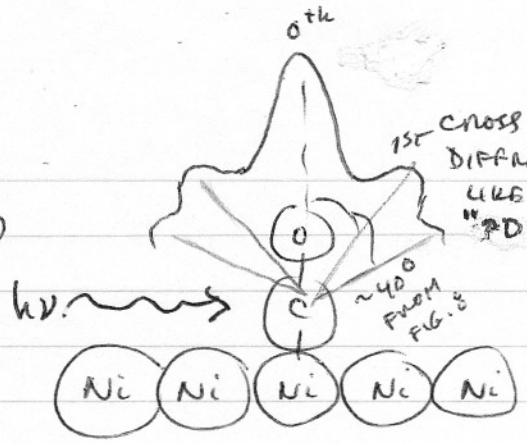
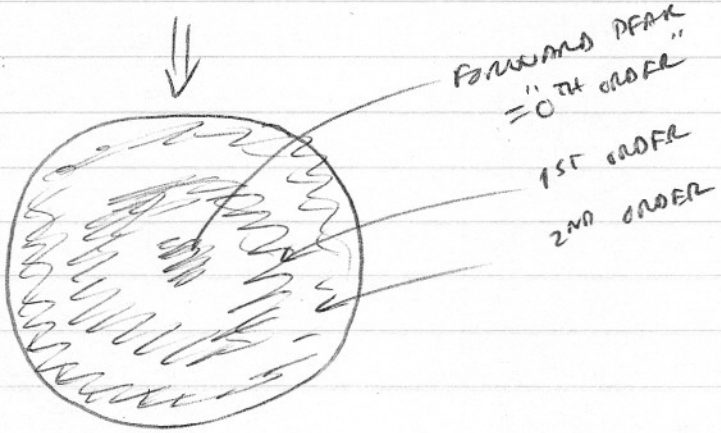
20 points

[4.5] (a)





SO 2D PLOT OF HEMISPHERE DATA IS LIKE:

(b) JUST USE $\ell_{max} = kr_{MUFFIN-TIN}$

WITH:

$E_{kin} \approx 1486.6 - 284 \approx 1202\ eV$

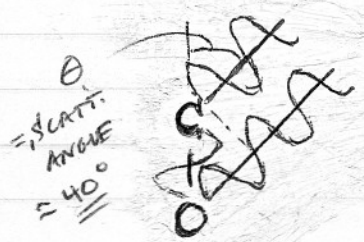
$k = 0.512\,(1202)^{1/2} = 17.8\ \text{Å}^{-1}$,

SO

$$\ell_{max} = (17.8)(1.1) = 19.5 \Rightarrow \underline{\underline{20}}$$

(c) FOR FIRST-ORDER INTERFERENCE: $n = 1$

$$2\pi = kr_{C\text{-}O}(1 - \cos\theta_1) + \psi_0(\theta_1)$$

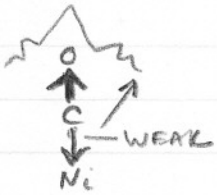


$$2\pi = 17.8\,(1.18)\,(1 - \cos(40°)) + \psi_0(\theta_1)$$

$$6.28 - 4.91 = \psi_0(\theta_1)$$

$$\psi_0(\theta_1) = \underline{\underline{1.37\ \text{rad} \approx 78°}}$$

(d) See following pages, with brief answers as:
1st order = 6th order, due to dominance of single forward scattering like:



(e) See following pages as well, with brief answers as:
Lowering energy increases photoe⁻ wavelength and makes rings larger in diameter
" " also increases importance of multiple scattering, as well as Ni backscattering, but single-scattering picture still an excellent description.

Answers to parts (d) and (e):

Cluster definition

The cluster and the list of emitters are defined by a list of commands with the following format (click here or on the items of this list for further details):

atom symbol $x\ y\ z$ layer symbol $x\ y\ z\ a\ b\ \alpha_1\ \alpha_2$

surface symbol $x\ y\ z\ a$ type emitter $x\ y\ z$

Fill in the text box with these commands according to the cluster specifications that you need. Some examples are provided by clicking here (you may cut and paste them to this page and modify them further).

```
atom O 0 0 1.18
atom C 0 0 0
atom Ni 0 0 -1.83
emitter 0 0 0
end
```

The cluster consists of a maximum of 3 **atoms. (Warning: a finite number of atoms generally introduces symmetry breaking.)**

The size of the cluster is determined by the distance d_{max} = 10 **Å and the reference point** x_0 = 0 **Å,** y_0 = 0 **Å,** z_0 = 0 **Å.**

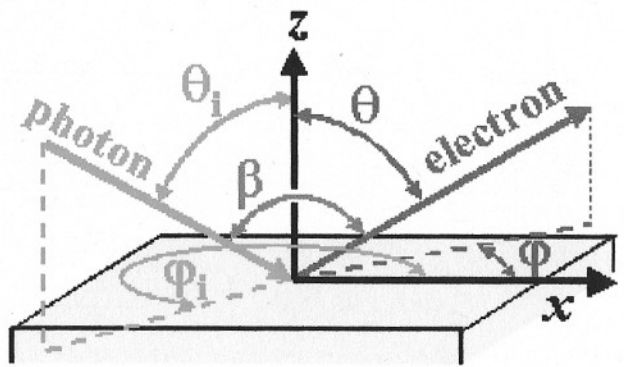
See cluster shape **for more details.**

Geometry of beam and analyzer

Incoming beam parameters (see figure)

Polar angle θ_i = 0 degrees

Azimuthal angle φ_i = 0 degrees



Schematic representation of the geometry

Polarization:
- (•) p-polarization
- ( ) s-polarization
- ( ) RCP
- ( ) LCP

Mobility of cluster beam, and sample (click here for details):
- (•) Only the sample moves with constant β = 90 degrees
- ( ) Only the analyzer moves
- ( ) Both the sample and the analyzer move

Could do it this way too: see later

Note: the parameter β specifies the angle between beam and analyzer when this is kept constant during the simulation (i.e., everything happens as if it is only the sample that is rotated); therefore, this parameter is not required when only the analyzer moves or when both the sample and the analyzer move (click here for details).

Energy and angle scanning parameters (see figure above)

The following entries will select the range of photoelectron energies and angles of emission.

Energy scans for a given emission angle can be chosen by selecting more than one energy of emission and only one polar angle and one azimuthal angle (the value of each angle is then taken as the lower limit of the selected angular range, and the value of the upper limits are disregarded). In this case, the output is a 1D plot with the photoelectron intensity as a function of photoelectron energy.

Angular scans can be chosen by selecting only one photoelectron energy. Then, if the polar and the azimuthal angles take both more than one value, the output is a 2D polar plot of the photoelectron intensity. Otherwise, if only one polar angle is selected, a 1D plot is generated (an azimuthal scan), whereas if only one azimuthal angle is selected then a 1D polar plot is given in the output.

For 2D angular scans, a linear or logarithmic scale of the photoelectron intensities can be selected for the grey scale (see below). More details about the 2D representation (e.g., type of projection on 2D) are given in the caption of the output.

Electron energy range: 1 equally-spaced value(s) of the electron energy from 1202 eV to 1202 eV

Polar angle: 50 equally-spaced value(s) of the polar angle θ from 0 degrees to 89 degrees

Azimuthal angle: 61 equally-spaced value(s) of the azimuthal angle φ from 0 degrees to 360 degrees

Type of 2D angular representation: ○ Linear scale ◉ Logarithmic scale

Type of azimuthal of polar angular representation: ◉ Cartesian ○ Polar

Use Ni Nearest-neighbor distance

Multiple scattering parameters

Additional solid parameters

Inner potential V_0 = 14.0 eV

Use band structure plus work function

Electronic edge z_0 = 2.5 Å

Internal code parameters

Maximum orbital quantum number l_{max} = 20

Scattering order = 1

Iteration method: ○ Jacobi (regular MS) ◉ Recursion + 6 for second part

Inelastic mean free path: **either choose a fixed value** = -10 Å

or (if that last entry is <0) use the TPP-2M formula for Ni

with parameters ρ = 8.91 g/cm^3, N_v = 10, E_p = 35.5 eV, and E_g = 0.0 eV

TPP-2M

Temperature (K) = 298 and Debye emperature (K) = 450

Initial core-state quantum numbers

Radial matrix elements: ◉ Automatic: core level (e.g. 1s, 2s, 2p, etc.) = 1s

○ Manual: l_0 = 0, R_{l0+1} = 1.0, δ_{l0+1} = 0.0, R_{l0-1} = 0.0, δ_{l0-1} = 0.0

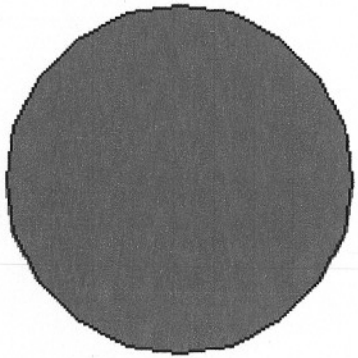
Calculate* Download Input File** Reset***

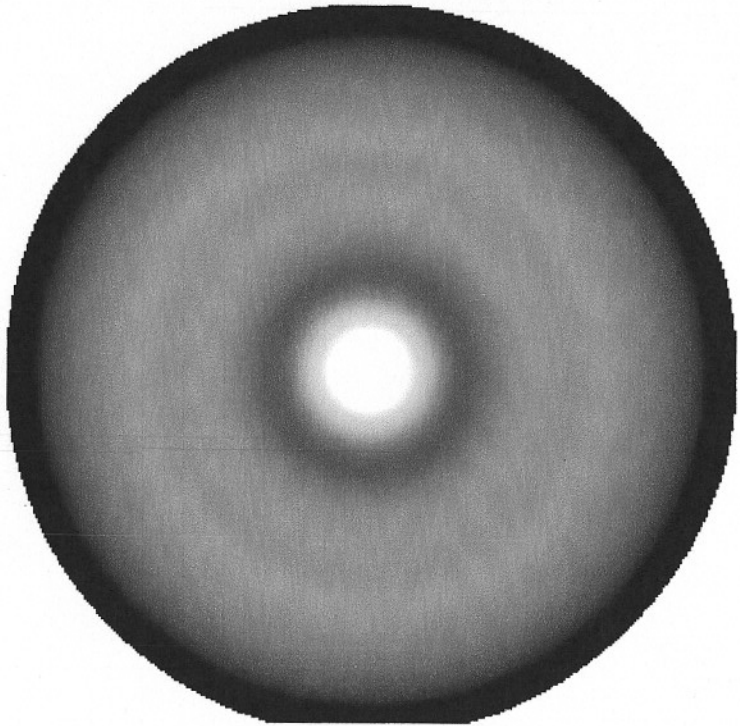
COMPUTATION TIME: the CPU time needed for the calculation using the default cluster and input parameters (use Reset to recover default input) is 1.24 seconds on a Pentium III @ 733 MHz. This gives a time scale to estimate the computation time for other input parameters, keeping in mind that it scales like ~ (n_{scat} -

EDAC output for O-C-Ni

Click on the figure to download data.

1202 eV
1st order only

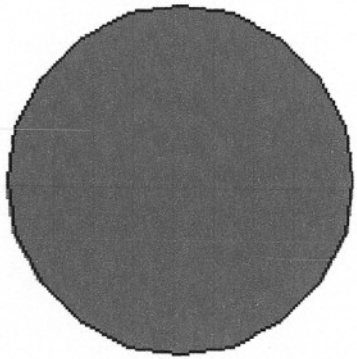


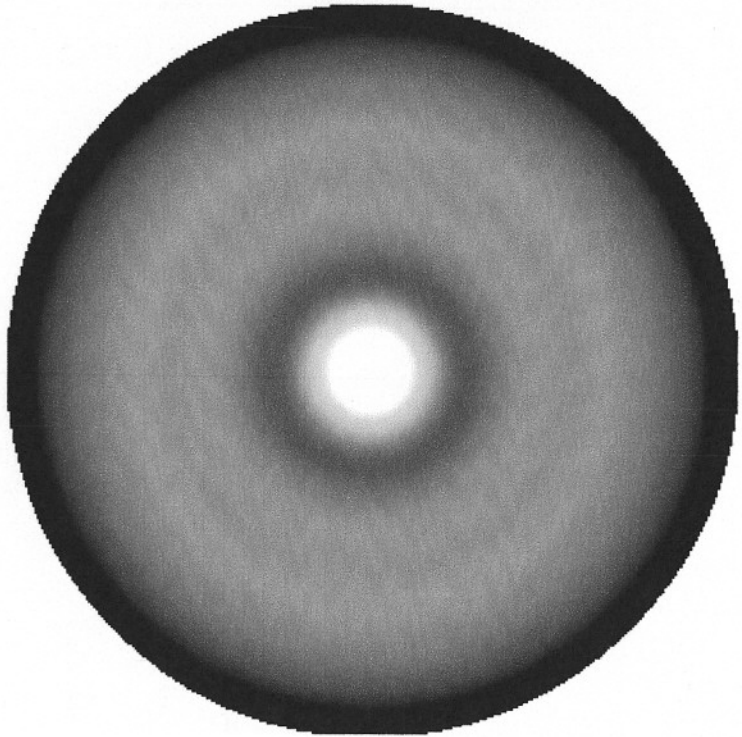


EDAC output for O-C-Ni

Click on the figure to download data.

1202 eV, 6th order—
no difference,
fwd. scatt. dominant





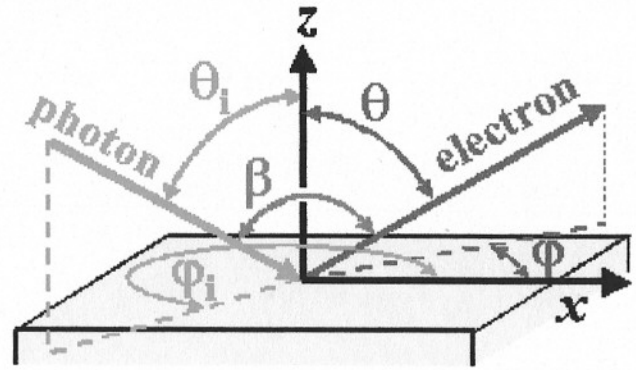
Alternate geometry setup, with analyzer moving only

Geometry of beam and analyzer

Incoming beam parameters (see figure)

Polar angle θ_i = 89 degrees

Azimuthal angle φ_i = 0 degrees



Schematic representation of the geometry

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- (•) Only the analyzer moves
- ( ) Both the sample and the analyzer move

Note: the parameter β specifies the angle between beam and analyzer when this is kept constant during the simulation (i.e., everything happens as if it is only the sample that is rotated); therefore, this parameter is not required when only the analyzer moves or when both the sample and the analyzer move (click here for details).

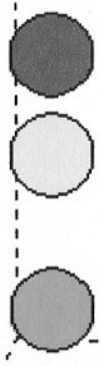
Alternate geometry setup, with analyzer moving only

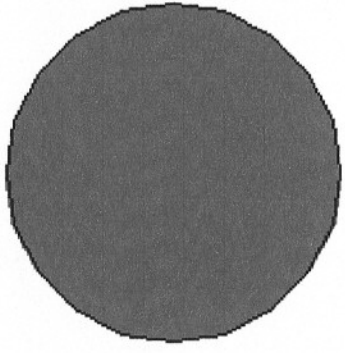
EDAC output for O-C-Ni

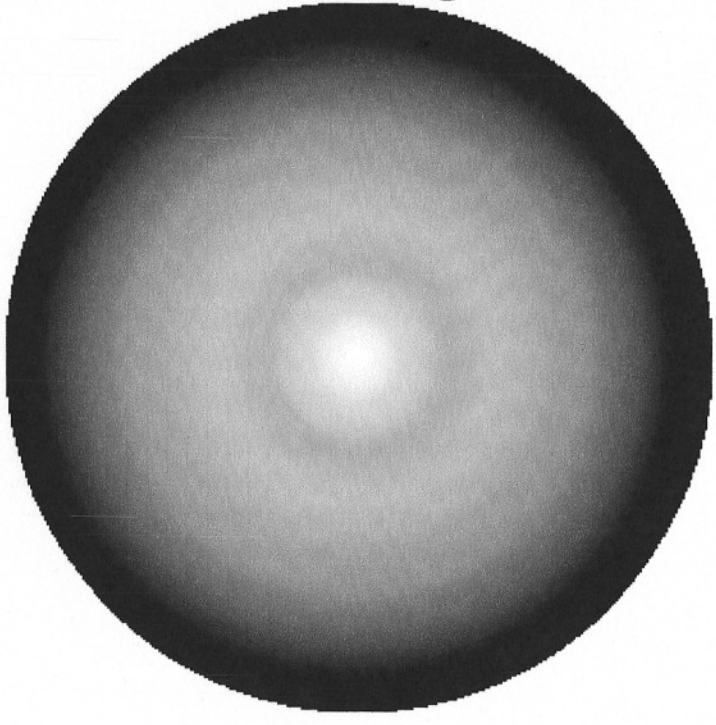
Click on the figure to download data.

1202 eV

6th order—rings more clear





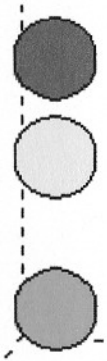


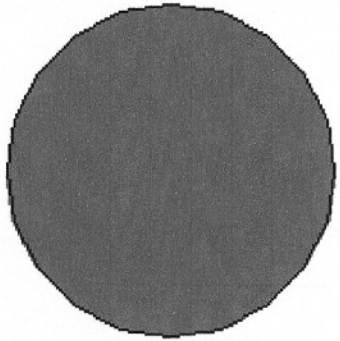
Back to first geometry inputs, sample rotating

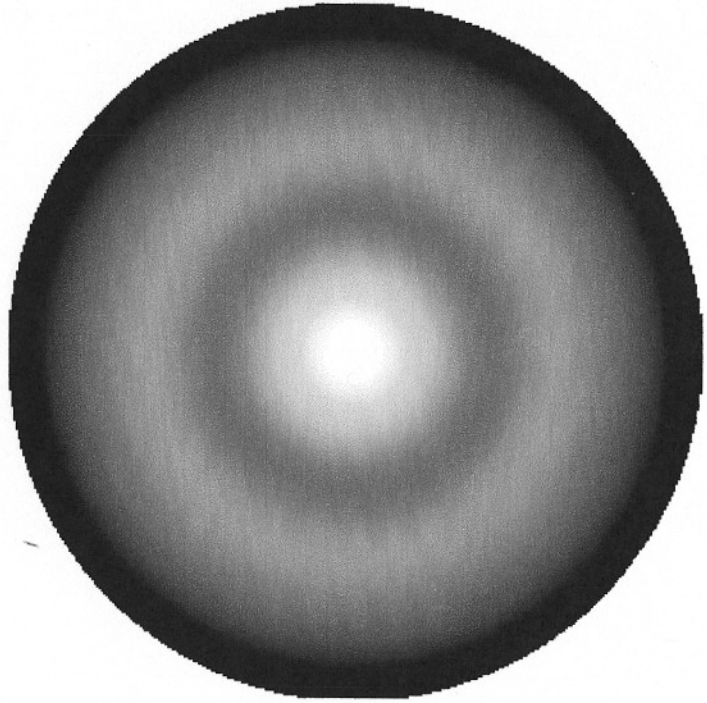
EDAC output for O-C-Ni

Click on the figure to download data.

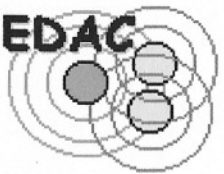
100 eV
1st order







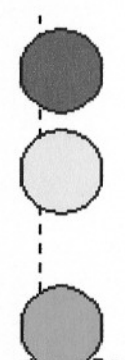
EDAC output for O-C-Ni

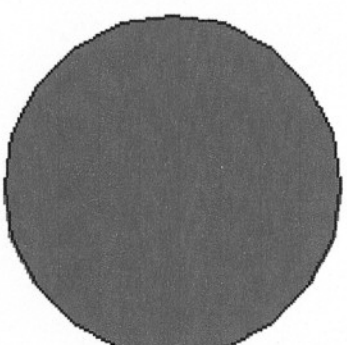


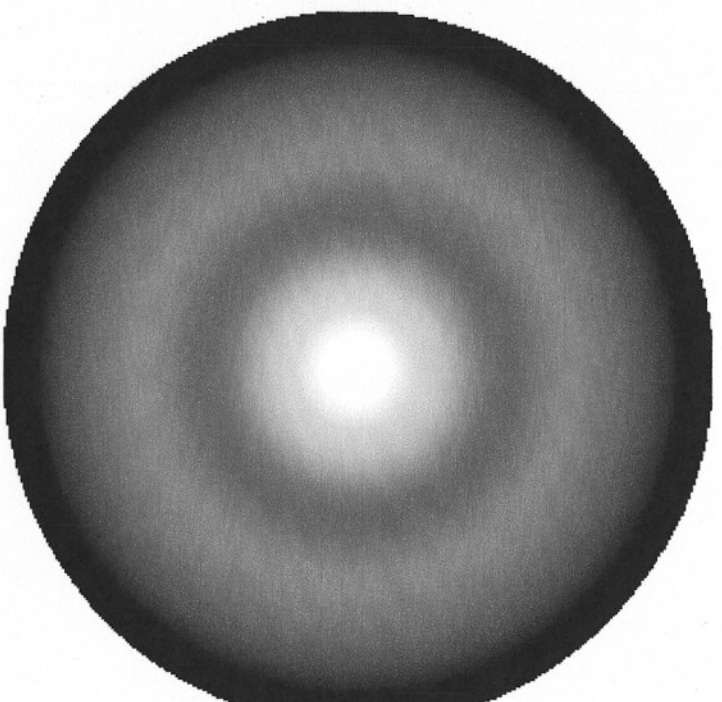
Click on the figure to download data.

100 eV

6th order—slight difference





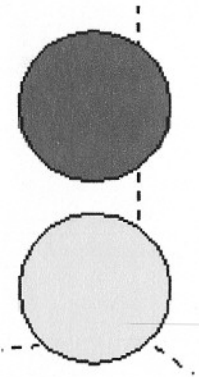


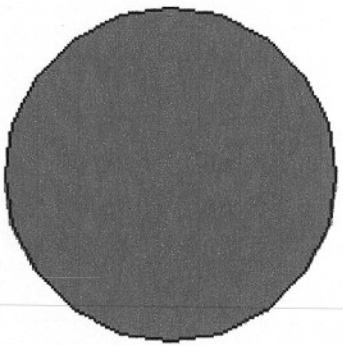
EDAC output for O-C-Ni

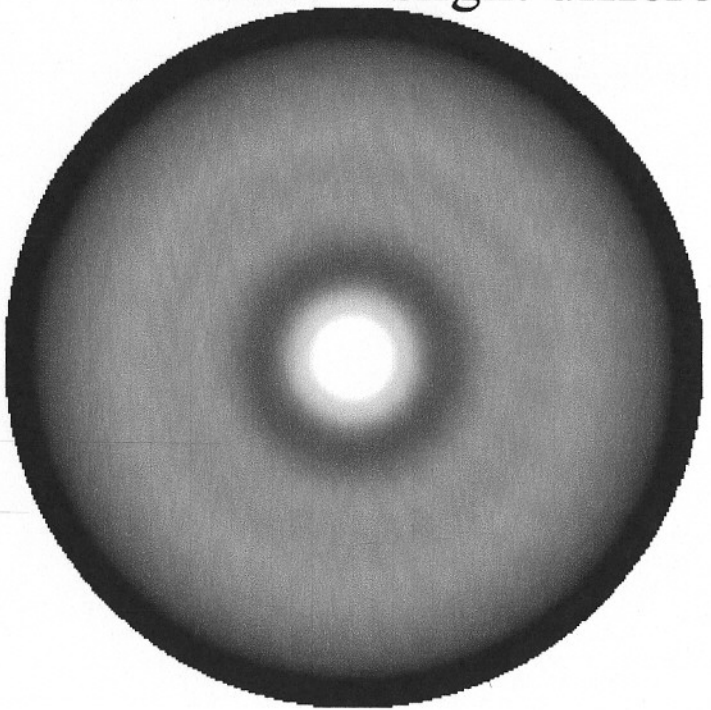
Click on the figure to download data.

1202 eV, no Ni

6th order—slight difference





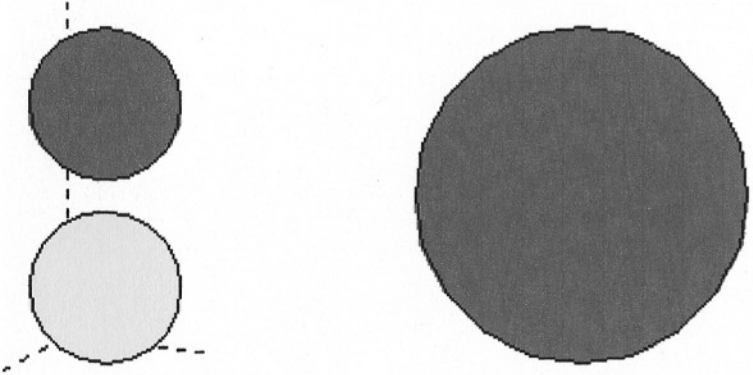


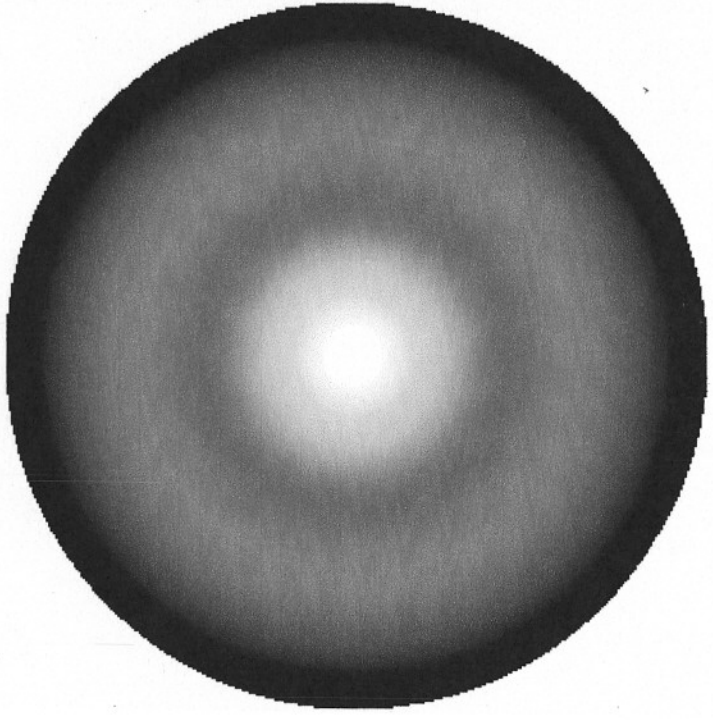
EDAC output for O-C-Ni

Click on the figure to download data.

100 eV, no Ni

6th order—slight difference





[4.7]

(a) The relevant equation is:

$$\sin\theta_{inc} + \sin\theta_{refl} = m\lambda_x/d$$

or

$$\sin\theta_{refl} = m\lambda_x/d - \sin\theta_{inc}$$

With fixed θ_{inc}, the derivative is calculated via:

$$d\sin\theta_{refl}/d\theta_{refl} = \cos\theta_{refl} = (m/d)d\lambda_x/d\theta_{refl}$$

Thus,

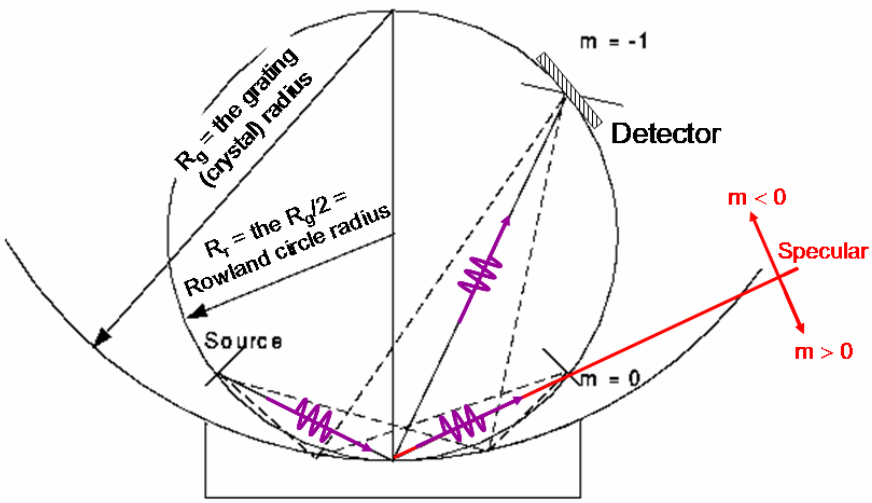
$$d\theta_{refl}/d\lambda_x = m/(d\cos\theta_{refl}),$$

5

a quantity which is larger for higher order *m*, smaller line spacing *d*, or larger reflection angle θ_{refl}.

(b) The geometry is as introduced in lecture:

The (Focusing) Rowland Circle
X-Ray Monochromator/Spectrometer Geometry



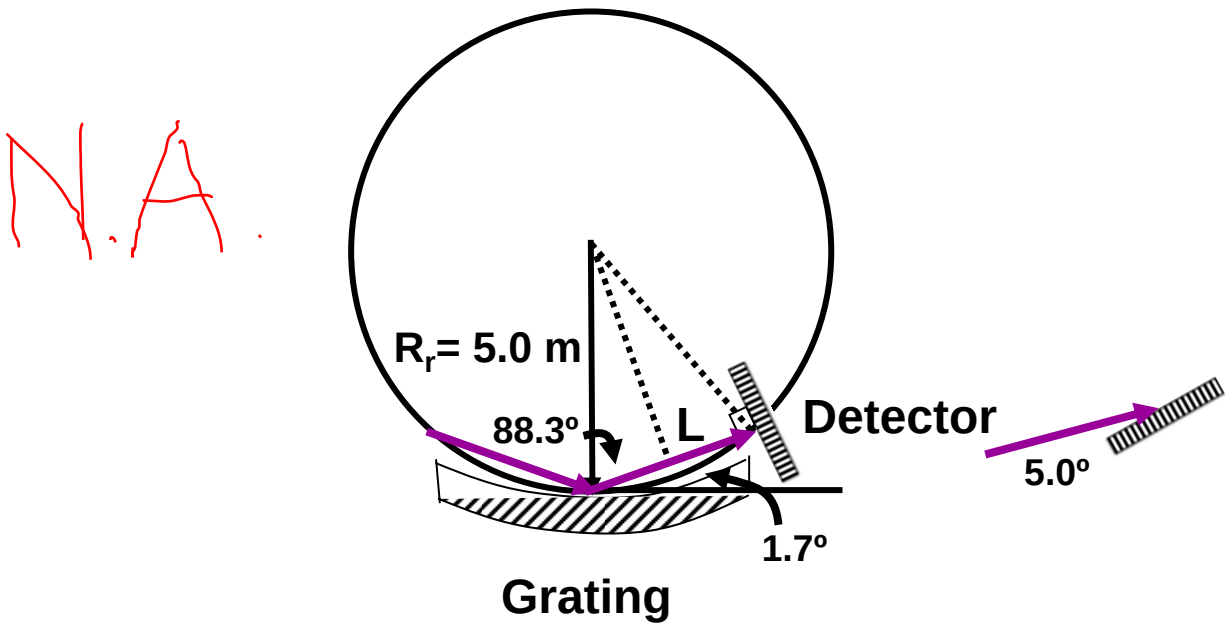
Curved grating (soft x-rays)
or single crystal (hard x-rays)

First use the grating equation to determine θ_{refl},
with parameters of d = 1/1200 mm = 8.33 x 10^{-4} mm = 8.33 x 10^{-7} m,
***θ_{inc} = 1.9º, λ_x = 12,398/500 Å = 24.8 Å = 2.48 x 10^{-9} m,* and assuming**
first-order reflection so *m* = 1, we have:
$\sin\theta_{refl} = m\lambda_x/d - \sin\theta_{inc}$ = 1(2.48x10^{-9})/8.33x10^{-7} - sin(1.9º) = 0.0029-
0.033 = -0.030, or θ_{refl} = 1.7º. (cont'd)

So this is nearly specular reflection, and the reflectivity is high for soft x-rays, another important consideration in the design.

Thus also,
$d\theta_{refl}/d\lambda_x = m/(d\cos\theta_{refl}) = 1/(8.33 \times 10^{-7}\ m)\cos(1.7^o)$
$= 1.2 \times 10^6$ **radians/m =** 1.2×10^3 **radians/mm**

The change in wavelength for 0.1% energy resolution is from say 500 eV to 500.5 eV or from 24.796 Å to 24.771 and thus $\Delta\lambda_x$ **= 0.025 Å =** 2.5×10^{-9} **mm, so** $\Delta\theta_{refl} = (1.2x10^3)x(2.5x10^{-9}) = 3.0 \times 10^{-6}$ ***radians***

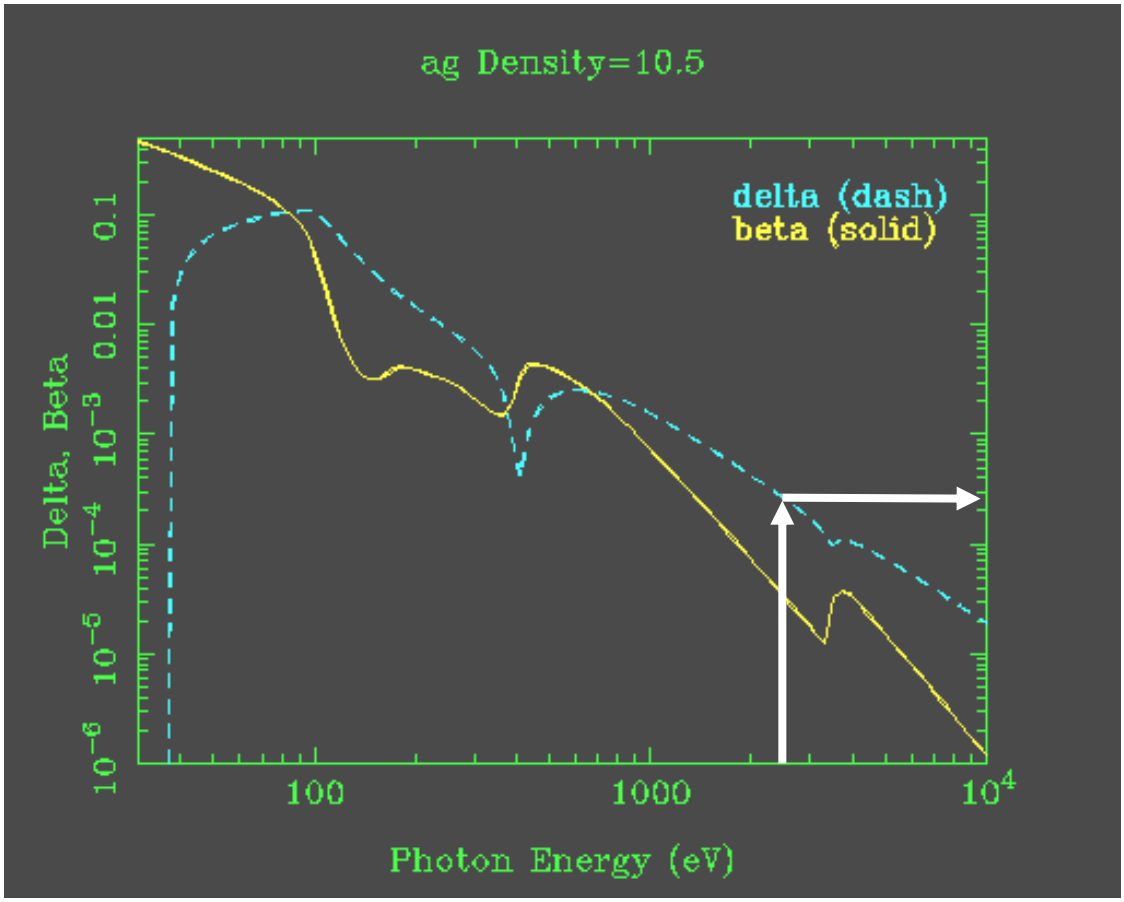


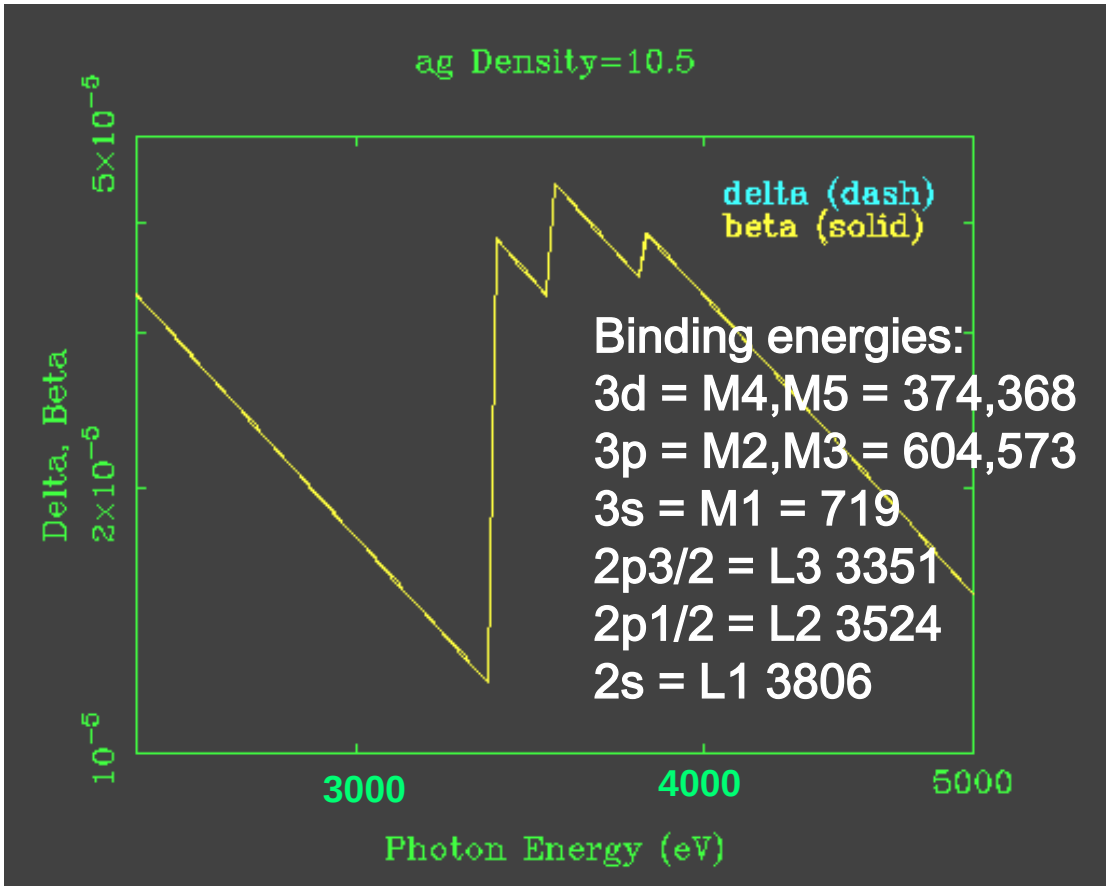
From the geometry above, the distance of the detector from the center of the grating is L = $2R_r\cos(88.3^o)$ **= 2(5.0m)(0.029) = 0.296 m = 296 mm.**

Thus, the distance between two points separated by $\Delta\lambda_x$ **at the detector will be** $(3.0x10^{-6})(296) = 8.88 \times 10^{-4}$ **mm =** 8.88×10^{-7} **m = 88.8 microns. So we would need resolution in the detector about 1/10th of this or about 9 microns to adequately resolve this change in energy.**

Reorienting the detector so that the light hits at a grazing incidence angle of 5º (see above left) simply increases the spacing of the detector channels as $1/(\sin\theta_{det}) = 11.5$**, so we could relax the detector resolution to about 100 microns.**

5.1 (a)

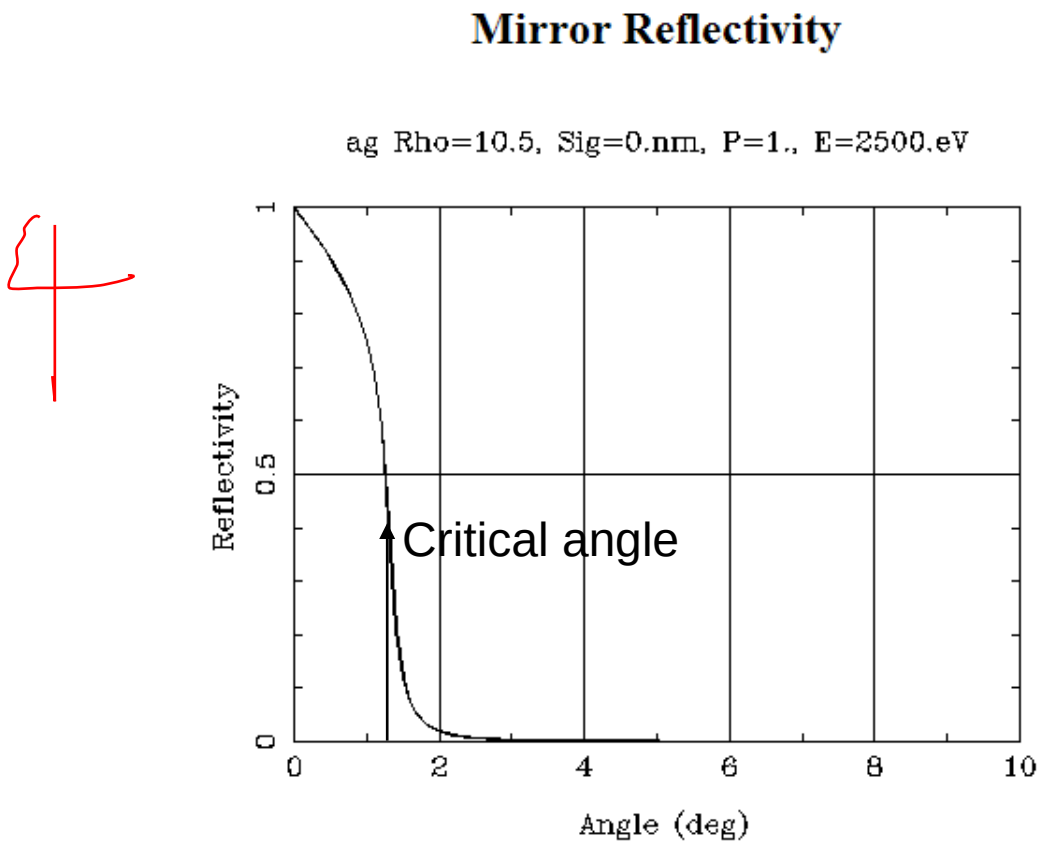

ag Density=10.5
delta (dash)
beta (solid)
Delta, Beta
0.1
0.01
10^{-3}
10^{-4}
10^{-5}
10^{-6}
100
1000
10^4
Photon Energy (eV)


ag Density=10.5
delta (dash)
beta (solid)
Delta, Beta
5×10^{-5}
2×10^{-5}
10^{-5}
3000
4000
5000
Photon Energy (eV)
Binding energies:
3d = M4,M5 = 374,368
3p = M2,M3 = 604,573
3s = M1 = 719
2p3/2 = L3 3351
2p1/2 = L2 3524
2s = L1 3806

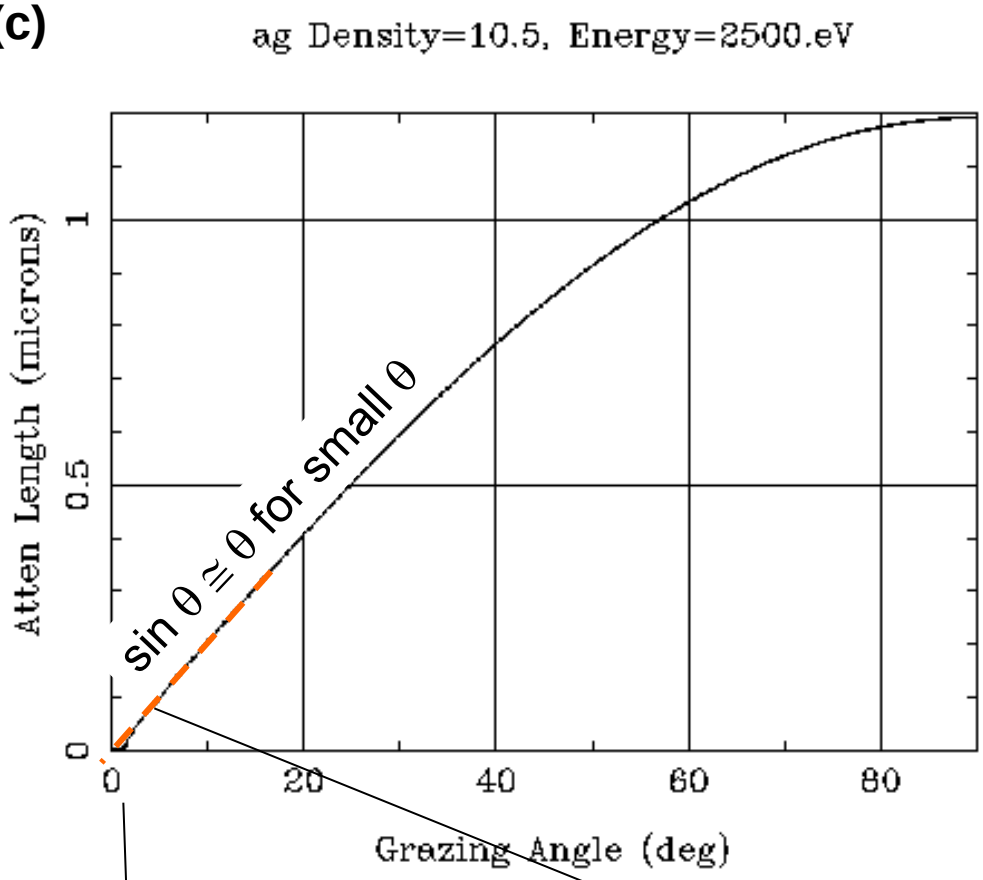
5.1 (a) (cont'd)
Yes, increases in beta over 2500-5000 eV are associated with turning on the absorption of the various levels in the n = 2 or L shell.

From binding energies for Ag L shell (see prior page), we see that three are needed, and three steps are seen in beta. Therefore, spin-orbit is included in this range of the tabulation of index of refraction.

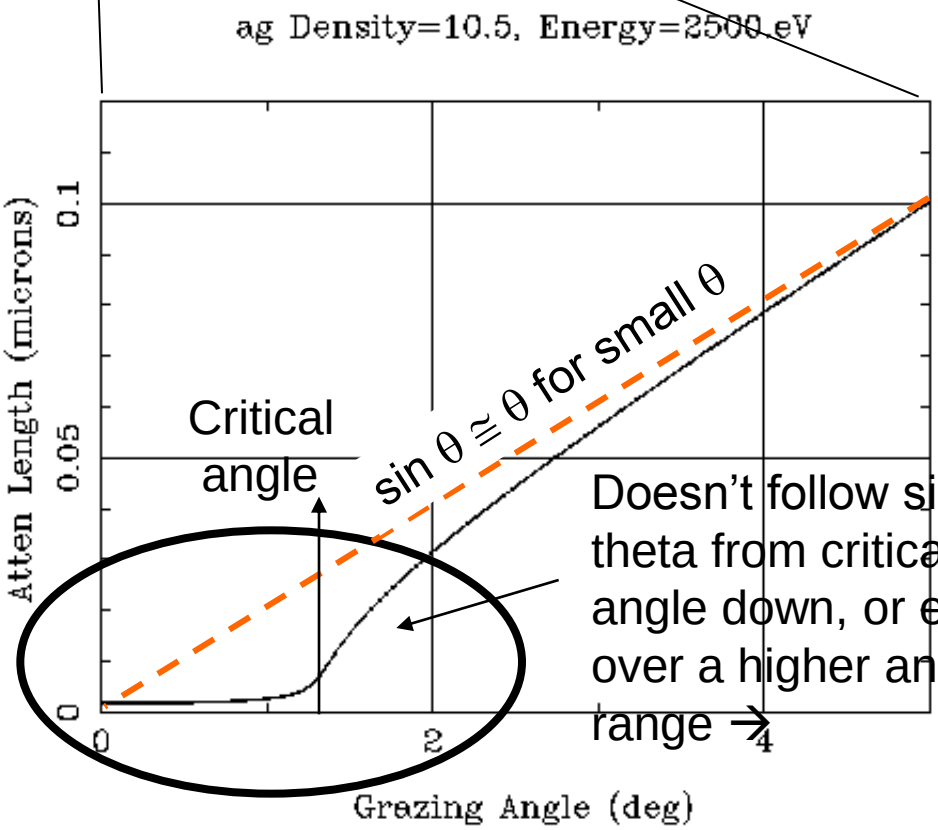
(b) From the first plot on the prior page, the critical angle in this regime should be about sqrt(2delta)$^{1/2}$ in radians, or with delta ≅ 2.5x10^{-4} over the n = 3 absorption edges, this gives 0.223 radians or 0.0223(360/2π) = 0.0223(57.3 deg./radian) = 1.3 deg. Plot below shows R ≅ 0.4 at this angle.



5.1 (c)



4

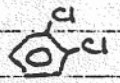
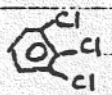
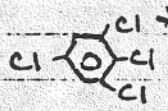


Doesn't follow sin theta from critical angle down, or even over a higher angle range →

[5.2] (a) In each molecule, carbons at lower E_{kin} (higher E_b) are those bonded to Cl. Electronegative Cl withdraws valence charge, thereby increasing binding energy.

Relative intensities should to first order be proportional to no. of atoms, so

5

Molecule	Predicted Relative Intensity C(Cl)/C(H)
	$2.0/4.0 = 0.5$
	$3.0/3.0 = 1.0$
 *	$4.0/2.0 = 2.0$

These intensities are in good agreement with experiment, as can be verified by visual inspection.

---

* For this molecule, one might expect three kinds of carbon, three grouped C(Cl)'s, one isolated C(Cl), and 2 C(H)'s. However, nearest neighbor effects dominate the C(Cl) shift, so that all C(Cl)'s occur at the same E_b.

(b) This result is consistent with the potential model, which predicts that

$$E_b^V(\text{C 1s, molecule}) = E_b^V(\text{C 1s, free ion of charge } q_c) + \sum_{i \neq C} \frac{q_i}{r_{ci}}$$

or

$$E_b^V(\text{C 1s, molecule}) - \sum_{i \neq C} \frac{q_i}{r_{ci}} = E_b^V(\text{C 1s, Free ion of charge } q_c),$$

provided that we make the identification

$$E_b^V(\text{C 1s, free ion of charge } q_c) = 284.9 + 23.3\, q_c .$$

The significance of the constants is thus:

$$284.9 = E_b^V(\text{C 1s, free atom, } q_c = 0)$$

$$23.3 = C_c \approx J_{\text{1s-valence}}$$

(c) From the last line above

$$J_{\text{1s-valence}} \approx 23.3 \text{ eV}$$

(d) Answer above.

[5.3] (a) NO – 15 e^- TOTAL IN CONFIG.

$$\underbrace{(1s_O)^2(1s_N)^2}_{(1s)^2}\underbrace{(2s)^2}_{(2s)^2}(2p_z)^2(2p_x)^2(2p_y)^4(2p_z)^2(2p_x)^1$$

$(2p_y)^2$ $(2p_z)^2$ UNPAIRED $e^- \Rightarrow$ PARAMAGNETIC MOLECULE WITH $S = 1/2$

5

(b) FOR O 1s EMISSION: $\Delta E_b(O1s) \propto K_{O1s,2p}$

FOR N 1s EMISSION: $\Delta E_b(N1s) \propto K_{N1s,2p}$

5

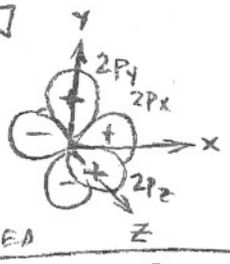
(c) $2p$ MO IS MORE LOCALIZED ON N END OF MOLECULE. THUS, N1s, $2p$ OVERLAP IS LARGER AND $K_{N1s,2p}$ ALSO IS LARGER.

5

Nitric Oxide

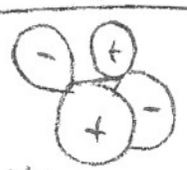
Symmetry: $C_{\infty v}$

[2]

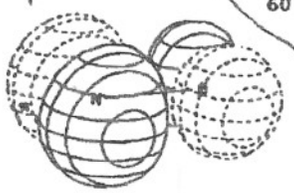


UNOCCUPIED

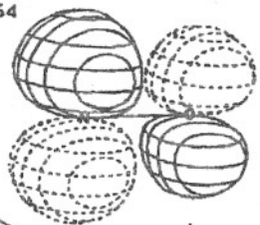
OCCUPIED



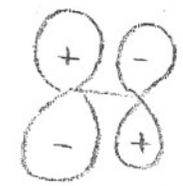
$N2p_z - O2p_z$



$2\Pi_z$ E=-0.3359

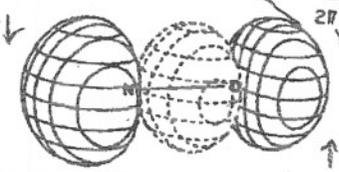


$2\Pi_y$ E=-0.3359

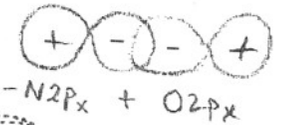


$N2p_y - O2p_y$

π ANTI-BONDING

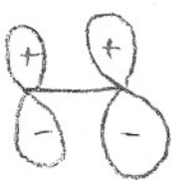


5σ E=-0.5371



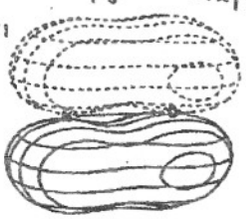
$-N2p_x + O2p_x$

σ BONDING

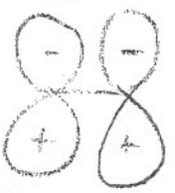


$-N2p_z - O2p_z$

1Π E=-0.5592

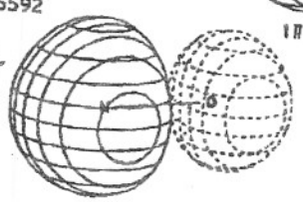


1Π E=-0.5592



$-N2p_y - O2p_y$

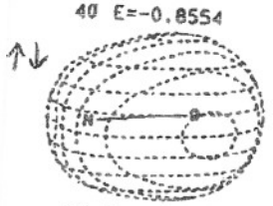
π BONDING



4σ E=-0.8554

$\approx N2s - O2s$

σ ANTI-BONDING



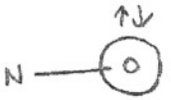
3σ E=-1.4825

$-N2s - O2s$

σ BONDING

CORE LEVELS

2σ = N1s $E \approx -410\,eV = -E_b(N1s)$



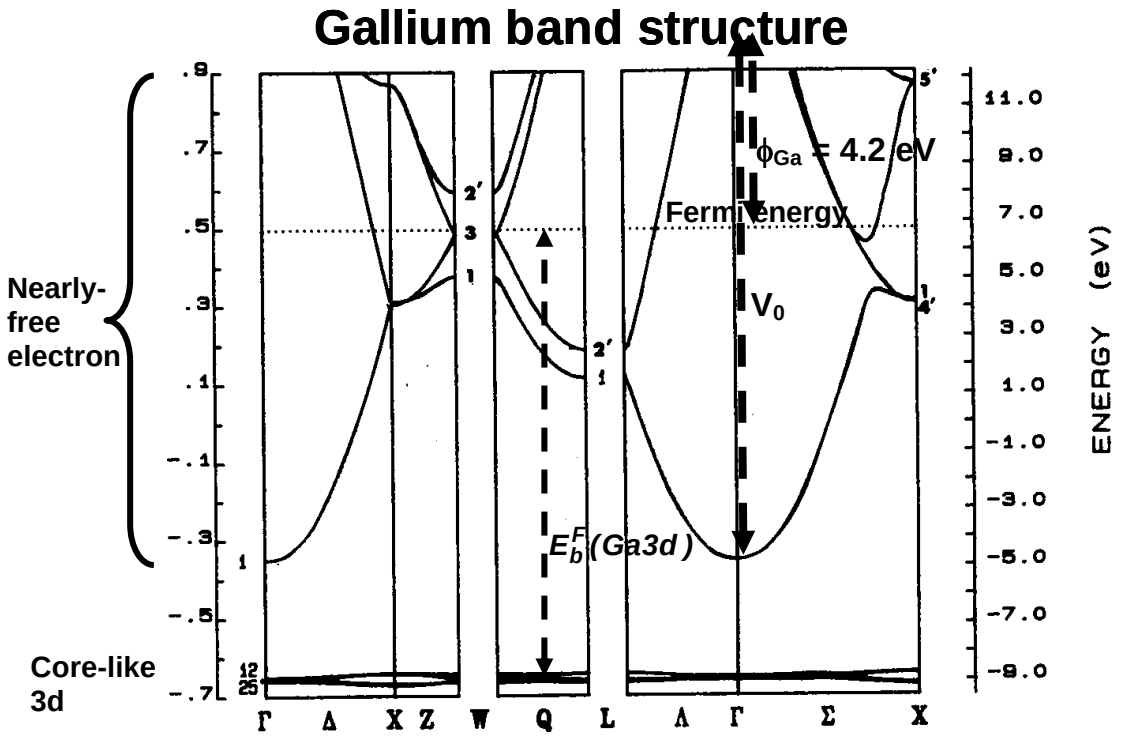
1σ = O1s $E \approx -543\,eV = -E_b(O1s)$

[5.4]

5 (a) The electron configuration of Ga is $3d^{10}4s^24p^1$. The 3d electrons are really core electrons, and the 4s and 4p occupation is like Ga's chemical relative Al with $3s^23p^1$. Not surprisingly, then, all of the bands above -5.0 eV are free-electron like, with splittings here and there due to the crystal potential, as in the nearly-free-electron model (e.g. Ashcroft and Mermin, pp. 152-173).

5 (b) These flat bands are the highly-localized, nearly-dispersionless, 3d bands of these core-like electrons. Checking the X-Ray Data Book for binding energy shows a Fermi-referenced 3d binding energy of 18.7 eV. The Fermi-referenced binding energy of these flat bands is 8.0 + 6.8 = 14.8 eV, in good enough agreement with the tabulated value.

5 (c) With a work function of 4.0 eV (lecture slide) or 4.2 eV (from J. Phys.: Condens. Matter 10 (1998) 10815), the inner potential is from the bottom of the free-electron bands at -5.0 eV to the Fermi level, an energy of 5.0 +6.8, plus the work function of 4.2, to give V_0 = 16 eV.



[5.5] (a) Initially: $\psi = \psi_1$ = grd. state ($n=1$) of particle in box of width ℓ

$\therefore \quad = \left(\frac{2}{\ell}\right)^{1/2} \sin\frac{\pi x}{\ell}$ for $0 \le x \le \ell$; zero elsewhere (1)

$$E = E_1 = \frac{h^2}{8m\ell^2}$$

After instantaneous change of box to width 2ℓ:

No wave function can change instantaneously; it must obey the t-dep. Schroedinger Eqn., which has solutions continuous in time. Therefore, just after the change in box width, we still have

ψ = Eq. (1) above.

However, the new set of allowed individual solutions to the t-indep. Schroed. Eqn. are given by:

$$\psi_n' = \left(\frac{2}{2\ell}\right)^{1/2} \sin\left(\frac{n\pi x}{2\ell}\right) \text{ for } 0 \le x \le 2\ell; \text{ zero elsewhere} \quad (2)$$

$$E_n' = n^2 \frac{h^2}{8m(2\ell)^2} = \frac{n^2}{4}\left(\frac{h^2}{8m\ell^2}\right), \quad n = 1, 2, 3, 4, \cdots \quad (3)$$

Expressing ψ now as a linear combination of the complete set in (2) gives formally

$$\psi = \sum_{n=1}^{\infty} a_n \psi_n'$$

with a_n's determined in usual way (see your favorite quantum mechanics book), from

$$a_n = \int_{-\infty}^{\infty} \psi_n' \psi \, dx = \int_0^{\ell} \left(\frac{1}{\ell}\right)^{1/2} \sin\left(\frac{n\pi x}{2\ell}\right)\left(\frac{2}{\ell}\right)^{1/2} \sin\left(\frac{\pi x}{\ell}\right) dx$$

↑ RANGE OF NON-ZERO ψ

$$= \frac{2^{1/2}}{\ell}\int_0^{\ell} \sin\left(\frac{n\pi x}{\ell}\right)\sin\left(\frac{\pi x}{\ell}\right) dx = \frac{2^{1/2}}{\ell}\cdot\frac{\ell}{\pi}\int_0^{\ell} \sin\left(\frac{n\pi x}{2\ell}\right)\sin\left(\frac{\pi x}{\ell}\right)\frac{\pi\, dx}{\ell}$$

or, with change of variable to $u = \pi x/\ell$:

$$= \frac{2^{1/2}}{\pi}\int_0^{\pi} \sin\left(\frac{nu}{2}\right)\sin u \, du = \begin{cases} \text{if } n=2: \ \frac{2^{1/2}}{\pi}\cdot\frac{\pi}{2} = \frac{1}{2^{1/2}} \\ \text{if } n\neq 2: \ \frac{2^{1/2}}{\pi}\left[\frac{\sin\left(\frac{n}{2}-1\right)\pi}{2\left(\frac{n}{2}-1\right)} - \frac{\sin\left(\frac{n}{2}+1\right)}{2\left(\frac{n}{2}+1\right)}\right] \end{cases} \quad (4)$$

For $n \neq 2$, simplifying yields

$$a_n = \frac{2^{1/2}}{\pi}\left[\frac{(n/2+1)\sin(\frac{n}{2}-1)\pi - (n/2-1)\sin(\frac{n}{2}+1)\pi}{2(n^2/4-1)}\right],$$

plus with

$$\sin(\tfrac{n}{2}-1)\pi = \sin(\tfrac{n}{2}+1)\pi \quad \text{(they are } 2\pi \text{ different in argument)},$$

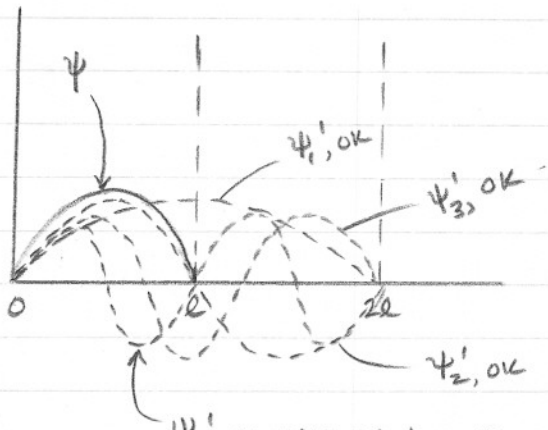
and $\sin(\frac{n}{2}-1)\pi = -\sin(\frac{n\pi}{2})$.

$$\boxed{a_n = -\frac{2^{1/2}}{\pi}\left[\frac{2\sin(\frac{n\pi}{2})}{2(n^2/4-1)}\right] = -\frac{2^{1/2}\sin(n\pi/2)}{\pi(n^2/4-1)} \quad ; \; n \neq 2} \quad (5)$$

∴ (4) + (5) dictate that a_n non-zero only for

$n = 1, 2, 3, 5, 7, \ldots$.

Symmetry restriction against all even $n > 2$ easily seen from net overlaps in integral for a_n:



∴ overall

$$\boxed{\psi = \psi_1 = \frac{1}{(2\ell)^{1/2}}\sin(\frac{\pi x}{\ell}) + \sum_{n=1,3,5}^{\text{ODD}}\left(\frac{2^{1/2}\sin(n\pi/2)}{\pi(n^2/4-1)\ell^{1/2}}\right)\sin(\frac{n\pi x}{2\ell})}$$

(b) The average energy will be given by:

$$\langle E \rangle = \sum_{n=1}^{\infty} |a_n|^2 E_n',$$

where $|a_n|^2$ = probability of measuring the energy

E_n' associated with the final-state eigenfunction ψ_n'. Thus, we have:

$$\langle E \rangle = |a_2|^2 E_2 + \sum_{n=1,3,5\ldots}^{\text{ODD}} |a_n|^2 E_n$$

→ Always +1, since squared.

$$= \frac{\hbar^2}{8mL^2}\left[\frac{1}{2} + \sum_{n=1,3,\ldots} \frac{2\sin^2(n\pi/2)}{\pi^2(n^2/4-1)^2}\cdot\frac{n^2}{4}\right]$$

$$= \frac{\hbar^2}{8mL^2}\left[\frac{1}{2} + \sum_{n=1,3,\ldots}^{8} \frac{16\, n^2}{2\pi^2(n^2-4)^2}\right]$$

$$= E_1\left[\frac{1}{2} + \frac{8}{\pi^2}\sum_{n=1,3,5\ldots} \frac{n^2}{(n^2-4)^2}\right]$$

→ a standard series $= \frac{\pi^2}{16}$

$$= E_1\left[\frac{1}{2} + \frac{1}{2}\right]$$

$$= \underline{\underline{E_1}}, \quad \text{Q.E.D.}$$

Thus, although each measurement of E may yield any one of the E_n' values, the average over a large number of measurements will give the same energy as before the sudden expansion of the box.

(c) This problem thus has 1:1 correspondences to the Sudden Approximation in photoemission as:

		THIS PROBLEM	CORE PHOTOE⁻ EMISSION
(1)	SUDDEN CHANGE IN $\hat{V}$	BOX(L) → BOX(2L)	EMISSION OF CORE e^- TO FORM k HOLE
(2)	INITIAL ψ	ψ IN BOX(L)	$(N-1)\,e^-$ ψ_R IN INITIAL N e^- $\hat{H}$
(3)	FINAL ψ_j's	ψ_n' IN BOX(2L)	$(N-1)\,e^-$ ψ_j^f OF ACTUAL ION (k-hole)
(4)	PROBAB. OF ψ_j	$\left\lvert\int \psi_n' \psi\, dx\right\rvert^2$	$\left\lvert\int \psi_j^f \psi_R\, d\tau\right\rvert^2 = \left\lvert\langle \psi_j^f(N-1) \mid \psi_R(N-1)\rangle\right\rvert^2$
(5)	CONSTANCY OF $\langle$ENERGY$\rangle$	$\langle E\rangle = E_1$	"MANNE-ÅBERG" OR "HEDIN-LUNDQVIST" THEOREM: $\left(\begin{matrix}\text{AVER. } E_B \\ \text{OVER ALL} \\ \text{PEAKS}\end{matrix}\right) = -\varepsilon_k$ = KOOPMANS' RESULT

[5.6]

Overall transition is:

$He\,1s^2\ (^1S,\ S=0,\ L=0) \xrightarrow[\text{PERTURBATION},\ \Delta S=0]{\text{DIPOLE}} He\,1s'\ (^2S,\ s=1/2,\ \ell=0),\ E^f p_{+1}\ (^2P,\ s=1/2,\ \ell=1,\ m_\ell=+1)\ (^1P,\ S=0,\ L=1,\ M_L=+1)$

relaxed; photoe⁻: Taken arbitrarily to be $\ell=0$ (P), $m_\ell=+1$ (+1); one choice allowed by dipole selection rule.

N. A.

(a) The ^1S ground state of $He\ 1s^2$ is, in a Slater determinant approximation (see your favorite q.m. book):

$$\psi^i(2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$$

$$= 1s(1)1s(2) \cdot \underbrace{\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]}_{\text{The } S=0 \text{ spin function for } 2\ e^-} \qquad (1)$$

(b) The final state must also be a singlet state (with $S=0$), because the dipole operator cannot change spin. Thus, its 2-e^- spin function must be the same as that in (1). The new total configuration is different however, in having electrons in 2 inequivalent orbitals. I.e., the overall 2-e^- configuration is $He^+ + \text{photo}e^- = 1s'(\text{relaxed}),\ E^f p_{+1}$, where the photoelectron is at energy E^f, with $\ell=1$, $m_\ell=1$, as stated in problem. The wave function here must be a sum of two Slater determinants in order to yield the correct $S=0$ state (see your q.m. book again):

MANY PEOPLE MISS THIS PIECE.

$$\psi^f(2) = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}} \underbrace{\begin{vmatrix} 1s'(1)\alpha(1) & E^f p_{+1}(1)\beta(1) \\ 1s'(2)\alpha(2) & E^f p_{+1}(2)\beta(2) \end{vmatrix}}_{(A)} - \frac{1}{\sqrt{2}} \underbrace{\begin{vmatrix} 1s'(1)\beta(1) & E^f p_{+1}(1)\alpha(1) \\ 1s'(2)\beta(2) & E^f p_{+1}(2)\alpha(2) \end{vmatrix}}_{(B)}\right]$$

$$= \underbrace{\frac{1}{\sqrt{2}}\left[1s'(1)E^f p_{+1}(2) + E^f p_{+1}(1)1s'(2)\right]}_{\text{SYMMETRIC}} \cdot \underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]}_{\text{ANTI-SYMMETRIC}} \qquad (2)$$

$S=0$ spin function

The matrix element desired is thus:

$$\langle \Psi^f(2) | \vec{r}_1 + \vec{r}_2 | \Psi^i(2) \rangle = \left\langle \frac{1}{\sqrt{2}} \left[1s'(1)\, E^f_{p+1}(2) + E^f_{p+1}(1)\, 1s'(2) \right] \cdot (\text{S=0 spin}) \middle| \vec{r}_1 + \vec{r}_2 \middle| 1s(1)\, 1s(2) \cdot (\text{S=0 spin}) \right\rangle$$

Integration on two spin coordinates σ_1 and σ_2 gives 1, because S=0 function is normalized.

Integration on two spin coordinates can be done separately, since $\vec{r}_1 + \vec{r}_2$ does not affect them; this yields 1, as indicated above.

Remaining spatial integrals can now be evaluated by expanding products and noting $\vec{r}_1$ affects dV_1 integration only and $\vec{r}_2$ affects dV_2 integration only. This yields:

$$\begin{aligned}
\langle \Psi^f(2) | \vec{r}_1 + \vec{r}_2 | \Psi^i(2) \rangle = \frac{1}{\sqrt{2}} \Big\{ & \langle 1s'(1)\, E^f_{p+1}(2) | \vec{r}_1 | 1s(1)\, 1s(2) \rangle \\
& + \langle 1s'(1)\, E^f_{p+1}(2) | \vec{r}_2 | 1s(1)\, 1s(2) \rangle \\
& + \langle E^f_{p+1}(1)\, 1s'(2) | \vec{r}_1 | 1s(1)\, 1s(2) \rangle \\
& + \langle E^f_{p+1}(1)\, 1s'(2) | \vec{r}_2 | 1s(1)\, 1s(2) \rangle \Big\}
\end{aligned}$$

Or, separating dV_1 and dV_2 integrations into products:

$$\begin{aligned}
= \frac{1}{\sqrt{2}} \Big\{ & \underset{①}{\langle 1s'(1) | \vec{r}_1 | 1s(1) \rangle} \cdot \underset{②}{\langle E^f_{p+1}(2) | 1s(2) \rangle} \\
& + \underset{③}{\langle 1s'(1) | 1s(1) \rangle} \cdot \underset{④}{\langle E^f_{p+1}(2) | \vec{r}_2 | 1s(2) \rangle} \\
& + \underset{⑤}{\langle E^f_{p+1}(1) | \vec{r}_1 | 1s(1) \rangle} \cdot \underset{⑥}{\langle 1s'(2) | 1s(2) \rangle} \\
& + \underset{⑦}{\langle E^f_{p+1}(1) | 1s(1) \rangle} \cdot \underset{⑧}{\langle 1s'(2) | \vec{r}_2 | 1s(2) \rangle} \Big\} \qquad (3)
\end{aligned}$$

This is easily simplified by recalling certain orthogonality relations among the orbitals. I.e., the orbitals all can be written as:

$$1s(\vec{r}) = R_{1s}(r)\, Y_0^0(\theta,\phi)$$

$$1s'(\vec{r}) = R'_{1s}(r)\, Y_0^0(\theta,\phi)$$

$$E^f p_{+1}(\vec{r}) = R_{E^f,\ell=1}(r)\, Y_1^1(\theta,\phi).$$

Therefore, integrals ② and ⑦ in Eq. ③ are <u>zero</u>, because Y_0^0 and Y_1^1 are orthogonal when integrated over all θ and ϕ. By a similar argument, integrals ① and ⑧ are also zero. $1s'(\vec{r}) \cdot 1s(\vec{r})$ is an even function of $\vec{r}$, but $\vec{r}$ itself is odd; thus the overall integrand is odd and integrates to zero.

Also, in integrals ③ – ⑥, once the dV_1 and dV_2 integrals are separated, the labels 1 and 2 can be interchanged. Thus, ③ = ⑥ and ④ = ⑤, and we have finally

$$\boxed{\langle \Psi^f(2) | \vec{r}_1 + \vec{r}_2 | \Psi^i(2) \rangle = \sqrt{2}\, \langle E^f_{P+1} | \vec{r} | 1s \rangle \langle 1s' | 1s \rangle.} \qquad (4)$$

This is indeed equivalent to Eq. (68) in "Basic Concepts" I, with the identifications:

$$\phi^f = E^f_{P+1} \quad ; \quad \psi^f(N-1) = \psi^f(1) = 1s' \text{ (relaxed)};$$
$$\phi_k = 1s \quad ; \quad \psi_R(N-1) = \psi_R(1) = 1s.$$

The extra factor of $\sqrt{2}$ relative to Eq. (68) comes about because two Slater dets. are involved in the final state. This extra factor has a simple physical significance that can be seen by noting that the <u>intensity</u> of the $\Psi^i(2) \to \Psi^f(2)$ excitation will be proportional to the square of Eq. ④ or

$$I \propto |\langle \Psi^f(2) | \vec{r}_1 + \vec{r}_2 | \Psi^i(2) \rangle|^2 = \underline{2} \cdot |\langle E^f p_{+1} | \vec{r} | 1s \rangle|^2 |\langle 1s' | 1s \rangle|^2 \quad . \quad (5)$$

I.e., the intensity seems to be twice that expected for a simple $1s \rightarrow E^f p_{+1}$ transition with 1s relaxing to 1s'. However, if we look back at the two determinants (A) and (B) in Eq. (2) for $\Psi^f(2)$, we can see that (A) represents a $1s\beta \rightarrow E^f p_{+1}\beta$ transition, whereas (B) represents a $1s\alpha \rightarrow E^f p_{+1}\alpha$ transition. (Recall that 1-e$^-$ spin cannot change either.) Thus, the factor 2 represents a unit of intensity for either the spin up excitation channel or the spin down channel, which act independently so as to add to 2. If we were to <u>detect photoelectron spin</u> somehow, the final state would have to be modified so as to project out only that spin, and the intensity would be reduced to ½ of Eq. (5).

(c) $He^+ 1s'$ is just a hydrogenic atom with $Z = 2$. So

$$\varphi_{1s'} = \varphi_{1s}(Z = 2).$$

20 points

[5.7] (a) All subshells initially filled except $4f^7$, so we can write 3s emission as

$$Gd^{3+}\ 1s^2 \cdots 3s^2 \cdots 4s^2 \cdots 4f^7 \cdots {}^8S \longrightarrow$$

$$\xrightarrow{-3s} \begin{cases} Gd^{4+}\ 1s^2 \cdots 3s \cdots 4s^2 \cdots 4f^7 & {}^7S \\ Gd^{4+}\ 1s^2 \cdots 3s \cdots 4s^2 \cdots 4f^7 & {}^9S \end{cases}$$

$$\Delta E_b(3s) = 8\,K_{3s,4f}$$ (Eq. (148))

BASIC CONCEPTS...

or, with 4s emission as

$$\xrightarrow{-4s} \begin{cases} Gd^{4+}\ 1s^2 \cdots 3s^2 \cdots 4s \cdots 4f^7 & {}^7S \\ Gd^{4+}\ 1s^2 \cdots 3s^2 \cdots 4s \cdots 4f^7 & {}^9S \end{cases}$$

$$\Delta E_b(4s) = 8\,K_{4s,4f}$$

with in both cases an intensity ratio of

$$\frac{I({}^7S)}{I({}^9S)} = \frac{7}{9}$$ (Eq. (146)).

(b) 4s, because 4s and 4f electrons overlap more and therefore $K_{4s,4f} > K_{3s,4f}$.

(c) 3s more accurately predicted by simple HF theory, because the higher overlap of 4s and 4f leads to greater $e^- - e^-$ correlation corrections in the uncorrelated ${}^7S$ state. (Recall that exchange correlates the spin-parallel electrons in the ${}^9S$ states somewhat.)

(d) No multiplet splitting, because the F^- ions have an inert-gas valence configuration. So, no net valence spin to couple remaining 1s electron with.

(e) Easy to do if we note that e^- configuration is identical to neon example of lecture and "Basic Concepts - -". So, the final F^0 states are like:

F^0 $1s\,2s^2\,2p^6$ ^2S — no shake-up, shake-off

F^0 $1s\,2s\,2p^6\,3s$
" $4s$
" ns
" εs

s series shake-up → shake-off (ns) (εs)

F^0 $1s\,2s^2\,2p^5\,3p$
" $4p$
" np
" εp

p series shake-up → shake-off (np) (εp)

→ With overlaps for this typical case like:

$$I \propto |\langle \underbrace{1s\,2s\,2p^6\,3s}_{\text{Relaxed}} | \underbrace{1s\,2s^2\,2p^6}_{\text{Initial}} \rangle|^2 = |\langle \underline{1s}|1s\rangle\langle \underline{2s}|2s\rangle\langle \underline{3s}|2s\rangle \cdot$$

$\overset{9\text{-}e^-}{}$

$$\langle \underline{2p_x}|2p_x\rangle\langle \underline{2p_x}|2p_x\rangle\langle \underline{2p_y}|2p_y\rangle\langle \underline{2p_y}|2p_y\rangle\langle \underline{2p_z}|2p_z\rangle\langle \underline{2p_z}|2p_z\rangle$$

(f) Cooper minima evident for Gd 4d at $h\nu \approx 220$ eV and for Gd 5d at $h\nu \approx 155$ eV.

(g) Gd 4f may exhibit resonant photoemission with the Gd 4d shell just adjacent to it in spatial extent and binding energy. This would be expected to occur at $h\nu \approx$ Gd 4d BINDING ENERGY ≈ 128 eV (VALUE OF 162.0 eV IN YEH & LINDAU IS CALCULATED, AND SO IN ERROR BY dE_{RELAX} ETC.)

ELECTRONIC STATES LIKE:

$Gd^{3+} \rightarrow Gd^{4+}\ldots 4f^6$ NORMAL

$\rightarrow Gd^{3+}\ldots 4d^9\ldots 4f^7\varepsilon f$ RESONANT εf EP

$Gd^{4+}\ldots 4d^{10}\ldots 4f^6$ AUTO IONIZ.

(h) E_{KIN} VALUES FOR ALL THREE VALENCE SUBSHELLS ESSENTIALLY EQUAL, SINCE $E_b << h\nu = 1486$ eV. THUS, WE CAN FORGET ALL ENERGY-DEPENDENT ANALYZER FACTORS ($A_0 \Omega_0 D_0$). ALSO, ALL e^- ARE FROM SAME ATOM, SO ATOMIC DENSITIES ARE EQUAL. MEAN FREE PATHS ARE ALSO EQUAL, SINCE E_{KIN} VALUES SO CLOSE.

∴ ALL THIS LEAVES IS A RATIO OF SUBSHELL DIFFERENTIAL CROSS SECTIONS:

$$I_{4f} : I_{5d} : I_{6s} = \frac{d\sigma_{4f}}{d\Omega} : \frac{d\sigma_{5d}}{d\Omega} : \frac{d\sigma_{6s}}{d\Omega}$$

FOR ALL THREE $= -0.1198$ (at $\alpha = 50°$)

$$= \sigma_{4f}\left[1 + \tfrac{1}{2}\beta_{4f}\left(\tfrac{3}{2}\sin^2\alpha - 1\right)\right] : \sigma_{5d}\left[1 + \tfrac{1}{2}\beta_{5d}\left(\tfrac{3}{2}\sin^2\alpha - 1\right)\right]$$

$$: \sigma_{6s}\left[1 + \tfrac{1}{2}\beta_{6s}\left(\tfrac{3}{2}\sin^2\alpha - 1\right)\right]$$

YEH + LINDAU TABLES

$$= 0.021\left[1 - \tfrac{1}{2}(1.039)(0.1198)\right] : 0.00094\left[1 - \tfrac{1}{2}(1.388)(0.1198)\right]$$

ALL S SUBSHELLS

$$: 0.00043\left[1 - \tfrac{1}{2}(2.000)(0.1198)\right]$$

$$= 0.0197 : 0.000862 : 0.000378 = \underline{1.000 : 0.044 : 0.019}$$

SO, VERY LITTLE OF 5d AND 6s INTENSITY SEEN IN XPS OF Gd (OR OTHER RARE EARTHS).

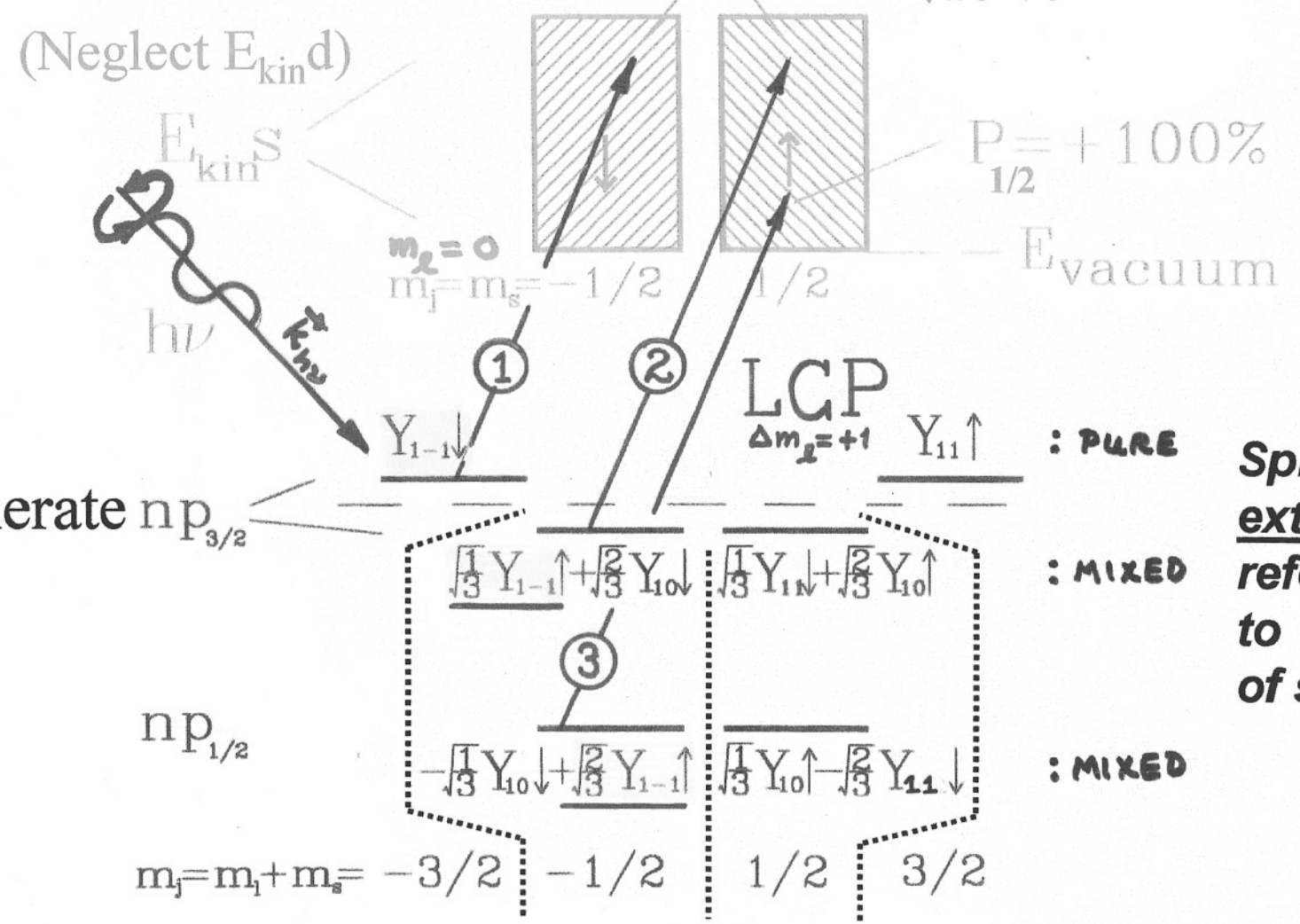
(i) Just use reasoning in following example discussed in lectures, but spins reversed since RCP↑ This gives $P = +50\%$

(and $\Delta m_z = -1$.)

PHOTOELECTRON SPIN POLARIZATION FROM CIRCULAR POLARIZATION AND SPIN–ORBIT SPLITTING

(THE FANO EFFECT)

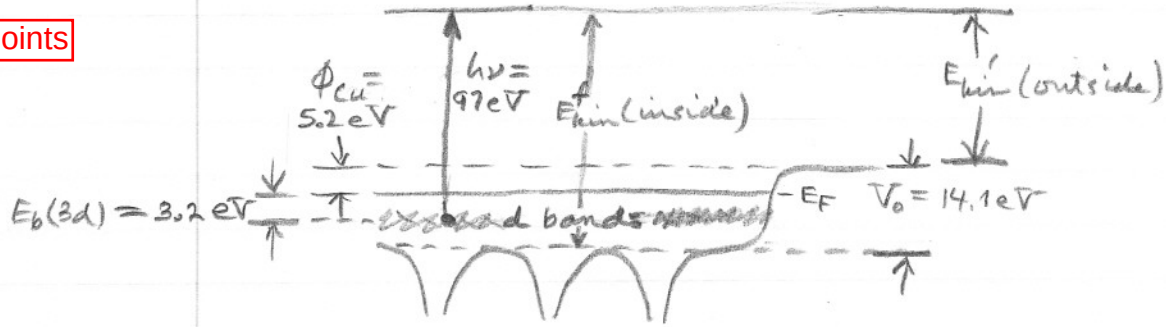
$$P_{3/2} = -50\% = \frac{\sqrt{1/3^2} - 1^2}{\sqrt{1/3^2} + 1^2} x100 = \frac{-2/3}{4/3} x100 = -50\%$$



Spin externally referenced to $\vec{k}_{h\nu}$ and $\vec{M}$ of sample

15 points

[5.8] Relevant energy + potential diagram is:



(a) From diagram, $E^f_{min}(\text{inside}) = 97\text{ eV} + (14.1 - 5.2 - 3.2)\text{ eV}$

$= 97\text{ eV} + 5.7\text{ eV}$

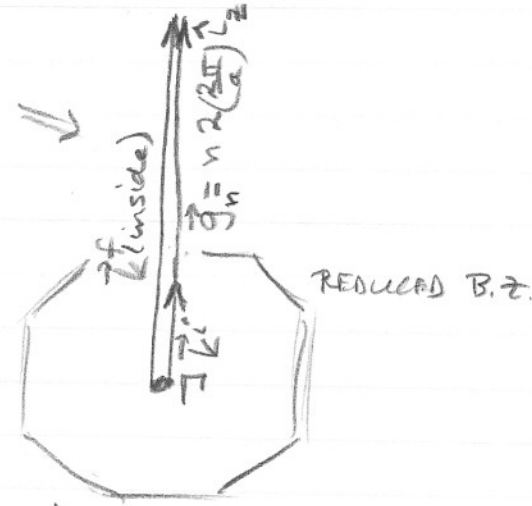
$= 102.7\text{ eV}$

$\therefore |\vec{k}^f(\text{inside})| = 0.512\,[102.7]^{0.5}$

$= 5.189\ \text{Å}^{-1}$

and $\vec{k}$ conservation looks like:

$\vec{k}^f(\text{inside}) = \vec{k}^i(\text{in RBZ}) + \vec{g}_n$ ⟹



Assume $n = 1$ for $\vec{g}$ as first try:

$|\vec{g}_1| = 2\left(\frac{2\pi}{a}\right) = \frac{4\pi}{3.61\text{ Å}} = 3.481\ \text{Å}^{-1}$

$\therefore |\vec{k}^i| = |\vec{k}^f(\text{inside})| - |\vec{g}_1| = 5.189\ \text{Å}^{-1} - 3.481\ \text{Å}^{-1}$

$= 1.709\ \text{Å}^{-1}$

But X point is at $\frac{2\pi}{a}$ along z direction $= \frac{2\pi}{3.61} = \underline{1.741}\ \text{Å}^{-1}$

or very close to $|\vec{k}^i|$ for 97 eV excitation.

(b) Just outside the surface, $\bar{V}_0$ is lost to give $102.7\ eV - 14.1\ eV = \underline{\underline{88.6\ eV}}$

(c) $p_{h\nu} = \hbar k_{h\nu} = \frac{h}{\lambda}$ (de Broglie rel'n.)

$\therefore\ k_{h\nu} = \frac{2\pi}{\lambda_{h\nu}}$ (the usual relationship)

For $h\nu = 97\ eV$, $\lambda_{h\nu} = \frac{12,398}{97} = 127.8\ \text{Å}$, so

$$k_{h\nu} = \frac{2\pi}{127.8} = 0.0492\ \text{Å}^{-1}$$

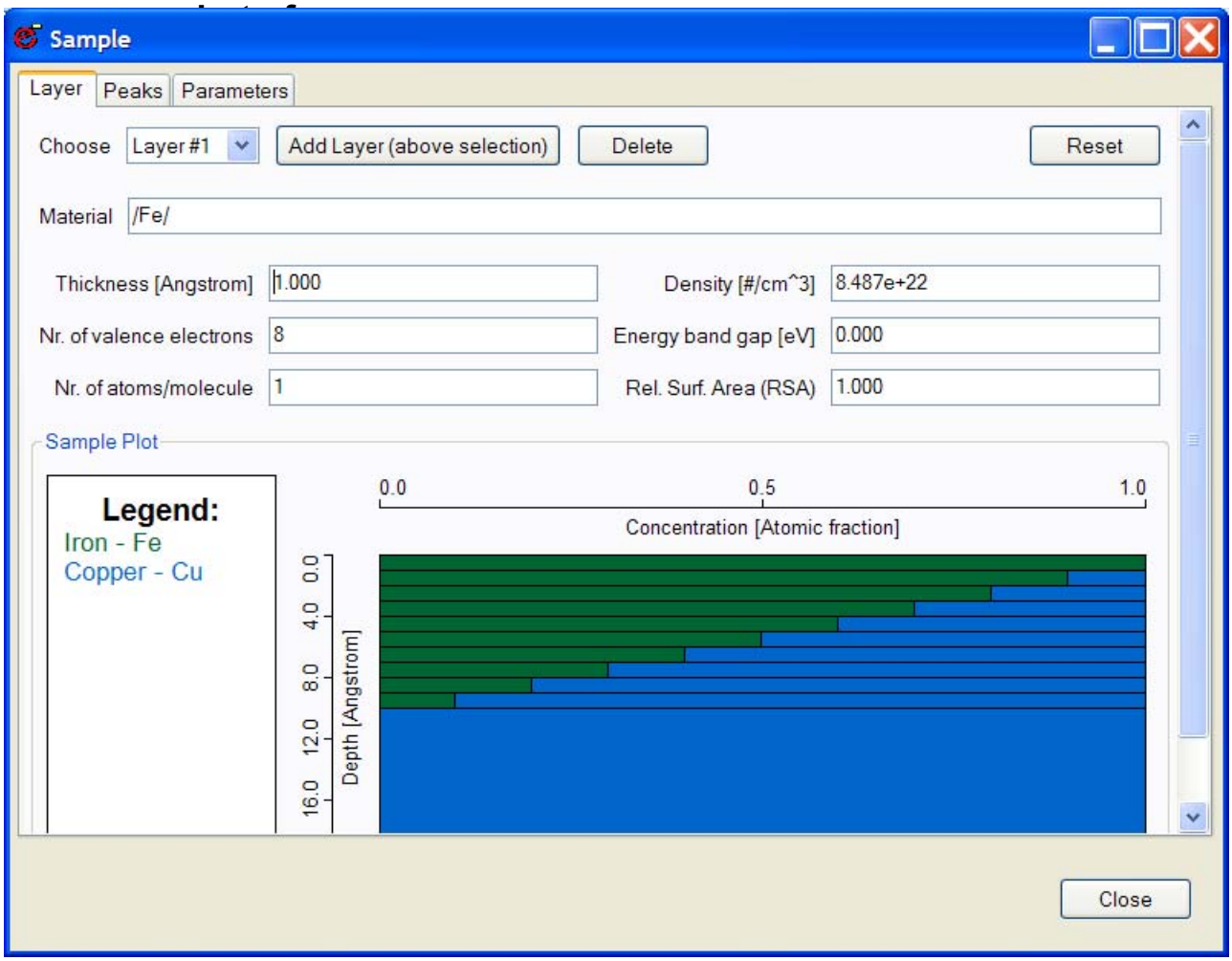
which is very small compared to the BZ radius of $1.708\ \text{Å}^{-1}$ (only about 3%), and so negligible.

20 points

[5.9.]

(a) Average no. electrons for Fe and Cu is (11+8)/2 = 9.5, but SESSA requires integers, so could use 9.0 or 10.0. I'll use 10 for the mixed layers.

Average atomic density is (8.50+8.45)/2 x 10^{22} = 8.48 x 10^{22}. Building up the sample from Cu substrate plus ten layers of Fe+Cu from /Fe10/Cu90/ to /Fe20/Cu80/ to /Fe30/Cu70/,....to /Fe/ yields finally



The source is just the default AlKα in the program, as shown in the screen shot on the next page.

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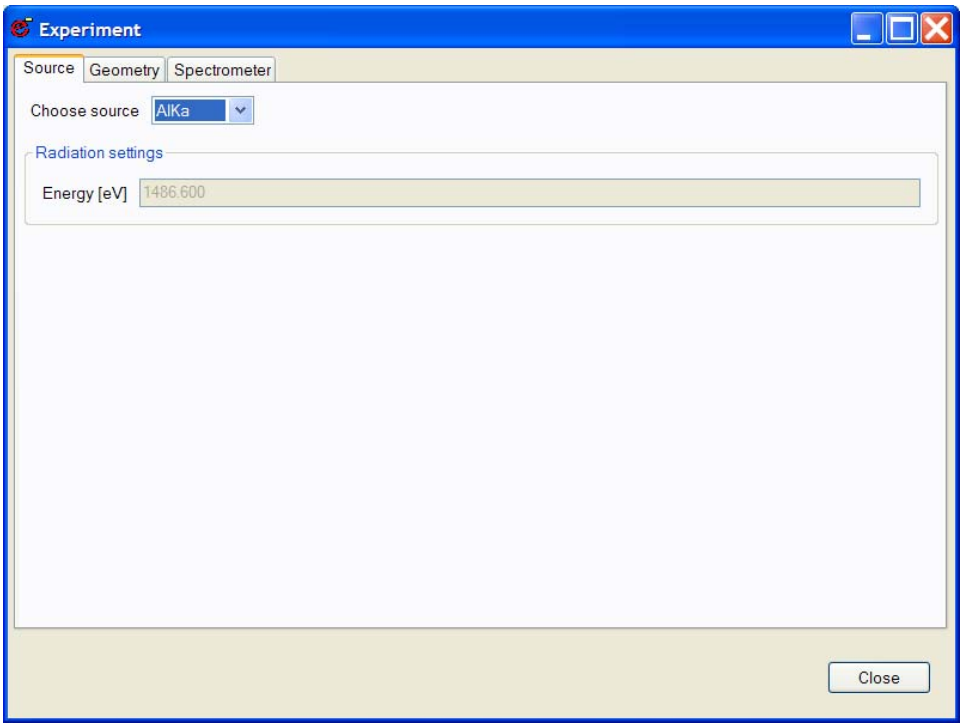
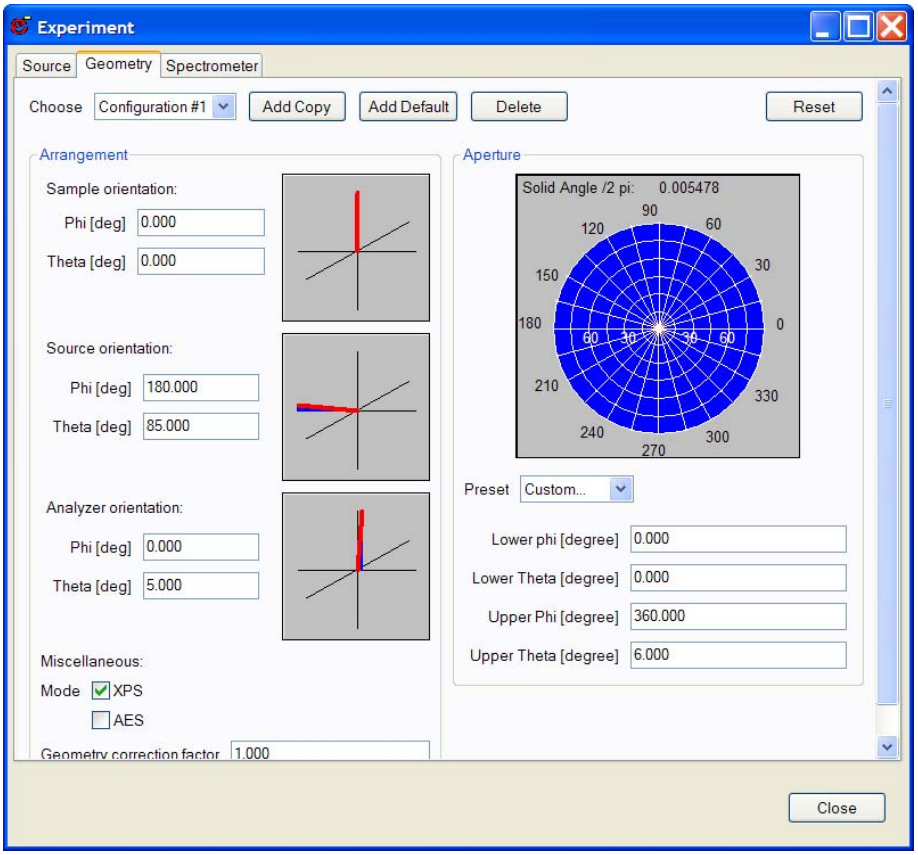
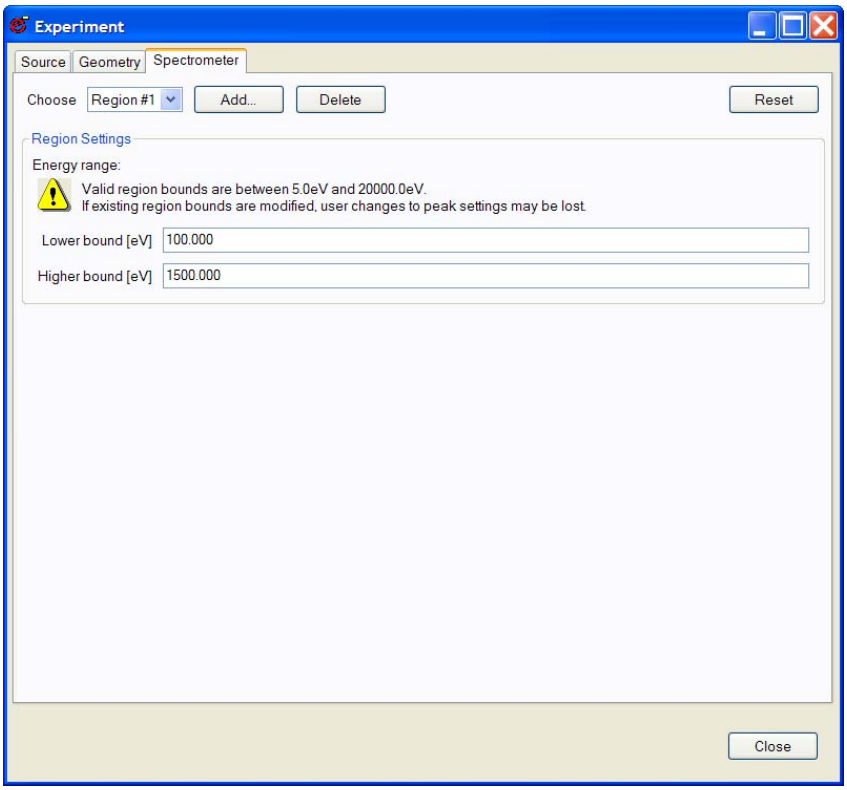


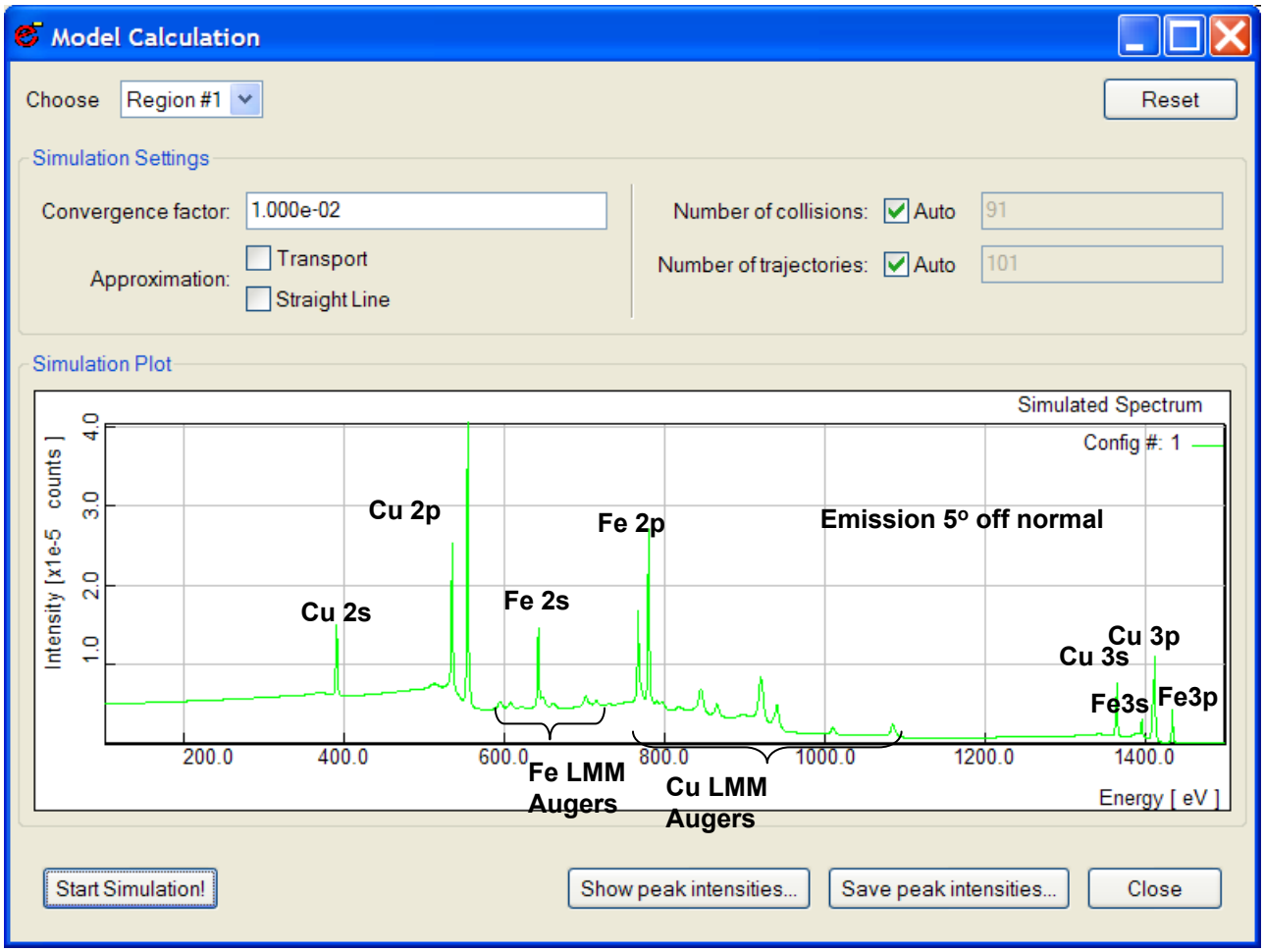
The geometry is as shown below:

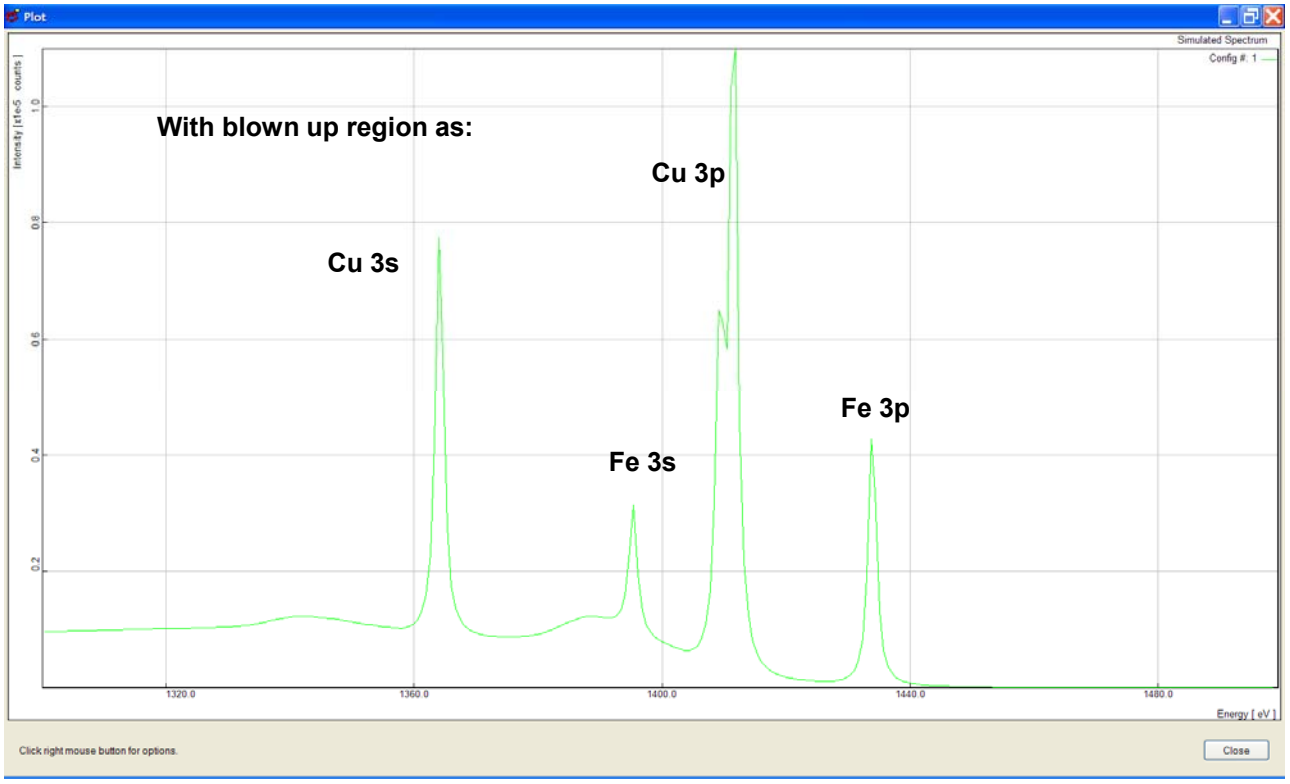


The spectrometer is defined as below:

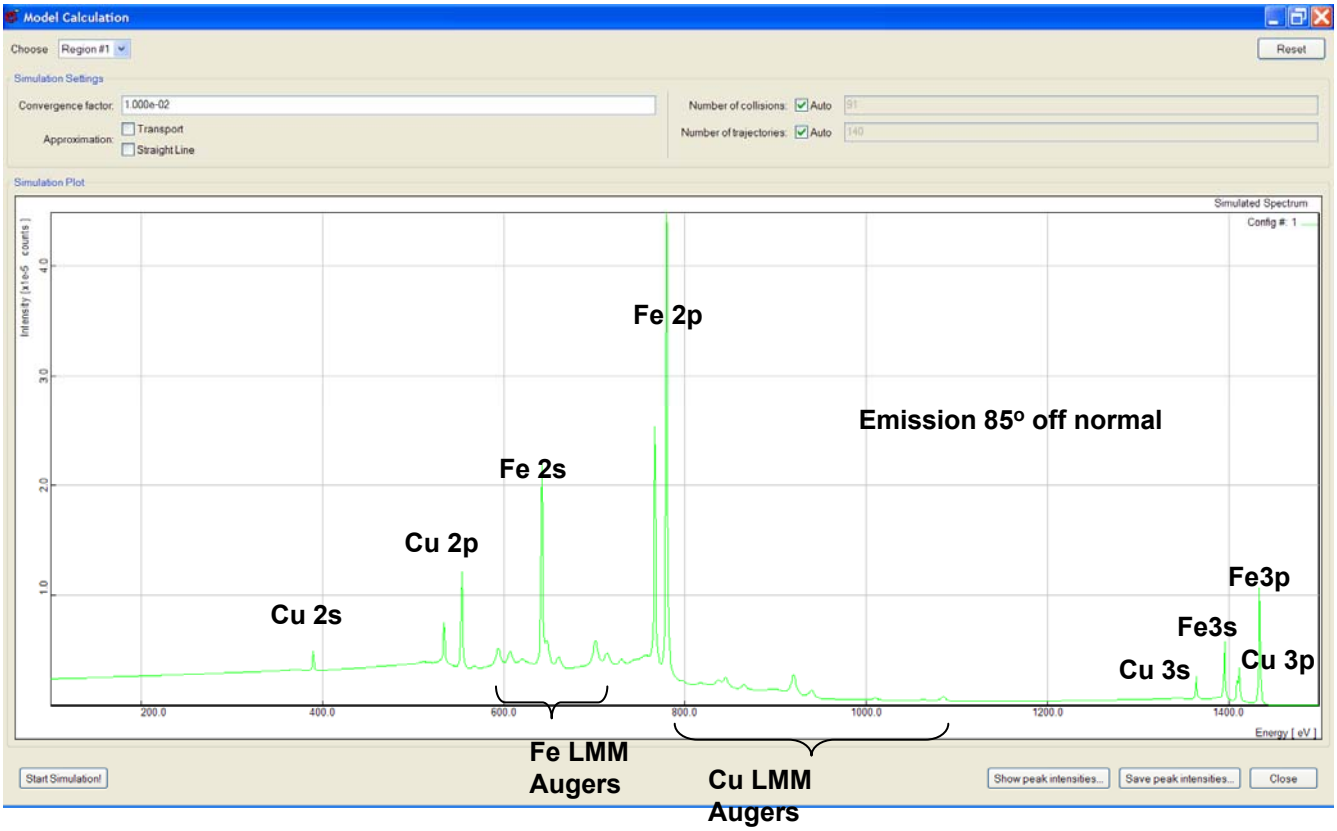


The result of the simulation is then:



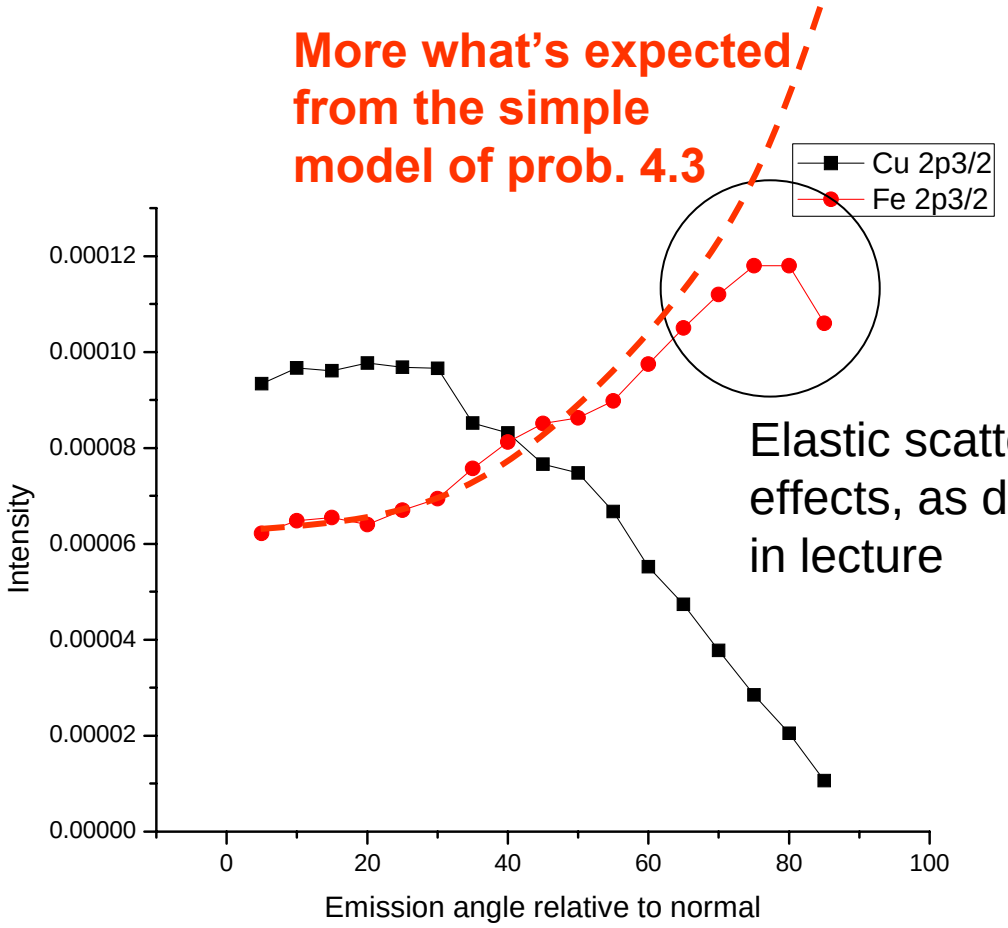


Changing only the takeoff angle to now be 85 deg.off normal = 5 degree takeoff angle dramatically enhances all Fe features:

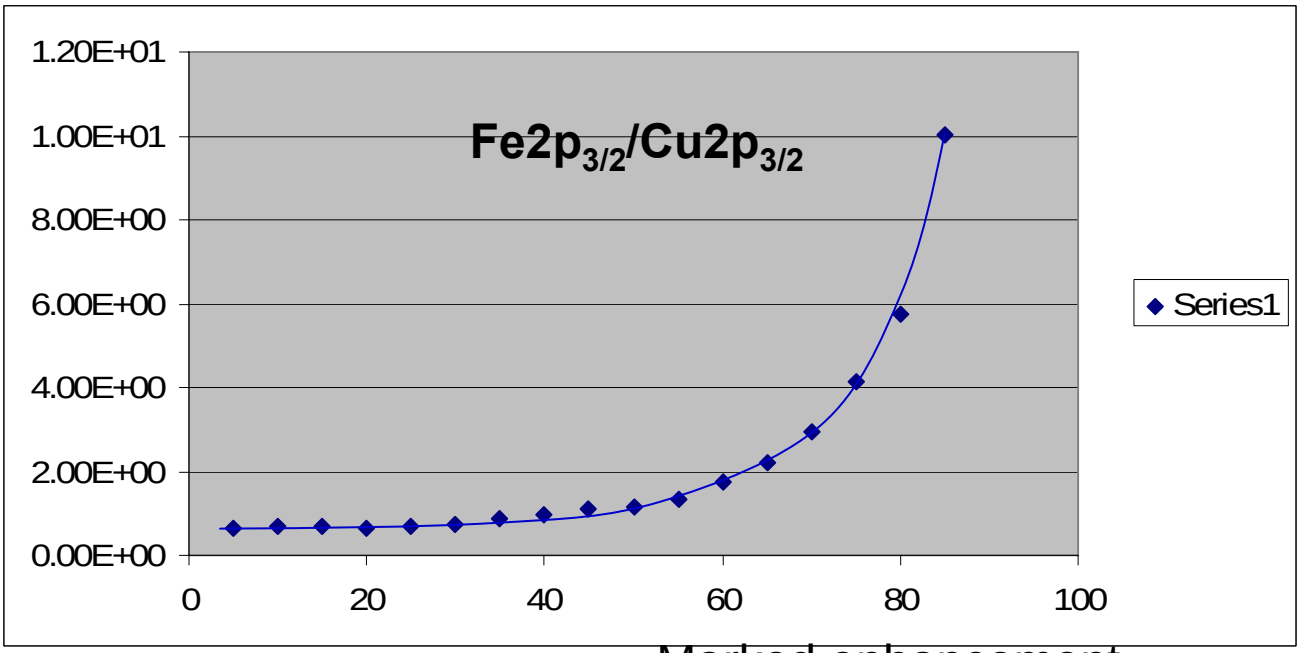


(b) Calculating Cu $2p_{3/2}$ and Fe $2p_{3/2}$ intensitiies now for the different angles requested now yields:

Electron emission angle (w.r.t. normal)	Cu $2p_{3/2}$	Fe $2p_{3/2}$	$Fe2p_{3/2}$/ $Cu2p_{3/2}$
85	1.06009e-05	1.06205e-04	1.00E+01
80	2.05254e-05	1.18011e-04	5.74951
75	2.84874e-05	1.18007e-04	4.142428
70	3.77737e-05	1.11802e-04	2.959784
65	4.73596e-05	1.04910e-04	2.215179
60	5.52105e-05	9.75318e-05	1.766544
55	6.67060e-05	8.98120e-05	1.346386
50	7.47551e-05	8.63412e-05	1.154987
45	7.65899e-05	8.50740e-05	1.110773
40	8.31061e-05	8.11802e-05	0.976826
35	8.52360e-05	7.57348e-05	0.888531
30	9.65751e-05	6.94172e-05	0.71879
25	9.67727e-05	6.70305e-05	0.692659
20	9.76668e-05	6.40239e-05	0.655534
15	9.60796e-05	6.55382e-05	0.682124
10	9.67096e-05	6.47569e-05	0.669602
5	9.33935e-05	6.21533e-05	0.665499

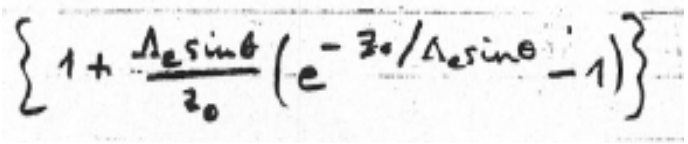


Elastic scattering effects, as discussed in lecture



Marked enhancement of Fe relative intensity for more grazing angles of emission

(c) The expected angular variation of Fe $2p_{3/2}$ is from the answer for proble 4.3 according to:



But with θ defined as the complement in the SESSA program. So this part of the problem involves calculating this function with z_0 = 10 Å, and Λ_e = 13 Å = an average no. from the "Parameters" list in SESSA for the Fe 2;$_{3/2}$ peak, which gives:

$$1+\frac{13\cos\theta}{10}\left[\exp(-\frac{10}{13\cos\theta})-1\right]=1+1.3\cos\theta\left[\exp(-0.769/\cos\theta)-1\right]$$

which has limits of 0.300 for θ = 5^o (where the simple model is expected to be better) and 1.11 for θ = 85^o or a factor of 3.7 enhancement at more grazing emission angles. However, the actual change over this range from SESSA is only about 1.7, so the effects of elastic scattering are important, particularly over the circled region of the red curve. You could go further and normalize experiment to simple theory at θ = 5^o and the plot them together, to see where they begin to diverge.

Running SESSA in a "straight-line" trajectory mode to should reduce the effects of elastic scattering in taking intensity away from a given initial emission direction, and leads to:

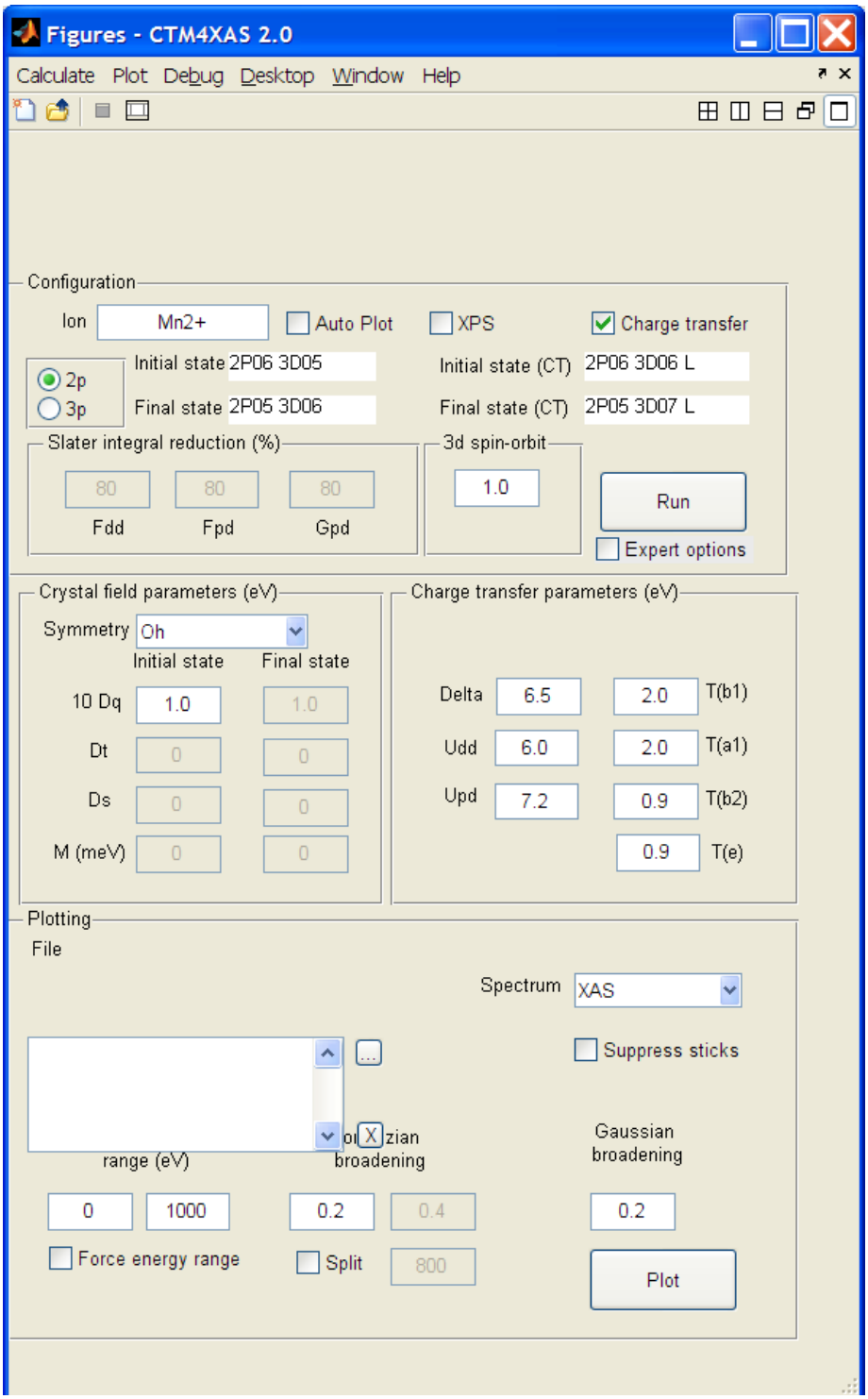
	θ = 85^o	θ = 5^o	85/5 ratio
Fe 2p3/2	1.57476e-04	5.89509e-05	2.67
		(1.7 from full SESSA, 3.7 from simple model)	
Cu 2p3/2	1.08118e-05	1.34945e-04	0.089
			(0.113 from full SESSA).

So two calculations for Fe close up a little this way, but deviations from simple model still persist.

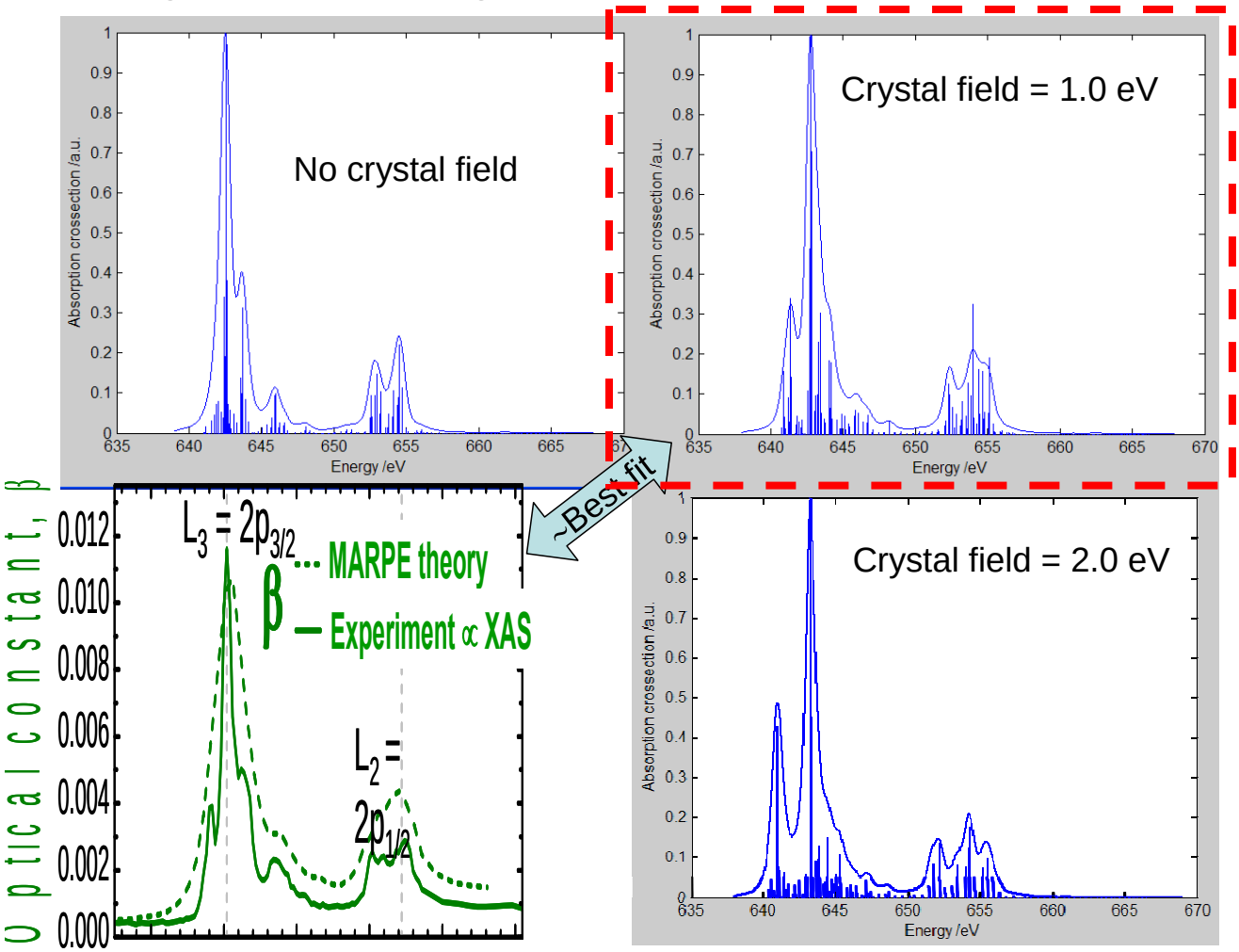
[5.10]

20 points

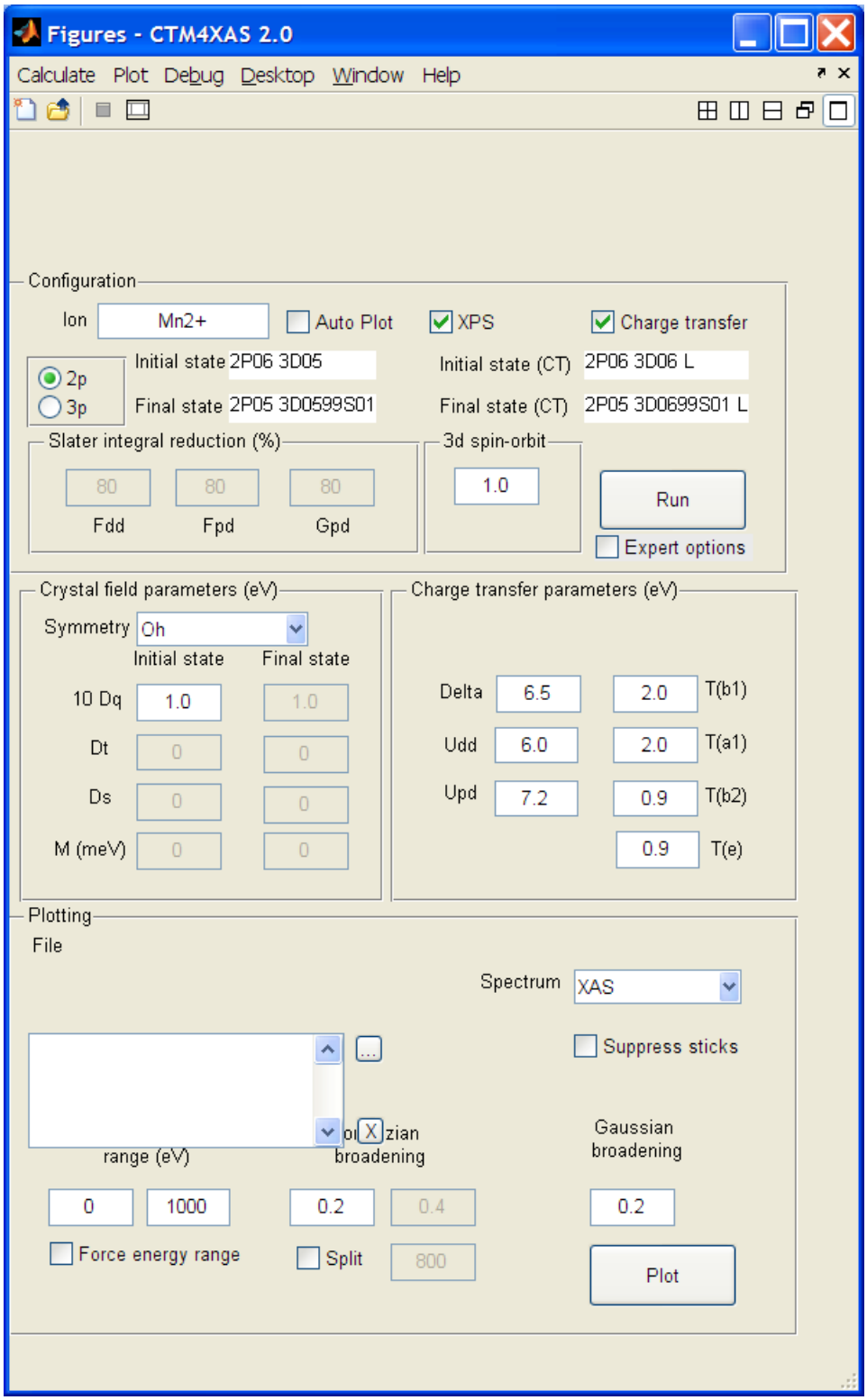
(a) Mn^{2+} is in an octahedral environment of O^{2-} ions in the NaCl crystal structure, and we can just go to the CTM4XAS manual posted at the website to get the relevant parameters. We'll add a crystal field splitting of 1.0 eV beyond the sample calculations done in our manual, so that the input formats for XAS looks like:



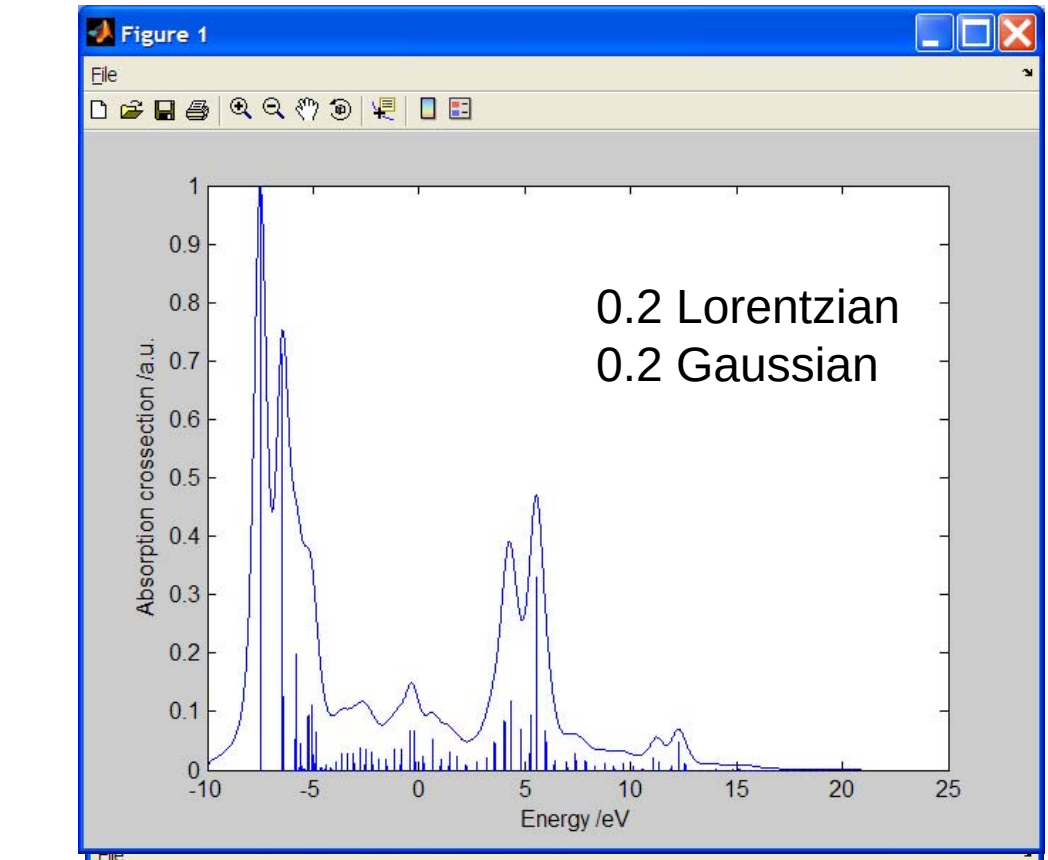
With a final result like that in our manual, where the effects of crystal field splitting were also investigated:

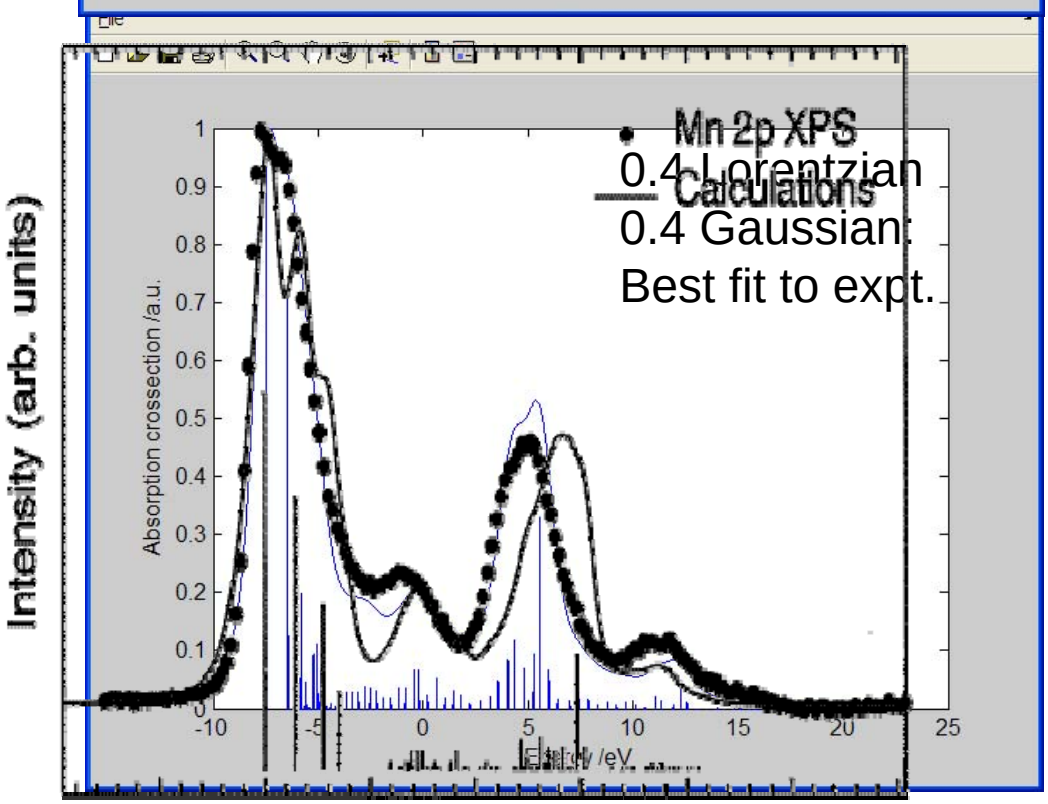


For XPS, the inputs look like:



And the XPS output looks like:





Intensity (arb. units)

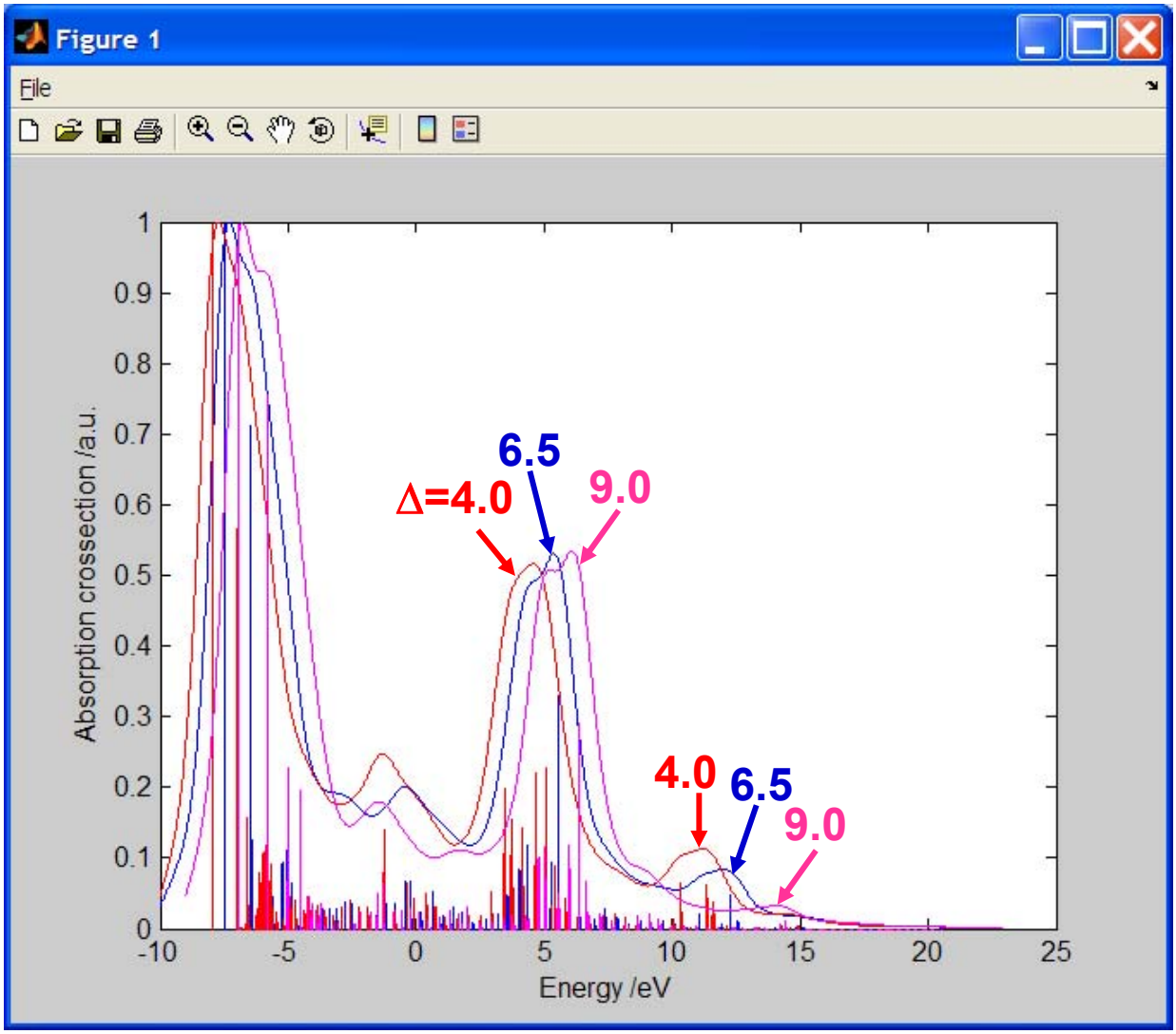
Relative Binding Energy (eV)

With trial-and-error selection of spectral broadening, excellent agreement with experiment!

(b) Everything in this calculation is done in the Sudden Approximation limit, and with the assumption that the matrix elements for 2p excitation do not change significantly with photon energy. So you don't need to know it to do the calculation. In real life, different transitions could have different angular dependences in a single crystal for example.

(c) Can try just some extreme values around those of the optimum calculated before:

Δ = 4 and 9 with 6.5 eV midway between them
U_{dd} = 4 and 8 with 6 midway
U_{dp} = 5.2 and 9.2 with 7.2 midway

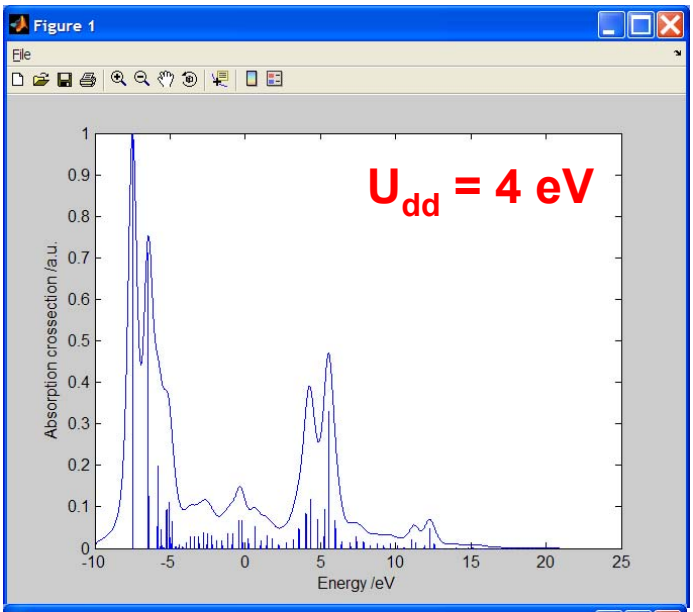


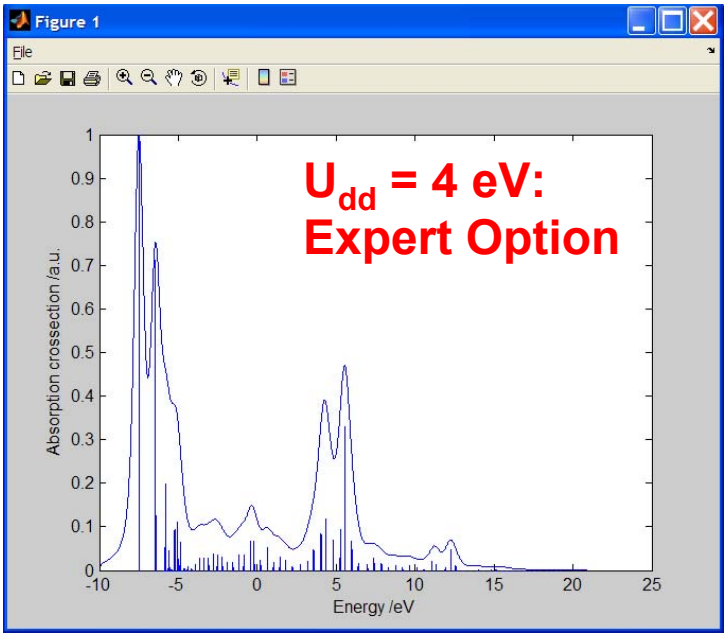
Increasing Δ with all other param. fixed decreases the unscreened satellite peak intensity, as seen also by Bocquet and Fujimori (see next page)

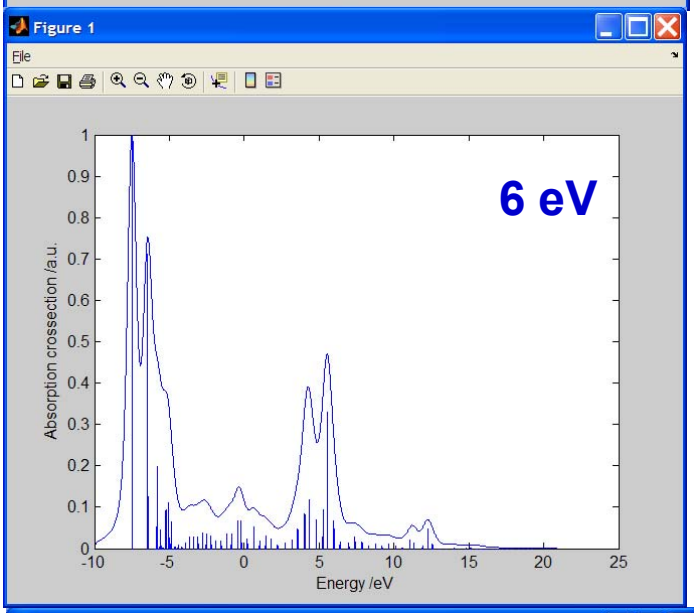
From Bocquet and Fujimori

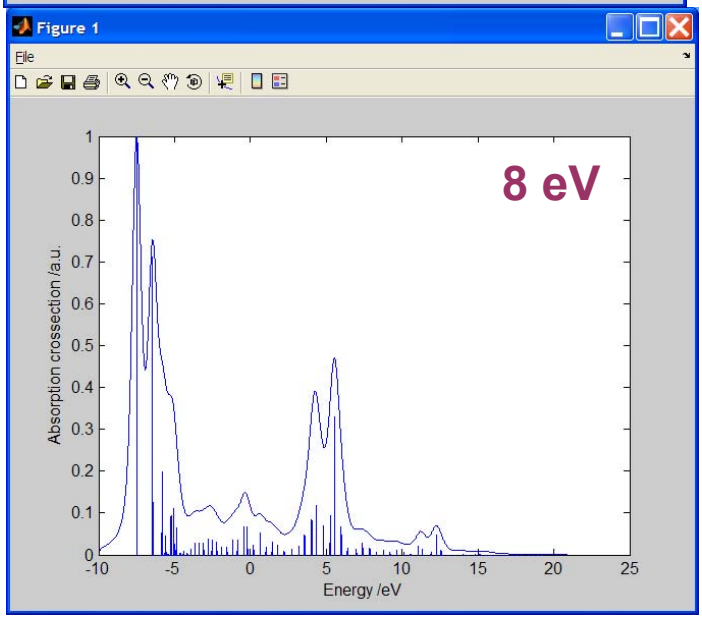
Journal of Electron Spectroscopy and Related Phenomena 82 (1996) 87–124

General trends as Δ, U and T are varied can be observed for all TM ions studied. Where only one satellite structure is predicted, an increase in Δ leads to a fall in the satellite intensity. For $\Delta < Q$, a second (or third) satellite at higher energy may appear due to increased weight in the $\underline{c}d^{n+2}\underline{L}^2$ final state (or higher final states). As Δ is increased, spectral weight from this satellite is transferred to the main satellite structure closer to the main peak, causing the main satellite first to increase and then finally to decrease as Δ approaches Q. Increasing U (and Q) with Δ and T held constant has the effect of increasing the weight of the satellite structure. As more polarizable ligands will screen the d-electrons to a greater extent, chalcogenides should be chosen with a smaller U than oxides [1]. As the hybridization strength T is increased, all satellites are found to become weaker and move away from the main peak. As T becomes larger the position and intensity of the satellite feature vary more slowly with Δ and U.

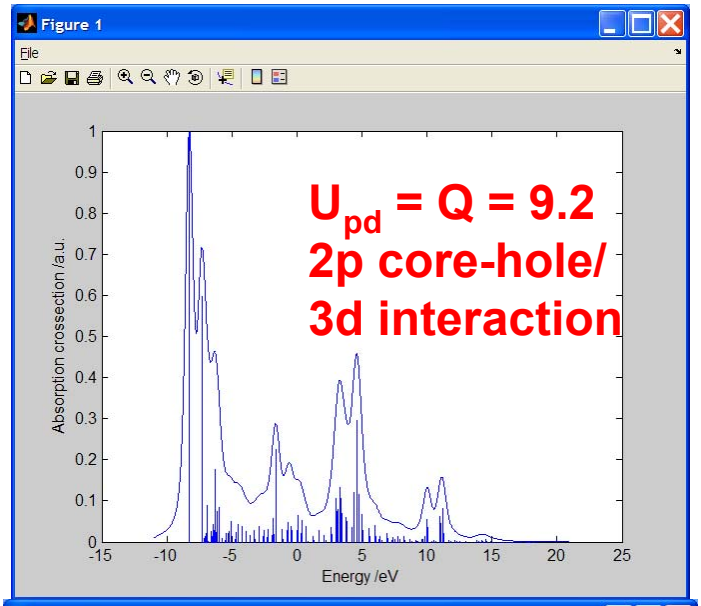


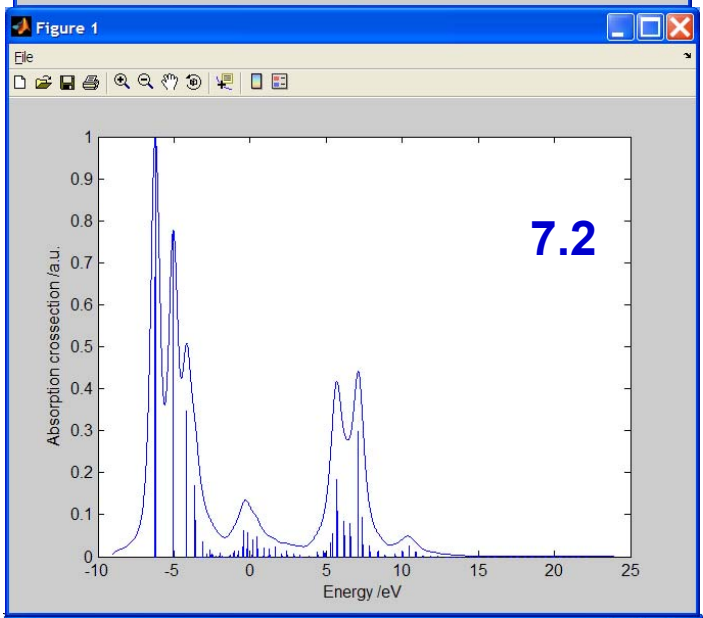


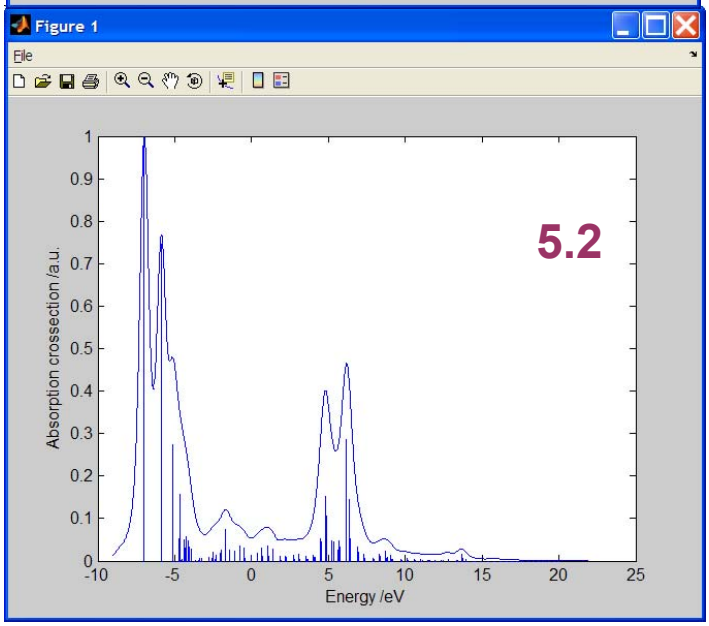




This variation didn't work: The program is obstinate in not letting one change Udd, so I'm sorry about asking for this!!! Next time the program or the problem statement will be fixed.





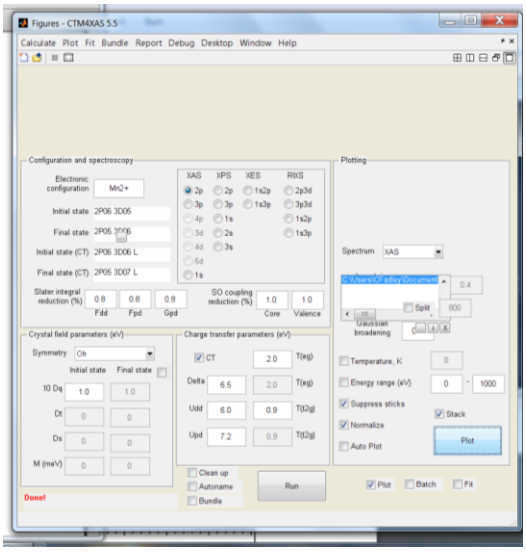


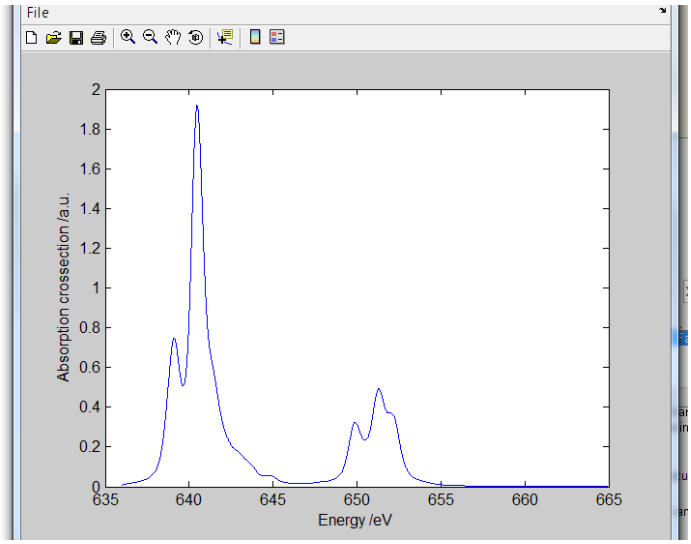
This variation works: As in Bocquet and Fujimori, Increasing U_{pd} increases satellite intensity. Spectrum shifts to higher binding energy also, as core hole drags states down.

[5.10]

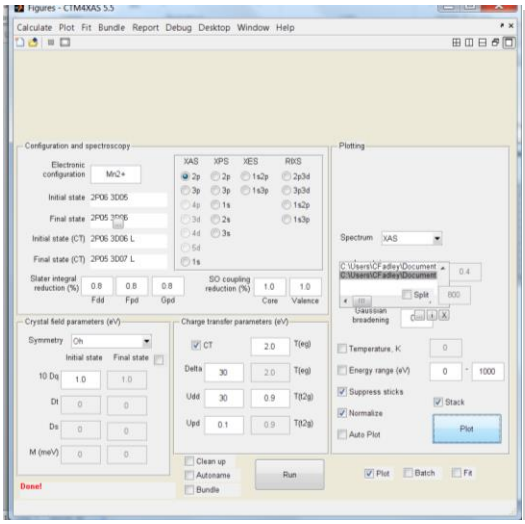
(d) Two calculations run with the new version of CTM4XAS5, one with charge transfer and one without, first by parameter trick of setting Δ to a very large number of 30, the core-hole attractive energy to a very small number of 0.1, and the dd repulsion to a very large number.

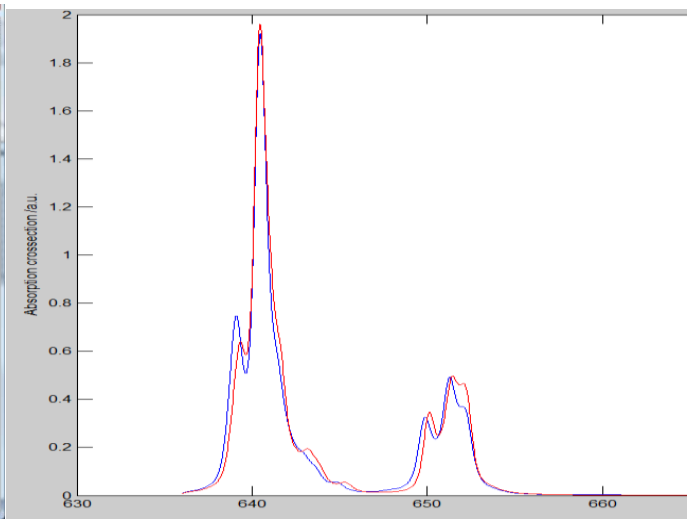
With charge transfer:





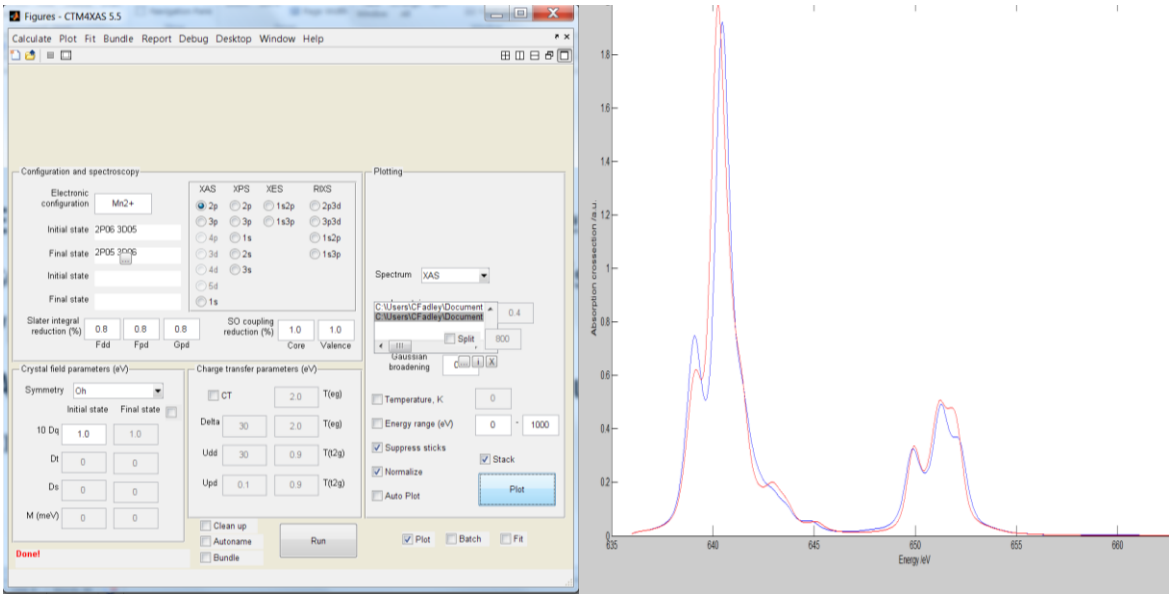
Without charge transfer using parameter trick-red curve





Effect is rather small in XAS, as the excited electron acts to screen the core hole, and the atom is in some sense left "neutral". Slight reduction in energy of two edges with charge transfer.

Without charge transfer done simply by unclicking the charge transfer option:



Gives very nearly the same result, as expected.