

# Photoelectric effect

photoelectric effect

produces

photon absorption

giving  $\left\{ \begin{array}{l} e^- \\ \text{Kinetic energy} \end{array} \right.$

electron emission

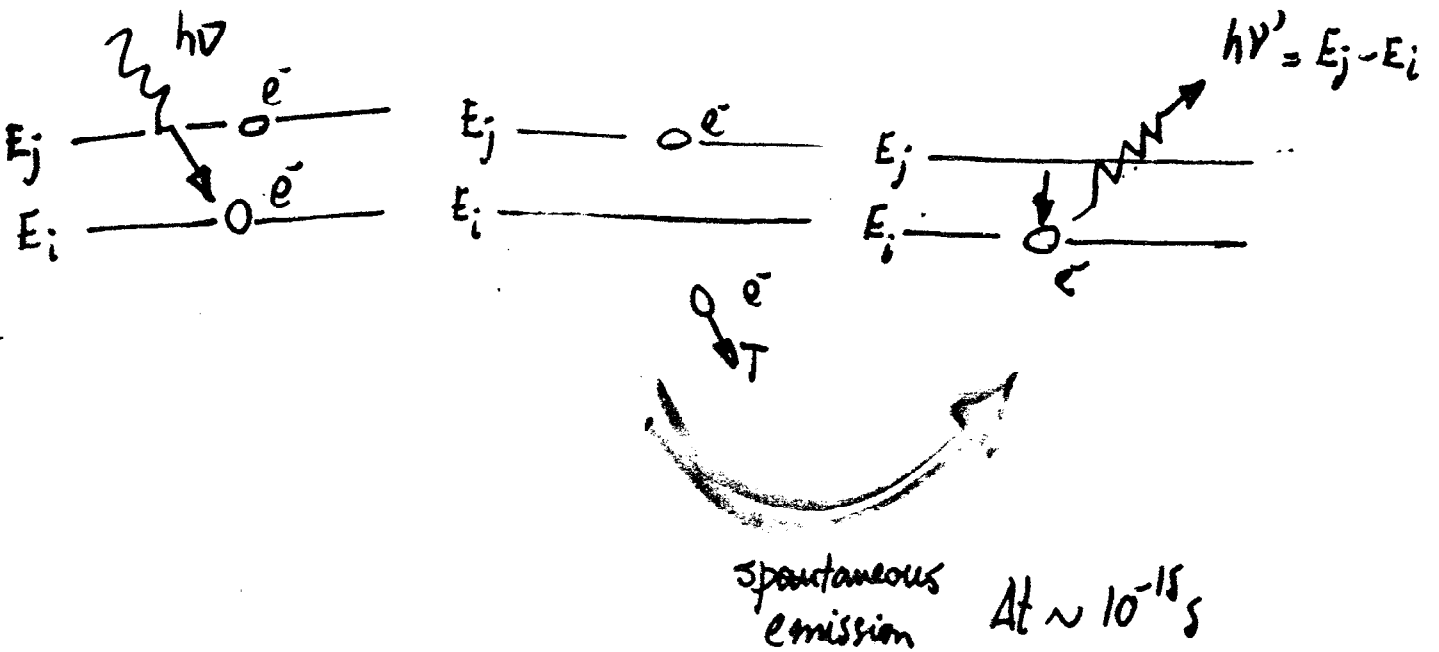
produces

hole

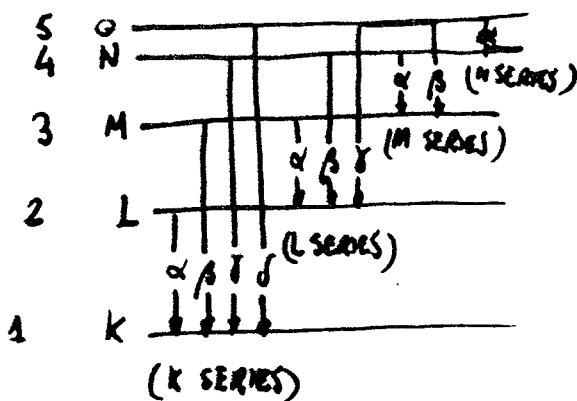
giving

transition from higher energy levels

## photon - photon interaction



## ELECTRONIC TRANSITIONS



# MOSELEY LAW

The energy levels for an hydrogenic atom  $Z$  are given by

$$E_n = - R_{\infty} hc \left( \frac{M}{M+m_e} \right) \frac{Z^2}{n^2} \quad n=1,2,3,\dots$$

$R_{\infty}$  Rydberg constant       $n$  the quantum number of the level

$$hcR_{\infty} = \frac{2\pi^2 m e^4}{8h^3 c} = 13.6 \text{ eV}$$

The energy of a transition from  $n_i$  to  $n_f$  is

$$h\nu = R_{\infty} hc \left( \frac{M}{M+m_e} \right) Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{hydrogenic atom}$$

Atom with many electrons

Nuclear charge  $\rightarrow (Z - \sigma) e$

$\sigma$  screening constant

$$h\nu_k \approx R_{\infty} hc (Z - \sigma_k)^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} R_{\infty} hc (Z - \sigma_k)^2$$

$$\left( \frac{\nu}{cR} \right)_{K_{\alpha}}^{1/2} = 0.874 (Z - 1.13) \quad (\text{Moseley law})$$

Straight line

Fig 3.5. K-series lines, illustrating Moseley's law. (White, 1934).

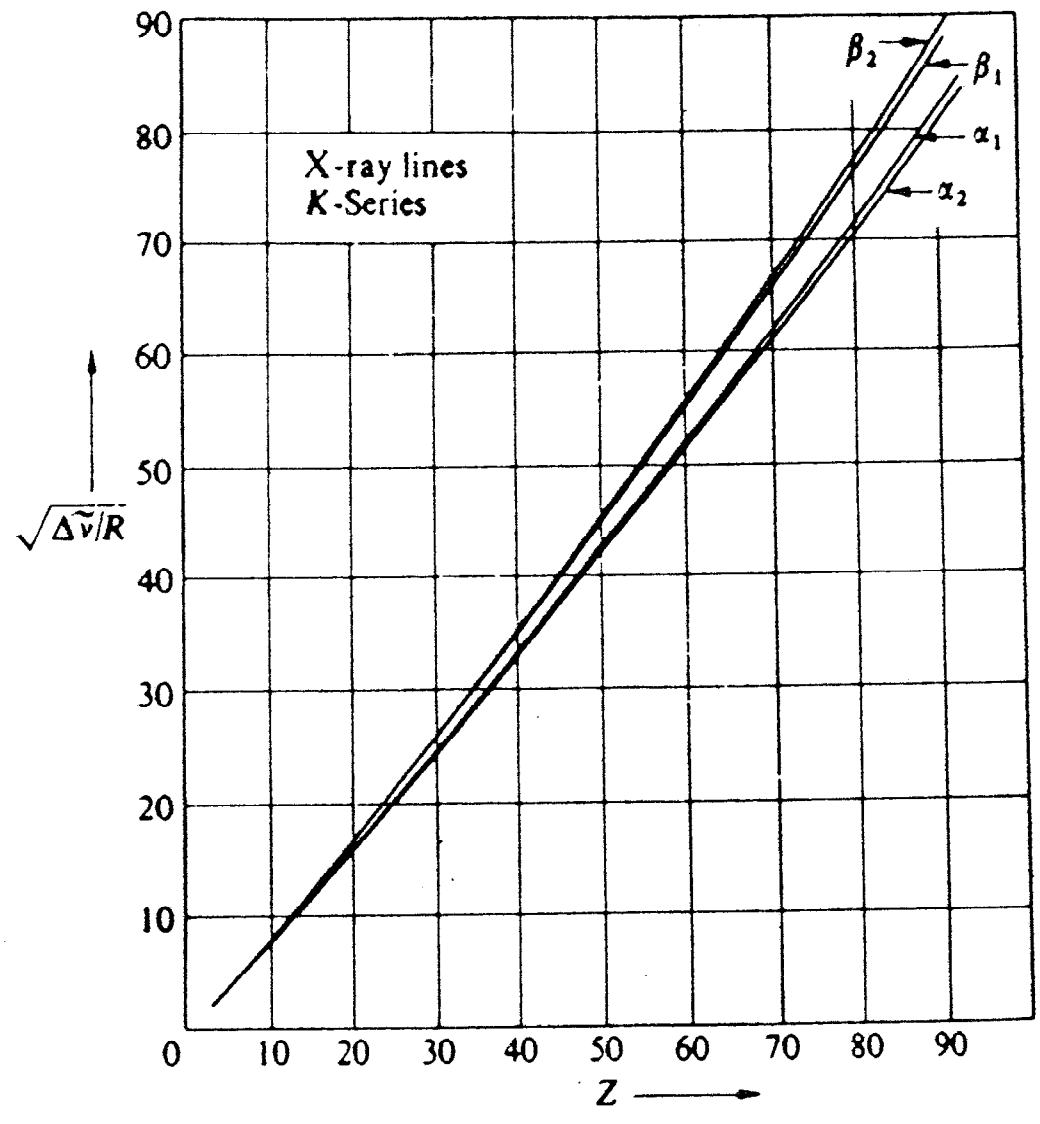
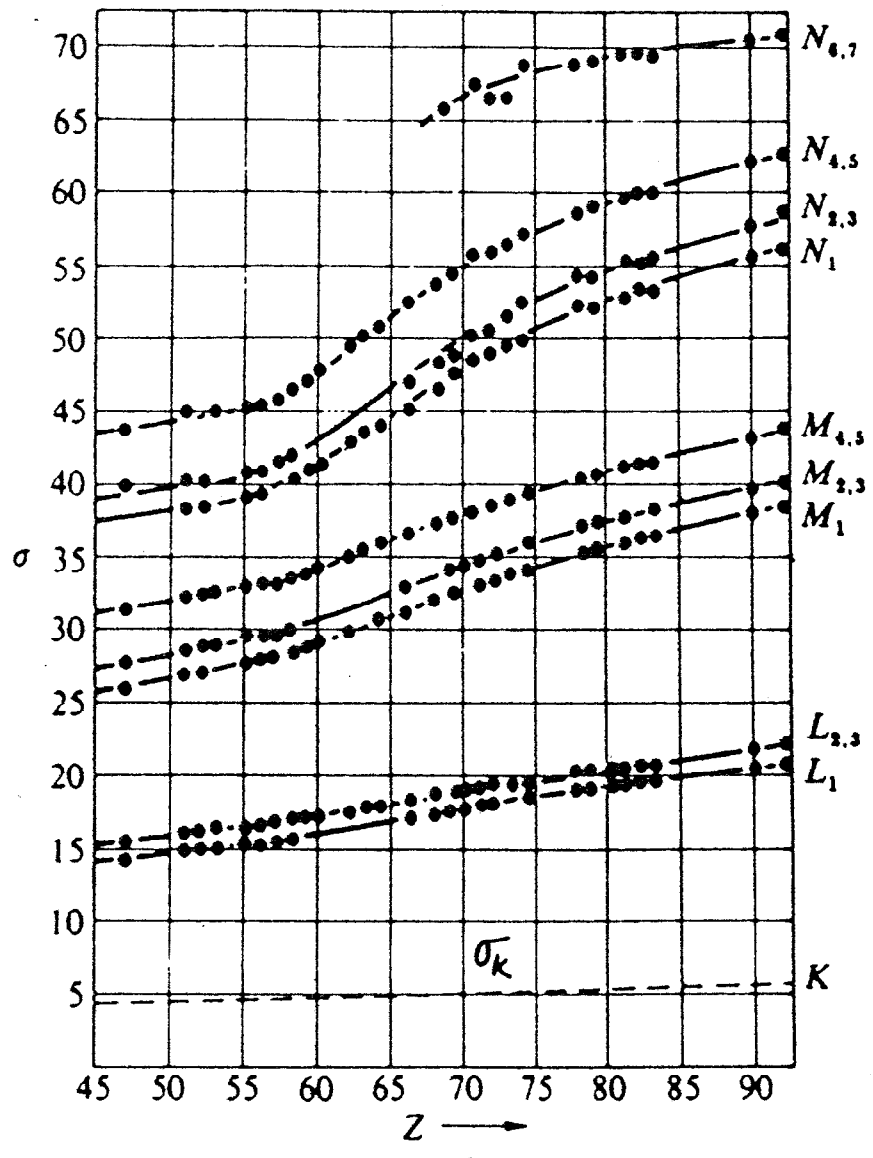


Fig. 3.6. Screening constant  $\sigma$ . (After A. Sömmmerfeld *Atombau and Spekrallinien*, 1944, Braunschweig: Vieweg. For an English translation of an earlier edition of this text, see Sömmmerfeld (1934)).



# X-Ray Terms

Wave function for the stationary state of the hydrogenlike atom

$$\psi_{nlm m_s} = R_{nl}(r) Y_l^m(\theta) Z_m(\phi) \psi_{spin}$$

$n = 1, 2, 3, \dots$  principal quantum number  $\rightarrow$  SHELL and ENERGY

K, L, M

$0 \leq l < n$  orbital angular momentum  $\rightarrow$  SUBSHELL

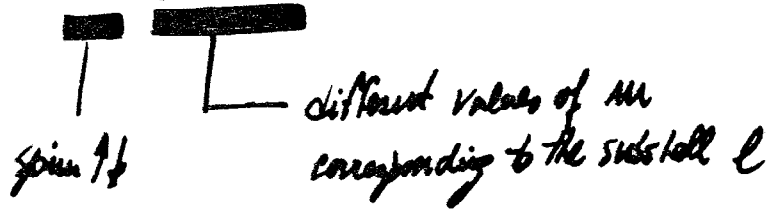
$-l \leq m \leq l$  magnetic quantum number

$m_s = \pm \frac{1}{2}$  spin orientation

CONFIGURATION

Pauli's exclusion principle: no two electrons in an atom can have the same four quantum numbers

# electrons in a subshell  $\rightarrow 2(2l+1)$



States with different energy are characterised by  $n$  ( $E_n$ )

$\Rightarrow$  degeneracy (many states  $\psi_{nlm m_s}$  have the same energy)

Degeneracy is broken if we consider spin-orbit interactions

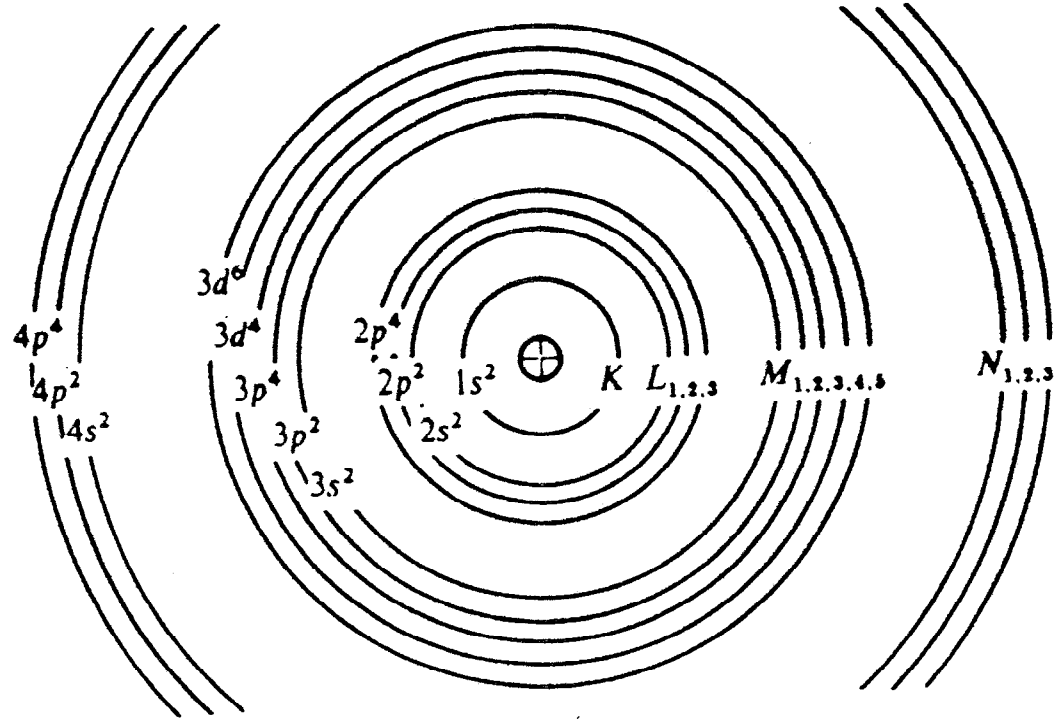
$j = l \pm m_s$  total angular momentum

$-j \leq m_j \leq j$  ]  $n, l, j, m_j$

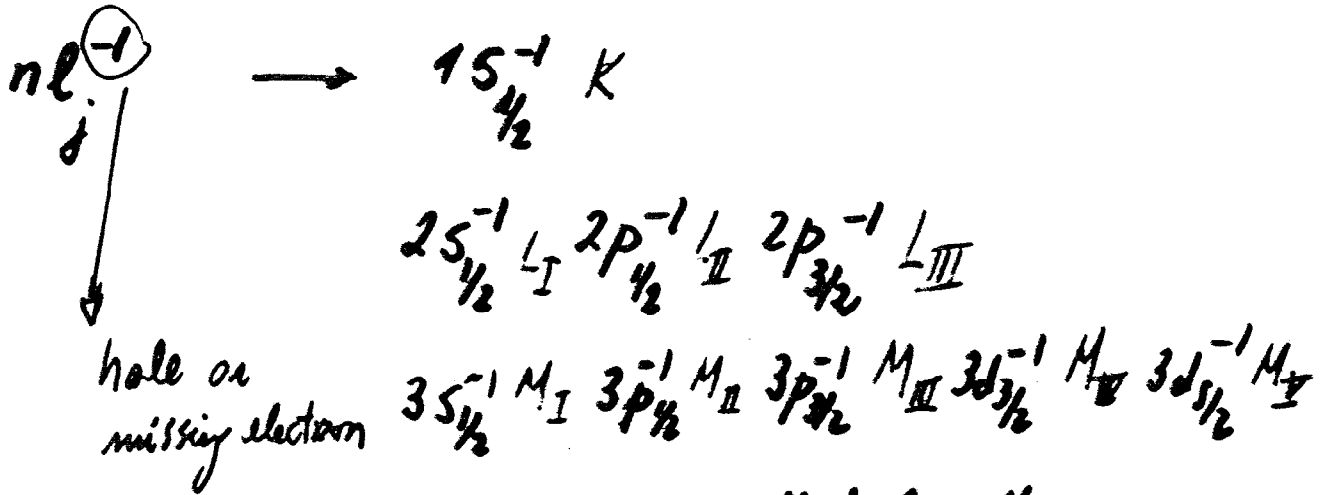
Table 3.1 Electronic orbits, with quantum numbers

$n$	$l$	$j$				
1	0	$\frac{1}{2}$	1s	K	1s	
2	0	$\frac{1}{2}$	$2s_{\frac{1}{2}}$	} $L_1$	2s	
2	1	$\frac{1}{2}$	$2p_{\frac{1}{2}}$		} $L_2$	2p
2	1	$\frac{3}{2}$	$2p_{\frac{3}{2}}$			
3	0	$\frac{1}{2}$	$3s_{\frac{1}{2}}$	$M_1$	3s	
3	1	$\frac{1}{2}$	$3p_{\frac{1}{2}}$	} $M_2$	3p	
3	1	$\frac{3}{2}$	$3p_{\frac{3}{2}}$			} $M_3$
3	2	$\frac{3}{2}$	$3d_{\frac{3}{2}}$			
3	2	$\frac{5}{2}$	$3d_{\frac{5}{2}}$	$M_5$	3d	
4	0	$\frac{1}{2}$	$4s_{\frac{1}{2}}$	$N_1$	4s	
4	1	$\frac{1}{2}, \frac{3}{2}$	$4p_{\frac{1}{2}}, \frac{3}{2}$	$N_{2, 3}$	4p	
4	2	$\frac{3}{2}, \frac{5}{2}, \frac{7}{2}$	$4d_{\frac{3}{2}}, \frac{5}{2}, \frac{7}{2}$	$N_{4, 5}$	4d	
4	3	$\frac{5}{2}, \frac{7}{2}$	$4f_{\frac{5}{2}}, \frac{7}{2}$	$N_{6, 7}$	4f	

Fig. 3.1. The Bohr atom-shells and sub-shells of krypton. In the designation  $3d^6$  (for example), 3 refers to the principal quantum number  $n$ ,  $d$  refers to the angular momentum quantum number  $l$  ( $l=0, 1, 2, 3, \dots$  is indicated by the letters  $s, p, d, f, \dots$ ) and the superscript indicates the number of the electrons in the sub-shell.



# Spectroscopic notation



x-rays are produced by transitions that fill the holes created by photoelectric effect

## Energies of Atomic X-Rays

Non relativistic hamiltonian  $H_0$  (unperturbed)

$$H_0 = \frac{p^2}{2m} - \frac{ze^2}{r}$$

$$H_0 \psi_{nlm} = E_n \psi_{nlm} \quad (\text{Ec. Schrödinger})$$

$$E_n = -R_{\infty} hc \frac{z^2}{n^2} = -\frac{m \alpha^2 c^2}{2} \frac{z^2}{n^2}$$

Relativistic hamiltonian (perturbation)

$$H = H_0 + H' \quad H' = -\frac{1}{2mc^2} \left( H_0 + \frac{ze^2}{r} \right)^2 = -\frac{p^4}{8m^3 c^2}$$

$$E_{nl} = E_n + E'_{rel} = E_n \left[ 1 - (\alpha z)^2 \frac{1}{n} \left( \frac{3}{4n} - \frac{1}{l+1/2} \right) \right]$$

Removes degeneracy between states with same  $n$  and different  $l$

# Spin-orbit interaction

$$H = H_0 + H' \quad H' = \frac{Ze^2 \hbar^2}{2m^2 c^2 r^3} \overbrace{1}^{3(r)} \vec{L} \cdot \vec{S}$$

$$\Psi_{nlm m_s} = \Psi_{nlm} \Psi_{spin} = |nl m_l\rangle |m_s\rangle = |nl m_l m_s\rangle$$

$$E'_{spin-orbit} = \langle nl | 3(r) | nl \rangle \begin{cases} \frac{l}{2} & \text{if } j = l + \frac{1}{2} \\ -\frac{1}{2}(l+1) & \text{if } j = l - \frac{1}{2} \end{cases}$$

$$\langle nl | 3(r) | nl \rangle = \frac{R_\infty hc a^2 Z^4}{m^3 l(l+1)(l+\frac{1}{2})}$$

Removes  $m_l, m_s$  degeneracy within each configuration (same  $nl$ )

$$E_{nlj} = -R_\infty hc \frac{Z^2}{n^2} + \frac{a^2 Z^4}{n^4} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right)$$

valid for  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$

## Screening correction

first term)  $Z \rightarrow Z - \sigma_1(n, l)$   
└ total screening constant

second term)  $Z \rightarrow Z - \sigma_2(n, l)$   
└ internal screening constant

Atomic x-ray levels

$$E_{nlj} = \frac{I_{hole}}{h} + R_\infty hc \left\{ \frac{[Z - \sigma_1(n, l)]^2}{n^2} + \frac{a^2 [Z - \sigma_2(n, l, j)]^4}{n^4} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right\}$$

# Energy of x-ray lines

x-ray levels

- hole states have positive energy
- neutral atom in its ground state is the zero for energy measurements

x-ray line

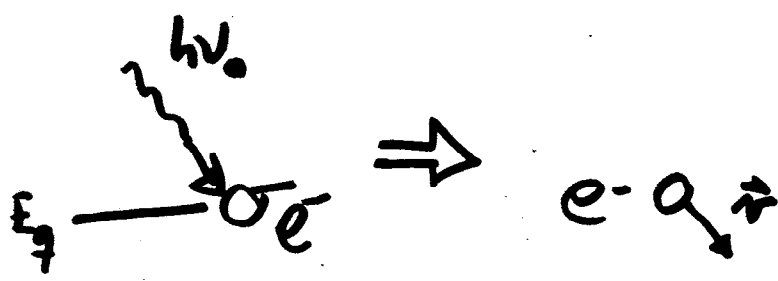
- hole transition from a higher level to a lower level on this energy diagram with selection rules

DIAGRAM LINES

$$\left\{ \begin{array}{l} \Delta n \neq 0 \\ \Delta l = \pm 1 \\ \Delta j = 0, \pm 1 \end{array} \right\} \text{electric-dipole selection rules}$$

suffer further selection depending on parity of the wave function.

# Photoelectric effect



$$h\nu_0 = \frac{1}{2}mv^2 + E_f$$

Labels for the energy levels in the equation above:

- $h\nu_0$ : incident quantum
- $\frac{1}{2}mv^2$ : Kinetic energy of the photoelectron
- $E_f$ : Binding energy of the electron

Energy balance of the photoelectric effect

# Quantum theory of the photoelectric effect

For a K shell electron

$$E_g = E_x = \frac{1}{2} m c^2 \alpha^2 Z^2 \quad (\text{unperturbed})$$

The matrix element for the absorption of a photon is

$$H' = - \frac{e}{m} \left( \frac{\hbar}{v v_0} \right)^{1/2} \int \psi_f^\dagger (\vec{p} \cdot \vec{e}_0) e^{i \vec{k}_0 \cdot \vec{r}} \psi_i \, d\tau$$

↑ volume
↑ momentum operator
↑ polarization Vector
↑ propagator Vector

For K shell electron

$$\psi_i = \left( \frac{a^3}{\pi} \right)^{1/2} e^{-ar} \quad a = \frac{Z}{a_0} \quad a_0 = \frac{\hbar^2}{m e^2}$$

In Born approximation

$$\psi_f = v^{-1/2} e^{i \vec{p} \cdot \vec{r} / \hbar}$$

↑ momentum of free electron

Since  $\psi_f$  is an eigenstate of the momentum, we can write

$$\langle f | \vec{p}_0 \cdot \vec{e}_0 e^{i \vec{k}_0 \cdot \vec{r}} | i \rangle = \vec{p}_0 \cdot \vec{e}_0 \langle f | e^{i \vec{k}_0 \cdot \vec{r}} | i \rangle$$

↑ is a number

then

$$H' = - \frac{e}{mv} \left( \frac{a^3 \hbar}{\pi v_0} \right)^{1/2} \vec{p} \cdot \vec{e}_0 \int_V e^{i(\vec{k}_0 - \vec{p}) \cdot \vec{r}} e^{-ar} d^3r$$

$$= - \frac{e}{mv} \left( \frac{a^3 \hbar}{\pi v_0} \right)^{1/2} (\vec{p} \cdot \vec{e}_0) \frac{8\pi a}{(a^2 + k^2)^2} \quad \vec{k} = \frac{\vec{k}_0 - \vec{p}}{\hbar}$$

The differential cross section is given by

$$d\sigma = \frac{V}{c} \frac{2\pi}{\hbar} \rho_f |H'|^2 d\Omega$$

density of final states =  $\frac{\rho(mc^2)}{h^3 c^2} = \frac{mp}{h^3}$

$$\frac{d\sigma}{d\Omega} = \frac{64 Z^5 a_0^2 \alpha^8 (2E/mc^2)^{1/2} (\vec{p} \cdot \vec{e}_0)^2}{\left[ (\alpha Z)^2 + \frac{ZE}{mcc} \left( 1 - \frac{v}{c} \vec{k}_0 \cdot \vec{p} \right) \right]^4}$$

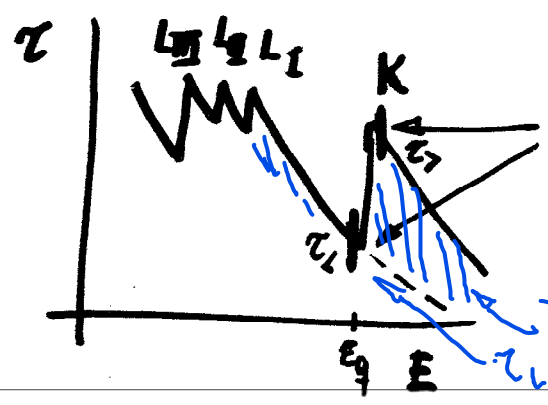
↑ takes into account the photon polarization

Integrated coefficient is

$$\tau_m \propto v_0^{-3/2} Z^5 \quad \text{as observed}$$

Observed coefficient

$$\tau = \tau_K + \tau_{L_2} + \tau_{L_1} + \dots$$



two values on either side of the absorption edge at  $E_K$   
We define the absorption edge jump

$$r = \frac{\tau_K}{\tau_L} > 1$$

In the region  $E > E_k$

$\tau_k = (1 - \frac{1}{r_k}) \tau$  gives the fraction of the total number of photoelectrons that come from the k shell

Ways of Filling the vacancy

**Radiative**

Fluorescence  
characteristic lines spectra

**Non radiative**

Auger effect  
an electron is emitted rather than a photon

Coster-Kronig transitions  
double ionization giving high energy satellites

Radiative fraction

$\omega_f$  fluorescence yield of the g-series  
(fraction of radiative transitions in its own series)

Photoelectric kernel

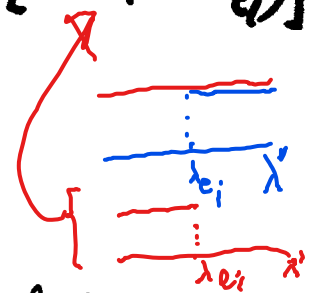
Isotropic (since radiative emission is an spontaneous process separated from photoelectric)

$$k_p(\omega, \lambda, \omega_0; \lambda') = \frac{1}{4\pi} \sum_i Q_{\lambda_i}(\lambda') \tau_{k_s}(\lambda) \delta(\lambda - \lambda_i) [1 - u(\lambda' - \lambda_i)]$$

$$Q_{\lambda_i}(\lambda') = W_s \tau_s(\lambda') (1 - \frac{1}{r_i}) \omega_{\lambda_i} \Gamma_{\lambda_i}$$

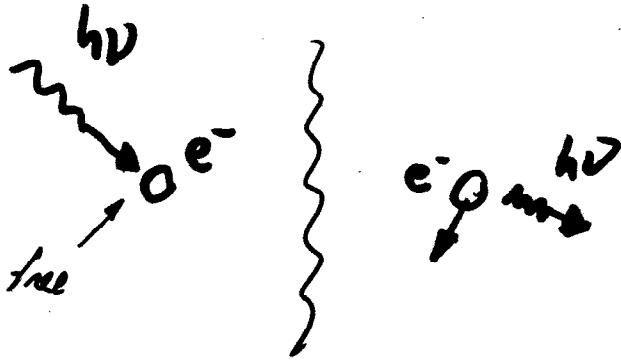
Weight fraction of element s

intensity fraction of the line i in its own series

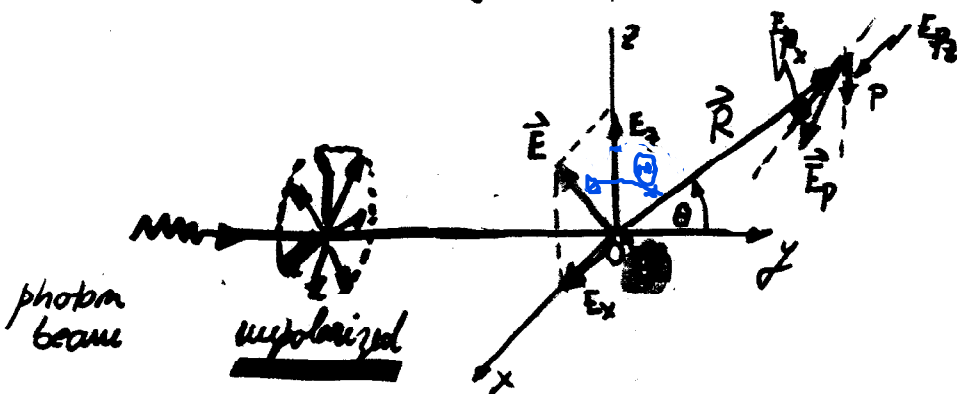


# Scattering of x rays

## Coherent scattering (Rayleigh) Elastic



## Classical electrodynamics (THOMSON)



Electric field of the incident wave at point O (time t):  $E = E_0 e^{i\omega t}$

The electron receives an acceleration  $\vec{a}$

$$\vec{a} = \frac{e \vec{E}}{m_e} \text{ and as an accelerated charge becomes a radiation source (same } \omega \text{)}$$

Then there is a scattered wave at point P (at the same t) ↑  
since is nonrelativistic motion

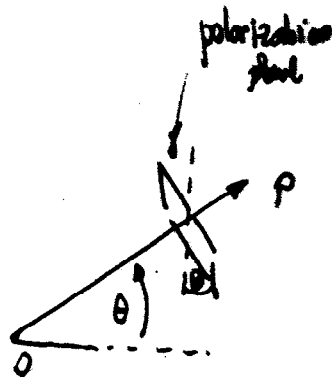
$$\vec{E}_p = - \vec{E} \frac{e^2}{mc^2 R} \sin^2 \theta$$

$$\vec{E} = \vec{E}_0 e^{i\omega(t - \frac{R}{c})}$$

Let P in the plane yz

$$\vec{E}_{p_x} = \frac{e^2}{mc^2 R} \vec{E}_x$$

$$\vec{E}_{p_z} = \frac{e^2}{mc^2 R} \vec{E}_z \cos \theta$$



The ENERGY per unit volume that flows at P is

$$E_p^2 = E_{p_x}^2 + E_{p_z}^2$$

and since  $\langle \vec{E}_x \rangle^2 = \langle E_z \rangle^2 = \frac{\langle E \rangle^2}{2}$  (unpolarized beam)

$$\langle E_p \rangle^2 = \frac{e^4 \langle E \rangle^2}{m^2 c^4 R^2} \left( \frac{1 + \cos^2 \theta}{2} \right)$$

The INTENSITY ( $I = \frac{c}{4\pi} |E|^2$ ) is

$$I = I_0 \frac{r_e^2}{R^2} \left( \frac{1 + \cos^2 \theta}{2} \right)$$

$$r_e = \frac{e^2}{mc^2} \text{ 'classical radius of electron'}$$

The classical differential cross section per electron is

$$\left( \frac{d\sigma_e}{d\Omega} \right)_{\text{Thomson}} = \frac{\text{Energy radiated / unit time / unit solid angle}}{\text{Incident energy flux in energy / unit area / unit time}}$$

$$= \frac{I_e R^2}{I_0} = \frac{r_e^2}{2} (1 + \cos^2 \theta)$$

The integrated scattering cross section per electron is

$$\int_{4\pi} d\vec{\omega} \left( \frac{d\sigma_e}{d\vec{\omega}} \right)_{Th} = 2\pi \int_{-1}^1 d\eta \frac{r_e^2}{2} (1+\eta^2) = \boxed{\frac{8\pi}{3} r_e^2} = 0.66 \text{ b}$$

For an atom with Z electrons  $\sigma_a_{Th} = Z \frac{8\pi}{3} r_e^2$

and for a pure material of atomic number Z

$$\sigma_{Th} = \frac{N_e Z}{A} \sigma_{e, Th} \left[ \frac{cm^2}{g} \right] \approx 0.2 \frac{cm^2}{g} \text{ (should be a universal constant)}$$

Since  $\frac{Z}{A} \approx 0.5$

But not all the electrons contribute in the same way to the atomic cross-section because they are bound with different bindings

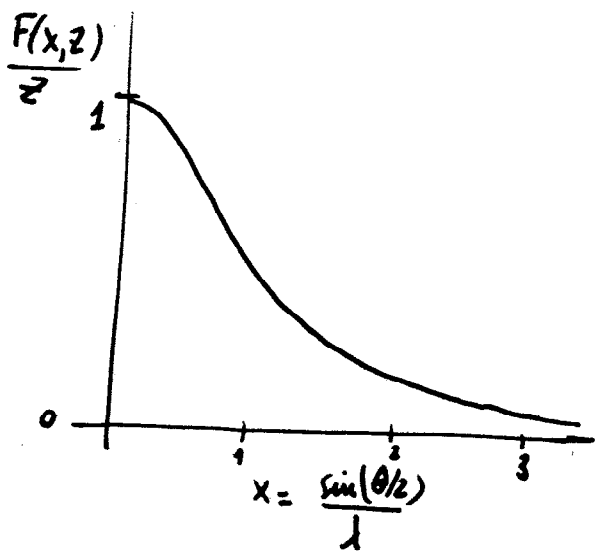
$$\left( \frac{d\sigma_a}{d\Omega} \right)_{Rayleigh} = \left( \frac{d\sigma_e}{d\Omega} \right)_{Th} \underbrace{F^2(\theta, z)}_{\text{scattering form factor}}$$

$$F(\theta, z) = \int \underbrace{\rho(\vec{r})}_{\text{electron density at } \vec{r}} \underbrace{e^{i\vec{q} \cdot \vec{r}}}_{\text{wave contribution from } \vec{r}} d^3r$$

$|\vec{q}| = \frac{2k}{\lambda} \sin\left(\frac{\theta}{2}\right)$  "momentum transfer"

# Rayleigh scattering kernel

$$K_R(\vec{\omega}, \lambda, \vec{\omega}', \lambda') = \underbrace{\delta(\lambda - \lambda')}_{\text{scatt-elastico}} \underbrace{\frac{r_0^2}{2} (1 + (\vec{\omega} \cdot \vec{\omega}')^2)}_{\text{Thomson differential cross section}} \underbrace{F^2(\lambda', \vec{\omega}, \vec{\omega}', z)}_{\text{form factor (scidij)}}$$



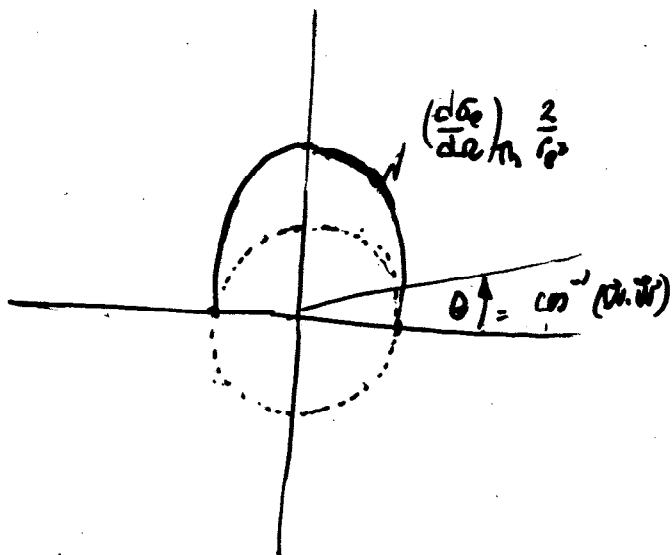
$$x = \frac{\sin(\theta/2)}{1} = \frac{E}{hc} \sin(\theta/2)$$

$$\sin(\theta/2) = \sqrt{\frac{1 - \vec{\omega} \cdot \vec{\omega}'}{2}}$$

$$E [\text{keV}] = \frac{hc}{\lambda} = \frac{12.39}{\lambda [\text{\AA}]}$$

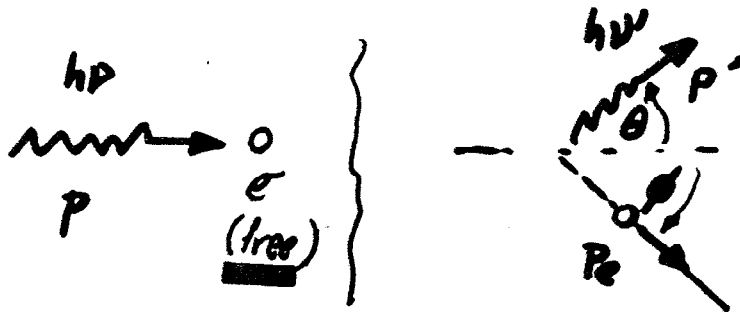
$$F \rightarrow z \begin{cases} \vec{\omega} \cdot \vec{\omega}' \rightarrow 1 \\ \lambda \rightarrow \infty \\ (E \rightarrow 0) \end{cases}$$

$$F \rightarrow 0 \begin{cases} \lambda \rightarrow 0 \\ (E \rightarrow \infty) \end{cases} \vec{\omega} \neq \vec{\omega}'$$



# Incoherent scattering (Compton)

(34)



Exchange of energy and momentum

Evidence of the particle nature of the photon

We can analyze energy and momentum conservation in the hit (relativistic particle)

Relativistic energy of a free particle  $\sqrt{(pc)^2 + (mc^2)^2}$

and momentum is  $p = \frac{E}{c}$

For the photon  $v=c$  and  $mc^2 \equiv 0$  (zero rest mass) then  $E = pc$

$$\text{or } p = \frac{E}{c} = \frac{h\nu}{c}$$

Conservation of momentum gives

$$\frac{h\nu}{c} = \left(\frac{h\nu'}{c}\right) \cos \theta + p_e \cos \phi \quad (C.1)$$

$$0 = \left(\frac{h\nu'}{c}\right) \sin \theta - p_e \sin \phi \quad (C.2)$$

Conservation of energy gives

$$h\nu + m_0 c^2 = h\nu' + \sqrt{p_e^2 c^2 + (m_0 c^2)^2} \quad (C.3)$$

From (C.1) and (C.2)

$$p_e^2 c^2 = (h\nu)^2 + (h\nu')^2 - 2(h\nu)(h\nu') \cos \theta$$

and from (C.3)

$$p_e^2 c^2 + (m_0 c^2)^2 = (h\nu - h\nu')^2 + 2m_0 c^2 (h\nu - h\nu') + (m_0 c^2)^2$$

then

$$m_0 c^2 (\nu - \nu') = h\nu\nu' (1 - \cos \theta)$$

or

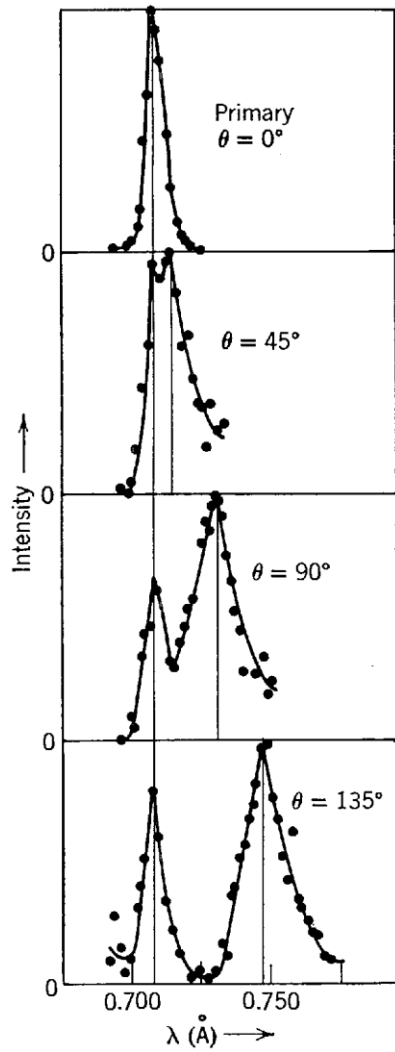
$$\lambda' - \lambda = \left[ \frac{h}{m_0 c} \right] (1 - \cos \theta)$$

Compton wavelength

Compton shift

Note that  $\lambda' > \lambda$

- The shift depends only on the scattering angle  $\theta$  not on the energy of the incident photon



**Figure 2-6** Compton's experimental results. The solid vertical line on the left corresponds to the wavelength  $\lambda$ , that on the right to  $\lambda'$ . Results are shown for four different angles of scattering  $\theta$ . Note that the Compton shift,  $\Delta\lambda = \lambda' - \lambda$ , for  $\theta = 90^\circ$ , agrees well with the theoretical prediction  $h/m_0c = 0.0243 \text{ \AA}$ .

Klein and Nishina computed (Dirac's relativistic theory of electron) the differential cross section for the Compton effect (unpolarized)

$$\left(\frac{d\sigma_e}{d\Omega}\right)_{KN} = \frac{r_e^2}{2} [1 + \alpha(1 - \cos\theta)]^{-2} \left[ 1 + \cos^2\theta + \frac{\alpha^2(1 - \cos\theta)^2}{1 + \alpha(1 - \cos\theta)} \right]$$

$$\text{where } \alpha = \frac{E}{m_e c^2} = \frac{h\nu}{m_e c^2}$$

Once more time the electrons contribute differently to the atomic cross section and we must introduce the incoherent scattering function S

$$\frac{d\sigma_a}{d\Omega} = \left(\frac{d\sigma_e}{d\Omega}\right)_{KN} S(\lambda', \theta, z)$$

S takes into account the binding of electrons with different energies and momenta.

Other processes may occur (they are neglected)

- Distribution of momenta of electrons produces a line broadening.
- Inverse Compton scattering

# Compton scattering kernel

$$K(\vec{w}, \lambda, \vec{w}'; \lambda') = \frac{e^2}{2} \underbrace{K_{\vec{w}}(\lambda, \lambda')}_{\text{Klein-Nishina electronic differential cross section}} \underbrace{S(\lambda', \vec{w}, \vec{w}', z)}_{\text{Scattering function}} \underbrace{\delta(\lambda' - \lambda + \lambda_c(1 - \vec{w} \cdot \vec{w}'))}_{\text{Compton shift}}$$

we have

$$K_{\vec{w}}(\lambda, \lambda') = \left(\frac{\lambda'}{\lambda}\right)^2 \left\{ \frac{\lambda}{\lambda'} + \frac{\lambda'}{\lambda} + \frac{\lambda - \lambda'}{\lambda_c} \left(\frac{\lambda - \lambda'}{\lambda_c} - z\right) \right\}$$

We can do the check (HOMEWORK)

$$\alpha' = \frac{E'}{mc^2}$$

$$\sigma(\nu') = \int_0^\infty d\nu \int_{4\pi} d\vec{w} \sigma_{\vec{w}}(\nu' \rightarrow \nu, \vec{w})$$

$$= \pi r_0^2 \int_{-1}^1 dz \frac{1}{[1 + \alpha'(1-z)]^2} \left[ \frac{1 + z^2 + \alpha'^2(1-z)^2}{1 + \alpha'^2(1-z)} \right]$$

to verify that the integral cross section coincides with the experimental behaviour.