IGOR PRO - selected applications

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Outline

Expression for an approximation Voigt profile
-application diatomic molecule and clusters

Post collision interaction (PCI)
in inner shell excitation-application fit-function

An expression for an approximation of the Voigt profile

Voigt integral

$$H(\alpha, v) = \frac{\alpha}{\pi} \int_{-\infty}^{\infty} \frac{e^{-y^2} dy}{(v - y)^2 + \alpha^2} \qquad (1)$$

The parameter α is defined as:

$$\alpha = \frac{\Gamma_L}{\Gamma_G} (\ln 2)^{\frac{1}{2}} \qquad (2)$$

Are the full widths at half maximum FWHM of the Lorentzian and Gaussian profiles

v is the dimensionless separation from the Voigtian line center

$$v = \frac{1}{\Gamma_G} 2(\nu - \nu_0)(\ln 2)^{\frac{1}{2}}$$

ν_0 is the frecuency at the line centre

an analytical expression with two fitting Voigtian parameters:

$$y = \frac{\left(2\, v \sqrt{\ln\ 2}\right)}{\Gamma_G}$$

the second one estimates the effective half-width w of Voigtian profile

$$\Gamma_G = 2\sqrt{2\ln 2}\,\sigma$$

Γ_V is FWHM of the Voigtian spectrum

$$w = (\ln\ 2)^{\frac{1}{2}} \frac{\Gamma_V}{\Gamma_G} \qquad (3)$$

Description of the method

The general theorem of convolution may be written as:

$$h(v) = \int_{-\infty}^{\infty} r(v - y)\, f(y)\, dy \qquad (4)$$

Where r(v-y) is the so-called resolution function and f(y) is the actual data distribution

- I will propose a general method for deconvoluting a function using a series expansion about y=v

- If the first n derivaties of f(y) on the real domain exist ,then eq.(4) may be written as:

$$h(v) = C_0 f(v) + \sum_{n=1}^{\infty} C_n \frac{f^n(v)}{n!} \qquad (5)$$

The following this method ,the first fewterms on the right hand side eq.(5) are good enough to approximate h(v),whenever the range of θ is so small that $r(\theta)$ has appreciable values $|\theta| << \xi$ where ξ is small.

The coefficients C_n are given by:

$$C_n = \int_{-\infty}^{\infty} \theta^n r(\theta) d\theta \qquad (6)$$

where $\theta = v - y$

Approximation of the Lorentzian-Gaussian profile convolution to third order

For the case of a Lorentzian –Gaussian convolution,the following expression is obtained:

$$H(v) = K \int_{-\infty}^{\infty} G(v - v') L(v') dv'$$

$K = \frac{1}{(\sqrt{\pi}\alpha)}$ normalization constant to be chosen so that this expression represent the Voigt integral (1)

$G(v - v')$ is a normalized Gaussian line of standard deviation σ

$G(\nu - \nu')$ is a normalized Gaussian line of standard deviation σ

Given by:

$$G(\nu - \nu') = \frac{1}{\sqrt{2\pi}\sigma} e^{-\left[\frac{(\nu-\nu')^2}{(2\sigma^2)}\right]}$$

$L(\nu')$ is the unnormalized Lorentzian line centred at frecuency ν_0

Given by:

$$L\left(v'\right) = \frac{1}{1 + \frac{\left(v' - v_0\right)^2}{\Delta^2}}$$

$\Delta = \frac{\Gamma_L}{2}$ being its half-width at half maximum

According to eq. (5) convolution may be written , keeping terms up to the third order in the ratio

$\frac{\sigma}{\Delta} << 1$ $\alpha >> \frac{1}{\sqrt{2}}$

$$H(\alpha,v)=\frac{\alpha}{\sqrt{\pi}}\frac{1}{\left(v^2+\alpha^2\right)}+\frac{\alpha}{2\sqrt{\pi}}\left[\frac{3v^2-\alpha^2}{\left(v^2+\alpha^2\right)^3}\right] \quad (8)$$

C_n coefficients of eq.(8) were obtained by using eq.(6):

$$C_0=1$$

$$C_1=0$$

$$C_2=\sigma^2$$

$$C_3=0$$

From eq.(8) the Voigtian height

$$H(\alpha,0)=\frac{1}{\sqrt{\pi}\alpha}\left(1-\frac{1}{2\alpha^2}\right)$$

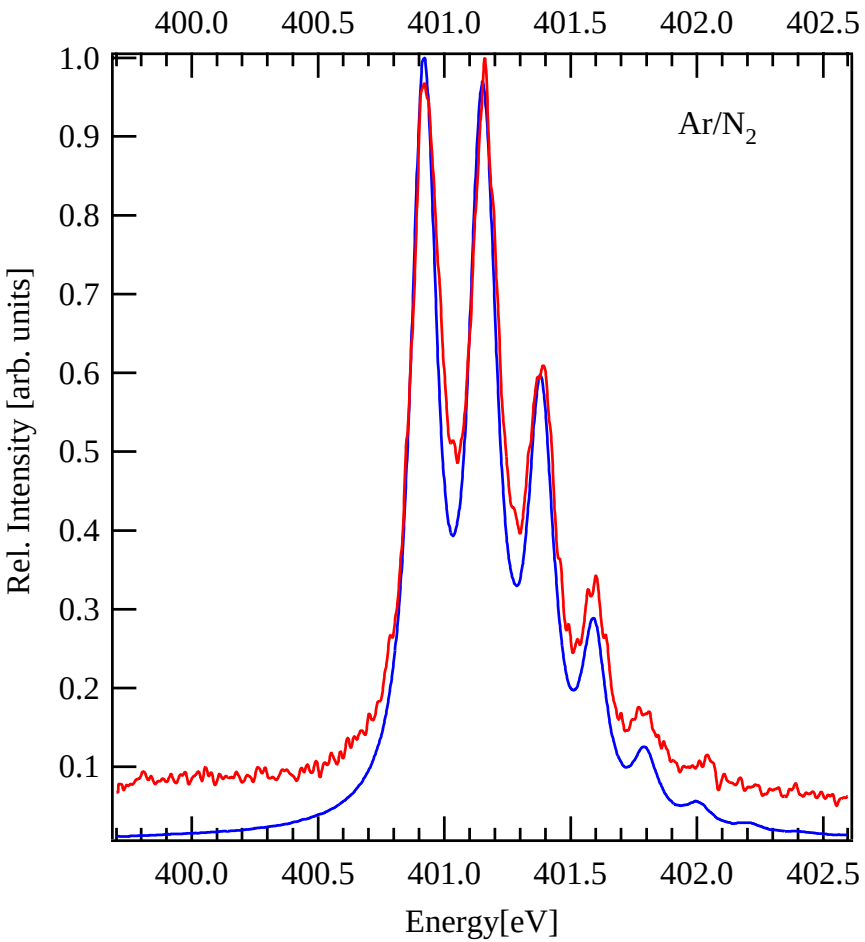
And its approximated half-width at half maximum w results to be:

$$w=\alpha\left(1+\frac{3}{4}\frac{1}{\alpha^2}\right)$$

Also ,the area under the curve(8) turns out to be equal to eq.(1)
The value of this area is $\sqrt{\pi}$

As becomes larger and larger ,the approximation given here produces heights and widths widths which approach the ones of the Voigt profile fast.

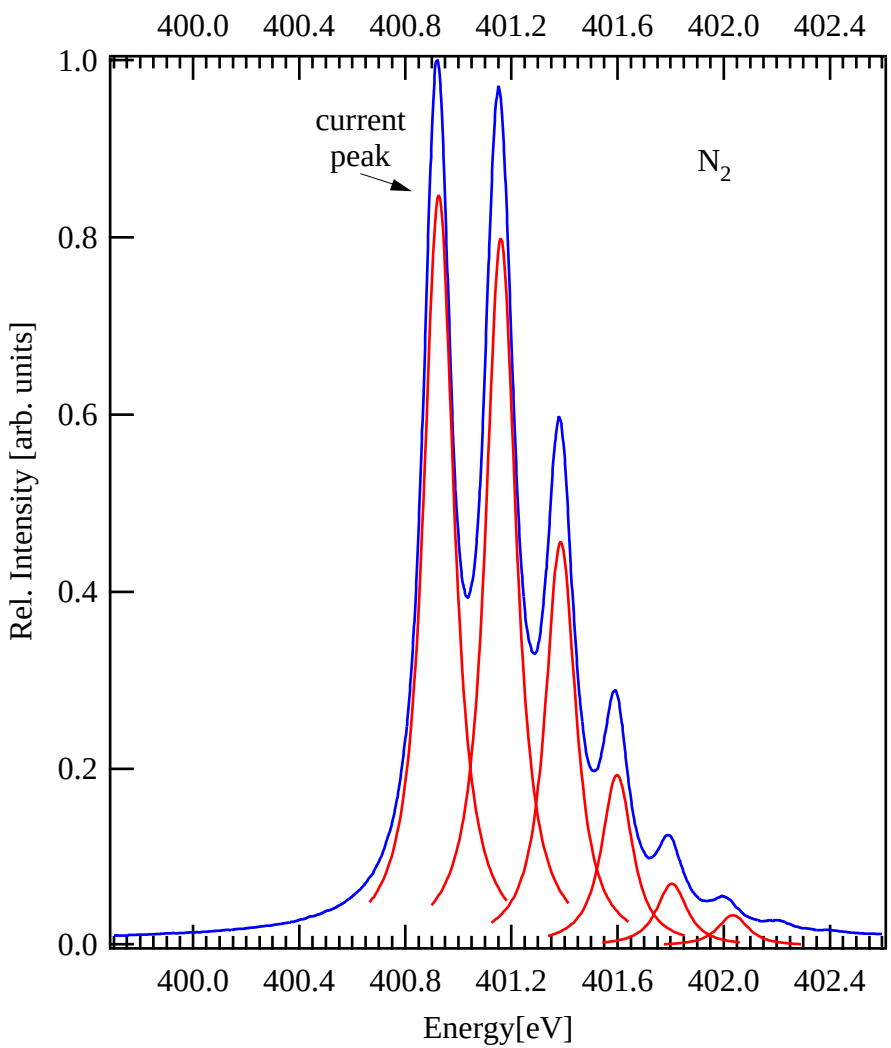
N 1s excitation of heterogeneous nitrogen clusters

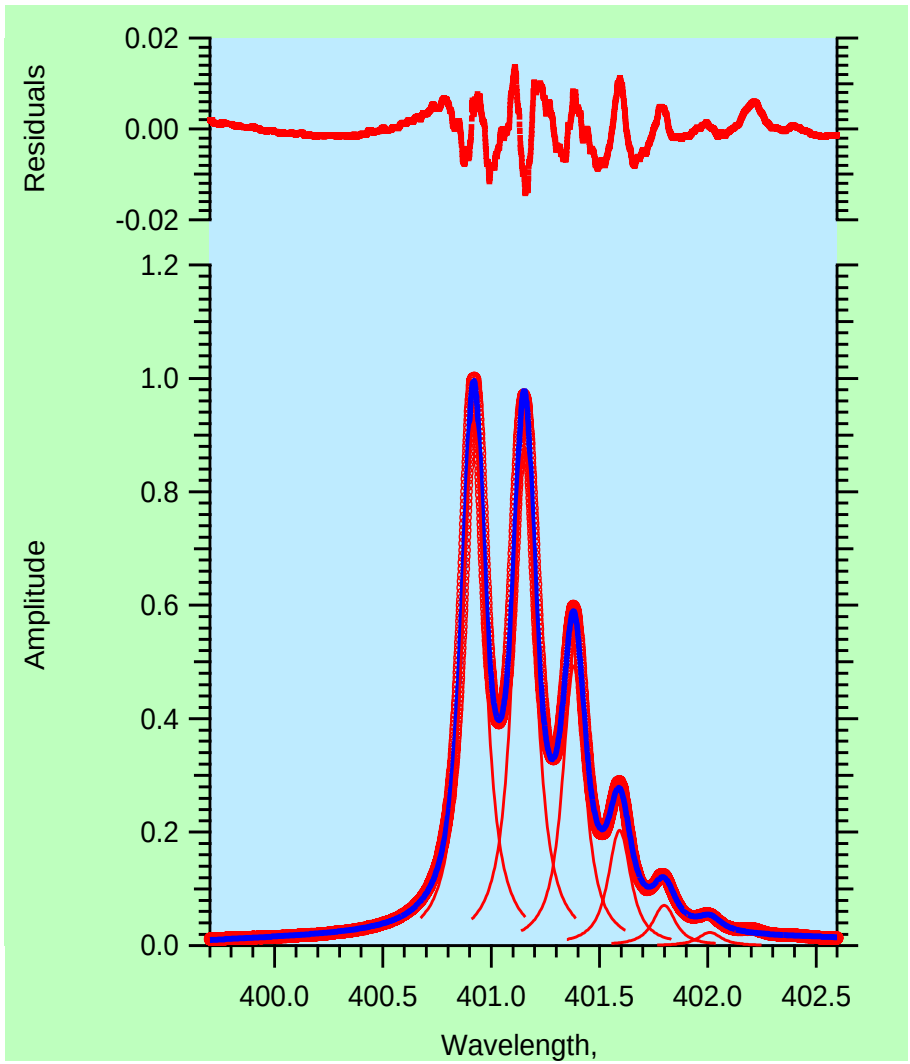


Comparison of the N 1 s- π^* transition of isolated nitrogen (blue) and heterogeneous Ar/N clusters(red) .

Voigt-fit

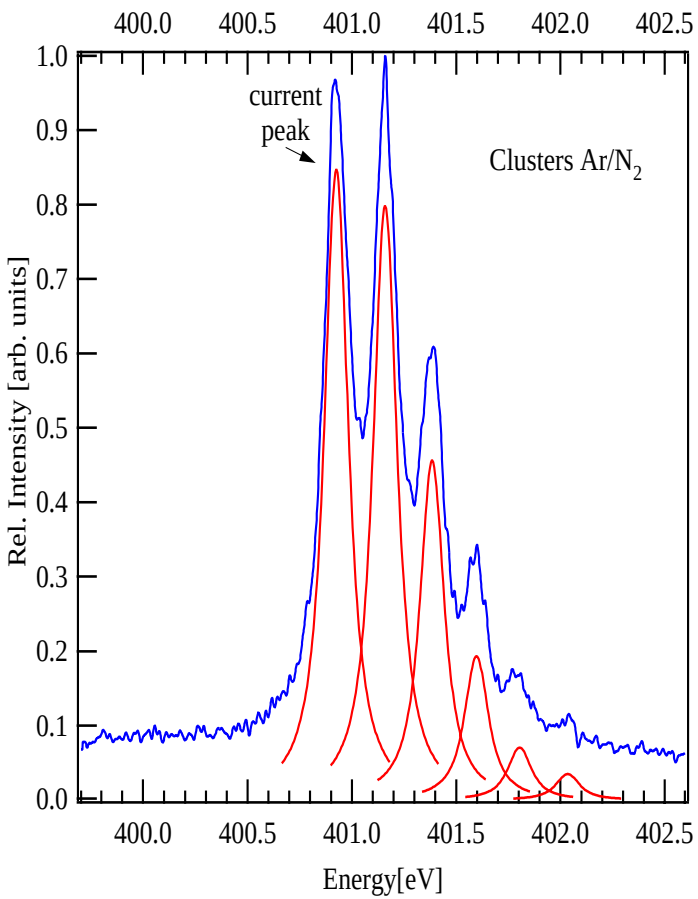
N_2

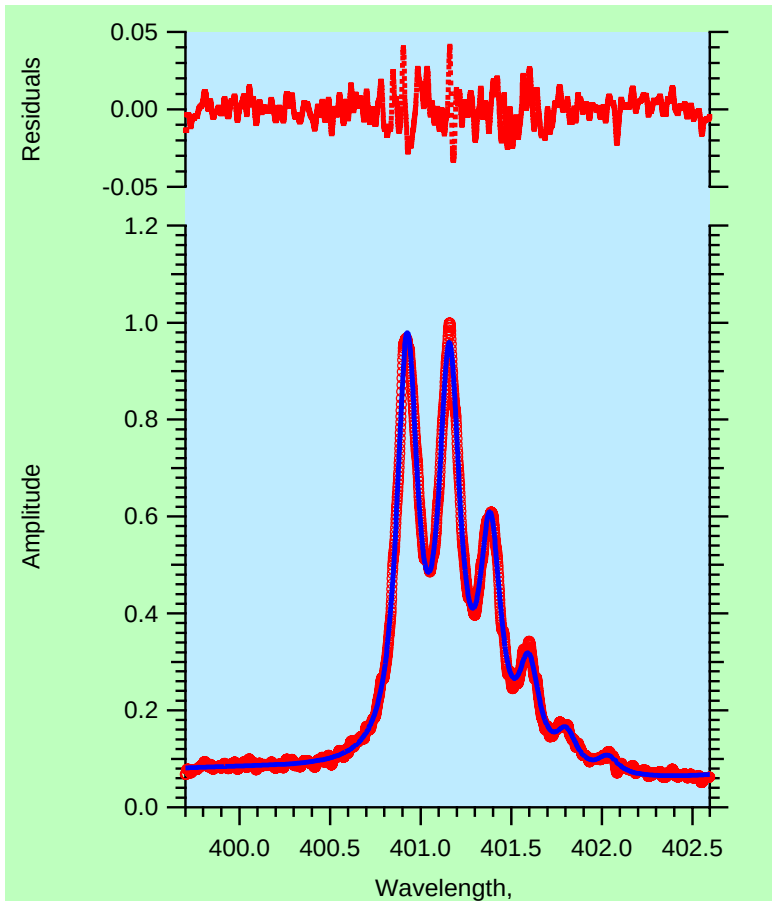

400.0
400.4
400.8
401.2
401.6
402.0
402.4
1.0
0.8
0.6
0.4
0.2
0.0
current
peak
N2
Rel. Intensity [arb. units]
Energy[eV]


Residuals
0.02
0.00
-0.02
Amplitude
1.2
1.0
0.8
0.6
0.4
0.2
0.0
400.0
400.5
401.0
401.5
402.0
402.5
Wavelength,

Voigt-fit gives the following results:

The width (FWHM) of vibrational bands increases from 123 meV in the isolated molecules to 130meV in heteroclusters.





Analysis of post-collision interaction in Auger processes following near-threshold inner-shell photo-ionization

Auger effect

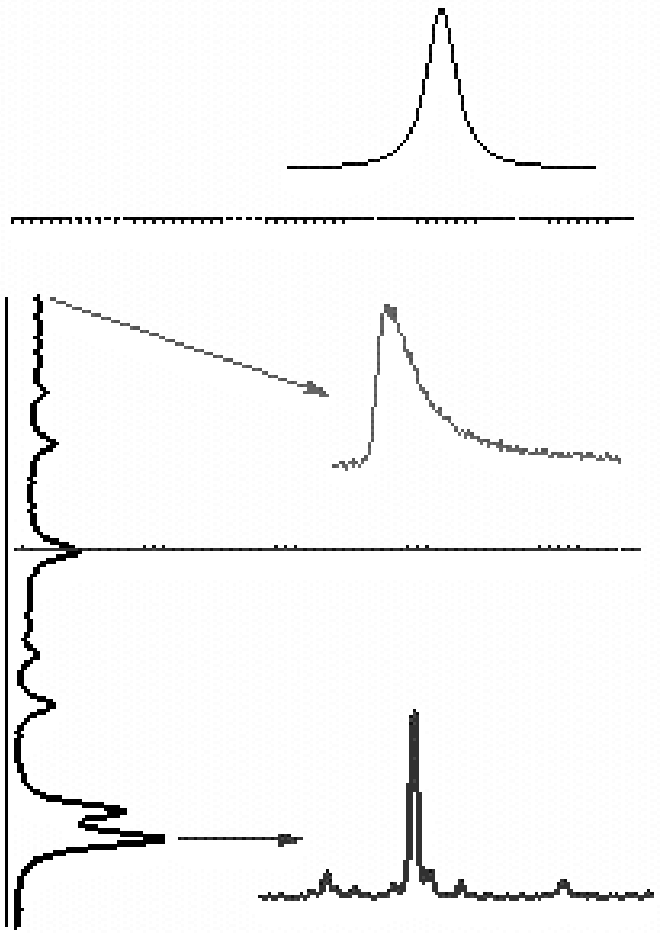
- Transition matrix element for one step Auger effects is described by time –independent scattering theory:

$$T_{\alpha\beta} = \langle \psi_\beta | H_{\text{int}} | \psi_\alpha \rangle + \sum_\tau \int \frac{\langle \psi_\beta | H - E | \psi_\tau \rangle \langle \psi_\tau | H_{\text{int}} | \psi_\alpha \rangle}{\hbar\omega - \hbar\omega_\tau + \frac{i\Gamma_\tau}{2}}$$

Direct ionization

Auger

Auger effect below/above ionization threshold



Normal Auger

$$E_{Auger} < h\nu - IP$$

+ Undisturbed Auger line shape

$$E_{Auger} > h\nu - IP > 0$$

Auger line shape is disturbed by the PCI

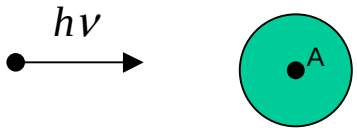
Resonant Auger

$$E_{Auger} > h\nu - IP < 0$$

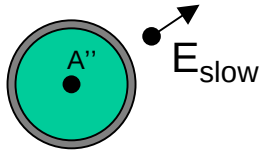
+shake up/ down

Post collision interaction process

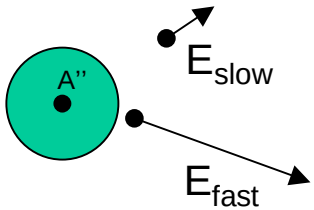
a) Inelastic collision (photo-ionization)



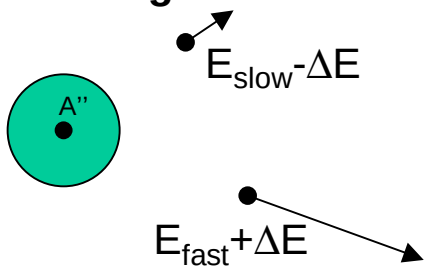
b) Excited atom

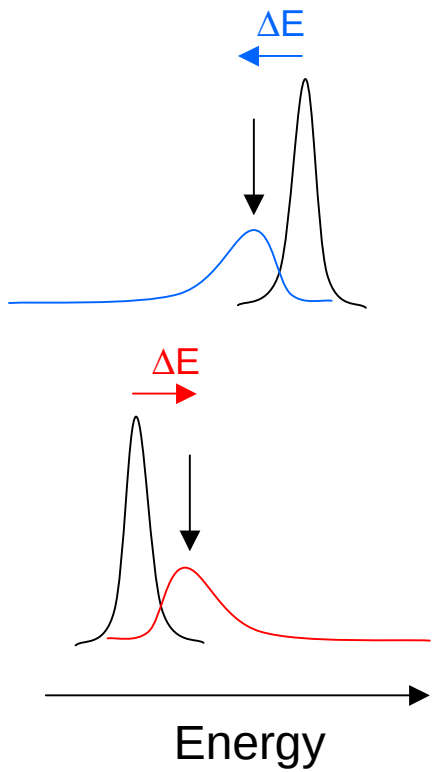


c) Auto-ionization (Auger effect)



d) Overtaking





After the photo-ionization ,the photoelectrons moves in the field of the singly ionized atom

After Overtaking the photoelectrons moves in the field of a doubly ionized atom and the Auger electron sees the field of the singly ionized atom.

ΔE =PCI (energy) shift

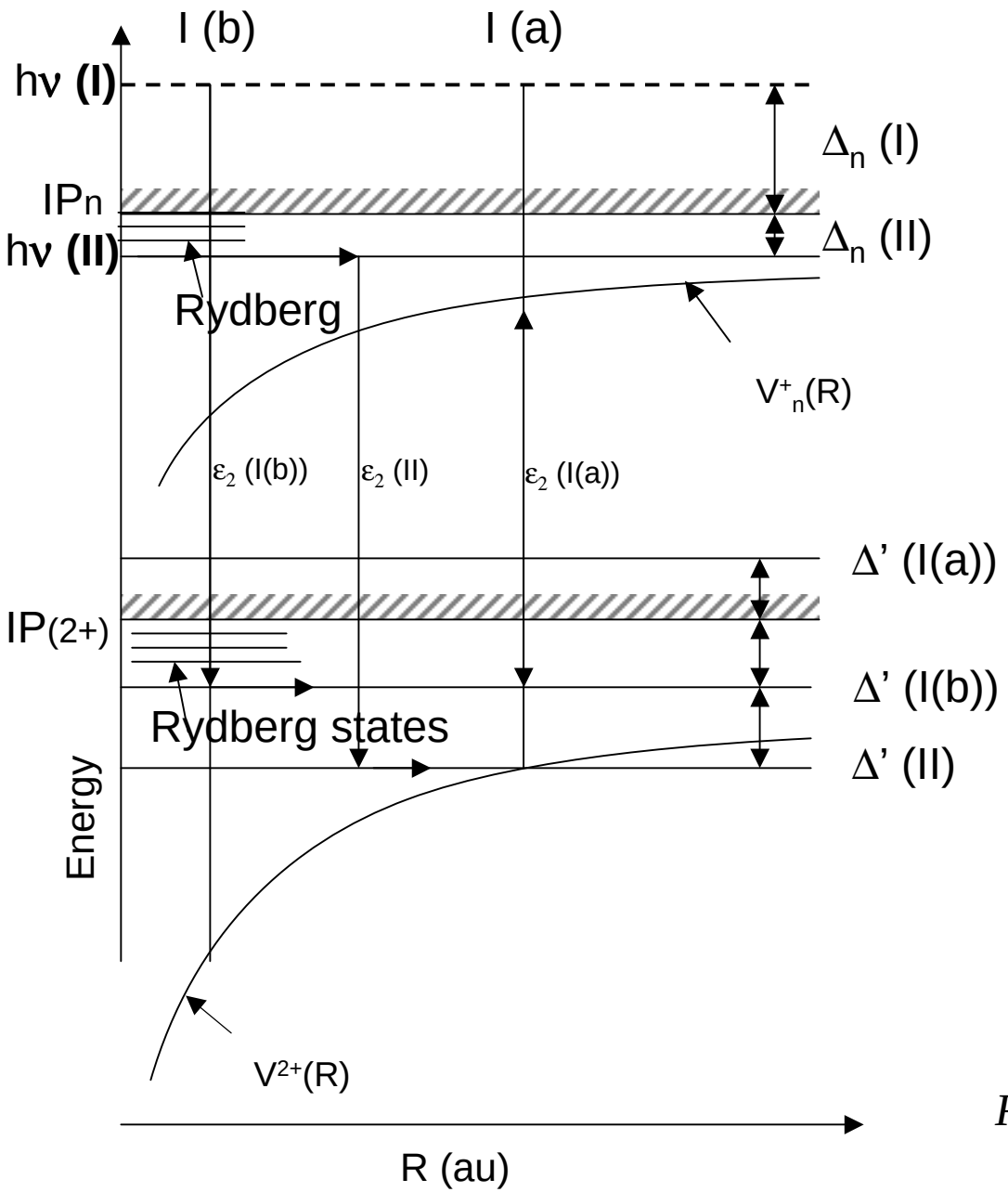
PCI occurs due to the relaxation of the system

PCI effects were for the first time observed by ion impact auto-ionization process.

$$A^{+} + B \rightarrow B^{**} + A^{+}\left(slow\right) \rightarrow B^{+} + e^{-}\left(\ fast\ \right)$$

Also been observed for the process of inner-shell ionization
Followed by Auger ejection of a fast electron.

$$h\nu + A \rightarrow A^{*+} + e^{-}(1)slow \rightarrow A^{**+} + e^{-}(\ fast\ )$$



$$\varepsilon_i^n = h\nu - V_n^+(R)$$

$$R \to \infty, Z = -1$$

$$\varepsilon_i^n \to \Delta_n = h\nu - IP_n$$

$$IP_n$$

$$Z = -2$$

$$\varepsilon_f(R) = h\nu - \varepsilon_2 - V^{2+}(R)$$

$$R \to \infty, \varepsilon_f(R) \to \Delta' = h\nu - \varepsilon_2 - IP(2+)$$

I would like to calculate the energy distribution for a system with certain lifetimes of the ions initially formed by inner-shell photo-ionization energy

found a method which is equivalent to calculating the transition amplitude with wave functions for a slow electron moving on the complex potential

$$V_n^{+}(R) - \frac{1}{2} i\Gamma \qquad (1)$$

- with kinetic energy Δ_n in the initial state ,and on $V^{2+}(R)$ with kinetic energy Δ' in the final state and again applying the stationary-phase approximation in the integration over distance.

-general expression which allows for the interferences between all contributions of processes leading to the final state characterized by detection of one electron of energy ε_2

-and one free electron of energy:

$$\Delta' = h\nu - \varepsilon_2 - IP(2+) \quad (2)$$

$$P(\varepsilon_2) = \left| A + \sum_n C_n(\varepsilon_2) \exp[-i\alpha(\varepsilon_2)] \right|^2 \quad (3)$$

A = population amplitude of a final state

In the present cases equally well as in the case of auto-ionization of a neutral atom in the presence of a slowly receding electron ,where
able to explain all observed details on the same level of approximation

The energy of Auger electron would have in the absence of PCI

$$\varepsilon_0^n = IP_n - IP(2+) \qquad (4)$$

- The amplitudes $C_n(\varepsilon_2)$

$$C_n(\varepsilon_2) = a_n(0)\exp\left(-\frac{t_*^{\,n}}{2\tau_n}\right)\left[2\tau_n^2\left(\Delta_n + \varepsilon_2 - \varepsilon_0^n\right)\right]^{-1/4}\left(\varepsilon_2 - \varepsilon_0^n\right)^{-1} \qquad (5)$$

where

$a_n(0)$ are the population amplitudes of the initial states by the inner -shell photo-ionization process

t_*^0 is given by:

$$t_*^n = \frac{1}{\sqrt{2}\Delta_n}\left\{\frac{\left(\varepsilon_2 - \varepsilon_0^n + \Delta_n\right)^{1/2}}{\varepsilon_2 - \varepsilon_0^n} - \frac{\left(E_a - \Delta_n\right)^{1/2}}{E_a} + \frac{1}{2\sqrt{\Delta_n}} \times \left[\ln\left(\frac{\left(\left(\varepsilon_2 - \varepsilon_0^n + \Delta_n\right)^{1/2} - \Delta_n^{1/2}\right)}{\left(\varepsilon_2 - \varepsilon_0^n + \Delta_n^{1/2}\right) + \Delta_n^{1/2}}\right) - \ln\left(\frac{\left(E_a + \Delta_n\right)^{1/2} - \Delta_n^{1/2}}{\left(E_a + \Delta_n\right)^{1/2} + \Delta_n^{1/2}}\right)\right]\right\}$$

(6)

and by: if $\Delta_n > 0$

$$t_*^n = \frac{1}{\sqrt{2}\Delta_n}\left\{\frac{\left(\varepsilon_2 - \varepsilon_0^2 + \Delta_n\right)^{1/2}}{\varepsilon_2 - \varepsilon_0^n} - \frac{\left(E_a - \Delta_n\right)^{1/2}}{E_a} + \frac{1}{\sqrt{-\Delta_n}} \times \left[\tan^{-1}\left(\frac{\varepsilon_2 - \varepsilon_0^n + \Delta_n}{-\Delta_n}\right)^{1/2} - \tan^{-1}\left(\frac{E_a + \Delta_n}{-\Delta_n}\right)^{1/2}\right]\right\}$$

(7)

If $\Delta_n < 0$

$E_a = 1\,\text{au}$ potential curves ,is of a order of a binding energies of electron to be ionized

Case I (a).

The photon energy is above the threshold IPn and ejected the electron energy ε_2 is smaller than $h\nu - IP(2+)$

The asymptotic energy of the slow electron is then positive ,so that in the final state one has a doubly ionized atom and two free electrons.

$$\Delta_n > 0, \Delta' = \Delta_n - \varepsilon_2 - \varepsilon_0^n > 0$$

In this case the Auger process leads to double ionization.

The phases are given by: $\alpha_n(\varepsilon_2) = I_1 - I_2$ (8)

$$I_1 = \sqrt{2}\left\{ \frac{1}{2\sqrt{\Delta_n}} \left[\ln\left(\frac{\left(E_a + \Delta_n\right)^{1/2} - \Delta_n^{1/2}}{\left(E_a - \Delta_n\right)^{1/2} + \Delta_n^{1/2}} \right) - \ln\left(\frac{\left(\varepsilon_2 - \varepsilon_0^n + \Delta_n\right)^{1/2} - \Delta_n^{1/2}}{\left(\varepsilon_2 - \varepsilon_0^n + \Delta_n\right)^{1/2} + \Delta_n^{1/2}} \right) \right] - \frac{\left(E_a + \Delta_n\right)^{1/2}}{E_a} \right\}$$

(9)

$$I_2 = \sqrt{2}\left\{ \frac{1}{\left[\Delta_n - \left(\varepsilon_n - \varepsilon_0^n\right)\right]^{1/2}} \left[\ln\left(\frac{\left(2E_a + \Delta_n - \left(\varepsilon_2 - \varepsilon_0^n\right)\right)^{1/2} - \left[\Delta_n - \left(\varepsilon_2 - \varepsilon_0^n\right)\right]^{1/2}}{\left[2E_a + \Delta_n - \left(\varepsilon_2 - \varepsilon_0^n\right)\right]^{1/2} + \left[\Delta_n - \left(\varepsilon_2 - \varepsilon_0^n\right)\right]^{1/2}} \right) - \ln\left(\frac{\left[\Delta_n + \left(\varepsilon_2 - \varepsilon_0^n\right)\right]^{1/2} - \left[\Delta_n - \left(\varepsilon_2 - \varepsilon_0^n\right)\right]^{1/2}}{\left[\Delta_n + \left(\varepsilon_2 - \varepsilon_0^n\right)\right]^{1/2} + \left[\Delta_n - \left(\varepsilon_2 - \varepsilon_0^n\right)\right]^{1/2}} \right) \right] - \frac{\left[2E_a + \Delta_n - \left(\varepsilon_2 - \varepsilon_0^n\right)\right]}{E_a} \right\}$$

(10)

Case I (b).

The photon energy is above the threshold ,but $\varepsilon_2 > h\nu - IP(2+)$
The final state in this case is an excited singly ionized (with the binding energy of the excited electron being $|\Delta'|$) and one free electron.

$$\Delta_n < 0; \Delta' = \Delta_n - \left(\varepsilon_2 - \varepsilon_0^n\right) < 0$$

In this case the slow electron is captured and bound by $|\Delta'|$ so that the Auger process leads to single ionization

$$\alpha_n\left(\varepsilon_2\right) = I_1 - I_3 \qquad (11)$$

$$I_3 = \sqrt{2}\left\{\frac{2}{\left[\left(\varepsilon_2 - \varepsilon_0^n\right) - \Delta_n\right]^{1/2}}\left[\tan^{-1}\left(\frac{2E_a}{\left(\varepsilon_2 - \varepsilon_0^n\right) - \Delta_n} + 1\right)^{1/2}\right] - \frac{\left[2E_a + \Delta_n - \left(\varepsilon_2 - \varepsilon_0^n\right)\right]^{1/2}}{E_a}\right\}$$

(12)

PCI phenomena should be describable by (3),(4),(5) with A=0
and only one contribution .

$$P(\varepsilon_2) = |C(\varepsilon_2)|^2 \qquad (13)$$

The shape and the position of this distribution depends on the lifetime and the excess energy .

$$t_*^{\,n} = \frac{1}{\sqrt{2}\Delta_n}\left\{\frac{\left(\varepsilon_2 - \varepsilon_0^n + \Delta_n\right)^{1/2}}{\varepsilon_2 - \varepsilon_0^n} - \frac{\left(E_a - \Delta_n\right)^{1/2}}{E_a} + \frac{1}{2\sqrt{\Delta_n}} \times \left[\ln\left(\frac{\left(\left(\varepsilon_2 - \varepsilon_0^n + \Delta_n\right)^{1/2} - \Delta_n^{1/2}\right)}{\left(\varepsilon_2 - \varepsilon_0^n + \Delta_n^{1/2}\right) + \Delta_n^{1/2}}\right) - \ln\left(\frac{\left(E_a + \Delta_n\right)^{1/2} - \Delta_n^{1/2}}{\left(E_a + \Delta_n\right)^{1/2} + \Delta_n^{1/2}}\right)\right]\right\}$$

A.Niehaus,J.Phys.B 10,1845(1977)

$$t_* = \frac{1}{2^{1/2}\Delta}\left\{\left(\frac{2}{\Delta}\right)^{1/2}(1+\Delta)^{1/2} - \frac{1}{2\Delta^{1/2}}\left[1.763 + \ln\left(\frac{(1+\Delta)^{1/2} - \Delta^{1/2}}{(1+\Delta)^{1/2} + \Delta^{1/2}}\right)\right]\right\}$$

P.A.Heimann,J.Phys.B 20,5005(1987)

Using semi-classical model ,calculate Auger line shapes with depends on the lifetime of a core hole state and excess photon energy above threshold.

Starting from eq.(3),(5),(6),(13) and setting the Auger energy shift equal to Δ because 0eV kinetic energy electrons are detected .

$$P(\Delta) = \frac{1}{2\tau\Delta^{\frac{5}{2}}} \exp(-\frac{t_*}{\tau})$$

$$t_* = \frac{1}{\sqrt{2}\Delta}\left\{\sqrt{\frac{2}{\Delta}}(\sqrt{1+\Delta}) - \frac{1}{2\sqrt{\Delta}}\left[1.763 + \ln\left(\frac{\left(\sqrt{1+\Delta}\right)-\sqrt{\Delta}}{\left(\sqrt{1+\Delta}\right)+\sqrt{\Delta}}\right)\right]\right\}$$

$$\Delta = h\nu - IP$$

(14)

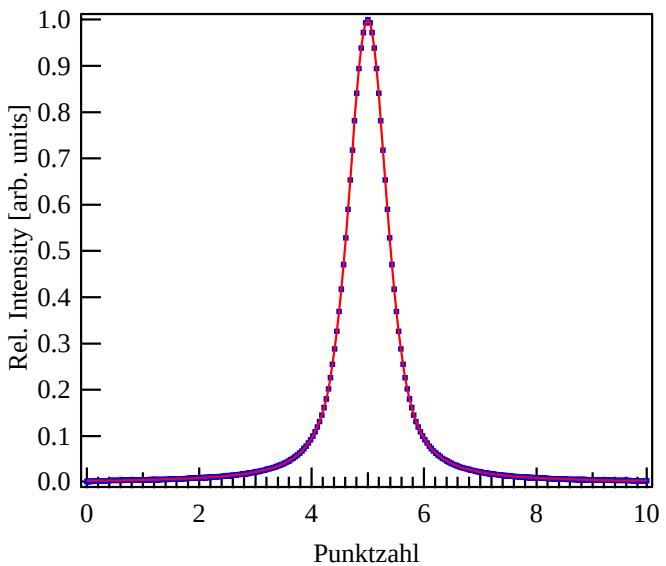
Convolution with a Gaussian

```
function gconv(wx, wy, w,sigma)
wave wx,wy,w
variable sigma

variable i,j,k,kmax,s,g
variable xi,xj,dx

kmax=numpnts(wx)-1
dx=wx[1]-wx[0]

k=-1
do
     k=k+1
     s=0
     i=-1
     do
          i=i+1
          j=i-k
          s=s+wy[i]*((2/sigma*dx)*
sqrt(ln(2)/pi))* exp(-(2*(j*dx)/sigma)^2*ln(2))
     while (j<kmax)
     w[k]=s
while (k<kmax)

end
```

- Igor implementation is similar to Fortran
- wx, wy: input wave x and y values
- sigma: FWHM of the Gaussian
- w: the result of the convolution
- The inner loop calculates the convolution at a given x value
- The outher loop iterates over the x values
- The Gaussian is normalized such that the sum over all x values is 1

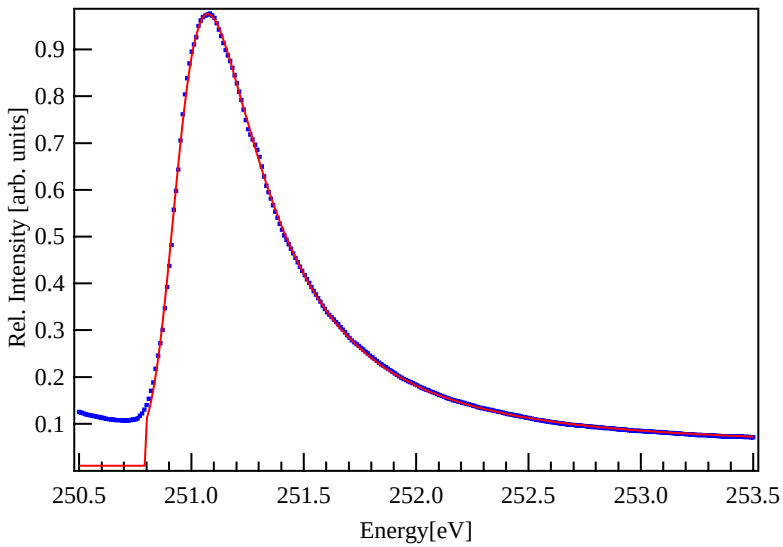
Convolution between Lorentzian and Gaussian function

```
#pragma rtGlobals=1                    // Use modern global access method.
Function lorxga(w,x) : FitFunc
wave w
variable x

variable result=0
variable lor=0
variable xi,xj,N
variable nh=0,ga,sga
variable sigma =w[3]

// we consider that the gaussiam is 0 outside of the [-deltax, deltax] range
// we will make the convolution only on this interval
// N is the number of sampling points, dx is the step for the x values
N=50
variable deltax=2.5*sigma
variable dx=2*deltax/N

// loop for calculating the convolution
// we only calculate the sum inside the cutoff region
sga=0
xi=x-deltax-dx
do
        xi=xi+dx
        xj=xi-x
        // we evaluate the nehaus function in xi and the gaussian in xj
        // in the way the ranges are choosen, abs(xj) < deltax

// lorentzian
        lor=w[2] * w[0]/(2*pi)/((xi - w[1])^2  + w[0]^2/4)

// gaussian
        ga= exp(-(2*xj/sigma)^2*ln(2))        // sigma=FWHM
        sga=sga+ga

// convolution
        result = result + lor*ga

while (xi<x+deltax+dx)

result=result/sga

return result

end
```



Convolution between Niehaus and Gauusian function

```
#pragma rtGlobals=1                    // Use modern global access method.
Function niehaus1ga(w,x) : FitFunc
wave w
variable x

variable result=0
variable result1,result1a,result1b,result1c,result1d,result1e,result1f,result1g,result1h


variable xi,xj,N
variable nh=0,ga,sga
variable sigma =w[3]

// we consider that the gaussiam is 0 outside of the [-deltax, deltax] range
// we will make the convolution only on this interval
// N is the number of sampling points, dx is the step for the x values
N=50
variable deltax=2.5*sigma
variable dx=2*deltax/N

// loop for calculating the convolution
// we only calculate the sum inside the cutoff region
sga=0
xi=x-deltax-dx
do
        xi=xi+dx
        xj=xi-x
        // we evaluate the nehaus function in xi and the gaussian in xj
        // in the way the ranges are choosen, abs(xj) < deltax

// compute niehaus
        if (xi-w[1]<=0)
                result1=0
        else
                result1a=(1/sqrt(4))*(1/(xi-w[1]))
                result1b=sqrt(2/(xi-w[1]))*sqrt(1+(xi-w[1]))
                result1c=1/(2*sqrt(xi-w[1]))
                result1d=sqrt(1+(xi-w[1]))-sqrt(xi-w[1])
                result1e=sqrt(1+(xi-w[1]))+sqrt(xi-w[1])
                result1f=1.763+ln(result1d/result1e)
                result1g=result1a*(result1b+result1c*result1f)
                result1h=1/(2*w[0]*(xi-w[1])^2.5)
                result1=result1h*exp(-(result1g/w[0]))
        endif

        nh=w[2]*result1

// the gaussian
        ga= exp(-(xj/sigma)^2)          // sigma='broadening'
//      ga= exp(-(2*xj/sigma)^2*ln(2))  // sigma=FWHM
        sga=sga+ga

// convolution
        result = result + nh*ga

while (xi<x+deltax+dx)

result=result/sga

return result

end


//Algorithmus folgt: Heimann et al., J. Phys. B 20, 5005 (1987)
```



Thank you for attention.