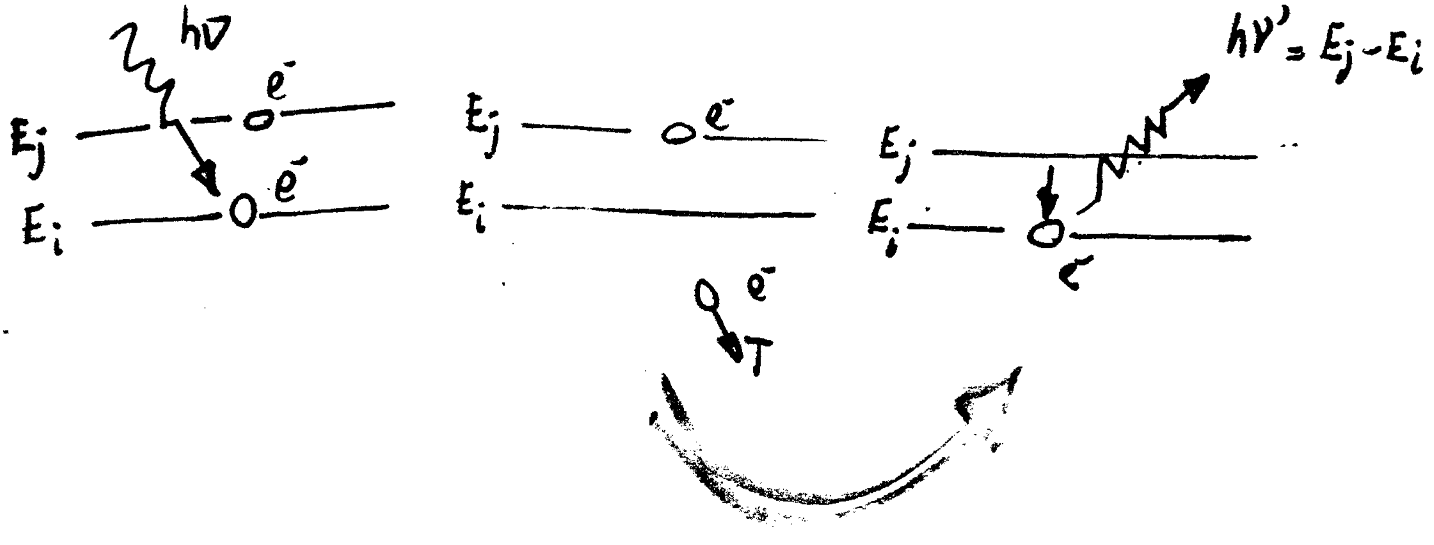
Photoelectric effect

photoelectric effect produces photon absorption giving { e^-, Kinetic energy

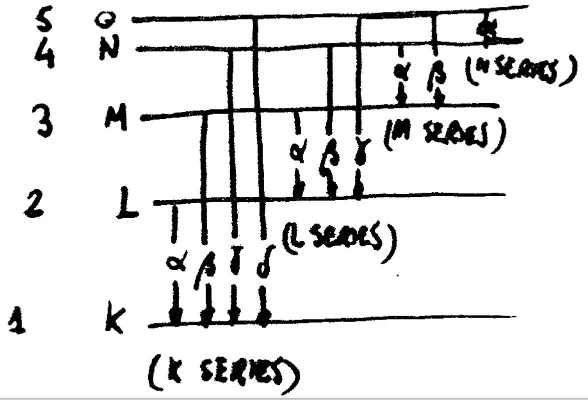
electron emission produces hole giving transition from higher energy levels

photon - photon interaction



spontaneous emission $\Delta t \sim 10^{-15}$ s

ELECTRONIC TRANSITIONS



MOSELEY LAW

The energy levels for an hydrogenic atom Z are given by

$$E_n = -\underbrace{R_\infty}_{\text{Rydberg constant}} hc\left(\frac{M}{M+m}\right)\frac{Z^2}{\underbrace{n^2}_{\text{the quantum number of the level}}} \qquad n=1,2,3,\ldots$$

$$hcR_\infty = 2\pi^2\frac{me^4}{\cancel{c}h^{\cancel{3}2}} = 13.6\ \text{eV}$$

The energy of a transition from n_i to n_f is

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

Atom with many electrons

$$\text{Nuclear charge} \longrightarrow (Z-\underbrace{\sigma}_{\text{screening constant}})e$$

$$h\nu_K \simeq R_\infty hc(Z-\sigma_K)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right) = \frac{3}{4}R_\infty hc(Z-\sigma_K)^2$$

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

$$\boxed{\text{Stright line}}$$

(22J)

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

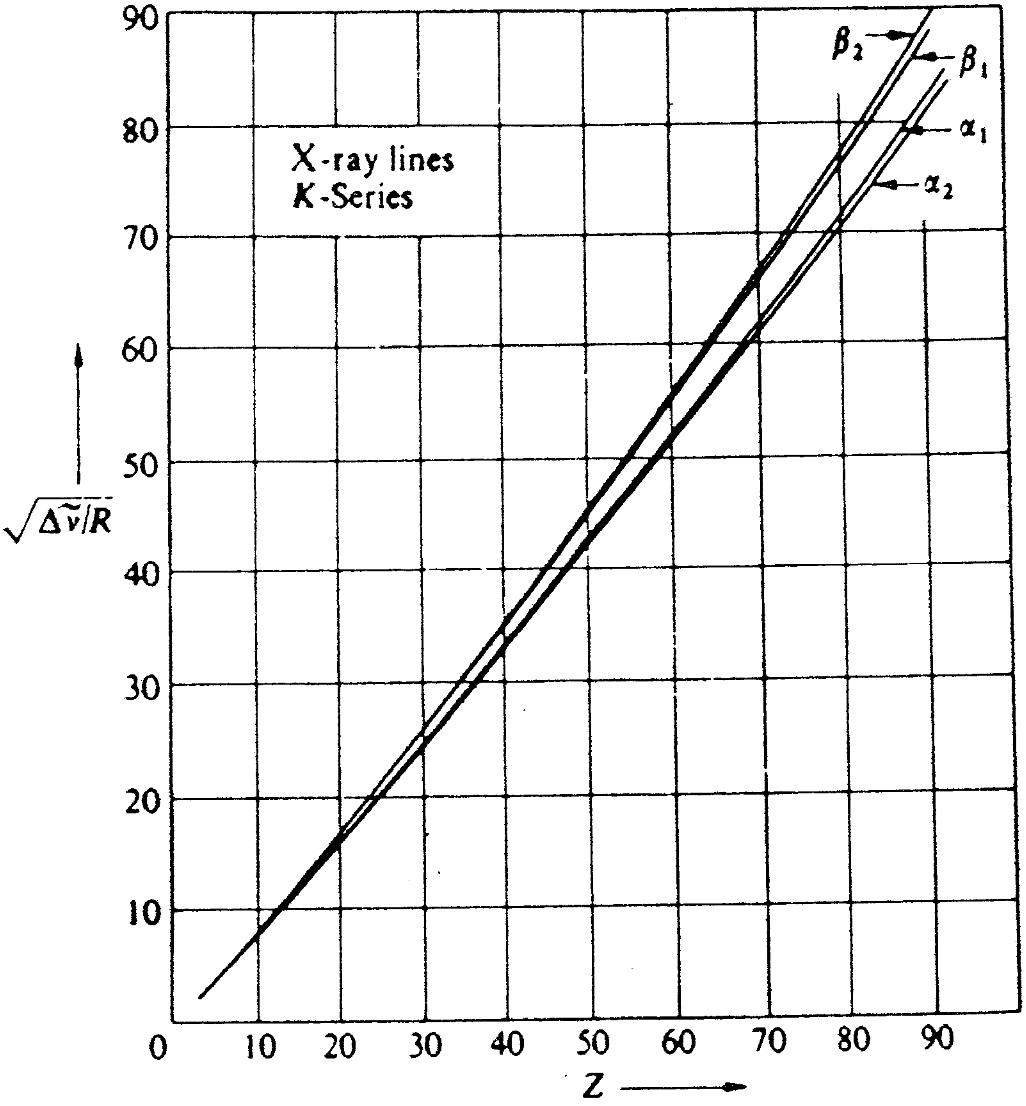
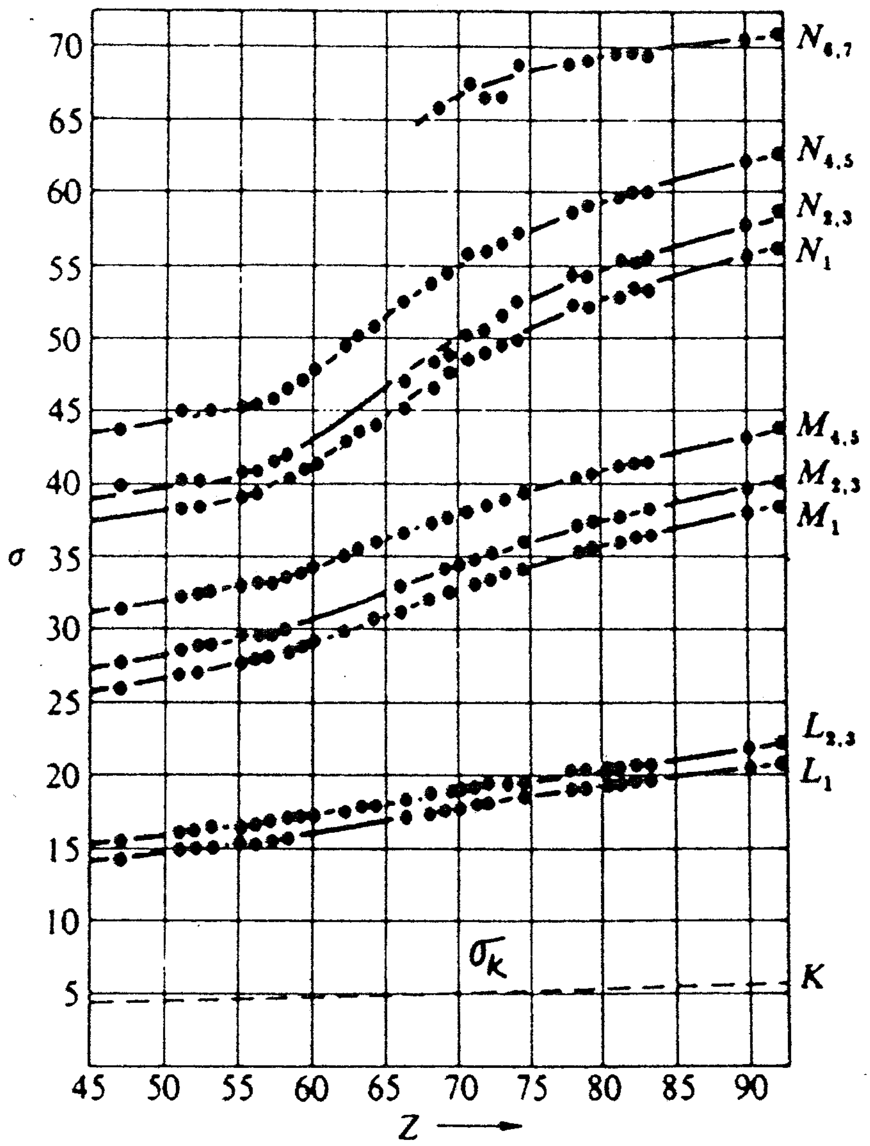


Fig. 3.6. Screening constant σ_s. (After A. Sömmerfeld *Atombau and Spekrallinien*, 1944, Braunschweig: Vieweg. For an English translation of an earlier edition of this text, see Sömmerfeld (1934)).



X-Ray Terms

Wave function for the stationary state of the hydrogen-like atom

$$\psi_{nlmm_s} = R_{nl}(r)\, Y_l(\theta)\, Z_m(\phi)\, \psi_{spin}$$

$n = 1, 2, 3 \ldots$ $\boxed{K, L, M}$ principal quantum number → SHELL and ENERGY

$0 \leq l < n$ $\boxed{1,2,3,4,5\ldots}$ $\boxed{s,p,d,f,g..}$ orbital angular momentum → SUBSHELL

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

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

→ $\boxed{\text{CONFIGURATION}}$

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

\# electrons in a subshell → $\underbrace{2}_{\text{spin } \uparrow\downarrow}\ \underbrace{(2l+1)}_{\text{different values of } m \text{ corresponding to the subshell } l}$

States with different energy are characterised by n (E_n)

⇒ degeneracy (many states ψ_{nlmm_s} have the same energy)

Degeneracy is broken if we consider spin-orbit interaction

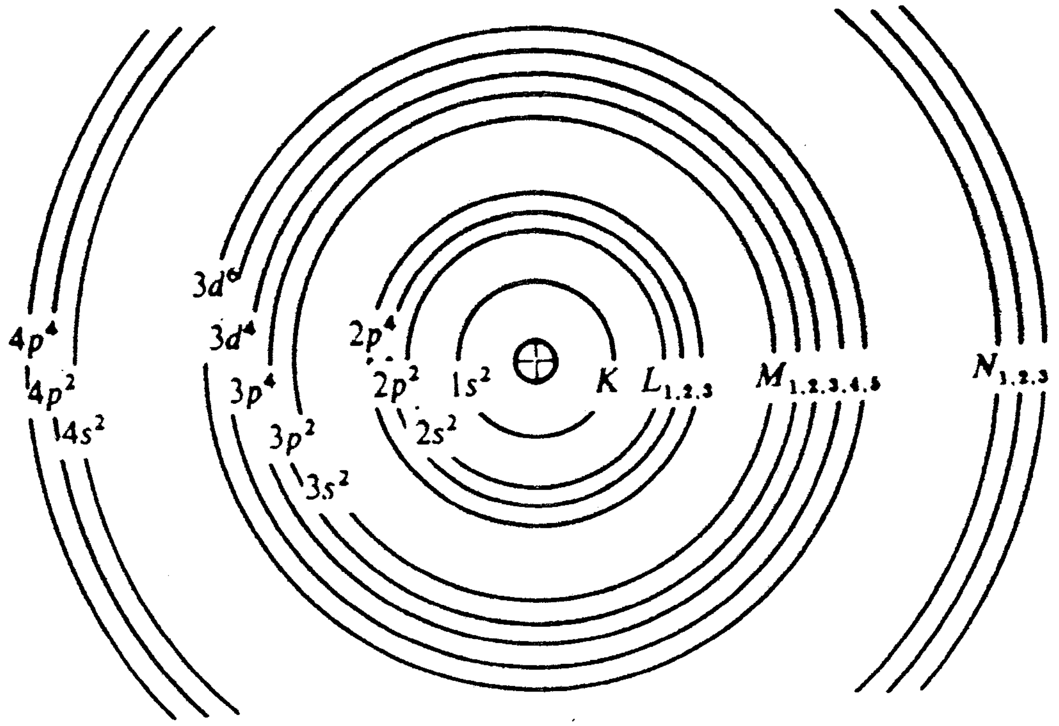
$j = l \pm m_s$ total angular momentum

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

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	$\frac{3}{2}$	$2p_{\frac{3}{2}}$	L_3	
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	$\frac{3}{2}$	$3d_{\frac{3}{2}}$	M_4	3d
3	2	$\frac{5}{2}$	$3d_{\frac{5}{2}}$	M_5	
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	$\frac{3}{2}, \frac{5}{2}$	$4d_{\frac{3}{2}}, \frac{5}{2}$	$N_{4,\ 5}$	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 ($\ell = 0, 1, 2, 3, \ldots$ is indicated by the letters $s, p, d, f, \ldots$) and the superscript indicates the number of the electrons in the sub-shell.



Spectroscopic notation

$n\ell_j^{(-1)} \longrightarrow 1s_{1/2}^{-1}\ K$

hole or missing electron

$2s_{1/2}^{-1}\ L_I \quad 2p_{1/2}^{-1}\ L_{II} \quad 2p_{3/2}^{-1}\ L_{III}$

$3s_{1/2}^{-1}\ M_I \quad 3p_{1/2}^{-1}\ M_{II} \quad 3p_{3/2}^{-1}\ M_{III} \quad 3d_{3/2}^{-1}\ M_{IV} \quad 3d_{5/2}^{-1}\ M_V$

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)

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

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

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

Relativistic hamiltonian (perturbation)

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

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

Removes degeneracy between states with same n and different l

Spin-orbit interaction

$$H = H_0 + H' \qquad H' = \overbrace{\frac{Ze^2\hbar^2}{2m^2c^2}\frac{1}{r^3}}^{\xi(r)}\,\vec{l}\cdot\vec{s}$$

$$\psi_{nlm m_s} = \psi_{nlm}\psi_{spin} = |n l m_l\rangle |m_s\rangle = |n l m_l m_s\rangle$$

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

$$\langle nl|\xi(r)|nl\rangle = \frac{R_\infty\, ch\, \alpha^2 Z^4}{n^3\, l(l+1)(l+\frac{1}{2})}$$

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

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

valid for $j = l + 1/2$ and $j = l - 1/2$

Screening correction

first term) $\quad Z \to Z - \underbrace{\underline{\sigma_1(n,l)}}_{\text{total screening constant}}$

second term) $\quad Z \to Z - \underbrace{\underline{\sigma_2(n,l)}}_{\text{internal screening constant}}$

Atomic x-ray levels

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

Energy of x-ray lines

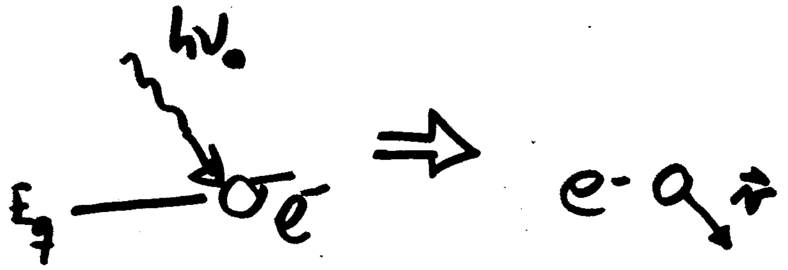
X-ray levels
- hole states have <u>positive</u> energy
- neutral atom in its ground state is the <u>zero</u> for energy measurements

X-ray line
- hole transition from a higher level to a lower level on this energy diagram with <u>selection rules</u>

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

suffer further selection depending on parity of the wave function.

Photoelectric effect



$$\underbrace{h\nu_0}_{\text{incident quantum}} = \underbrace{\frac{1}{2}mv^2}_{\text{Kinetic energy of the photoelectron}} + \underbrace{E_q}_{\text{Binding energy of the electron}}$$

Energy balance of the photoelectric effect

Quantum theory of the photoelectric effect

For a K shell electron

$$E_q = E_K = \frac{1}{2} m c^2 \alpha^2 Z^2 \qquad \text{(unperturbed)}$$

The matrix element for the absorption of a photon is

$$H' = -\frac{e}{m}\left(\frac{\hbar}{V\nu_0}\right)^{1/2} \int \psi_f^* (\vec{p}\cdot\vec{e}_0)\, e^{i\vec{k}_0\cdot\vec{r}}\, \psi_i \, dr$$

volume

polarization vector

propagation vector

momentum operator

For K shell electron

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

In Born approximation

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

momentum of free electron

Since ψ_f is an eigenstate of the momentum, we can write

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

is a number

then

$$H' = -\frac{e}{mV}\left(\frac{a^3\hbar}{\pi V_0}\right)^{1/2} \vec{p}\cdot\vec{e}_0 \int_V e^{i\frac{(\vec{k}_0-\vec{p})}{\hbar}\cdot\vec{r}}\, e^{-ar}\, d^3r$$

$$= -\frac{e}{mV}\left(\frac{a^3\hbar}{\pi V_0}\right)^{1/2} (\vec{p}\cdot\vec{e}_0)\, \frac{8\pi a}{(a^2+\lambda^2)^2} \qquad \vec{\lambda} = \frac{\vec{k}_0-\vec{p}}{\hbar}$$

The differential cross section is given by

$$d\sigma = \frac{V}{c}\,\frac{2\pi}{\hbar}\,\underbrace{\rho_f}_{\text{density of final states } = \frac{p(mc^2)}{h^3c^2} = \frac{mp}{h^3}}\, |H'|^2\, d\Omega$$

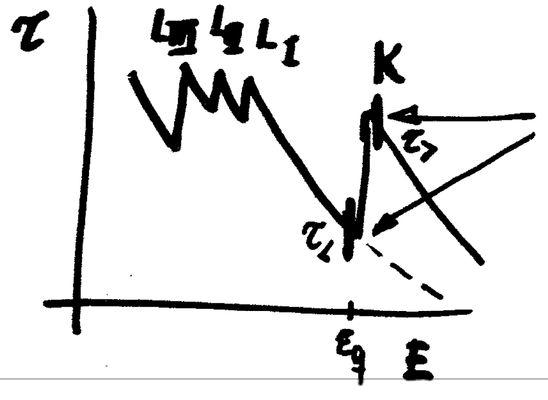
$$\frac{d\sigma}{d\Omega} = \frac{64\, Z^5 a_0^2 \alpha^8 \left(2E/mc^2\right)^{1/2} (\vec{p}\cdot\vec{e}_0)^2}{\left[(\alpha Z)^2 + \frac{2E}{mc^2}\left(1-\frac{v}{c}\,\vec{k}_0\cdot\vec{p}\right)\right]^4}$$

takes into account the photon polarization

Integrated coefficient is

$$\tau_m \propto \nu_0^{-7/2} Z^5 \quad \text{as observed}$$

Observed coefficient



two values on either side of the absorption edge at Eq

We define the absorption edge jump

$$r = \frac{\tau_>}{\tau_<} > 1$$

In the region $E > E_K$

$\left(1-\frac{1}{r_K}\right)\tau$ 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

ω_q fluorescence yield of the q-series

(fraction of radiative transitions in its own series)

Photoelectric kernel

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

$$k_p(\omega,\lambda,\vec{\omega};\lambda') = \boxed{\frac{1}{4\pi}} \sum_i Q_{\lambda_i}(\lambda')\,\delta(\lambda-\lambda_i)\left[1-U(\lambda'-\lambda_{e_i})\right]$$

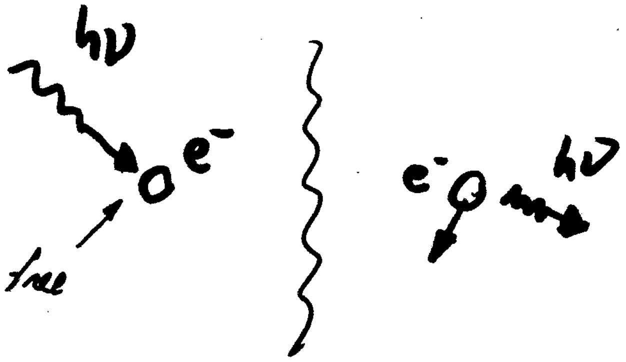
$$Q_{\lambda_i}(\lambda') = \underline{W_s}\,\overbrace{\tau_s(\lambda')\left(1-\frac{1}{r_{\lambda_i}}\right)}^{\tau_{K_s}(\lambda')}\,\omega_{\lambda_i}\,\underline{\Gamma_{\lambda_i}}$$

Weight fraction of element s

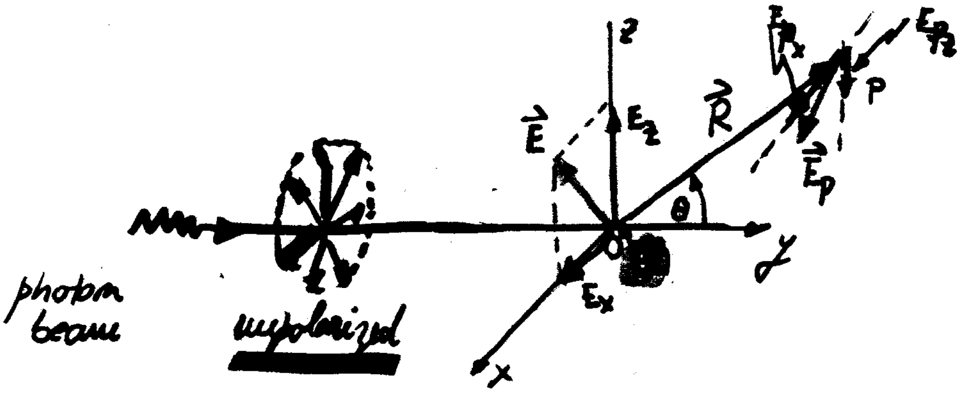
intensity fraction of the line i in its own series

Scattering of x rays

Coherent scattering (Rayleigh)



Classical electrodynamics (THOMPSON)



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

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

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

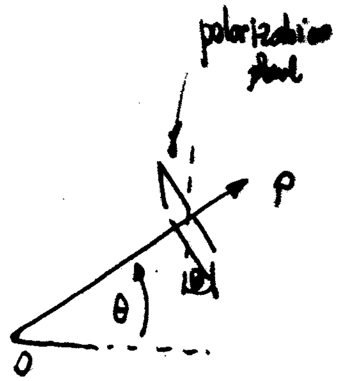
since is nonrelativistic motion

Then there is a scattered wave at point P (at the same t)

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

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

Let P in the plane yz



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

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

The ENERGY per unit volume that flows at P is

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

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

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

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

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

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

The classical differential cross section per electron is

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

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

The integrated scattering cross section per electron is

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

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

$$\sigma_{Th} = \frac{N_0 Z}{A} \sigma_{e_{Th}} \left[\frac{cm^2}{g}\right] \simeq 0.2 \, \frac{cm^2}{g}$$ (should be an universal constant)

since $\frac{Z}{A} \simeq 0.5$

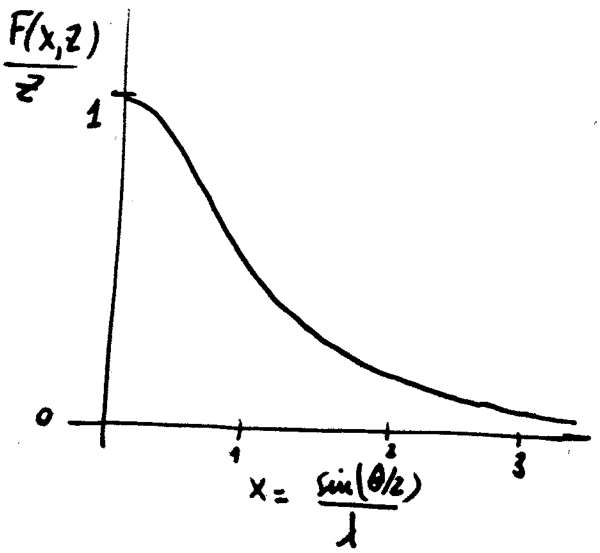
But not all the electrons contribute in the same way to the atomic cross-section because they are bound with different bindings

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

$$F(\theta, Z) = \int \underbrace{\rho(\vec{r})}_{\text{electron density at } \vec{r}} \, \underbrace{e^{i\vec{q}\cdot\vec{r}}}_{\text{wave contribution from } \vec{r}} \, d^3r \qquad |\vec{q}| = \frac{2k}{\hbar} \sin\left(\frac{\theta}{2}\right)$$ "momentum transfer"

Rayleigh scattering kernel

$$\underset{R}{k}(\vec{\omega},\lambda,\vec{\omega}',\lambda') = \underbrace{\delta(\lambda-\lambda')}_{\text{coherence}} \; \underbrace{\frac{r_e^2}{2}\left(1+(\vec{\omega}\cdot\vec{\omega}')^2\right)}_{\text{Thompson differential cross section}} \; \underbrace{F^2(\lambda', \vec{\omega}\cdot\vec{\omega}', Z)}_{\text{form factor (binding)}}$$

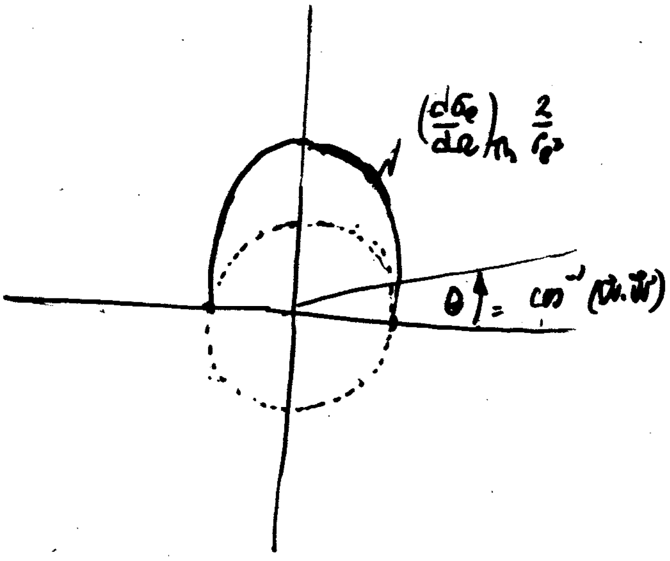


$$\sin\left(\frac{\theta}{2}\right) = \sqrt{\frac{1-\vec{\omega}\cdot\vec{\omega}'}{2}}$$

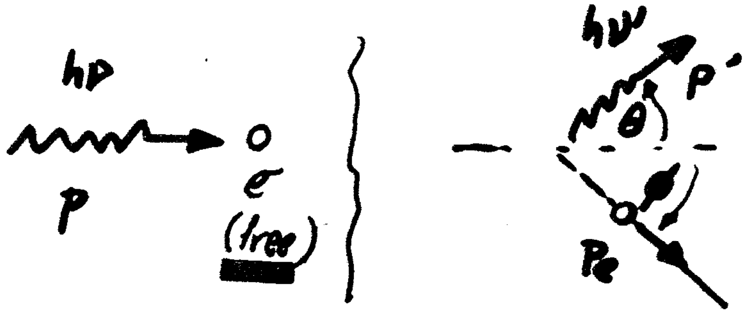
$$E\,[\text{KeV}] = \frac{hc}{\lambda} = \frac{12.39}{\lambda\,[\text{Å}]}$$

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

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



Incoherent scattering (Compton)



Exchange of energy and momentum

Evidence of the <u>particle</u> 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 $E=pc$

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

Conservation of momentum gives

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

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

Conservation of energy gives

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

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)

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

then

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

or

$$\lambda' - \lambda = \underbrace{\boxed{\left(\frac{h}{m_e c}\right)}}_{\substack{\lambda_c \\ \text{compton wavelength}}} (1 - \cos\theta)$$

<u>Compton shift</u>

Note that, $\lambda' > \lambda$

- the shift depends only on the scattering angle θ not on the energy of the incident photon

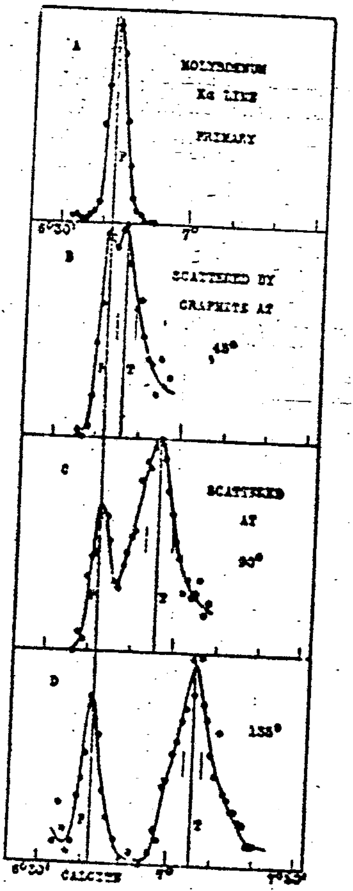


FIGURA 20A. *Questo grafico, tratto dall'articolo di Compton [A. H. Compton, in «Physical Review» 22, 1923, pag. 409], mostra lo spettro della radiazione diffusa in corrispondenza di tre angoli di diffusione differenti. Il grafico superiore mostra la riga della radiazione incidente, di lunghezza d'onda 0,71 Å. L'ascissa è proporzionale alla lunghezza di onda e l'ordinata è una misura dell'intensità. I picchi a sinistra nei tre grafici sottostanti indicano che parte della radiazione diffusa ha la stessa lunghezza di onda della radiazione incidente. I picchi a destra mostrano la radiazione diffusa per effetto Compton, di frequenza spostata. Lo spostamento nella frequenza cresce al crescere dell'angolo di diffusione, secondo la formula di Compton.* (Per gentile concessione di *Physical Review*).

4
I fotoni

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

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

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

$$k_C(\vec{\omega}, \lambda, \vec{\omega}'; \lambda') = \underbrace{\frac{\epsilon^2}{2} K_{KN}(\lambda,\lambda')}_{\text{Klein-Nishina electronic differential cross section}} \underbrace{S(\lambda', \hat{\omega}\cdot\hat{\omega}', Z)}_{\text{Scattering function}} \underbrace{\delta\left(\lambda' - \lambda + \lambda_c(1 - \hat{\omega}\cdot\hat{\omega}')\right)}_{\text{Compton shift}}$$

where

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

We can do the check (HOMEWORK)

$$\sigma(\nu') = \int_0^\infty d\nu \int_{4\pi} d\vec{\omega}\ \sigma_{Kd}(\nu' \to \nu, \zeta)$$

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

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