Reading and Problem Assignments for Physics 243A
Surface Physics of Materials: Spectroscopy, Fall, 2014

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 85-8, 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*
  - Chapter 10: pp. 244-249 on bond lengths, no ion scattering
- IBACH, "PHYSICS OF SURFACES AND INTERFACES", DOWNLOADABLE BOOK (SEE COURSE WEBSITE)—
  - Chapter 2: 2.1, 2.2
- DESJONQUERES AND SPANJAARD, "CONCEPTS OF SURFACE PHYSICS", EXCERPTS DOWNLOADABLE FROM COURSE WEBSITE:
  - On equilibrium shapes of surfaces, thermodynamics, kinetics and adsorption isotherms, and on STM current calculation. No need to follow every step, but this fills in the line of arguments in Zangwill and lecture
- FADLEY, "BASIC CONCEPTS OF XPS", HANDED OUT, BUT ALSO DOWNLOADEABLE—
  - Sections I, II, and III, with remaining sections by the end of the course
- FADLEY, "THE STUDY OF SURFACE STRUCTURES BY PHOTOELECTRON DIFFRACTION AND AUGER ELECTRON DIFFRACTION", PAGES 421-450 only, DOWNLOADABLE FROM COURSE WEBSITE with other examples and exercises using the EDAC web program introduced in lecture
- ATTWOOD, DOWNLOADEABLE EXCERPT ON SYNCHROTRON RADIATION FROM THE BOOK "Soft X-Rays and Extreme Ultraviolet Radiation" (see course website)
- SIX READING DOWNLOADS FROM THE COURSE WEBSITE:
  1) Molecular orbital basics
  2) Tight-binding basics
  3) Dejonqueres and Spanjaard handout-Photoelectron Diffraction Theory/Debye-Waller Factors
  4) Core-Hole Multiplets with Charge Transfer--Basic Theory
  5) Brief Manual for SESSA spectral simulation program
  6) Brief Manual for CTM4XAS20 charge-transfer multiplet simulation program

  [7) Optional only for physics students: Basic theory for the Hubbard Model of bonding]

PROBLEM SET 3-FINAL: Not all problems assigned

Problems 3.3, 3.4, 4.1, 4.2, 4.4, 4.5, 5.1, 5.2, 5.3, 5.4, 5.7, 5.8, 5.9(a),(b) only, 5.10, DUE FRIDAY, 12 DECEMBER

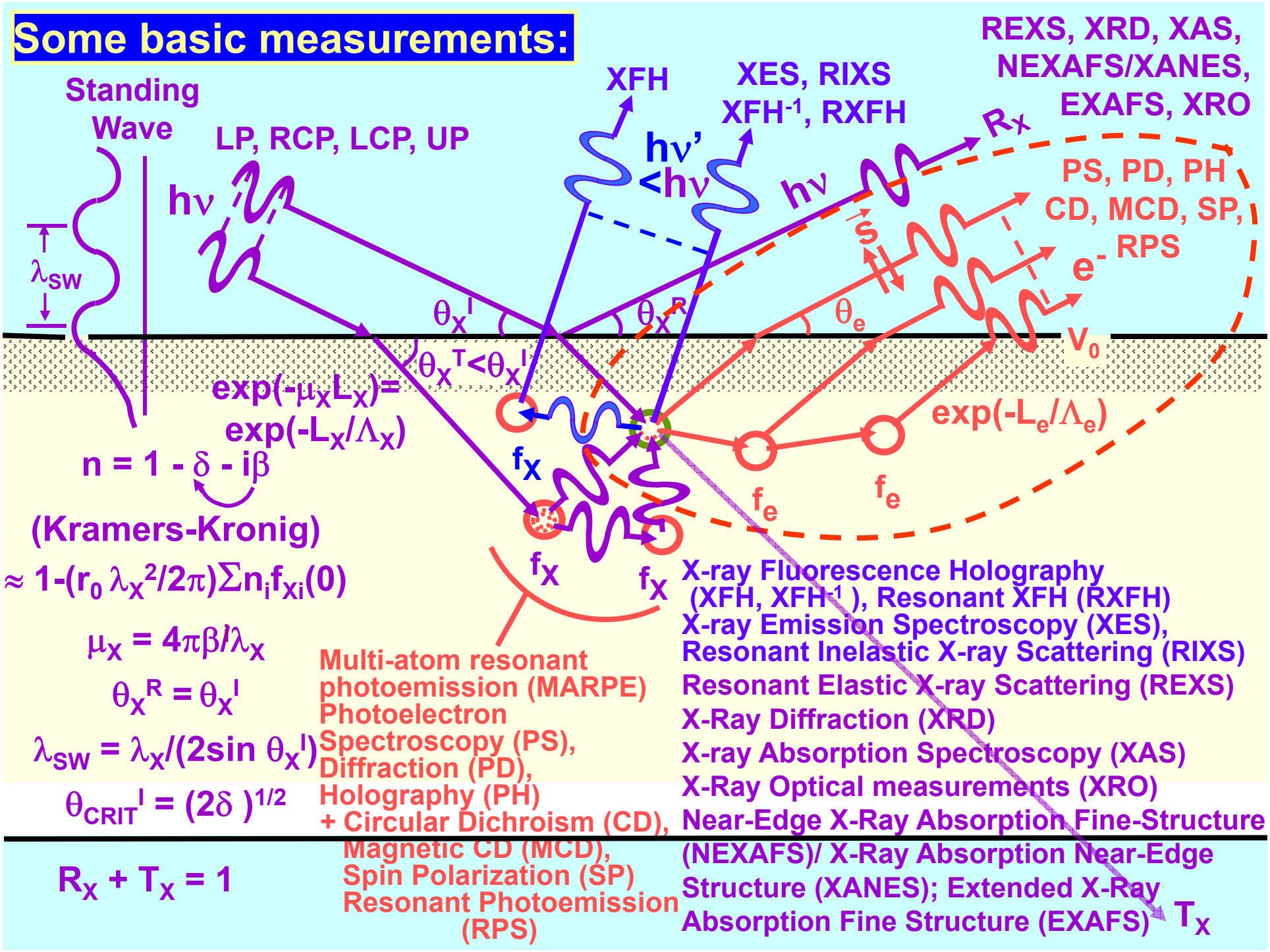
REMAINING LECTURE SCHEDULE:

NO LECTURES: 2 DECEMBER AND 9 DECEMBER

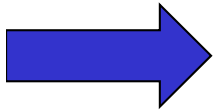
12:10 MAKEUP + 2:10 REGULAR LECTURES: 25 NOVEMBER, 4 DECEMBER, AND 11 DECEMBER

TOUR OF LBNL: SATURDAY, 13 DECEMBER

FINAL EXAMINATION: TUESDAY, 16 DECEMBER, 10:30 AM-12:30 PM, PHYSICS 285 (unless moved by unanimous consent)


Some basic measurements:
Standing Wave
LP, RCP, LCP, UP
hν
λsw
XFH
XES, RIXS
XFH-1, RXFH
hν'
<hν
hν
Rx
REXS, XRD, XAS,
NEXAFS/XANES,
EXAFS, XRO
PS, PD, PH
CD, MCD, SP,
RPS
e-
s
θx I
θx R
θx T<θx I
θe
V0
exp(-μxLx)=
exp(-Lx/Λx)
n = 1 - δ - iβ
(Kramers-Kronig)
≈ 1-(r0 λx2/2π)Σnifxi(0)
μx = 4πβ/λx
θx R = θx I
λsw = λx/(2sin θx I)
θCRIT I = (2δ)1/2
Rx + Tx = 1
fx
fe
exp(-Le/Λe)
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)
Tx

Outline—Here to end of quarter



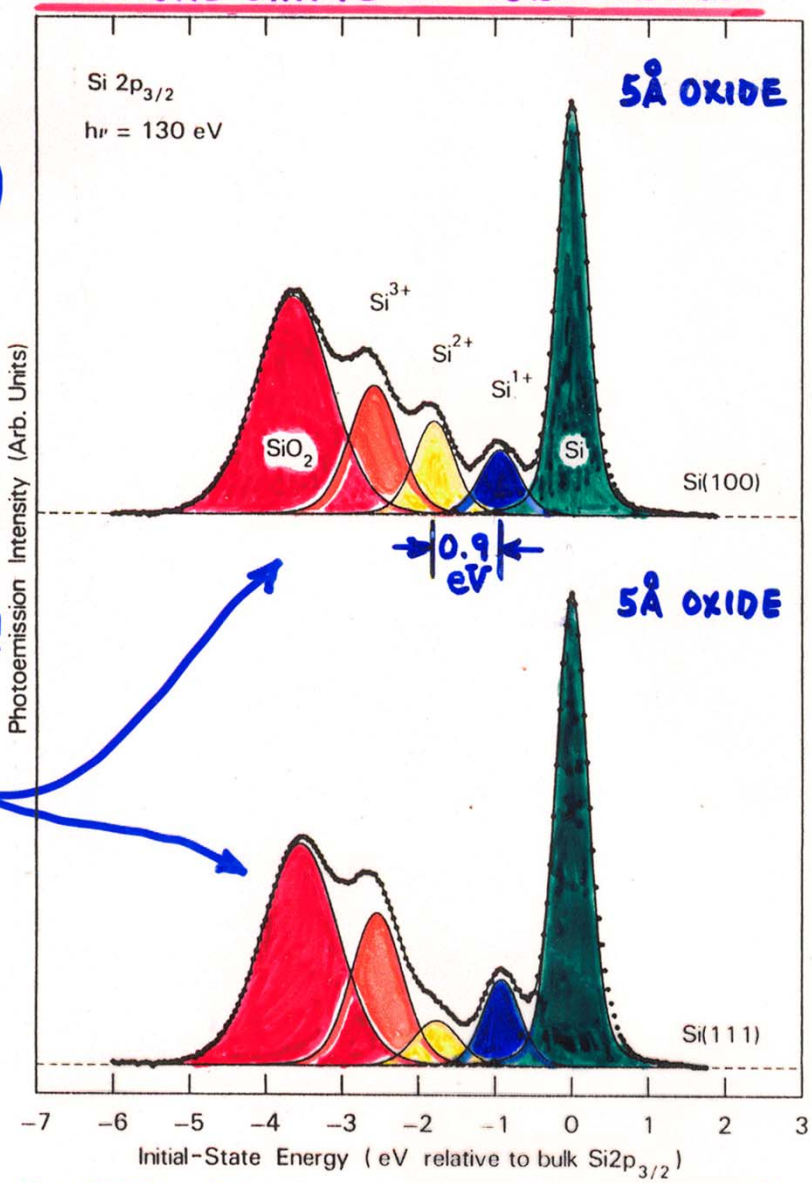
- Core-level chemical shifts: Koopmans', relaxation, the potential model
- Various other final state effects providing information in core-level spectra
- Valence-band spectra: low-energy UPS limit and high-energy XPS limit
- Photoelectron diffraction, extended x-ray absorption fine structure (EXAFS, XAFS)
- Photoelectron spectroscopy at realistic pressures in the multi-Torr range
- Photoelectron microscopy: adding lateral spatial resolution in 2 dimensions

PHOTOELECTRON SPECTRA

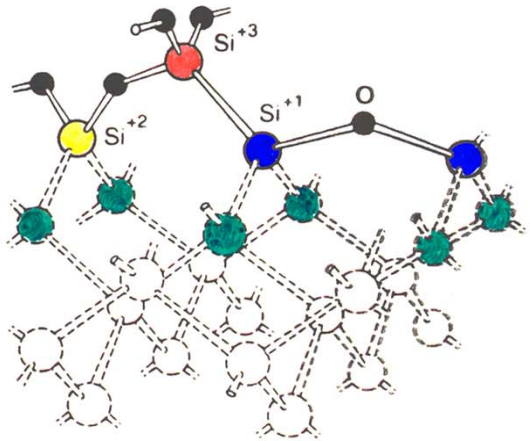
OXIDIZED SILICON

CHEMICAL SHIFTS OF CORE LEVELS

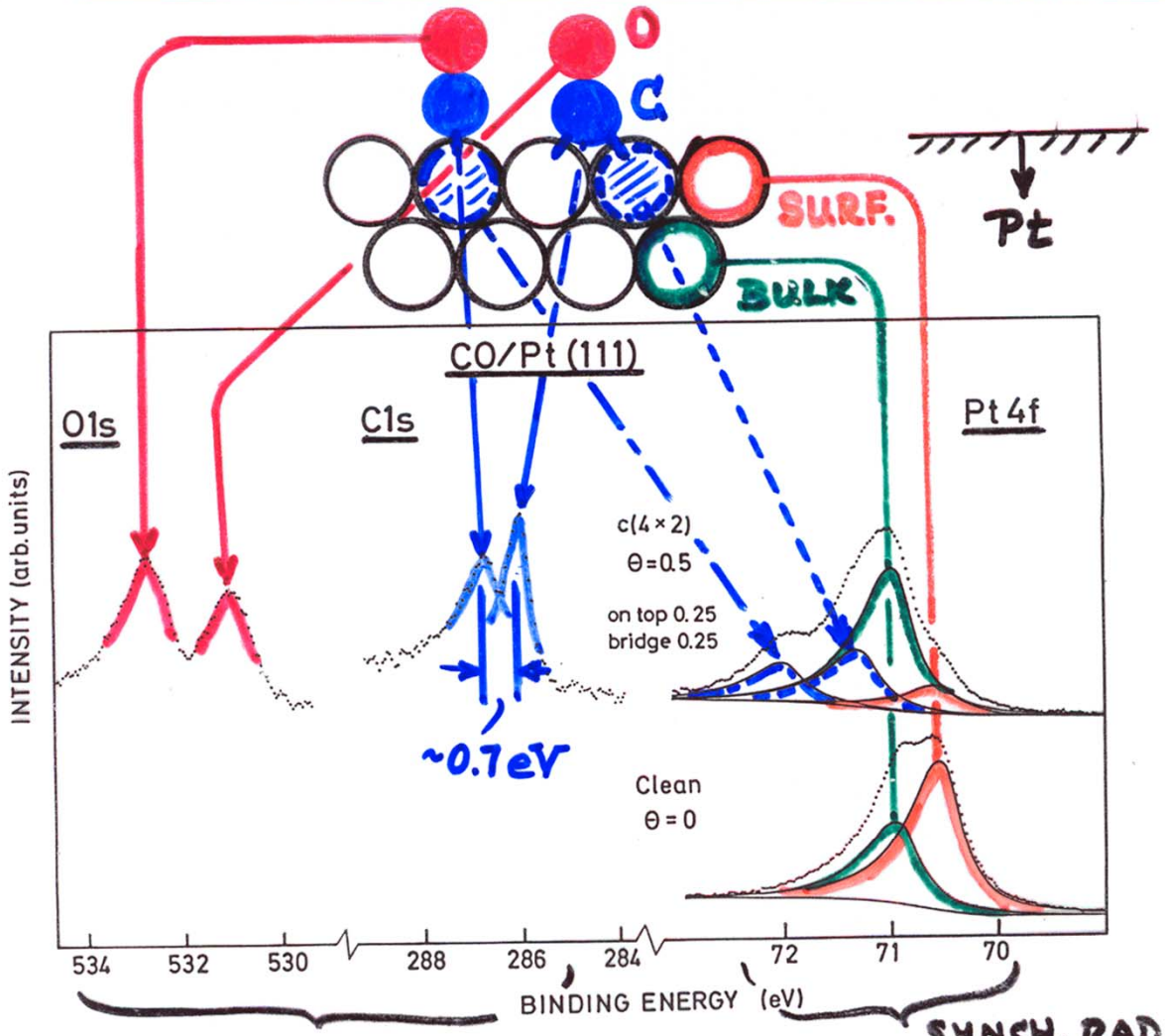
EXACTLY WHAT IS STRUCTURE OF INTERFACE? NEED STATE-SPECIFIC STRUCTURAL INFORMATION!



HIMPSEL ET AL., PHYS. REV. B, 38, 6084('90)



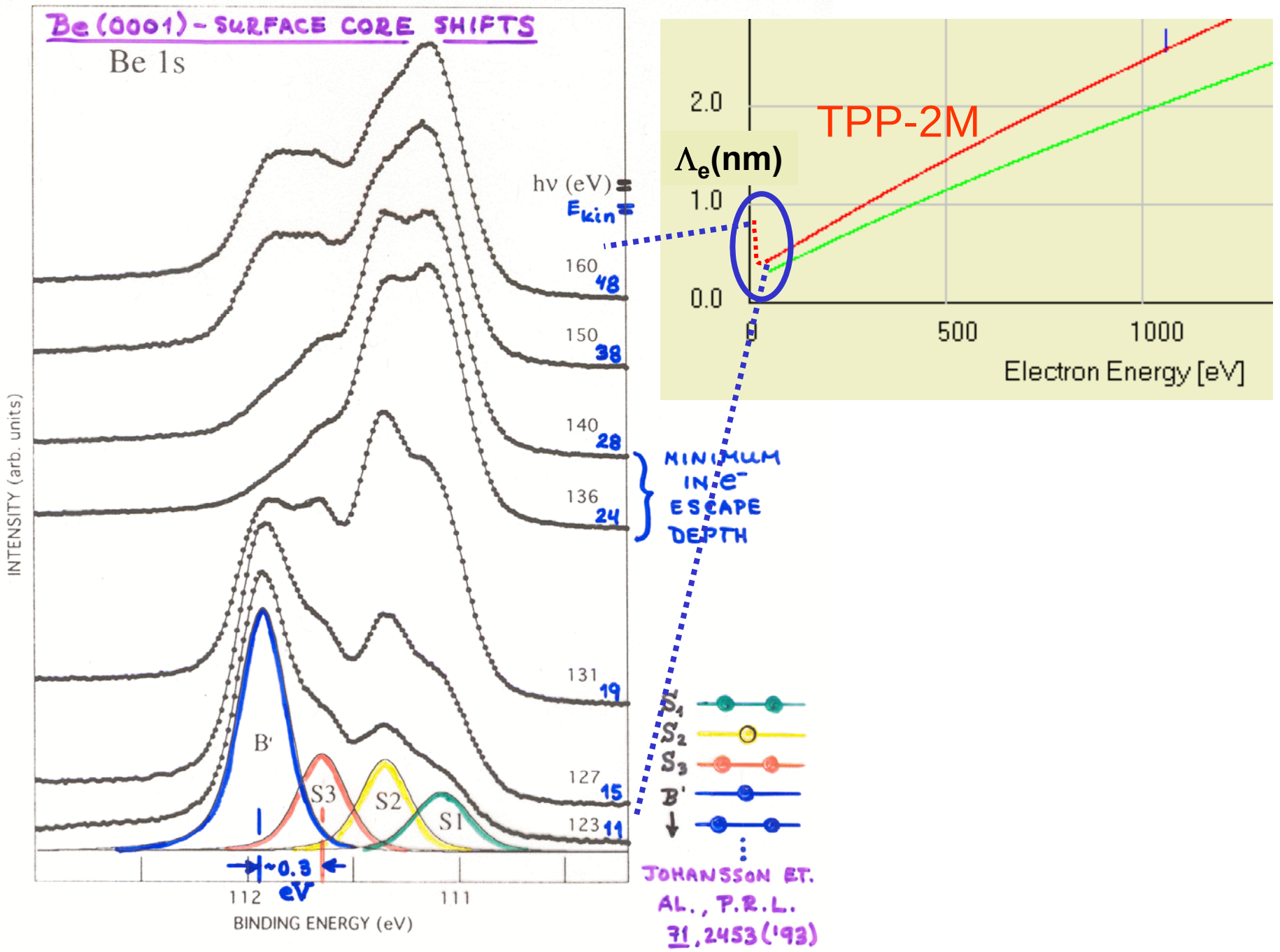
CHEMICAL SHIFTS IN ADSORBATE & SUBSTRATE



MONOCH. XPS,
ΔE ~ 0.3 eV

SYNCH. RAD., ΔE ~ 0.15 eV

BJÖRNEHOLM
ET AL.
(NILSSON GRP.,
UPPSALA)


Be (0001) - SURFACE CORE SHIFTS
Be 1s
hν (eV) =
E_kin =
160
48
150
38
140
28
136
24
131
19
127
15
123
11
B'
S3
S2
S1
~0.8 eV
112
111
BINDING ENERGY (eV)
INTENSITY (arb. units)
MINIMUM IN e⁻ ESCAPE DEPTH
S1
S2
S3
B'
JOHANSSON ET. AL., P.R.L. 71, 2453 ('93)
TPP-2M
Λe(nm)
2.0
1.0
0.0
0
500
1000
Electron Energy [eV]

BINDING ENERGIES & KOOPMANS' THEOREM:

N-e^- SCH. EQN. — $\hat{H}(N)\Psi_j(N) = E_j(N)\Psi_j(N)$, $j = 1, 2, \ldots$

MINIMIZE $E_j(N)$ $\Big\downarrow$ $\Psi_j \approx \Phi_j$ = SLATER DET.

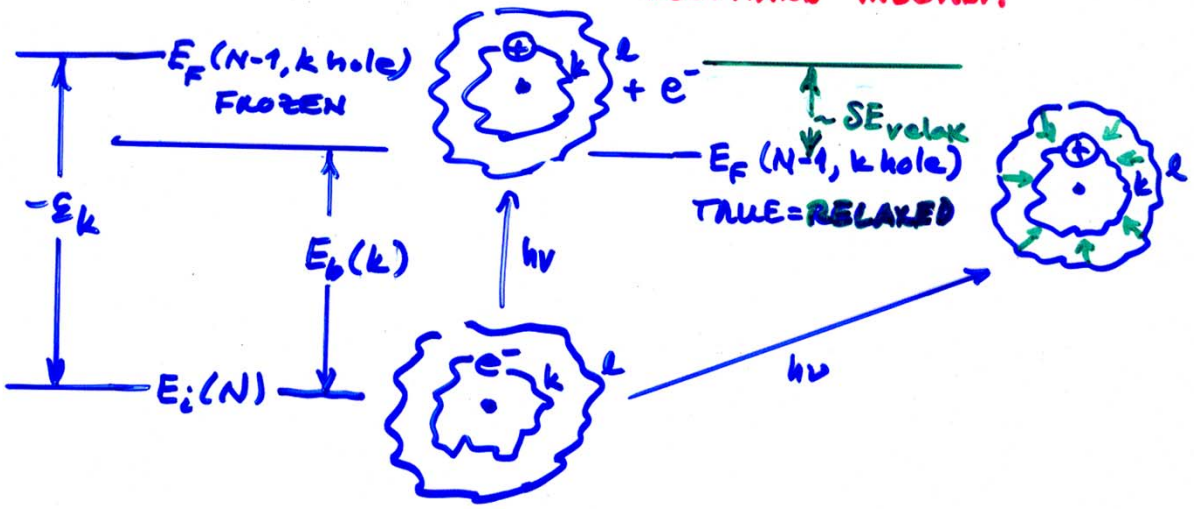
N 1-e^- HARTREE-FOCK EQNS. — $\hat{h}(1)\varphi_k(1) = \varepsilon_k(1)\varphi_k(1)$

- COUPLED INTEGRO-DIFF.
- COULOMB + EXCHANGE

$E_b(k)$ = k^{th} BINDING ENERGY = $E_f(N-1, k\ \text{hole}) - E_i(N)$ (+) EXACT

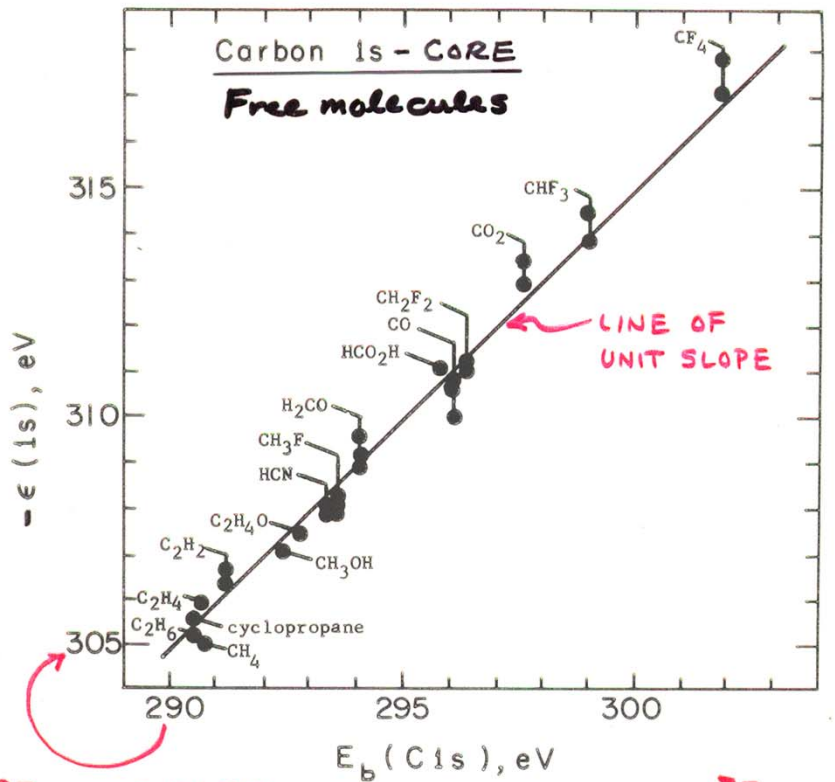
OR $E_b(k) = -\varepsilon_k$ IF $\varphi_{ki} = \varphi_{kf}$ (FROZEN ORBITAL)

KOOPMANS' THEOREM



⇒ RELAXATION, SCREENING, CONFIGURATION INTERACTION, SELF-ENERGY EFFECTS ALWAYS PRESENT; ANDERSON IMPURITY MODEL ETC.

KOOPMANS' THEOREM CALCULATION OF SHIFTS



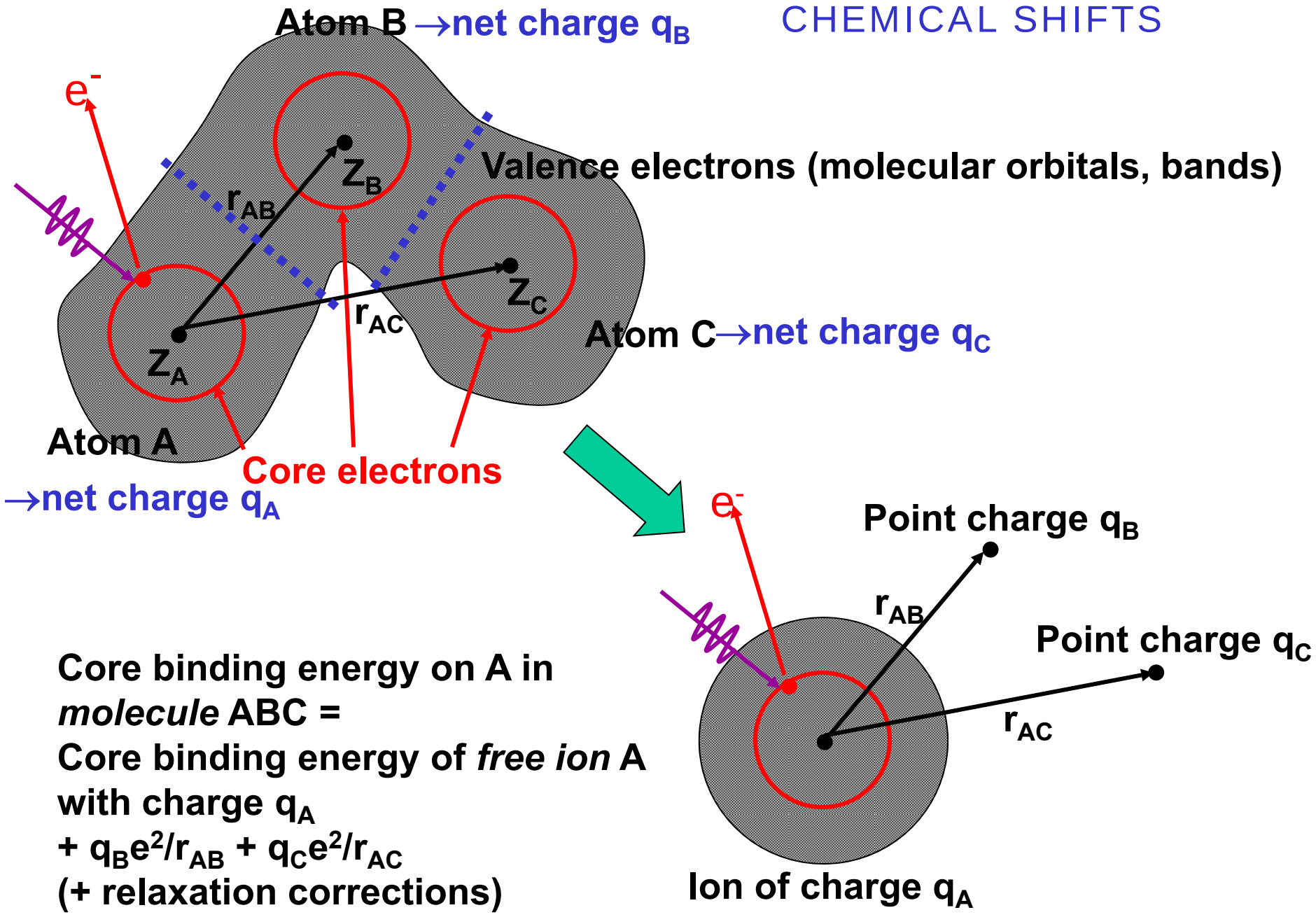
DIFF. = $\delta E_{relax} \approx 15$ eV = CONSTANT $\approx$ 5% OF E_b^V

$\hookrightarrow \Delta E_b$ (C1s, "1" - CH_4) = $-\Delta \varepsilon_{C1s,\ "1"-CH_4}$

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.)

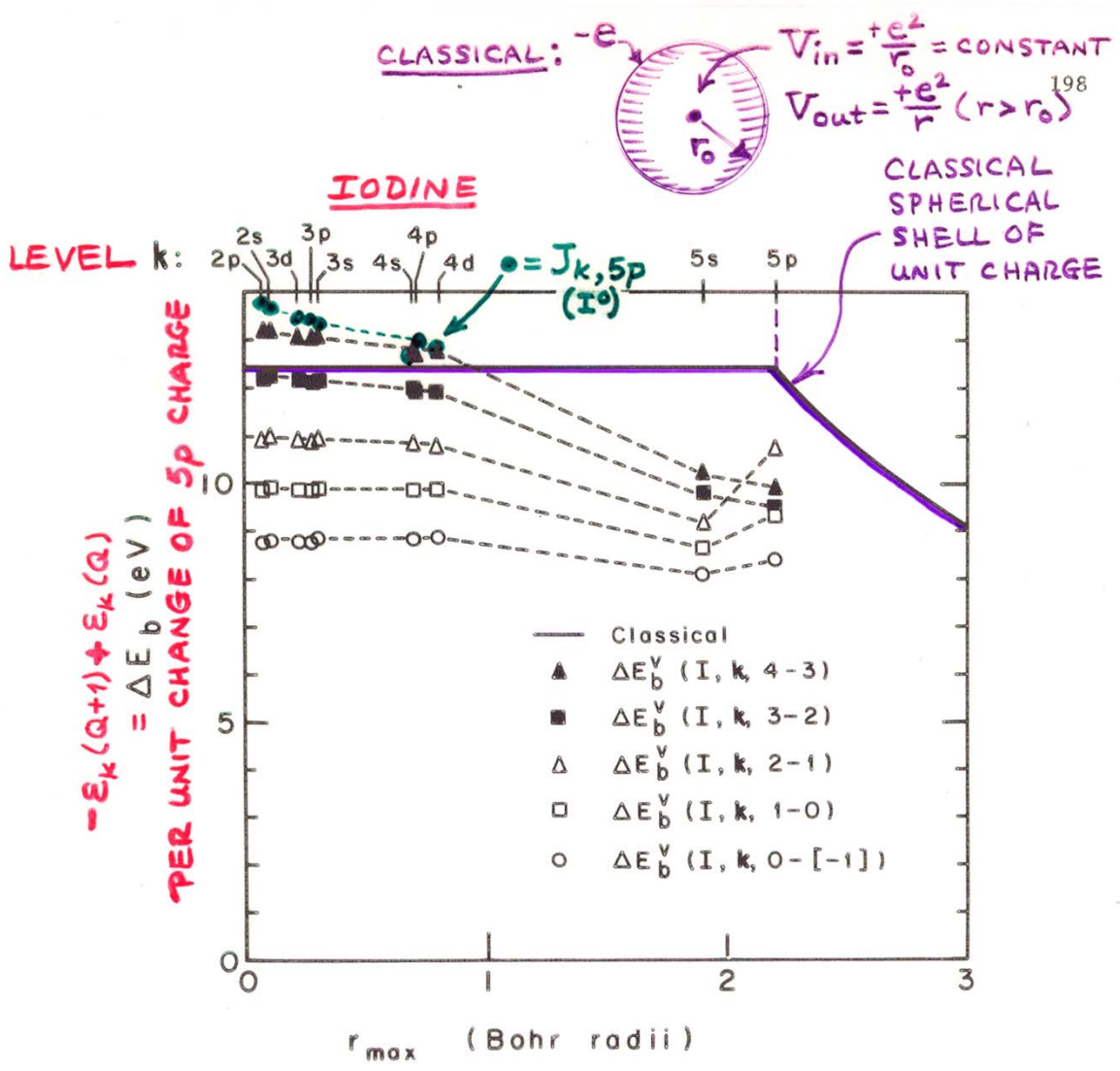
"Basic Concepts of XPS"
Figure 18

GROUND-STATE POTENTIAL MODEL FOR CORE-LEVEL CHEMICAL SHIFTS



Core binding energy on A in *molecule* ABC =
Core binding energy of *free ion* A with charge q_A
+ $q_B e^2/r_{AB}$ + $q_C e^2/r_{AC}$
(+ relaxation corrections)

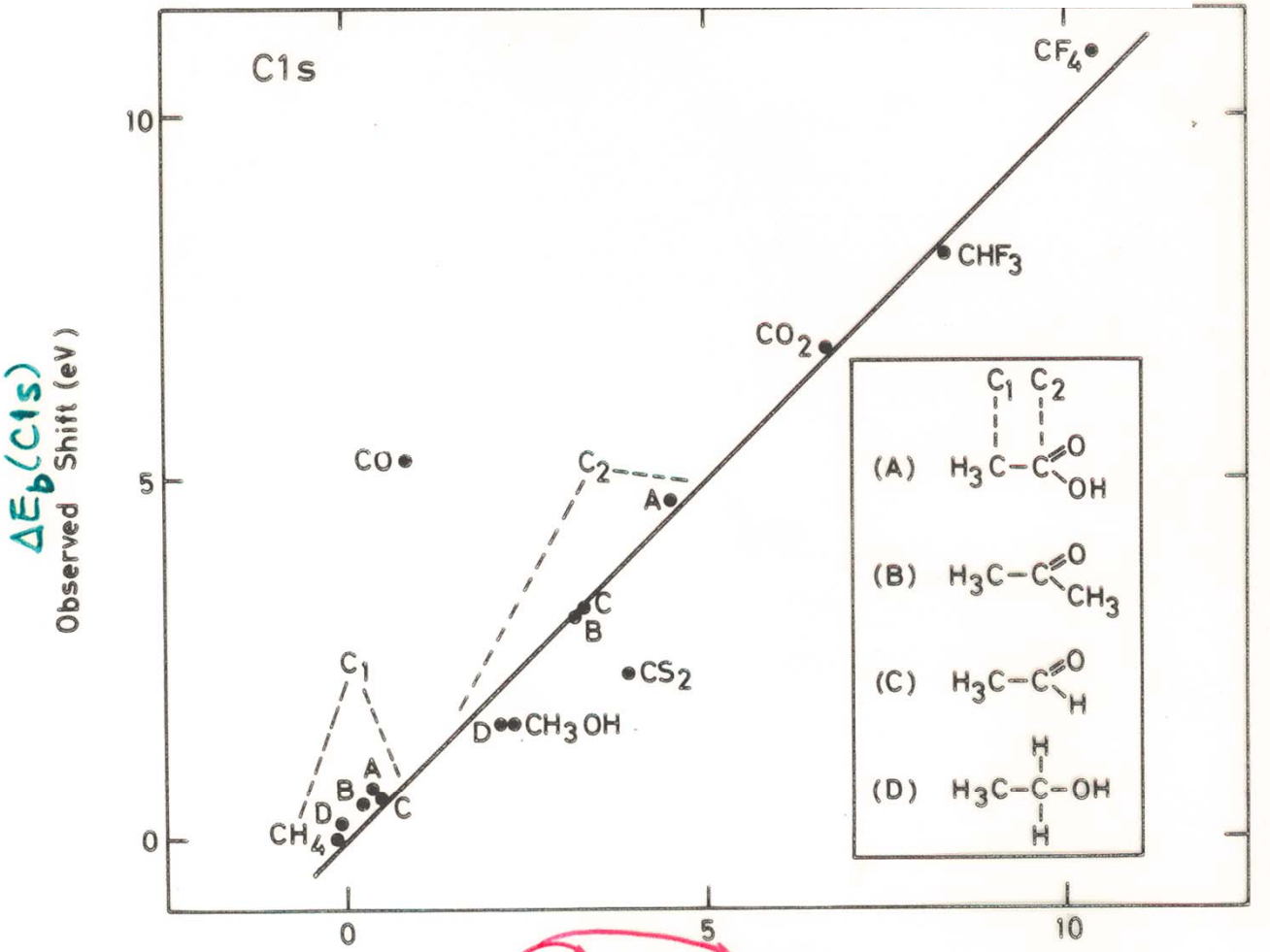
FREE-ION (INTRAATOMIC) ASPECTS OF SHIFTS: KOOPMANS' THEOREM & CLASSICAL CHARGED SHELL



⇒ REMOVAL/ADDITION OF VALENCE e^- CHARGE IN BONDING SHIFTS ALL INNER e^- E_b's ≈ E_K's BY ~SAME AMOUNT

"Basic Concepts of XPS"
Figure 19

POTENTIAL MODEL CALCULATION OF CARBON CHEMICAL SHIFTS



"Basic Concepts of XPS"
Figure 24

Outline—Here to end of quarter

- Core-level chemical shifts: Koopmans', relaxation, the potential model
- Various other final state effects providing information in core-level spectra
- Valence-band spectra: low-energy UPS limit and high-energy XPS limit
- Photoelectron diffraction, extended x-ray absorption fine structure (EXAFS, XAFS)
- Photoelectron spectroscopy at realistic pressures in the multi-Torr range
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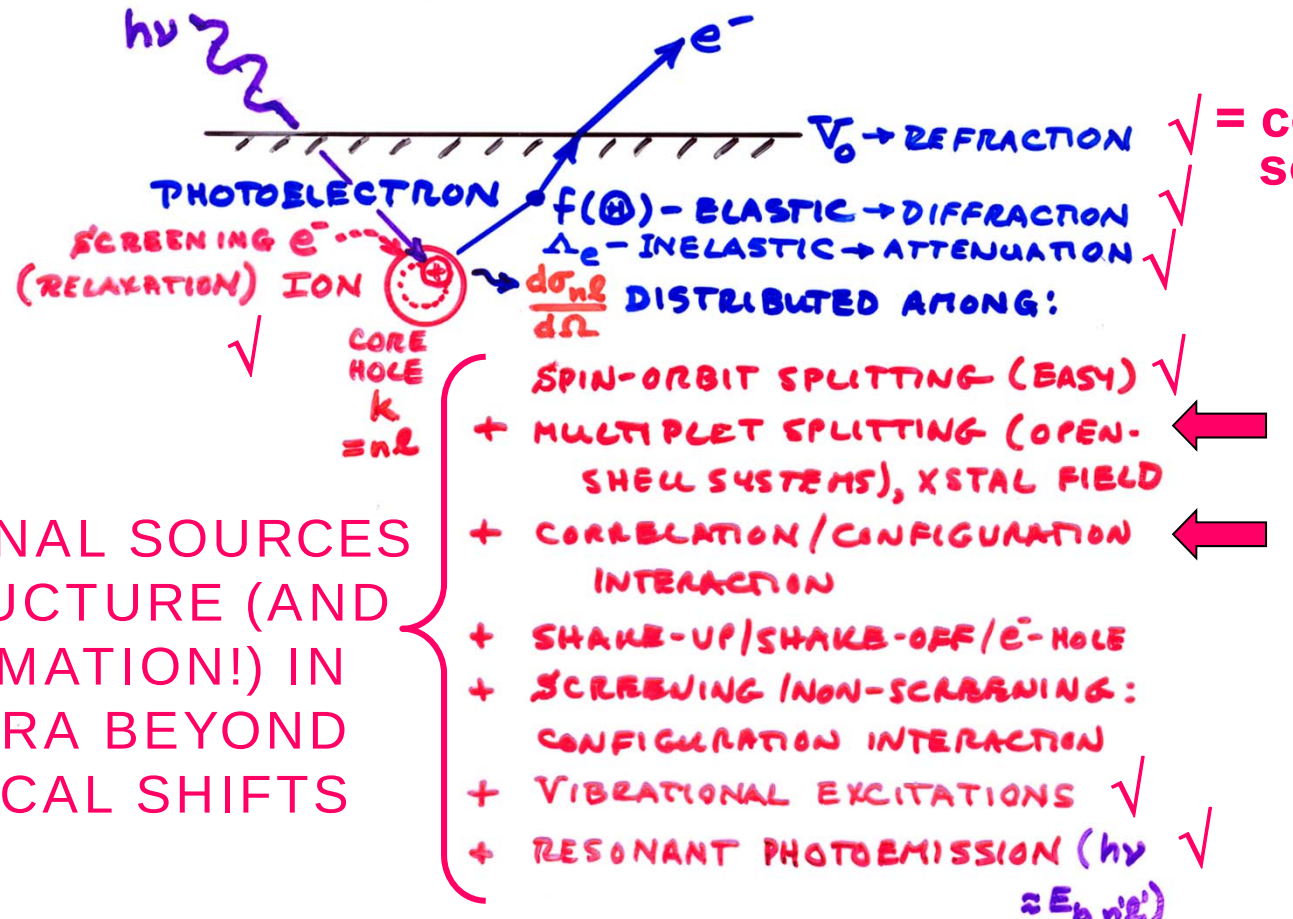
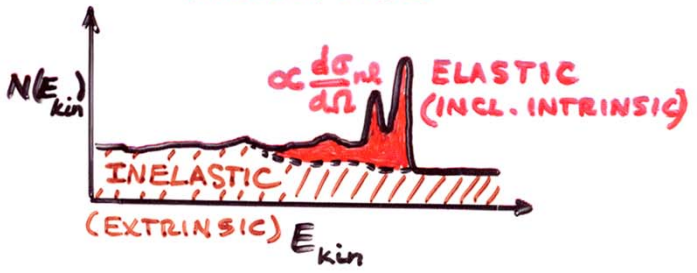


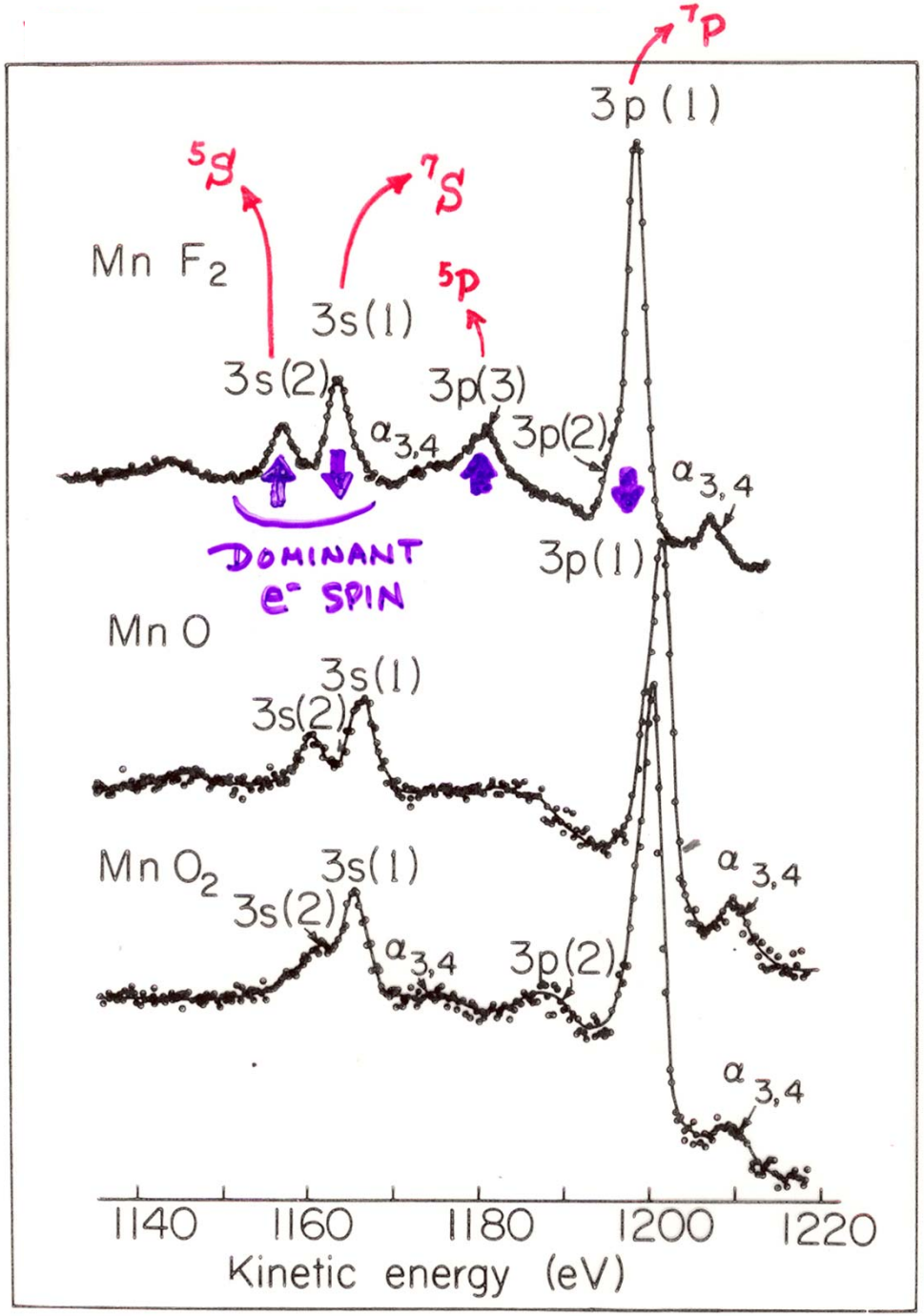
√ = covered so far

ADDITIONAL SOURCES OF STRUCTURE (AND INFORMATION!) IN SPECTRA BEYOND CHEMICAL SHIFTS

REALLY ALL AT ONCE, BUT SUM RULES + THEORY HELP

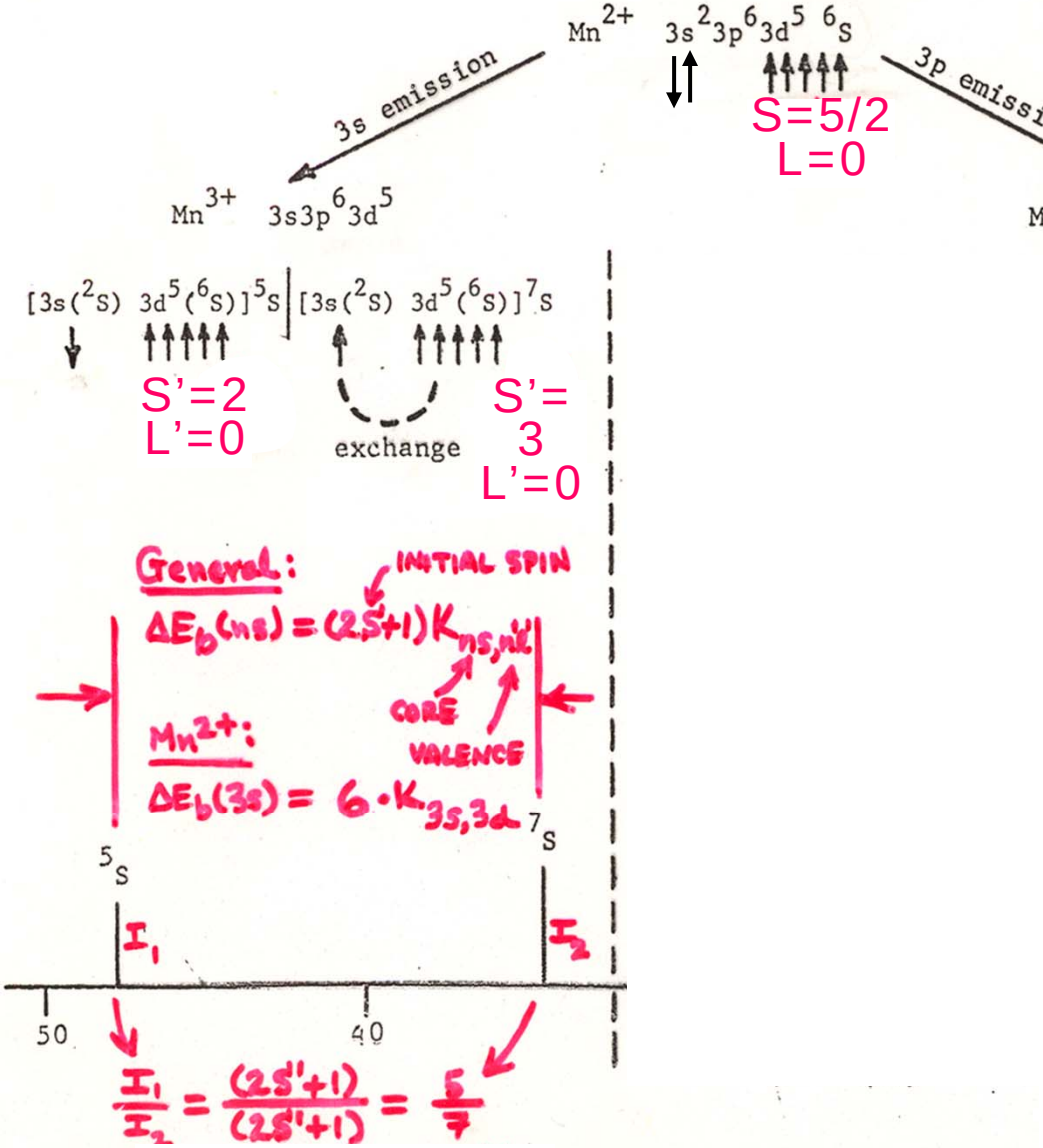


CORE-LEVEL MULTIPLET SPLITTINGS IN Mn COMPOUNDS



"Basic Concepts of XPS"
Figure 31

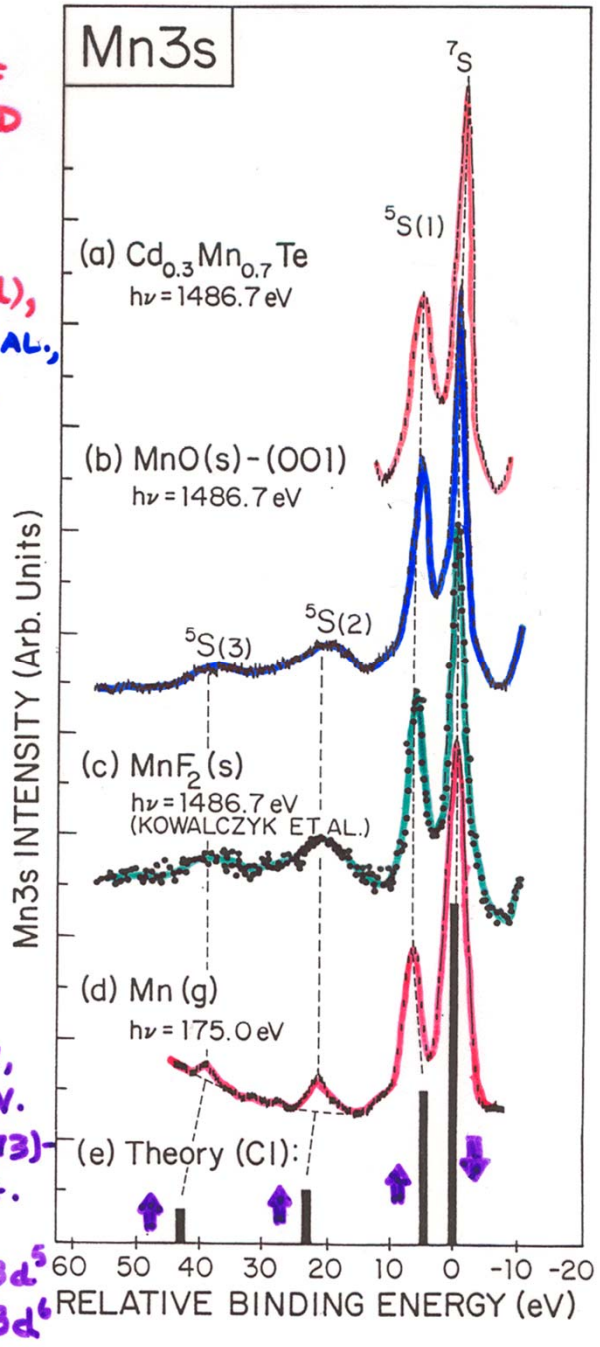
ORIGIN OF MULTIPLET SPLITTINGS IN Mn^{2+}: "ONE-ELECTRON" THEORY



General Mn^{2+} **"Basic Concepts of XPS" Figure 30**

COMPARISON OF GAS-PHASE AND SOLID-STATE SPECTRA

EXPT.: (a), (b), (d), HERMSMEIER ET AL., PHYS. REV. LETT. 61, 2592 (1988) (OUR GROUP)



Correlation CI effects: anti-parallel electrons

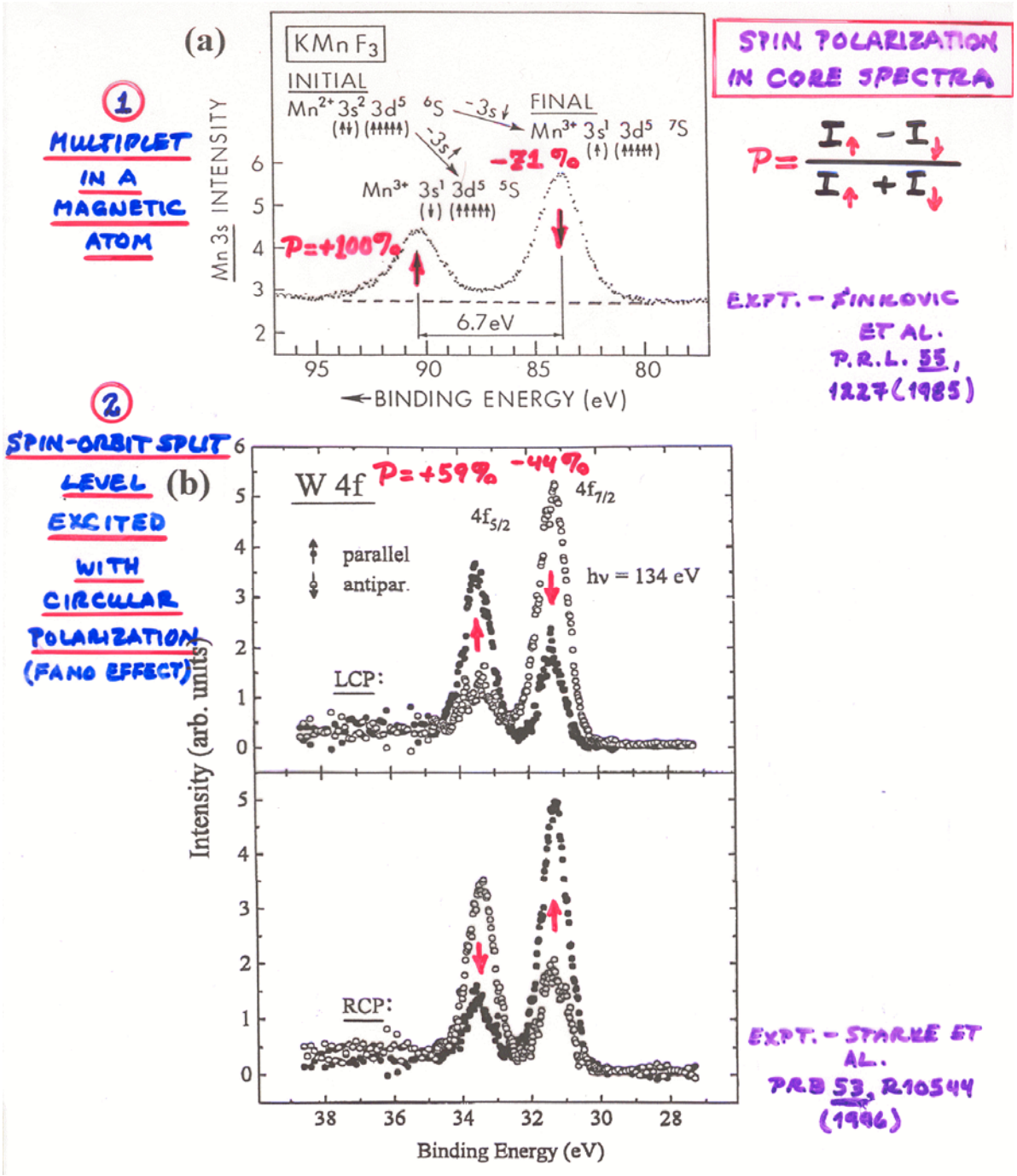
THEORY: BAGUS, FREEMAN, SASAKI, PHYS. REV. LETT. 30, 850 (1973) - ATOMIC CONFIG. INT. IN

$Mn^{3+}...3s^1...3d^5$

+ $Mn^{3+}...3s^2 3p^4 3d^6$

CI = configuration interaction

"Basic Concepts of XPS"
Figure 33

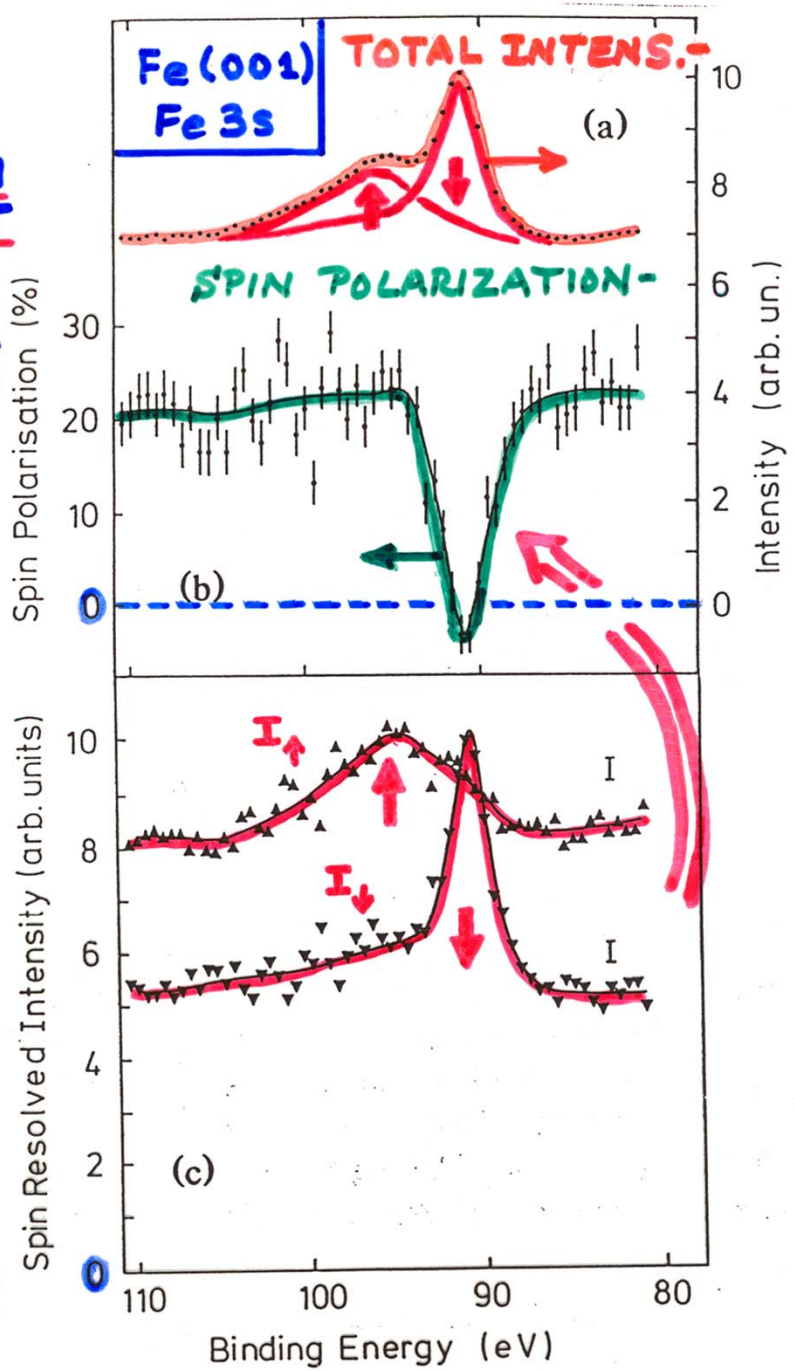


Spin <u>internally</u> referenced to spin of each ion

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

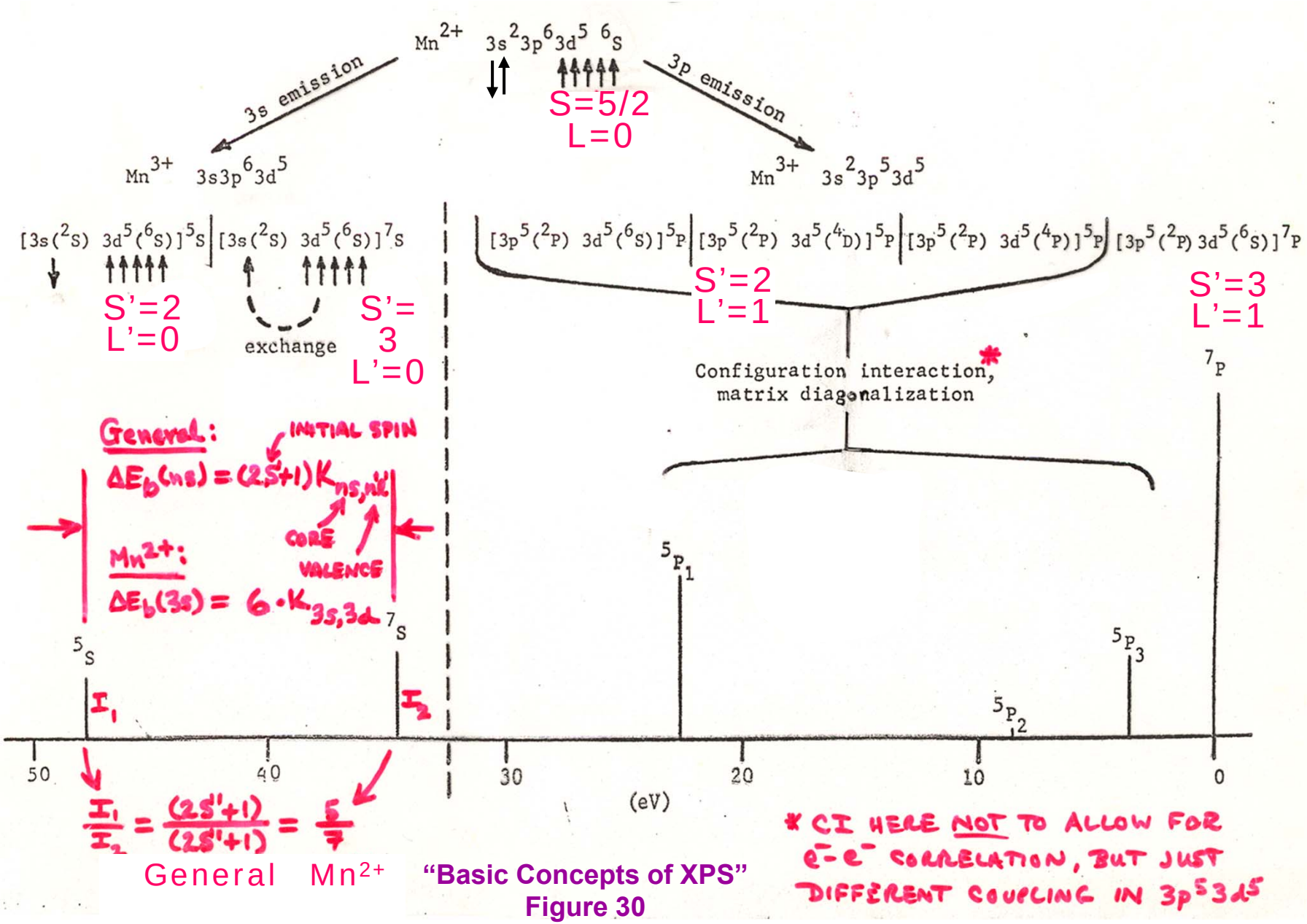
DIRECT OBSERVATION OF SPIN-SPLIT CORE LEVELS IN A FERROMAGNET

$$\frac{I_\uparrow - I_\downarrow}{I_\uparrow + I_\downarrow}$$



HILLEBRECHT ET AL., PHYS. REV. LETT. 65, 2450 (1990)

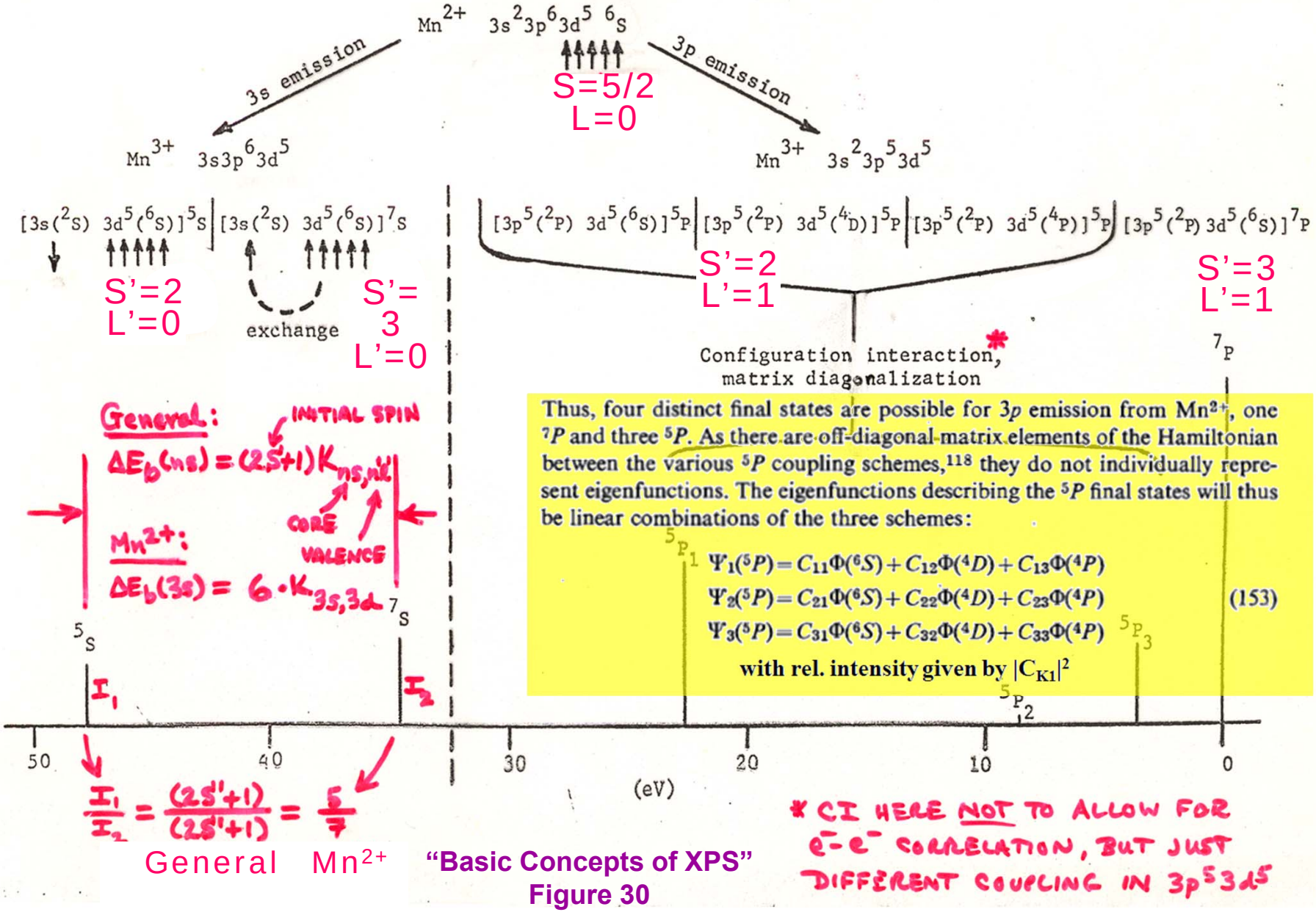
ORIGIN OF MULTIPLET SPLITTINGS IN Mn^{2+}: "ONE-ELECTRON" THEORY



General Mn^{2+}

"Basic Concepts of XPS"
Figure 30

ORIGIN OF MULTIPLET SPLITTINGS IN Mn^{2+}: "ONE-ELECTRON" THEORY



General Mn^{2+}

"Basic Concepts of XPS"
Figure 30

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

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

- SUDDEN APPROXIMATION: $\Psi_K \rightarrow \Psi_f$ = PHOTO e⁻ (FAST)

k HOLE → $\Psi_1 \rightarrow \Psi_1'$, …, $\Psi_{k-1} \rightarrow \Psi_{k-1}'$, $\Psi_{k+1} \rightarrow \Psi_{k+1}'$, …, $\Psi_N \rightarrow \Psi_N'$ (SLOW)

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

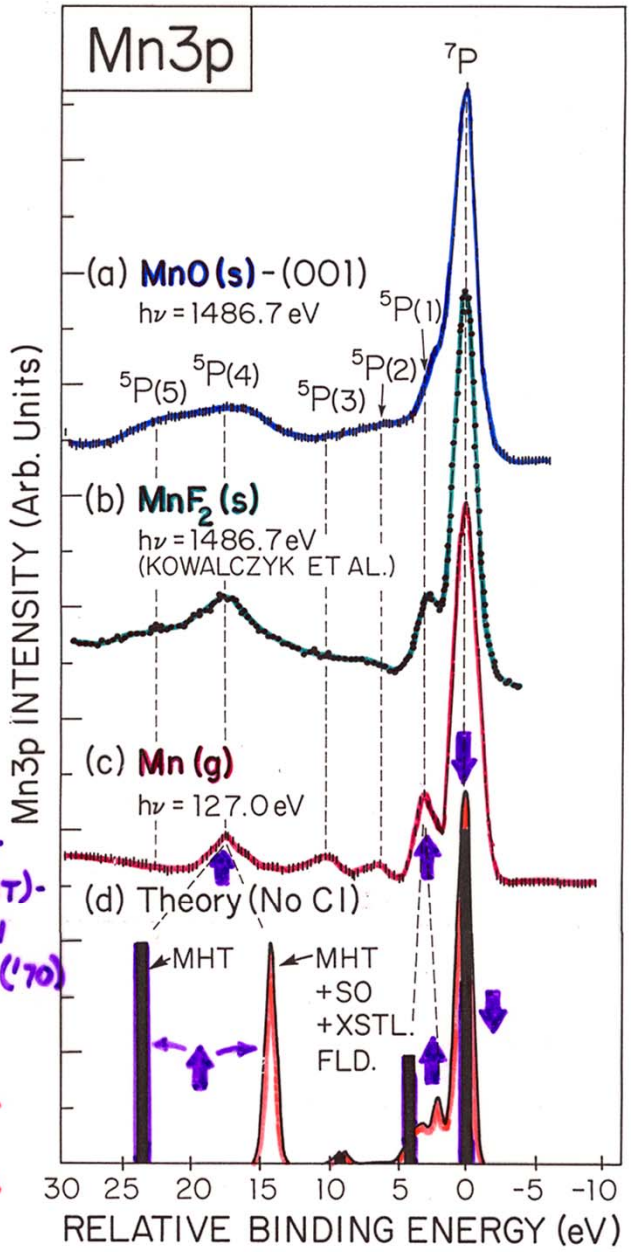
$$\left| \hat{e} \cdot \langle \Psi_f | \vec{r} | \Psi_K \rangle \right|^2$$

↳ NORMAL $\frac{d\sigma_K}{d\Omega}$

$\Phi(3s^1 3p^6 3d^5\ {}^6S)$ from initial state

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

Differential cross section: $d\sigma/d\Omega_{3s}$



THEORY: NO CI

SIMPLE MULTIPLET HOLE THEORY (MHT) - FADLEY, SHIRLEY PHYS. REV. A2, 1109 ('70)

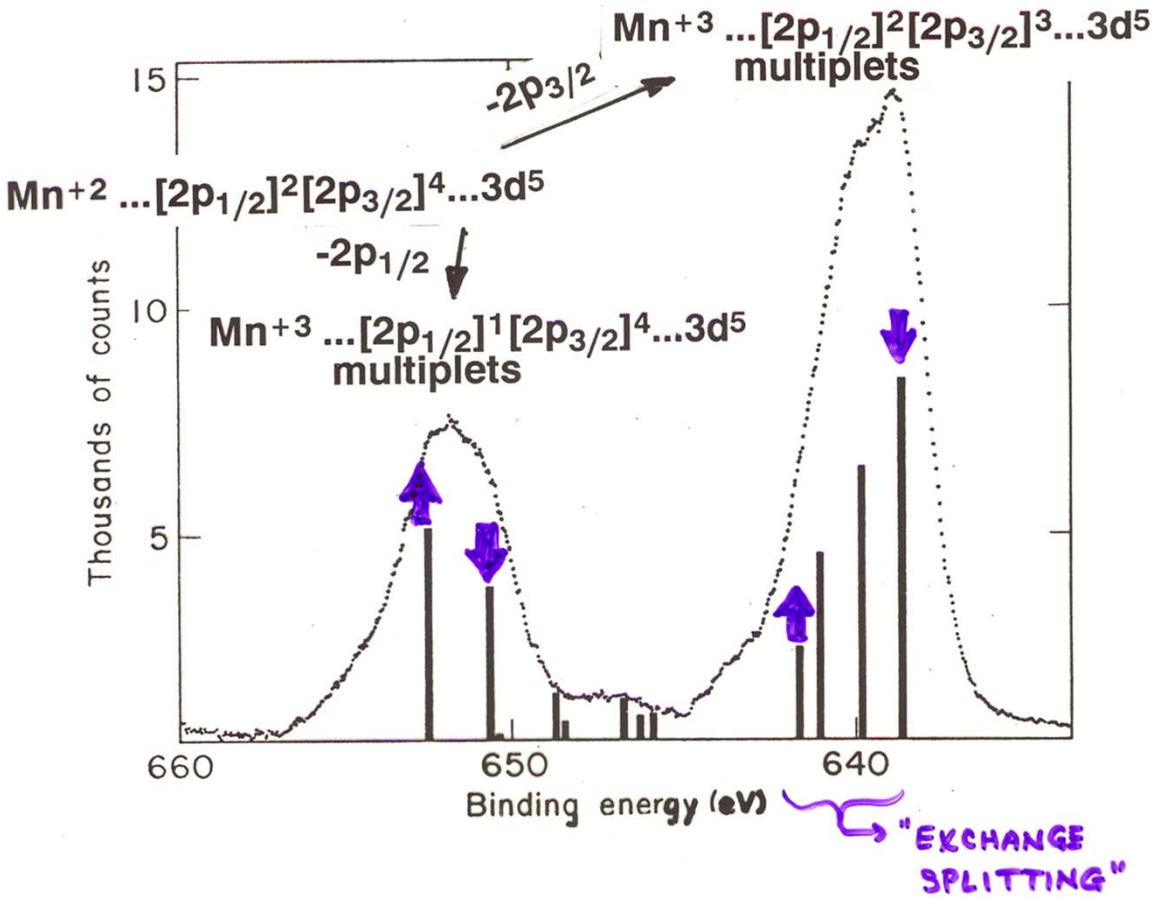
EMPIRICAL MHT WITH SPIN ORBIT & CRYSTAL FIELD - SUGANO ET AL., J. PHYS. C 15, 2625 (1982)

MHT = multiplet hole theory with CI
SO = spin-orbit
XSTAL FLD. = crystal field

HERMSMEIER ET AL., P.R.L. 61, 2592 ('88)

+ MORE COMPLEX MULTIPLETS FOR L > 0 WITH SPIN-ORBIT COUPLING:

Mn 2p emission from MnF_2:

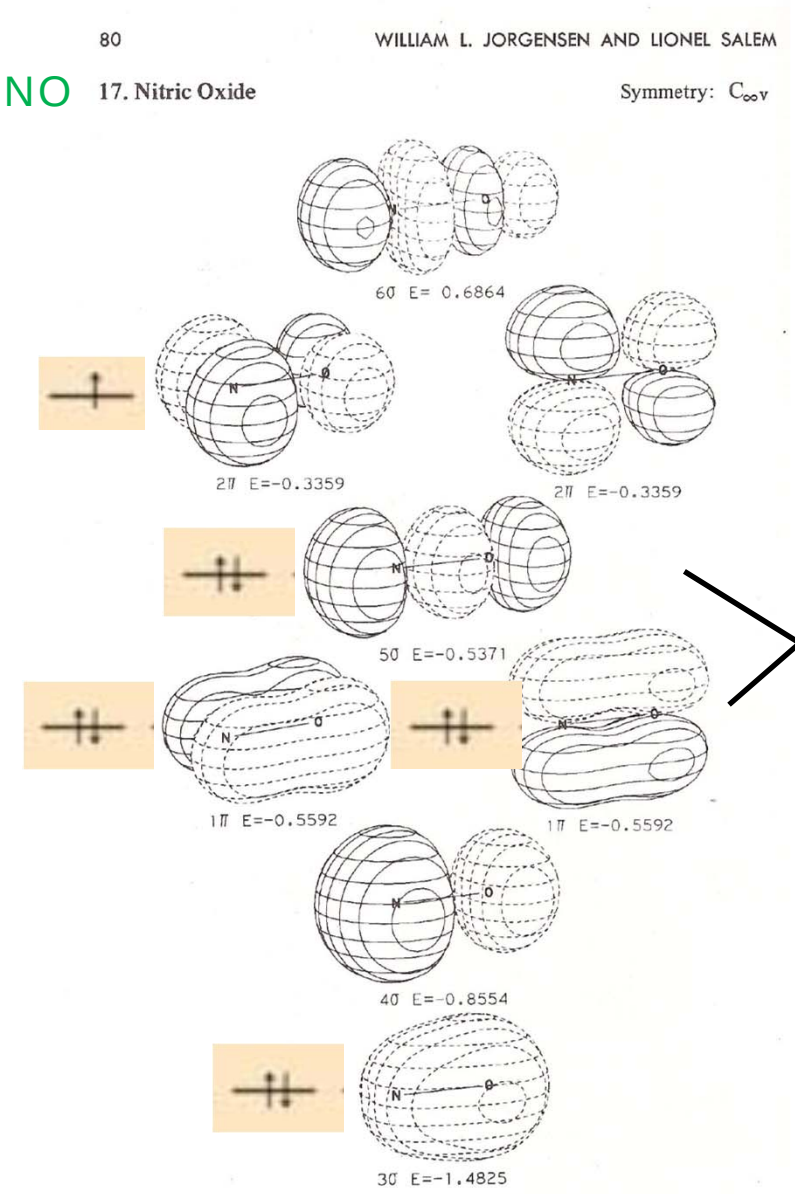


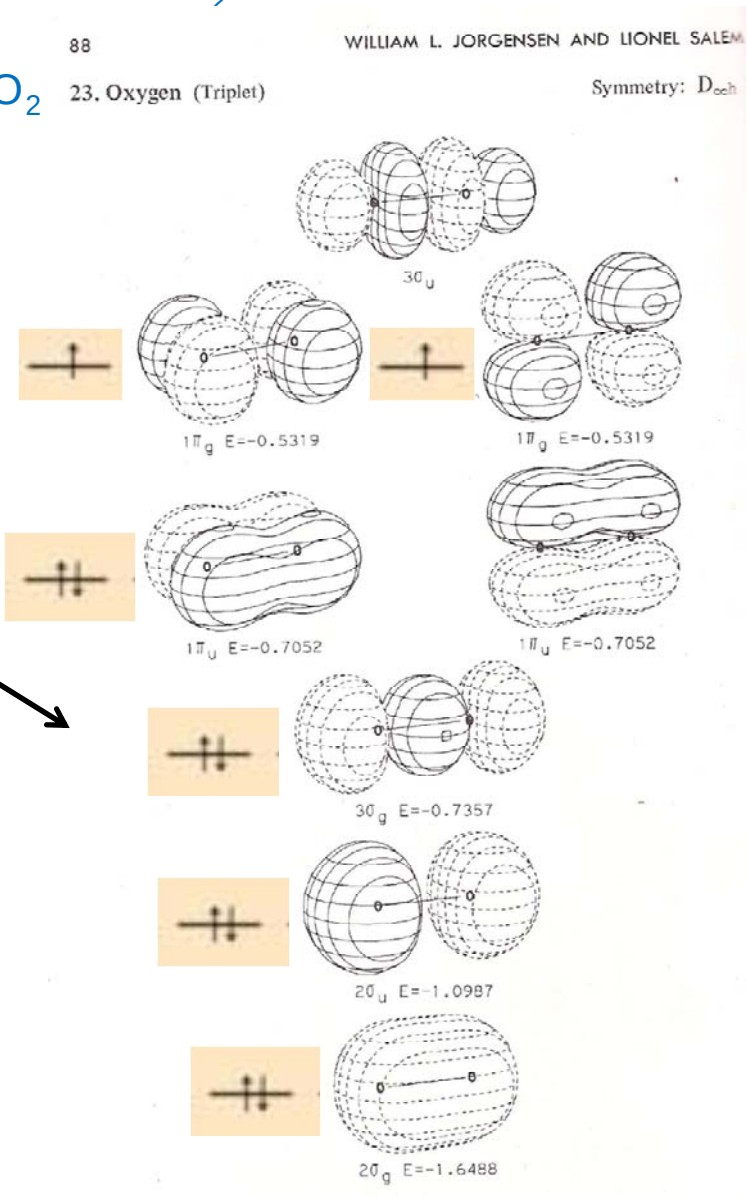
Expt.--Kowalczyk et al., Phys. Rev. B11, 1721 (1975)

Theory--Gupta and Sen, Phys. Rev. B10, 71 (1974)

Park et al., Phys. Rev. B37, 10867(1988)

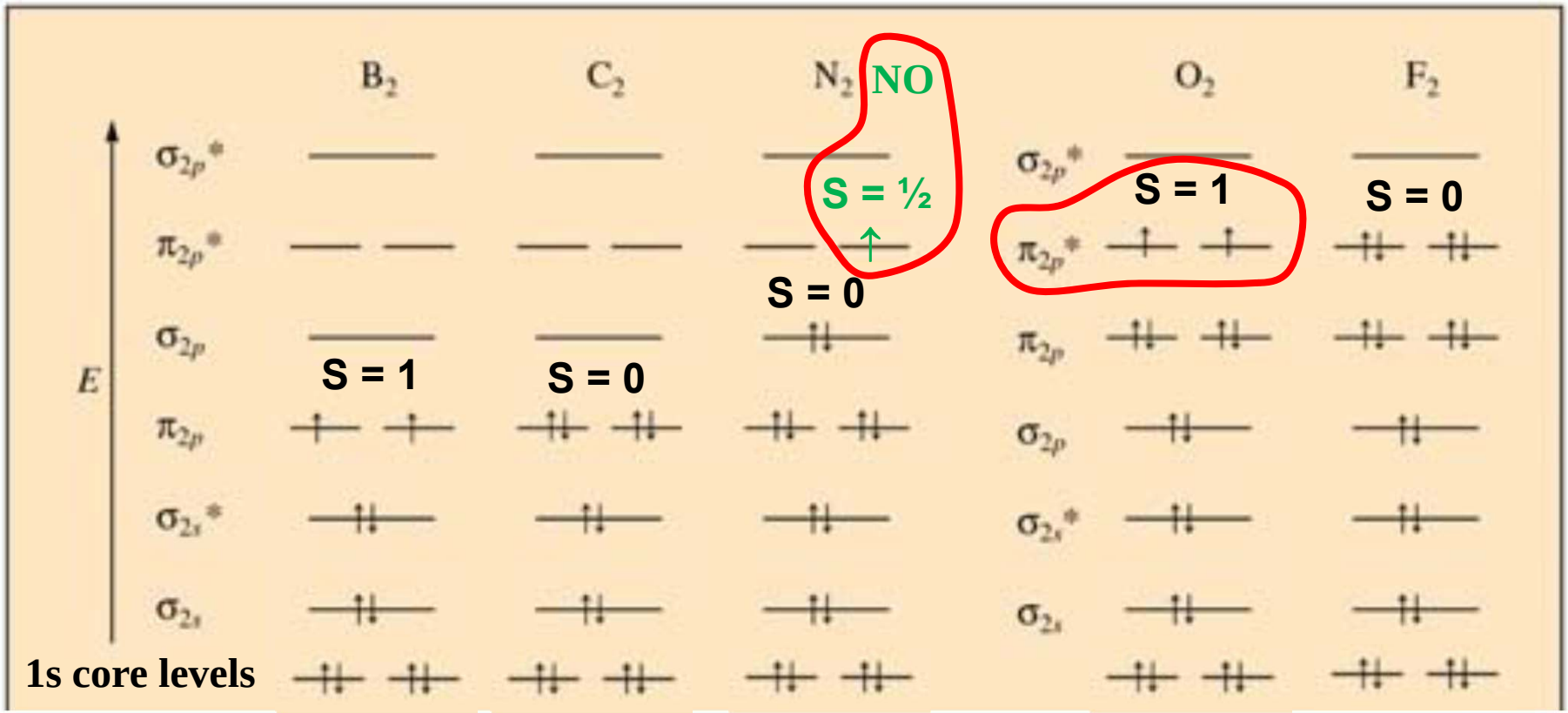
FILLING OF THE MOLECULAR ELECTRONIC STATES OF DIATOMIC NO AND O_2





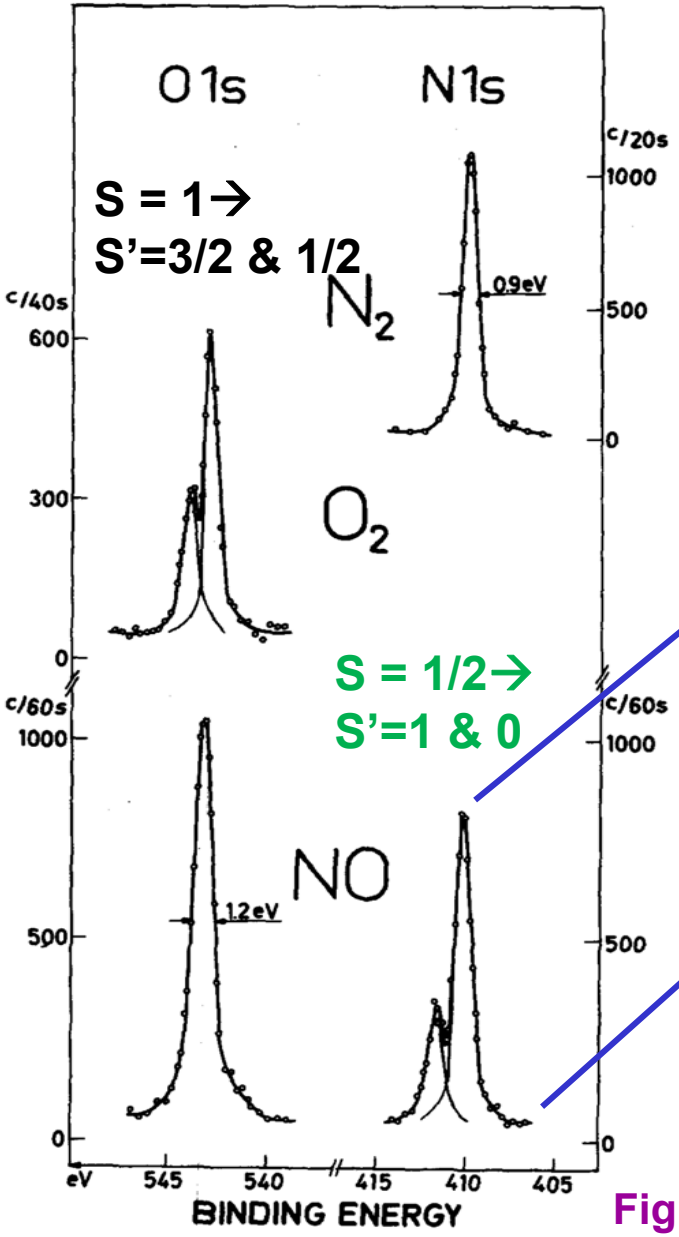
1s core levels

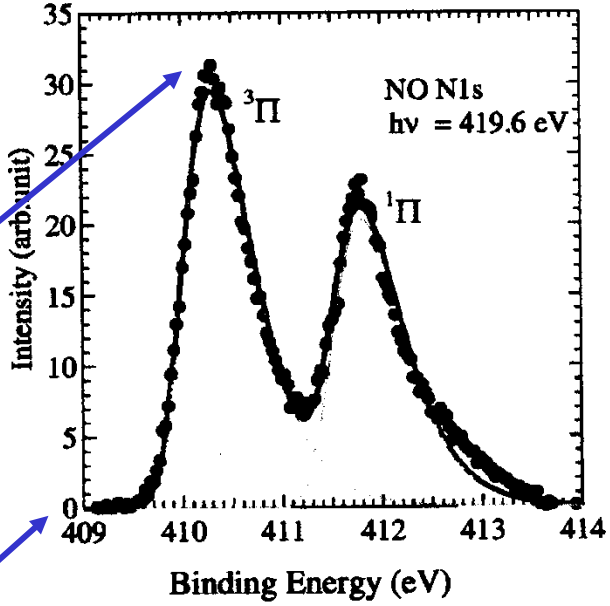
FILLING OF THE MOLECULAR ELECTRONIC STATES OF HOMONUCLEAR DIATOMIC MOLECULES & NO



Multiplet splitting ∝ $K_{1s,\pi 2p^*}$

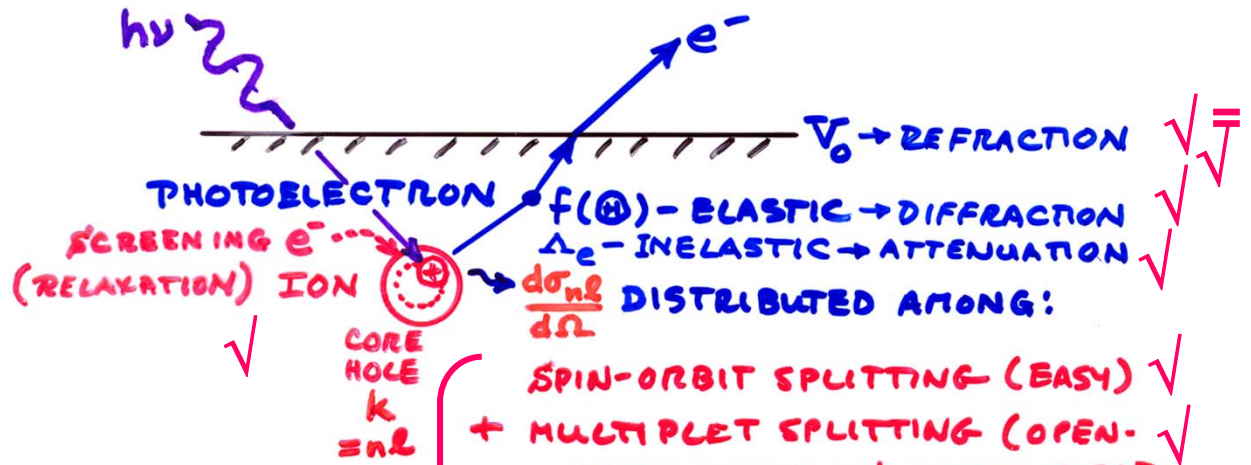
MULTIPLETS IN FREE MOLECULES





Hosaka et al., J. Phys. B 36, 4617 (2003), and earlier theory from Bagus and Schaefer, J. Chem. Phys. 55, 1474 (1971)

Fig. 34
Basic Concepts of XPS

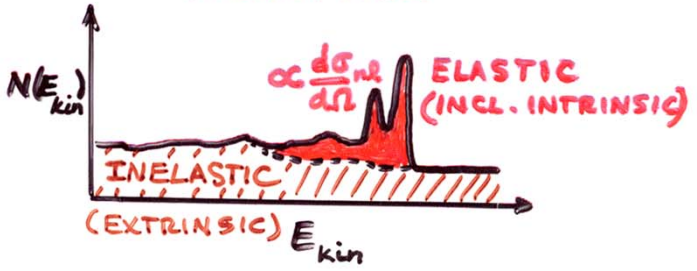


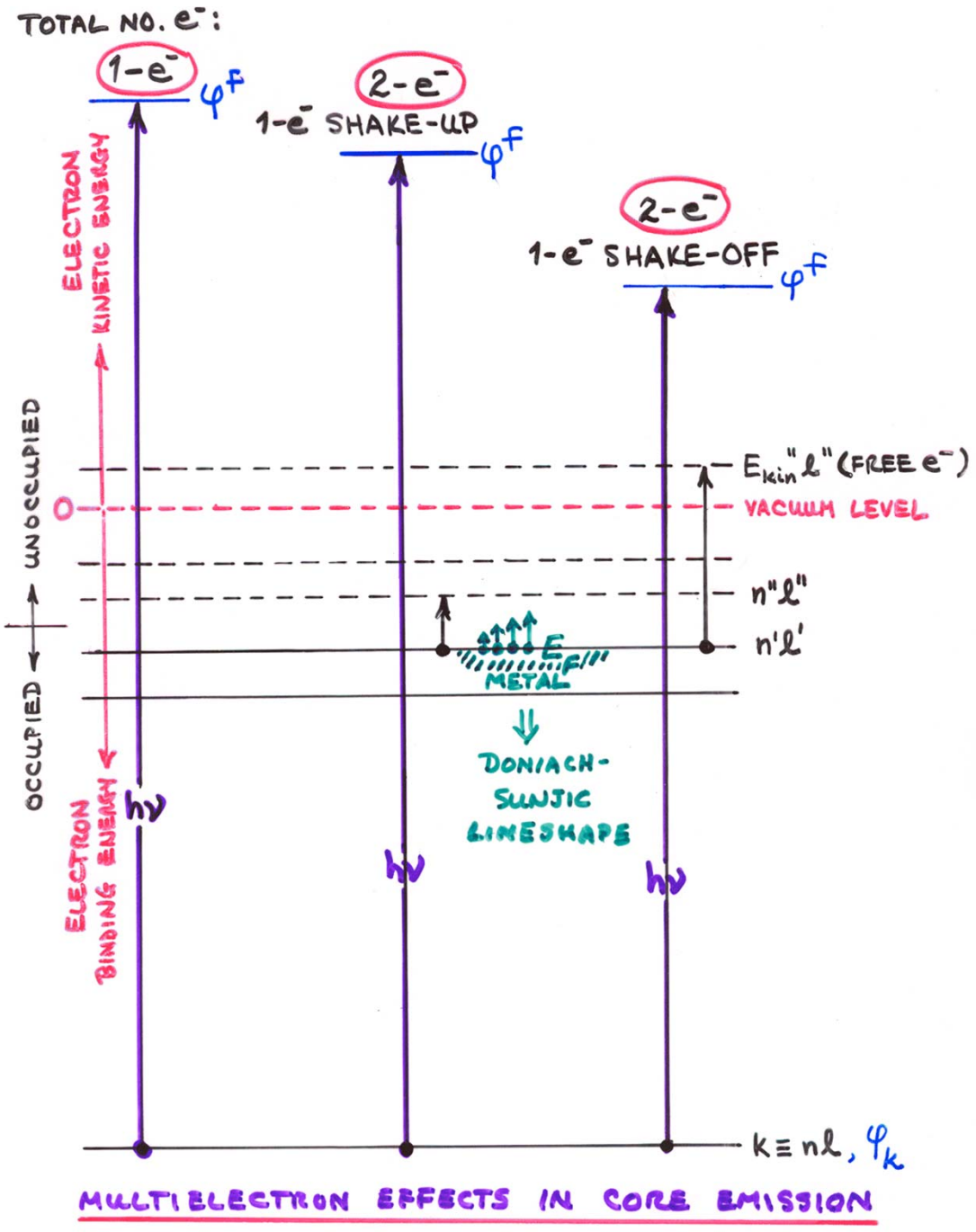
√ = covered so far

ADDITIONAL SOURCES OF STRUCTURE (AND INFORMATION!) IN SPECTRA BEYOND CHEMICAL SHIFTS

- SPIN-ORBIT SPLITTING (EASY) √
- + MULTIPLET SPLITTING (OPEN-SHELL SYSTEMS), XSTAL FIELD √
- + CORRELATION / CONFIGURATION INTERACTION √
- + SHAKE-UP / SHAKE-OFF / e⁻-HOLE
- + SCREENING / NON-SCREENING: CONFIGURATION INTERACTION
- + VIBRATIONAL EXCITATIONS
- + RESONANT PHOTOEMISSION (hν ≈ $E_{b,nl'}$) √

REALLY ALL AT ONCE, BUT SUM RULES + THEORY HELP





MULTIELECTRON EFFECTS IN CORE EMISSION

INTENSITIES IN PHOTOELECTRON SPECTRA:

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

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

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

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

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

k HOLE → $\psi_1 \to \psi'_1$, …, $\psi_{k-1} \to \psi'_{k-1}$, $\psi_{k+1} \to \psi'_{k+1}$, …, $\psi_N \to \psi'_N$ } (SLOW)

S_0^2 in EXAFS (LATER)

$$\text{INT.}_K \propto |\langle\psi^f_{VIB,v'}|\psi^i_{VIB,v}\rangle|^2 \underbrace{|\langle\Psi^f_{e^-}(N-1,K)|\Psi^{\uparrow}_{K}(N-1,K)\rangle|^2}_{\text{SAME SUBSHELL COUPLING + TOTAL L,S} \to \text{"MONOPOLE"}}$$

k MISSING

$$|\hat{e}\cdot\langle\psi_f|\vec{r}|\psi_K\rangle|^2$$

↳ NORMAL $\frac{d\sigma_K}{d\Omega}$

- SLATER DETS. FOR $\Psi^f_{e^-} = \det(\psi'_1\psi'_2\cdots\psi'_{k-1}\psi'_{k+1}\cdots\psi'_N)$

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

$$\text{INT.}_K \propto |\langle\psi^f_{VIB,v'}|\psi^i_{VIB,v}\rangle|^2 |\langle\psi'_1|\psi_1\rangle|^2 |\langle\psi'_2|\psi_2\rangle|^2 \cdots$$
$$|\langle\psi'_{k-1}|\psi_{k-1}\rangle|^2 |\langle\psi'_{k+1}|\psi_{k+1}\rangle|^2 \cdots |\langle\psi'_N|\psi_N\rangle|^2 \cdot$$

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

$$|\hat{e}\cdot\langle\psi_f|\vec{r}|\psi_K\rangle|^2$$

1e- DIPOLE → $d\sigma/d\Omega$

- PLUS DIFFRACTION EFFECTS IN ψ_f ESCAPE

NEON 1S SHAKE-UP / SHAKE-OFF:

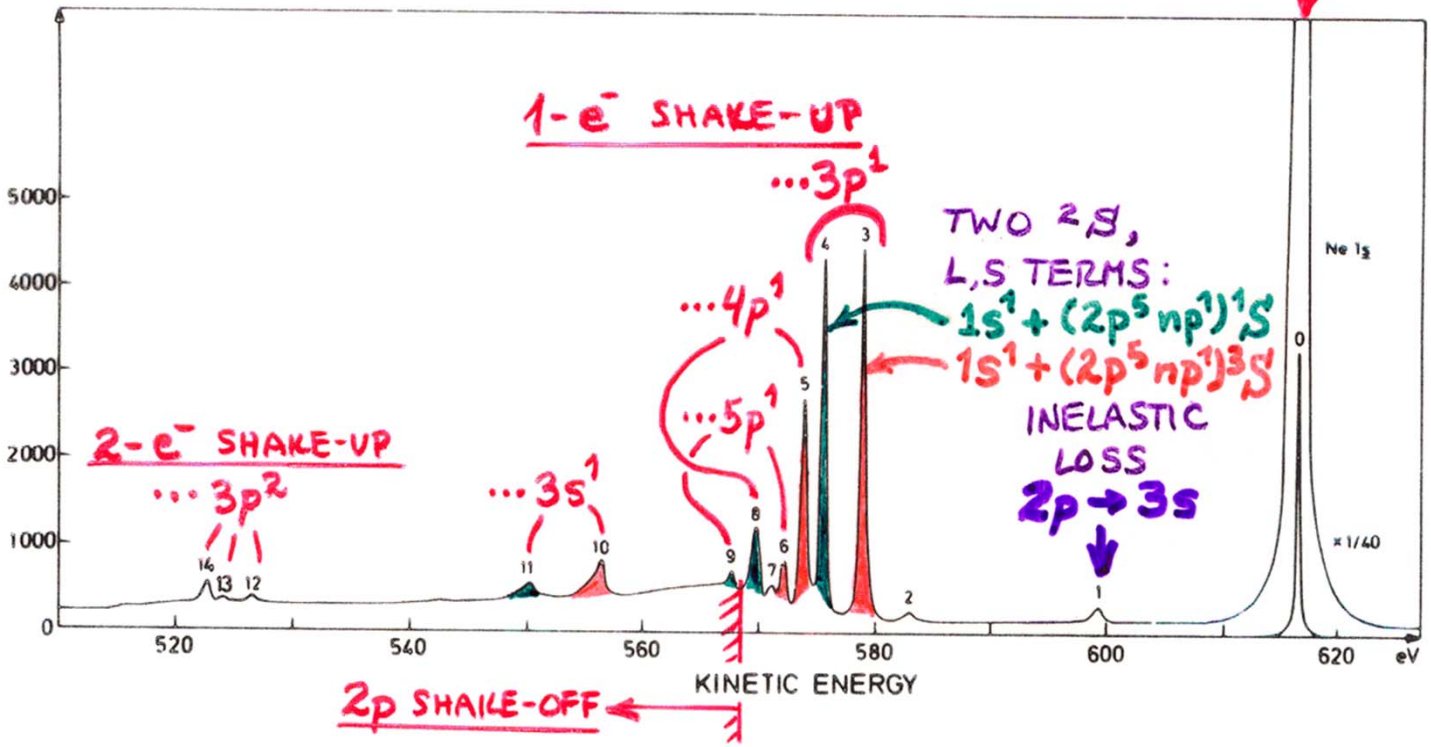
$Ne\ 1s^2 2s^2 2p^6\ {}^1S \xrightarrow{-e^-} Ne^+\ 1s^1 2s^2 2p^6\ {}^2S$

1-e^- SHAKE-UP: ($Ne^+\ 1s^1 2s^2 2p^5\ np^1\ (n=3,4,5,\dots)\ {}^2S$
$Ne^+\ 1s^1 2s^1 2p^6\ ns^1\ (n=3,\dots)\ {}^2S$

2-e^- SHAKE-UP: $Ne^+\ 1s^1 2s^2 2p^4 3p^2\ {}^2S$

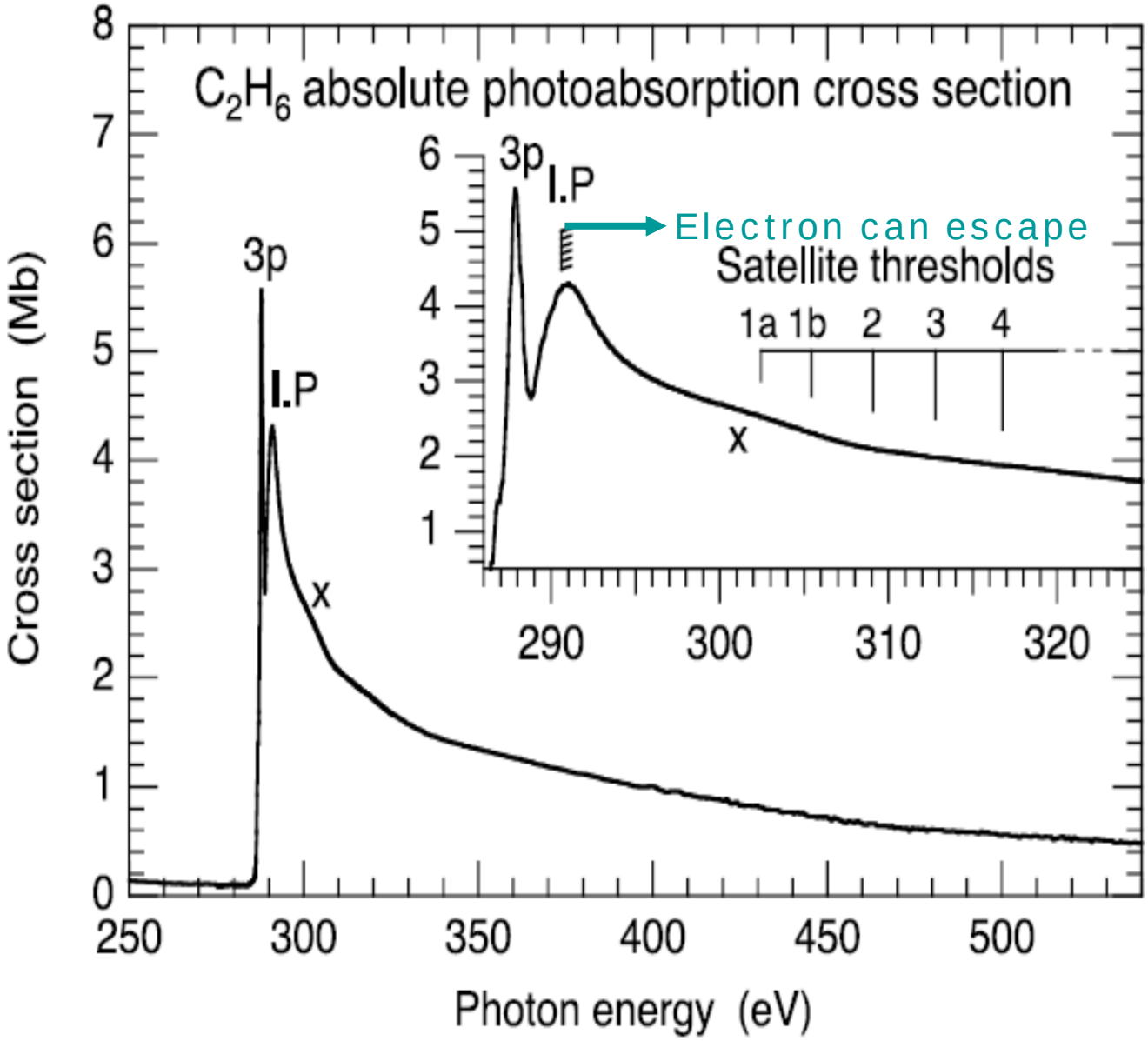
2p SHAKE-OFF: $Ne^+\ 1s^1 2s^2 2p^5, E_{kin}\text{"p"}\ {}^2S$

"Basic Concepts of XPS"
Figure 36



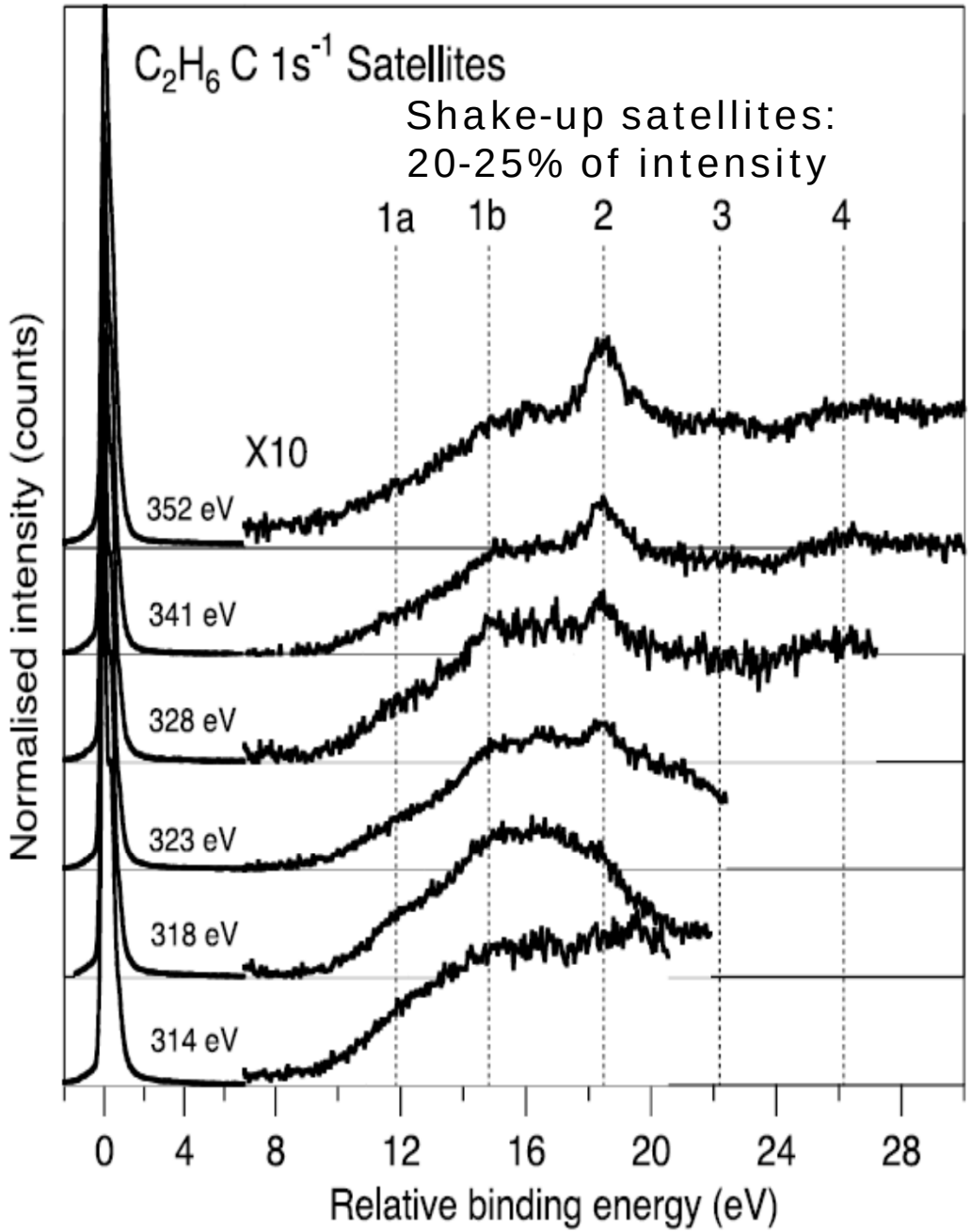
OVERALL: ~12% SHAKE-UP + 16% SHAKE-OFF ≈ 28% OF EVENTS

Ethane: C 1s NEXAFS, with shakeup also

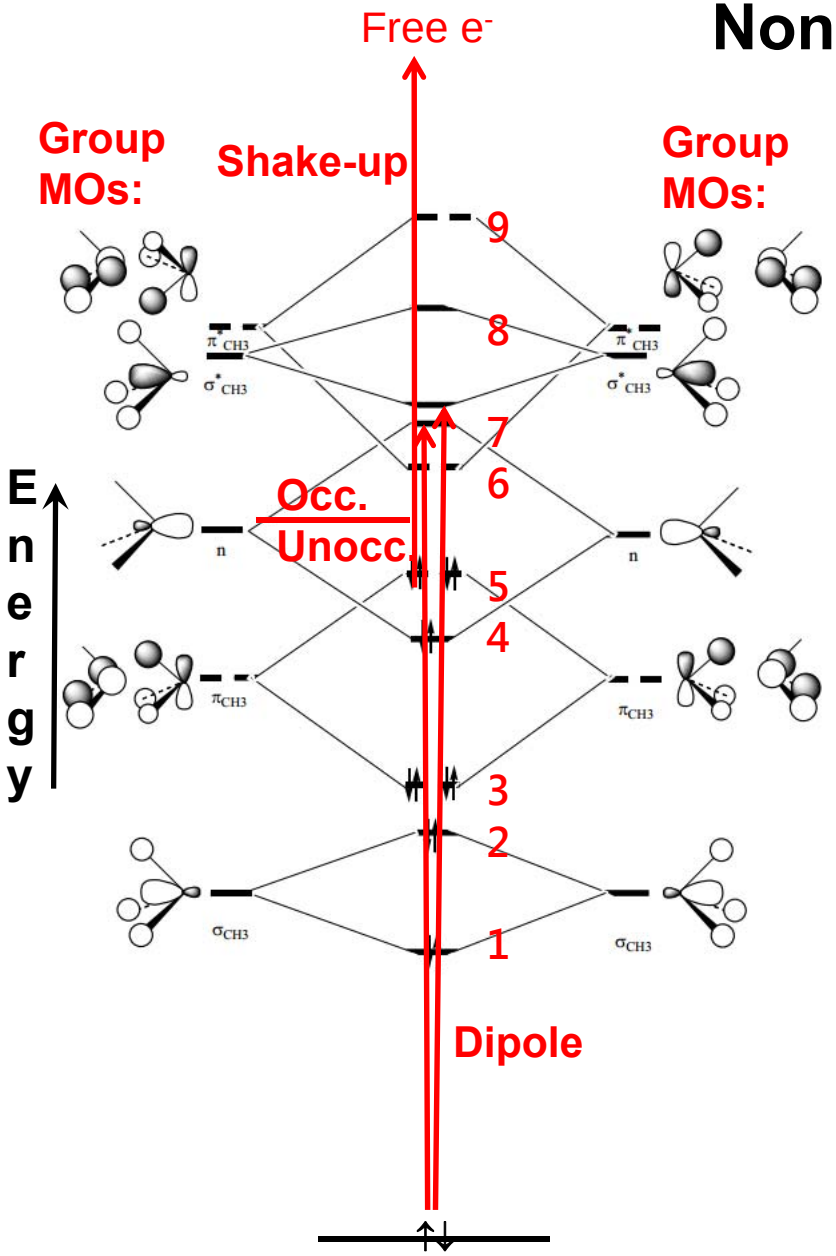


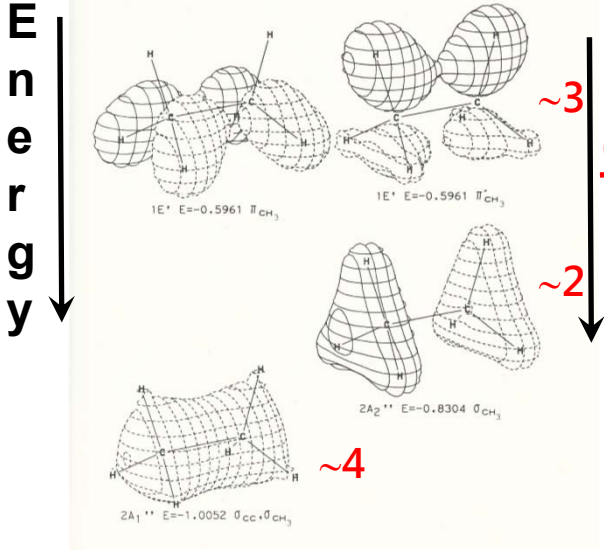
Rennie et al., J. Phys. B: At. Mol. Opt. Phys. 32 (1999) 2691

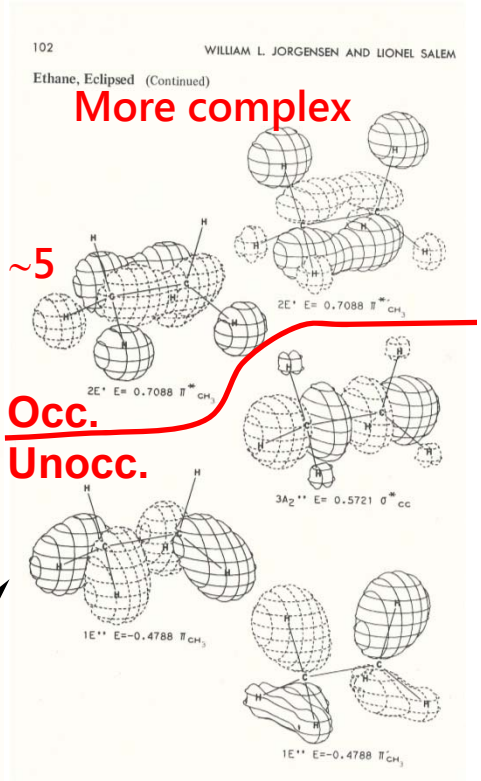
Ethane-
C 1s photoemission:
“Conjugate shake-up”
C 1s→unoccupied MO
+occupied MO to free
electron

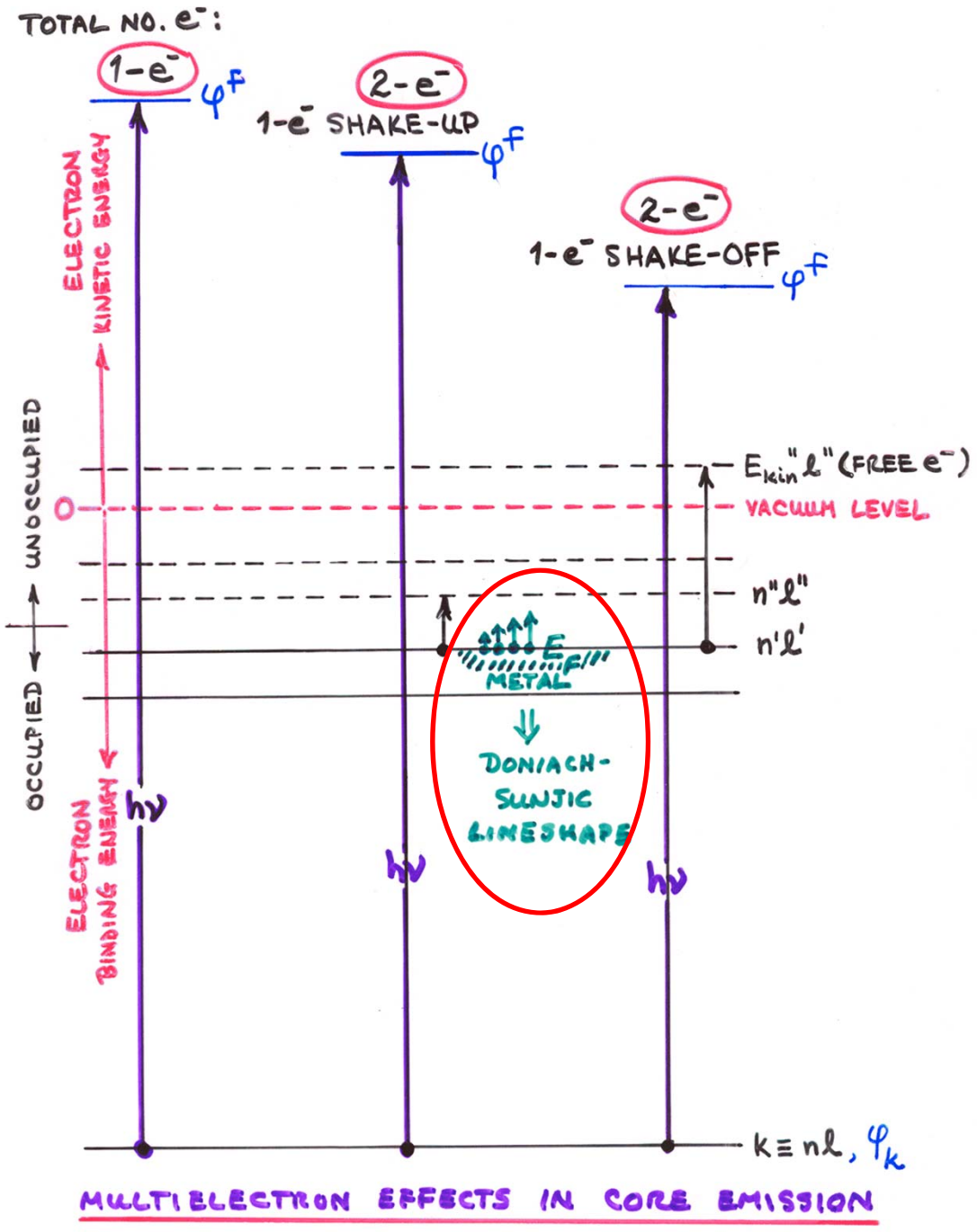


Non-sudden "Conjugate shake-up" in ethane: MO pictures

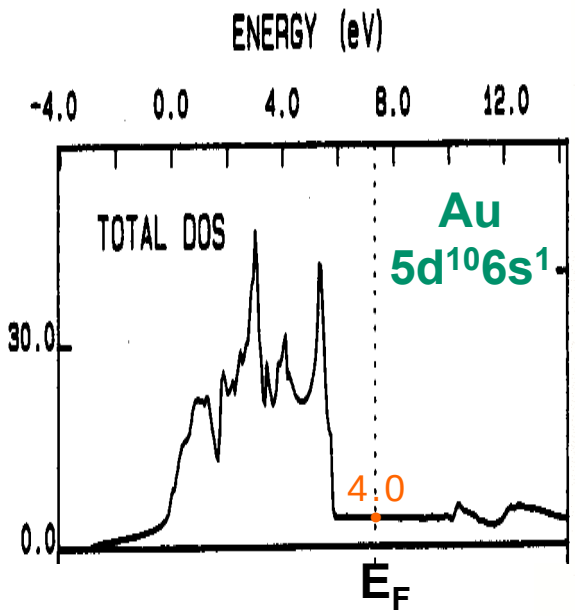


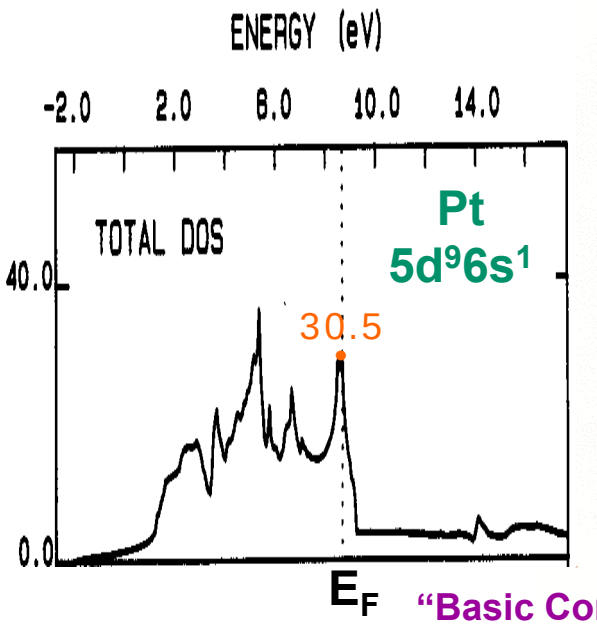




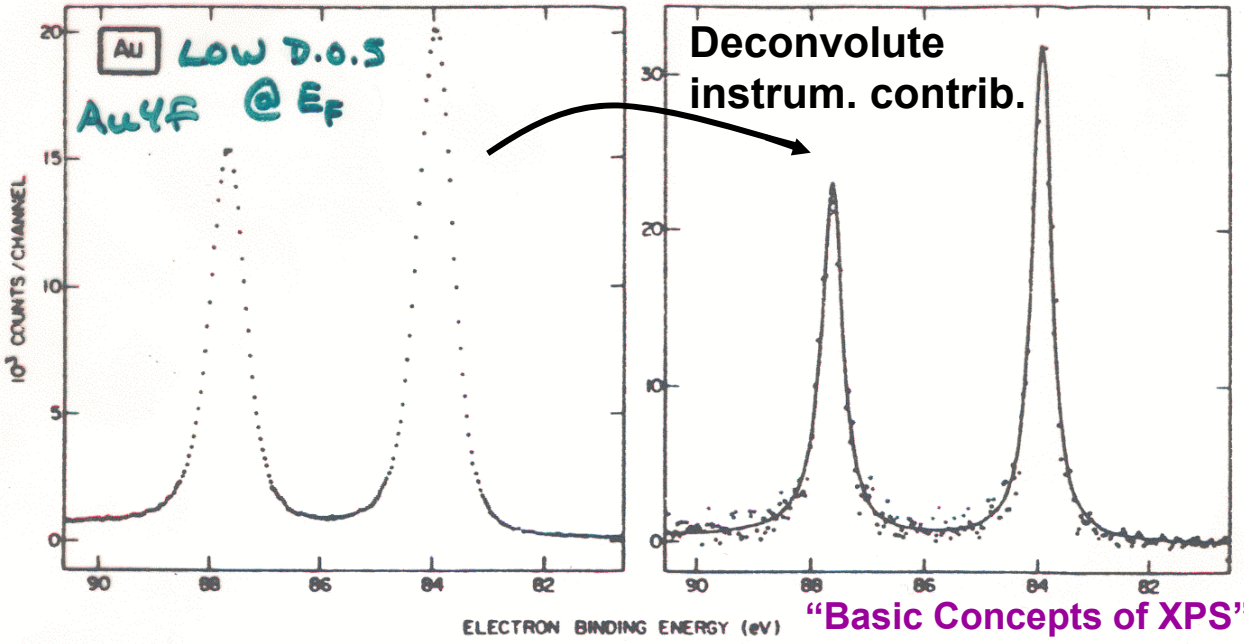

TOTAL NO. e⁻:
1-e⁻
φ^f
2-e⁻
1-e⁻ SHAKE-UP
φ^f
2-e⁻
1-e⁻ SHAKE-OFF
φ^f
ELECTRON KINETIC ENERGY
UNOCCUPIED
OCCUPIED
ELECTRON BINDING ENERGY
E_kin "l" (FREE e⁻)
0
VACUUM LEVEL
n"l"
n'l'
E_F
METAL
DONIACH-SUNJIC LINESHAPE
hν
hν
hν
k ≡ nl, φ_k
MULTIELECTRON EFFECTS IN CORE EMISSION

BAND THEORY—D.O.S:

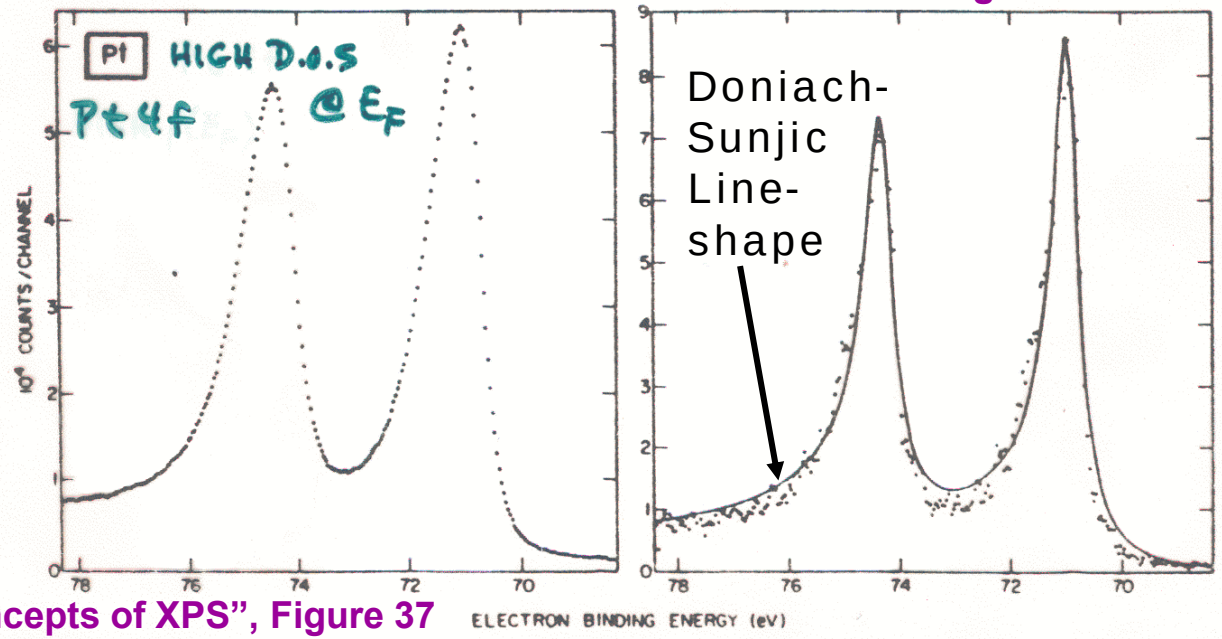




SHAKE-UP IN METALS— ∝ D.O.S AT E_F:



"Basic Concepts of XPS"
Figure 10



"Basic Concepts of XPS", Figure 37

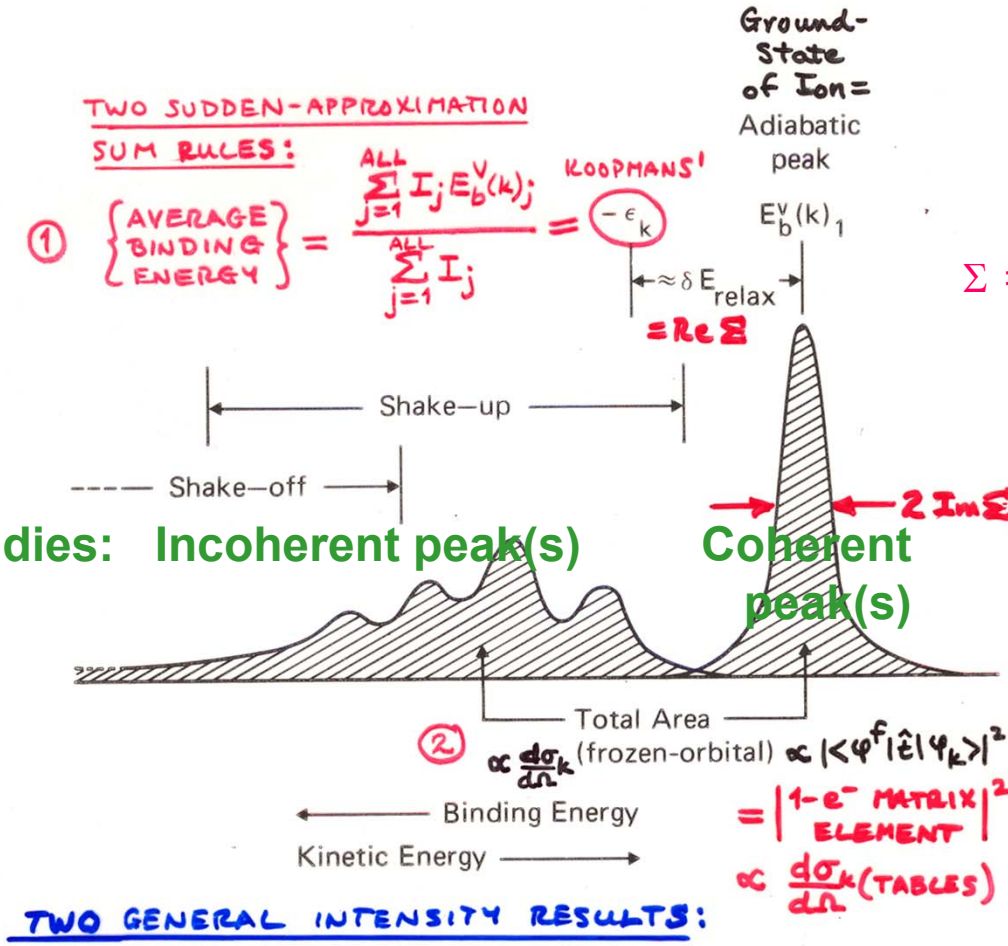
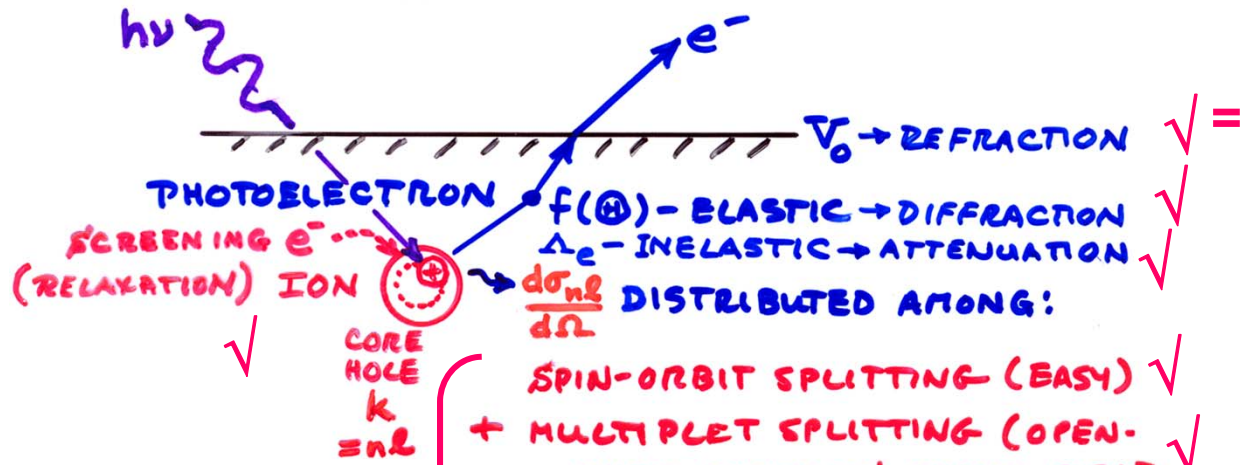


Figure 8 -- Schematic illustration of a photoelectron spectrum involving shake-up and shake-off satellites. The weighted average of all binding energies yields the Koopmans' Theorem binding energy $-\epsilon_k$ (sum rule (77)), and the sum of all intensities is proportional to a frozen-orbital cross section σ_k (sum rule (78)). The adiabatic peak corresponds to formation of the ground-state of the ion ($E_b(k)_1 \equiv E_b(K=1)$).

Σ = many-body "self energy" = $Re\Sigma + i Im\Sigma$

$\Delta E \times \tau_{lifetime} \approx \hbar / 2$

In valence-band studies: Incoherent peak(s) Coherent peak(s)

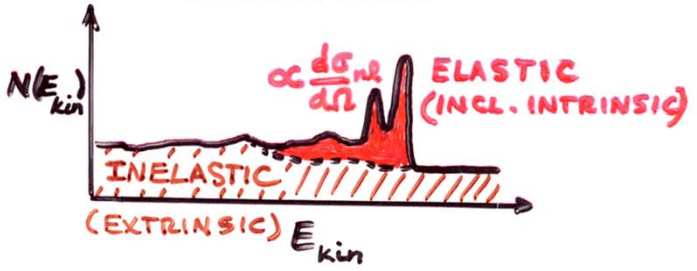


√ = covered so far

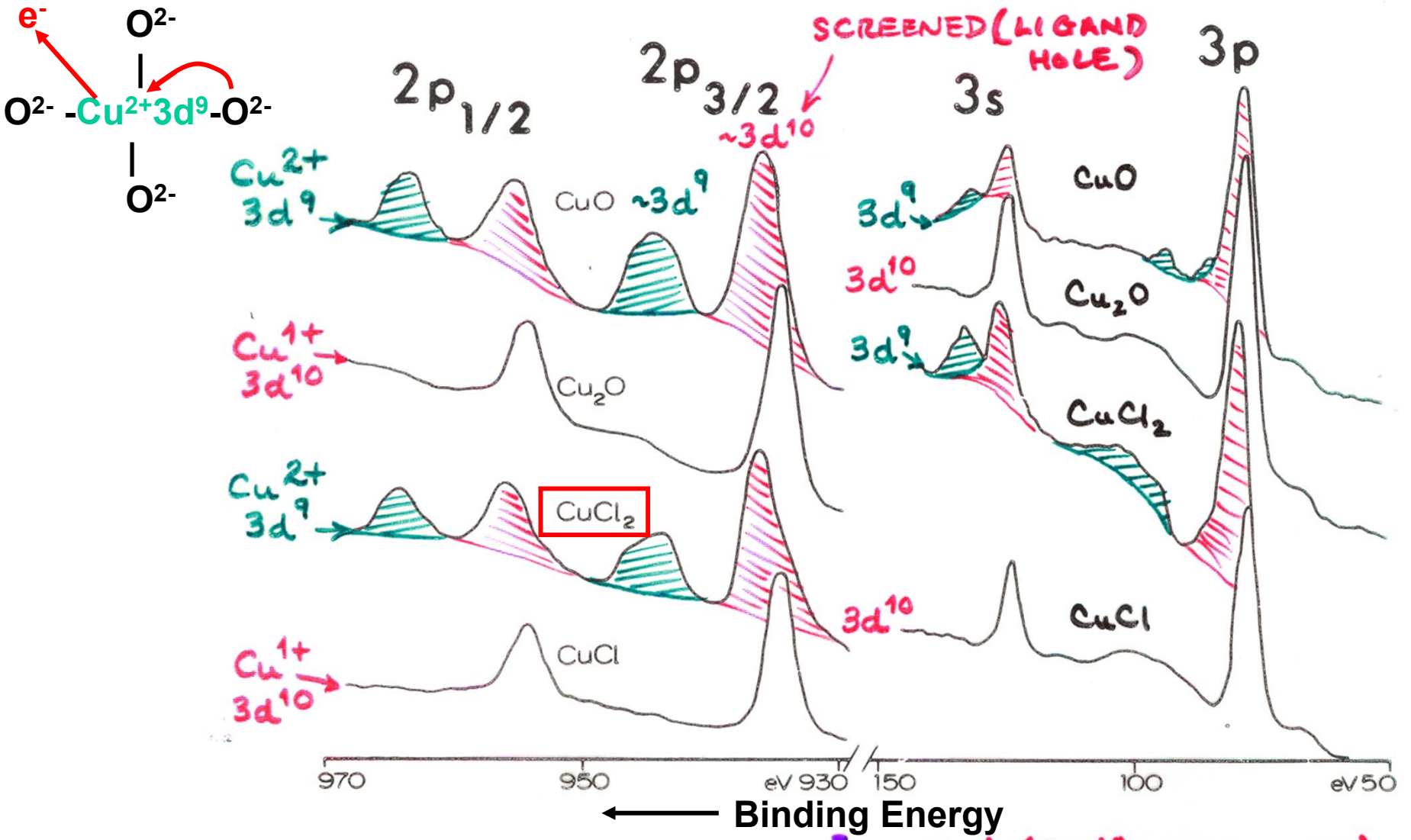
ADDITIONAL SOURCES OF STRUCTURE (AND INFORMATION!) IN SPECTRA BEYOND CHEMICAL SHIFTS

- SPIN-ORBIT SPLITTING (EASY) √
- \+ MULTIPLET SPLITTING (OPEN-SHELL SYSTEMS), XSTAL FIELD √
- \+ CORRELATION / CONFIGURATION INTERACTION √
- \+ SHAKE-UP/SHAKE-OFF/e⁻-HOLE √
- \+ SCREENING / NON-SCREENING: CONFIGURATION INTERACTION ←
- \+ VIBRATIONAL EXCITATIONS
- \+ RESONANT PHOTOEMISSION (hν ≈ $E_{b,nl'}$) √

REALLY ALL AT ONCE, BUT SUM RULES + THEORY HELP



SATELLITES & CHARGE-TRANSFER SCREENING



ACTUAL FINAL STATE $\Psi \approx C_1\Phi_1$ ($3d^{10}$ - SCREENED)
$+ C_2\Phi_2$ ($3d^9$ - UNSCREENED)

"Basic Concepts of XPS"
Figure 38

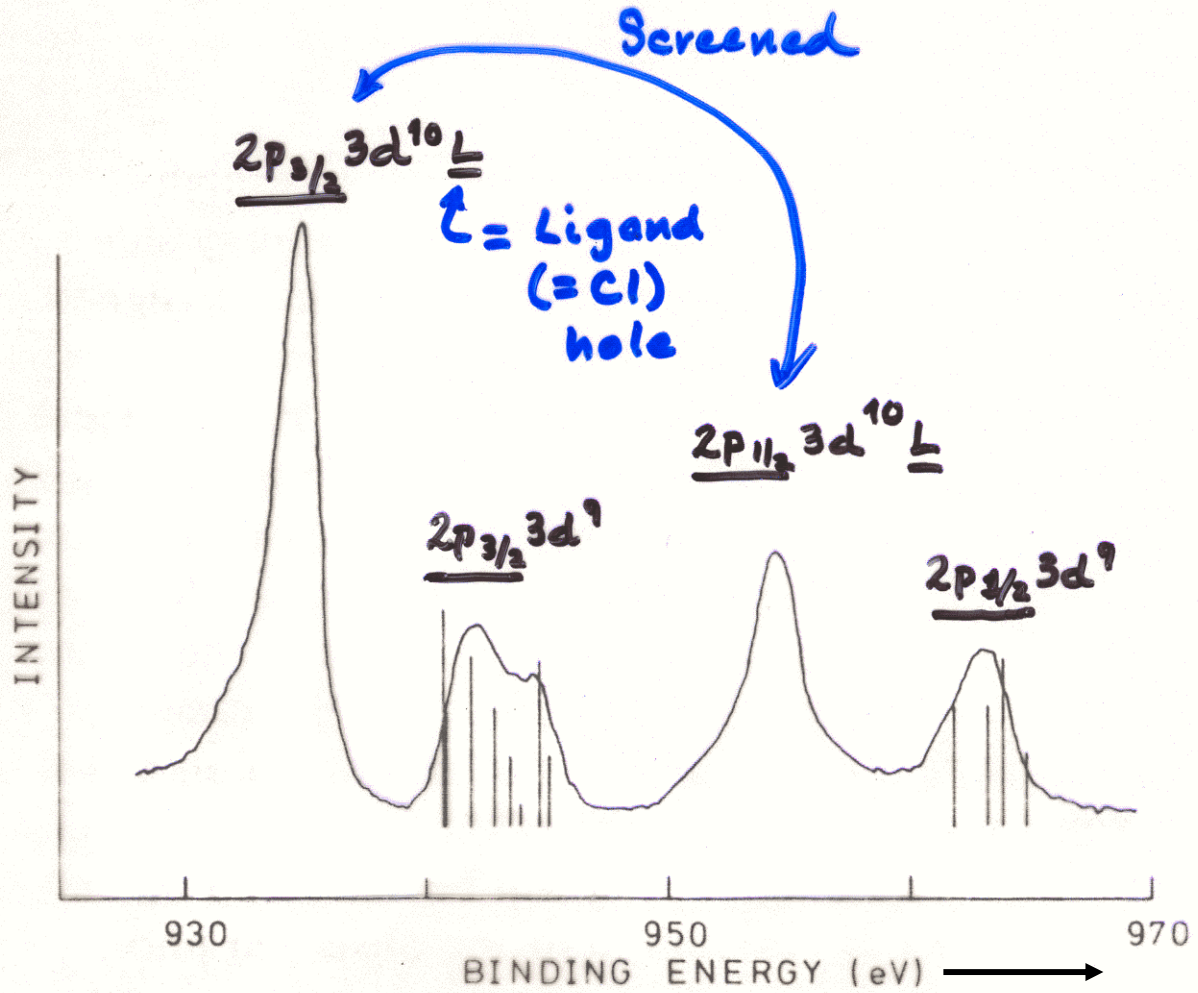


FIG. 2. The Cu $2p$ spectrum of $CuCl_2$ together with the expected multiplet splittings, represented by bars, for the $\underline{2p}3d^9$ level as calculated and discussed in the text.

VAN DER LAAN ET AL., PHYS. REV. B 23, 4369 (1981)

Screening depends on Ionicity/covalency→ satellite intensities can be used to measure interaction parameters

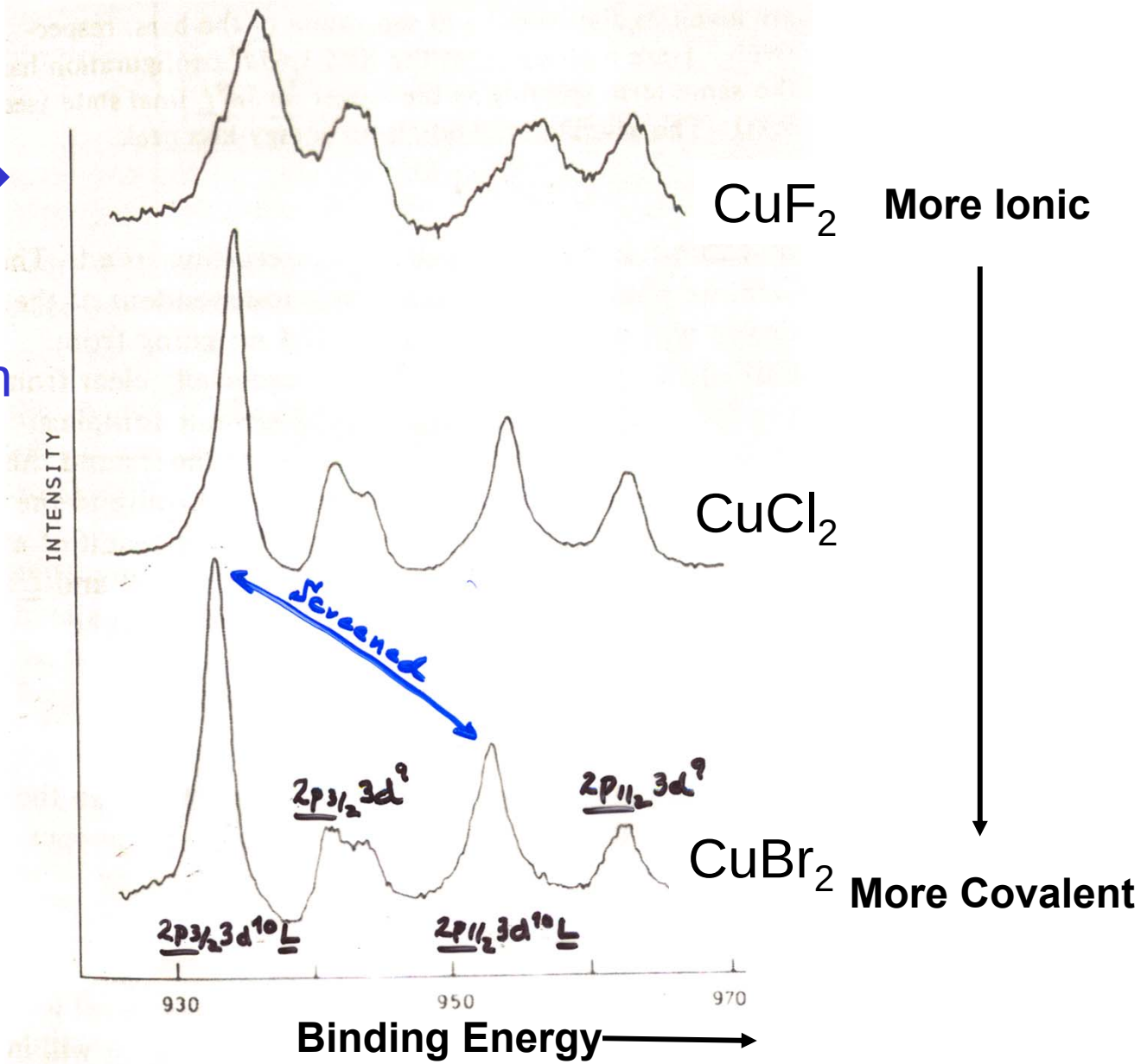


FIG. 1. Cu 2*p* photoelectron spectra of Cu dihalides. The lines leading to a final state with a ligand hole ($\underline{L}$) show a chemical shift.

Screening depends on Ionicity/covalency→ satellite intensities and energy spacings can be used to measure interaction parameters

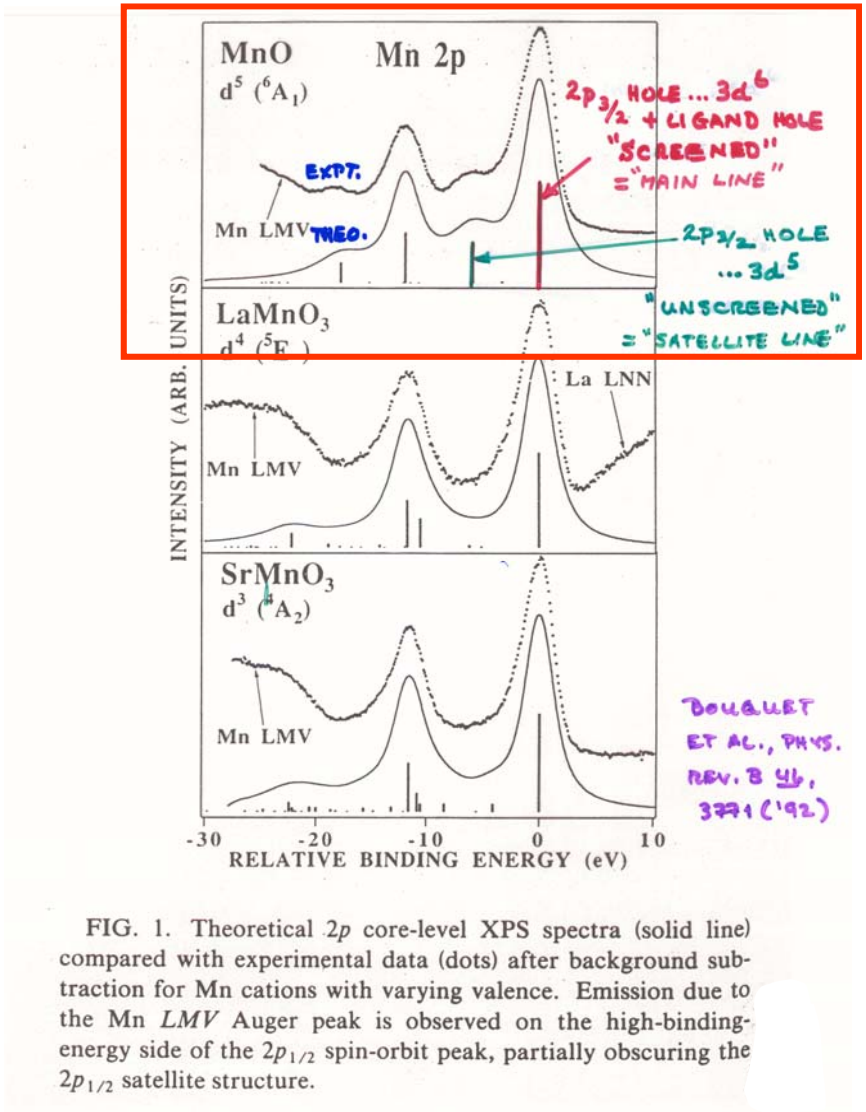
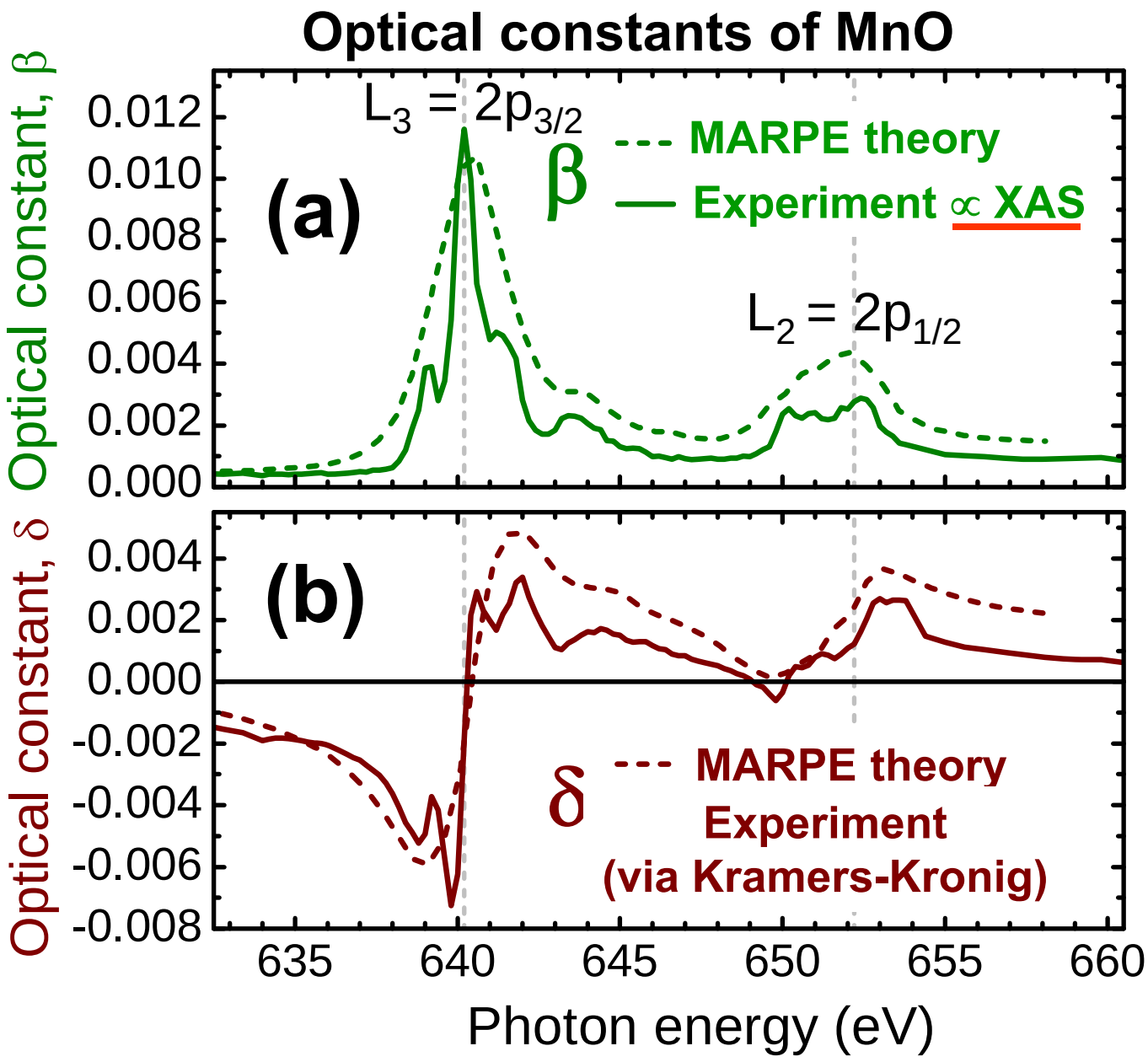
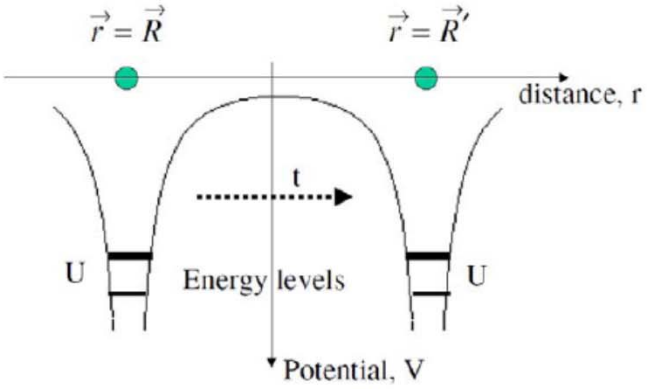


FIG. 1. Theoretical $2p$ core-level XPS spectra (solid line) compared with experimental data (dots) after background subtraction for Mn cations with varying valence. Emission due to the Mn *LMV* Auger peak is observed on the high-binding-energy side of the $2p_{1/2}$ spin-orbit peak, partially obscuring the $2p_{1/2}$ satellite structure.


Optical constants of MnO
Optical constant, β
Optical constant, δ
(a)
(b)
L3 = 2p3/2
L2 = 2p1/2
β
δ
MARPE theory
Experiment ∝ XAS
MARPE theory
Experiment
(via Kramers-Kronig)
0.012
0.010
0.008
0.006
0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008
635
640
645
650
655
660
Photon energy (eV)

The Hubbard model-mixing a localized on-site picture and a delocalized band picture



See problem 5 in Chapter 32 of Ashcroft and Mermin, "Solid State Physics", which this paper goes through in nice detail:

B Alvarez-Fernández and J A Blanco

Eur. J. Phys. **23** (2002) 11–16

+243A download at website

$$H = h_1 + h_2 + V_{12} \qquad (1)$$

= U below

where h_1 and h_2 are one-electron Hamiltonians and V_{12} is the Coulomb repulsion potential between the two electrons when they are found to be on the same atom. In order to solve the problem we shall use the following procedure. First we consider a hydrogen molecule in which an atom at $\vec{R}$ is described in the spatial representation by a single orbital electronic level $|\vec{R}\rangle$. When there is no electron on the atom $|\vec{R}, 0\rangle_{\text{vacuum}}$, i.e. an empty level, the energy is zero, if there is one electron of either spin in the level $|\vec{R}, \uparrow\rangle_{\text{up}}$ or $|\vec{R}, \downarrow\rangle_{\text{down}}$ its energy is E_0, and if there are two electrons of opposite spins in the level $|\vec{R}, \uparrow\downarrow\rangle_{\text{singlet}}$ the energy is $2E_0 + U$. The last additional positive energy U represents the intra-atomic Coulomb repulsion between the two localized electrons. = $\mathbf{J_{1s,1s}}$.

The amplitude for tunnelling is represented by the off-diagonal term in the one-electron Hamiltonian

bonding =

$$\langle \vec{R}|h|\vec{R}'\rangle = \langle \vec{R}'|h|\vec{R}\rangle = -t \qquad (2)$$

The same U and t used in the de Groot multiplet program (to come later)

T =

The Hubbard Model (continued)

Ground-state Hubbard energy:

$$E_{\text{Hubbard}} = 2E_0 + \tfrac{1}{2}U - \sqrt{4t^2 + \tfrac{1}{4}U^2}.$$

And wave function:

$$\Phi_{\text{Hubbard}} = \frac{1}{\sqrt{2}}\Phi_0 + \left(\sqrt{1 + \left(\frac{U}{4t}\right)^2} - \frac{U}{4t}\right)\frac{1}{2}(\Phi_1 + \Phi_2)$$

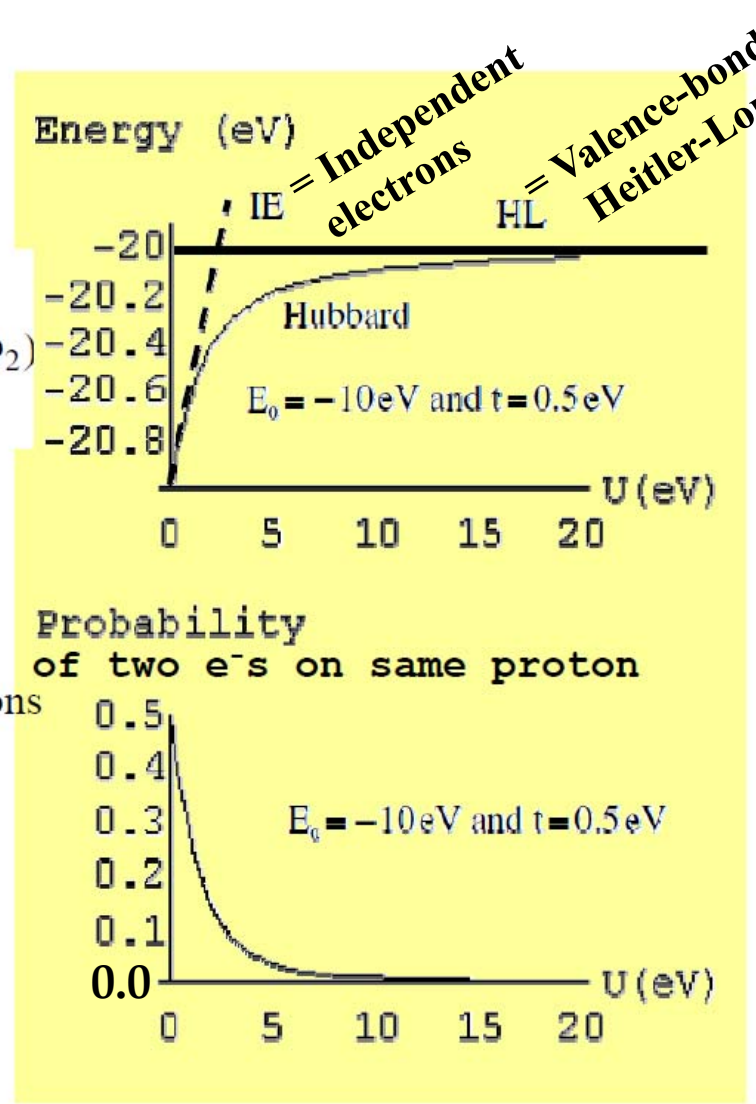
With $\Phi_0 = \dfrac{1}{\sqrt{2}}[|\vec{R}\rangle|\vec{R}'\rangle + |\vec{R}'\rangle|\vec{R}\rangle]$

$\Phi_1 = |\vec{R}\rangle|\vec{R}\rangle$

$\Phi_2 = |\vec{R}'\rangle|\vec{R}'\rangle$

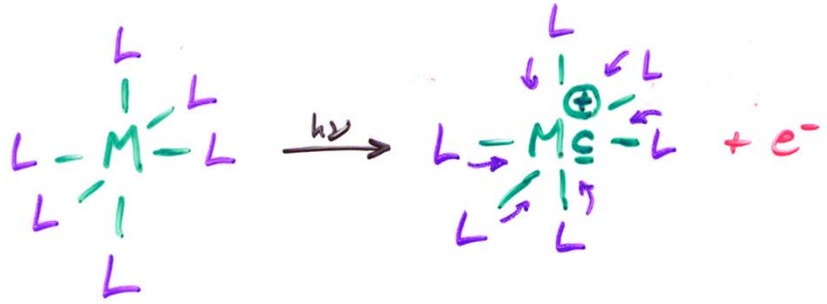
Electrons on different protons

Electrons on the same proton



Localized configuration interaction approach to spectrum simulation: Anderson impurity model for PS, XAS, XES

(SUGANO, LARSSON ~> SAWATZKY, VAN DER LAAN, FUJIMORI, OH, ET AL.)



$\underline{c}$ = CORE HOLE ON METAL

$\underline{L}$ = VALENCE ($\underline{\gamma}$) HOLE ON LIGAND

$$\psi_i = a_0|d^n\rangle + \sum_m a_m|d^{(n+m)}\underline{L}^m\rangle$$

$$\psi_f = b_0|\underline{c}\,d^n\rangle + \sum_m b_m|\underline{c}\,d^{(n+m)}\underline{L}^m\rangle$$

WITH INTERACTIONS OF:

$10Dq$ = CRYSTAL FIELD (OFTEN NEGLECTED)

Δ = LIGAND-TO-METAL CHARGE TRANSF. ENERGY
$= E(d^{n+1}\underline{L}) - E(d^n)$

$U_{dd} = U$ = d-d COULOMB REPULSION ENERGY
$= E(d^{n-1}) + E(d^{n+1}) - 2E(d^n) \approx J_{dd}$

T = LIGAND p-TO-METAL d HYBRIDIZATION
$= \langle d_\alpha|\hat{H}|p_\alpha\rangle$ (α = SAME SYMMETRY)

$U_{pd} \equiv U_{cd} = Q$ = CORE-HOLE-TO-d INTERACTION: $\langle \underline{c}|\hat{H}|d\rangle \approx J_{cd}$ = coulomb integral

Good discussion of model: Bocquet & Fujimori, J. Elect. Spect. & Rel. Phen. 82, 87 (1996)

$$\rho(e_k) = \sum_f |\langle \Psi_f|c|\Psi_g\rangle|^2 \delta(h\nu - e_k - E_f)$$

By now: CTM4XAS program for calculating this for some cases:
http://www.anorg.chem.uu.nl/CTM4XAS/

WITH INTENSITIES FROM SUDDEN APPROX. AS:

$$I(E_{kin}) \propto \sum_{f,k} |\langle \Psi_f(N-1,k)|\,\Psi_g(N-1,k)\rangle|^2 \cdot \delta(h\nu - E_f - E_{kin})$$

($\underline{c}$ = CORE HOLE)

WHERE: $\Psi_g(N-1,k) = \Psi_i$ (N WITH k HOLE = $\underline{c}$)

From Bocquet & Fujimori, J. Elect.Spect. & Rel. Phen. 82, 87 (1996):

The electronic structures of transition-metal (TM) compounds, particularly the 3d TM halides, oxides and chalcogenides, have long provided intriguing problems for physicists and chemists. These compounds are highly correlated electron systems where the essential physics can be described in terms of a few interaction strengths, namely the on-site d–d coloumbic repulsion energy U, the ligand-to-metal charge-transfer energy Δ, and the ligand p–metal d hybridization strength T. Core-level X-ray photoemission spectroscopy (XPS) is a useful probe of the valence electronic structures of TM compounds, and has been successfully used in recent years to extract parame values for these interaction strengths [1–5]. In

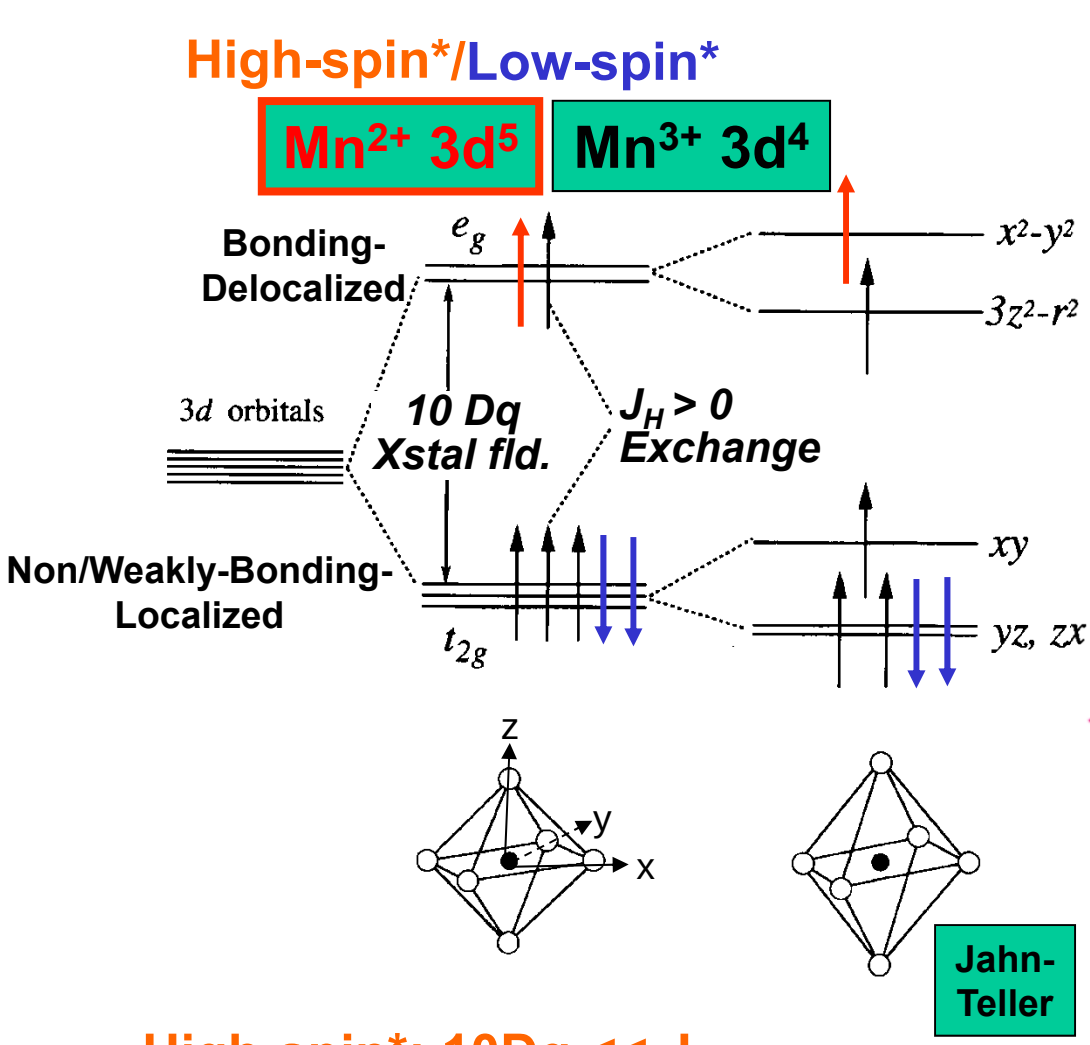
From CTM manual:

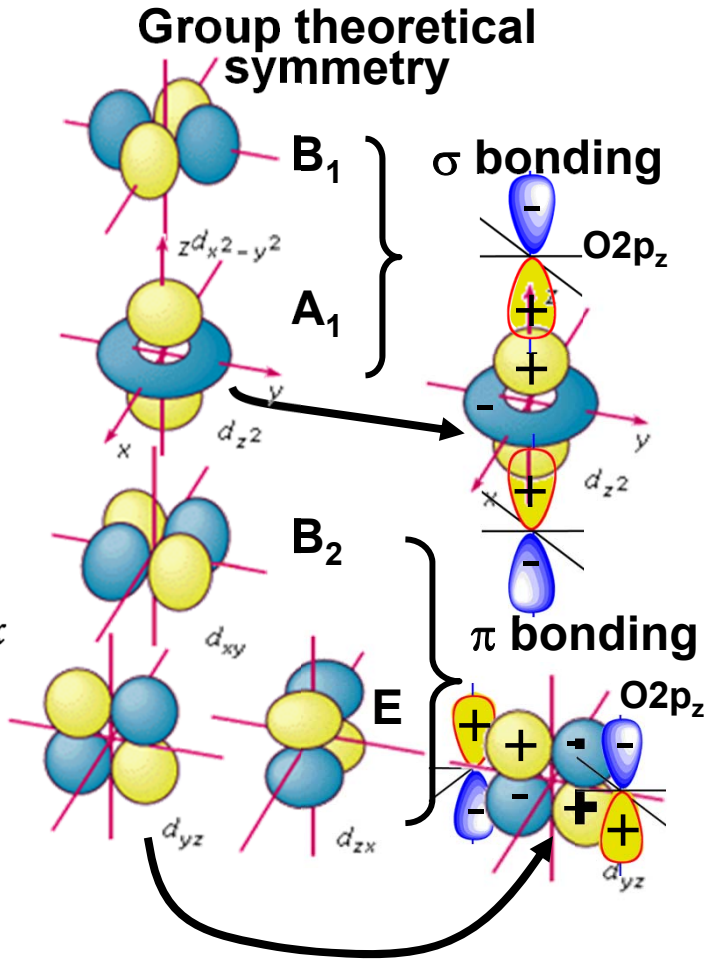
C: Charge Transfer Parameters

- **Delta:** This is the charge transfer parameter Δ, which gives the energy difference between the (centers of the) $3d^N$ and $3d^{N+1}\underline{L}$ configurations. The effective value of Δ (Δ_{eff}) is affected by the multiplet and crystal field effects on each configuration. In the next version, the value of Δ_{eff} will be given in a parameter-output file.
- **Udd:** This is the value of the Hubbard U.
- **Upd:** This is the core hole potential. In case of XAS spectra, only the difference between U_{pd} and U_{dd} is important.
- **Hopping T:** The hopping parameters are given for the 4 symmetries in tetragonal symmetry A_1, B_1, E and B_2. A_1 (z^2) and B1 (x^2-y^2) are part of the e_g-orbitals and E (xz, yz) and B_2 (xy) are part of the t_{2g} orbitals. In Oh symmetry the values of A_1=B_1 and E=B_2. (This is not yet automatic in the test-version).

Originated in the Hubbard Model: Ashcroft and Mermin, pp. 689-691

E.g.—Crystal field in Mn^{3+} & Mn^{2+} with negative octahedral ligands





High-spin*: 10Dq << J_H

Low-spin*: 10Dq >> J_H

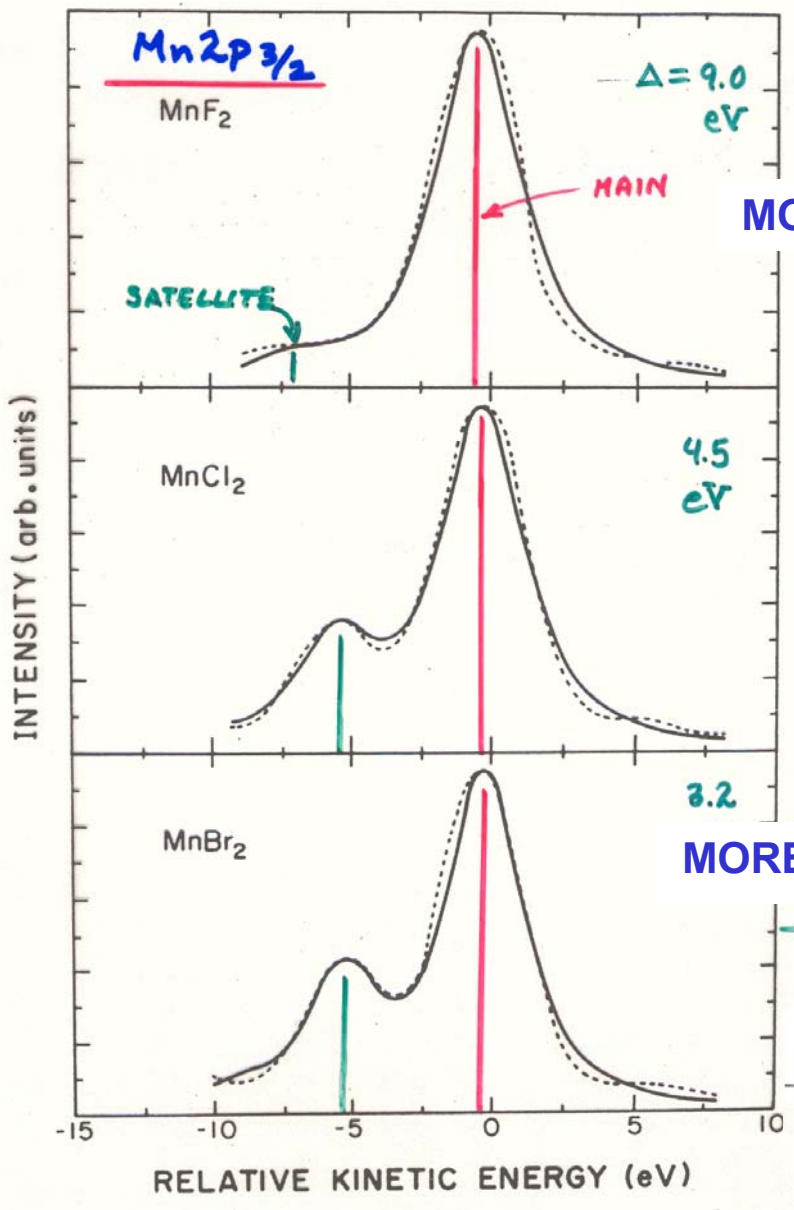


FIG. 6. Fits of the cluster model results with the experimental $2p_{3/2}$ spectra of the manganese dihalides. The parameters used are listed in Table II. A Lorentzian broadening is 2.6–3.0 eV, and a Gaussian broadening of 1.2 eV (FWHM) was used.

MORE IONIC

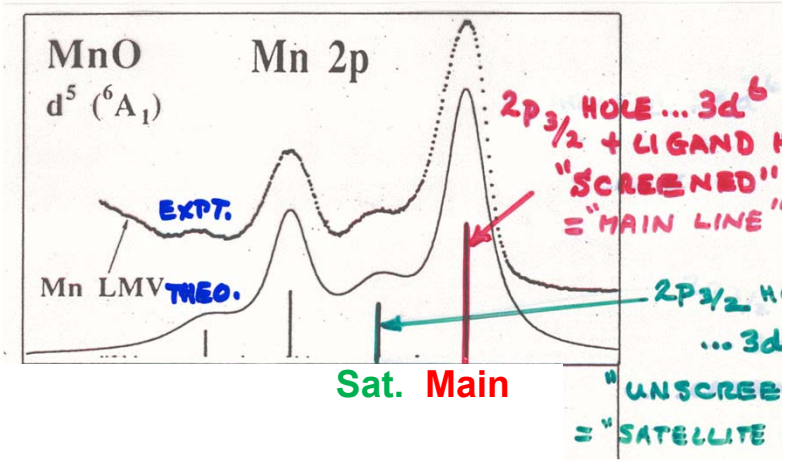
MORE COVALENT

Park et al. Phys. Rev. B 37, 10867 (1988)

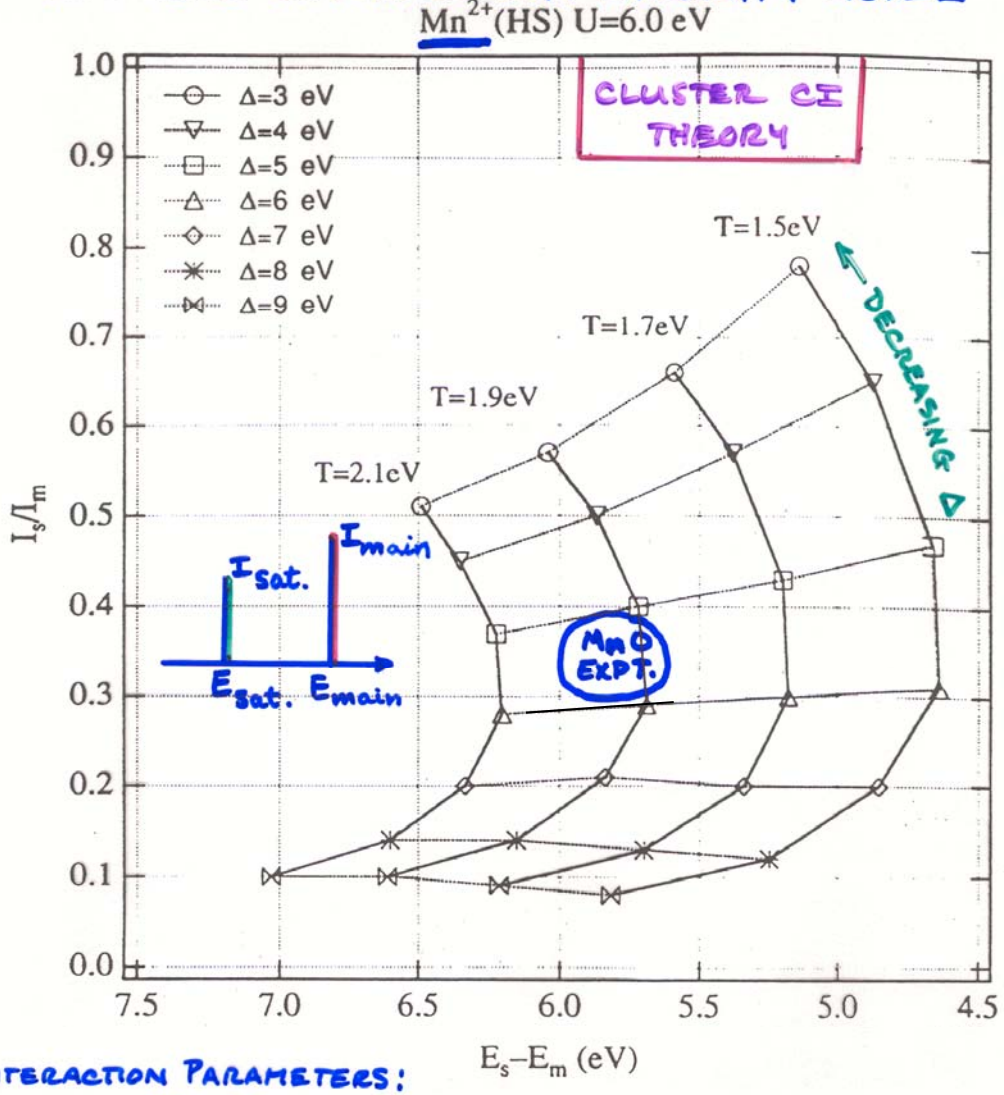
Core hole-d attraction
U_{pd} =
U_{cd} =

Compound	Δ (eV)	U (eV)	T (eV)	Q (eV)	$\langle n_d \rangle$
MnF_2	9.0	3.2	1.5	4.5	5.12
$MnCl_2$	4.5	3.2	1.5	4.5	5.32
$MnBr_2$	3.2	3.2	1.4	4.5	5.41

XPS satellites-MnO



ANALYSIS VIA ANDERSON IMPURITY MODEL



INTERACTION PARAMETERS:

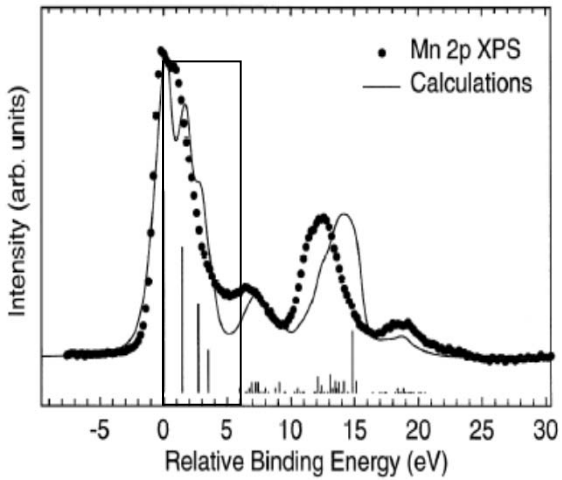
U = 3d-3d COULOMB REPULSION ENERGY

Δ = LIGAND-TO-METAL CHARGE TRANSFER ENERGY

T = LIGAND p — METAL 3d HYBRIDIZATION ENERGY

Q = CORE HOLE-3d COULOMB

BOURNET ET AL., J. EL. SP. 82, 87 (196



More recent data:
Phys. Rev. B 63, 115119 (2001)
In problem set

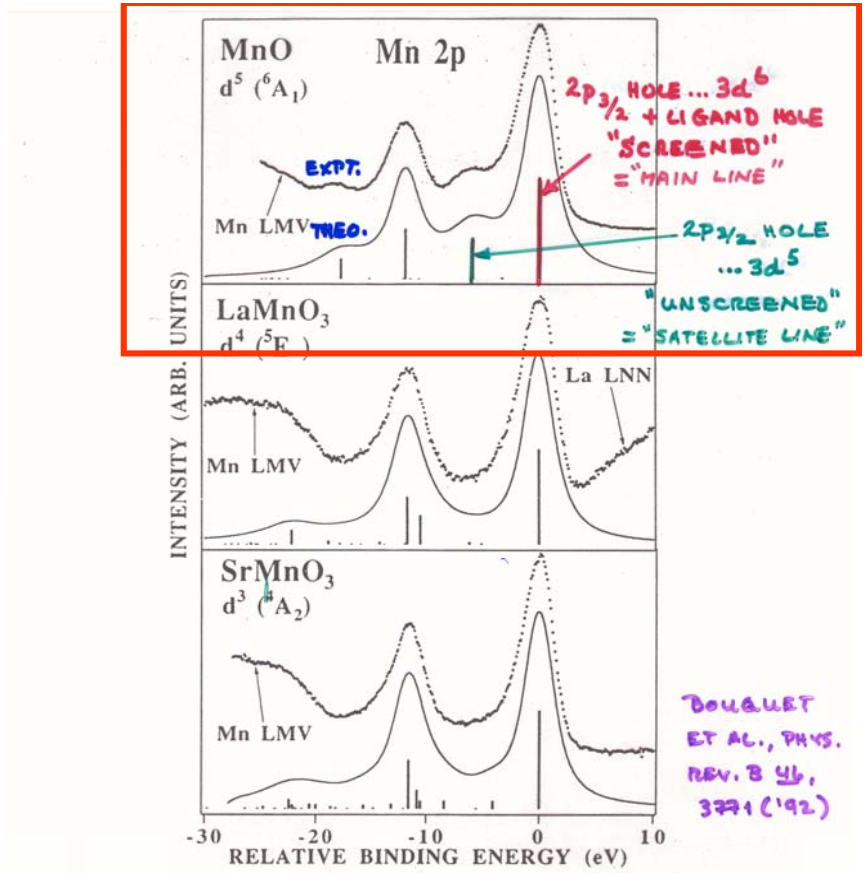


FIG. 1. Theoretical $2p$ core-level XPS spectra (solid line) compared with experimental data (dots) after background subtraction for Mn cations with varying valence. Emission due to the Mn *LMV* Auger peak is observed on the high-binding-energy side of the $2p_{1/2}$ spin-orbit peak, partially obscuring the $2p_{1/2}$ satellite structure.

For octahedral coord.:

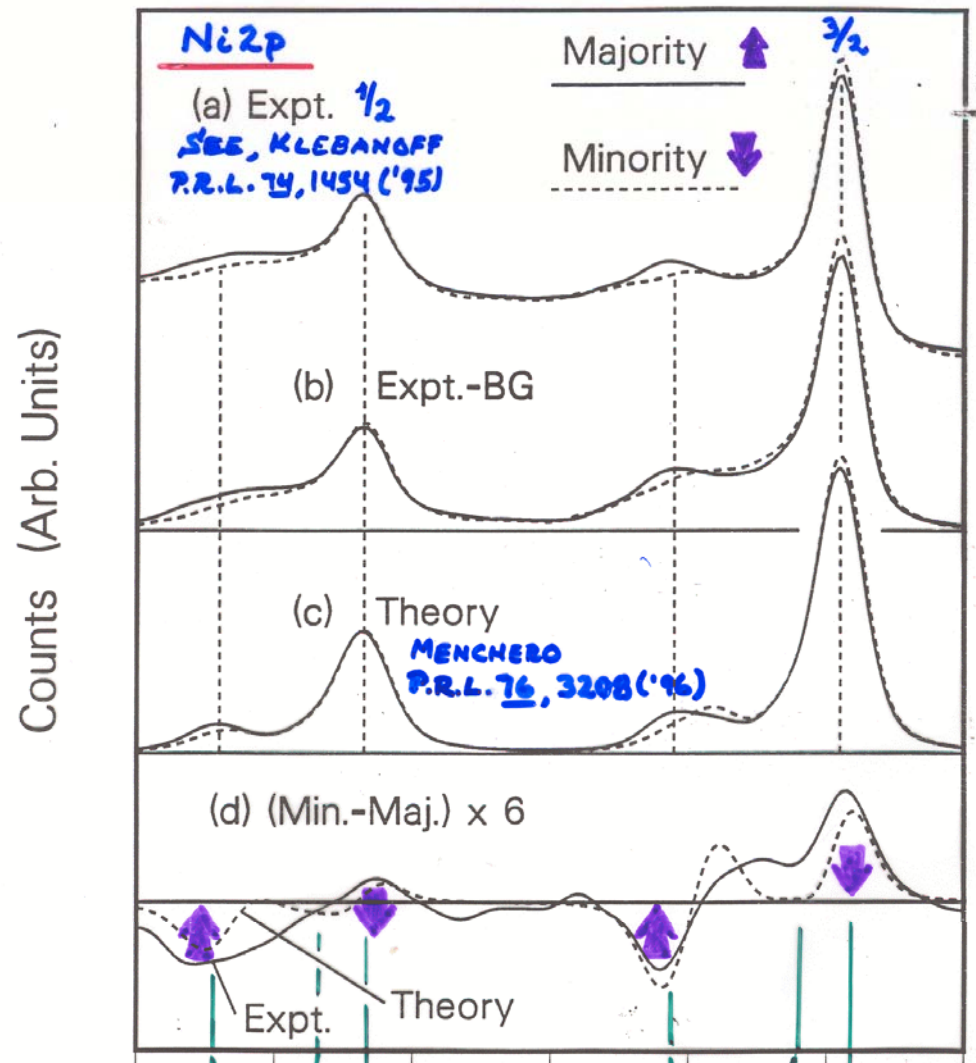
$$T_\sigma = \sqrt{3}(pd\sigma),\ T_\pi = 2(pd\pi)$$

$$T_\sigma / T_\pi \propto (pd\sigma)/(pd\pi) \approx -2.2$$

Compound	d^n	Valence	Δ	U	$(pd\sigma)$	Δ_{eff}	U_{eff}	Main peak	Satellite peak	Ref.
$SrMnO_3$	d^3	4+	2.0	7.8	−1.5	−0.2	7.1	$d^4\underline{L}$	$d^4\underline{L}$	This work
$LaMnO_3$	d^4	3+	4.5	7.5	−1.8	1.8	6.8	$d^5\underline{L}$	$d^6\underline{L}^2$	This work
MnO	d^5	2+	6.5	7.0	−1.1	8.8	11.6	$d^6\underline{L}$	d^5	This work
			7.0	7.5	−0.9					3

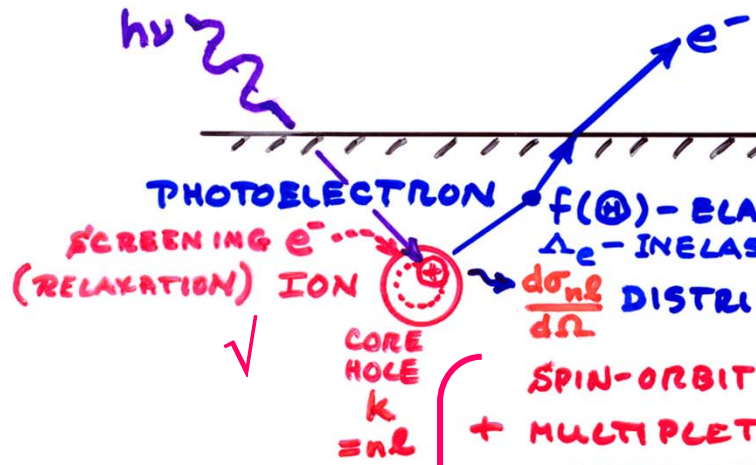
From later paper (see next slides) 6.5 6.0 -1.99/√3 = -1.1 U/Q = 0.7-1.0, a best fit no. is 0.83.

SPIN-ORBIT SPLITTING + MULTIPLETS + SCREENING IN A METAL : Ni - INITIAL CONFIG.: ~15% $3d^8$, 43% $3d^9$, 42% $3d^{10}$



FINAL CONFIG.: $3d^9$ 65% 15% 10% "UNSCREENED" {65% 15% 10%} "SCREENED"

$3d^{10}$ 35% 85% 90% {35% 85% 90%}

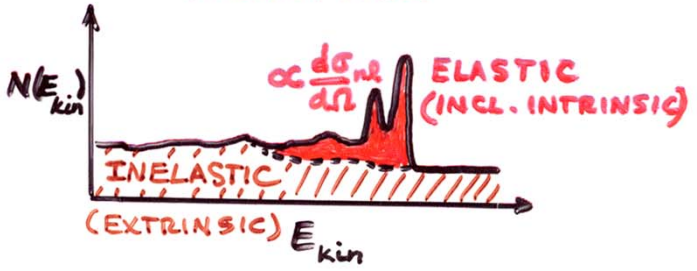


√ = covered so far

ADDITIONAL SOURCES OF STRUCTURE (AND INFORMATION!) IN SPECTRA BEYOND CHEMICAL SHIFTS

- SPIN-ORBIT SPLITTING (EASY) √
- + MULTIPLET SPLITTING (OPEN-SHELL SYSTEMS), XSTAL FIELD √
- + CORRELATION / CONFIGURATION INTERACTION √
- + SHAKE-UP/SHAKE-OFF/e⁻-HOLE √
- + SCREENING/NON-SCREENING: CONFIGURATION INTERACTION √
- + VIBRATIONAL EXCITATIONS √ Review
- + RESONANT PHOTOEMISSION (hν ≈ $E_{b,nl'}$) √

REALLY ALL AT ONCE, BUT SUM RULES + THEORY HELP



INTENSITIES IN PHOTOELECTRON SPECTRA:

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

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

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

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

FRANCK-CONDON FACTOR

- SUDDEN APPROXIMATION: $\varphi_k \rightarrow \varphi_f$ = PHOTO e^- (FAST)

$$\left.\begin{array}{l} \varphi_1 \rightarrow \varphi_1' \\ \vdots \\ \varphi_{k-1} \rightarrow \varphi_{k-1}' \\ \varphi_{k+1} \rightarrow \varphi_{k+1}' \\ \vdots \\ \varphi_N \rightarrow \varphi_N' \end{array}\right\} \text{(SLOW)}$$

k HOLE →

$$\text{INT.}_K \propto \left| \langle \psi^f_{VIB,v'} | \psi^i_{VIB,v} \rangle \right|^2 \left| \langle \psi^f_{e^-}(N-1,K) | \underbrace{\psi^f_K(N-1,K)}_{\text{k missing}} \rangle \right|^2$$

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

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

↳ NORMAL $\frac{d\sigma_K}{d\Omega}$

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

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

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

$$\left| \langle \varphi_{k-1}' | \varphi_{k-1} \rangle \right|^2 \left| \langle \varphi_{k+1}' | \varphi_{k+1} \rangle \right|^2 \cdots \left| \langle \varphi_N' | \varphi_N \rangle \right|^2 \cdot$$

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

1e- DIPOLE → $d\sigma/d\Omega$

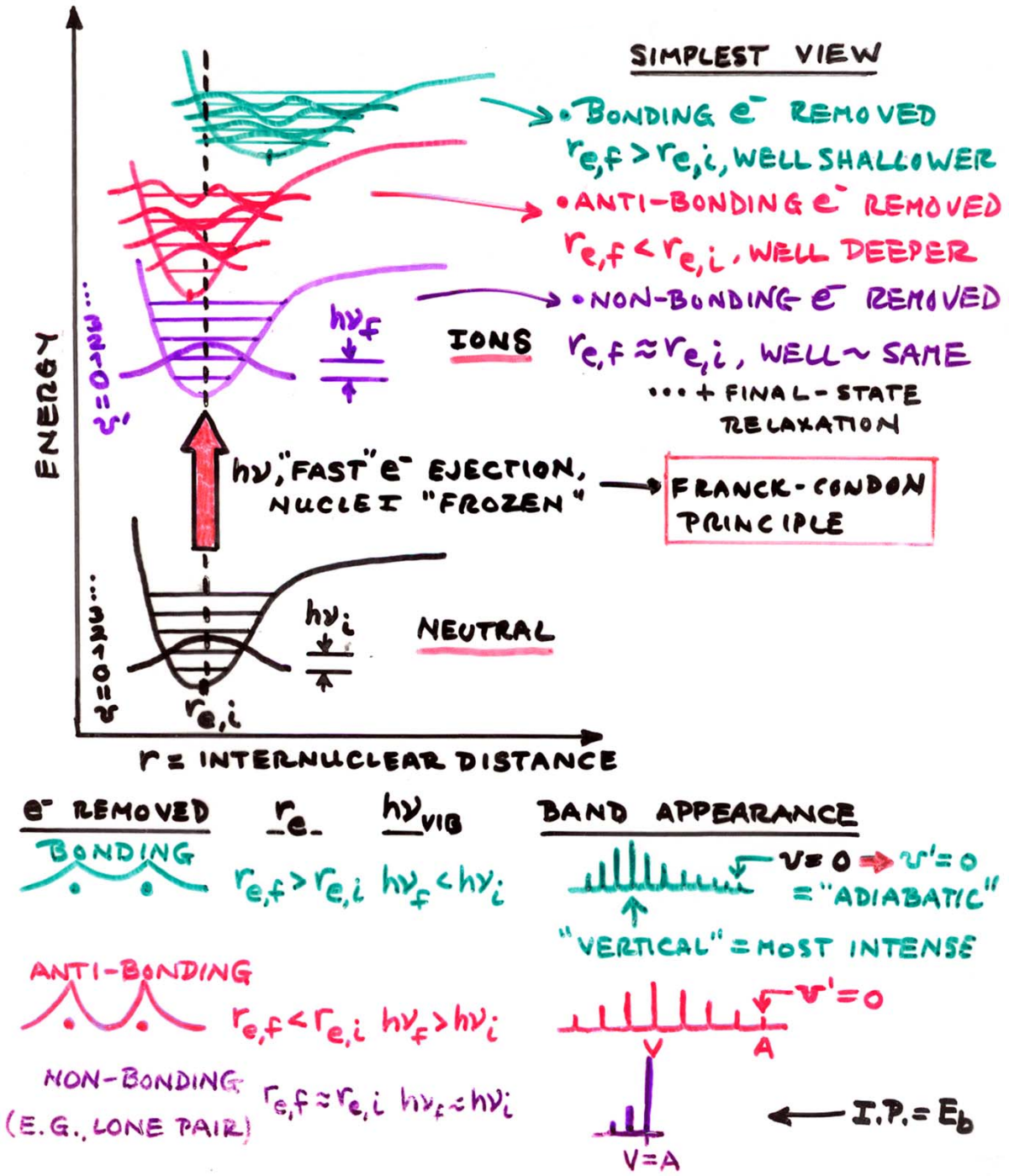
(N-1)e^- SHAKE-UP/ SHAKE-OFF → "MONOPOLE"

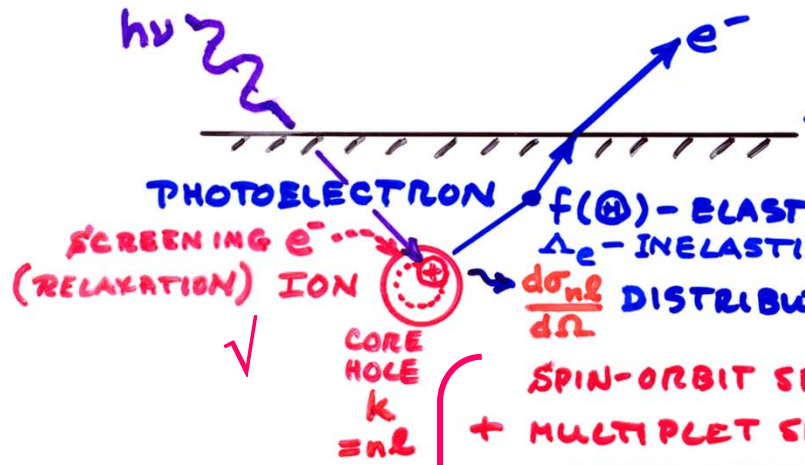
- PLUS DIFFRACTION EFFECTS IN φ_f ESCAPE

VIBRATIONAL STRUCTURE IN VALENCE-LEVEL (MO) SPECTRA

Diatomic A-B example

(Also applies to core-level emission if equilibrium distance changes on forming core hole)





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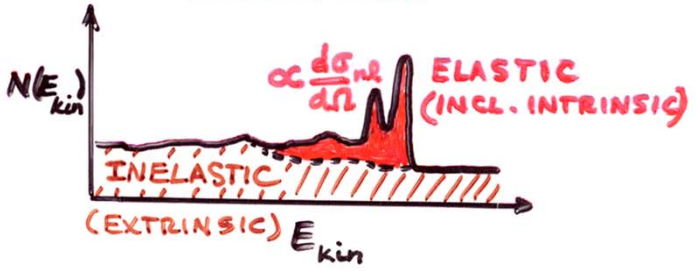
- + VIBRATIONAL EXCITATIONS √
- + RESONANT PHOTOEMISSION (hν ≈ $E_{b,nl'}$) √

REALLY ALL AT ONCE, BUT SUM RULES + THEORY HELP



Outline—Here to end of quarter

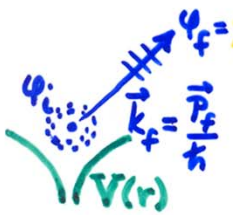
- Core-level chemical shifts: Koopmans', relaxation, the potential model
- Various other final state effects providing information in core-level spectra
- Valence-band spectra: low-energy UPS limit and high-energy XPS limit
- Photoelectron diffraction, extended x-ray absorption fine structure (EXAFS, XAFS)
- Photoelectron spectroscopy at realistic pressures in the multi-Torr range
- Photoelectron microscopy: adding lateral spatial resolution in 2 dimensions

PHOTOELECTRON EMISSION - BASIC MATRIX ELEMENTS + SELECTION RULES:

VALENCE BANDS IN SOLIDS:

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

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



$$\varphi_f(\vec{r},\vec{k}_f) = \varphi_{E_f}(\vec{r},\vec{k}_f)$$

$$= 4\pi \sum_{l_f,m_f} i^{l_f} e^{-i\delta_{l_f}} Y^*_{l_f m_f}(\theta_{k_f},\phi_{k_f}) Y_{l_f m_f}(\theta,\phi) R_{E_f l_f}(r)$$

(PHASE SHIFT OF l_f WAVE IN $V(r)$)

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

$\Delta l = l_f - l_i = \pm 1$ TWO CHANNELS

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

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

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

- **BLOCH-FUNCTION (DELOCALIZED) STATES ⇒ VALENCE:**

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

BRILLOUIN ZONE

$$\varphi_f(\vec{r}) = u_{\vec{k}_f}(\vec{r}) e^{i\vec{k}_f\cdot\vec{r}} \; ; \; E_f = \frac{p_f^2}{2m} = \frac{\hbar^2 k_f^2}{2m}$$

(USUALLY NEGLIG.)

$$|\langle \varphi_f | \hat{\varepsilon}\cdot\vec{p} | \varphi_i \rangle|^2 = |\hat{\varepsilon}\cdot\langle \varphi_f | \vec{p} | \varphi_i \rangle|^2 \Rightarrow \Delta\vec{k} = \vec{k}_f - \vec{k}_i - \vec{k}_{hv} + \vec{k}_{PHONON}$$

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

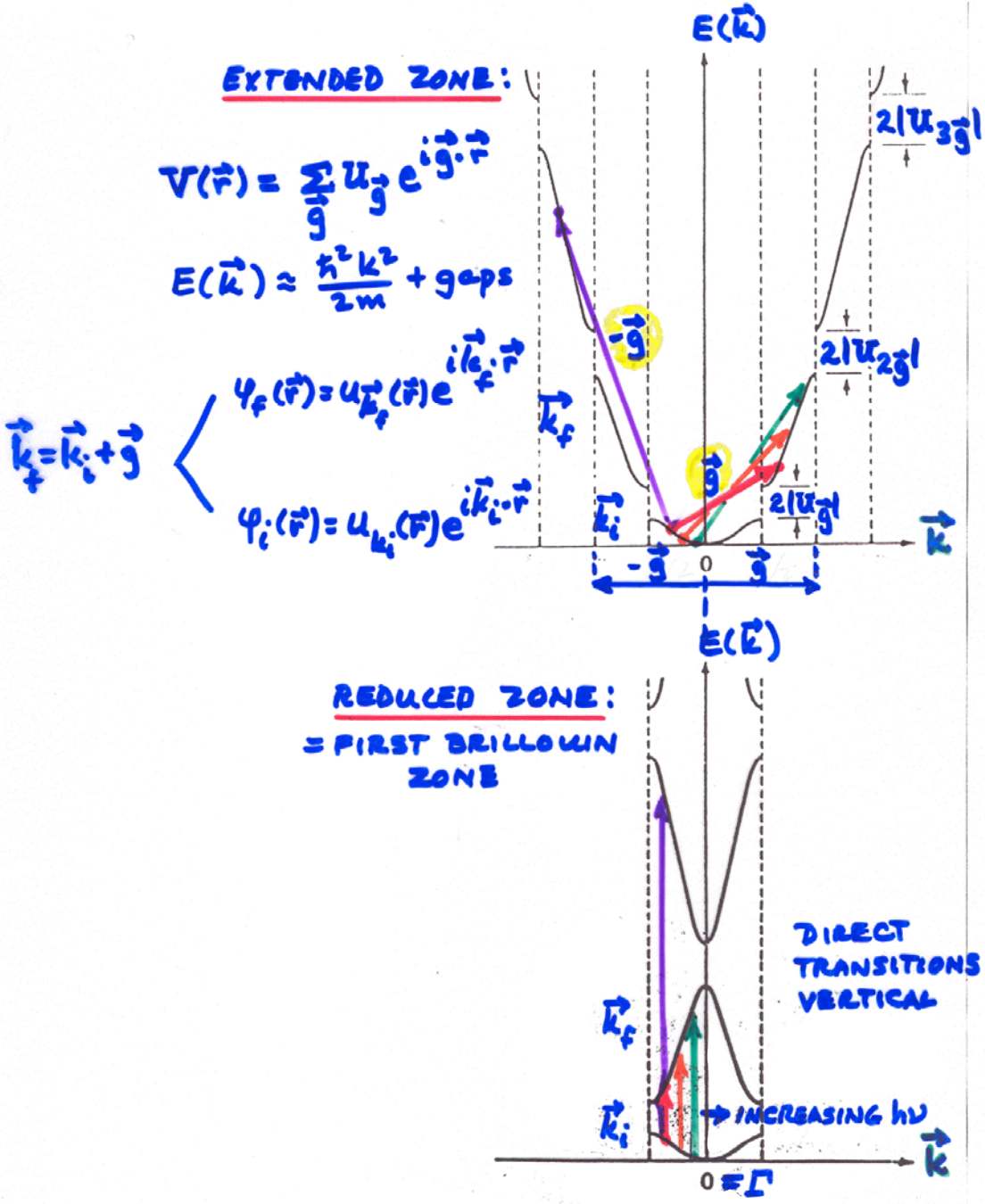
"DIRECT" TRANSITIONS

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

⇒ FRACTION DIRECT ≈ DEBYE-WALLER FACTOR

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

NEARLY-FREE ELECTRONS IN A WEAK PERIODIC POTENTIAL—1 DIM.

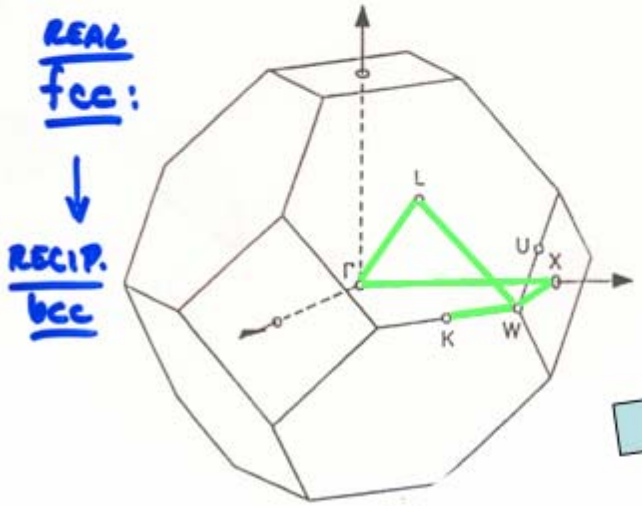


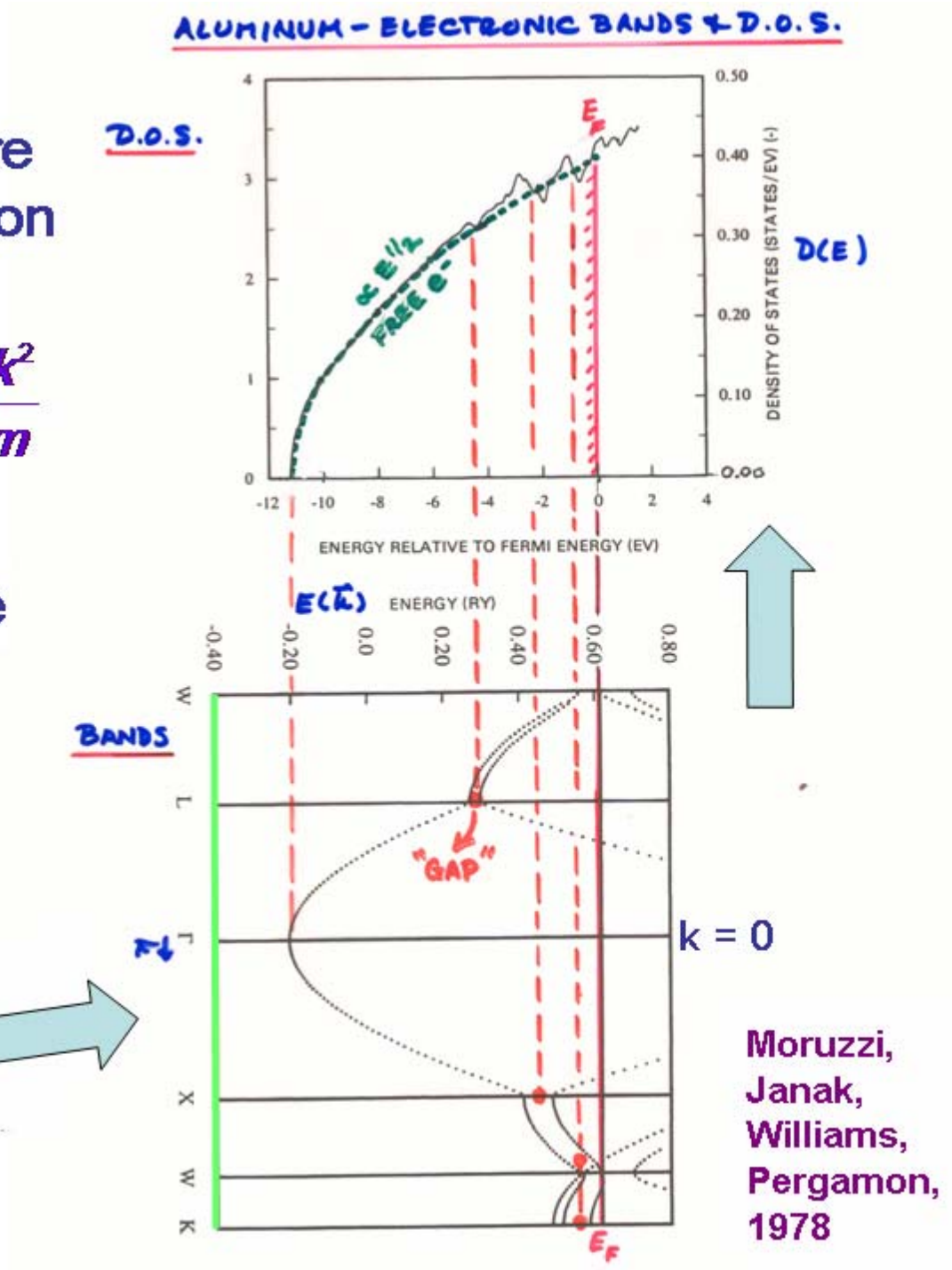
The electronic structure of a nearly free-electron metal—fcc Al

$$\phi(\vec{r}) = u_{\vec{k}}(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}; \quad E(\vec{k}) \approx \frac{\hbar^2 k^2}{2m}$$

(Bloch)

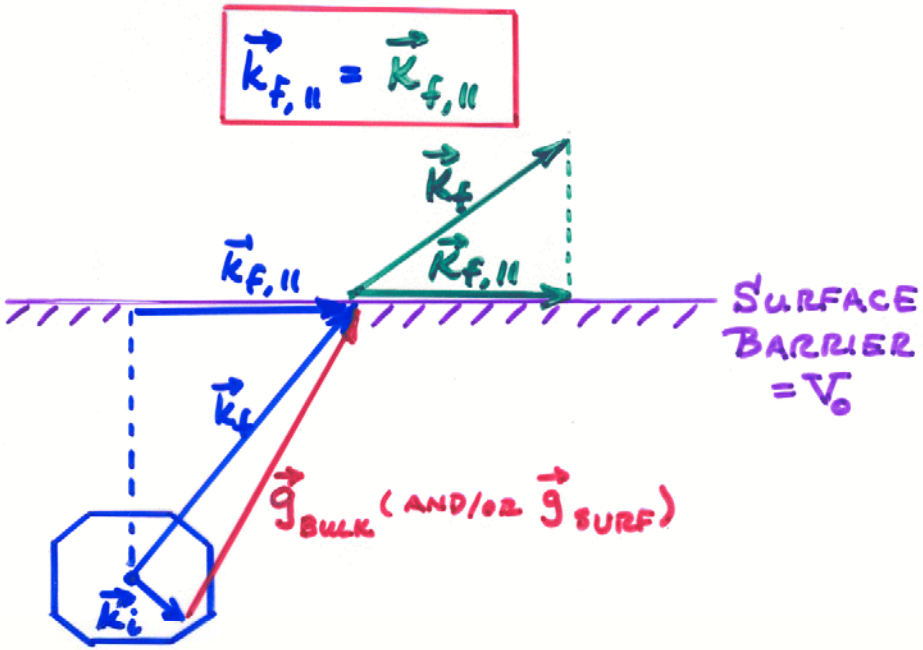
3D Brillouin zone





Moruzzi, Janak, Williams, Pergamon, 1978

Conservation Laws in Valence-Band Photoelectron Spectroscopy:



"The UPS Limit"

$$\vec{k}_f = \vec{k}_i + \vec{g}_{BULK}(\vec{g}_{SURFACE}) + \vec{k}_{h\nu} + \vec{k}_{PHONON}$$

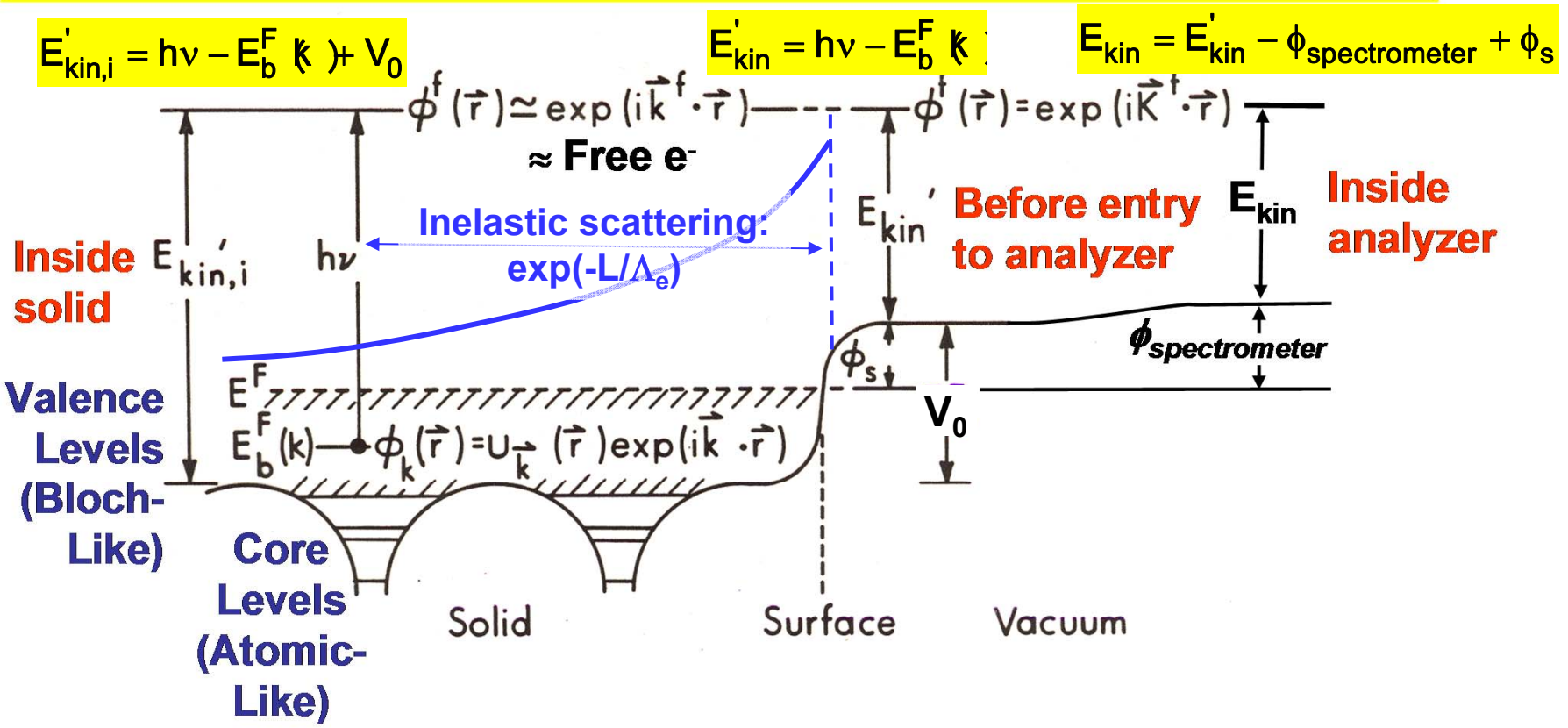
Negligible if $h\nu \lesssim 500$ eV

$h\nu$ and/or T low enough

Basic energetics

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

One-Electron Picture of Photoemission from a Surface



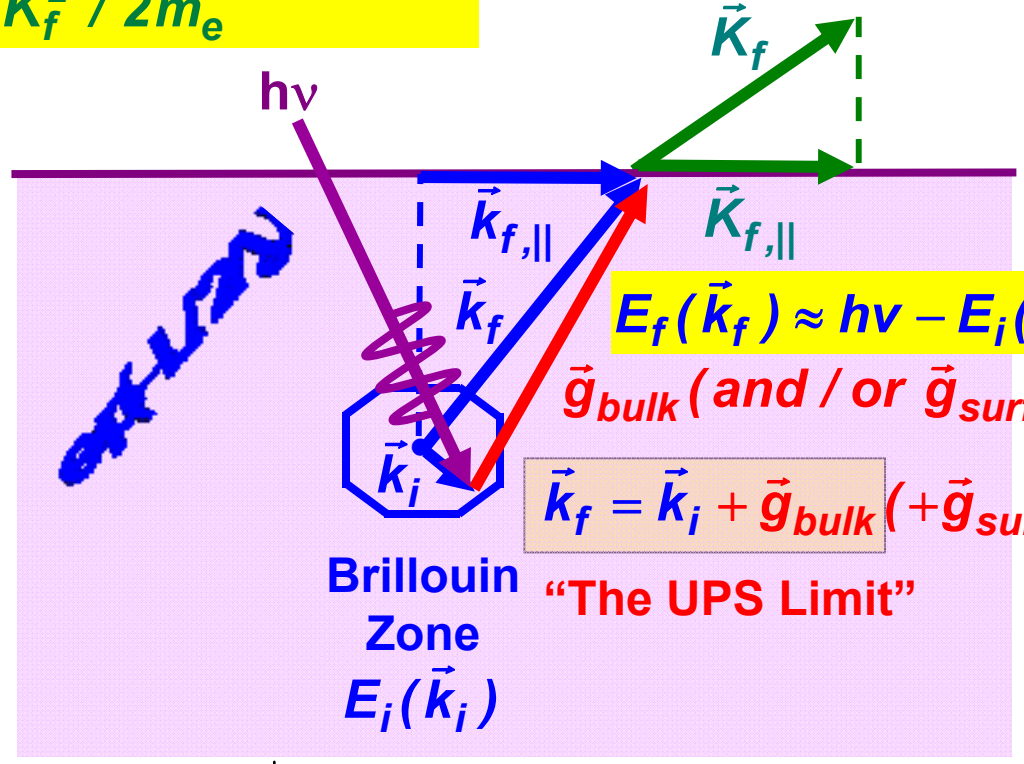
Valence-band photoemission: Angle-Resolved Photoemission (ARPES)

$E_f(\vec{K}_f) =$

$E_f(\vec{k}_f) - V_0 = h\nu - E_i(\vec{k}_i)$

$\approx \hbar^2 K_f^2 / 2m_e$

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



$E_f(\vec{k}_f) \approx h\nu - E_i(\vec{k}_i) + V_0 \approx \hbar^2 k_f^2 / 2m_e$

$\vec{g}_{bulk}$ (and / or $\vec{g}_{surf}$)

$\vec{k}_f = \vec{k}_i + \vec{g}_{bulk} (+\vec{g}_{surf}) + \vec{k}_{h\nu} + \vec{k}_{phonon}$

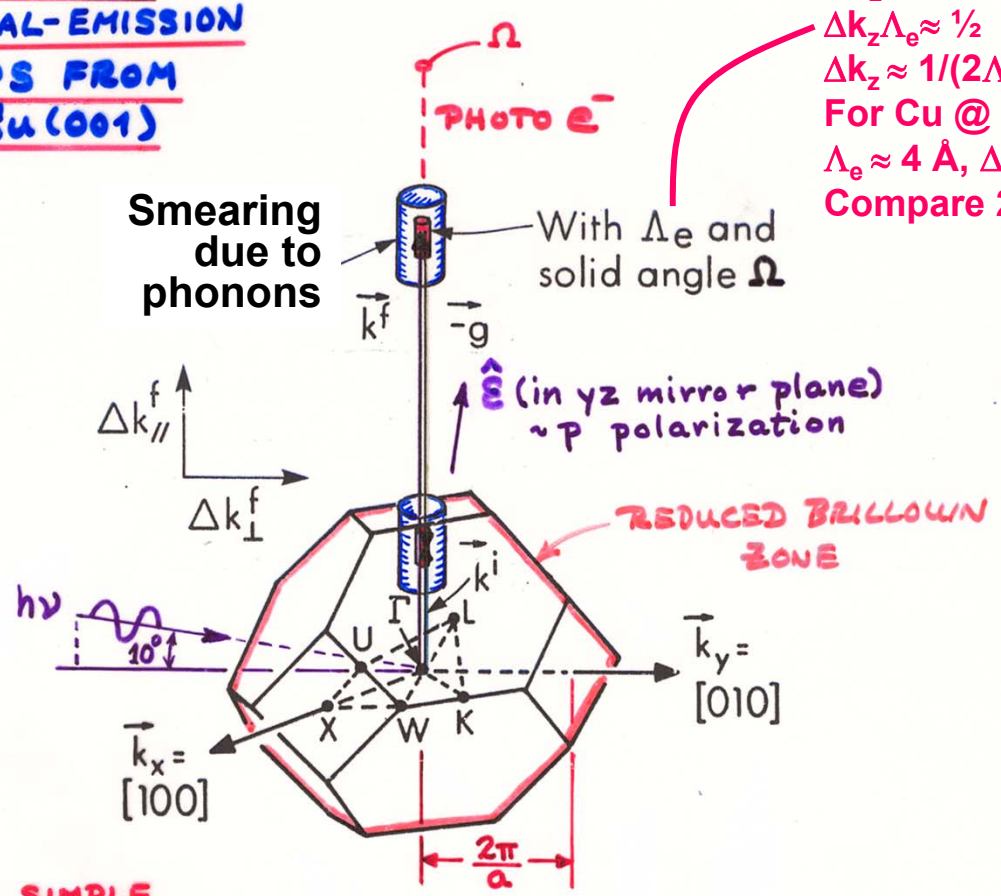
"The UPS Limit"

High energy a/o High temp.

$$I(E_f, \vec{k}_f) \propto \left| \hat{\varepsilon} \bullet \left\langle \varphi_{photoe}(E_f = h\nu + E_i, \vec{k}_f = \vec{k}_i + \vec{g}) \middle| \vec{r} \middle| \varphi(E_i, \vec{k}_i) \right\rangle \right|^2$$

"Direct" or k-conserving transitions

EXAMPLE: NORMAL-EMISSION UPS FROM Cu(001)



$\Delta p_z \Delta z \approx \hbar/2$
$\Delta k_z \Lambda_e \approx ½$
$\Delta k_z \approx 1/(2\Lambda_e)$
For Cu @ $E_{kin} \approx 80$ eV,
$\Lambda_e \approx 4$ Å, $\Delta k_z \approx 0.12$ Å^{-1}
Compare $2\pi/a = 0.98$ Å^{-1}

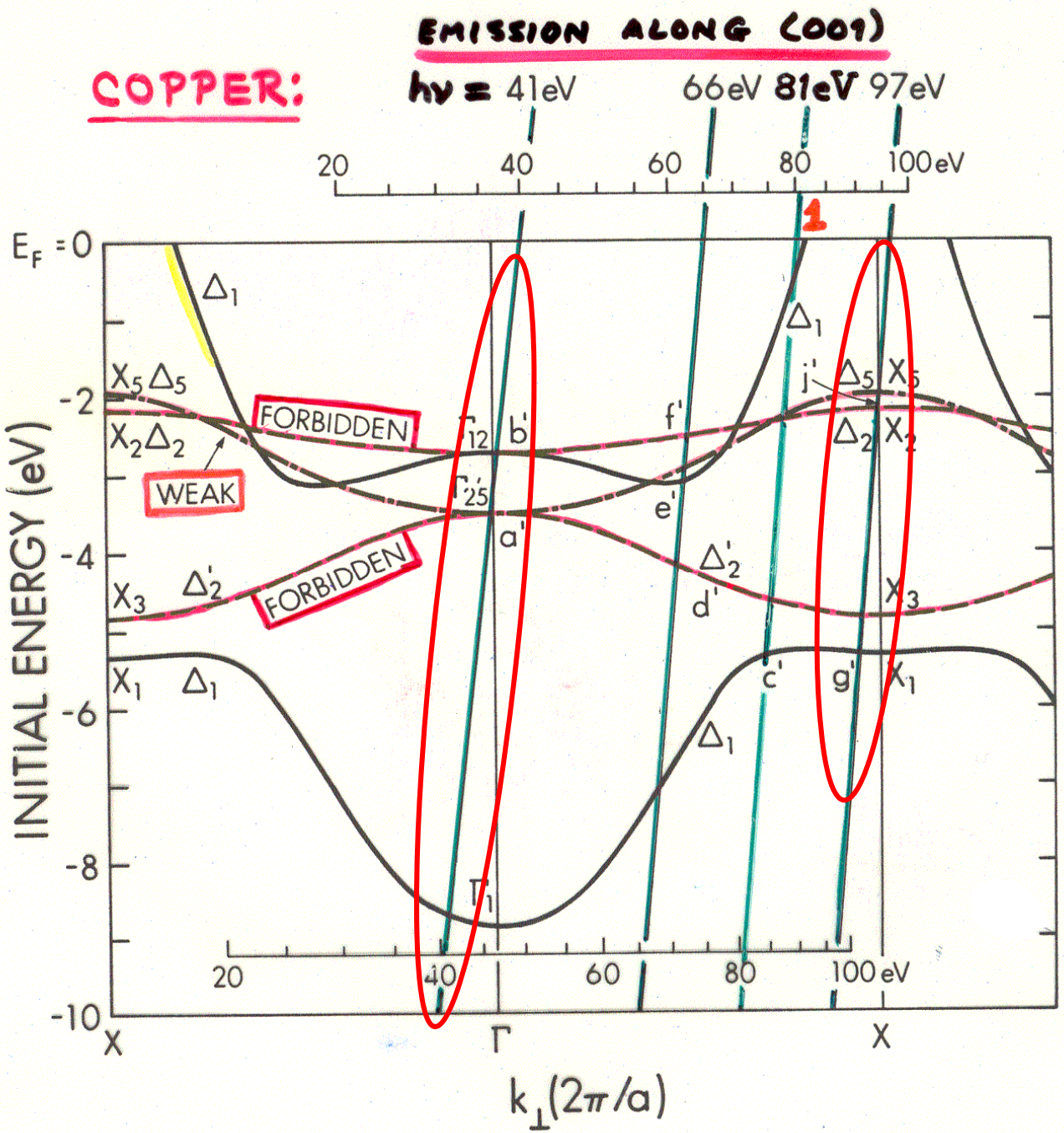
SIMPLE DT MODEL: Direct: $\vec{k}^f = \vec{k}^i + \vec{g} + \cancel{\vec{k}_{h\nu}}$

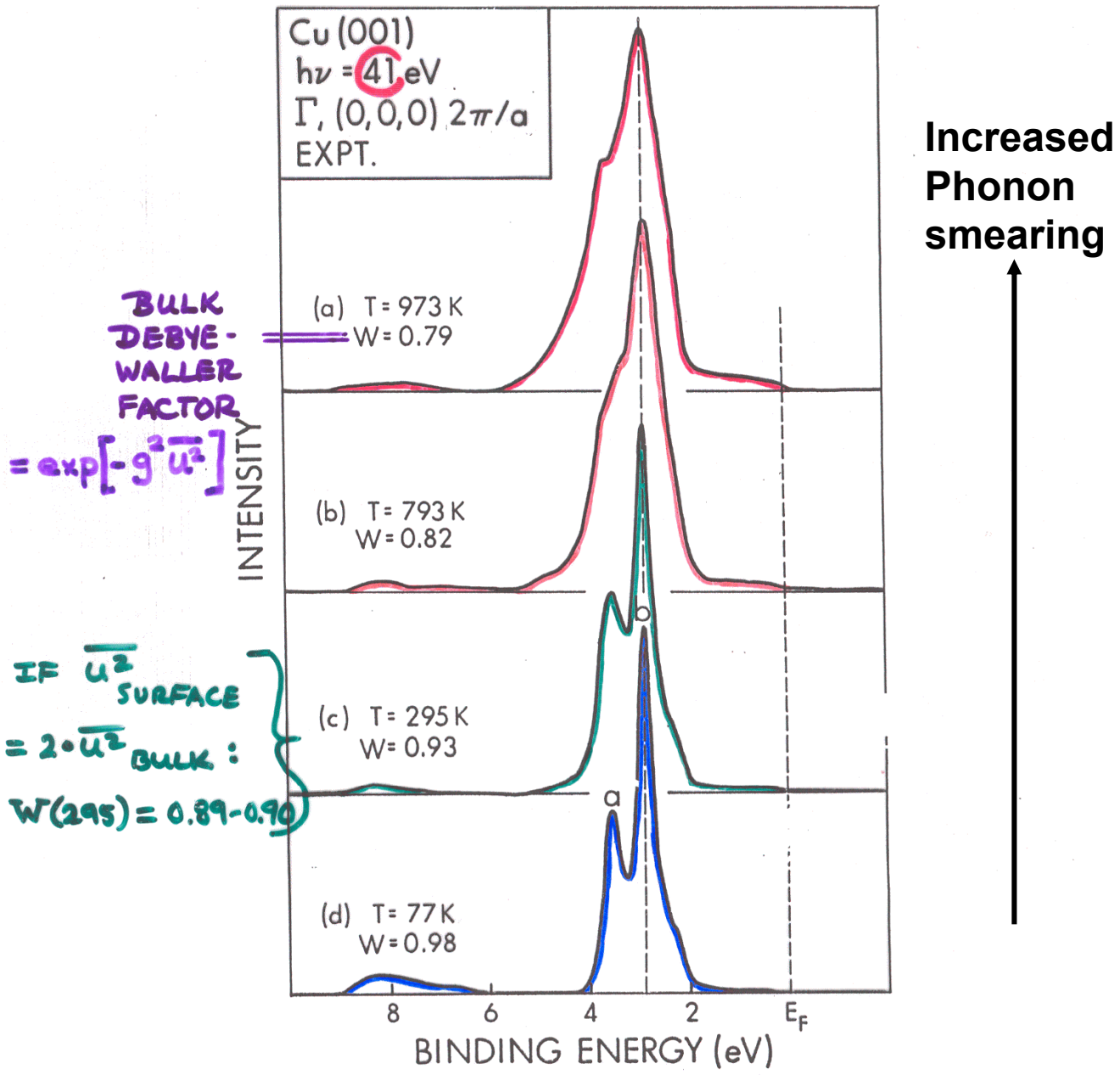
$E^i(\vec{k}^i)$ = initial band structure

$E^f(\vec{k}^f) \approx \hbar^2 (k^f)^2 / 2m$

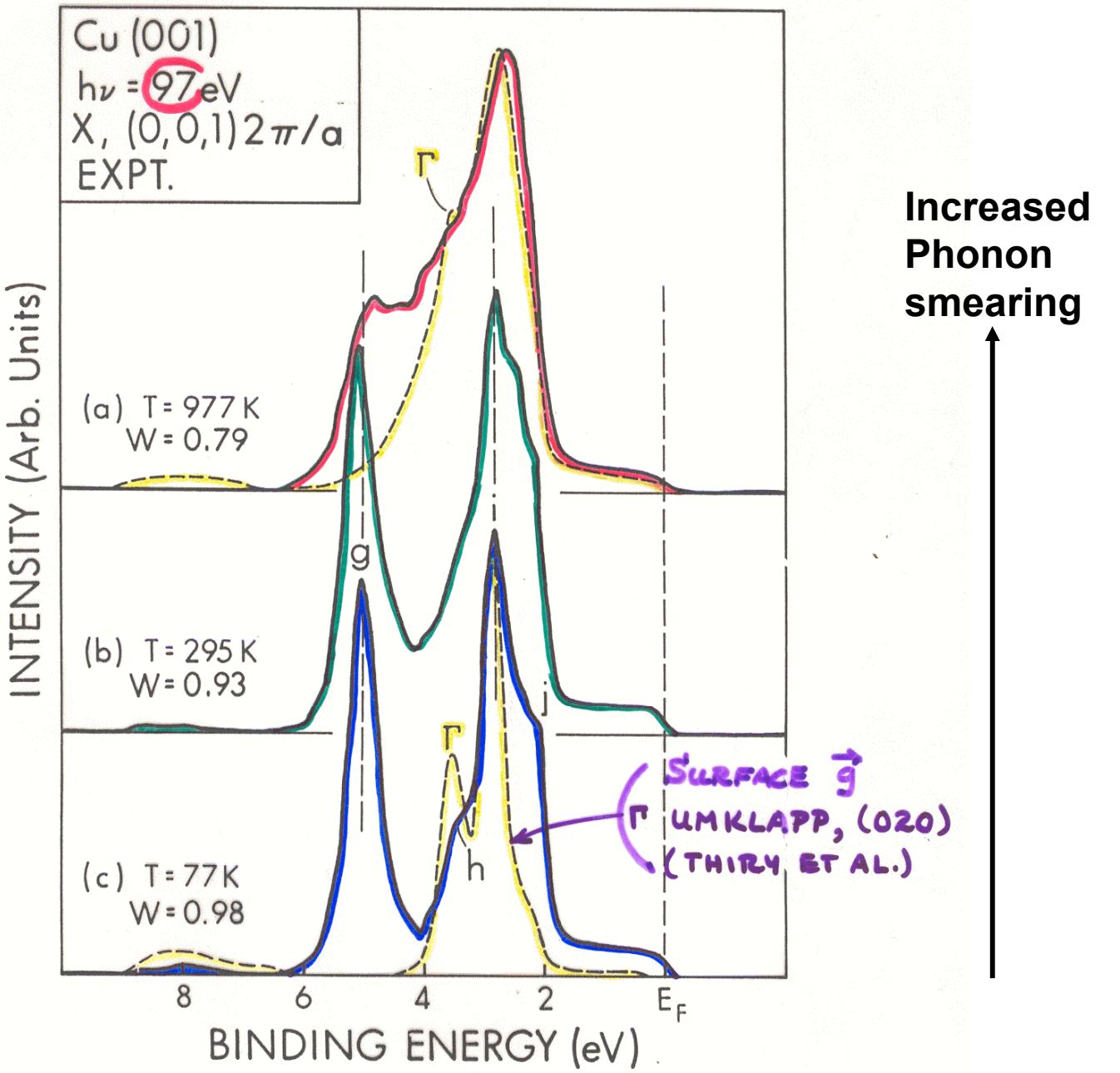
Constant matrix elements

Expectations from simple direct-transition theory + symmetry considerations in matrix elements

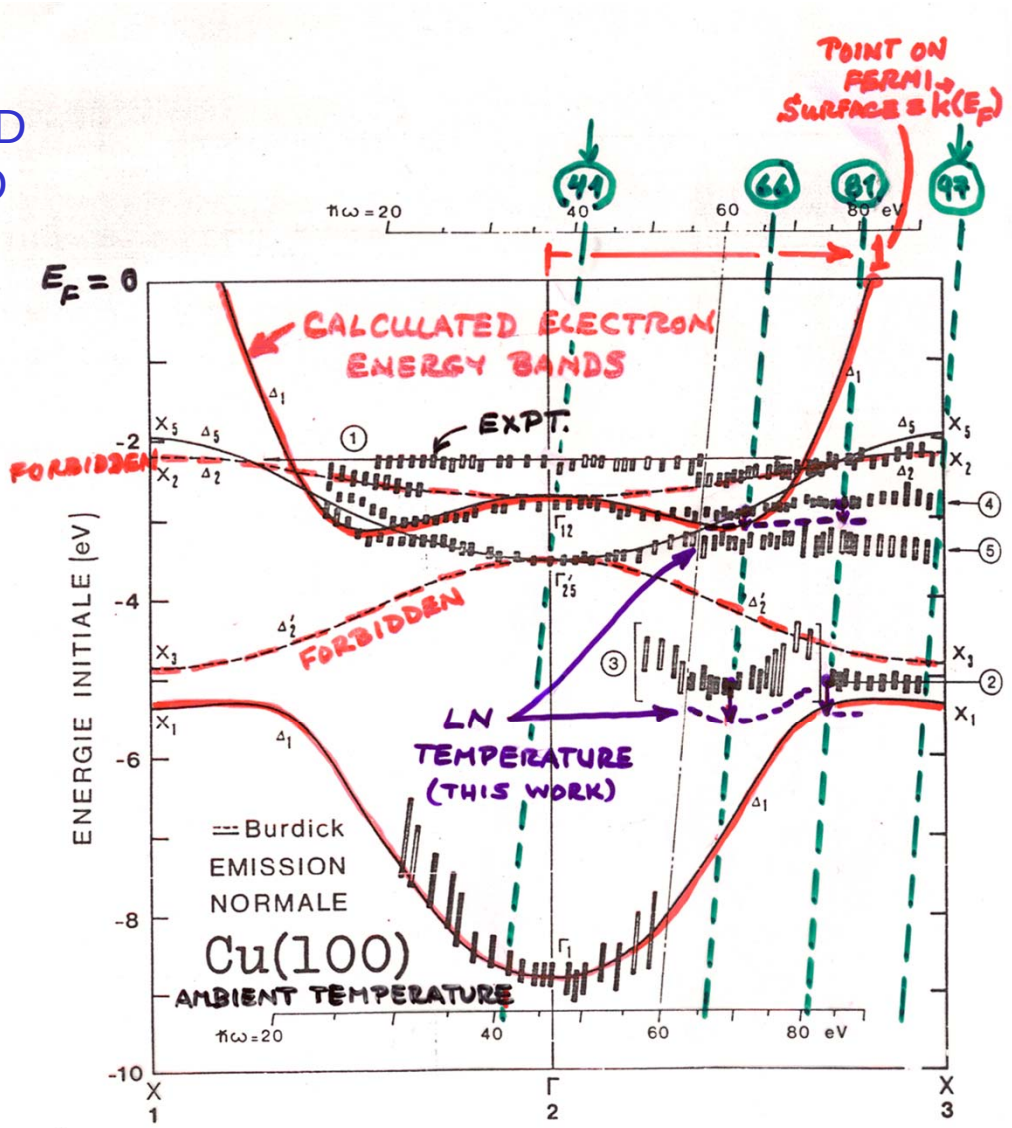




R.C. WHITE ET AL., PHYS. REV. B 35, 1147 (1987)


Cu (001)
hν = 97 eV
X, (0,0,1) 2π/a
EXPT.
Γ
(a) T = 977 K
W = 0.79
g
(b) T = 295 K
W = 0.93
Γ
h
(c) T = 77 K
W = 0.98
SURFACE g
Γ UMKLAPP, (020)
(THIRY ET AL.)
INTENSITY (Arb. Units)
8
6
4
2
E_F
BINDING ENERGY (eV)
Increased
Phonon
smearing

Cu: ANGLE-RESOLVED PHOTOEMISSION AND BAND-MAPPING ALONG (001)



P. THIRY, THESIS, UNIV. OF PARIS (1980)
+ WHITE ET AL.
P.R.B 35, 1147 (1987)

FIG.56

Cu: ANGLE-RESOLVED PHOTOEMISSION AND BAND-MAPPING ALONG (110)

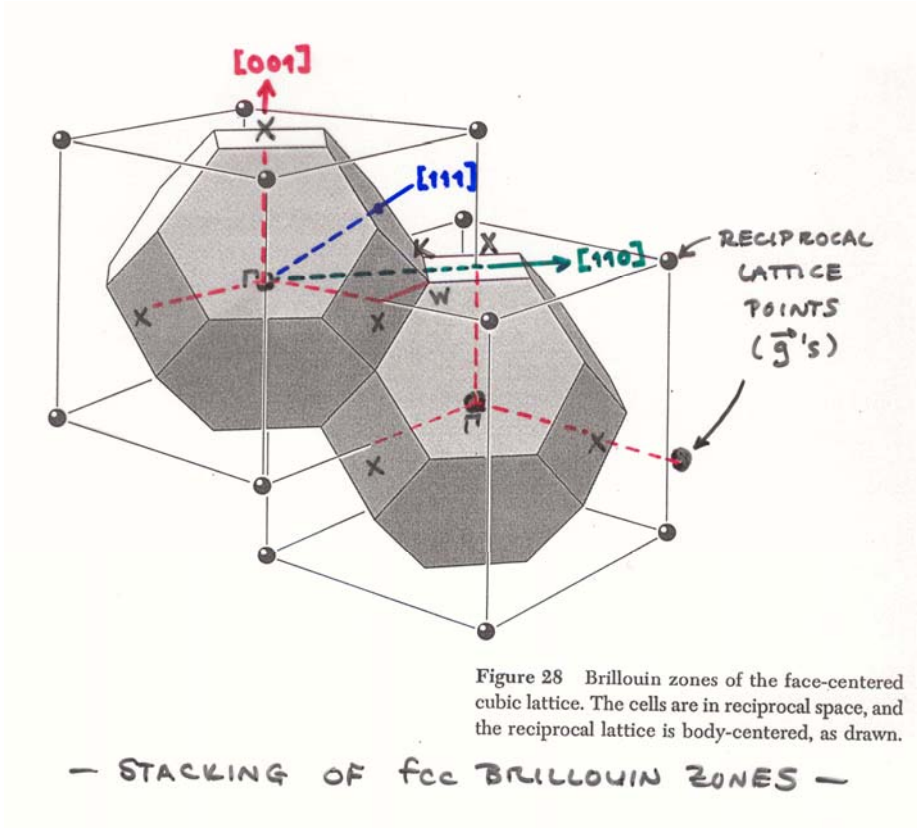
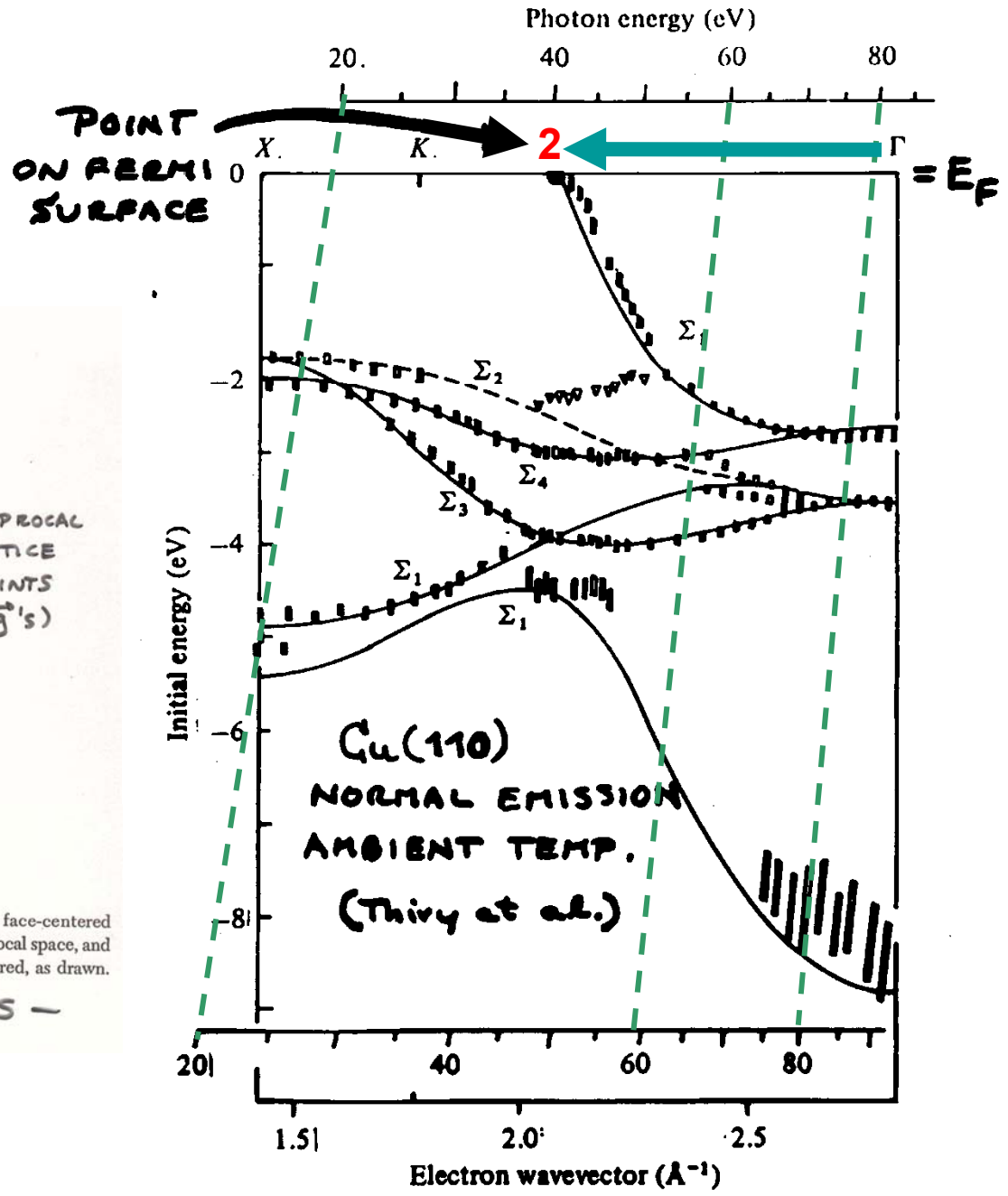
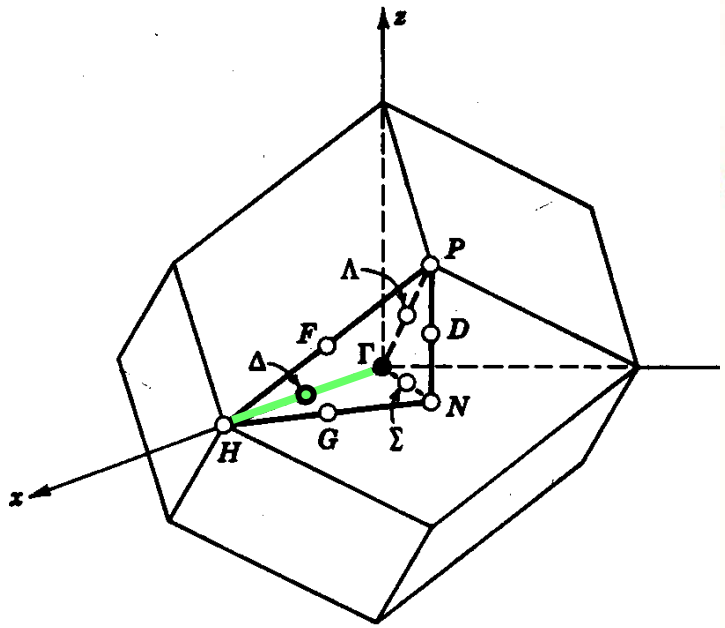


Figure 28 Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body-centered, as drawn.

— STACKING OF fcc BRILLOUIN ZONES —



P.Thiry, Ph.D. thesis, Univ. of Paris (1980)



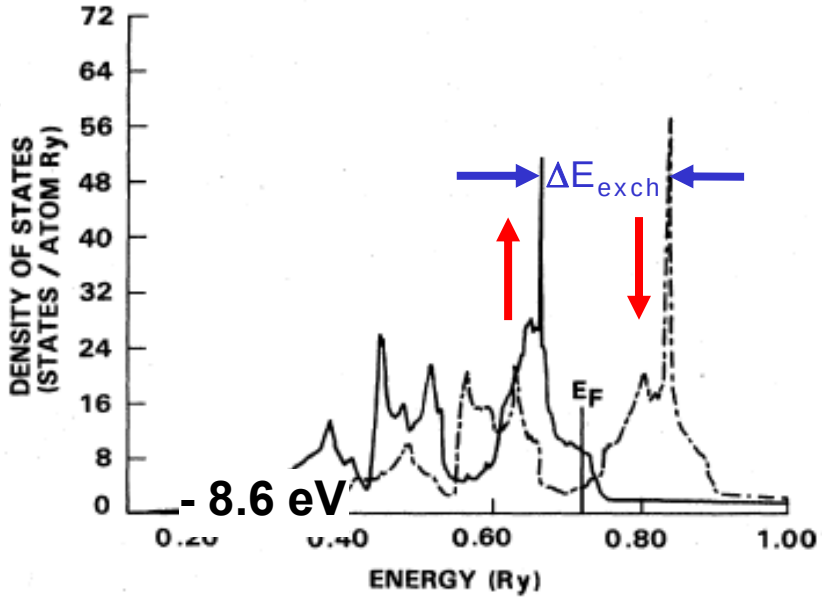
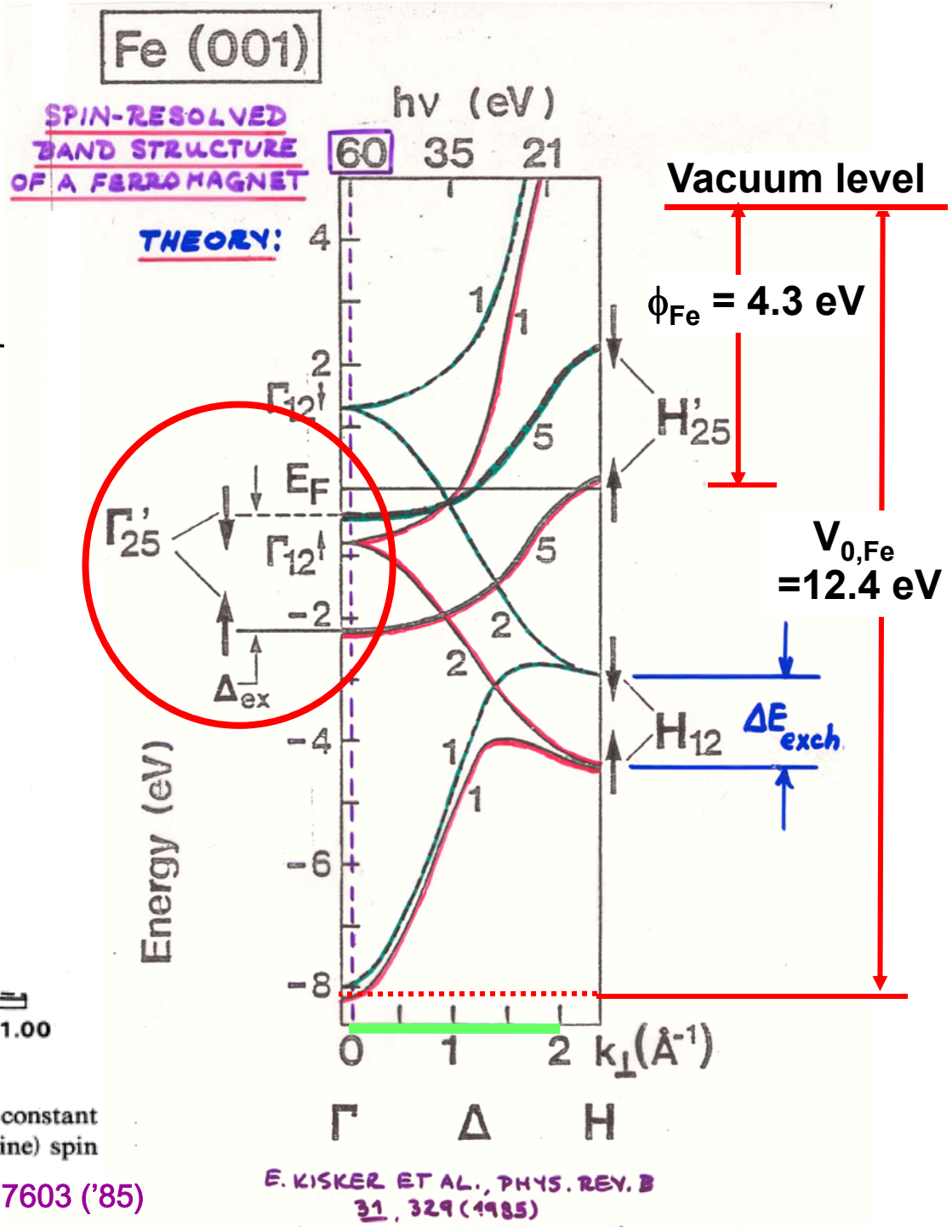
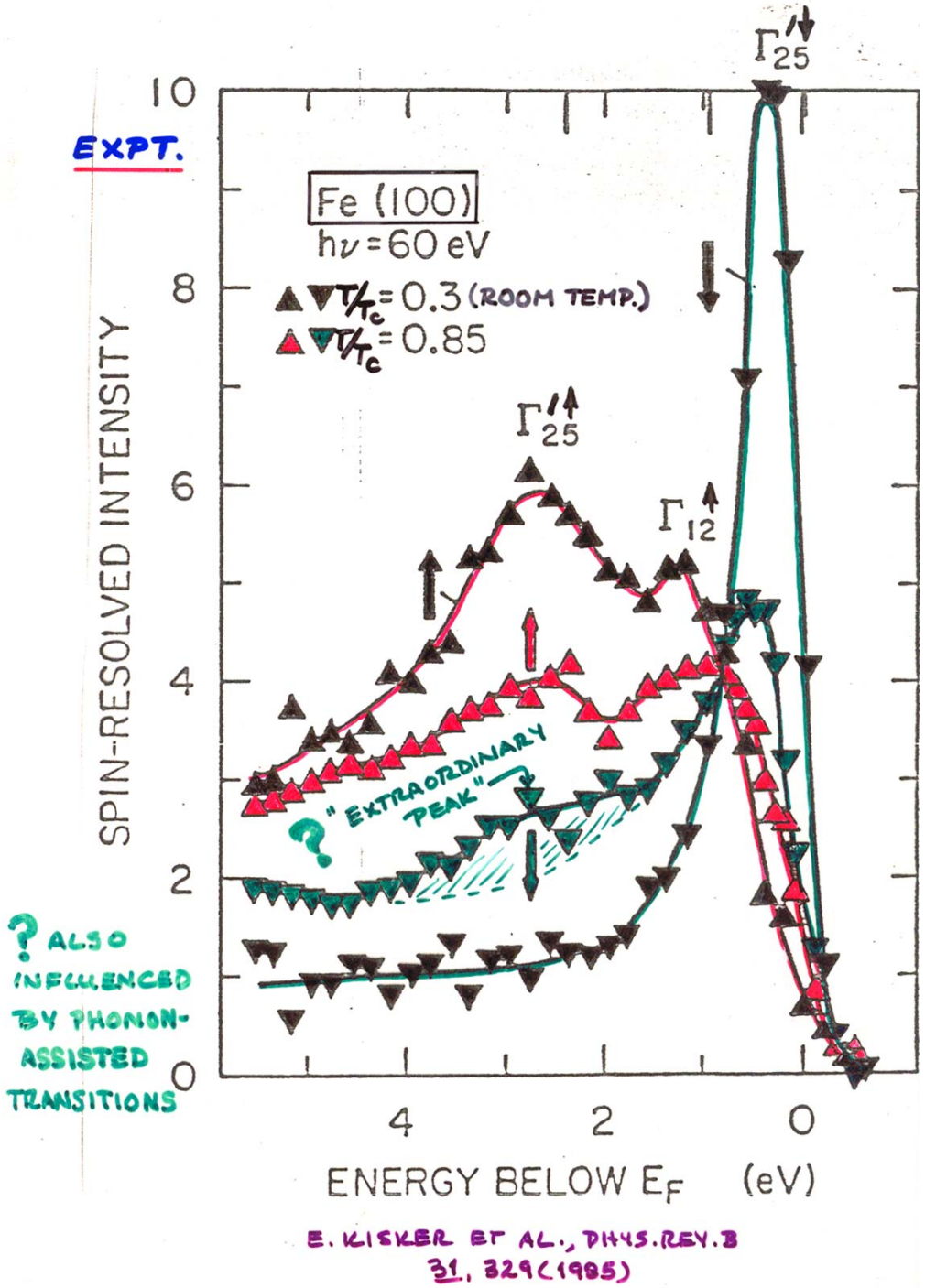


FIG. 4. Density of states at the equilibrium lattice constant of Fe for majority- (solid line) and minority- (broken line) spin states.

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



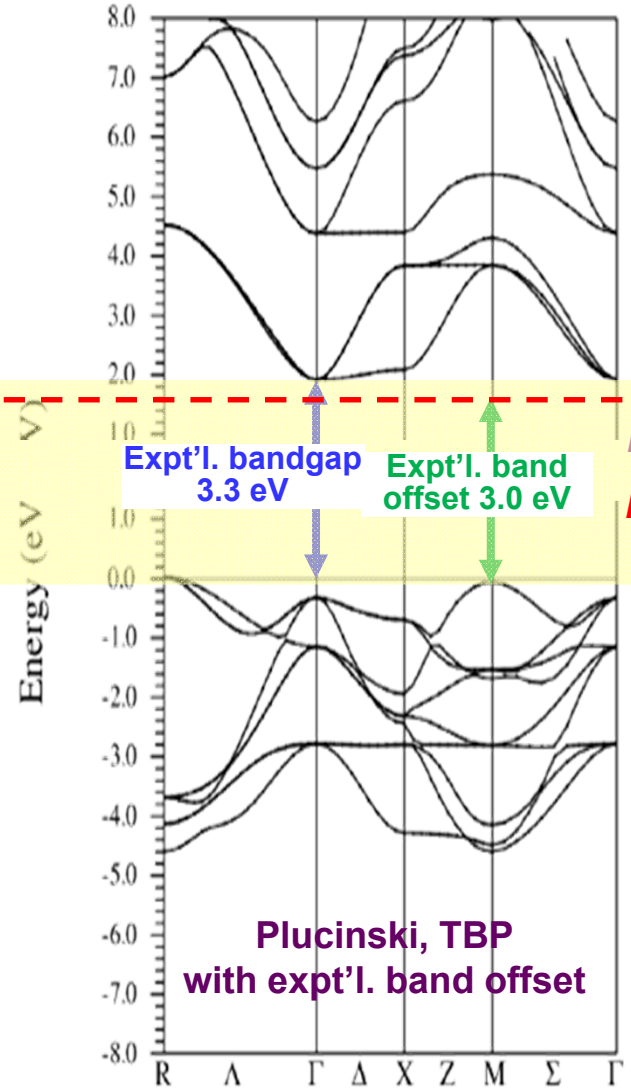
Fe: ANGLE AND SPIN-RESOLVED SPECTRA AT Γ POINT



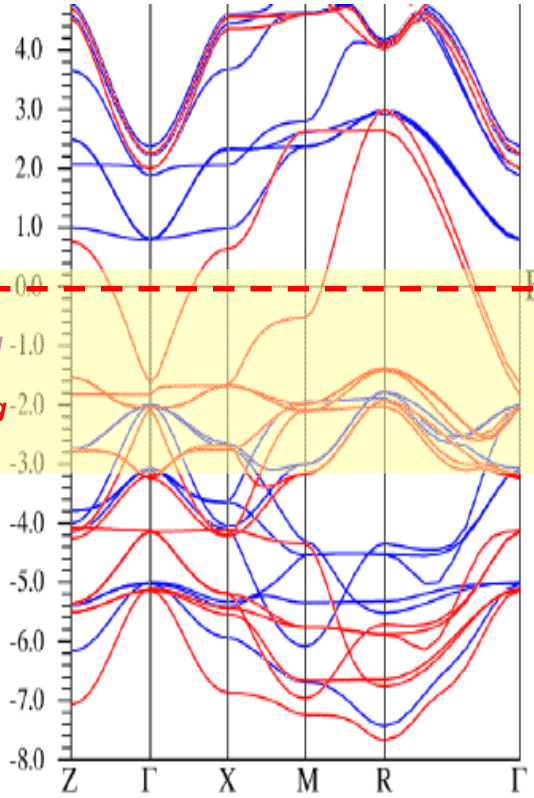
$SrTiO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ band structures and DOS

$SrTiO_3$-band insulator

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

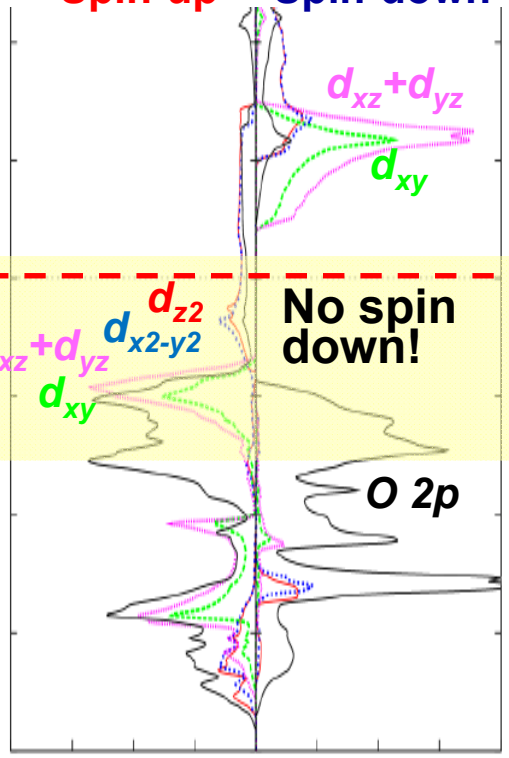


Plucinski, TBP
with expt'l. band offset



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

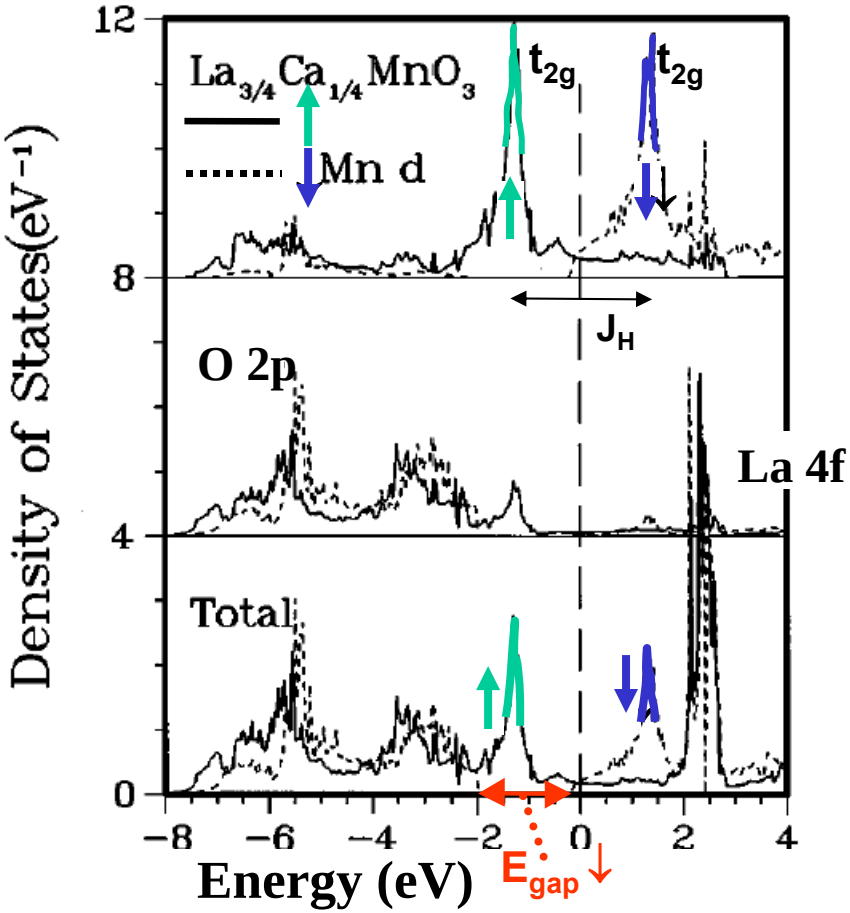
Projected DOSs



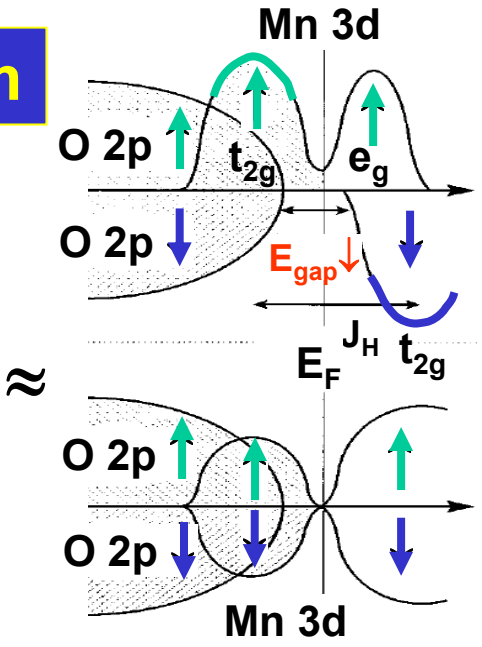
Zheng, Binggeli, J. Phys.
Cond. Matt. 21, 115602 (2009)
Plucinski, TBP

Half-Metallic Ferromagnetism

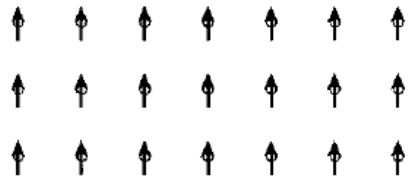
***LDA theory*- FM $La_{0.75}Ca_{0.25}MnO_3$**



Pickett and Singh, PRB 53, 1146 (1996)

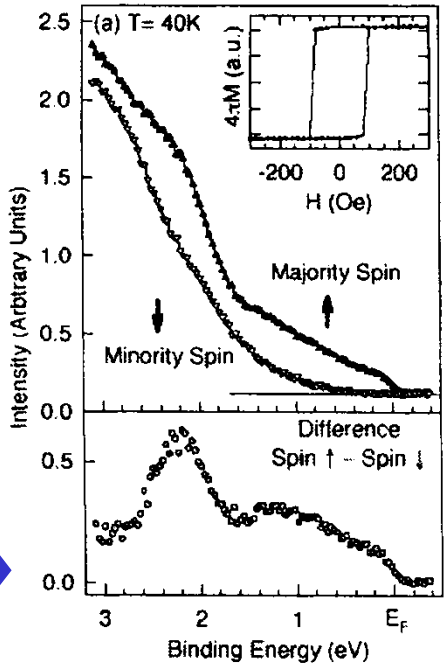


FM : $T \ll T_C$

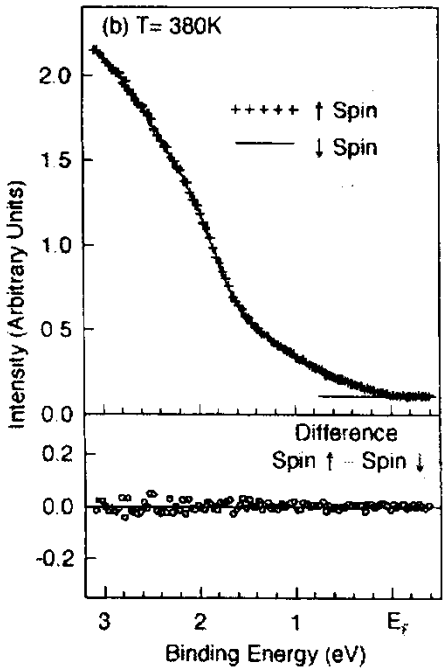


PM : $T > T_C$

$T \ll T_C$



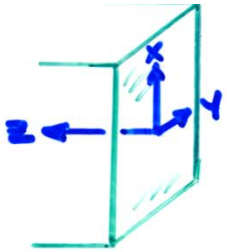
$T > T_C$



***Experiment*- spin-resolved PS**
$La_{0.70}Sr_{0.30}MnO_3$ as thin film

Park et al., Nature, PRB 392, 794 (1998)

SURFACE ELECTRONIC STATES



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

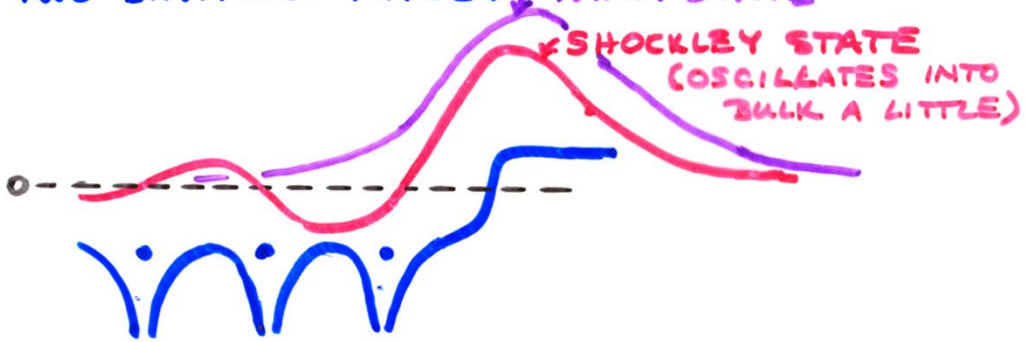
$k_z \Rightarrow \vec{k}_{\perp}$

- STRONGLY LOCALIZED NEAR SURFACE
- BLOCH FUNCTION IN x+y, BUT DECAYING IN z:

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

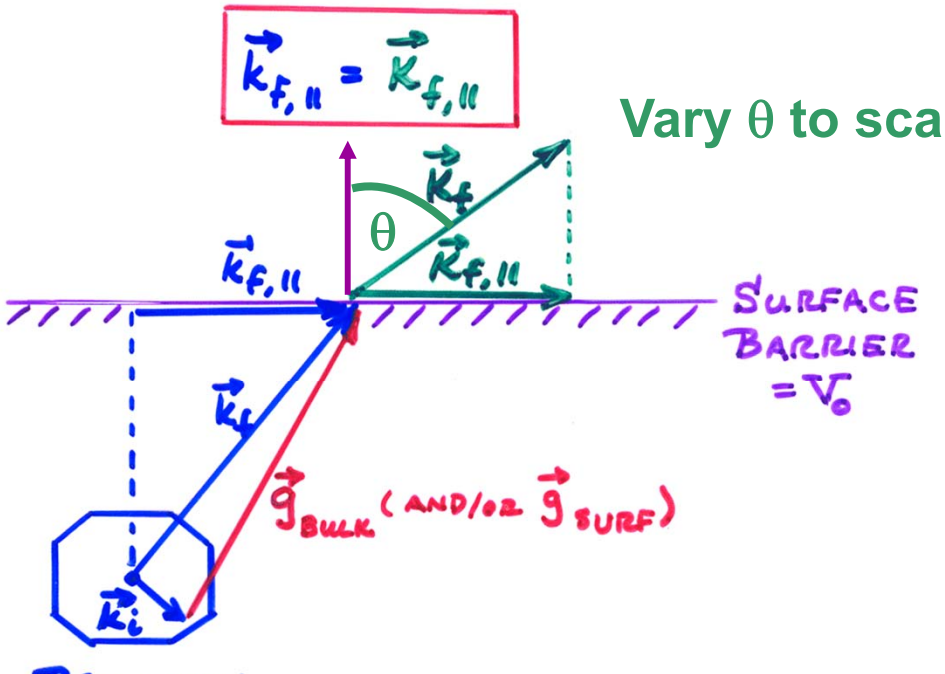
($\kappa_{\perp}$: DECAY CONSTANT)

- TWO LIMITING TYPES: TAMM STATE, SHOCKLEY STATE (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

Conservation Laws in Valence-Band Photoelectron Spectroscopy:



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

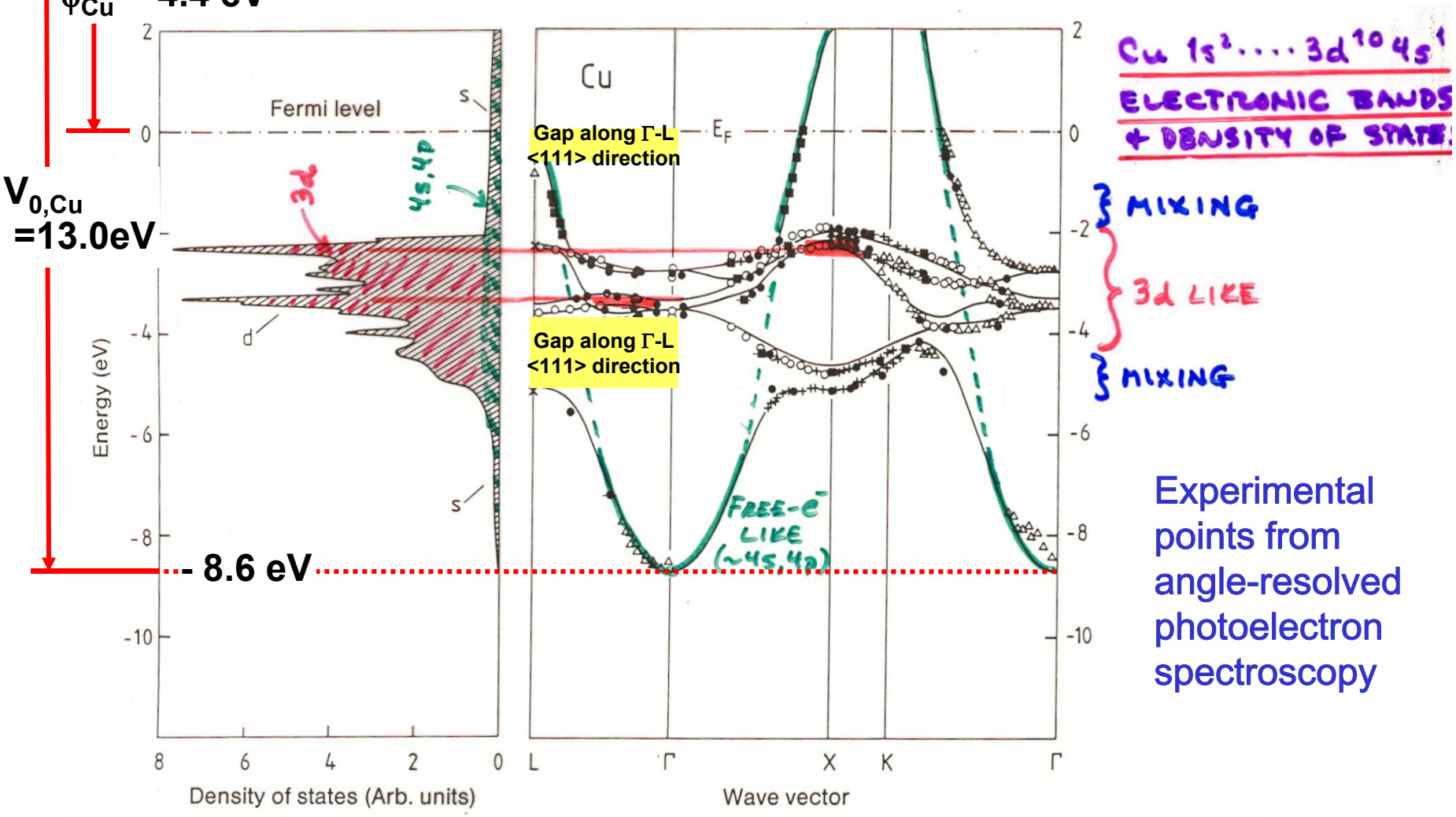
"The UPS Limit"

$$\vec{k}_f = \vec{k}_i + \vec{g}_{BULK}(\vec{g}_{SURFACE}) + \vec{k}_{h\nu} + \vec{k}_{PHONON}$$

NEGLIGIBLE IF: $h\nu \lesssim 500$ eV

$h\nu$ and/or T low enough

The electronic structure of a transition metal—fcc Cu



Experimental points from angle-resolved photoelectron spectroscopy

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

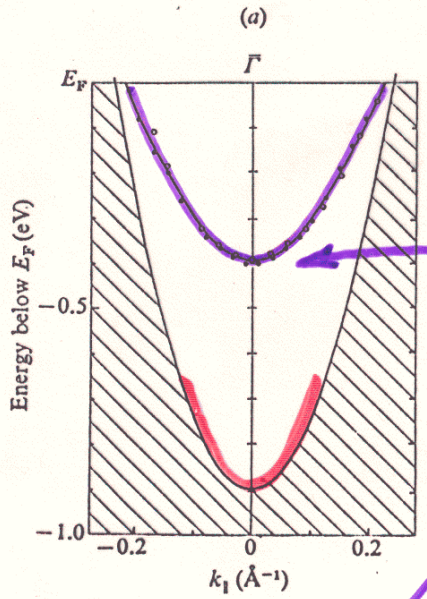
Surface states on Cu(111)

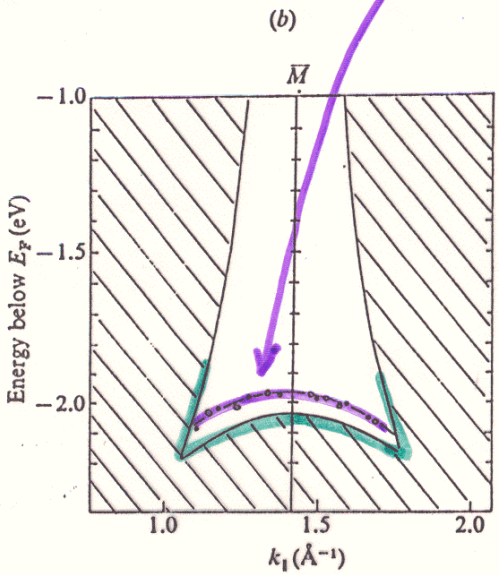
Shockley surface state

Tamm surface state

Zangwill, Surface Physics,

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.

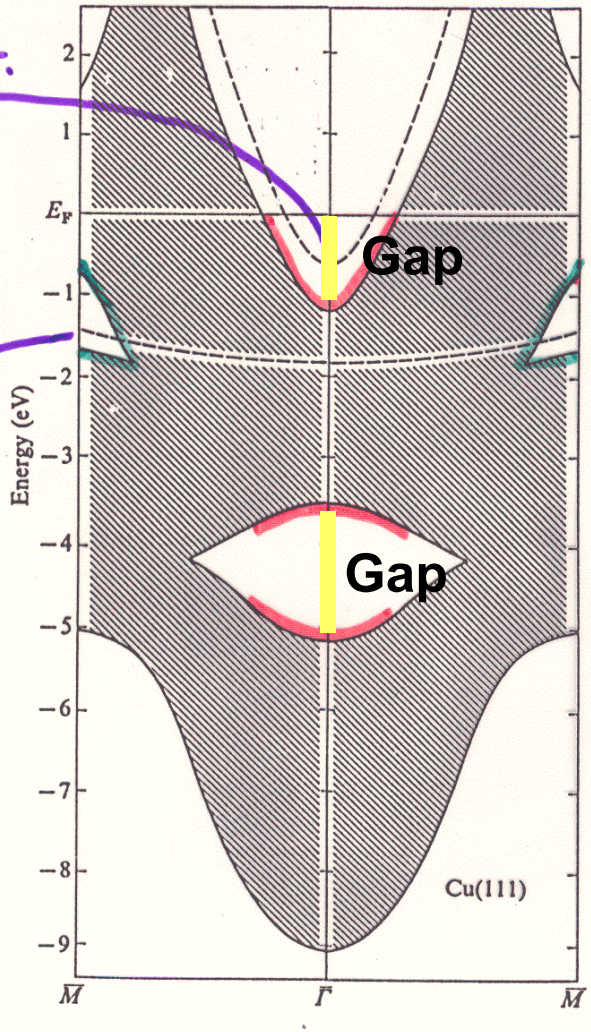
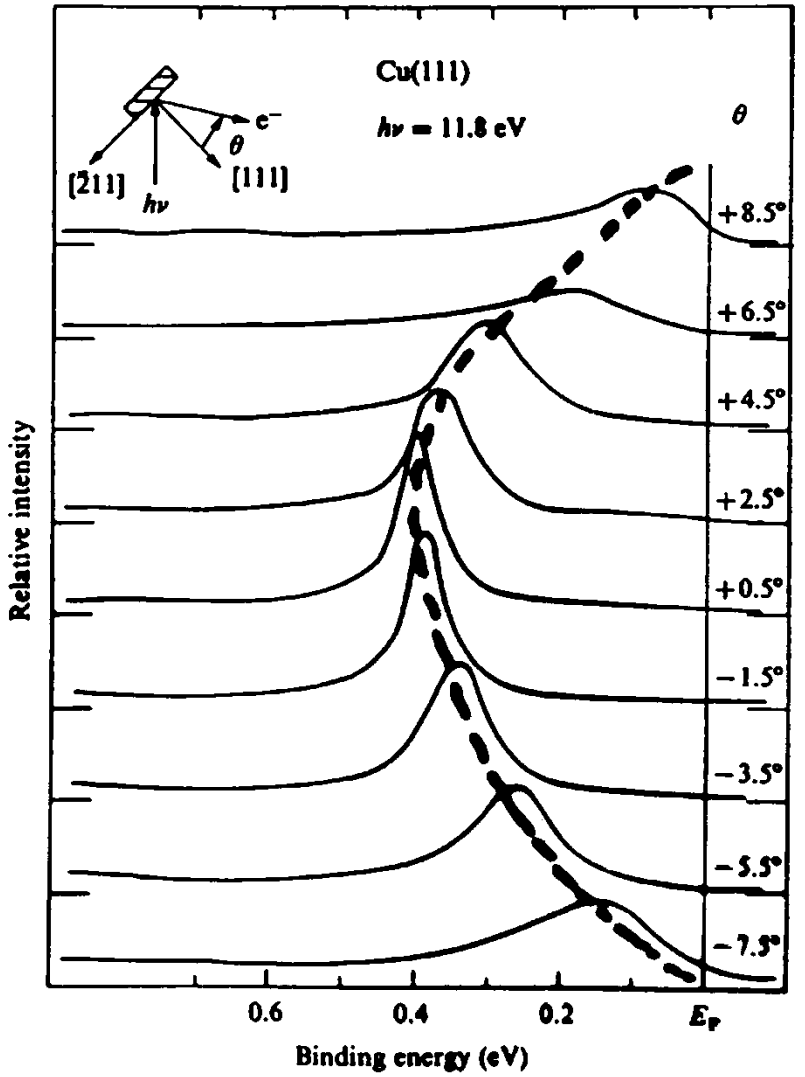
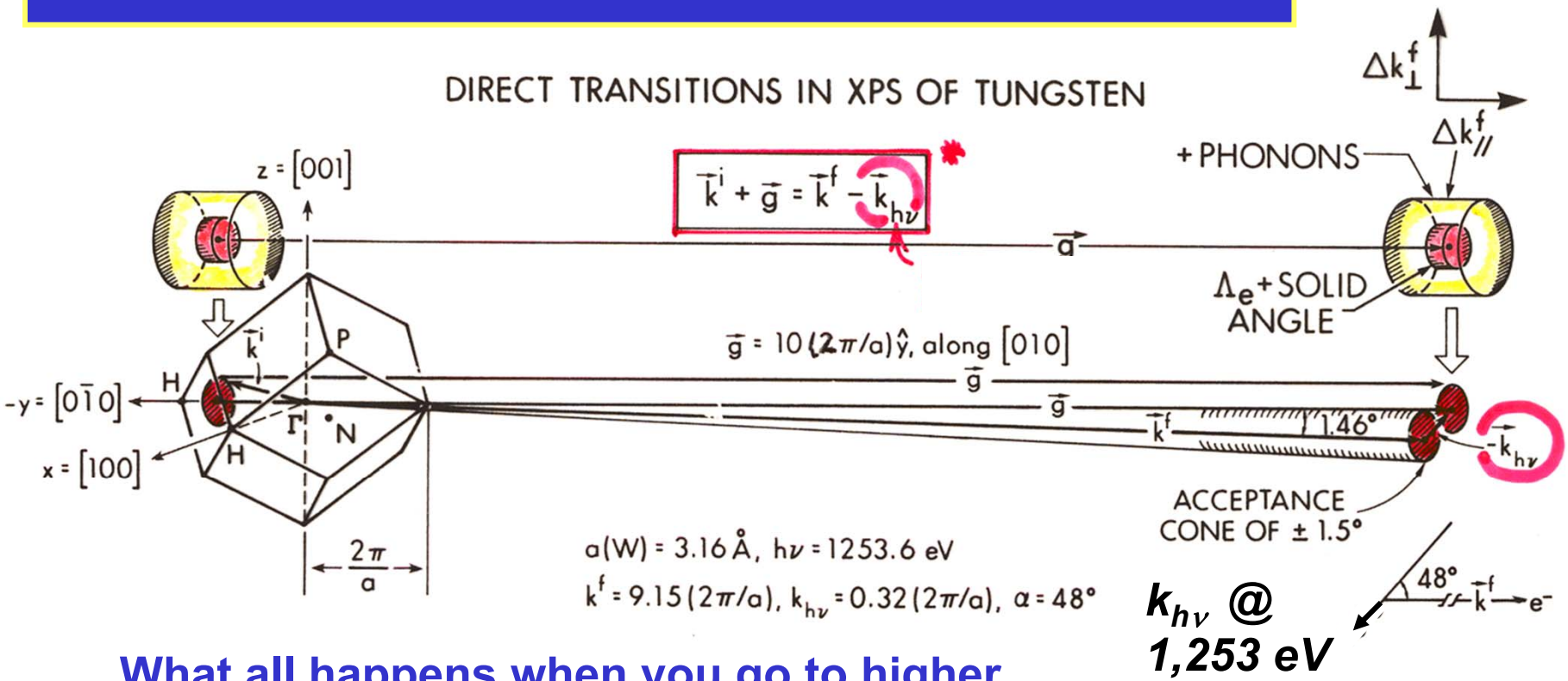


Fig. 4.20. Photoemission energy distribution curves from Cu(111) at different collection angles. Equation (4.32) has been used to express the electron kinetic energy in terms of the binding energy of the electron state (Kevan, 1983).



Zangwill,
Surface Physics,

Valence-Band Photoemission at High Energy-- What & Where is the "XPS Limit"?:



$k_{h\nu}$ @ 1,253 eV

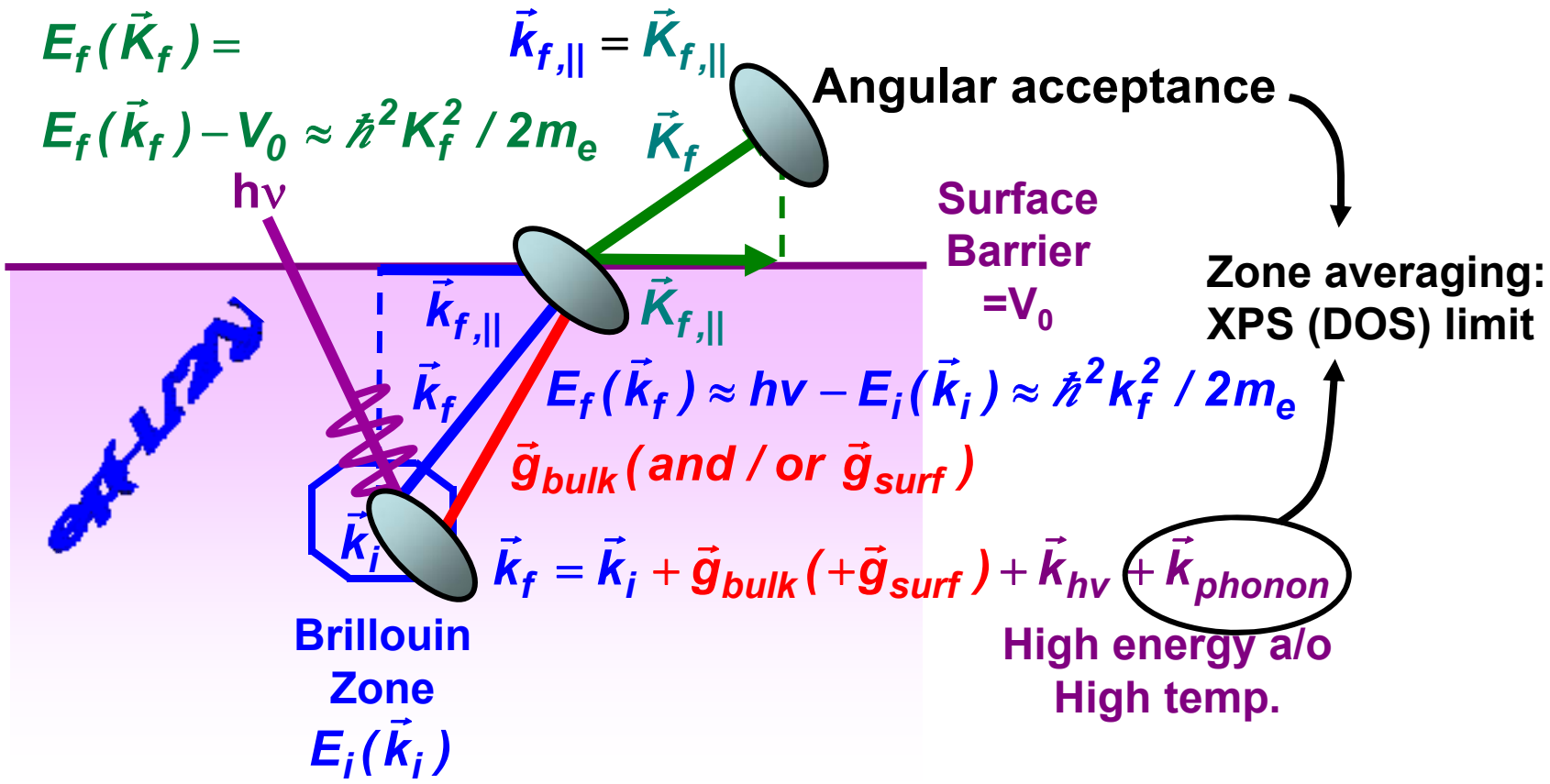
What all happens when you go to higher photon energies?

- **non-dipole effect→the photon momentum**
- **angular acceptance→B.Z. averaging**
- **lattice recoil, phonon creation→more B.Z. averaging, energy loss**

….the XPS limit of full B.Z. averaging and D.O.S. sensitivity

Hussain et al., Phys. Rev. B 22, 3750 ('80)

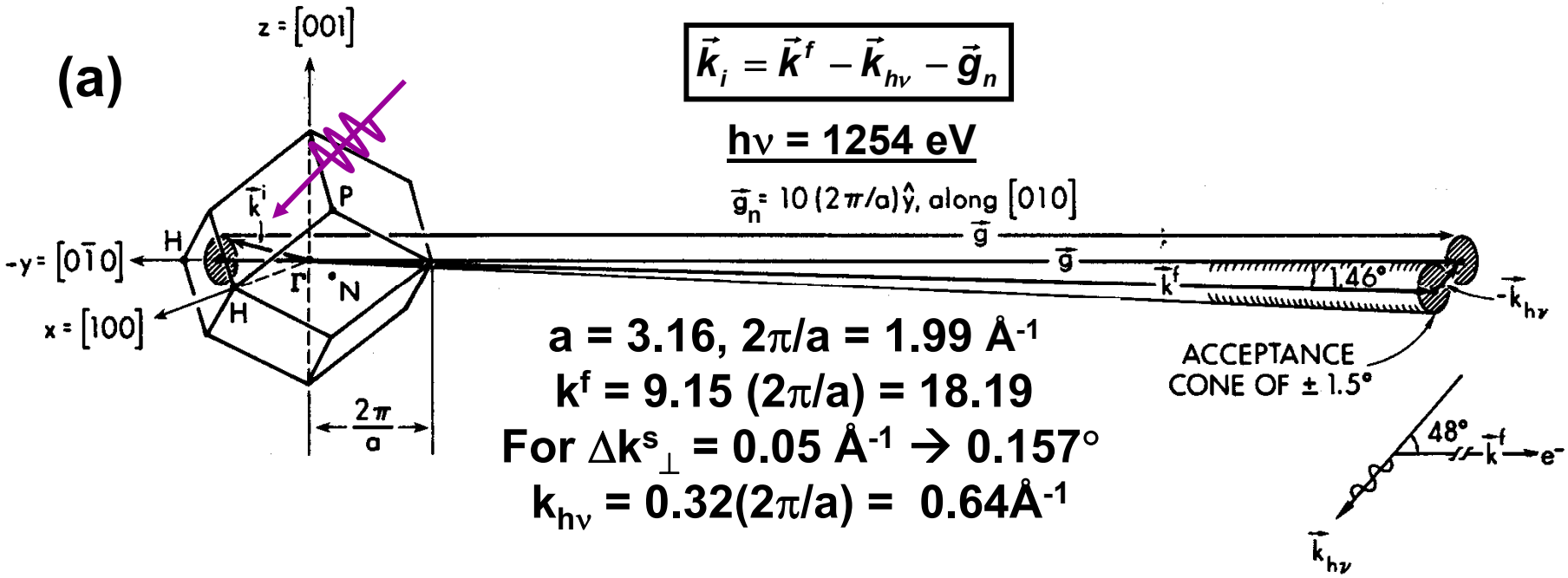
Valence-band photoemission—at higher energy



$$I(E_f, \vec{k}_f) \propto \left| \hat{\varepsilon} \bullet \left\langle \varphi_{photoe}(E_f = h\nu + E_i, \vec{k}_f = \vec{k}_i + \vec{g}) \middle| \vec{r} \middle| \varphi(E_i, \vec{k}_i) \right\rangle \right|^2$$

Hussain et al., Phys. Rev. B 34 (1986) 5226.

Angle-Resolved Photoemission at High Energy--



$$\vec{k}_i = \vec{k}^f - \vec{k}_{h\nu} - \vec{g}_n$$

$h\nu$ = 1254 eV

$a = 3.16$, $2\pi/a = 1.99$ Å^{-1}

$k^f = 9.15\ (2\pi/a) = 18.19$

For $\Delta k^s_{\perp} = 0.05$ Å^{-1} → 0.157°

$k_{h\nu} = 0.32(2\pi/a) = 0.64$Å^{-1}

Hussain et al.….CF, Phys. Rev. B 22 3750 (1980) Phys. Rev. B 34, 5226 (1986)

Additional effects at higher energies:

- Non-dipole--the photon momentum $k_{h\nu}$
- Angular acceptance→B.Z. averaging
- Lattice recoil→phonon creation→more B.Z. averaging,

  Fraction DTs ≈ **Debye-Waller factor** = $W(T) \approx \exp[-(k^f)^2 \langle u^2(T)\rangle]$

  $\approx \exp[-C_1 (k^f)^2 T/(m\Theta_D^2)] \approx \exp(-C_2 E_{kin} T)$

  →the "XPS limit" of full B.Z. averaging and D.O.S. sensitivity

  →core-like photoelectron diffraction

Shevchik, Phys. Rev. B 16, 3428 (1977)

Takata et al., Phys. Rev. B 75, 233404 (2007)

Alvarez et al., PR*B* 54, 14703 (1996)

- Recoil leads to peak shifts and broadening: $E_{recoil}(eV) \approx \left[\frac{m_e}{M}\right] E_{kin} \approx 5.5 \times 10^{-4} \left[\frac{E_{kin}(eV)}{M(amu)}\right]$

Table 1 Debye temperature and thermal conductivity[a]

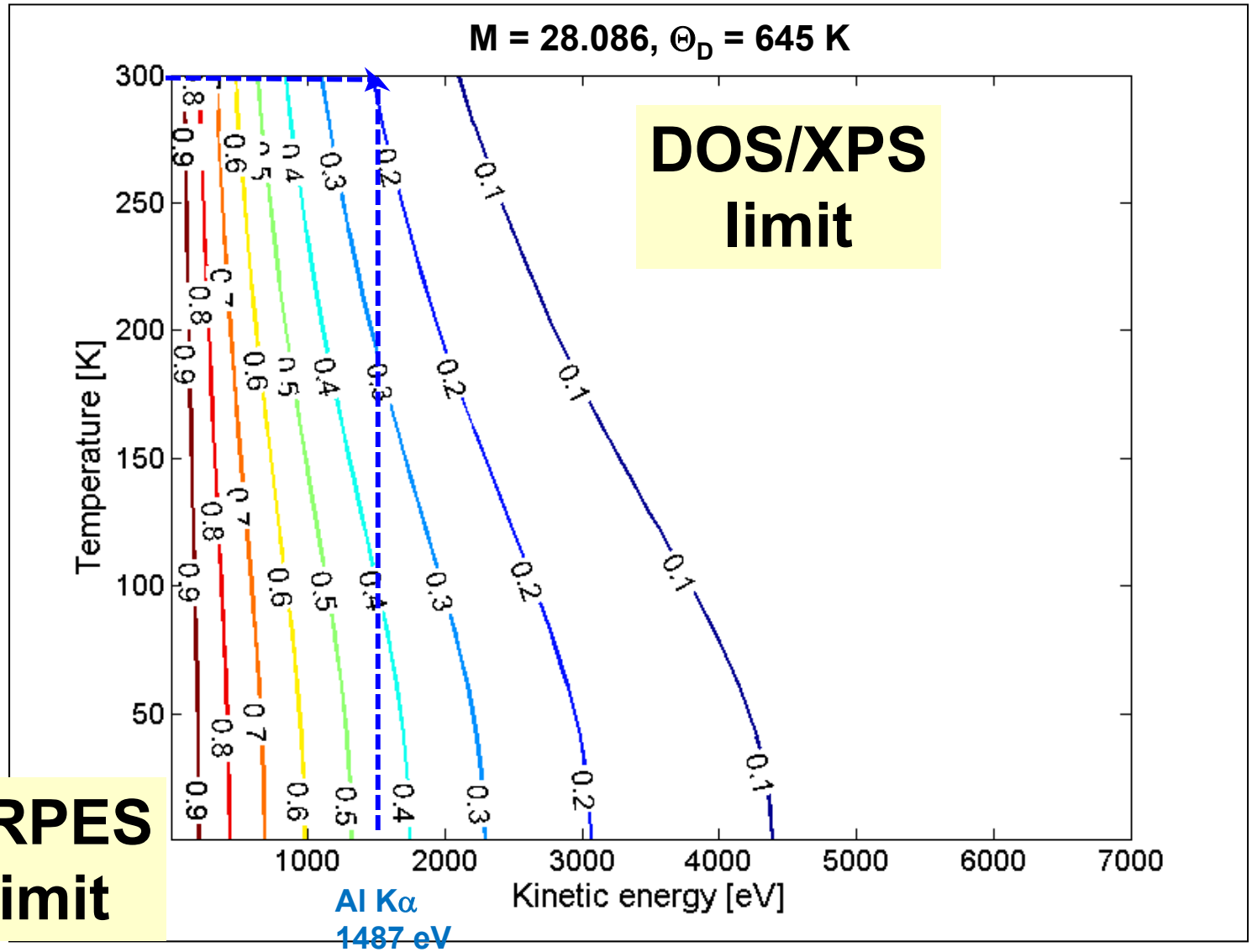
Li	Be											B	C	N	O	F	Ne
344	1440												2230				75
0.85	2.00											0.27	1.29				
Na	Mg											Al	Si	P	S	Cl	Ar
158	400	Low temperature limit of θ, in Kelvin										428	645				92
1.41	1.56	Thermal conductivity at 300 K, in W $cm^{-1}K^{-1}$										2.37	1.48				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
91	230	360.	420	380	630	410	470	445	450	343	327	320	374	282	90		72
1.02		0.16	0.22	0.31	0.94	0.08	0.80	1.00	0.91	4.01	1.16	0.41	0.60	0.50	0.02		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn w	Sb	Te	I	Xe
56	147	280	291	275	450		600	480	274	225	209	108	200	211	153		64
0.58		0.17	0.23	0.54	1.38	0.51	1.17	1.50	0.72	4.29	0.97	0.82	0.67	0.24	0.02		
Cs	Ba	La β	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
38	110	142	252	240	400	430	500	420	240	165	71.9	78.5	105	119			
0.36		0.14	0.23	0.58	1.74	0.48	0.88	1.47	0.72	3.17		0.46	0.35	0.08			
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
						200		210				120	210
0.11	0.12	0.16		0.13		0.11	0.11	0.11	0.16	0.14	0.17	0.35	0.16

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
163		207											
0.54		0.28	0.06	0.07									

[a] Most of the θ values were supplied by N. Pearlman; references are given the *A.I.P. Handbook*, 3rd ed; the thermal conductivity values are from R. W. Powell and Y. S. Touloukian, Science **181**, 999 (1973).

Silicon--Debye-Waller Factors

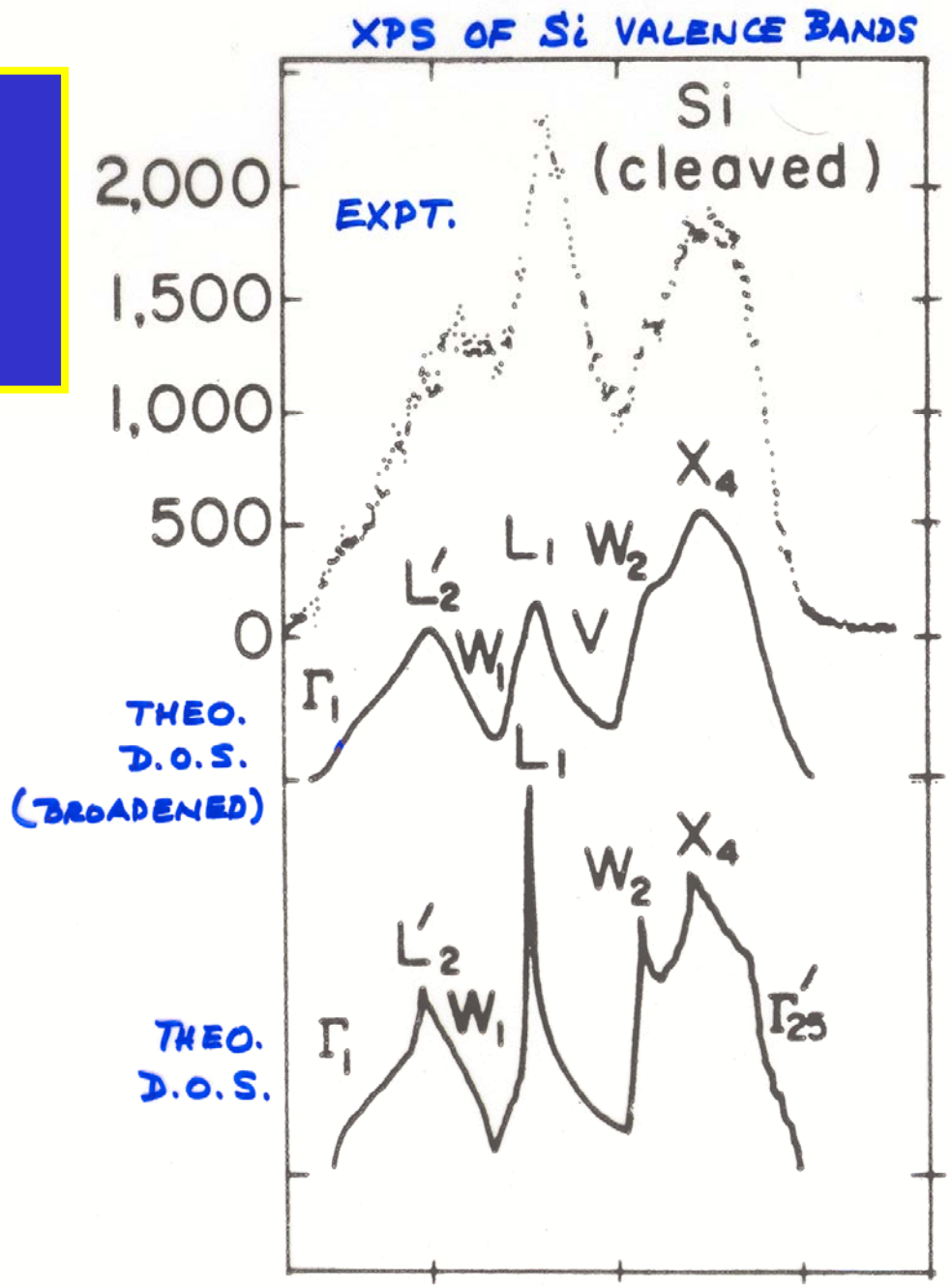


DOS/XPS limit

ARPES limit

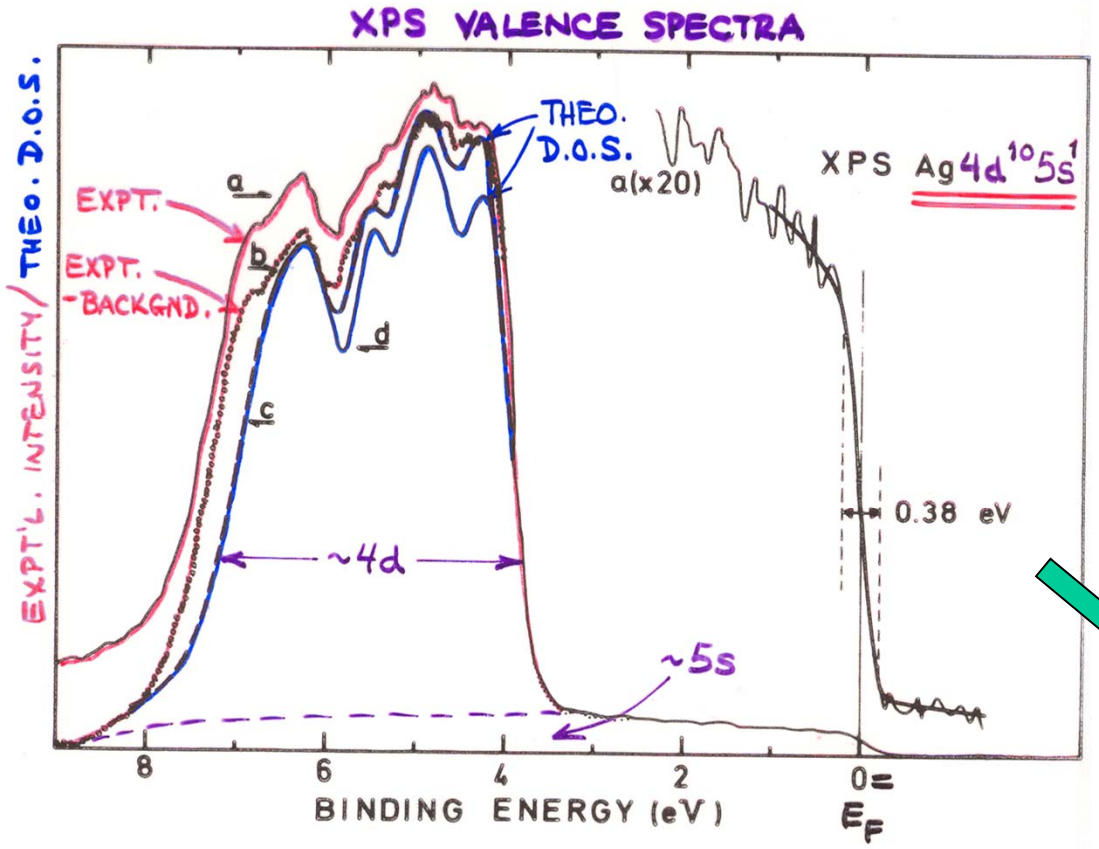
Plucinski, et al. PRB 78, 035108 (2008);
Phys. Rev. B 84, 045433 (2011)

Some classic cases in the XPS limit:

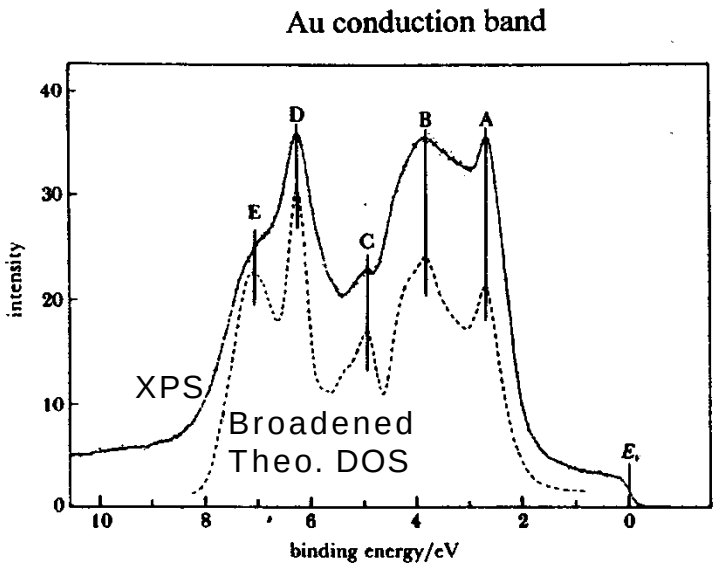


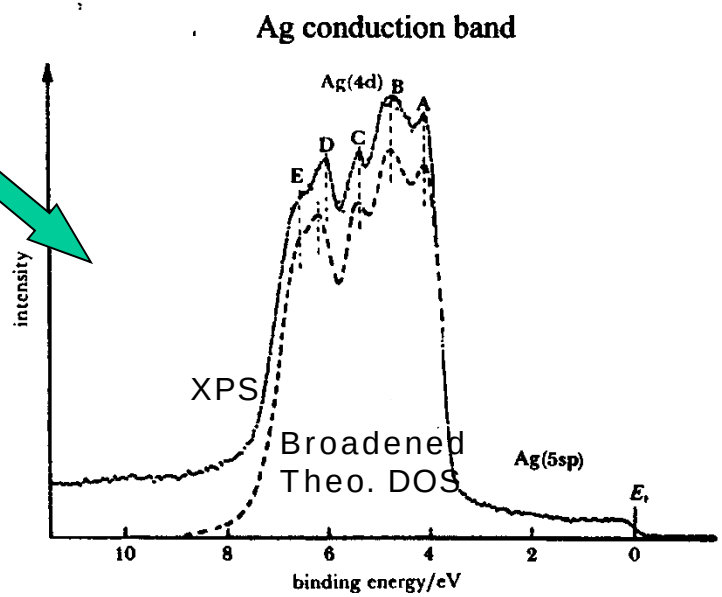
"Basic Concepts of XPS"
Figure 14

Densities of states From XPS spectra



- COMPLETE B.Z. AVERAGING DUE TO PHONON-ASSISTED NON-DIRECT TRANSITIONS ⇒ "XPS LIMIT"

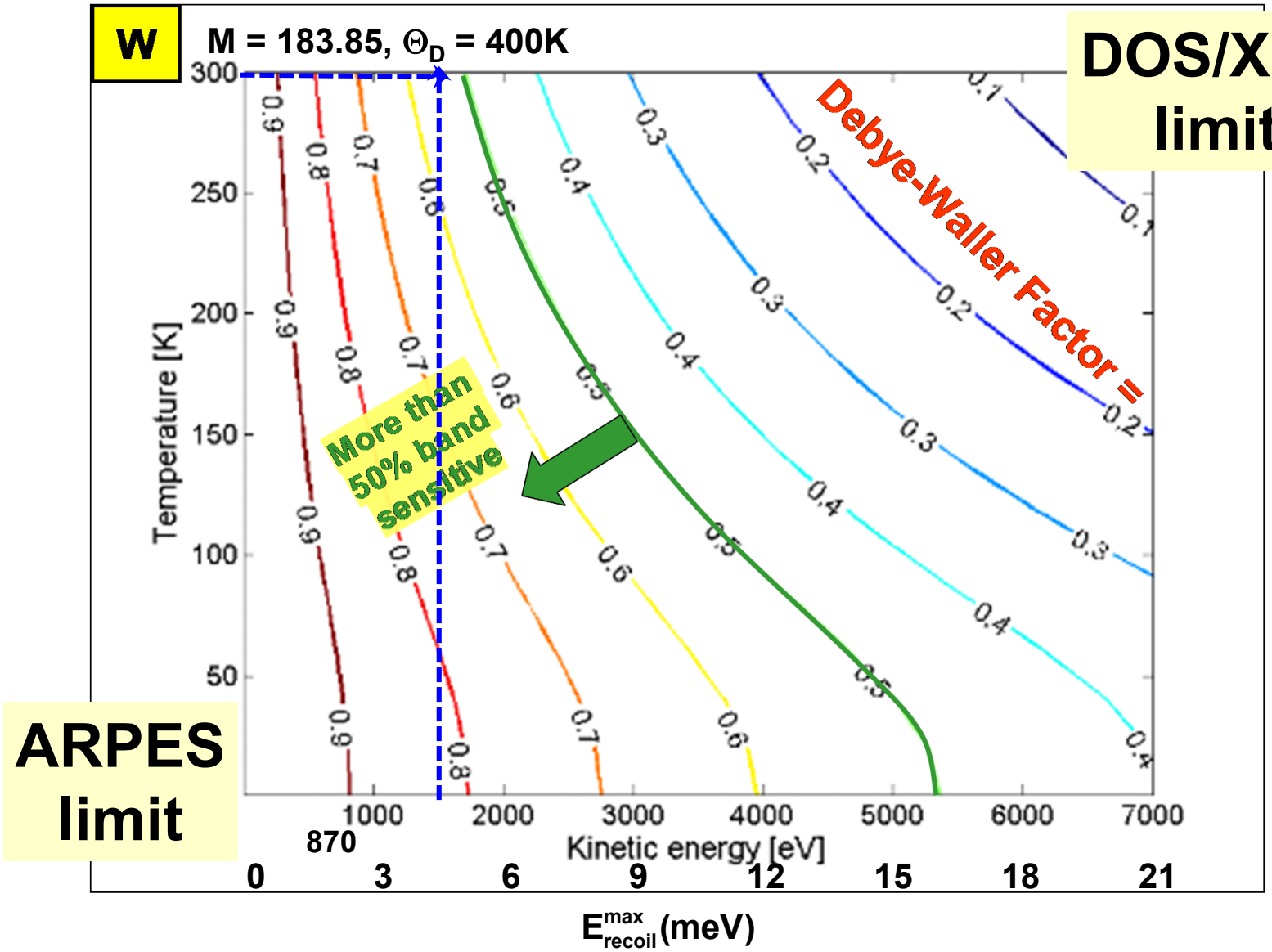




"Basic Concepts of XPS"
Figure 13

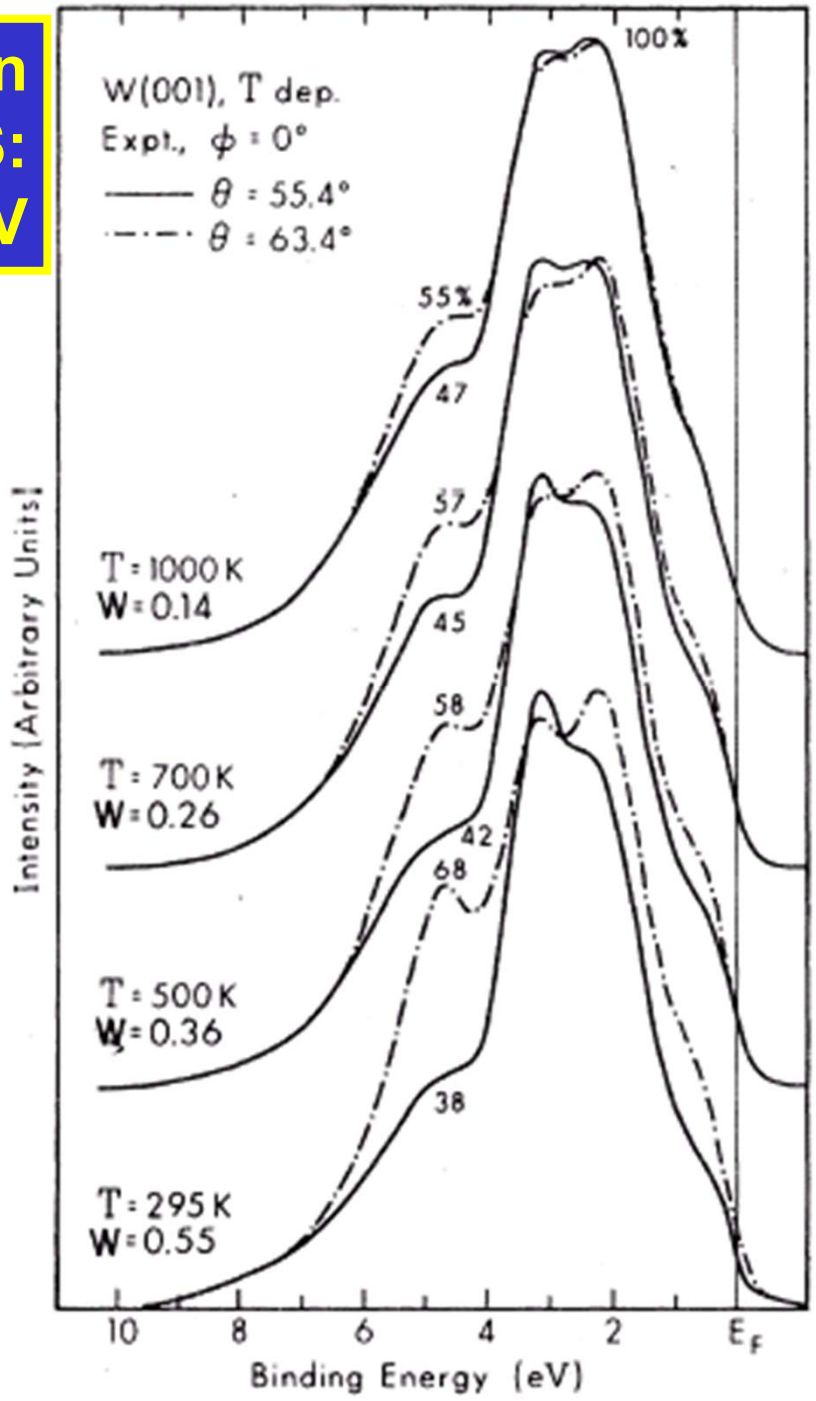
Siegbahn, 2003

Tungsten--Debye-Waller Factors and Recoil Energies



Plucinski, et al. PRB 78, 035108 (2008);
Phys. Rev. B 84, 045433 (2011)

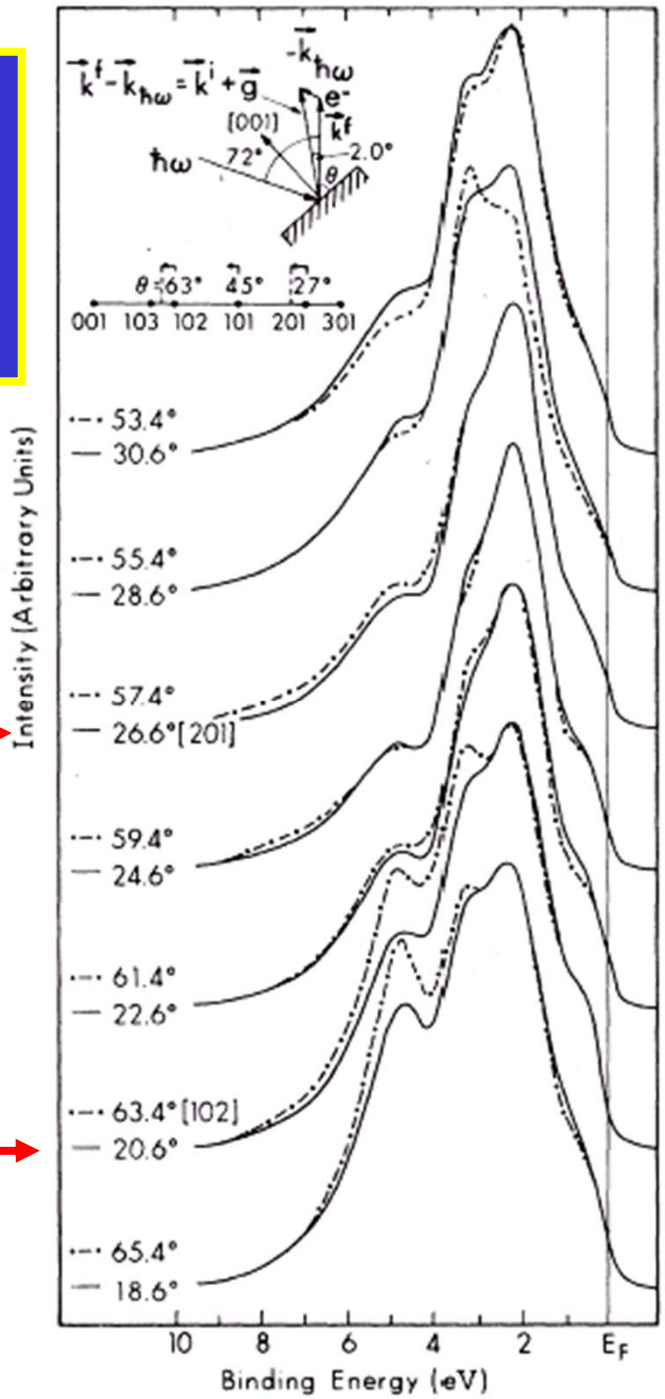
Direct-transition effects in XPS: W(110) at 1253.6 eV



Present if vibrations stiff enough (Debye T high enough), but suppressed as temperature is raised.

Hussain et al., Phys. Rev. 22, 3750 (1980)

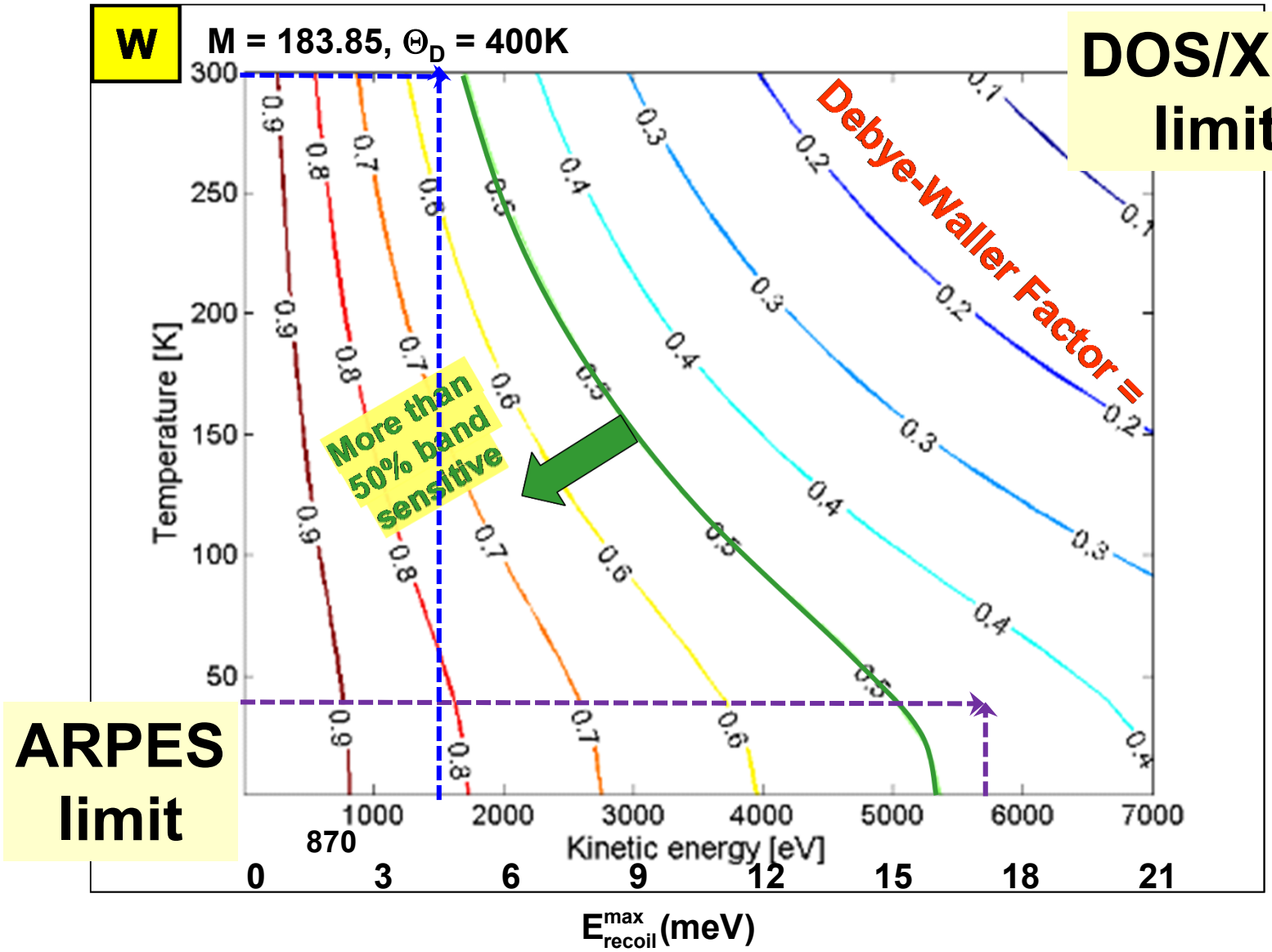
Effect of photon momentum on k conservation: W(110) at 1253.6 eV



Symmetry-related spectra shifted by 6.0° for best match. Theoretical 4.8° due to $k_{h\nu}$

Hussain et al., Phys. Rev. 22, 3750 (1980)

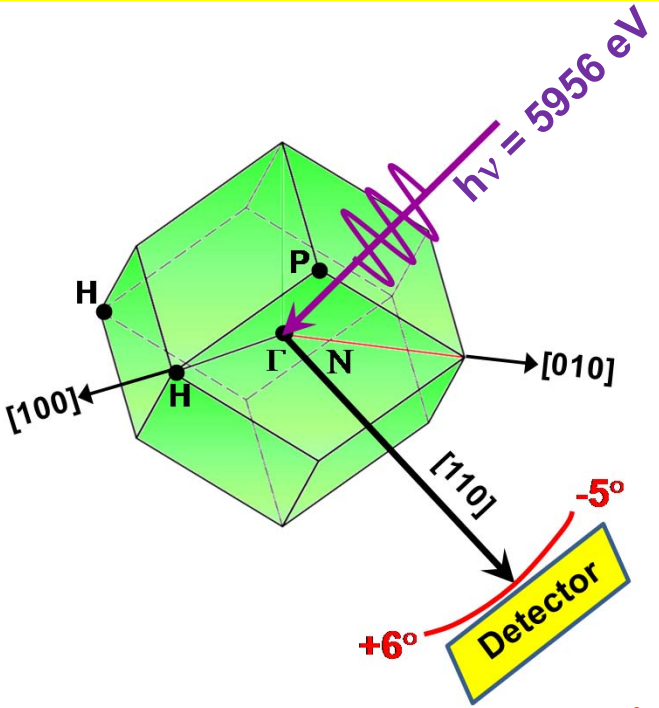
Tungsten--Debye-Waller Factors and Recoil Energies



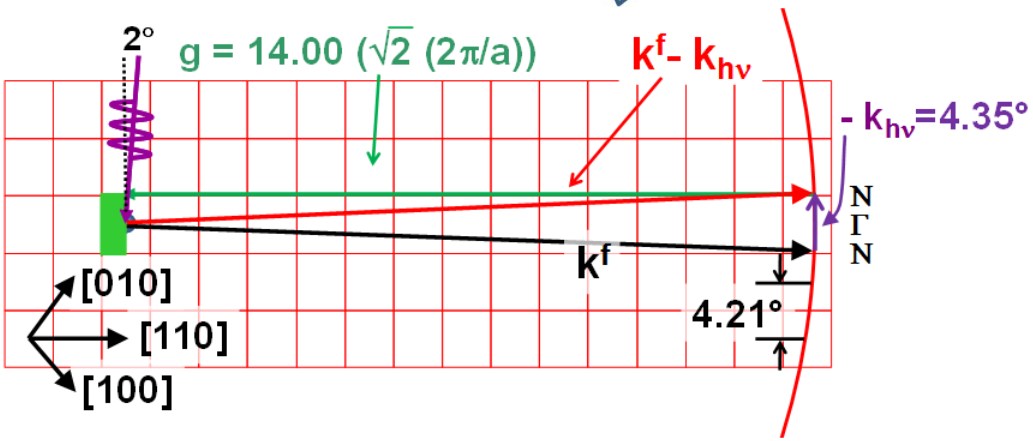
Plucinski, et al. PRB 78, 035108 (2008);
Phys. Rev. B 84, 045433 (2011)

Hard x-ray ARPES for W(110): 5.96 keV

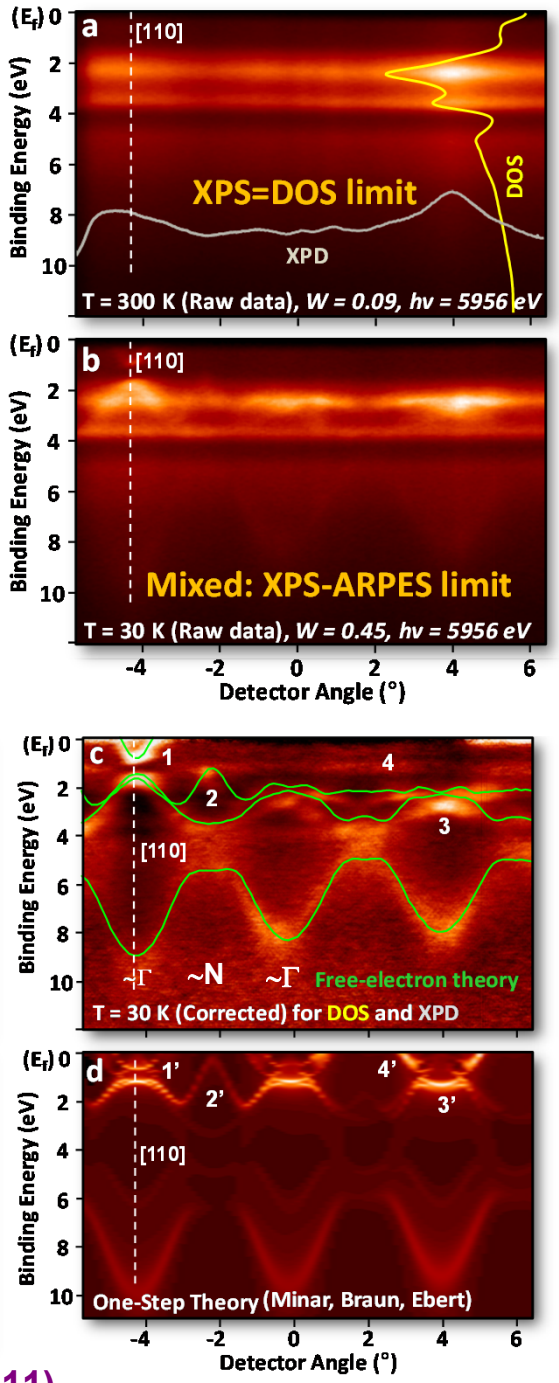
(i)



(ii)

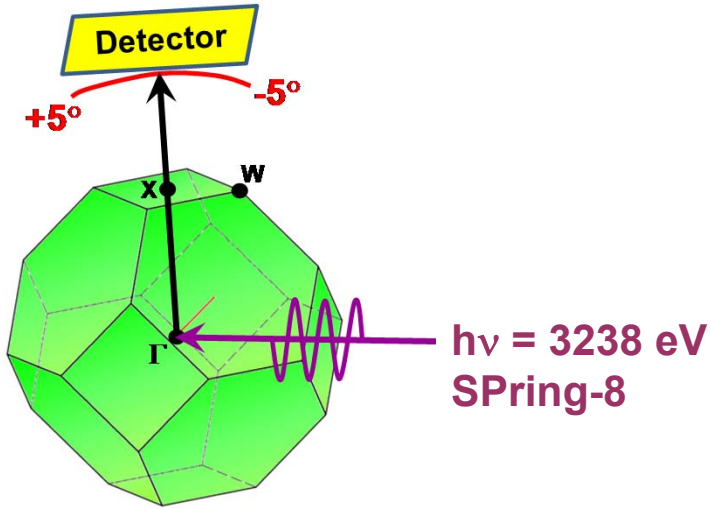


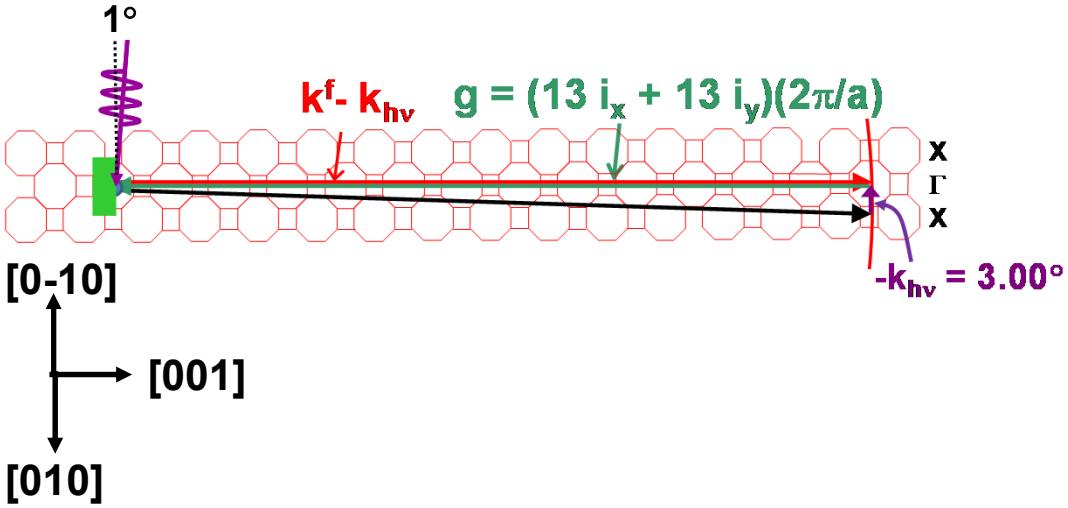
(iii)

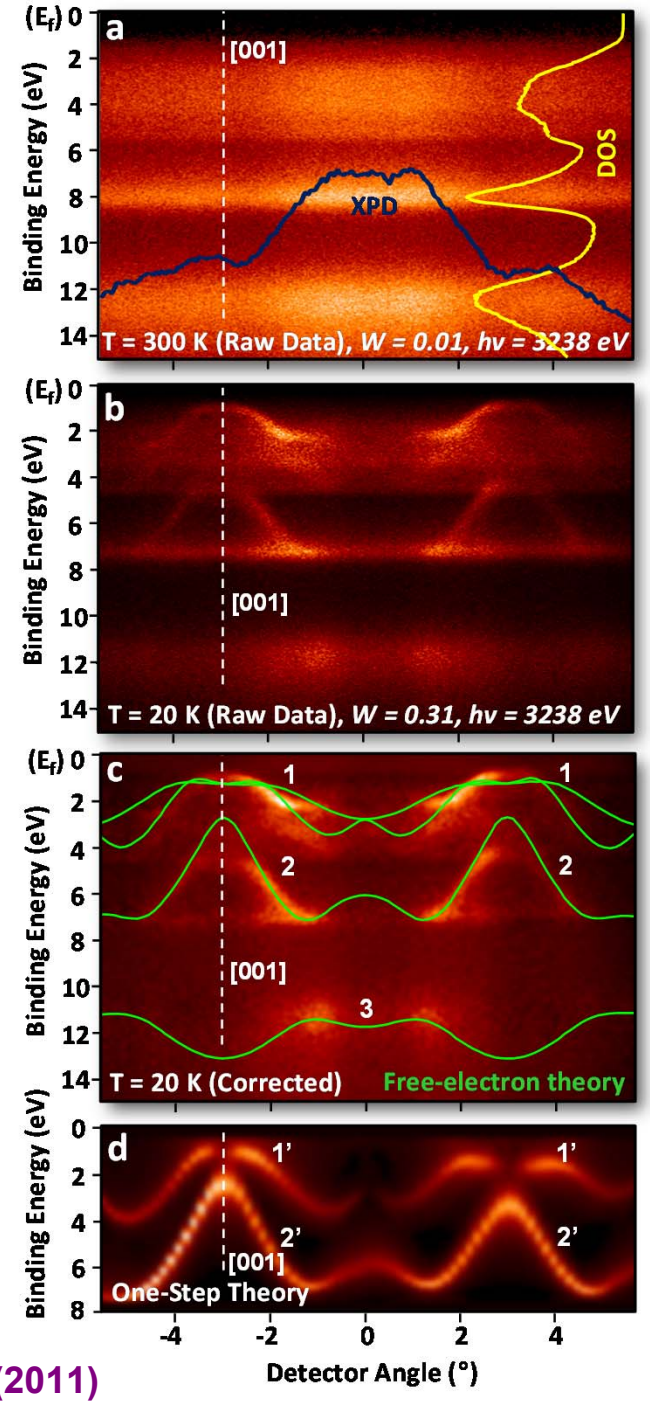


Gray, Minar et al., Spring-8, Nature Materials 10, 759 (2011)

Hard x-ray ARPES for GaAs(001): 3.2 keV

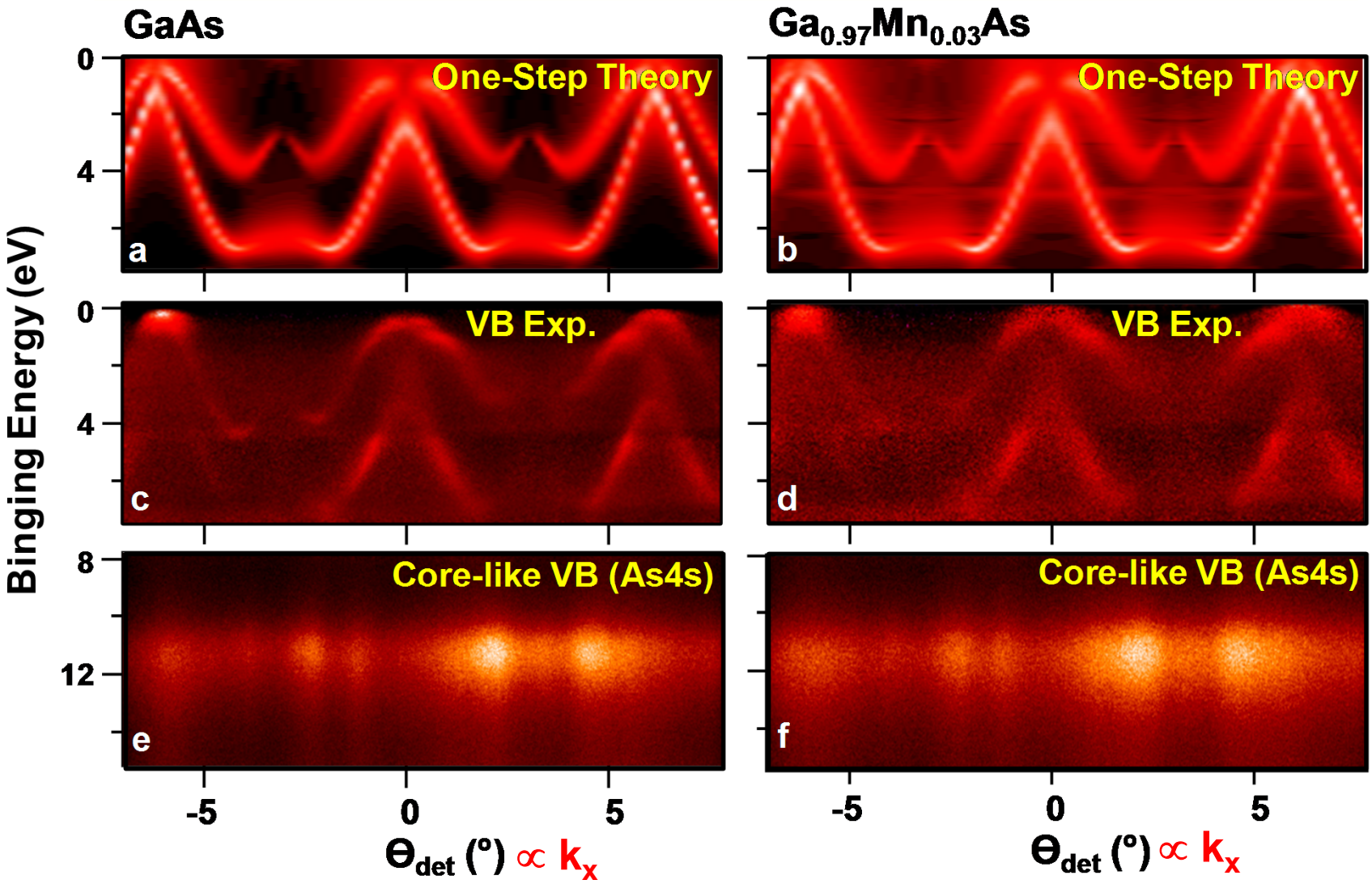






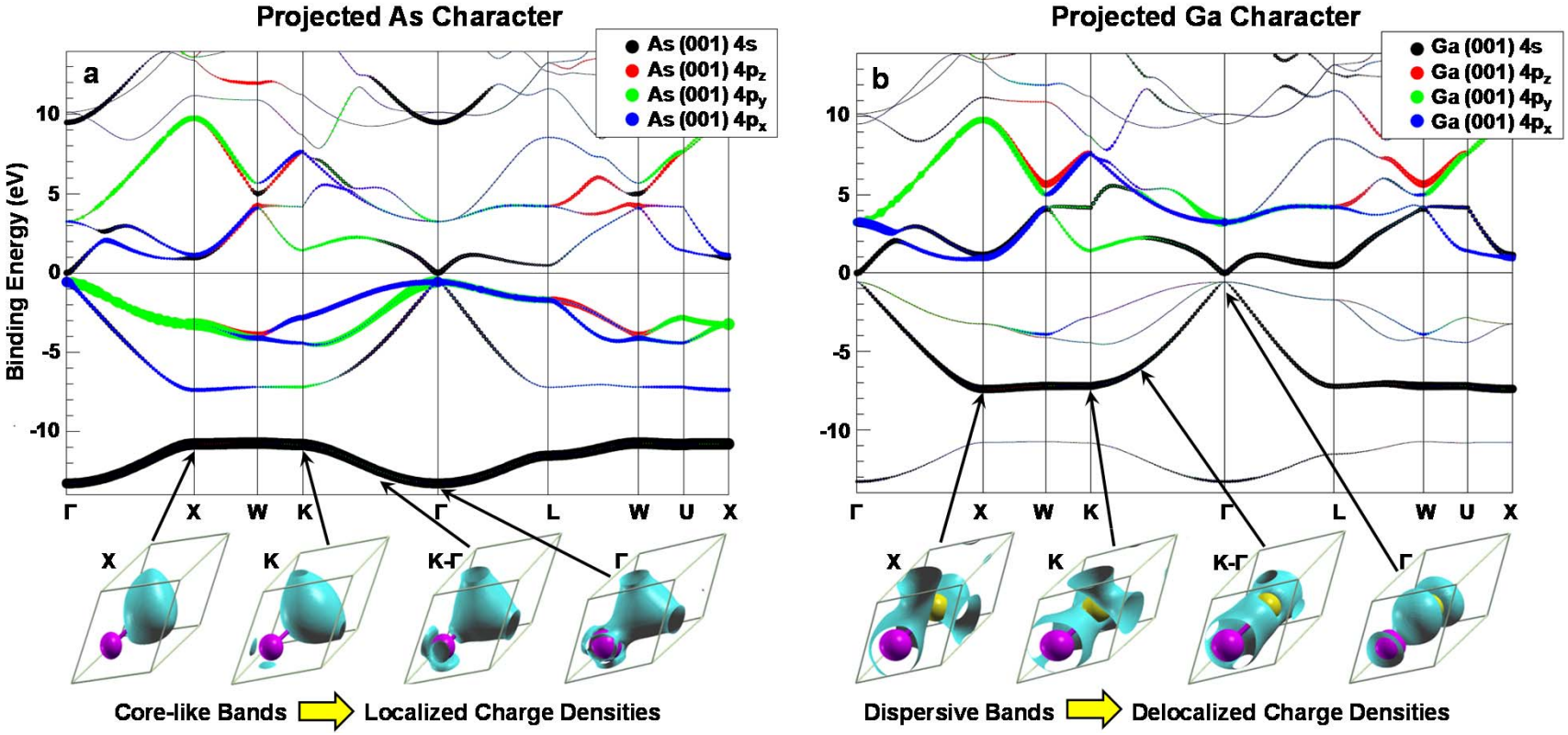
Gray, Minar et al., Spring-8, Nature Materials 10, 759 (2011)

Hard x-ray ARPES--GaAs and DMS $Ga_{0.97}Mn_{0.03}As$ Comparing Experiment and One-Step KKR Theory



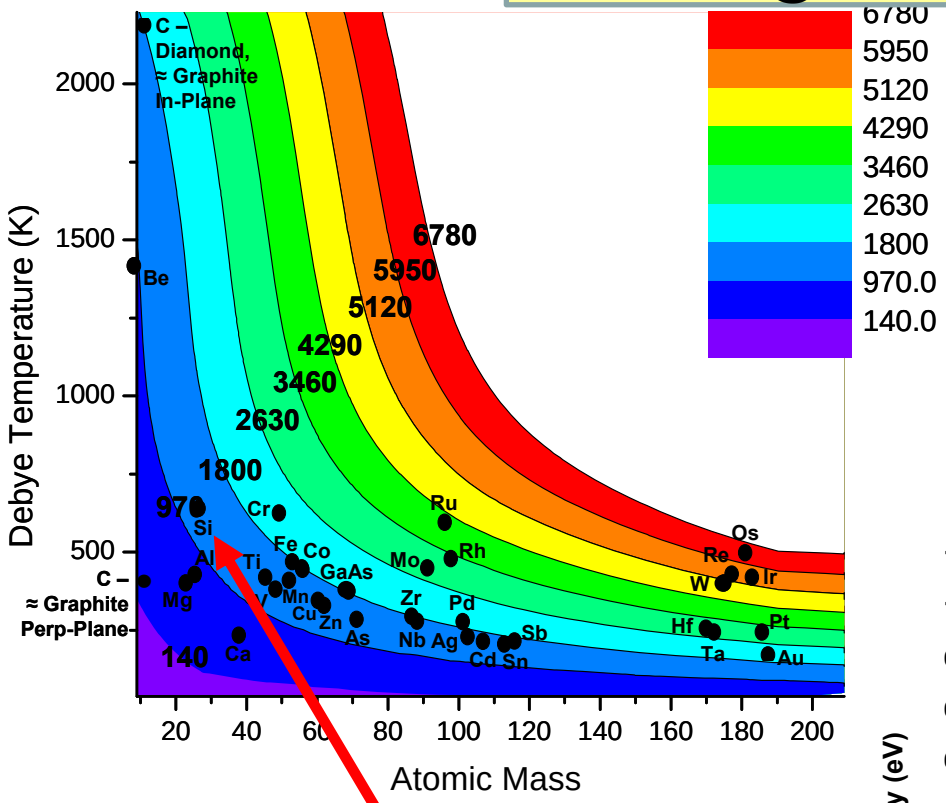
Gray, Minar, Dubon (sample) et al., TBP

GaAs Band Structure
Atomic-Orbital Character and Charge Density Contours

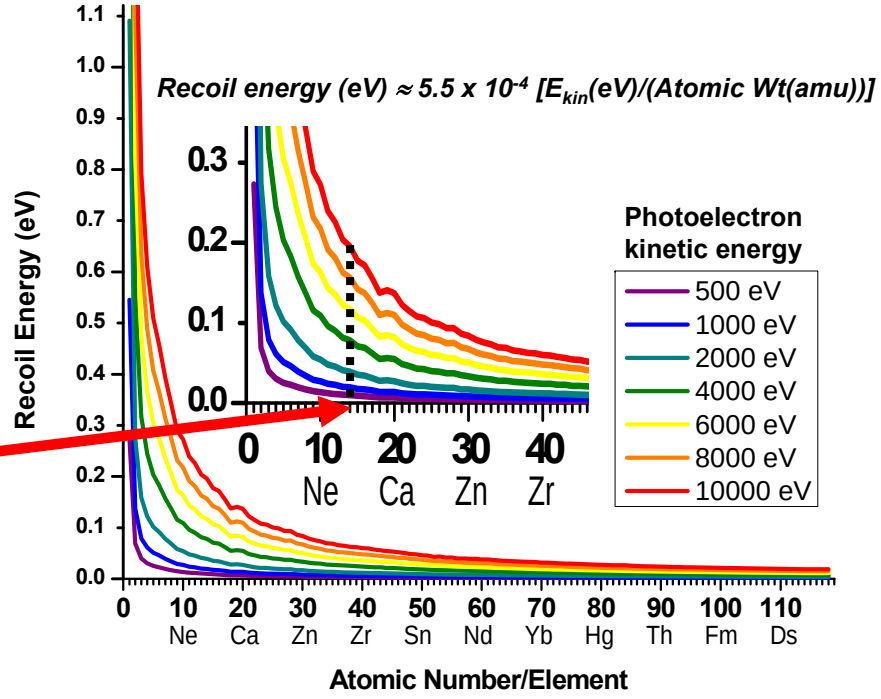


Ylvisaker and Pickett

Photon energy for D-W = O.5 @ 20K



HARPES-How high can we go? Photoemission Debye-Waller Factors and Recoil Energies



E.g.-Si

C. Papp. L. Plucinski, et al.,
Phys. Rev. B 84, 045433 (2011)

Outline—Here to end of quarter

- Core-level chemical shifts: Koopmans', relaxation, the potential model
- Various other final state effects providing information in core-level spectra
- Valence-band spectra: low-energy UPS limit and high-energy XPS limit
- Photoelectron diffraction, extended x-ray absorption fine structure (EXAFS, XAFS)
- Photoelectron spectroscopy at realistic pressures in the multi-Torr range
- Photoelectron microscopy: adding lateral spatial resolution in 2 dimensions