin 12 \theta)}{\text{is the Klein-Nishina cross section}}$ 

and  $\frac{E\downarrow p = E\downarrow 0 / 1 + E\downarrow 0 / mc12 (1 - \cos\theta)}{\text{is the Compton peak energy}}$ 



## Single shell Compton cross sections



Ag - mass Compton scattering coefficient [cm2/g]



# XRF from Compton ionization: evaluation strategy

By replacing the IA single shell and total cross sections we obtain

 $\frac{\sigma \downarrow i \downarrow IA / \sigma \downarrow IA = n \downarrow i \int 0 \uparrow \pi \# KN(E \downarrow 0, E \downarrow p, \theta) \int -\infty \uparrow Q \downarrow i MAX \# J \downarrow i}{(Q) dQ \sin\theta d\theta / \sum i = 1 \uparrow shell number \# n \downarrow i \int 0 \uparrow \pi \# KN(E \downarrow 0, E \downarrow p, \theta) \int -\infty \uparrow Q \downarrow i MAX \# J \downarrow i (Q) dQ \sin\theta d\theta}$ 

Which replaces the crude constant approximation used by Pavlinski and Portnoy (G.V. Pavlinski and Yu. Pornoy, X-ray Spectrometry 43 (2014), 118-121)



# XRF from Compton ionization: evaluation strategy

The single shell Compton cross section is computed by means of a mixed procedure involving both the Waller-Hartree (WH) and the impulse (IA) approximations as:

$$\sigma_{C_i} = \left(\frac{\sigma_{C_i}{}^{IA}}{\sigma_{C}{}^{IA}}\right) \sigma_{C}{}^{WH}$$

This mixed procedure allows the computation of the single shell Compton cross section by preserving all the advantages of both the WH and the IA approximation:

- The IA approximation allows the computation of the Compton cross section for each shell starting from the single shell profiles data library from Biggs et al.<sup>[1]</sup>
- The WH approximation gives a better description of the cross section in the energy ranges close to the binding energies of the considered element

[1] Biggs, F.; Mendelsohn, L.B. and Mann, J.B. (1975), Hartree-Fock Compton profiles for the elements. Atomic Data and Nuclear Data Tables 16:210-309. doi:10.1016/0092-640X(75)90030-3



## XRF from Compton ionization: evaluation strategy

The single shell photoelectric cross section  $t_i$  is computed by using two different data libraries:

The EPDL97 Database from Cullen et al <sup>[1]</sup>

Allows a better description of the single shell photoelectric cross section

 The attenuation coefficient data tables and fitting functions from McMaster et al <sup>[2]</sup>

The ratio  $s_{Ci}/t_i$  is evaluated as a function of the primary photon energy E' for a fixed grid of energy values in the range 1 - 1000 keV for the K, L and M shells of all elements with Z = 11 - 92

[1]Cullen et al (1989), Tables and Graphs of Photon-Interaction Cross Sections from 10 eV to 100 GeV Derived from the LLNL Evaluated Photon Data Library (EPDL). Lawrence Livermore National Laboratory Report UCRL-5400, 6(A-B)

[2] McMaster et al. (1969), Compilation of X-ray cross-sections. Lawrence Livermore National Laboratory Report UCRL-50174, Sect. 2, Rev. 1.



# Single shell photoelectric-Compton cross section ratio

For all the shells from K to M5 it is assessed with good precision the atomic number at which the Compton interaction becomes the main process of ionization ( $s_{Ci}/t_i > 100\%$ ) within the energy range 1-150 keV

- $Z \le 17$  for the K shell
- $Z \le 29$  for the L1 shell
- $Z \le 48$  for the L2 shell
- $Z \le 52$  for the L3 shell
- $Z \le 44$  for the M1 shell
- $Z \le 62$  for the M2 shell
- $Z \le 68$  for the M3 shell
- $Z \le 92$  for the M4 shell
- $Z \le 92$  for the M5 shell

The obtained results show that the XRF contribution from Compton single shell ionization plays a relevant role in the description of the radiation field in X-ray spectrometry that up to now has been neglected



# Compton ionization kernel refinement

The kernel for the XRF from Compton ionization was introduced in the Boltzmann model as a correction of the emission kernel

The contribution due to Compton scattering can be added to the photoelectric cross section as a corrective term

$$\Delta k_{P_{E_i}}^{p \to p}(\vec{\omega}, E, \vec{\omega}', E') = \frac{1}{4\pi} \sum_{i=1}^{n_{e_i}} Q_{E_i}(E') f_{e_i}^C(E') \delta(E - E_i) \left[ \bigcup_{j \in I} (E' - E_j - I_i) \right]$$

Extent of the correction

$$f_{e_i}^C(E') = \frac{\sigma_{e_i}(E')}{\tau_{e_i}(E')}$$

Compton ionization occurs when the energy transferred to the electron  $(E\hat{l}' - E\hat{l}p)$ exceeds the binding energy of the shell  $I\hat{l}i$ 

A general parametric function capable of describing the energy dependences of the XRF correction from Compton ionization has been investigated



### Extent of the correction: Comptonphotoelectric cross section ratio

For each shell *i* (*K*, *L* and *M*) of all elements Z=11-92, it was computed the energy value E'(Z) for which the ratio  $s_{Ci}/t_i$  becomes equal to a given fixed percent value



## Extent of the correction: Comptonphotoelectric cross section ratio





### Conclusions on XRF from Compton ionization

□ The XRF emission due to Compton ionization was computed for the shells K, L1-L3 and M1-M5 of all elements with Z from 11 to 92

□ A new kernel which includes the XRF emission from Compton ionization has been introduced in the Boltzmann model

□ The energy to reach a given extent of the correction as a function of Z has been computed for the shells K, L1-L3 and M1-M5 (1, 5, 10, 20, 50, 100%)

□ It is demonstrated that the XRF contribution from single shell Compton ionization plays a role in the description of the radiation field in X-ray spectrometry, specially for L and M shells



# Minor contributions to the x-ray characteristic lines

#### 1) Compton ionization

- 2) Inner shell impact ionization
- 3) Self-absorbtion of the Lorentzian tail

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Radiation Physics and Chemistry

Detailed calculation of inner-shell impact ionization to use in photon (transport codes



Jorge E. Fernandez <sup>a,\*</sup>, Viviana Scot <sup>a</sup>, Luca Verardi <sup>b</sup>, Francesc Salvat <sup>c</sup>

#### **Research article**



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#### Electron contribution to photon transport in coupled photon-electron problems: inner-shell impact ionization correction to XRF

Jorge E. Fernandez,<sup>a</sup>\* Viviana Scot,<sup>a</sup> Luca Verardi<sup>b</sup> and Francesc Salvat<sup>c</sup>



# Electron contributions to photon transport

- The aim is to evaluate the contribution due to electrons to be included in photon transport codes without solving the complete coupled problem.
- The code PENELOPE (coupled electron-photon Monte Carlo) was used to study the effect of secondary electrons into the photon transport.
- An ad-hoc code KERNEL was developed to simulate a forced first collision at the origin of coordinates. We considered a point source of monochromatic photons.
- The physics of the interaction was described using the **PENELOPE** subroutine library.
- All the secondary electrons were followed along their multiple-scattering until their energy become lower of a predefinite threshold value.
- All photons produced by the electrons at every stage were accumulated.
- Polarization was not considered.



# **Electron-photon coupling**





Adopted solution

#### **Problem**

The solution of the coupled transport problem is very time consuming because electrons

interact continuously

**Possible Solution** 

<u>Compute an off-line corrective term</u> to the photon kernel which fully describes <u>the effect of secondary electrons in pure photon</u> <u>transport codes</u>

Bremsstrahlung

contributes a continuous distribution

Inner shell impact ionization (ISII)

modifies the intensity of the characteristic lines



# **Adopted Solution**

- The code PENELOPE<sup>[1]</sup> (coupled electron-photon Monte Carlo) is used to study the effect of secondary electrons into the photon transport
- PENELOPE uses refined hybrid techniques to describe the multiple scattering of electrons
- □ For Bremsstrahlung uses its own scaled differential cross sections data base generated from the original database of Seltzer and Berger<sup>[2] [3]</sup>
- □ The ad-hoc code KERNEL was developed to simulate a forced first collision at the origin of coordinates
- □ We consider a point source of monochromatic photons
- □ All the secondary electrons were followed along their multiple-scattering until their energy become lower of a predefinite threshold value
- □ All photons produced by the electrons at every stage were accumulated
- □ The ISII contribution have been computed for electrons generated by Compton interactions and photoelectric effect for all source shells

[1] F. Salvat, J.M. Fernandez-Varea, and J. Sempau, PENELOPE, a code system for Monte Carlo simulation of electron and photon transport, Nuclear Energy Agency (NEA), Paris 2008.

[2]Seltzer, S.M., Berger, M.J., 1985. Bremsstrahlung spectra from electron interactions with screened atomic nuclei and orbital electrons. Nucl. Instrum. Meth. B 12, 95–134.

[3]Seltzer, S.M., Berger, M.J., 1986. Bremsstrahlung energy spectra from electrons with kinetic energy 1 keV–10GeV incident on screened nuclei and orbital electrons of neutral atoms with Z ¼ 1–100. At. Data Nucl. Data Tables 35, 345–418.



Characterization of the correction





# Energy distribution for the ISII correction

- Since the electrons loose their energy more efficiently in the low energy range, the computed contribution is higher for low energy lines.
- To compute the correction for a generic energy the whole interval is divided into 5 energy regions.

	Region 5	4	3	Region 2	Region 1	1
1	keV E	E <sub>ab L3</sub> E	<sub>ab L2</sub> E	E <sub>ab L1</sub> E	<sub>ab K</sub> 150	keV

• The best fit of the energy correction at each energy region R is computed using a fitting model with 4 coefficients.

$$f_R(E) = \exp\left(\sum_{k=0}^3 \alpha_{kR} \ln(E)^k\right)$$



## Kernel correction due to inner shell impact ionization

$$\Delta k_{P_{E_i}}^{e \to p}(\vec{\omega}, E, \vec{\omega}', E') \Big|_{electron} = \frac{1}{4\pi} Q_{\lambda_i}(E') \Big|_{electron} \delta(E - E_i) U(E' - I_i)$$

• To avoid data-base differences between PENELOPE and other transport codes the electron correction  $f_{E_i}(E')|_{pe}$  is computed in units of the photon contribution  $Q_{E_i}(E')$ .

$$\Delta k_{P_{E_i}}^{e \to p}(\vec{\omega}, E, \vec{\omega}', E')\Big|_{electron} = \frac{1}{4\pi} \left[ f_{E_i}(E')\Big|_{ISII} Q_{E_i}(E') \,\delta(E - E_i) \,\mathrm{U}(E' - I_i) \right]_{ISII}$$

$$f_{E_i}(E')\Big|_{ISII} = \frac{Q_{E_i}(E')\Big|_{electron}}{Q_{E_i}(E')} \qquad \begin{array}{c} \text{Computed with} \\ \text{PENELOPE} \end{array}$$

$$Q_{E_i}(E') = \tau_{s,e_i}(E') p_{E_i}$$

• To compute the correction for a generic energy the whole interval is divided into 5 regions. The best fit of the energy correction at each energy interval requires 4 coefficients.

$$f_{E_i}(E')\Big|_{ISII} = \exp\left(\sum_{k=0}^3 \alpha_k \ln(E')^k\right)$$

### STUDIORUM On NOTOCA

### **ISII** correction on K-lines





### **ISII** correction on L-lines





### **ISII** correction on M-lines





Absolute value of the correction  $\Delta Q = Q_{corrected} - Q$ . has been computed for all lines of the elements with atomic number Z=1-92.



Q and  $Q_{corrected}$  for Al K $\alpha$ 1, as a function of the excitation energy (1-150 keV). Note that the y-axis is in logarithmic scale.

Absolute value of the correction  $\Delta Q = Q_{corrected}$ -Q. It is apparent that the correction is significant only within a restricted energy interval. It has maximum for excitation energy of 7 keV ( $\Delta Q$ /Q=3.4%). The vertical line near the left border represents the K edge.



Absolute value of the correction  $\Delta Q = Q_{corrected} - Q$ . has been computed for all lines of the elements with atomic number Z=1-92.





### $\Delta Q$ maximum (in % of Q ) as a function of Z





### Energy of the maximum as a function of Z

#### K lines (comprising K $\alpha$ 1, K $\alpha$ 2 and K $\beta$ 1





Absolute value of the correction  $\Delta Q = Q_{corrected} - Q$ . has been computed for all lines of the elements with atomic number Z=1-92.









### Energy of the maximum as a function of Z





### **Conclusions ISII contribution**

The inner shell impact ionization correction has been studied in terms of: spatial, angular and energy distribution.

It is shown that the correction is point wise and isotropic.

The energy dependence of the correction has been parameterized using 20 parameters (5 energy regions, 4 parameters each) for all K and L lines and few M lines for the elements Z=1-92 in the range of 1-150 keV.

The new kernel brings to deterministic or MC photon transport codes the effect of inner-shell impact ionization (ISII) computed off-line with the code PENELOPE.

The limited energy range where the absolute correction is relevant makes it this correction more relevant for monochromatic excitation than for polychromatic one.



# Minor contributions to the x-ray characteristic lines

### 1) Compton ionization

2) Inner shell impact ionization

3) Self-absorbtion of the Lorentzian tail

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#### Self-enhancement effects on XRF K-lines due to natural width

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Deterministic and Monte Carlo codes for multiple scattering photon transport

Jorge E. Fernández<sup>a,b,\*</sup>, Viviana Scot<sup>a</sup>



# The width of the atomic levels is responsible for the natural width of the lines



The widths of the atomic levels are the recommended values in Campbell and Papp, *At. Data and Nucl. Data Tables* **77**, 1–56 (2001)



### Lorentzian shape of the line





sometimes is used the Half Width at Half Maximum (HWHM)

$$\gamma_{E_{\ell}} = \Gamma_{E_{\ell}}/2$$



## **Emission of a Lorentzian K-line**





### Example for K-line (pure element) First order approx. (tail attenuation)





# Second order contribution (self-enhancement by the tail)



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### Transport kernel for a single Lorentzian line

$$k_{P_{E_i}}(\vec{\omega}, E, \vec{\omega}', E')\Big|_{L} = \frac{1}{4\pi} Q_{E_i}^*(E') \ell(E, E_i; \gamma_{E_i}) [1 - U(E - E_0)]$$
  
Emission probability  
with the previous  
modifications  

$$Q_{E_i}^*(E') = Q_{E_i}(E') \left\{ 1 + f_{E_i}(E') \right\}$$
  
Lorentzian  
distribution  

$$\ell(E, E_i; \gamma_{E_i}) = \frac{1}{\pi} (E - e^{-1})$$



# Discretization of the Lorentzian distribution (wavelength regime)

We define a new normalized distribution between the finite limits  $\left[-(2t+1)\gamma_i,(2t+1)\gamma_i\right]$ 

$$\ell_{\nu}(\lambda,\lambda_{i};\gamma_{\lambda_{i}}) = \frac{1}{\nu\pi} \frac{\gamma_{\lambda_{i}}}{\left(\left(\lambda-\lambda_{i}\right)^{2}+\gamma_{\lambda_{i}}^{2}\right)}$$

where  $V = \int_{\lambda_i - (2t+1)\gamma_i}^{\lambda_i + (2t+1)\gamma_i} \ell(\lambda, \lambda_i; \gamma_{\lambda_i}) d\lambda = \frac{2}{\pi} \arctan(2t+1)$ 

and use a discrete  $\delta\text{-expansion}$  for the Lorentzian

$$\ell_{v}(\lambda,\lambda_{i};\gamma_{\lambda_{i}}) = \sum_{k=-t}^{t} p_{k} \,\delta(\lambda - [\lambda_{i} + 2k\gamma_{i}])$$

with coefficients

$$p_{k} = \int_{\lambda_{i}+2k\gamma_{i}+\gamma_{i}}^{\lambda_{i}+2k\gamma_{i}+\gamma_{i}} \left(\lambda, \lambda_{i}; \gamma_{\lambda_{i}}\right) d\lambda$$
  
$$= \frac{1}{\nu\pi} \left[\arctan(2k+1) - \arctan(2k-1)\right] , \quad (k = -t..t)$$

 $2\gamma_i$ 

 $2t\gamma_i$ 



# Discretized kernel for the Lorentzian line (wavelength regime)

$$k_{P_{\lambda_{i}}}(\vec{\omega},\lambda,\vec{\omega}',\lambda')\Big|_{L} = \frac{1}{4\pi}Q_{\lambda_{i}}(\lambda')\sum_{k=-t}^{t}p_{k}\,\delta(\lambda-\lambda_{ik})[1-U(\lambda'-\lambda_{e_{i}})]U(\lambda-\lambda')$$
$$= \frac{1}{4\pi}Q_{\lambda_{i}}(\lambda')[1-U(\lambda'-\lambda_{e_{i}})]\sum_{k=k_{\min}}^{t}p_{k}\,\delta(\lambda-\lambda_{ik})$$

with

$$\lambda_{ik} = \lambda_i + 2k\gamma_i$$
$$k_{\min} = \max\left[-t, -\left|\frac{\lambda_i - \lambda'}{2\gamma_i}\right|\right]$$

(energy conservation cut-off)



### Primary XRF intensity of a Lorentzian line

The primary intensity of the line centered at the peak wavelength  $\lambda_i$  for an infinite thickness specimen is computed within an infinitely large acquisition window

$$I_{\lambda_{i}}^{(1)}(0,\vec{\omega})\Big|_{L} = \frac{I_{0}}{4\pi} \left|\eta\right| Q_{\lambda_{i}}(\lambda_{0}) [1 - U(\lambda_{0} - \lambda_{e_{i}})] \sum_{k=k_{0}}^{t} \frac{p_{k}}{\mu_{ik} |\eta_{0}| + \mu_{0} |\eta|}$$

where



 $\mu_{ik} = \mu(\lambda_{ik})$ 





### Secondary XRF intensity of a Lorentzian line

The secondary intensity of the line centered at the peak wavelength  $\lambda_i$  for an infinite thickness specimen is computed within an infinitely large acquisition window.









# Secondary fluorescence for Lorentzian contributions can be very asymmetric



Sometimes the asymmetry is large ...



# Conclusions for the Lorentzian shape contribution

✓When the Lorentzian tail crosses the edge, i.e. the energy of the emitted photon is high enough to produce another vacancy and, therefore, a selfenhancement effect.

✓ Since the high energy tail has always a low probability, this case requires refined variance reduction techniques in order to get significant results in MC codes.

✓The slow asymptotic decrease of the Lorentzian distribution introduces a further complication to describe multiple scattering with reasonable statistics.

 $\checkmark$  Therefore, is better to use either

- (a) a deterministic method based on the energy (wavelength) discretization of the Lorentzian distribution, or
- (b) an approximate analytical solution.



## Minor contributions: Final Conclusions

Minor contributions may give no negligible contributions to the intensity and the shape of the characteristic lines

All these minor contributions considered are **positive**, therefore they **sum-up giving a larger modification**.

By considering only the major contribution (photoelectric ionization) it is introduced a systematic error in the line intensity evaluation which makes it more difficult the comparison between experimental intensities and theoretical probablities.

This error increases with the number of minor contributions neglected.

The atomic parameters more affected by these errors are the line probabilities and the fluorescence yields.

This work puts together and sumarizes three corrections which can be added to MC and deterministic codes of photon transport.



# Summary of the contributions

Contribution	Туре	Origin	Main characteri stic	Lines more affected	MS
Photoelectric ionization	Major	Primary photon	Dominant effect	All	Increase the effect
Inner Shell Impact Ionization	Minor	Secondary electrons	Important with monochro matic excitation	low energy K, L, M lines	Increase the effect
Compton ionization	Minor	Primary photon	Depends on source polarization	L, M lines at medium- high source energy	Increase the effect
Self- enhancement	Minor	Secondary photon	Asymmetry of the line	Broader lines	Increase the effect



# Thanks for your attention

jorge.fernandez@unibo.it



ALMA MATER STUDIORUM Università di Bologna