

**Atomic Theory:**  
**Atoms in external fields**  
**— Lecture script —**  
**WS 2015/16**

<http://www.atomic-theory.uni-jena.de/>  
→ Teaching → Atomic Theory  
(Script and additional material)

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Wednesday 7<sup>th</sup> October, 2015



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# 0. Preliminary remarks

## 0.1. Schedule and agreements

Lecture period:	19. 10. 2015 – 12. 2. 2016
Lecture:	Thu 8 – 10, Max-Wien-Platz (Physik, SR 1)
Tutorial:	Tue 8 – 10, every 2nd week, to be agreed
Language:	German / English ??
ECTS points:	4 (inclusive the tasks and exam).
Exam:	Tasks (40 %), oral <u>or</u> written exam.
Requirements for exam:	<i>Modulanmeldung</i> within the first 6 weeks; at least 50 % of the points from tutorials.
A few questions ahead:	How much have you heard about atomic theory so far ?? Who makes regularly use of Maple oder Mathematica ?? ...

## 0.2. Further reading

- K. Blum: *Density Matrix Theory and Applications: Physics of Atoms and Molecules* (Plenum Press, New York, 1981, 1996).
- B. H. Brandsen and C. J. Joachain: *Physics of Atoms and Molecules* (Benjamin Cummings, 2nd Edition, 2003).
- R. D. Cowan: *Theory of Atomic Structure and Spectra* (Los Alamos Series, 1983).
- W. R. Johnson: *Atomic Structure Theory: Lectures on Atomic Physics* (Springer, Berlin, 2007).
- J. Foot: *Atomic Physics* (Oxford Master Series, Oxford University Press, 2005).
- H. Friedrich: *Theoretical Atomic Physics* (Springer, 3rd edition, 2003).
- M. Metcalf, J. Reid and M. Cohen: *Fortran 95/2003 Explained: Numerical Mathematics and Scientific Computation* (Oxford University Press, Oxford, 2007).
- G. K. Woodgate: *Elementary Atomic Structure* (Oxford University Press, 2nd Edition, 1983).
- *Controlling the Quantum World: The Science of Atoms, Molecules and Photons* (The National Academy Press, Washington, 2007).

Additional texts: ... (Blackboard)



# 1. Atomic theory: A short overview

## 1.1. Atomic spectroscopy: Structure & collisions

### Atomic processes & interactions:

- **Spontaneous emission/fluorescence:** occurs without an ambient electromagnetic field; related also to absorption, and it shows the **deep quantum nature** of atoms and light.
- **Stimulated emission:** from excited atoms leads to **photons with basically the same phase, frequency, polarization, and direction of propagation** as the incident photons.
- **Photoionization:** results in free electrons.
- **Rayleigh and Compton scattering:** **Elastic and inelastic scattering** of X-rays and gamma rays by atoms and molecules. Compton scattering often leads to an decrease in the photon energy but a energy transfer from matter to the photon can also be observed under certain circumstances (**inverse Compton scattering**).
- **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:** shows the non-linear electron-photon interaction and is **presently a very active field of research**.
- **Autoionization:** Nonradiative electron emission from (inner-shell) excited atoms.
- **Electron-impact excitation & ionization:** results in excited and ionized atoms and occurs frequently in **astro-physical and laboratory plasmas**.
- **Elastic & inelastic electron scattering:** reveals the electronic structure of atoms and ions; it is important for plasma physics.
- **Pair production:** creation of an elementary particle and its antiparticle from light (electron-positron pairs); pairs from the vacuum.
- **Delbrück scattering:** the deflection of high-energy photons in the Coulomb field of atomic nuclei as 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 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 applying even field-theoretical techniques. — In short, the knowledge of the fundamental constants of Nature, the basic equations, and a bundle of proper approximation techniques will be enough to predict the energies and properties of ions, atoms and molecules with spectroscopic accuracy or even better.

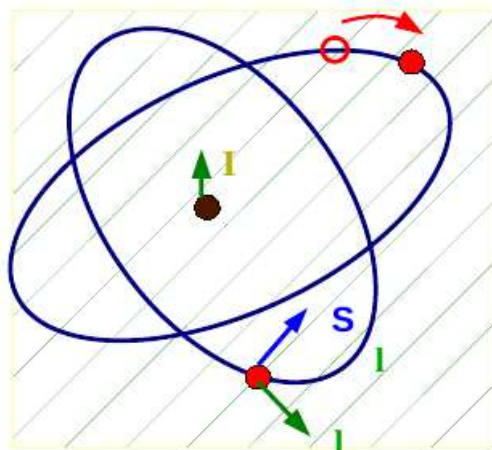
Well, ... this is quite an ambitious task with a lot of surprises when it comes to details.

Atomic theory is a great playground, indeed.

Requires good physical intuition, or this is often at least beneficial.

### Hierarchy of inner-atomic interactions

-- self-consistent fields vs. perturbation theory



External fields

★ Motion of the nucleus: Reduced mass and mass polarization

- Nuclear potential
- Instantaneous Coulomb repulsion between all pairs of electrons
- Spin-orbit interaction
- Relativistic electron velocities; magnetic contributions and retardation
- QED: radiative corrections
- Hyperfine structure
- Electric and magnetic nuclear moments (isotopes)

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



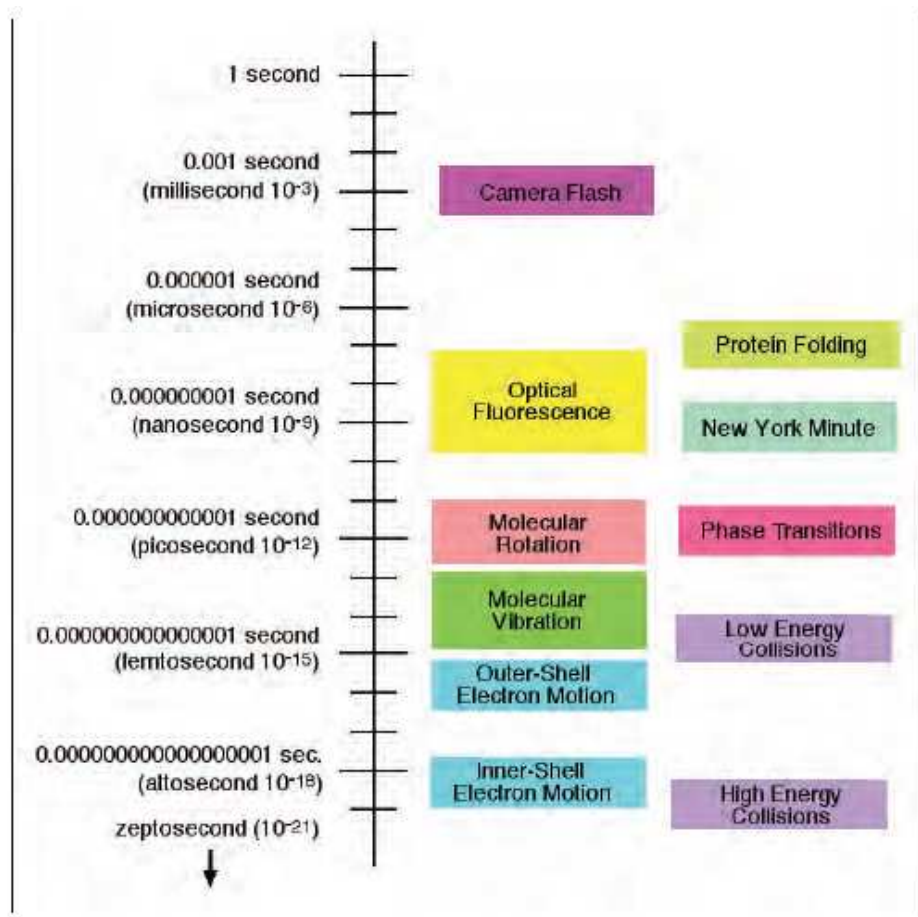


Figure 1.2.: Characteristic time scales of atomic and molecular motions; taken from: *Controlling the Quantum World*, page 99.

### 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 (upon which the quantum system does not couple back).
- This semi-classical treatment is suitable for a very large class of problems, sometimes by including quantum effects of the field in some ‘ad-hoc’ manner (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). QED is important for problems with definite photon statistics or in cavities in order to describe single-photon-single-atom interactions.

### Combination of different (theoretical) techniques:

- Special functions from mathematical physics (spherical harmonics, Gaussian, Legendre- and Laguerre polynomials, Whittaker functions, etc.).
- Racah's algebra: Quantum theory of angular momentum.
- Group theory and spherical tensors.
- Many-body perturbation theory (MBPT, coupled-cluster theory, *all-order* methods).
- Multiconfigurational expansions (CI, MCDF).
- Density matrix theory.
- Green's functions.
- Advanced computational techniques (object-oriented; computer algebra; high-performance computing).

## 1.3. Applications of atomic theory

### 1.3.a. 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 lithographic techniques (13.5 nm).
- **Atomic clocks:** design of new frequency standards; requires very accurate data on hyperfine structures, atomic polarizabilities, light shift, blackbody radiation, etc.
- **Search for super-heavy elements:** beyond fermium ( $Z = 100$ ); '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 ?
- ...

### 1.3.b. Laser-particle acceleration: An alternative route

- **High power short-pulse lasers** with peak powers at the Terawatt or even Petawatt level enables one to reach focal intensities of  $10^{18} - 10^{23} \text{ W/cm}^2$ . These lasers are able also to produce a variety of **secondary radiation**, from **relativistic electrons and multi-MeV/nucleon ions** to **high energetic x-rays and gamma-rays**.
- **Applications:** The development of this **novel tool of particle acceleration** is presently explored in many different labs, and includes studies in fundamental and high-field physics as well as on medical technologies for diagnostics and tumor therapy.
- **Extreme Light Infrastructure (ELI):** a new EU-funded large-scale research infrastructure in which one (out of four) pillar is exclusively devoted to nuclear physics based on high intensity lasers. The aim is to push the limits of laser intensity three orders towards  $10^{24} \text{ W/cm}^2$ .
- This ELI project, a collaboration of 13 European countries, comprises three branches:
  - **Ultra High Field Science** to explore laser-matter interactions in an energy range where relativistic laws could stop to be valid;
  - **Attosecond Laser Science** to conduct temporal investigations of the electron dynamics in atoms, molecules, plasmas and solids at the attosecond scale;
  - **High Energy Beam Science**.

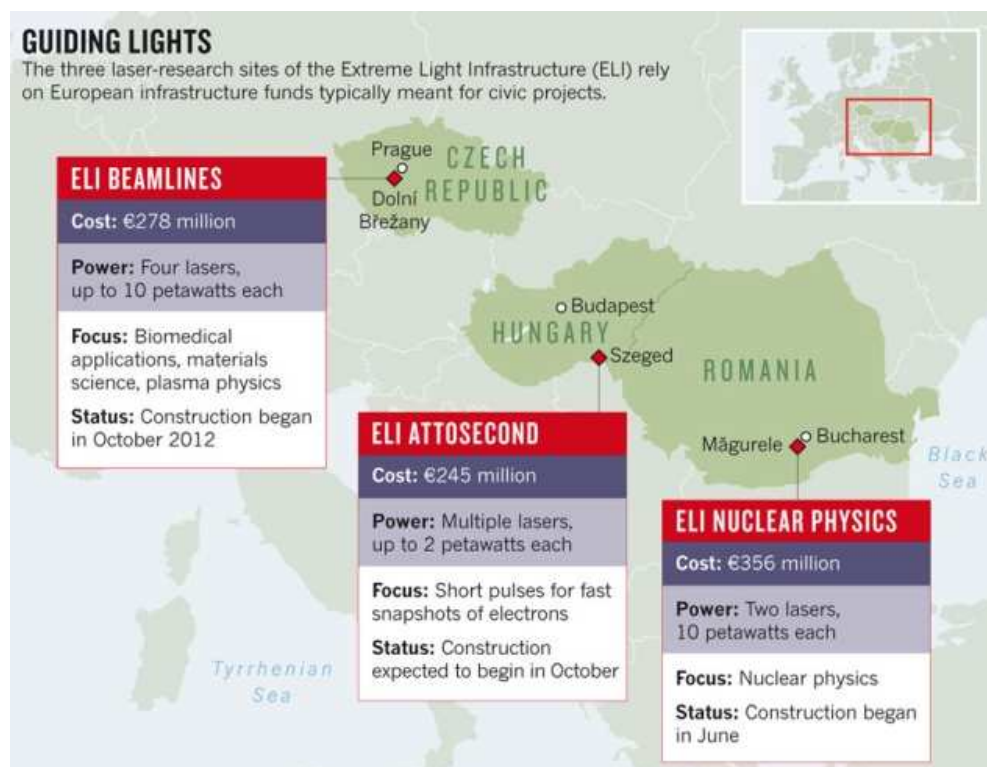


Figure 1.3.: Status of the ELI project 2014 (from: <http://www.nature.com>).

## 1. Atomic theory: A short overview

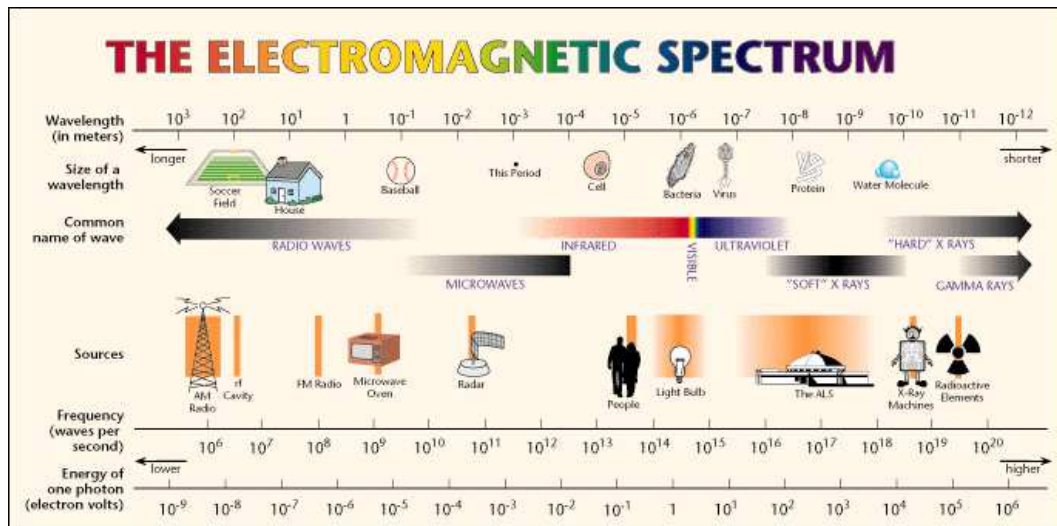


Figure 1.4.: Electromagnetic spectrum.

## 1.4. Overview to light-matter interactions

### 1.4.a. Properties of light

- Speed of light:  $3 \times 10^8$  m/s.
- Frequency & line width
- Intensity
- Propagation direction
- Polarization, angular momentum of light
- Duration, pulse length
- Coherence
- Amplitude and phase for mathematical description; complex notation.
- Artificial light sources have given rise to new and unmatched properties of light (maser, laser, FEL, ...).

### 1.4.b. Origin of light and its interaction with matter

- Atomic & molecular emission: spontaneous and stimulated emission of atoms; line frequency and frequency distributions; atomic emission spectrum is formed when lines are displayed a function of the wavelength or frequency.
- Synchrotron radiation: The emitted electromagnetic radiation when charged particles are accelerated radially; use of bending magnets, wigglers, undulators.
- Plasma radiation: Electromagnetic radiation emitted from a plasma, primarily by free electrons undergoing transitions to other free states or to bound states of atoms and ions, but also bound-bound transitions; bremsstrahlung and Compton radiation.

- **Blackbody radiation:** best possible emitter of thermal radiation which results in a characteristic, continuous spectrum that depends on the body's temperature. As the temperature increases beyond a few hundred degrees Celsius, black bodies start to emit visible wavelengths, appearing red, orange, yellow, white, and blue with increasing temperature. Planck's law; Rayleigh-Jeans law.

### Interactions of light with atoms and matter:

- Light can also undergo **reflection**, **scattering** and **absorption**; sometimes, the energy/heat transfer through a material is mostly radiative, i.e. by emission and absorption of photons (for example, in the core of the Sun).
- Light of different frequencies may travel through matter at different speeds; this is called **dispersion**. In some cases, it can result in extremely slow speeds of light in matter **slow light**.
- The factor by which the speed of light is decreased in a material is called the **refractive index** of the material. In a classical wave picture, the slowing can be explained by the light inducing electric polarization in the matter; the polarized matter then radiates new light, and the new light interferes with the original light wave to form a **delayed wave**.
- Alternatively, photons may be viewed as always traveling at  $c$ , even in matter. Due to the **interaction atomic scatters**, the photons get a shifted (delayed or advanced) phase. In this **bare-photon** picture, photons are scattered and phase shifted, while in the **dressed-state photon** picture, the photons are **dressed** by their interaction with matter and move with lower speed but, otherwise, without scattering or phase shifts.
- **Nonlinear optical processes** are another active research area, including topics such as two-photon absorption, self-phase modulation, and optical parametric oscillators. Though these processes are often explained in the **photon picture**, they do not require the assumption of photons. These processes are often modeled by treating some atoms or molecules as nonlinear oscillators.
- **Light-matter interactions:**
  - dispersion ➡ frequency spectrum
  - diffraction ➡ spatial frequency spectrum
  - absorption ➡ central frequency
  - scattering ➡ change in wavelength

### Different approaches for studying light-matter interactions:

- **Geometrical optics:**  $\lambda \ll$  object size ➡ daily experience; optical instrumentation; optical imaging.  
**intensity, direction, coherence, phase, polarization, photons**
- **Wave optics:**  $\lambda \approx$  object size ➡ interference, diffraction, dispersion, coherence; laser, resolution issues, pulse propagation, holography.  
**intensity, direction, coherence, phase, polarization, photons**
- **Laser and electro-optics:** reflection and transmission in wave guides; resonators, ...  
lasers, integrated optics, photonic crystals, Bragg mirrors, ...  
**intensity, direction, coherence, phase, polarization, photons**

## 1. Atomic theory: A short overview

- **Quantum optics:** photons and photon number statistics, fluctuation, atoms in cavities, laser cooling techniques ...  
intensity, direction, coherence, phase, polarization, photons

### 1.4.c. Light sources

#### Traditional light sources:

- **Celestial and atmospheric light:** Sun, stars, aurorae, Cherenkov, ...
- **Terrestrial sources:** bioluminescence (glowworm), volcanic (lava, ...)
- **Combustion-based:** candles, lantern, argon flash, ...
- **Electric-powered:** halogen lamps, ...
- **Gas discharge lamps:** neon and argon lamps; mercury-vapor lamps, ...
- **Laser & laser diodes:** gas, semi-conductor, organic, ...

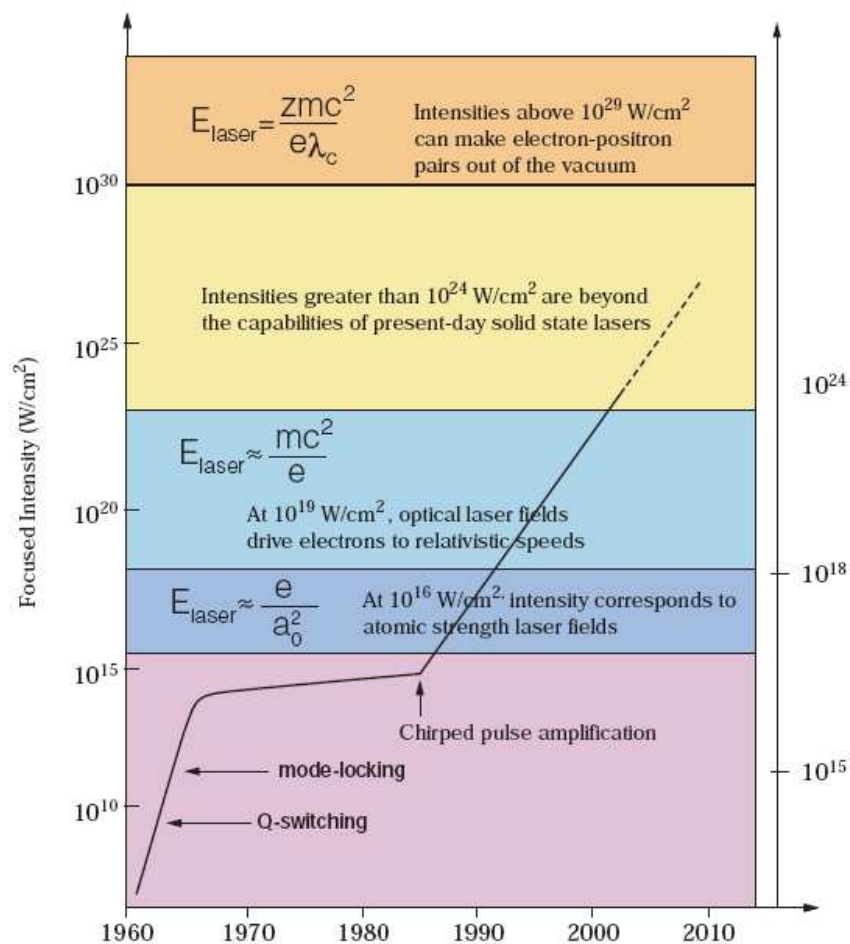


Figure 1.5.: The exponential increase in achievable laser intensity over the last 50 years; taken from: *Controlling the Quantum World*, page 88.

#### Recently developed (new) light sources:



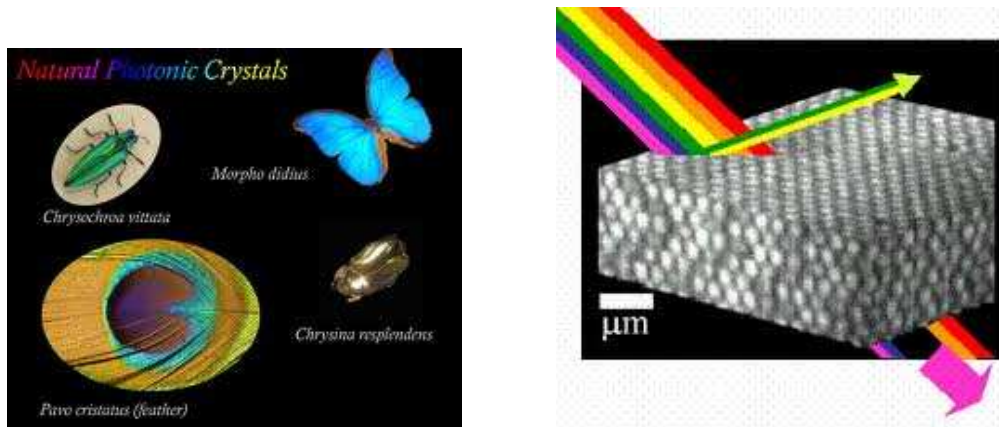


Figure 1.6.: Left: Photonic crystals from nature. Right: Photonic crystals from artificial nanostructures.

- **LED's:** Semiconductor diodes that consists out of a chip of semi-conducting material and a **p-n (positive-negative) junction**. When connected to a power source, the current flows from the p- to the n-side. **LED's generate little or no long wave IR or UV**, but convert only 15-25 % of the power into visible light; the remainder is converted to heat that must be conducted from the LED die (p-n junction) to the underlying circuit board and heat sinks.
- **Laser-plasma light sources:** The application of a dense plasma focus as a **light source for extreme ultraviolet (EUV) lithography**.
- **High-harmonic generation (HHG):** tunable table-top source of **XUV/Soft X-rays** that is usually synchronised with the driving laser and produced with the same repetition rate; HHG strongly depends on the driving laser field and, therefore, the high harmonics have similar temporal and spatial coherence properties.
- **Free-electron lasers (FEL):** use a relativistic electron beam as the lasing medium which moves freely through a magnetic structure. **FEL's can cover a very wide frequency range and are well tunable**, ranging currently from microwaves, through terahertz radiation and infrared, to the visible spectrum, to ultraviolet, to X-rays.

#### Further reading (Attosecond Light Sources):

- Read the article by David Villeneuve, La Physique au Canada **63** (2009) 65; cf. 1.2-Villeneuve.pdf on the web page of the lecture.

#### 1.4.d. Atomic physics & photonics: Related areas and communities

- **Spectroscopy:** to study details of the medium, for instance, photon spectroscopy, **electron spectroscopy**, Raman spectroscopy, ...  
Spectroscopic data are often represented by a spectrum, a plot of the response of interest as a function of wavelength or frequency.
- Different spectroscopic techniques are often distinguished by their **type of radiative energy** (infrared-, x-ray-, etc.) **nature of interaction** (absorption-, emission-, coherent-, ...) or **type of materials** (atoms, molecular, crystal, nuclei, ...).

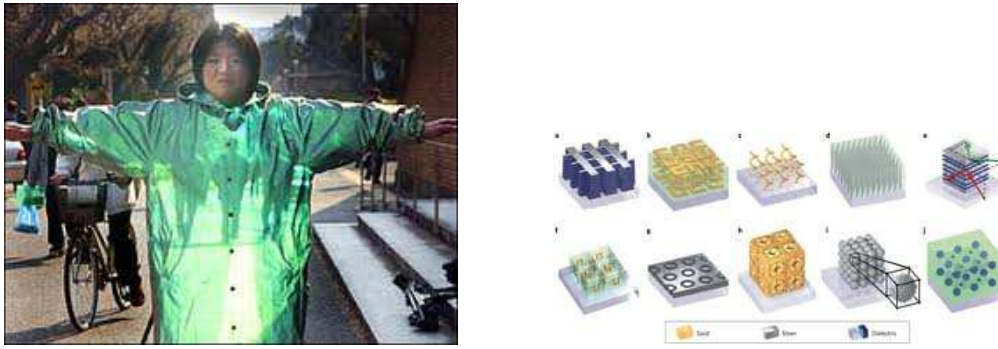


Figure 1.7.: Left: The invisibility of meta materials. Right: Some 3d structures.

- **Interferometry:** family of techniques in which electromagnetic waves are superimposed in order to extract information about the waves and their properties. An instrument used for that is called an **interferometer**. Interferometry is an important investigative technique in the fields of **astronomy**, **fiber optics**, **engineering metrology**, **optical metrology**, **oceanography**, **seismology**, **quantum mechanics**, **nuclear and particle physics**, **plasma physics**, **remote sensing** and **biomolecular interactions**.
- **Metrology:** is the science of measurement. Metrology includes all theoretical and practical aspects of measurement.
- **Design of ‘new’ media:** **Photonic crystals** are periodic optical nanostructures that are designed to affect the motion of photons in a similar way that periodicity of a semiconductor crystal affects the motion of electrons. **Photonic crystals occur in nature and in various forms.**  
**Meta materials** are artificial materials engineered to have properties that may not be found in nature. Metamaterials usually **gain their properties from structure rather than composition**. Materials with **negative refractive index**; **creation of superlenses** which may have a spatial resolution below that of the wavelength; invisibility and cloaking.
- **Electro-magnetic optics:** the study of the propagation and evolution of electromagnetic waves, including topics of interference and diffraction. Besides the usual branches of analysis, this area **includes geometric topics such as the paths of light rays**.
- **Relativistic optics:** The generation of ultrahigh intense pulse has open up a new field in optics, the field of relativistic nonlinear optics, where the nonlinearity is dictated by the **relativistic character of the electron**. This young field has already produced a series of landmark experiments. Among them are the generation of energetic beams of particles (electrons, protons, ions, positrons), as well as beams of X-rays and  $\gamma$ -rays.
- **Quantum electronics:** A term that is sometimes used for dealing with the effects of quantum mechanics on the behavior of electrons in matter as well as their interactions with photons. Nowadays, it is not seen so much as a sub-field of its own but has been absorbed into **solid state physics**, **semiconductor physics**, and several others.



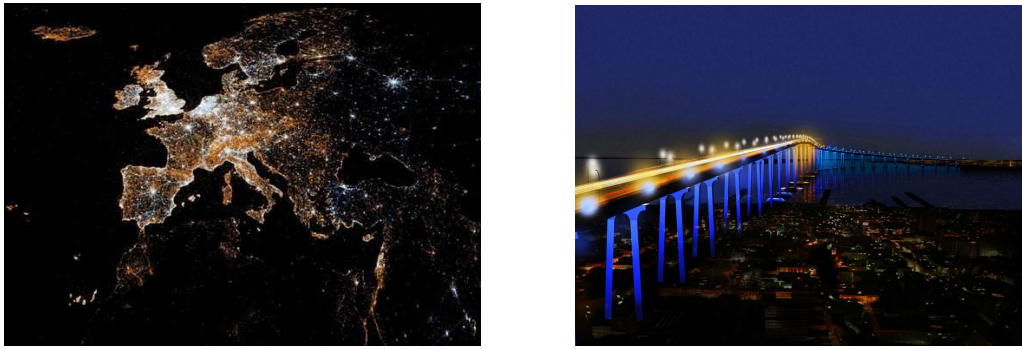


Figure 1.8.: Left: Europe at night. Right: Lighting up the famous, 2.5 mile long San Diego Bridge..

### 1.4.e. Applications of light-atom interactions

#### Photonics and light-atom interactions everywhere

From: Harnessing Light; Optical Science and Engineering for the 21st Century (The National Academies of Sciences, Engineering, and Medicine, 2001).

John reached over and shut off the alarm (1) clock. He turned on the lights (2) and got up. Downstairs, he began to make his morning coffee and turned (3) on the television to check the weather (4) and (5) forecast. Checking the time on the kitchen clock (6) he poured his coffee and went to the solarium (7) to sit and read the newspaper (8).

Upstairs, the kids were getting ready for school. Julie was listening to music (9) while getting dressed (10). Steve felt sick, so Sarah, his mother, checked his temperature (11). Julie would go to school and Steve would stay home.

John drove to work in his new car (12), a high-tech showcase. He drove across a bridge (13), noticing the emergency telephones (14) along the side of the freeway. He encountered traffic signals (15), highway signs (16), and a police officer scanning for speeders (17).

- (1) light-emitting diode (LED) displays.
- (2) energy saving compact fluorescent lamps.
- (3) infrared remote controls.
- (4) optical fibers for distributed cable television.
- (5) satellite-based optical weather images.
- (6) liquid crystal displays (LCDs).
- (7) temperature-moderating window coatings.
- (8) phototypesetting.
- (9) compact disks.
- (10) laser fabric cutting.
- (11) infrared non-contact 'ear' thermometers.
- (12) infrared automobile security systems; optical monitors for antilock brakes; LED, LCD, and optical fiber dashboard displays; LED taillights.
- (13) optical-fiber sensors to monitor bridge integrity.
- (14) solar power for emergency services.
- (15) LED traffic lights.
- (16) high-reflectivity surfaces for highway signs.
- (17) laser traffic radar.

#### Web link (A Day in the Life with Photonics):

➤ [http://www.quebecphotonic.ca/a\\_propos\\_en.html](http://www.quebecphotonic.ca/a_propos_en.html)

#### LED light sources: Advantages and shortcomings

- **High conversion efficiency:** When designed properly, an LED circuit will approach 80 % efficiency, which means 80 % of the electrical energy is converted to light energy.
- The **long operational life** of current white LED lamps is 100,000 hours. This is 11 years of continuous operation, or 22 years of 50 % operation.

## 1. Atomic theory: A short overview

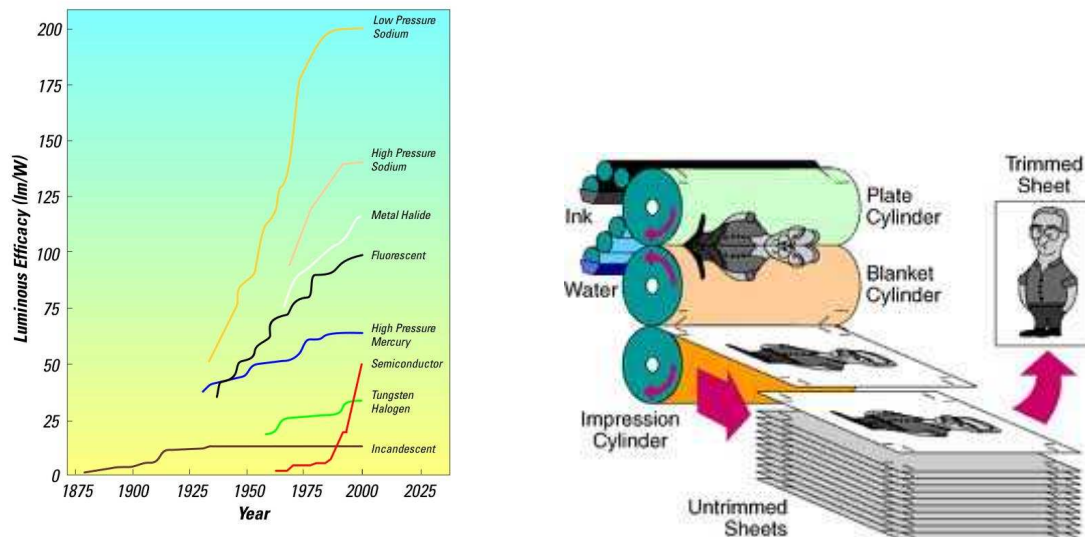


Figure 1.9.: Left: Increase in light efficiency over the last 100 years. Right: Principle of lithography.

- A new technology appeared since the mid 1990s, based on InGaAlP and InGaN compound semiconductors, and quickly opened up large markets for LEDs; between 1995 and 2005, the LED market grew at a remarkable average annual rate of 42 %.
- **Three large application areas:** signalling (traffic signals, automobile brake lights); displays (outdoor full-colour video screens, single-colour variable-message signs); and back-lighting (automobile instrument panels, mobile-phone LCD displays and keypads). In 2005, the LED market had grown to 3.9 billion dollars.
- LEDs are (still) much more expensive, though this need to be compared with costs for replacement, etc.
- In the (near) future, white LED lighting applications are going to be powerful and cheap enough to replace incandescent lighting at home and in street lights, outdoor signs, and offices.

## Lithography

Lithography is a method for printing using a stone (lithographic limestone) or a metal plate with a completely smooth surface. Invented in 1796 by Bavarian author Alois Senefelder as a cheap method of publishing. In modern lithography, the image is made of a polymer coating applied to a flexible aluminum plate. To print an image lithographically, the flat surface of the stone plate is roughened slightly etched and divided into hydrophilic regions that accept a film of water, and thereby repel the greasy ink; and hydrophobic regions that repel water and accept ink because the surface tension is greater on the greasy image area, which remains dry. Today, this term refers to a large class of such 'printing' techniques.

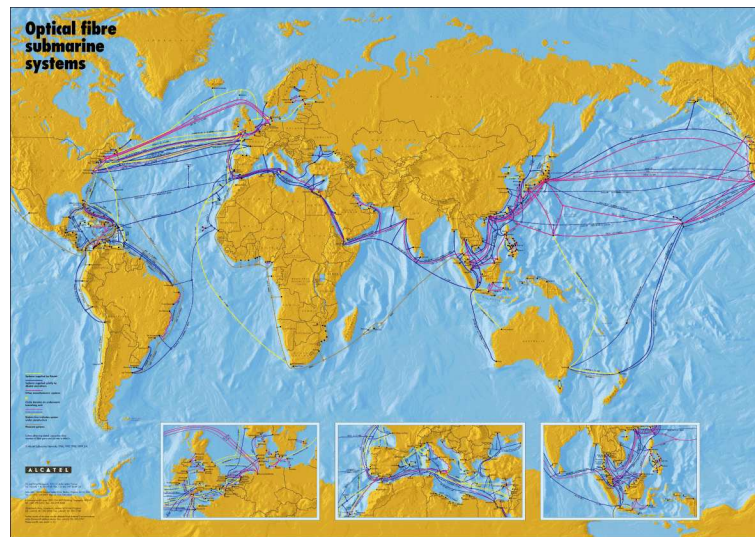


Figure 1.10.: The transatlantic cable system continues to grow.

**Telecommunication, Medicine & life sciences**

**Sensorics**

**Micro- and nano-optics**



## 2. Atoms in static external fields

### Change of level structure and line spectra in external fields due to:

- Splitting of degenerate levels.
- Shift of energy levels.
- Superposition and hybridization of energy levels.

Usually, the level splitting in external fields is treated perturbatively by studying the Hamiltonian:  $H = H_o + H'$ .

### 2.1. Atoms in homogeneous magnetic effects (Zeeman effect)

#### Splitting in external B-field due to:

- Particle with magnetic moment  $\boldsymbol{\mu}$  has energy:  $e = -\boldsymbol{\mu} \cdot \mathbf{B}$
- Magnetic moment of electron due to its orbital angular momentum:

$$\boldsymbol{\mu}_l = -\frac{e\hbar}{2m} \mathbf{l} = -\mu_B \frac{\mathbf{l}}{\hbar} \quad \mu_B = \frac{e\hbar}{2m} \quad \dots \text{Bohr's magneton.}$$

- Spin magnetic moment:  $\boldsymbol{\mu}_s = -g_s \frac{e\hbar}{2m} \mathbf{s} = -g_s \mu_B \frac{\mathbf{s}}{\hbar}$  with  $g_s = 2$  (Dirac theory).
- *g-factor*: one of the most accurate quantities in physics; differs for free and bound electrons and generally depends on the details of binding  $\rightsquigarrow$   *$g_J$ -factor of atomic levels*.
- Total Hamiltonian (atom 'plus' magnetic field):

$$\begin{aligned} H &= -\frac{\Delta}{2} - \frac{Z}{r} + \underbrace{\xi(r) \mathbf{l} \cdot \mathbf{s}}_{\text{fine-structure, } H_{\text{FS}}} + \underbrace{\mu_B (\mathbf{l} + 2\mathbf{s}) \cdot \mathbf{B}}_{\text{B-field interaction, } H_{\text{B}}} \\ &= H_o + H_{\text{FS}} + \mu_B (\mathbf{l}_z + 2\mathbf{s}_z) \cdot B_z \quad \mathbf{B} \parallel \mathbf{e}_z. \end{aligned}$$

#### Often, one distinguishes three effects of a homogeneous magnetic field:

- Normal Zeeman effect: Splitting of atomic level (energies) with total spin  $S = 0$  into usually three  $\sigma^\pm$  and  $\pi$ -components.
- Anomalous Zeeman effect: Splitting of atomic level (energies) with total spin  $S \neq 0$ .
- Paschen-Back effect: Limit of the anomalous Zeeman effect for strong fields, in which the spin-orbit coupling is broken by the external magnetic field.

## 2. Atoms in static external fields

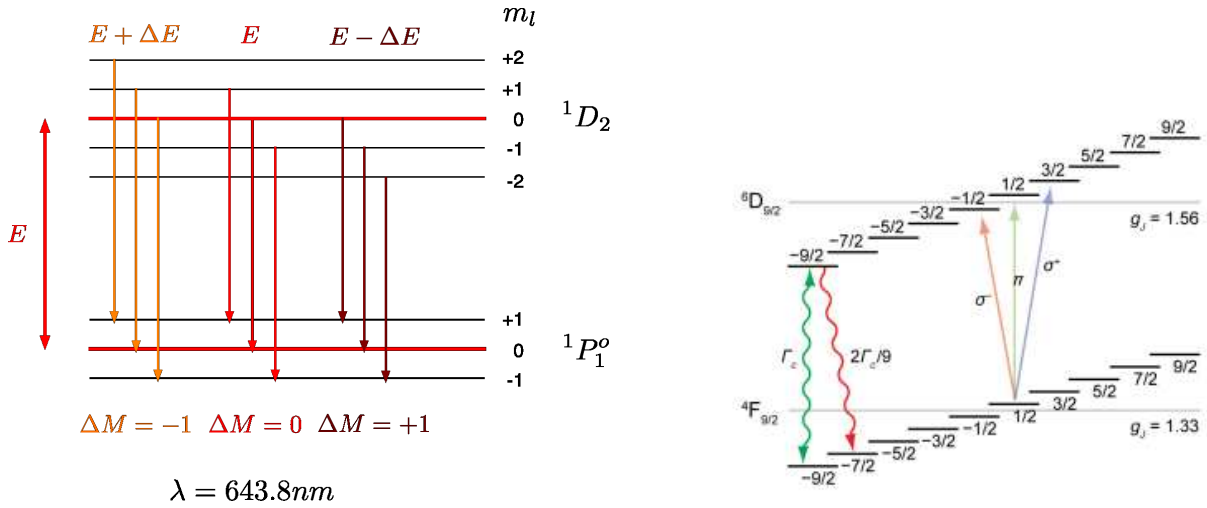


Figure 2.1.: Left: Scheme of the energy levels and dipole transitions that lead to the red Cd line. Without the magnetic field, all levels with different  $m_l$  values are degenerate. Right: Calculated energy level diagram of  $^{192}\text{Os}^-$  in an external magnetic field including the hyperfine structure. From [wanda.fiu.edu/teaching](http://wanda.fiu.edu/teaching) and [www.mpi-hd.mpg.de/kellerbauer](http://www.mpi-hd.mpg.de/kellerbauer)

### 2.1.a. Normal Zeeman effect ( $S = 0$ )

Atomic Hamiltonian & level splitting: ... (Blackboard)

### 2.1.b. Anomalous Zeeman & Paschen-Back effect

Coupling of different strength:

- In practice, both the orbital and spin motion gives rise to a magnetic moment and, hence, to the potential energy in the field:

$$\begin{aligned}
 H' &= -(\boldsymbol{\mu}_l + \boldsymbol{\mu}_s) \cdot \mathbf{B} \quad \text{with} \quad \mathbf{B} = B \mathbf{e}_z \\
 &= -(\mu_{l,z} + \mu_{s,z}) \cdot B = \frac{e\hbar B}{2m} (l_z + g_s s_z) = \frac{e\hbar B}{2m} (j_z + (g_s - 1) s_z)
 \end{aligned}$$

- This interaction (term) has to be compared with the spin-orbit interaction

$$H'' = H^{so} = \frac{g\hbar\alpha Z}{4m^2 c} \frac{\mathbf{l} \cdot \mathbf{s}}{r^3}$$

- There are three cases due to this comparison:

- anomalous Zeeman effect:  $H' \ll H^{so}$
- Paschen-Back effect:  $H' \gg H^{so}$
- Intermediate case:  $H' \simeq H^{so}$

i)  $H' \ll H^{so}$ : ... (Blackboard)

ii)  $H' \gg H^{so}$ : ... (Blackboard)

### 2.1.c. Zeeman effect for different field strengths B

With increasing field strength B: ... (Blackboard)

## 2.2. Atoms in homogenous electric fields (Stark effect)

### 2.2.a. Linear Stark effect

Atom-field Hamiltonian: ... (Blackboard)

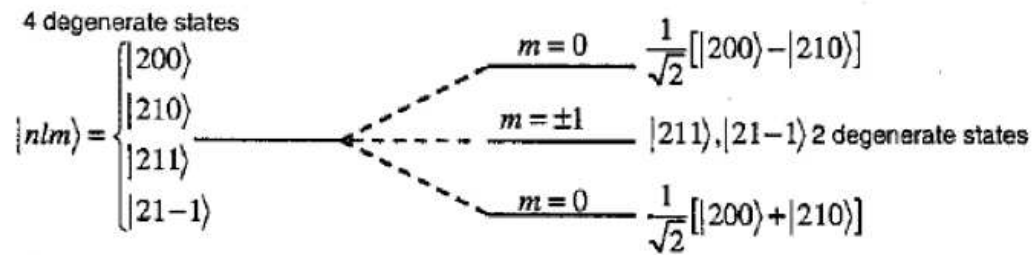


Figure 2.2.: The 1st excited state is split from 4 degenerate states to 2 distinct, and 1 degenerate state.

### 2.2.b. Quadratic Stark effect

Hydrogen in the 1s ground state: ... (Blackboard)

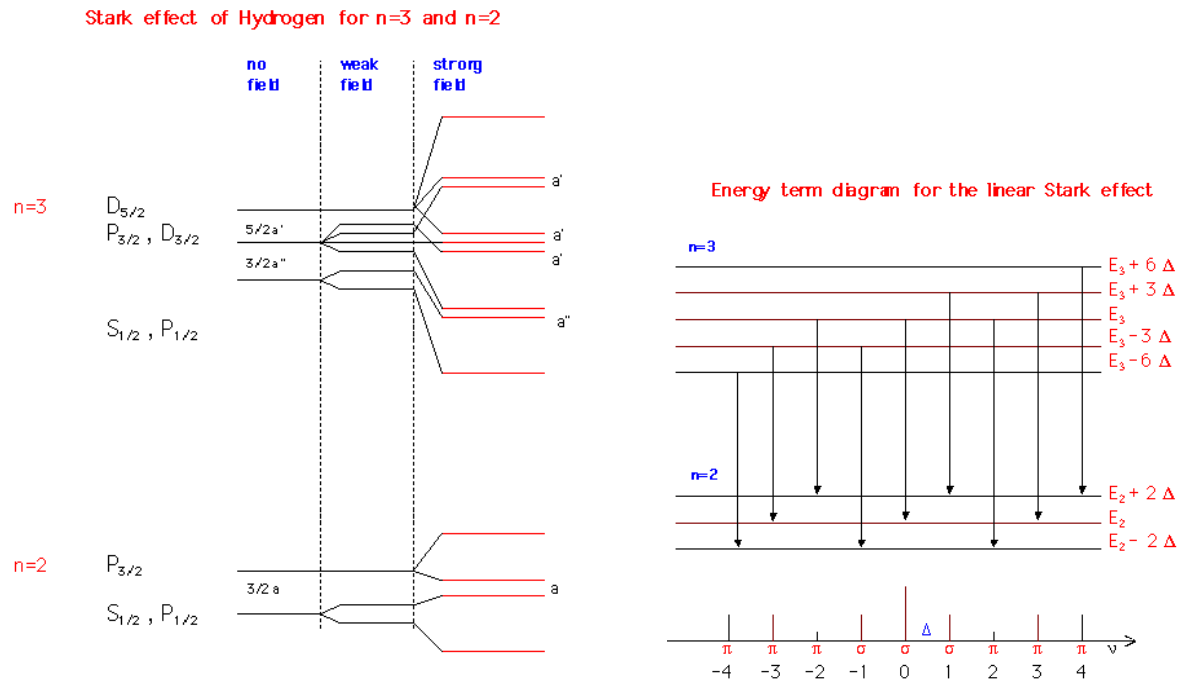


Figure 2.3.: Stark effect on the  $n = 2 \rightarrow 3$  transitions in atomic hydrogen. Left: The electric field is said to be *strong* when the splitting of the energy levels becomes larger than the fine-structure splitting. Right: The transition energy without the fine-structure. From <http://www.afs.enea.it/apruzzes/Spectr/Stark>.



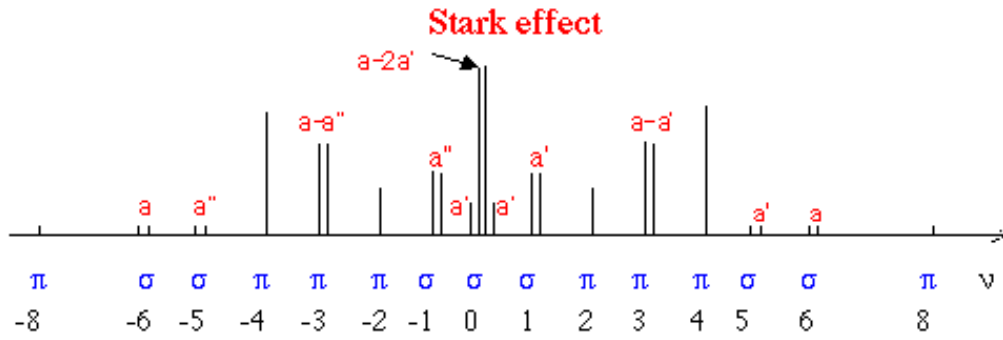


Figure 2.4.: The  $n = 2 \rightarrow 3$  transition energy including the fine-structure of the levels. From <http://www.afs.enea.it/apruzzes/Spectr/Stark>.



### 3. Interactions of atoms in weak (light) fields

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

#### 3.1. Radiative transitions

##### 3.1.a. Einstein's A and B coefficients

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

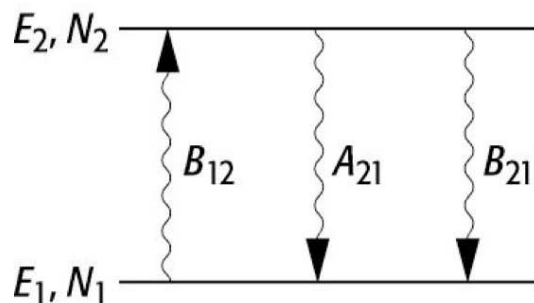


Figure 3.1.: Model of the induced and spontaneous processes.

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

#### Einstein's argumentation and coefficients:

➤ Einstein's rate equation

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

$$= P_{\text{emission}} N_2 - P_{\text{absorption}} N_1$$

➤ No field,  $\rho(\omega) = 0$ :

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

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

### 3. Interactions of atoms in weak (light) fields

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

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

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

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

For each pair  $ij$  of atomic levels, the emission and absorption is in equilibrium, and independent of other possible transition processes.

➤ **Generalized field-free case:**

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

➤ **Ratio  $A_{ji} : B_{ji} : B_{ij}$ :**

Thermal equilibrium:

$$-\frac{N_j}{N_i} = \frac{g_j}{g_i} \exp\left(-\frac{\hbar\omega_{ij}}{kT}\right)$$

$$g(\omega_{ij}) = \frac{\omega_{ij}^2}{\pi^2 c^3} \frac{\hbar\omega_{ij}}{\exp\left(-\frac{\hbar\omega_{ij}}{kT}\right) - 1}$$

Planck's black-body radiation

➤ **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 the state of the atomic ensemble.

#### 3.1.b. Additional material to Einstein relations and others

Some additions: ... (Blackboard)

Photoabsorption and emission of  $\sigma$ - vs.  $\pi$ -light ... (Blackboard)

Line-width contributions in atomic spectroscopy ... (Blackboard)

**Example (Line-width contributions for the yellow sodium line):** This 'yellow 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.

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 widths.

### 3.1.c. Transition amplitudes and probabilities

radiation 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: ... (Blackboard)

Hamiltonian function of a particle in an electro-magnetic field:

$$\begin{aligned}
 H &= \frac{1}{2m}(\mathbf{p} + e\mathbf{A})^2 - e\phi + V & \mathbf{E} &= -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t} \\
 & & \mathbf{B} &= \text{rot } \mathbf{A} \\
 & & (\phi, \mathbf{A}) & \dots 4 - \text{comp. vector potential}
 \end{aligned}$$

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

Special case: Superposition of plane waves

$$\begin{aligned}
 \phi &= 0 \\
 \mathbf{A} &= \mathbf{A}_o e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + \mathbf{A}_1 e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \\
 \text{div } \mathbf{A} &= 0 & \text{Coulomb gauge} & \quad [\mathbf{p}, \mathbf{A}] = 0
 \end{aligned}$$

$$H' = \frac{e}{m} \mathbf{A} \cdot \mathbf{p} + \underbrace{\frac{e^2}{2m} \mathbf{A}^2}_{\text{negligible}}$$

### 3. Interactions of atoms in weak (light) fields

$H_0 \oplus$  time-dependent perturbation  $\Rightarrow$  time-dependent perturbation theory.

Absorption probability: ... (Blackboard)

## 3.2. Electric-dipole interactions and higher multipoles

### 3.2.a. Electric-dipole approximation

Consider a light field with plane-wave structure  $\sim e^{i\mathbf{k}\cdot\mathbf{r}}$  and  $|\mathbf{k}| = \frac{2\pi}{\lambda}$ ;

$\Rightarrow$  visible light:  $\lambda \approx 500 \text{ nm}$  ... 1000-10000 atomic radii

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

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

Evaluation of the Einstein A coefficients: ... (Blackboard)

### 3.2.b. Selection rules and discussion

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

Electron temperature  $T_e$ :

$$\frac{N_j}{N_i} = \frac{g_j}{g_i} e^{-\frac{(E_j - E_i)}{kT}}$$

- $T_e \approx 10^4 \text{ K} \rightsquigarrow kT_e \sim 1 \text{ eV}$
- $T_e \approx 300 \text{ K} \rightsquigarrow kT_e \sim 1/40 \text{ eV}$
- $T_e \rightarrow \infty$

Selection rules for bound-bound transitions: ... (Blackboard)

### 3.2.c. Higher multipole components

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

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

$$(M1) \sim \frac{\omega^2}{c^2} \left| \left\langle j \left| \frac{e\hbar}{2m} \mathbf{l}_a \right| i \right\rangle \right|^2 = \frac{\omega^2}{c^2} |\langle j | \boldsymbol{\mu}_a | i \rangle|^2$$

$$\boldsymbol{\mu} = \frac{e\hbar}{2m} \mathbf{l} \quad \dots \text{magnetic moment of electron}$$

$$(E2) \sim \frac{\omega^4}{c^2} |\langle j | e x_a x_b | i \rangle|^2$$

$x_a x_b$  ... second-order tensor (components)

Intensity ratio for hydrogen-like wave functions:

$$E1 : M1 : E2 = 1 : \alpha^2 : \alpha^2$$

### 3.2.d. Dipole transitions in many-electron atoms

For a weak radiation field, its interaction with the atom can be described perturbatively by the Hamiltonian

$$H' = \frac{e}{m} \mathbf{A} \cdot \sum_k \mathbf{p}_k$$

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

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

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

**spherical component of the (many-electron) dipole operator**

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

Spherical tensor operators: ... (Blackboard)

Gauge forms of the transition probabilities: ... (Blackboard)

Selection rules for electric-dipole radiation: ... (Blackboard)

## 3.3. Multipole expansions of the radiation field

Multipoles ... ... (Blackboard)

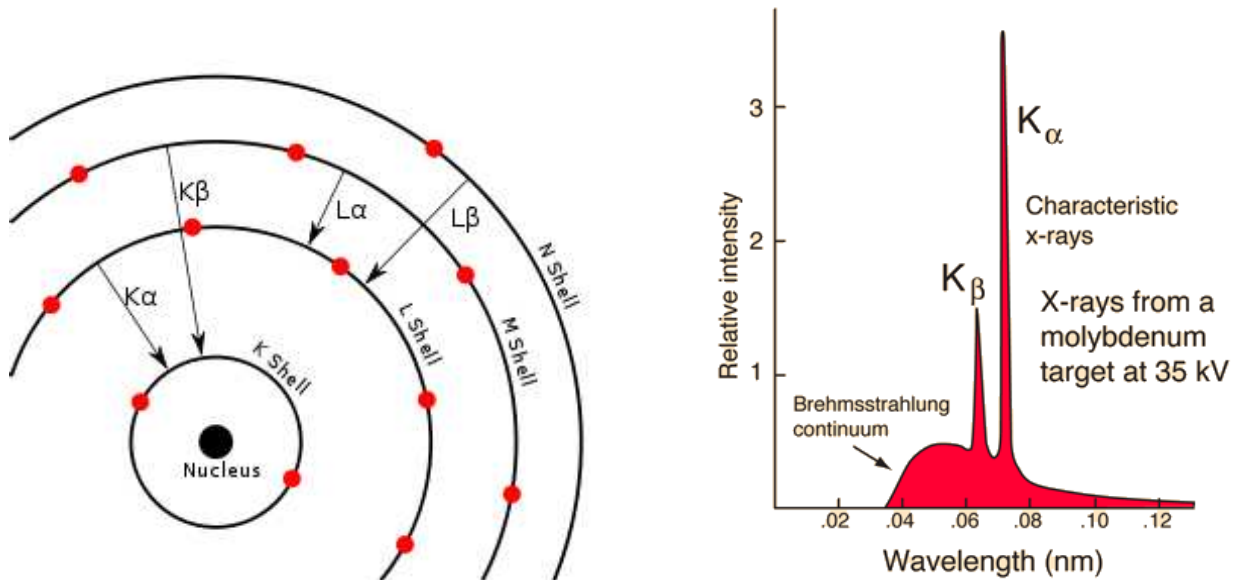


Figure 3.2.: Left: Characteristic x-rays are emitted from heavy elements when their electrons make transitions between the lower atomic energy levels. Right: The characteristic  $K_{\alpha,\beta}$  x-ray emission appears as two sharp peaks in the photon spectra following the production of a vacancy in 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

### 3.4. Characteristic radiation

- **Notation:**  $e^- + A \longrightarrow e^- + A^{*+} \longrightarrow e^- + A^+ + \hbar\omega; \quad \hbar\omega = E_i - E_f.$
- **Mosley's law:** The energies of the characteristic radiation (and absorption edges) follow approximately Balmer's rule:

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

where  $Z_{\text{eff}} = Z - S$  with screening number  $S$  varies also for the same element if different lines and scenarios are considered.

➤

Characteristic x-ray absorption ... (Blackboard)

### 3.5. Atomic photoionization

**Photo excitation with subsequent fluorescence emission:**

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



Siegbahn	IUPAC	Siegbahn	IUPAC	Siegbahn	IUPAC	Siegbahn	IUPAC
K $\alpha_1$	K-L <sub>3</sub>	L $\alpha_1$	L <sub>3</sub> -M <sub>5</sub>	L $\gamma_1$	L <sub>2</sub> -N <sub>4</sub>	M $\alpha_1$	M <sub>5</sub> -N <sub>7</sub>
K $\alpha_2$	K-L <sub>2</sub>	L $\alpha_2$	L <sub>3</sub> -M <sub>4</sub>	L $\gamma_2$	L <sub>1</sub> -N <sub>2</sub>	M $\alpha_2$	M <sub>5</sub> -N <sub>6</sub>
K $\beta_1$	K-M <sub>3</sub>	L $\beta_1$	L <sub>2</sub> -M <sub>4</sub>	L $\gamma_3$	L <sub>1</sub> -N <sub>3</sub>	M $\beta$	M <sub>4</sub> -N <sub>6</sub>
K $^I\beta_2$	K-N <sub>3</sub>	L $\beta_2$	L <sub>3</sub> -N <sub>5</sub>	L $\gamma_4$	L <sub>1</sub> -O <sub>3</sub>	M $\gamma$	M <sub>3</sub> -N <sub>5</sub>
K $^{II}\beta_2$	K-N <sub>2</sub>	L $\beta_3$	L <sub>1</sub> -M <sub>3</sub>	L $\gamma_4'$	L <sub>1</sub> -O <sub>2</sub>	M $\zeta$	M <sub>4,5</sub> -N <sub>2,3</sub>
K $\beta_3$	K-M <sub>2</sub>	L $\beta_4$	L <sub>1</sub> -M <sub>2</sub>	L $\gamma_5$	L <sub>2</sub> -N <sub>1</sub>		
K $^I\beta_4$	K-N <sub>5</sub>	L $\beta_5$	L <sub>3</sub> -O <sub>4,5</sub>	L $\gamma_6$	L <sub>2</sub> -O <sub>4</sub>		
K $^{II}\beta_4$	K-N <sub>4</sub>	L $\beta_6$	L <sub>3</sub> -N <sub>1</sub>	L $\gamma_8$	L <sub>2</sub> -O <sub>1</sub>		
K $\beta_{4x}$	K-N <sub>4</sub>	L $\beta_7$	L <sub>3</sub> -O <sub>1</sub>	L $\gamma_8'$	L <sub>2</sub> -N <sub>6(7)</sub>		
K $^I\beta_5$	K-M <sub>5</sub>	L $\beta_7'$	L <sub>3</sub> -N <sub>6,7</sub>	L $\eta$	L <sub>2</sub> -M <sub>1</sub>		
K $^{II}\beta_5$	K-M <sub>4</sub>	L $\beta_9$	L <sub>1</sub> -M <sub>5</sub>	L $\iota$	L <sub>3</sub> -M <sub>1</sub>		
		L $\beta_{10}$	L <sub>1</sub> -M <sub>4</sub>	L $\varsigma$	L <sub>3</sub> -M <sub>3</sub>		
		L $\beta_{15}$	L <sub>3</sub> -N <sub>4</sub>	L $\tau$	L <sub>3</sub> -M <sub>2</sub>		
		L $\beta_{17}$	L <sub>2</sub> -M <sub>3</sub>	L $\upsilon$	L <sub>3</sub> -N <sub>6,7</sub>		
				L $\nu$	L <sub>2</sub> -N <sub>6(7)</sub>		

Figure 3.3.: While the x-ray (analytical) community still largely uses the so-called Siegbahn notation, the IUPAC notation is consistent with notation used for Auger electron spectroscopy, though the latter one is slightly more cumbersome. From nau.edu/cefns/labs

### 3.5.a. Photoionization amplitudes

- Photoionization from the ground state for  $\hbar\omega > I_p$  (1st ionization potential).
- For a weak photon field, this ionization is again caused by the Hamiltonian

$$H' = \frac{e}{m} \mathbf{A} \cdot \sum_i \mathbf{p}_i$$

- The (induced) photo excitation and ionization is usually described by means of cross sections:

$$\sigma_{i \rightarrow f}(\omega) \sim \omega^3 \sum_q \left| \langle (\gamma_f J_f, \epsilon_f \kappa_f) J' M' | P_q^{(1)} | \gamma_i J_i M_i \rangle \right|^2.$$

## 3.6. Radiative electron capture

➤

$$e^-(E_{\text{kin}}) + A \longrightarrow A^{+*}(E_i) + \hbar\omega \longrightarrow$$

➤

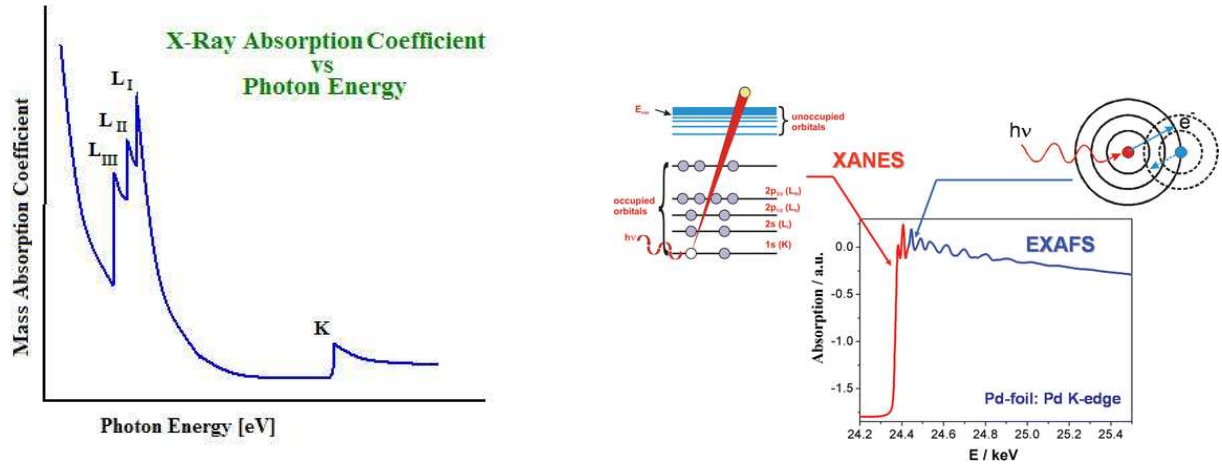


Figure 3.4.: Left: Edges in the x-ray absorption coefficients as function of the photon energy. Right: Principle of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. From chemwiki.ucdavis.edu and pubs.rsc.org

### 3.7. Bremsstrahlung

- $e^- + A \Rightarrow e^- + A + \gamma$
- Maximal electron energy  $E_{\max} = eU$  leads to a minimum wave lengths

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

- **Examples:**  $U = 10\text{kV} \rightsquigarrow \lambda \sim 1 \text{ \AA}$ ;  $U = 100\text{kV} \rightsquigarrow \lambda \sim 0.1 \text{ \AA}$

### 3.8. Non-radiative transitions: Auger transitions and autoionization

- Auger transitions and autoionization are caused by the inter-electronic interactions.
- Kinetic energy of emitted electrons:

$$E_{kin} = E(\text{initial}, N) - E(\text{final}, N - 1)$$

- **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 theoretically ver similar; they are both described by the **Auger rate**

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

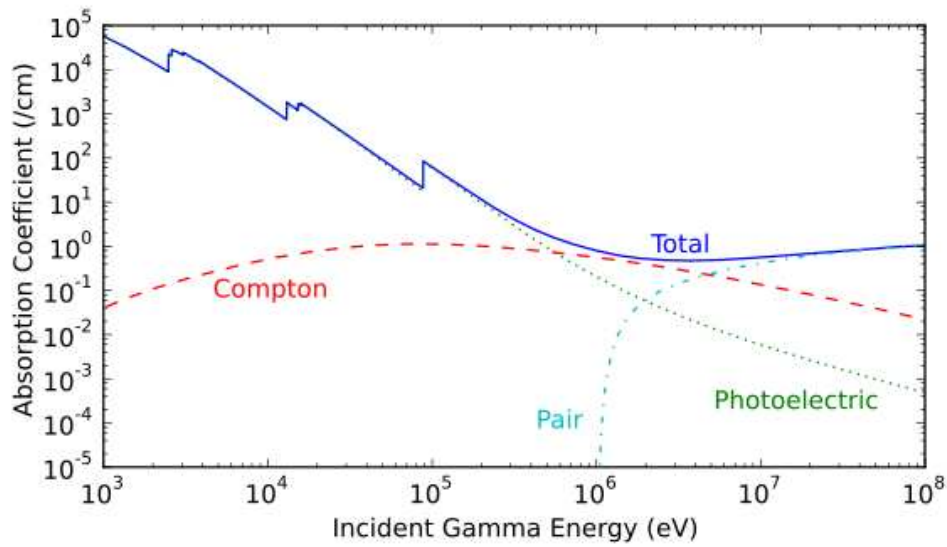


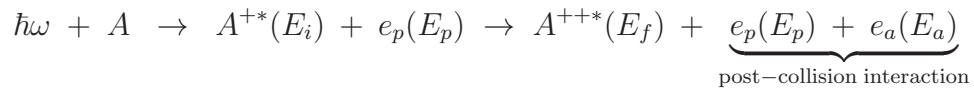
Figure 3.5.: The total absorption coefficient of lead (atomic number 82) for gamma rays, plotted versus gamma energy, and the contributions by the three effects. Above 5 MeV, pair production starts to dominate.

➤ Selection rules for Auger transitions:

$$\Delta J = \Delta M = 0 \quad (\text{strict})$$

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

➤ Excitation and subsequent decay:



### 3.9. Beyond single-photon or single-electron transitions

Weak processes with several photons and/or electrons: ... (Blackboard)

### 3. Interactions of atoms in weak (light) fields

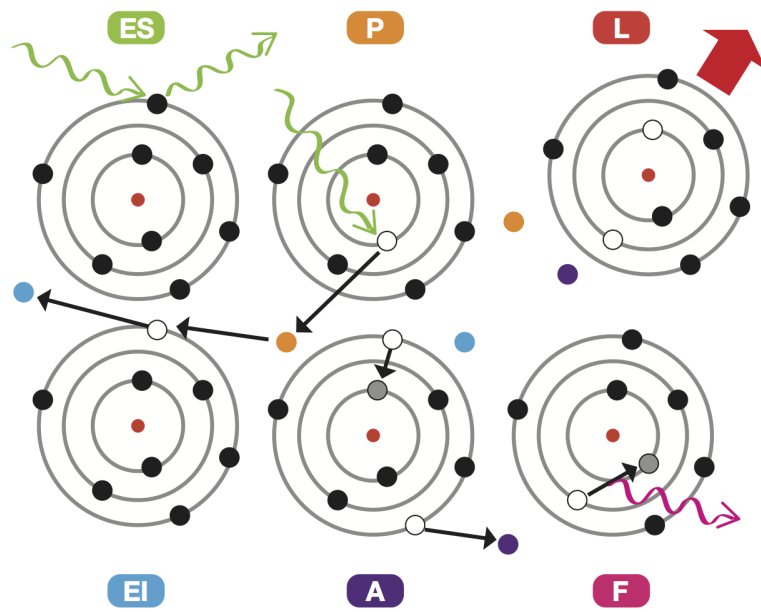


Figure 3.6.: Comparison of different ionization and subsequent decay processes in atoms.

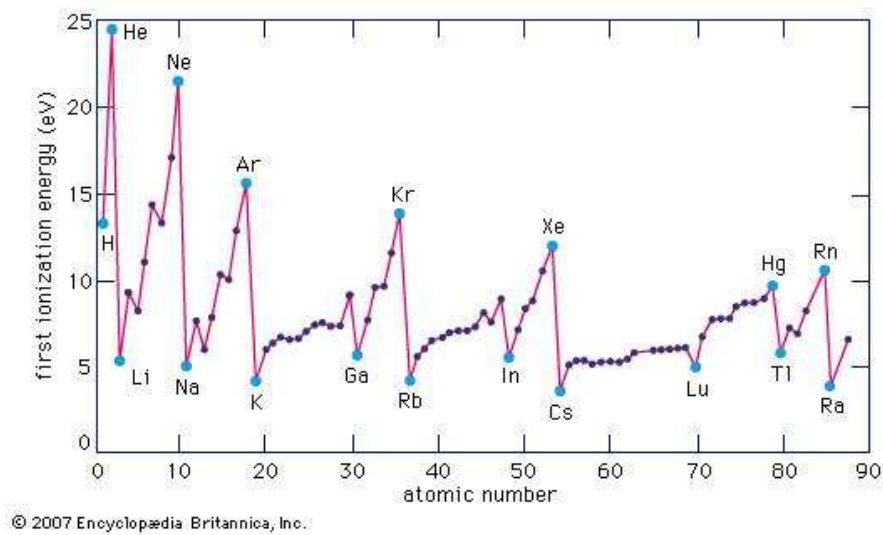


Figure 3.7.: First ionization potential as function of the nuclear charge of elements.

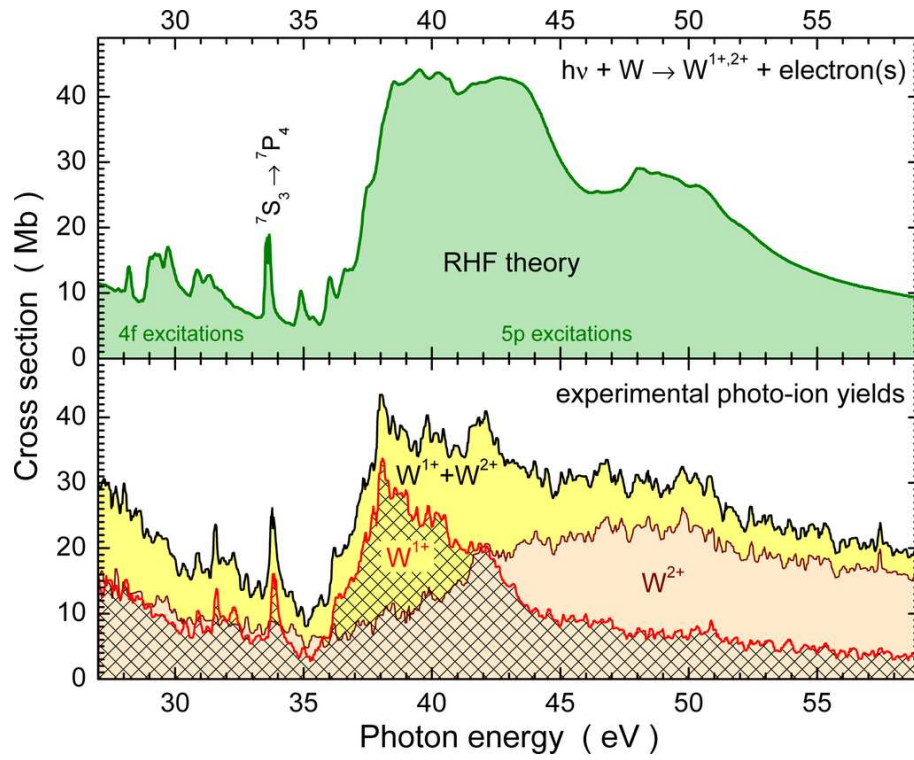


Figure 3.8.: Cross sections for photoionization of neutral W atoms. The upper panel shows the result of relativistic Hartree-Fock (RHF) calculations for photoabsorption by neutral tungsten atoms brought into the gas phase by evaporating tungsten at 3200 K. From [www.mdpi.com](http://www.mdpi.com).

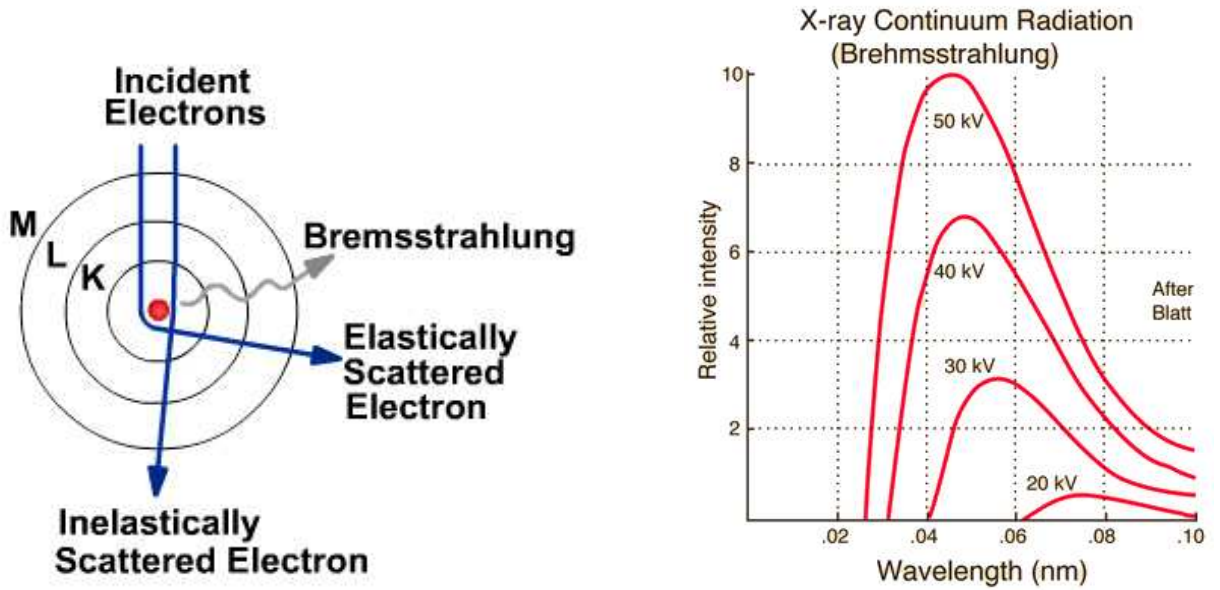


Figure 3.9.: Left: Different elastic and inelastic electron scattering processes on atoms, including bremsstrahlung. Right: Bremsstrahlung is characterized by a continuous distribution of radiation that is shifted towards higher photon energies and becomes more intense with increasing electron energy. From: [www.nde-ed.org/EducationResources](http://www.nde-ed.org/EducationResources) and [hyperphysics.phy-astr.gsu.edu](http://hyperphysics.phy-astr.gsu.edu)

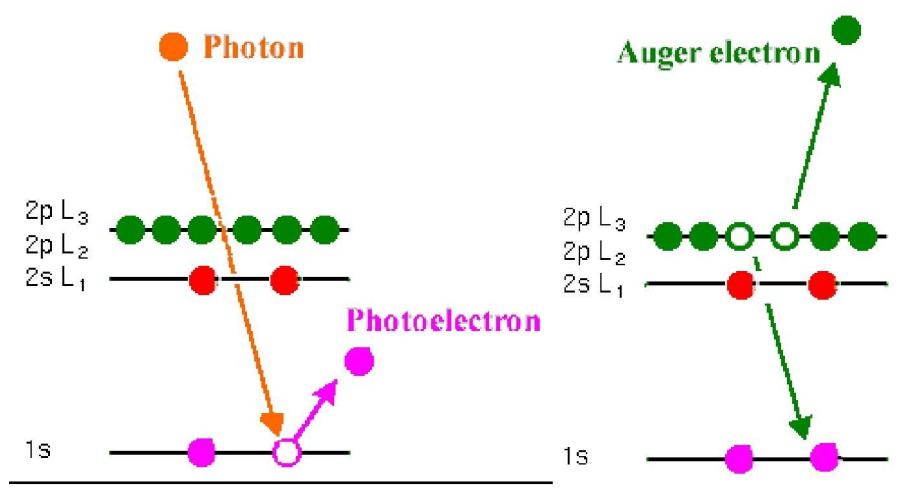


Figure 3.10.: Schematic diagram for the XPS emission process (left). An incoming photon causes the ejection of the photoelectron. Relaxation process (right) resulting in the emission of an Auger KLL electron; from <http://www.vub.ac.be/>

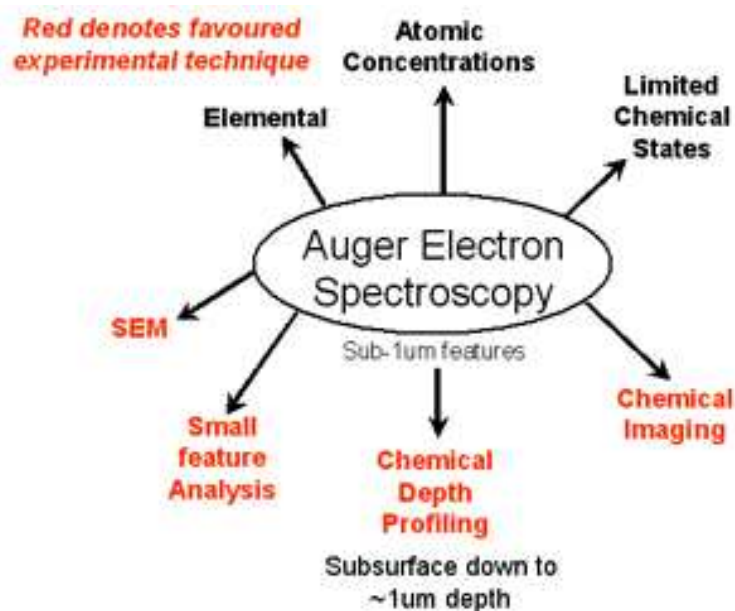


Figure 3.11.: Information Available from Auger electron spectroscopy. From and <http://www.lpdlabsservices.co.uk>

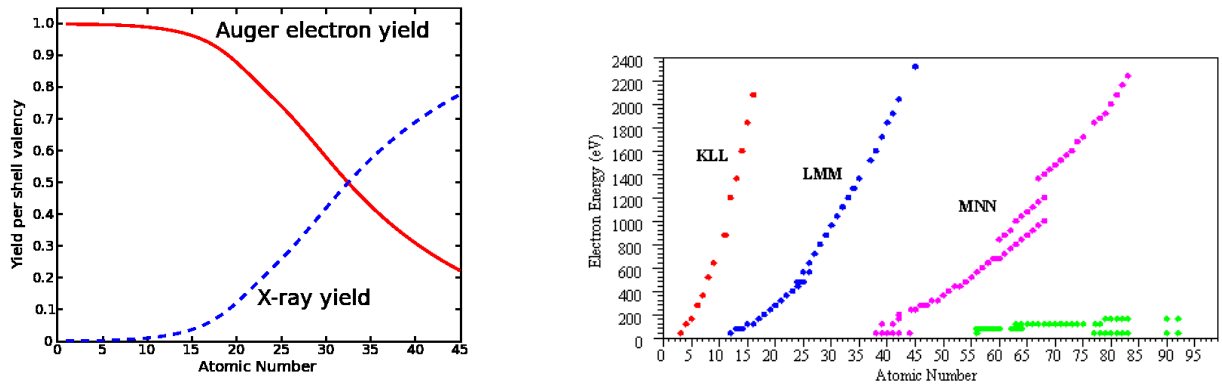


Figure 3.12.: Left: Comparison of Auger yield and fluorescence yield as a function of atomic number. Right: Auger characteristic energies. From [commons.wikimedia.org](https://commons.wikimedia.org) and [www.semitracks.com](http://www.semitracks.com).





## 4. Interaction of atoms with driving light fields

**Web link (Lecture by the nobel laureate Claude Cohen-Tannoudji):**

➤ For more motivation, listen to [cdsweb.cern.ch/record/423817](https://cdsweb.cern.ch/record/423817)

### 4.1. Time-dependent Schrödinger eq. for two-level atoms

Let us consider the time-dependent Schrödinger equation with  $H = H_0 + H_I(t)$ , where  $H_0$  is the Hamiltonian of the free (unperturbed) atom and  $H_I(t)$  describes the interaction with the oscillating electric field.

For a finite set of levels with energy  $E_n$ , the eigenfunctions can be written as

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-\frac{i}{\hbar} E_n t}.$$

For a **two-level atom**, that evolves under the influence of a perturbation  $H_I(t)$ , the time-dependent wave function can therefore be written as

$$\begin{aligned}\Psi(\mathbf{r}, t) &= c_1(t) \psi_1(\mathbf{r}) e^{-\frac{i}{\hbar} E_1 t} + c_2(t) \psi_2(\mathbf{r}) e^{-\frac{i}{\hbar} E_2 t} \\ &= c_1 |1\rangle e^{-i\omega_1 t} + c_2 |2\rangle e^{-i\omega_2 t}\end{aligned}$$

with  $c_i \equiv c_i(t)$  and  $\omega_i = E_i/\hbar$ , and with  $|c_1|^2 + |c_2|^2 = 1$  due to normalization.

#### Perturbation due to an oscillating electric field:

➤ For a bound electron  $e$  with position vector  $\mathbf{r}$  (with regard to the center of mass), an oscillating **electric field**  $\mathbf{E} = \mathbf{E}_0 \cos \omega t$  gives rise to the Hamiltonian

$$H_I(t) = e \mathbf{r} \cdot \mathbf{E}_0 \cos(\omega t)$$

➤ Substitution of ansatz  $\Psi(\mathbf{r}, t)$  into the time-dependent SE gives

$$i \dot{c}_1 = \Omega \cos(\omega t) e^{-\omega_0 t} c_2 \quad i \dot{c}_2 = \Omega^* \cos(\omega t) e^{\omega_0 t} c_1$$

with  $\omega_0 = (E_2 - E_1)/\hbar$  and the (so-called) **Rabi-frequency**  $\Omega$ .

➤ **Rabi-frequency**

$$\begin{aligned}\Omega &= \frac{\langle 1 | e \mathbf{r} \cdot \mathbf{E}_0 | 2 \rangle}{\hbar} = \frac{e}{\hbar} \int d^3 \mathbf{r} \psi_1^*(r) \mathbf{r} \cdot \mathbf{E}_0 \psi_2(r) \\ &\approx \frac{e \mathbf{E}_0}{\hbar} \int d^3 \mathbf{r} \psi_1^*(r) \mathbf{r} \psi_2(r)\end{aligned}$$

#### 4. Interaction of atoms with driving light fields

- The **dipole approximation** in the last line holds when the radiation has a wavelength greater than the size of the atom, i.e.  $\lambda \gg a_0$ .
- Especially for **linear-polarized radiation along  $x$ -axis**, i.e.  $\mathbf{E} = E_0 \mathbf{e}_x \cos(\omega t)$ :

$$\Omega = \frac{eX_{12}E_0}{\hbar} \quad \text{with} \quad X_{12} = \langle 1|x|2 \rangle .$$

➤ In general, further approximations are needed to solve Eqs. (4.1) for  $c_1(t)$  and  $c_2(t)$ . Consider the **initial (population) condition**  $c_1(0) = 1$  and  $c_2(0) = 0$ , a reasonable ‘first-order’ solution is

$$c_1(t) = 1$$

$$c_2(t) = \frac{\Omega^*}{2} \left\{ \frac{1 + \exp[i(\omega_0 + \omega)t]}{\omega_0 + \omega} + \frac{1 + \exp[i(\omega_0 - \omega)t]}{\omega_0 - \omega} \right\}$$

i.e. as long as  $c_2(t)$  remains small.

Rotating-wave approximation: ... (Blackboard)

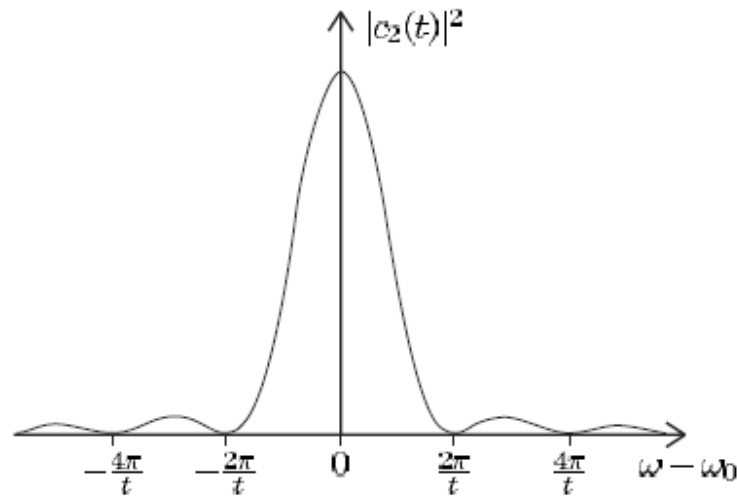


Figure 4.1.: The excitation probability function of the radiation frequency has a maximum at the atomic resonance. The line width is inversely proportional to the interaction time; from Foot (2006).

#### 4.2. Einstein's $B$ coefficient revisited

So far, we considered the effect of an oscillating electric field  $\mathbf{E}_0 \cos(\omega t)$  on the atom. **How is this (quantum-mechanical) behavior of the excitation probability related to Einstein's statistical treatment of the atom-field interaction ?** Especially, what do we expect if some broadband radiation with the energy density  $\rho(\omega) d\omega = \epsilon_0 E_0^2(\omega)/2$  interacts with a two-level atom ?

Einstein's coefficients expressed by the dipole amplitude:

- If we square the Rabi frequency  $\Omega$  for linear-polarized radiation and use the energy density from above, we find

$$|\Omega|^2 = \left| \frac{eX_{12} E_0(\omega)}{\hbar} \right|^2 = \frac{e^2 |X_{12}|^2}{\hbar^2} \frac{2\rho(\omega) d\omega}{\epsilon_0},$$

and together with  $c_2(t)$  (by integration over the frequency)

$$|c_2(t)|^2 = \frac{2e^2 |X_{12}|^2}{\epsilon_0 \hbar^2} \int_{\omega_0 - \Delta/2}^{\omega_0 + \Delta/2} d\omega \rho(\omega) \frac{\sin^2\{(\omega_0 - \omega)t/2\}}{(\omega_0 - \omega)^2}.$$

This is the **excitation probability for broadband radiation**.

- This expression for the makes use of the assumption that contributions at different frequencies do not interfere with each other.
- Since for broadband radiation, the energy density  $\rho(\omega)$  does not change significantly over the 'major' extent of the sinc-function, one can take the density out of the integral and write

$$|c_2(t)|^2 \simeq \frac{2e^2 |X_{12}|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) \times \frac{t}{2} \int_{-\phi}^{\phi} dx \frac{\sin^2 x}{x^2}.$$

**steady-state excitation rate for broadband radiation**

Apparently, the probability for a transition from level 1 to 2 increases linearly with time.

- **Steady-state excitation rate for broadband radiation:** This rate (i.e. the transition probability per time) is given by

$$R_{12} = \frac{|c_2(t)|^2}{t} = \frac{e^2 |X_{12}|^2}{\epsilon_0 \hbar^2}.$$

- Comparison with Einstein's treatment of the upward rate,  $B_{12} \rho(\omega_0)$  shows:

$$B_{12} = \frac{\pi e^2 |D_{12}|^2}{3\epsilon_0 \hbar^2},$$

if we replace  $|X_{12}|^2 \rightarrow |D_{12}|^2/3$ , i.e. by the (magnitude of the) standard **dipole matrix element**

$$\mathbf{D}_{12} = \langle 1 | \mathbf{r} | 2 \rangle = \int d^3\mathbf{r} \psi_1^* \mathbf{r} \psi_2.$$

- Here,  $\mathbf{D}_{12}$  is a vector, and the factor  $1/3$  arises from the average of  $\mathbf{D} \cdot \mathbf{e}_{\text{rad}}$  (with  $\mathbf{e}_{\text{rad}}$  being the unit vector along the electric field) over all spatial directions.
- From the known relation between the Einstein coefficients  $A_{21}$  and  $B_{21}$ , we finally find

$$A_{12} = \frac{g_1}{g_2} \frac{4\alpha}{3c^2} \times \omega^3 |D_{12}|^2$$

where  $\alpha = e^2/4\pi\epsilon_0 \hbar c$  is the **fine-structure constant**. The matrix element  $\mathbf{D}_{12}$  between the initial and final states depends only on the wave functions of the atom, that is the **Einstein coefficients are properties of the atom or molecule**.

#### 4. Interaction of atoms with driving light fields

- For some typical (allowed) transition, the matrix element above has a value  $D_{12} \simeq 3a_0$  (taking the wave functions from hydrogen), and this gives  $A_{21} \simeq 2\pi \times 10^7 / s^{-1}$  for a transition of the wavelength  $\lambda = 6 \times 10^{-7}$  m and  $g_1 = g_2 = 1$ .

In conclusion, although we have no real explanation for the spontaneous emission of atoms and molecules, Einstein's treatment provides us with a relation between  $A_{21}$  and  $B_{21}$ , and we have used time-dependent perturbation theory to derive an expression for  $B_{21}$ .

### 4.3. Interaction of atoms with monochromatic radiation

#### 4.3.a. Rabi oscillations

- If  $c_2(t)$  is not small for all times, we re-write Eq. (4.1) as:

$$i\dot{c}_1 = c_2 \left\{ e^{i(\omega - \omega_0)t} + e^{-i(\omega + \omega_0)t} \right\} \frac{\Omega}{2}$$

and analogue for  $i\dot{c}_2$ .

- Since the term  $(\omega + \omega_0)t$  oscillates very quickly, it averages to zero for any reasonable interaction time, and we obtain a second-order differential equation for  $c_2(t)$ :

$$\frac{d^2 c_2}{dt^2} + i(\omega - \omega_0) \frac{dc_2}{dt} + \left| \frac{\Omega}{2} \right|^2 c_2 = 0.$$

- This initial-value equations can be solved for the conditions  $c_1(0) = 1$  and  $c_2(0) = 0$

$$|c_2(t)|^2 = \frac{\Omega^2}{W^2} \sin^2 \left( \frac{Wt}{2} \right) \quad \text{with} \quad W^2 = \Omega^2 + (\omega - \omega_0)^2$$

- At resonance ( $\omega = \omega_0$ ), we find

$$|c_2(t)|^2 = \sin^2 \left( \frac{\Omega t}{2} \right)$$

Rabi oscillations, i.e. the population oscillates between the two levels.

- When  $\Omega t = \pi$ , all the population has gone from level 1 into the upper state,  $|c_2(t)|^2 = 1$ , and when  $\Omega t = 2\pi$  the atom has returned back to the lower state.

$\pi$ - and  $\pi/2$ -pulses: ... (Blackboard)

Bloch sphere representation: ... (Blackboard)

**Web link (how a pulse acts upon a two-level atom):**

- [www.youtube.com/watch?v=eONhmaVKw\\_c](http://www.youtube.com/watch?v=eONhmaVKw_c)  
➤ [www.youtube.com/watch?v=n4iX8XuJIU](http://www.youtube.com/watch?v=n4iX8XuJIU)

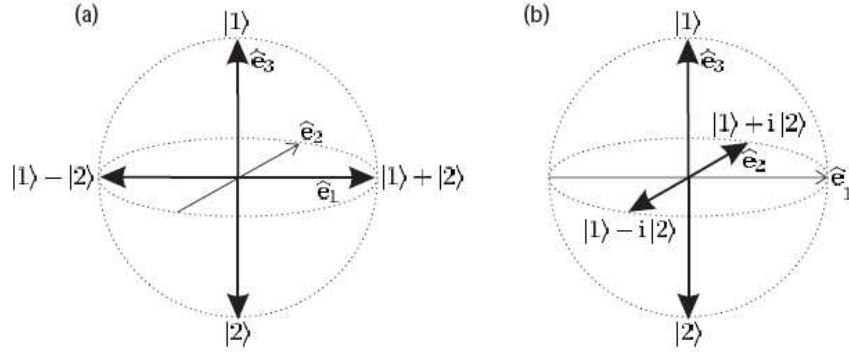


Figure 4.2.: The Bloch sphere. The position vectors of points on its surface represent the states of a two-level system (in Hilbert space). Examples of states are shown in (a) and (b); from: Foot: Atomic Physics, Fig. 7.2..

#### 4.3.b. Ramsay fringes

- Let us consider an atom that interacts with a **square pulse of radiation**, i.e. an oscillating electric field of constant amplitude in the interval  $t = [0, \tau_p]$  (and  $E_0 = 0$  otherwise).
- For a weak excitation ( $|c_2|^2 \ll 1$ ), the excitation probability is [cf. Eq. (?? and Figure 4.1]

$$|c_2(t)|^2 = \left| \Omega \frac{\sin\{(\omega_0 - \omega)t/2\}}{\omega_0 - \omega} \right|^2.$$

- The frequency spread of the first minimum of the  $\text{sinc}^2$  function has the width

$$\Delta f = \frac{\Delta \omega}{2\pi} = \frac{1}{\tau_p}$$

i.e. the frequency spread is inversely proportional to the interaction time as we might have expected from the Fourier transform relationship between the frequency and time domains.

- **What happens when an atom interacts with two separate pulses of radiation, from time  $t = [0, \tau_p]$  and again from  $t = [T, T + \tau_p]$ .**
- Integration of Eq. (4.1) with the initial condition  $c_2(0) = 0$  yields

$$c_2(t) = \frac{\Omega^*}{2} \left\{ \frac{1 - \exp[i(\omega_0 - \omega)\tau_p]}{\omega_0 - \omega} + \exp[i(\omega_0 - \omega)T] \frac{1 - \exp[i(\omega_0 - \omega)\tau_p]}{\omega_0 - \omega} \right\}$$

Amplitude of upper level after both pulses ( $t > T + \tau_p$ )  
in the rotating wave approximation.

- However, **when two pulses act together, there excitation amplitude into the excited state will interfere**

$$|c_2|^2 = \left| \Omega \frac{\sin\{(\omega_0 - \omega)\tau_p/2\}}{\omega_0 - \omega} \right|^2 \times |1 + \exp[i(\omega_0 - \omega)T]|^2$$

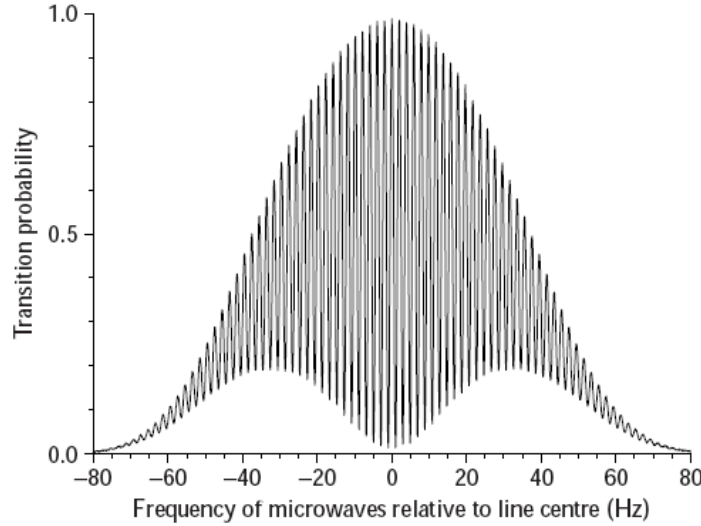


Figure 4.3.: Ramsey fringes from an atomic fountain of caesium, showing the transition probability for the  $F = 3, M_F = 0$  to  $F' = 4, M'_F = 0$  transition versus the frequency of the microwave radiation in the interaction region. The height of the fountain is 31 cm, giving a fringe width just below 1 Hz (i.e.  $\Delta f = 1/(2T) = 0.98$  Hz; from: Foot: Atomic Physics, Fig. 7.3..

$$= \left| \frac{\Omega \tau_p}{2} \right|^2 \left[ \frac{\sin(\delta \tau_p / 2)}{\delta \tau_p / 2} \right]^2 \cos^2 \left( \frac{\delta T}{2} \right),$$

where  $\delta = \omega - \omega_0$  is the frequency detuning.

- The double-pulse sequence produces a signal of the form shown in Figure 4.3.b, named after Norman Ramsey.
- How to interpret this figure ? The overall envelope is proportional to  $\text{sinc}^2$ — function and is caused by a single-slit diffraction, while the  $\cos^2$  term determines the width of the central peak in Eq. (4.1).
- From the maximum value at  $\omega = \omega_0$ , moreover, the excitation falls to zero when  $\delta T / 2 = \pi / 2$ ; the central peak has a width (FWHM) of  $\Delta \omega = \pi / T$  or
 
$$\Delta f = \frac{1}{2T}.$$
- This shows that Ramsey fringes from the interaction of a two-level atom with two squared pulses, separated by time  $T$ , have half the width of the signal from a single interaction of time  $T$ .

## 4.4. Radiative damping

### 4.4.a. Damping of a classical dipole

- Newton's second law for a damped harmonic oscillator with eigen frequency  $\omega_0$ ,

$$\ddot{x} + \beta \dot{x} + \omega_0^2 x = \frac{F(t)}{m} \cos(\omega t)$$

for a driving frequency  $\omega$  and a friction force  $F_{friction} = -m\beta \dot{x}$ . The amplitude of  $F(t)$  is assumed to vary slowly when compared with  $\omega$ .

- Solution can be found with ansatz, see classical mechanics:

$$x(t) = \mathcal{U}(t) \cos \omega t - \mathcal{V}(t) \sin \omega t.$$

- For ( $F(t) = 0$ ), i.e. no driving force, we obtain

$$x(t) = x_0 e^{-\beta t/2} \cos(\omega' t + \phi)$$

with  $\omega' \simeq \omega_0$  for light damping  $\beta/\omega_0 \ll 1$ . The energy is proportional to the amplitude of the motion squared,  $E \propto \exp(-\beta t)$ .

- For a (nearly) constant driving force ( $F(t) =$ , the energy of the classical oscillator

$$E = \frac{|F\mathcal{V}|\omega}{2\beta}$$

increases linearly with the strength of the driving force.

- In a two-level atom, in contrast, the energy must have an upper limit

#### 4.4.b. Density matrix of a two-level system

For a semi-classical description of an atom in the radiation field, we need to know the [electric dipole moment of the atom as induced by the radiation](#)

$$-e D_x(t) = - \int d^3\mathbf{r} \Psi^+(t) e x \Psi(t).$$

#### (Optical) Bloch equations:

- The [electric dipole moment](#) of the two-level atom can be either in terms of the (time-dependent) amplitudes  $c_1(t)$ ,  $c_2(t)$  or by means of the [density matrix](#)

$$|\Psi\rangle\langle\Psi| = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \begin{pmatrix} c_1^* & c_2^* \end{pmatrix} = \begin{pmatrix} |c_1|^2 & c_1 c_2^* \\ c_1^* c_2 & |c_2|^2 \end{pmatrix} = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}.$$

- In the density matrix, the diagonal elements  $|c_1|^2$  and  $|c_2|^2$  represent the (level) population, while the off-diagonal matrix elements are (sometimes) called the [coherences which describe the response of the system to the frequency of the driving fields](#).
- In the expression of the [electric dipole moment](#), the (modified) coherences appear in the form  $\tilde{\rho}_{12} = \rho_{12} \exp(-i\delta t)$  with  $\delta = \omega - \omega_0$  as well as  $\tilde{\rho}_{21} = \rho_{21} \exp(i\delta t) = (\tilde{\rho}_{12})^*$ .
- With these definitions (of combined density matrix elements), the Schrödinger equation for the driven two-level atoms can be expressed in the compact form

$$\dot{u} = \delta v$$

$$\dot{v} = -\delta u + \Omega \omega$$

$$\dot{w} = -\Omega v$$

(optical) Bloch equations

#### 4. Interaction of atoms with driving light fields

- In these Bloch equations, the three real and time-dependent functions are defined as

$$u = \tilde{\rho}_{12} + \tilde{\rho}_{21}$$

$$v = -i(\tilde{\rho}_{12} - \tilde{\rho}_{21})$$

$$w = \rho_{11} - \rho_{22}$$

i.e. as the real and imaginary parts of the density matrix.

- In addition, these three functions can be interpreted also as components of the (so-called) **Bloch vector**

$$\mathbf{R} = u \mathbf{e}_1 + v \mathbf{e}_2 + w \mathbf{e}_3$$

(Optical) Bloch equations with damping: ... (Blackboard)

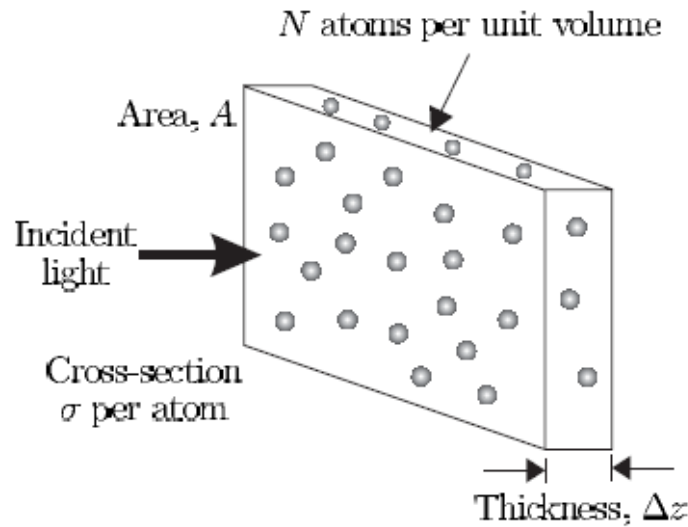


Figure 4.4.: Atoms with number density  $N$  distributed in a slab of thickness  $\Delta z$  absorb a fraction  $N \sigma \Delta z$  of the incident beam intensity, where  $\sigma$  is defined as the (absorption) cross-section.  $N \Delta z$  is the number of atoms per ‘unit area’ and  $\sigma$  is the ‘target area’ which each atom presents; from Foot: Atomic Physics, Fig. 7.4.

### 4.5. Optical absorption cross sections

(Classical) optical absorption cross-section: ... (Blackboard)

#### 4.5.a. Optical absorption cross sections for intense light

- Stimulated emission of already excited atoms **reduce** the absorption; we write the differential attenuation as

$$\frac{dI}{dz} = -\kappa(\omega) I(\omega) = -(N_1 - N_2) \sigma(\omega) I(\omega)$$



since absorption and stimulated emission have the same cross-section (see Einstein's analysis).

- In steady state, the conservation of energy further requires

$$(N_1 - N_2) \sigma(\omega) I(\omega) = N_2 A_{21} \hbar \omega,$$

because the net rate of the absorbed energy per unit volume (lhs) must be equal to the rate of spontaneous emission times  $\hbar \omega$  (rhs).

- Since  $w = \frac{N_2 - N_1}{N}$ , we can write the absorption cross section as

$$\begin{aligned} \sigma(\omega) &= \frac{\rho_{22}}{w} \frac{A_{21} \hbar \omega}{I} = \frac{\Omega^2/4}{(\omega - \omega_0)^2 + \Gamma^2/4} \times \frac{A_{21} \hbar \omega}{I} \\ &= 3 \times \frac{\pi^2 c^2}{\omega_0^2} A_{21} g_L(\omega) \end{aligned} \quad (4.1)$$

- The particular frequency dependence is described by the (normalized) **Lorentzian line shape**

$$g_L(\omega) = \frac{1}{2\pi} \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2/4};$$

- The pre-factor (3) in (4.1) can take any value between 0 ... 3; for unpolarized light and randomly oriented atoms, this factor is 1.
- Under these conditions and for degenerate levels, the optical absorption cross section become

$$\sigma(\omega) = \frac{g_2}{g_1} \times \frac{\pi^2 c^2}{\omega_0^2} A_{21} g_L(\omega)$$

**Example (Zeeman level  $M_F$  interacts with polarized laser beam):** Consider

atoms in a specific  $M_F$  state and a polarized laser beam, e.g. sodium atoms in a magnetic trap that absorb a circularly polarized probe beam, Figure 4.5.a.

To drive the  $\Delta M_F = +1$  transition, we need circularly polarized light and a beam direction parallel to the quantization axis of the atoms (magnetic field).

#### 4.5.b. Cross sections for pure radiative broadening

- For  $\omega = \Omega_0$ , the absorption cross section (4.1) becomes

$$\sigma(\omega_0) = 3 \times \frac{2\pi c^2}{\omega_0^2} \frac{A_{21}}{\Gamma}$$

- With  $\lambda_0 = 2\pi c/\omega_0$  and  $\Gamma = A_{21}$ , we also have

$$\sigma(\omega_0) = 3 \times \frac{\lambda_0^2}{2\pi} \simeq \frac{\lambda_0}{2},$$

an absorption cross section much larger than the size of an atom.

- However, the optical cross-section decreases rapidly off resonance.

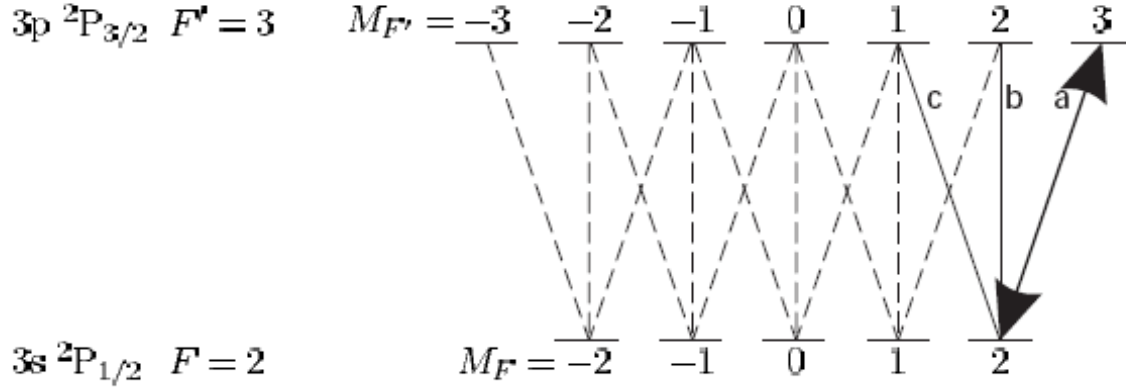


Figure 4.5.: The Zeeman states of the  $3s\ ^2P_{1/2}\ F = 2$  and  $3p\ ^2P_{3/2}\ F' = 3$  hyperfine levels of sodium, and the allowed electric dipole transitions between them. The other hyperfine levels ( $F = 1$  and  $F' = 0, 1$  and  $2$ ) have not been shown. Excitation of the transition  $F = 2, M_F = 2$  to  $F' = 3, M_{F'} = 3$  (labelled a) gives a closed cycle that has similar properties as a two-level atom: Due to the selection rules, the atoms in the state  $F' = 3, M_{F'} = 3$  will decay back spontaneously to the initial state. (Circularly polarized light that excites  $\Delta M_F = +1$  transitions leads to cycles of absorption and emission that tend to drive the population in the  $F = 2$  level towards the state of maximum  $M_F$ , and this optical pumping process provides a way of preparing a sample of atoms in this state.) When all the atoms have the correct orientation, i.e. they are in the  $F = 2, M_F = 2$  state for this example, then Eq. (4.1) applies. Atoms in this state give less absorption for linearly-polarized light (transition b), or circular polarization of the wrong handedness (transition c); from Foot: Atomic Physics, Fig. 7.5.

#### 4.5.c. Saturation intensity

- Let us define the (dimensionless) ratio and difference in the population density

$$r = \frac{N_2}{N_1 - N_2} = \frac{\sigma(\omega) I(\omega)}{\hbar\omega A_{21}}$$

$$N_1 - N_2 = \frac{N}{1 + 2r} = \frac{N}{1 + I/I_s(\omega)}.$$

and use this to define the [saturation intensity](#)

$$I_s(\omega) = \frac{\hbar\omega A_{21}}{2\sigma(\omega)}$$

- Then, the same saturation intensity can be used to express the [intensity dependence of the absorption coefficient](#)

$$\kappa(\omega, I) = \frac{N\sigma(\omega)}{1 + I/I_s(\omega)}$$

- The minimum saturation occurs at resonance where the cross section is largest; it is often this value which is called [the saturation intensity](#)

$$I_{sat} = I_s(\omega_0) = \frac{\pi\hbar c \Gamma}{3\lambda^3}.$$

- For the resonance transition in sodium at  $\lambda = 589 \text{ nm}$ , for example, we have:

$$\text{lifetime } \tau = 16 \text{ ns} \quad \rightsquigarrow \quad \text{intensity } I_{\text{sat}} = 6 \text{ mW/cm}^2$$

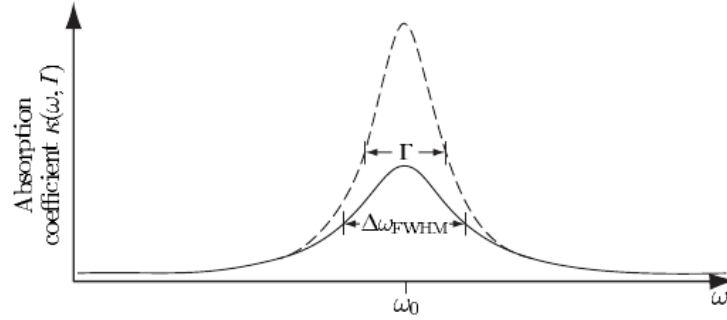


Figure 4.6.: The absorption coefficient  $\kappa(\omega, I)$  is a Lorentzian function of the frequency that peaks at  $\omega_0$ , the atomic resonance. Saturation causes the absorption line shape to change from the curve for a low intensity ( $I \ll I_s$ , dashed line), to a broader curve (solid line), with a lower peak value but still described by a Lorentzian function.

#### 4.5.d. Power broadening

- Absorption coefficient  $\kappa(\omega, I)$  ... depends on both, the frequency and the intensity of light.
- This coefficient can be expressed also in terms of  $\sigma_0 = \sigma(\omega_0)$ :

$$\kappa(\omega, I) = \frac{N\sigma(\omega)}{1 + I/I_s(\omega)} = N\sigma_0 \frac{\Gamma^2/4}{(\omega - \omega_0)^2 + \Gamma^2/4(1 + I/I_s)}$$

- Therefore, the absorption coefficient  $\kappa(\omega, I)$  also has a Lorentzian line shape and a FWHM of

$$\Delta\omega_{FWHM} = \Gamma \sqrt{1 + \frac{I}{I_s}}. \quad (4.2)$$

$$(4.3)$$

## 4.6. Light shifts

- Difference between the unperturbed energies and energy eigenvalues of the system when perturbed by a light field ('dressed-atom' picture)..

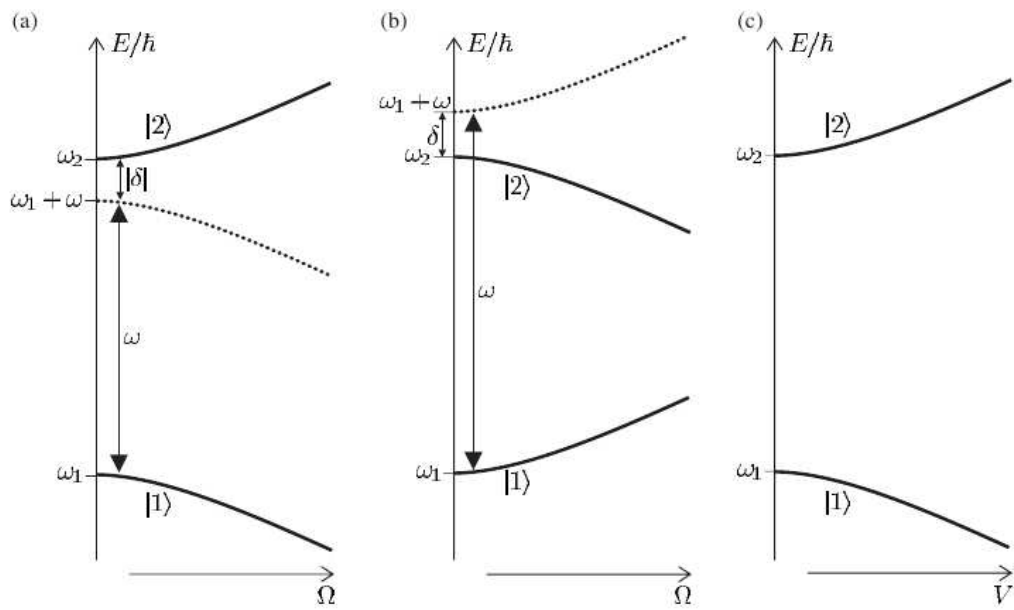


Figure 4.7.: Eigenenergies of a two-level atom interacting with an external electric field. (a) and (b) show the a.c. Stark effect for negative and positive frequency detunings respectively, as a function of the Rabi frequency. (c) The d.c. Stark effect as a function of the applied field strength.

## 5. Hyperfine interactions and isotope shifts

### 5.1. Magnetic-dipole interactions

Nucleus with (total) nuclear spin:  $|I M_I\rangle$  ... fixed for given isotope.

Apart from the total charge (electric monopole), a nucleus generally also possesses multipole moments of higher order; in fact, these multipole moments due to non-spherical charge and magnetization distributions cause the hyper-fine structure of all atomic levels. A multipole expansion for a rotational symmetric nucleus gives rise to:

- magnetic multipoles: odd
- electric multipoles: even

Hamiltonian of the magnetic dipole interaction:

$$H' = - \underbrace{\boldsymbol{\mu}_I}_{\text{nuclear coordinates}} \cdot \underbrace{\mathbf{B}(0)}_{\text{electronic coordinates}}$$

$\mathbf{B}(0)$  ... field as caused by the electrons at the nucleus (origin).

For a sufficiently isolated electronic level  $E_J$  with total angular momentum  $J$ , the hyperfine splitting is much smaller than the fine-structure splitting, and we can make use of the  $IJF$  coupling scheme:  $|(IJ)FM_F\rangle$ .

Nuclear magnetic moment:

$$\boldsymbol{\mu}_I = g_I \mu_N \mathbf{I} \quad (\text{sign!}) \quad \mu_N = \frac{e\hbar}{2M} \approx \frac{\mu_B}{1836} \ll \mu_B$$

$$\mathbf{B} \sim \mathbf{J} \quad \text{weak splitting; isolated level}$$

$$H' = A \mathbf{I} \cdot \mathbf{J}$$

magnetic dipole interaction;  $A$  can often be determined experimentally.

Magnetic-dipole interaction Hamiltonian: ... (Blackboard)

Energy splitting in first-order: ... (Blackboard)

## 5.2. Electric-quadrupole interactions

Deviations from the spherical symmetry of the nuclear charge distribution leads to (even) higher-order electrical multipole moments of the nucleus; again, a multipole expansion help result for  $r_e \gg r_N$  into a separation of the nuclear and electron coordinates.

For this electric-quadrupole interaction, a Hamiltonian  $H''$  can be written as scalar product of a nuclear tensor and an electronic tensor (of each second rank).

The effects of the electric-quadrupole interaction is often seen as (more or less small) deviations from the  $\Delta E(F)$  rule to the dominant magnetic-dipole interaction.

## 5.3. Isotope shifts

### Reasons for isotope shifts:

- Finite nuclear mass.
- Extended and non-uniform charge distribution inside of the nucleus.

### 5.3.a. Mass shift

Consider an atom at rest with total momentum  $\mathbf{P} + \sum_i \mathbf{p}_i = 0$ .

Kinetic energy:

$$T = \frac{P^2}{2M} + \sum_i \frac{p_i^2}{2m} = \underbrace{\frac{\sum_i p_i^2}{2M} + \frac{\sum_i p_i^2}{2m}}_{\text{normal mass shift}} + \underbrace{\frac{1}{M} \sum_{i < j} \mathbf{p}_i \cdot \mathbf{p}_j}_{\text{specific mass shift}}$$

Normal mass shift: ... (Blackboard)

Specific mass shift: ... (Blackboard)

### 5.3.b. Field shifts

Different charge distributions of isotopes affect first of all the  $s$  electrons (as well as the  $p_{1/2}$  electrons within a relativistic treatment). The major contribution arises from differences in the volume

$$r_o = 1.2 \cdot 10^{-15} \text{ m } \sqrt[3]{A}; \quad \frac{\delta r_o}{r_o} = \frac{1}{3} \frac{\delta A}{A}$$

$$\Delta E = 4\pi \int_0^\infty dr r^2 (V(r) - V_o(r))$$

volume shift