FOTOABSORPCIJSKI PRESEK

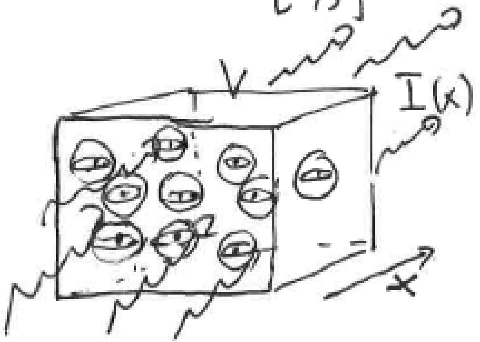
$$\dot N_i = -\Gamma N_i = \dot N = -\sigma_{ef} I$$

- σ_{ef} … EFEKTIVNI ABSORPCIJSKI PRESEK TARČE $[m^2]$
- I … GOSTOTA TOKA FOTONOV, KI VPADAJO NA TARČO $\left[\frac{1}{m^2 s}\right]$
- $\dot N_i$ … $(-1)\times$ ŠT. ATOMOV V TARČI, KI ABSORBIRAJO FOTON, NA ČASOVNO ENOTO $\left[\frac{1}{s}\right]$
- Γ … VERJETNOST ZA ABSORPCIJO FOTONA ZA ATOM NA ČASOVNO ENOTO $\left[\frac{1}{s}\right]$
- $\dot N$ … ŠT. ABORBIRANIH FOTONOV NA ČASOVNO ENOTO $\left[\frac{1}{s}\right]$

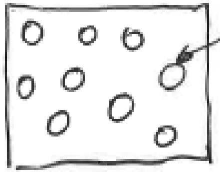
$$I(x) = I(0) - \frac{\dot N}{S}$$

γ

$I(0)$



"TLORIS"



σ_{abs}

ABSORPCIJSKI PRESEK ATOMA

$$\sum \sigma = \sigma_{ef} = N_i \sigma_{abs}$$

$$\sigma_{ef} I = \Gamma N_i = \sigma_{abs} I N_i \longrightarrow \sigma_{abs} = \frac{\Gamma}{I}$$

$$I = \frac{j}{\hbar\omega} = \frac{w c}{\hbar\omega} = \frac{\frac{1}{2}\varepsilon_0\omega^2 A_0^2\cdot c}{\hbar\omega} \xrightarrow{a.u.} \frac{\omega A_0^2}{8\pi\alpha} \longrightarrow \sigma_{abs}$$

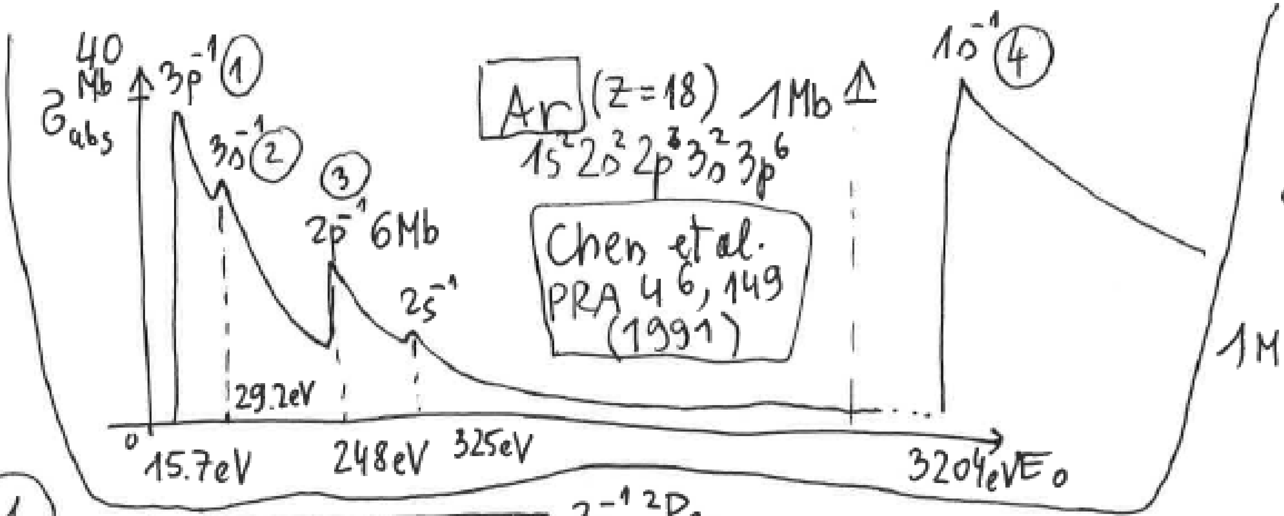
$$\Gamma = 2\pi\omega^2 \left|\langle i|\, \tfrac{1}{2} A_0 \hat\varepsilon\, e^{i\vec k\cdot\vec r - i\omega t}\cdot\vec r\, |j\rangle\right|^2 \approx \frac{\pi}{2} A_0^2\omega^2 \left|\langle i|\hat\varepsilon\cdot\vec r|j\rangle\right|^2$$

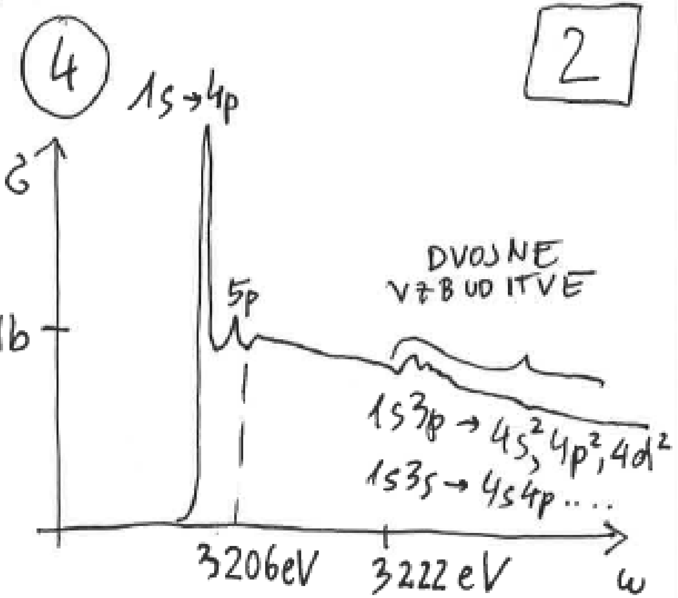
$$\boxed{\sigma_{abs} = 4\pi^2\alpha\omega\left|\langle i|\hat\varepsilon\cdot\vec r|j\rangle\right|^2}$$

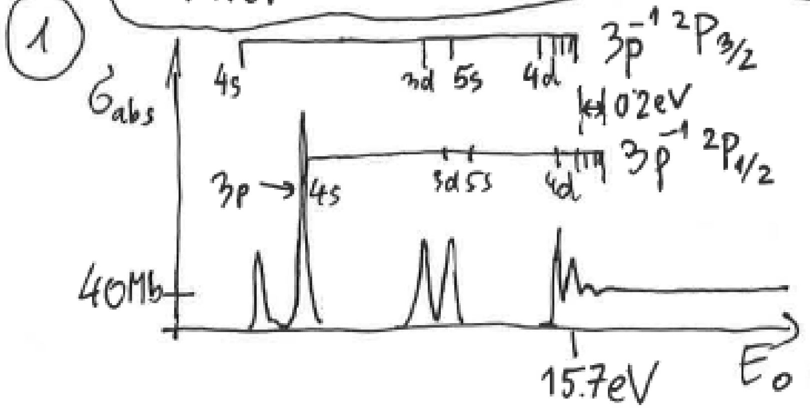
$n_i = \frac{N_i}{V}$ … GOSTOTA ATOMOV $\left[\frac{1}{m^3}\right]$

$$\big(I(x) - I(0)\big)S = -N_i\sigma_{abs} I(0) \quad \text{"TANKA TARČA"} \longrightarrow \text{BEER-LAMBERT}$$

$$n_i S\,dx\,\sigma_{abs} I(0) = \frac{dI}{dx}\Big|_0 S\,dx \rightarrow \boxed{\frac{dI}{dx} = -\sigma_{abs} n_i I}$$







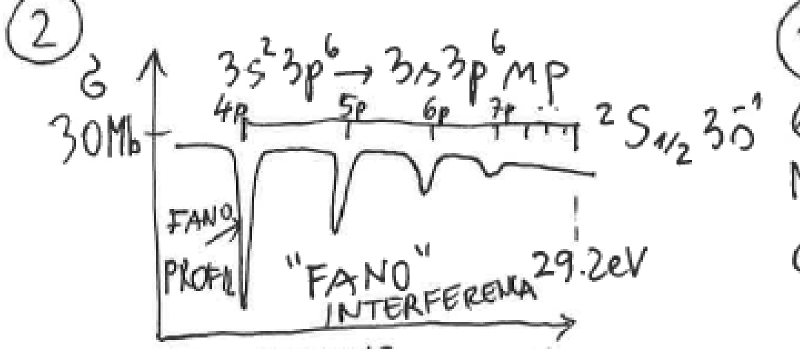
ABSORPCIJA V VEZANA STANJA PRI NIZKIH ENERGIJAH FOTONOV

$$\sigma(\omega) = 4\pi^2 \alpha \omega \left|\langle i | \hat{\varepsilon} \cdot \sum_i \vec{r}_i | j \rangle\right|^2 \delta(E_j - E_i - \omega)$$

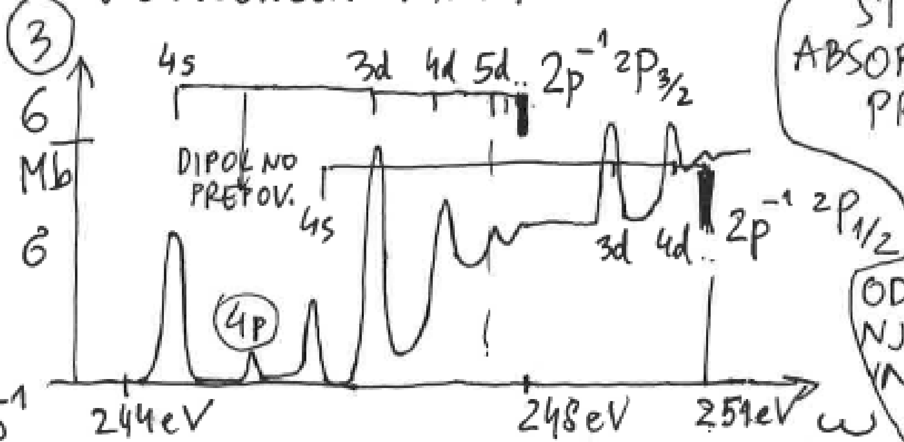
$$\to \frac{\Gamma_j / 2\pi}{(\omega - E_j + E_i)^2 + \frac{\Gamma_j^2}{4}}$$

Lorentzova funkcija

RAZŠIRITEV ZARADI KONČNEGA ŽIVLJ. ČASA VZBUJENEGA STANJA



MED DIREKTNO IONIZACIJO V $3p^{-1}$ KONTINUUM TER AVTOIONIZACIJO PREKO $3s^{-1}$



STRUKTURA ABSORPCIJSKEGA PRESEKA BLIZU (POD) ROBOM JE ODVISNA OD VRSTE ATOMA, NJEGOVE OKOLICE IN ZAČETNE LUPINE ELEKTRONA

FOTOABSORPCIJA RENTGENSKIH ŽARKOV

$E_0 = 500\,eV - 500\,keV$

$\lambda = 2500\,pm - 25\,pm$

FOTOEFEKT: foton absorbira (močno) vezan elektron (Einstein 1905)

Absorbcijski koeficient $\mu(E_0)$:

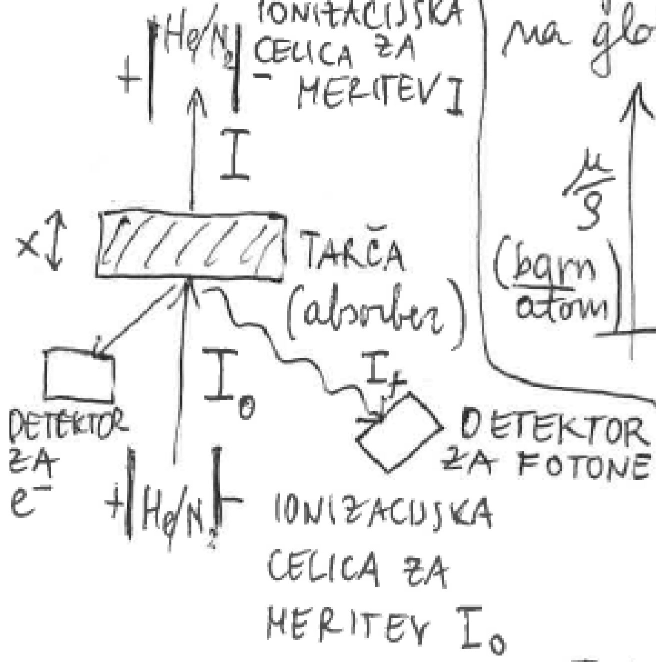
$$I(E_0, x) = I_0(E_0, 0)\, e^{-\mu(E_0)x} \quad \dots \text{ BEER-LAMBERT}$$

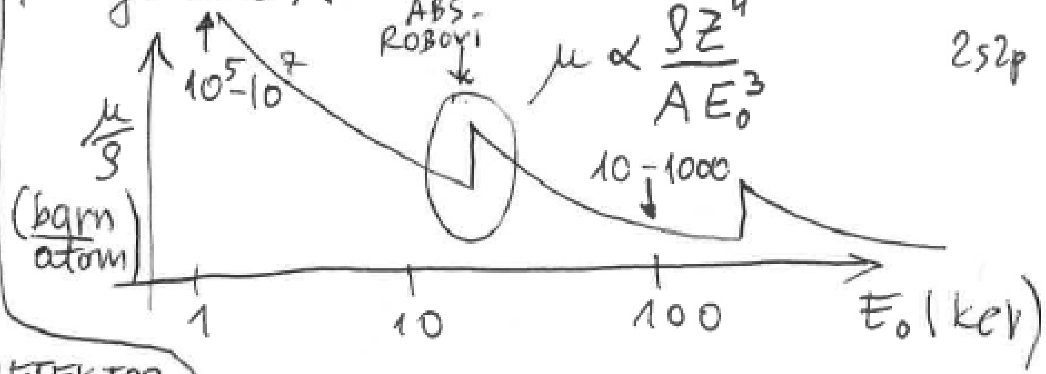
x ← globina tarče

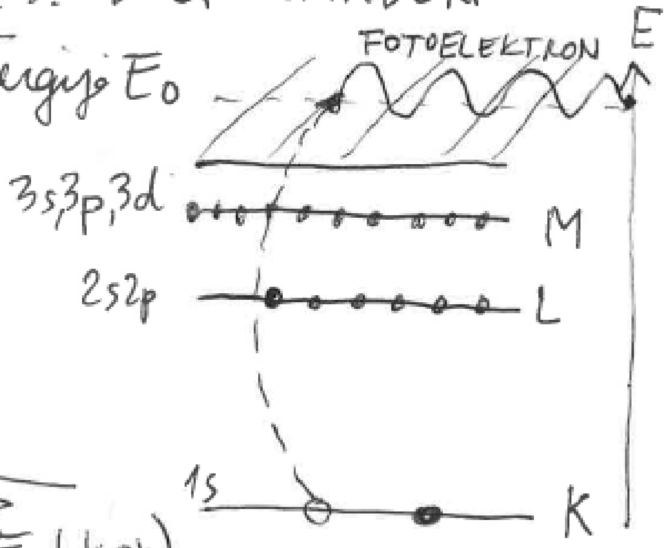
$\mu = \sigma_{abs}\, n$

$I_0(E_0,0)$: vpadni tok fotonov z energijo E_0

$I(E_0,x)$: tok fotonov z energijo E_0 na globini x





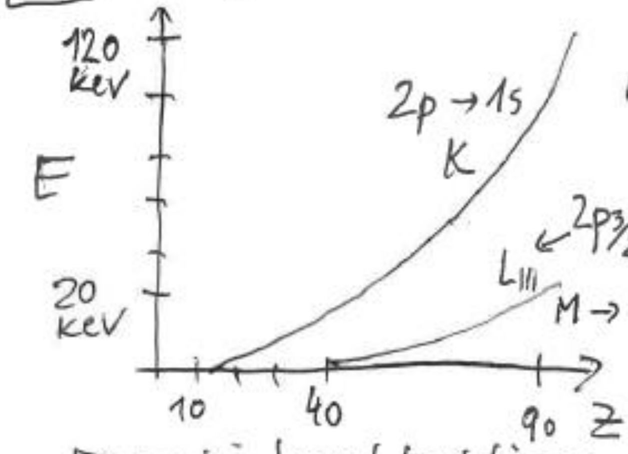


$$1\,\text{barn} = 10^{-28}\,m^2 = 10^{-24}\,cm^2$$

$$1\,a.u. = r_B^2 = 0{,}28 \cdot 10^{-16}\,cm^2 = 28\,\text{Mbarn}$$

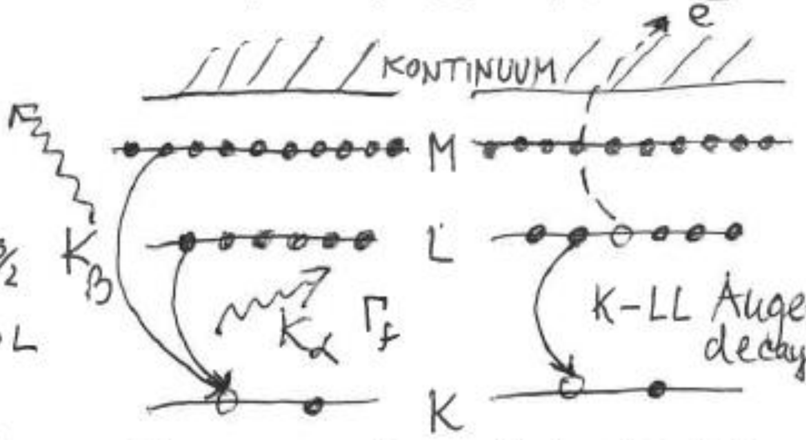
$$\mu(E_0) = \ln\left(\frac{I_0}{I}\right) \quad \text{TRANSMISSION}, \qquad \mu(E_0) \propto \frac{I_f}{I_0} \quad \text{FLUORESCENCE, AUGER EMISSION}$$

4 ABSORPCIJSKI ROBOVI



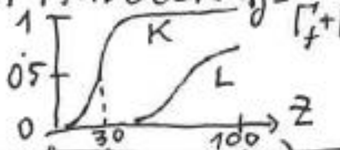
Energija karakterističnih rentgenskih žarkov

RAZPAD VRZELI K

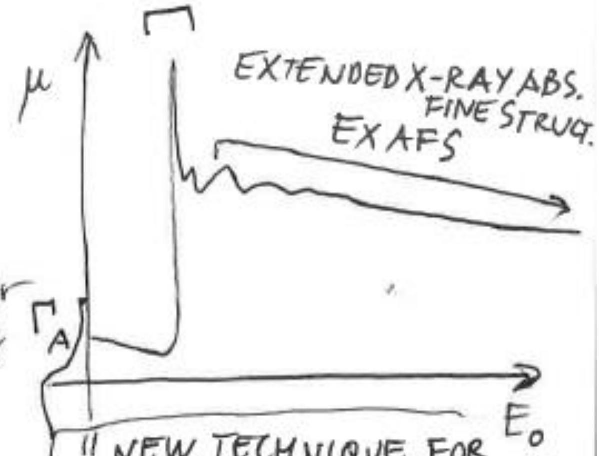


FLUORESCENČNI RAZPAD / AUGERJEV RAZPAD

FLUORESCENČNI PRIDELEK $\eta = \frac{\Gamma_f}{\Gamma_f + \Gamma_A}$

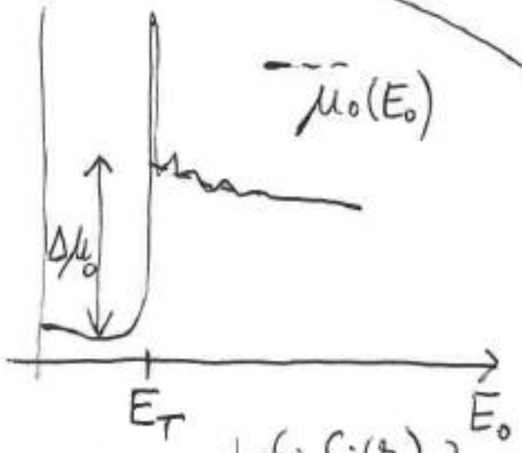


X-RAY ABSORPTION NEAR EDGE STRUCT. XANES



"NEW TECHNIQUE FOR INVESTIGATING NONCRYSTALLINE STRUCTURES: FOURIER ANALYSIS OF THE EXTENDED X-RAY ABSORPTION FINE STRUCTURE"
D.E. SAYERS, E.A. STERN & F.W. LYTLE, PRL 27, 1204 (1971)

EXAFS:



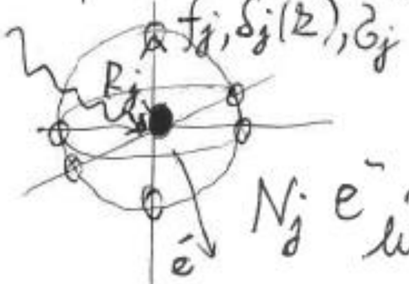
$$\chi(E_0) = \frac{\mu(E_0) - \mu_0(E)}{\Delta\mu_0}$$

$$\left[\frac{1}{m}\right] \quad k = \sqrt{\frac{2m(E_0 - E_T)}{\hbar^2}}$$

valovni vektor elektrona s kinetično energijo $E_0 - E_T$

MODELSKA ENAČBA:

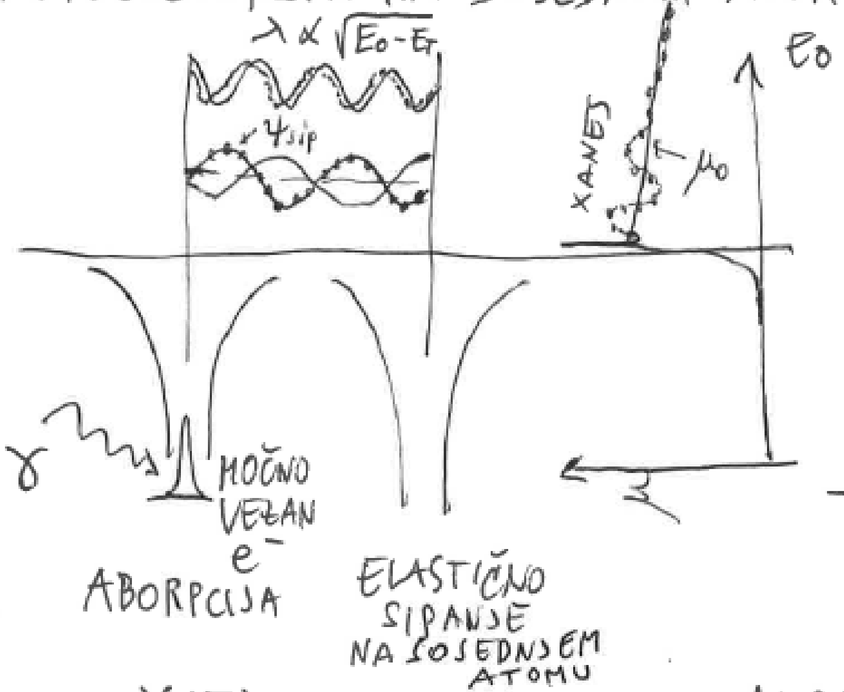
$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{k R_j^2} \sin(2kR_j + \delta_j(k))$$



N_j e^- v koordinacijski lupini j z radijem R_j

PREPROSTA "IZPELJAVA" FORMULE EXAFS:

UNDULACIJA ABSORPCIJSKEGA PRESEKA SE ZGODI ZARADI SIPANJA FOTOELEKTRONA NA SOSEDNJIH ATOMIH.



$$\mu(E_0) \propto |\langle i|H|f\rangle|^2$$

$$|f\rangle = |f_0\rangle + |\Delta f\rangle$$

$$\mu(E_0) \propto |\langle i|H|f_0\rangle|^2 \left(1 + \frac{\langle i|H|\Delta f\rangle \langle f_0|H|i\rangle^*}{|\langle i|H|f_0\rangle|^2} + c.c.\right)$$

$$\mu(E_0) = \mu_0(E_0)\left(1 + \chi(E_0)\right)$$

$$\rightarrow \chi(E_0) \propto \langle i|H|\Delta f\rangle \propto \int dr\, \delta(r) e^{ikr} \psi_{sip}(r)$$

$$\propto \psi_{sip}(0)$$

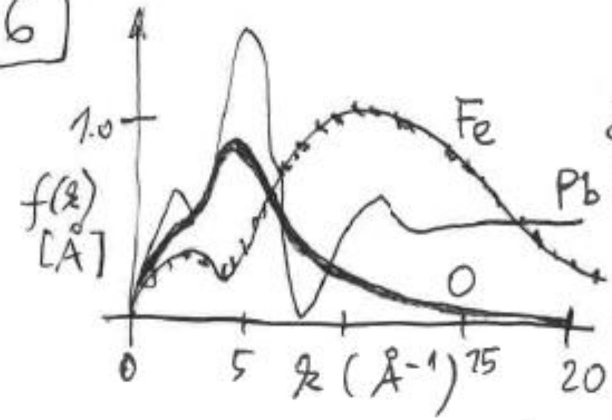
EXAFS $\chi(E)$ JE SORAZMEREN Z AMPLITUDO VALOVNE FUNKCIJE SIPANEGA ELEKTRONA NA MESTU IZVIRA.

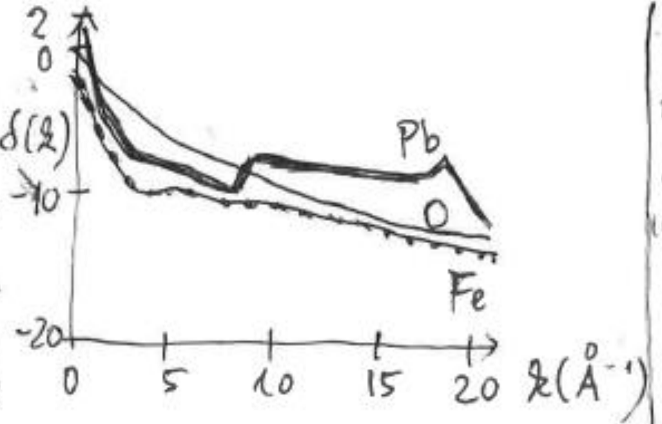
$$\psi(k,r) = \frac{e^{ikr}}{kr}, \quad \chi(k) \propto \psi_{sip}(k, r=0) = \frac{e^{ikR}}{kR}\left(2k f(k) e^{i\delta(k)}\right)\frac{e^{ikR}}{kR} + c.c.$$

PRISPEVEK ENEGA SOSEDNJEGA ATOMA $\longrightarrow$ $\chi(k) = \frac{f(k)}{kR^2} \sin(2kR + \delta(k))$ ODVISNA OD Z SIPALCA

N atomov na razdalji R $\longrightarrow$ $\chi(k) = \frac{N e^{-2k^2\sigma^2} f(k)}{kR^2} \sin(2kR + \delta(k))$

"RAZMAZANOST" DOLŽINE VEZI

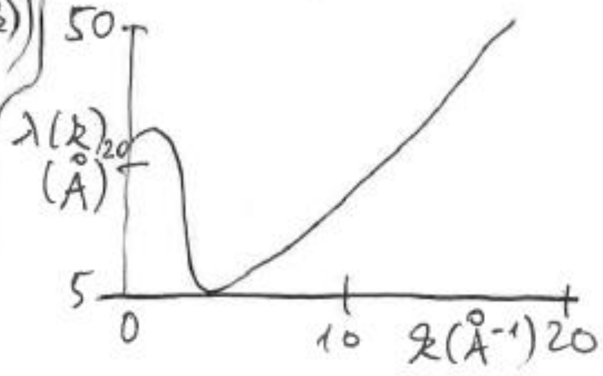




DODATNO DUŠENJE SIPANEGA KROGELNEGA VALA ZARADI NEELASTIČNEGA SIPANJA IN "ČASOVNE STISKE" (NA IZVIK SE MORA VRNITI PREDEN NOTRANJA VRZEL RAZPADE)

$$\psi(k,r) = \frac{e^{ikr}}{kr}\, e^{-\frac{2r}{\lambda(k)}}$$

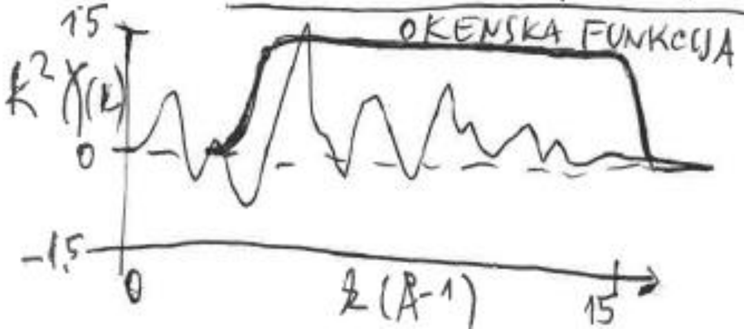
$$\chi(k) = \sum_j \frac{N_j\, e^{-2k^2\sigma_j^2}\, e^{-2R_j/\lambda(k)}\, f_j(k)}{k R_j^2} \sin\left(2kR_j + \delta_j(k)\right)$$

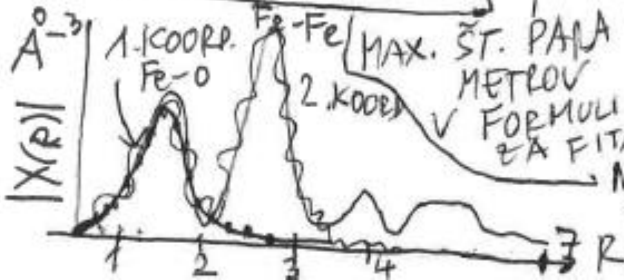


ODVISNOST $\lambda(k)$ TER $1/R_j^2$ NAREDITA EXAFS "LOKALNO" OBČUTLJIVEGA. MERITEV REDA KRATKEGA DOSEGA (~ 0.5 nm DOSEGA).

PRISPEVKE RAZLIČNIH "FREKVENC" V EXAFS SIGNALU (KOORDINACIJSKIH LUPIN Z RAZLIČNIMI R_j) LOČIMO S FOURIEROVO ANALIZO.

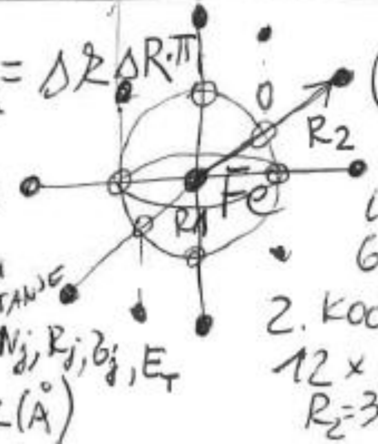
FEFF PROGRAM





$N_{MAX} = \Delta k\, \Delta R \cdot \pi$

MAX. ŠT. PARAMETROV V FORMULI ZA FITANJE → N_j, R_j, σ_j, E_T



FeO

1. KOORD. LUPINA 2.10 Å 6 × O ATOMOV

2. KOORD. LUPINA 12 × Fe ATOMOV $R_2 = 3.05$ Å

MERITEV ABSORPCIJE:

10% < KONCENTRIRANI VZORCI ⇒ **MERITEV V TRANSMISIJI**

VZOREC MORA BITI DOVOLJ TANEK, DA JE PREPUŠČENI TOK SVETLOBE I DOVOLJ VELIK. $\mu x \approx 2.5$ NAD PRAGOM IN $\Delta\mu_0 x \approx 1$

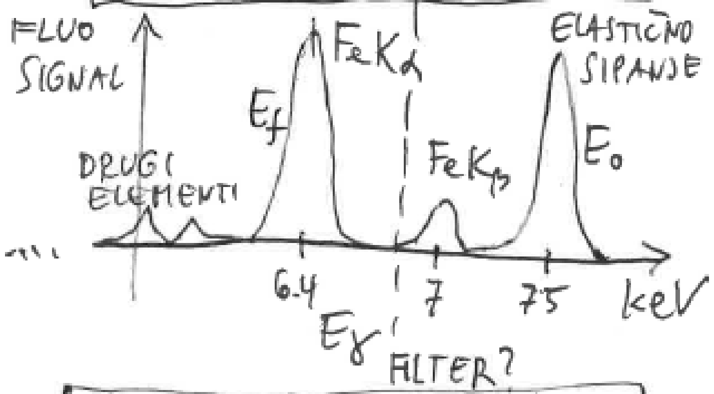
ZA KOVINE ~ NEKAJ 10 μm (Fe : 7 μm), mm ZA RAZREDČENE VZORCE V RAZTOPINAH

VZOREC MORA BITI HOMOGEN IN BREZ LUKENJ.

FLUORESCENČNA MERITEV → POLVODNIŠKI DETEKTOR SiLi

IMA ENERGIJSKO LOČLJIVOST ~ 150 eV NA K ROBU MANGANA 6.5 keV,

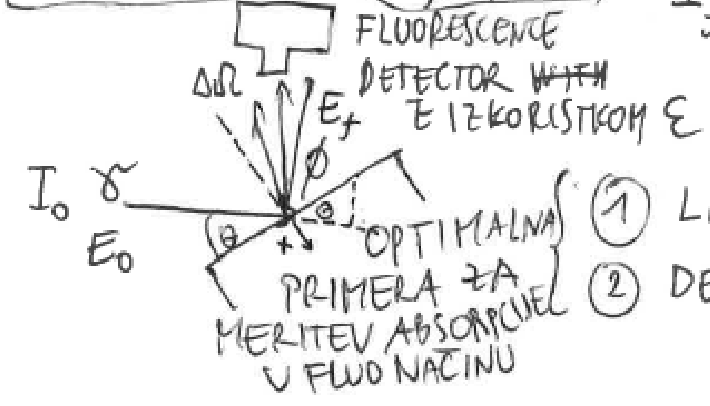
VELIK PROSTORSKI KOT DETEKCIJE $\Delta\Omega$?



SAMOABSORPCIJA: $I_f \not\propto \mu I_0$

$$I_f = I_0 \frac{\varepsilon \Delta\Omega}{4\pi} \mu_x(E_0) \frac{\left\{1 - e^{-(\mu_{TOT}(E_0)/\sin\theta + \mu_{TOT}(E_f)/\sin\phi)\cdot x}\right\}}{\mu_{TOT}(E_0)/\sin\theta + \mu_{TOT}(E_f)/\sin\phi}$$

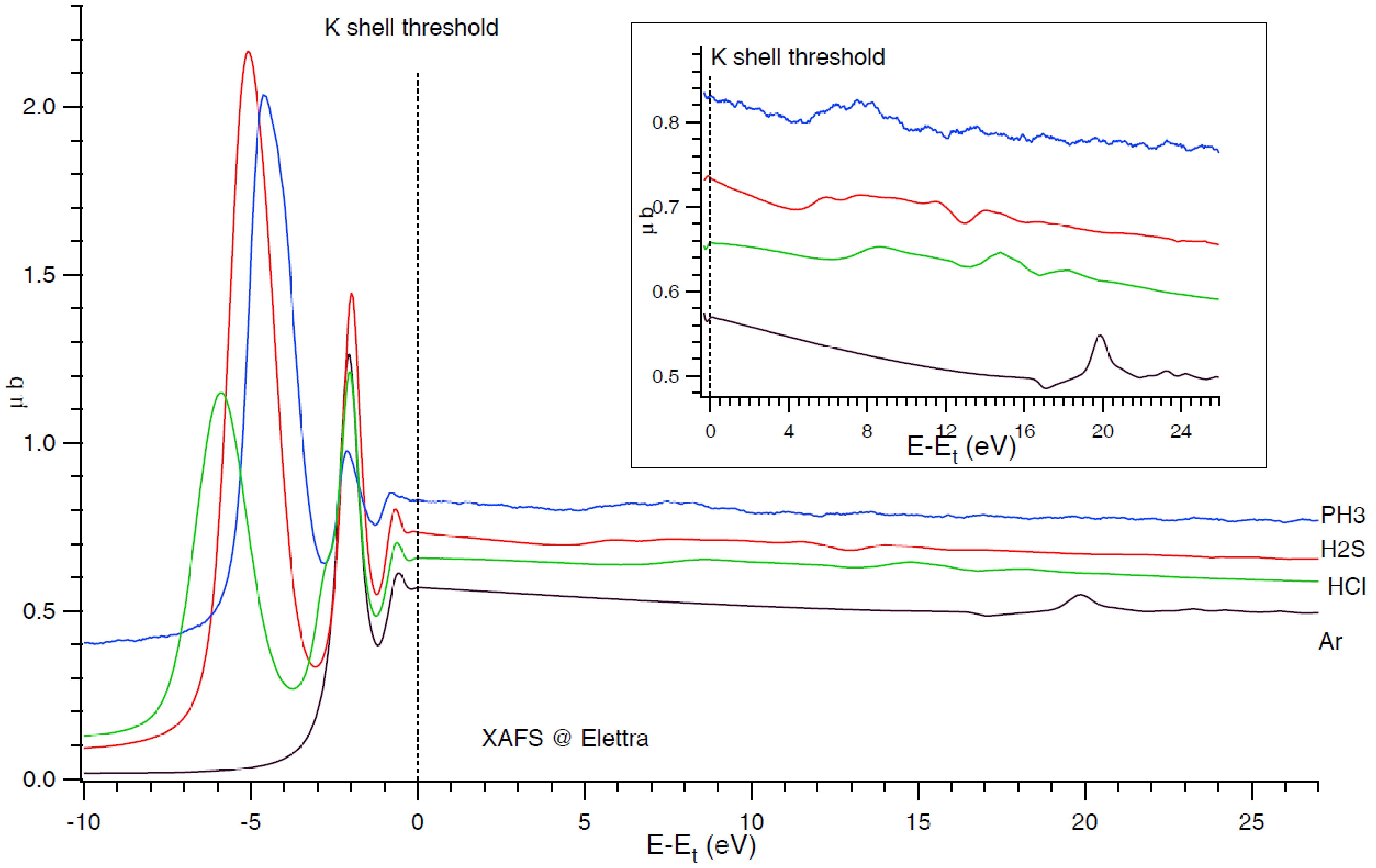
$$\mu_{TOT} = \mu_x + \mu_{DRUGI}$$



① LIMITA TANKEGA VZORCA: $\mu x \ll 1 \rightarrow I_f \approx I_0 \frac{\varepsilon \Delta\Omega}{4\pi} \mu_x(E_0)\cdot x$

② DEBEL VZOREC Z MAJHNO KONC. X: $\mu x \gg 1$, $\mu_x \ll \mu_{DRUGI}$

$$I_f = I_0 \frac{\varepsilon \Delta\Omega}{4\pi} \frac{\mu_x(E_0)}{\mu_{TOT}(E_0)/\sin\theta + \mu_{TOT}(E_f)/\sin\phi} \propto I_0 \mu_x(E_0)$$


K shell threshold
XAFS @ Elettra
μ b
E-E$_t$ (eV)
PH3
H2S
HCl
Ar
0.0
0.5
1.0
1.5
2.0
-10
-5
0
5
10
15
20
25
K shell threshold
0.5
0.6
0.7
0.8
0
4
8
12
16
20
24