

# Hybridization effects in 4*f* systems as observed by photoemission spectroscopy

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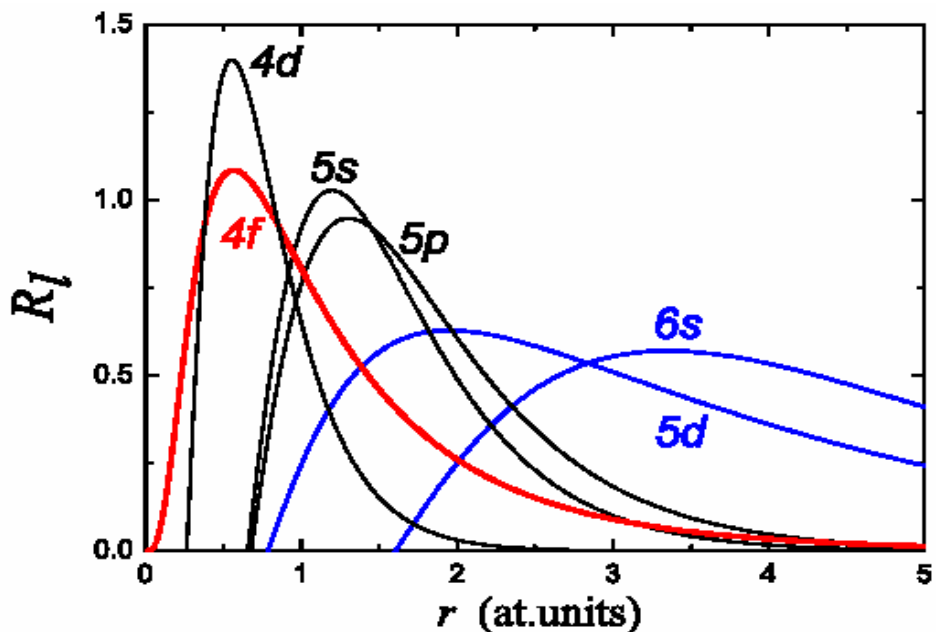
**Experiment**

# Outline

1. Introduction
2. Single-impurity Anderson model
  - Gunnarsson-Schönhammer approach
  - Spectral density for  $f$  emission
3. Resonant photoemission: interference of excitation channels
4. Simple model: analytic solution
5. PES of rare-earth – transition-metal compounds
6. Angle-resolved PES and simplified periodic Anderson model

## Rare-earth atoms:

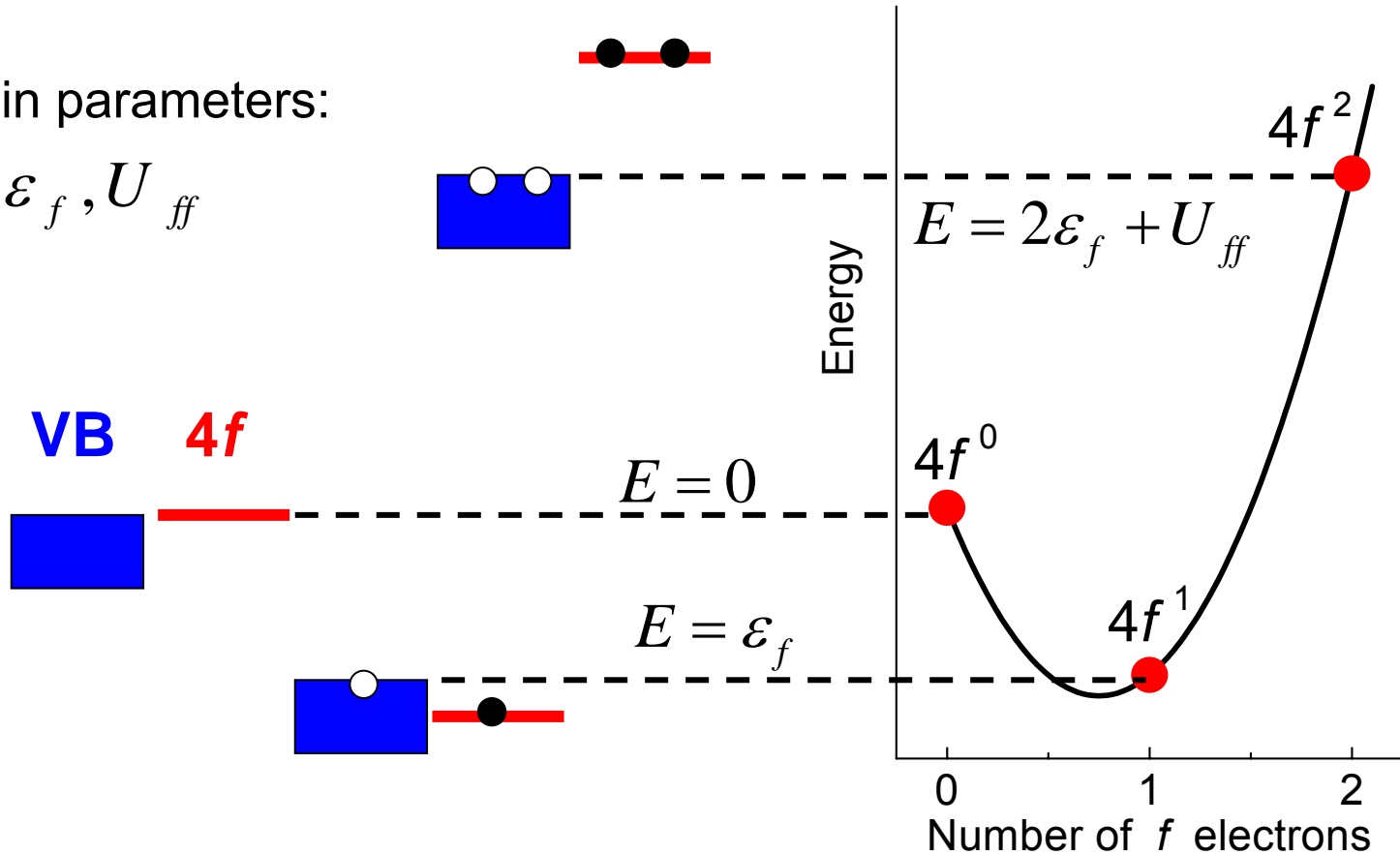
strongly localized  $4f$  levels +  
extended VB ( $5d, 6s$ ) states



# $4f^n$ configurations in Ce

Main parameters:

$$\varepsilon_f, U_{ff}$$



# Single-impurity Anderson model

$$\text{Hamiltonian: } H = H_{VB} + H_f + H_{\text{int.}}$$

$$H_{VB} = \sum_{\mathbf{k}, \sigma} \varepsilon_{\mathbf{k}} d_{\mathbf{k}\sigma}^+ d_{\mathbf{k}\sigma},$$

$$H_f = \varepsilon_f \sum_{m\sigma} f_{m\sigma}^+ f_{m\sigma} +$$

$$+ \frac{U_{ff}}{2} \sum_{mm', \sigma\sigma'} f_{m\sigma}^+ f_{m\sigma} f_{m'\sigma'}^+ f_{m'\sigma'},$$

$$H_{\text{int.}} = \sum_{\mathbf{k}m\sigma} V_{\mathbf{k}m} (d_{\mathbf{k}\sigma}^+ f_{m\sigma} + f_{m\sigma}^+ d_{\mathbf{k}\sigma})$$

*Localized degenerated  
4f state in the sea of  
valence electrons*

-- the valence-band states are transformed to **the same symmetry representation** as the 4*f* states:

$$|\varepsilon m \sigma\rangle = \frac{1}{V_m(\varepsilon)} \sum_{\mathbf{k}} V_{\mathbf{k}m} \delta(\varepsilon - \varepsilon_{\mathbf{k}}) |\mathbf{k} \sigma\rangle$$

These states are orthogonal to each other if  $\sum_{\mathbf{k}} V_{\mathbf{k}m}^* V_{\mathbf{k}m'} \delta(\varepsilon - \varepsilon_{\mathbf{k}}) = |V_m(\varepsilon)|^2 \delta_{mm'}$

-- VB states are discretized in  $N$  degenerated energy states (labeled by the index  $i$ )

-- assumption:  $V_m(\varepsilon) \rightarrow V(\varepsilon_i) \equiv V_i$

$$\longrightarrow H = \sum_{i=1}^N \sum_{\nu=1}^{N_f} \varepsilon_i d_{i\nu}^+ d_{i\nu} + \varepsilon_f \sum_{\nu=1}^{N_f} f_{\nu}^+ f_{\nu} +$$

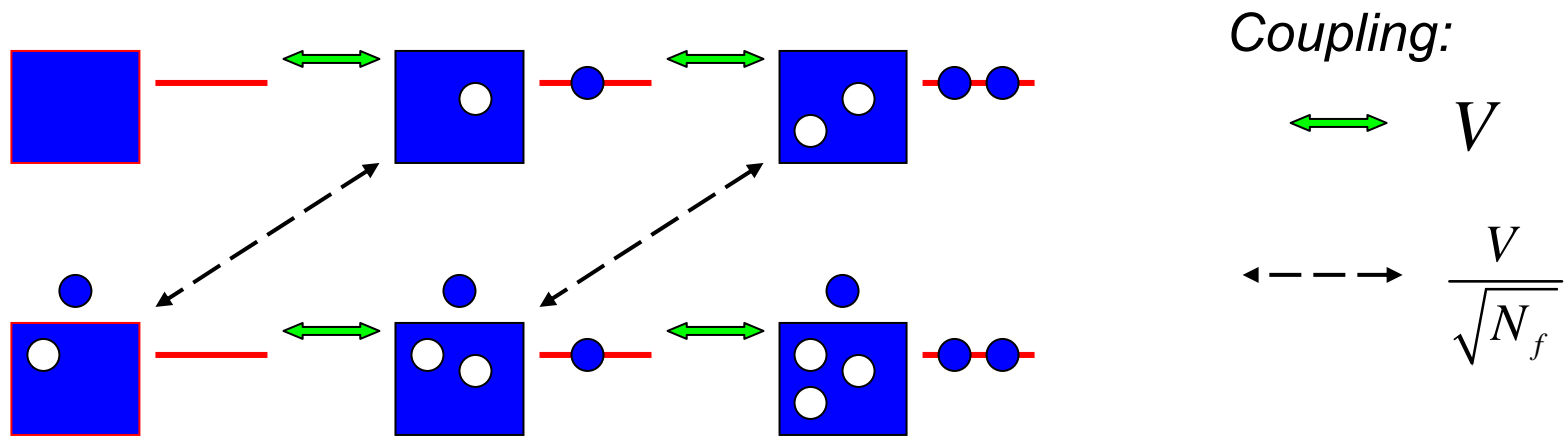
$$+ \frac{U_{ff}}{2} \sum_{\nu, \nu'}^{\nu \neq \nu'} f_{\nu}^+ f_{\nu} f_{\nu'}^+ f_{\nu'} + \sum_{i=1}^N \sum_{\nu=1}^{N_f} V_i (d_{i\nu}^+ f_{\nu} + f_{\nu}^+ d_{i\nu}) + \tilde{H}$$

$$\nu = (m, \sigma)$$

-- contains the VB states which  do not couple to the localized 4*f* states

# Gunnarsson-Schönhammer approach

The variational set of basis functions:



→ The eigenstates of  $H$  with energies  $E^{(m)}$  are expressed as

$$|m\rangle = \alpha_0^{(m)} |0, N\rangle + \sum_{i=1}^N \alpha_i^{(m)} |1, N-1; i\rangle + \sum_{i,j} \alpha_{ij}^{(m)} |2, N-2; ij\rangle \dots$$

The state with a minimal energy  $E_g$  – **ground state**  $|g\rangle$

$N_f \rightarrow \infty$ , finite  $U_{ff}$  : **minimal version** of GS approach

The hybridization parameters  $V_i$  have to be scaled to  $\Delta_i = V_i \sqrt{N \cdot N_f}$

$$H = \begin{pmatrix} 0 & \dots & \Delta_i/\sqrt{N} & \dots & 0 & \dots & 0 \\ \vdots & \ddots & & & \vdots & & \vdots \\ \Delta_i/\sqrt{N} & & \varepsilon_f - \varepsilon_i & & \Delta_i\sqrt{2/N} & & \Delta_j/\sqrt{N} \\ \vdots & & & \ddots & & \ddots & \vdots \\ 0 & & \Delta_i\sqrt{2/N} & & 2\varepsilon_f + U_{ff} - 2\varepsilon_i & & 0 \\ \vdots & & & \ddots & & \ddots & \vdots \\ 0 & & \Delta_j/\sqrt{N} & & 0 & & 2\varepsilon_f + U_{ff} - \varepsilon_i - \varepsilon_j \\ \vdots & & & \ddots & & \ddots & \vdots \end{pmatrix}$$

$$N_m = 1 + 2N + \frac{N(N-1)}{2} \text{ basis functions}$$

Hybridization  $\Delta_i = \Delta \sqrt{\rho(\varepsilon_i) N \delta E_i}$    $\rho(\varepsilon)$  is the local valence-band DOS around 4f site allowed for hybridization

# 4f photoexcitation

Electron removal states:  $E_{i_0}^{(m)} = E^{(m)} - \varepsilon_{i_0}$ ,  $|m, i_0\rangle = \sum_{\phi} \alpha_{\phi}^{(m)} |\phi, i_0\rangle$

The spectral density in the PE process (sudden approximation):

$$I(\omega, E_{kin.}) = -\frac{1}{\pi} \Im \sum_{m=1}^{N_m} \sum_{i=1}^N \frac{|\langle m, i | T(\omega) | g \rangle|^2}{\hbar\omega - E_{kin.} - (E^{(m)} - \varepsilon_i - E_g) + i\Gamma}$$

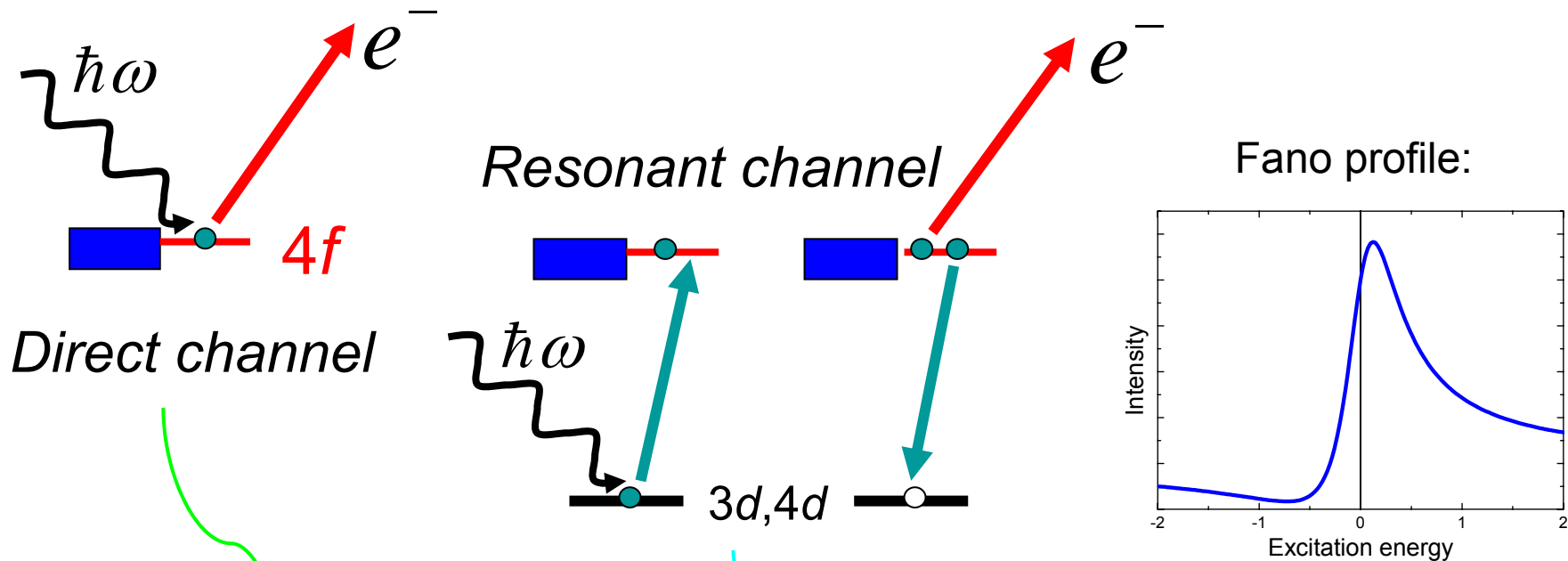
with the transition operator  $T(\omega) = t_f(\omega) f_v + t_d(\omega) d_{iv}$

$$\longrightarrow I(\omega, E_{kin.}) = I_f(\omega, E_{kin.}) + I_d(\omega, E_{kin.}) + \cancel{I_{int.}(\omega, E_{kin.})}$$

For VB photoemission – a trivial result:  $I_d(\omega, E_{kin.}) = t_d^2(\omega) \tilde{\rho}(E_{kin.} - \hbar\omega)$

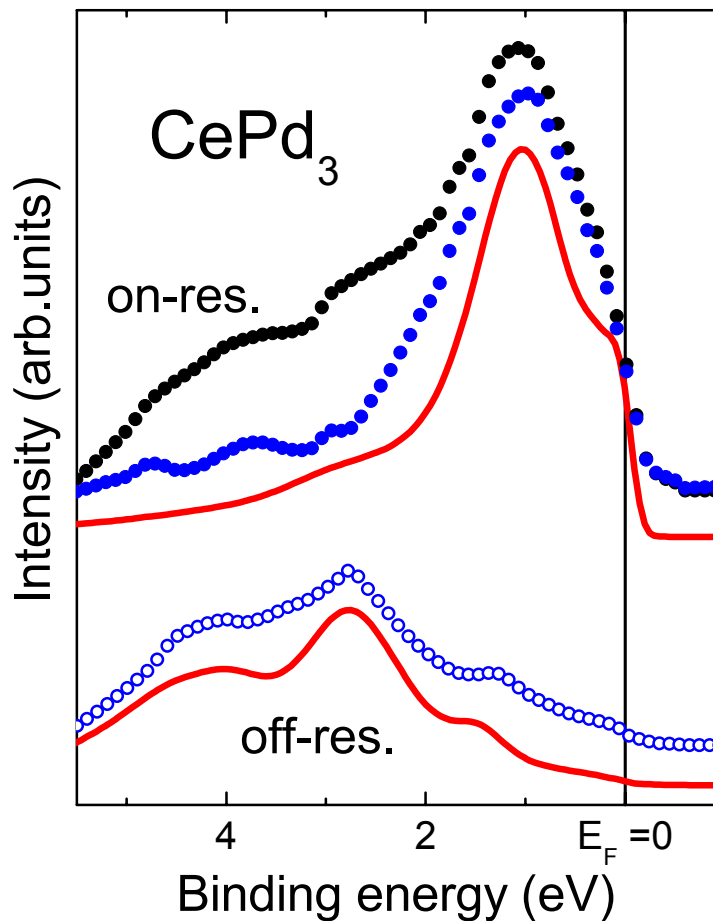


# Resonant photoemission spectra



Transition operator:

$$T = t_f f_v + \sum_r v_A \sum_{v'} c_{v'}^+ f_{v'} f_v \frac{|r\rangle\langle r|}{\hbar\omega - (E_{\text{int.}}^{(r)} - E_g) + i\Gamma_{\text{int.}}} t_c f_{v'}^+ c_{v'}$$

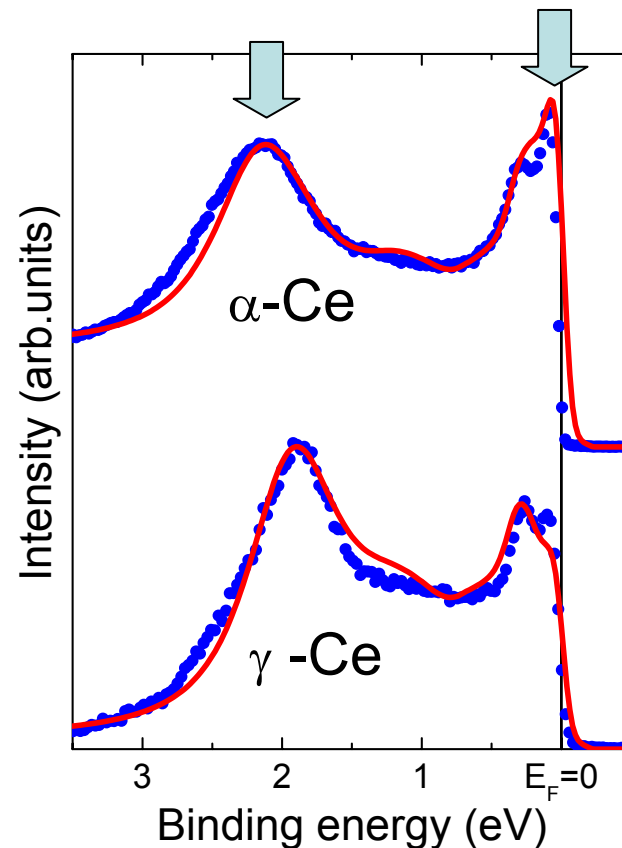


on-res. → 4f emission,  
off-res. → Pd d DOS

**Effect of  
the resonant  
channel:**

$$\tau = \frac{v_A t_c}{t_f}$$

Parameters  
estimated  
for bulk α-Ce:



$\tau$	0	1.4
$\varepsilon_f$	-1.45	-1.30
$\Delta$	0.82	0.87
$n_f$	0.976	0.918

# Simple(st) model

$$H = \begin{pmatrix} 0 & \Delta & 0 \\ \Delta & \varepsilon_f & \Delta\sqrt{2} \\ 0 & \Delta\sqrt{2} & 2\varepsilon_f + U_{ff} \end{pmatrix}$$

$$E_1 = \frac{1}{2} \left( \varepsilon_f - \sqrt{\varepsilon_f^2 + 4\Delta^2} \right) = E_g$$

$$E_0 = \frac{1}{2} \left( \varepsilon_f + \sqrt{\varepsilon_f^2 + 4\Delta^2} \right)$$

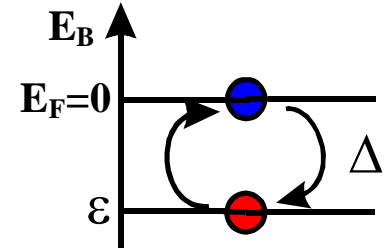
$$|\Psi^1\rangle = A|f^0\rangle + B|f^1\rangle$$

$$|\Psi^0\rangle = B|f^0\rangle - A|f^1\rangle$$

$$A = \frac{\Delta}{\sqrt{\varepsilon_f^2 - \Delta^2}} \quad B = \sqrt{1 - A^2}$$

$$n_f = B^2$$

*f* state interacts with only one degenerated VB state at  $E_F$

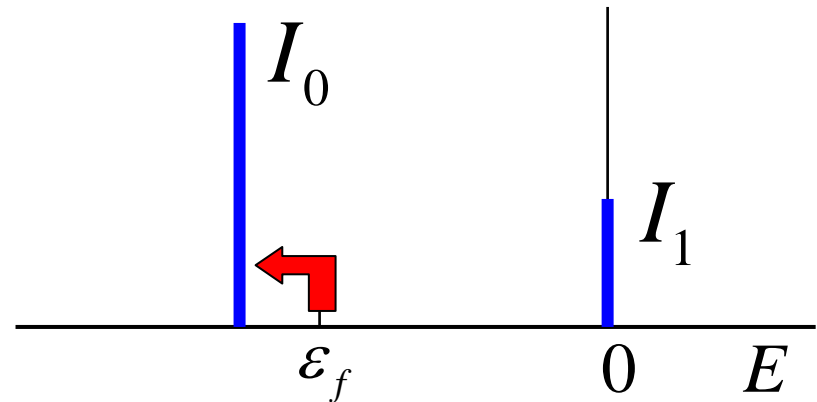


Photoemission:  $E_{kin} = \hbar\omega - (E_m^{(f)} - E_g)$

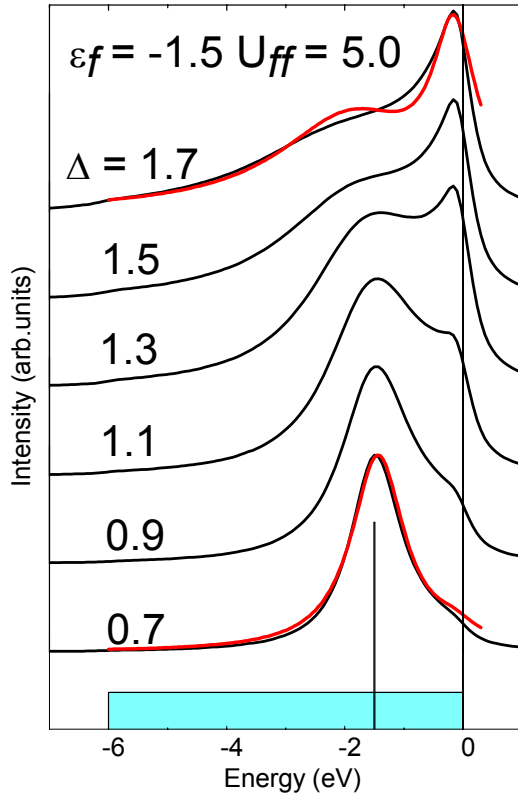
$$(E_1^{(f)} - E_g) = 0$$

$$\frac{I_1}{I_0} \approx \frac{\Delta^2}{\varepsilon_f^2 - \Delta^2}$$

$$(E_0^{(f)} - E_g) = \sqrt{\varepsilon_f^2 + 4\Delta^2}$$

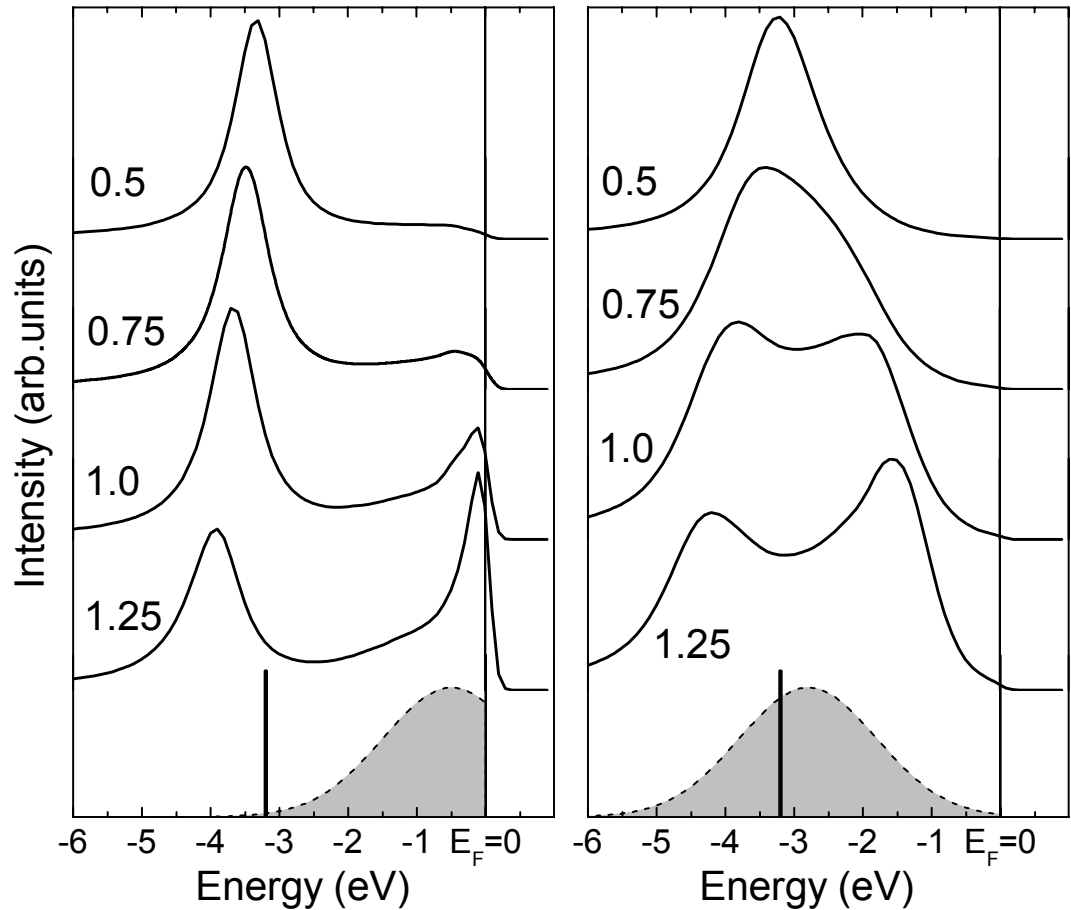


## Effect of the VB DOS on the 4f emission



Imer:  
 $\varepsilon_f = -1.16 \pm 0.02$   
 $\Delta = 0.18 \text{ _ to _ } 0.57$

*Imer model is oversimplified  
and can not be used for  
estimation of parameters for  
real systems!*



# GS approach to Pr, Nd...

Energy of (bare)  $f$  levels:

Configuration	Ce ( $n=1$ )	Pr ( $n=2$ )	Nd ( $n=3$ )
$f^{n-1}$	0	$\varepsilon_f$	$2\varepsilon_f + U_{ff}$
$f^n$	$\varepsilon_f$	$2\varepsilon_f + U_{ff}$	$3\varepsilon_f + 3U_{ff}$
$f^{n+1}$	$2\varepsilon_f + U_{ff}$	$3\varepsilon_f + 3U_{ff}$	$4\varepsilon_f + 6U_{ff}$

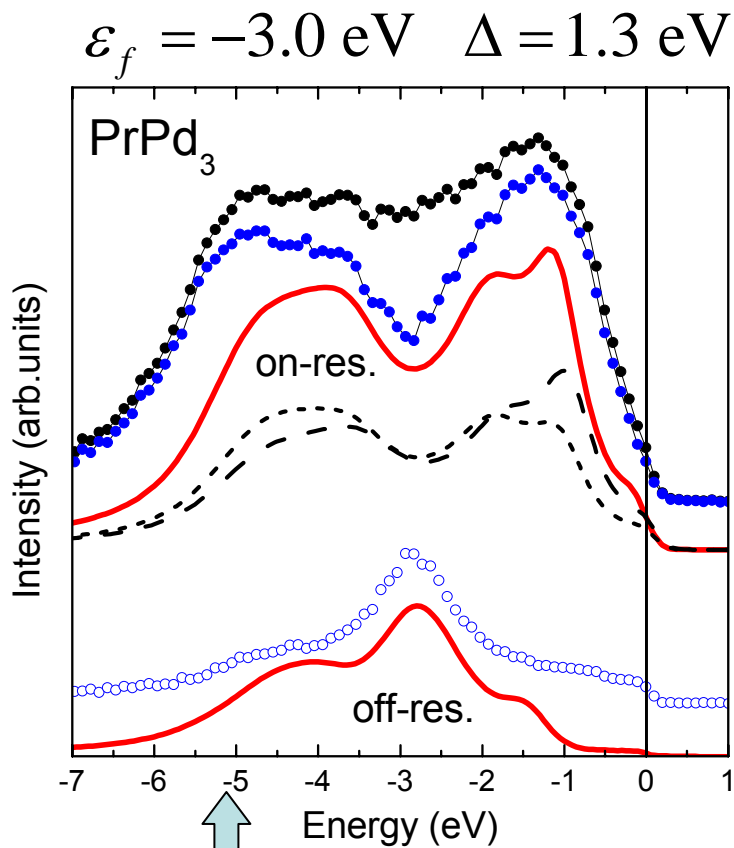
- introducing an **energy shift** for diagonal matrix elements  $\rightarrow E(f^{n-1})=0$  :

Configuration	Ce ( $n=1$ )	Pr ( $n=2$ )	Nd ( $n=3$ )
$f^{n-1}$	0	0	0
$f^n$	$\varepsilon_f$	$\varepsilon_f + U_{ff}$	$\varepsilon_f + 2U_{ff}$
$f^{n+1}$	$2\varepsilon_f + U_{ff}$	$2(\varepsilon_f + U_{ff}) + U_{ff}$	$2(\varepsilon_f + 2U_{ff}) + U_{ff}$

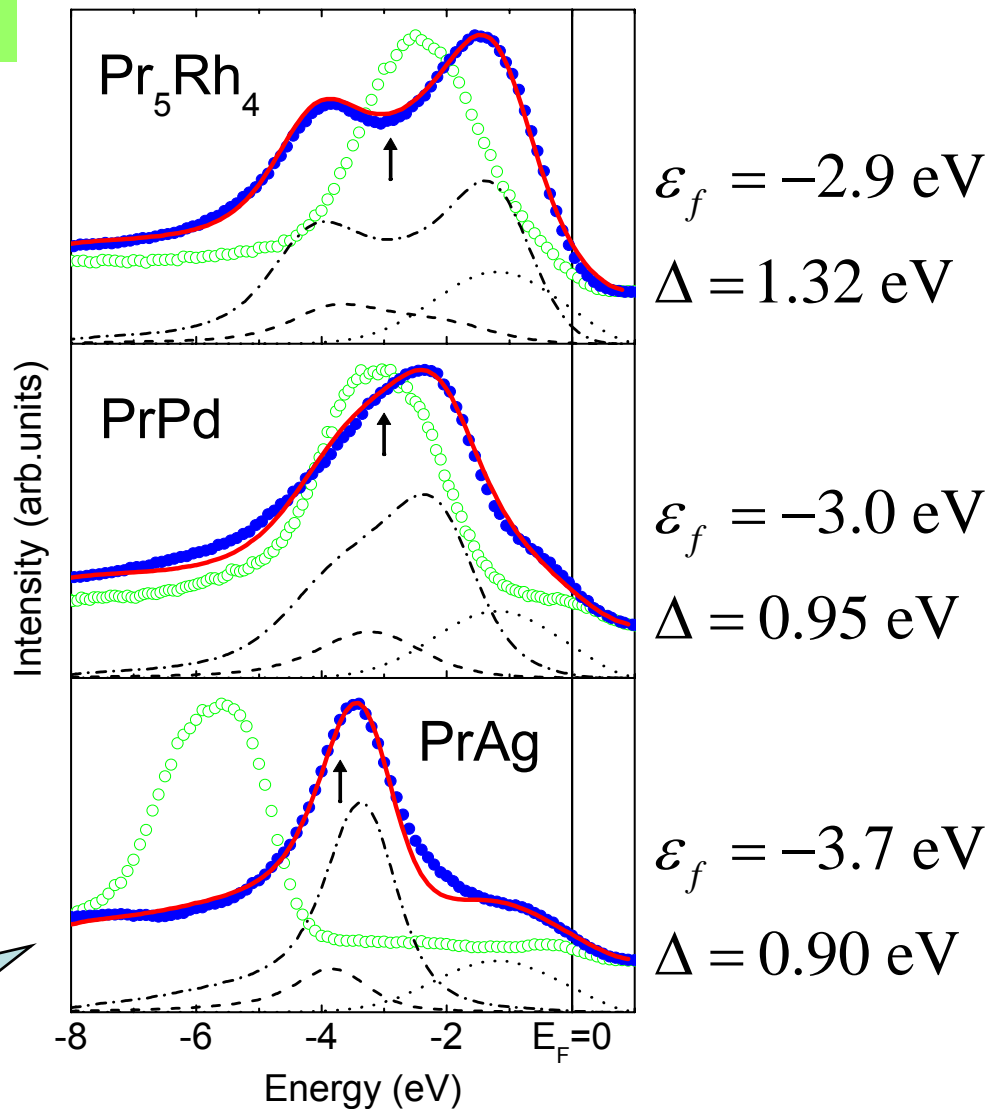
-- **new definition** for  $\varepsilon_f$ :  $\tilde{\varepsilon}_f = \varepsilon_f + (n-1) U_{ff} \rightarrow$  the same form of **H matrix**

$$\tilde{\varepsilon}_f = E(f^n) - E(f^{n-1})$$

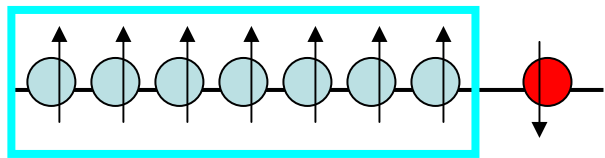
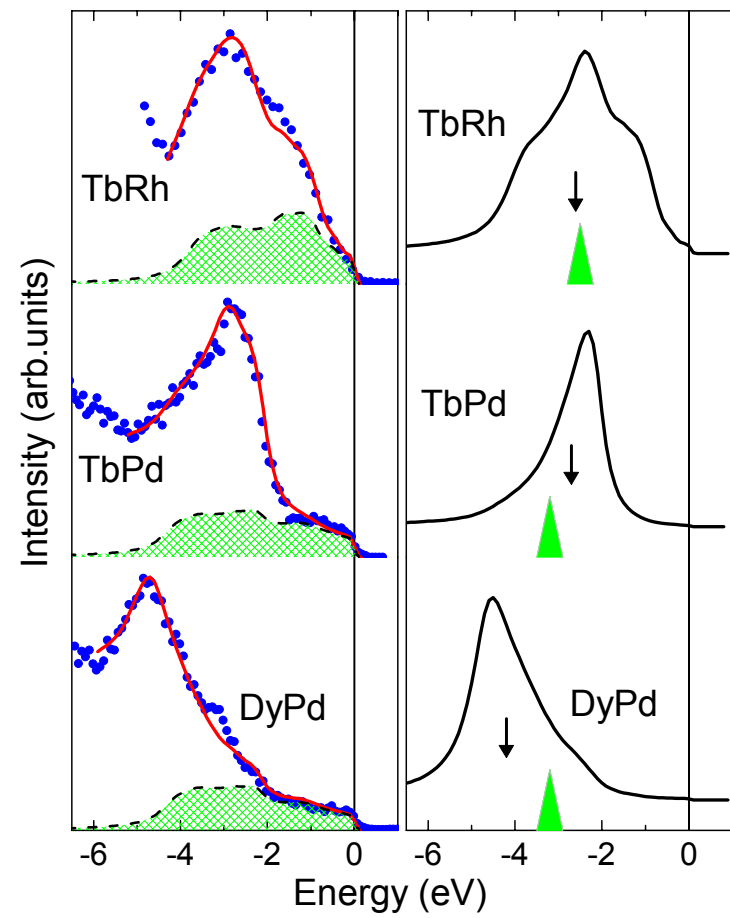
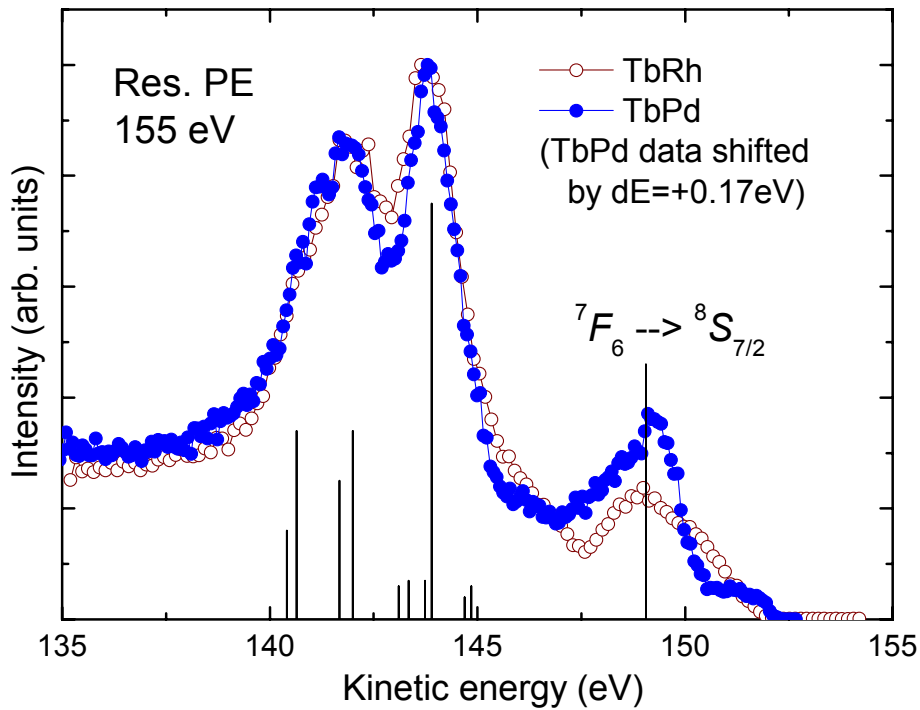
# Pr-TM compounds



4d-4f resonance  
3d-4f resonance



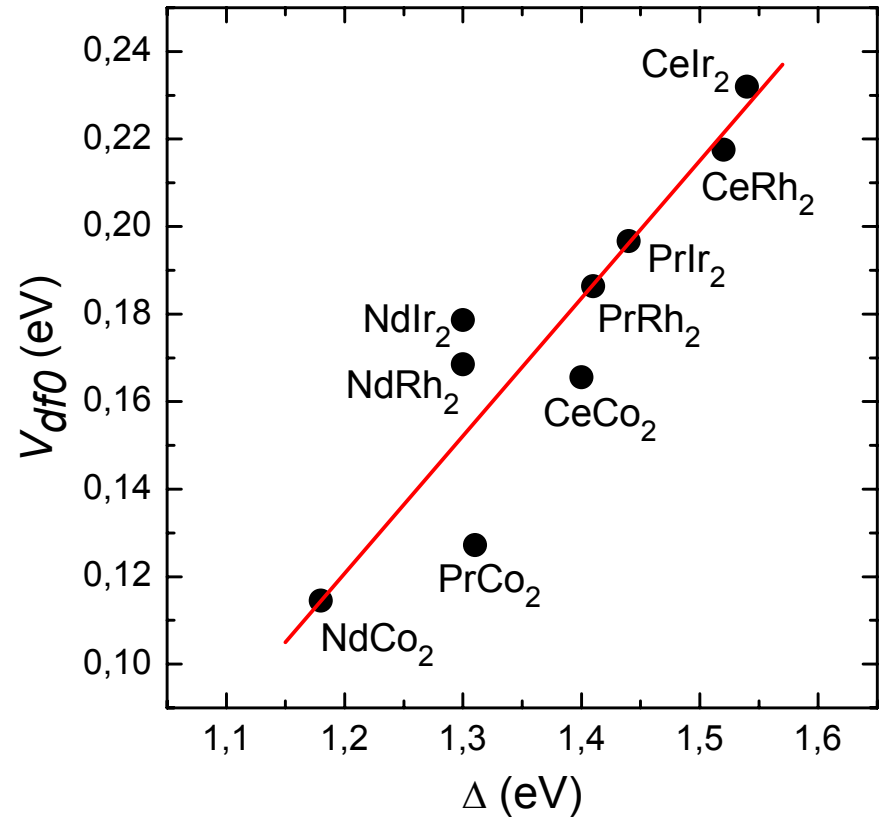
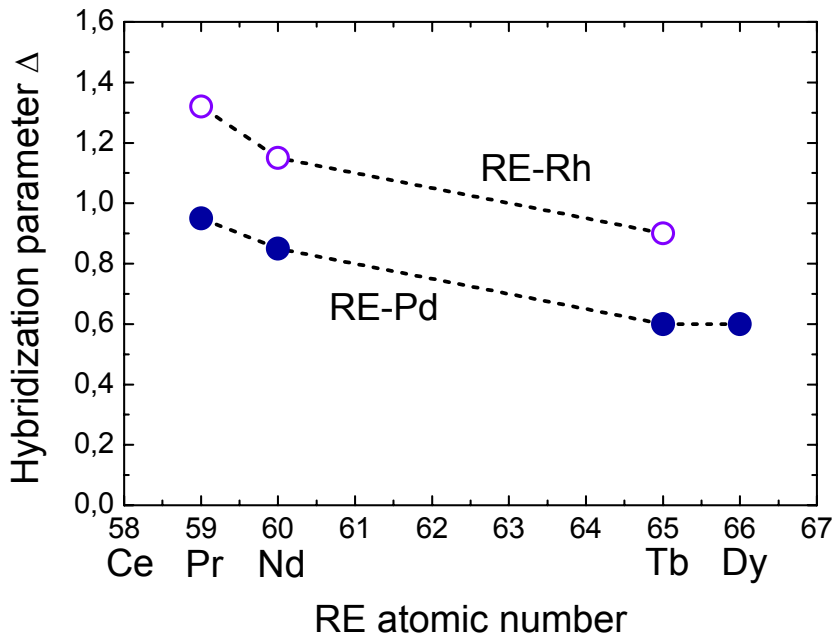
# Tb-*TM* compounds



W.A.Harrison, G.K.Straub, Phys.Rev.B **36**, 2695 (1987):

Hybridization matrix element:

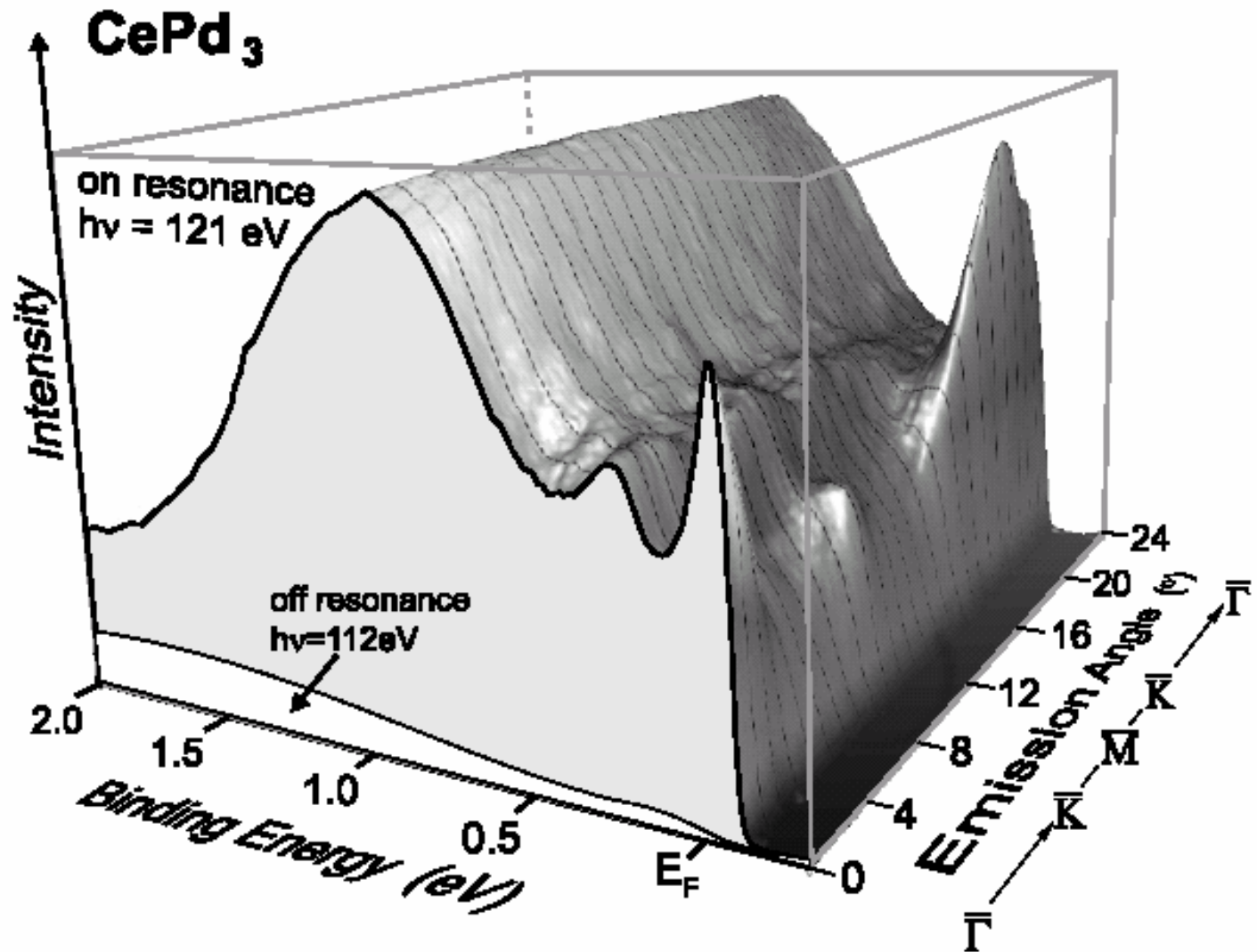
$$V_{ll'm} = \left( \eta_{ll'm} \frac{\hbar^2}{m_e} \right) \frac{\left( r_l^{2l-1} r_{l'}^{2l'-1} \right)^{1/2}}{d^{l+l'+1}}$$



Yu.Kucherenko *et al.*, Phys.Rev.B **70**, 045105 (2004)



# Angle-resolved photoemission spectra



# Periodic Anderson model

$$H = \sum_{\mathbf{k}\sigma} \varepsilon(\mathbf{k}) d_{\mathbf{k}\sigma}^{\dagger} d_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma} \varepsilon_f(\mathbf{k}) f_{\mathbf{k}\sigma}^{\dagger} f_{\mathbf{k}\sigma} + \frac{U_{ff}}{2} \sum_{i,\sigma} n_{i,\sigma}^f n_{i,-\sigma}^f$$

$$+ \sum_{\mathbf{k}\sigma} V_{\mathbf{k}}(\varepsilon) (d_{\mathbf{k}\sigma}^{\dagger} f_{\mathbf{k}\sigma} + f_{\mathbf{k}\sigma}^{\dagger} d_{\mathbf{k}\sigma})$$

-- leads to a mixing of states with different  $\mathbf{k}$  values

$$= \sum_{\mathbf{k}} h_0(\mathbf{k}) + u$$

$U_{ff}$  large  $\rightarrow$  contribution of the  $4f^2$  configuration small

$$U_{ff} \rightarrow \infty$$

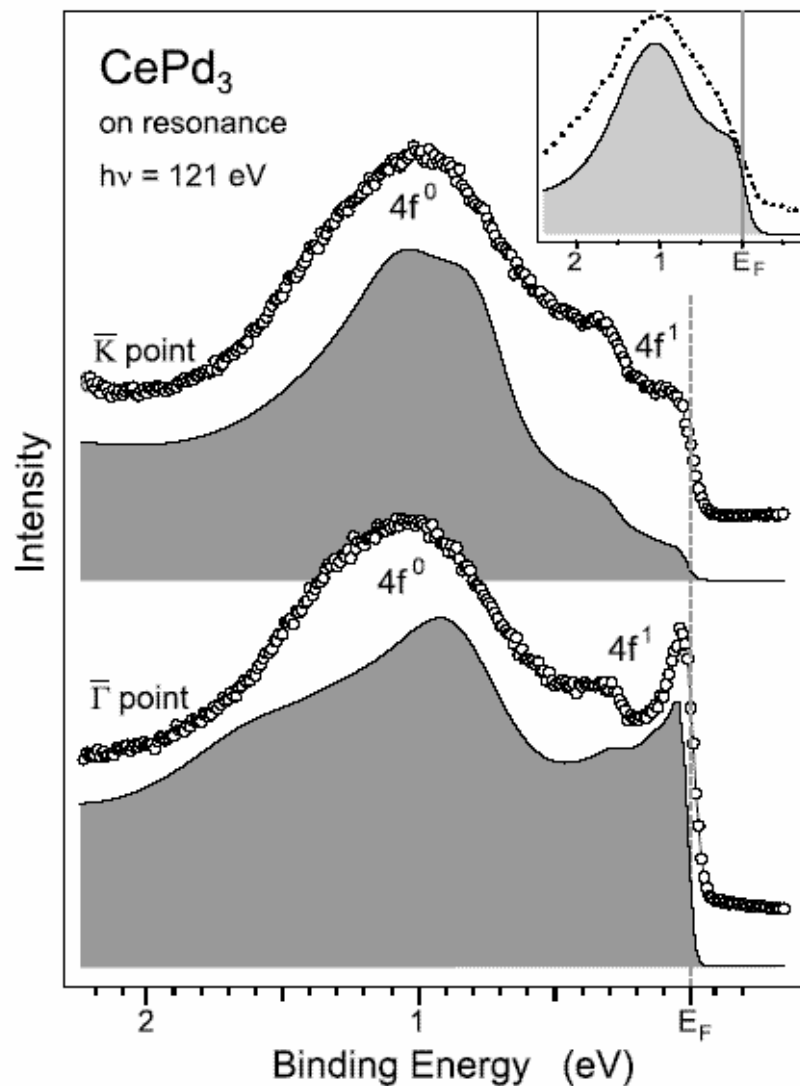
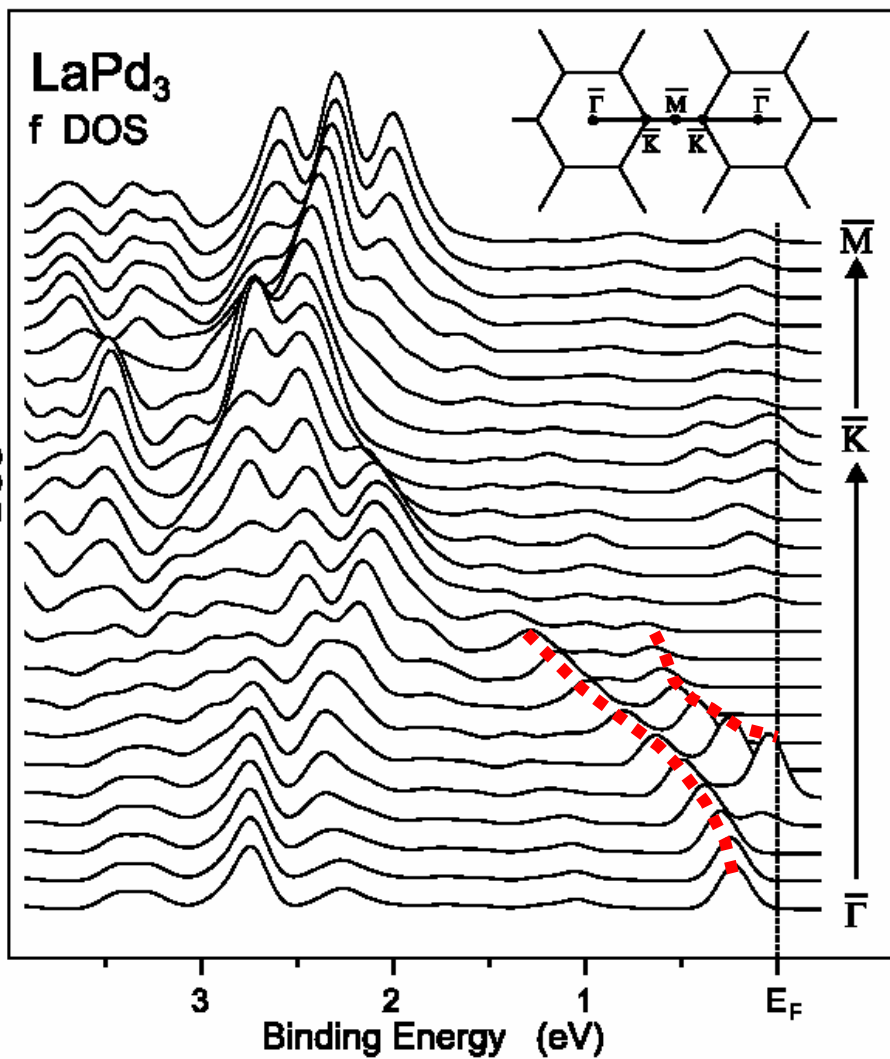
Non-hybridized  $f$  states create a band with no dispersion

$$\varepsilon_f(\mathbf{k}) = \varepsilon_f$$

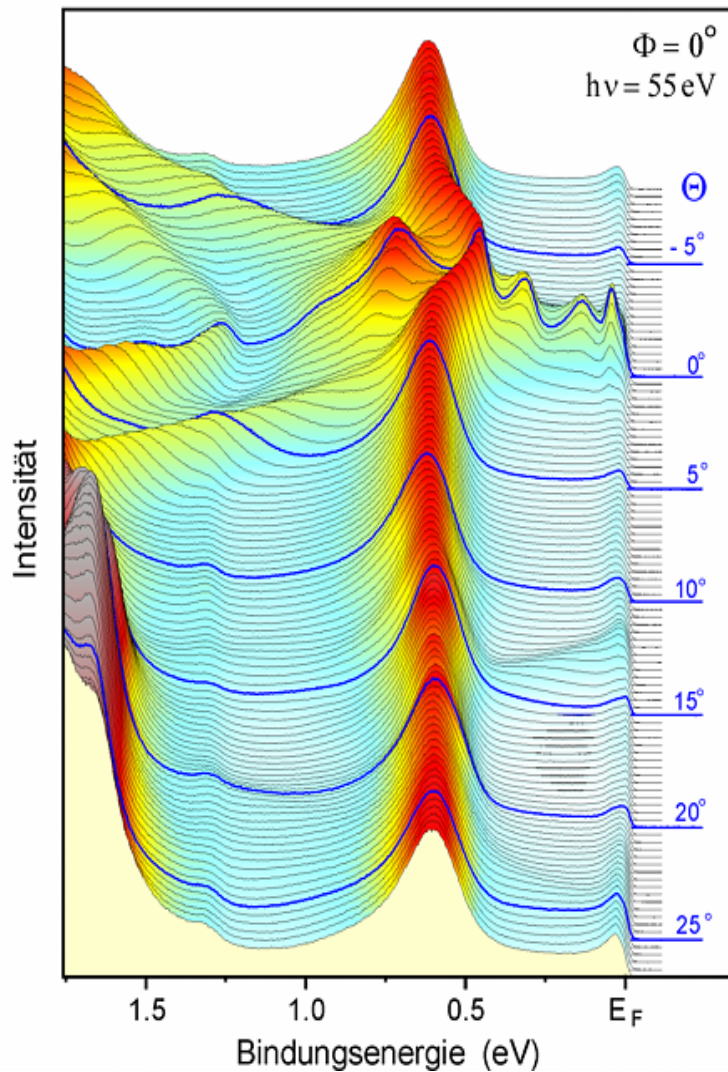
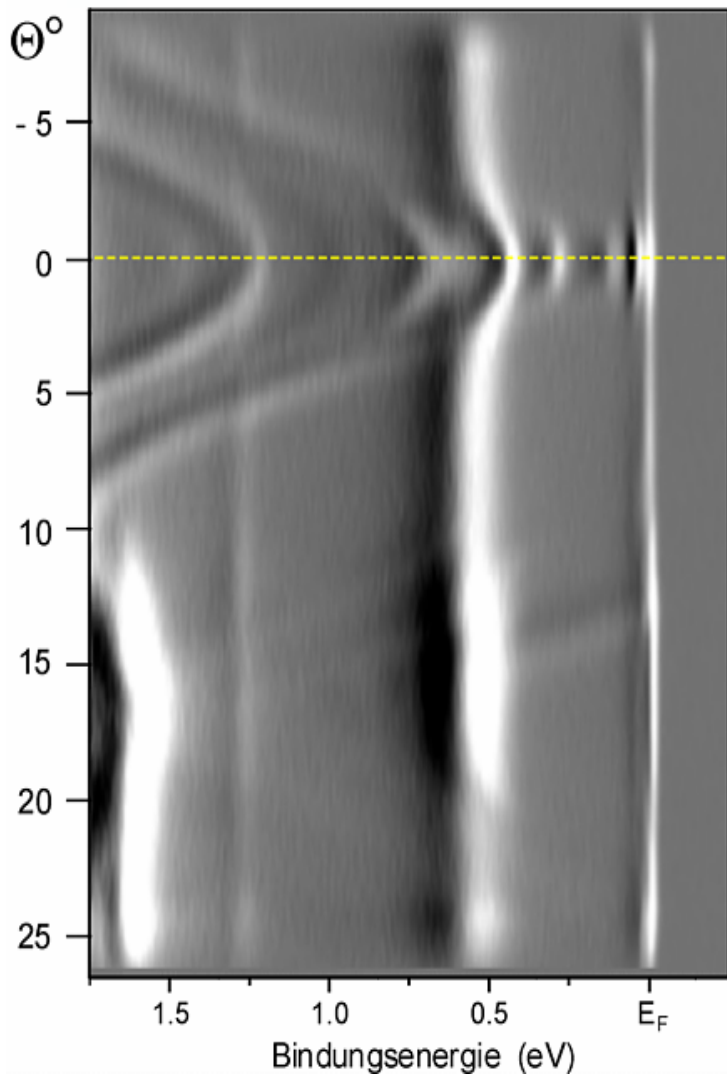
$$V_{\mathbf{k}}(\varepsilon) = \Delta \cdot c_f(\varepsilon, \mathbf{k})$$

$\rightarrow$  Diagonalizing  $h_0(\mathbf{k})$ ; two parameters:  $\varepsilon_f$  and  $\Delta$

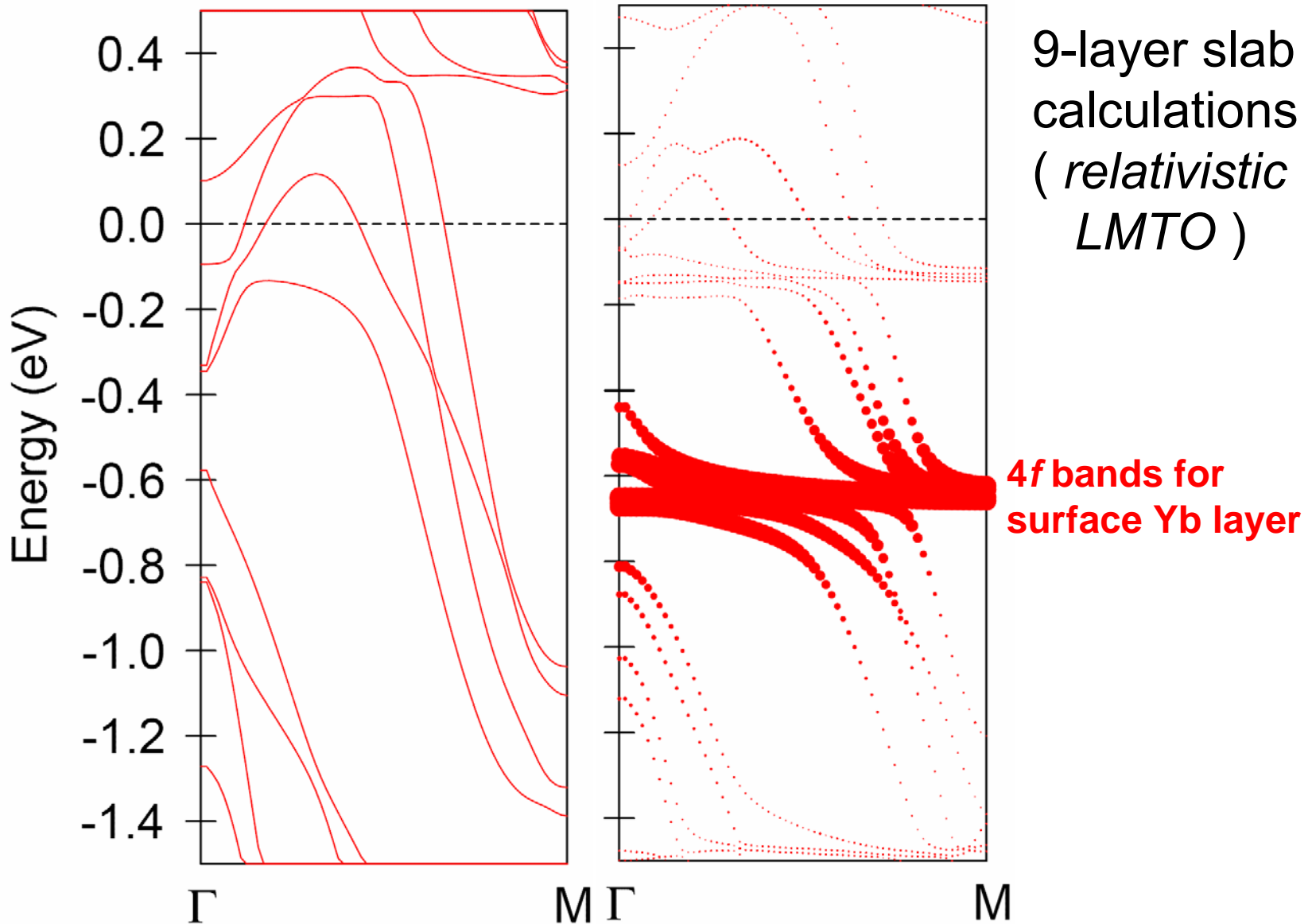
# ARPES: CePd<sub>3</sub>

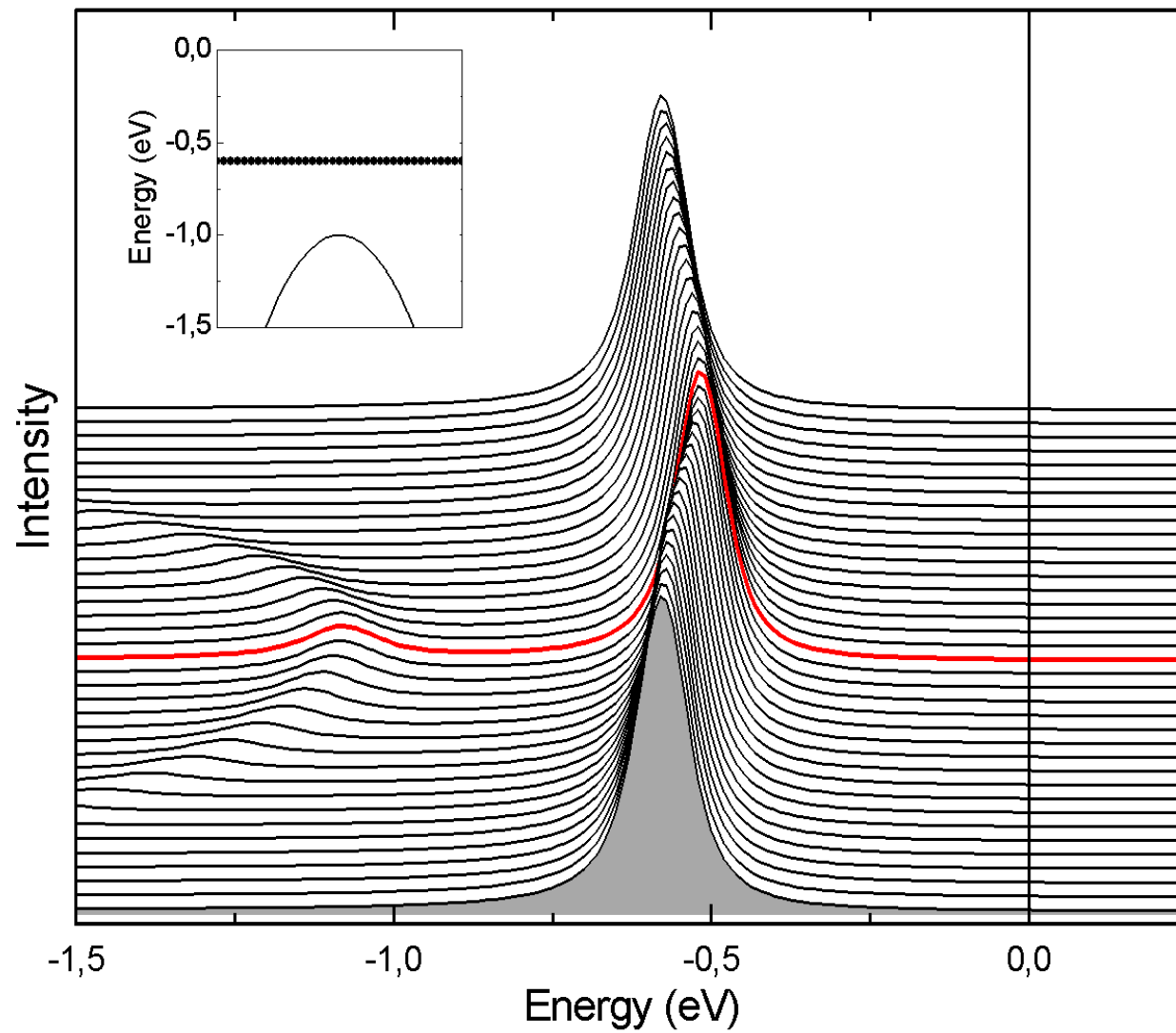


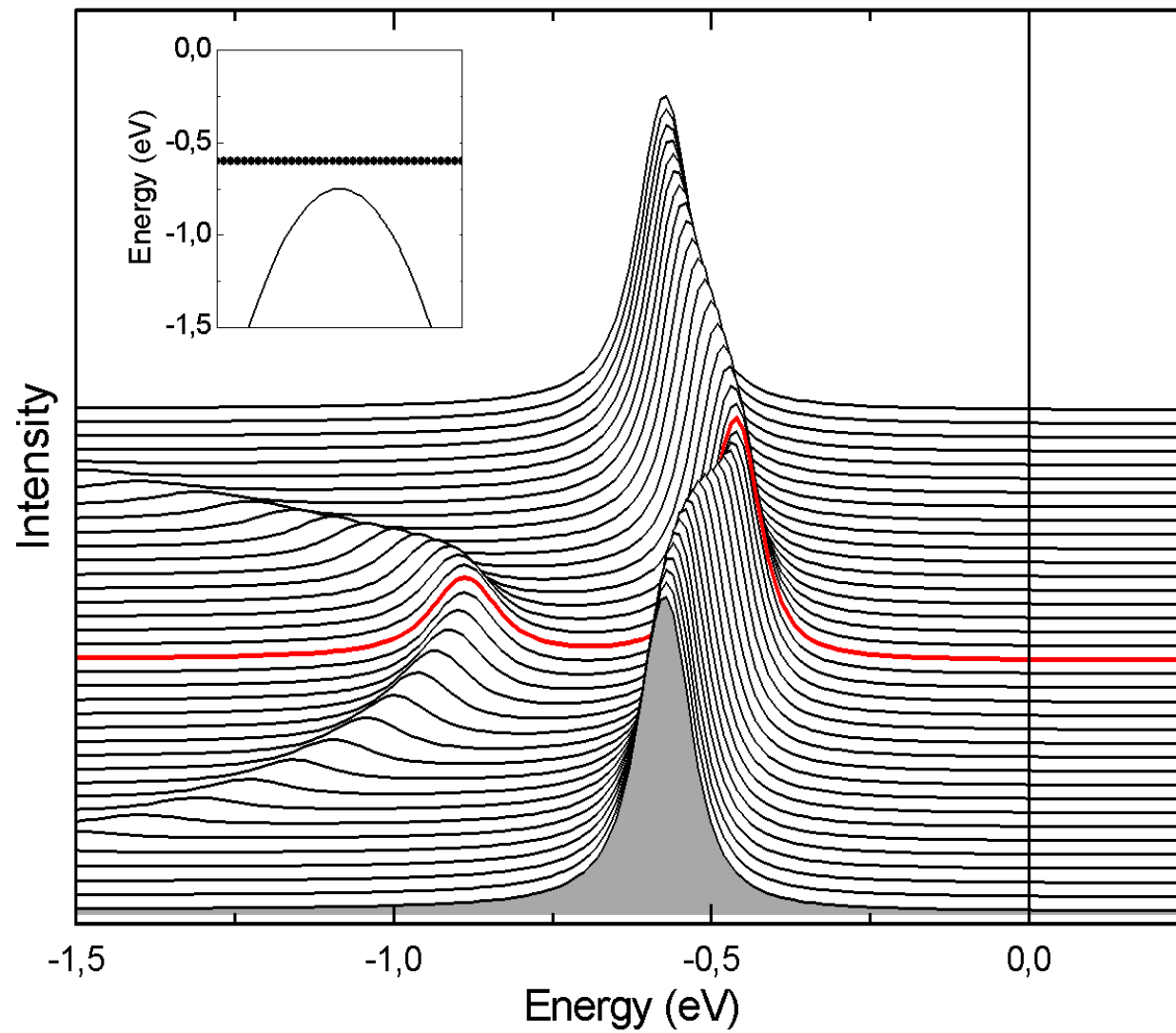
# ARPES: $\text{YbIr}_2\text{Si}_2$

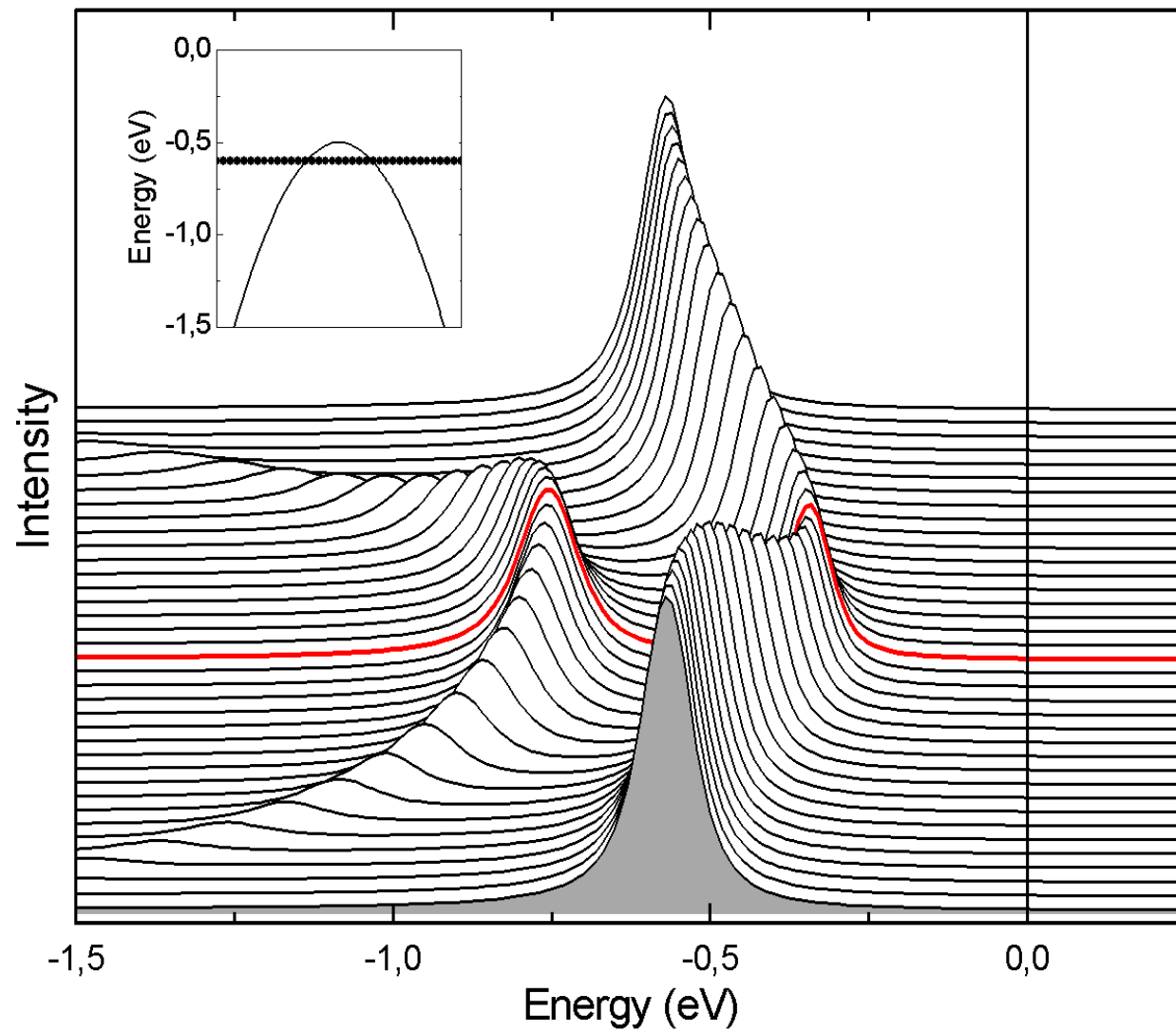


# LDA+ $U$ : YbIr<sub>2</sub>Si<sub>2</sub>

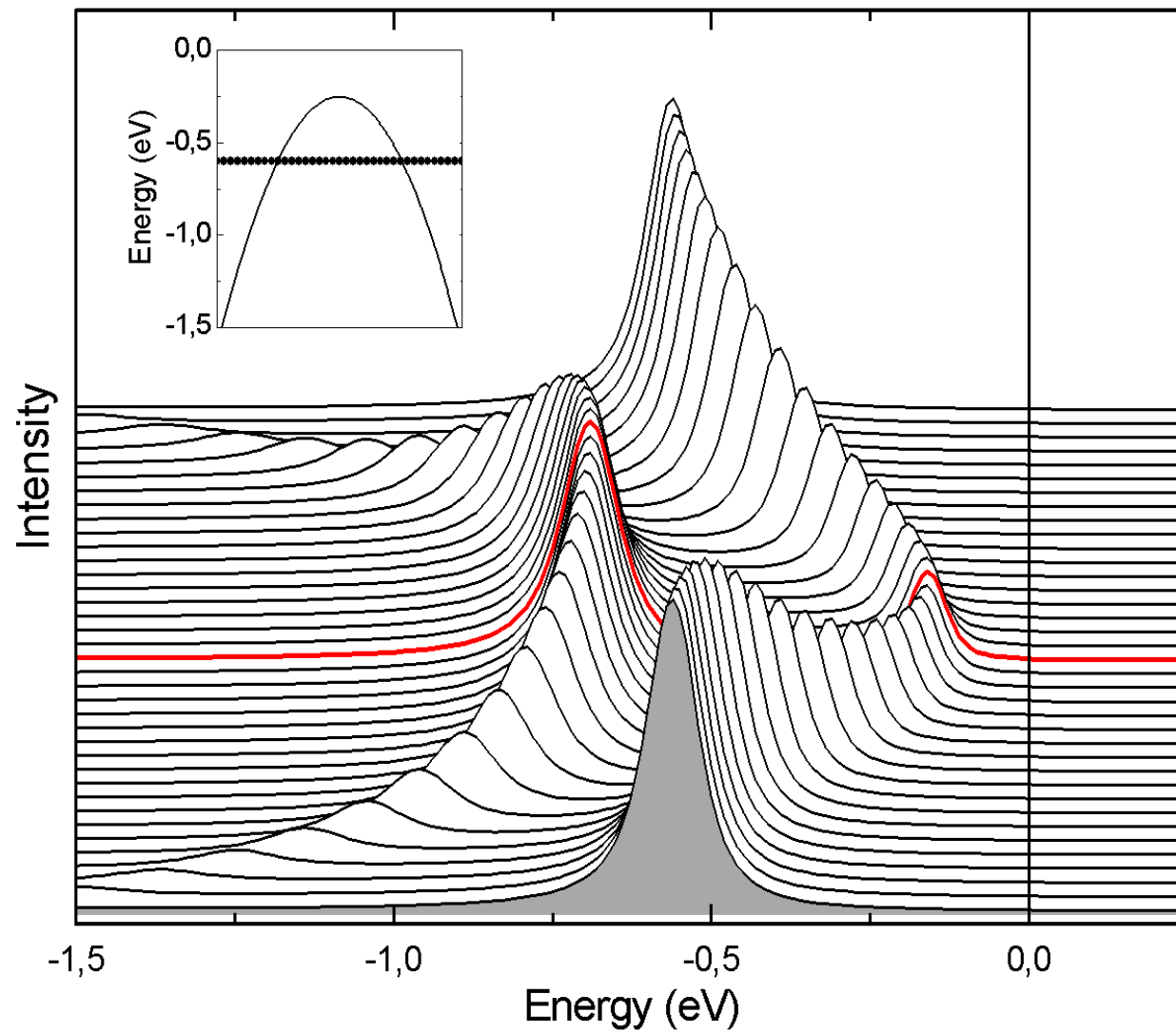








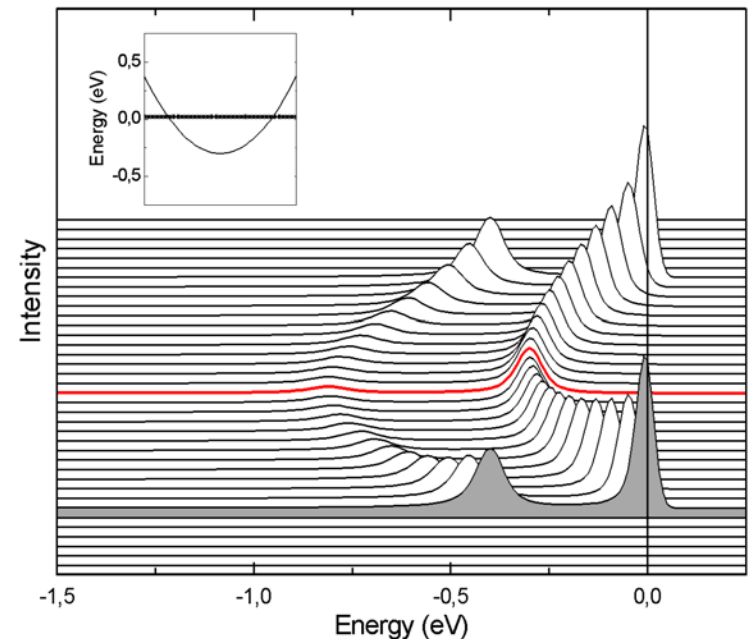
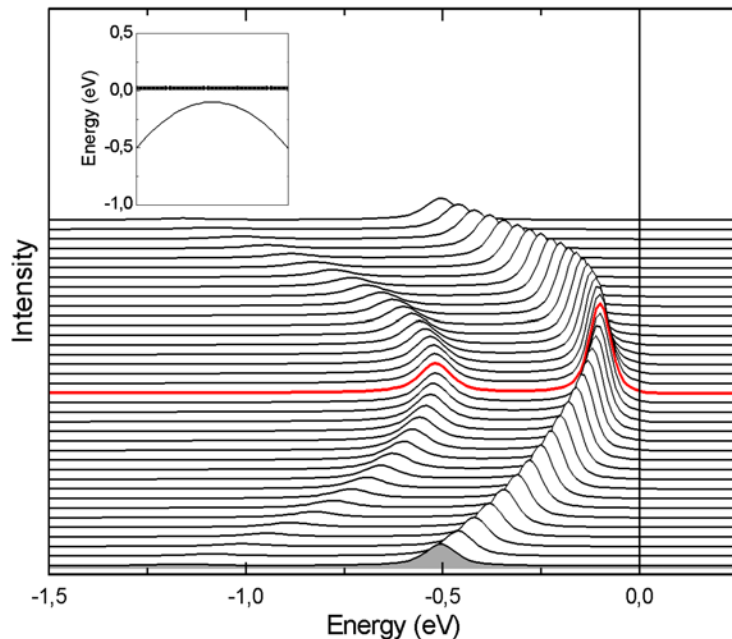




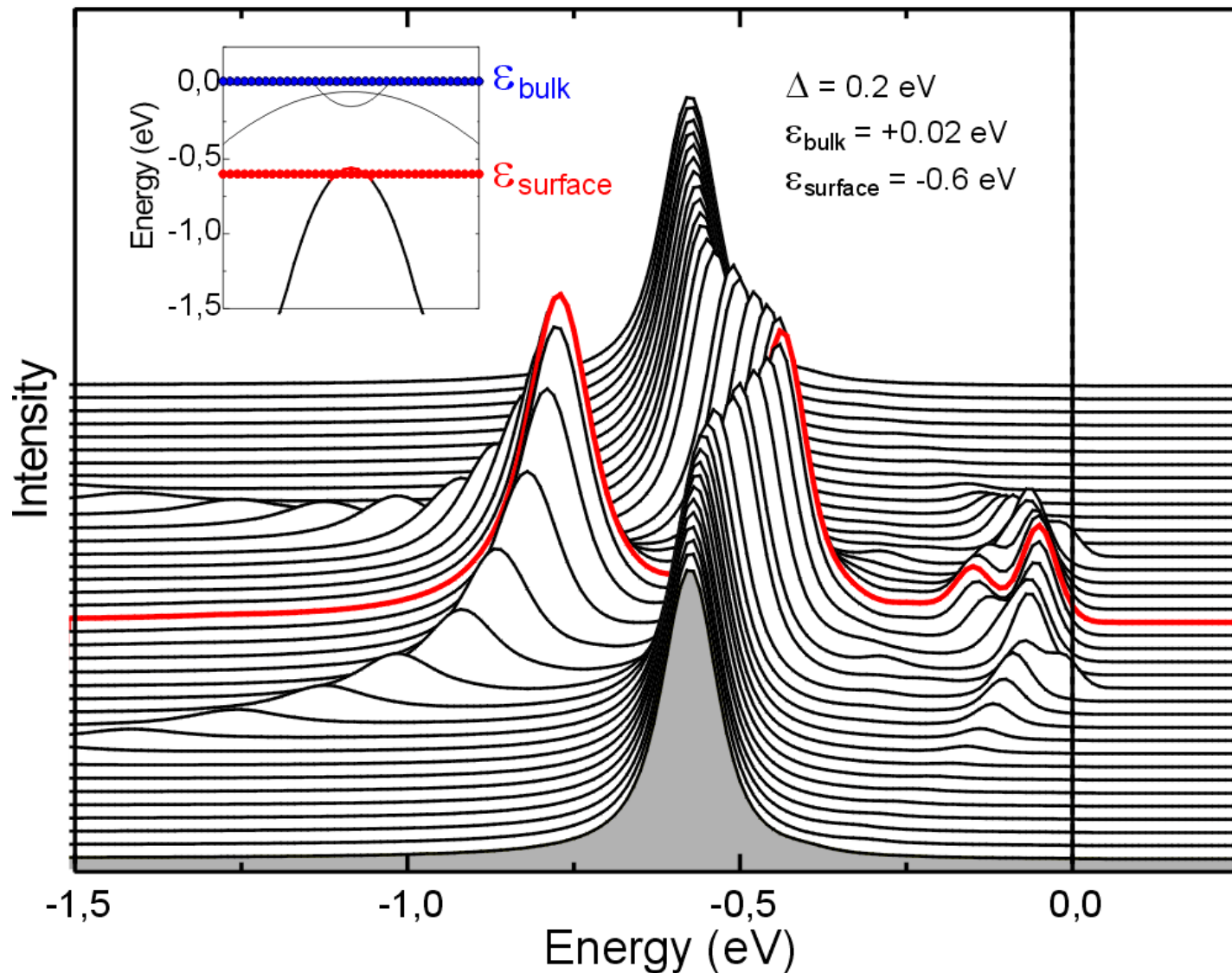
Yb: considering  $f$  holes instead of  $f$  electrons

Configurations  $h^0$  ( $4f^{14}$ ),  $h^1$  ( $4f^{13}$ ),  $h^2$  ( $4f^{12}$ )

- for divalent atoms the  $h^2$  configuration may be neglected
- photoemission:  $h^0 \rightarrow h^1$  transitions
- main peak ( $h^1$  final state) and satellite ( $h^0$  final state due to hybridization)
- energy spacing about  $2\Delta$



# ARPES simulation: $\text{YbIr}_2\text{Si}_2$



# Conclusions:

- The 4*f* photoemission lineshapes in Ce, Pr, Nd, and even (under some assumptions) in Tb, Dy systems are properly described within the framework of **SIAM**
- Large **energy splittings** of the 4*f* “ionization” peak are obtained, if the energy position of the expected electron-removal state is close to the maximum of the valence-band DOS
- The hybridization of the 4*f* states with the VB decreases (as expected) in the series of rare earth. However, even for heavier 4*f* elements it is **not negligible**
- A simplified version of PAM explains the **main features** of the angle-resolved Ce 4*f* photoemission using a realistic band structure
- **k** dependence of **hybridization strength** is caused by the dispersive properties of VB states and their local *f* character at the *RE* site.