

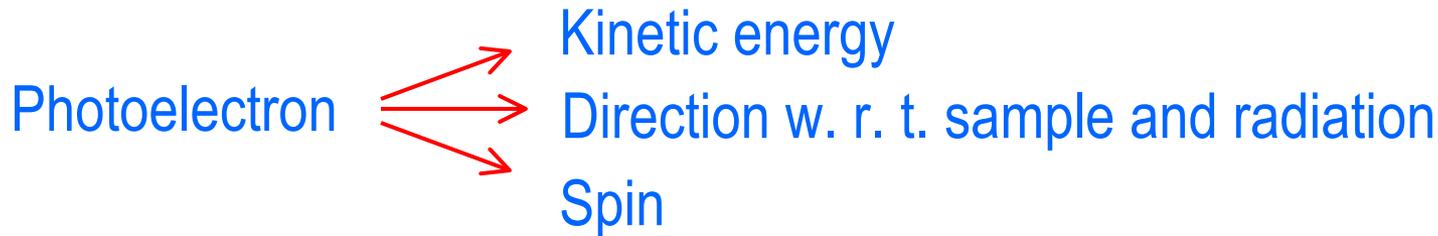
## Lecture 8

# X-Ray Photoelectron Spectroscopy

# X – ray Photoelectron spectroscopy

$$h\nu = E_b^v(k) + E_{\text{kin}}$$

Spectrum is composed of  
Photoelectrons, Auger electrons, secondary electrons



All these measurements are possible.

The basic PE measurements involve only kinetic energy analysis

The aluminium spectrum

- (1) narrow PE features
- (2) inelastic tail after each peak

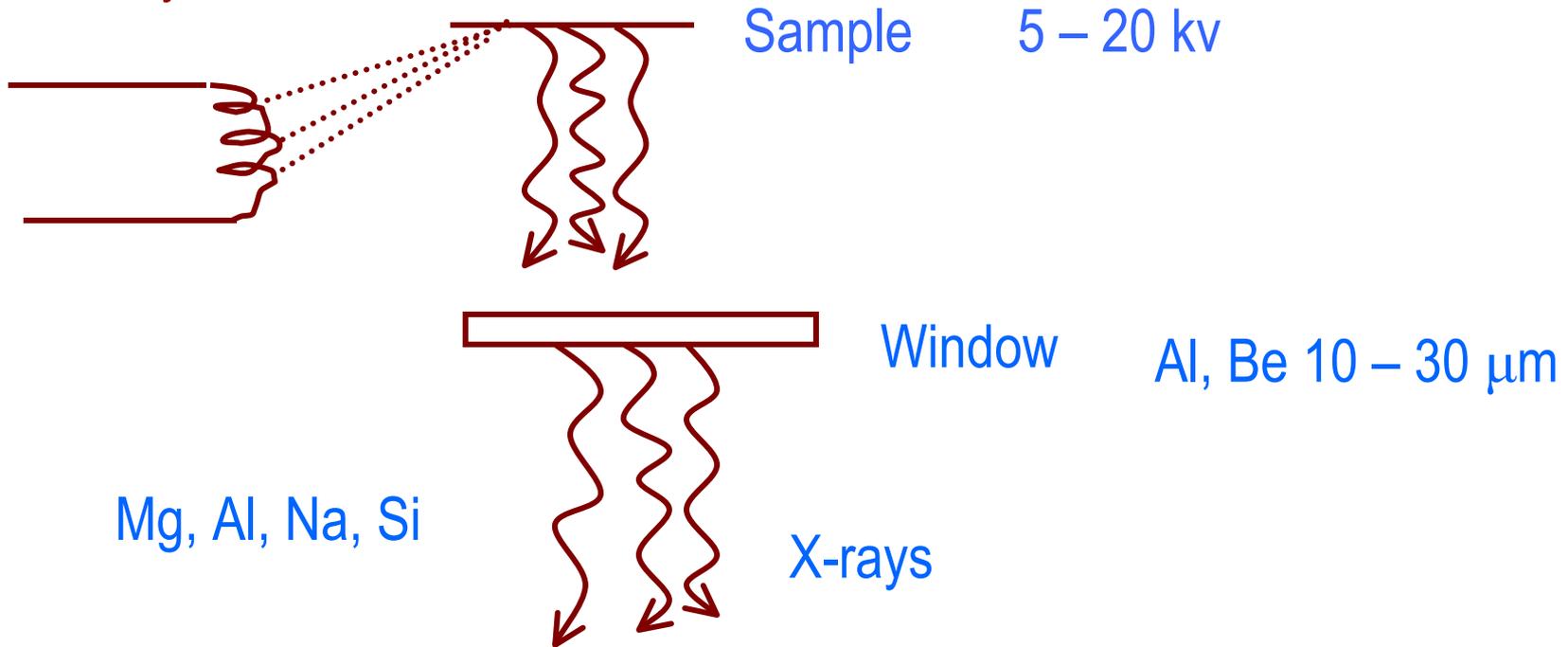
What are the additional features due to?

Plasmons

Valence excitations OLS

Weak inelastic tail for C

X – ray Source



**Mg, Al, Na, Si**

**K $\alpha_1$**

**K $\alpha_2$**

**2p $_{3/2}$   $\rightarrow$  1s**

**2p $_{1/2}$   $\rightarrow$  1s**

<b>Name</b>	<b>Energy</b>	<b>FWHM</b>
<b>NaK<math>\alpha_{1,2}</math></b>	<b>1041.0</b>	<b>0.4</b>
<b>MgK<math>\alpha_{1,2}</math></b>	<b>1253.6</b>	<b>0.7</b>
<b>AlK<math>\alpha_{1,2}</math></b>	<b>1486.6</b>	<b>0.8</b>
<b>SiK<math>\alpha_{1,2}</math></b>	<b>1739.5</b>	<b>1.0-1.2</b>

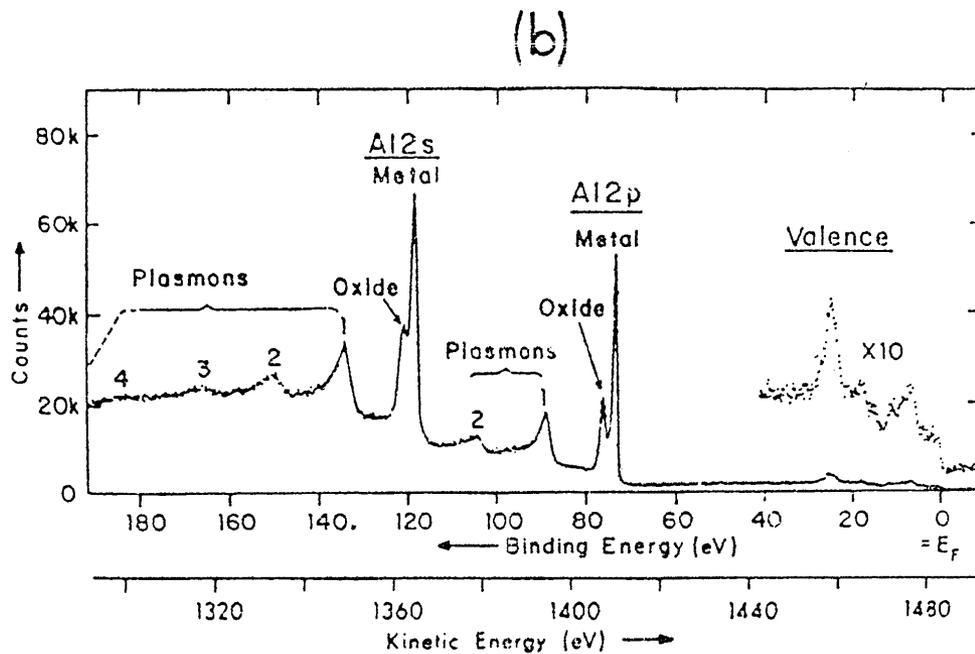
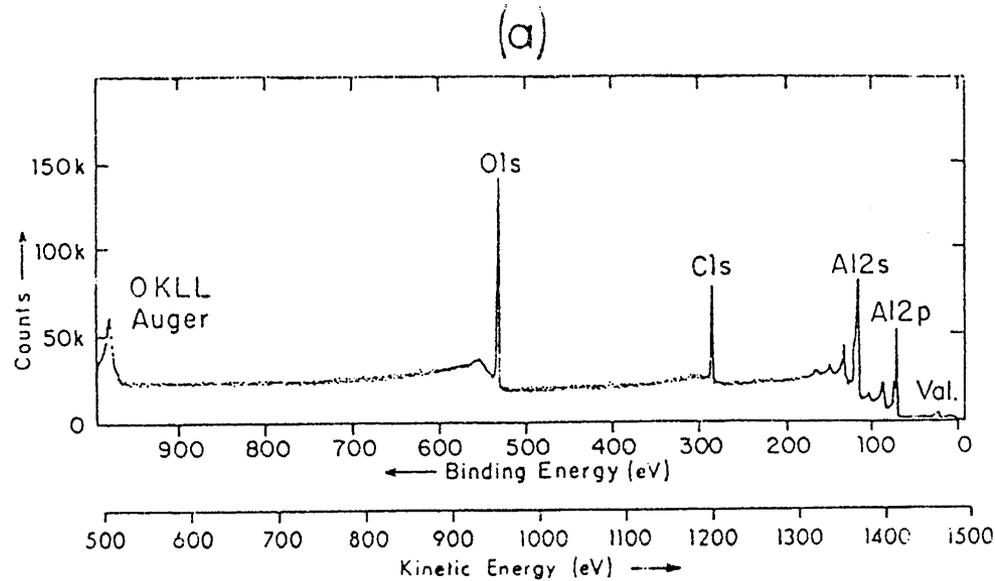


Fig. 1. Typical XPS spectra obtained from an oxidized aluminium specimen with carbonaceous contaminant overlayer. Monochromatized  $AlK\alpha$  radiation was used for excitation. (a) Overall spectrum with all major no-loss features labelled. (b) Expanded-sca spectrum of the  $Al2s$ ,  $Al2p$ , and valence regions. Chemically-shifted oxide- and metal-co peaks are indicated, as well as inelastic loss peaks due to bulk plasmon creation.

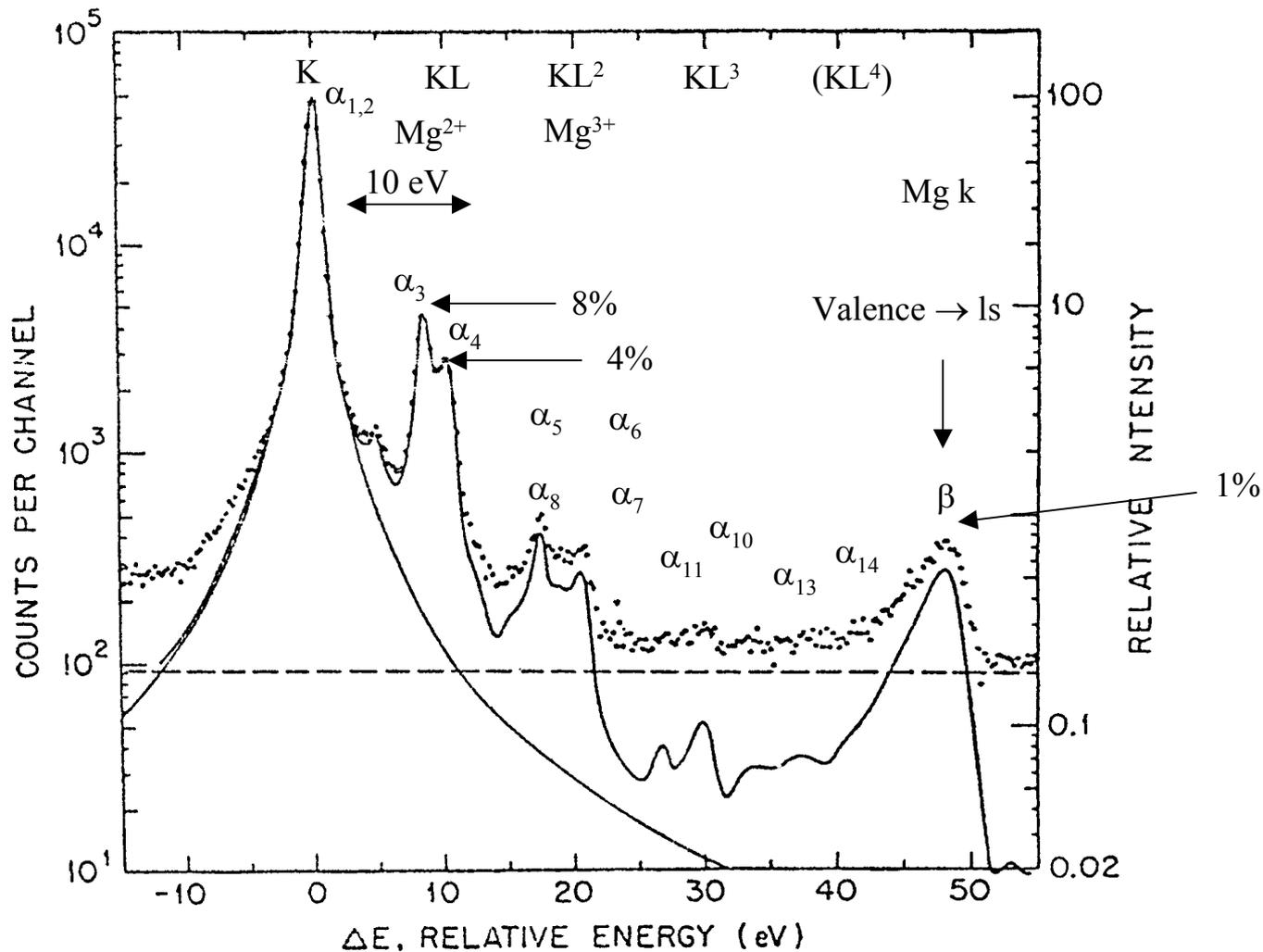


Fig. 2. The K x-ray emission spectrum of Mg metal as emitted by a non-monochromatized x-ray source. The peaks indicated  $\alpha_1, 2, \dots, \beta$  correspond to various transitions into the  $K=1s$  subshell. The dashed line is an average background and the solid line is the net spectrum. Note the logarithmic intensity scale. The notation K corresponds to a single initial  $1s$  hole, KL to initial holes in both  $1s$  and  $2s$  or  $2p$ ,  $KL^2$  to a single initial hole in  $1s$  and two initial holes in  $2s, 2p$ , etc. (From Krause and Ferreira, ref. 37.)

FWHM decreases with at.no. due to decrease in  $\alpha_{3/2,1/2}$  splitting and an increase in core hole life time.

Elements below Ne are not used since 2p levels are broadened due to bonding. However,  $k_{\alpha 1,2}$  of F, from highly ionic compounds is used.

Bragg reflection can get monochromatic radiation:  $\text{Alk}_{\alpha 1,2} \rightarrow 0.4 \text{ eV}$

Soft x-ray  $\text{M}\zeta(4p_{3/2} \rightarrow 3d_{5/2})$  Y – Mo  $100 \leq h\nu \leq 200 \text{ eV}$

Element	Energy	FWHM
Y	132.3 eV	0.5 eV
Zr	151.4	0.8

low penetration

# Charging

Charging potential  $V_c$

$$h\nu = E_b^v(k)^0 + E_{\text{kin}}(r) + V_c(r)$$

Peak position Vs. x-ray flux

Gaseous samples → variation of gas pressure

Use of internal standards

Solid Specimens

Inelastic scattering  $10 - 80 \text{ \AA}$

Sample volume  $10^{-6} \text{ cm}^3$  or  $1 - 10 \text{ \mu g}$

Detection limit –  $10^{-9} \text{ gm}$

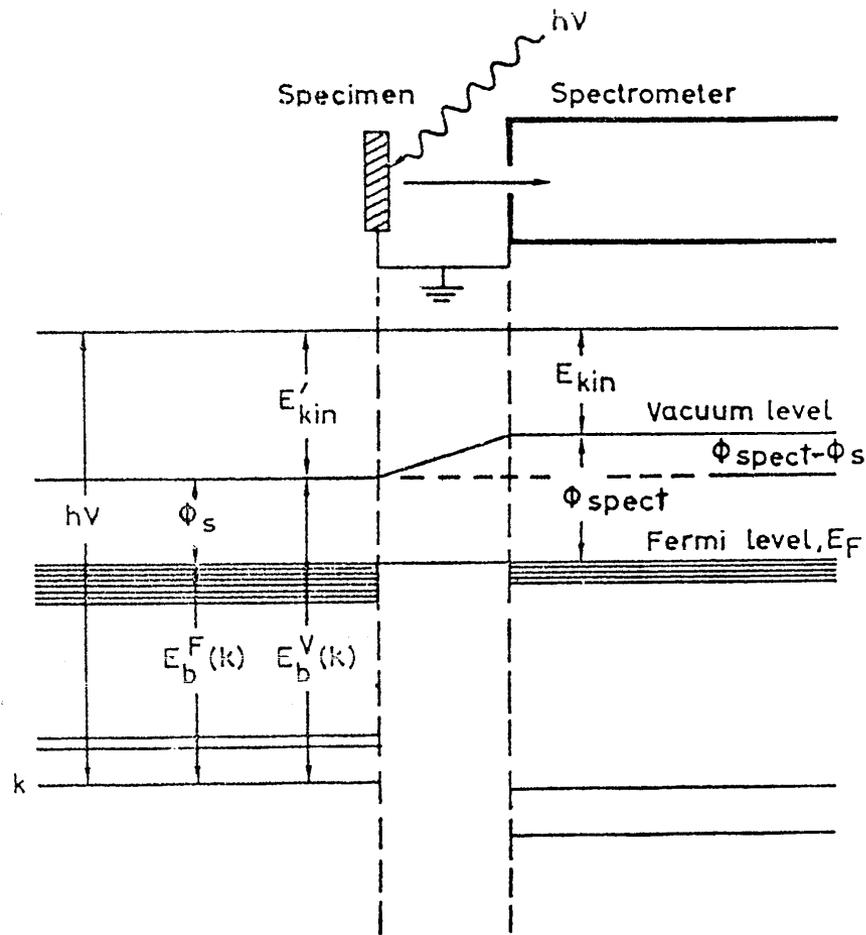
Surface sensitivity  $\leq 10^{-9} \text{ torr pressure}$

$\text{O}_2$  at  $10^{-9} \text{ torr } 25^\circ\text{C}$ , sticking coefficient  $\sim 1.0$

1 atomic layer takes – 50 minutes

∴ Clean surface requires  $10^{-10} \text{ torr}$

Depending on the type of sample to be analyzed, the kinetic energies of the ejected photoelectrons vary. In the simple case of a metal in a metallic spectrometer, the electron chemical potentials of both should be equal.



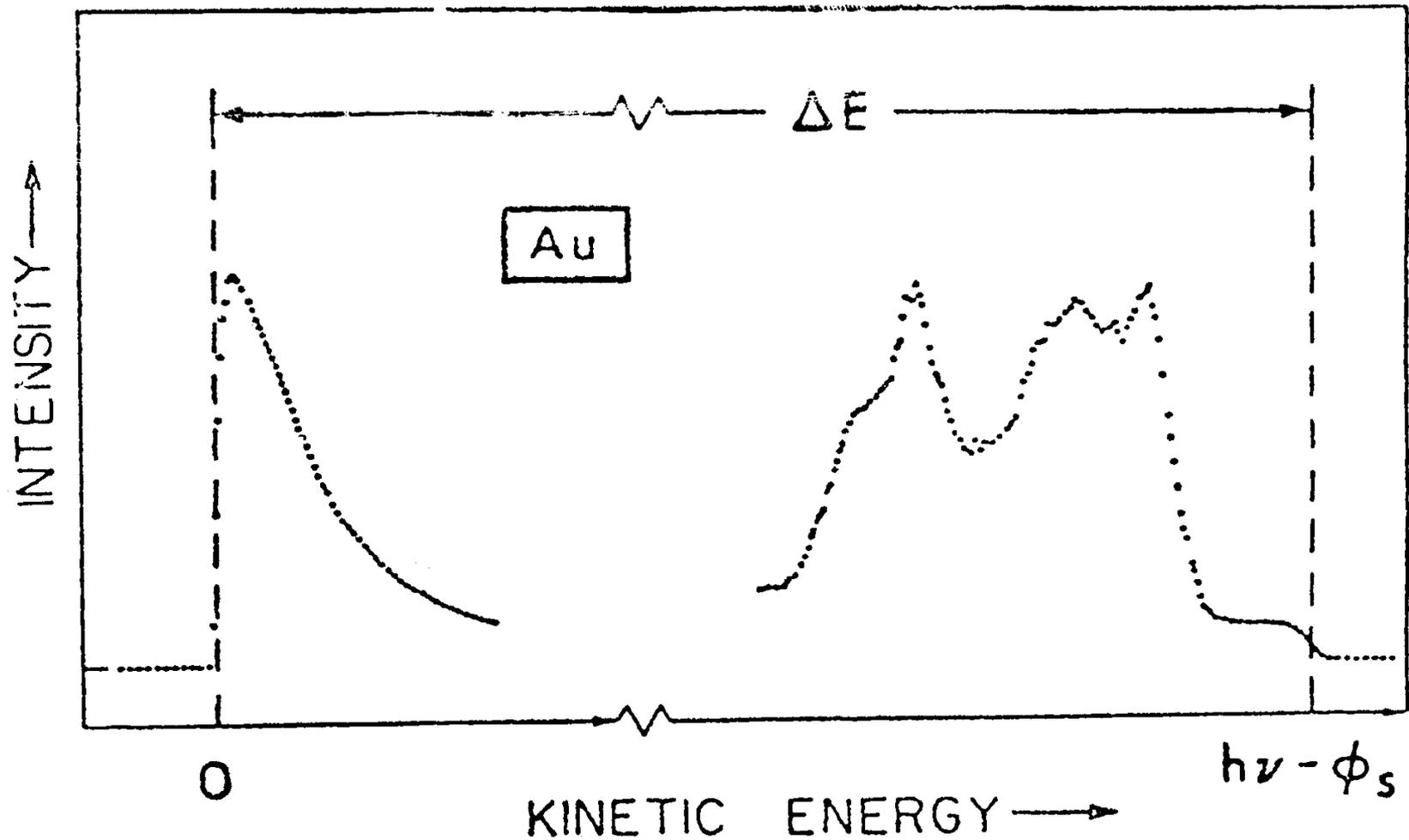
Energy level diagram for a metallic specimen in electrical equilibrium with an electron spectrometer. The closely spaced levels near the Fermi level  $E_F$  represent the filled portions of the valence bands in specimen and spectrometer. The deeper levels are core levels. An analogous diagram also applies to semi-conducting or insulating specimens, with the only difference being that  $E_F$  lies somewhere between the filled valence bands and the empty conduction bands above.

**Accelerating or retarding  $\phi_s - \phi_{\text{spec}}$**

$$E_{\text{kin}} = E'_{\text{kin}} + \phi_s - \phi_{\text{spec}}$$

$$h\nu = E_b^{\text{F}}(\mathbf{k}) + E_{\text{kin}} + \phi_{\text{spec}}$$

$$E_b^{\text{V}}(\mathbf{k}) = E_b^{\text{F}}(\mathbf{k}) + \phi_s$$



Full XPS spectral scan for a polycrystalline Au specimen, showing both the cutoff of the secondary electron peak at zero kinetic energy and the high-energy cut-off for emission from levels at the metal Fermi level. The measurable distance  $\Delta E$  thus equals  $h\nu - \phi_s$ , provided that suitable specimen biasing has been utilized. For this case,  $h\nu$  was 1253.6 eV and  $\phi_s$  was 5.1 eV.

# Efficiency and retardation

Overall efficiency  $E \propto B A \Omega \delta E_{kin}$

B is the brightness of the electron source in unit area per unit solid angle, A area of the source,  $\Omega$  the solid angle of electron acceptance  $\delta E_{kin}$  is the range of kinetic energies measured by the analyzer at one time B, A and  $\Omega$  vary with  $E_{kin}$ .

$$E \propto \int (B \Omega dA) \delta E_{kin}$$

Most of the time, the electron source seen by the analyzer depends on the slit width and B,  $\Omega$  and A refer to this. For a multichannel detector,  $\delta E_{kin}$  may be 10% of  $E_{kin}$ , whereas resolution  $\Delta E_{kin}$  will be 0.01%.

The detector may correspond to  $\geq 1000$  channels.

# Data analysis

Location

Intensities

Peak shape

## Complexities

1. Inelastic tail may or may not have structure asymptotically constant
2. All peaks sit on a background of high KE peaks.
3. XPS peak shape is a convolution of
  - (a) exciting x-ray line shape
  - (b) satellites of x-rays
  - (c) analyzer line shape
  - (d) non-uniform specimen charging
  - (e) lorentzian life time distribution of the core hole

- (f) doppler broadening in gases
- (g) many electron processes in the final state
- (h) vibrational excitations

No simple function can be used to represent the XPS lineshape.

Deconvolution and peak-fitting

# Photo emission process

$$\Psi_{\text{tot}}^i(N), E_{\text{tot}}^i(N) \rightarrow \Psi_{\text{tot}}^f(N, K), E_{\text{tot}}^f(N, K)$$

$\Psi_{\text{tot}}^f(N, K) \rightarrow K^{\text{th}}$  final state of N electron system.

(involves both the emitter and the photoelectron)

Energy conservation equation.

$$E_{\text{tot}}^i(N) + h\nu = E_{\text{tot}}^f(N, K)$$

k refers to one electron orbital k from which electron emission occurred, in the simplest case. In general it should include all modes of excitation, electronic, vibrational and translational.

In general, it is assumed that the photoelectron is weakly coupled to the (N – 1) electron system so that separation of final state is possible

$$\Psi_{\text{tot}}^i(N), E_{\text{tot}}^i(N) \rightarrow h\nu \Psi_{\text{tot}}^f(N-1, k), E_{\text{tot}}^f(N-1, k) + \phi^f(1) \chi^f(1), E_{\text{kin}}$$

Initial state
Final state ion
Photoelectron

$\phi^f(1)$  is the spatial part and  $\chi^f(1)$  is the spin part.

$\Psi_{\text{tot}}^f(N-1, k)$  and  $\phi^f(1)$  can be combined suitably to yield correct antisymmetry. This can be done with antisymmetrizing operator  $\hat{A}$ .

$$\Psi_{\text{tot}}^f(N, K) = \hat{A} (\phi^f(1) \chi^f(1), \Psi_{\text{tot}}^f(N-1, k))$$

The energy conservation equation then yields

$$E_{\text{tot}}^i(N) + h\nu = E_{\text{tot}}^f(N-1, k) + E_{\text{kin}}$$

The binding energy corresponding to producing the  $\Psi_{\text{tot}}^{\text{f}}(N-1, K)$  state is,

$$E_{\text{b}}^{\text{v}}(K) = E_{\text{tot}}^{\text{(f)}}(N - 1, K) - E_{\text{tot}}^{\text{i}}(N)$$

The photoelectron is referred w.r.t the vacuum level.

Line width  $\rightarrow$  lifetime of initial and final states

Initial lifetimes are large, for a final state life time  $t$  the lorentzian width of the peak is  $\sim \hbar/t = 6.58 \times 10^{-16}/t(\text{s})$  in eV. For life time of  $10^{-18}$ sec this width can be large (initial state lifetime in most cases is high and there is no contribution to line width)

System containing  $N$  electrons with spatial coordinates  $r_1, r_2 \dots r_N$  and spin coordinates  $\sigma_1, \sigma_2, \dots \sigma_N$  and  $p$  nuclei with coordination  $R_1, R_2 \dots R_N$  the total wave function,

$$\Psi_{\text{tot}}(N) = \Psi_{\text{tot}}(r_1, \sigma_1, r_2, \sigma_2 \dots r_N \sigma_N; R_1, R_2 \dots R_N)$$

Nuclear coordinates can be neglected in the resolution scale of electron spectroscopy. In the non-relativistic limit, the Hamiltonian in electrostatic units,

$$\hat{H}_{\text{tot}} = \underbrace{\hbar^2/2m \sum_{i=1}^N \mathcal{Q}_i^2}_{\text{e-kinetic}} - \underbrace{\sum_{i=1}^N \sum_{l=1}^P Z_l e^2/r_{il}}_{\text{e-n attraction}} + \underbrace{\sum_{i=1}^N \sum_{j>i}^N e^2/r_{ij}}_{\text{e-e repulsion}} \\ + \underbrace{\sum_{l=1}^P \sum_{m>l}^P Z_l Z_m e^2/r_{lm}}_{\text{n-n repulsion}} - \underbrace{\hbar^2/2 \sum_{l=1}^P \mathcal{Q}_l^2 / M_l}_{\text{Nuclear kinetic}}$$

$M$  – electron mass,  $Z_l$  charge of  $l^{\text{th}}$  nucleus  $r_{il} = |r_i - R_l|$ ,  $r_{ij} = |r_i - r_j|$

$R_{lm} = |R_l - R_m|$   $M_l$  – mass of  $l^{\text{th}}$  nucleus.

To this relativistic effects may be added by perturbation. Hamiltonian most often added is due to spin-orbit splitting.

$$\hat{H}_{so} = \sum_{i=1}^N \xi(r_i) \hat{l}_i \cdot \hat{S}_i$$

$\xi(r_i)$  is the appropriate function of radial coordinate  $r_i$ ,  $\hat{l}_i$  and  $\hat{S}_i$  are the one electron orbital and spin angular momentum operations.

The total wave function must satisfy the time independent Schrodinger equation,

$$\hat{H}_{tot} \Psi_{tot}(N) = E_{tot}(N) \Psi_{tot}(N)$$

Bohn-oppenheimer approximation permits separation of the total wave function into a product of electronic and nuclear parts.

$\Psi_{tot}(r_1 \dots r_N; R_1 \dots R_p) = \Psi(r_1, \sigma_1 \dots r_N, \sigma_N) \Psi_{nuc}(R_1 \dots R_p)$   
 $\Psi(N)$ , the electronic wave function depends on  $R_1 \dots R_N$  only parametrically through nuclear-nuclear coulombic repulsion.

The electronic Hamiltonian will be  $\hat{H}_{\text{tot}}$  minus the nuclear kinetic term.

$$(\hat{H}_{\text{tot}} + \hbar^2/2 \sum_{l=1}^P \nabla_l^2/m_l) \Psi(N) \equiv \hat{H}(N) \Psi(N) = E(N) \Psi(N)$$

$\hat{H}_{\text{tot}}$  can be include S-O effects. The total energy

$$\begin{aligned} E_{\text{tot}} &= E + E_{\text{nuc}} \\ &= E + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}} + \dots \end{aligned}$$

The quantum number K should represent all

For diatomic harmonic oscillator,

$$E_{\text{vib}} = \hbar \nu_{\text{vib}} (\nu + 1/2)$$

$$\nu_{\text{vib}} = 0, 1, 2, \dots$$

Translational motions of the atom or molecule can influence the energies in two ways.

1. Conservation of linear momentum requires

$$P_{h\nu} + 0 = P^f + P_r$$

$P_{h\nu}$  → Photon momentum  $h\nu/c$  momentum of  $E_i$  taken to be zero.

$P^f$  → photoelectron momentum  $P_r$  recoil momentum of the atom.

Recoil energy of two atom vary as  $E_r = P^2/2m$  and increases with decreasing at. No. For  $Alk_{\alpha}$ , the  $E_r$  value for various elements are, H – 0.9 eV, Li – 0.1 eV, Na – 0.04 eV, K – 0.02 eV Rb – 0.01 eV.

Therefore, this is important only in H, as far as XPS is concerned XPS instrumental line widths are 0.4 – 0.9 eV. Thus  $E_r$  can be neglected.

2. Doppler broadening can be significant.

Thermal motion of emitters.

If the atom of mass  $M$  moves with a centre of mass velocity  $V$ , the electron kinetic energy

$$E_{\text{kin}}'' = 1/2m|v - V|^2$$

The measured  $E_{\text{kin}} = 1/2mv^2$  will be different from this. The difference depends on thermal velocities. If the mean kinetic energy measured is  $E_{\text{kin}}$ , the Doppler width,  $\Delta E_d$

$$= 0.723 \times 10^{-3} (T \cdot E_{\text{kin}}/M)^{1/2}$$

At room temperature, for XPS energy of 1000 eV, the value of  $\Delta E_d \leq 0.1$  eV for  $M \geq 10$ . Thus it is not significant in comparison with FWHM important in gas phase.

Normally it is a practice to neglect nuclear motion.

The  $N$  and  $N - 1$  electron states represent the various irreducible representations of the point group.

In atoms where spin-orbit splitting is small, the states are specified by  $L$ ,  $S$  and perhaps also  $M_L$  and  $M_S$ .  $M_L$  and  $M_S$  are  $z$  components of  $L$  and  $S$ . For zero spin orbit splitting, energies depend only on  $z$  and  $s$ . and the degeneracies would be  $(2L + 1) (2S + 1)$ . Such states also occur in molecules, but they are seldom used