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Assumptions

The following assumptions are needed
to measure an ideal spectrum.

$T = 0 \text{ K}$

Heisenberg's uncertainty does not exist

electrons have no spin

all electrons that are created leave the
sample with no losses

all events are equally likely to occur

ideal source

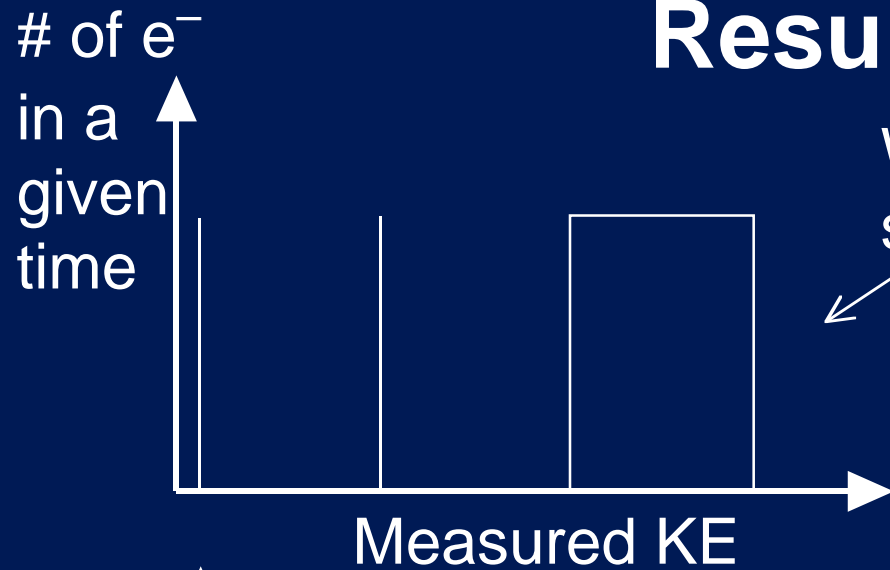
ideal analyzer (and detector)

sample is a single element

sample is a conductor (metal)

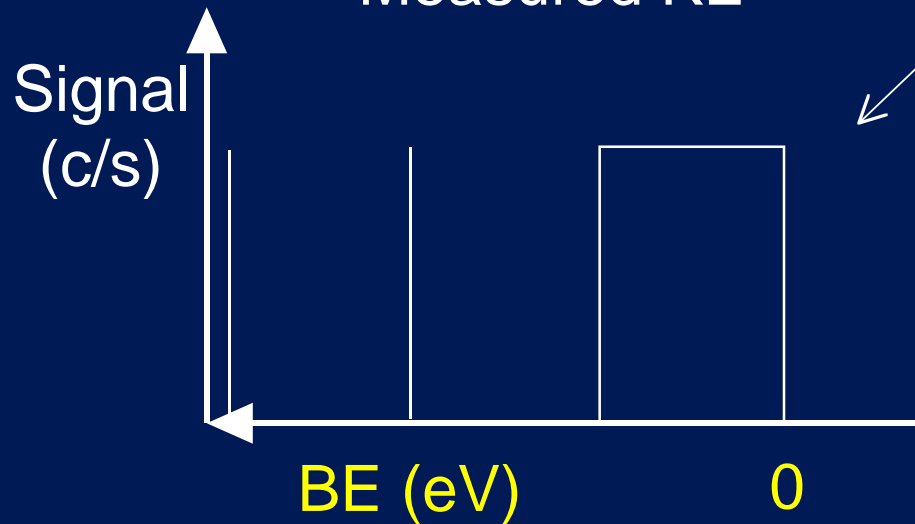
We will relax
these
assumptions
each in turn.

Result



We should measure signals in KE ...

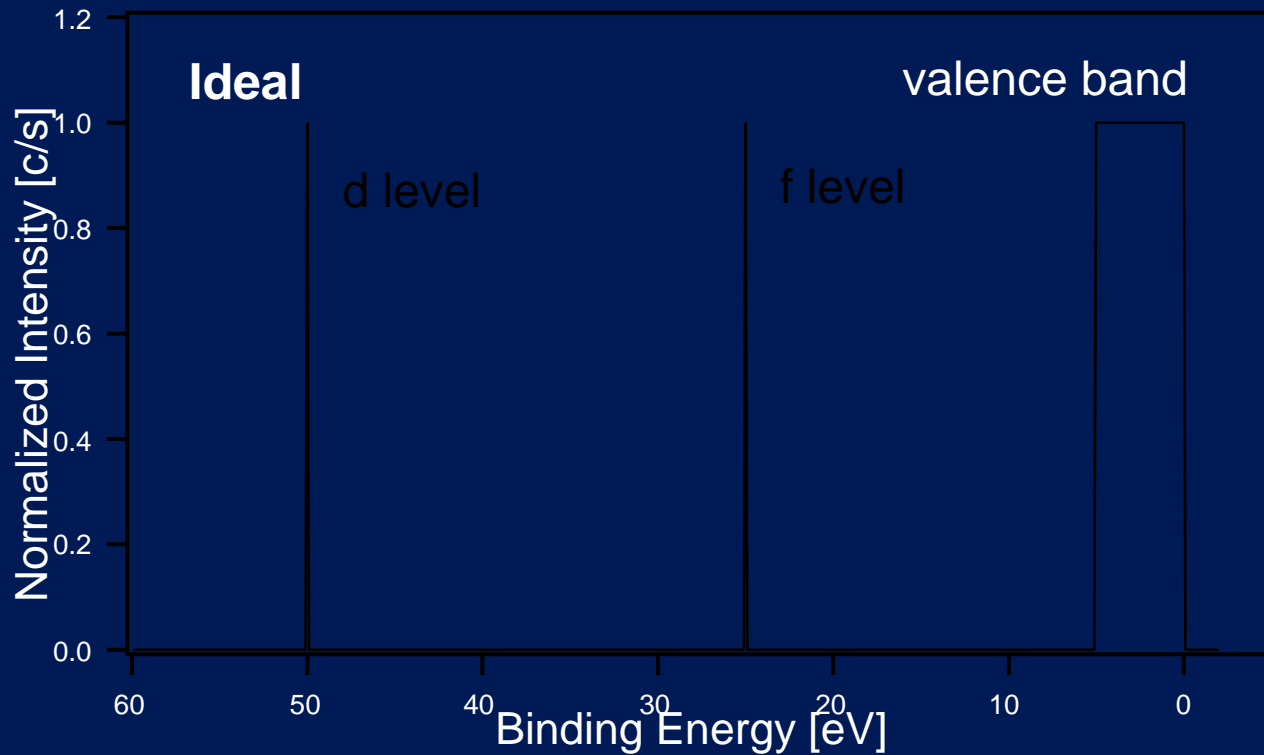
... that should map the BE levels of the element



A **survey spectrum** covers a wide range of BE, typically from 0 eV to 1000 eV or higher.

Ideal Survey Spectrum

For the examples that follow, intensity will be normalized from 0 to 1.



The core level peaks are delta functions of zero width. The valence band model does not consider electron density of states.

Fermi Distribution Function

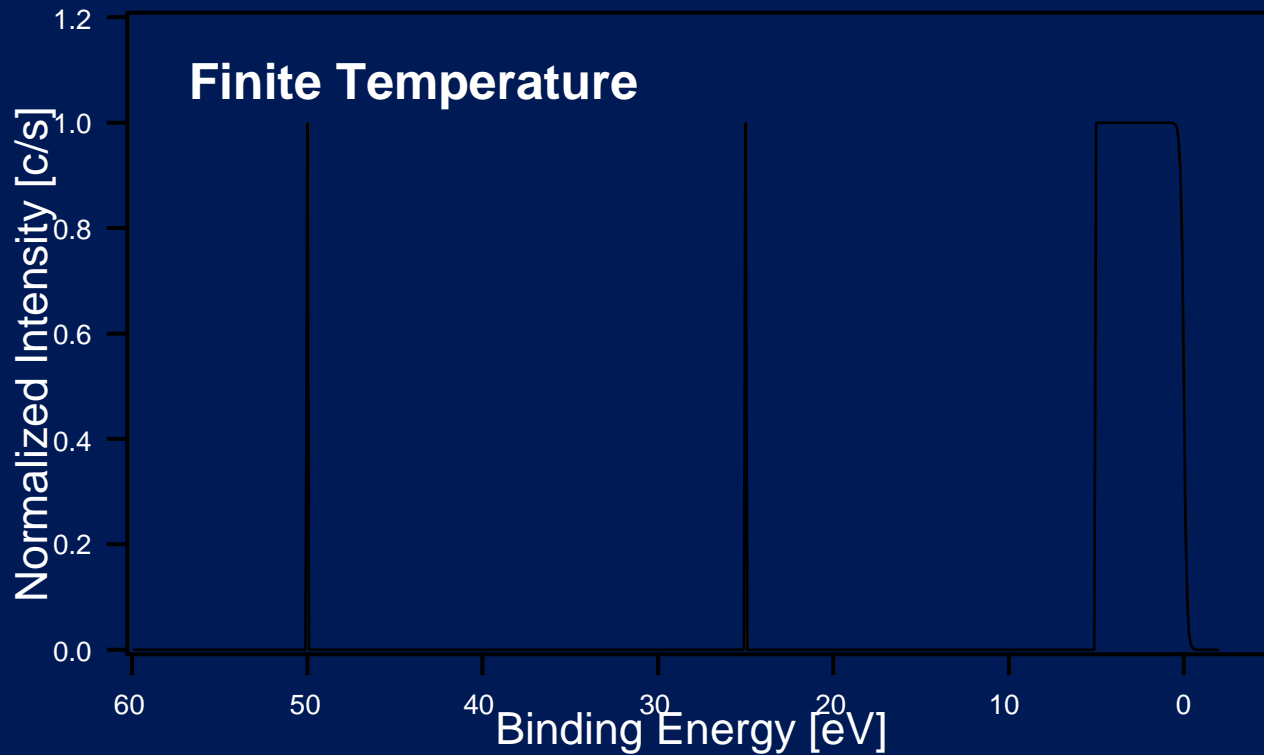
At temperatures other than 0 K, the Fermi level is smeared out according to the Fermi distribution function.

$$f = 1 / (1 + \exp(-(E - E_F) / k T))$$

The shape of this function can be found in a wide variety of materials texts.

Result

This is the magnitude of the effect expected at $T \sim 1000$ K.



The position of the Fermi energy become harder to determine.

Definition

According to the uncertainty principle in quantum mechanics, we can only measure the energy of an event to a certainty no better than

$$\Delta E \Delta t < h / 4 \pi$$

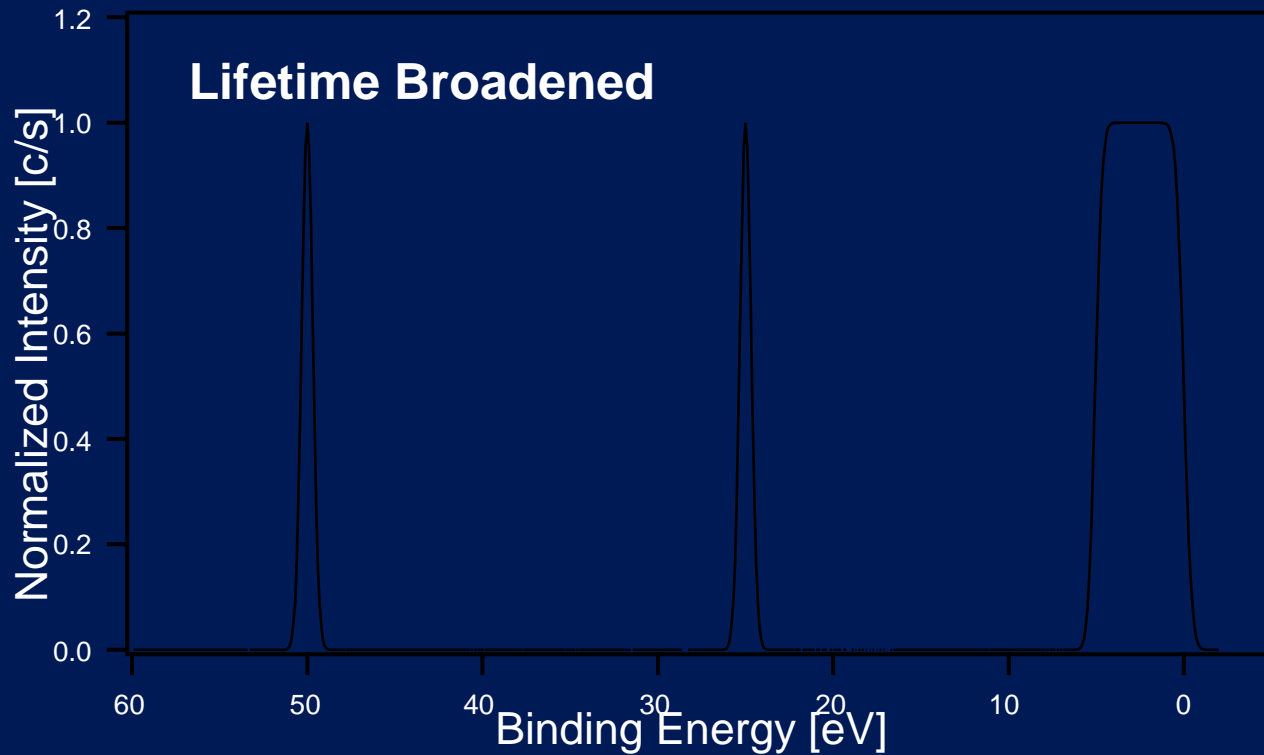
The value Δt is the lifetime of the electron in the state we are attempting to define.

The energy broadening, ΔE , that arises because of this is called lifetime broadening.

All levels will be broadened due to our intrusion during the measuring process.

Result

Lifetime broadening is a Gaussian or Lorentzian $\sim 0.5 - 0.7$ eV in width.



The broadening occurs throughout the spectrum and is different for different orbitals.

Principles

Electrons have spin. Their total angular momentum depends on spin and orbital quantum numbers.

Electrons with different spin-orbit coupling will have different binding energies.

We recognize two types of spin-orbit couplings.

j-j coupling - important for $Z > \sim 75$

determine the momenta for all electrons individually, then sum the values over all electrons to get the total

L-S coupling (Russell-Sanders) - for $Z < \sim 20$

sum the orbit angular momenta for all electrons, then sum the spin angular momenta, then add the two sums

jj Spin-Orbit Coupling

This appears often in XPS spectra.

Consider the electron with spin s of $1/2$.

Each orbital has a orbital angular momentum of l .

The vector sum is $(l \pm s)$, leading to splitting into two distinct energy levels for all but s orbitals.

level	l	$(l \pm s)$
s	0	$1/2$
p	1	$1/2$ or $3/2$
d	2	$3/2$ or $5/2$
f	3	$5/2$ or $7/2$

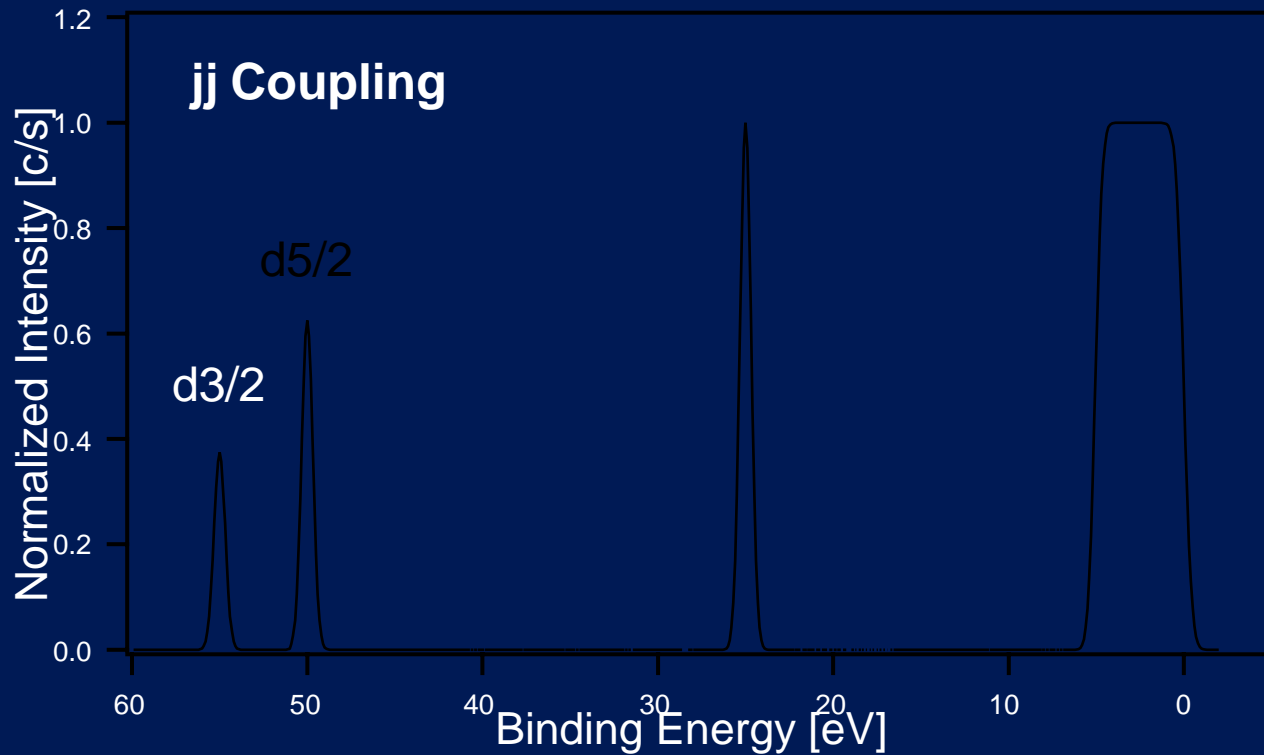
The relative ratio of occupancy in each level is in rough proportion to the ratio of $(l \pm s)$ values.

example

the $d_{5/2}$ level has $\sim 5/3$ more electrons than the $d_{3/2}$ level

Result

For clarity, only the d level has been split due to jj coupling.



The total intensity in the two d levels (the sum of the two peak areas) is equal to the value it was without spin-orbit splitting.

Event Non-Idealities

The factors that follow can be broken down into three areas

those involved with additional processes that occur along with the photoemission event

spin-orbit coupling electron scatter Auger transitions

those that are due to a non-ideal source

line-broadening satellites ghosts

those that are due to a non-ideal analyzer

line-broadening signal loss

Principles

The intensity of a peak depends on how efficiently the x-ray interacts with the electron to cause the photoemission process to occur.

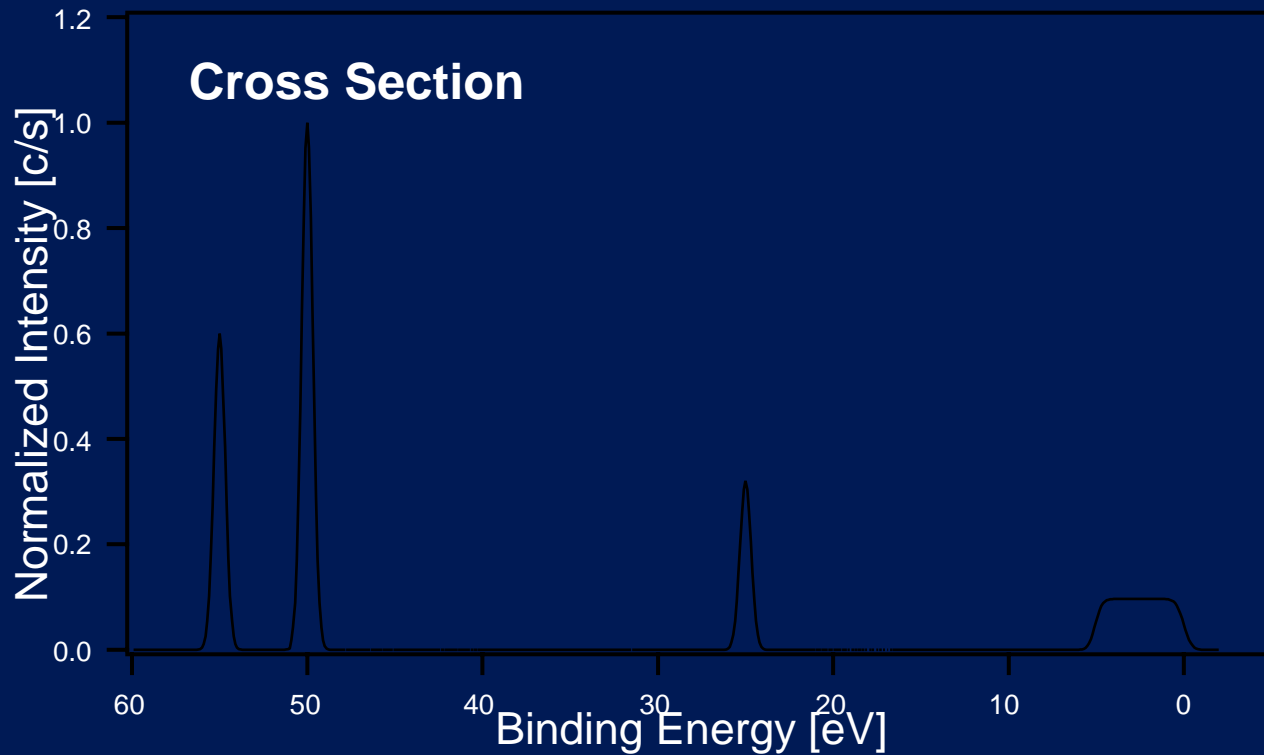
The efficiency of the photon interaction with the electron is determined by the **photoelectron cross section**, σ .

Each orbital has its own cross section - the number of electrons emitted by an incident x-ray photon depends on σ for the orbital.

The intensities of XPS peaks will not be identical in a survey spectrum even when all else is ideal.

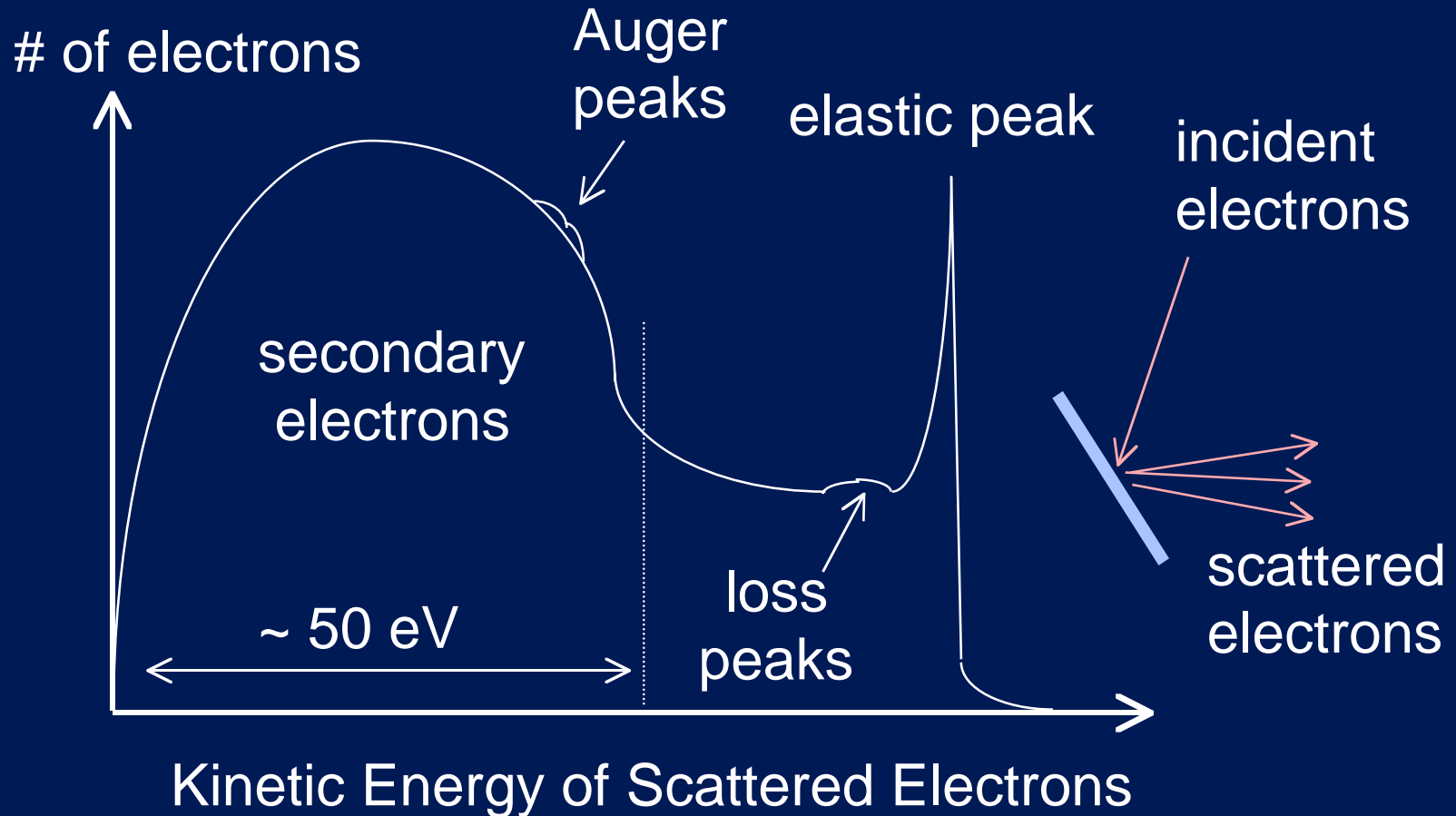
Result

Orbitals with lower cross sections will have lower intensity.



The cross sections for the f level and valence band in this example spectrum are lower than the cross section for the d levels.

Electron Distribution Curve



Scattering

Electrons scatter from surrounding atoms as they exit a material.

Inelastic scattering events lead to electrons with kinetic energies lower than the primary electron.

loss peaks - when the primary electron loses energy due to a single scattering event as it leaves the sample

secondary electrons - when the primary electron scatters multiple times and causes other (low energy) electrons to be ejected from the material

Inelastic scattering causes an increase in the background level on the high binding energy side of all peaks in an XPS spectrum.

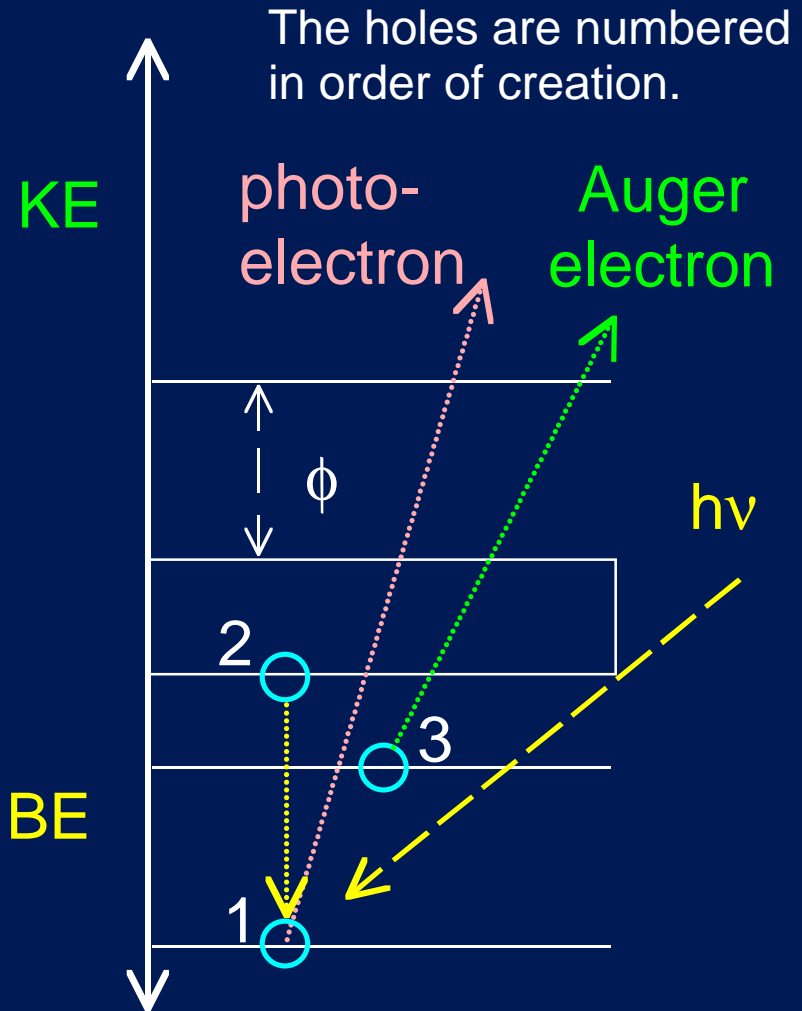
Auger Process

The Auger process can occur anytime we create a hole in a core level.

We create holes using either x-rays (in XPS) or electrons (in AES).

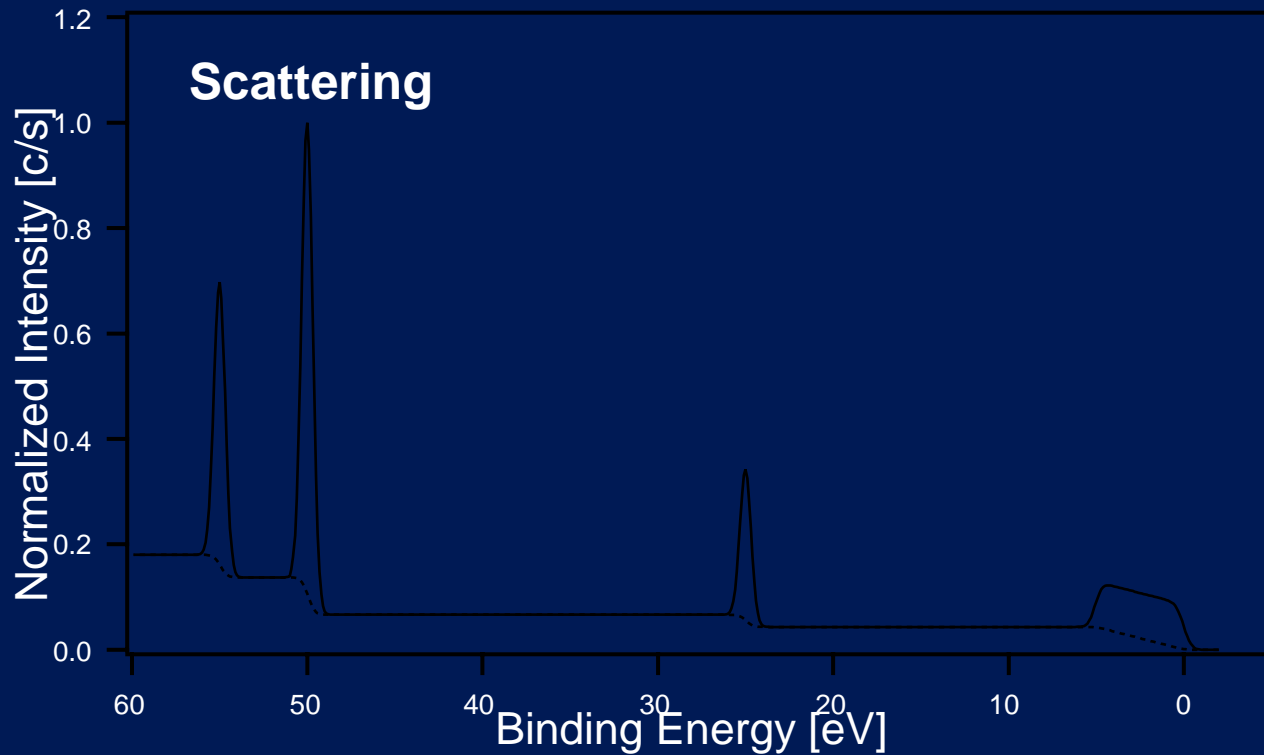
Auger peaks can also appear in XPS spectra.

The energy lost by the electron falling from 2 to 1 ejects the electron from 3.



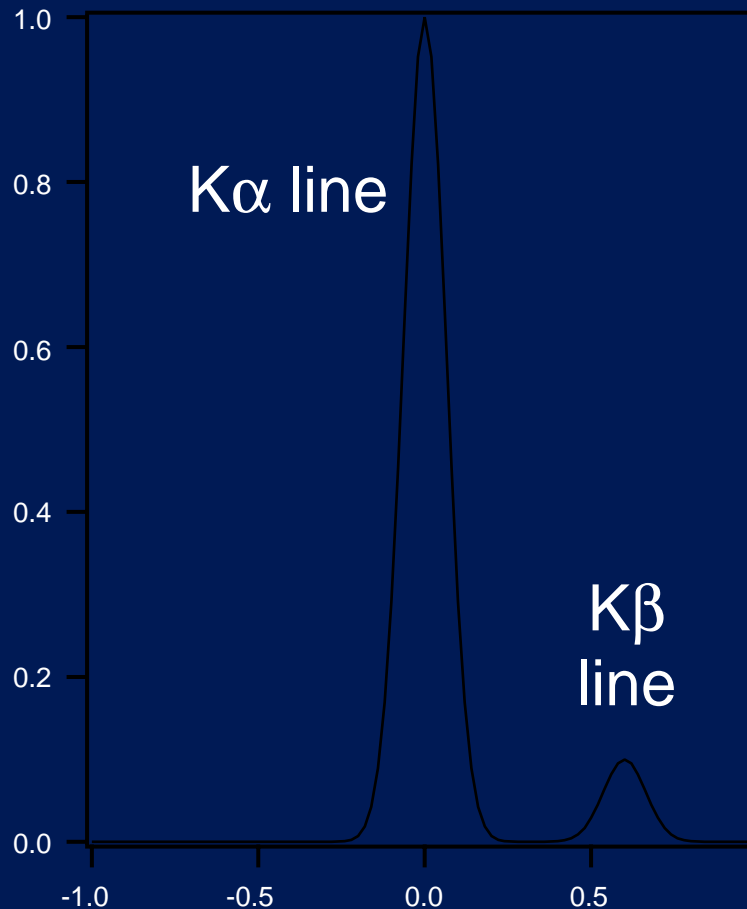
Result

Loss peaks and Auger peaks are not included in this example.



An integrated background was used for illustration. In principle, the background should decrease to zero about 50 eV above the main peak.

Source Lineshape



excitation energy relative to main peak

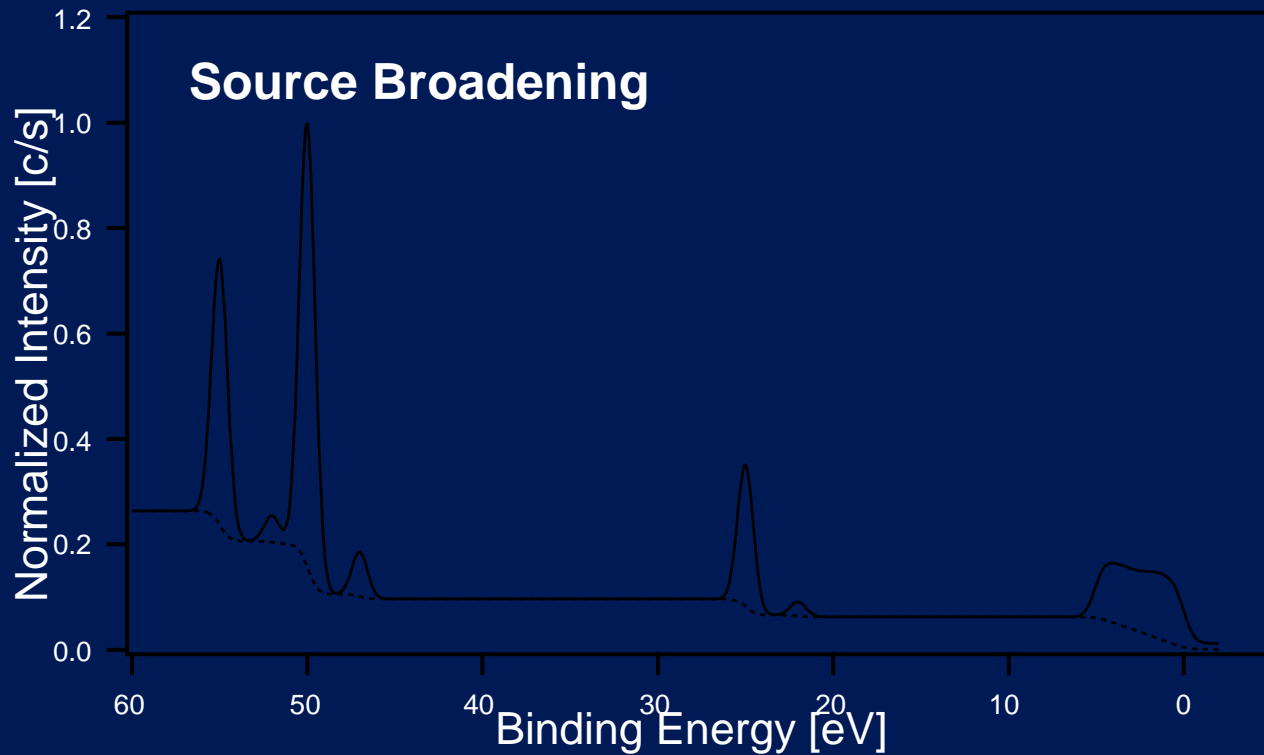
X-ray sources have finite line widths (and are not symmetric in shape).

They also have one or more secondary emission lines. This will cause **x-ray satellites** at higher kinetic energy (lower binding energy).

We can take care of these problems with deconvolution routines.

Result

The x-ray satellites always appear at lower BE from the main peak.



This effect extends to above the Fermi level too!

Other Factors

A number of problems that arise with x-ray sources can cause additional peaks in the XPS spectrum.

Ghost Peaks

When the x-ray source is either contaminated (with another metal) or oxidized, the spectrum will show ghost peaks due to excitation radiation from the other metal or the oxidized metal.

Increased Background

When the x-ray source window has been damaged such that electrons can escape from the filament to the sample, we will see an increase in background signal.

Analyzer Transmission

The analyzer has a finite acceptance aperture. This causes broadening in peaks.

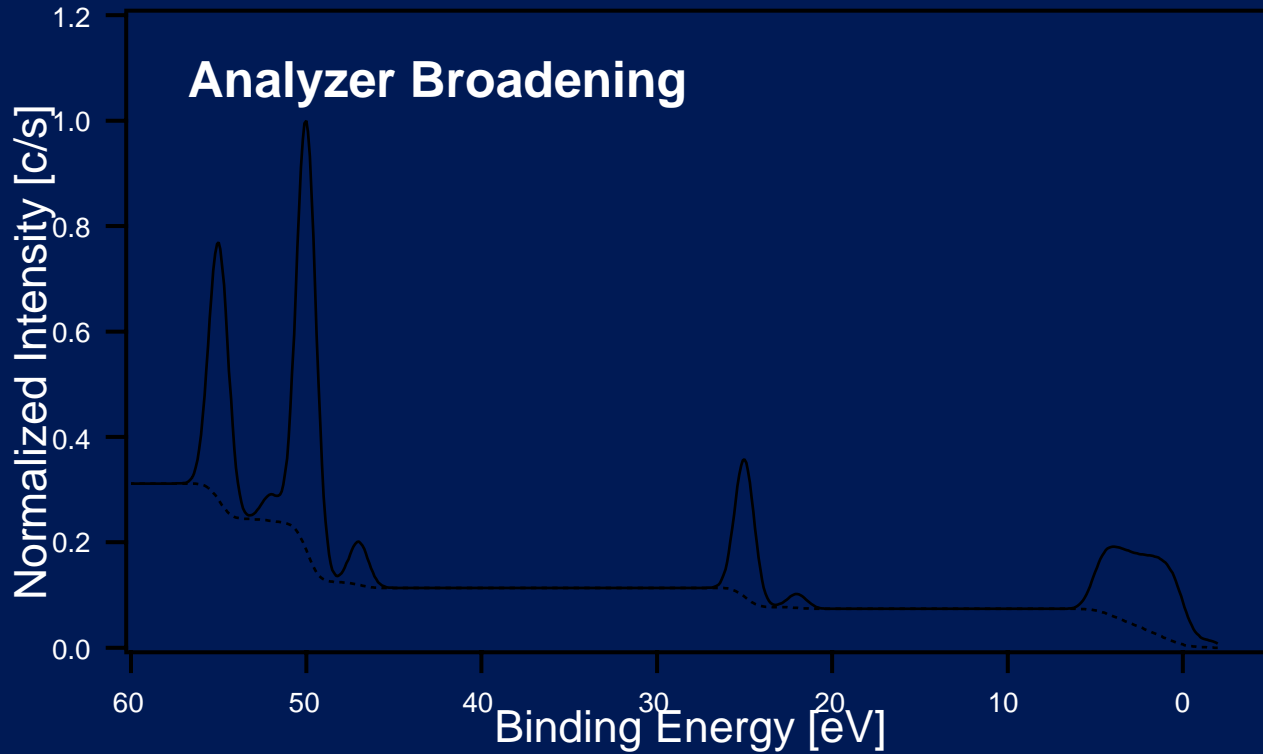
The analyzer does not transmit electrons of all kinetic energies equally well. This causes discrepancies in peak heights across the spectrum.

We can use peak deconvolution processes to take care of any problems due to analyzer broadening.

We must account for non-idealities in the analyzer transmission function if we want to have accurate measures of peak heights and areas.

Result

The peaks are further broadened when passing through the analyzer.



This sample spectrum does not consider non-idealities in the transmission function of the analyzer.