Radiation & Autoionization Processes

Atomic Theory and Computations

— Lecture script —

IAEA-ICTP School, Trieste, February 2017

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Monday 27$^{\text{th}}$ February, 2017

1. Atomic theory and computations in a nut-shell

1.1. Atomic spectroscopy: Structure & collisions

Atomic processes & interactions:

- Spontaneous emission/fluorescence: ... occurs without an ambient electromagnetic field; related also to absorption.
- Stimulated emission: ... leads to photons with basically the same phase, frequency, polarization, and direction of propagation as the incident photons.
- Photoionization: ... release of free electrons.
- Rayleigh and Compton scattering: ... Elastic and inelastic scattering of X-rays and gamma rays by atoms and molecules.
- Thomson scattering: ... elastic scattering of electromagnetic radiation by a free charged particle (electrons, muons, ions); low-energy limit of Compton scattering.
- Multi-photon excitation, ionization and decay: ... non-linear electron-photon interaction.
- Autoionization: ... nonradiative electron emission from (inner-shell) excited atoms.
- Electron-impact excitation & ionization: ... excited and ionized atoms; occurs frequently in astro-physical and laboratory plasmas.

- ➢ Elastic & inelastic electron scattering: ... reveals electronic structure of atoms and ions; important for plasma physics.
- ➢ Pair production: ... creation of particles and antiparticles from the internal of light with matter (electron-positron pairs).
- ➢ Delbrück scattering: ... deflection of high-energy photons in the Coulomb field of atomic nuclei; a consequence of vacuum polarization.
- ➢ ...
- ➢ In practice, the distinction and discussion of different atomic and electron-photon interaction processes also depends on the particular community/spectroscopy.

1.2. Atomic theory

Covers a very wide range of many-body methods and techniques, from the simple shell model of the atom to various semi-empirical method to mean-field approaches ... and up to advanced ab-initio and quantum-field theories. The aim of ab-initio atomic structure and collision theory is to describe the (electronic) level structure, properties and dynamical behaviour on the basis of the (many-electron) Schrödinger equation or by even applying field-theoretical techniques.

Well, ... this is quite an ambitious task, and with a lot of surprises when it comes to details.

Atomic theory is a great playground, indeed.

Requires good physical intuition, or this is typically benefitial, at least.

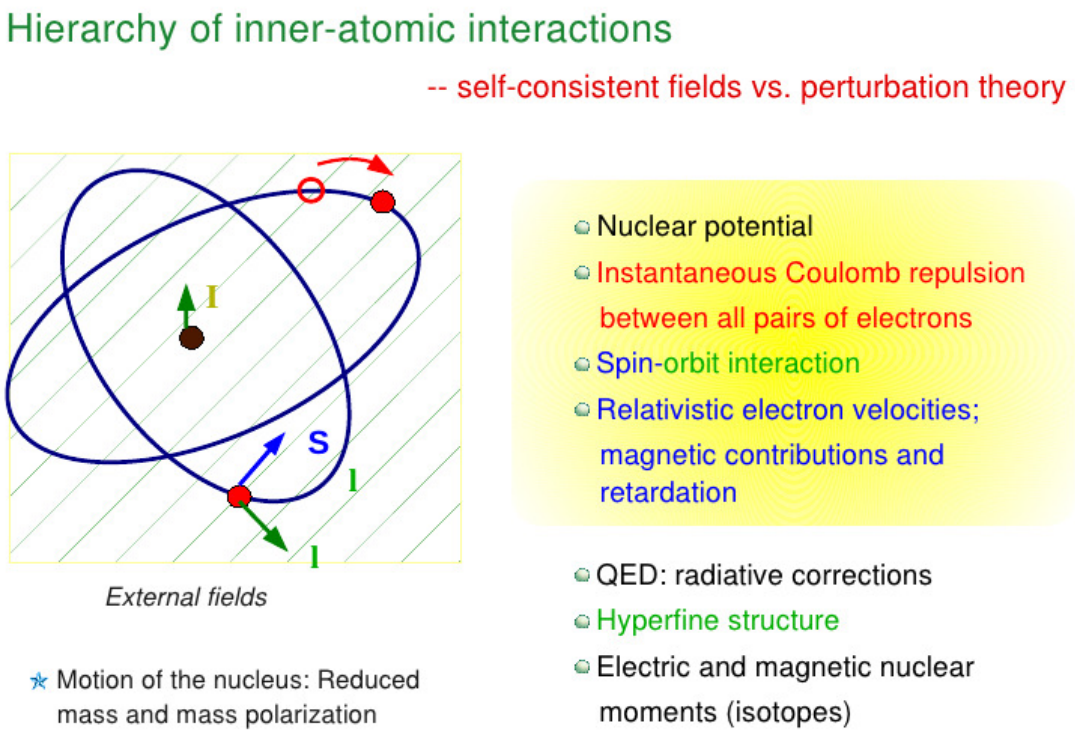

Figure 1.1.: Atomic interactions that need to be considered for a quantitative description/prediction of atoms.

Theoretical models:

- ➢ Electronic structure of atoms and ions: is described quantum mechanically in terms of wave functions, energy levels, ground-state densities, etc., and is usually based on some atomic (many-electron) Hamiltonian.
- ➢ Interaction of atoms with the radiation field: While the matter is treated quantum-mechanically, the radiation is — more often than not (> 99 % of all case studies) — described as a classical field.

Figure 1.2.: Characteristic time scales of atomic and molecular motions; taken from: *Controlling the Quantum World*, page 99.

➢ This semi-classical treatment is suitable for a very large class of problems, sometimes by incorporating 'ad-hoc' quantum effects of the em field (for instance, spontaneous emission).

➢ Full quantum treatment: of the radiation field is very rare in atomic and plasma physics and requires to use quantum-field theoretical techniques; for example, atomic quantum electrodynamics (QED).

1.3. Need of (accurate) atomic theory and data

➢ Astro physics: Analysis and interpretation of optical and x-ray spectra.

➢ Plasma physics: Diagnostics and dynamics of plasma; astro-physical, fusion or laboratory plasma.

➢ EUV lithography: Development of UV/EUV light sources and lithograhpic techniques (13.5 nm).

➢ Atomic clocks: Design of new frequency standards; requires accurate data on hyperfine structures, atomic polarizibilities, light shift, blackbody radiation, etc.

➢ Search for super-heavy elements: beyond fermium (Z = 104); 'island of stability'; better understanding of nuclear structures and stabilities.

➢ Nuclear physics: Accurate hyperfine structures and isotope shifts to determine nuclear parameters; formation of the medium and heavy elements.

➢ Surface & environmental physics: Attenuation, autoionization and light scattering.

➢ X-ray science: Ion recombination and photon emission; multi-photon processes; development of x-ray lasers; high-harmonic generation (HHG).

➢ Fundamental physics: Study of parity-nonconserving interactions; electric-dipole moments of neutrons, electrons and atoms; 'new physics' that goes beyond the standard model.

➢ Quantum theory: 'complete' experiments; understanding the frame and boundaries of quantum mechanics ?

➢ ...

2. Interactions of atoms in weak (light) fields

Basic assumption: Weak coupling of atoms with the radiation field, i.e. the field itself does not affect the electronic structure of the atoms and ions.

2.1. Radiative transitions

2.1.a. Einstein's A and B coefficients

Consider two levels of an atom: $\hbar\omega = E_2 - E_1 > 0$.

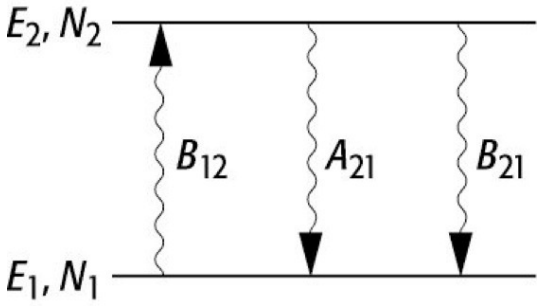

Figure 2.1.: Model of the induced and spontaneous processes.

Spectral energy density:

$$\rho(\omega) \quad ... \quad \text{energy density}/d\nu \;=\; \frac{\text{number of photons}}{\text{volume} \cdot d\nu}$$

Einstein's argumentation and coefficients:

➢ Einstein's rate equation:

$$\underbrace{-\frac{dN_2}{dt} \;=\; \frac{dN_1}{dt}}_{\text{particle conservation}} \;=\; A\,N_2 \;+\; B_{21}\,\rho(\omega)\,N_2 \;-\; B_{12}\,\rho(\omega)\,N_1 \;=\; P_{emission}\,N_2 \;-\; P_{absorption}\,N_1$$

➢ No field, $\rho(\omega) \;=\; 0$:

$$N_2(t) \;=\; N_2(0)\,e^{-At} \qquad\qquad A \;=\; \frac{1}{\tau}$$

A ... inverse lifetime, transition rate [1/s]

➢ Equilibrium state: $\frac{dN_2}{dt} \;=\; 0$:

$$\frac{P_{absorption}}{P_{emission}} \;=\; \frac{N_2}{N_1} \;=\; \frac{B_{12}\,\rho(\omega)}{A \;+\; B_{21}\,\rho(\omega)}$$

➢ Atoms with more than two levels: We here assume additionally the principle of detailed balance

$$\frac{P_{ij}}{P_{ji}} \;=\; \frac{N_j}{N_i} \;=\; \frac{B_{ij}\;\rho(\omega_{ij})}{A_{ji}\;+\;B_{ji}\;\rho(\omega_{ij})}$$

In equilibrium, the emission and absorption probability is equal for each pair ij of atomic levels, and this equivalence is independent of any other possible transition processes that the atoms may undergo.

➢ Generalized field-free case:

$$-\frac{dN_j}{dt} \;=\; \sum_i A_{ji}\,N_j \qquad\qquad \rightsquigarrow \qquad\qquad \tau_j \;=\; \left[\sum_i A_{ji}\right]^{-1}$$

➢ Ratio $A_{ji} \;:\; B_{ji} \;:\; B_{ij}$: ... in thermal equilibrium

$$\frac{N_j}{N_i} \;=\; \frac{g_j}{g_i}\,\exp\left(-\frac{\hbar\omega_{ij}}{kT}\right);\qquad\qquad \rho(\omega_{ij}) \;=\; \frac{\omega_{ij}^2}{\pi^2\,c^3}\,\frac{\hbar\omega_{ij}}{\exp\left(-\frac{\hbar\omega_{ij}}{kT}\right)\;-\;1}$$

Planck's black-body radiation: Power density radiation law

➢ Power density radiation law is a product of three quantities

- state density: $g(\omega) \;=\; \frac{\omega^2}{\pi^2\,c^3}$ [modes/m^3/Hz];
- photon energy: $\hbar\omega$ [Joule/photon; eV/photon];
- mean occupation number of mode ω: $\langle n_{ij}\rangle \;=\; \left(e^{\frac{\hbar\omega_{ij}}{kT}}\;-\;1\right)^{-1}$ [photons/mode].

➢ Einstein's relation (1917): Relation of detailed balance is fulfilled for

$$A_{ji} \;=\; \frac{\omega_{ij}^2}{\pi^2\,c^3}\,\hbar\,\omega_{ij}\,B_{ji} \;=\; \frac{\omega_{ij}^2}{\pi^2\,c^3}\,\hbar\,\omega_{ij}\,\frac{g_i}{g_j}\,B_{ij}$$

Einstein's coefficients depend on the internal structure of the atoms and they are (assumed to be) independent of the radiation field and its spectral density.

➢ Apparently, spontaneous emission increases rapidly with the frequency of the modes, $\propto\ \omega_{ij}^3$.

Example (Line-width contributions for the orange sodium line): This 'orange line' (known from sodium vapor lamps, for instance) has the frequency $\omega_o \sim 2\pi \cdot 4 \cdot 10^{14}$ Hz, a lifetime $\tau \sim 10^{-8}$ s and a natural width $\Delta\,\omega_o \sim 10^8$ Hz $= 0.1$ GHz — This gives a relative contribution $\Delta\,\omega_o/\omega_o \sim 4 \cdot 10^{-8}$.

For sodium with mass number $A = 23$ and for a temperature $T = 500$ K, we find a Doppler width $\Delta\,\omega/\omega \sim 3 \cdot 10^{-6}$ or $\Delta\,\omega \approx 12$ GHz.

In general: Doppler widths $\gg$ natural widts.

2.1.b. Transition amplitudes and probabilities

radiation field	atom – field interaction	atomic structure
(time – dependent)	$\Longleftrightarrow$	and motion

Time-dependent perturbation theory:

- semi-classical: quantized atom $\oplus$ classical em field.
- QED: quantized atom $\oplus$ quantized em field (Dirac 1927).

Limitations of the semi-classical description:

➢ Spontaneous emission is dominant for atoms in weak fields but can be understood only ad-hoc via the Einstein relation; this semi-classical picture is inappropriate for real weak fields, i.e. classical fields ... but this picture can be saved by applying these relations.

➢ Way out: Use the semi-classical picture to describe the induced emission/absorption.

➢ In classical light fields, the relative importance of the spontaneous emission is reduced (when compared to the action of the driving field), although it is generally not negligible.

Hamiltonian function of a particle in an electro-magnetic field: ... with $(\phi,\ \mathbf{A})$ the 4-vector potential

$$H = \frac{1}{2m}(\mathbf{p} + e\mathbf{A})^2 - e\,\phi + V, \qquad \mathbf{E} = -\boldsymbol{\nabla}\,\phi - \frac{\partial \mathbf{A}}{\partial t}, \qquad \mathbf{B} = \mathrm{rot}\,\mathbf{A}$$

$$= \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{e}{2m}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2}{2m}\mathbf{A}^2 - e\phi = H_{\text{atom}} + H_{\text{atom-field interaction}} = H_o + H'$$

Special case: Superposition of plane waves

$$\phi \;=\; 0$$

$$\mathbf{A} \;=\; \mathbf{A}_{-}\, e^{i\,(\mathbf{k}\cdot\mathbf{r}-\omega t)} \;+\; \mathbf{A}_{+}\, e^{i\,(\mathbf{k}\cdot\mathbf{r}+\omega t)}, \qquad \operatorname{div}\mathbf{A} \;=\; 0 \qquad \text{Coulomb gauge;} \qquad [\mathbf{p},\,\mathbf{A}] \;=\; 0$$

$$H' \;=\; \frac{e}{m}\,\mathbf{A}\cdot\mathbf{p} \;+\; \underbrace{\frac{e^2}{2m}\,\mathbf{A}^2}_{\text{neglegible for weak fields}}$$

$H_o \oplus$ time-dependent perturbation ➥ time-dependent perturbation theory.

Absorption probability:

➢ Fermi's Golden rule gives rise to

$$P_{\text{absorption}} \;=\; B_{ij}\,\rho(\omega_{ij}) \;=\; \frac{\pi}{\epsilon_o\,\hbar^2\,\omega_{ij}^2}\,\left|\left\langle j\left|\frac{e}{m}\,\boldsymbol{\epsilon}\cdot\mathbf{p}\,e^{i\,\mathbf{k}\cdot\mathbf{r}}\right|i\right\rangle\right|^2\,\rho(\omega_{ij}) \qquad \Longrightarrow \qquad A_{ji} \;\propto\; \omega_{ij}\,\frac{g_i}{g_j}\,B_{ij}$$

where $\boldsymbol{\epsilon}$ is the polarization vector of the emitted/absorbed light and $\mathbf{k} \equiv \mathbf{k}_{ij}$ the corresponding wave vector.

➢ Non-degenerate case: $B_{ij} \;=\; B_{ji}$ (microscopic reversible)

➢ Many-electron atoms:

$$\mathbf{p}\,e^{i\,\mathbf{k}\cdot\mathbf{r}} \quad\longrightarrow\quad \sum_a \mathbf{p}_a\,e^{i\,\mathbf{k}_a\cdot\mathbf{r}_a}\;.$$

➢ Merely the matrix element $\langle j \,|\, \boldsymbol{\epsilon}\cdot\mathbf{p}\, e^{i\,\mathbf{k}\cdot\mathbf{r}} \,|\, i\rangle$ depends on the electron coordinates; its mathematical analysis gives rise to the (so-called) selection rules.

2.2. Electric-dipole interactions and higher multipoles

2.2.a. Electric-dipole approximation

Consider a light field with plane-wave structure $\sim e^{i\,\mathbf{k}\cdot\mathbf{r}}$ and $|\mathbf{k}| = \frac{2\pi}{\lambda}$; for instance, ➥ visible light: $\lambda \approx 500$ nm ... 1000-10000 atomic radii

$$e^{i\,\mathbf{k}\cdot\mathbf{r}} = 1 + i\,\mathbf{k}\cdot\mathbf{r} + \ldots \approx 1$$

Dipole approximation: light wave is constant over the size of the atom.

Evaluation of the Einstein A coefficients:

➢ Consider polarization $\boldsymbol{\epsilon} \,||\, \mathbf{e}_x$, then $\langle j \,|\boldsymbol{\epsilon}\cdot\mathbf{p}\, e^{i\,\mathbf{k}\cdot\mathbf{r}}|\, i\rangle$

$$\langle j\,|p_x|\,i\rangle = \langle j\,|m\,\dot{x}|\,i\rangle = \frac{im}{\hbar}\,\langle j\,|\,[H_o,\,x]\,|\,i\rangle \qquad \Longrightarrow \qquad \left\langle j\left|\frac{e}{m}\,p_x\right|i\right\rangle = \frac{i}{\hbar}\,(E_j - E_i)\,\langle j\,|\,e\,x\,|\,i\rangle$$

$$B_{ij} = \frac{\pi}{\epsilon_o\,\hbar^2}\,|\langle j\,|\,e\,x\,|\,i\rangle|^2 \quad (\mathrm{x}-\text{polarization}); \qquad B_{ij} = \frac{1}{3}\cdot\frac{\pi}{\epsilon_o\,\hbar^2}\,|\langle j\,|e\,\mathbf{r}|\,i\rangle|^2 \quad (\text{unpolarized})$$

dipole operator in length gauge $e\,\mathbf{r}$.

➢ Spontaneous decay for non-degenerate and degenerate levels:

$$A_{ji} = \frac{1}{3}\frac{\omega_{ij}^3}{\pi c^3 \epsilon_o \hbar} |\langle j \,|\, e\mathbf{r} \,|\, i\rangle|^2 \qquad \text{...non} - \text{degenerate } |j\rangle$$

$$A_{ji} = \frac{1}{3}\frac{\omega_{ij}^3}{\pi\, c^3\, \epsilon_o \hbar} \sum_{m_i} |\langle j m_j \,|\, e\mathbf{r} \,|\, i m_i\rangle|^2 \qquad \neq f(m_j) \qquad \text{...degenerate } |jm\rangle$$

m_i ... additional quantum number to account all degenerate levels.

➢ Especially, optical transitions: $A \sim 10^8/s$ or $\tau = \frac{1}{A} = 10^{-8}\, s$ ... spontaneous decay dominates

$A \sim \omega^3$ ... Radio frequencies; spontaneous decay negligible. %

➢ Scaling with nuclear charge: $A_{if}^{(\mathrm{E1})} \propto Z^3$

2.2.b. Selection rules and discussion

Intensity of lines $\sim$ (i) occpuation of levels; (ii) transition probability.

Selection rules for bound-bound transitions:

➢ Matrix elements between bound states: $\langle jm_j \,|\, e\,\mathbf{r} \,|\, im_i\rangle$

➢ Expectation value of the electric-dipole moment $\langle e\mathbf{r}\rangle$ for stationary states:

$$\langle e\mathbf{r}\rangle \;=\; e\int d^3r\;\psi^*_{n\ell m}\,\mathbf{r}\,\psi_{n\ell m} \;=_{\mathbf{r}\to-\mathbf{r}}\; e\,(-1)^{2\ell+1}\int d^3r\;\psi^*_{n\ell,m}\,\mathbf{r}\,\psi_{n\ell m}\,.$$

➢ Electric-dipole transitions can connect only states with different parity:

- even $\longleftrightarrow$ odd
- $\Delta\,\ell \;=\; \pm 1$ (odd)

➢ The electric-dipole operator is an (odd-partiy) rank-1 operator.

➢ General form of the intensity for electric-dipole radiation:

$$I \;\sim\; N_j\,\omega^4\left[\int dr\,r^2\,R^*_{nl}\;r\;R_{n'l'}\right]^2 F\,(\ell m_\ell,\,\ell' m'_\ell)\,.$$

(i) Calculation of intensities $\rightsquigarrow$ evaluation of radial integrals.

(ii) Angular part of the intensity that can be obtained analytically within the central-field approximation.

➢ Further selection rules for an additional weak magnetic field **B**:

- $\boldsymbol{\epsilon} \,||\, \mathbf{n}_\mathrm{B}$ $\qquad \Delta m_\ell = 0 \qquad$ ... π-polarization
- $\boldsymbol{\epsilon} \perp \mathbf{n}_\mathrm{B}$ $\qquad \Delta m_\ell = \pm 1 \qquad$ ... σ-polarization.

2.2.c. Higher multipole components ("forbidden transition")

$$e^{i\,\mathbf{k}\cdot\mathbf{r}} = 1 + i\,\mathbf{k}\cdot\mathbf{r} + \ldots$$

magnetic-dipole (M1) and electric-quadrupole (E2) radiation

$$(\mathrm{M1}) \sim \frac{\omega^2}{c^2}\left|\left\langle j\left|\frac{e\,\hbar}{2m}\,\mathbf{l}_q\right|i\right\rangle\right|^2 = \frac{\omega^2}{c^2}\left|\langle j\,|\,\boldsymbol{\mu}_{l_q}\,|\,i\rangle\right|^2, \qquad \boldsymbol{\mu} = \frac{e\,\hbar}{2m}\,\mathbf{l} = \mu_\mathrm{B}\,\mathbf{l}$$

... magnetic moment of electron

$$(\mathrm{E2}) \sim \frac{\omega^4}{c^2}\,|\langle j\,|\,e\,x_q x_r|\,i\rangle|^2$$

$x_q x_r$ ... second-order tensor (components).

Intensity ratio for hydrogen-like wave functions:

$$\mathrm{E1} : \mathrm{M1} : \mathrm{E2} = 1 : \alpha^2 : \alpha^2$$

2.2.d. Dipole transitions in many-electron atoms

For a weak radiation field, the interaction of the radiation field with the (electrons of an) atom can be described perturbatively by the Hamiltonian

$$H' \;=\; \frac{e}{m}\,\mathbf{A}\cdot\sum_k \mathbf{p}_k \qquad\qquad \mathbf{A} = \text{ constant} \qquad \text{... over extent of atom}$$

and where the spontenous emission rates are obtained from the induced rates via the Einstein relation above. In this very common semi-classical approach, the spontanoeus emission rates is

$$A_{ji} \;=\; \frac{32\,\pi^3 e^2\,a_o^2}{3h}\;(E_j \;-\; E_i)^3\;\sum_q\;\left|\left\langle \gamma_j J_j M_j \left| P_q^{(1)} \right| \gamma_i J_i M_i \right\rangle\right|^2$$

$$P_q^{(1)} \;=\; \sum_{i=1}^{N} r_q^{(1)}(i) \;=\; \sum_{i=1}^{N} r_i\,\sqrt{\frac{4\pi}{3}}\,Y_{1q}(\vartheta_i,\varphi_i)$$

spherical components of the (many-electron) dipole operator

Analogue formulas also apply for the multipole radiation of higher order.

transition	selection rules
Electric dipole (E1)	$\lvert j_a - j_b \rvert = 0, \pm 1$ $\pi_a = -\pi_b$
Magnetic dipole (M1)	$\lvert j_a - j_b \rvert = 0, \pm 1$ $\pi_a = \pi_b$
Electric quadrupole (E2)	$\lvert j_a - j_b \rvert = 0, \pm 1, \pm 2$ $\pi_a = \pi_b$
Magnetic quadrupole (M2)	$\lvert j_a - j_b \rvert = 0, \pm 1, \pm 2$ $\pi_a = -\pi_b$

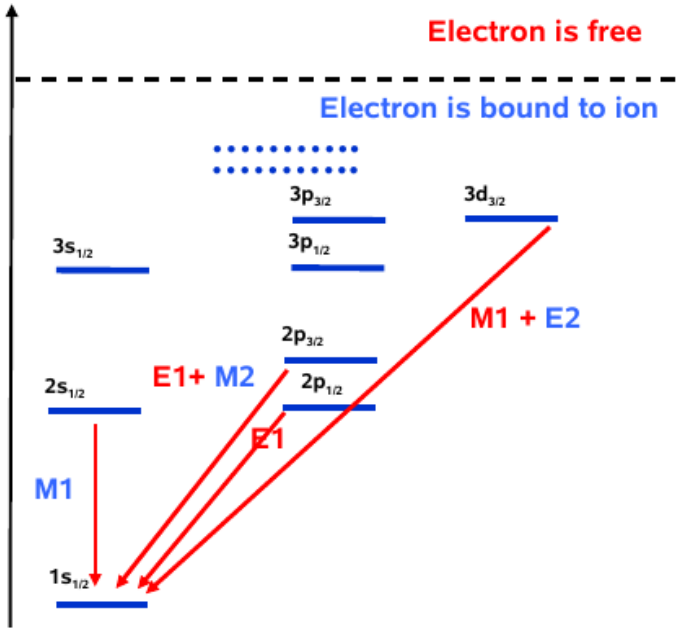

Figure 2.2.: Left: Selection rules for higher multipole transitions, and where $\pi_{a,b}$ refer to the parities of the initial and final states. Although the notation refers here for one-electron atoms, the same rules also apply for many-electron atoms and ions. Right: Selective multipole transitions are shown for hydrogen-like ions.

2.2.e. Multipol expansions of the radiation field

Multipoles radiation

➢ Non-relativistic time-dependent perturbation for weak fields: $H' = e\,\boldsymbol{p}\cdot\mathbf{A}$.

➢ Relativistic time-dependent perturbation: $H' = ce\,\boldsymbol{\alpha}\cdot\mathbf{A}$.

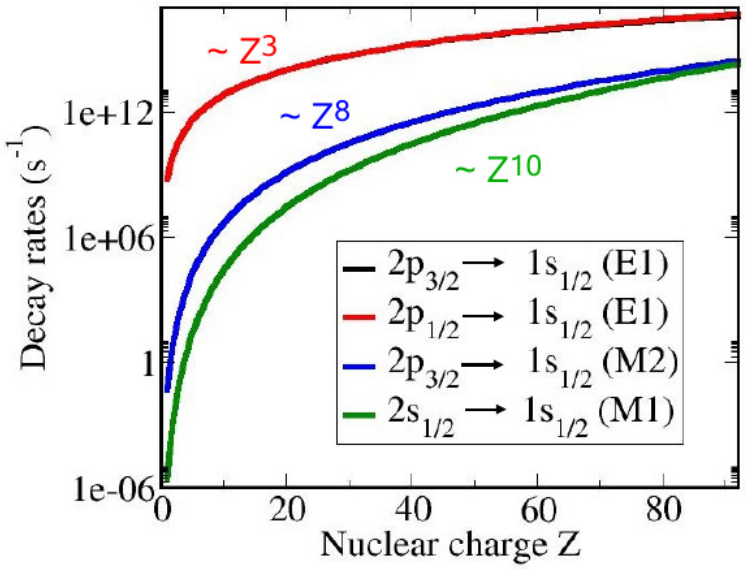

Figure 2.3.: Decay rates and scaling of the high multipole transitions with the nuclear charge, Z, for hydrogen-like ions.

➢ Electron-photon operator: gives rise (for instance, in time-dependent perturbation theory) to the transition amplitude

$$M_{fi} \;=\; \int d^3r\; \psi_f^*\; \boldsymbol{\alpha}\cdot\boldsymbol{\epsilon}\; e^{i\mathbf{k}\cdot\mathbf{r}}\; \psi_i\;.$$

➢ Selection rules:

$$|J_a \,-\, J_b| \;\leq\; L \;\leq\; J_a \,+\, J_b \qquad\qquad \delta(J_a, L, J_b), \qquad\qquad \begin{cases} \pi \;=\; (-1)^L & \text{electric multipoles} \\ \pi \;=\; (-1)^{L+1} & \text{magnetic multipoles} \end{cases}$$

➢ For low-Z, all high(er) multipole transition are negligible compared to the leading electric dipole (E1) term.

➢ For heavy and superheavy elements, the high multipoles become rapidly important with nuclear charge Z.

➢ Scaling rules with nuclear charge Z:

$$\propto Z^4\,(\mathrm{E1}); \qquad \propto Z^{10}\,(\mathrm{M1}); \qquad \propto Z^8\,(\mathrm{M2}); \qquad \propto Z^6\,(\mathrm{E1E1}); \qquad \propto Z^{12}\,(\mathrm{E1M1})\,.$$

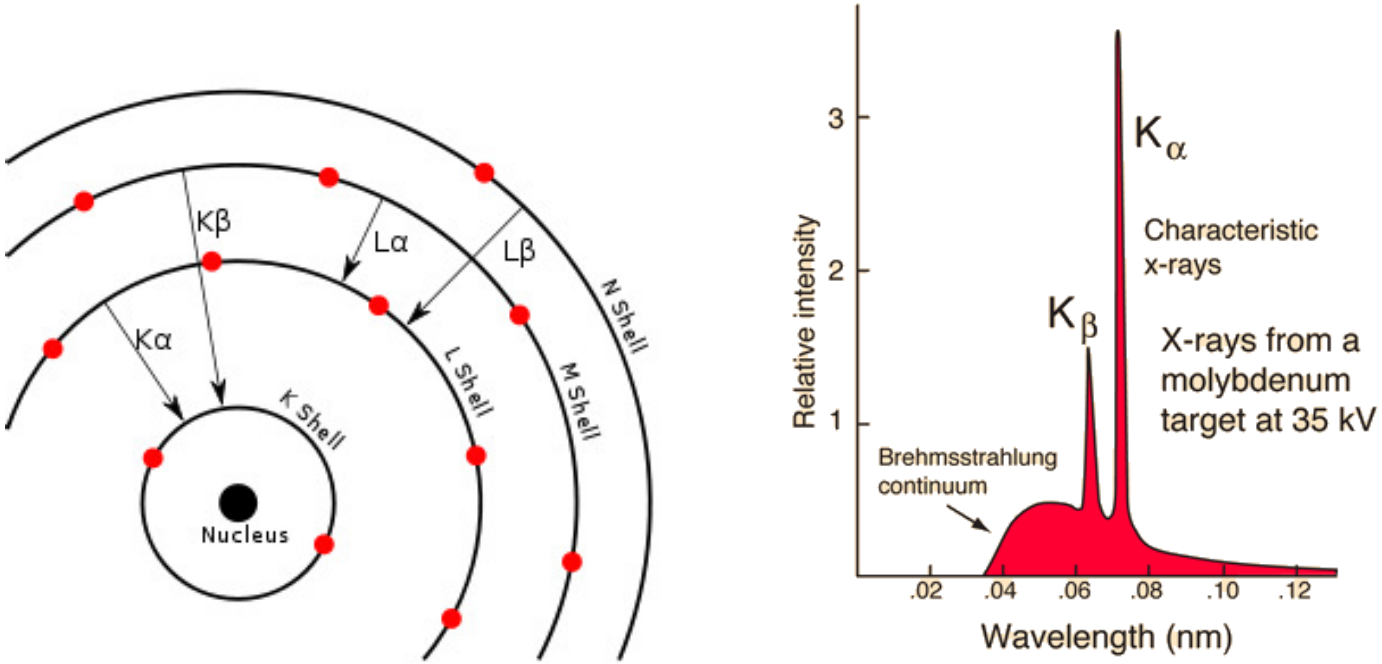

Figure 2.4.: Left: Characteristic x-rays are emitted from heavy elements when their electrons make transitions between atomic energy levels. Right: The characteristic $K_{\alpha,\beta}$ x-ray emission appears as two sharp peaks in the photon spectra following the production of a vacancy in the K-shell ($n = 1$). The background in the emitted x-ray spectra arises from Compton and bremsstrahlung radiation. From en.wikipedia.org/wiki and

2.3. Photo excitation and photo emission processes

2.3.a. Photo excitation and fluorescence

➢ Notation: $\hbar\omega + A \longrightarrow A^* \longrightarrow A^{*'} + \hbar\omega'$.

➢ Photoexcitation is often discussed together with photoionization or even photofragmentation (for molecules).

➢ Fluorescence: spontaneous photon emission that results in some lower-lying level of the atoms or ions.

Photoabsorption and emission of σ- *vs.* π-light

➢ Left- and right-circular light are often called also $\sigma^{\pm}$ light, in contrast to the linear-polarized π-light.

➢ If the atom is aligned along the z-axis (quantization axis), the π-light is emitted in the $x-y$ plane, oscillates predominantly along the z-axis and combines substates with $\Delta m = 0$.

➢ Angular distributions:

- $\sigma^{\pm}$: $W(\vartheta) \propto \left(1 + \cos^2\vartheta\right)$
- π : $W(\vartheta) \propto \sin^2\vartheta$

Siegbahn	IUPAC	Siegbahn	IUPAC	Siegbahn	IUPAC	Siegbahn	IUPAC
$K\alpha_1$	K-L_3	$L\alpha_1$	L_3-M_5	$L\gamma_1$	L_2-N_4	$M\alpha_1$	M_5-N_7
$K\alpha_2$	K-L_2	$L\alpha_2$	L_3-M_4	$L\gamma_2$	L_1-N_2	$M\alpha_2$	M_5-N_6
$K\beta_1$	K-M_3	$L\beta_1$	L_2-M_4	$L\gamma_3$	L_1-N_3	$M\beta$	M_4-N_6
$K^I\beta_2$	K-N_3	$L\beta_2$	L_3-N_5	$L\gamma_4$	L_1-O_3	$M\gamma$	M_3-N_5
$K^{II}\beta_2$	K-N_2	$L\beta_3$	L_1-M_3	$L\gamma_4'$	L_1-O_2	$M\zeta$	$M_{4,5}$-$N_{2,3}$
$K\beta_3$	K-M_2	$L\beta_4$	L_1-M_2	$L\gamma_5$	L_2-N_1		
$K^I\beta_4$	K-N_5	$L\beta_5$	L_3-$O_{4,5}$	$L\gamma_6$	L_2-O_4		
$K^{II}\beta_4$	K-N_4	$L\beta_6$	L_3-N_1	$L\gamma_8$	L_2-O_1		
$K\beta_{4x}$	K-N_4	$L\beta_7$	L_3-O_1	$L\gamma_8'$	L_2-$N_{6(7)}$		
$K^I\beta_5$	K-M_5	$L\beta_7'$	L_3-$N_{6,7}$	$L\eta$	L_2-M_1		
$K^{II}\beta_5$	K-M_4	$L\beta_9$	L_1-M_5	Ll	L_3-M_1		
		$L\beta_{10}$	L_1-M_4	Ls	L_3-M_3		
		$L\beta_{15}$	L_3-N_4	Lt	L_3-M_2		
		$L\beta_{17}$	L_2-M_3	Lu	L_3-$N_{6,7}$		
				Lv	L_2-$N_{6(7)}$		

Figure 2.5.: While the x-ray (analytical) community still largely uses the so-called Siegbahn notation, the IUPAC notation is consistent with the notation used for Auger electron spectroscopy, though the latter one is slightly more cumbersome. From nau.edu/cefns/labs.

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2.3.b. Characteristic x-ray radiation

➢ X-ray transitions: $\mathrm{K}_{\alpha 1}(2p_{3/2} \to 1s)$; $\mathrm{K}_{\alpha 2}(2p_{1/2} \to 1s)$; $\mathrm{K}_{\beta 1}(3p_{3/2} \to 1s)$, ...

➢ X-ray fluorescence following electron impact:

$$e^- + A \longrightarrow e^- + A^* \longrightarrow e^- + A^+ + \hbar\omega; \qquad \hbar\omega = E_i - E_f\,.$$

➢ Mosley's law: The energies of the characteristic radiation and of the absorption edges follow (very) approximately Balmer's rule: ... with $Z_{\mathrm{eff}} = Z - S$, and with the screening number S.

$$\hbar\omega = Z_{\mathrm{eff}}^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

➢ X-ray satellite and hypersatellite lines: $\mathrm{K}^s_{\alpha 1}\left((1s2p)^{-2} \to (2p_{3/2}2p)^{-2}\right)$, $\mathrm{K}^h_{\alpha 1}\left((1s)^{-2} \to (1s2p_{3/2})^{-2}\right)$, ...

2.3.c. Characteristic x-ray absorption

➢ Beer's law: $\frac{dN}{N} = -\sigma_a\, n\, dx$ with number density n; ... n – number of atoms per cm^3 of the material (atomic density).

$$N(x) = N(0)\,\exp(-x/\xi); \qquad \xi = \frac{1}{\sigma_a\, n}$$ ... mean free path length.

➢ X-ray Absorption Spectroscopy: measurement of the x-ray absorption coefficient of a material as a function of energy (EXAFS and XANES).

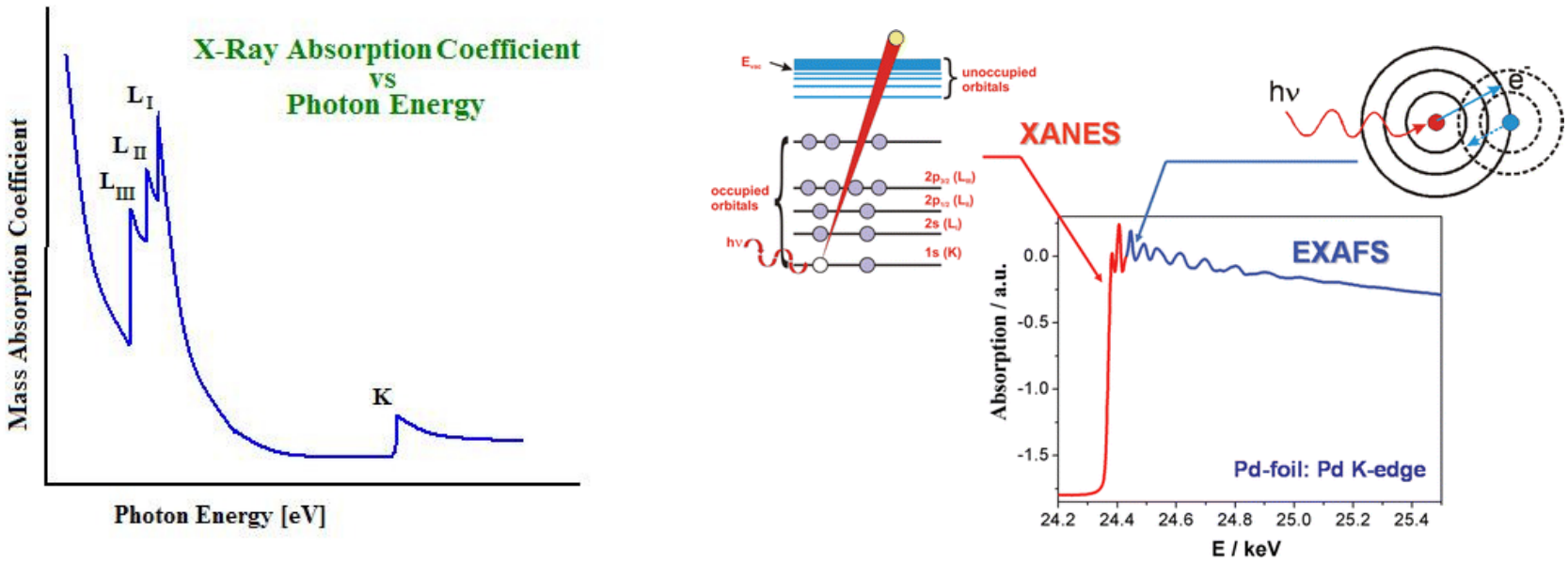

Figure 2.6.: Left: Edges in the x-ray absorption coefficients as function of the photon energy. Right: Principle of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. From chemwiki.ucdavis.edu and pubs.rsc.org

➢ Note that the 'edges' are often displayed as function of the wavelength ... which virtually leads to a 'mirror' image of the figure.

➢ Usually, the photoelectric effect is largest at low energies, Compton scattering dominates at intermediate energies, and pair production dominates at high energies.

2.3.d. Rayleigh and Compton scattering

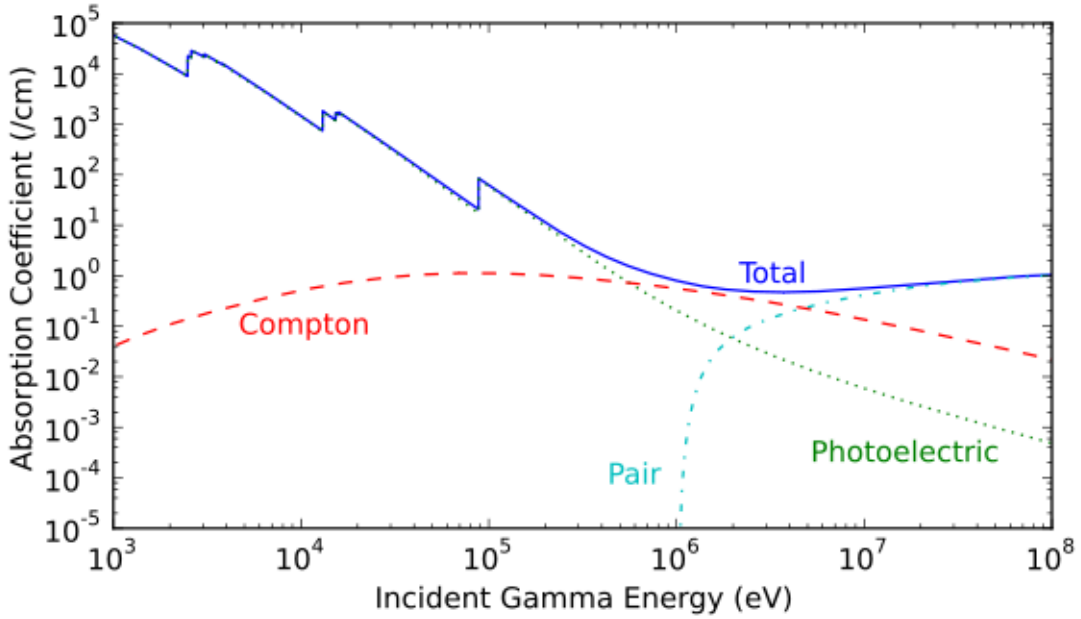

Figure 2.7.: The total (x-ray) absorption coefficient as function of the photon energy, and up to very high γ energies. The figure displays the relative importance of the three major effects, the photoionization, Compton and pair-creation process. Above 5 MeV, pair production starts to dominate the photoabsorption of matter.

- Rayleigh: $\hbar\omega + A \longrightarrow A + \hbar\omega$ ... elastic scattering of high-energetic photons
- Compton: $\hbar\omega + A \longrightarrow A^* + \hbar\omega'$ ... inelastic scattering of high-energetic photons with a simultaneous atomic excitation/de-excigtation

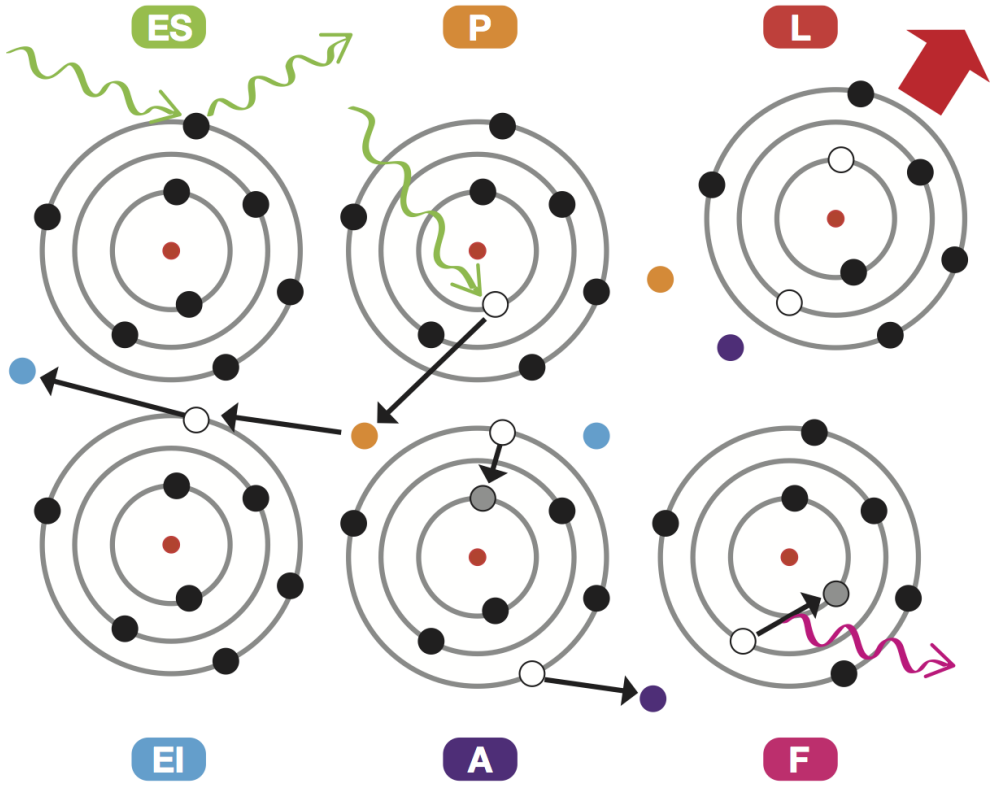

Figure 2.8.: Comparison of different ionization and subsequent decay processes in atoms.

2.3.e. Bremsstrahlung

➢ $e^-(E_e) + A \longrightarrow e^-(E'_e) + A + \hbar\omega, \qquad \hbar\omega = E_e - E'_e$ ... energy conservation.

➢ Maximal loss of kinetic energy of the electron, $E_{\max} = eU$ leads to a minimum wave lengths

$$\lambda_{\min} = \frac{hc}{E_{\max}} = \frac{hc}{eU}; \qquad \lambda[nm] = \frac{1240}{E[eV]}.$$

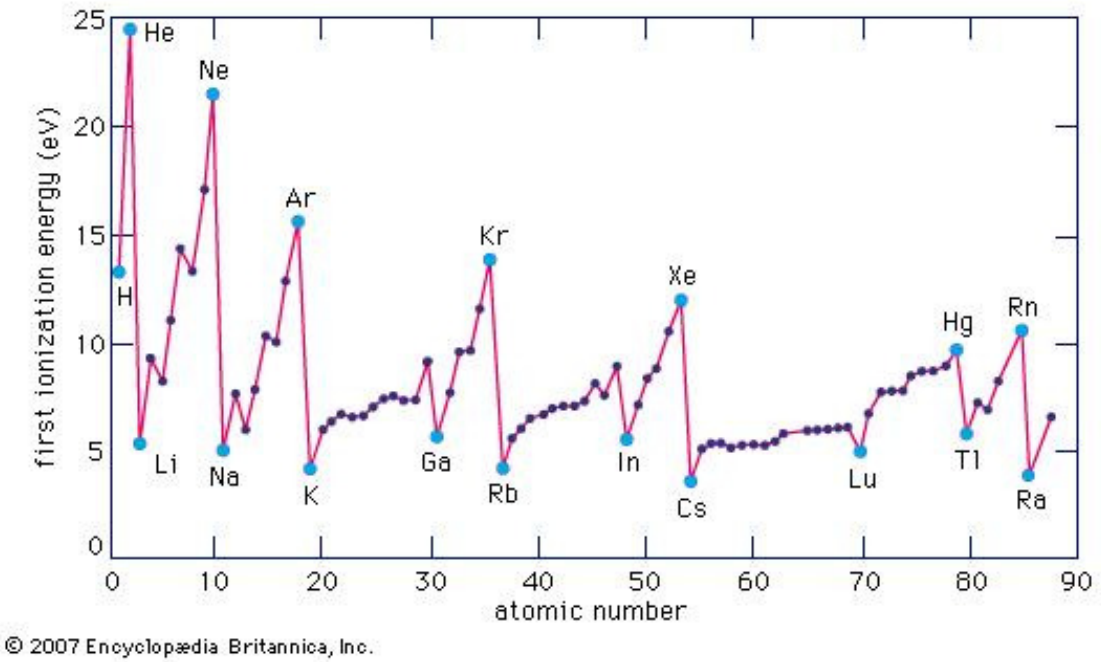

Figure 2.9.: First ionization potential as function of the nuclear charge of elements. From: www1.aps.anl.gov.

➢ Examples: $U = 10\,\text{kV} \quad \rightsquigarrow \lambda \sim 1\ \text{Å}$; $U = 100\,\text{kV} \quad \rightsquigarrow \lambda \sim 0.1\ \text{Å}$.

➢ Continuation of the radiative recombination (RR) process if the 'capture' occurs into the continuum of the ions.

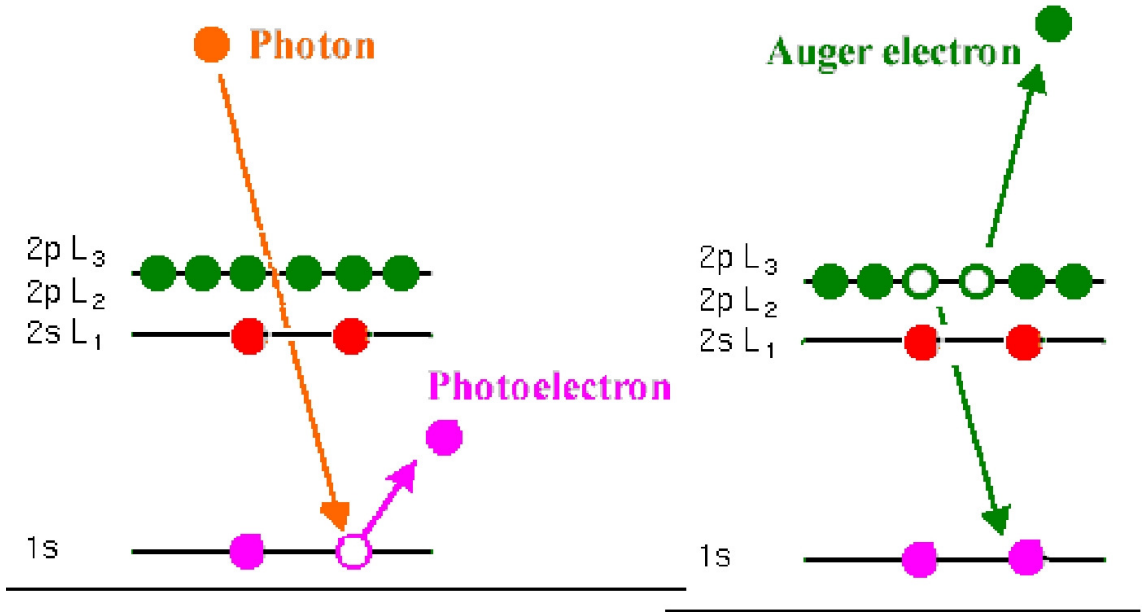

Figure 2.10.: Schematic diagram for the XPS emission process (left). An incoming photon causes the ejection of a photoelectron. The subsequent relaxation process (right) leads to the emission of an Auger KLL electron; from http://www.vub.ac.be/

2.3.f. Radiative electron capture (REC)

➢ Capture of a (quasi-) free electron by an ion under the releases of a photon; important for multiply and highly-charged ions.

$$e^-(E_e) \; + \; A^{q+} \; \longrightarrow \; A^{(q-1)+*}(E_n) \; + \; \hbar\omega \; \longrightarrow \; A^{(q-1)+}(E_f) \; + \; \hbar\omega \; + \; \underbrace{\hbar\omega'}_{\text{characteristic radiation}}$$

➢ In multiply and highly-charged ions, the REC or radiative recombination (RR) are non-resonant process, while the

dielectronic recombination (DR) is a resonant process:

$$e^- + A^{q+} \longrightarrow A^{(q-1)+} + \hbar\omega \qquad \text{... RR or REC}$$

$$e^- + A^{q+} \longrightarrow A^{(q-1)+*} \longrightarrow A^{(q-1)+} + \hbar\omega \qquad \text{... DR.}$$

➢ In laser physics, RR is known as a process that destroyes the carriers, i.e. the electrons and holes.

2.3.g. Two-photon absorption (TPA) and two-photon emission

➢ Simultaneous absorption or emission of two photons:

$$\hbar\omega + \hbar\omega' + A \longrightarrow A^* \longrightarrow A + \hbar\omega + \hbar\omega'$$

➢ Atomic transition rate depends quadratically on the light intensity: $A_{\text{absorption}} \sim I^2$.

➢ Different selection rules for TPA than for one-photon absorption.

➢ Examples:

- Helium-like ions: $1s2s\ {}^1S_0 \to 1s^2\ {}^1S_0$ decay by E1E1 + M1M1 + E2E2 + ... emission; the E1E1 channel clearly dominates by several orders of magnitude.
- Beryllium-like ions: $1s^22s2p\ {}^3P_0 \to 1s^22s^2\ {}^1S_0$ decay by E1M1 + E2M2 + 3E1 + ... emission; the ${}^3P_0$ level is the lowest excited level and has extreme long lifetimes up to many thousands of years near to the neutral end of the sequence.

➢ Scaling with nuclear charge: $A_{if} \propto Z^{-6}$

2.4. Atomic photoionization

Photoionization with subsequent Auger electron emission (autoionization):

$$\hbar\omega \;+\; A(E_i) \;\longrightarrow\; A^{+*}(E_n) \;+\; e_p(E_p) \;\longrightarrow\; A^{++*}(E_f) \;+\; \underbrace{e_p(E_p) \;+\; e_a(E_a)}_{\text{post-collision interaction}}$$

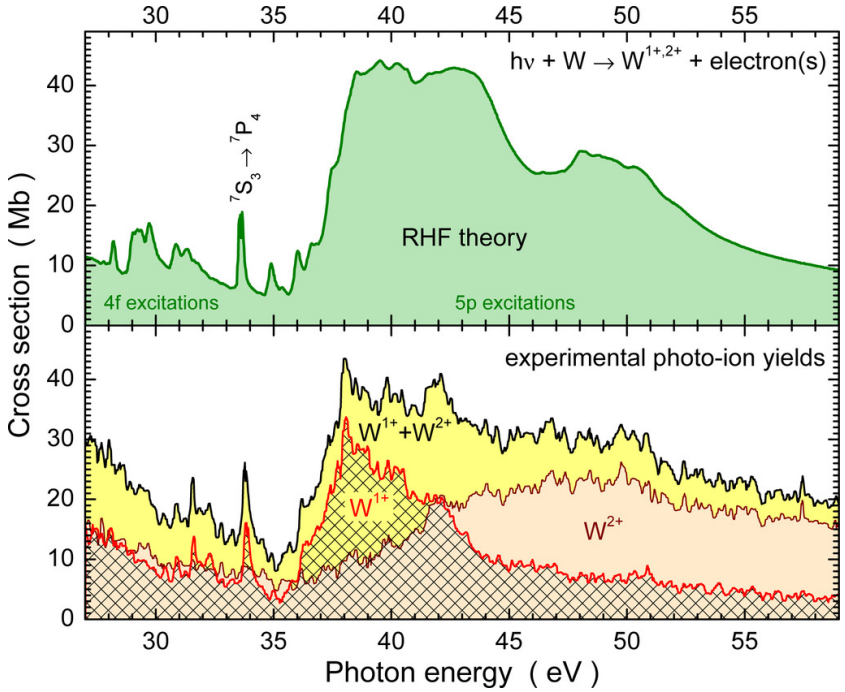

Figure 2.11.: Cross sections for the photoionization of neutral W (tungsten) atoms. The upper panel shows the result of relativistic Hartree-Fock (RHF) calculations for the photoabsorption by neutral tungsten. The tungsten atoms are brought into the gas phase by evaporating tungsten at 3200 K. From www.mdpi.com.

2.4.a. Photoionization amplitudes and transition amplitudes

➢ Photoionization from the ground state of an atom or ion is possible for $\hbar\omega > I_p$ (1st ionization potential).

➢ For a weak photon field, this ionization is again caused by the Hamiltonian

$$H' = \frac{e}{m}\,\mathbf{A}\cdot\sum_i \mathbf{p}_i \;=_{\text{(in E1 approximation)}}\; \mathbf{E}\cdot\sum_i \mathbf{r}_i$$

with $\mathbf{E} = \Re\left[F_o\, e^{-i\omega t}\,\mathbf{n}\right]$, and where F_o denotes the magnitude of the electric field.

➢ Cross section for the photoionization of an atom for a transition from $|i\rangle \to |f\rangle$: ... $P(\omega)$ is the ionization probability per atom and time unit

$$\sigma(\omega) = \frac{P(\omega)}{F}$$

➢ Photon flux F : is the number of photons per unit area and unit time

$$F = \frac{|F_o|^2\, c}{8\pi\,\omega}$$

➢ Transition probability: ... k_f – asymptotic momentum of the free electron.

$$P_{if}(\omega, k_f) = 2\pi \left|\left\langle f\left|\frac{F_o}{2}\,\mathbf{r}\cdot\mathbf{n}\right|i\right\rangle\right|^2 , \rho_f(E_f)$$

➢ Density of states:

$$\rho(E_f) = \rho_o\,\delta\left(\hbar\omega + E_i - E_f\right) = \rho_o\,\delta\left(\hbar\omega + I_f - \frac{k_f^2}{2}\right)$$

➢ Total transition probability:

$$P_{if}(\omega) \;=\; \sum_{k_f} P_{if}(\omega, k_f)$$

➢ Free (outgoing) electron: is often approximated by Coulomb waves

$$\lim_{r\to\infty} R_{k\ell}(r) \;\sim\; \frac{1}{r}\cos\left(kr \;+\; \frac{q}{k}\ln(2kr) \;-\; \frac{(\ell+1)\pi}{2} \;+\; \delta_\ell^{\text{Coulomb}} \;+\; \delta_\ell\right)$$

$\delta_\ell^{\text{Coulomb}}$ ... Coulomb phase shift

δ_ℓ ... non − Coulomb phase shift

q ... (screened) charge that is seen asymptotically by the electron

➢ Summation over k_f: ... $\frac{2}{\pi}$ – normalization factor of free electrons in the momentum scale.

$$\sum_{k_f} \to \frac{2}{\pi}\int dk_f \qquad \Longrightarrow \; P_{if}(\omega)\sum_{k_f} = \frac{2}{\pi}\int dk_f\, P_{if}(\omega, k_f)$$

2.4.b. Shake-up and shake-off processes; direct double photoionization

➢ Photoionization with excitation and direct double photoionization:

$$\begin{aligned}
\hbar\omega \;+\; A \;&\longrightarrow\; A^{+*} \;+\; e_p^- \;\longrightarrow\; A^{++} \;+\; e_p^- \;+\; e_A^- && \text{ionization} - \text{excitation with subs. Auger}\\
&\longrightarrow\; A^{++} \;+\; 2\,e_p^- && \text{direct double ionization}\\
&\longrightarrow\; A^{*} \;\longrightarrow\; A^{++} \;+\; 2\,e_A^- && \text{excitation with Auger with shake} - \text{off}\\
&\longrightarrow\; A^{*} \;\longrightarrow\; A^{+*} \;+\; e_A^- \;\longrightarrow\; A^{++} \;+\; 2\,e_A^- && \text{excitation with two} - \text{step Auger cascade}
\end{aligned}$$

➢ Transition amplitude:

$$\langle((\gamma_f J_f,\, \epsilon_1\kappa_1)X_f, \epsilon_2\kappa_2)\, J'M' \,|\, Z_{\rm op} \,|\, \gamma_i\, J_i M_i\rangle$$

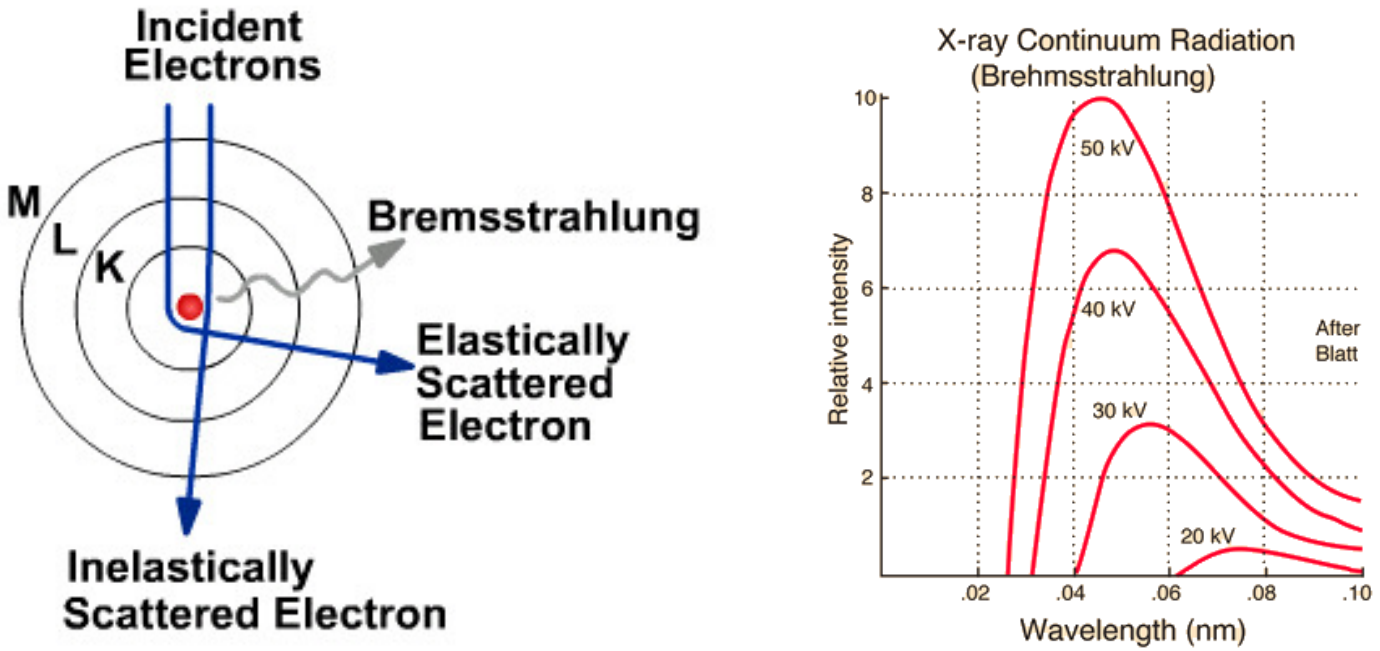

Figure 2.12.: Left: Different elastic and inelastic electron scattering processes on atoms, including bremsstrahlung. Right: Bremsstrahlung is characterized by a continuous distribution of radiation that is shifted towards higher photon energies and becomes more intense with increasing electron energy. From: www.nde-ed.org/EducationResources and hyperphysics.phy-astr.gsu.edu.

2.5. Non-radiative transitions: Auger transitions and autoionization

➢ Single- or two-step Auger decay:

$$A^{q+} \longrightarrow A^{(q+1)+} + e_A^- \longrightarrow A^{(q+2)+} + e_{A,1}^- + e_{A,2}^-$$

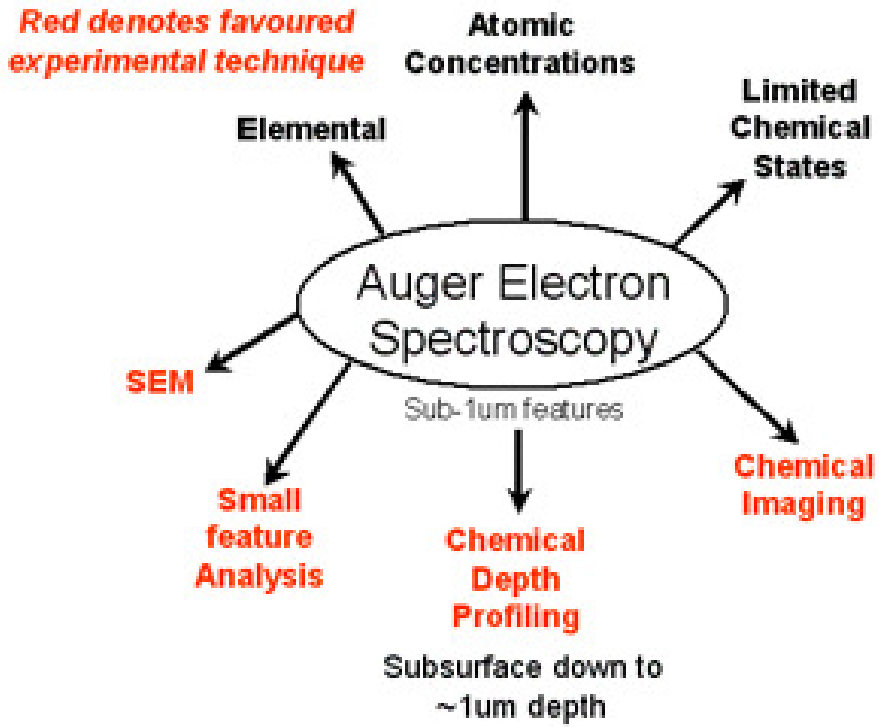

Figure 2.13.: Information that is available from Auger electron spectroscopy. From www.lpdlabservices.co.uk

➢ Examples:

$K-LL,\ K-LM,\ L-MM,\ L_3-M_1M_{23},\ ...$	normal Auger transitions
$L-LM,\ M-MN,\ ...$	Coster − Kronig transitions
$L-LL,\ L_1-L_2L,\ M--MM,\ ...$	super.Coster − Kronig transitions

➢ For an autoionization, the excited atom $A^{q+,*}$ must lay energetically in the continuum of the next higher charge state.

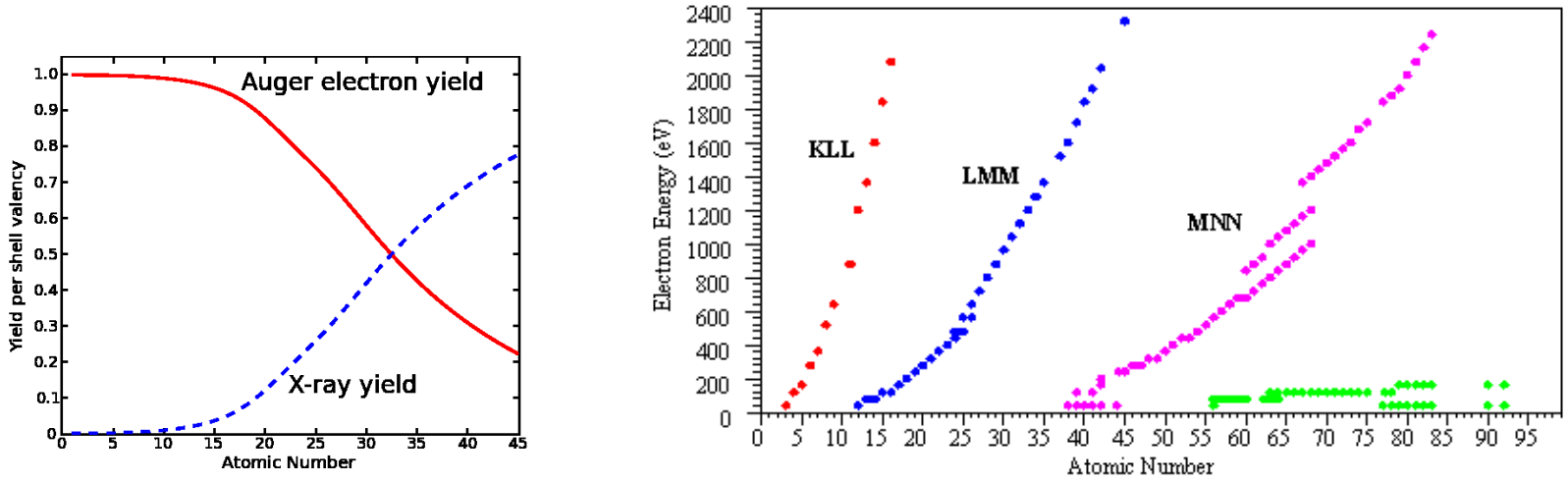

Figure 2.14.: Left: Comparison of Auger yield and fluorescence yield as a function of atomic number. Right: Auger characteristic energies. From and commons.wikimedia.org and www.semitracks.com.

- Auger transitions and autoionization are caused by inter-electronic interactions.
- Kinetic energy of emitted electrons: $E_{kin} = E_i(N) - E_f(N-1)$.
- Autoionization: (Low-energy) emission of valence electrons.
  Auger decay: (High-energetic) electron emission after decay of an inner-shell hole.
- Autoionization and Auger decay are very similar in their theoretical treatment; they are both described by the Auger (autoionization) rate

$$A_{fi} \sim 2\pi \left| \left\langle (\gamma_f J_f, \epsilon_f \kappa_f)\, J' M' \right| \sum_{i<j} \frac{1}{r_{ij}} \left| \gamma_i J_i M_i \right\rangle \right|^2$$

➢ Selection rules for Auger transitions:

$$\Delta J \;=\; |J_i \,-\, J_f| \;=\; \Delta M \;=\; |M_i \,-\, M_f| \;=\; 0 \qquad \text{(strict, since caused by inner interactions)}$$

$$\Delta L \;=\; \Delta M_L \;=\; \Delta S \;=\; \Delta M_S \;=\; 0 \qquad \text{(in the non} - \text{relativistic framework)}$$

However, no simple rules apply for J_i, J_f or M_i, M_f , since the access angular momentum is carried away by the outgoing electron.

➢ Scaling with nuclear charge Z: $A_{fi} \;\propto\; Z^0 \;=\;$ const.

➢ Auger electron spectroscopy (AES): common analytical technique for studying surfaces and materials.

➢ Excitation and subsequent decay of a neutral atom:

$$\hbar\omega \;+\; A \;\rightarrow\; A^{+*}(E_i) \;+\; e_p(E_p) \;\rightarrow\; A^{++*}(E_f) \;+\; \underbrace{e_p(E_p) \;+\; e_a(E_a)}_{\text{post}-\text{collision interaction}}$$

➢ Auger vs. fluorescence yield:

$$\omega \;=\; \frac{\Gamma_x}{\Gamma_x \;+\; \Gamma_A} \;=\; \frac{\Gamma_x}{\sum_i \Gamma_i} \;\propto\; \frac{Z^4}{Z^4 \;+\; Z^0} \;\rightarrow\; 1 \qquad\qquad \text{for } Z \;>\; 50\,.$$

➢ Shake-up and shake-off processes: Excitation and (auto-) ionization due to a sudden change in the potential; often estimated in terms of probabilities due to the overlap of wave functions that are obtaine for a N-electron atom:

$$P_{\text{shake}} \;=\; 1 \;-\; \int d^3r\; \psi_f^*(N-1)\; \psi_i(N)$$

$$P_{\text{orbital}} \;=\; \int d^3r\; \psi_f^*(N-1)\; \psi_i(N) \qquad \text{... probability to stay in given orbital.}$$

2.6. Beyond single-photon or single-electron transitions

Weak processes with several photons and/or electrons:

➢ E1E1 (or 2E1) decay of excited states:

$$A^* \longrightarrow A + \hbar\omega_1 + \hbar\omega_2, \qquad \Delta E = \hbar\omega_1 + \hbar\omega_2 = E(A^*) - E(A)\,.$$

Example: He-like $1s2s\ ^1S_0 \rightarrow 1s^2\ ^1S_0$ can only decay by 2E1 and, hence, the $1s2s\ ^1S_0$ level in neutral helium is metastable with a lifetime of about 19 ms.

Hyperfine quenching:

➢ Radiative Auger decay: $A^{+*} \longrightarrow A^{++} + \hbar\omega + e^-_A$

➢ Two-photon double ionization: $2\hbar\omega + A^{+*} \longrightarrow A^{++} + e^-_{p,1}(E_1) + e^-_{p,2}(E_2)$

➢ Two-color single ionization: $\hbar\omega_1 + \hbar\omega_2 + A \longrightarrow A^+ + e^-_p$

➢ Two-color double ionization: $\hbar\omega_1 + \hbar\omega_2 + A \longrightarrow A^{++} + e^-_{p,1}(E_1) + e^-_{p,2}(E_2)$

➢ Multi-photon ionization: $n \cdot \hbar\omega + A \rightarrow A^+ + e^-_p$

➢ Quantum mechanics allows many more but often (very) weak transitions.

➢ Conservation of energy typically leads to a unique condition(s) for the (sum of) energies of the emitted particles.