Topic Outline

VA1. Fundamentals

Electron Configurations

The beginning point for discussions of XPS is the electron configurations of elements.

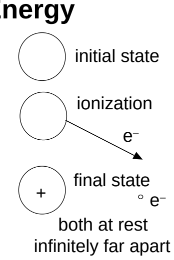
You should know how to find electron configurations for any element using the Periodic Table and be aware of the elements that deviate from expectations.

Ionization Energy

The ionization energy of an element is defined as the energy required to remove an electron to an infinite distance at rest from an atom, molecule, or ion.

Since we require energy to remove an electron, the process is endothermic.

How we remove the electron is irrelevant to the discussion.



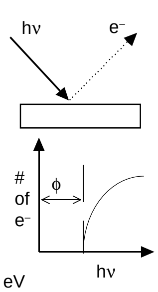
example: C IE_1 = 11.6 eV/atom

Photoelectric Effect

The process of using photons (light) to remove electrons from a bulk material is called photo-emission.

The photoelectric effect was the observation that a minimum frequency (energy) of light was needed to remove any electrons.

This minimum energy corresponds to the work function ϕ of the material.



ϕ for graphite ~ 3 - 4 eV

Molecular vs Bulk

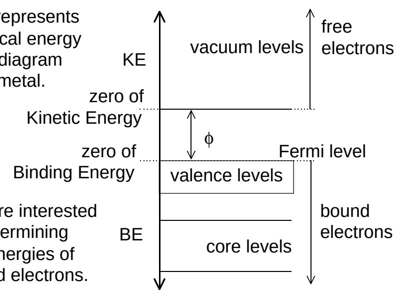
Work functions of bulk materials are always less than the first ionization energy of the element. This is due to relaxation effects in the bulk material that we will consider later as part of the photoemission process.

Work functions can be altered by changes in the chemistry and composition of the surface of a material.

For metals, work functions depend on the lattice plane.

Energy Diagram

This represents a typical energy level diagram for a metal.



We are interested in determining the energies of bound electrons.

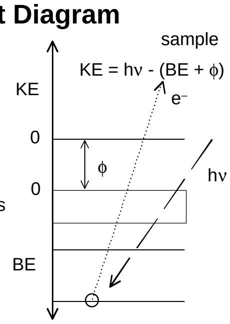
Event Diagram

In photoemission spectroscopy, we use photons to eject electrons.

In XPS, the photons are x-rays.

An energy balance gives the KE of the leaving electron.

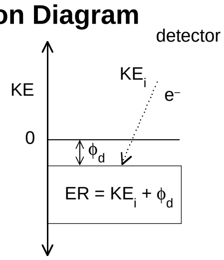
The photoemission process leaves behind a hole. We will deal with this later.



Detection Diagram

Electrons are detected (counted) by a detector when they reach the Fermi energy of the detector.

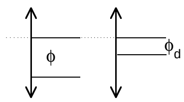
Their KE is measured relative to the zero point of KE for the detector. This may or may not be the same as the zero point of KE for the inital source of electrons.



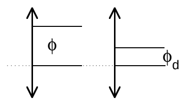
Energy Level Alignment

When two materials are not connected, their zero levels of KE are aligned. An electron above either one sees the same vacuum levels.

When two materials are connected, their Fermi energies are aligned. A potential energy appears between them (the basis behind thermocouples).

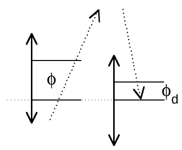


unconnected materials



connected materials

Consequences



An electron that leaves the material on the left with KE_L will gain additional KE falling into the material on the right.

It will gain $(\phi - \phi_d)$ in KE.

$KE_L = h\nu - (BE + \phi)$ and $KE_R = KE_L + (\phi - \phi_d)$

Therefore $KE_R = h\nu - BE - \phi_d$

The KE we record for the electron depends on the source energy, its initial binding energy, and the work function of the detector (or spectrometer).

Conclusions

In order to measure the proper BE of electrons using XPS, we must

- make sure the sample and detector are at the same potential (typically ground)
- have an accurate value for the energy of the source
- have an accurate value for the work function of the detector