



Electron Spectroscopy

Method	Particle In	Particle Out	Information	Technique
Photoemission	Photon	Electron	Filled core states	XPS
Photoemission	Photon	Electron	Filled valence states	UPS
Inverse photoemission	Electron	Photon	Empty states	IPES
Electron energy loss	Electron	Electron	Electronic & vibrational transitions	EELS, HREELS
Auger	Electron	Electron	Filled states	AES
Absorption / emission*	Photon	Photon	Electronic transitions, filled states	UV-Vis, XRF

* not normally surface sensitive

Photoelectron spectroscopy is based upon a single photon in/electron out process.

The energy of a photon is given by the Einstein relation :

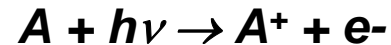
$$E = h \nu$$

where

***h - Planck constant (6.62
x 10⁻³⁴ J s)***

***ν – frequency (Hz) of the
radiation***

The process of photoionization can be considered in several ways : one way is to look at the overall process as follows :



Conservation of energy then requires that :


$$E(A) + h\nu = E(A^+) + E(e^-)$$

Since the electron's energy is present solely as kinetic energy (KE) this can be rearranged to give the following expression for the KE of the photoelectron :

$$KE = h\nu - (E(A^+) - E(A))$$

The final term in brackets, representing the difference in energy between the ionized and neutral atoms, is generally called the binding energy (BE) of the electron - this then leads to the following commonly quoted equation :

$$KE = h\nu - BE$$



Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy).

In XPS the photon is absorbed by an atom in a molecule or solid, leading to ionization and the emission of a core (inner shell) electron. By contrast, in UPS the photon interacts with valence levels of the molecule or solid, leading to ionisation by removal of one of these valence electrons.

The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyser and a photoelectron spectrum can thus be recorded.

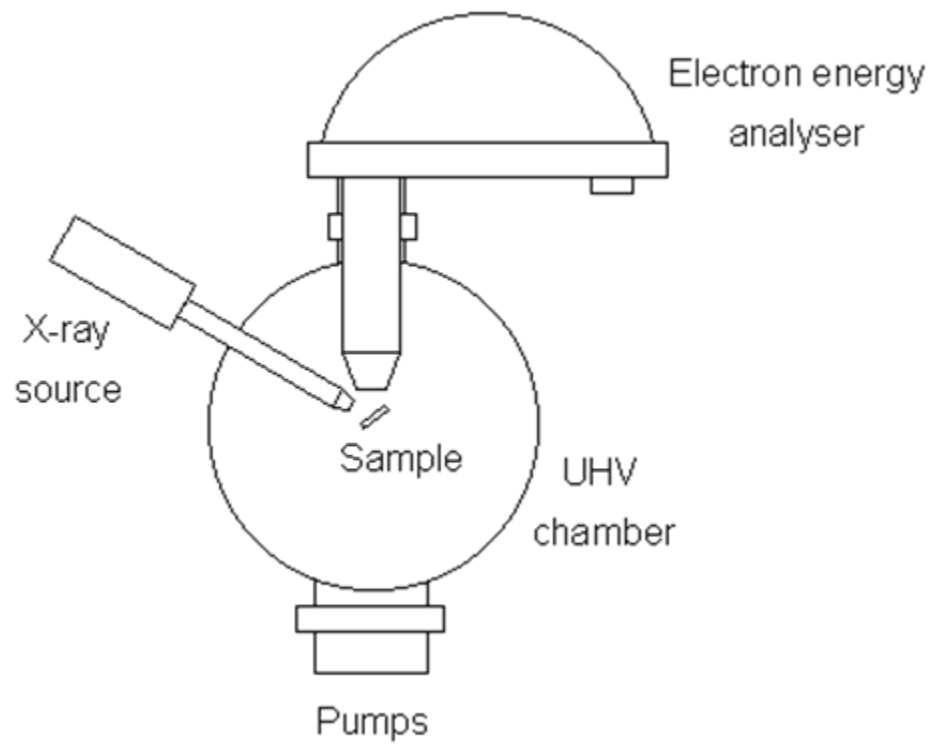
Experimental Details

The basic requirements for a photoemission experiment (XPS or UPS) are:

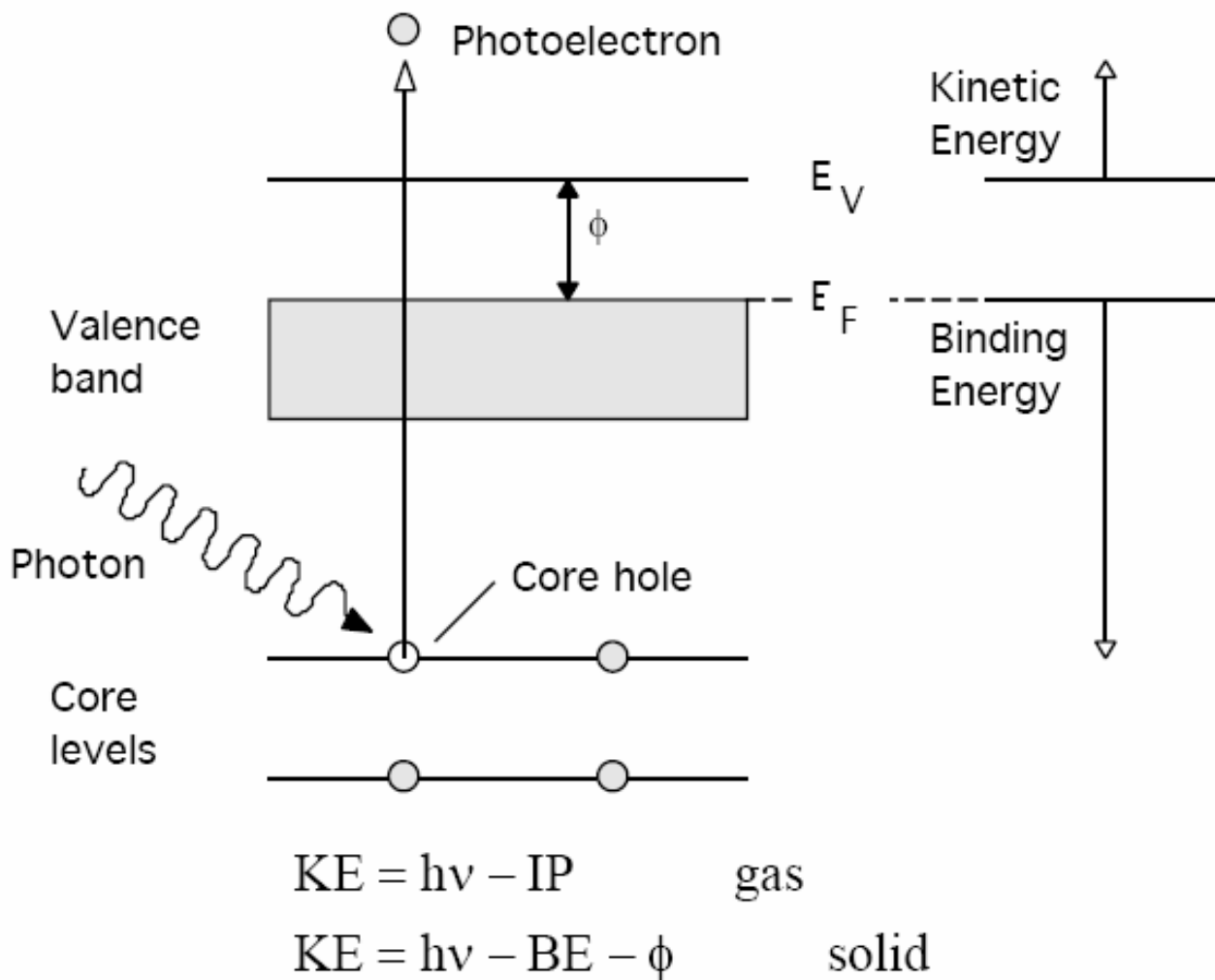
a source of fixed-energy radiation (an x-ray source for XPS or a He discharge lamp for UPS, or a tunable source such as synchrotron radiation for both)

an electron energy analyser (which can disperse the emitted electrons according to their kinetic energy, and thereby measure the flux of emitted electrons of a particular energy)

a high vacuum environment (to enable the emitted photoelectrons to be analysed without interference from gas phase collisions)



The Photoemission Process



Absorption very fast - $\sim 10^{-16}$ s

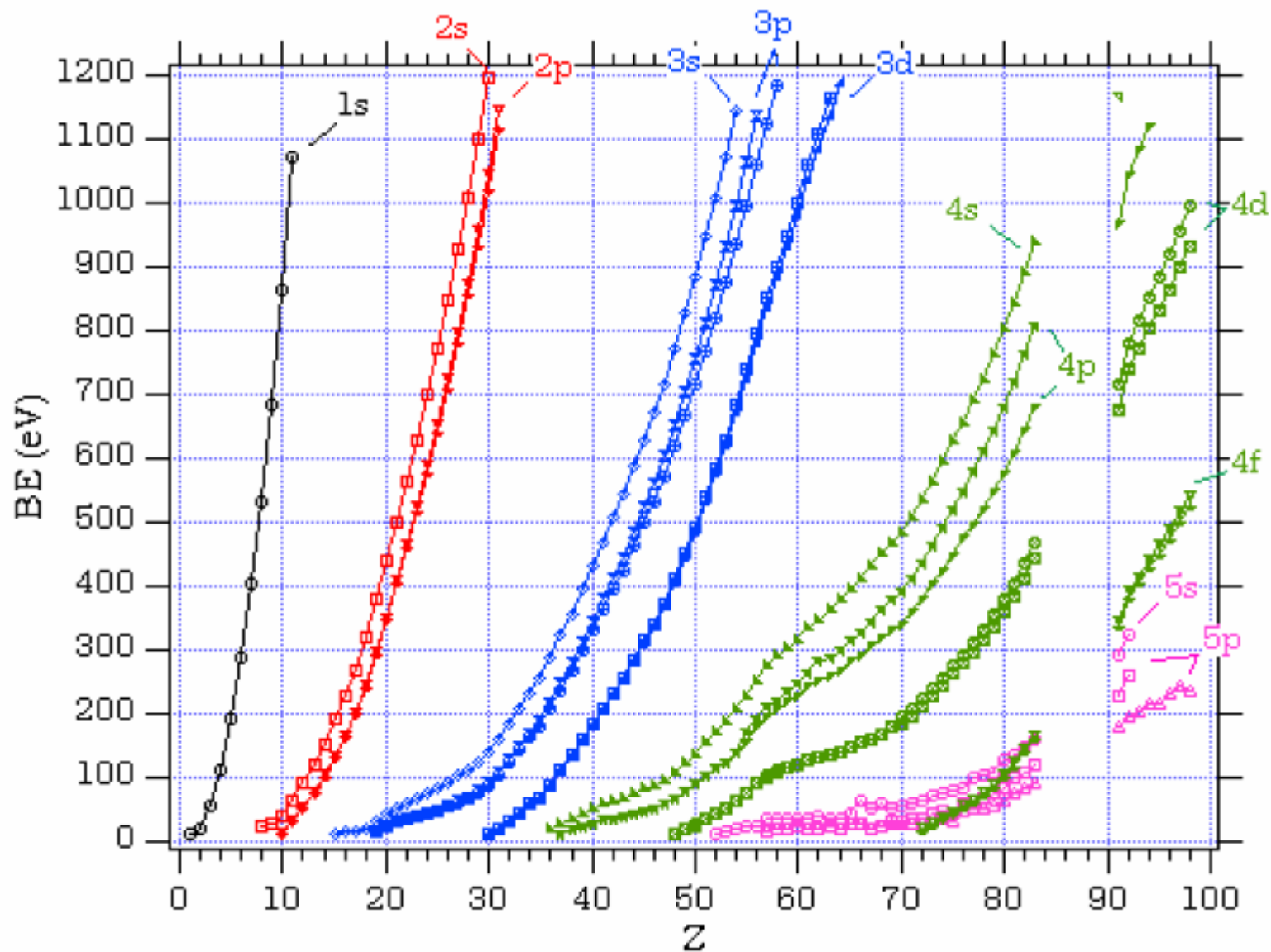
Clearly from picture above,

- no photoemission for $h\nu < \phi$
- no photoemission from levels with $BE + \phi > h\nu$
- KE of photoelectron increases as BE decreases
- intensity of photoemission \propto intensity of photons

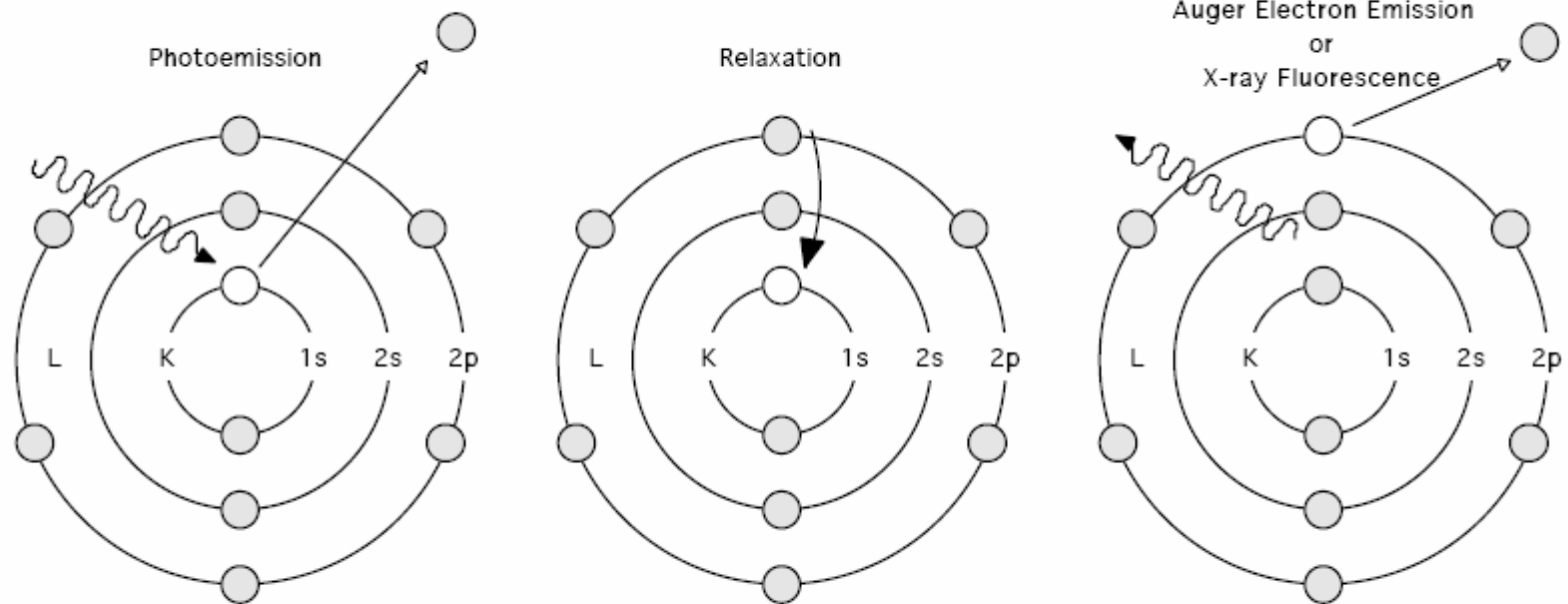
- need monochromatic (x-ray) incident beam
- a range of KE's can be produced if valence band is broad
- since each element has unique set of core levels, KE's can be used to fingerprint element

Binding energy (BE) represents strength of interaction between electron (n, l, m, s) and nuclear charge


- in gases, $BE \equiv IP$ (n, l, m, s)
- BE follows energy of levels: $BE(1s) > BE(2s) > BE(2p) > BE(3s) \dots$
- BE of orbital increases with Z: $BE(\text{Na } 1s) < BE(\text{Mg } 1s) < BE(\text{Al } 1s) \dots$



What is fate of core hole?



- Auger electron emission - basis of Auger electron spectroscopy (AES)
- X-ray fluorescence



The application of photoemission as a technique to study the chemical and electronic structure of solids has its origins in the work of Kai Siegbahn and coworkers at Uppsala University, Sweden in the fifties. That group made dramatic improvements in the energy resolution and sensitivity of electron spectrometers, enabling a determination of the binding energies of electrons in a wide range of materials. As we'll see, from an analysis of the electronic binding energies it was possible to build up a chemical "fingerprint" of the solid.


X-ray photoelectron spectroscopy (XPS)
(X-ray photoemission)

is thus also commonly referred to as *Electron Spectroscopy for Chemical Analysis* (ESCA). (Siegbahn's pioneering work earned him the Nobel prize in 1981).

The mean free path and surface sensitivity

The photoelectrons that are detected in a photoemission experiment originate only from the uppermost layers of a solid. As we'll see, with the correct choice of experimental parameters photoemission can be used to probe just the first few *monolayers* at the surface of a solid. This surface sensitivity arises from the strong interaction of electrons with matter.

An electron travelling through a solid will have a certain inelastic mean free path – a characteristic length that it can travel without suffering an energy loss.




Thus, electrons ejected from a solid via the photoelectric effect will be of two types:

Elastically scattered electrons which have escaped from the solid without suffering an energy loss

Inelastically scattered electrons which have lost kinetic energy on their way out of the solid.

An electron with energy in the 5 – 2000 eV range passing through a solid can lose energy via a number of processes.




Electron-electron scattering processes. In particular, the photoelectron can excite plasmons in the solid.

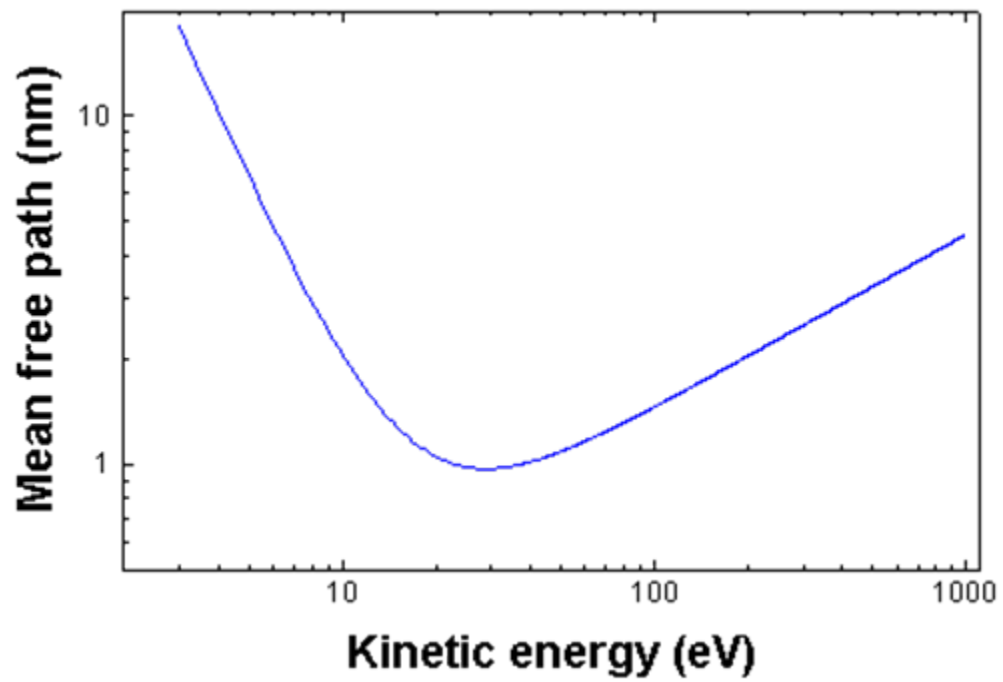
A plasmon is a collective excitation of the electron gas whose energy is quantised in, typically, the 5 –25 eV range.


An electron can excite an interband transition, e.g. the excitation of a valence electron to a conduction band state or excite a core-electron to an empty state.

The photoelectron on its way out of the solid may have sufficient energy to ionise a core-level with the creation of another photoelectron or an Auger electron



The net effect of these processes is that the (inelastic) mean free path of an electron in a solid is strongly dependent on its kinetic energy. At very low kinetic energies the electron simply does not have enough energy to excite the processes listed in 1- 3 above so its mean free path is long. At high kinetic energies the electron spends less time passing through a given thickness of solid and thus is less likely to suffer an energy loss. Hence its mean free path in the solid is again quite long. However between these two regions the mean free path passes through a minimum



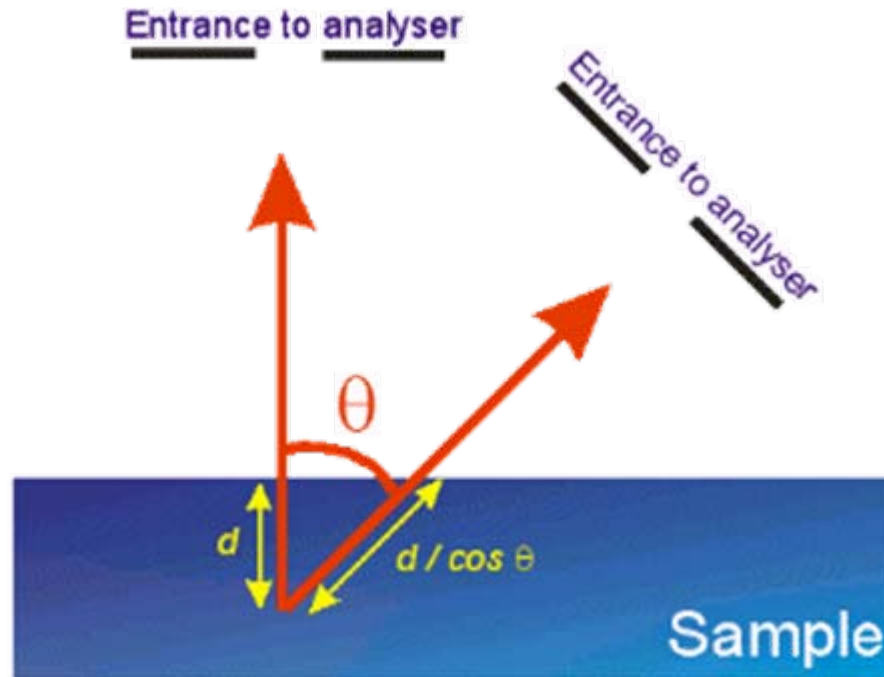


Electrons with kinetic energies in the $\sim 40 - 150$ eV range have the shortest mean free paths and at the minimum of the "universal" curve the mean free path is ~ 1 nm. Even for quite high electron energies (1-2 keV) the mean free path is still only a few nm.

This is a very significant result as regards the use of photoelectron spectroscopy as a surface sensitive probe. It means that even though the penetration depth of the incident X-rays is typically of the order of microns, the electrons that escape from the solid, due to their mean free path, will only have originated from the top few layers.

Surface sensitivity achieved by experimental geometry

If we rotate the spectrometer (or sample) so that the electrons are collected at a glancing angle, the electrons have to traverse a longer distance in the solid ($d \cos \theta$). The larger the angle, the greater the path length for the electrons and, thus, the higher the surface sensitivity of the photoemission measurement



Electronic energy levels and the photoemission spectrum

As mentioned above, in XPS we are concerned with the excitation of electrons lying in the tightly bound core-levels whereas UPS is used to probe the valence levels. The key equation underlying both processes is Einstein's equation:


$$E_{KE} = h\nu - E_B$$

where E_{KE} is the kinetic energy of the electron ejected from the solid, $h\nu$ is the photon energy and E_B is the binding energy of the electron in the solid.

XPS may be used to provide a chemical "fingerprint" of a surface.

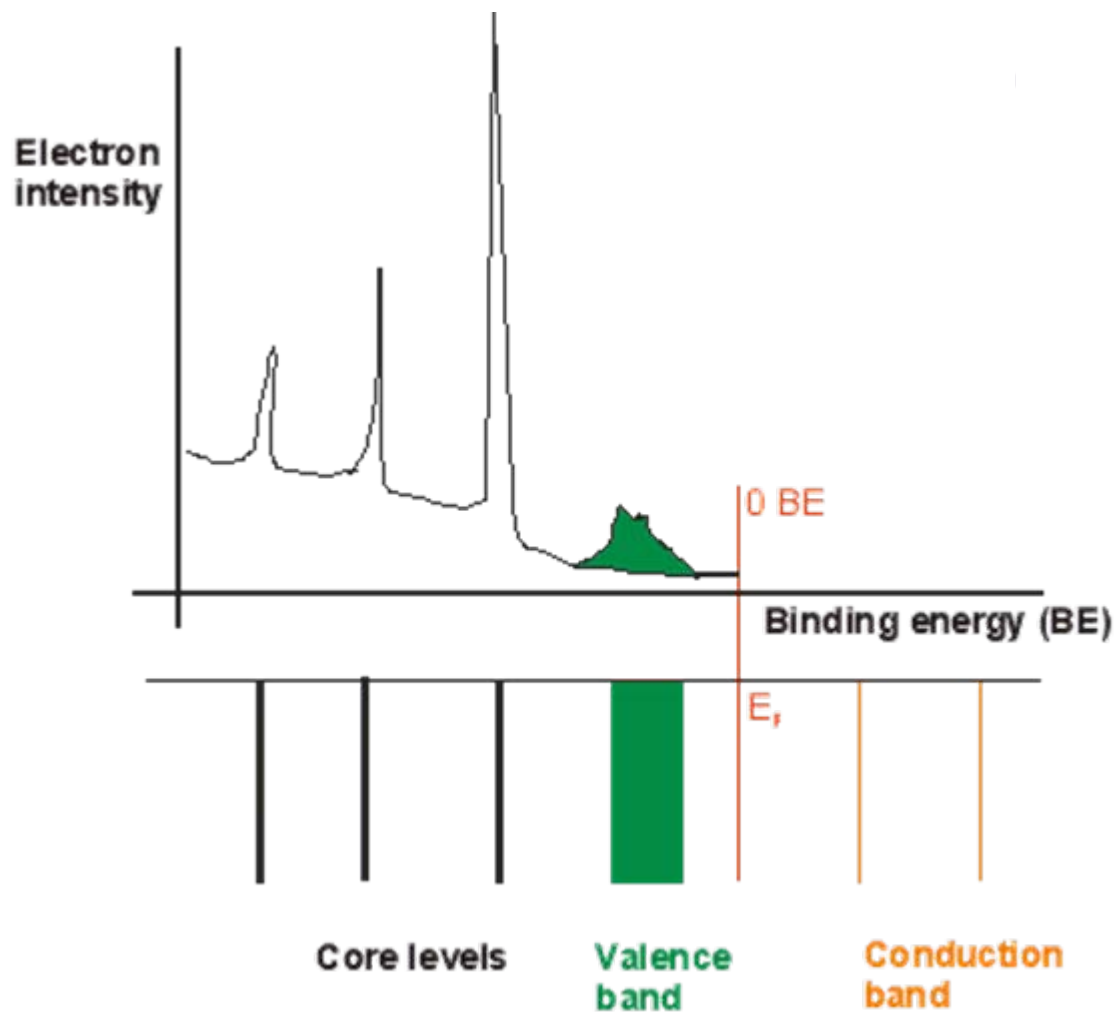
This is because the binding energies of the electrons in the core-levels are representative of the atomic species.

That is, an electron in a 1s level of oxygen has a particular binding energy which will differ from that of a Si 1s electron, a Ga 3d electron, a C 1s electron etc...



Although the binding energy will vary depending on the chemical environment of the atom in the solid, the energy differences are generally small enough so that the presence of a particular element may be unequivocally identified from an XPS spectrum.

Electrons are excited from filled states out of the solid with a particular kinetic energy. Measurement of the intensities and energies of the outgoing electrons with an electron spectrometer produces a photoemission spectrum that mirrors the distribution of filled levels in the solid.



Koopman's theorem


If we assume that no rearrangement of the electrons – either within the atom from which the photoelectron originated *or* in the neighbouring atoms of the material - occurs following the ejection of the photoelectron (an approximation known as *Koopman's theorem*) then the binding energy of the electron is simply the negative of the atomic orbital energy ($-e_k$, where the subscript k labels the energy level from which the electron was removed).

Koopman's Theorem

The BE of an electron is simply difference between initial state (atom with n electrons) and final state (atom with $n-1$ electrons (ion) and free photoelectron)

$$BE = E_{\text{final}}(n-1) - E_{\text{initial}}(n)$$

If no relaxation followed photoemission, $BE = -$ orbital energy which can be calculated from Hartree-Fock



Measured BE's and calculated orbital energies different by 10-30 eV because of:

- electron rearrangement to shield core hole - the frozen orbital approximation is not accurate
- electron correlation (small)
- relativistic effects (small)

Really, both *initial state effects* and *final state effects* affect measured BE

Final state effects

Koopman's theorem is a severe approximation.

The ejection of a photoelectron creates a positively charged core-hole in the atom.

Electrons in the vicinity of the positive charge will rearrange to *screen* it i.e. reduce its energy. The energy reduction is called the *relaxation energy* and can originate both from the electrons on the atom containing the core-hole (intra-atomic screening) and from those on surrounding atoms (interatomic screening).

Relaxation/screening is thus a *final state effect*.

The photoelectron can also interact with other electrons when departing the atom. For example, it may excite a valence electron to an unfilled (conduction band) state and lose an amount of kinetic energy equal to the excitation energy. This is called a *shake-up* process.

Similarly, the departing photoelectron might transfer sufficient energy to the valence electron to remove it entirely from the atom: a *shake-off* process.

Spin-orbit (l-s) coupling

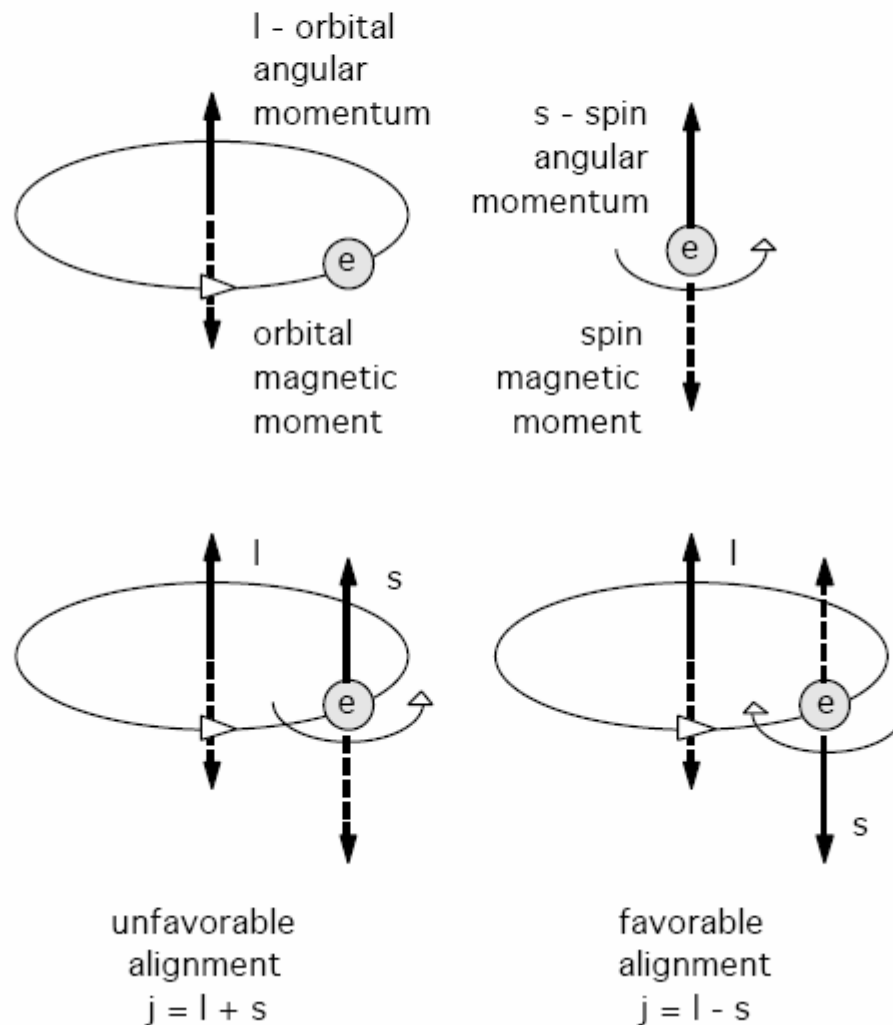
A very important initial state effect for any orbital with orbital angular momentum > 0 is *spin-orbit coupling/ splitting*. This is a magnetic interaction between an electron's spin and its orbital angular momentum. We'll consider a *p* orbital (though spin/orbit coupling holds equally for *d* and *f* orbitals).

After removal of an electron from the *p* orbital through photoemission, the remaining electron can adopt one of two configurations - a *spin-up* or *spin-down* state.

With no spin-orbit interaction these states would have equal energy. However, spin-orbit coupling lifts the degeneracy and we need to consider the quantum number, *j*, the *total angular momentum quantum number*. The value of *j* is given by $l + s$ where *s* is the spin quantum number ($\pm 1/2$). For a *p* orbital $j=1/2$ or $3/2$. Thus the final state of the system may be either $p_{1/2}$ or $p_{3/2}$ and this gives rise to a splitting of the core-level into a doublet.

Spin-orbit splitting is an *initial state effect*

For any electron in orbital with orbital angular momentum, coupling between magnetic fields of spin (s) and angular momentum (l) occurs



Total angular momentum $j = |l \pm s|$

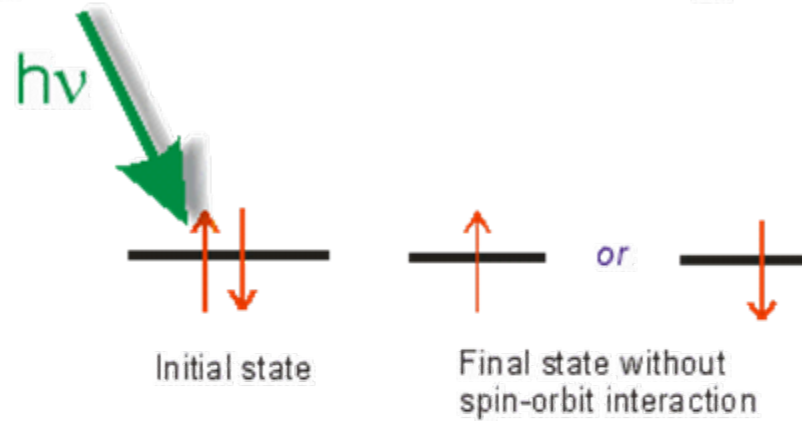
Quantum numbers				Atomic notation	X-ray notation
n	l	s	j	n l _j	
1	0	$\pm 1/2$	1/2	1s _(1/2)	K ₁
2	0	$\pm 1/2$	1/2	2s _(1/2)	L ₁
2	1	+ 1/2	3/2	2p _{3/2}	L ₂
2	1	- 1/2	1/2	2p _{1/2}	L ₃
3	0	$\pm 1/2$	1/2	3s	M ₁
3	1	- 1/2	1/2	3p _{1/2}	M ₂
3	1	+ 1/2	3/2	3p _{3/2}	M ₃
3	2	-1/2	3/2	3d _{3/2}	M ₄
3	2	+ 1/2	5/2	3d _{5/2}	M ₅

But how many spin-orbit split levels at each j value?

$$\text{Degeneracy} = 2j + 1$$

Subshell	j values	Degeneracy
s	1/2	-
p	1/2, 3/2	2, 4 = 1, 2
d	3/2, 5/2	4, 6 = 2, 3
f	5/2, 7/2	6, 8 = 3, 4

(i)



(ii)

Spin orbit interaction lifts degeneracy



Initial state effects: chemical shifts

The valence electron distribution at the surface of a solid will differ from that of the bulk solid (sometimes weakly, as for certain metal surfaces, or dramatically, as for a large number of semiconductors). Variations in the valence electron distribution will affect the potential a core-level electron feels. Therefore, the binding energy of a core-level electron in an atom at the surface will generally differ from that in a bulk atom.

The precise binding energy of a core-level electron depends critically on its chemical environment.

Both clean and adsorbate covered surfaces represent chemical environments that differ from that "seen" by an atom in the bulk.

The change in the chemical environment produces a shift in the core-level. The magnitude of this chemical shift varies dramatically (from <0.1 eV to ~ 10 eV) **from system to system.**

Chemical shifts are generally interpreted in terms of the initial state of the system (i.e. before the photoelectron has been ejected).

Charge transfer will either decrease or increase the charge density of an atom, leading to increased or decreased Coulombic attraction between the nucleus and the core electrons. Thus an atom that has donated a considerable amount of valence charge will produce an XPS peak at a higher binding energy than that of an atom in a lower oxidation state.

As an example we can look at the oxidized and clean Si(100) surface. The Si 2p core-level (doublet) peak appears at ~ 100 eV binding energy. However, at approximately 4 eV above the Si 2p peak lies a broad peak due to the oxidised atoms at the Si surface. As we anneal the sample surface we can desorb this oxidised layer and produce a clean Si(100) surface.

Binding energy referencing

For this type of core-level analysis we must have accurate measurements of the core-level binding energies.

The photoemission measurements are usually for conducting samples (metals or semiconductors).

Both the spectrometer and the sample are electrically grounded and, hence their Fermi levels will align. The sample and spectrometer will have different work functions as shown. The binding energy of the photoelectron is referenced to the Fermi level (i.e. the zero of the binding energy scale is at the Fermi level).

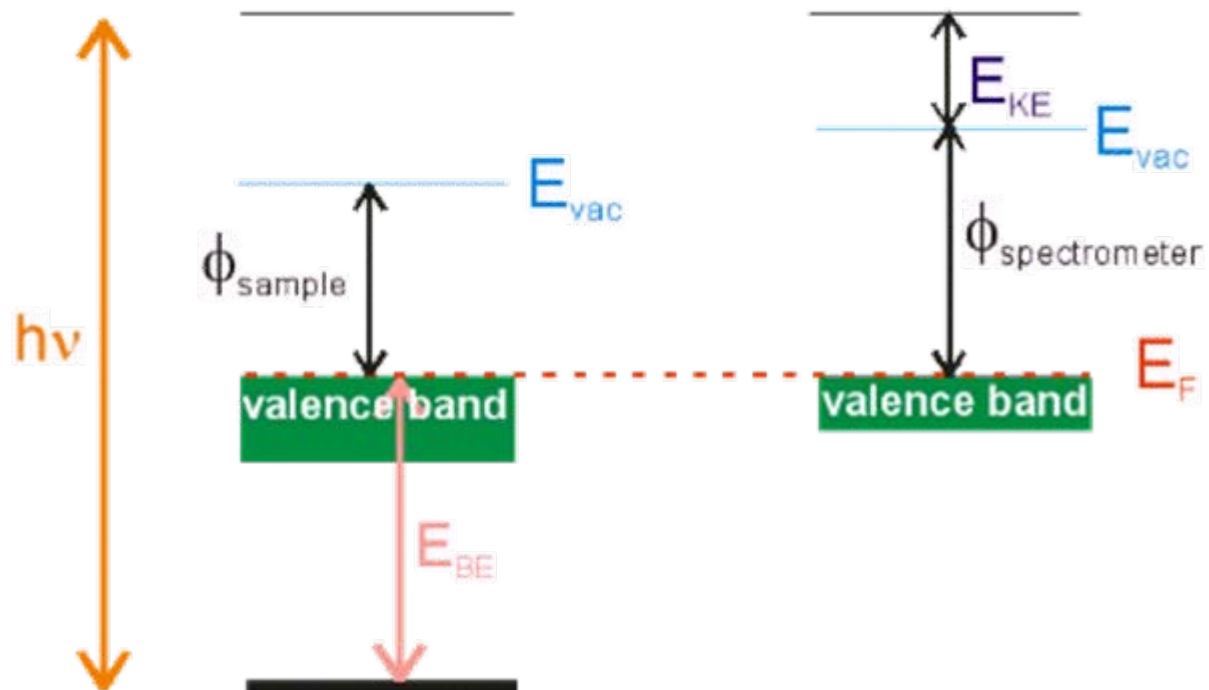
The binding energy of the photoelectron is given by:

$$E_B = h\nu - E_{KE} - \varphi_{SP}$$

where φ_{SP} is the spectrometer work function.

Hence, it is the spectrometer and not the sample work function that must be accurately known.

The spectrometer is generally calibrated using standard samples prior to the photoemission experiments and its work function determined.



Auger Electron Spectroscopy (AES)

A second important electron spectroscopy used in surface science is *Auger electron spectroscopy (AES)*. Auger electrons are named after their discoverer, Pierre Auger and arise from what is termed an *autoionisation* process.

An electron is ejected from a core-level either by a photon (as in conventional photoemission) or by an incident high energy electron. The core-hole is filled by an electron from a higher energy level. The energy lost by that electron may be given up in the form of an X-ray photon *or* the quantum of energy is transferred (non-radiatively) to another electron in the atom.

That electron (the Auger electron) is thus released from the atom.

X-ray and high energy electron bombardment of atom can create core hole

Core hole will eventually decay via either

(i) photon emission (x-ray fluorescence -XRF)

more likely for deep core hole (high BE)

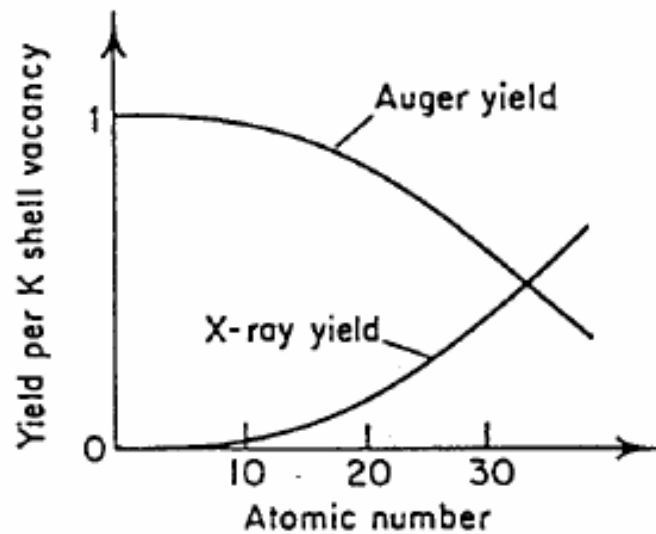
high Z elements

or (ii) radiationless internal rearrangement (Auger process)

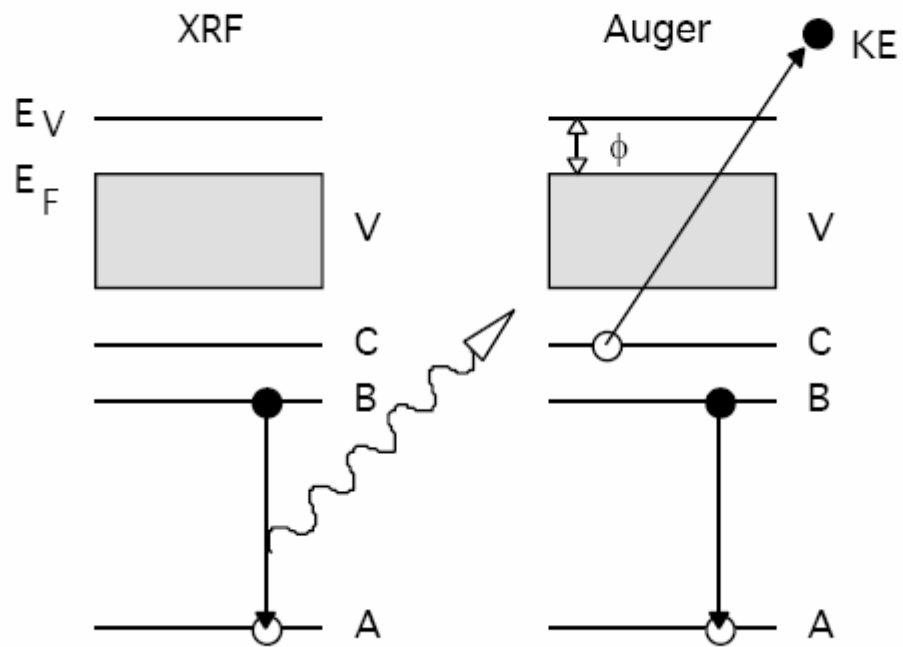
more likely for shallow core hole (low BE)

low Z elements (almost exclusively for $Z < 15$)

↓



The relative probabilities of X-ray emission and Auger electron emission in the decay of K (1s) holes in the lighter elements.



- Photon not much use for surface analysis since propagates large distances in solid (but is used for x-ray microprobe analysis in SEM/TEM)
- Auger electrons produced with similar kinetic energies to photoelectrons so similar surface sensitivity
- Initial core hole can be generated by *x-rays*

see Auger peaks in XPS

or *electrons* (most common in AES)


spectrum contains Auger, incident and inelastically scattered electrons

but *no photoemission* peaks!

In simple, one-electron picture (ignoring *relaxation* or *final state* effects),

$$\text{X-ray photon} \quad h\nu \approx E_A - E_B$$

$$\text{Auger electron} \quad \text{KE} \approx \underbrace{E_A - E_B}_{\substack{\text{energy gained} \\ \text{by core-hole} \\ \text{annihilation}}} - \underbrace{E_C}_{\substack{\text{energy needed} \\ \text{to overcome BE} \\ \text{of Auger electron}}} - \phi$$

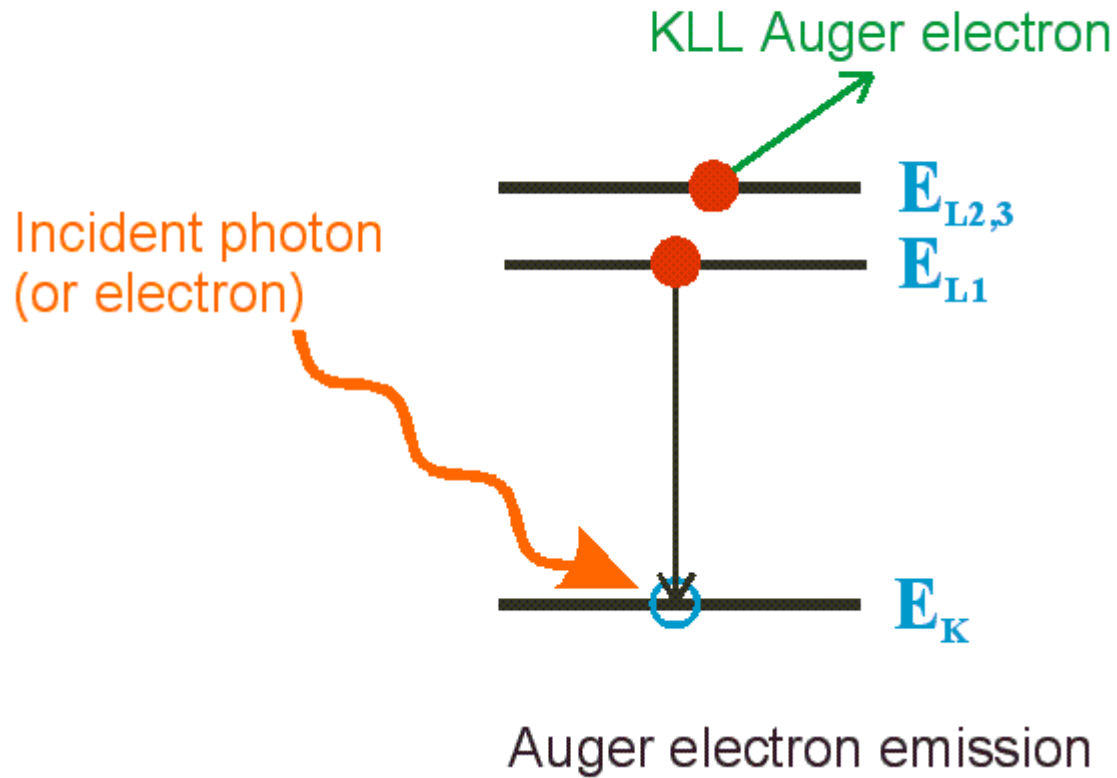



The kinetic energy of the Auger electron, unlike that of a photoelectron, is not dependent on the energy of the incident radiation (or electron) that produced the initial core hole.

Thus, Auger electrons have energies that are characteristic of the atom from which they arose and may be used for elemental identification.

The notation associated with Auger transitions relies on the shell nomenclature. Note that if the valence levels are involved in the Auger process these are denoted by a *V*.

$$\text{Energy of Auger electron} = E_K - E_{L1} - E_{L2,3}$$





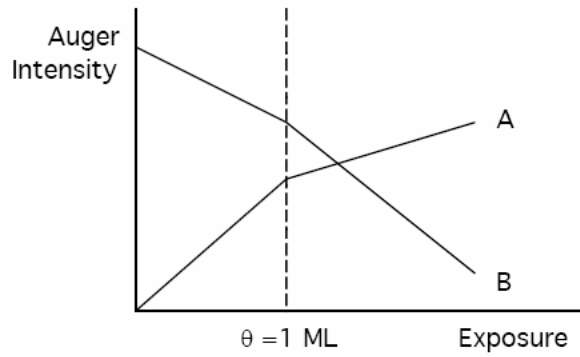
Generally Auger electron spectroscopy is carried out using an electron gun to produce relatively high energy electrons (in the 2 to 5 keV range) for initial core-level excitation.

The Auger peaks are superimposed on the secondary electron background and are generally quite weak.

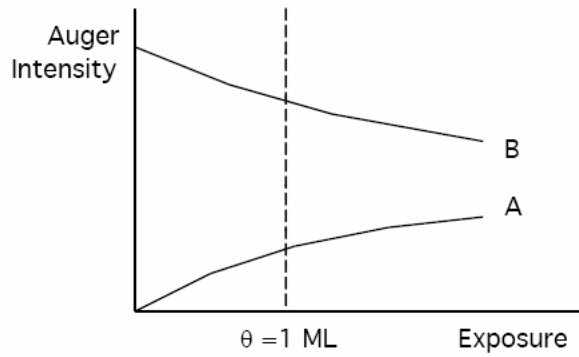
Therefore, the Auger spectrum is usually electronically (sometimes numerically) differentiated to highlight the Auger peaks.

In addition to chemical "fingerprinting" of a sample, a very common application of Auger spectroscopy is in the determination of growth modes.

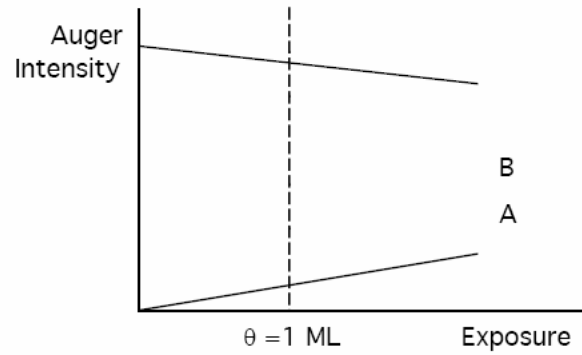
An analysis of the attenuation of a substrate Auger peak as a function of coverage enables a determination of whether the growth mode is of Frank-van der Merwe, Vollmer-Weber or Stranski-Krastanov character.



Frank-van der Merwe
(layer-by-layer)



Stranski-Krastinov
(3-D islands)



Alloying