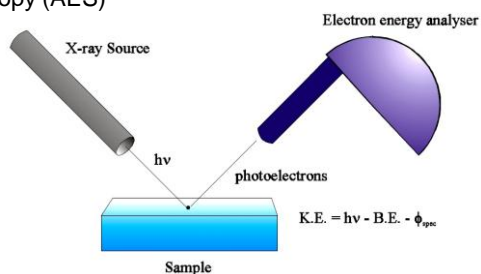


## Lecture 7

### X-ray Photoelectron Spectroscopy (XPS)

- 7. Photoemission Spectroscopy (XPS)
  - 7.1 Principles
  - 7.2 Interpretation
    - 7.2.1 Notations
    - 7.2.2 Electron workfunction
    - 7.2.3 Chemical shifts
  - 7.3 Instrumentation
  - 7.4 XPS vs UV photoelectron spectroscopy (UPS)
  - 7.5 Auger Electron Spectroscopy (AES)
  - 7.6 Quantitative Analysis

Appendix I:  
Workfunction  
Electron Emission



## References

- 1) Vickerman, Chapter 2 and 3
- 2) Zangwill; Chapter 2, pp. 20-24 and 4
- 3) Kolasinski, Chapter 2.6
- 4) Woodruff, and Delchar, Chapter 3
- 5) Briggs, Seah, *Practical Surface Analysis*. 1991; Vol. 1.
- 6) Luth, Chapter 6

Useful web-sites:

- 1) <http://www.phy.cuhk.edu.hk/course/surfacesci/index2.html>
- 2) <http://www.chem.qmul.ac.uk/surfaces/scc/>
- 3) <http://www.cem.msu.edu/~cem924sg/>

Electron Spectroscopy for Chemical Analysis

Spectroscopy	Particles involved	Incident Energy	What you learn
XPS X-ray Photoelectron	X-ray in e out	1-4 keV	Chemical state, composition
UPS UV Photoelectron	UV photon e out	5-500 eV	Valence band
AES Auger Electron	e in, e out; radiationless process, filling of core hole	1-5 keV	Composition, depth profiling
IPS Inverse Photoelectron	e in photon out	8-20eV	Unoccupied states
EELS Electron Energy Loss	e in e out	1-5 eV	Vibrations

3

7.1 Photoemission Spectroscopy: Principles

Electrons absorb X-ray photon and are ejected from atom  
 Energy balance:

Photon energy
 

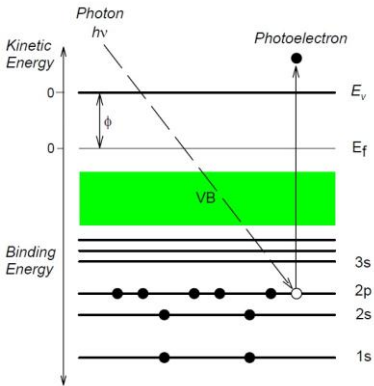
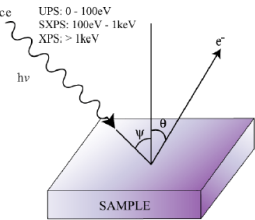
$h\nu$

− Kinetic Energy
 

$- KE$

= Binding Energy
 

$= BE$

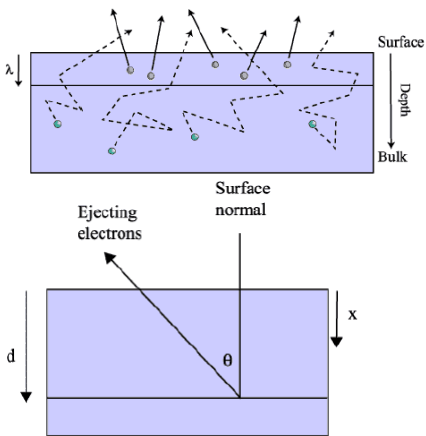


- Spectrum – Kinetic energy distribution of photoemitted e’s
- Different orbitals give different peaks in spectrum
- Peak intensities depend on photoionization cross section (largest for C 1s)
- Extra peak: Auger emission

4

Photoelectron Spectroscopy: Basics

Electrons from the sample surface:



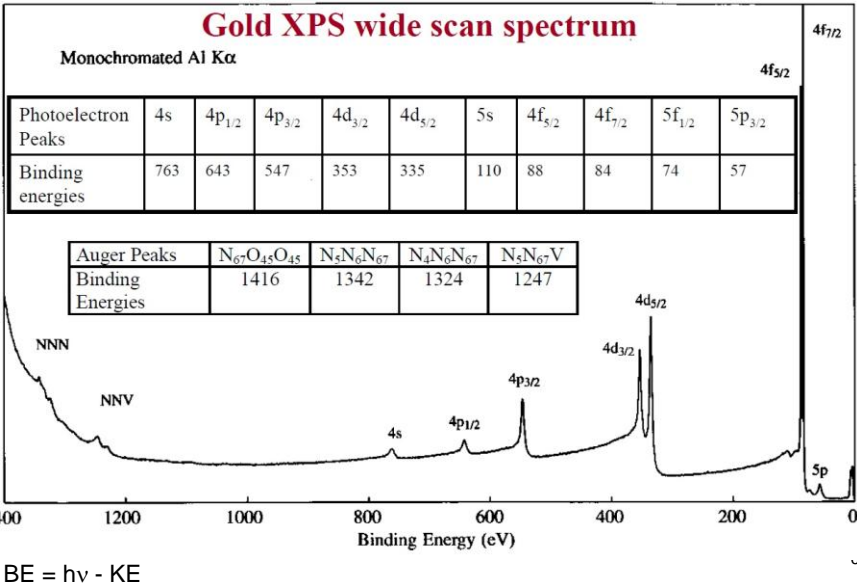
$$I(d) = K \int_0^d \exp\left(\frac{-x}{\lambda \cos \theta}\right) dx$$

Fraction of signal from various depth in term of λ

Depth	Equation	Fraction of signal ( θ= 0)
λ	$\frac{I(\lambda)}{I(\infty)} = \frac{\int_0^\lambda \exp\left(\frac{-x}{\lambda \cos \theta}\right) dx}{\int_0^\infty \exp\left(\frac{-x}{\lambda \cos \theta}\right) dx}$	0.63
2λ	$\frac{I(2\lambda)}{I(\infty)} = \frac{\int_0^{2\lambda} \exp\left(\frac{-x}{\lambda \cos \theta}\right) dx}{\int_0^\infty \exp\left(\frac{-x}{\lambda \cos \theta}\right) dx}$	0.86
3λ	$\frac{I(3\lambda)}{I(\infty)} = \frac{\int_0^{3\lambda} \exp\left(\frac{-x}{\lambda \cos \theta}\right) dx}{\int_0^\infty \exp\left(\frac{-x}{\lambda \cos \theta}\right) dx}$	0.95

1. C. J. Powell, A. Jablonski, S. Tanuma, et al. *J. Electron Spectrosc. Relat. Phenom*, 68, P. 605 (1994).
- 2 D. F. Mitchell, K. B. Clark, W. N. Lennard, et al. , *Surf. Interface Anal.* 21, P. 44 (1994).

7.2 Typical XPS (ESCA) spectrum



7.2.1 X-ray and spectroscopic notations

	Quantum numbers			X-ray suffix	X-ray level	Spectroscopic Level
	<i>n</i>	<i>l</i>	<i>j</i>			
Principle quantum number: <i>n</i> = 1, 2, 3, ...	1	0	1/2	1	K	1s <sub>1/2</sub>
Orbital quantum number: <i>l</i> = 0, 1, 2, ..., ( <i>n</i> -1)	2	0	1/2	1	L <sub>1</sub>	2s <sub>1/2</sub>
	2	1	1/2	2	L <sub>2</sub>	2p <sub>1/2</sub>
Spin quantum number: <i>s</i> = ± ½	2	1	3/2	3	L <sub>3</sub>	2p <sub>3/2</sub>
	3	0	1/2	1	M <sub>1</sub>	3s <sub>1/2</sub>
Total angular momentum: <i>j</i> = <i>l</i> + <i>s</i> = 1/2, 3/2, 5/2	3	1	1/2	2	M <sub>2</sub>	3p <sub>1/2</sub>
	3	1	3/2	3	M <sub>3</sub>	3p <sub>3/2</sub>
	3	2	3/2	4	M <sub>4</sub>	3d <sub>3/2</sub>
	3	2	5/2	5	M <sub>5</sub>	3d <sub>5/2</sub>
<b>Spin-orbit split doublets</b>	Etc.			Etc.	Etc.	Etc.

Sub-shell	<i>j</i> values	Area ratio
<i>s</i>	1/2	-
<i>p</i>	1/2; 3/2	1: 2
<i>d</i>	3/2; 5/2	2: 3
<i>f</i>	5/2; 7/2	3: 4

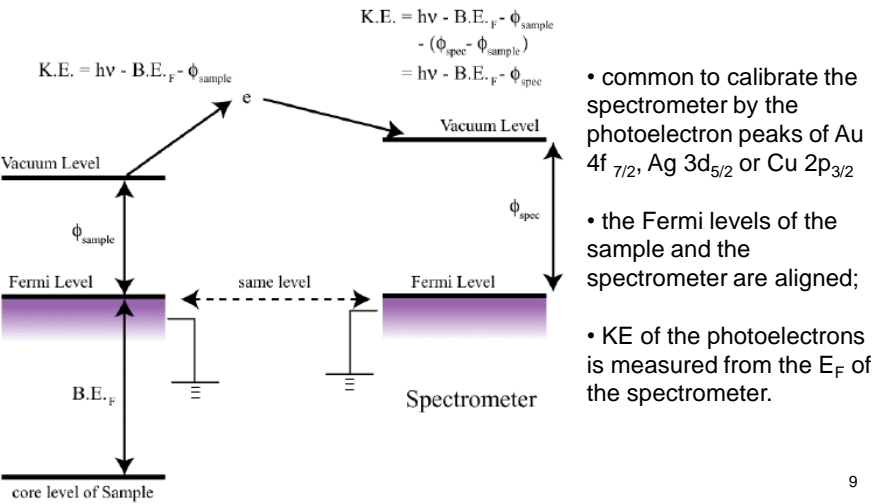
7

- Determine all of the X-ray levels that all possible for *n*=3 shell?

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## Binding energy reference in XPS

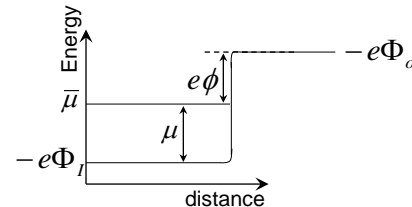
Energy level diagram for an electrically conductive sample grounded to the spectrometer



## 7.2.2 Work Function: Uniform Surfaces

- The “true work function”  $e\phi$  of a uniform surface of an electronic conductor is defined as the difference between the electrochemical potential  $\bar{\mu}$  of the electrons just inside the conductor, and the electrostatic potential energy  $(-e\Phi_o)$  of an electron in the vacuum just outside

- $\bar{\mu}$  is work required to bring an electron isothermally from infinity to solid



- Note:  $\bar{\mu}$  is function of internal AND surface/external (e.g., shifting charges, dipoles) conditions;
- We can define quantity  $\mu$  which is function of internal state of the solid

Chemical potential of electrons:  $\mu = \bar{\mu} + e\Phi_f$  Average electrostatic potential inside

## Work Function

- The Fermi energy  $[E_F]$ , the highest filled orbital in a conductor at  $T=0K$ , is measured with respect to  $(-e\Phi_I)$  and is equivalent to  $\mu$ .
- We can write:
 

$e\phi = -e\Phi_o + e\Phi_I - \mu$ 
(5.4)

$\phi = \Delta\Phi - \frac{\mu}{e}$ 
(5.5)
- $\Delta\Phi$  depends on surface structure and adsorbed layers. The variation in  $\phi$  for a solid is contained in  $\Delta\Phi$ .
- What do we mean by potential just outside the surface???

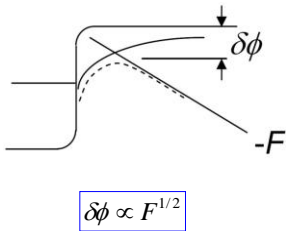
11

## Potential just outside the surface

The potential experienced by an electron just outside a conductor is:

For a uniform surface this corresponds to  $\Phi_o$  in (5.1):

In many applications, an accelerating field,  $F$ , is applied:



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Selected Values of Electron Workfunctions\*

Element	$\phi$ (eV)	Element	$\phi$ (eV)	Element	$\phi$ (eV)
Ag	4.26	Cu	4.65	Si	4.85
Ag (100)	4.64	Cu(100)	4.59	Ru	4.71
Ag (110)	4.52	Cu(110)	4.48	Ta	4.25
Ag (111)	4.74	Cu(111)	4.98	Ta (100)	4.15
Ba	2.52	Ir (110)	5.42	Ta (110)	4.80
C	5.0	Ir(111)	5.76	Ta (111)	4.00
Ce	2.9	K	2.30	Ti	4.53
Cr	4.5	LaB <sub>6</sub>	2.66	W	4.55
Cs	2.14	Mo	4.60	Zr	4.05

Units: eV electron Volts;  
 \*Reference: CRC handbook on Chemistry and Physics version 2008, p. 12-114.

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7.2.3 Interpretation: Typical spectral features

Binding energies = Orbital energies, BUT ... USE CAUTION!

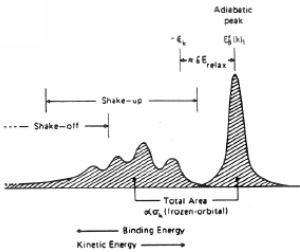
Energy conservation:  $E_i(N) + h \nu = E_f(N-1) + KE$   
 $\Rightarrow h \nu - KE = E_f(N-1, k) - E_i(N) = E_B$

Binding energy is more properly associated with ionization energy.

In HF approach, **Koopmans' Theorem**:  $E_B = -E_k$  (orbital energy of  $k^{th}$  level)  
 Formally correct within HF. Wrong when “relaxation” effects are included.

ALSO: Photoexcitation is rapid event  
 $\Rightarrow$  sudden approximation

Gives rise to chemical shifts and plasmon peaks



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## Qualitative results

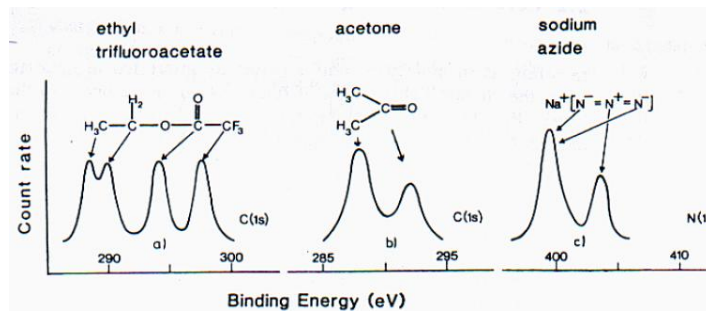
A: Identify element

B: Chemical shifts of core levels:

Consider core levels of the same element in different chemical states:

$$\Delta E_B = E_B(2) - E_B(1) = E_K(2) - E_K(1)$$

Often correct to associate  $\Delta E_B$  with change in local electrostatic potential due to change in electron density associated with chemical bonding ("initial state effects").



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## Chemical Shifts

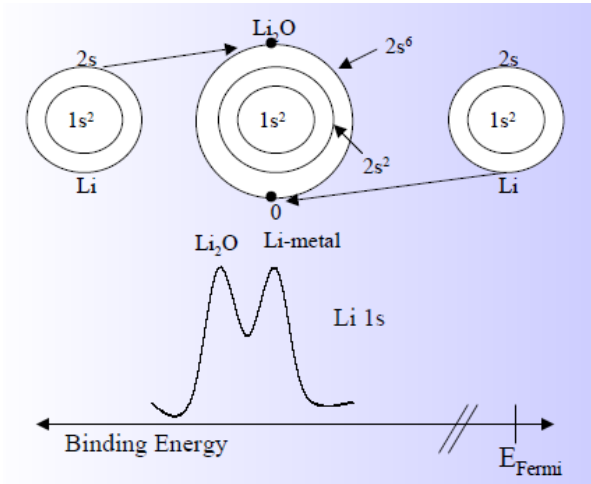
Core binding energies are determined by:  
electrostatic interaction between it and the nucleus, and reduced by

- ...
- ...

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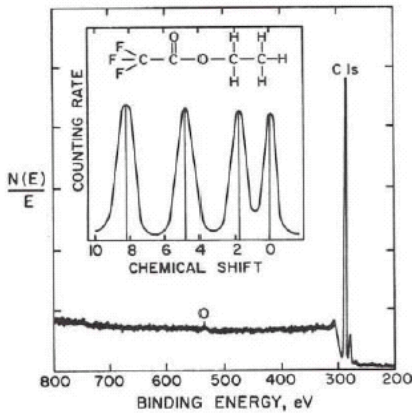


### Chemical Shifts: Oxide Compared to Metal



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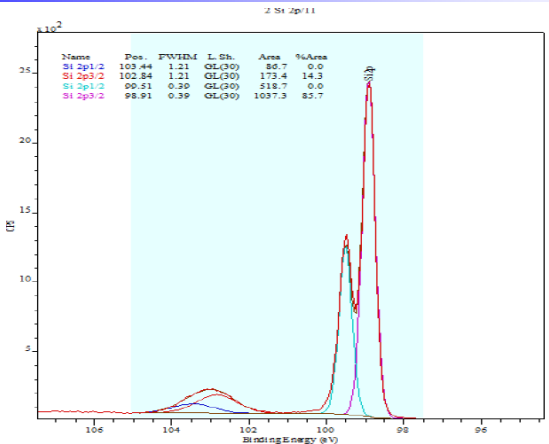
### Chemical Shifts



- Carbon 1s chemical shifts in ethyl trifluoroacetate
- The four carbon lines correspond to the four atoms within the molecule

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Peak Width:



$\Delta E$  measured as FWHM; if assume Gaussian:

$$\Delta E = (\Delta E^2_{\text{natural}} + \Delta E^2_{\text{photons}} + \Delta E^2_{\text{analyzer}})^{1/2}$$

Lifetime width:  $\Gamma = \hbar/\tau$  for  $\Gamma \sim 1$  eV,  $\tau \sim 10^{-15}$  s

<http://www.lasurface.com/database/liaisonxps.php>

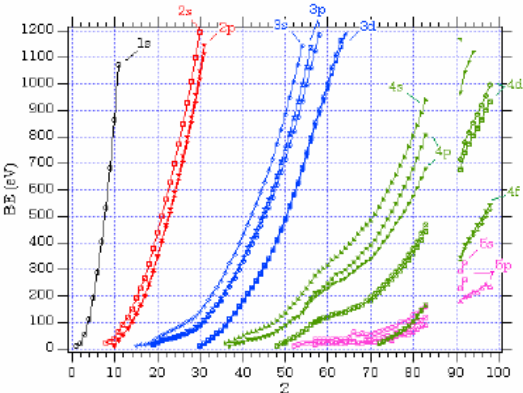
19

Peak Identification: Core level binding energies

XPS Photoelectron Binding Energies\* versus Atomic Number

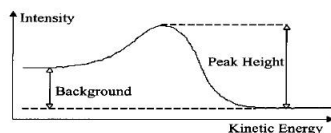
Where the same BE is quoted for different spin-orbit split subshells, the individual subshells are either not resolved or have a complex structure. Spin-orbit coupling: 2p1=2p1/2, 2p3=2p3/2 etc.

Z	1s	2s	2p1	2p3	3s	3p1	3p3	3d3	3d5	4s	4p1	4p3	4d3	4d5	4f5	4f7	5s	5p1	5p3
1	14																		
2	21																		
3	56																		
4	113																		
5	191																		
6	287																		
7	402																		
8	531	23																	
9	686	30																	
10	863	41	14	14															
11	1072	64	31	31															
12		90	51	51															
13		119	74	74															
14		153	103	102															
15		191	134	133	14														
16		229	166	165	17														
17		270	201	199	17														
18		319	243	241	22														
19		378	296	293	33	17	17												
20		439	350	347	44	25	25												
21		501	407	402	53	31	31												
22		565	464	458	62	37	37												
23		630	523	515	69	40	40												
24		698	586	577	77	46	45												
25		770	652	641	83	49	48												

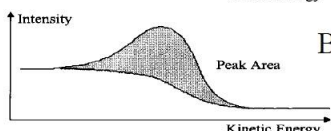
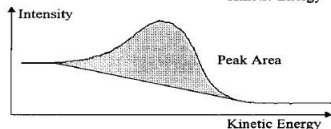
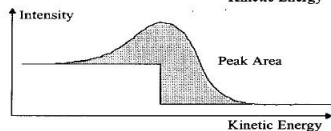


<http://www.lasurface.com/database/elementxps.php>

## How to measure peak intensities?



Worst



Best

Must include or correct for (i) x-ray satellites (ii) chemically shifted species (iii) shake-up peaks (iv) plasmon or other losses

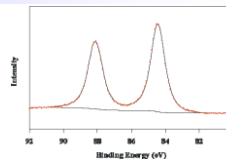
- Accuracy better than 15%
- Use of standards measured on same instrument or full expression above accuracy better than 5%
- In both cases, reproducibility (precision) better than 2%

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## Quantification of XPS

Primary assumption for quantitative analysis: ionization probability (photoemission cross section) of a core level is nearly independent of valence state for a given element

⇒ intensity ∝ number of atoms in detection volume



$$I_A = \sigma_A(\hbar\omega) D(E_A) \int_{\gamma=0}^{\pi} \int_{\phi=0}^{2\pi} L_A(\gamma) \int_{x,y} J_0(x,y) T(x,y,\gamma,\phi,E_A) \int_x N_A(x,y,z) \exp\left(\frac{-z}{\lambda \cos \theta}\right) dx dy dz d\gamma d\phi$$

where:

$\sigma_A$  = photoionization cross section

$D(E_A)$  = detection efficiency of spectrometer at  $E_A$

$L_A(\gamma)$  = angular asymmetry of photoemission intensity

$\gamma$  = angle between incident X-rays and detector

$J_0(x,y)$  = flux of primary photons into surface at point  $(x,y)$

$T$  = analyzer transmission

$\phi$  = azimuthal angle

$N_A(x,y,z)$  = density of A atoms at  $(x,y,z)$

$\lambda_M$  = electron attenuation length of e's with energy  $E_A$  in matrix M

$\theta$  = detection angle (between sample normal and spectrometer)

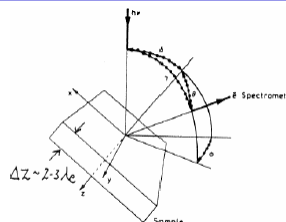


Figure 5.13 Geometry of the XPS analysis configuration

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Quantitative analysis

For small entrance aperture (fixed  $\phi, \gamma$ ) and uniform illuminated sample:

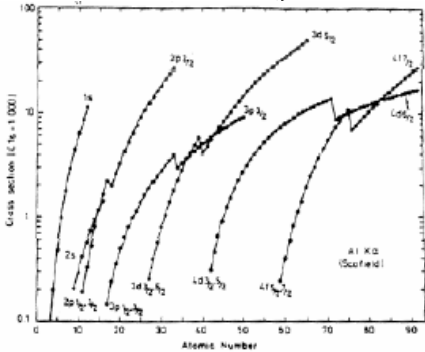
$$I_A = \sigma_A(\hbar\omega) D(E_A) L_A(\gamma_i) J_0 N_A \lambda_M(E_A) \cos \theta_i G(E_A)$$

Angles  $\gamma_i$  and  $\theta_i$  are fixed by the sample geometry and  $G(E_A) = \iint_{x,y} T(x, y, E_A) dx dy$

$G(E_A)$ =product of area analyzed and analyzer transmission function

$D(E_A)$ =const for spectrometers  
 Operating at fixed pass energy

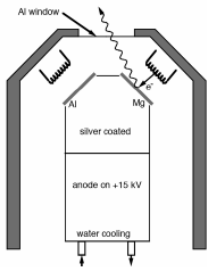
$\sigma_A$ : well described by Scofield  
 Calculation of cross-section



5.14 Calculated values of the cross-section  $\sigma_A(h\nu)$  for Al K $\alpha$  radiation in terms of the C L $\alpha$  cross-section. (After Scofield<sup>18</sup>)

7.3 Photoemission Spectroscopy: Instrumentation

X-ray source



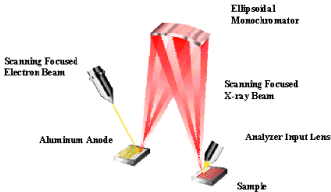
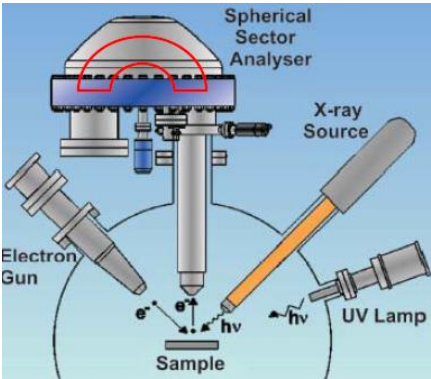
X-ray lines		
Line	Energy, eV	Width, eV
Ti L $\alpha$	395.3	3.0
Cu L $\alpha$	929.7	3.8
Mg K $\alpha$	1253.6	0.7
Al K $\alpha$	1486.6	0.85
Ti K $\alpha$	4510.0	2.0

How to choose the material for a soft X-ray source:
 

1. the line width must not limit the energy resolution;
2. the characteristic X-ray energy must be high enough to eject core electrons for an unambiguous analysis;
3. the photoionization cross section of e in different core levels varies with the wavelength of the X-ray, a suitable characteristic X-ray wavelength is crucial to obtain a strong enough photoelectron signal for analysis.

Instrumentation

- Essential components:
- **Sample:** usually 1 cm<sup>2</sup>
  - **X-ray source:** Al 1486.6 eV;  
Mg 1256.6 eV
  - **Electron Energy Analyzer:**  
100 mm radius concentric hemispherical analyzer (CHA); vary voltages to vary pass energy.
  - **Detector:** electron multiplier (channeltron)
  - Electronics, Computer
  - **Note:** All in **ultrahigh vacuum** (<10<sup>-8</sup> Torr) (<10<sup>-11</sup> atm)
  - **State-of-the-art small spot**
- ESCA: 5 μm spot size  
Sputtering gun for profiling

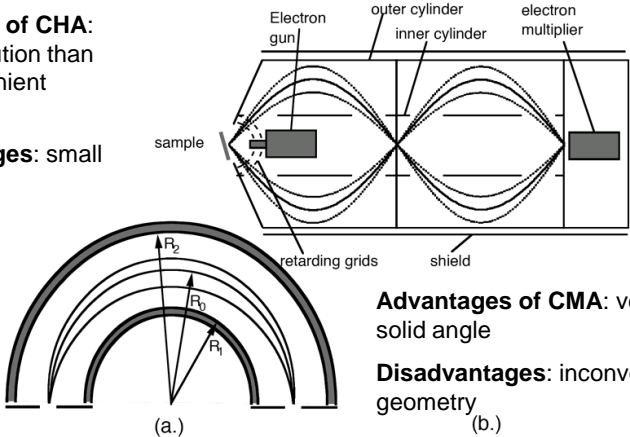


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Electron Energy Analyzers

(a) Concentric Hemispherical Analyzer (CHA) and (b) (Double Pass) Cylindrical Mirror Analyser (CMA)

- Advantages of CHA:**  
higher resolution than CMA, convenient geometry
- Disadvantages:** small solid angle



- Advantages of CMA:** very large solid angle
- Disadvantages:** inconvenient geometry

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## Surface Science Western- XPS

<http://www.uwo.ca/ssw/services/xps.html>

<http://xpsfitting.blogspot.com/>

<http://www.casaxps.com/>

<http://www.lasurface.com/database/elementxps.php>

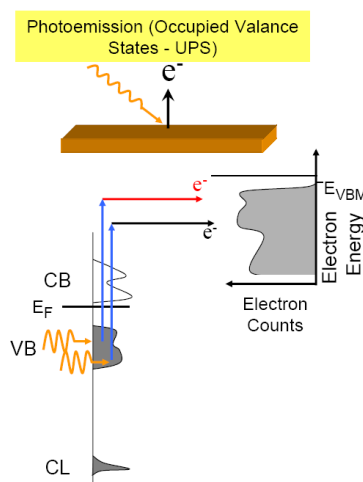


Kratos Axis Ultra (left)  
Axis Nova (right)

Contact:  
Mark Biesinger  
[biesinger@uwo.ca](mailto:biesinger@uwo.ca)

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## 7.4 Comparison XPS and UPS



XPS: photon energy  $h\nu=200\text{-}4000\text{ eV}$  to probe core-levels (to identify elements and their chemical states).

UPS: photon energy  $h\nu=10\text{-}45\text{ eV}$  to probe filled electron states in **valence band** or adsorbed molecules on metal.

Angle resolved UPS can be used to map band structure ( to be discussed later)

UPS source of irradiation: He discharging lamp (two strong lines at 21.2 eV and 42.4 eV, termed He I and He II) with narrow line width and high flux

Synchrotron radiation source

continuously variable photon energy, can be made very narrow, very intense, now widely available, require a monochromator

Introduction to Photoemission Spectroscopy in solids, by F. Boscherini

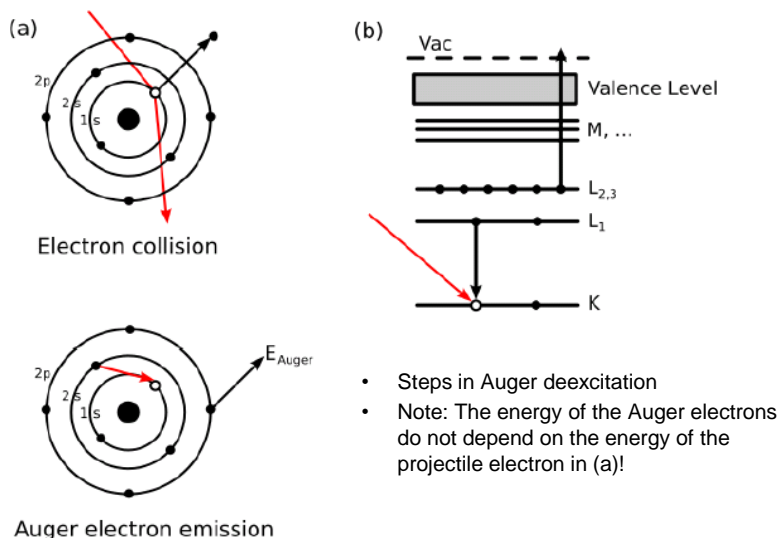
[http://amscampus.cib.unibo.it/archive/00002071/01/photoemission\\_spectroscopy.pdf](http://amscampus.cib.unibo.it/archive/00002071/01/photoemission_spectroscopy.pdf)

## Studies with UV Photoemission

- The electronic structure of solids -detailed angle resolved studies permit the complete band structure to be mapped out in  $k$ -space
- The adsorption of molecules on solids-by comparison of the molecular orbitals of the adsorbed species with those of both the isolated molecule and with calculations.
- The distinction between UPS and XPS is becoming less and less well defined due to the important role now played by synchrotron radiation.

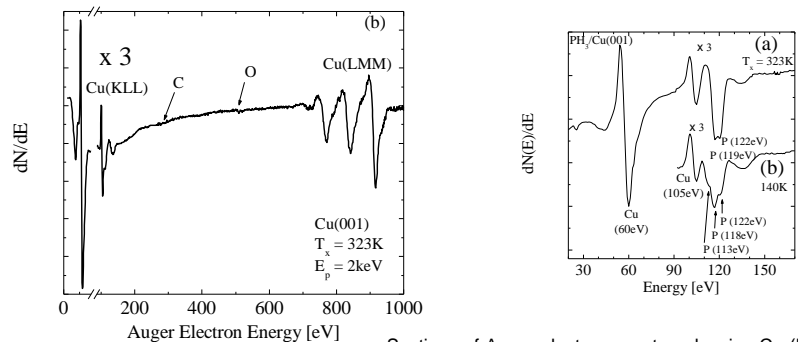
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## 7.5 Auger Electron Spectroscopy (AES)



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Auger spectrum of Cu(001) and CuP



Use  $dN/dE$  (derivative mode)  $\Rightarrow$   
 Why?

Sections of Auger electron spectra, showing Cu (M2,3VV) and P (L2,3VV) transitions, for a low temperature PH3 overlayer phase at 140K and (b) for a P c (6 $\times$ 8) structure obtained by annealing the surface of (a) to  $T_x > 450\text{K}$ . Both spectra have been normalized to give the same Cu (60 eV) feature peak height.

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- Are Auger peaks recorded at 60eV, 350eV and 1500eV equally surface sensitive?

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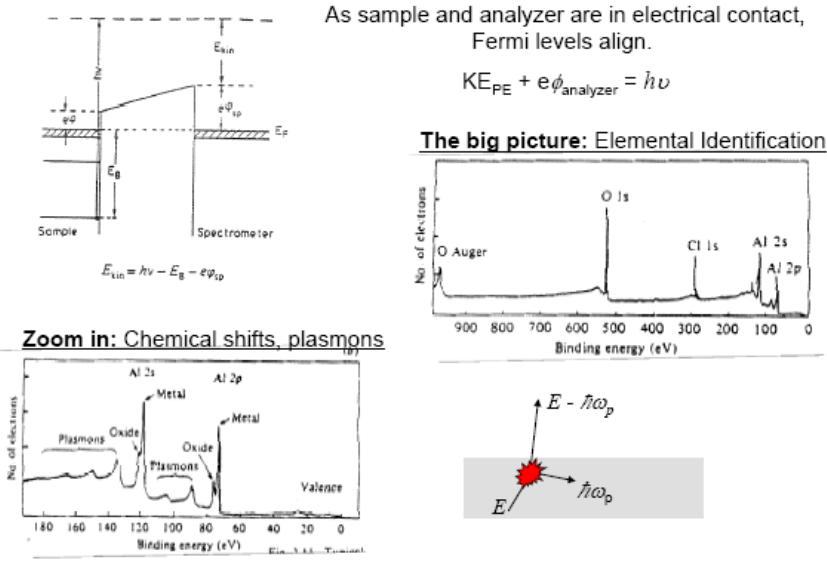


Applications of AES

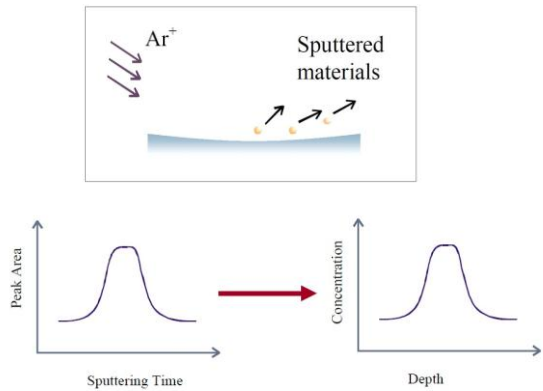
- A means of monitoring surface cleanliness of samples
- High sensitivity (typically ca. 1% monolayer) for all elements except H and He.
- Quantitative compositional analysis of the surface region of specimens, by comparison with standard samples of known composition.
- The basic technique has also been adapted for use in :
  - Auger Depth Profiling : providing quantitative compositional information as a function of depth below the surface (through sputtering)
  - Scanning Auger Microscopy (SAM) : providing spatially-resolved compositional information on heterogeneous samples (by scanning the electron beam over the sample)

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7.6 Quantitative analysis



## Depth Profiling



### Calibration of depth scale

1. Sputtering rate determined from the time required to sputter through a layer of the same material of known thickness.
2. After the sputtering analysis, the crater depth is measured using depth profilometer. A constant sputtering rate is assumed.

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## Quantitative Analysis

- Estimate **chemical concentration**, **chemical state**, **spatial distribution of surface species**
- Simplest approximation is that sample is in single phase

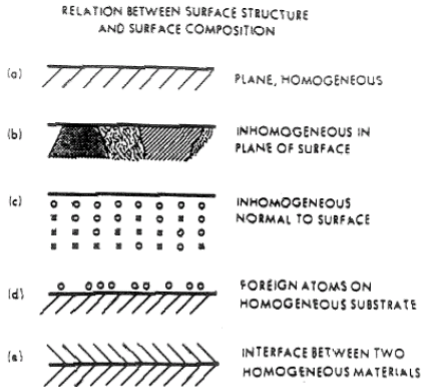


FIG. 1. Idealized surface structures: (a) plane homogeneous surface; (b) a surface with lateral inhomogeneities consisting of several different surface phases; (c) a surface with depth inhomogeneities (the circles and the crosses represent different types of atoms); (d) a surface phase consisting of a submonolayer of foreign atoms on an otherwise homogeneous surface; and (e) an interface between two homogeneous bulk phases (Ref. 1).

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Appendix I

- Workfunction of polycrystalline materials
- Electron emission

References:

- 1) Zangwill, p.57-63
- 2) Woodruff & Delchar, pp. 410-422, 461-484
- 3) Luth, pp.336, 437-443, 464-471
- 4) A. Modinos, "Field, Thermionic and Secondary Electron Spectroscopy", Plenum, NY 1984.

Work Function: Polycrystalline Surfaces

Consider polycrystalline surface with "patches" of different workfunction, and different value of surface potential

i, $\Phi_{oi}$	j, ...	k	l
m	m	o	p

At small distance  $r_o$  above  $i^{th}$  patch electrostatic potential is  $\Phi_{oi}$

At distances large w/r/t/ patch dimension:

$$\Phi_o = \sum_i f_i \Phi_{oi}, f_i = \text{fractional area of } i^{th} \text{ patch}$$

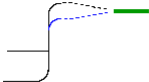
So mean work function is given by:

$$e\bar{\phi} = \sum_i f_i e\phi_i \quad (5.10)$$

- at **low** applied field, electron emission controlled by:  $e\bar{\phi}$

- at **high** field (applied field  $\gg$  patch field)

electron emission related to individual patches:  $e\phi_i$



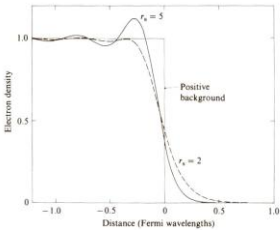
On real surfaces, patch dimension  $< 100\text{\AA}$ , if  $\Delta\phi \sim 2\text{ eV}$  then patch field  $F \sim 2V/(10^{-6}\text{ cm}) \sim 2 \times 10^6\text{ Volts/cm}$ . work required to bring an electron from infinity to solid

Workfunction

Factors that influence work function differences on clean surfaces:

- Adsorbed layers
- Surface dipoles (cf. Zangwill, p 57)
- Smooth surface: electron density “spillover”

Fig. 4.2. Electron density profile at a jellium surface for two choices the background density,  $r_s$  (Lang & Kohn, 1970).



- Electron density outside rough surface
- For tungsten

$e\phi$ , eV	W plane
5.70	(110)
4.93	(211)
4.39	(111)
4.30	(116)

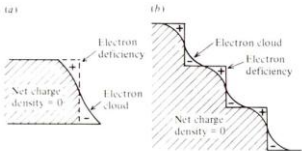
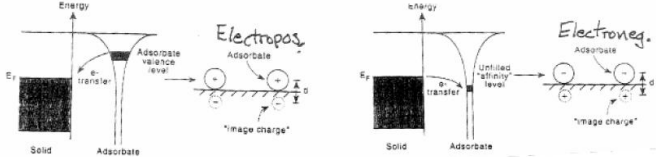


Fig. 7.2 Charge distribution at a metal surface (schematic): (a) an atomically smooth surface; (b) an atomically stepped surface.

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Work function change upon adsorption

- Charge transfer at interface: electrop**ositive** (K, Na, ...) or electrop**egative** (Cl, O, F, ...)

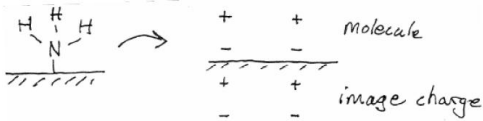


- Model dipole layer as parallel plate capacitor:

$$\Delta\phi = \frac{n\mu}{\epsilon_0} \quad \mu - \text{dipole moment [C m]}; n - \text{surface charge density [m}^{-2}\text{]}; \epsilon_0 = 8.85 \times 10^{-12} \text{ [C/Vm]}$$

Suppose  $\Delta\phi = 1.5\text{V}$  for  $1 \times 10^{15}/\text{cm}^2$  O atoms on W (100). What is  $\mu$ ?

For molecules with a permanent dipole moment:



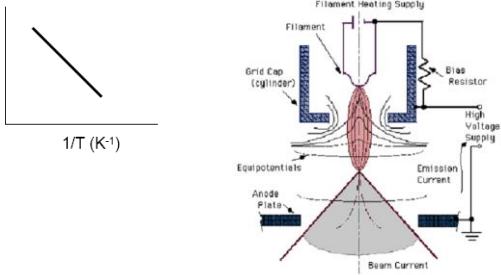
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## Electron Sources: Thermionic Emission

**Thermionic emission** occurs when sufficient heat is supplied to the emitter so that e's can overcome the work function, the energy barrier of the filament,  $E_w$ , and escape from it

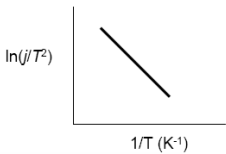
- Richardson's Equation:** (derivation – aside)  
 Current density,  $j$ :  $j = A_o(1-\bar{r})T^2 \exp(-\frac{e\phi}{kT})$   
 $r$  = reflection coefficient;  $A_o = \frac{4\pi me k^2}{h^3} = 120.4 \frac{\text{Amp}}{\text{cm}^2 \text{ deg}^2}$

- Richardson plot:**  
 $\ln(j/T^2)$  vs  $1/T \Rightarrow$   
 $\Rightarrow$  straight line



## Electron Emission: Thermionic Emission

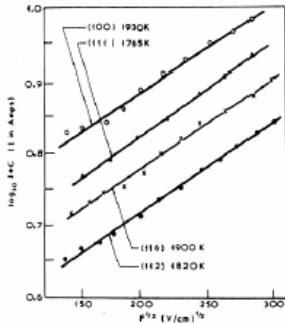
- Richardson plot:**  
 $\ln(j/T^2)$  vs  $1/T \Rightarrow$   
 $\Rightarrow$  straight line



- Schottky Plot**

$$e\phi \rightarrow e\Phi_o - bF^{1/2} \quad (\text{cf. eq.5.9})$$

$$\ln j \text{ vs } F^{1/2} \Rightarrow \text{straight line}$$



**FIGURE 2.3**  
 Schottky plots for four faces of tungsten.  $C = 8, 9, 7.9, 8.0$  for the (100), (111), (110), and (112) planes, respectively. (From Smith, 1954).

Field Electron Emission

- Electron tunneling through low, thin barrier
  - Field emission, when  $F > 3 \times 10^7 \text{ V/cm} \sim 0.3 \text{ V/\AA}$
- General relation for electron emission in high field:

$$j = e \int_0^\infty P(E_z, F) v(E_z) dE_z$$

- P is given by WKB approximation

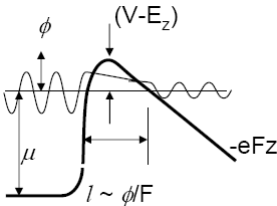
$$P = \text{const} \times \exp \left( - \frac{2^{2/3} m^{1/2}}{\hbar} \int_0^l (V - E_z)^{1/2} dz \right)$$

- If approximate barrier by triangle:  $\int \sim \frac{1}{2} \phi^{1/2} \frac{\phi}{F} \sim \frac{1}{2} \frac{\phi^{3/2}}{F}$

$$P = \text{const} \times \exp \left( - \frac{2^{2/3} m^{1/2}}{\hbar} \frac{\phi^{3/2}}{F} \right)$$

- Fowler – Nordheim eqn, including potential barrier:

$$j = 1.54 \times 10^{-6} \frac{F^2}{\phi} t^2(y) \exp \left\{ - 6.83 \times 10^7 \frac{\phi^{3/2} f(y)}{F} \right\}; \text{ where } y = \frac{e^{3/2} F^{1/2}}{\phi}$$



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How do we get high fields: Field Emission Microscope!

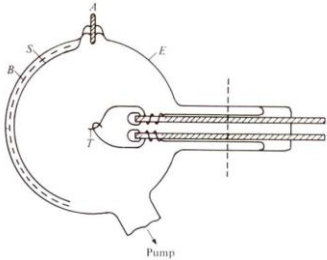
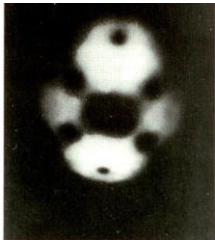


Fig. 6.5 Schematic drawing of one form of the field emission microscope. E, glass envelope; S, phosphorescent screen; B, tin oxide backing; A, anode connector; T, emitter tip.

Get high field by placing sharp tip at center of spherical tube.

Mag:  $R/r \sim 5\text{cm}/10^{-5}\text{cm} \sim 500,000$   
 $F = cV$ ;  $c \sim 5/r$   $F \sim 5 \times 10^7 \text{ V/cm}$   
 For  $V = 2,500 \text{ Volts}$ .



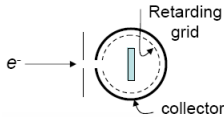
W single crystal wire as tip.  
 Typical pattern on phosphor screen

Fig. 6.7 Field emission image from a clean W field emitter showing the symmetry typical of such patterns.

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Secondary Electron Emission

Electrons emitted from surfaces after electron bombardment  
 In general complicated phenomenon  
 involving several interrelated processes



Generally classify secondaries into three categories:

- (I) Elastic ;
- (II) Inelastic;
- (III) “true” secondaries (KE < 50 eV)

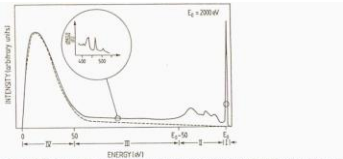
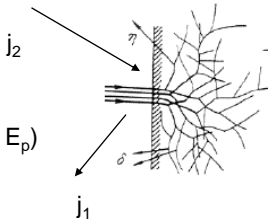


Fig. V.2. Qualitative large-scale overview of the energy distribution of electrons emitted from a surface which is irradiated by an electron beam of primary energy  $E_0$ .

Total coefficient for secondary emission,  
 $\sigma = j_2/j_1 = r + \eta + \delta$

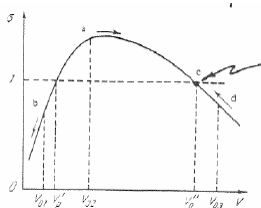


For metals, max values:  $r \sim 0.2$  ( $E_p \sim \text{eV}$ );  $\sim 0.02$  (large  $E_p$ )  
 $\eta \sim 0.3$  to  $0.4$ ;  $\delta \sim 0.5$  to  $1.8$  ( $E_p \sim \text{few hundred eV}$ )  
 For insulators,  $\sigma$  can be MUCH higher ( $\sim 20$ !!!!)



Secondary Electron Emission

- Establishment of stable potential for insulators and dielectric materials



In practice, steady state potential reached by dielectric is due mainly to incomplete extraction of secondary electrons

- For metals and semiconductors: Correlation between  $\delta$  and density,  $\rho$

