Surface Analysis of Nanomaterials

(나노소재표면분석)

Surface and Thin Film Analysis (표면 및 박막 분석)

장소: E6, Room 116

시간: 월7A-8A, 수7A-8A

2. Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

Previous section

The general concept of the electron binding energy and its relationship to the energy of the incident X-ray and the emitted photoelectron was introduced

=> What the quantities that affect the E_B magnitude?

How measurement of the E_B can be used to characterize materials?

Chemical Shifts

depend on the bonding environment around the atom, in particular, on the oxidation state of the atom

Electron Spectroscopy for Chemical Analysis

Binding Energy Reflects the Electronic Environment of an Atom

The binding energy of a core electron is primarily determined by the electrostatic interaction between the electron and the nucleus.

$$E_B \propto \text{interaction between the nucleus and the electron}$$

Major factors affecting E_B

- Nuclear charge (Z)

  A larger nuclear charge generally results in stronger attraction of the electron.

- Electron shell and orbital

  Electrons closer to the nucleus are more strongly bound.

- Shielding by other electrons

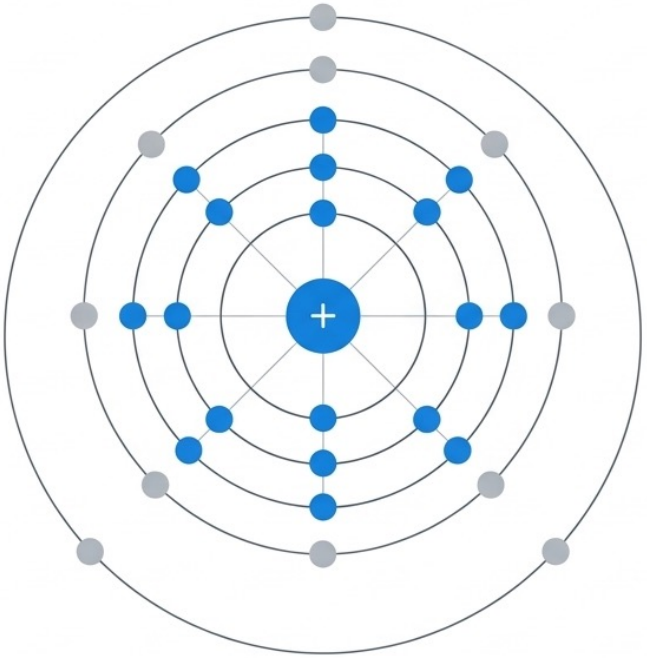
  Inner and outer electrons modify the effective nuclear charge experienced by a core electron.

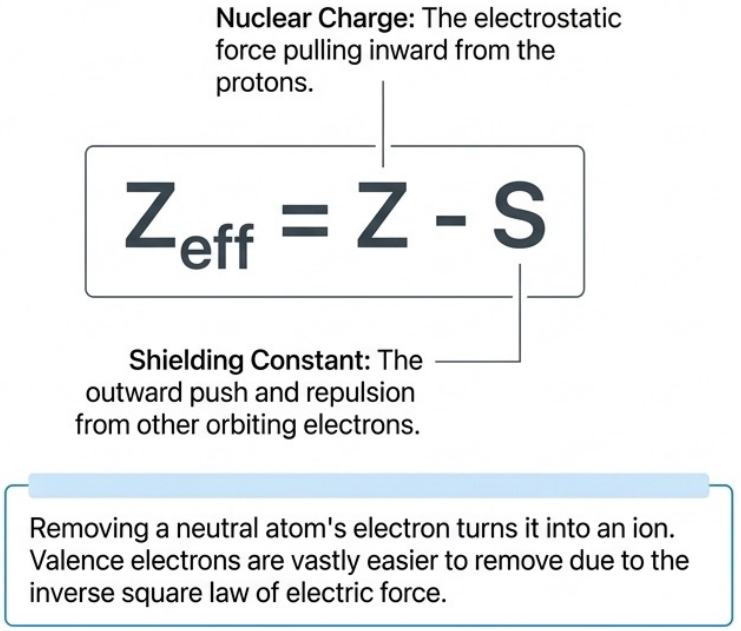
Electron Spectroscopy for Chemical Analysis

Binding Energy Reflects the Electronic Environment of an Atom

$Z_{eff} = Z - S$ (Effective Nuclear Charge = Atomic Number − Shielding Constant)

- Local chemical environment
  Bonding and charge transfer change the electron density around an atom.





Electron Spectroscopy for Chemical Analysis

Binding Energy Reflects the Electronic Environment of an Atom

- How Chemical Environment Shifts Peak Positions

Step 01. Oxidation State Changes

-> Atom loses valence electrons (e.g., Cu^0 -> Cu^{+1}).

Step 02. Shielding (S) Drops

-> Lower electron density means less repulsion between remaining electrons.

Step 03. Nucleus Pulls Harder.

->Z_{eff} increases, gripping core electrons more tightly.

- Naive Expectation:

Higher Oxidation State -> Smaller Shielding (S) -> **Higher Binding Energy (E_B).**

Note: While this rule works perfectly for most main-group elements, it heavily breaks down in transition metals.

Electron Spectroscopy for Chemical Analysis

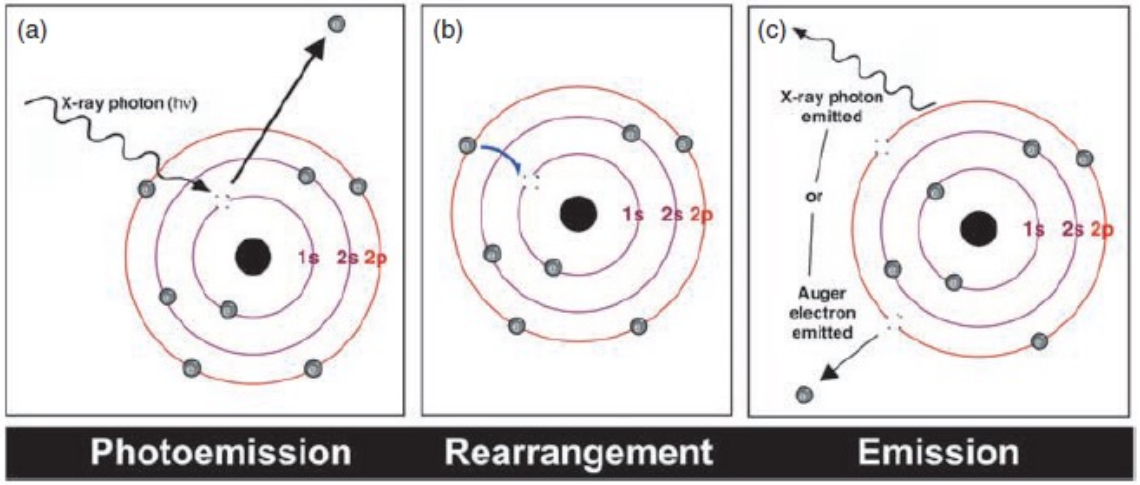
Binding Energy and the Chemical Shift

KOOPMANS' THEOREM

The E_B of an emitted photoelectron is simply the energy difference between the (n – 1)–electron final state and the n–electron initial state (see below).
This is written as:

$$E_B = E_f(n - 1) - E_i(n)$$

where $E_f(n - 1)$ is the final state energy and $E_i(n)$ is the initial state energy



(a) The X–ray photon transfers its energy to a core–level electron leading to photoemission from the *n*–electron initial state.

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

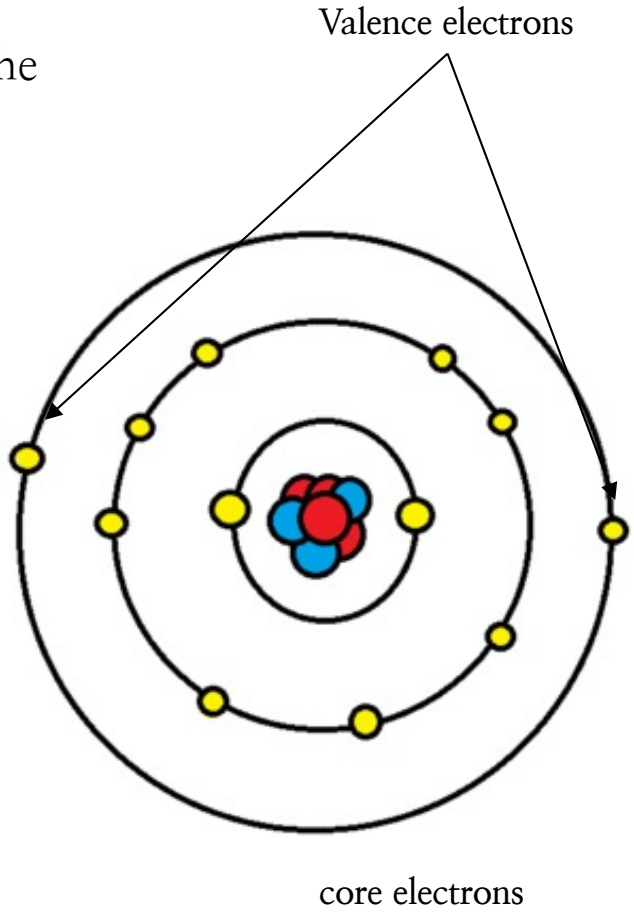
Valance and Core electrons

Valence electrons are the electrons orbiting the nucleus in the outermost atomic shell of an atom.

Electrons that are closer to the nucleus are in filled orbitals and are called **core electrons.**

Valence electrons are the farthest from the positive charge (the protons) and thus tend to be easier to remove than core electrons; this means that it takes them less energy to move far away from the atom. This difference comes from the electric force being an inverse square law. Removing an electron (any of them) from a neutral atom turns the atom into an ion.

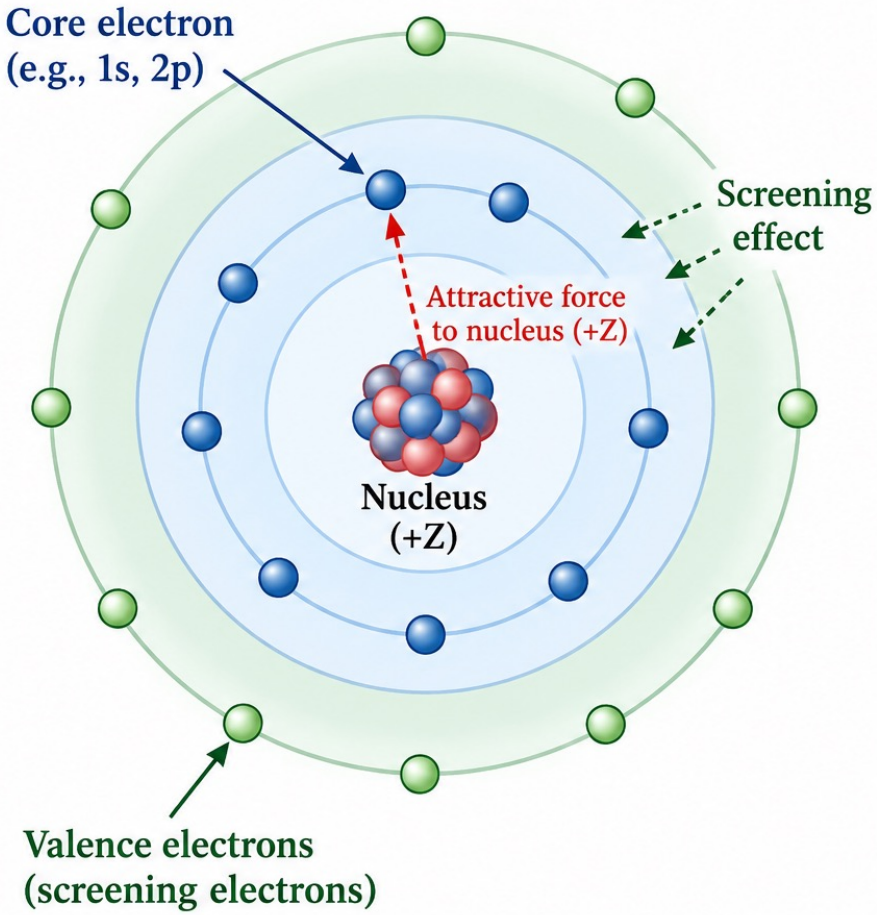
Valence electrons also tend to be the electrons that specifically participate in a chemical bond, like ionic bonds or covalent bonds.



Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

Valance and Core electrons



Core electron

- Strongly attracted to the nucleus by Coulombic interaction.
- Its binding energy depends on the effective nuclear charge (Z_{eff}).

Valence electrons

- Partially screen (shield) the nuclear charge.
- Reduce the effective nuclear charge felt by the core electron.
- Changes in the valence electron density (e.g., due to chemical bonding or oxidation state) lead to shifts in the core-level binding energy.

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

KOOPMANS' THEOREM

If no rearrangement of other electrons in the atom or material occurred during the photoemission process, then the observed E_B would be just the negative orbital energy, $-\varepsilon_k$ for the ejected photoelectron.

This approximation comes from Koopmans' theorem and is written as:

$$E_B \approx -\varepsilon_k$$

The values of ε_k can be calculated using the Hartree–Fock method.

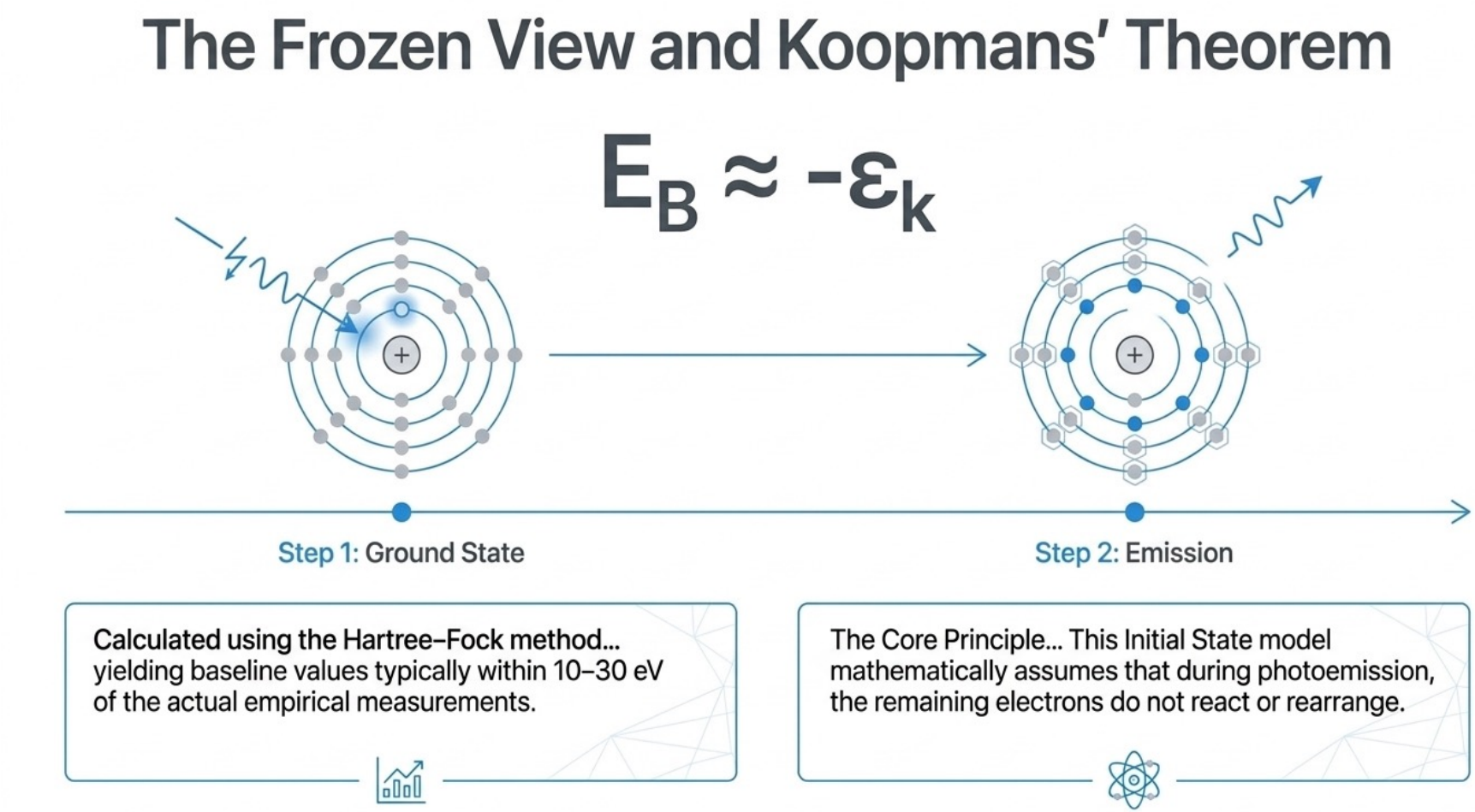
The values of ε_k can be calculated using the Hartree–Fock method. These values are typically within 10–30 eV of the actual E_B values.

The disagreement between E_B and $-\varepsilon_k$ is because Koopmans' theorem and the Hartree–Fock calculation method do not provide a complete accounting of the quantities that contribute to E_B

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

KOOPMANS' THEOREM

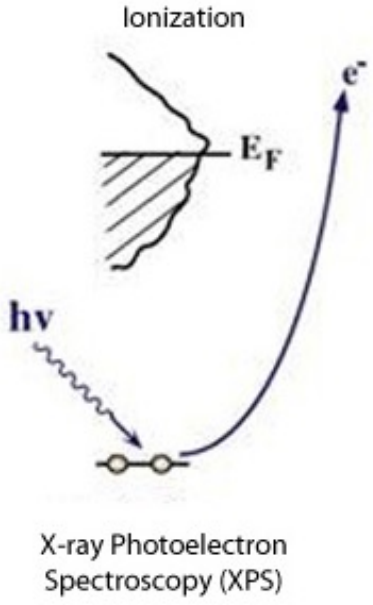


Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

KOOPMANS' THEOREM

In particular, the assumption that other electrons remain 'frozen' during the photoemission process is not valid.
During emission of the photoelectron, other electrons in the sample will respond to the creation of the core hole by rearranging to shield, or minimize, the energy of the ionized atom.



X-ray Photoelectron Spectroscopy (XPS)

The energy reduction caused by this rearrangement of electrons is called the 'relaxation energy'

Relaxation occurs for both electrons on the atom containing the core hole (atomic relaxation) and on surrounding atoms (extra-atomic relaxation)

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

KOOPMANS' THEOREM

- Koopmans' / Hartree-Fock Approximation: Assumes other electrons stay completely "frozen" when an electron is emitted ($E_B = -\varepsilon k$).
- The Reality: The system is highly dynamic, not frozen. Three major physical phenomena are neglected in the simple view.

Thus, a more complete description of E_B is given by:

$$E_B = -\varepsilon_k - E_r(k) - \delta\,\varepsilon_{corr} - \delta\,\varepsilon_{rel}$$

Where, $E_r(k)$ is the relaxation energy

$\delta\,\varepsilon_{corr}$ and $\delta\,\varepsilon_{rel}$ are corrections for the differential correlation and relativistic energies.

-> Both the correlation and relativistic terms are typically small and usually can be neglected.

Electron Spectroscopy for Chemical Analysis

What Makes Up the Real Binding Energy E_B?

When an electron is ejected, the atom undergoes an immediate quantum-level adjustment:

1. Relaxation Energy (E_r) : *The Rush*

   The sudden loss of an electron leaves a "core hole" (+ charge).

   Surrounding electrons immediately collapse inward to screen this new charge, releasing extra energy.

2. Electron Correlation ($\delta\,\varepsilon_{corr}$) : *The Social Distancing*

   Electrons don't just sit around in a smooth cloud; they actively dodge and avoid each other.

   Simple models forget this "cooperative movement."

3. Relativistic Effects ($\delta\,\varepsilon_{rel}$) : *The Speed Zone*

   In heavy atoms, inside electrons circle the nucleus at near the speed of light.

   This extreme speed changes their mass and artificially alters the expected energy.

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

INITIAL STATE EFFECTS

Again

The E_B of an emitted photoelectron is simply the energy difference between the (n – 1) electron final state and the (n) electron initial state (see below).

This is written as:

$$E_B = E_f(n-1) - E_i(n)$$

=〉 both initial and final state effects contribute to the observed E_B.

the binding energy is equal to the difference in energies between the atom with n electrons [$E_i(n)$]and the ion with n – 1 electrons [$E_f(n-1)$]

The initial state is just the ground state of the atom prior to the photoemission process

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

INITIAL STATE EFFECTS

If the energy of the atom's initial state is changed by formation of chemical bonds with other atoms, then the E_B of electrons in that atom will change.

The change in E_B, ΔE_B, is called the chemical shift.

To a first approximation,
All core-level E_B for an element will undergo the same chemical shift

〈Example〉
If a silicon atom is bound to a chlorine atom, i.e. a Si—Cl bond, the chemical shift for the Si2p and Si2s Si—Cl peaks relative to the position of the Si^0 state for each peak will be similar.

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

INITIAL STATE EFFECTS

Initial state effects are responsible for the observed chemical shifts,
as the formal oxidation state of an element increases, the E_B of photoelectrons ejected from that element will increase.

final state effects such as relaxation have similar magnitudes for different oxidation states.

For most samples, the interpretation of E_B solely in terms of initial state effects

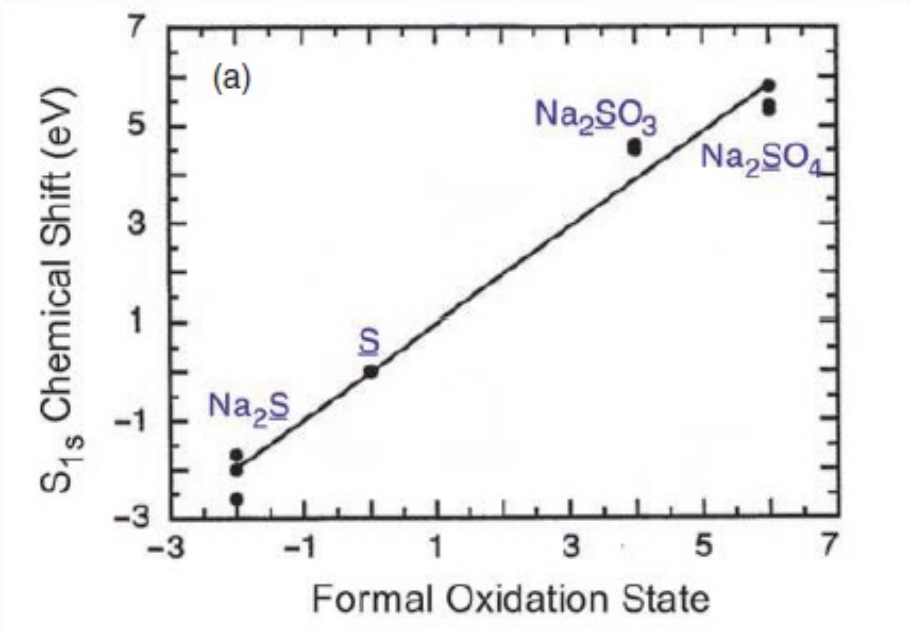
$$E_B = -\Delta\varepsilon_k$$

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

INITIAL STATE EFFECTS

Correlation between the initial state of an element and its E_B



E_B for the S1s orbital increased by nearly 8 eV as the formal oxidation state of sulfur increased from −2 (Na_2S) to +6 (Na_2SO_4)

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

INITIAL STATE EFFECTS

Correlation between the initial state of an element and its E_B

Functional group		Binding energy (eV)
Hydrocarbon	C—H, C—C	285.0
Amine	C—N	286.0
Alcohol, ether	C—O—H, C—O—C	286.5
Cl bound to carbon	C—Cl	286.5
F bound to carbon	C—F	287.8
Carbonyl	C=O	288.0
Amide	N—C=O	288.2
Acid, ester	O—C=O	289.0
Urea	N—C(=O)—N	289.0
Carbamate (urethane)	O—C(=O)—N	289.6
Carbonate	O—C(=O)—O	290.3
2F bound to carbon	$—CH_2CF_2—$	290.6
Carbon in PTFE	$—CF_2CF_2—$	292.0
3F bound to carbon	$—CF_3$	293–294

[a]The observed binding energies will depend on the specific environment where the functional groups are located. Most ranges are ±0.2 eV, but some (e.g., fluorocarbon samples) can be larger.

Typical C 1s binding energies for organic samples

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

INITIAL STATE EFFECTS

Correlation between the initial state of an element and its E_B

Functional group		Binding energy (eV)
Carbonyl	C=O, O–C=O	532.2
Alcohol, ether	C–O–H, C–O–C	532.8
Ester	C–O–C=O	533.7

[a]The observed binding energies will depend on the specific environment where the functional groups are located. Most ranges are ±0.2 eV.

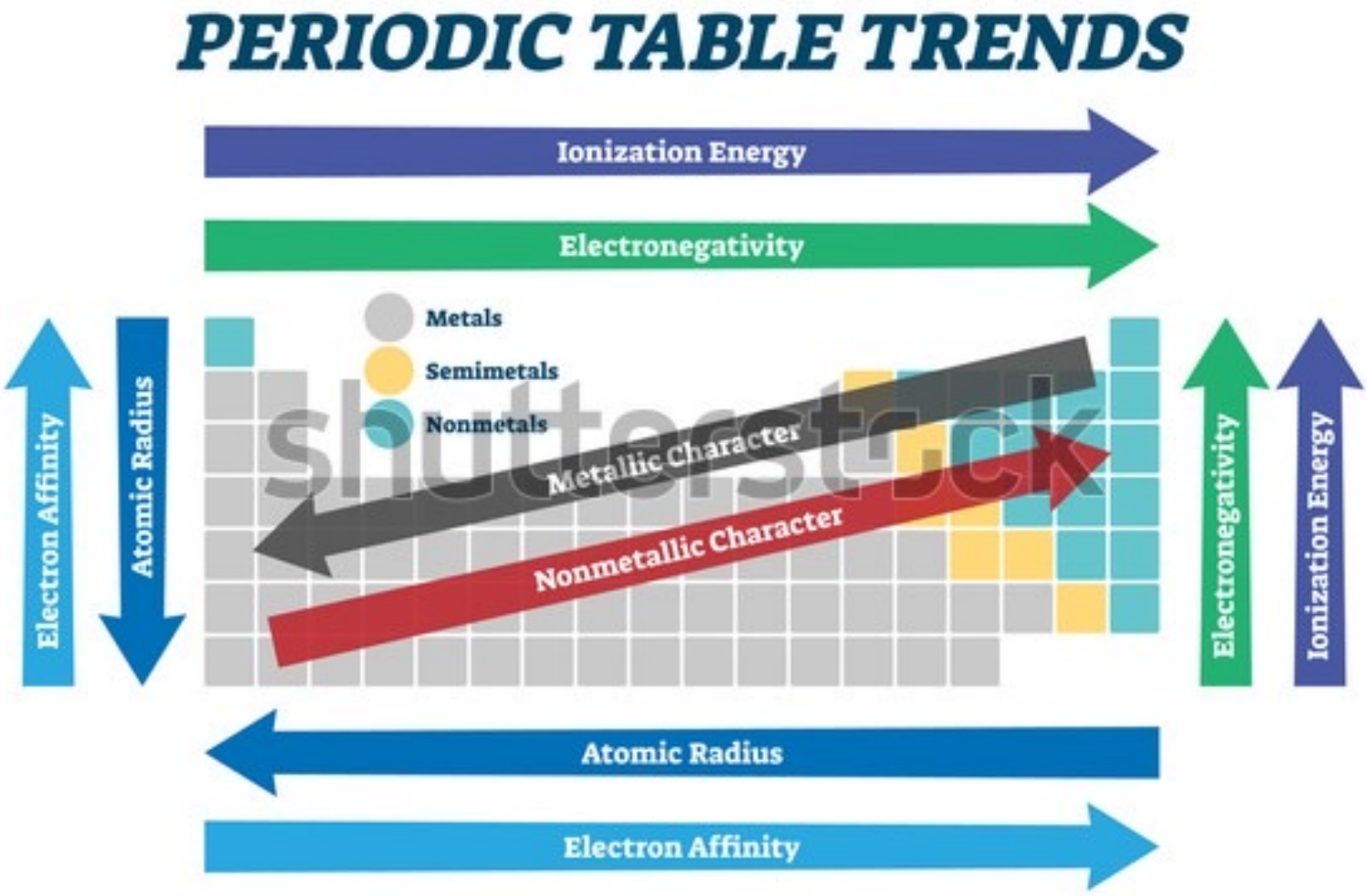
Typical O 1s binding energies for organic samples

The C1s E_B is observed to increase monotonically as the number of oxygen atoms bonded to carbon increases (C–C < C–O < C=O < O–C=O < O–(C=O)O–), since oxygen is more electronegative than carbon and will draw electrons away from carbon.

This is consistent with an initial state effect, since, as the number of oxygen atoms bonded to a carbon increase, the carbon should become more positively charged, resulting in an increase in the C1s E_B.

Electron Spectroscopy for Chemical Analysis

Electronegativity (전기음성도)



Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

INITIAL STATE EFFECTS

A caution must be made against solely using initial state effects for interpreting chemical shifts.
There are examples where final state effects can significantly alter the relationship between the formal oxidation state and E_B.

Also, it is the changes in the distribution and density of electrons of an atom resulting from changes in its chemical environment that contribute to E_B.

These quantities do not necessarily have a straightforward relationship to the formal oxidation state.

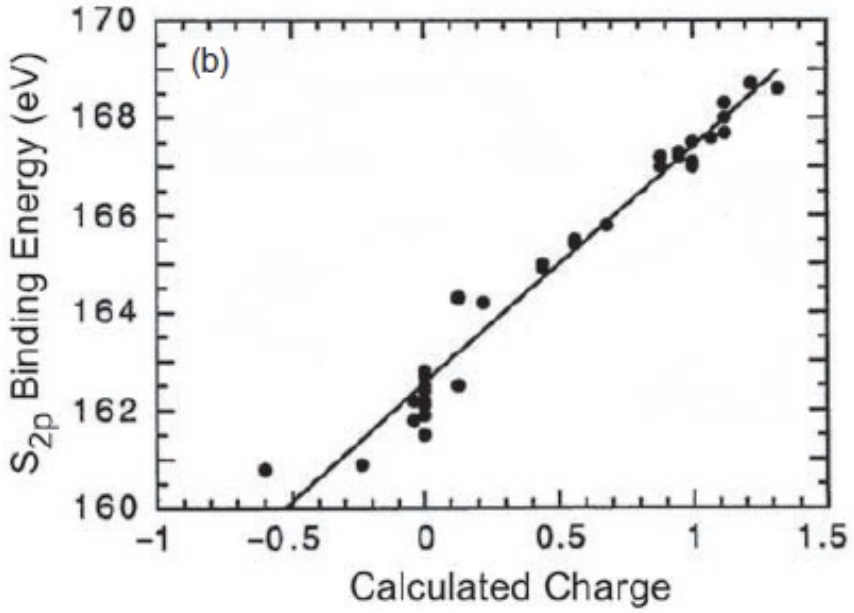
For example,
Formal oxidation states only give the full charge in 100% ionic bonds. Because most bonds share electrons (covalent character), the real charge on an atom changes depending on its environment. Therefore, **we should E_B to the atom's actual charge, not just its official oxidation number.**

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

Consistent correlations for both inorganic and organic sulfur species

Linear relationship observed for the S 2p E_B versus calculated charge on the sulfur (S) atom



The sulfur(S) 2p binding energy versus calculated charge for several inorganic and organic sulfur species.

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

Charge potential model

This model relates the observed E_B to a reference energy E^0_B, the charge q_i on atom i, and the charge q_j on the surrounding atoms j at distances r_{ij} as follows:

$$E_B = E_B^\circ + kq_i + \sum_{j \neq i} (q_j / r_{ij})$$

with the constant k. Generally, the reference state is considered to be E_B for the neutral atom.

It is then apparent that, as the positive charge on the atom increases by formation of chemical bonds, E_B will increase.

Madelung potential because of its similarity to the lattice potential of a crystal,

$$V_i = \Sigma(q_j / r_{ij}).$$

This term represents the fact that the charge q_i removed or added by formation of a chemical bond is not displaced to infinity, but rather to the surrounding atoms.

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

Charge potential model

Using following Equation $E_B = E_B^\circ + kq_i + \sum_{j \neq i}(q_j/r_{ij})$

chemical shift between states 1 and 2 can now be written as:

$$\Delta E_B = k[q_i(2) - q_i(1)] + V_i(2) - V_i(1)$$

$$\Delta E_B = k\Delta q_i + \Delta V_i$$

Where, ΔV_i the potential change in the surrounding atoms

Electron Spectroscopy for Chemical Analysis

INITIAL STATE EFFECT

- **Concept:** "The Frozen View"

  The electronic structure of the atom BEFORE photon absorption (Ground state).

- **Key Driving Forces:**

  Chemical oxidation state (e.g., $Si^{0} \rightarrow Si^{+1}$).

  Local electrostatic potential changes around the nucleus.

  Structural bonding and coordination environment.

- **Real-World Case (Silicon):**

  Highly Predictable & Uniform.

  When Si bonds with Cl, valence electrons are drawn away, altering the inner potential field uniformly. Both Si 2s and 2p core lines shift by virtually the same energy amount (ΔE_B).

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

FINAL STATE EFFECTS

Relaxation effects can have a significant impact on the measured E_B. In all cases the electron rearrangements that occur during photoemission result in the lowering of E_B.

If the magnitude of the relaxation energy varies significantly as the chemical environment of an atom is changed, the E_B ranking that would be expected based on initial state considerations, can be altered

the ranking of the $Co_{2p3/2}$ E_B values

$$Co^0\ (778.2\,eV) < Co^{+3}\ (779.6\,eV) < Co^{2+}\ (780.5\,eV)$$

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

FINAL STATE EFFECTS

For Copper

both Cu^0 and Cu^{+1} have $2_{p3/2}$ but, E_B values of 932.5 eV ($\Delta E_B \approx 0$)

=> for the Co and Cu systems, final state effects cause deviations in the E_B versus oxidation state ranking expected from initial state considerations

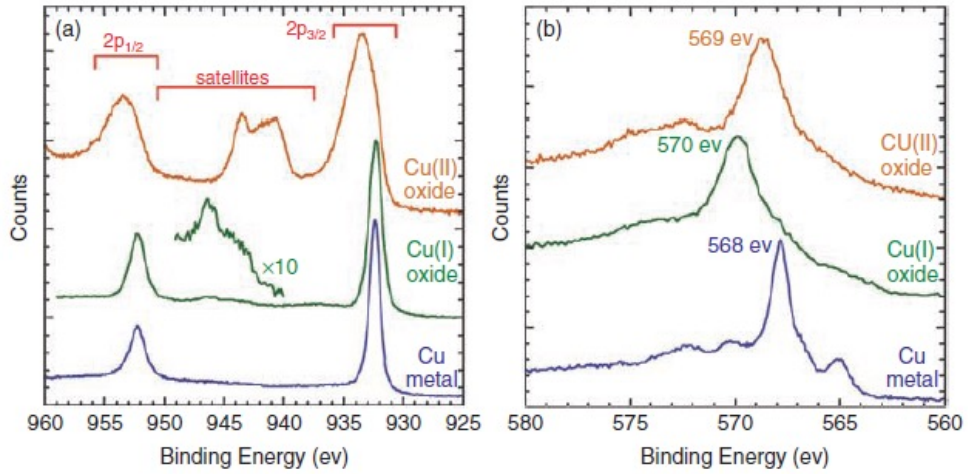


Figure 3.4 (a) The copper 2p photoemission spectra for metallic Cu (Cu^0), Cu_2O (Cu^{+1}) and CuO (Cu^{+2}). (b) The X-ray induced copper Auger LVV spectra for metallic Cu (Cu^0), Cu_2O (Cu^{+1}) and CuO (Cu^{+2})

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

FINAL STATE EFFECTS

Final State Effects in Copper

- The Initial State Misconception

  Based solely on $Z_{eff} = Z - S$

  Cu^{+1} has lower electron density than Cu^{0}

  Expectation: Smaller shielding (S) -> Higher E_B for Cu^{+1}

- The Reality (Experimental Observation)

  Paradoxical overlap of Cu $2p_{3/2}$ peaks

  Both Cu^{0} and Cu^{+1} appear around **932.5 eV**

- The Origin: Final State Screening

  Photoemission leaves behind a core hole.

  Orbital relaxation and polarization stabilize the core hole.

  Differential screening counterbalances the initial state energy difference.

Electron Spectroscopy for Chemical Analysis

FINAL STATE EFFECT

- **Concept:** "The Dynamic Response"

  The sudden rearrangement of remaining electrons AFTER photoelectron ejection.

- **Key Driving Forces:**

  Core-hole screening & polarization.

  Orbital Relaxation (E_r): Remaining electrons collapse inward to shield the core hole.

  Multiplet splitting & Shake-up features.

- **Real-World Case (Copper/Cobalt):**

  Anomalous & Peak-Specific.

  Dynamic final-state screening heavily dictates the spectrum. Relaxation energy varies between states, completely erasing the expected initial-state chemical shift (e.g., Cu^0 and Cu^{+1} peaks overlap perfectly at ~932.5 eV).

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

FINAL STATE EFFECTS

Contributions to the relaxation energy arise from both the atom containing the core hole (atomic relaxation) and its surrounding atoms (extra-atomic relaxation).
Most of the atomic relaxation component results from rearrangement of outer shell electrons, which have a **smaller E_B than the emitted photoelectron.**

In contrast, the inner shell electrons (E_B larger than the emitted photoelectron) make only a small contribution to the atomic relaxation energy and can usually be neglected.

For electrically conducting samples such as metals, valence band electrons can move from one atom to the next to screen the core hole.

For ionically bonded solids such as the alkali halides, electrons are not free to move from one atom to the next

Electron Spectroscopy for Chemical Analysis

Binding Energy and the Chemical Shift

FINAL STATE EFFECTS

Other types of final state effects such as multiplet splitting and shake-up satellites can contribute to E_B.

Multiplet splitting
arises from interaction of the core hole with unpaired electrons in the outer shell orbitals

Shake-up
satellites arise from the outgoing photoelectron losing part of its kinetic energy to excite a valence electron into an unoccupied orbital
(e.g. $\pi \rightarrow \pi^*$ transition).

Electron Spectroscopy for Chemical Analysis

Binding Energy Referencing

E_B is determined by measuring the KE of the emitted photoelectron

-> a calibrated and suitably referenced ESCA spectrometer is required!

How to set up an ESCA spectrometer to measure accurately the photoelectron KE (and therefore E_B) for different types of samples.

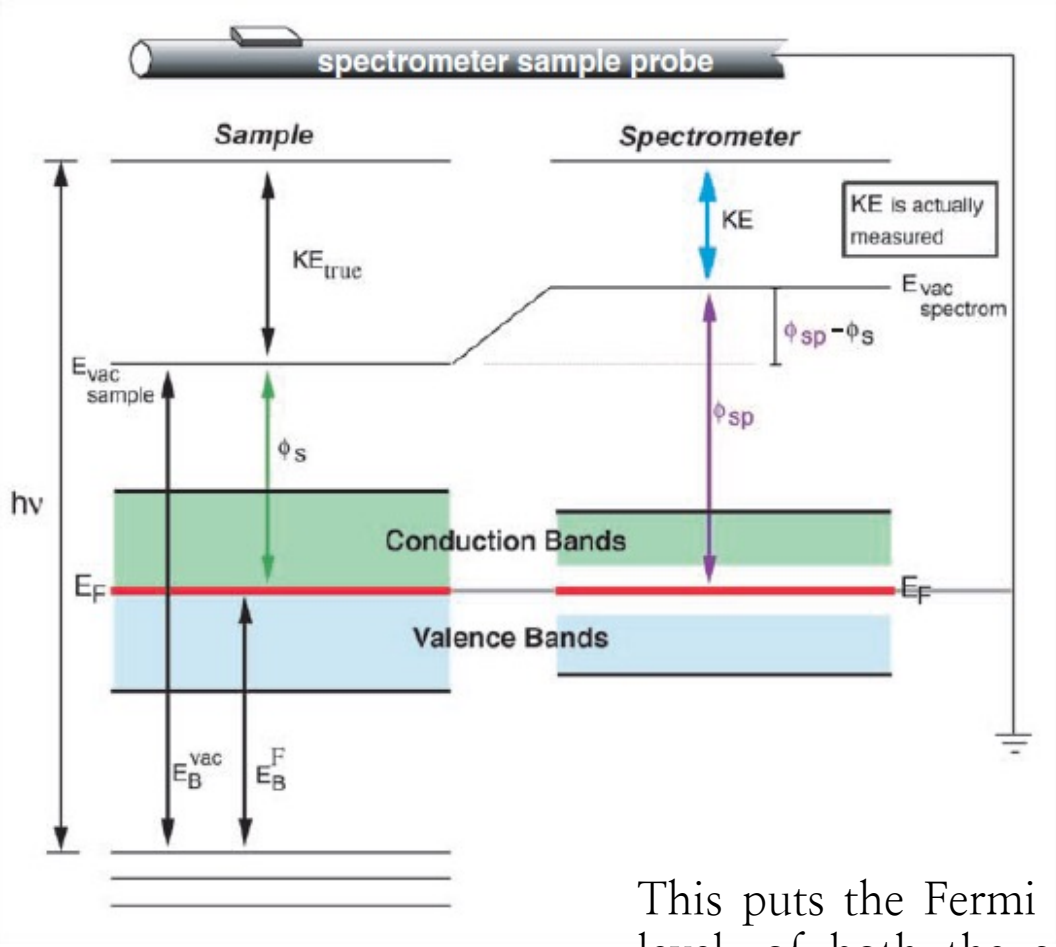
Conducting samples

metals are placed in electrical contact with the spectrometer, typically by grounding both the sample and the spectrometer.
This puts the Fermi level (E_F), the highest occupied energy level, of both the sample and spectrometer, at the same energy level.

Binding Energy Referencing

Electron Spectroscopy for Chemical Analysis

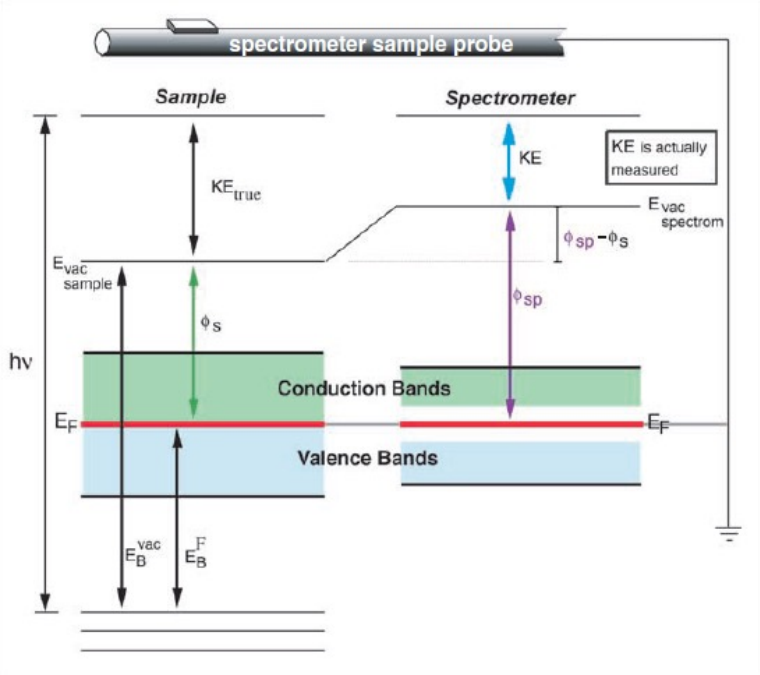
Binding Energy Referencing



This puts the Fermi level (E_F), the highest occupied energy level, of both the sample and spectrometer, at the same energy level.
Then the photoelectron KE can be measured

Electron Spectroscopy for Chemical Analysis

Binding Energy Referencing



The sum of the KE and E_B does not exactly equal the X-ray energy

The difference is the work function of the spectrometer (ϕ_{sp})

The work function, ϕ, is related to the E_F and vacuum level (E_{vac}) by:

$$\phi = E_F - E_{vac}$$

ϕ is the minimum energy required to eject an electron from the highest occupied level into vacuum. The Einstein equation now becomes:

$$E_B^F = h\nu - KE - \phi_{sp}$$

both KE and ϕ_{sp} must be measured to determine E^F_B.
The superscript F on E_B means that E_B is referenced to E_F.

Electron Spectroscopy for Chemical Analysis

Binding Energy Referencing

Calibration for conducting samples

The work function of the spectrometer (ϕ_{sp}) that is important

Can be calibrated by placing a clean Au standard in the spectrometer and adjusting the instrumental settings such that the known E_B values for Au are obtained (e.g. $E_F = 0$ eV, Au $4f_{7/2} = 83.96$ eV).

The linearity of the E_B scale is then calibrated by adjusting the energy difference between two widely spaced lines of a sample (e.g. the 3s and $2p_{3/2}$ peaks of clean Cu) to their known values.

ISO Standard 15472:2001 https://www.iso.org/standard/55796.html

Surface chemical analysis — X-ray photoelectron spectrometers — Calibration of energy scales

Electron Spectroscopy for Chemical Analysis

Binding Energy Referencing

Validity of Calibration

Once the spectrometer energy scale has been calibrated, it is assumed to remain constant.

This is valid as long as the spectrometer is maintained in an UHV environment.

If the pressure of the spectrometer is raised above the UHV range, particularly when exposed to a reactive gas, different species can adsorb to components in the analyzer.

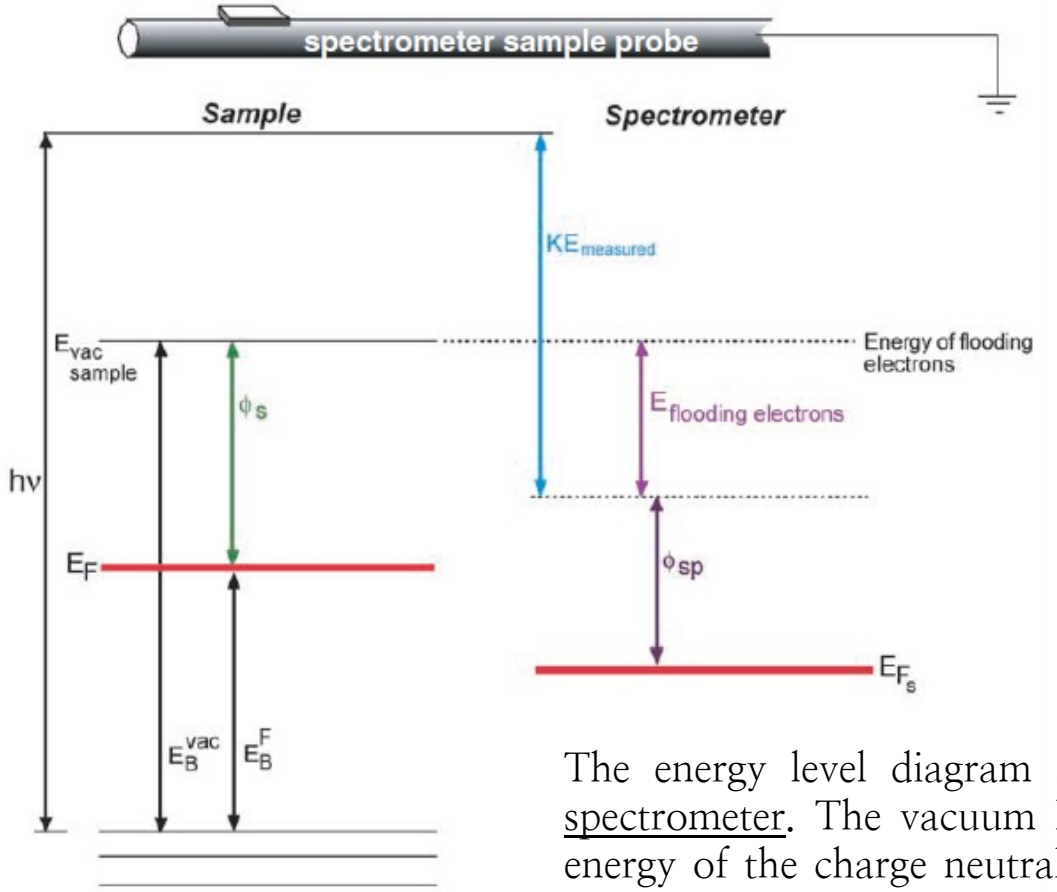
This will change the ϕ_{sp} and necessitate recalibration.

It is always good practice to regularly (i.e., daily to weekly) check the instrument calibration.

Electron Spectroscopy for Chemical Analysis

Charge Compensation in insulators

When some materials do not have sufficient electrical conductivity or cannot be mounted in electrical contact with the ESCA spectrometer.

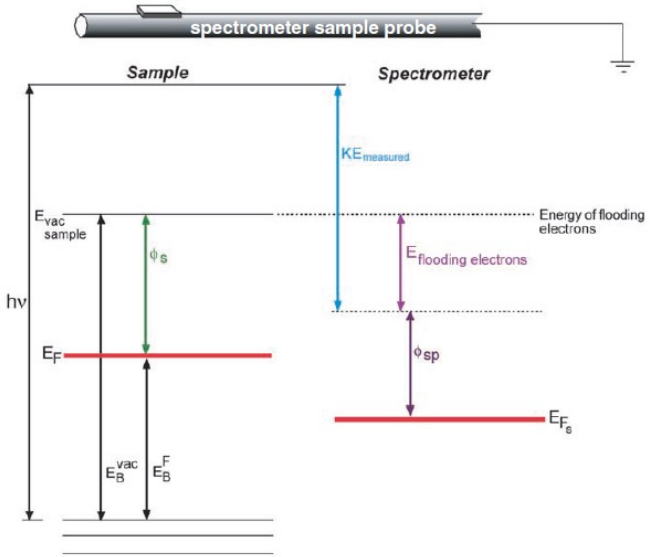


The energy level diagram for a sample electrically insulated from the spectrometer. The vacuum level of the sample (E^{s}_{vac}) is aligned with the energy of the charge neutralization electrons (ϕ_s) so that E_B is referenced with respect to ϕ_e. The measurement of E_B is dependent on the sample work function, ϕ_s

Electron Spectroscopy for Chemical Analysis

Charge Compensation in insulators

Insulating samples



the measured E_B of an insulated sample depends on its work function (ϕ_s) and the energy of the flooding electrons, ϕ_e,

$$E_B^{vac} = E_B^F + \phi_s = h\nu - KE + \phi_e$$

for insulators E_B is referenced to E_{vac} and ϕ_e.

This makes it difficult or impossible to measure absolute E_B values for samples not in electrical contact with the spectrometer.

For polymer and organic samples, the hydrocarbon component (C–C/C–H) of the C1s peak is typically set to 285.0 eV.

For supported catalysts, a major peak of the oxide support (Si2p, Al2p, etc.) is typically used. Internal referencing of the E_B scale allows the accurate measurement of other E_B values in the sample.

Electron Spectroscopy for Chemical Analysis

Charge Compensation in insulators

Insulating samples

- The Challenge: Surface Charging
  - Insulators cannot conduct electrons from the ground to replace ejected photoelectrons.
  - The surface becomes positively charged (+), pulling photoelectrons back.
  - *Result:* Measured kinetic energy (KE) drops -> **Artificial upward shift in Binding Energy (E_B)**.
- The Solution: Charge Compensation
  - Using a **Flood Gun** to supply low-energy electrons onto the insulator surface.
  - Neutralizes the positive surface charge to restore the true, unshifted XPS peak positions.

Electron Spectroscopy for Chemical Analysis

Charge Compensation in insulators

Effect of flooding electrons

Usually the energy of the flooding electrons is varied to obtain the narrowest width of the photoemission peak

→ It is important to have the entire sample either electrically grounded or fully isolated!!

A sample in partial electrical contact with the spectrometer can lead to differential charging, which will produce distorted peak shapes and, under extreme conditions, new peaks

Must be **aware of the electrical properties of the sample** and **how they can affect the ESCA experiment.**

Electron Spectroscopy for Chemical Analysis

Charge Compensation in insulators

Effect of flooding electrons

Example

a conducting metal substrate with a thin (~5nm or less) insulating overlayer can usually be analyzed with the sample grounded.

However, if the insulating overlayer becomes too thick (**~10nm or more**), differential charging can occur.

Then the entire sample must be electrically isolated from the spectrometer for proper analysis.

For samples with electrical properties that vary with location on the sample, carefully designed experiments can be used to gain further information about the electrical and **spatial** properties of a sample

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