

Supporting information:
I4P : an *Igor Pro* suite for photoemission analysis

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Abstract

This supporting information gives the equations of the peak profiles $P(E)$ available in the *I4P* fit menu. Each peak is defined by:

- A : a scale or intensity factor which corresponds to the integrated peak area only for symmetric profiles (such as gaussian or lorentzian);
- E_0 : the peak central value (in eV) which matches with the peak maximum and centroid for symmetric profiles;
- FWHM : the characteristic peak width (in eV) which is the actual Full-Width at Half-Maximum only for symmetric profiles.

Nevertheless, actual peak maximum positions, FWHMs and areas over the fit range are given in the fit report. In what follows, the following notations are used:

- E : binding energy (in eV);
- $\Gamma(x)$: Gamma function;
- $\text{Erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(-t^2) dt$: complementary error function;
- $\Theta_H(x)$: the Heaviside function [$\Theta_H(x) = 0$ if $x < 0$; $\Theta_H(x) = 1$ if $x > 0$];
- $\text{sign}(x)$: the sign function ($\text{sign}(x) = -1$ if $x < 0$; $\text{sign}(x) = +1$ if $x > 0$);
- \otimes : convolution product.

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- Lorentzian:

$$P_{\text{Lorentz}}(E) = \frac{1}{\pi} \frac{A\sigma}{(E - E_0)^2 + \sigma^2}$$

with FWHM = 2σ (1)

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- Gaussian:

$$P_{Gauss}(E) = \frac{A}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right]$$

with $\text{FWHM} = 2\sqrt{2\ln(2)}\sigma$ (2)

- Voigt:

$$P_{Voigt}(E) = P_{Gauss}(E) \otimes P_{Lorentz}(E) \quad (3)$$

- Pseudo-Voigt:

$$P_{Pseudo-Voigt}(E) = \eta P_{Gauss}(E) + (1-\eta)P_{Lorentz}(E)$$

with $\text{FWHM}_{Lorentz} = \text{FWHM}_{Gauss} = \text{FWHM}$
 $0 \leq \eta \leq 1$ (4)

η is the mixing ratio ($0 \leq \eta \leq 1$).

- Lorentzian-Gaussian product:

$$P_{LorXGauss}(E) = \frac{A\sigma_L}{\pi \exp\left[\frac{\sigma_L^2}{2\sigma_G^2}\right] \text{Erfc}\left[\frac{\sigma_L}{\sqrt{2}\sigma_G}\right]} \frac{\exp\left[-\frac{(E-E_0)^2}{2\sigma_G^2}\right]}{(E-E_0)^2 + \sigma_L^2}$$

with $\text{FWHM}_L = 2\sigma_L, \text{FWHM}_G = 2\sqrt{2\ln(2)}\sigma_G$ (5)

- Oscillator:

$$P_{Oscillator}(E) = \frac{A_L}{\pi} \frac{4E_0^2\sigma}{(E^2 - E_0^2)^2 + \sigma_L^2 E^2}$$

with $\text{FWHM} = \sigma_L$ (6)

- Doniach-Sunjic [1]:

$$P_{Doniach-Sunjic}(E) = \frac{1}{\pi} \frac{A\Gamma[1-\alpha]}{[(E-E_0)^2 + \sigma^2]^{(1-\alpha)/2}} \cos\left[\frac{\pi\alpha}{2} - (1-\alpha) \arctan\left(\frac{E-E_0}{\sigma}\right)\right]$$

with $\text{FWHM} = 2\sigma; 0 \leq \alpha < 1$ (7)

α is the asymmetry parameter ($\alpha = 0$ for a pure Lorentz function).

- Generalized Doniach-Sunjic:

$$P_{GenDoSu}(E) = \frac{2\mu\sigma A}{\pi^2(\mu+2)} \frac{\frac{\pi}{2} + \frac{\pi}{\mu} + \arctan(\frac{E}{\sigma})}{[(E-E_0)^2 + \sigma^2]^\gamma}$$

with $\text{FWHM} = 2\sigma; \gamma > 0; \mu > 0$ (8)

γ, μ are asymmetry parameters ($\gamma = 1; \mu = 0$ for pure Lorentz function).

- Mahan [2]:

$$P_{Mahan}(E) = \left\{ \frac{A}{\xi^\alpha \Gamma(\beta)} (E - E_0)^{\beta-1} \exp \left[-\frac{E - E_0}{\xi} \right] \right\} \otimes P_{Lorentz}(E)$$

with $\text{FWHM} = \text{FWHM}_{Lorentz}; \beta > 0; \xi > 0$ (9)

α, β are the asymmetry parameters of the Mahan peak and ξ its width ($\xi \rightarrow +\infty$ for Doniach-Sunjic with $\alpha = \beta$).

- Post-collision interaction [3]:

$$P_{PCI}(E) = \frac{1}{\pi} \frac{A\sigma}{[(E - E_0 + \delta\sigma)^2 + \sigma^2]} \times \exp \left[2\delta \arctan \left(\frac{E - E_0 + \delta\sigma}{\sigma} \right) \right]$$

with $\text{FWHM} = 2\sigma; \delta \geq 0$ (10)

δ is the asymmetry parameter ($\delta = 0$ for pure Lorentz function).

- Asymmetric Voigt:

$$P_{Asym-Lorentz}(E) = \frac{A}{\pi(\sigma_1 + \sigma_2)} \left\{ \frac{[1 + \text{sign}(E - E_0)]\sigma_1^2}{(E - E_0)^2 + \sigma_1^2} + \frac{[1 - \text{sign}(E - E_0)]\sigma_2^2}{(E - E_0)^2 + \sigma_2^2} \right\}$$

with $\text{FWHM}_{HighBE} = 2\sigma_1; \text{FWHM}_{LowBE} = 2\sigma_2$ (11)

- Asymmetric pseudo-Voigt [4]:

Same as Eq. 4 with (12)

$$\text{FWHM}_{Pseudo-Voigt} = \frac{2FWHM}{1 + \exp[-\epsilon(E - E_0 - E_{sf})]}; \epsilon \geq 0$$

ϵ is asymmetry parameter of the asymmetric pseudo-Voigt ($\epsilon = 0$ for pure Lorentz function) and E_{sf} the sigmoidal shift.

- Step functions (Fermi edge and secondary electron cut off):

$$P_{step}(E) = \frac{H_s}{2\text{Erfc}\left(-\frac{E-E_0}{\sigma_{Erf}}\right)} + H_s \left[\frac{1}{2} + \frac{1}{\pi} \arctan \left(\frac{E - E_0}{\sigma_{arctan}} \right) \right] + \frac{H_s}{1 + \exp\left(-\frac{E-E_0}{k_B T}\right)}$$

(13)

with:

$$\sigma_{Erf} = \text{FWHM}_{Erf}/2\sqrt{\ln 2}; \sigma_{arctan} = 2\sqrt{\pi \ln 2} \text{FWHM}_{Arctan}.$$

The following background decay is further applied to this step function:

$$P_{step}(E) \times \exp \left[-\frac{E - E_0}{\lambda_d} \right] \times [1 + B_s(E - E_0) + C_s(E - E_0)^2 + D_s(E - E_0)^3].$$

H_s is the step height times the number of functions with FWHMs different from zero, $k_B T$ the Boltzmann constant times temperature (K), λ_d the exponential decay coefficient of the step function and B_s, C_s, D_s the polynomial coefficients of the step function decay.

- Fano:

$$P_{Fano}(E) = \frac{A\sigma}{\pi(1+q^2\sigma^2)} \frac{(E-E_0+q\sigma)^2}{(E-E_0)^2+\sigma^2}$$

with FWHM = 2σ ; $q = \frac{1-\nu}{\nu}$; $-1 < \nu < 1$ (14)

- Plasmon [5]:

$$P_{Plasmon}(E) = \frac{A}{\pi} \frac{1}{\frac{a}{1-a} + e^b - 1} \sum_{n=1}^{\infty} \left[a^n + \frac{b^n}{n!} \right] \frac{\sigma_0 + n\sigma_P}{(E-E_0 - nE_P)^2 + (\sigma_0 + n\sigma_P)^2}$$

with FWHM = 2σ ; $0 \leq a < 1$; $0 \leq b < 1$ (15)

E_P is the plasmon energy (eV), σ_P its width (eV), a_P its extrinsic damping and b_P its intrinsic damping.

- Lorentzian band bending [6]:

$$P_{BandBending}(E) = \frac{1}{\lambda_{bb}} \int_0^{+\infty} \exp(-z/\lambda_{bb}) P_{Lorentz}[E_0(z)] dz$$

$$E_0(z) = E_0 - eV_{bb} \left[1 - \frac{z}{W} \right]^2 \quad \text{if } z < W$$

$$E_0(z) = E_0 \quad \text{if } z > W$$

$W > 0$; $\lambda_{bb} > 0$ (16)

V_{bb} is the band bending amplitude (V), W the width of the space charge layer (\AA) and λ_{bb} the escape depth of the photoelectron (\AA).

- Gadzuk-Sunjic [7]:

$$P_{Gadzuk-Sunjic}(E) = \frac{A}{\pi} \left(\frac{1}{\eta_c^2} + \frac{1}{\omega_c^2} \right)^{\alpha/2} \exp\left(-\frac{E-E_0}{\eta_c}\right) \frac{\Gamma(1-\alpha)}{[(E-E_0)^2 + \sigma^2]^{(1-\alpha)/2}} \cos\theta$$

$$- \eta_c^{\alpha-1} \delta P(E-E_0)$$

$$\theta = (1-\alpha) \arctan\left(\frac{E-E_0}{\sigma}\right) - \frac{1}{2}\pi\alpha - \frac{\sigma}{\eta_c}$$

$$\delta P(E-E_0) = A \cos(\sigma/\eta_c) - B \sin(\sigma/\eta_c)$$

$$A = \int_0^1 z^{-\alpha} \exp\left(z\frac{E-E_0}{\eta_c}\right) \sin(z\sigma/\eta_c) dz$$

$$B = \int_0^1 z^{-\alpha} \exp\left(z\frac{E-E_0}{\eta_c}\right) \cos(z\sigma/\eta_c) dz$$

with FWHM = 2σ ; $0 \leq \alpha \leq 1$; $0 < \eta_c$; $0 < \omega_c$ (17)

η_c is the damping amplitude of the core hole potential and ω_c the cut-off amplitude of the order of the Fermi energy.

- Peak pair due to spin-orbit splitting:

$$\begin{aligned} P_{pair}(E) &= P(E) + B_r P(E + E_{so}) \\ B_r &> 0; E_{so} > 0 \end{aligned} \quad (18)$$

where E_{so} is the spin-orbit splitting and B_r the branching ratio.

- Gaussian broadening of $P(E)$:

$$P_{GaussBroad}(E) = P_{Gauss}(E) \otimes P(E) \quad (19)$$

- Polynomial background:

$$B_{pol}(E) = A_p + B_p \Delta E + C_p \Delta E^2 + D_p \Delta E^3 \quad \text{with} \quad \Delta E = E - \langle E \rangle \quad (20)$$

The polynomial background is defined on the middle of the binding energy range $\langle E \rangle$ to prevent divergence during fit of coefficients A_p, B_p, C_p, D_p .

- Shirley background [8]:

$$B_{Shirley}(E) = S_h \int_{E_0}^E P^*(E') dE' \quad (21)$$

where $P^*(E) = P(E) - P(E_0)$ with E_0 is chosen on the low binding energy side of the peak [9, 10].

- Generalized Shirley background [11]:

$$\begin{aligned} B_{GenShir}(E) &= S_h \int_{E_0}^E P^*(E') dE' + S_l \int_{E_0}^E dE' \int_{E_0}^{E'} P^*(E'') dE'' \\ &+ S_c \int_{E_0}^E dE' \int_{E_0}^{E'} dE'' \int_{E_0}^{E''} P^*(E''') dE''' \end{aligned} \quad (22)$$

Same definitions as for the Shirley background.

- Two or three parameters Tougaard background [12]:

$$\begin{aligned} B_{Tougaard}(E) &= \int_{E_0}^E \lambda_i K(E - E') M^*(E') dE' \\ \text{or} \quad \lambda_i K(T) &= \frac{B(T - G)}{[C + (T - G)^2]^2} \Theta_H(T - G) \\ \text{or} \quad \lambda_i K(T) &= \frac{B(T - G)}{[C - (T - G)^2]^2 + D(T - G)^2} \Theta_H(T - G) \end{aligned} \quad (23)$$

$M^*(E) = P(E) - P(E_0)$ is the measured spectrum *i.e.* the sum of the intrinsic peak and inelastic background $M(E) = P(E) + B(E)$ [9, 10]. When only the intrinsic peak $P(E)$ is known as in case of simulation/fit, $B_{Tougaard}$ is calculated iteratively [9, 10] up to a relative accuracy of 0.005. B, C, D parameters for selected materials can be found in Refs. [12, 13] (for universal background $B \simeq 3006 \text{ eV}^2$, $C = 1643 \text{ eV}^2$). G is the material gap.

- Distorted Shirley [9, 14]:

$$B_{DistortedShirley}(E) = \int_{E_0}^E \lambda_i K(E - E') M^*(E') dE' \quad (24)$$

$$\text{with } \lambda_i K(T) = \frac{B [1 - \exp[-D(T - G)]]}{C + (T - G)^2} \Theta_H(T - G)$$

Same remark as for the Tougaard background.

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