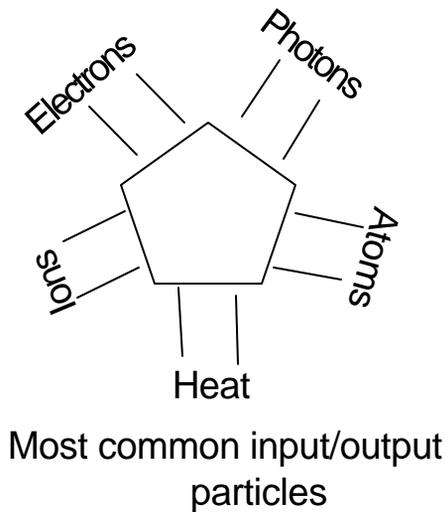


Surface Sensitive Techniques

- Large number of surface sensitive techniques have been developed to study surface properties including structure, Composition, Oxidation states, electronic and mechanical properties of the surface.
- Surface equipment is continually being improved to be able to detect smaller volumes, numbers of atoms as well as higher spatial resolution and energy resolving power.



- Usually either the input or output particle must be surface sensitive.
- Several of these particles have a large scattering cross-section and thus need a vacuum to be able to get to the surface from the source and after interacting with the surface to get from the surface to the detector.
- Vacuum required for techniques for which input/output particles have a large scattering cross-section. Without a vacuum the particles would not be able to travel to the detector without undergoing a collision with gases between sample and the detector.

Some Surface Sensitive Techniques

<i>Acronym</i>	<i>Name</i>	<i>Surface Information</i>
	Adsorption or chemisorption	Surface area; # adsorption sites
AES	Auger Electron Spectroscopy	Composition
AFM	Atomic Force Microscopy	Surface structure
ARUPS	Angle-resolved ultraviolet photoemission spec.	Valence band information, bonding
ARXPS	Angle-resolved X-ray photoelectron spectroscopy.	Surface Structure
ELS or EELS	Electron energy loss spec.	Electronic structure (functional groups)
ESDIAD or PSD	Electron (photon)-stimulated ion angular distribution.	Bonding Geometry, molecular orientation
FIM	Field ionization microscopy	Surface structure
FTIR	Fourier transform IR	Bonding geometry and strength.
ISS	Ion scattering spec.	Surface structure, composition.
LEED	Low-energy electron diffraction.	Surface structure
SIMS	Secondary ion mass spec.	Surface composition
TPD	Temperature programmed desorption	Composition, heat of adsorption, surface structure.
XPS	X-ray photoelectron spec.	Composition and oxidation state.

X-ray Photoelectron Spectroscopy (XPS)

- Historical
 - 1905 Einstein – Photoelectric effect explained.
 - 1923 Pierre Auger – discovered the effect which is named after him.
 - Prior to WW1 – β -rays were being studied with magnetic sector instruments.
 - 1959 Kai Siegbahn (Sweden) showed that binding energies (BEs) of core-level electrons could be determined. Also observed **chemical shifts**. Chemical shifts were found for many substances which made XPS a very useful tool for determining the chemical environment of a substance.
 - 1962 Turner (England) determined BEs of molecular orbitals. Work done in parallel to Siegbahn's work.

- Absorption of a photon by matter causes annihilation of the photon and transfer of energy to that atom – actually the electrons of the atom; called **photoelectric effect**.

Conservation of energy gives

$$h\nu = E_B + E_K \text{ or } E_B = h\nu - E_K$$

where E_B = binding energy and E_K = kinetic energy of electron

- Kinetic energy actually measured and BE calculated.
- Very low BE gives measure of the population of various molecular orbitals. Low energy photons needed
- Photon energy must be greater than BE;
- Greatest intensities obtained when photon energy is fairly close to BEs.
- He UV source most commonly used.
 - Narrow line width makes it possible to access individual orbitals (gas phase, natural line widths few hundredths to a few tenths of eV). Solid state line widths are broader.

Ultraviolet Photoelectron Spectroscopy (UPS)

- Greatest cross-section for ionization observed when photon energy is similar to orbital energy.
- MOs (valence band) observed with conventional photon sources but are very weak since the photon energy is much larger than the orbital energy.
- Rotational and vibrational effects on the spectra observed in gas phase when high resolution photon sources used.

BINDING ENERGIES

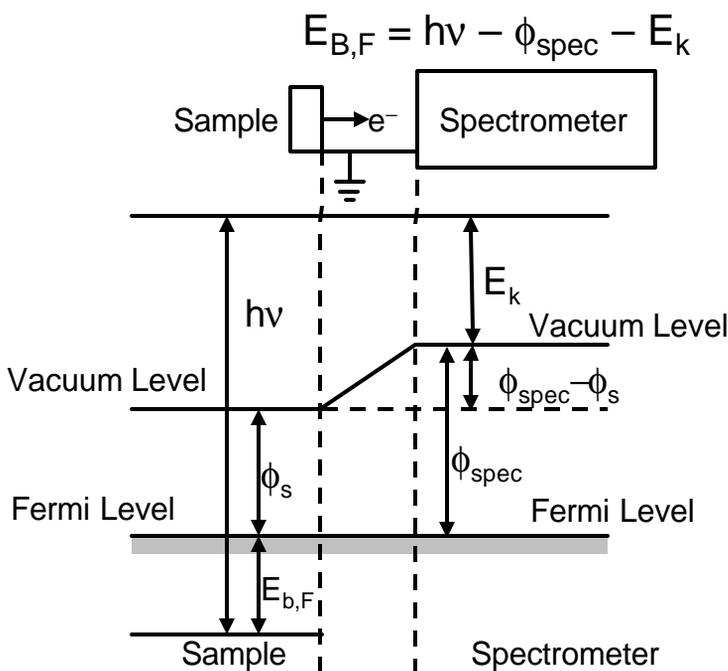
- All electrons with $BE < h\nu - \phi$, where ϕ = work function, are ejected upon irradiation with photons.
- Theoretical Ionization Probability for an orbital defined as probability per unit time for excitation from initial state to final state and is obtained from the wave functions.
- Relative cross-section is function of energy as well as incident photon angle as well as the direction of photoelectron detection.
- Plots of normalized cross-section for 3s/3d and 3p/3d orbitals vs photon energy agrees with experiment.
 - Higher energies 3s and 3p dominate;
 - Lower energies 3d dominates.
- Scofield using relativistic Hartree – Fock Slater wave functions, unrelaxed in final state, calculated cross – sections for elements from $Z = 2 - 103$ at energies of 1254 and 1487.
 - Unrelaxed wave functions are about 20% higher than experimental values.
- Solids more commonly studied than gases, because of their technological importance; e.g. microelectronics, catalysis, corrosion.
- Spectra from solids tend to be somewhat broader than those of gases.
- Unique fingerprint of peaks obtained when the spectrum scanned over wide BE range.
- Auger peaks also observed in XPS spectrum, but changing source causes a relative shift in Auger peaks.

Information Obtained from XPS

- Spectra are a plot of detected electron current (Intensity) vs KE (plotted as BE).
- Peaks occur at characteristic BEs.
- Survey scan gives information about the elements present; it is a plot of intensity over a wide BEs at low instrumental resolution.
- Narrow scans at high instrumental resolution are often used for
 - more quantitative estimate of the composition (from peak areas)
 - Chemical states of the different elements on the surface.
 - Relative intensity measurements can provide information about the thickness of an overlayer.

Extra Atomic Relaxation

- Binding Energies of Solids are not what gas phase measurements indicate they should be, because
 - Extra atomic relaxation, ≈ 10 eV; interaction of extra atomic screening electrons.
 - Different referencing point. Gas referenced to Vacuum level; solid reference to Fermi level:



Binding Energy Measurements

- Fermi Level = highest populated molecular orbital in metal (HOMO)
- Recall metals are large molecules with HOMO and LUMO very close to each other.
- Some electrons have BE very close to 0 eV, causing the intensity to be something other than zero at that point. Half-way point considered Fermi level.
- Semi-conductors will have a band gap since there is an energy separation between HOMO and LUMO.

Work Function

- Work function, ϕ , = amount of work required to remove the electron from the Fermi level to the Vacuum level.
- Metals are in close contact with the instrument (sample is grounded to the instrument).
- Electron gets back to the sample from the instrument; thus work function of instrument must be included in the calculation of the BE.
- Because metals are in close contact with the instrument the Fermi levels are pinned together and the BE is measured KE (used to calculate the BE) is referenced to the instrument Vacuum level.
 - Gold is often used as a BE calibrant (instrument calibration) and the Au $4f_{7/2}$ line occurs at 83.8 eV.

KOOPMAN'S THEOREM (theoretical estimates of BE)

- Self-consistent field (SCF) calculations used to calculate “orbital energies” of atomic core-levels.
- The orbital energy, $\epsilon(i)$ is approximately equal to the BE of electron i ; i.e. $E_B(i) \approx \epsilon(i)$.
- Assumes that all of the other electrons remain “frozen” orbitals; their energy does not change during the ionization process (***Koopman's Theorem***).
- Koopman's theorem not correct because no allowance for the relaxation of passive orbitals toward the positive hole (*Intra-atomic Relaxation*).
- Relaxation increases screening of the core hole towards the exiting electron and gives it a higher KE as it leaves than would be predicted.

Theoretical Estimation of BE (cont)

- SCF calculation results improved by Bagus when he showed that they could be carried out directly on the final “hole” state yielding total energies of these states.
- BEs were calculated by subtraction of initial state (un-ionized atom) and the final state. E.g. consider an atom which loses an electron from the i th orbital of an atom with an atomic # of Z , Let $E_B(Z,i)$ = measured BE, then

$$E_B(Z,i) = E(Z^+,i) - E(Z)$$

where $E(Z^+,i)$ = final energy after ionization and relaxation
and $E(Z)$ = energy of the initial state before ionization

- Calculation of the “hole state” was a difficult enough task that it was not feasible to use this method as routinely to determine binding energies of the orbitals of very many elements.
- Method of “Equivalent Cores”:
 - Assumes that the electron from a inner shell almost completely shields an outer electron from 1 unit of charge.
 - Outer orbital in an atom of nuclear charge Ze with a hole in an inner shell will then be closely approximated by the corresponding outer orbital in the ground state of the next element ($Z+1$).
 - Relaxation energies for the Noble gases estimated using orbital energies from SCF calculation:

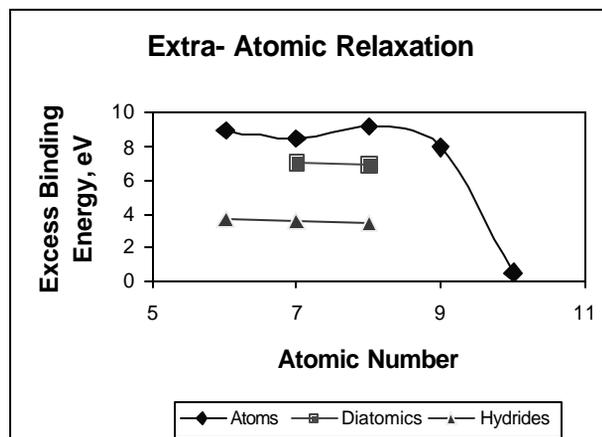
Gas	E_R	Hole, E_B^H	Eq. Core, E_B^R	Exp't, E_B
Ne 1s	25.6	870	868.4	870.2
Ar 1s	37	3209	3203	3205.9
Kr 2p _{1/2}	32	1735	1730	1730.9
Xe 2s	44	5472	5462	5453.2

“Equivalent Cores” cont.

- Conclusions:
 - Close agreement between E_B^H and E_B^R especially for heavy atoms.
 - Agreement between these shows that “equivalent core” method is a good alternative to determine relaxation energies.
 - Even with these predictions discrepancy between predicted and observed BE is greater than the chemical shifts.

Extra-atomic Relaxation

- Core – level BEs measured in the gas phase differ by ≈ 10 eV from the measured BEs for the same atom in the solid phase.
 - E.g. carbon has an estimated gas phase C 1s BE of 299 eV (theoretical and experimental estimates). Remember theoretical values were within a few eV of the experimental value. Solid carbon: C 1s BE = 284 eV; add work function correction to get 288 eV relative to the vacuum level. A difference of about 11 eV.



Extra-Atomic Relaxation

- The excess BE is the discrepancy between estimated and experimental values. Excess BE shows
 - points out similarities between atoms and more complicated systems.
 - the magnitude of the discrepancy is related to the chemical structure since discrepancy was not the same for different structures.
- Discrepancies are attributed to ***extra – atomic relaxation*** accompanying photoemission.
- ***Intra-atomic relaxation***: relaxation in a free atom (also called adiabatic relaxation) estimated by assuming “outward diffusion” of a quantity of charge of value $+e$, that has been introduced near the center of the atom, to reduce the energy of the system.
- Polyatomic systems:
 - Charge distribution in CH_4^+ from emission of C 1s electron approximated by a neutral atom and charges of $+e/4$ on each H.
 - In a diatomic molecule such as CO^+ , each atom has a charge of about $+e/2$ following ejection of a C 1s electron.
 - Hydrides: positive charge migrates to the hydrogen ligands.
 - Solid sample = charge migrates farther than the nearest ligand during photoemission; net effect = core-electron BE is even further reduced.
 - Molecules discussed so far are the simplest since the host atoms are neutral (or nearly so) since very little difference in electronegativities between atoms in the compound.

Extra-atomic Relaxation cont.

- From earlier figure and discussion we note that
 $E_B(\text{free atom}) > E_B(\text{diatomic}) > E_B(\text{hydride}) > E_B(\text{solid})$
- Conclusions:
 - Extra-atomic relaxation very important in determining the exact binding energy of electrons in solid networks of atoms; “extra-molecular relaxation” due to polarization of neighboring molecules in the solid when comparing BE of molecules in the solid with those in the gas.
 - When adsorbing gas molecules on a surface, the substrate is different from the surface atoms; relaxation would be expected to have a large affect on the BEs of atoms on the surface; might give information about surface chemical bond.
- Lifetime of the Final State: *Heisenberg uncertainty principle* gives the lifetime of the final state:

$$\Delta E = \frac{\hbar}{\Delta t}$$

where ΔE = width of the photoelectron line and Δt = mean lifetime of the final state and $h = 6.58 \times 10^{-16} \text{ eV*s}$

–*Valence shell*: natural line widths are a few meV; assume 0.010 eV; $\Delta t = (6.58 \times 10^{-16} \text{ eV*s}) / 0.010 \text{ eV} \approx 10^{-13} \text{ s}$

–*Core shell*: natural line width ranges from 1-5 eV which means that $\Delta t = (6.58 \times 10^{-16} \text{ eV*s}) / 2 \text{ eV} \approx 10^{-16} \text{ s}$

–Thus, lifetime of MO states is roughly the same order of magnitude as molecular processes; lifetime of atomic orbitals is quite a bit shorter.

Spin – Orbit Splitting

- Each electron is spinning on its axis and generates its own magnetic field.
- Each electron also has an orbital angular momentum and is a current circulating around the atom; this gives rise to a magnetic field that is proportional to the angular momentum.
- These will interact with each in a process referred to as **spin – orbit interaction** and will produce two subshells.
 - Let j = quantum # describing the two states, then $j = l + s$ where $s = \pm \frac{1}{2}$, and l = angular momentum quantum #
 - All orbitals exhibit spin – orbit splitting except the s orbital.
 - Occupancy of each subshell is $2j + 1$
 - Two states have slightly different energies, which is usually detectable in the XPS spectrum.

E.g. f spectra: $l = 3$; $j = 3 + \frac{1}{2} = \frac{7}{2}$ and $j = 3 - \frac{1}{2} = \frac{5}{2}$; occupancy would be: $2 \cdot \frac{5}{2} + 1 = 6$ and $2(\frac{7}{2}) + 1 = 8$. Thus intensity ratio expected to be $\frac{8}{6} = \frac{4}{3}$

Orbital	l	j level	occupancy	Intensity
p	1	$\frac{1}{2}$	2	1
		$\frac{3}{2}$	4	2
d	2	$\frac{3}{2}$	4	2
		$\frac{5}{2}$	6	3
f	3	$\frac{5}{2}$	6	3
		$\frac{7}{2}$	8	4

- Experimental results qualitatively and quantitatively confirm the number and relative areas of the peaks.

Spin-Orbit (LS) Splitting cont.

- LS splitting increases with Z (actually Z^5)

LS Splitting for the Inert Gases						
Shell	Ar		Kr		Xe	
	$\Delta\varepsilon(\text{calc})$	$\Delta\varepsilon(\text{exp})$	$\Delta\varepsilon(\text{calc})$	$\Delta\varepsilon(\text{exp})$	$\Delta\varepsilon(\text{calc})$	$\Delta\varepsilon(\text{exp})$
2p	2.23	2.03	55.1	52.5	329.6	319.9
3p	0.17	0.18	8.2	7.8	63.2	61.5

Multiplet Splitting, Cont.

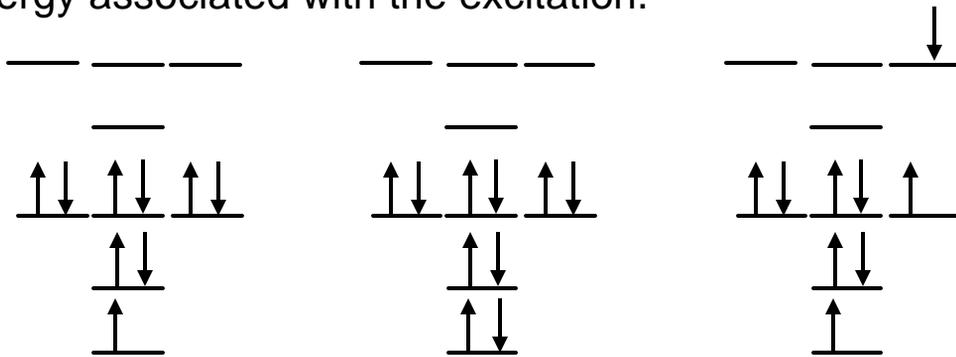
- XPS spectra of the 3s electrons from Cr, Mn, Fe show the presence of multiplet splitting. The second peak must be due to the interactions occurring during ionization and are large enough to observe as separate peaks.
- Multiplet splitting is an indication of the local environment. The intensity of peaks associated with these different interactions depends upon the ligand attached to the metal. Notice the second spectrum for iron which contains no significant indication of a second peak.
- Intensity and shift is then determined by:
 - Extent of decoupling in d orbital of the interaction due to strong ligand bonding.
 - Extent that d electrons are localized around the metal ion.
- Recall Fe 3s spectrum from $\text{K}_3\text{Fe}(\text{CN})_6$ shows no second peak. Magnetic susceptibility measurements of the $\text{K}_3\text{Fe}(\text{CN})_6$ compound indicate all unpaired spins in the d orbitals of iron are couple to the ligand; the electrons are so localized that no splitting occurs.
- In general, greater covalency between metal and ligand, means smaller splitting.
 - splitting is greater for O than S and $\text{F} > \text{Cl} > \text{Br} > \text{I}$.
- For a given ligand the experimental splitting correlates well with the number of unpaired spins in the metal. Fig. 5.26 shows that the greatest splitting occurs when there are the largest number of unpaired spins and least splitting when there are the least number.

Shake-up and Shake – off

- Shake – up: peaks resulting from electron's loss of energy as it leaves during the ionization process with associated promotion of valence band electrons to either an excited state or continuum.
 - Transition of a valence electron to a higher energy state causes the leaving electron to lose energy. Peaks associated with this loss observed on the high BE (lower KE) side of the main peak. It appears as a small usually broad peak.
 - Changes in the screening of the outer electrons during the emission of one of the core electrons (relaxation energy) causes the electrons to be excited.
 - Excitation of an outer occurs with only a change in the principal quantum number ($\Delta l = \Delta s = \Delta j = 0$).
 - Shake – up peaks have significant intensity when unpaired electrons in the 3d or 4f levels and are usually associated with the formation of a compound.
 - E.g. Cu in Cu_2O has a filled d subshell and CuO an unfilled shell in this compound. Shake –up observed for CuO, but not for Cu_2O . The existence of shake-up can be used to assign chemical environment.
 - Cu compounds: presence of shake-up in Cu spectrum was related to the geometry of the ligands around the metal. Square planar = no shake-up.
 - Intensity of shake-up peak with open d orbitals is approximately 30% of the main peak. When there are no open d orbitals intensities of shake –up peaks are greatly reduced.

Shake-up, cont.

- Consider the ionization of Mg: normal electron configuration is $1s^2 2s^2 2p^6 3s^2$; after ionization and interaction with electrons in the atom, possible electron configurations from this monopole excitation are:
 - $1s^1 2s^2 2p^5 3s^2 3p$,
 - $1s^1 2s^2 2p^5 3s^2 4p$ (energy separation from the simple ionized state is 42.4 eV)
 - $1s^1 2s^2 2p^5 3s^2 5p$ (energy separation from the simple ionized state is 44.4 eV)
- Since there is a discrete energy associated with an electronic transition, it is possible to calculate the shift in energy associated with the excitation.



Normal Ionization, Ne⁺*

Ground state

Shake-up, Ne⁺⁺

- The separation of the 2p and 3p orbitals is 41.0 eV.
- Normal Ionization: $E_k = h\nu - E(1s)$
 $= 1486.6 - 867.0$
 $= 620.0 \text{ eV}$
- Shake – up:
 $E_k = h\nu - E(1s) - [E(2p) - E(3p)]$
 $= 1486.6 - 867.0 - 41.0$
 $= 579.0 \text{ eV}$
- Relative intensities only about 2% of the Ne 1s peak.

Shake-Off and Energy Loss Structures

- **Shake – off**: structure associated with a second ionization.
 - Instead of having a transition to an excited state as discussed earlier, an additional electron can be excited all the way to the vacuum (valence electron).
 - Starts at a discrete energy, but a broad band is observed instead of discrete peaks.
 - Probability of shake-off related to energy level; and is greatest for low Z elements.
- **Energy loss features**: background and plasmons
- **Background**: Electrons emitted from atoms below the first layer must travel to the surface through the surface layer to get to the vacuum and be eventually measured by the detector.
 - Some electrons traveling through this region undergo a collision with an atom and transfer some of the energy to the atom.
$$A + h\nu \rightarrow A^{*+} + e^{-}(E_1) \text{ (photoejection)}$$
$$A + e^{-}(E_1) \rightarrow A^{*} + e^{-}(E_2) \text{ (collision)}$$
$$E_2 > E_1 \text{ (kinetic energy; on BE scale intensity appears on high BE side of the main peak).}$$
 - Gas phase: process is pressure dependent.
 - Energy loss structures can interfere with the interpretation of XPS results, since they decrease S/N ratio.
- **Plasmon loss features**: characteristic energy losses in metals.
 - Electron traveling through solid excites one of the collective modes of oscillation of the sea of conduction electrons.
 - Oscillations of sea of electrons have characteristic frequencies.
 - Excitation to a given frequency requires a characteristic loss of energy from the exiting electron.
 - Plasmon features observed in both XPS and AES.
 - Energy losses are directly related to the characteristic IR frequencies; **EELS** (electron energy loss spectroscopy) surface scientist' version of IR!

Plasmons and Satellites peaks

- Plasmon cross-section decreases with increasing energy according to $\sigma \propto E^{1/2}$
- Bulk plasmons (those coming from beneath the top layer) as well as Surface Plasmons are observed:

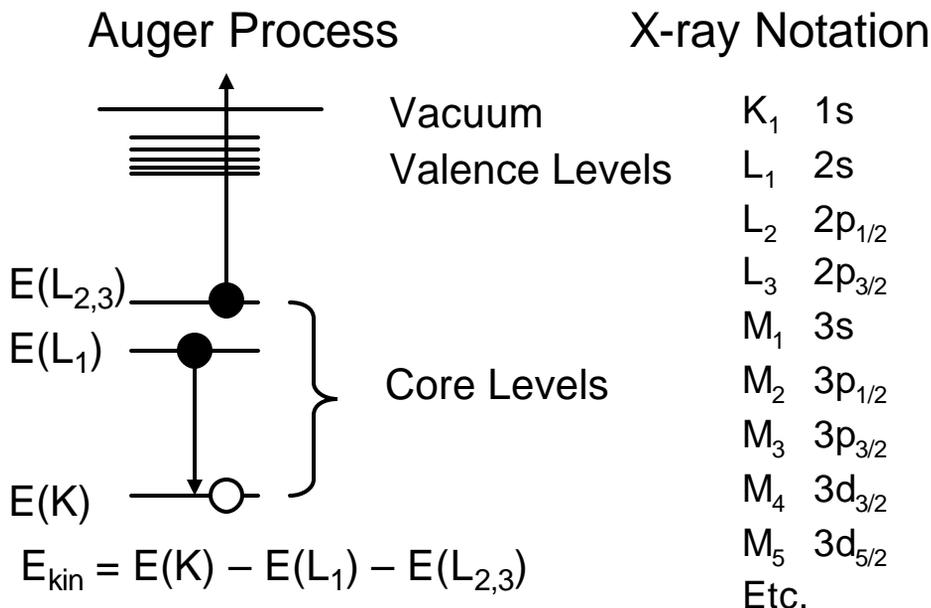
$$E_{sp} = E_{bp}/(\epsilon + 1)^{1/2}$$

where ϵ = the dielectric constant.

- Energy loss from the bulk is generally greater than that from the surface. In spectrum surface plasmons are closer to the original peak than bulk plasmons (see Fig.).
- X-ray satellites: X-rays (Al $K\alpha$ and Mg $K\alpha$) have radiation at a characteristic energy, but have other photons too. The narrow band is of most interest to us.
 - Others at lower energy (and intensity) also observed and can interfere with the interpretation of observed spectra. $K\alpha_{3,4}$ observed at about 10 eV lower photon energy at about 10% of the intensity of the $K\alpha_{1,2}$ photons.
 - Observed spectra contain peaks associated with both sources of photons as well as peaks from the less intense photons.

Auger Peaks

- Auger Electron Spectroscopy (AES) sister technique to XPS, used to study surface composition, and will be discussed in more detail later.
- Auger Peaks are also observed in XPS spectra; the Auger process will be discussed here first so that we know the source of these peaks.
- Auger electrons emitted from the surface atoms at the same time as photoelectrons;
- they are the result of relaxation of electrons after a hole is created (in this case from photons);
- Hole creation can be by any process.
- Description of Auger peaks given by the three orbitals involved in the process. X-ray notation used.
- XAES Peaks differentiated from XPS peaks by
 - Width: Auger peaks tend to be broader.
 - K.E. is constant no matter what the source is; K.E. of photoelectrons varies with photon source.



Chemical Shifts

- Chemical shift has made this technique one of the pre-eminent surface sensitive techniques since it provides information about the chemical environment of the surface.
- Chemical shift is a small change in the BE of either a core or valence electron that is a result of
 - Molecular environment
 - Formal oxidation differences
 - Differences in lattice sites
 - Anything that changes the electron density around the atom emitting the electron.
- Chemical shifts are often quite easy to measure and makes it possible to distinguish between the different chemical environments.
- Shifts can be predicted from a know of the total wave functions for the neutral and singly ionized species.
- Shift for orbital n/l between free atom A and the molecular state would be:
$$\Delta E_{nl} = E_{nl}(M) - E_{nl}(A) = [T^*_{nl}(M) - T(M)] - [T^*_{nl}(A) - T(A)]$$
where T^*_{nl} and T are the total energies for the ionized and neutral states respectively.
- Rigorous determination of these states difficult, but using Koopmann's theorem energies of the orbitals for molecular and atomic core electrons can be calculated using Hartree – Fock calculations; differences provide an estimate of the chemical shift:

$$-\Delta E_{nl} \approx \varepsilon_{nl}(M) - \varepsilon_{nl}(A)$$

Chemical Shifts, cont.

- Calculations should also account for relaxation, which as discussed earlier is result of contraction of orbital radii during emission.

$$-\Delta E_{nl} \approx \varepsilon_{nl}(M) - \varepsilon_{nl}(A) + \Delta R_{nl,in} + \Delta R_{nl,ex}$$

where $\Delta R_{nl,in}$ and $\Delta R_{nl,ex}$ are changes in the intraatomic and extraatomic relaxation energies.

- **Charge potential model:** method of estimating chemical shift by ignoring relaxation effects and assuming the atom behaves as a hollow sphere of radius r over the surface of which is distributed a charge q due to valence electrons; inside the sphere the charge is q/r .
 - All core electrons would then have the same chemical shift;
 - BE of an electron in a core level l of an atom A surrounded by other atoms B given by:

$$\Delta E_A(i) = I + k_l \Delta q_A + \Delta \sum_B q_B / 4\pi \epsilon r_{AB}$$

- Reasonable agreement between calculated and measured shifts for a series of gases are observed as seen in Fig. 10.22 (Rivière).
- **Partial charge chemical shift:** XPS BEs are a measure of the relative electron density around the atom which is affected by its nearest neighbors.

- Electron density around the atom related to the Pauling (or Sanderson) electronegativity
- Charge on the atom calculated from

$$q = \sum_i I + Q$$

where Q is the formal charge on the atom and the summation is the partial ionic character of each bond.

- Partial ionic contribution determined by considering the difference between electronegativities of the two species:

$$I = \frac{c_A - c_B}{|c_A - c_B|} \cdot \left[1 - e^{-0.25(c_A - c_B)^2} \right]$$

where χ_B and χ_A are electronegativities for atoms studied and its neighbor.

Estimation of Chemical Shift, cont 2

- ***Ab Initio Calculation of Chemical Shift:*** Charge density calculated using wave functions from semiempirical methods such as CNDO, INDO, MINDO programs.
 - Linear variations of BE with calculated charge have been observed (see Fig. 5.3, Carlson).
 - Many studies have appeared in the literature relating small BE changes with changes in the chemical environment of the surface.

Valence Band spectra

- Valence band spectra can be used to tell details about the bonding of the atoms; Peaks are
 - broad in the solid phase and badly overlap each other;
 - Weak in conventional XPS instruments due to the low cross-section of excitation associated with a higher energy source (Al $K\alpha$ and Mg $K\alpha$).
 - Some modern instruments have very intense X-ray sources making it more feasible to acquire valence band spectra.
- In principle spectra should be best for determining the chemical environment of the atoms involved in bonding, but broadness of peaks limit the usefulness.
- $X\alpha$ calculations of model compounds have facilitated the interpretation by looking where peaks for certain types of groups would exist.
- Subtle differences in the valence band structure are often used to distinguish different chemical environments even when shifts not observed in core-level spectra.
- Temperature dependence spectra can show the transition from insulating to conducting, because of a decrease in the gap between the Fermi edge and the first peak.

BE Referencing

- Fermi level of metals used as reference for metals and vacuum level for gases; for metals we have:

$$E_B = h\nu - E_k - \phi.$$

- Fermi level only works for solids having a well-defined Fermi level and are in good electrical contact with the spectrometer.
- Many (most) samples are non-conducting; band gap exists; no well defined band gap.
- The instrument work function can be calibrated using a metal, then BEs from spectra of a sample that is not very conducting, but is in good electrical contact with the instrument can be obtained.
- Non-conducting samples which are thick enough not to be in good electrical contact will develop a steady-state positive charge as a result of resistance of the sample (like a capacitor).
- Monochromatic X-ray sources have larger amounts of charging; polychromatic x-ray sources have a filter to remove some of the background, it produces a stream of low energy electrons which at least partially neutralize any charging (Fig. A21).
- Solutions to surface charging:
 - **Low energy flood gun-** surface is flooded with low energy electrons (<6 eV) from an external source (hot filament).
 - Charge can be partially neutralized or even made negative on the surface depending upon the current from the flood gun.
 - Difficult to determine exactly correct amount of current to flood the surface.
 - *Differential charging* can be observed because of inhomogeneous areas on the surface (see fig. from PHI handbook).

Charging Correction or Elimination

- Physical mixtures- finely ground particles of a reference material mixed with the compound to be analyzed. Surface assumed to be in intimate contact with the reference material.
 - BE of reference material provides measure of the shift on the sample. BE calculated from

$$E_B = E'_B - C$$

where C = static charge; E_B = correct BE and E'_B = observed BE

- Variations in particle size make this method difficult to use; LiF, K salts, Pb_3O_4 , MoO_3 and Au have been used.
- Differential charging often a problem with this reference.
- Internal Standards: BE of a group in the material that is part of the system being studied used as a BE reference. Extensively used in polymer systems as well as catalysts.
- Implanted noble gas ions: implantation of inert gases at relatively low doses and XPS analysis produces spectra from the inert gas in the matrix which can allow the determination of C, but relaxation effects in different surfaces makes this technique of limited value.
- Deposited surface layers: intentional deposition of a reference material such as an organic material or a metal ensures electrical contact with the surface. Reference material at same potential as rest of surface.
 - Knowledge of the correct BE of the reference material leads to C.
 - Chemical interaction of the reference material can change the BE expected and C will be incorrectly determined.
 - Thickness of film important so that extra-atomic relaxation won't be a problem. BEs of reference material on different surfaces should be the same.
 - Nano particles (e.g. 20 nm Au particles) have been deposited from a suspension.

Referencing: Adventitious Carbon and Auger Parameter

- Adventitious Carbon: Any sample treated *ex situ* from the analysis system will have a small amount of carbon containing layer deposited from the atmosphere prior to sample introduction into the instrument.
 - This carbon is in intimate contact with the surface; many studies have shown that the C 1s for this contaminant occurs at a consistent value of 284.6 eV.
 - BE of this contaminant determined on conducting metal surfaces, which are referenced to Fermi level.
 - Contaminant not always well defined so that the source sometimes from different types of carbon.
 - E.g. preparation of the surface *in situ* (under UHV conditions) main contaminant would be CO or CO₂, which are major vacuum impurities at that pressure, and not hydrocarbon.
- Auger Parameter (AP): Wagner proposed the AP method of determining the chemical state in spite of an charging.

$$\begin{aligned}\alpha &= E_k(\text{jkl}) - E_k(i) \\ &= E_k(\text{jkl}) + E_k(i) - h\nu.\end{aligned}$$

where $E_k(\text{jkl})$ = kinetic energy of the Auger transition jkl and $E_k(i)$ is the kinetic energy from atomic level i.

- This separation between Auger and photoelectrons peaks is sensitive to chemical state and reduces the influence of charging on the interpretation.
- Modified AP parameter sometimes used instead:
$$\alpha' = h\nu + \alpha = E_k(\text{jkl}) + E_B(i)$$
- Eliminates needs for accurate BE energy measurement, but accurate shifts between Auger and photoelectron peaks necessary.
- AP plots have been tabulated to determine chemical states of uncharacterized surfaces.

Auger Parameter, cont.

- Auger parameter (AP) introduced as an empirical way of determining the Chemical state, but AP has been shown to be related to extra-atomic relaxation with a core-hole. Relaxation energy given by

$$R_{ea} = \frac{(1 - \epsilon_o^{-1})q_o^2}{2r_o} \quad 1$$

where ϵ_o = static dielectric constant; r_o = effective screening distance; q_o = point charge.

- This equation indicates relaxation energy related to the polarizability of the material.
- Polarizability larger with 2 hole final state. Auger chemical shifts greater than XPS shifts, but Auger peaks too broad to be used by themselves for chemical state determination.
- Chemical shift between BEs of two chemical environments can be expressed as: $\Delta E_B(i) = -\Delta\epsilon(i) - \Delta R_{ea}(i)$ where ϵ is orbital energy and ΔR_{ea} is the extra-atomic relaxation energy for creation of the core hole.
- Assume that changes in orbital energy is independent upon orbit; leads to $\Delta\epsilon(j) = \Delta\epsilon(k) = \Delta\epsilon(l)$.
- Kinetic energy change is for a core-core-core peaks would be: $\Delta E_k(jkl) = \Delta\epsilon(j) - \Delta R_{ea}(j) - \Delta R_{ea}(kl)$ where $\Delta R_{ea}(kl)$ = relaxation energy from second ionization.
- After second ionization charge is +2 instead of +1; squared dependence of relaxation energy with charge (eq. 1) leads to

$$\Delta R_{ea}(kl) = 4\Delta R_{ea}(j) \text{ and } \Delta E_k(jkl) = \Delta\epsilon(j) + 3\Delta R_{ea}(j)$$
- Shift in modified AP would be: $\Delta\alpha' = \Delta E_B(j) + \Delta E_k(jkl) = \Delta E_k(jkl) - \Delta E_k(j) = \Delta\epsilon(j) + 3\Delta R_{ea}(j) - (\Delta\epsilon(j) + \Delta R_{ea}(j)) = 2\Delta R_{ea}(j)$.

$$\Delta\alpha' = 2\Delta R_{ea}(j) \quad 2$$
- This relationships (eq 2) allows us to determine the change in relaxation energy between two compounds, but assumption that the shifts of all levels is same not always true.

Auger Electron Spectroscopy, AES

- Recall in AES, an electron fills an empty core hole and emits a second electron which has an energy related to the energy differences of the three orbitals involved.
- What created the first core-hole is not important; electrons usually used, since larger electron fluxes possible than X-ray fluxes.
- Emission curve after electron excitation shows large background with very little useful structure (Fig. 3.2, Briggs).
- Electrons elastically scattered by single crystals; basis of Low Energy Electron Diffraction, LEED.
- Plasmon losses observed at lower energies than main Auger peaks;
 - Contain information on surface bonding; exactly analogous to IR and basis of Electron Energy Loss Spectroscopy, EELS.
- Intense peak at 10-50 eV from secondary electrons; result of charge migration from core electrons to valence.
- XAES peaks “Gaussian” peak shape; Electron excited AES spectra acquire in derivative mode to remove large background (Fig. 3.3, Briggs).
- Because of the energy mismatch between the first and second orbital, we have described the emission of electrons to release the excess energy; photon can be emitted instead (Fig. 3.5, Briggs).
 - Auger emission greatest for light elements and decreases with heavier elements \Rightarrow AES is very sensitive to low Z elements.

AES – Energies, Qual and Chem Analysis

- Energy of transition given by $E_{ABC}(Z) = E_A(Z) - E_B(Z) - E^*_C(Z)$
 - Energies of B,C are difficult to determine because of relaxation effects.
- Solution:
$$E_{ABC}(Z) = E_A(Z) - \frac{1}{2}[E_B(Z) + E_B(Z+1)] - \frac{1}{2}[E_C(Z) + E_C(Z+1)]$$
- Energies of Auger transitions have been compiled and are useful for identifying the element.
- Elemental Analysis: Both AES and XPS detect elements on the surface.
 - Kinetic energies of electrons from the same transitions are very different making it easy to distinguish between them (Fig. 4.4, Briggs).
 - Presence of several Auger peaks in a “survey scan” make it possible to identify all elements (except H, He: 3 energy levels needed) from its “fingerprint” (Fig. 4.5, Briggs).
- Chemical Analysis: AES is generally not used for analysis of chemical states.
 - Broad peaks compared to the chemical shifts make it of limited value.
 - Fine structure of spectra is often result of chemical effects and is of value in determining chemical environment. Especially true when valence electrons involved in the transition (e.g. C KVV).
 - Changes in line shape make it possible to distinguish between carbide and graphite (Fig. 3.11, Briggs).
 - Integral form of spectra show more dramatic effects. B. Rye demonstrated many differences in C KVV spectra of carbon containing compounds (3.12, Briggs). Showed can determine hybridization (i.e. sp , sp^2 , sp^3).

AES – Diffraction Features

- As stated earlier, one can observe diffraction peaks with a well ordered surface.
 - Occurs when electron energy is equal to energy required to satisfy Bragg equation.
 - Constructive interference enhances signal that energy compared with other energies and one observed a peak as a result (Fig. 3.18, Briggs). Peak may not be due to an Auger transition.

Surface Sensitivity

- Elemental and chemical state ID are useful capabilities of AES and XPS; often used to determine composition of homogeneous mixtures and compounds.
- Surface sensitivity makes these very valuable techniques.
- Depth from which signal arises is related to the attenuation length, λ , of the electrons in a solid. As with solutions a linear decrease in signal observed as it passes through a solid.
- Leads to an exponential variation in signal vs depth. λ is distance an electron travels before undergoing a collision.
- Attenuation length related to matrix and energy of electron.
 - Tables giving attenuation lengths in various matrices (elements, inorganic and organic compounds) have been compiled (Fig. 2.7, Rivière).
 - Attenuation lengths can be obtained from the appropriate table or an empirical relationship relating electron energy to the attenuation length.
 - Most electrons have energy in the range of 20-1000 eV which means the signal comes from the top 2-10 monolayers.
- Escape ($\lambda \sin \theta$) sometimes used to describe surface sensitivity, but has an angular dependence. Variation in angle of detection changes escape depth.
- 95% of signal comes from a depth $d = 3 \lambda \sin \theta$ or 6-30 monolayers (Fig. 5.43, Carlson).
- Changing angle from normal to glancing reduces amount of signal coming from bulk since signal must travel a larger distance to escape.

Surface sensitivity, cont.

- Thin film analysis: as long as the film $< 3\lambda$ in thickness, the signal can be analyzed since the signal coming from the substrate and overlayer will vary according to

$$I_s^d = I_s e^{-d/\lambda \sin \theta} \wedge I_o^d = I_o (1 - e^{-d/\lambda \sin \theta})$$

- Overlayer intensity is enhanced with small θ (Fig. 3.36, Briggs) relative to substrate.
- Ratio of signals from substrate and film vary in well-defined way:

$$R = \frac{I_s^d}{I_o^d} = \frac{I_s e^{-d/\lambda \sin \theta}}{I_o (1 - e^{-d/\lambda \sin \theta})}$$

- Quantitative Analysis:**

- XPS Signal intensity from a given subshell is related to several factors that can be reduced to $I_A \propto [A]$ and is given by

$$I_A(X) = I_o r s (h\nu : E_x) T(E_x) D(E_x) L(h\nu : X) \int_0^\infty N_A(z) \exp(-z/\lambda) I_m(E_X) \cos \theta dz$$

Where

I_o = x-ray flux

X = the orbital of element A with energy E_x

σ = cross-section

T = analyzer transmission of electron with energy E_x

ρ = surface roughness factor

D = Efficiency of the detector at given Kinetic energy

N = distribution of atoms A at depth z

λ = inelastic mean free path in the matrix M for atom A

θ = emission angle relative to the surface normal

L = asymmetry parameter for emission from X.

z = depth of A

XPS Intensity

- For a given surface and set of experimental conditions, this equation can be simplified:

$$I_A(X) = K\sigma(h\nu : E_X)L(h\nu : X)\int_0^\infty N_A(z) \exp(-z/\lambda_m(E_X)) \cos\theta dz$$

- Assume we have a uniform distribution of A with depth and defining \bar{N}_A = average atomic density, then

$$I_A(X) = K\sigma L\bar{N}_A\lambda \cos\theta$$

- Linear variation of signal intensity with number density is predicted; number density can be predicted if the following are known:
 - Inelastic mean free path (Fig. 2.7, Seah); can be obtained from known graphs of it vs. Energy, but is a function of matrix.
 - Angle, θ , known; should be able to know this because of instrument configuration.
 - Cross section, σ , calculated for AlK α X-rays by Scofield (Fig. 10.23, Rivière).
 - K and L are difficult to determine.

- Intensities are often normalized to a standard such as F 1s peak.

$$\frac{I_A(X)}{I_F(1s)} = \frac{K}{K} \cdot \frac{s(h\nu : X)}{s(h\nu : 1s)} \cdot \frac{L(h\nu : X)}{L(h\nu : 1s)} \cdot \frac{\bar{N}_A}{\bar{N}_F} \cdot \frac{I_A(E_X)}{I_F(E_{1s})} \cdot \frac{\cos q}{\cos q}$$

- Let $I_F(1s) = 1$ then

$$I_A(X) = \frac{K}{K} \cdot \frac{s(h\nu : X)}{s(h\nu : 1s)} \cdot \frac{L(h\nu : X)}{L(h\nu : 1s)} \cdot \frac{1}{\bar{N}_F} \cdot \frac{I_A(E_X)}{I_F(E_{1s})} \cdot \bar{N}_A$$

- Ratios of remaining parameters in the equation relative to a well characterized F standard and pure A determined.

XPS: Quantitative Analysis, cont.

- These sensitivity factors can be used to determine the relative composition of each component in our spectrum.
- Mole fraction determined using relative sensitivities, S:

$$X_A = \frac{I_A / S_A}{\sum I_x / S_x}$$

- S values are specific to the type of analyzer used; they must be determined for each.
- Does not always include some of the extra peaks (e.g. shake-up peaks).
- Leads to an estimated error of $\pm 5-20\%$ for the surface concentration.

AES Signal Intensity

- Surface concentrations are similarly determined from intensities by AES. Equations are modified to account for the different excitation source and processes involved:

$$I_{XYZ} = I_0 \rho \gamma_{XYZ} \sigma(E_P : E_X) [1 + r_M(E_X : \alpha)] T(E_{XYZ}) D(E_{XYZ}) \int_0^{\infty} N_A(z) \exp(-z/\lambda_M(E_{XYZ})) \cos \theta dz$$

where

ρ = surface roughness factor,

γ_{XYZ} = probability of Auger transition XYZ,

σ = cross-section for ionization of a core level with binding energy E_X by an electron of energy E_p ,

r_M = back-scattering factor,

α = angle of incident that e^- makes to surface normal,

T = transmission factor, and

D = detector efficiency.

N_A = distribution of atoms, A, with depth z.

- Backscattering factor most important in determining the intensity of the signal.

- With constant experimental conditions:

$$I_{XYZ} = K \sigma(E_P : E_X) R \int_0^{\infty} N_A(z) \exp(-z/\lambda_M(E_{XYZ})) \cos \theta dz$$

where $R = (1 + r_m)$

AES Signal

- For a homogeneous distribution, use average atomic density:

$$I_{XYZ} = KsR\bar{N}_A \cos \theta$$

- As with XPS standards are used to calibrate relative sensitivity of each transition; leads to

$$\frac{\bar{N}_A}{\bar{N}_{A,s}} = \frac{I_{XYZ}}{I_{XYZ,s}} \cdot \frac{R_s}{R} \cdot \frac{I_s}{I}$$

- We can define a sensitivity factor:

$$\bar{N}_A = I_{XYZ} S_A$$

where

$$S_A = \frac{\bar{N}_{A,s}}{I_{XYZ,s}} \cdot \frac{R_s}{R} \cdot \frac{I_s}{I}$$

- Mole fractions can then be determined as with XPS
- Sensitivity factors must be determined for the particular analyzer being used.
- Common way of determining composition, but suffers from large errors in absolute composition.

Matrix effects strongly affect λ in XPS and AES spectra:

Elements	$\lambda = 538E^{-2} + 0.41(\alpha E)^{1/2}$ monolayers
Inorganic compounds	$\lambda = 2170E^{-2} + 0.72(\alpha E)^{1/2}$ monolayers
Organic compounds	$\lambda = 49E^{-2} + 0.11(\alpha E)^{1/2}$ monolayers

where a = monolayer thickness

Thin Film Analysis

- Film with a sharp interface of constant composition until the interface can be analyzed using the equations:

$$I_s^d = I_s e^{-d/\lambda \sin \theta} \wedge I_o^d = I_o \left(1 - e^{-d/\lambda \sin \theta} \right)$$

- Film thickness and composition can be derived from our fundamental intensity equations for XPS or AES if one assumes a well-defined composition variation with depth into film (E.g. linear variation in composition with depth).
 - Often more than one solution to the equations.
- **Real Surfaces** have much more complicated structure making impossible to even assume the surface is perfectly flat.
 - Surface roughness plays a large role; consider a surface made up of spherical particles; to determine composition of a uniform film, it is necessary to account for variations in sampling depth depending upon the place for the emission of the electron (Fig. 3, Cross & Dewing, SIA 1(1), 1979, 26-31).
 - Modeling of a surface as a sinusoidal structure has shown estimated thickness very sensitive to emission angle; a two fold overestimation can be observed.