
Prof. Dr. Ismael Graff – Multo multo obrigado!!!

# *Fundamentals and New Directions in Photoelectron Spectroscopy (Photoemission)*


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**and**
**Materials Sciences Division**
**Lawrence Berkeley National Laboratory**



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**APTCOM Project, Labex Program (France)**


***Lectures at***
***Federal University of Parana State, Curitiba, Brazil***
***04-08 April, 2016***



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# Bem Vindo a Berkeley

Class statistics:

Total no. of students: 23

Physics? 15

Chemistry? 3

Other?: 5

Used photoelectron spectroscopy before?

- Laboratory XPS? 6
- Synchrotron radiation XPS? 5
- Laboratory low-energy ARPES? 1
- Synchrotron radiation ARPES? 1

Done other synchrotron radiation experiments?

- X-ray absorption, XMCD? 5
- EXAFS?3
- Other? 1

LNLS: 6


Prof. Ismael Graff


ATLANTIC
Ismael
Graff

**Some key references:**

**"Basic Concepts of X-ray Photoelectron Spectroscopy", C. S. Fadley, invited chapter for Electron Spectroscopy: Theory, Techniques, and Applications, C. R. Brundle and A. D. Baker, Eds. (Academic Press, London, 1978) Vol. II, Chap. 1, 145 pp., 53 figs, available at:**
**http://www.physics.ucdavis.edu/Classes/Physics243A/BasicConceptsofXPS.Fadley.pdf**

**"X-ray Photoelectron Spectroscopy : Progress and Perspectives", C.S. Fadley, invited review, Journal of Electron Spectroscopy and Related Phenomena 178–179, 2 (2010), 30 pp., 35 figs., available at:**
**http://www.physics.ucdavis.edu/Classes/Physics243A/XPS.Present&Future.JESRP.Fadley.pdf**

**And others downloadable from two websites:**

**http://www.physics.ucdavis.edu/fadleygroup/ Lecture slides from this course will be posted there**

**http://www.physics.ucdavis.edu/Classes/Physics243A/ A ten-week course of 20 lectures, with slides and videos posted**

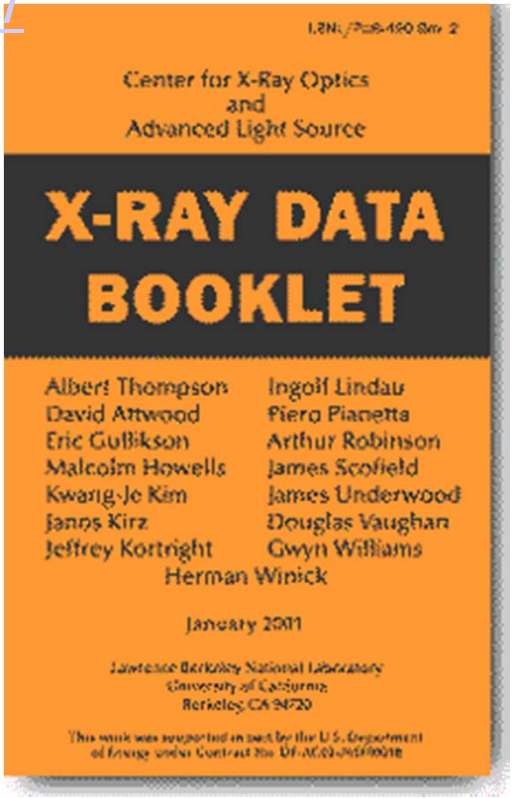
# X-RAY DATA BOOKLET

## *Center for X-ray Optics and Advanced Light Source*

## *Lawrence Berkeley National Laboratory*

http://xdb.lbl.gov/






**Basic Concepts:**

A Little Electronic Structure
The X-Ray-Based Experiments
X-Ray Sources, Synchrotron Radiation, Free Electron Lasers

**Core-Level Photoemission**

Intensities and Quantitative Analysis, the 3-Step Model
Varying Surface and Bulk Sensitivity
Chemical Shifts
Multiplet Splittings
Electron Screening and Satellite Structure
Magnetic and Non-Magnetic Dichroism
Resonant Photoemission
Photoelectron Diffraction and Holography

**Valence-Level Photoemission**

Band-Mapping in the Ultraviolet Photoemission Limit
Densities of States in the X-Ray Photoemission Limit

**Some New Directions**

Photoemission with Hard X-Rays (throughout lectures)
Photoemission with Standing Wave Excitation
Photoemission with: Higher Pressures→multi-Torr→Atmosphere?
Spatial Resolution-Photoelectron Microscopy
Temporal Resolution

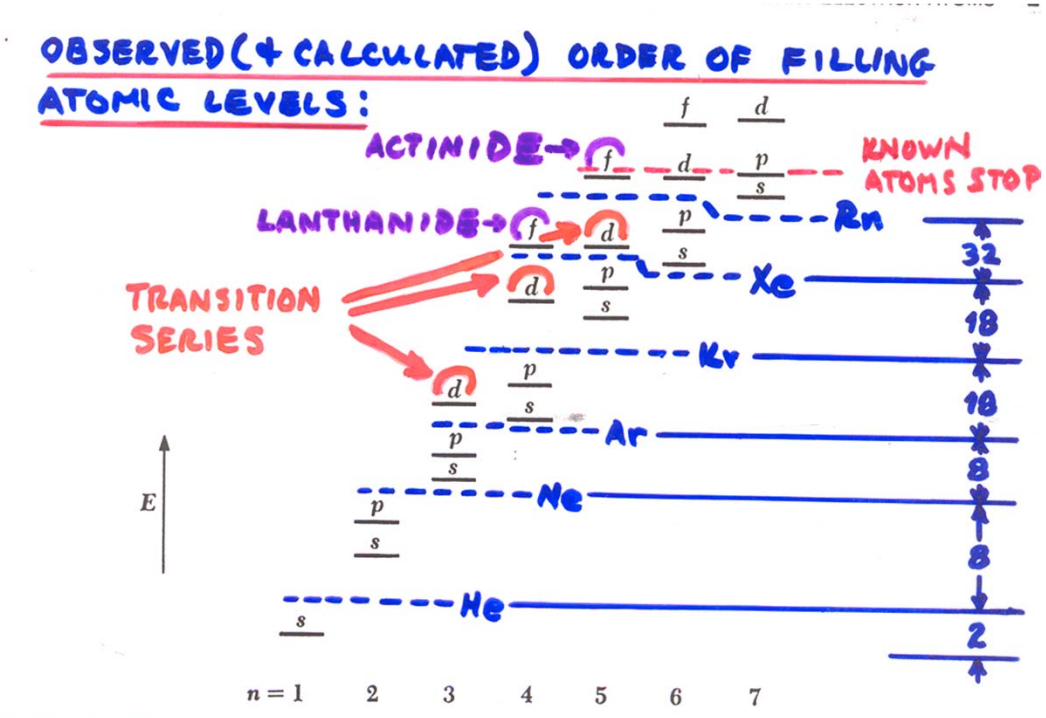
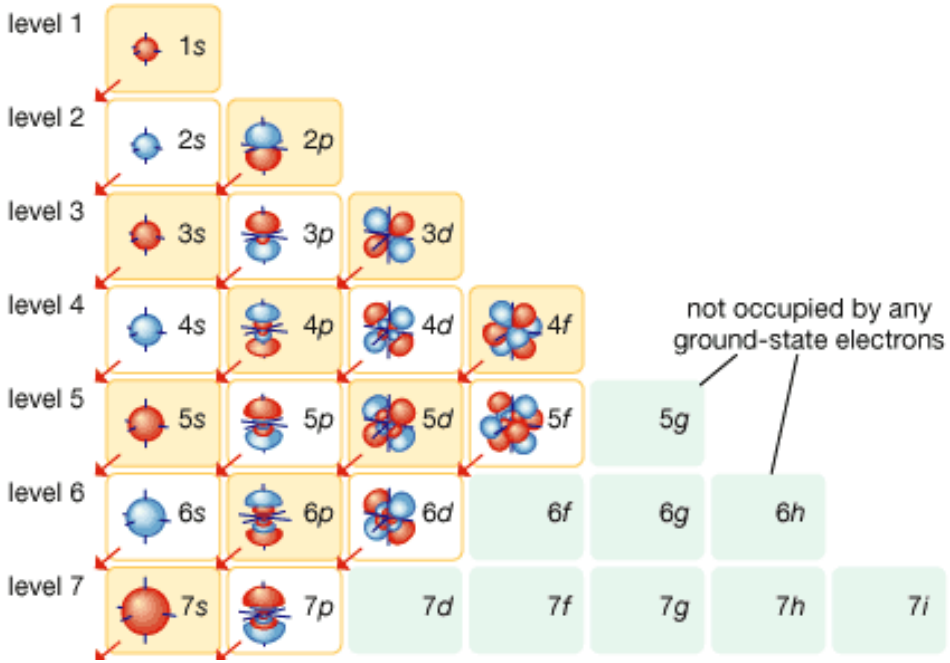



FIGURE 7.13 The sequence of quantum states in an atom. Not to scale.




## EXAMPLE CONFIGURATIONS:

| Z | ATOM | CONFIG. |
|---|---|---|
| 8 | O | $1s^2 2s^2 2p^4$ |
| 26 | Fe | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ |
| 63 | Eu | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^7 6s^2$ |

GROUND-STATE OPEN SHELL COUPLING?



⇒ LARGE $M_{3d}$ + MAGNETISM

ALSO MAGNETIC!


**Exchange interaction.**
**Hund's First Rule:**
**highest total spin angular momentum**

TRANSITION METALS

# Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States

The notation used to describe the electronic configuration of atoms and ions is discussed in all textbooks of introductory atomic physics. The letters $s$, $p$, $d$, . . . signify electrons having orbital angular momentum 0, 1, 2, . . . in units $\hbar$; the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H^{1}$ $1s$ | | | | | | | | | | | | | | | | | $He^{2}$ $1s^2$ |
| $Li^{3}$ $2s$ | $Be^{4}$ $2s^2$ | | | | | | | | | | | $B^{5}$ $2s^22p$ | $C^{6}$ $2s^22p^2$ | $N^{7}$ $2s^22p^3$ | $O^{8}$ $2s^22p^4$ | $F^{9}$ $2s^22p^5$ | $Ne^{10}$ $2s^22p^6$ |
| $Na^{11}$ $3s$ | $Mg^{12}$ $3s^2$ | | | | | | | | | | | $Al^{13}$ $3s^23p$ | $Si^{14}$ $3s^23p^2$ | $P^{15}$ $3s^23p^3$ | $S^{16}$ $3s^23p^4$ | $Cl^{17}$ $3s^23p^5$ | $Ar^{18}$ $3s^23p^6$ |
| $K^{19}$ $4s$ | $Ca^{20}$ $4s^2$ | $Sc^{21}$ $3d$ $4s^2$ | $Ti^{22}$ $3d^2$ $4s^2$ | $V^{23}$ * $3d^3$ $4s^2$ | $Cr^{24}$ $3d^5$ $4s$ | $Mn^{25}$ $3d^5$ $4s^2$ | $Fe^{26}$ $3d^6$ $4s^2$ | $Co^{27}$ $3d^7$ $4s^2$ | $Ni^{28}$ $3d^8$ $4s^2$ | $Cu^{29}$ $3d^{10}$ $4s$ | $Zn^{30}$ $3d^{10}$ $4s^2$ | $Ga^{31}$ $4s^24p$ | $Ge^{32}$ $4s^24p^2$ | $As^{33}$ $4s^24p^3$ | $Se^{34}$ $4s^24p^4$ | $Br^{35}$ $4s^24p^5$ | $Kr^{36}$ $4s^24p^6$ |
| $Rb^{37}$ $5s$ | $Sr^{38}$ $5s^2$ | $Y^{39}$ $4d$ $5s^2$ | $Zr^{40}$ * $4d^2$ $5s^2$ | $Nb^{41}$ $4d^4$ $5s$ | $Mo^{42}$ $4d^5$ $5s$ | $Tc^{43}$ $4d^6$ $5s$ | $Ru^{44}$ $4d^7$ $5s$ | $Rh^{45}$ $4d^8$ $5s$ | $Pd^{46}$ $4d^{10}$ – | $Ag^{47}$ $4d^{10}$ $5s$ | $Cd^{48}$ $4d^{10}$ $5s^2$ | $In^{49}$ $5s^25p$ | $Sn^{50}$ $5s^25p^2$ | $Sb^{51}$ $5s^25p^3$ | $Te^{52}$ $5s^25p^4$ | $I^{53}$ $5s^25p^5$ | $Xe^{54}$ $5s^25p^6$ |
| $Cs^{55}$ $6s$ | $Ba^{56}$ $6s^2$ | $La^{57}$ $5d$ $6s^2$ | $Hf^{72}$ $4f^{14}$ $5d^2$ $6s^2$ | $Ta^{73}$ $5d^3$ $6s^2$ | $W^{74}$ $5d^4$ $6s^2$ | $Re^{75}$ $5d^5$ $6s^2$ | $Os^{76}$ $5d^6$ $6s^2$ | $Ir^{77}$ $5d^9$ – | $Pt^{78}$ $5d^9$ $6s$ | $Au^{79}$ $5d^{10}$ $6s$ | $Hg^{80}$ $5d^{10}$ $6s^2$ | $Tl^{81}$ $6s^26p$ | $Pb^{82}$ $6s^26p^2$ | $Bi^{83}$ $6s^26p^3$ | $Po^{84}$ $6s^26p^4$ | $At^{85}$ $6s^26p^5$ | $Rn^{86}$ $6s^26p^6$ |
| $Fr^{87}$ $7s$ | $Ra^{88}$ $7s^2$ | $Ac^{89}$ $6d$ $7s^2$ | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Ce^{58}$ $4f^2$ $6s^2$ | $Pr^{59}$ $4f^3$ $6s^2$ | $Nd^{60}$ $4f^4$ $6s^2$ | $Pm^{61}$ $4f^5$ $6s^2$ | $Sm^{62}$ $4f^6$ $6s^2$ | $Eu^{63}$ $4f^7$ $6s^2$ | $Gd^{64}$ $4f^7$ $5d$ $6s^2$ | $Tb^{65}$ $4f^8$ $5d$ $6s^2$ | $Dy^{66}$ $4f^{10}$ $6s^2$ | $Ho^{67}$ $4f^{11}$ $6s^2$ | $Er^{68}$ $4f^{12}$ $6s^2$ | $Tm^{69}$ $4f^{13}$ $6s^2$ | $Yb^{70}$ $4f^{14}$ $6s^2$ | $Lu^{71}$ $4f^{14}$ $5d$ $6s^2$ |
| $Th^{90}$ – $6d^2$ $7s^2$ | $Pa^{91}$ $5f^2$ $6d$ $7s^2$ | $U^{92}$ $5f^3$ $6d$ $7s^2$ | $Np^{93}$ $5f^5$ $7s^2$ | $Pu^{94}$ $5f^6$ $7s^2$ | $Am^{95}$ $5f^7$ $7s^2$ | $Cm^{96}$ $5f^7$ $6d$ $7s^2$ | $Bk^{97}$ | $Cf^{98}$ | $Es^{99}$ | $Fm^{100}$ | $Md^{101}$ | $No^{102}$ | $Lr^{103}$ |

$s^1$ $s^2$ $p^1$ $p^2$ $p^3$ $p^4$ $p^5$ $p^6$

$d^1$ $d^2$ $d^3$ $d^4$ $d^5$ $d^6$ $d^7$ $d^8$ $d^9$ $d^{10}$

$4f^1$ ... $4f(5d)$ FILLING ... $4f^{14}$

... $5f(6d)$ FILLING ...

RARE EARTHS

ACTINIDES

* = EXCEPTIONS

= EXCEPTIONS

→ $d^5 + d^{10}$ : ½ FILLED / FILLED MORE STABLE

# A first try at many-electron wave functions: The Hartree-Fock Method

**Assume N-electron, P nucleus wave function to be:**

$$\Psi \approx \Phi = \textit{Slater}\ \text{det}\,\textit{er}\,\text{min}\,\textit{ant}$$

space: like 1s, 2s,…
spin: α(↑) or β(↓)

$$= \frac{1}{\sqrt{N!}} \begin{pmatrix} \phi_1(\vec{r}_1)\chi_1(\sigma_1) & \cdots & \phi_N(\vec{r}_1)\chi_N(\sigma_1) \\ \vdots & \ddots & \vdots \\ \phi_1(\vec{r}_N)\chi_1(\sigma_N) & \cdots & \phi_N(\vec{r}_N)\chi_N(\sigma_N) \end{pmatrix} \qquad (35a)$$

**and also require orthonormality of one-electron orbitals**

$$\int \phi_i^*(\vec{r})\phi_j(\vec{r})dV = \delta_{ij}$$

**Minimize total energy→ Hartree-Fock equations**

$$\hat{H}(\vec{r}_1)\phi_i(\vec{r}_1) = \varepsilon_i\phi_i(\vec{r}_1);\ i = 1,2,...N \qquad (42)$$

**with:**

$$\varepsilon_i = \varepsilon_i^0 + \sum_{j=1}^{N} J_{ij} - \delta_{m_{s_i},m_{s_j}} K_{ij} \qquad (47)$$

↑↑ or ↓↓

If $\varphi_j$ ($j \neq i$) don't relax around a $\varphi_i$ *hole* → Koopmans' Theorem:
- One-electron energies (eigenvalues) =
$-\varepsilon_i \approx E_{Binding}$

**One-electron integral:**

$$\varepsilon_i^0 = \left\langle \phi_i(\vec{r}_1) \left| -\frac{1}{2}\nabla_1^2 - \sum_{\ell=1}^{P} \frac{Z_\ell}{r_{1\ell}} \right| \phi_i(\vec{r}_1) \right\rangle \qquad (48)$$

**Two-electron coulomb integral:**

$$J_{ij} \equiv \left\langle \phi_i(\vec{r}_1) \left| \hat{K}_j \right| \phi_i(\vec{r}_1) \right\rangle = \iint \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\frac{1}{r_{12}}\phi_i(\vec{r}_1)\phi_j(\vec{r}_2)dV_1dV_2 \qquad (45)$$

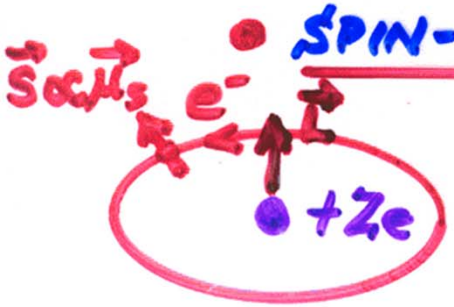
*Note—$K_{ij} \leftrightarrow J_{ij}$ in solid state*

**Two-electron exchange integral:**

$$K_{ij} \equiv \left\langle \phi_i(\vec{r}_1) \left| \hat{J}_j \right| \phi_i(\vec{r}_1) \right\rangle = \iint \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\frac{1}{r_{12}}\phi_j(\vec{r}_1)\phi_i(\vec{r}_2)dV_1dV_2 \qquad (46)$$

**Lowers energy—"attractive"**

# Spin-orbit: Final important relativistic interaction




- SPIN-ORBIT SPLITTING OF LEVELS:

$\Rightarrow$ EFFECTIVE $\vec{B}$ (NUCLEUS AROUND $e^-$) $\propto \vec{L}$

$$\hat{H}_{s\text{-}o} = \xi(r)\,\vec{l}\cdot\vec{s}$$

- SPLITS ALL $nl$ LEVELS $2(2l+1)$
  - $nlj = l+1/2$ — $2l+2$
  - $nlj = l-1/2$ — $2l$

- MIXES SPIN + ORBITAL ANGULAR MOM.:

$$\psi_{nljm_j} = C_1\psi_{nl,m_j-1/2}\begin{pmatrix}1\\0\end{pmatrix} + C_2\psi_{nl,m_j+1/2}\begin{pmatrix}0\\1\end{pmatrix}$$

$\begin{pmatrix}1\\0\end{pmatrix} = m_s = +1/2 = \uparrow$ $\qquad$ $\begin{pmatrix}0\\1\end{pmatrix} = m_s = -1/2 = \downarrow$

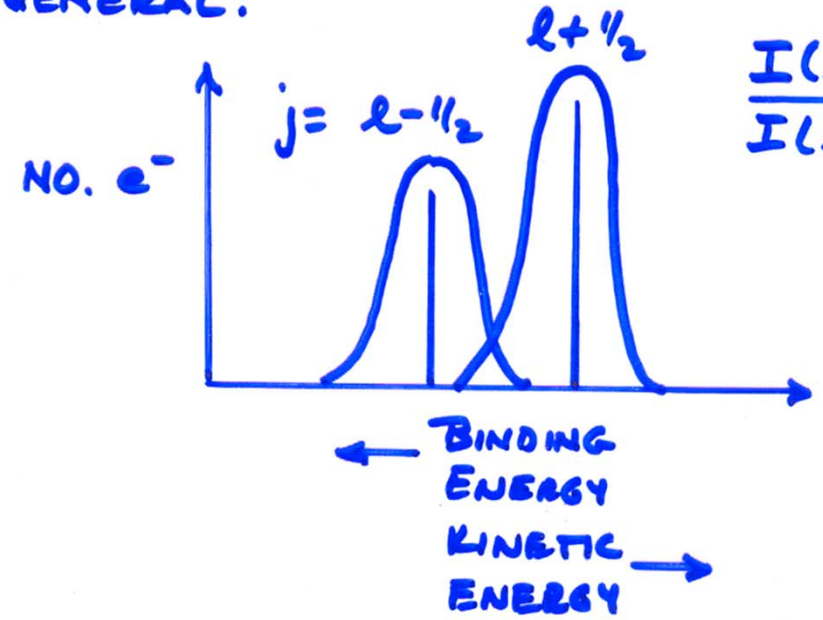
WITH C1 AND C2 TABULATED CLEBSCH-GORDAN OR WIGNER 3j SYMBOLS

# SOME SPIN-ORBIT SPLITTINGS: (IN eV)

| | Z = 13 (Al) | 28 (Ni) | 46 (Pd) |
|---|---|---|---|
| $2p^6$ | | | |
| $2p_{1/2}^2$ | 0.4 | 17.8 | 157.0 |
| $2p_{3/2}^4$ | | | |
| $3d^{10}$ | Z = 30 (Zn) | 48 (Cd) | 64 (Gd) |
| $3d_{3/2}^4$ | 0.1 | 6.7 | 32.3 |
| $3d_{5/2}^6$ | | | |
| $4f^{14}$ | Z = 74 (W) | 84 (Pb) | 92 (U) |
| $4f_{5/2}^6$ | 2.2 | 7.0 | 64 |
| $4f_{7/2}^8$ | | | |

INCREASE WITH Z FOR A GIVEN LEVEL.

IN GENERAL:




$$\frac{I(\ell+1/2)}{I(\ell-1/2)} = \frac{2\ell+2}{2\ell}$$

# X-Ray Data Booklet--Section 1.1 ELECTRON BINDING ENERGIES

**The energies are given in eV relative to the vacuum level for the rare gases and for $H_2$, $N_2$, $O_2$, $F_2$, and $Cl_2$; relative to the Fermi level for the metals; and relative to the top of the valence bands for semiconductors (and insulators).**

| Electronic configuration | Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ | $M_1$ 3s | $M_2$ $3p_{1/2}$ | $M_3$ $3p_{3/2}$ |
|---|---|---|---|---|---|---|---|---|
| $1s$ | 1 H | 13.6 | | | | | | |
| $1s^2$ | 2 He | 24.6* | | | | | | |
| $1s^2\,2s$ | 3 Li | 54.7* | | | | | | |
| $1s^2\,2s^2$ | 4 Be | 111.5* | | | | | | |
| $1s^2\,2s^2\,2p$ | 5 B | 188* | | | | | | |
| $1s^2\,2s^2\,2p^2$ | 6 C | 284.2* | | | | | | |
| $1s^2\,2s^2\,2p^3$ | 7 N | 409.9* | 37.3* | ~ 9 | ~ 9 | | | |
| $1s^2\,2s^2\,2p^4$ | 8 O | 543.1* | 41.6* | ~ 13 | ~ 13 | | | |
| $1s^2\,2s^2\,2p^5$ | 9 F | 696.7* | ~ 45 | ~ 17 | ~ 17 | | | |
| $1s^2\,2s^2\,2p^6$ | 10 Ne | 870.2* | 48.5* | 21.7* | 21.6* | | | |
| [Ne] $3s$ | 11 Na | 1070.8† | 63.5† | 30.65 | 30.81 | | | |
| [Ne] $3s^2$ | 12 Mg | 1303.0† | 88.7 | 49.78 | 49.50 | | | |
| [Ne] $3s^2\,3p$ | 13 Al | 1559.6 | 117.8 | 72.95 | 72.55 | | | |
| [Ne] $3s^2\,3p^2$ | 14 Si | 1839 | 149.7*b | 99.82 | 99.42 | | | |
| [Ne] $3s^2\,3p^3$ | 15 P | 2145.5 | 189* | 136* | 135* | | | |
| [Ne] $3s^2\,3p^4$ | 16 S | 2472 | 230.9 | 163.6* | 162.5* | | | |
| [Ne] $3s^2\,3p^5$ | 17 Cl | 2822.4 | 270* | 202* | 200* | | | |
| [Ne] $3s^2\,3p^6$ | 18 Ar | 3205.9* | 326.3* | 250.6† | 248.4* | 29.3* | 15.9* | 15.7* |
| [Ar] $4s$ | 19 K | 3608.4* | 378.6* | 297.3* | 294.6* | 34.8* | 18.3* | 18.3* |
| [Ar] $4s^2$ | 20 Ca | 4038.5* | 438.4† | 349.7† | 346.2† | 44.3 † | 25.4† | 25.4† |
| | 21 Sc | 4492 | 498.0* | 403.6* | 398.7* | 51.1* | 28.3* | 28.3* |
| | 22 Ti | 4966 | 560.9† | 460.2† | 453.8† | 58.7† | 32.6† | 32.6† |

Valence levels

Interpolated, extrapolated

Missing valence B.E.s

Valence levels

# X-Ray Data Booklet--Section 1.1 ELECTRON BINDING ENERGIES

| Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ | $M_1$ 3s | $M_2$ $3p_{1/2}$ | $M_3$ $3p_{3/2}$ | $M_4$ $3d_{3/2}$ | $M_5$ $3d_{5/2}$ | $N_1$ 4s | $N_2$ $4p_{1/2}$ | $N_3$ $4p_{3/2}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 23 V | 5465 | 626.7† | 519.8† | 512.1† | 66.3† | 37.2† | 37.2† | | | | | |
| 24 Cr | 5989 | 696.0† | 583.8† | 574.1† | 74.1† | 42.2† | 42.2† | | | | | |
| 25 Mn | 6539 | 769.1† | 649.9† | 638.7† | 82.3† | 47.2† | 47.2† | | | | | |
| 26 Fe | 7112 | 844.6† | 719.9† | 706.8† | 91.3† | 52.7† | 52.7† | | | | | |
| 27 Co | 7709 | 925.1† | 793.2† | 778.1† | 101.0† | 58.9† | 59.9† | | | | | |
| 28 Ni | 8333 | 1008.6† | 870.0† | 852.7† | 110.8† | 68.0† | 66.2† | | | | | |
| 29 Cu | 8979 | 1096.7† | 952.3† | 932.7 | 122.5† | 77.3† | 75.1† | | | | | |
| 30 Zn | 9659 | 1196.2* | 1044.9* | 1021.8* | 139.8* | 91.4* | 88.6* | 10.2* | 10.1* | | | |
| 31 Ga | 10367 | 1299.0*b | 1143.2† | 1116.4† | 159.5† | 103.5† | 100.0† | 18.7† | 18.7† | | | |
| 32 Ge | 11103 | 1414.6*b | 1248.1*b | 1217.0*b | 180.1* | 124.9* | 120.8* | 29.8 | 29.2 | | | |
| 33 As | 11867 | 1527.0*b | 1359.1*b | 1323.6*b | 204.7* | 146.2* | 141.2* | 41.7* | 41.7* | | | |
| 34 Se | 12658 | 1652.0*b | 1474.3*b | 1433.9*b | 229.6* | 166.5* | 160.7* | 55.5* | 54.6* | | | |
| 35 Br | 13474 | 1782* | 1596* | 1550* | 257* | 189* | 182* | 70* | 69* | | | |
| 36 Kr | 14326 | 1921 | 1730.9* | 1678.4* | 292.8* | 222.2* | 214.4 | 95.0* | 93.8* | 27.5* | 14.1* | 14.1* |
| 37 Rb | 15200 | 2065 | 1864 | 1804 | 326.7* | 248.7* | 239.1* | 113.0* | 112* | 30.5* | 16.3* | 15.3 * |
| 38 Sr | 16105 | 2216 | 2007 | 1940 | 358.7† | 280.3† | 270.0† | 136.0† | 134.2† | 38.9† | 21.3 | 20.1† |
| 39 Y | 17038 | 2373 | 2156 | 2080 | 392.0*b | 310.6* | 298.8* | 157.7† | 155.8† | 43.8* | 24.4* | 23.1* |
| 40 Zr | 17998 | 2532 | 2307 | 2223 | 430.3† | 343.5† | 329.8† | 181.1† | 178.8† | 50.6† | 28.5† | 27.1† |
| 41 Nb | 18986 | 2698 | 2465 | 2371 | 466.6† | 376.1† | 360.6† | 205.0† | 202.3† | 56.4† | 32.6† | 30.8† |
| 42 Mo | 20000 | 2866 | 2625 | 2520 | 506.3† | 411.6† | 394.0† | 231.1† | 227.9† | 63.2† | 37.6† | 35.5† |
| 43 Tc | 21044 | 3043 | 2793 | 2677 | 544* | 447.6 | 417.7 | 257.6 | 253.9* | 69.5* | 42.3* | 39.9* |
| 44 Ru | 22117 | 3224 | 2967 | 2838 | 586.1* | 483.5† | 461.4† | 284.2† | 280.0† | 75.0† | 46.3† | 43.2† |
| 45 Rh | 23220 | 3412 | 3146 | 3004 | 628.1† | 521.3† | 496.5† | 311.9† | 307.2† | 81.4*b | 50.5† | 47.3† |
| 46 Pd | 24350 | 3604 | 3330 | 3173 | 671.6† | 559.9† | 532.3† | 340.5† | 335.2† | 87.1*b | 55.7†a | 50.9† |
| 47 Ag | 25514 | 3806 | 3524 | 3351 | 719.0† | 603.8† | 573.0† | 374.0† | 368.3 | 97.0† | 63.7† | 58.3† |

Valence levels

Valence levels

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The X-Ray-Based Experiments

X-Ray Sources, Synchrotron Radiation, Free Electron Lasers

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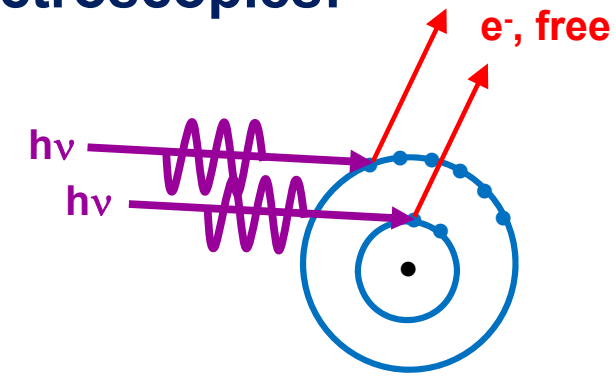
Photoemission with: Higher Pressures→multi-Torr→Atmosphere?

Spatial Resolution-Photoelectron Microscopy

Temporal Resolution

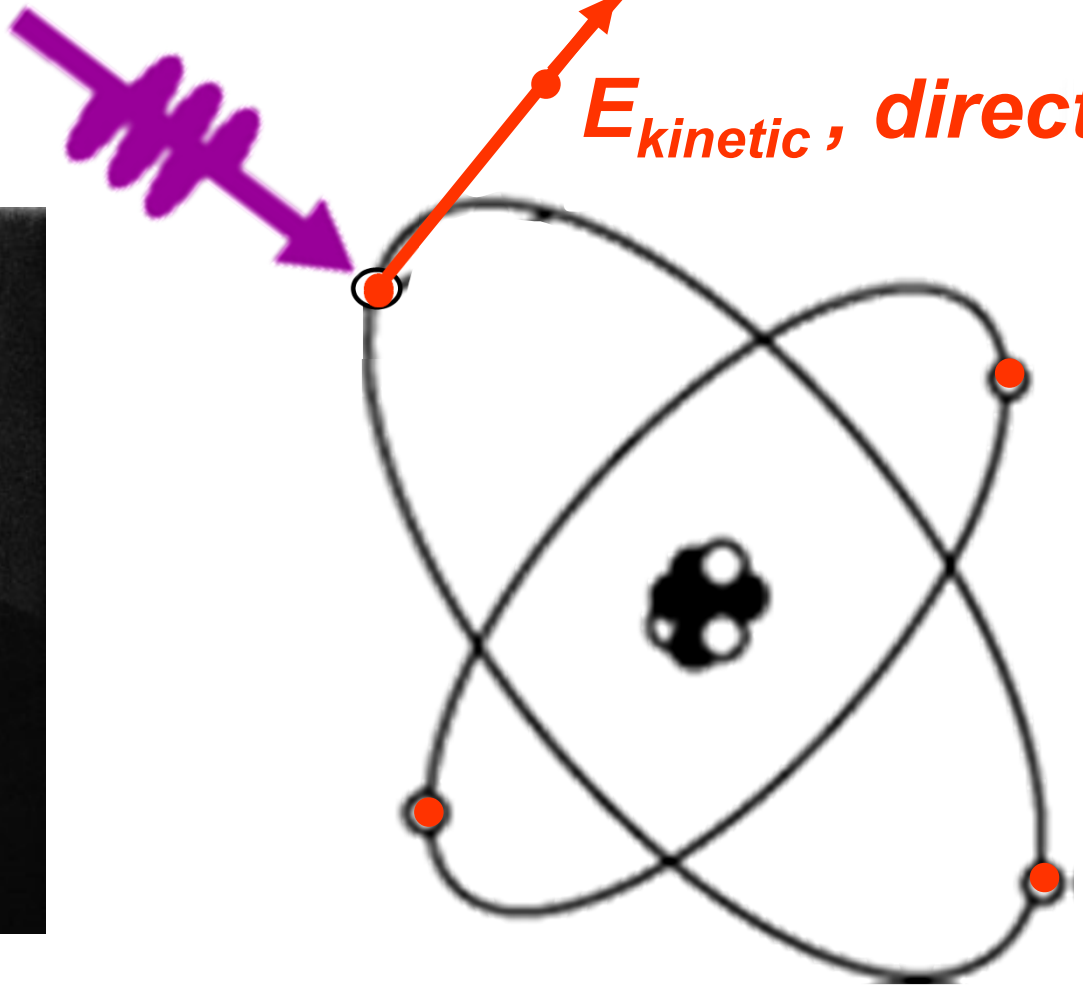
# The vacuum ultraviolet, soft x-ray, hard x-ray measurements:

## The spectroscopies:




PHOTOELECTRON SPECTROSCOPY=
PHOTOEMISSION – PS, PES, UPS, XPS
+ DIFFRACTION-XPD, PhD
+ HOLOGRAPHY-PH
+ MICROSCOPY-PEEM

# The Photoelectric Effect, Einstein, 1905
# Light can behave like a Particle!



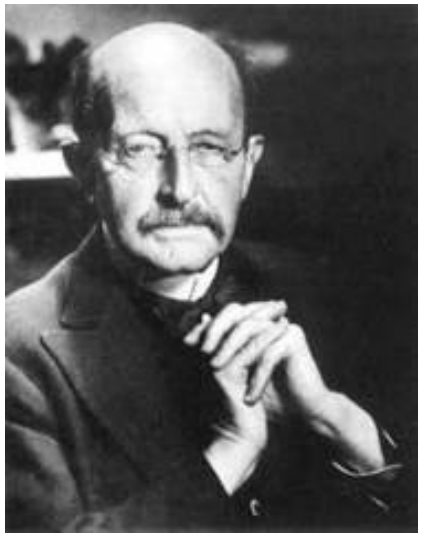

$$h\nu = E_{initial} - E_{final} = E_{binding} + E_{kinetic}$$

# But not everybody liked this idea to start with!

*"I would like to tell you how pleased I am that you have given up your light-quantum theory"*

***von Laue to Einstein, 1907 letter***

# …and even Planck



***In his 1913 letter nominating Einstein for the membership of Prussian Academy of Science, Max Planck et al. wrote:***

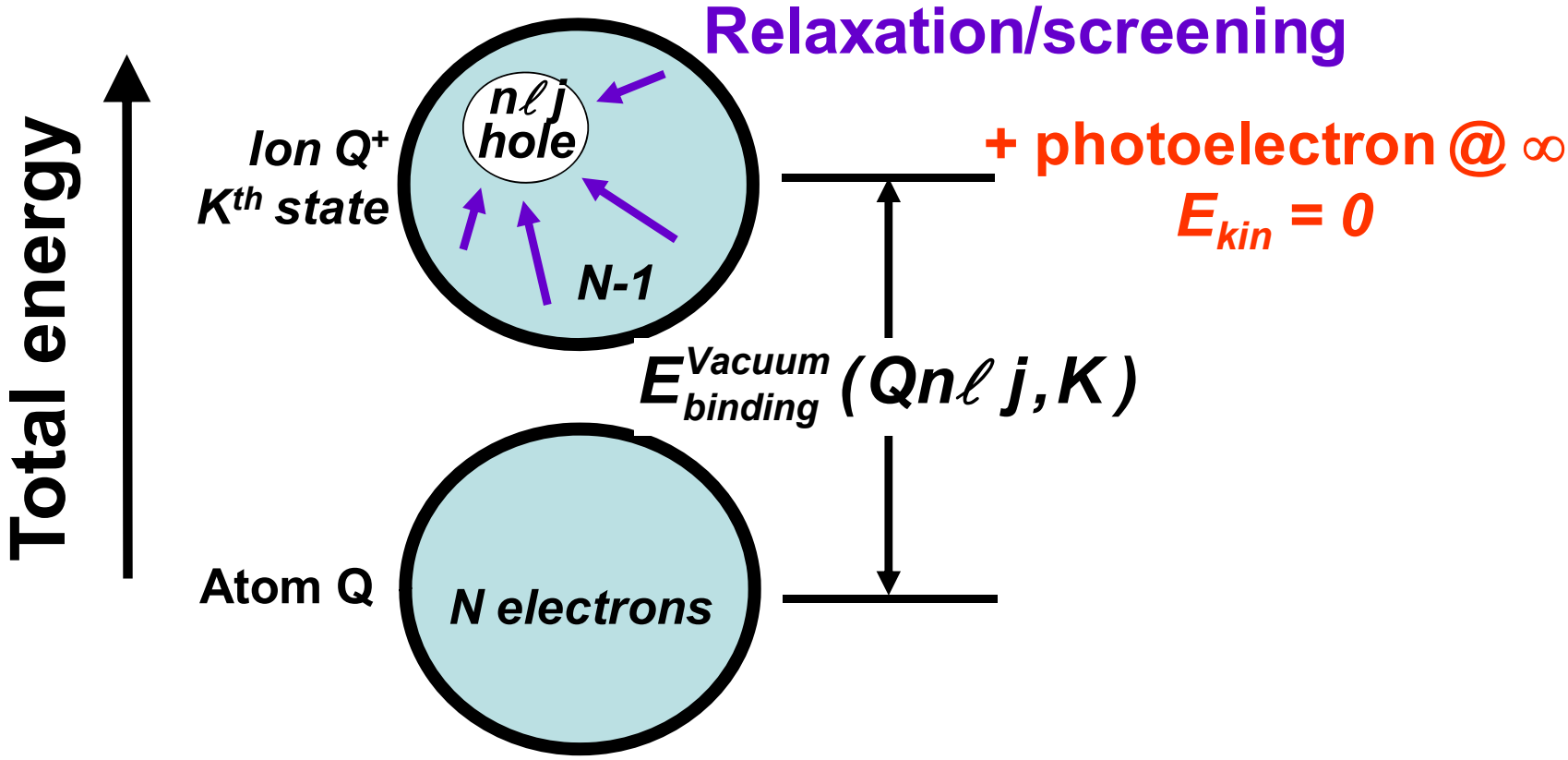
*"In sum, one can say there is hardly one among the great problems in which modern physics is so rich to which Einstein has not made a remarkable contribution. That he may sometimes have missed the target in his speculations, as, for example, in his hypothesis of light quanta, cannot really be held too much against him, for it is not possible to introduce really new ideas even in the most exact sciences without sometimes taking a risk."*

# Basic energetics—Many e⁻ picture

$$h\nu = E^{Vacuum}_{binding} + E_{kinetic} = E^{Fermi}_{binding} + \varphi_{spectrometer} + E_{kinetic}$$

Many states, many values

$$E^{Vacuum}_{binding}(Qn\ell\, j, K) = E_{final}(N-1, Qn\ell\, j\ hole, K) - E_{initial}(N)$$



# The vacuum ultraviolet, soft x-ray, hard x-ray measurements:

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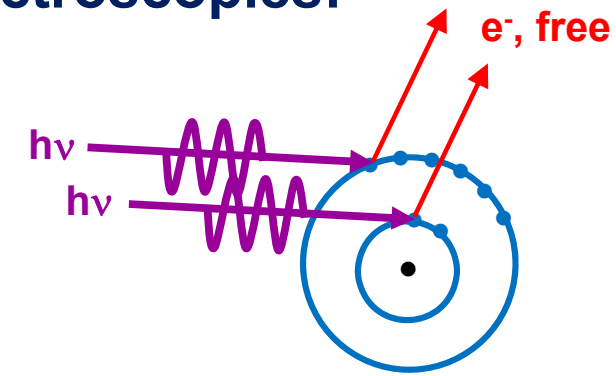
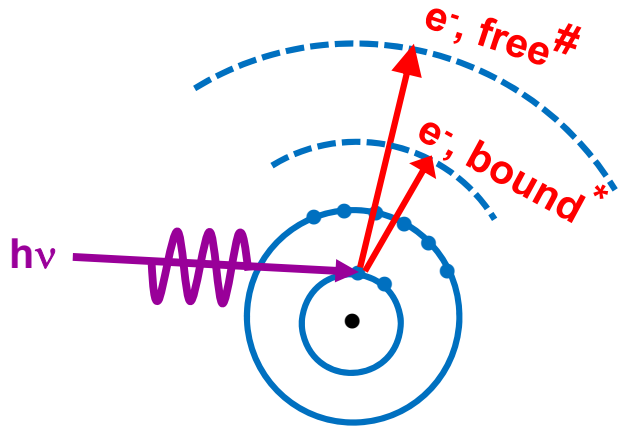
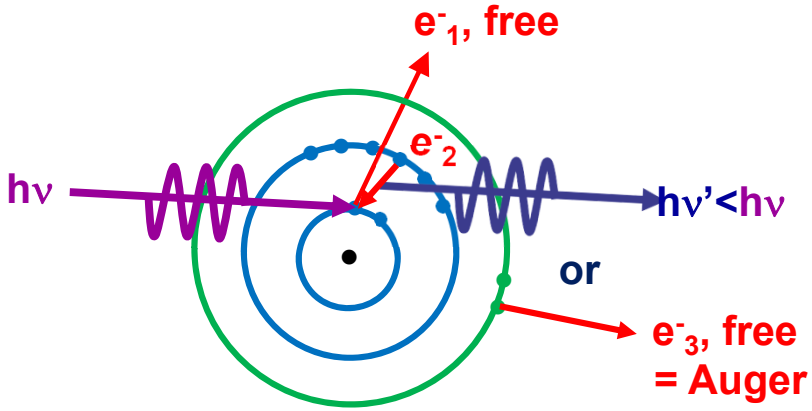



PHOTOELECTRON SPECTROSCOPY=
PHOTOEMISSION – PS, PES, UPS, XPS
+ DIFFRACTION-XPD, PhD
+ HOLOGRAPHY-PH
+ MICROSCOPY-PEEM




X-RAY ABSORPTION SPECTROSCOPY- XAS
*NEAR-EDGE – NEXAFS, XANES
#EXTENDED- EXAFS, XAFS
+ X-RAY MAGNETIC CIRCULAR/LINEAR
DICHROISM- XMCD, XMLD



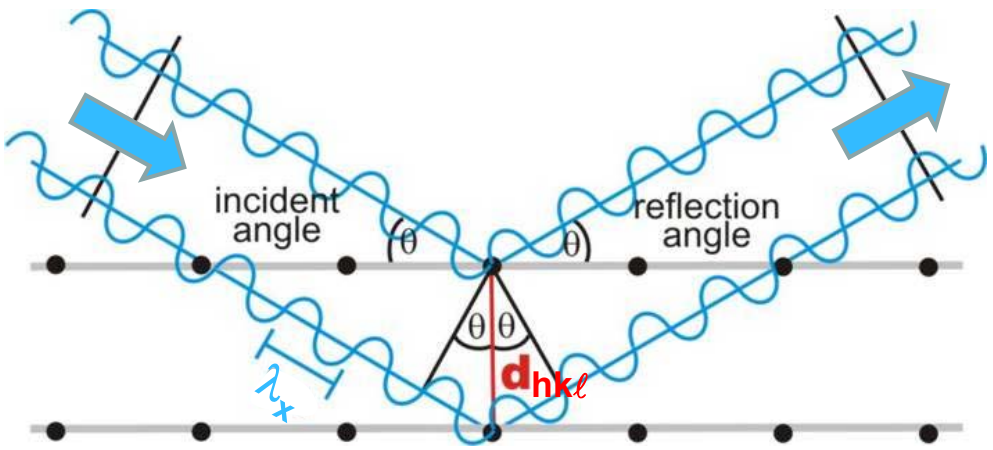

X-RAY EMISSION (FLUORESCENCE)
SPECTROSCOPY

+ AUGER ELECRON SPECTROSCOPY

# The vacuum ultraviolet, soft x-ray, hard x-ray measurements:

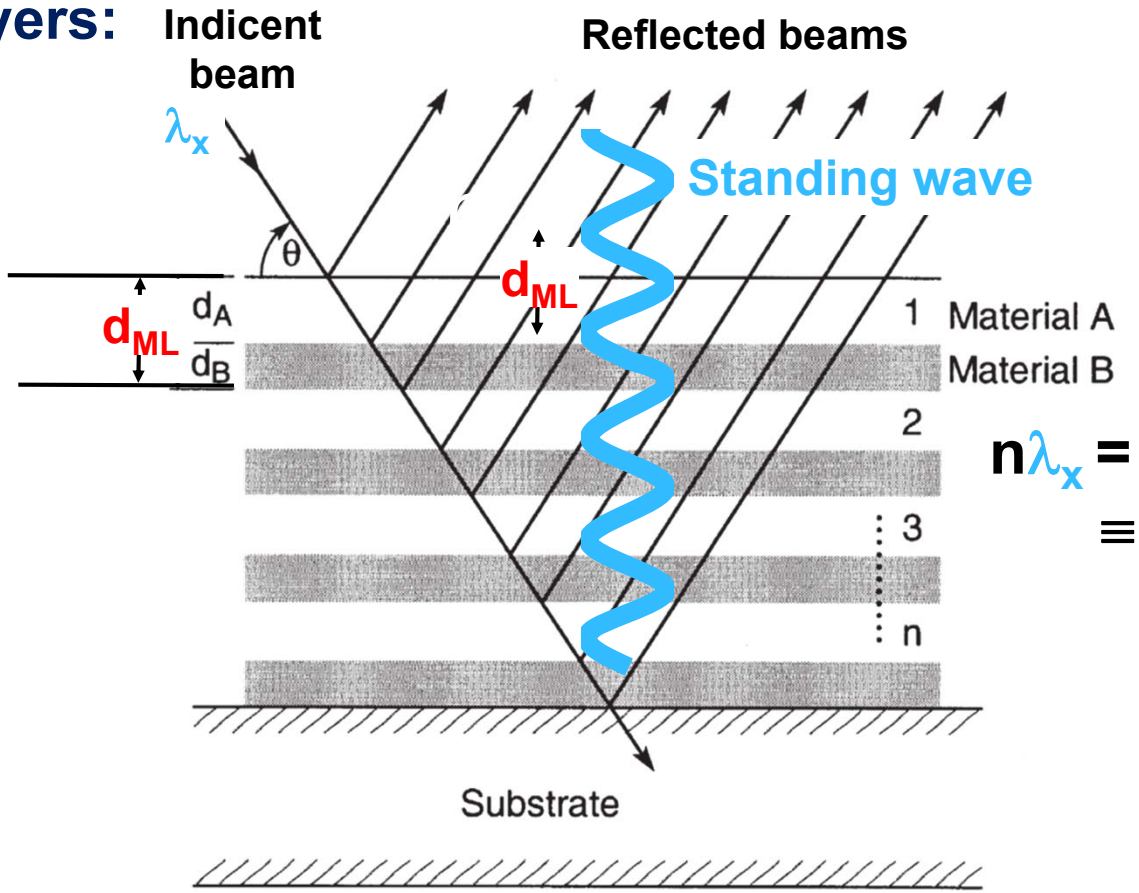
## Plus diffraction and scattering:

## From crystals:



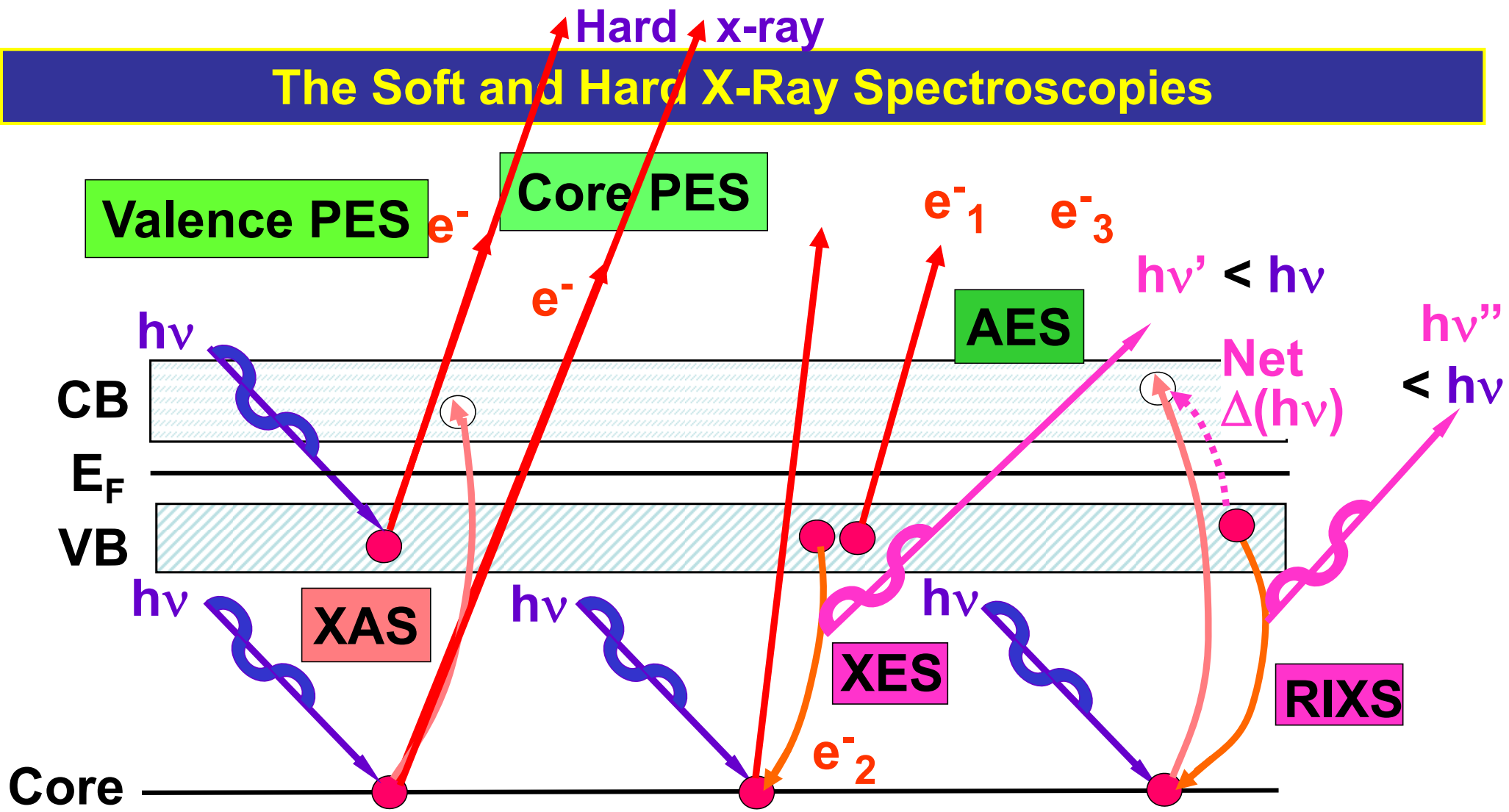

$$n\lambda_x = 2d_{hk\ell}\sin\theta$$

## From multilayers:




$$n\lambda_x = 2(d_A+d_B)\sin\theta$$
$$\equiv 2d_{ML}\sin\theta$$

# The Soft and Hard X-Ray Spectroscopies




PES = photoemission = photoelectron spectroscopy

XAS = x-ray absorption spectroscopy

AES = Auger electron spectroscopy

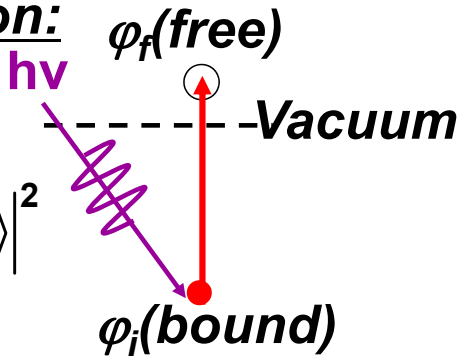
XES = x-ray emission spectroscopy

RIXS = resonant inelastic x-ray scattering / x-ray Raman scatt.

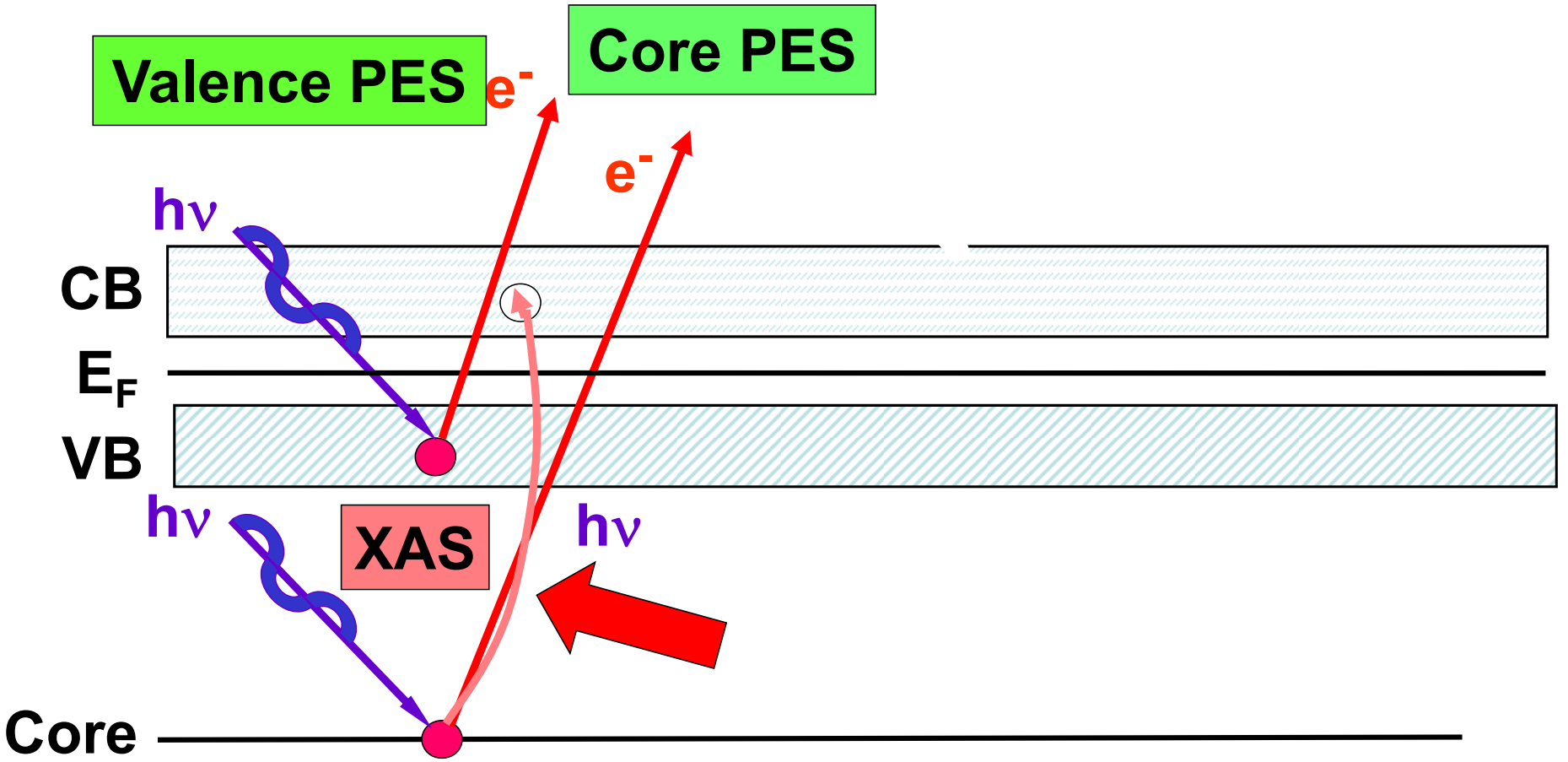
# MATRIX ELEMENTS IN The Soft and Hard X-Ray Spectroscopies: DIPOLE LIMIT

- ***Photoelectron spectroscopy/photoemission:***

$$I \propto \left| \hat{e} \bullet \left\langle \varphi_f(1) \middle| \vec{r} \middle| \varphi_i(1) \right\rangle \right|^2$$



# The Soft and Hard X-Ray Spectroscopies

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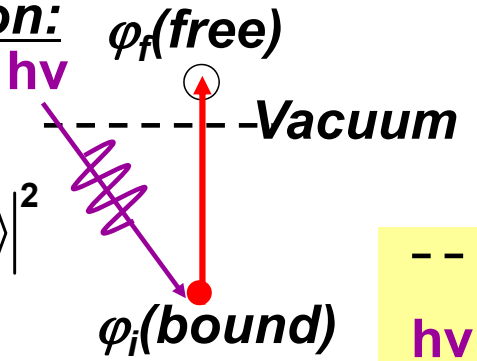
# MATRIX ELEMENTS IN The Soft and Hard X-Ray Spectroscopies: DIPOLE LIMIT

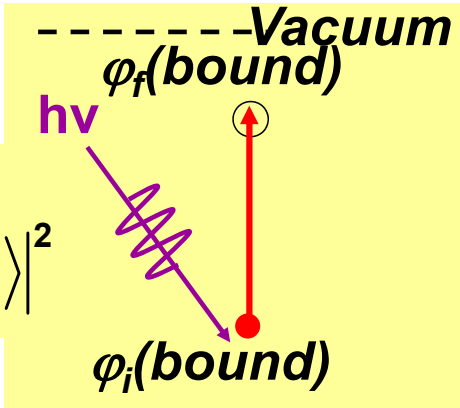
- ***Photoelectron spectroscopy/photoemission:***

$$I \propto \left| \hat{e} \bullet \left\langle \varphi_f(1) \middle| \vec{r} \middle| \varphi_i(1) \right\rangle \right|^2$$



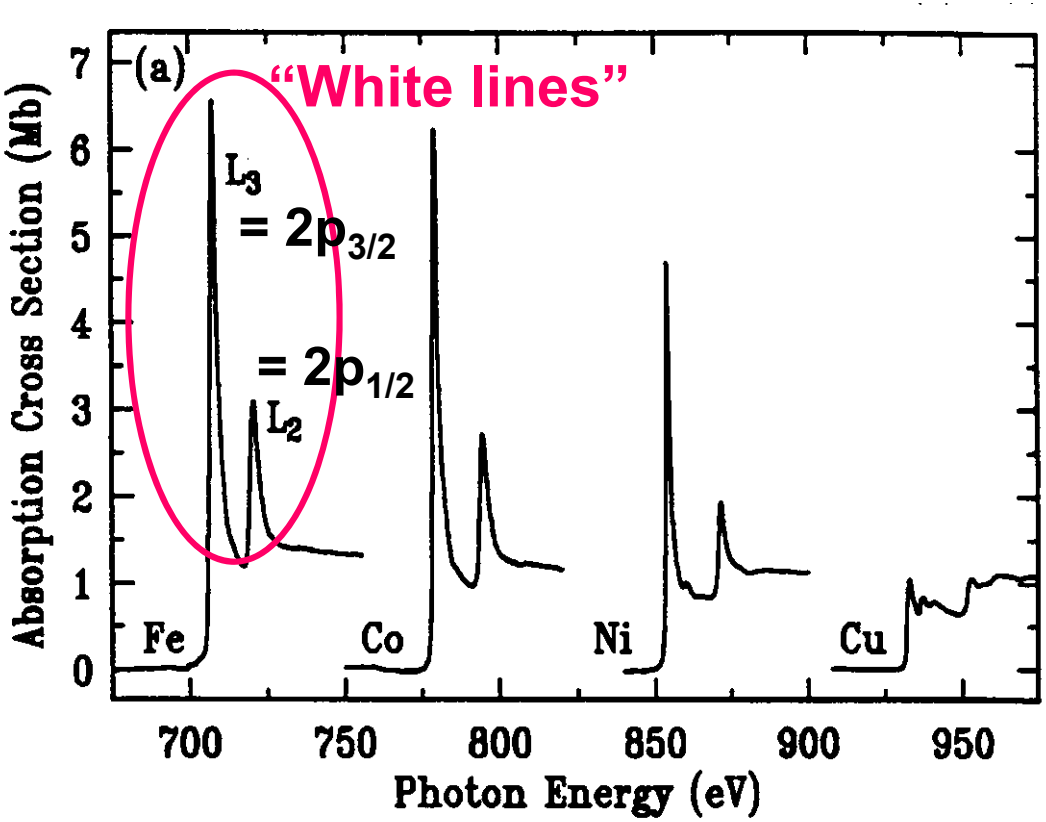

- ***Near-edge x-ray absorption:***

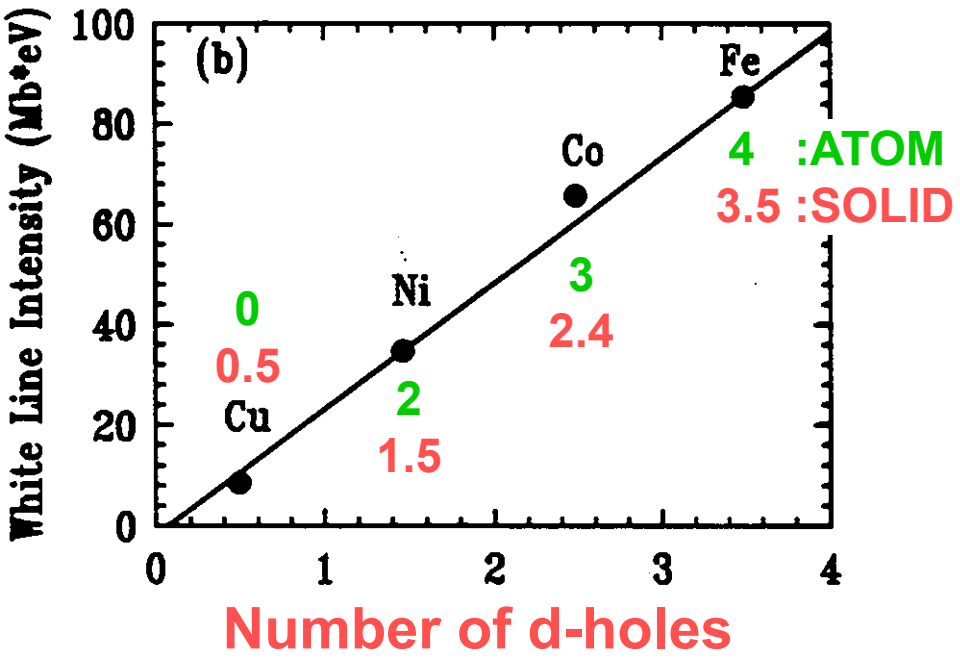
$$I \propto \left| \hat{e} \bullet \left\langle \varphi_f(1) \middle| \vec{r} \middle| \varphi_i(1) \right\rangle \right|^2$$



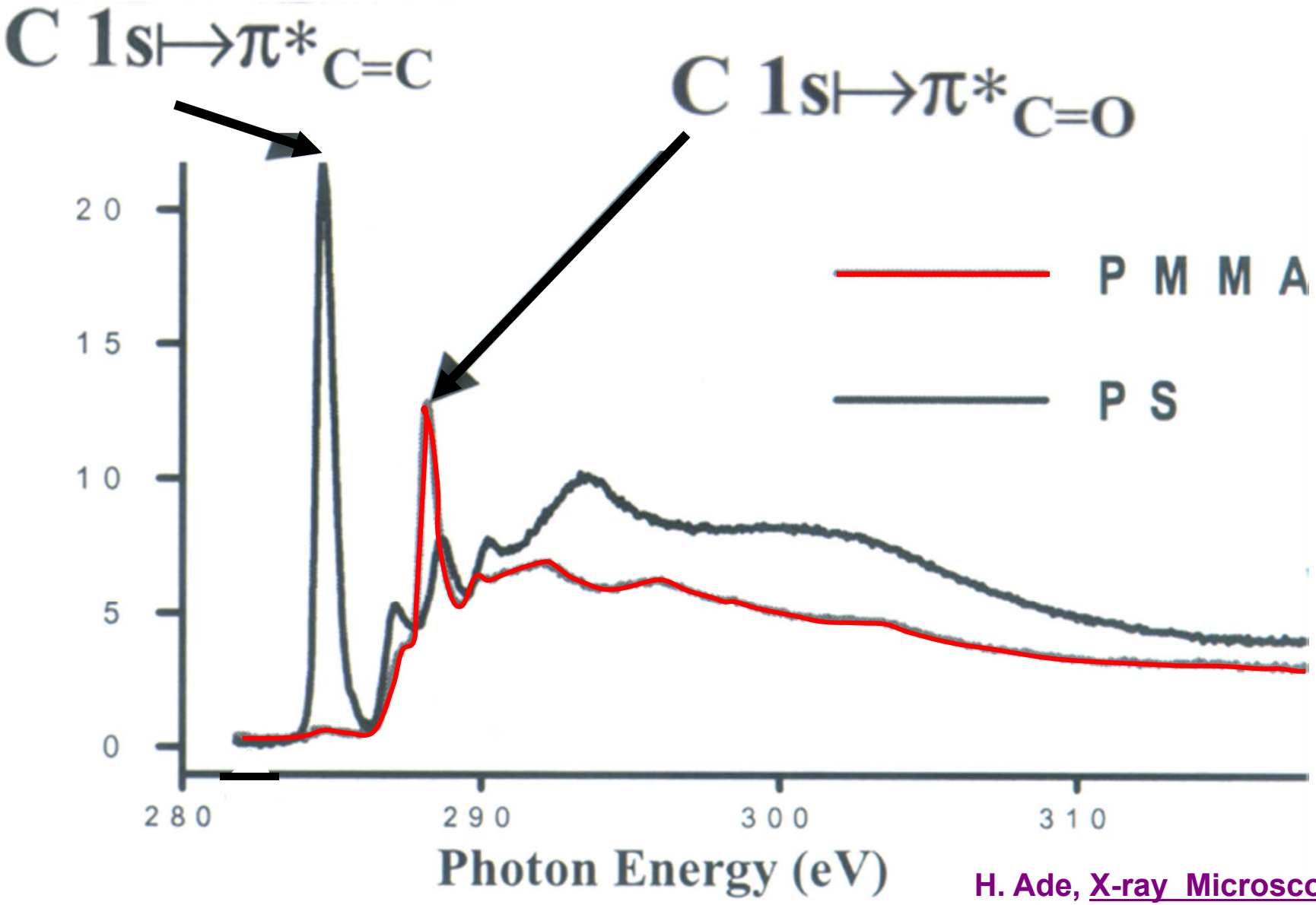
# Variation of Near-Edge X-Ray Absorption Fine Structure (NEXAFS) with Atomic No. for Some 3d Transition Metals

J. Stohr, "NEXAFS Spectroscopy" (Spring, 1992), Stohr and Siegmann, "Magnetism: From Fundamentals to Nanoscale Dynamics" (Springer Series in Solid-State Sciences, 2006), Chapter 9
Download from 243A website:
http://physics.ucdavis.edu/Classes/Physics243A/XMCD.stohr.siegmann.abridged-for-emailing.pdf



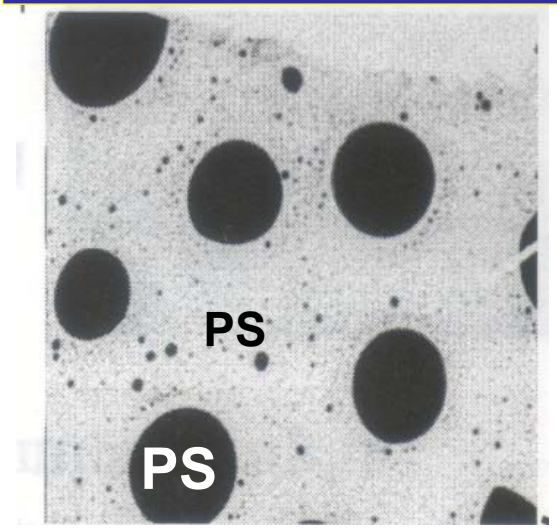



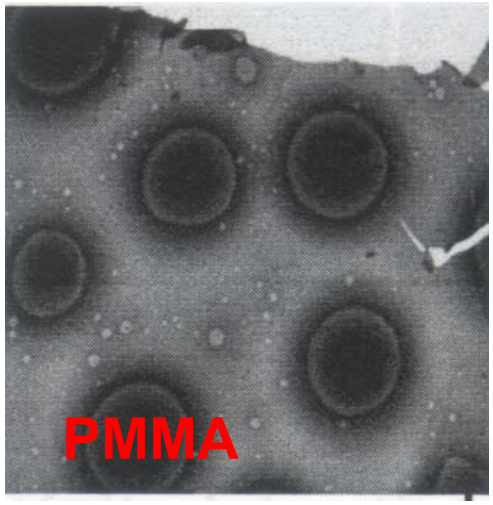
# Variation of Near-Edge X-Ray Absorption Fine Structure (NEXAFS) for Different Polymers

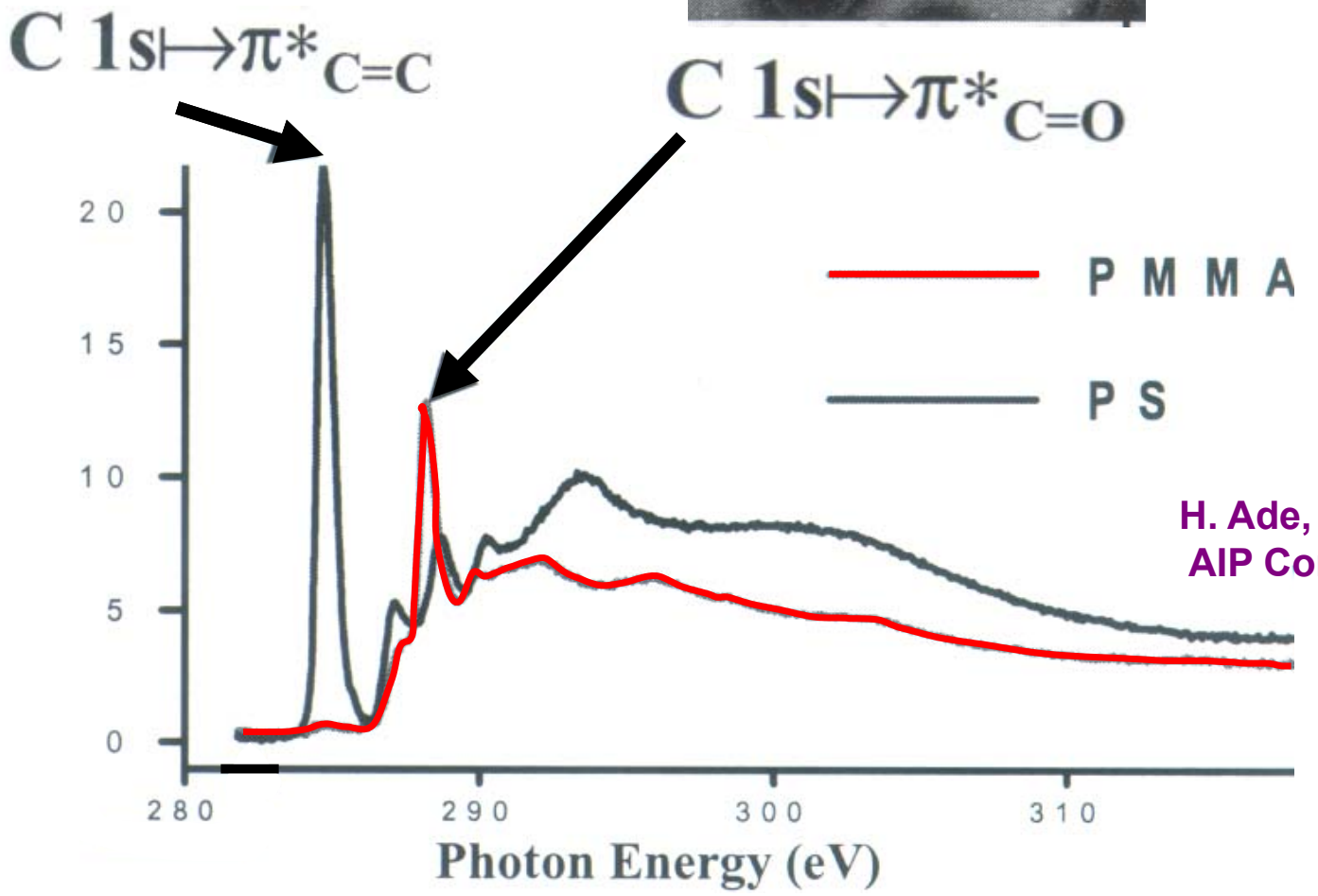



H. Ade, X-ray Microscopy 99, AIP Conf. Proc. 507, p.197

# SCANNING TRANSMISSION X-RAY MICROSCOPY OF POLYMER BLEND

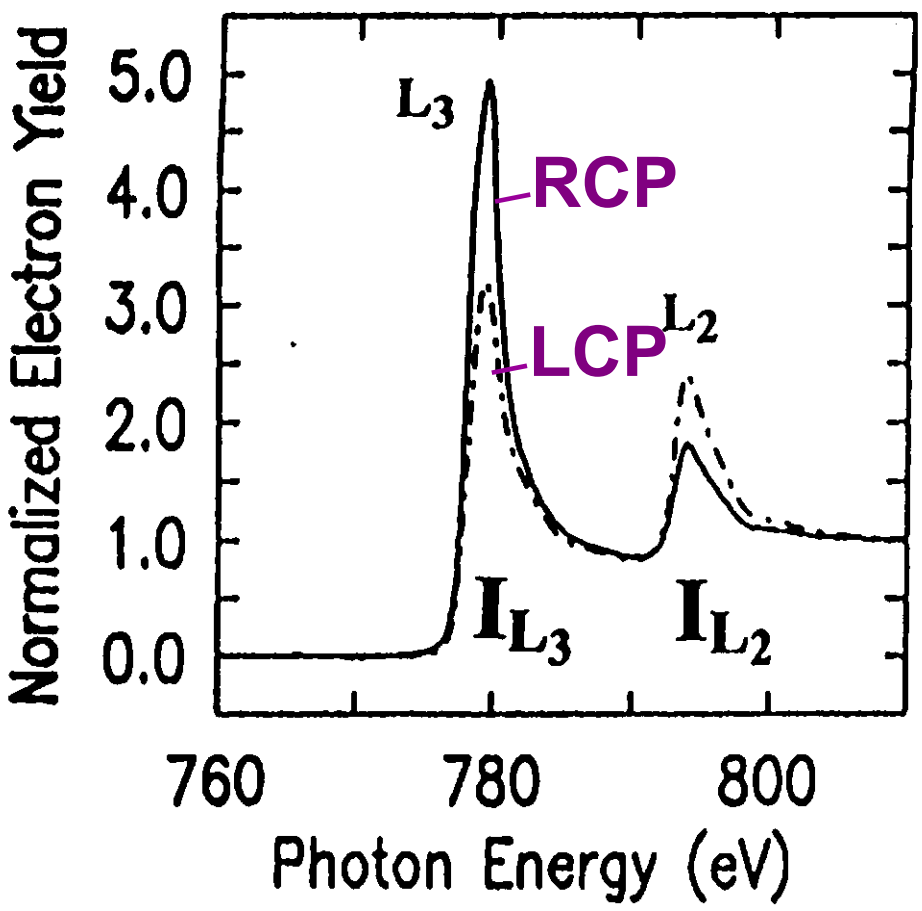


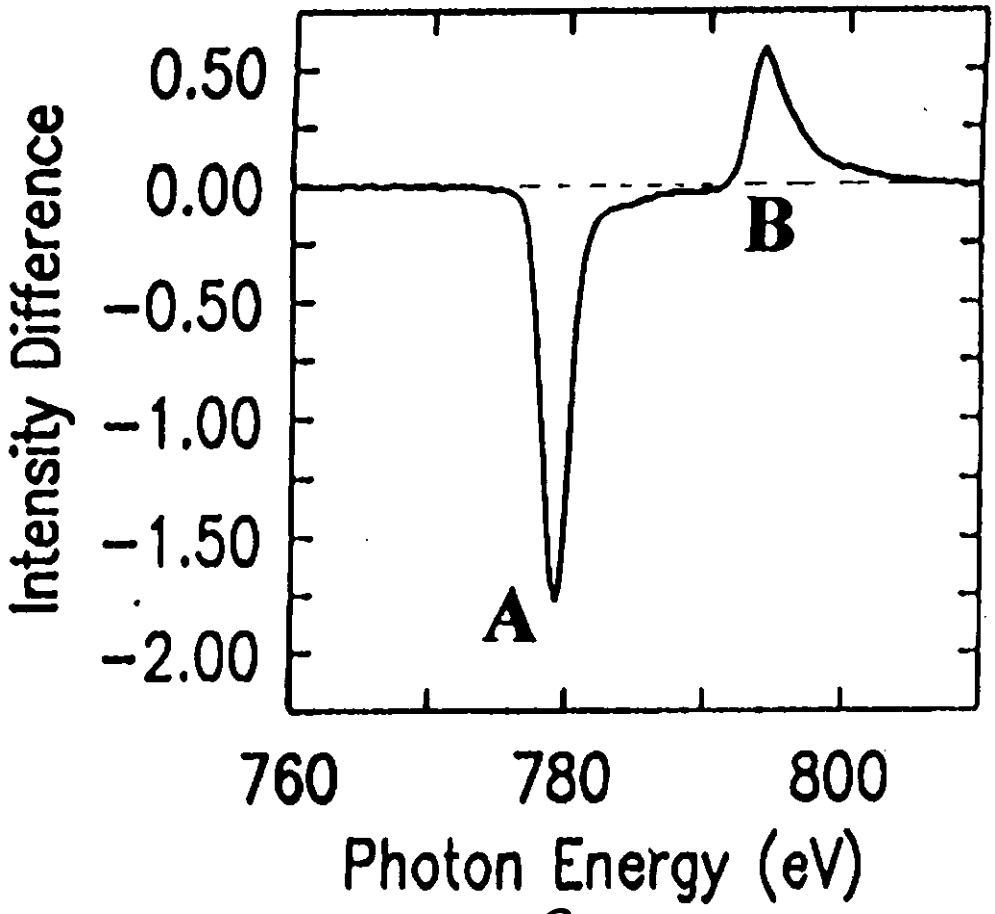




H. Ade, X-ray Microscopy 99, AIP Conf. Proc. 507, p.197

# Magnetic Circular Dichroism in X-Ray Absorption (XMCD)
## Ferromagnetic cobalt with magnetization along incident light direction




Very useful sum rules: Spin magnetic moment—

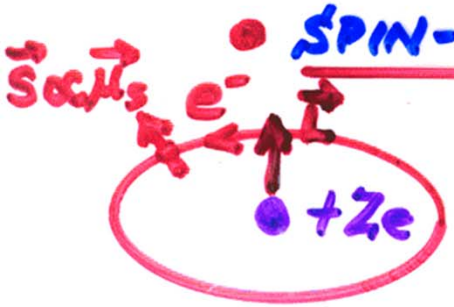
$$[A-2B]_\alpha = -\frac{C}{\mu_B}(m_{spin})$$

Orbital magnetic moment—

$$[A+B]_\alpha = -\frac{3C}{2\mu_B} m^\alpha_{orbital}$$

($\alpha \rightarrow$ component along magnetic field)

# Magnetic Circular Dichroism in X-Ray Absorption (XMCD): Only happens because of the spin-orbit effect




- SPIN-ORBIT SPLITTING OF LEVELS:

$\Rightarrow$ EFFECTIVE $\vec{B}$ (NUCLEUS AROUND $e^-$) $\propto \vec{L}$

$$\hat{H}_{S\text{-}O} = \xi(r)\,\vec{l}\cdot\vec{s}$$

- SPLITS ALL $nl$ LEVELS $2(2l+1)$
  - $nlj = l + 1/2$ — $2l+2$
  - $nlj = l - 1/2$ — $2l$

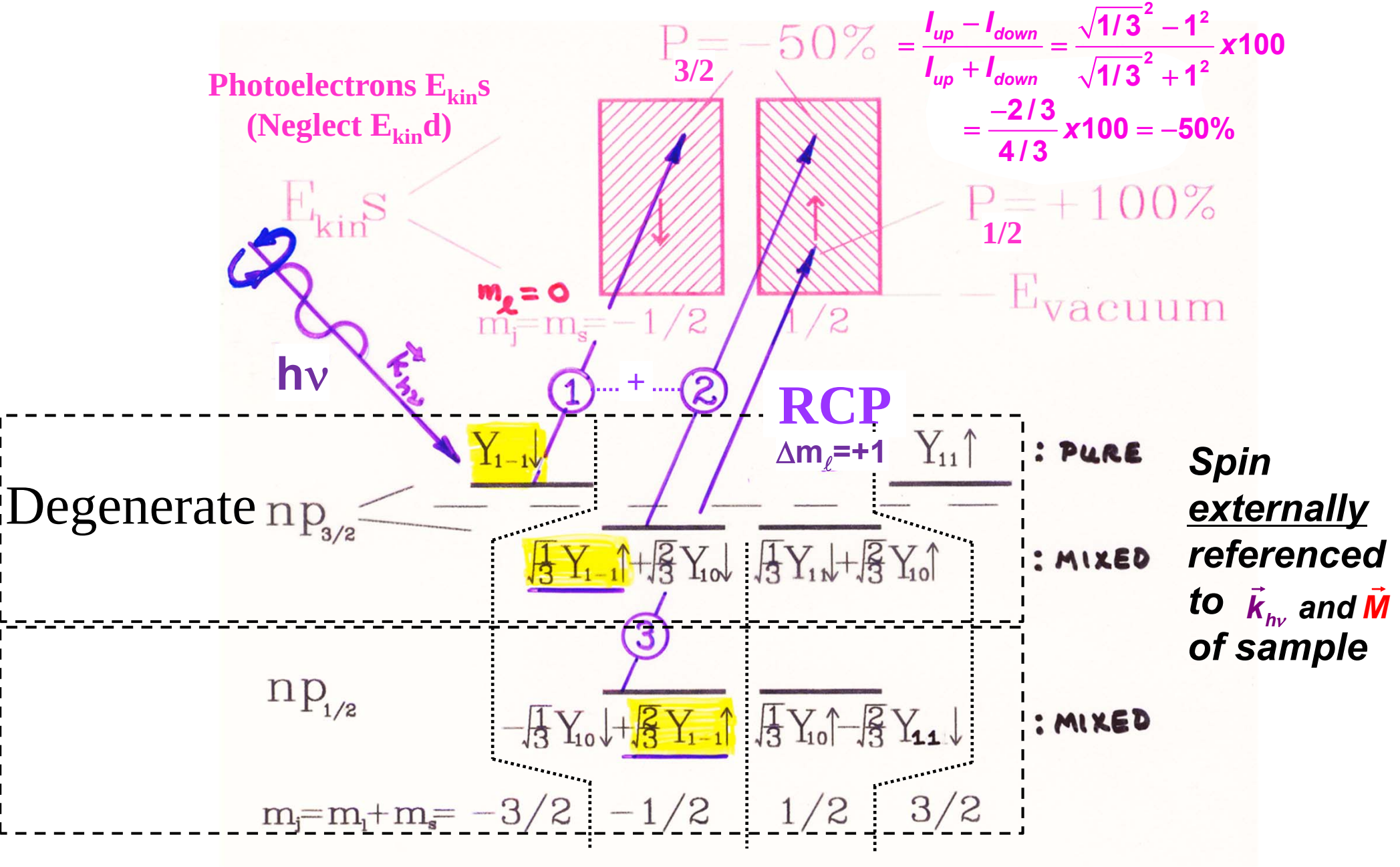
- MIXES SPIN + ORBITAL ANGULAR MOM.:

$$\psi_{nljm_j} = C_1 \psi_{nl,m_j-1/2}\begin{pmatrix}1\\0\end{pmatrix} + C_2 \psi_{nl,m_j+1/2}\begin{pmatrix}0\\1\end{pmatrix}$$

$\begin{pmatrix}1\\0\end{pmatrix}$ = $m_s = +1/2$ = $\uparrow$ ; $\begin{pmatrix}0\\1\end{pmatrix}$ = $m_s = -1/2$ = $\downarrow$

WITH C1 AND C2 TABULATED CLEBSCH-GORDAN OR WIGNER 3j SYMBOLS

# Example: Photoelectron spin polarization from spin-orbit coupling and circularly-polarized radiation—The Fano Effect

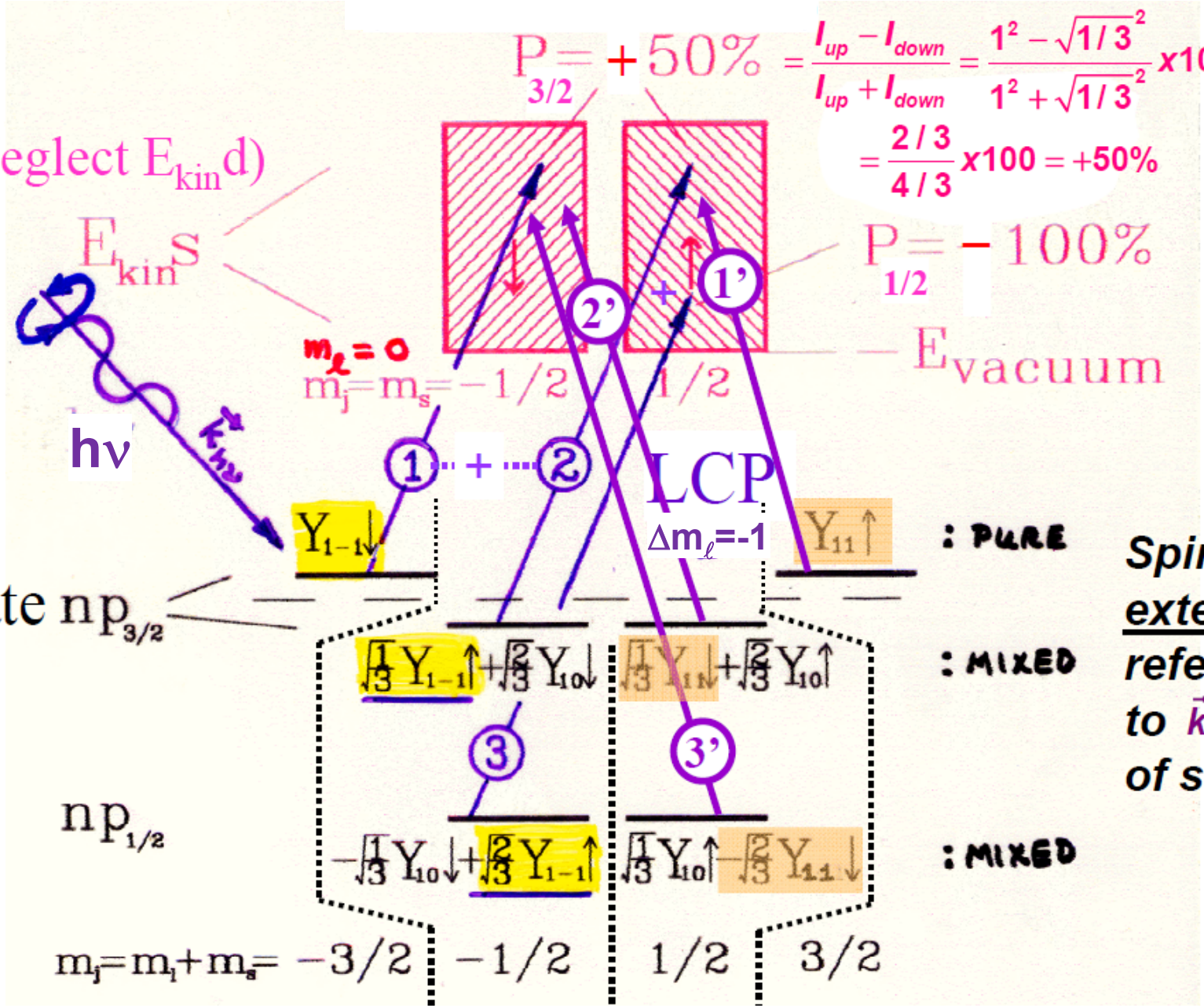



$$= \frac{I_{up} - I_{down}}{I_{up} + I_{down}} = \frac{\sqrt{1/3}^2 - 1^2}{\sqrt{1/3}^2 + 1^2} x100$$

$$= \frac{-2/3}{4/3} x100 = -50\%$$

***Spin <u>externally</u> referenced to $\vec{k}_{h\nu}$ and $\vec{M}$ of sample***

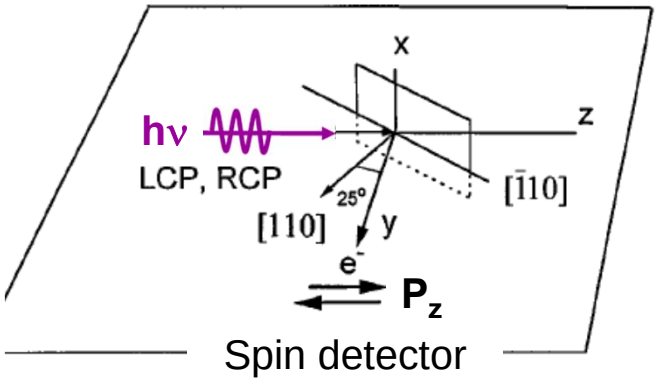
# Photoelectron spin polarization from spin-orbit coupling and circularly-polarized radiation—The Fano Effect

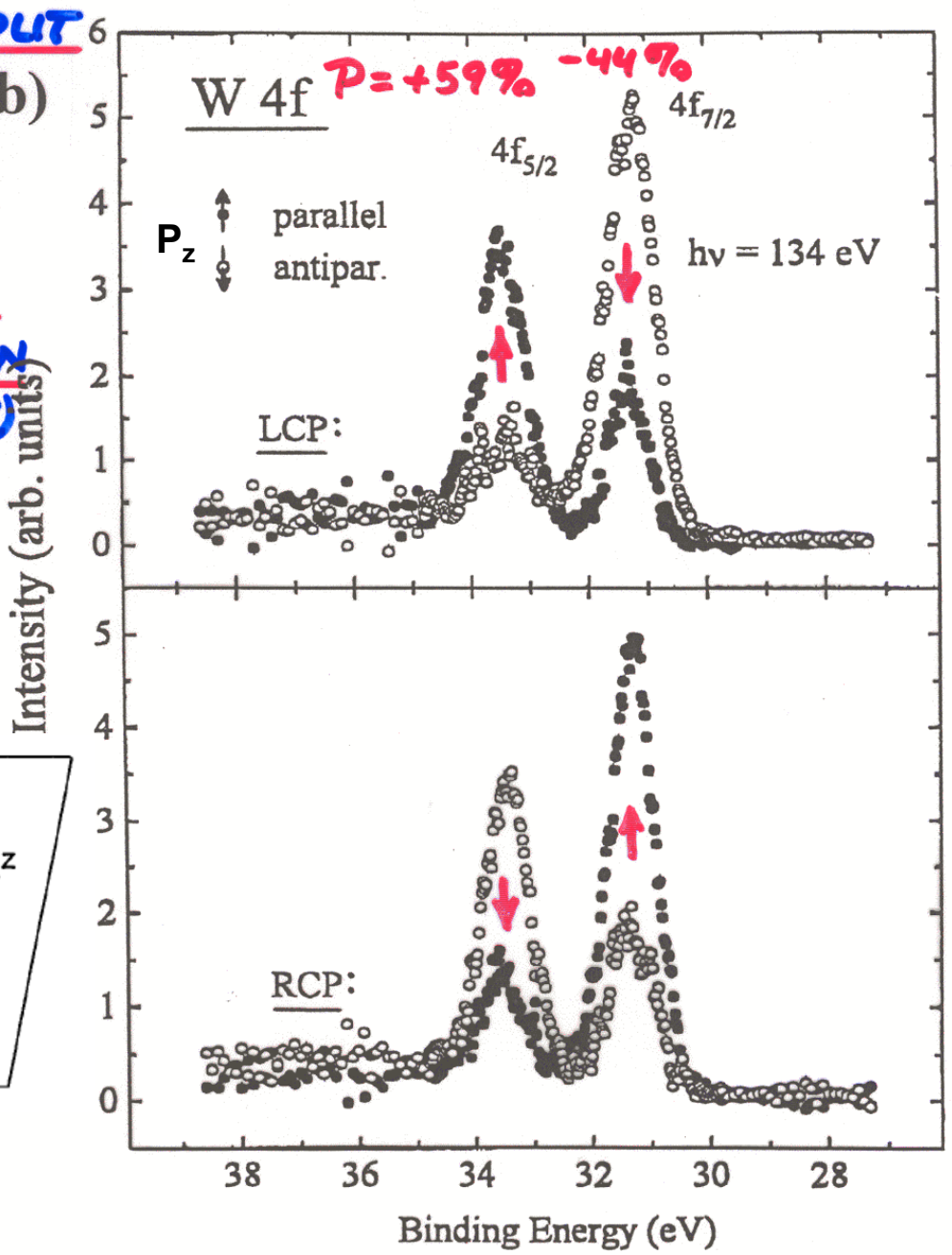



***Spin <u>externally</u> referenced to $\vec{k}_{h\nu}$ and $\vec{M}$ of sample***

# Fano effect and spin polarization (SP) in core photoelectron spectra—expt.

SPIN-ORBIT SPLIT LEVEL (b) EXCITED WITH CIRCULAR POLARIZATION (FANO EFFECT)

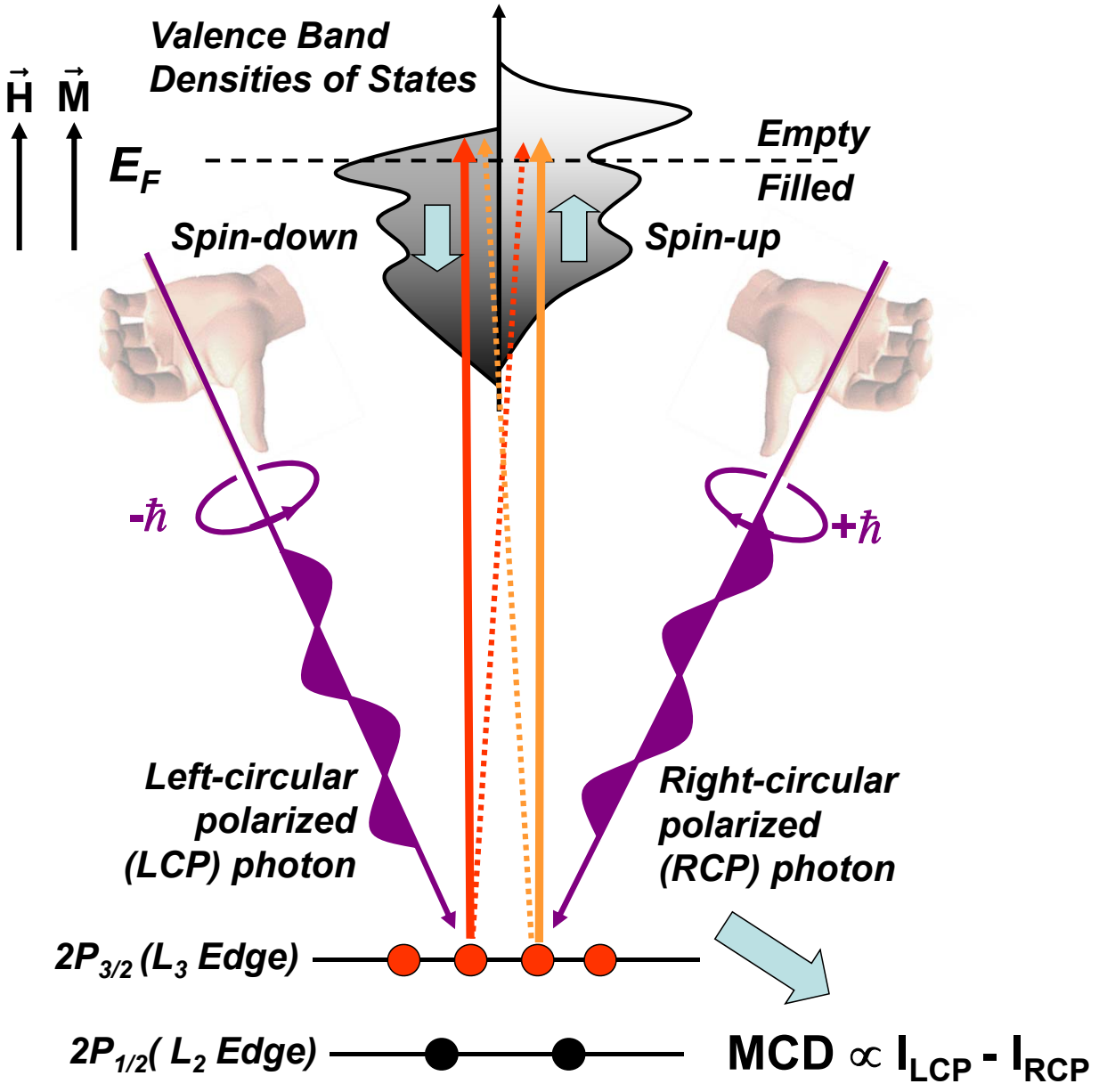


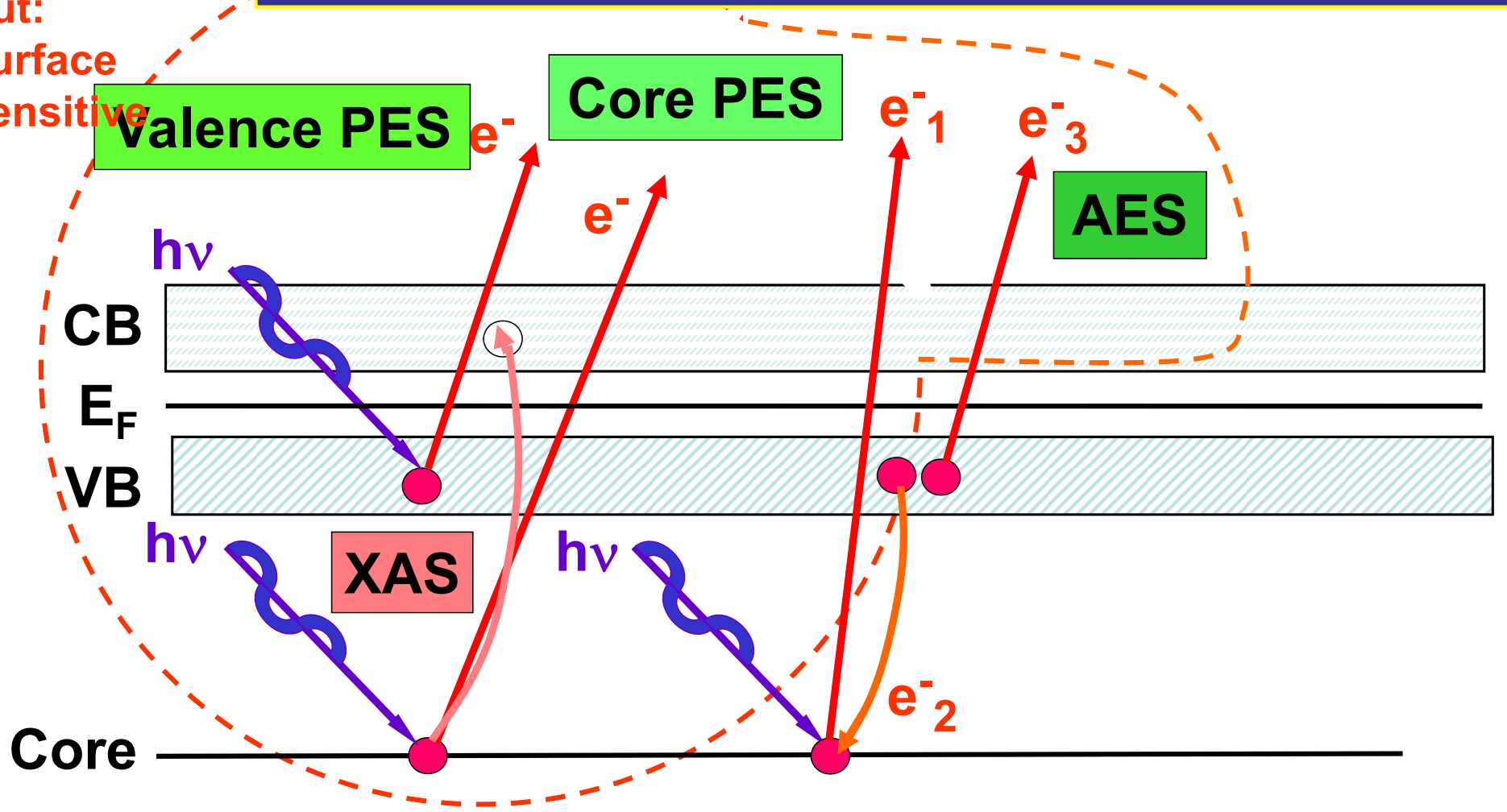

EXPT. – STARKE ET AL. PRB 53, R10544 (1996)

# Magnetic Circular Dichroism in X-Ray Absorption (XMCD)

J. Stohr, Journal of Magnetism and Magnetic Materials 200 (1999) 470–497



# The Soft and Hard X-Ray Spectroscopies




PES = photoemission = photoelectron spectroscopy

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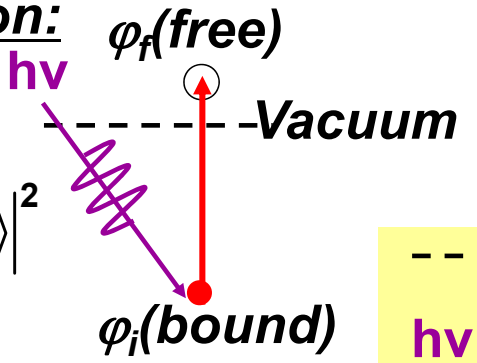
XES = x-ray emission spectroscopy

REXS/RIXS = resonant elastic/inelastic x-ray scattering

# MATRIX ELEMENTS IN The Soft and Hard X-Ray Spectroscopies: DIPOLE LIMIT

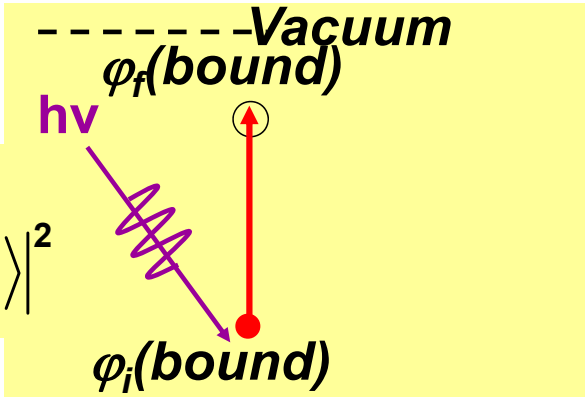
- ***Photoelectron spectroscopy/photoemission:***

$$I \propto \left|\hat{e} \bullet \left\langle \varphi_f(1) \middle| \vec{r} \middle| \varphi_i(1) \right\rangle\right|^2$$




- ***Near-edge x-ray absorption:***

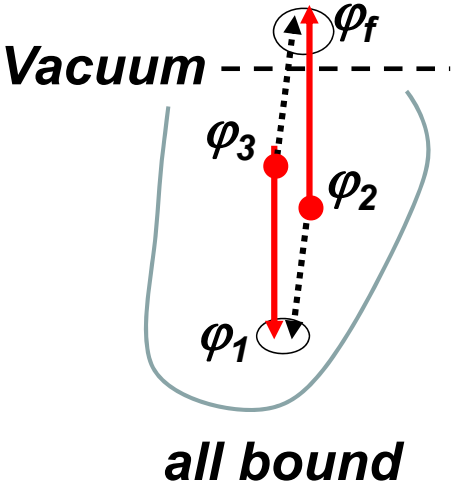
$$I \propto \left|\hat{e} \bullet \left\langle \varphi_f(1) \middle| \vec{r} \middle| \varphi_i(1) \right\rangle\right|^2$$




- ***Auger electron emission:***

$$I \propto \left| \left\langle \varphi_f(1)\varphi_1(2) \middle| \frac{e^2}{r_{12}} \middle| \varphi_3(1)\varphi_2(2) \right\rangle - \left\langle \varphi_1(1)\varphi_f(2) \middle| \frac{e^2}{r_{12}} \middle| \varphi_3(1)\varphi_2(2) \right\rangle \right|^2$$

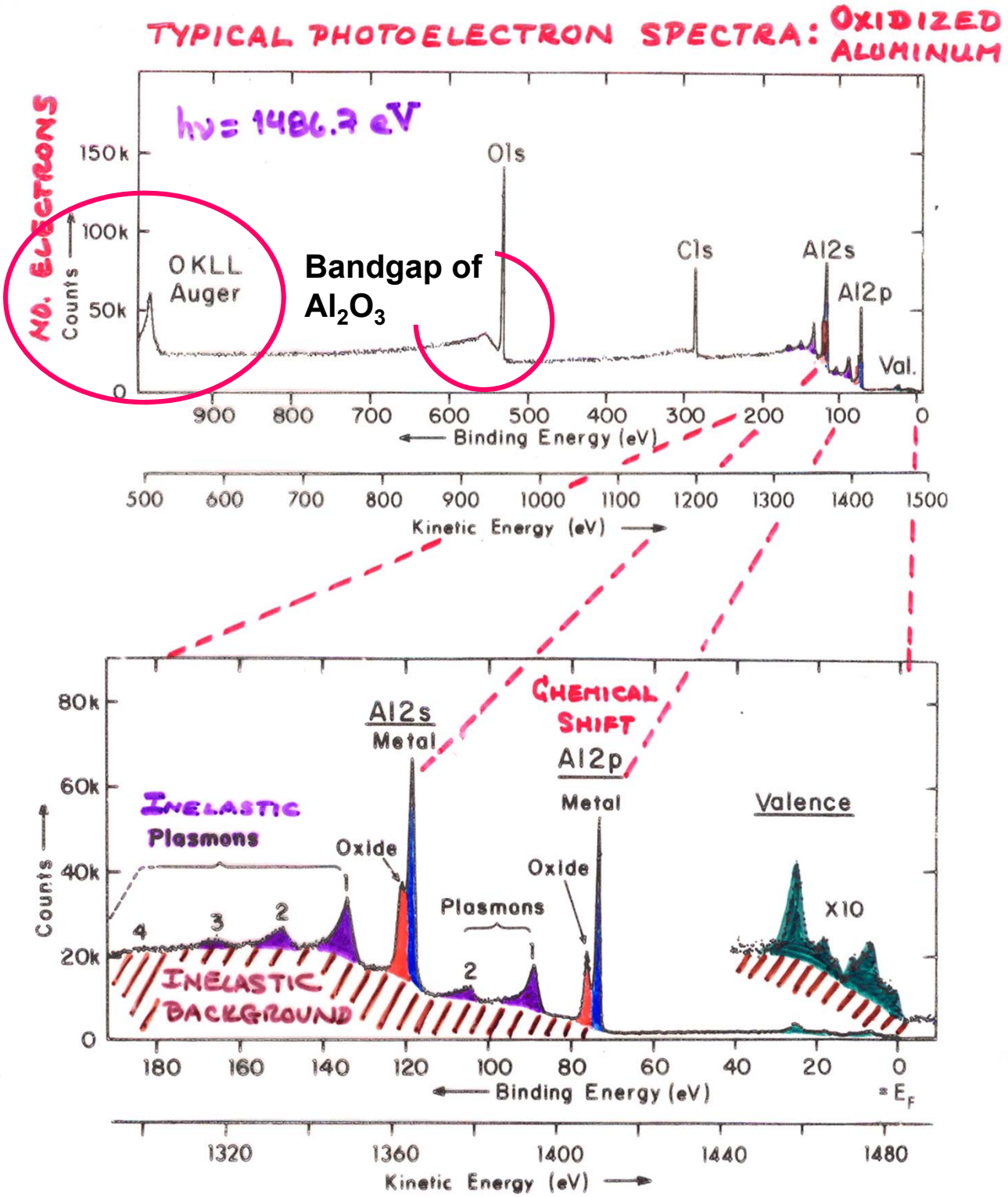
Direct — Exchange

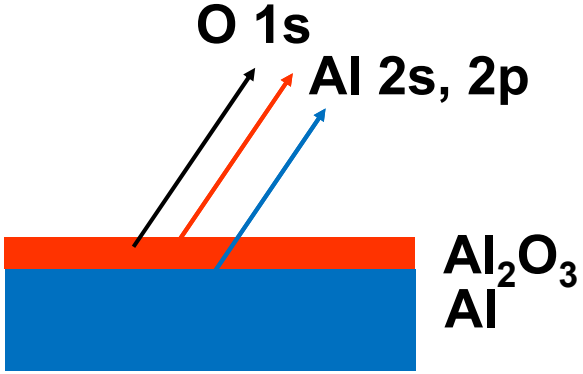



*with* $r_{12} = \left|\vec{r}_1 - \vec{r}_2\right|$, and

$$\frac{e^2}{\left|\vec{r}_1 - \vec{r}_2\right|} = 4\pi e^2 \sum_{\ell=0}^{\infty} \sum_{m_\ell=-\ell}^{\ell} \frac{1}{2\ell+1} \frac{r_<^\ell}{r_>^{\ell+1}} Y_\ell^{m_\ell}(\theta_1,\phi_1)[Y_\ell^{m_\ell}(\theta_2,\phi_2)]^*$$

**a complex operator, no simple selection rules**

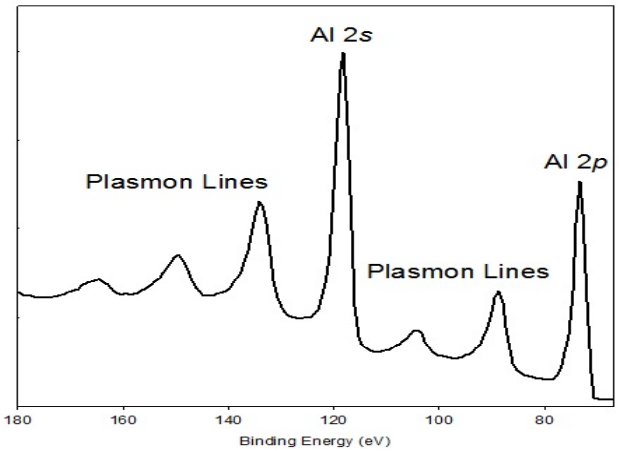



**Plasmons:**

$E_{plasmon} = \hbar\omega_p = \hbar(n_{valence}e^2/m_e\varepsilon_0)^{1/2}$

**CLEAN ALUMINUM**




"Basic Concepts of XPS"
Figure 1

# THE AUGER PROCESS

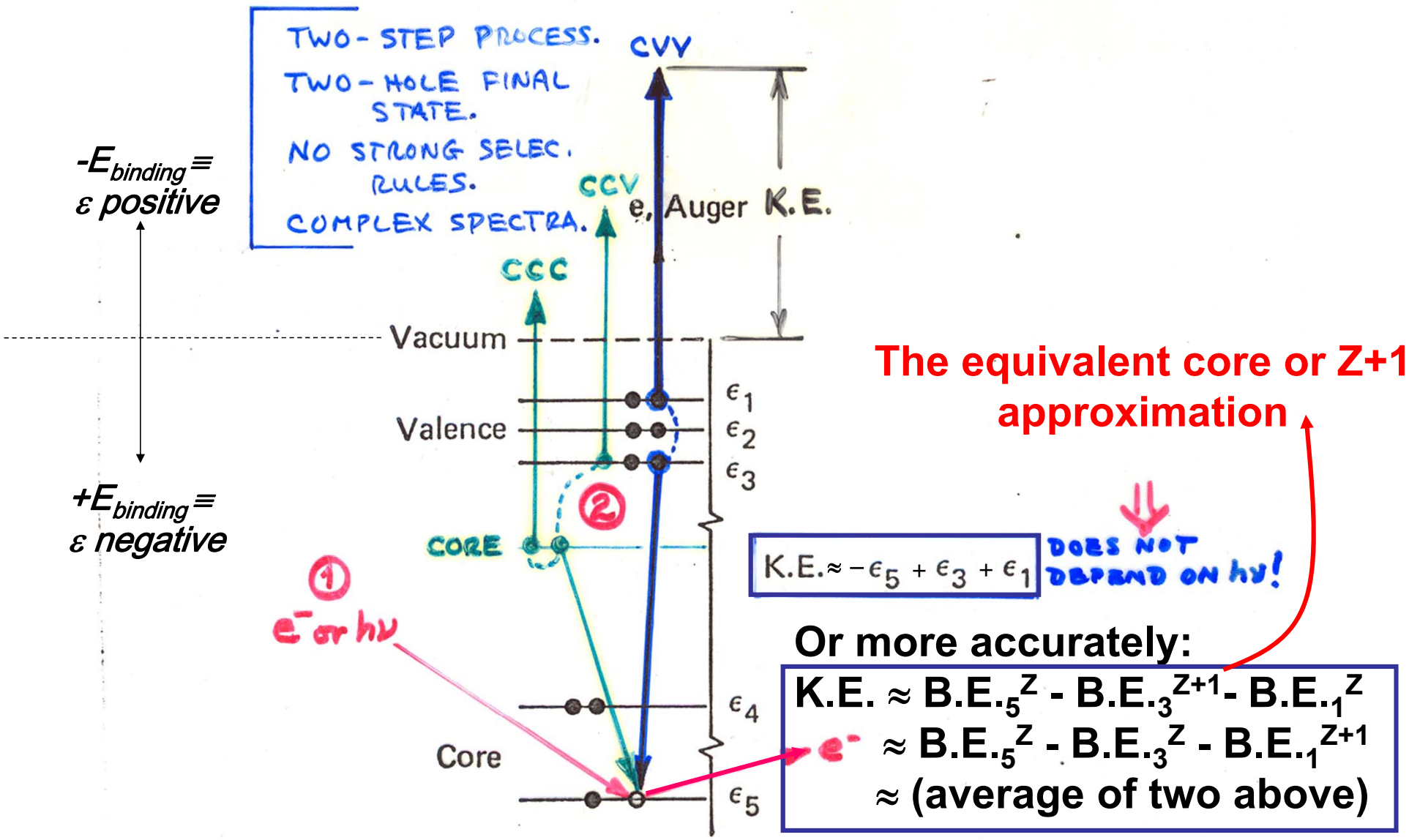
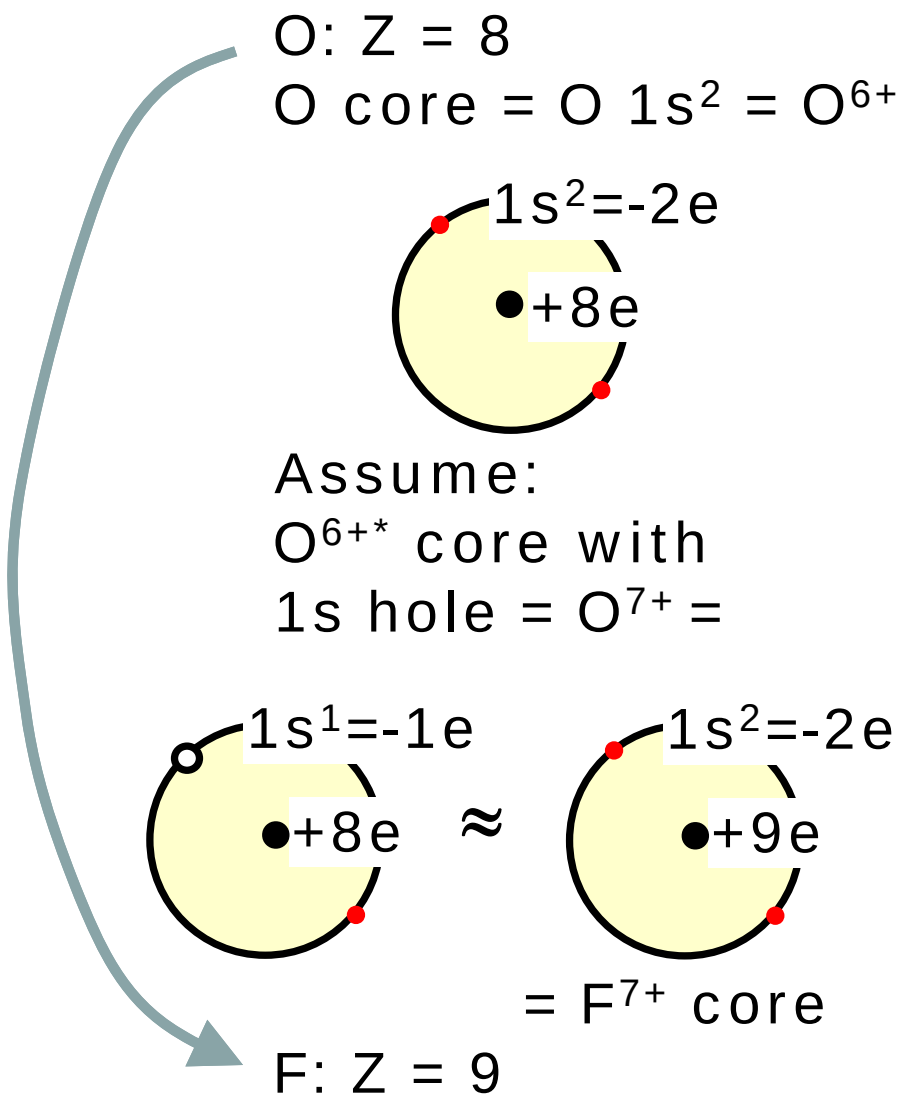
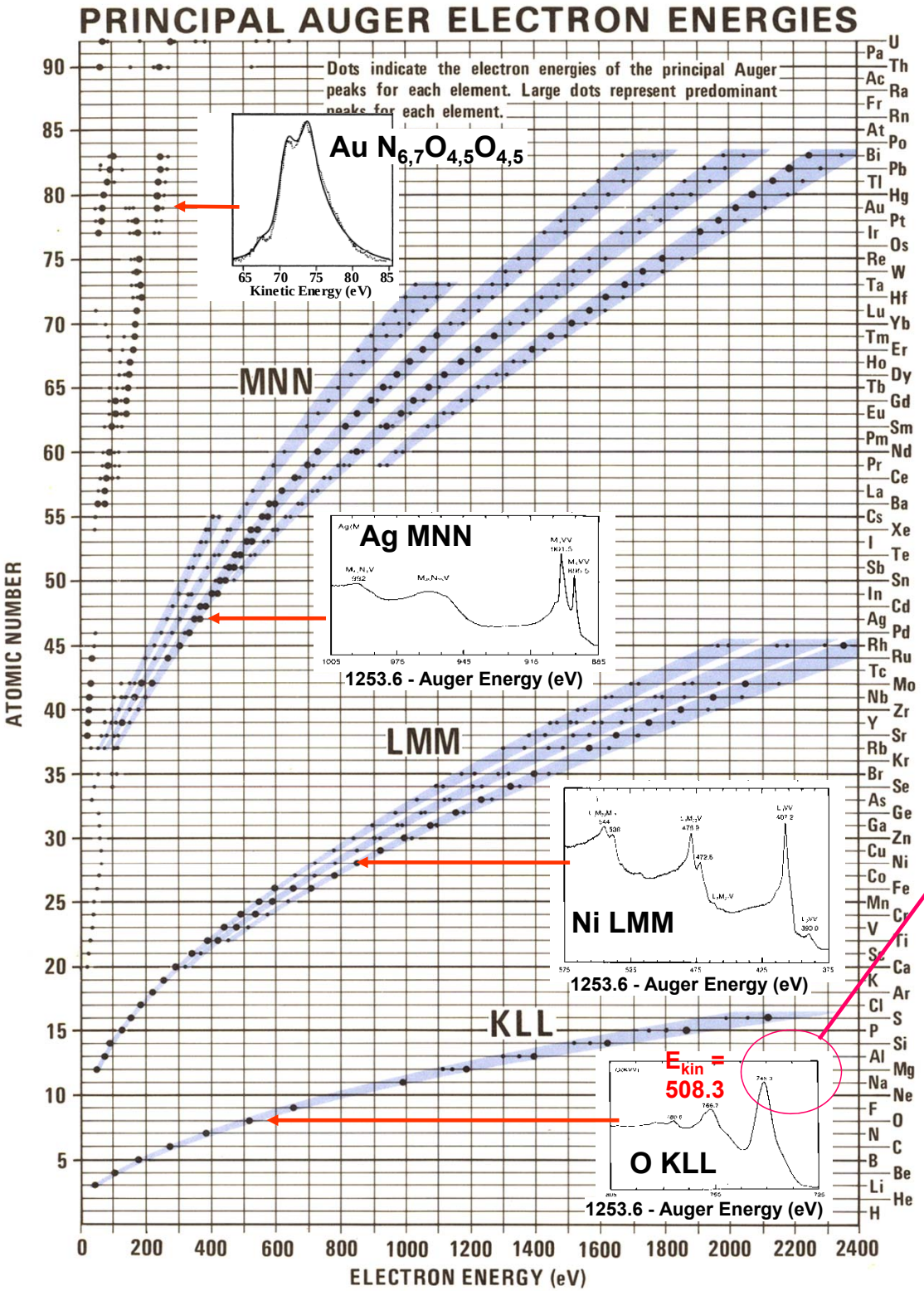



*Figure 2. Scheme of the Auger process. A valence-level involved Auger emission is illustrated here, but the two electrons involved also could have come from core level, $\epsilon_4$, provided $\epsilon_5 - 2\epsilon_4 > 0$.*

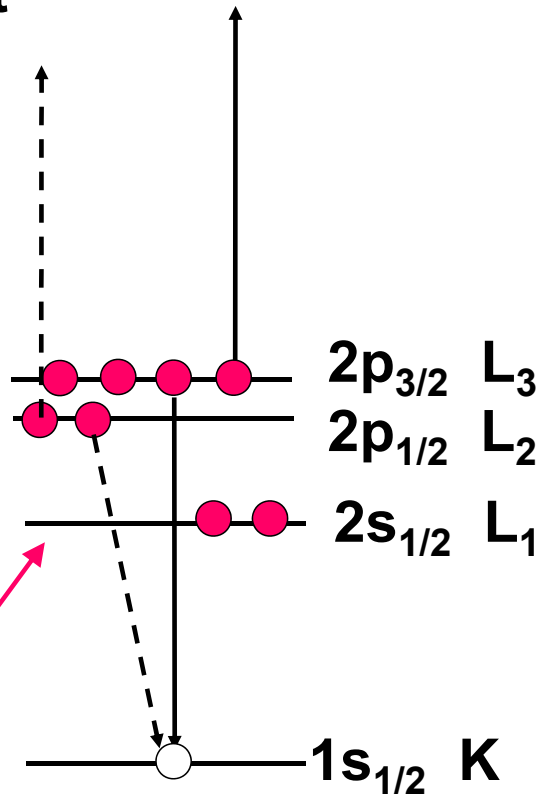
# The equivalent core or Z+1 approximation




**Plus see pp. 92-93 in**
**"Basic Concepts of XPS"**




**X-Ray Data Booklet Fig. 1.4**




$$K.E. \approx B.E._{1s}{}^{Z=8} - B.E._{2p}{}^{9} - B.E._{2p}{}^{8}$$
$$\approx B.E._{1s}{}^{8} + B.E._{2p}{}^{8} - B.E._{2p}{}^{9}$$
$$\approx 543.1 - 17 - 13 \approx 513 \text{ eV}$$

# X-Ray Data Booklet--Section 1.1 ELECTRON BINDING ENERGIES

**The energies are given in eV relative to the vacuum level for the rare gases and for $H_2$, $N_2$, $O_2$, $F_2$, and $Cl_2$; relative to the Fermi level for the metals; and relative to the top of the valence bands for semiconductors (and insulators).**

| Electronic configuration | Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ | $M_1$ 3s | $M_2$ $3p_{1/2}$ | $M_3$ $3p_{3/2}$ |
|---|---|---|---|---|---|---|---|---|
| $1s$ | 1 H | 13.6 | | | | | | |
| $1s^2$ | 2 He | 24.6* | | | | | | |
| $1s^2\,2s$ | 3 Li | 54.7* | | | | | | |
| $1s^2\,2s^2$ | 4 Be | 111.5* | | | | | | |
| $1s^2\,2s^2\,2p$ | 5 B | 188* | | | | | | |
| $1s^2\,2s^2\,2p^2$ | 6 C | 284.2* | | | | | | |
| $1s^2\,2s^2\,2p^3$ | 7 N | 409.9* | 37.3* | ~ 9 | ~ 9 | | | |
| $1s^2\,2s^2\,2p^4$ | 8 O | 543.1* | 41.6* | ~ 13 | ~ 13 | | | |
| $1s^2\,2s^2\,2p^5$ | 9 F | 696.7* | ~ 45 | ~ 17 | ~ 17 | | | |
| $1s^2\,2s^2\,2p^6$ | 10 Ne | 870.2* | 48.5* | 21.7* | 21.6* | | | |
| [Ne] $3s$ | 11 Na | 1070.8† | 63.5† | 30.65 | 30.81 | | | |
| [Ne] $3s^2$ | 12 Mg | 1303.0† | 88.7 | 49.78 | 49.50 | | | |
| [Ne] $3s^2\,3p$ | 13 Al | 1559.6 | 117.8 | 72.95 | 72.55 | | | |
| [Ne] $3s^2\,3p^2$ | 14 Si | 1839 | 149.7*b | 99.82 | 99.42 | | | |
| [Ne] $3s^2\,3p^3$ | 15 P | 2145.5 | 189* | 136* | 135* | | | |
| [Ne] $3s^2\,3p^4$ | 16 S | 2472 | 230.9 | 163.6* | 162.5* | | | |
| [Ne] $3s^2\,3p^5$ | 17 Cl | 2822.4 | 270* | 202* | 200* | | | |
| [Ne] $3s^2\,3p^6$ | 18 Ar | 3205.9* | 326.3* | 250.6† | 248.4* | 29.3* | 15.9* | 15.7* |
| [Ar] $4s$ | 19 K | 3608.4* | 378.6* | 297.3* | 294.6* | 34.8* | 18.3* | 18.3* |
| [Ar] $4s^2$ | 20 Ca | 4038.5* | 438.4† | 349.7† | 346.2† | 44.3 † | 25.4† | 25.4† |
| | 21 Sc | 4492 | 498.0* | 403.6* | 398.7* | 51.1* | 28.3* | 28.3* |
| | 22 Ti | 4966 | 560.9† | 460.2† | 453.8† | 58.7† | 32.6† | 32.6† |

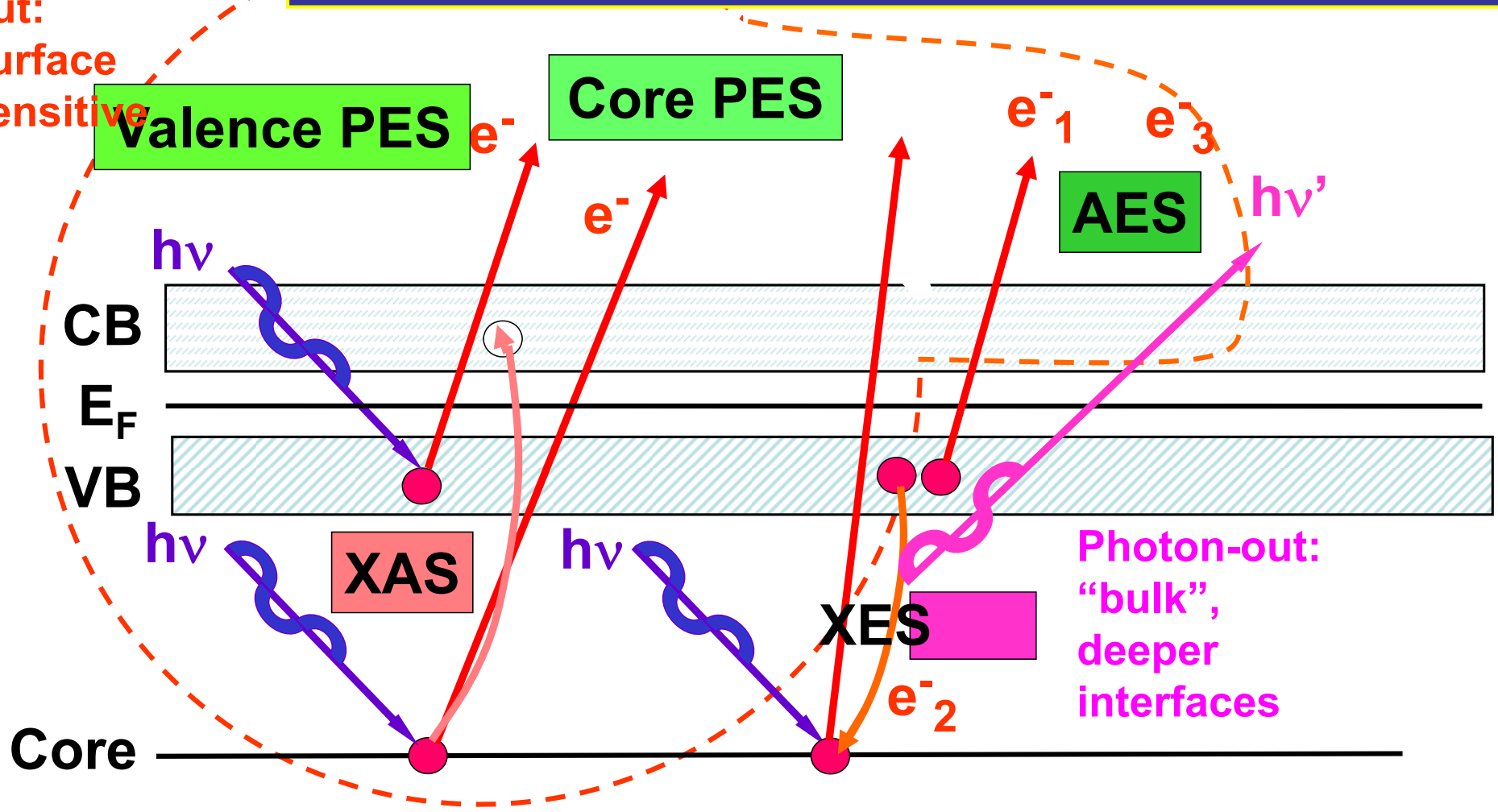
Valence levels

Interpolated, extrapolated

Missing valence B.E.s

Valence levels

# The Soft and Hard X-Ray Spectroscopies




PES = photoemission = photoelectron spectroscopy

XAS = x-ray absorption spectroscopy

AES = Auger electron spectroscopy

XES = x-ray emission spectroscopy

REXS/RIXS = resonant elastic/inelastic x-ray scattering

# THE AUGER PROCESS

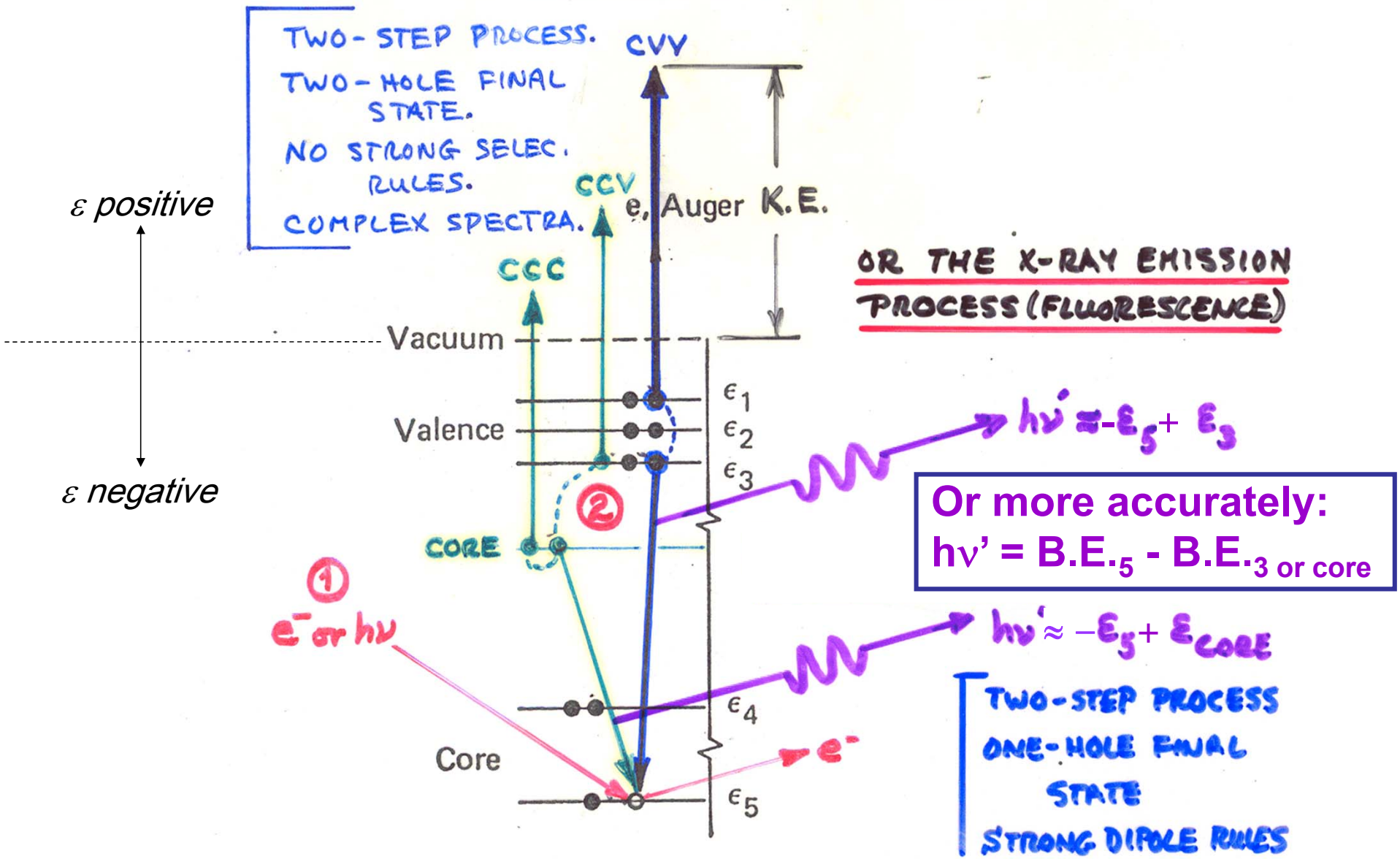



*Figure 2. Scheme of the Auger process. A valence-level involved Auger emission is illustrated here, but the two electrons involved also could have come from core level, $\epsilon_4$, provided $\epsilon_5 - 2\epsilon_4 > 0$.*

## X-Ray Nomenclature (from "X-Ray Data Booklet")

**In general:**

$nl$ — Spin-orbit — $nl_{j=l+1/2}$, $nl_{j=l-1/2}$

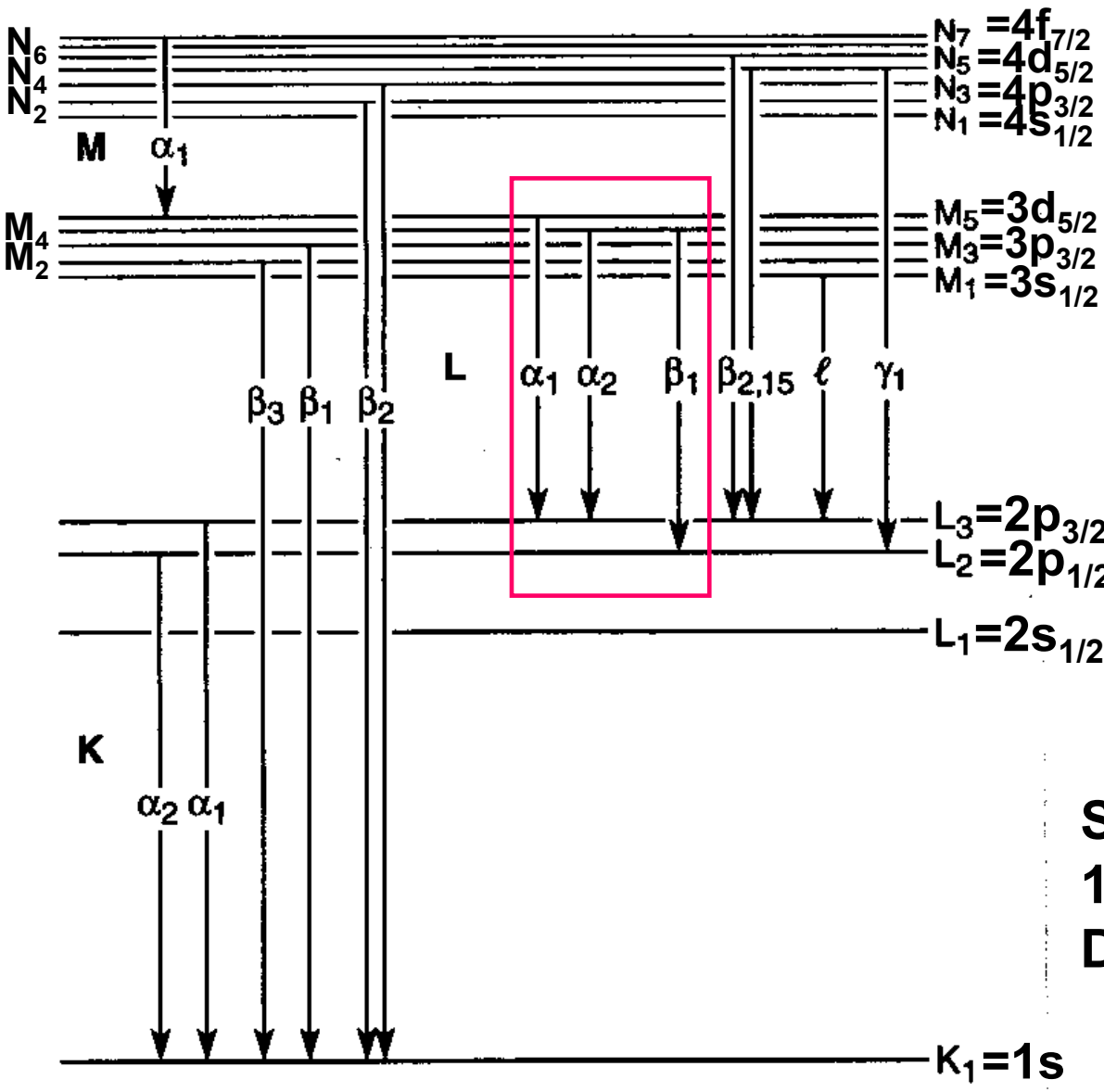



*Fig. 1-1. Transitions that give rise to the emission lines in Table 1-3.*

$\Delta j = 0, \pm 1$

**See Section 1.2 in "X-Ray Data Booklet"**

## *Electron binding energies*

| Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ | $M_1$ 3s | $M_2$ $3p_{1/2}$ | $M_3$ $3p_{3/2}$ | $M_4$ $3d_{3/2}$ | $M_5$ $3d_{5/2}$ |
|---|---|---|---|---|---|---|---|---|---|
| 23 V | 5465 | 626.7† | 519.8† | 512.1† | 66.3† | 37.2† | 37.2† | | |
| 24 Cr | 5989 | 696.0† | 583.8† | 574.1† | 74.1† | 42.2† | 42.2† | | |
| 25 Mn | 6539 | 769.1† | 649.9† | 638.7† | 82.3† | 47.2† | 47.2† | | |
| 26 Fe | 7112 | 844.6† | 719.9† | 706.8† | 91.3† | 52.7† | 52.7† | | |
| 27 Co | 7709 | 925.1† | 793.2† | 778.1† | 101.0† | 58.9† | 59.9† | | |
| 28 Ni | 8333 | 1008.6† | 870.0† | 852.7† | 110.8† | 68.0† | 66.2† | | |
| 29 Cu | 8979 | 1096.7† | 952.3† | 932.7 | 122.5† | 77.3† | 75.1† | | |
| 30 Zn | 9659 | 1196.2* | 1044.9* | 1021.8* | 139.8* | 91.4* | 88.6* | 10.2* | 10.1* |

Diff. = 11.2

***Table 1-2.** Energies of x-ray emission lines (continued).*

| Element | $K\alpha_1$ | $K\alpha_2$ | $K\beta_1$ | $L\alpha_1$ | $L\alpha_2$ | $L\beta_1$ | $L\beta_2$ | $L\gamma_1$ | $M\alpha_1$ |
|---|---|---|---|---|---|---|---|---|---|
| 22 Ti | 4,510.84 | 4,504.86 | 4,931.81 | 452.2 | 452.2 | 458.4 | | | |
| 23 V | 4,952.20 | 4,944.64 | 5,427.29 | 511.3 | 511.3 | 519.2 | | | |
| 24 Cr | 5,414.72 | 5,405.509 | 5,946.71 | 572.8 | 572.8 | 582.8 | | | |
| 25 Mn | 5,898.75 | 5,887.65 | 6,490.45 | 637.4 | 637.4 | 648.8 | | | |
| 26 Fe | 6,403.84 | 6,390.84 | 7,057.98 | 705.0 | 705.0 | 718.5 | | | |
| 27 Co | 6,930.32 | 6,915.30 | 7,649.43 | 776.2 | 776.2 | 791.4 | | | |
| 28 Ni | 7,478.15 | 7,460.89 | 8,264.66 | 851.5 | 851.5 | 868.8 | | | |
| 29 Cu | 8,047.78 | 8,027.83 | 8,905.29 | 929.7 | 929.7 | 949.8 | | | |
| 30 Zn | 8,638.86 | 8,615.78 | 9,572.0 | 1,011.7 | 1,011.7 | 1.034.7 | | | |

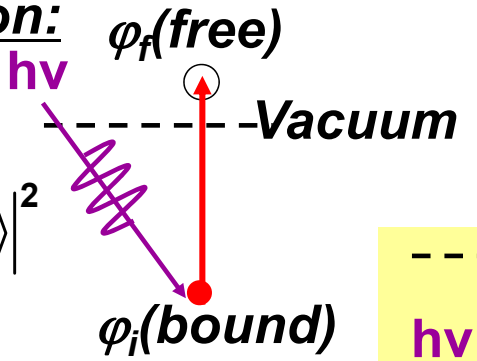
Diff. = 11.4

**See Tables 1.1 and 1.2 in X-Ray Data Booklet**

# MATRIX ELEMENTS IN The Soft and Hard X-Ray Spectroscopies: DIPOLE LIMIT

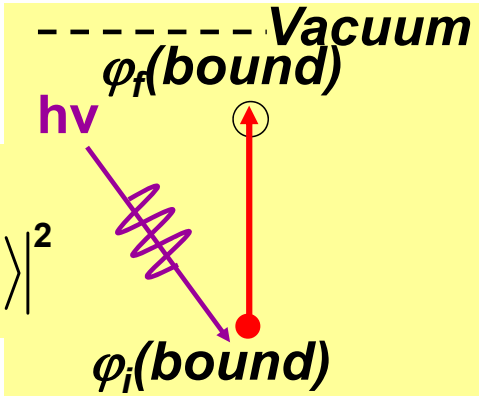
- ***Photoelectron spectroscopy/photoemission:***

$$I \propto \left|\hat{e} \bullet \left\langle \varphi_f(1) \middle| \vec{r} \middle| \varphi_i(1) \right\rangle\right|^2$$




- ***Near-edge x-ray absorption:***

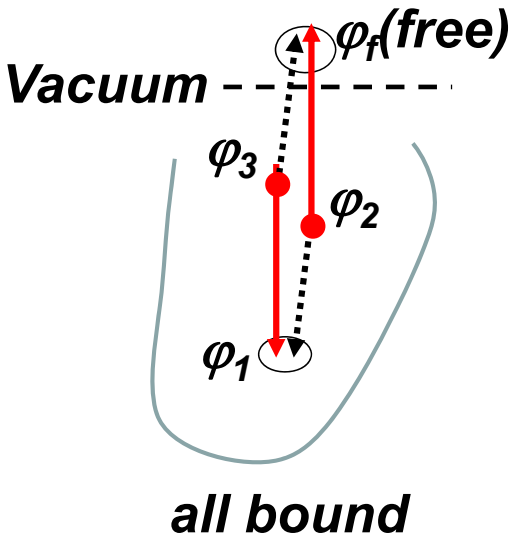
$$I \propto \left|\hat{e} \bullet \left\langle \varphi_f(1) \middle| \vec{r} \middle| \varphi_i(1) \right\rangle\right|^2$$




- ***Auger electron emission:***

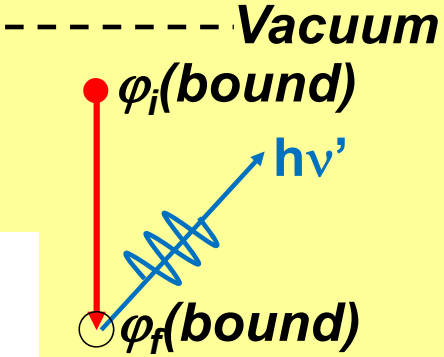
$$I \propto \left| \left\langle \varphi_f(1)\varphi_1(2) \middle| \frac{e^2}{r_{12}} \middle| \varphi_3(1)\varphi_2(2) \right\rangle - \left\langle \varphi_1(1)\varphi_f(2) \middle| \frac{e^2}{r_{12}} \middle| \varphi_3(1)\varphi_2(2) \right\rangle \right|^2$$

Direct — Exchange




- ***X-ray emission:***

$$I \propto \left|\hat{e} \bullet \left\langle \varphi_f(1) \middle| \vec{r} \middle| \varphi_i(1) \right\rangle\right|^2$$



## 1.3 FLUORESCENCE YIELDS FOR *K* AND *L* SHELLS

*Jeffrey B. Kortright*

Fluorescence yields for the $K$ and $L$ shells for the elements $5 \leq Z \leq 110$ are plotted in Fig. 1-2; the data are based on Ref. 1. These yields represent the probability of a core hole in the $K$ or $L$ shells being filled by a radiative process, in competition with nonradiative processes. Auger processes are the only nonradiative processes competing with fluorescence for the $K$ shell and

**Fluorescence yield ≡ FY**

**FY = probability of radiative decay → x-ray emission)**

**1 - FY = probability of non-radiative decay → Auger electron emission**

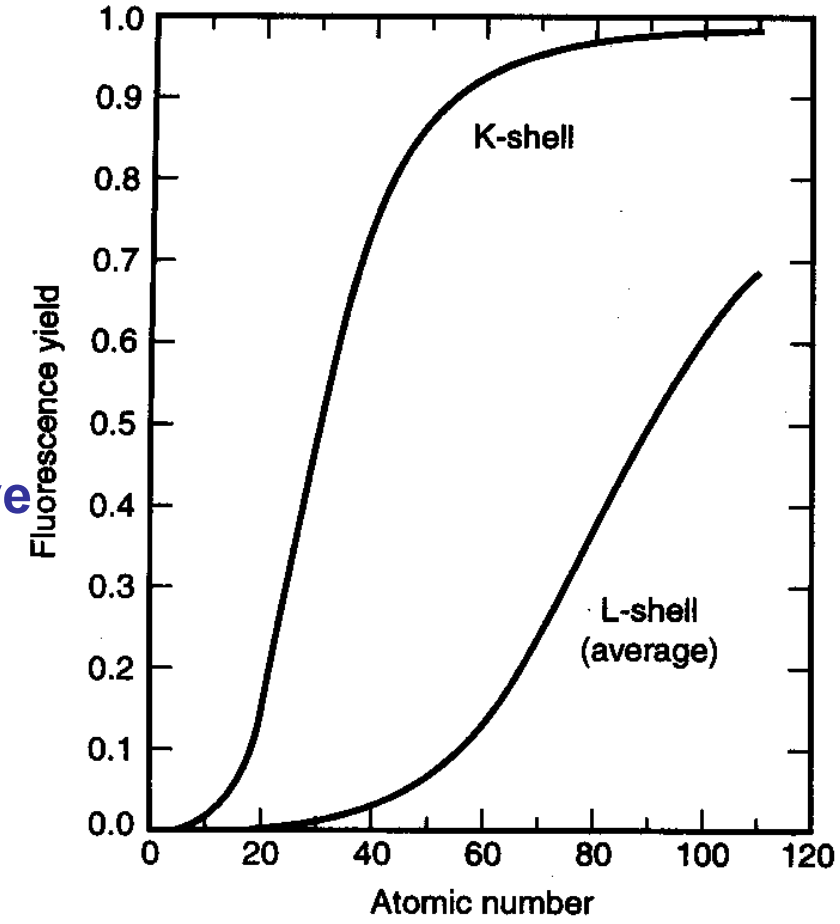
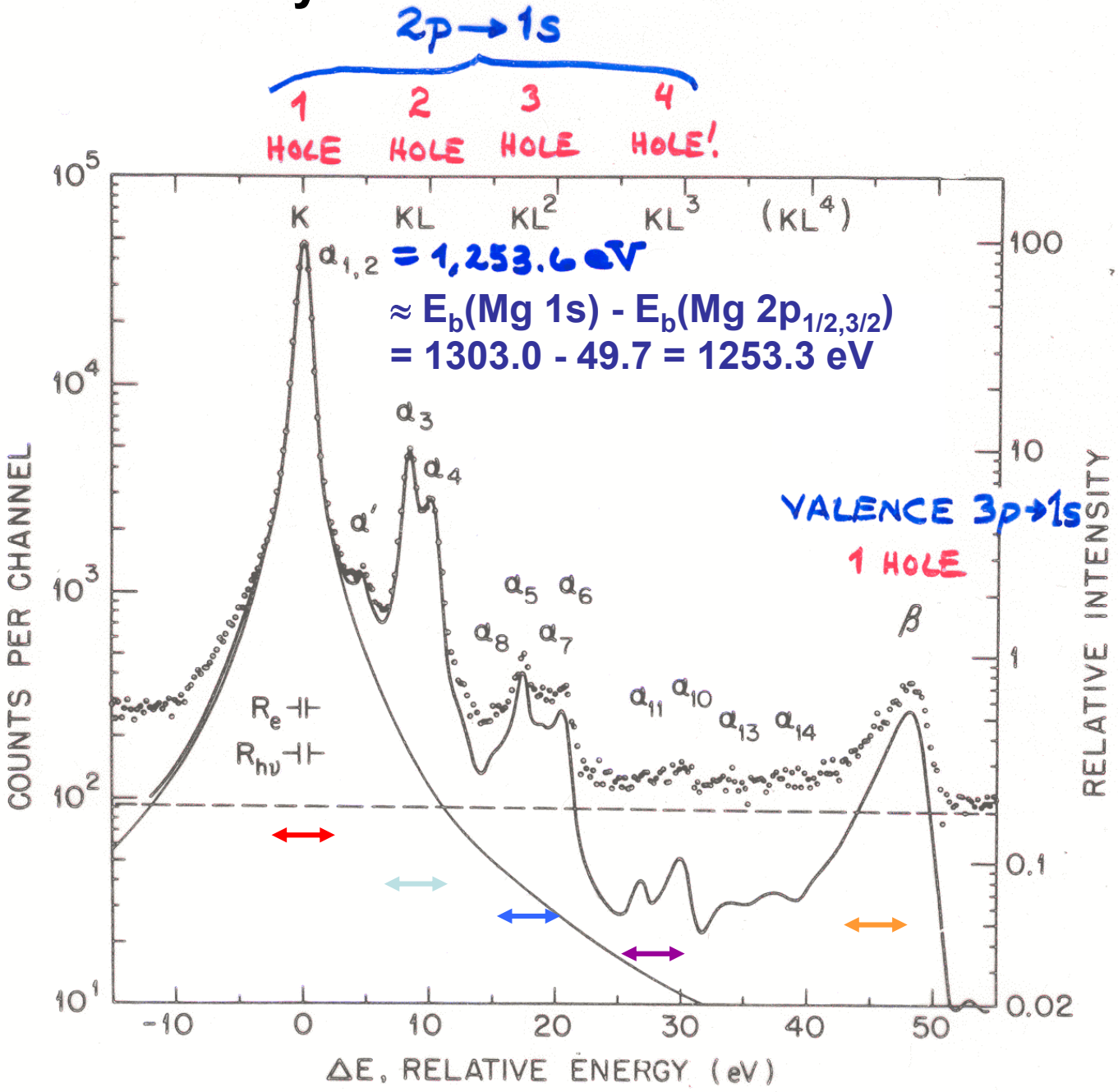
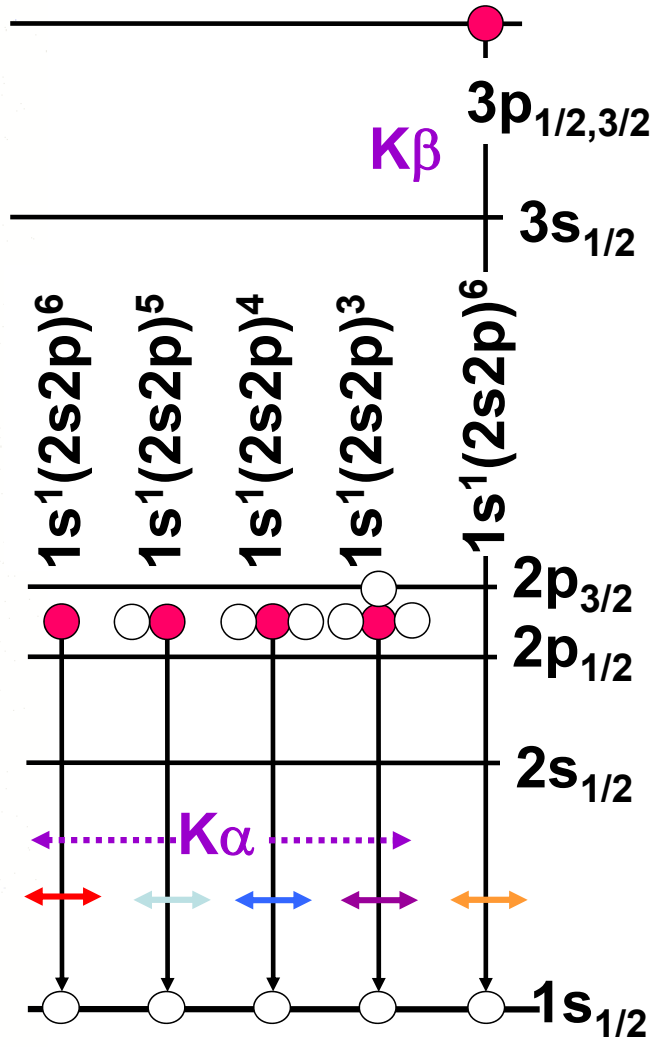



*Fig. 1-2. Fluorescence yields for K and L shells fo 110. The plotted curve for the L shell rep average of $L_1$, $L_2$, and $L_3$ effective yields*

**"X-Ray Data Booklet" Section 1.3**

# Many electron effects and satellites in x-ray emission

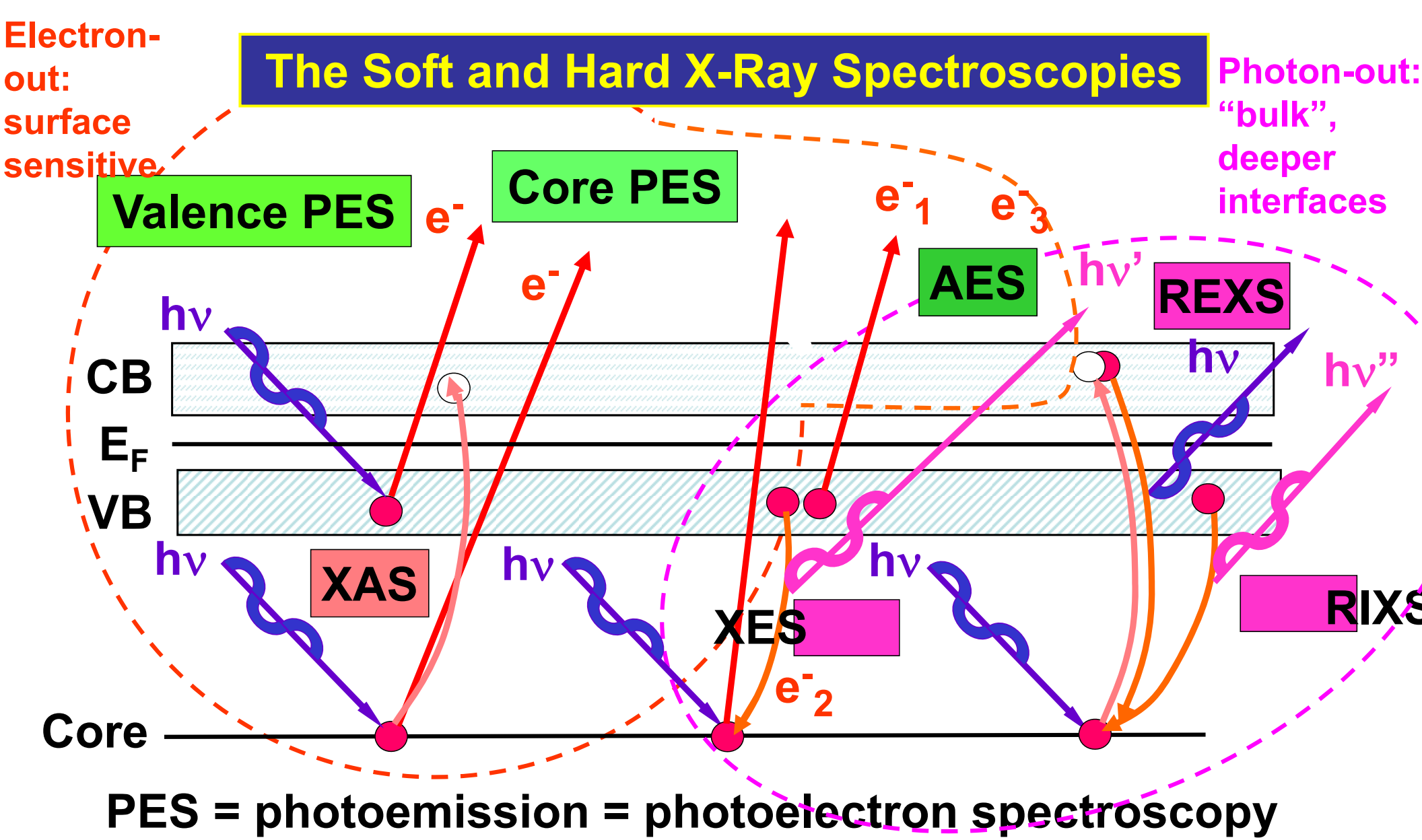



**Mg K series of x-rays:**
**atomic no. = 12**
**Fluorescence Yield ≈ 0.03**

"Basic Concepts of XPS"
Figure 2

# The Soft and Hard X-Ray Spectroscopies




PES = photoemission = photoelectron spectroscopy

XAS = x-ray absorption spectroscopy

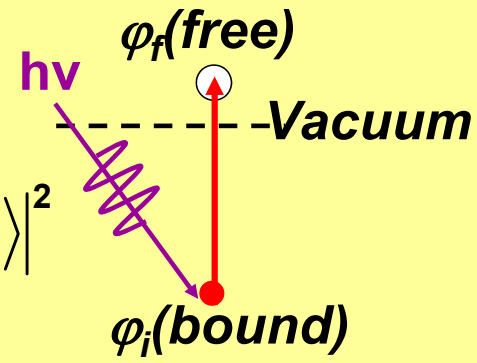
AES = Auger electron spectroscopy

XES = x-ray emission spectroscopy

REXS/RIXS = resonant elastic/inelastic x-ray scattering

# MATRIX ELEMENTS IN The Soft and Hard X-Ray Spectroscopies: RESONANT EFFECTS

- ***Non-resonant photoemission:***

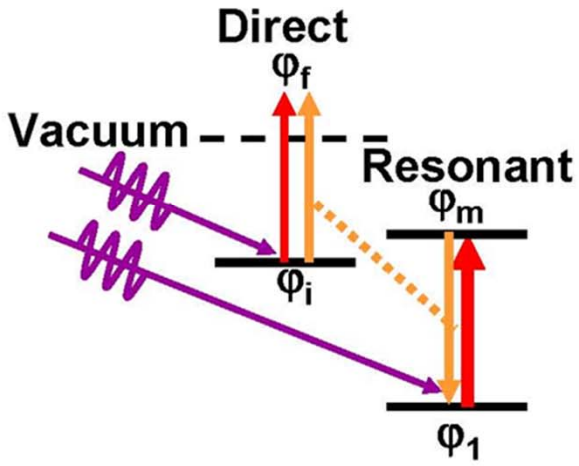



$$I \propto \left|\hat{e} \bullet \langle \varphi_f(1) | \vec{r} | \varphi_i(1) \rangle\right|^2$$

- ***Resonant photoemission:***

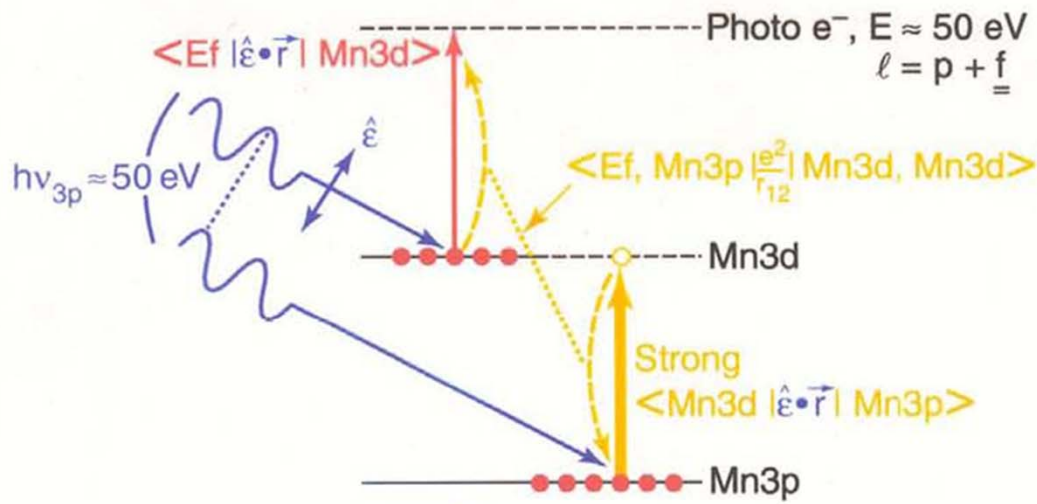
$$I \propto \left| \langle \varphi_f(1) | \hat{e} \bullet \vec{r} | \phi_i(1) \rangle + \sum_m \langle \varphi_f(1)\varphi_1(2) | \frac{e^2}{r_{12}} | \varphi_i(1)\varphi_m(2) \rangle \langle \varphi_m(1) | \hat{e} \bullet \vec{r} | \varphi_1(1) \rangle \right|^2$$

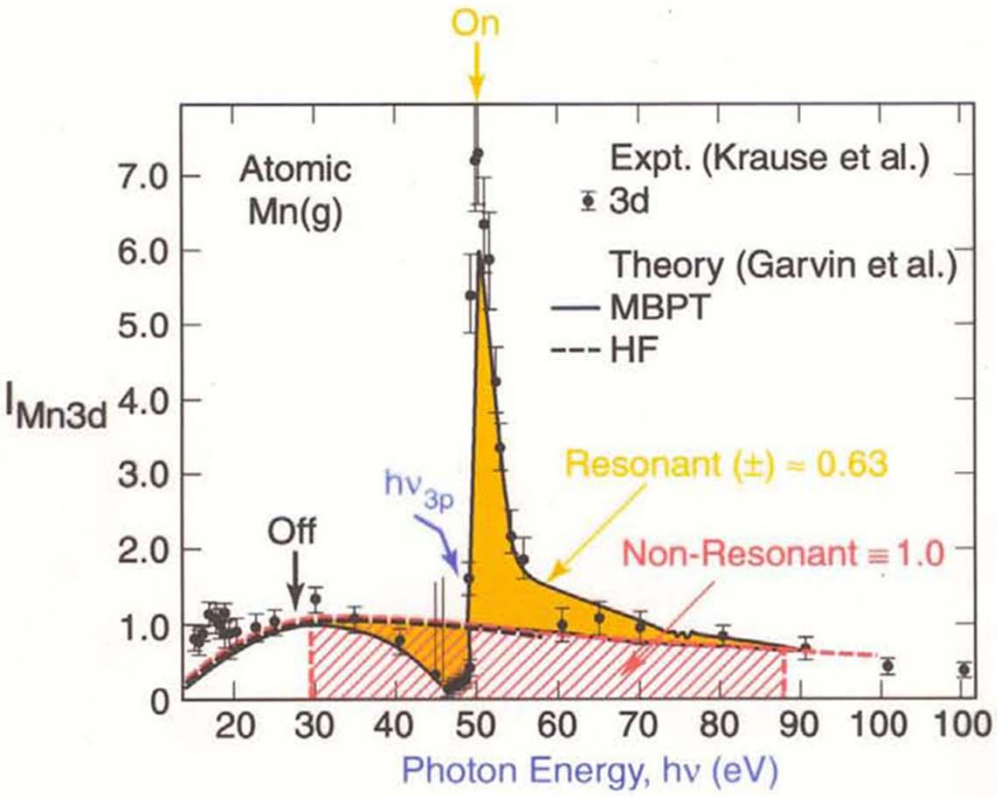
$$\times \delta(h\nu - (E_m - E_1))$$



## Single-atom resonant photoemission:

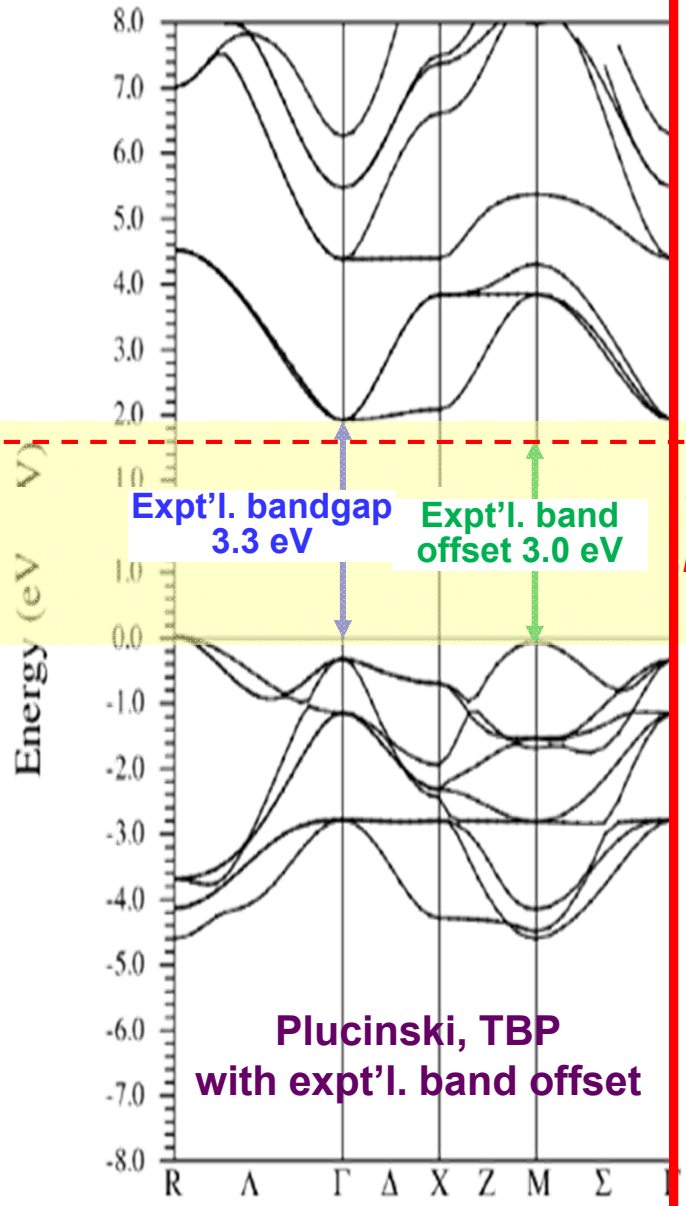
Ex. – Mn atom: Mn3d emission, resonance with Mn3p



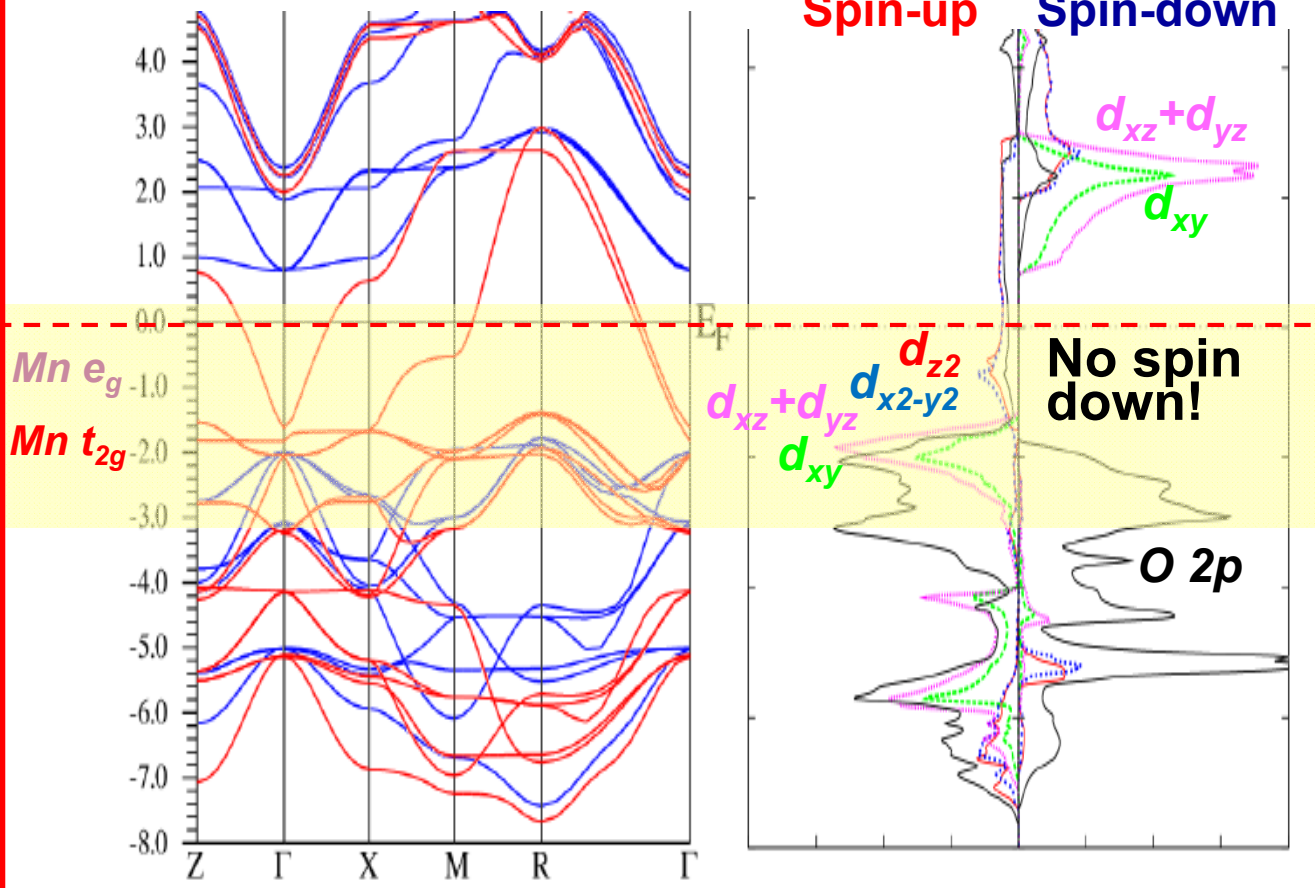
# $SrTiO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ band structures and DOS

## $SrTiO_3$-band insulator




Plucinski, TBP
with expt'l. band offset

## $La_{0.67}Sr_{0.33}MnO_3$- Half-Metallic Ferromagnet

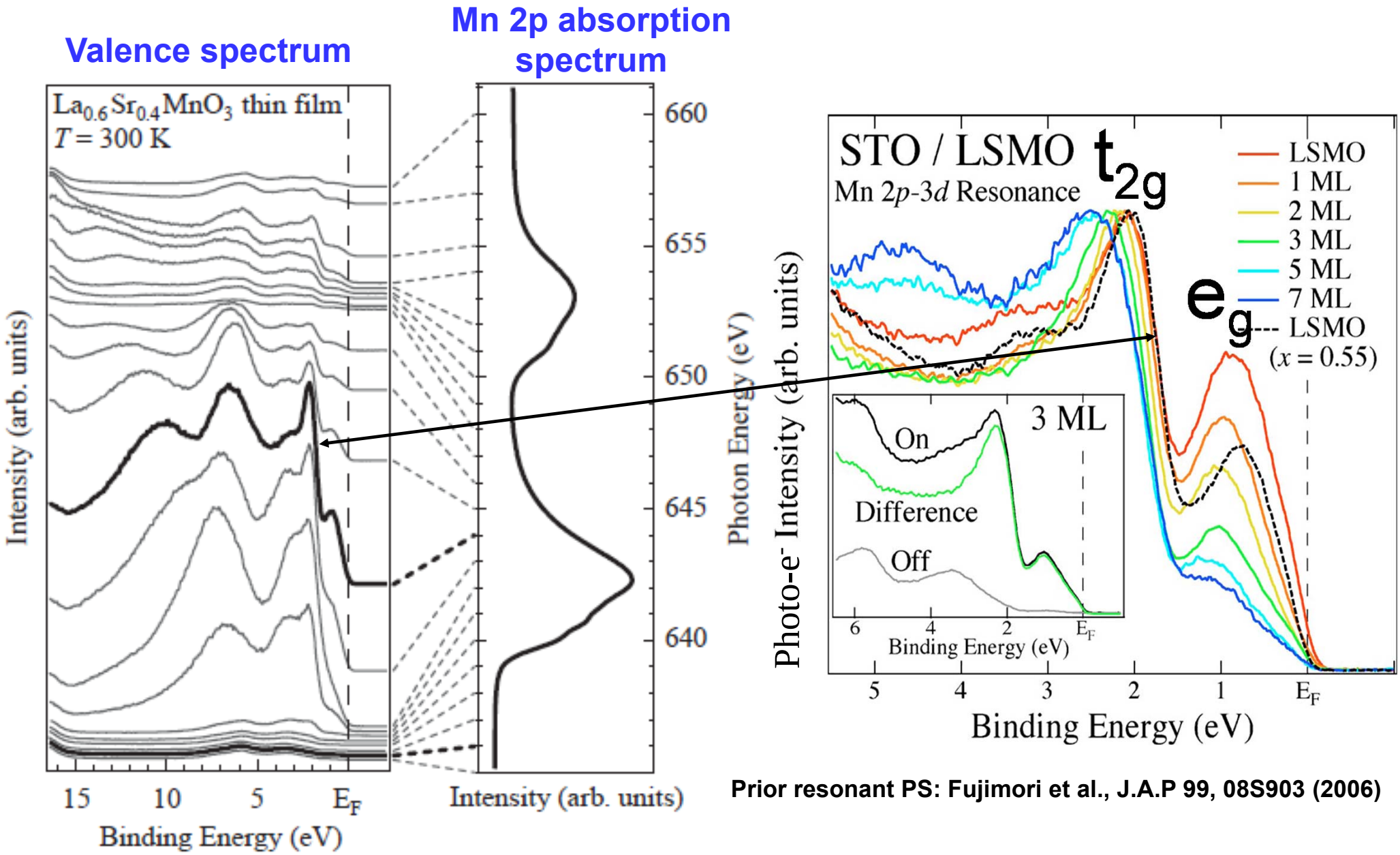



Spin-up
Spin-down

Chikamatsu et al.,
PRB 73, 195105 (2006);
Plucinski, TBP

Zheng, Binggeli, J. Phys. Cond. Matt. 21, 115602 (2009)
Plucinski, TBP

# Resonant Photoemission—$La_{0.6}Sr_{0.4}MnO_3$, Mn 3d with Mn 2p

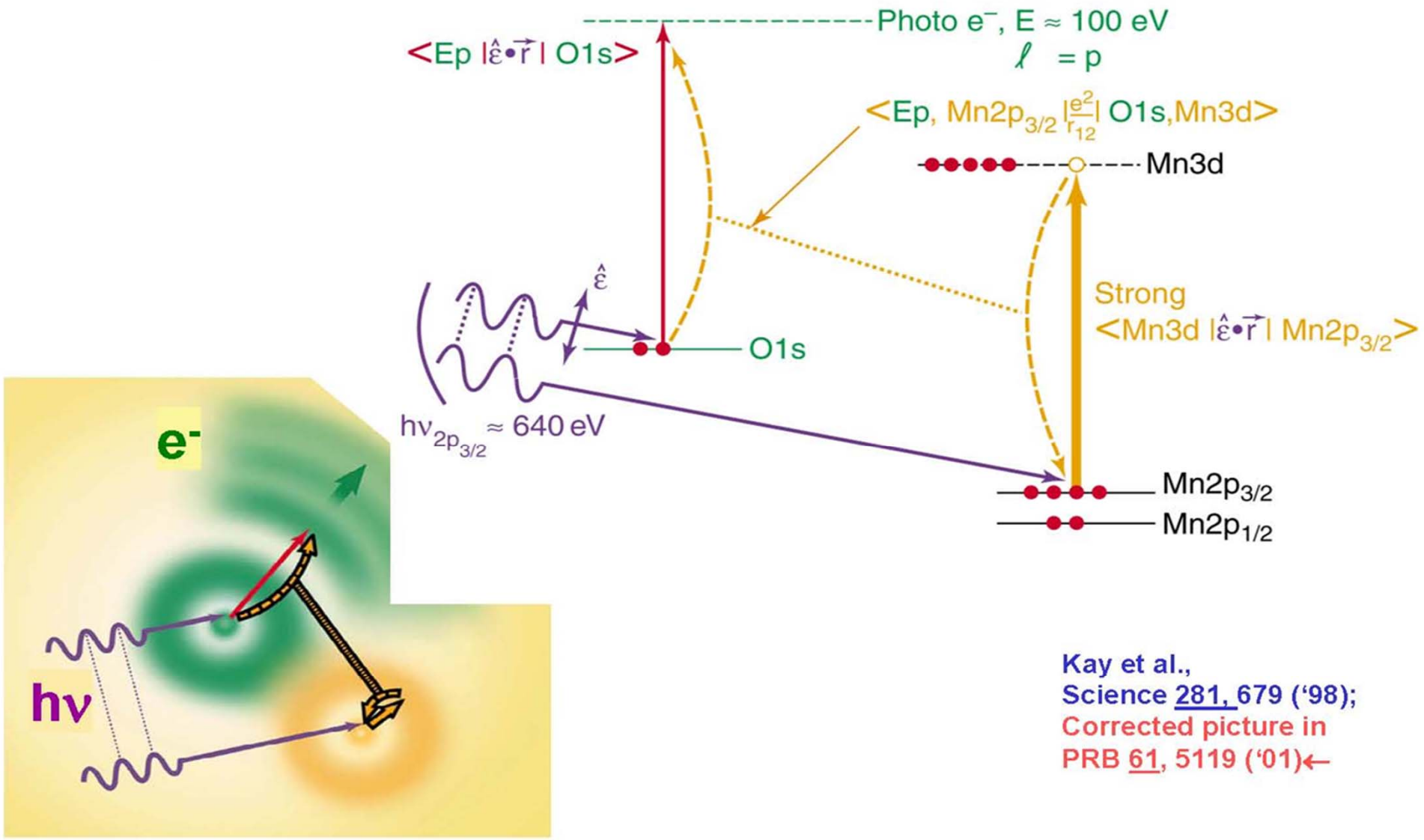



**Prior resonant PS: Fujimori et al., J.A.P 99, 08S903 (2006)**

*K. Horiba et al. / Journal of Magnetism and Magnetic Materials 272–276 (2004) 436–437*

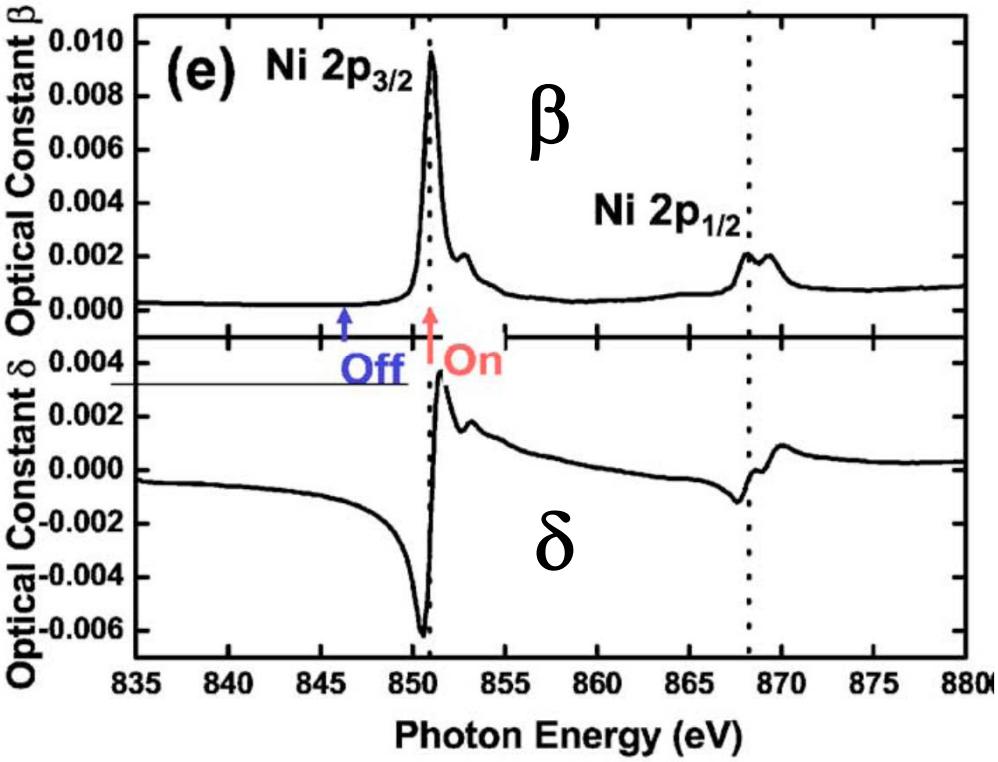
# Multi-Atom Resonant Photoemission

Ex. – MnO(001): O1s emission, resonance with $Mn2p_{3/2}$

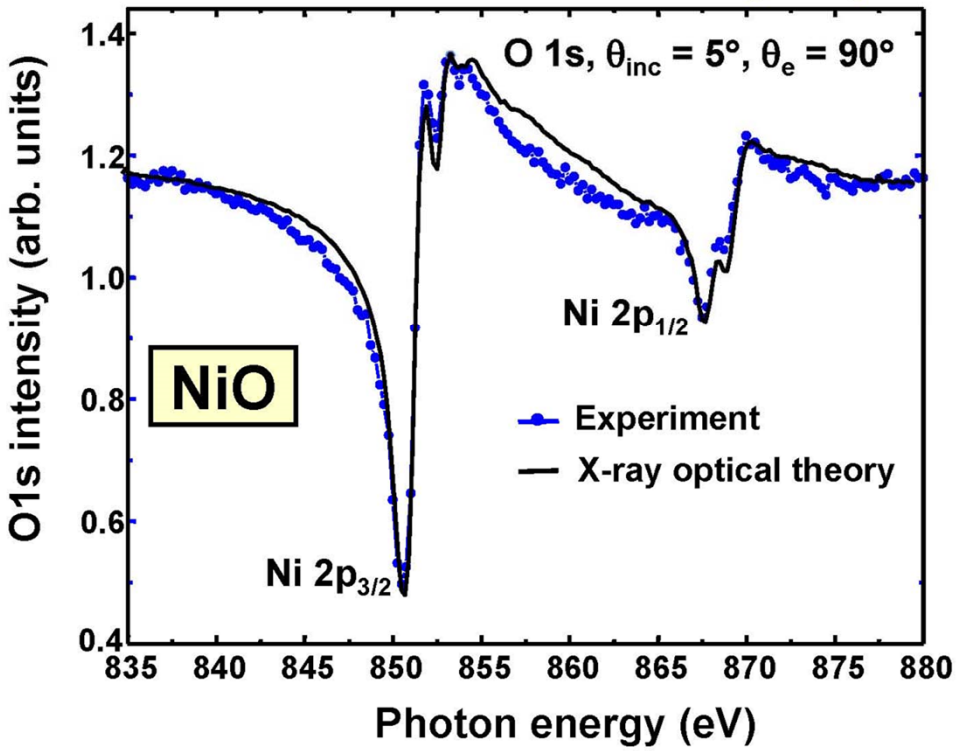



Kay et al.,
Science 281, 679 ('98);
Corrected picture in
PRB 61, 5119 ('01)←

Index of refraction over
Ni 2p resonances in NiO




**Multi-Atom Resonant Photoemission—
O 1s emission from NiO(001)**

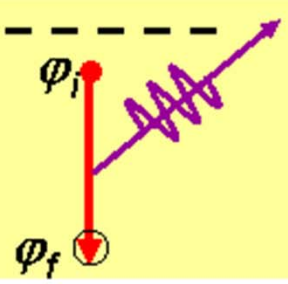



Mannella et al., Phys. Rev. B. 74, 165106 (2006)

# MATRIX ELEMENTS IN The Soft and Hard X-Ray Spectroscopies: RESONANT EFFECTS

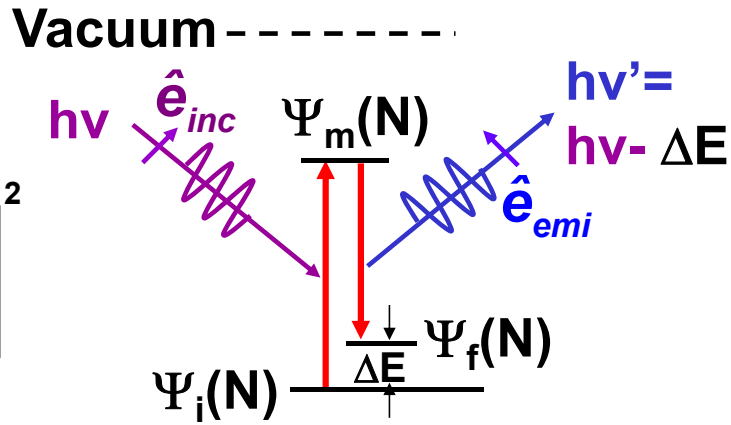
- ***X-ray emission:***

$$I \propto \left| \hat{e} \bullet \left\langle \varphi_f(1) \middle| \vec{r} \middle| \varphi_i(1) \right\rangle \right|^2$$




- ***Resonant inelastic x-ray scattering:***

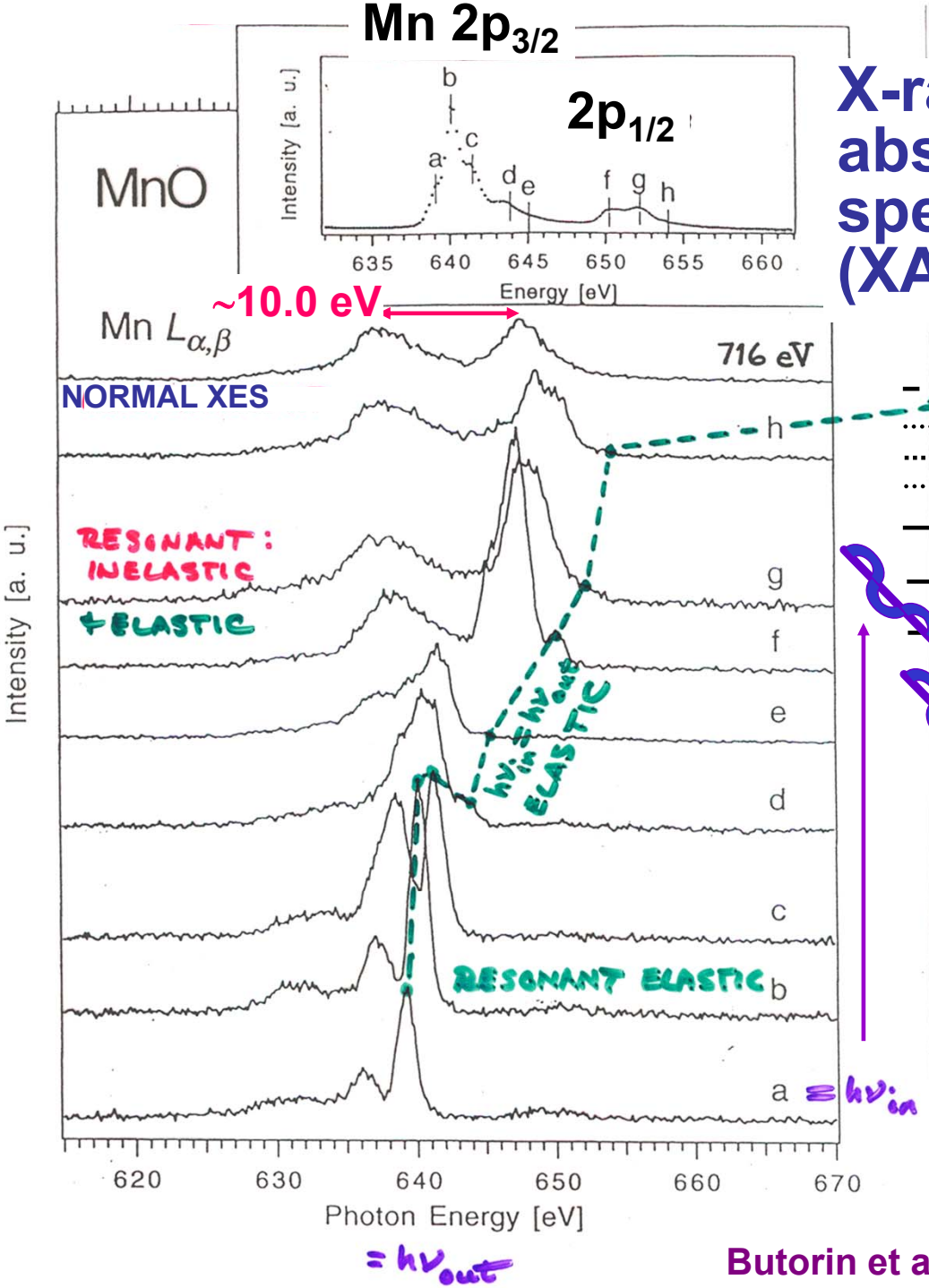
$$I \propto \sum_f \left| \sum_m \frac{\left\langle \Psi_f(N) \middle| \hat{e}_{emi} \bullet \vec{r} \middle| \Psi_m(N) \right\rangle \left\langle \Psi_m(N) \middle| \hat{e}_{inc} \bullet \vec{r} \middle| \Psi_i(N) \right\rangle}{h\nu + E_i(N) - E_m(N) - i\Gamma_m} \right|^2 \times \delta(h\nu - (E_m(N) - E_i(N)))$$



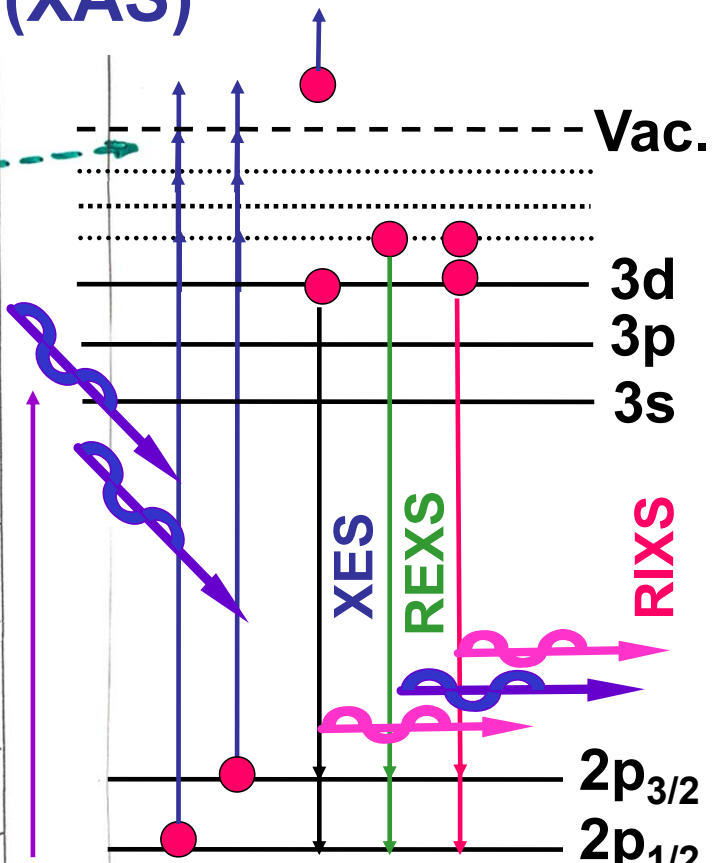

$$N_m(t) = N_m(0)e^{-\frac{2\Gamma_m t}{\hbar}} = N_m(0)e^{-\frac{t}{\tau_{lifetime}}}$$

**X-ray fluorescence spectroscopy =X-ray emission spectroscopy (XES) and Resonant inelastic x-ray scattering (RIXS)**

**Resonant inelastic x-ray scattering (RIXS) and Resonant elastic x-ray scattering (REXS)**

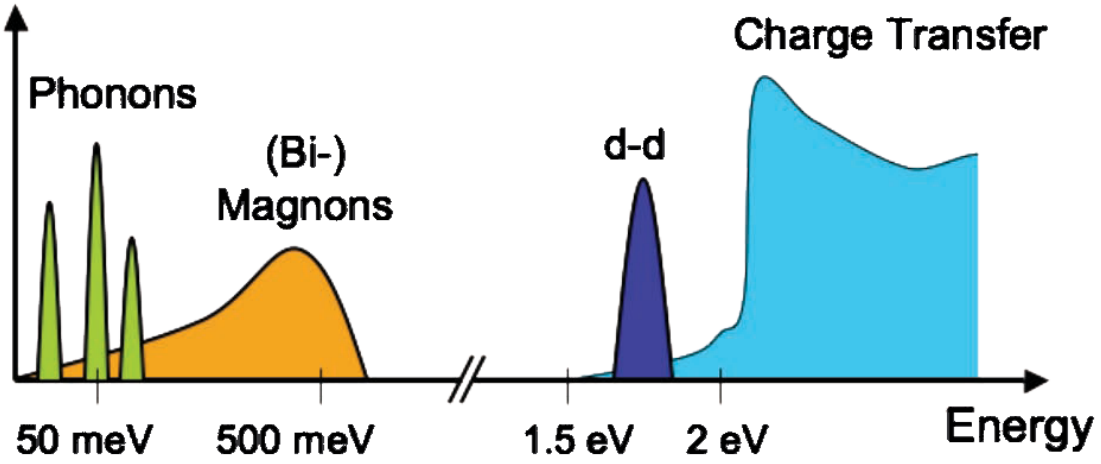



**X-ray absorption spectroscopy (XAS)**

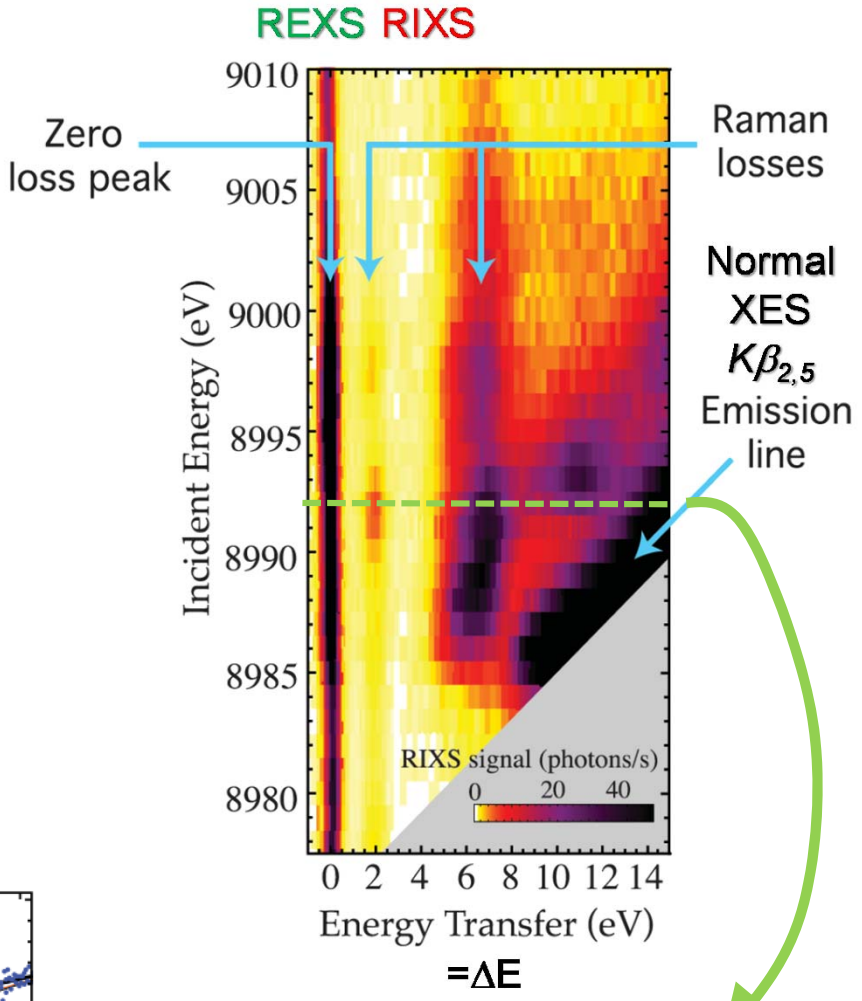



Butorin et al., Phys. Rev. B 54, 4405 ('96)

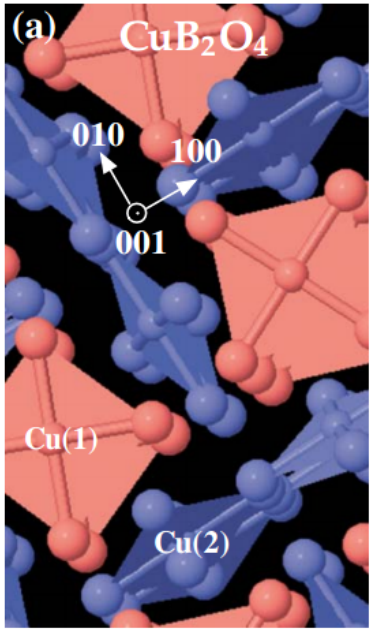
# Excitations probed by RIXS

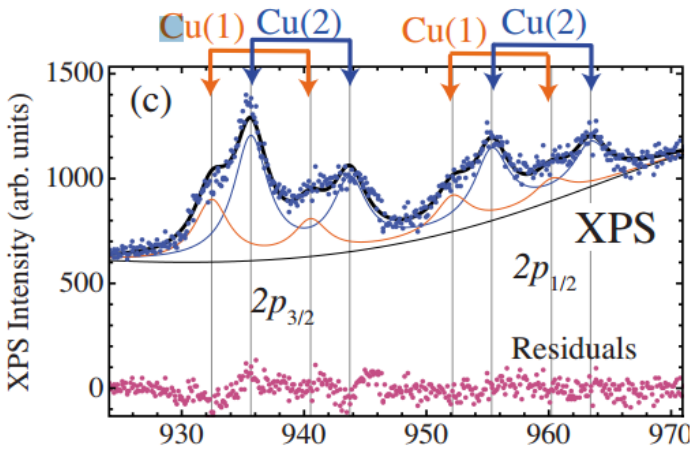



Aments et al., Rev. Mod. Phys. 83, 705 (2011)

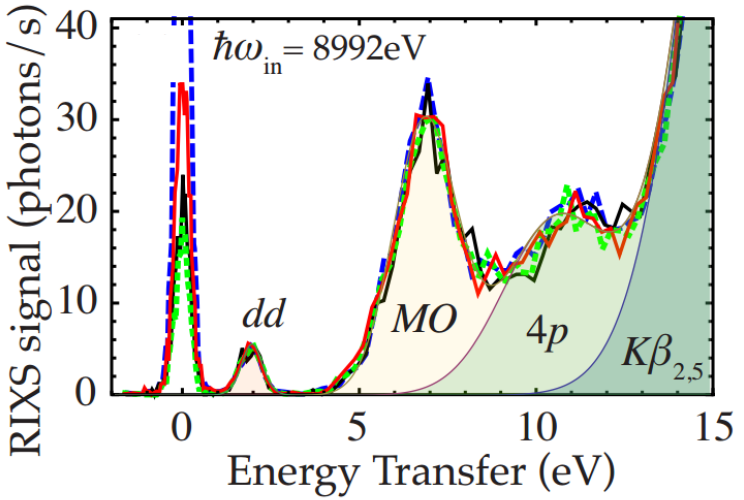



## Example: $CuB_2O_4$ plaquets




Hancock et al., Phys. Rev. B 80, 092509 (2009)



# The Soft and Hard X-Ray Spectroscopies

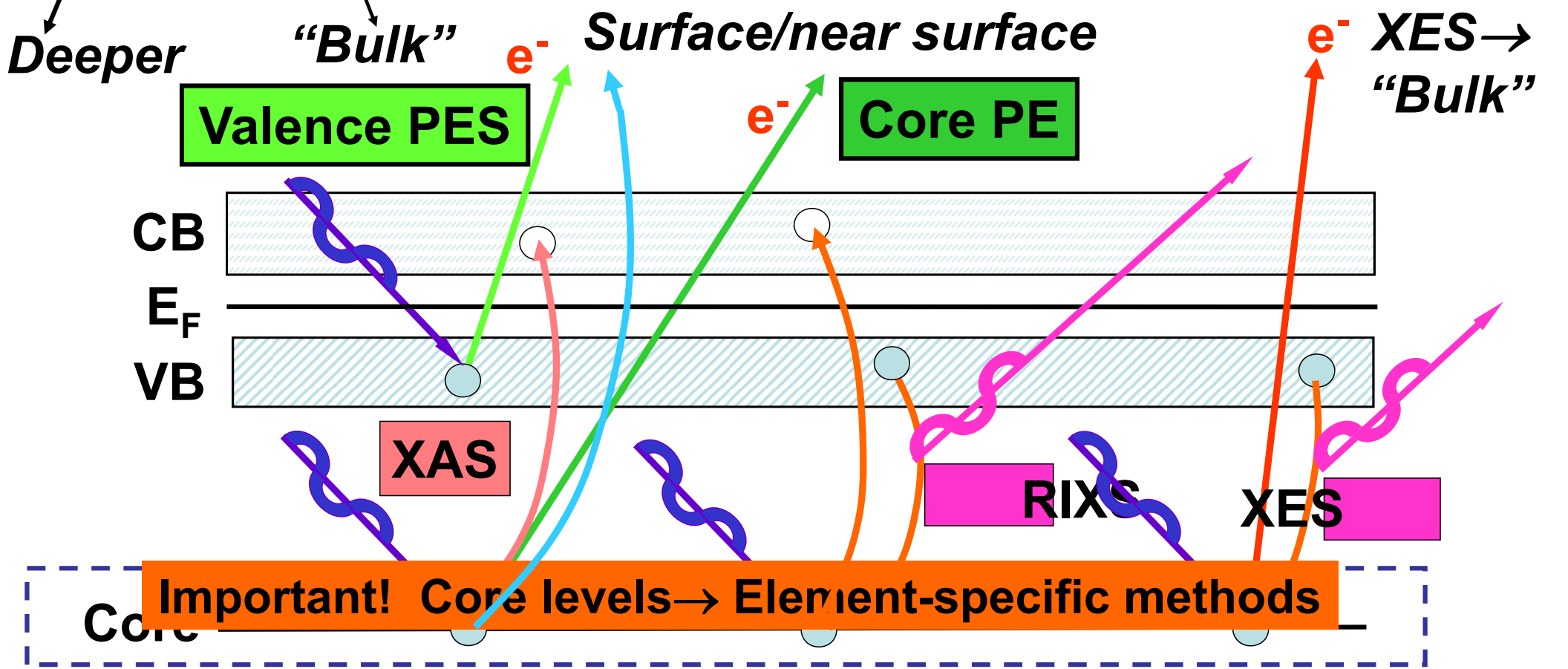
**EXAFS**
Atomic structure

**XAS**
unoccupied DOS
(2° e- and hν Detection)

**Valence PES -**
band struct.,
quasipart. exc.,
DOS, spin pol.

**Core PES -**
stoichiometry
BE shifts
splittings, MCD
spin polarization
diffraction

**XES, RIXS –**
band structure,
partial DOS,
d-d/other
excitations



The five ways in which x-rays interact with matter:

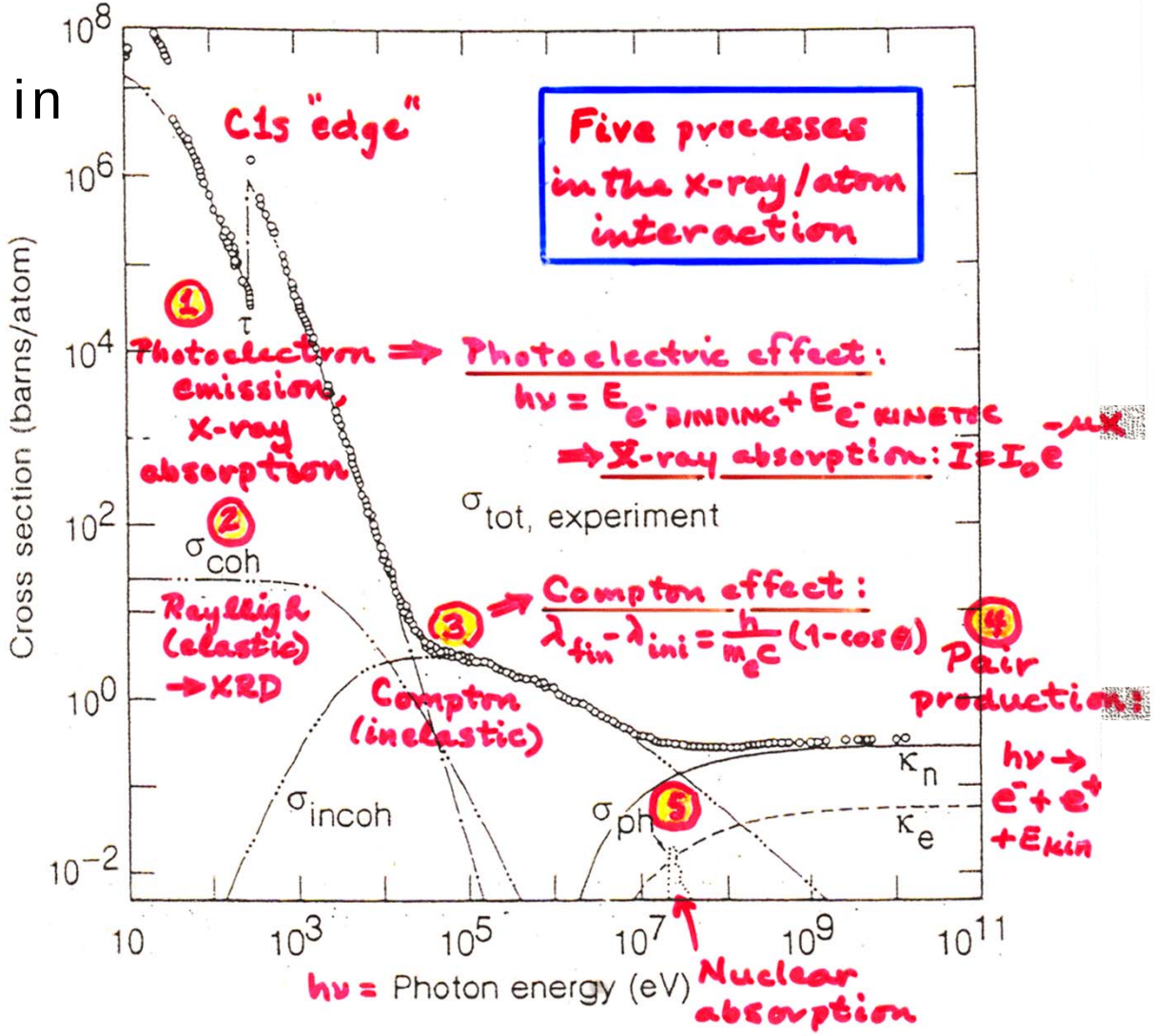
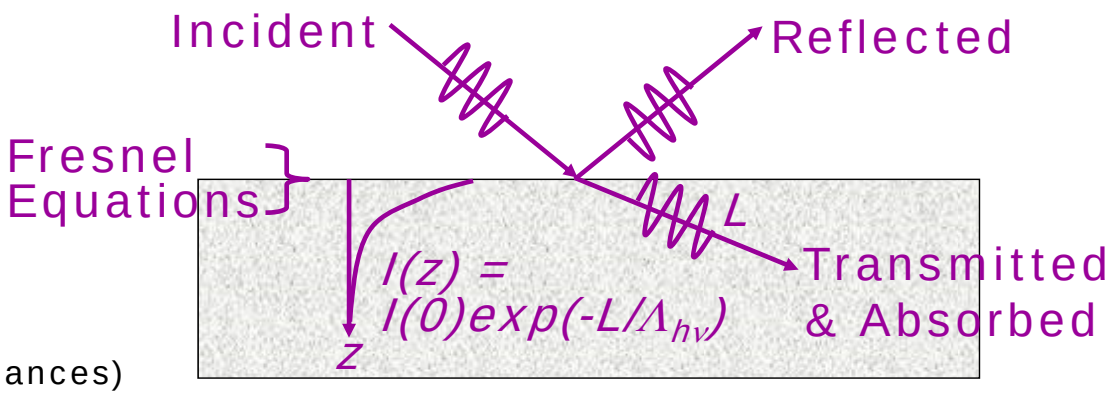



*Fig. 3-1.* *Total photon cross section $\sigma_{tot}$ in carbon, as a function of energy, showing the contributions of different processes: $\tau$, atomic photo-effect (electron ejection, photon absorption); $\sigma_{coh}$, coherent scattering (Rayleigh scattering—atom neither ionized nor excited); $\sigma_{incoh}$, incoherent scattering (Compton scattering off an electron) $\kappa_n$, pair production, nuclear field; $\kappa_e$, pair production, electron field; $\sigma_{ph}$, photonuclear absorption (nuclear absorption usually followed by emission of a neutron or other particle). (From Ref. 3; figure courtesy of J. H. Hubbell.)*

**LBNL Center for X-Ray Optics**
**"X-Ray Data Booklet"**
**Section 3.1**
**http://cxro.lbl.gov/x-ray-data-booklet**

# A LITTLE X-RAY OPTICS




**Index of refraction = n = 1 - δ - iβ**

(Sometimes with + signs on δ and/or β)

**δ = + no. = refractive decrement << 1**

(Sometimes changes sign through absorption resonances)

**β = + no. = absorptive decrement << 1**

**δ and β linked by Kramers-Kronig transform**

(See next page)

**n also = 1 – $(r_e/2\pi)\lambda_{hv}^2\Sigma n_i f_i$(0=fwd. scatt.)**

**$r_e$ = classical electron radius**

$= e^2/4\pi\varepsilon_0 m_e e^2 = 2.817 \times 10^{-15}$ m

**$\lambda_{hv}$ = x-ray wavelength**

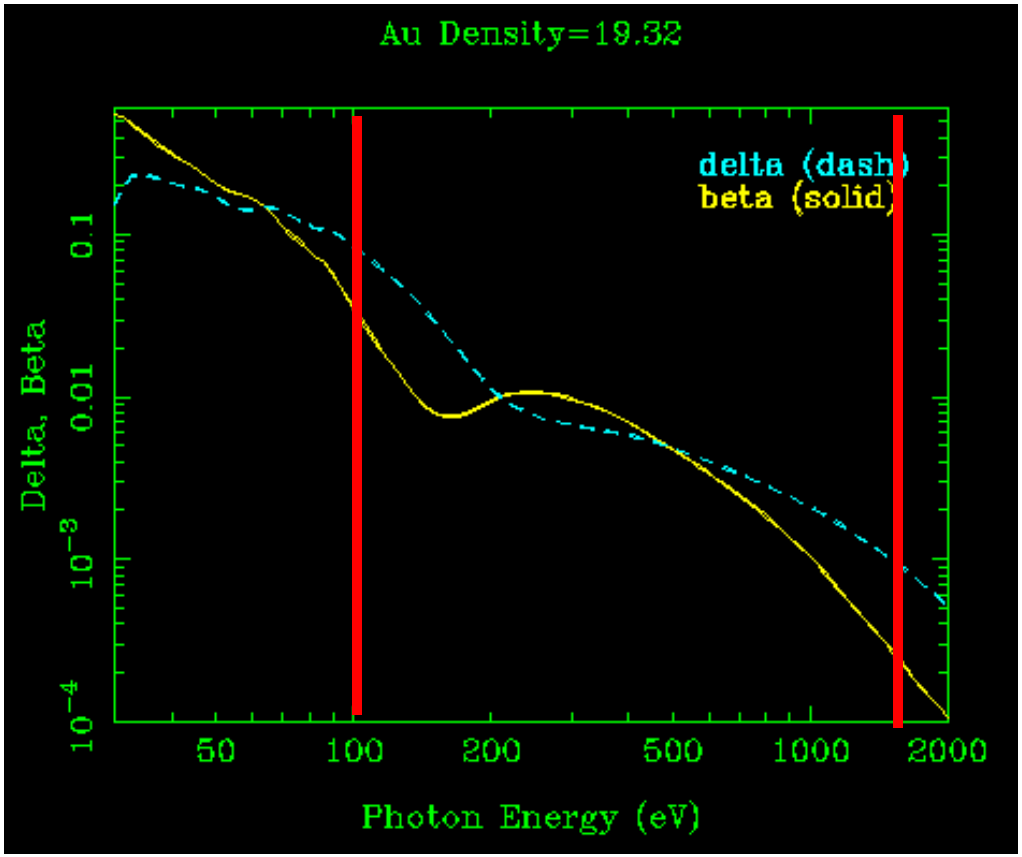
**$n_i$ = no. i atoms per unit volume**

**$f_i$ = x-ray scattering factor for ith type of atom, in forward direction**

**Exponential absorption length = $l_{abs} = \lambda_{hv}/(4\pi\beta) = \Lambda_{hv}$**

$\theta_{CRIT}$ = critical grazing angle at which reflectivity begins (R ≈ 0.20) = $[2\delta]^{0.5}$

Online data and calculations excluding resonant behavior at:
http://henke.lbl.gov/optical_constants/getdb2.html




**Sections 1.6 and 1.7 of X-Ray Data Booklet**

## 1.7 ATOMIC SCATTERING FACTORS

*Eric M. Gullikson*

The optical properties of materials in the photon energy range above about 30 eV can be described by the atomic scattering factors. The index of refraction of a material is related to the scattering factors of the individual atoms by

$$n = 1 - \delta - i\beta = 1 - \frac{r_e}{2\pi}\lambda^2 \sum_i n_i f_i(0) \quad , \tag{1}$$

where $r_e$ is the classical electron radius, $\lambda$ is the wavelength, and $n_i$ is the numb[illegible]e. The parameters $\delta$ and $\beta$ are called the refractive index decrement and the absorption index, respectively. The complex atomic scattering factor for the forward scattering direction is

$$f(0) = f_1 + if_2 \quad . \tag{2}$$

The imaginary part is derived from the atomic photoabsorption cross section:

$$f_2 = \frac{\sigma_a}{2r_e\lambda} \quad . \tag{3}$$

The real part of the atomic scattering factor is related to the imaginary part by the Kramers-Kronig dispersion relation:

$$f_1 = Z^* + \frac{1}{\pi r_e hc}\int_0^\infty \frac{\varepsilon^2 \sigma_a(\varepsilon)}{E^2 - \varepsilon^2}\, d\varepsilon \quad . \tag{4}$$

In the high-photon-energy limit, $f_1$ approaches $Z^*$, which differs from the atomic number $Z$ by a small relativistic correction:

$$Z^* \approx Z - (Z/82.5)^{2.37} \quad . \tag{5}$$

**Sections 1.6 and 1.7 of X-Ray Data Booklet**
**Plus the "Bible" of Soft X-Ray Optics:**
**Henke, Gullikson, Davis, Atomic and Nuclear Data Tables 54, 181-342 (1993)**

$=1/\Lambda_{h\nu}$

$\wedge$

$= 4\pi\beta/\lambda_x \quad \mu_\ell = (N_A/A)\rho\sigma_a = 1/\Lambda_{h\nu}$

$h\nu$

$(h\nu)^2$

www.cxro.lbl.gov/optical_constants/]. The mass absorption coefficient $\mu$ (cm$^2$/g) is related to the transmitted intensity through a material of density $\rho$ (g/cm$^3$) and thickness $d$ by

$$I = I_0 e^{-\mu\rho d} \quad . \tag{1}$$

Thus, the linear absorption coefficient is $\mu_\ell$ (cm$^{-1}$) $= \mu\rho$. For a pure material, the mass absorption coefficient is directly related to the total atomic absorption cross section $\sigma_a$ (cm$^2$/atom) by

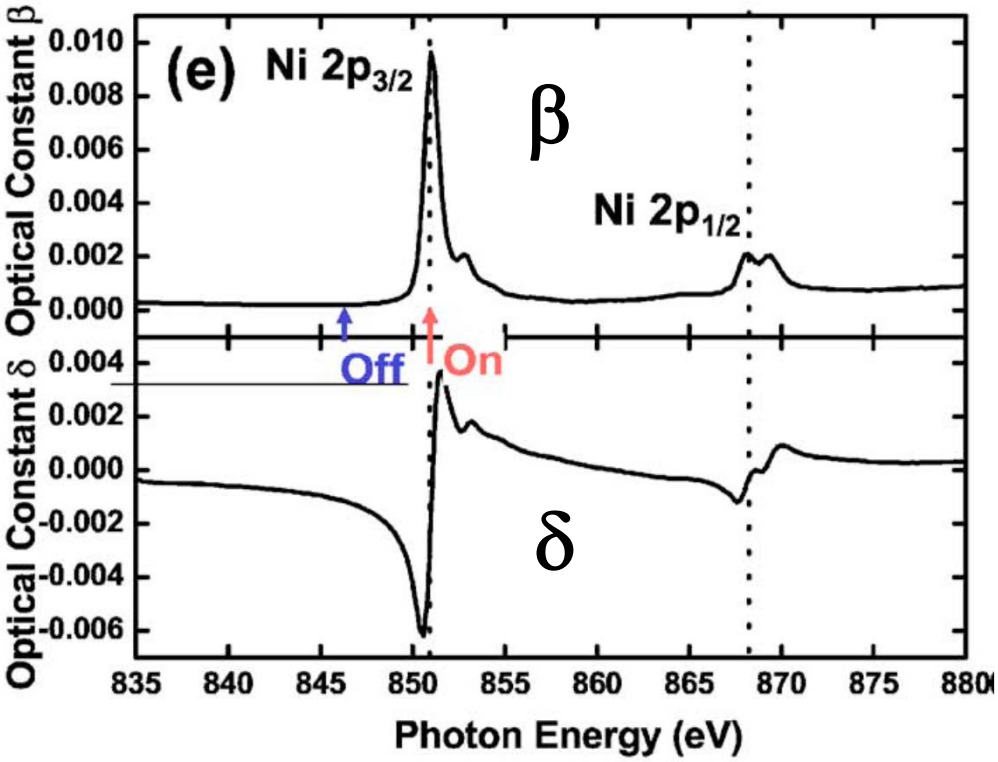
$$\mu = \frac{N_A}{A}\sigma_a \quad , \tag{2}$$

where $N_A$ is Avogadro's number and $A$ is the atomic weight. For a compound material, the mass absorption coefficient is obtained from the sum of the absorption cross sections of the constituent atoms by

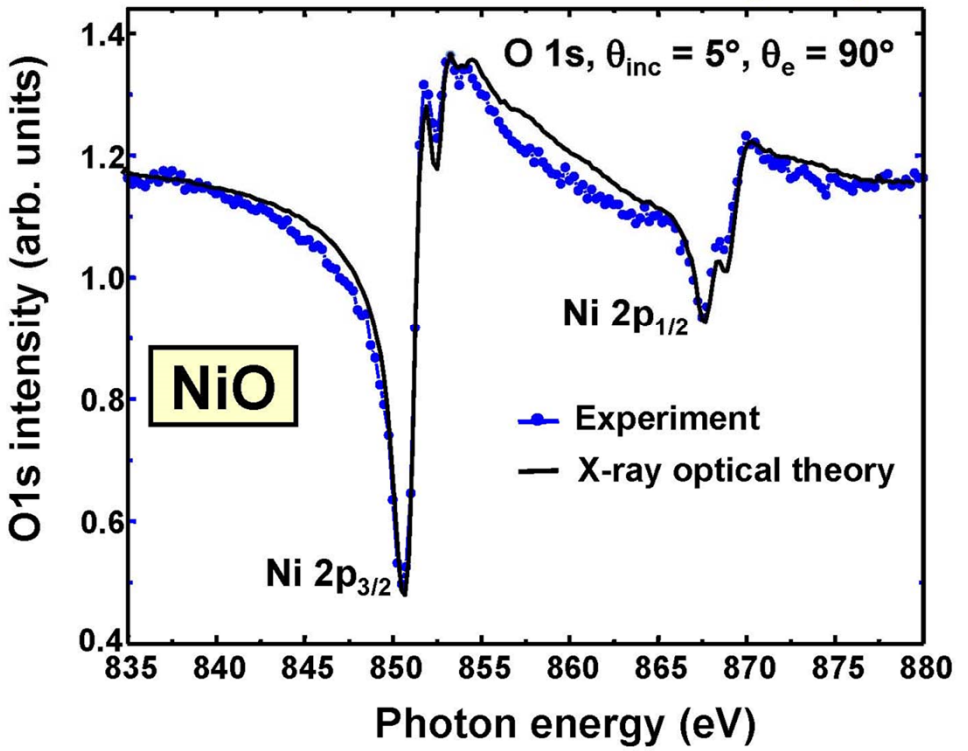
$$\mu = \frac{N_A}{MW}\sum_i x_i \sigma_{ai} \quad , \tag{3}$$

where the molecular weight of a compound containing $x_i$ atoms of type $i$ is $MW = \Sigma_i x_i A_i$. This approximation, which neglects interactions among the atoms in the material, is generally applicable for photon energies above about 30 eV and sufficiently far from absorption edges.

Index of refraction over
Ni 2p resonances in NiO




**Multi-Atom Resonant Photoemission—
O 1s emission from NiO(001)**




Mannella et al., Phys. Rev. B. 74, 165106 (2006)

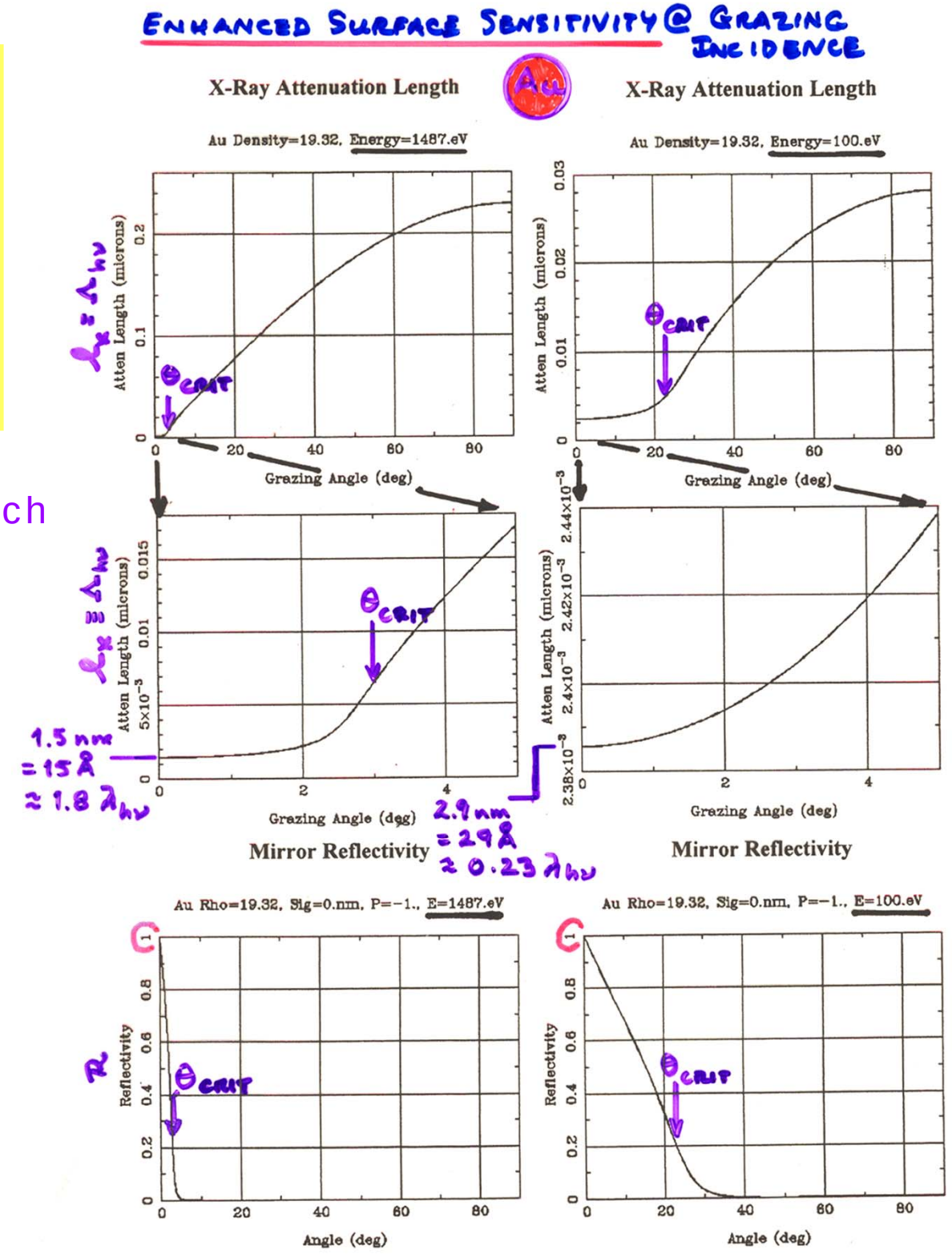
# SOME X-RAY OPTICAL EFFECTS: REDUCED PENETRATION DEPTHS AND INCREASED REFLECITIVITY AT GRAZING INCIDENCE ANGLES

$\theta_{CRIT}$ = Grazing angle at which reflectivity begins ($R \approx 0.20$)

$= [2\delta]^{0.5}$

**Regardless of energy, in total reflection the mean depth of x-ray penetration shrinks to nm range**

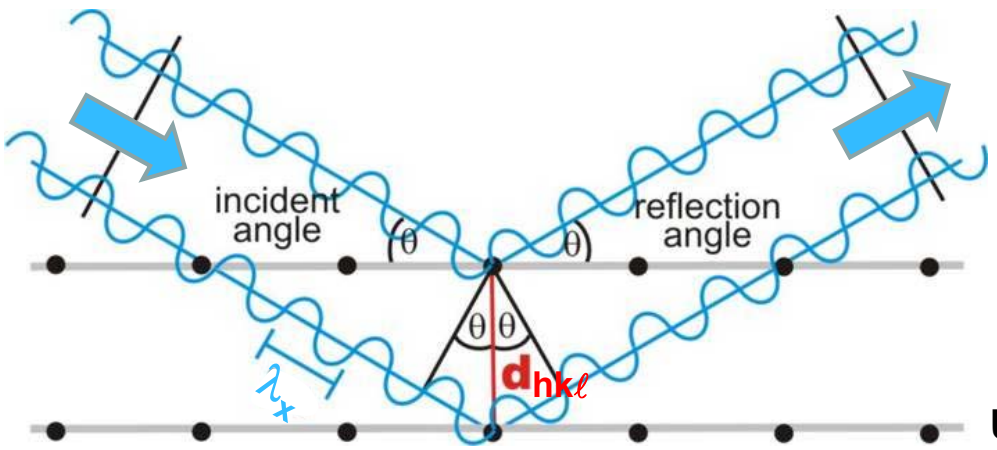
**Calculated online from: http://henke.lbl.gov/optical_constants/atten2.html**



# The ultraviolet, soft x-ray, hard x-ray measurements:

## Plus diffraction and scattering:

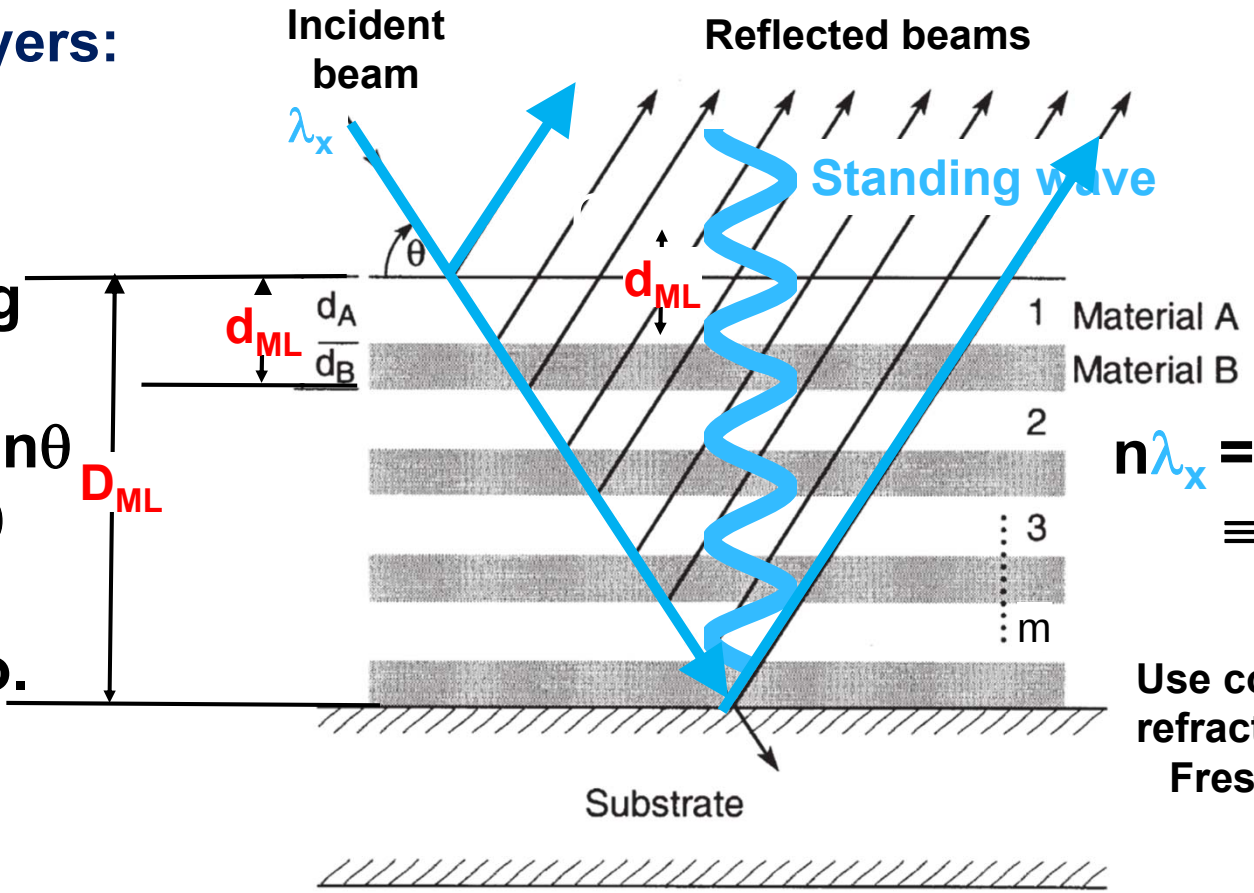
## From crystals:




$$n\lambda_x = 2d_{hk\ell}\sin\theta$$

Use atomic scattering factors $f_i$

## From multilayers:




**Plus Kiessig fringes:**

$$p\lambda_x = 2md_{ML}\sin\theta \equiv 2D_{ML}\sin\theta$$

p = 1, 2,…

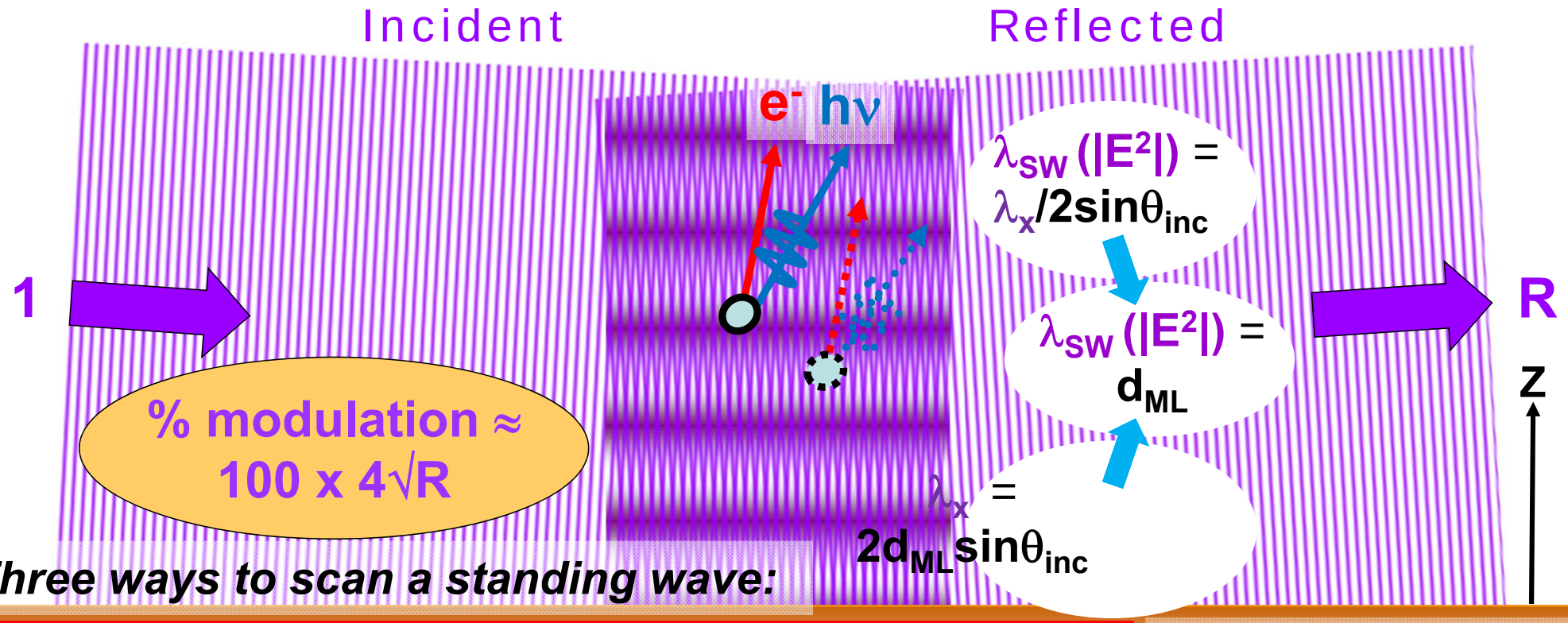
unknown no.

$$n\lambda_x = 2(d_A+d_B)\sin\theta \equiv 2d_{ML}\sin\theta$$

Use complex index of refraction $n = 1 - \delta - i\beta$

Fresnel Equations

# Three ways to scan a standing wave formed in reflection from single-crystal Bragg planes, or a multilayer mirror*




***Three ways to scan a standing wave:***

***1. Rocking curve:***

$$I(\theta_{inc}) \propto 1 + R(\theta_{inc}) + 2\sqrt{R(\theta_{inc})}\, f \cos[\varphi(\theta_{inc}) - 2\pi(\Delta z / \lambda_{SW})]$$

**Multilayer Mirror**

***2. Photon energy scan:***

$$I(h\nu) \propto 1 + R(h\nu) + 2\sqrt{R(h\nu)}\, f \cos[\varphi(h\nu) - 2\pi(\Delta z / \lambda_{SW})]$$

$d_{ML}$

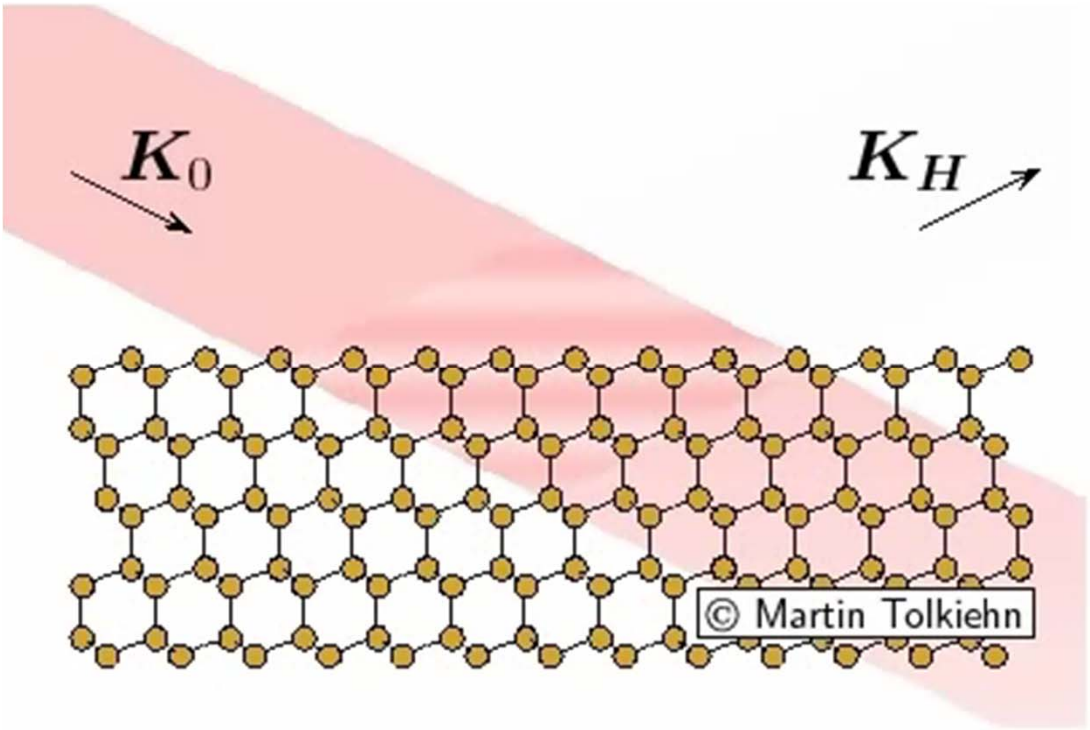
***with: f = coherent fraction of atoms, $\Delta z / \lambda_{SW}$ = phase of coherent-atom position***

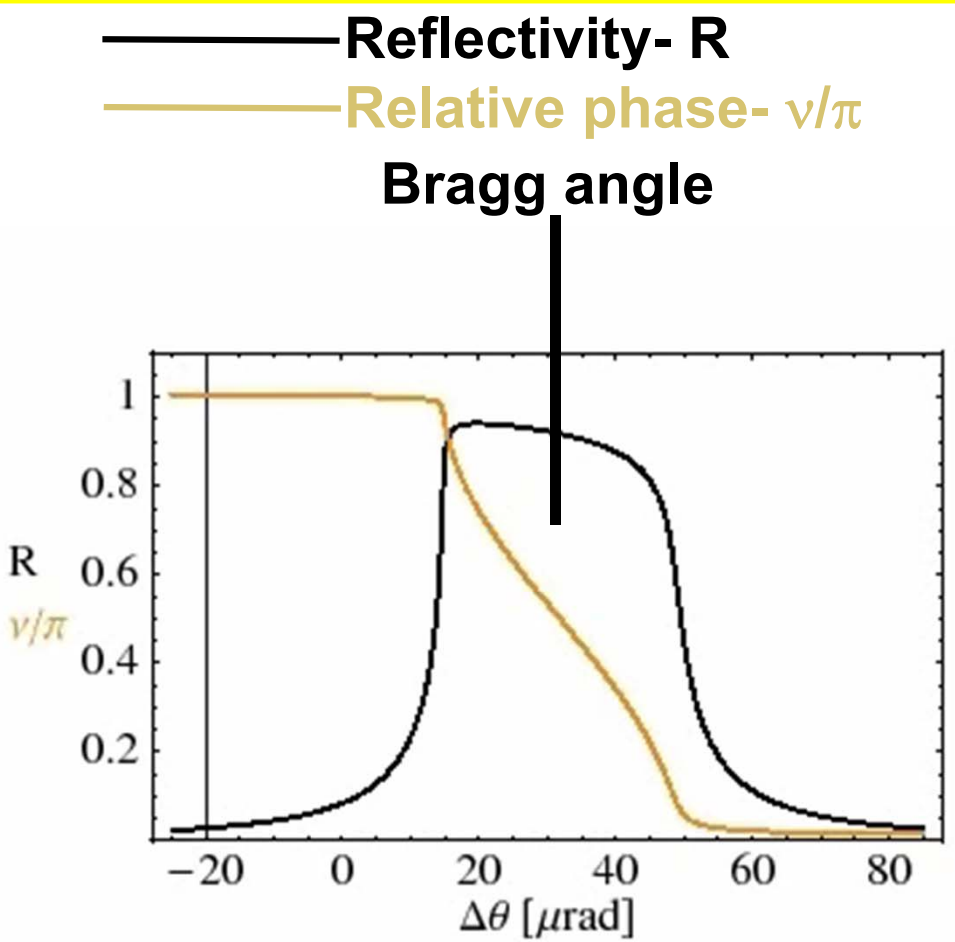
***3. Phase scan with wedge-shaped sample ("Swedge" method)***

+Standing waves via Bragg reflection of hard x-rays: Batterman, Phys. Rev A 133, 759 (1964)

*In x-ray magnetic circular dichroism (XMCD)—Kim, Kortright, PRL 86, 1347(2001)

# Standing Wave Behavior During a Rocking Curve or Photon-Energy Scan



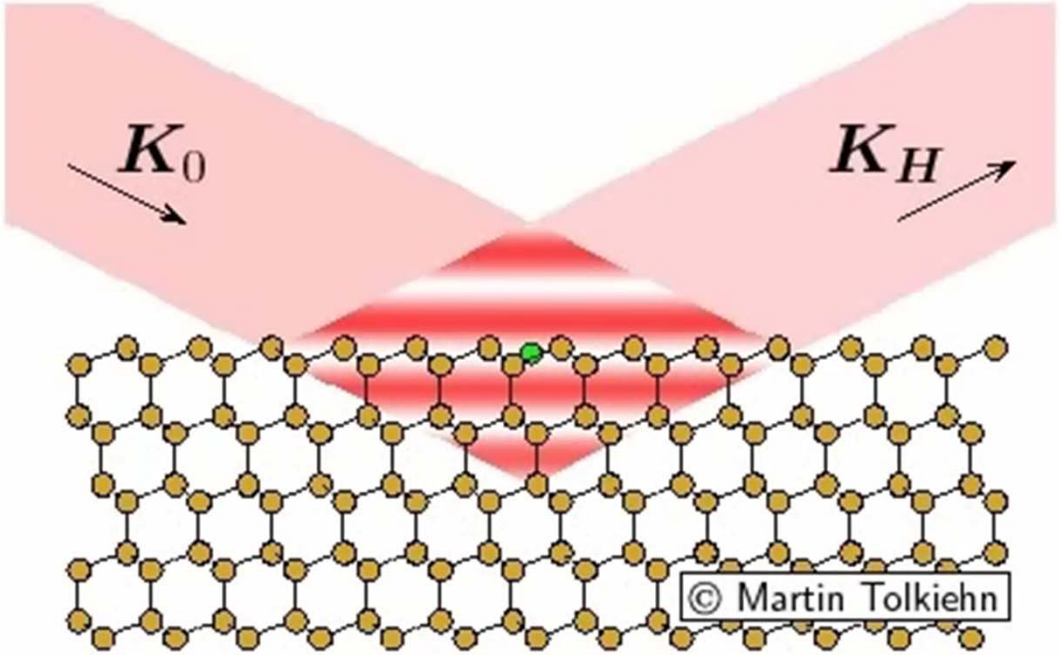



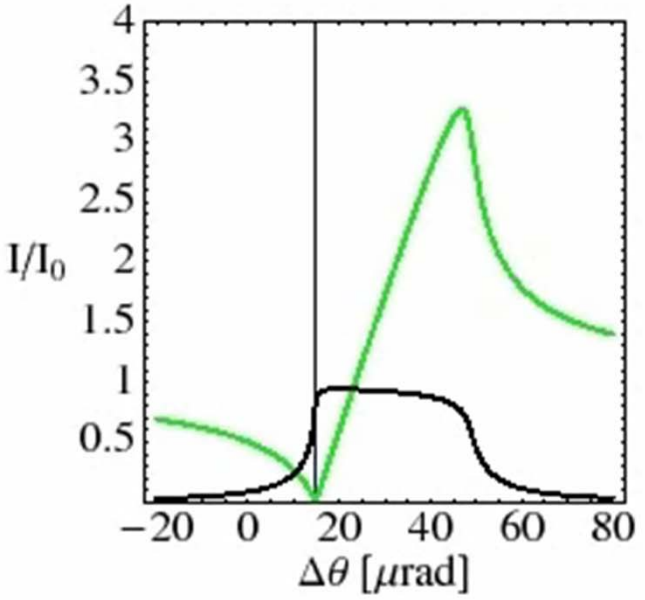

**+Same general forms if photon energy is scanned**

Woodruff and Delchar, Modern Techniques of Surface Science (Cambridge, 1994) pages 97-104

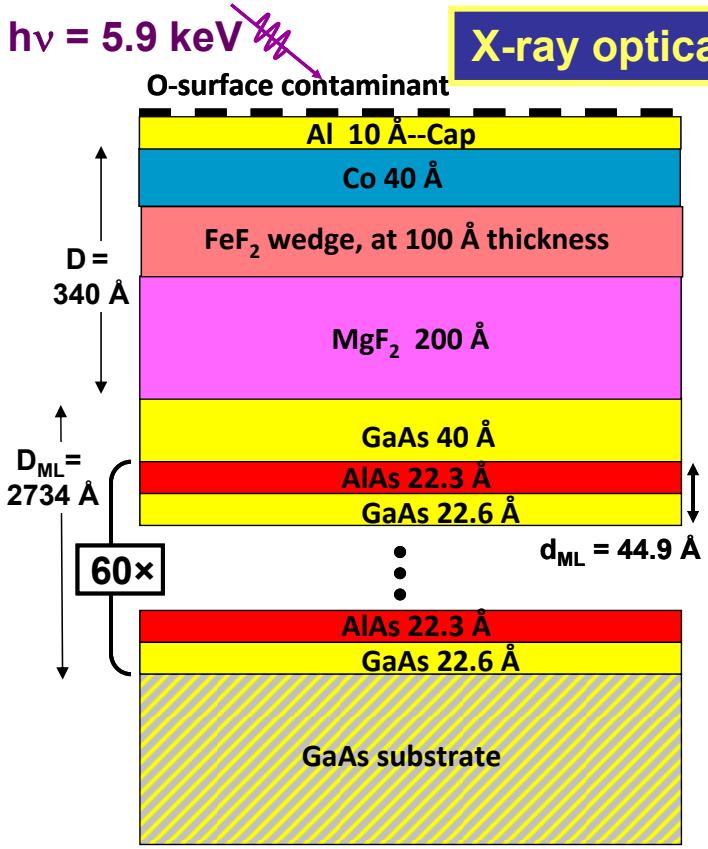
# Form of rocking curve is unique to position of emitter

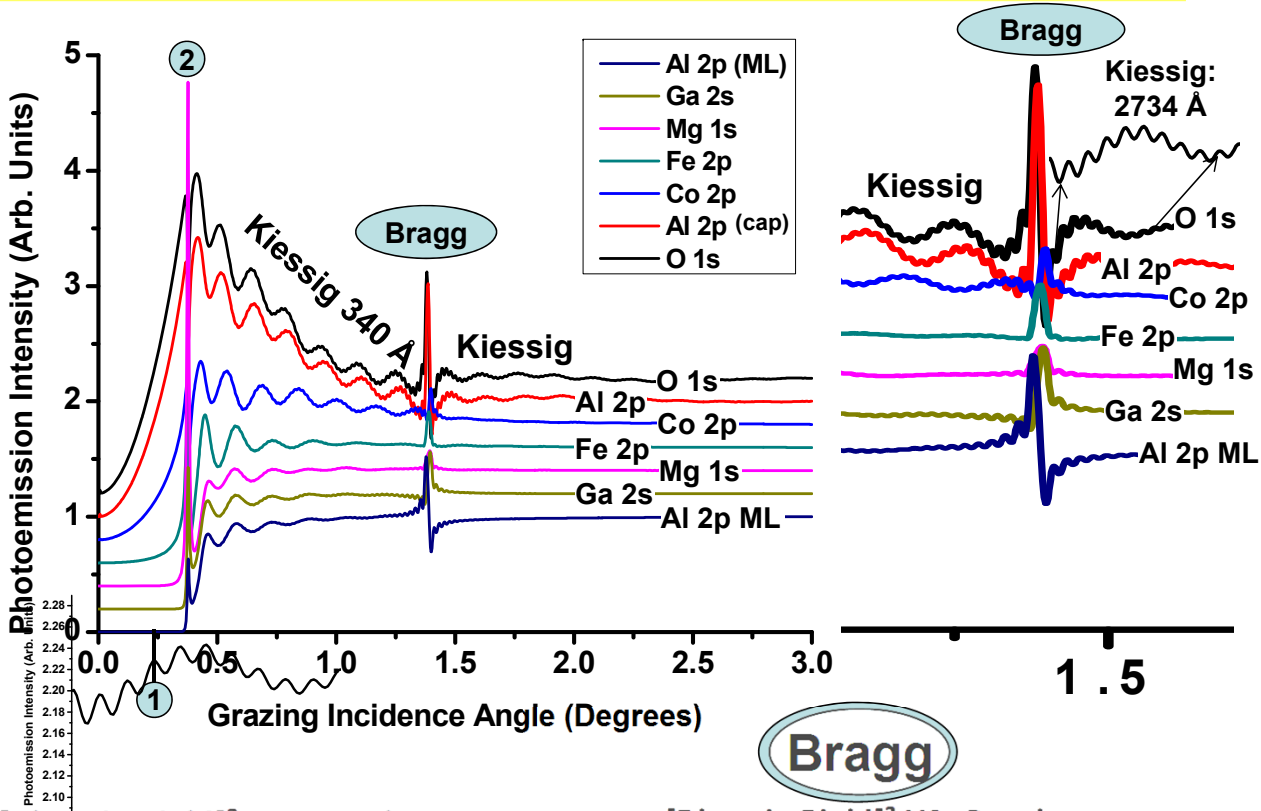
Intensity vs atomic position

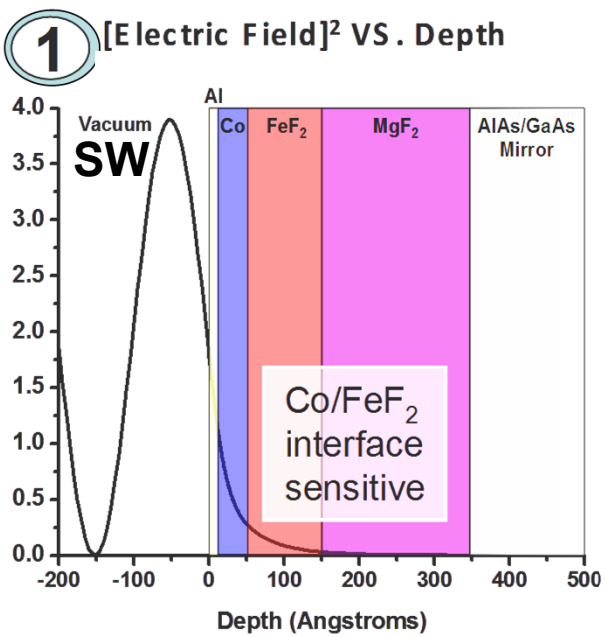


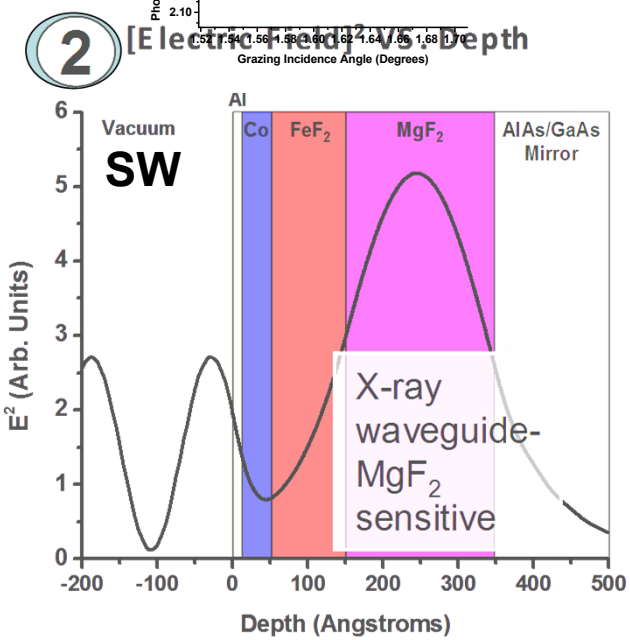



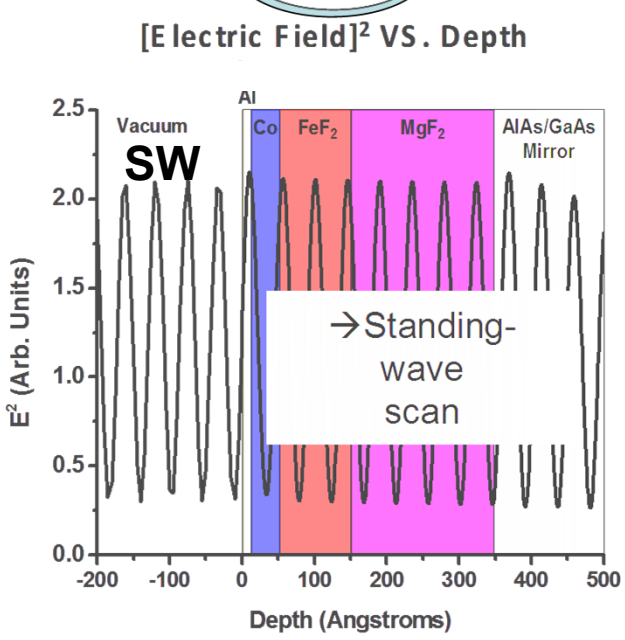
# X-ray optical effects in hard x-ray reflectivity from a multilayer structure



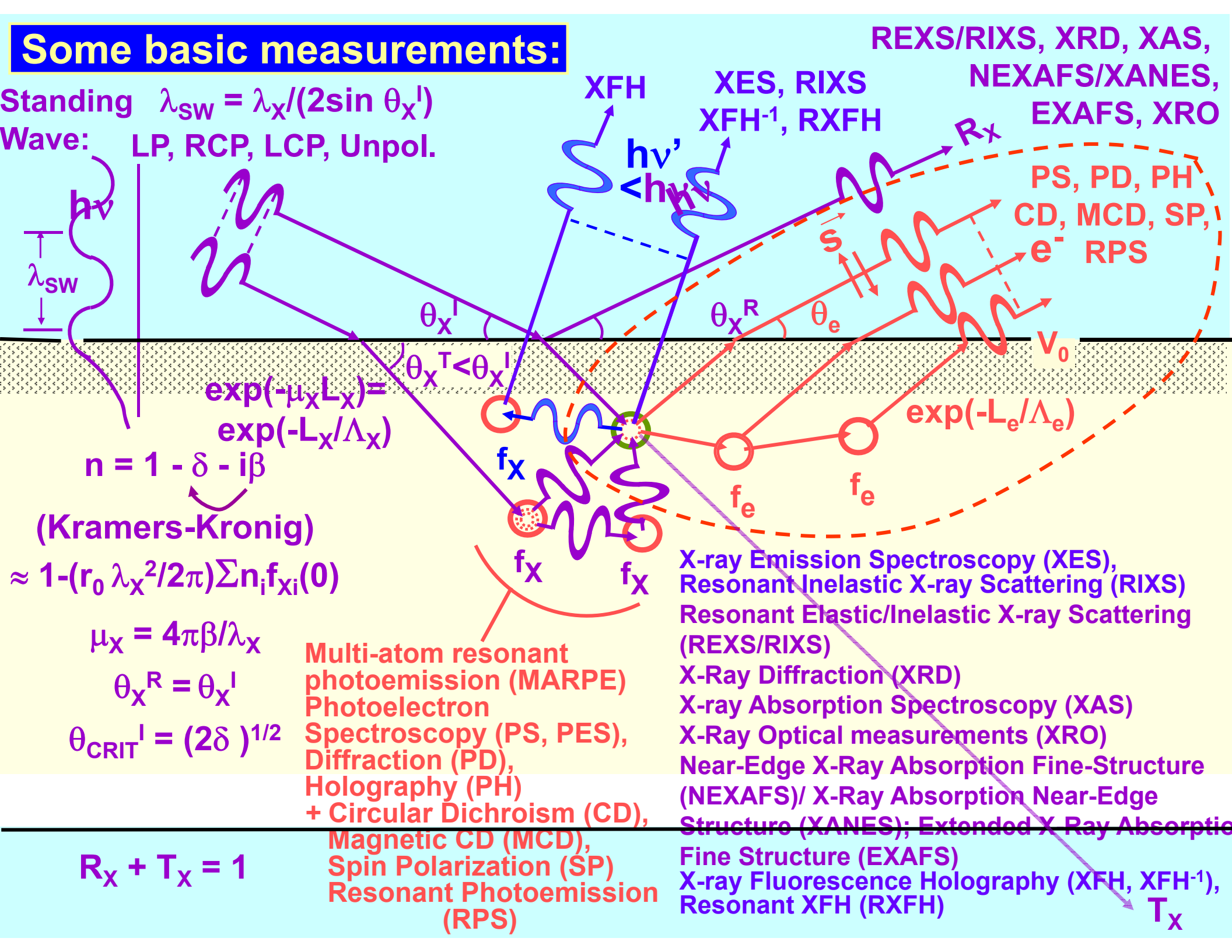




Yang et al., J. Appl. Phys. 113, 073513 (2013)

# Some basic measurements:



**Basic Concepts:**

A Little Electronic Structure
The X-Ray-Based Experiments
X-Ray Sources, Synchrotron Radiation, Free Electron Lasers

**Core-Level Photoemission**

Intensities and Quantitative Analysis, the 3-Step Model
Varying Surface and Bulk Sensitivity
Chemical Shifts
Multiplet Splittings
Electron Screening and Satellite Structure
Magnetic and Non-Magnetic Dichroism
Resonant Photoemission
Photoelectron Diffraction and Holography

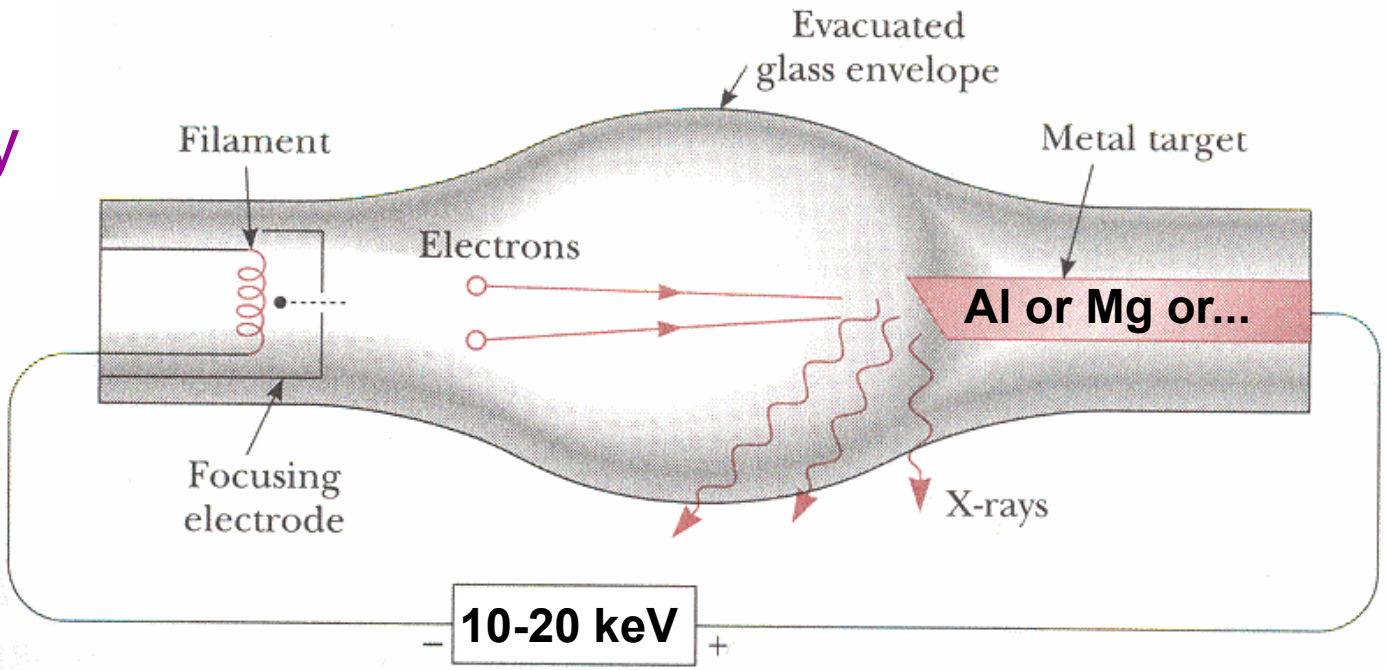
**Valence-Level Photoemission**

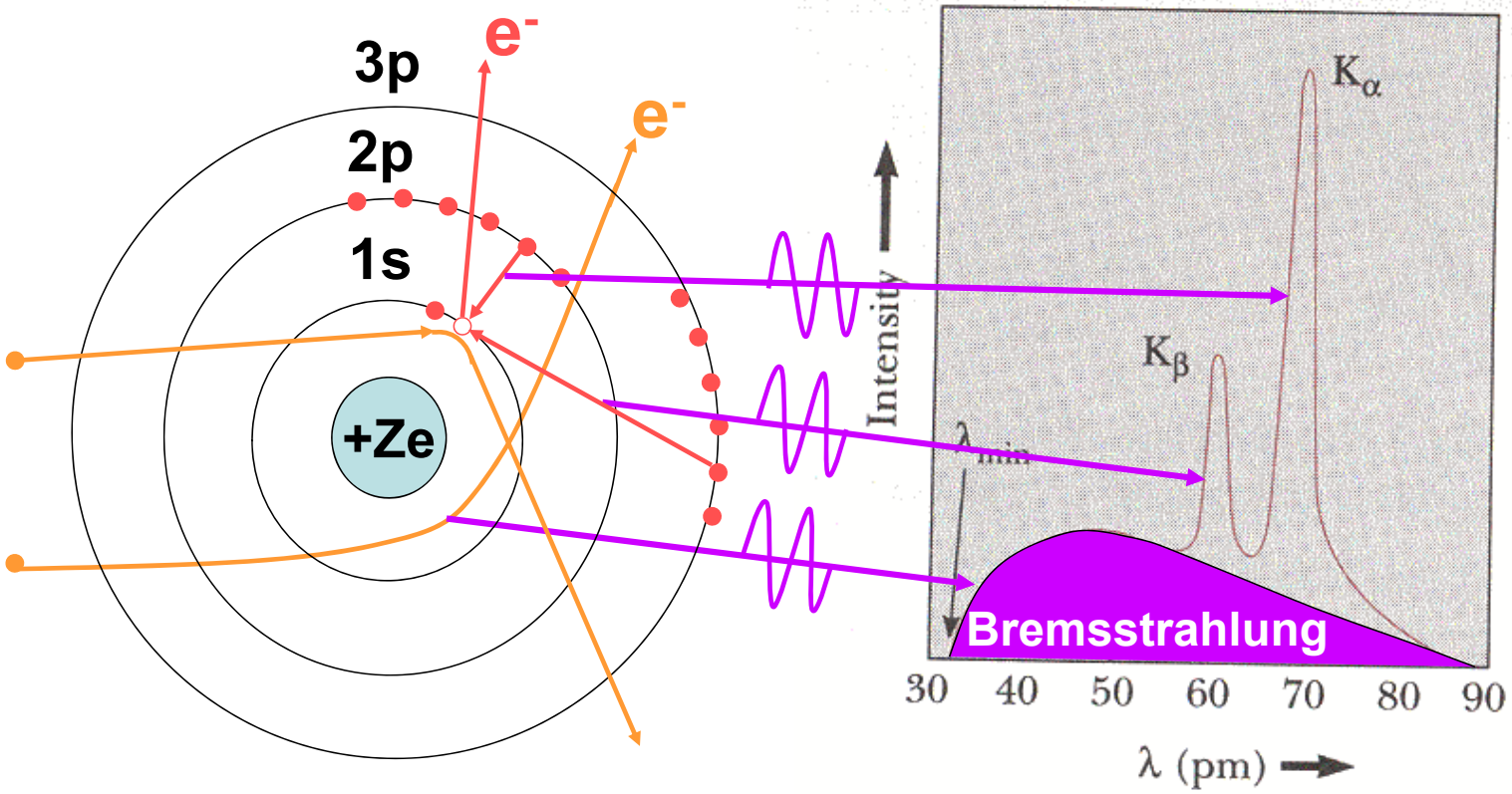
Band-Mapping in the Ultraviolet Photoemission Limit
Densities of States in the X-Ray Photoemission Limit

**Some New Directions**

Photoemission with Hard X-Rays (throughout lectures)
Photoemission with Standing Wave Excitation
Photoemission with: Higher Pressures→multi-Torr→Atmosphere?
Spatial Resolution-Photoelectron Microscopy
Temporal Resolution

# Producing x-rays: the good old-fashioned way



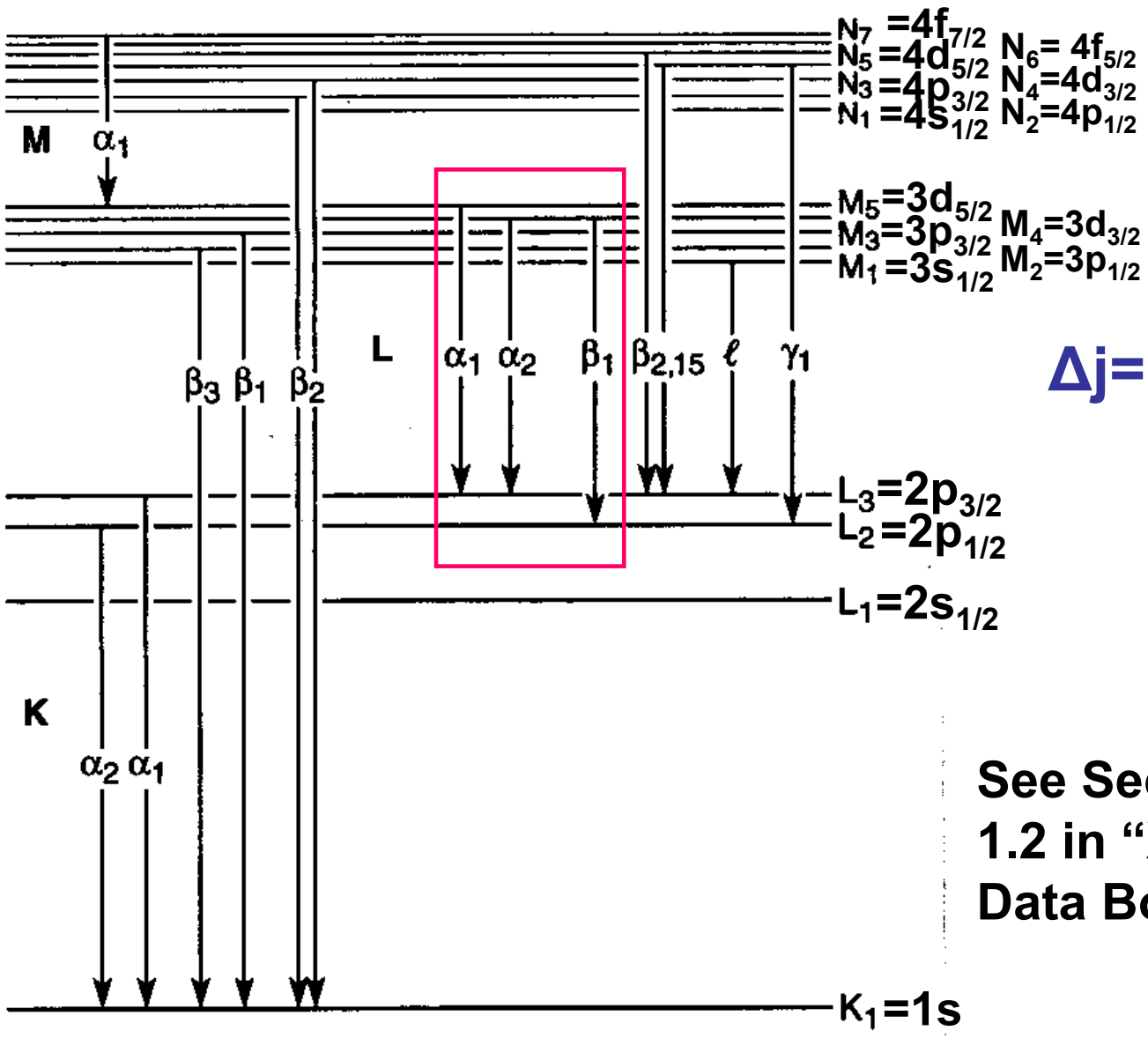




**See Section 1.2 in "X-Ray Data Booklet"**

## X-Ray Nomenclature (from "X-Ray Data Booklet")

**In general:**

$nl$ — Spin-orbit — $nl_{j=l+1/2}$, $nl_{j=l-1/2}$




**Δj=0,±1**

**See Section 1.2 in "X-Ray Data Booklet"**

*Fig. 1-1. Transitions that give rise to the emission lines in Table 1-3.*

# X-Ray energies from the "X-Ray Data Booklet"

*Table 1-2. Photon energies, in electron volts, of principal K-, L-, and M-shell emission lines.*

| Element | $K\alpha_1$ | $K\alpha_2$ | $K\beta_1$ | $L\alpha_1$ | $L\alpha_2$ | $L\beta_1$ | $L\beta_2$ | $L\gamma_1$ | $M\alpha_1$ |
|---|---|---|---|---|---|---|---|---|---|
| 3 Li | 54.3 | | | | | | | | |
| 4 Be | 108.5 | | | | | | | | |
| 5 B | 183.3 | | | | | | | | |
| 6 C | 277 | | | | | | | | |
| 7 N | 392.4 | | | | | | | | |
| 8 O | 524.9 | | | | | | | | |
| 9 F | 676.8 | | | | | | | | |
| 10 Ne | 848.6 | 848.6 | | | | | | | |
| 11 Na | 1,040.98 | 1,040.98 | 1,071.1 | | | | | | |
| 12 Mg | 1,253.60 | 1,253.60 | 1,302.2 | | | | | | |
| 13 Al | 1,486.70 | 1,486.27 | 1,557.45 | | | | | | |
| 14 Si | 1,739.98 | 1,739.38 | 1,835.94 | | | | | | |
| 15 P | 2,013.7 | 2,012.7 | 2,139.1 | | | | | | |
| 16 S | 2,307.84 | 2,306.64 | 2,464.04 | | | | | | |
| 17 Cl | 2,622.39 | 2,620.78 | 2,815.6 | | | | | | |
| 18 Ar | 2,957.70 | 2,955.63 | 3,190.5 | | | | | | |
| 19 K | 3,313.8 | 3,311.1 | 3,589.6 | | | | | | |
| 20 Ca | 3,691.68 | 3,688.09 | 4,012.7 | 341.3 | 341.3 | 344.9 | | | |
| 21 Sc | 4,090.6 | 4,086.1 | 4,460.5 | 395.4 | 395.4 | 399.6 | | | |

Popular laboratory sources for common soft x-ray photoelectron spectroscopy

# X-Ray energies from the "X-Ray Data Booklet"

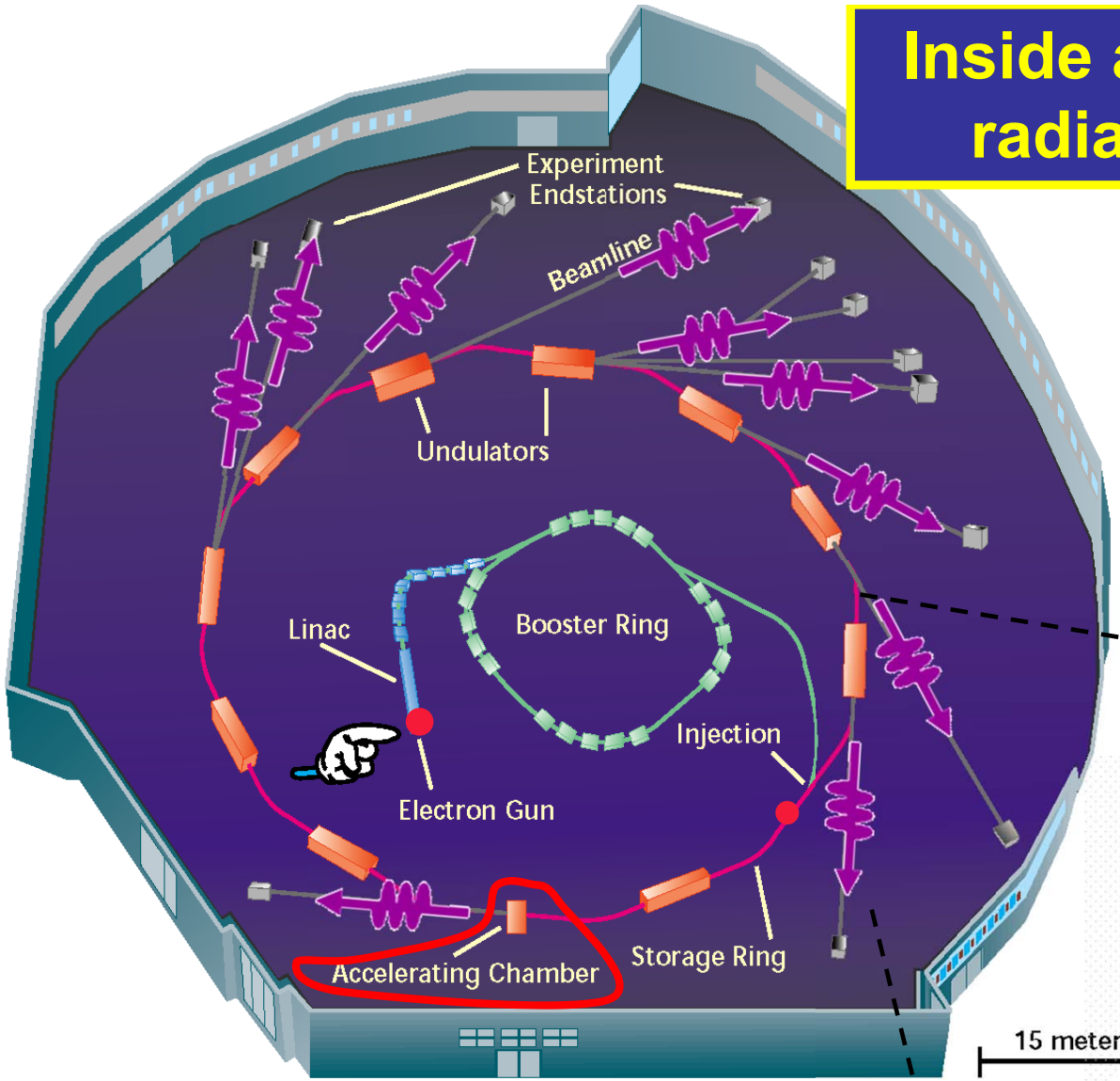
*Table 1-2. Energies of x-ray emission lines (continued).*

| Element | $K\alpha_1$ | $K\alpha_2$ | $K\beta_1$ | $L\alpha_1$ | $L\alpha_2$ | $L\beta_1$ | $L\beta_2$ | $L\gamma_1$ | $M\alpha_1$ |
|---|---|---|---|---|---|---|---|---|---|
| 22 Ti | 4,510.84 | 4,504.86 | 4,931.81 | 452.2 | 452.2 | 458.4 | | | |
| 23 V | 4,952.20 | 4,944.64 | 5,427.29 | 511.3 | 511.3 | 519.2 | | | |
| 24 Cr | 5,414.72 | 5,405.509 | 5,946.71 | 572.8 | 572.8 | 582.8 | | | |
| 25 Mn | 5,898.75 | 5,887.65 | 6,490.45 | 637.4 | 637.4 | 648.8 | | | |
| 26 Fe | 6,403.84 | 6,390.84 | 7,057.98 | 705.0 | 705.0 | 718.5 | | | |
| 27 Co | 6,930.32 | 6,915.30 | 7,649.43 | 776.2 | 776.2 | 791.4 | | | |
| 28 Ni | 7,478.15 | 7,460.89 | 8,264.66 | 851.5 | 851.5 | 868.8 | | | |
| 29 Cu | 8,047.78 | 8,027.83 | 8,905.29 | 929.7 | 929.7 | 949.8 | | | |
| 30 Zn | 8,638.86 | 8,615.78 | 9,572.0 | 1,011.7 | 1,011.7 | 1,034.7 | | | |
| 31 Ga | 9,251.74 | 9,224.82 | 10,264.2 | 1,097.92 | 1,097.92 | 1,124.8 | | | |
| 32 Ge | 9,886.42 | 9,855.32 | 10,982.1 | 1,188.00 | 1,188.00 | 1,218.5 | | | |
| 33 As | 10,543.72 | 10,507.99 | 11,726.2 | 1,282.0 | 1,282.0 | 1,317.0 | | | |
| 34 Se | 11,222.4 | 11,181.4 | 12,495.9 | 1,379.10 | 1,379.10 | 1,419.23 | | | |
| 35 Br | 11,924.2 | 11,877.6 | 13,291.4 | 1,480.43 | 1,480.43 | 1,525.90 | | | |
| 36 Kr | 12,649 | 12,598 | 14,112 | 1,586.0 | 1,586.0 | 1,636.6 | | | |
| 37 Rb | 13,395.3 | 13,335.8 | 14,961.3 | 1,694.13 | 1,692.56 | 1,752.17 | | | |
| 38 Sr | 14,165 | 14,097.9 | 15,835.7 | 1,806.56 | 1,804.74 | 1,871.72 | | | |
| 39 Y | 14,958.4 | 14,882.9 | 16,737.8 | 1,922.56 | 1,920.47 | 1,995.84 | | | |
| 40 Zr | 15,775.1 | 15,690.9 | 17,667.8 | 2,042.36 | 2,039.9 | 2,124.4 | 2,219.4 | 2,302.7 | |

**Popular laboratory sources for hard x-ray photoelectron spectroscopy**

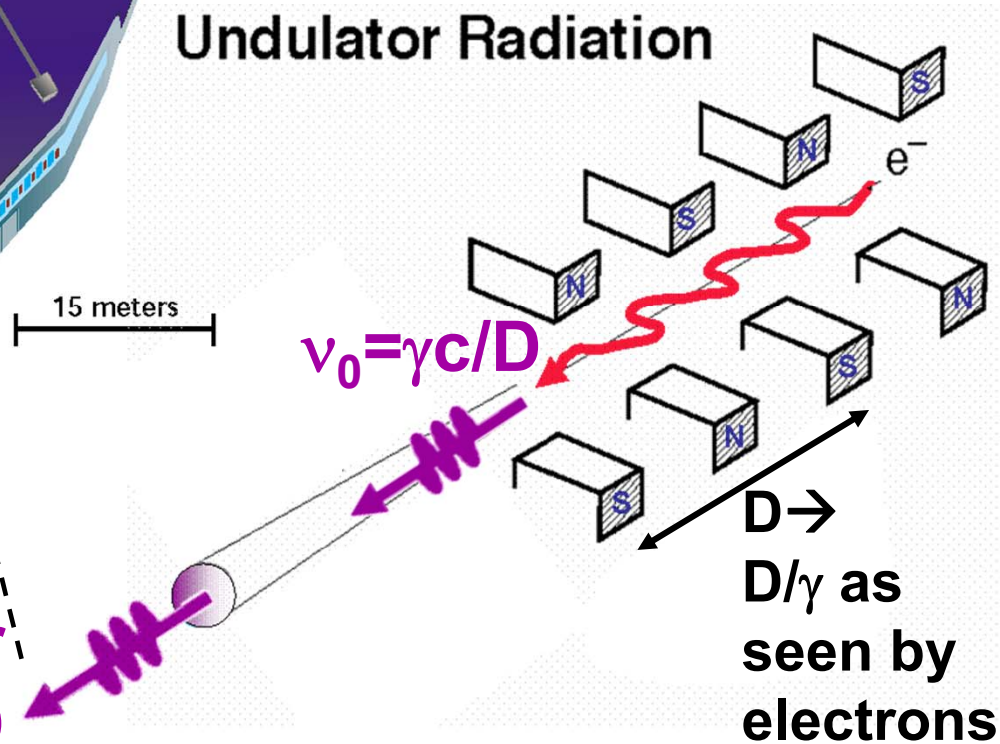
Liquid jet-Scienta

# Inside a synchrotron radiation source



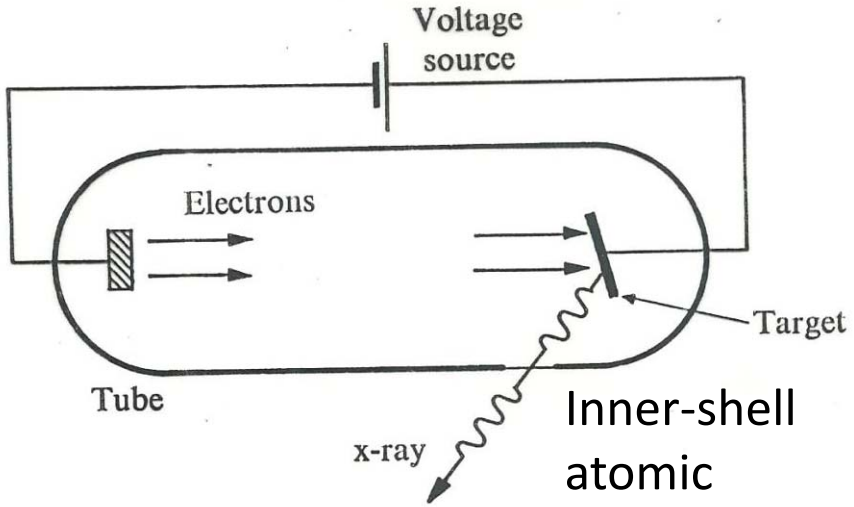

Radiofrequency Cavity

Electron speed near c: 0.99999994 c, $\gamma$ = 3719 Einstein needed again—Special Relativity



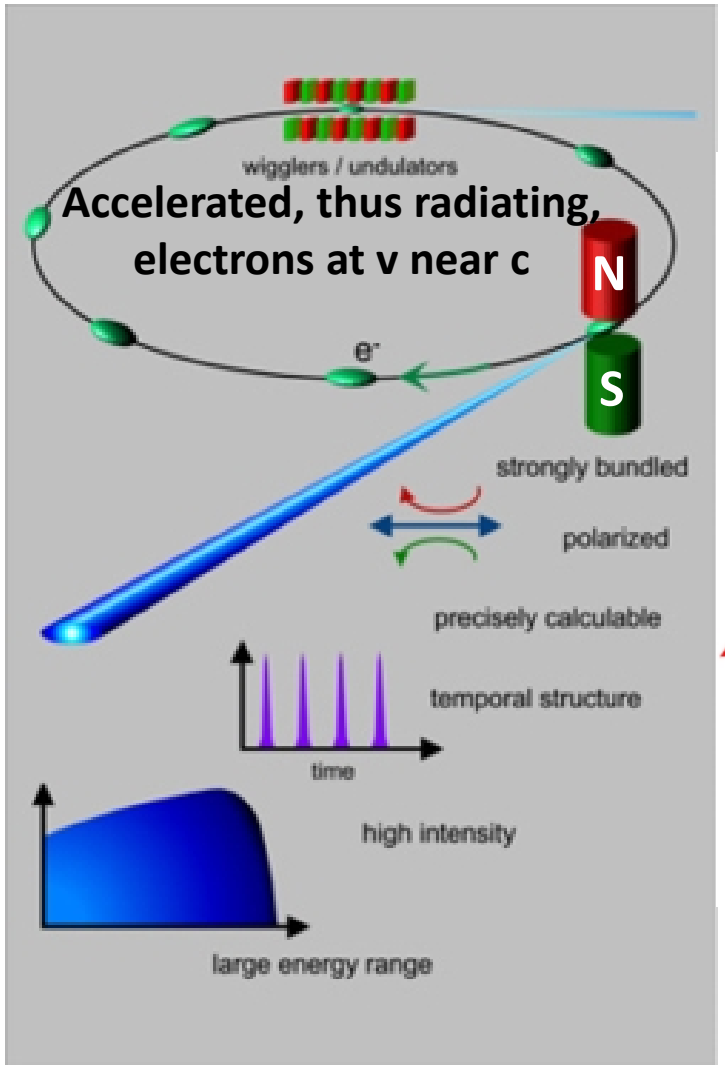
# The generation of x-rays:

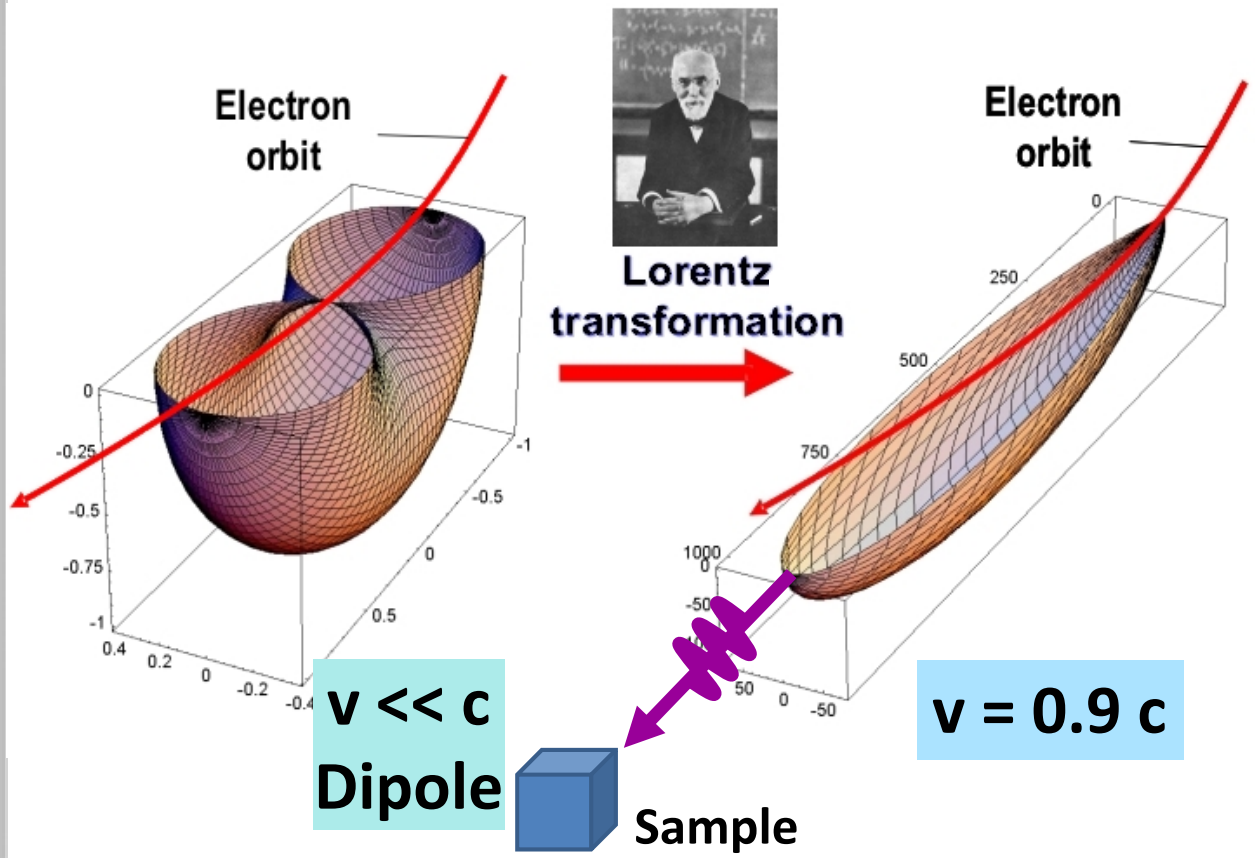
## An x-ray tube:



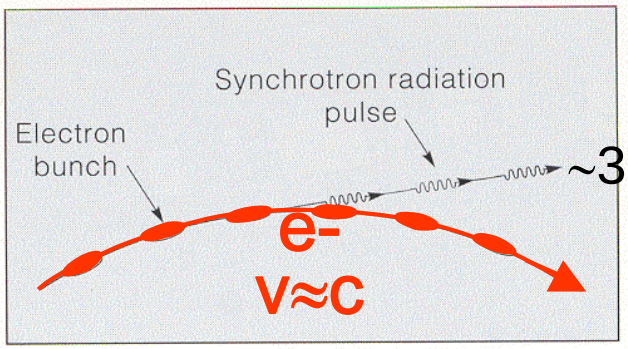

Inner-shell atomic transitions

## Synchrotron radiation: e.g. the Berkeley Advanced Light Source

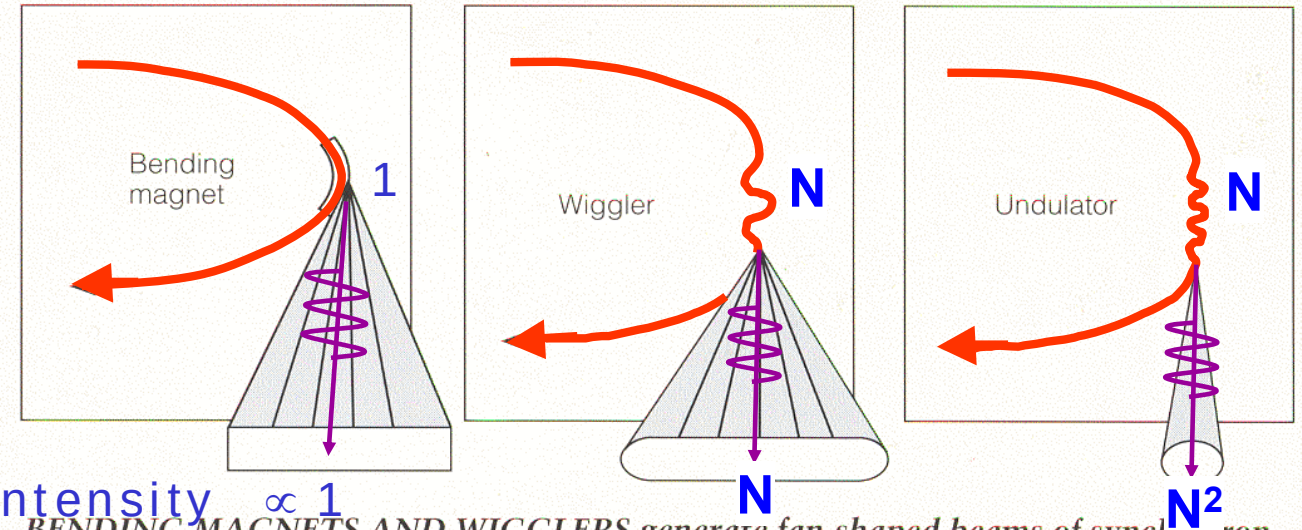


# Synchrotron Radiation Sources:

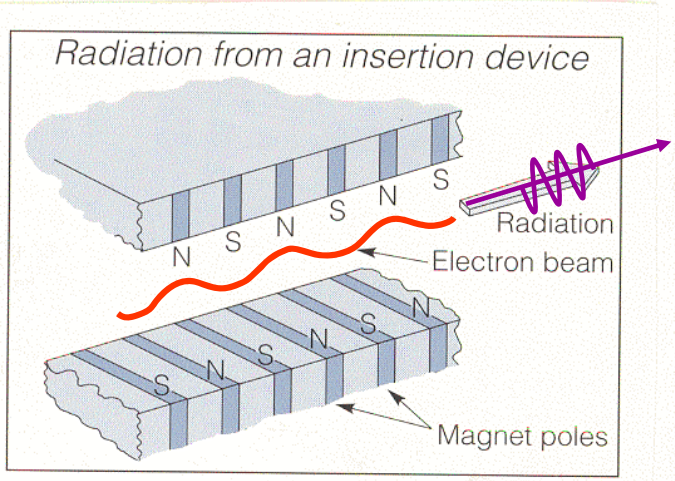



~30 psec long



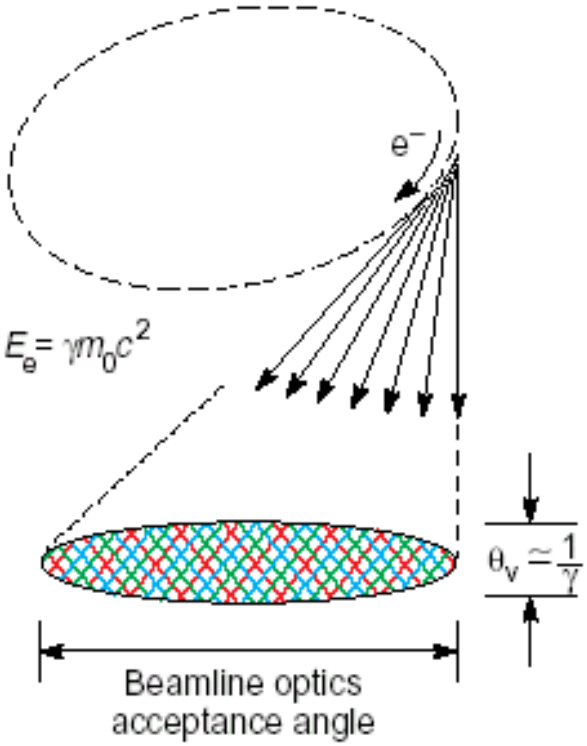

Intensity ∝ 1

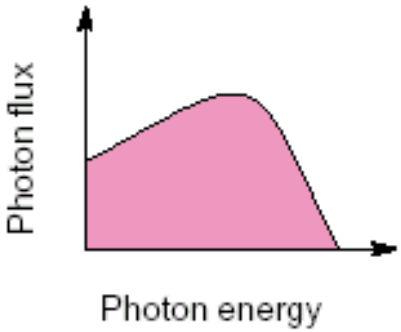
*BENDING MAGNETS AND WIGGLERS generate fan-shaped beams of synchrotron radiation, whereas undulators emit pencil-thin beams.*



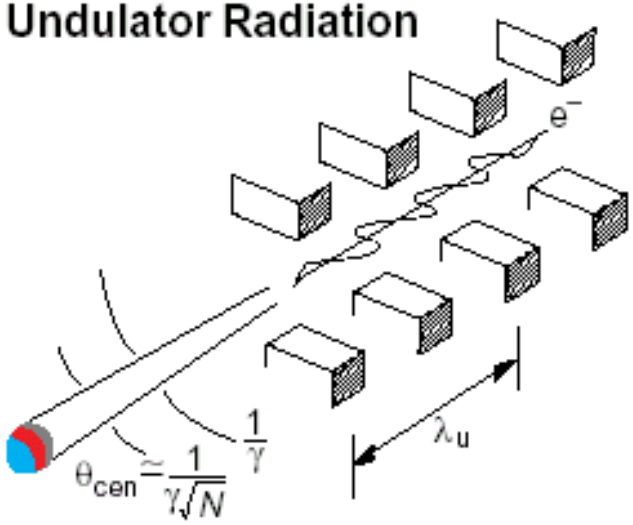
## Bend-Magnet Radiation

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$




## Undulator Radiation



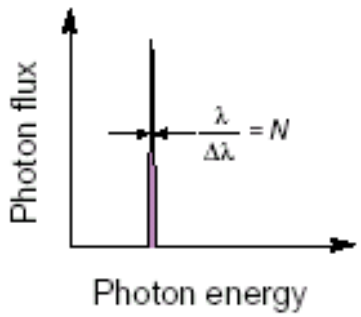

$$\lambda_x = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2} + \gamma^2\theta^2\right)$$

$$K = \frac{eB_0\lambda_u}{2\pi m_0 c}$$

In the central radiation cone:

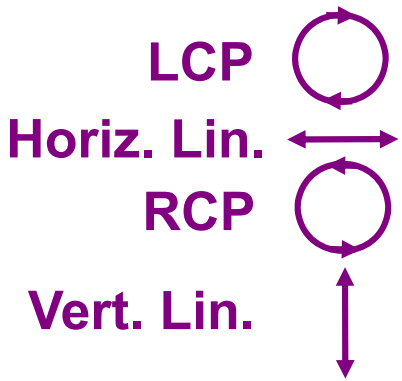
$$\frac{\Delta\omega}{\omega} \simeq \frac{1}{N}$$

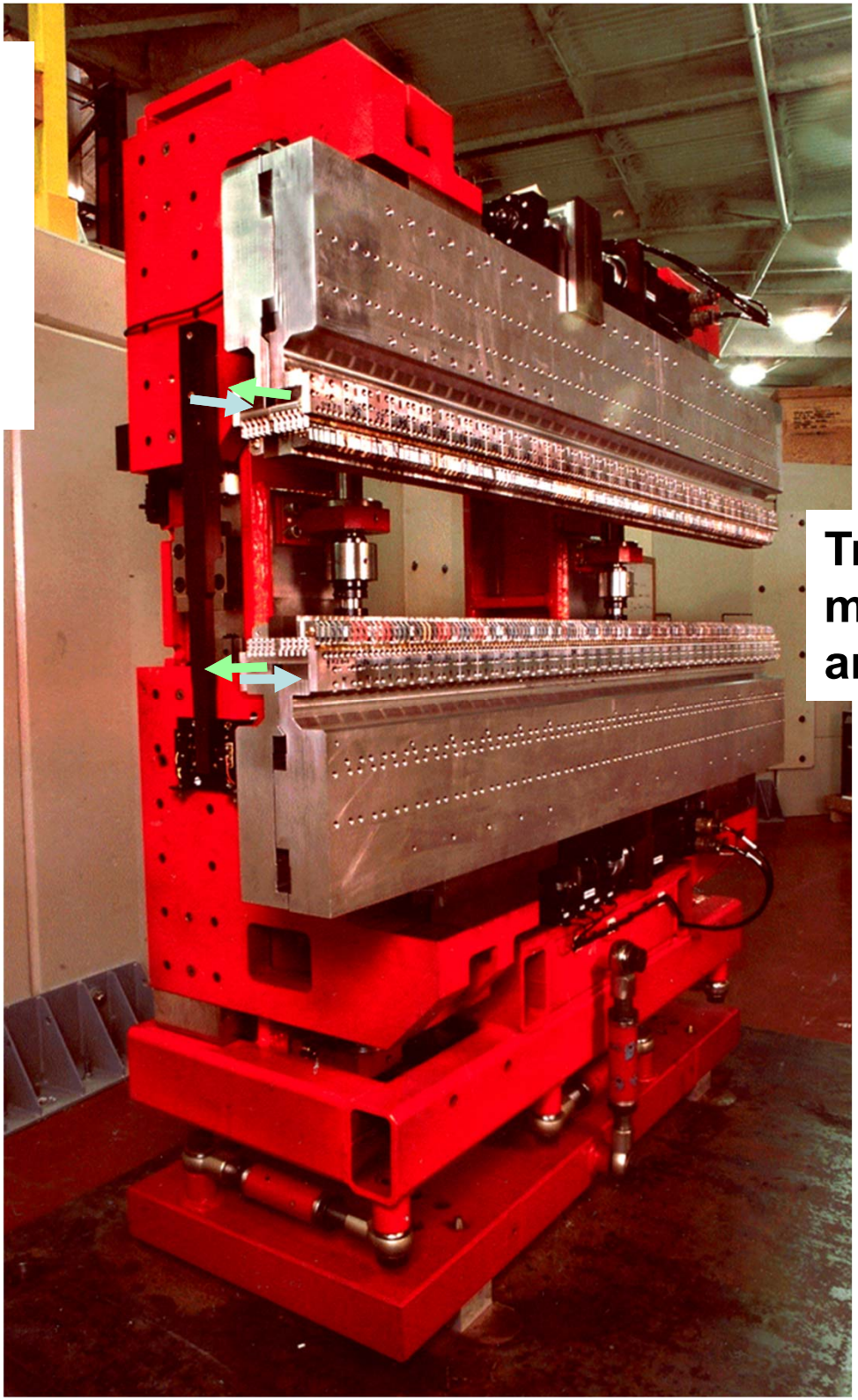
$$\theta_{cen} \simeq \frac{1}{\gamma\sqrt{N}}$$




***$\lambda_x$ as observed will increased if the magnetic field $B_0$ is increased or if viewed away from the axis by an angle θ***

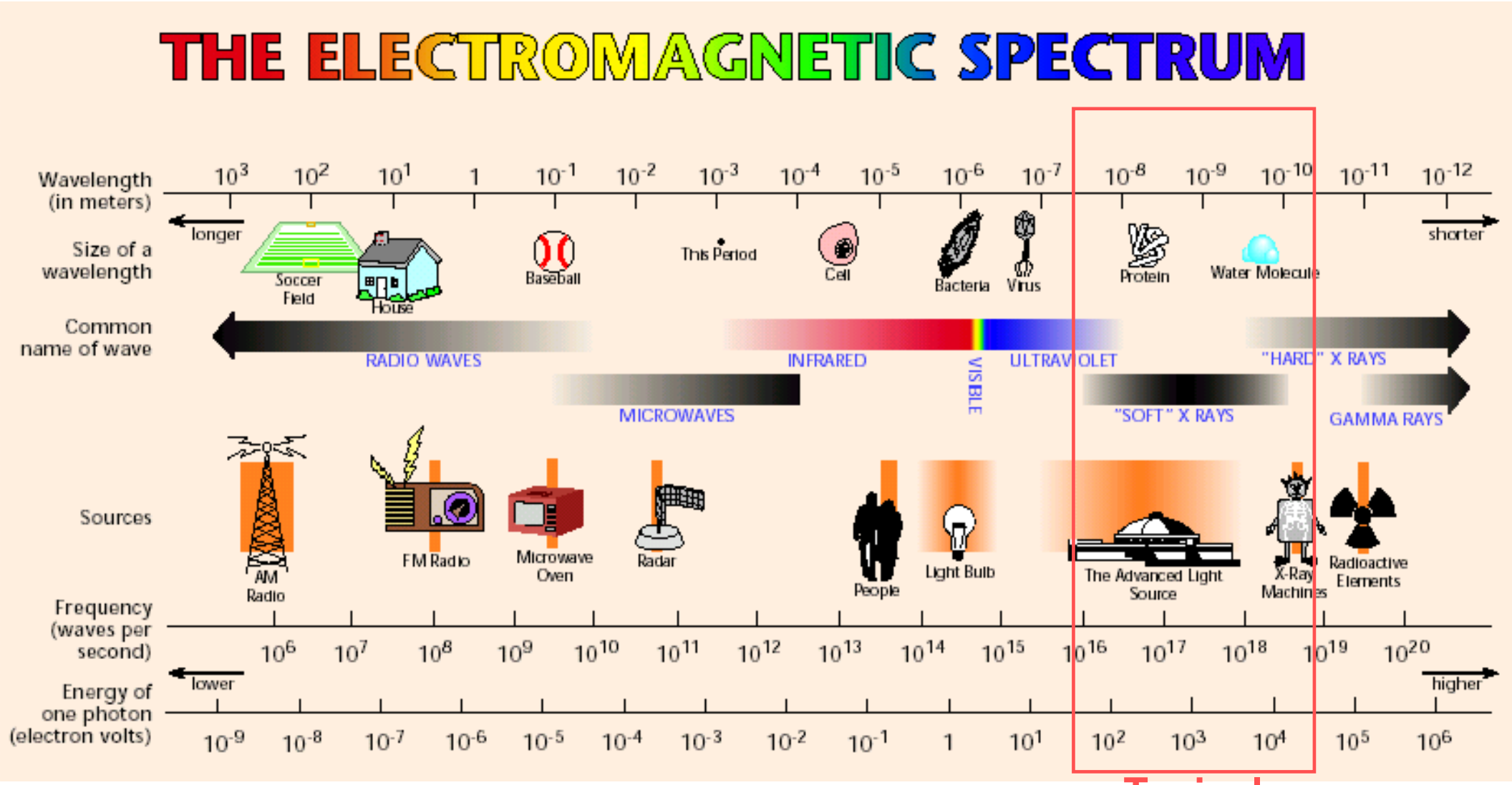
**Advanced Light Source-- Sasaki-Carr Elliptically-Polarized Undulator: Variable light polarization**



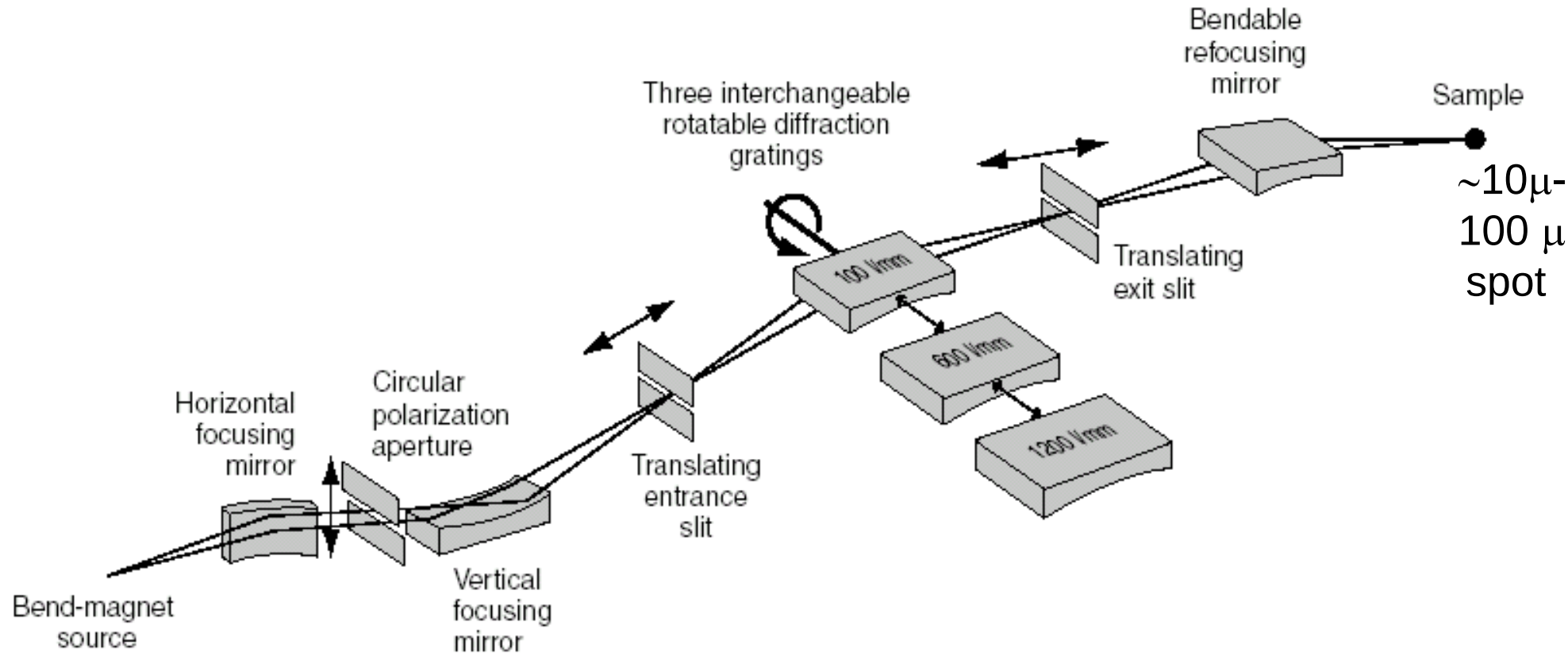
**Translating magnet arrays**

**[Can also vary polarization to LCP, RCP by going above and below the orbit plane in a bend magnet]**



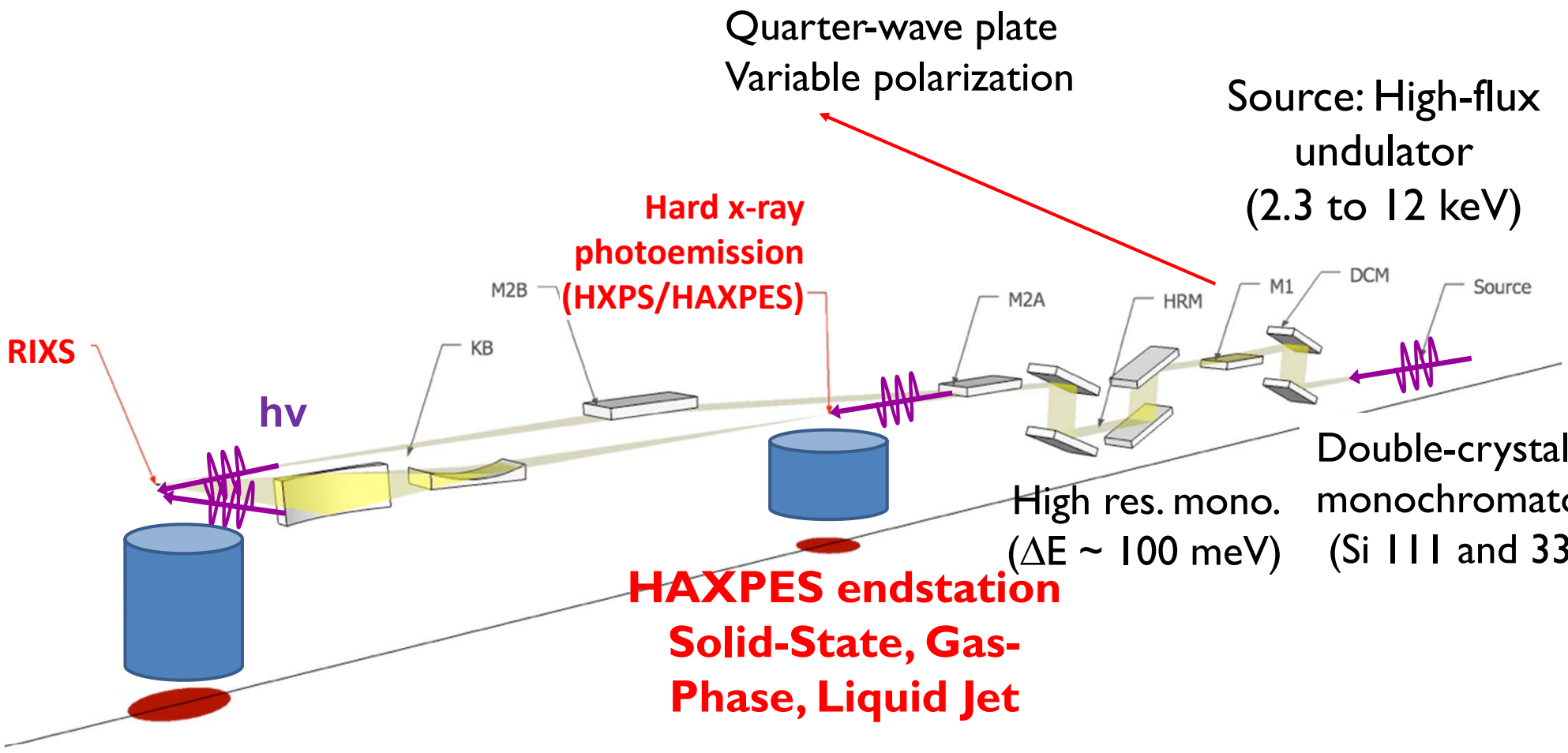

**Typical surface/materials science expts.**

# Advanced Light Source--
# Typical Soft X-Ray Spectroscopy Beamline Layout: to ca. 1500 eV



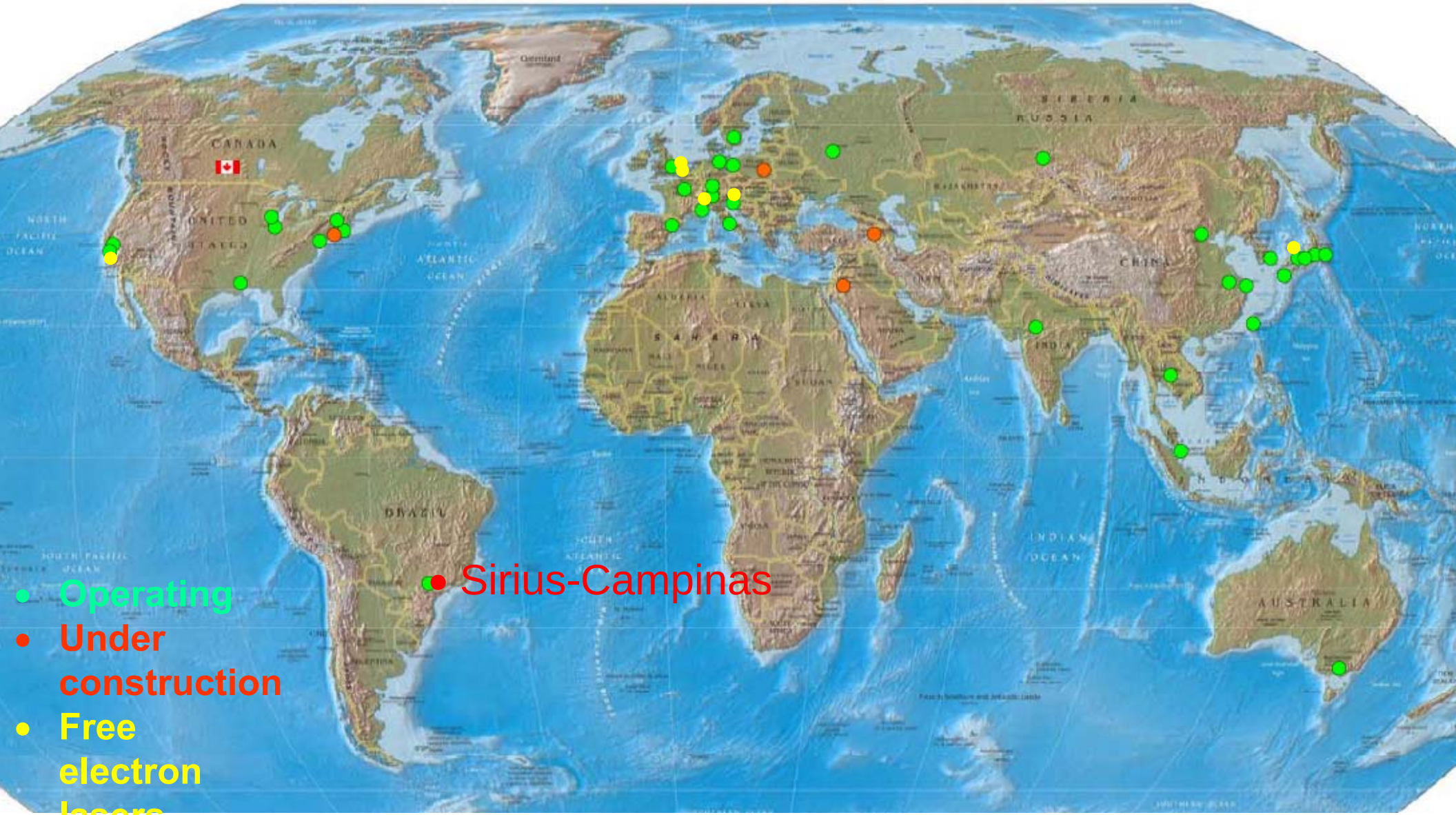

*Schematic layout of Beamline 9.3.2.*

# Soleil (Paris)—Typical hard x-ray spectroscopy beamline




J.-P. Rueff, D. Ceolin, M. Simon, J. Rault

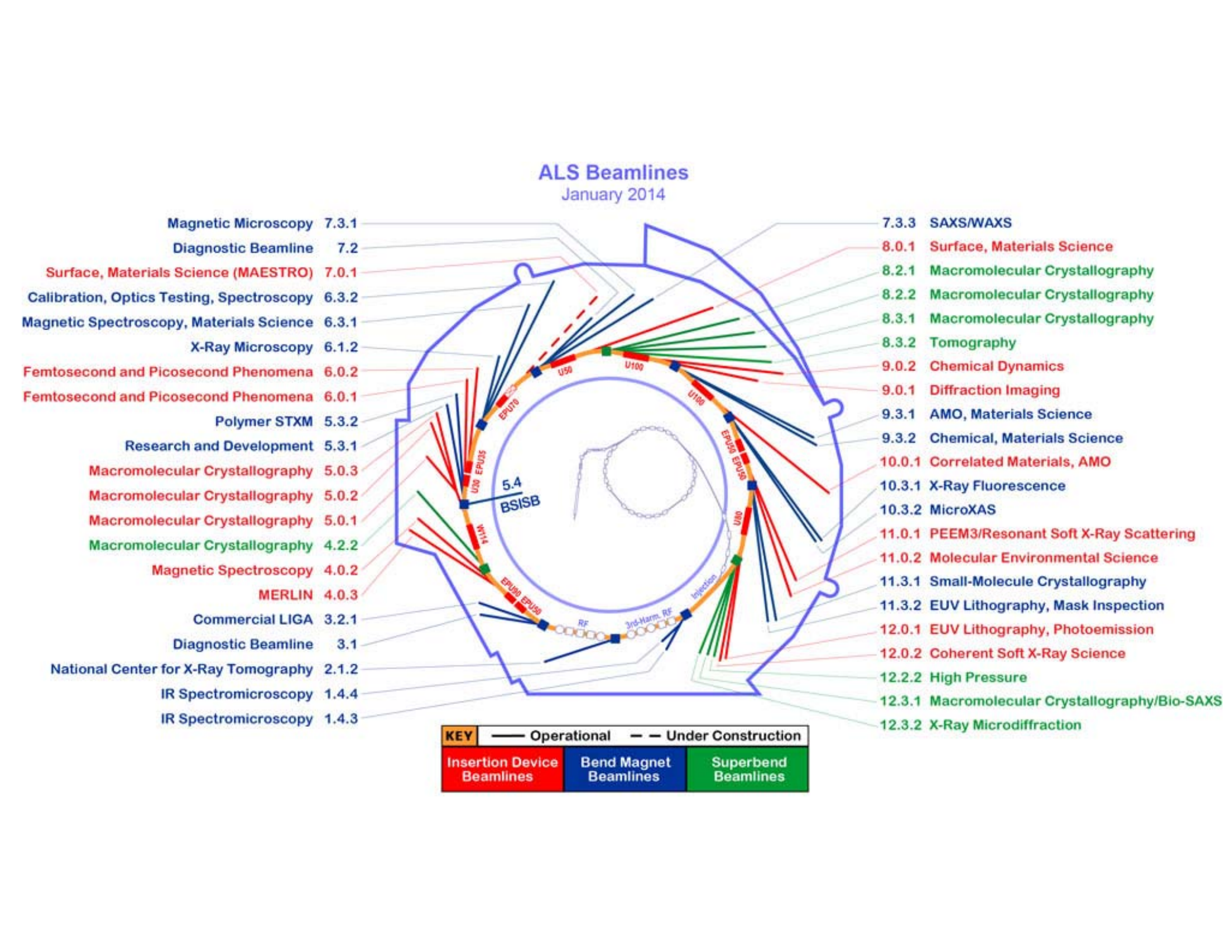
# Synchrotron radiation sources of the world- about 41 and growing
# Free-electron laser (VUV, X-ray)- about 5 and growing




San Francisco
Marin County
UC Berkeley
Advanced
Light Source
Group offices
& lab.

# ALS Beamlines

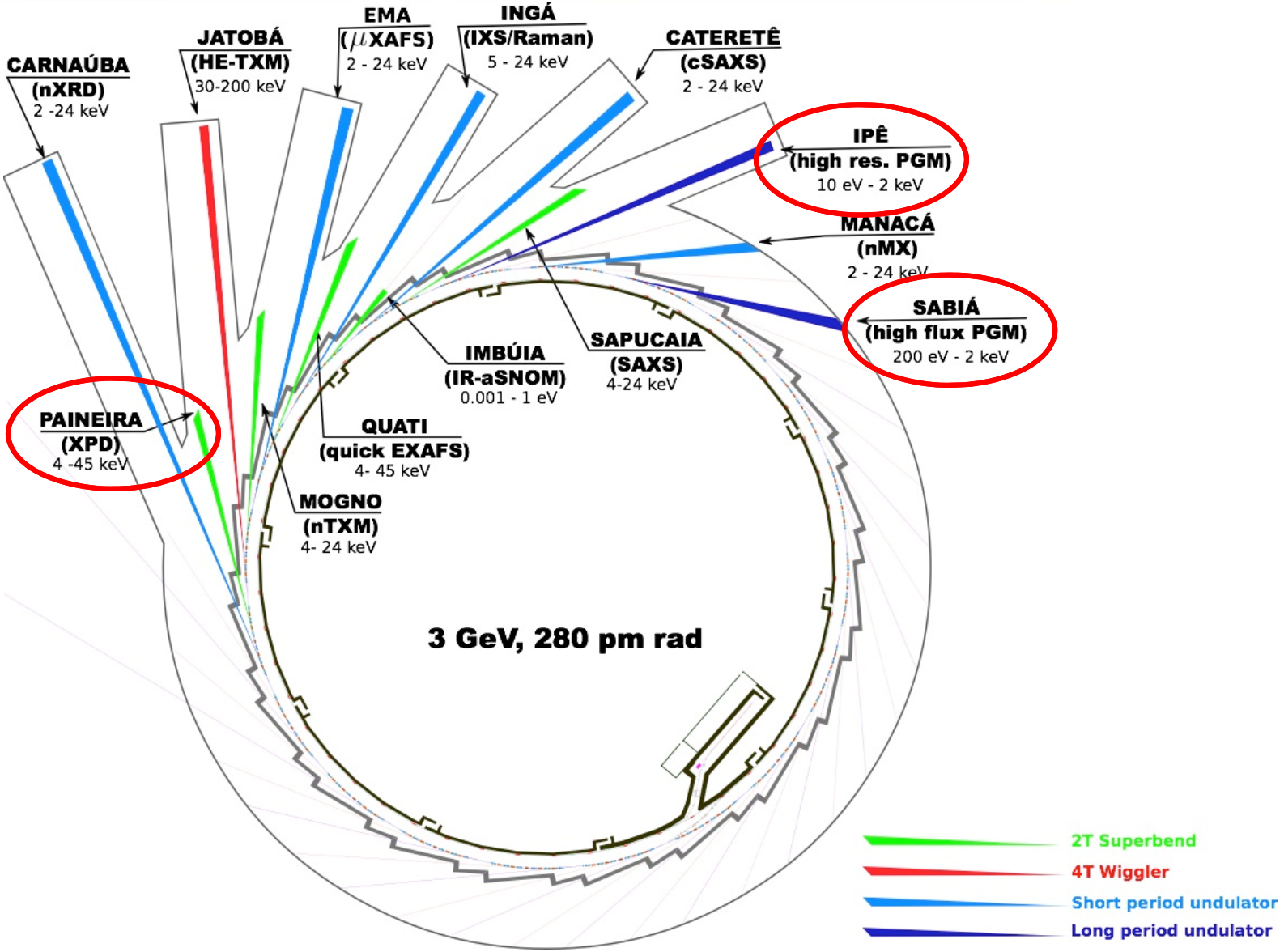
January 2014



# SIRIUS

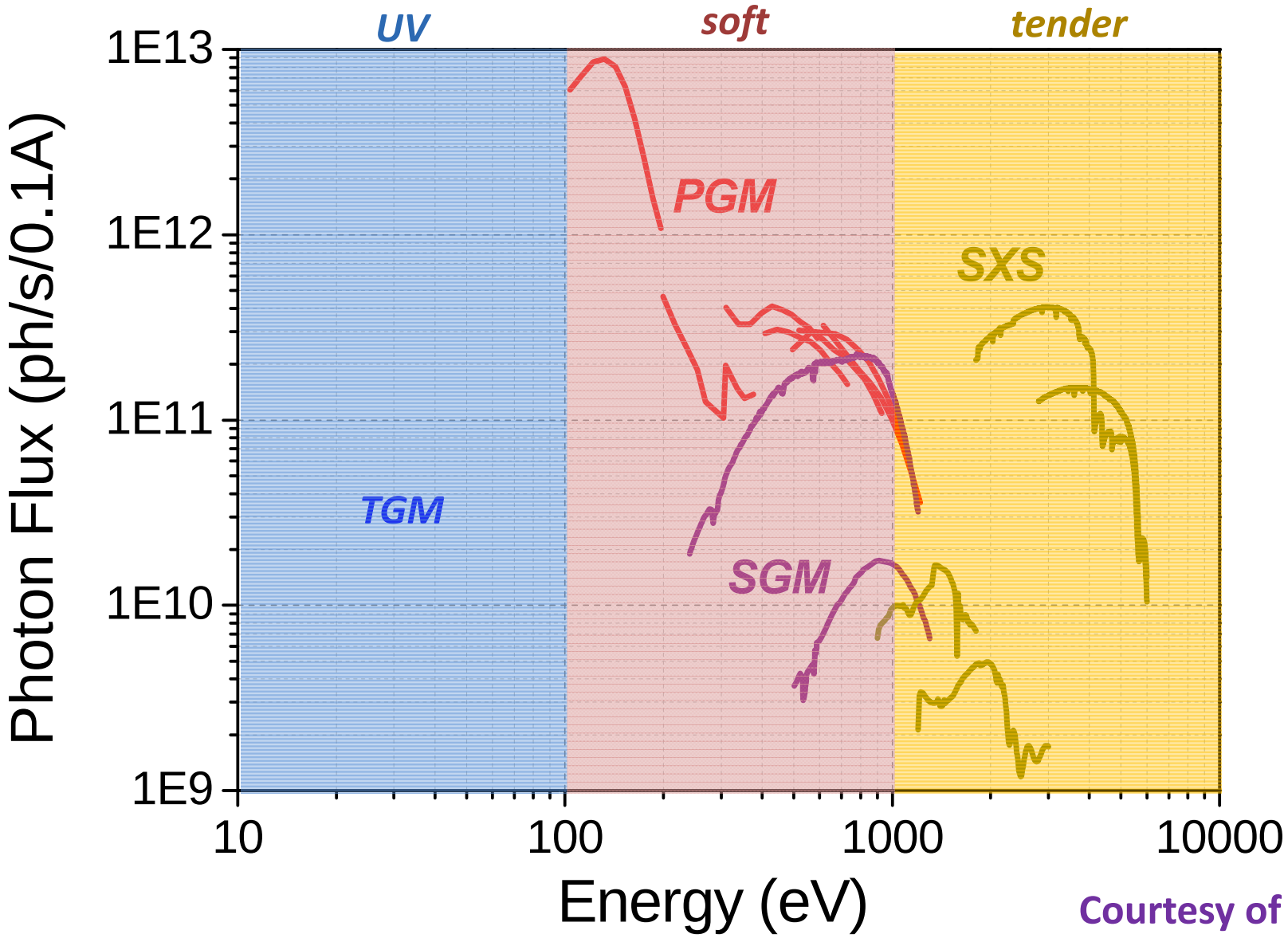
- 3 GeV
- 13 beam lines in phase 1
- 280 pm electrons emittance
- Open to users in 2018→2019?

# SIRIUS: initial beam lines



# Low energy synchrotron radiation at UVX

4 beamlines covering from 3 eV to 6 KeV




***Spectroscopy***

- ✓ *XANES*
- ✓ *XMCD*
- ✓ *ARPES*
- ✓ *XPS*
- ✓ *XPD*
- ✓ *PEPICO*

***Scattering***

- ✓ *(M)RXRR*
- ✓ *RSAXS*

***Imaging***

- ✓ *PEEM*

**Courtesy of Tulio Rocha, LNLS**

# Soft X-ray Beamlines at Sirius

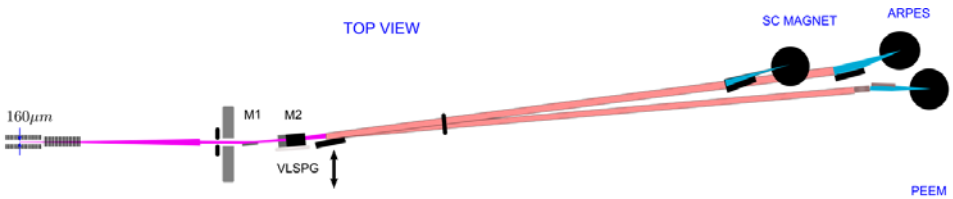
Laboratório Nacional de Luz Síncrotron

CNPEM

- ✓ EPU with 50mm period
- ✓ VLS PGM monochromator
- ✓ Multi-branches
- ✓ KB focusing

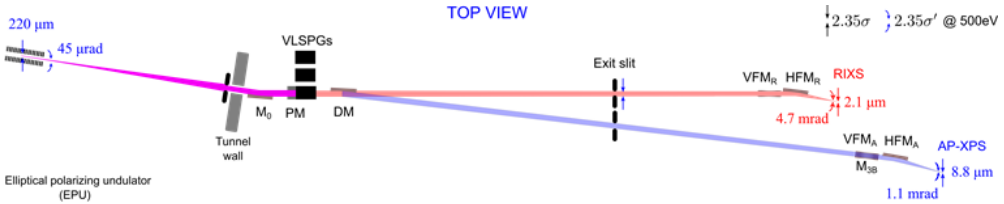
## *SABIÁ*

(Soft Xray Absorption spectroscoy and Imaging)




## *IPÊ*

(Inelastic and Photoelectron Spectroscopy)




## *ARPES, PEEM, XMCD/XMLD*

### *UHV condensed matter research*

- ✓ ***In situ sample preparation***
- ✓ *Magnetism*
- ✓ *Multiferroic materials*
- ✓ *Superconductivity*
- ✓ *Topological insulators*
- ✓ *Surface science*

## *Ambient Pressure XPS (AP-XPS), RIXS*

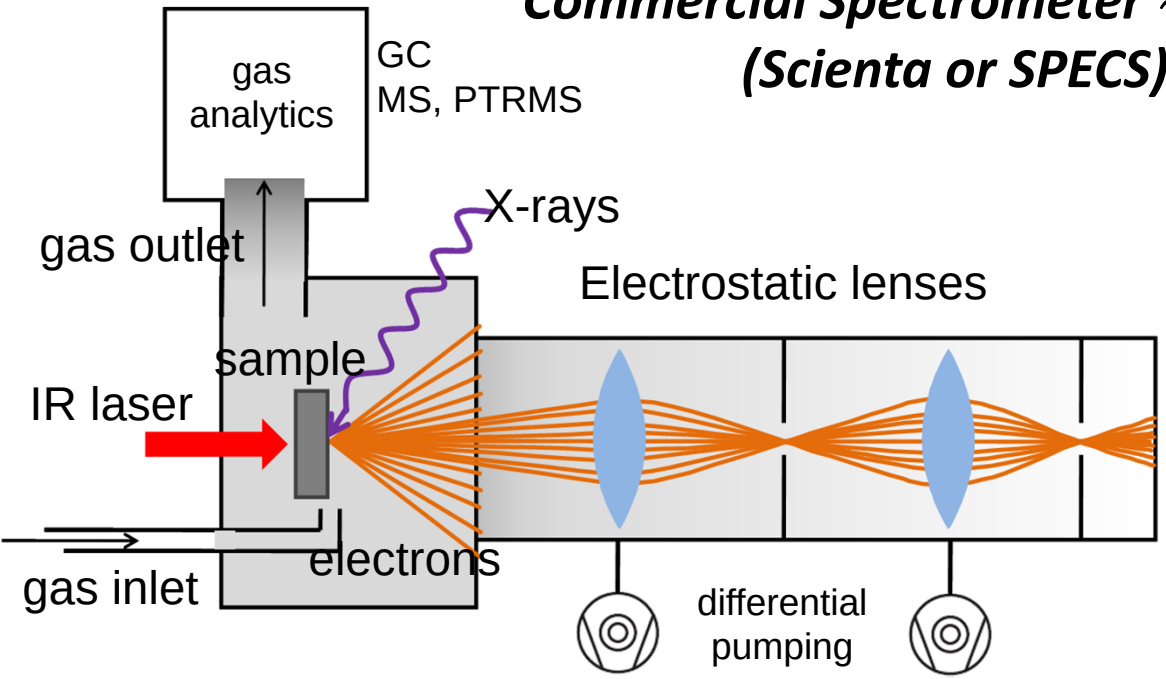
### *Environmental conditions*

- ✓ ***In situ measurements***
- ✓ *Catalysis*
- ✓ *Corrosion*
- ✓ *Hydrated surfaces*
- ✓ *Solvated molecules*
- ✓ *Correlated materials*

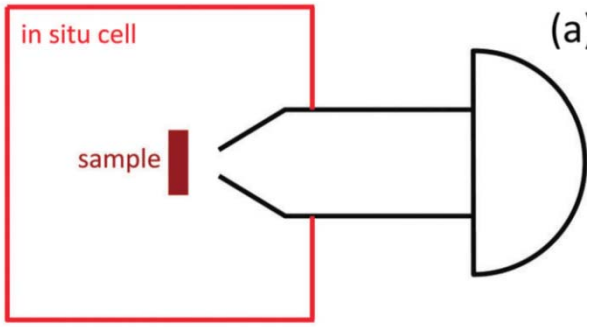
**Courtesy of Tulio Rocha, LNLS**

# APXPS endstation

***Commercial Spectrometer ~10 mbar (Scienta or SPECS)***

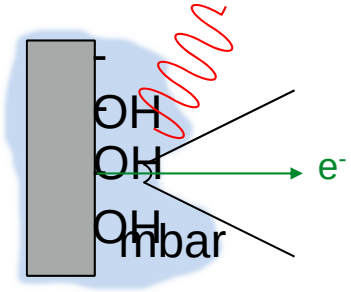



***Interchangeable Chambers***

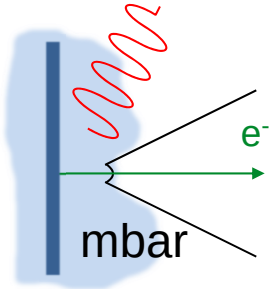



Probing interfaces

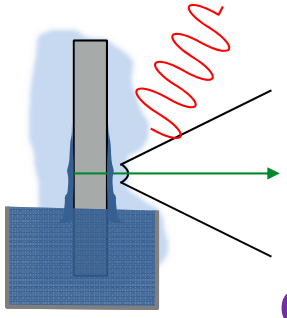
***Solid-gas***




***Liquid-gas***




***Solid-liquid***



***Requirements:***

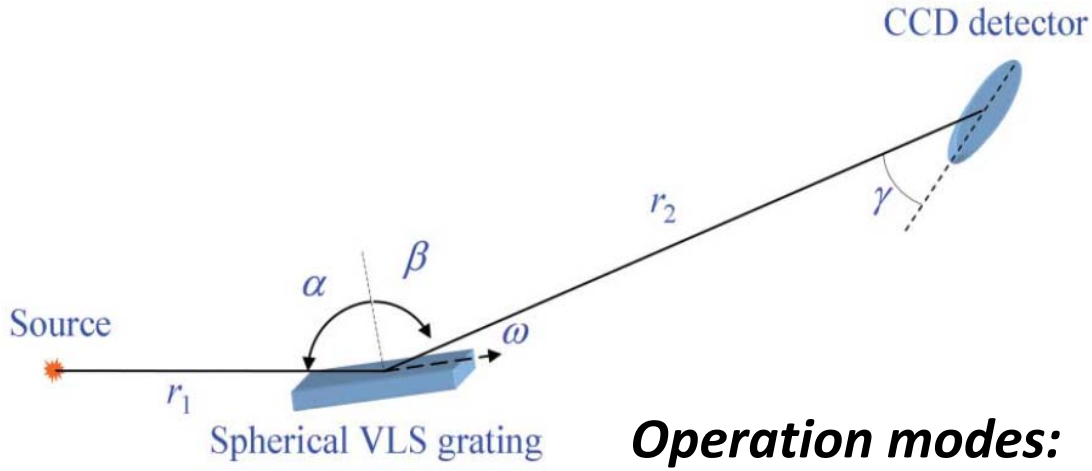
Spot size < 10 μm

E/ΔE ~ 5000

**Courtesy of Tulio Rocha, LNLS**

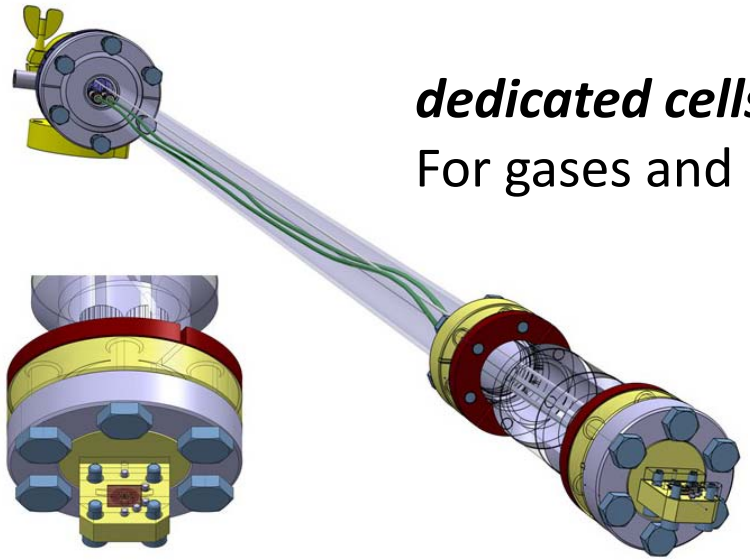
# RIXS endstation

- ✓ Spherical VLS
- ✓ Electron Multiplying CCD
- ✓ Variable 4-6 m arm




***Operation modes:***

- ✓ High resolution ~ 50000
- ✓ High transmission



***dedicated cells***
For gases and liquids

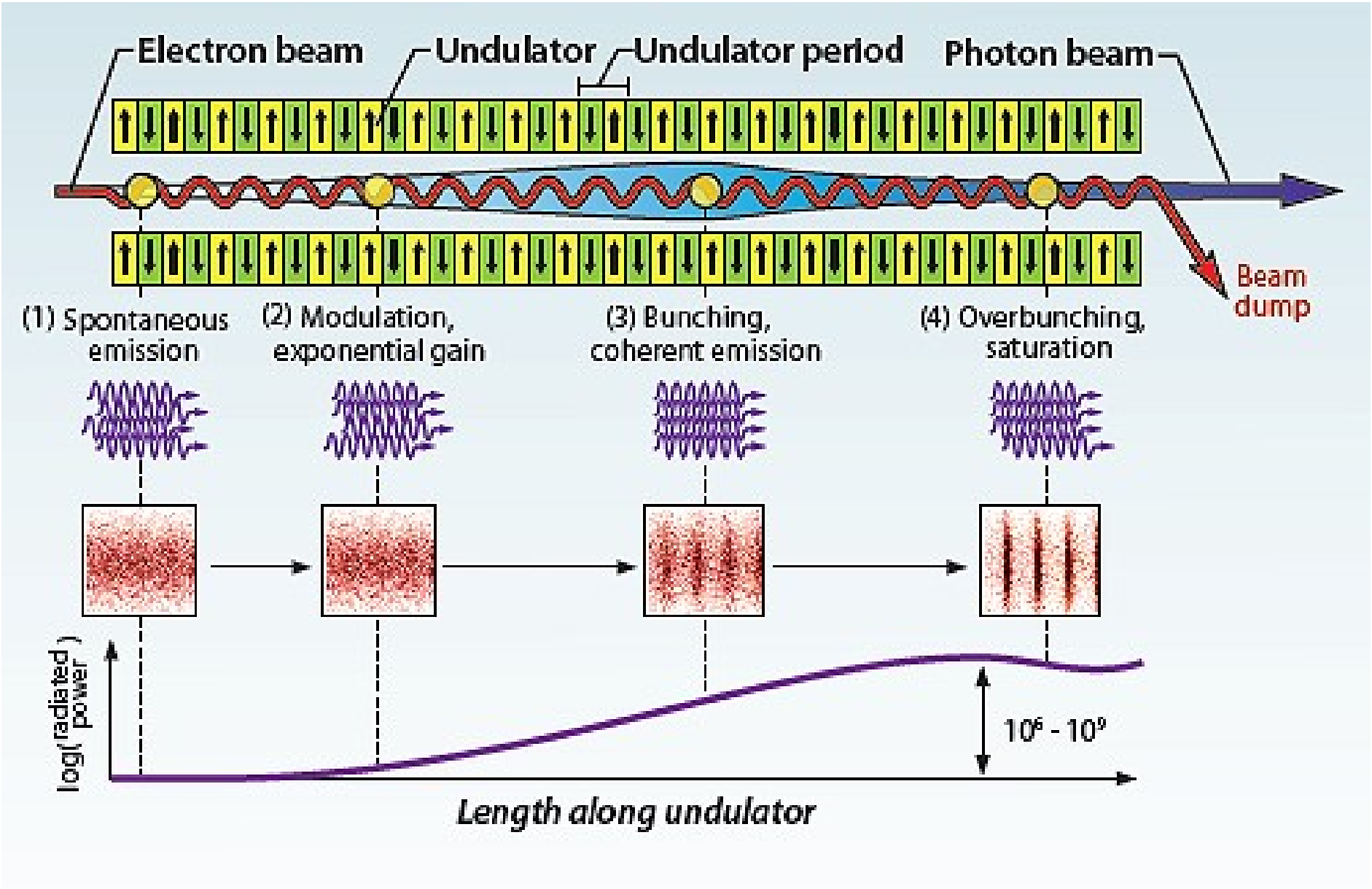
***Requirements:***

Spot size < 1 μm

E/ΔE ~ 60000 @ 500eV

Courtesy of Tulio Rocha, LNLS

# The Next Generation: The Free-Electron Laser



Average brightness

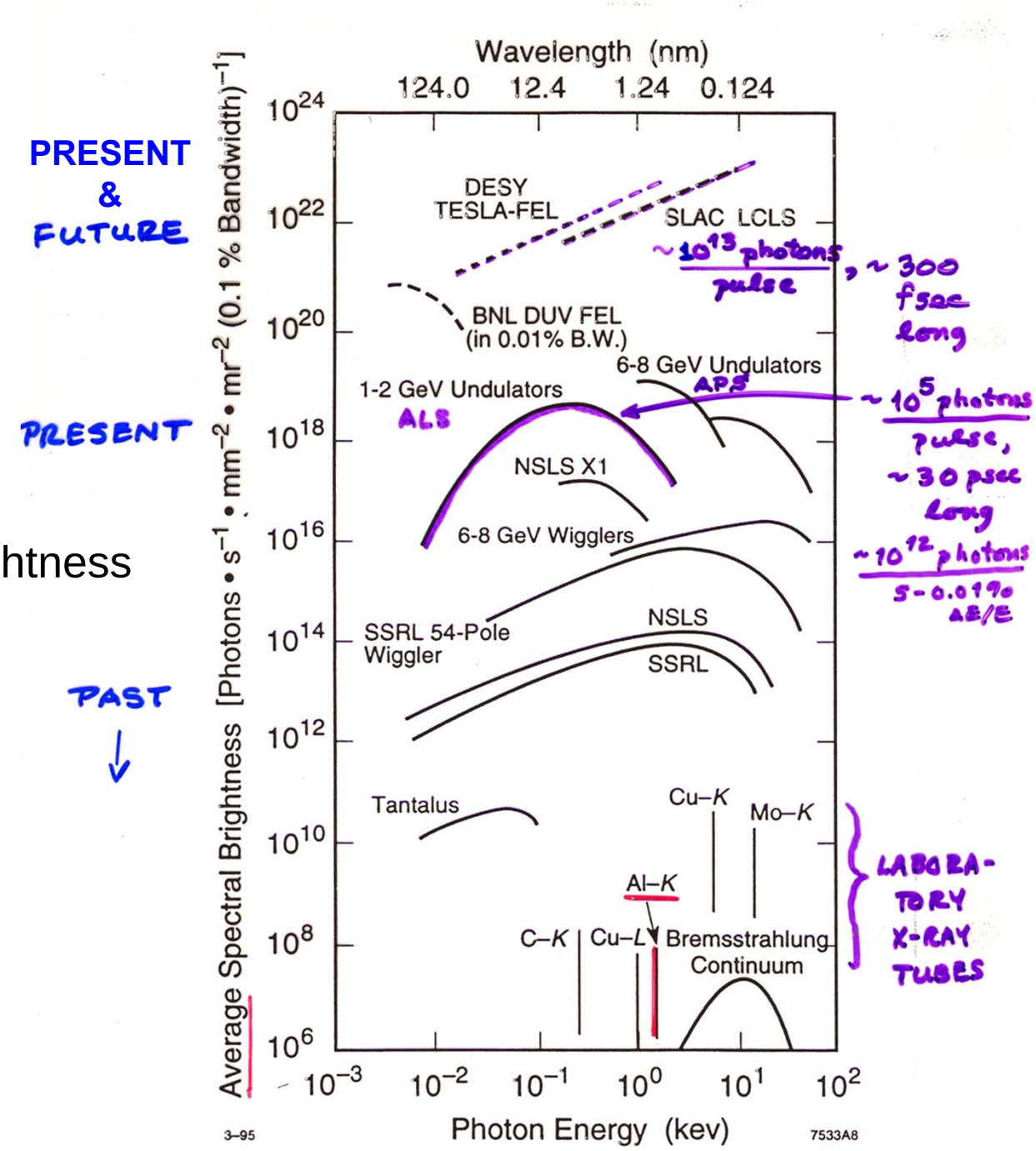



Fig. 2. Average brightness comparisons of the LCLS and other light sources, including proposed FELs at Brookhaven [14] and DESY [15].

Peak brightness

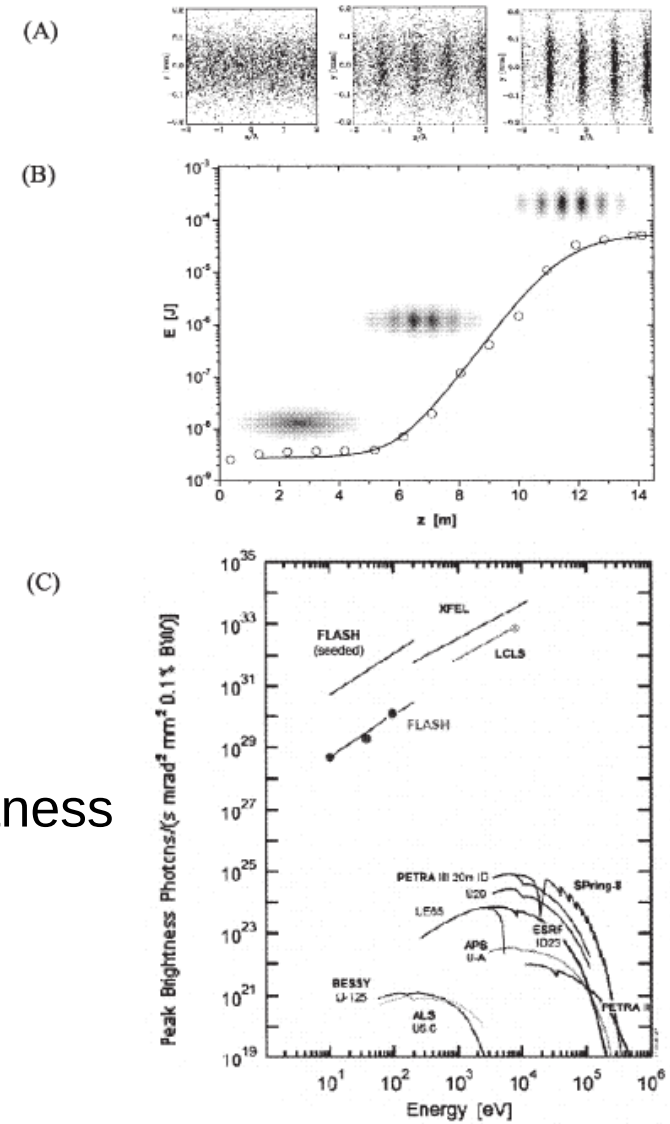
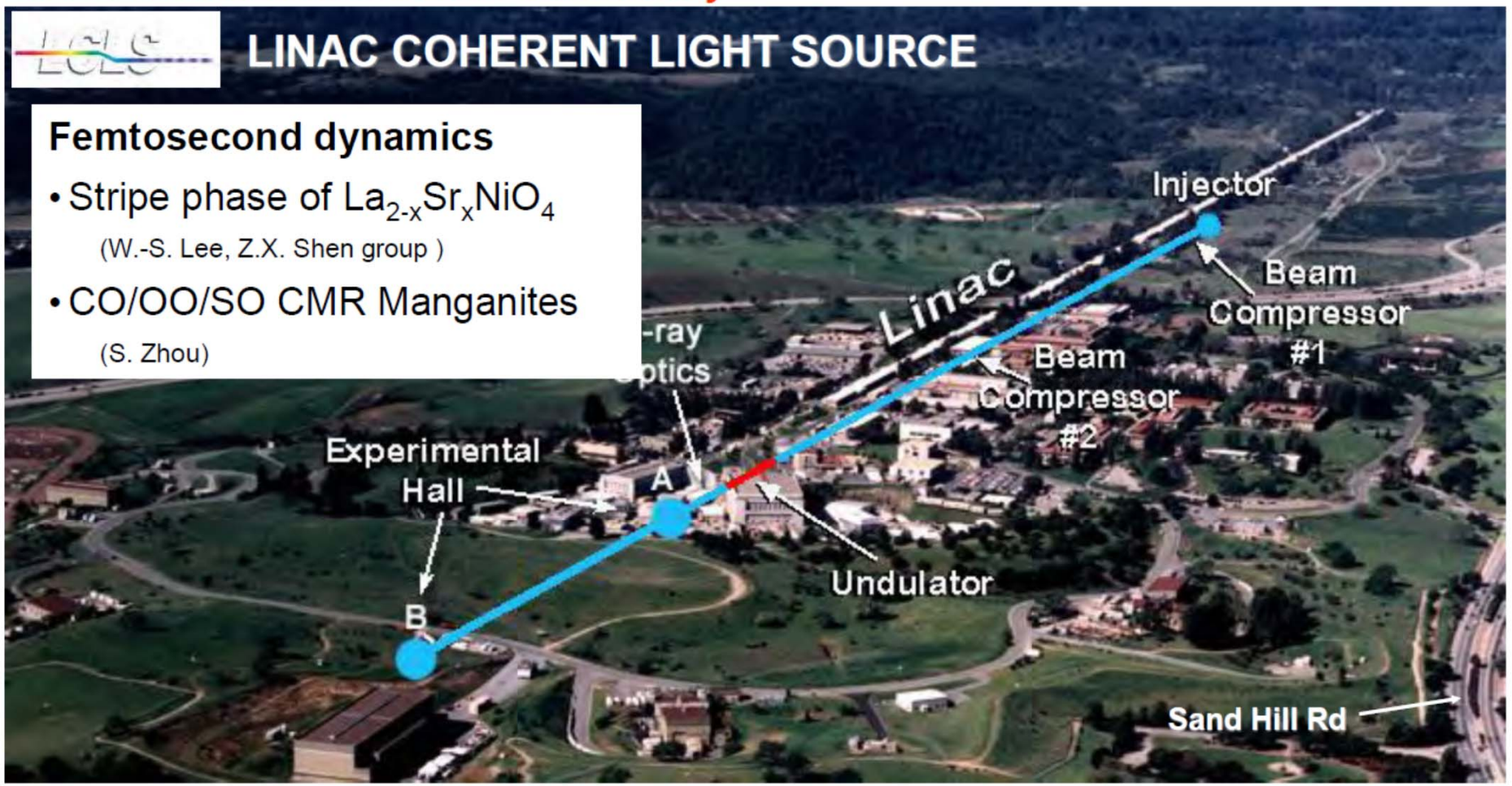



***Figure 2-10.*** *(A) Simulation of the electron microbunching process and (B) the exponential growth of FEL output energy due to microbunching (following S. Reiche and K.-J. Kim). (C) FEL beams have very short pulse duration and full spatial coherence, with peak brightness many orders of magnitude higher than 3rd generation synchrotron facilities [4, modified].*

**"X-Ray Data Booklet" Fig. 2.10**

# An operational vuv/x-ray free-electron laser

*SLAC National Accelerator Laboratory*




**Plus: FLASH (Hamburg)**
**Fermi (Trieste)**
**SACLA (Japan)**
**XFEL-soon (Hamburg)**

# Typical experimental geometry for energy- and angle-resolved photoemission measurements

Ferromagnet

Tailoring the photon field:
Polarization, Standing wave
Measuring spin

Photon

Up to 10-20 keV
Down to 5 eV (Lasers, UV lamps)

$\theta_{inc}$

$\theta$

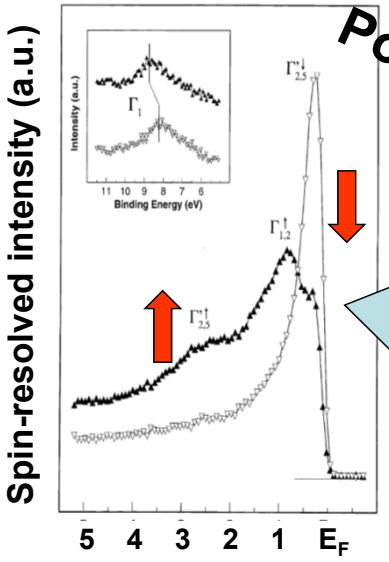
Ultrahigh Vacuum

Multi-torr at sample

$\phi$

Space & Time resolution (Lasers, Free e⁻ lasers)

Sample



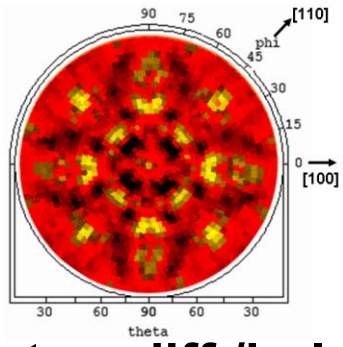

Surf. Sci. 478, 193 ('01)

$\vec{k}$ $\vec{s}$ e-

y
x
z

Irradiated Area

Core-level $I(\theta,\phi)$




Photoe⁻ diff./holog.

Analyzer Slit

Angle

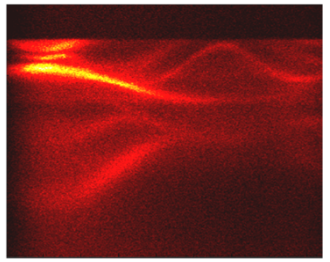
Energy

Imaging Detector

No. e⁻ →

Kinetic Energy →

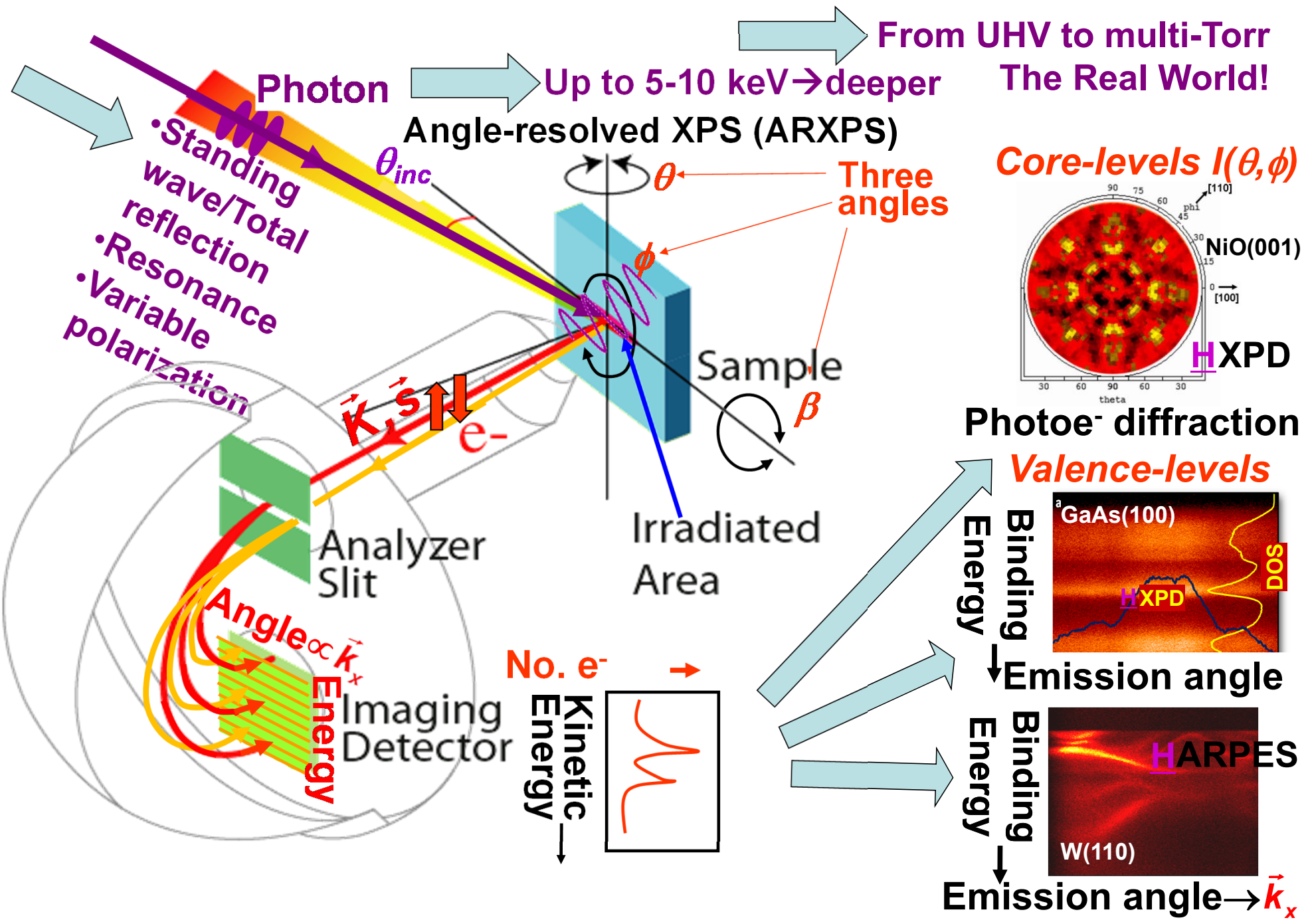
Valence-levels-ARPES



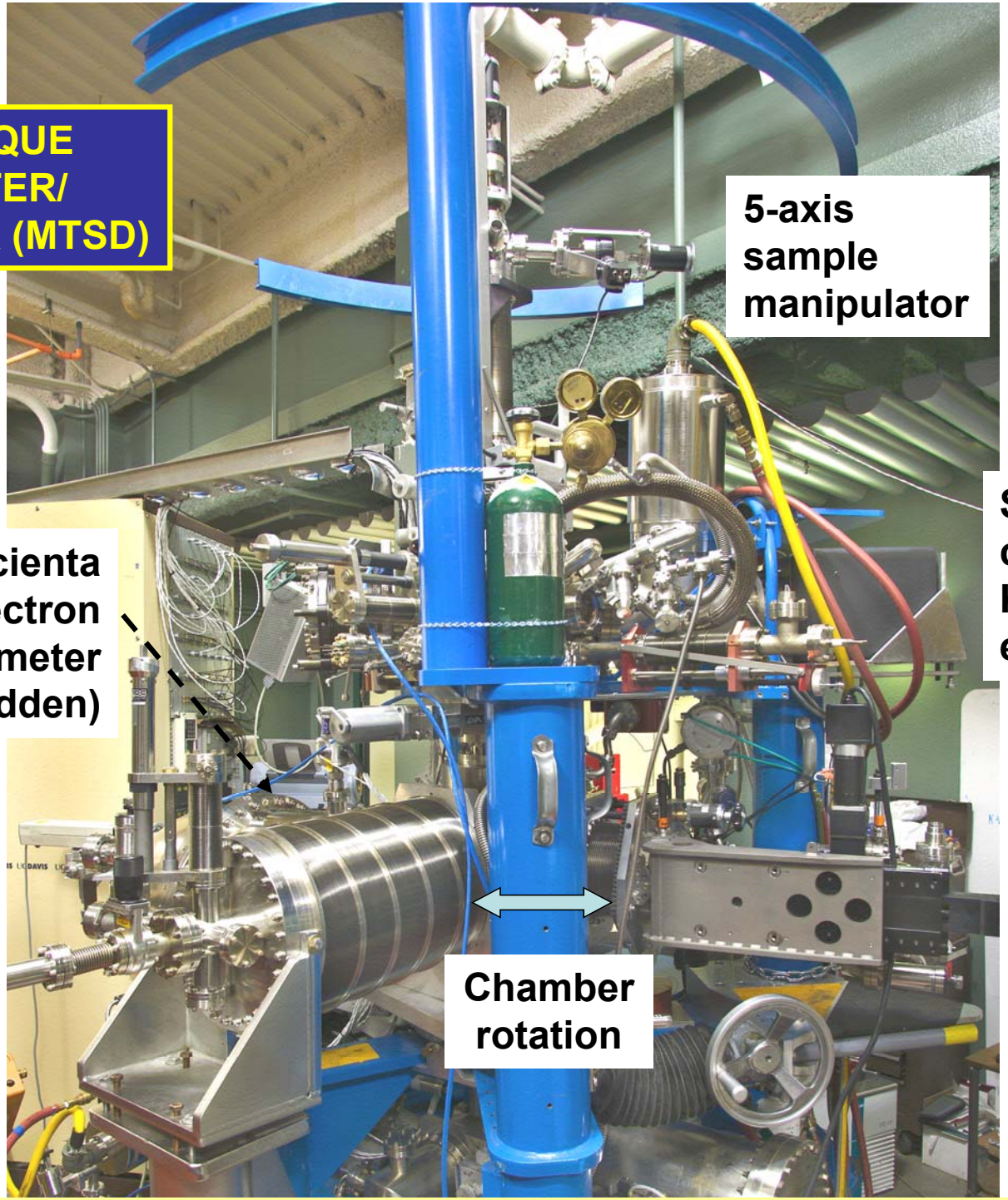
Binding Energy →

Emission angle → $\vec{k}_x$

# X-ray photoemission: some key elements



# MULTI-TECHNIQUE SPECTROMETER/ DIFFRACTOMETER (MTSD)



5-axis sample manipulator

Sample prep. chamber: LEED, Knudsen cells, electromagnet,...

Scienta electron spectrometer (hidden)

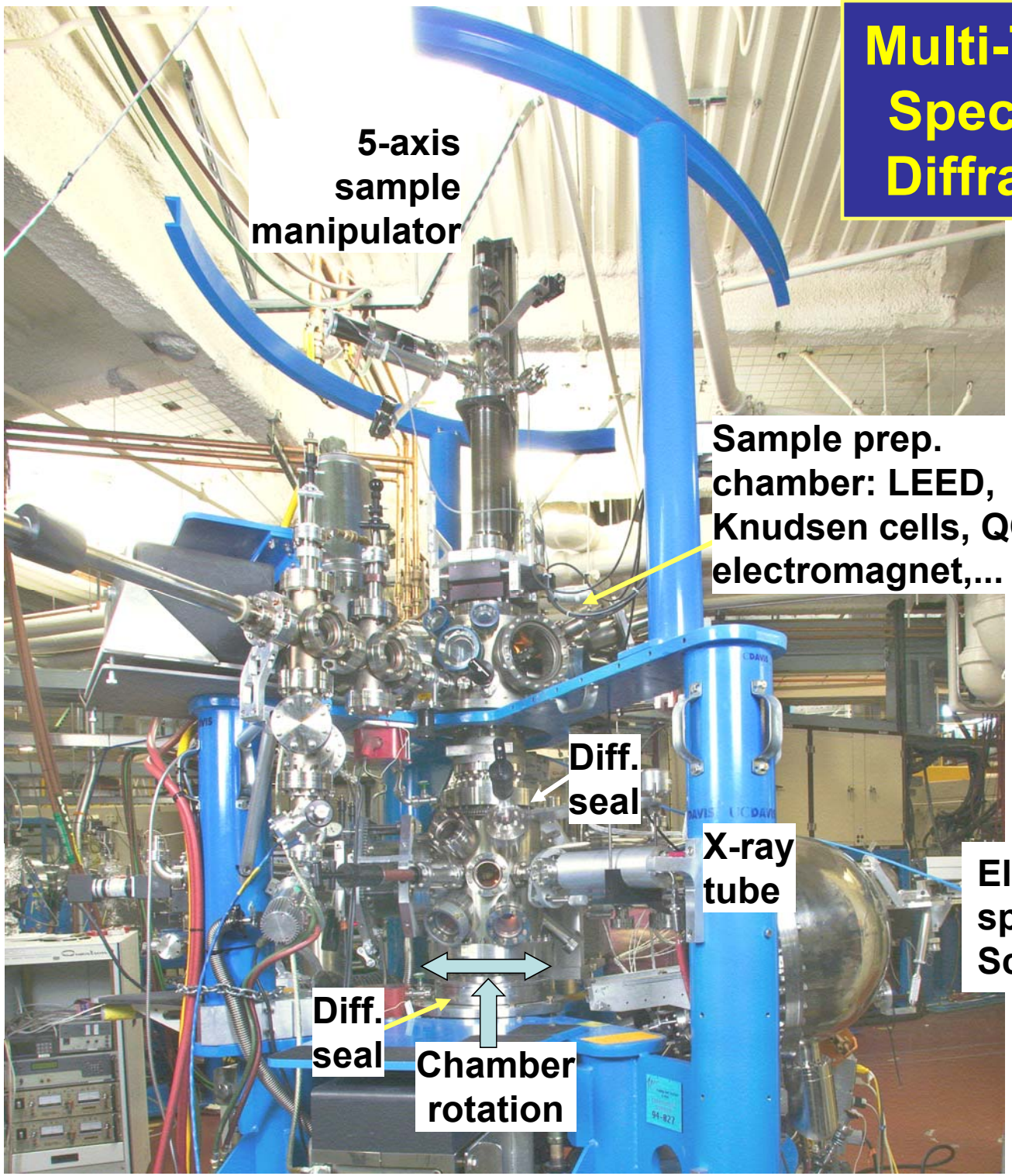
ALS
BL 9.3.1
hν = 2-5 keV

Chamber rotation

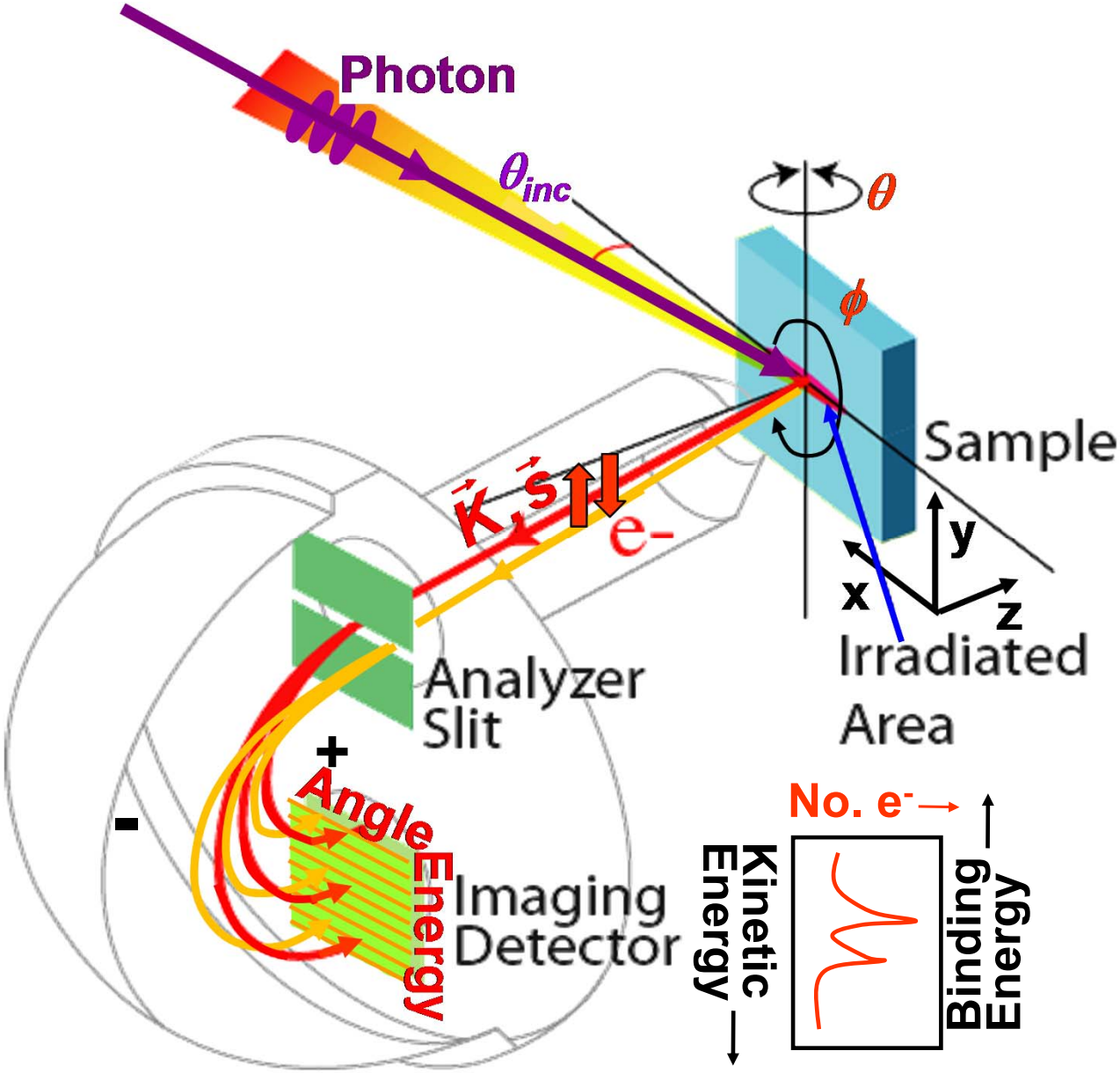
Scienta soft x-ray spectrometer

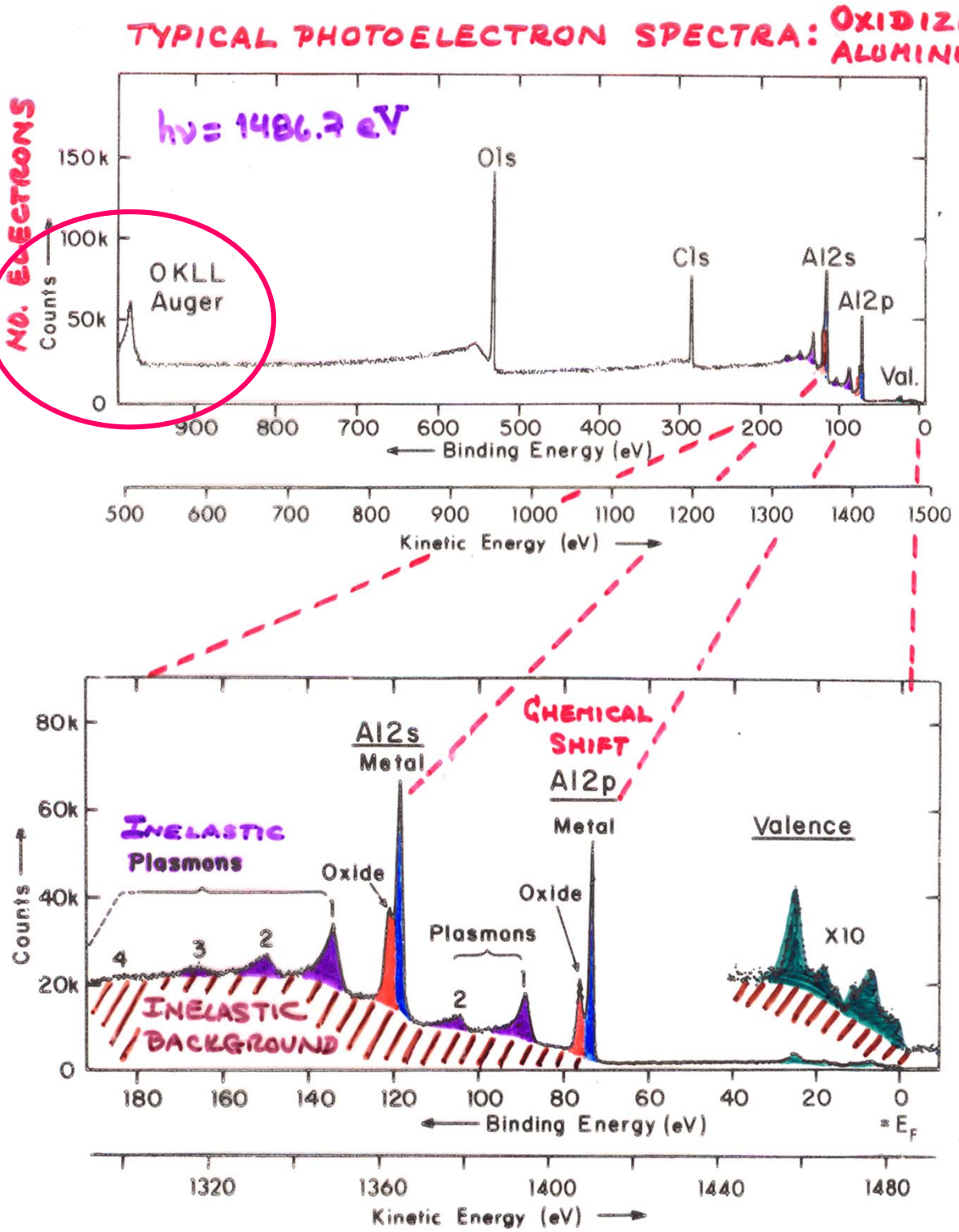
**Permits using all relevant soft and hard x-ray spectroscopies on a single sample: PS, PD, PH; XAS ($e^-$ or photon detection), XES/RIXS, with MCD, MLD**

# Multi-Technique Spectrometer/ Diffractometer



# Typical experimental geometry for energy- and angle-resolved photoemission measurements





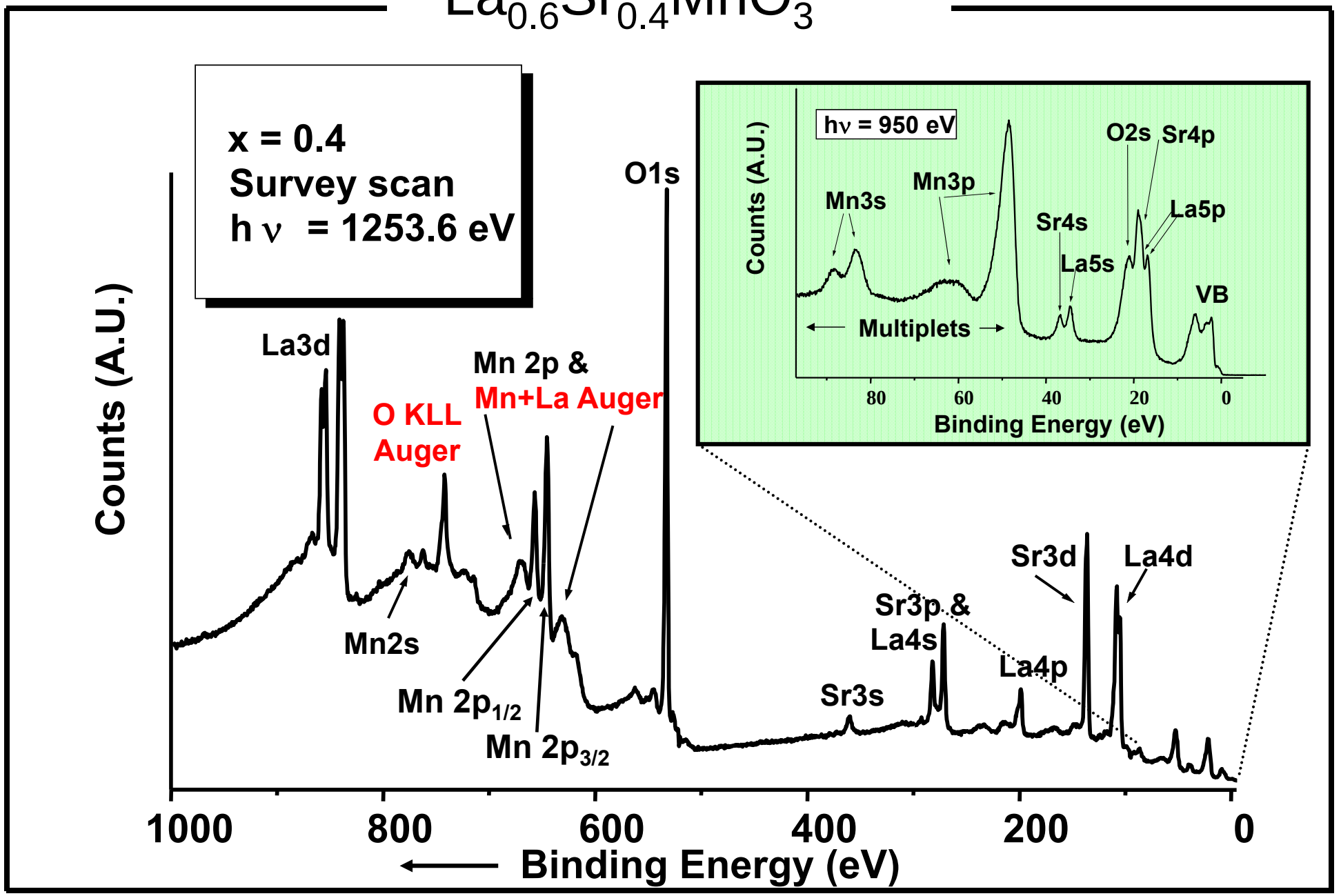

**Auger kinetic energies do not change with photon energy**

**Photoelectron kinetic energies shift linearly with photon energy**

"Basic Concepts of XPS"
Figure 1

# Core and valence photoemission

$La_{0.6}Sr_{0.4}MnO_3$



**Basic Concepts:**

A Little Electronic Structure
The X-Ray-Based Experiments
X-Ray Sources, Synchrotron Radiation, Free Electron Lasers

**Core-Level Photoemission**

Intensities and Quantitative Analysis, the 3-Step Model
Varying Surface and Bulk Sensitivity
Chemical Shifts
Multiplet Splittings
Electron Screening and Satellite Structure
Magnetic and Non-Magnetic Dichroism
Resonant Photoemission
Photoelectron Diffraction and Holography

**Valence-Level Photoemission**

Band-Mapping in the Ultraviolet Photoemission Limit
Densities of States in the X-Ray Photoemission Limit

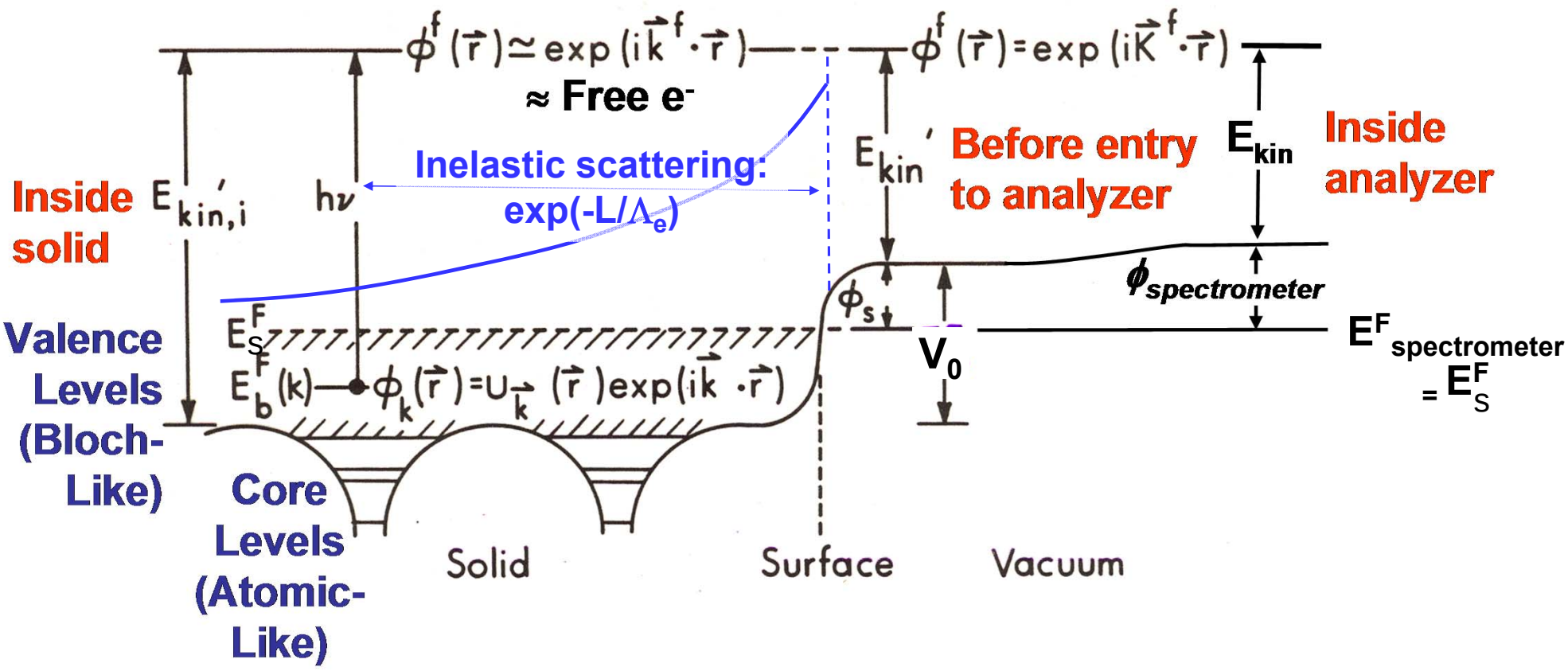
**Some New Directions**

Photoemission with Hard X-Rays (throughout lectures)
Photoemission with Standing Wave Excitation
Photoemission with: Higher Pressures→multi-Torr→Atmosphere?
Spatial Resolution-Photoelectron Microscopy
Temporal Resolution

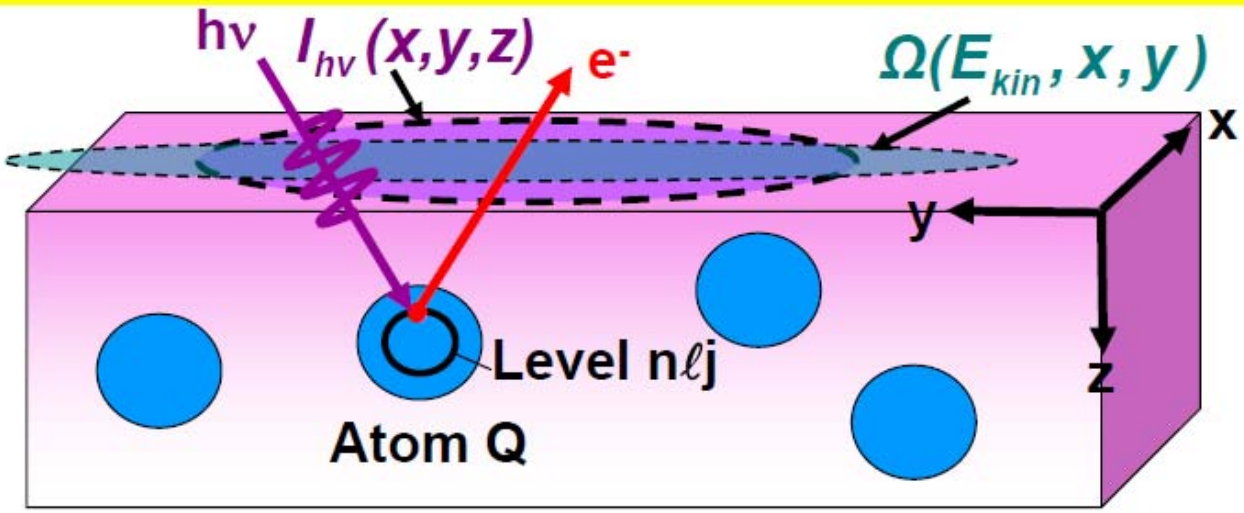
# Basic energetics

$$h\nu = E^{Vacuum}_{binding} + E_{kinetic} = E^{Fermi}_{binding} + \varphi_{spectrometer} + E_{kinetic}$$

## One-Electron Picture of Photoemission from a Surface



# CORE PHOTOELECTRON INTENSITIES AND COMPOSITION




$$I(Qn\ell j) =$$

$$C\int_0^{\infty} I_{h\nu}(x,y,z)\rho_Q(x,y,z)\frac{d\sigma_{Qn\ell j}(h\nu)}{d\Omega}\exp\left[-\frac{z}{\Lambda_e(E_{kin})\sin\theta}\right]\Omega(E_{kin},x,y)dxdydz$$

$I_{h\nu}(x,y,z)$ = x-ray flux

$\rho_Q(x,y,z)$ = density of atoms Q → quantitative analysis

$\frac{d\sigma_{Qn\ell j}(h\nu)}{d\Omega}$ = energy-dependent differential photoelectric cross section for subshell $Qn\ell j$

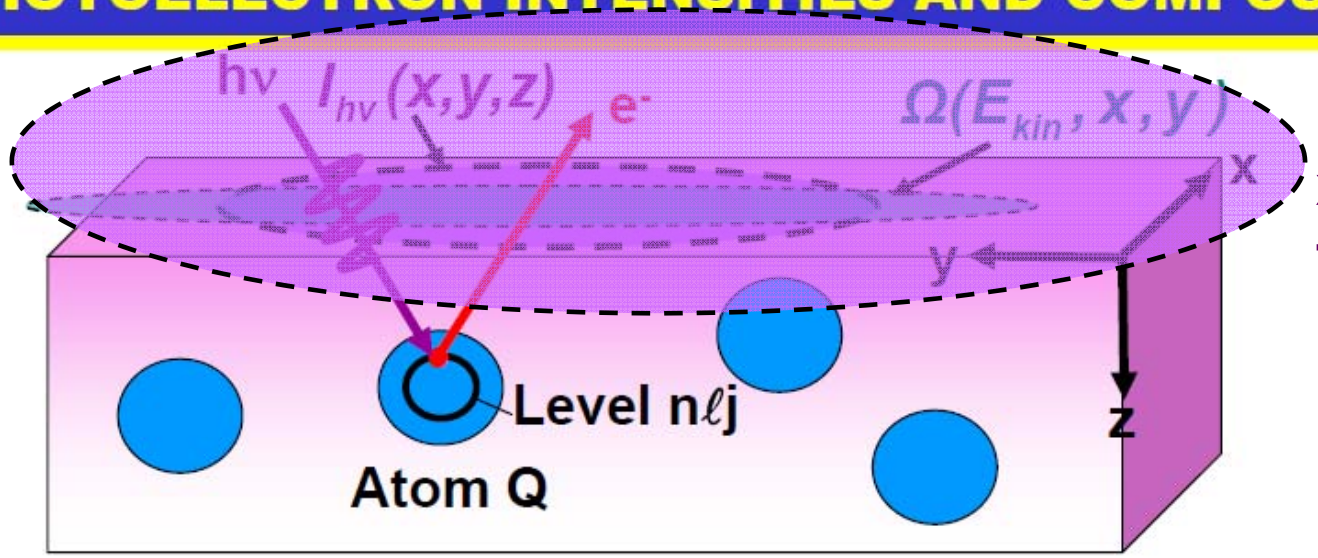
$\Lambda_e(E_{kin})$ = energy-dependent inelastic attenuation length

→ Effective Attenuation Length (EAL) → Mean Emission Depth (MED)

$\Omega(E_{kin},x,y)$ = energy-dependent spectrometer acceptance solid angle

C.S.F., Journal of Electron Spectroscopy and Related Phenomena 178–179 (2010) 2–32

# CORE PHOTOELECTRON INTENSITIES AND COMPOSITION




Normal x-ray tube

$$I(Qn\ell j) = C\int_0^\infty I_{hv}(x,y,z)\rho_Q(x,y,z)\frac{d\sigma_{Qn\ell j}(hv)}{d\Omega}\exp\left[-\frac{z}{\Lambda_e(E_{kin})\sin\theta}\right]\Omega(E_{kin},x,y)\,dx\,dy\,dz$$

$I_{hv}(x,y,z)$ = x-ray flux

$\rho_Q(x,y,z)$ = density of atoms Q → quantitative analysis

$\frac{d\sigma_{Qn\ell j}(hv)}{d\Omega}$ = energy-dependent differential photoelectric cross section for subshell $Qn\ell j$

$\Lambda_e(E_{kin})$ = energy-dependent inelastic attenuation length

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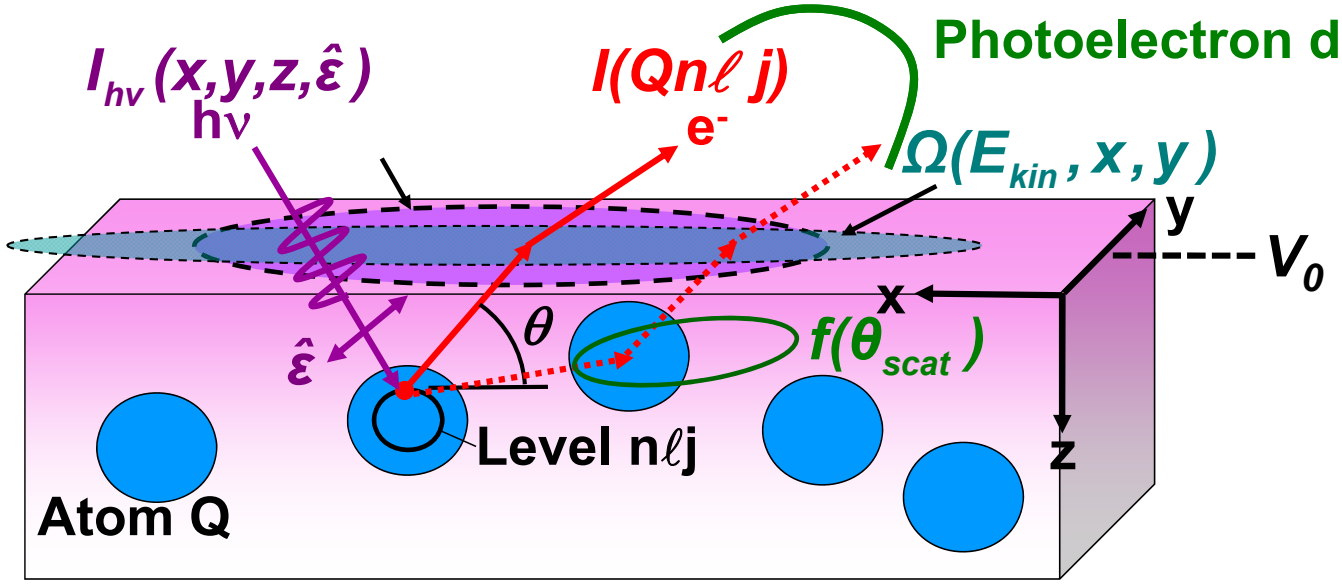
C.S.F., Journal of Electron Spectroscopy and Related Phenomena 178–179 (2010) 2–32

# ATOMIC (CORE) PHOTOELECTRON INTENSITIES: THE THREE-STEP MODEL




$I(Qn\ell\, j)$ =

$$C\int_0^{\infty} I_{h\nu}(x,y,z,\hat{\varepsilon})\rho_Q(x,y,z)\frac{d\sigma_{Qn\ell j}(h\nu,\hat{\varepsilon})}{d\Omega}\exp\left[-\frac{z}{\Lambda_e(E_{kin})\sin\theta}\right]\Omega(E_{kin},x,y)\,dx\,dy\,dz$$

$I_{h\nu}(x,y,z,\hat{\varepsilon})$ = x-ray flux, $\hat{\varepsilon}$ = polarization

$\rho_Q(x,y,z)$ = density of atoms Q → quantitative analysis

$\frac{d\sigma_{Qn\ell j}(h\nu,\hat{\varepsilon})}{d\Omega}$ = energy-dependent differential photoelectric cross section for subshell $Qn\ell\, j$

$\Lambda_e(E_{kin})$ = energy-dependent inelastic attenuation length + elastic scattering: $f(\theta_{scatt})$

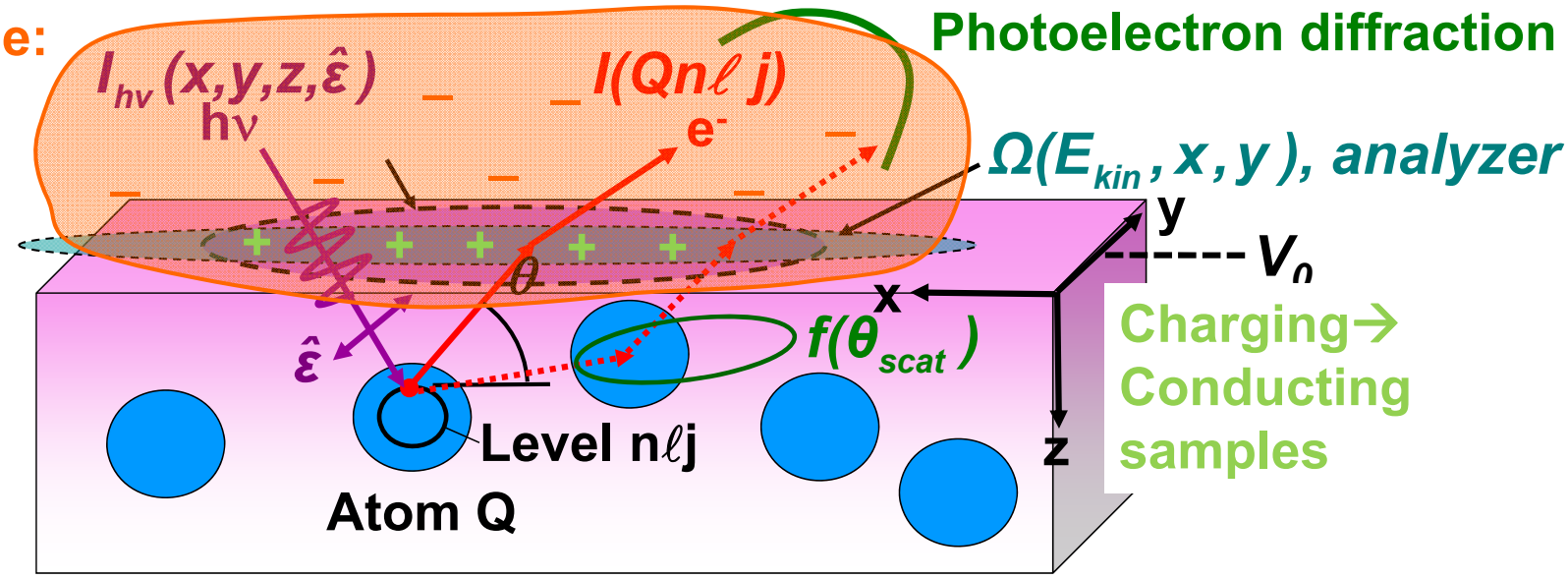
→ Effective Attenuation Length (EAD) → Mean Emission Depth (MED)

$\Omega(E_{kin},x,y)$ = energy-dependent spectrometer acceptance solid angle = transmission function

$V_0$ = inner potential

# ATOMIC (CORE) PHOTOELECTRON INTENSITIES: THE "FOUR-STEP" MODEL

**e⁻ space charge:** Hellman et al. (FLASH), Phys. Rev. B 85, 075109 (2012); Oloff et al. (SACLA), New J. Phys. 16, 123045 (2014); J.Sync.Rad.Res. 21, 183 (2014): Turn down the light!




$I(Qn\ell j)$ =

Non-dipole effects and resonant interchannel

$$C\int_0^{\infty} I_{hv}(x,y,z,\hat{\varepsilon})\rho_Q(x,y,z)\frac{d\sigma_{Qn\ell j}(hv,\hat{\varepsilon})}{d\Omega}\exp\left[-\frac{z}{\Lambda_e(E_{kin})\sin\theta}\right]\Omega(E_{kin},x,y)dxdydz$$

$I_{hv}(x,y,z,\hat{\varepsilon})$ = x-ray flux, $\hat{\varepsilon}$ = polarization

$\rho_Q(x,y,z)$ = density of atoms Q → quantitative analysis

$\frac{d\sigma_{Qn\ell j}(hv,\hat{\varepsilon})}{d\Omega}$ = energy-dependent differential photoelectric cross section for subshell $Qn\ell j$

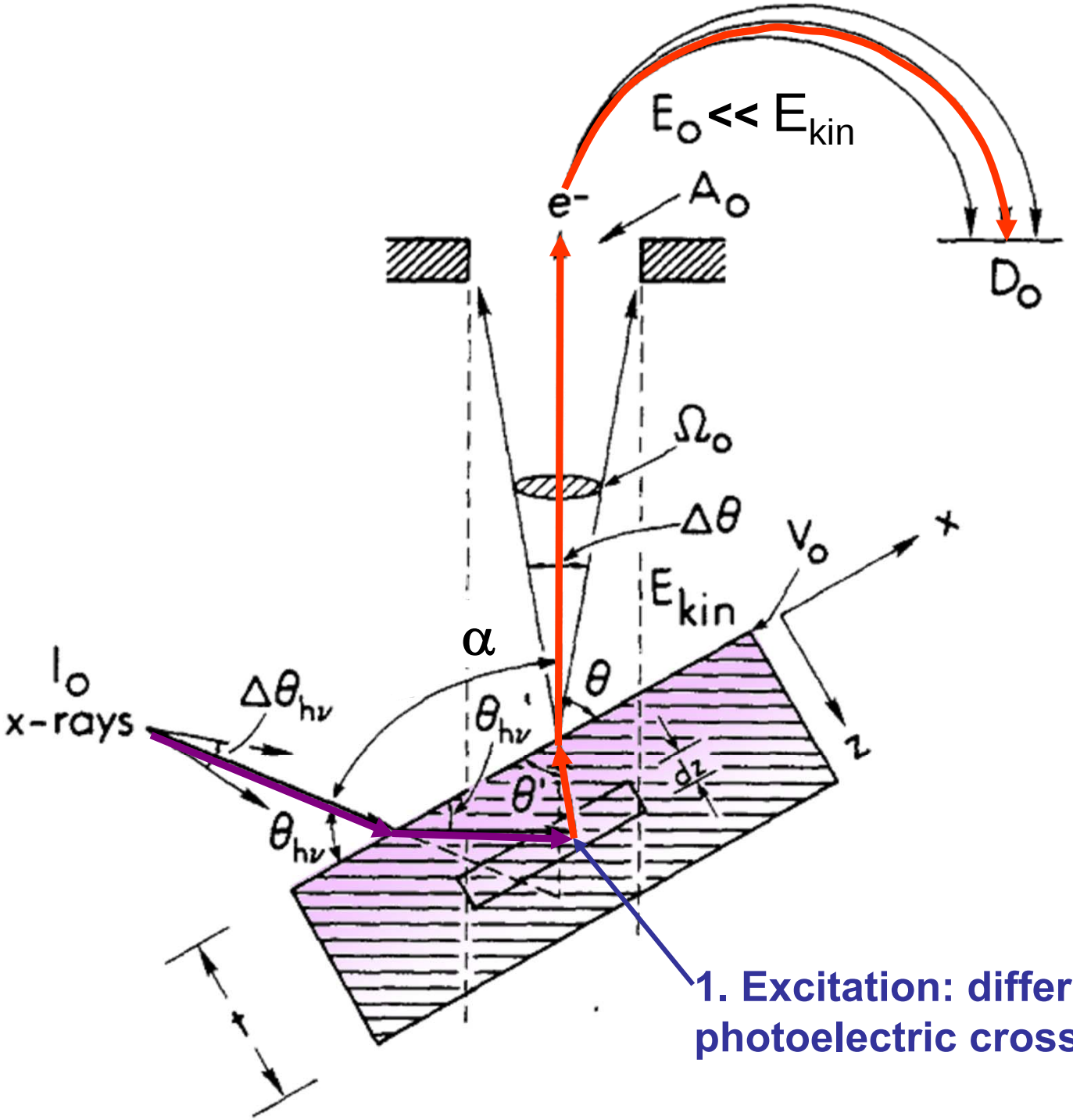
$\Lambda_e(E_{kin})$ = energy-dependent inelastic attenuation length + elastic scattering: $f(\theta_{scatt})$

→ Effective Attenuation Length (EAD) → Mean Emission Depth (MED)

$\Omega(E_{kin},x,y)$ = energy-dependent analyzer acceptance solid angle = transmission function

$V_0$ = inner potential

# PHOTOELECTRON INTENSITIES—THE 3-STEP MODEL



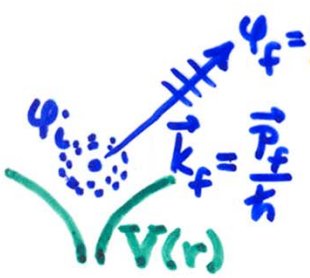

**1. Excitation: differential photoelectric cross section ($d\sigma/d\Omega$)**

# PHOTOELECTRON EMISSION-
# BASIC MATRIX ELEMENTS + SELECTION RULES:

- **ATOMIC-LIKE (LOCALIZED) STATES ⇒ CORE:**

$$\varphi_i(\vec{r}) = \varphi_{n_i \ell_i m_i}(r,\theta,\phi) = R_{n_i \ell_i}(r) Y_{\ell_i m_i}(\theta,\phi)$$

PLUS SPIN:
$\alpha(\sigma) = m_{si} = +½ = \uparrow$
$\beta(\sigma) = m_{si} = -½ = \downarrow$




$$\varphi_f(\vec{r},\vec{k}_f) = \varphi_{E_f}(\vec{r},\vec{k}_f) \begin{cases}\alpha(\sigma)\\ \beta(\sigma)\end{cases}$$

$$= 4\pi \sum_{\ell_f, m_f} i^{\ell_f} e^{-i\delta_{\ell_f}} Y^*_{\ell_f m_f}(\theta_{k_f}, \phi_{k_f}) Y_{\ell_f m_f}(\theta,\phi) R_{E_f \ell_f}(r) \begin{cases}\alpha(\sigma)\\ \beta(\sigma)\end{cases}$$

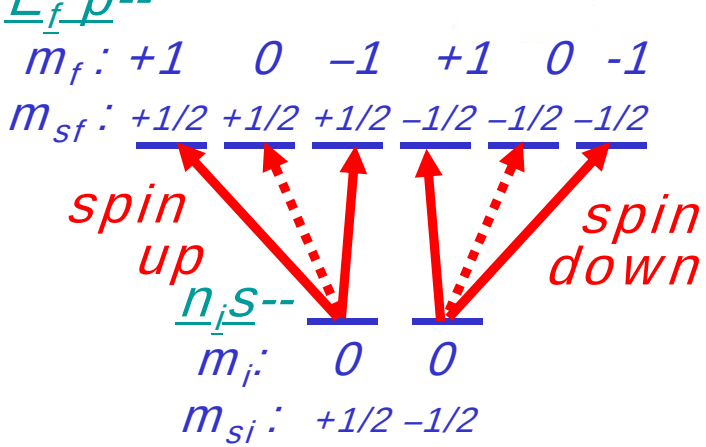
($\delta_{\ell_f}$: PHASE SHIFT OF $\ell_f$ WAVE IN V(r))

DIPOLE APPROX.: INT. $\propto |\langle \varphi_f | \hat{\varepsilon}\cdot\vec{r} | \varphi_i \rangle|^2 = |\hat{\varepsilon}\cdot\langle \varphi_f | \vec{r} | \varphi_i \rangle|^2 \Rightarrow$

EQUIVALENT WITHIN CONSTANT FACTOR ( $\vec{p}$ ↕ $\vec{\nabla}V(r)$ )

- $\Delta\ell = \ell_f - \ell_i = \pm 1$ TWO CHANNELS
- $\Delta m = m_f - m_i = 0, \pm 1$ LINEAR POLARIZ.
- $\Delta m = \pm 1$, CIRCULAR POLARIZATION

$\Delta m_s = m_{sf} - m_{si} = 0$ !




FOR A GIVEN $n_i/_i m_i m_{si}$: SUM OVER DEGENERATE INITIAL STATES $m_i m_{si}$ AND AVERAGE OVER FINAL STATES $E_f/_f m_f m_{sf}$ ACCESSED FROM EACH $m_i$ TO YIELD DIFFERENTIAL SUBSHELL PHOTOELECTRIC CROSS SECTION :

$$d\sigma_{n_i \ell_i} / d\Omega$$

∝ PROBABILITY PER UNIT SOLID ANGLE OF EXCITING ONE ELECTRON FROM SUBSHELL $n_i/_i$ INTO THE DIRECTION $k_f$

- **RADIATION POLARIZATION:** $\hat{\varepsilon}\cdot\vec{r} = \hat{\varepsilon}\cdot(x\hat{x}+y\hat{y}+z\hat{z})$


**LINEARLY POLARIZED -** $\propto Y_{\ell=1,m_\ell=+1}(\theta,\phi) + Y_{\ell=1,m_\ell=-1}(\theta,\phi)$

x: $\hat{\varepsilon}\cdot\vec{r} \Rightarrow x \Rightarrow$ INT.$_x$

y: $\hat{\varepsilon}\cdot\vec{r} \Rightarrow y \Rightarrow$ INT.$_y$

$\propto Y_{\ell=1,m_\ell=+1}(\theta,\phi) - Y_{\ell=1,m_\ell=-1}(\theta,\phi)$

**CIRCULARLY POLARIZED** $\propto Y_{\ell=1,m_\ell=1}(\theta,\phi)$

LEFT $\equiv$ LCP: $\hat{\varepsilon}\cdot\vec{r} \Rightarrow x - iy \Rightarrow$ INT.$_{LCP}$

RIGHT $\equiv$ RCP: $\hat{\varepsilon}\cdot\vec{r} \Rightarrow x + iy \Rightarrow$ INT.$_{RCP}$

$\propto Y_{\ell=1,m_\ell=+1}(\theta,\phi)$

**UNPOLARIZED -**

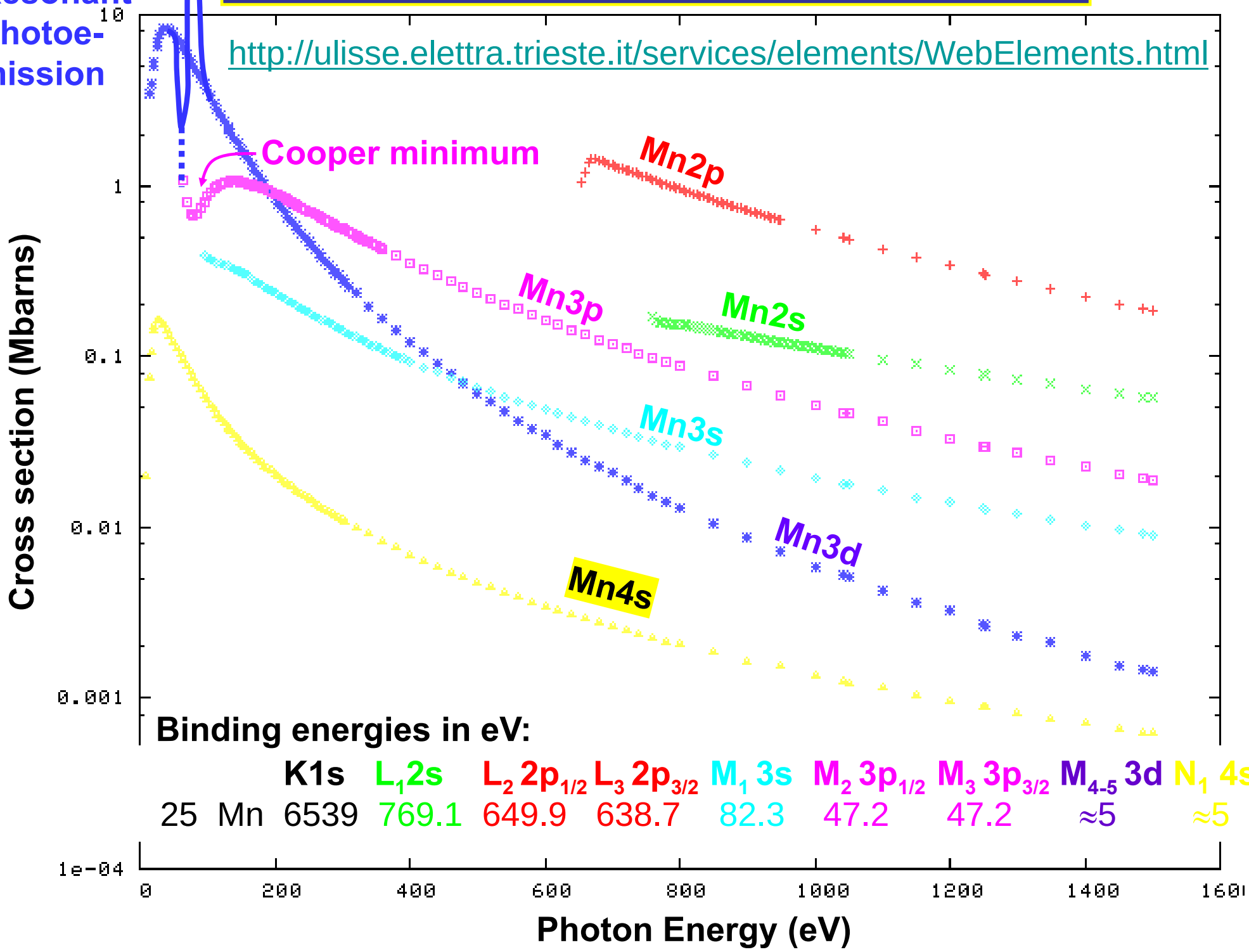
INT.$_{UNP}$ = INT.$_x$ + INT.$_y$

= INT.$_{LCP}$ + INT.$_{RCP}$

# PHOTOELECTRIC CROSS SECTIONS FOR Mn

Resonant Photoe-mission

http://ulisse.elettra.trieste.it/services/elements/WebElements.html

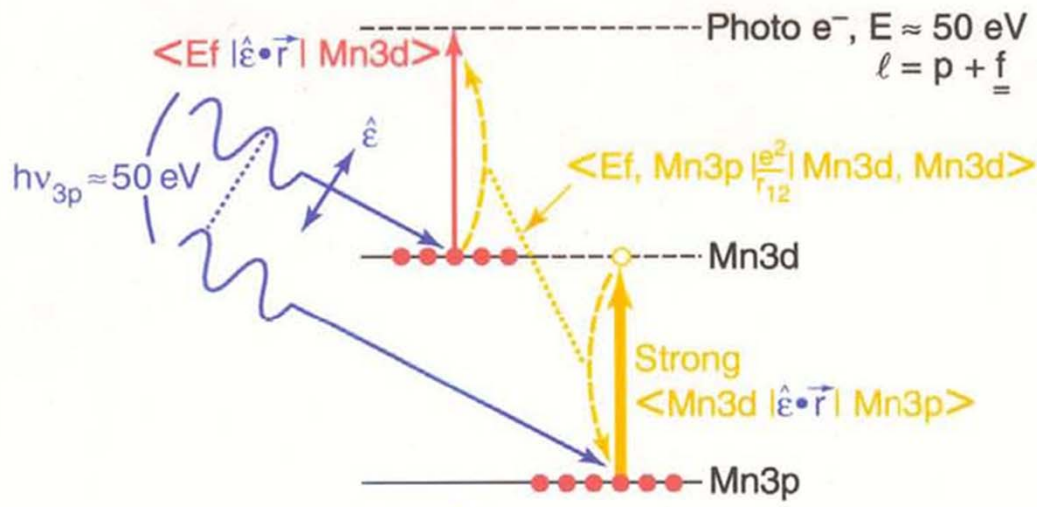


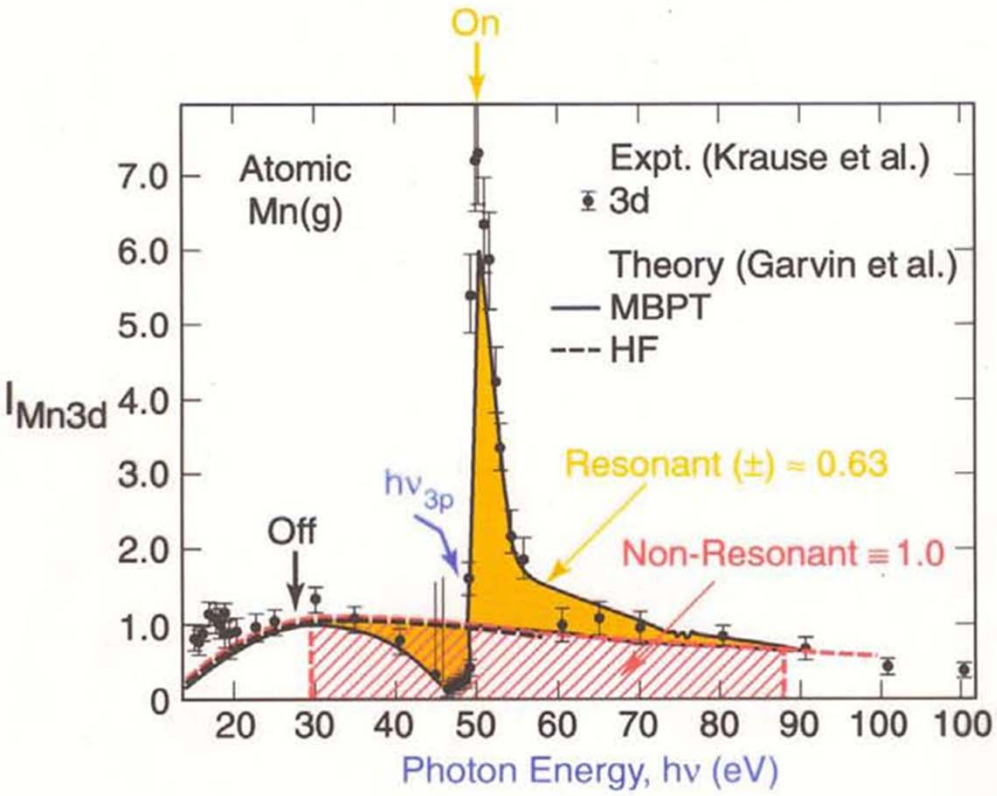

**Binding energies in eV:**

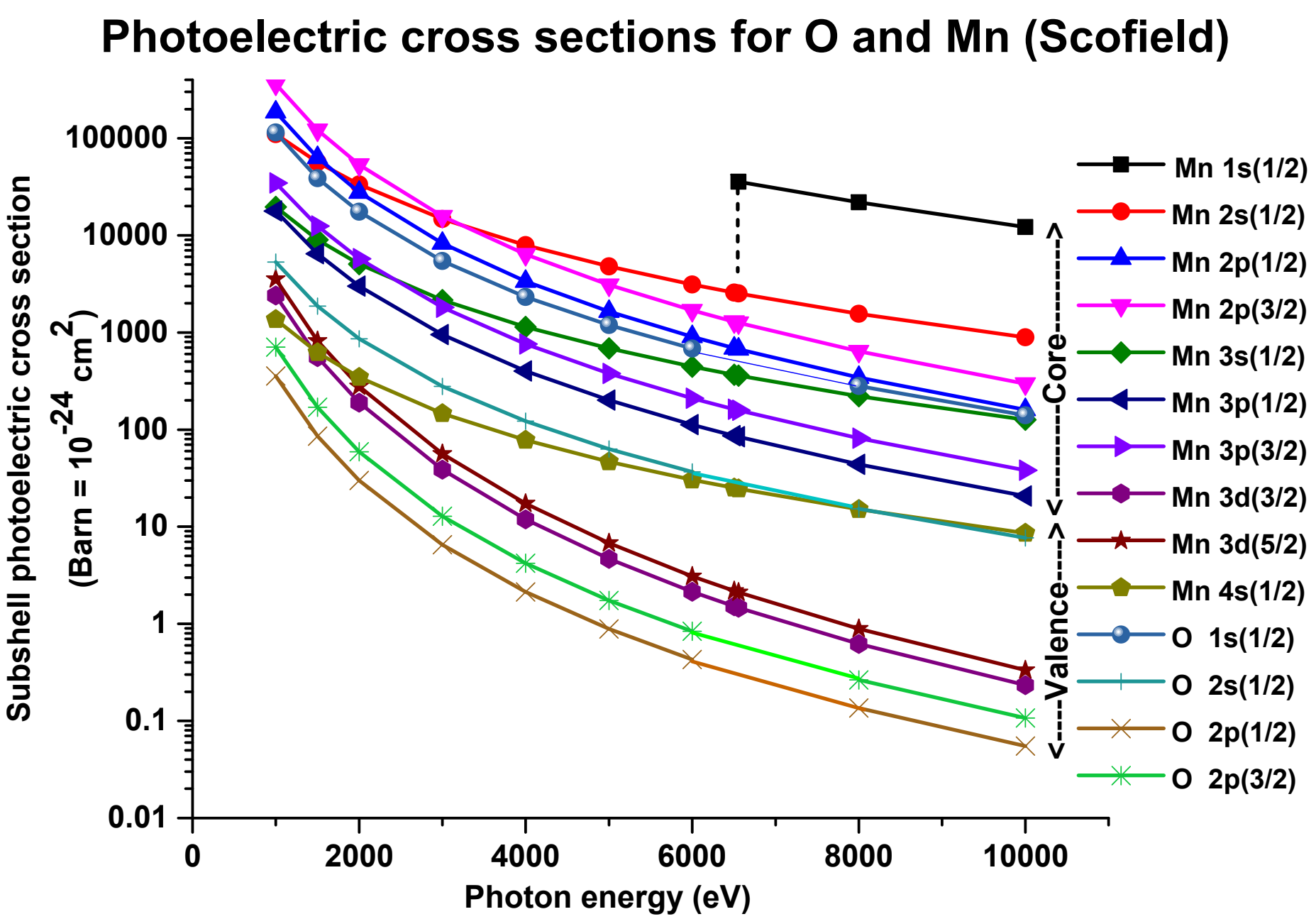
| | | K1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ | $M_1$ 3s | $M_2$ $3p_{1/2}$ | $M_3$ $3p_{3/2}$ | $M_{4-5}$ 3d | $N_1$ 4s |
|---|---|---|---|---|---|---|---|---|---|---|
| 25 | Mn | 6539 | 769.1 | 649.9 | 638.7 | 82.3 | 47.2 | 47.2 | ≈5 | ≈5 |

## Single-atom resonant photoemission:

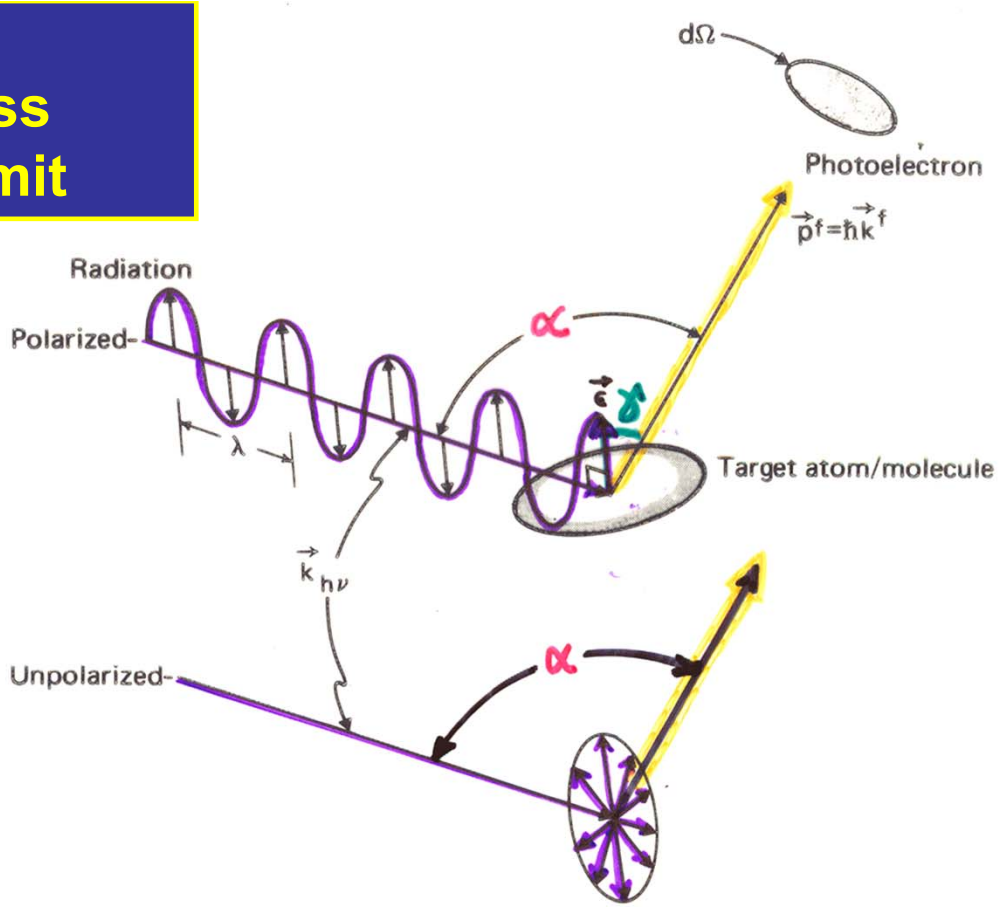
Ex. – Mn atom: Mn3d emission, resonance with Mn3p




Photoelectric cross sections for O and Mn (Scofield)
Subshell photoelectric cross section
(Barn = 10^-24 cm^2)
100000
10000
1000
100
10
1
0.1
0.01
0
2000
4000
6000
8000
10000
Photon energy (eV)
Core
Valence
Mn 1s(1/2)
Mn 2s(1/2)
Mn 2p(1/2)
Mn 2p(3/2)
Mn 3s(1/2)
Mn 3p(1/2)
Mn 3p(3/2)
Mn 3d(3/2)
Mn 3d(5/2)
Mn 4s(1/2)
O 1s(1/2)
O 2s(1/2)
O 2p(1/2)
O 2p(3/2)

# The differential photoelectric cross section—dipole limit




FOR ATOMIC-LIKE EMISSION:

LIN. POLARIZED: $\frac{d\sigma_{n\ell}(E_f)}{d\Omega} = \frac{\sigma_{n\ell}(E_f)}{4\pi}\left[1 + \beta_{n\ell}(E^f)\left(\frac{3}{2}\cos^2\gamma - \frac{1}{2}\right)\right]$

UNPOLARIZED: $\frac{d\sigma_{n\ell}(E_f)}{d\Omega} = \frac{\sigma_{n\ell}(E_f)}{4\pi}\left[1 + \frac{1}{2}\beta_{n\ell}(E^f)\left(\frac{3}{2}\sin^2\alpha - 1\right)\right]$

Figure 7 -- General geometry for defining the differential cross section $d\sigma/d\Omega$, showing both polarized and unpolarized incident radiation. The polarization vector $\vec{e}$ is parallel to the electric field $\vec{E}$ of the radiation. In order for the dipole approximation to be valid, the radiation wave length $\lambda$ should be much larger than typical target dimensions (that is, the opposite of what is shown here).

WITH:

$\sigma_{n\ell}$ = TOTAL CROSS SECTION

$\beta_{n\ell}$ = ASYMMETRY PARAMETER

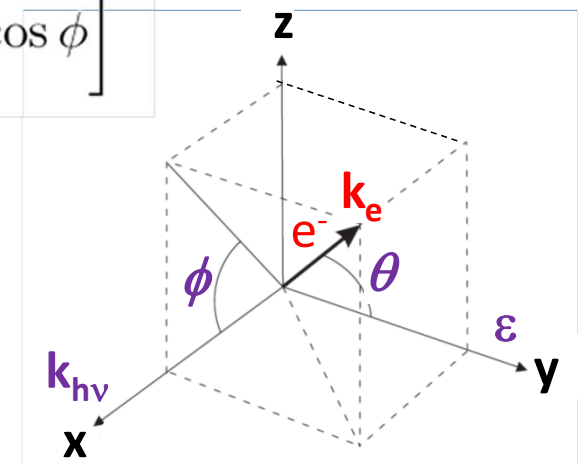
$\sigma_{n\ell}$, $\beta_{n\ell}$ TABULATIONS IN: GOLDBERG ET AL., J. ELECT. SPECT. & YEH, LINDAU, AT. NUC. DATA 32, 1 ('85) \ 21, 285 ('91)

# Differential photoelectric cross sections for filled $n\ell$ subshells, incl. non-dipole

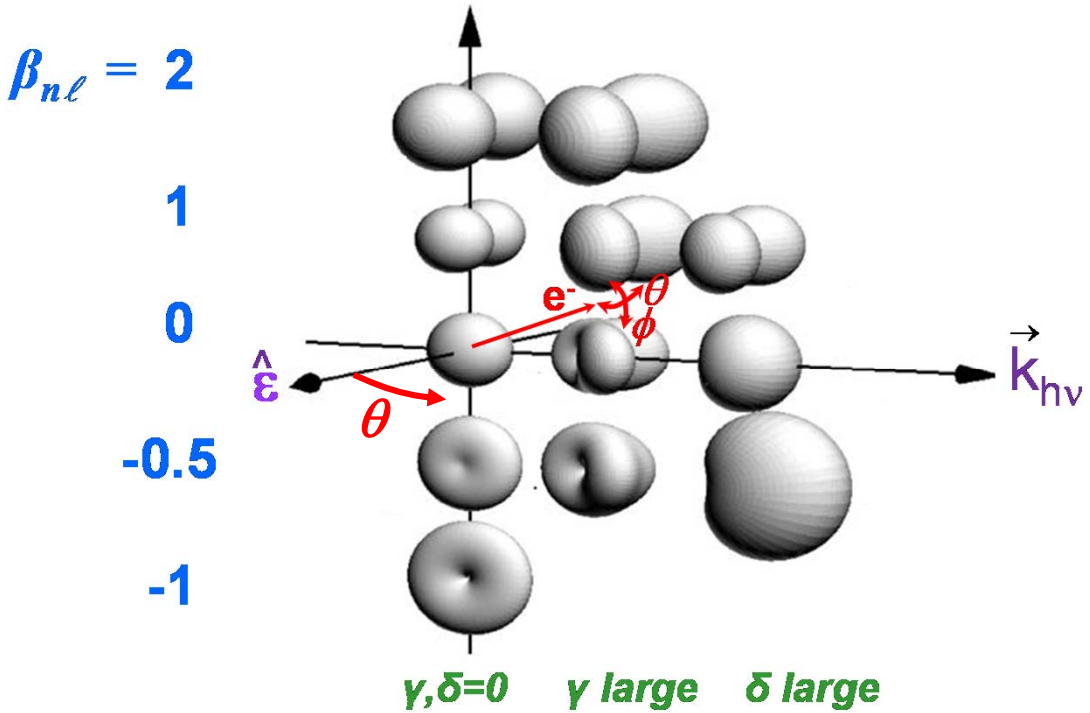
$$\frac{d\sigma_{n\ell}(h\nu)}{d\Omega} = \frac{\sigma_{n\ell}(h\nu)}{4\pi}\left[1 + \frac{\beta_{n\ell}}{2}(3\cos^2\theta - 1) + (\delta_{n\ell} + \gamma_{n\ell}\cos^2\theta)\sin\theta\cos\phi\right]^*$$

Dipole Non-dipole

$$\beta_{nl}(E^f) = \frac{\{l(l-1)R_{l-1}^2(E^f) + (l+1)(l+2)R_{l+1}^2(E^f) - 6l(l+1)R_{l+1}(E^f)R_{l-1}(E^f)\cos[\delta_{l+1}(E^f) - \delta_{l-1}(E^f)]\}}{(2l+1)[lR_{l-1}^2(E^f) + (l+1)R_{l+1}^2(E^f)]}$$




**Dipole $d\sigma_{n\ell}/d\Omega$ calculated from $R_{\ell-1}$, $R_{\ell+1}$, $\delta_{\ell-1}$, and $\delta_{\ell+1}$**




*γ,δ=0* *γ large* *δ large*

#At higher energies, valence cross sections are dominated by atomic-like part near the nucleus

*Guilleumin et al., Radiation Physics and Chemistry 75, 2258 (2006)

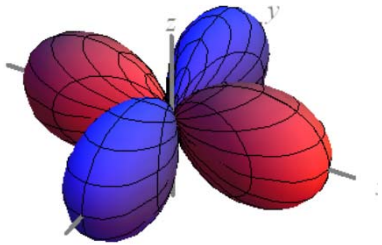
And for individual $d\sigma_{2p(x,y,z)}/d\Omega$ or $d\sigma_{3d(xy,yz,xz,z2,x2\text{-}y2)}/d\Omega$?&

&Goldberg, Fadley, Kono, J. Electr. Spectr. 21, 285-363 (1985)

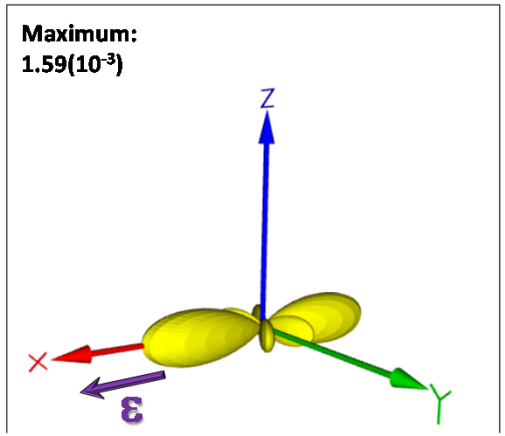
→Nemšák et al.

# Gelius, in *Electron Spectroscopy*, D.A. Shirley, Ed. (North Holland, 1971) p. 311; Solterbeck et al., Phys. Rev. Lett. 79, 4681 (1997)

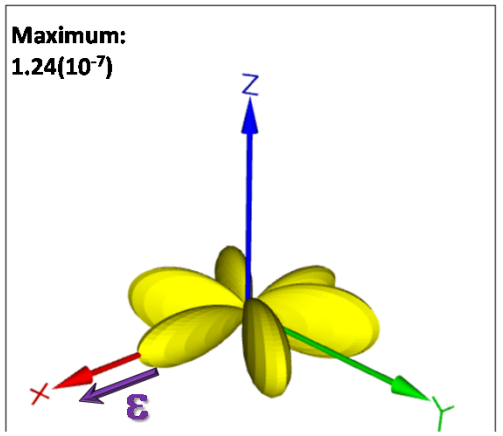
# Energy and polarization dependence of orbital-specific differential cross sections: Cu $3d_{x2-y2}$ @ 800 and 5000 eV



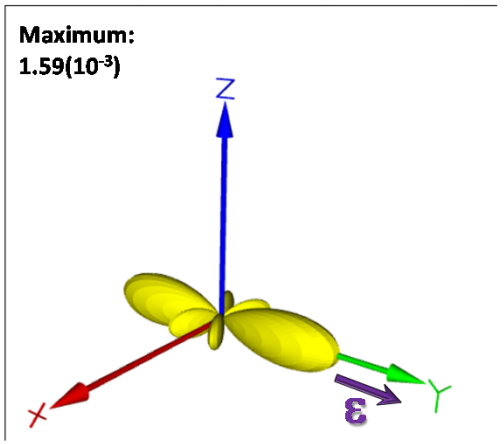
Cu $3d_{x2-y2}$



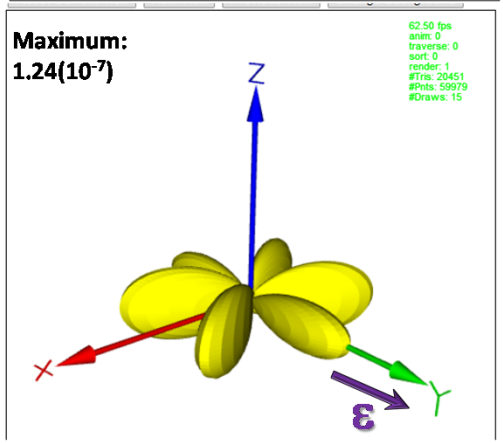

Cu $3d_{x2-y2}$ (hv=800 eV; E ∥ [100])



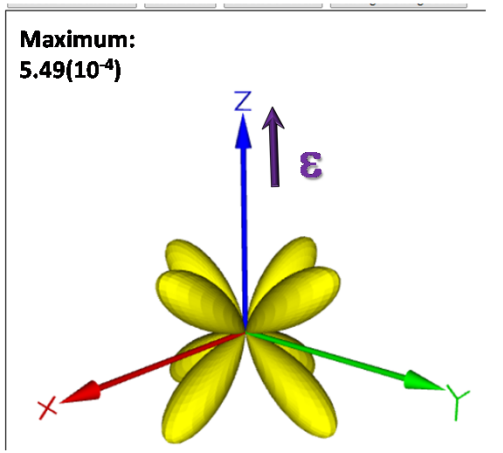

Cu $3d_{x2-y2}$ (hv=5000 eV; E ∥ [100])



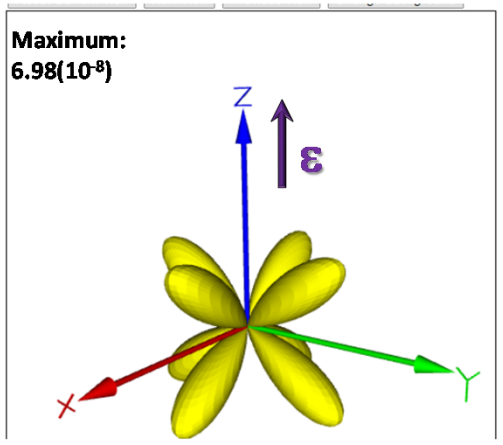

Cu $3d_{x2-y2}$ (hv=800 eV; E ∥ [010])




Cu $3d_{x2-y2}$ (hv=5000 eV; E ∥ [010])



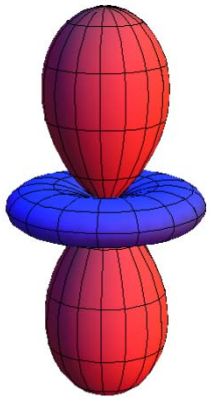

Cu $3d_{x2-y2}$ (hv=800 eV; E ∥ [001])



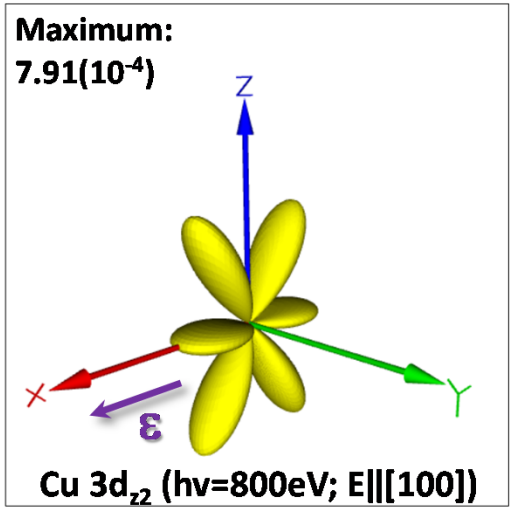

Cu $3d_{x2-y2}$ (hv=5000 eV; E ∥ [001])

**Nemšák et al., TBP; based on equations in Goldberg, Fadley, Kono, J. Electr. Spectr. 21, 285-363 (1985); CSF and S. Nemšák, J. Electron Spect. 195, 409–422 (2014)**

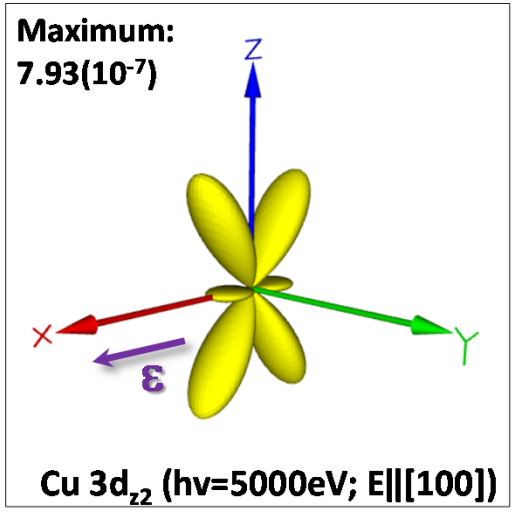
# Energy and polarization dependence of orbital-specific differential cross sections: Cu $3d_{z2}$@ 800 and 5000 eV



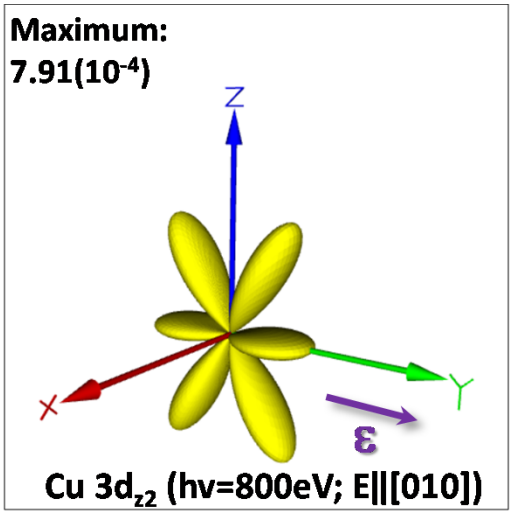
*Cu $3d_{z^2}$*



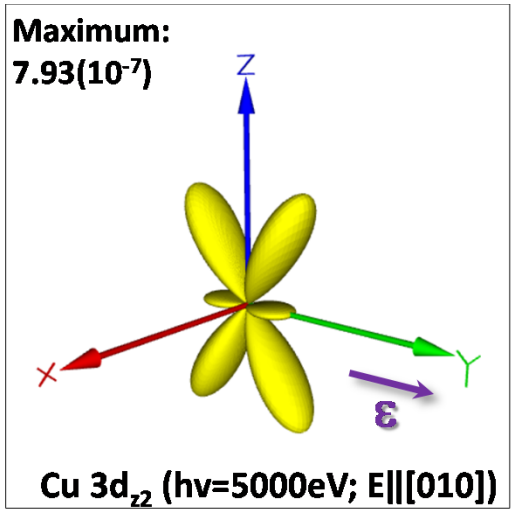

Cu $3d_{z2}$ (hv=800eV; E||[100])



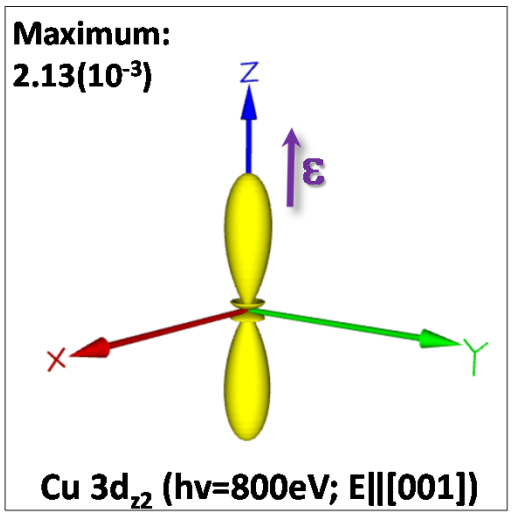

Cu $3d_{z2}$ (hv=5000eV; E||[100])



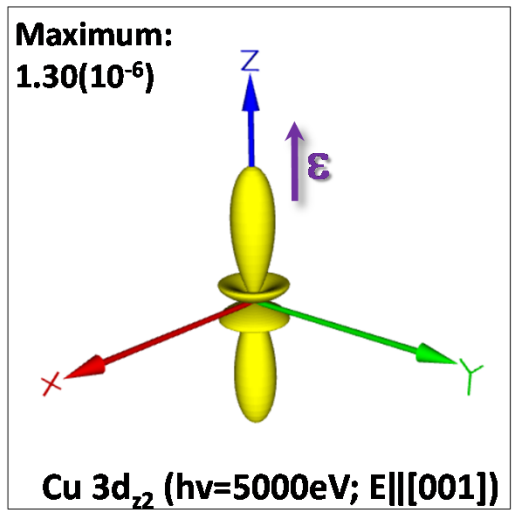

Cu $3d_{z2}$ (hv=800eV; E||[010])




Cu $3d_{z2}$ (hv=5000eV; E||[010])

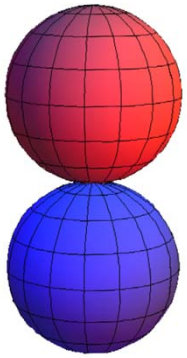



Cu $3d_{z2}$ (hv=800eV; E||[001])

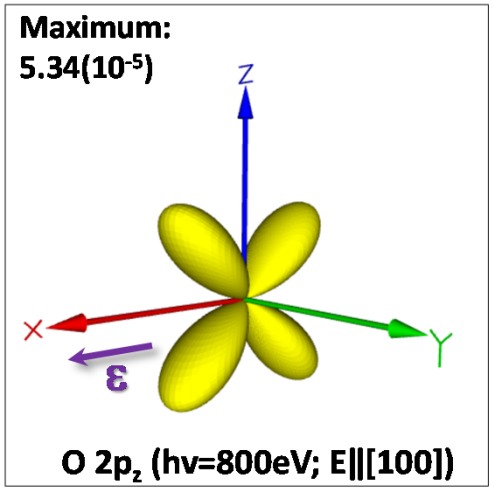



Cu $3d_{z2}$ (hv=5000eV; E||[001])

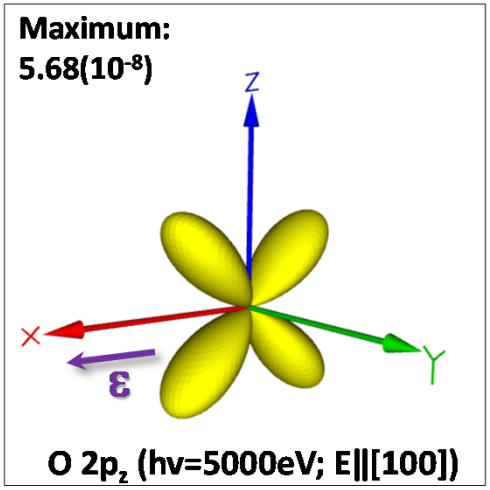
# Energy and polarization dependence of orbital-specific differential cross sections: O $2p_z$ @ 800 and 5000 eV



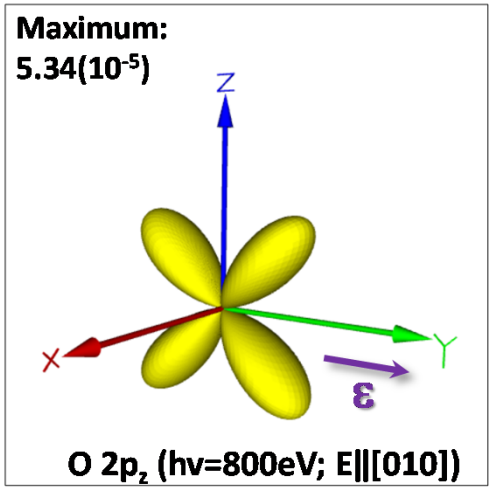
$O\ 2p_z$



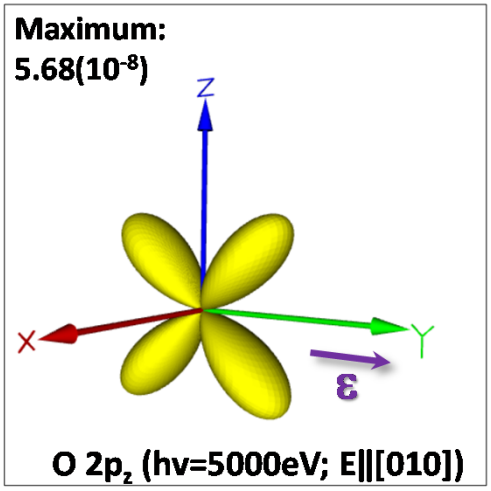

O $2p_z$ (hv=800eV; E||[100])



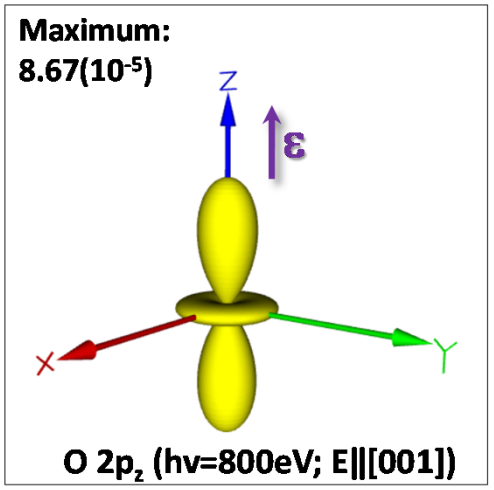

O $2p_z$ (hv=5000eV; E||[100])



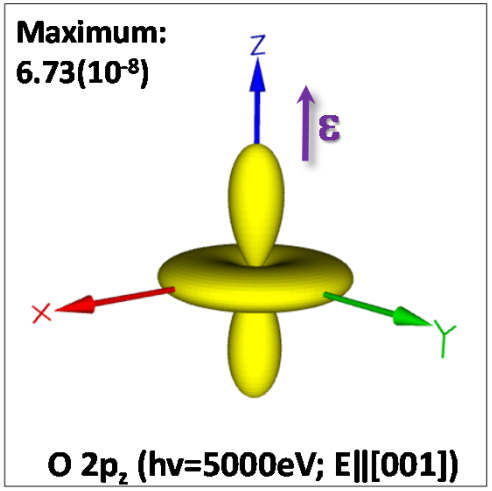

O $2p_z$ (hv=800eV; E||[010])




O $2p_z$ (hv=5000eV; E||[010])

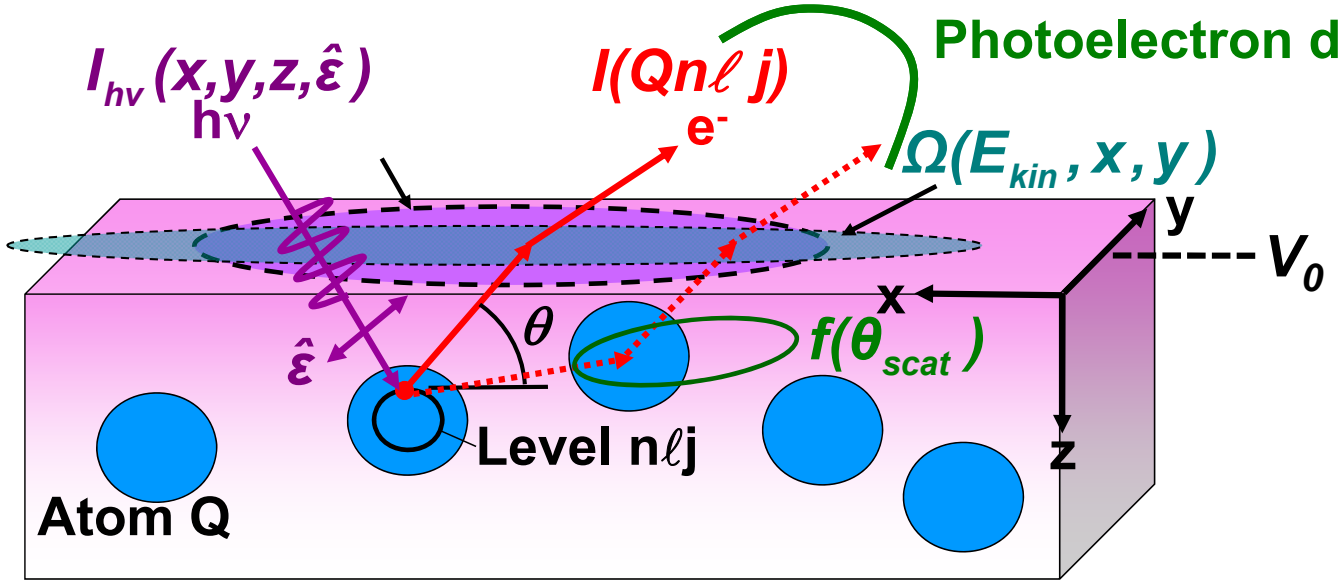



O $2p_z$ (hv=800eV; E||[001])




O $2p_z$ (hv=5000eV; E||[001])

# ATOMIC (CORE) PHOTOELECTRON INTENSITIES: THE THREE-STEP MODEL




$I(Qn\ell\, j)$ =

$$C\int_0^{\infty} I_{h\nu}(x,y,z,\hat{\varepsilon})\,\rho_Q(x,y,z)\,\frac{d\sigma_{Qn\ell j}(h\nu,\hat{\varepsilon})}{d\Omega}\,\exp\left[-\frac{z}{\Lambda_e(E_{kin})\sin\theta}\right]\Omega(E_{kin},x,y)\,dxdydz$$

$I_{h\nu}(x,y,z,\hat{\varepsilon})$ = x-ray flux, $\hat{\varepsilon}$ = polarization

$\rho_Q(x,y,z)$ = density of atoms Q → quantitative analysis

$\frac{d\sigma_{Qn\ell j}(h\nu,\hat{\varepsilon})}{d\Omega}$ = energy-dependent differential photoelectric cross section for subshell $Qn\ell\, j$

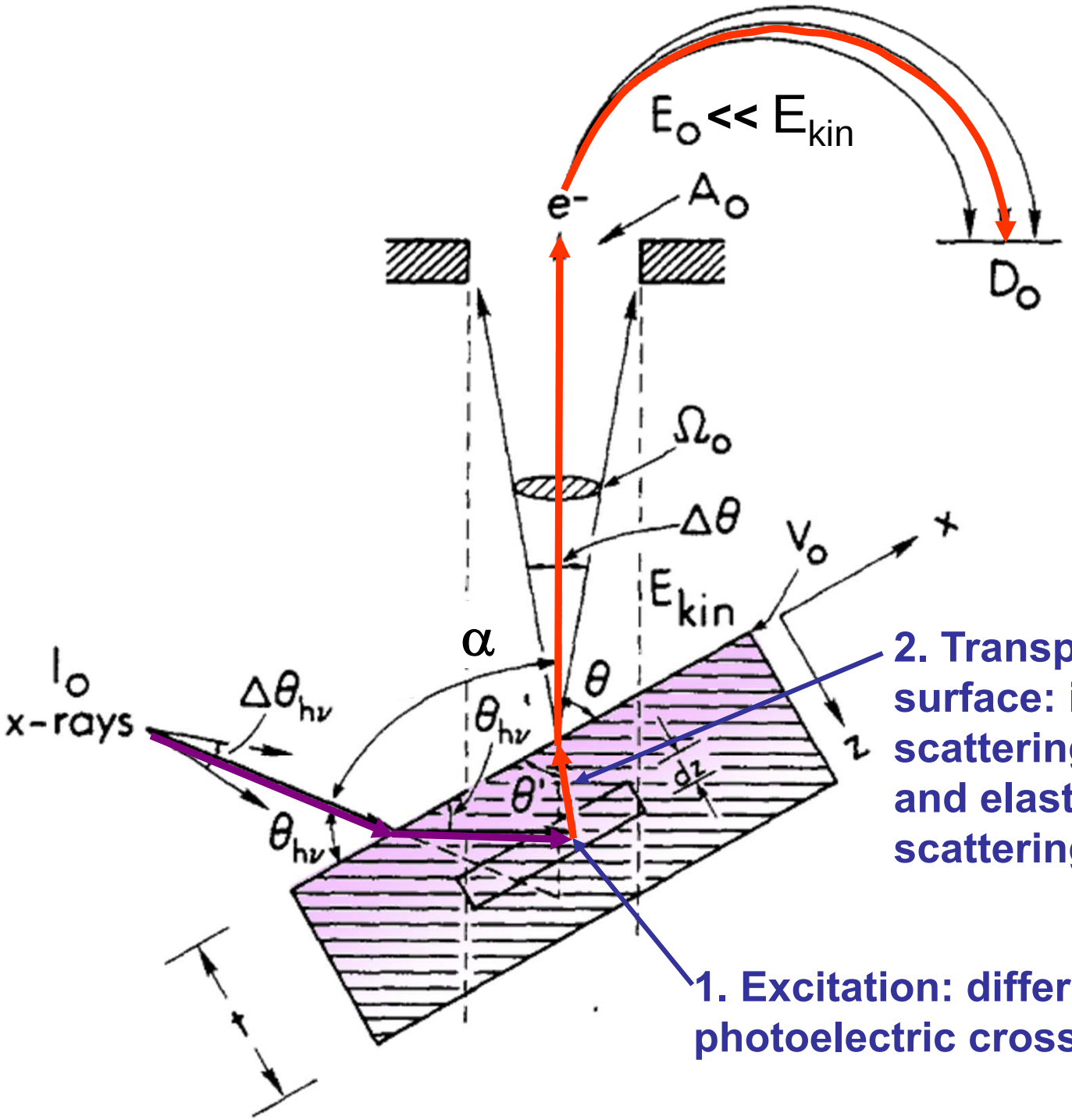
$\Lambda_e(E_{kin})$ = energy-dependent inelastic attenuation length + elastic scattering: $f(\theta_{scatt})$

→ Effective Attenuation Length (EAD) → Mean Emission Depth (MED)

$\Omega(E_{kin},x,y)$ = energy-dependent spectrometer acceptance solid angle = transmission function

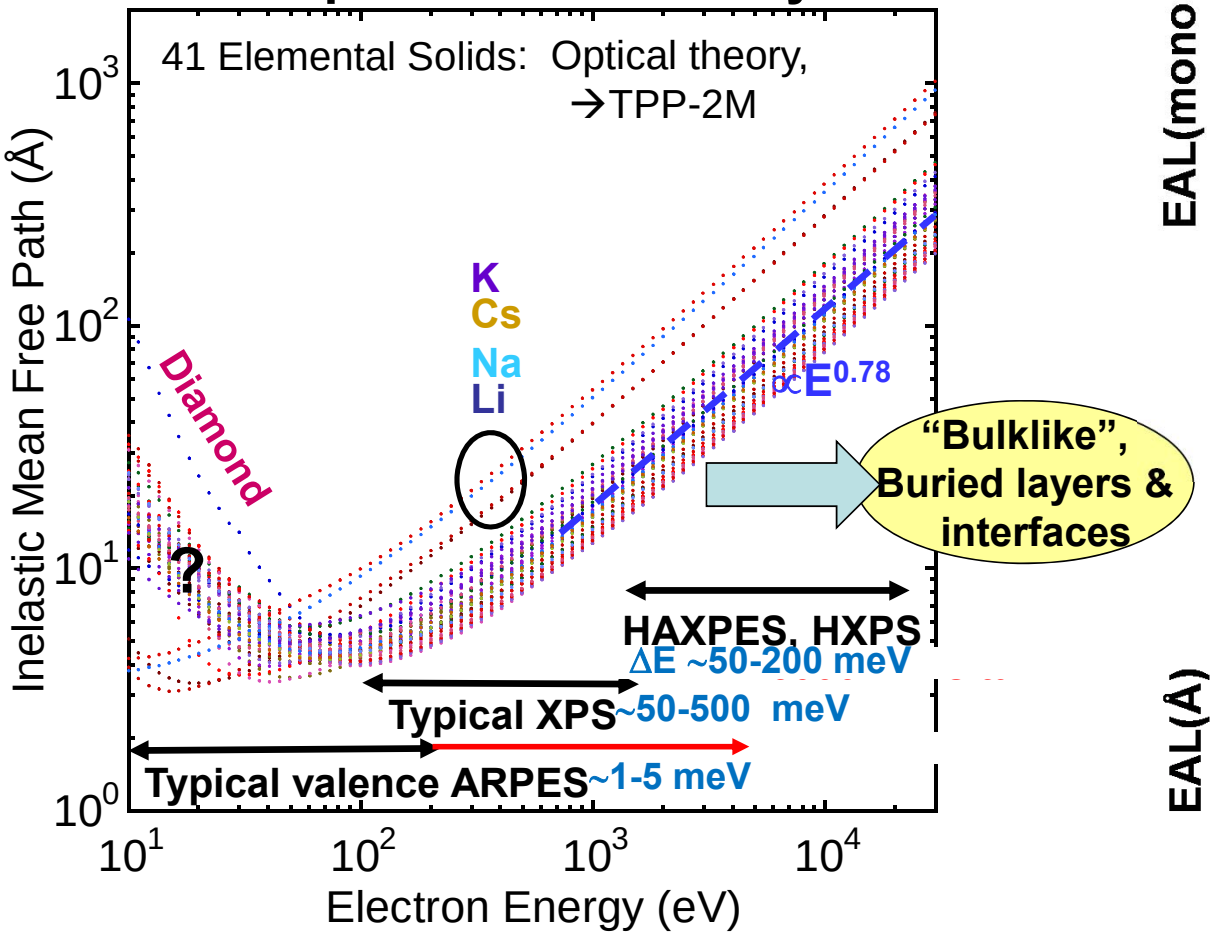
$V_0$ = inner potential

# PHOTOELECTRON INTENSITIES—THE 3-STEP MODEL



# More bulk sensitivity in photoemission by going to hard x-rays

## Optical-based theory

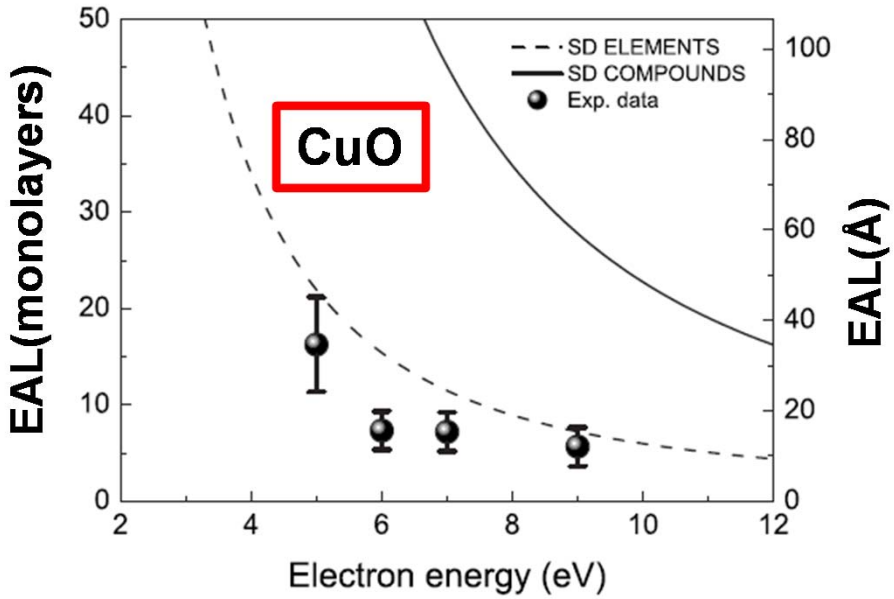



Tanuma, Powell, Penn, Surf. and Interf. Anal. 43, 689 (2011)

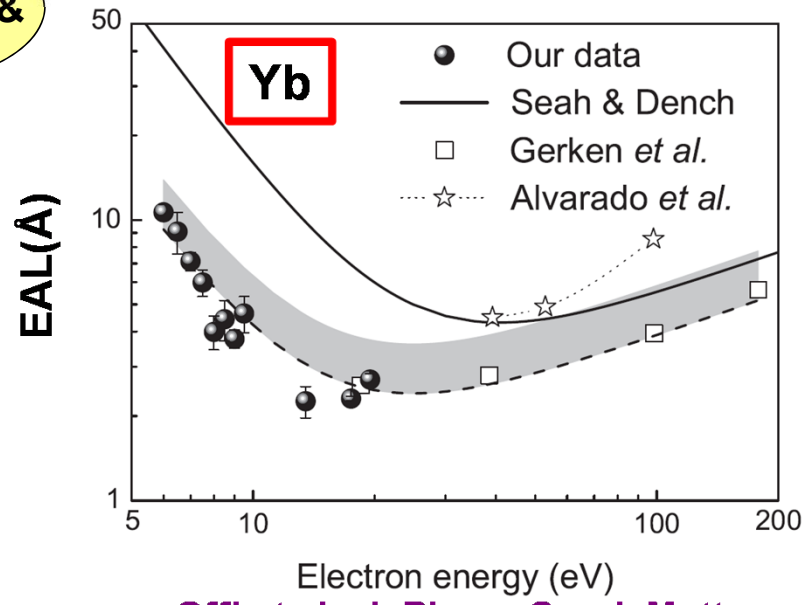
**→The only certain way to obtain more bulk sensitivity**

**And with competitive energy resolutions**

## Experiment




Offi et al., PRB 77, 201101R (2008)




Offi et al., J. Phys.: Cond. Matt. 22 (2010) 305002

**Basic Concepts:**

A Little Electronic Structure
The X-Ray-Based Experiments
X-Ray Sources, Synchrotron Radiation, Free Electron Lasers

**Core-Level Photoemission**

Intensities and Quantitative Analysis, the 3-Step Model

Varying Surface and Bulk Sensitivity
Chemical Shifts
Multiplet Splittings
Electron Screening and Satellite Structure
Magnetic and Non-Magnetic Dichroism
Resonant Photoemission
Photoelectron Diffraction and Holography

**Valence-Level Photoemission**

Band-Mapping in the Ultraviolet Photoemission Limit
Densities of States in the X-Ray Photoemission Limit

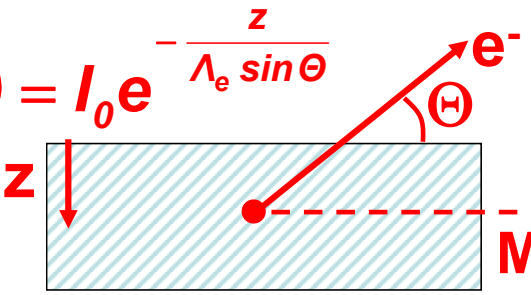
**Some New Directions**

Photoemission with Hard X-Rays (throughout lectures)
Photoemission with Standing Wave Excitation
Photoemission with: Higher Pressures→multi-Torr→Atmosphere?
Spatial Resolution-Photoelectron Microscopy
Temporal Resolution

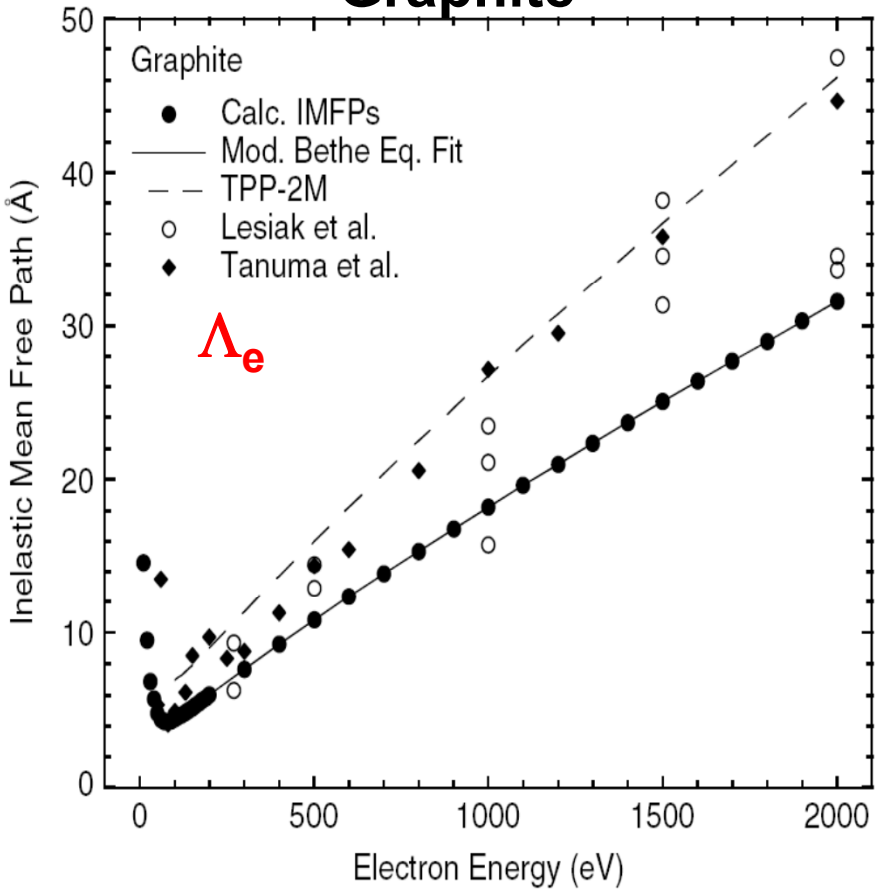
# Electron inelastic attenuation length in solids—the "universal curve"
# Photoemission is a surface sensitive experiment

**Changing angle:**
**1st way to vary surface sensitivity**

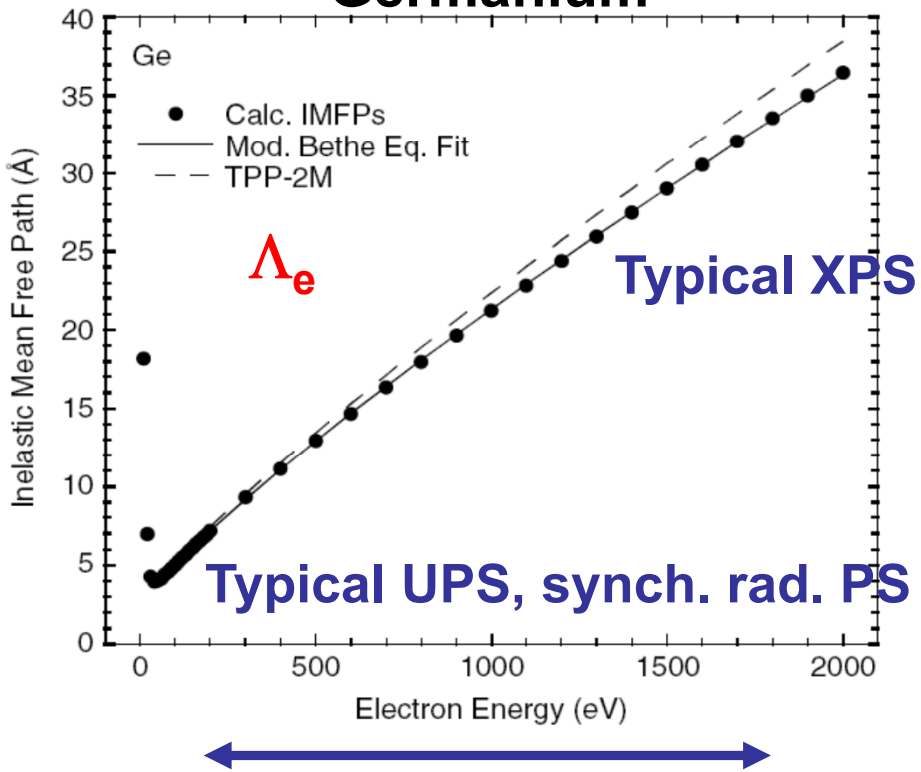
$$I(z) = I_0 e^{-\frac{z}{\Lambda_e \sin\Theta}}$$




## Graphite

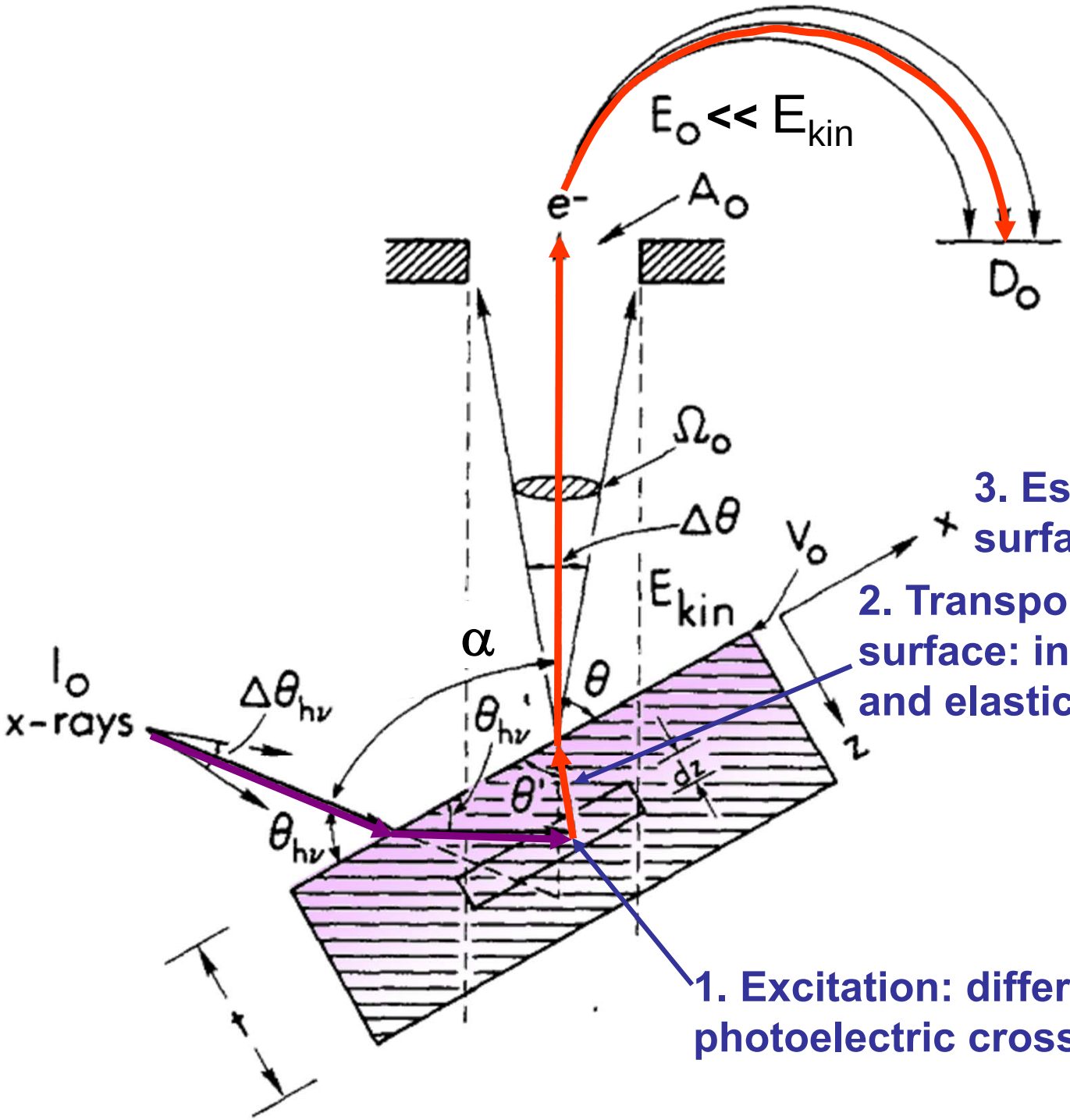



## Germanium




**Changing photon energy:**
**2nd way to vary surface sensitivity**

# PHOTOELECTRON INTENSITIES—THE 3-STEP MODEL

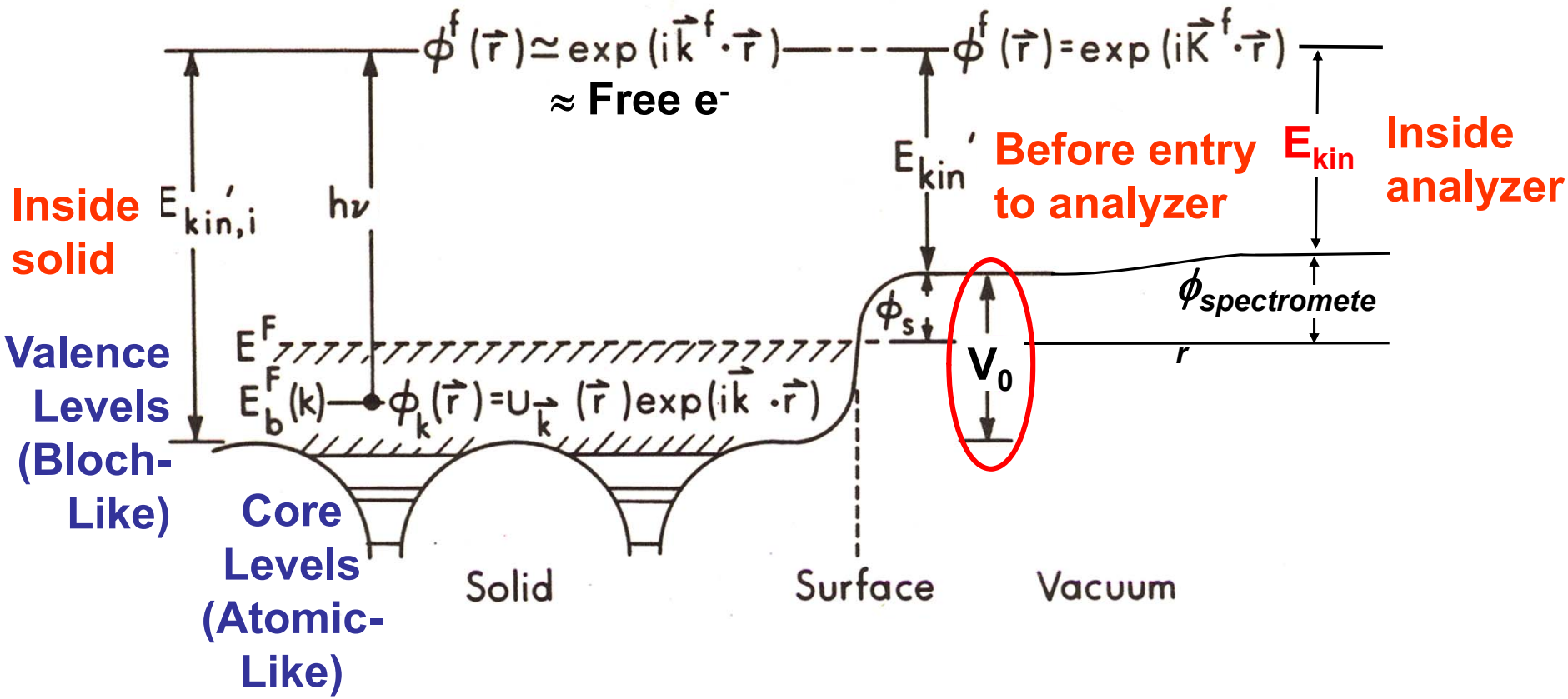



**3. Escape across the surface barrier ($V_0$)**

**2. Transport to the surface: inelastic ($\Lambda_e$) and elastic ($f(\theta)$) scattering**

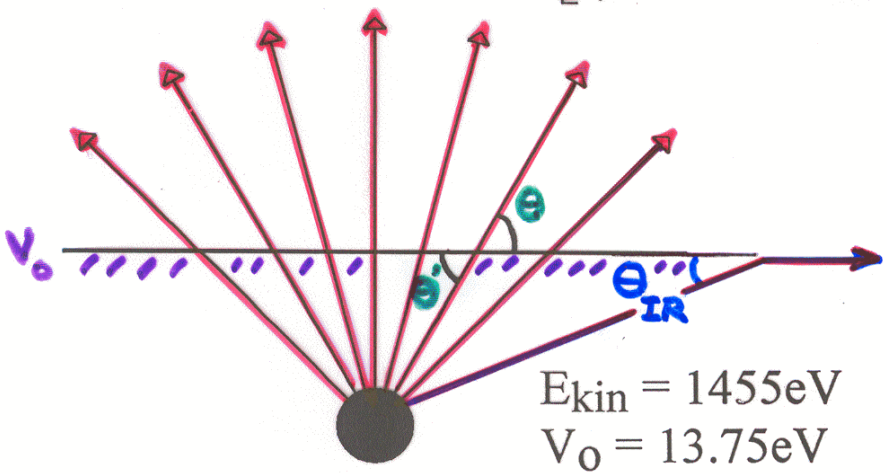
**1. Excitation: differential photoelectric cross section ($d\sigma/d\Omega$)**

# One-Electron Picture of Photoemission from a Surface

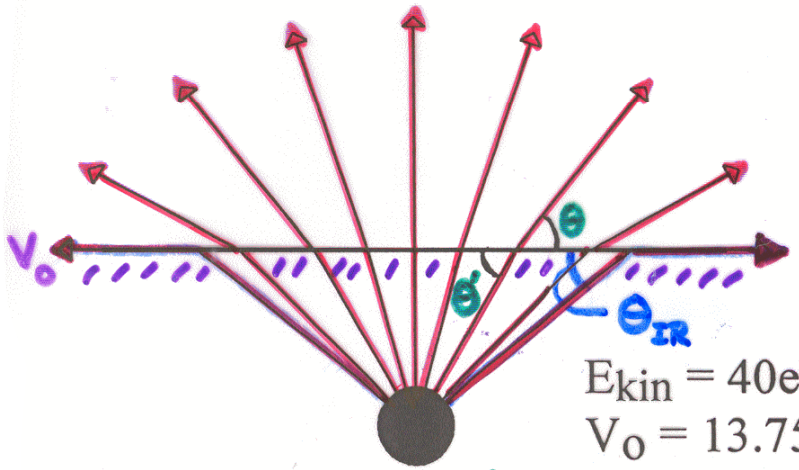


# Electron Refraction at the Surface Due to the Inner Potential

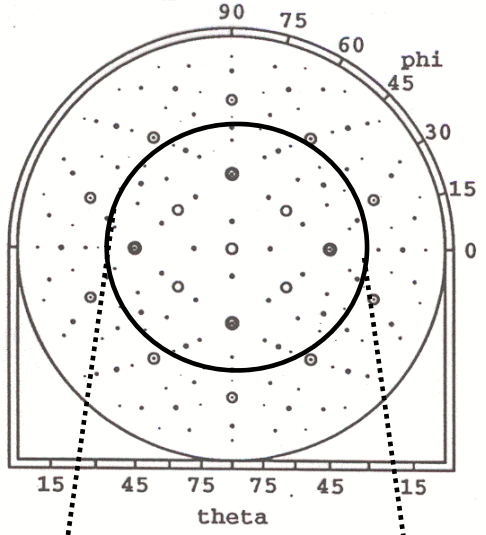
$$\theta = \tan^{-1}\left[\sqrt{\sin^2\theta' - \frac{V_o}{E_{kin}}} \Big/ \cos\theta'\right]$$, $\theta_{IR}$ = total internal reflection

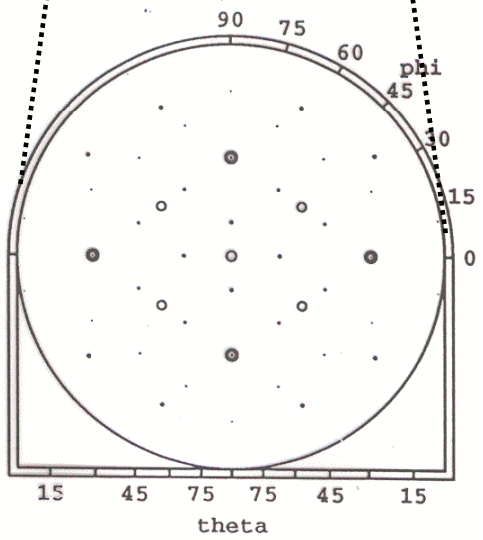



$E_{kin} = 1455eV$
$V_o = 13.75eV$
$\theta'_{min} = \theta_{IR} \approx 6°$



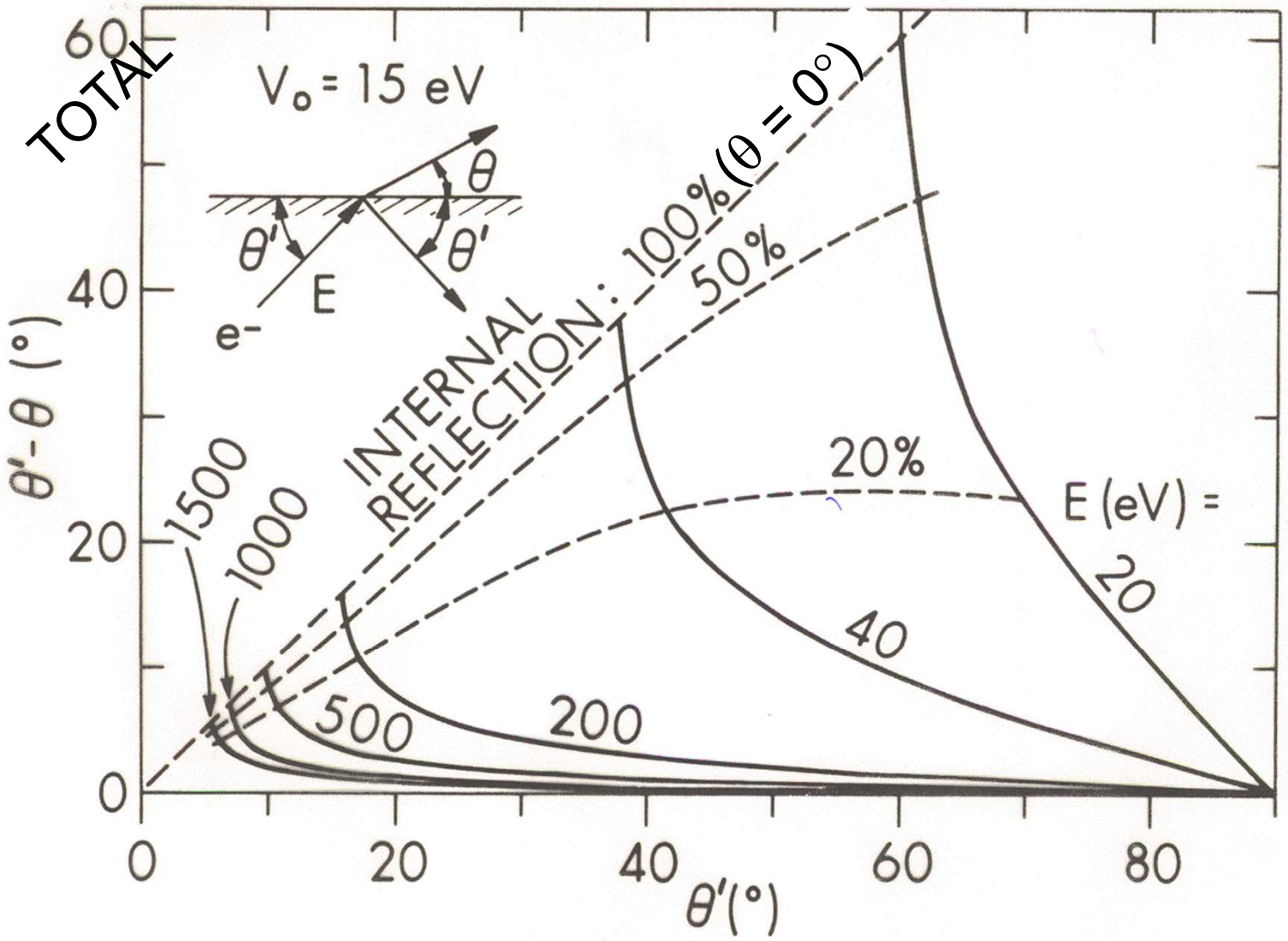

$E_{kin} = 40eV$
$V_o = 13.75eV$
$\theta'_{min} = \theta_{IR} \approx 39°$



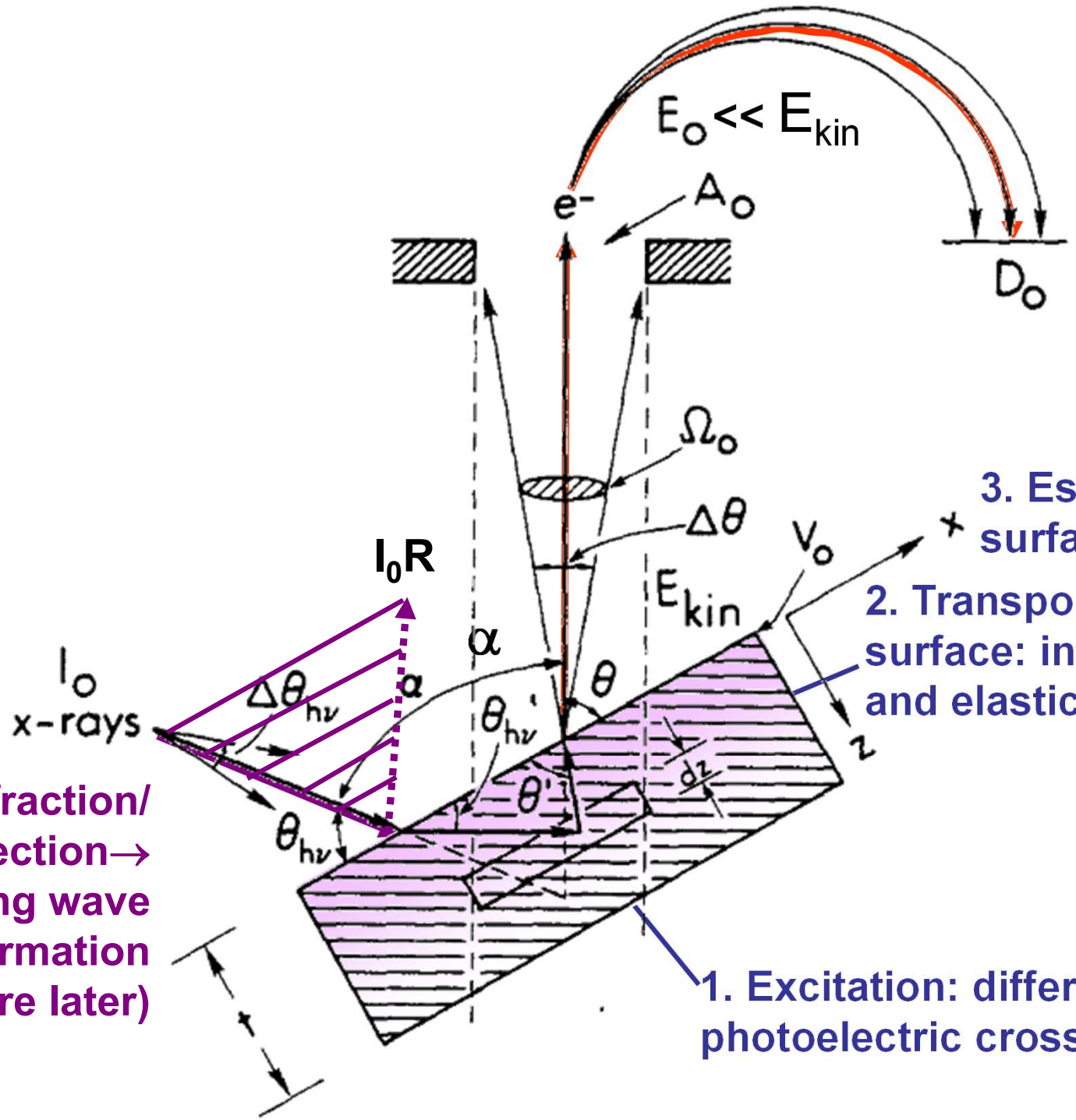

**Observed Low-Index Directions Above W(110)**

# Electron Refraction at the Surface Due to the Inner Potential




C. S. F., *Prog. Surf. Sci.* 1984, *16*, 275

# PHOTOELECTRON INTENSITIES—THE 3-STEP MODEL



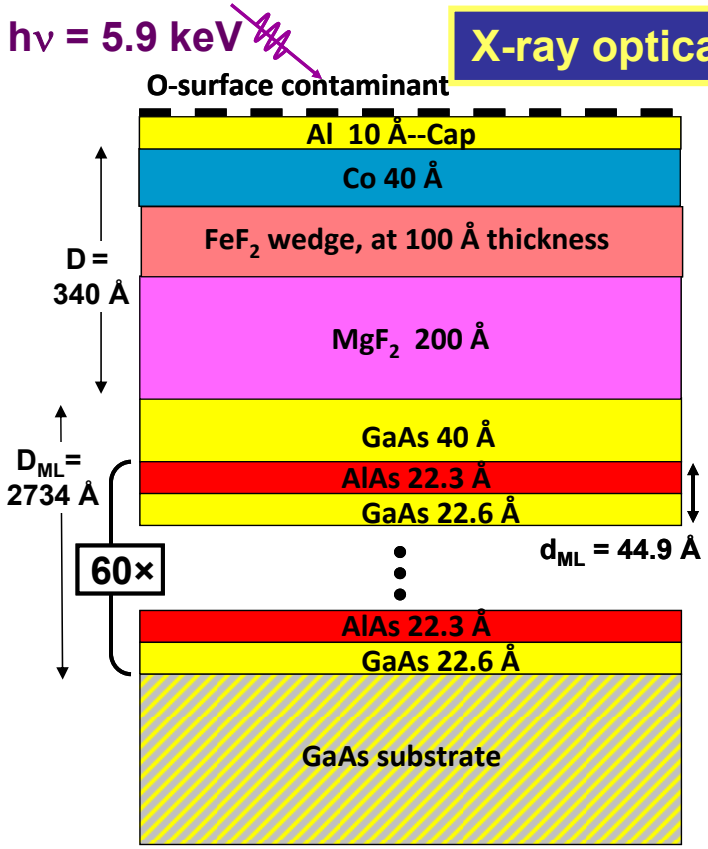

3. Escape across the surface barrier ($V_0$)

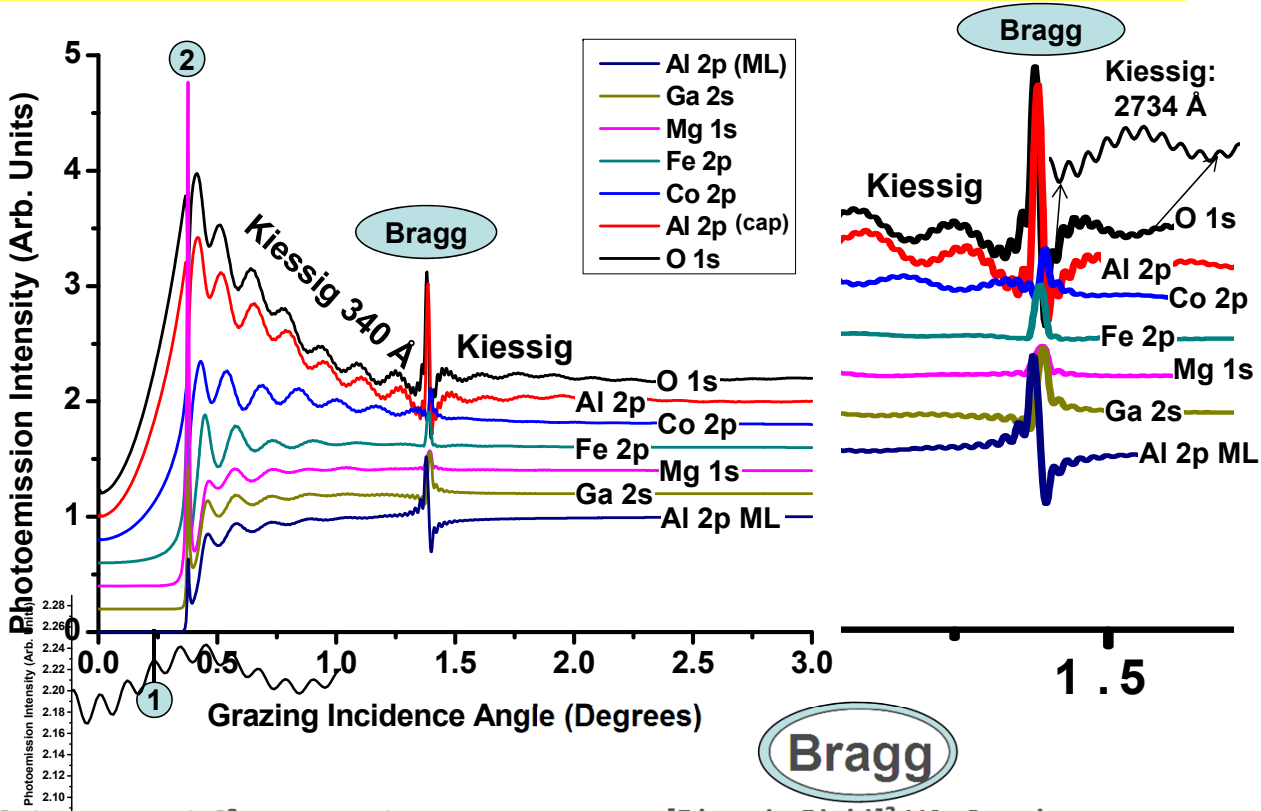
2. Transport to the surface: inelastic ($\Lambda_e$) and elastic ($f(\theta)$) scattering

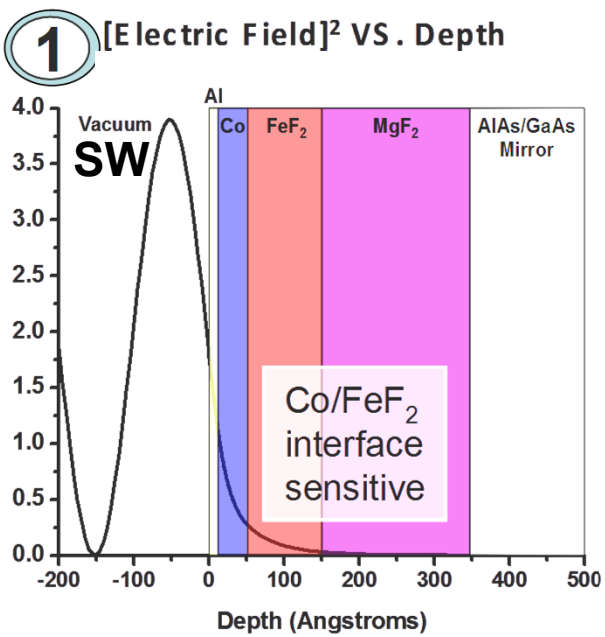
+X-ray refraction/ reflection→ standing wave formation (more later)

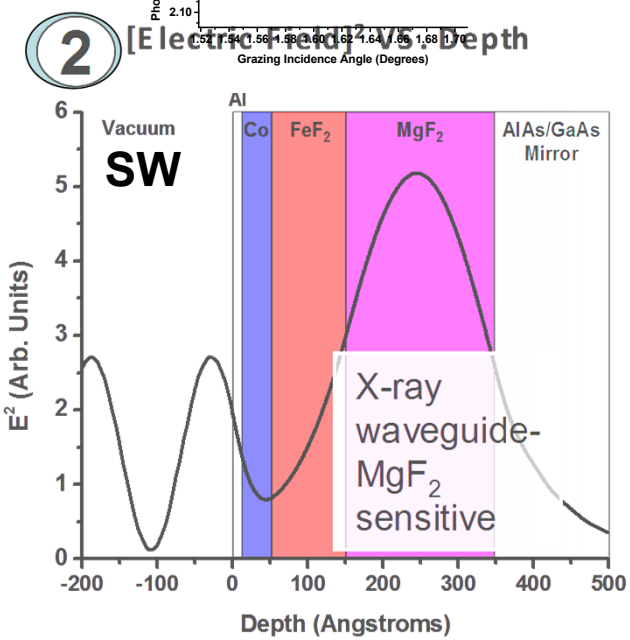
1. Excitation: differential photoelectric cross section ($d\sigma/d\Omega$)

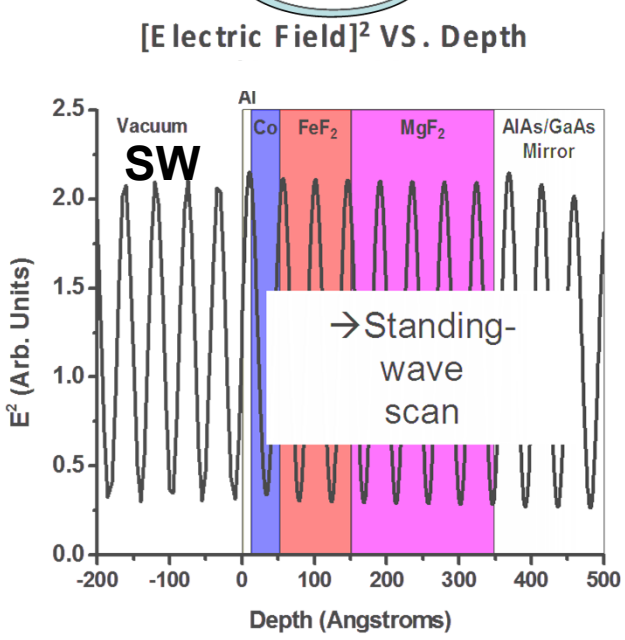
# X-ray optical effects in hard x-ray reflectivity from a multilayer structure




Yang et al., J. Appl. Phys. 113, 073513 (2013)

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**Changing angle:**
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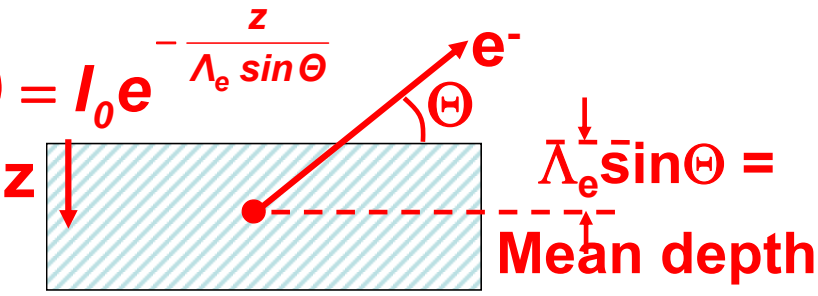
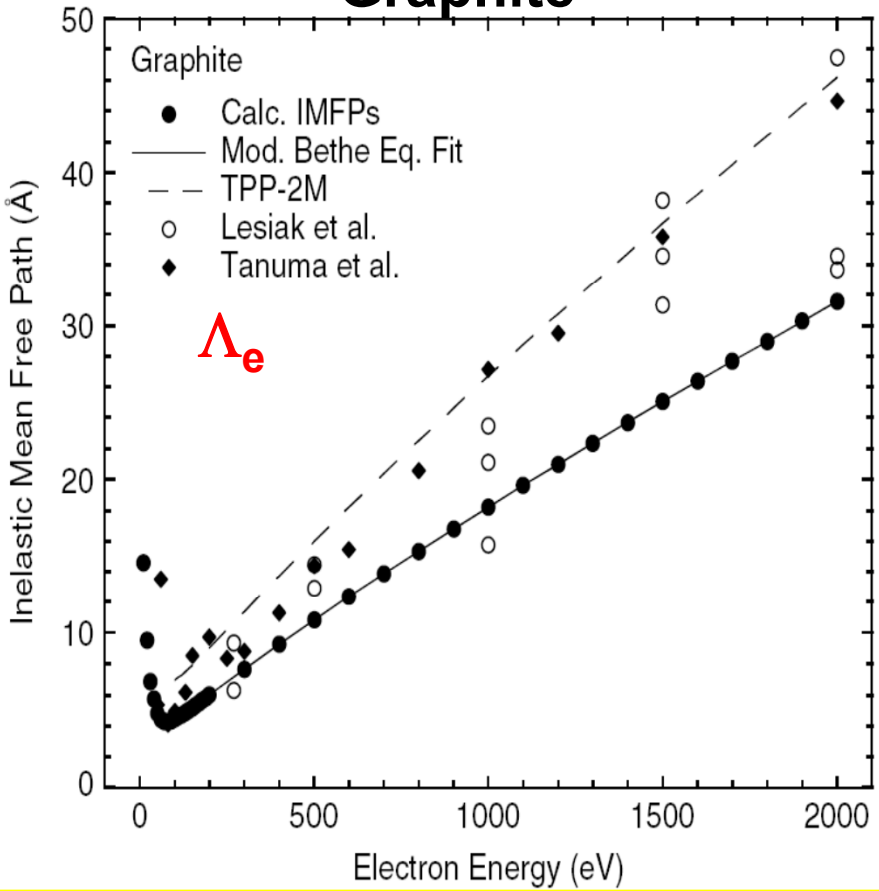
$$I(z) = I_0 e^{-\frac{z}{\Lambda_e \sin\Theta}}$$




## Graphite

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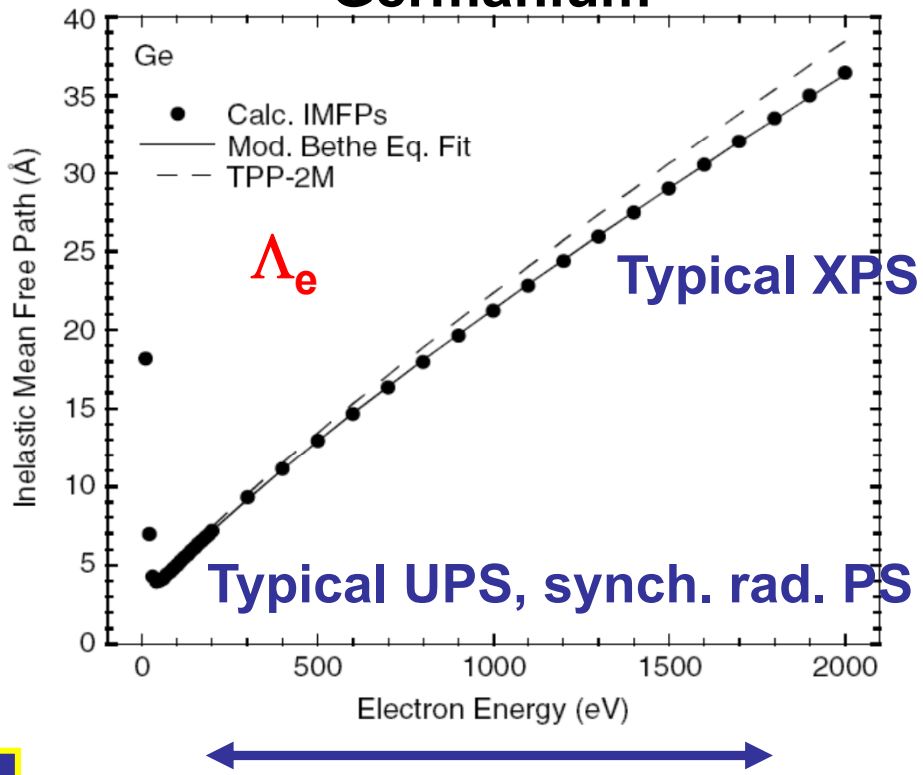
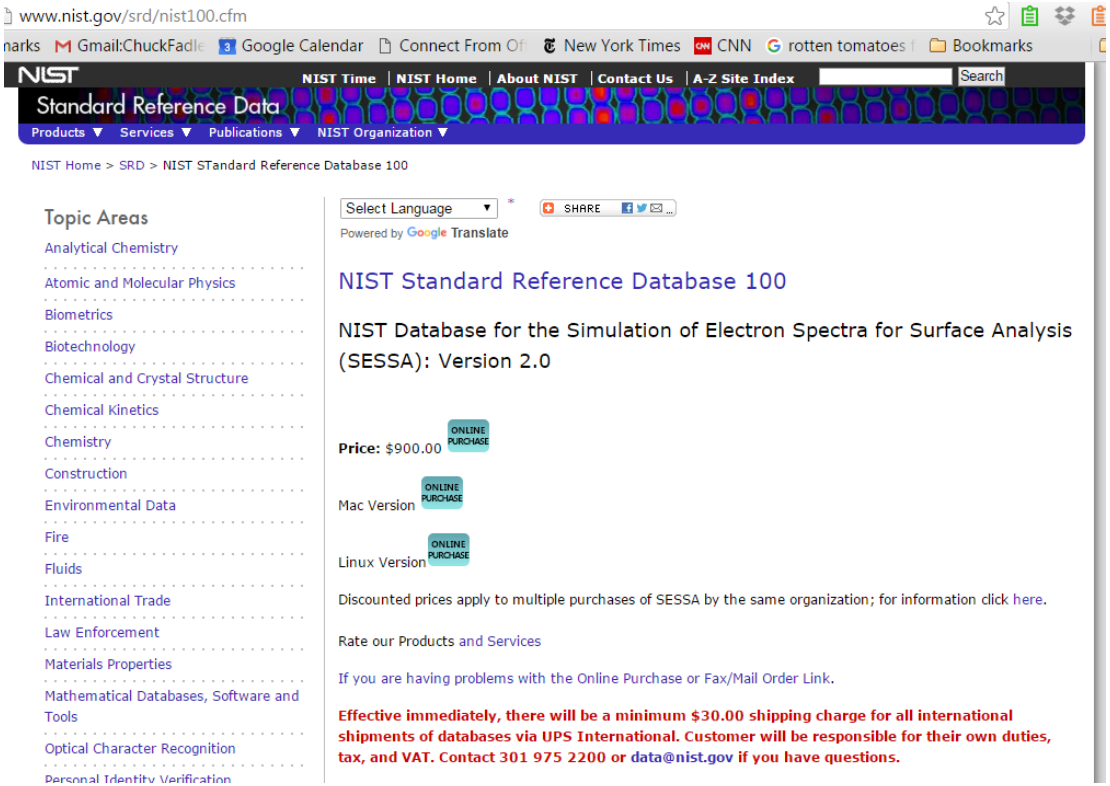



**Changing x-ray penetration/**
**standing wave/total reflection:**
**3rd way to vary surface sensitivity**

**Changing photon energy:**
**2nd way to vary surface sensitivity**

# SIMULATING XPS SPECTRA-WITH ELASTIC SCATTERING THE SESSA PROGRAM FROM NIST

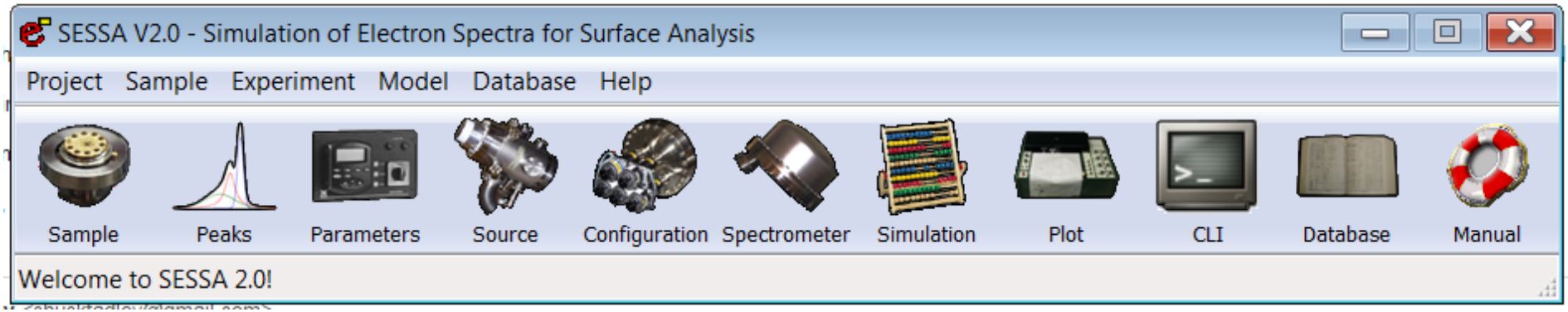



***Includes:***

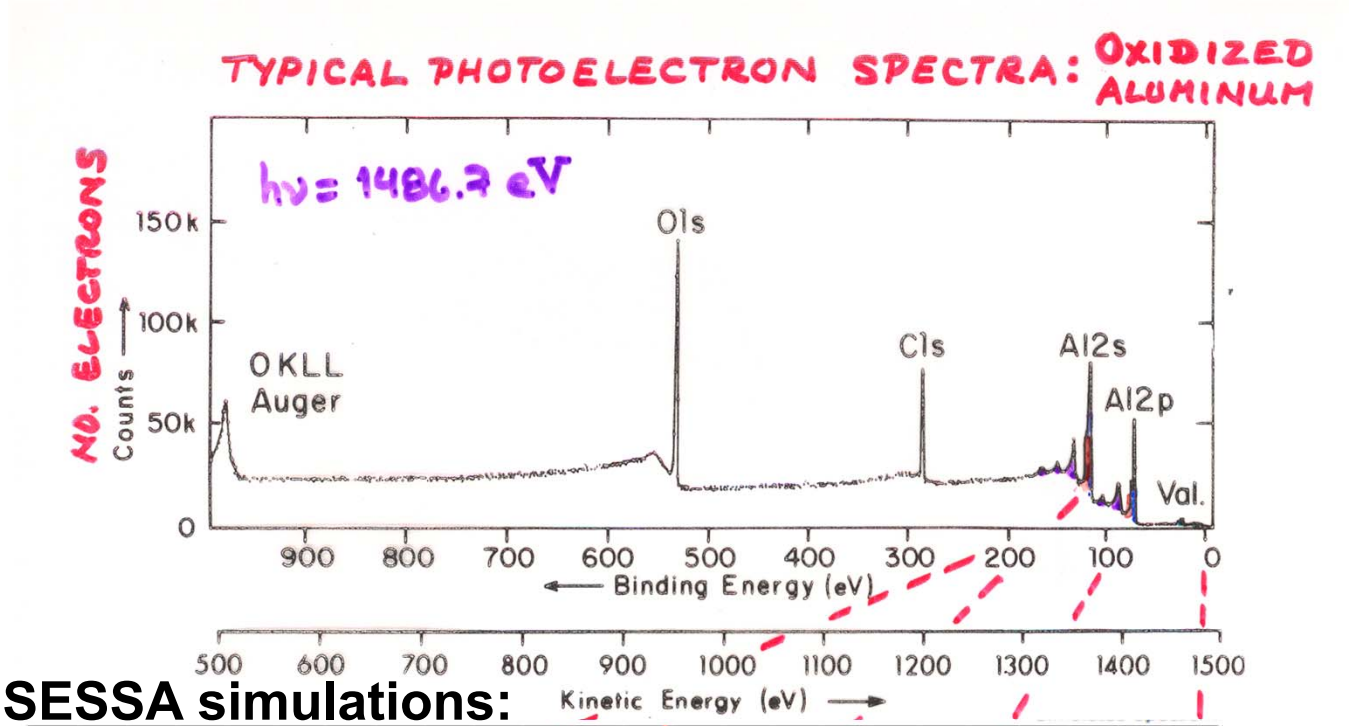
- **Cross sections**
- **Radiation polarization**
- **Inelastic mean free path**
- **Elastic scattering**
- **Exact experimental geometry**
- **Estimate of Auger intensities**

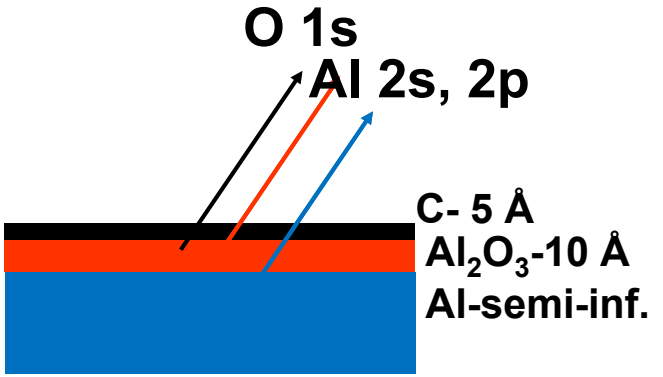
***Does not include:***

- **Trajectory bending at the inner potential $V_0$**
- **Any x-ray optical effects (for that our YXRO program: Yang et al., J. Appl. Phys. 113, 073513 (2013)**

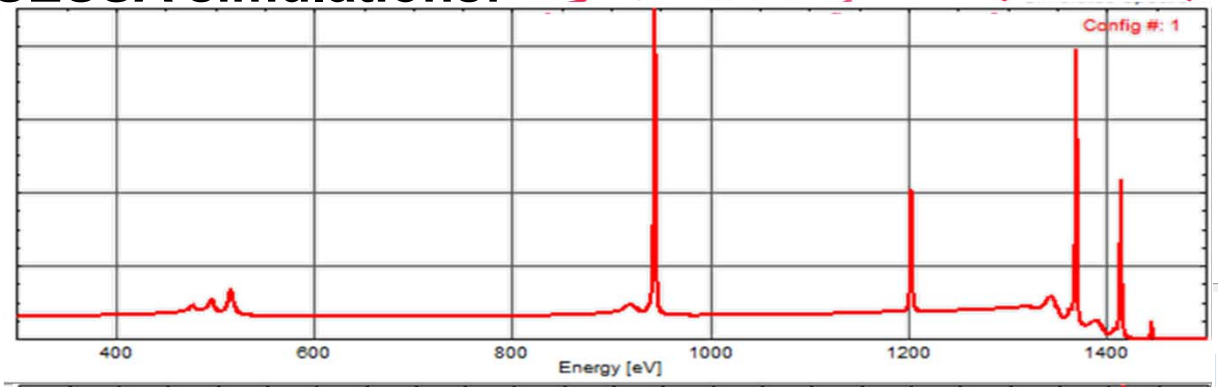


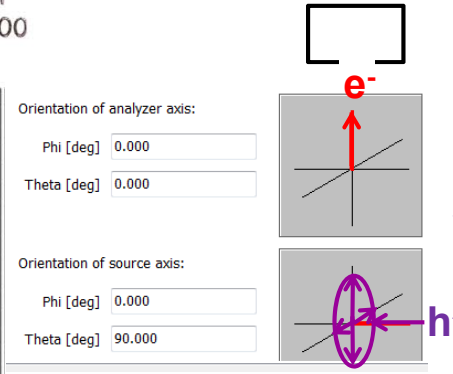

**W. Smekal, W. S. M. Werner and C. J. Powell, Surf. Interface Anal. 3, 1059 (2005); W. S.M. Werner, W. Smekal, T. Hisch, J. Himmelsbach, C. J. Powell, J. Electron Spectrosc. 190, 137 (2013).**



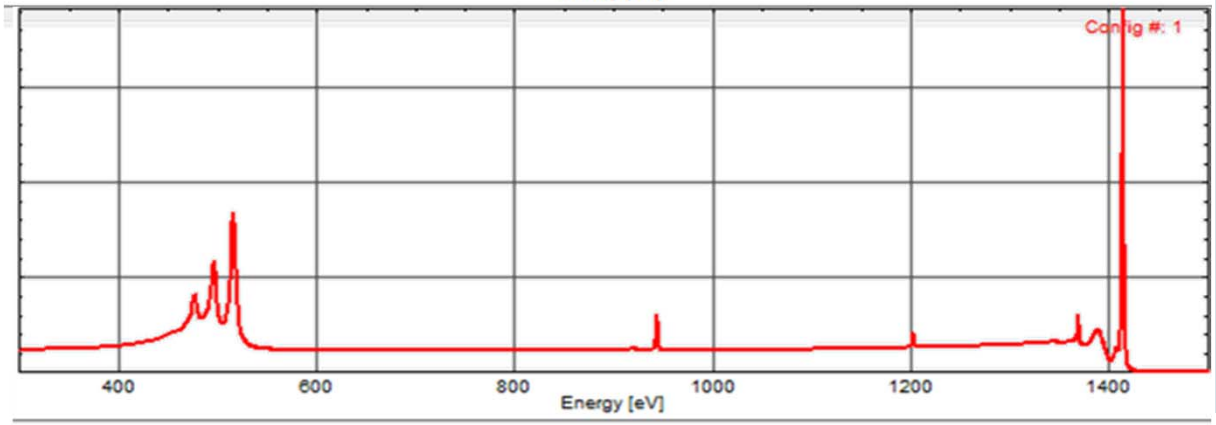



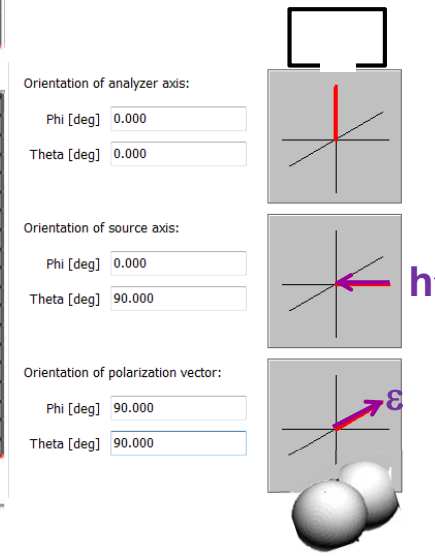

## SESSA simulations:




Unpolarized, with some components pointing into analyzer




Polarized along axis perp. to plane of x-ray incidence and electron exit, and so yielding electron emission into the nodal line of any s-shell cross section

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