

Plan of lectures

- 1 15.04.2015 Preliminary Discussion / Introduction
- 2 22.04.2015 Experiments (discovery of the positron, formation of antihydrogen, ...)
- 3 29.04.2015 Experiments (Lamb shift, hyperfine structure, quasimolecules and MO spectra)
- 4 06.05.2015 Theory (from Schrödinger to Dirac equation, solutions with negative energy)
- 5 13.05.2015 Theory (bound-state solutions of Dirac equation, quantum numbers)
- 6 20.05.2015 Theory (bound-state Dirac wavefunctions, QED corrections)
- 7 27.05.2015 Experiment (photoionization, radiative recombination, ATI, HHG...)
- 8 03.06.2015 Theory (description of the light-matter interaction)
- 9 10.06.2015 Experiment (Kamiokande, cancer therapy,)
- 10 17.06.2015 Theory (interaction of charged particles with matter)
- 11 24.06.2015 Experiment (Auger decay, dielectronic recombination, double ionization)
- 12 01.06.2015 Theory (interelectronic interactions, extension of Dirac (and Schrödinger) theory for the description of many-electron systems, approximate methods)
- 13 08.07.2015 Experiment (Atomic physics PNC experiments (Cs,...), heavy ion PV research)

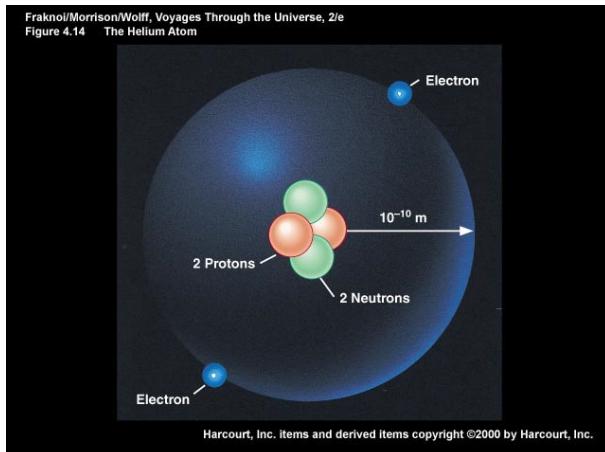
The helium atom and

many-electron-systems

Auger decay, dielectronic recombination,
double ionization

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

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

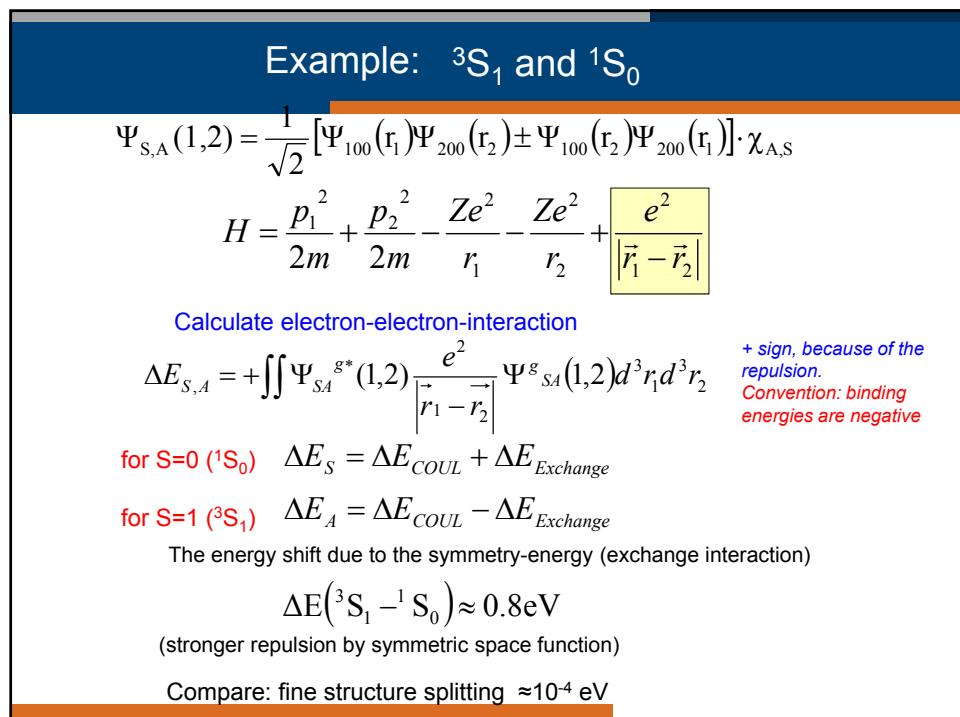
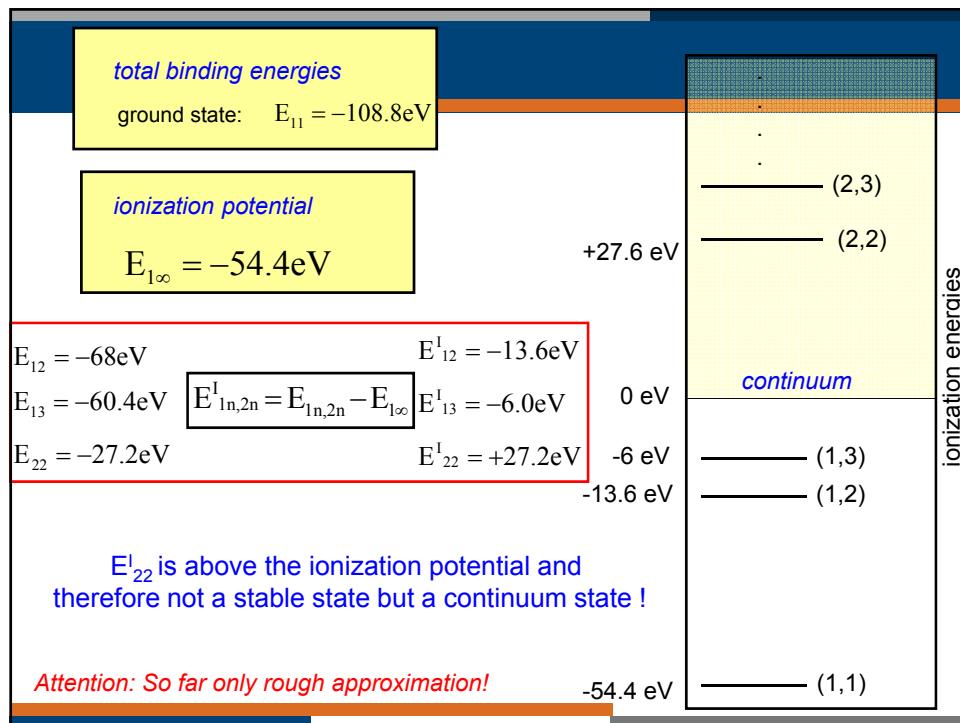
and we get

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

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

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

*total binding-energies
(without Coulomb repulsion)*



States in He-atoms: a current problem of physics

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).

| N | E_{nr} (in a.u.) |
|-------------------------|---------------------------------|
| 4200 | -2.9037243770341195983111540 |
| 4600 | -2.9037243770341195983111572 |
| 5200 | -2.9037243770341195983111587 |
| extrop | -2.9037243770341195983111594(4) |
| Sims and Hagstrom [1] | -2.9037243770341195982999 |
| Drake <i>et al.</i> [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]:

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

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

| N | β |
|----------------------------|----------------|
| 1200 | 4.3701692290 |
| 1600 | 4.3701692323 |
| 4000 | 4.3701692322 |
| Drake, Goldman [4] | 4.370169218(3) |
| J. Baker <i>et al.</i> [5] | 4.370159(2) |
| C. Schwartz [6], (1961) | 4.370(4) |

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

$$E_{11} = -79.0034 \text{ eV}$$

ionization potential

$$24.5874 \text{ eV}$$

contribution of the electron-electron interaction

$$\Delta E = +29.8 \text{ eV}$$

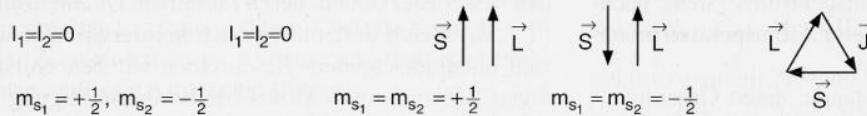
References

- [1] J.S. Sims and S.A. Hagstrom, Int. J. Quantum Chem., to be published.
- [2] G.W.F. Drake, M.M. Casper, 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. Farley, M. Jozwiak, and J.D. Morgan III, unpublished.
- [6] C. Schwartz, Phys. Rev. 123 1700 (1961).

LS-coupling (light atoms)

The spins couple independently of the orbital angular momentum

$$\left. \begin{aligned} \vec{S} &= \vec{s}_1 + \vec{s}_2; \vec{S} = \sum_i \vec{s}_i \\ \vec{L} &= \vec{\ell}_1 + \vec{\ell}_2; \vec{L} = \sum_i \vec{\ell}_i \end{aligned} \right\} \quad \vec{J} = \vec{L} + \vec{S}$$



| | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 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 $S(L=0), P(L=1), \dots$

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

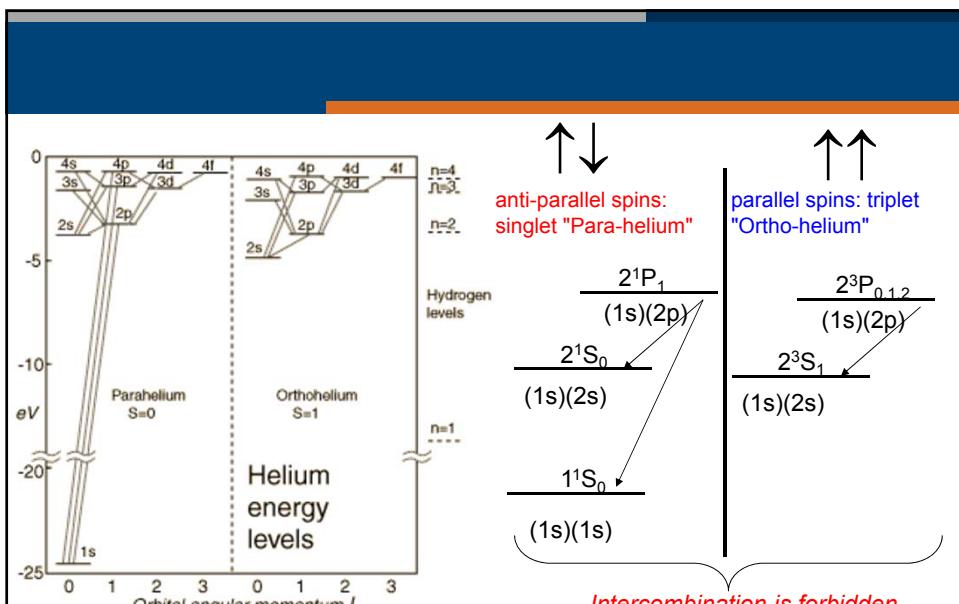
2 gives the principle quantum number (1s)(2p)

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)

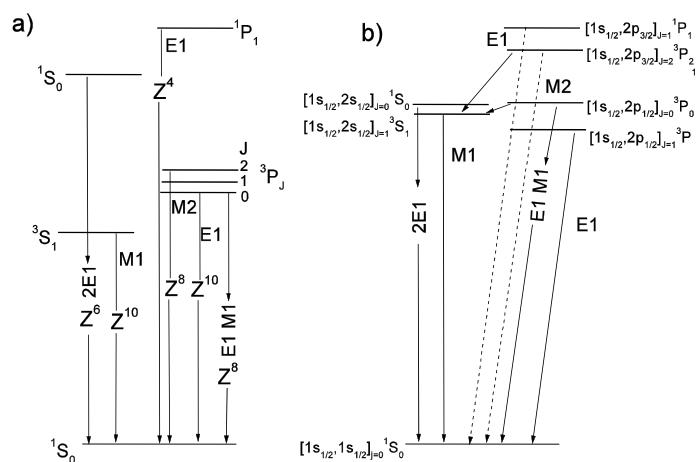
$$\vec{J}_1 = \vec{\ell}_1 + \vec{s}_1 \quad \vec{J} = \vec{j}_1 + \vec{j}_2 \quad \vec{J} = \sum_i \vec{j}_i$$

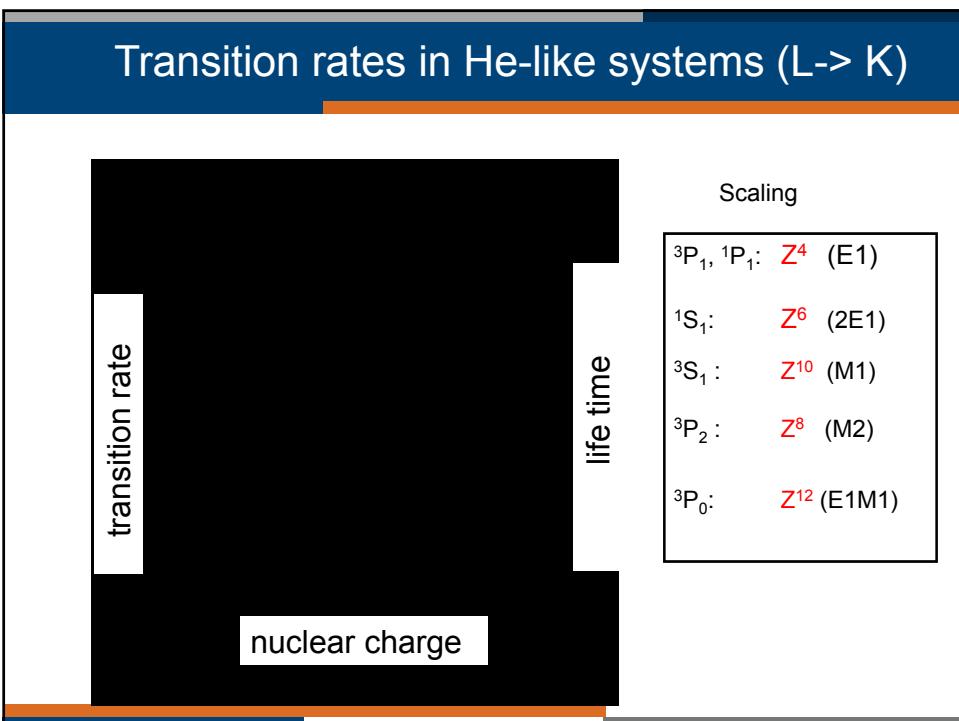
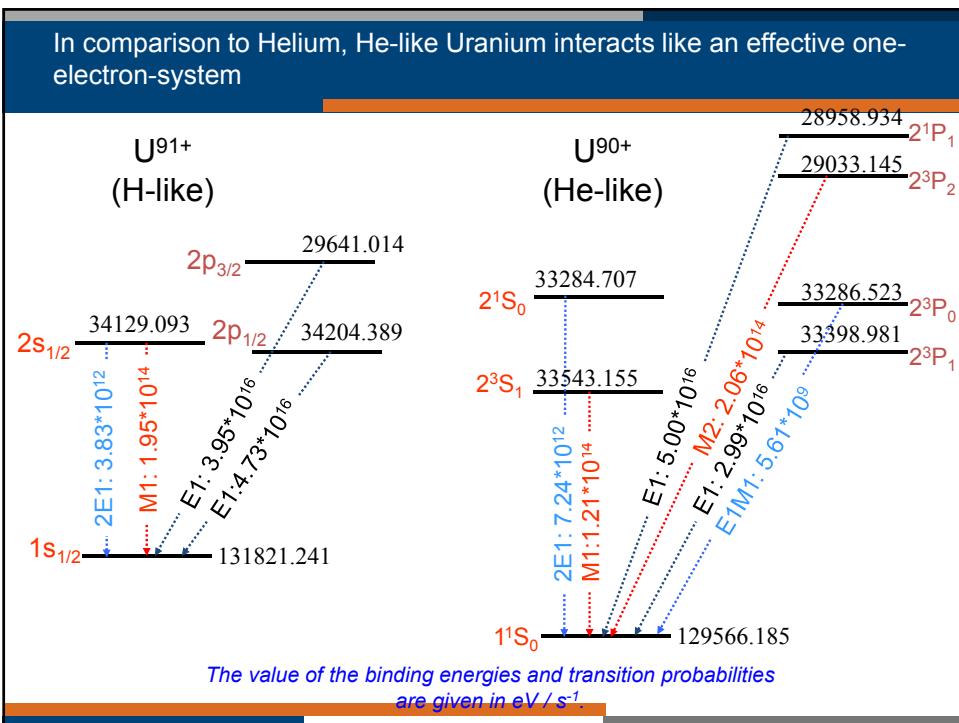
In heavy atoms the jj-coupling dominants. Here the spin-orbit-interaction (fine structure) is much stronger than the exchange interaction. The electrons behave like in an effective one-electron-system.

Example: Uran L-shell

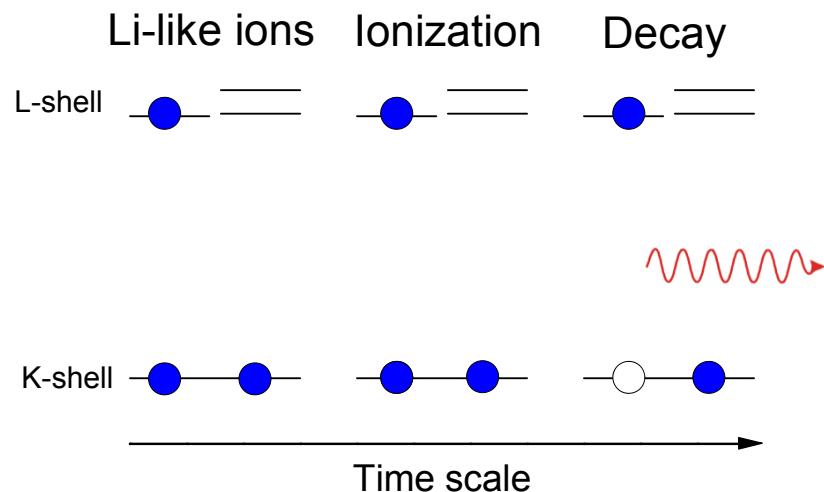
Spin-orbit-coupling: $\approx 4.5 \text{ keV}$
Exchange interaction: $\approx 100 \text{ eV}$

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



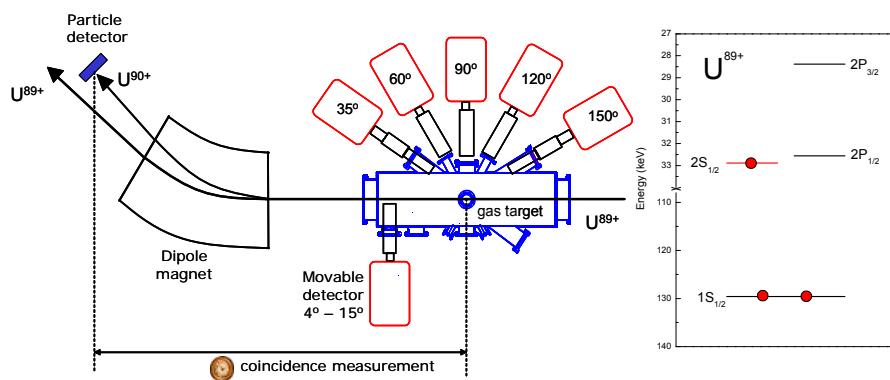


Structure investigation with U^{90+}



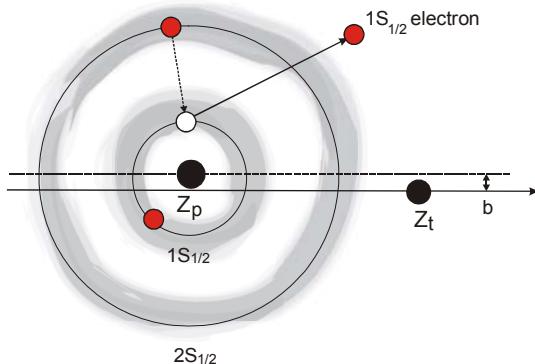
Experiment

- Li-like Uranium (U^{89+}) with a velocity of about $\beta \approx 0.6$.
- The produced x-ray radiation (in collisions with N_2) is measured in coincidence with ions, which have lost an electron during the collision.



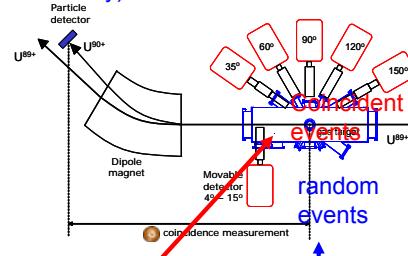
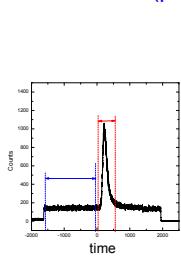
Selective K-shell Ionization

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

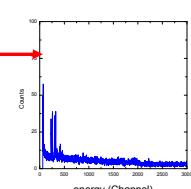


Coincidence technique

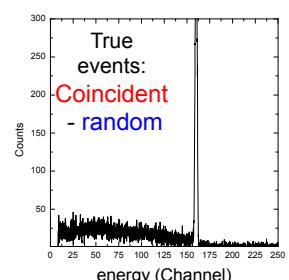
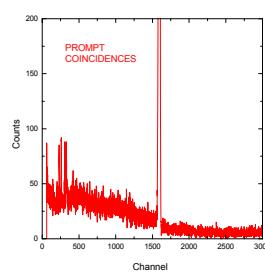
Time: Δt (particle – x-ray)



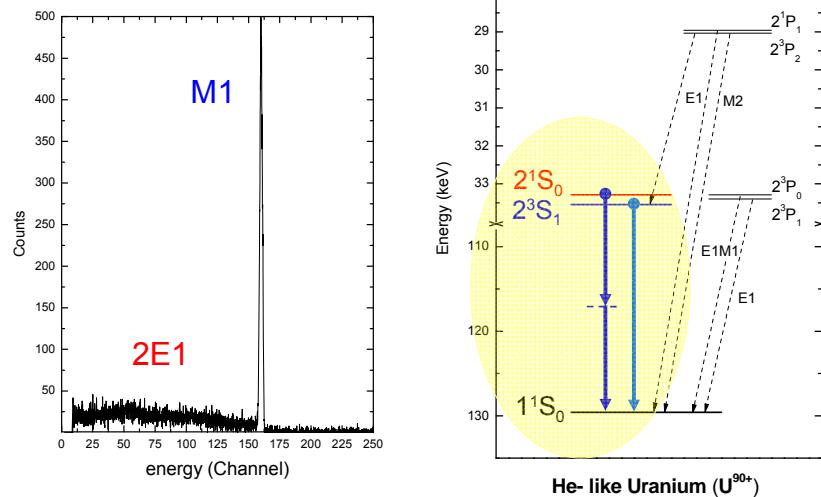
Time-spectrum
 Δt (particle – x-ray)



Time

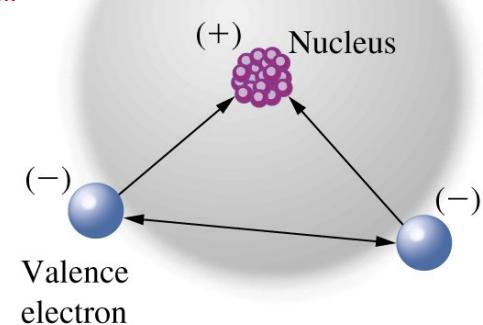


Coincident x-ray-spectra



Many-electron systems

→ Use effective nuclear charge Z_{eff}



The effective nuclear charge

$$Z_{\text{eff}} = Z - S$$

Z: nuclear charge

Z_{eff} : effective or shielded nuclear charge

S: shielding constant



Binding energies

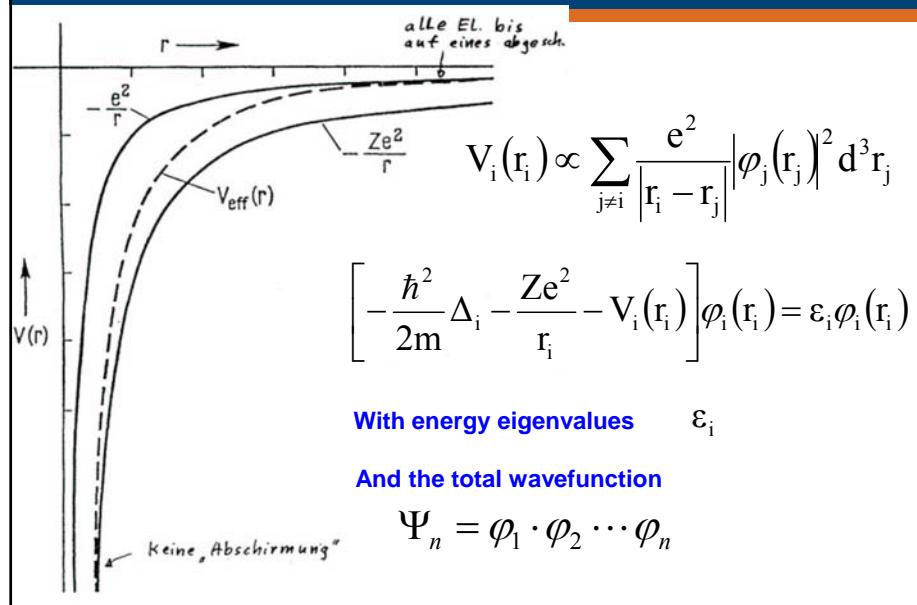
$$E_B = Ry \cdot \frac{Z_{\text{eff}}^2}{n^2} \quad \xrightarrow{\text{Compare}} \quad E_B = Ry \cdot \frac{Z^2}{n^2}$$

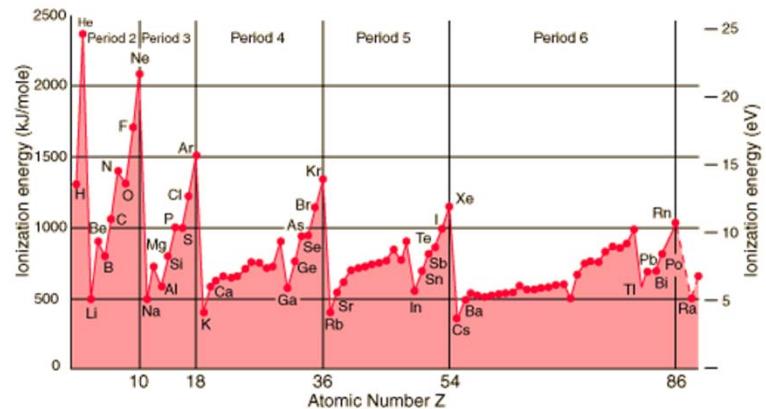
Orbit radius

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

$$(a_0 = 0.53 \cdot 10^{-8} \text{ cm})$$

The many-electron potential



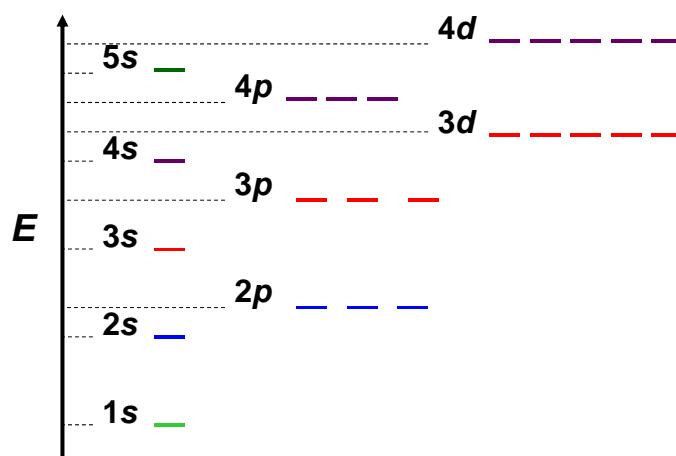


Ionization potential:

At least this energy has to be deposited to remove an electron.

$$E_I = Ry \cdot \frac{Z_{\text{eff}}^2}{n^2}$$

Energy levels in a many-electron system

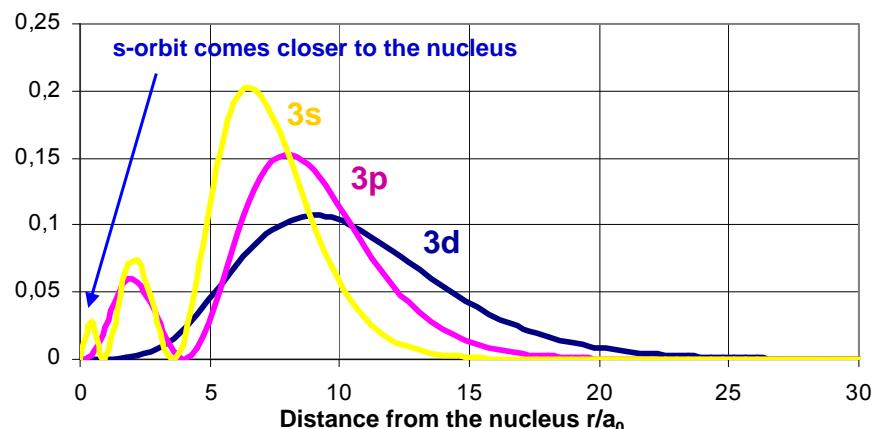


The many-electron wavefunctions

The order of the energy levels changes

$$Z_{\text{eff}}(\text{s}) > Z_{\text{eff}}(\text{p}) > Z_{\text{eff}}(\text{d}) \quad E_B = Ry \cdot \frac{Z_{\text{eff}}^2}{n^2}$$

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.

18

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

Potassium Z=19 for [3d¹] follows: $s=18 \Rightarrow Z_{\text{eff}}=1$

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

10 8×0.85

for [4s] follows: $S=10+6.8 = 16.8 \Rightarrow Z_{\text{eff}}=2.2$

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

Sodium Z=11 2 8×0.85

for [3s] follows: $S=2+6.8 = 8.8 \Rightarrow Z_{\text{eff}}=2.2$

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 \rightarrow Auger electrons

pure electron-electron interaction

$$\Gamma_A \propto \left| \left\langle \Psi_1^i \cdot \Psi_2^i \left| \frac{1}{|r_1 - r_2|} \right| \Psi_1^f \cdot \Psi_2^f \right\rangle \right|^2$$

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.

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

$$\Gamma_A \propto \left| \left\langle \Psi_1^{i_1} \cdot \Psi_2^{i_2} \left| \frac{1}{|r_1 - r_2|} \right| \Psi_1^{f_1} \cdot \Psi_2^{f_2} \right\rangle \right|^2$$

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

$\Psi_1^{i_1}$: initial bound state of electron 1 $\propto Z^{3/2}$

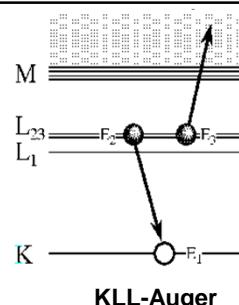
$\Psi_2^{i_2}$: initial bound state of electron 2 $\propto Z^{3/2}$

$\Psi_1^{f_1}$: final bound state of electron 1 $\propto Z^{3/2}$

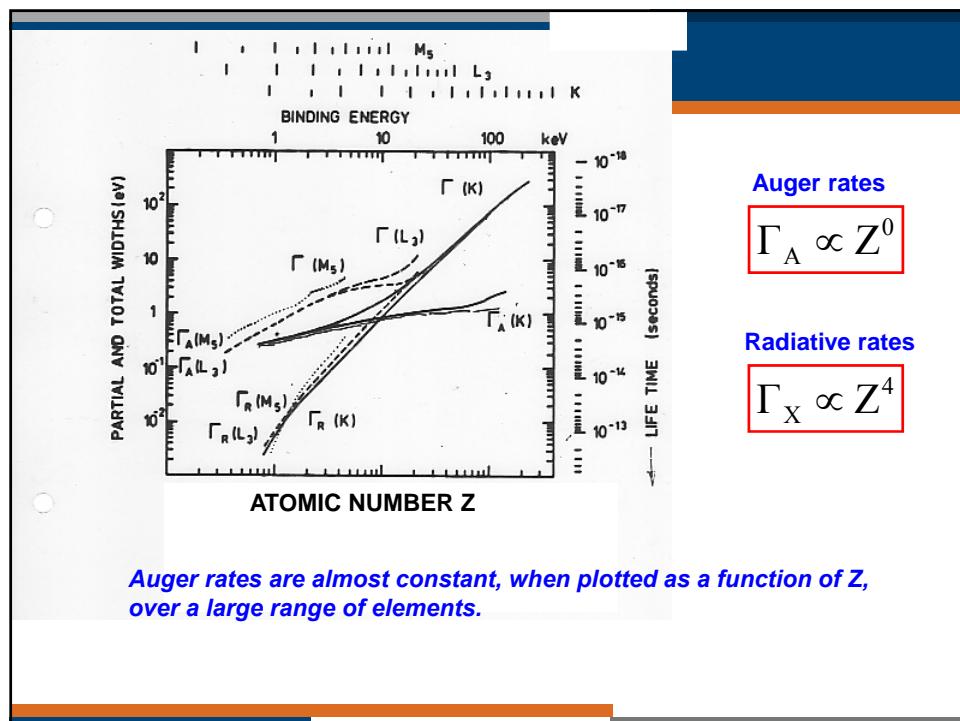
$\Psi_1^{f_1}$: final free state of electron 1 $\propto Z^{1/2}$

$$\frac{1}{r} \propto Z; \quad d^3 r_i \propto \frac{1}{Z^3};$$

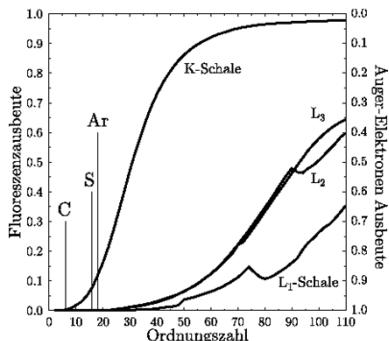
$$d^3 r_2 \propto \frac{1}{Z^3};$$



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



Fluorescence yield



Fluorescence yield

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

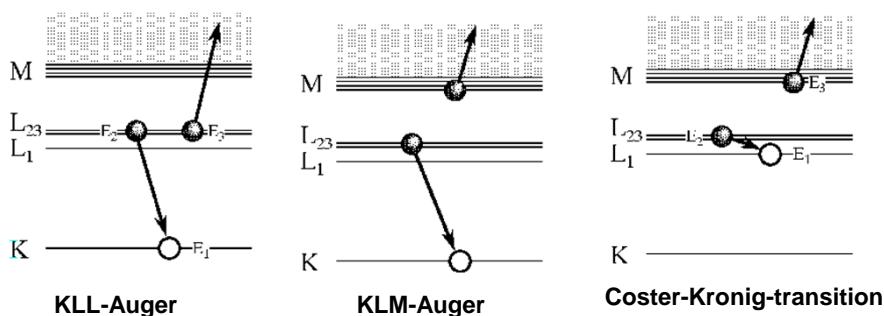
$$\omega \propto \frac{Z^4}{Z^4 + Z^0} \rightarrow 1 \text{ for } Z > 50$$

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



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.

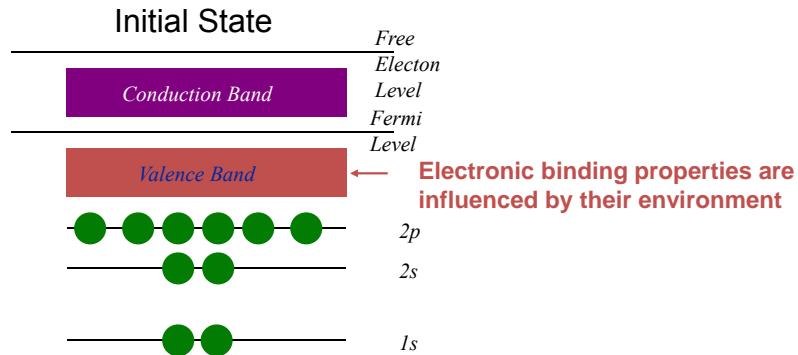
hole
Auger electron
decaying electron

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

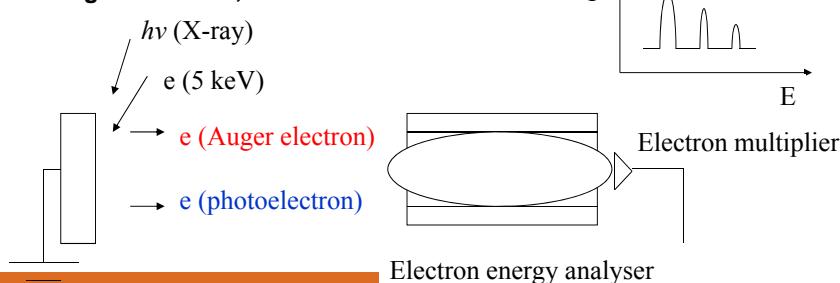
-how to identify elements and binding properties
e.g. of atoms in their environment =



Analysis of materials, chemical 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 |

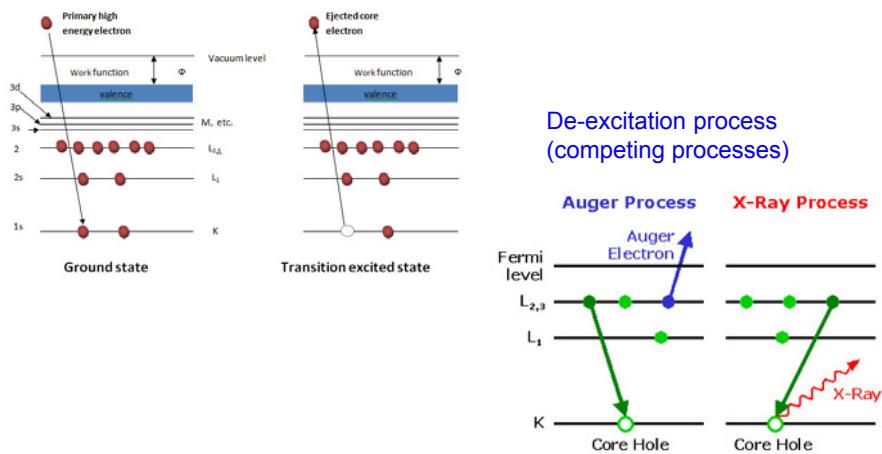
chematic diagram for XPS, AES



- 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



Binding energies (BE)

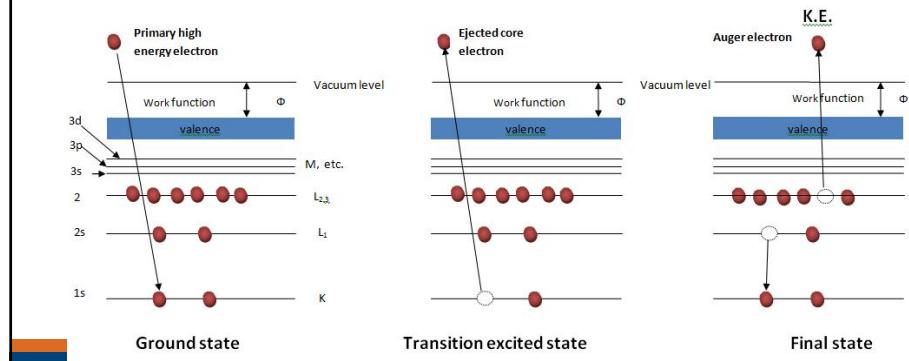
$$BE = h\nu - KE - \Phi_{\text{spec}} - E_{\text{ch}}$$

BE= Electron-binding energy

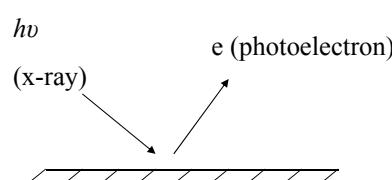
KE= Kinetik electron energy

Φ_{spec} = Spectrometer Work Function

E_{ch} = Surface energy (Ablösearbeit)

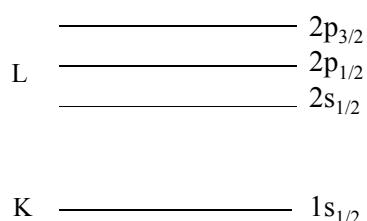


XPS (X-ray photoelectron spectroscopy) oder ESCA (electron spectroscopy for chemical analysis)



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

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

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

$$E_{K_{L_1}L_{III}} = E_K - E_{L_1} - E_{L_{III}}$$

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

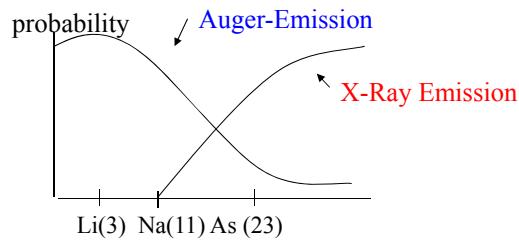
$$E_{K\alpha_1} = E_K - E_{L_{III}}$$

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

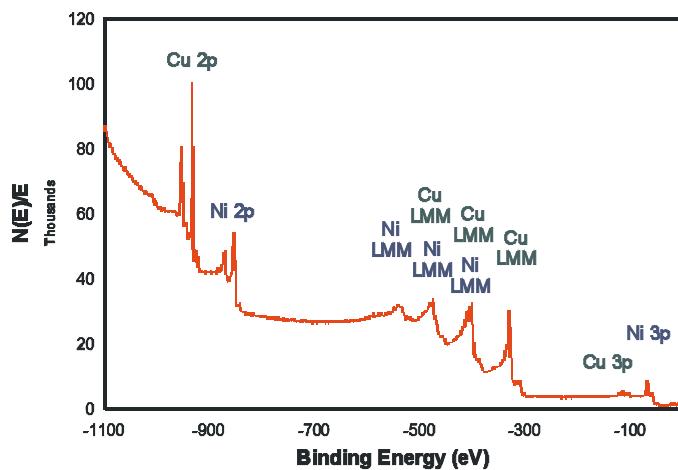
$K_\alpha : L \rightarrow K$

$K_\beta : M \rightarrow K$

Effective probe thickness $\sim 1 \mu\text{m}$, sensitivity $\sim 0.1\%$



Element identification



Element identification

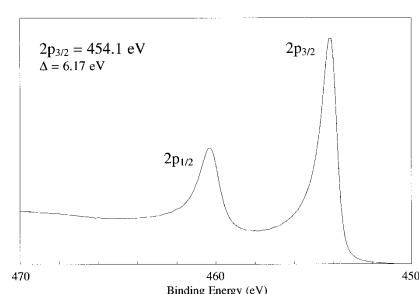
| Binding Energy (eV) | | | |
|---------------------|-------------------|----|-----|
| Element | 2p _{3/2} | 3p | Δ |
| Fe | 707 | 53 | 654 |
| Co | 778 | 60 | 718 |
| Ni | 853 | 67 | 786 |
| Cu | 933 | 75 | 858 |
| Zn | 1022 | 89 | 933 |

Electron-nucleus interaction is used for the element analysis

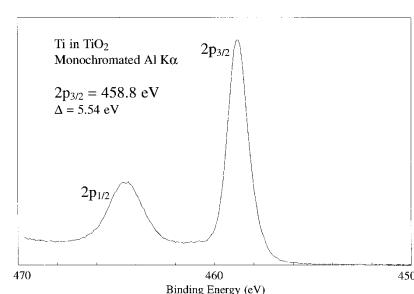
Chemical properties

Spin-Orbit Coupling

Ti Metal

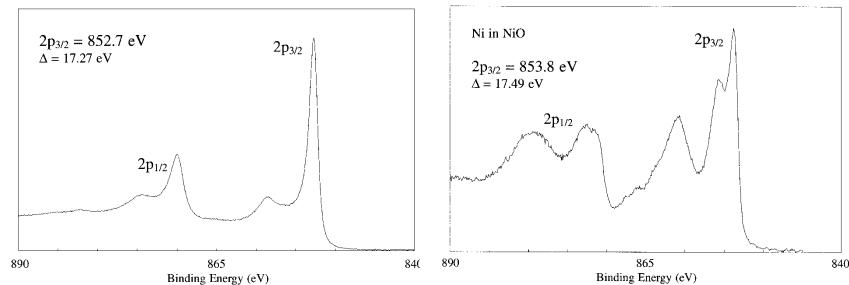


Ti Oxide



Shakeoff/Shakeup

Ni Metal



Ni Oxide

Final State Effects Shake-up/ Shake-off

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

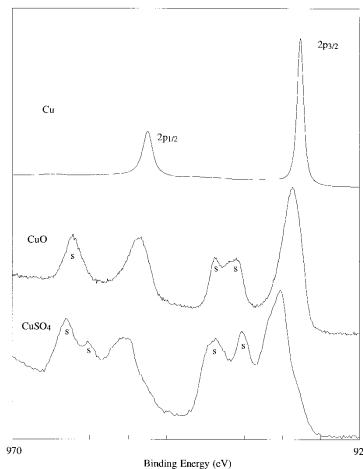
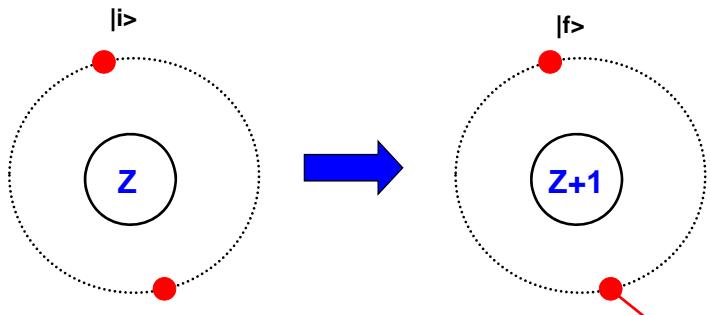


Figure 8. Examples of shake-up lines (s) of the copper 2p observed in copper compounds.

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:

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

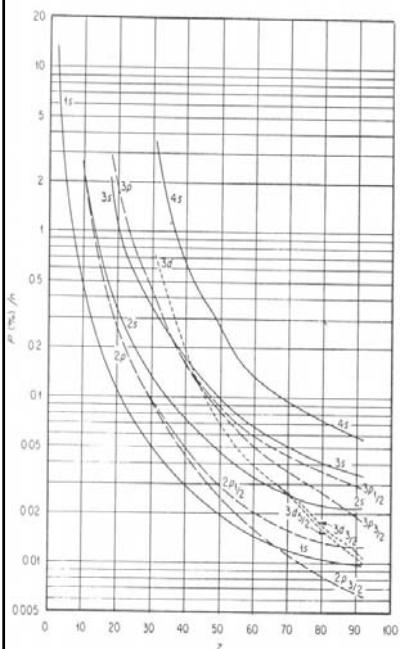
This probability is given by the overlap between the wavefunctions of the initial state $\Psi(Z)$ and the final state. $\Psi(Z+1)$

The probability that an electron is being ionized is:

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

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).

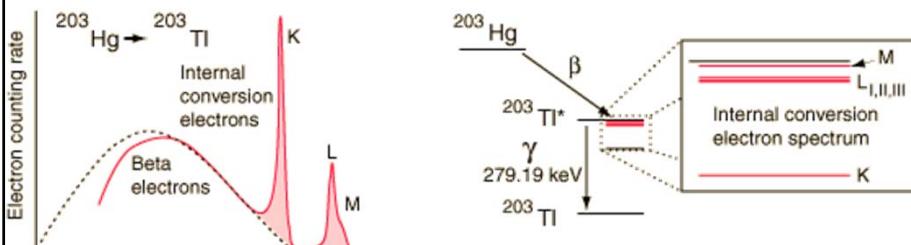
These calculations are based on the sudden approximation.

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)

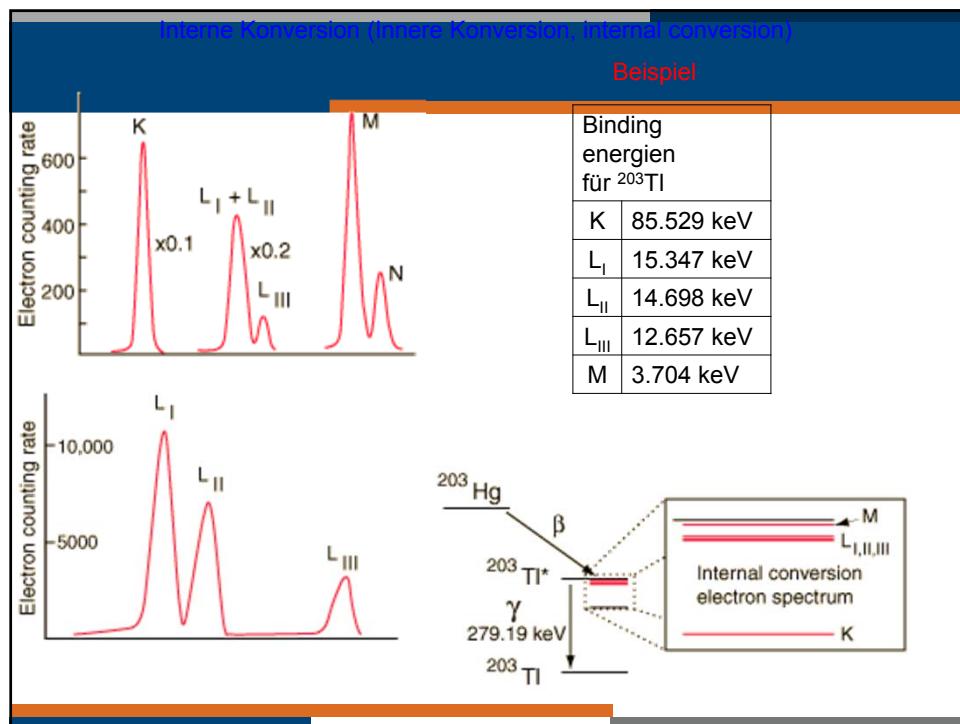
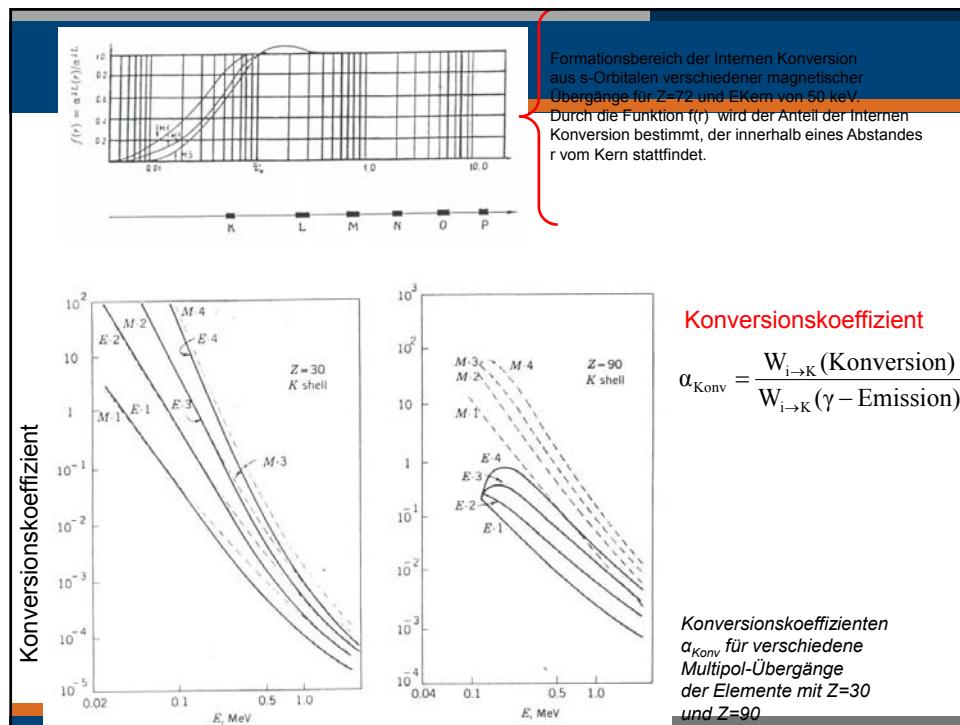
Elektromagnetische Abregung von Kernen

- a) Emission eines γ -Quants
- b) Emission eines H̄llenelektrons
- c) Emission eines Elektron-Postriton Paars

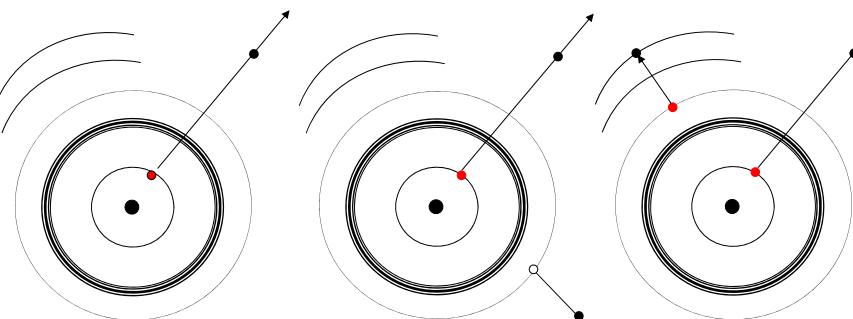


Energie des Konversionselektrons

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

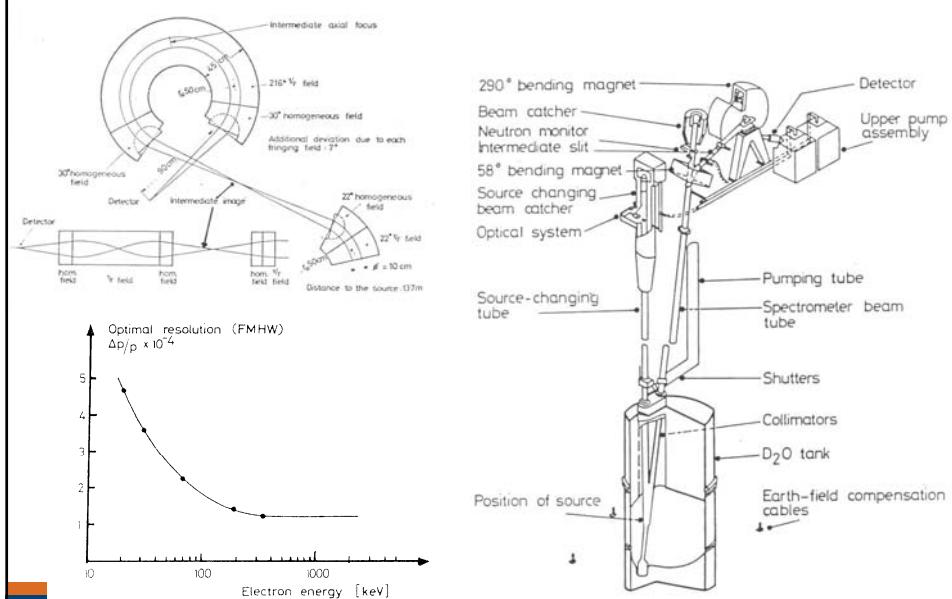


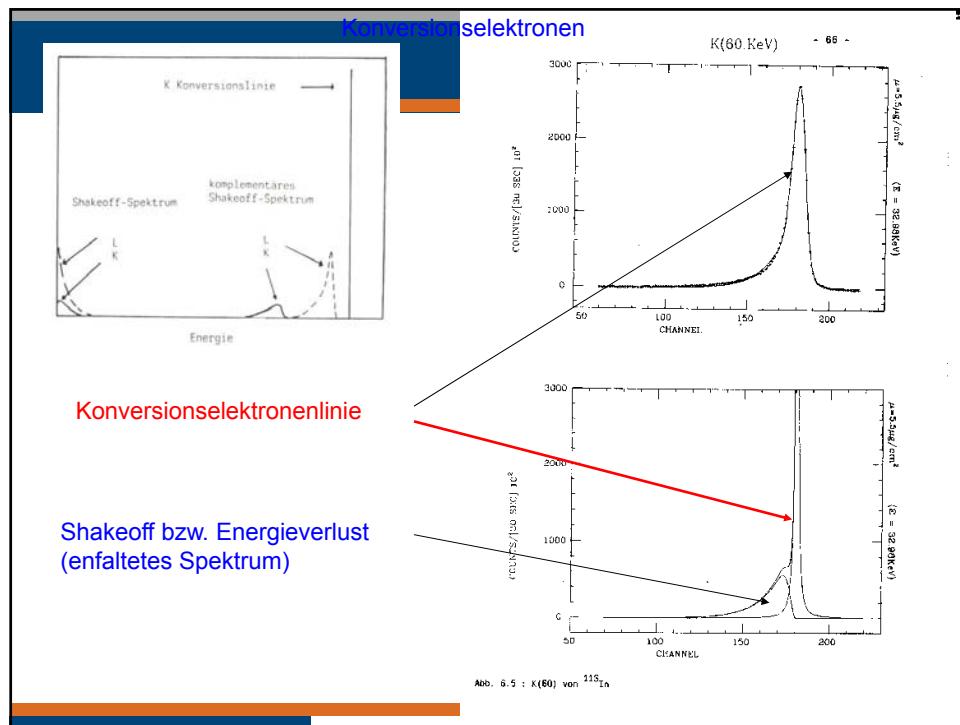
Interne Konversion (Innere Konversion, internal conversion)



- 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)

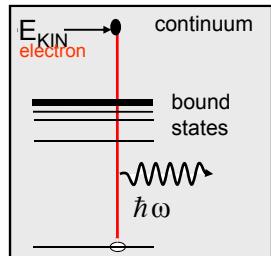




- Dielectronic Recombination

Electron Pickup Processes of HCl in Collisions with Electrons (Dynamic Processes)

Radiative Recombination/Electron Capture



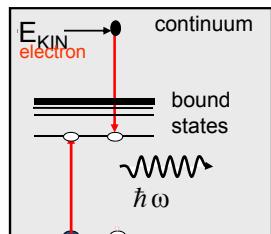
- Electron capture into a bound ionic state by emission of a photon

$$\hbar\omega = E_B + E_{KIN}$$

- Time-reversed photionization

- Only possible capture/recombination process for bare ions colliding with electrons

Dielectronic Recombination/Electron Capture



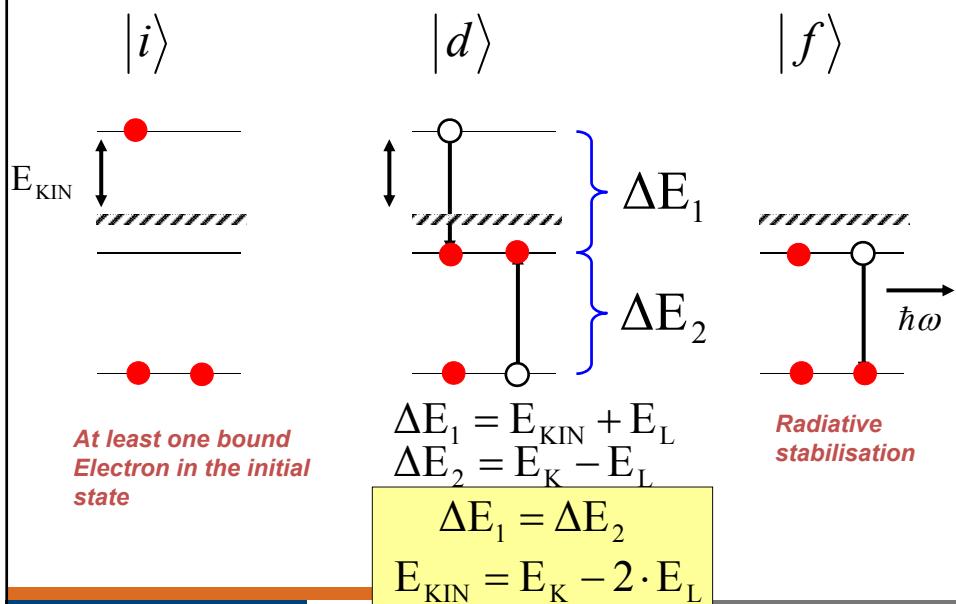
- Resonant (non-radiative) capture of an electron into a bound state

- Time-reversed Auger process

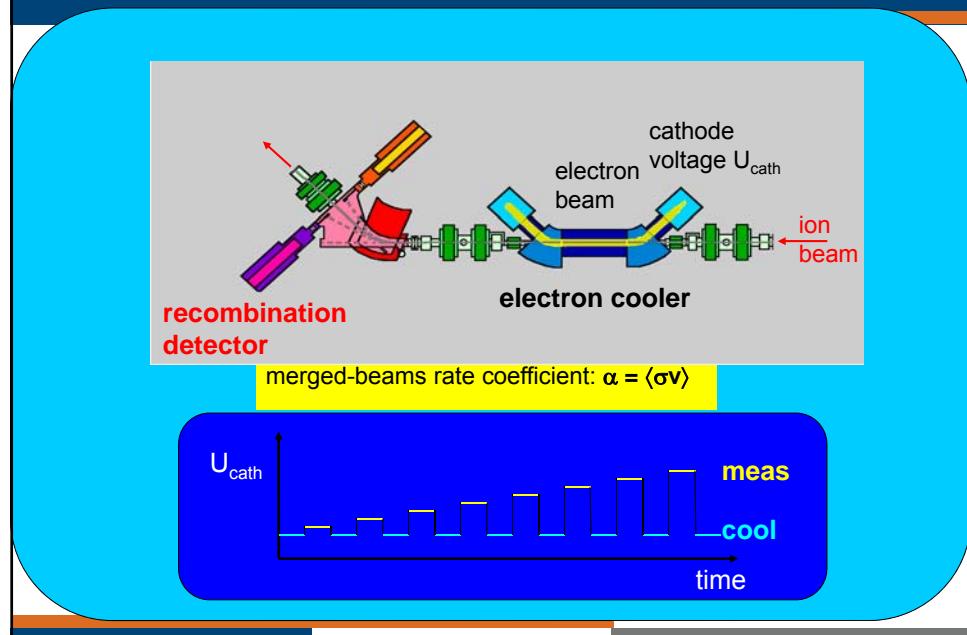
- Important charge exchange process for multi-electron ions

Dielectronic Recombination

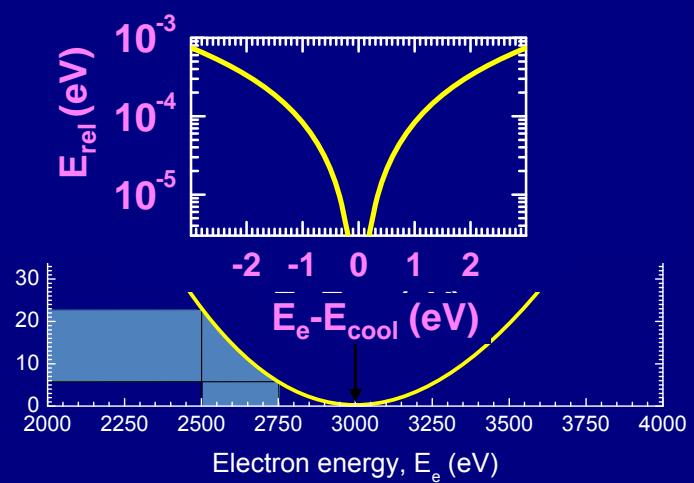
Resonance process => time reversed Auger effect



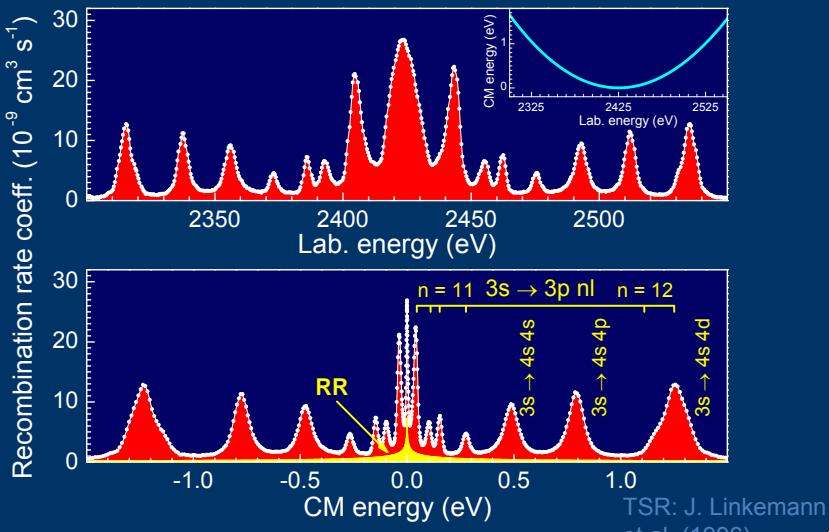
Dielectronic recombination: the technique



Merged-Beams Kinematics (access to low relative energies)



Recombination of Na-like Se^{23+}



Experimental Energy Spread

vs. Time (DR of Li-like C^{3+})

