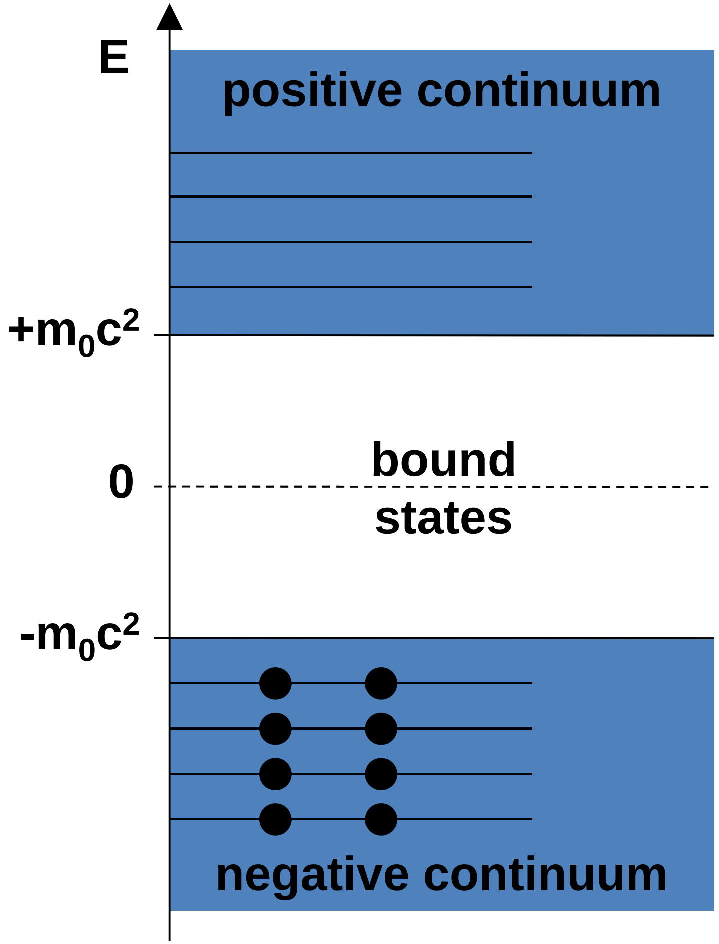
Atomic Decay Modes and Radiation Properties

Lecture 3

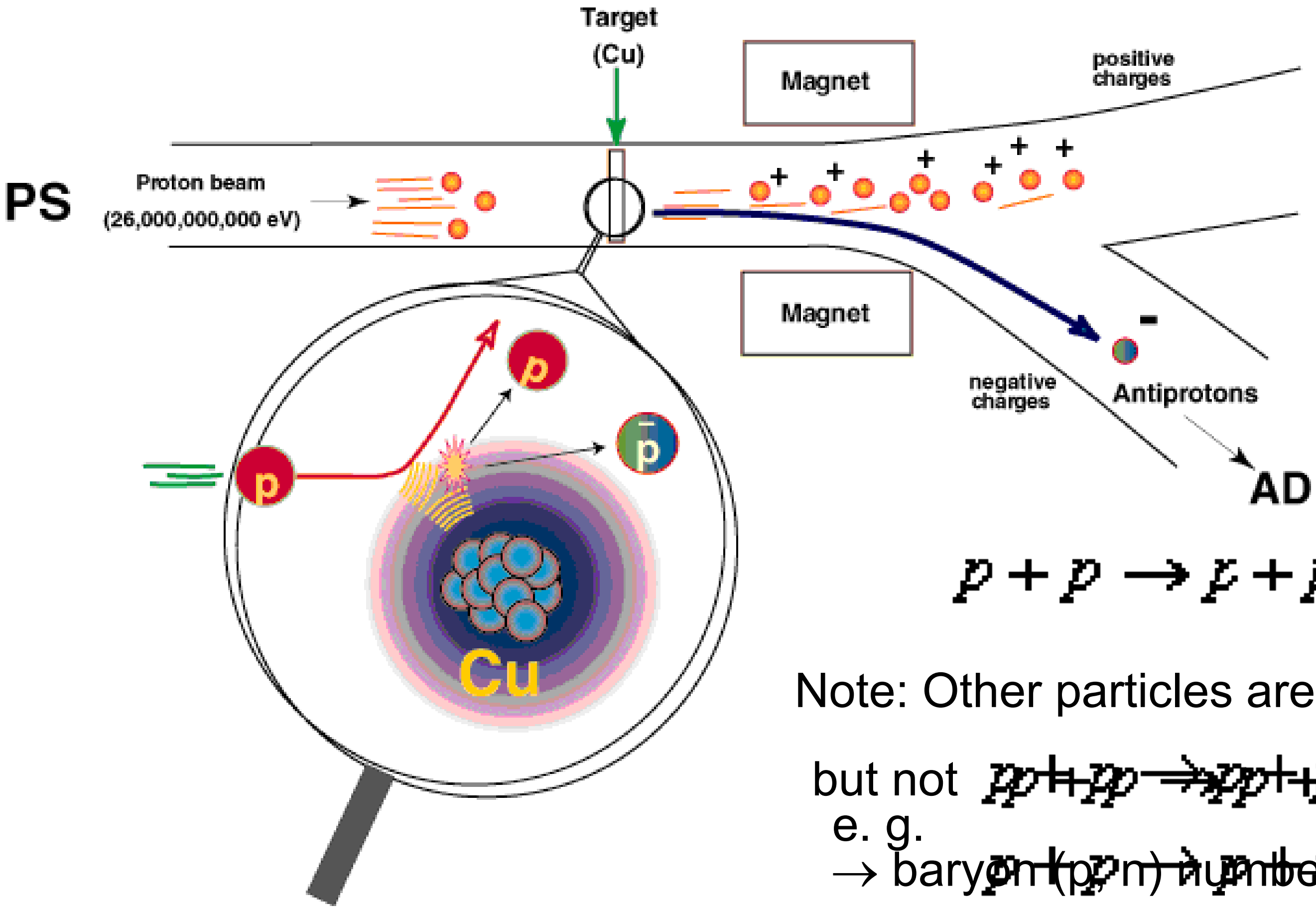
6 November 2013

Dirac Theory: Prediction of anti-matter



Dirac, Anderson, the Positron and the anti-matter. In his famous equation Paul Dirac combined (**1929**) the fundamental equation of quantum mechanics, the Schrödinger-equation with the theory of special relativity. He did not discard the negative energy –solutions of his equation as unphysical but interpreted them as states of the anti-particle of the electron (positron, having the same mass but opposite charge). In **1932** Carl Anderson discovered the positron the first time in the cosmic radiation. This was the proof of the existence of 'anti-matter', with incalculable consequences for the future of physics.

Principle of Antiproton Production



$$p + p \rightarrow p + p + p + \bar{p}$$

Note: Other particles are produced as well.

but not $p + p \rightarrow p + p + \pi^{+} + \bar{p}$

e. g. $p + p \rightarrow p + n + \pi^{+}$

→ baryon (p, n) number conservation!

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Our "road map"

Lectures

- 1 16.10.2012 Preliminary Discussion / Introduction

Basics concepts, Dirac sea, Creation of Particles

- 2 23.10.2013 Dirac Theory
- 3 30.10.2013 Atomic Decay Modes and Radiation Properties
- 4 06.11.2013 Interaction of Photons with Matter
- 5 13.11.2013 Interaction of Charged Particles with Matter
- 6 20.11.2013 Key Experiments

Sources of High Energetic Radiation

- 7 27.11.2013 Nuclei and their Decay Modes
- 8 04.12.2013 Cosmic Radiation

Detectors

- 9 11.12.2013 Photon-, x-ray-, gamma-detectors
- 10 18.12.2013 Particle Detectors

Applications

- 11 08.01.2014 Radiation and their Biological Effectiveness
- 12 15.01.2014 Application of Charged Particle to Cancer Therapy

Novel Accelerators

- 13 22.01.2014 Novel Photon Sources
- 14 29.01.2014 Modern Accelerators for Ions and Exotic Nuclei

Summary

- 15 05.02.2014 Excursion to GSI

Exercises

Basics concepts, Dirac sea, Creation of Particles

- 1 31.10.2013
- 2 14.11.2013
- 3 28.11.2013

Sources of High Energetic Radiation

- 4 12.12.2013

Detectors

- 5 09.01.2014

Applications

- 6 23.01.2014

Novel Accelerators

- 7 06.02.2014

Topics for Presentation

- Lamb shift studies in Hydrogen
  (high-precision spectroscopy)

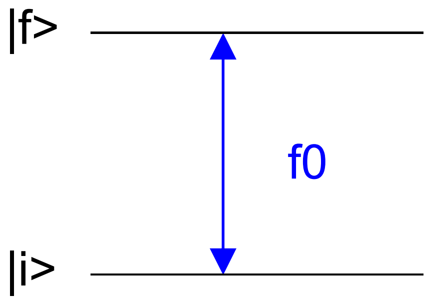
- Lamb shift in H- and He-like Uranium
  (storage ring physics, hard x-rays)

Contents

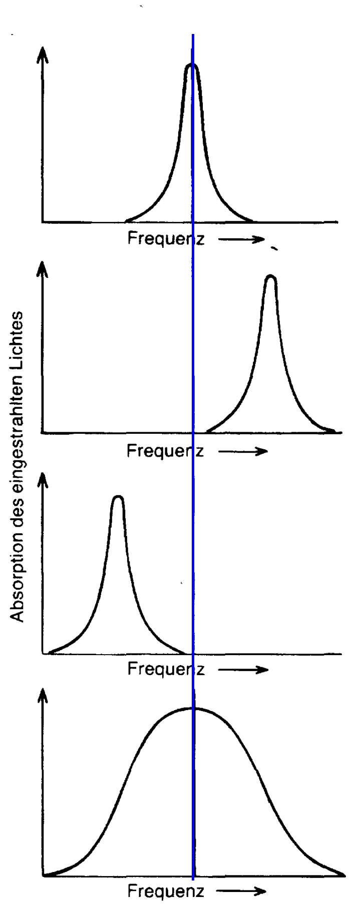
Laser spectroscopy

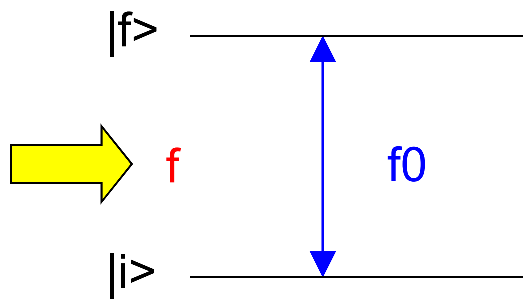
Laserfrequenz: f

Anregungsfrequenz: f_0



$v \ll c$





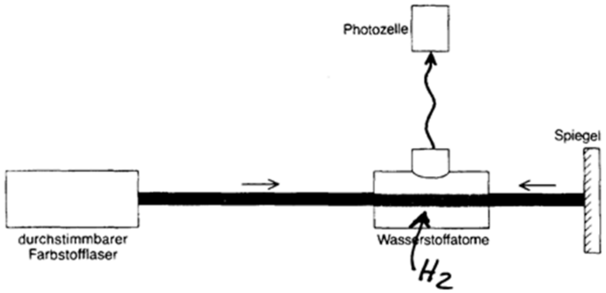
$$f = f_0$$

$$f = f_0\left(1 + \frac{v}{c}\right)$$

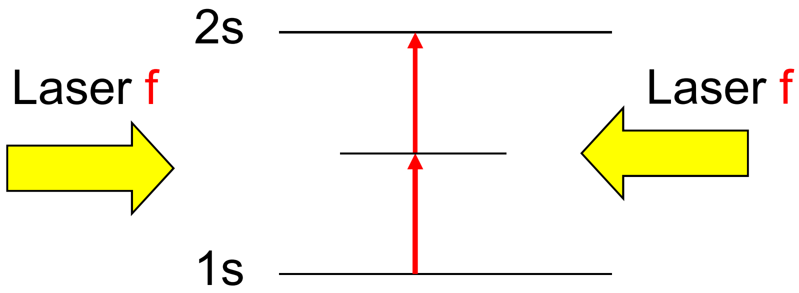
$$f = f_0\left(1 - \frac{v}{c}\right)$$

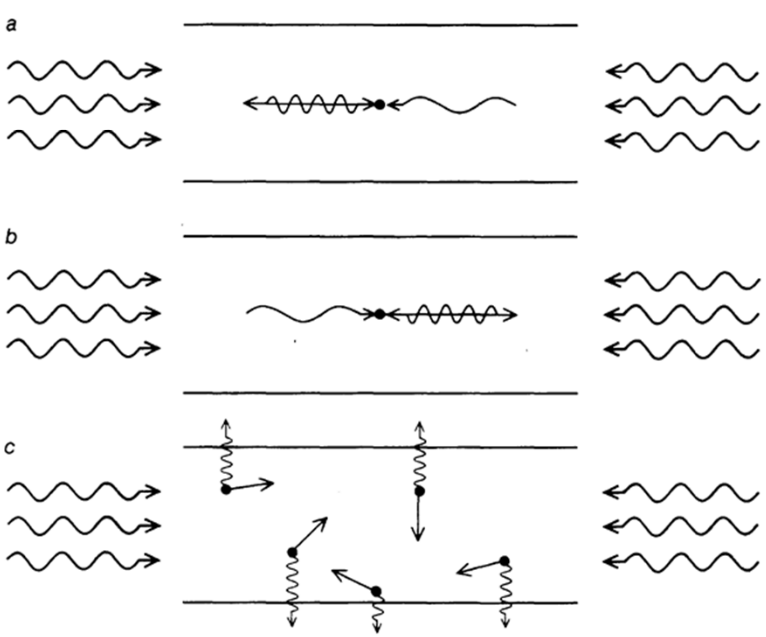
large Doppler broadening caused by temperature

Two Photon Spectroscopy



$f_0 = 2 \times f$





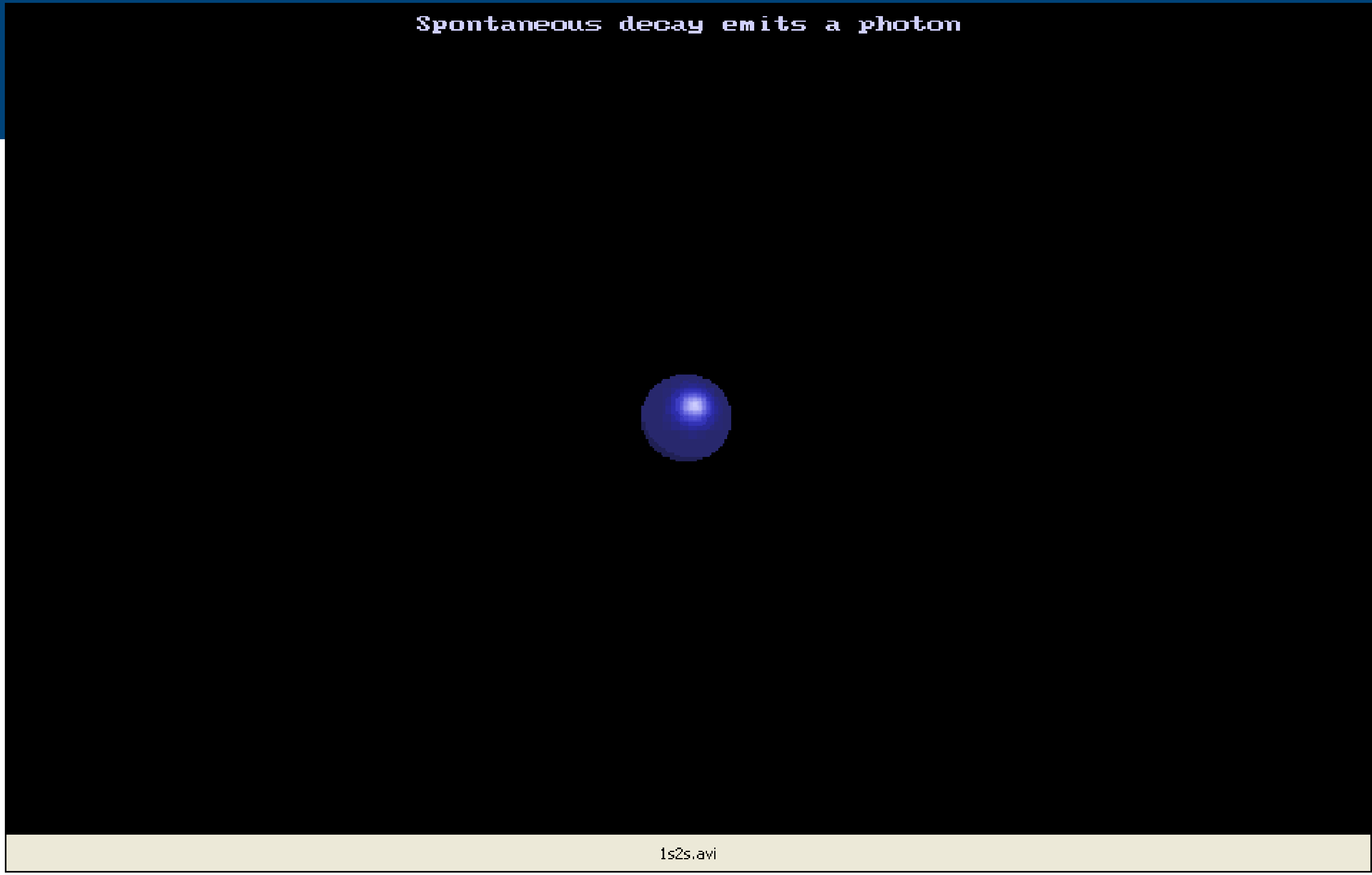
$$f_1 = \frac{f_0}{2}\left(1 + \frac{v}{c}\right)$$

$$f_2 = \frac{f_0}{2}\left(1 - \frac{v}{c}\right)$$

$$f = f_1 + f_2$$

Doppler free spectroscopy

Detection of fluorescenz radiation as function of laser frequency



Shows a complete measuring cycle: Excitation to the 1S state by using two photons from oposite directions so that the first order doppler shift cancels. Here it is shown as a complete transition (driven by a pi pulse) while in reality the excitation is much less. Then there is a time delay to select the slow atoms to reduce the second order doppler shift. An electric field that is applied downstream the flow of excited atoms mixes the metastable 2S state with the fast decaying 2P state.
This causes the emission of a photon in an arbitrary direction that we use to detect weather the 1S - 2S transition frequency was chosen correctly.

http://www.mpq.mpg.de/~haensch/chain/move.html

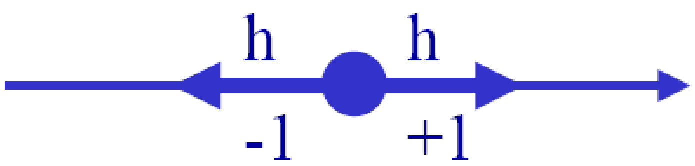
Photons: conservation of angular momentum, helicity

Particle with Spin S and Momentum p;
Axis of quantization is along p:

$$h = \frac{\vec{s} \cdot \vec{p}}{\left|\vec{s}\right| \cdot \left|\vec{p}\right|}$$

- Helicity h depends on the reference system for particles with rest mass > 0.
- For mass-less particles it is a constant quantity.

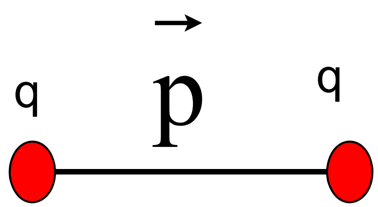
Photons have a helicity of 1, i.e. an angular momentum of 1, whose projections onto the direction of motion can have only values of +1 and -1.

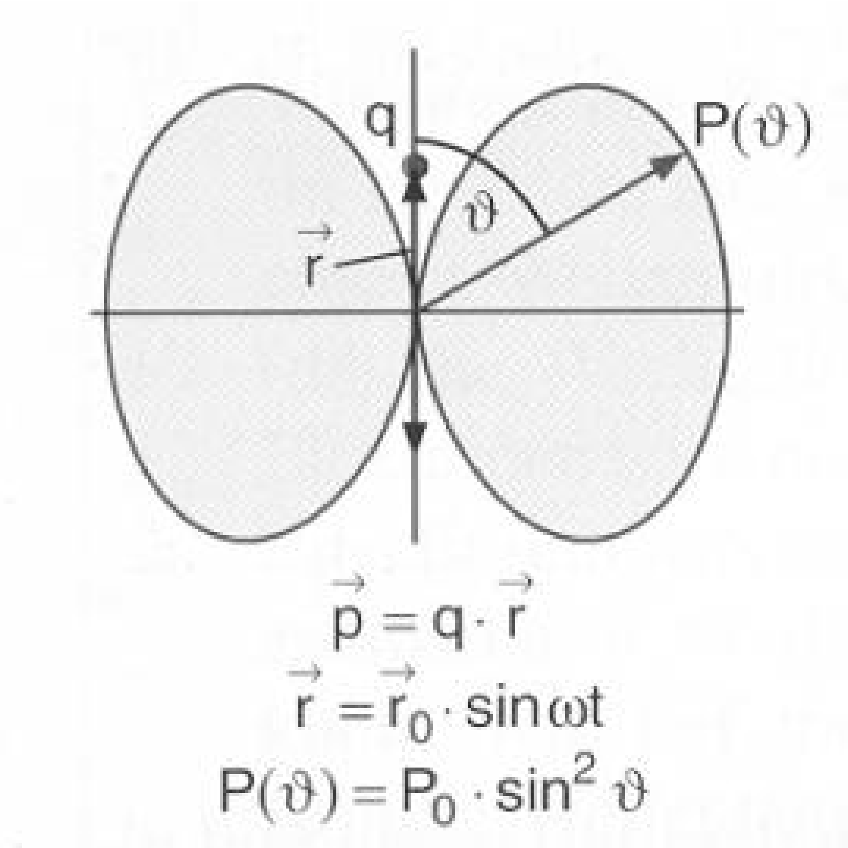


Absorption and emission processes conserve the helicity of the involed particles.

Interaction between Radiation and Matter

Emission and absorption can be treated within the oscillator picture.





Classical dipole with dipole moment p

$$\vec{p} = q \cdot \vec{r} = p_0 \cdot \sin \omega t$$

$$\vec{p} = p_0 \cdot \sin \omega t \qquad \vec{F} \propto \omega^2 \vec{p}$$

$$P(\vartheta) = P_0 \cdot \sin^2 \vartheta$$

Average Power: $$\overline{P} = \frac{2}{3} \frac{\overline{p}^2 \omega^4}{4\pi\varepsilon_0 c^3}$$

Quantum mechanical treatment

$$\langle p \rangle = e\langle r \rangle = e\int \psi^* r\, \psi d^3 r$$

Transition maxtrix $$M_{if} = \int \psi^* r\, \psi d^3 r$$

Decay probability/rate $$W_{i\to f} \propto \left|M_{i\to f}\right|^2 \propto \left|\int \psi_i^* r \psi_f d^3 r\right|^2$$

$$S_{i\to f} = \left|M_{i\to f}\right|^2$$ in literature S is called *line strength*

A_{if} is the decay probability per second that an atoms undergoes a transition from |i> to |f> and emits a photon $\hbar\omega$

N_i Atomen, mean power <P> emittiert

$$\langle P \rangle = N_i \cdot A_{if} \cdot \hbar\omega$$

The factor A_{if} is called Einstein-Coefficient and also *spontaeous decay rate*

$$A_{if} = \frac{2}{3}\frac{e^2}{\varepsilon_0 c^3 h}\omega^3 \cdot \left|M_{if}\right|^2$$

Selection Rules

For dipole radiation:

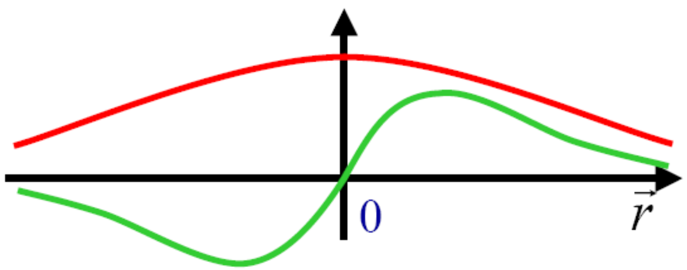
Dipolmatrixelement

$$M_{if} = \left| \int \psi_i^{*} \cdot r \cdot \psi_f d^3 r \right|$$

Decay probability

R is an odd operator!

Parity needs to change!



$$\langle \varphi_{End} | \hat{\vec{r}} | \varphi_{Anf} \rangle = \int \varphi \vec{r} \varphi \; d^3 r$$

The Integral M_{if}=0 musst be an even function, i.e. f(r)=-f(-r). Because r must be an odd function also the product $\psi_i^{*} \psi_f$ must be an odd function.

The dipole matrix element is ZERO
for transitions between states of same parity !

Selection rules for parity

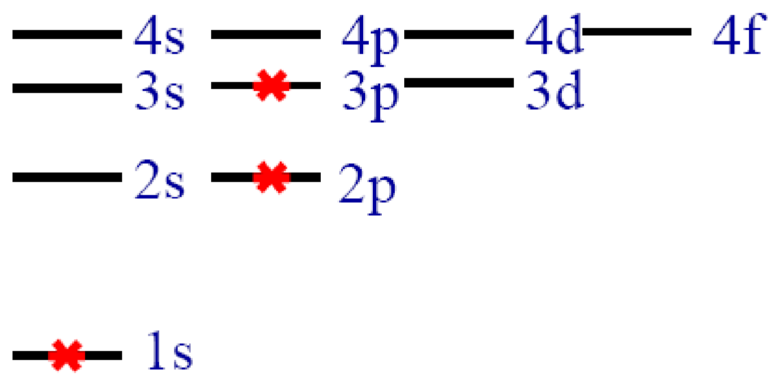
The parity of an electron wavefunction in an atom is given by:

$$\pi = (-1)^{\ell}$$

Parity operator: $\vec{r} \rightarrow -\vec{r}$

Selection rules for dipole radiation:

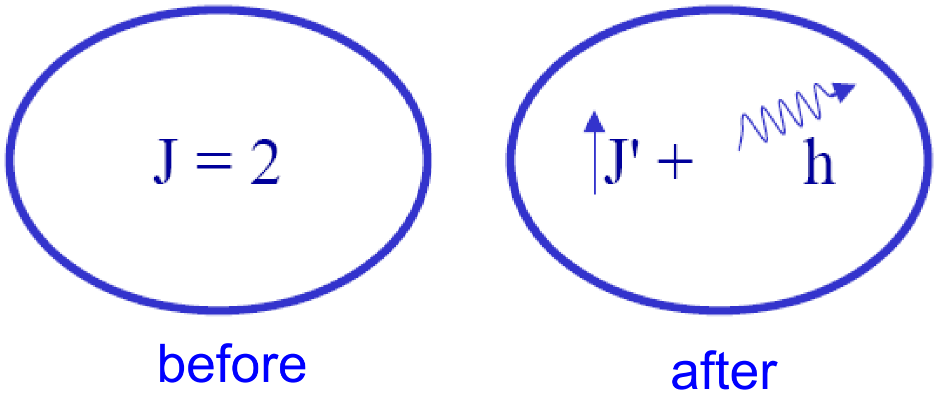
$$\boxed{\Delta l = \pm 1}$$



This is can also be understood in terms of a $\Delta l = \pm 1$ restriction in order to conserve the angular momentum in single-photon transitions.

Selection Rules for the Angular Momentum

$$\Delta J = 0, \pm 1$$



Achtung:
J=0 $\rightarrow$ J'=0 is not allowed
for single-photon transitions because of h=1

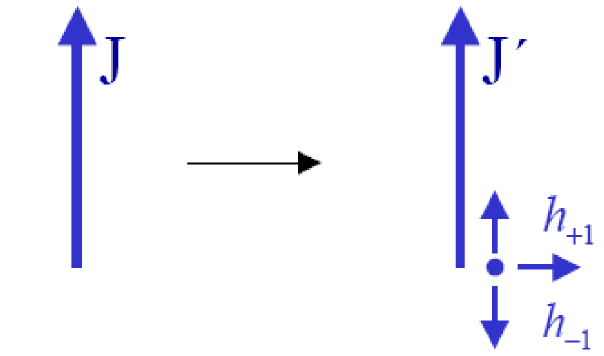
Coupling of angular momenta

$$|J' - J| \leq \ell \leq |J' + J|$$

ℓ Angular momentum of the photon

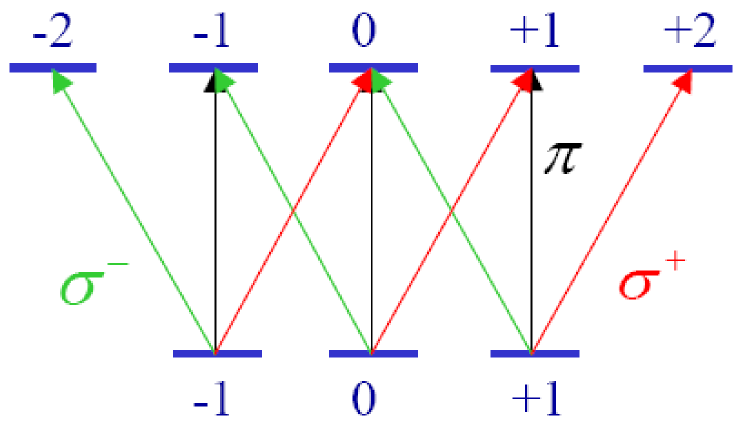
Conservation rules for the magnetic quantum number

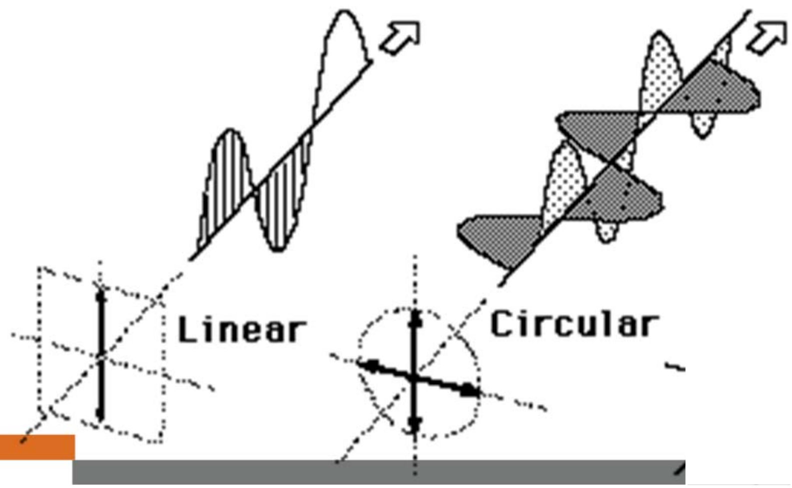
$$\Delta m_J = 0, \pm 1$$



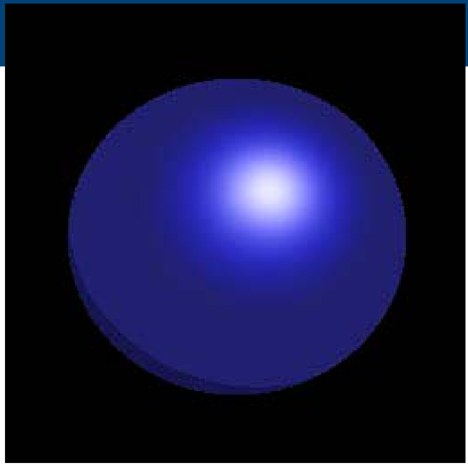
Observation:

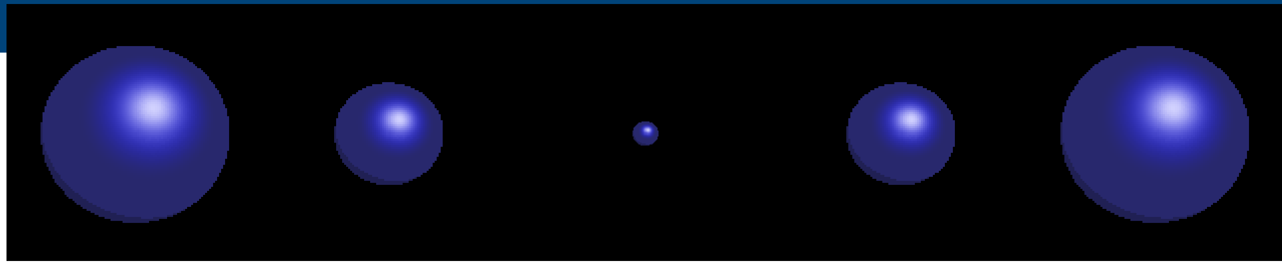
$\Delta m = 0:$	Linearly polarized light	$\pi - \text{Licht}$
$\Delta m = +1:$	Right-circularly polarized light	$\sigma^+ - \text{Licht}$
$\Delta m = -1:$	Left-circularly polarized light	$\sigma^- - \text{Licht}$



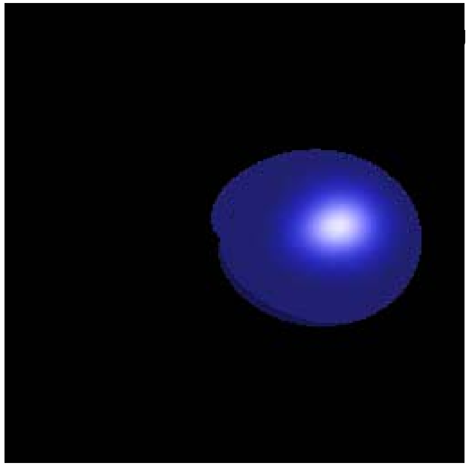


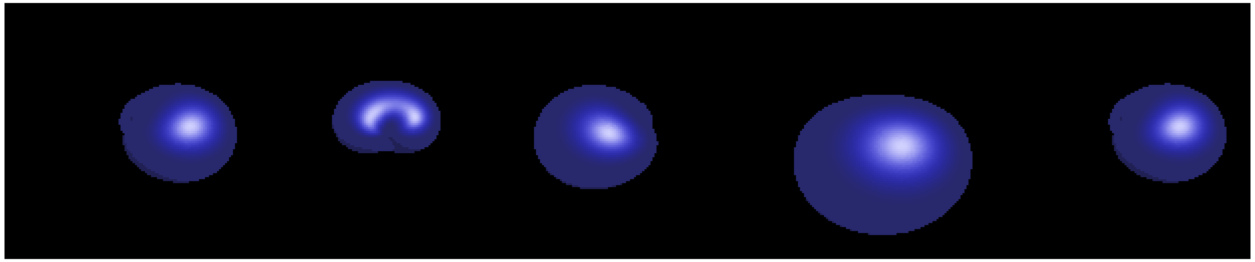
The 1S - 2S transition





The l=1, m=1 to l=0, m=0 transition





http://www.mpq.mpg.de/~haensch/chain/move.html

The scaling of transition rates

$$M_{if} = \left| \int \psi_i^* r \psi_f d^3r \right| \propto Z^{3/2} \frac{1}{Z} Z^{3/2} \frac{1}{Z^3} = \frac{1}{Z}$$

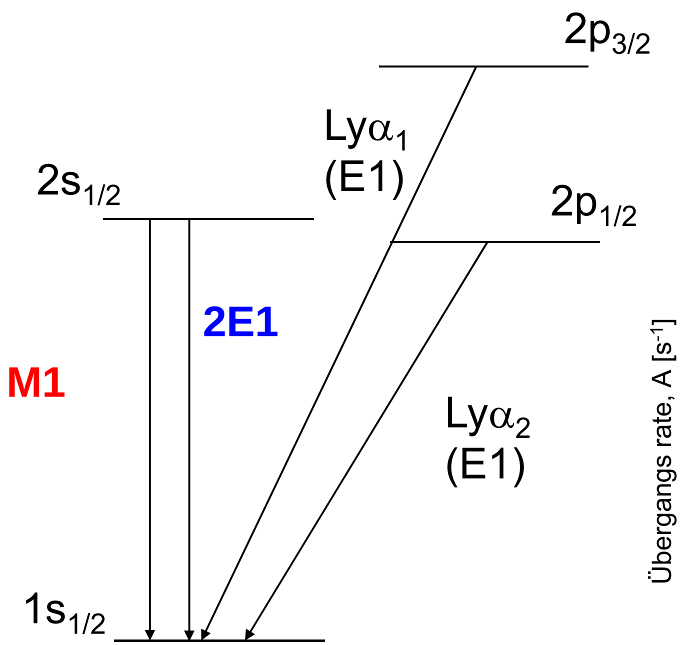
$$r \propto \frac{1}{Z}$$

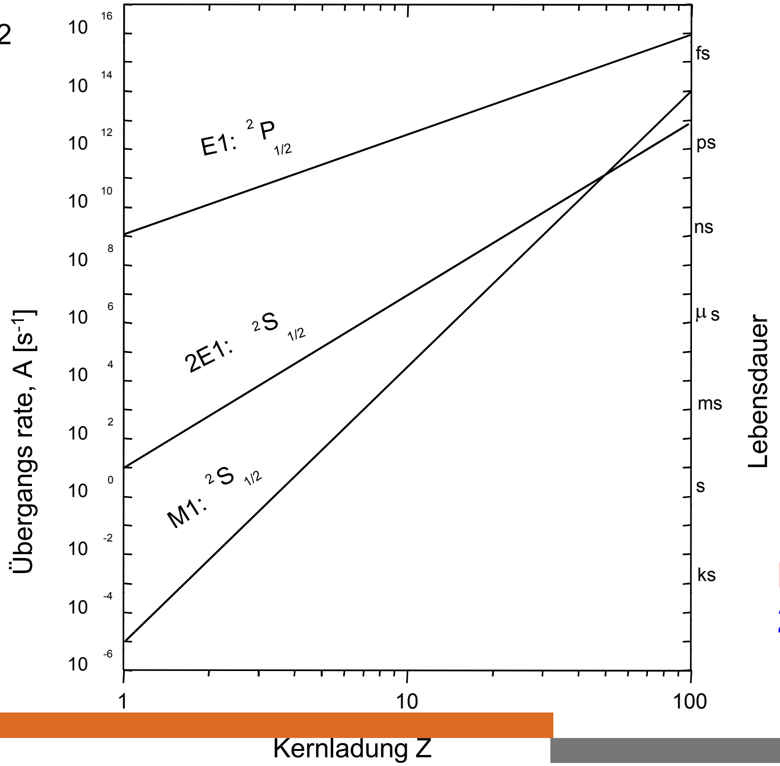
$$\omega \propto (E_f - E_i) \propto Z^2$$

$$A_{if} \propto \omega^3 \cdot |M_{if}|^2$$

$$A_{if} \propto Z^4$$

for dipole matrix elements





Scaling of transition rates

E1: Z^4

M1: Z^{10}

2E1: Z^6

M1: magnetic dipole
2E1: two-photon decay

Multipole expansion

Hamiltonian of the photon–electron interaction: $H = e\frac{\vec{p}}{mc}\vec{A}$

The matrixelement for a transition of an electron from the initial state Ψ_i to the final state Ψ_f is:

$$\left|M_{if}\right| = \int \Psi^*{}_i\, p e^{ikr} \Psi_f\, d^3r$$

where **p** is the momentum of the electron, and **k** is the momentum of the emitted photon

The photon wavelength is: $\lambda = \frac{2\pi}{k}$

assumptions: plane wave,
vector potential, wave function:

$$A \propto e^{-i(kr-\omega t)}$$

$$e^{-ikr} = 1 - ikr + \frac{(kr)^2}{2} + \ldots$$

Multipole expansion

$$e^{-ikr} = 1 - i\mathrm{kr} + \frac{(\mathrm{kr})^2}{2} + \ldots$$

dipole approximation

$$\mathrm{k} \cdot \mathrm{r} << 1 \rightarrow \mathrm{r} << \lambda$$

i.e. the wavelength is much larger than the size of the atom (orbit radius)

higher order multipoles

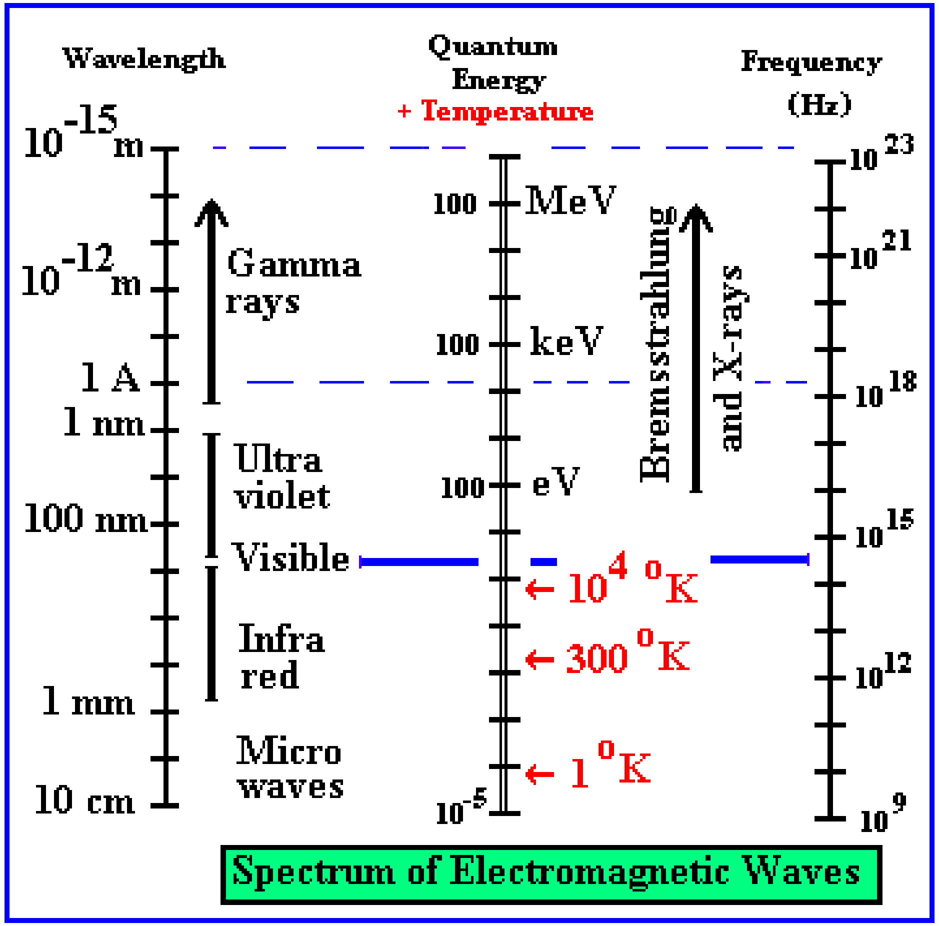
$$\mathrm{k} \cdot \mathrm{r} \approx 1 \text{ oder } \mathrm{k} \cdot \mathrm{r} \geq 1$$

There will be higher order multipoles:
Quadrupole, etc.
e.g.: nuclear decay, or atoms with high Z

For higher order multipole radiation the following rules apply to the parity ℓ :

$\pi = (-1)^{\ell}$ **electric multipole radiation**

$\pi = (-1)^{\ell+1}$ **magnetic multipole radiation**



dipole approximation

$$k \cdot r << 1 \rightarrow r << \lambda$$

i.e. the wavelength is much larger than the size of the atom (orbit radius)

example: 2p→1s transition

$$\frac{h \cdot c}{E} = \lambda$$ **with h= 4.14*10^15 eVs**

(Bohr-Radius a_0=0.529x10^-8 cm)

Natural line width

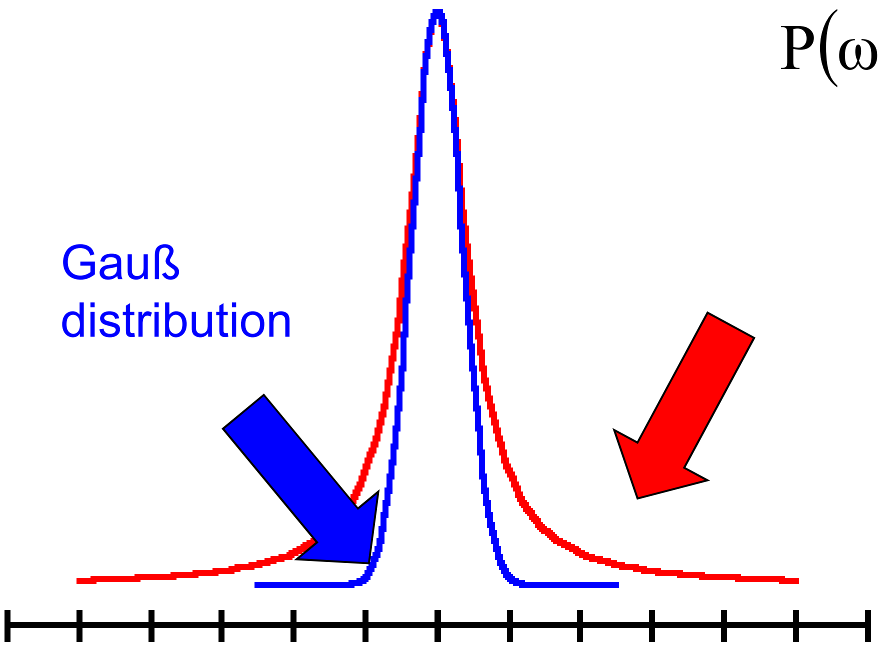
$$A_{if}\left[\frac{1}{s}\right] = \Gamma_{if} = \frac{1}{\Delta t}$$ rate, with Δt as the mean lifetime of an excited state

$$\Delta E \cdot \Delta t \geq \hbar \qquad \Delta E = \hbar \cdot \Gamma$$ width of the transition

Fast transition -> broad line width

Lorentz profile (Lorentz distribution)

$$P(\omega) = P_0 \frac{\frac{\Gamma}{2\pi}}{(\omega-\omega_0)^2 + \left(\frac{\Gamma}{2}\right)^2}$$



derived from a damped oscillator

$$\ddot{x} + \Gamma\dot{x} + \omega_0^{\ 2} x = 0$$

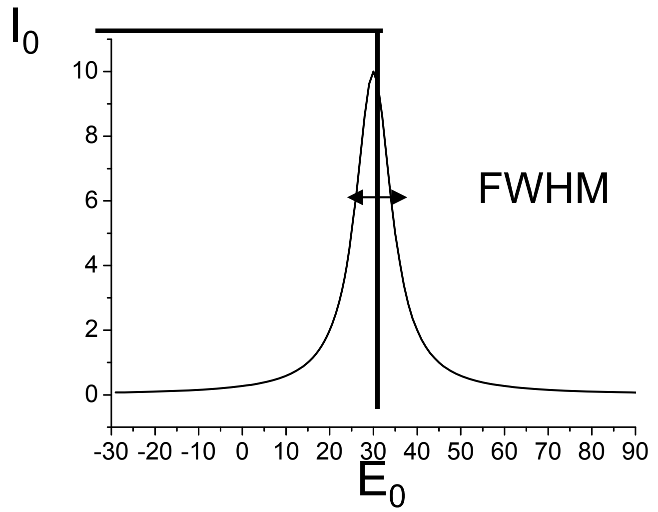
with resonance frequency ω_0

(c.f. Demtröder III p. 214).

Line profiles

Lorentz (natural line shape)

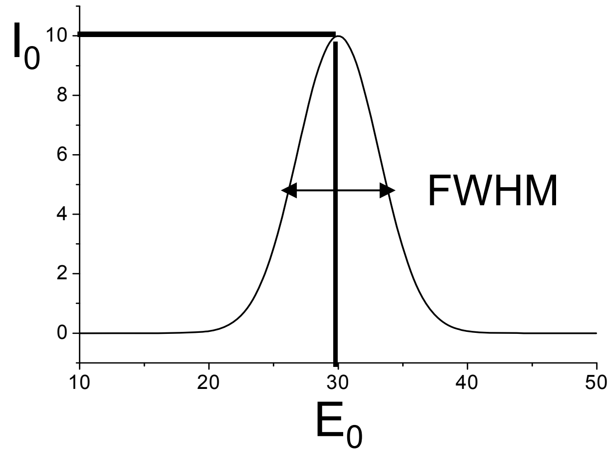
$$I_L(E) = I_0 \frac{\left(\frac{\Gamma_{FWHM}}{2}\right)^2}{(E - E_0) + \left(\frac{\Gamma_{FWHM}}{2}\right)^2}$$



Folding of two Lorentz profiles leads to: $\Gamma = \Gamma_1 + \Gamma_2$

Gauß (instumental resolution)

$$I_G(E) = I_0 \cdot \exp\left(-(E - E_0)^2 \frac{4 \cdot \log 2}{G^2_{FWHM}}\right)$$



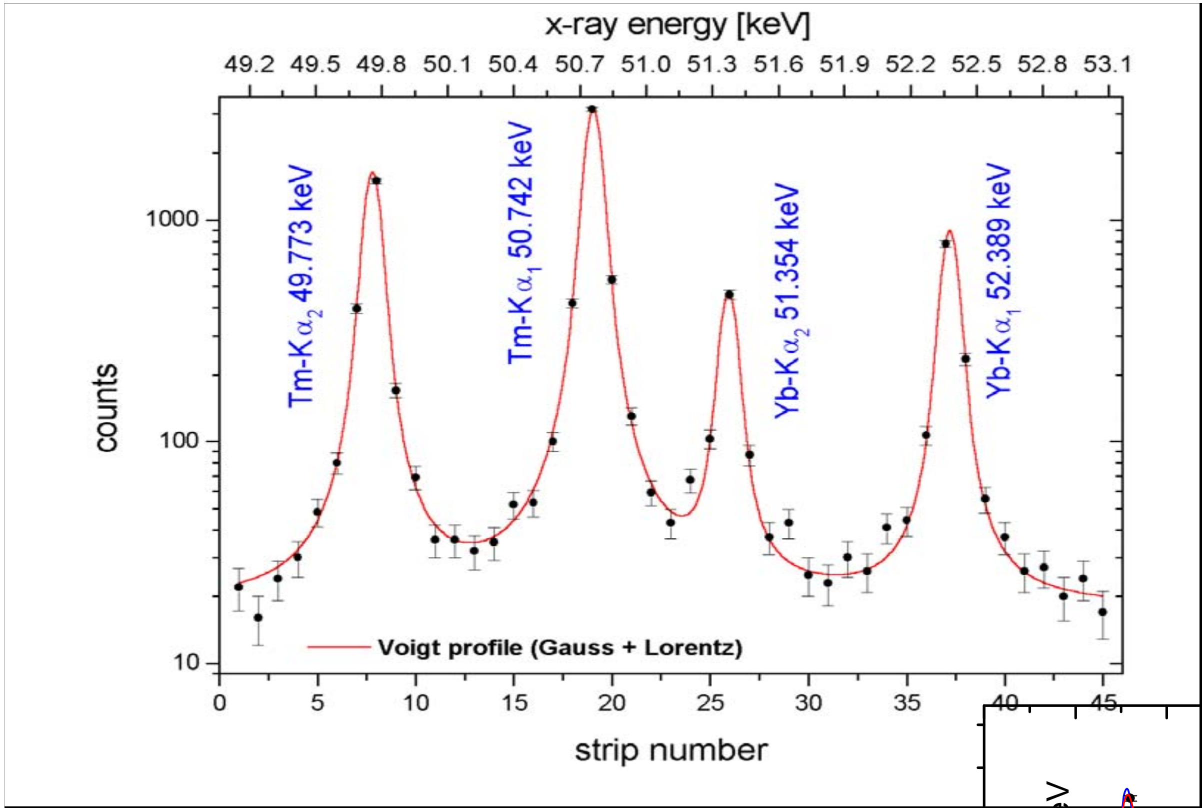
Folding of two Gaussian distributions leads to: $\Gamma^2 = \Gamma_1^{\,2} + \Gamma_2^{\,2}$

Voigt (convolution)

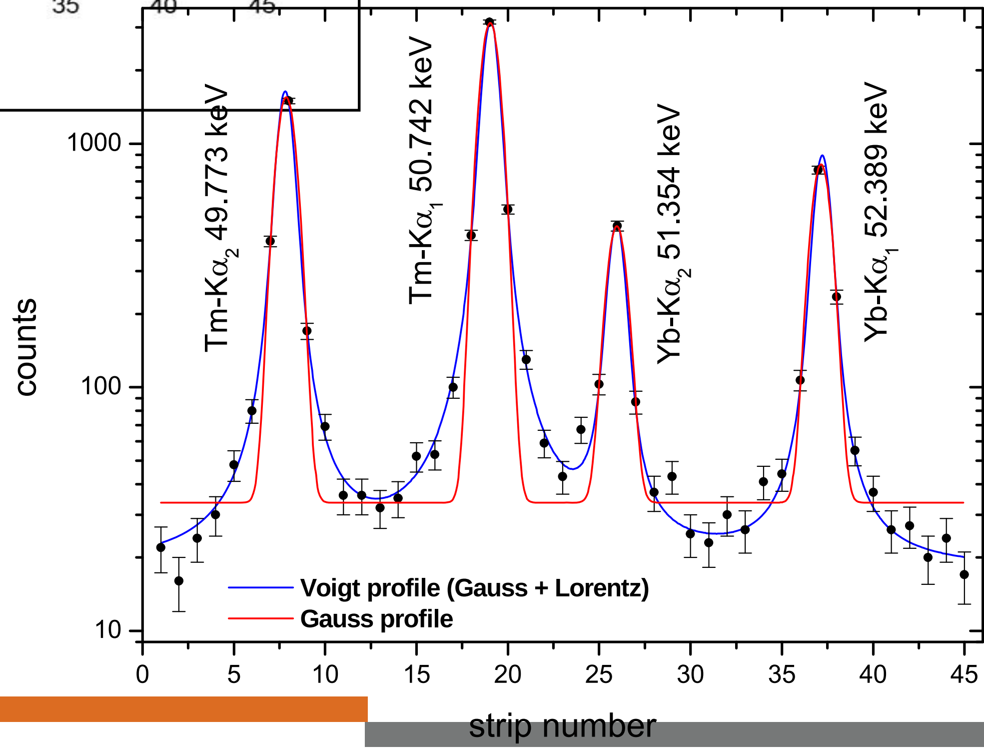
$$I(E) = \int_{-\infty}^{+\infty} I_L(E - E_0) \cdot I_G(E - E_x)\, dE_x$$

FWHM: Full Width at Half Maximum

Voigt profile is relevant if instrumental resolution is in the order of the natural line width, e.g. crystal spectroscopy



x-ray energy [keV]
49.2 49.5 49.8 50.1 50.4 50.7 51.0 51.3 51.6 51.9 52.2 52.5 52.8 53.1
Tm-Kα2 49.773 keV
Tm-Kα1 50.742 keV
Yb-Kα2 51.354 keV
Yb-Kα1 52.389 keV
counts
10
100
1000
Voigt profile (Gauss + Lorentz)
0 5 10 15 20 25 30 35 40 45
strip number



Tm-Kα2 49.773 keV
Tm-Kα1 50.742 keV
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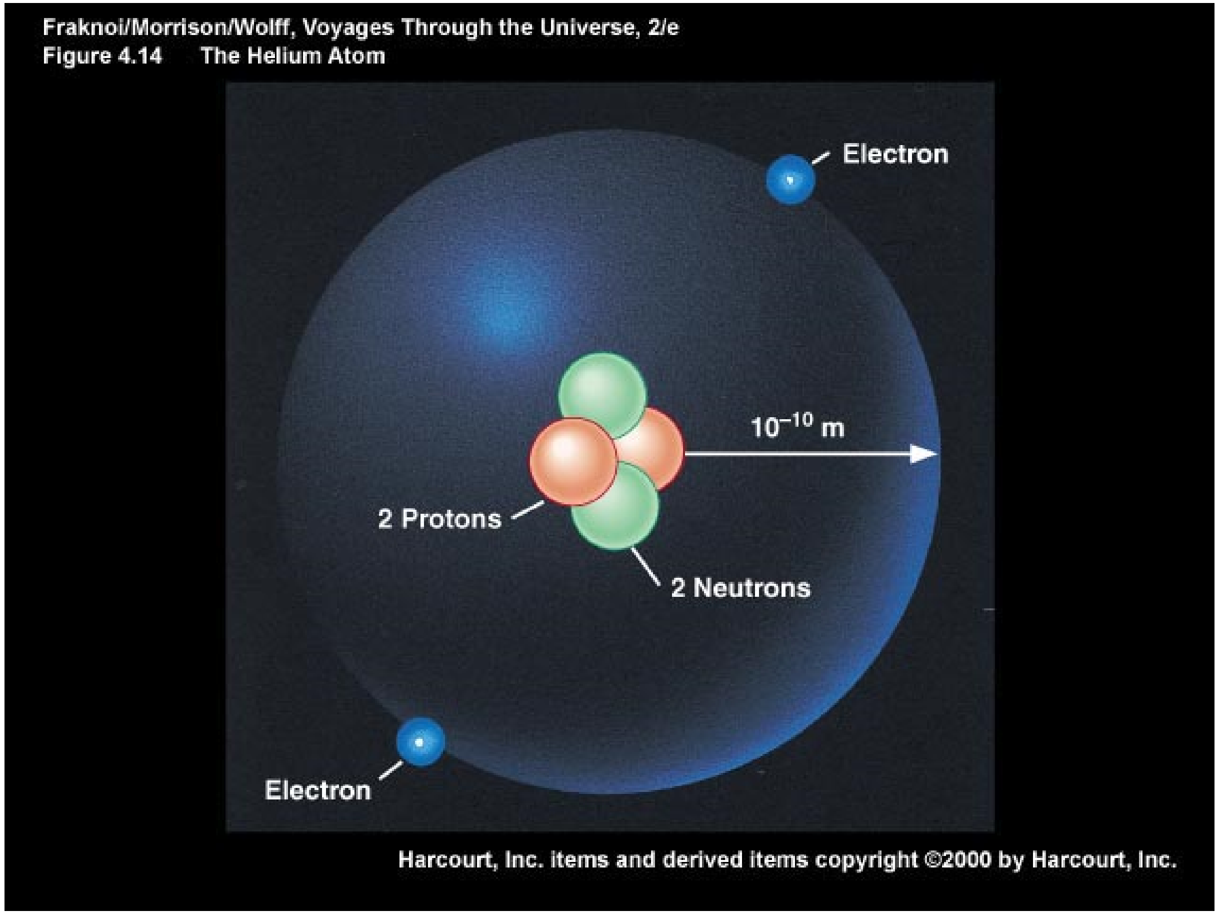
counts
10
100
1000
Voigt profile (Gauss + Lorentz)
Gauss profile
0 5 10 15 20 25 30 35 40 45
strip number

The helium atom and

many-electron-systems

The helium atom

Three-body Coulomb-problem: No accurate solution



States in the helium atom

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Therefore we have two times the Hamilton operator for the hydrogen atom (but Z=2) and in addition the repulsion-term V

$$H = H_1 + H_2 + V \quad \text{with} \quad V(\vec{r}_1, \vec{r}_2) = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

In 0th approximation we neglect the term V, die Coulomb repulsion between the electrons – and use the product-states of the hydrogen atom

$$u(\vec{r}_1, \vec{r}_2) = \Psi_{n_1 l_1 m_1}(\vec{r}_1) \bullet \Psi_{n_2 l_2 m_2}(\vec{r}_2)$$

U are not eigenfunctions of the Hamiltonian, if the repulsion V is taken into account

According to this, the problem would be accurately solvable because both electrons can be separated as

$$(H_1 + H_2)u = Eu$$

and we get

$$E_{n_1,n_2} = E_{n1} + E_{n2} = -Ry \cdot Z^2 \left(\frac{1}{n_1^2} + \frac{1}{n_1^2} \right) = -54.4\,eV \cdot \left(\frac{1}{n_1^2} + \frac{1}{n_1^2} \right)$$

ground state: $E_{11} = -108.8 eV$

1st excited state: $E_{12} = -68 eV$

total binding-energies (without Coulomb repulsion) *total binding energies*

ground state: $E_{11} = -108.8\text{eV}$

ionization potential

$$E_{1\infty} = -54.4\text{eV}$$

$E_{12} = -68\text{eV}$

$E_{13} = -60.4\text{eV}$

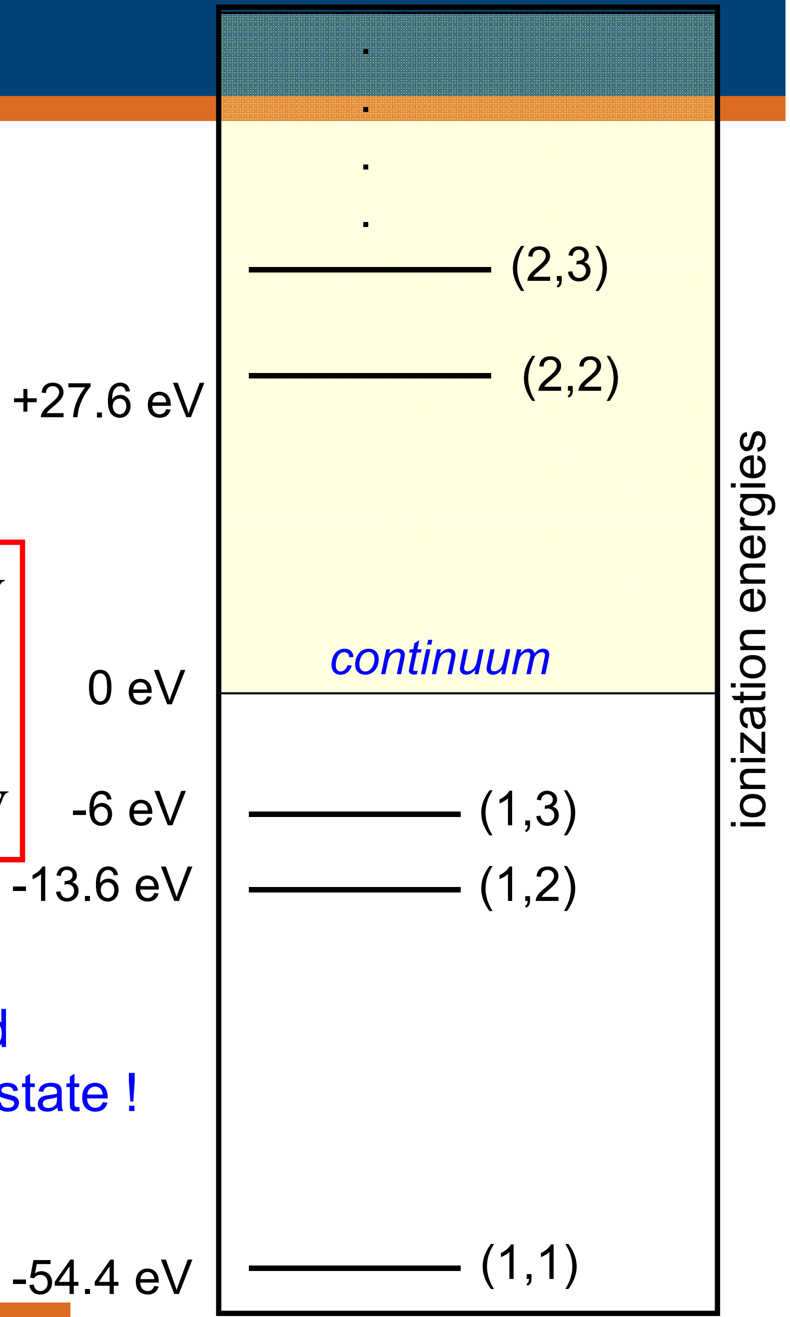
$E_{22} = -27.2\text{eV}$

$$E^{I}_{1n,2n} = E_{1n,2n} - E_{1\infty}$$

$E^{I}_{12} = -13.6\text{eV}$

$E^{I}_{13} = -6.0\text{eV}$

$E^{I}_{22} = +27.2\text{eV}$



E^{I}_{22} is above the ionization potential and therefore not a stable state but a continuum state !

Attention: So far only rough approximation!

spin	particle	exchange-behavior of the wave function
integral	bosons (e.g. photons)	symmetric
half-integral	fermions (e.g. electrons)	anti-symmetric

Pauli-Prinziple: Two particles with the same quantum numbers
=> particles have the same state

A quantum mechanical state can only be occupied by one particle
=> wave function of the system has to be anti-symmetrical

$$\Psi^g(1,2) = -\Psi^g(2,1)$$

The total wave function (= the product of the space wave function and the spin wave function) of a many-electron-system is always anti-symmetrical to the permutation of two electrons (Pauli-prinziple).

space wave function: Ψ

$$\Psi^g = \Psi \cdot \chi$$

spin wave function: χ

Symmetry of the states:
For the ground state of two identical electrons the space function is symmetrical.
Therefore the spin functions have to be anti-symmetrical.

Example: $^3S_1$ and $^1S_0$

$$\Psi_{S,A}(1,2) = \frac{1}{\sqrt{2}}\left[\Psi_{100}(r_1)\Psi_{200}(r_2) \pm \Psi_{100}(r_2)\Psi_{200}(r_1)\right] \cdot \chi_{A,S}$$

$$H = \frac{p_1^{\;2}}{2m} + \frac{p_2^{\;2}}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \boxed{\frac{e^2}{\left|\vec{r}_1 - \vec{r}_2\right|}}$$

Calculate electron-electron-interaction

$$\Delta E_{S,A} = +\iint \Psi_{SA}^{g*}(1,2)\frac{e^2}{\left|\vec{r}_1 - \vec{r}_2\right|}\Psi^{g}{}_{SA}(1,2)\,d^3r_1 d^3r_2$$

+ sign, because of the repulsion.
Convention: binding energies are negative

for S=0 ($^1S_0$) $\quad \Delta E_S = \Delta E_{COUL} + \Delta E_{Exchange}$

for S=1 ($^3S_1$) $\quad \Delta E_A = \Delta E_{COUL} - \Delta E_{Exchange}$

The energy shift due to the symmetry-energy (exchange interaction)

$$\Delta E\left({}^3S_1 - {}^1S_0\right) \approx 0.8\,\mathrm{eV}$$

(stronger repulsion by symmetric space function)

Compare: fine structure splitting $\approx 10^{-4}$ eV

Some numerical results for the helium ground state

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In this contribution we would like to report about two numerical results related to the ground state of the helium atom. The first one is precise determination of the ground state nonrelativistic energy (Table 1).

Table 1: Nonrelativistic energies for the ground state of a helium atom $^{\infty}$He. N is the number of basis functions.

N	E_{nr} (in a.u.)
4200	−2.903724377034119598311540
4600	−2.903724377034119598311572
5200	−2.903724377034119598311587
extrap	−2.903724377034119598311594(4)
Sims and Hagstrom[1]	−2.9037243770341195982999
Drake *et al.* [2]	−2.903724377034119598305

The next result (see Table 2) is a very accurate calculation of the Bethe logarithm. It is known that this quantity has been considered for many years as most difficult for numerical evaluation. It is formally defined as follows [3]

$$\beta = \ln k_0/\mathrm{Ry} = \sum_n |\langle 0|\mathbf{p}|n\rangle|^2 (E_n - E_0) \ln\{|E_n - E_0|/\mathrm{Ry}\} / \sum_n |\langle 0|\mathbf{p}|n\rangle|^2 (E_n - E_0).$$

Table 2: The Bethe logarithm for the ground state of a helium atom $^{\infty}$He.

N	β
1200	4.3701602230
1400	4.3701602223
1600	4.3701602222
Drake, Goldman [4]	4.370160218(3)
J. Baker *et al.* [5]	4.370159(2)
C. Schwartz [6], (1961)	4.370(4)

References

[1] J.S. Sims and S.A. Hagstrom, Int. J. Quantum Chem., to be published.

[2] G.W.F Drake, M.M. Cassar, and R.A. Nistor, Phys. Rev. A 65, 054501 (2002).

[3] H. Bethe and E. Salpeter, *Quantum Mechanics of One– and Two–Electron Atoms*, Springer-Verlag, Berlin-Göttingen-Heidelberg 1957.

[4] G.W.F. Drake and S.P. Goldman, Can. J. Phys. 77, 835 (1999).

[5] J. Baker, R.C. Forrey, M. Jeziorska, and J.D. Morgan III, unpublished.

[6] C. Schwartz, Phys. Rev. 123 1700 (1961).

For the ground state the prevailing value of the binding energies is

E_{11} = -79.0034 eV

ionization potential

24.5874 eV

contribution of the electron-electron interaction

ΔE=+29.8 eV

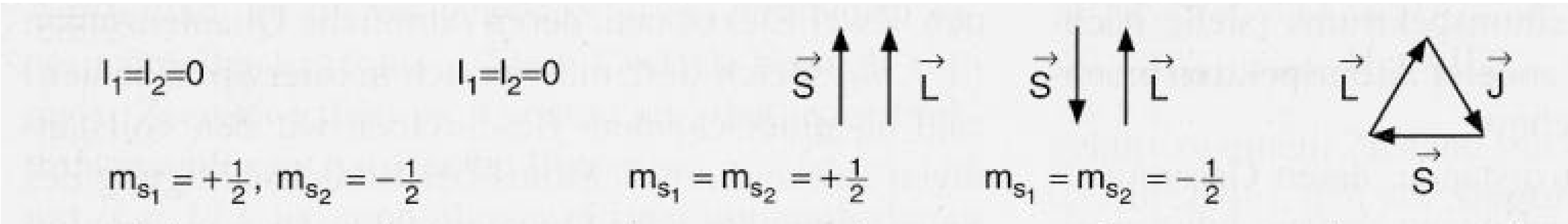
LS-coupling (light atoms)

The spins couple independently of the orbital angular momentum

$$\vec{S} = \vec{s}_1 + \vec{s}_2; \vec{S} = \sum_i \vec{s}_i$$

$$\vec{L} = \vec{\ell}_1 + \vec{\ell}_2; \vec{L} = \sum_i \vec{\ell}_i$$

$$\vec{J} = \vec{L} + \vec{S}$$



1^1S_0	2^1S_0	2^3S_1	2^3P_2	2^3P_0	2^3P_1
L=0, S=0, J=0		L=0, S=1 J=1	L=1, S=1 J=2	L=1, S=1 J=0	L=1, S=1 J=1

The first excited electrons of helium

Nomenclature for an atomic state (n, l, m, s)

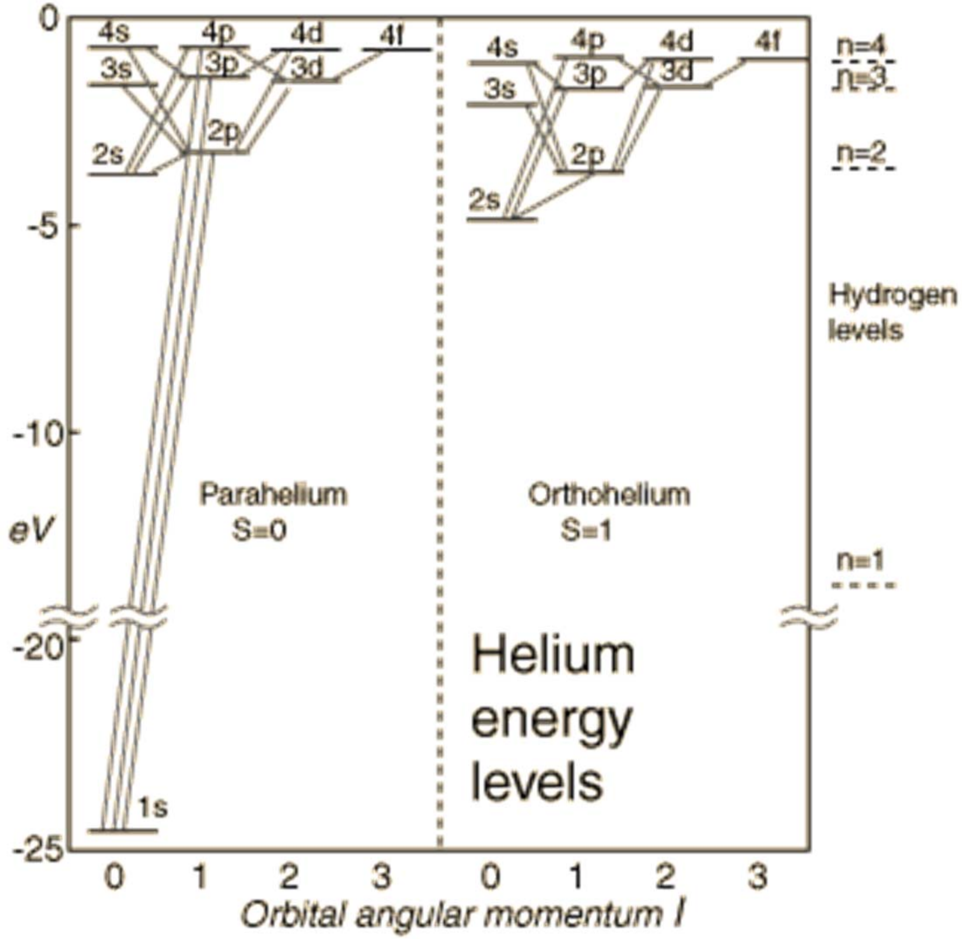
$$n^{2s+1}X_J$$

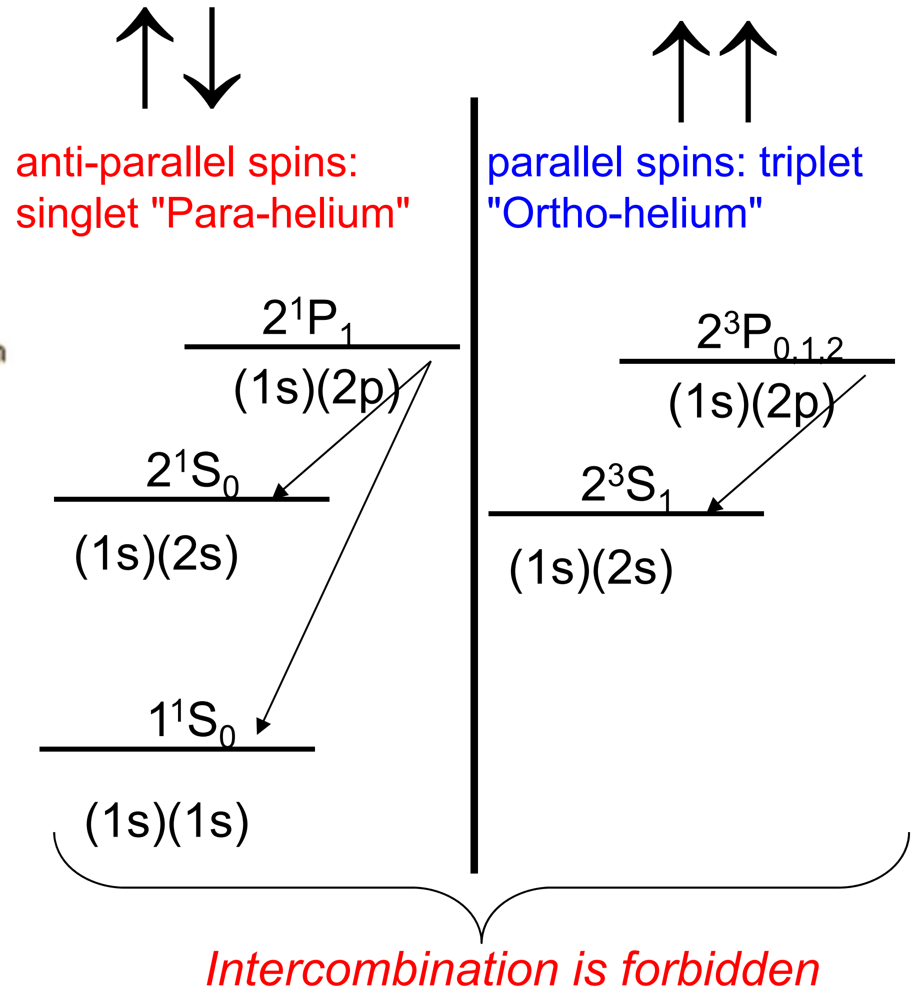
N gives the principle quantum number
X is the total angular momentum S(L=0), P(L=1),…
The index (top left) describes the multiplicity (total spin $S = \sum_i s_i$)
The total angular momentum is given by J=L+S

Example:

$$2^3P_1$$

2 gives the principle quantum number (1s)(2p)
P is the total angular momentum L=1
The index (top left) describes the multiplicity ($S=s_1+s_2=1$)
The total angular momentum is given by L=1, S=1.
They couple to J=1





Level scheme of the He-atom: A few of the permitted transitions are plotted. There are two term-systems between which the radiative transitions are forbidden: the singlet- and the triplet-system. In the singlet-system the transitions cover an energy range of 25 eV, in the triplet-system only 5 eV.

jj-coupling (heavy atoms)

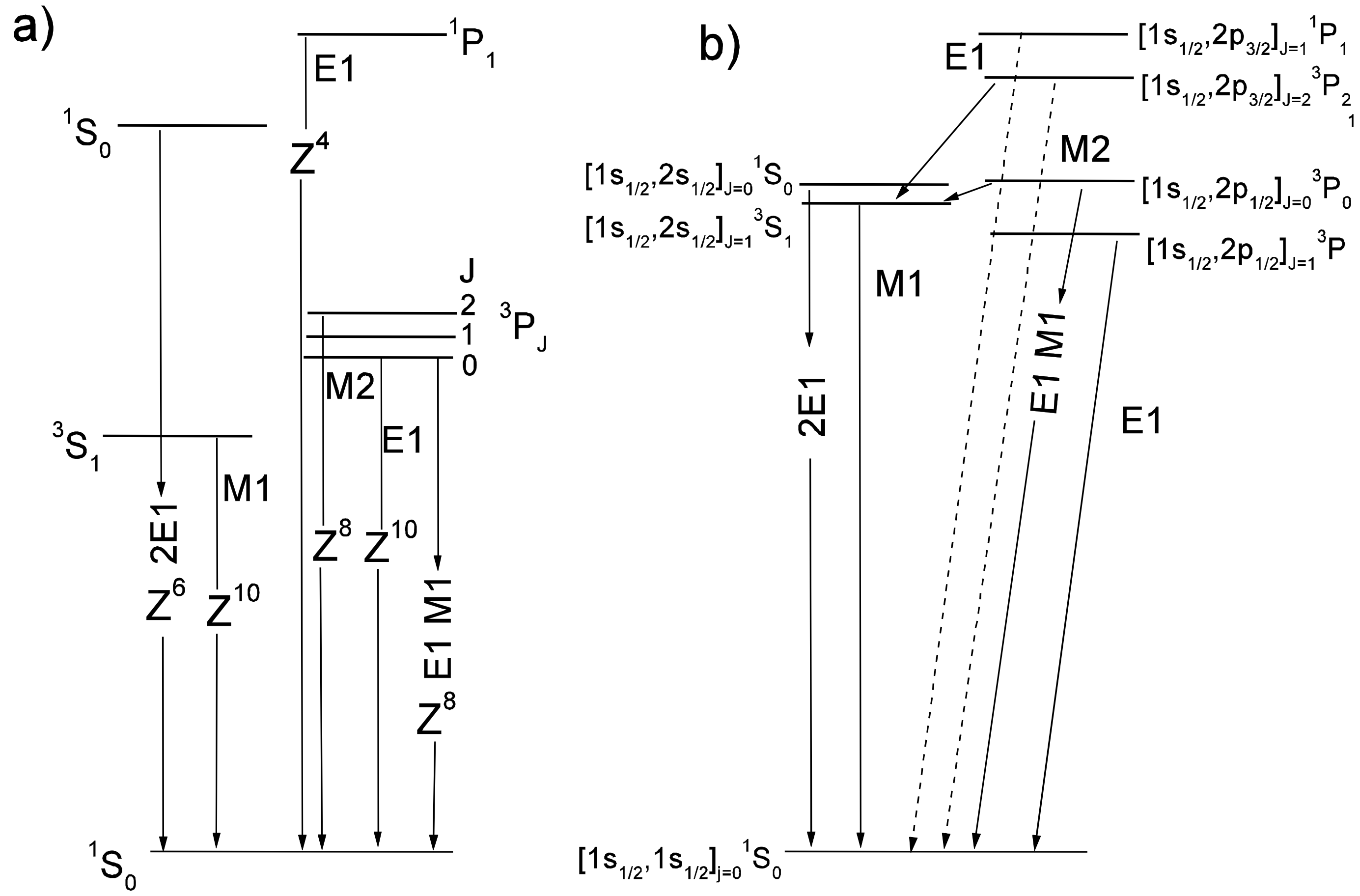
$$\vec{J_1} = \vec{\ell_1} + \vec{s_1} \qquad \vec{J} = \vec{j_1} + \vec{j_2} \qquad \vec{J} = \sum_i \vec{j_i}$$

In heavy atoms the jj-coupling dominants. Here the spin-orbit-interaction (fine structure) is much stronger than the exchange interaction. The electrons behave like in an effective one-electron-system.

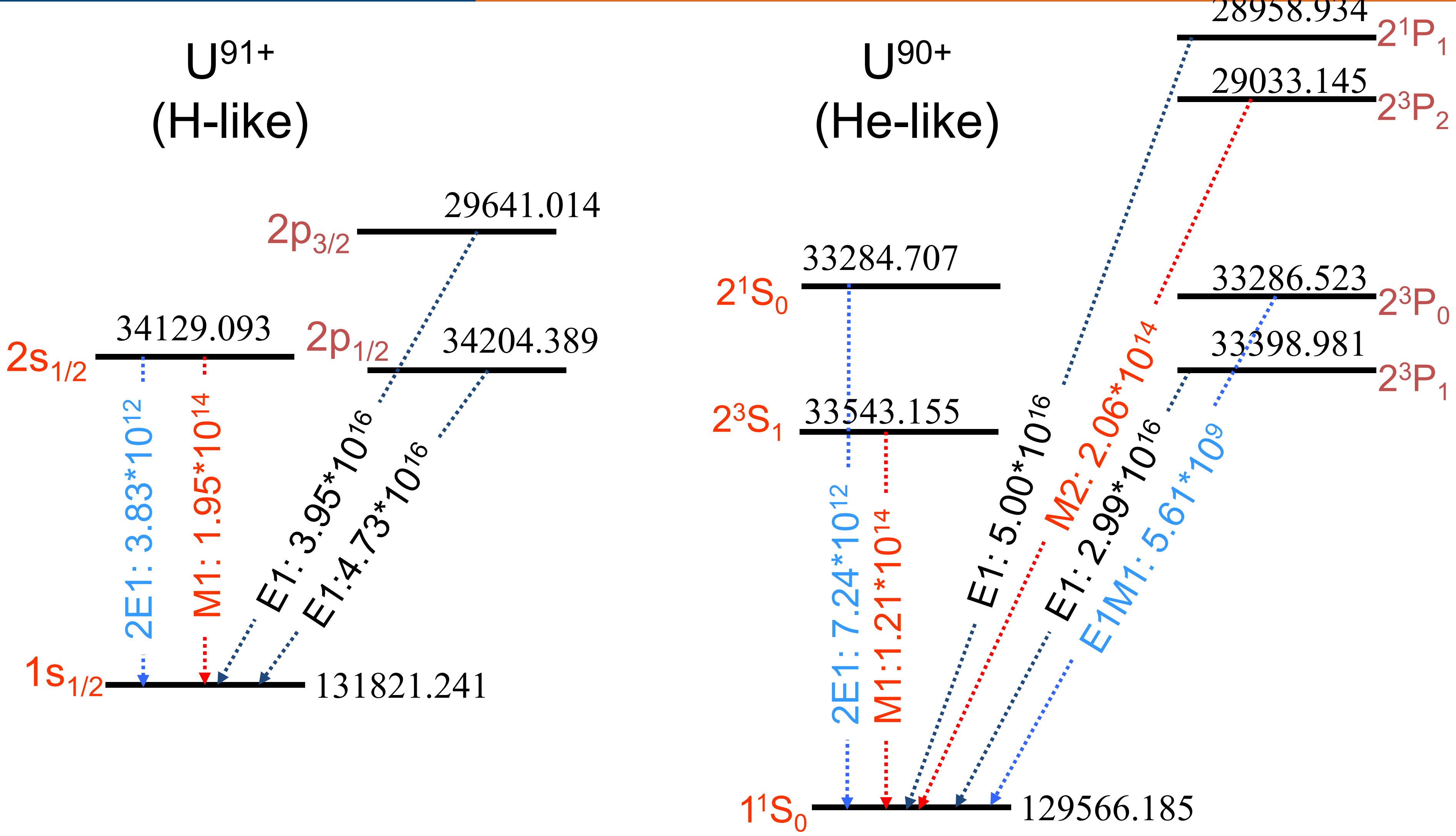
Example: Uran L-shell

Spin-orbit-coupling: *≈ 4.5 keV*
Exchange interaction: *≈ 100 eV*

Compare: Helium and Helium-like Uranium (ls-coupling und jj-coupling)

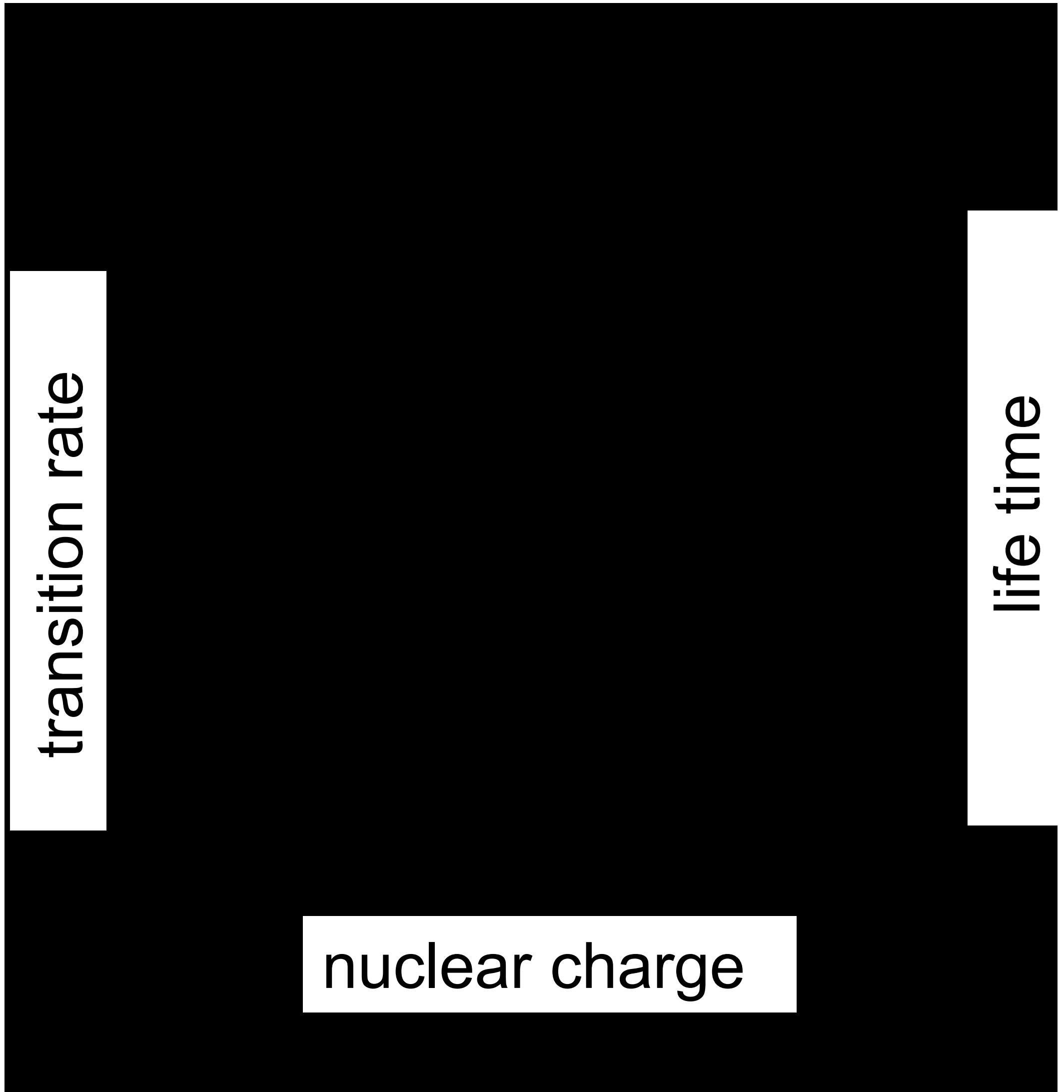


In comparison to Helium, He-like Uranium interacts like an effective one-electron-system



The value of the binding energies and transition probabilities are given in eV / s^{-1}.

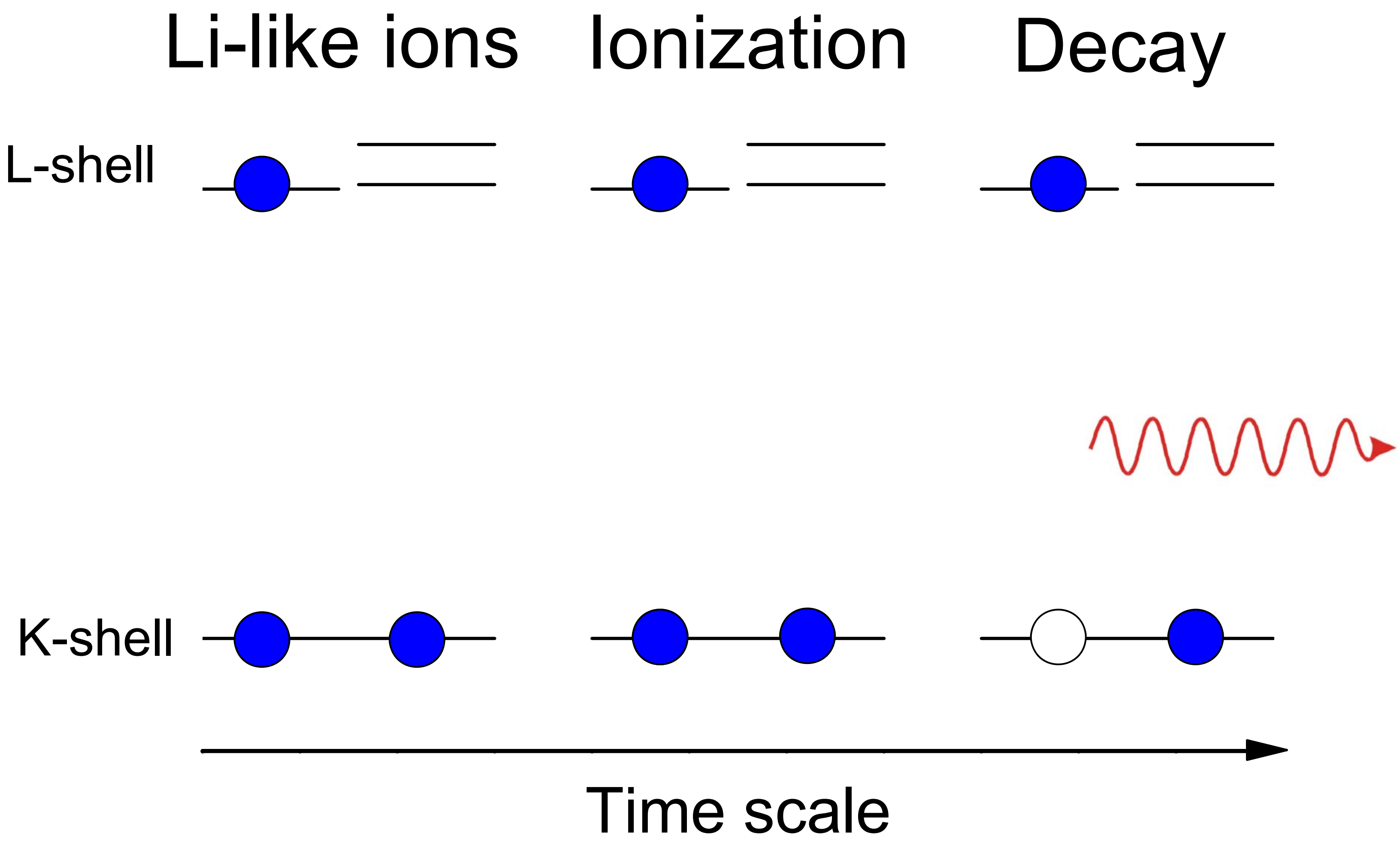
Transition rates in He-like systems (L-> K)



Scaling

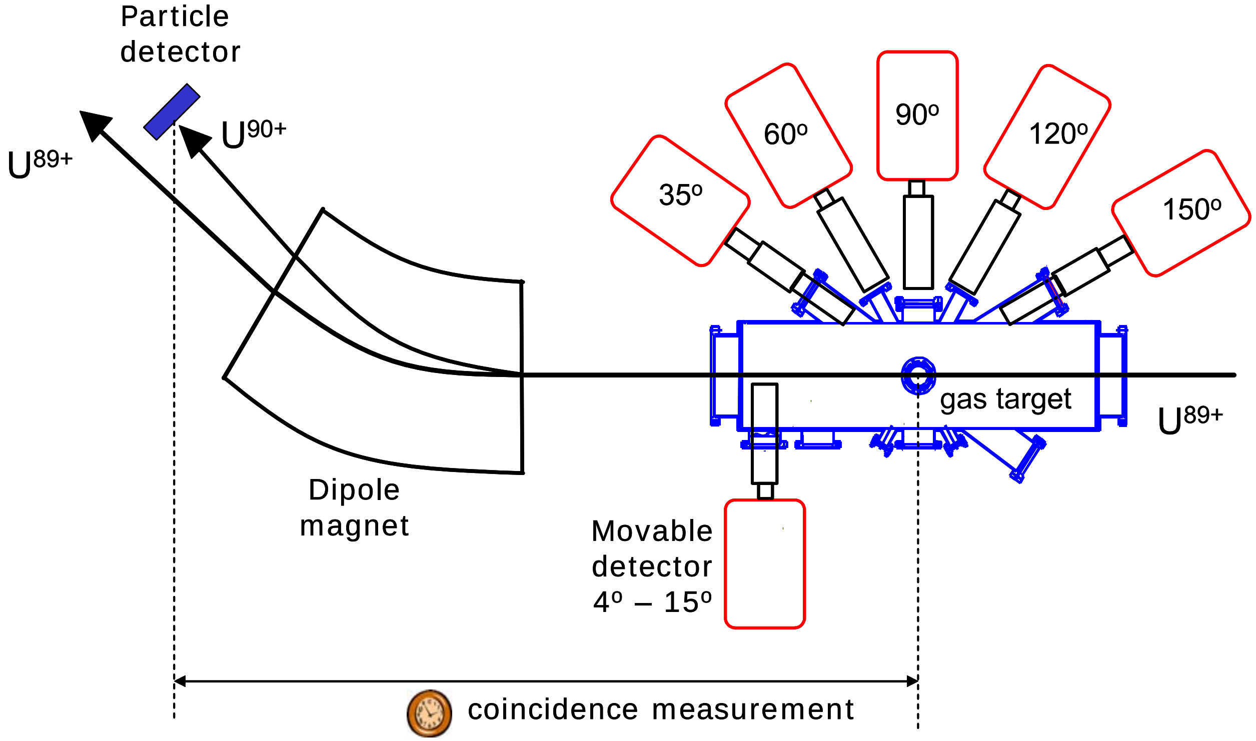
$^3P_1$, $^1P_1$:	Z^4	(E1)
$^1S_1$:	Z^6	(2E1)
$^3S_1$:	Z^{10}	(M1)
$^3P_2$:	Z^8	(M2)
$^3P_0$:	Z^{12}	(E1M1)

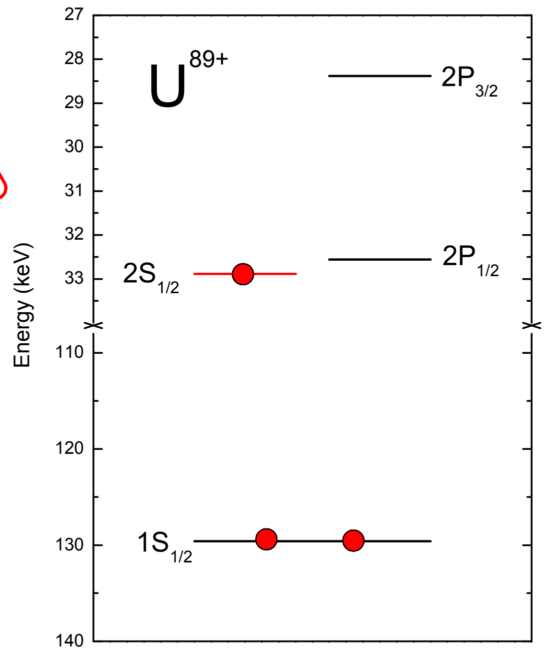
Structure investigation with U^{90+}



Experiment

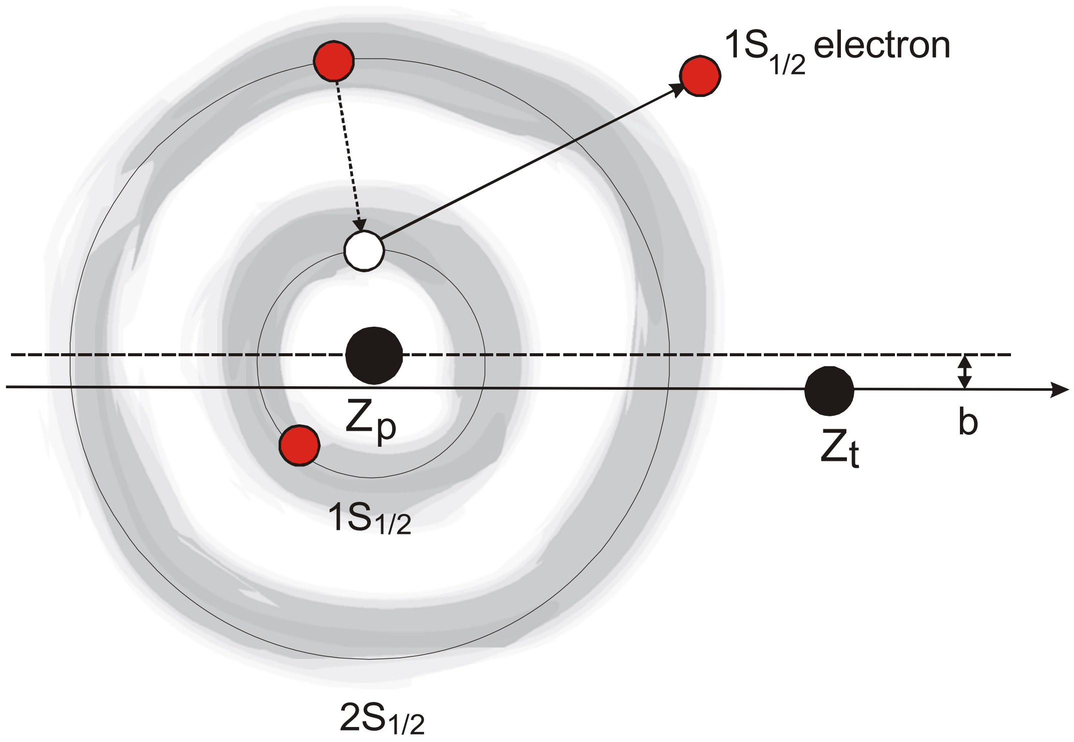
- Li-like Uranium (U89+) with a velocity of about $\beta \cong 0.6$.
- The produced x-ray radiation (in collisions with N_2) is measured in coincidence with ions, which have lost an electron during the collision.



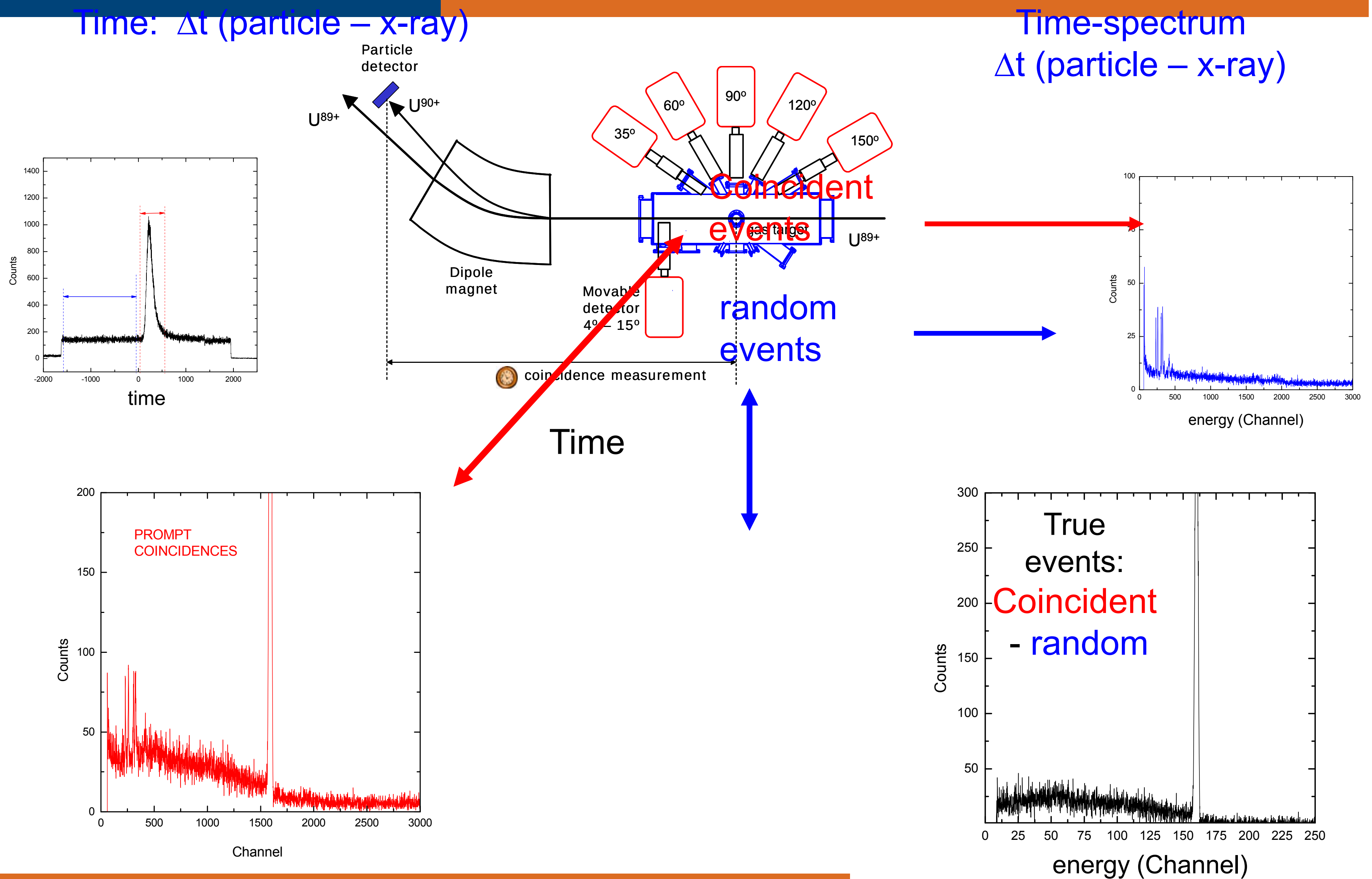


Selective K-shell Ionization

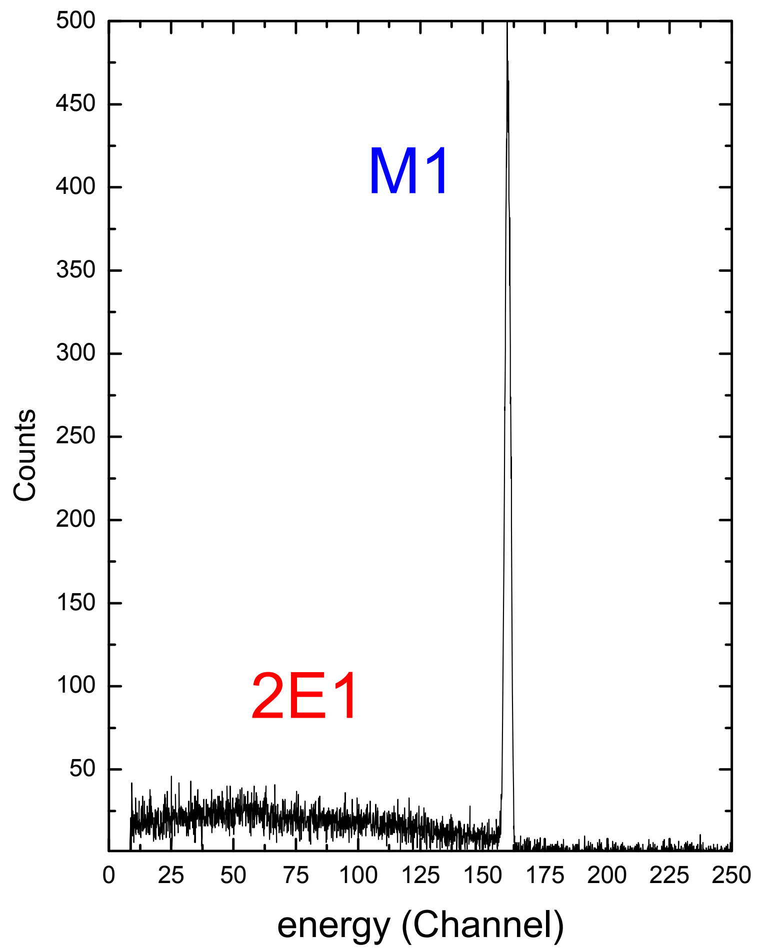
- Ionization of a K-shell electron. The L-shell-electron stays undisturbed.

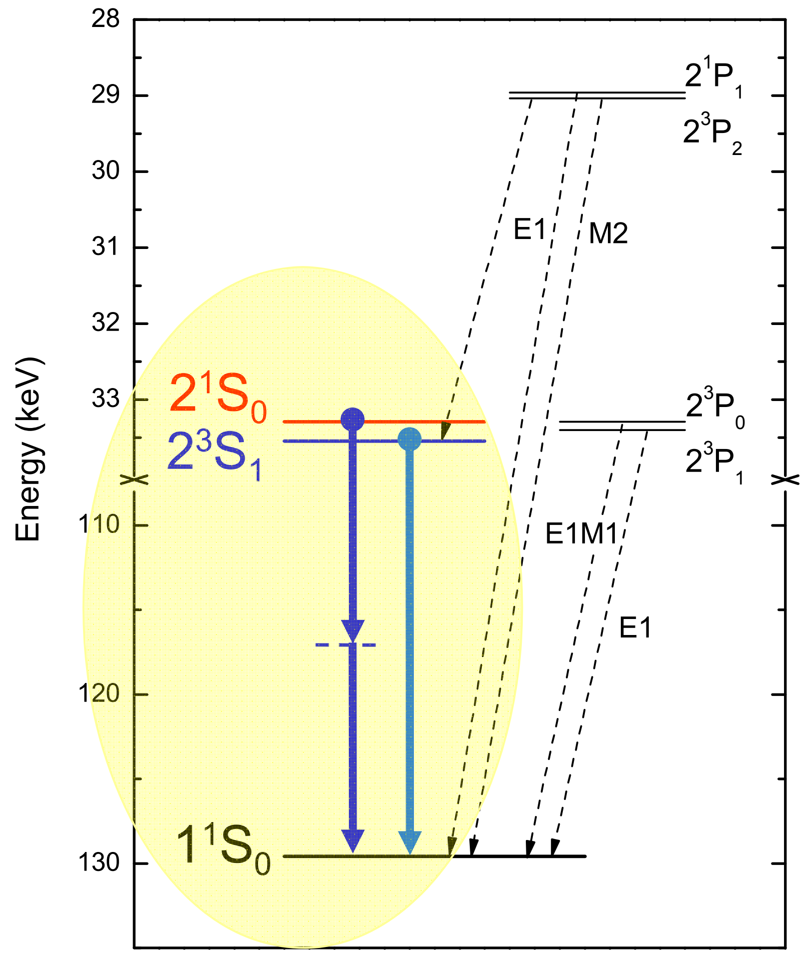


Coincidence technique



Coincident x-ray-spectra

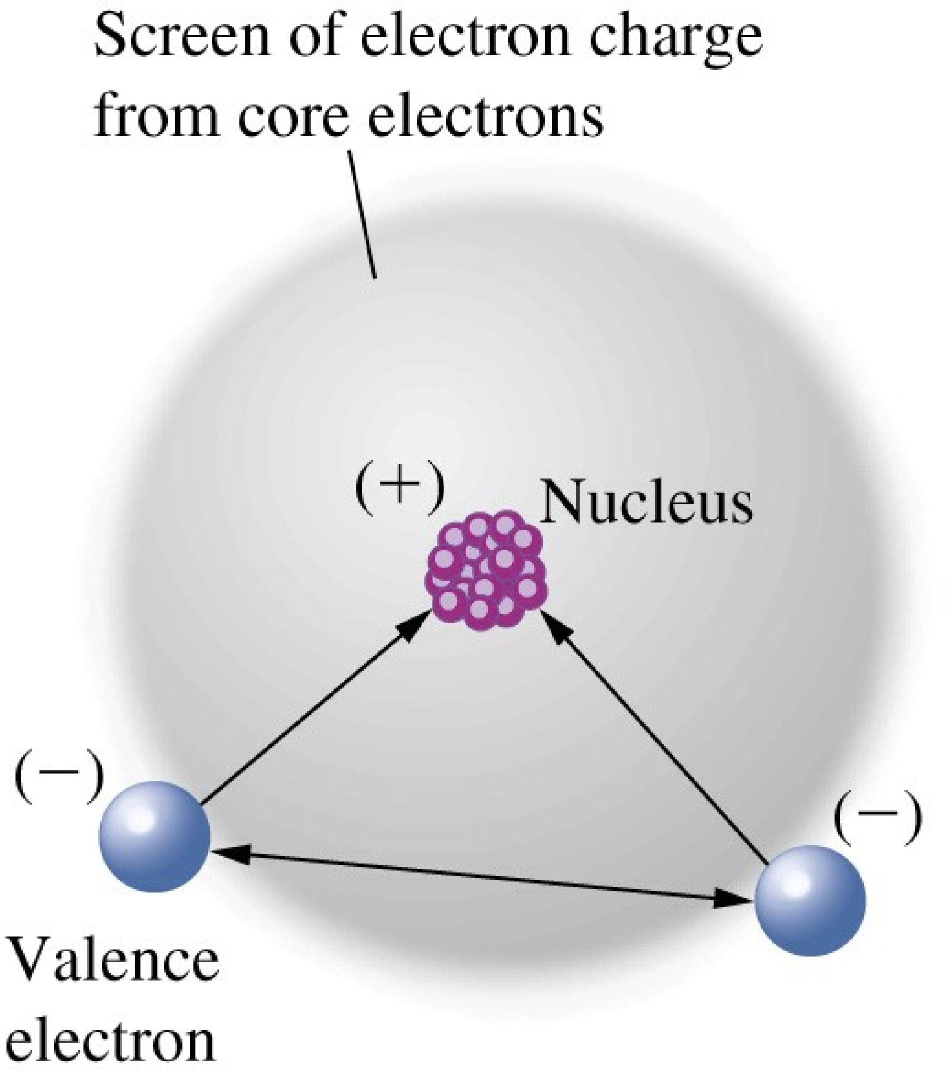




He- like Uranium (U^{90+})

Many-electron systems

→ **Use effective nuclear charge Z_{eff}**



The effective nuclear charge

$$Z_{eff} = Z - s$$

Z: nuclear charge
Z_{eff}: effective or shielded nuclear charge
S: shielding constant

Binding energies

$$E_B = Ry \cdot \frac{Z^2{}_{eff}}{n^2} \quad \longrightarrow \quad E_B = Ry \cdot \frac{Z^2}{n^2}$$

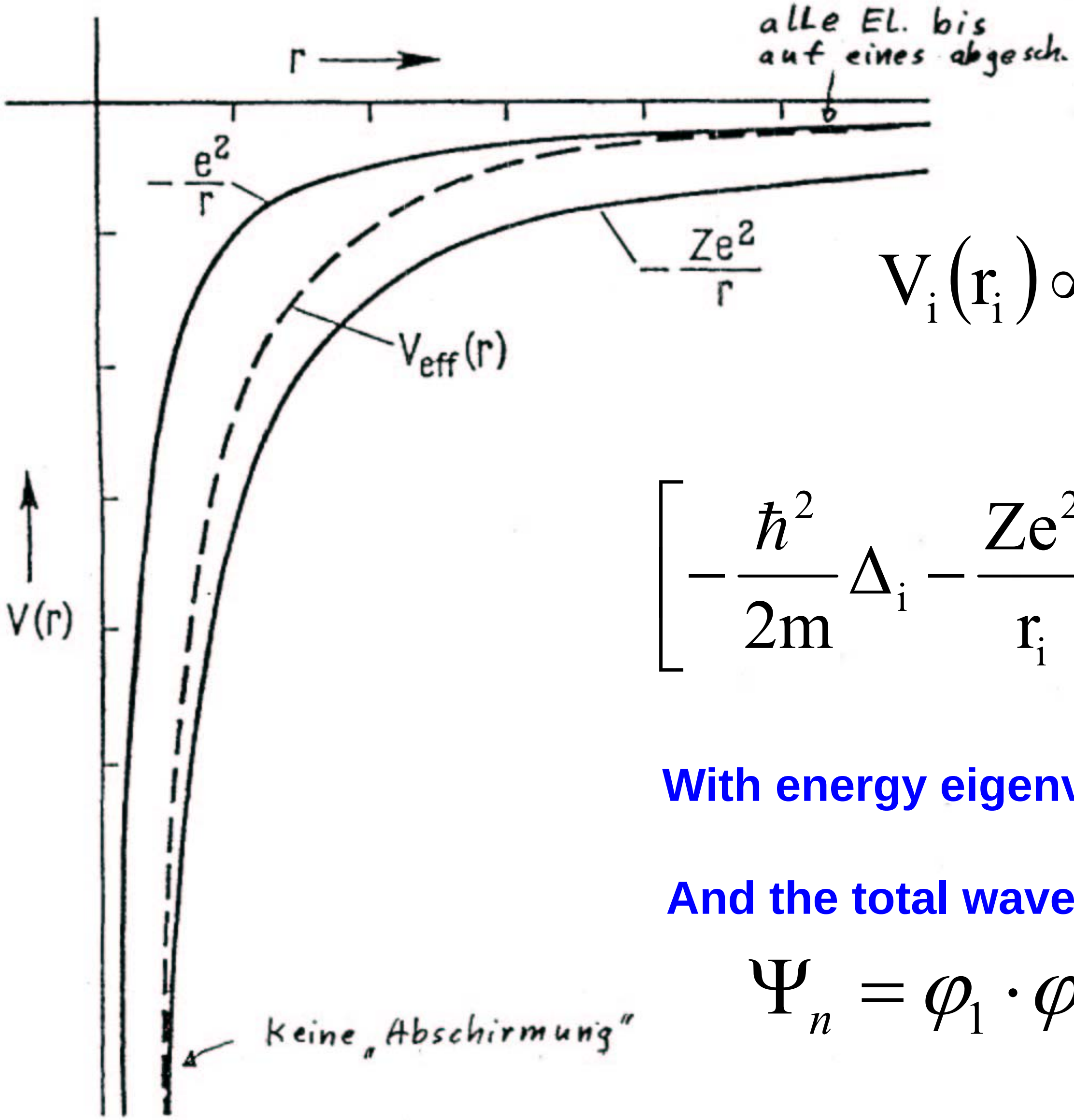
Compare

Orbit radius

$$r_{eff} = a_0 \cdot \frac{n^2}{Z_{eff}} \quad \longrightarrow \quad r = a_0 \cdot \frac{n^2}{Z}$$

(a_0=0.53*10^{-8} cm)

The many-electron potential



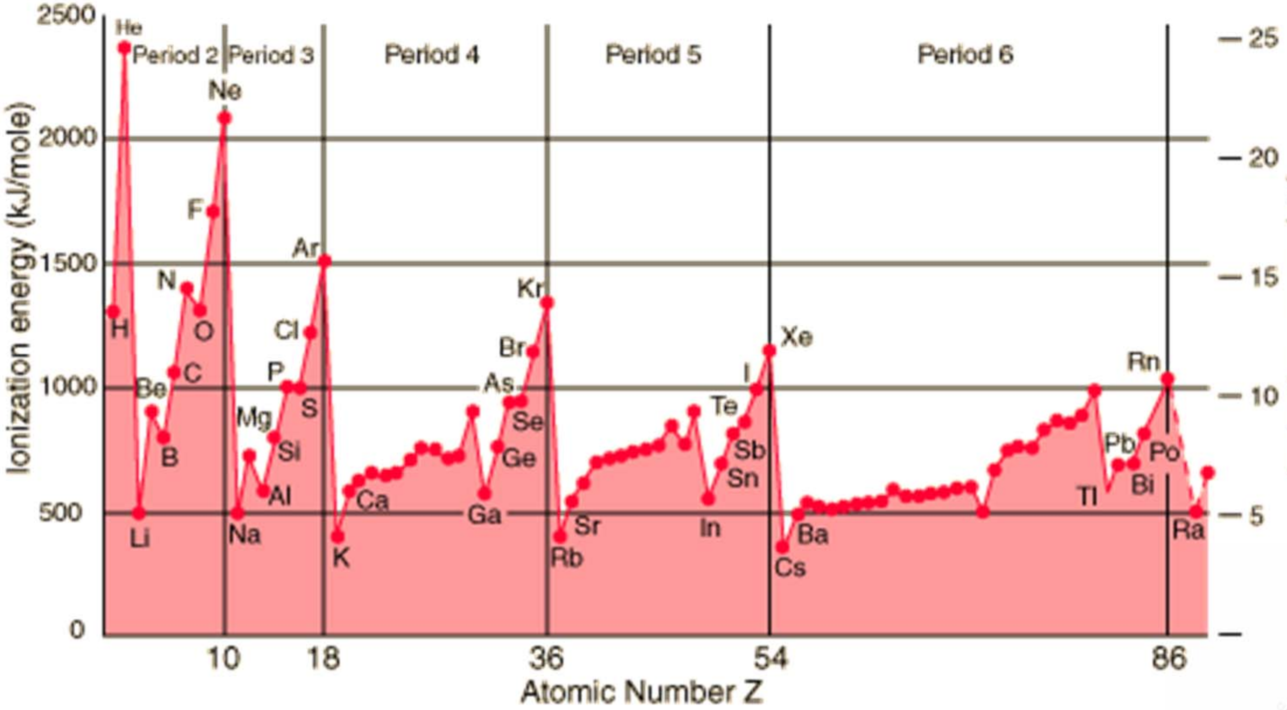
$$V_i(r_i) \propto \sum_{j\neq i} \frac{e^2}{|r_i - r_j|} |\varphi_j(r_j)|^2 d^3 r_j$$

$$\left[-\frac{\hbar^2}{2m}\Delta_i - \frac{Ze^2}{r_i} - V_i(r_i)\right]\varphi_i(r_i) = \varepsilon_i \varphi_i(r_i)$$

With energy eigenvalues ε_i

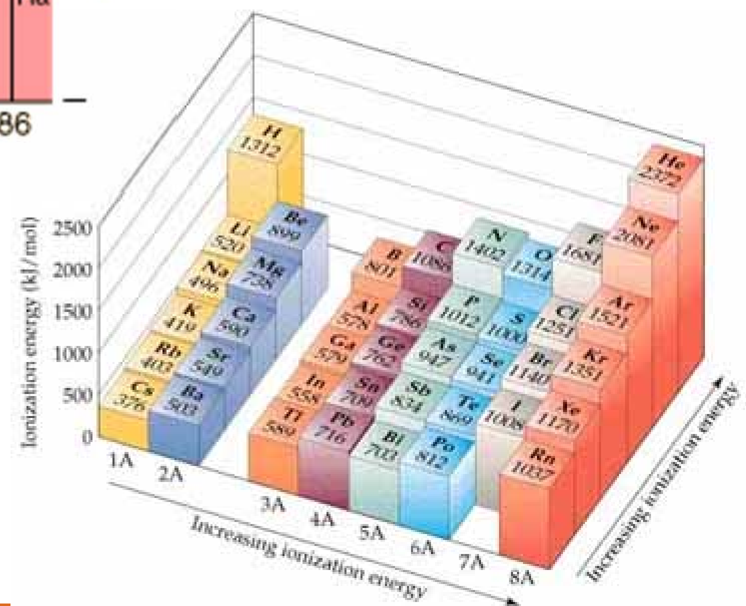
And the total wavefunction

$$\Psi_n = \varphi_1 \cdot \varphi_2 \cdots \varphi_n$$

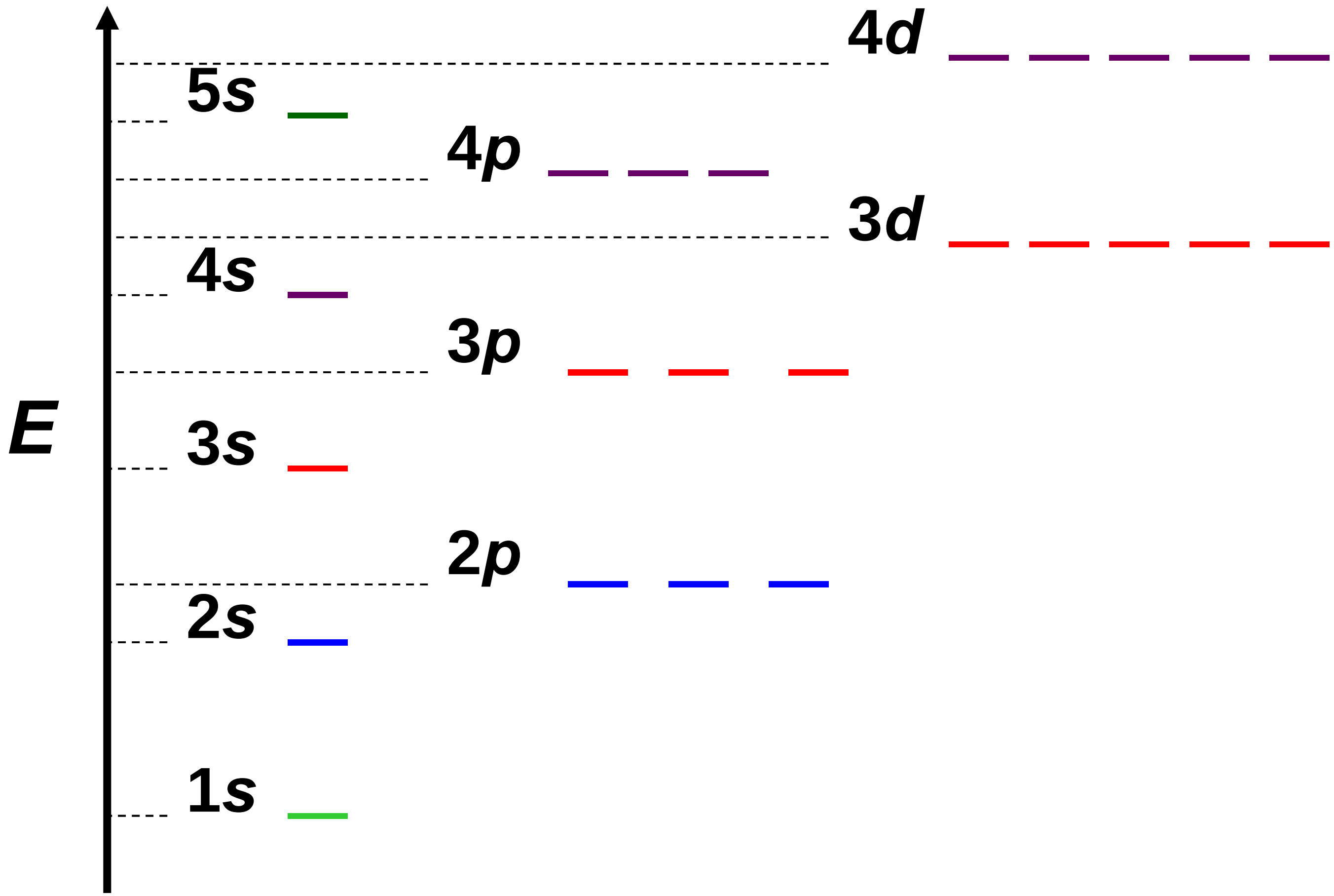


Ionization potential: *At least this energy has to be deposited to remove an electron*.

$$E_I = Ry \cdot \frac{Z^2_{eff}}{n^2}$$



Energy levels in a many-electron system



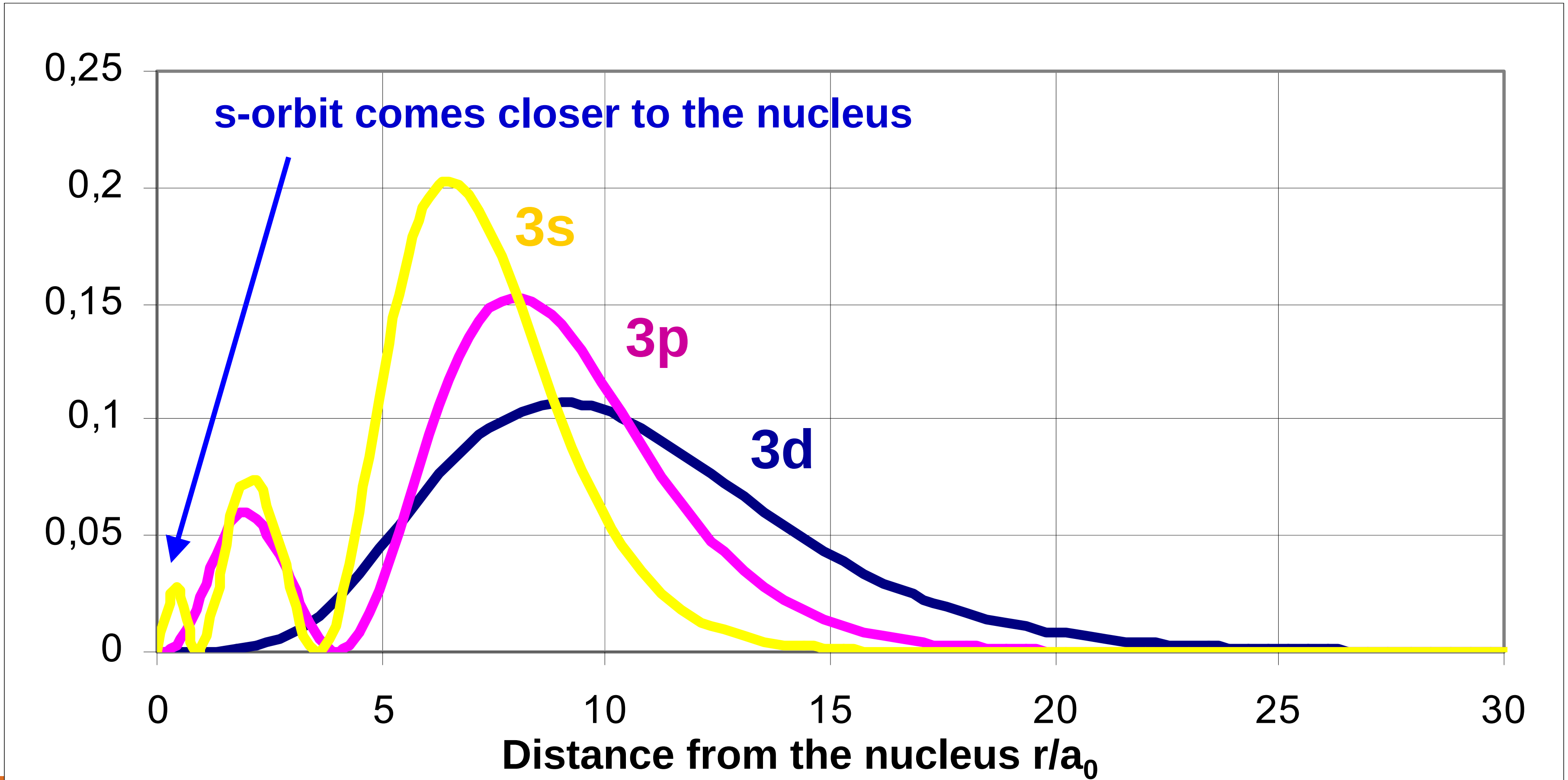
The many-electron wavefunctions

The order of the energy levels changes

$$Z_{eff}(s) > Z_{eff}(p) > Z_{eff}(d)$$

$$E_B = Ry \cdot \frac{Z^2_{eff}}{n^2}$$

e.g. $E_{4s} < E_{3d}$



Slater-rules for calculate Z_{eff}

Electron orbitals are classified as follows

$$[1s][2s2p][3s3p][3d][4s4p][4d][4f][5s5p][5d][5f]\,etc.$$

Rules for calculate the screening constant s

1.) [ns np] Group: Electrons in a higher group do not shield.

2.) [ns np] Group : Electrons in the same group contribute with -0.35 in shielding.

3.) [ns np] Group : Electrons in the next lower group [n-1] shield with -0.85.

4.) [ns np] Group : Electrons in the [n-2] group (and lower) shield with -1.

5.) [nd nf] Group : Rule 1.) and 2.) but electrons in [n-1] shield with -1.

6.) [1s] Shielding by the second 1s-electron: -0.3.

Example

Potassium Z=19

18

[1s^2] [2s^2 2p^6] [3s^2 3p^6] [3d^1]

for [3d^1] follows: s=18 => Z_{eff}=1

[1s^2] [2s^2 2p^6] [3s^2 3p^6] [3d^0] [4s]

10 8x 0.85

for [4s] follows: S=10+6.8 = 16.8 => Z_{eff}=2.2

Example

Sodium Z=11

[1s^2] [2s^2 2p^6] [3s^1]

2 8x 0.85

for [3s] follows: S=2+6.8 = 8.8 => Z_{eff}=2.2

Exact calculations: Z=2.51

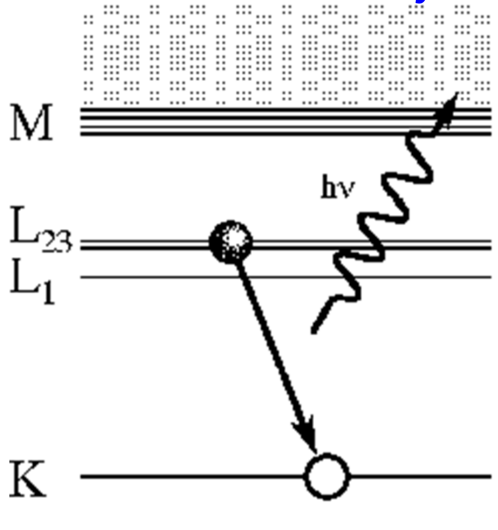
The Auger-effect (many-electron systems)

An excited atomic system can, besides emitting photons, also de-excite by (radiationless) emission of electrons → Auger electrons

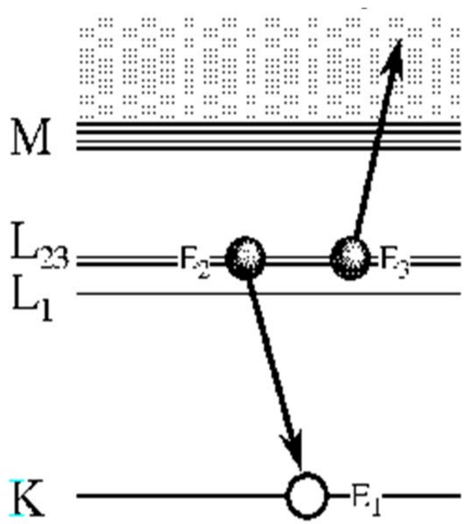
pure electron-electron interaction

$$\Gamma_A \propto \left| \left\langle \Psi^i{}_1 \cdot \Psi^i{}_2 \left| \frac{1}{|r_1 - r_2|} \right| \Psi^f{}_1 \cdot \Psi^f{}_2 \right\rangle \right|^2$$

In general, doubly-excited states are formed,
e.g. as a consequence of a produced K-shell vacancy,
and an excited many-electron system can decay by the emission of Auger electrons.



fluorescence



KLL-Auger

Pierre Auger (1899*-1998+):
Studied atomic physics and cosmic radiation. In 1926 he discovered the effect named after him.
(Herder Lexikon)

Auger rates are in first order approximation independent of the nuclear charge

$$\Gamma_A \propto \left| \left\langle \Psi^{i}{}_1 \cdot \Psi^{i}{}_2 \left| \frac{1}{|r_1 - r_2|} \right| \Psi^{f}{}_1 \cdot \Psi^{f}{}_2 \right\rangle \right|^2$$

(non-relativistic, while all distances scale with Z)

$$\frac{1}{\mathrm{r}} \propto Z; \quad \mathrm{d}^3\mathrm{r}_1 \propto \frac{1}{Z^3}; \quad \mathrm{d}^3\mathrm{r}_2 \propto \frac{1}{Z^3};$$

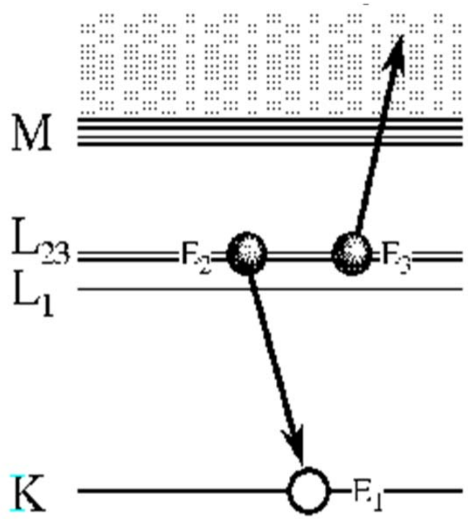
$\Psi^{i}{}_1$ **: initial bound state of electron 1** $\propto Z^{3/2}$

$\Psi^{i}{}_2$ **: initial bound state of electron 2** $\propto Z^{3/2}$

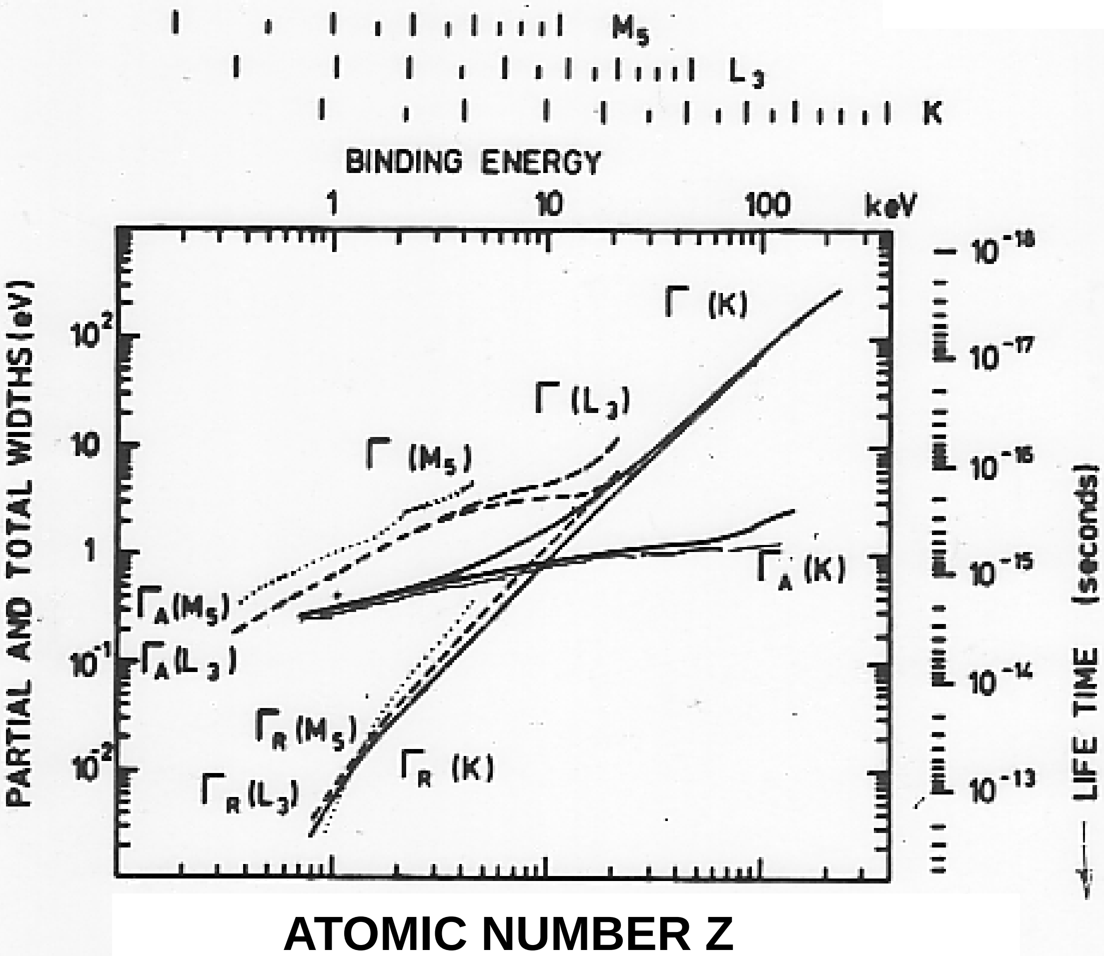
$\Psi^{f}{}_1$ **: final bound state of electron 1** $\propto Z^{3/2}$

$\Psi^{f}{}_1$ **: final free state of electron 1** $\propto Z^{1/2}$

$$\Gamma_A \propto \left| Z^{3/2} \cdot Z^{3/2} \cdot Z \cdot Z^{3/2} \cdot Z^{1/2} \cdot \frac{1}{Z^3} \cdot \frac{1}{Z^3} \right|^2 = Z^0$$



KLL-Auger



Auger rates

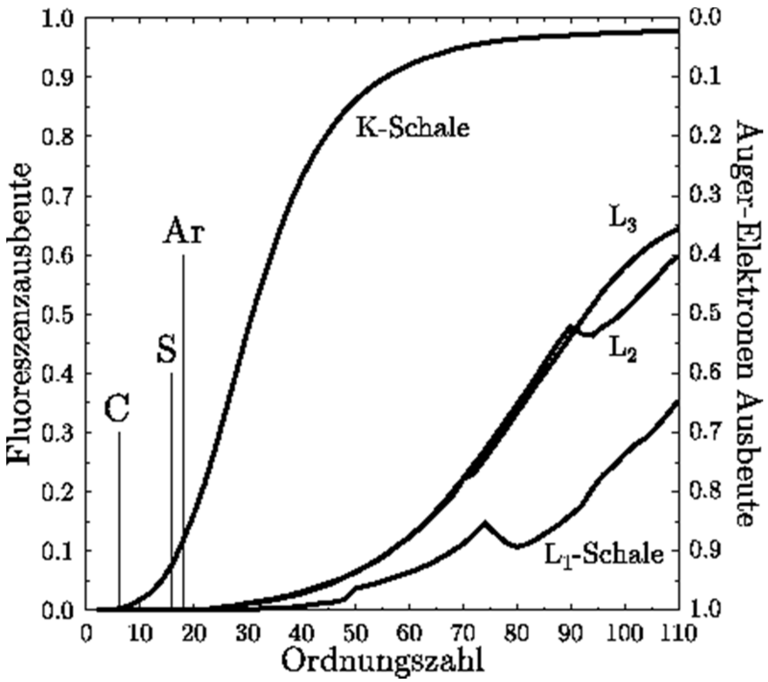
$$\Gamma_A \propto Z^0$$

Radiative rates

$$\Gamma_X \propto Z^4$$

Auger rates are almost constant, when plotted as a function of Z, over a large range of elements.

Fluorescence yield



Fluorescence yield

$$\omega = \frac{\Gamma_x}{\Gamma_x + \Gamma_A} = \frac{\Gamma_x}{\sum_i \Gamma_i}$$

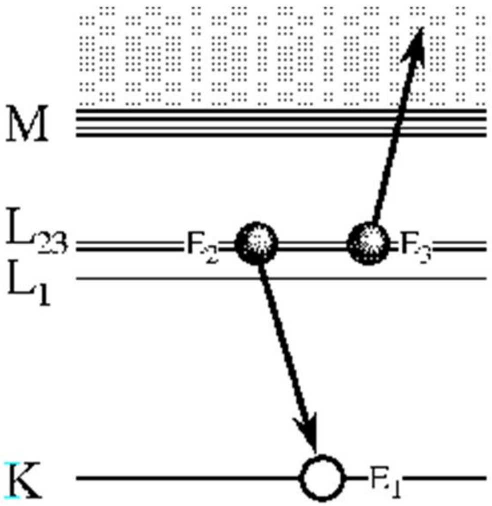
$$\omega \propto \frac{Z^4}{Z^4 + Z^0} \rightarrow 1 \text{ for } Z > 50$$

Fluorescence yield: **ratio of the fluorescence yield to the total yield Γ_i is also called *Fluorescence coefficient* ω.**

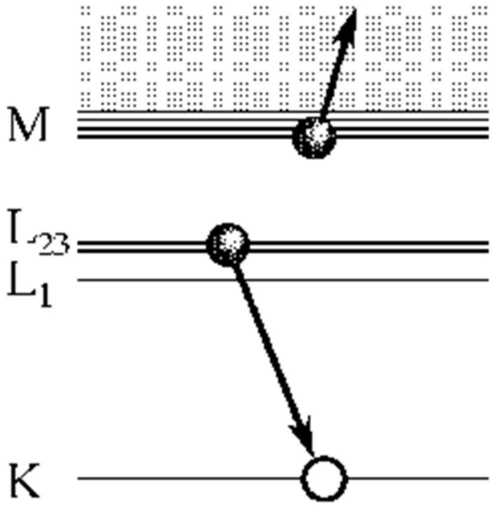
Note: so far we only treated approximations: The complete electron-electron interaction is given by the function f, also called the current-current-interaction. For certain states this function could also be the dominant term.

$$\frac{1}{|r_1 - r_2|} + f(j_1, j_2)$$

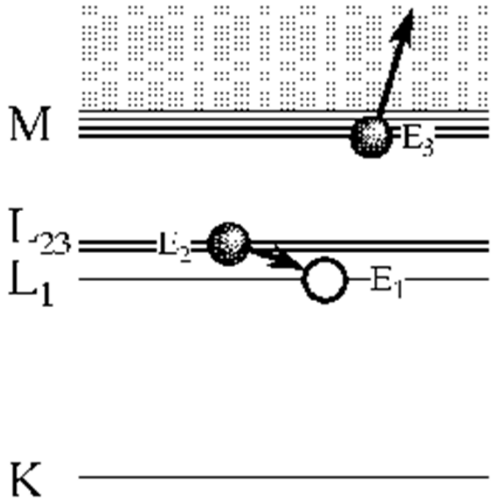
Nomenclature of the Auger-effect



KLL-Auger



KLM-Auger



Coster-Kronig-transition

Radiationless transitions from state X (L-shell) to state Y (K-shell) and electron emission from the state Z (L-shell) into the continuum are termed XYZ, e.g. KLL, KLM, KMN, etc.

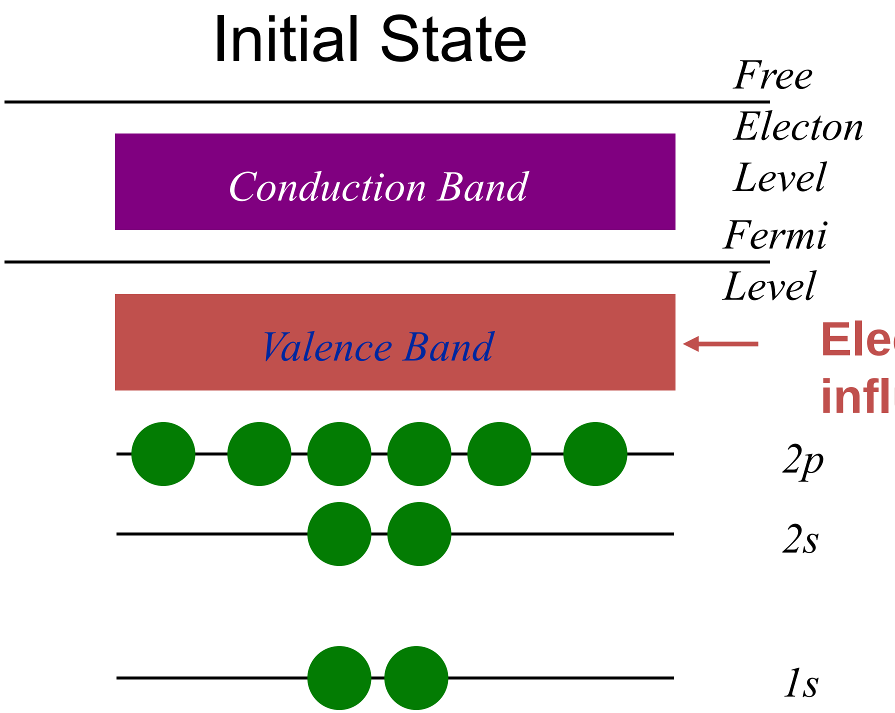
hole (X) – decaying electron (Y) – Auger electron (Z)

Coster-Kronig-transitions

If x_i and x_f are the lower states of level X and Y is an excited state, then $x_i \rightarrow x_f Y$ is a Coster-Kronig-transition

Binding energies

-how to identify elements and binding properties
e.g. of atoms in their environment =

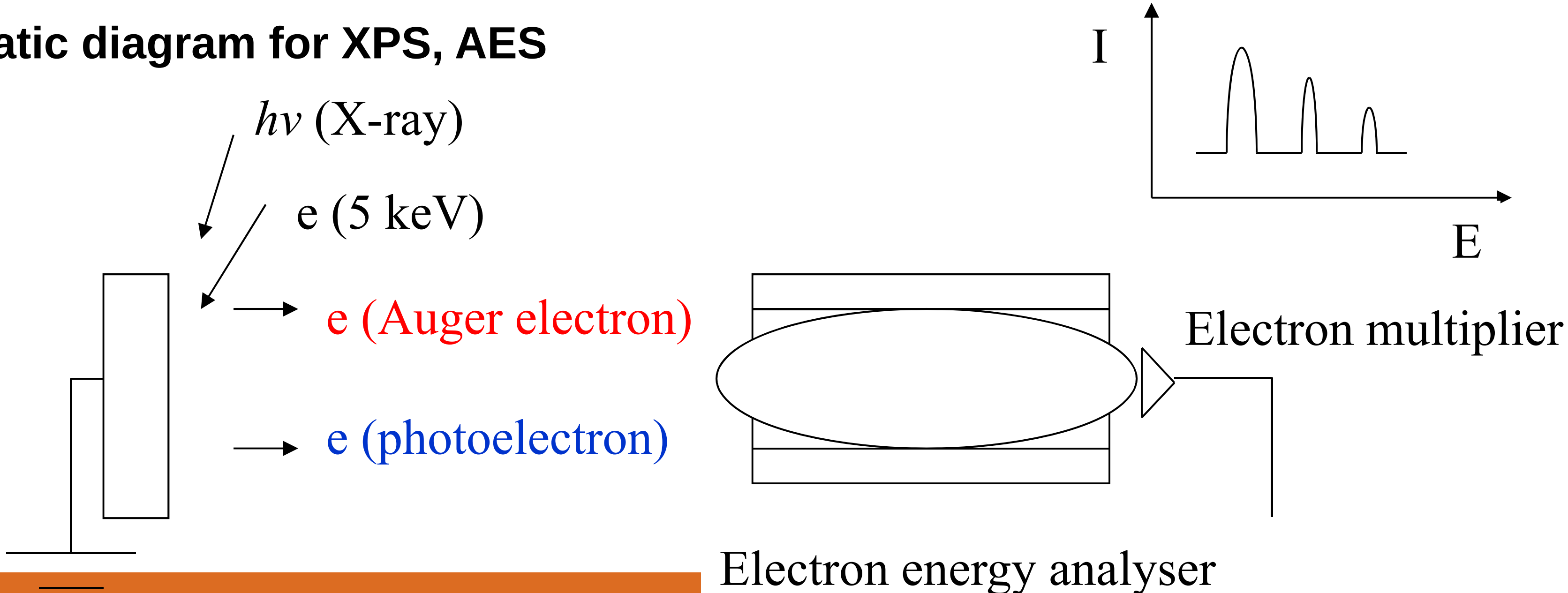


Electronic binding properties are influenced by their environment

Analysis of materials, chemcal properties

	Probe beam	detection
XPS	photons (X-ray)	X-ray photo electron spectroscopy (core electrons)
UPS	photons (UV)	UV Photo electron spectroscopy (valence electrons)
AES	electrons	Auger electron spectroscopy
SIMS	ions	secondary ion mass spectroscopy

chematic diagram for XPS, AES



- XPS(x-ray photoelectron spectroscopy) was developed in the mid-1960s by Kai Siegbahn & his research groups

  (at the Univ. of Uppsala, Sweden)

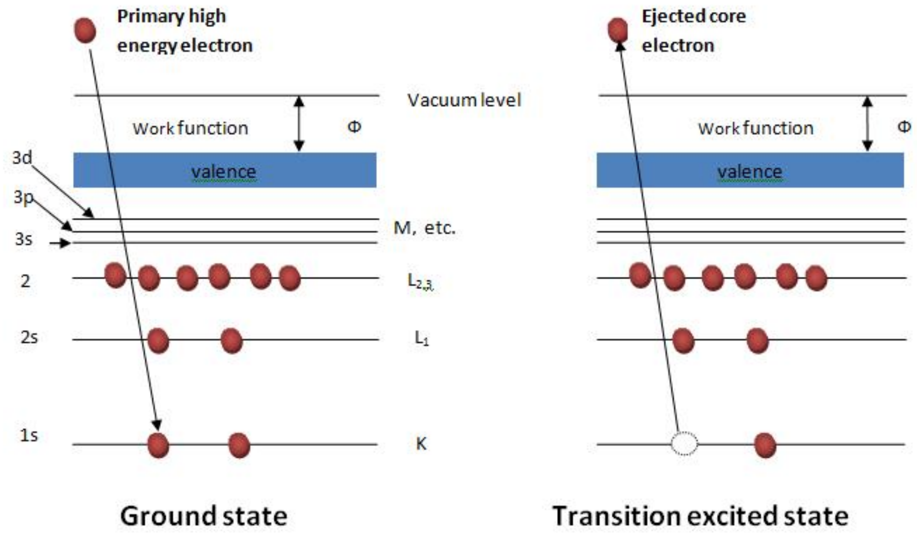
- The technique was first known by the acronym

  ESCA(electron spectroscopy for chemical analysis)

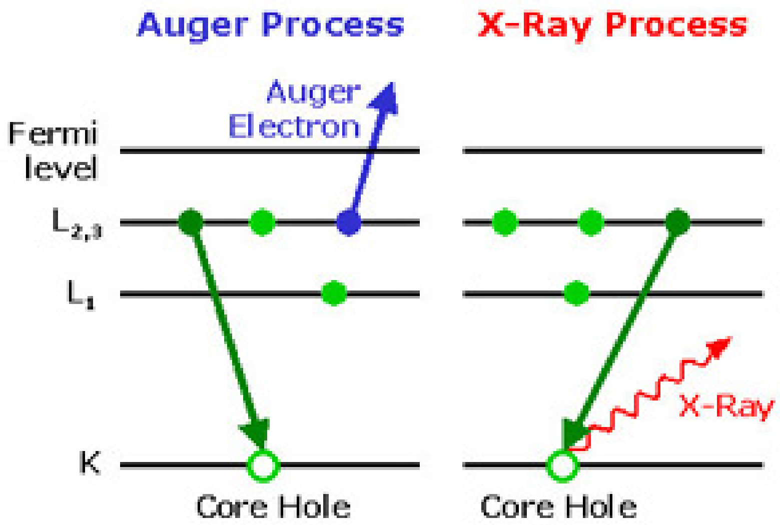
- The advent of commercial manufacturing of surface analysis equipment in the early 1970s => equipment in laboratories
- In 1981, Siegbahn was awarded the Nobel Prize for Physics for his work with XPS

AES: Auger electron spectroscopy (1925)

Excitation by primary electrons (5keV)
or x-rays



De-excitation process
(competing processes)



Binding energies (BE)

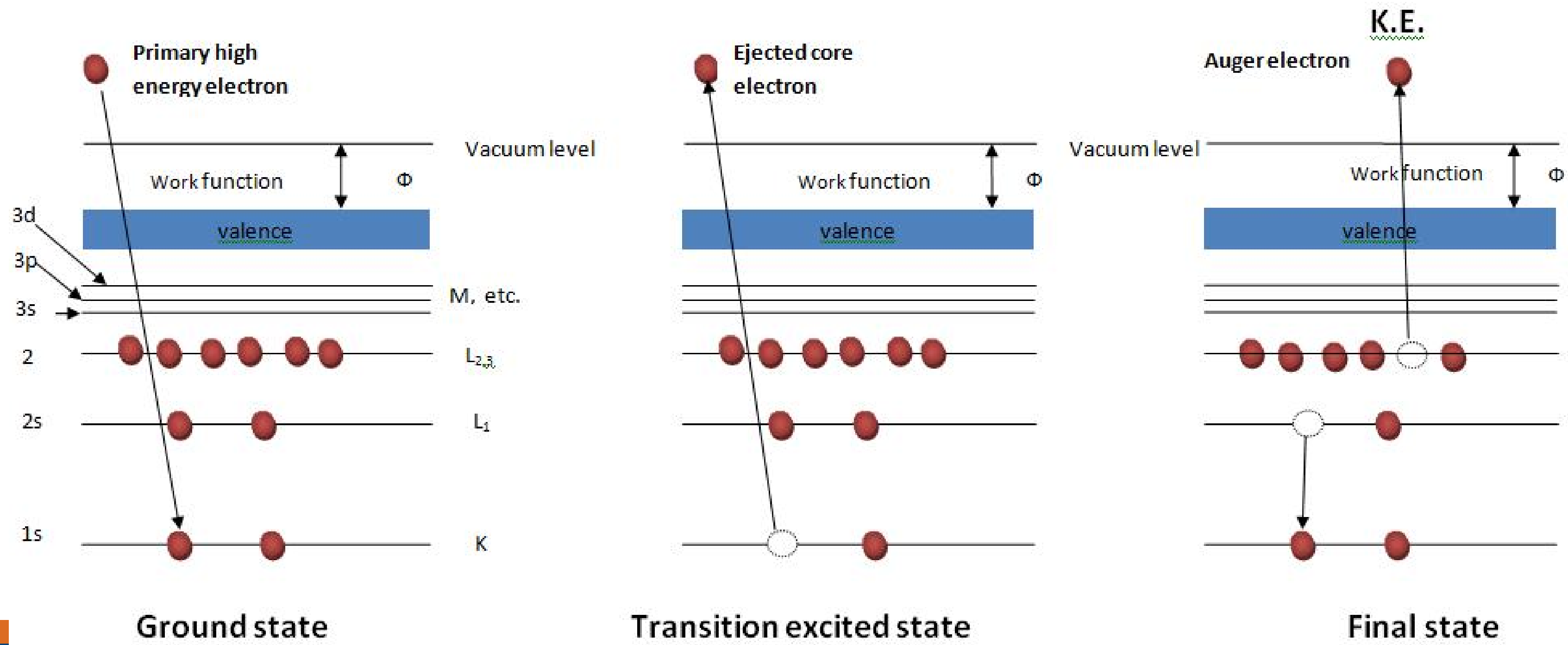
$$BE = h\nu - KE - \Phi_{spec} - E_{ch}$$

BE= *Electron-binding energy*

KE= *Kinetik electron energy*

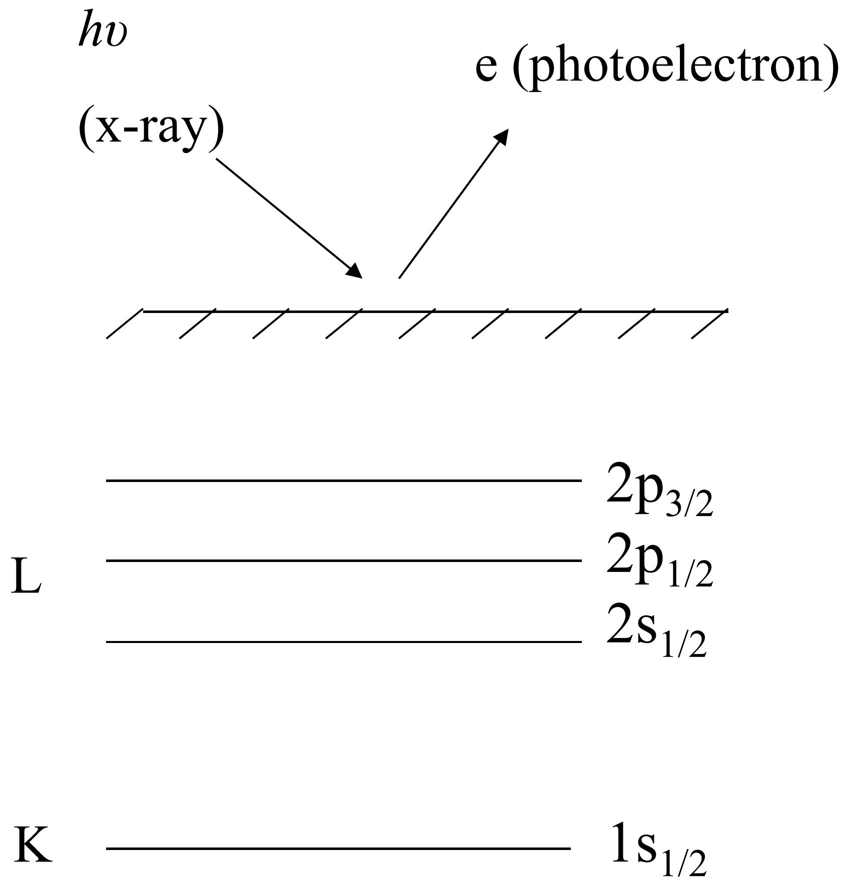
Φ_{spec}= *Spectrometer Work Function*

E_{ch}= *Surface energy (Ablösearbeit)*



XPS (X-ray photoelectron spectroscopy) oder ESCA (electron spectroscopy for chemical analysis)

by Siegbahn



Mg K_α	: 1253.6 eV	half width: 0.8 eV
Al K_α	: 1486.6 eV	: 0.9 eV
Cu K_α	: 8047.8 eV	: ~ 3 eV

Photoelectron kinetic energy

Photoelectron kinetic energy

$$E_{K.E} = h\upsilon - E_B$$

photon energy (constant)

"Binding energy" of the electron in the orbital in the atom

Auger-Electron-spectroscopy: typically used for elements between Li and U

$$E_{\mathrm{K\,L_I\,L_{III}}} = E_{\mathrm{K}} - E_{\mathrm{L_I}} - E_{\mathrm{L_{III}}}$$

X-ray spectroscopy: typically used for elements between Li and U

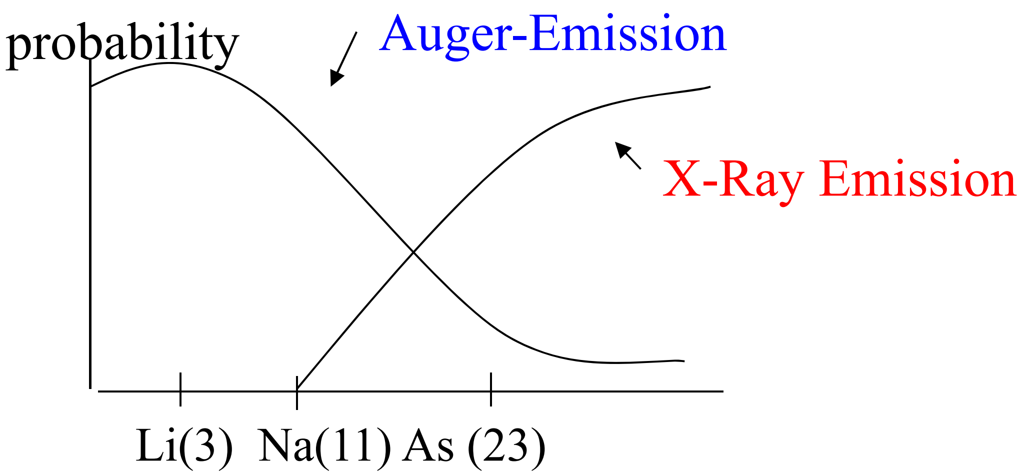
$$E_{\mathrm{K}\alpha_{\mathrm{I}}} = E_{\mathrm{K}} - E_{\mathrm{L_{III}}}$$

$$E_{\mathrm{K}\alpha_2} = E_{\mathrm{K}} - E_{\mathrm{L_{II}}}$$

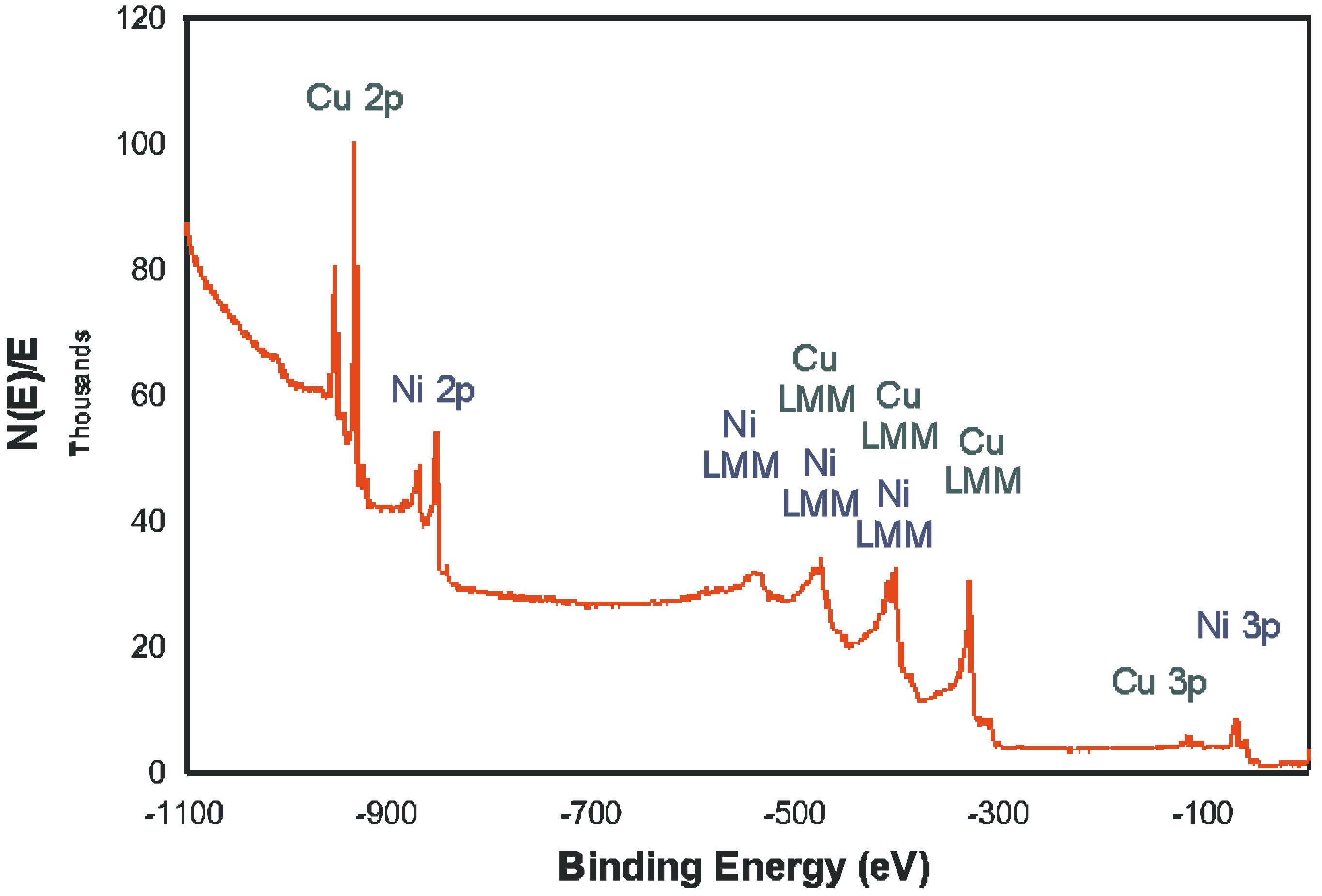
K_α : L → K

K_β : M → K

Effective probe thickness ~ 1 µm, sensitivity ~ 0.1%



Element identification



Element identification

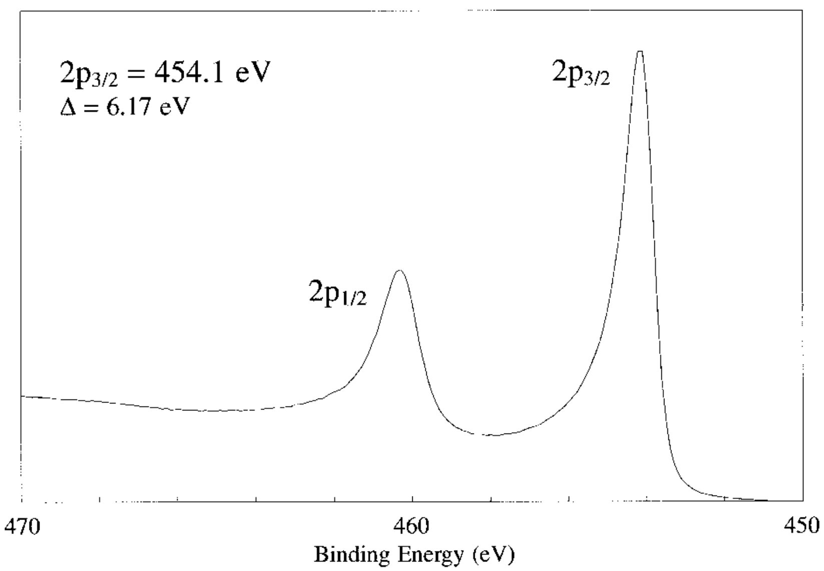
	Binding Energy (eV)		
Element	***$2p_{3/2}$***	***3p***	Δ
Fe	707	53	654
Co	778	60	718
Ni	853	67	786
Cu	933	75	858
Zn	1022	89	933

Electron-nucleus interaction is used for the element analysis

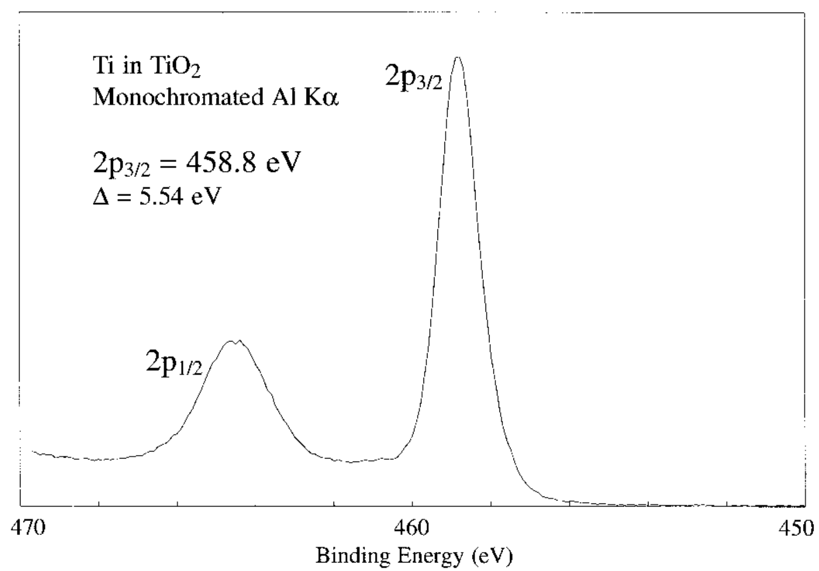
Chemical properties

Spin-Orbit Coupling

Ti Metal

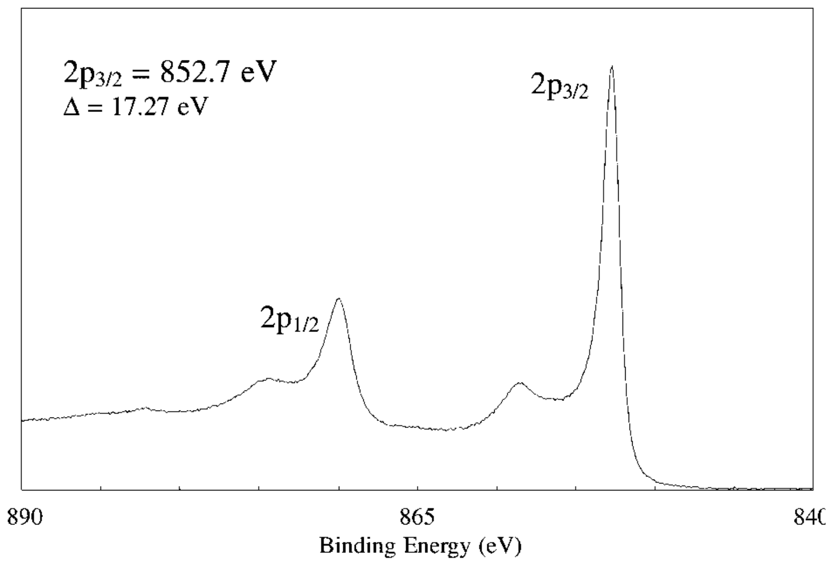


Ti Oxide

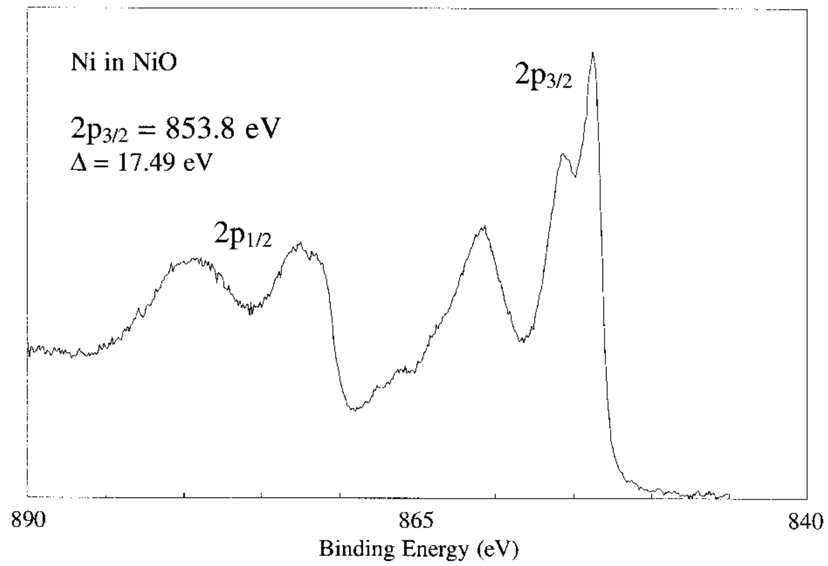


Shakeoff/Shakeup

Ni Metal



Ni Oxide



Final State Effects
Shake-up / Shake-off

L(2p) -> Cu(3d)

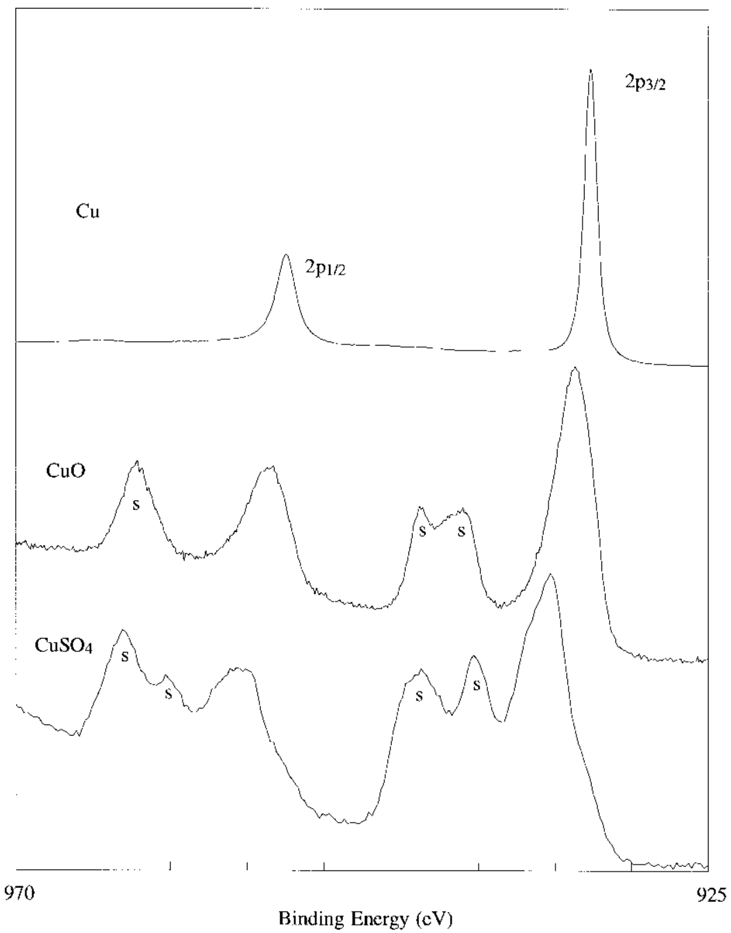
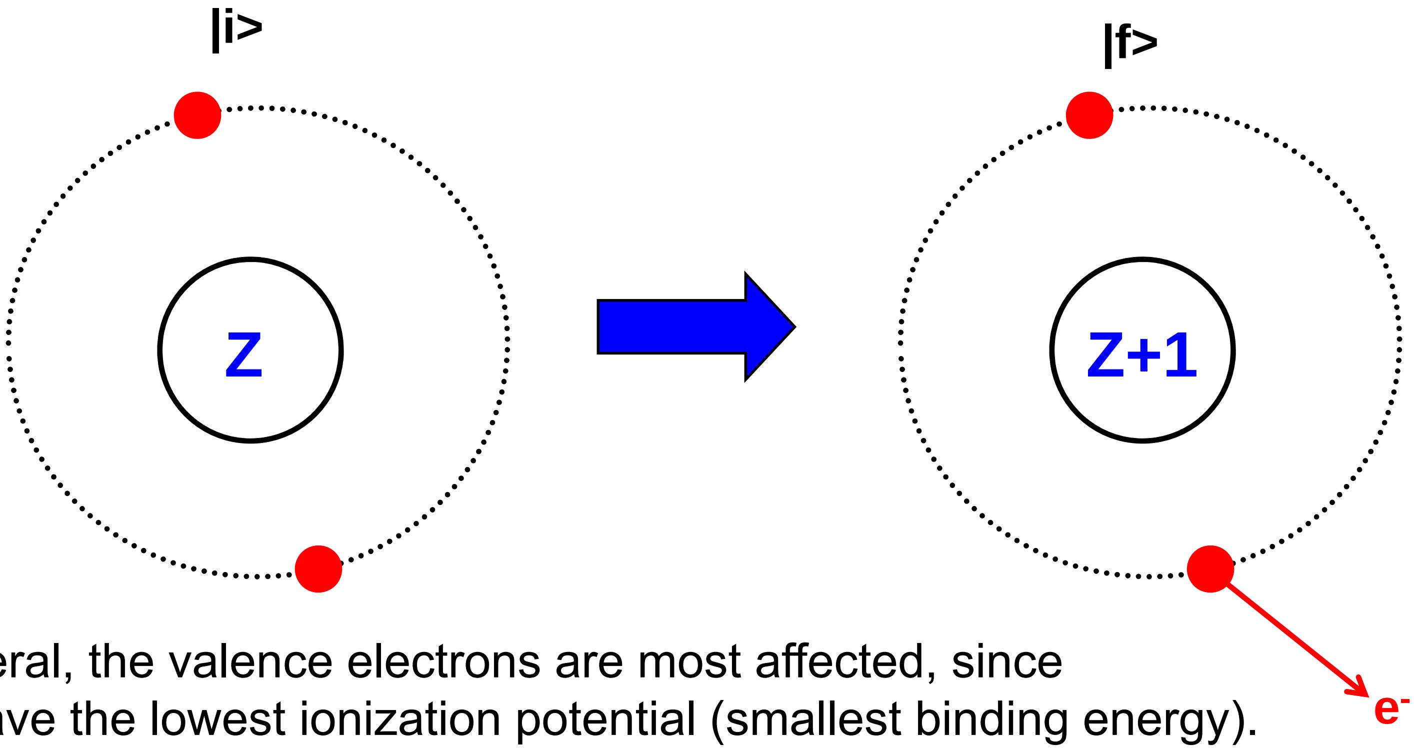


Figure 8. Examples of shake-up lines (s) of the copper 2p observed in copper compounds.

Shake-off process

The *shake-off process* occurs when the effective Coulomb potential changes its strength and leads to an autoionization of the electron cloud. Examples are: K-shell ionization and β-decay.



In general, the valence electrons are most affected, since they have the lowest ionization potential (smallest binding energy).

Non-adiabatic regime:
Two-step process `sudden approximation´. The first process (e.g. K-shell ionization) does not influence the second one (emission).

Shake-off process

The probability that an electron remains in its orbit is:

$$P = \int \Psi^*(Z) \cdot \Psi(Z+1) d^3r$$

This probability is given by the overlap between the wavefunctions of the initial state $\Psi(Z)$

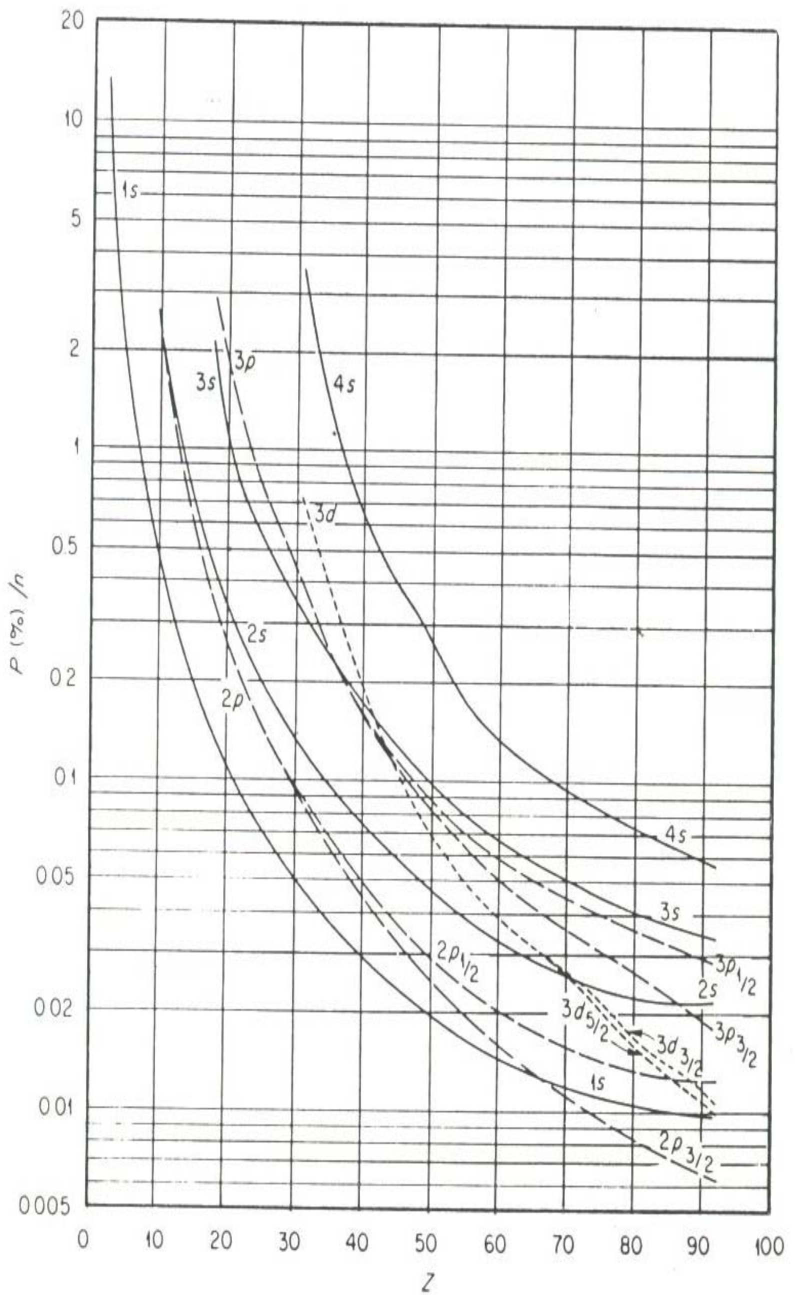
and the final state. $\Psi(Z+1)$

The probability that an electron is being ionized is:

$$P_{ION} = 1 - \int \Psi^*(Z) \cdot \Psi(Z+1) d^3r \qquad (P_{ION} = 1 - P)$$

Note: High-energy approximation!

Question: What is the energy distribution of the electrons ?



Calculated relative shake-off probabilities for the 1s to 4s orbitals as a function of the nuclear charge (Carlson 1968).

These calculations are based on the sudden approximation.

For complex atoms and changes of the effective nuclear charge by 1 unit, the total shake-off probability is close to 30%.

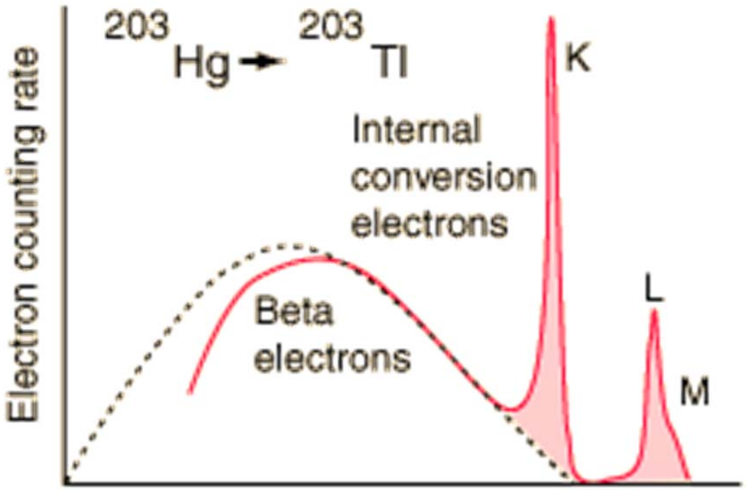
Interne Konversion (Innere Konversion, internal conversion)

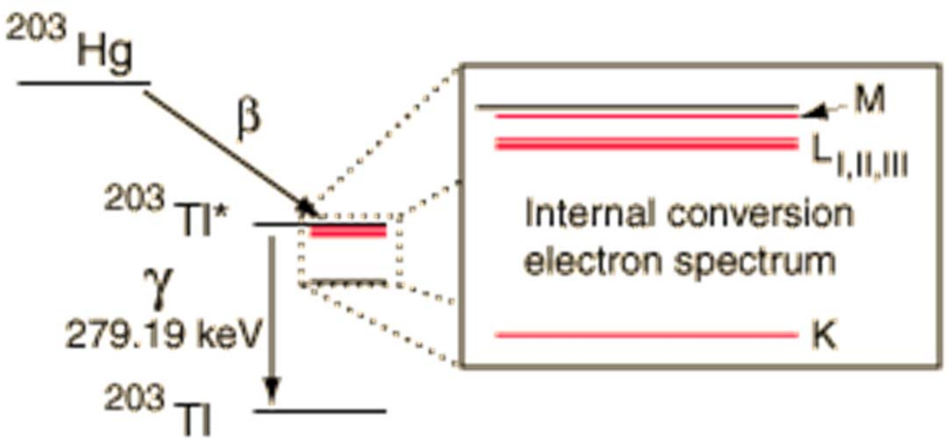
Elektromagnetische Abregung von Kernen

a) Emission eine γ-Quants

b) Emission eines Hüllenelektrons

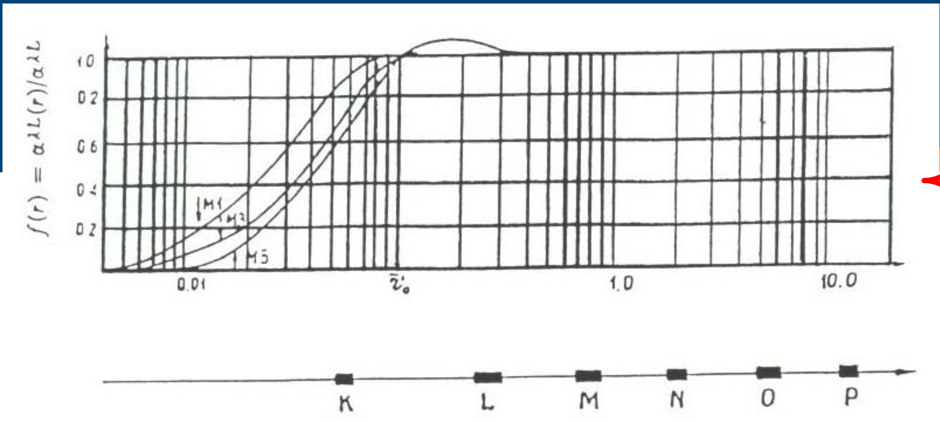
c) Emission eines Elektron-Postritron Paares





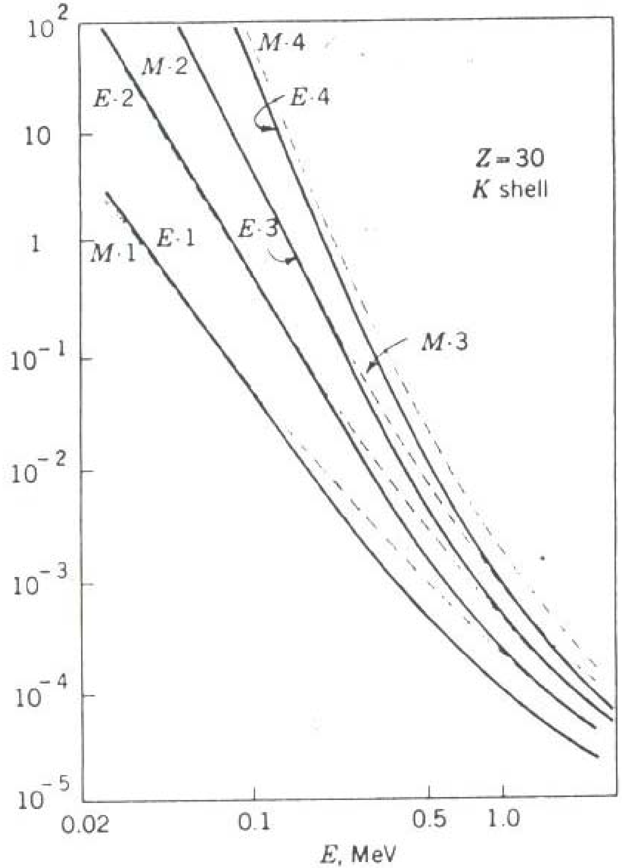
Energie des Konversionselektrons

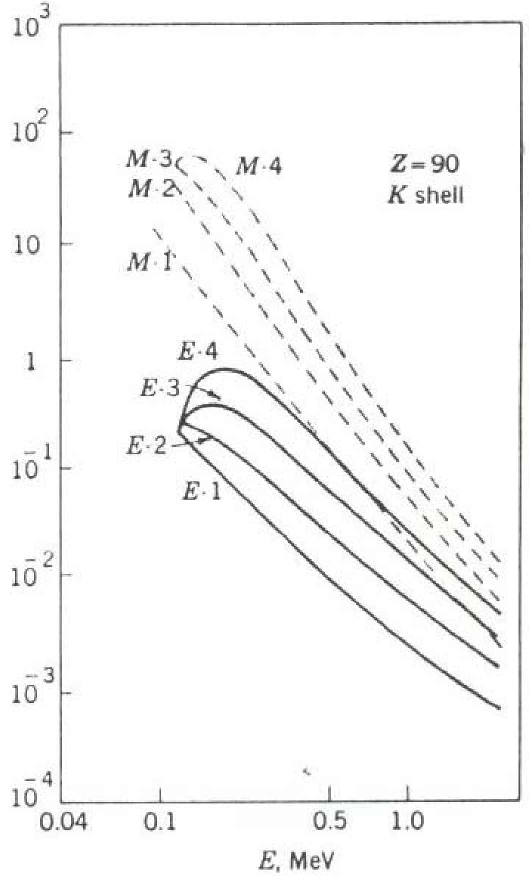
$$E_{Konv} = E_{\gamma} - E_{Bind}$$



Formationsbereich der Internen Konversion aus s-Orbitalen verschiedener magnetischer Übergänge für Z=72 und EKern von 50 keV.
Durch die Funktion f(r) wird der Anteil der Internen Konversion bestimmt, der innerhalb eines Abstandes r vom Kern stattfindet.

Konversionskoeffizient





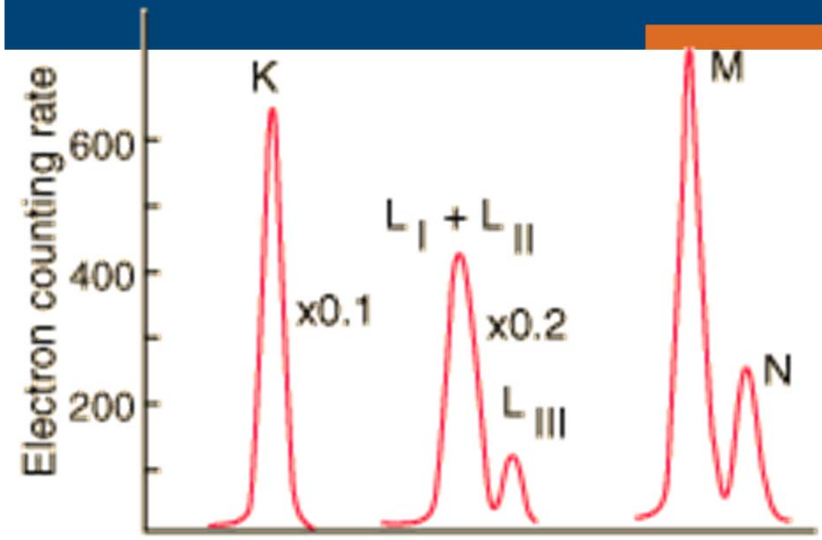
Konversionskoeffizient

$$\alpha_{Konv} = \frac{W_{i \to K}(\text{Konversion})}{W_{i \to K}(\gamma - \text{Emission})}$$

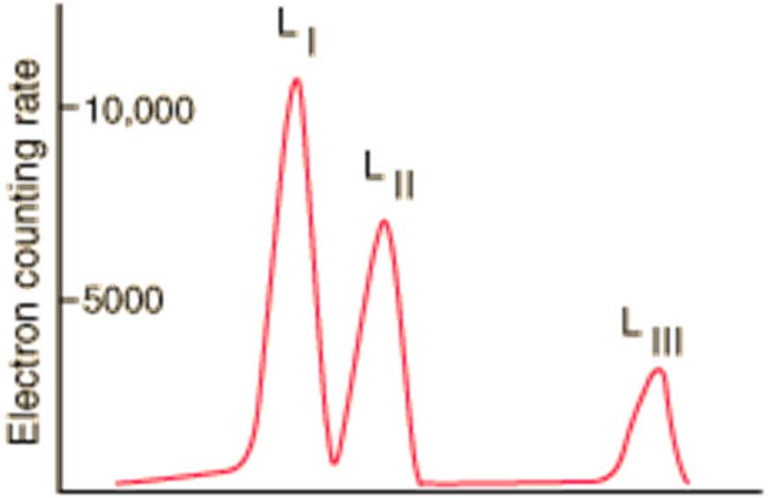
Konversionskoeffizienten α_{Konv} für verschiedene Multipol-Übergänge der Elemente mit Z=30 und Z=90

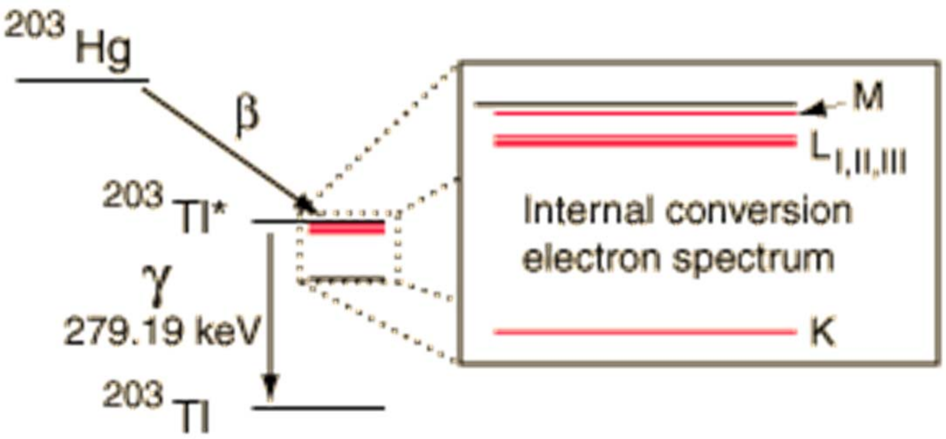
Interne Konversion (Innere Konversion, internal conversion)

Beispiel

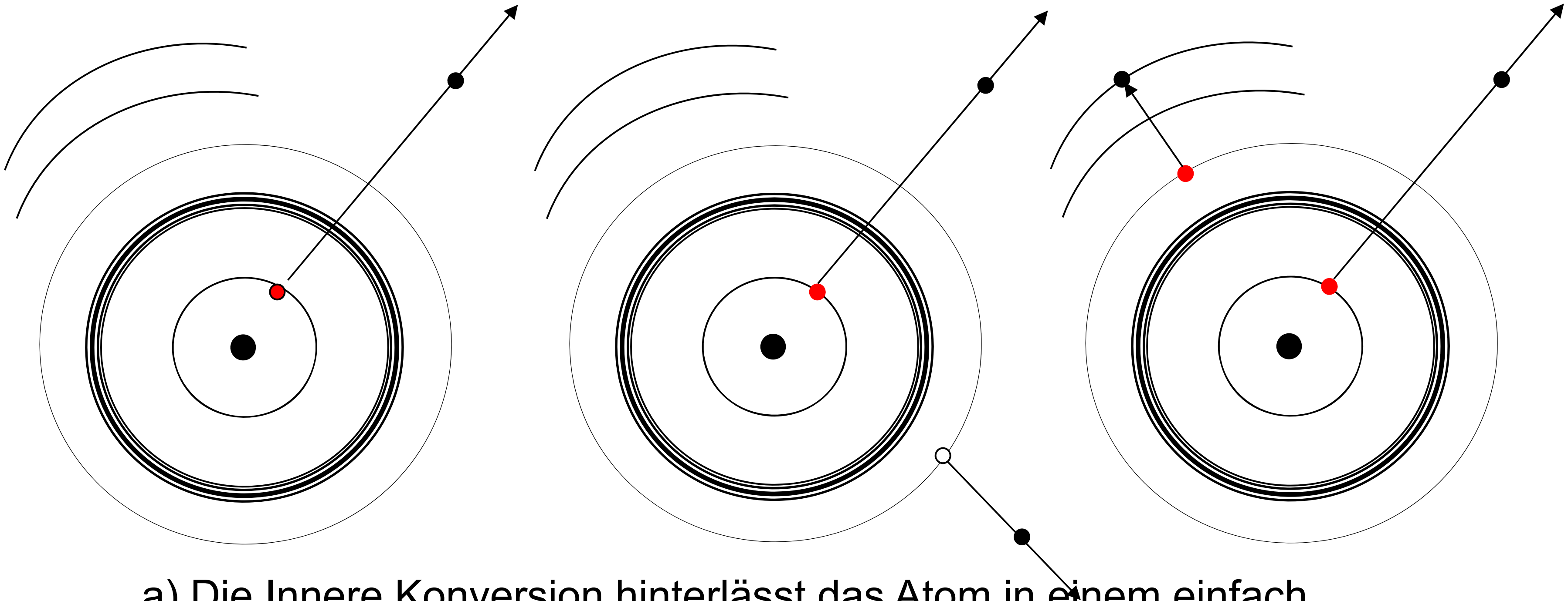


Binding energien für ^{203}Tl	
K	85.529 keV
L_I	15.347 keV
L_{II}	14.698 keV
L_{III}	12.657 keV
M	3.704 keV





Interne Konversion (Innere Konversion, internal conversion)

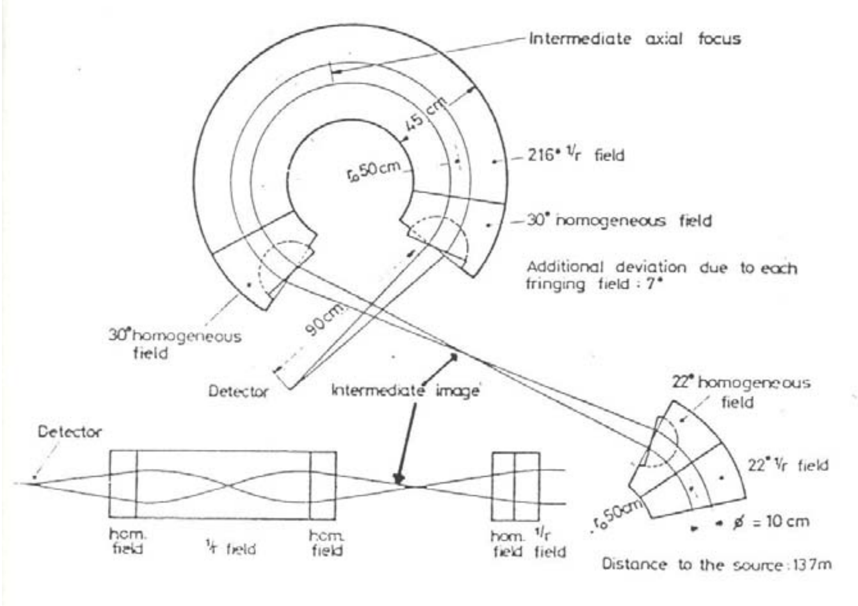


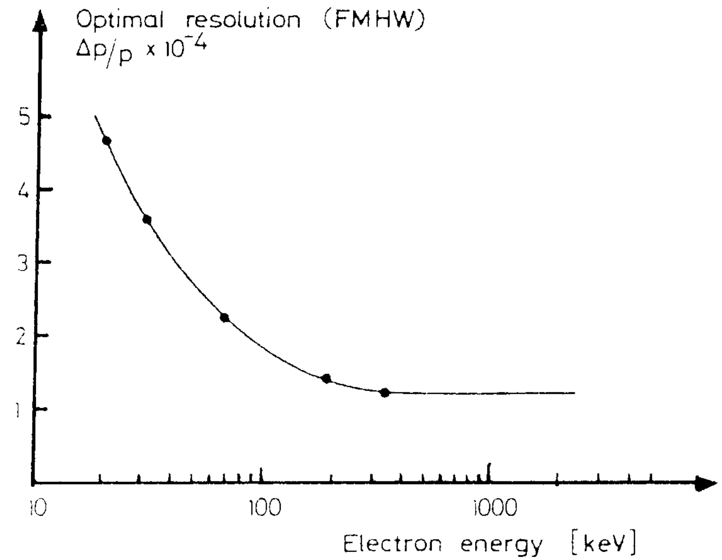
a) Die Innere Konversion hinterlässt das Atom in einem einfach ionisierten Zustand

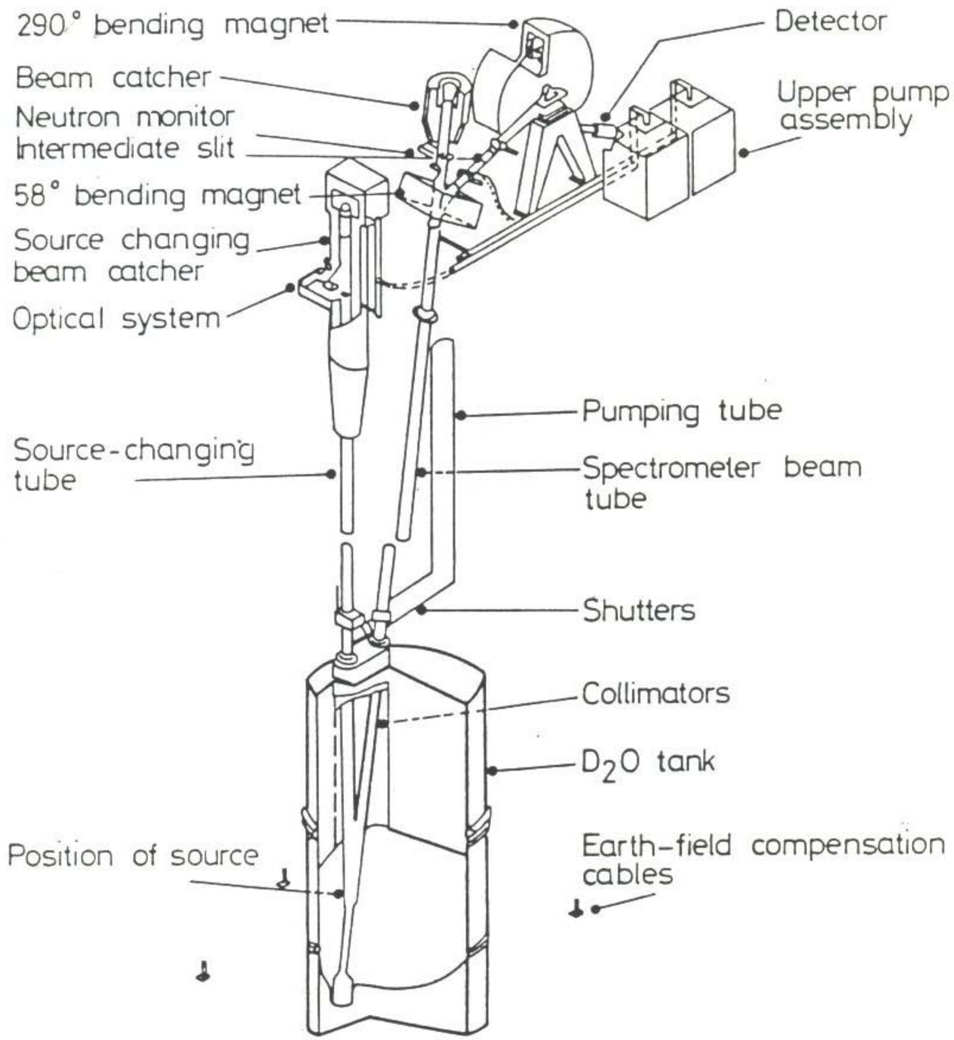
b) *Shakeoff im Prozess der Inneren Konversion*: das Atom wird zweifach ionisiert

c) *Shakeup:* Das Atom wird in einem einfach ionisierten und angeregten Zustand hinterlassen

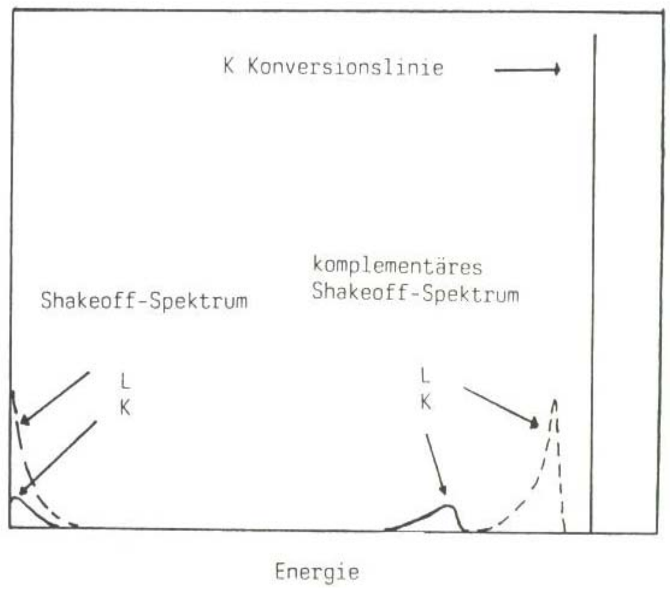
Magnetisches Elektronenspektrometer für hohe Energien (15 keV bis 10 MeV)







Konversionselektronen



Konversionselektronenlinie

Shakeoff bzw. Energieverlust (enfaltetes Spektrum)

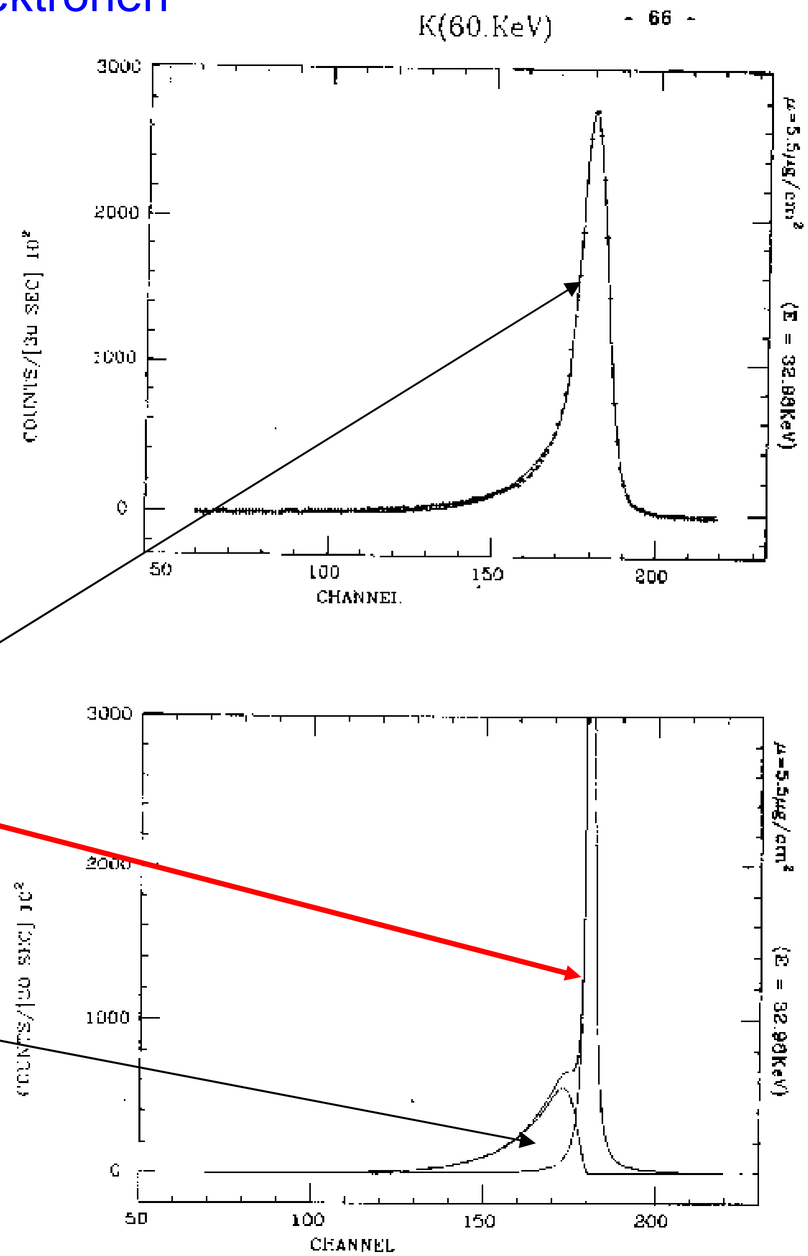


Abb. 6.5 : K(60) von ^{113}In