Photoelectron Spectroscopy --- Basics
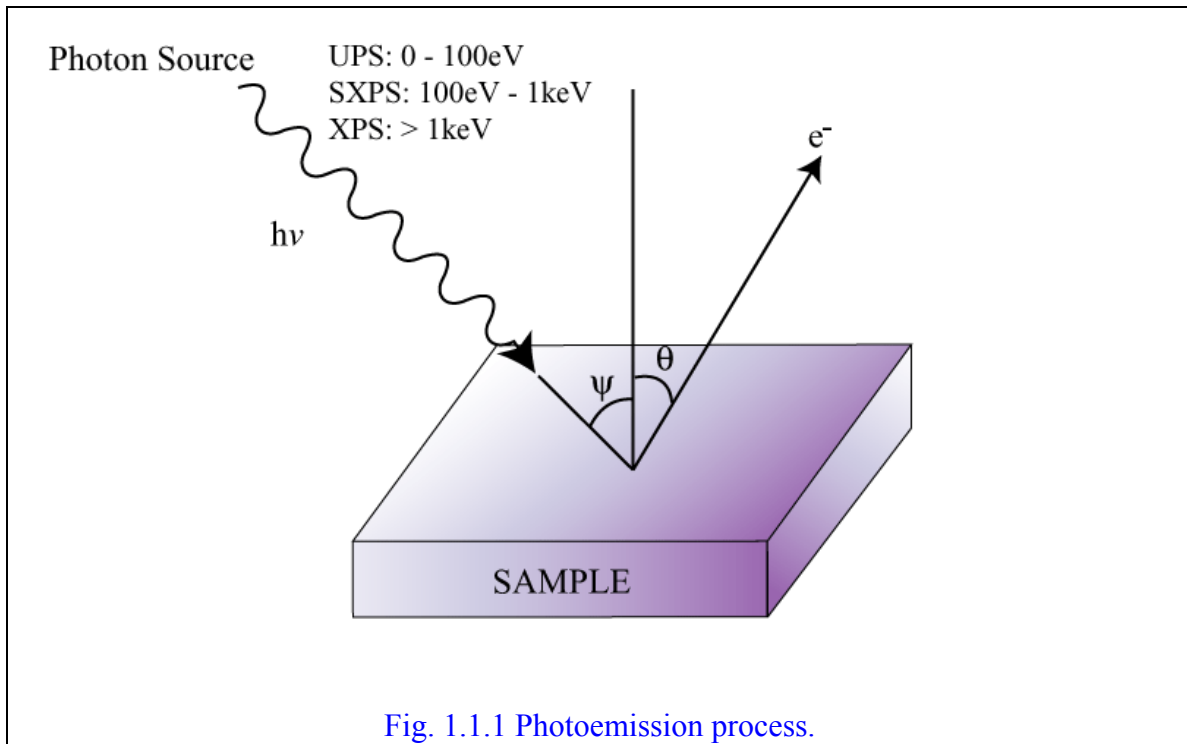
1.1 Photoemission process (Ref. 3.1, P. 43)

When a sample surface is irradiated with photons of energy $h\upsilon$, electrons are emitted from the sample surface. Figure 1.1.1 shows the essence of this photoemission process.

<p style="text-align:center">Fig. 1.1.1 Photoemission process.</p>

This process was first reported by H.Hertz in 1887. The excitation source was a UV lamp. Nowadays, the excitation source can be X-ray or synchrotron radiation. In this module, we concentrate on the X-ray photoelectron spectroscopy.

Reference:
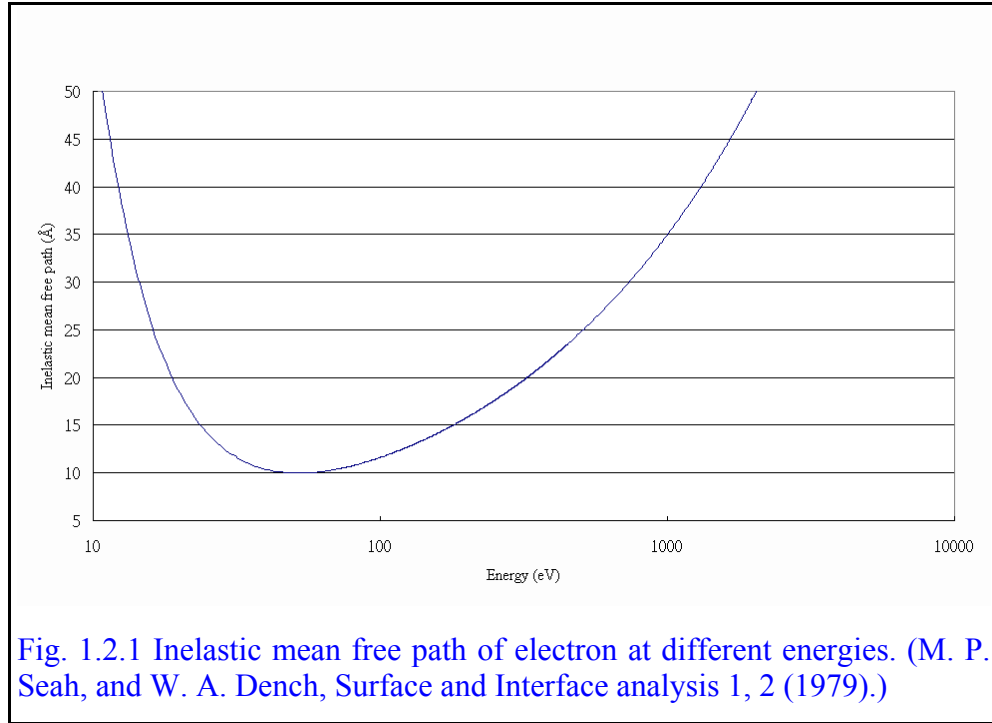3.1 J. C. Vickerman, *Surface analysis – the principal techniques,* John Wiley & Sons (1997).

1.2 Surface Sensitivity of XPS (Ref. 3.1, P. 58-61)

Photoelectron spectroscopy is a surface sensitive technique. Its surface sensitivity can be explained in terms of the inelastic mean free path of electrons, λ.
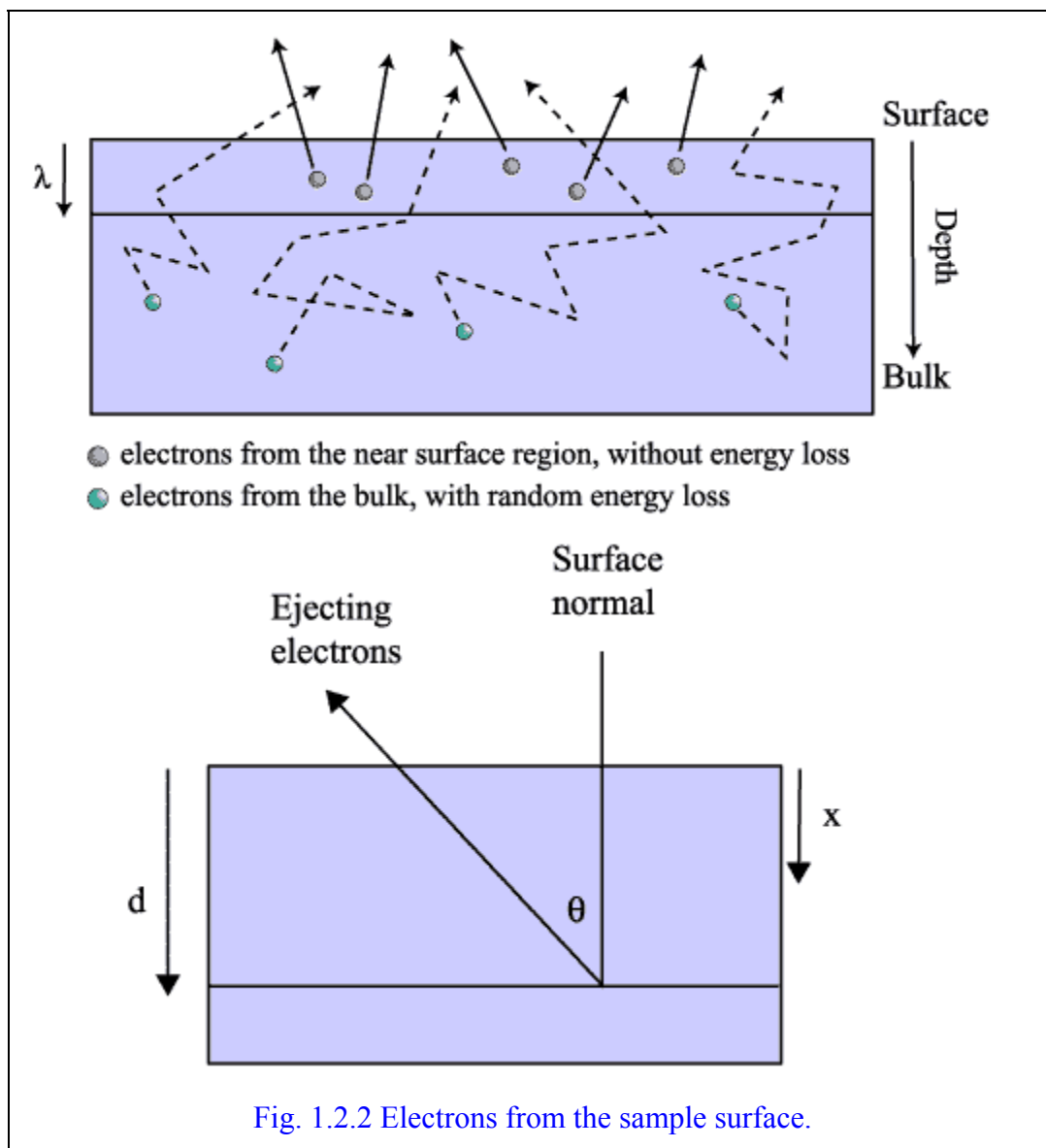
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Inelastic mean free path is defined as the distance traveled by an electron between successive inelastic collisions. When the energy of the electron is larger than 100 eV, the higher the kinetic energy of the electron the longer the inelastic mean free path.

Fig. 1.2.1 Inelastic mean free path of electron at different energies. (M. P. Seah, and W. A. Dench, Surface and Interface analysis 1, 2 (1979).)

When X-ray photons enter below a sample surface, photoelectrons (or photoinduced electrons) are produced. Some travel out from the surface without losing any energy. Some of them lose energy owing to inelastic collisions.

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○ electrons from the near surface region, without energy loss
○ electrons from the bulk, with random energy loss

Fig. 1.2.2 Electrons from the sample surface.

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It has been shown theoretically by a Monte Carlo simulation[1] and proved experimentally[2] that the intensity of ejecting electrons through a medium with no energy loss will follow an exponential decay function, *i.e.*

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

[1] C. J. Powell, A. Jablonski, S. Tanuma and D. R. Penn, *J. Electron Spectrosc. Relat. Phenom*, 68, P.605 (1994).

[2] D. F. Mitchell, K. B. Clark, J. A. Bardwell, W. N. Lennard, G. R. Massoumi and I. V. Mitchell, *Surf. Interface Anal.* 21, P.44 (1994).

Fraction of signal from various depth in term of λ

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

Thus 95% of the photoelectron signals come from the surface region of 3 λ thick. (3 λ is about several tens of Å). The remaining 5% of signals come from the deeper region. This explains the surface sensitivity of XPS.

Activities on web:
Visit http://www.lasurface.com/IMFP/Ag_IMFP_1.htm You can learn why XPS is a surface sensitive technique in this website. Also, try the program at http://www.lasurface.com/IMFP/Ag_IMFP_3.htm to calculate the inelastic mean free path. The site is created with the help of VG Scientific.

Question:
"The penetration depth of X-ray used in XPS is in the order of μm, therefore the surface sensitivity of XPS is restricted to analysis in μm level."

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Please comment upon the above statement. Is it true or false? Answer with appropriate argument based on the origin of the surface sensitivity of XPS in terms of the inelastic mean free path of electron, λ, and the exponential decay function of photoelectron from within the sample.

Reference:
3.1 J. C. Vickerman, *Surface analysis – the principal techniques,* John Wiley & Sons (1997).
Goto: Section 1.3 – History of photoelectron spectroscopy

1.3 History of photoelectron spectroscopy (Ref. 3.1, P. 44-46)
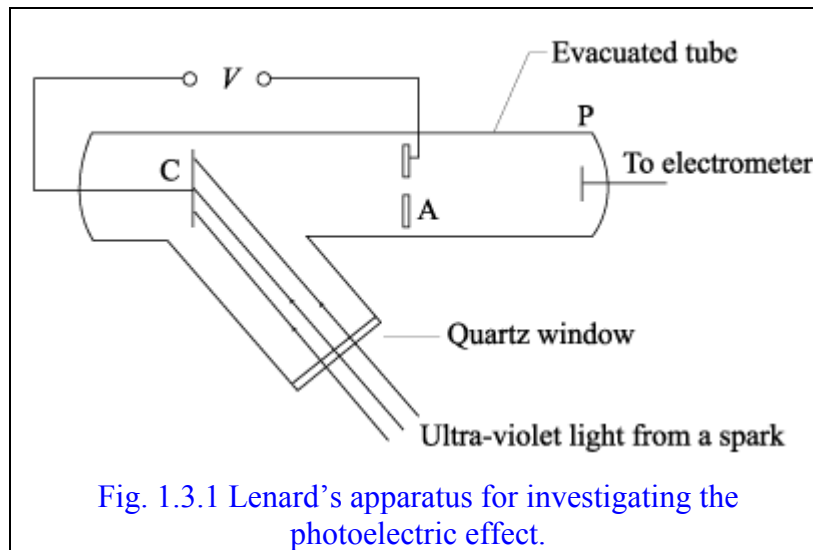
1.3.1. Photoemission in the Pre-Siegbahn period

1887: Heinrich Hertz published, "On an effect of UV light upon the electric discharge" (Sitzungsber d. Berl. Akad. d. Wiss., June 9, 1887).
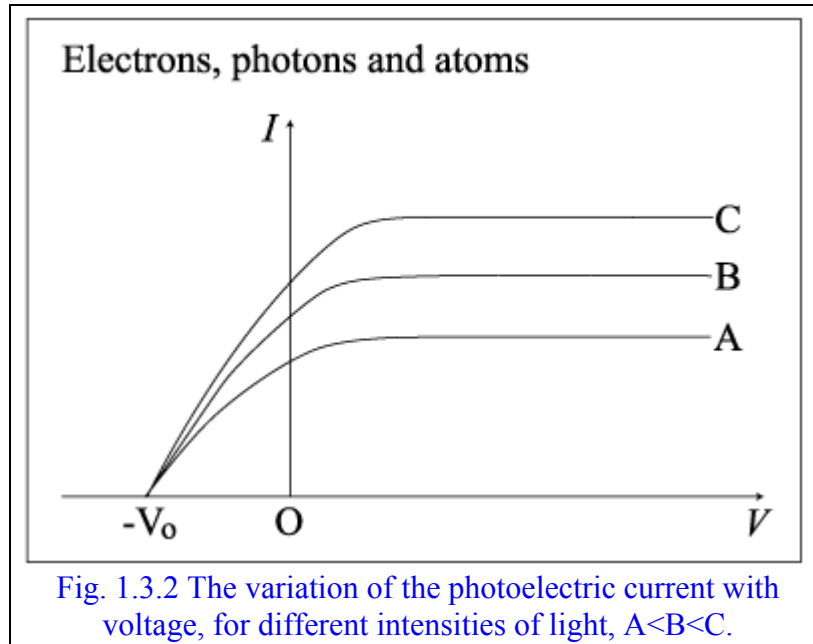
1895: Discovery of X-rays by W.K. Röntgen.

1897: J.J. Thomson's cathode ray tube experiments for measuring e/m of electrons: a primitive electron spectrometer.

1905: Einstein equation for the photoelectric effect: $eV_0 = h\upsilon - \phi$.

Fig. 1.3.1 Lenard's apparatus for investigating the photoelectric effect.

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Fig. 1.3.2 The variation of the photoelectric current with voltage, for different intensities of light, A<B<C.

1907: Innes, a Ph.D. student, conducted research on: "....the velocity of the cathode particles emitted by various metals under the influence of Röntgen rays...." (Proc. Roy. Sec.. Ser. A 79, 442(1907)). A photographic plate was used to measure the deflection of photoelectrons in a magnetic field.

1918: First XPS paper by a Chinese(!) A Harvard University researcher, Mang-Fuh Hu, reported, "some preliminary results in a determination of the maximum emission velocity of the photoelectrons from metals at X-ray frequencies" (Phys. Rev. 11, 505(1918)).

1925: H. Robinson, a pioneer who devoted his entire research career to XPS, wrote that, "...an accurate knowledge of the energies associated with the different electronic orbits within the atoms is essential to the further development of the theory of atomic structure" (Proc. Roy. Sec., Ser. A, 104, 455(1923)).

Reference:
3.1 J. C. Vickerman, *Surface analysis – the principal techniques,* John Wiley & Sons (1997).

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1.3.2 Developments of Quantum Mechanics in the Pre-Siegbahn period

1911: Rutherford backscattering experiment for probing atomic structures.

1913: Bohr's primitive atom model.

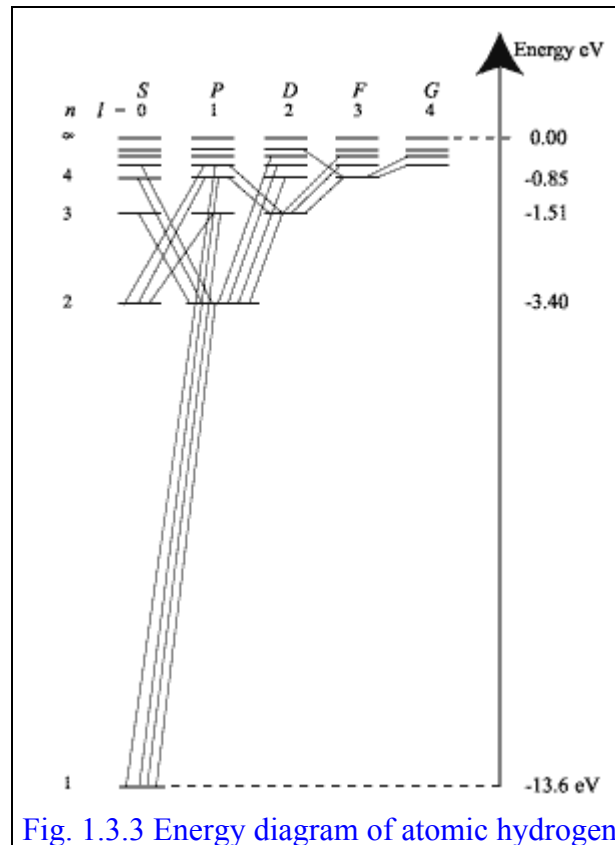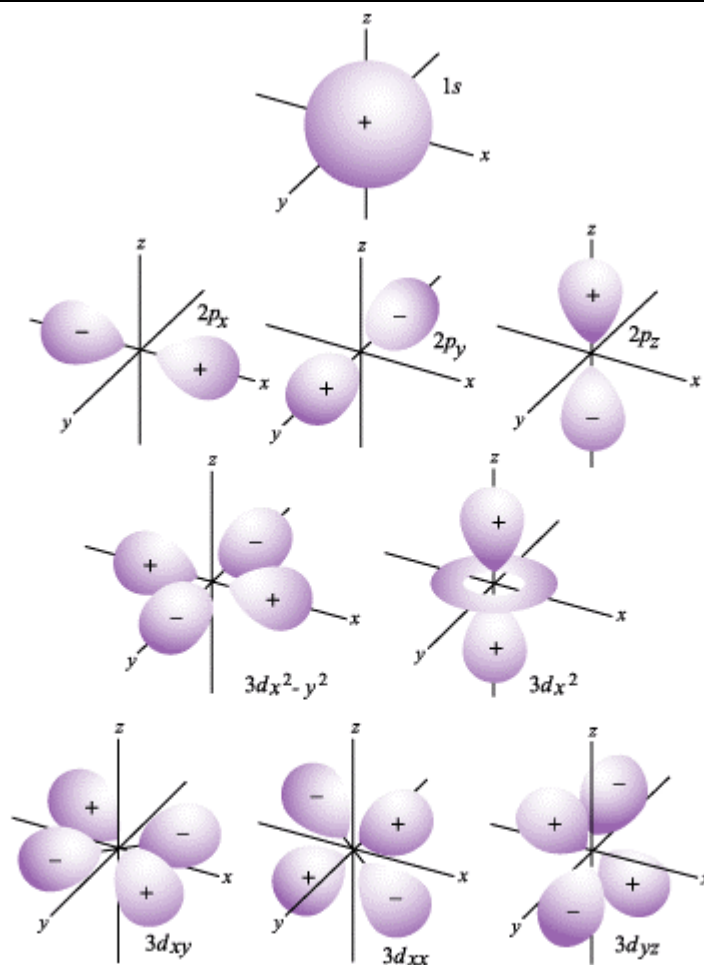1925: Schrödinger's quantum mechanics.

Fig. 1.3.3 Energy diagram of atomic hydrogen

3D Plots showing the angular dependence of 1s, 2p and 3d functions for a fixed value of r. The indicated signs are those of the wave function.

Fig. 1.3.4 Orbital wavefunction of Schrödinger's equation for a hydrogen atom

Reference:
3.1 J. C. Vickerman, *Surface analysis – the principal techniques,* John Wiley & Sons (1997).
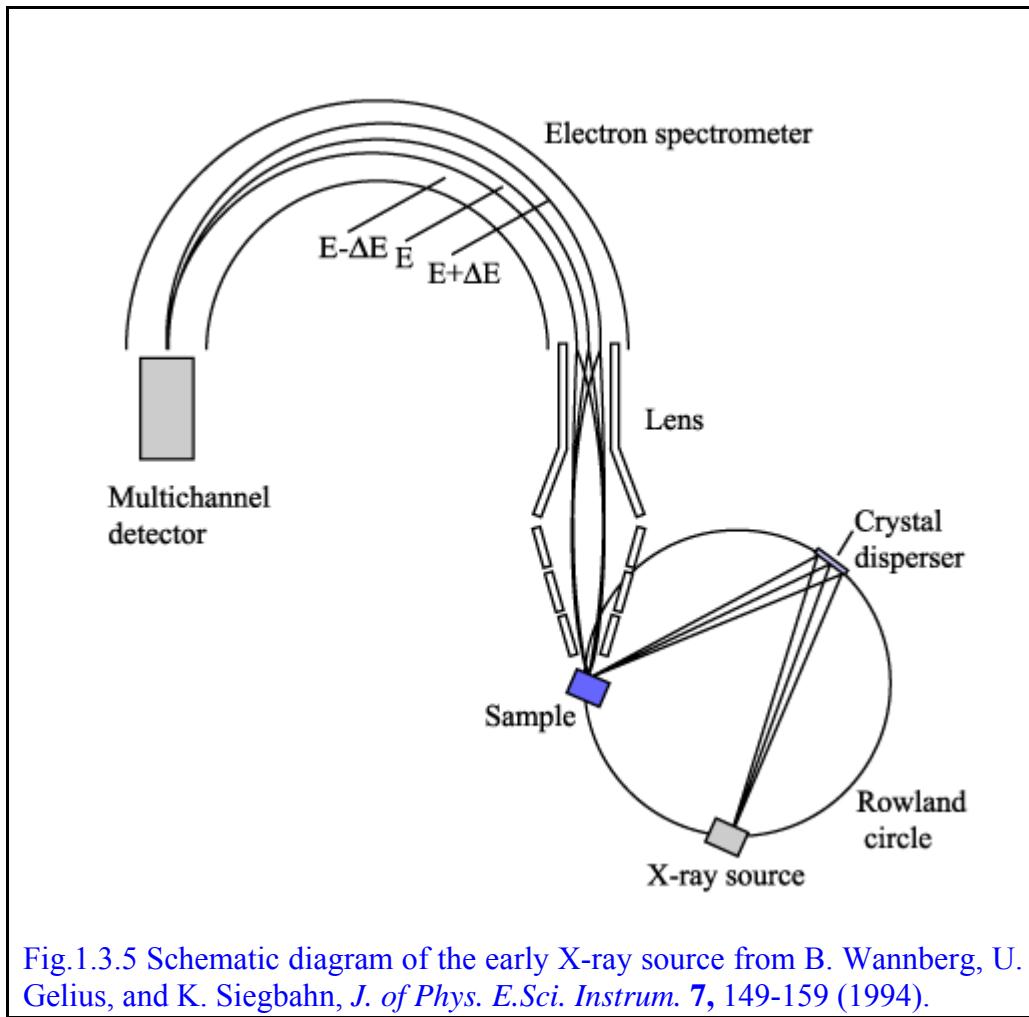**Goto: Section 1.3.2 Modern Photoemission Spectroscopy**

1.3.3 Modern Photoemission Spectroscopy

1950: R.G. Steinhardt Jr. published his PhD thesis, "An X-ray photoelectron spectrometer for chemical analysis" (Leihigh University). He was also the first to recognize that "X-ray photoelectron spectra are profoundly influenced by the chemical and physical nature of the surface under investigation" (Anal. Chem. 25, 697(1953)).

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1954: Kai Siegbahn built his high resolution photoelectron spectrometer, and subsequently established XPS as an important research and analysis tool. (Figure 3.2.2 from K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johnsson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, Nova Acta Regiae Soc. Sci. Ups. 20, 7 (1967).)

In 1981: Kai M. Siegbahn was awarded the Nobel Prize for "his contribution to the development of high-resolution electron spectroscopy". (Nobel Lectures in physics (1981-1990), World Scientific Publishing Co. Pte. Ltd 1993)

Fig.1.3.5 Schematic diagram of the early X-ray source from B. Wannberg, U. Gelius, and K. Siegbahn, *J. of Phys. E.Sci. Instrum.* **7,** 149-159 (1994).

Reference:
3.1 J. C. Vickerman, *Surface analysis – the principal techniques,* John Wiley & Sons (1997).

Goto: Section 1.2 Surface Sensitivity of XPS