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Advanced School on Synchrotron and Free Electron Laser Sources and their Multidisciplinary Applications

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Surface, interface, and nanoscience—short introduction

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Outline

Surface, interface, and nanoscience—short introduction

Some surface/interface concepts and techniques

Experimental aspects:
intro. to laboratory-based and SR-based

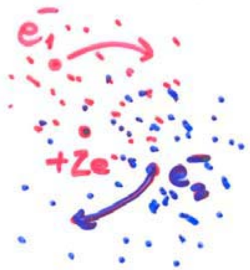
➡ Electronic structure—a brief review

The basic synchrotron radiation techniques:
more experimental and theoretical details

Core-level photoemission

Valence-level photoemission

What properties do wave functions of overlapping (thus indistinguishable) particles have?—electrons as example:



$\psi = \psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2)$, *including spin of both electrons*

But labels can't affect any measurable quantity.

E.g. – probability density :

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

Therefore

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

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

and eigenvalues of ± 1

Finally, all particles in two classes :

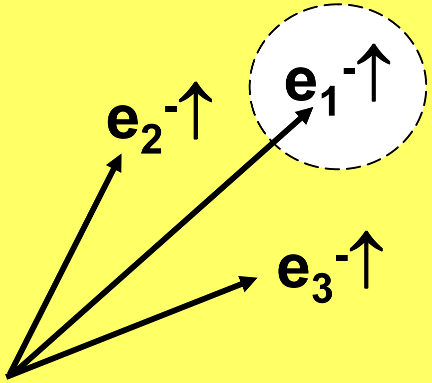
FERMIONS : (incl. e⁻'s) : ψ *antisymmetric*

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

BOSONS : (incl. photons) : ψ *symmetric*

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

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



→the Exchange Interaction

→Hund's 1st rule & magnetism

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

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

space: like 1s, 2s,…

spin: α(↑) or β(↓)

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

and also require orthonormality of one-electron orbitals

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

Minimize total energy→ Hartree-Fock equations:

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

with:

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

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

One-electron integral:

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

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

Two-electron coulomb integral:

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

Two-electron exchange integral:

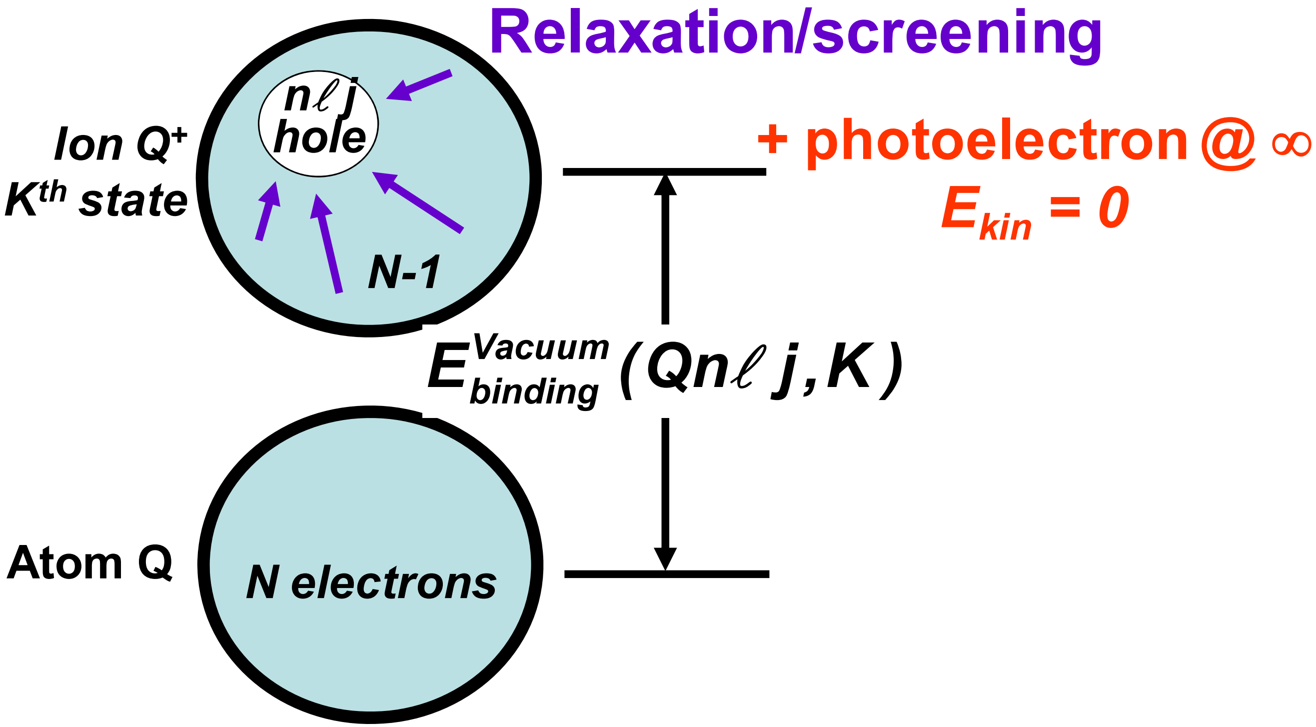
$$K_{ij} \equiv \left\langle \phi_i(\vec{r}_1) \middle| \hat{K}_j \middle| \phi_i(\vec{r}_1) \right\rangle = \iint \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\frac{1}{r_{12}}\phi_j(\vec{r}_1)\phi_i(\vec{r}_2)dV_1dV_2 \qquad (46)$$

Lowers energy—"attractive"

Basic energetics—Many e$^-$ picture

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

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



Relaxation/screening

Ion Q$^+$
Kth state

$n\ell j$
hole

N-1

+ photoelectron @ ∞
$E_{kin} = 0$

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

Atom Q

N electrons

What does the hole do?

BINDING ENERGIES + KOOPMANS' THEOREM:

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

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

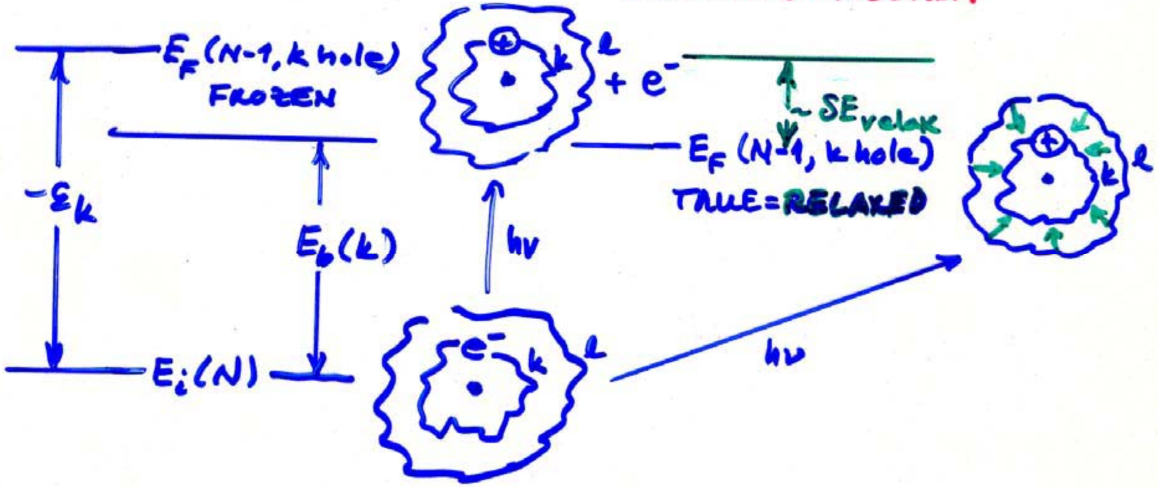
N 1-e⁻ HARTREE-FOCK EQNS.— $\hat{\mathcal{H}}(1)\varphi_k(1) = \varepsilon_k(1)\varphi_k(1)$

- COUPLED INTEGRO-DIFF.
- COULOMB + EXCHANGE

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

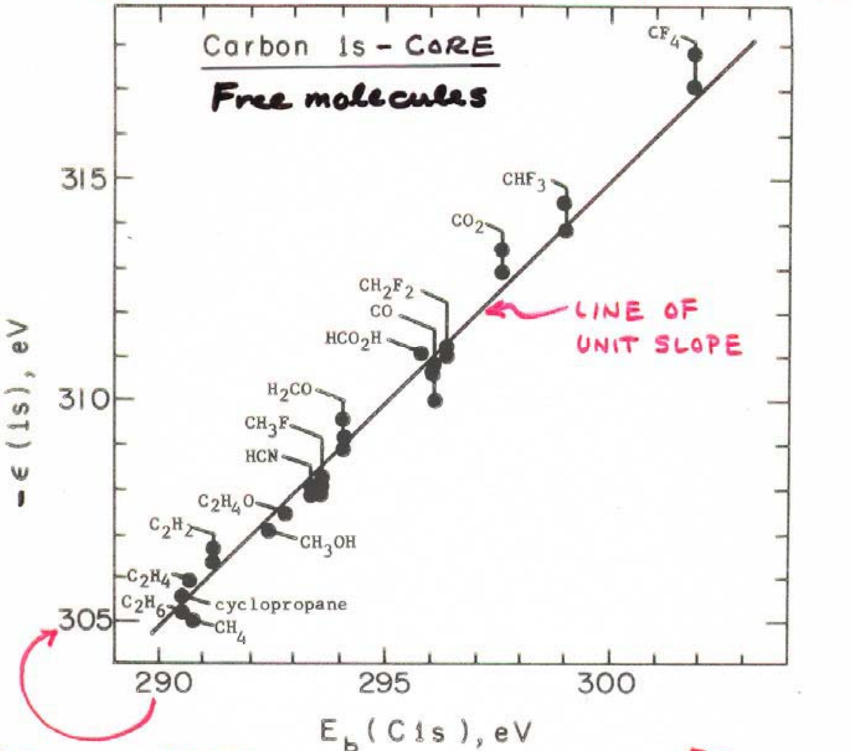
OR $E_b(k) = -\varepsilon_k$ IF $\varphi_{ki} = \varphi_{kf}$ (FROZEN ORBITAL)

KOOPMANS' THEOREM



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

KOOPMANS' THEOREM CALCULATION OF SHIFTS



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

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

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.)

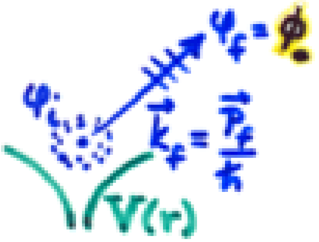
Paper [1]--"Basic
Concepts of XPS"
Figure 18

PHOTOELECTRON EMISSION-
BASIC MATRIX ELEMENTS + SELECTION RULES:

- ATOMIC-LIKE (LOCALIZED) STATES ⇒ CORE:

PLUS SPIN:

$$\varphi_i(\vec{r}) = \varphi_{n_i \ell_i m_i}(r,\theta,\phi) = R_{n_i \ell_i}(r) Y_{\ell_i m_i}(\theta,\phi) \begin{cases} \alpha(\sigma) = m_{si} = +\tfrac{1}{2} = \uparrow \\ \beta(\sigma) = m_{si} = -\tfrac{1}{2} = \downarrow \end{cases}$$



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

PHASE SHIFT OF ℓ_f WAVE IN V(r)

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

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

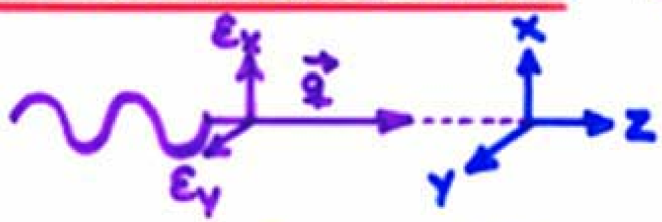
- $\Delta\ell = \ell_f - \ell_i = \pm 1$ TWO CHANNELS
- $\Delta m = m_f - m_i = 0, \pm 1$ LINEAR POLARIZ.
- $\Delta m = \pm 1$, CIRCULAR POLARIZATION

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

EQUIVALENT WITHIN CONSTANT FACTOR

$$\vec{r} \updownarrow \vec{p} \updownarrow \vec{\nabla} V(r)$$

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



LINEARLY POLARIZED –

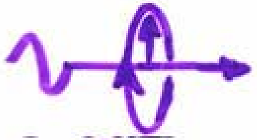
x: $\hat{\varepsilon}\cdot\vec{r} \Rightarrow x \Rightarrow \text{INT.}_x$

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

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

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

CIRCULARLY POLARIZED –



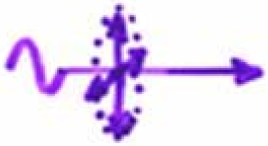
LEFT ≡ LCP: $\hat{\varepsilon}\cdot\vec{r} \Rightarrow x-iy \Rightarrow \text{INT.}_{LCP}$

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

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

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

UNPOLARIZED –



$$\text{INT.}_{UNP} = \text{INT.}_x + \text{INT.}_y$$
$$= \text{INT.}_{LCP} + \text{INT.}_{RCP}$$

Atomic orbitals:

COMPLEX, IF $m \neq 0$

TABLE 6.1

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

n	ℓ	m_ℓ	$\Phi_{m_\ell}(\phi)$	$\Theta_{\ell m_\ell}(\theta)$	$R_{n\ell}(r)$	$\psi_{n\ell m_\ell}(r,\theta,\phi)=\Phi_{m_\ell}\Theta_{\ell m_\ell}R_{n\ell}$
1	0 1s	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
2	0 2s	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1 $2p_0$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$
2	1 $2p_{\pm 1}$	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$
3	0 3s	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\, a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\, a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1 $3p_0$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos\theta$
3	1 $3p_{\pm 1}$	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin\theta\, e^{\pm i\phi}$
3	2 $3d_0$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3\cos^2\theta - 1)$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3\cos^2\theta - 1)$
3	2 $3d_{\pm 1}$	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin\theta\cos\theta\, e^{\pm i\phi}$
3	2 $3d_{\pm 2}$	±2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2\theta\, e^{\pm 2i\phi}$

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

IS SAME FOR MANY e^- ATOMS

CHANGES FOR MANY e^- ATOMS

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

$$\underbrace{\psi_{n\ell m_\ell}(r,\theta,\phi)}_{\text{COMPLEX}} = \underbrace{R_{n\ell}(r)}_{\text{REAL}}\,\underbrace{\Theta_{\ell m_\ell}(\theta)}_{\text{REAL}}\,\frac{1}{\sqrt{2\pi}}\underbrace{e^{im_\ell\phi}}_{\text{COMPLEX IF } m_\ell \neq 0}$$

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

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

$\underline{\text{REAL}}$

EXAMPLE: 2p ORBITALS

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

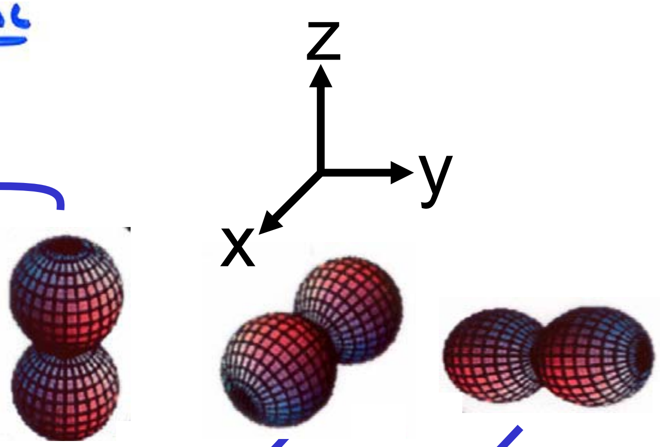
$$\psi_{211} = \psi_{2p_{+1}} \propto r\sin\theta\, e^{i\phi} = r\sin\theta[\cos\phi + i\sin\phi]$$

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

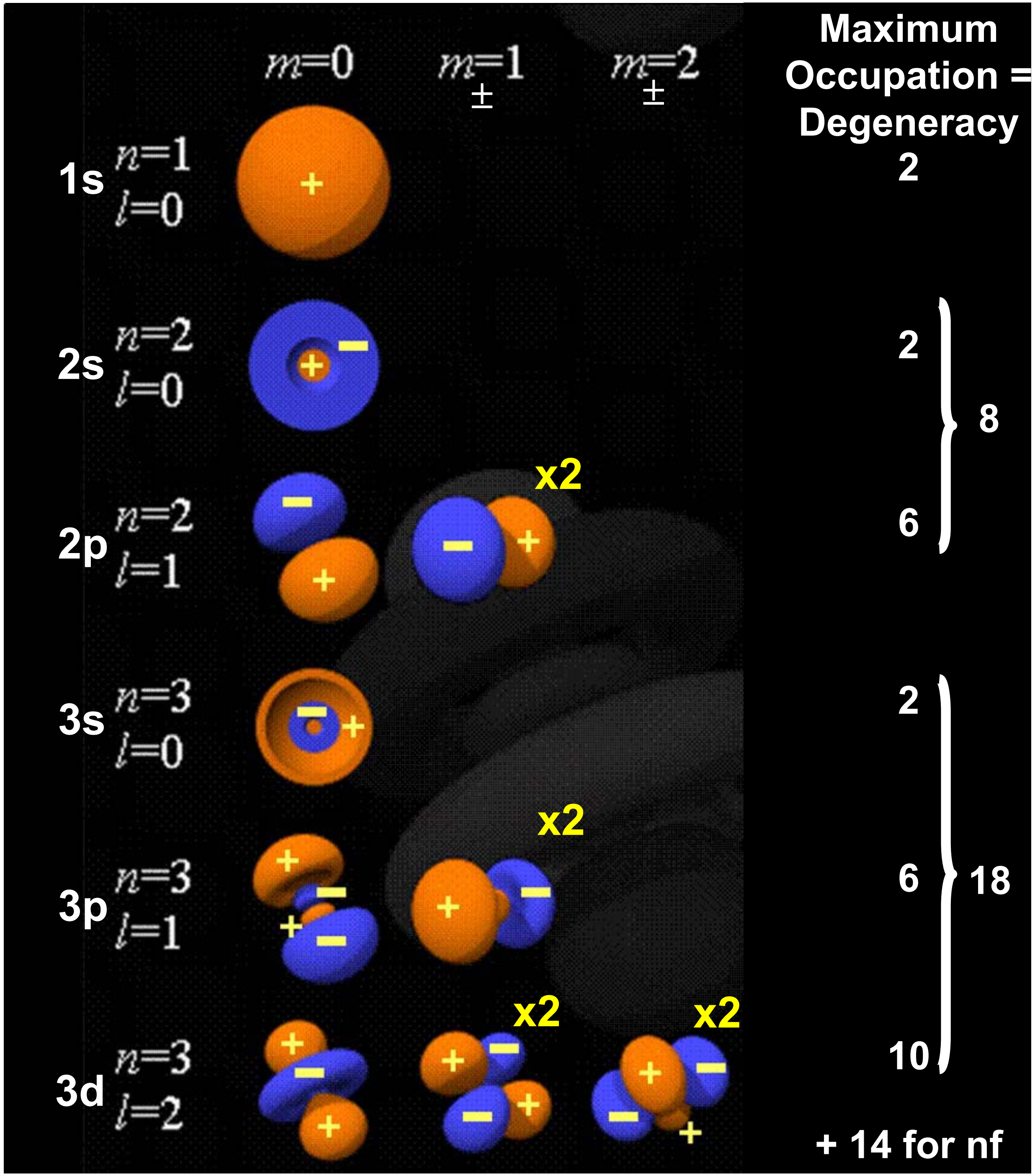
$\therefore$

$$\frac{1}{2}\left[\psi_{2p_{+1}} + \psi_{2p_{-1}}\right] = \underline{\psi_{2p_x} \propto r\sin\theta\cos\phi = x}$$

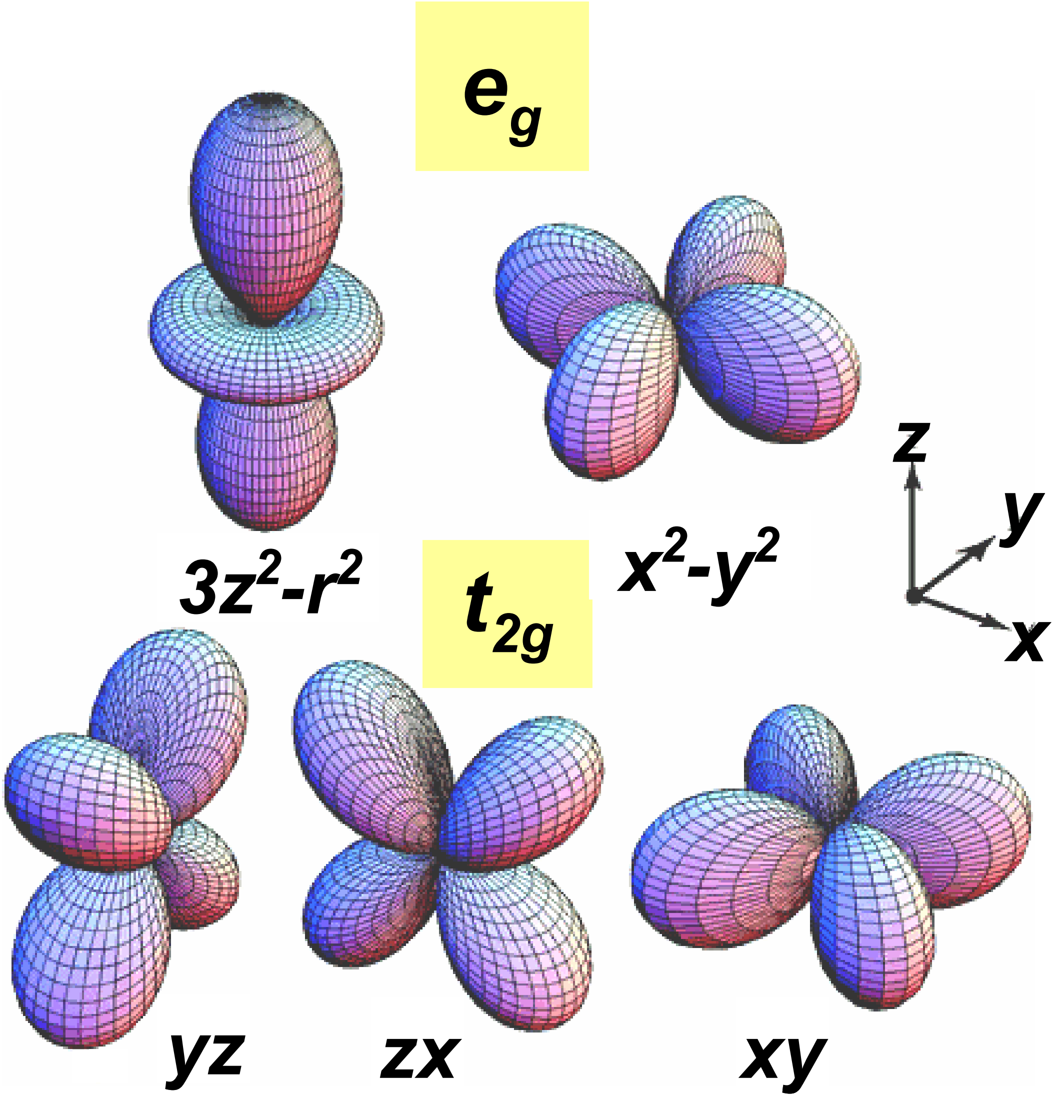
$$\frac{1}{2i}\left[\psi_{2p_{+1}} - \psi_{2p_{-1}}\right] = \underline{\psi_{2p_y} \propto r\sin\theta\sin\phi = y}$$

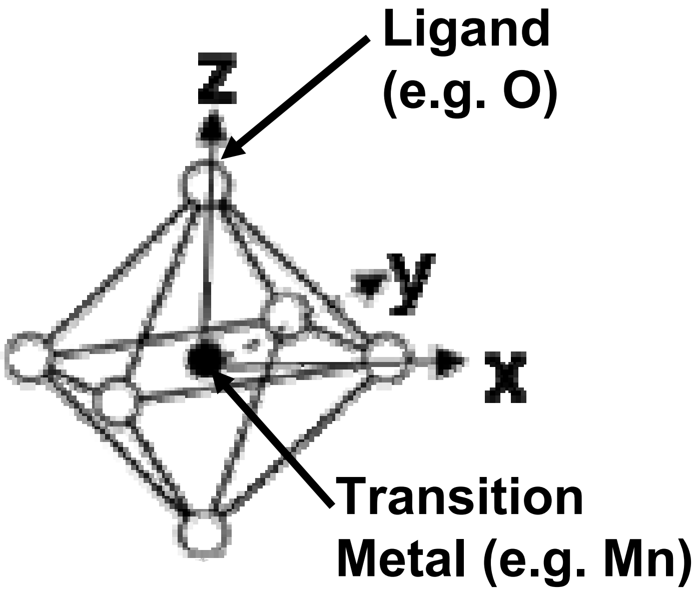


Filling the Atomic Orbitals:



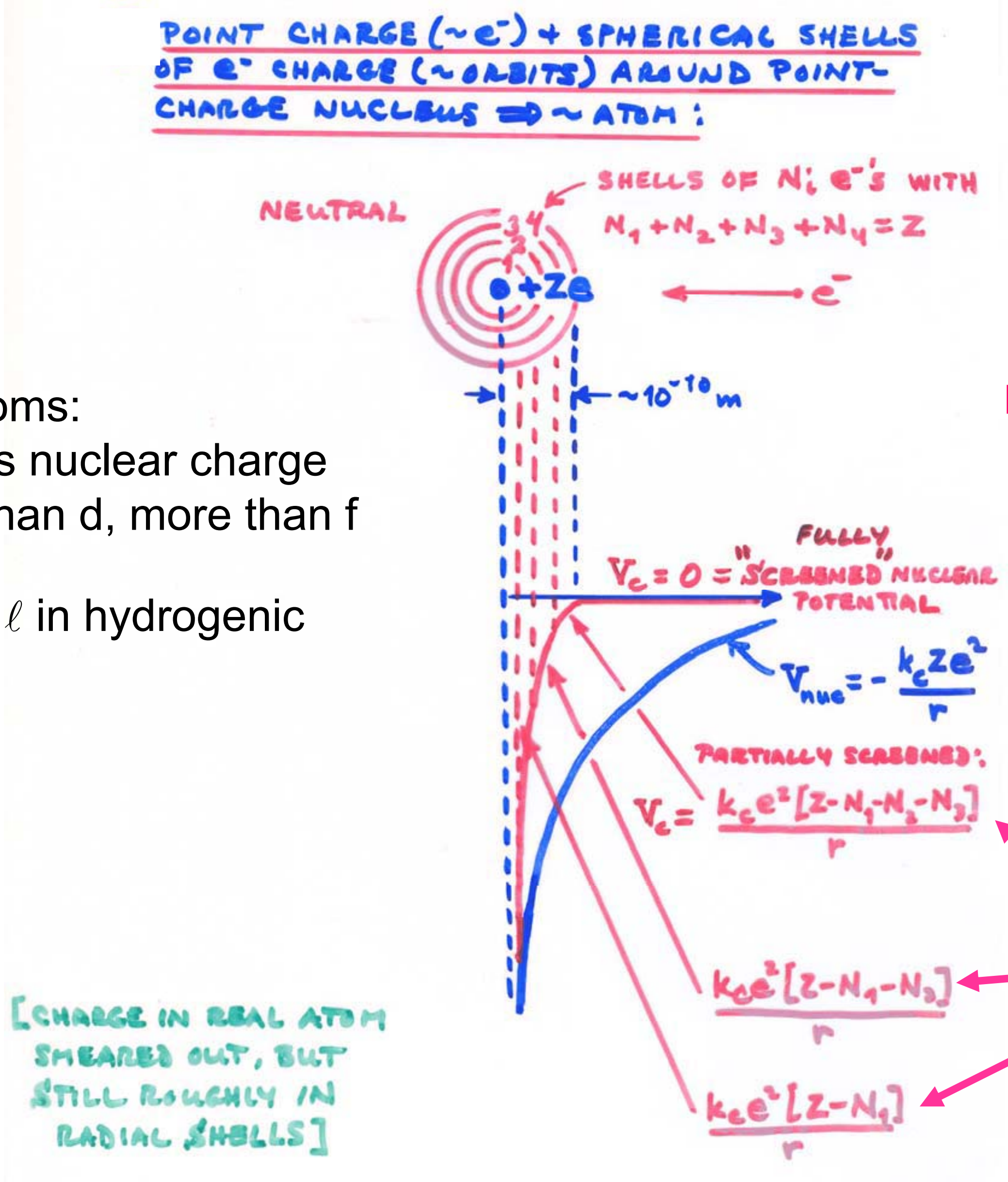
And the same thing for the d orbitals:





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

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


POINT CHARGE (~e⁻) + SPHERICAL SHELLS OF e⁻ CHARGE (~ORBITS) AROUND POINT-CHARGE NUCLEUS ⇒ ~ ATOM :

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

In many-electron atoms:
For a given n, s feels nuclear charge more than p, more than d, more than f

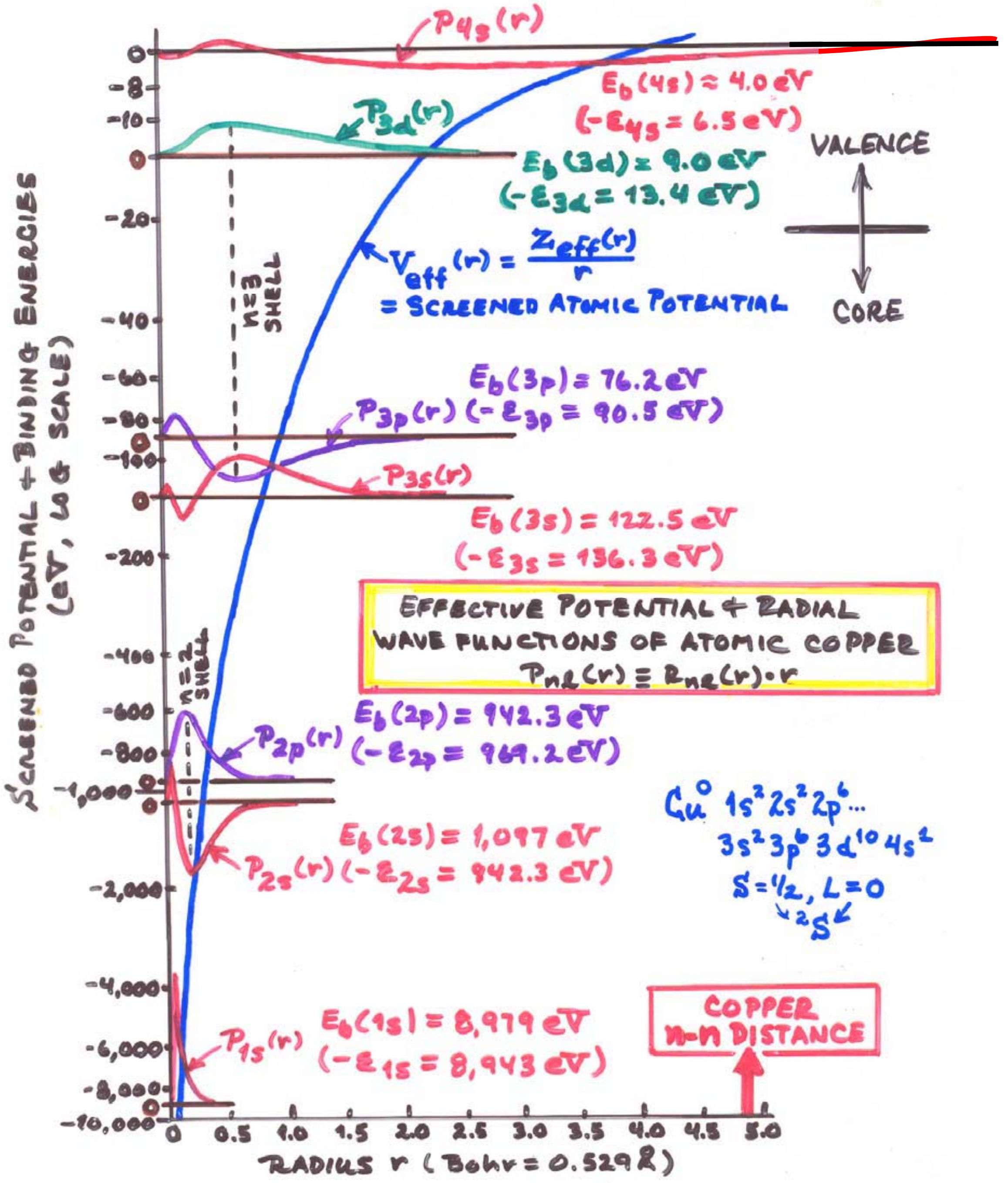
Lifts degeneracy on ℓ in hydrogenic atom

$k_C \equiv 1/(4\pi\varepsilon_0)$

$[Z_{eff}]$

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

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



OBSERVED (+ CALCULATED) ORDER OF FILLING ATOMIC LEVELS:

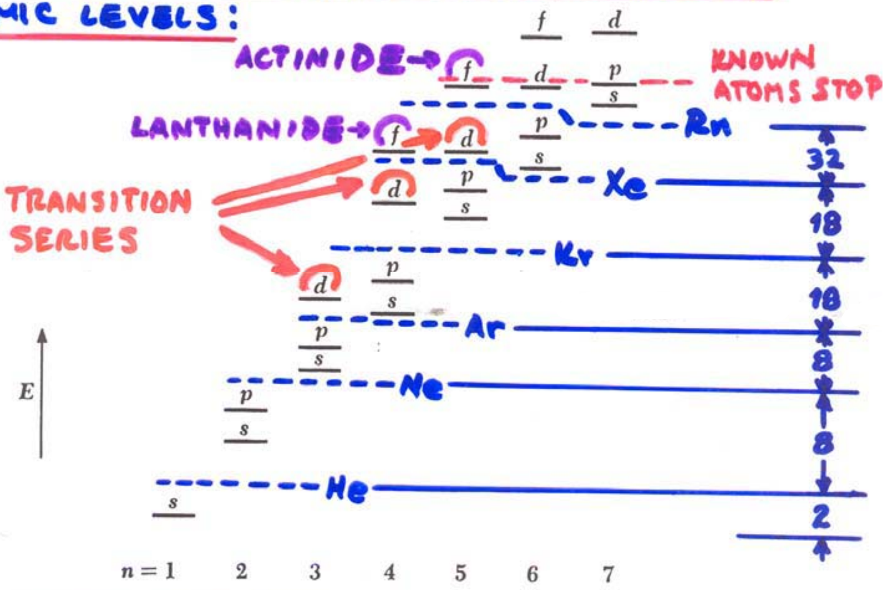
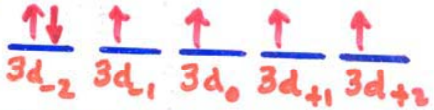


FIGURE 7.13 The sequence of quantum states in an atom. Not to scale.

EXAMPLE CONFIGURATIONS:

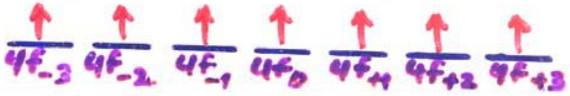
Z	ATOM	CONFIG.
8	O	$1s^2 2s^2 2p^4$
26	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
63	Eu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^7 6s^2$

GROUND-STATE OPEN SHELL COUPLING?



⇒ LARGE μ_{3d} + MAGNETISM

ALSO MAGNETIC!



TRANSITION METALS

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

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

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

$4f^1$ … $4f(5d)$ FILLING … $4f^{14}$

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

… $5f(6d)$ FILLING …

*

☐ = EXCEPTIONS

☐ = EXCEPTIONS

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

• 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 $2(2l+1)$
  - $\rightarrow nl_j \; j = l + 1/2$ — $2l+2$
  - $\rightarrow nl_j \; j = l - 1/2$ — $2l$

- MIXES SPIN + ORBITAL ANGULAR MOM.:

$$\psi_{nljm_j} = C_1\psi_{nl,m_j-1/2}\underset{\substack{\| \\ m_s=+1/2 \\ \| \\ \uparrow}}{\begin{pmatrix}1\\0\end{pmatrix}} + C_2\psi_{nl,m_j+1/2}\underset{\substack{\| \\ m_s=-1/2 \\ \| \\ \downarrow}}{\begin{pmatrix}0\\1\end{pmatrix}}$$

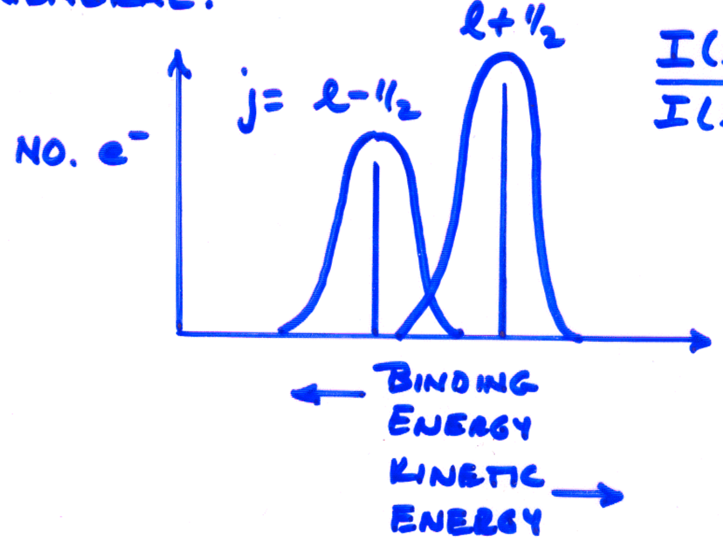
WITH C1 AND C2 TABULATED CLEBSCH-GORDAN OR WIGNER 3j SYMBOLS

SOME SPIN-ORBIT SPLITTINGS: (IN eV)

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

INCREASE WITH Z FOR A GIVEN LEVEL.

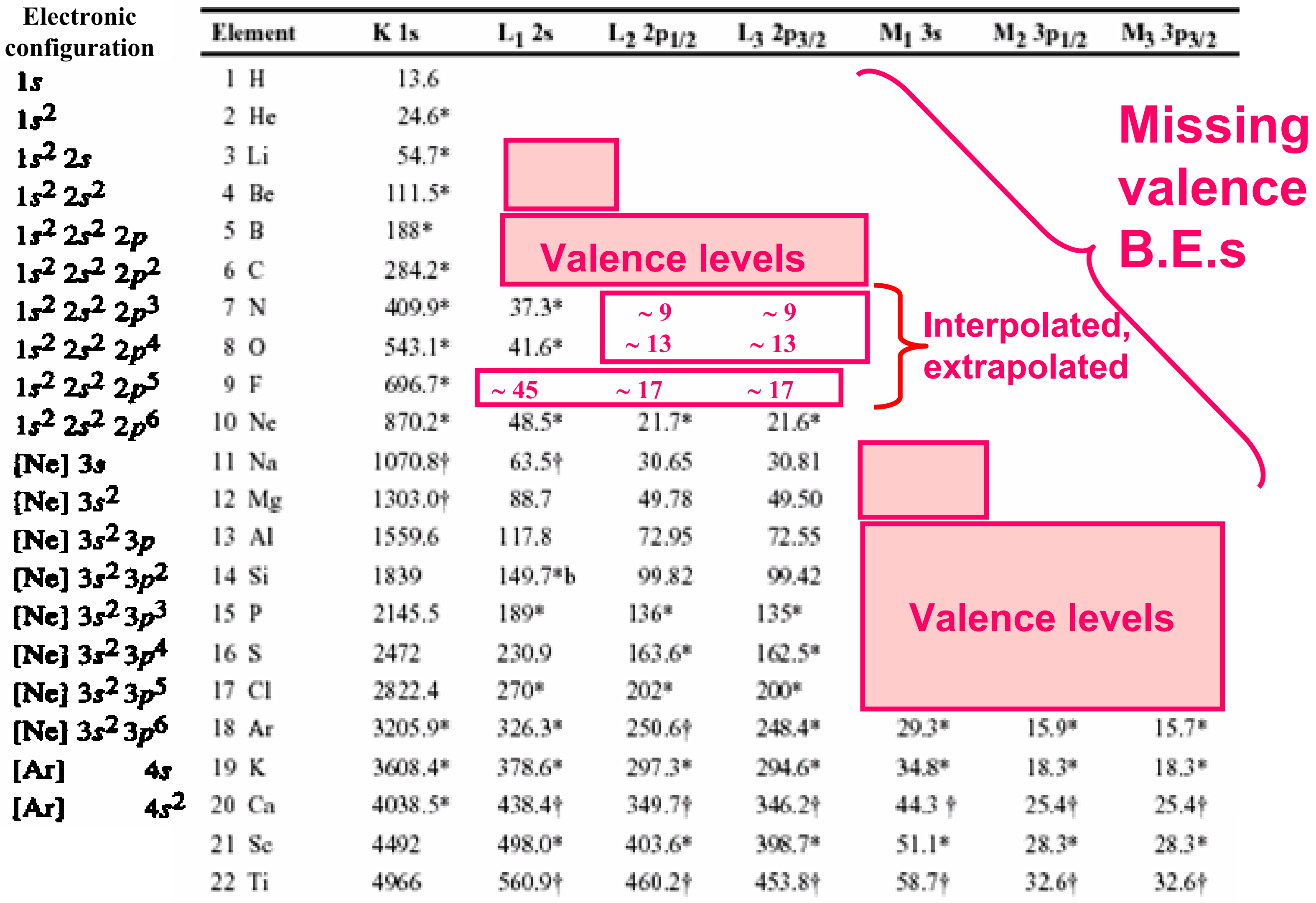
IN GENERAL:



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

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

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



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

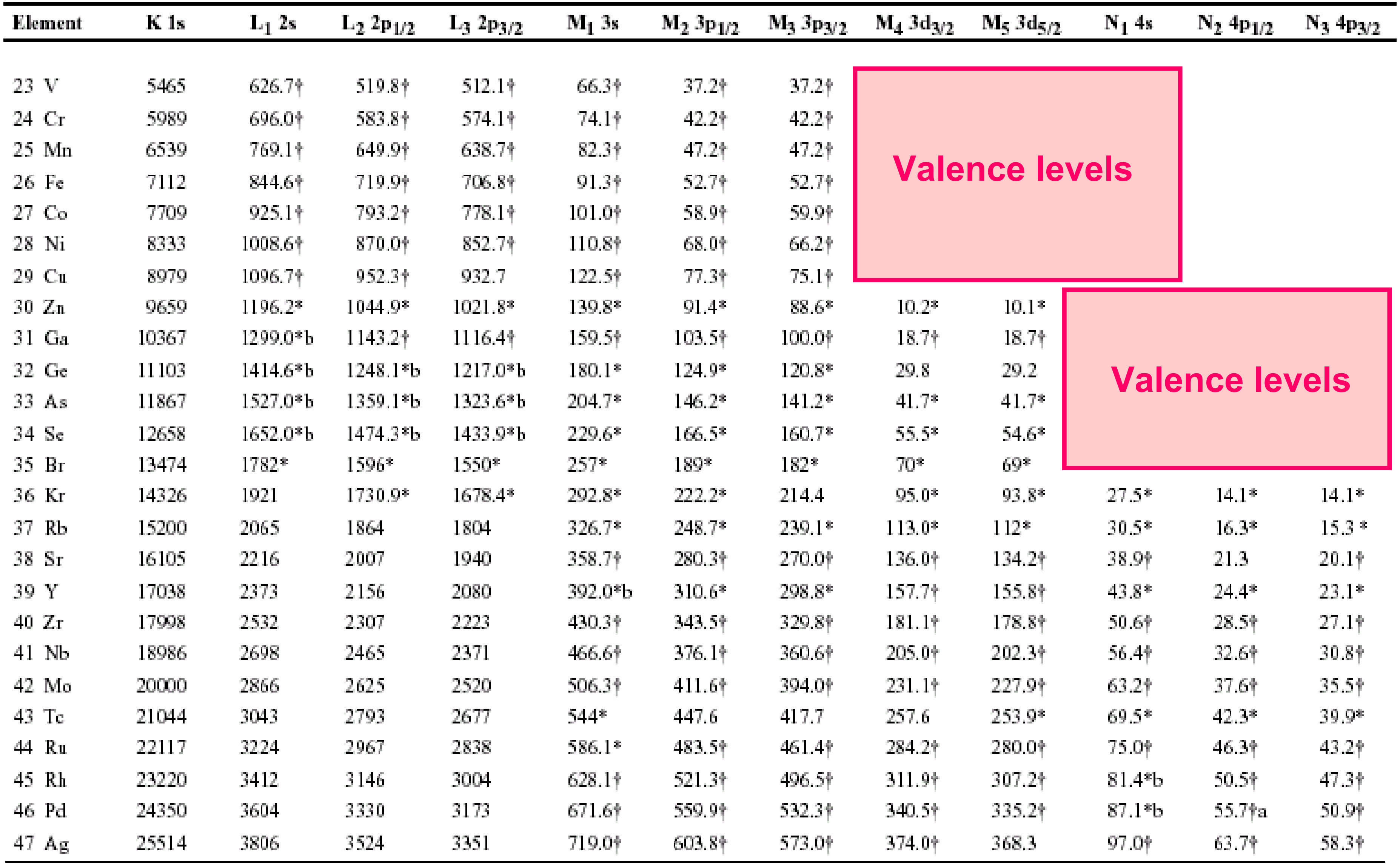
Valence levels

Interpolated, extrapolated

Missing valence B.E.s

Valence levels

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



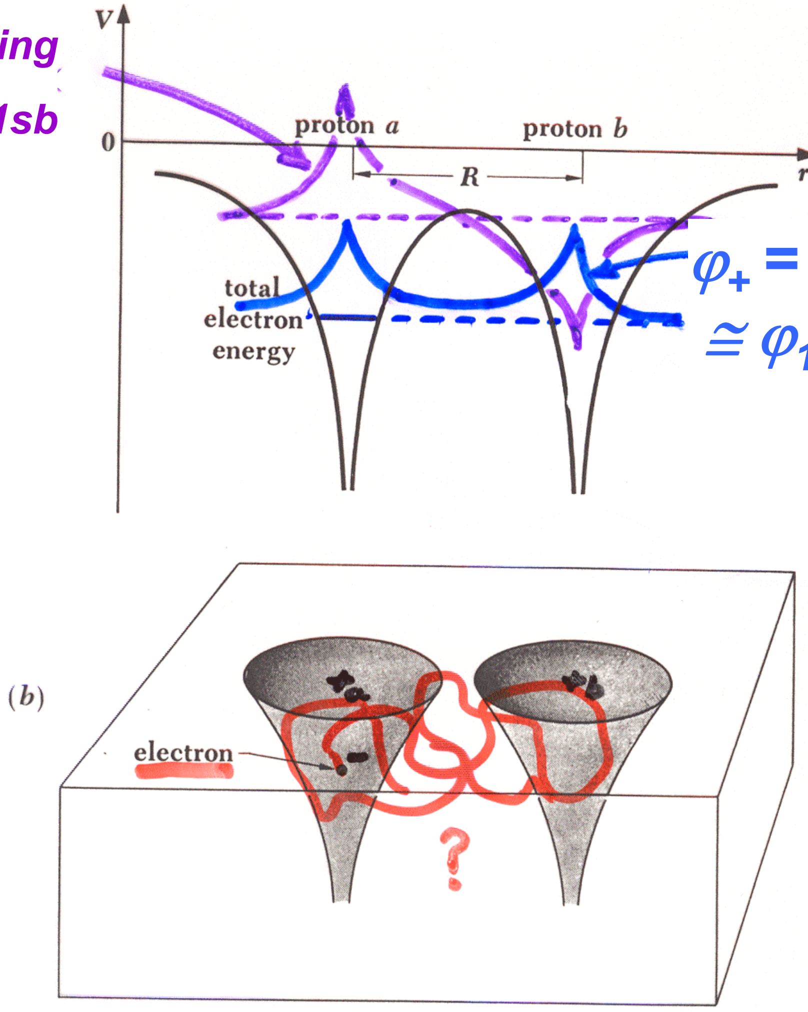
Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$	N_3 $4p_{3/2}$
23 V	5465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†					
24 Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2†					
25 Mn	6539	769.1†	649.9†	638.7†	82.3†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

Valence levels

Valence levels

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

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



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

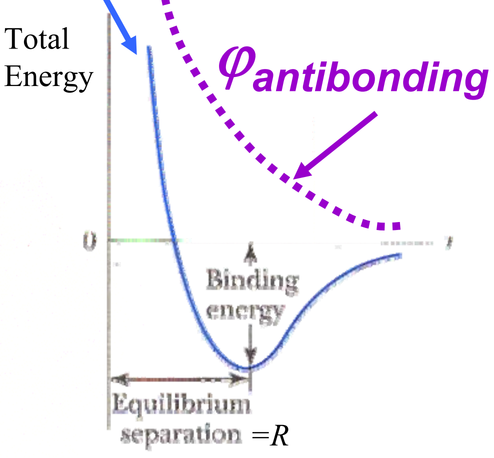
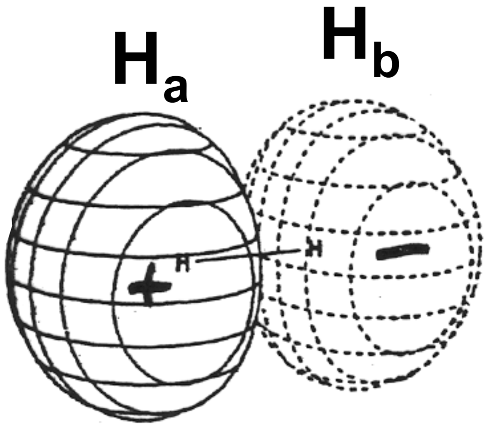


FIGURE 10.2 The net potential energy curve, showing the equilibrium separation and binding energy.

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

1. Hydrogen

Symmetry: $D_{\infty h}$



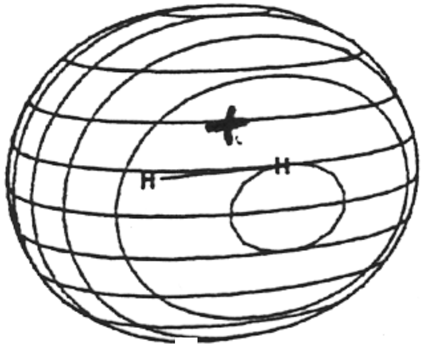
Anti-Bonding

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

ε *positive*
(unoccupied)

$1\sigma_u$ $\varepsilon = 0.2656$ a.u. = +7.21 eV

ε *negative*
(occupied)



Bonding

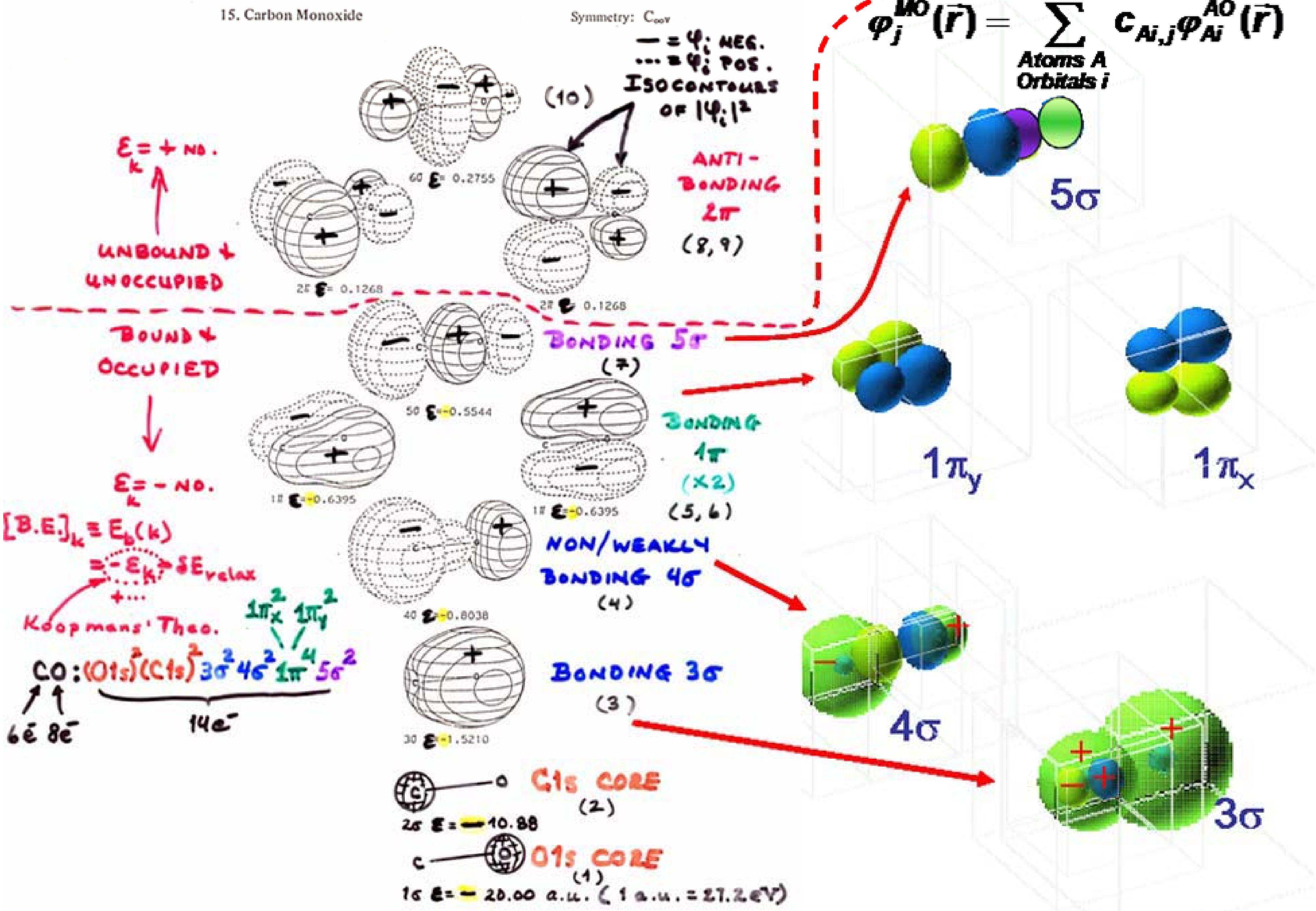
$$\varphi_{bonding}^{MO} \cong \varphi_{1sa} + \varphi_{1sa}$$

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

THE ELECTRONS IN CARBON MONOXIDE:

Atomic orbital makeup

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



$$[\mathrm{B.E.}]_k \equiv E_b(k) = -\varepsilon_k + \delta E_{relax} + \cdots$$

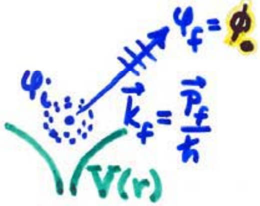
$$\mathrm{CO}: (\mathrm{O1s})^2 (\mathrm{C1s})^2\, \underbrace{3\sigma^2\, 4\sigma^2\, 1\pi^4\, 5\sigma^2}_{14e^-}$$

$$1\pi^4 = 1\pi_x^2\; 1\pi_y^2$$

PHOTOELECTRON EMISSION-
BASIC MATRIX ELEMENTS + SELECTION RULES:

● ATOMIC-LIKE (LOCALIZED) STATES ⇒ CORE:

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



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

PHASE SHIFT OF l_f WAVE IN V(r)

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

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

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

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

● BLOCH-FUNCTION (DELOCALIZED) STATES ⇒ VALENCE:

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

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

$$|\langle\varphi_f|\hat{\varepsilon}\cdot\vec{p}|\varphi_i\rangle|^2 = |\hat{\varepsilon}\cdot\langle\varphi_f|\vec{p}|\varphi_i\rangle|^2 \Rightarrow \Delta\vec{k} = \vec{k}_f - \vec{k}_i - \underset{\text{USUALLY NEGLIG.}}{\vec{k}_{h\nu}} + \vec{k}_{\text{PHONON}}$$

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

"DIRECT" TRANSITIONS

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

⇒ FRACTION DIRECT ≈ DEBYE-WALLER FACTOR

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

"Basic Concepts of XPS"
Chapter 3

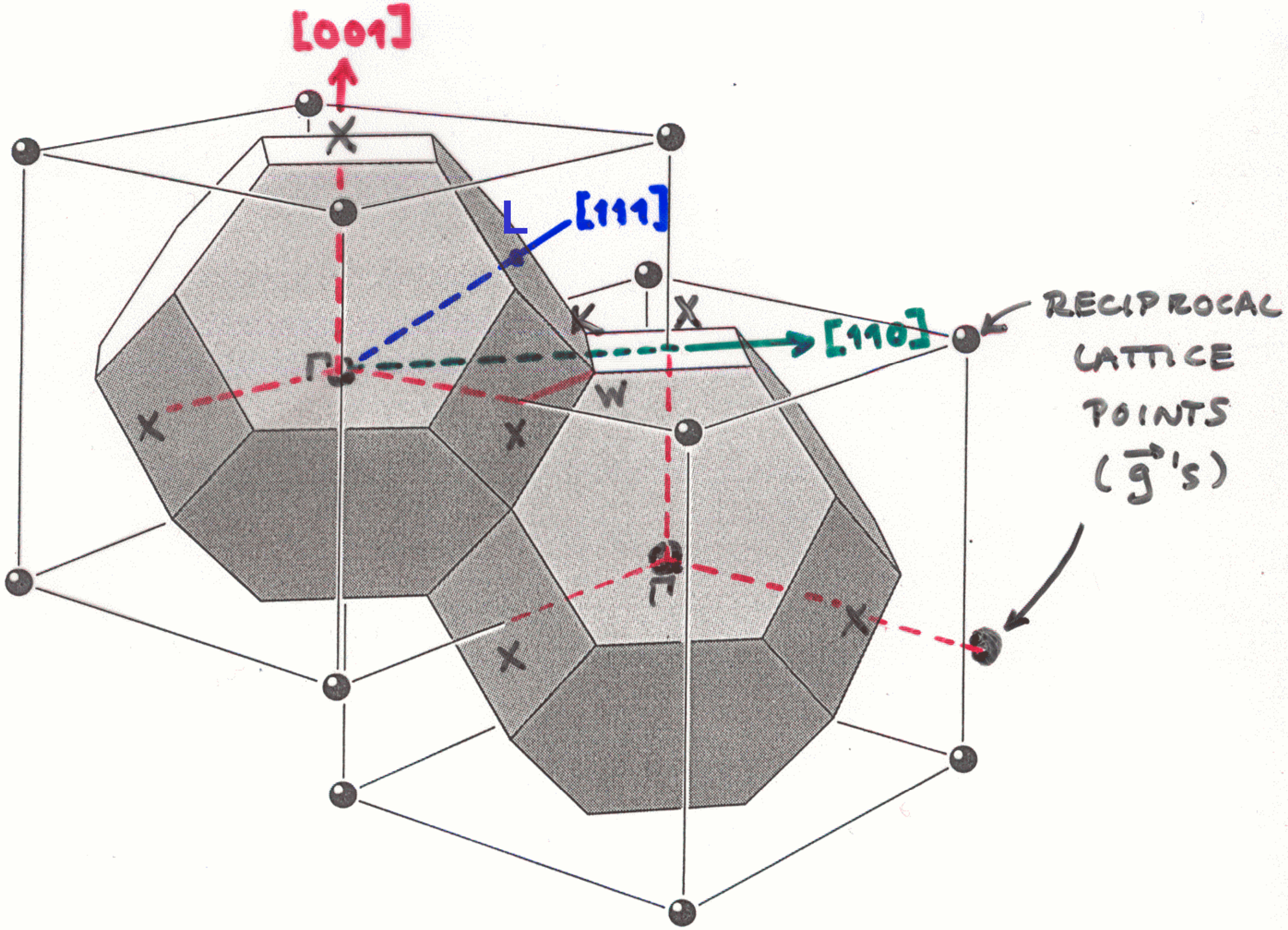


Figure 28 Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body-centered, as drawn.

— STACKING OF fcc BRILLOUIN ZONES —

The electronic structure of a transition metal—fcc Cu

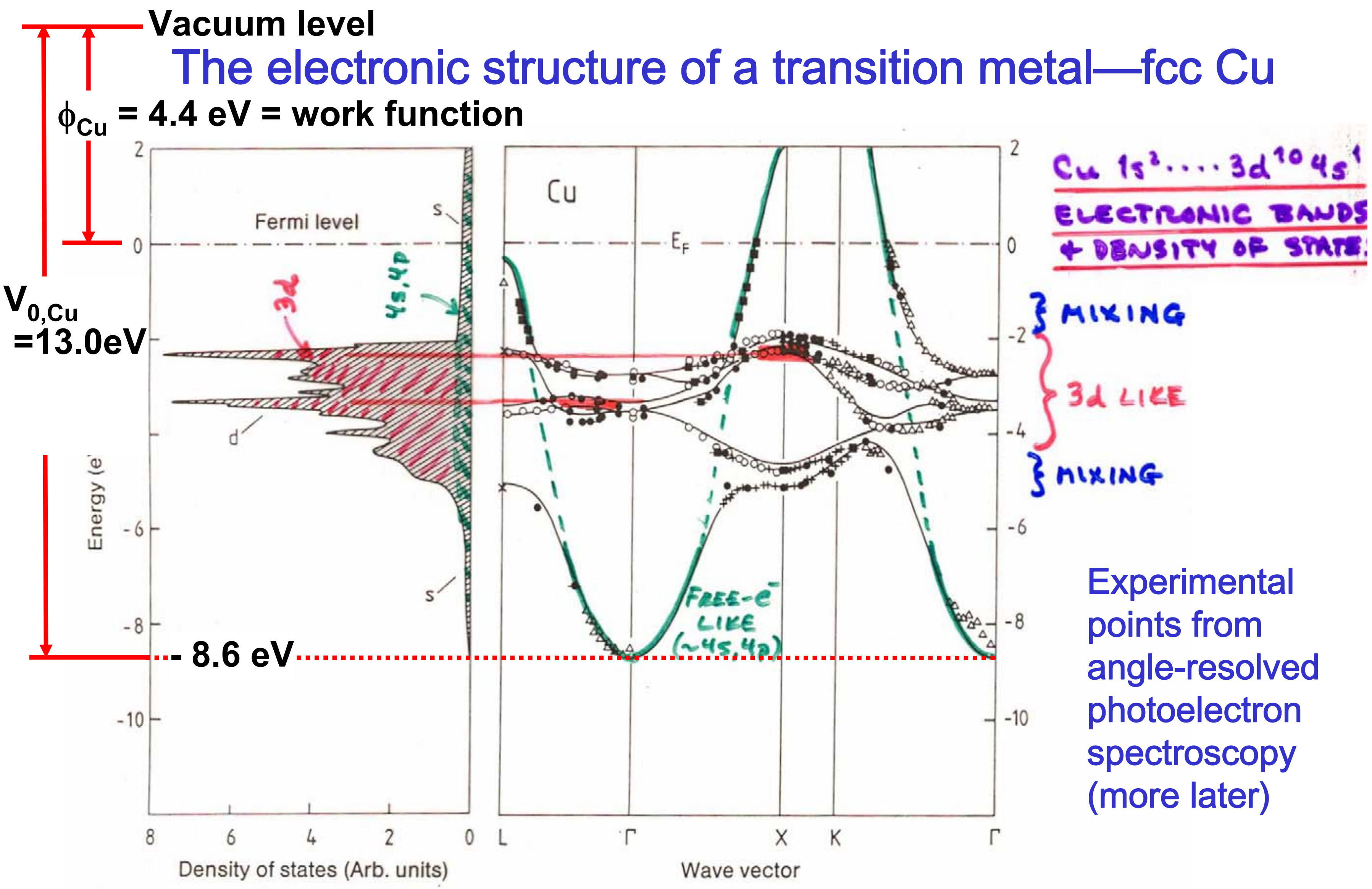
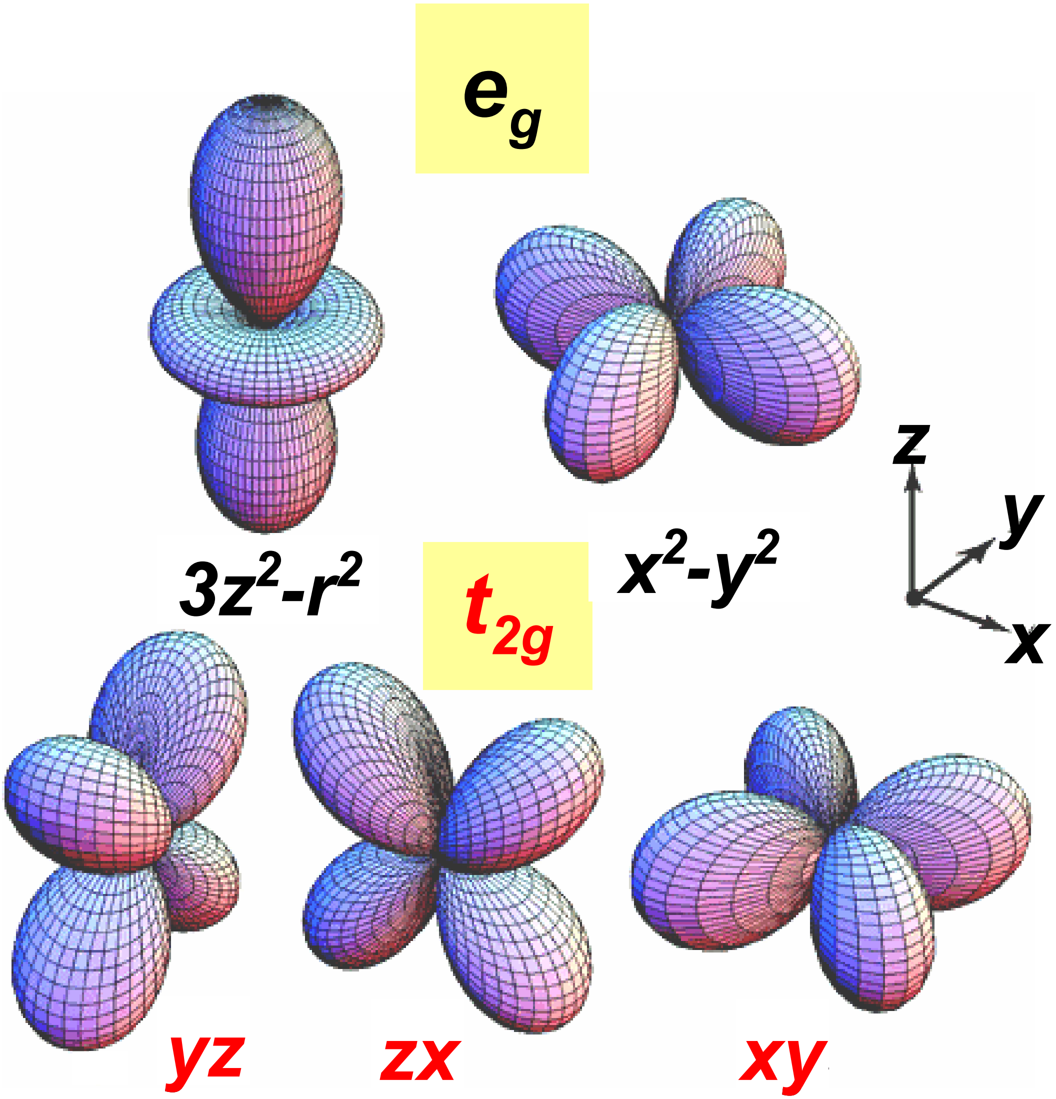
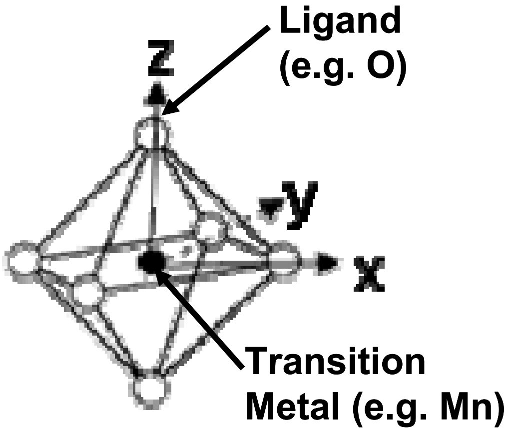


Fig. 7.12. Bandstructure $E(k)$ for copper along directions of high crystal symmetry (*right*). The experimental data were measured by various authors and were presented collectively by Courths and Hüfner [7.4]. The full lines showing the calculated energy bands and the density of states (*left*) are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

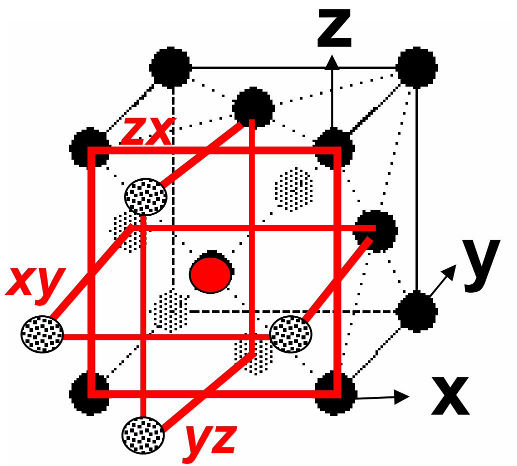
Experimental points from angle-resolved photoelectron spectroscopy (more later)

And the d orbitals are not equivalent in different bonding environments:



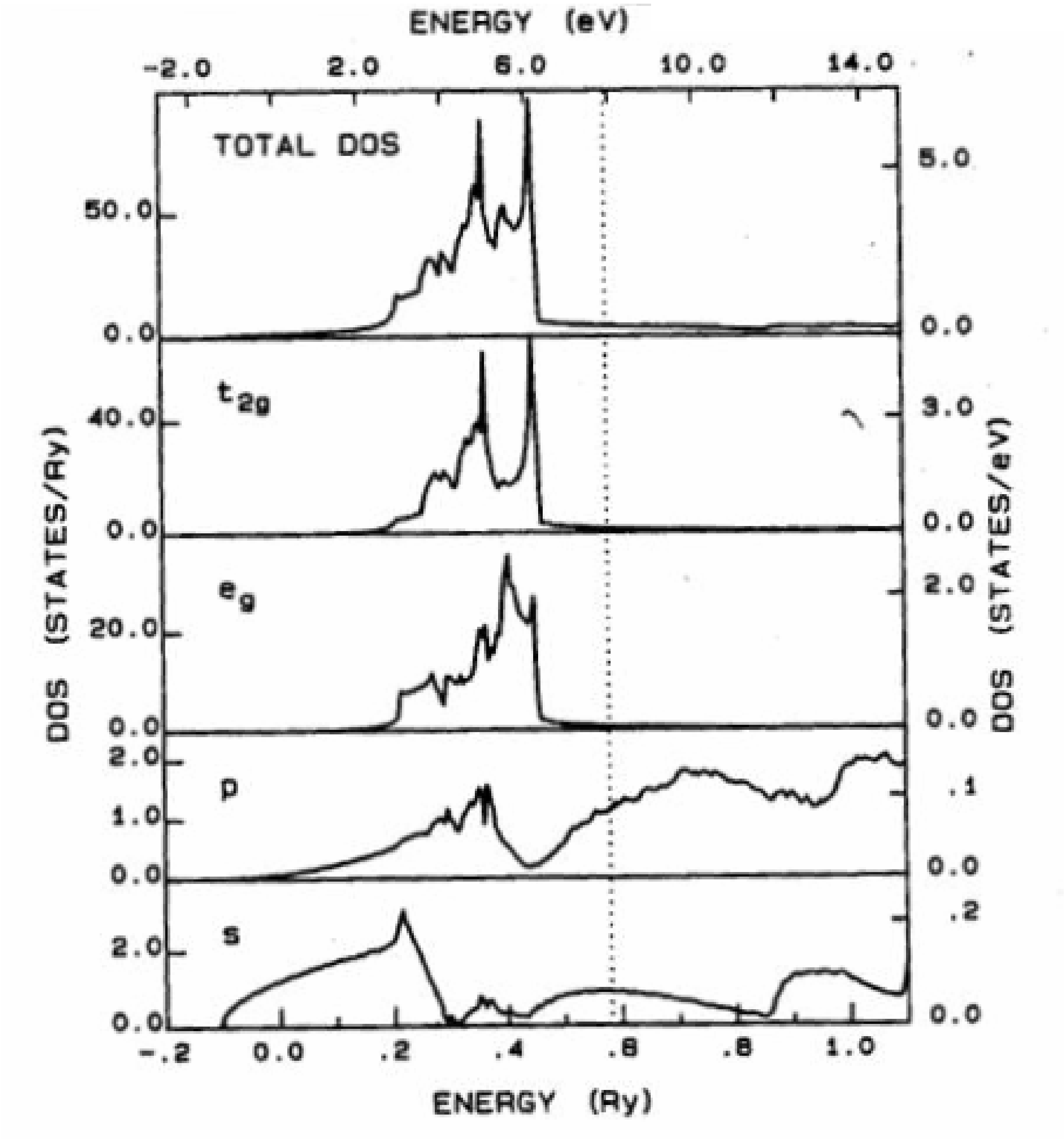


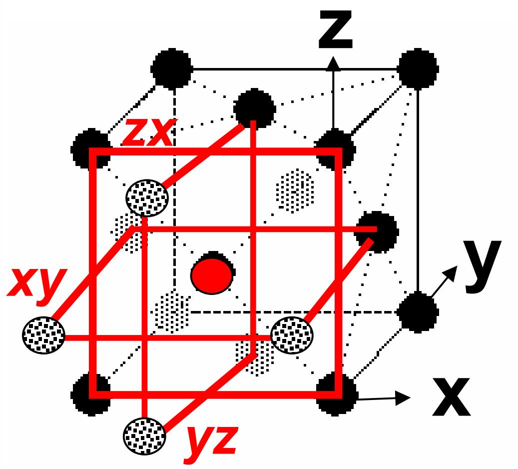
e_g and t_{2g} not equivalent in octahedral (cubic) environment



Face-centered cubic—
12 nearest neighbors

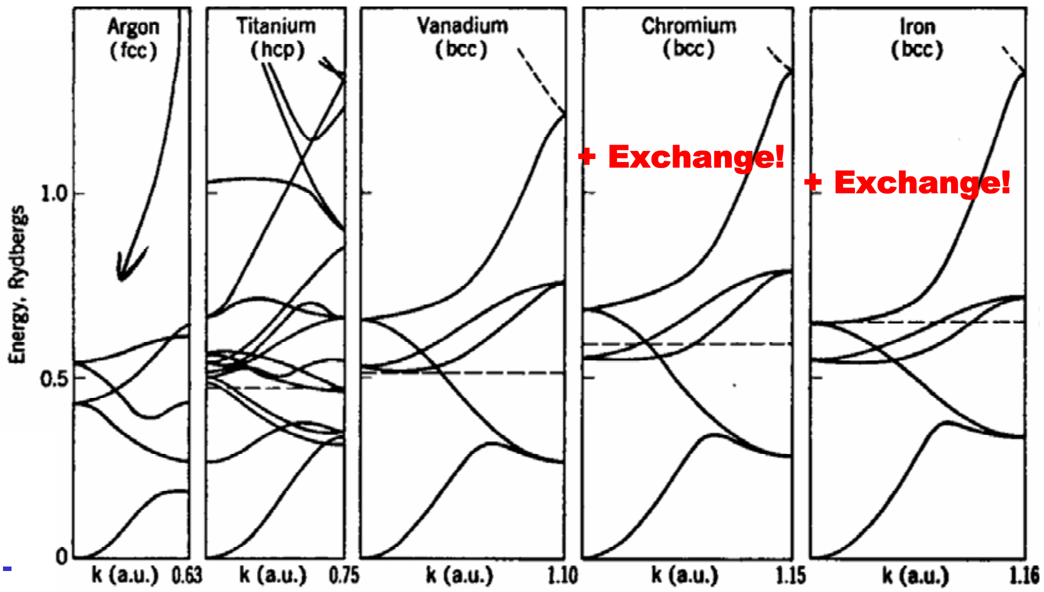
Copper densities of states-total and by orbital type:





The electronic structures of the 3d transition metals—≈ “rigid-band model”

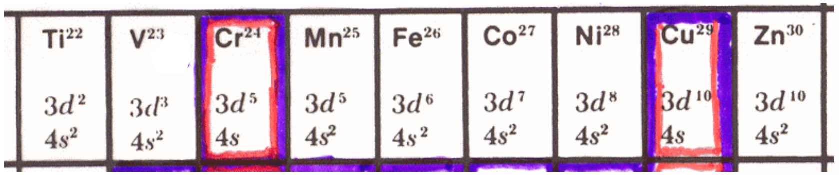
$3s^2 3p^6$ filled + 3d,4s CB $3d^2 4s^2$ $3d^3 4s^2$ $3d^5 4s^1$ $3d^6 4s^2$



+ Exchange!

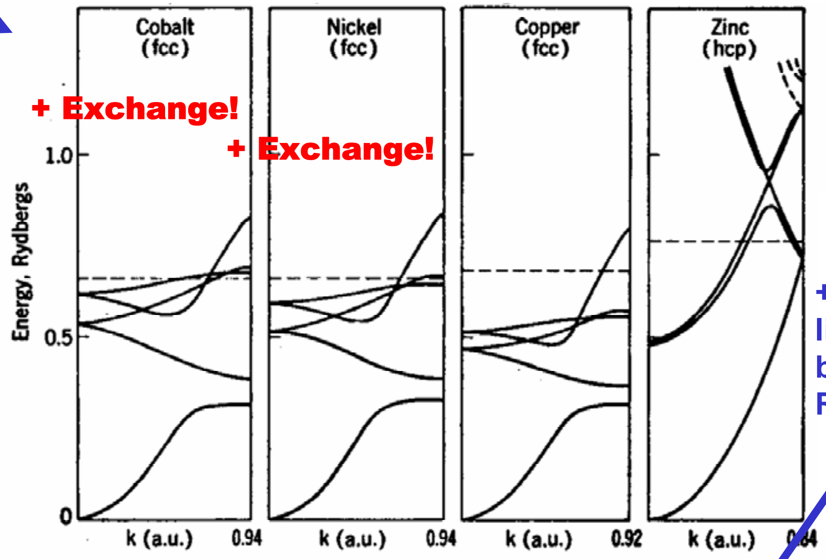
+ Exchange!

+ Flat “core-like” Ar 3s, 3p bands at ~-1.0-1.5 Rydbergs



Ti^{22}	V^{23}	Cr^{24}	Mn^{25}	Fe^{26}	Co^{27}	Ni^{28}	Cu^{29}	Zn^{30}
$3d^2$ $4s^2$	$3d^3$ $4s^2$	$3d^5$ $4s$	$3d^5$ $4s^2$	$3d^6$ $4s^2$	$3d^7$ $4s^2$	$3d^8$ $4s^2$	$3d^{10}$ $4s$	$3d^{10}$ $4s^2$

$3d^7 4s^2$ $3d^8 4s^2$ $3d^{10} 4s^1$ $3d^{10} 4s^2$

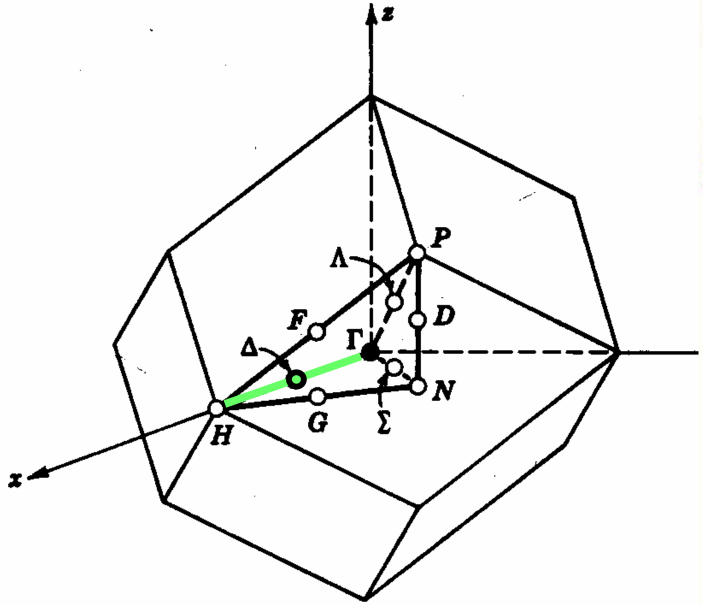


+ Exchange!

+ Exchange!

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

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



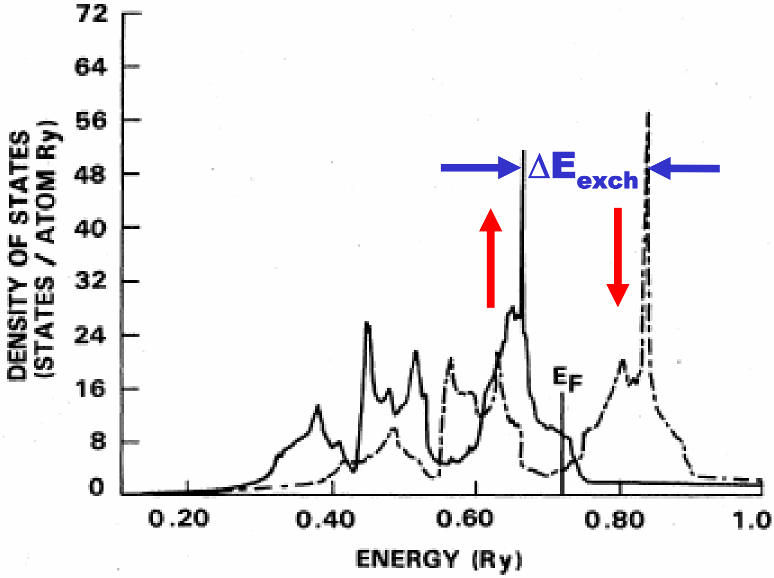
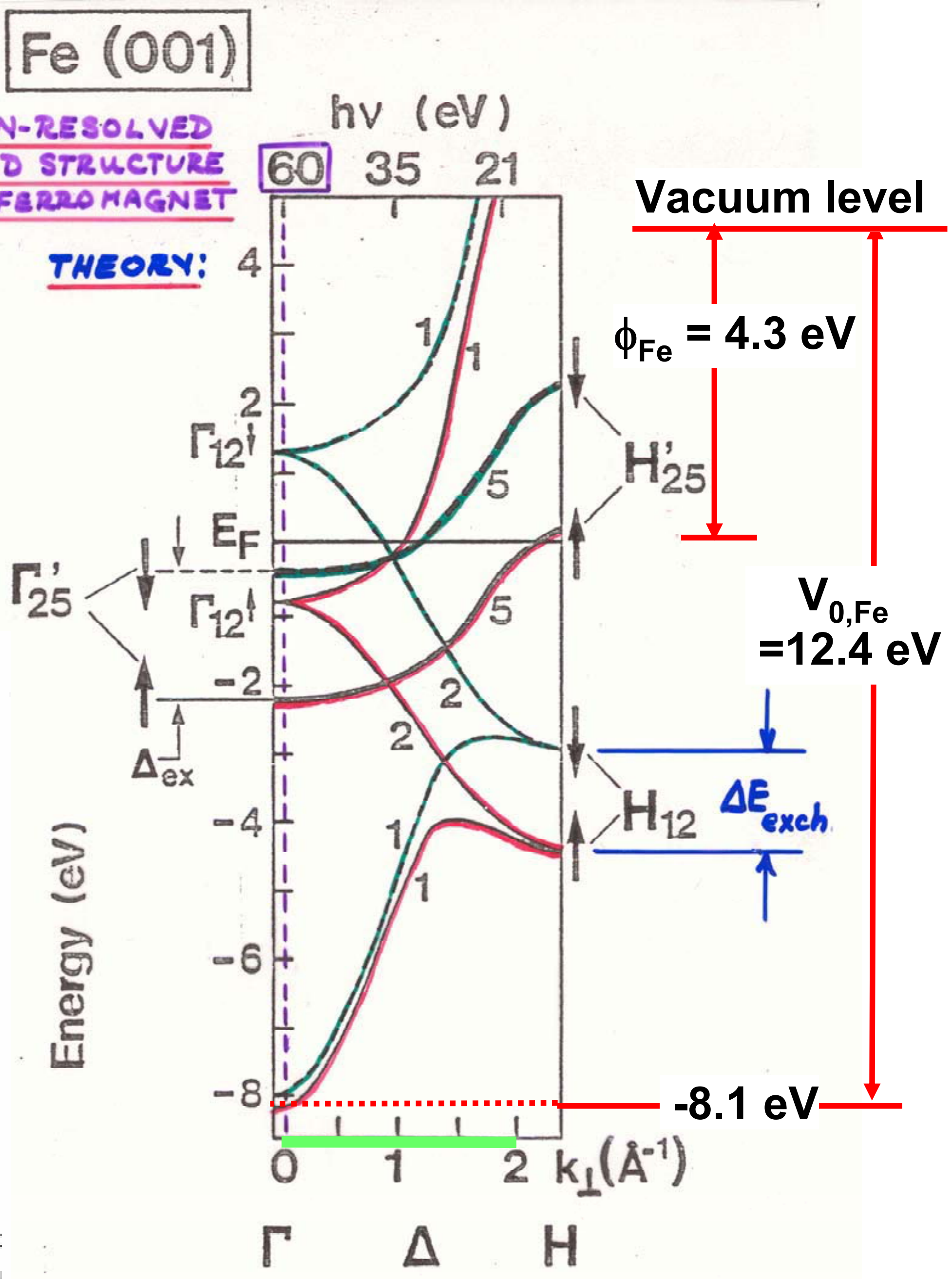


FIG. 4. Density of states at the equilibrium lattice constant of Fe for majority- (solid line) and minority- (broken line) spin states.

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

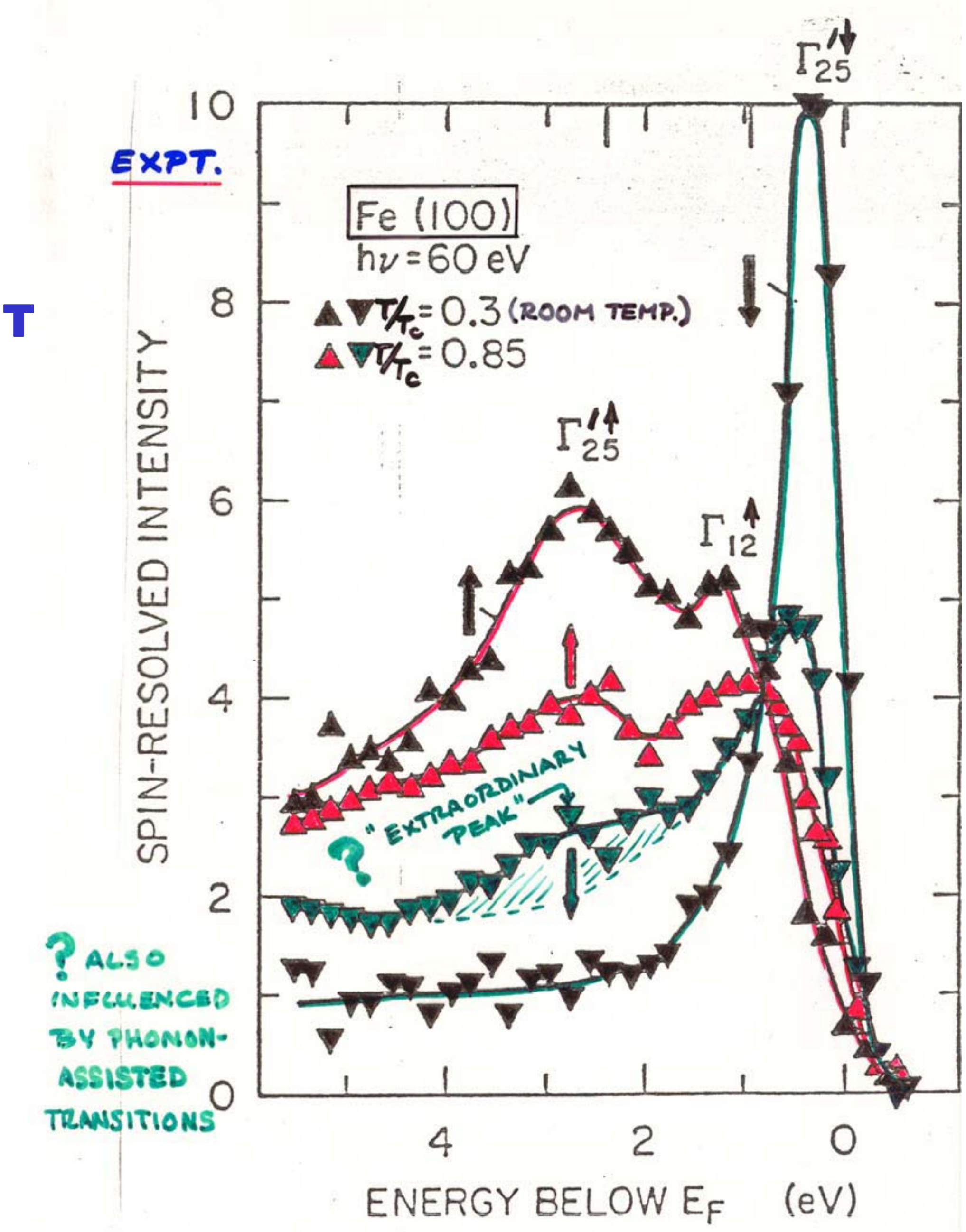
SPIN-RESOLVED BAND STRUCTURE OF A FERROMAGNET

THEORY:



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

Fe: ANGLE AND SPIN-RESOLVED SPECTRA AT Γ POINT

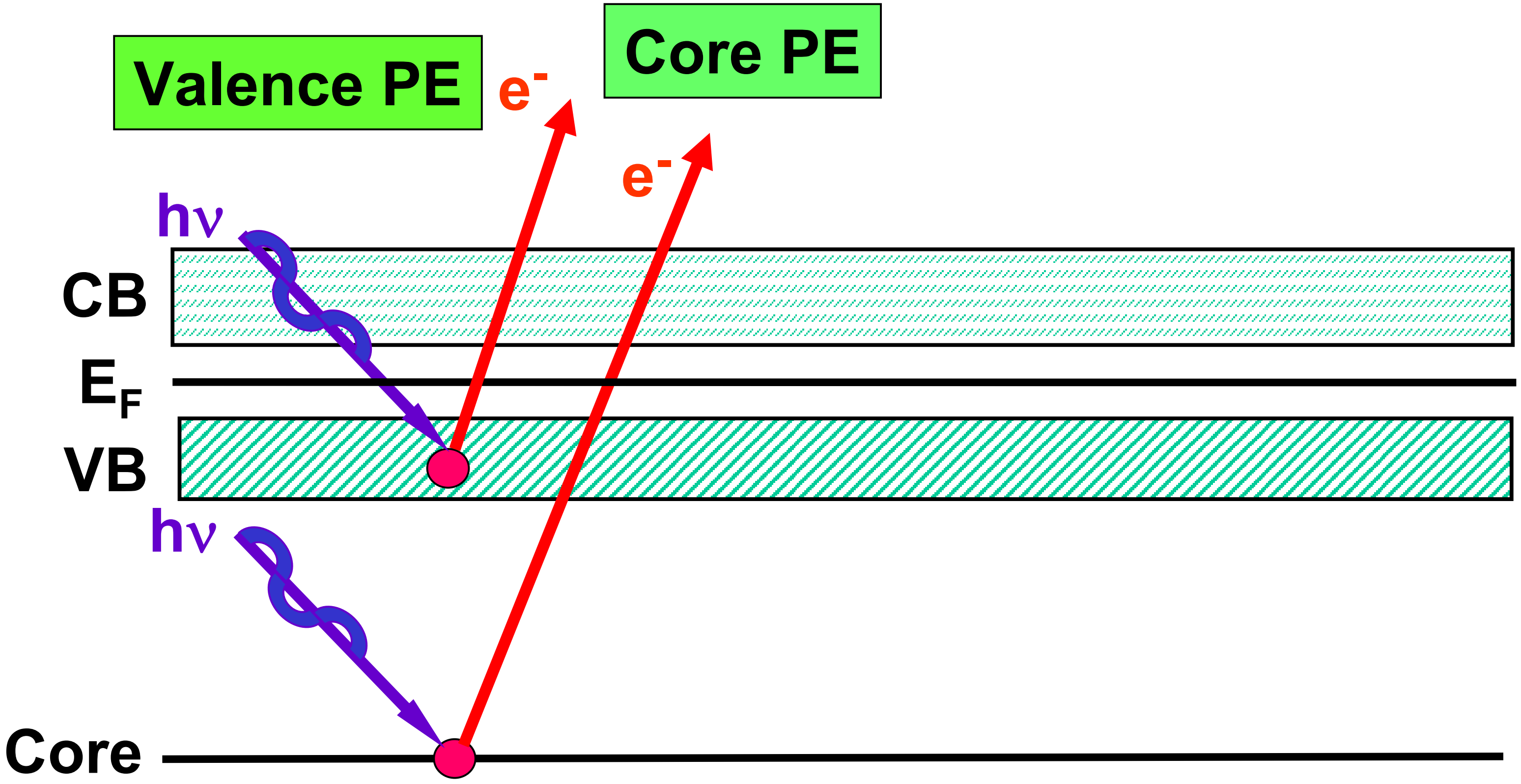


EXPT.

? ALSO INFLUENCED BY PHONON-ASSISTED TRANSITIONS

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

The Soft X-Ray Spectroscopies



PE = photoemission = photoelectron spectroscopy

XAS = x-ray absorption spectroscopy

AES = Auger electron spectroscopy

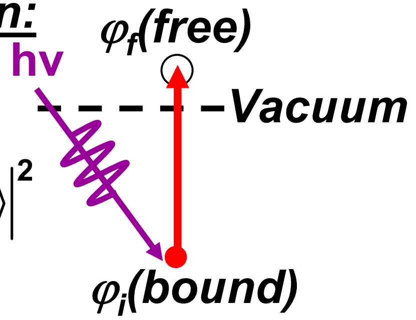
XES = x-ray emission spectroscopy

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

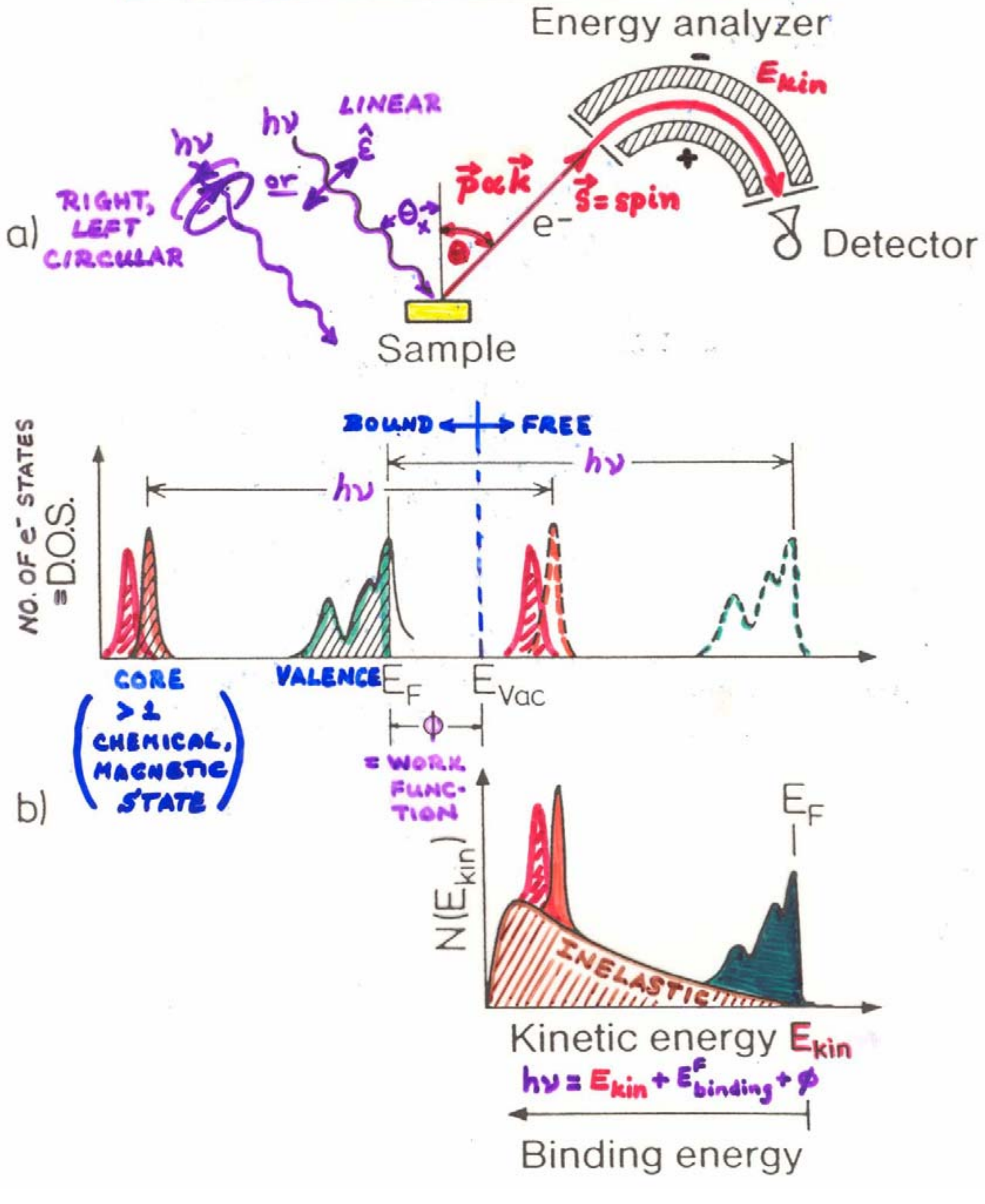
MATRIX ELEMENTS IN THE SOFT X-RAY SPECTROSCOPIES: DIPOLE LIMIT

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

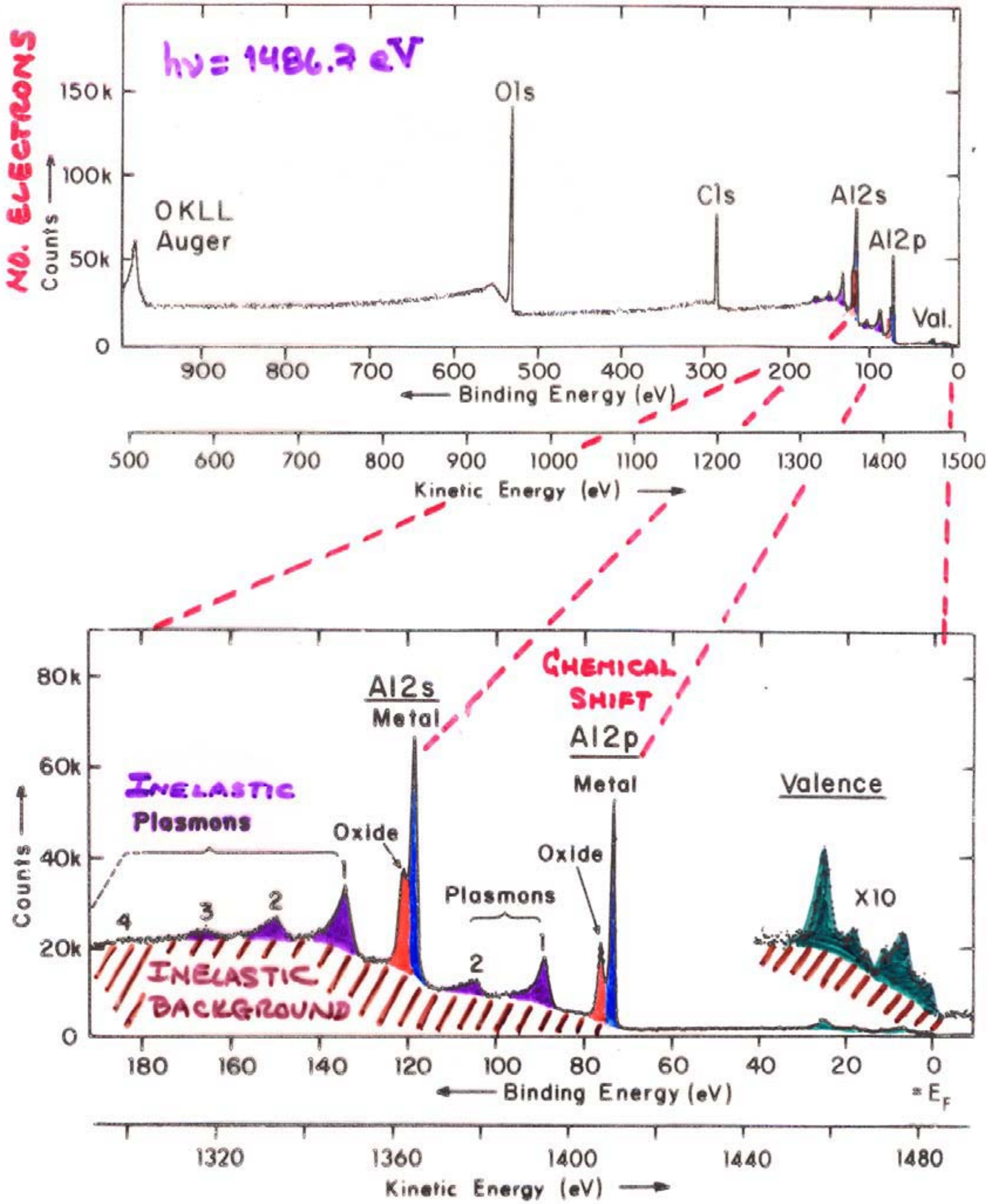
$$I \propto \left| \hat{e} \bullet \left\langle \varphi_f(1) \middle| \vec{r} \middle| \varphi_i(1) \right\rangle \right|^2$$



PHOTOELECTRON SPECTROSCOPY



TYPICAL PHOTOELECTRON SPECTRA: OXIDIZED ALUMINUM



"Basic Concepts of XPS"
Figure 1

PHOTOELECTRON SPECTROSCOPY

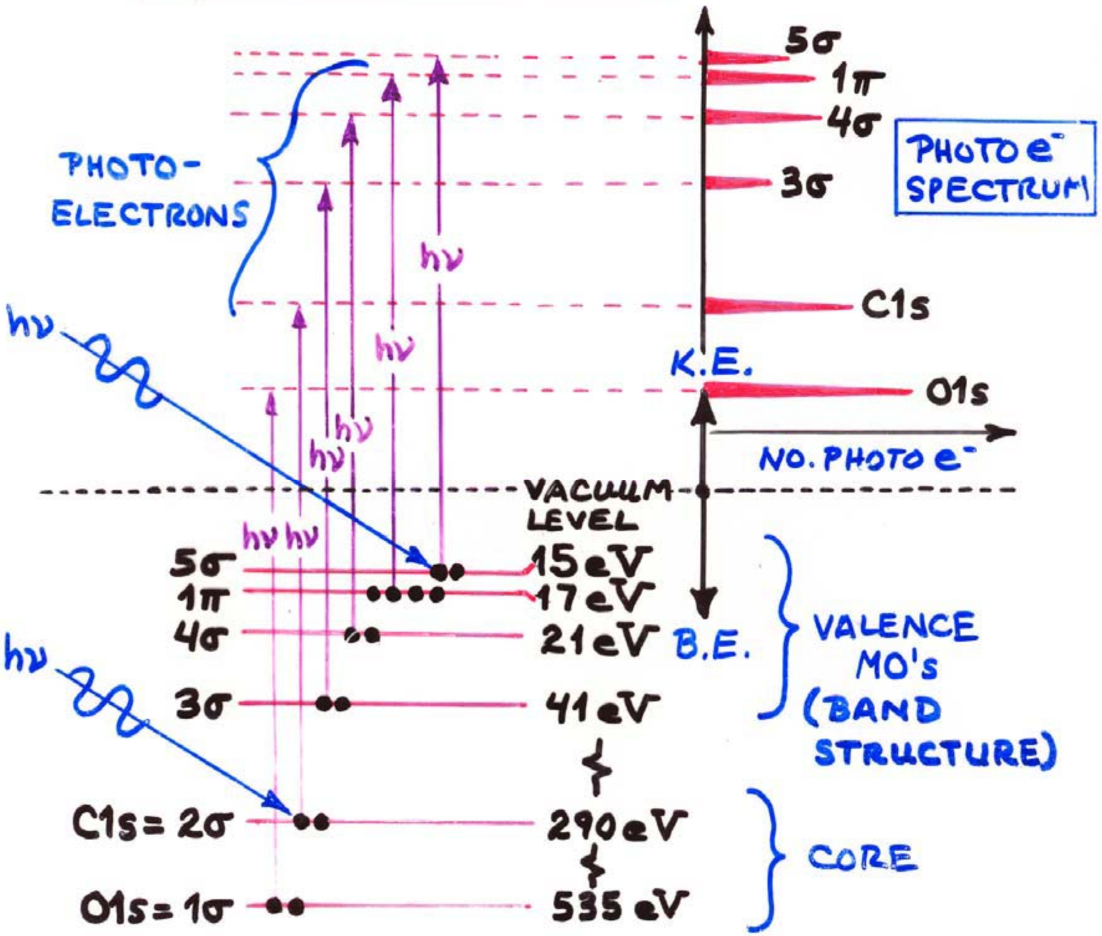
THE PHOTOELECTRIC EFFECT (EINSTEIN, 1905):

$$\begin{pmatrix}\text{PHOTON}\\ \text{ENERGY}\end{pmatrix} = \begin{pmatrix}e^- \text{ BINDING ENERGY}\\ \text{IN SYSTEM}\end{pmatrix} + \begin{pmatrix}\text{PHOTOELECTRON}\\ \text{KINETIC ENERGY}\end{pmatrix}$$

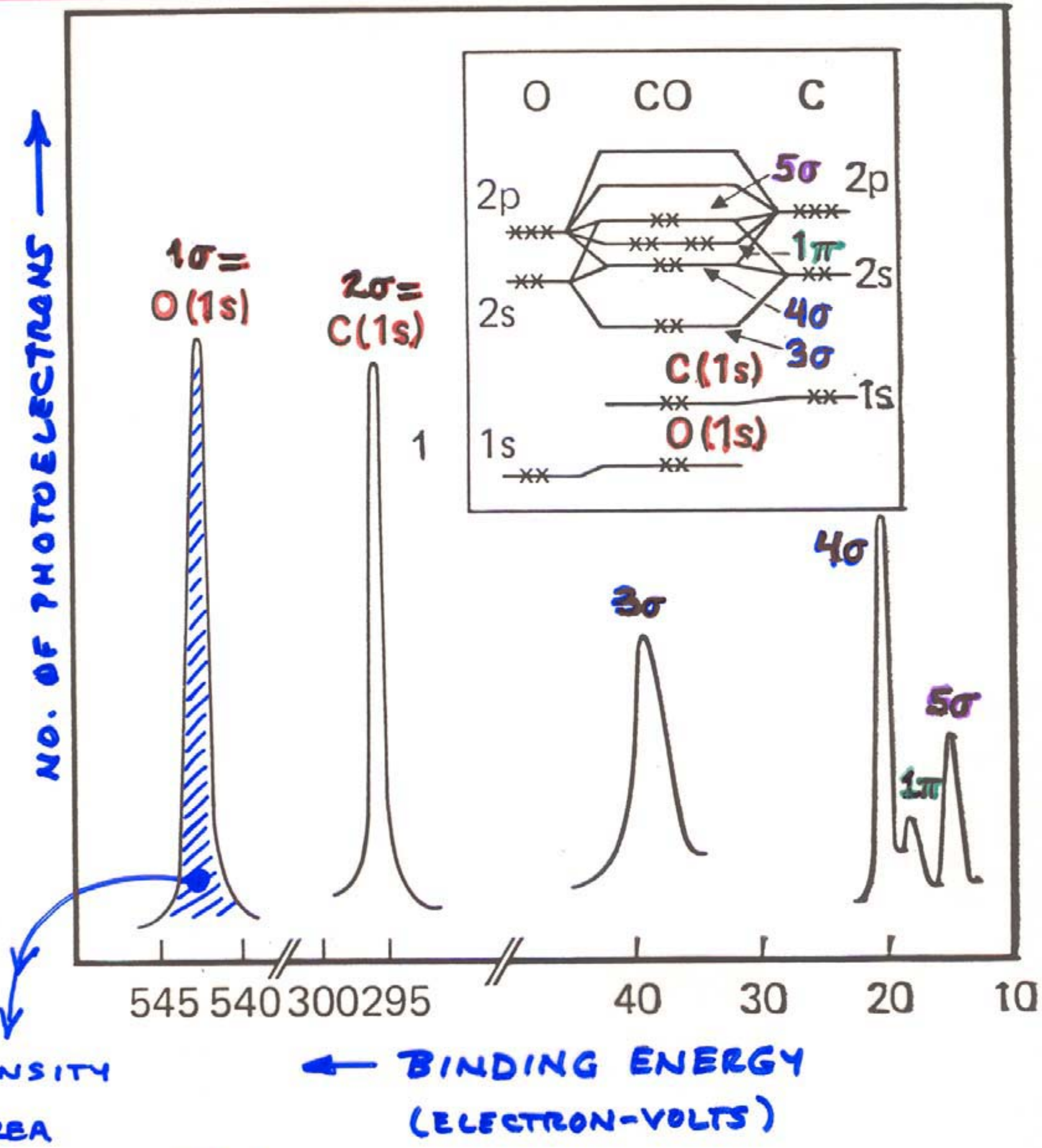
(ABSORBED) (EMITTED)

$$= \quad \text{B.E.} \quad + \quad \text{K.E.}$$

EXAMPLE – CO MOLECULE:



X-RAY PHOTOELECTRON SPECTRUM OF CO



INTENSITY

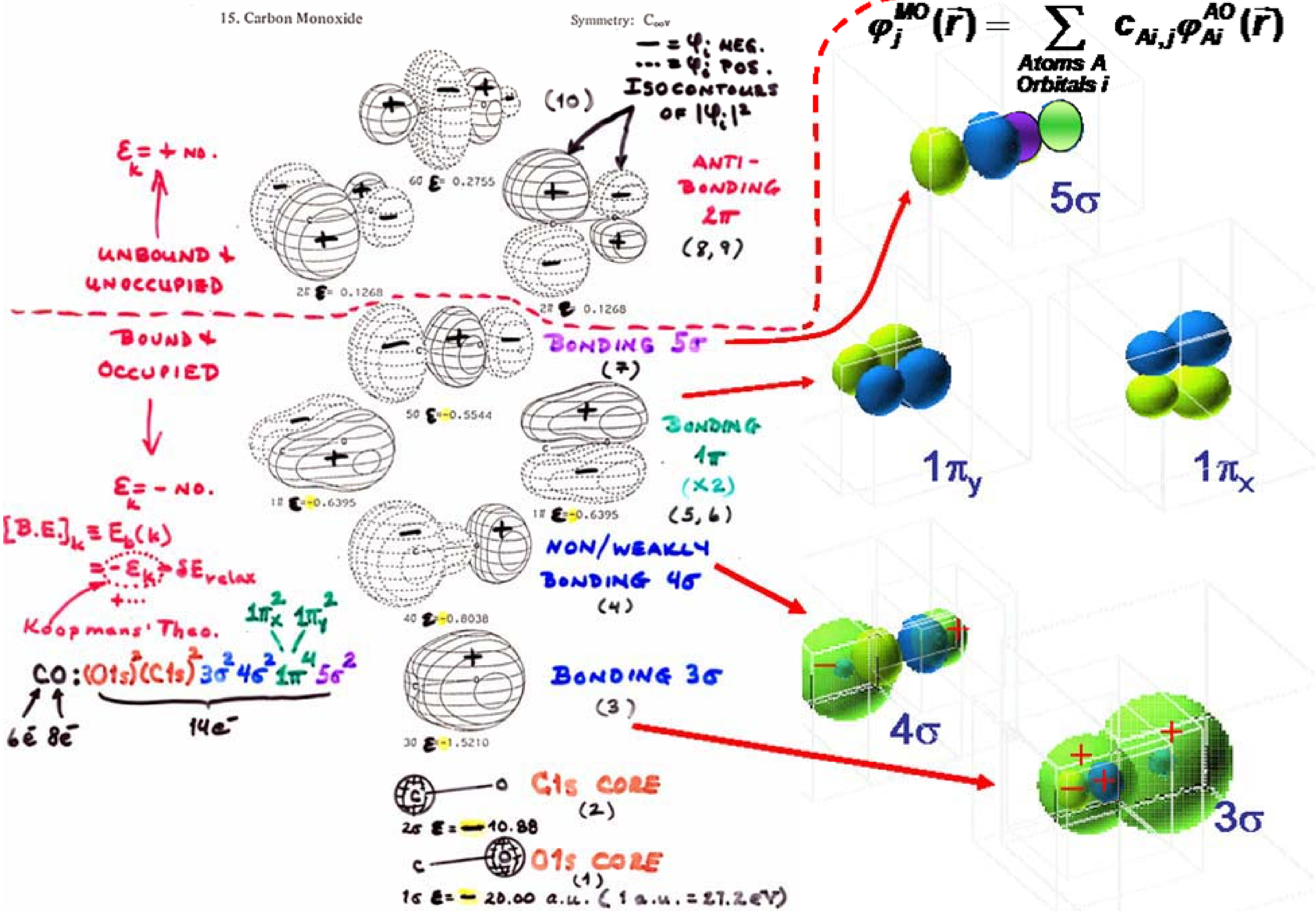
∝ AREA

∝ PHOTOELECTRIC CROSS SECTION × NO. ATOMS → QUANTITATIVE SURFACE ANALYSIS

THE ELECTRONS IN CARBON MONOXIDE:

Atomic orbital makeup

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



$[B.E.]_k \equiv E_b(k) = -\varepsilon_k + \delta E_{relax} + \cdots$

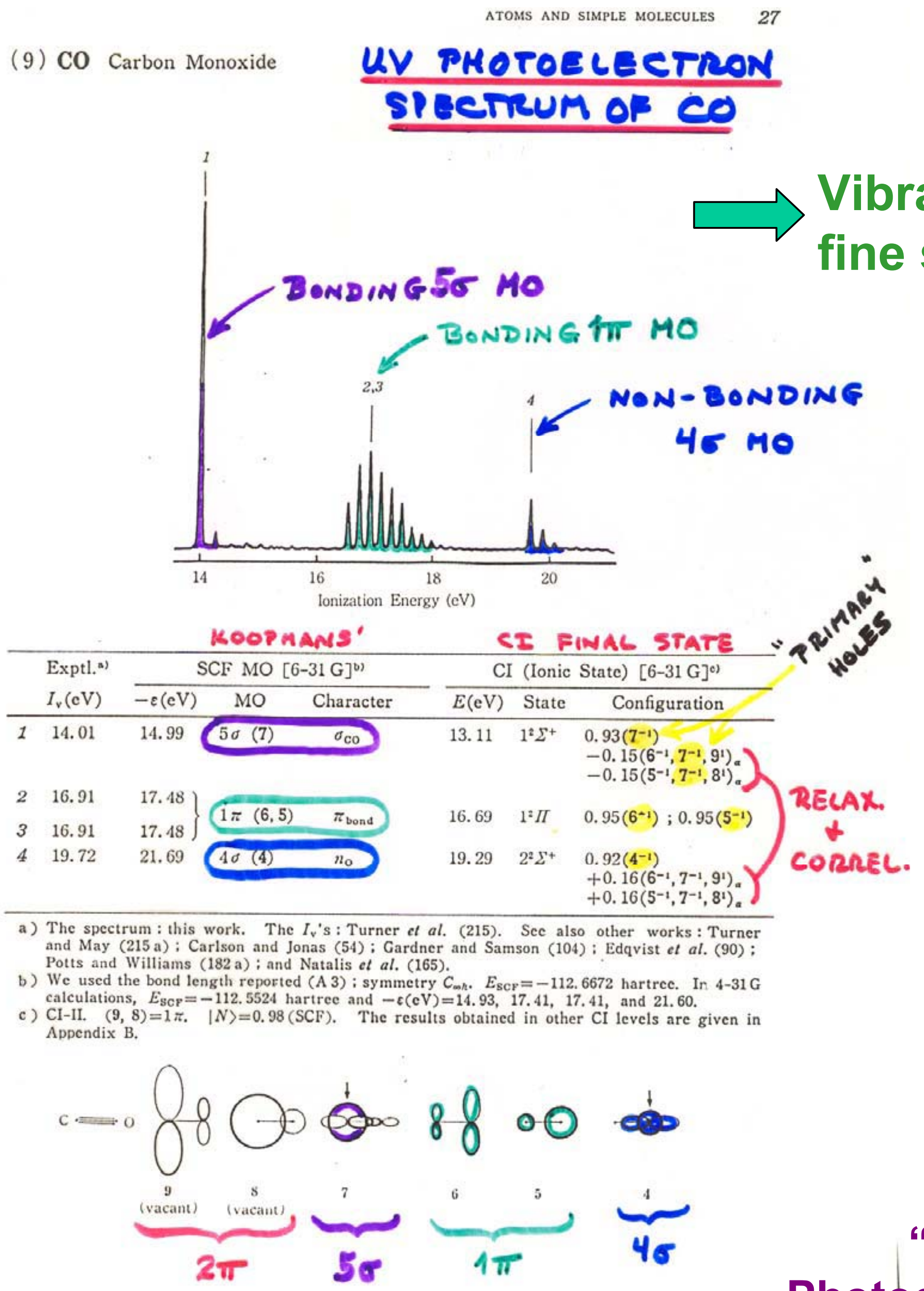
Koopmans' Theo.

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

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

6e⁻ 8e⁻

14e⁻



ATOMS AND SIMPLE MOLECULES 27

(9) **CO** Carbon Monoxide

UV PHOTOELECTRON SPECTRUM OF CO

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.

Vibrational fine structure

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

INTENSITIES IN PHOTOELECTRON SPECTRA:

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

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

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

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

- SUDDEN APPROXIMATION: $\varphi_k \to \varphi_f$ = PHOTOE (FAST)

k HOLE →

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

$$\text{INT.}_k \propto |\langle \psi^f_{VIB,v'}|\psi^i_{VIB,v}\rangle|^2 |\langle \underbrace{\psi^f_{e^-}(N-1,k)|\psi_R\overset{\overset{k \text{ MISSING}}{\uparrow}}{(N-1,k)}\rangle}_{\text{SAME SUBSHELL COUPLING + TOTAL L,S}\rightarrow\text{"MONOPOLE"}}|^2$$

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

↳ NORMAL $\frac{d\sigma_k}{d\Omega}$

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

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

$$\text{INT.}_k \propto |\langle\psi^f_{VIB,v'}|\psi^i_{VIB,v}\rangle|^2 \left.\begin{array}{l} |\langle\varphi_1'|\varphi_1\rangle|^2|\langle\varphi_2'|\varphi_2\rangle|^2\cdots \\ |\langle\varphi_{k-1}'|\varphi_{k-1}\rangle|^2|\langle\varphi_{k+1}'|\varphi_{k+1}\rangle|^2\cdots|\langle\varphi_N'|\varphi_N\rangle|^2. \end{array}\right\}$$

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

1e- DIPOLE→dσ/dΩ

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

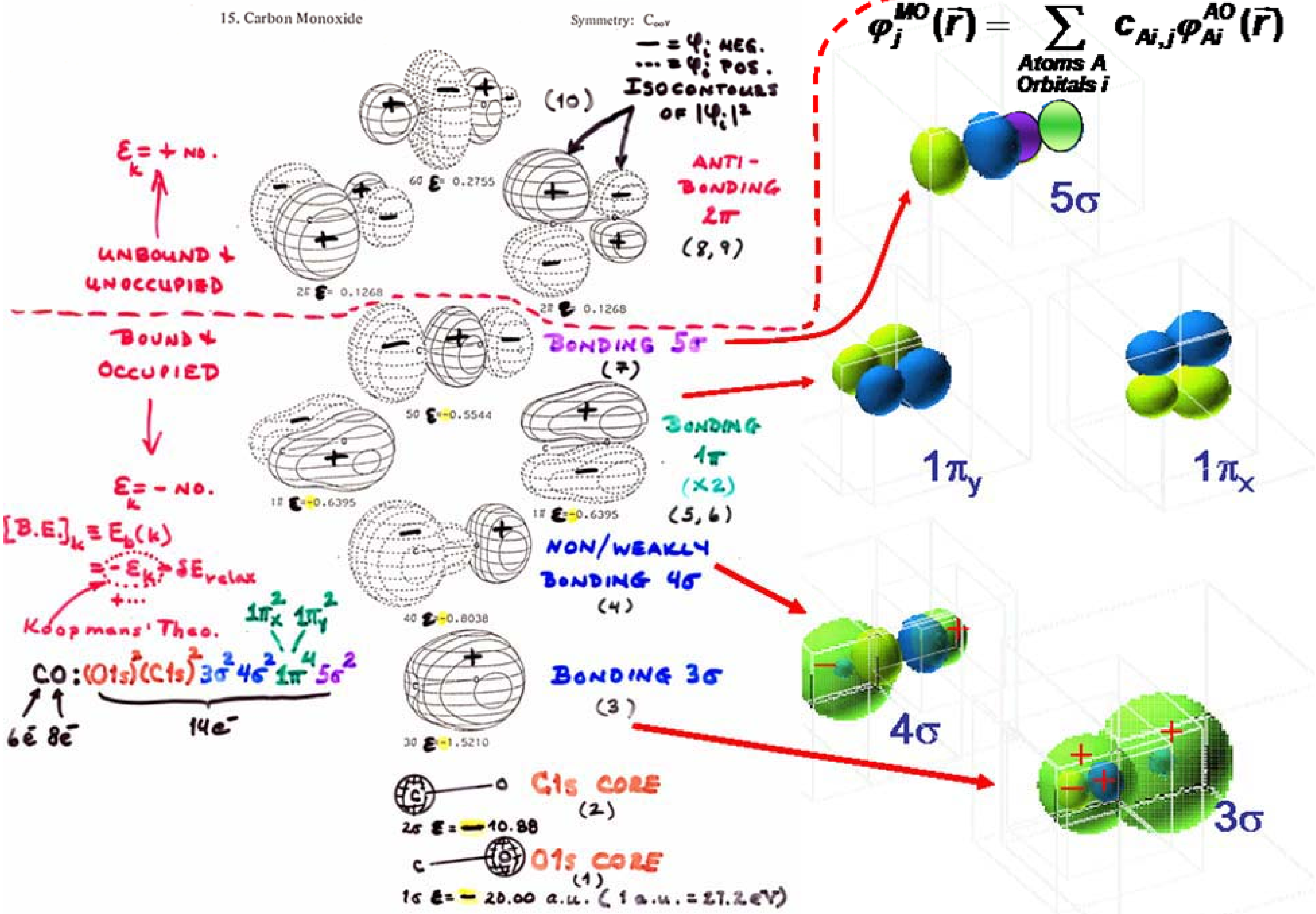
- PLUS DIFFRACTION EFFECTS IN φ_f ESCAPE

“Basic Concepts of XPS”
Chapter 3

THE ELECTRONS IN CARBON MONOXIDE:

Atomic orbital makeup

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



$$[B.E.]_k \equiv E_b(k) = -\varepsilon_k + \delta E_{relax} + \cdots$$

Koopmans' Theo.

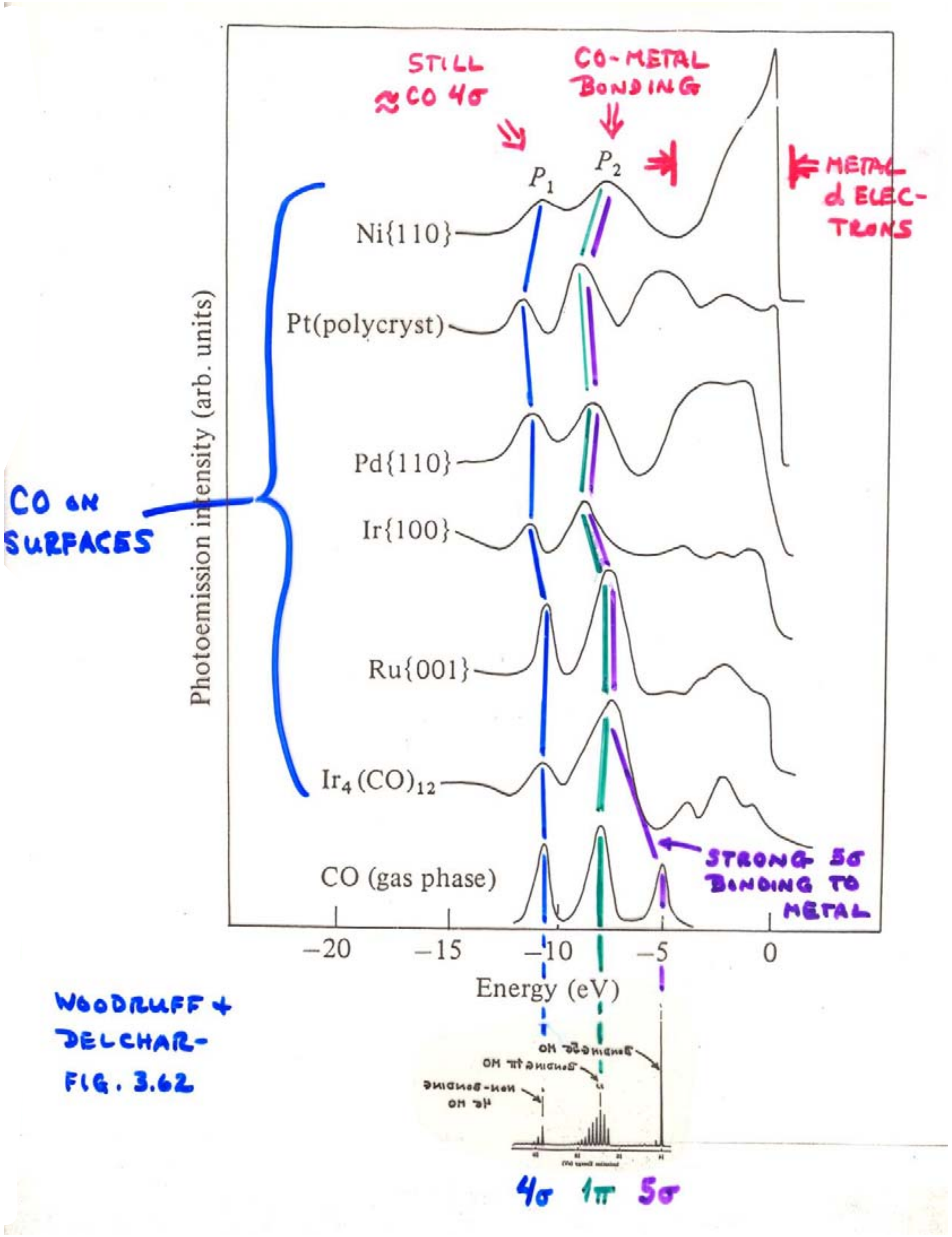
$$\mathrm{CO} : (O1s)^2 (C1s)^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$$

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

6e⁻ 8e⁻

14e⁻

Valence-level Photoelectron spectra of CO adsorbed on various transition metal surfaces

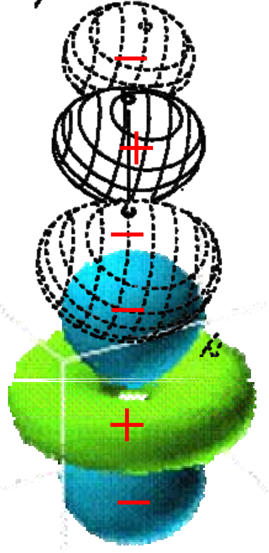


WOODRUFF + DELCHAR-
FIG. 3.62

Theoretical Calculations of charge density for CO bound to Ni(001)- “on-top”:

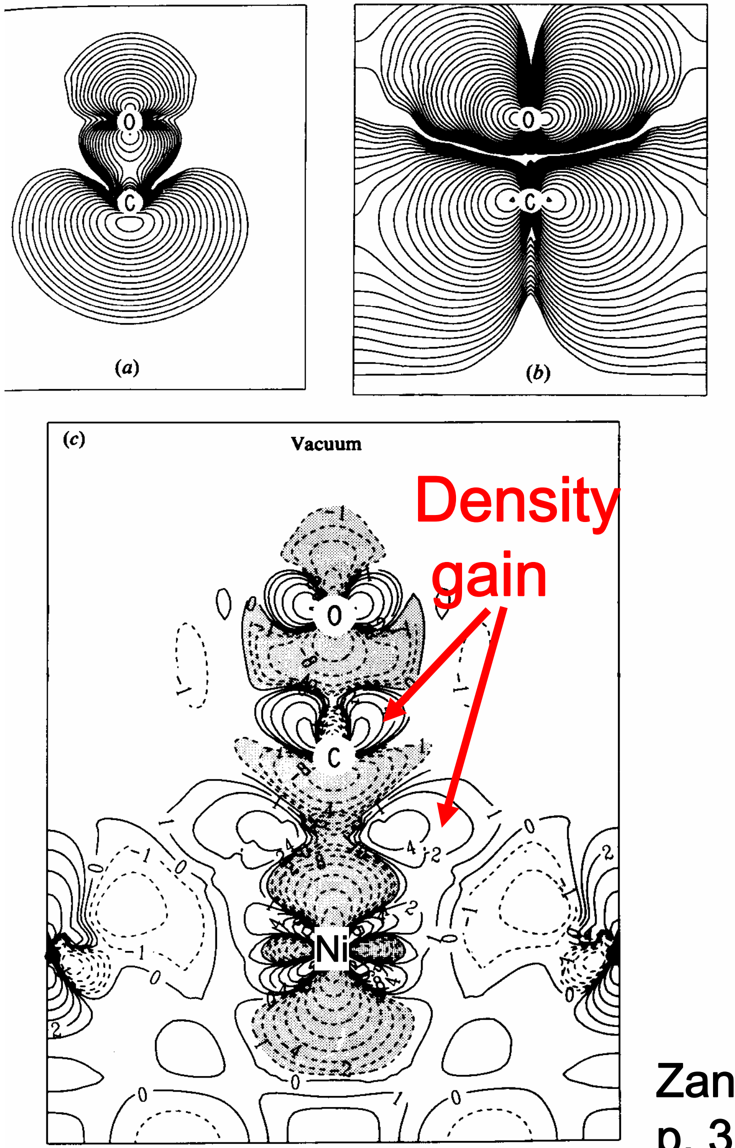
O
|
C
|
Ni

CO 5σ



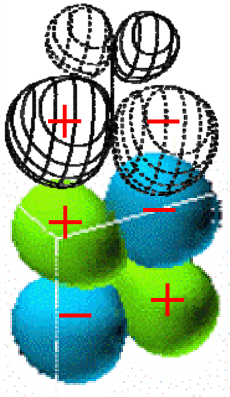
Ni 3d$_{z^2}$
σ bond

Fig. 12.14. Charge density contour plots appropriate to Ni(100) c(2 × 2)-CO: (*a*) free molecule 5σ orbital; (*b*) free molecule 2π orbital; (*c*) difference between CO/Ni(100) and the superposition of clean Ni(100) and an unsupported CO monolayer. Solid (dashed) lines indicate a gain (loss) of electronic charge (Wimmer, Fu & Freeman, 1985).



Density gain

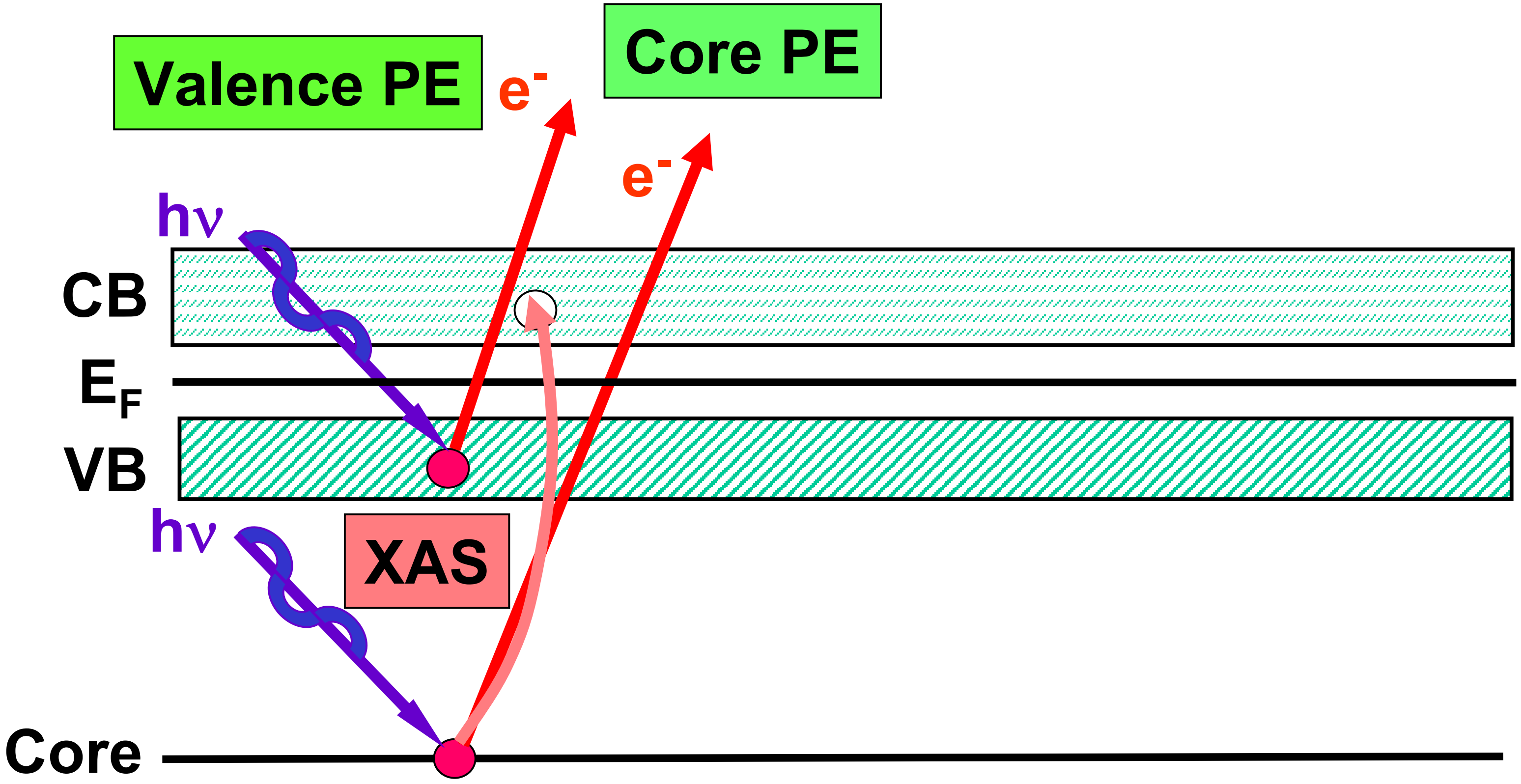
CO 2π = π*



Ni 3d$_{xy}$
π “back bond”

Zangwill,
p. 307, plus
PRL 55, 2618 (’85)

The Soft X-Ray Spectroscopies

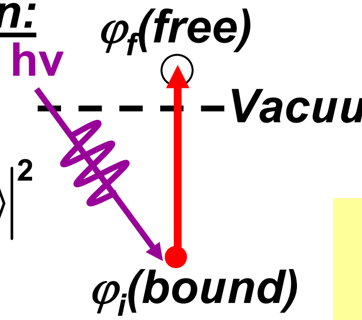


PE = photoemission = photoelectron spectroscopy
XAS = x-ray absorption spectroscopy
AES = Auger electron spectroscopy
XES = x-ray emission spectroscopy
RIXS = resonant inelastic x-ray scattering / x-ray Raman scatt.

MATRIX ELEMENTS IN THE SOFT X-RAY SPECTROSCOPIES: DIPOLE LIMIT

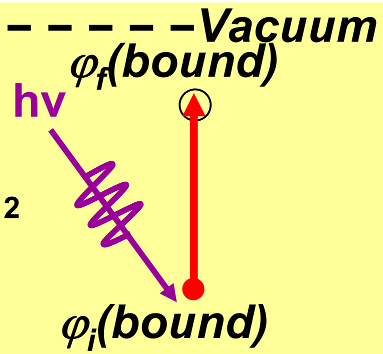
- ***Photoelectron spectroscopy/photoemission:***

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

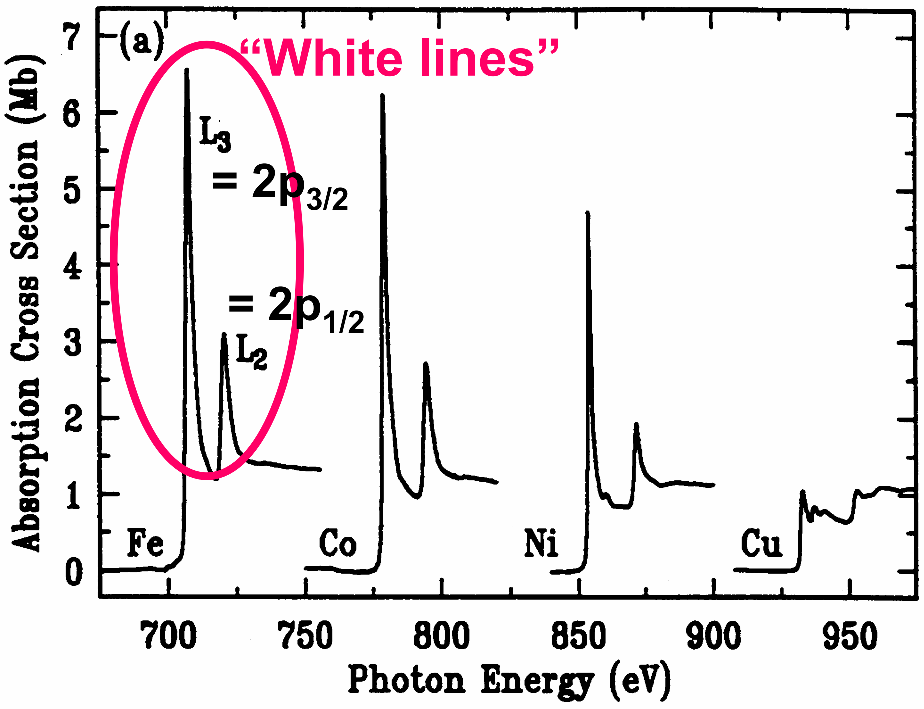


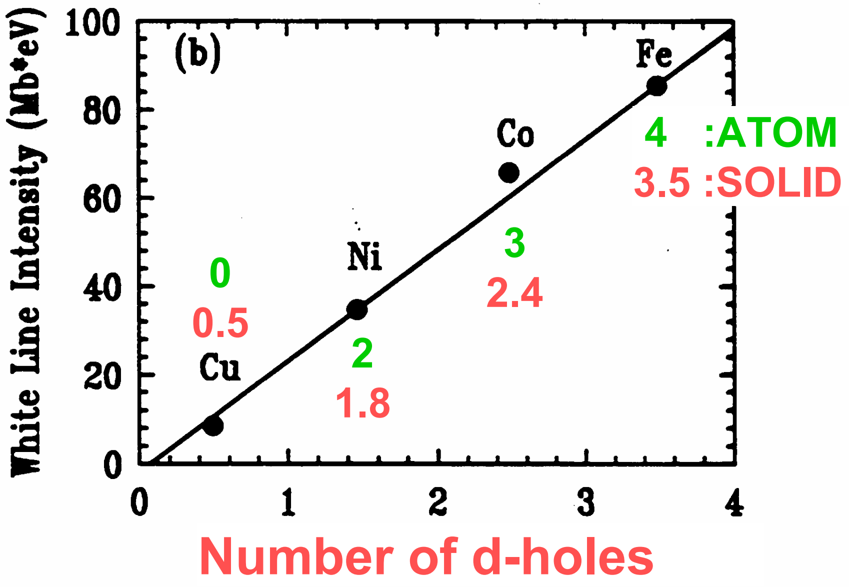
- ***Near-edge x-ray absorption:***

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



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

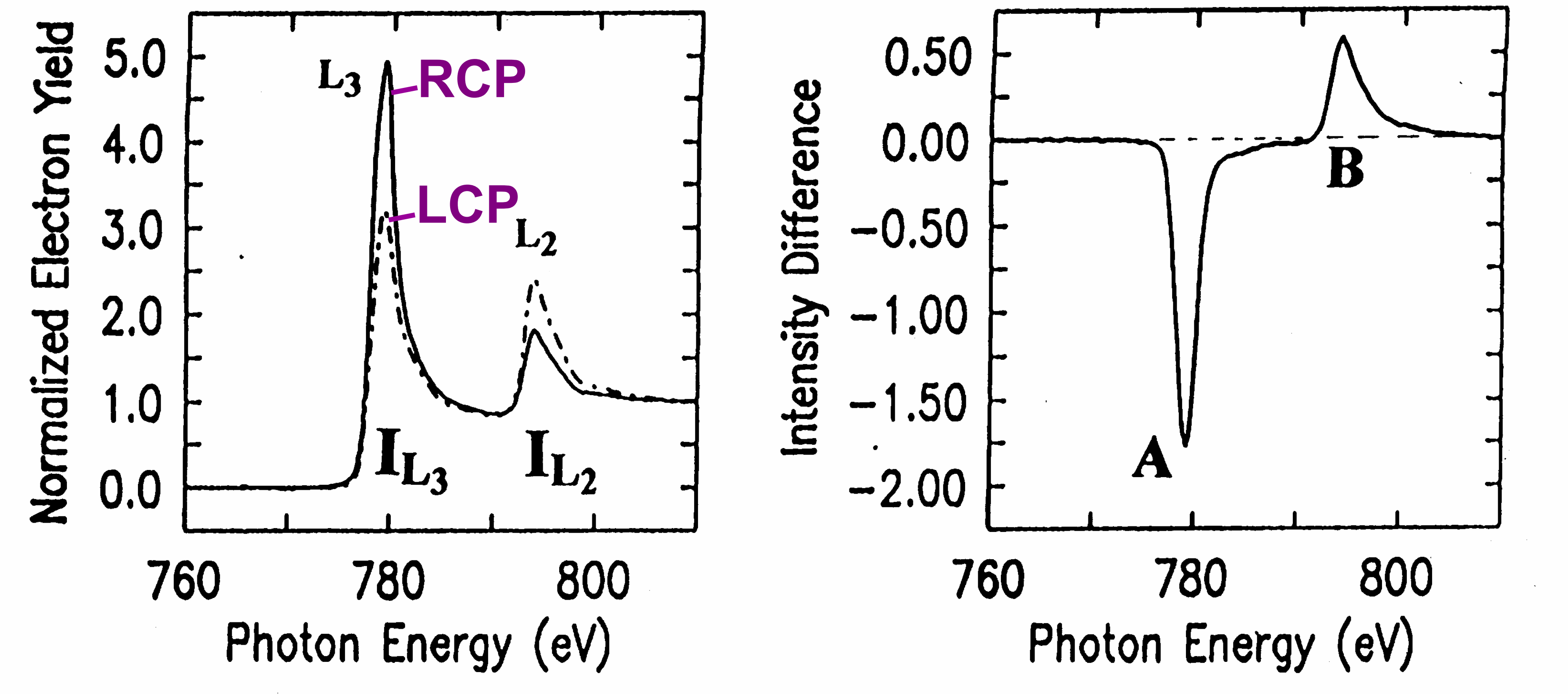




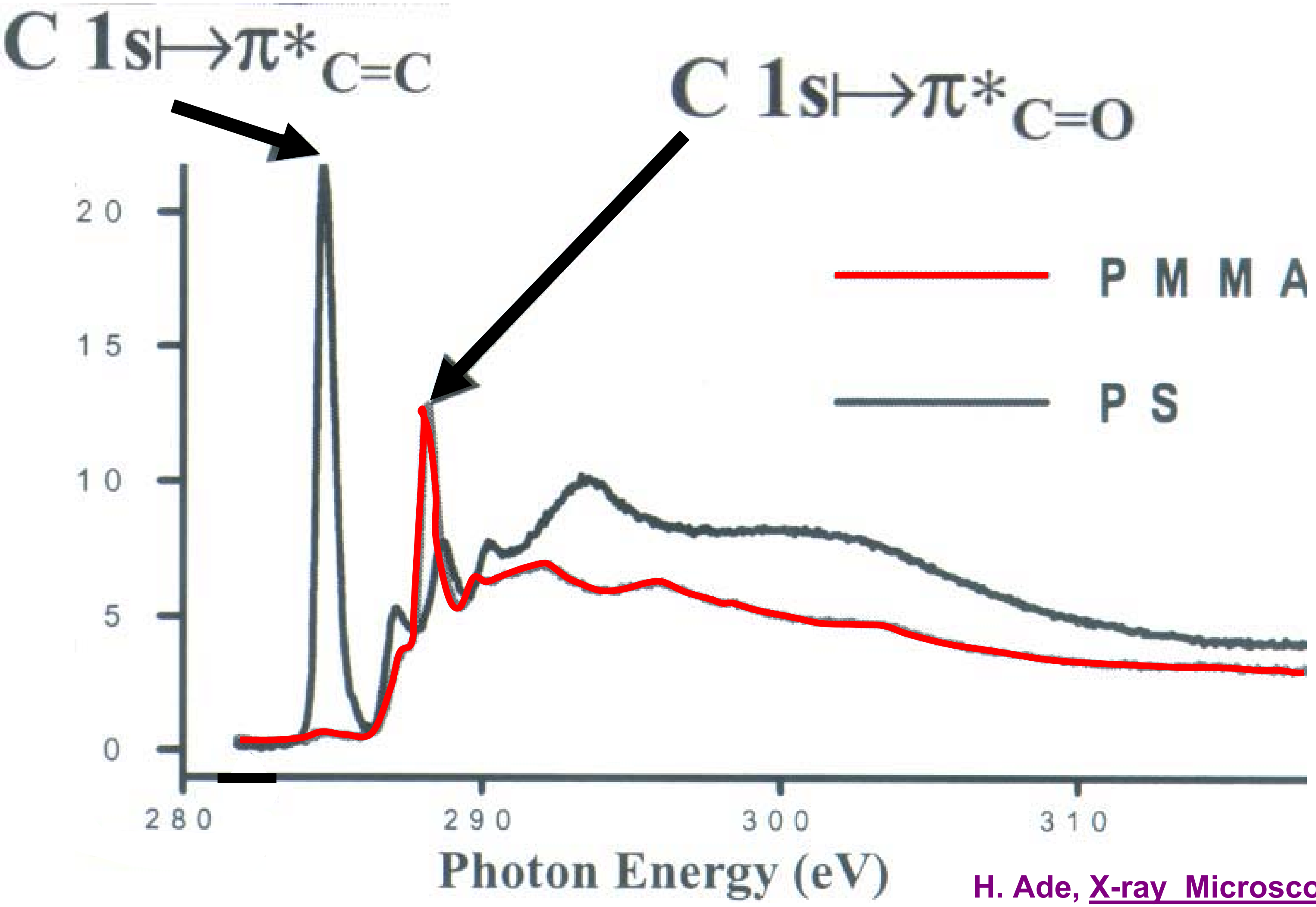
J. Stohr, "NEXAFS Spectroscopy"

Magnetic Circular Dichroism in X-Ray Absorption (XMCD)

Ferromagnetic cobalt with magnetization along incident light direction

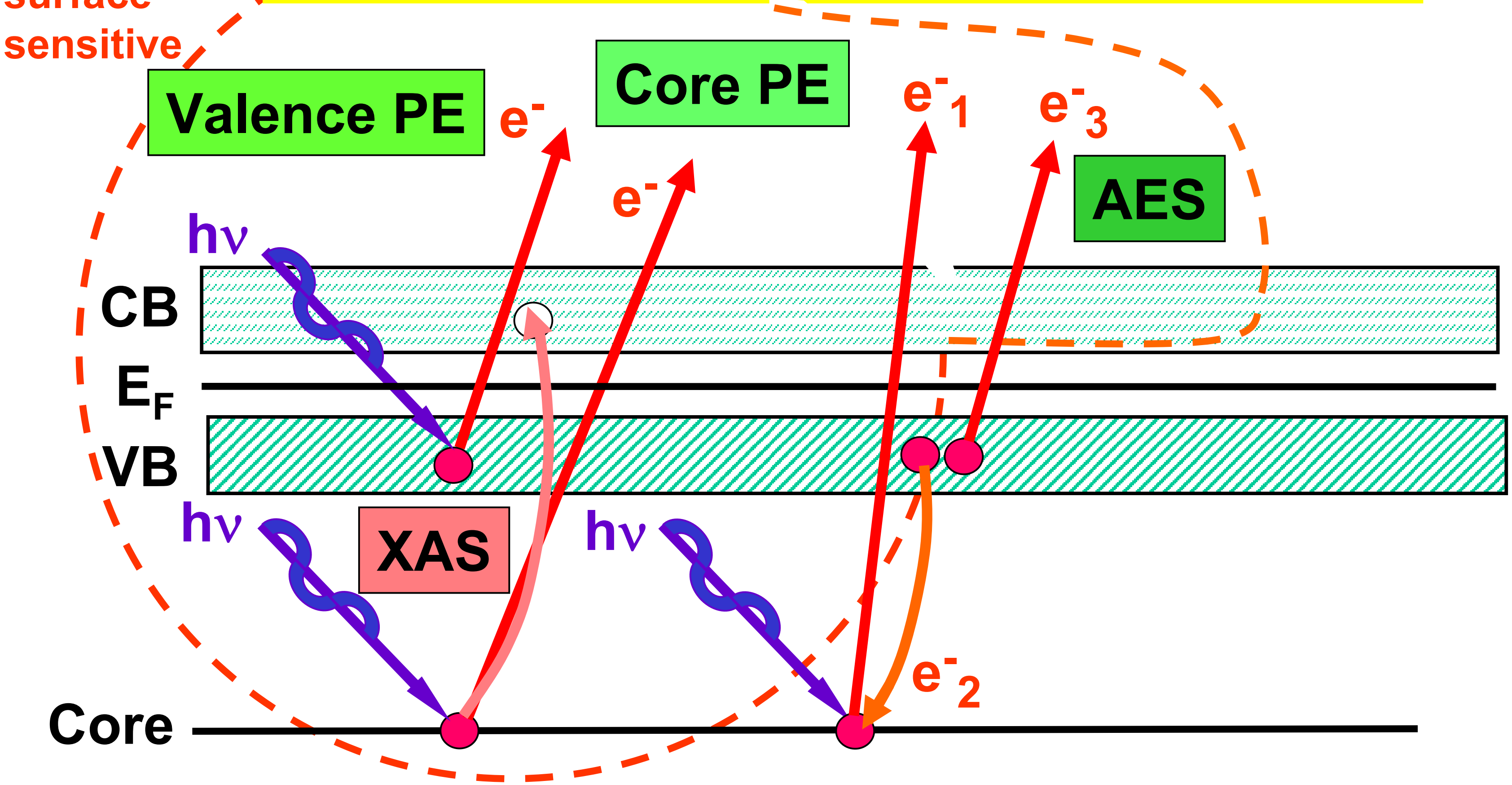


Variation of Near-Edge X-Ray Absorption Fine Structure (NEXAFS) for Different Polymers



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

The Soft X-Ray Spectroscopies

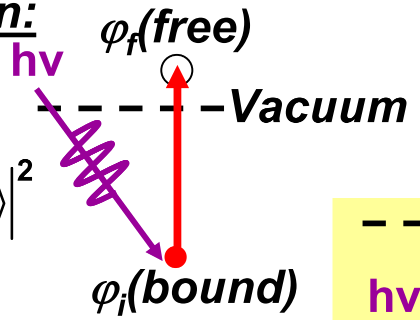


PE = photoemission = photoelectron spectroscopy
XAS = x-ray absorption spectroscopy
AES = Auger electron spectroscopy
XES = x-ray emission spectroscopy
REXS/RIXS = resonant elastic/inelastic x-ray scattering

MATRIX ELEMENTS IN THE SOFT X-RAY SPECTROSCOPIES: DIPOLE LIMIT

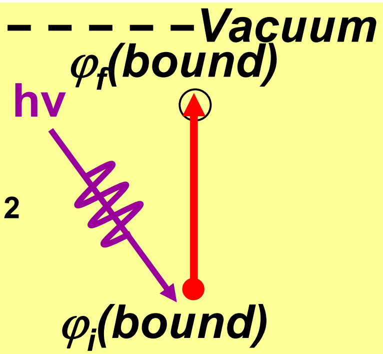
- ***Photoelectron spectroscopy/photoemission:***

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



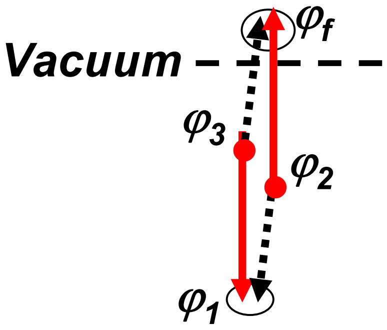
- ***Near-edge x-ray absorption:***

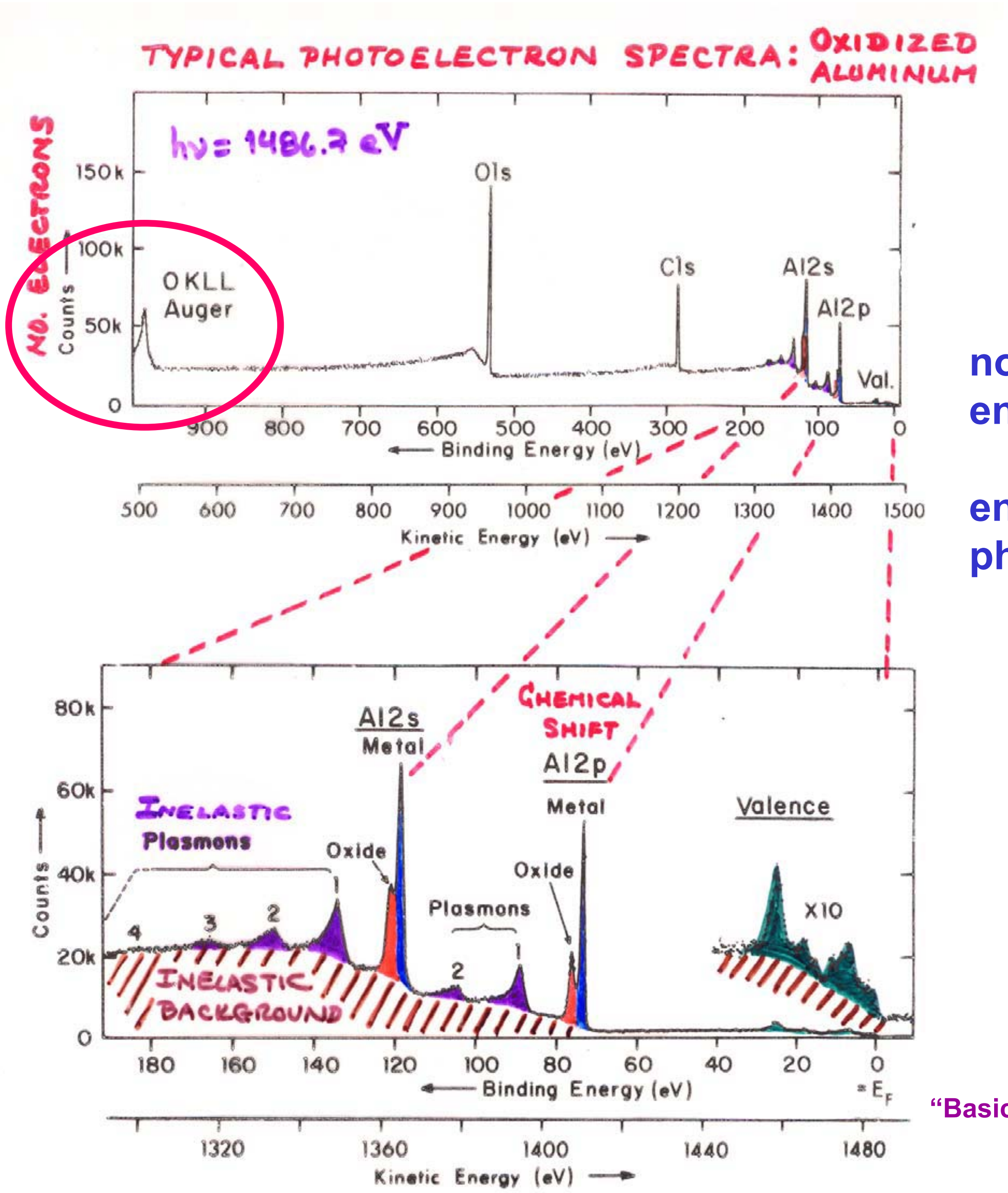
$$I \propto \left|\hat{e}\bullet\langle\varphi_f(1)|\vec{r}\,|\varphi_i(1)\rangle\right|^2$$



- ***Auger electron emission:***

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





Auger kinetic energies do not change with photon energy

Photoelectron kinetic energies shift linearly with photon energy

"Basic Concepts of XPS"
Figure 1

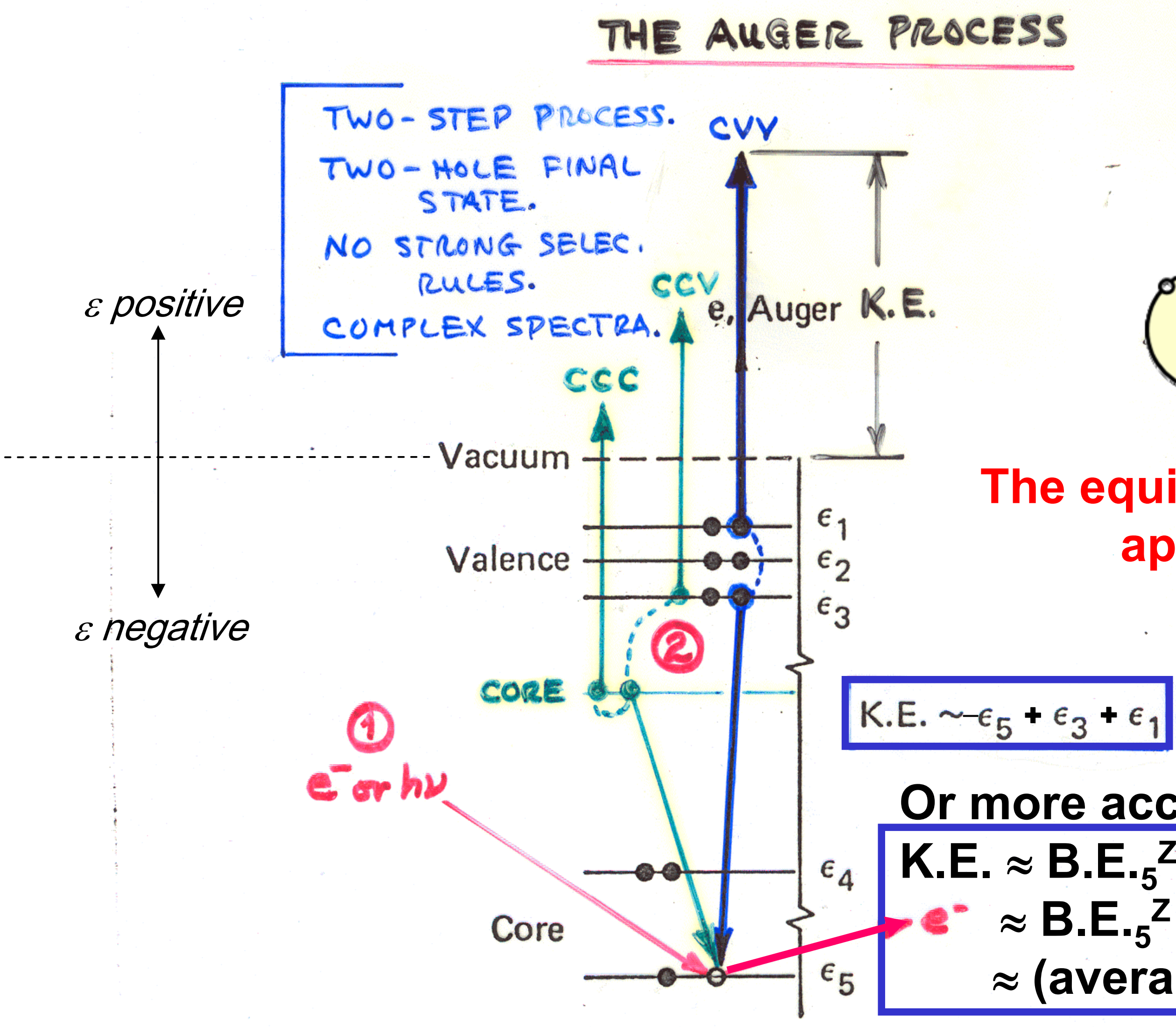
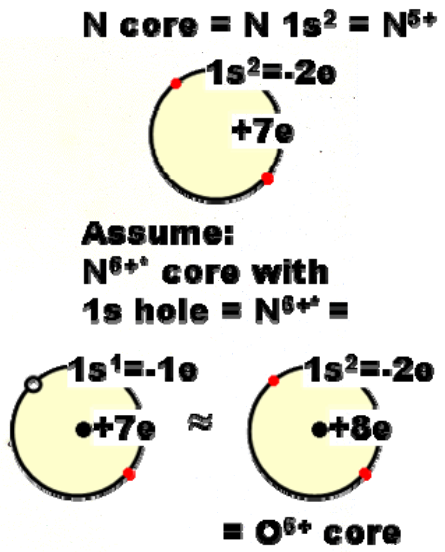


Figure 2. Scheme of the Auger process. A valence-level involved Auger emission is illustrated here, but the two electrons involved also could have come from core level, ϵ_4, provided $\epsilon_5 - 2\epsilon_4 > 0$.



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

$1s^2$=-2e

+7e

Assume:

N^{6+*} core with

1s hole = N^{6+*} =

$1s^1$=-1e

+7e ≈

$1s^2$=-2e

+8e

= O^{6+} core

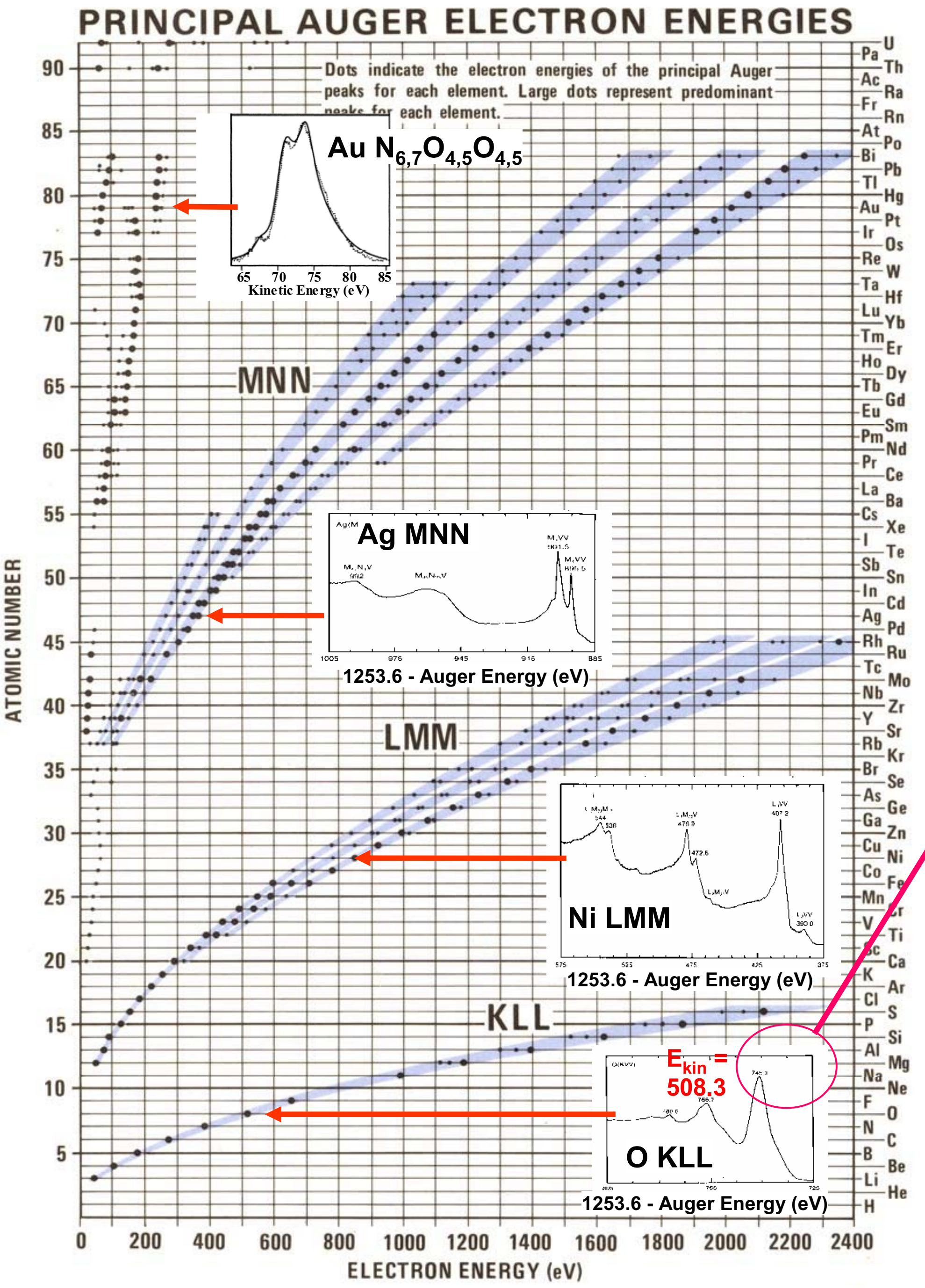
The equivalent core or Z+1 approximation

Or more accurately:

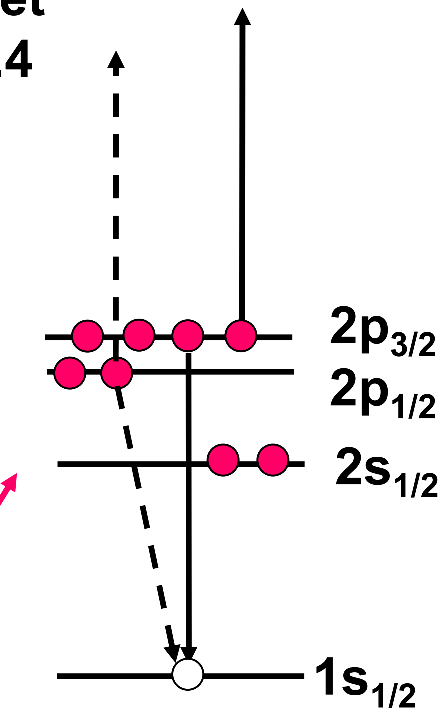
$$\text{K.E.} \approx \text{B.E.}_5^{Z} - \text{B.E.}_3^{Z+1} - \text{B.E.}_1^{Z}$$

$$\approx \text{B.E.}_5^{Z} - \text{B.E.}_3^{Z} - \text{B.E.}_1^{Z+1}$$

$$\approx \text{(average of two above)}$$



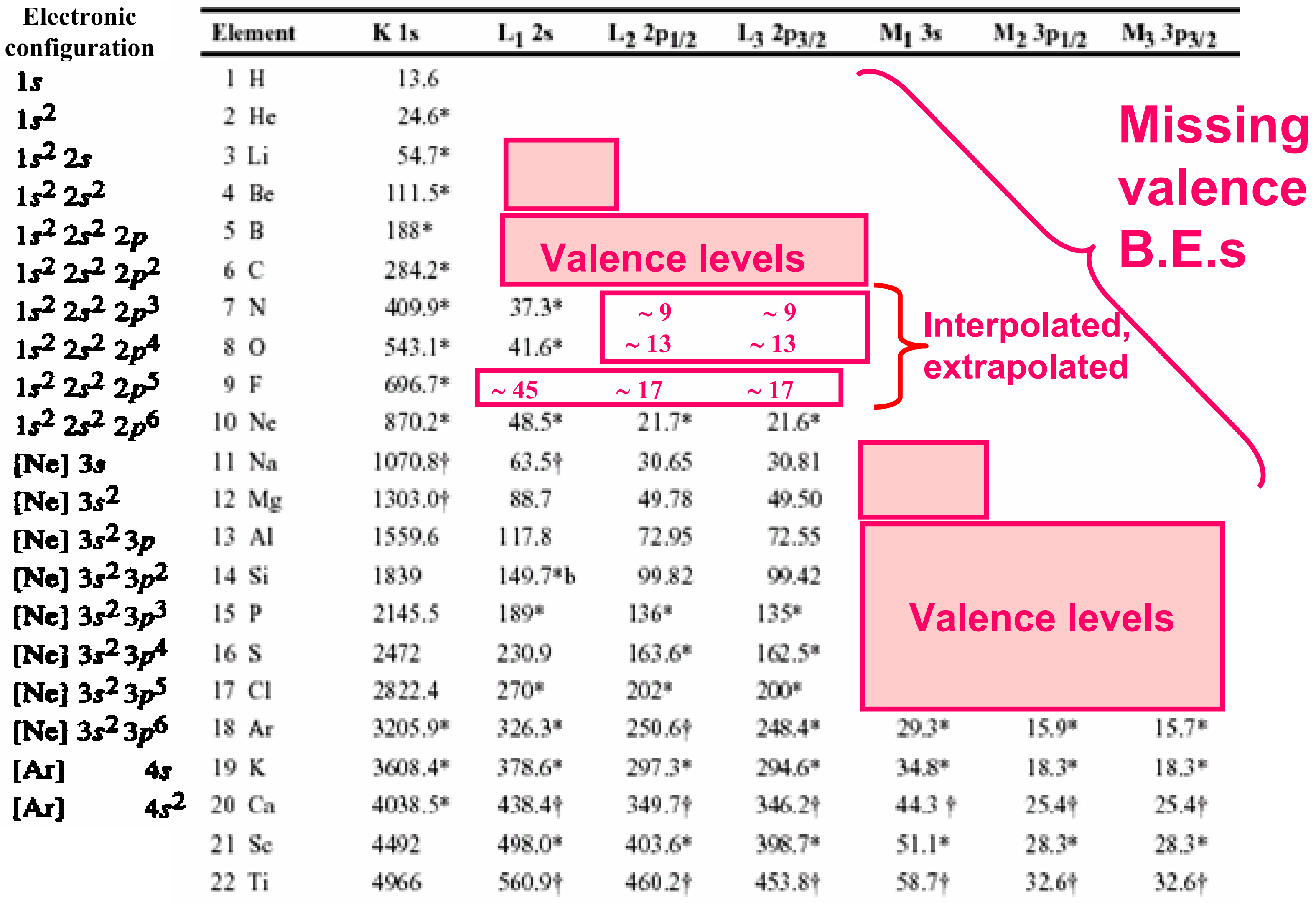
X-Ray Data Booklet Fig. 1.4



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

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

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



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

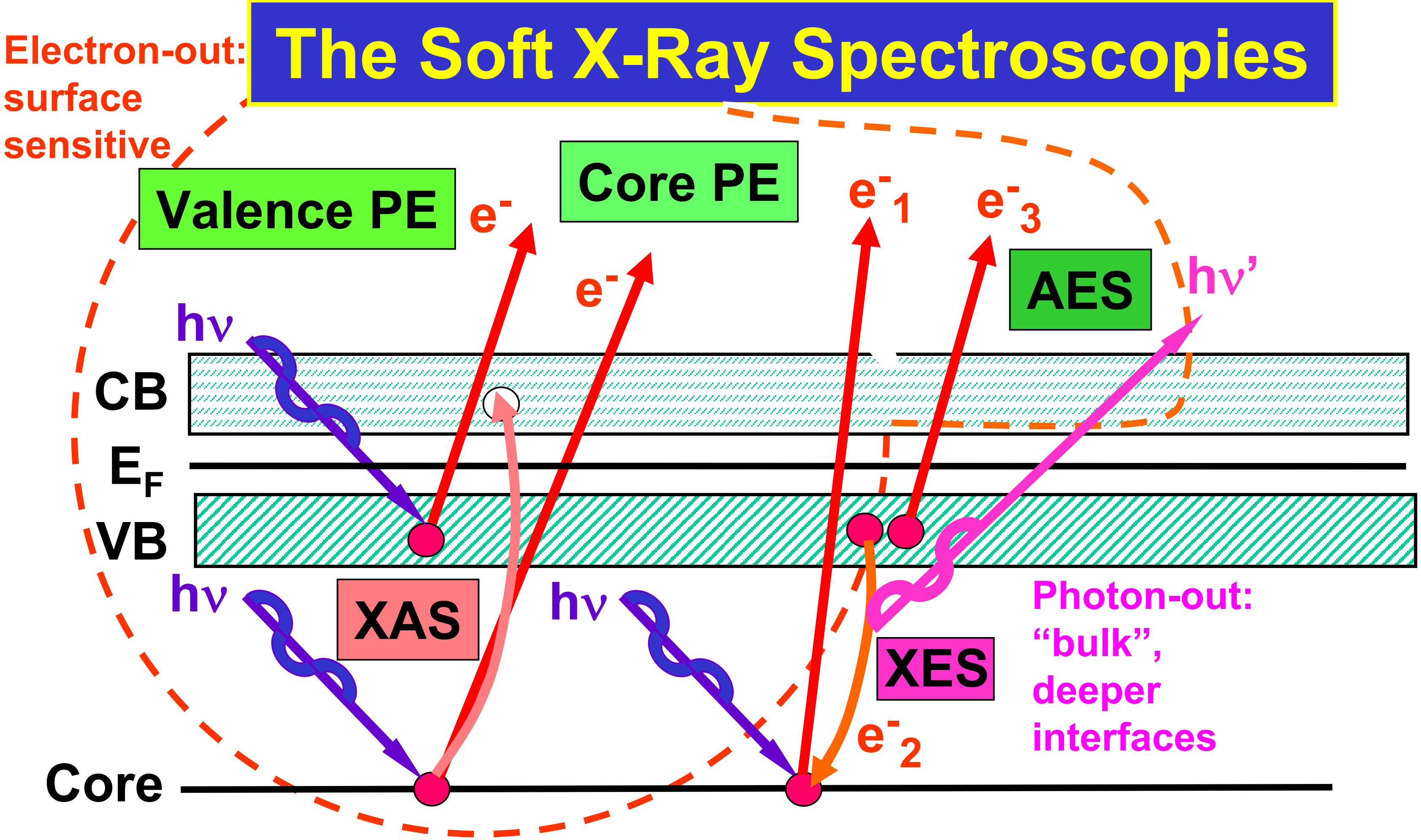
Valence levels

Interpolated, extrapolated

Missing valence B.E.s

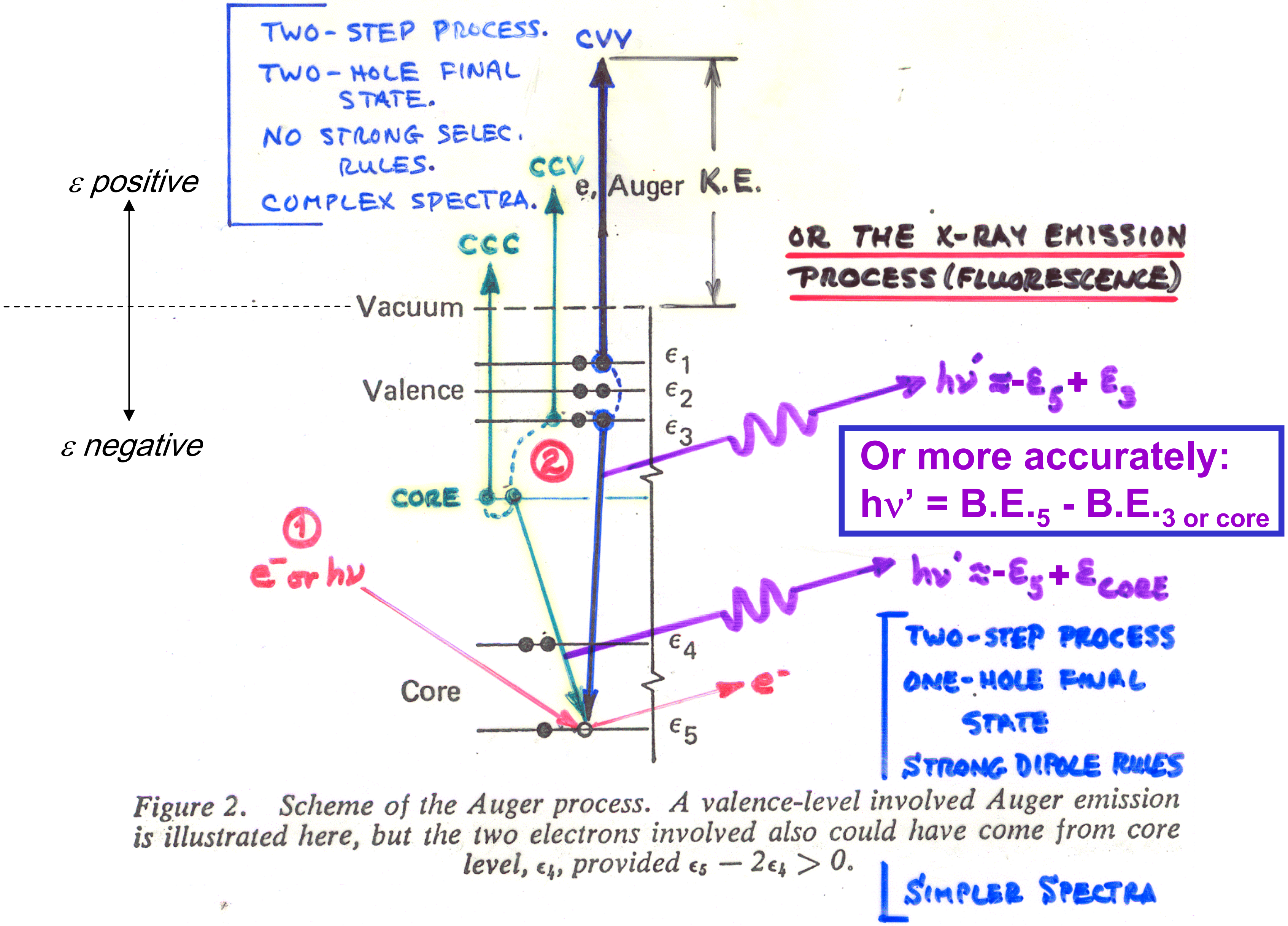
Valence levels

The Soft X-Ray Spectroscopies



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

THE AUGER PROCESS



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

OR THE X-RAY EMISSION PROCESS (FLUORESCENCE)

Or more accurately:
$h\nu' = B.E._5 - B.E._{3 \text{ or core}}$

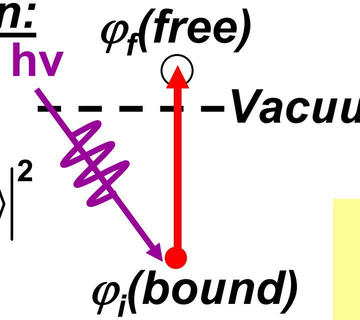
TWO-STEP PROCESS
ONE-HOLE FINAL STATE
STRONG DIPOLE RULES
SIMPLER SPECTRA

Figure 2. Scheme of the Auger process. A valence-level involved Auger emission is illustrated here, but the two electrons involved also could have come from core level, ϵ_4, provided $\epsilon_5 - 2\epsilon_4 > 0$.

MATRIX ELEMENTS IN THE SOFT X-RAY SPECTROSCOPIES: DIPOLE LIMIT

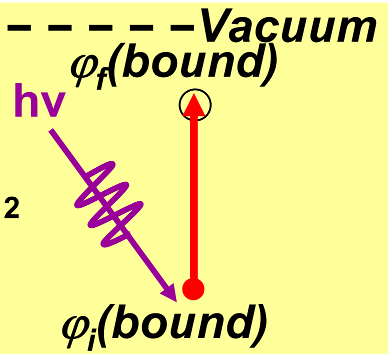
- ***Photoelectron spectroscopy/photoemission:***

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



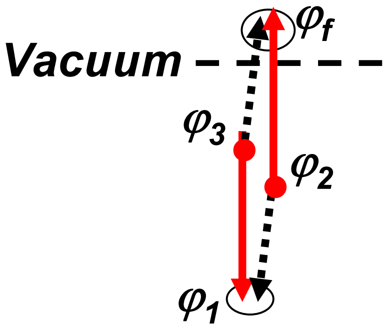
- ***Near-edge x-ray absorption:***

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



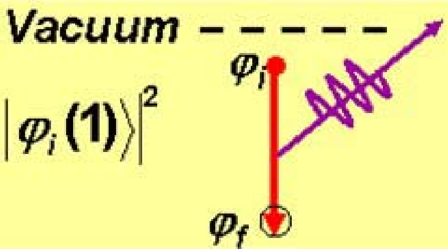
- ***Auger electron emission:***

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



- *X-ray emission:*

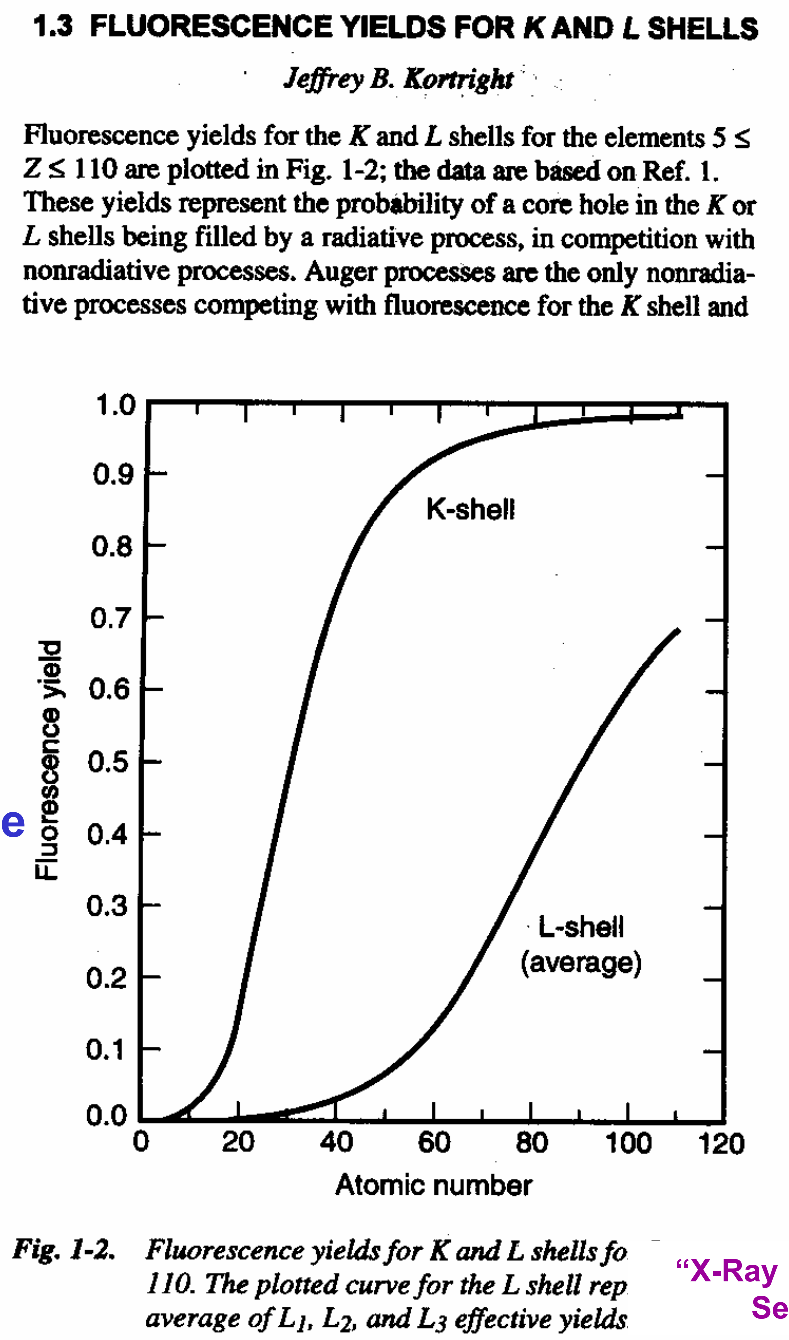
$$I \propto \left| \hat{e} \bullet \langle \varphi_f(1) | \vec{r} | \varphi_i(1) \rangle \right|^2$$



If fluorescence yield ≡ FY

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

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



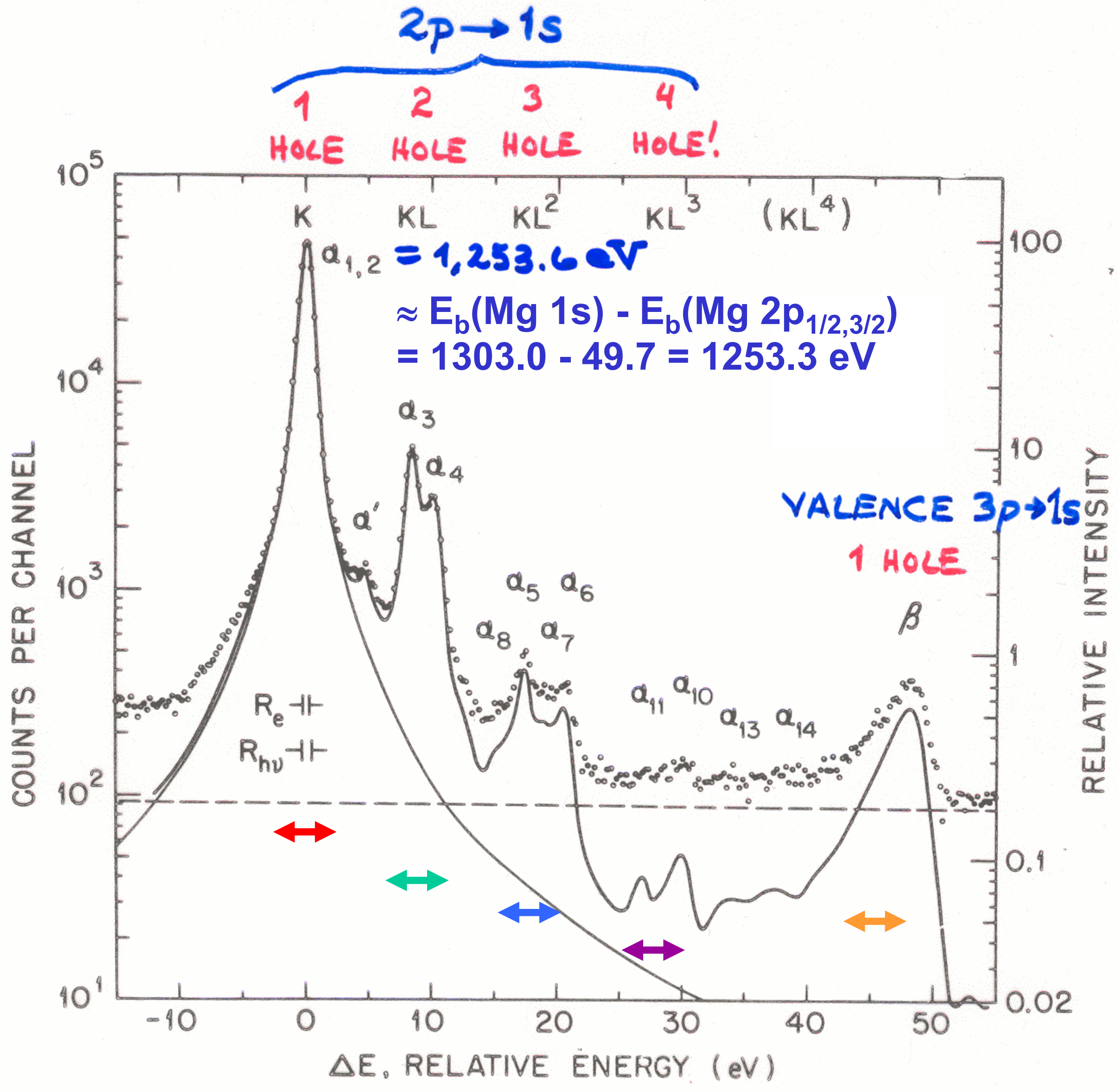
1.3 FLUORESCENCE YIELDS FOR *K* AND *L* SHELLS

Jeffrey B. Kortright

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

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

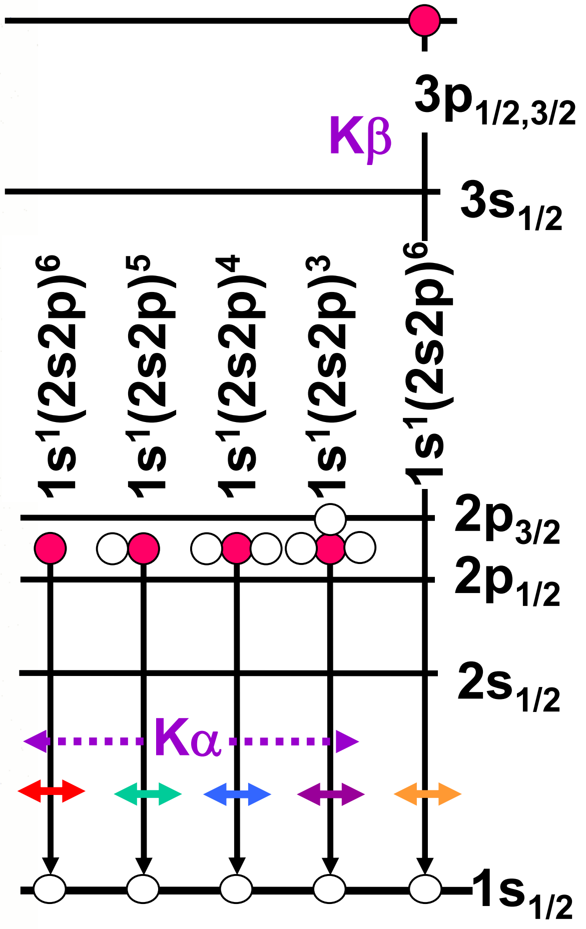
"X-Ray Data Booklet"
Section 1.3



$= 1{,}253.6$ eV

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

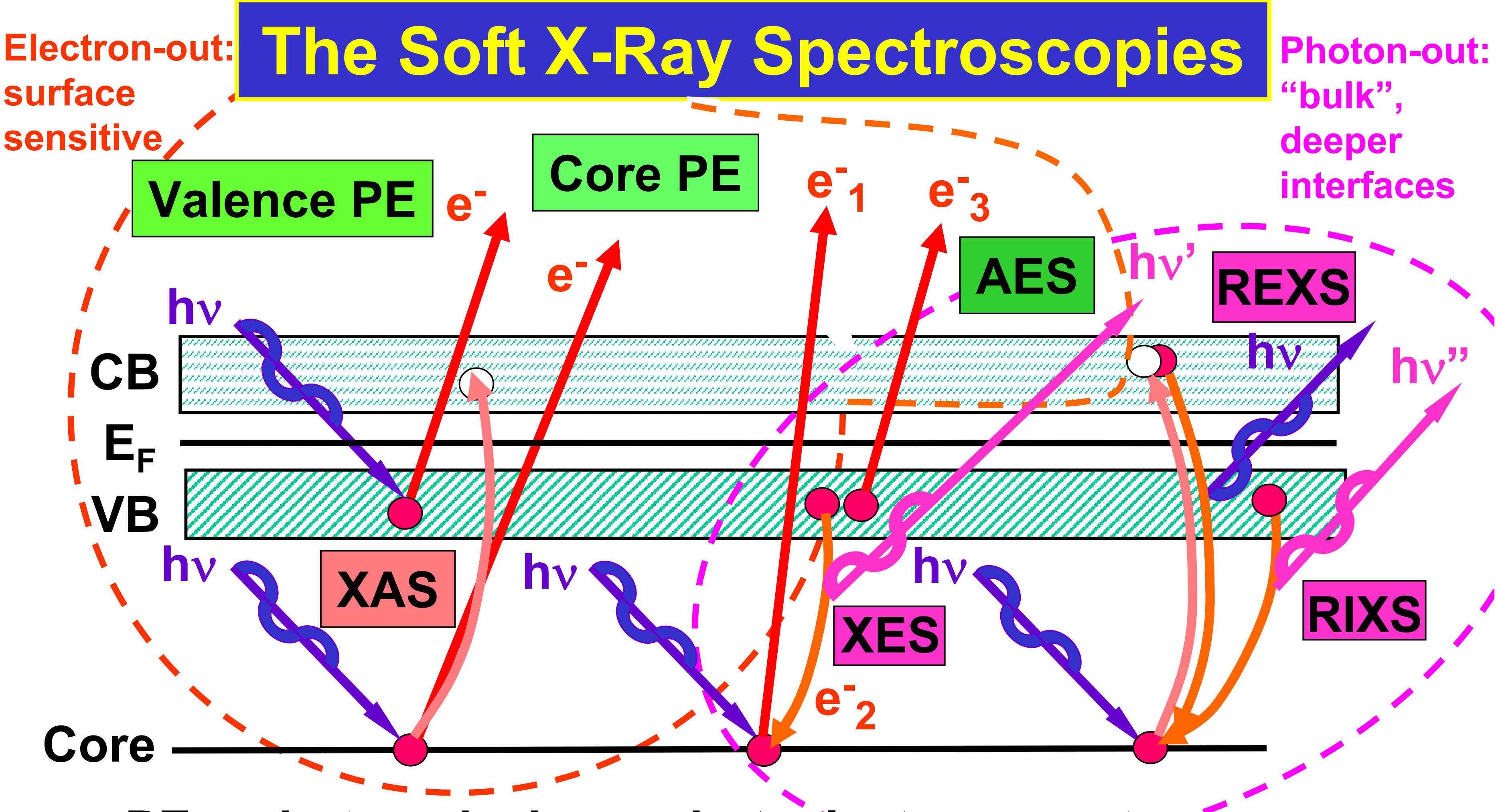
A STANDARD LABORATORY X-RAY SOURCE



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

"Basic Concepts of XPS"
Figure 2

The Soft X-Ray Spectroscopies



PE = photoemission = photoelectron spectroscopy

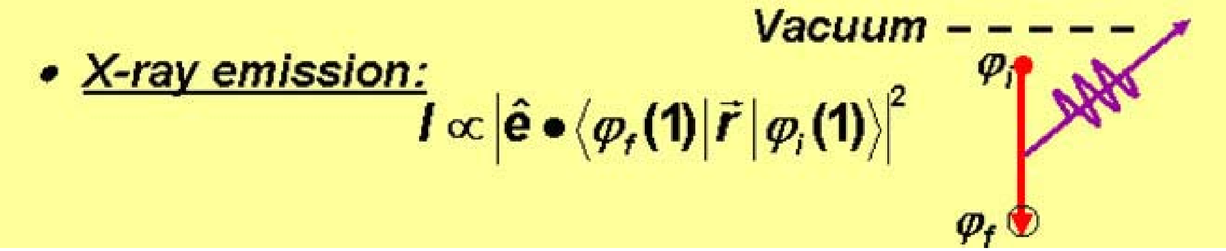
XAS = x-ray absorption spectroscopy

AES = Auger electron spectroscopy

XES = x-ray emission spectroscopy

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

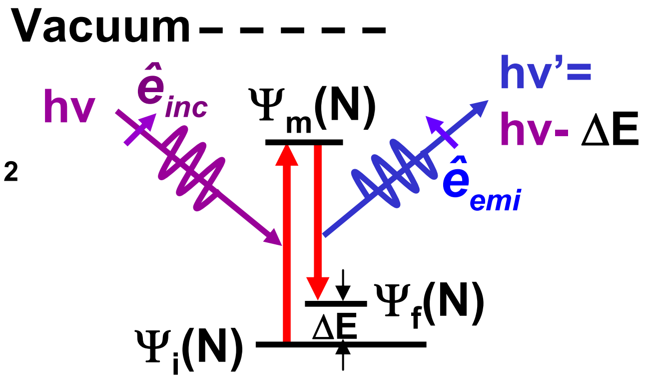
MATRIX ELEMENTS IN THE SOFT X-RAY SPECTROSCOPIES: RESONANT EFFECTS



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

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

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



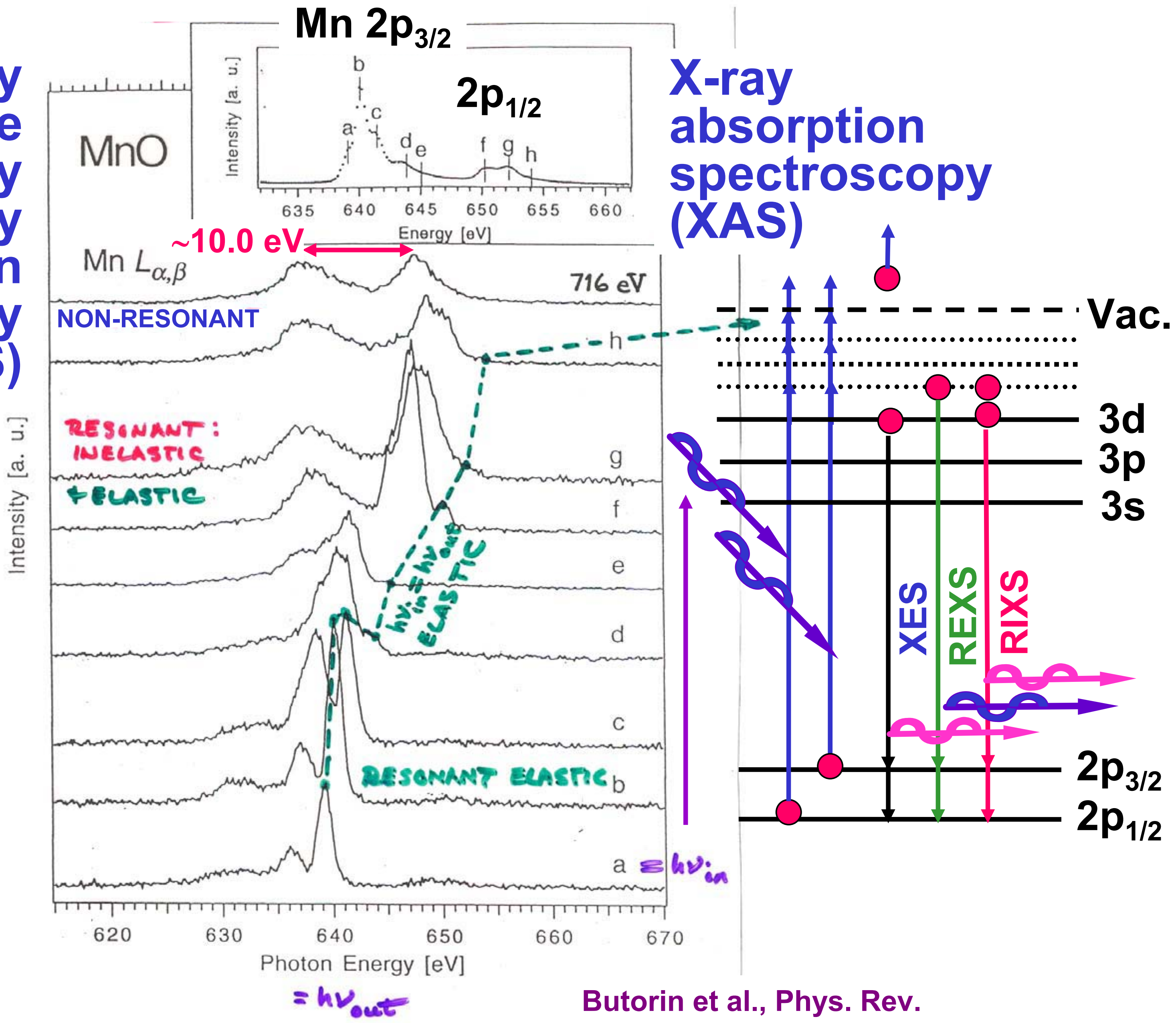
$$I \propto \sum_f \left| \sum_m \frac{\langle \Psi_f(N) | \hat{e}_{emi} \bullet \vec{r} | \Psi_m(N) \rangle \langle \Psi_m(N) | \hat{e}_{inc} \bullet \vec{r} | \Psi_i(N) \rangle}{h\nu + E_i(N) - E_m(N) - i\Gamma_m} \right|^2 \times \delta(h\nu - (E_m(N) - E_i(N)))$$

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

X-ray fluorescence spectroscopy =X-ray emission spectroscopy (XES)

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

X-ray absorption spectroscopy (XAS)



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

X-Ray Nomenclature (from “X-Ray Data Booklet”)

In general:

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

1-14

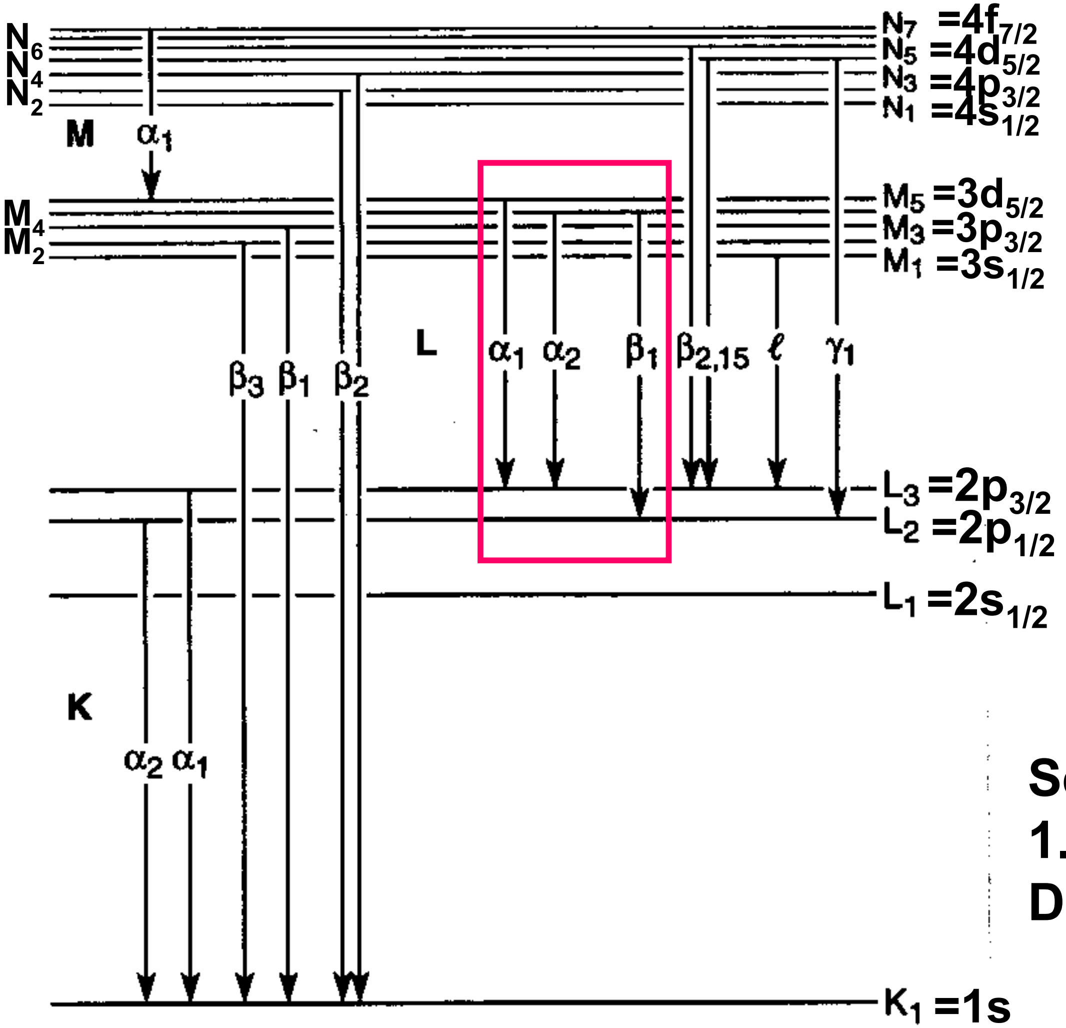
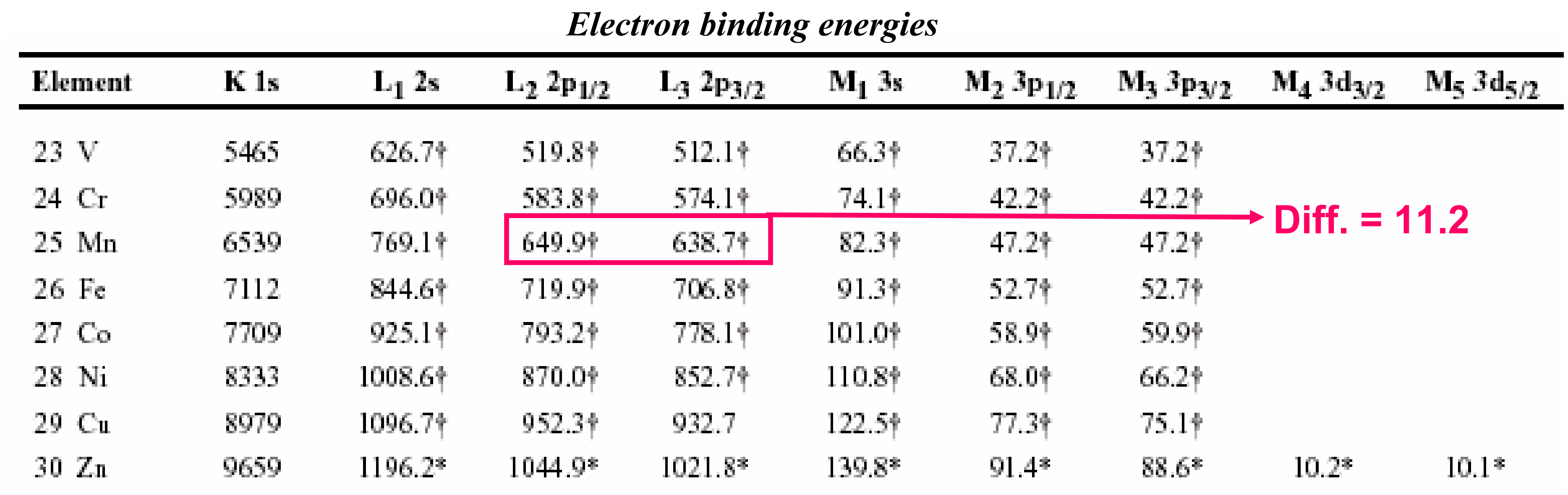


Fig. 1-1. Transitions that give rise to the emission lines in Table 1-3.

$\Delta j = 0, \pm 1$

See Section 1.2 in “X-Ray Data Booklet”



Electron binding energies

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

Diff. = 11.2

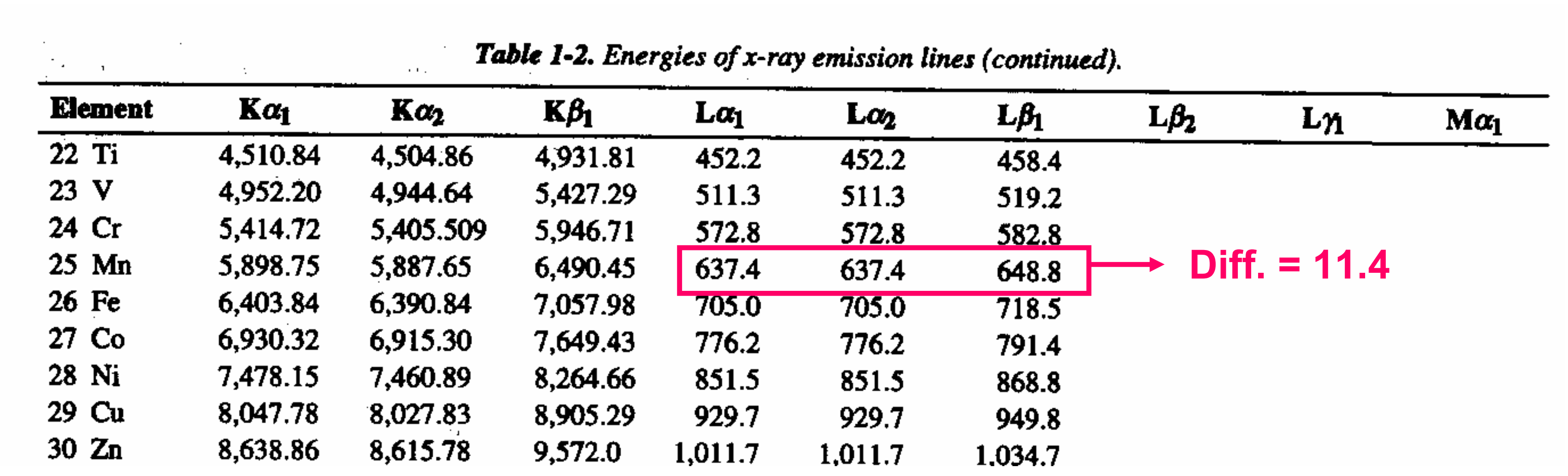
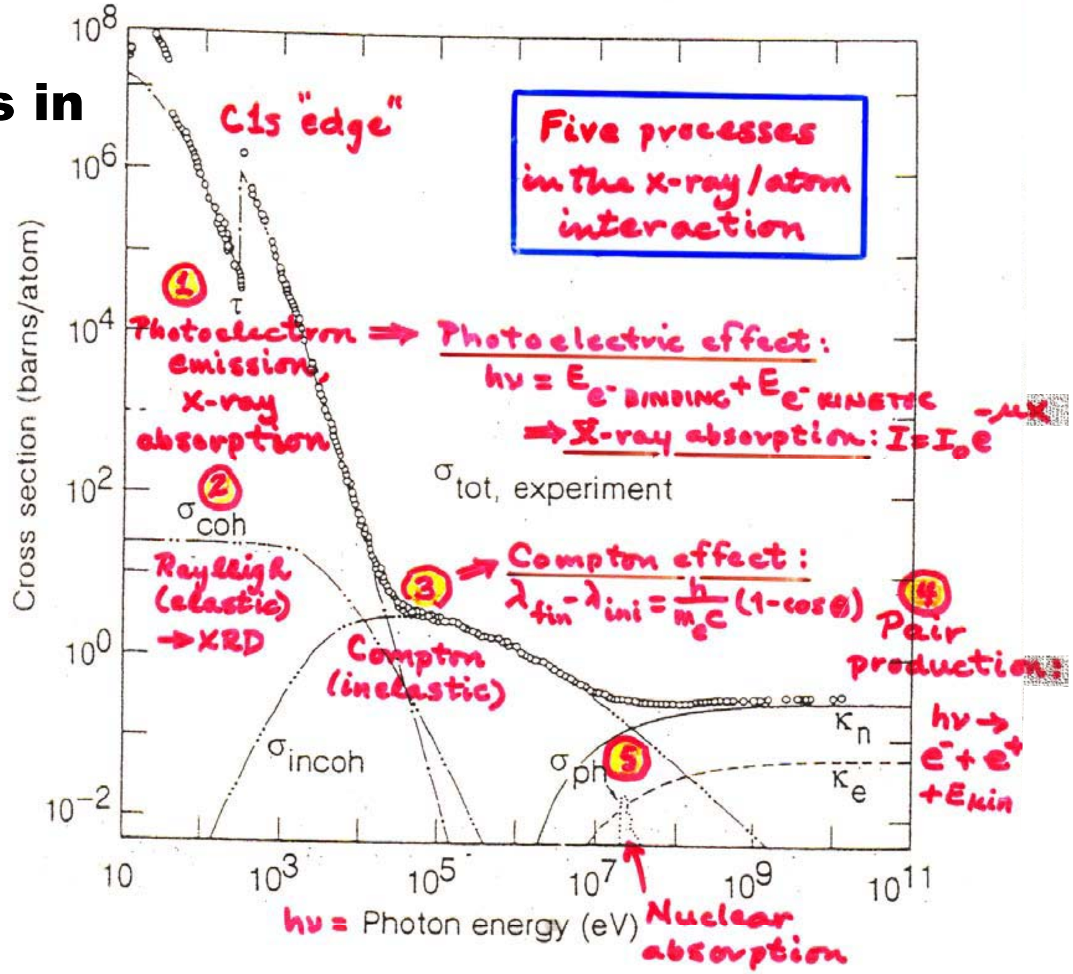


Table 1-2. Energies of x-ray emission lines (continued).

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

Diff. = 11.4

The five ways in which x-rays Interact with Matter:



C1s "edge"

Five processes in the x-ray/atom interaction

① Photoelectron emission, x-ray absorption ⟹ Photoelectric effect: $h\nu = E_{e^- \text{ BINDING}} + E_{e^- \text{ KINETIC}}$ ⟹ X-ray absorption: $I = I_0 e^{-\mu x}$

② Rayleigh (elastic) → XRD

③ Compton (inelastic) ⟹ Compton effect: $\lambda_{fin} - \lambda_{ini} = \frac{h}{m_e c}(1 - \cos\theta)$

④ Pair production: $h\nu \rightarrow e^- + e^+ + E_{kin}$

⑤ Nuclear absorption

$h\nu$ =

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

"X-Ray Data Booklet"
Section 3.1