Outline

Surface, interface, and nanoscience—short introduction

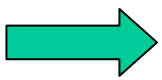
Some surface concepts and techniques→photoemission

Synchrotron radiation: experimental aspects

Electronic structure—a brief review

The basic synchrotron radiation techniques:
more experimental and theoretical details

Core-level photoemission



Valence-level photoemission

Microscopy with photoemission

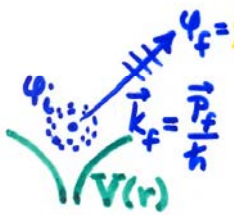
Outline

- Valence-band spectra: low-energy UPS limit and high-energy XPS limit
- Core-level chemical shifts: the potential model
- Core-level chemical shifts: equivalent-core (Z+1) and thermochemical energies
- Multiplet splittings
- Spin-orbit splitting, the Fano effect, and spin-polarized outgoing electrons
- Magnetic circular dichroism (MCD) in core-level emission
- Non-magnetic circular dichroism in core-level emission: a.k.a. circular dichroism in angular distributions (CDAD)
- Various other final state effects providing information in core-level spectra

PHOTOELECTRON EMISSION - BASIC MATRIX ELEMENTS & SELECTION RULES:

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

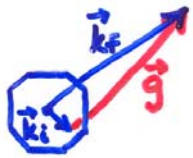
- $\Delta l = l_f - l_i = \pm 1$ TWO CHANNELS
- $\Delta m = m_f - m_i = 0, \pm 1$ LINEAR POLARIZ.
- $\Delta m = \pm 1$, CIRCULAR POLARIZATION

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

VALENCE BANDS IN SOLIDS:

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.

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

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

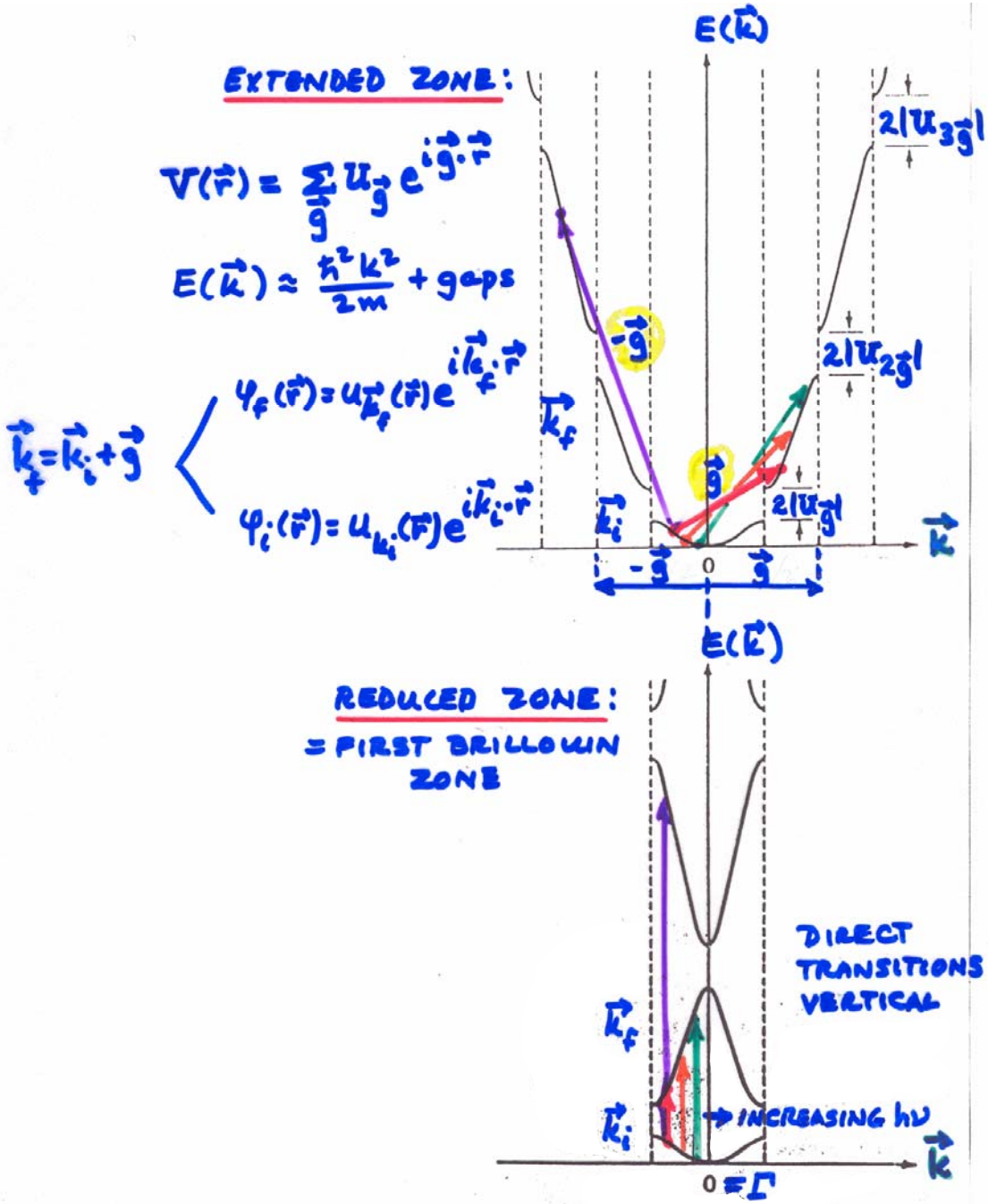
"DIRECT" TRANSITIONS

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.



ALUMINUM – ELECTRONIC BANDS & D.O.S.

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

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

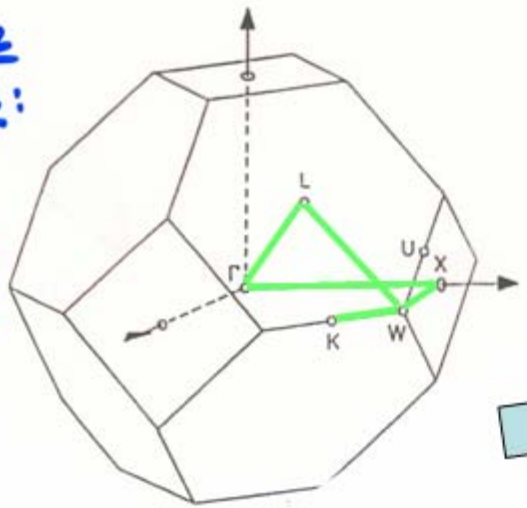
(Bloch)

3D Brillouin zone

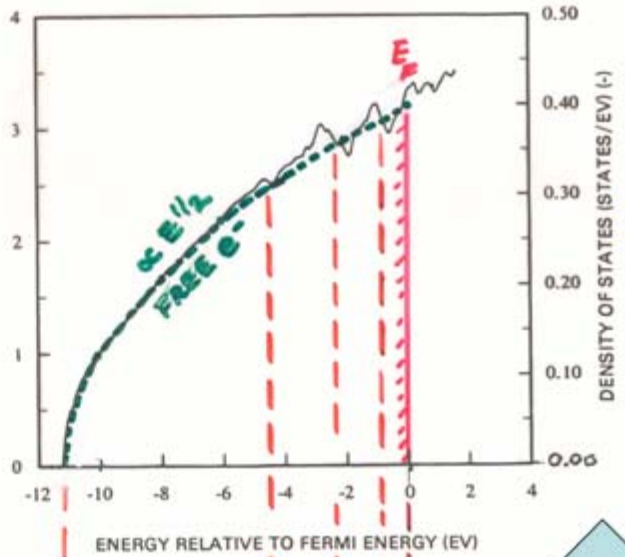
REAL fcc:

↓

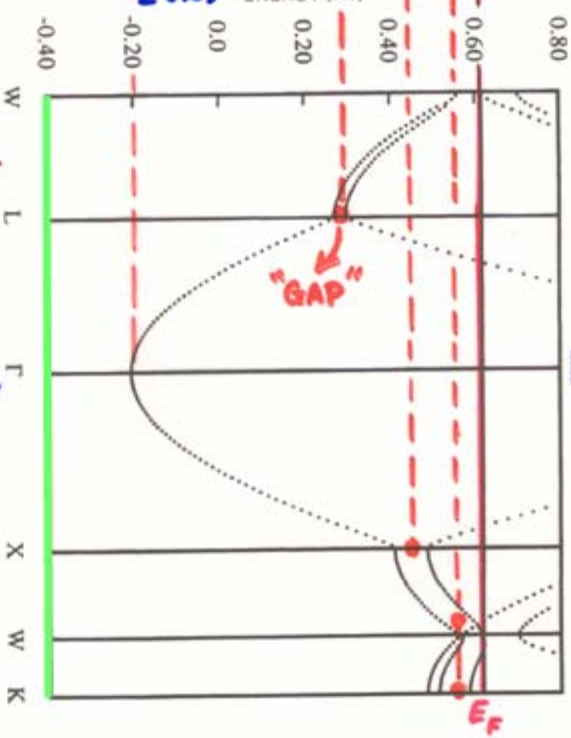
RECIP. bcc



D.O.S.



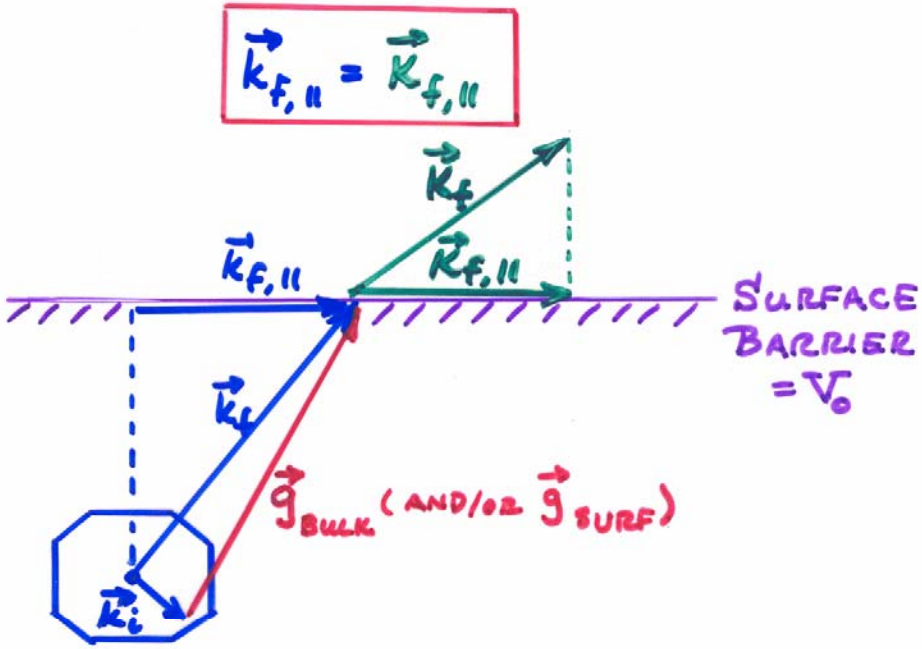
BANDS



k = 0

Moruzzi, Janak, Williams, Pergamon, 1978

Conservation Laws in Valence-Band Photoelectron Spectroscopy:



"The UPS Limit"

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

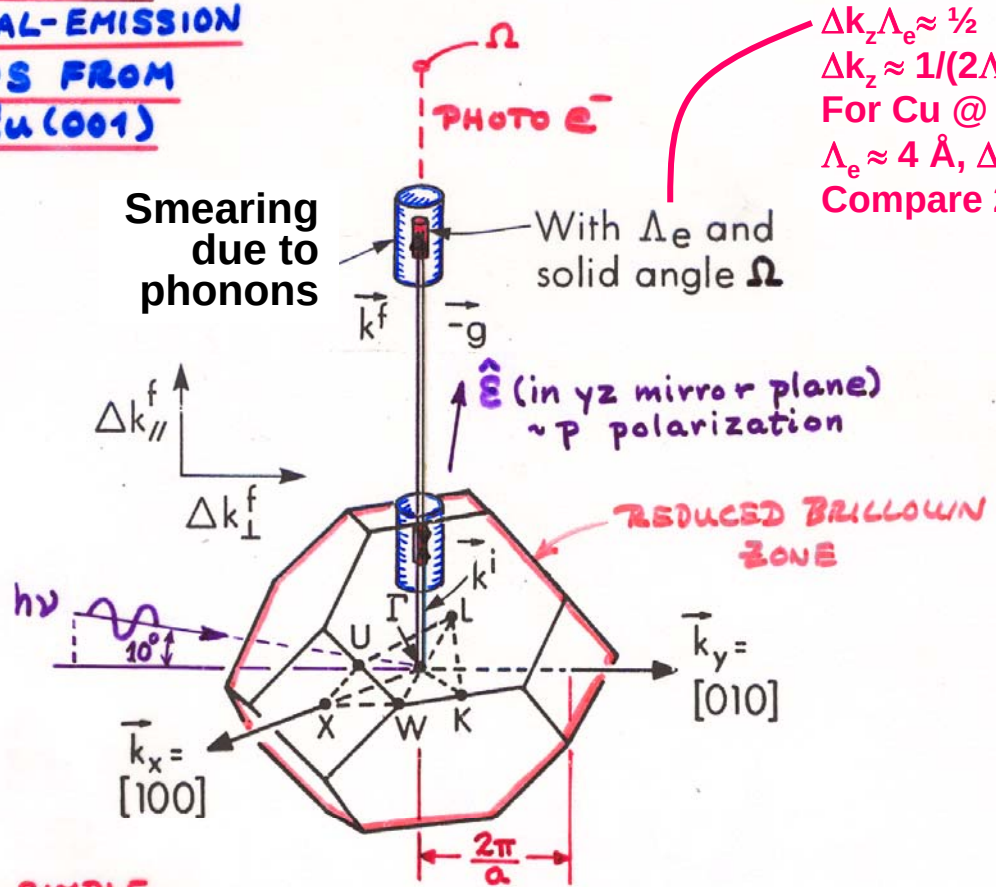
NEGLIGIBLE IF: $h\nu \lesssim 500$ eV

$h\nu$ and/or T low enough

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}

Smearing due to phonons



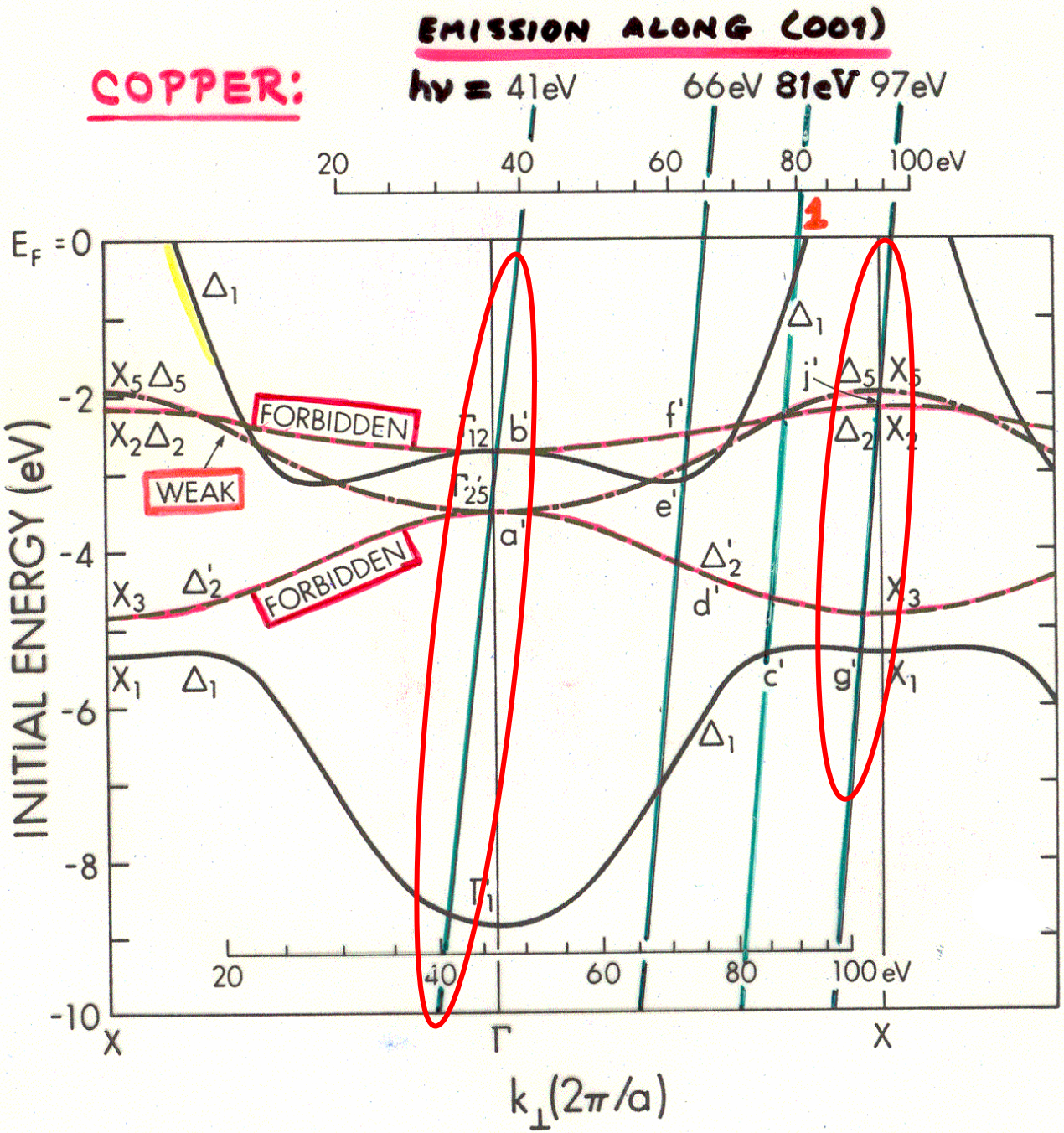
SIMPLE DT MODEL: Direct: $\vec{k}^f = \vec{k}^i + \vec{g} + \cancel{\vec{k}_{h\nu}}$

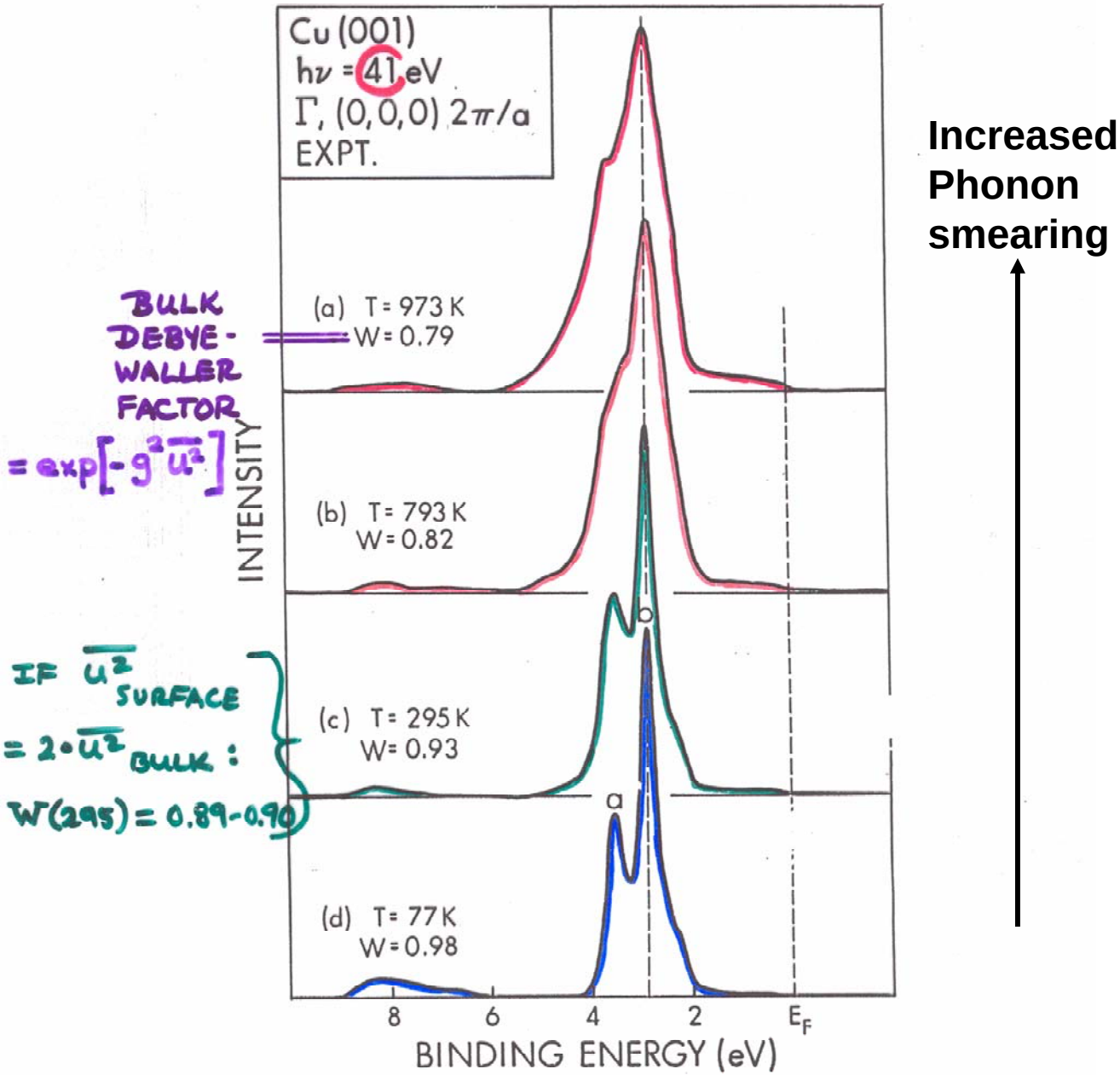
$E^i(\vec{k}^i)$ = initial band structure

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

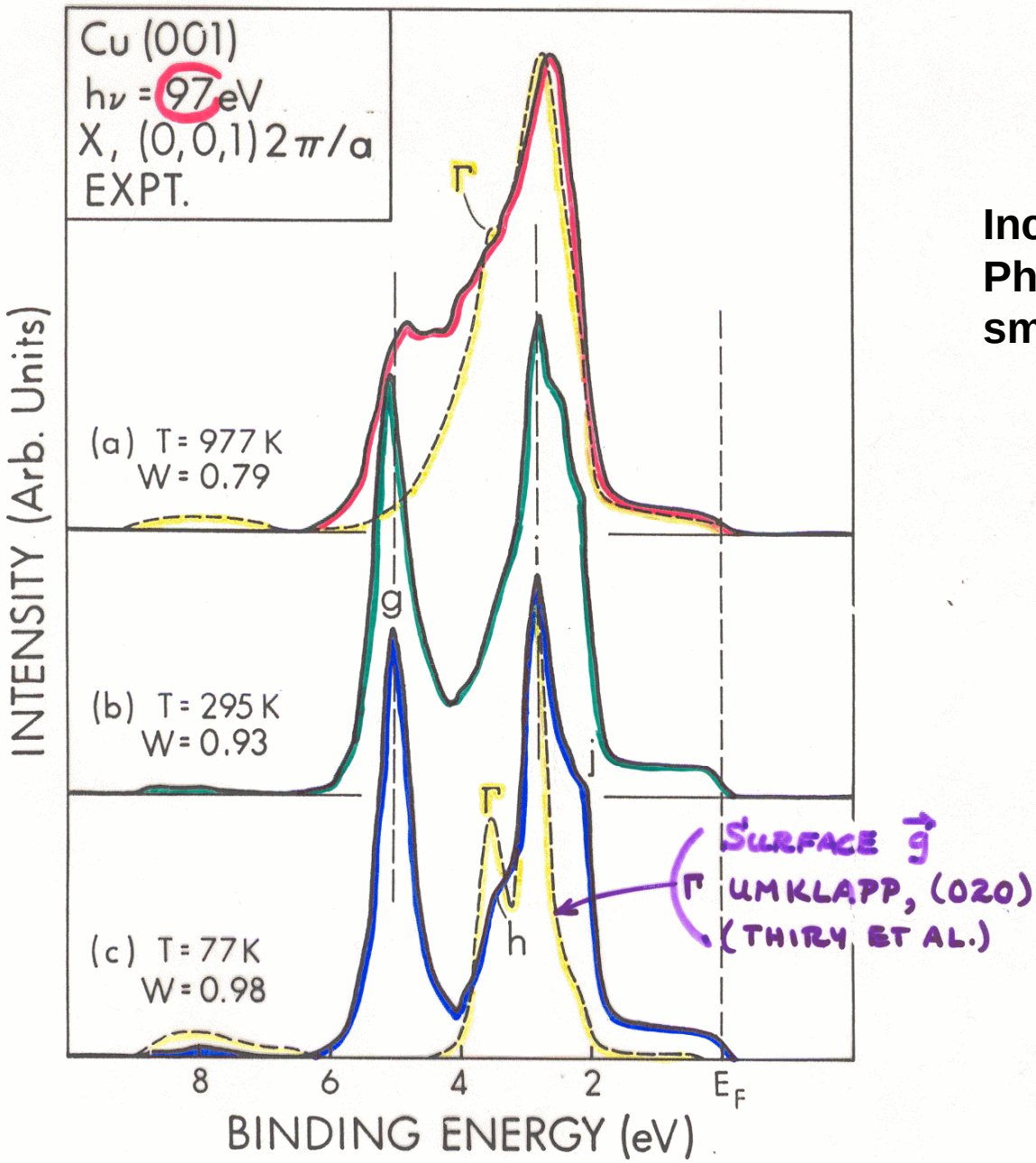
Constant matrix elements

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



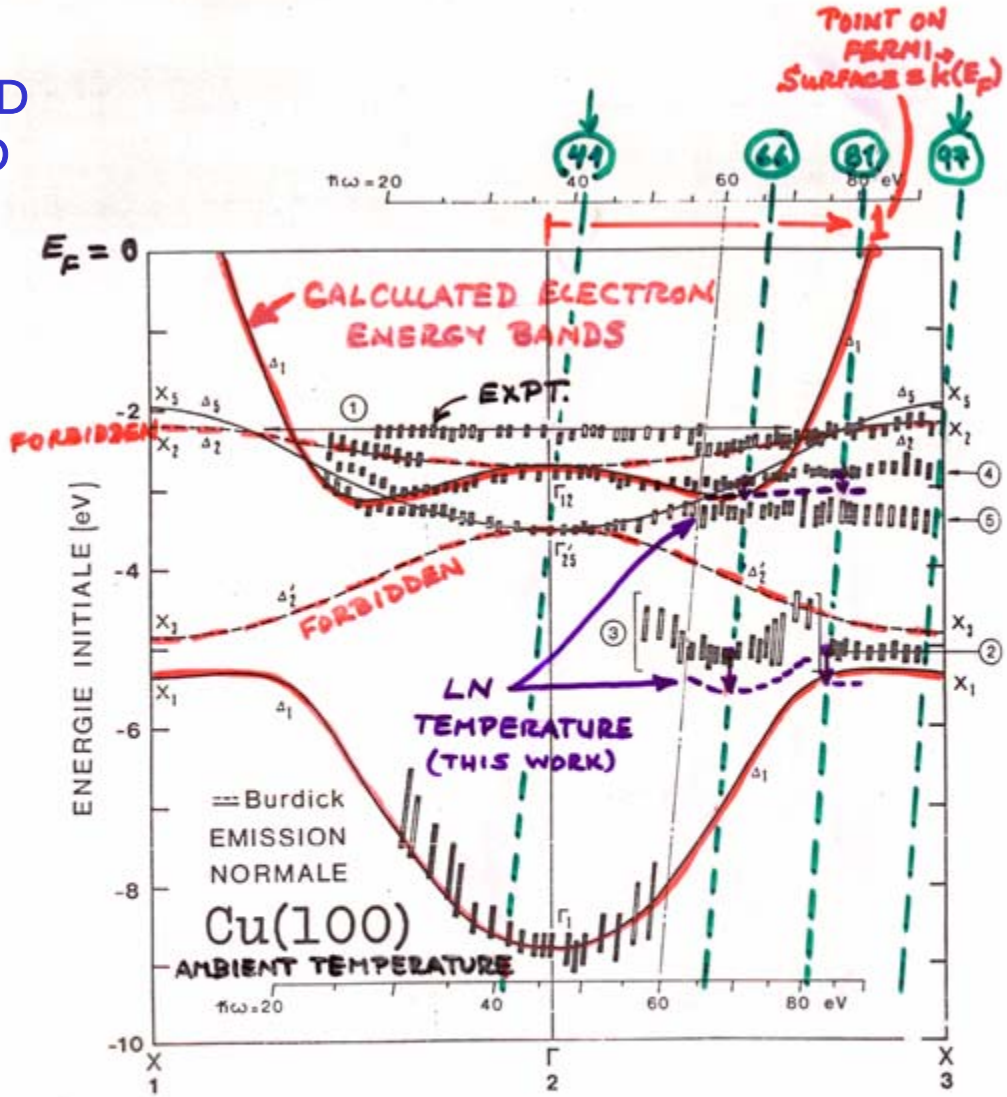


R.C. WHITE ET AL., PHYS. REV. B 35, 1147 (1987)



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)

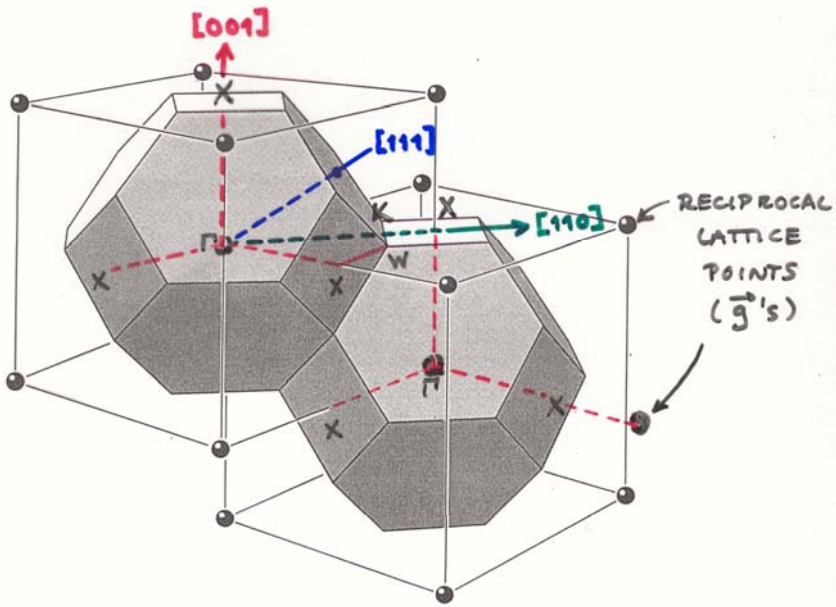
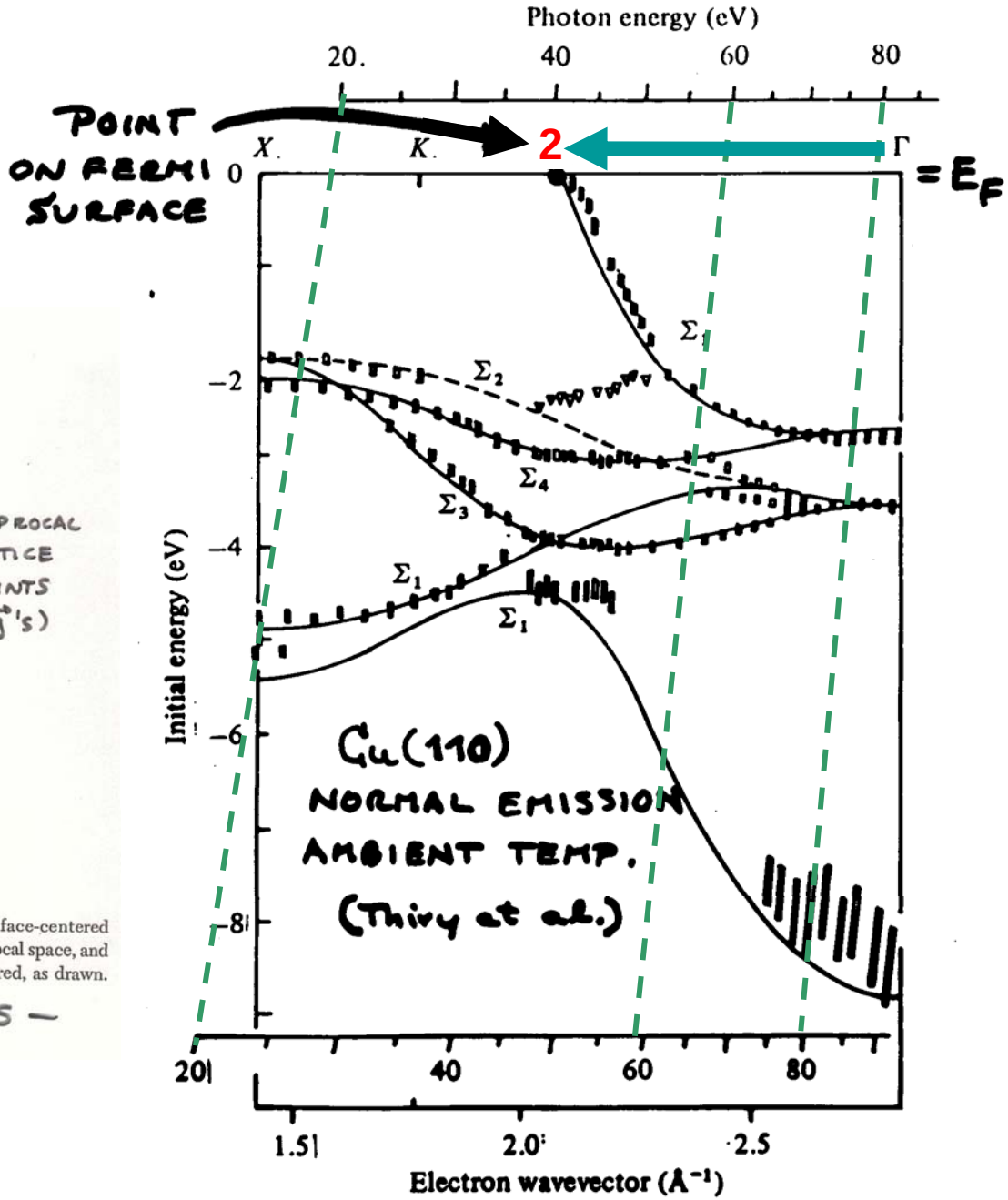
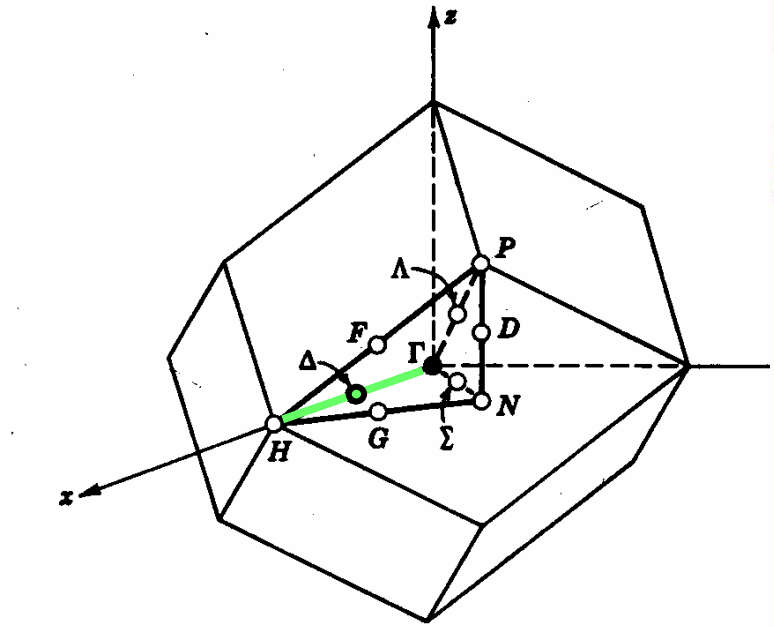


Figure 28 Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body-centered, as drawn.

— STACKING OF fcc BRILLOUIN ZONES —



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



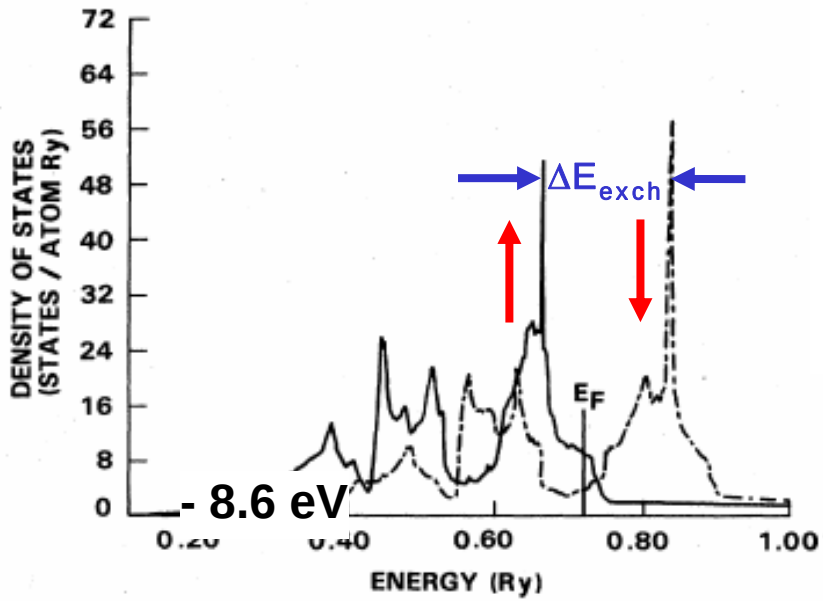
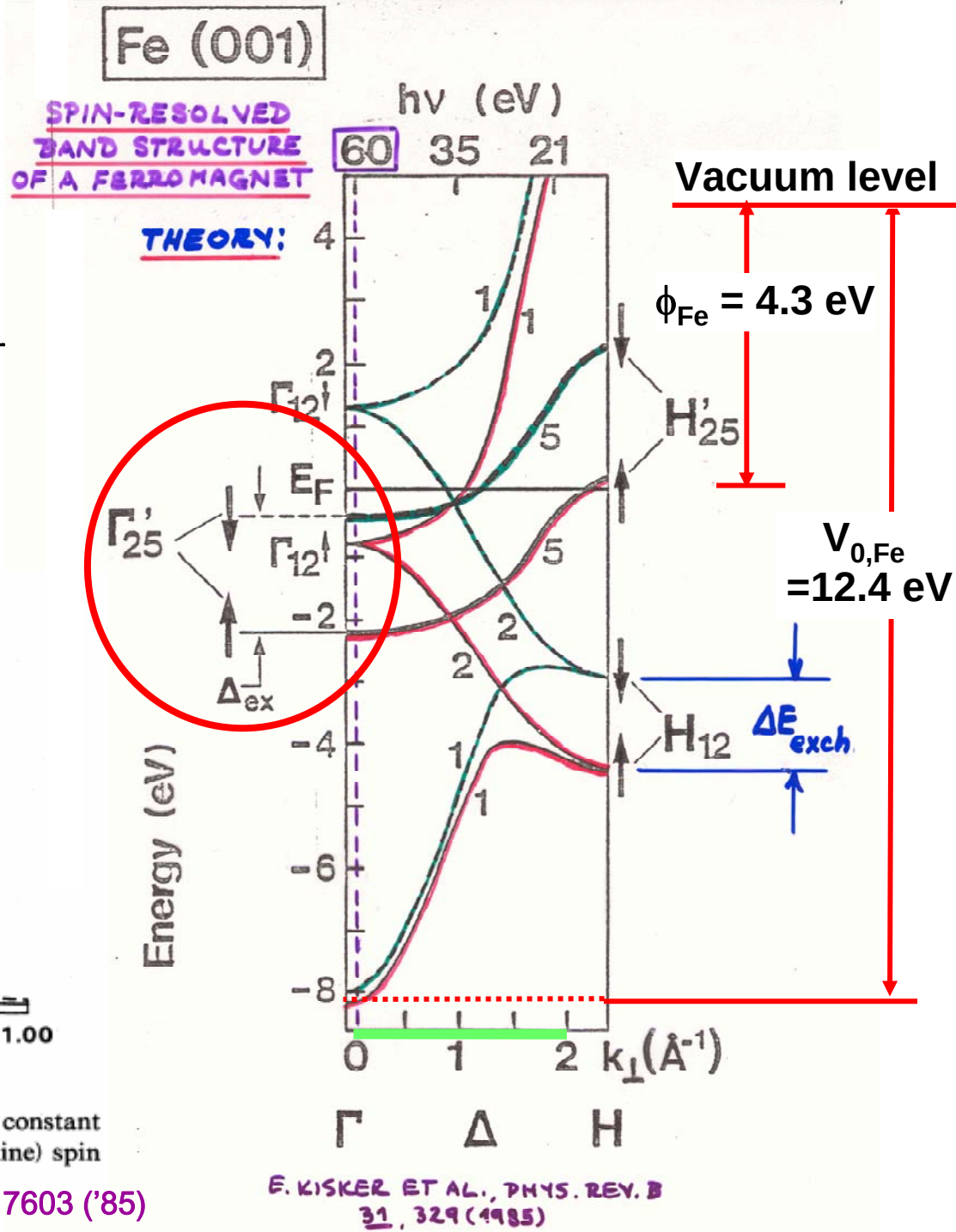
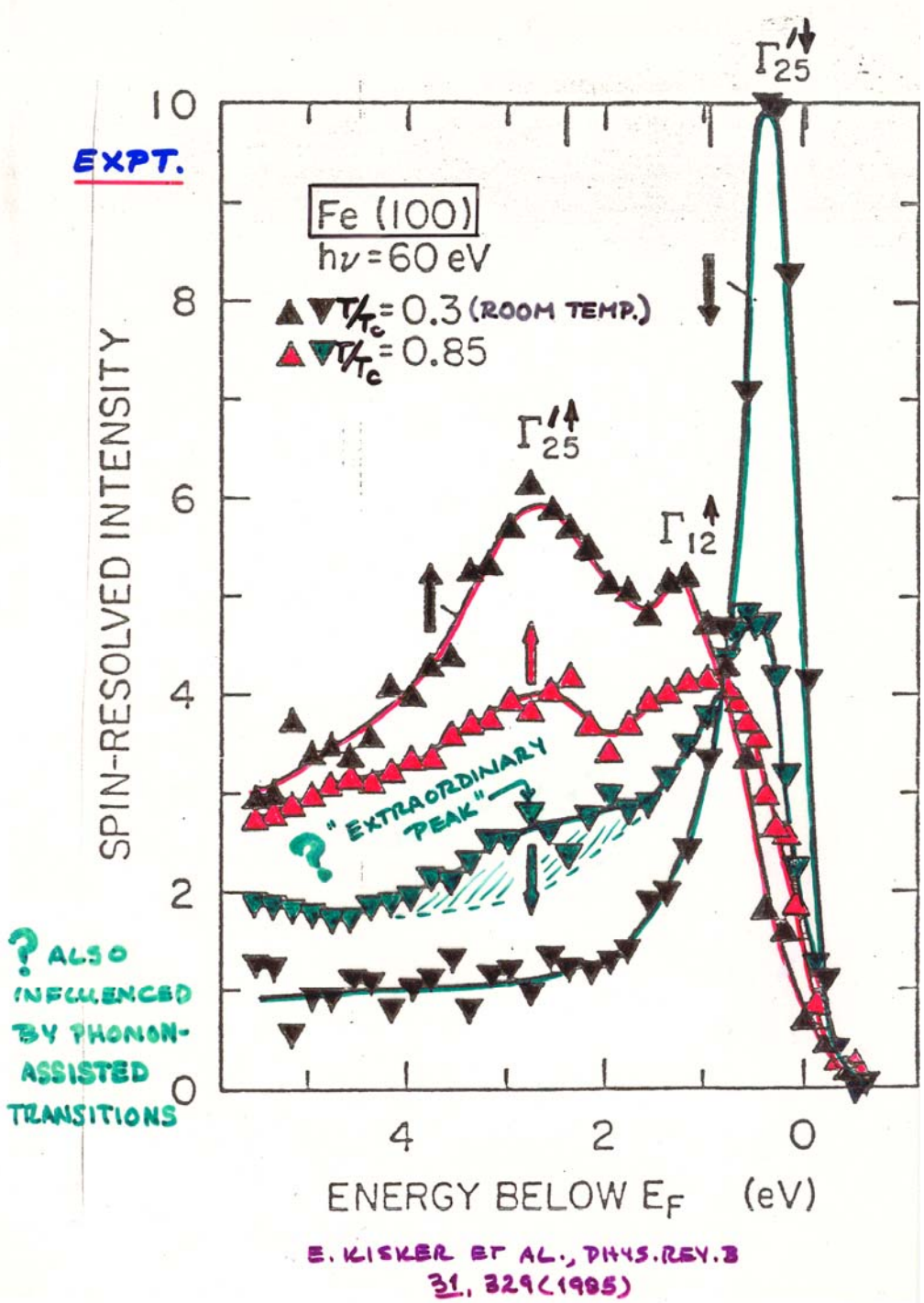


FIG. 4. Density of states at the equilibrium lattice constant of Fe for majority- (solid line) and minority- (broken line) spin states.

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

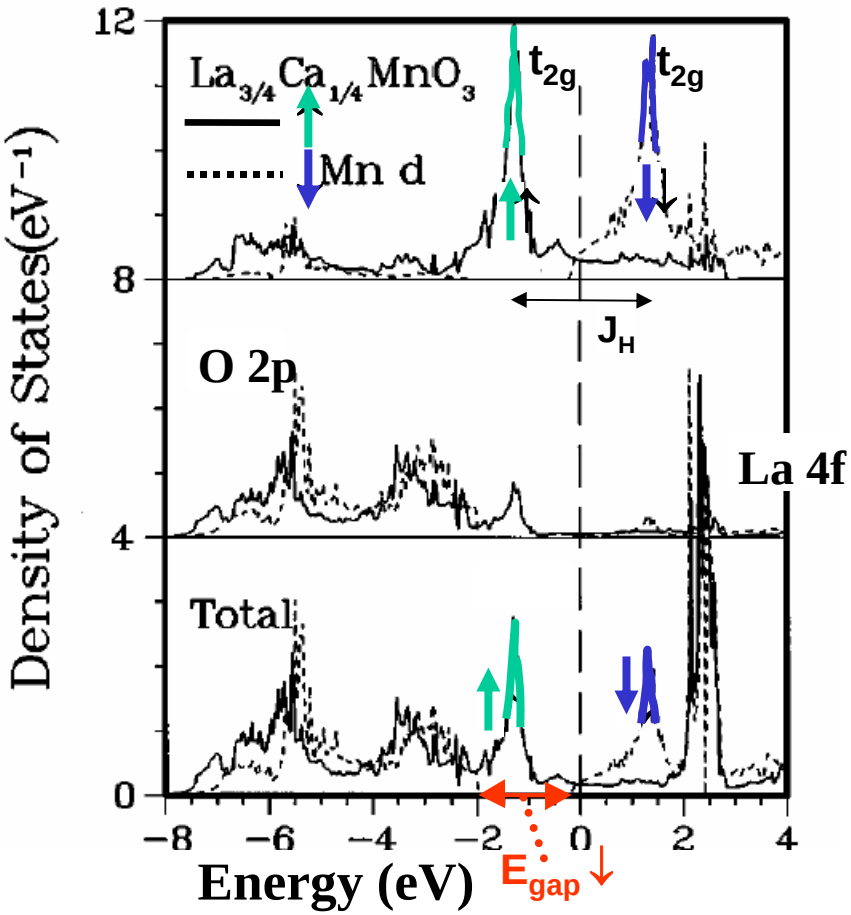


Fe: ANGLE AND SPIN-RESOLVED SPECTRA AT Γ POINT



Half-Metallic Ferromagnetism

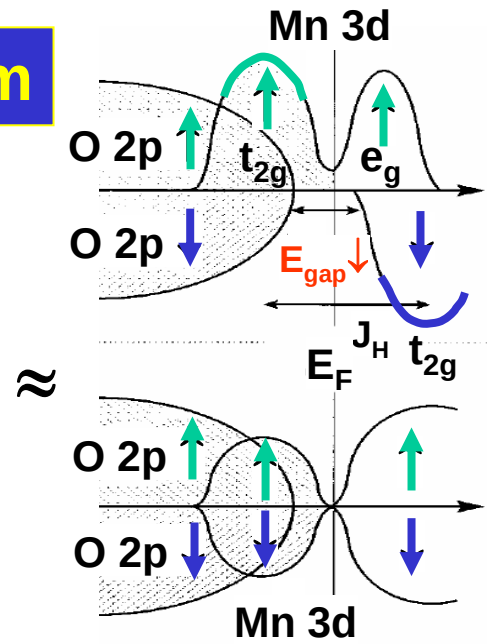
***LDA theory*- FM $La_{0.75}Ca_{0.25}MnO_3$**



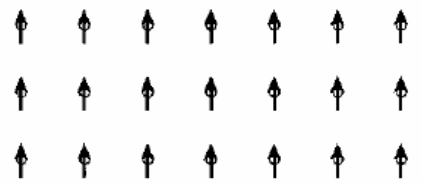
Pickett and Singh, PRB 53, 1146 (1996)

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

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

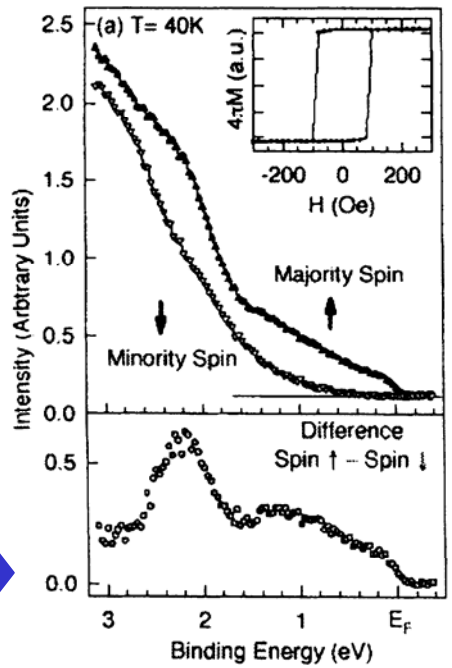


FM : $T \ll T_C$

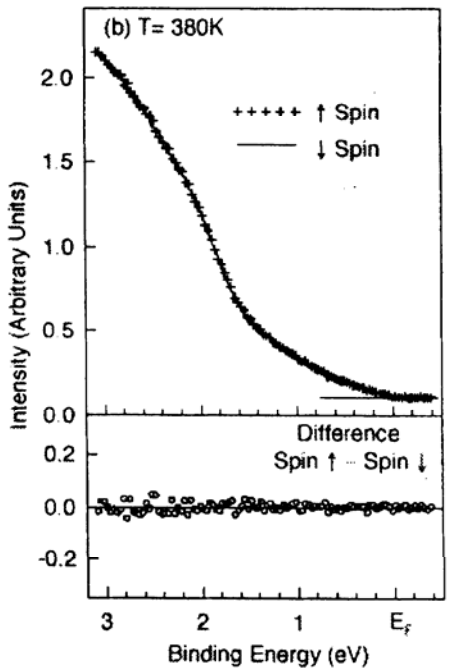


PM : $T > T_C$

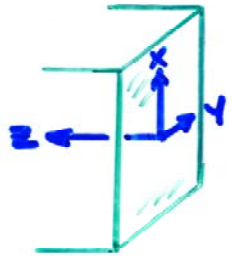
$T \ll T_C$



$T > T_C$



SURFACE ELECTRONIC STATES



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

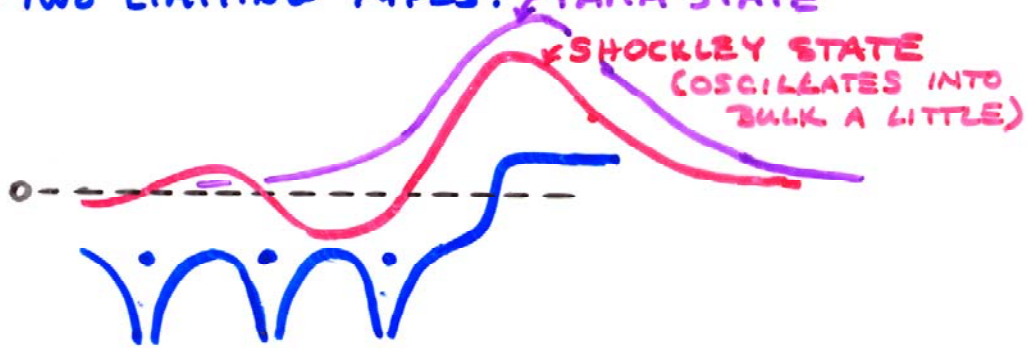
$k_z \Rightarrow \vec{k}_{\perp}$

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

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

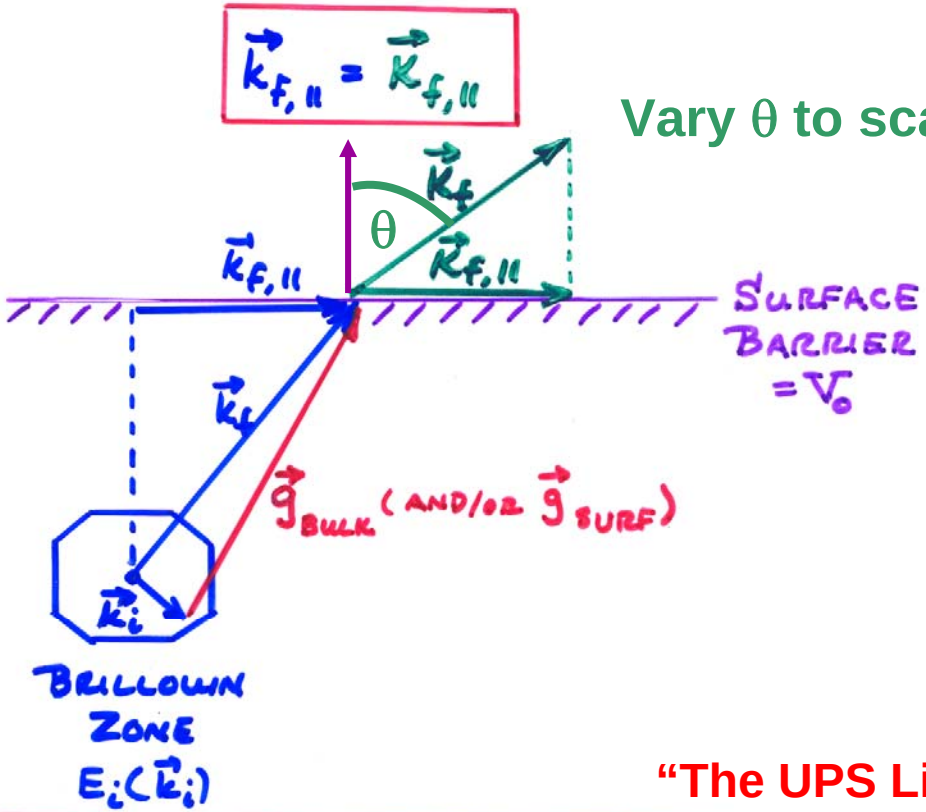
($\kappa_{\perp}$: DECAY CONSTANT)

- TWO LIMITING TYPES:



- 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:



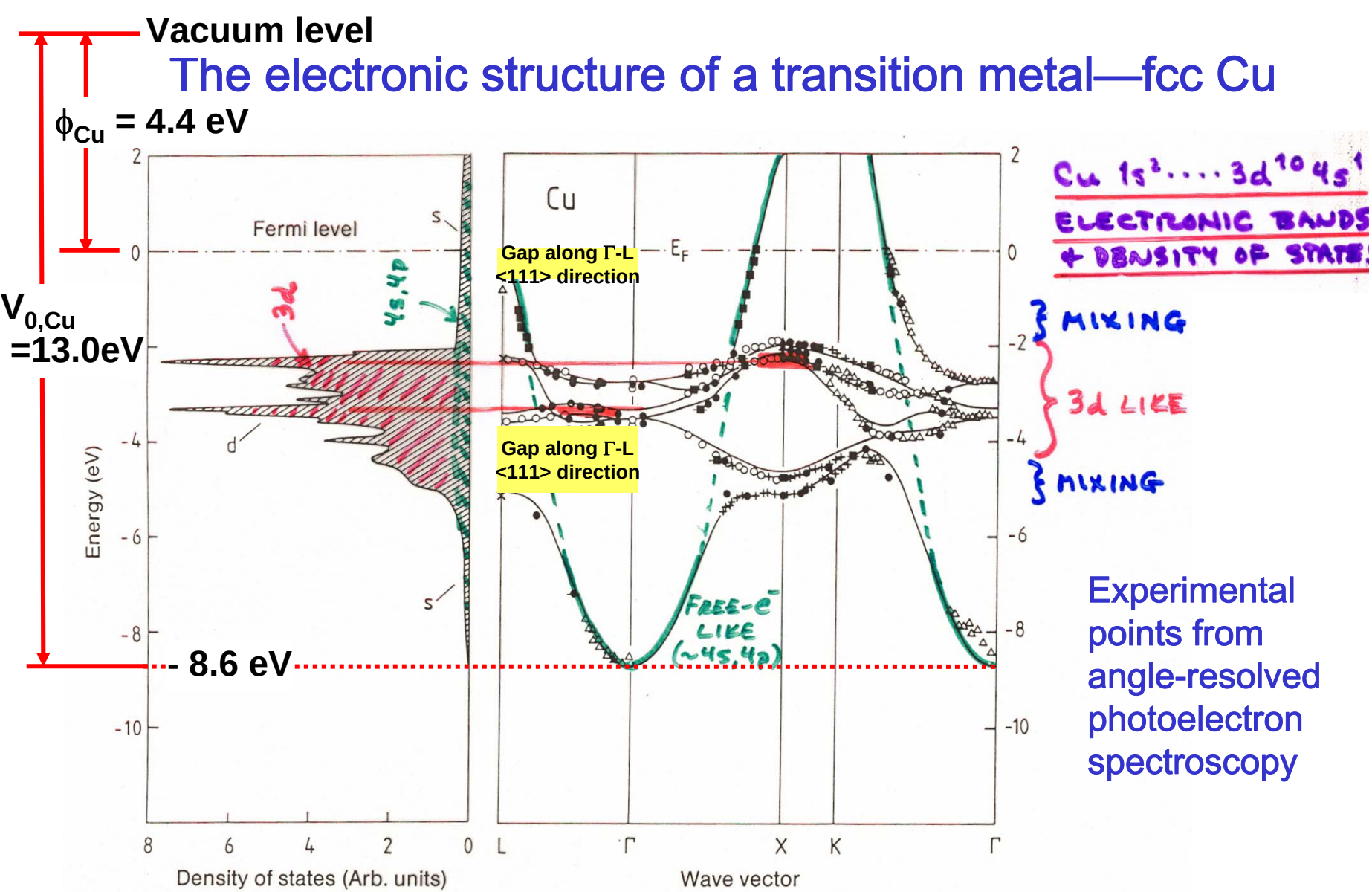
Vary θ to scan $\vec{K}_{f,\parallel} = \vec{k}_{f,\parallel}$

"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

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.

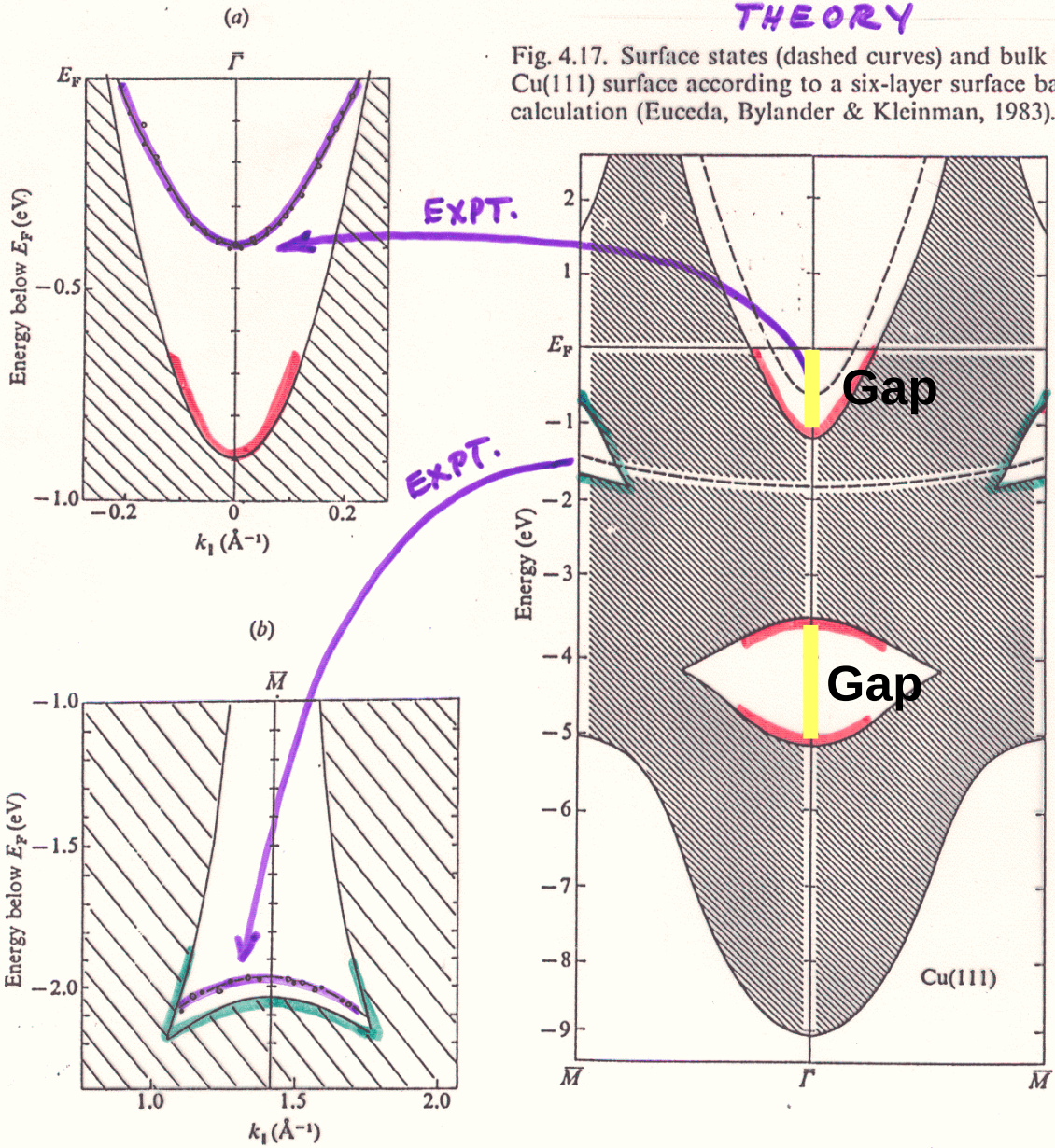
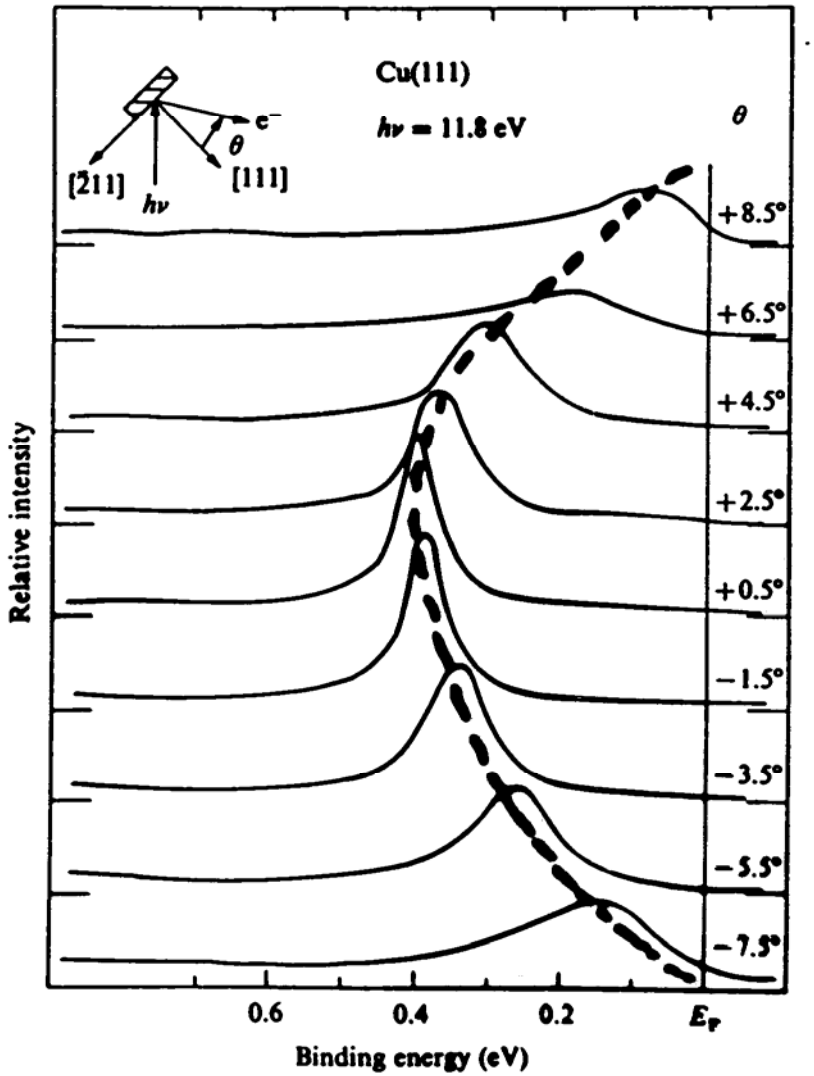


Fig. 4.17. Surface states (dashed curves) and bulk projected ban Cu(111) surface according to a six-layer surface band structure calculation (Euceda, Bylander & Kleinman, 1983).

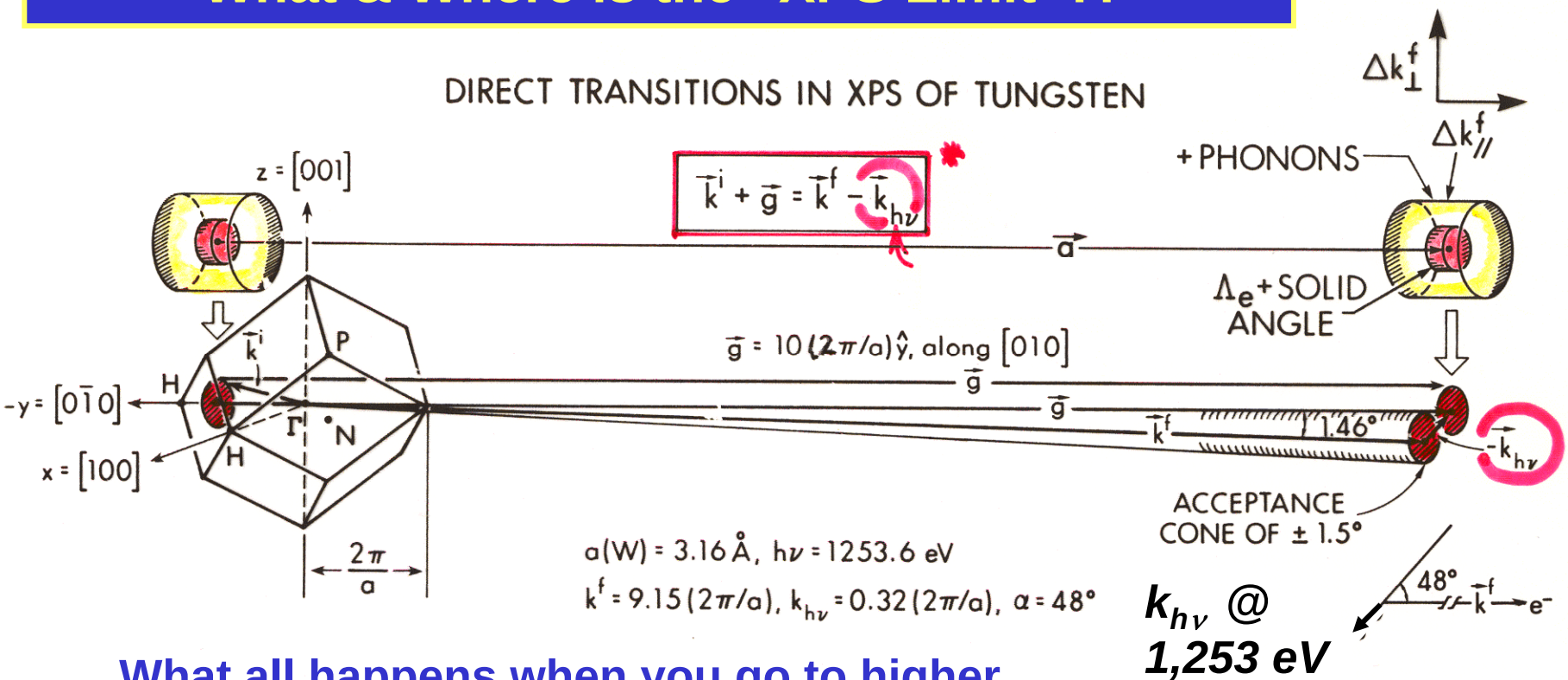
Zangwill, Surface Physics,

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

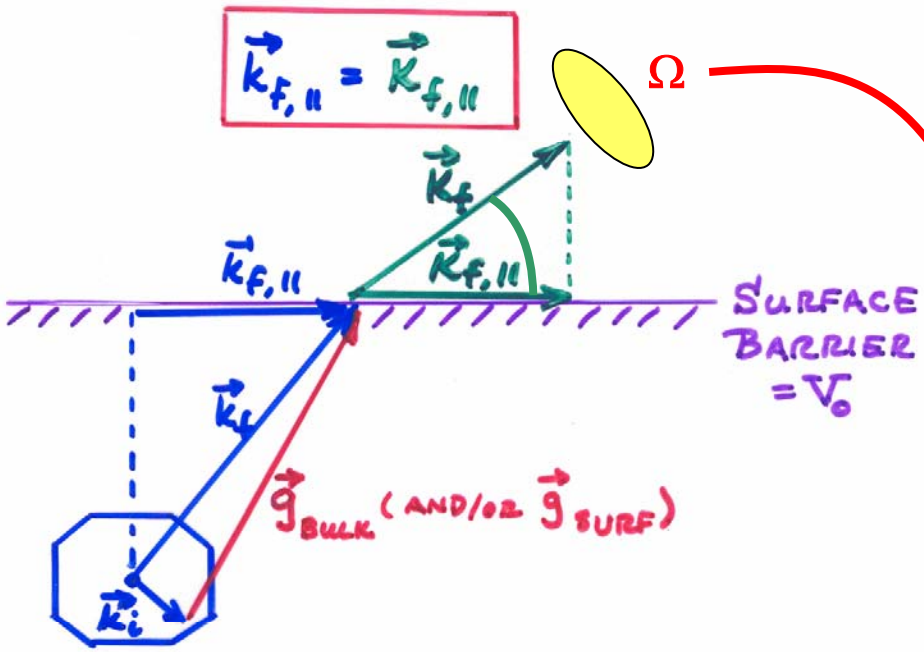
What all happens when you go to higher photon energies?

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

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

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

Conservation Laws in Valence-Band Photoelectron Spectroscopy:



"The XPS Limit"

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

Smears over full BZ→ ~densities of states

Not negligible ← NEGLIGIBLE IF: $h\nu \lesssim 500$ eV; $h\nu$ and/or T low enough

hν = 1487 eV

Estimating phonon effects: 1st approx.

$$W(T) = \text{Debye-Waller factor} = \exp\left(-\frac{1}{3}g^2\left\langle U^2(T)\right\rangle\right)$$

$$I(E,T) = W(T)I_{DT} + [1-W(T)]I_{NDT}$$

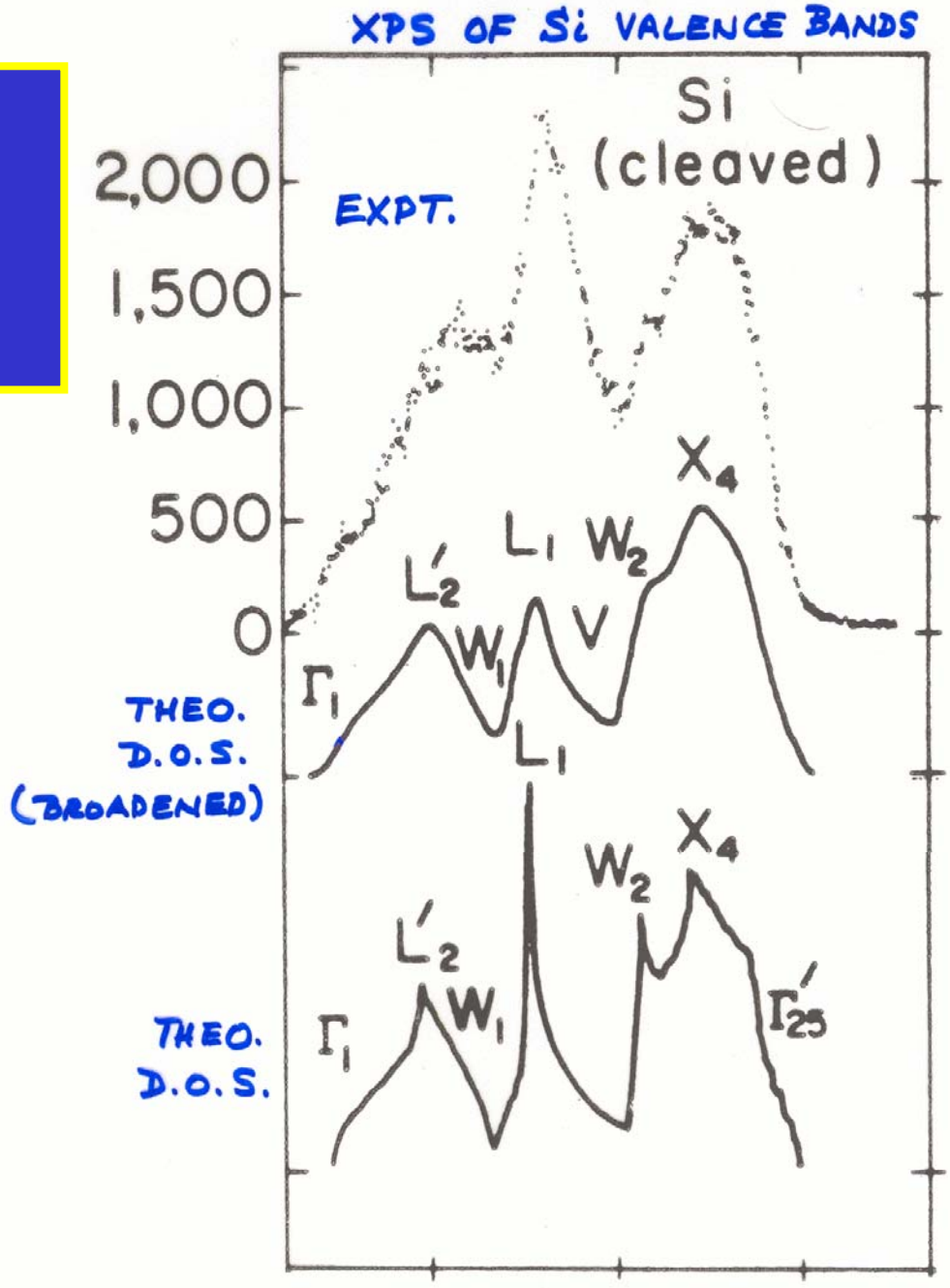
TABLE I. Tabulation of thermal displacements ($\langle U^2\rangle$) and Debye–Waller factors [$W(T)=\exp(-\frac{1}{3}\langle U^2\rangle g^2)$] in the XPS regime ($E_{kin}=1482$ eV) for various elements. The Debye temperatures are taken from Ref. 30. The solid line divides the Debye–Waller factors so as to indicate when $\geq\frac{1}{2}$ of the transitions will be direct. Elements are in order of Z.

Element	Θ_D (K)	A (amu)	$T=4$ K $\langle U^2\rangle$ (10^{-18} cm^2)	W	$T=77$ K $\langle U^2\rangle$ (10^{-18} cm^2)	W	$T=300$ K $\langle U^2\rangle$ (10^{-18} cm^2)	W	$T=1000$ K $\langle U^2\rangle$ (10^{-18} cm^2)	W
Be	1440	9.012	0.84	0.34	0.86	0.33	1.07	0.25	2.47	0.04
C	2230	12.001	0.41	0.59	0.41	0.59	0.46	0.35	0.83	0.34
Mg	400	24.312	1.12	0.23	1.40	0.16	3.53	0.01		
Al	428	26.981	0.95	0.29	1.15	0.22	2.79	0.03		
Si	645	28.086	0.60	0.46	0.66	0.42	1.26	0.19	3.07	0.02
Ca	230	40.08	1.19	0.21	1.94	0.08	6.24	0.0		
Ti	420	47.9	0.54	0.49	0.66	0.42	1.63	0.12	5.16	0.0
V	380	50.942	0.56	0.48	0.72	0.39	1.85	0.09	5.93	0.0
Cr	630	51.996	0.33	0.65	0.37	0.62	0.71	0.40	2.15	0.06
Mn	410	54.938	0.48	0.53	0.60	0.46	1.49	0.14	4.72	0.0
Fe	470	55.847	0.42	0.58	0.49	0.53	1.13	0.23	3.58	0.01
Co	445	58.933	0.42	0.58	0.50	0.52	1.19	0.21	3.74	0.0
Ni	450	58.71	0.41	0.58	0.49	0.53	1.17	0.22	3.67	0.01
Cu	343	63.54	0.50	0.52	0.67	0.42	1.82	0.09	5.84	0.0
Zn	327	65.37	0.51	0.51	0.70	0.40	1.92	0.08		
Ge	374	72.59	0.40	0.58	0.51	0.51	1.34	0.17	4.28	0.0
As	282	74.922	0.52	0.51	0.77	0.37	2.25	0.05	7.33	0.0
Zr	291	91.22	0.41	0.58	0.60	0.46	1.74	0.10	5.65	0.0
Nb	275	92.906	0.43	0.57	0.65	0.43	1.90	0.08	6.21	0.0
Mo	450	95.94	0.25	0.72	0.30	0.68	0.71	0.39	2.25	0.05
Ru	600	101.07	0.18	0.78	0.20	0.77	0.40	0.60	1.21	0.21
Rh	480	102.905	0.22	0.75	0.26	0.71	0.59	0.46	1.84	0.09
Pd	274	106.4	0.37	0.61	0.57	0.48	1.68	0.11	5.46	0.0
Ag	225	107.87	0.45	0.56	0.75	0.38	2.44	0.04	8.00	0.0
Cd	209	112.40	0.47	0.55	0.81	0.35	2.70	0.03		
Sn	200	118.69	0.46	0.55	0.83	0.34	2.55	0.04		
Sb	211	121.75	0.43	0.57	0.79	0.35	2.46	0.04		
Hf	252	178.49	0.24	0.73	0.30	0.60	1.18	0.22	3.85	0.01
Ta	240	180.948	0.25	0.72	0.43	0.58	1.28	0.19	4.19	0.0
W	400	183.85	0.15	0.82	0.18	0.79	0.47	0.55	1.48	0.14
Re	430	186.2	0.16	0.84	0.17	0.81	0.40	0.58	1.23	0.19
Os	500	190.2	0.11	0.86	0.13	0.84	0.30	0.68	0.92	0.30
Ir	420	192.2	0.14	0.84	0.17	0.81	0.41	0.59	1.29	0.19
Pt	240	195.09	0.23	0.74	0.39	0.60	1.19	0.21	3.88	0.01
Au	165	196.967	0.24	0.65	0.82	0.35	2.46	0.04	8.14	0.0
Pb	105	207.19	0.51	0.52	1.54	0.13	5.75	0.0		

Greater than 50% direct transitions

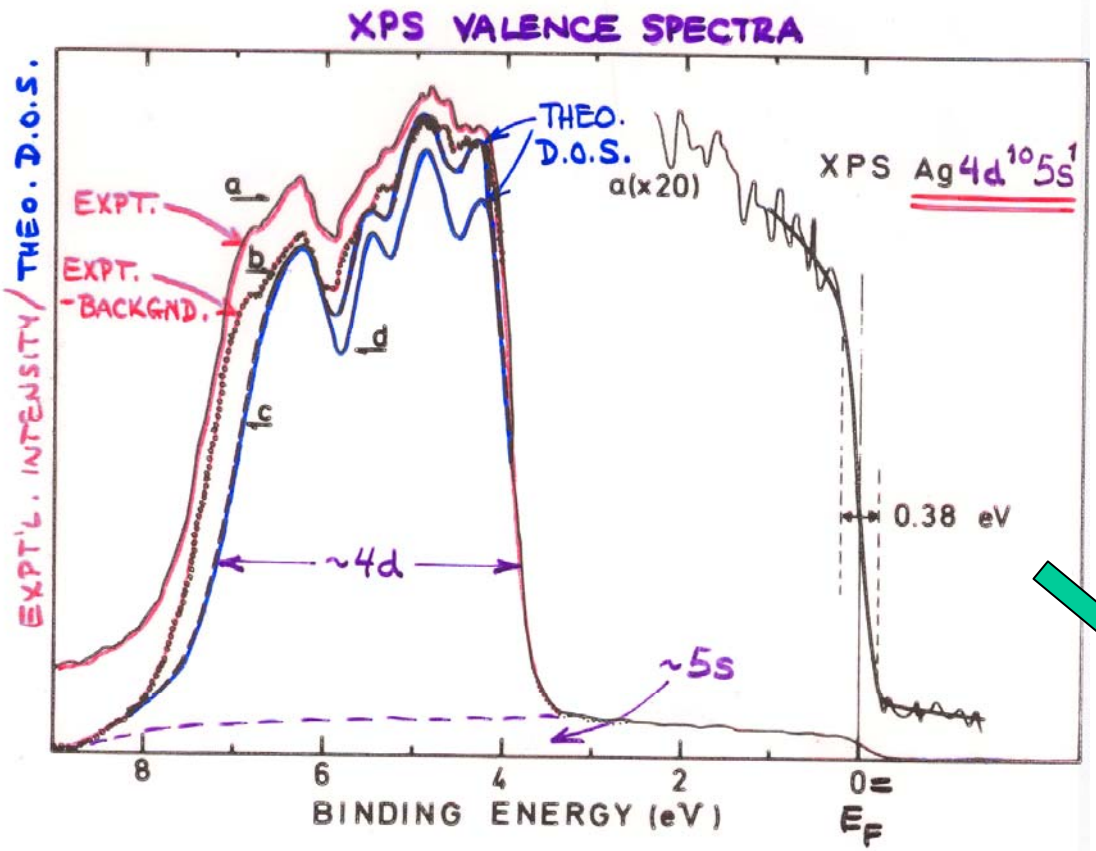
Shevchik, Phys. Rev. B 20, 3020 ('79); Hussain et al., Phys. Rev. 22, 3750 ('80)

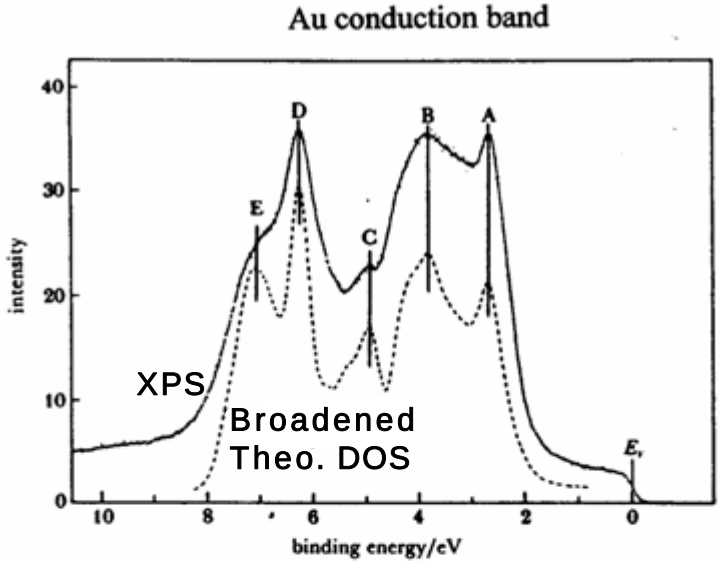
Some classic cases in the XPS limit:

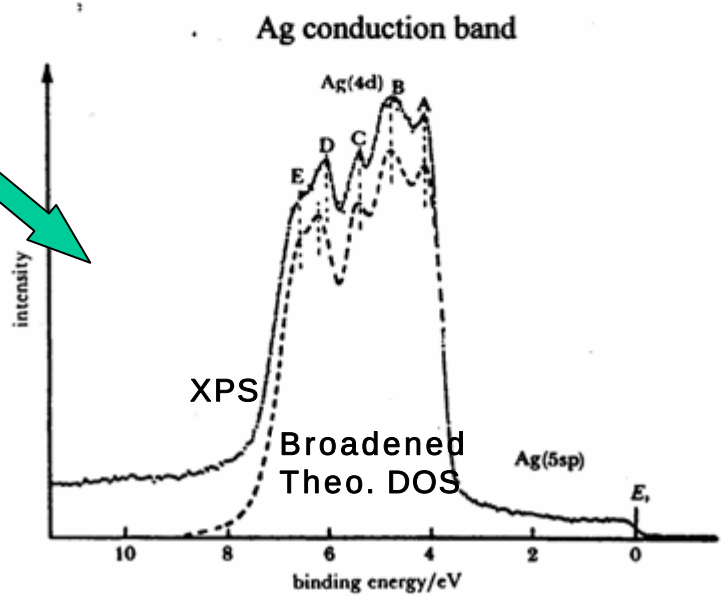


"Basic Concepts of XPS"
Figure 14

Densities of states From XPS spectra



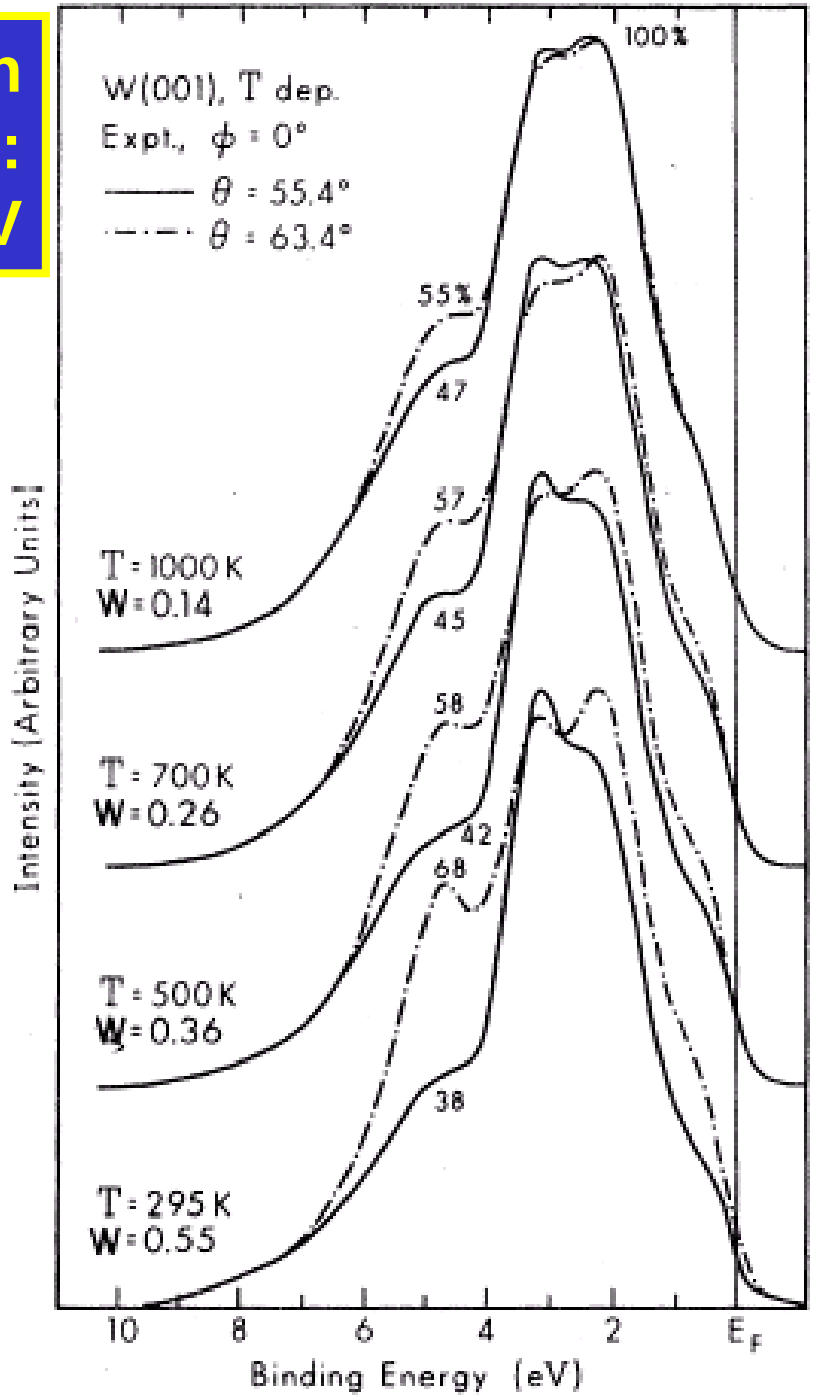




"Basic Concepts of XPS"
Figure 13

Siegbahn, 2003

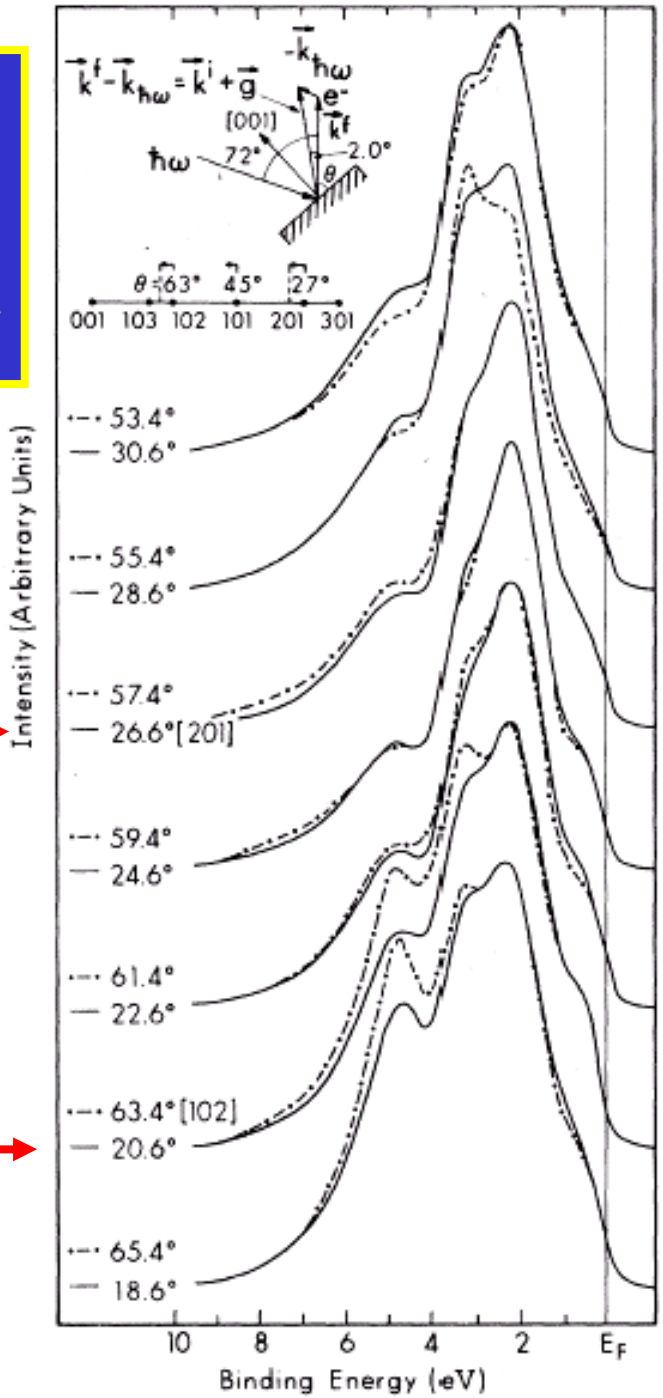
Direct-transition effects in XPS: W(110) at 1253.6 eV



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 $k_{h\nu}$

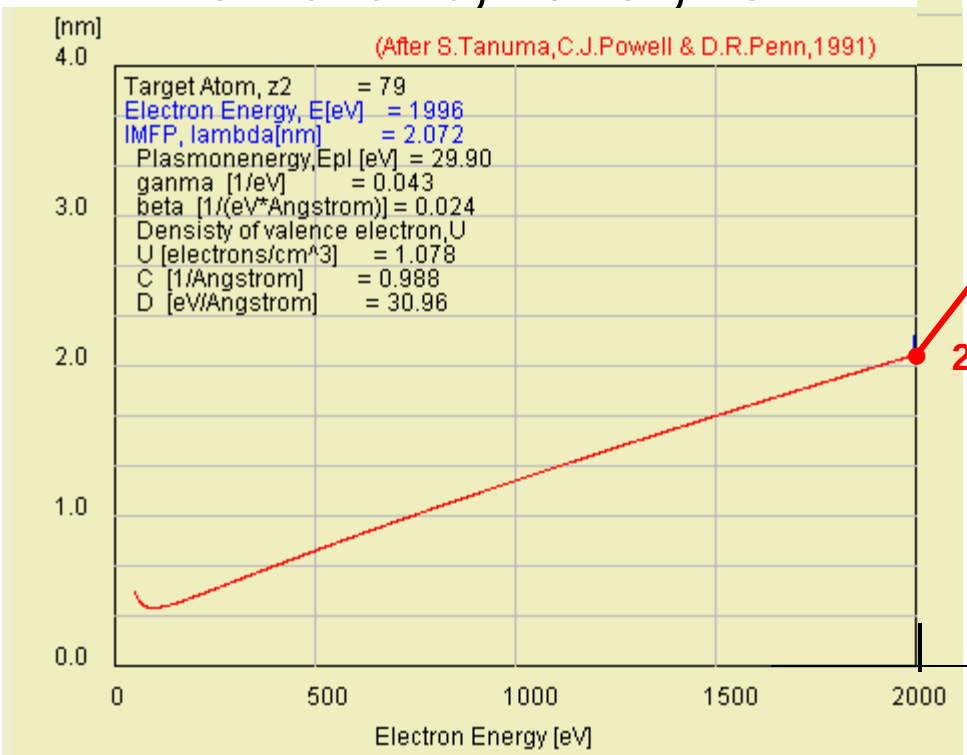
Hussain et al., Phys. Rev. 22, 3750 (1980)

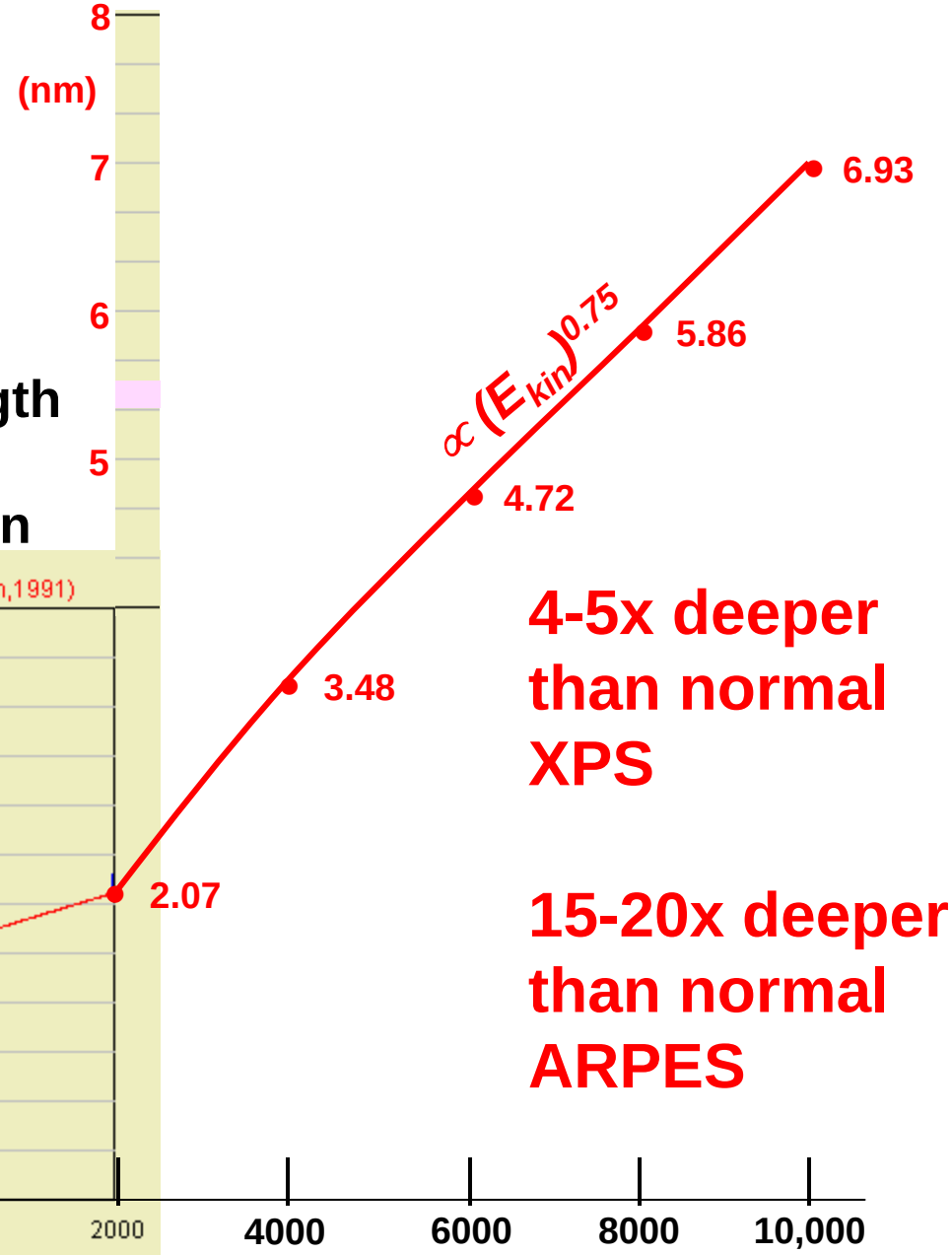
Outline

- Valence-band spectra: low-energy UPS limit and high-energy XPS limit: Taking the excitation energy up to 5-15 keV
- Core-level chemical shifts: the potential model
- Core-level chemical shifts: equivalent-core (Z+1) and thermochemical energies
- Multiplet splittings
- Spin-orbit splitting, the Fano effect, and spin-polarized outgoing electrons
- Magnetic circular dichroism (MCD) in core-level emission
- Non-magnetic circular dichroism in core-level emission: a.k.a. circular dichroism in angular distributions (CDAD)
- Various other final state effects providing information in core-level spectra

How much deeper do we probe at 10 keV?

Au
Inelastic attenuation length
TPP-2M formula
of Tanuma, Powell, Penn

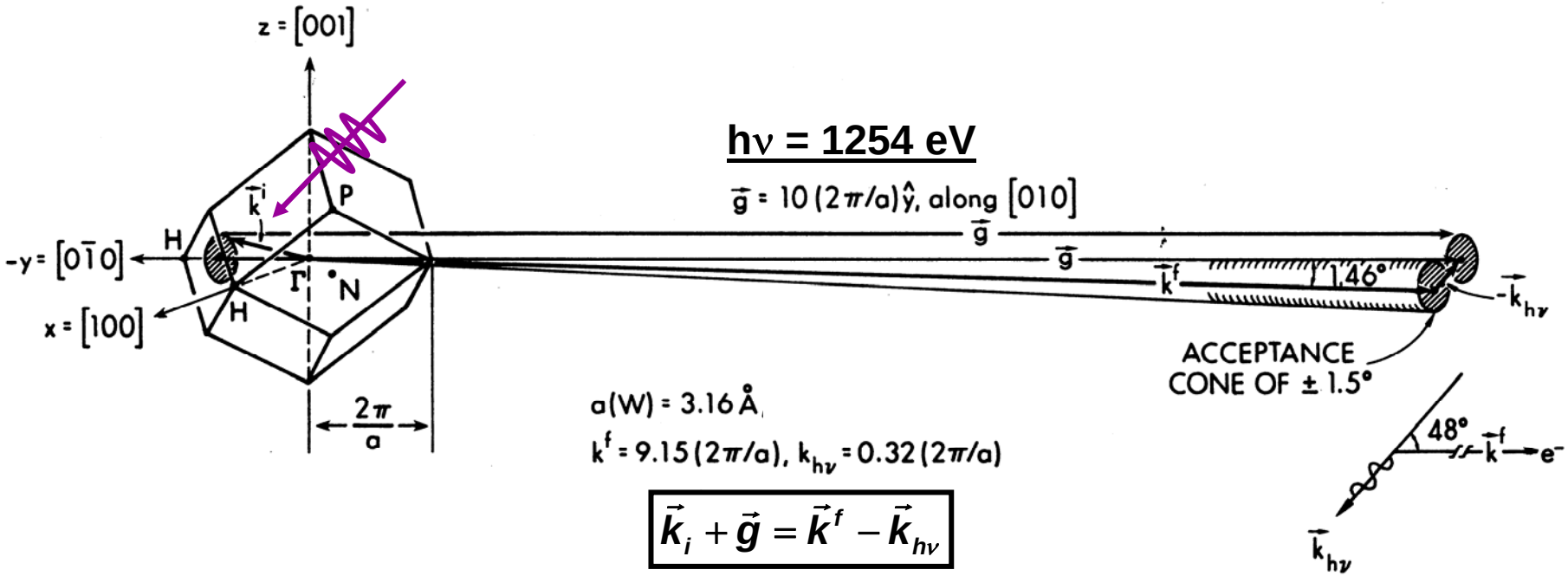


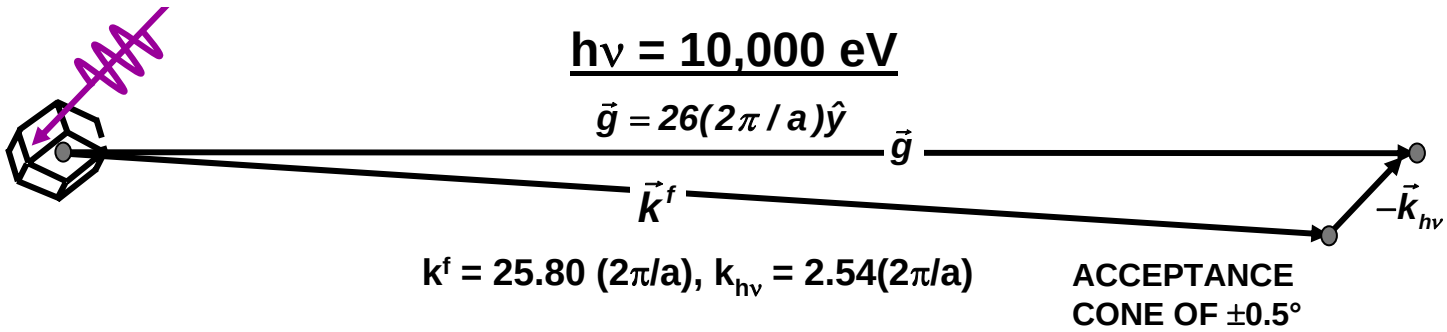


4-5x deeper than normal XPS

15-20x deeper than normal ARPES

http://www.ss.teen.setsunan.ac.jp/e-imfp.html

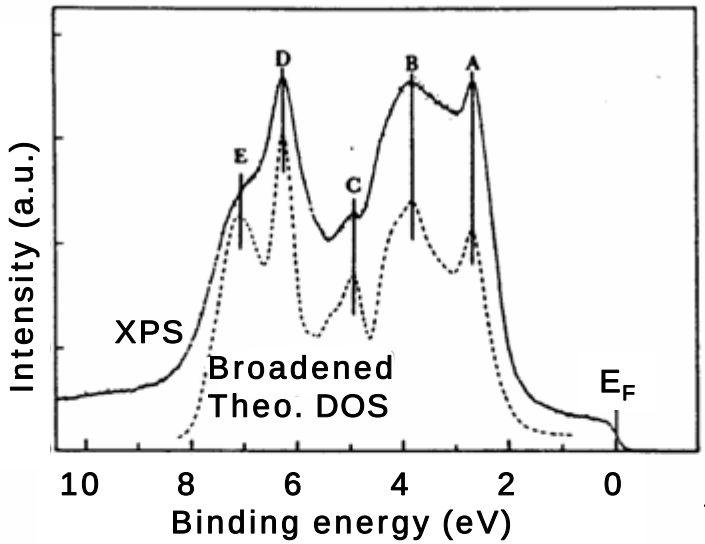




But angular resolutions of 0.01° with an acceptance ±2° may be possible!

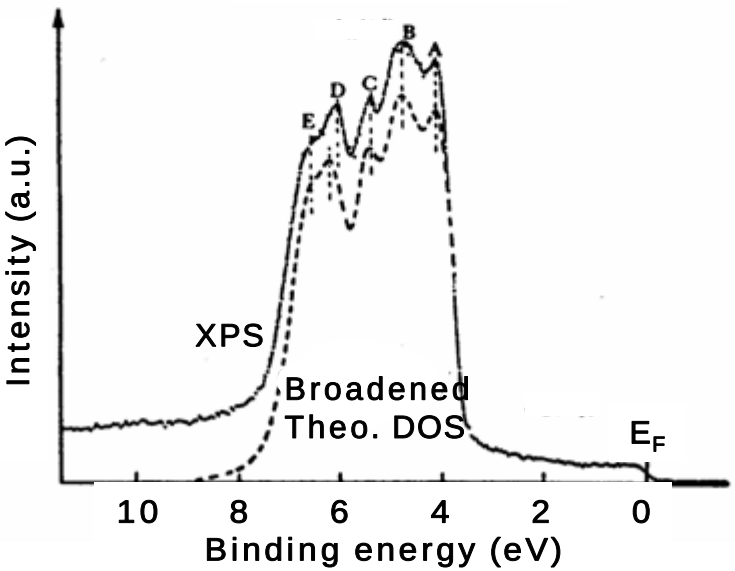
B. Wannberg

Gold Valence Spectrum



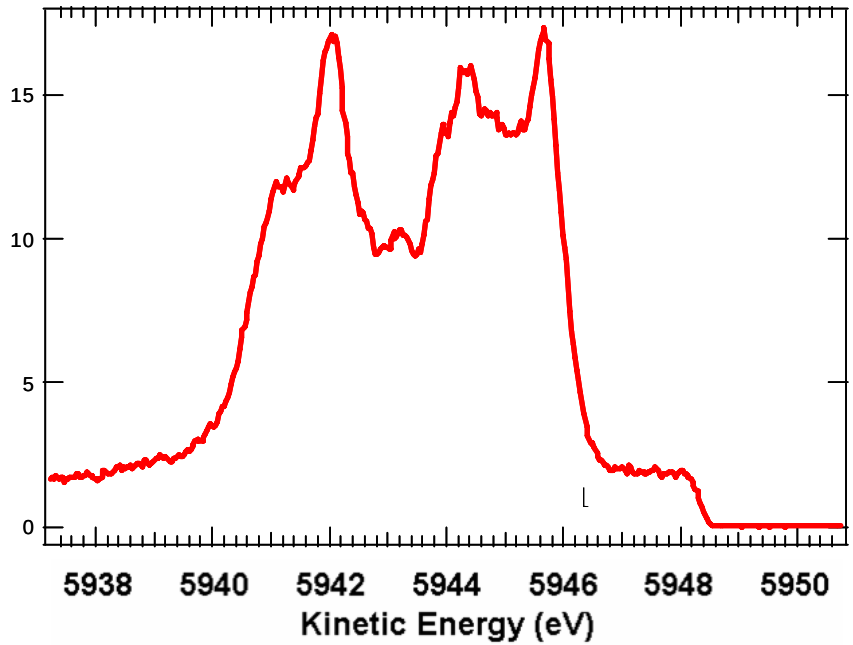
Siegbahn XPS @ 1.487 keV

Silver Valence Spectrum



In the XPS Limit

Gold Valence Spectrum



Measurement time: 3 min 40 s
Total resolution: ca. 80 meV

Takata et al., Spring8 @ 5.495 keV

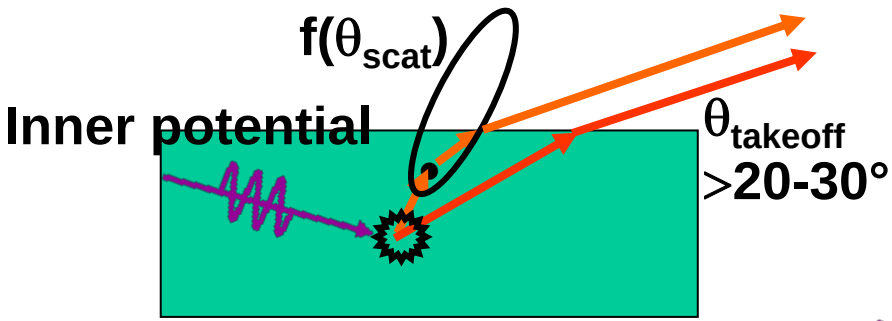
Varying surface sensitivity for lower electron takeoff angles

Simplest interpretation:

Average emission depth = $\Lambda_{inelastic} \sin\theta_{takeoff}$

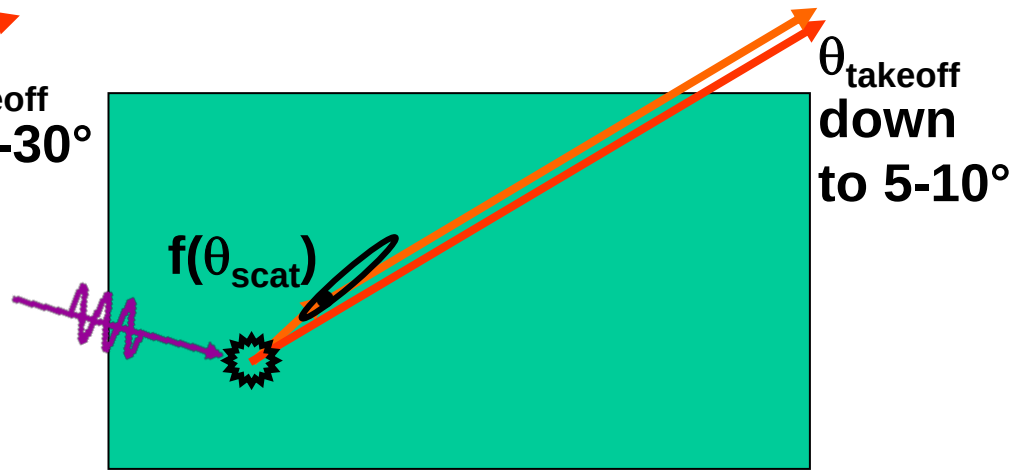
How valid?

$E_{kin} \approx$ 500-1000 eV



E.g.: A. Jablonski and C. J. Powell, J. Vac. Sci. Tech. A 21, 274 (2003):
→ Mean Emission Depth (MED) more relevant than $\Lambda_{inelastic}$

$E_{kin} \approx$ 10,000 eV



Simpler analysis

Cleaner bulk & surface distinction

C. J. Powell, W. Werner et al., priv. comm.;
C.S.F., Nucl. Inst. & Meth. A 547, 24 (2005)

Outline

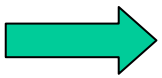
Surface, interface, and nanoscience—short introduction

Some surface concepts and techniques→photoemission

Synchrotron radiation: experimental aspects

Electronic structure—a brief review

The basic synchrotron radiation techniques:
more experimental and theoretical details



Core-level photoemission

Valence-level photoemission

Microscopy with photoemission

Outline

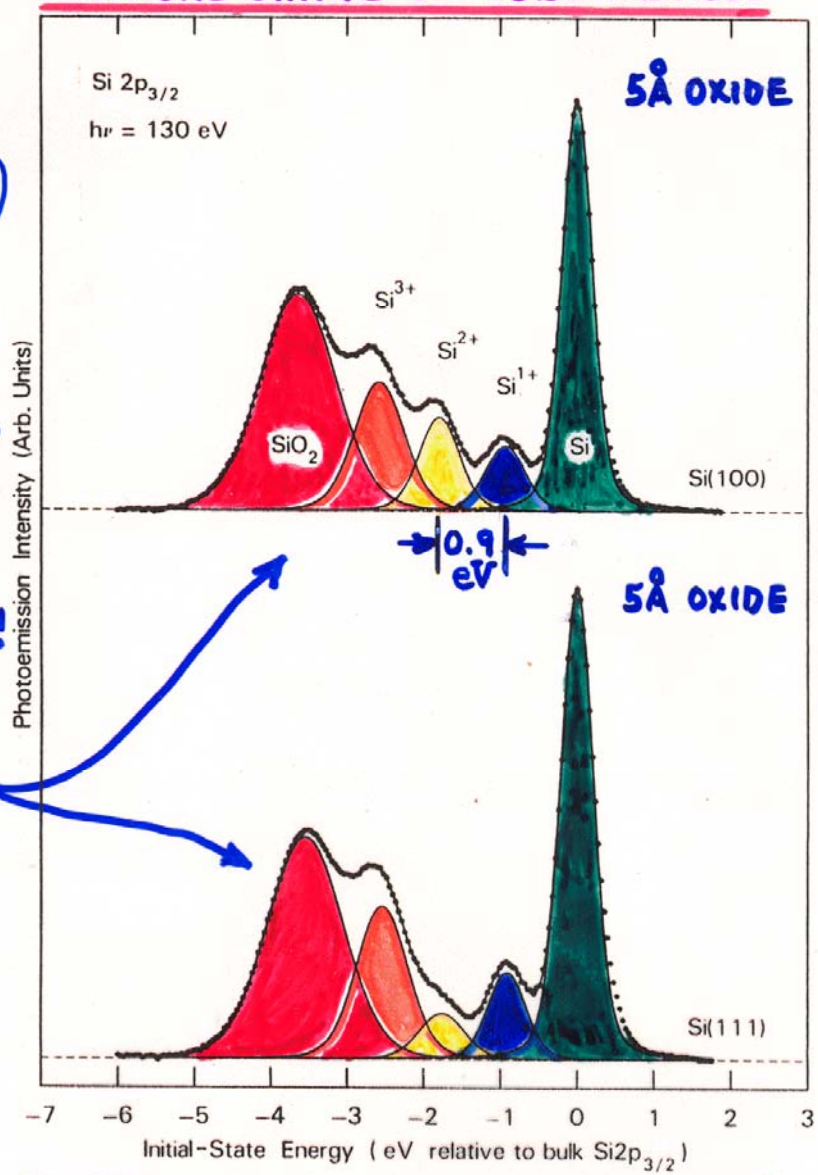
- Valence-band spectra: low-energy UPS limit and high-energy XPS limit
- Core-level chemical shifts: the potential model
- Core-level chemical shifts: equivalent-core (Z+1) and thermochemical energies
- Multiplet splittings
- Spin-orbit splitting, the Fano effect, and spin-polarized outgoing electrons
- Magnetic circular dichroism (MCD) in core-level emission
- Non-magnetic circular dichroism in core-level emission: a.k.a. circular dichroism in angular distributions (CDAD)
- Various other final state effects providing information in core-level spectra

PHOTOELECTRON SPECTRA

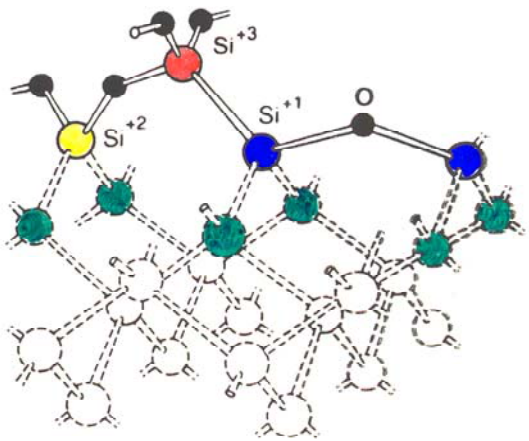
OXIDIZED SILICON

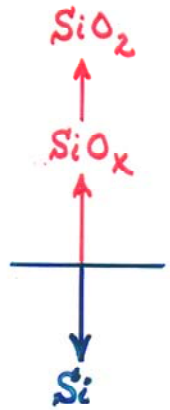
CHEMICAL SHIFTS OF CORE LEVELS

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

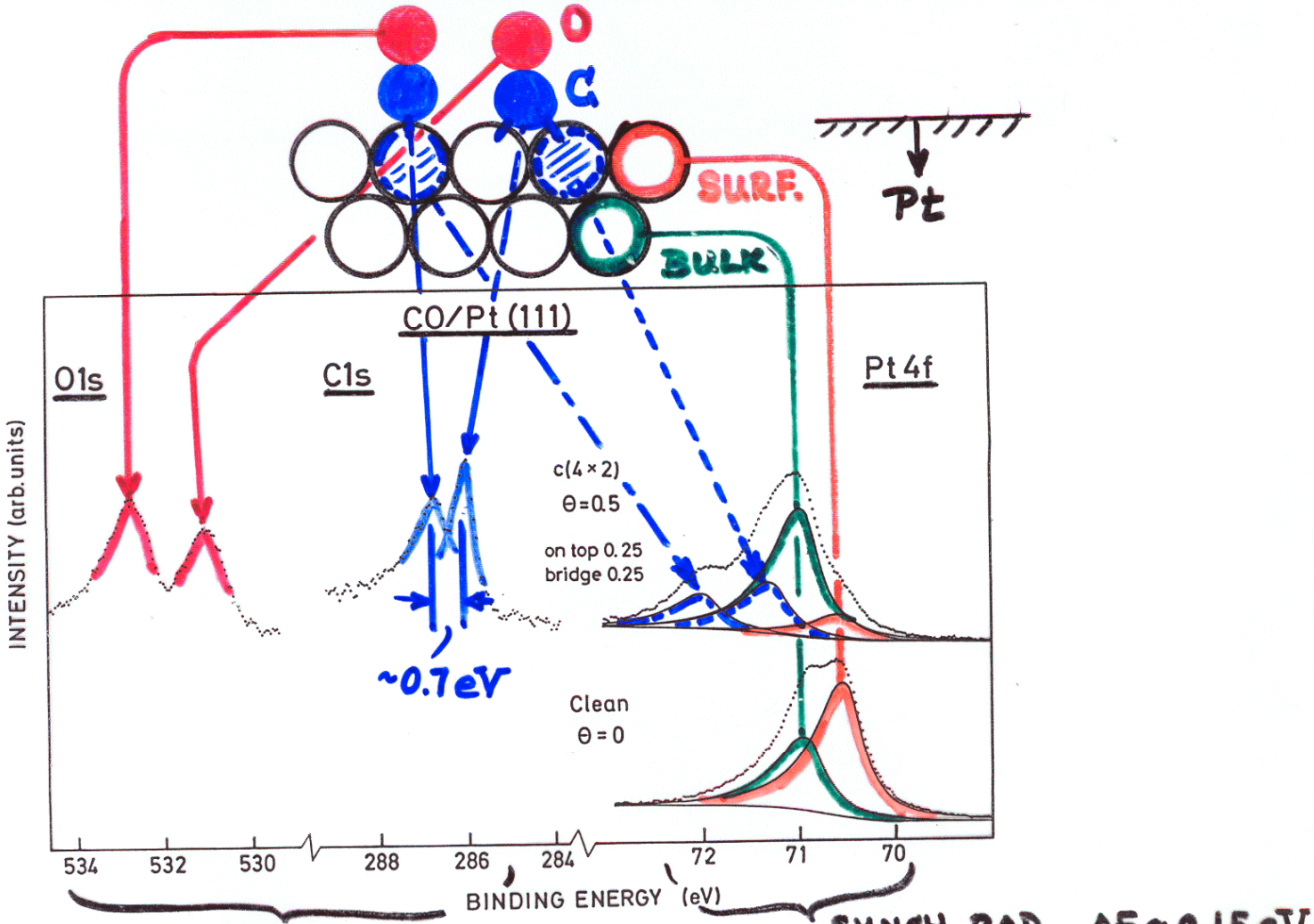


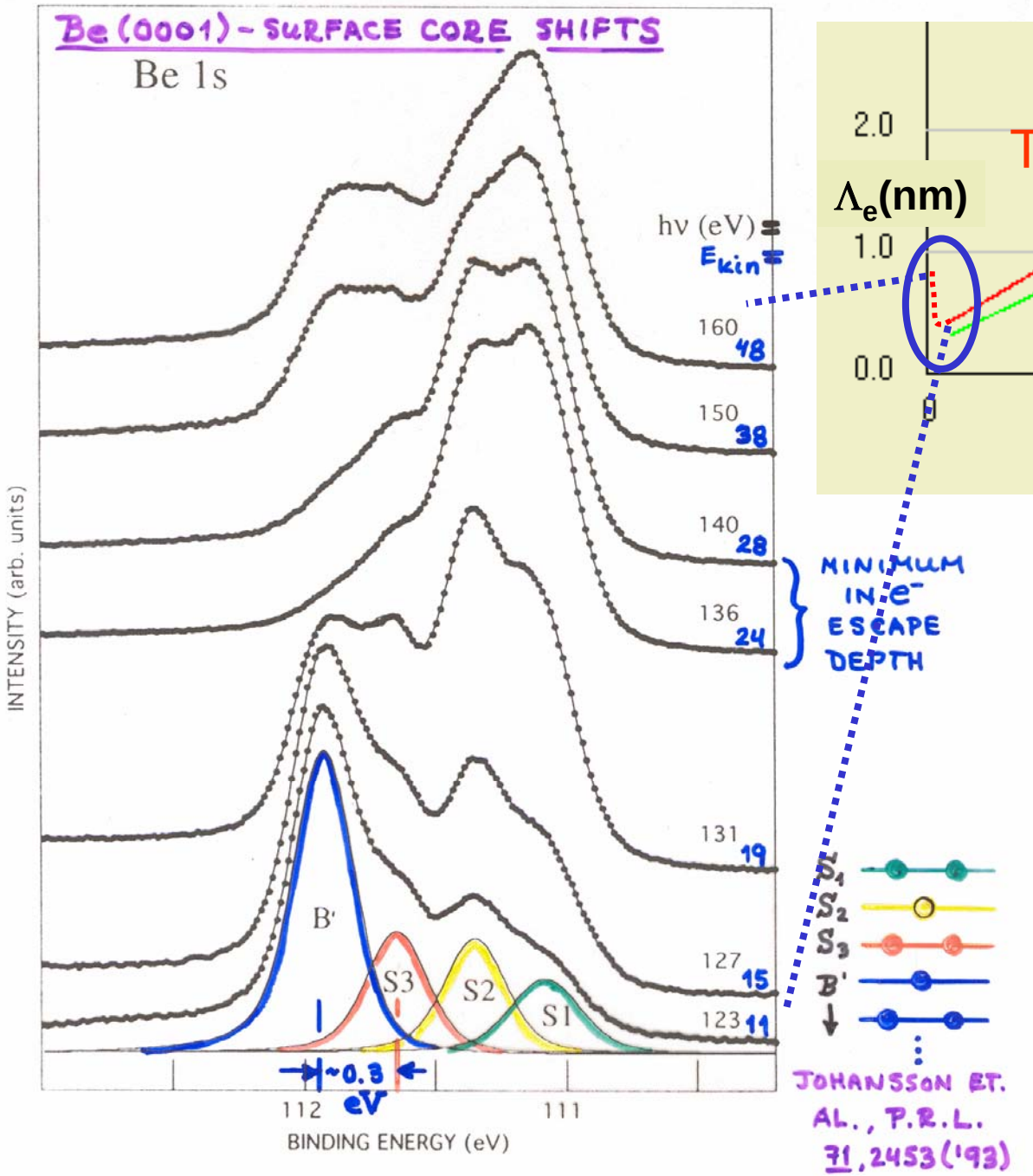
HIMPSEL ET AL., PHYS. REV. B, 38, 6084('90)

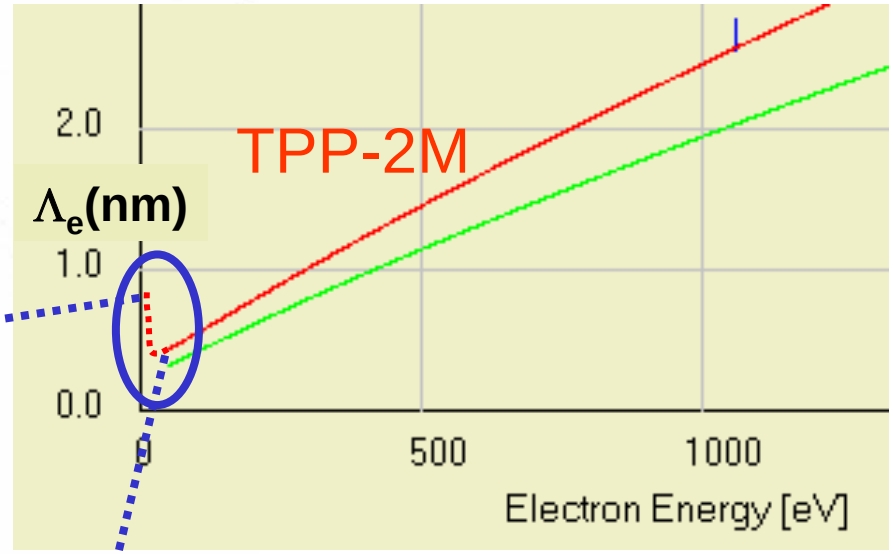




CHEMICAL SHIFTS IN ADSORBATE & SUBSTRATE




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
MINIMUM IN e⁻ ESCAPE DEPTH
B'
S3
S2
S1
~0.3 eV
112
111
BINDING ENERGY (eV)
INTENSITY (arb. units)
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 $E_j(N)$ $\Big\{$ $\Psi_j \approx \Phi_j$ = SLATER DET.

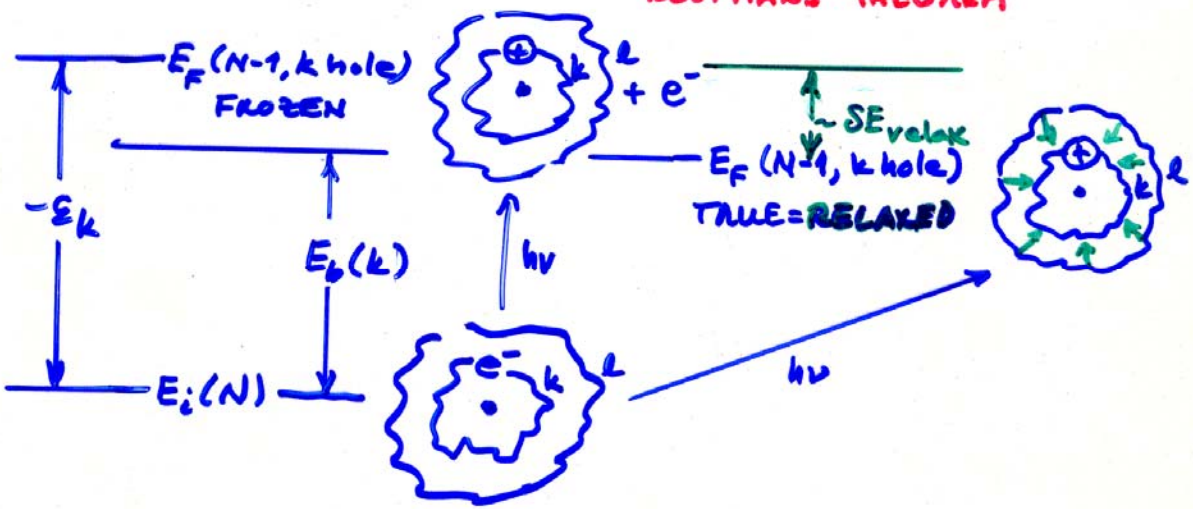
N 1-e^- HARTREE-FOCK EQNS. — $\hat{h}(1)\varphi_k(1) = \varepsilon_k(1)\varphi_k(1)$

- COUPLED INTEGRO-DIFF.
- COULOMB + EXCHANGE

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

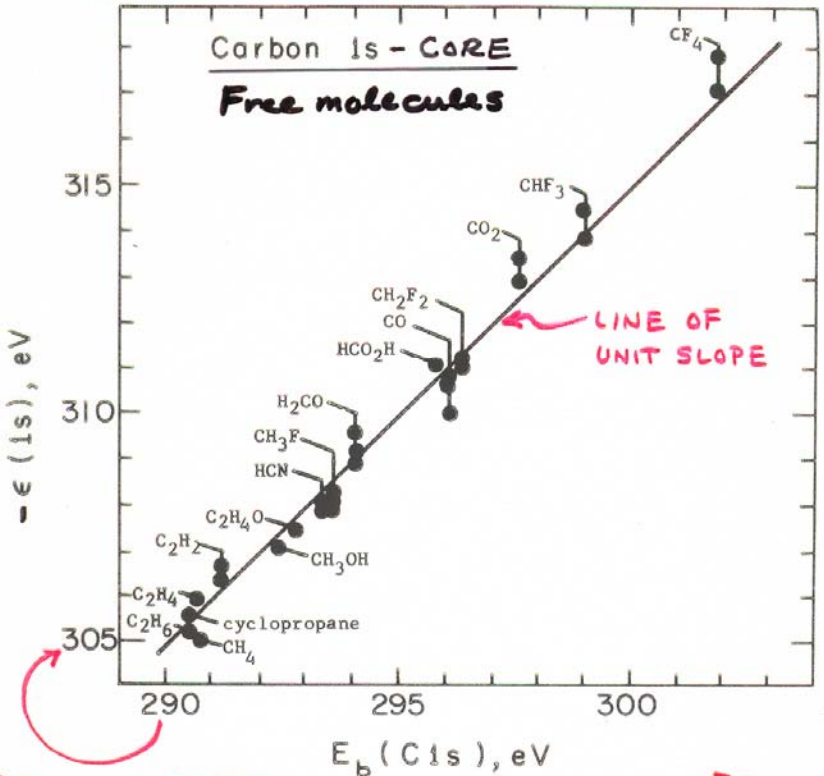
OR $E_b(k) = -\varepsilon_k$ IF $\varphi_{ki} = \varphi_{kf}$ (FROZEN ORBITAL)

KOOPMANS' THEOREM



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

KOOPMANS' THEOREM CALCULATION OF SHIFTS



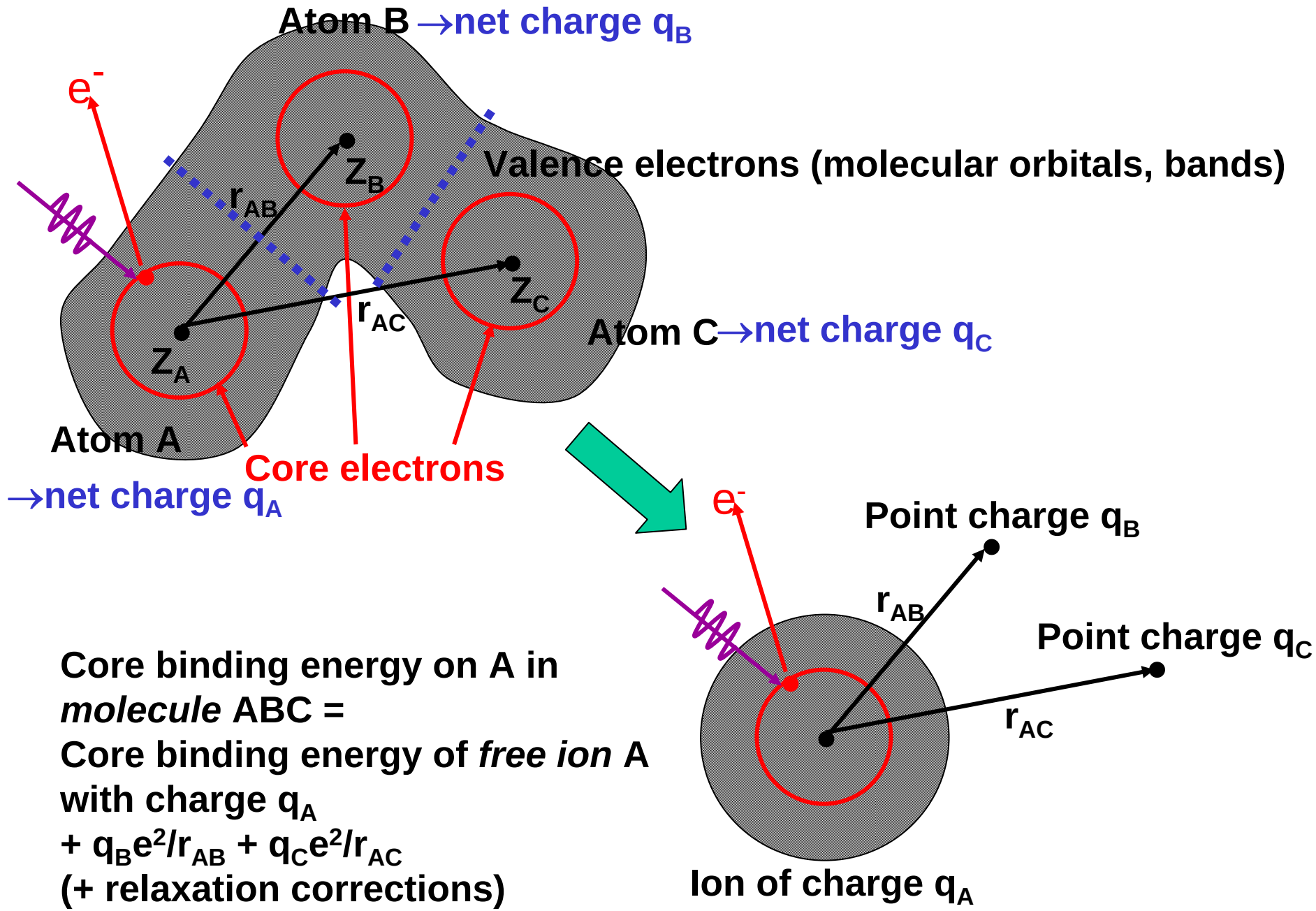
DIFF. = $\delta E_{relax} \approx 15$ eV ≈ CONSTANT ≈ 5% OF E_b^V

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

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.)

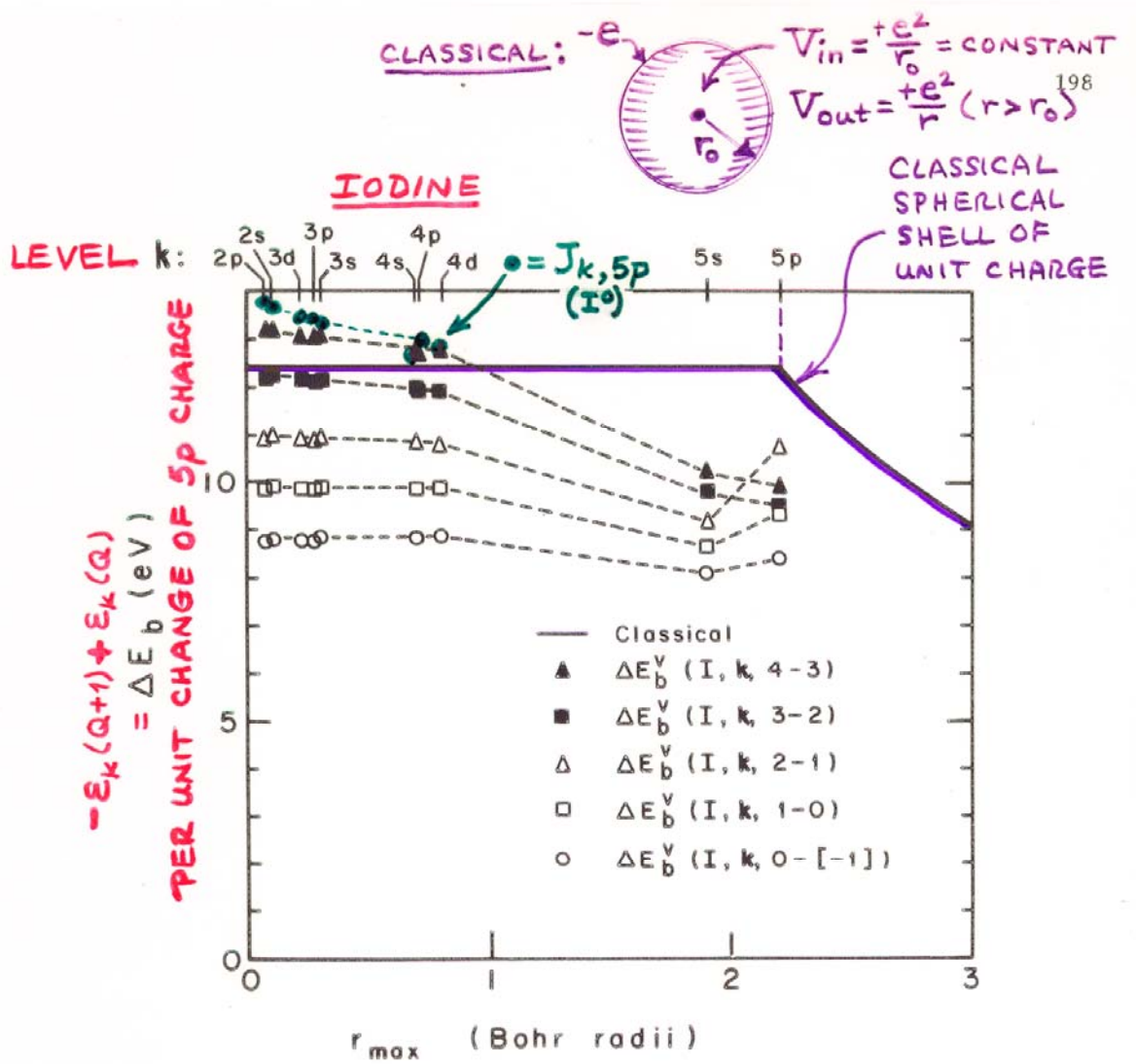
"Basic Concepts of XPS"
Figure 18

POTENTIAL MODEL FOR CORE-LEVEL CHEMICAL SHIFTS



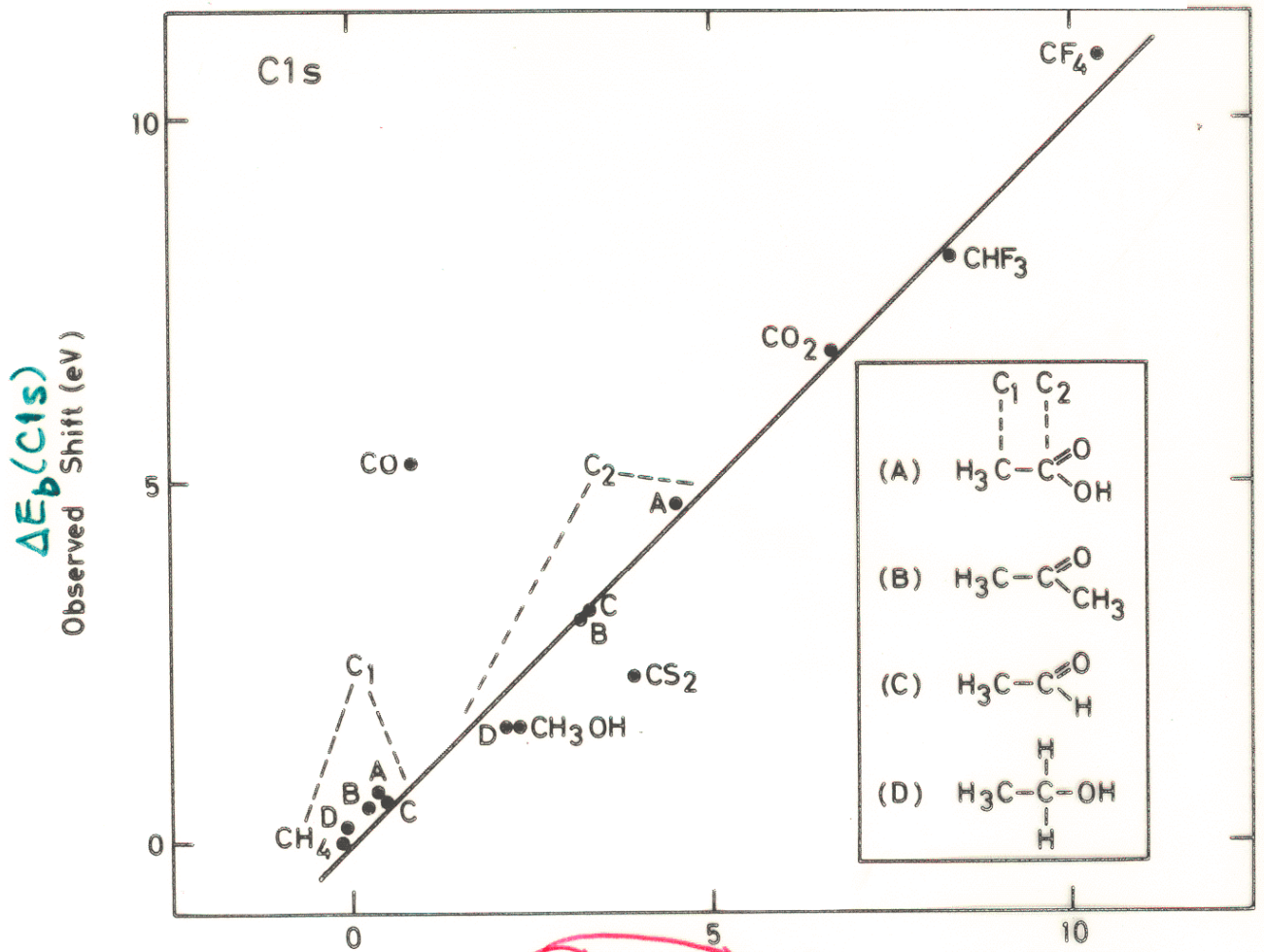
Core binding energy on A in *molecule* ABC =
Core binding energy of *free ion* A with charge q_A
+ $q_B e^2/r_{AB}$ + $q_C e^2/r_{AC}$
(+ relaxation corrections)

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



"Basic Concepts of XPS"
Figure 19

POTENTIAL MODEL CALCULATION OF CARBON CHEMICAL SHIFTS



"Basic Concepts of XPS"
Figure 24

Outline

- Valence-band spectra: low-energy UPS limit and high-energy XPS limit
- Core-level chemical shifts: the potential model
- Core-level chemical shifts: equivalent-core (Z+1) and thermochemical energies
- Multiplet splittings
- Spin-orbit splitting, the Fano effect, and spin-polarized outgoing electrons
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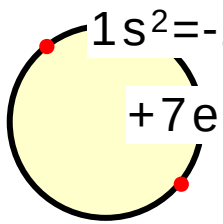
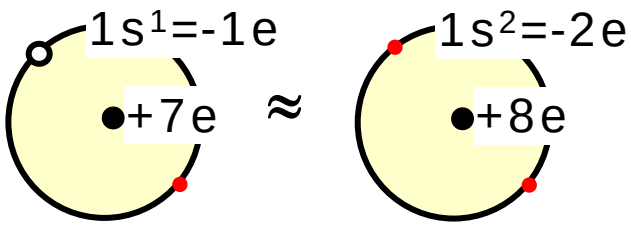
CORRELATION OF THERMOCHEMICAL DATA WITH CHEMICAL SHIFTS: EQUIVALENT-CORE OR (Z+1) MODEL

N core = N $1s^2$ = N^{5+}

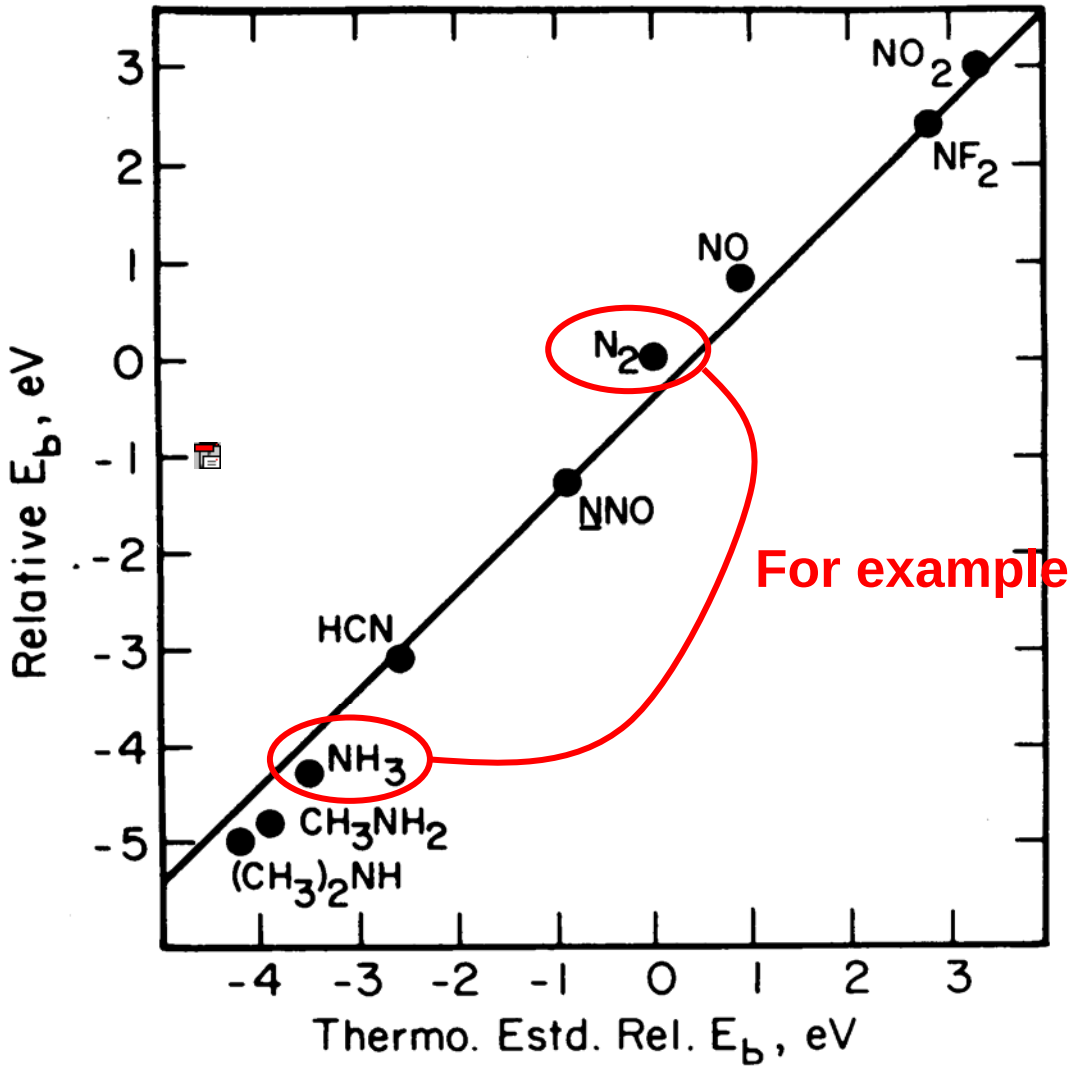


Assume:
N^{6+*} core with
1s hole = N^{6+*} =



= O^{6+} core

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



Jolly et al.

Binding energies: * = N 1s core hole present

$$NH_3 \rightarrow NH_3^{+*} + e^- : \Delta E_1 = E_b^V(N1s, NH_3)$$

$$N_2 \rightarrow N_2^{+*} + e^- : \Delta E_2 = E_b^V(N1s, N_2)$$

Adding and subtracting:

$$NH_3 + N_z^{+*} \rightarrow NH_3^{+*} + N_2 : \quad \Delta E = \Delta E_1 - \Delta E_2$$

$$= E_b^V(N1s, NH_3) - E_b^V(N1s, N_2)$$

$$= \Delta E_b^V(N1s, NH_3 - N_2)$$

The chemical shift

Replacing real N 1s core with equivalent O 1s core:

$$NH_3 + NO^+ \rightarrow OH_3^+ + N_2 : \quad \Delta E = \Delta E_b^V(N1s, NH_3 - N_2) + \Delta E_{ce} - \Delta E_{ce}$$

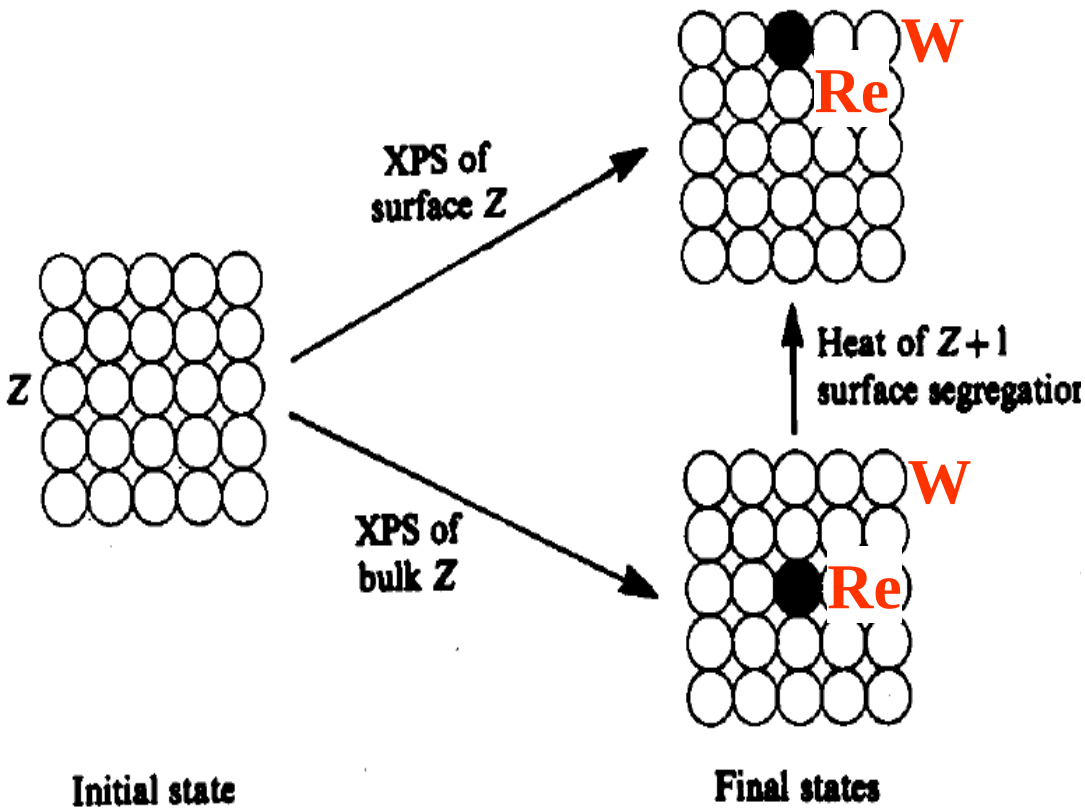
$$= \Delta E_b^V(N1s, NH_3 - N_2)$$

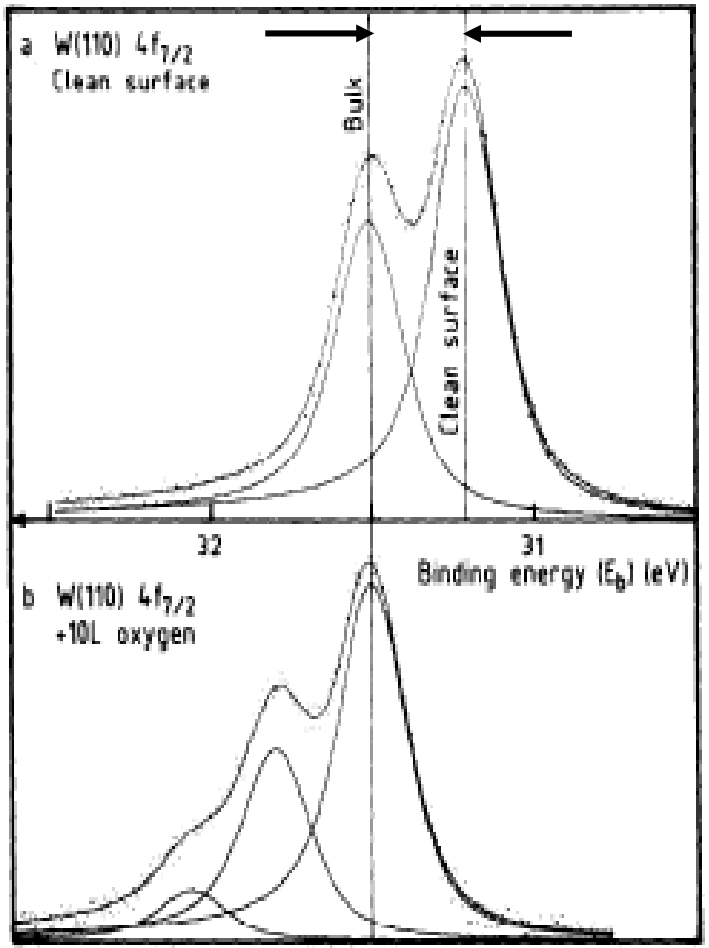
A thermochemical energy

DERIVATION OF HEAT OF SURFACE SEGREGATION FROM SURFACE CORE-LEVEL CHEMICAL SHIFTS

Fig. 4.30. The XPS surface core level shift approach to the heat of segregation of a binary alloy (Egelhoff, 1983). **(Zangwill, p. 87)**

$$\Delta E_b = \Delta H_{segregation}$$





Spanjaard et al., Surf. Sci. Repts. 5, 1 (1985)

Outline

- Valence-band spectra: low-energy UPS limit and high-energy XPS limit
- Core-level chemical shifts: the potential model
- Core-level chemical shifts: equivalent-core (Z+1) and thermochemical energies
- Multiplet splittings and magnetism
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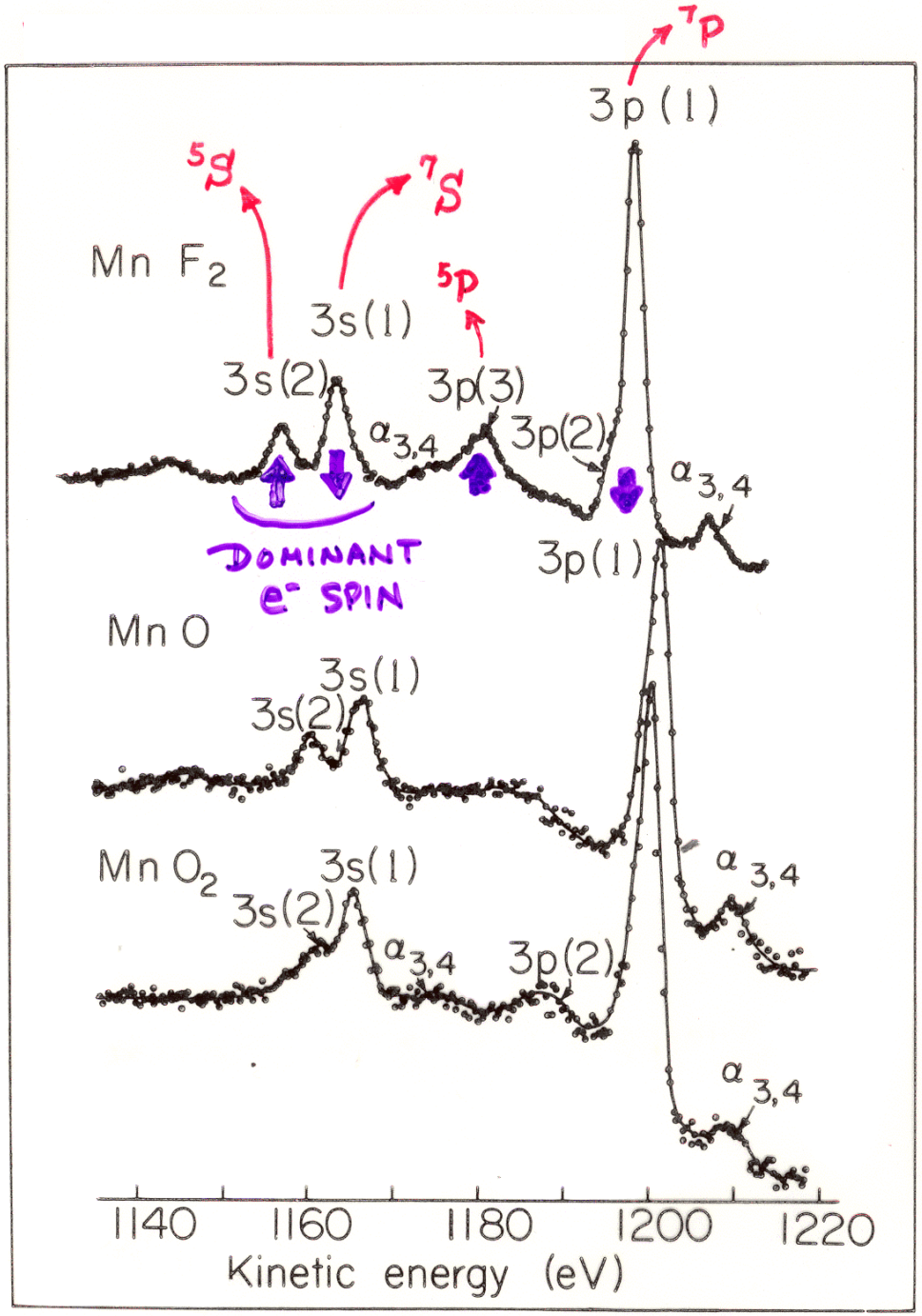
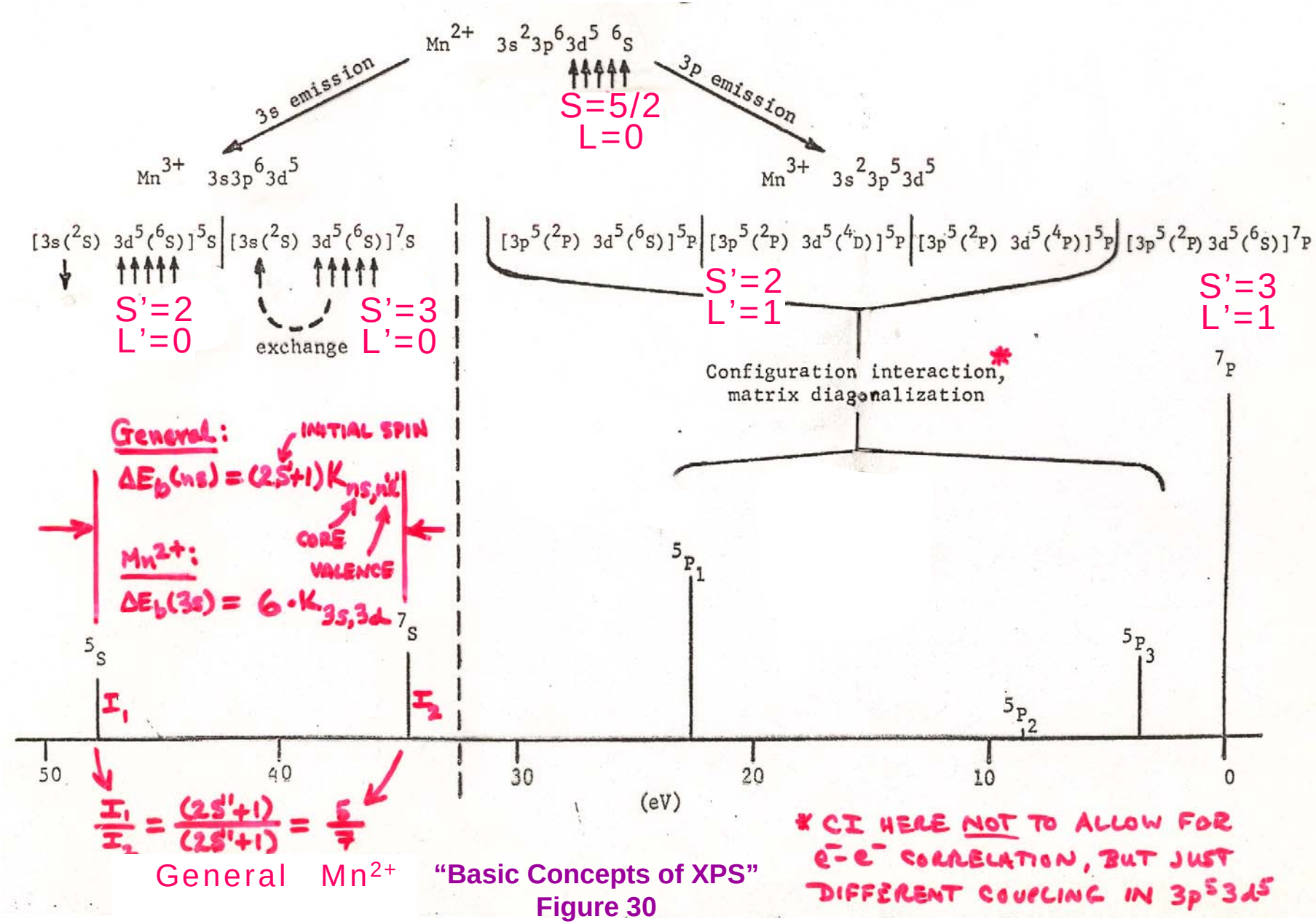
- Various other final state effects providing information in core-level spectra

CORE-LEVEL MULTIPLET SPLITTINGS IN Mn COMPOUNDS



"Basic Concepts of XPS"
Figure 31

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

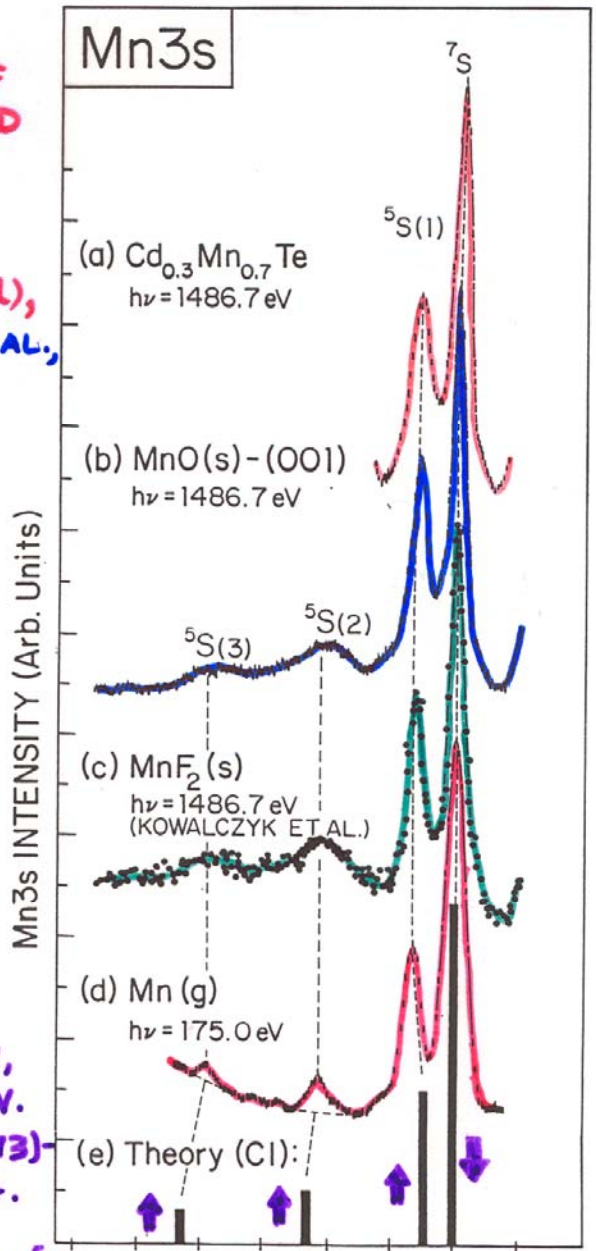


General Mn^{2+}

"Basic Concepts of XPS"
Figure 30

COMPARISON OF GAS-PHASE AND SOLID-STATE SPECTRA

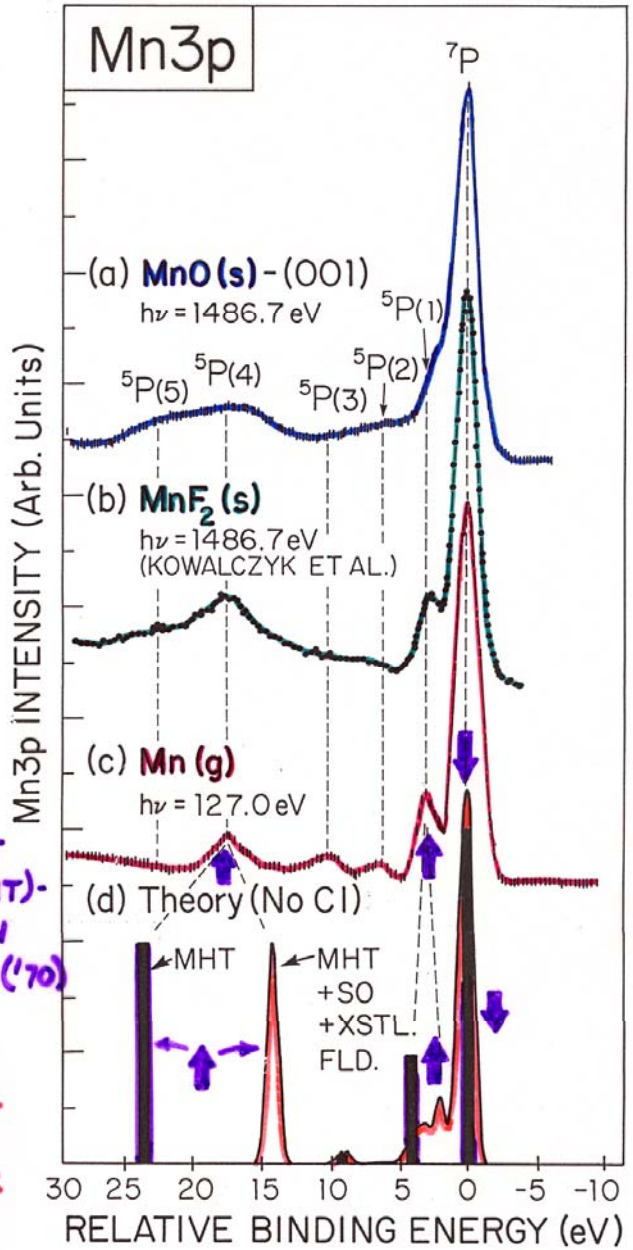
EXPT.: (a), (b), (d), HERMSMEIER ET AL., PHYS. REV. LETT. 61, 2592 (1988) (OUR GROUP)



THEORY:
BAGUS, FREEMAN, SASAKI, PHYS. REV. LETT. 30, 850 (1973)-
ATOMIC CONFIG. INT. IN
$Mn^{3+}...3s^1...3d^5$
+ $Mn^{3+}...3s^2 3p^4 3d^6$

Correlation CI effects: anti-parallel electrons

"Basic Concepts of XPS"
Figure 33



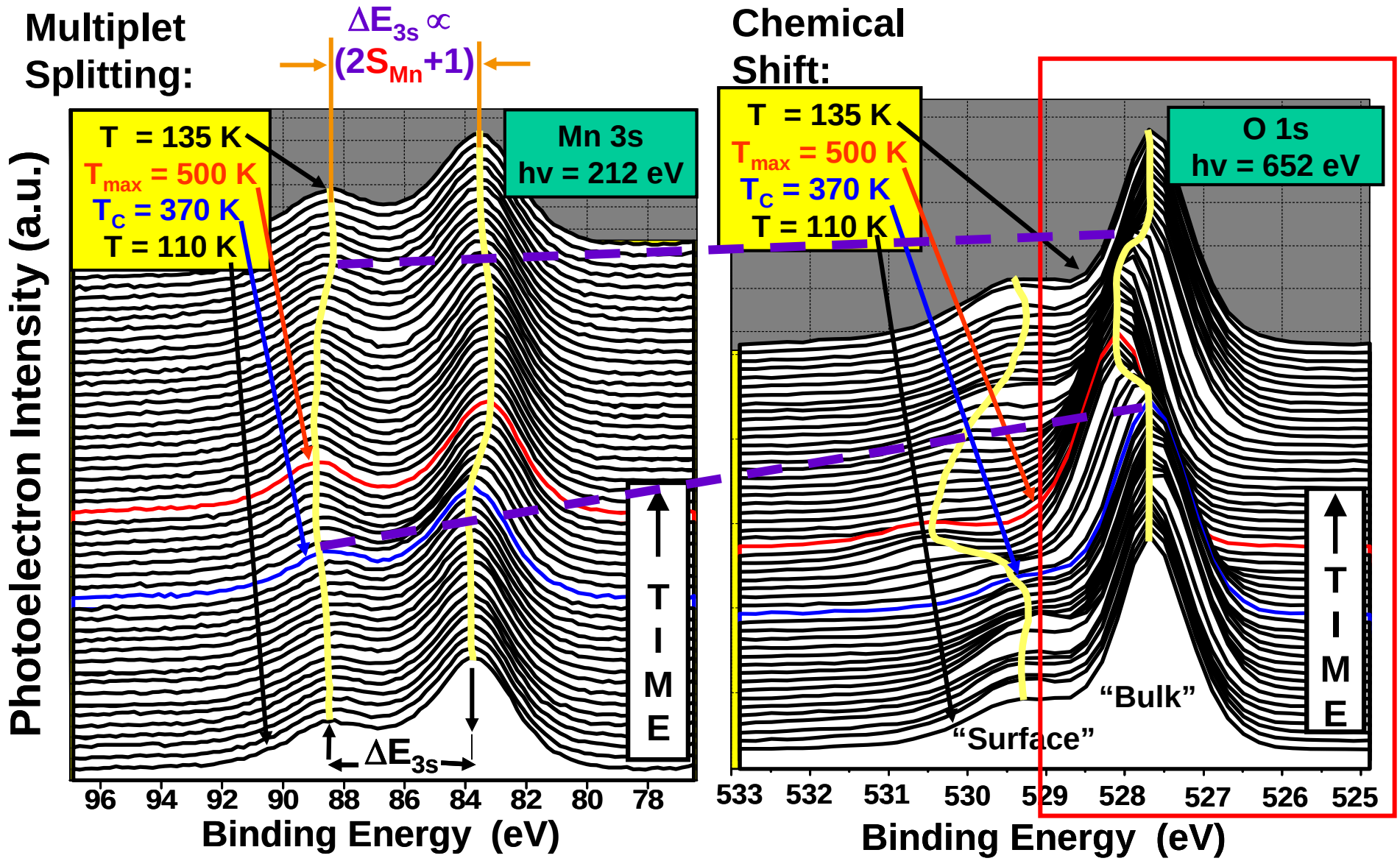
THEORY: NO CI

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)

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

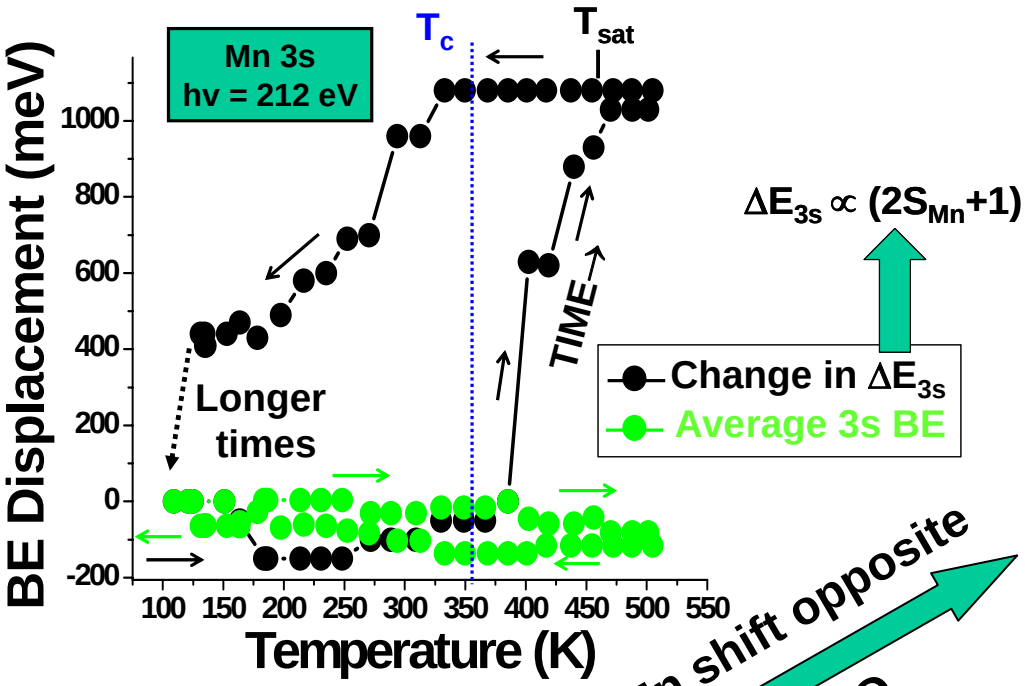
Temperature dependence of Mn3s and O1s spectra in a colossal magnetorestive (CMR) oxide: $La_{0.7}Sr_{0.3}MnO_3$



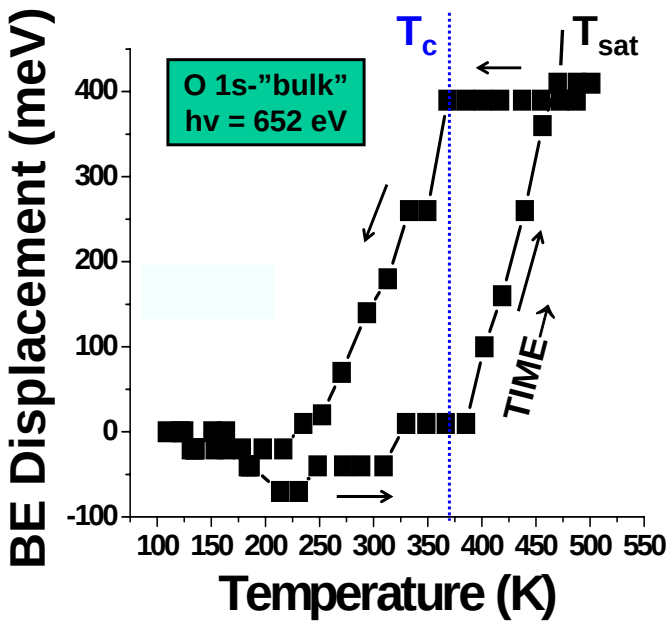
Increase of the Mn3s splitting-reversible

Increase of O1s BE-reversible

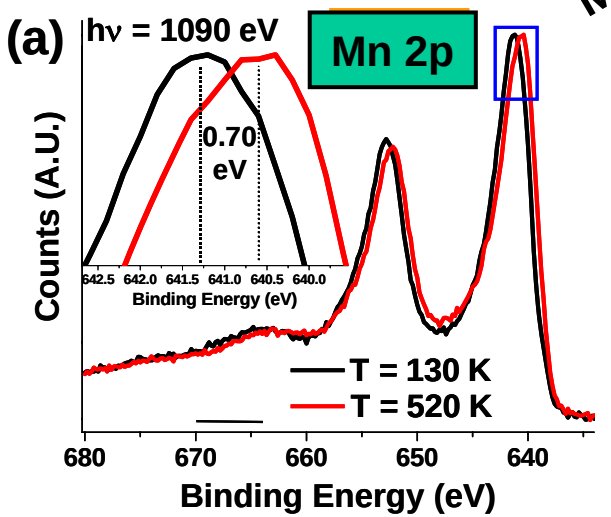
T dependence of Mn 3s binding energies

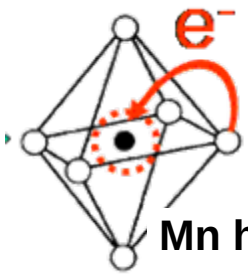


T dependence of bulk O 1s binding energy



Mn shift opposite to O





O more positive

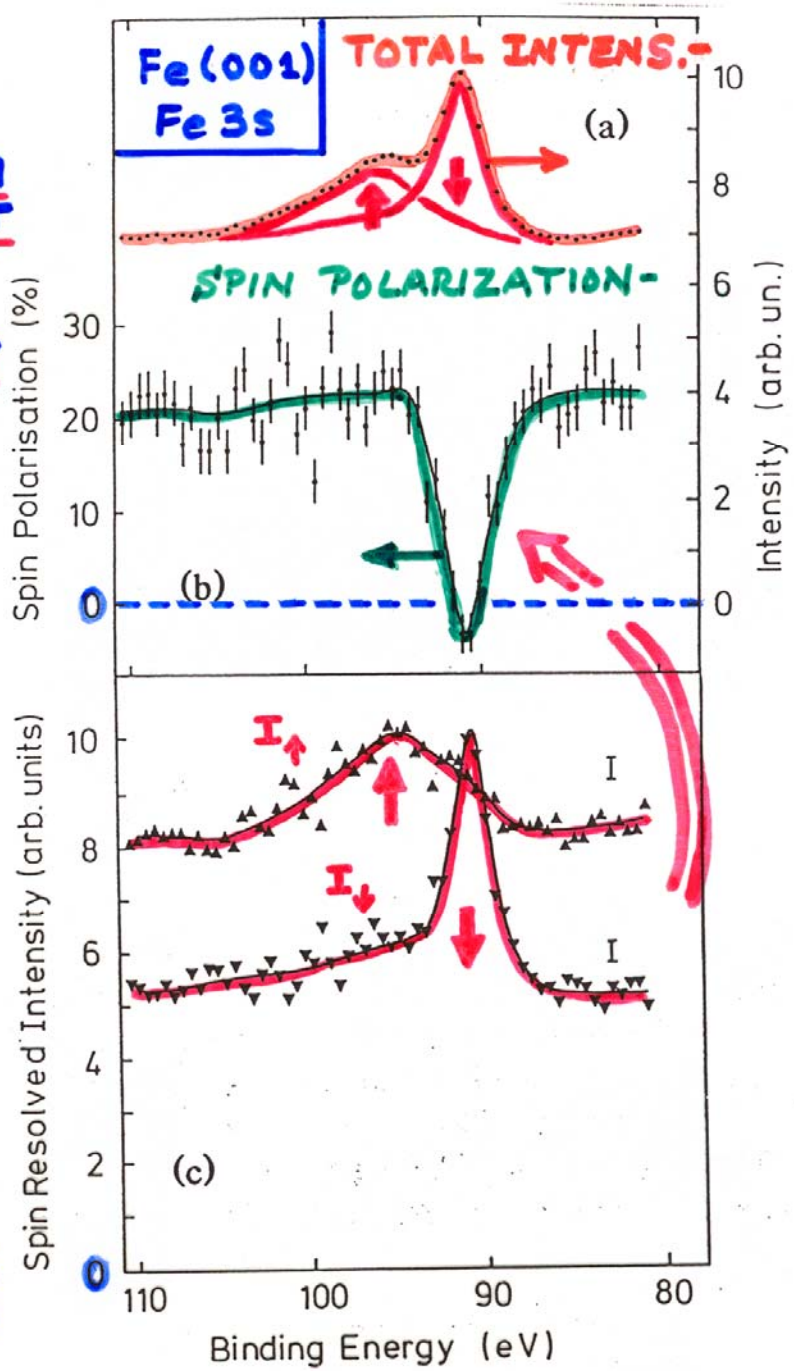
Mn higher spin, more negative

Theory: self-interaction corrected local spin density results for LSMO → elongating octahedron makes Mn^{3+} more stable than Mn^{4+}
Banach, Temmerman, PRB 69, 054427 ('04)

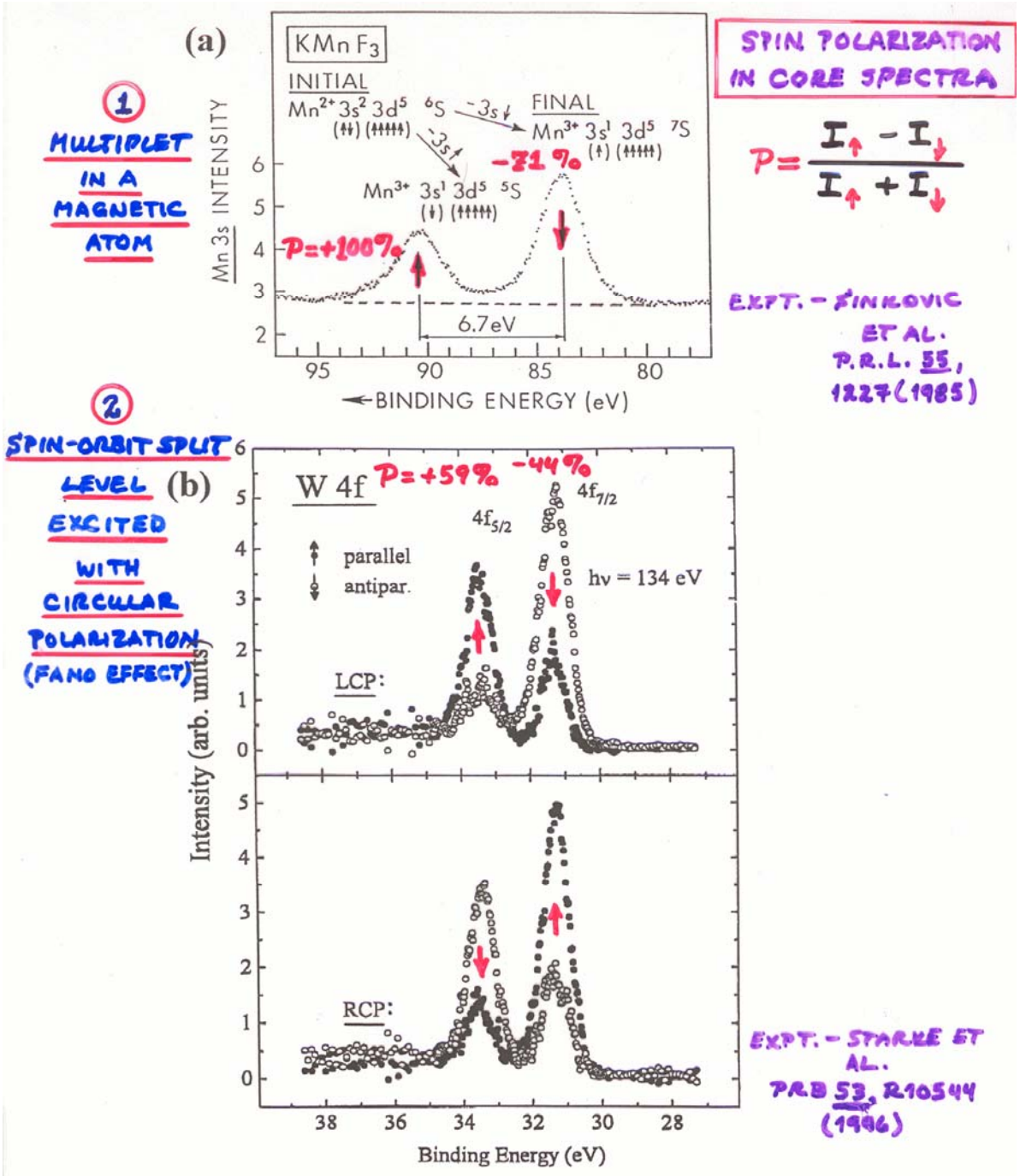
Mannella et al., Phys. Rev. Lett. 92, 166401 (2004)

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)

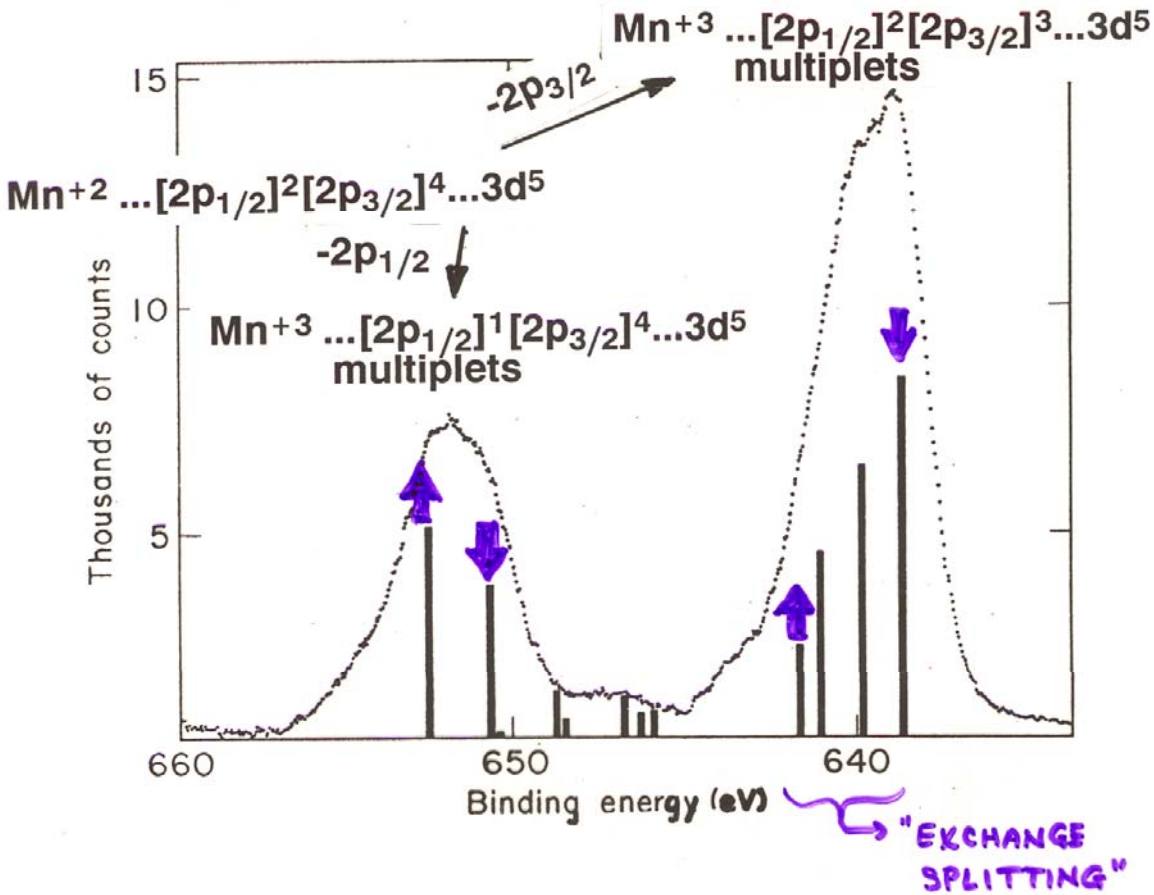


Spin <u>internally</u> referenced to spin of each ion

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

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

Mn 2p emission from MnF_2:

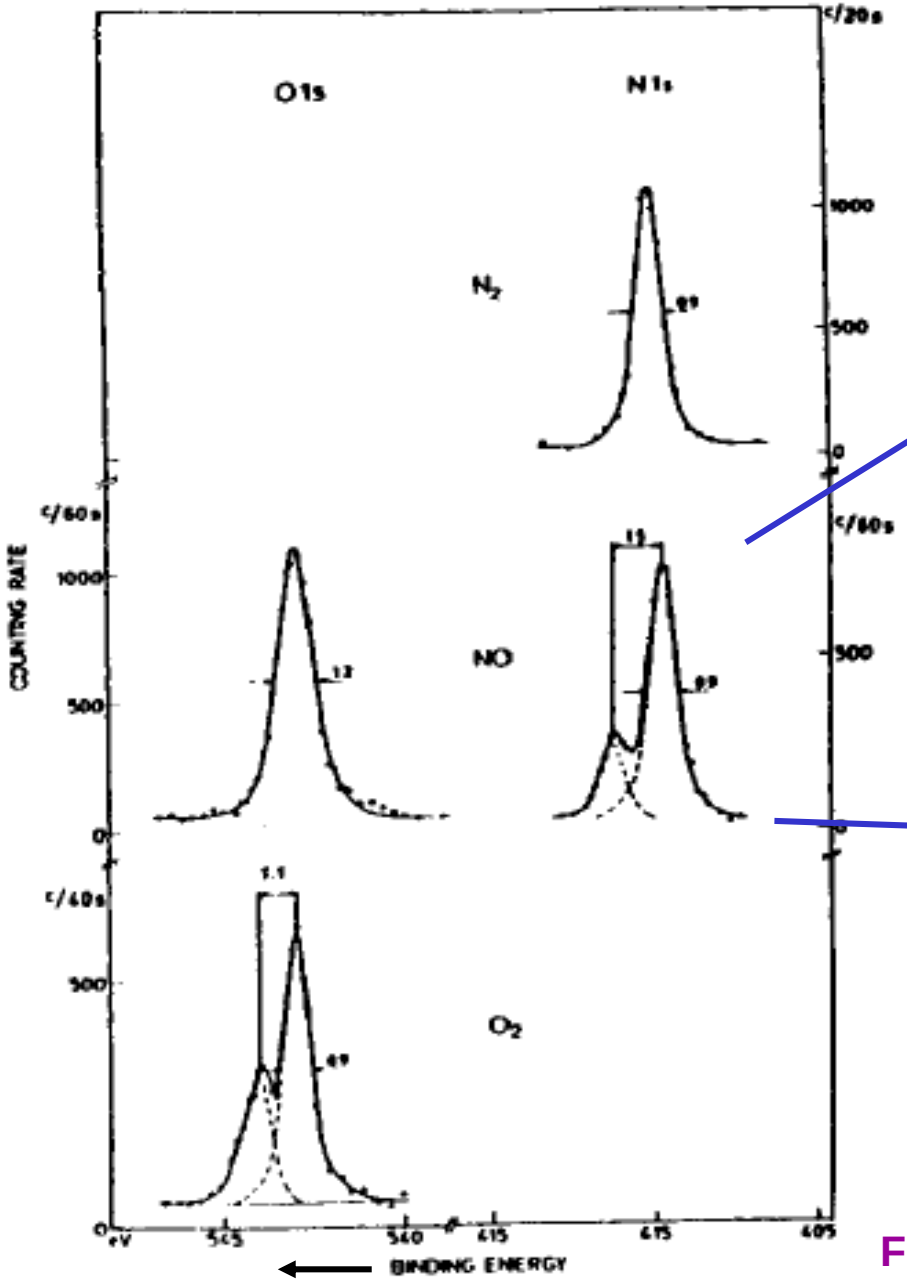


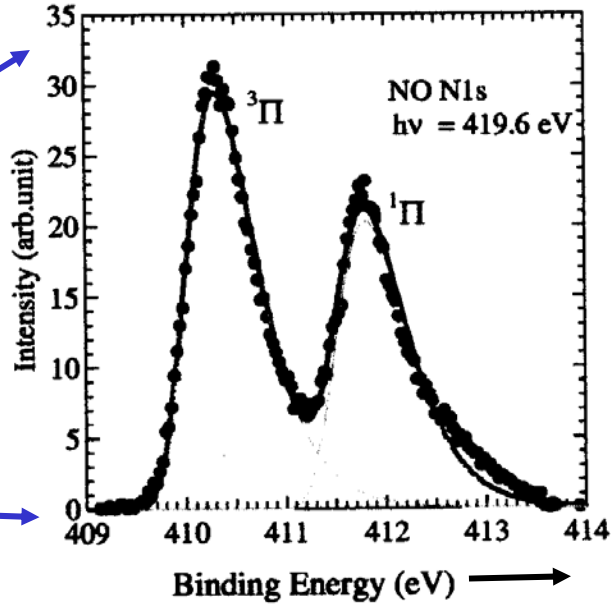
Expt.--Kowalczyk et al., Phys. Rev. B11, 1721 (1975)

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

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

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

Outline

- Valence-band spectra: low-energy UPS limit and high-energy XPS limit
- Core-level chemical shifts: the potential model
- Core-level chemical shifts: equivalent-core (Z+1) and thermochemical energies
- Multiplet splittings
- Spin-orbit splitting, the Fano effect, and spin-polarized outgoing electrons
- Magnetic circular dichroism (MCD) in core-level emission
- Non-magnetic circular dichroism in core-level emission: a.k.a. circular dichroism in angular distributions (CDAD)
- Various other final state effects providing information in core-level spectra

PHOTOELECTRON EMISSION - BASIC MATRIX ELEMENTS + SELECTION RULES:

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

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

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

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

$\varphi_f = \phi$, $\vec{k}_f = \frac{\vec{p}_f}{\hbar}$, φ_i, $V(r)$

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

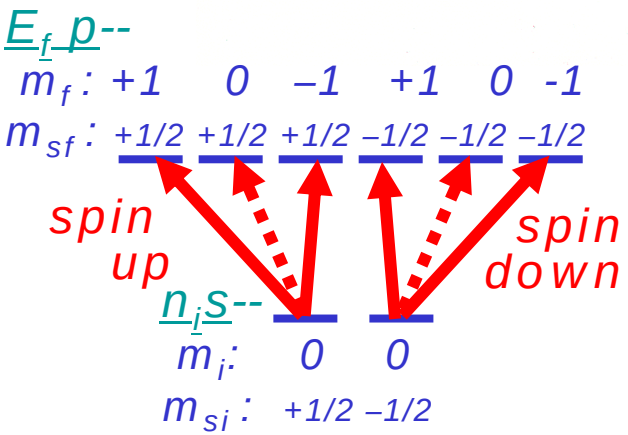
$$= 4\pi \sum_{l_f,m_f} i^{l_f} e^{-i\delta_{l_f}} Y^*_{l_f m_f}(\theta_{k_f},\phi_{k_f}) Y_{l_f m_f}(\theta,\phi) R_{E_f l_f}(r)\{\alpha(\sigma),\beta(\sigma)$$

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

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

- $\Delta l = l_f - l_i = \pm 1$ TWO CHANNELS
- $\Delta m = m_f - m_i = 0, \pm 1$ LINEAR POLARIZ.
- $\Delta m = \pm 1$, CIRCULAR POLARIZATION

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

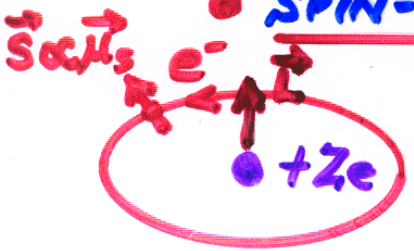


FOR A GIVEN $n_i l_i m_i m_{si}$: SUM OVER DEGENERATE INITIAL STATES $m_i m_{si}$ AND AVERAGE OVER FINAL STATES $E_f l_f m_f m_{sf}$ ACCESSED FROM EACH m_i TO YIELD DIFFERENTIAL SUBSHELL PHOTOELECTRIC CROSS SECTION :

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

$\propto$ PROBABILITY PER UNIT SOLID ANGLE OF EXCITING ONE ELECTRON FROM SUBSHELL $n_i l_i$ INTO THE DIRECTION k_f

• SPIN-ORBIT SPLITTING OF LEVELS:



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

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

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

• MIXES SPIN + ORBITAL ANGULAR MOM.:

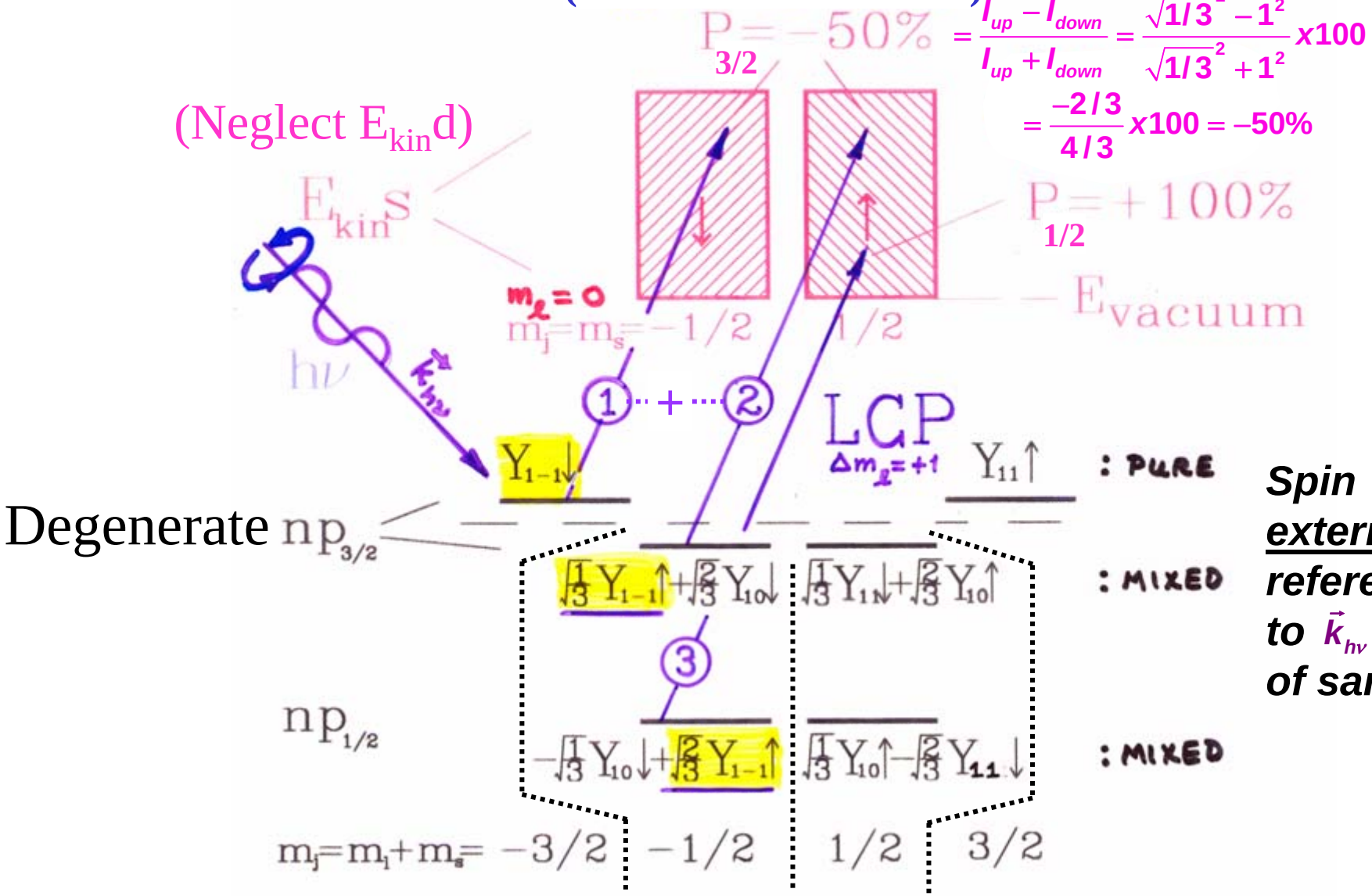
$$\psi_{nljm_j} = C_1 \psi_{nl,m_j-1/2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + C_2 \psi_{nl,m_j+1/2} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

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

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

PHOTOELECTRON SPIN POLARIZATION FROM CIRCULAR POLARIZATION AND SPIN–ORBIT SPLITTING

(THE FANO EFFECT)



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

Spin polarization in core photoelectron spectra—expt.

Outline

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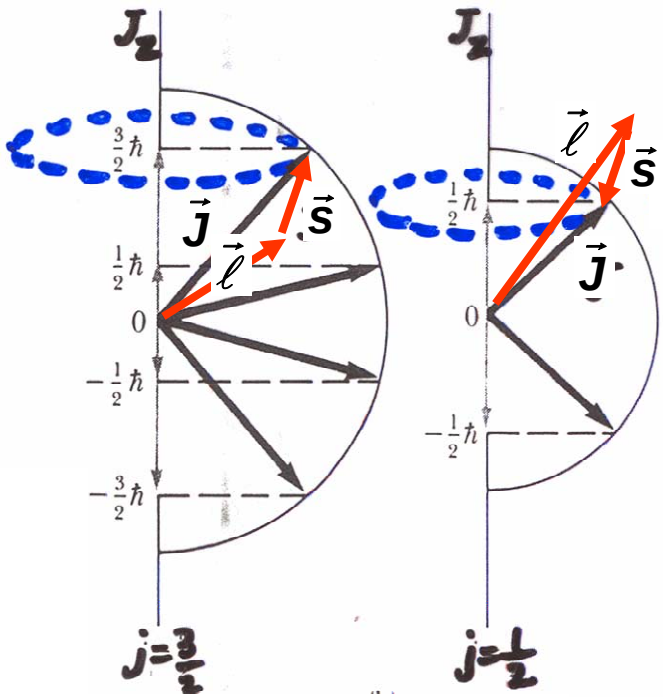
MCD IN 2p EMISSION - 1-e⁻ THEORY

$\vec{J} = \vec{\ell} + \vec{s}$ $\qquad$ $\vec{J} = \vec{\ell} - \vec{s}$

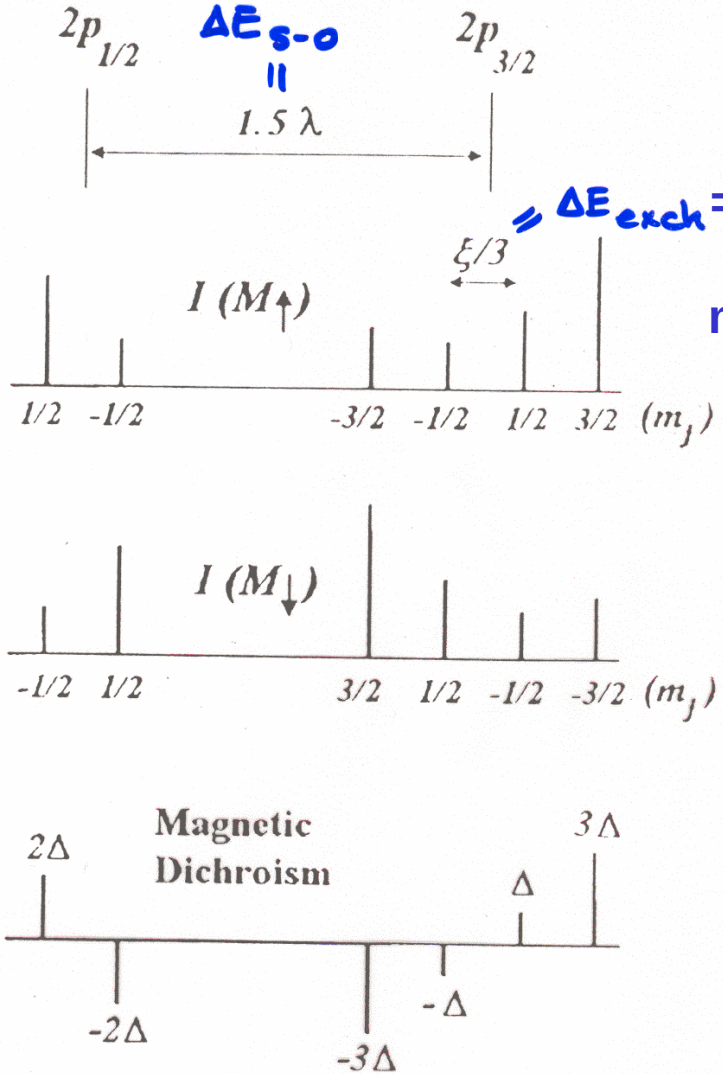


$$|\vec{J}| = \hbar\sqrt{j(j+1)}$$

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

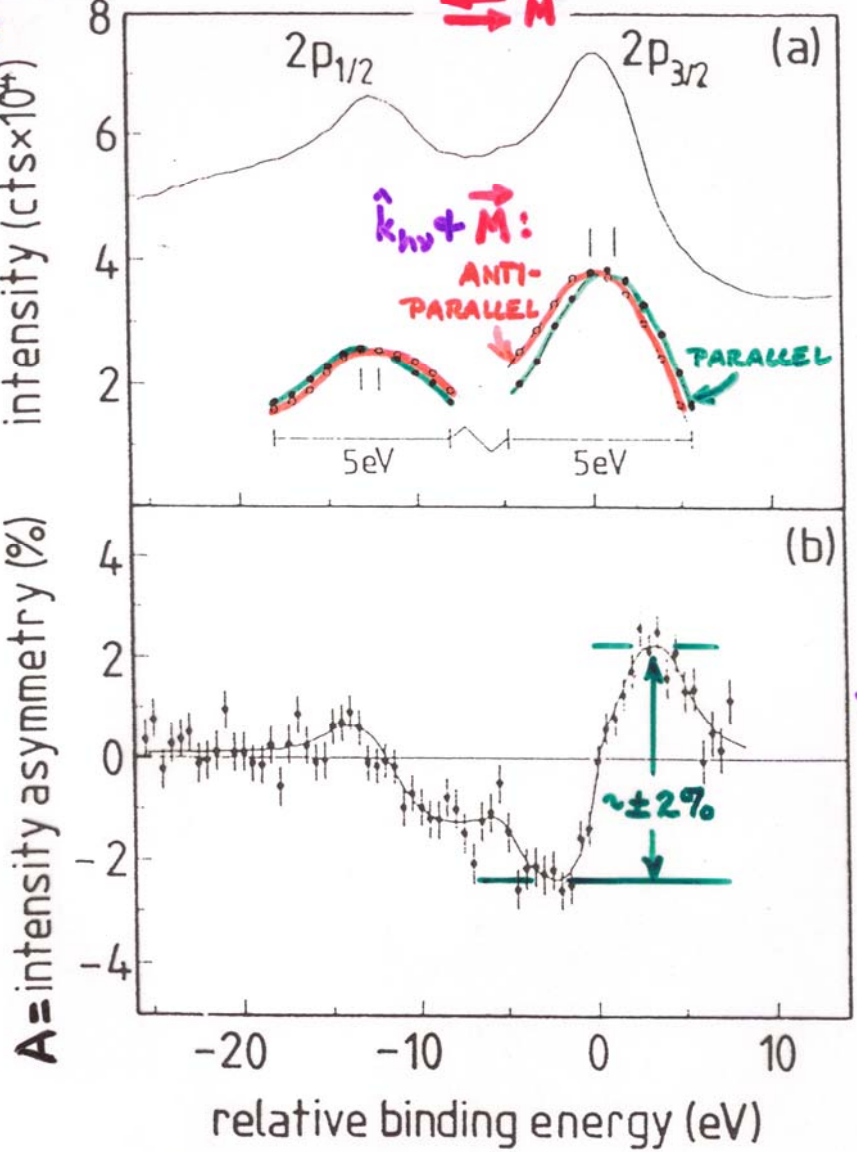
$$J_z = \hbar m_j$$

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



MENCHERO, P.R.B 57, 993('98)

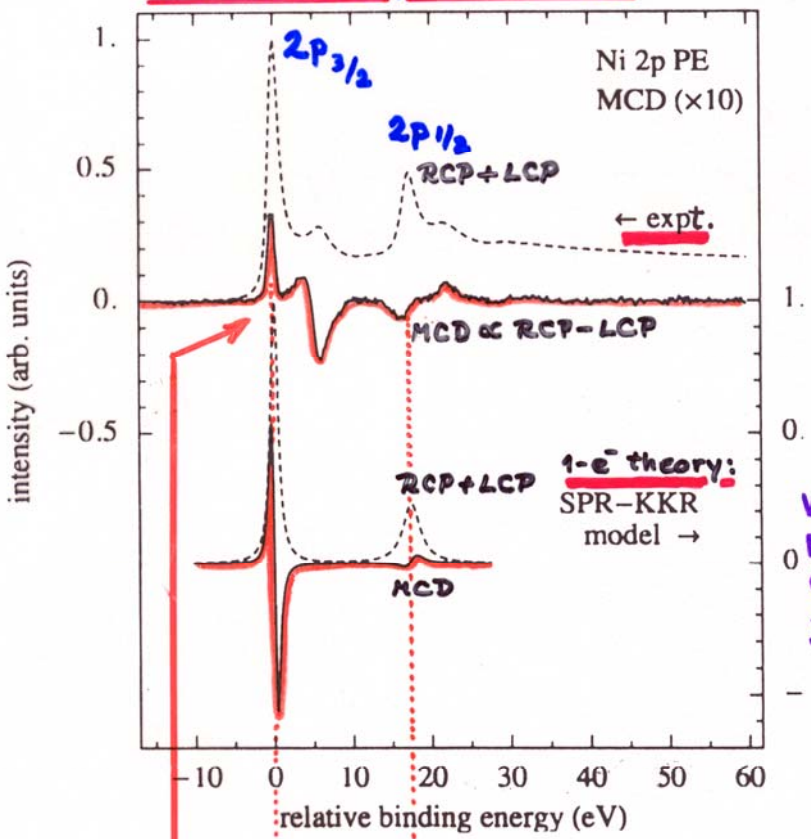
MAGNETIC CIRCULAR DICHROISM IN CORE-LEVEL PHOTOE⁻ EMISSION



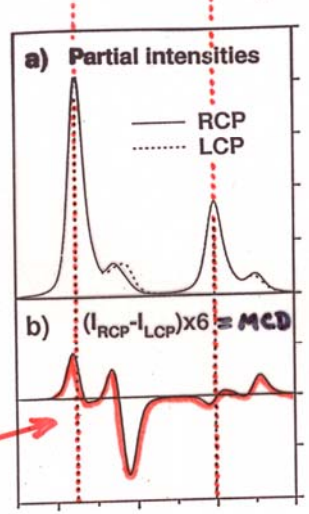
BAUM-GARTEN ET AL., P.R.L. 65, 492 (1990)

⇒ DIFFRACTION EFFECTS WILL BE IMPORTANT HERE ALSO

MCD IN Ni2p EMISSION:



VAN DER LAAN ET AL., J. PHYS. COND. MATT. 12, L295 (2000)

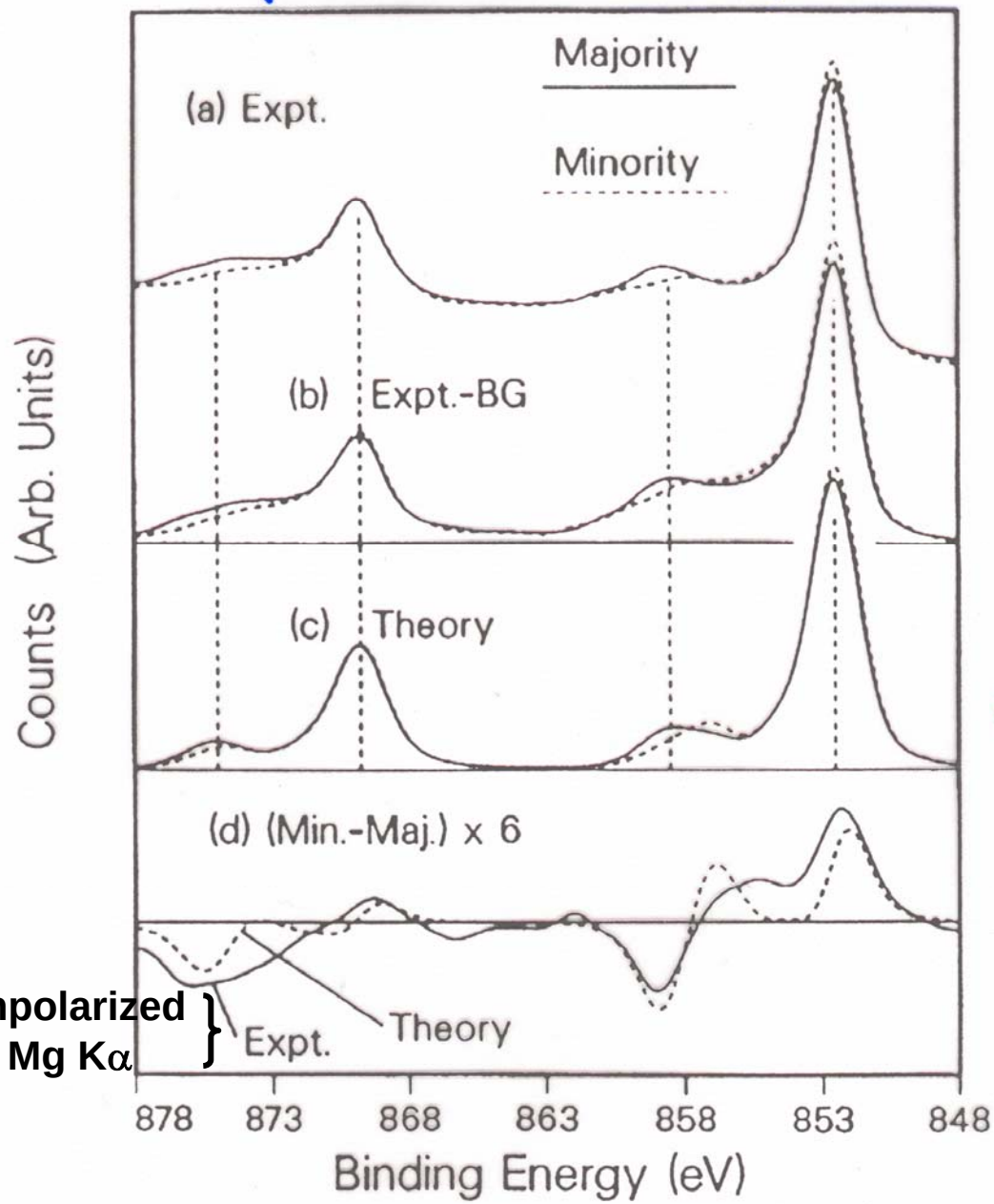


Many-e⁻ theory:
CI, screening

MENCHERO, PRL 76, 3208 ('96)
PRB 57, 1001 ('98)

MANY-e^- THEORY

Ni 2p – SPIN-RESOLVED SPECTRA

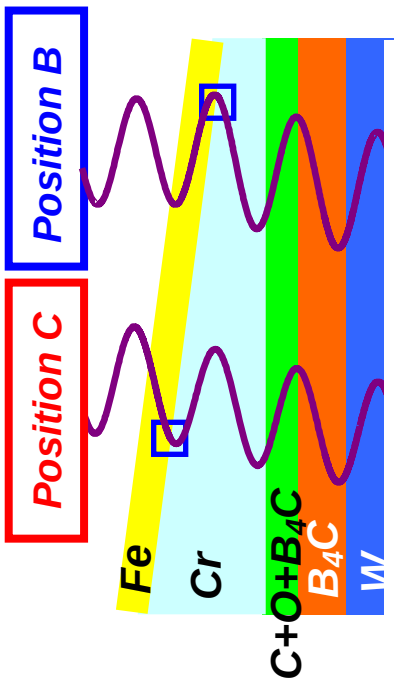


⇒ FORM OF MCD APPROX. of FORM OF SPIN POLARIZATION: MCD + POLARIZATION DIRECTLY LINKED

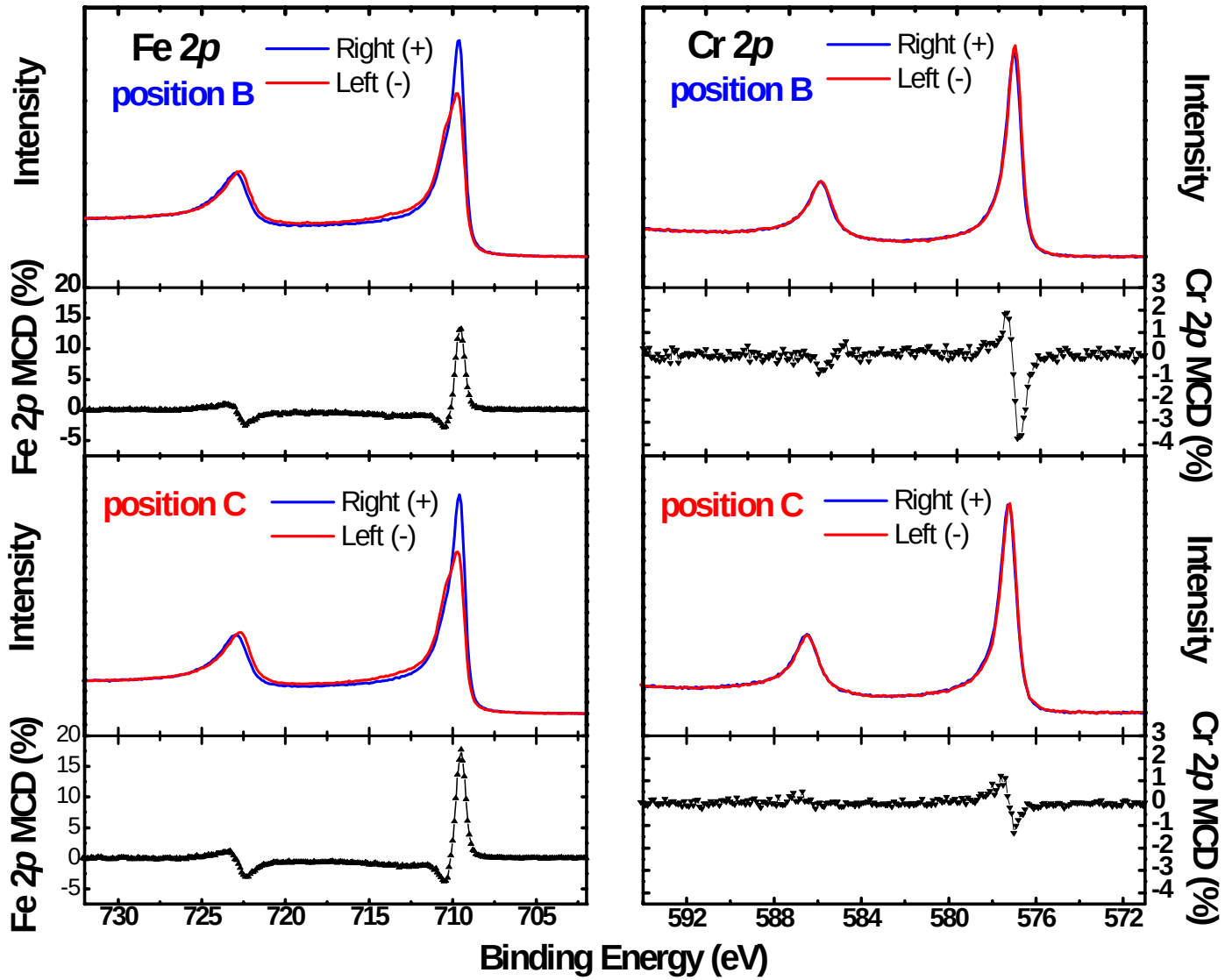
MENCHERO P.R.L. 76, 3208 ('96)

Application to a buried interface: with standing wave excitation

Cr magnetization Is antiparallel to Fe; systematic variation of MCD strengths vs d_{cr}



Fe & Cr 2p MCD Data from wedge (Fe/Cr)+SWG



S.H. Yang , B.S. Mun et al., J. Phys. Cond. Matt. 14, L406 (2002)

Outline

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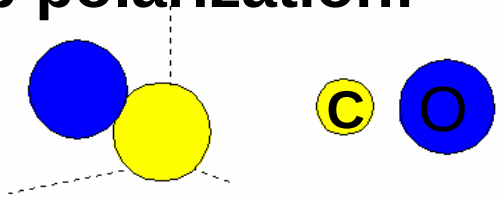
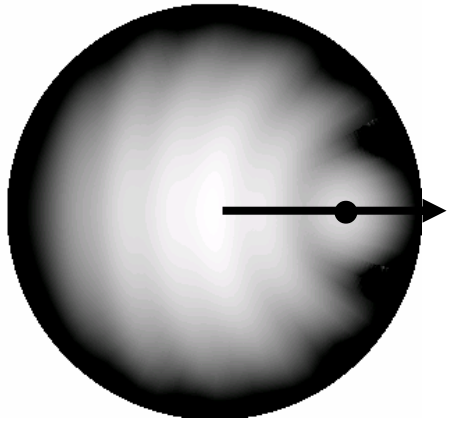
Circular dichroism in angular distributions:
C 1s emission from CO, E_{kin} = 200 eV

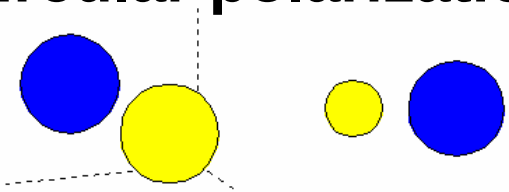
Linear p polarization:

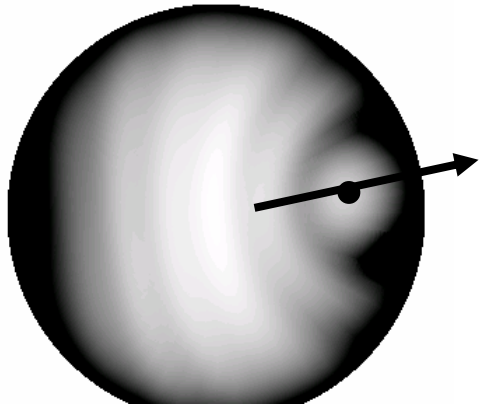




Oxygen forward scattering peak

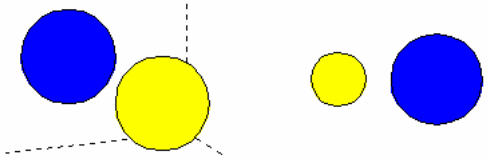
Right circular polarization:

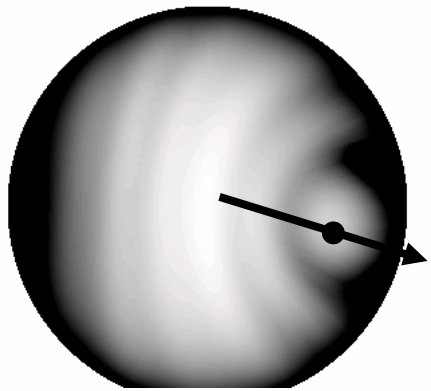




Circular dichroism! Why?

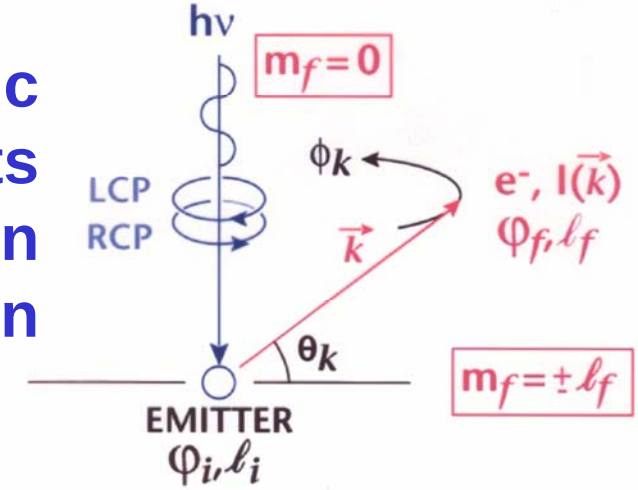
Left circular polarization:

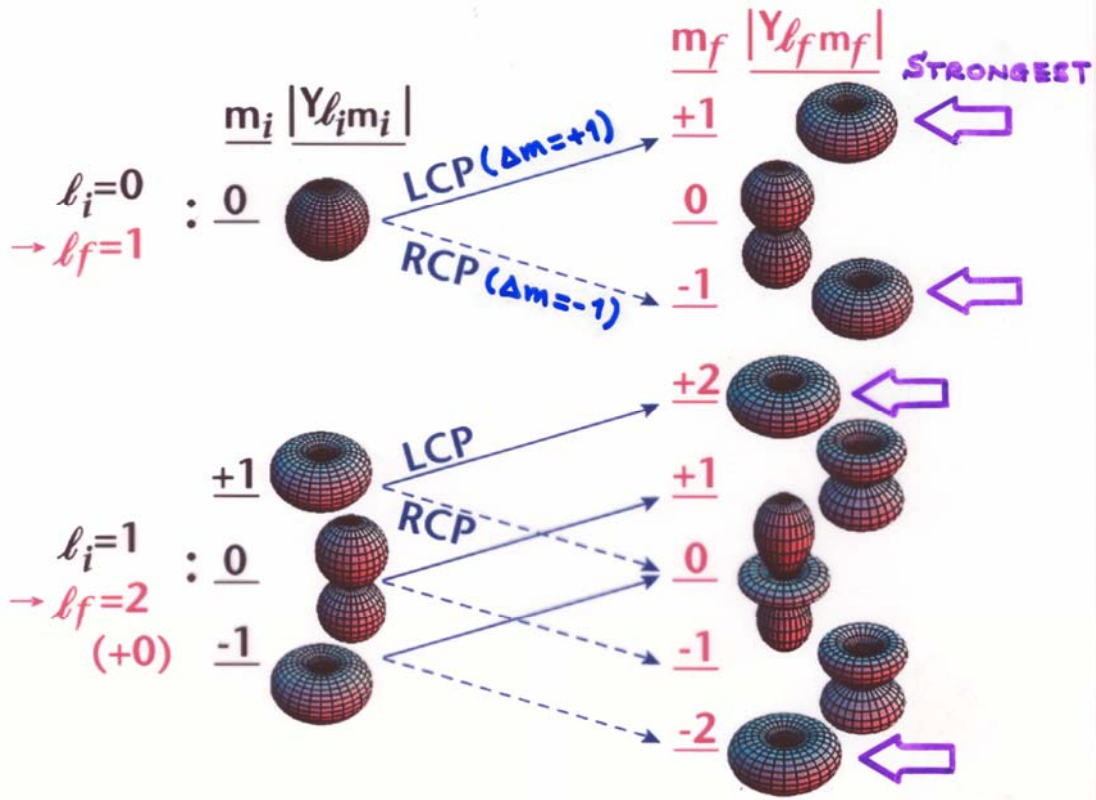




CIRCULAR DICHROISM IN PHOTOELECTRON ANGULAR DISTRIBUTIONS (CDAD)

Non-magnetic dichroism effects due to photoelectron diffraction

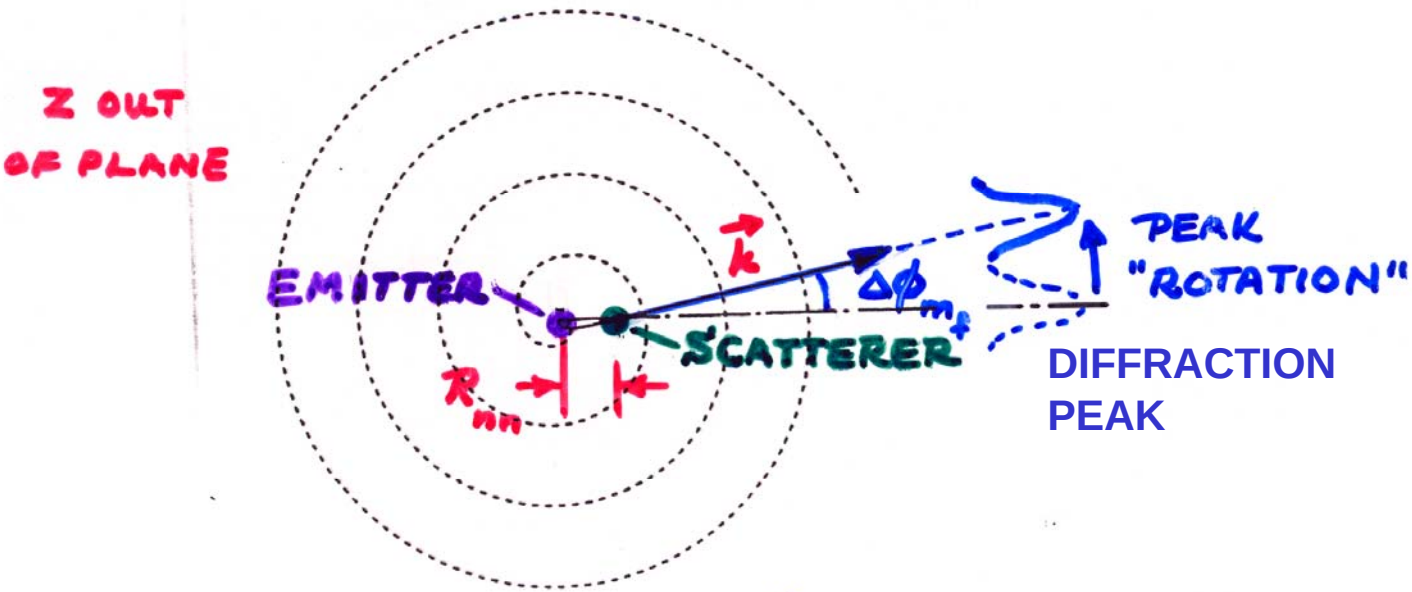




CIRCULAR DICHROISM IN PHOTOELECTRON DIFFRACTION

CONSTANT-PHASE SURFACE OF:

$$\psi_{\text{PHOTOE}^-}(r,\theta,\phi) \propto \frac{e^{ikr}}{r} \Theta_{lm} e^{im_f\phi}$$



$$\Delta\phi_{m_f} = \frac{m_f}{R_{nn,\parallel} k_\parallel}$$

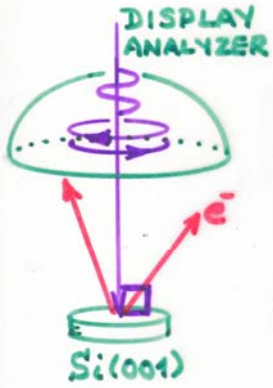
$$\overline{m_f} \approx m_{f,\max}$$

DAIMON ET AL.
JPN. J. APPL. PHYS.
32, L1480('93)

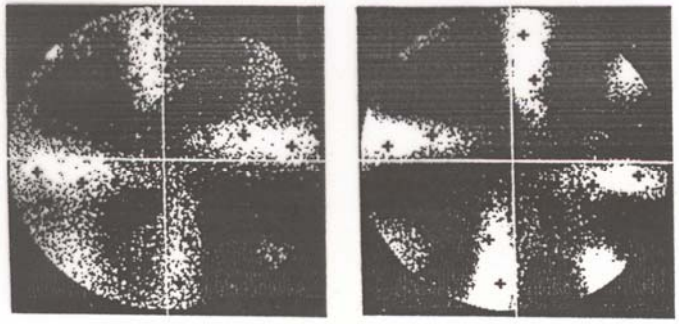
CIRCULAR DICHROISM - NON-MAGNETIC SYSTEMS

Si2p -- 250eV = E_{kin}

EXPERIMENT



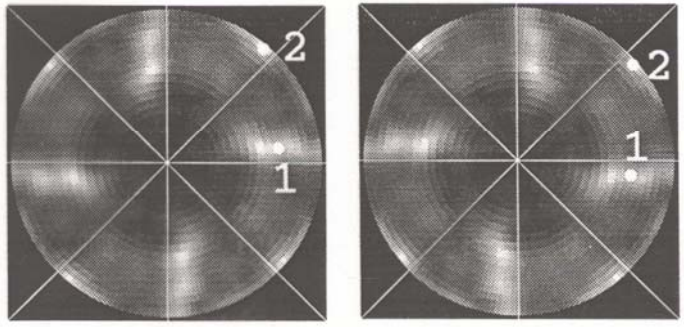
(a) LCP (b) RCP



DAIMON ET AL.
JPN. J. APPL. PHYS.
32, L1480 ('93)

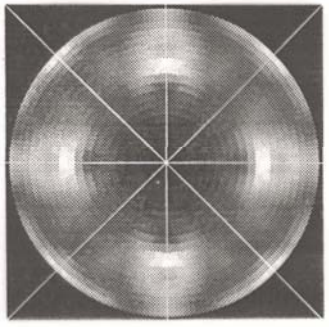
THEORY

(c) LCP (d) RCP



KADUWELA ET AL.
P. R. B 50, 6203 ('94)

(e) UNPOLARIZED



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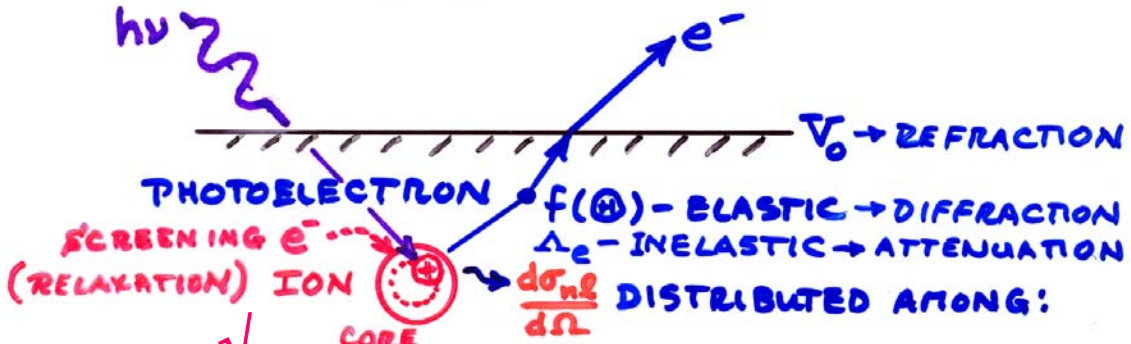
- Spin-orbit splitting, the Fano effect, and spin-polarized outgoing electrons
- Magnetic circular dichroism (MCD) in core-level emission
- Non-magnetic circular dichroism in core-level emission: a.k.a. circular dichroism in angular distributions (CDAD)
- Various other final state effects providing information in core-level spectra

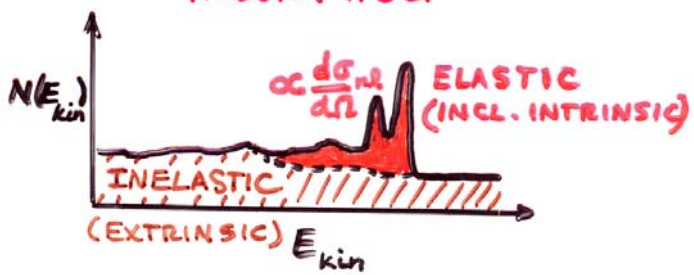


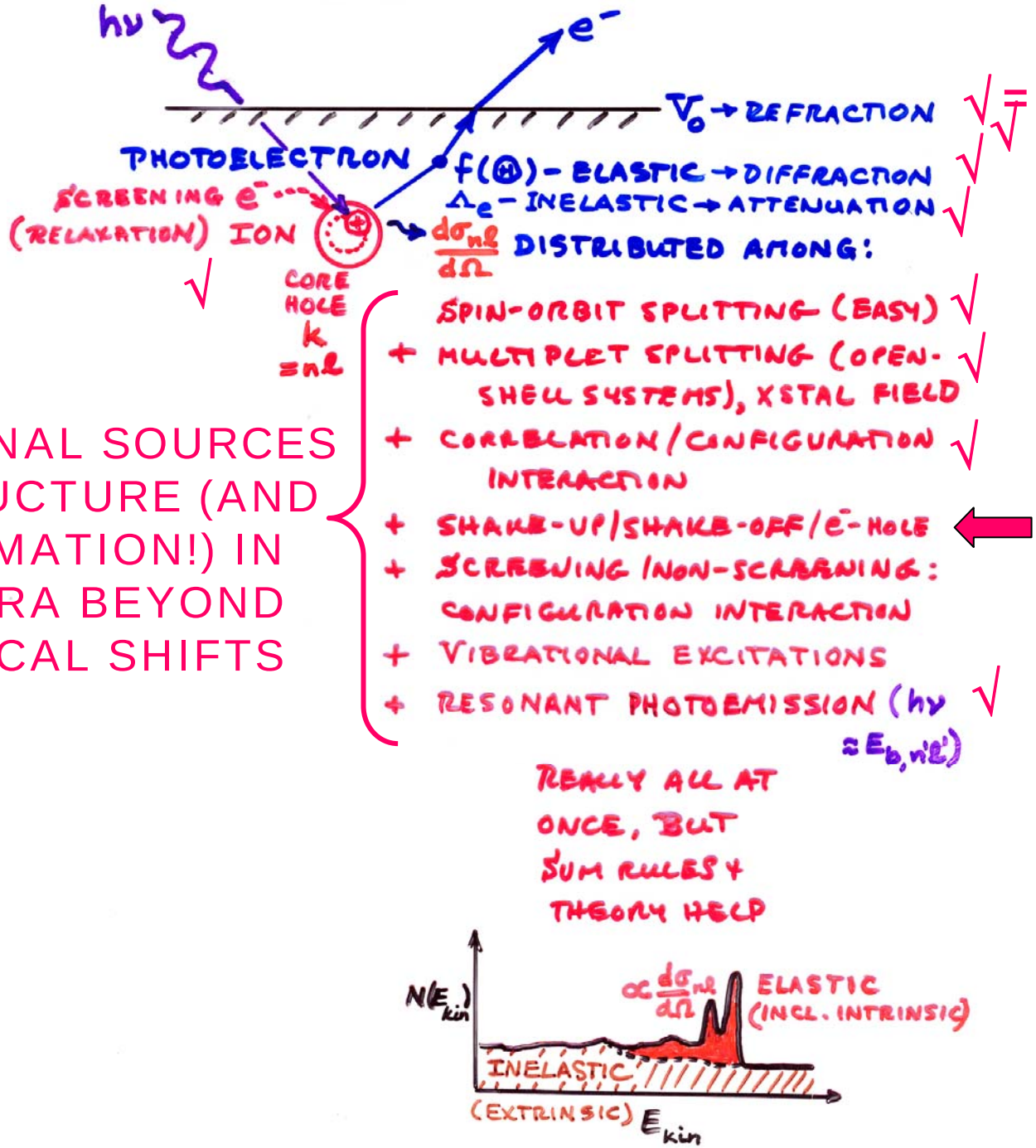
√ = covered so far

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 ($h\nu \approx E_{b,n'l'}$) √

REALLY ALL AT ONCE, BUT SUM RULES + THEORY HELP





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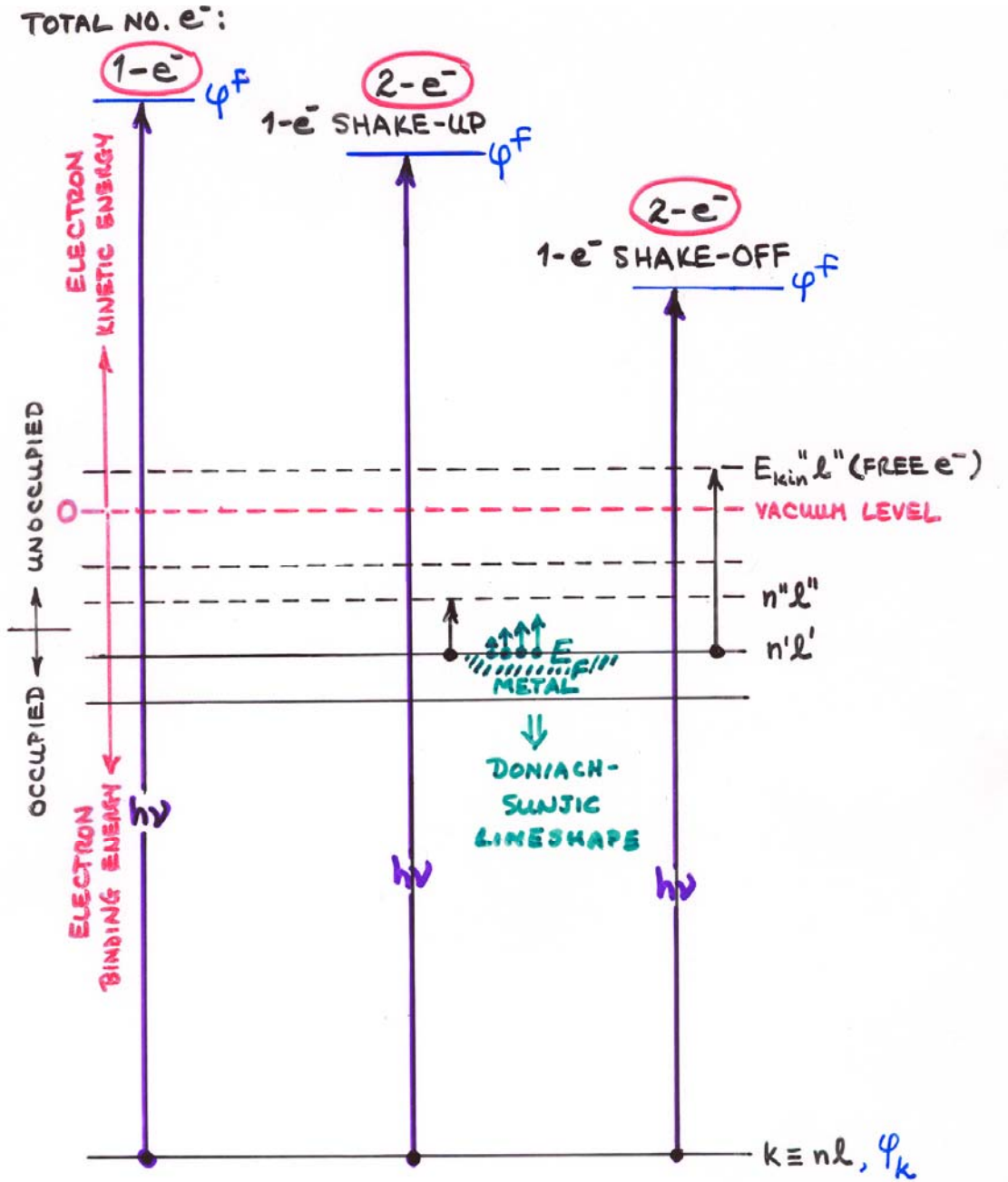


MULTIELECTRON EFFECTS IN CORE EMISSION

INTENSITIES IN PHOTOELECTRON SPECTRA:

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

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

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

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

- SUDDEN APPROXIMATION: $\Psi_K \rightarrow \Psi_f = \text{PHOTO}e^-$ (FAST)

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

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

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

↳ NORMAL $\dfrac{d\sigma_K}{d\Omega}$

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

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

$$\text{INT.}_K \propto |\langle \Psi^f_{VIB,v'} | \Psi^i_{VIB,v} \rangle|^2 |\langle \varphi_1' | \varphi_1 \rangle|^2 |\langle \varphi_2' | \varphi_2 \rangle|^2 \cdots$$
$$|\langle \varphi_{K-1}' | \varphi_{K-1} \rangle|^2 |\langle \varphi_{K+1}' | \varphi_{K+1} \rangle|^2 \cdots |\langle \varphi_N' | \varphi_N \rangle|^2 \cdot$$
$$|\hat{e} \cdot \langle \varphi_f | \vec{r} | \varphi_K \rangle|^2$$

1e- DIPOLE → $d\sigma/d\Omega$

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

- PLUS DIFFRACTION EFFECTS IN φ_f ESCAPE

NEON 1s SHAKE-UP / SHAKE-OFF:

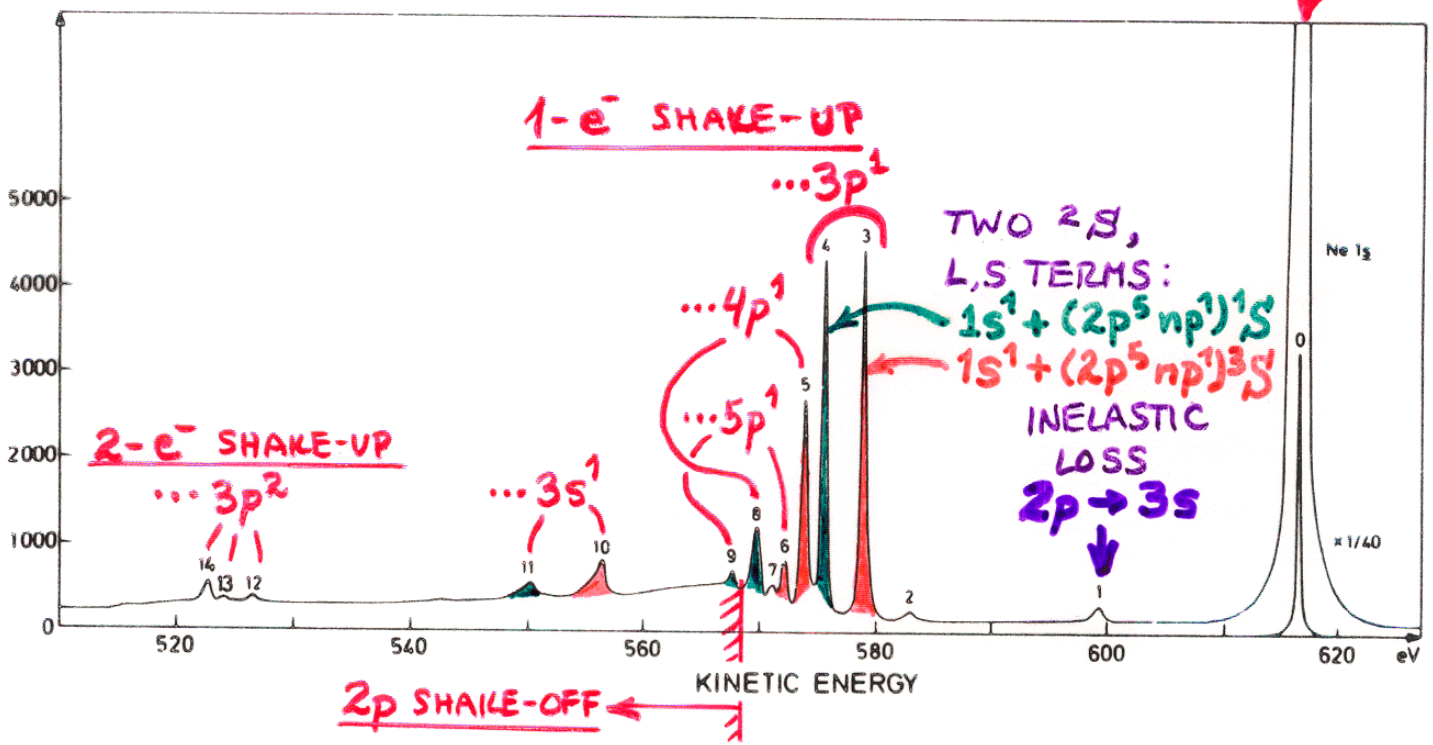
$Ne\ 1s^2 2s^2 2p^6\ {}^1S \xrightarrow{-e^-} Ne^+\ 1s^1 2s^2 2p^6\ {}^2S$

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

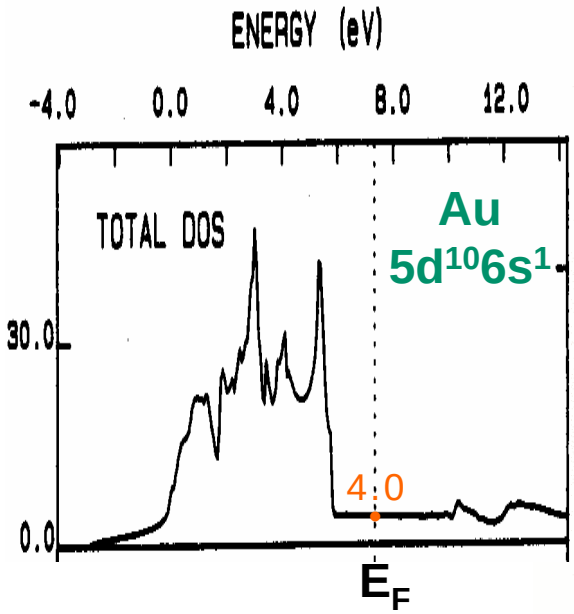
"Basic Concepts of XPS"
Figure 36

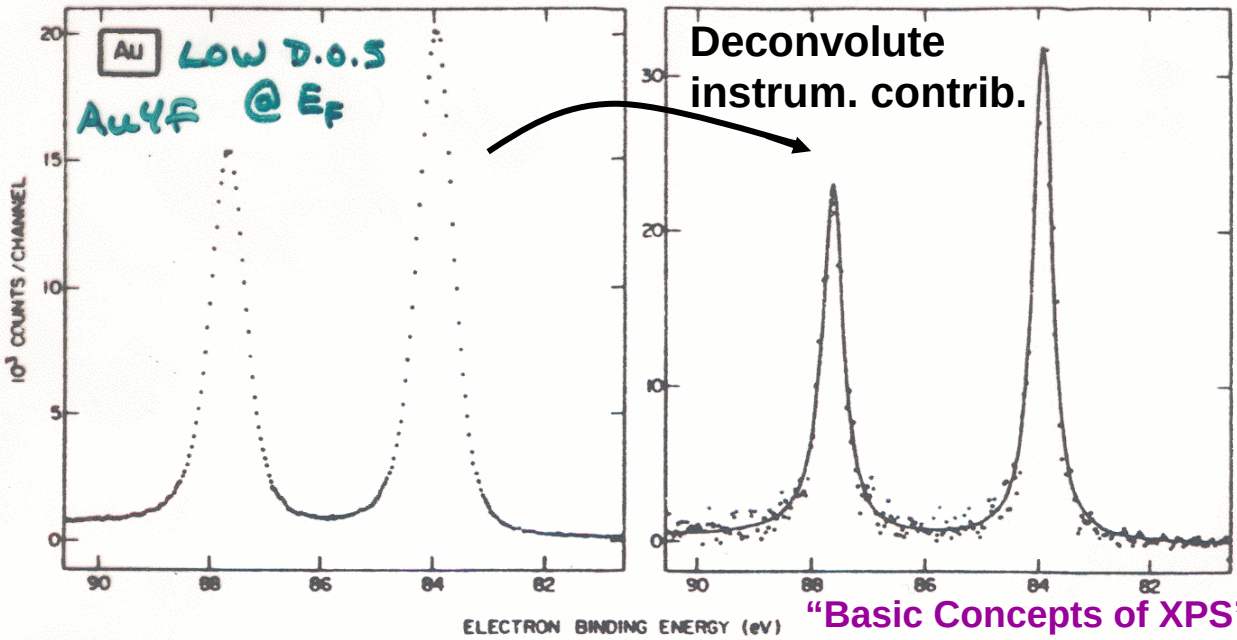


OVERALL: ~12% SHAKE-UP + 16% SHAKE-OFF ≈ 28% OF EVENTS

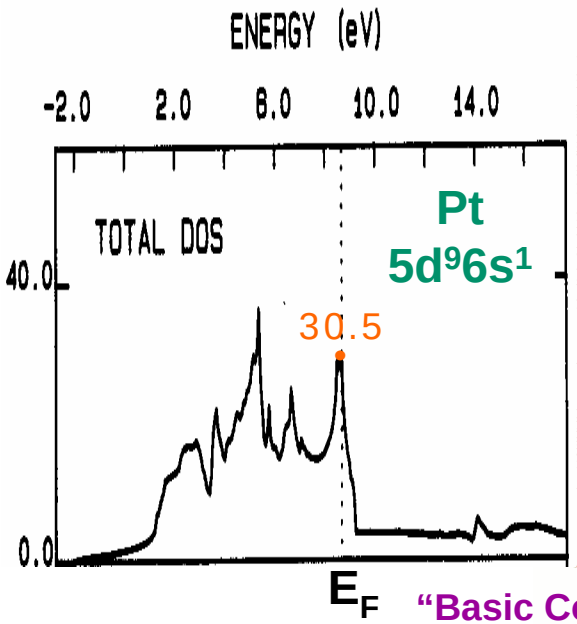
BAND THEORY—D.O.S:

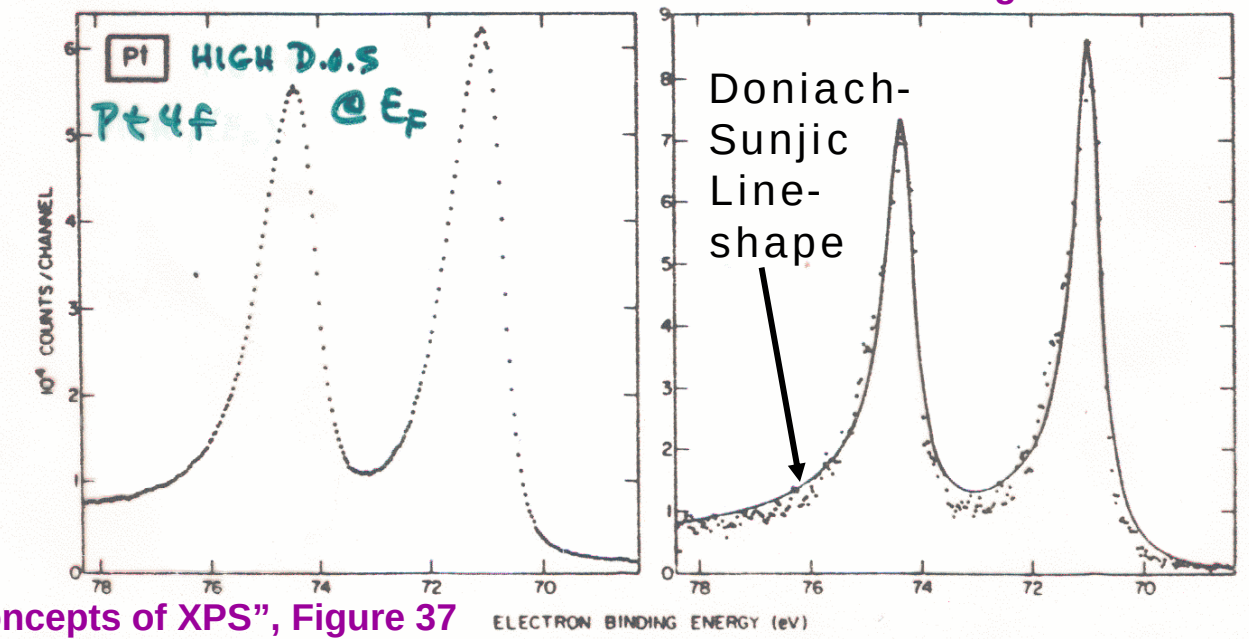
ELECTRON-HOLE EXCITATIONS IN METALS:



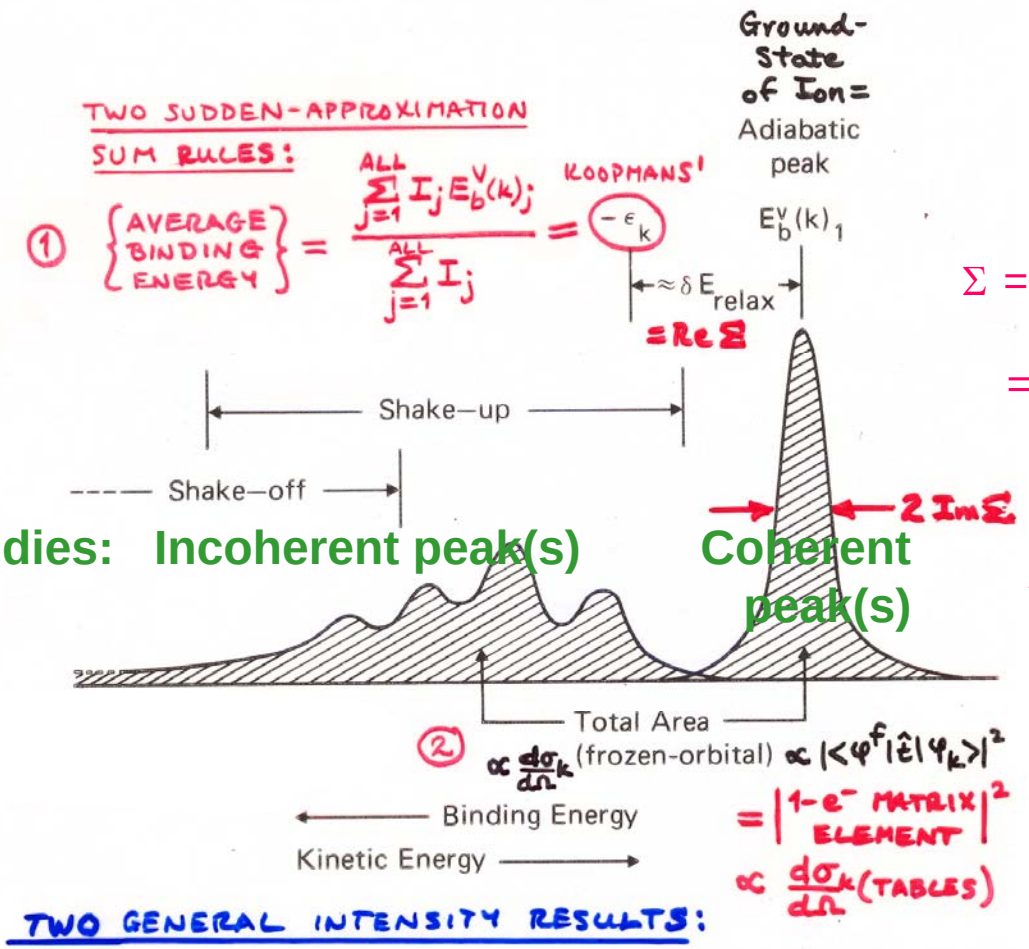


"Basic Concepts of XPS"
Figure 10





"Basic Concepts of XPS", Figure 37



TWO SUDDEN-APPROXIMATION SUM RULES:

① $\left\{\begin{matrix}\text{AVERAGE}\\ \text{BINDING}\\ \text{ENERGY}\end{matrix}\right\} = \dfrac{\sum_{j=1}^{ALL} I_j E_b^v(k)_j}{\sum_{j=1}^{ALL} I_j} = -\epsilon_k$ (KOOPMANS')

② $\propto \dfrac{d\sigma_k}{d\Omega}$(frozen-orbital) $\propto |\langle \varphi^f | \hat{\epsilon} | \varphi_k \rangle|^2$ $= |1\text{-}e^-$ MATRIX ELEMENT$|^2$ $\propto \dfrac{d\sigma_k}{d\Omega}$(TABLES)

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

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

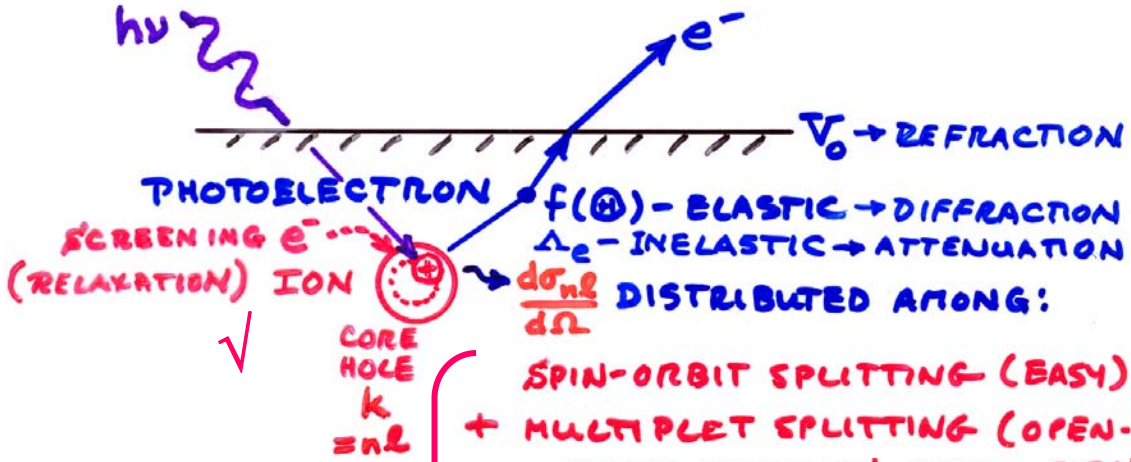
In valence-band studies: Incoherent peak(s) Coherent peak(s)

TWO GENERAL INTENSITY RESULTS:

① $I_j \propto |\langle \varphi^f(1) | \hat{\epsilon} | \varphi_k(1) \rangle|^2 |\langle \Psi^f(N-1,j) | \Psi_R(N-1) \rangle|^2$ (k e^- MISSING)

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 $(E_b(k)_1 \equiv E_b(K=1))$.

② (TOTAL SHAKE-UP + SHAKE-OFF) $= 1 - |\langle \Psi^f(N-1,1) | \Psi_R(N-1) \rangle|^2$ $\approx$ 15-25 % FOR ATOMS/MOLEC.



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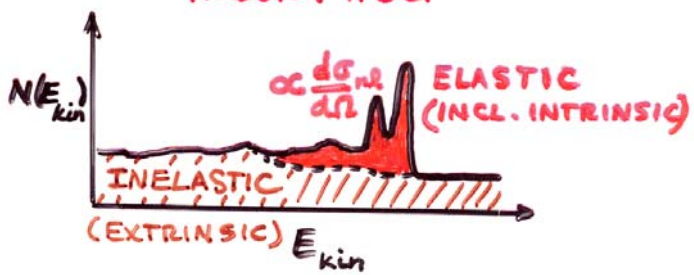
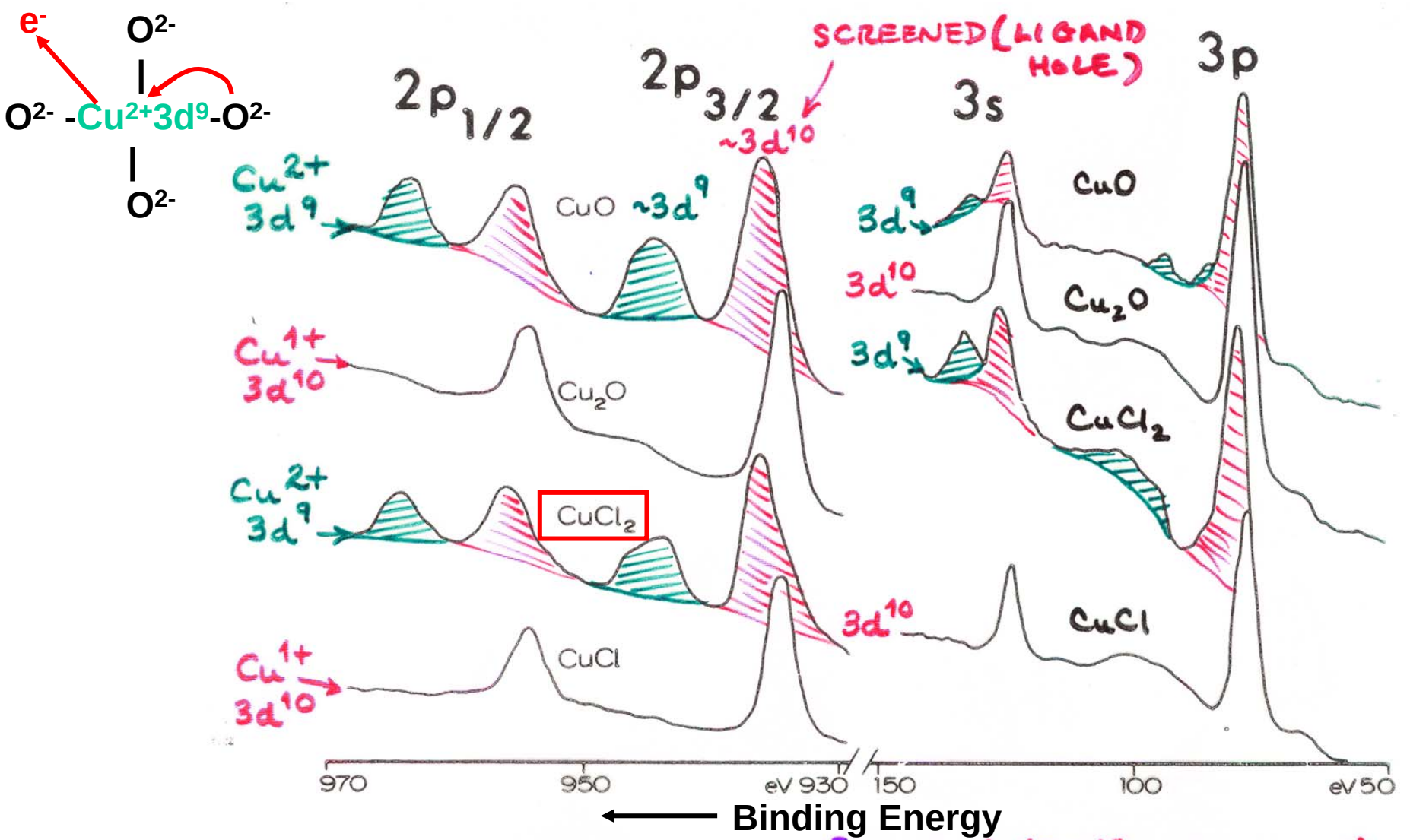
- + MULTIPLET SPLITTING (OPEN-SHELL SYSTEMS), XSTAL FIELD √
- + CORRELATION / CONFIGURATION INTERACTION √
- + SHAKE-UP / SHAKE-OFF / e^--HOLE √
- + SCREENING / NON-SCREENING: CONFIGURATION INTERACTION ⬅
- + VIBRATIONAL EXCITATIONS
- + RESONANT PHOTOEMISSION ($h\nu \approx E_{b,n'l'}$) √

REALLY ALL AT ONCE, BUT SUM RULES + THEORY HELP



SATELLITES & CHARGE-TRANSFER SCREENING



ACTUAL FINAL STATE $\Psi \approx C_1\Phi_1$ (3d10 - SCREENED)
$+ C_2\Phi_2$ (3d9 - UNSCREENED)

"Basic Concepts of XPS"
Figure 38

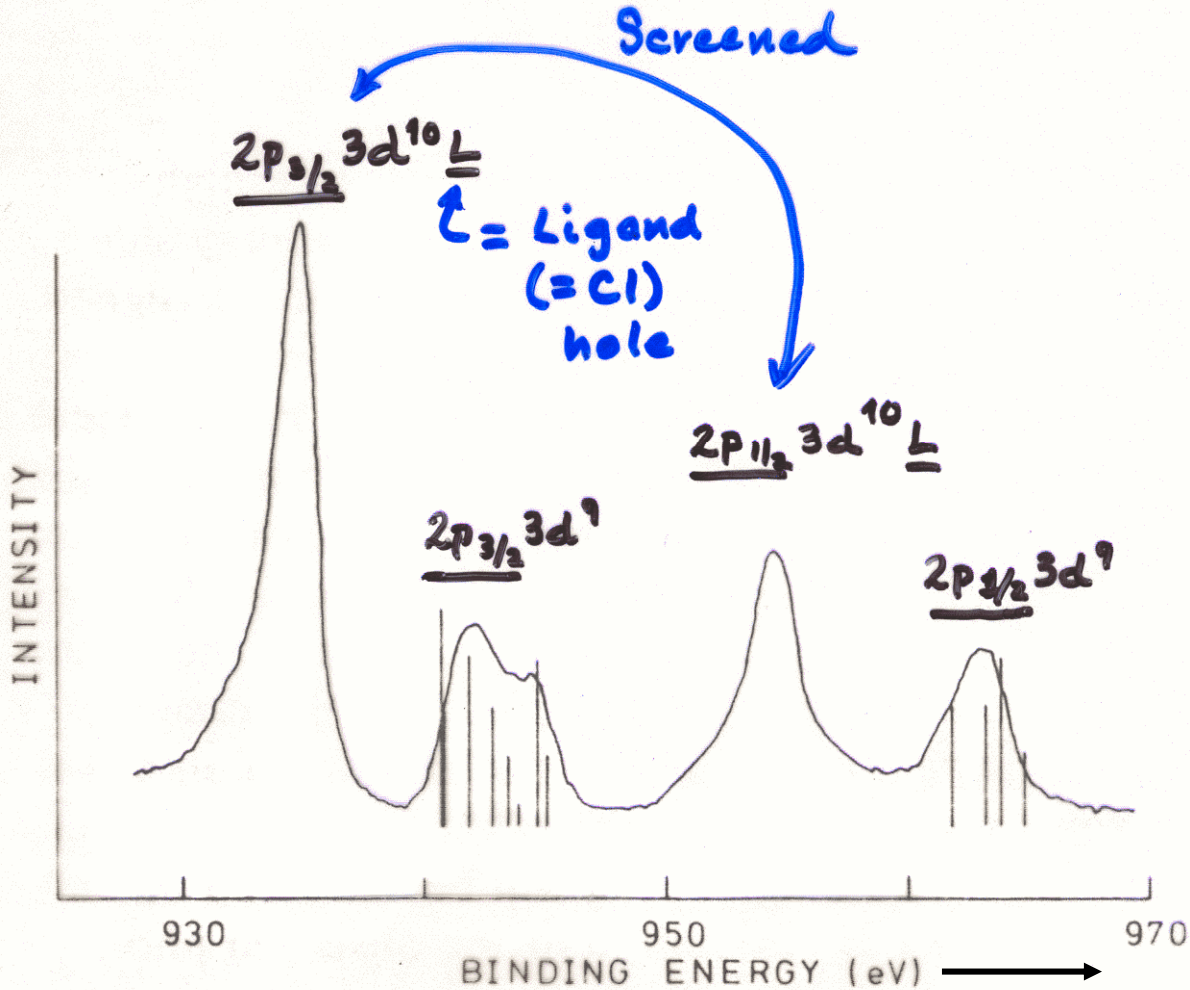


FIG. 2. The Cu $2p$ spectrum of $CuCl_2$ together with the expected multiplet splittings, represented by bars, for the $\underline{2p}3d^9$ level as calculated and discussed in the text.

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

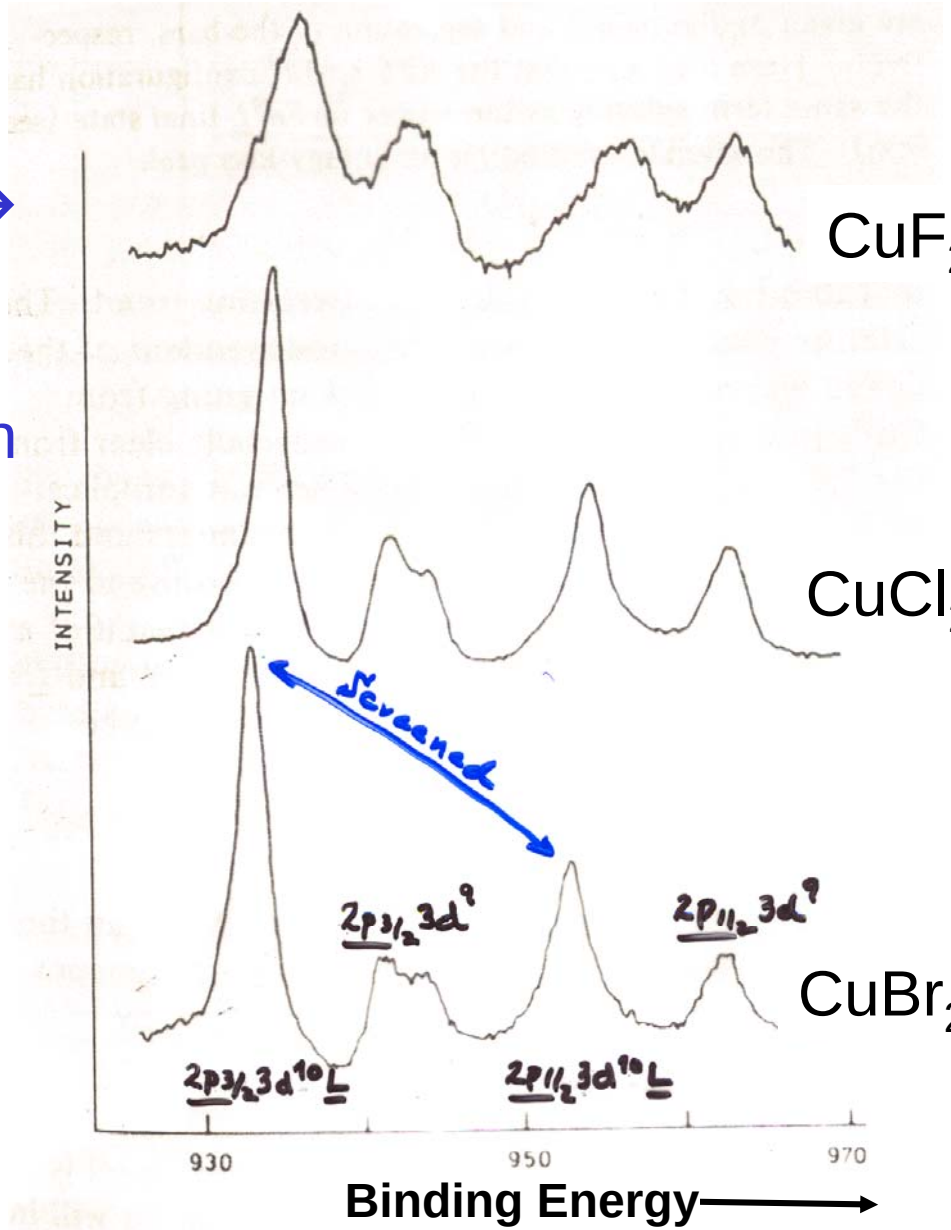


FIG. 1. Cu 2*p* photoelectron spectra of Cu dihalides. The lines leading to a final state with a ligand hole ($\underline{L}$) show a chemical shift.

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

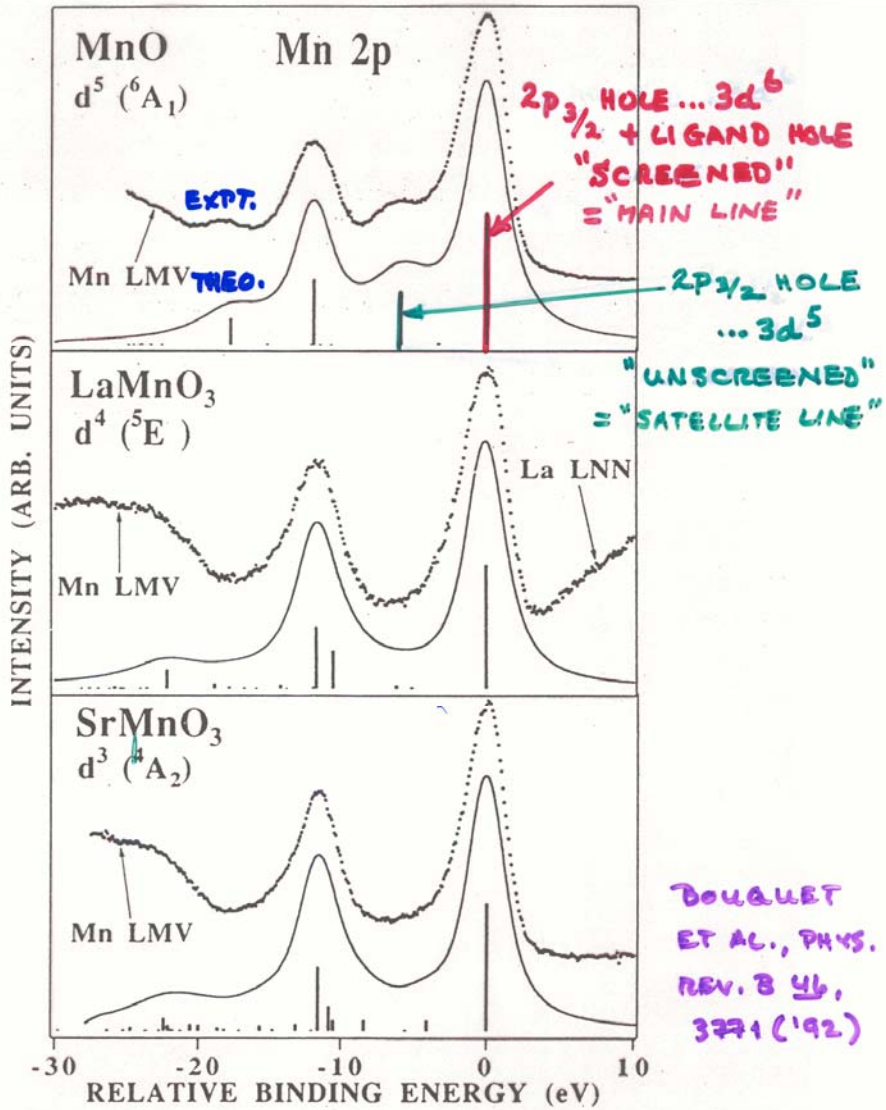
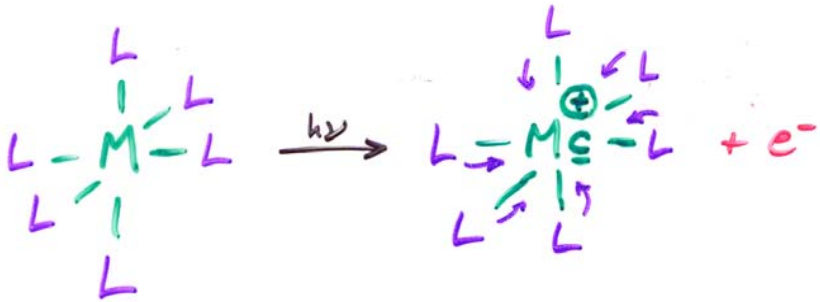


FIG. 1. Theoretical $2p$ core-level XPS spectra (solid line) compared with experimental data (dots) after background subtraction for Mn cations with varying valence. Emission due to the Mn *LMV* Auger peak is observed on the high-binding-energy side of the $2p_{1/2}$ spin-orbit peak, partially obscuring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

CONFIGURATION INTERACTION APPROACH TO SCREENING IN TRANSITION-METAL (RARE-EARTH) COMPOUNDS:

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



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

$\underline{L}$ = VALENCE (π) 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 = d-d COULOMB REPULSION ENERGY
$= E(d^{n-1}) + E(d^{n+1}) - 2E(d^n)$

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

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

WITH INTENSITIES FROM SUDDEN APPROX.

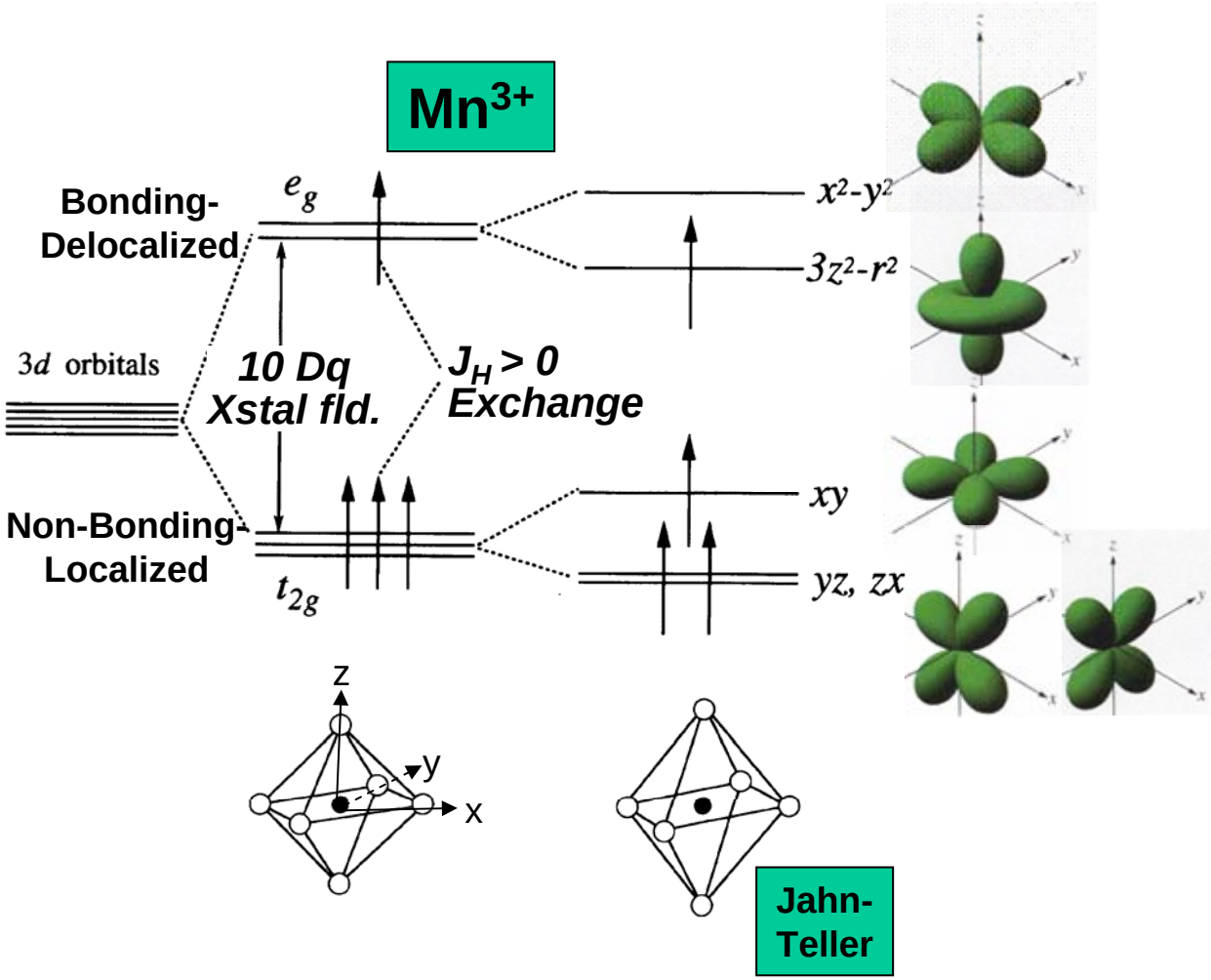
AS:

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

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

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

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



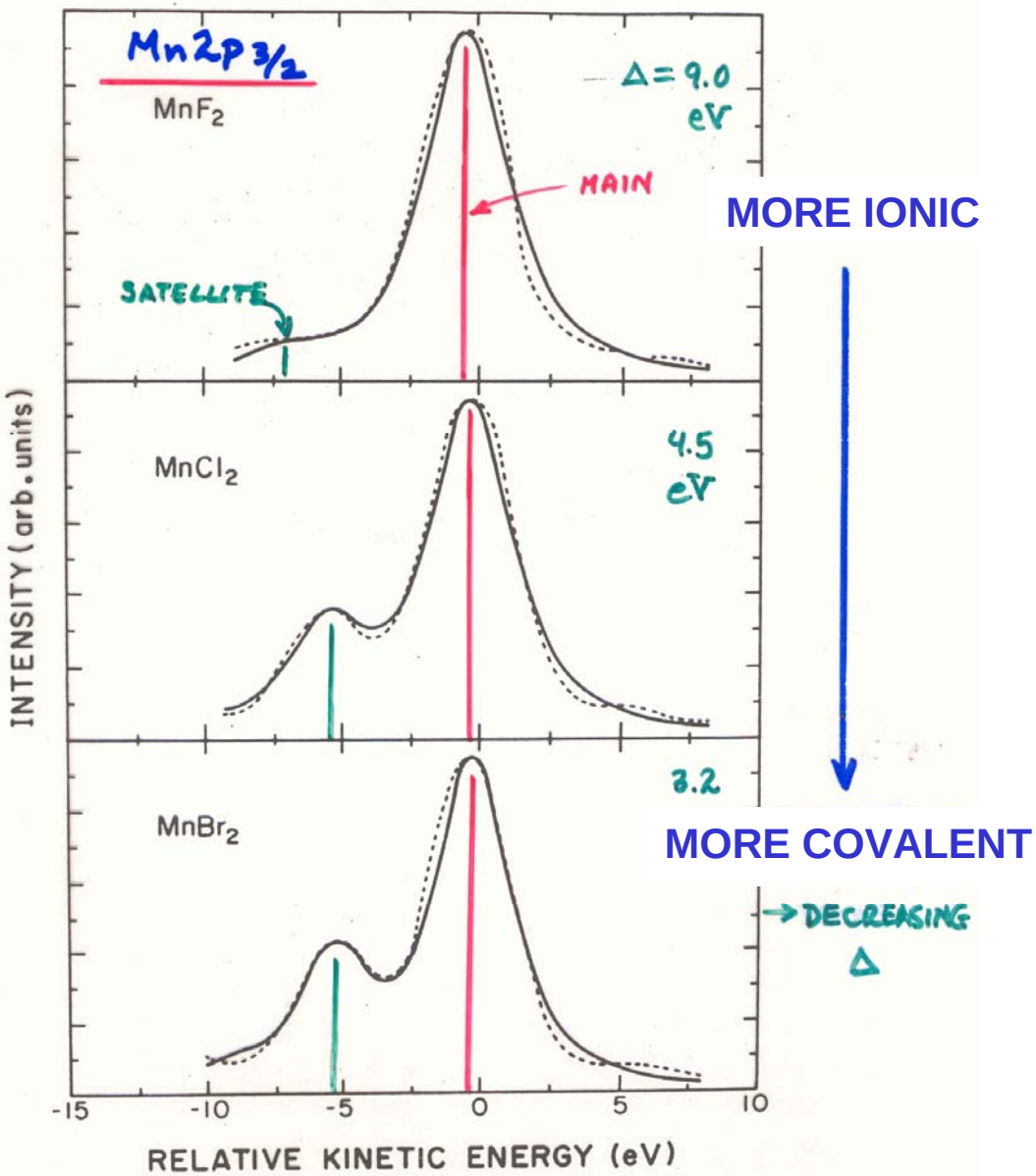
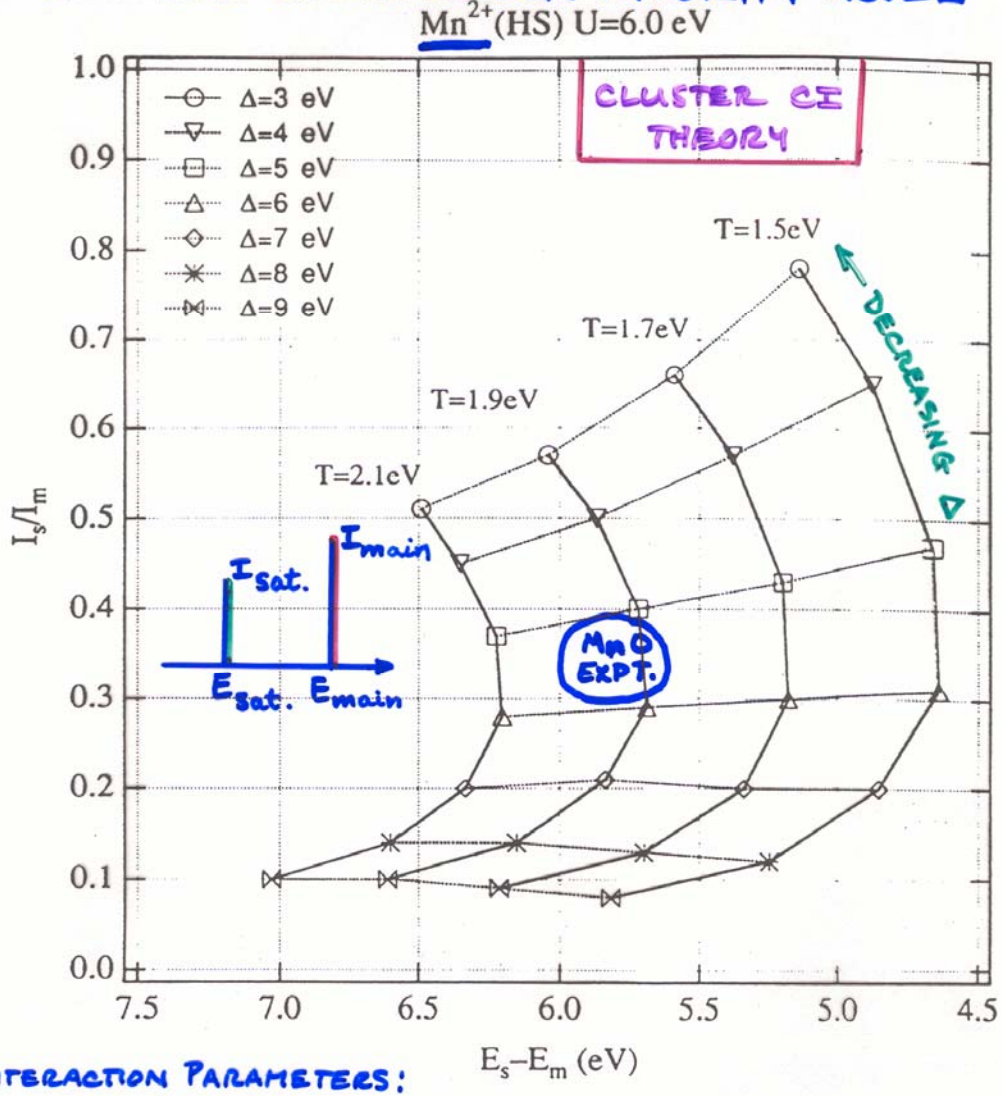


FIG. 6. Fits of the cluster model results with the experimental $2p_{3/2}$ spectra of the manganese dihalides. The parameters used are listed in Table II. A Lorentzian broadening is 2.6–3.0 eV, and a Gaussian broadening of 1.2 eV (FWHM) was used.

ANALYSIS VIA ANDERSON IMPURITY MODEL



INTERACTION PARAMETERS:

U = 3d-3d COULOMB REPULSION ENERGY

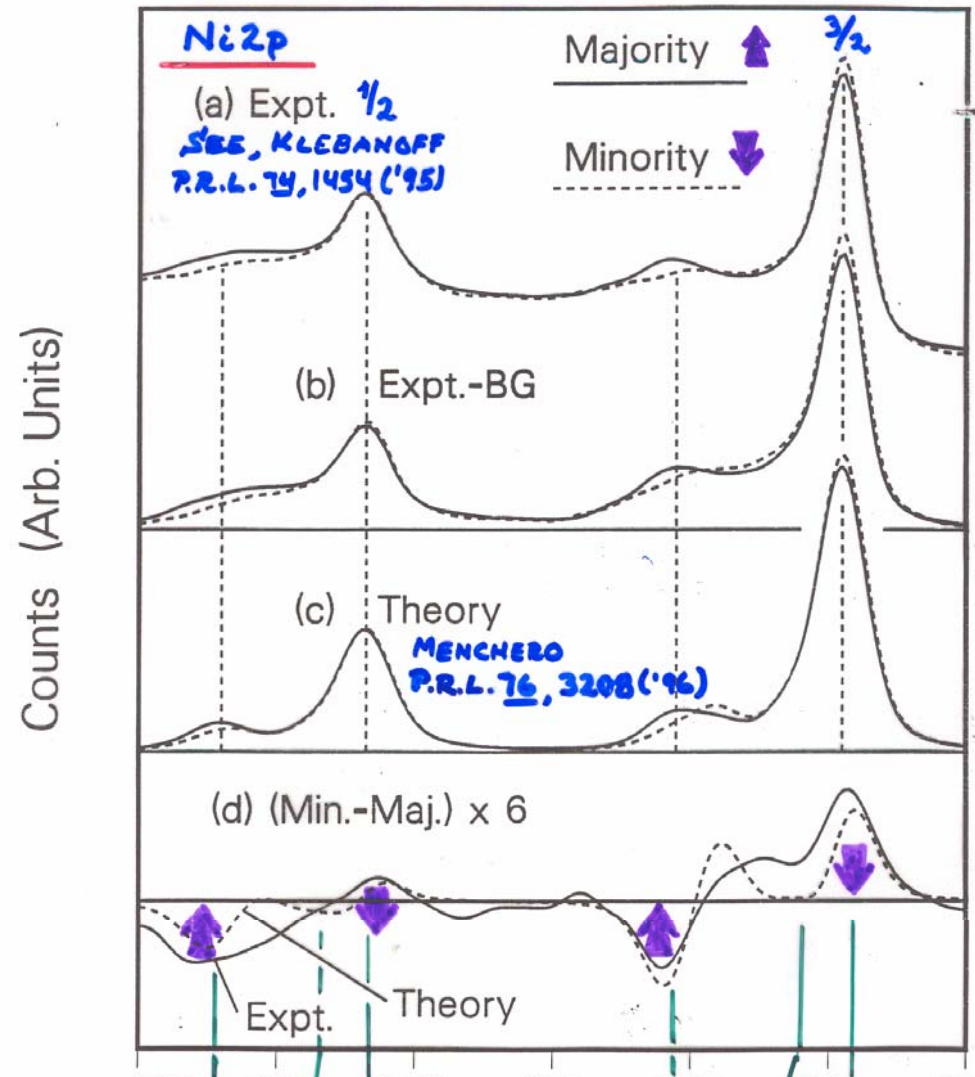
Δ = LIGAND-TO-METAL CHARGE TRANSFER ENERGY

T = LIGAND p — METAL 3d HYBRIDIZATION ENERGY

Q = CORE HOLE-3d COULOMB

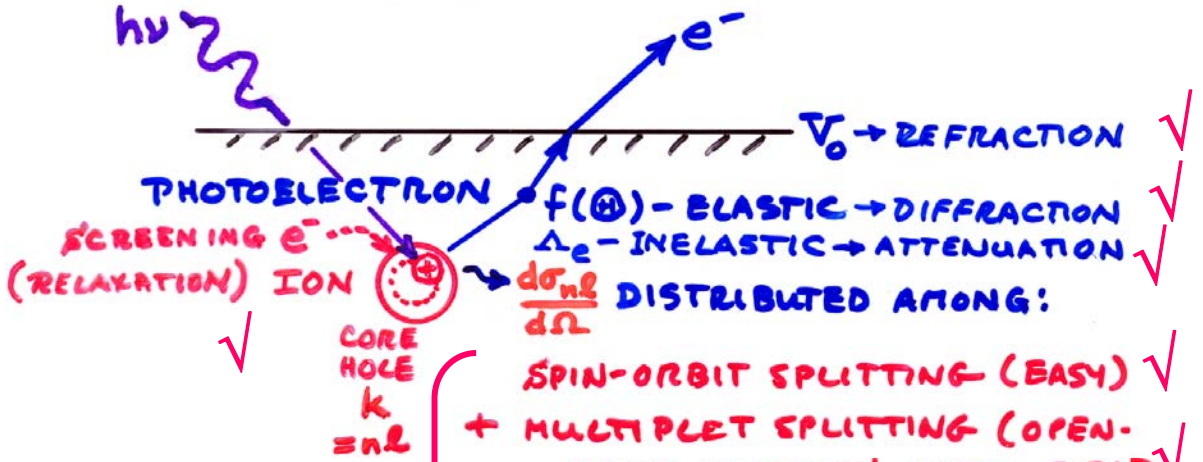
DOUGUET ET AL., J. EL. SP. 82, 87 (1996)

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%}



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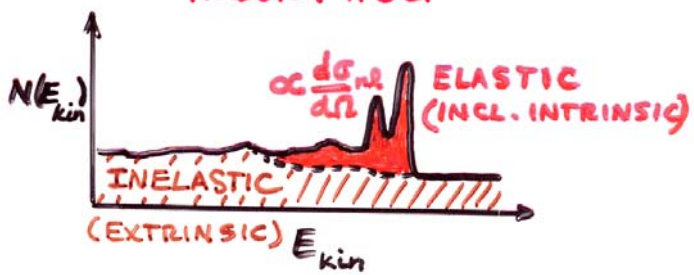
REALLY ALL AT ONCE, BUT SUM RULES + THEORY HELP



INTENSITIES IN PHOTOELECTRON SPECTRA:

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

- 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: $\Psi_K \rightarrow \Psi_f$ = 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)

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

(k MISSING)

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

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

↳ NORMAL $\frac{d\sigma_K}{d\Omega}$

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

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

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

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

1e- DIPOLE → $d\sigma/d\Omega$

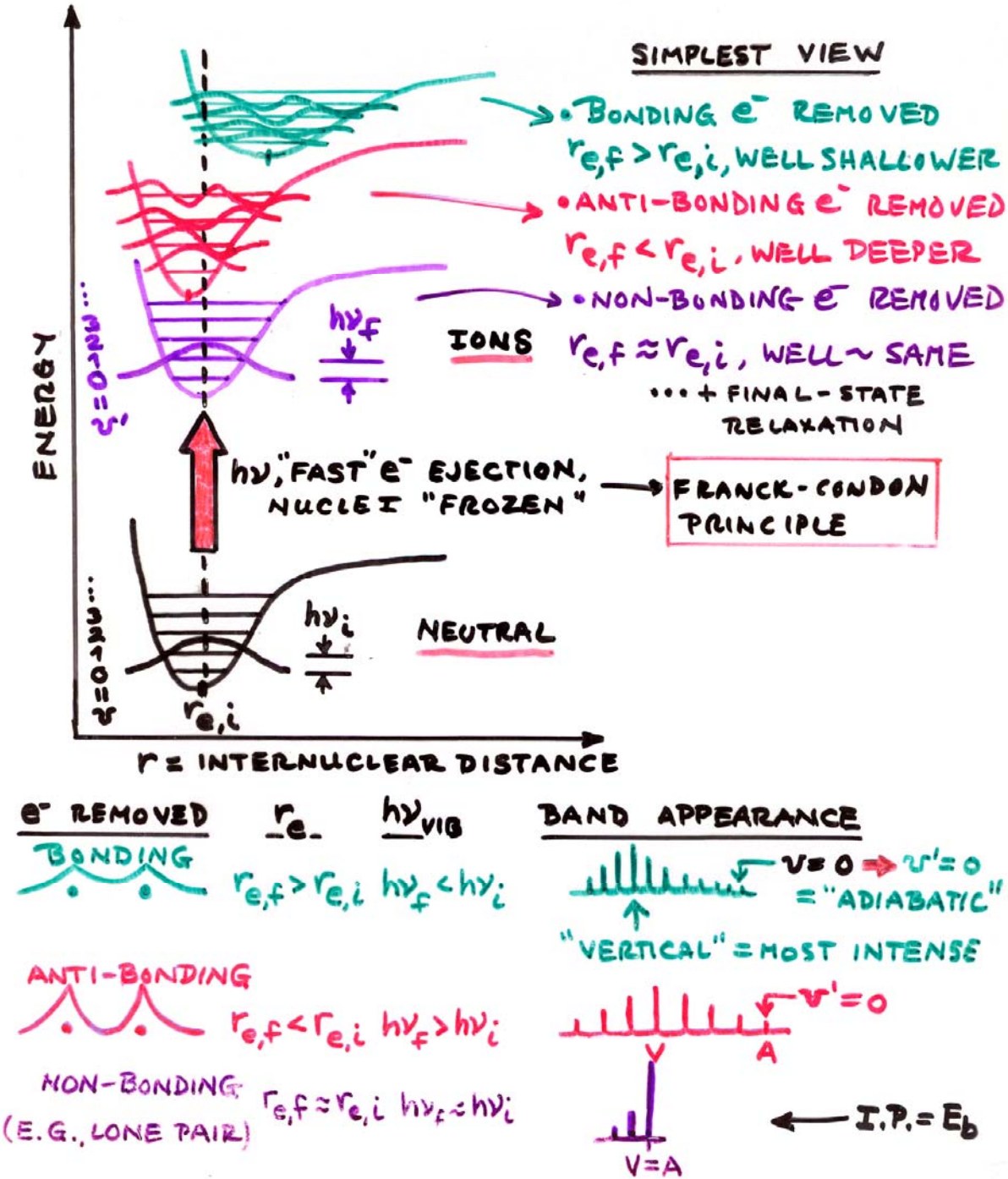
$(N-1)e^-$ SHAKE-UP/ SHAKE-OFF → "MONOPOLE"

- PLUS DIFFRACTION EFFECTS IN ψ_f ESCAPE

VIBRATIONAL STRUCTURE IN VALENCE-LEVEL (MO) SPECTRA

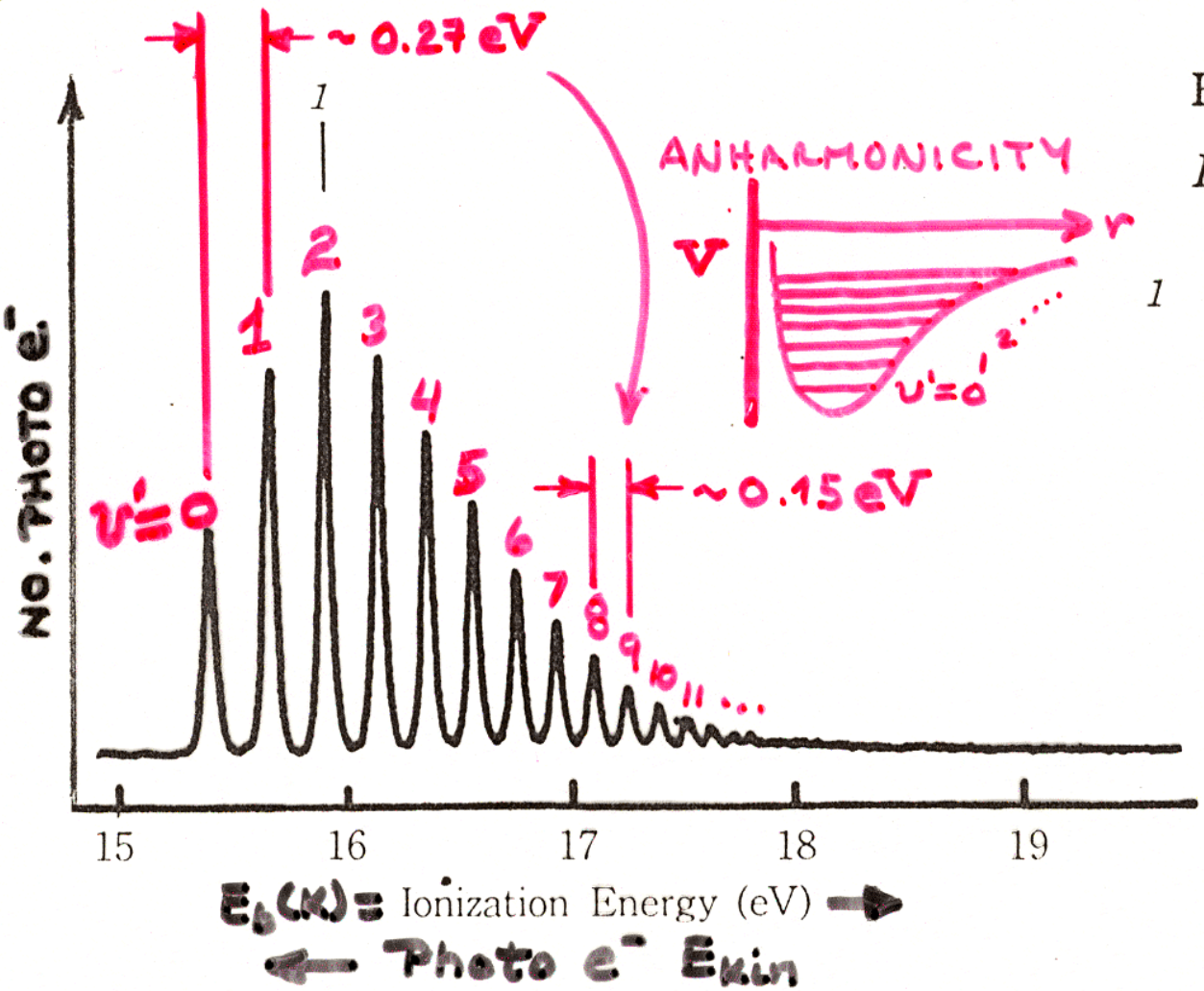
Diatomic A-B example

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



VIBRATIONAL STRUCTURE IN VALENCE-LEVEL (MO) SPECTRA

H_2 Hydrogen

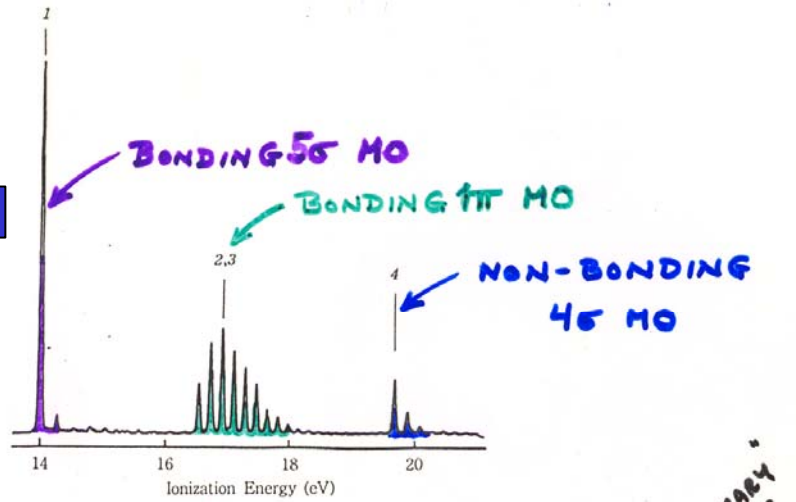


	Exptl.[a] I_v (eV)
1	15.98

(9) **CO** Carbon Monoxide

UV PHOTOELECTRON SPECTRUM OF CO

Vibrational fine structure

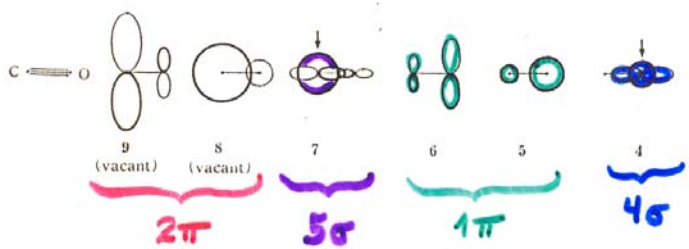


KOOPMANS' — CI FINAL STATE — "PRIMARY HOLES"

	Exptl.[a]	SCF MO [6-31 G][b]			CI (Ionic State) [6-31 G][c]		
	I_v(eV)	$-\varepsilon$(eV)	MO	Character	E(eV)	State	Configuration
1	14.01	14.99	5σ (7)	σ_{CO}	13.11	$1^2\Sigma^+$	$0.93(7^{-1})$ $-0.15(6^{-1},7^{-1},9^1)_a$ $-0.15(5^{-1},7^{-1},8^1)_a$
2	16.91	17.48	1π (6, 5)	π_{bond}	16.69	$1^2\Pi$	$0.95(6^{-1})$; $0.95(5^{-1})$
3	16.91	17.48					
4	19.72	21.69	4σ (4)	n_O	19.29	$2^2\Sigma^+$	$0.92(4^{-1})$ $+0.16(6^{-1},7^{-1},9^1)_a$ $+0.16(5^{-1},7^{-1},8^1)_a$

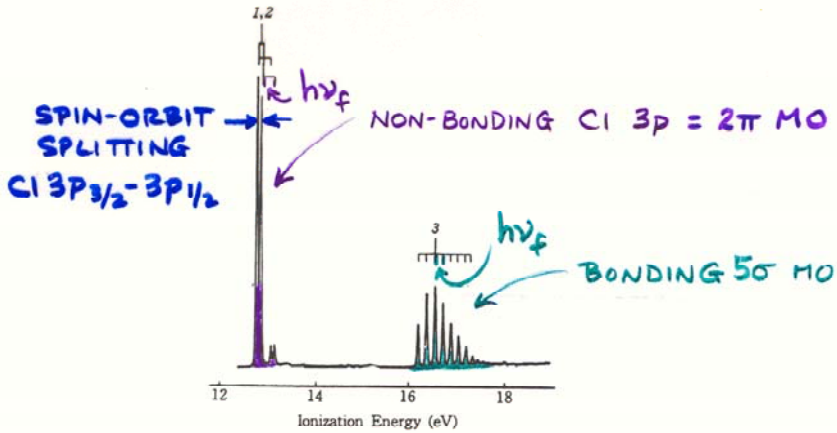
RELAX. + CORREL.

a) The spectrum : this work. The I_v's : Turner *et al.* (215). See also other works : Turner and May (215 a) ; Carlson and Jonas (54) ; Gardner and Samson (104) ; Edqvist *et al.* (90) ; Potts and Williams (182 a) ; and Natalis *et al.* (165).
b) We used the bond length reported (A 3) ; symmetry $C_{\infty h}$. $E_{SCF}=-112.6672$ hartree. In 4-31 G calculations, $E_{SCF}=-112.5524$ hartree and $-\varepsilon$(eV)=14.93, 17.41, 17.41, and 21.60.
c) CI-II. (9, 8)=1π. $|N\rangle=0.98$ (SCF). The results obtained in other CI levels are given in Appendix B.



Kimura et al., "Handbook of Hel Photoelectron Spectra"

THE UV PHOTOELECTRON SPECTRUM OF HCl



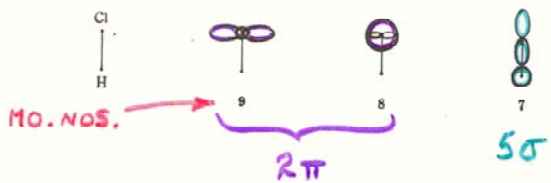
KOOPMANS' THEO. CONFIG. INT. ON FINAL STATE

	Exptl.[a]	SCF MO [4-31 G][b]			CI (Ionic State) [4-31 G][c]		
	I_v(eV)	$-\varepsilon$(eV)	MO	Charactor	E(eV)	State	Configuration
1	12.75	12.77	2π (9, 8)	π_{Cl}	11.97	$1^2\Pi$	0.98(9⁻¹) ; 0.98(9⁻¹)
2	12.85	12.77					
3	16.28	16.50	5σ (7)	σ_{HCl}	16.10	$1^2\Sigma^+$	0.98(7⁻¹)

CI HOLE

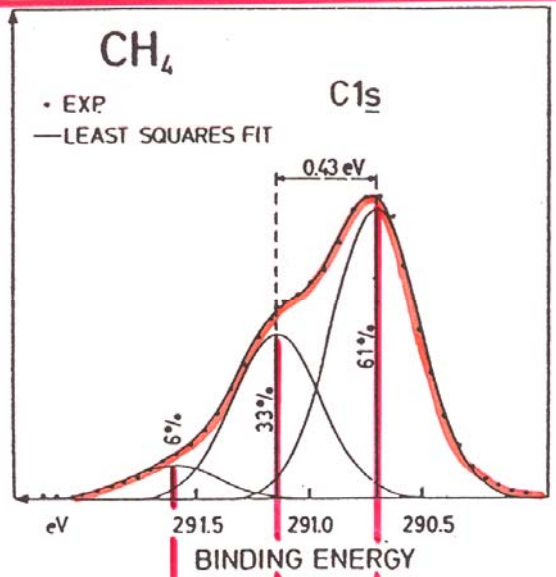
WEIGHTING

a) The spectrum : this work. The I_v's : Frost *et al.* (102). See also other works : Lempka *et al.* (150) ; Turner *et al.* (215) ; and Weiss *et al.* (224).
b) We used the bond length reported in Ref. (A 5) ; symmetry $C_{\infty h}$. E_{SCF} = −459.5631 hartree.
c) CI-V. $|N\rangle$=0.99 (SCF).
CI-V' : E(eV)=12.01 and 16.11.
CI-III : E(eV)=12.60 and 16.79.



(FROM KIMURA ET AL., "HANDBOOK OF He I PHOTOELECTRON SPECTRA OF FUND. ORGANIC MOLECULES")

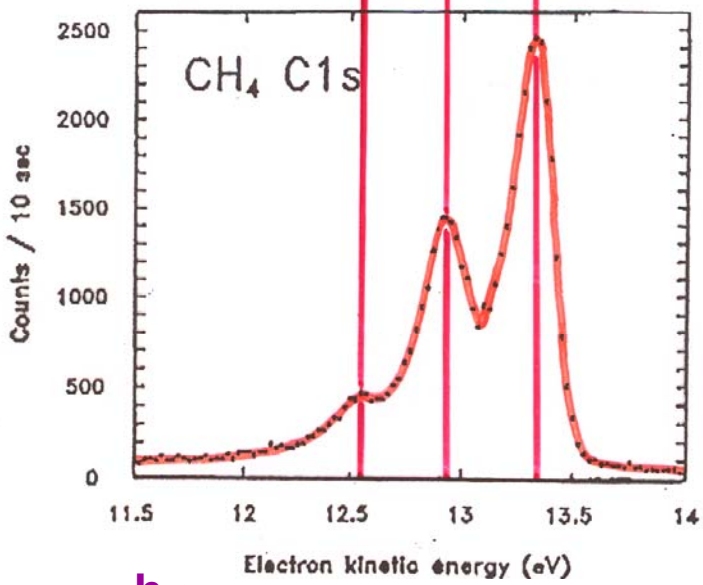
VIBRATIONAL FINE STRUCTURE IN CORE SPECTRA



MONOCHROMATIZED LABORATORY X-RAY SOURCE

1970 SIEGBAHN, GELIUS, ET AL.

"Basic Concepts of XPS"
Figure 40



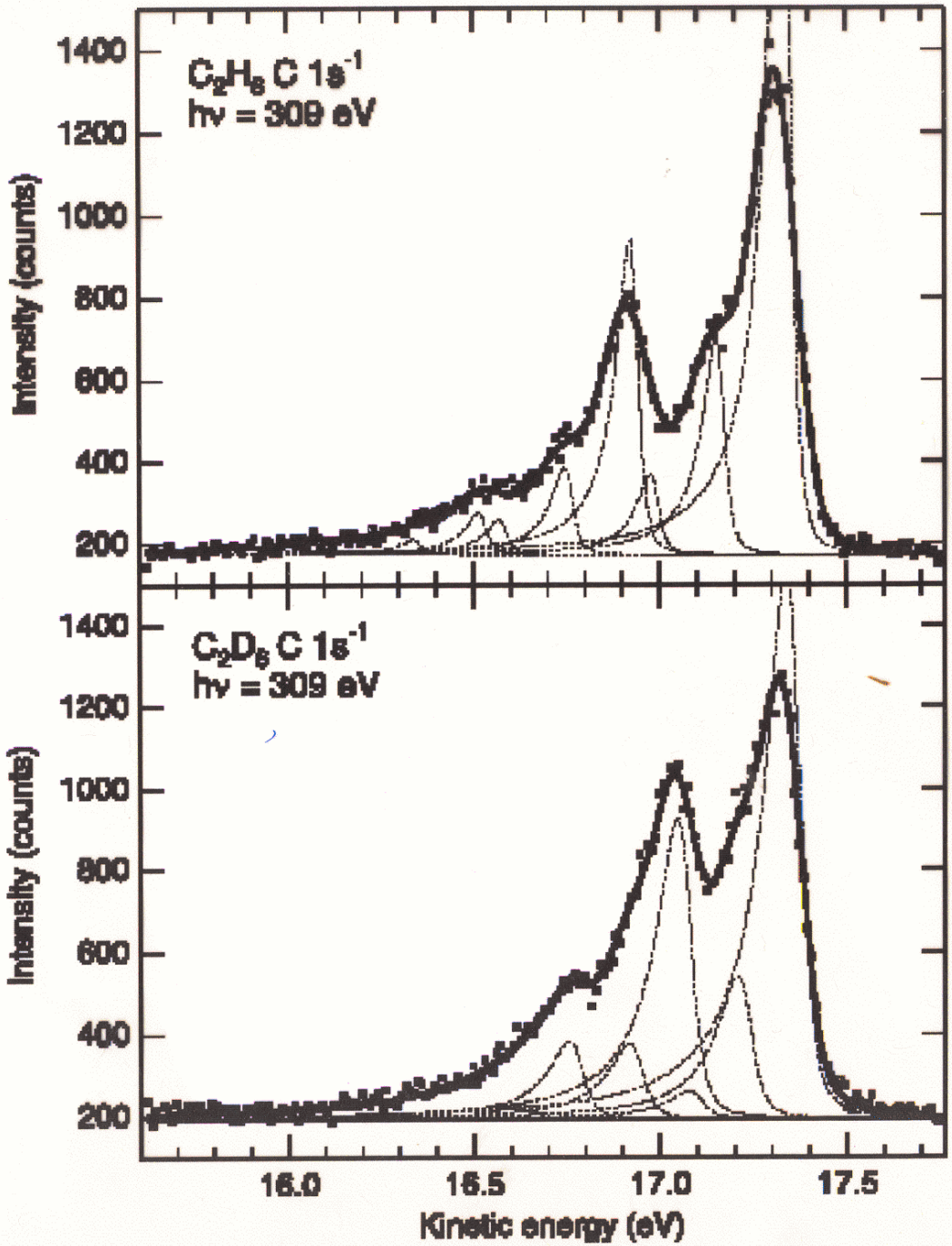
NEW SR BEAMLINE AT BROOK-HAVEN (~5-10X FASTER @ALS)

1991 BRADSHAW, KAINDL, ET AL.

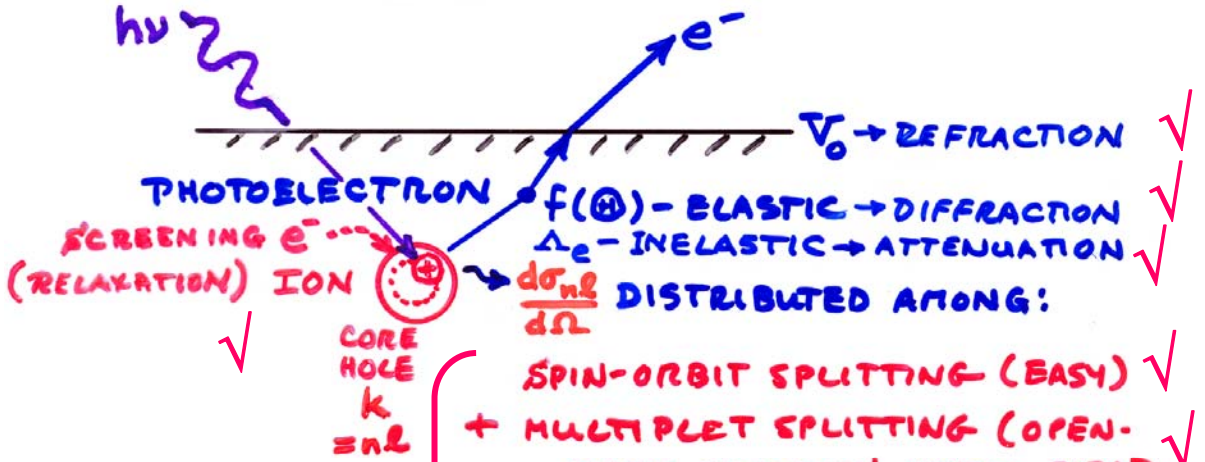
CH distance = 1.10 Å
NH distance = 1.00 Å
Equivalent-core

$$CH_4 \xrightarrow{h\nu} [C(1s\ hole)H_4]^{+*} + e^- \approx [NH_4]^+ + e^-$$

Vibrational fine structure in C 1s photoemission from ethane: two progressions v_a at 0.407 eV and v_b at 0.176 eV and various excitations (v_a ,v_b)



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

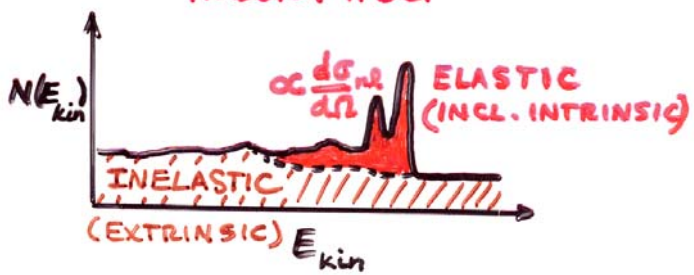


√ = covered so far

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 ($h\nu \approx E_{b,n'l'}$) √

REALLY ALL AT ONCE, BUT SUM RULES + THEORY HELP



Outline

Surface, interface, and nanoscience—short introduction

Some surface concepts and techniques→photoemission

Synchrotron radiation: experimental aspects

Electronic structure—a brief review

The basic synchrotron radiation techniques:
more experimental and theoretical details

Core-level photoemission

Valence-level photoemission

→ Microscopy with photoemission:
All of the above with lateral spatial resolution
of ca. 20 nm, going down to few nm in future
(Next lecturers)

Thank your for your attention!