Slides from 2012 in videos assigned for lectures on 8 and 10 November

2012-Lecture 10 starting from 0:33 until the end, all of lecture 11 and lecture 12 from start to 1:02.

INTENSITIES IN PHOTOELECTRON SPECTRA:

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

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

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

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

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

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

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

k HOLE → $\varphi_1 \rightarrow \varphi_1'$, …, $\varphi_{k-1} \rightarrow \varphi_{k-1}'$, $\varphi_{k+1} \rightarrow \varphi_{k+1}'$, …, $\varphi_N \rightarrow \varphi_N'$ (SLOW)

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

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

↳ NORMAL $\frac{d\sigma_K}{d\Omega}$

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

INTENSITIES IN PHOTOELECTRON SPECTRA:

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

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

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

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

↳ NORMAL $\frac{d\sigma_K}{d\Omega}$

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

- SLATER DETS. FOR $\Psi^f_{e^-} = \det(\psi_1' \psi_2' \cdots \psi_{k-1}' \psi_{k+1}' \cdots \psi_N')$

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

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

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

1e- DIPOLE → $d\sigma/d\Omega$

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

"Basic Concepts of XPS"
Section 3.D.

INTENSITIES IN PHOTOELECTRON SPECTRA:

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

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

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

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k HOLE → $\varphi_1 \rightarrow \varphi_1'$, $\varphi_{k-1} \rightarrow \varphi_{k-1}'$, $\varphi_{k+1} \rightarrow \varphi_{k+1}'$, $\varphi_N \rightarrow \varphi_N'$ } (SLOW)

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

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

↳ NORMAL $\frac{d\sigma_K}{d\Omega}$

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

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

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

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

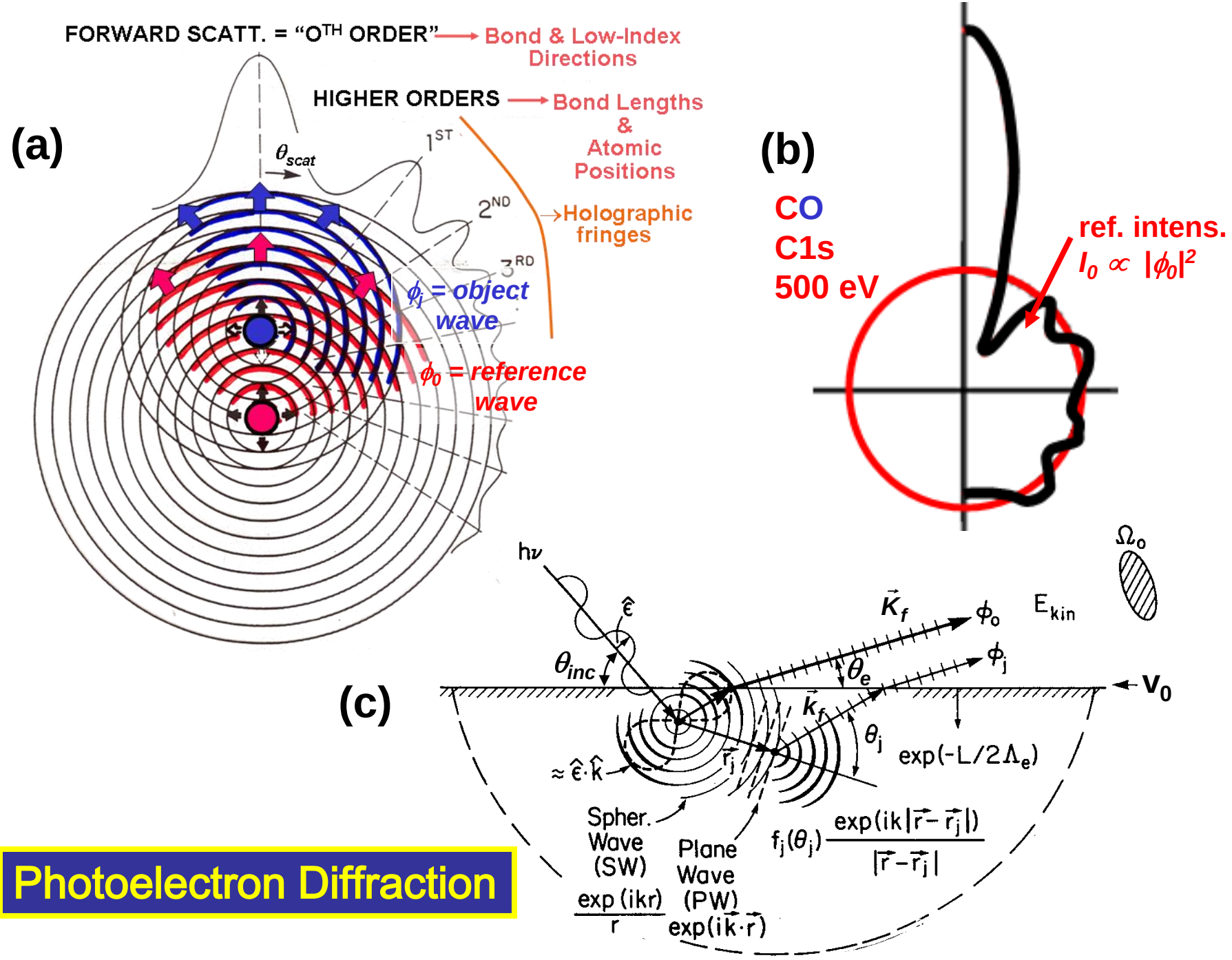
1e- DIPOLE → $d\sigma/d\Omega$

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

- PLUS DIFFRACTION EFFECTS IN φ_f ESCAPE

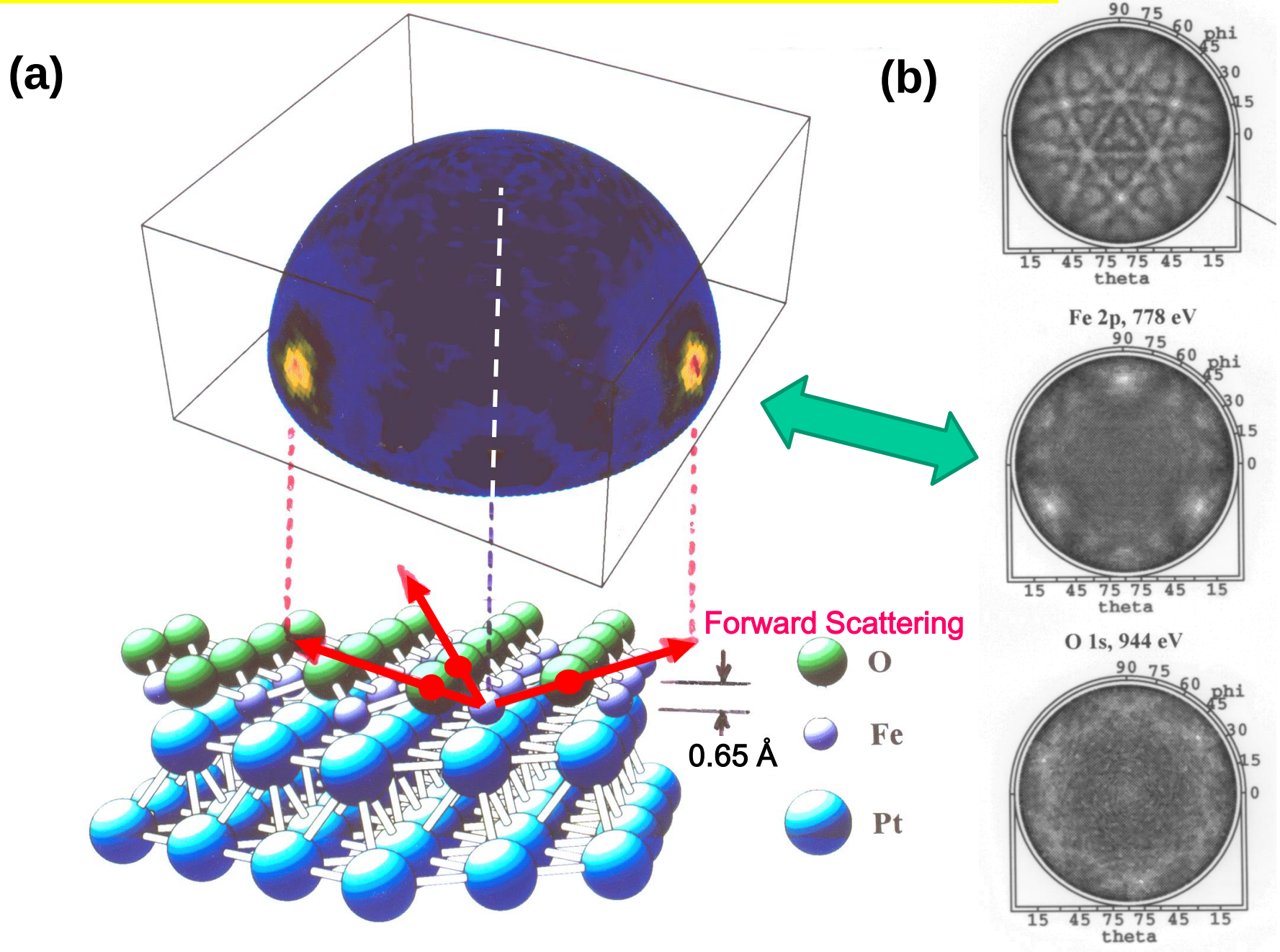
"Basic Concepts of XPS" Section 3.D.

Section 6.D.



Photoelectron Diffraction

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



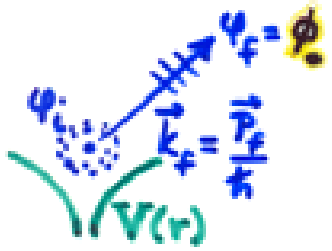
PHOTOELECTRON EMISSION - BASIC MATRIX ELEMENTS + SELECTION RULES:

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

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

PLUS SPIN:

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



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

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

(δ_{ℓ_f}: PHASE SHIFT OF ℓ_f WAVE IN $V(r)$)

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

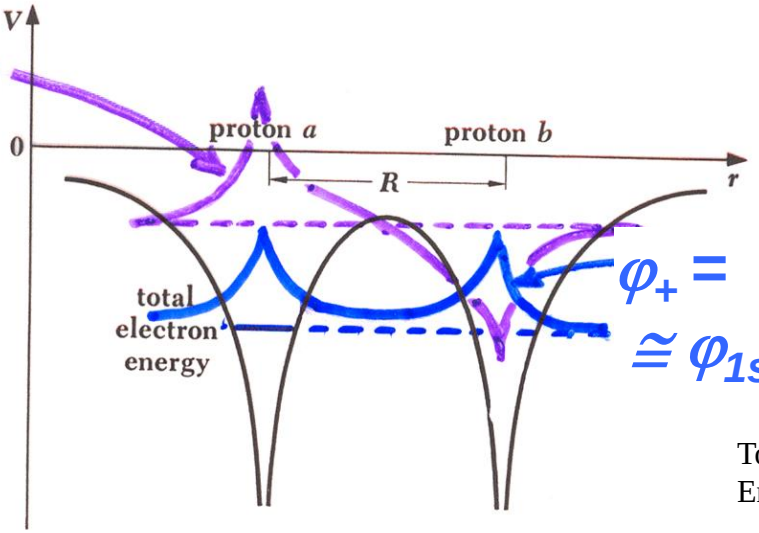
EQUIVALENT WITHIN CONSTANT FACTOR ($\vec{p} \leftrightarrow \vec{\nabla} V(r)$)

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

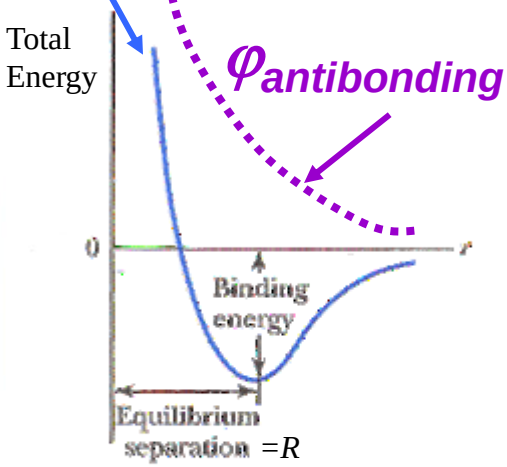
$\Delta m_s = m_{sf} - m_{si} = 0$!

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

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



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



$\varphi_{antibonding}$

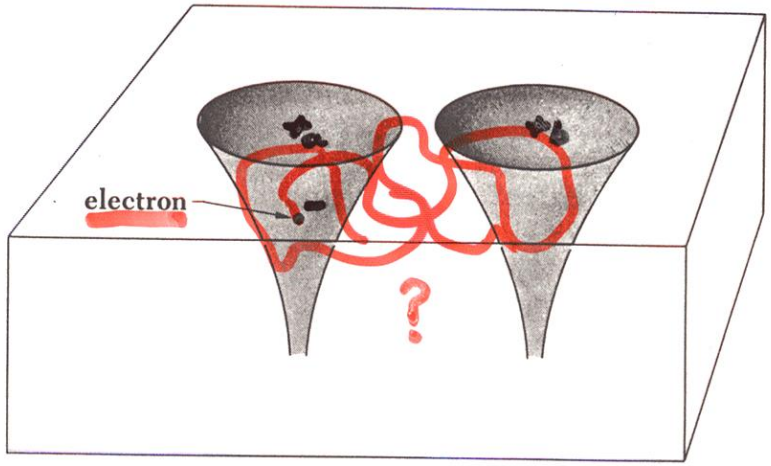
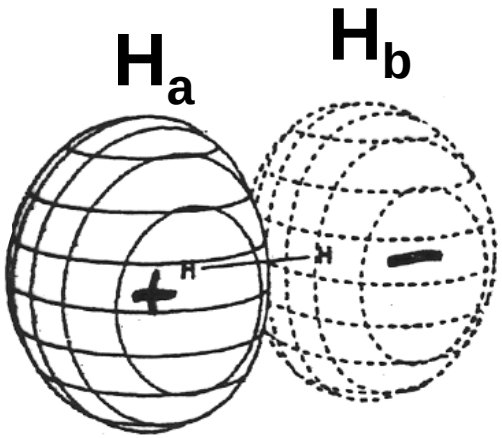


FIGURE 8.4 (*a*) Potential energy of an electron in the electric field of two nearby protons. The total energy of a ground-state electron in the hydrogen atom is indicated. (*b*) Two nearby protons correspond quantum-mechanically to a pair of boxes separated by a barrier.

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

III. MOLECULAR ORBITAL DRAWINGS 61

1. Hydrogen Symmetry: $D_{\infty h}$



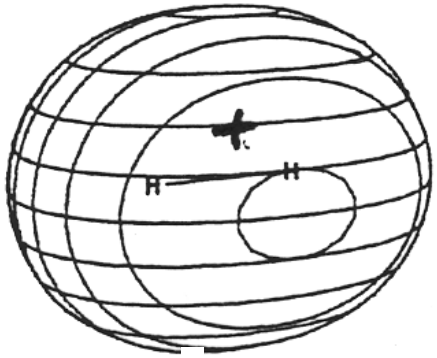
$1\sigma_u$ ε= 0.2656 a.u. = +7.21 eV

Anti-Bonding

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

ε *positive (unoccupied)*

ε *negative (occupied)*



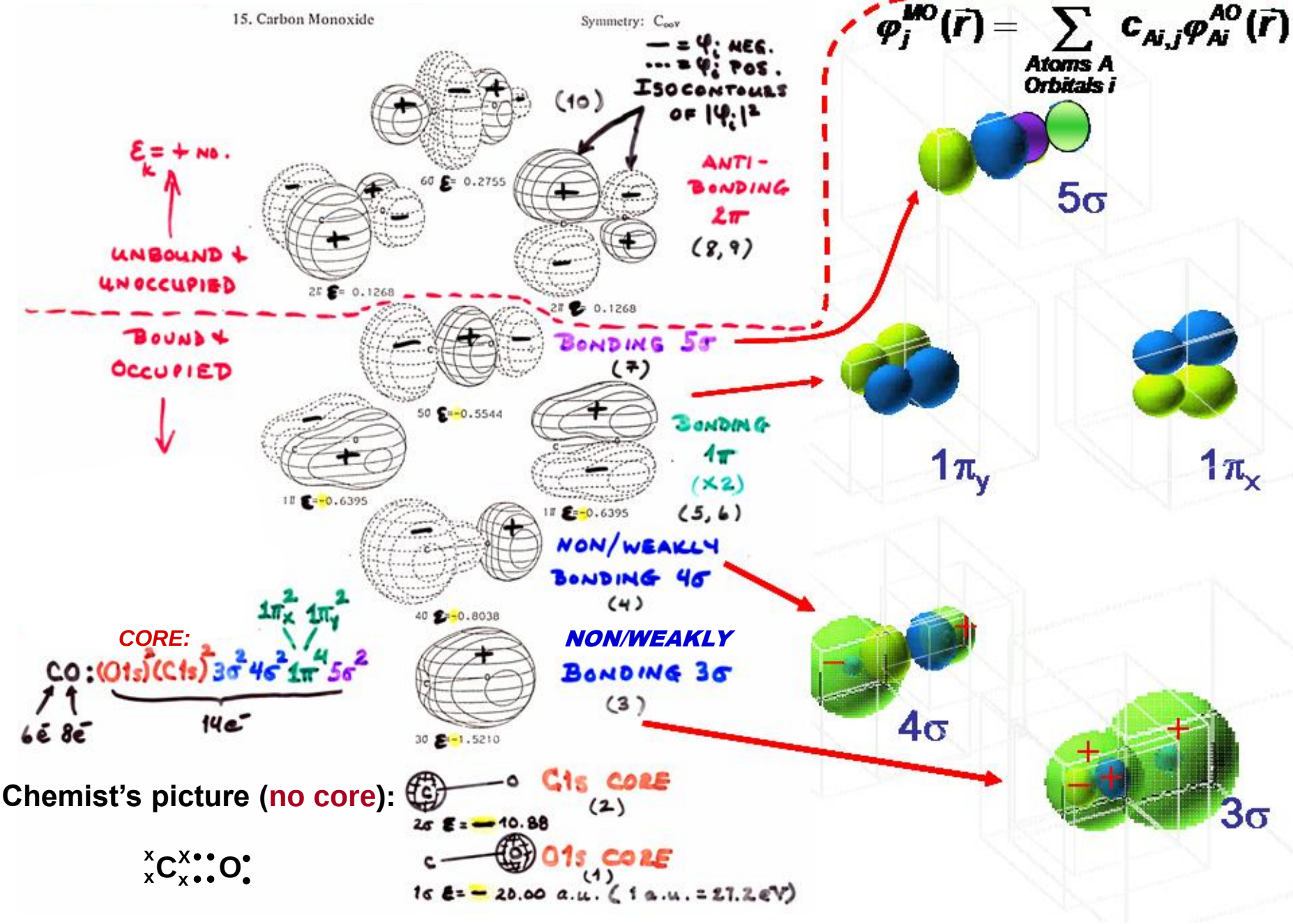
$1\sigma_g$ ε=-0.5944 a.u. = -16.16 eV

(Compare – 13.61 for H atom 1s)

Bonding

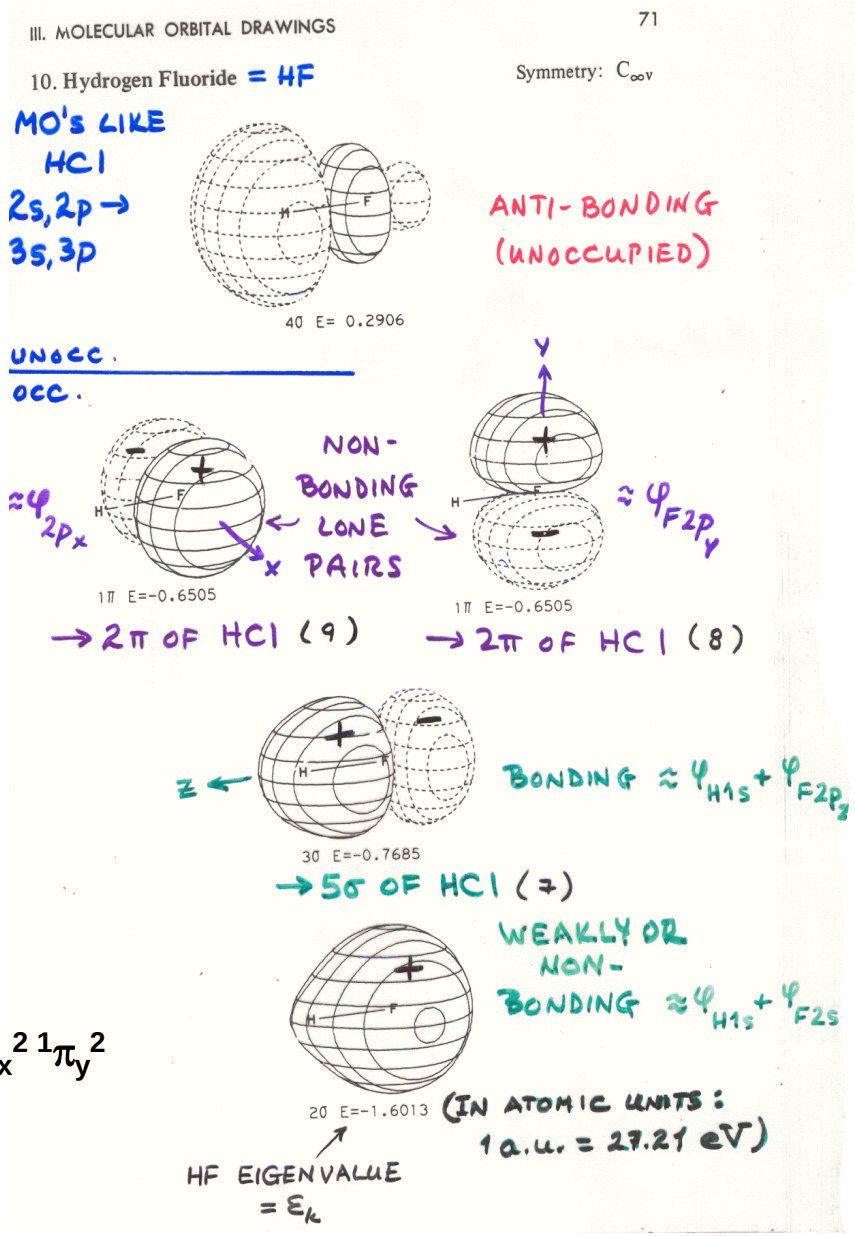
$\varphi_{bonding}^{MO} \cong \varphi_{1sa} + \varphi_{1sa}$

The LCAO or tight-binding picture for CO:



Chemist's picture (no core):

THE ELECTRONS IN HF (OR HCl): ionic molecules



$1\sigma^2$

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

1 e⁻ 9 e⁻

H — F **F 1s core**

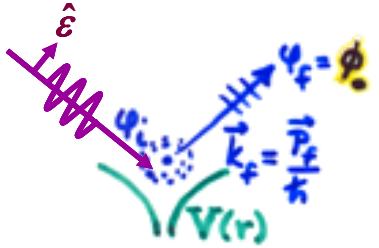
1σ E = -25.6 a.u.

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: $\alpha(\sigma) = m_{sl} = +\tfrac{1}{2} = \uparrow$, $\beta(\sigma) = m_{sl} = -\tfrac{1}{2} = \downarrow$



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

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

(δ_{l_f}: PHASE SHIFT OF l_f WAVE IN V(r))

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

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

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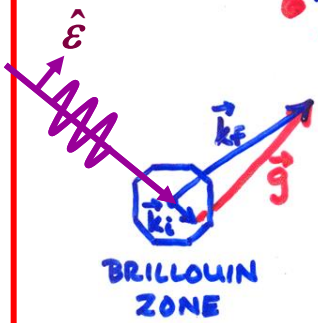
- $\Delta m = m_f - m_i = 0, \pm 1$ LINEAR POLARIZ.
- $\Delta m = \pm 1$, CIRCULAR POLARIZATION

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

BLOCH-FUNCTION (DELOCALIZED) STATES ⇒ VALENCE:



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

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

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

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

"DIRECT" TRANSITIONS

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

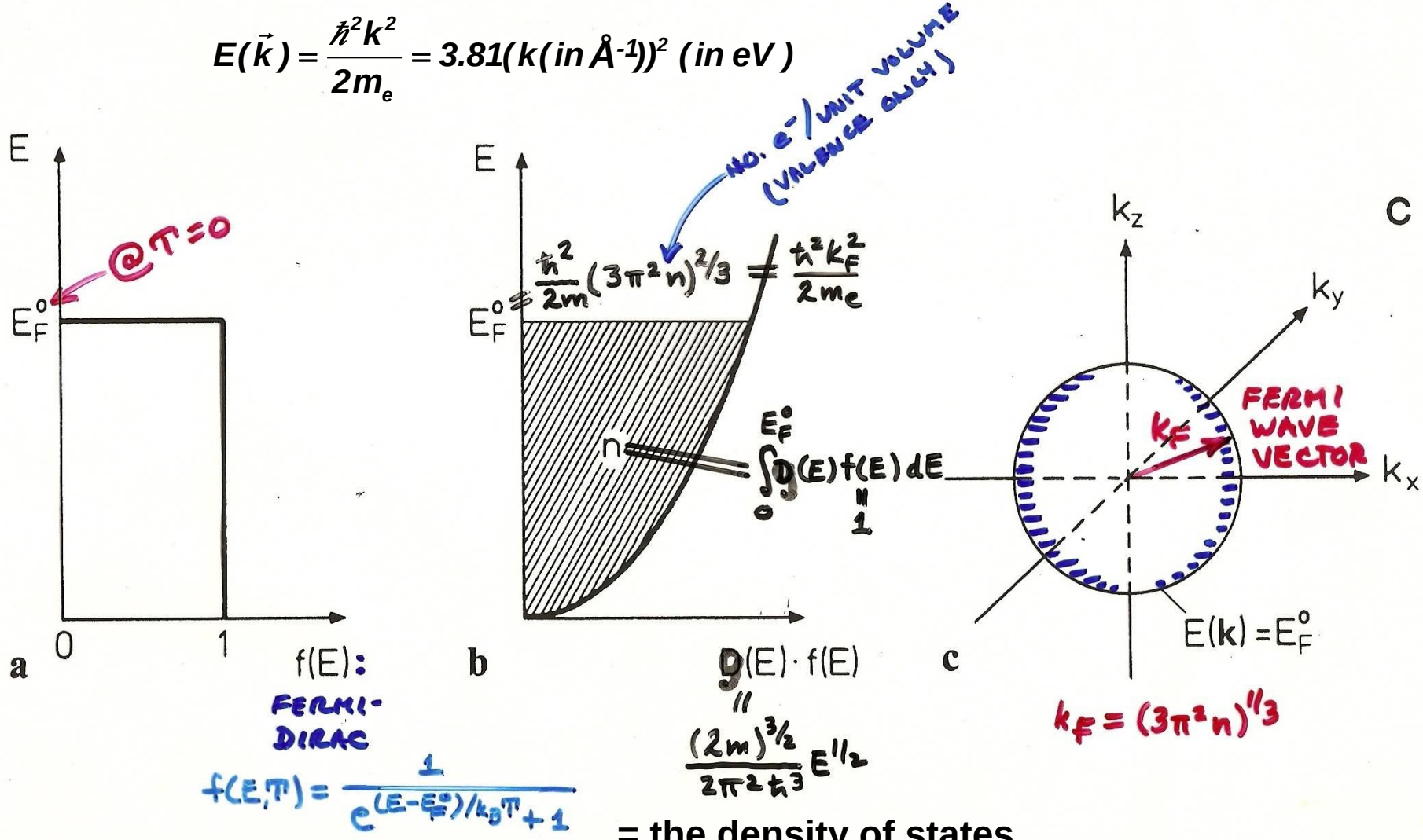
⇒ FRACTION DIRECT ≈ DEBYE-WALLER FACTOR

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

"Basic Concepts of XPS"
Chapter 3

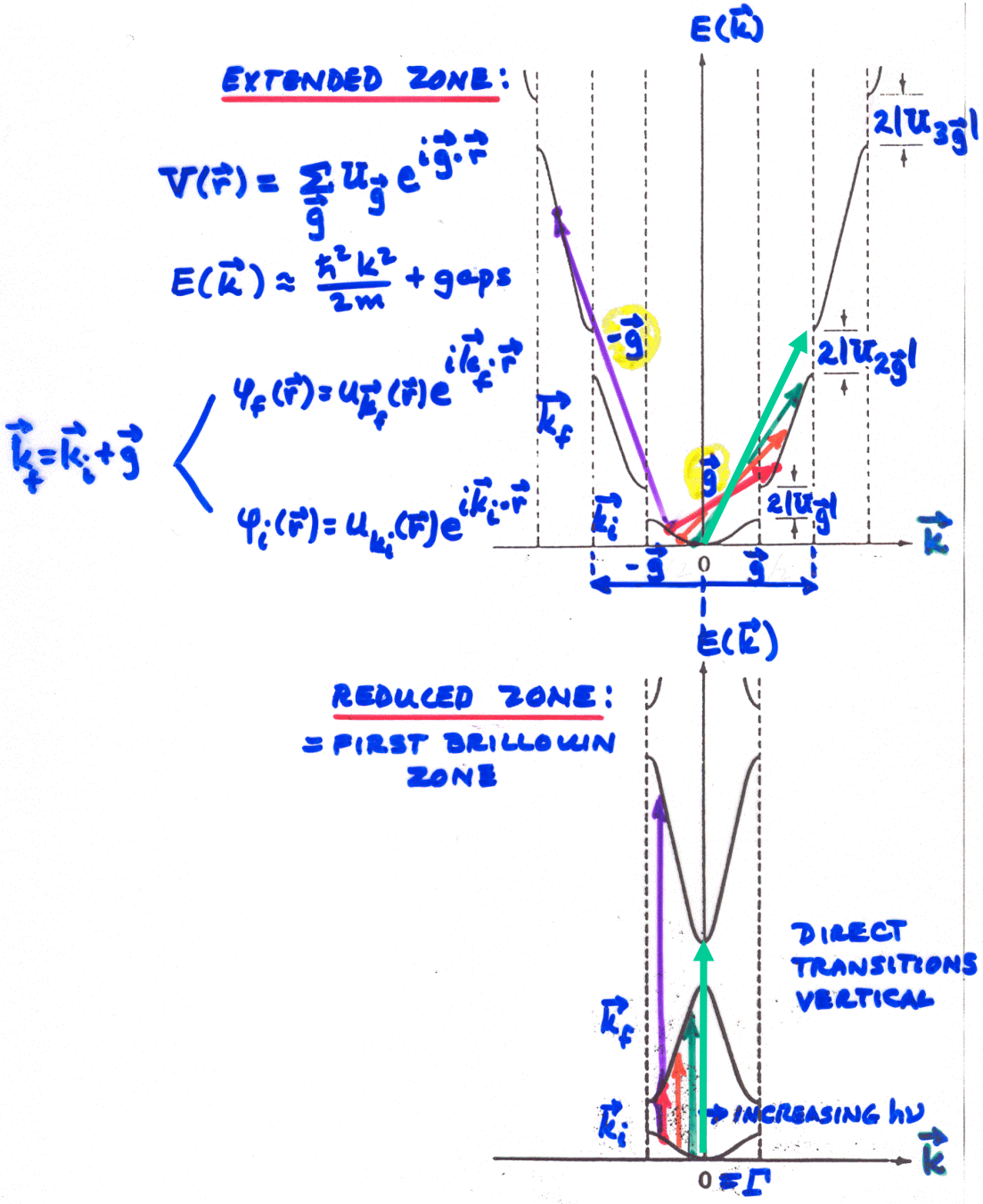
The free-electron solid at absolute zero

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



= the density of states

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



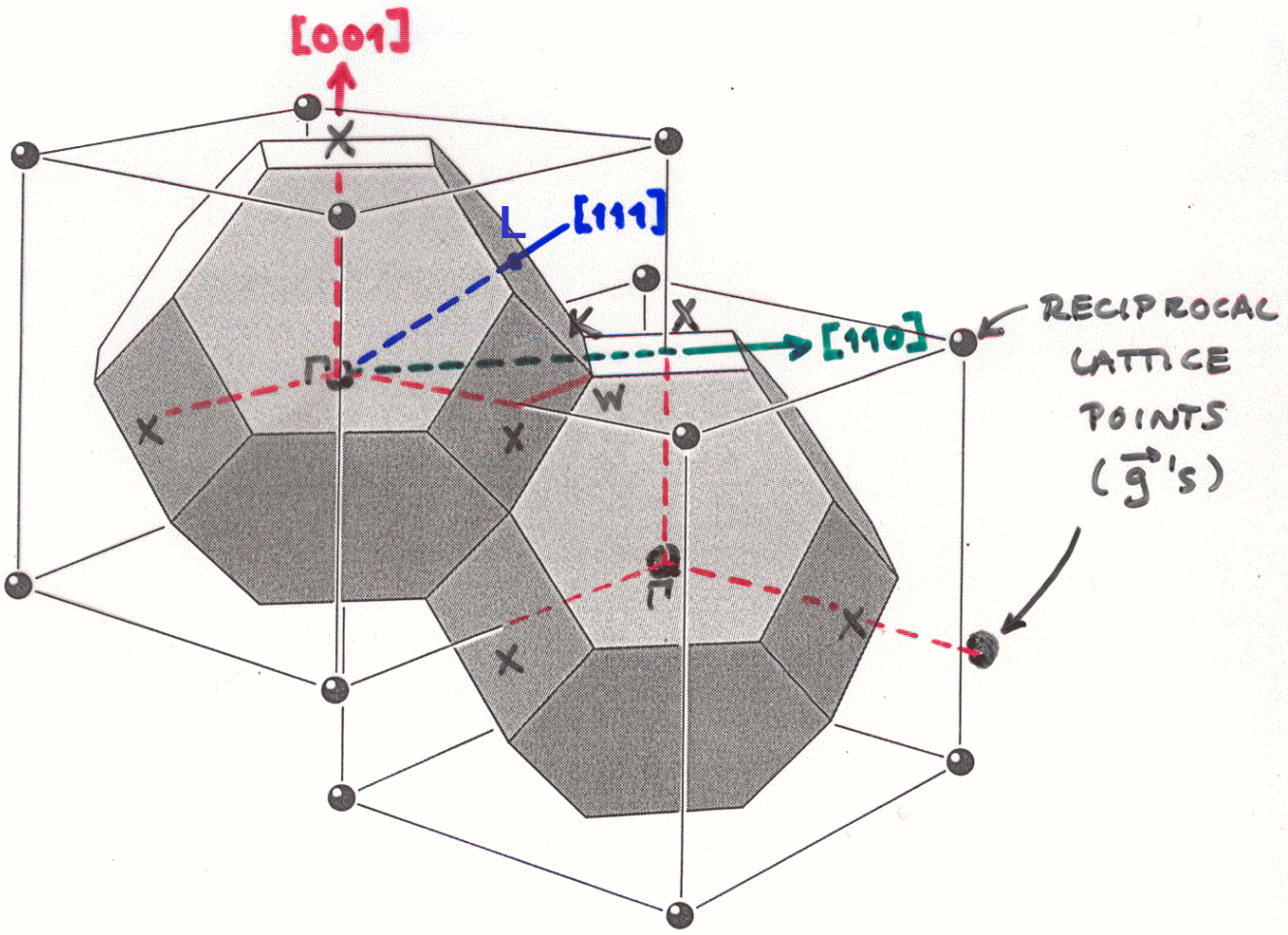


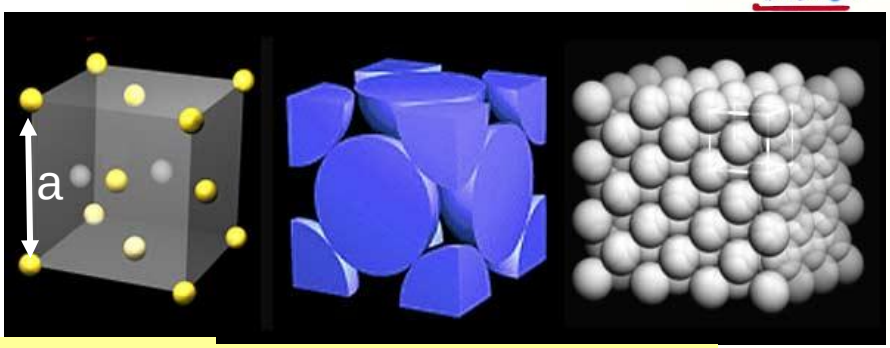
Figure 28 Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body-centered, as drawn.

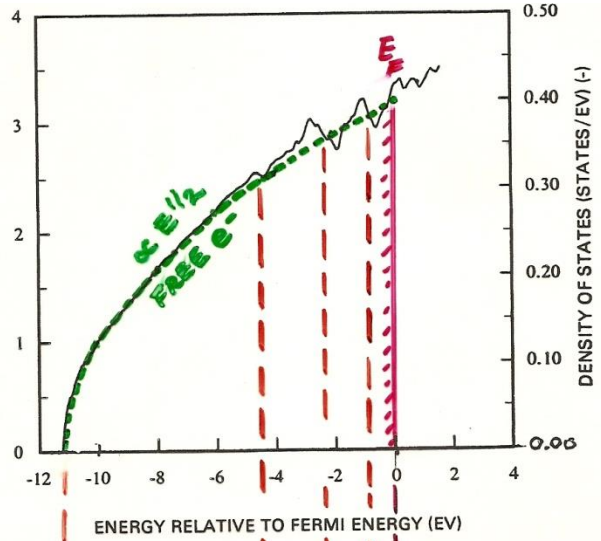
— STACKING OF fcc BRILLOUIN ZONES —

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

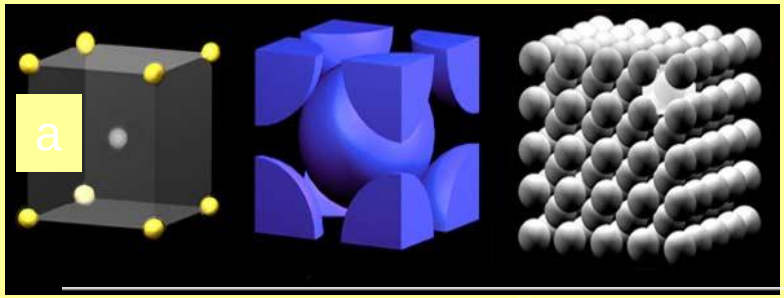
Rydberg = 13.605 eV

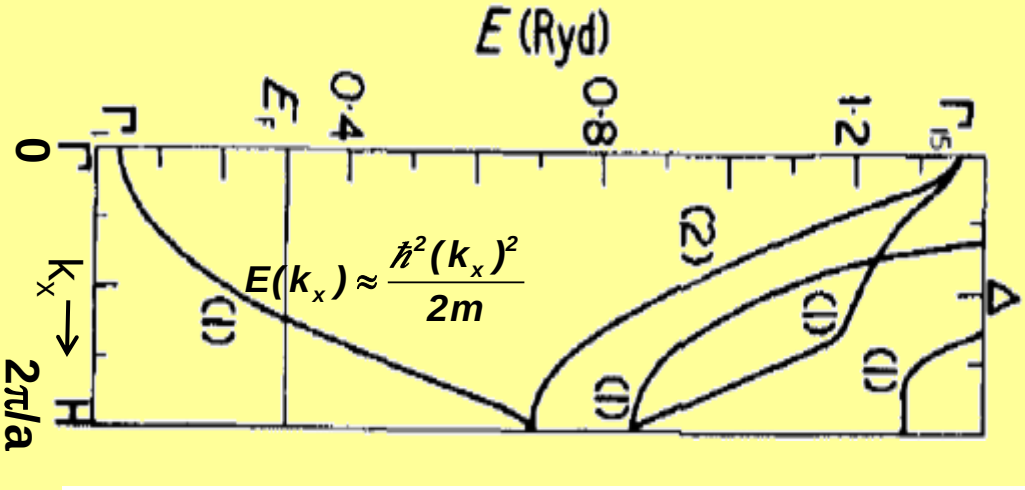
Aluminum—fcc,
a = 4.05 Å
$1s^2 2s^2\ 2p^6 3s^2\ 3p^1$

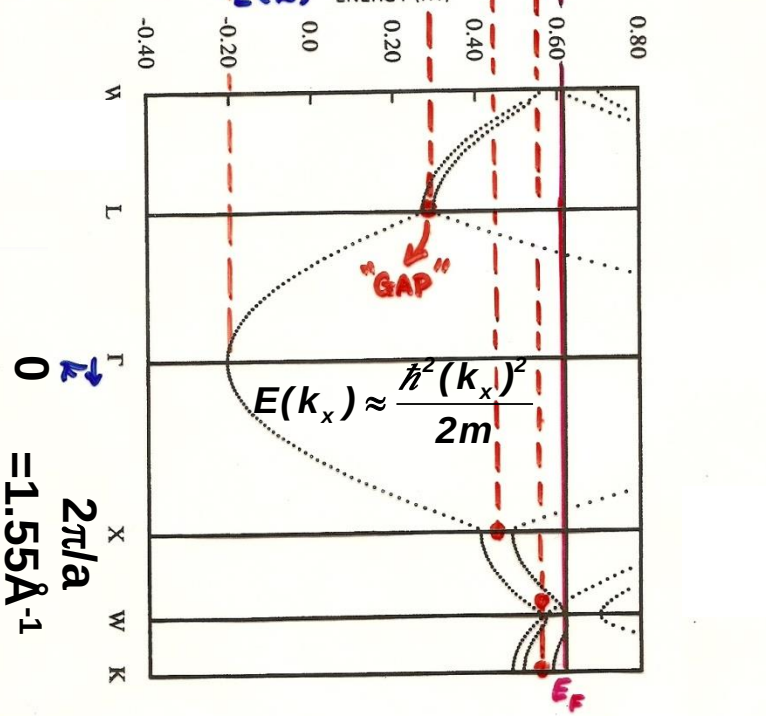




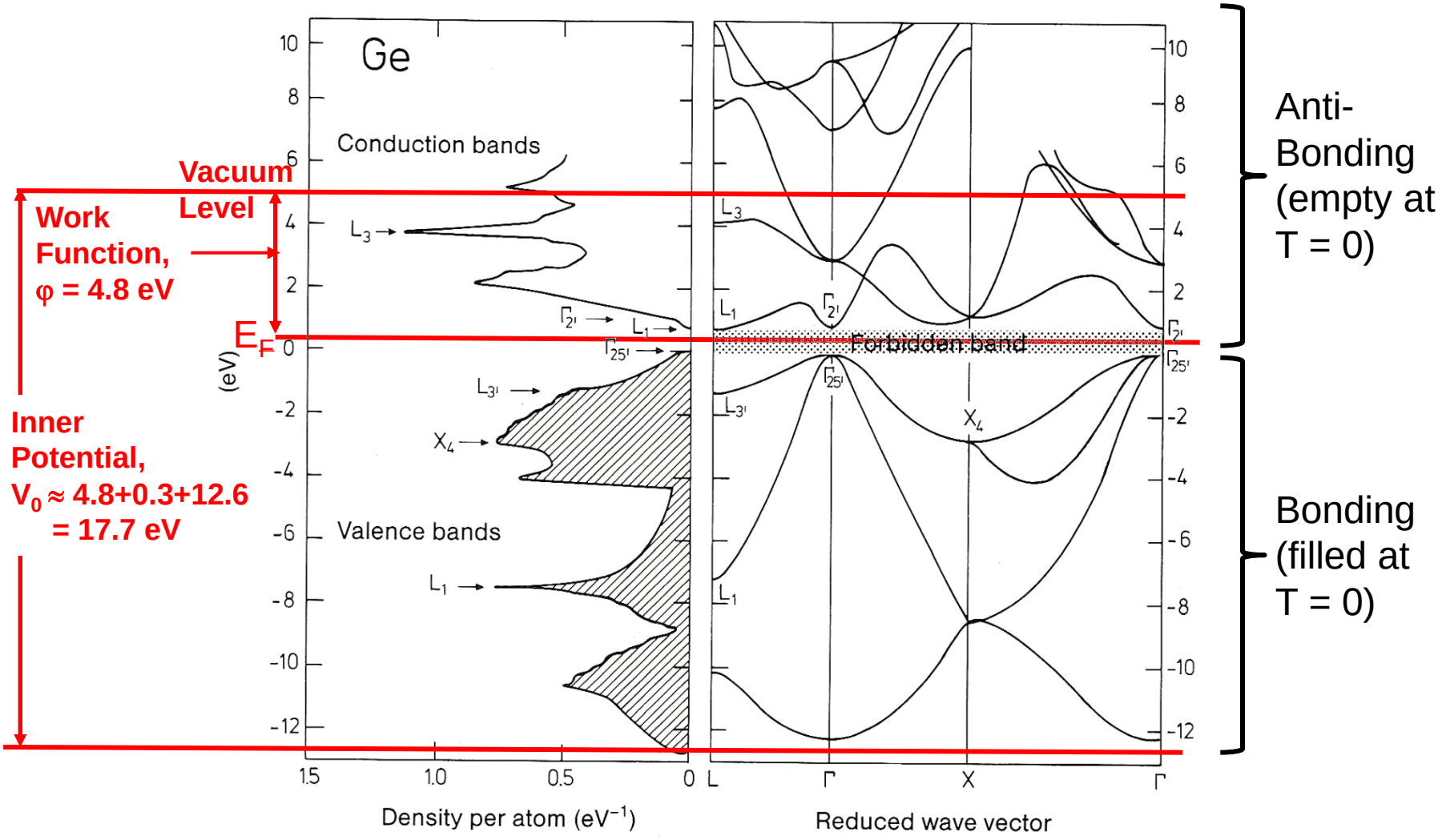
Lithium—bcc, a = 3.49 Å
$1s^2 2s^1$







Electronic bands and density of states for a semiconductor-Germanium—
$1s^2 2s^2\ 2p^6 3s^2\ 3p^6 3d^{10} 4s^2 4p^2$



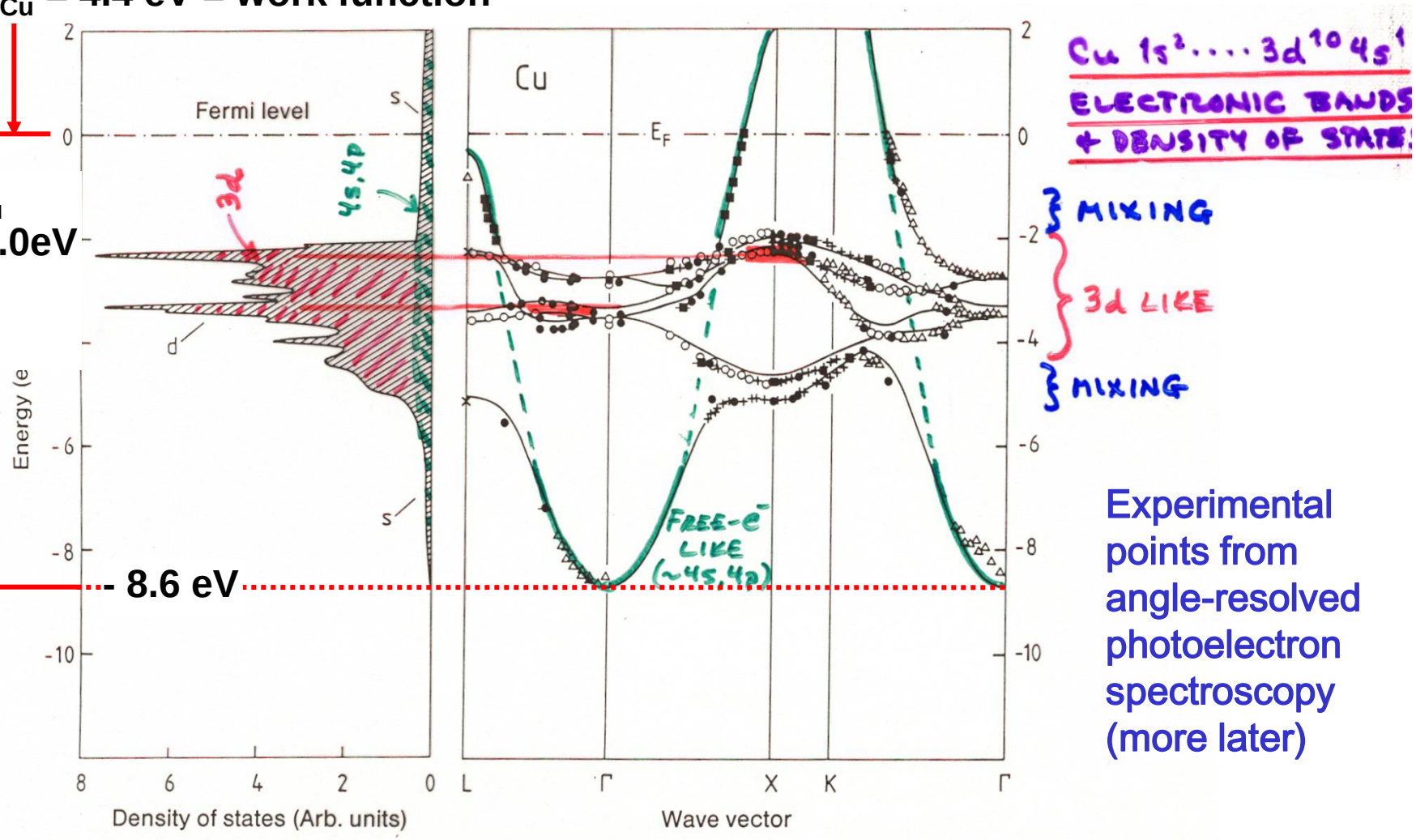
The electronic structure of a transition metal —fcc Cu

Vacuum level

ϕ_{Cu} = 4.4 eV = work function

$V_{0,Cu}$ =13.0eV

- 8.6 eV



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

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

Atomic orbital makeup

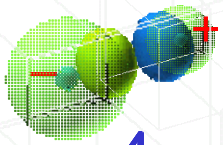
$$\varphi_j^{MO}(\vec{r}) = \sum_{\substack{\text{Atoms A} \\ \text{Orbitals i}}} c_{Ai,j}\varphi_{Ai}^{AO}(\vec{r})$$

Molecular orbital approach

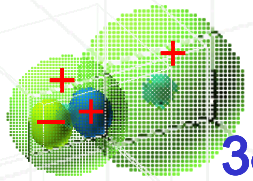
5σ

$1\pi_y$

$1\pi_x$



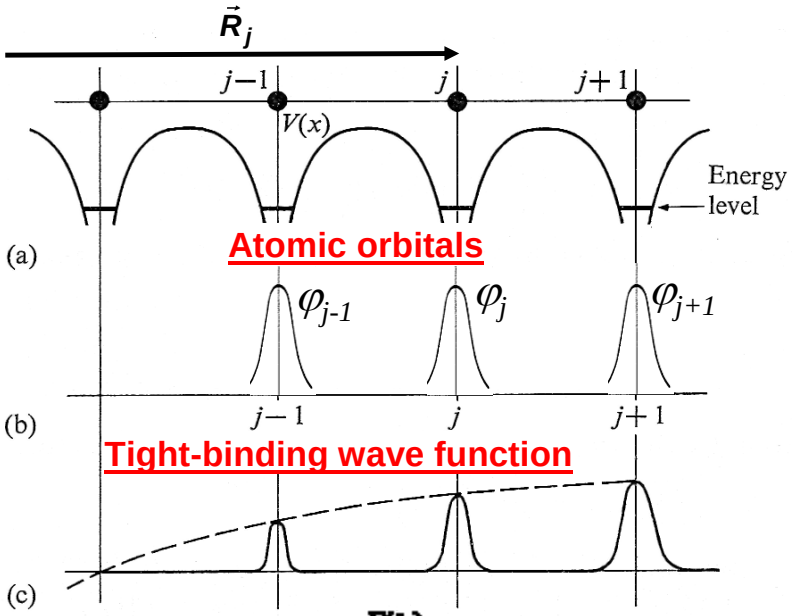
4σ

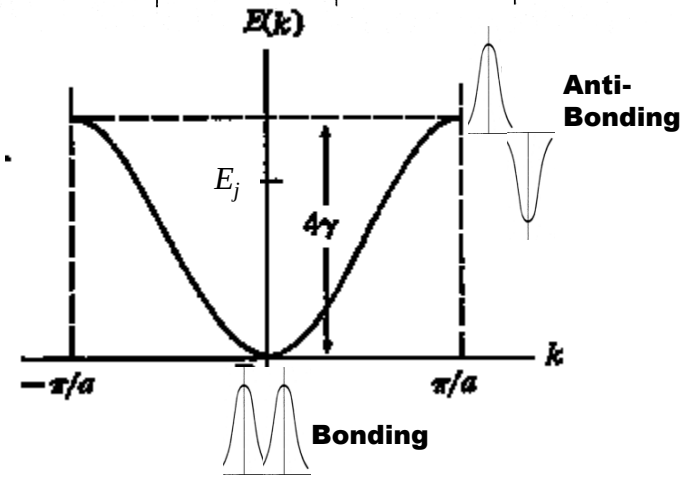


3σ

Solid state tight-binding approach

Crystal potential-1D

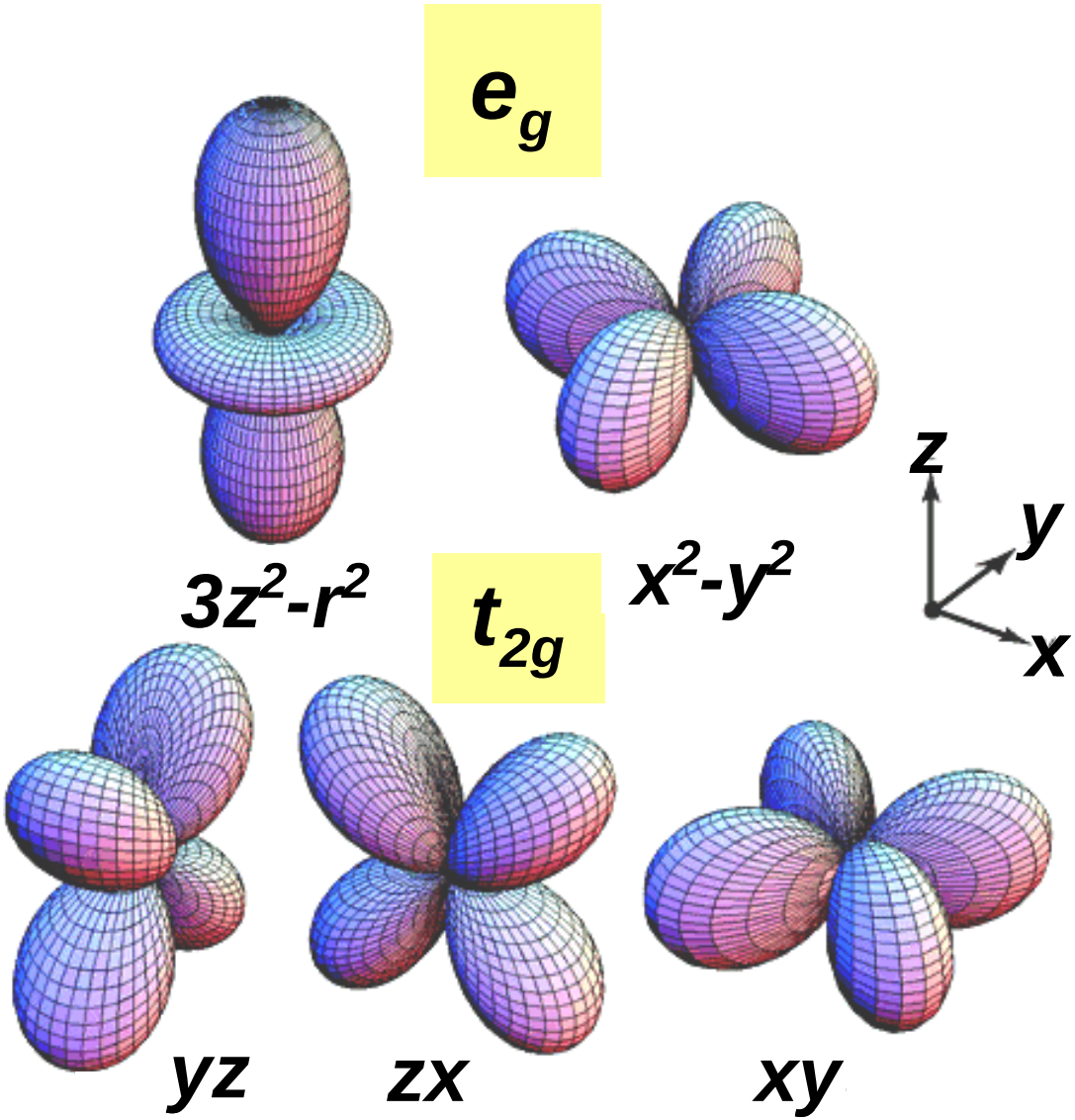


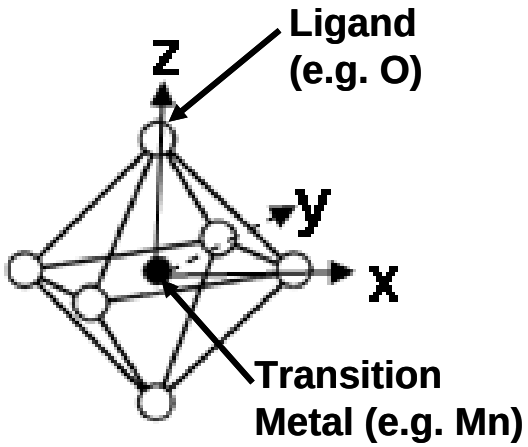


$$\varphi_{\vec{k}}^{BF}(\vec{r}) = \text{a Bloch function}$$

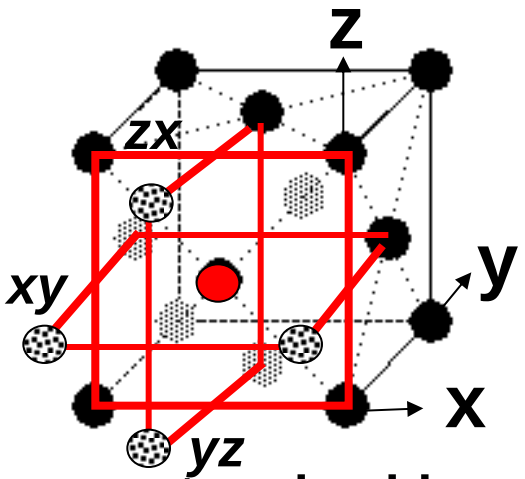
$$\propto \frac{1}{N^{1/2}} \sum_{j=1.....N \text{ unit cells at } \vec{R}_j} e^{i\vec{k}\bullet\vec{R}_j} \sum_{\substack{Ai = \text{basis set of AOs} \\ \text{in unit cell}}} c_{Ai,\vec{k}}\varphi_{Ai}^{AO}(\vec{r} - \vec{R}_j)_{21}$$

And the same thing for the d orbitals:



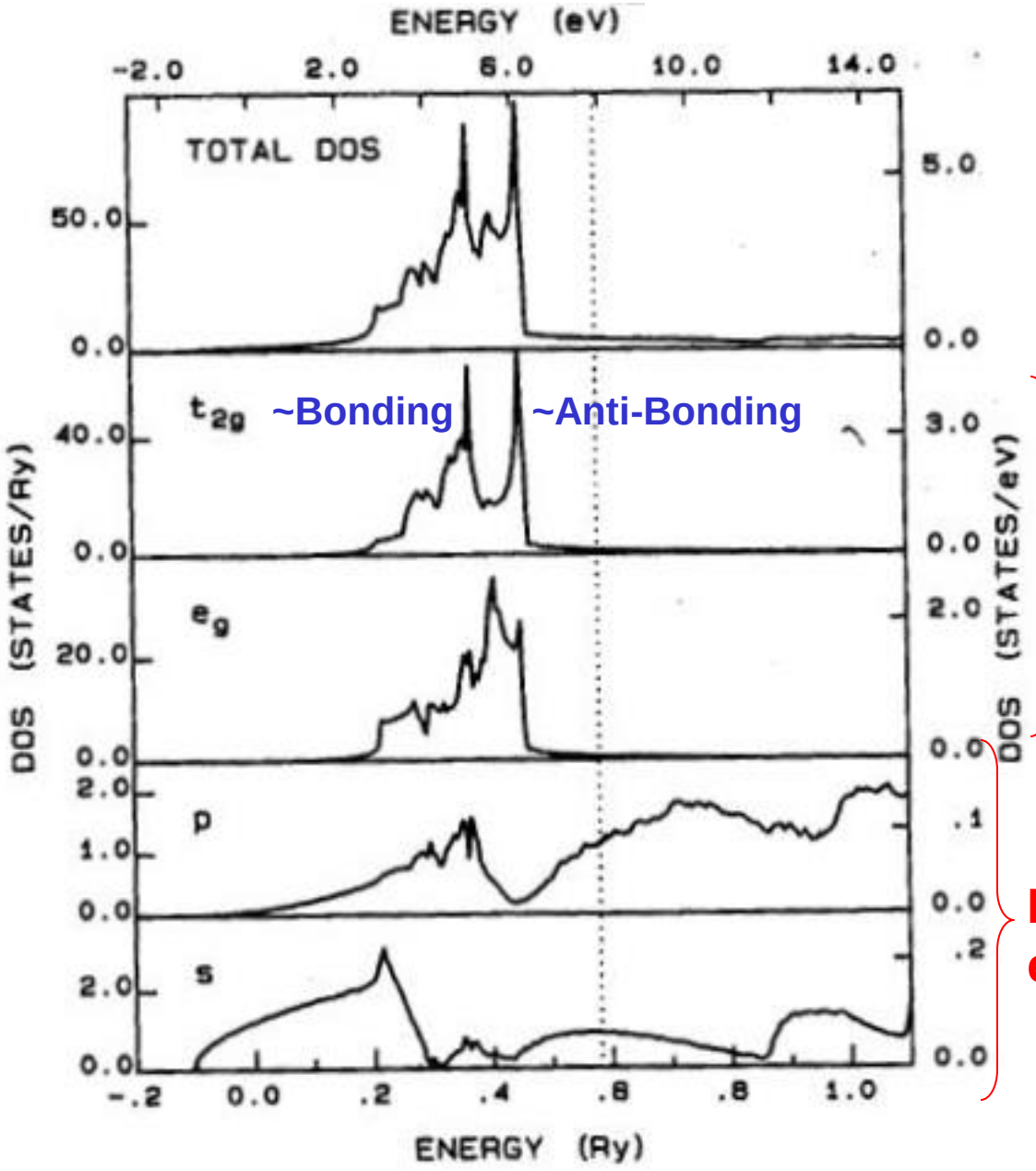


e_g and t_{2g} not equivalent in octahedral (cubic) environment



Face-centered cubic—12 nearest neighbors

Copper densities of states-total and by orbital type:

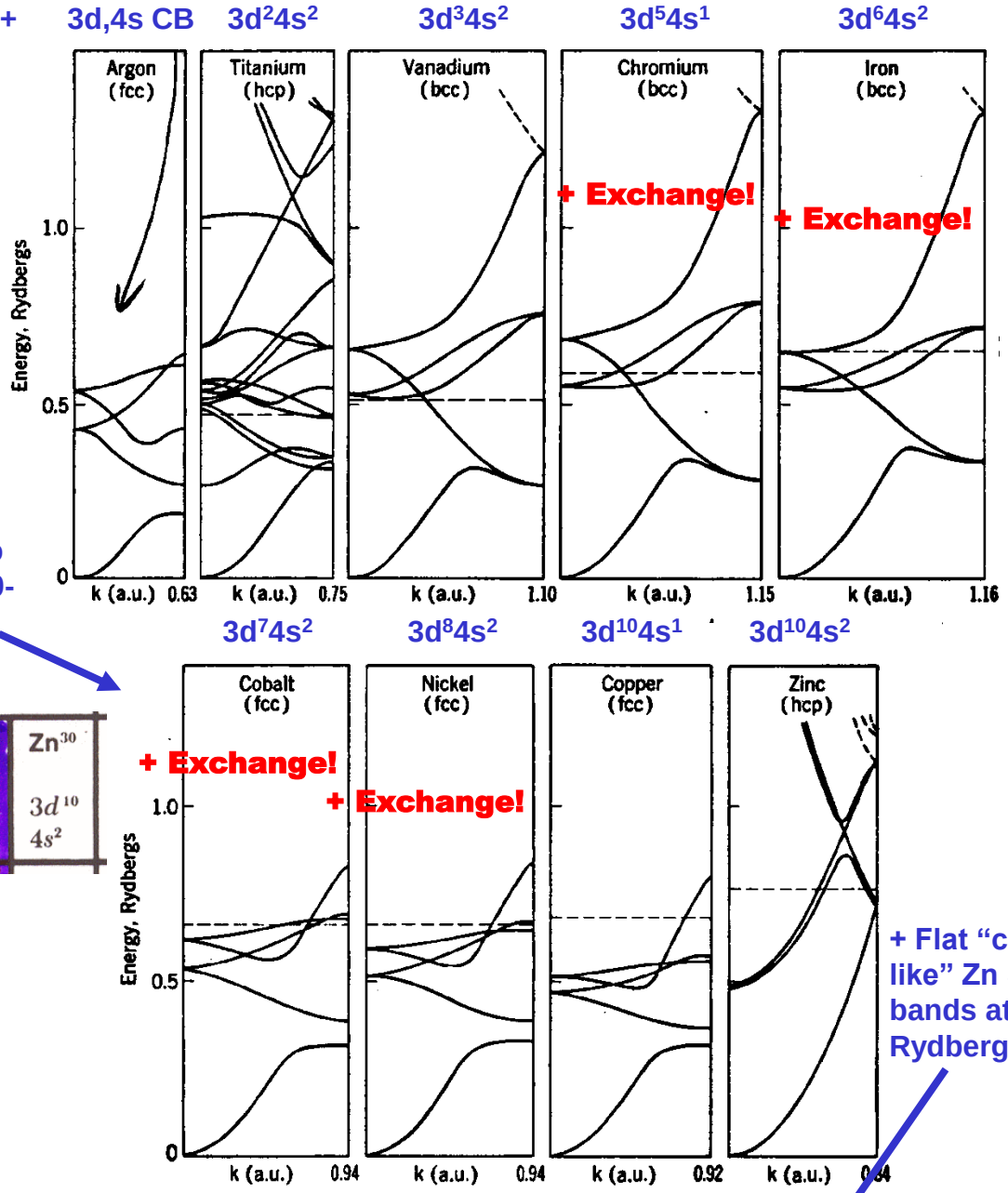


More localized 3d-like

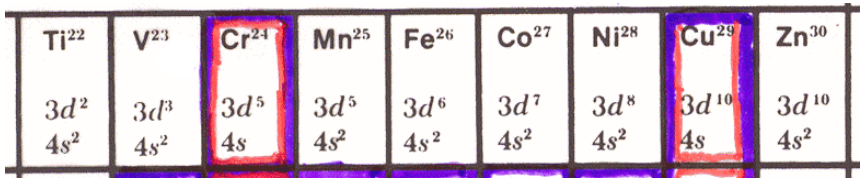
Delocalized free electron-like

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

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



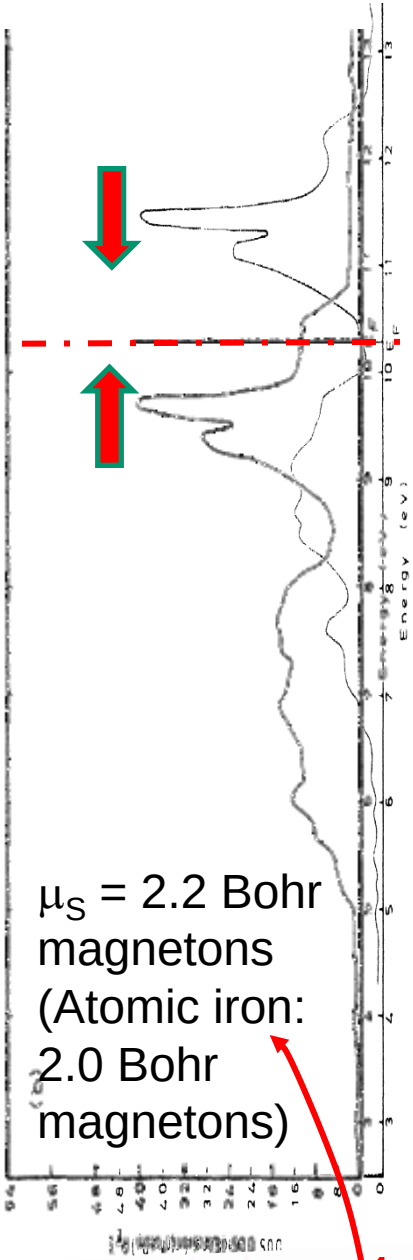
+ Flat "core-like" Ar 3s, 3p bands at ~-1.0-1.5 Rydbergs



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

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

The electronic bands and densities of states of ferromagnetic iron



μ_S = 2.2 Bohr magnetons (Atomic iron: 2.0 Bohr magnetons)

4 x ½ = 2

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

$3d_{z^2}$ $3d_{xz}$ $3d_{yz}$ $3d_{x^2-y^2}$ $3d_{xy}$

⇒ LARGE μ_{3d} + MAGNETISM

Energy (Ry)

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

E_F

Exchange splitting

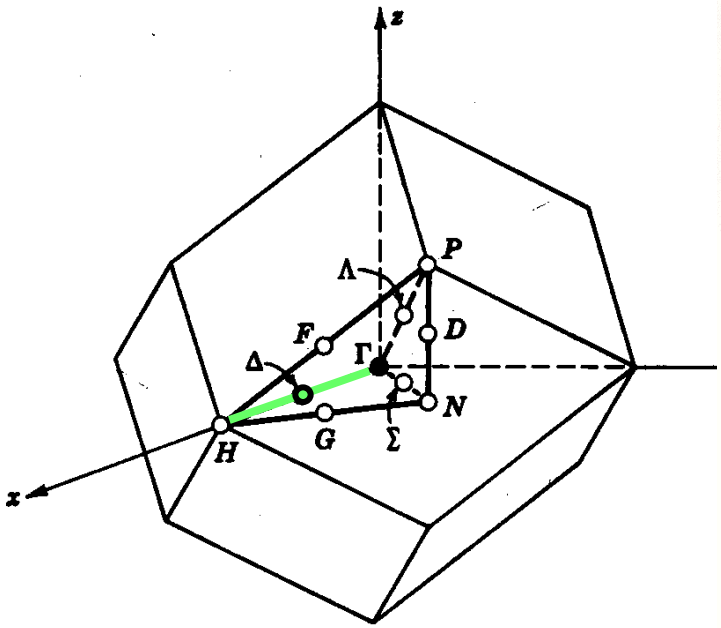
Spin-down (Minority)

Spin-up (Majority)

Γ Δ H F P D N Σ Γ Λ F

k = 0

k = 0



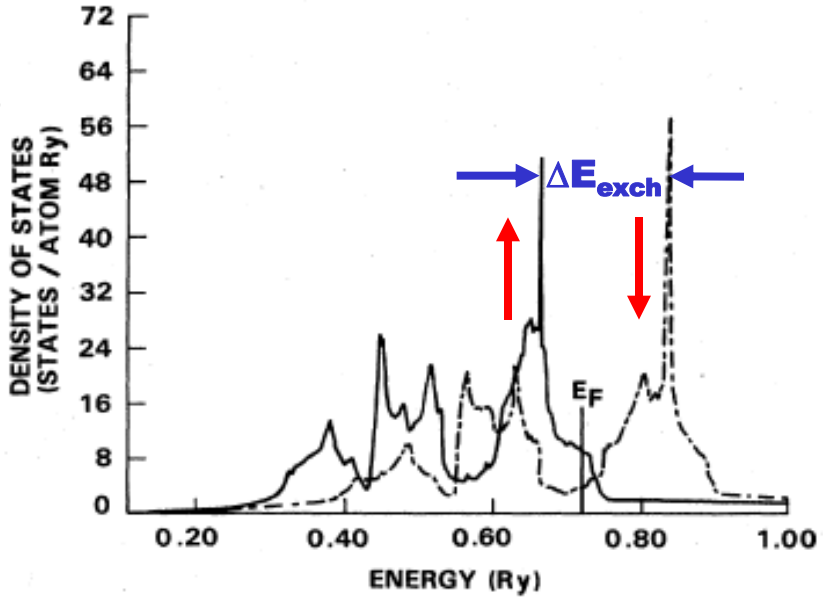
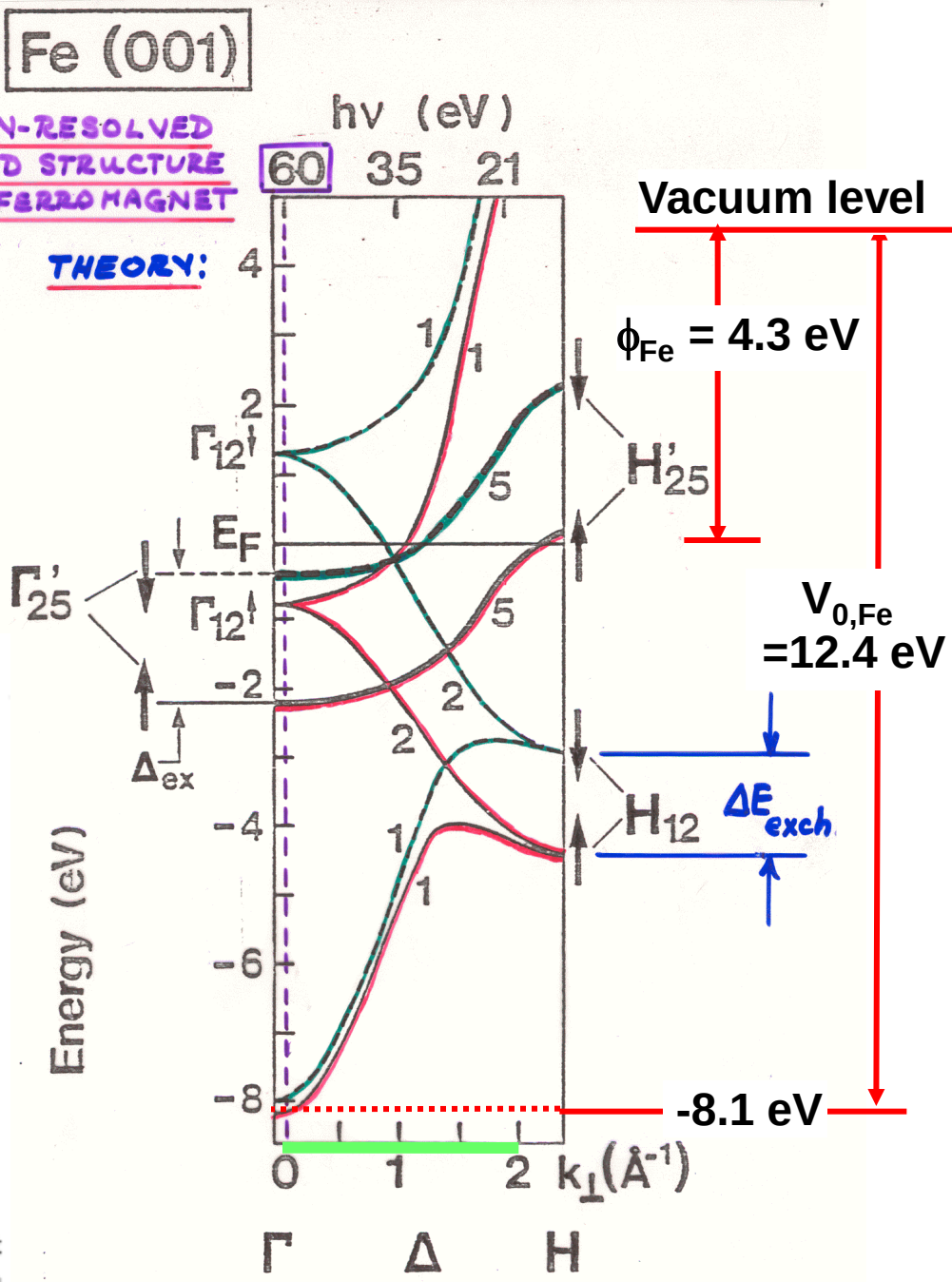
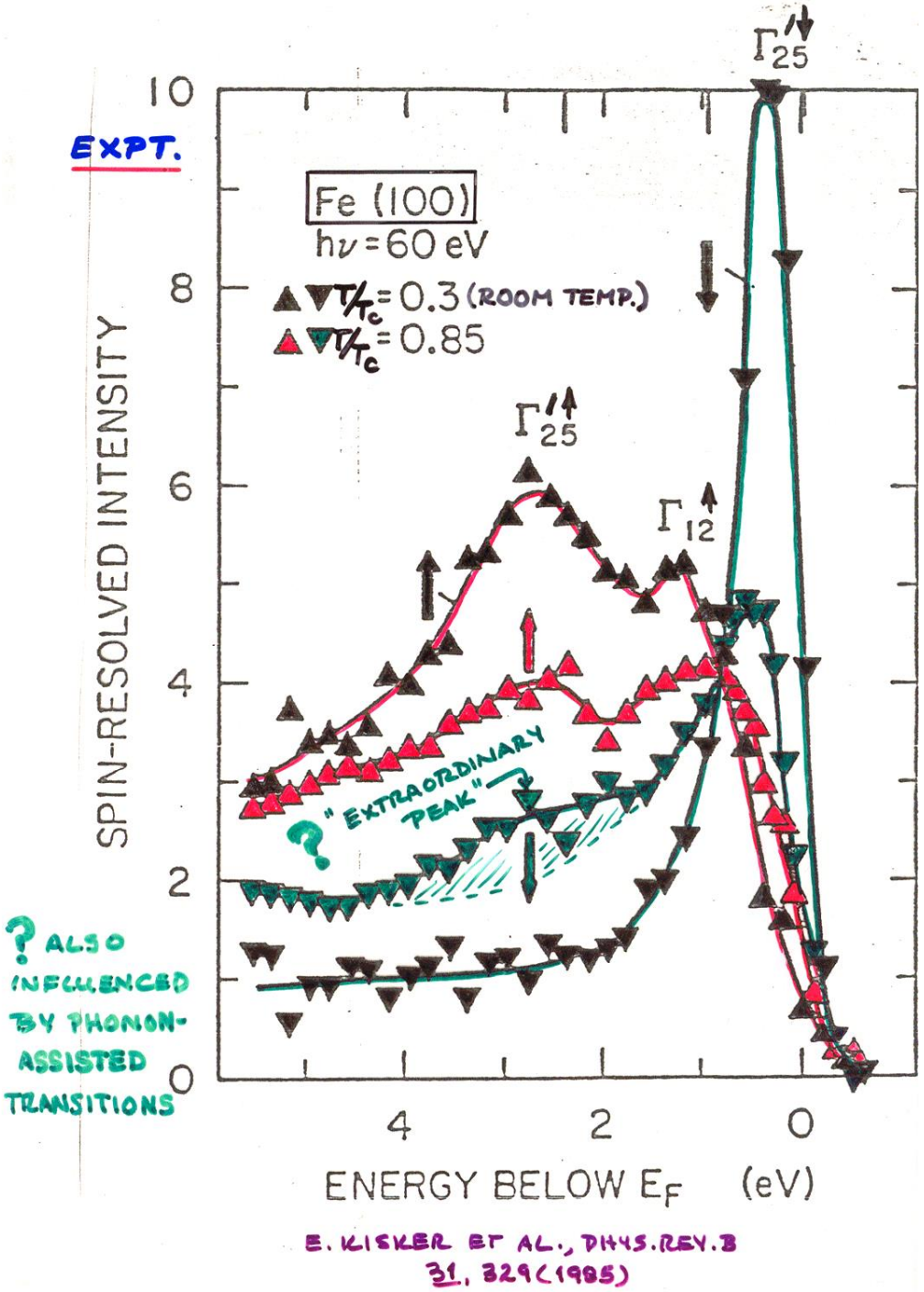


FIG. 4. Density of states at the equilibrium lattice constant of Fe for majority- (solid line) and minority- (broken line) spin states.

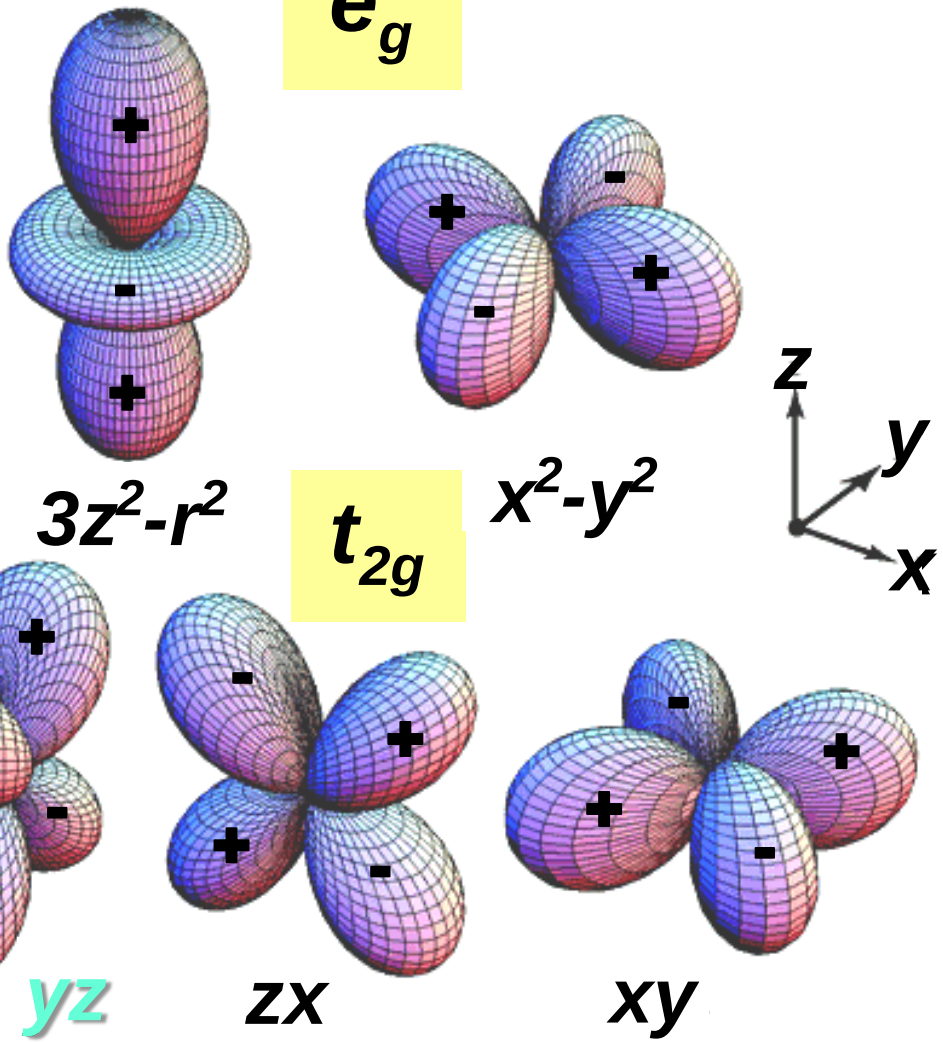
Hathaway et al., Phys. Rev. B 31, 7603 ('85)

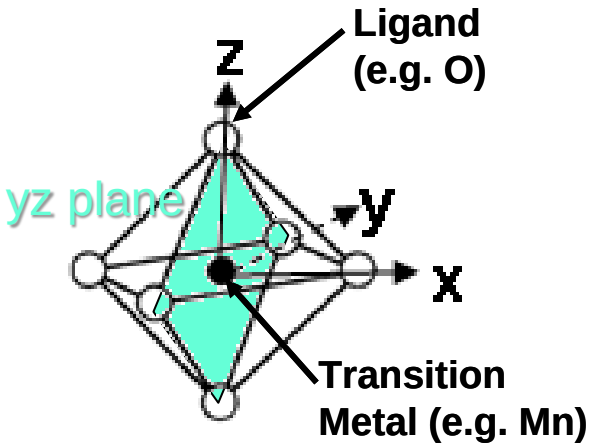


Fe: ANGLE AND SPIN-RESOLVED SPECTRA AT Γ POINT

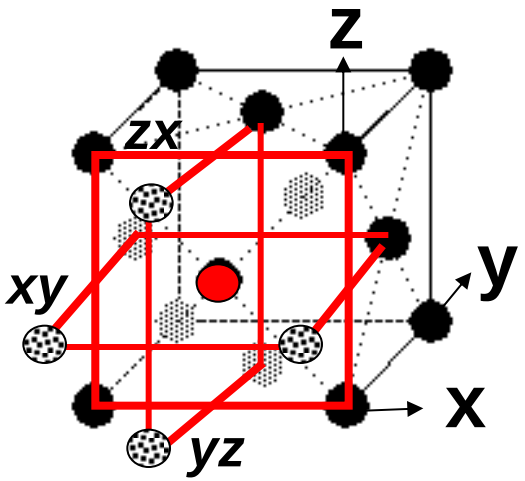


And the same thing for the d orbitals:





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

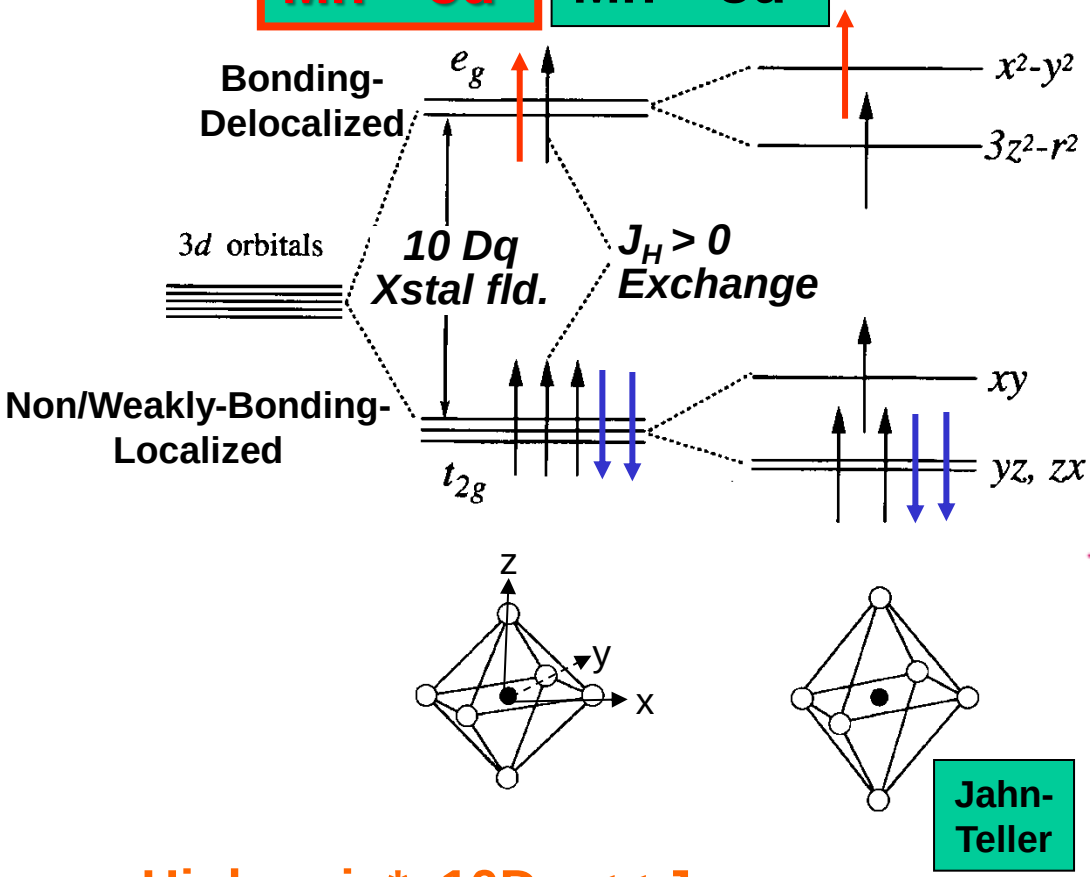


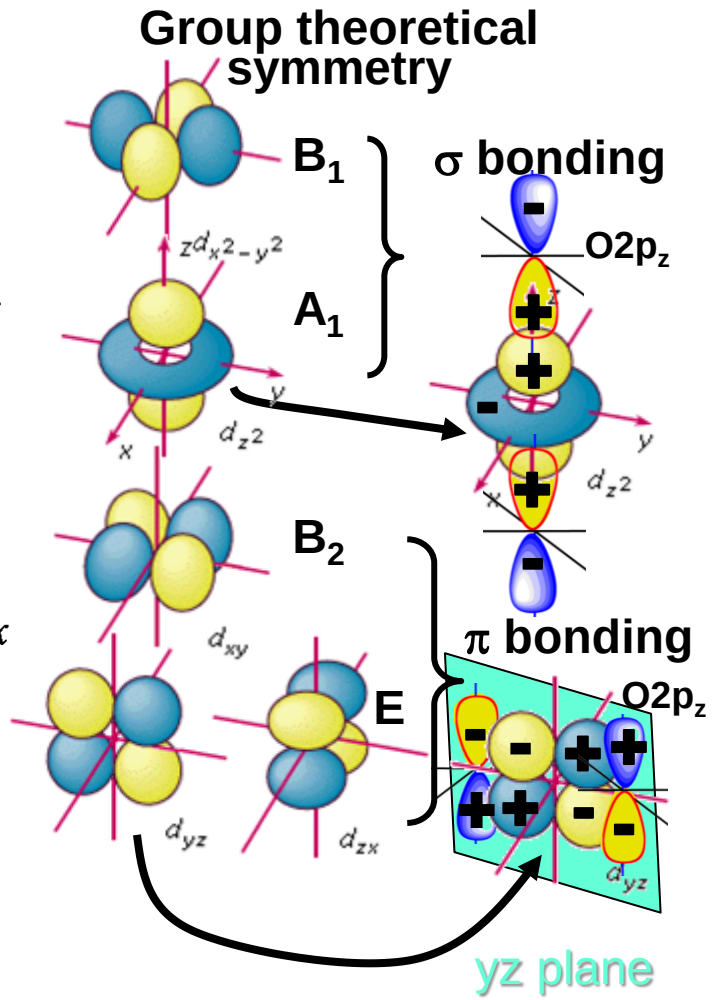
Face-centered cubic—12 nearest neighbors

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

High-spin*/Low-spin*

Mn^{2+} $3d^5$ | **Mn^{3+} $3d^4$**





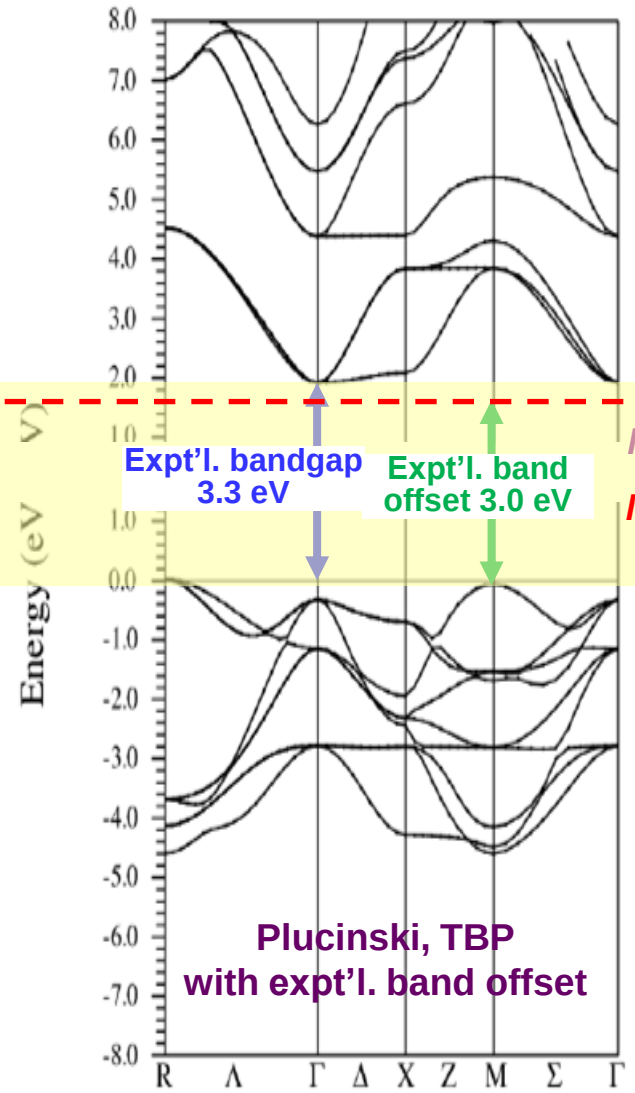
High-spin*: 10Dq << J_H

Low-spin*: 10Dq >> J_H

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

$SrTiO_3$-band insulator

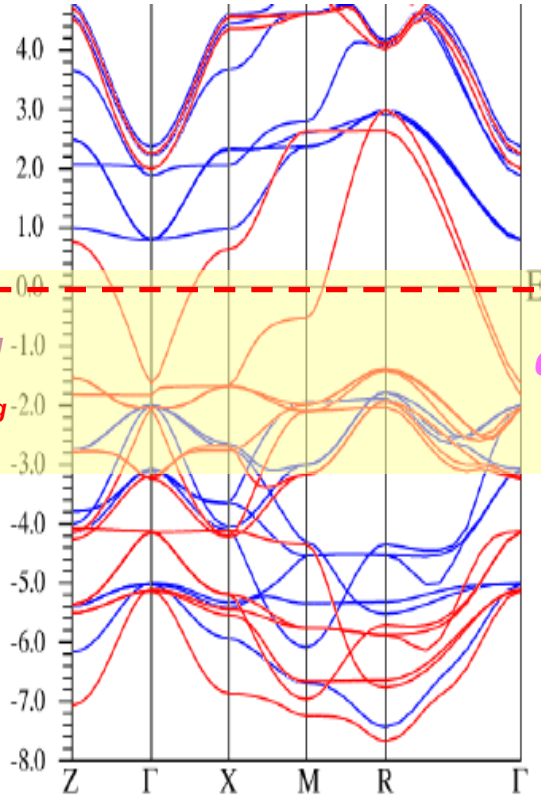
$La_{0.67}Sr_{0.33}MnO_3$- Half-Metallic Ferromagnet



Expt'l. bandgap 3.3 eV

Expt'l. band offset 3.0 eV

Plucinski, TBP with expt'l. band offset



Mn e_g

Mn t_{2g}

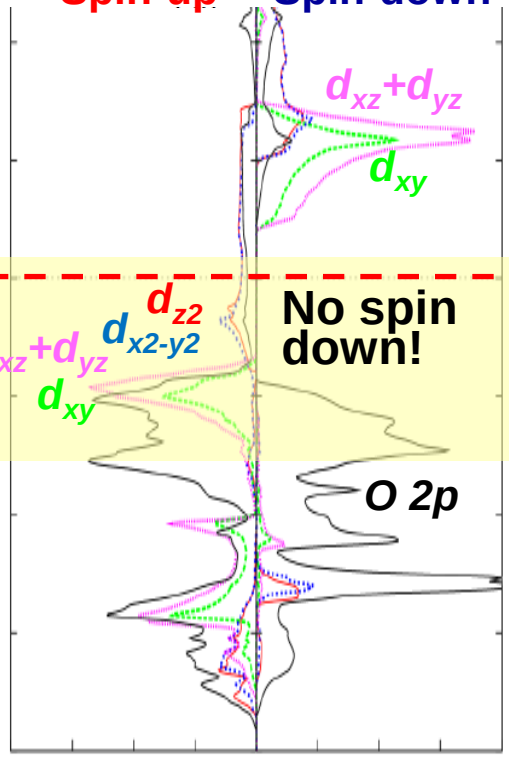
Spin-up

Spin-down

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

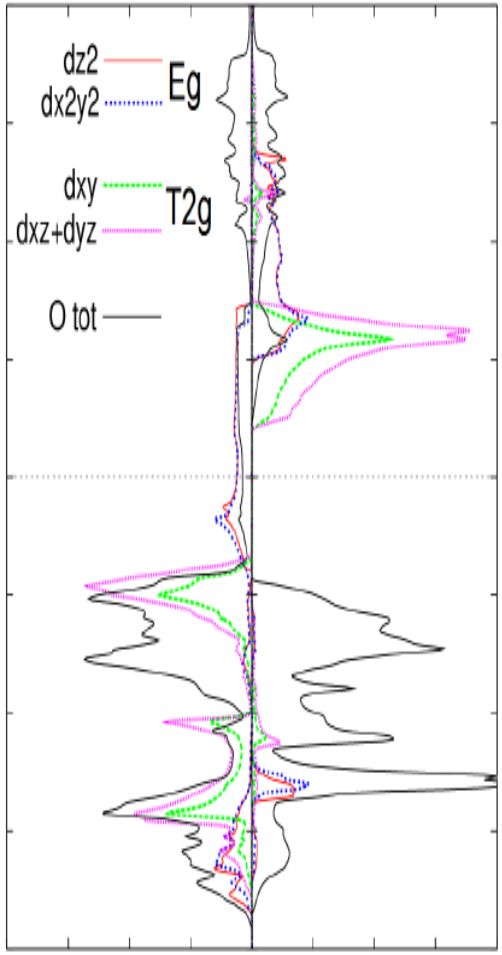
Projected DOSs

Spin-up Spin-down



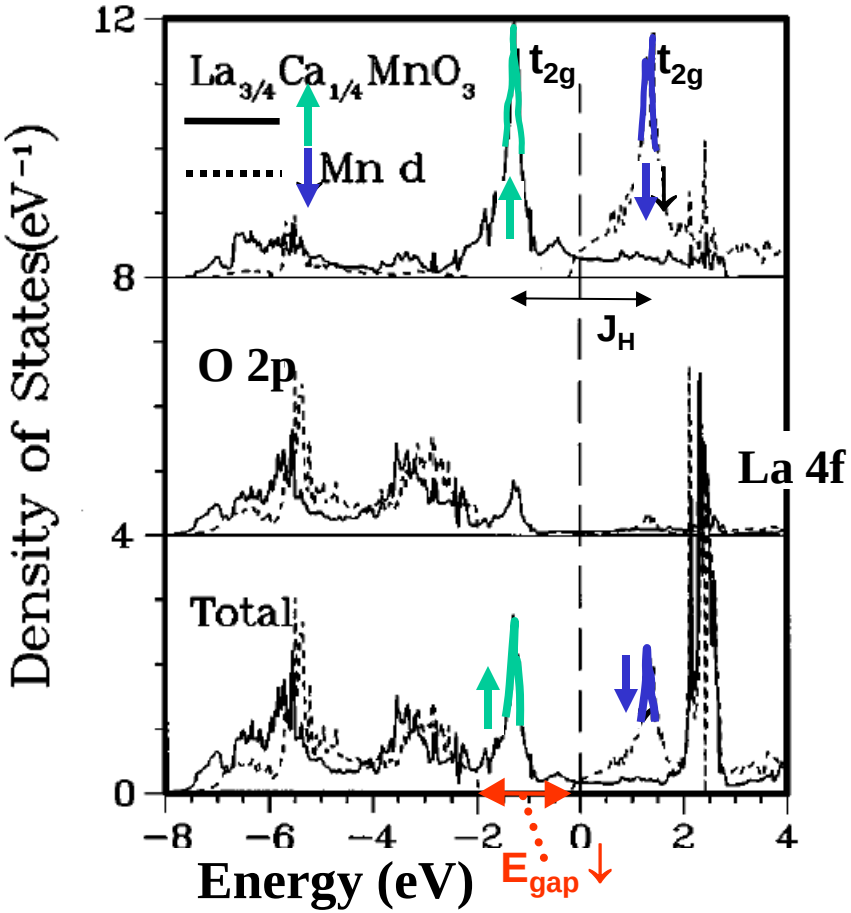
Zheng, Binggeli, J. Phys. Cond. Matt. 21, 115602 (2009) Plucinski, TBP

LSMO partial DOS



Half-Metallic Ferromagnetism

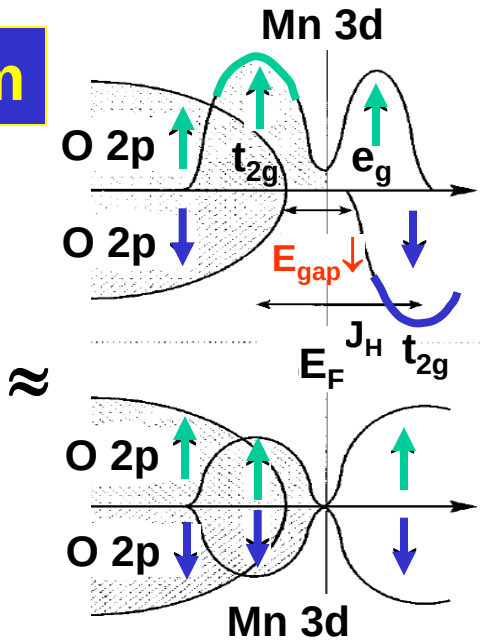
***LDA theory*- FM $La_{0.75}Ca_{0.25}MnO_3$**



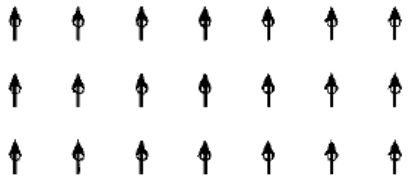
Pickett and Singh, PRB 53, 1146 (1996)

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

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

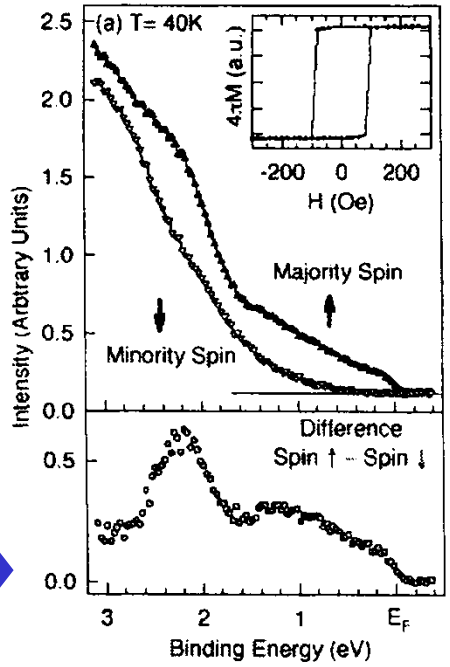


FM : $T \ll T_C$

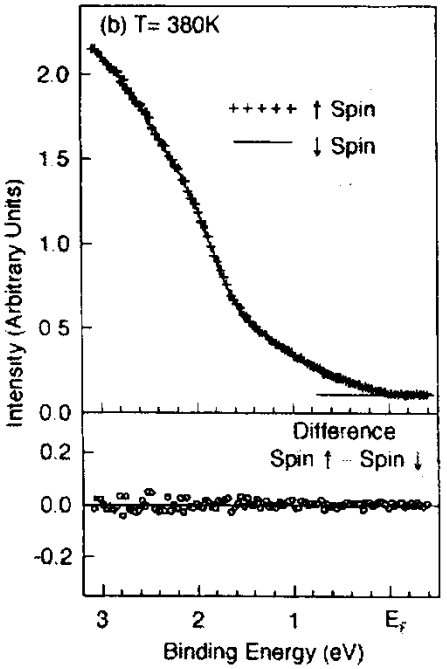


PM : $T > T_C$

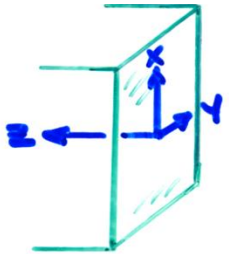
$T \ll T_C$



$T > T_C$



SURFACE ELECTRONIC STATES



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

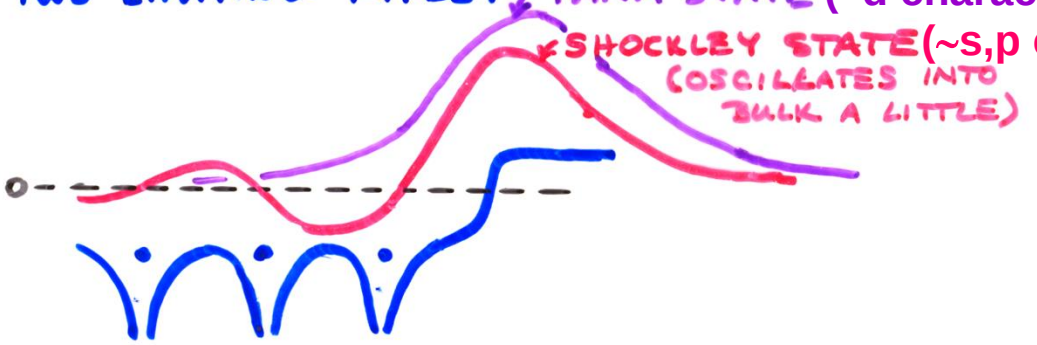
$k_z \Rightarrow \vec{k}_{\perp}$

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



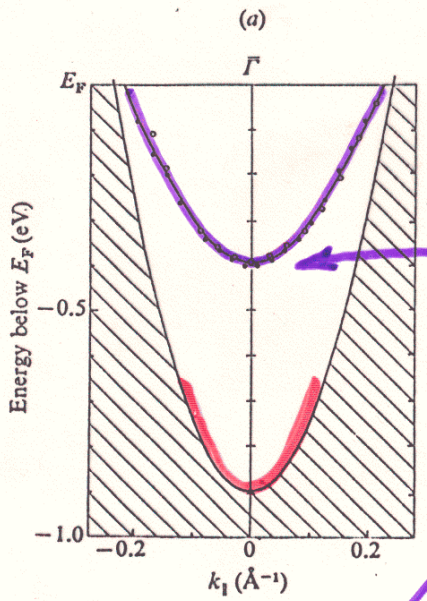
- ONLY EXIST WHEN NO BULK STATE EXISTS AT SAME $\vec{k}_{\parallel} = k_x\hat{i} + k_y\hat{j}$; OTHERWISE MIXING OCCURS + NOT SURFACE-LOCALIZED

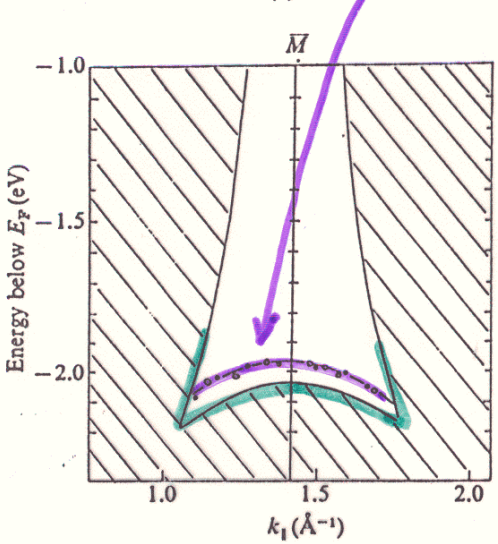
Surface states on Cu(111)

Shockley surface State: s,p makeup

Tamm surface state: 3d makeup

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



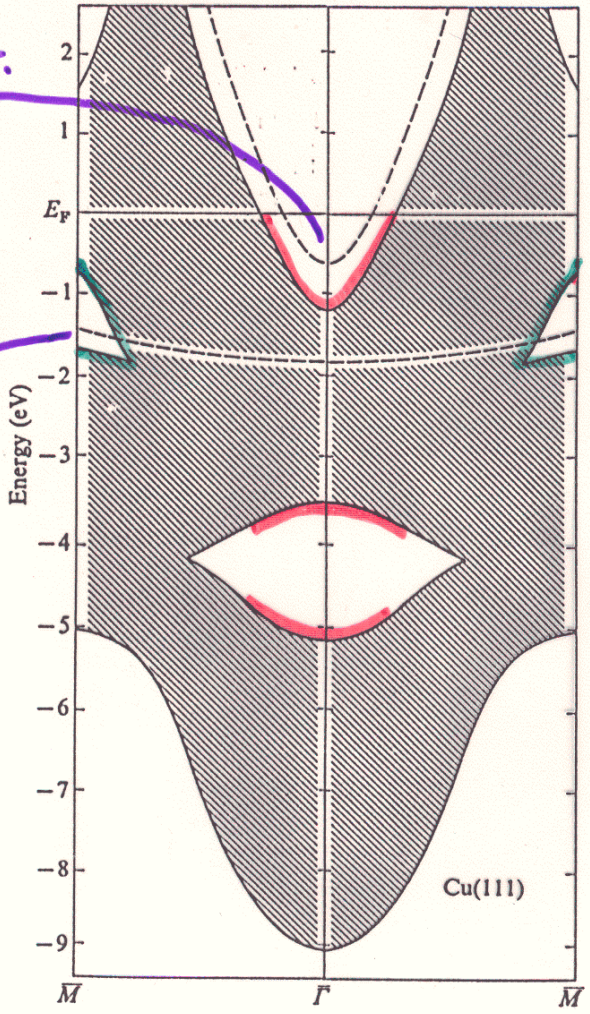


THEORY

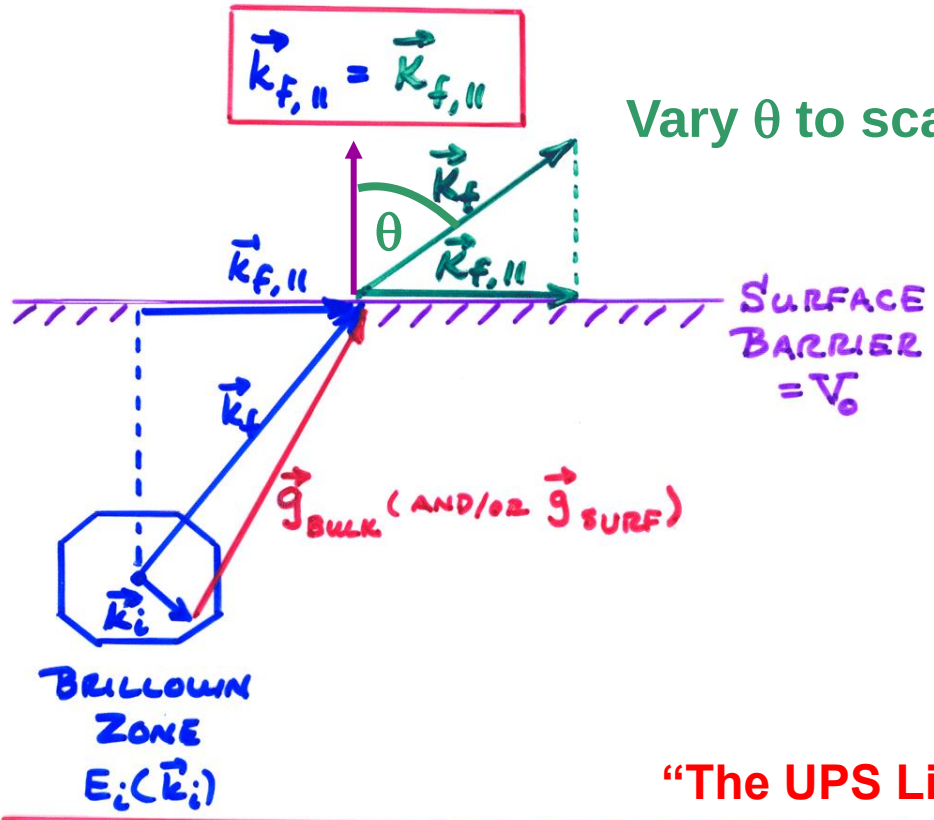
Fig. 4.17. Surface states (dashed curves) and bulk projected ban Cu(111) surface according to a six-layer surface band structure calculation (Euceda, Bylander & Kleinman, 1983).

EXPT.

EXPT.



Conservation Laws in Valence-Band Photoelectron Spectroscopy:



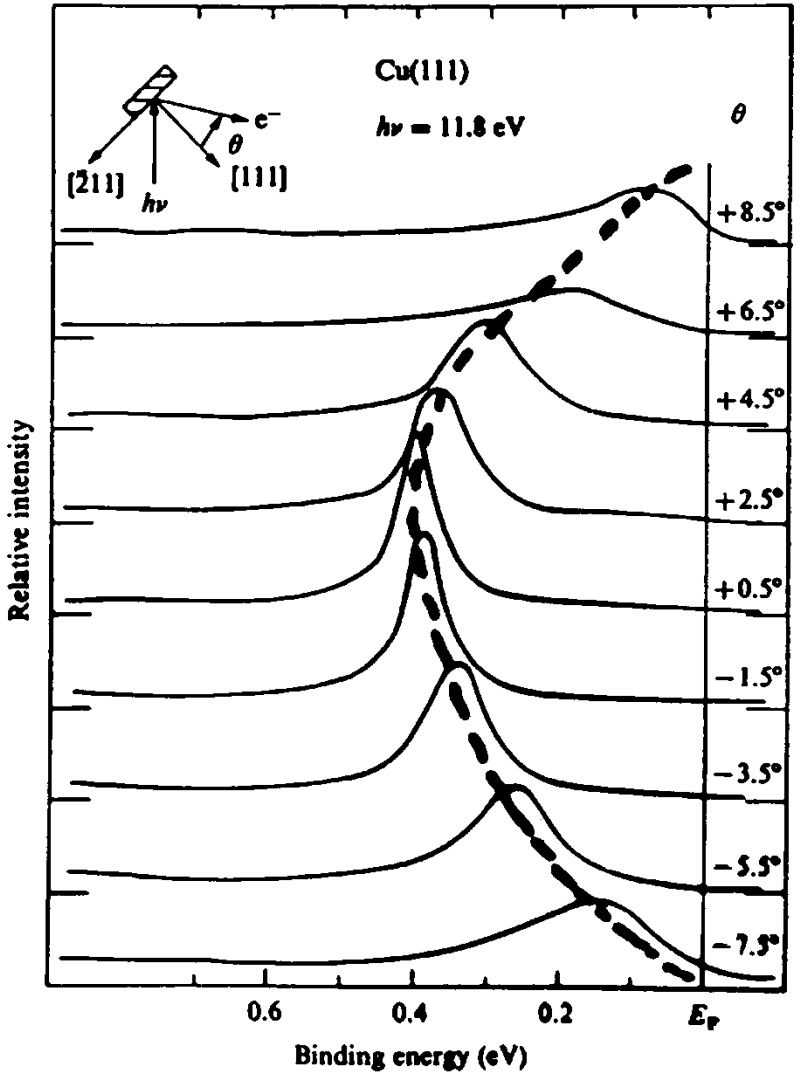
Vary θ to scan $\vec{K}_{f,\parallel} = \vec{k}_{f,\parallel}$

"The UPS Limit"

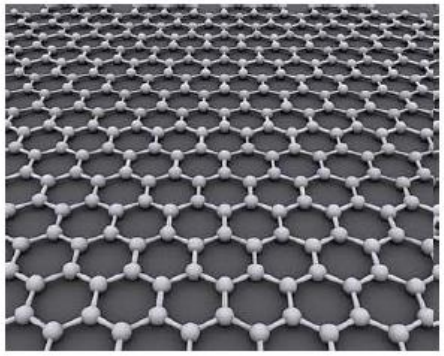
$$\vec{k}_f = \vec{k}_i + \vec{g}_{BULK}(\vec{g}_{SURFACE}) + \vec{k}_{h\nu} + \vec{k}_{PHONON}$$

NEGLIGIBLE IF: $h\nu \lesssim 500$ eV; $h\nu$ and/or T low enough

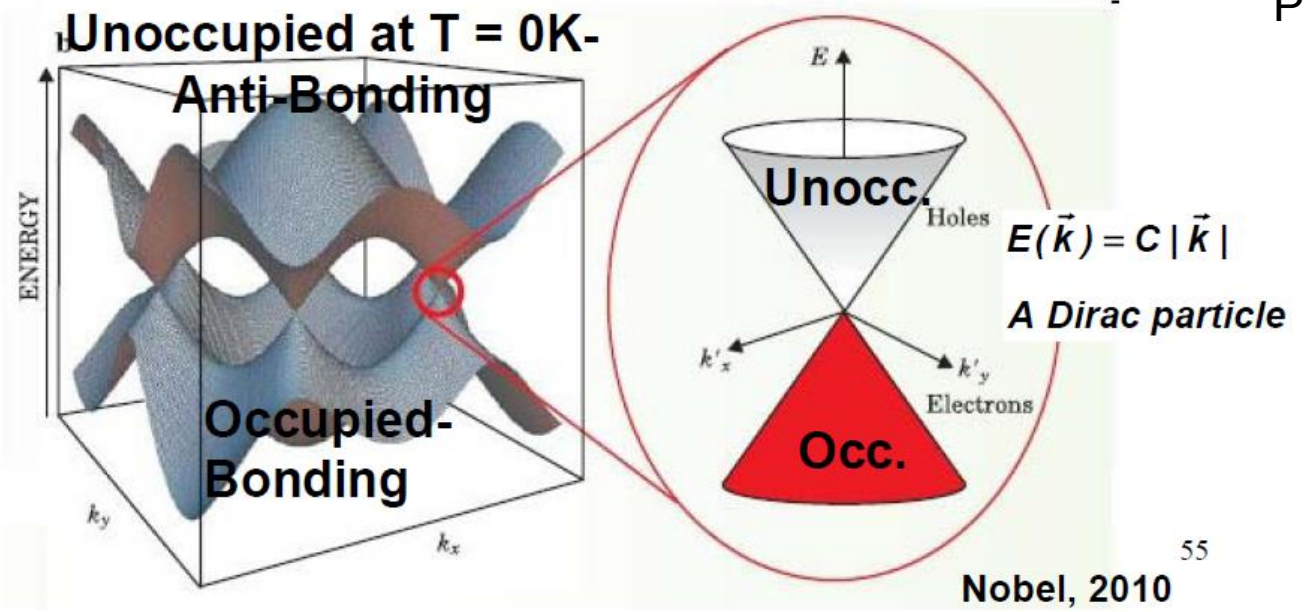
Fig. 4.20. Photoemission energy distribution curves from Cu(111) at different collection angles. Equation (4.32) has been used to express the electron kinetic energy in terms of the binding energy of the electron state (Kevan, 1983).



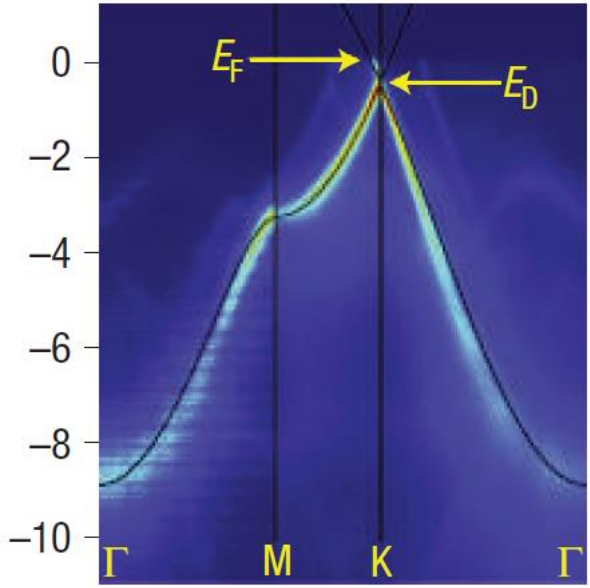
Graphene- A very special 2D case



The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov
…"for groundbreaking experiments regarding the two-dimensional material graphene"



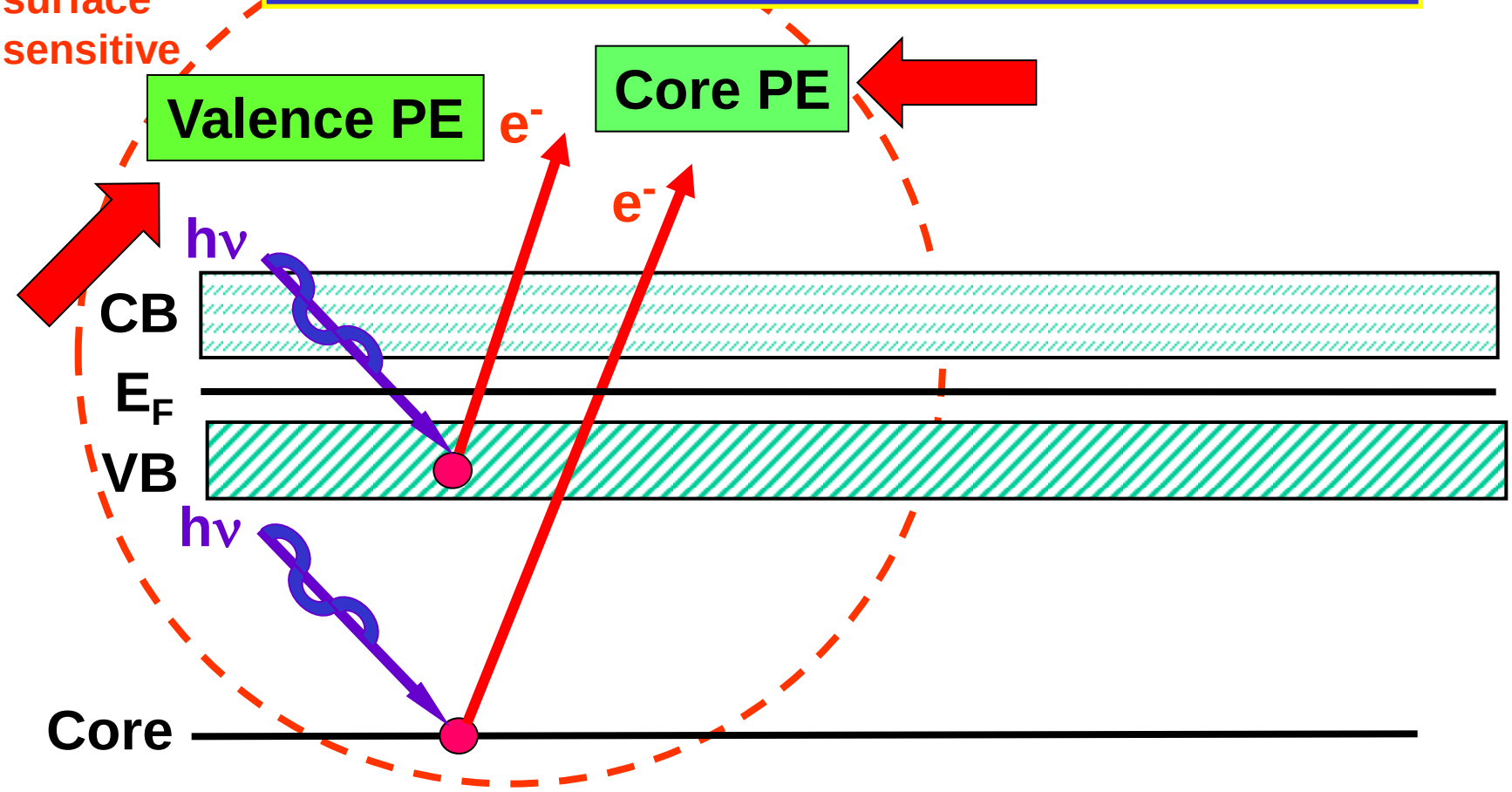
Photoelectron spectroscopy



Bostwick et al., Nature Physics 3, 36 - 40 (2007)

The Soft X-Ray Spectroscopies

Electron-out: surface sensitive



PE = photoemission = photoelectron spectroscopy

XAS = x-ray absorption spectroscopy

AES = Auger electron spectroscopy

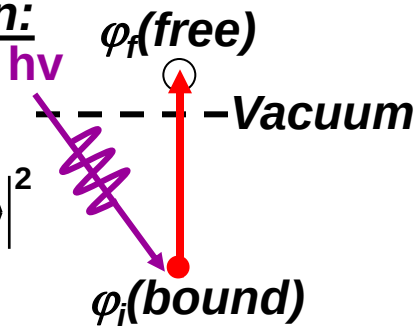
XES = x-ray emission spectroscopy

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

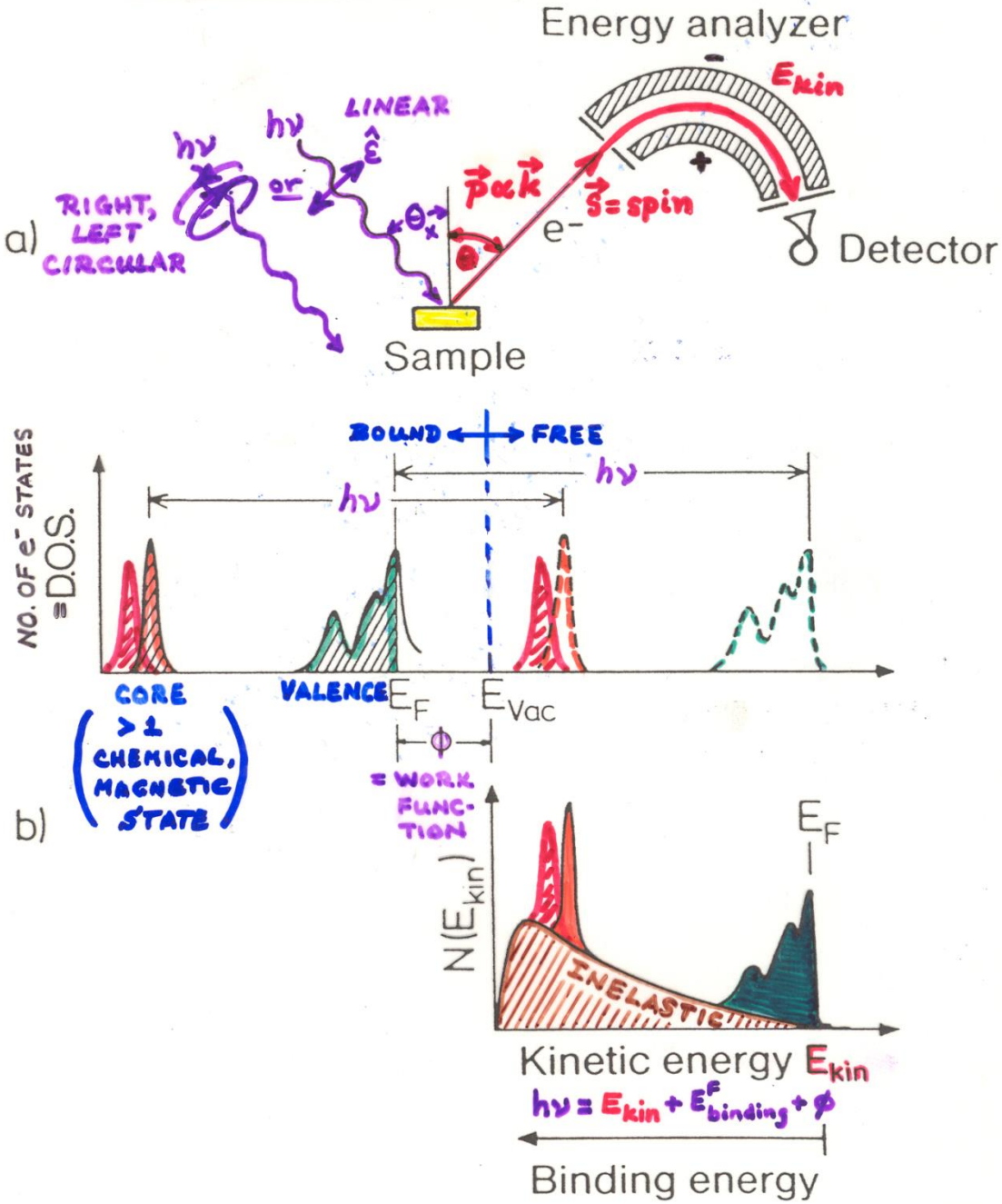
MATRIX ELEMENTS IN THE SOFT X-RAY SPECTROSCOPIES: DIPOLE LIMIT

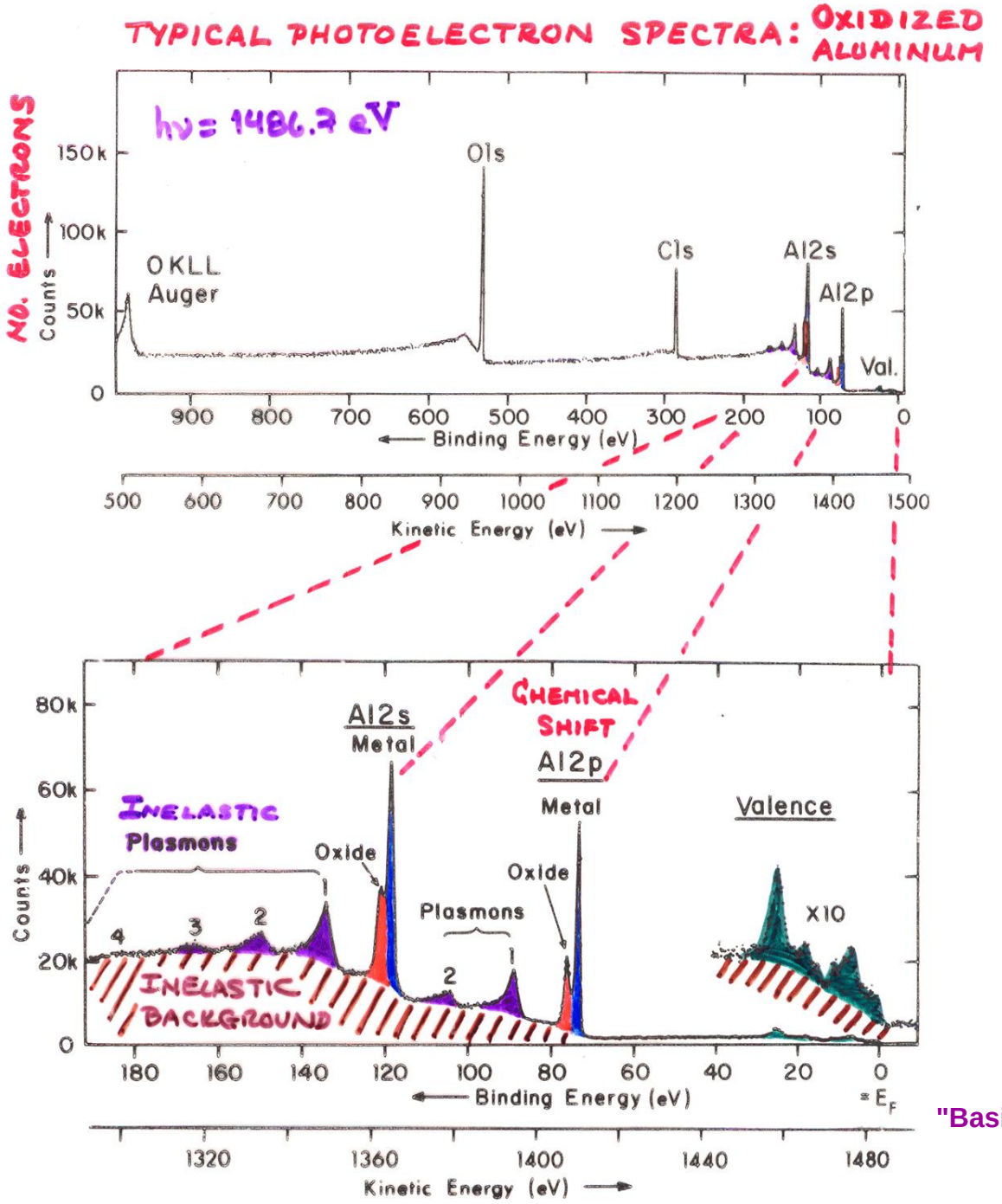
- ***Photoelectron spectroscopy/photoemission:***

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



PHOTOELECTRON SPECTROSCOPY





"Basic Concepts of XPS"
Figure 1

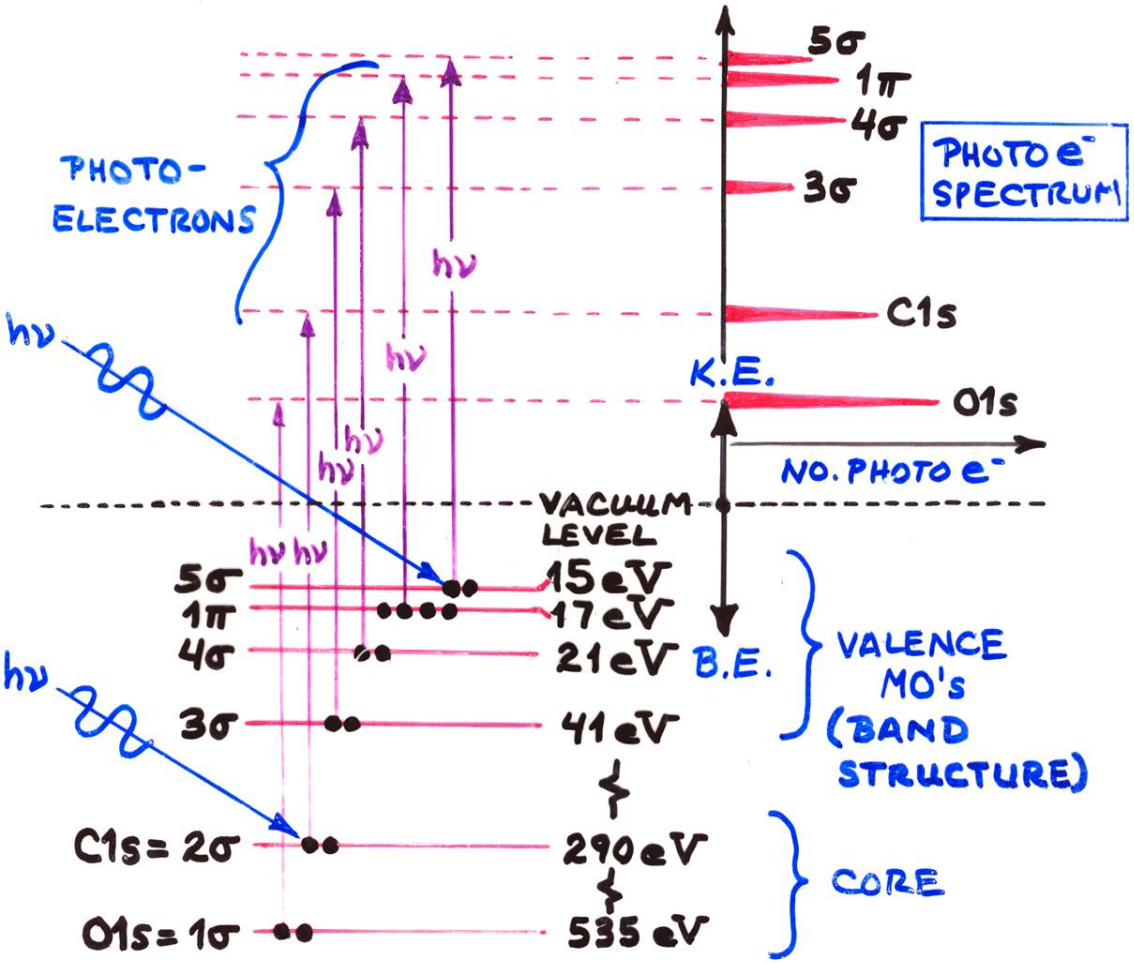
PHOTOELECTRON SPECTROSCOPY

THE PHOTOELECTRIC EFFECT (EINSTEIN, 1905):

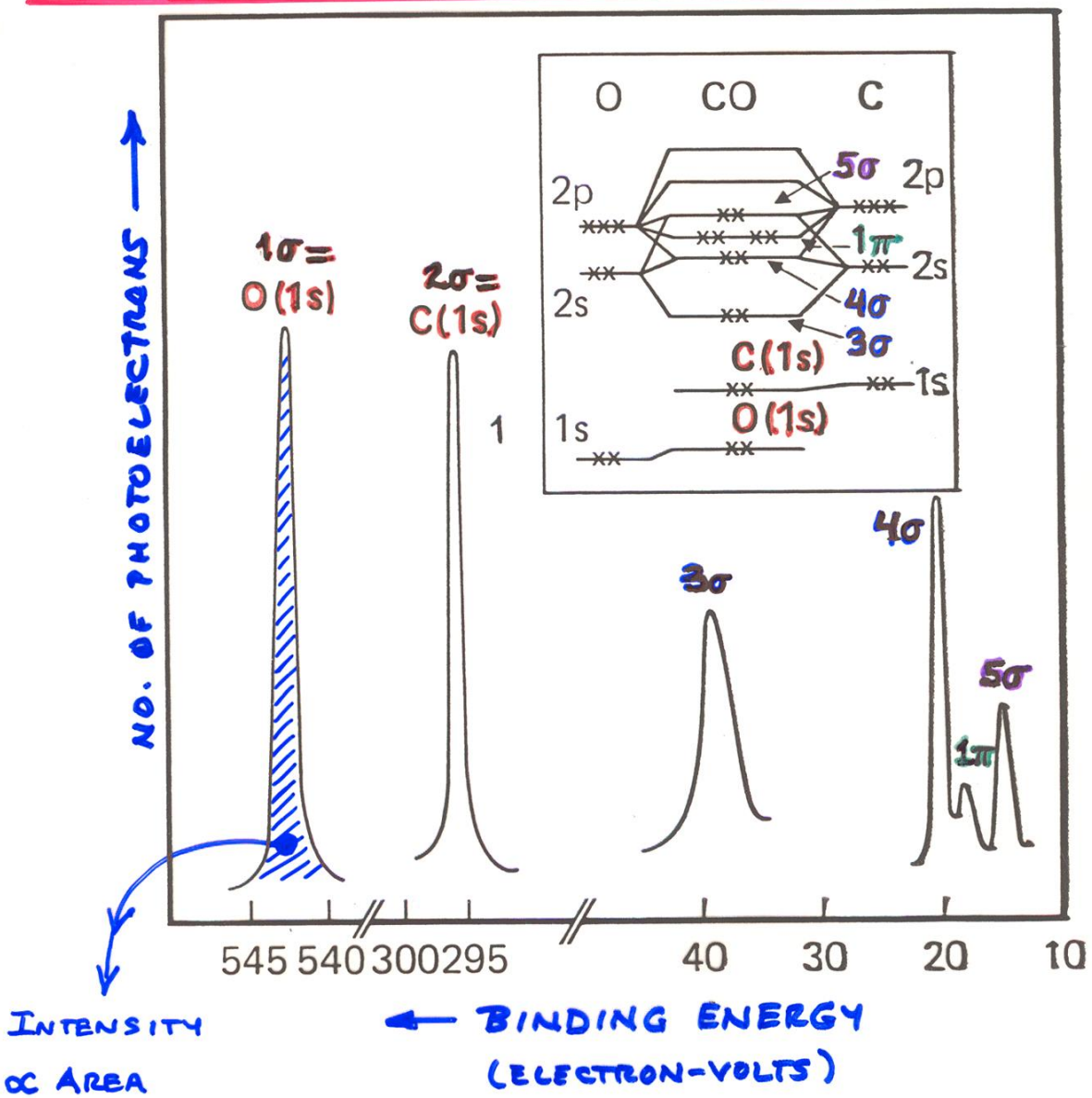
(PHOTON ENERGY) (ABSORBED) = (e⁻ BINDING ENERGY IN SYSTEM) + (PHOTOELECTRON KINETIC ENERGY) (EMITTED)

= B.E. + K.E.

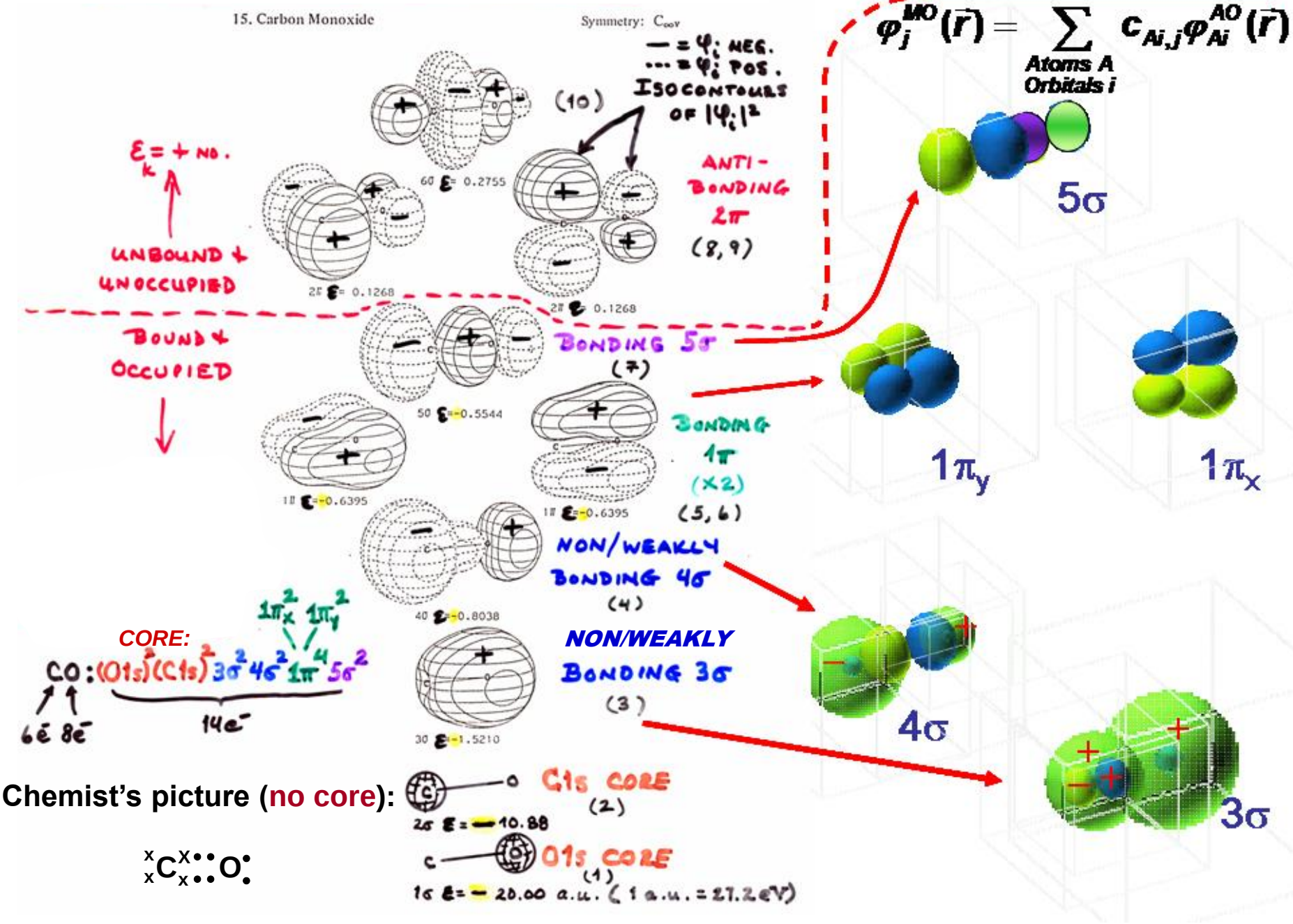
EXAMPLE – CO MOLECULE:



X-RAY PHOTOELECTRON SPECTRUM OF CO

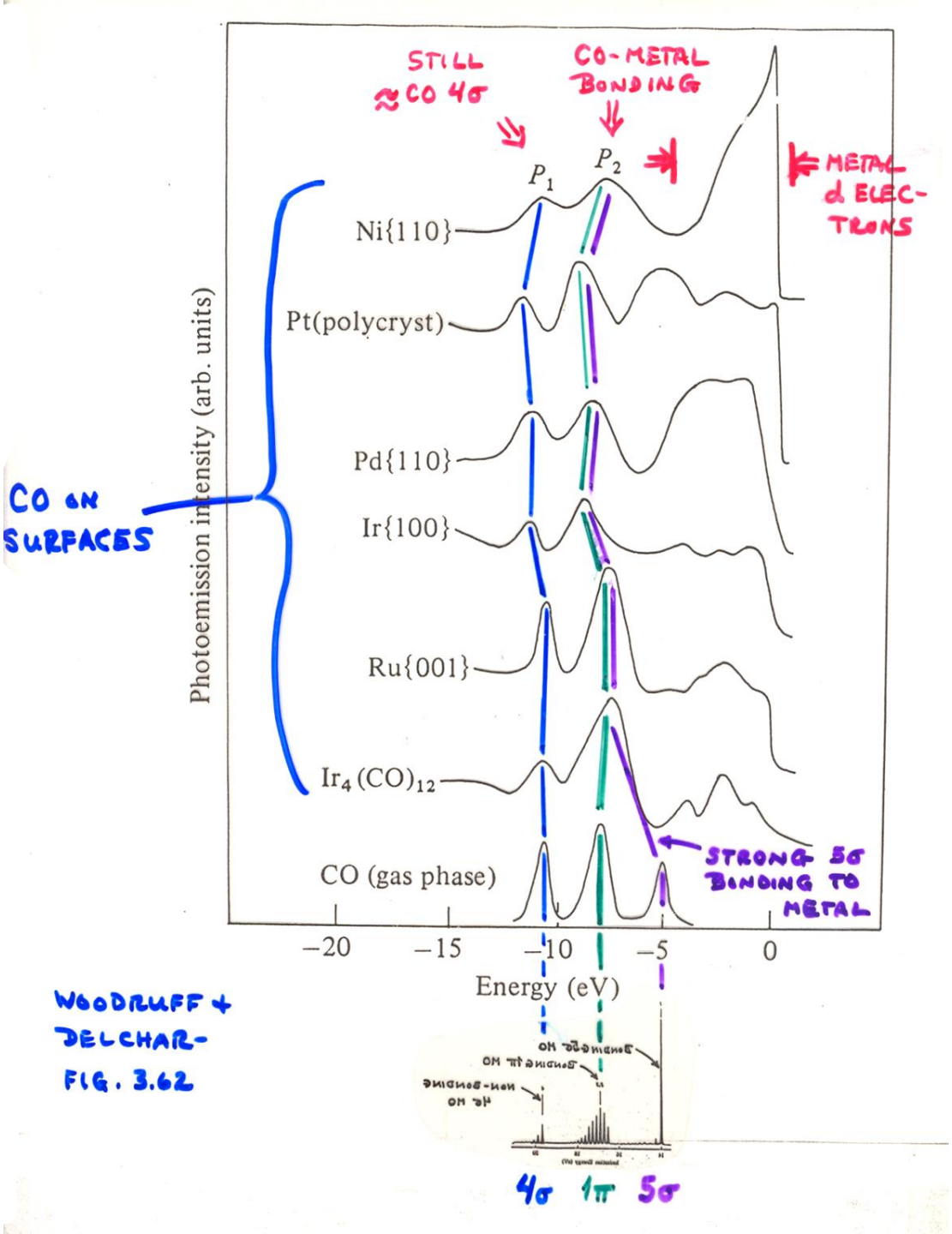


The LCAO or tight-binding picture for CO:



Chemist's picture (no core):

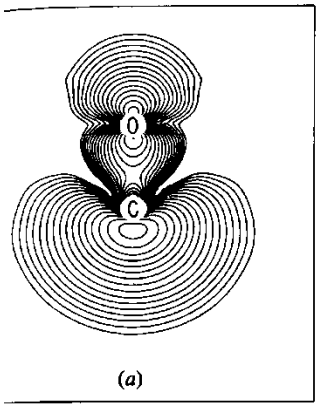
Valence-level Photoelectron spectra of CO adsorbed on various transition metal surfaces

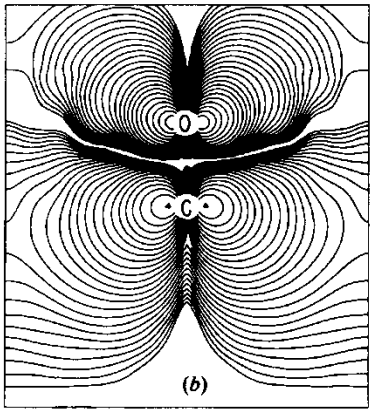


Theoretical Calculations of charge density for CO bound to Ni(001)- "on-top":

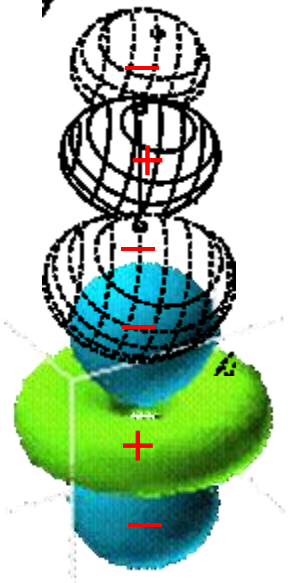
O
|
C
|
Ni

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).

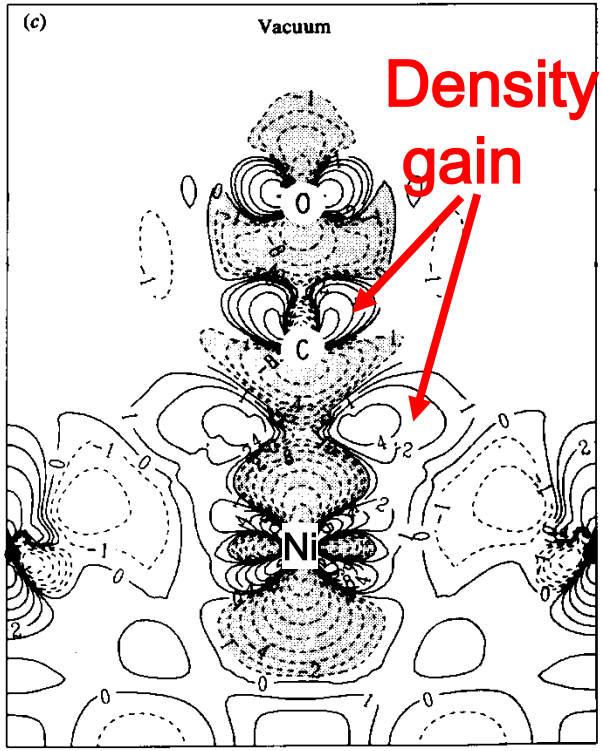




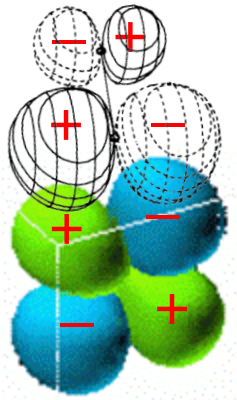
CO 5σ



Ni $3d_{z^2}$
σ bond



CO 2π = π*

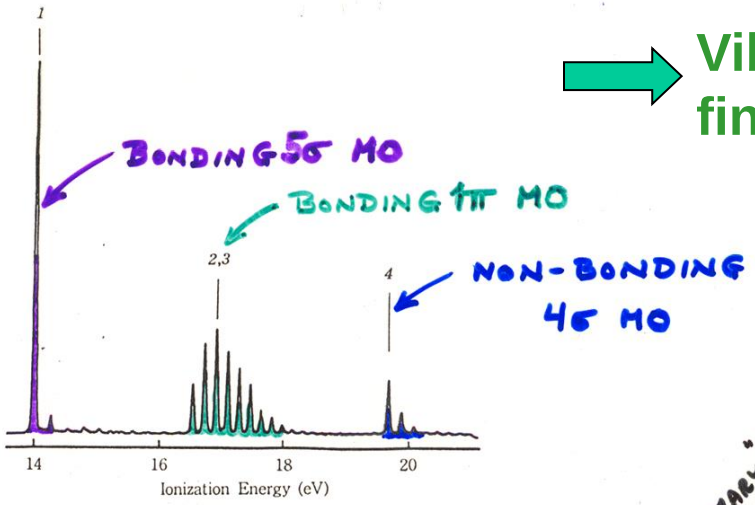


Ni $3d_{xy}$
π "back bond"

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

(9) **CO** Carbon Monoxide

UV PHOTOELECTRON SPECTRUM OF CO



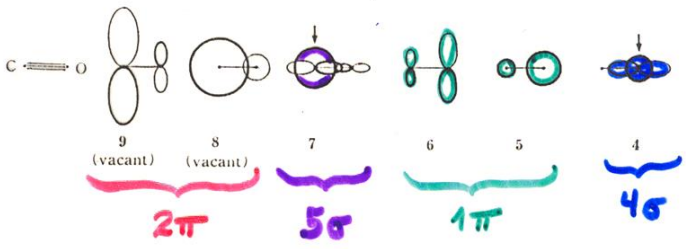
Vibrational fine structure

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"

INTENSITIES IN PHOTOELECTRON SPECTRA:

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

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

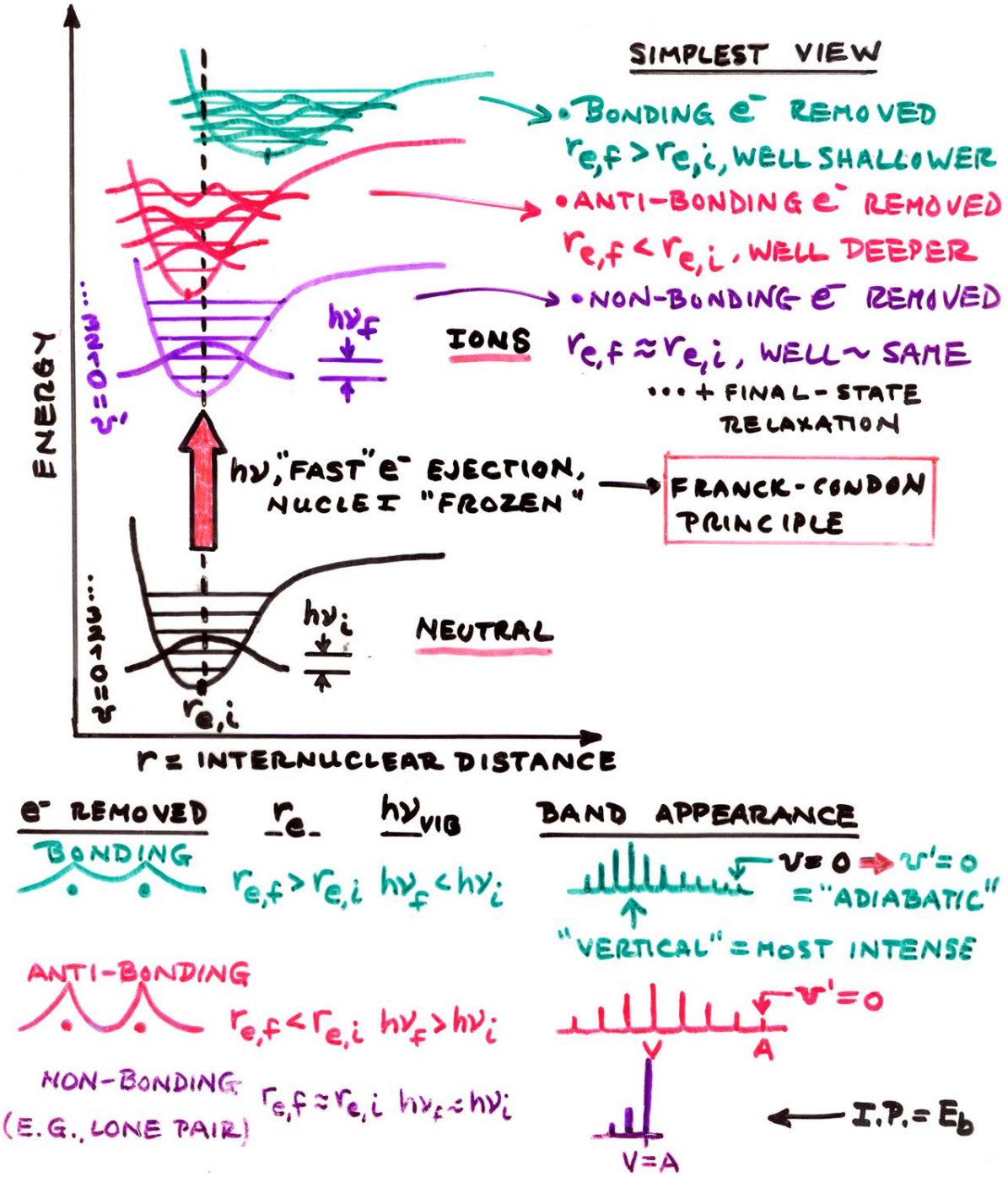
- BORN-OPPENHEIMER: e^-'s FAST, VIBRATIONS SLOW

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

VIBRATIONAL STRUCTURE IN VALENCE-LEVEL (MO) SPECTRA

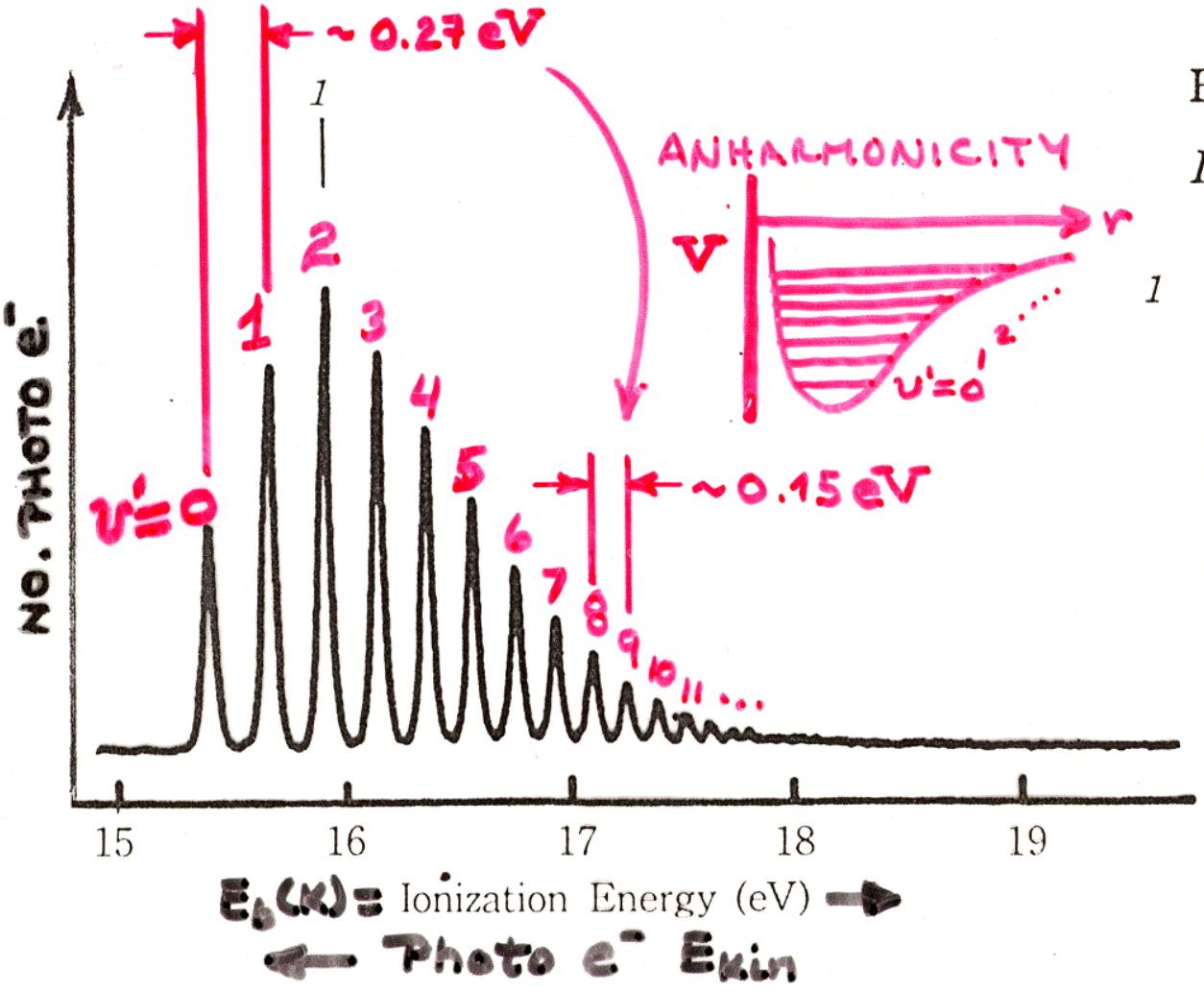
Diatomic A-B example

(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

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: $\psi_K \rightarrow \psi_f$ = PHOTOe^- (FAST)

k HOLE → $\psi_1 \rightarrow \psi_1'$, $\psi_{k-1} \rightarrow \psi_{k-1}'$, $\psi_{k+1} \rightarrow \psi_{k+1}'$, $\psi_N \rightarrow \psi_N'$ (SLOW)

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

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

↳ NORMAL $\frac{d\sigma_K}{d\Omega}$

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

- SLATER DETS. FOR $\Psi^f_{e^-} = \det(\psi_1' \psi_2' \cdots \psi_{k-1}' \psi_{k+1}' \cdots \psi_N')$

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

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

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

spin-orbit + $\left| \hat{e} \cdot \langle \psi_f | \vec{r} | \psi_K \rangle \right|^2$ **1e- DIPOLE → $d\sigma/d\Omega$**

- PLUS DIFFRACTION EFFECTS IN ψ_f ESCAPE

"Basic Concepts of XPS" Chapter 3.D.