Reading and Problem Assignments for Physics 243A
Surface Physics of Materials: Spectroscopy, Fall, 2016
(In order of coverage in lecture)

Reading:

- **Woodruff and Delchar, "Modern Techniques of Surface Science", 2nd Edition--**
  - Chapter 1
  - Chapter 2: Sections 2.1, pp.22 (bottom)-23(top) on Wood notation for surface structures, 2.4, and 2.5 (pp. 31-37), 2.9.6 on standing waves
  - Chapter 6: 6.9, 6.10, 6.11
  - Chapter 3: Sections 3.1, 3.2, 3.3, 3.5

- **Zangwill, "Physics at Surfaces", downloadable Chapters 1-5 (see course website)--**
  - Chapter 1: Everything except "The roughening transition"
  - Chapter 3: pp. 28-34, pp. 49-52 on STM
  - Pages 85-86, 192-196, 204-212
  - Chapter 2: All
  - Chapter 4: Introduction, with lighter reading of *The jellium model, One-dimensional band theory, and Three-dimensional band theory*, and detailed reading of *Photoelectron spectroscopy, Metals, and Alloys*

- **Ibach, "Physics of Surfaces and Interfaces", downloadable book (see course website)—**
  - Chapter 2: 2.1, 2.2
  - Chapter 8: 8.2

- **Desjonqueres and Spanjaard, "Concepts of Surface Physics", excerpts downloadable from Course website:** On STM current calculation, equilibrium shapes of surfaces, thermodynamics, kinetics and adsorption isotherms. No need to follow every step, but this fills in the line of arguments in Zangwill and lecture

- **Fadley, "Basic Concepts of XPS", to be handed out, but also downloadeable—**
  - Sections I, II, and III. A-C, with remaining sections by the end of the course

- **Attwood, Downloadeable excerpt on synchrotron radiation from the book "Soft X-Rays and Extreme Ultraviolet Radiation" (see course website)**

Problem assignments:
Problem set 1-all. Due Thursday, October 13th
Problem set 2-all. Due Thursday, October 27th

Midterm exam: Tuesday, November 1st, open book and open notes. Computers OK, but no cell phones, or use of material from prior offerings of this course beyond that at the website.

Reading coverage for midterm

Next reading in blue: Rest of "Basic Concepts" +Molecular Orbital Basics &Tight-Binding Basics (from website)

Office hours:

TA: Galina Malovichko- 2:00-3:00 PM, Mondays, Physics 416

Instructor: Chuck Fadley, 2:30-3:30, Tuesdays and Thursdays, Physics 241 (others by special appointment)

Class consultant: Shih-Chieh Lin- 4:20-5:20, Wednesdays, Physics 221

Handing in problem sets:

Hand in problem sets in class, or in secure submission box with class number on it. The new homework submission boxes are located in the east wing at the first floor north entrance to the Physics Building – the same hallway where our student computer lab. is located (rm 106 Physics)

Table 1 Cohesive Energies* of the elements

Energy required to form separated neutral atoms from the solid at 0°K; the values in parentheses are at 298.15°K or at the melting point, whichever temperature is lower. To obtain the energy in J mol^{-1}, multiply the energy in kcal mol^{-1} by $4.184 = 10^3$. To obtain the energy in ergs per atom, multiply the energy in eV per atom by 1.60219×10^{-12}.

← eV per atom →
← kcal per mole →

H 4.48 / 103																	**He**
Li 1.65 / 38.0	**Be** 3.33 / 76.9											**B** 5.81 / 134.	**C** 7.36 / 170.	**N** (114)	**O** (60)	**F** (20)	**Ne** 0.02 / 0.45
Na 1.13 / 26.0	**Mg** 1.53 / 35.3											**Al** 3.34 / 76.9	**Si** 4.64 / 107	**P** (79.2)	**S** 2.86 / 66.1	**Cl** (32.2)	**Ar** 0.080 / 1.85
K 0.941 / 21.7	**Ca** 1.825 / 42.1	**Sc** 3.93 / 90.6	**Ti** 4.855 / 112.0	**V** 5.30 / 122.	**Cr** 4.10 / 94.5	**Mn** 2.98 / 68.7	**Fe** 4.29 / 98.9	**Co** 4.387 / 101.2	**Ni** 4.435 / 102.3	**Cu** 3.50 / 80.8	**Zn** 1.35 / 31.1	**Ga** 2.78 / 64.2	**Ge** 3.87 / 89.3	**As** 3.0 / 69.	**Se** 2.13 / 49.2	**Br** 1.22 / (28.2)	**Kr** 0.116 / 2.67
Rb 0.858 / 19.8	**Sr** (39.1)	**Y** 4.387 / 101.2	**Zr** 6.316 / 145.7	**Nb** 7.47 / 172.	**Mo** 6.810 / 157.1	**Tc**	**Ru** 6.615 / 152.6	**Rh** 5.752 / 132.7	**Pd** 3.936 / 90.8	**Ag** 2.96 / 68.3	**Cd** 1.160 / 26.76	**In** 2.6 / 59	**Sn** 3.12 / 71.9	**Sb** 2.7 / 62.	**Te** 2.0 / 46	**I** (25.6)	**Xe** (3.57)
Cs 0.827 / 19.1	**Ba** 1.86 / (42.8)	**La** 4.491 / 103.6	**Hf** 6.35 / 146.	**Ta** 8.089 / 186.6	**W** 8.66 / 200.	**Re** 8.10 / 187.	**Os** (187)	**Ir** 6.93 / 160.	**Pt** 5.852 / 135.0	**Au** 3.78 / 87.3	**Hg** (0.694) / (16.0)	**Tl** 1.87 / 43.2	**Pb** 2.04 / 47.0	**Bi** 2.15 / 49.6	**Po** (34.5)	**At**	**Rn**
Fr	**Ra**	**Ac**															

Ce 4.77 / 110	**Pr** 3.9 / 89	**Nd** 3.35 / 77.2	**Pm**	**Sm** 2.11 / 48.6	**Eu** 1.80 / 41.5	**Gd** 4.14 / 95.4	**Tb** 4.1 / 94	**Dy** 3.1 / 71	**Ho** 3.0 / 70	**Er** 3.3 / 77	**Tm** 2.6 / 59	**Yb** 1.6 / 36	**Lu** (4.4) / (102)
Th 5.926 / 136.7	**Pa** 5.46 / 126	**U** 5.405 / 124.7	**Np** 4.55 / 105	**Pu** 4.0 / 92	**Am** 2.6 / 60	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lw**

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Cohesive energies and surface tension

ELEMENT	E_{COH} $\left(\dfrac{kcal}{mol}\right)$	ΔH_{FUS} $\left(\dfrac{kcal}{mol}\right)$	$\dfrac{\Delta H_{FUS}}{E_{COH}}$ (%)
Si	107	9.47	8.9 %
Ca	42.1	2.23	5.3 %
Sc	90.6	3.80	4.2 %
Mn	68.7	3.45	5.0 %
Fe	98.7	3.56	3.6 %
Cu	80.8	3.11	3.8 %
Zn	31.1	1.60	5.1 %
Ge	89.3	8.30	9.3 %

METALS → SEMICOND.

$\sim 4-9$ %

$$\Delta H_{FUS} << E_{COH}$$

$$\text{BOND STRENGTHS}\big|_{LIQ} \approx \text{BOND STRENGTHS}\big|_{SOLID}$$

$$\therefore \quad \gamma_{SOLID} \approx \gamma_{LIQUID}$$

$$\gamma_{SOLID} > \gamma_{LIQUID}$$

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Fig. 1.4. Surface tension of the elements in the liquid phase (Schmit, 1974).
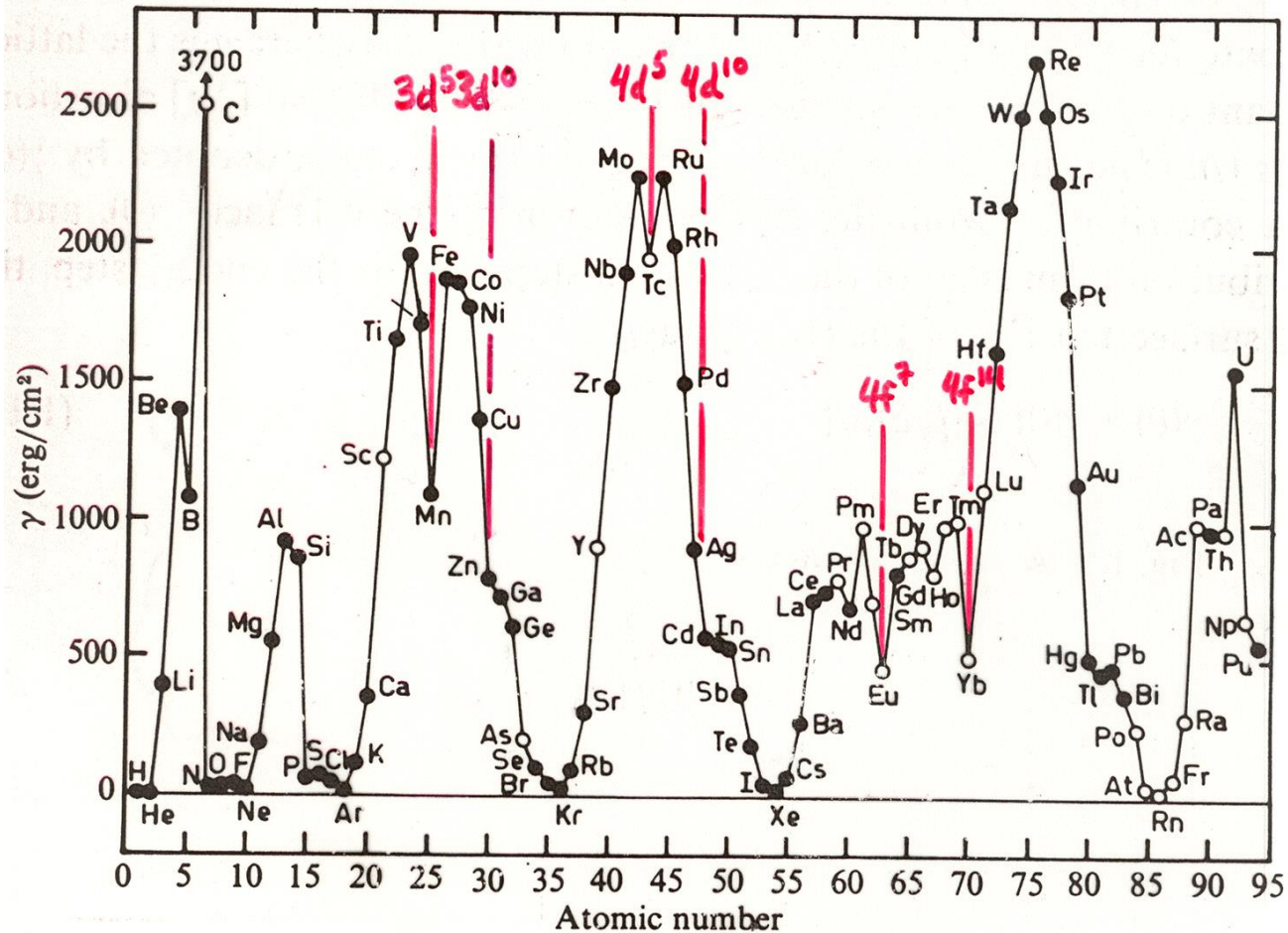
NOTE LOWER VALUES FOR HALF-FILLED HUND'S RULE STATES WITH REDUCED BONDING HYBRIDIZATION (d^5, f^7) AS WELL AS FOR FILLED-SHELL STATES

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SURFACE TREATMENT OF A LOW-FRICTION POLYMERIC COATING FOR TOOLS

"TEFLON S" = A MIXTURE OF EPOXY AND $(CF_2)_x$

Chemical shifts In core electron binding energies

Carbon 1s   Oxygen 1s   Fluorine 1s

WETTING
$\Theta_a = 45°$

Teflon S dried at 70 °F
C−O$_x$ C−C

C−F$_x$

Teflon S baked at 450 °F
$\Theta_a = 109°$

NON-WETTING

FEP film control = PURE $(CF_2)_x$
C−F$_x$
$\Theta_a = 109°$

300   290   280   540   530   700   690   eV

Binding energy
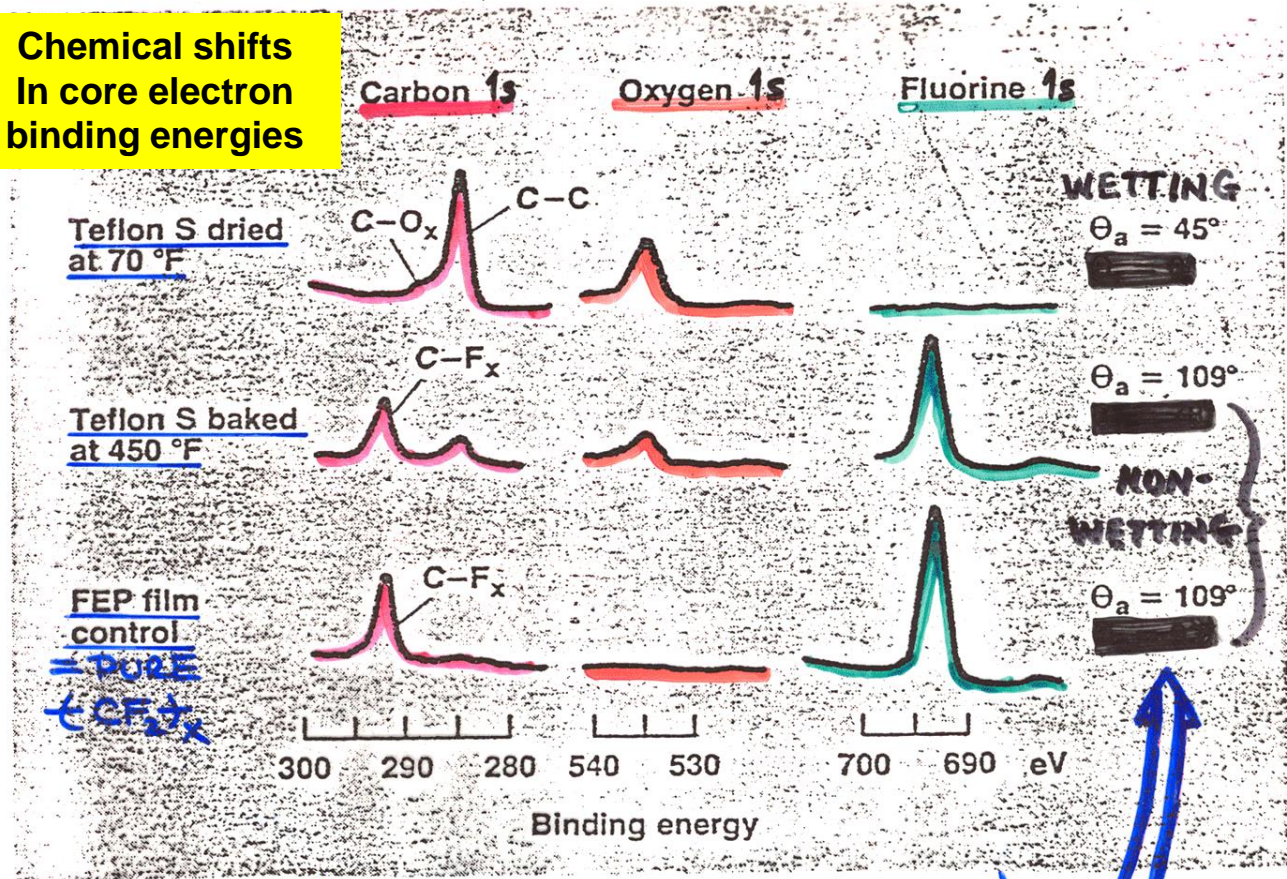
X-RAY PHOTOELECTRON SPECTRA

(D. DWIGHT, CHEMTECH, MARCH 1982)

CONTACT ANGLES:
WATER DROP Θ_a
POLYMER

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$$\gamma(\theta) = \gamma(0) + (\beta/a)|\theta|.$$
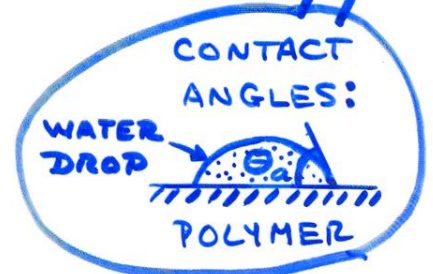
ENERGY TO PRODUCE EACH STEP

+ ENERGY OF INT. BETWEEN STEPS

The Wulff construction

Fig. 1.5. A vicinal surface.

[01] [1n]

θ

a
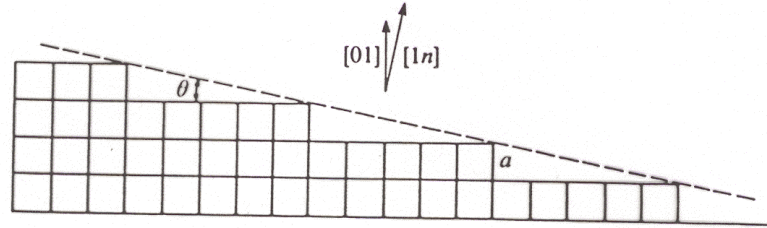
Fig. 1.6. Polar plot of the surface tension at $T = 0$ (solid curve) and the Wulff construction of the equilibrium crystal shape (dashed curve) (Herring, 1951b).
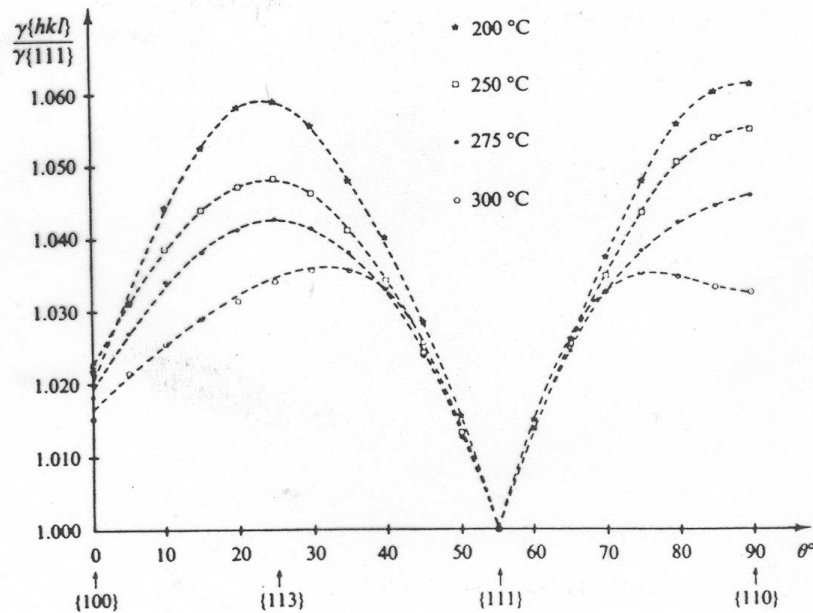
CUSPS AT [hkl] DIRECTIONS
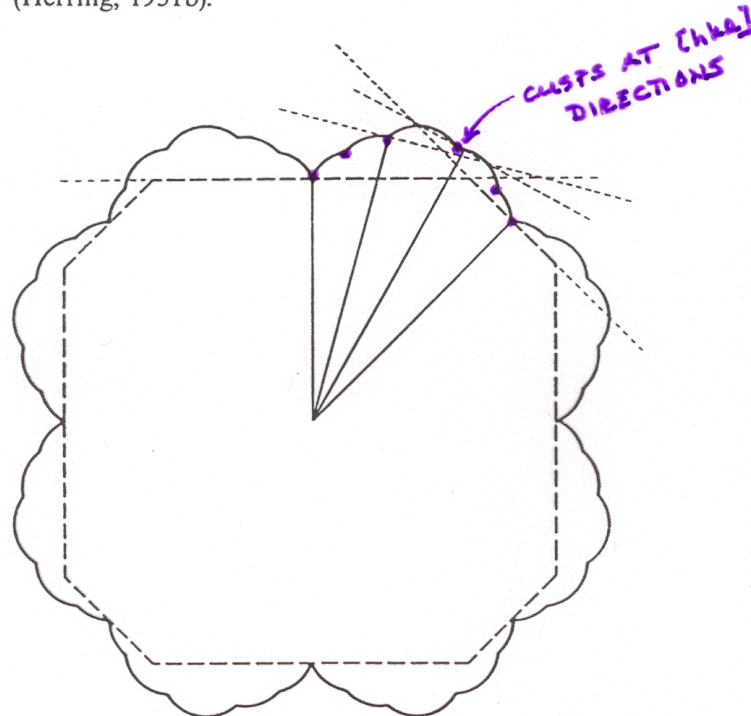
Scanning electron microscopy Images of Pb crystallites

Fig. 1.7. Electron micrograph of a lead crystal at 473 K (Heyraud & Metois, 1983).

⟨111⟩

γ_i

⟨100⟩

⟨111⟩

h_i
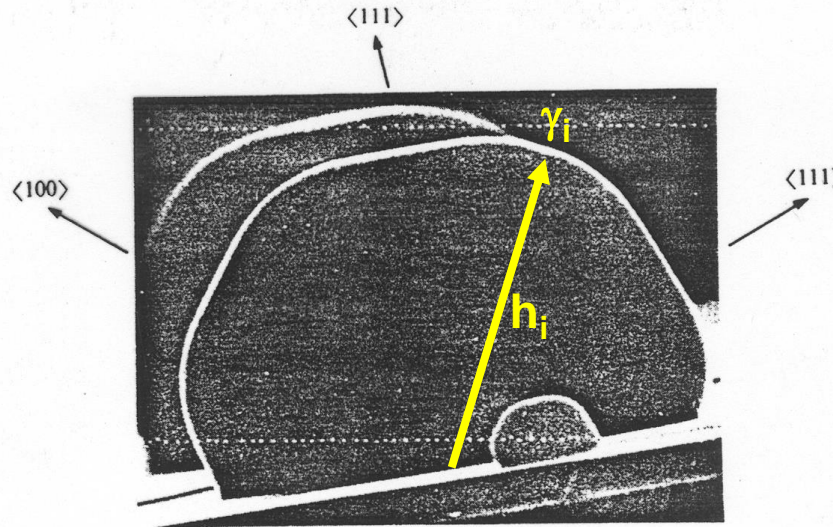
Wulff theorem:
γ_i/h_i = constant

Fig. 1.8. Anisotropy of γ relative to ⟨111⟩ for lead as a function of temperature (Heyraud & Metois, 1983).

$\frac{\gamma\{hkl\}}{\gamma\{111\}}$

- 200 °C
- 250 °C
- 275 °C
- 300 °C

1.060

1.050

1.040

1.030

1.020

1.010

1.000

0   10   20   30   40   50   60   70   80   90   θ°

{100}   {113}   {111}   {110}

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Scanning tunneling microscopy Images of Pb crystallites

C. Bombis et al., Surface Science 511 (2001) 83-96
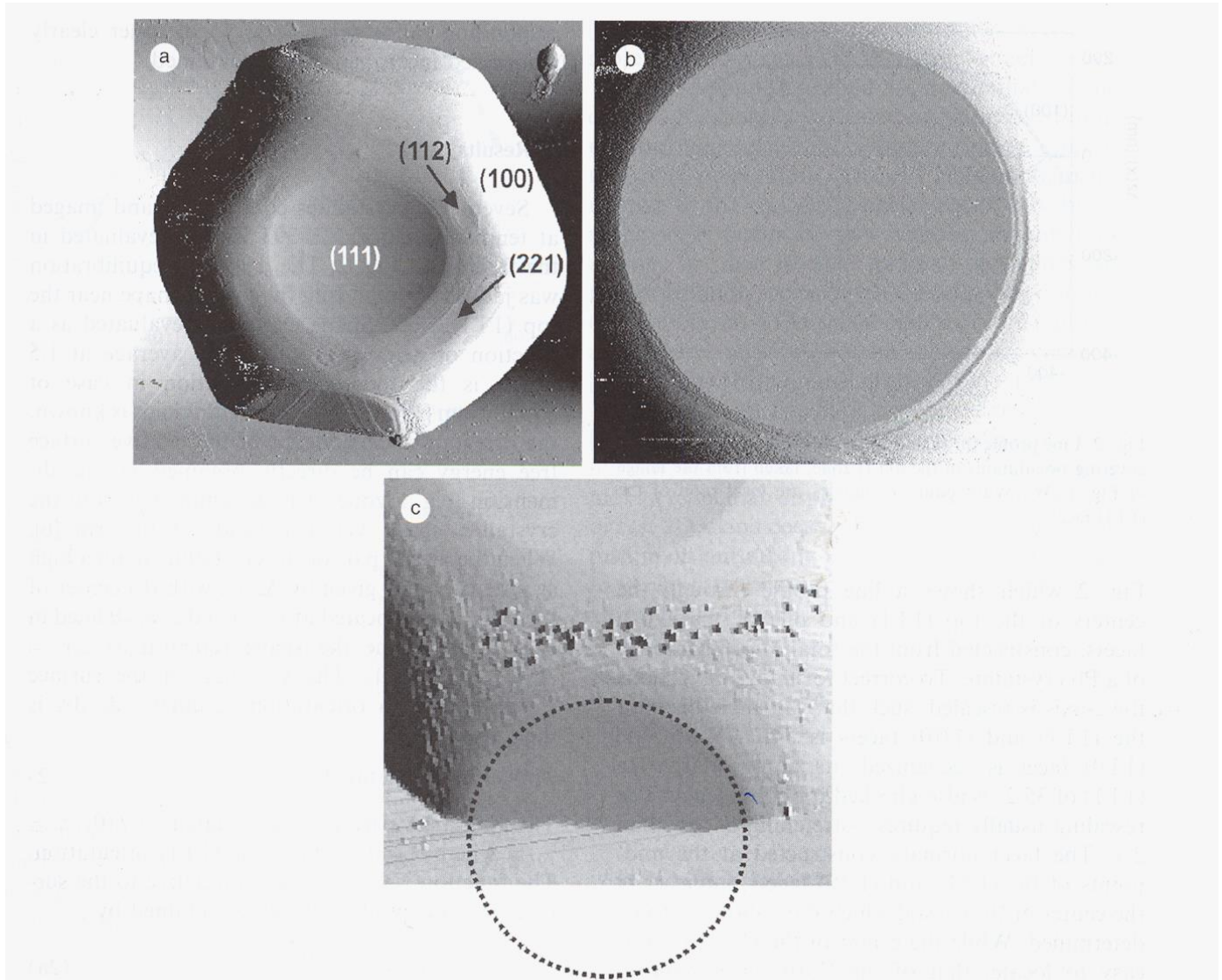
Fig. 1. STM images of equilibrated Pb crystallite. (a) Vertical projection of complete crystallite, with the (1 1 1) facet parallel to the substrate, $T = 323$ K. Note (1 1 2) and (2 2 1) facets near the periphery of the (1 1 1) facet. Large (1 0 0) facets are visible at the contact line. Image size: 1300×1300 nm^2. (b) Image of the (1 1 1) facet and vicinal range of same crystallite as in (a). A double tip effect is seen on the r.h.s. of the facet. Image size: 670×670 nm^2. (c) 3D image of crystallite at $T = 393$ K, with the (1 0 0) facet rotated into the paper plane; center of the (1 0 0) facet approximately at the contact line. Due to the higher temperature, some bumps have been generated by local surface-to-tip contacts. Lateral dimension: 600 nm.

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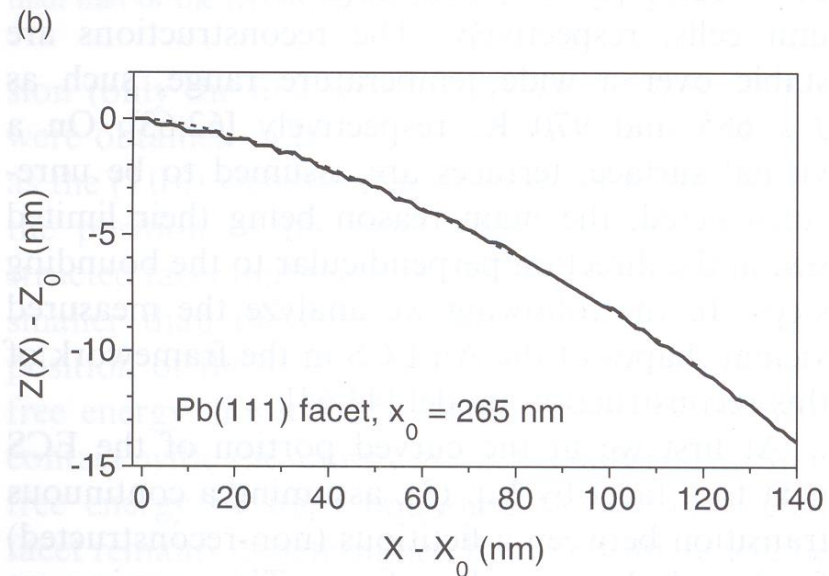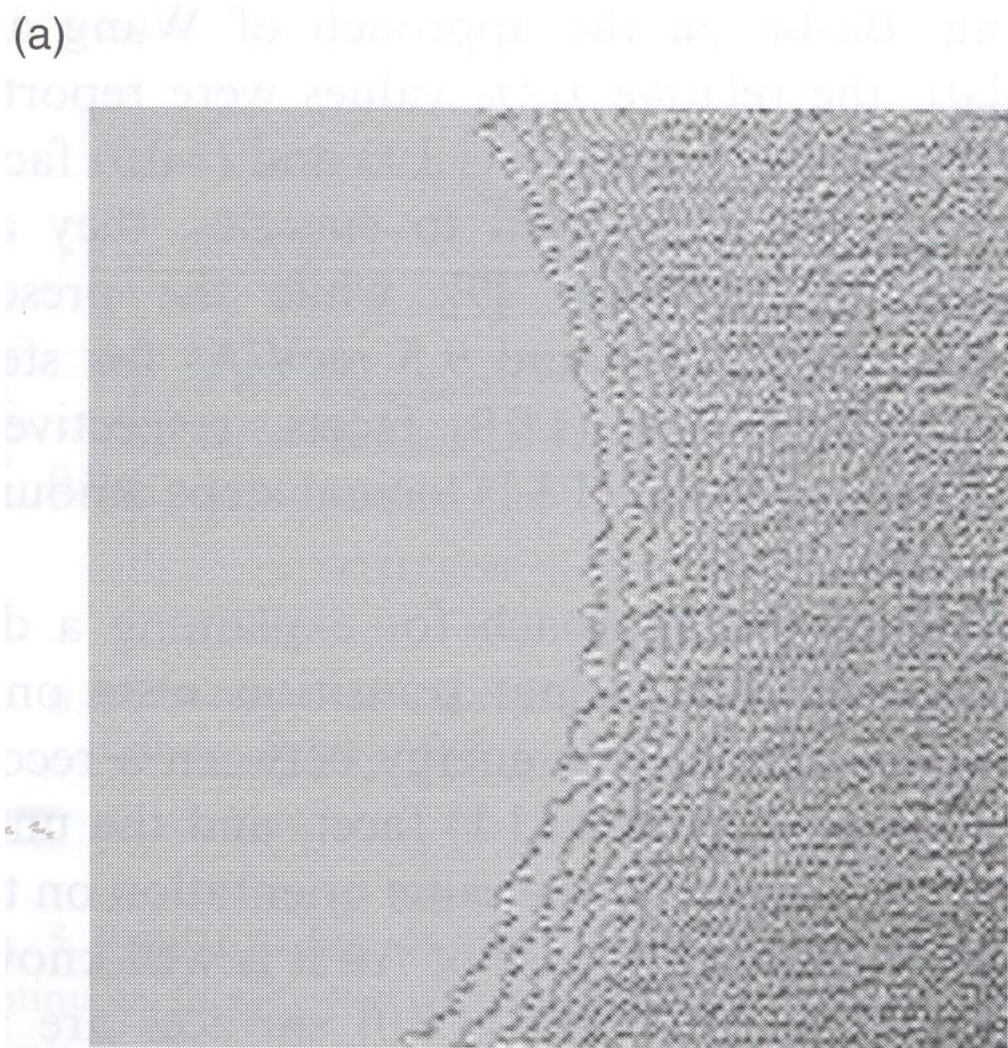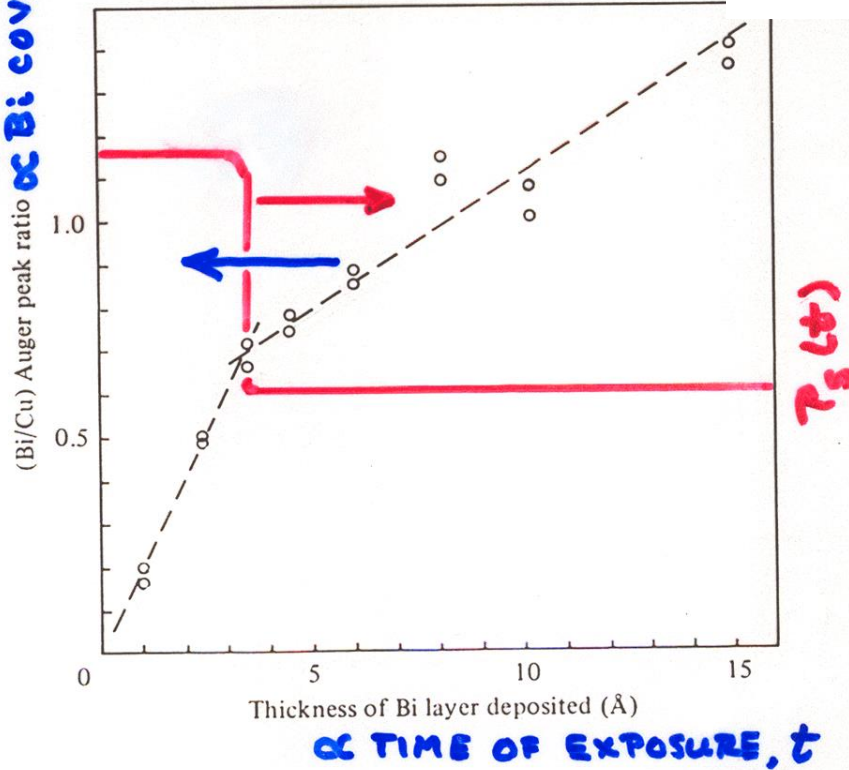# Scanning tunneling microscopy images of Pb crystallites

Fig. 2. (a) STM image of a section of the ECS of a Pb crystallite at 383 K. The image shows the facet to vicinal surface transition where the latter is characterized by a train of monatomic steps. (b) Example of a line scan across the ECS in the area of facet to vicinal surface transition. The line scan, $z(x) - z_0$ versus $x - x_0$, normalized relative to the facet edge at z_0, x_0, is fitted by Eq. (3) without the f_4 term.

Emundts et al., Surf. Sci. 481, 13 (2001)

10
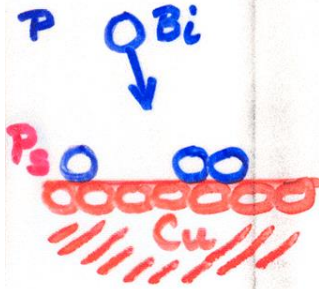
Fig. 3.44 Auger peak height ratio of 102 eV Bi peak to Cu 62 eV peak for Bi grown on an evaporated Cu substrate. Note the break or 'knee' corresponding to monolayer coverage (from Powell & Woodruff, 1976).
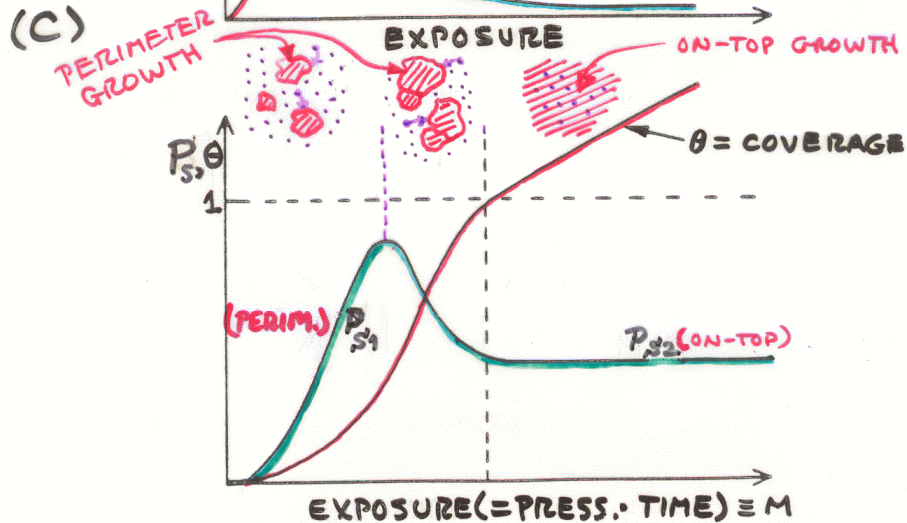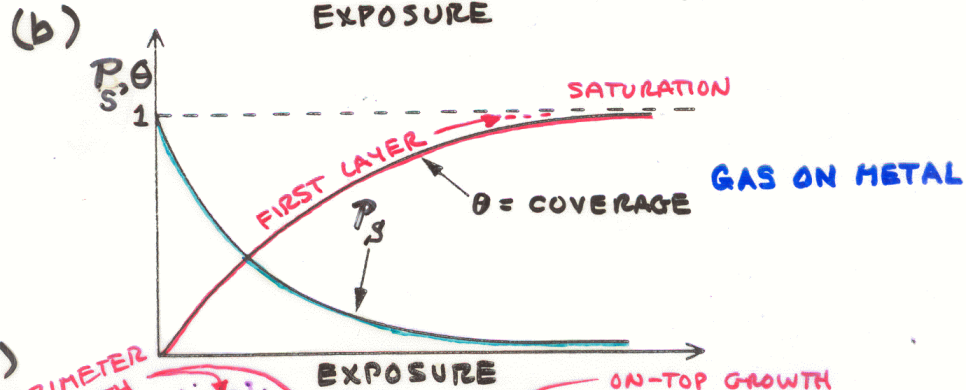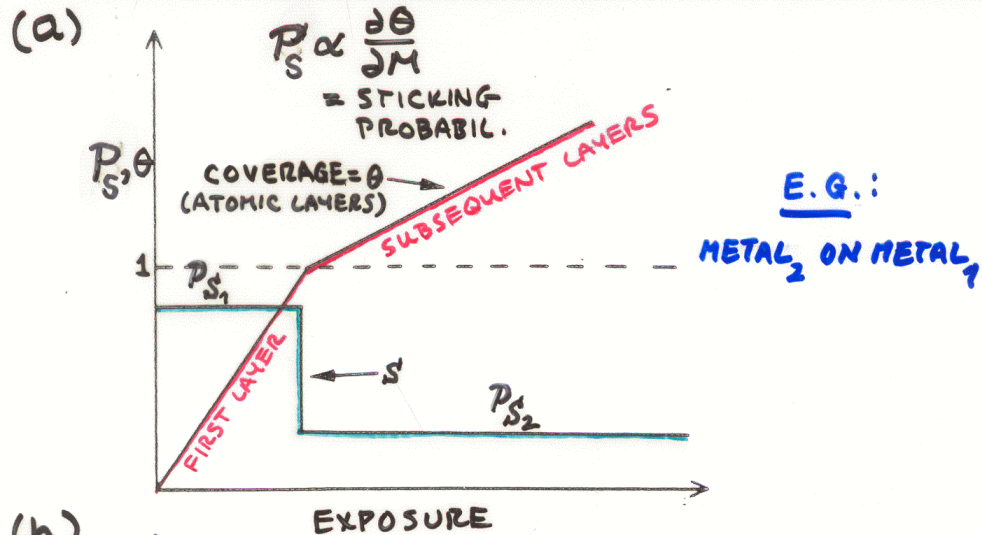
P $\bigcirc$ Bi

P_S $\bigcirc$ $\bigcirc$ $\bigcirc$ Cu

(Bi/Cu) Auger peak ratio $\propto$ Bi COVERAGE

1.0

0.5

0   5   10   15

Thickness of Bi layer deposited (Å)

$\propto$ TIME OF EXPOSURE, t

P_S

$$\left(\begin{array}{c}\text{RATE OF OVERLAYER (Bi)} \\ \text{GROWTH AT } t\end{array}\right) = \frac{P_S(t)\,P(t)}{(2\pi k_B m T)^{1/2}}$$

$$\left(\begin{array}{c}\text{OVERLAYER THICKNESS} \\ \text{AT } t_0\end{array}\right) \propto \int_0^{t_0} \frac{P_S(t)\,P(t)}{(2\pi k_B m T)^{1/2}}\,dt$$

$\therefore$ $P_S(t) \propto$ SLOPE IF $P(t)$ CONSTANT

Woodruff and Delchar, p. 191

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SOME TYPICAL COVERAGE/STICKING PROB. CURVES

(a)

$$P_S \propto \frac{\partial \theta}{\partial M}$$

= STICKING PROBABIL.

COVERAGE=θ
(ATOMIC LAYERS)

SUBSEQUENT LAYERS

P_{S_1}

1

S

FIRST LAYER

P_{S_2}

P_S, θ

EXPOSURE

E.G.:

METAL$_2$ ON METAL$_1$

(b)

P_S, θ

SATURATION

1

FIRST LAYER

θ = COVERAGE

P_S

GAS ON METAL

EXPOSURE

(c)

PERIMETER GROWTH

ON-TOP GROWTH

θ = COVERAGE

P_S, θ

1

(PERIM.) P_{S_1}

P_{S_2}(ON-TOP)

EXPOSURE(=PRESS.·TIME) $\equiv$ M

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Oxidation of Silicon: Time evolution at 580℃, Langmuir form

Normalized Si⁴⁺ Intensity vs. time (graph)

1x10⁻⁶ Torr
5x10⁻⁷ Torr
2x10⁻⁷ Torr
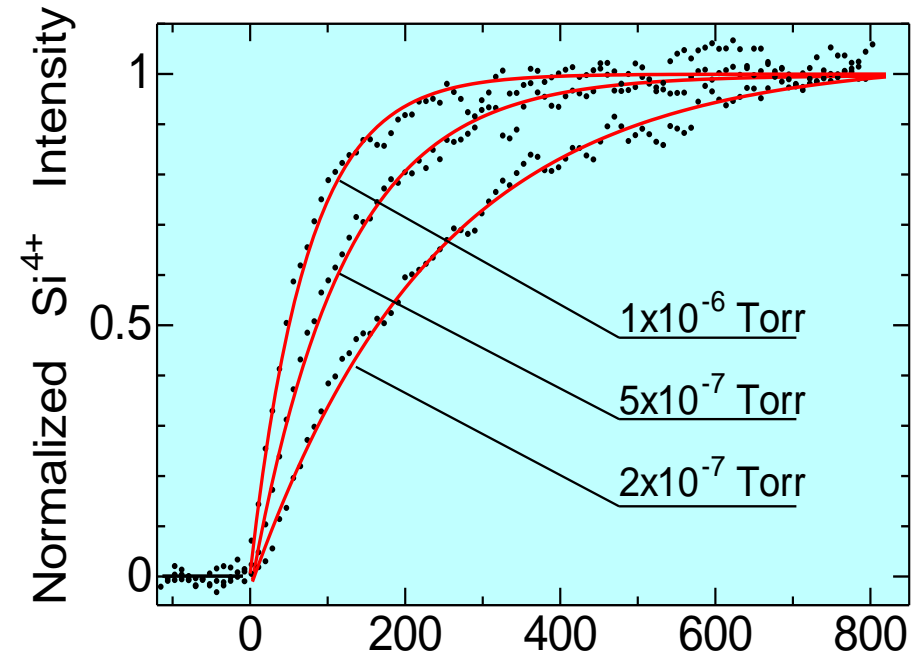
Langmuir-type adsorption:
Growth rate is proportional to bare Si surface

$$\frac{d\theta}{dt} \propto P_S P (1-\theta)^n$$

θ = oxide coverage
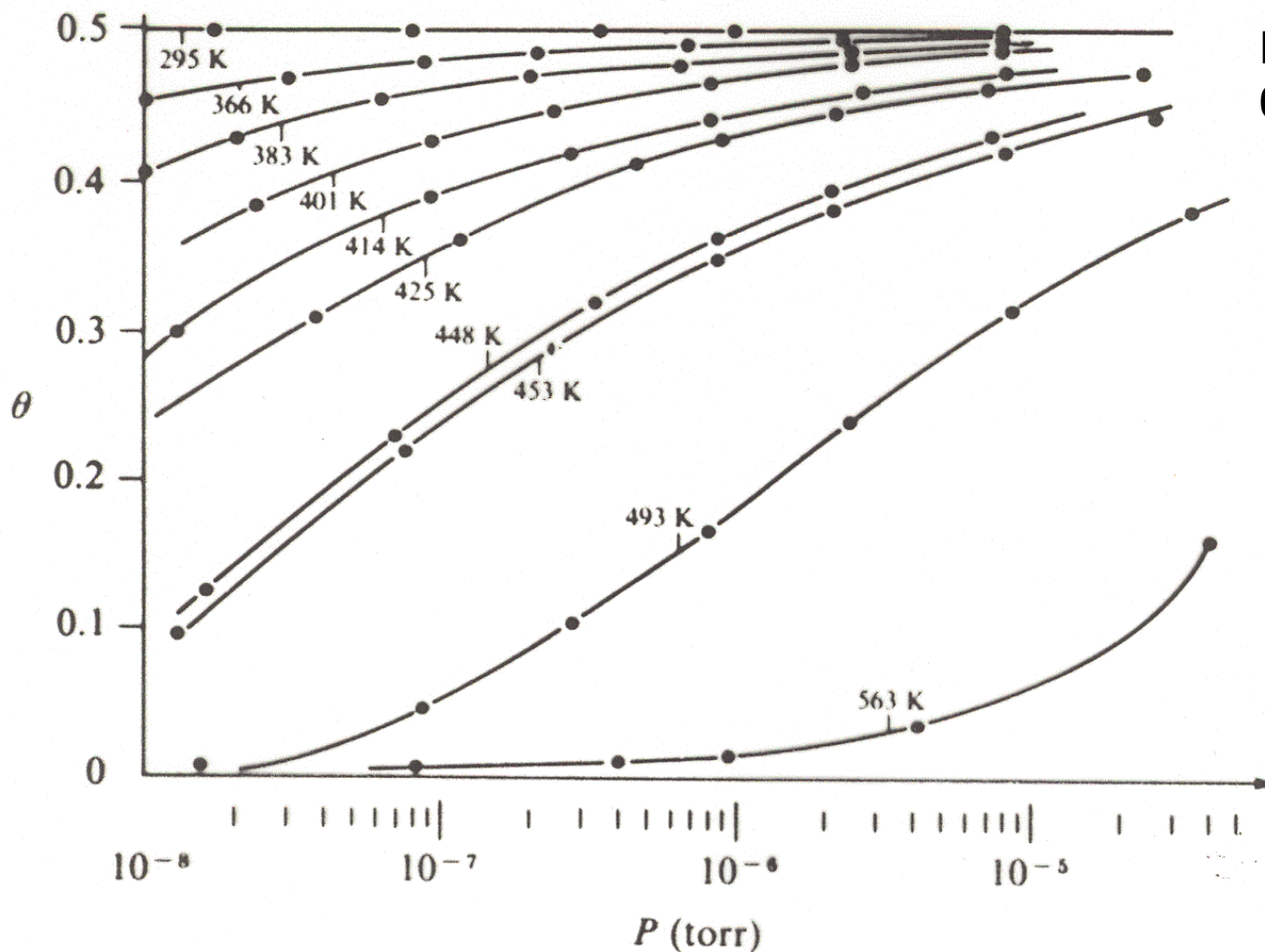P_S = sticking probability
P = oxygen pressure
n = reaction order

The time evolution follows
$n = 1 \rightarrow$ first-order Langmuirian

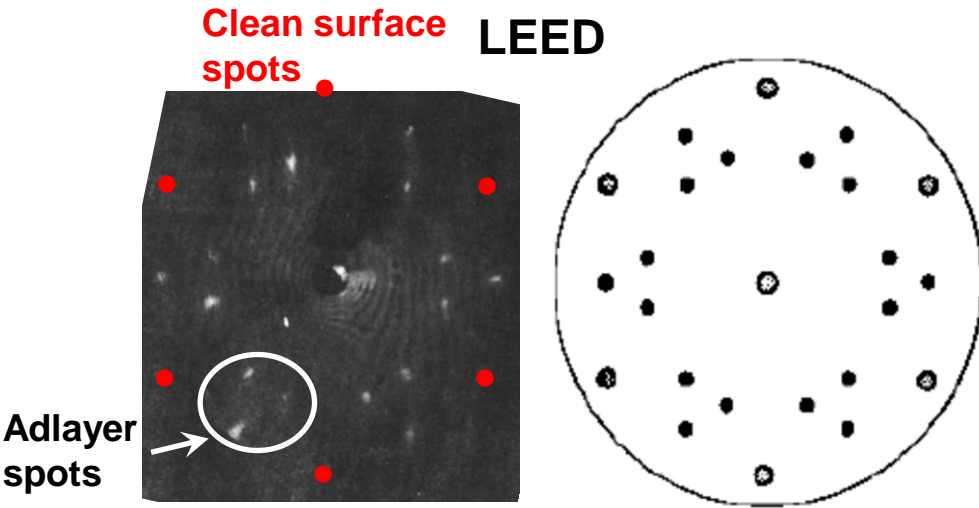Sticking probability, P_S = 0.016—constant if no interaction between adsorbed species

Enta et al., PRB 57, 6294 (1998)

Fig. 9.2. Adsorption isotherms for CO/Pd(111) (Ertl & Koch, 1970).

Final saturation for 0.5 coverage

FROM
ZANGWILL

14

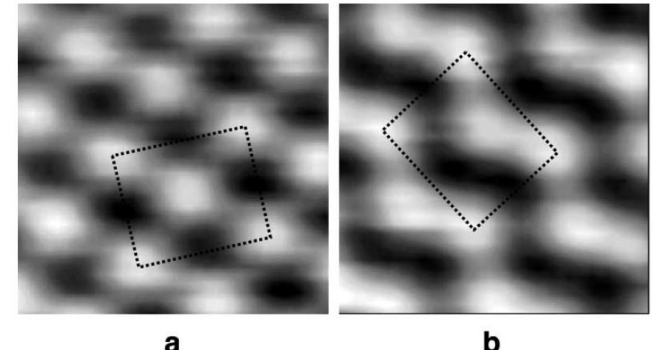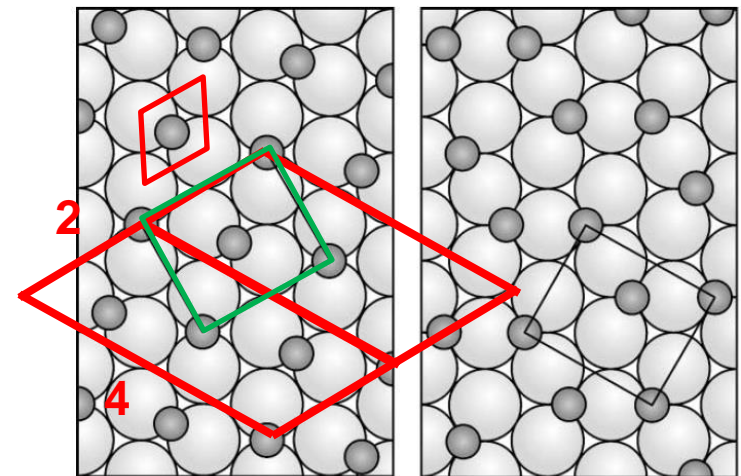# CO on Pd(111)- The 0.5 ML saturation structures-at equilibrium!

Clean surface spots

LEED

STM

Adlayer spots

J. Electroanal. Chem., 353 (1993) 281–287

Pd(111)c(4×2)
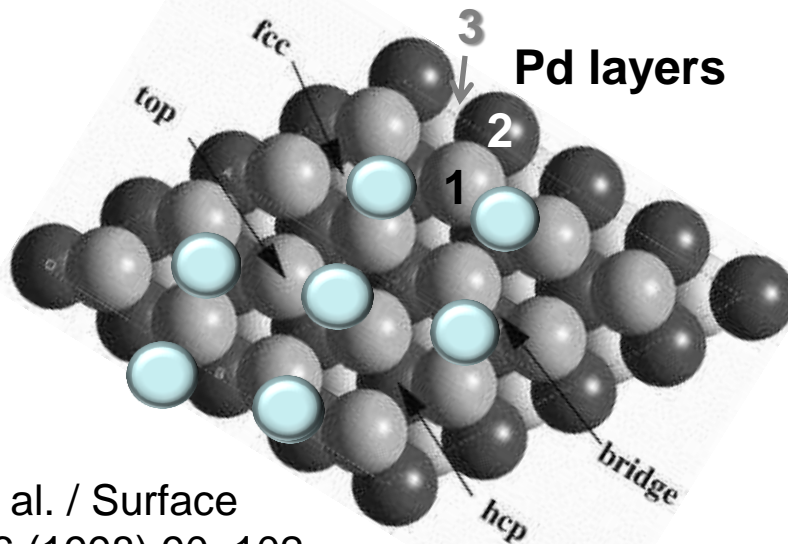
Coexistent- **a** slightly preferred at 120K

Pd layers

3

2

1

top

fcc

bridge

hcp

2

4

2 COs per rectangular cell, **4 COs per c(4x2)**

Fig. 5. c(4 × 2)-2CO models. (a) CO molecules occupying bridge sites. (b) CO molecules in fcc and hcp threefold hollow sites. A primitive cell of each c(4 × 2) structure is indicated.

Diffusion of water on TiO$_2$ and dissociation at an oxygen vacancy defect on the surface

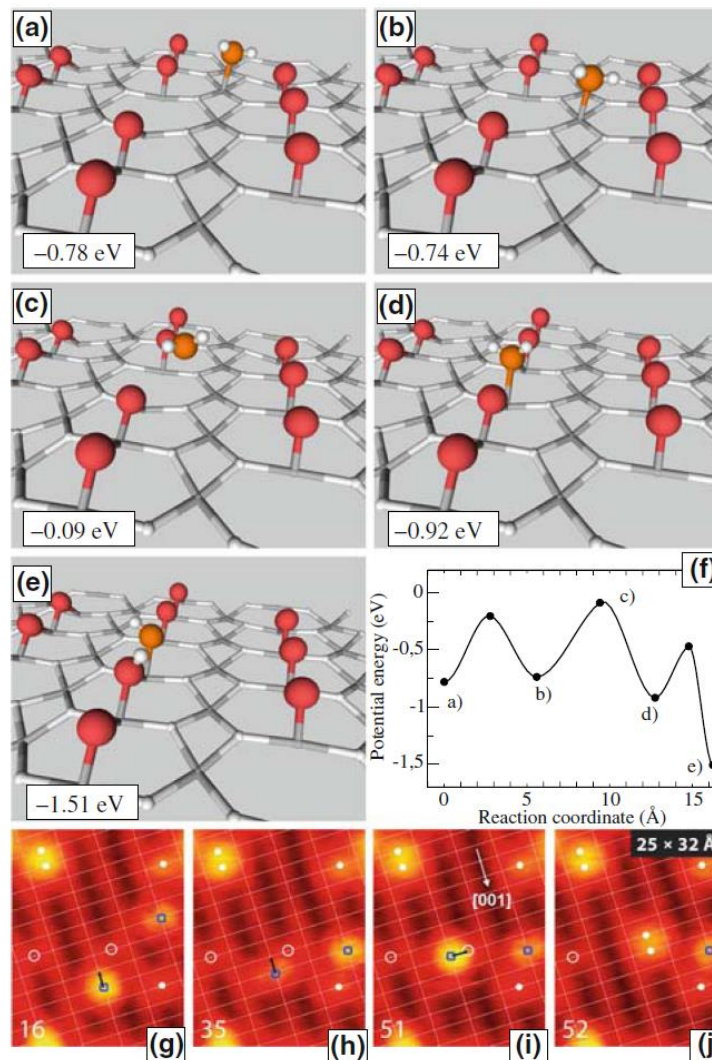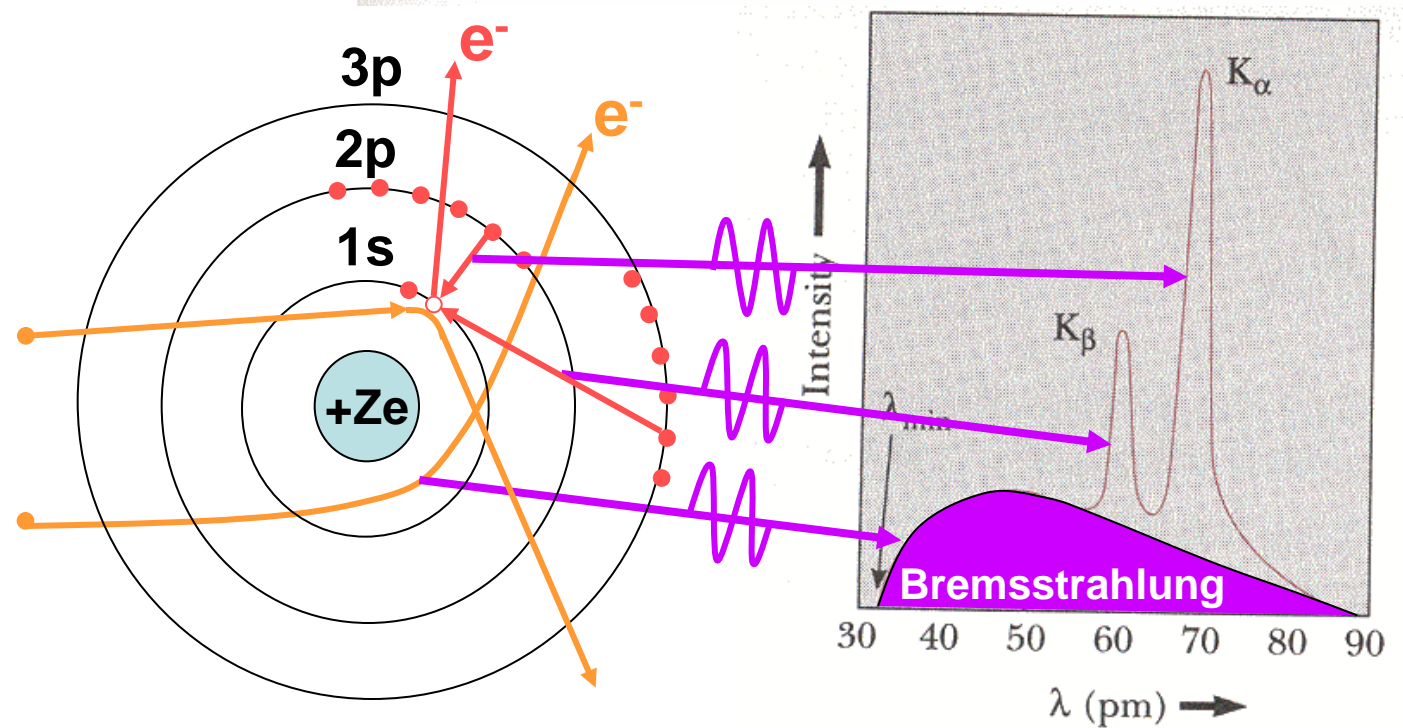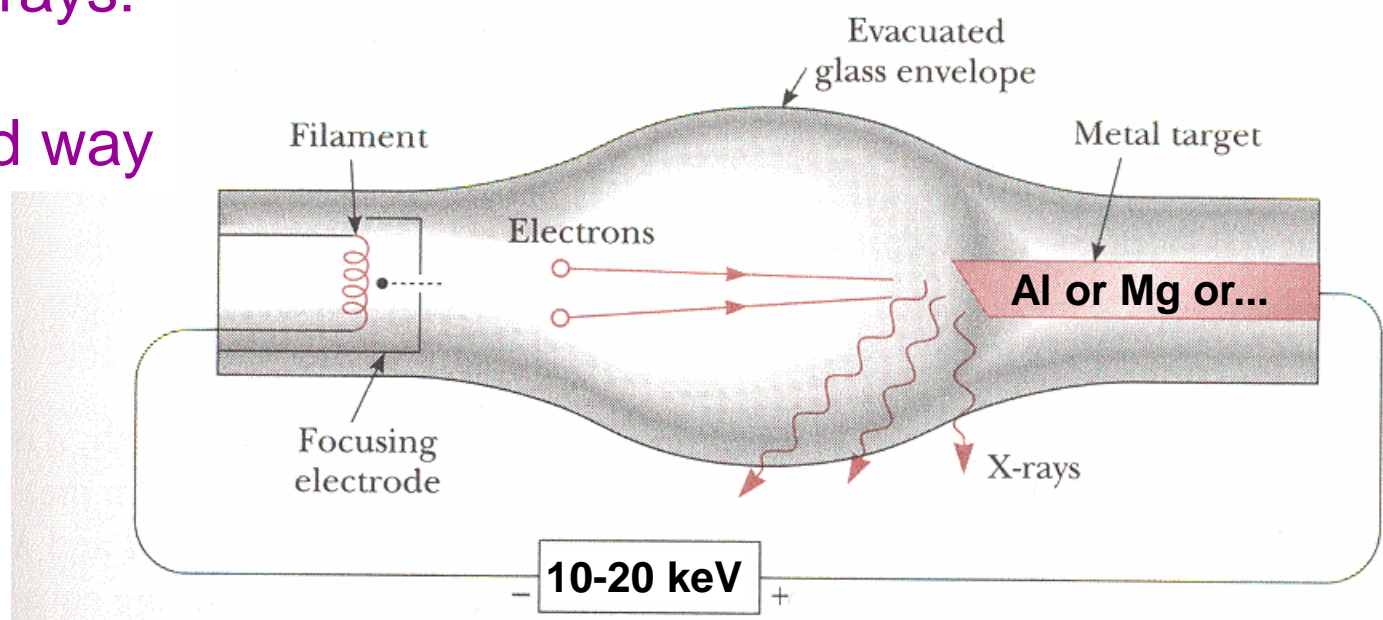Topics in Catalysis (2010) 53:423–430
doi 10.1007/s11244-010-9454-3

Other STM movies at:
http://phys.au.dk/forskning/forskning
somraader/condensed-matter-
physics/spm/stm-movies/

Fig. 4 **a–b** Configuration and adsorption potential energy (PW91) of adsorbed monomeric water at Ti$_{5f}$ sites close to an O$_{br}$ vacancy. **c–d** Transition and final state of an adsorbed water molecule that jumps into an O$_{br}$ vacancy. **e** Configuration with a pair of H adatoms in the O$_{br}$ row after the water has dissociated. **f** Potential energy diagram. **g–j** STM images showing the diffusion of an adsorbed water molecule (*blue square*) that dissociates in an O$_{br}$ vacancy (*white circle*) forming a pair of H adatoms (two neighboring *white dots*). STM images are extracted from movie "dissociation" published with [22]

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Producing x-rays: the good old-fashioned way

Evacuated glass envelope

Filament

Electrons

Metal target

Al or Mg or...

Focusing electrode

X-rays

10-20 keV

3p

2p

1s

e⁻

e⁻

+Ze

Intensity

K_α

K_β

λ_{min}

Bremsstrahlung

30 40 50 60 70 80 90

λ (pm) ➔

See Section 1.2 in "X-Ray Data Booklet"

X-ray spectrum from a rhodium target at 60 keV electron energy

Bremsstrahlung: $K \propto$ atomic number

$$I(\lambda)d\lambda = K \left(\frac{\lambda}{\lambda_{min}} - 1 \right) \frac{1}{\lambda^2}d\lambda$$

K_α

K_β

$h\nu_{max} = eV$

$c/\nu_{max} = \lambda_{min} = \frac{hc}{eV} \approx \frac{1239.8 \text{ pm}}{V \text{ in kV}}$

counts per second

Wavelength, pm
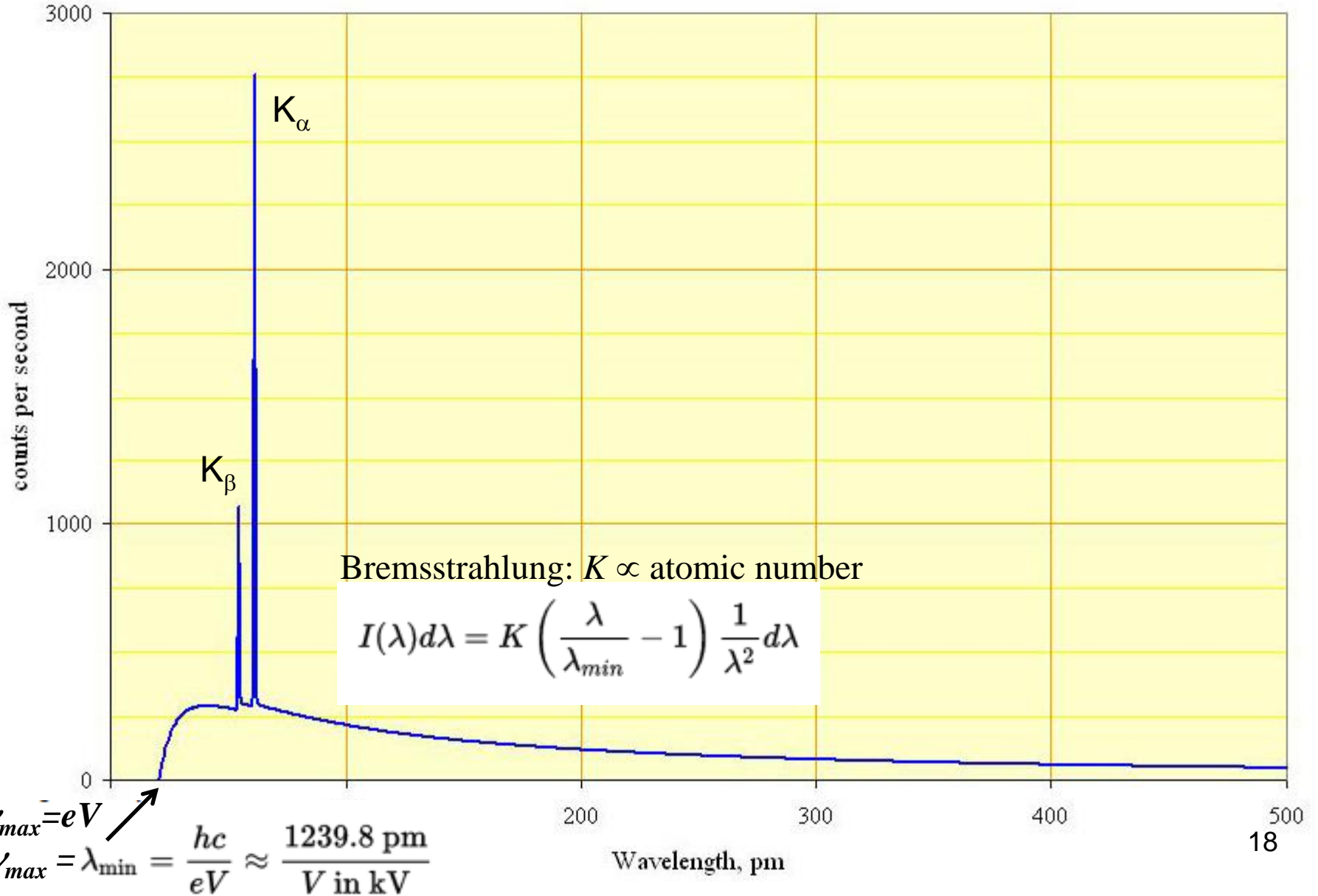
ALLOWED TRANSITIONS IN X-RAY EMISSION:

Spin-orbit splitting in high-resolution x-ray spectra
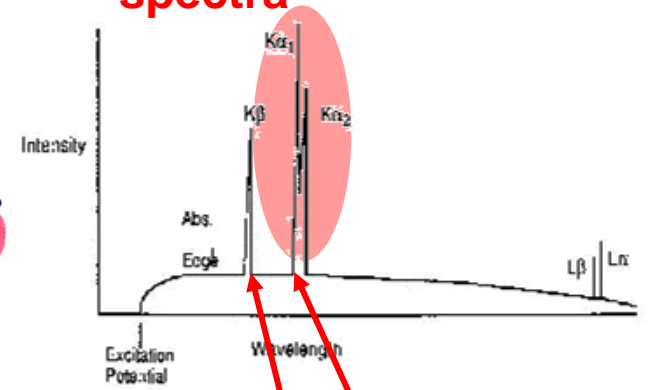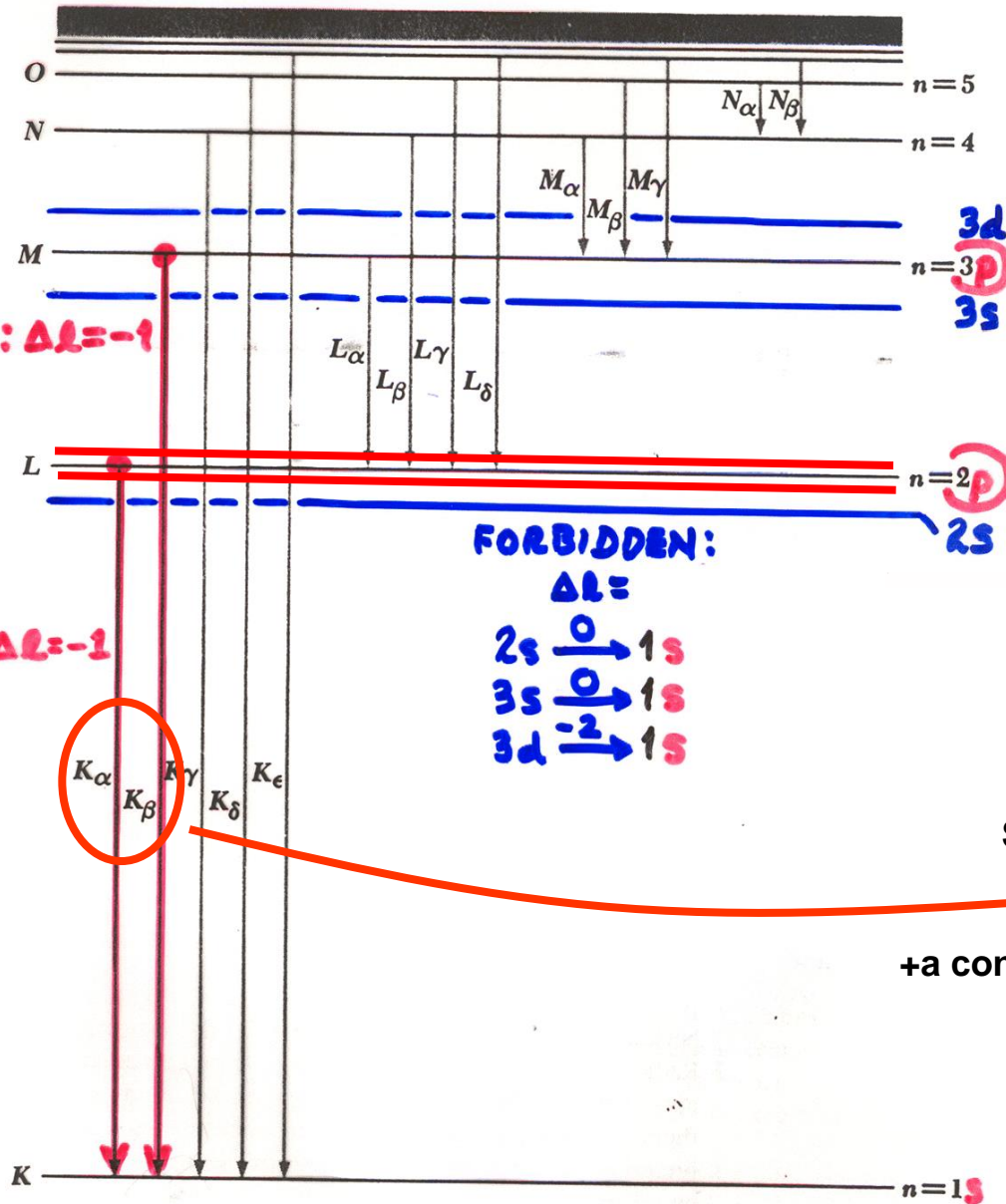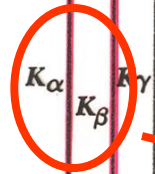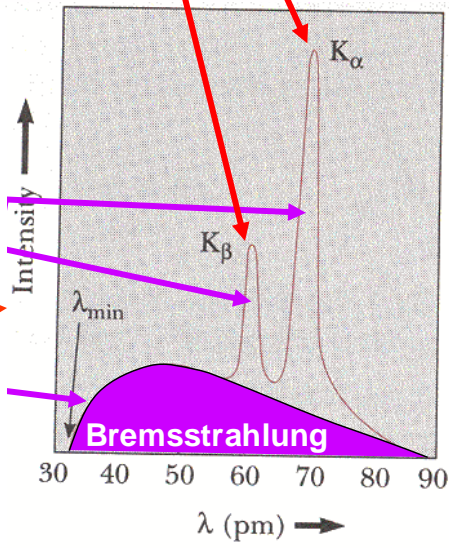
O $n = 5$

N $n = 4$

N_α N_β

M_α M_β M_γ

$3d$

M $n = 3p$

$3s$

ALLOWED: $\Delta \ell = -1$

L_α L_β L_γ L_δ

L $n = 2p$

2p, j = 3/2
2p, j = 1/2
2s

FORBIDDEN:
$\Delta \ell =$

$2s \xrightarrow{0} 1s$
$3s \xrightarrow{0} 1s$
$3d \xrightarrow{-2} 1s$

$\Delta \ell = -1$

K_α K_β K_γ K_δ K_ϵ

K $n = 1s$

Intensity

$K\alpha_1$

$K\beta$ $K\alpha_2$

Abs.

Edge

$L\beta$ $L\alpha$

Excitation Potential

Wavelength

Line Spectra

Intensity

K_α

K_β

λ_{min}

+a continuum

Bremsstrahlung

30   40   50   60   70   80   90

λ (pm)

Slide Set 5   19

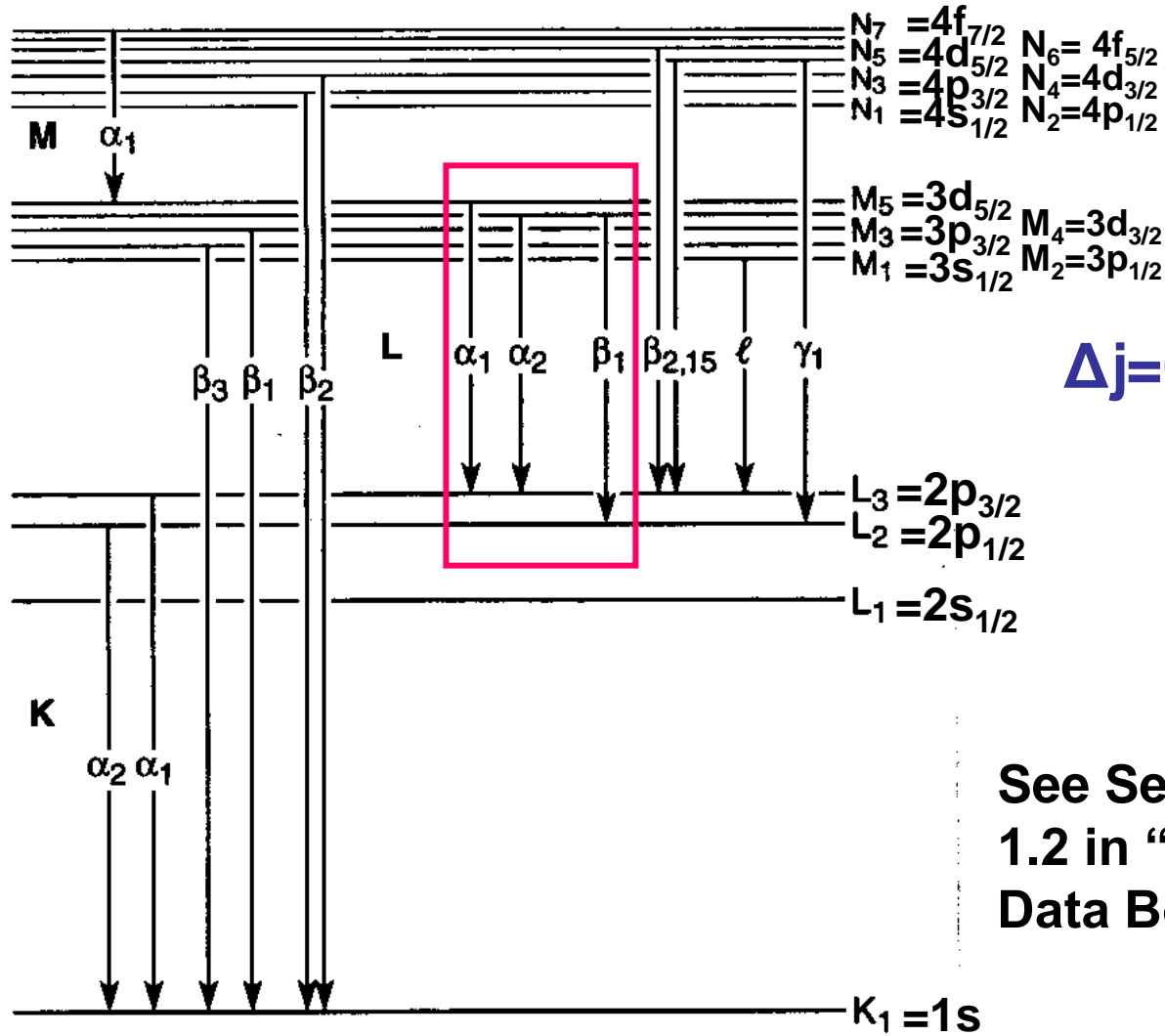**X-Ray Nomenclature (from "X-Ray Data Booklet")**

In general:

$$nl \begin{cases} \text{Spin-} & nl_{j=l+1/2} \\ \text{orbit} & nl_{j=l-1/2} \end{cases}$$

$N_7 = 4f_{7/2}$ $N_6 = 4f_{5/2}$
$N_5 = 4d_{5/2}$ $N_4 = 4d_{3/2}$
$N_3 = 4p_{3/2}$ $N_2 = 4p_{1/2}$
$N_1 = 4s_{1/2}$

M α_1

$M_5 = 3d_{5/2}$ $M_4 = 3d_{3/2}$
$M_3 = 3p_{3/2}$ $M_2 = 3p_{1/2}$
$M_1 = 3s_{1/2}$

L α_1 α_2 β_1 $\beta_{2,15}$ ℓ γ_1

β_3 β_1 β_2

Δj=0,±1

$L_3 = 2p_{3/2}$
$L_2 = 2p_{1/2}$
$L_1 = 2s_{1/2}$

K

α_2 α_1

See Section 1.2 in "X-Ray Data Booklet"

$K_1 = 1s$

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.*

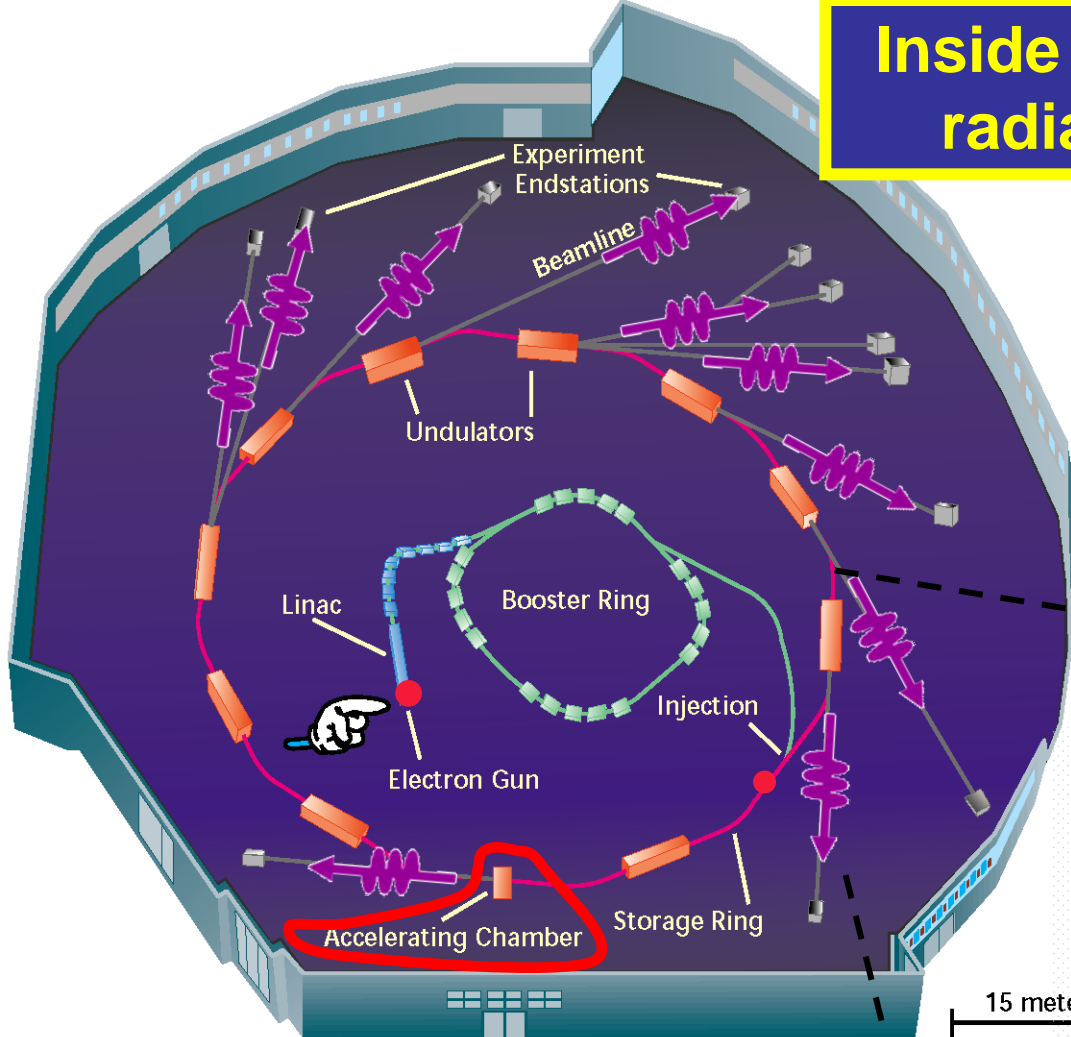| Element	$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\gamma_1$	$M\alpha_1$
3 Li	54.3								
4 Be	108.5								
5 B	183.3								
6 C	277								
7 N	392.4								
8 O	524.9								
9 F	676.8								
10 Ne	848.6	848.6							
11 Na	1,040.98	1,040.98	1,071.1						
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 photoelectron spectroscopy

X-Ray energies from the "X-Ray Data Booklet" (cont'd.)

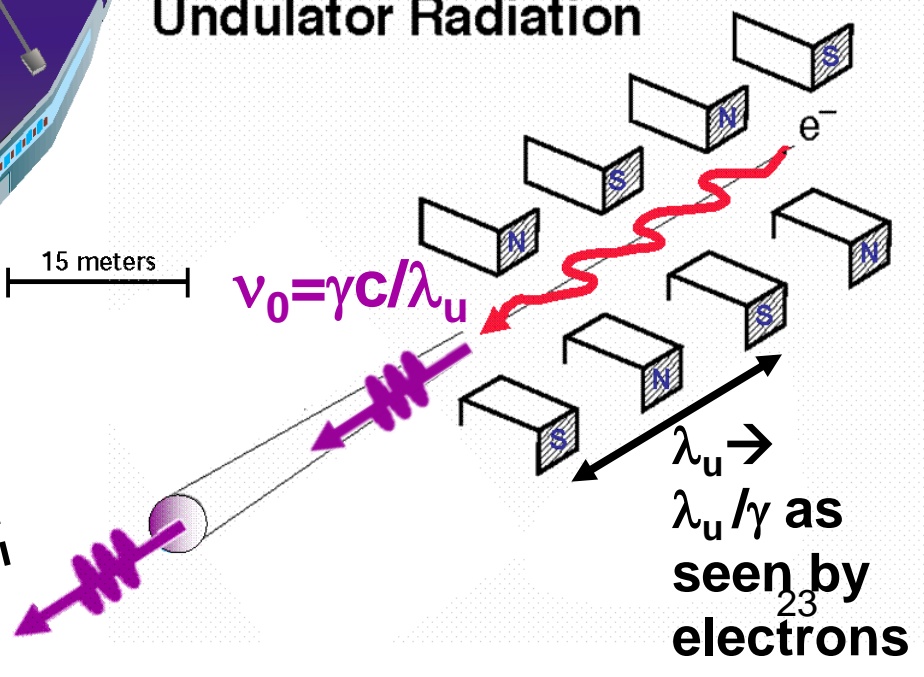Table 1-2. Energies of x-ray emission lines (continued).

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	
41 Nb	16,615.1	16,521.0	18,622.5	2,165.89	2,163.0	2,257.4	2,367.0	2,461.8	
42 Mo	17,479.34	17,374.3	19,608.3	2,293.16	2,289.85	2,394.81	2,518.3	2,623.5	
43 Tc	18,367.1	18,250.8	20,619	2,424	2,420	2,538	2,674	2,792	
44 Ru	19,279.2	19,150.4	21,656.8	2,558.55	2,554.31	2,683.23	2,836.0	2,964.5	
45 Rh	20,216.1	20,073.7	22,723.6	2,696.74	2,692.05	2,834.41	3,001.3	3,143.8	
46 Pd	21,177.1	21,020.1	23,818.7	2,838.61	2,833.29	2,990.22	3,171.79	3,328.7	
47 Ag	22,162.92	21,990.3	24,942.4	2,984.31	2,978.21	3,150.94	3,347.81	3,519.59	
48 Cd	23,173.6	22,984.1	26,095.5	3,133.73	3,126.91	3,316.57	3,528.12	3,716.86	
49 In	24,209.7	24,002.0	27,275.9	3,286.94	3,279.29	3,487.21	3,713.81	3,920.81	
50 Sn	25,271.3	25,044.0	28,486.0	3,443.98	3,435.42	3,662.80	3,904.86	4,131.12	
51 Sb	26,359.1	26,110.8	29,725.6	3,604.72	3,595.32	3,843.57	4,100.78	4,347.79	
52 Te	27,472.3	27,201.7	30,995.7	3,769.33	3,758.8	4,029.58	4,301.7	4,570.9	
53 I	28,612.0	28,317.2	32,294.7	3,937.65	3,926.04	4,220.72	4,507.5	4,800.9	
54 Xe	29,779	29,458	33,624	4,109.9	—	—	—	—	
55 Cs	30,972.8	30,625.1	34,986.9	4,286.5	4,272.2	4,619.8	4,935.9	5,280.4	
56 Ba	32,193.6	31,817.1	36,378.2	4,466.26	4,450.90	4,827.53	5,156.5	5,531.1	
57 La	33,441.8	33,034.1	37,801.0	4,650.97	4,634.23	5,042.1	5,383.5	5,788.5	833
58 Ce	34,719.7	34,278.9	39,257.3	4,840.2	4,823.0	5,262.2	5,613.4	6,052	883
59 Pr	36,026.3	35,550.2	40,748.2	5,033.7	5,013.5	5,488.9	5,850	6,322.1	929
60 Nd	37,361.0	36,847.4	42,271.3	5,230.4	5,207.7	5,721.6	6,089.4	6,602.1	978
61 Pm	38,724.7	38,171.2	43,826	5,432.5	5,407.8	5,961	6,339	6,892	—
62 Sm	40,118.1	39,522.4	45,413	5,636.1	5,609.0	6,205.1	6,586	7,178	1,081

Inside a synchrotron radiation source

Electron speed near c: 0.99999994 c, γ = 3719 Einstein needed again— Special Relativity
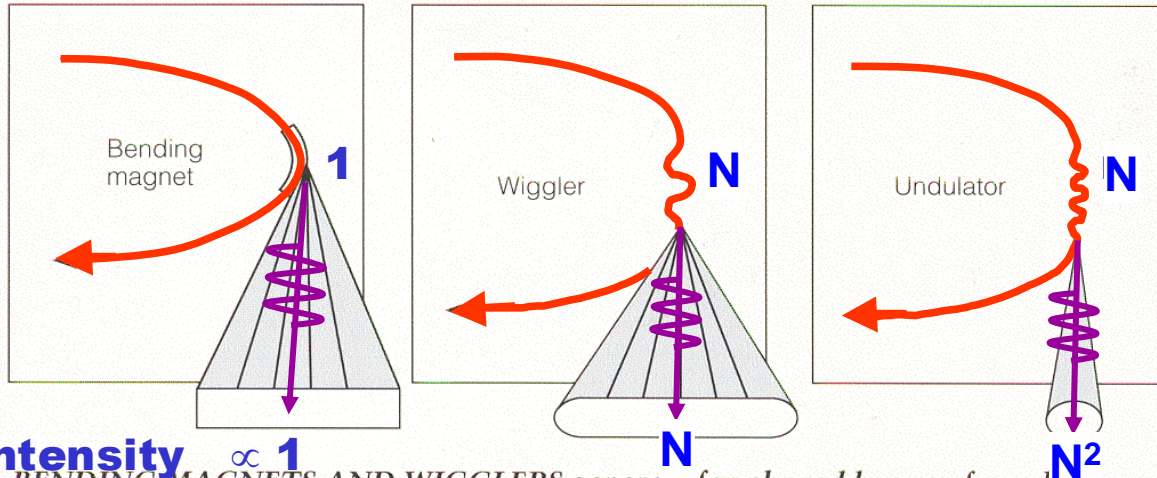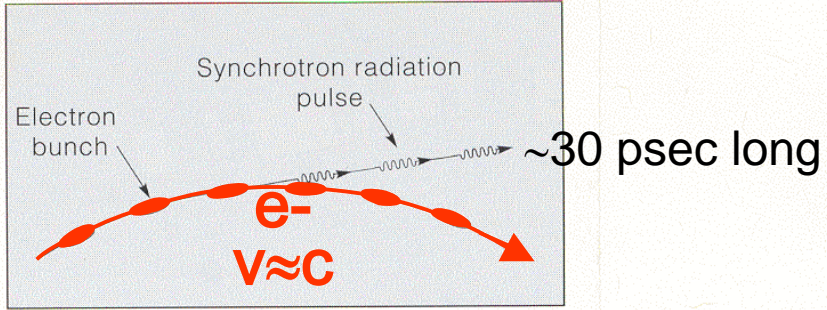
Experiment Endstations
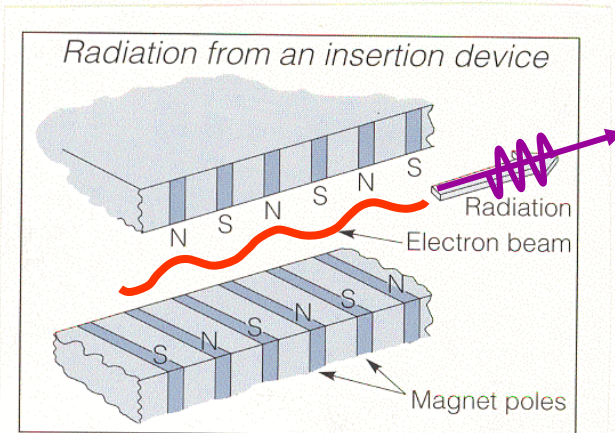
Beamline

Undulators

Linac

Booster Ring

Injection

Electron Gun

Storage Ring

Accelerating Chamber

Radiofrequency Cavity

Undulator Radiation

15 meters

$\nu_0 = \gamma c / \lambda_u$

e^-

$\lambda_u \rightarrow$

λ_u / γ as seen by electrons

+Doppler

$\nu = \gamma^2 c / \lambda_u$

See Attwood: page 137

23

Synchrotron Radiation Sources:

Electron bunch

Synchrotron radiation pulse

~30 psec long

e-
V≈C

Bending magnet **1**

Wiggler **N**

Undulator **N**

Intensity ∝ **1**   **N**   **N²**

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

Radiation from an insertion device

S N S N S
N S N S N

Radiation
Electron beam

S N S N S
S N S N S

Magnet poles

Synchrotron Radiation Sources

$$v = \beta c = 0.99999994\,c \rightarrow \gamma \approx 2{,}900$$

① e^- t_1 t_2 t_3 t_4 t_5 γ^{-1}

Bending Magnet — A "Sweeping Searchlight"

+ DOPPLER SHIFT:

② e^- (10-50) γ^{-1} $\nu_o = \nu \sqrt{\dfrac{1+\beta}{1-\beta}}$

Wiggler — Incoherent Superposition

$$\frac{dP}{d\Omega} \propto N$$

$\approx 5{,}700\,\nu$!

③ $v = \beta c$ e^- $|\!-\lambda_u-\!|$ $(\gamma \sqrt{N})^{-1}$

Undulator — Coherent Interference
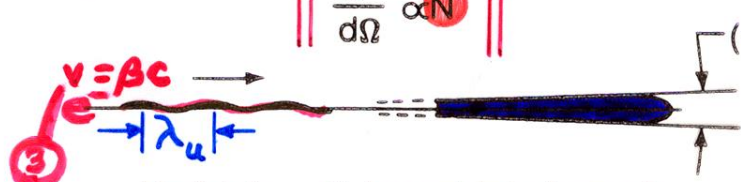
CHARACTERISTIC λ:

$$\frac{\lambda}{c} = \frac{\lambda_u}{\beta c} - \frac{\lambda_u}{c}$$

PLUS HARMONICS AT
$\lambda/2, \lambda/3, \lambda/4, \ldots$

$$\frac{dP}{d\Omega} \propto N^2$$
$$\Omega \propto \frac{1}{N}$$
$$P \propto N$$

$t = 0$: c c
e^- βc

$t = \dfrac{\lambda_u}{\beta c}$: c
e^- βc
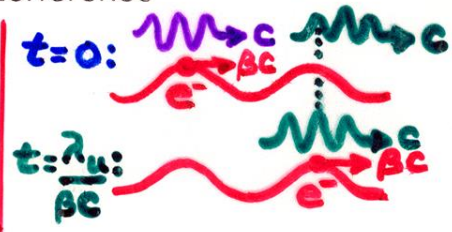
N = number of magnetic periods (~100)

IN GENERAL: $\gamma^{-1} = \dfrac{m_o c^2}{E_e} = \dfrac{0.511}{E_e(\text{GeV})}$ mrad = θ_v = VERTICAL ANGULAR WIDTH
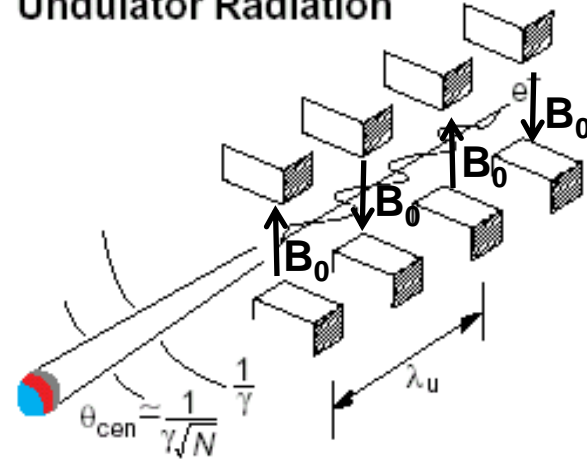
≈ 0.34 mrad FOR ALS

Bend-Magnet Radiation

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

$E_e = \gamma m_0 c^2$

ψ

$\psi_{max} \simeq \frac{1}{\gamma}$

Beamline optics acceptance angle

ε_c = Critical energy [keV] = 0.665 E^2[GeV]B[T]

Photon flux

ε_c

Photon energy

Undulator Radiation

$\theta_{cen} \simeq \frac{1}{\gamma\sqrt{N}}$ $\frac{1}{\gamma}$ λ_u
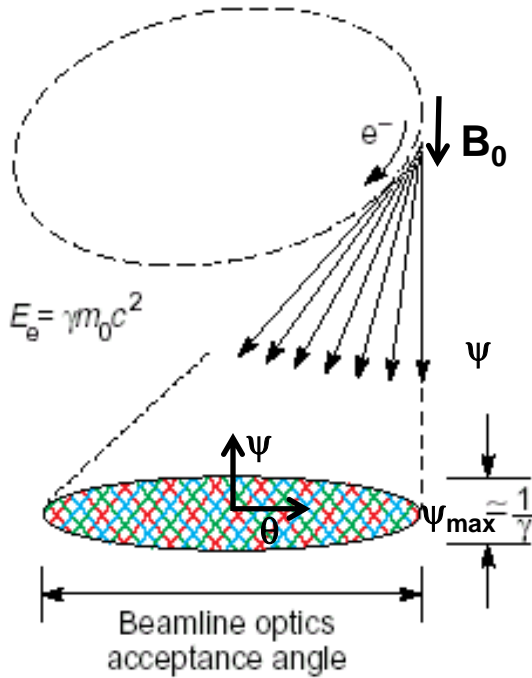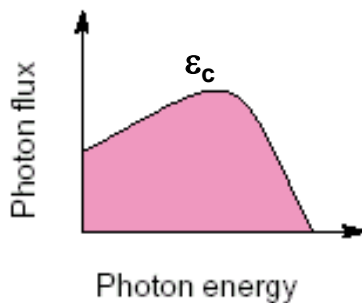
$$\lambda_x = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2} + \gamma^2\theta^2\right) \qquad K = \frac{eB_0\lambda_u}{2\pi m_0 c}$$

In the central radiation cone:

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

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

λ_x as observed will increase if the magnetic field B_0 is increased and/or the gap of the magnets is made smaller, or if viewed away from the axis by an angle θ
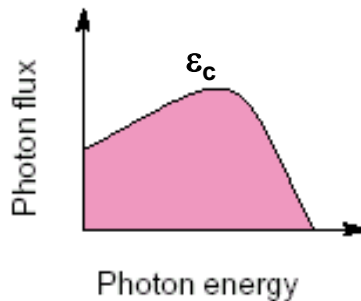*Odd harmonics are much stronger than even harmonics*

1st

Measured undulator brilliance from the Advanced Photon Source: Z. Cai et al., 1995

3rd

2nd   4th   5th   6th

Brilliance (ph/s/0.1%BW/mrad²/mm²/mA)×10⁻¹⁶

Energy (keV)

26

Bend-Magnet Radiation

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

$E_e = \gamma m_0 c^2$

$\psi_{max} \cong \dfrac{1}{\gamma}$

Beamline optics acceptance angle
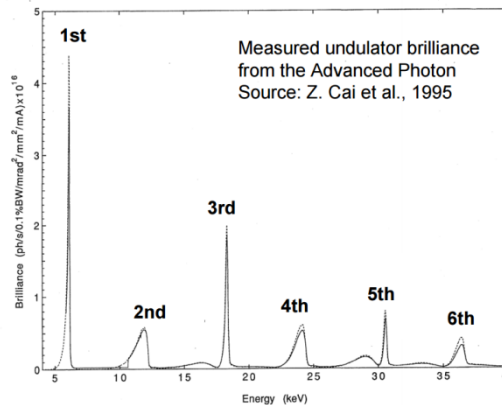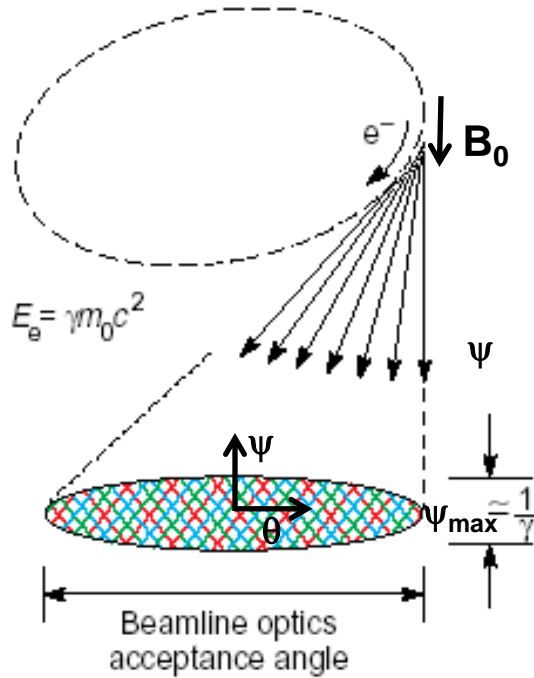
ε_c = Critical energy [keV] = 0.665 E^2[GeV]B[T]

In practical units [photons·s^{-1}·mr^{-2}·(0.1% bandwidth)$^{-1}$],

$$\dfrac{d^2 \check{S}_B}{d\theta d\psi}\bigg|_{\psi=0} = 1.327 \times 10^{13} E^2[\text{GeV}] I[\text{A}] H_2(y)$$

$$1 \text{ mrad} = 10^{-2}(360/2\pi) = 0.0572°$$

The function $H_2(y)$ is shown in Fig. 2-1.

$G_1(y)$

$H_2(y)$

$G_1(y)$ and $H_2(y)$

$y = \varepsilon/\varepsilon_c$
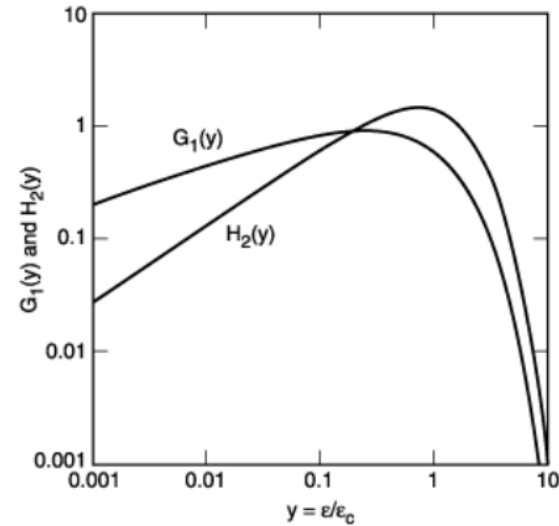
Fig. 2-1. *The functions $G_1(y)$ and $H_2(y)$, where y is the ratio of photon energy to critical photon energy.*

The distribution integrated over ψ is given by

In practical units [photons·s^{-1}·mr^{-1}·(0.1% bandwidth)$^{-1}$],

$$\dfrac{dS_B}{d\theta} = 2.457 \times 10^{13} E[\text{GeV}] I[\text{A}] G_1(y)$$

Photon flux

ε_c

Photon energy

27

Variable polarization with a bend magnet: above and below plane

Bending magnet

1

LCP

Horiz. Lin.

RCP
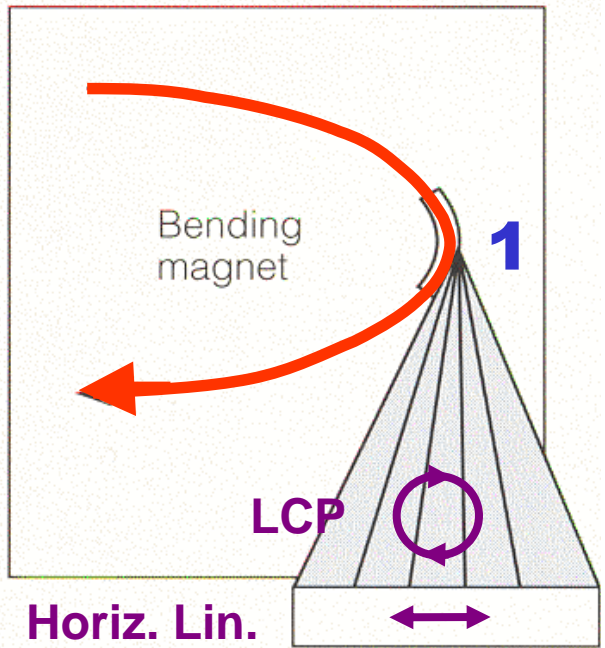
Above plane **LCP**

Horiz. Lin.

Below plane **RCP**

28

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

LCP
Horiz. Lin.
RCP

Vert. Lin.

Translating magnet arrays

[Can also vary polarization to LCP, RCP by going above and below the orbit plane in a bend magnet]
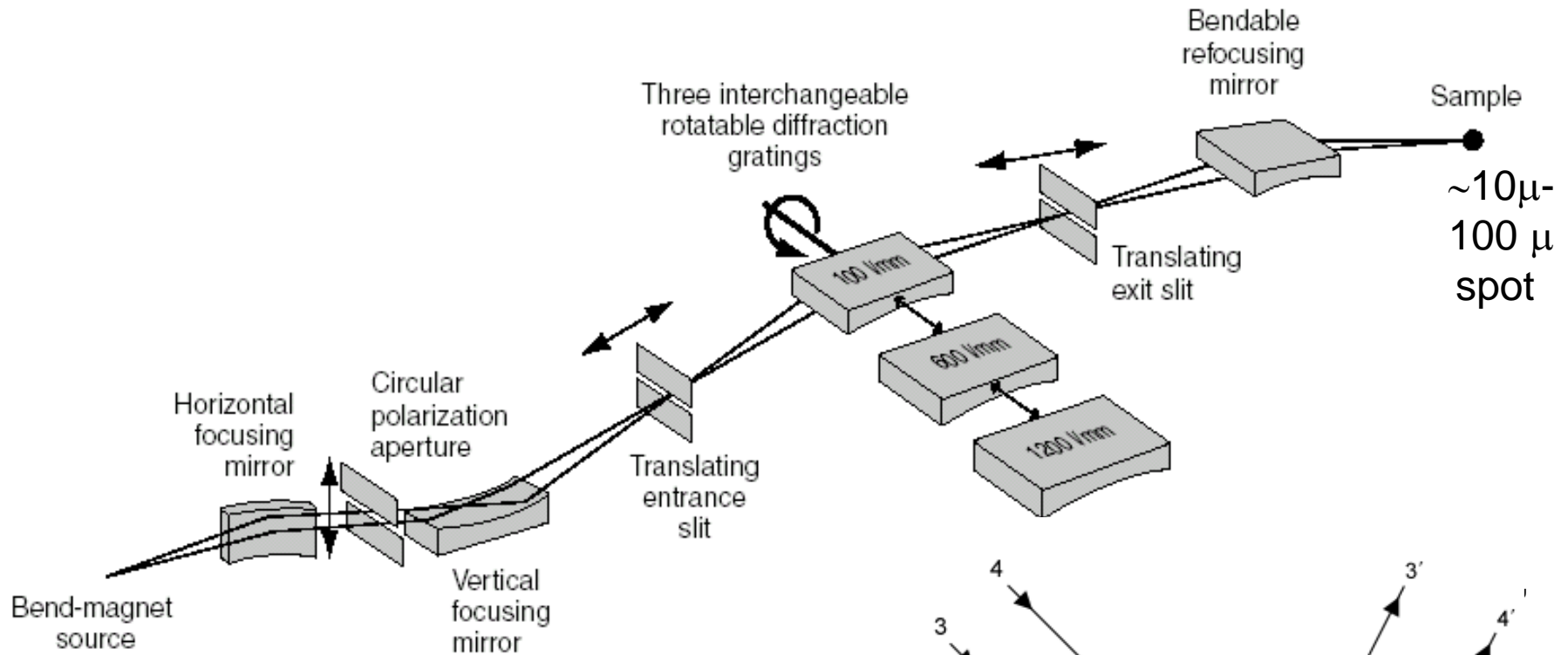
29

$$\lambda_x(\text{Å}) = 12{,}398/[h\nu(\text{eV})]$$

Vacuum Ultraviolet (VUV)- ~8-200 eV

Soft x-rays ~200-2000 eV

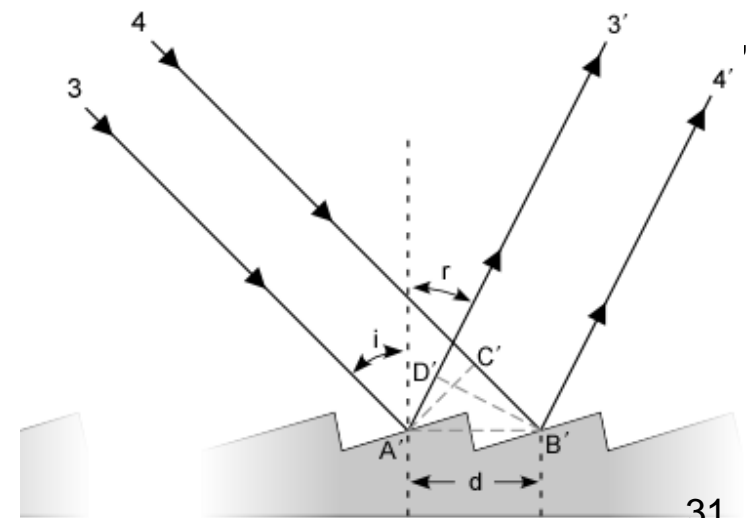**"Tender" x-rays ~2000-10000 eV**

THE ELECTROMAGNETIC SPECTRUM

| Wavelength (in meters) | 10^3 | 10^2 | 10^1 | 1 | 10^{-1} | 10^{-2} | 10^{-3} | 10^{-4} | 10^{-5} | 10^{-6} | 10^{-7} | 10^{-8} | 10^{-9} | 10^{-10} | 10^{-11} | 10^{-12} |

longer ← → shorter

Size of a wavelength

Soccer Field • House • Baseball • This Period • Cell • Bacteria • Virus • Protein • Water Molecule

Common name of wave

RADIO WAVES — INFRARED — VISIBLE — ULTRAVIOLET — "HARD" X RAYS

MICROWAVES — "SOFT" X RAYS — GAMMA RAYS

Sources

AM Radio • FM Radio • Microwave Oven • Radar • People • Light Bulb • The Advanced Light Source • X-Ray Machines • Radioactive Elements

| Frequency (waves per second) | 10^6 | 10^7 | 10^8 | 10^9 | 10^{10} | 10^{11} | 10^{12} | 10^{13} | 10^{14} | 10^{15} | 10^{16} | 10^{17} | 10^{18} | 10^{19} | 10^{20} |

lower ← → higher

$h\nu$ = Energy of one photon (electron volts)

| 10^{-9} | 10^{-8} | 10^{-7} | 10^{-6} | 10^{-5} | 10^{-4} | 10^{-3} | 10^{-2} | 10^{-1} | 1 | 10^1 | 10^2 | 10^3 | 10^4 | 10^5 | 10^6 |

Typical surface/materials science expts.

30

Bendable refocusing mirror

Sample

Three interchangeable rotatable diffraction gratings

100 l/mm

600 l/mm

1200 l/mm

Translating exit slit

~10µ-100 µ spot

Horizontal focusing mirror

Circular polarization aperture

Translating entrance slit

Bend-magnet source

Vertical focusing mirror

Schematic layout of Beamline 9.3.2.

$$n\lambda_x = d(\sin(i) - \sin(r))$$

Quarter-wave plate
Variable polarization

Source: High-flux undulator
(2.3 to 12 keV)

M2B

HAXPES

M2A

HRM

M1

DCM

Source

KB

RIXS

hv

RIXS

Double-crystal monochromator
(Si 111 and 333)

High res. mono.
($\Delta E \sim 100$ meV)

**HAXPES endstation
Solid-State, Gas-
Phase, Liquid Jet**

RIXS endstation

30×80 µm² beam spot

10×10 µm² beam spot

λ_x

continuous

θ

λ_x

λ_x

θ

Bragg:
$n\lambda_x = 2d_{hk\ell}\sin\theta$
$n = 1, 2, \ldots$
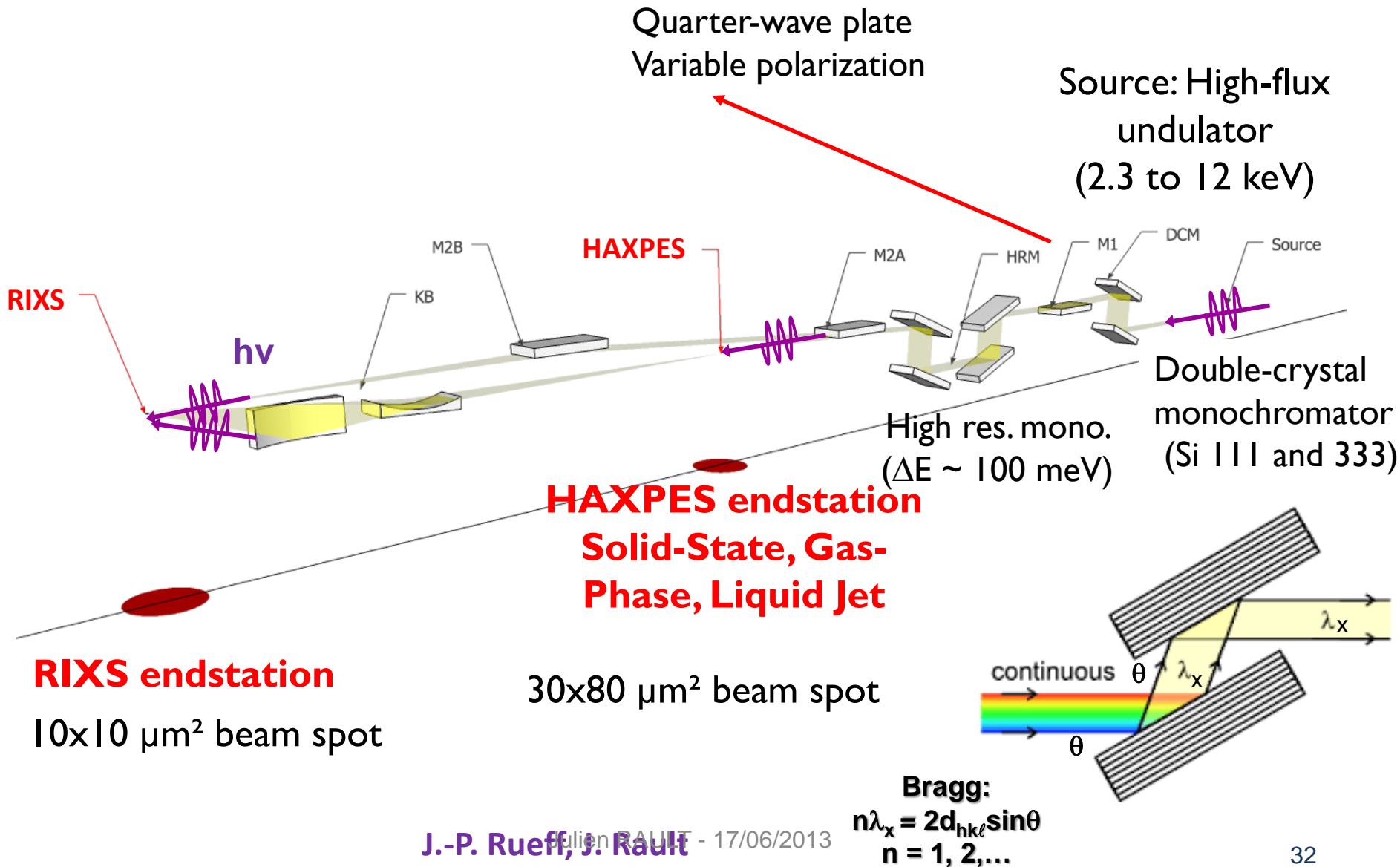
MULTI-TECHNIQUE SPECTROMETER/ DIFFRACTOMETER (MTSD)

5-axis sample manipulator

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

Scienta electron spectrometer (hidden)

ALS
BL 9.3.1
$h\nu$ = 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
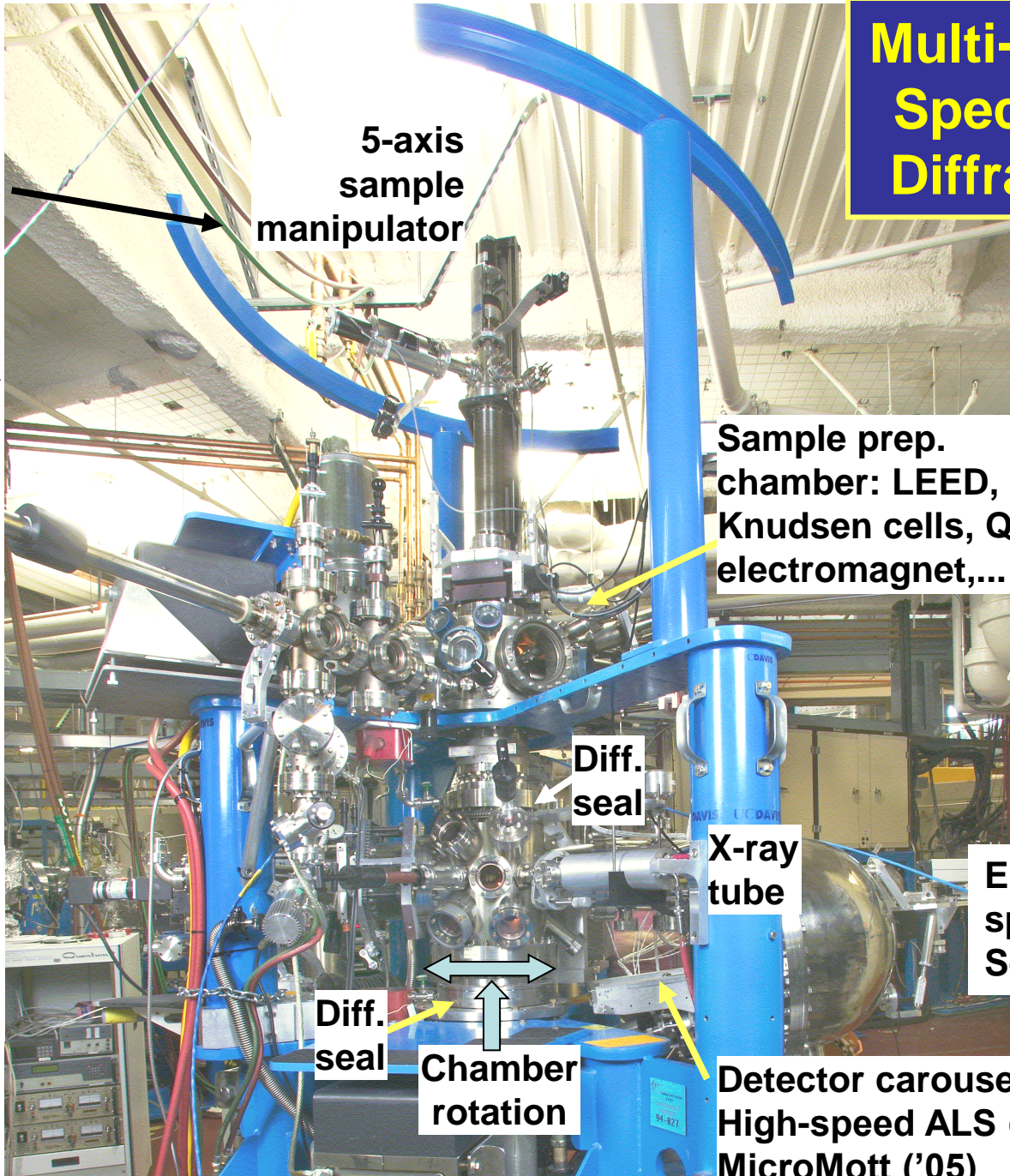
Sample manipulator: to be upgraded, '05: T down to ~6 K

5-axis sample manipulator

Loadlock for sample introduction

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

Diff. seal

X-ray tube

Soft x-ray spectrometer: Scienta XES 300

Electron spectrometer: Scienta SES 200

Diff. seal

Chamber rotation

Detector carousel: High-speed ALS detector ('05), MicroMott ('05)

34

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

Nature Photonics 9, 281 (2015)

San Francisco

Marin County

UC Berkeley

Advanced
Light Source

Group offices
& lab.

ALS Beamlines
January 2014

Magnetic Microscopy 7.3.1
Diagnostic Beamline 7.2
Surface, Materials Science (MAESTRO) 7.0.1
Calibration, Optics Testing, Spectroscopy 6.3.2
Magnetic Spectroscopy, Materials Science 6.3.1
X-Ray Microscopy 6.1.2
Femtosecond and Picosecond Phenomena 6.0.2
Femtosecond and Picosecond Phenomena 6.0.1
Polymer STXM 5.3.2
Research and Development 5.3.1
Macromolecular Crystallography 5.0.3
Macromolecular Crystallography 5.0.2
Macromolecular Crystallography 5.0.1
Macromolecular Crystallography 4.2.2
Magnetic Spectroscopy 4.0.2
MERLIN 4.0.3
Commercial LIGA 3.2.1
Diagnostic Beamline 3.1
National Center for X-Ray Tomography 2.1.2
IR Spectromicroscopy 1.4.4
IR Spectromicroscopy 1.4.3

7.3.3 SAXS/WAXS
8.0.1 Surface, Materials Science
8.2.1 Macromolecular Crystallography
8.2.2 Macromolecular Crystallography
8.3.1 Macromolecular Crystallography
8.3.2 Tomography
9.0.2 Chemical Dynamics
9.0.1 Diffraction Imaging
9.3.1 AMO, Materials Science
9.3.2 Chemical, Materials Science
10.0.1 Correlated Materials, AMO
10.3.1 X-Ray Fluorescence
10.3.2 MicroXAS
11.0.1 PEEM3/Resonant Soft X-Ray Scattering
11.0.2 Molecular Environmental Science
11.3.1 Small-Molecule Crystallography
11.3.2 EUV Lithography, Mask Inspection
12.0.1 EUV Lithography, Photoemission
12.0.2 Coherent Soft X-Ray Science
12.2.2 High Pressure
12.3.1 Macromolecular Crystallography/Bio-SAXS
12.3.2 X-Ray Microdiffraction

5.4 BSISB

KEY — Operational – – Under Construction

Insertion Device Beamlines **Bend Magnet Beamlines** **Superbend Beamlines**

37

Average brightness

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

"X-Ray Data Booklet" See Fig. 2.10

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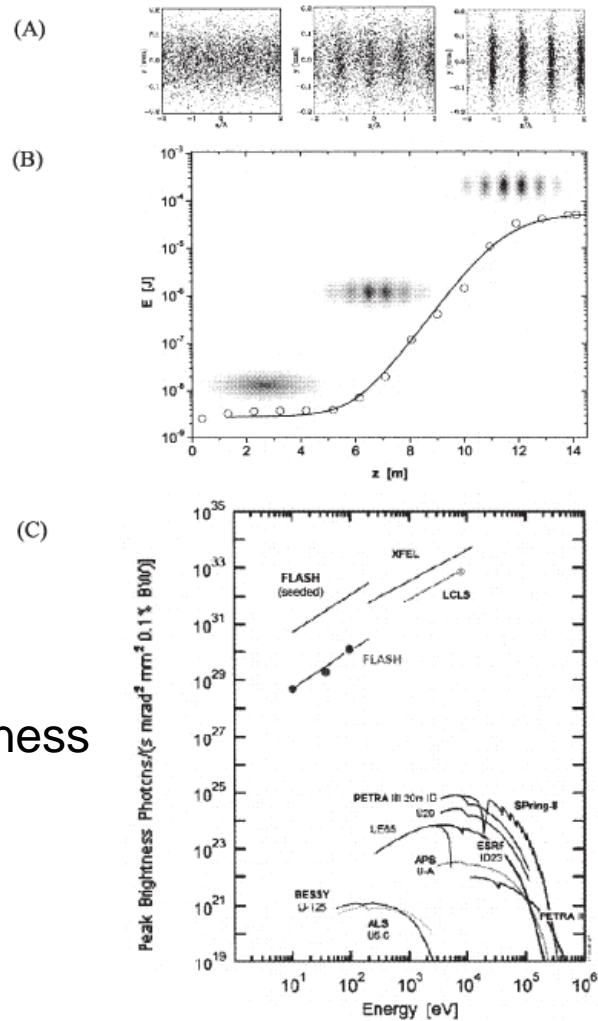
Figure 2-10. (A) Simulation of the electron microbunching process and (B) the exponential growth of FEL output energy due to microbunching (following S. Reiche and K.-J. Kim). (C) FEL beams have very short pulse duration and full spatial coherence, with peak brightness many orders of magnitude higher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

Future – Ultrafast X-ray Science

X-ray Free-Electron Lasers!

SLAC National Accelerator Laboratory

LINAC COHERENT LIGHT SOURCE

Femtosecond dynamics

- Stripe phase of $La_{2-x}Sr_xNiO_4$
  (W.-S. Lee, Z.X. Shen group)

- CO/OO/SO CMR Manganites
  (S. Zhou)

Injector

Beam Compressor #1

Beam Compressor #2

Linac

X-ray optics

Experimental Hall

A

B

Undulator

Sand Hill Rd
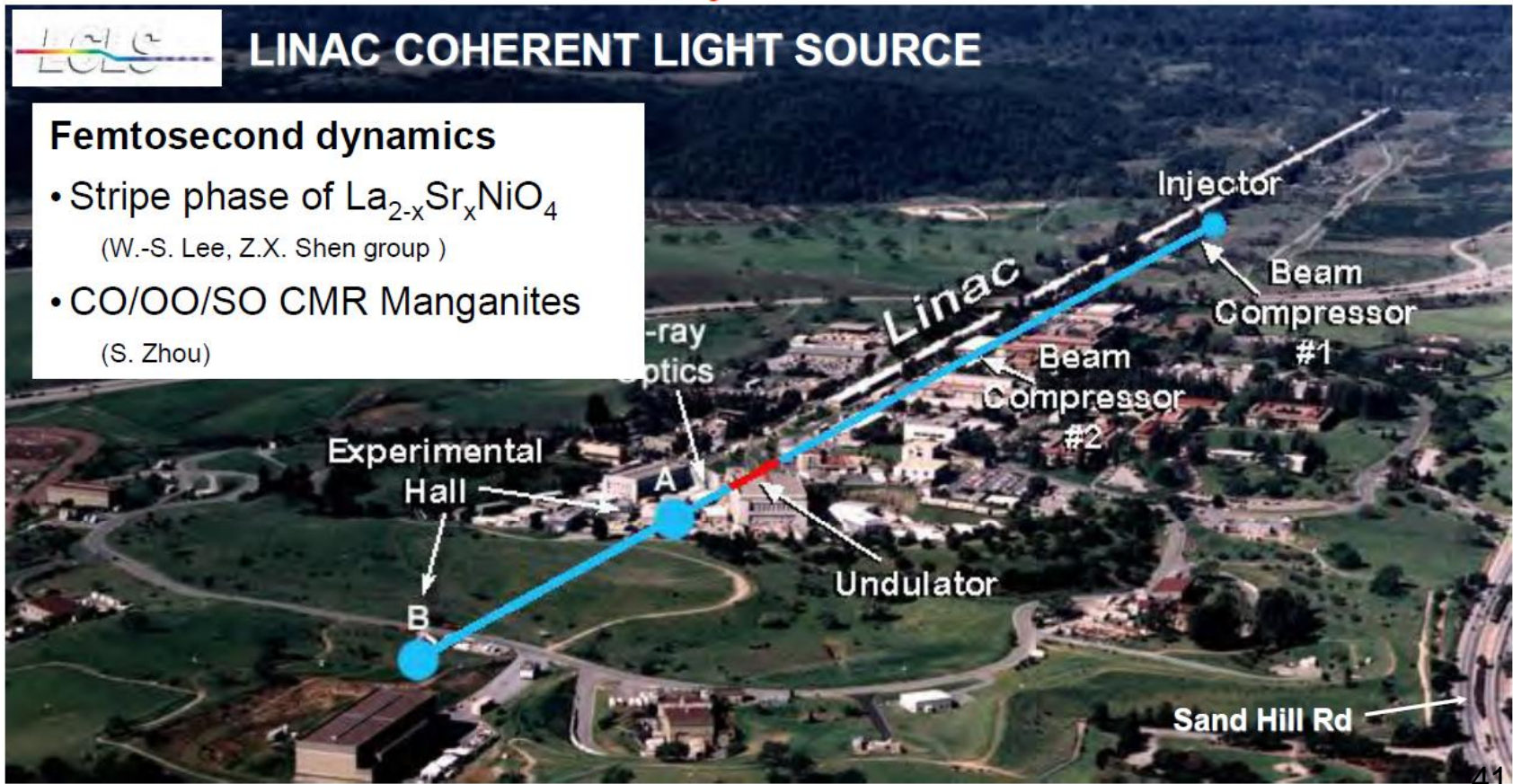
The five ways in which x-rays Interact with Matter:
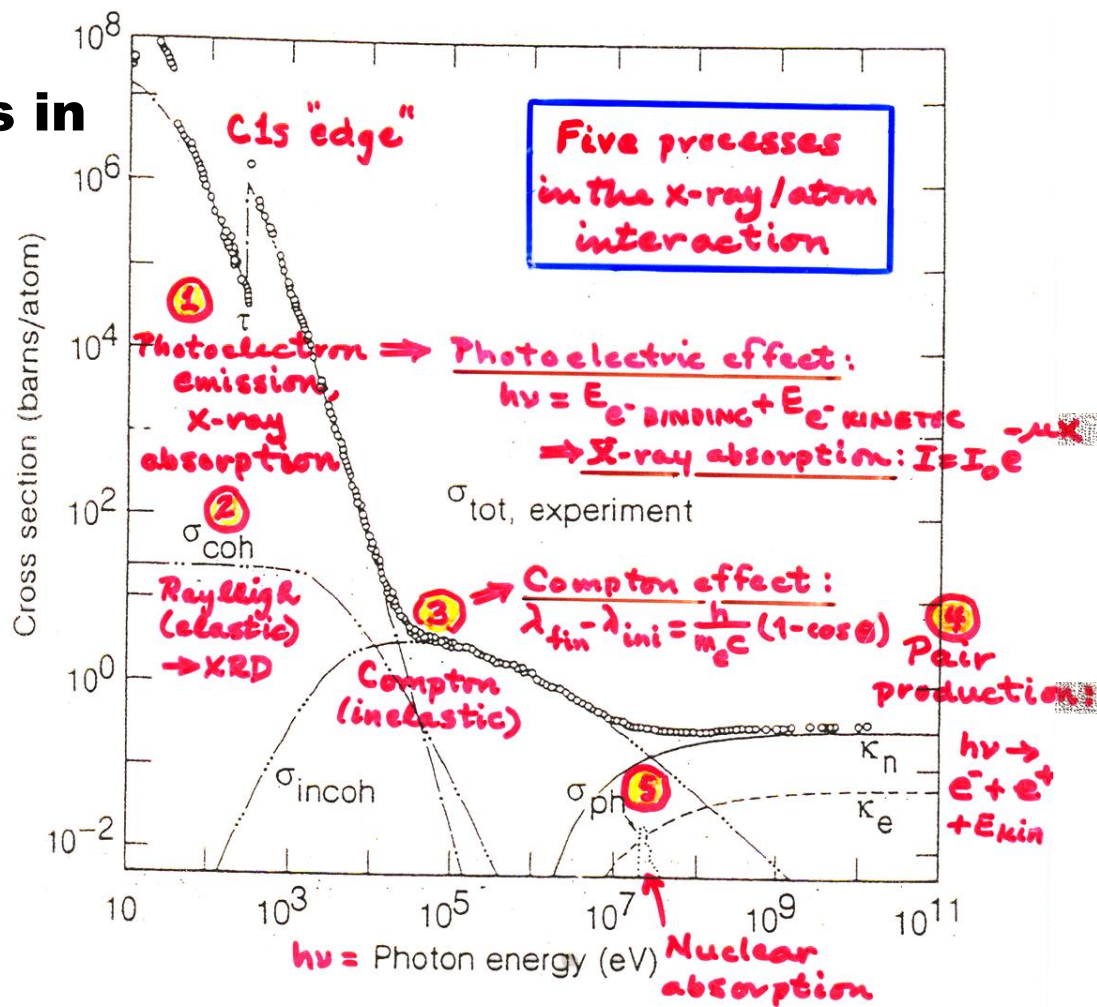
Fig. 3-1. Total photon cross section σ_{tot} in carbon, as a function of energy, showing the contributions of different processes: τ, atomic photo-effect (electron ejection, photon absorption); σ_{coh}, coherent scattering (Rayleigh scattering—atom neither ionized nor excited); σ_{incoh}, incoherent scattering (Compton scattering off an electron) κ_n, pair production, nuclear field; κ_e, pair production, electron field; σ_{ph}, photonuclear absorption (nuclear absorption, usually followed by emission of a neutron or other particle). (From Ref. 5; figure courtesy of J. H. Hubbell.)

The spectroscopies:

e⁻, free

hν

hν

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

e⁻, free #

e⁻, bound *

hν

X-RAY ABSORPTION SPECTROSCOPY- XAS

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

e⁻₁, free

e⁻₂

hν

hν' < hν

or

e⁻₃, free
= Auger

X-RAY EMISSION (FLUORESCENCE)
SPECTROSCOPY

+ AUGER ELECRON SPECTROSCOPY
(Always accompanies photoelectron emission)

43
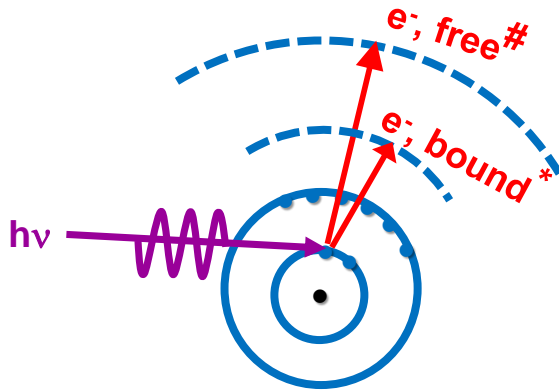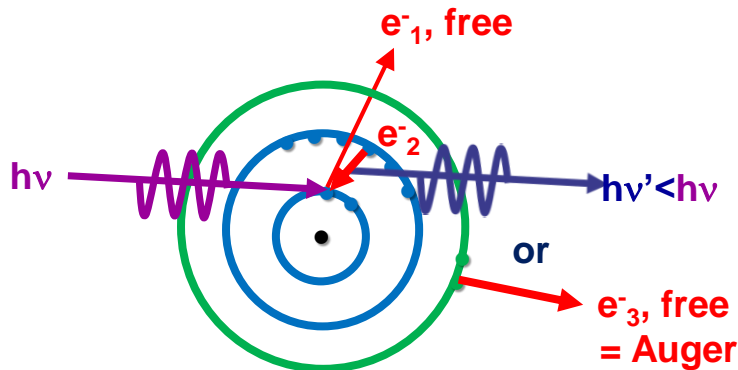
X-ray diffraction from crystals and multilayers, standing waves:
From crystals:

incident angle (θ)   reflection angle (θ)

$d_{hk\ell}$

$nk\ell$

λ_x

Atomic scattering factor $f_i(\theta)$

Bragg:
$$n\lambda_x = 2d_{hk\ell}\sin\theta$$
$$n = 1, 2,\ldots$$

From multilayers:

Incident beam

Reflected beams

Standing wave

λ_x

θ

d_{ML} $\dfrac{d_A}{d_B}$

d_{ML}

1 Material A
Material B

2

3

N

$D_{ML} = Nd_{ML}$

$n_A = 1-\delta_A-i\beta_A$
$n_B = 1-\delta_B-i\beta_B$
Index of refraction
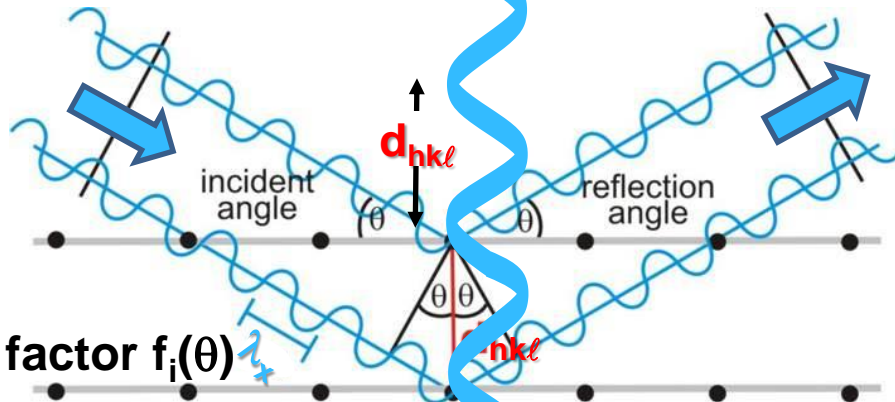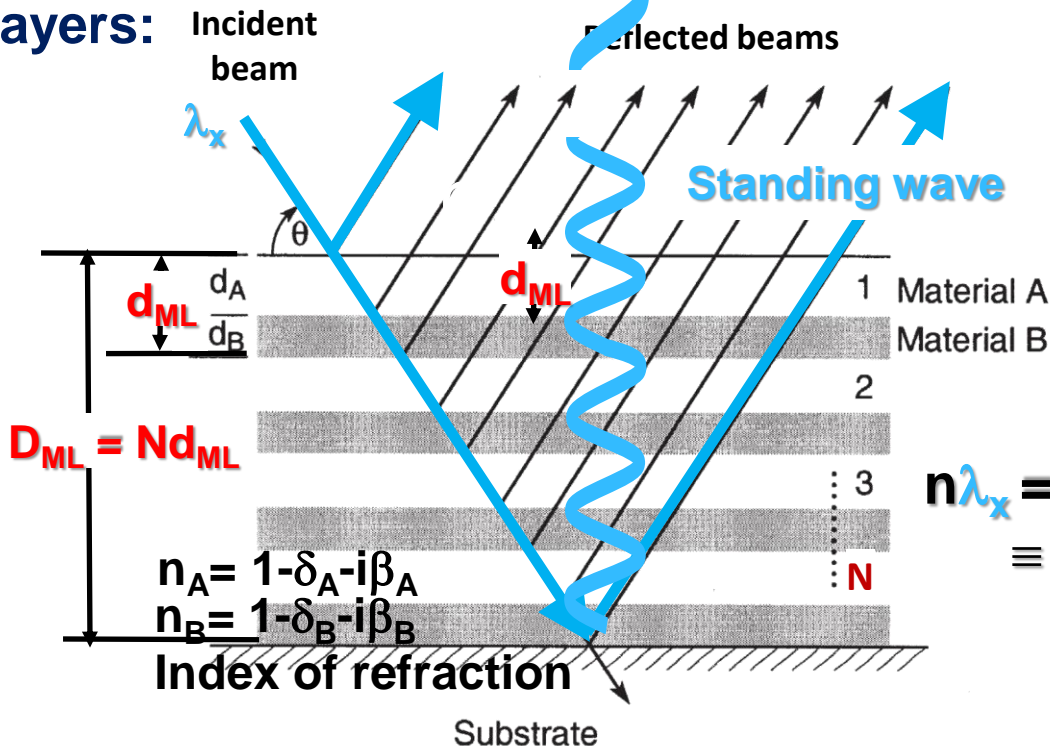
+Kiessig fringes:
$$m\lambda_x = 2\sin\theta_m$$
$$= 2D_{ML}\sin\theta_m$$
m = usually large (often unknown) number

Bragg:
$$n\lambda_x = 2(d_A+d_B)\sin\theta_n$$
$$\equiv\ 2d_{ML}\sin\theta_n$$
$$n = 1,2,\ldots$$

Substrate

A LITTLE X-RAY OPTICS

Incident **Reflected**

Fresnel Equations }

$I(z) = I(0)exp(-L/\Lambda_{h\nu})$

L

Transmitted & Absorbed

z
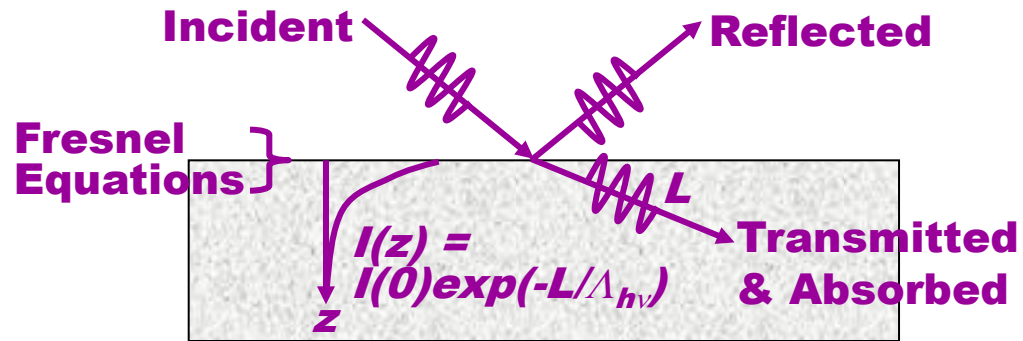
(E.G. See pp. 1-38, 1-44, 5-18-5-19 in X-Ray Data Booklet)

Index of refraction = $n = 1 - \delta - i\beta$
(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

n also = $1 - (r_e/2\pi)\lambda_{h\nu}^2\sum n_i f_i(0=$fwd. scatt.$)$

r_e = classical electron radius
= $e^2/4\pi\varepsilon_0 m_e e^2$ = **2.817 x 10^{-15} m**
$\lambda_{h\nu}$ = 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 = $l_{abs} = \lambda_{h\nu}/(4\pi\beta) = \Lambda_{h\nu}$

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

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

Au Density=19.32

delta (dash)
beta (solid)

Delta, Beta

Photon Energy (eV)

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[x] 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, λ is the wavelength, and n_i is the number of atoms of type i per unit volume. The parameters[x] δ and β 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)

The mass absorption coefficient μ (cm^2/g) is related to the transmitted intensity through a material of density ρ (g/cm^3) and thickness d by

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

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

$$\mu = \frac{N_A}{A}\sigma_a \quad , \quad 4\pi\beta/\lambda_X = \mu_\ell = (N_A/A)\rho\sigma_a = 1/\Lambda_{h\nu} \tag{2}$$

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

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

where the molecular weight of a compound containing x_i atoms of type i is $MW = \sum_i x_i A_i$. 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.

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

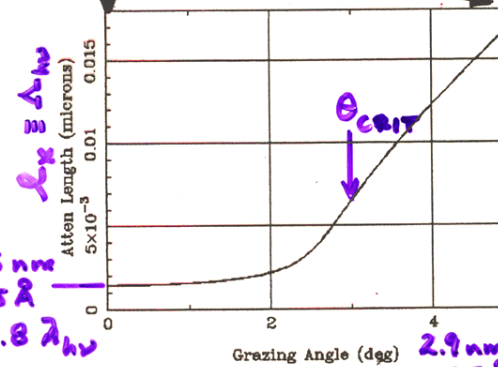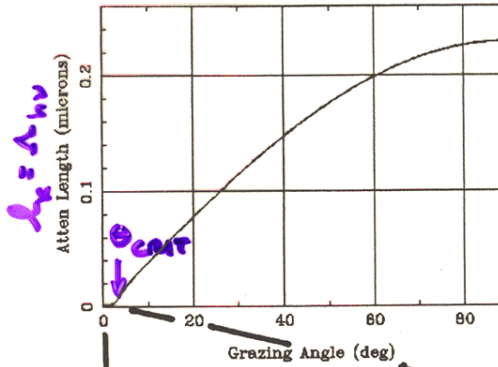θ_{CRIT} = Grazing angle at which reflectivity begins (R ≈ 0.20)

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

Calculated online from: http://henke.lbl.gov/optical _constants/atten2.html

X-Ray Attenuation Length

Au Density=19.32, Energy=1487.eV

X-Ray Attenuation Length

Au Density=19.32, Energy=100.eV

θ_{CRIT}

1.5 nm = 15 Å ≈ 1.8 $\lambda_{h\nu}$

2.9 nm = 29 Å ≈ 0.23 $\lambda_{h\nu}$

Mirror Reflectivity

Au Rho=19.32, Sig=0.nm, P=-1., E=1487.eV
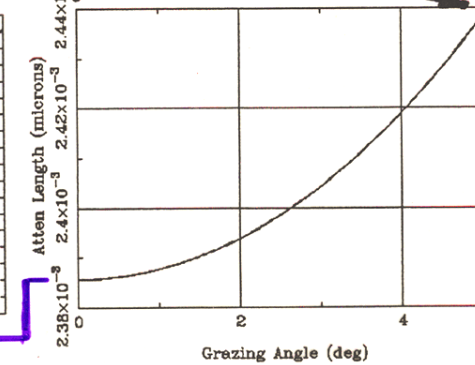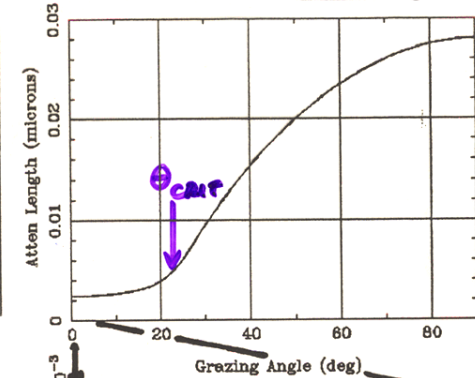
Mirror Reflectivity

Au Rho=19.32, Sig=0.nm, P=-1., E=100.eV

47
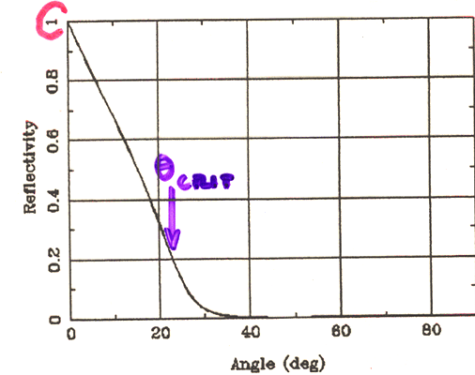
Multilayer Reflectivity

- Top Material: Si . Density: -1 gm/cm^3.
  (enter negative value to use tabulated density.)
- Bottom Material: Mo . Density: -1 gm/cm^3.
- Multilayer Period: 3.0 nm.
- Ratio of (Bottom layer thickness)/(Period): 0.5 .
- Interdiffusion thickness : 0 nm (Sigma).
- Number of periods: 20 (enter negative value for semi-infinite multilayer.)
- Substrate Material: SiO2 . Density: -1 gm/cm^3.
- Polarization: -1 (-1 < pol < 1) where s=1, p=-1 and unpolarized=0.
- Scan Grazing Angle (deg) ▾ from 0 to 20 in 500 steps (< 500).
  (NOTE: Energies must be in the range 30 eV < E < 30,000 eV, Wavelength between 0.041 nm < Wavelength < 41 nm, and Angles between 0 & 90 degrees.)
- At fixed Energy (eV) = 1000

To request a LinLog ▾ Plot ▾ press this button: Submit Request

To reset to default values, press this button: Reset .

http://henke.lbl.gov/optical_constants/multi2.html

Multilayer Reflectivity

Si/Mo d=3.nm s=0.nm N=20 at 1000.eV, P=−1.

Bragg

Kiessig

48
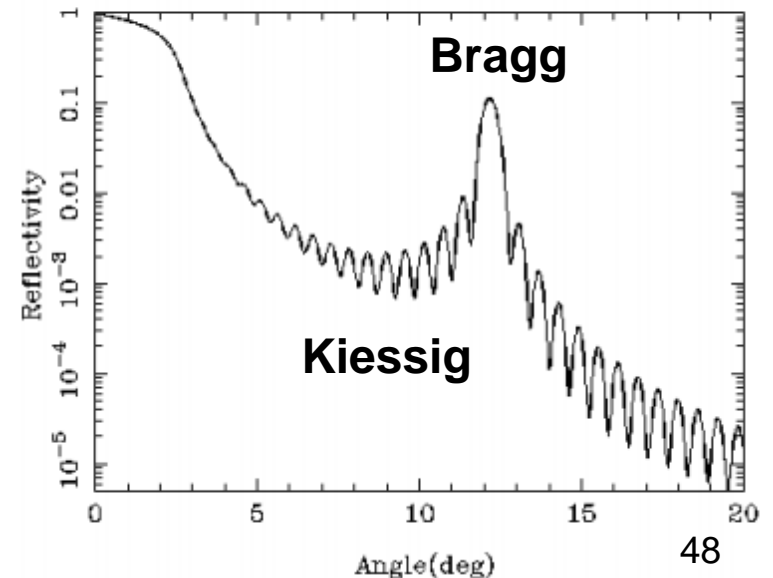
What properties do wave functions of overlapping (thus indistinguishable) particles have?—electrons as example:
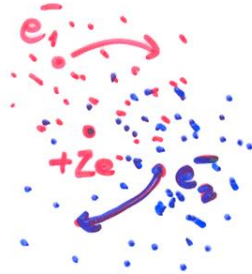
$\psi = \psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2)$, *including spin of both electrons*

But labels can't affect any measurable quantity.

E.g. – probability density :

$$\left|\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2)\right|^2 = \left|\psi(\vec{r}_2, \vec{s}_2; \vec{r}_1, \vec{s}_1)\right|^2$$

Therefore

$$\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) = \pm 1 \psi(\vec{r}_2, \vec{s}_2; \vec{r}_1, \vec{s}_1)$$
$$\equiv \hat{P}_{12}\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2)$$

with $\hat{P}_{12}$ = *permutation operator* $\rightarrow \vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2$

and eigenvalues of ± 1

Finally, all particles in two classes :

FERMIONS : (incl. e^- 's) : ψ antisymmetric

$$s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} ... \qquad \hat{P}_{12}\psi = -1\psi$$

BOSONS : (incl. photons) : ψ symmetric

$$s = 0, 1, 2, ... \qquad \hat{P}_{12}\psi = +1\psi$$

A brief review of electronic structure in atoms, molecules, and solids

Probability of finding two electrons at the same point in space with the same spin is zero: "the Fermi Hole"

$e_2 - \uparrow$ $e_1 - \uparrow$

$e_3 - \uparrow$
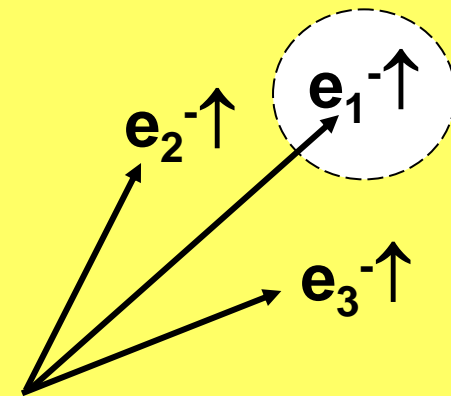
→**the Exchange Interaction**
→**Hund's 1st rule & magnetism**

Antisymmetry and the Pauli Exclusion Principle:

Try Helium, 2 electrons in ground state 1s wave functions, "1s^2"

Simple normalized antisymmetric trial wave function is

$$\psi(\vec{r}_1,\vec{s}_1;\vec{r}_2,\bar{s}_2) = \frac{1}{\sqrt{2}}\left[\varphi_{1s}(\vec{r}_1,\vec{s}_1=\uparrow)\varphi_{1s}(\vec{r}_2,\vec{s}_2=\downarrow) - \varphi_{1s}(\vec{r}_1,\vec{s}_1=\downarrow)\varphi_{1s}(\vec{r}_2,\vec{s}_2=\uparrow)\right]$$

interchanging labels gives

$$\psi(\vec{r}_2,\vec{s}_2;\vec{r}_1,\bar{s}_1) = \frac{1}{\sqrt{2}}\left[\varphi_{1s}(\vec{r}_2,\vec{s}_2=\uparrow)\varphi_{1s}(\vec{r}_1,\vec{s}_1=\downarrow) - \varphi_{1s}(\vec{r}_2,\vec{s}_2=\downarrow)\varphi_{1s}(\vec{r}_1,\vec{s}_1=\uparrow)\right]$$

$$= -\psi(\vec{r}_1,\vec{s}_1;\vec{r}_2,\bar{s}_2), \textit{ as required}$$

Can't tell which electron is spin up--indistinguishable

Also, if we try to put both electrons in 1s with spin-up ($\uparrow$), first term always cancels second term, and $\psi = 0!$ Therefore, we have the Pauli Exclusion Principle

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

$$\Psi \approx \Phi = Slater\ \det er\min ant$$

space: like 1s, 2s,...
spin: $\alpha(\uparrow)$ or $\beta(\downarrow)$

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

(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:

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

with:

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

$\uparrow\uparrow$ or $\downarrow\downarrow$

One-electron energies or eigenvalues ≈ binding energy→ Koopmans' Theorem

One-electron integral:

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

Note--K_{ij} often J_{ij} in solid-state

Two-electron coulomb integral:

$$J_{ij} \equiv \left\langle \phi_i(\vec{r}_1) \mid \hat{J}_j \mid \phi_i(\vec{r}_1) \right\rangle = \iint \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\frac{1}{r_{12}}\phi_i(\vec{r}_1)\phi_j(\vec{r}_2)dV_1 dV_2 \quad \text{(45)}$$
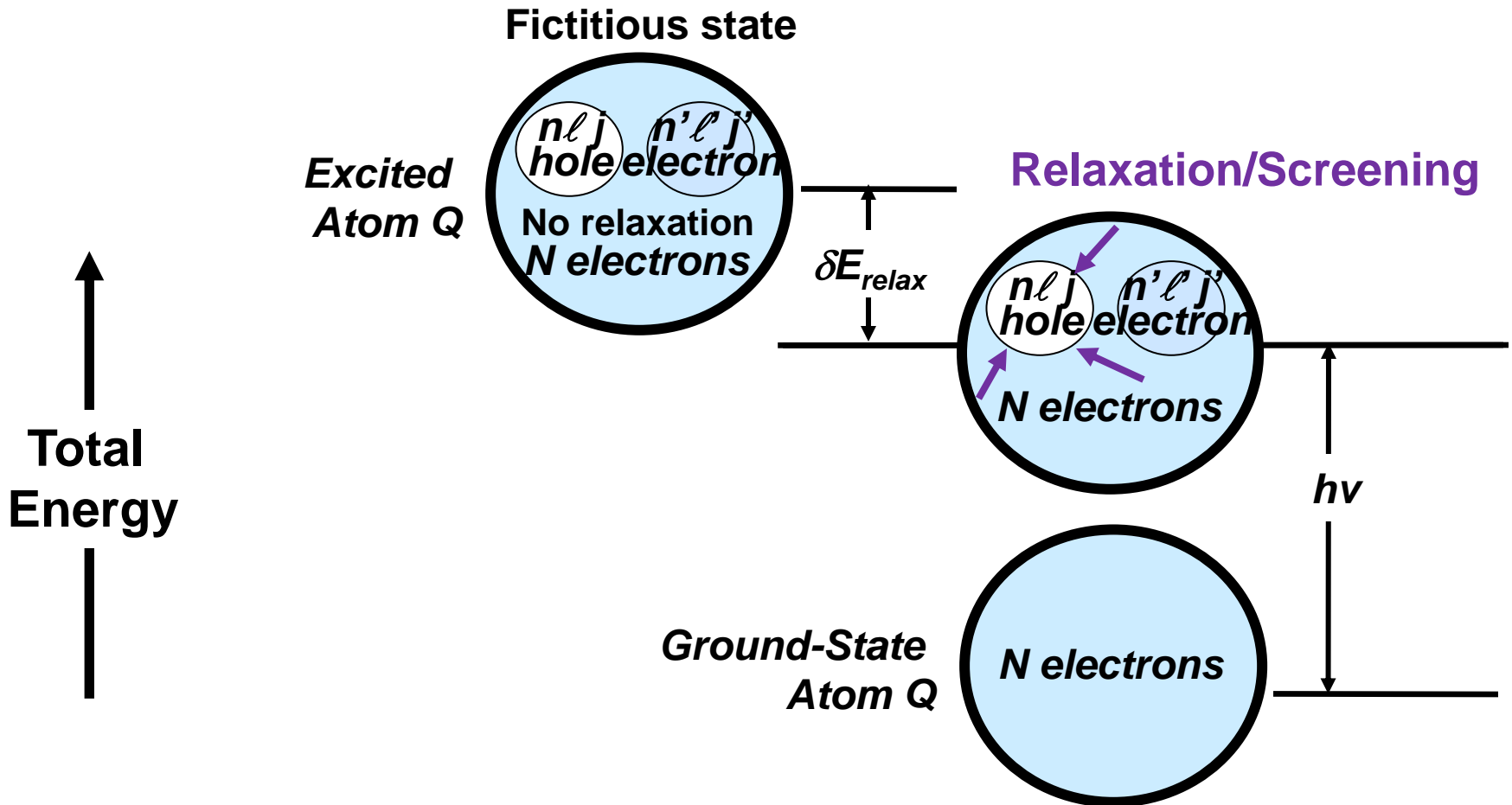
Two-electron exchange integral:

$$K_{ij} \equiv \left\langle \phi_i(\vec{r}_1) \mid \hat{K}_j \mid \phi_i(\vec{r}_1) \right\rangle = \iint \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\frac{1}{r_{12}}\phi_j(\vec{r}_1)\phi_i(\vec{r}_2)dV_1 dV_2 \quad 51 \text{(46)}$$

Lowers energy—"attractive"

X-ray absorption: $n\ell\, j \rightarrow n'\ell'\, j'$

Fictitious state

Excited Atom Q

$n\ell\, j$ hole $n'\ell'\, j'$ electron

No relaxation N electrons

Relaxation/Screening

δE_{relax}

$n\ell\, j$ hole $n'\ell'\, j'$ electron

N electrons
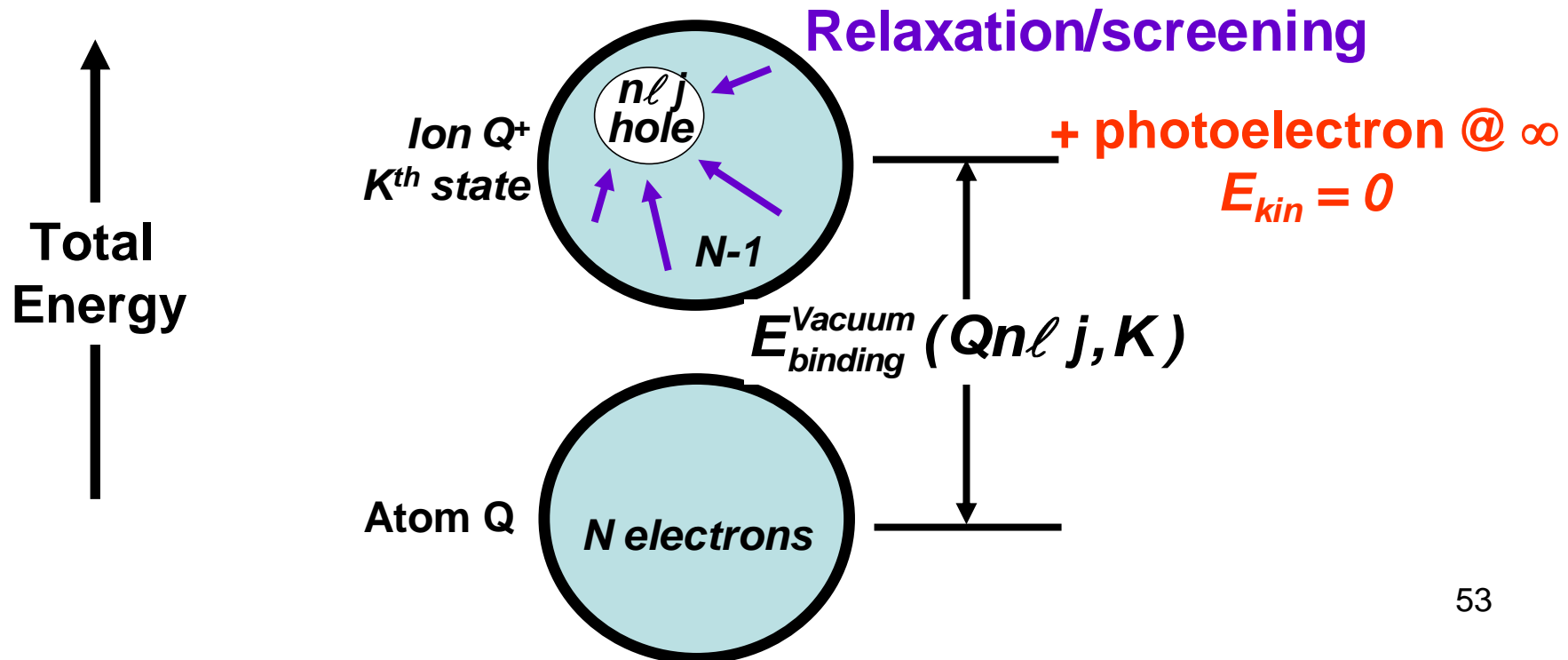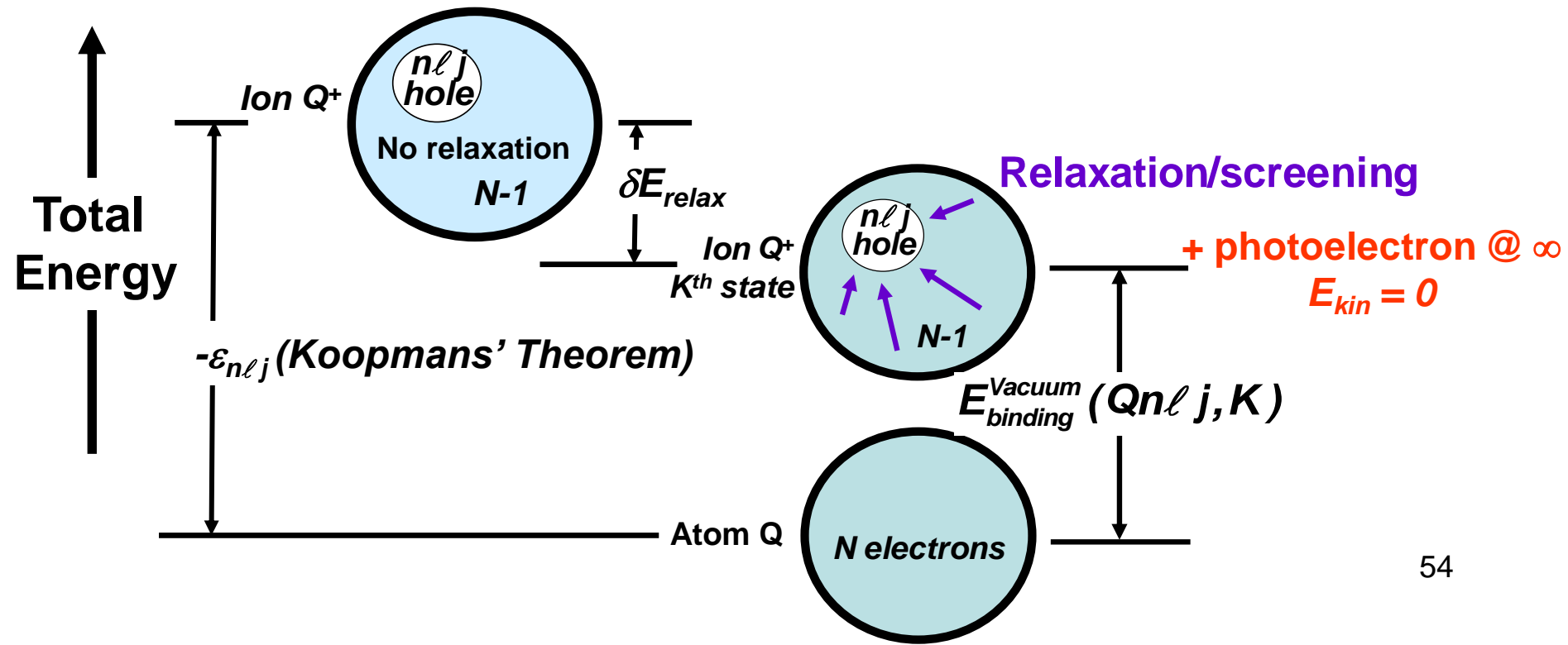
Total Energy

$h\nu$

Ground-State Atom Q   **N electrons**

Basic energetics—Many e⁻ picture

Photoelectron emission: $n\ell\,j \rightarrow$ *photoelectron at* $E_{kinetic}$

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

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

Total Energy

Relaxation/screening

Ion Q⁺
Kᵗʰ state

$n\ell\,j$ *hole*

N-1

+ photoelectron @ ∞
$E_{kin} = 0$

$E_{binding}^{Vacuum}(Qn\ell\,j,K)$

Atom Q

N electrons

Photoelectron emission: $n\ell\, j \rightarrow$ *photoelectron at* $E_{kinetic}$

$$hv = E_{binding}^{Vacuum} + E_{kinetic} = E_{binding}^{Fermi} + \varphi_{spectrometer} + E_{kinetic}$$

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

Fictitious state

Total Energy

Ion Q⁺

n ℓ j hole

No relaxation

N-1

δE_{relax}

Ion Q⁺

Kth state

Relaxation/screening

n ℓ j hole

N-1

+ photoelectron @ ∞

$E_{kin} = 0$

$-\varepsilon_{n\ell j}$ *(Koopmans' Theorem)*

$E_{binding}^{Vacuum}(Qn\ell\, j, K)$

Atom Q

N electrons

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Koopmans' Theorem Calculation of C 1s Chemical Shifts in Small C-Containing Molecules
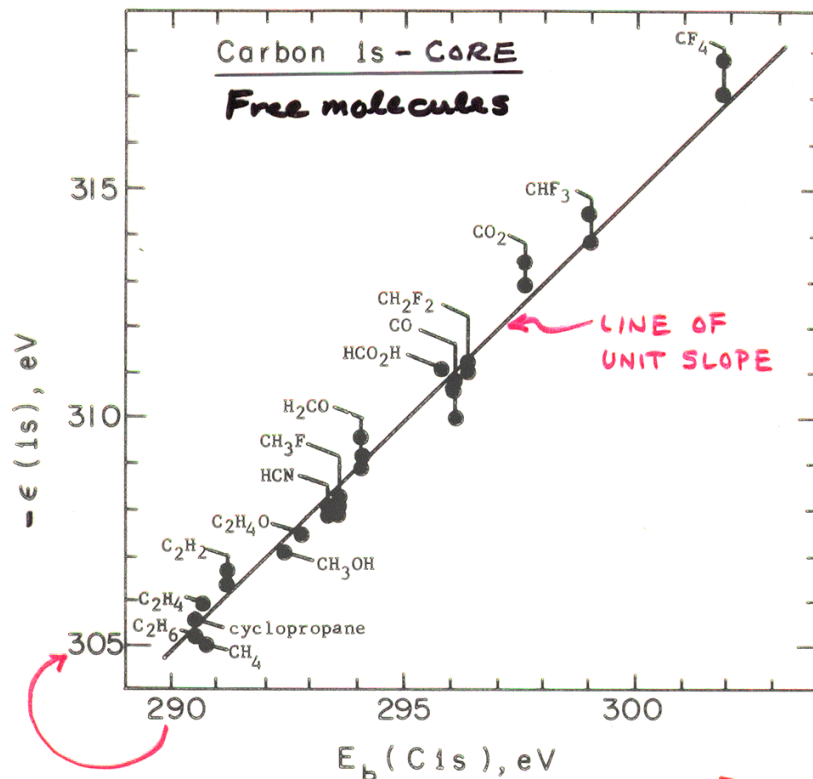
Figure 18 -- Plot of carbon 1s binding energies calculated via Koopmans' Theorem against experimental binding energies for several carbon-containing gaseous molecules. For some molecules, more than one calculated value is presented. The slope of the straight line is unity. The two scales are shifted with respect to one another by 15 eV, largely due to relaxation effects. All of the theoretical calculations were of roughly double-zeta accuracy or better. (From Shirley, reference 7.)

For general N-electron state K:

$\Psi_K(N) = $ *weighted sum of Slater determinants* Φ_j

$$= \sum_j C_{jK} \Phi_j$$

with probability of each $\left|C_{jK}\right|^2$

For example, for Ne, a highly accurate CI calculation by Barr involving 1071 distinct configurations of spatial orbitals[123] yields the following absolute values for the coefficients multiplying the various members of a few more important configurations: $\Phi_1 = 1s^2 2s^2 2p^6 =$ Hartree–Fock configuration— 0·984; $\Phi_2 = 1s^2 2s^1 2p^6 3s^1$—0·005; $\Phi_3 = 1s^2 2s^2 2p^5 3p$—0·009; $\Phi_4 = 1s^2 2s^2 2p^4 4p^2$ —0·007–0·030; and $\Phi_5 = 1s^2 2s^2 2p^4 3p 4p$—0·007–0·022. Approximately 70 distinct configurations have coefficients larger than 0·010 in magnitude, but only that for Φ_1 is larger than 0·030.

Effects of <u>non-local</u> exchange

$$K_{ij} \equiv \left\langle \phi_i(\vec{r}_1) \mid \hat{K}_j \mid \phi_i(\vec{r}_1) \right\rangle = \iint \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\frac{1}{r_{12}}\phi_j(\vec{r}_1)\phi_i(\vec{r}_2)dV_1 dV_2$$

and additional correlation effects are replaced in solving for ground-state one-electron orbitals by a <u>local</u> exchange-correlation potential:

$$V_{ec,\uparrow(\downarrow)}(\vec{r}) \approx -\frac{3}{4}\left[\frac{3\rho_{\uparrow(\downarrow)}(\vec{r})}{\pi}\right]^{1/3} - \frac{0.056\rho_{\uparrow(\downarrow)}^{1/3}(\vec{r})}{0.079 + \rho_{\uparrow(\downarrow)}^{1/3}(\vec{r})}$$

Where $\rho_{\uparrow(\downarrow)}(\vec{r}) = \sum_{i=1,...N} \phi_{i,\uparrow(\downarrow)}^*(\vec{r})\phi_{i,\uparrow(\downarrow)}(\vec{r}) = \sum_{i=1,...N} \left|\phi_{i,\uparrow(\downarrow)}(\vec{r})\right|^2$

+ Various corrections/approximations going beyond this: generalized gradient approximation (GGA), GW and GW + cumulant expansions, dynamical mean field theory (DMFT), hybrid functionals mixing Hartree-Fock and LDA, quantum Monte Carlo,…

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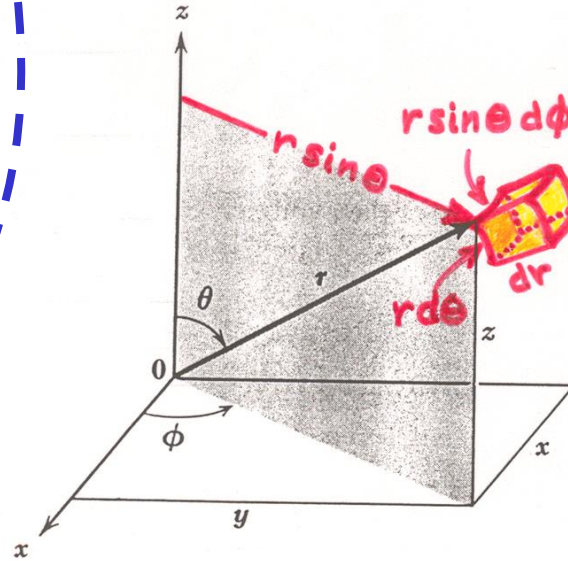**The Hydrogenic Atom Schroedinger Equation: Spherical Polar Coordinates**

Classically:

e⁻ $\vec{p}$

$\vec{r}$

+Ze
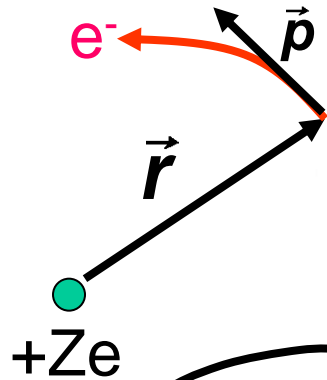
V(r) = -Ze²/4πε₀r

$\vec{L} = \vec{r} \times \vec{p}$

is conserved

Quantum mechanically:

$\Rightarrow dV = r^2 dr \sin\theta d\theta d\phi$

$\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = -\cos\theta \Big|_0^\pi \times 2\pi = 4\pi$

$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

Polar angle = θ = arc cos(z/r)
Azimuthal angle = ϕ = arc tan(y/x)

Converting to new coordinates

$\hat{K} = -\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$

$= -\frac{\hbar^2}{2\mu} \cdot \frac{1}{r^2 \sin\theta}\left[\sin\theta \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\phi^2}\right]$

$= -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$

$\hookrightarrow Z_{eff}(r)$ IN MANY-e ATOM

♣ H-ATOM SCH. EQN. IS:

$\hat{H}\Psi(r,\theta,\phi) = \hat{K}\Psi(r,\theta,\phi) - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = E\Psi$

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- Use separation of variables:

$$\Psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\underline{\Phi}(\phi)$$

− ASSUMED FORM −

- Substitute, rearrange ⟶

$\phi:$ $\quad \dfrac{d^2\underline{\Phi}}{d\phi^2} + C_\phi\,\underline{\Phi} = 0 \implies \underline{\Phi}(\phi) = Ae^{\pm iC_\phi \phi}$ ①

$\quad\quad\quad \Downarrow$

$\quad\quad m_\ell = 0,\pm 1,\dots \quad \boxed{\underline{\Phi}_{m_\ell}(\phi) = \dfrac{1}{\sqrt{2\pi}}\,e^{\pm im_\ell \phi}}$ − COM-PLEX

$\theta:$ $\quad \dfrac{1}{\sin\theta}\dfrac{d}{d\theta}\left(\sin\theta\,\dfrac{d\Theta}{d\theta}\right) + \left[\,C_\theta - \dfrac{m_\ell^2}{\sin^2\theta}\,\right]\Theta = 0$ ②

$\quad\quad\quad\quad\quad\quad \Downarrow$

$\quad\quad\quad\quad\quad \ell(\ell+1)$ ⟶ $Z_{eff}(r)$ IN MANY e^- ATOM

$R:$ $\left[\,-\dfrac{\hbar^2}{2\mu}\left(\dfrac{\partial^2}{\partial r^2} + \dfrac{2}{r}\dfrac{\partial}{\partial r}\right) + \dfrac{\ell(\ell+1)}{2\mu r^2} - \dfrac{Ze^2}{4\pi\varepsilon_0 r}\,\right]R = ER$ ③

A "RADIAL SCHROEDINGER EQN."

$$H_{op,\,radial}\,R = ER \implies \boxed{\begin{array}{l} E = E_n \\ = -\dfrac{Ze^2}{8\pi\varepsilon_0 a_0}\cdot\dfrac{1}{n^2} \\ n = 1,2,3,\dots \end{array}}$$

- Solving for Θ with ② ⟹

$$\boxed{\begin{array}{l}\Theta_{\ell m_\ell}(\theta) = \text{ASSOC. LEGENDRE POLYNOMIALS} \\ \quad\quad\quad\quad\quad \text{IN } (\cos\theta) - \text{REAL}\end{array}}$$

$$\ell = 0, 1, 2, 3, \dots (n-1)$$

$$m_\ell = -\ell, -\ell+1, \dots 0 \dots +\ell-1, +\ell$$

$$\underbrace{}_{2\ell+1}$$

Solving for R with ③ ⟹

$$\boxed{\begin{array}{l} R_{n\ell}(r) = \text{ASSOC. LAGUERRE FUNCTIONS} \\ \quad = (\text{POLYNOMIAL IN } r)\cdot e^{-Zr/a_0} - \text{REAL} \end{array}} \text{ ALSO}$$

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Atomic orbitals:

COMPLEX, IF $m \neq 0$

TABLE 6.1

NORMALIZED WAVE FUNCTIONS OF THE HYDROGEN ATOM FOR $n = 1, 2,$ AND 3^* ($Z = 1 = $ HYDROGEN)

n	l	m_l	$\Phi_{m_l}(\phi)$	$\Theta_{l,m_l}(\theta)$	$R_{nl}(r)$	$\Psi_{n,l,m_l}(r,\theta,\phi) = \Phi_{m_l}\Theta_{l,m_l}R_{nl}$
1 — 1s	0	0	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{1}{\sqrt{2}}$	$\dfrac{2}{a_0^{3/2}}e^{-r/a_0}$	$\dfrac{1}{\sqrt{\pi}\,a_0^{3/2}}e^{-r/a_0}$
2 — 2s	0	0	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{1}{\sqrt{2}}$	$\dfrac{1}{2\sqrt{2}\,a_0^{3/2}}\left(2-\dfrac{r}{a_0}\right)e^{-r/2a_0}$	$\dfrac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\left(2-\dfrac{r}{a_0}\right)e^{-r/2a_0}$
2 — 2p₀	1	0	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{\sqrt{6}}{2}\cos\theta$	$\dfrac{1}{2\sqrt{6}\,a_0^{3/2}}\dfrac{r}{a_0}e^{-r/2a_0}$	$\dfrac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\dfrac{r}{a_0}e^{-r/2a_0}\cos\theta$
2 — 2p±1	1	±1	$\dfrac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\dfrac{\sqrt{3}}{2}\sin\theta$	$\dfrac{1}{2\sqrt{6}\,a_0^{3/2}}\dfrac{r}{a_0}e^{-r/2a_0}$	$\dfrac{1}{8\sqrt{\pi}\,a_0^{3/2}}\dfrac{r}{a_0}e^{-r/2a_0}\sin\theta\,e^{\pm i\phi}$
3 — 3s	0	0	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{1}{\sqrt{2}}$	$\dfrac{2}{81\sqrt{3}\,a_0^{3/2}}\left(27-18\dfrac{r}{a_0}+2\dfrac{r^2}{a_0^2}\right)e^{-r/3a_0}$	$\dfrac{1}{81\sqrt{3\pi}\,a_0^{3/2}}\left(27-18\dfrac{r}{a_0}+2\dfrac{r^2}{a_0^2}\right)e^{-r/3a_0}$
3 — 3p₀	1	0	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{\sqrt{6}}{2}\cos\theta$	$\dfrac{4}{81\sqrt{6}\,a_0^{3/2}}\left(6-\dfrac{r}{a_0}\right)\dfrac{r}{a_0}e^{-r/3a_0}$	$\dfrac{\sqrt{2}}{81\sqrt{\pi}\,a_0^{3/2}}\left(6-\dfrac{r}{a_0}\right)\dfrac{r}{a_0}e^{-r/3a_0}\cos\theta$
3 — 3p±1	1	±1	$\dfrac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\dfrac{\sqrt{3}}{2}\sin\theta$	$\dfrac{4}{81\sqrt{6}\,a_0^{3/2}}\left(6-\dfrac{r}{a_0}\right)\dfrac{r}{a_0}e^{-r/3a_0}$	$\dfrac{1}{81\sqrt{\pi}\,a_0^{3/2}}\left(6-\dfrac{r}{a_0}\right)\dfrac{r}{a_0}e^{-r/3a_0}\sin\theta\,e^{\pm i\phi}$
3 — 3d₀	2	0	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{\sqrt{10}}{4}(3\cos^2\theta-1)$	$\dfrac{4}{81\sqrt{30}\,a_0^{3/2}}\dfrac{r^2}{a_0^2}e^{-r/3a_0}$	$\dfrac{1}{81\sqrt{6\pi}\,a_0^{3/2}}\dfrac{r^2}{a_0^2}e^{-r/3a_0}(3\cos^2\theta-1)$
3 — 3d±1	2	±1	$\dfrac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\dfrac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\dfrac{4}{81\sqrt{30}\,a_0^{3/2}}\dfrac{r^2}{a_0^2}e^{-r/3a_0}$	$\dfrac{1}{81\sqrt{\pi}\,a_0^{3/2}}\dfrac{r^2}{a_0^2}e^{-r/3a_0}\sin\theta\cos\theta\,e^{\pm i\phi}$
3 — 3d±2	2	±2	$\dfrac{1}{\sqrt{2\pi}}e^{\pm 2i\phi}$	$\dfrac{\sqrt{15}}{4}\sin^2\theta$	$\dfrac{4}{81\sqrt{30}\,a_0^{3/2}}\dfrac{r^2}{a_0^2}e^{-r/3a_0}$	$\dfrac{1}{162\sqrt{\pi}\,a_0^{3/2}}\dfrac{r^2}{a_0^2}e^{-r/3a_0}\sin^2\theta\,e^{\pm 2i\phi}$

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.3 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

IS SAME FOR MANY e^- ATOMS

CHANGES FOR MANY e^- ATOMS

$\Psi_{n\ell m_\ell m_s}(r,\theta,\varphi,spin) = \Psi_{n\ell m_\ell}(r,\theta,\varphi) \times [\alpha(\uparrow) \text{ or } \beta(\downarrow)]$

The atomic orbitals:

With spin

$Y_{\ell m_\ell}(\theta,\phi) =$ *"spherical harmonics"*

COMPLEX, IF m ≠ 0 *But we can make them real for convenience*

TABLE 6.1

NORMALIZED WAVE FUNCTIONS OF THE HYDROGEN ATOM FOR n = 1, 2, AND 3* **(Z = 1 = HYDROGEN)**

n	ℓ	m_ℓ	$\Phi(\phi)$ m_ℓ	$\Theta_{\ell m_\ell}(\theta)$	$R_{n\ell}(r)$	$\Psi_{n\ell m_\ell}(r,\theta,\phi) = \Phi\,\Theta\,R_{n\ell}$ $m_\ell\ \ell m_\ell\ n\ell$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\,a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\,a_0^{3/2}}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}\cos\theta$ →**node for θ = 90°**
2	1	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\,a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\,a_0^{3/2}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\,a_0^{3/2}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{4}{81\sqrt{6}\,a_0^{3/2}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\,a_0^{3/2}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\cos\theta$ → **node for r = 6a_0**
3	1	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{4}{81\sqrt{6}\,a_0^{3/2}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\,a_0^{3/2}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\sin\theta\, e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4}(3\cos^2\theta - 1)$	$\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}(3\cos^2\theta - 1)$ → **nodes for cos²θ = 1/3**
3	2	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$ **θ= 54.7°, 125.3°**
3	2	±2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$

Handwritten row labels: 1S, 2S, 2P₀, 2P±1, 3S, 3P₀, 3P±1, 3d₀, 3d±1, 3d±2

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.3 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

IS SAME FOR MANY e⁻ ATOMS

CHANGES FOR MANY e⁻ ATOMS

$e^{-r/na_0} \to e^{-Zr/na_0}$ for hydrogenic $Z \to Z_{eff}(r)$ in many-e⁻ atoms

Overall, in a many-electron system:

●**Anti-symmetry of total wave function implies:**

Pauli Exclusion Principle:
No two electrons can have all the same quantum nos.
n, ℓ, m_ℓ, m_s
or, if spin-orbit split
n, ℓ, j, m_j

●**Electronic structure determined by filling** n, ℓ *(or n, ℓ, j)* **levels from lowest to highest energy** *($E_{n\,\ell}$ or $E_{n\ell\,j}$ from radial Schroedinger Eqn. with Z_{eff})*

●**Partially filled subshells** n, ℓ *(or n, ℓ, j)* **have their lowest energy when a maximum no. of electrons have parallel spins = highest <u>total</u> spin angular momentum = $\vec{S}$ (Hund's First Rule), and then they couple to yield highest <u>total</u> orbital angular momentum = $\vec{L}$ (Hund's Second Rule)**

MAKING THE ATOMIC ORBITALS REAL (E.G., FOR CHEMICAL BONDING):

$$\Psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r) \, \Theta_{\ell m_\ell}(\theta) \, \frac{1}{\sqrt{2\pi}} \, e^{i m_\ell \phi}$$

COMPLEX   REAL   REAL   COMPLEX IF $m_\ell \neq 0$

SO JUST TAKE COMB. OF $\pm m_\ell$ AS:

$$\Psi_{n\ell(\rightarrow)}(r, \theta, \phi) = \begin{cases} \frac{1}{2}\left[\Psi_{n\ell m_\ell} + \Psi_{n\ell -m_\ell}\right] \propto R_{n\ell} \, \Theta_{\ell m_\ell} \cos m_\ell \phi \\ \frac{1}{2i}\left[\Psi_{n\ell m_\ell} - \Psi_{n\ell -m_\ell}\right] \propto R_{n\ell} \, \Theta_{\ell m_\ell} \sin m_\ell \phi \end{cases}$$

REAL

EXAMPLE: 2p ORBITALS

$$\Psi_{210} = \Psi_{2p_0} = \underline{\Psi_{2p_z} \propto r \cos\theta = z} \quad \text{(ALREADY REAL)}$$

$$\Psi_{211} = \Psi_{2p_{+1}} \propto r \sin\theta \, e^{i\phi} = r\sin\theta[\cos\phi + i\sin\phi]$$

$$\Psi_{21-1} = \Psi_{2p_{-1}} \propto r \sin\theta \, e^{-i\phi} = r\sin\theta[\cos\phi - i\sin\phi]$$

$$\therefore$$

$$\tfrac{1}{2}[\Psi_{2p_{+1}} + \Psi_{2p_{-1}}] = \Psi_{2p_x} \propto r\sin\theta\cos\phi = x$$

$$\tfrac{1}{2i}[\Psi_{2p_{+1}} - \Psi_{2p_{-1}}] = \Psi_{2p_y} \propto r\sin\theta\sin\phi = y$$

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Filling the Atomic Orbitals:

		$m=0$	$m=1$ $\pm$	$m=2$ $\pm$	Maximum Occupation = Degeneracy
1s	$n=1$ $l=0$				2
2s	$n=2$ $l=0$				2
2p	$n=2$ $l=1$		x2		6
3s	$n=3$ $l=0$				2
3p	$n=3$ $l=1$		x2		6
3d	$n=3$ $l=2$		x2	x2	10

8

18

+ 14 for nf
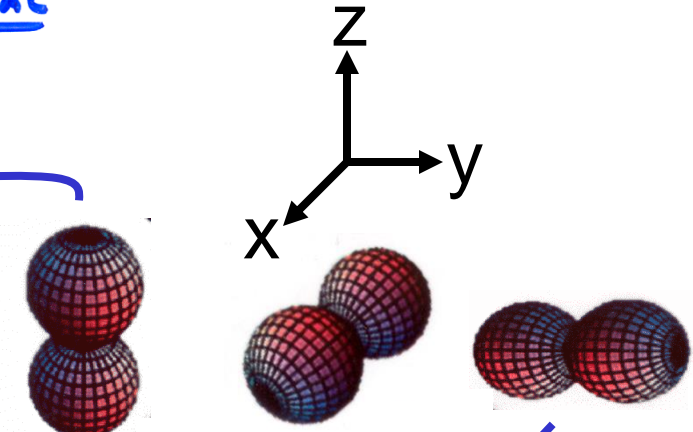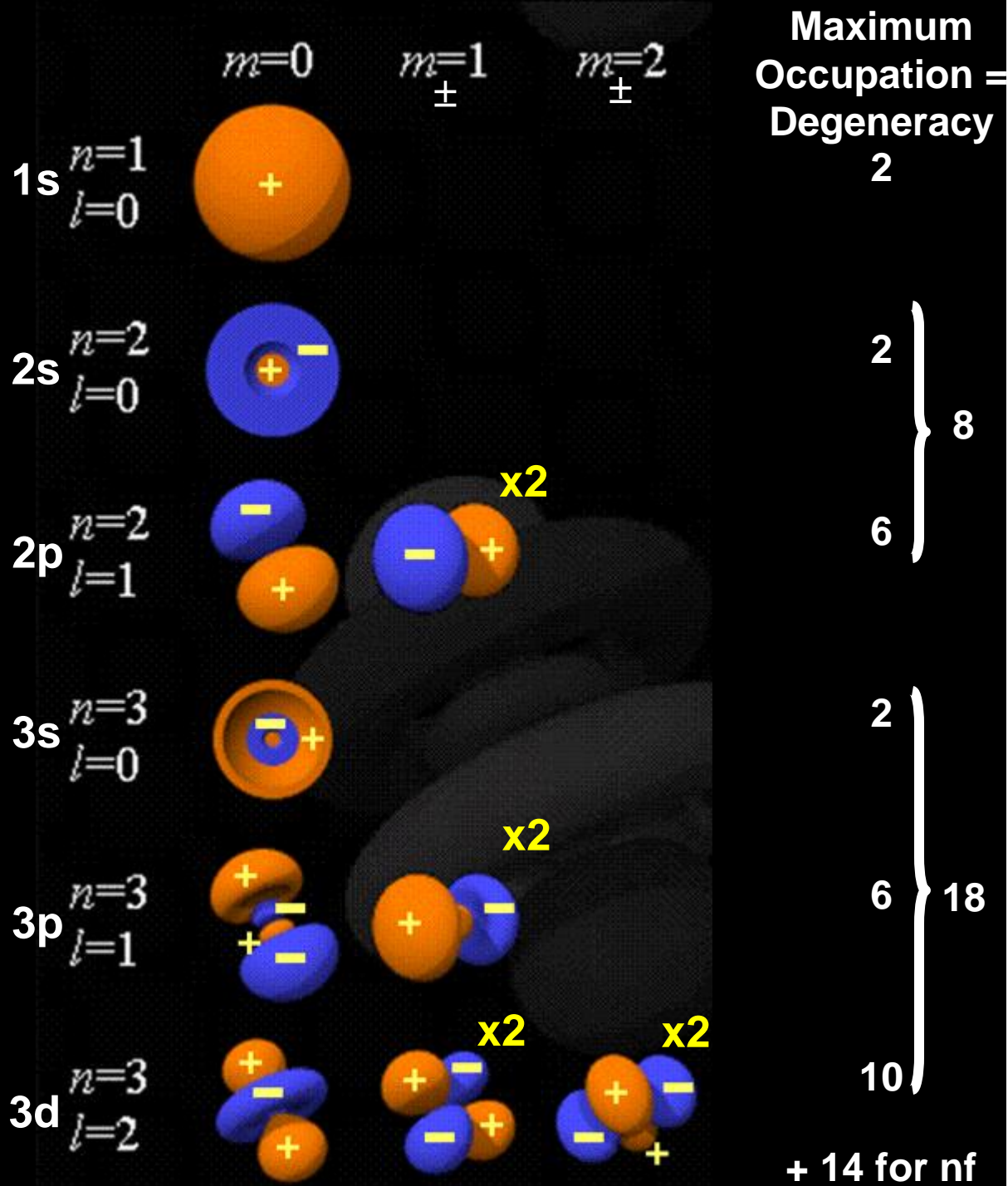
And the same thing for the d orbitals:

e_g

Point at neighbors

Ligand (e.g. O^{-q} repulsive)

z

y

x

Transition Metal (e.g. Mn)

$3z^2-r^2$

t_{2g}

x^2-y^2

z

y

x

yz zx xy

Point between neighbors

e_g and t_{2g} not equivalent in octahedral (cubic) environment

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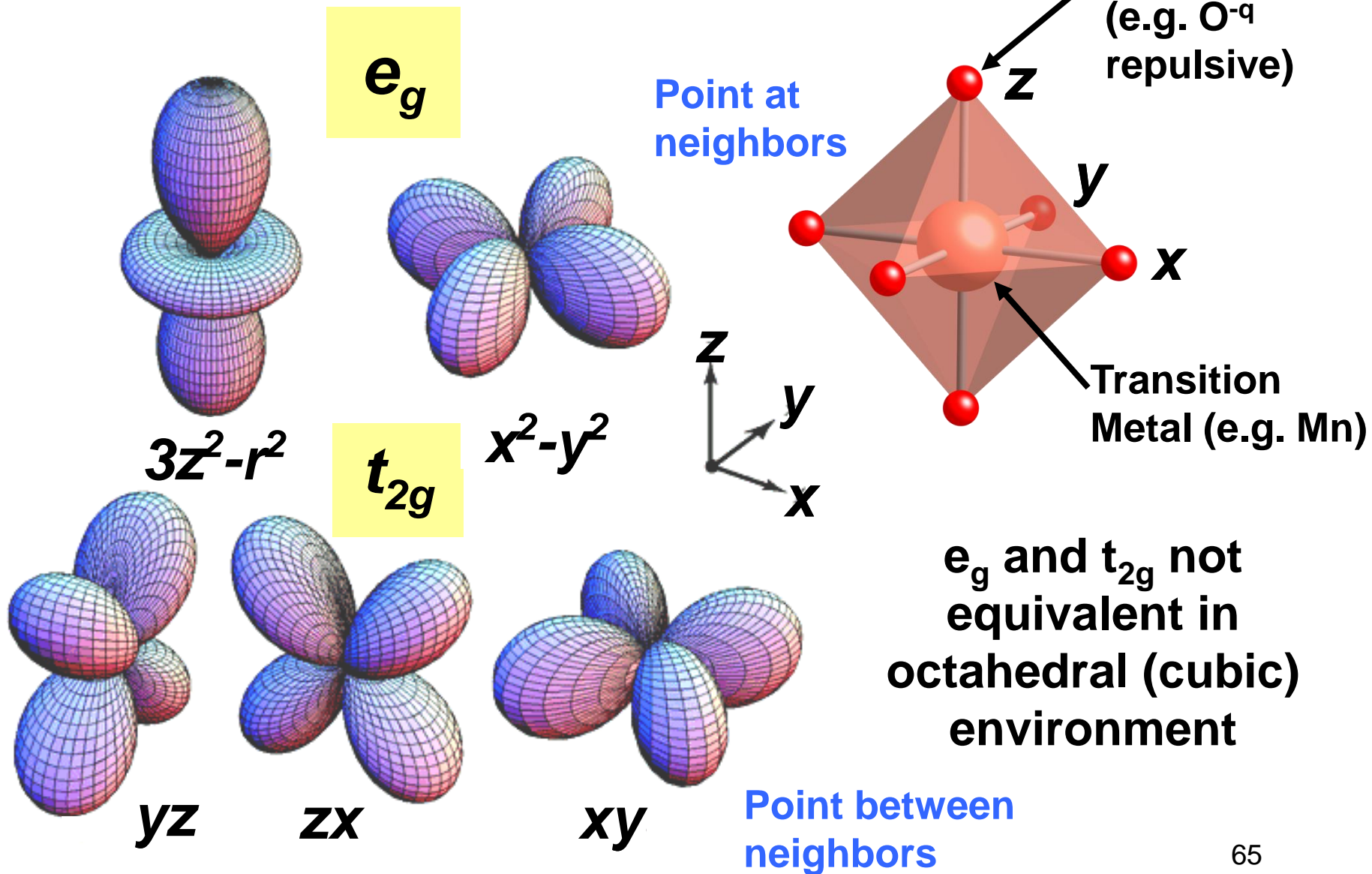
Intraatomic electron screening
in many-electron atoms--a simple model

POINT CHARGE ($\sim e^-$) + SPHERICAL SHELLS
OF e^- CHARGE ($\sim$ ORBITS) AROUND POINT-
CHARGE NUCLEUS $\Rightarrow \sim$ ATOM:

SHELLS OF N_i e^-'s WITH
$N_1 + N_2 + N_3 + N_4 = Z$

NEUTRAL

$+Ze$

e^-

$\sim 10^{-10}$ m

$k_C \equiv 1/(4\pi\varepsilon_0)$
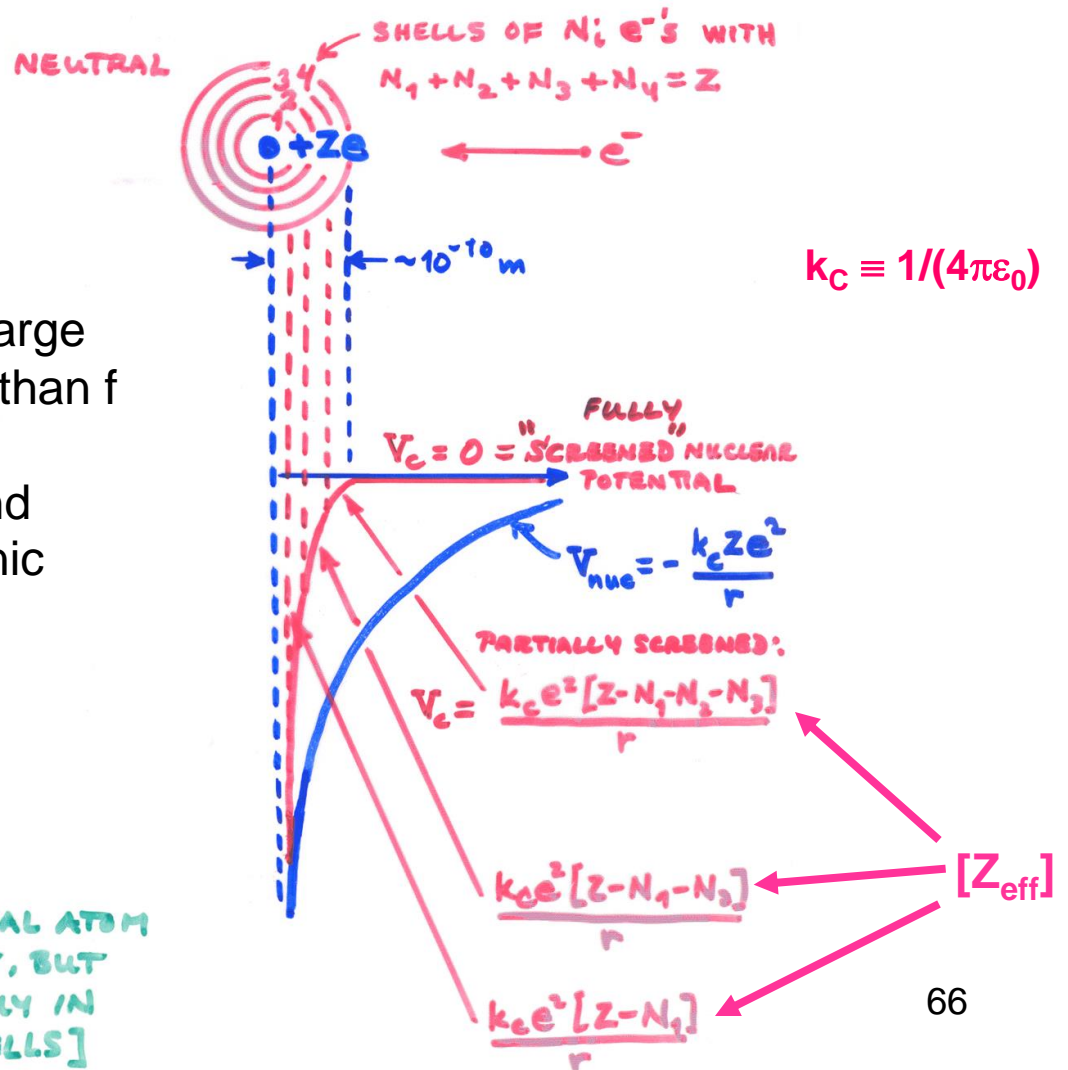
In many-electron atoms:
For a given n, s feels nuclear charge
more than p, more than d, more than f

Yields $Z_{eff}(r)$ in simple picture, and
lifts degeneracy on ℓ in hydrogenic
atom

FULLY
$V_e = 0 = $ "SCREENED" NUCLEAR
POTENTIAL

$V_{nuc} = -\dfrac{k_C Ze^2}{r}$

PARTIALLY SCREENED:

$V_e = \dfrac{k_C e^2 [Z - N_1 - N_2 - N_3]}{r}$

$[Z_{eff}]$

$\dfrac{k_C e^2 [Z - N_1 - N_2]}{r}$

[CHARGE IN REAL ATOM
SMEARED OUT, BUT
STILL ROUGHLY IN
RADIAL SHELLS]

$\dfrac{k_C e^2 [Z - N_1]}{r}$

66

Intraatomic electron screening in many-electron atoms--a self-consistent Q.M. calculation

Plus radial one-electron functions:
$$P_{n\ell}(r) \equiv rR_{n\ell}(r)$$

General useful rule:

(n-ℓ) maxima in radial probability density $P_{n\ell}(r)^2 \equiv r^2 R_{n\ell}(r)^2$

EFFECTIVE POTENTIAL & RADIAL WAVE FUNCTIONS OF ATOMIC COPPER
$$P_{n\ell}(r) \equiv R_{n\ell}(r) \cdot r$$

$P_{4s}(r)$

$E_b(4s) \approx 4.0 \text{ eV}$
$(-\varepsilon_{4s} = 6.5 \text{ eV})$

$P_{3d}(r)$

$E_b(3d) = 9.0 \text{ eV}$
$(-\varepsilon_{3d} = 13.4 \text{ eV})$

VALENCE

CORE

$V_{eff}(r) = \dfrac{Z_{eff}(r)}{r}$ = SCREENED ATOMIC POTENTIAL

$E_b(3p) = 76.2 \text{ eV}$
$P_{3p}(r)$ $(-\varepsilon_{3p} = 90.5 \text{ eV})$

$P_{3s}(r)$

$E_b(3s) = 122.5 \text{ eV}$
$(-\varepsilon_{3s} = 136.3 \text{ eV})$

$E_b(2p) = 942.3 \text{ eV}$
$P_{2p}(r)$ $(-\varepsilon_{2p} = 969.2 \text{ eV})$

Cu^0 $1s^2 2s^2 2p^6 \ldots$
$3s^2 3p^6 3d^{10} 4s^2$
$S = \frac{1}{2}, L = 0$
$\downarrow 2S \downarrow$

$E_b(2s) = 1,097 \text{ eV}$
$P_{2s}(r)$ $(-\varepsilon_{2s} = 942.3 \text{ eV})$

COPPER n-n DISTANCE

$E_b(1s) = 8,979 \text{ eV}$
$P_{1s}(r)$ $(-\varepsilon_{1s} = 8,943 \text{ eV})$

SCREENED POTENTIAL & BINDING ENERGIES (eV, LOG SCALE)

n=3 SHELL
n=2 SHELL

0, -8, -10, -20, -40, -60, -80, -100, -200, -400, -600, -800, -1,000, -2,000, -4,000, -6,000, -8,000, -10,000

RADIUS r (Bohr = 0.529 Å)
0   0.5   1.0   1.5   2.0   2.5   3.0   3.5   4.0   4.5   5.0

OBSERVED (+ CALCULATED) ORDER OF FILLING
ATOMIC LEVELS:

ACTINIDE → f — d — p — s   KNOWN ATOMS STOP

LANTHANIDE → f — d — p — s ——— Rn

TRANSITION SERIES → d — p — s ——— Xe   32

d — p — s ——— Kr   18

d — p — s ——— Ar   18

p — s ——— Ne   8

E ↑   8

s ——— He   2

$n = 1$ 2   3   4   5   6   7
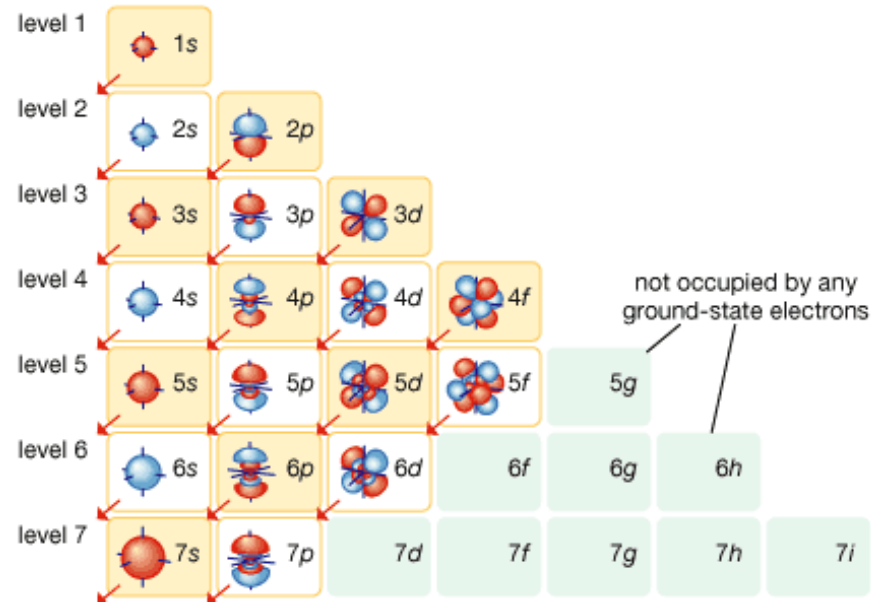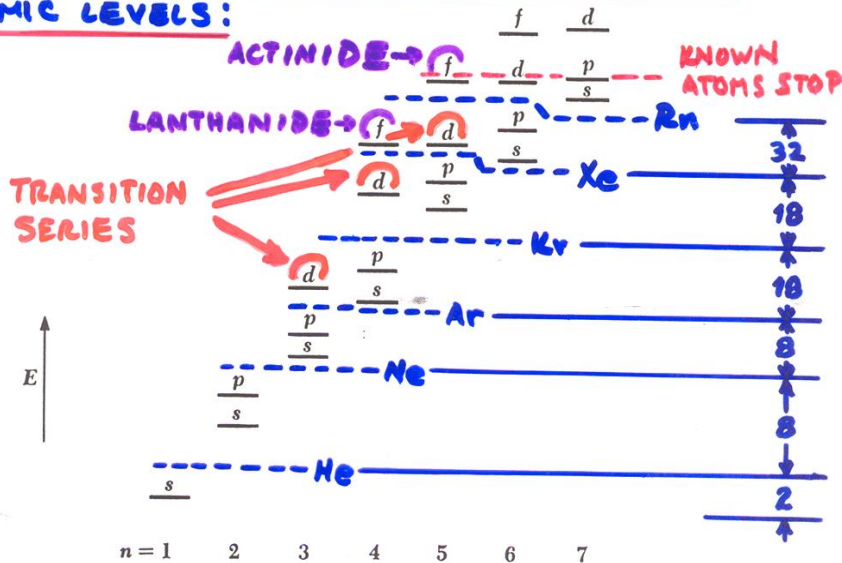
FIGURE 7.13   The sequence of quantum states in an atom. Not to scale.

level 1	1s						
level 2	2s	2p					
level 3	3s	3p	3d				
level 4	4s	4p	4d	4f			not occupied by any ground-state electrons
level 5	5s	5p	5d	5f	5g		
level 6	6s	6p	6d	6f	6g	6h	
level 7	7s	7p	7d	7f	7g	7h	7i

EXAMPLE CONFIGURATIONS:

Z	ATOM	CONFIG.
8	O	$1s^2 2s^2 2p^4$

GROUND-STATE OPEN SHELL COUPLING?

↑↓   ↑   ↑
$2p_{-1}$ $2p_0$ $2p_{+1}$

| 26 | Fe | $1s^2 2s^2 2p^6 3s^2 3p^6$ $3d^6 4s^2$ |

↑↓ ↑ ↑ ↑ ↑
$3d_{-2}$ $3d_{-1}$ $3d_0$ $3d_{+1}$ $3d_{+2}$

⇒ LARGE μ_{3d} + MAGNETISM

| 63 | Eu | $1s^2 2s^2 2p^6 3s^2 3p^6$ $3d^{10} 4s^2 4p^6 4d^{10}$ $4f^7 6s^2$ |

ALSO MAGNETIC!

↑ ↑ ↑ ↑ ↑ ↑ ↑
$4f_{-3}$ $4f_{-2}$ $4f_{-1}$ $4f_0$ $4f_{+1}$ $4f_{+2}$ $4f_{+3}$

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

Slide Set 5   68

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.

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}

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} $6d$ $7s^2$															

$4f1$ ... $4f(5d)$ FILLING ... $4f14$

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}

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

RARE EARTHS

ACTI-NIDES

✱ ☐ = EXCEPTIONS
☐ = EXCEPTIONS
→ d^5 & d^{10} : ½ FILLED / FILLED MORE STABLE

SPIN-ORBIT SPLITTING OF LEVELS:

$\vec{S} \propto \vec{\mu}_S$ e^-

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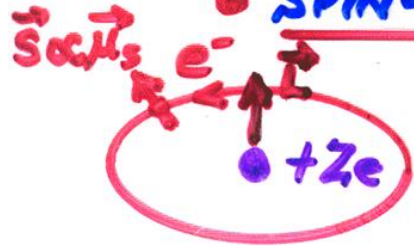
$\Rightarrow$ EFFECTIVE $\vec{B}$ (NUCLEUS AROUND e^-) $\propto \vec{L}$

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

- SPLITS ALL $n\ell$ LEVELS $\quad \longrightarrow n\ell j = \ell + \frac{1}{2} \rule{1cm}{0.4pt} 2\ell + 2$
  $2(2\ell+1) \qquad\qquad \searrow n\ell j = \ell - \frac{1}{2} \rule{1cm}{0.4pt} 2\ell$

- MIXES SPIN & ORBITAL ANGULAR MOM.:

$$\Psi_{n\ell j m_j} = C_1 \Psi_{n\ell, m_j - \frac{1}{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + C_2 \Psi_{n\ell, m_j + \frac{1}{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$m_s = +\frac{1}{2} \qquad\qquad m_s = -\frac{1}{2}$$

$$\uparrow \qquad\qquad\qquad \downarrow$$

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

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SOME SPIN-ORBIT SPLITTINGS: (IN eV)

$2p^6$ — $Z = 13$ (Al)   28 (Ni)   46 (Pd)

$2p^2_{1/2}$ $2p^4_{3/2}$ 0.4   17.8   157.0

$3d^{10}$ — $Z = 30$ (Zn)   48 (Cd)   64 (Gd)

$3d^4_{3/2}$ $3d^6_{5/2}$ 0.1   6.7   32.3

$4f^{14}$ — $Z = 74$ (W)   84 (Pb)   92 (U)

$4f^6_{5/2}$ $4f^8_{7/2}$ 2.2   7.0   64

INCREASE WITH Z FOR A GIVEN LEVEL.

IN GENERAL:

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

NO. e^-

$j = \ell - 1/2$ $\ell + 1/2$

← BINDING ENERGY

KINETIC → ENERGY
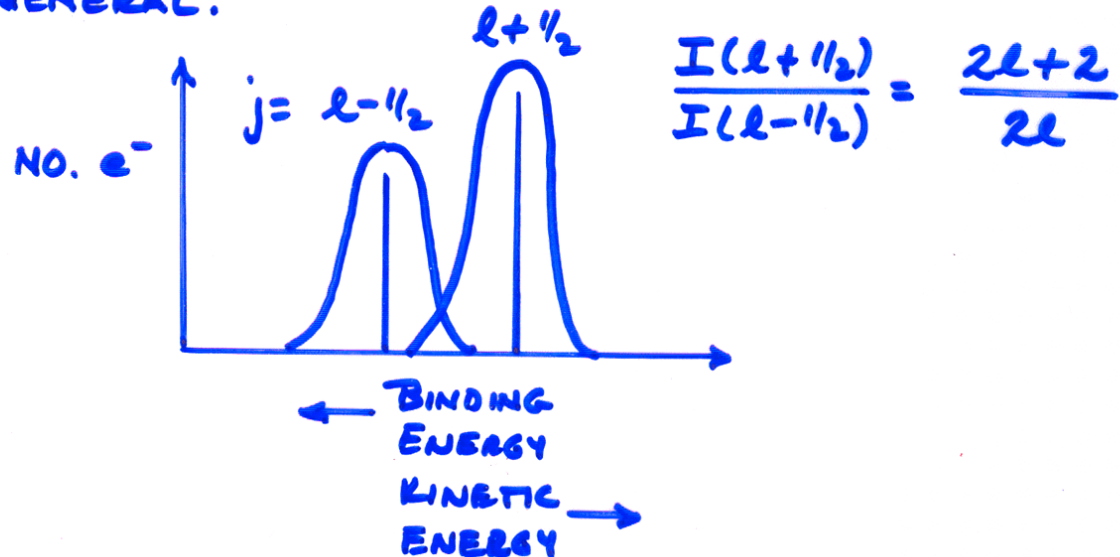
X-Ray Data Booklet--Section 1.1 ELECTRON BINDING ENERGIES

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

Electronic configuration	Element	K 1s	L₁ 2s	L₂ 2p₁/₂	L₃ 2p₃/₂	M₁ 3s	M₂ 3p₁/₂	M₃ 3p₃/₂
$1s$	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

Missing valence B.E.s

Interpolated, extrapolated

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†
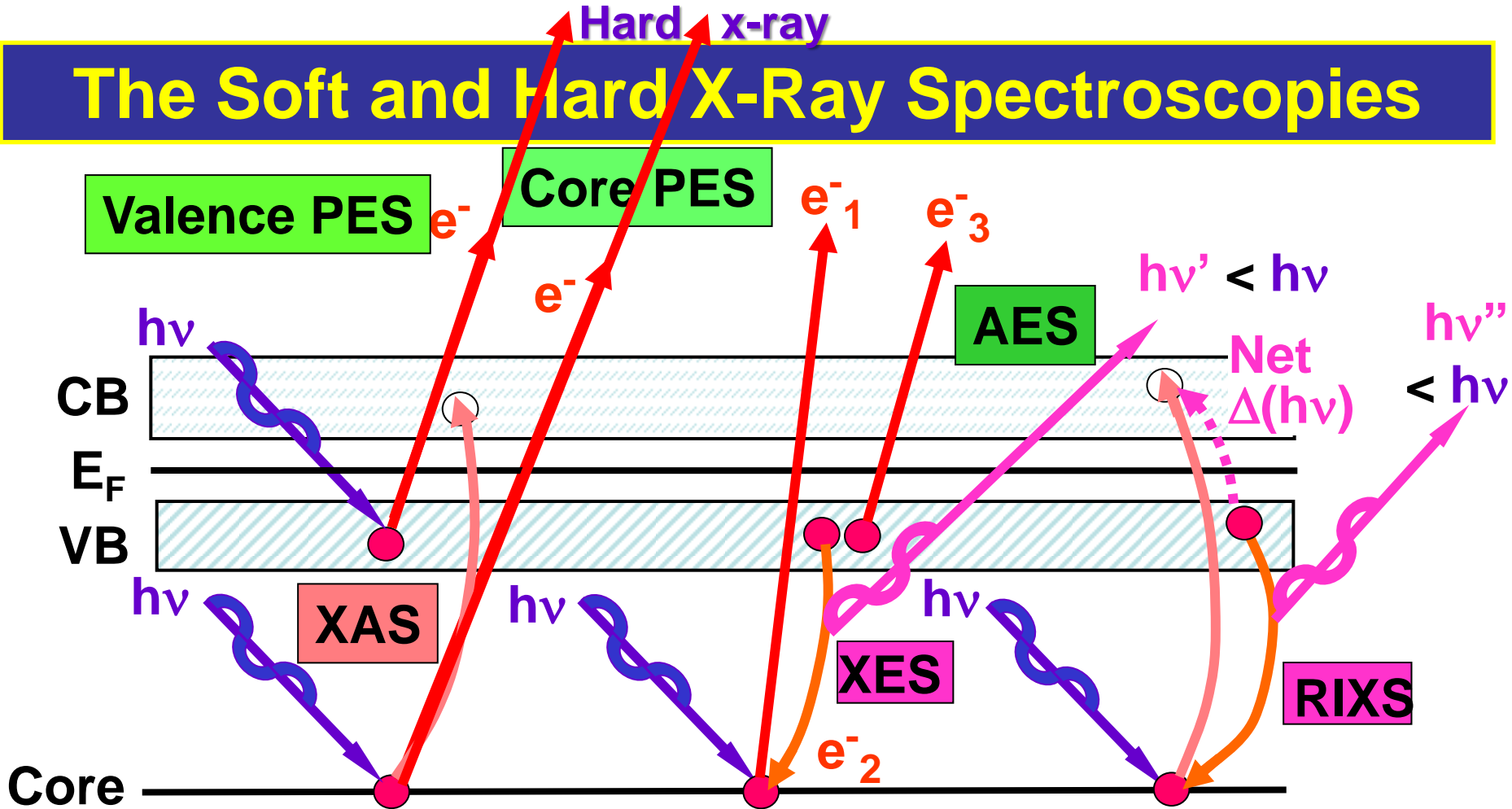
Valence levels

Valence levels

The Soft and Hard X-Ray Spectroscopies

Hard x-ray

Valence PES   **Core PES**

e^- e^-_1 e^-_3

e^-

$h\nu$ **AES**

$h\nu' < h\nu$

CB   **Net** $\Delta(h\nu)$

$h\nu''$

E_F $< h\nu$

VB

$h\nu$ **XAS** $h\nu$ $h\nu$

XES   **RIXS**

e^-_2

Core

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.

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The Soft and Hard X-Ray Spectroscopies

Valence PES   Core PES

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

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- **_Photoelectron spectroscopy/photoemission:_**

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

φ_f*(free)*

hν

– – – –*Vacuum*

φ_i*(bound)*

Core and valence photoemission

$La_{0.6}Sr_{0.4}MnO_3$

The Soft and Hard X-Ray Spectroscopies

Valence PES **Core PES**

CB

E_F

VB

XAS

Core

$h\nu$ e^- e^-

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

- *Photoelectron spectroscopy/photoemission:*

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

$\varphi_f(free)$

hv

$- - - -$ *Vacuum*

$\varphi_i(bound)$

- *Near-edge x-ray absorption:*

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

$- - - - -$ *Vacuum*

$\varphi_f(bound)$

hv

$\varphi_i(bound)$

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

(a) "White lines"

$L_3 = 2p_{3/2}$

$L_2 = 2p_{1/2}$

Fe   Co   Ni   Cu

Absorption Cross Section (Mb) vs Photon Energy (eV)

(b)

White Line Intensity (Mb·eV) vs Number of d-holes

Fe, Co, Ni, Cu

4 :ATOM
3.5 :SOLID

3
2.4

0
0.5

2
1.5

80
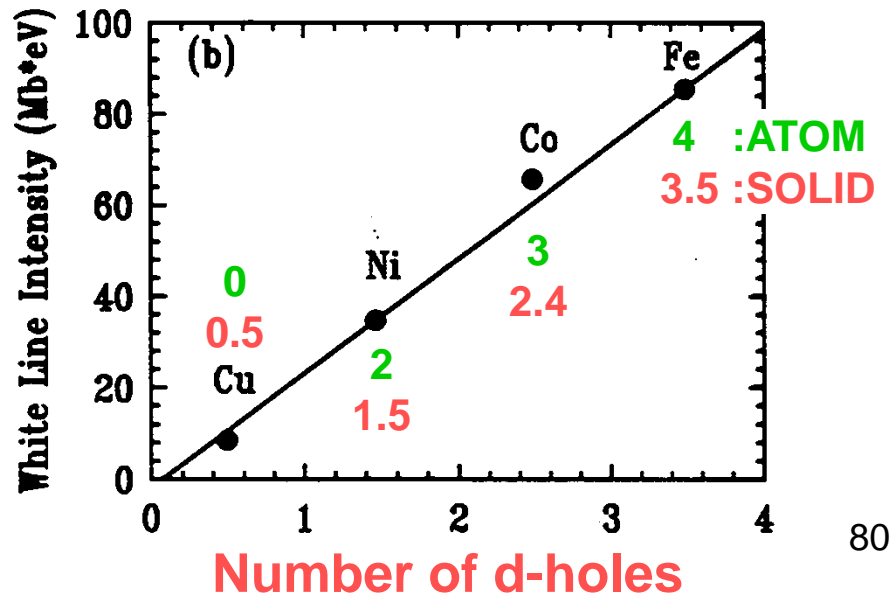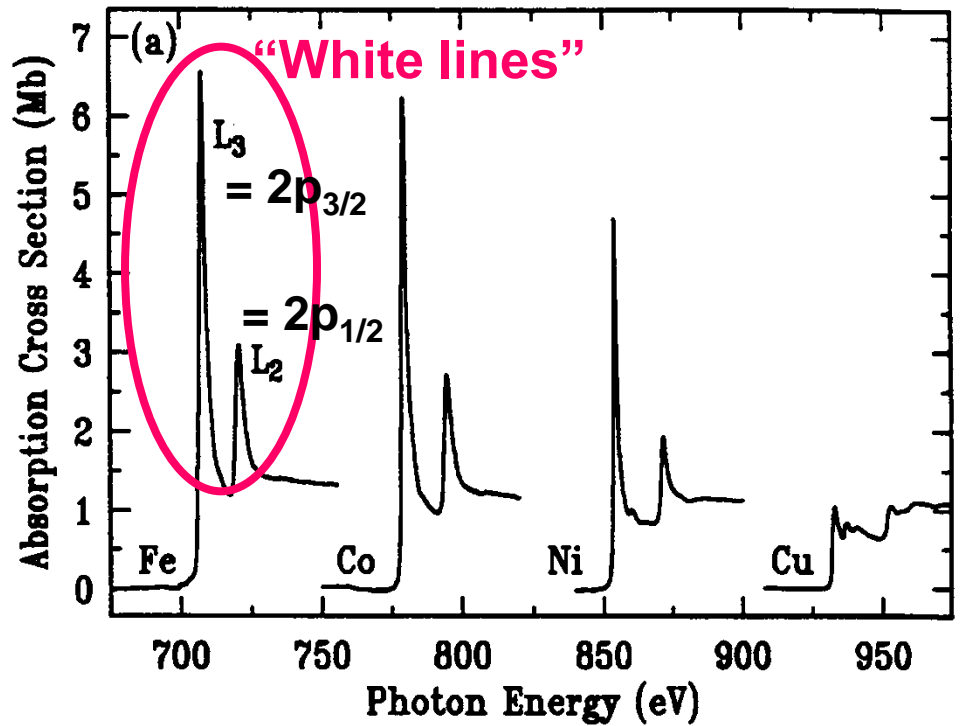
Variation of Near-Edge X-Ray Absorption Fine Structure (NEXAFS) for Different Polymers

C 1s $\mapsto \pi^*_{C=C}$

C 1s $\mapsto \pi^*_{C=O}$

PMMA

PS

Photon Energy (eV)

H. Ade, X-ray Microscopy 99, AIP Conf. Proc. 507, p.197
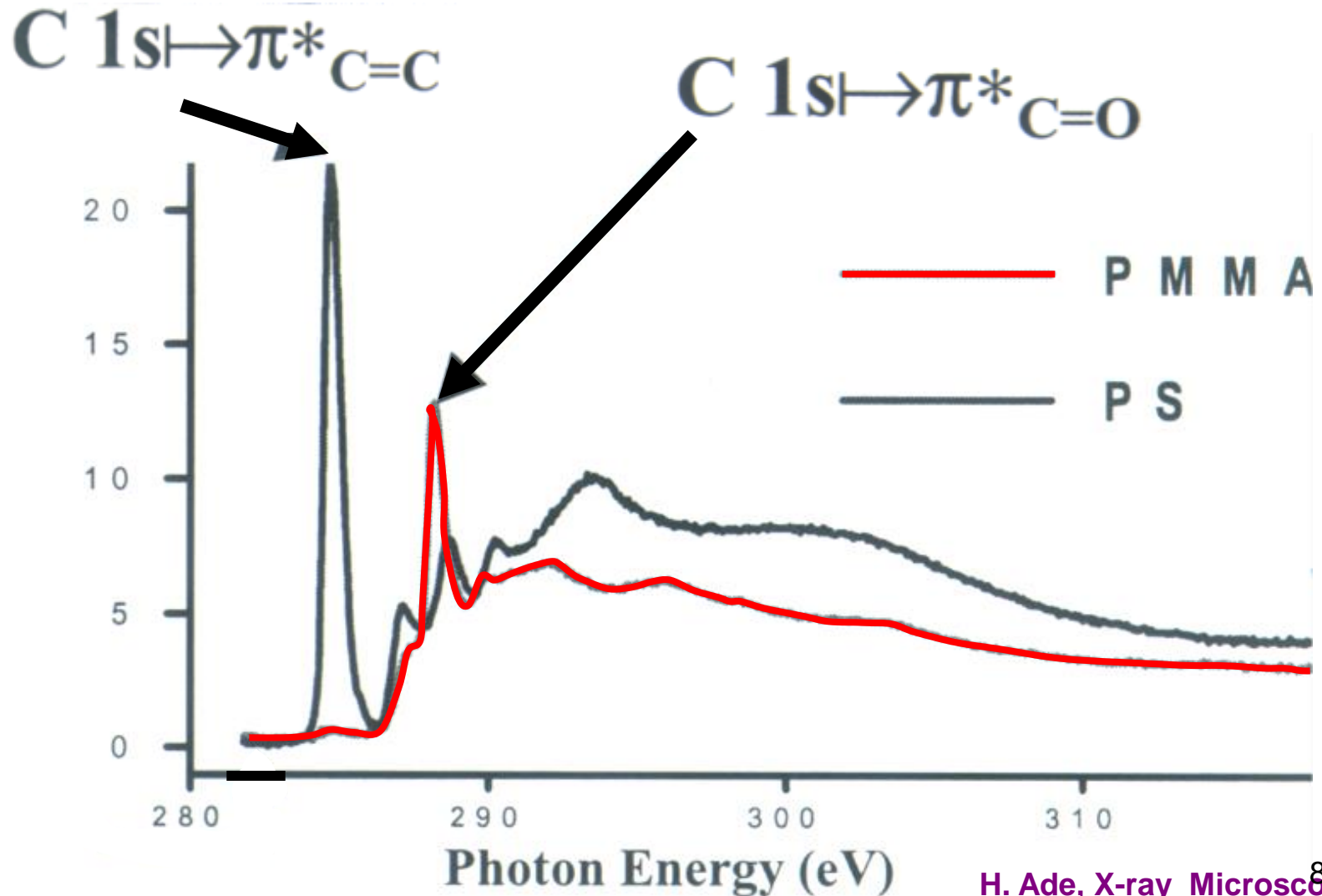
SCANNING TRANSMISSION X-RAY MICROSCOPY OF POLYMER BLEND

PS

PS

PMMA

C 1s $\mapsto \pi^*_{C=C}$

C 1s $\mapsto \pi^*_{C=O}$

PMMA

PS

Photon Energy (eV)
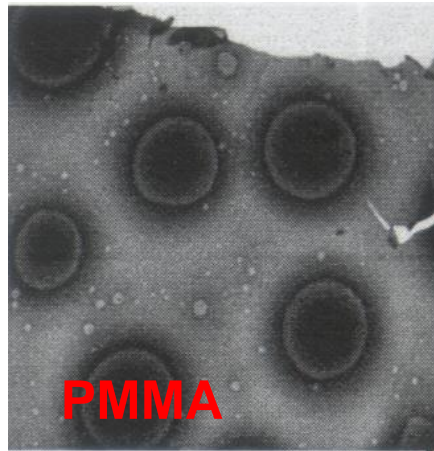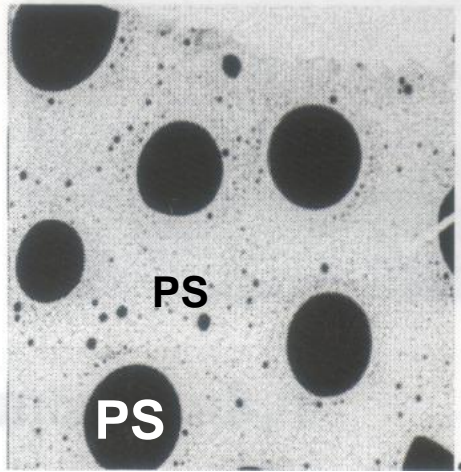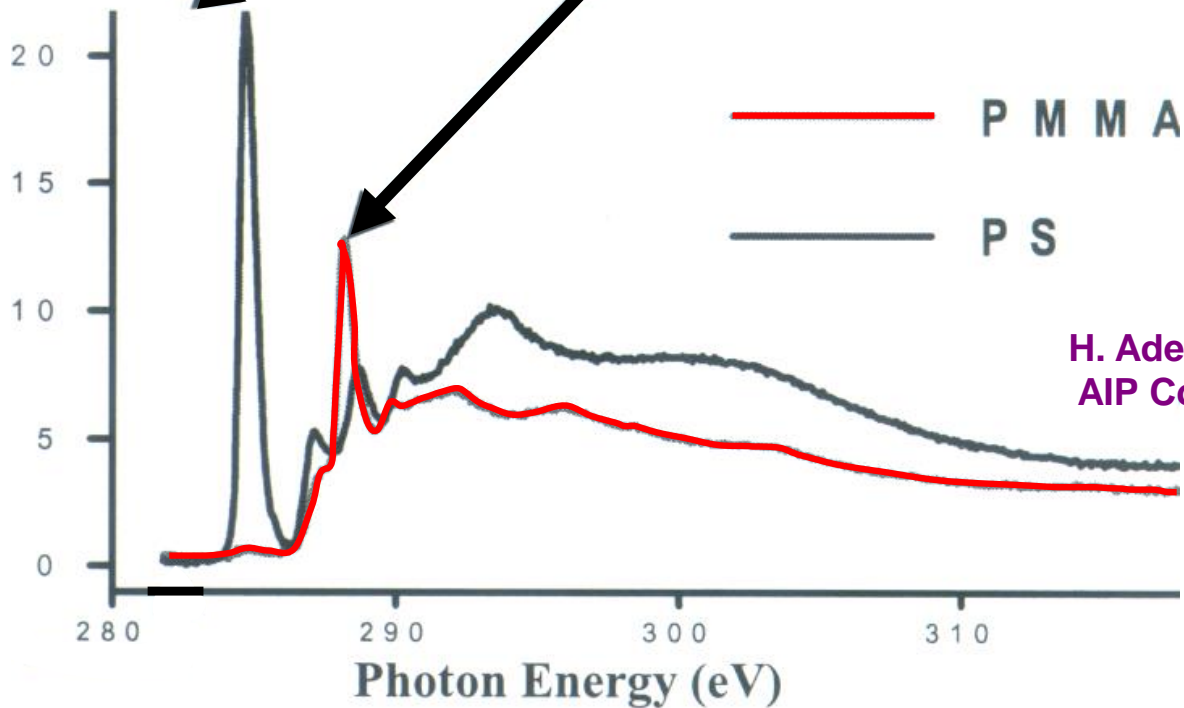
H. Ade, X-ray Microscopy 99, AIP Conf. Proc. 507, p.197

Magnetic Circular Dichroism in X-Ray Absorption (XMCD)
Ferromagnetic cobalt with magnetization along incident light direction
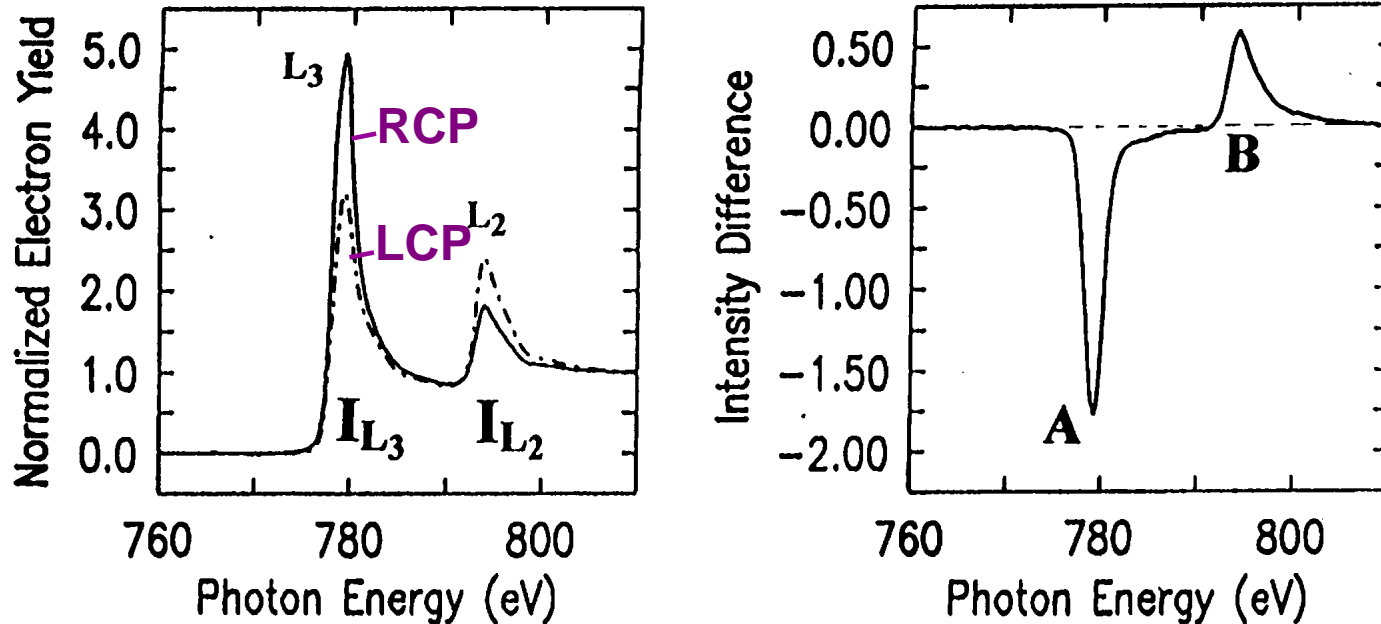
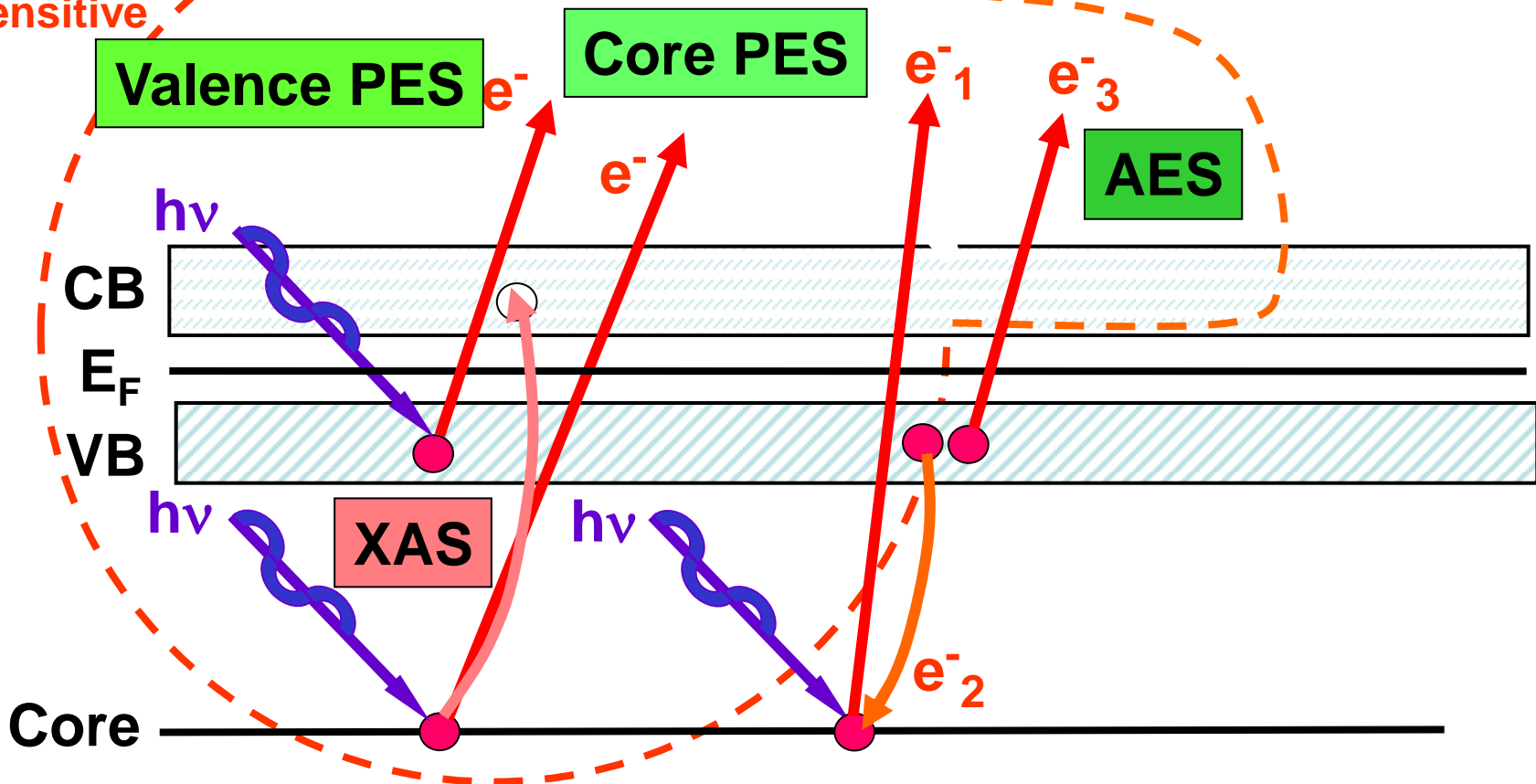Very useful sum rules:

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

Orbital magnetic moment —
$$[A + B]_\alpha = -\frac{3C}{2\mu_B} m_{orbital}^\alpha$$

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$$C = (cons\tan t)\,x\,(radial\ matrix\ element\ squared)\frac{L_{Final}}{3\left[2L_{Final} +1\right]}$$

$\alpha \rightarrow$ component along magnetic field

(a) An electron circles an atomic nucleus, as viewed from the frame of reference of the nucleus. (b) From the electron's frame of reference, the nucleus is circling it. The magnetic field the electron experiences as a result is directed upward from the plane of the paper. Th interaction between the electron's spin magnetic moment and this magnetic field leads to th phenomenon of spin-orbit coupling.

r

v

$\vec{S}$

$-e$

$+Ze$
NUC.

$\vec{B}_L$ INTO PLANE

$i \propto L$
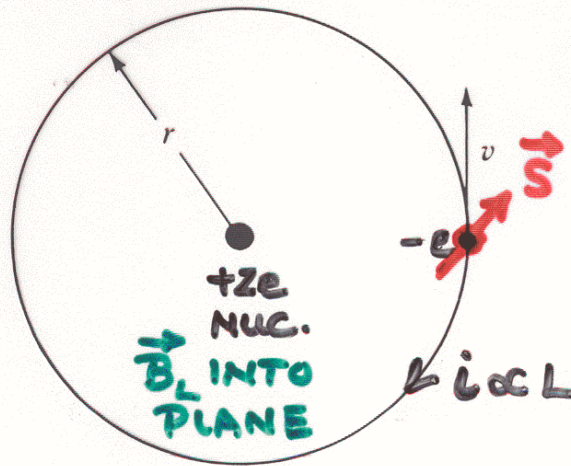
(a)

NUCLEAR

REST FRAME

r

$\vec{S}$

$+Ze$
NUC.

$-e$

$\vec{B}_L$ OUT OF PLANE

v

$i \propto L$

(b)

$B_L = \dfrac{\mu_o i}{2r}$

(CLASS.)
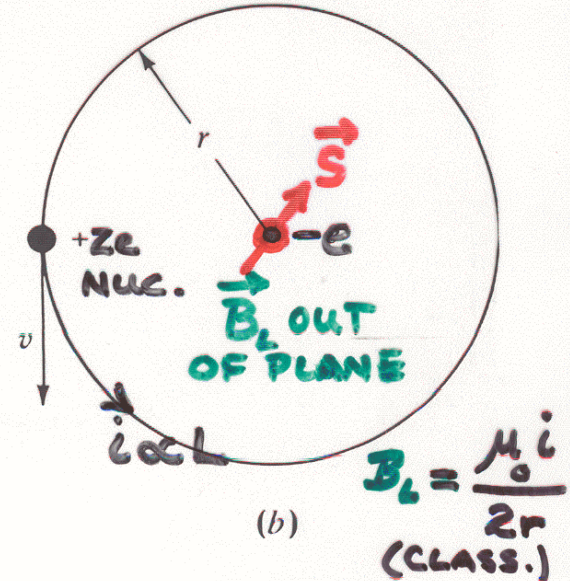
ELECTRON

REST FRAME

$$E_{S-0} = -\vec{\mu}_S \cdot \vec{B}_L$$

$$E_{S-0} \propto + \vec{S} \cdot \vec{L}$$

ADDS TO $\hat{H}$ IN SCHROED. EQN.

$$\hat{H}\Psi = \hat{K}\Psi + V\Psi + \hat{H}_{S-0}\Psi = E\Psi$$

Slide Set 5

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Spin=orbit coupling and a new angular momentum J

$\hat{H}_{s-o}$

E_{s-o} COUPLES $\vec{s}$ AND $\vec{L}$ TO NEW "CONSERVED" $\vec{J}$:

$j = \ell - \frac{1}{2}$ $j = \ell + \frac{1}{2}$

LOWER E   (a)   HIGHER E

Figure 8.12 (a) A vector model for determining the total angular momentum $J = L + S$ of a single electron. (b) The allowed orientations of the total angular momentum J for the states $j = \frac{3}{2}$ and $j = \frac{1}{2}$. Notice that there are now an even number of orientations possible, not the odd number familiar from the space quantization of L alone.

$j = \frac{3}{2}$ $j = \frac{1}{2}$ (b)
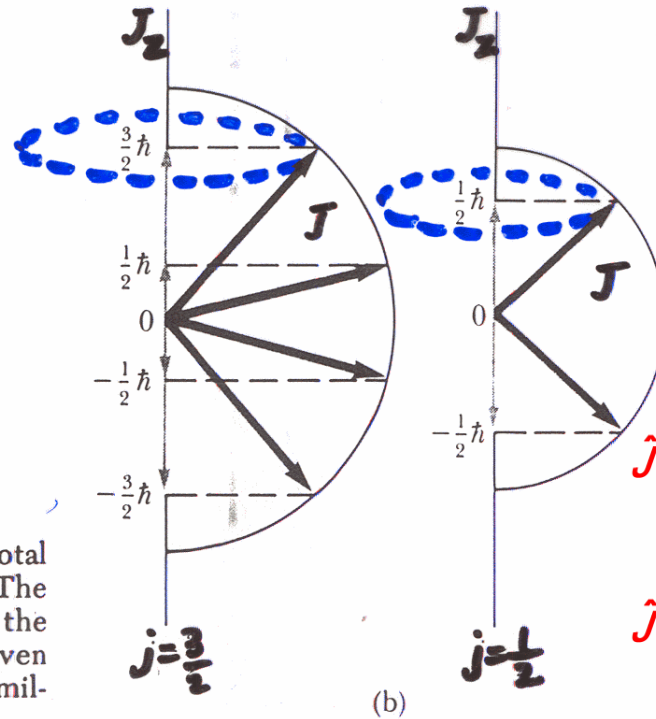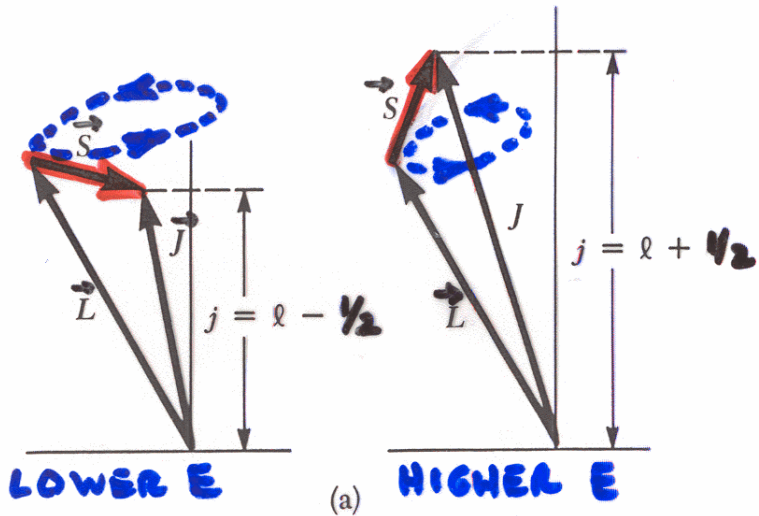
AGAIN PRECESSING VECTOR MODEL

Eigenfunctions:

$$\hat{J}^2 \Psi_{n,\ell,s=1/2,j,m_j} =$$

$$\hbar^2 j(j+1) \Psi_{n,\ell,s=1/2,m_j}$$

$$\hat{J}_z \Psi_{n,\ell,s=1/2,j,m_j} =$$

$$\hbar m_j \Psi_{n,\ell,s=1/2,j,m_j}$$

$$|\vec{J}| = \hbar \sqrt{j(j+1)}$$

WITH: $j = \begin{cases} \ell - \frac{1}{2} \\ \ell + \frac{1}{2} \end{cases}$

$$J_z = \hbar m_j$$

WITH: $m_j = -j, -j+1, \cdots +j$

$\Bigg\} \Rightarrow$

$2j+1$ DEGENERACY

$\Psi_{n,\ell,s=1/2,j,m_j} \Rightarrow$ NOTATION "nL_j"

$\Psi_{n,\ell,s=1/2,j,m_j}$

GOOD QUANTUM NOS. IF E_{s-o} STRONG

Slide Set 5   85

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^-) $\propto \vec{L}$

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

SPLITS ALL $n\ell$ LEVELS $2(2\ell+1)$

$\rightarrow n\ell j = \ell + \frac{1}{2} \longrightarrow 2\ell+2$

$\rightarrow n\ell j = \ell - \frac{1}{2} \longrightarrow 2\ell$

MIXES SPIN & ORBITAL ANGULAR MOM.:

$$\Psi_{n\ell j m_j} = C_1 \Psi_{n\ell, m_j - \frac{1}{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + C_2 \Psi_{n\ell, m_j + \frac{1}{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$m_s = +\frac{1}{2} \qquad\qquad m_s = -\frac{1}{2}$$

$$\uparrow \qquad\qquad\qquad \downarrow$$

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

86

Photoelectrons $E_{kin}s$ (Neglect $E_{kin}d$)

$E'_{kin}s$

$P = -50\% = \dfrac{I_{up} - I_{down}}{I_{up} + I_{down}} = \dfrac{\sqrt{1/3}^2 - 1^2}{\sqrt{1/3}^2 + 1^2} \, x100$

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

3/2

$P = +100\%$

1/2

E_{vacuum}

$m_\ell = 0$

$m_j = m_s = -1/2 \qquad 1/2$

$h\nu$

$\vec{k}_{h\nu}$

① $\cdots + \cdots$ ②   **RCP**

$Y_{1-1}\downarrow$ $\Delta m_\ell = +1$ $Y_{11}\uparrow$: PURE

Degenerate $np_{3/2}$

$\sqrt{\dfrac{1}{3}}Y_{1-1}\uparrow + \sqrt{\dfrac{2}{3}}Y_{10}\downarrow$ | $\sqrt{\dfrac{1}{3}}Y_{11}\downarrow + \sqrt{\dfrac{2}{3}}Y_{10}\uparrow$: MIXED

③

$np_{1/2}$

$-\sqrt{\dfrac{1}{3}}Y_{10}\downarrow + \sqrt{\dfrac{2}{3}}Y_{1-1}\uparrow$ | $\sqrt{\dfrac{1}{3}}Y_{10}\uparrow - \sqrt{\dfrac{2}{3}}Y_{11}\downarrow$: MIXED

$m_j = m_l + m_s = -3/2$: $-1/2$: $1/2$: $3/2$

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

87

$$P = +50\% = \frac{I_{up} - I_{down}}{I_{up} + I_{down}} = \frac{1^2 - \sqrt{1/3}^2}{1^2 + \sqrt{1/3}^2} \times 100$$

$$= \frac{2/3}{4/3} \times 100 = +50\%$$

$$P = -100\%$$

(Neglect E_{kin}d)

E'_{kin} s

$P_{3/2}$

$P_{1/2}$

$m_\ell = 0$

$m_j = m_s = -1/2 \quad 1/2$

E_{vacuum}

hν

$\mathbf{k}_{h\nu}$

① ... + ... ②   LCP

$\Delta m_\ell = -1$

$Y_{1-1}\downarrow$ $Y_{11}\uparrow$: PURE

Degenerate $np_{3/2}$

$\sqrt{\frac{1}{3}} Y_{1-1}\uparrow + \sqrt{\frac{2}{3}} Y_{10}\downarrow$ $\sqrt{\frac{1}{3}} Y_{11}\downarrow + \sqrt{\frac{2}{3}} Y_{10}\uparrow$: MIXED

③   ③'

$np_{1/2}$

$-\sqrt{\frac{1}{3}} Y_{10}\downarrow + \sqrt{\frac{2}{3}} Y_{1-1}\uparrow$ $\sqrt{\frac{1}{3}} Y_{10}\uparrow - \sqrt{\frac{2}{3}} Y_{11}\downarrow$: MIXED

$m_j = m_l + m_s = -3/2 \quad -1/2 \quad 1/2 \quad 3/2$

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

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

W 4f $P = +59\%$ -44%

$4f_{5/2}$ $4f_{7/2}$

P_z ↑ parallel ↓ antipar. $h\nu = 134$ eV

LCP:

RCP:

P_z

$h\nu$ LCP, RCP
[110]   [$\bar{1}$10]
25°
y
e⁻
P_z
Spin detector

Intensity (arb. units)

Binding Energy (eV)

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

Magnetic Circular Dichroism in X-Ray Absorption (XMCD)

$$MCD \propto I_{LCP} - I_{RCP}$$

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—

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

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

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The Soft and Hard X-Ray Spectroscopies

Electron-out: surface sensitive

Valence PES

Core PES

AES

XAS

$h\nu$ ... e^- ... e^-_1 ... e^-_3 ... e^-_2

CB

E_F

VB

Core

PES = photoemission = photoelectron spectroscopy
XAS = x-ray absorption spectroscopy
AES = Auger electron spectroscopy
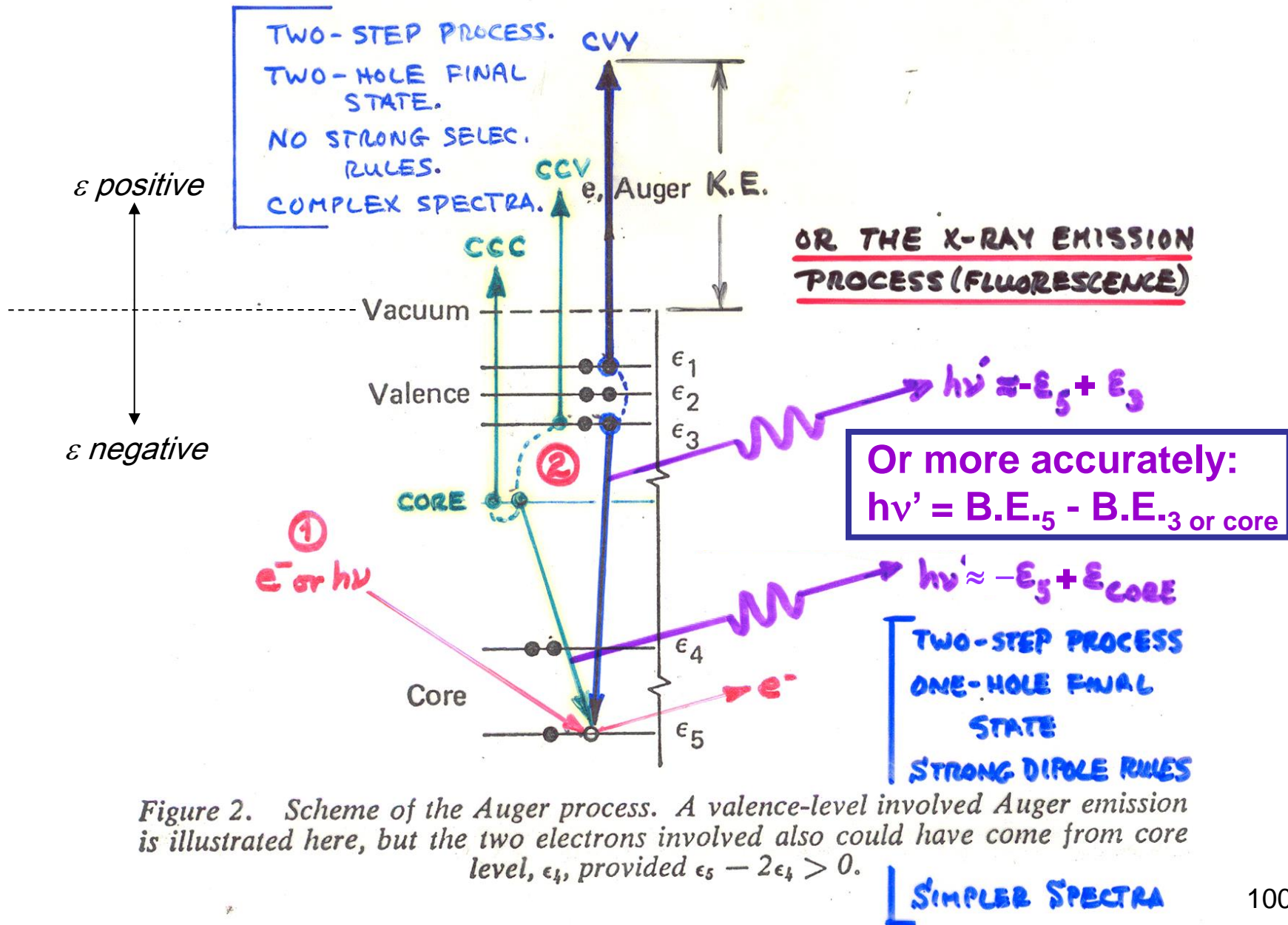XES = x-ray emission spectroscopy
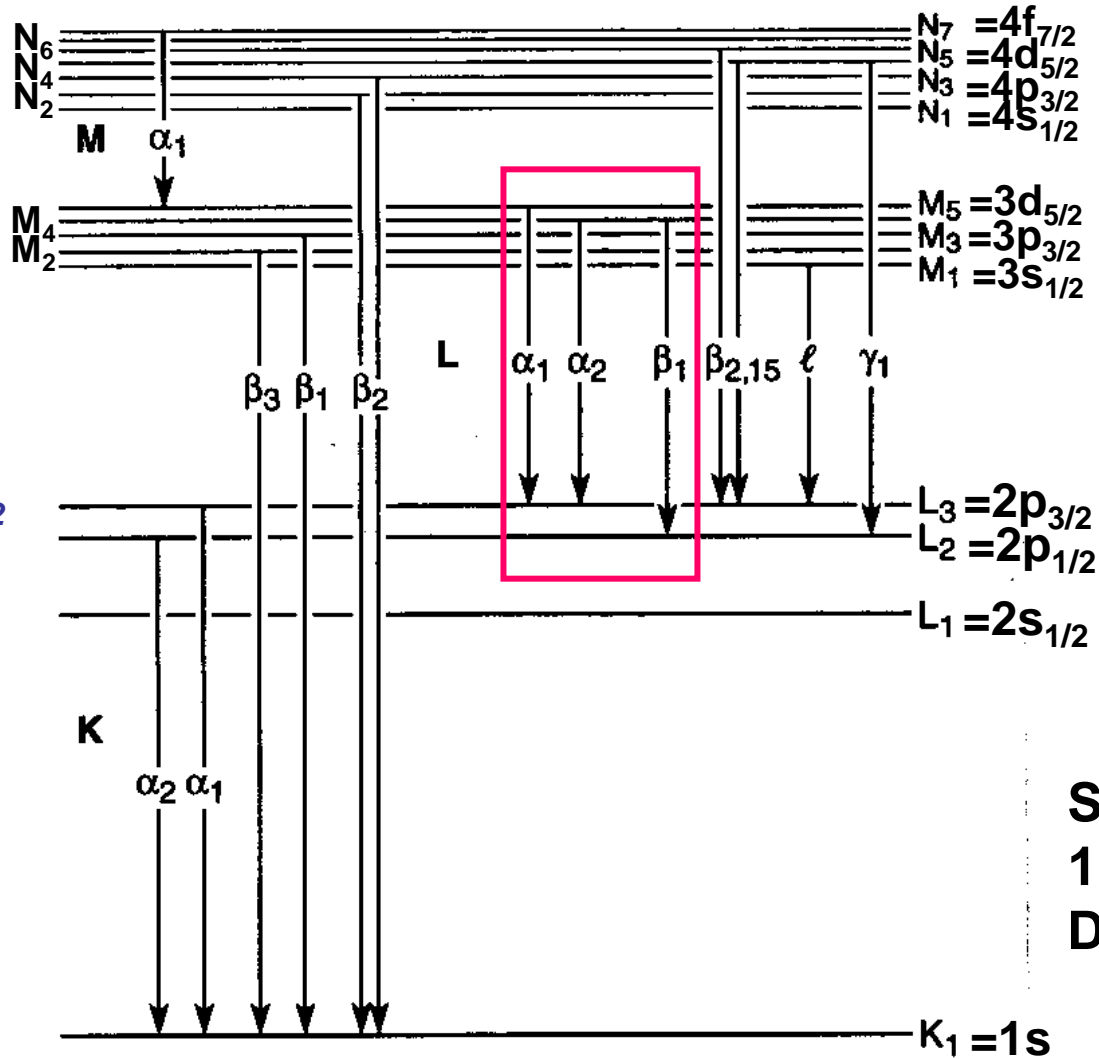REXS/RIXS = resonant elastic/inelastic x-ray scattering

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- *Photoelectron spectroscopy/photoemission:*

φ_f*(free)*

hv

— — — — *Vacuum*

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

φ_i*(bound)*

— — — — *Vacuum*

φ_f*(bound)*

hv

- *Near-edge x-ray absorption:*

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

φ_i*(bound)*

- *Auger electron emission:*

φ_f

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

Vacuum — — — —

φ_3

φ_2

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

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

φ_1

all bound

a complex operator, no simple selection rules

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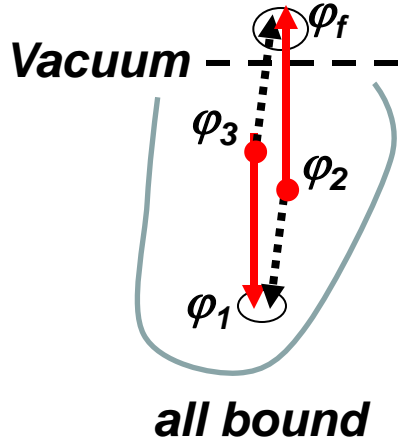
TYPICAL PHOTOELECTRON SPECTRA: OXIDIZED ALUMINUM

$h\nu = 1486.7$ eV

O KLL Auger

Bandgap of Al₂O₃ — Al_2O_3

O1s
C1s
Al2s
Al2p
Val.

NO. ELECTRONS

Counts

← Binding Energy (eV)

900 800 700 600 500 400 300 200 100 0

Kinetic Energy (eV) →

500 600 700 800 900 1000 1100 1200 1300 1400 1500

O 1s

Al 2s, 2p

Al_2O_3
Al
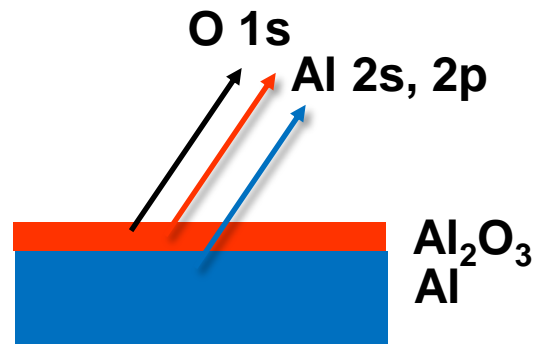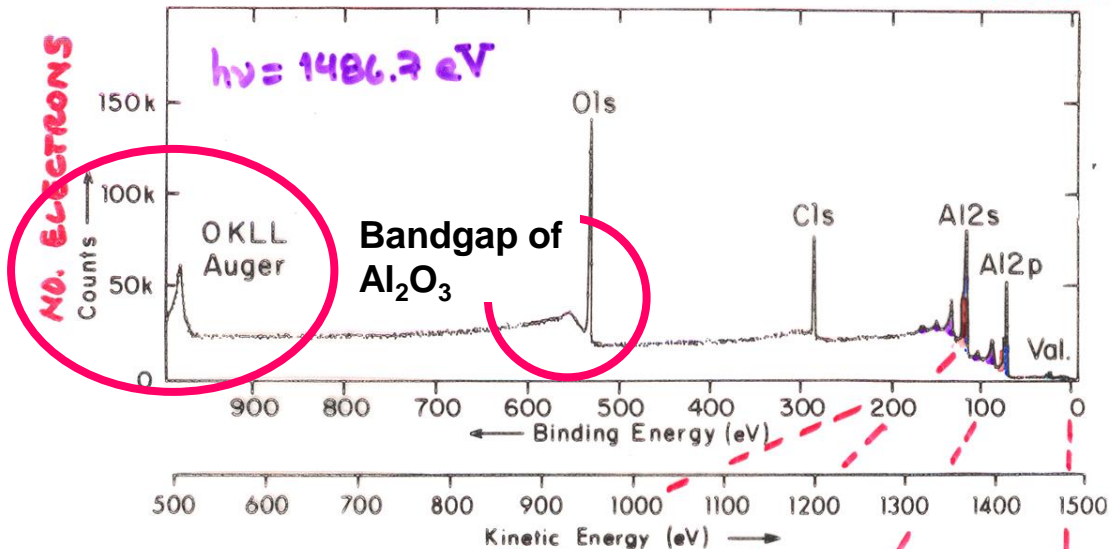
Plasmons:

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

CLEAN ALUMINUM

Al 2s

Plasmon Lines

Al 2p

Plasmon Lines

180   160   140   120   100   80
Binding Energy (eV)

Al2s Metal

CHEMICAL SHIFT

Al2p Metal

INELASTIC Plasmons

Oxide

Valence

Oxide

Plasmons

X10

4   3   2

2

1

INELASTIC BACKGROUND

Counts →

180 160 140 120 100 80 60 40 20 0 ≈ E_F
← Binding Energy (eV)

1320   1360   1400   1440   1480
Kinetic Energy (eV) →
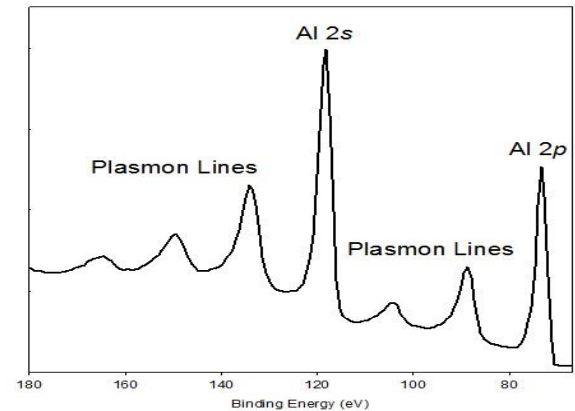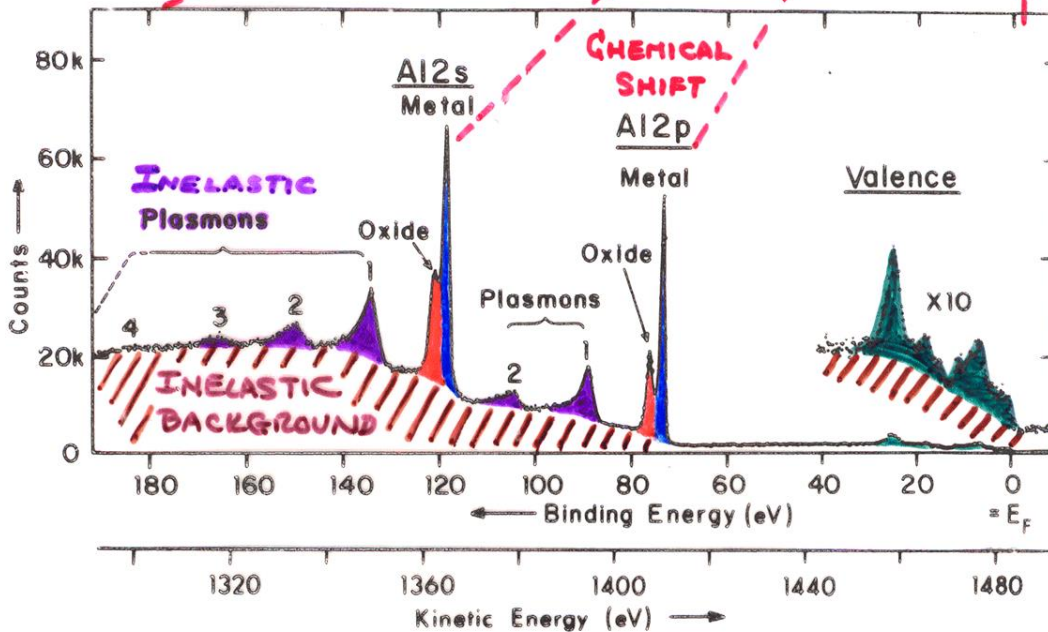
"Basic Concepts of XPS"
Figure 1

THE AUGER PROCESS
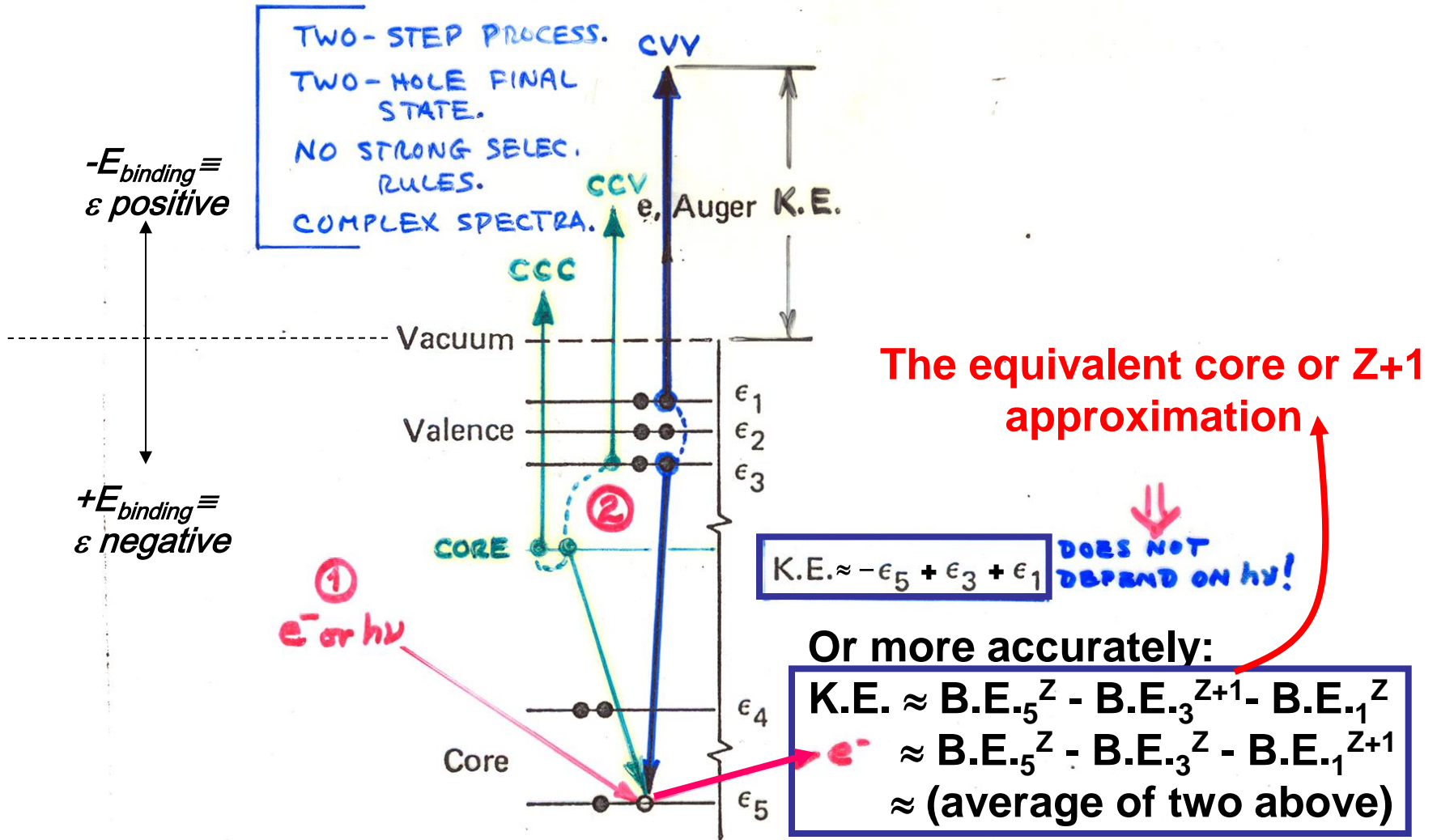
TWO-STEP PROCESS.
TWO-HOLE FINAL STATE.
NO STRONG SELEC. RULES.
COMPLEX SPECTRA.

$-E_{binding} \equiv \varepsilon$ positive

$+E_{binding} \equiv \varepsilon$ negative

CVV

CCV

CCC

e, Auger K.E.

Vacuum

Valence

ε_1
ε_2
ε_3

CORE

②

①

e^- or $h\nu$

ε_4

Core

ε_5

The equivalent core or Z+1 approximation

$$K.E. \approx -\varepsilon_5 + \varepsilon_3 + \varepsilon_1$$ DOES NOT DEPEND ON $h\nu$!

Or more accurately:
$$K.E. \approx B.E._{-5}{}^Z - B.E._{-3}{}^{Z+1} - B.E._{-1}{}^Z$$
$$\approx B.E._{-5}{}^Z - B.E._{-3}{}^Z - B.E._{-1}{}^{Z+1}$$
$$\approx \text{(average of two above)}$$

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, ε_4, provided $\varepsilon_5 - 2\varepsilon_4 > 0$.

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The equivalent core or Z+1 approximation

O: Z = 8
O core = O $1s^2$ = O^{6+}

$1s^2 = -2e$
$\bullet +8e$
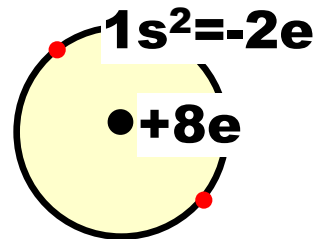
Assume:
O^{6+*} core with
1s hole = O^{7+} =

$1s^1 = -1e$
$\bullet +8e$ $\approx$ $1s^2 = -2e$
$\bullet +9e$

= F^{7+} core

F: Z = 9

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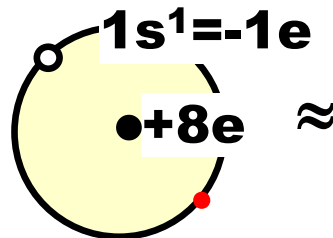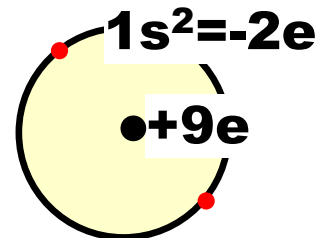
PRINCIPAL AUGER ELECTRON ENERGIES

Dots indicate the electron energies of the principal Auger peaks for each element. Large dots represent predominant peaks for each element.

Au N$_{6,7}$O$_{4,5}$O$_{4,5}$

Kinetic Energy (eV)

MNN

Ag MNN

M$_4$N$_{4.5}$V
992

M$_4$N$_4$V
899.2

M$_5$VV
901.5

M$_4$VV
895.5

1253.6 - Auger Energy (eV)

LMM

L$_3$M$_{23}$M$_{23}$
544

L$_3$M$_{23}$V
476.9

472.5

L$_3$VV
401.2

L$_2$VV
390.0

Ni LMM

1253.6 - Auger Energy (eV)

KLL

E$_{kin}$ = 508.3

748.3

766.7

O KLL

1253.6 - Auger Energy (eV)

ATOMIC NUMBER (y-axis)

ELECTRON ENERGY (eV) (x-axis)

Atomic number axis labels: U Pa Th Ac Ra Fr Rn At Po Bi Pb Tl Hg Au Pt Ir Os Re W Ta Hf Lu Yb Tm Er Ho Dy Tb Gd Eu Sm Pm Nd Pr Ce La Ba Cs Xe I Te Sb Sn In Cd Ag Pd Rh Ru Tc Mo Nb Zr Y Sr Rb Kr Br Se As Ge Ga Zn Cu Ni Co Fe Mn Cr V Ti Sc Ca K Ar Cl S P Si Al Mg Na Ne F O N C B Be Li H

2p$_{3/2}$ **L$_3$**

2p$_{1/2}$ **L$_2$**

2s$_{1/2}$ **L$_1$**

1s$_{1/2}$ **K**

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

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The energies are given in eV relative to the <u>vacuum level</u> for the rare gases and for H_2, N_2, O_2, F_2, and Cl_2; relative to the <u>Fermi level</u> for the metals; and relative to the <u>top of the valence bands</u> 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†

Missing valence B.E.s

Valence levels

Interpolated, extrapolated

Valence levels

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The Soft and Hard X-Ray Spectroscopies

Electron-out: surface sensitive

Valence PES

Core PES

e⁻₁   e⁻₃

hν'

AES

hν

CB
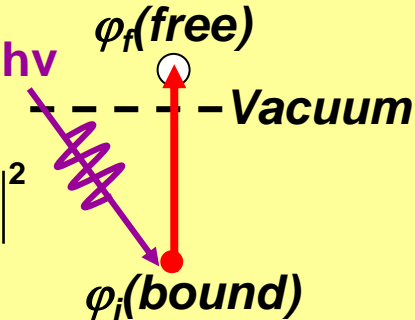
E_F

VB

hν   **XAS**   hν

XES

Photon-out: "bulk", deeper interfaces

e⁻₂

Core

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

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THE AUGER PROCESS

TWO-STEP PROCESS.
TWO-HOLE FINAL STATE.
NO STRONG SELEC. RULES.
COMPLEX SPECTRA.

CVV

CCV e, Auger K.E.

CCC

ε positive

ε negative

OR THE X-RAY EMISSION PROCESS (FLUORESCENCE)

Vacuum

Valence

ϵ_1
ϵ_2
ϵ_3

②

CORE

①

e^- or $h\nu$

$h\nu' \approx -\epsilon_5 + \epsilon_3$

Or more accurately:
$h\nu' = B.E._{-5} - B.E._{-3 \text{ or core}}$

$h\nu' \approx -\epsilon_5 + \epsilon_{CORE}$

ϵ_4

Core

$\rightarrow e^-$

ϵ_5

TWO-STEP PROCESS
ONE-HOLE FINAL STATE
STRONG DIPOLE RULES

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, ϵ_4, provided $\epsilon_5 - 2\epsilon_4 > 0$.

SIMPLER SPECTRA

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

In general:

$$nl \begin{cases} \text{Spin-} & nl_{j=l+1/2} \\ \text{orbit} & nl_{j=l-1/2} \end{cases}$$

$$\Delta j = 0, \pm 1$$

See Section 1.2 in "X-Ray Data Booklet"

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

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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 (649.9† − 638.7†, Mn row)

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 (637.4 − 648.8, Mn row)

See Tables 1.1 and 1.2 in X-Ray Data Booklet

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- **_Photoelectron spectroscopy/photoemission:_**

$\varphi_f(free)$

$h\nu$ — — — — — —_Vacuum_

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

$\varphi_i(bound)$

— — — — — — _Vacuum_

$\varphi_f(bound)$

$h\nu$

- **_Near-edge x-ray absorption:_**

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

$\varphi_i(bound)$
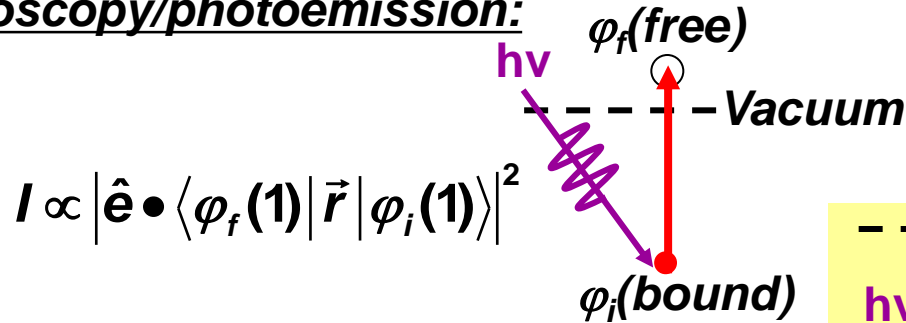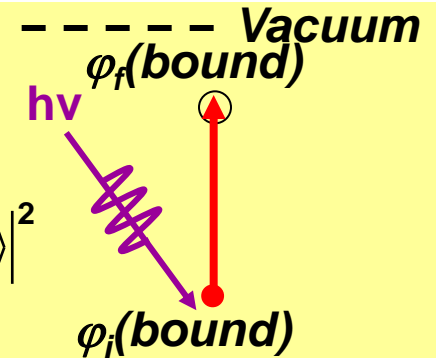
- **_Auger electron emission:_**

Direct   **Exchange**

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

$\varphi_f(free)$

Vacuum — — — — —

φ_3

φ_2

φ_1

- **_X-ray emission:_**

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

— — — — — _Vacuum_

$\varphi_i(bound)$

$h\nu'$

$\varphi_f(bound)$

all bound

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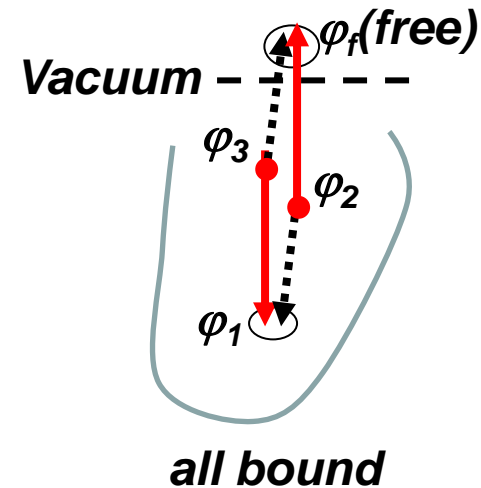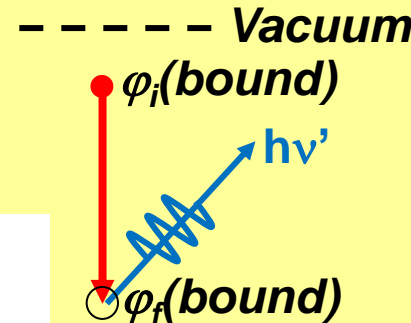
1.3 FLUORESCENCE YIELDS FOR K AND L SHELLS

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 $\equiv$ FY

FY = probability of radiative decay $\rightarrow$ x-ray emission)

1 - FY = probability of non-radiative decay $\rightarrow$ Auger electron emission
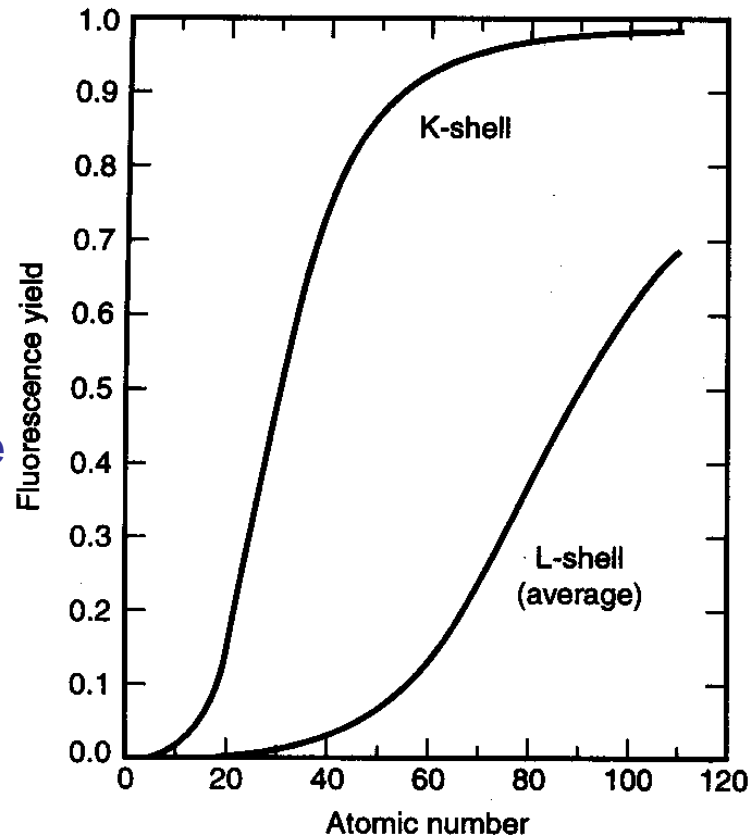
Fig. 1-2. Fluorescence yields for K and L shells fo 110. The plotted curve for the L shell rep average of L_1, L_2, and L_3 effective yields.

Many electron effects and satellites in x-ray emission

$2p \rightarrow 1s$

1   2   3   4
HOLE   HOLE   HOLE   HOLE!

K   KL KL^2 KL^3 (KL^4)

$\alpha_{1,2} = 1,253.6 \text{ eV}$

$\approx E_b(\text{Mg 1s}) - E_b(\text{Mg } 2p_{1/2,3/2})$
$= 1303.0 - 49.7 = 1253.3 \text{ eV}$

α_3
α_4
α'

VALENCE $3p \rightarrow 1s$
1 HOLE

$\alpha_5 \; \alpha_6$
$\alpha_8 \; \alpha_7$
β

$\alpha_{11} \; \alpha_{10}$
$\alpha_{13} \; \alpha_{14}$

R_e
$R_{h\nu}$

$3p_{1/2,3/2}$

$K\beta$

$3s_{1/2}$

$1s^1(2s2p)^6$ $1s^1(2s2p)^5$ $1s^1(2s2p)^4$ $1s^1(2s2p)^3$ $1s^1(2s2p)^6$

$2p_{3/2}$
$2p_{1/2}$

$2s_{1/2}$

$K\alpha$

$1s_{1/2}$
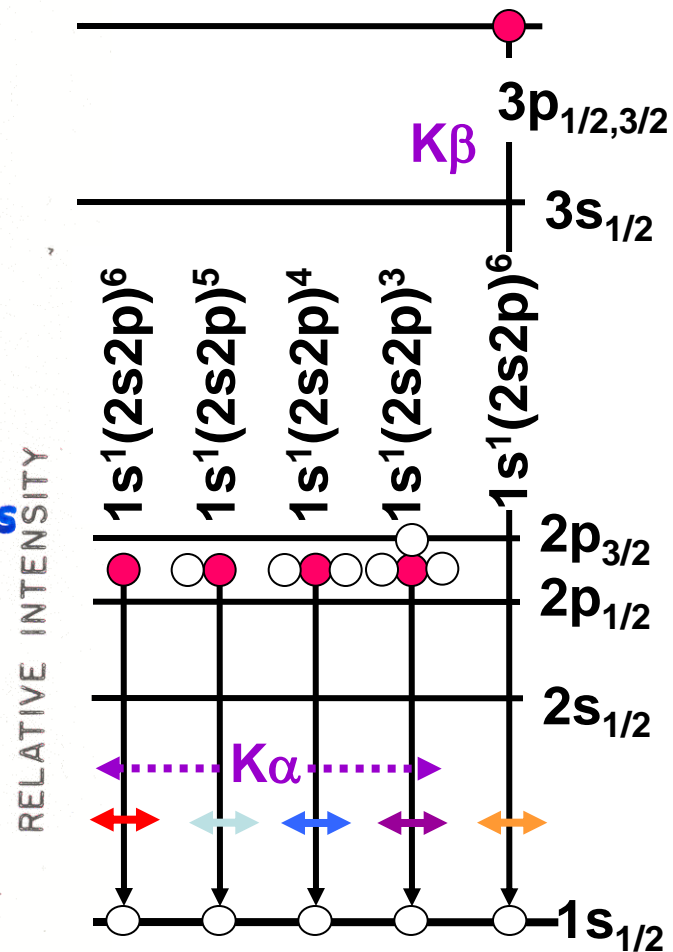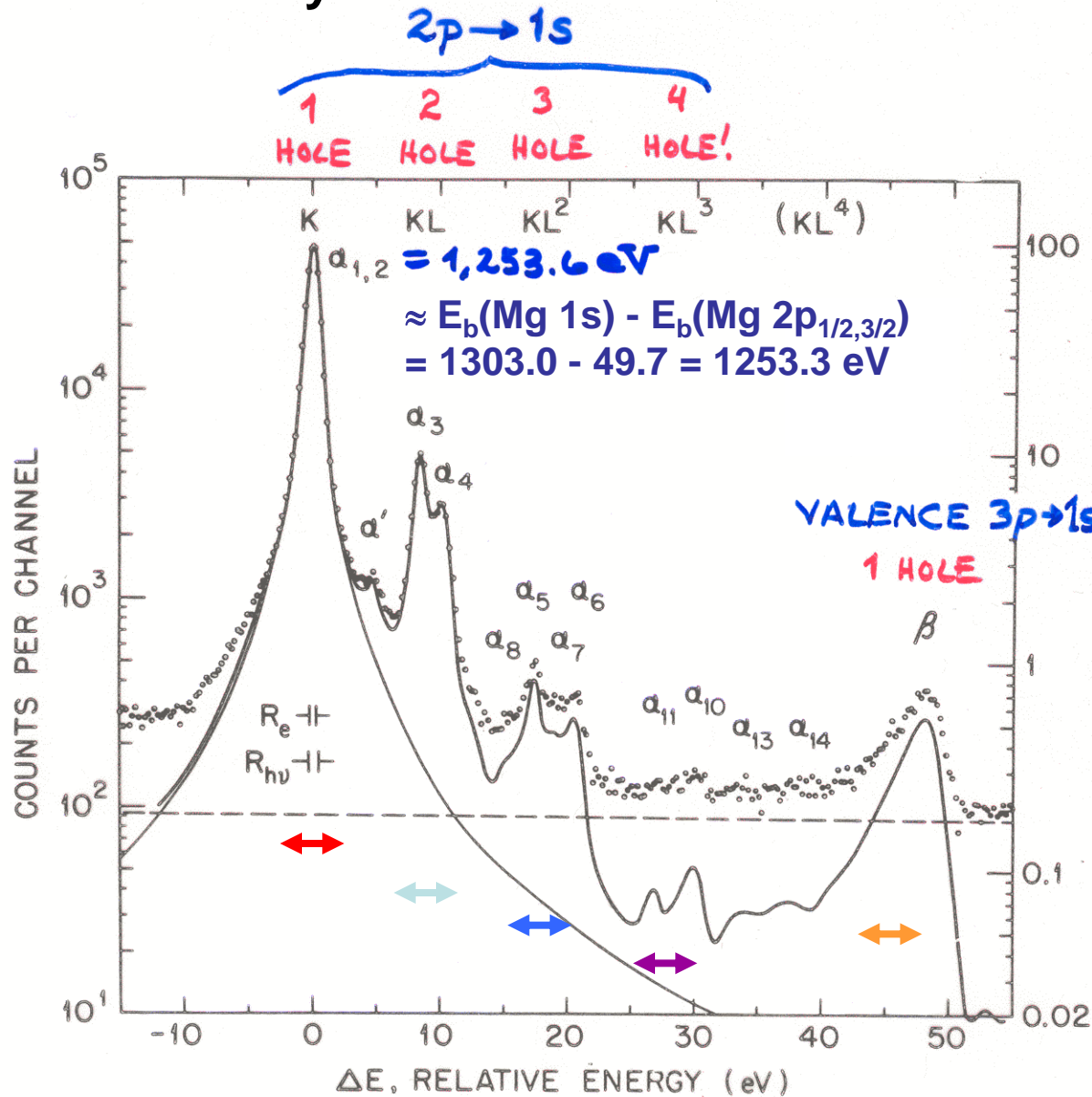
Mg K series of x-rays:
atomic no. = 12
Fluorescence Yield ≈ 0.03

A STANDARD LABORATORY X-RAY SOURCE

The Soft and Hard X-Ray Spectroscopies

Electron-out: surface sensitive

Photon-out: "bulk", deeper interfaces

Valence PES

Core PES

AES

REXS

XAS

XES

RIX

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

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● **Non-resonant photoemission:**

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

hv

$\varphi_f(free)$

$-\ -\ -\ -\ -Vacuum$

$\varphi_i(bound)$

● **Resonant photoemission:**

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

$$\times \delta(hv - (E_m - E_1))$$

Direct
φ_f

Vacuum $-\ -\ -\ -\ -$

Resonant
φ_m

φ_i

φ_1

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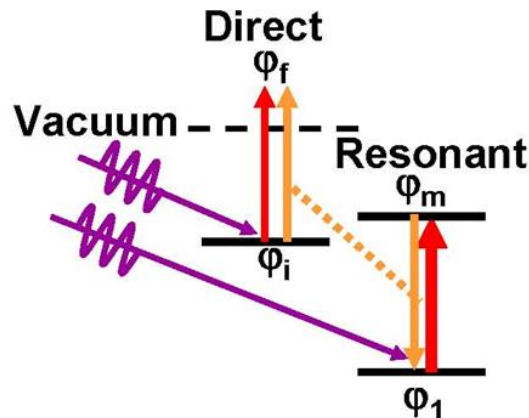
Single-atom resonant photoemission:

Ex. – Mn atom: Mn3d emission, resonance with Mn3p
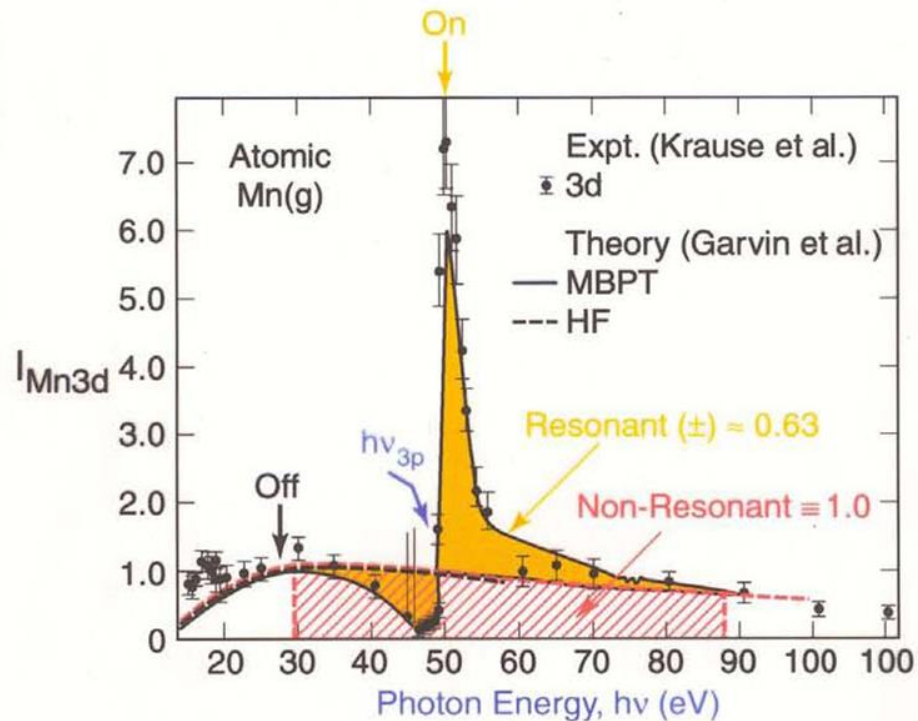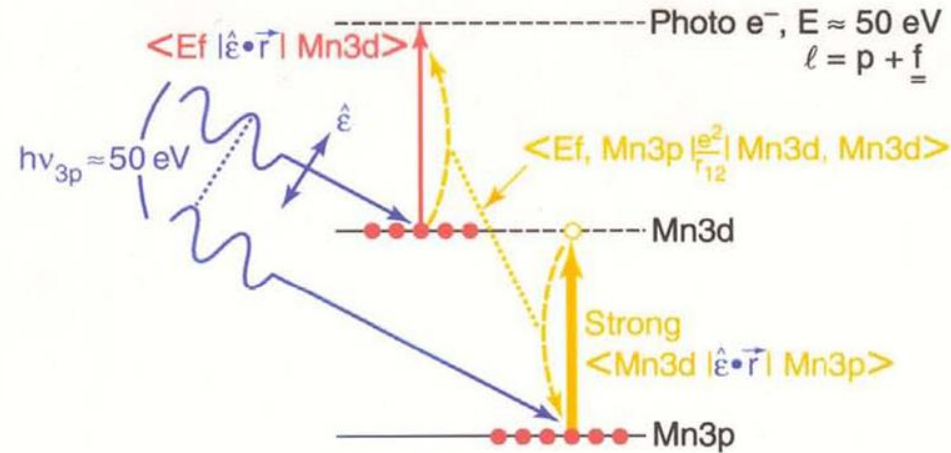
$\langle Ef | \hat{\varepsilon} \cdot \vec{r} | Mn3d \rangle$

$h\nu_{3p} \approx 50$ eV

$\hat{\varepsilon}$

Photo e⁻, E ≈ 50 eV

$\ell = p + \underline{f}$

$\langle Ef, Mn3p | \frac{e^2}{r_{12}} | Mn3d, Mn3d \rangle$

Mn3d

Strong

$\langle Mn3d | \hat{\varepsilon} \cdot \vec{r} | Mn3p \rangle$

Mn3p

On

Atomic Mn(g)

Expt. (Krause et al.)

3d

Theory (Garvin et al.)

—— MBPT

--- HF

I_{Mn3d}

Resonant (±) ≈ 0.63

$h\nu_{3p}$

Off

Non-Resonant ≡ 1.0

7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

20 30 40 50 60 70 80 90 100 100

Photon Energy, hν (eV)

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SrTiO$_3$ and La$_{0.67}$Sr$_{0.33}$MnO$_3$ band structures and DOS

SrTiO$_3$-band insulator

La$_{0.67}$Sr$_{0.33}$MnO$_3$- Half-Metallic Ferromagnet

Projected DOSs

Spin-up **Spin-down**

$d_{xz}+d_{yz}$

d_{xy}

No spin down!

d_{z2}

d_{x2-y2}

$d_{xz}+d_{yz}$

d_{xy}

$O\ 2p$

Expt'l. bandgap 3.3 eV

Expt'l. band offset 3.0 eV

Mn e$_g$

Mn t$_{2g}$

Energy (eV)

Plucinski, TBP with expt'l. band offset

— **Spin-up**
— **Spin-down**
Chikamatsu et al., PRB 73, 195105 (2006); Plucinski, TBP

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

Valence spectrum

Mn 2p absorption spectrum

Prior resonant PS: Fujimori et al., J.A.P 99, 08S903 (2006)
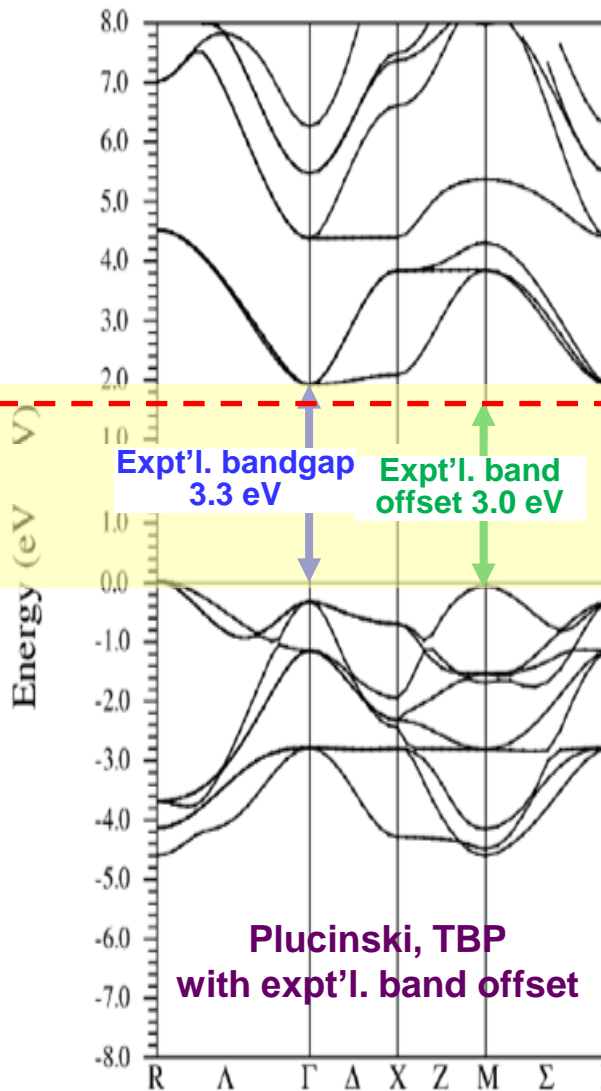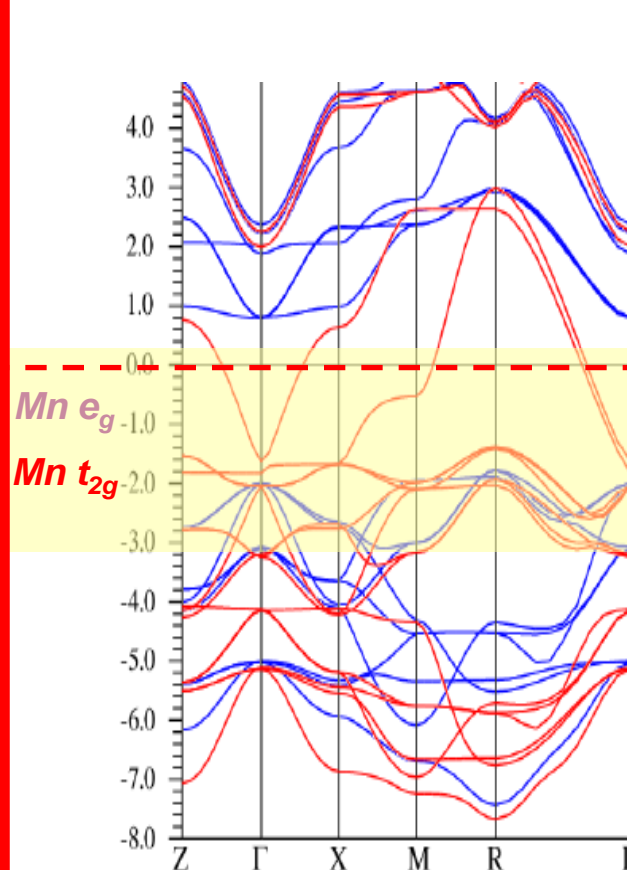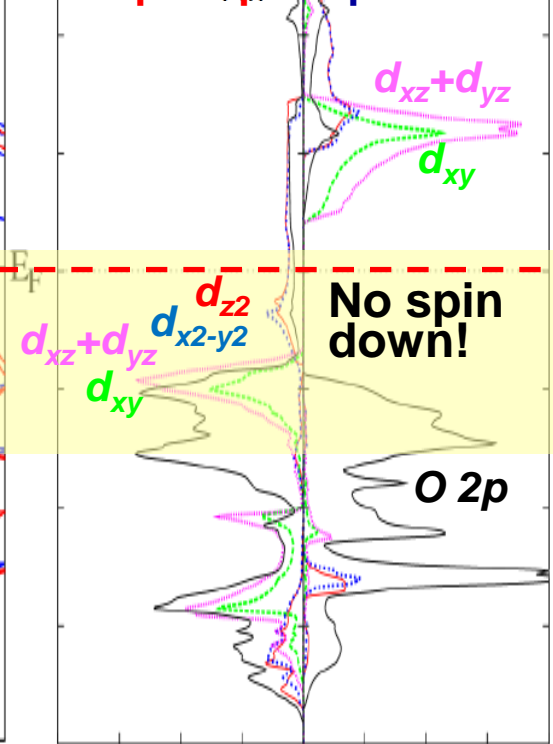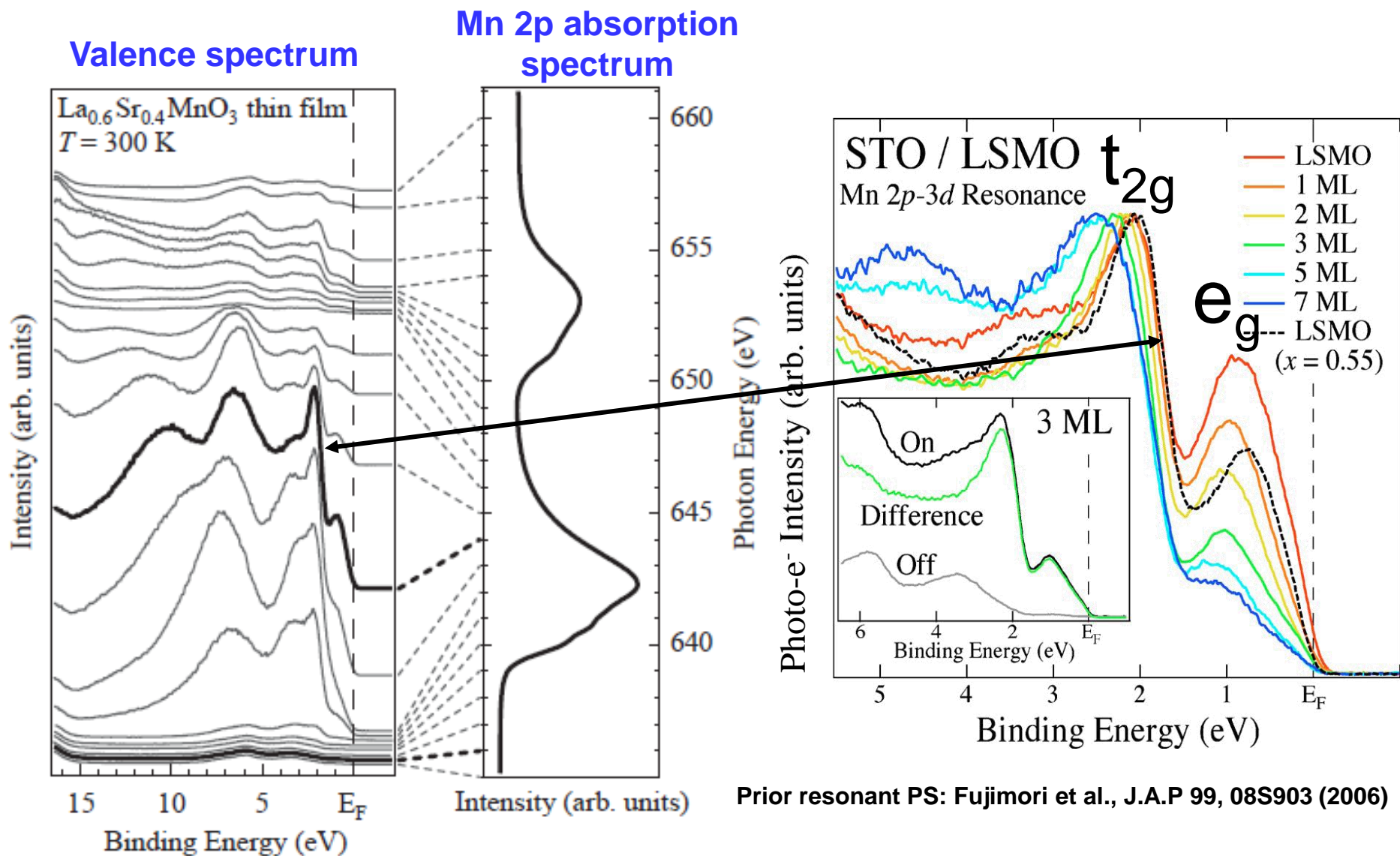
K. Horiba et al. / Journal of Magnetism and Magnetic Materials 272–276 (2004) 436–437

110

The Soft and Hard X-Ray Spectroscopies

Electron-out: surface sensitive

Photon-out: "bulk", deeper interfaces

Valence PES

Core PES

AES

REXS

XAS

XES

RIXS

CB

E_F

VB

Core

PES = photoemission = photoelectron spectroscopy
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111
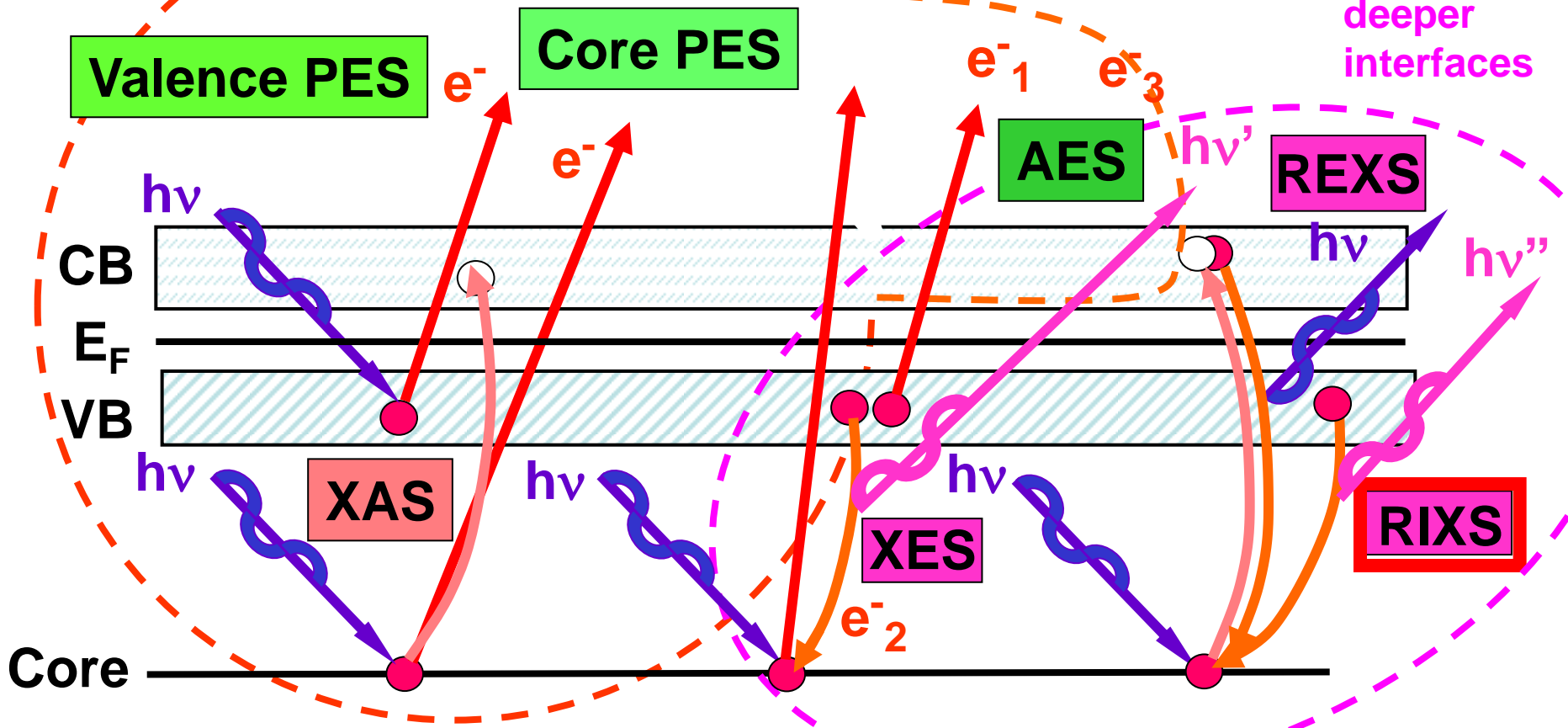
MATRIX ELEMENTS IN The Soft and Hard X-Ray Spectroscopies: RESONANT EFFECTS

- **_X-ray emission:_**

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

Vacuum $-\ -\ -\ -\ -$

φ_i

φ_f
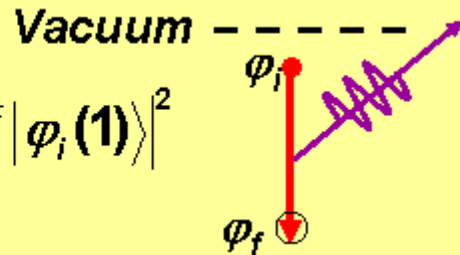
- **_Resonant inelastic x-ray scattering--The Kramers-Heisenberg Equation:_**

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

$$\times \delta(h\nu - (E_m(N) - E_i(N)))$$

Vacuum $-\ -\ -\ -\ -$

$h\nu$ $\hat{e}_{inc}$ $\Psi_m(N)$

$h\nu' = h\nu - \Delta E$

$\hat{e}_{emi}$

$\Psi_f(N)$

ΔE

$\Psi_i(N)$

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

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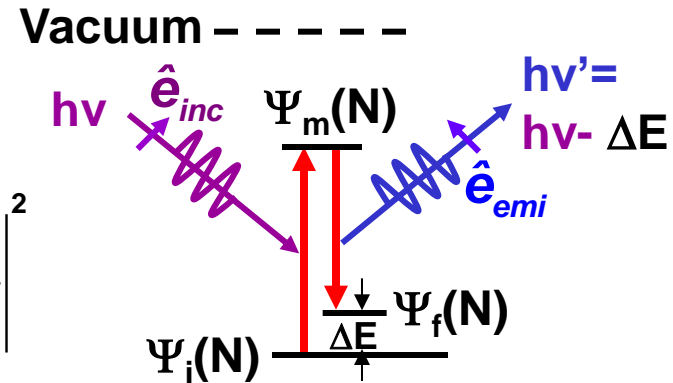
X-ray fluorescence spectroscopy =X-ray emission spectroscopy (XES) and Resonant inelastic x-ray scattering (RIXS)

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

X-ray absorption spectroscopy (XAS)

Mn 2p$_{3/2}$

2p$_{1/2}$

~10.0 eV

MnO

Mn L$_{\alpha,\beta}$ 716 eV

NORMAL XES

RESONANT: INELASTIC + ELASTIC

hν$_{in}$ hν$_{out}$ ELASTIC

RESONANT ELASTIC

a ≡ hν$_{in}$

= hν$_{out}$

Vac.

3d
3p
3s

XES   REXS   RIXS

2p$_{3/2}$
2p$_{1/2}$

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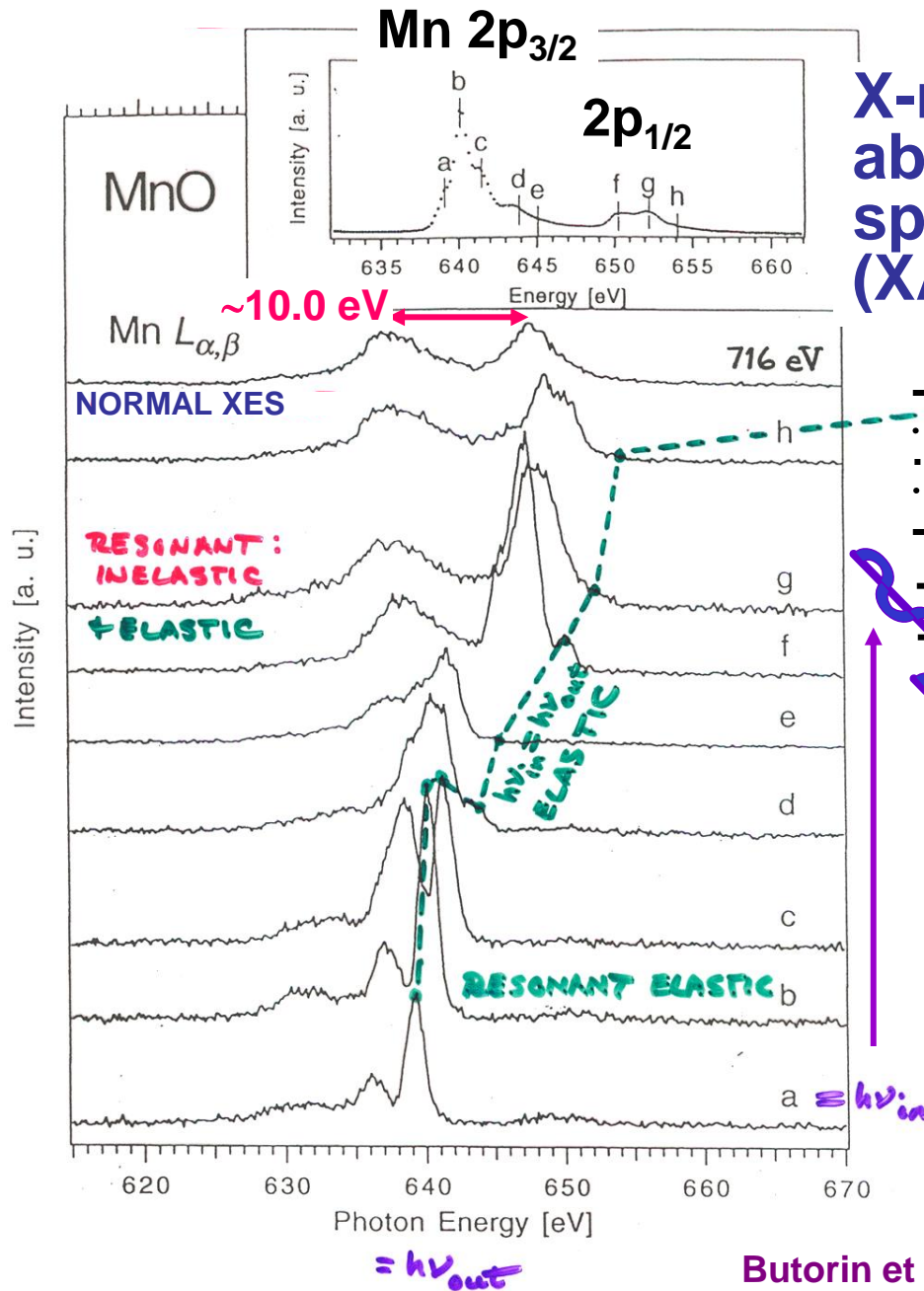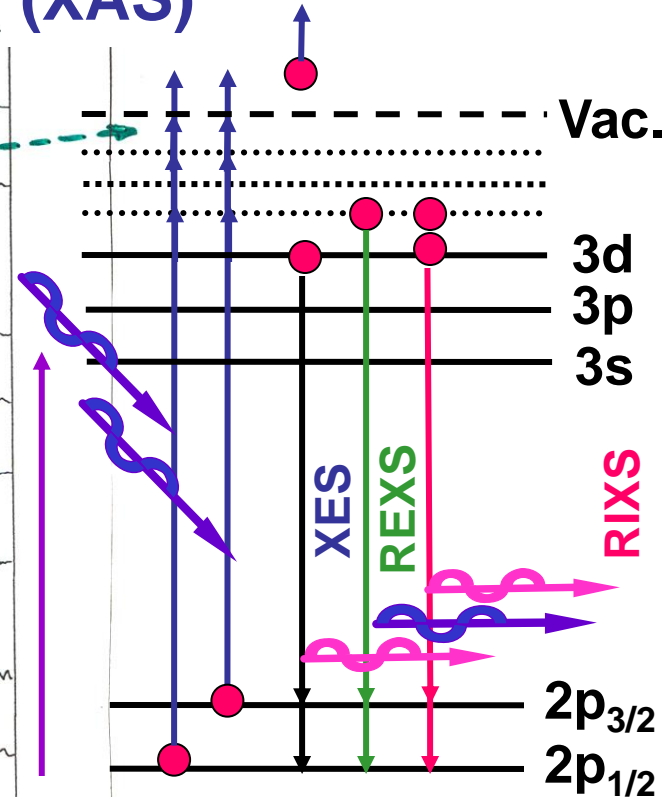
Excitations probed by RIXS

Phonons

(Bi-) Magnons

d-d

Charge Transfer

Energy

50 meV   500 meV   1.5 eV   2 eV
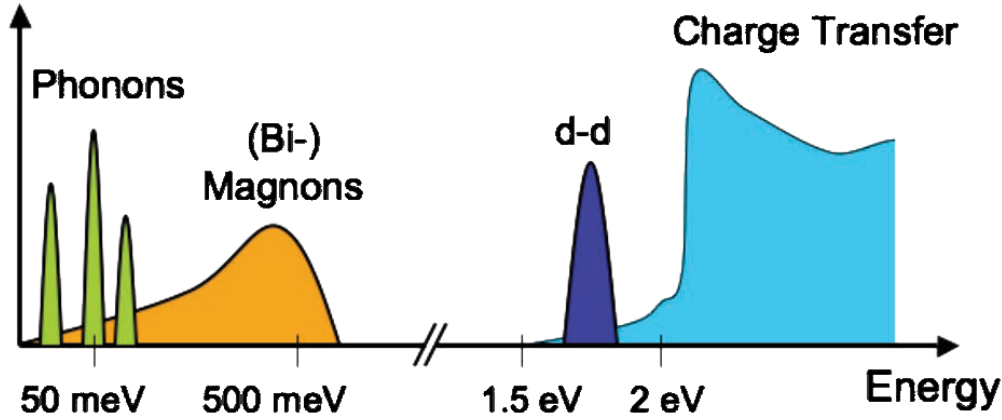
Aments et al., Rev. Mod. Phys. 83, 705 (2011)

Example: CuB$_2$O$_4$ plaquets

(a) CuB$_2$O$_4$

010 100 001

Cu(1)

Cu(2)

Cu(1) Cu(2)   Cu(1) Cu(2)

(c)

XPS

$2p_{1/2}$

$2p_{3/2}$

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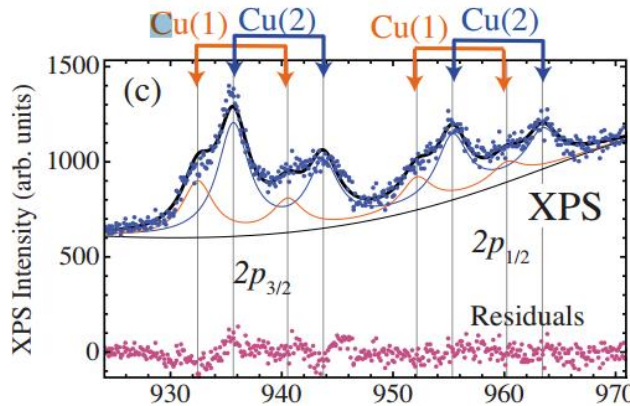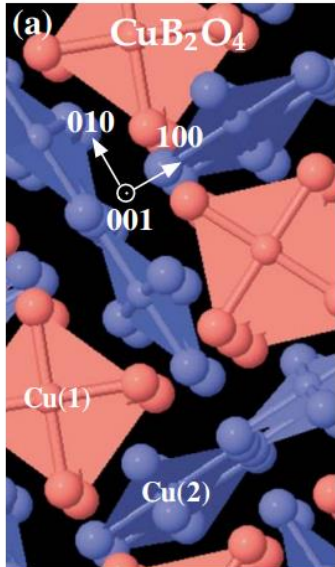
Hancock et al., Phys. Rev. B 80, 092509 (2009)

REXS RISS

Zero loss peak

Raman losses

Normal XES $K\beta_{2,5}$ Emission line

RIXS signal (photons/s)
0   20   40

Incident Energy (eV)

Energy Transfer (eV)

=ΔE

$\hbar\omega_{in} = 8992\,eV$

dd MO 4p $K\beta_{2,5}$

RIXS signal (photons/s)

Energy Transfer (eV)
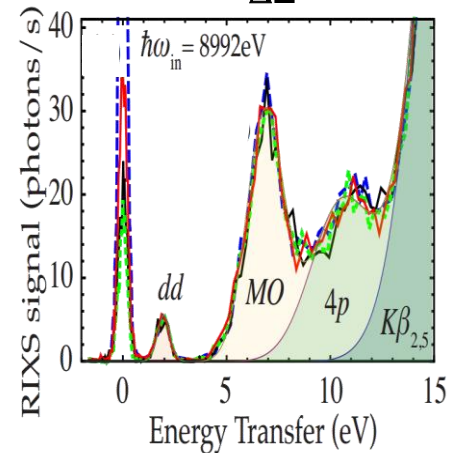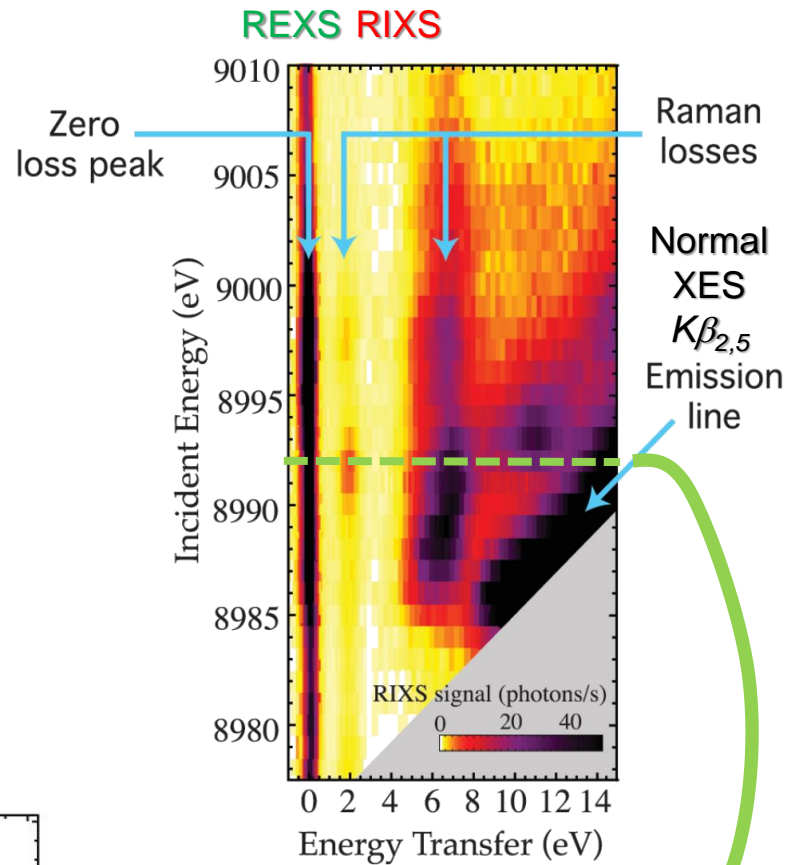
EXAFS
Atomic structure

The Soft and Hard X-Ray Spectroscopies

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

Deeper   *"Bulk"*   *Surface/near surface*   e-   *XES→*
                                                                                    "Bulk"

e-   e-

Valence PES   **Core PE**

CB

E_F

VB

XAS   **RIXS**   **XES**

Core

Important! Core levels→ Element-specific methods   115
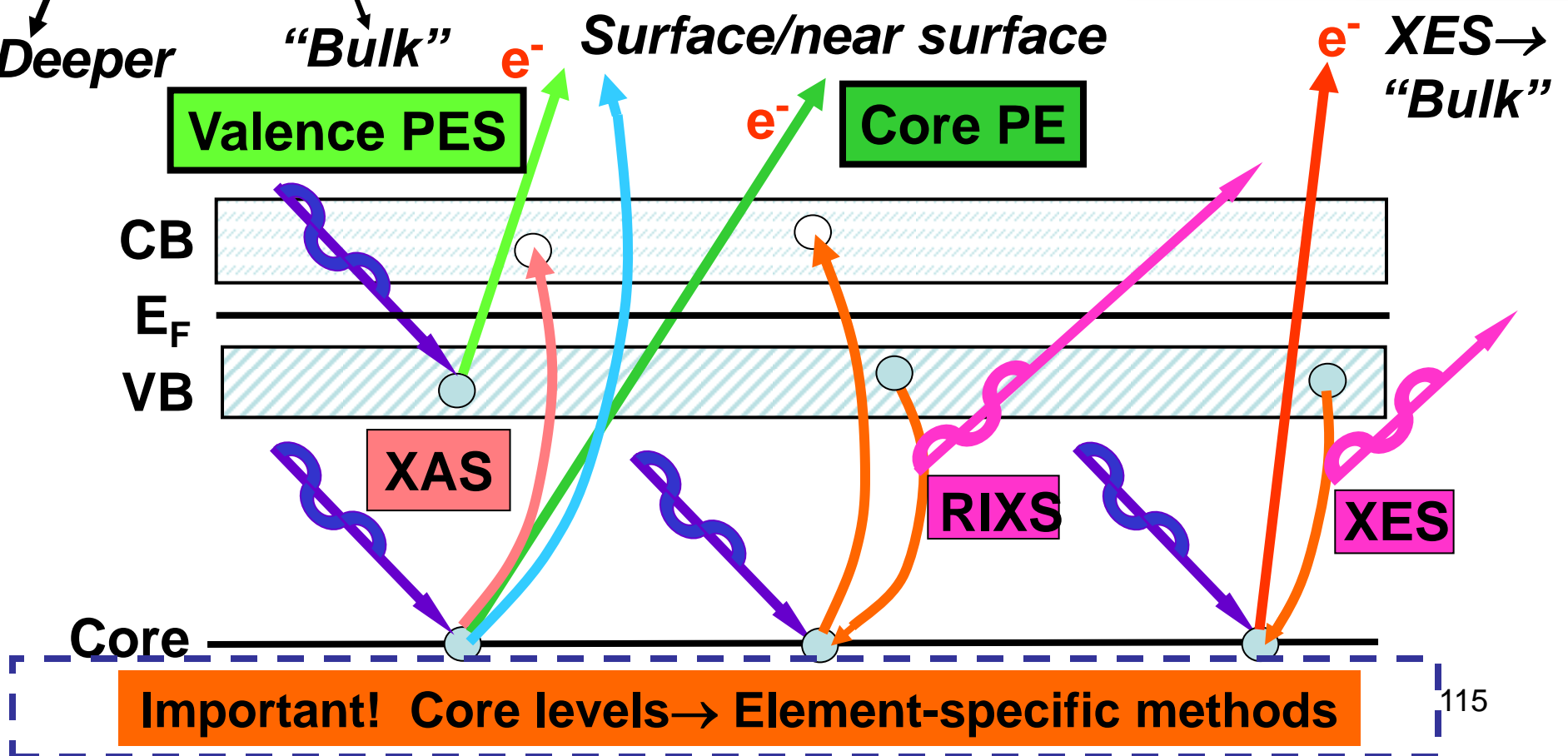
INTENSITIES IN PHOTOELECTRON SPECTRA:

- **GENERAL:** FINAL STATE K (k-SUBSHELL + ALL OTHER DESIG.)

$$\text{INT.}_K \propto \left| \hat{e} \cdot \langle \Psi^f_{tot}(N,K) | \sum_{i=1}^{N} \vec{r}_i | \Psi^i_{tot}(N) \rangle \right|^2 \quad (\text{DIPOLE APPROX.}$$

INTENSITIES IN PHOTOELECTRON SPECTRA:

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- **BORN-OPPENHEIMER:** e^-'s FAST, VIBRATIONS SLOW

$$INT._K \propto \left| \langle \Psi_{VIB,v'}^f | \Psi_{VIB,v}^i \rangle \right|^2 \left| \hat{e} \cdot \langle \Psi_{e^-}^f (N,K) | \sum_{i=1}^N \vec{r}_i | \Psi_{e^-}^i (N) \rangle \right|^2$$

$$\underbrace{\phantom{\langle \Psi_{VIB,v'}^f | \Psi_{VIB,v}^i \rangle}}_{\text{FRANCK-CONDON FACTOR}}$$

INTENSITIES IN PHOTOELECTRON SPECTRA:

- **GENERAL:** FINAL STATE K (k-SUBSHELL + ALL OTHER DESIG.)

$$INT._K \propto \left| \hat{e} \cdot \langle \Psi^f_{tot}(N,K) | \sum_{i=1}^{N} \vec{r}_i | \Psi^i_{tot}(N) \rangle \right|^2 \quad (\text{DIPOLE APPROX.})$$

- **BORN-OPPENHEIMER:** e^-'s FAST, VIBRATIONS SLOW

$$INT._K \propto \left| \langle \Psi^f_{VIB,v'} | \Psi^i_{VIB,v} \rangle \right|^2 \left| \hat{e} \cdot \langle \Psi^f_{e^-}(N,K) | \sum_{i=1}^{N} \vec{r}_i | \Psi^i_{e^-}(N) \rangle \right|^2$$

  $\underbrace{\qquad\qquad}_{\text{FRANCK-CONDON FACTOR}}$

- **SUDDEN APPROXIMATION:** $\psi_K \rightarrow \psi_F = PHOTO\, e^- \ (\text{FAST})$

$$\left. \begin{array}{l} \psi_1 \rightarrow \psi'_1 \\ \vdots \\ \text{k HOLE} \rightarrow \begin{array}{l} \psi_{k-1} \rightarrow \psi'_{k-1} \\ \psi_{k+1} \rightarrow \psi'_{k+1} \\ \vdots \\ \psi_N \rightarrow \psi'_N \end{array} \end{array} \right\} \ (\text{SLOW})$$

$$INT._K \propto \left| \langle \Psi^f_{VIB,v'} | \Psi^i_{VIB,v} \rangle \right|^2 \left| \langle \Psi^f_{e^-}(N-1,K) | \underset{\substack{\text{k MISSING} \\ \pm}}{\Psi_R}(N-1,k) \rangle \right|^2$$

$$\left| \hat{e} \cdot \langle \varphi_f | \vec{r} | \psi_k \rangle \right|^2$$

$\qquad \hookrightarrow \text{NORMAL} \ \dfrac{d\sigma_k}{d\Omega}$

SAME SUBSHELL COUPLING + TOTAL L,S→"MONOPOLE"

INTENSITIES IN PHOTOELECTRON SPECTRA:

- **GENERAL:** FINAL STATE K (k-SUBSHELL + ALL OTHER DESIG.)

$$\text{INT.}_K \propto \left| \hat{e} \cdot \langle \Psi^f_{tot}(N,K) | \sum_{i=1}^{N} \vec{r}_i | \Psi^i_{tot}(N) \rangle \right|^2 \quad \text{(DIPOLE APPROX.}$$

- **BORN-OPPENHEIMER:** e^-'s FAST, VIBRATIONS SLOW

$$\text{INT.}_K \propto \left| \langle \Psi^f_{VIB,v'} | \Psi^i_{VIB,v} \rangle \right|^2 \left| \hat{e} \cdot \langle \Psi^f_{e^-}(N,K) | \sum_{i=1}^{N} \vec{r}_i | \Psi^i_{e^-}(N) \rangle \right|^2$$

$$\underbrace{\qquad\qquad\qquad}_{\text{FRANCK-CONDON FACTOR}}$$

- **SUDDEN APPROXIMATION:** $\psi_k \to \psi_f = $ PHOTO e^- (FAST)

$$\begin{array}{c} \psi_1 \to \psi_1' \\ \vdots \\ k\text{ HOLE} \to \psi_{k-1} \to \psi_{k-1}' \\ \psi_{k+1} \to \psi_{k+1}' \\ \vdots \\ \psi_N \to \psi_N' \end{array} \Bigg\} \text{(SLOW)}$$

$$\text{INT.}_k \propto \left| \langle \Psi^f_{VIB,v'} | \Psi^i_{VIB,v} \rangle \right|^2 \left| \langle \underbrace{\Psi^f_{e^-}(N-1,k)}_{} | \Psi^{\pm}_R \overset{k\text{ MISSING}}{\overbrace{(N-1,k)}} \rangle \right|^2$$

$$\underbrace{\qquad\qquad\qquad\qquad}_{}$$

SAME SUBSHELL COUPLING + TOTAL L,S→"MONOPOLE"

$$\left| \hat{e} \cdot \langle \varphi_f | \vec{r} | \psi_k \rangle \right|^2$$

$$\hookrightarrow \text{ NORMAL } \frac{d\sigma_k}{d\Omega}$$

- **SLATER DETS. FOR** $\Psi^f_{e^-} = \det(\varphi_1' \varphi_2' \cdots \varphi_{k-1}', \varphi_{k+1}' \cdots \varphi_N')$

$$\Psi_R = \det(\varphi_1 \varphi_2 \cdots \varphi_{k-1} \varphi_{k+1} \cdots \varphi_N)$$

$$\text{INT.}_k \propto \left| \langle \Psi^f_{VIB,v'} | \Psi^i_{VIB,v} \rangle \right|^2 |\langle \varphi_1' | \varphi_1 \rangle|^2 |\langle \varphi_2' | \varphi_2 \rangle|^2 \cdots \Big\}$$

$$|\langle \varphi_{k-1}' | \varphi_{k-1} \rangle|^2 |\langle \varphi_{k+1}' | \varphi_{k+1} \rangle|^2 \cdots |\langle \varphi_N' | \varphi_N \rangle|^2 . \Big\}$$

$$\left| \hat{e} \cdot \langle \varphi_f | \vec{r} | \psi_k \rangle \right|^2$$

1e- DIPOLE→dσ/dΩ

(N-1)e- SHAKE-UP/ SHAKE-OFF→ "MONOPOLE"

"Basic Concepts of XPS" Section 3.D.

INTENSITIES IN PHOTOELECTRON SPECTRA:

- **GENERAL:** FINAL STATE K (k-SUBSHELL + ALL OTHER DESIG.)

$$INT._K \propto |\hat{e} \cdot \langle \Psi^f_{tot}(N,K)| \sum_{i=1}^{N} \vec{r}_i | \Psi^i_{tot}(N)\rangle|^2 \quad (DIPOLE\ APPROX.$$

- **BORN-OPPENHEIMER:** e^-'s FAST, VIBRATIONS SLOW

$$INT._K \propto |\langle \Psi^f_{VIB,v'}| \Psi^i_{VIB,v}\rangle|^2 |\hat{e} \cdot \langle \Psi^f_{e^-}(N,K)| \sum_{i=1}^{N} \vec{r}_i | \Psi^i_{e^-}(N)\rangle|^2$$

underbrace: **FRANCK-CONDON FACTOR**

- **SUDDEN APPROXIMATION:** $\psi_k \rightarrow \psi_f = PHOTO\ e^-$ (FAST)

$$\begin{array}{c} \psi_1 \rightarrow \psi_1' \\ \vdots \quad \vdots \\ \textcolor{orange}{k\ HOLE \rightarrow} \psi_{k-1} \rightarrow \psi_{k-1}' \\ \psi_{k+1} \rightarrow \psi_{k+1}' \\ \vdots \quad \vdots \\ \psi_N \rightarrow \psi_N' \end{array} \Big\} (SLOW)$$

$$INT._k \propto |\langle \Psi^f_{VIB,v'}| \Psi^i_{VIB,v}\rangle|^2 |\langle \Psi^f_{e^-}(N-1,k)| \Psi^\pm_R(N-1,k)\rangle|^2$$

k MISSING

SAME SUBSHELL COUPLING + TOTAL L,S→"MONOPOLE"

$$|\hat{e} \cdot \langle \varphi_f| \vec{r} | \psi_k\rangle|^2$$

$\hookrightarrow$ NORMAL $\dfrac{d\sigma_k}{d\Omega}$

- **SLATER DETS. FOR** $\Psi^f_{e^-} = det(\varphi_1' \varphi_2' \cdots \varphi_{k-1}', \varphi_{k+1}' \cdots \varphi_N')$

$$\Psi_R = det(\psi_1, \psi_2 \cdots \psi_{k-1}, \psi_{k+1} \cdots \psi_N)$$

$$INT._k \propto |\langle \Psi^f_{VIB,v'}| \Psi^i_{VIB,v}\rangle|^2 |\langle \varphi_1'|\psi_1\rangle|^2 |\langle \varphi_2'|\psi_2\rangle|^2 \cdots$$

$$|\langle \varphi_{k-1}'|\psi_{k-1}\rangle|^2 |\langle \varphi_{k+1}'|\psi_{k+1}\rangle|^2 \cdots |\langle \varphi_N'|\psi_N\rangle|^2 .$$

(N-1)e^- SHAKE-UP/ SHAKE-OFF→ "MONOPOLE"

$$|\hat{e} \cdot \langle \varphi_f| \vec{r} | \psi_k\rangle|^2$$

1e- DIPOLE→dσ/dΩ

- **PLUS DIFFRACTION EFFECTS IN** φ_f ESCAPE: PD or EXAFS

The spectroscopies:

e^-, free

$h\nu$

$h\nu$

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

e^-, free #

e^-, bound *

$h\nu$

X-RAY ABSORPTION SPECTROSCOPY- XAS

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

e^-_1, free

e^-_2

$h\nu$

$h\nu' < h\nu$

or

e^-_3, free
= Auger

**X-RAY EMISSION (FLUORESCENCE)
SPECTROSCOPY**

**+ AUGER ELECRON SPECTROSCOPY
(Always accompanies photoelectron emission)**

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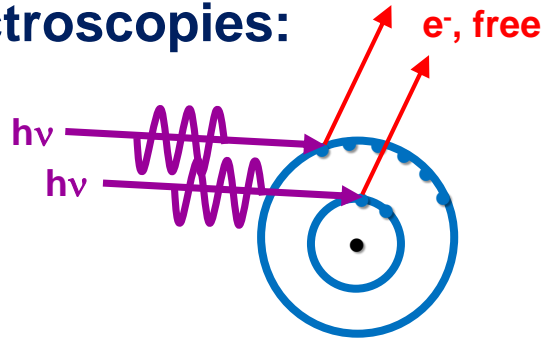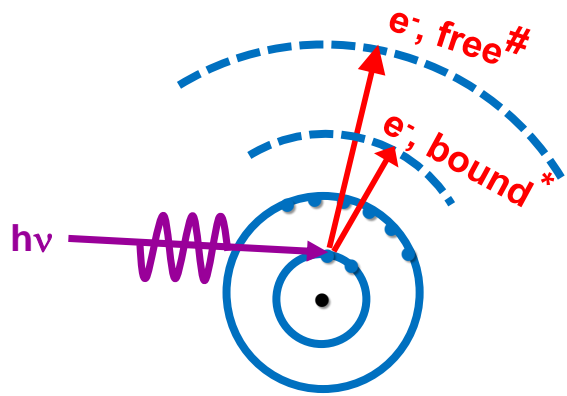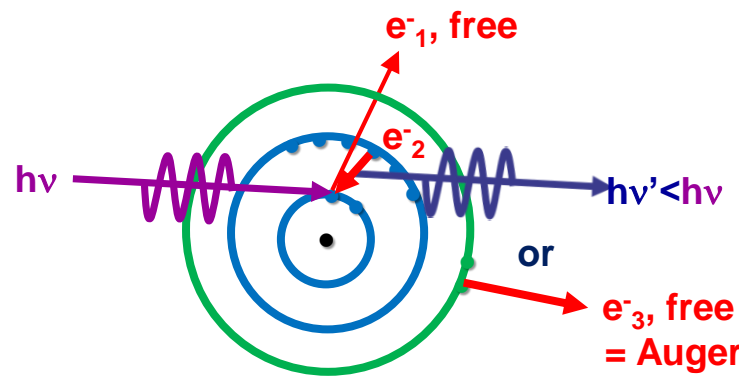
(a) FORWARD SCATT. = "0TH ORDER" → Bond & Low-Index Directions

HIGHER ORDERS → Bond Lengths & Atomic Positions

→ Holographic fringes

θ_{scat}

1ST
2ND
3RD

ϕ_j = object wave

ϕ_0 = reference wave

(b) CO C1s 500 eV

ref. intens.
$I_0 \propto |\phi_0|^2$

(c)

$h\nu$

$\hat{\epsilon}$

θ_{inc}

$\vec{K}_f$ ϕ_o E_{kin}

ϕ_j

θ_e

$\vec{k}_f$

θ_j

v_0

Ω_o

$\exp(-L/2\Lambda_e)$

$\approx \hat{\epsilon} \cdot \hat{k}$

$\vec{r}_j$

$f_j(\theta_j) \dfrac{\exp(ik|\vec{r} - \vec{r}_j|)}{|\vec{r} - \vec{r}_j|}$

Spher. Wave (SW)

Plane Wave (PW)

$\dfrac{\exp(ikr)}{r}$

$\exp(i\vec{k} \cdot \vec{r})$

Photoelectron Diffraction

122
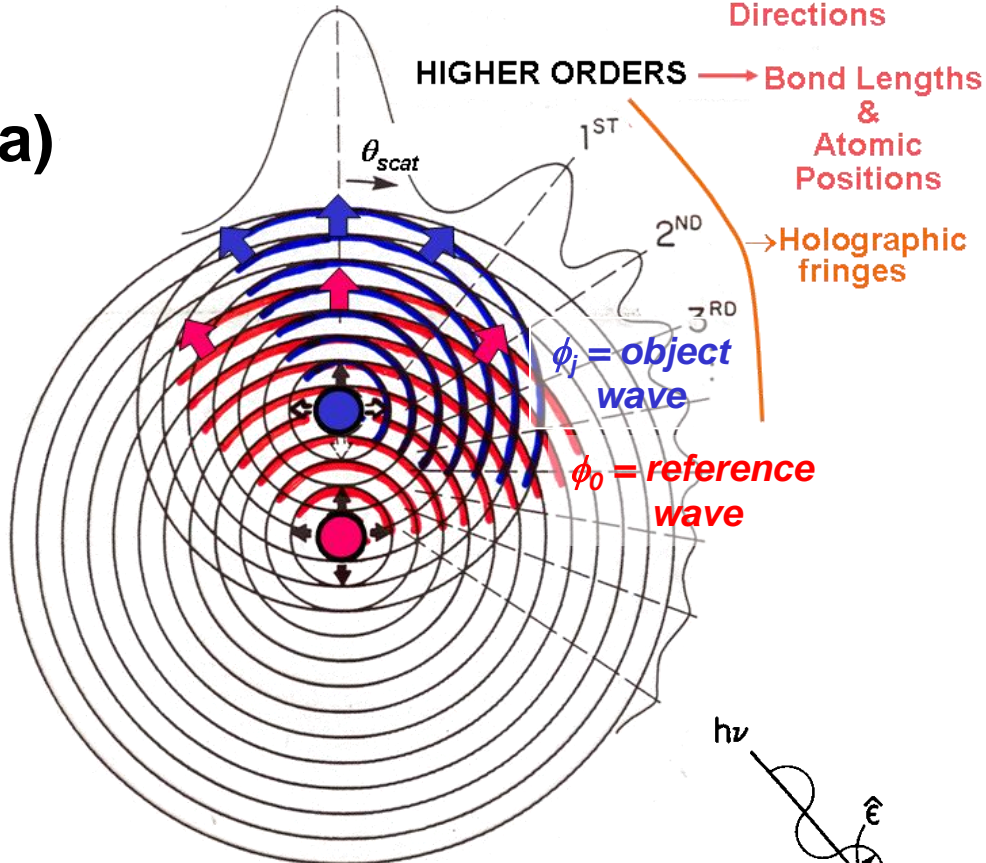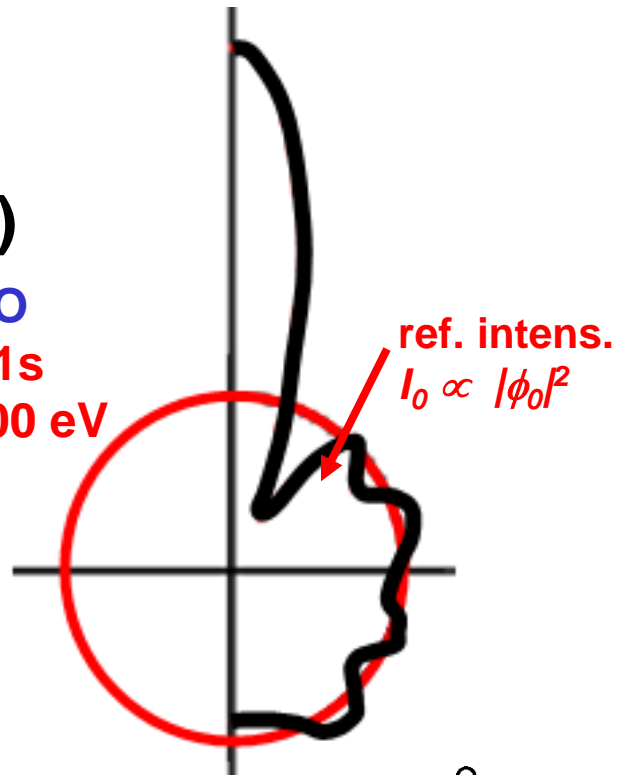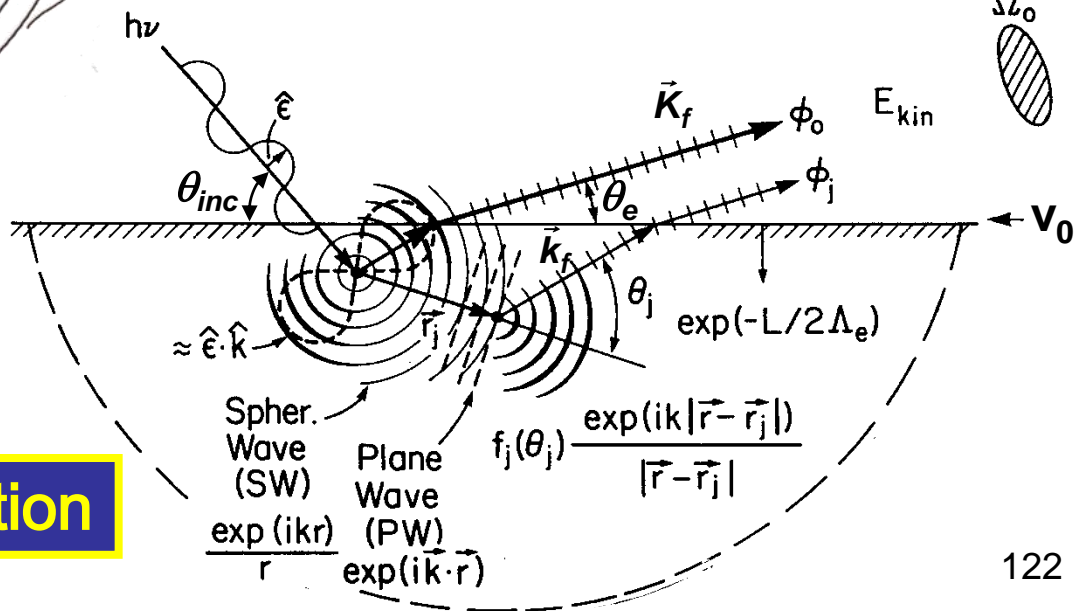
X-ray Photoelectron Diffraction: 1ML FeO on Pt(111)

(a)

(b)

Forward Scattering

0.65 Å

O

Fe

Pt

Pt 4f, 1414 eV

Fe 2p, 778 eV

O 1s, 944 eV

123
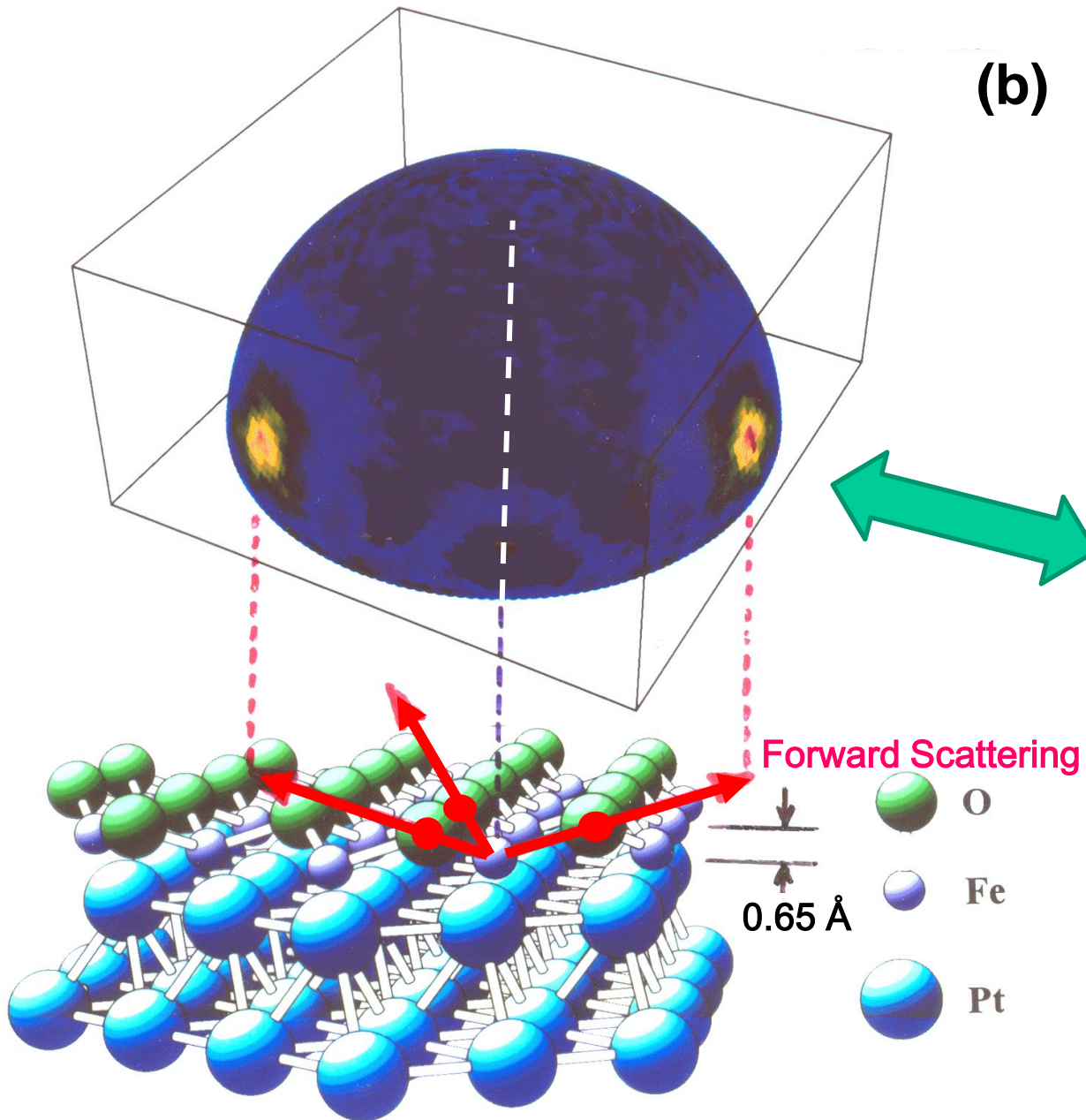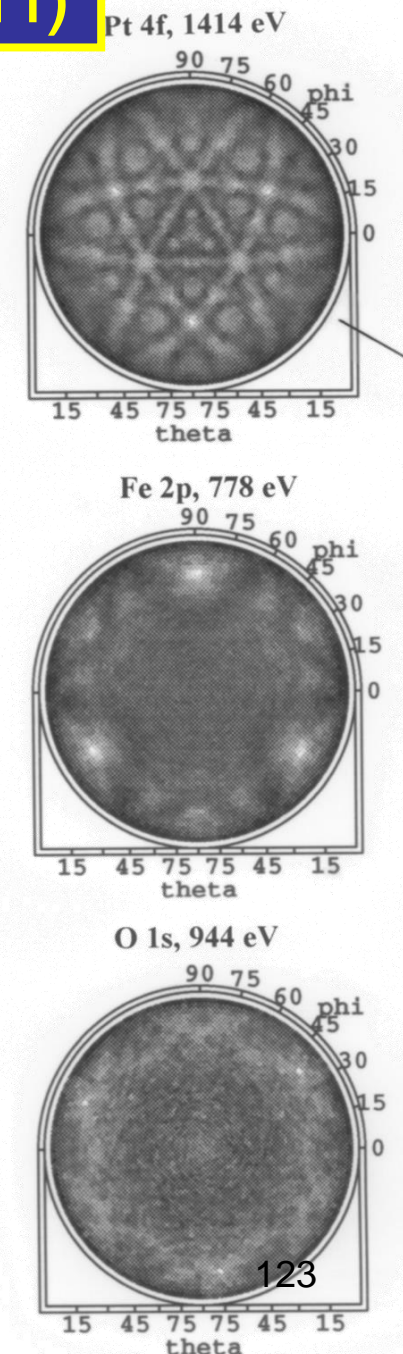
Scanned-energy photoelectron diffraction—an alternative approach (Shirley, Woodruff/ Bradshaw, Lapeyre, Chiang et al.)

SCANNED - ENERGY PHOTOELECTRON DIFF.

$(\sqrt{3} \times \sqrt{3})$ AL ON Si(111)

* 41 diffraction curves χ taken from Al 2p
* $\theta = 0 \sim 70°$, $\varphi = 0 \sim 60°$ } ~1100 DATA POINTS

Si 2p   Si(111)√3x√3−Al   hν=150eV

Al 2p

Intensity(Arb. Unit)

Kinetic Energy(ev)

WU ET AL., P.R.L. 71, 251('93) P.R. B 51, 14549('95)

PHOTON ENERGY(ev)

$\phi = 0.0°$ $\theta =$

6: 75.0°
5: 60.0°
4: 45.0°
3: 30.0°
2: 15.0°
1: 0.0°

Al 2p INTENSITY I(k), I₀(k)

MOMENTUM k(1/Å)

$E_{kin} =$ 34 eV   94 eV   184 eV

Photoelectron diffraction: Simple single-scattering theory for s-subshell emission

Various papers by Shirley et al., Woodruff, Bradshaw et. al.
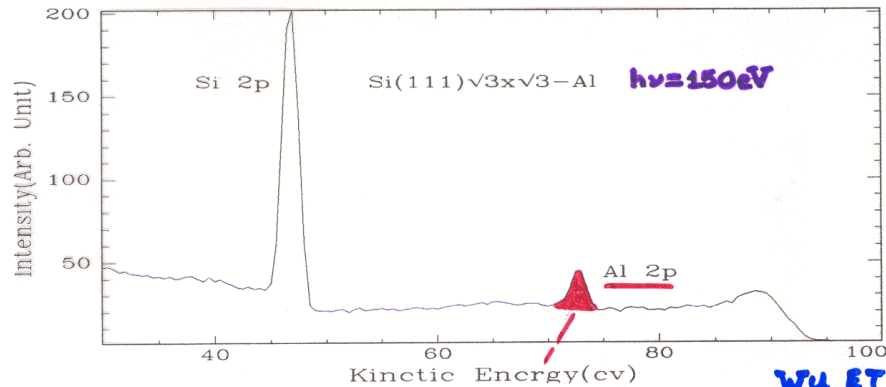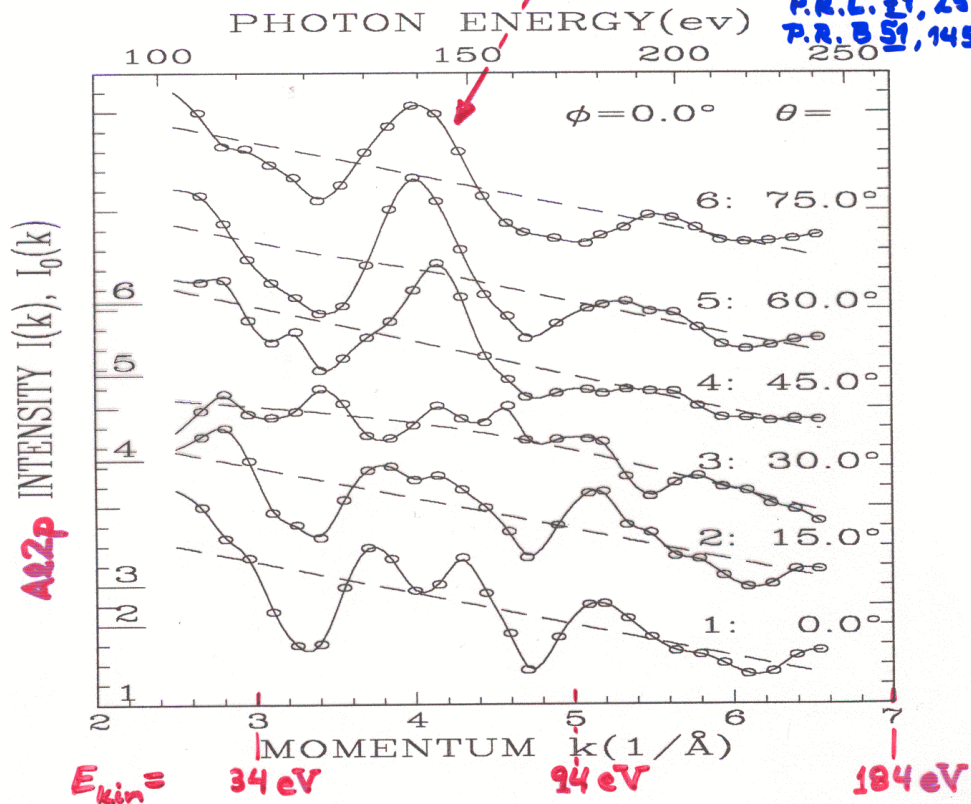
SINGLE SCATTERING THEORY
(Orders, Fadley, P.R.B 27, 781 ('83))

$h\nu$

$\hat{\varepsilon}$

$\dfrac{\exp(ikr)}{r}$

$\phi_o \propto A_o$ e^- $\vec{k}$

θ

$\phi_j \propto A_j$ $\leftarrow V_o$

$\sim \left(\dfrac{d\sigma}{d\Omega}\right)^{\frac{1}{2}}$ $\vec{r}_j$

θ_j $\exp(-L/2\Lambda_e)$

Ω_o

SPHERICAL WAVE (SW)

PLANE WAVE (PW) $f_j(\theta_j)\dfrac{\exp(ik|\vec{r}-\vec{r}_j|)}{|\vec{r}-\vec{r}_j|}$

$$\chi(E \text{ or } \vec{k}) \propto \sum_j \dfrac{F_j(k)}{F_o} \cos\left[kr_j(1-\cos\theta_j) + \psi_j(\theta_j,k)\right]$$

(CLUSTER)

Ω_o

ELASTIC e^-–ATOM SCATTERING

PATH LENGTH DIFFERENCE (P.L.D.)

SCATTERING PHASE SHIFT

INELASTIC e^-–e^- SCATTERING

$$F_j(k) = (\hat{\varepsilon}\cdot\hat{r}_j)\dfrac{|f_j(\theta_j,k)|}{r_j} W_j(\theta_j,k) \exp(-L_j/2\Lambda_e)$$

DEBYE-WALLER

= amplitude of scattered wave

$$F_o = (\hat{\varepsilon}\cdot\hat{k}) \exp(-L_o/2\Lambda_e)$$

= amplitude of direct wave

∴ FOURIER TRANSFORM OF $\chi(k) \Rightarrow$ PEAKS AT $\sim$ P.L.D. $= r_j(1-\cos\theta_j)$

COMPARISON OF SCANNED-ENERGY PD TO EXTENDED X-RAY ABSORPTION FINE STRUCTURE

"NEAR-EDGE"= XAS, XANES, NEXAFS
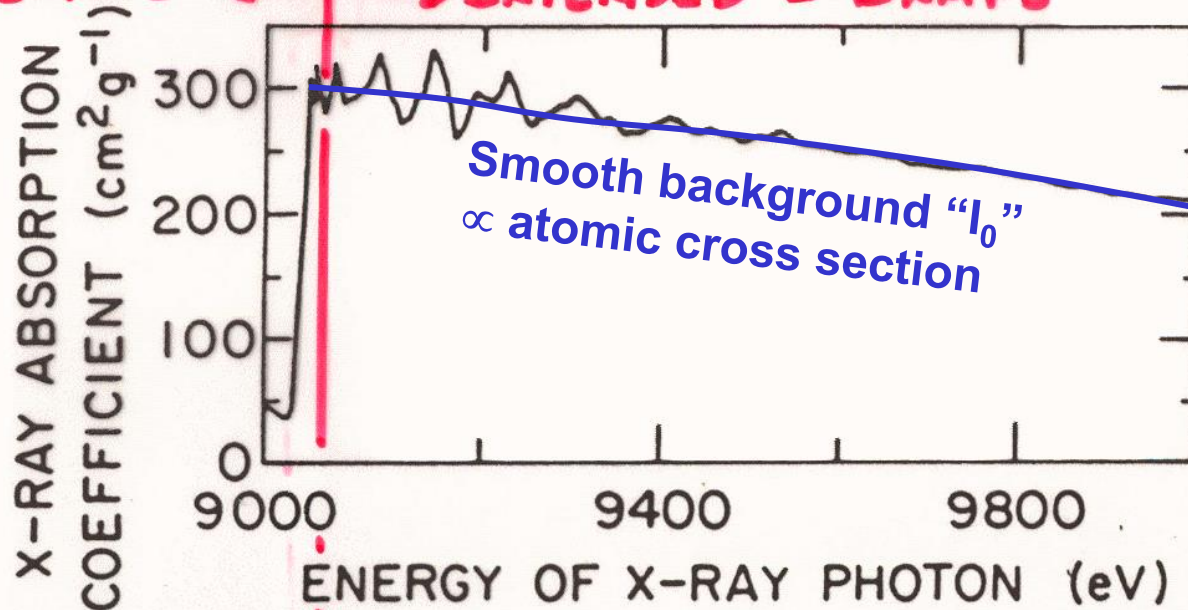
THEORY OF EXAFS

"EXTENDED" = EXAFS

Smooth background "I_0" $\propto$ atomic cross section

Figure 1.1. The x-ray absorption coefficient for the *K*-edge of copper metal.

~ COPPER 1S BINDING ENERGY

Also scanned-energy, but integrates over all electron emission directions

k (ATOMIC UNIT)

1 2 3 4 5 6 7

EXPERIMENT Cu

Glitsch = Bragg reflection in crystal
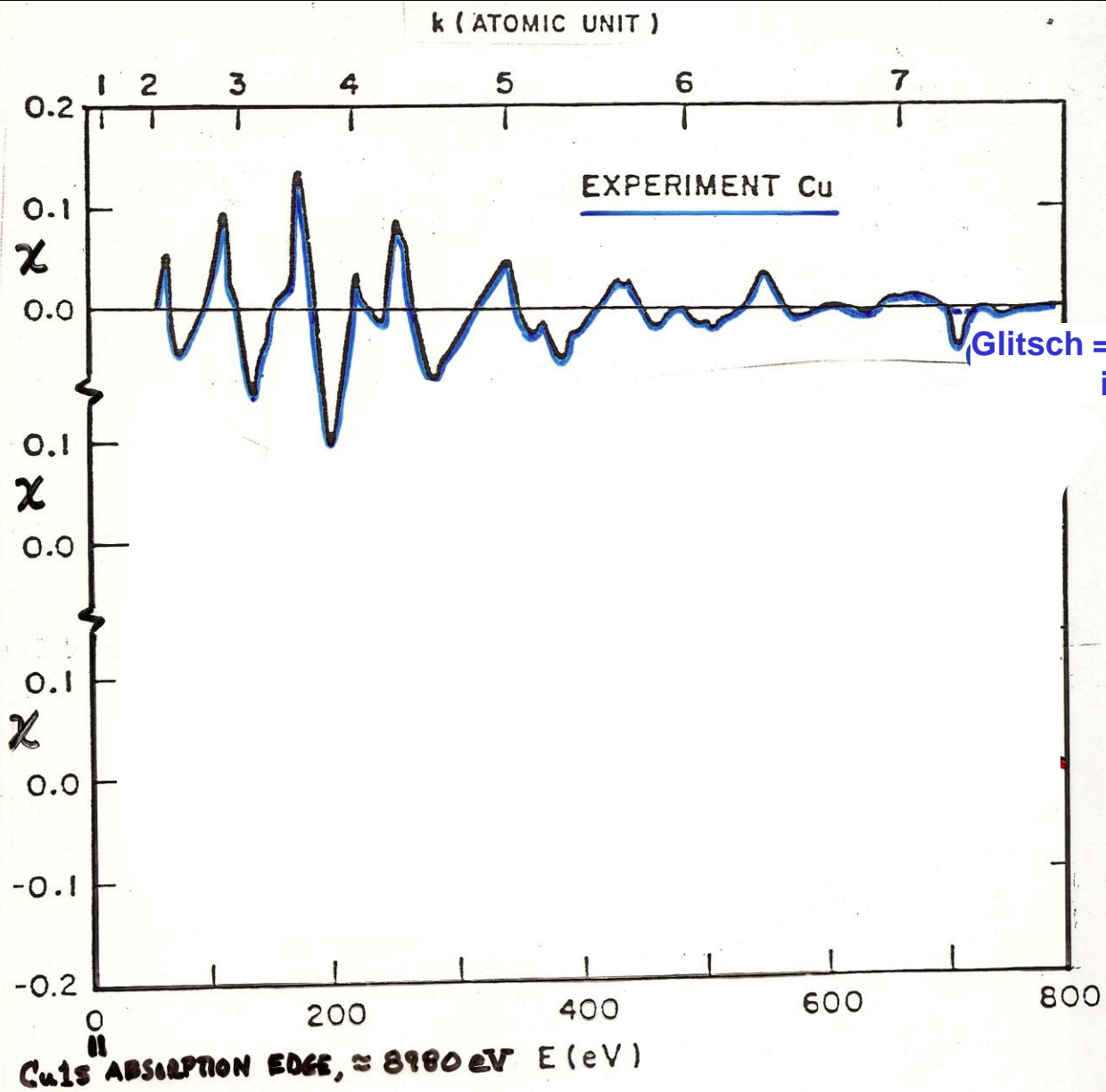
Cu 1s ABSORPTION EDGE, ≈ 8980 eV   E (eV)

EXAFS OF THE 1s SHELL OF COPPER

LEE + PENDRY, PHYS. REV. B 11, 2795 (1975)

SINGLE SCATTERING PLUS DOUBLE SCAT-
TERING BACK TO EMITTER FROM A CLUSTER
OF ~20-100 ATOMS ABOUT EMITTER-

SUM OVER ALL ϕ_1, ϕ_2, $I \propto |\phi_0 + \Sigma\phi_1 + \Sigma\phi_2|^2$,

THEN OVER ALL (UNOBSERVED) $\vec{k}$ DIRECTIONS

$$\chi(k) = \frac{\Delta\mu}{\mu_0} = -\sum_j \frac{N_j}{kr_j^2} |f_j(k,\pi)| S_0^2$$

∴ FOURIER
TRANSFORM
OF $\chi(k)$
➡ PEAKS
AT ≈ $2r_j$
➡ BOND
DISTANCES

$$\times \sin[2kr_j + \phi_j(k,\pi)] e^{-2\overline{u_j^2}k^2} e^{-2r_j/\Lambda_e(k)}$$

PHASES DUE TO: PATH   ELASTIC   DEBYE-   INELASTIC
            LENGTH   SCATT.   WALLER   SCATT.
            DIFF.   FACTOR

WITH: N_j = NO. SCATTERERS AT DISTANCE r_j.

$k = e^-$ WAVE VECTOR $= \sqrt{2mE'}/\hbar$

$|f_j(k,\pi)|$ = BACKSCATTERING AMPLITUDE

$\phi_j(k,\pi) = \psi_j(k,\pi) + 2\delta_1$ = OVERALL BACKSCATT. PHASE SHIFT

S_0^2 = FRACTION
     FREE OF "SHAKE"
$= |\langle \Psi_L | \Psi_R \rangle|^2$

$\overline{u_j^2}$ = MEAN-SQUARED VIBRATIONAL MOTION

$\Lambda_e(k)$ = INELASTIC MEAN FREE PATH

EXAFS OF THE 1s SHELL OF COPPER
LEE & PENDRY, PHYS. REV. B **11**, 2795 (1975)

Cu 1s EXAFS FOURIER TRANSF.
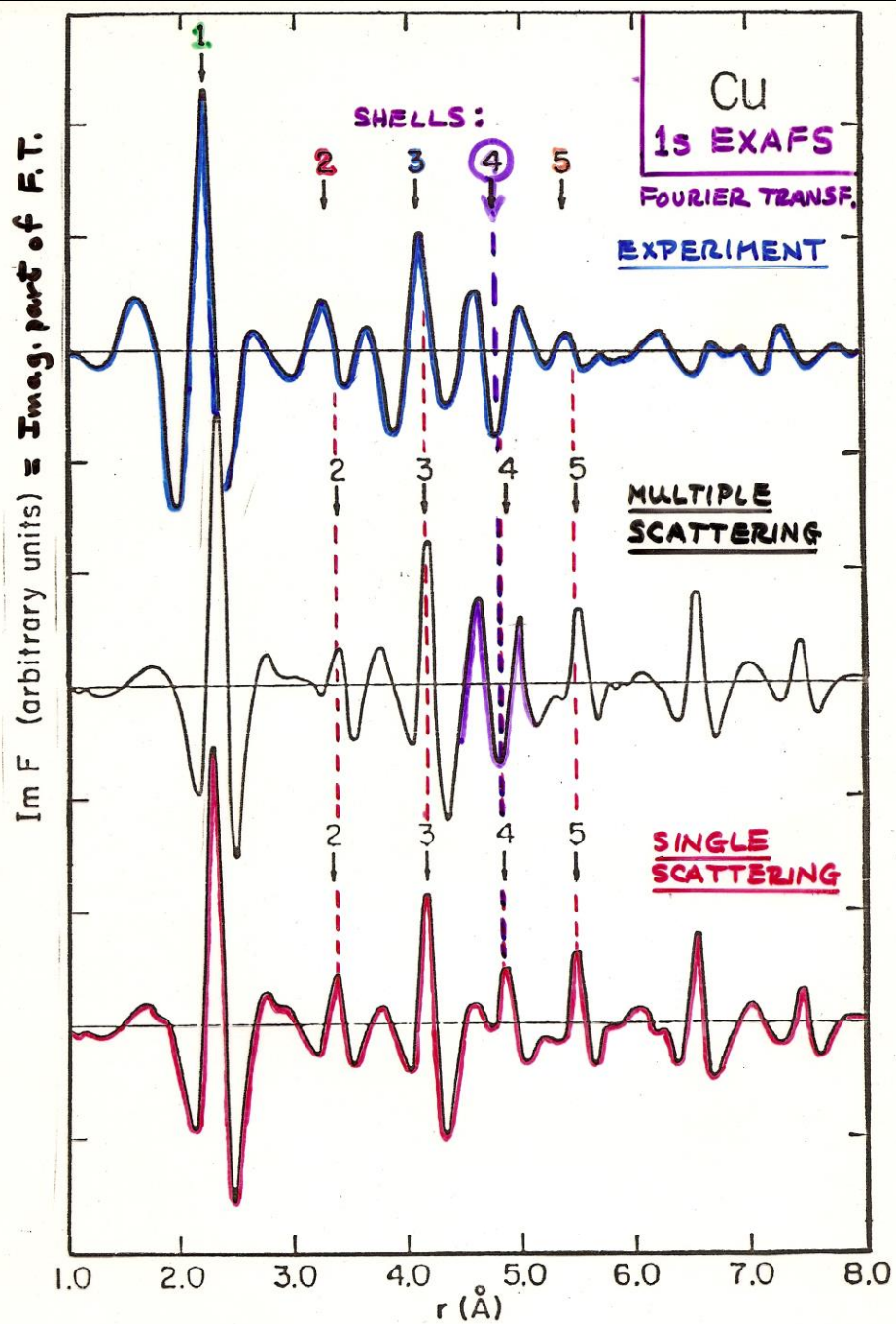
LEE & PENDRY, PHYS. REV. B **11**, 2795 (1975)

SURFACE EXTENDED X-RAY ABSORP- TION FINE STRUCTURE (SEXAFS)
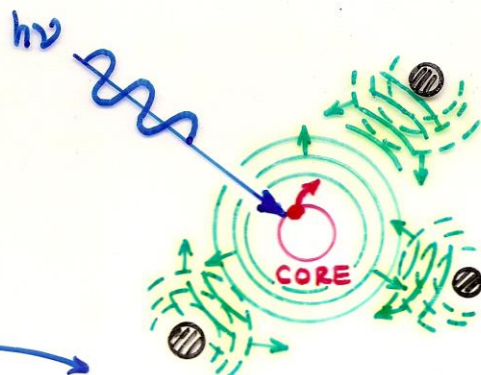
FOR PHOTOELECTRON:

$$E_{kin} = h\nu - E_b(core)$$

$$k = \frac{\sqrt{2mE}}{\hbar}$$

$$\lambda_{e^-} = \frac{2\pi}{k}$$

$h\nu$

CORE

NEAR EDGE X-RAY ABSORP- TION FINE STRUCTURE

"NEXAFS"

"EXAFS"

$\propto$ Abs. Coeff. $= \mu$

Backgnd. μ_0

BOUND | FREE

$E_b(core)$ $h\nu$

$\chi = \frac{\Delta \mu}{\mu_0}$

$\Rightarrow$ 0

E_{kin} (or k)
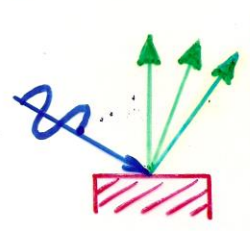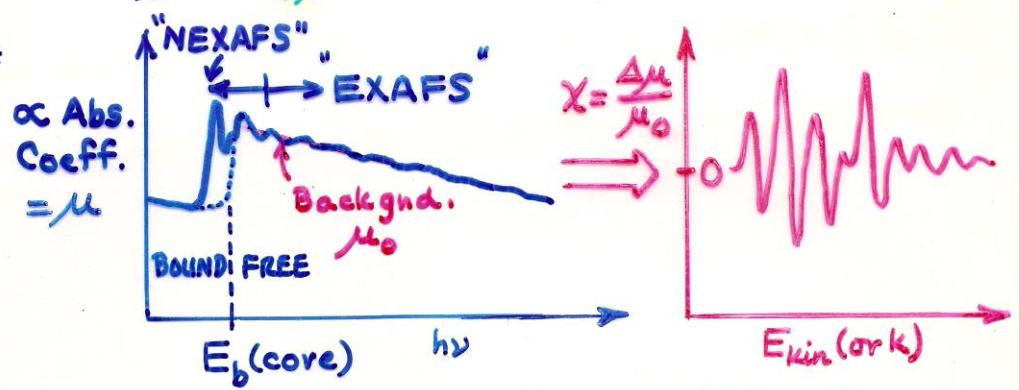
SEXAFS detection by: Auger yield.(CMA), $2° e^-$ yield, or Ions due to Photon stimu- lated desorption, or

(P.A. Lee et al., Rev. Mod. Phys. 53, 769 (1981))

X-ray Fluorescence (for adsorbates)

SINGLE SCATTERING PLUS DOUBLE SCAT-
TERING BACK TO EMITTER FROM A CLUSTER
OF ~20-100 ATOMS ABOUT EMITTER -

ϕ_o = DIRECT

SUM OVER ALL ϕ_1, ϕ_2, $I \propto |\phi_o + \Sigma\phi_1 + \Sigma\phi_2|^2$,

THEN OVER ALL (UNOBSERVED) $\vec{k}$ DIRECTIONS

$$\chi(k) = \frac{\Delta\mu}{\mu_o} = -\sum_j \frac{N_j}{k r_j^2} |f_j(k,\pi)| S_o'^2$$

$$\times \sin\left[2kr_j + \phi_j(k,\pi)\right] e^{-2\overline{u_j^2}k^2} e^{-2r_j/\Lambda_e(k)}$$

∴ FOURIER
TRANSFORM
OF $\chi(k)$
➡ PEAKS
AT ≈ $2r_j$
➡ BOND
DISTANCES

PHASES DUE TO: PATH LENGTH DIFF.   ELASTIC SCATT.   DEBYE-WALLER FACTOR   INELASTIC SCATT.

WITH: N_j = NO. SCATTERERS AT DISTANCE r_j.

$k = e^-$ WAVE VECTOR $= \sqrt{2mE'}/\hbar$

$|f_j(k,\pi)|$ = BACKSCATTERING AMPLITUDE

$\phi_j(k,\pi) = \psi_j(k,\pi) + 2\delta_l$ = OVERALL BACKSCATT. PHASE SHIFT

$S_o'^2$ = FRACTION FREE OF "SHAKE" $= |\langle\Psi_i|\Psi_R\rangle|^2$

$\overline{u_j^2}$ = MEAN-SQUARED VIBRATIONAL MOTION

$\Lambda_e(k)$ = INELASTIC MEAN FREE PATH

"NEAR-EDGE" =
XAS, XANES,
NEXAFS ← →"EXTENDED" = EXAFS
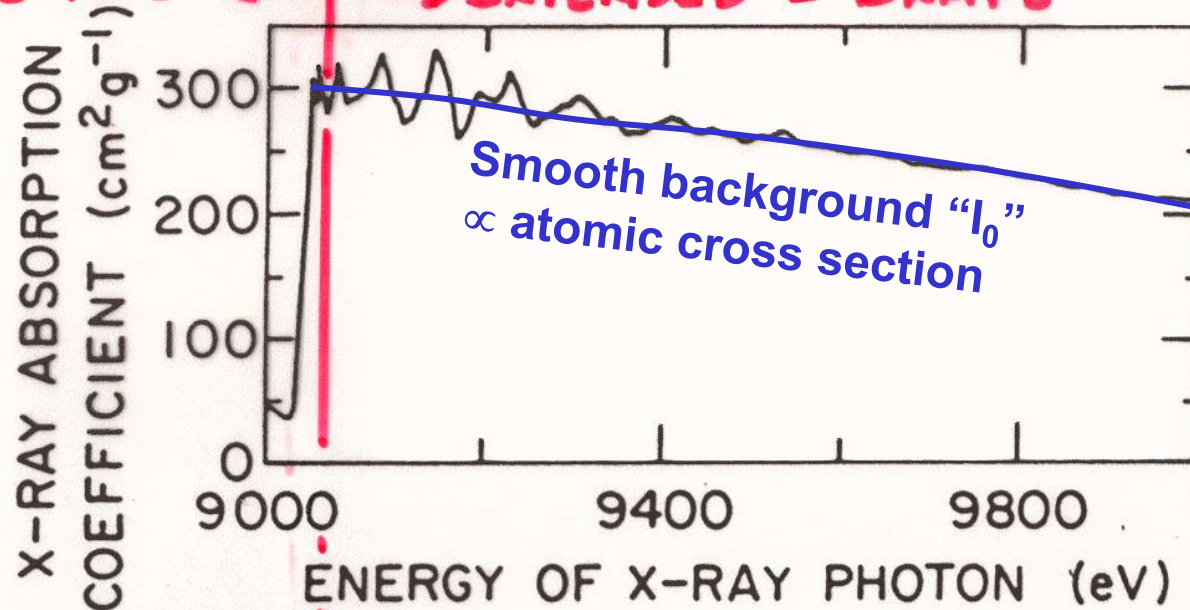
Smooth background "I_0"
$\propto$ atomic cross section

Figure 1.1. The x-ray absorption coefficient for the K-edge of copper metal.

~ COPPER
1S BINDING
ENERGY

Also scanned-energy, but integrates over all electron emission directions

133

EXAFS OF THE 1s SHELL OF COPPER
LEE & PENDRY, PHYS. REV. B **11**, 2795 (1975)

The quantum mechanics of covalent bonding in molecules: H_2^+ with one electron

$\varphi_- = \varphi_{antibonding}$
$\cong \varphi_{1sa} - \varphi_{1sb}$

$\varphi_+ = \varphi_{bonding}$
$\cong \varphi_{1sa} + \varphi_{1sb}$

$\varphi_{antibonding}$

proton *a*   proton *b*

R

total electron energy

Total Energy

0

Binding energy

Equilibrium separation $= R$

FIGURE 10.2 The net potential energy curve, showing the equilibrium separation and binding energy.

(*b*)

electron

?
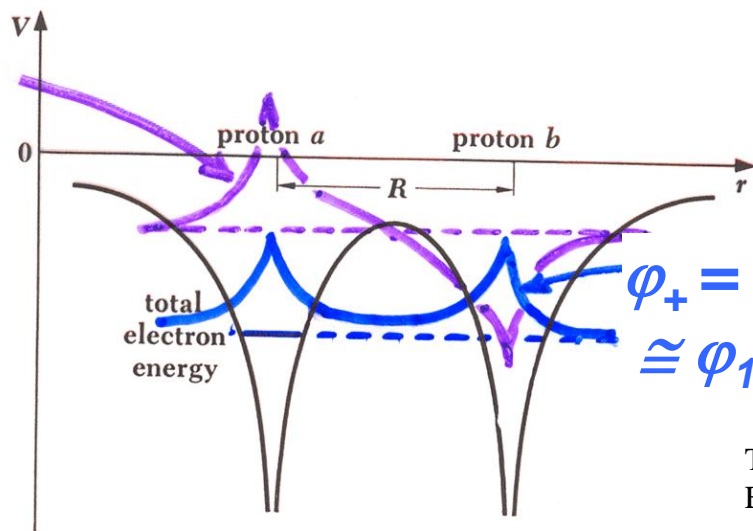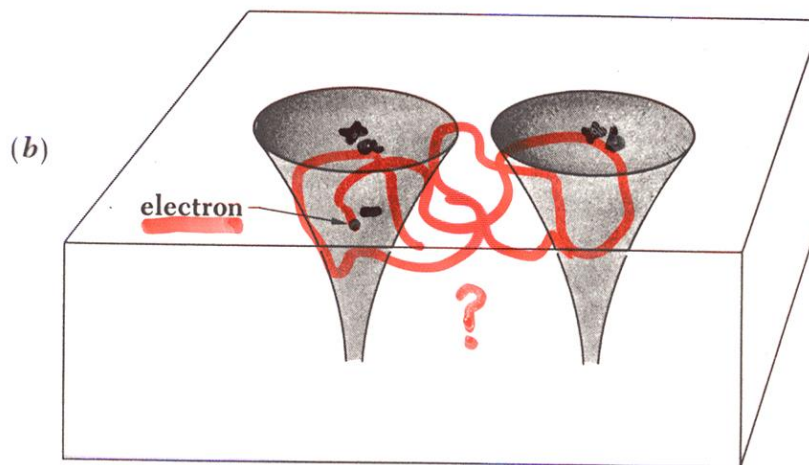
FIGURE 8.4 (*a*) Potential energy of an electron in the electric field of two nearby protons. The total energy of a ground-state electron in the hydrogen atom is indicated. (*b*) Two nearby protons correspond quantum-mechanically to a pair of boxes separated by a barrier.

135

1. Hydrogen

H_a H_b

Symmetry: $D_{\infty h}$
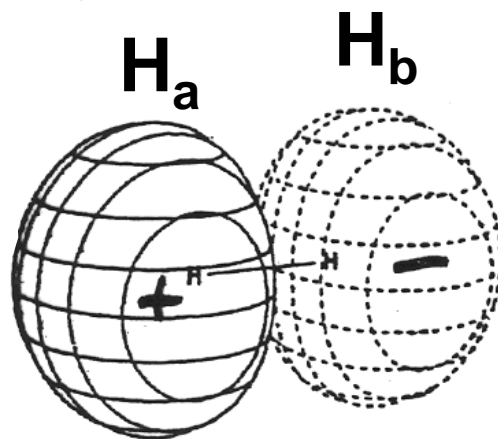
Anti-Bonding

$$\varphi_{anti}^{MO} \cong \varphi_{1sa} - \varphi_{1sa}$$

ε *positive*
(unoccupied)

$1\sigma_u$ $\varepsilon = 0.2656$ a.u. = +7.21 eV
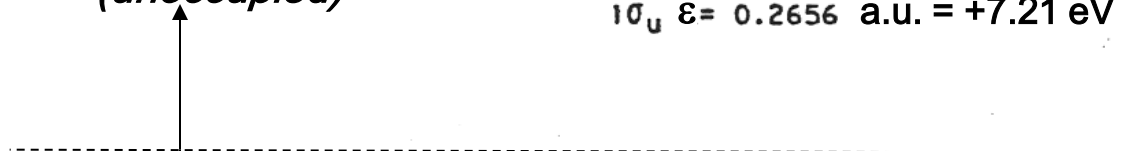
ε *negative*
(occupied)
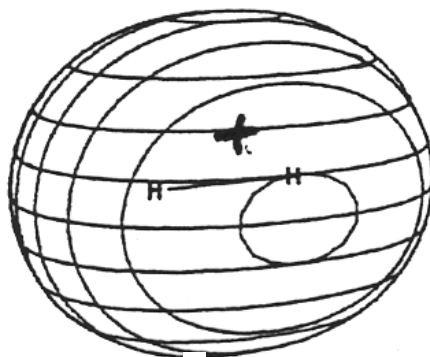
Bonding

$$\varphi_{bonding}^{MO} \cong \varphi_{1sa} + \varphi_{1sa}$$

$1\sigma_g$ $\varepsilon = -0.5944$ a.u. = -16.16 eV
(Compare – 13.61 for H atom 1s)   136

The LCAO or tight-binding picture for CO:

Atomic orbital makeup

$$\varphi_j^{MO}(\vec{r}) = \sum_{\substack{Atoms\ A \\ Orbitals\ i}} c_{Ai,j}\,\varphi_{Ai}^{AO}(\vec{r})$$

15. Carbon Monoxide   Symmetry: $C_{\infty v}$

— = φ_i NEG.
··· = φ_i POS.
ISOCONTOURS OF $|\varphi_i|^2$

(10)

$\varepsilon_k = +$ NO.

UNBOUND &
UNOCCUPIED

ANTI-
BONDING
2π
(8,9)

5σ

$6\,\varepsilon = 0.2755$

$2\sigma\ \varepsilon = 0.1268$

$2\pi\ \varepsilon = 0.1268$

BOUND &
OCCUPIED

BONDING 5σ
(7)

$5\sigma\ \varepsilon = -0.5544$

BONDING
1π
(×2)
(5,6)

$1\pi_y$ $1\pi_x$

$1\pi\ \varepsilon = -0.6395$ $1\pi\ \varepsilon = -0.6395$

NON/WEAKLY
BONDING 4σ
(4)

CORE:

$1\pi_x^2\ 1\pi_y^2$

$4\sigma\ \varepsilon = -0.8038$

NON/WEAKLY
BONDING 3σ
(3)

4σ

CO: $(O1s)^2(C1s)^2\,3\sigma^2\,4\sigma^2\,1\pi^4\,5\sigma^2$

$6\bar{e}\ 8\bar{e}$ $14e^-$

$3\sigma\ \varepsilon = -1.5210$

3σ

**Chemist's picture
(no core):**

$_x^x C_x^x {:}{:} O {:}$

C1s CORE
(2)

$2\sigma\ \varepsilon = -10.88$

O1s CORE
(1)

$1\sigma\ \varepsilon = -20.00$ a.u. (1 a.u. = 27.2 eV)

137
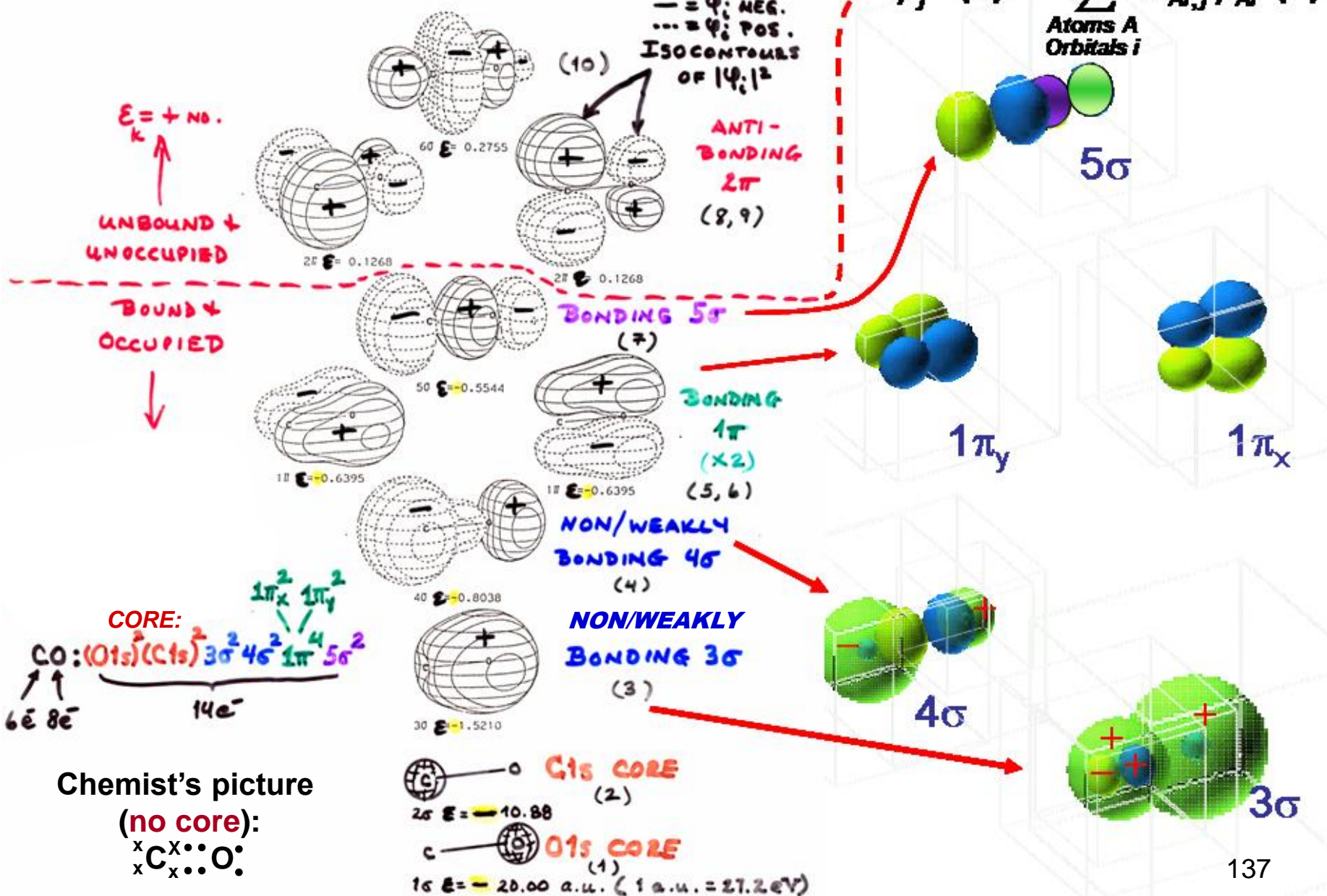
(9) **CO** Carbon Monoxide

UV PHOTOELECTRON SPECTRUM OF CO

+Vibrational (and rotational) excitations

e⁻ @ infinity

BONDING 5σ MO

BONDING π MO

NON-BONDING 4σ MO

e⁻

C-O ⟹ C-O⁺ **excited**

Photoelectric effect

Ionization Energy (eV)

138
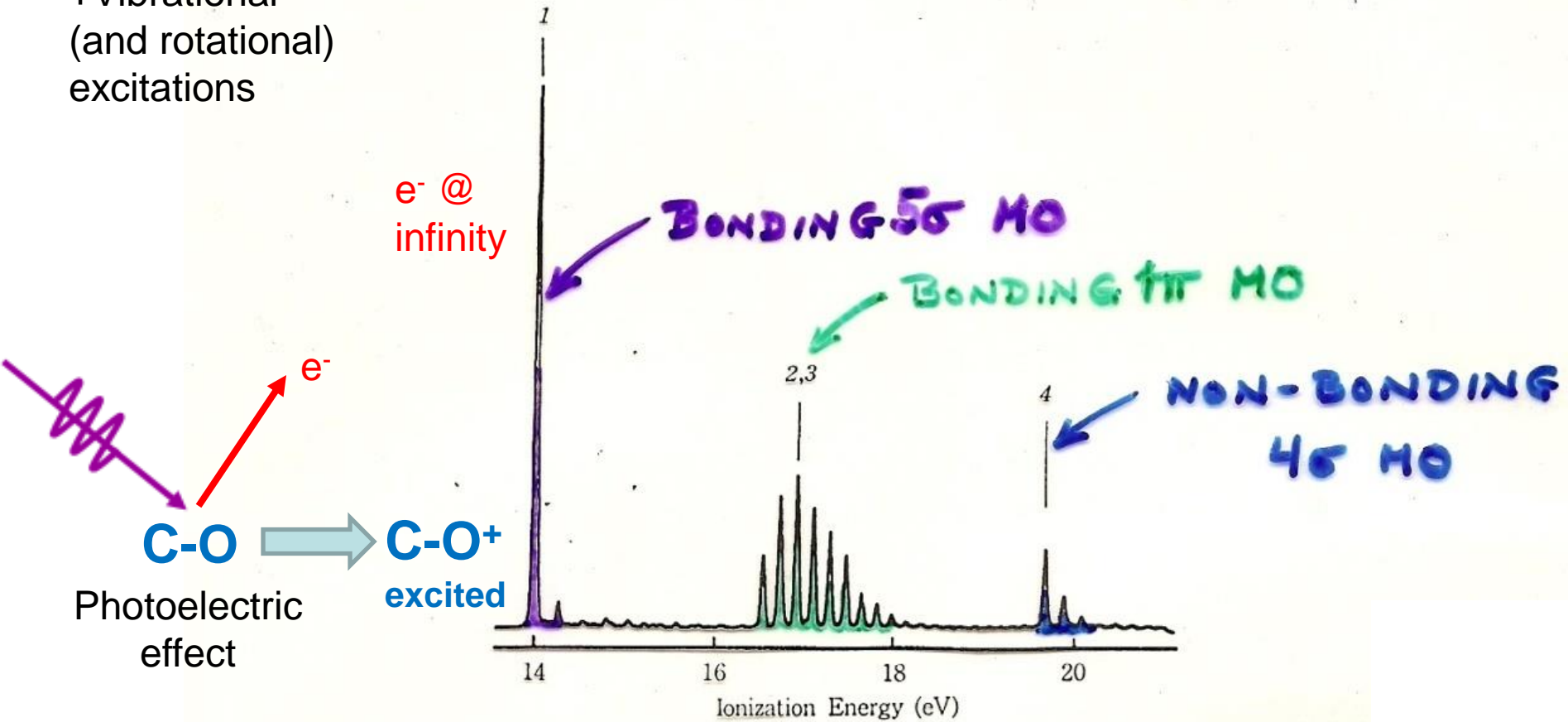
THE ELECTRONS IN HF (OR HCl): ionic molecules

10. Hydrogen Fluoride = HF   Symmetry: $C_{\infty v}$

MO's LIKE HCl

$2s, 2p \rightarrow$
$3s, 3p$
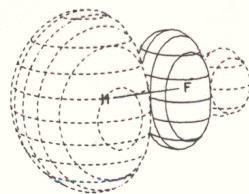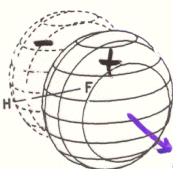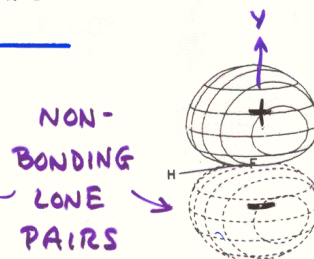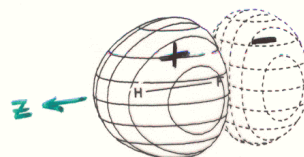
ANTI-BONDING (UNOCCUPIED)

4σ E= 0.2906

UNOCC.
OCC.

NON-BONDING LONE PAIRS

$\approx \psi_{2p_x}$

$\approx \psi_{F2p_y}$

1π E=-0.6505   1π E=-0.6505

→ 2π OF HCl (9)   → 2π OF HCl (8)

BONDING $\approx \psi_{H1s} + \psi_{F2p_z}$

But kind of the third "lone pair"

3σ E=-0.7685

→ 5σ OF HCl (7)

WEAKLY OR NON-BONDING $\approx \psi_{H1s} + \psi_{F2s}$

$1\sigma^2$

HF: **F1s^2**$2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2$

1 e$^-$ 9 e$^-$

Chemist's picture (no core):
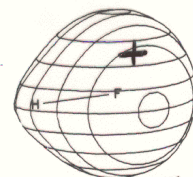
2σ E=-1.6013 (IN ATOMIC UNITS: 1 a.u. = 27.21 eV)

HF EIGENVALUE = ε_k

H $\overset{x}{\underset{\cdot\cdot}{\cdot}}$ F $\cdot\cdot$

Three "lone pairs"

H —⊜ F   **F 1s core**

1σ   E = -25.6 a.u.

PHOTOELECTRON EMISSION–
BASIC MATRIX ELEMENTS + SELECTION RULES:

● ATOMIC-LIKE (LOCALIZED) STATES ⇒ CORE:

$$\Psi_i(\vec{r}) = \Psi_{n_i \ell_i m_i}(r, \theta, \phi) = R_{n_i \ell_i}(r) Y_{\ell_i m_i}(\theta, \phi) \begin{cases} \end{cases}$$

PLUS SPIN:
$$\begin{cases} \alpha(\sigma) = m_{si} = +\tfrac{1}{2} = \uparrow \\ \beta(\sigma) = m_{si} = -\tfrac{1}{2} = \downarrow \end{cases}$$

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

PHASE SHIFT OF ℓ_f WAVE IN $V(r)$

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

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

$\langle \Delta\ell = \ell_f - \ell_i = \pm 1$ TWO CHANNELS

$\langle \Delta m = m_f - m_i = 0, \pm 1$ LINEAR POLARIZ.

$\langle \Delta m = \pm 1$, CIRCULAR POLARIZATION

EQUIVALENT WITHIN CONSTANT FACTOR
$$\left(\begin{array}{c} \vec{P} \\ \vec{\nabla} V(r) \end{array} \right.$$

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

+ with spin-orbit:
$\Delta j = 0, \pm 1$

PHOTOELECTRON EMISSION —
BASIC MATRIX ELEMENTS + SELECTION RULES:

● ATOMIC-LIKE (LOCALIZED) STATES ⇒ CORE:

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

PLUS SPIN:
$$\begin{cases} \alpha(\sigma) = m_{si} = +\tfrac{1}{2} = \uparrow \\ \beta(\sigma) = m_{si} = -\tfrac{1}{2} = \downarrow \end{cases}$$

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

PHASE SHIFT OF ℓ_f WAVE IN $V(r)$

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

$\hat{\varepsilon}$ $\psi_f = \phi_e$ $\vec{k}_f = \dfrac{\vec{P}_f}{\hbar}$ $V(r)$

DIPOLE APPROX:
$$\text{INT.} \propto \left| \langle \psi_f | \hat{\varepsilon} \cdot \vec{r} | \psi_i \rangle \right|^2 = \left| \hat{\varepsilon} \langle \psi_f | \vec{r} | \psi_i \rangle \right|^2 \Rightarrow$$

$$\begin{aligned} &\Delta\ell = \ell_f - \ell_i = \pm 1 \quad \text{TWO CHANNELS} \\ &\Delta m = m_f - m_i = 0, \pm 1 \quad \text{LINEAR POLARIZ.} \\ &\Delta m = \pm 1, \text{CIRCULAR POLARIZATION} \end{aligned}$$

EQUIVALENT WITHIN CONSTANT FACTOR $\begin{cases} \vec{P} \\ \vec{\nabla}V(r) \end{cases}$

$\Delta m_s = m_{sf} - m_{si} = 0\,!$ + with spin-orbit: $\Delta j = 0, \pm 1$

● BLOCH-FUNCTION (DELOCALIZED) STATES ⇒ VALENCE:
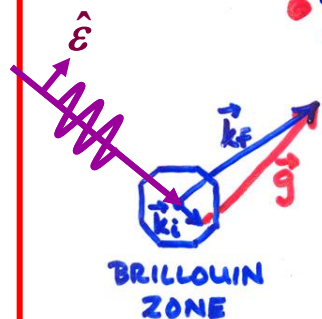
$$\psi_i(\vec{r}) = u_{\vec{k}_i}(\vec{r})\, e^{i\vec{k}_i \cdot \vec{r}}$$

$$\psi_f(\vec{r}) = u_{\vec{k}_f}(\vec{r})\, e^{i\vec{k}_f \cdot \vec{r}} \,; \quad E_f = \frac{P_f^2}{2m} = \frac{\hbar^2 k_f^2}{2m}$$ USUALLY NEGLIG.

$\hat{\varepsilon}$ $\vec{k}_f$ $\vec{g}$ $\vec{k}_i$ BRILLOUIN ZONE

$$\left| \langle \psi_f | \hat{\varepsilon} \cdot \vec{P} | \psi_i \rangle \right|^2 = \left| \hat{\varepsilon} \cdot \langle \psi_f | \vec{P} | \psi_i \rangle \right|^2 \Rightarrow \Delta\vec{k} = \vec{k}_f - \vec{k}_i - \vec{k}_{h\nu} + \vec{k}_{\text{PHONON}}$$

$$= \vec{g}_{\text{BULK}} \ (\text{OR } \vec{g}_{\text{SURF}})$$

"DIRECT" TRANSITIONS

BUT LATTICE VIBRATIONS ⇒ SUM OVER $\vec{k}_{\text{PHONON}}$

⇒ FRACTION DIRECT ≈ DEBYE-WALLER FACTOR

$$\approx \exp[-g^2 \overline{u^2}]$$

"Basic Concepts of XPS"
Chapter 3

The free-electron solid at absolute zero

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m_e} = 3.81(k(in\,\text{Å}^{-1}))^2 \ (in\ eV)$$

E

@T=0

E_F^o

a   0   1   f(E):

FERMI-
DIRAC

$$f(E,T) = \frac{1}{e^{(E-E_F^o)/k_B T} + 1}$$

E

NO. e^-/UNIT VOLUME
(VALENCE ONLY)

$$\frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} = \frac{\hbar^2 k_F^2}{2m_e}$$

E_F^o

$$n = \int_0^{E_F^o} D(E)\,f(E)\,dE = 1$$
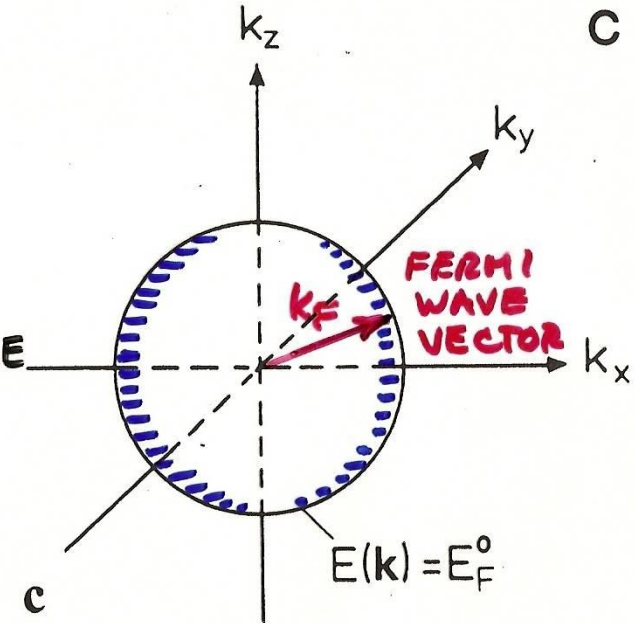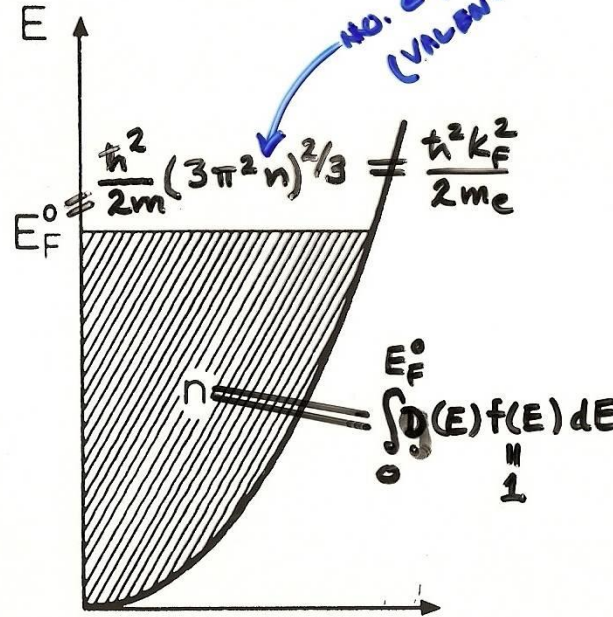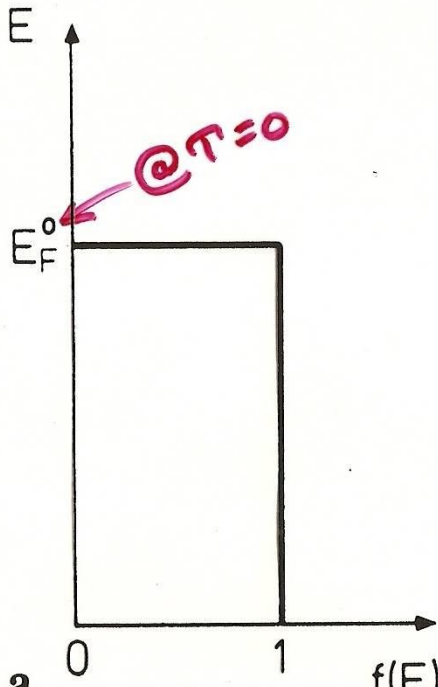
b   D(E)·f(E)

$$\frac{(2m)^{3/2}}{2\pi^2 \hbar^3} E^{1/2}$$

= the density of states

k_z C

k_y

FERMI
WAVE
VECTOR

k_F k_x

$E(k) = E_F^o$

c

$$k_F = (3\pi^2 n)^{1/3}$$

$$v_f = \hbar k_f / m_e$$

EXTENDED ZONE:

$$V(\vec{r}) = \sum_{g} U_{g} \, e^{i\vec{g}\cdot\vec{r}}$$

$$E(\vec{k}) \approx \frac{\hbar^2 k^2}{2m} + \text{gaps}$$

$$\vec{k}_f = \vec{k}_i + \vec{g} \begin{cases} \psi_f(\vec{r}) = u_{\vec{k}_f}(\vec{r})\, e^{i\vec{k}_f\cdot\vec{r}} \\[2mm] \varphi_i(\vec{r}) = u_{k_i}(\vec{r})\, e^{i\vec{k}_i\cdot\vec{r}} \end{cases}$$

$E(\vec{k})$

$2|U_{3g}|$

$2|U_{2g}|$

$2|U_{g}|$

$-\vec{g}$

$\vec{g}$

$\vec{k}_f$

$\vec{k}_i$

$-\vec{g}$ 0 $\vec{g}$

$\vec{k}$

$E(\vec{k})$

143

EXTENDED ZONE:

$$V(\vec{r}) = \sum_{\vec{g}} U_{\vec{g}}\, e^{i\vec{g}\cdot\vec{r}}$$

$$E(\vec{k}) \approx \frac{\hbar^2 k^2}{2m} + \text{gaps}$$

$$\psi_f(\vec{r}) = u_{\vec{k}_f}(\vec{r})\, e^{i\vec{k}_f\cdot\vec{r}}$$

$$\vec{k}_f = \vec{k}_i + \vec{g}$$

$$\varphi_i(\vec{r}) = u_{\vec{k}_i}(\vec{r})\, e^{i\vec{k}_i\cdot\vec{r}}$$

$2|U_{3g}|$

$2|U_{2g}|$

$2|U_g|$

$-\vec{g}$ $\vec{g}$

$-\vec{g}$ 0 $\vec{g}$
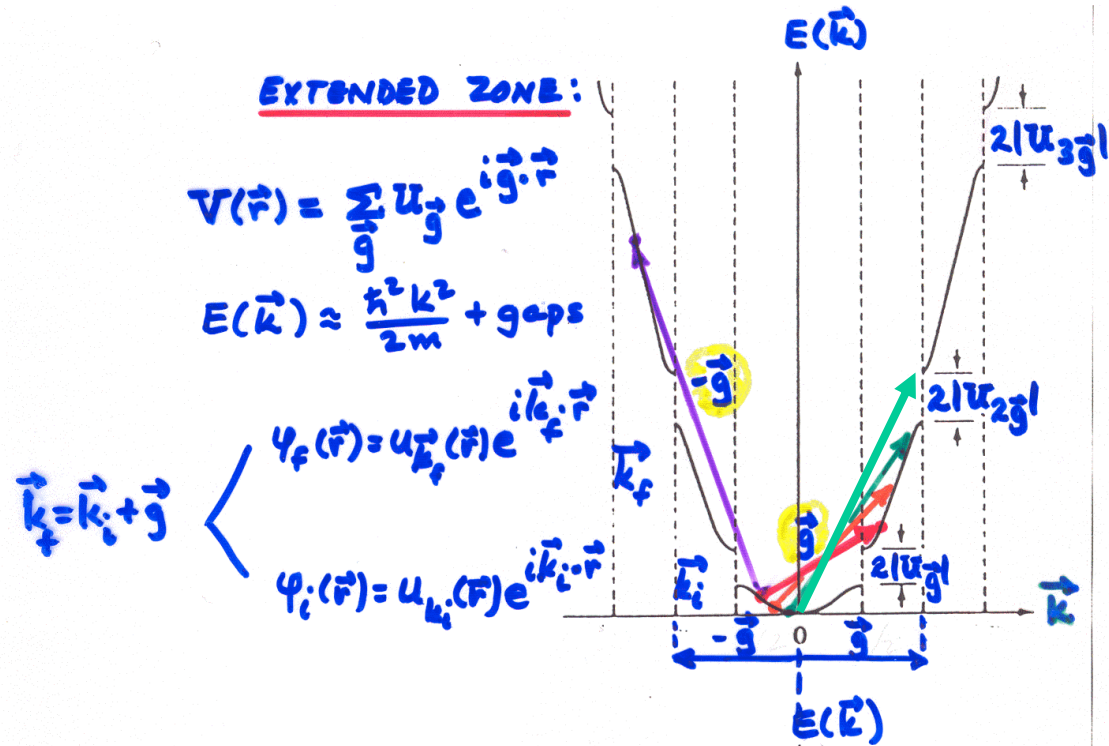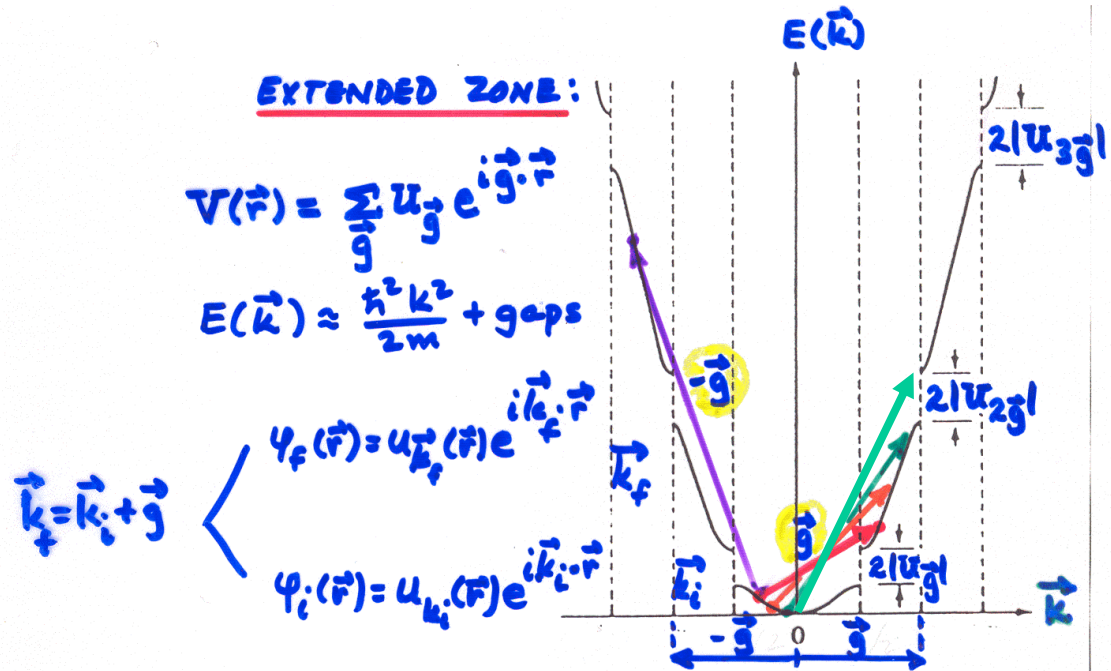
REDUCED ZONE:
= FIRST BRILLOUIN ZONE

DIRECT TRANSITIONS VERTICAL

INCREASING $h\nu$

0 = Γ

144

[001]

L   [111]

[110]

RECIPROCAL
LATTICE
POINTS
($\vec{g}$'s)
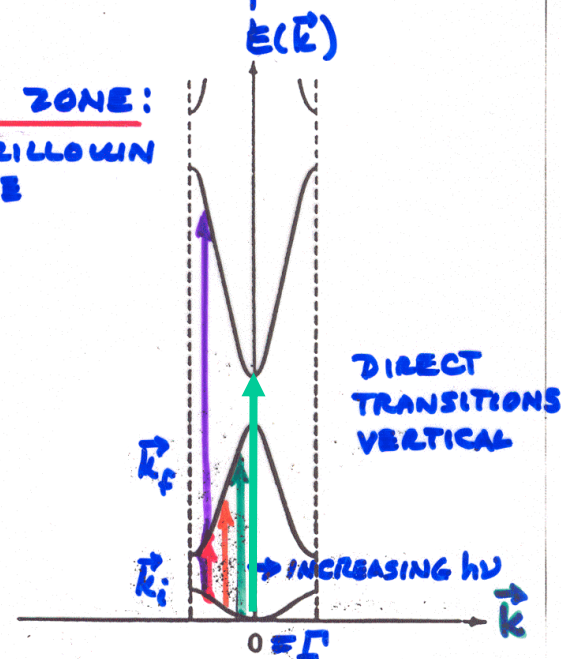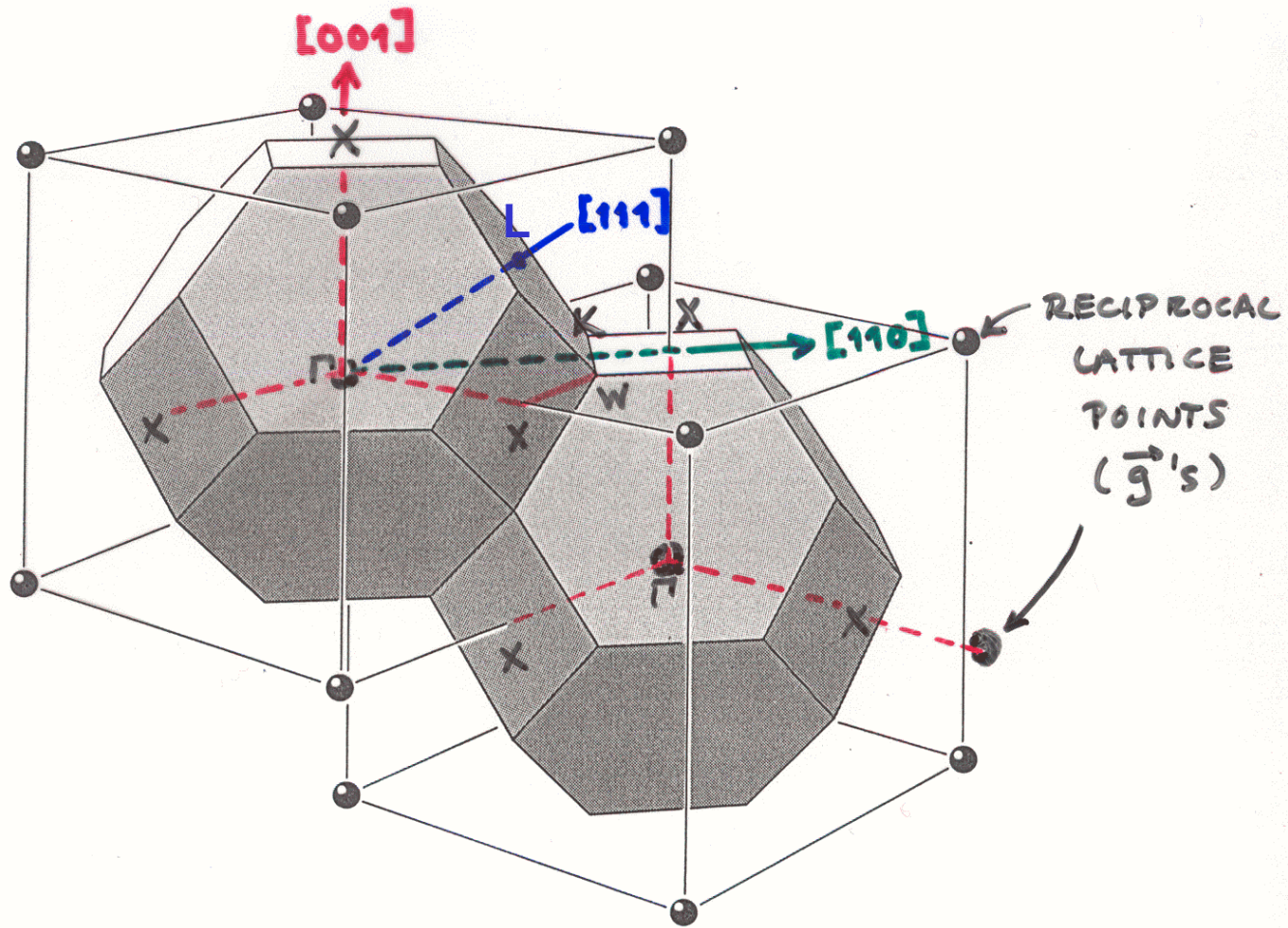
Figure 28 Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body-centered, as drawn.

— STACKING OF fcc BRILLOUIN ZONES —

Electronic bands and density of states for "free-electron" metals -

Rydberg = 13.605 eV

Aluminum—fcc,
a = 4.05 Å
$1s^2 2s^2 2p^6 3s^2 3p^1$

Lithium—bcc, a = 3.49 Å
$1s^2 2s^1$

D.O.S.

$\propto E^{1/2}$ FREE e⁻

DENSITY OF STATES (STATES/EV) (-)

ENERGY RELATIVE TO FERMI ENERGY (EV)

$E(\vec{k})$ ENERGY (RY)

ENERGY (RY)

"GAP"

$E(k_x) \approx \dfrac{\hbar^2 (k_x)^2}{2m}$

$\dfrac{2\pi}{a} = 1.55\text{Å}^{-1}$

E_F

E (Ryd)

$E(k_x) \approx \dfrac{\hbar^2 (k_x)^2}{2m}$

$k_x \longrightarrow$

$\dfrac{2\pi}{a} = 1.8\text{Å}^{-1}$
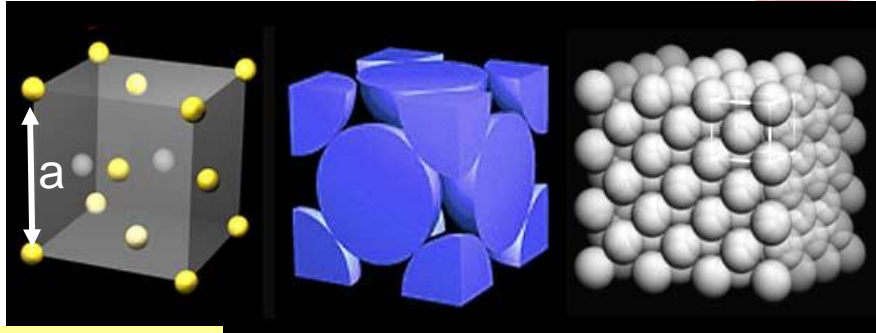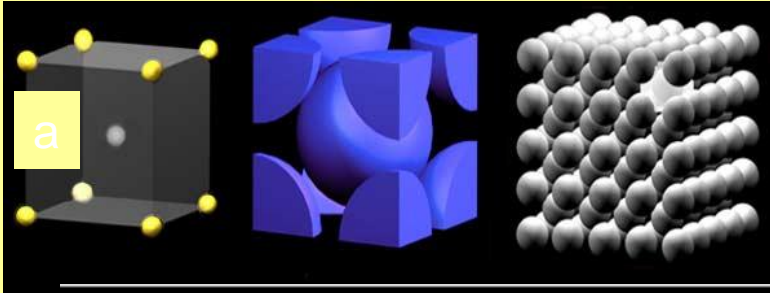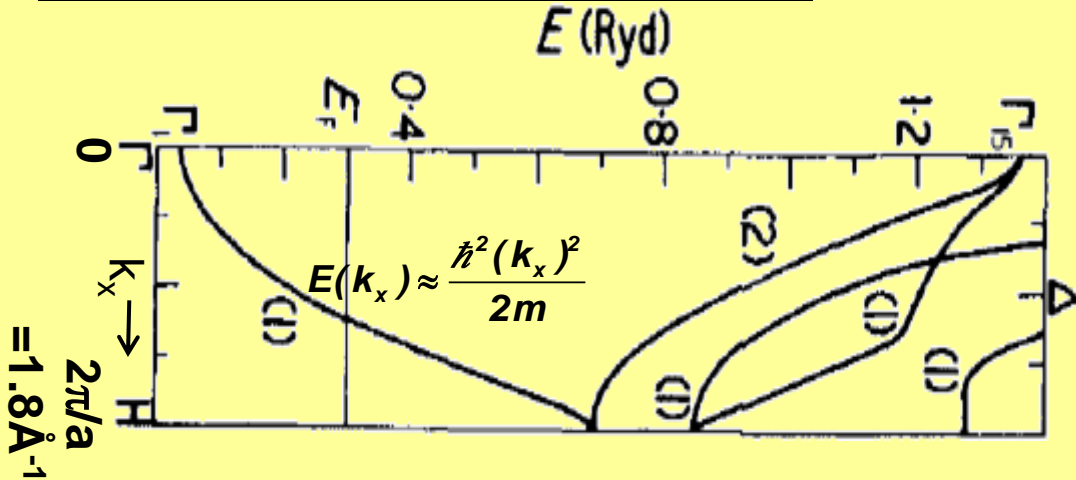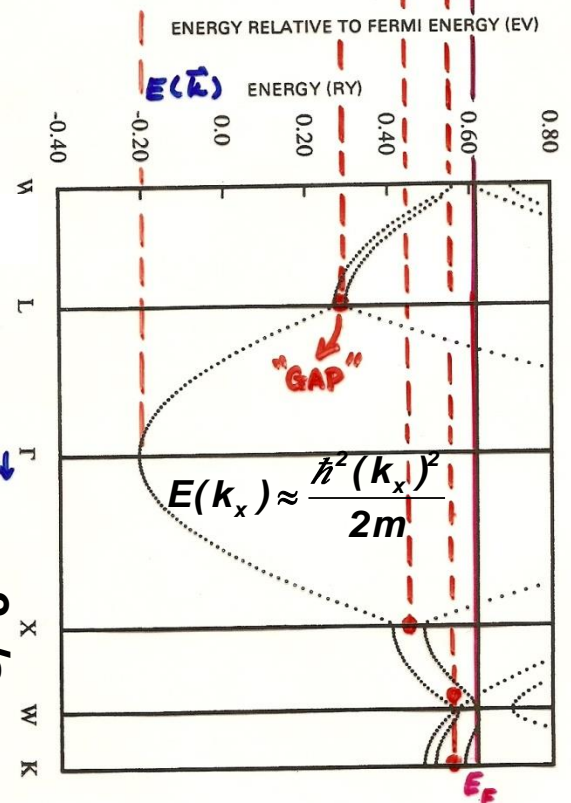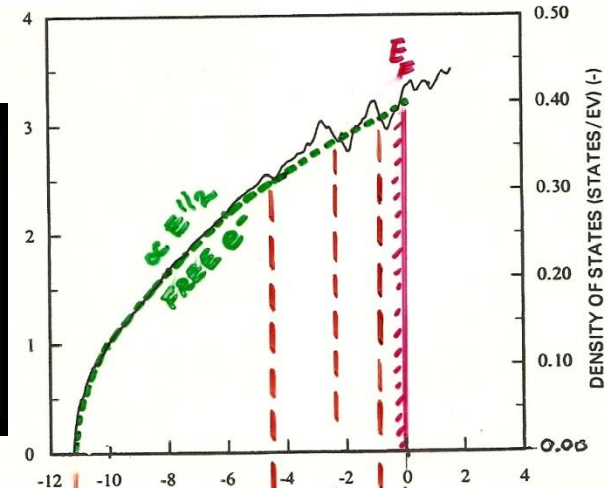
Electronic bands and density of states for a <u>semiconductor</u>-Germanium—
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$

Vacuum Level

Work Function, $\varphi = 4.8$ eV

E_F

Inner Potential, $V_0 \approx 4.8 + 0.3 + 12.6 = 17.7$ eV

Anti-Bonding (empty at T = 0)

Bonding (filled at T = 0)
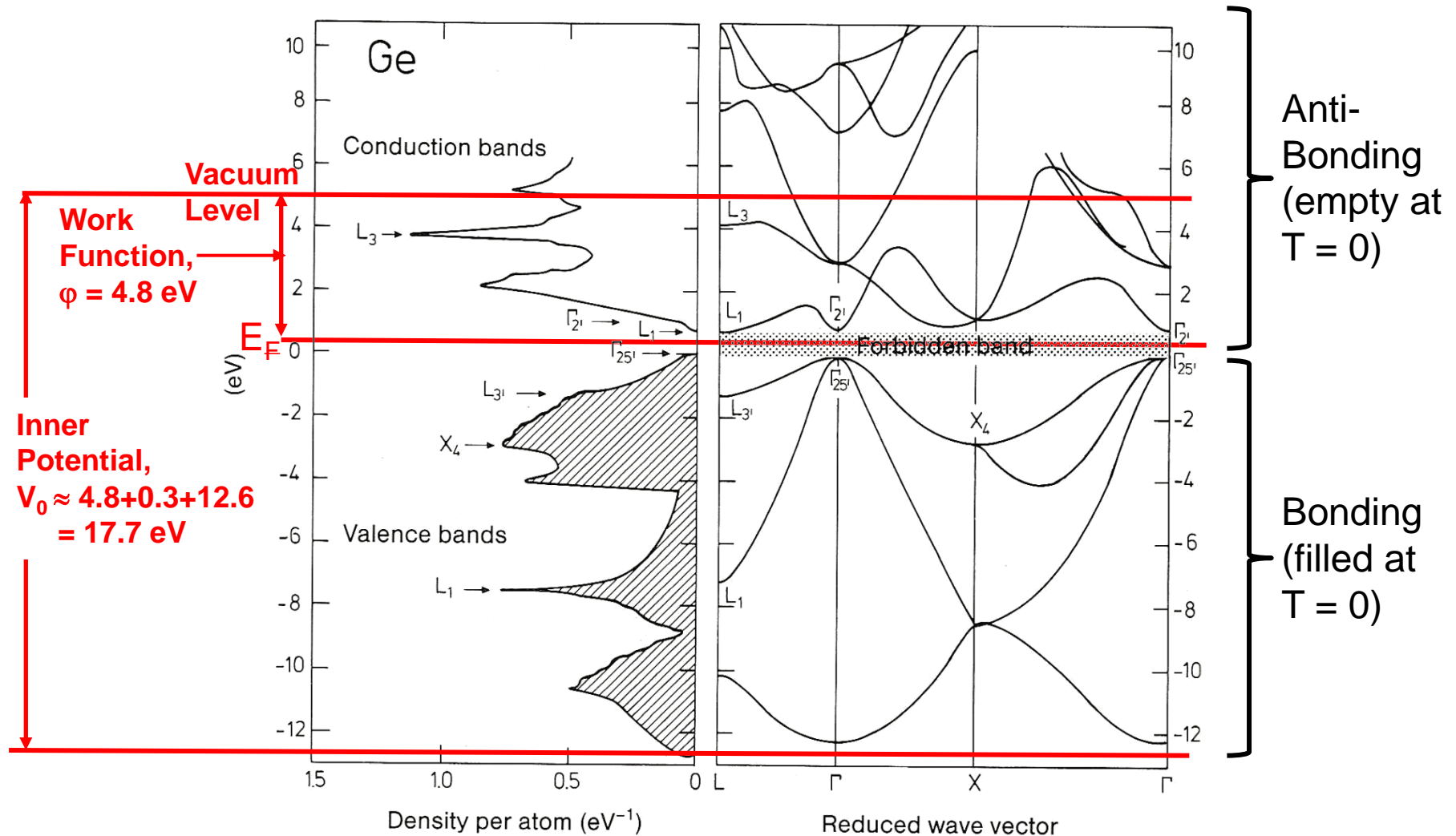
The electronic structure of a transition metal —fcc Cu

Vacuum level

ϕ_{Cu} = 4.4 eV = work function

$V_{0,Cu}$ =13.0eV

Energy (e

- 8.6 eV
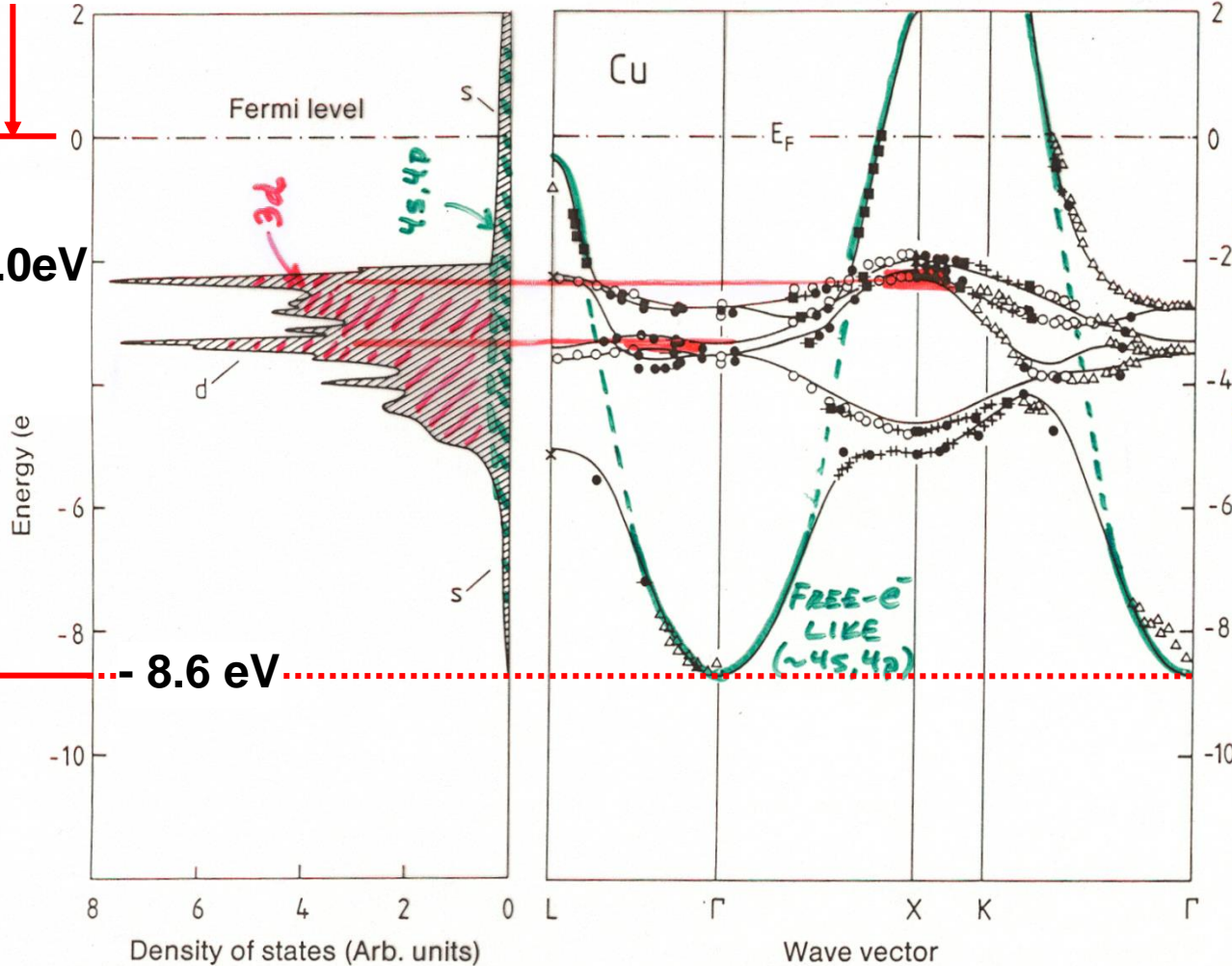
Cu $1s^2$.....$3d^{10}4s^1$

ELECTRONIC BANDS + DENSITY OF STATES

MIXING

3d LIKE

MIXING

FREE-e^- LIKE (~4s,4p)

Fermi level

E_F

Cu

L   Γ   X K   Γ

Density of states (Arb. units)

Wave vector

Experimental points from angle-resolved photoelectron spectroscopy (more later)

Fig. 7.12. Bandstructure $E(k)$ for copper along directions of high crystal symmetry (*right*). The experimental data were measured by various authors and were presented collectively by Courths and Hüfner [7.4]. The full lines showing the calculated energy bands and the density of states (*left*) are from [7.5]. The experimental data agree very well, not only among themselves, but also with the calculation

Atomic orbital makeup

$$\varphi_j^{MO}(\vec{r}) = \sum_{\substack{Atoms\ A \\ Orbitals\ i}} c_{Ai,j}\varphi_{Ai}^{AO}(\vec{r})$$

Solid state tight-binding approach

Molecular orbital approach

5σ

$1\pi_y$ $1\pi_x$

4σ

3σ

Crystal potential-1D

$\vec{R}_j$

$j-1$ j $j+1$

$V(x)$

Energy level

(a)

Atomic orbitals

φ_{j-1} φ_j φ_{j+1}

$j-1$ j $j+1$

(b)

Tight-binding wave function

(c)

$E(k)$

E_j

4γ

Anti-Bonding

Bonding

$-\pi/a$ π/a k
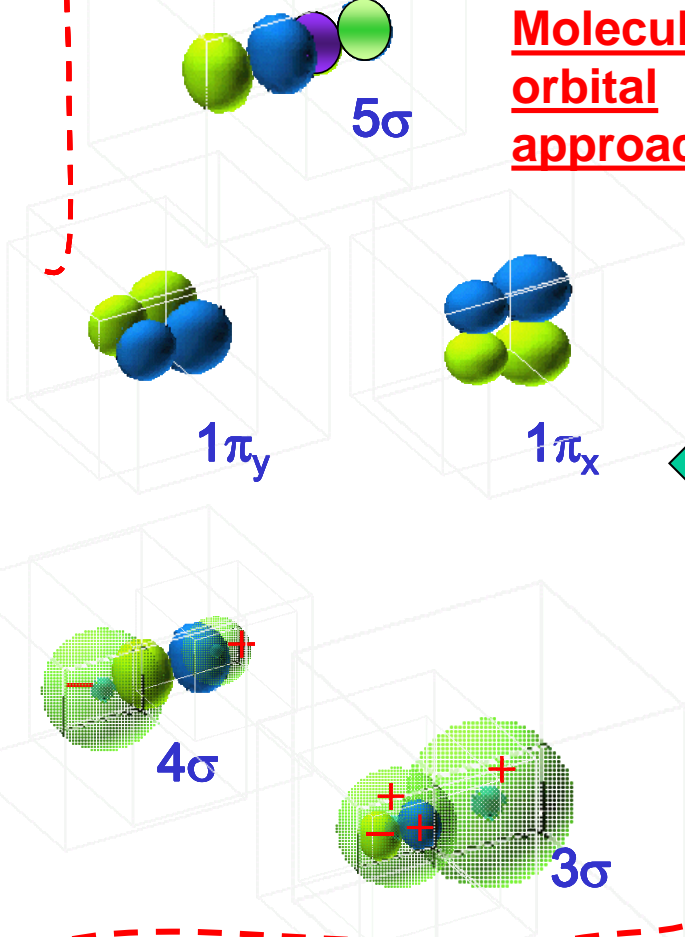
$\varphi_{\vec{k}}^{BF}(\vec{r}) = a$ Bloch function

$$\propto \frac{1}{N^{1/2}} \sum_{\substack{j = 1.....N\ unit\ cells\ at\ \vec{R}_j}} e^{i\vec{k}\bullet\vec{R}_j} \sum_{\substack{Ai = basis\ set\ of\ AOs \\ in\ unit\ cell}} c_{Ai,\vec{k}}\varphi_{Ai}^{AO}(\vec{r} - \vec{R}_j)$$

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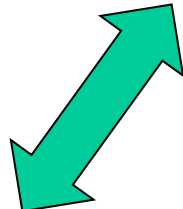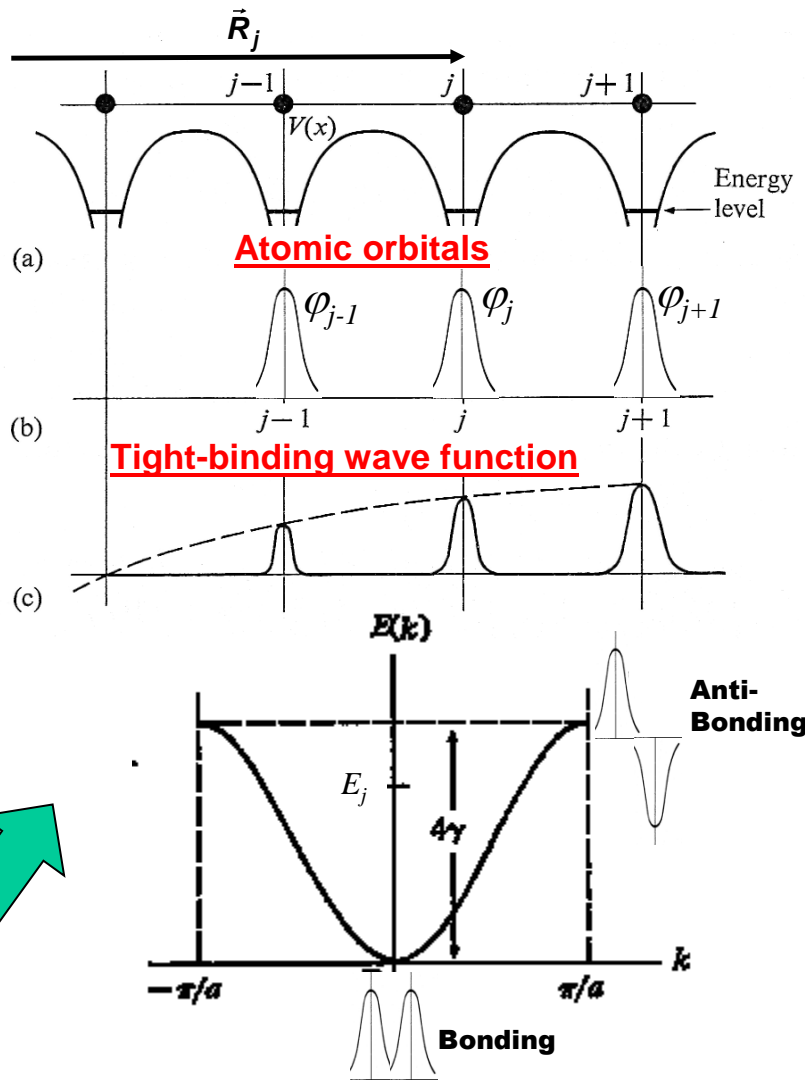
And for the real d orbitals in fcc:

e_g

$3z^2 - r^2$
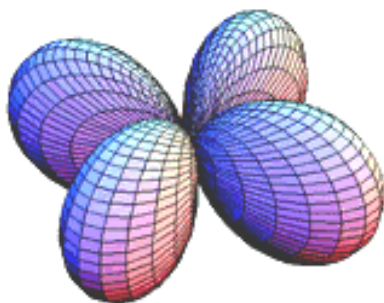
$x^2 - y^2$

t_{2g}

yz   *zx*   *xy*

Ligand (e.g. O)

z

y

x

Transition Metal (e.g. Mn)

e_g and t_{2g} not equivalent in octahedral (cubic) environment

z

zx

xy

y

x

yz
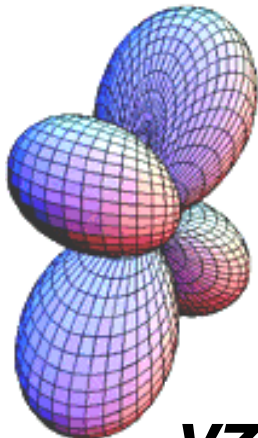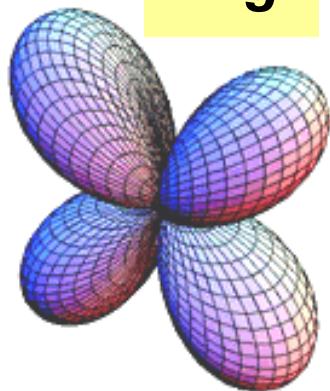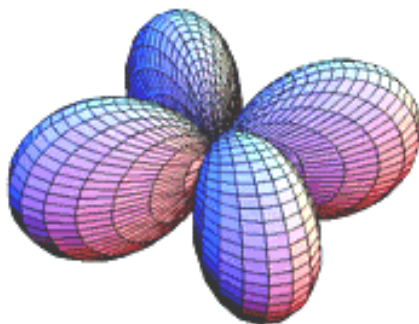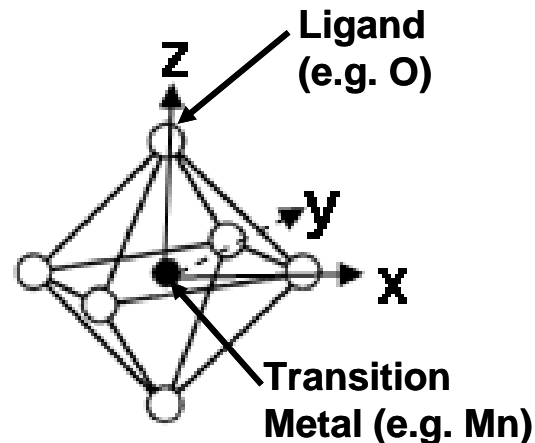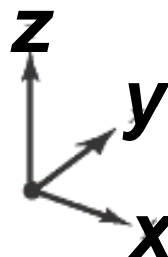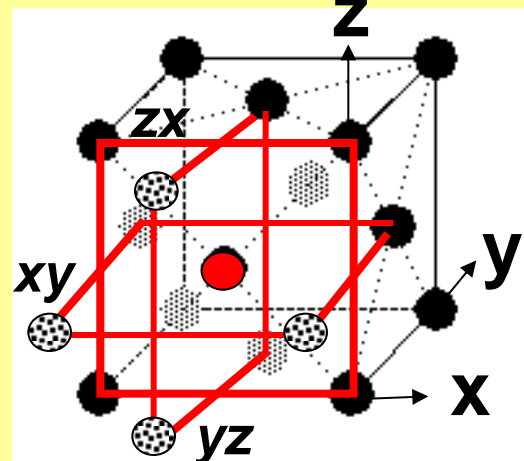
Face-centered cubic— t_{2g} pointing at 12 nearest neighbors

150

Copper densities of states-total and by orbital type:
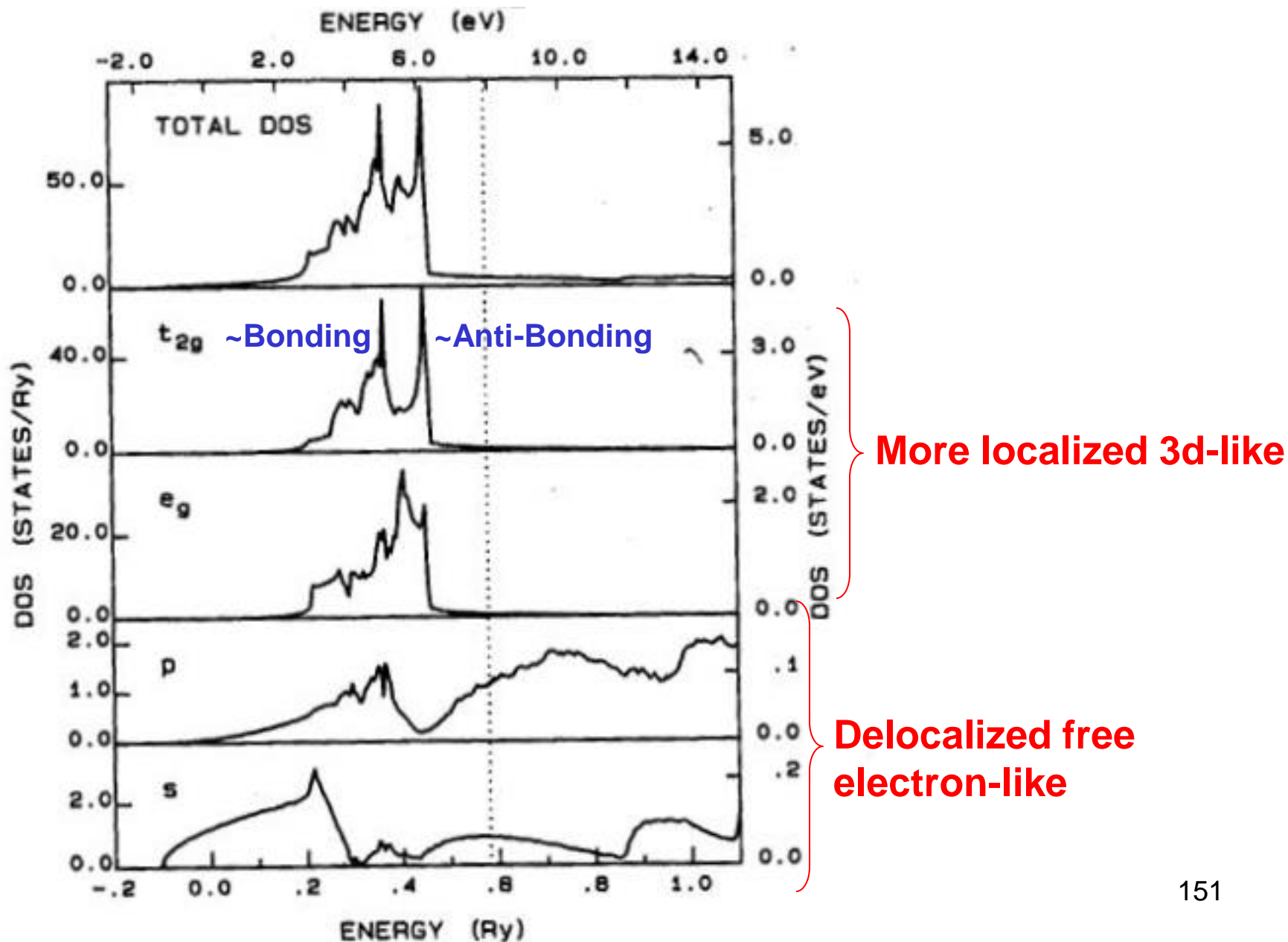
The electronic structures of the 3d transition metals— ≈ "rigid-band model"

3s²3p⁶ filled +   3d,4s CB   3d²4s²   3d³4s²   3d⁵4s¹   3d⁶4s²
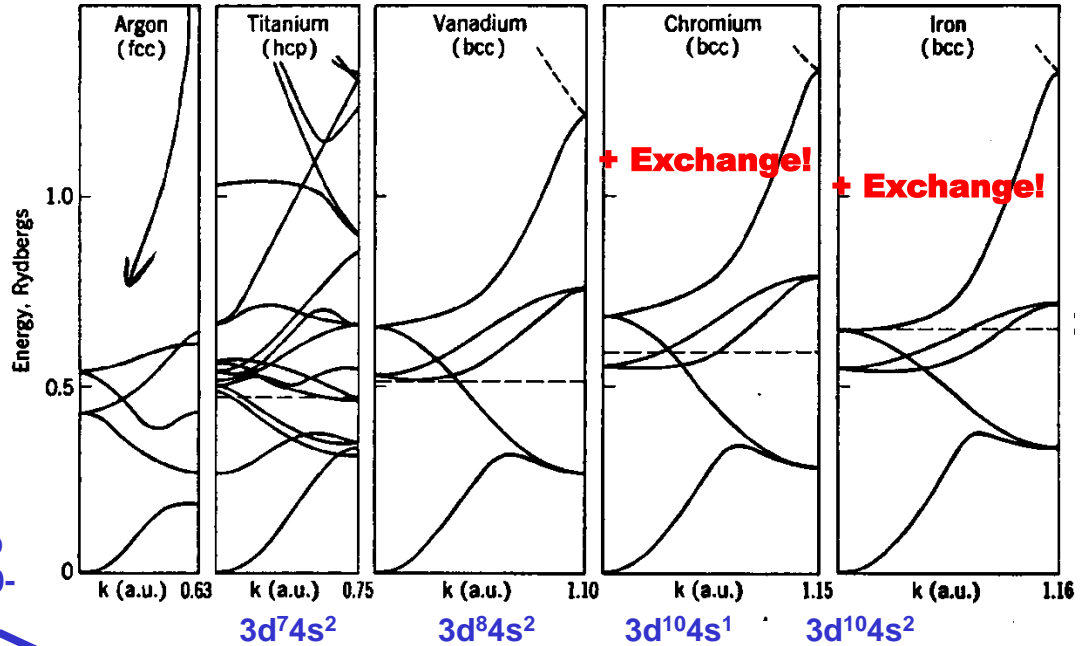
+ Flat "core-like" Ar 3s, 3p bands at ~-1.0-1.5 Rydbergs

+ Exchange!   + Exchange!

3d⁷4s²   3d⁸4s²   3d¹⁰4s¹   3d¹⁰4s²

+ Exchange!   + Exchange!

+ Flat "core-like" Zn 3d bands at ~-0.8 Rydberg

FIG. 10-20.   Energy bands of 3d transition elements, along a single direction, from Mattheiss.

The electronic bands and densities of states of ferromagnetic iron
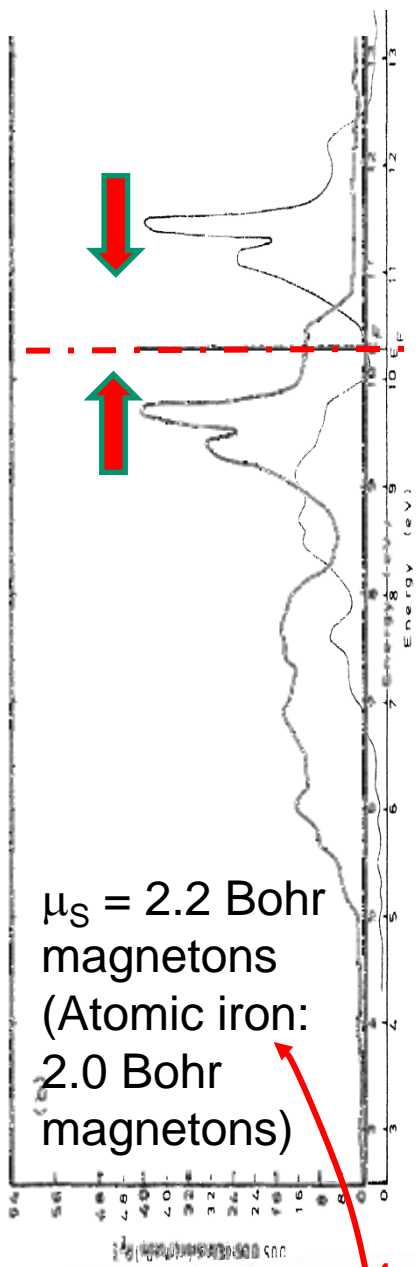
μ_S = 2.2 Bohr magnetons (Atomic iron: 2.0 Bohr magnetons)
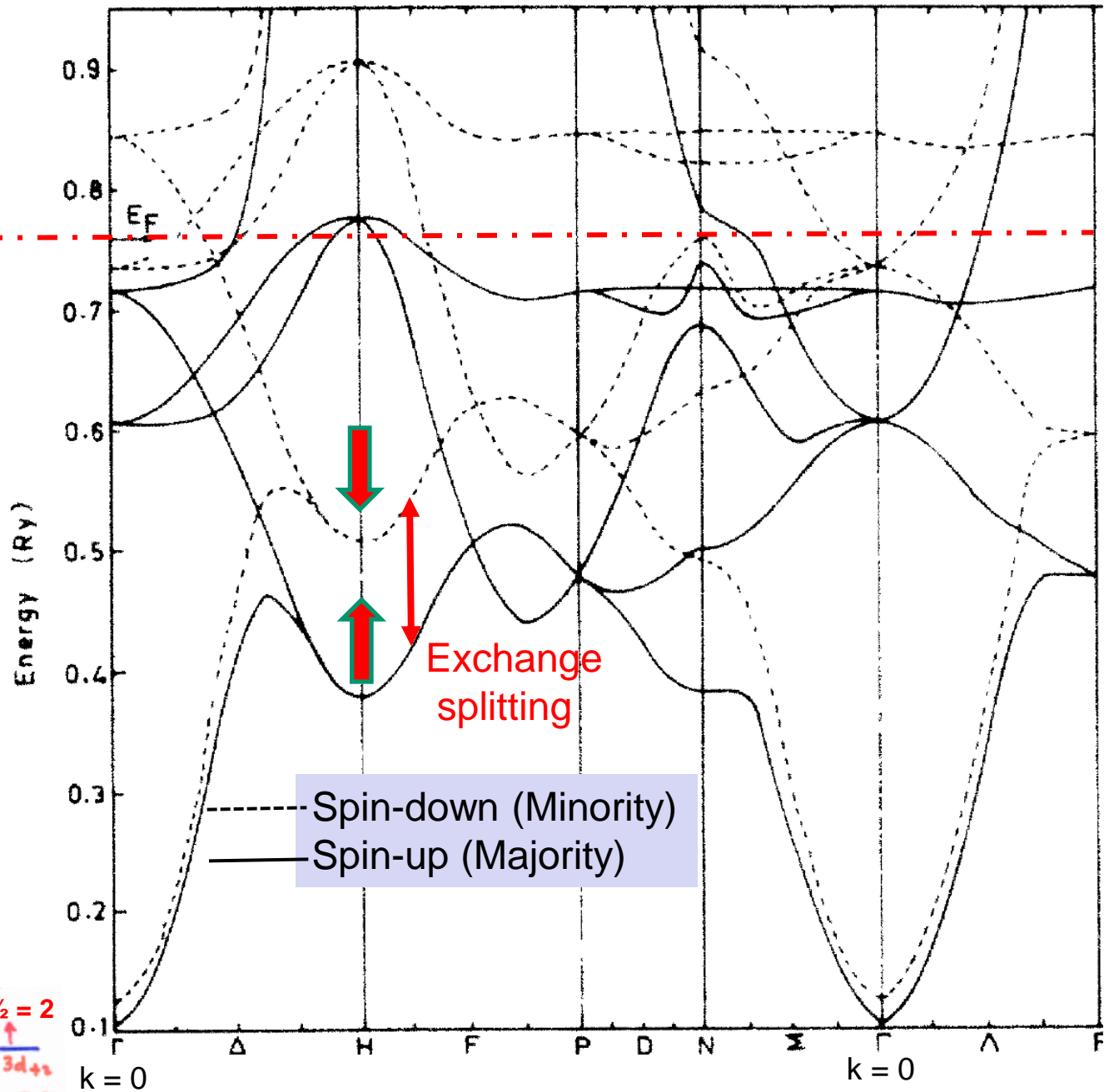
Exchange splitting

------ Spin-down (Minority)
———— Spin-up (Majority)

ε_F

Energy (Ry)

Γ   Δ   H   F   P   D   N   Σ   Γ   Λ   F

k = 0   k = 0

Fe $1s^2 2s^2 2p^6 3s^2 3p^6$
    $3d^6 4s^2$

$3d_{-2}$ $3d_{-1}$ $3d_0$ $3d_{+1}$ $3d_{+2}$

⟹ LARGE μ_{3d} + MAGNETISM

4 × ½ = 2

FIG. 4. Density of states at the equilibrium lattice constant of Fe for majority- (solid line) and minority- (broken line) spin states.

Hathaway et al., Phys. Rev. B 31, 7603 ('85)

Fe (001)

SPIN-RESOLVED BAND STRUCTURE OF A FERROMAGNET

THEORY:

ϕ_{Fe} = 4.3 eV

$V_{0,Fe}$ = 12.4 eV

Vacuum level

ΔE_{exch}

-8.1 eV

hv (eV)

$\Gamma_{12'}$
$\Gamma_{25'}$
$\Gamma_{12\downarrow}$
Δ_{ex}

H_{25}'
H_{12}

E_F

Energy (eV)

$k_\perp$(Å^{-1})

Γ   Δ   H

E. KISKER ET AL., PHYS. REV. B 31, 329 (1985)

Fe: ANGLE AND SPIN-RESOLVED SPECTRA AT Γ POINT

EXPT.

Fe (100)
$h\nu = 60$ eV

▲ ▼ $T/T_c = 0.3$ (ROOM TEMP.)
▲ ▼ $T/T_c = 0.85$

$\Gamma_{25}'^{\uparrow\downarrow}$

$\Gamma_{25}'^{\uparrow}$

$\Gamma_{12}^{\uparrow}$

"EXTRAORDINARY PEAK"
?
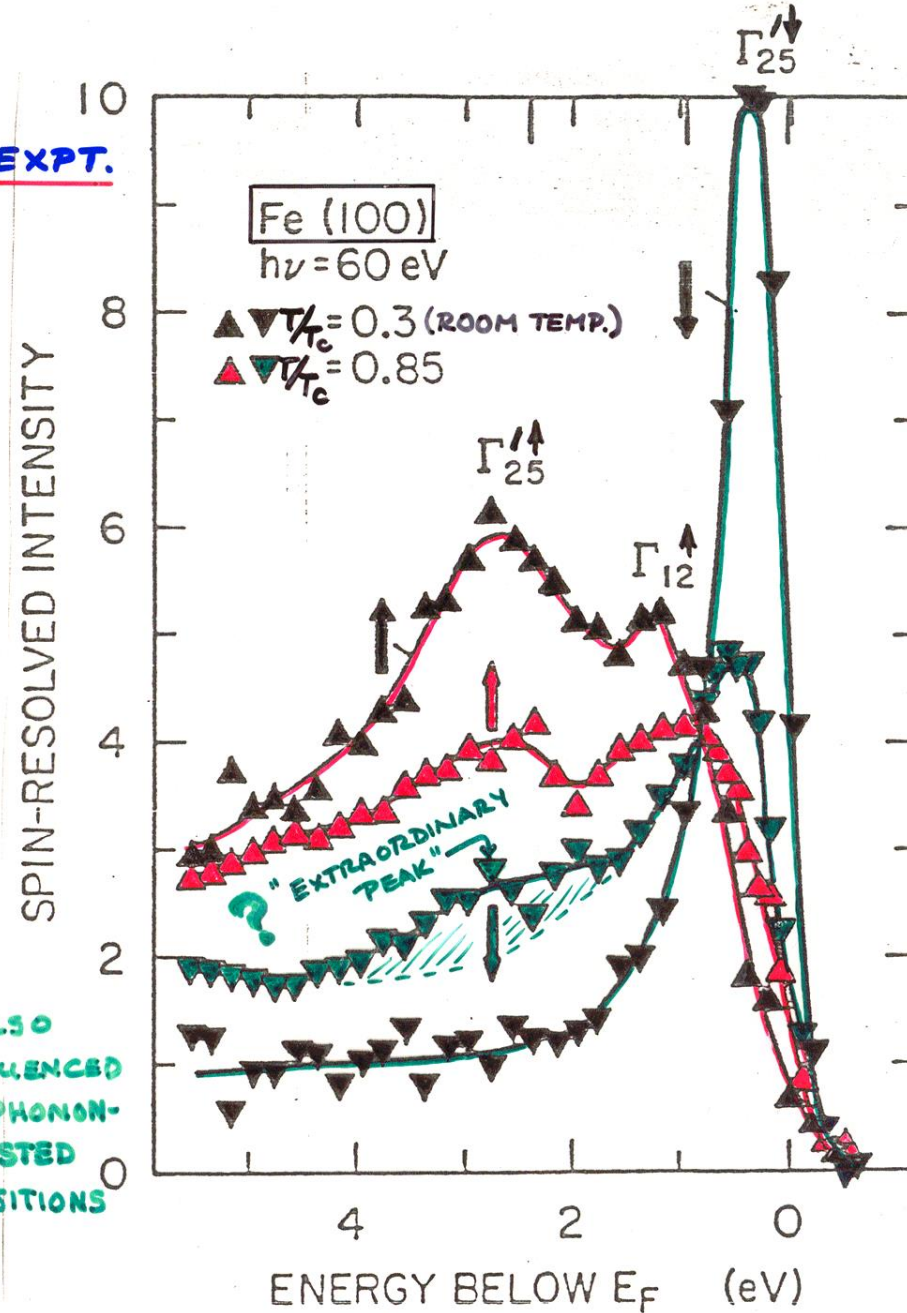
? ALSO INFLUENCED BY PHONON-ASSISTED TRANSITIONS

SPIN-RESOLVED INTENSITY

ENERGY BELOW E_F (eV)

E. KISKER ET AL., PHYS. REV. B 31, 329 (1985)

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And for the real d orbitals in octahedral:

e_g

$3z^2-r^2$ x^2-y^2

t_{2g}

yz   zx   xy

Ligand (e.g. O)

yz plane

Transition Metal (e.g. Mn)

e_g and t_{2g} not equivalent in octahedral (cubic) environment

zx

xy

yz
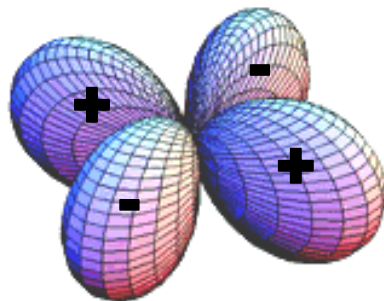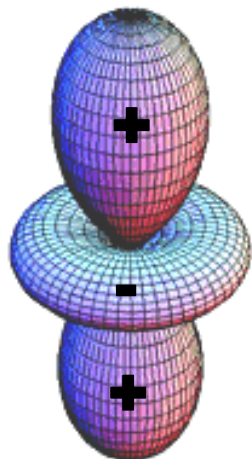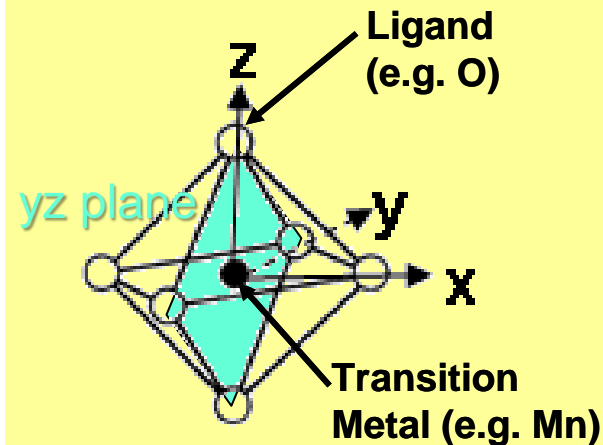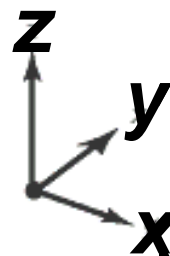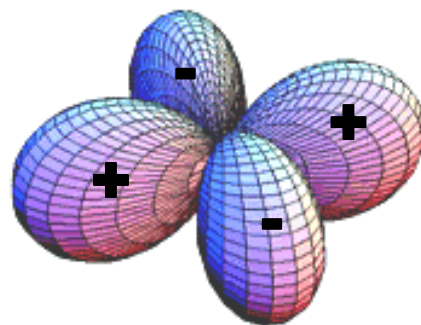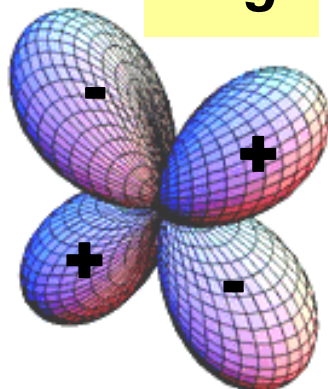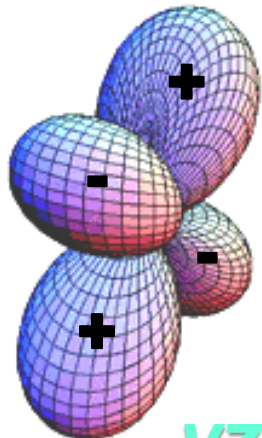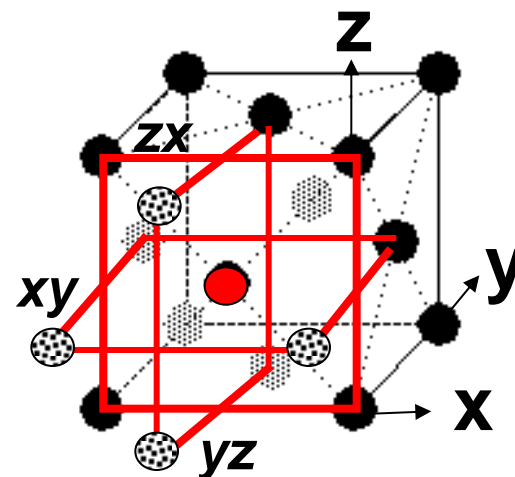
Face-centered cubic— 12 nearest neighbors

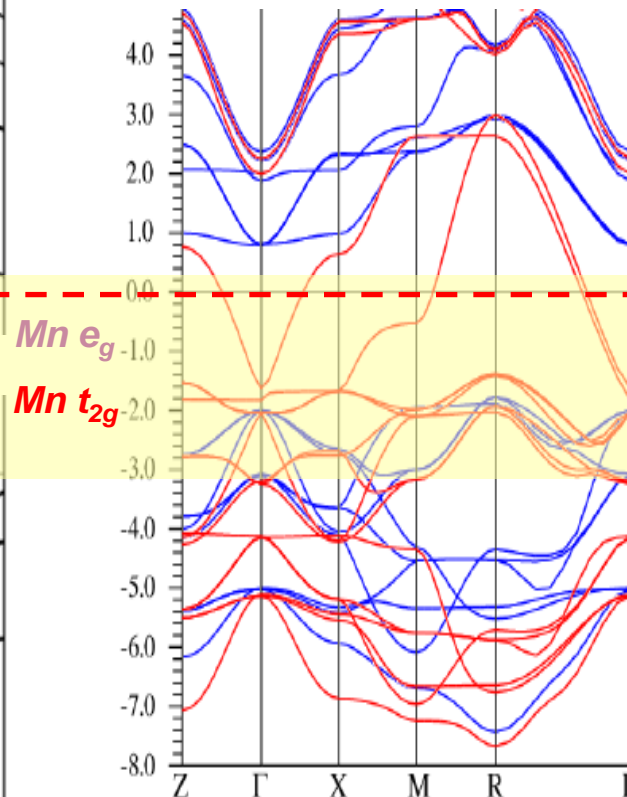# E.g.—Crystal field in Mn³⁺ & Mn²⁺ with negative octahedral ligands
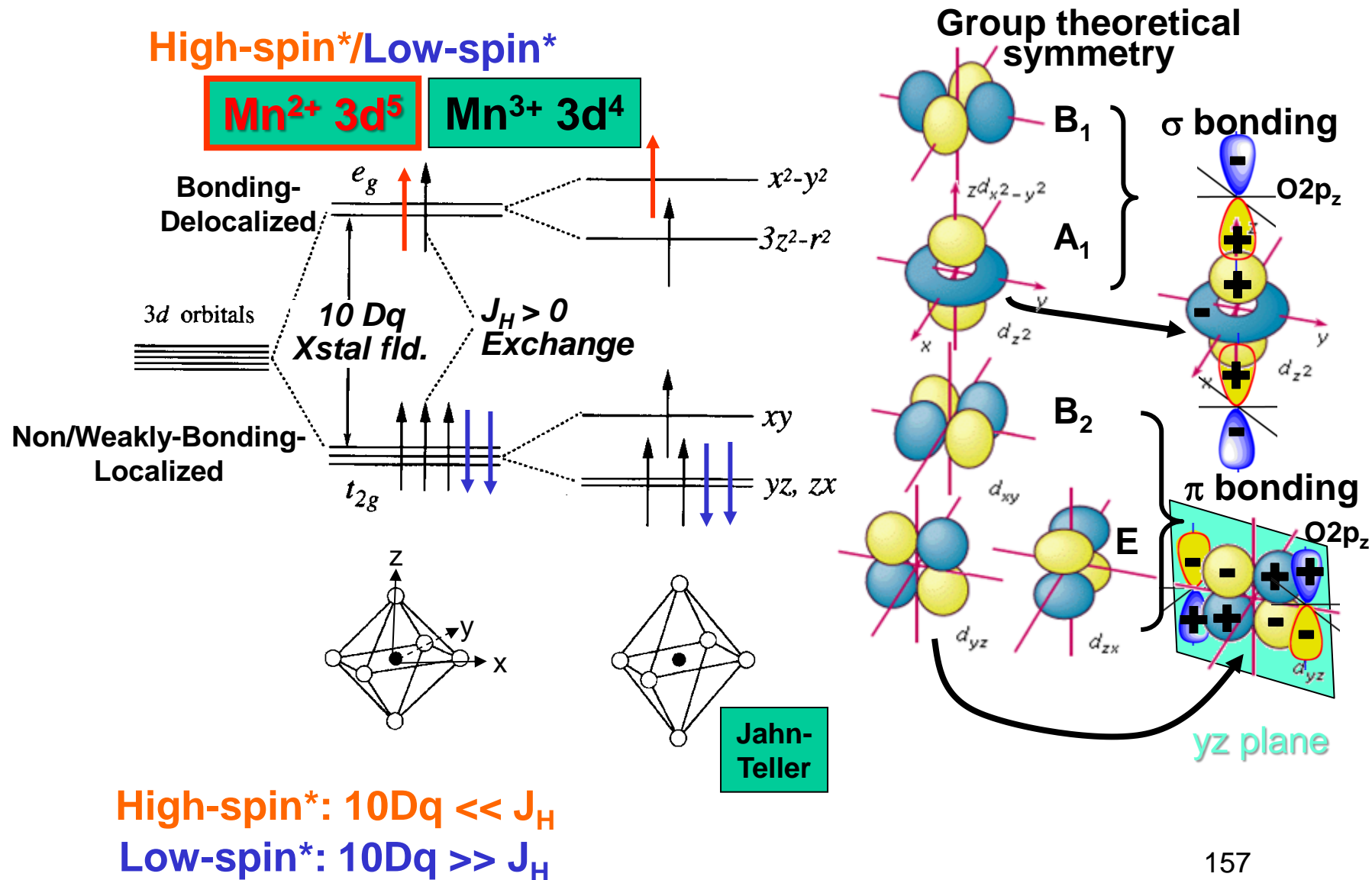
High-spin*/Low-spin*

| Mn²⁺ 3d⁵ | Mn³⁺ 3d⁴ |

Group theoretical symmetry

High-spin*: 10Dq << J_H
Low-spin*: 10Dq >> J_H

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SrTiO₃ and La₀.₆₇Sr₀.₃₃MnO₃ band structures and DOS

SrTiO₃-band insulator

La₀.₆₇Sr₀.₃₃MnO₃- Half-Metallic Ferromagnet

Projected DOSs

Spin-up **Spin-down**

$d_{xz}+d_{yz}$

d_{xy}

No spin down!

Mn e_g

Mn t_{2g}

d_{z2}

d_{x2-y2}

$d_{xz}+d_{yz}$

d_{xy}

O $2p$

Expt'l. bandgap 3.3 eV

Expt'l. band offset 3.0 eV

Plucinski, TBP with expt'l. band offset

— Spin-up
— Spin-down
Chikamatsu et al., PRB 73, 195105 (2006); Plucinski, TBP

Zheng, Binggeli, J. Phys. Cond. Matt. 21, 115602 (2009) Plucinski, TBP
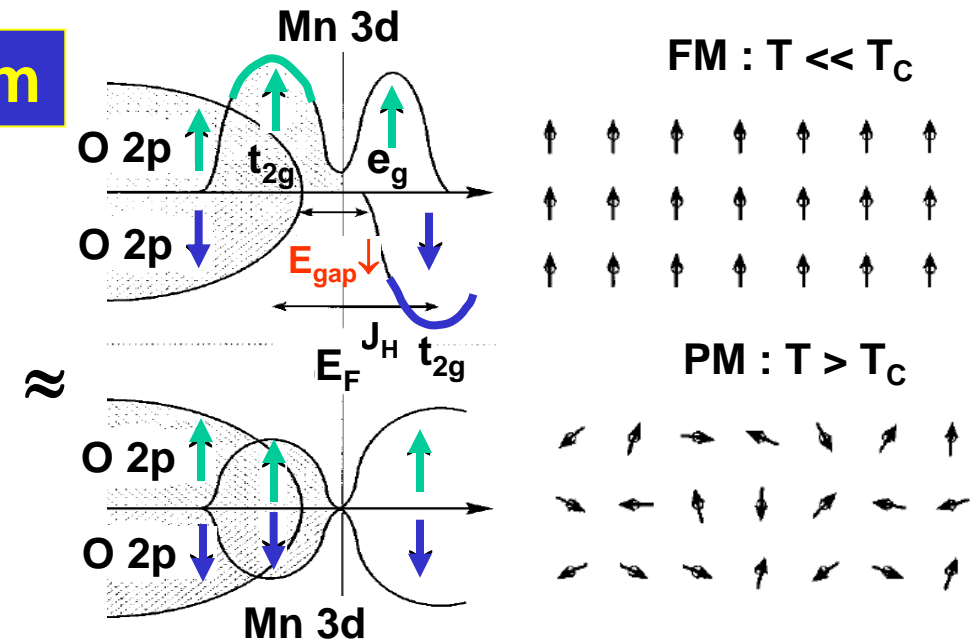
158
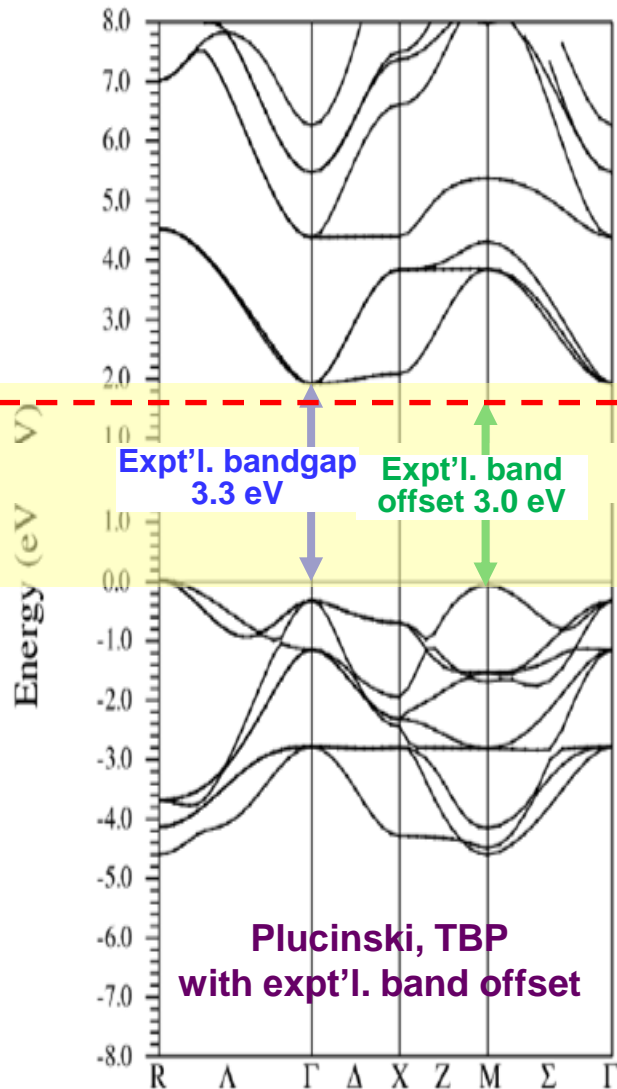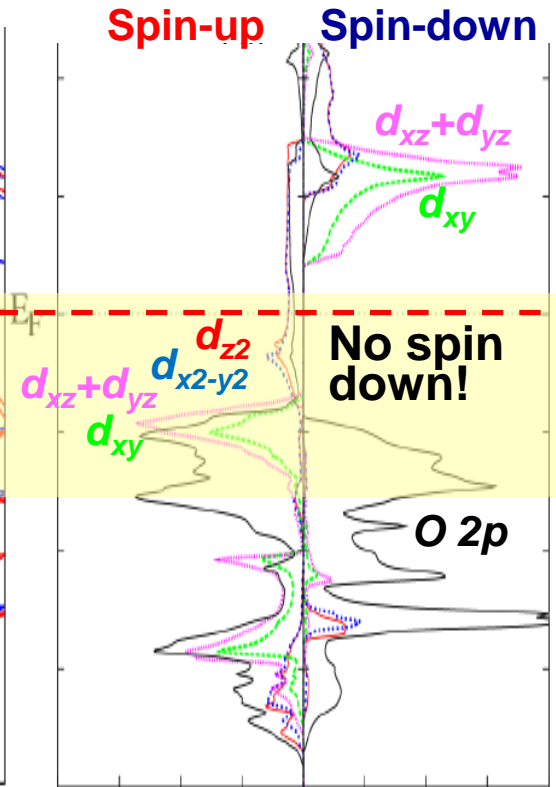
Half-Metallic Ferromagnetism

LDA theory- FM $La_{0.75}\underline{Ca}_{0.25}MnO_3$

Mn 3d

FM : $T \ll T_C$

O 2p t_{2g} e_g

O 2p E_{gap}

$\approx$

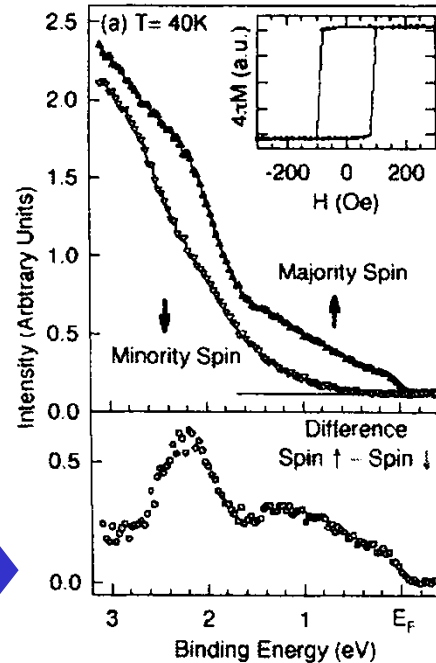O 2p

O 2p

Mn 3d

E_F J_H t_{2g}
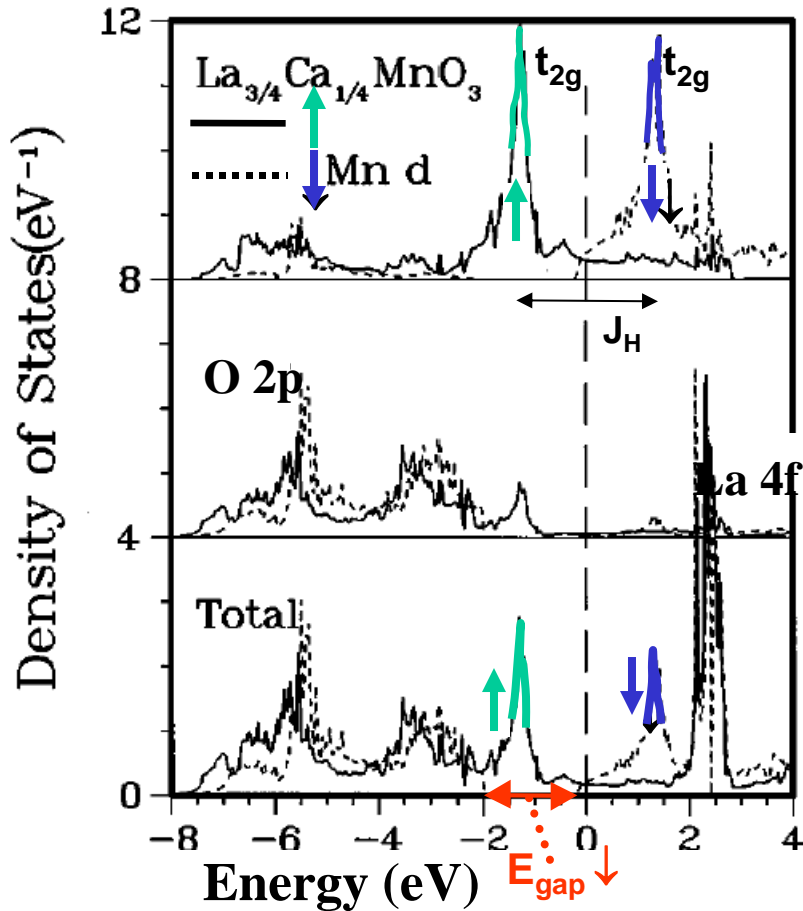
PM : $T > T_C$

Pickett and Singh, PRB <u>53</u>, 1146 (1996)

Experiment- spin-resolved PS $La_{0.70}\underline{Sr}_{0.30}MnO_3$ as thin film
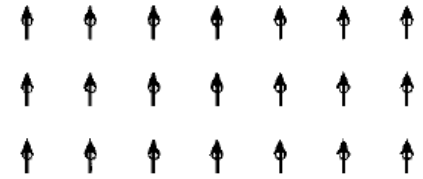
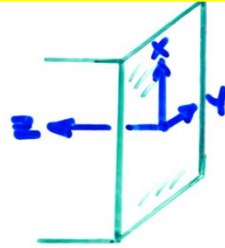Park et al., Nature, PRB <u>392</u>, 794 (1998)

$T \ll T_C$
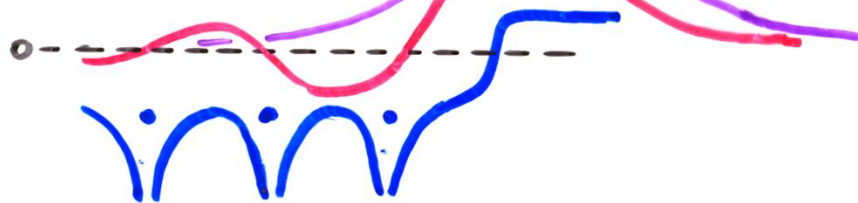
$T > T_C$

159
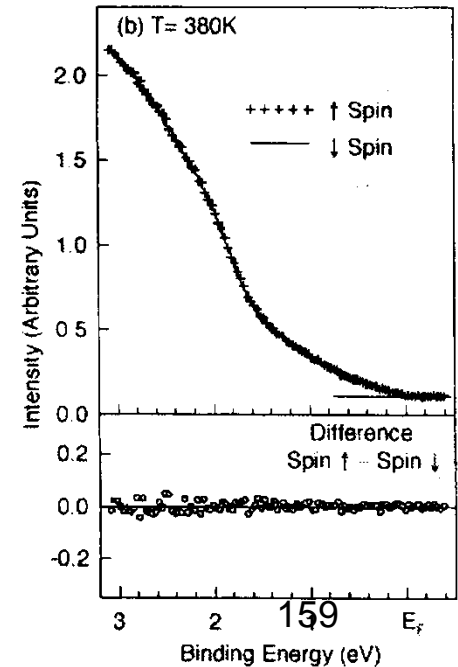
$$k_x, k_y \Rightarrow \vec{k}_{\parallel}$$
$$k_z \Rightarrow \vec{k}_{\perp}$$

- STRONGLY LOCALIZED NEAR SURFACE

- BLOCH FUNCTION IN $x + y$, BUT DECAYING IN z:

$$\psi_{\vec{k}_{\parallel}}(\vec{r}) = u_{\vec{k}_{\parallel}}(\vec{r}) e^{i\vec{k}_{\parallel} \cdot \vec{r}} e^{-\kappa_{\perp} z}$$

DECAY CONSTANT

- TWO LIMITING TYPES: TAMM STATE **(~d character, localized)**
 SHOCKLEY STATE **(~s,p character, delocalized)**
  (OSCILLATES INTO BULK A LITTLE)

- ONLY EXIST WHEN NO BULK STATE EXISTS AT SAME $\vec{k}_{\parallel} = k_x \hat{i} + k_y \hat{j}$; OTHERWISE MIXING OCCURS + NOT SURFACE-LOCALIZED

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Surface states on Cu(111)

Shockley surface State: s,p makeup

Tamm surface state: 3d makeup

Fig. 4.21. Experimental dispersion of Cu(111) surface states plotted with a projection of the bulk bands: (a) Shockley state near the zone center (Kevan, 1983); (b) Tamm state near the zone boundary (Heimann, Hermanson, Miosga and Neddermeyer, 1979). Compare with Fig. 4.17.
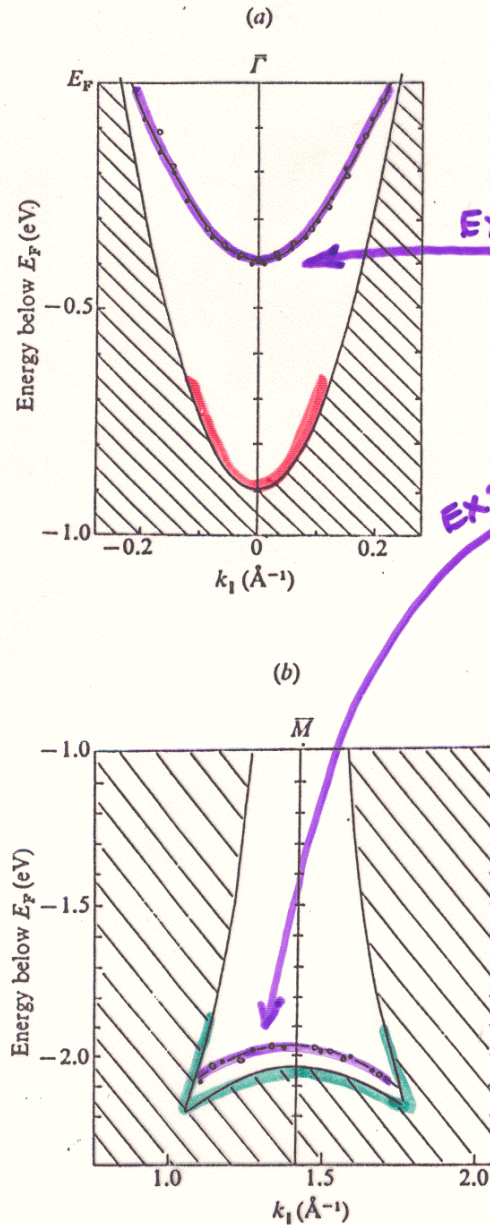
THEORY

Fig. 4.17. Surface states (dashed curves) and bulk projected ban Cu(111) surface according to a six-layer surface band structure calculation (Euceda, Bylander & Kleinman, 1983).

EXPT.

EXPT.
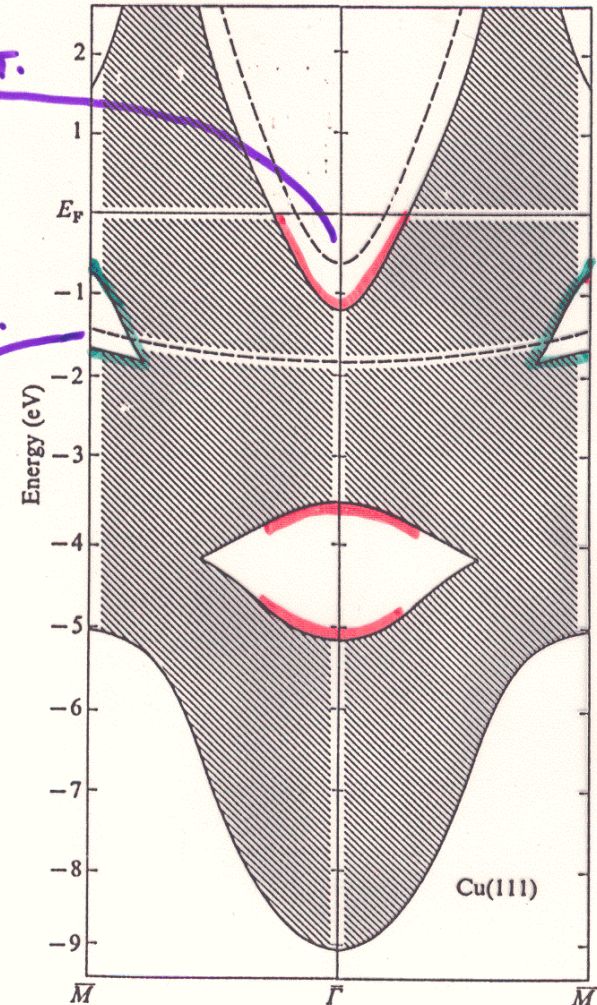
CONSERVATION LAWS IN VALENCE-BAND PHOTOELECTRON SPECTROSCOPY:

$$\vec{k}_{f,\parallel} = \vec{K}_{f,\parallel}$$

Vary θ to scan $\vec{K}_{f,\parallel} = \vec{k}_{f,\parallel}$

SURFACE BARRIER $= V_o$

$\vec{g}_{BULK}$ (AND/OR $\vec{g}_{SURF}$)

BRILLOUIN ZONE
$E_i(\vec{k}_i)$

"The UPS Limit"
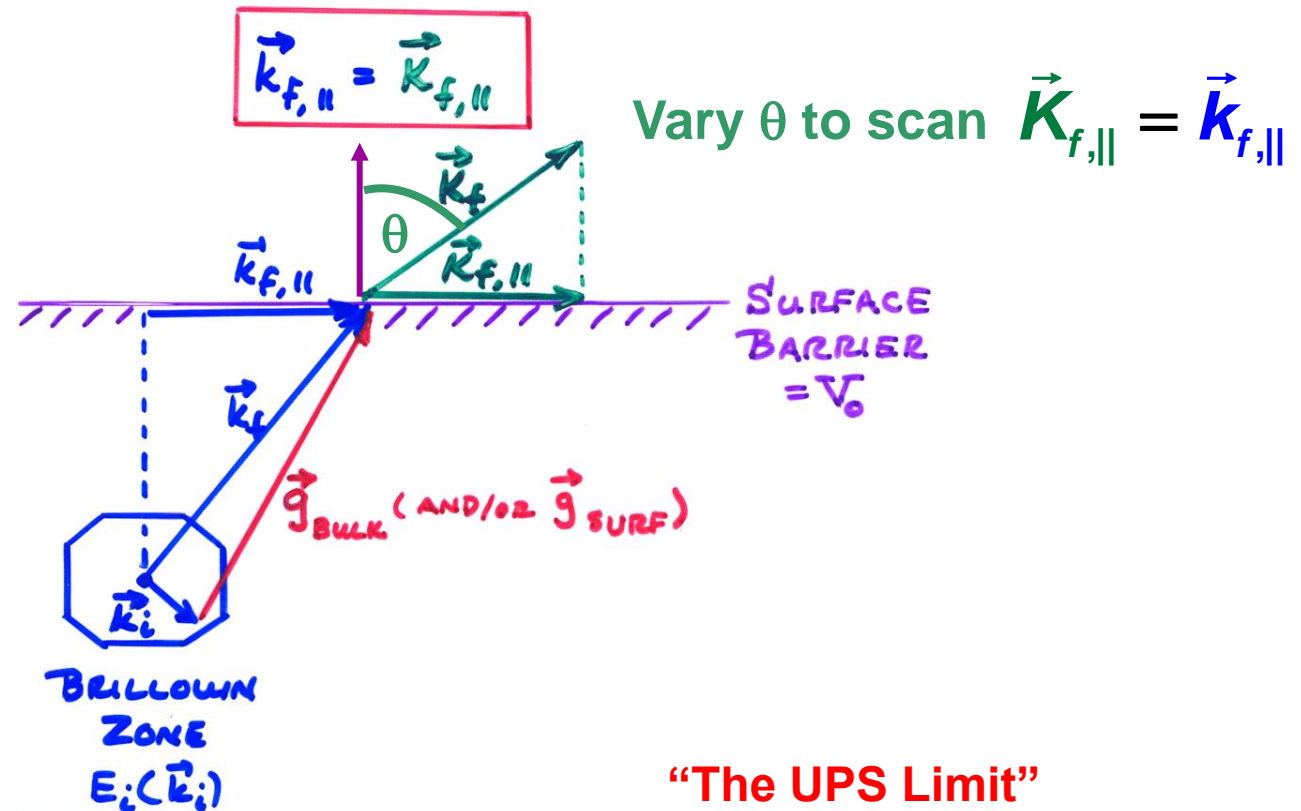
$$\vec{k}_f = \vec{k}_i + \vec{g}_{BULK}(\vec{g}_{SURFACE}) + \cancel{\vec{k}_{h\nu}} + \cancel{\vec{k}_{PHONON}}$$

NEGLIGIBLE: $h\nu \lesssim 500$ $h\nu$ AND/OR T
IF   eV   LOW ENOUGH

Fig. 4.20. Photoemission energy distribution curves from Cu(111) at different collection angles. Equation (4.32) has been used to express the electron kinetic energy in terms of the binding energy of the electron state (Kevan, 1983).
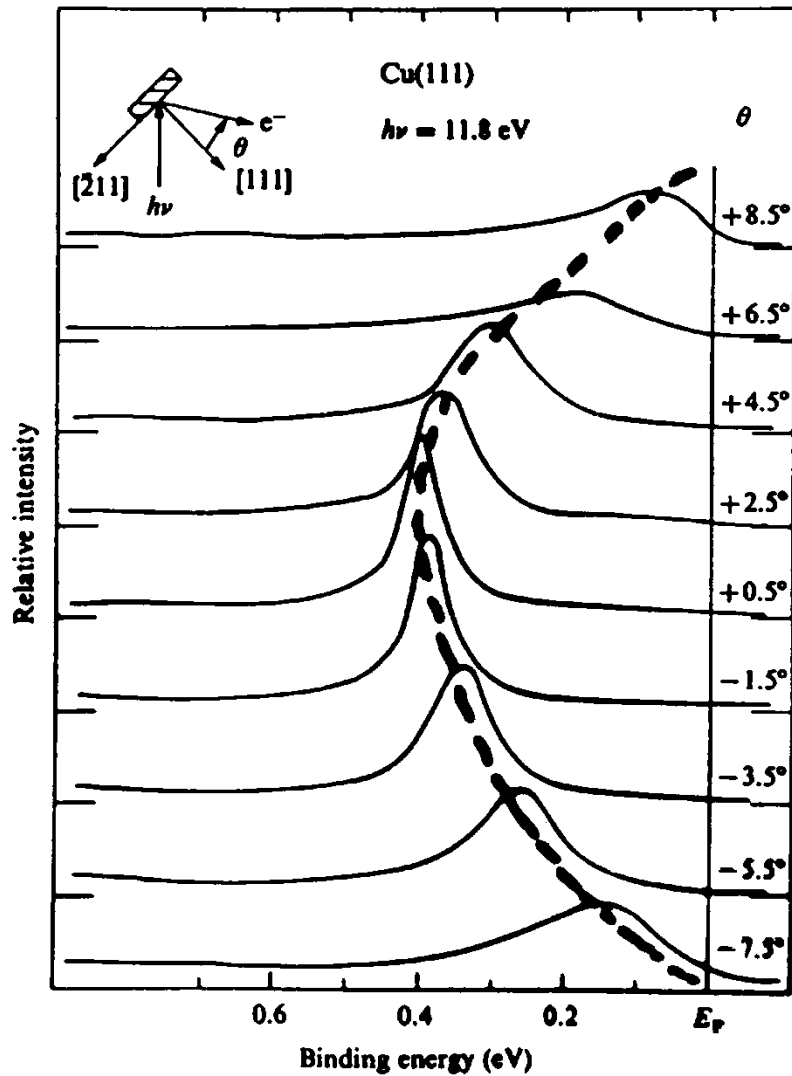
Graphene- A very special 2D case
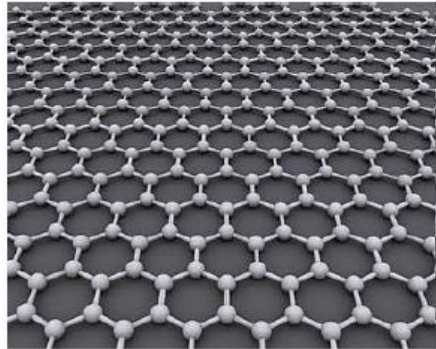
The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov
…"for groundbreaking experiments
regarding the two-dimensional
material graphene"

Photoelectron spectroscopy

Unoccupied at T = 0K-
Anti-Bonding

Occupied-
Bonding

Unocc.

Holes

$$E(\vec{k}) = C \, |\vec{k}|$$

A Dirac particle

Electrons

Occ.

Nobel, 2010

55

Bostwick et al., Nature Physics 3, 36 - 40 (2007)
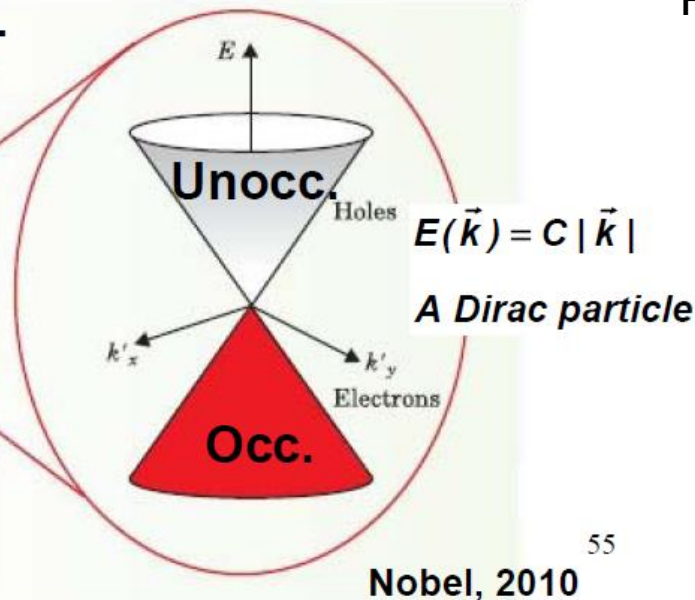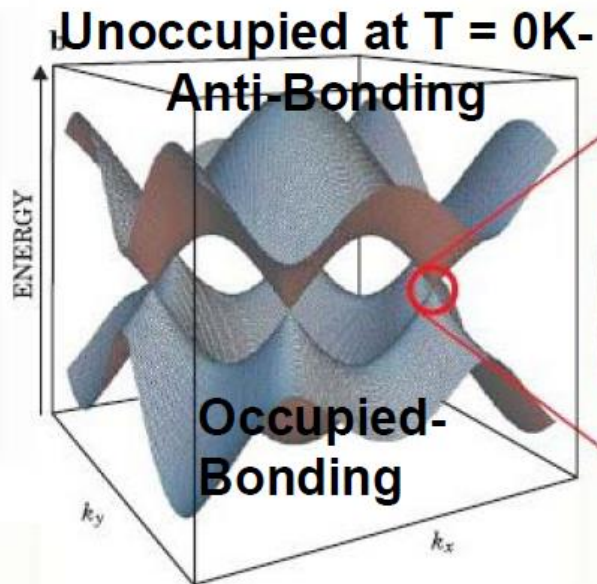
Some basic measurements:

Standing Wave: $\lambda_{SW} = \lambda_X/(2\sin\theta_X^I)$

LP, RCP, LCP, UP

XFH

XES, RIXS XFH^{-1}, RXFH

REXS, XRD, XAS, NEXAFS/XANES, EXAFS, XRO

$h\nu$

λ_{SW}

$h\nu' < h\nu$

$h\nu$

R_X

PS, PD, PH CD, MCD, SP, RPS

$\vec{s}$

e^-

θ_X^I

θ_X^R

θ_e

$\theta_X^T < \theta_X^I$

V_0

$\exp(-\mu_X L_X) = \exp(-L_X/\Lambda_X)$

$\exp(-L_e/\Lambda_e)$

$n = 1 - \delta - i\beta$

f_X

(Kramers-Kronig)

f_e f_e

$\approx 1-(r_0 \lambda_X^2/2\pi)\sum n_i f_{Xi}(0)$
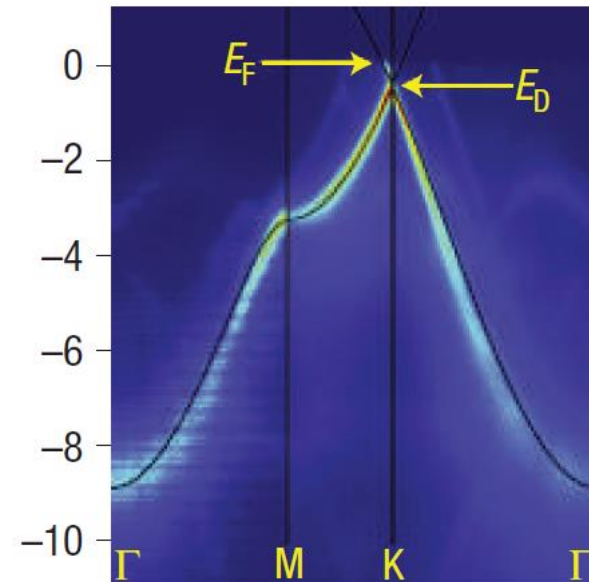
f_X

f_X

$\mu_X = 4\pi\beta/\lambda_X$

$\theta_X^R = \theta_X^I$

$\theta_{CRIT}^I = (2\delta)^{1/2}$

Multi-atom resonant photoemission (MARPE) Photoelectron Spectroscopy (PS), Diffraction (PD), Holography (PH) + Circular Dichroism (CD), Magnetic CD (MCD), Spin Polarization (SP) Resonant Photoemission (RPS)

X-ray Fluorescence Holography (XFH, XFH^{-1}), Resonant XFH (RXFH) X-ray Emission Spectroscopy (XES), Resonant Inelastic X-ray Scattering (RIXS) Resonant Elastic X-ray Scattering (REXS) X-Ray Diffraction (XRD) X-ray Absorption Spectroscopy (XAS) X-Ray Optical measurements (XRO) Near-Edge X-Ray Absorption Fine-Structure (NEXAFS)/ X-Ray Absorption Near-Edge Structure (XANES); Extended X-Ray Absorption Fine Structure (EXAFS)

$R_X + T_X = 1$

T_X

165