

# **Atomic Theory:**

## **Electronic structure of atoms and their interaction with light and particles**

### **— Lecture notes, —**

### **WS 2019/20**

<http://www.atomic-theory.uni-jena.de/>  
→ Teaching → Atomic Theory

**(Notes and additional material)**

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# 0. Preliminary remarks

## 0.1. Schedule and agreements

- Lecture period: 14. 10. 2019 – 7. 2. 2020
- Lecture: We 12 – 14, SR 5 HHW 4
- Tutorial: We 14 – 16, every 2nd week, to be agreed
- Language: German / English ??
- ECTS points: 4 or 8 (inclusive the tasks and exam).
- Exam: Tasks (40 %), oral or written exam (last week of term).
- Requirements for exam: *Modulanmeldung* 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, Mathematica ?? ... Which other languages ??

## 0.2. Further reading

- K. Blum: *Density Matrix Theory and Applications: Physics of Atoms and Molecules* (Plenum Press, N. York, 1996).
- B. H. Brandsen and C. J. Joachain: *Physics of Atoms and Molecules* (Benjamin Cummings, 2nd Edition, 2003).
- R. D. Cowan: *Theory of Atomic Struture and Spectra* (Los Alamos Series, 1983).
- J. Foot: *Atomic Physics* (Oxford Master Series, Oxford University Press, 2005).
- H. Friedrich: *Theoretical Atomic Physics* (Springer, 3rd edition, 2003).
- W. R. Johnson: *Atomic Structure Theory: Lectures on Atomic Physics* (Springer, Berlin, 2007).
- G. K. Woodgate: *Elementary Atomic Structure* (Oxford University Press, 2nd Edition, 1983).
- *Controlling the Quantum World: The Science of Atoms, Molecules and Photons* (National Acad. Press, 2007).

### Additional texts:

- K. Blaum: *High-accuracy mass spectroscopy with stored ions*, Phys. Rep. **425**, 1 (2006).
- L. S. Brown and G. Gabrielese: *Geonium Theory: Physics of a single electron or ion in a Penning trap*, Rev. Mod. Phys. **58**, 233 (1986).
- C. Froese Fischer: *The Hartree-Fock Method for Atoms* (John Wiley, New York, 1977).
- H. Haken and H. C. Wolf *Atom und Quantenphysik* (Springer, Berlin, 1984).
- H. Haken and H. C. Wolf *Molekülphysik und Quantenchemie* (Sprimger, Berlin, 1992).

# 1. Atomic theory: A short overview

## 1.1. Atomic spectroscopy: Level structures & collisions

### Atomic processes & interactions:

- Spontaneous emission/fluorescence: ... occurs without an ambient electromagnetic field; related also to absorption.
- Stimulated emission: ... leads to photons with 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- & 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 at a *fixed* potential.
- Multi-photon excitation, ionization and decay: ... non-linear electron-photon interaction.
- Autoionization: ... nonradiative electron emission from (inner-shell) excited atoms.
- Electron-impact excitation & ionization: ... occurs frequently in astro-physical and laboratory plasmas.
- Elastic & inelastic electron scattering: ... reveals electronic structure of atoms and ions; important for plasma physics.

## 1. Atomic theory: A short overview

- Pair production: ... creation of particles and antiparticles due to light-matter interactions ( $e^+ - e^-$  pairs).
- Delbrück scattering: ... deflection of high-energy photons in nuclear Coulomb fields; caused by vacuum polarization.
- ...
- In practice, however, a more detailed 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 methods to mean-field approaches ... and, eventually, up to advanced ab-initio and quantum-field theories. The goal 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 still 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 beneficial, at least.

### Theoretical models:

- **Electronic structure of atoms and ions:** is described quantum mechanically in terms of (many-electron) wave functions, energy levels, ground-state densities, etc., and is usually based on some atomic Hamiltonian.
- **Interaction of atoms with the radiation field:** While the atoms/matter is treated quantum-mechanically, the radiation is — more often than not ( $> 99\%$  of all studies in atomic physics) — described as a classical field.
- Such a 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) or quantum optics, though often without spatial degrees of freedom.

### Requires different (theoretical) techniques and skills:

- 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.

## 1.3. Applications of atomic theory

### 1.3.a. Need of (accurate) atomic 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

#### Acceleration by high-power short-pulse lasers:

- High power short-pulse lasers with peak powers at the Terawatt or even Petawatt level enables one to reach focal intensities of  $10^{18} - 10^{23}$  W/cm<sup>2</sup>. These lasers are able 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.
- Extreme Light Infrastructure (ELI): a new EU-funded large-scale research infrastructure; aims to push the limits of laser intensity three orders towards 10<sup>24</sup> W/cm<sup>2</sup>. The
- ELI comprises three branches:
  - Ultra-high-field science: ... to explore laser-matter interactions in the relativistic regime;
  - Attosecond physics: ... to conduct temporal investigations of the electron dynamics in atoms, molecules, plasmas and solids at the attosecond scale;
  - High-energy beam science: ... to explain laser-matter interactions in intense fields.

## 1.4. Overview to light-matter interactions

### 1.4.a. Properties of light

#### Characteristics of light:

- Frequency & line width
- Intensity

## 1. Atomic theory: A short overview

- Propagation direction; speed of light:  $3 \times 10^8$  m/s
- Polarization, angular momentum of light
- Duration, pulse length
- Coherence

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

#### Emission of light:

- **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:** Emitted electromagnetic radiation when charged particles are accelerated radially; use of bending magnets, wigglers, undulators.
- **Plasma radiation:** Electromagnetic radiation emitted from a plasma; primarily, if free electrons undergo transitions to other continuum or bound states of atoms and ions; bound-bound transitions; bremsstrahlung & Compton radiation.
- **Blackbody radiation:** best possible emitter of **thermal radiation with its characteristic (continuous) spectrum** that just depends on the temperature of the body. Black bodies start to emit visible wavelengths for temperatures beyond a few hundred degrees Celsius, and this blackbody radiation appears red, orange, yellow, white and even blue as the temperature increases; Planck's law; Rayleigh-Jeans law.

## Interactions of light with atoms and matter:

- Light can also undergo **reflection**, **scattering** and **absorption**; In particular, the energy/heat transfer through a material is mostly radiative, i.e. due to the emission and absorption of photons (for example, in the core of the Sun).
- **Dispersion:** Light of different frequencies may travel through matter at different speeds; under certain circumstances, the speed of light in matter can be extremely slow (**slow light**).
- **Refractive index of materials:** Relative factor by which the speed of light is decreased in a given material. Classically, this slow-down is often explained by the light-inducing electric polarization of the matter which by itself emits new light, and which then interferes with the original light wave, giving rise to a **delayed wave**.
- **Photon picture:** Photons always travel with  $c$ , even in matter. Due to their **interaction with atoms**, 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:** Active research area that include topics such as two-photon absorption, self-phase modulation and optical parametric oscillators. Though these processes are often explained in terms of the **photon picture**, no photons need to be assumed or treated explicitly. These processes are often modeled theoretically 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 concepts for studying light-matter interactions:

- Geometrical optics:  $\lambda \ll$  object size ➔ daily experience; optical instrumentation; optical imaging; use of **intensity profiles, direction, coherence, phase, polarization, photons**.
- Wave optics:  $\lambda \approx$  object size ➔ interference, diffraction, dispersion, coherence; laser, resolution issues, pulse propagation, holography; use of: **intensity, direction, coherence, phase, polarization, photons**.
- Laser and electro-optics: reflection and transmission in wave guides; resonators, lasers, integrated optics, photonic crystals, Bragg mirrors; use of: **intensity, direction, coherence, phase, polarization, photons**
- Quantum optics: photons and photon number statistics, fluctuation, atoms in cavities, laser cooling techniques; use of: **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, latern, argon flash, ...
- Electric-powered: halogen lamps, ...
- Gas discharge lamps: neon and argon lamps; mercury-vapor lamps, ...
- Laser & laser diodes: gas, semi-conductor, organic, ...

### Recently developed (new) light sources:

- **LED:** Semiconductor (light-emitting) diodes that consists out of a chip of semi-conducting material and a p-n (positive-negative) junction. LED generate little or even no long-wave IR or UV, but convert about 15-25 % of the power into visible light.
- **Laser-plasma light sources:** A dense plasma focus can act 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; since HHG strongly depends on the driving laser field, the high harmonics have generally rather similar temporal and spatial coherence properties.
- **Free-electron lasers (FEL):** Use of relativistic electron pulses as the lasing medium that 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.
- **Attosecond Light Sources:** Read the article by David Villeneuve, La Physique au Canada **63** (2009) 65.

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

#### Recently emerged research areas:

- **Spectroscopy:** ... to study details of medium/atomic clouds, for instance, photon spectroscopy, electron spectroscopy, Raman spectroscopy, ... . Spectroscopic data are often represented by a spectrum, a plot of cross sections, count numbers, intensity ratios, ... as a function of wavelength or frequency.  
Different spectroscopic techniques are often distinguished by their photon or electron energies (infrared-, x-ray-, VUV,

## 1. Atomic theory: A short overview

...), the **nature** of interaction (absorption-, emission-, coherent-, ...) or the **type** of materials (atoms, molecular, crystal, nuclei, ...).

- **Interferometry:** ... family of techniques where different electromagnetic waves are superimposed in order to extract information about the waves and their properties; **interferometers** are the corresponding instruments.
- 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**.
- **(Quantum) Metrology:** ... is the science of measurement; metrology includes all theoretical and practical aspects of measurements.
- **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.
- **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**.
- **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.

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

#### Photonics and light-atom interactions everywhere:

- A Day in the Life with Photonics: Cf. [http://www.quebecphotonic.ca/a\\_propos\\_en.html](http://www.quebecphotonic.ca/a_propos_en.html)
- 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.

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.

### LED light sources: Advantages and shortcomings:

- High conversion efficiency: ... LED circuit can approach 80 % efficiency.
- Long operational lifetimes: ... of current white LED lamps is 100,000 hours.
- New technology since mid 1990s: ... based on InGaAlP and InGaN compound semiconductors.
- Application areas: **signalling** (traffic signals, automobile brake lights); **displays** (outdoor full-colour video screens, single-colour variable-message signs); **lighting** (home and in street lights, outdoor signs, and offices); **backlighting** (automobile instrument panels, mobile-phone LCD displays and keypads).

### Lithography:

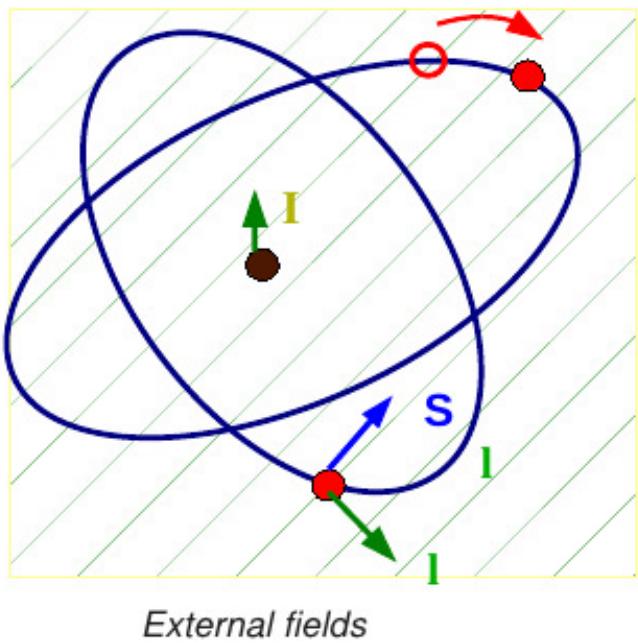
- Lithography: ... is a method for printing using a stone (lithographic limestone) or a metal plate.
- Modern lithography: ... the image is made of a polymer coating applied to a flexible aluminum plate.

### Further application areas:

- Telecommunication, medicine & life sciences
- Sensorics
- Micro- and nano-optics, ...

## Hierarchy of inner-atomic interactions

-- self-consistent fields vs. perturbation theory



- ★ 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.

## 1. Atomic theory: A short overview

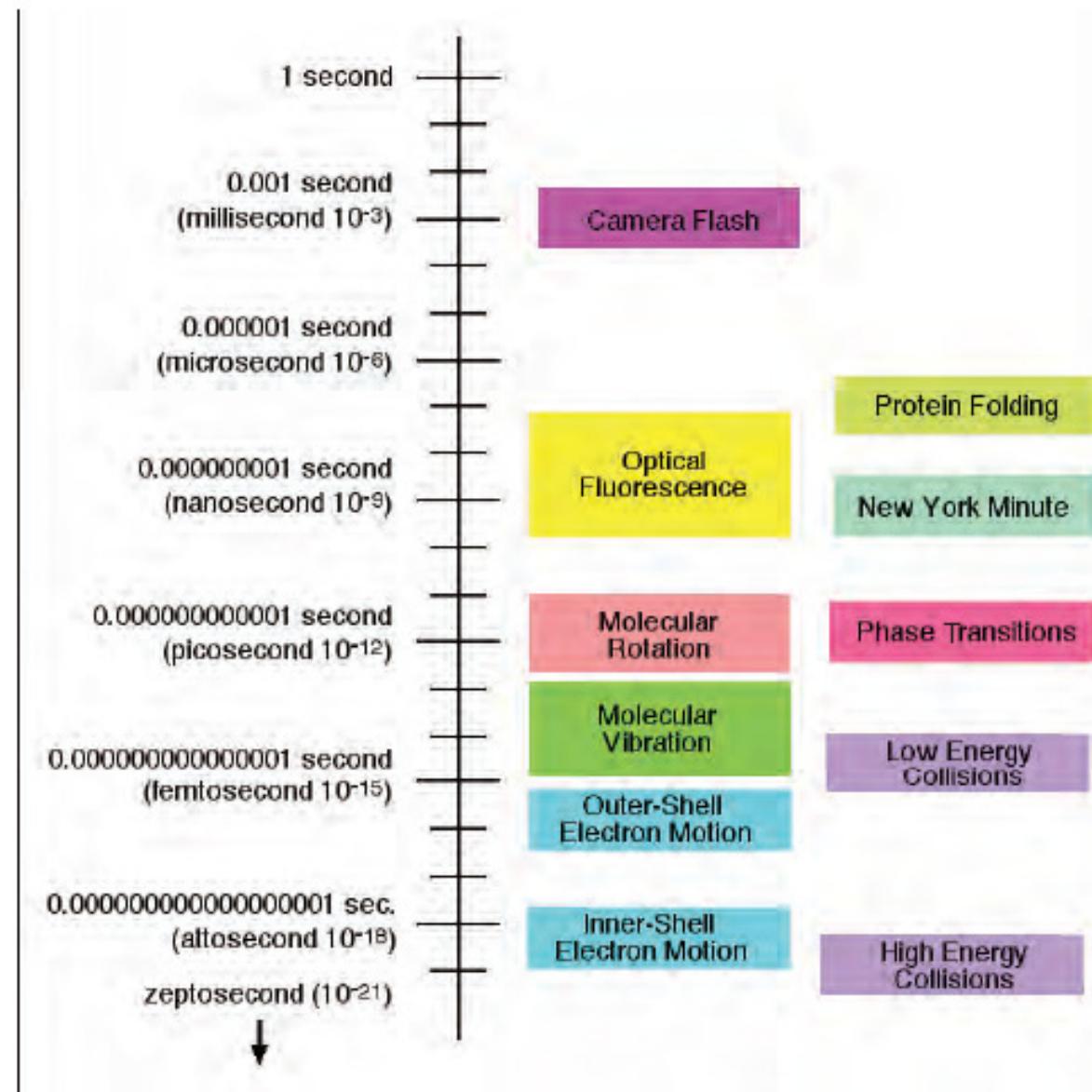
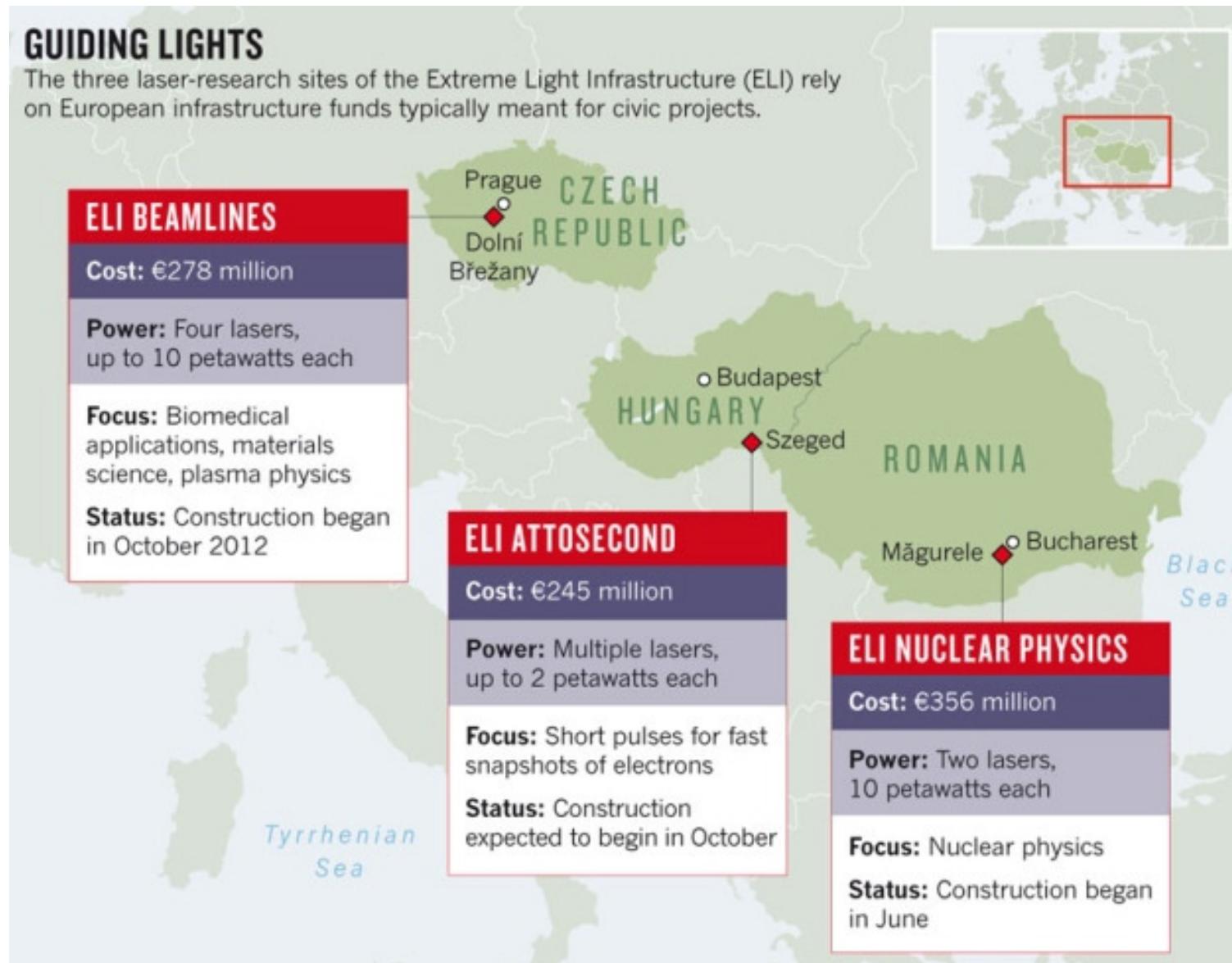


Figure 1.2.: Characteristic time scales of atomic and molecular motions; taken from: *Controlling the Quantum World*, page 99.

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

# 1. Atomic theory: A short overview

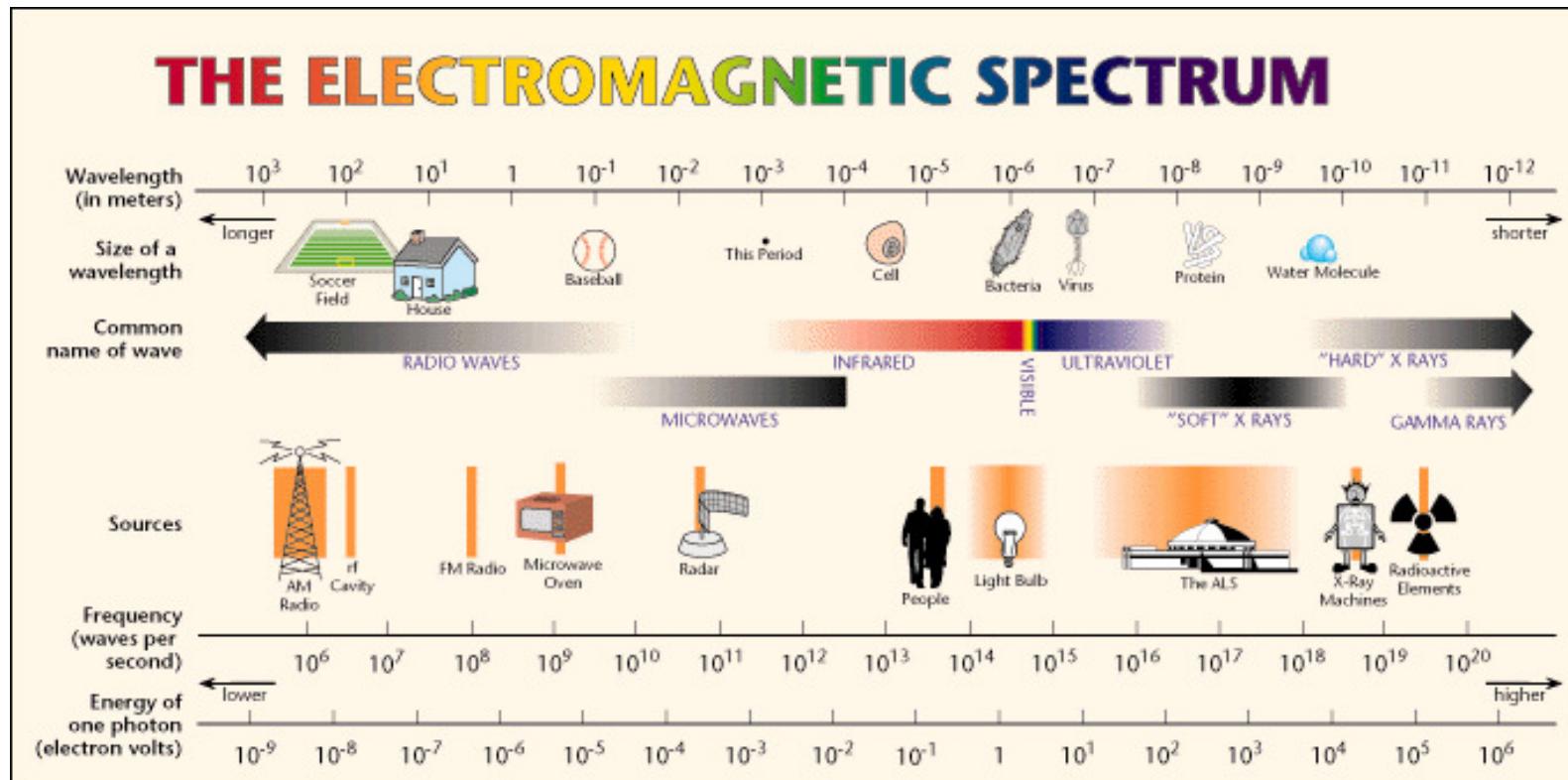


Figure 1.4.: Electromagnetic spectrum.

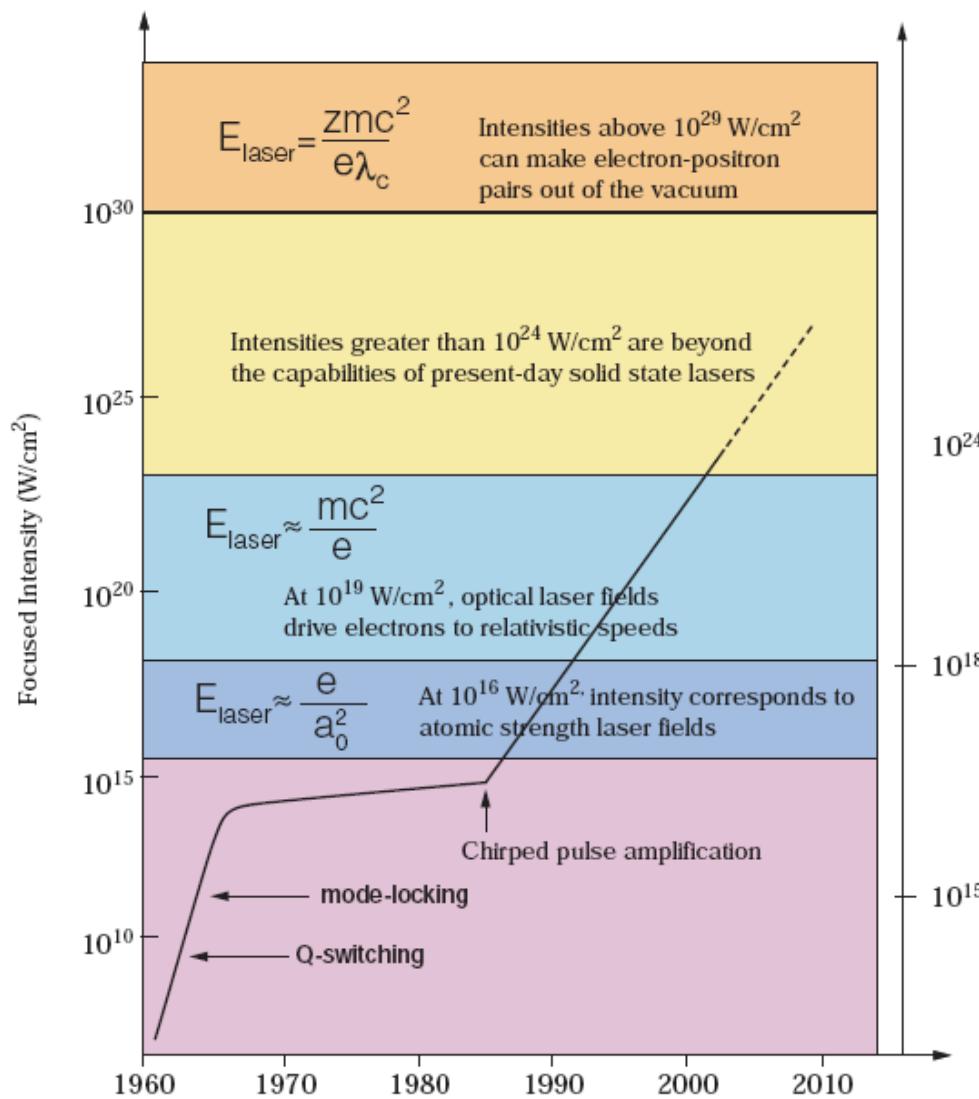


Figure 1.5.: The exponential increase in achievable laser intensity over the last 50 years; taken from: *Controlling the Quantum World*, page 88.

## 1. Atomic theory: A short overview

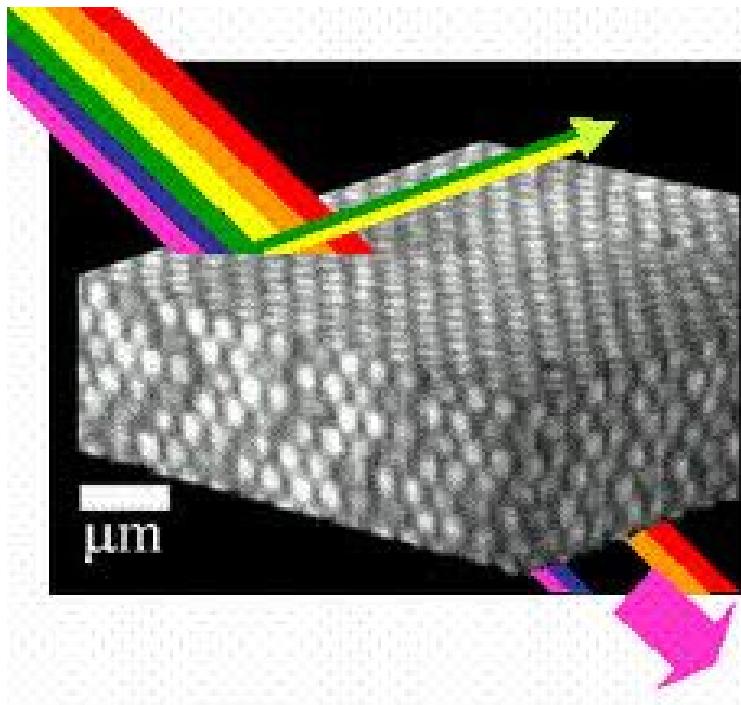


Figure 1.6.: Left: Photonic crystals from nature. Right: Photonic crystals from artificial nanostructures.

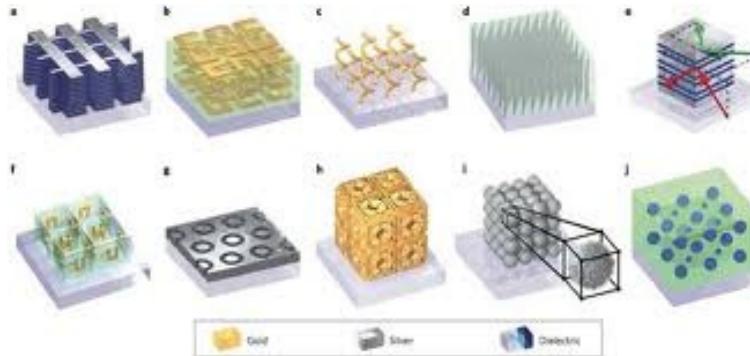


Figure 1.7.: Left: The invisibility of meta materials. Right: Some 3d structures.

## 1. Atomic theory: A short overview



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

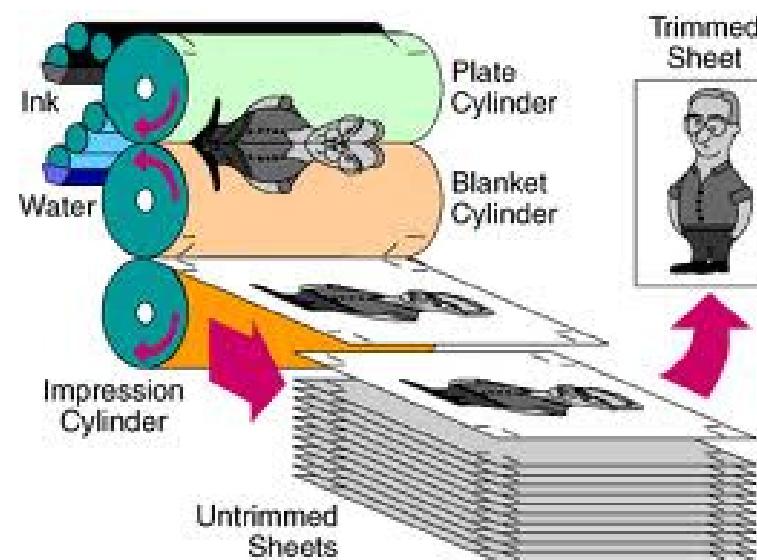
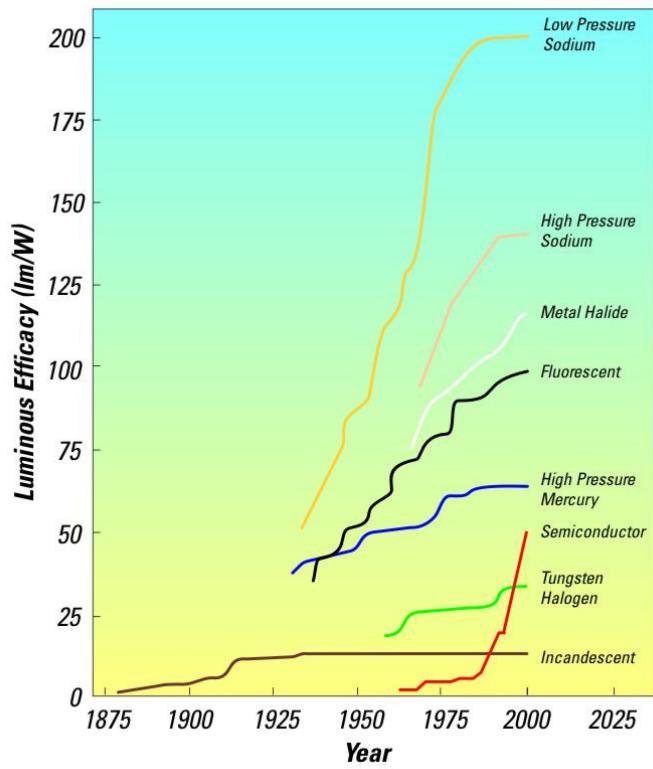


Figure 1.9.: Left: Increase in light efficiency over the last 100 years. Right: Principle of lithography.

## 1. Atomic theory: A short overview

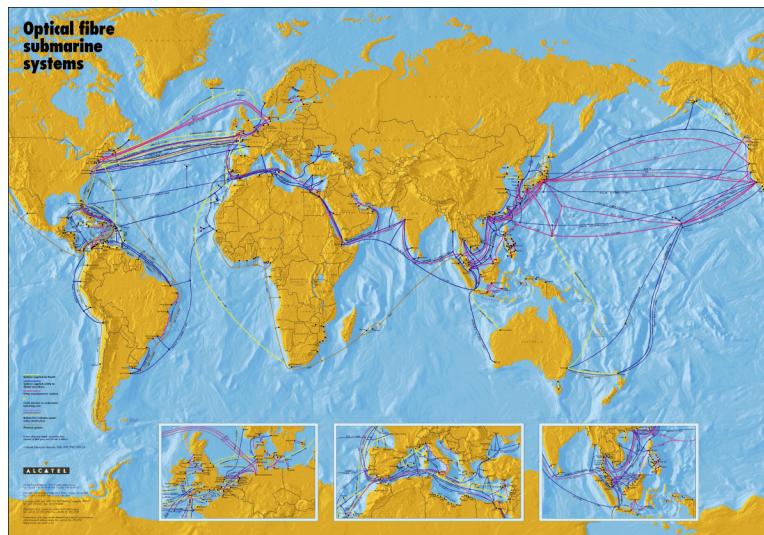


Figure 1.10.: The transatlantic cable system continues to grow.

## 2. Review of one-electron atoms (hydrogen-like)

### 2.1. Hydrogen: The 'key model' of atomic and molecular theory

#### Reminder:

- One of the simplest quantum systems that can be solved analytically.
- Basis of atomic shell model: ... ‘products’ of some radial function *times* spherical harmonics.
- The shell model has large impact for the understanding of most atomic processes.
- The shell model is closely related also to the Hartree-Fock theory of atoms and molecules.
- Hydrogenic ions: In the framework of quantum electrodynamics, the treatment of hydrogen (and hydrogenic ions) provides the most accurate test of quantum mechanics, up to the relative level  $10^{-11} \dots 10^{-13}$ .

#### 2.1.a. Separation of the center-of-mass motion

##### Separation of nuclear and electronic coordinates:

- Atomic hydrogen is already a system of two interacting particles. ... interaction (potential) only depends on the distance between them.

## 2. Review of one-electron atoms (hydrogen-like)

- Decoupling of the center-of-mass motion from the relative motion.
- Nonrelativistic treatment: ... owing to the (large) mass ratio  $m_p/m_e \approx 1836$ .
- (Classical) Hamiltonian functions of ‘nucleus + electron’:

$$H = K + V = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + V(\mathbf{r}_1, \mathbf{r}_2) = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}_r^2}{2\mu} + V(\mathbf{x}_r) \quad \text{if } V = V(\mathbf{x}_1 - \mathbf{x}_2).$$

- Final form makes use of **relative coordinates**:

$$\begin{array}{lll} \mathbf{x}_1, \mathbf{x}_2 & \implies & \mathbf{r}_r = \mathbf{r}_2 - \mathbf{r}_1; \\ \mathbf{p}_1, \mathbf{p}_2 & \implies & \mathbf{R} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}; \end{array} \quad \begin{array}{lll} \mathbf{p}_r = \mu \dot{\mathbf{r}}_r; & \mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \\ \mathbf{P} = M \dot{\mathbf{R}}; & M = m_1 + m_2 \end{array}$$

- Separation of the Hamilton function:

- (i) a trivial part  $\frac{\mathbf{P}^2}{2M}$
- (ii) the Hamiltonian function for the relative coordinates.
- Separation ansatz:  $\Psi(\mathbf{R}, \mathbf{r}_r) = S(\mathbf{R})\psi(\mathbf{r}_r)$  and **symmetric potential**:  $V = V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{\alpha\hbar c Z}{r}$

$$\frac{\partial^2 S}{\partial X^2} + \frac{\partial^2 S}{\partial Y^2} + \frac{\partial^2 S}{\partial Z^2} + \frac{2M}{\hbar^2} W S = 0$$

$$\left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right] \psi(\mathbf{r}_r) + \frac{2\mu}{\hbar^2} \left( E + \frac{\alpha Z \hbar c}{r} \right) \psi = 0$$

$$E = E_{\text{total}} - W, \quad \mathbf{R} = (X, Y, Z), \quad \mathbf{r}_r = (r, \vartheta, \varphi)$$

- Agreement: We usually assume  $\mu \approx m_{\text{electron}}$  and  $\mathbf{r}_r \approx \mathbf{r}_{\text{electron}} \equiv \mathbf{r}$ , and simply refer to the SE of the electron with  $\psi = \psi(\mathbf{r})$ .

## 2.1.b. Atomic units

### Atomic units:

- Use of SI units can be rather tedious in writing down most equations, cf. SE.
- atomic units (au):

$$\hbar = m_{\text{electron}} = \frac{e^2}{4\pi\epsilon_0} \equiv 1 .$$

- Length in Bohr units:  $1 \text{ a}_0 = 0.5291 \cdot 10^{-10} \text{ m}$
- Energies in Hartree units:  $1 \text{ Hartree} = 27.211 \text{ eV} = 4.359 \cdot 10^{-18} \text{ J}$
- Time:  $1 \text{ a.u.} = 2.418 \cdot 10^{-17} \text{ s}$
- Velocity:  $1 \text{ a.u.} = 2.187 \cdot 10^6 \text{ m/s}$

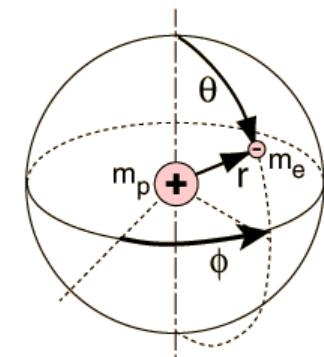
## 2.2. Nonrelativistic theory: A short reminder

### 2.2.a. Schrödinger equation for hydrogenic atoms

#### Solving the SE in a nutshell:

- Correspondence principle:

$$\begin{aligned} \mathbf{r} &\longrightarrow \hat{\mathbf{r}} \\ \text{classical mechanics} &\implies \mathbf{p}_r \longrightarrow -i\hbar \frac{\partial}{\partial \mathbf{r}} \implies \text{quantum mechanics} \\ E &\longrightarrow i\hbar \frac{\partial}{\partial t} \end{aligned}$$



hyperphysics.phy-astr.gsu.edu

## 2. Review of one-electron atoms (hydrogen-like)

➤ Separation of relative motion:

$$\psi = \psi(r, \vartheta, \varphi) = R(r) Y(\vartheta, \varphi) = R(r) \Theta(\vartheta) \Phi(\varphi)$$

$$Y_{lm}(\vartheta, \varphi) = \Theta(\vartheta) \Phi(\varphi) = A_{lm} A_m P_{l|m|}(\cos \vartheta) e^{im\varphi}$$

➤ Three independent ODE's: ... two separation constants  $\lambda, \beta^2$

$$\frac{d}{dr} \left( r^2 + \frac{dR}{dr} \right) + \left[ \frac{2\mu r^2}{\hbar^2} \left( E + \frac{\alpha \hbar c Z}{r} \right) - \lambda \right] R(r) = 0$$

$$\frac{1}{\sin \vartheta} \frac{d}{d\vartheta} \left( \sin \vartheta \frac{d\Theta}{d\vartheta} \right) + \left( \lambda - \frac{\beta^2}{\sin^2 \vartheta} \right) \Theta(\vartheta) = 0$$

$$\frac{d^2 \Phi}{d\varphi^2} + \beta^2 \Phi(\varphi) = 0, \quad \mathbf{l}^2 Y(\vartheta, \varphi) = \lambda \hbar^2 Y(\vartheta, \varphi)$$

➤ In atomic units: ... SE simplifies to:

$$\left( -\frac{1}{2} \nabla^2 + V(\mathbf{r}) \right) \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad V(r) = -\frac{Z}{r}$$

➤ Common set of eigenfunctions:  $H, \mathbf{l}^2$  and  $l_z$ .

➤ Spherical harmonics  $Y_{lm}(\vartheta, \varphi)$ : ... eigenfunctions of  $\mathbf{l}^2$  and  $l_z$ :

$$\mathbf{l}^2 Y_{lm}(\vartheta, \varphi) = l(l+1) \hbar^2 Y_{lm}(\vartheta, \varphi) \quad l_z Y_{lm}(\vartheta, \varphi) = m \hbar Y_{lm}(\vartheta, \varphi).$$

➤ Good quantum numbers:  $\psi(r, \vartheta, \varphi) = R_{nl}(r) Y_{lm}(\vartheta, \varphi)$

➤ With each degree of freedom, there is generally one (good) quantum number associated which helps in classifying the solutions.

## 2.2.b. Spherical harmonics

### Building blocks of atomic physics:

- Spherical harmonics  $Y_{lm}(\vartheta, \phi)$ : ... very important for atomic physics owing to their properties.
- Eigenfunctions of:  $\mathbf{l}^2$  and  $l_z$ .

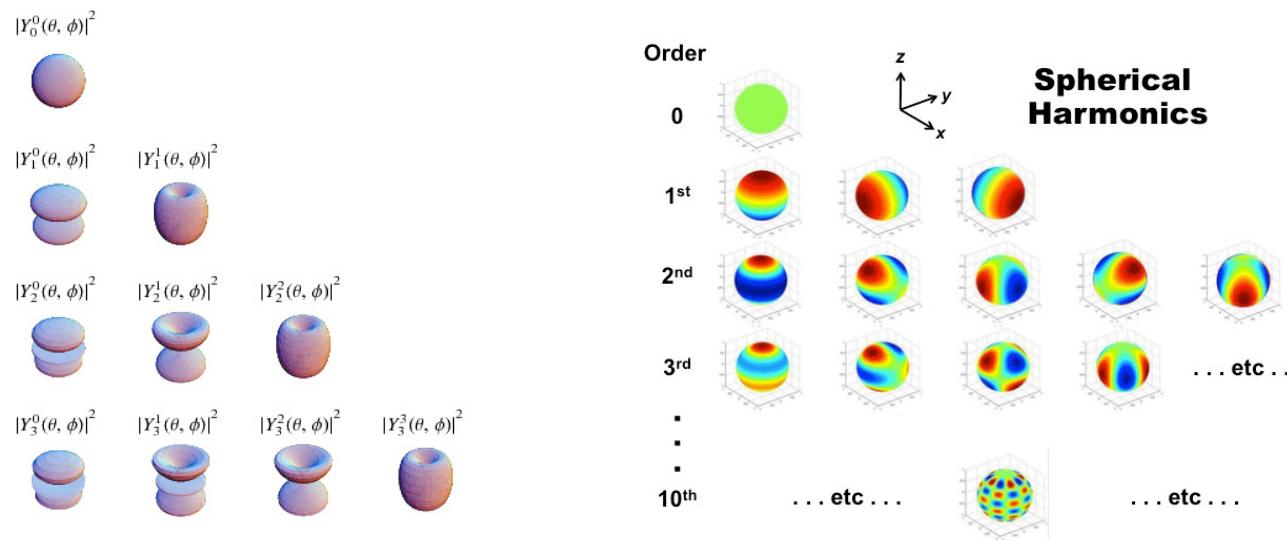


Figure 2.1.: Left: There are many different representations of the spherical harmonics, in which one displays the modulus, real or imaginary parts of these functions, or changes in the (complex) phase; from: mathworld.wolfram.com. Right: from <http://mri-q.com/uploads>.

## 2. Review of one-electron atoms (hydrogen-like)

➤ Explicit representation in coordinate space:

$$Y_{00}(\vartheta, \varphi) = \frac{1}{\sqrt{4\pi}}$$

$$Y_{10}(\vartheta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos \vartheta,$$

$$Y_{1,\pm 1}(\vartheta, \varphi) = \mp \sqrt{\frac{3}{8\pi}} \sin \vartheta e^{\pm i\varphi}$$

$$Y_{20}(\vartheta, \varphi) = \frac{1}{4} \sqrt{\frac{5}{\pi}} (3 \cos^2 \vartheta - 1),$$

$$Y_{2,\pm 1}(\vartheta, \varphi) = \mp \frac{1}{2} \sqrt{\frac{15}{2\pi}} \sin \vartheta \cos \vartheta e^{\pm i\varphi},$$

$$Y_{2,\pm 2}(\vartheta, \varphi) = \frac{1}{2} \sqrt{\frac{15}{2\pi}} \sin^2 \vartheta e^{\pm 2i\varphi}$$

➤ Make use of properties, whenever possible:

$$\langle Y_{lm} | Y_{l'm'} \rangle = \delta_{ll'} \delta_{mm'}, \quad Y_{lm}^*(\vartheta, \varphi) = (-1)^m Y_{l,-m}(\vartheta, \varphi), \quad Y_{lm}(\pi - \vartheta, \pi + \varphi) = (-1)^l Y_{lm}(\vartheta, \varphi).$$

➤ Wigner 3-j symbols:

$$Y_{lm}(\vartheta, \varphi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \vartheta) e^{im\varphi}$$

$$\langle Y_{l_1 m_1} | Y_{l_2 m_2} | Y_{l_3 m_3} \rangle = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

➤ Addition theorem: For any two unit vectors  $\mathbf{x} = \mathbf{x}(\vartheta, \varphi)$  and  $\mathbf{y} = \mathbf{y}(\vartheta', \varphi')$  and Legendre polynomial of order  $l$

$$P_l(\mathbf{x} \cdot \mathbf{y}) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}^*(\vartheta', \varphi') Y_{lm}(\vartheta, \varphi).$$

➤ Unsöld's theorem: ... for  $\mathbf{x} = \mathbf{y}$  (see below).

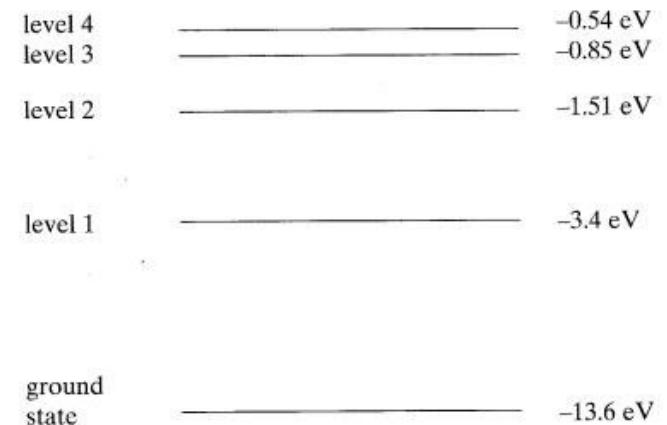
## 2.2.c. Complete set of commutable operators

### Reminder:

- A set of operators  $A_i$  ( $i = 1, \dots, n$ ) is called **complete**, if no additional (linear-independent) operator exist which commutes with all  $A_i$ .
- A complete set of operators has a simultaneous set of eigenfunctions which is not degenerate.
- H-atom:  $H$ ,  $\mathbf{l}^2$  and  $l_z$  are a complete set:  $[H, \mathbf{l}^2] = [H, l_z] = [\mathbf{l}^2, l_z] = 0$ .

## 2.2.d. Energies and quantum numbers

### Solutions $\psi(\mathbf{r}) = R_{nl}(r) Y_{lm}(\vartheta, \varphi)$ :



- Are classified by three quantum numbers
  - principal quantum number:  $n = 1, 2, 3, \dots$
  - orbital angular momentum quantum number:  $l = 0, 1, 2, \dots$
  - magnetic quantum number:  $m = -l, -l + 1, \dots, l$

- Eigen energies: ... degenerate in  $l$  and  $m$

$$Z = -\frac{Z^2}{2n^2} = -\frac{-\mu \alpha^2 c^2 Z^2}{2n^2} = -\frac{Z^2}{n^2} \cdot R_\infty \frac{M}{M+m}$$

- For given  $n$ , all  $\sum_{l=0}^{n-1} (2l+1) = n^2$  eigenstates have the **same energy within the non-relativistic theory**.

From: sciwebhop.net

## 2.2.e. Radial equation

### Radial orbitals:

➤ Radial equation:

$$\frac{1}{R(r)} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + 2r^2 \left( E + \frac{Z}{r} \right) = -\frac{1}{Y} l^2 Y(\theta, \phi) = \lambda, \quad \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left[ 2r^2 \left( E + \frac{Z}{r} \right) - \lambda \right] = 0$$

➤ Radial orbitals (functions)  $P(r) = r R(r)$ :

### How to find solutions for $R(r) = P(r)/r$ ??

➤ QM I or textbooks: Make proper substitutions and (try to) recognize the Whittaker equation or the defining equation for the Laguerre polynomials; with  $n_r$  denotes the number of radial knots.

$$R_{nl}(r) = -A_{nl} e^{-\beta_n r} (2\beta_n r)^l L_{n-l-1}^{2l+1}(2\beta_n r), \quad \beta_n = \sqrt{2E_n} au = \sqrt{-\frac{2\mu E_n}{\hbar^2}} = \frac{\mu \alpha c Z}{n \hbar}, \quad n = l + n_r + 1.$$

➤ The functions  $L_q^p(x)$  are called the generalized Laguerre polynomials of order  $p$  and grad  $q$ . — H'm ...

➤ Numerical solutions, direct integration:

$$\frac{d^2 P(r)}{dr^2} = F(r, E)$$

- Boundary behaviour:  $P(r \rightarrow 0) = A r^{l+1}; \quad P(r \rightarrow \infty) = B e^{-\alpha r}$
- Choose a proper (numerical) grid:  $\{r_1, r_2, \dots, r_N; \quad r_i \leq r_{i+1}\}$ .
- Take initial values  $P(r_1), P(r_2)$  due to the near-zero behavior  $P(r \rightarrow 0) \sim r^{l+1}$ .

➤ **Algebraic ansatz:** ... to transform the ode into an algebraic equation.

$$P(r) = \sum_i^N X_i g_i(r)$$

### Algebraic solutions; choice of basis functions:

➤ Generalized eigenvalue equation for  $\{E, \mathbf{X}\}$ : ... using matrix notation

$$(\mathbf{P} + \mathbf{V}^Z + \mathbf{V}) \mathbf{X} = E \mathbf{S} \mathbf{X}$$

➤ Frequently utilized atomic basis sets: (tempered functions)

- i) **Slater functions (STO):**  $g_i(r) = A_i r^{l+1} e^{-\alpha_i r}, \quad i = 1, \dots, N$
- ii) **Gaussian functions (GTO):**  $g_i(r) = B_i r^{l+1} e^{-\alpha_i r^2}, \quad i = 1, \dots, N$

➤ Parameter:

- Independent optimization on a nearby atomic configuration (quantum chemistry).
- Tempered functions (complete for  $N \rightarrow \infty$ )

$$\alpha_i = \lambda_N \cdot \beta_N^{(i-1)}, \quad i = 1, \dots, N, \quad \lim_{N \rightarrow \infty} \lambda_N = 0, \quad \lim_{N \rightarrow \infty} \beta_N = 1.$$

## 2. Review of one-electron atoms (hydrogen-like)

➤ Normalization and expectation values with hydrogenic wave functions:  $\bar{A} = \langle A \rangle = \langle \psi | A | \psi \rangle$

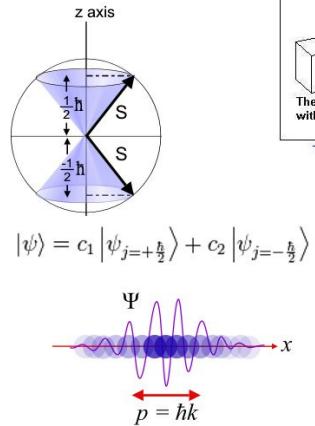
$$\begin{aligned}\langle \psi_{n\ell m} | \psi_{n'\ell' m'} \rangle &\equiv \langle n\ell m | n'\ell' m' \rangle = \int d^3r \psi_{n\ell m}^* \psi_{n'\ell' m'} = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'} \\ &= \int_0^\infty dr r^2 R_{nl}^*(r) R_{n'l'}(r) \int_0^\pi d\vartheta \sin \vartheta \Theta_{lm}^* \Theta_{l'm'} \int_0^{2\pi} d\varphi \Phi_m^* \Phi_{m'} \\ \langle r^k \rangle &= \int_0^\infty dr r^2 R_{nl}^*(r) \textcolor{blue}{r^k} R_{n'l'}(r); \quad \langle r \rangle_{l=n-1} = n^2 \left(1 + \frac{1}{2n}\right) \frac{a_0}{Z}; \quad \langle r^{-1} \rangle = \frac{1}{n^2} \left(\frac{Z}{a_0}\right); \quad \dots\end{aligned}$$

### 2.2.f. Pauli's wave mechanics: Fine structure

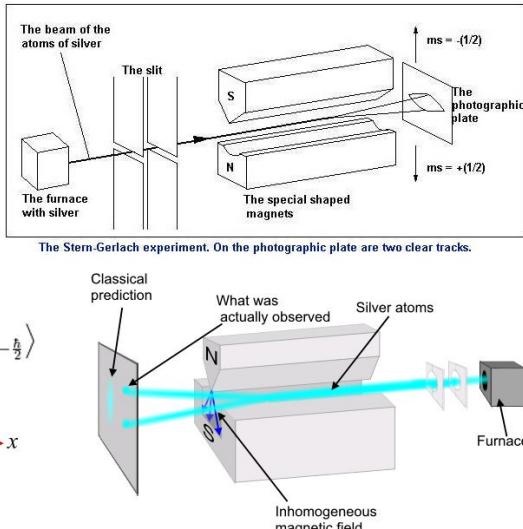
#### Observations that suggest an electron spin $s = 1/2$ :

- For given  $n$ , all solutions  $\psi(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta, \phi)$  are degenerate within the non-relativistic theory, more detailed observations show a line and level splitting which cannot be explained without the **spin of the electron(s)**.
- **magnetic spin quantum number  $m_s$ :** ... Uhlenbeck and Goudsmit (1925) postulated a further quantum number, the electron spin, with just two space projections.
- **Stern-Gerlach experiment:** Deflection of atomic beams in an inhomogenous magnetic field;  $\mu \sim \mathbf{l}, \mathbf{s}$ .  
Inhomogeneous field (and magnetic moment  $\mu_z$ ):  $\frac{\partial \mathbf{B}}{\partial z} \neq 0, \quad \mathbf{F} = -\mu_z \cdot \frac{\partial \mathbf{B}}{\partial z}$
- **Anomalous Zeeman effect:** Line and level splittings in the magnetic field that cannot be explained in terms of  $l$  and  $m$  alone. Especially, there even occurs a splitting of atomic levels in magnetic field even for  $l = 0$ .
- **Dublett structure of the alkali metals:** e.g., splitting of the yellow D-line in sodium by  $17 \text{ cm}^{-1}$ .

E4



## Stern-Gerlach



S6

## Zeeman Effect

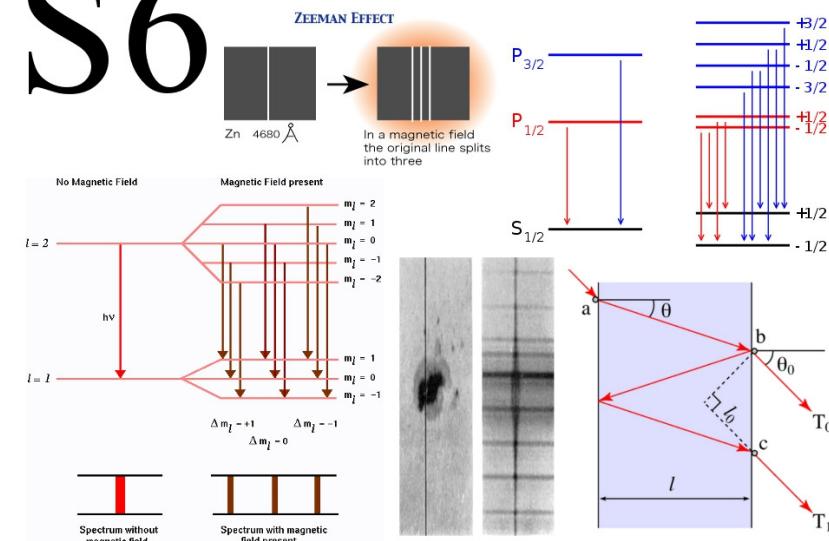


Figure 2.2.: Left: From: <http://pages.physics.cornell.edu/> Right: **Normal Zeeman effect:** splitting of a spectral line into several components in the presence of a static magnetic field. **Anomalous Zeeman effect:** There are a lot of observations that cannot be explained alone in terms of the magnetic and angular momentum quantum numbers, however. From: <http://pages.physics.cornell.edu/>.

➤ Spin (angular momentum) operators: ... acts only upon the spin space with  $s = 1/2$  and  $m_s = \pm 1/2$ :

$$\mathbf{s}^2 \chi_{sm_s} = s(s+1) \hbar^2 \chi_{sm_s}, \quad s_z \chi_{sm_s} = m_s \hbar \chi_{sm_s} \quad m_s = -s, -s+1, \dots, s$$

$$\chi_{1/2} = \chi(+) = |\uparrow\rangle = \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \chi_{-1/2} = \chi(-) = |\downarrow\rangle = \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

## 2. Review of one-electron atoms (hydrogen-like)

➤ Commutation relations: ... cf. orbital angular momentum

$$[s_x, s_y] = i\hbar s_z, \quad [s_y, s_z] = i\hbar s_x, \quad [s_z, s_x] = i\hbar s_y.$$

➤ Pauli matrices: Spin operator can be written as

$$\begin{aligned} \mathbf{s} &= \frac{\hbar}{2} \boldsymbol{\sigma} = \frac{\hbar}{2} (\sigma_x \mathbf{e}_x + \sigma_y \mathbf{e}_y + \sigma_z \mathbf{e}_z) \\ \sigma_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ [\sigma_i, \sigma_k] &= 2i \epsilon_{ikm} \sigma_m; \quad \{\sigma_i, \sigma_k\} = 0. \end{aligned}$$

➤ Schrödinger operators: are diagonal in this representation; within Pauli's wave mechanics, all operators are  $2 \times 2$  matrices.

$$(p_x)_{\text{Pauli}} = \begin{pmatrix} p_x & 0 \\ 0 & p_x \end{pmatrix} = \begin{pmatrix} -i\hbar \frac{\partial}{\partial x} & 0 \\ 0 & -i\hbar \frac{\partial}{\partial x} \end{pmatrix}; \quad (L_z)_{\text{Pauli}} = \begin{pmatrix} l_z & 0 \\ 0 & l_z \end{pmatrix} = \begin{pmatrix} -i\hbar \frac{\partial}{\partial \phi} & 0 \\ 0 & -i\hbar \frac{\partial}{\partial \phi} \end{pmatrix}$$

➤ Spin is a quantum mechanically concept without direct classical analogs. No classical limit for the spin).

### 2.2.g. Vector model: Constants of motion in a central field

#### Complete set of quantum numbers:

➤ So far: ...  $n, l, m, m_s$  according to the set of commutable operators  $\{H, \mathbf{l}^2, l_z, s_z\}$ .

➤ Alternative set of commutable operators:  $\{H, \mathbf{l}^2, \mathbf{j}^2, j_z\}$

- with operators  $\mathbf{j} = \mathbf{l} + \mathbf{s}$ ;  $j_z = l_z + s_z$ ;  $\mathbf{j}^2 = \mathbf{l}^2 + \mathbf{s}^2 + 2\mathbf{l} \cdot \mathbf{s}$
- principal quantum number:  $n = 1, 2, 3, \dots$
- orbital angular momentum quantum number:  $\ell = 0, 1, 2, \dots$
- total angular momentum quantum number:  $j = \ell \pm 1/2$
- magnetic quantum number of the total angular momentum:  $m = -j, -j+1, \dots, j$

➤ In Pauli representation, we have

$$(j_z)_{\text{Pauli}} = (l_z)_{\text{Pauli}} + \frac{\hbar}{2} \sigma_z = \begin{pmatrix} l_z + \frac{\hbar}{2} & 0 \\ 0 & l_z - \frac{\hbar}{2} \end{pmatrix} \quad (\mathbf{j}^2)_{\text{Pauli}} = \begin{pmatrix} \mathbf{l}^2 + \hbar l_z + \frac{3}{4} \hbar^2 & \hbar(l_x - il_y) \\ \hbar(l_x + il_y) & \mathbf{l}^2 - \hbar l_z + \frac{3}{4} \hbar^2 \end{pmatrix}.$$

➤ Commutation relations: ... follow immediately from those of  $\mathbf{l}^2$  and  $l_z$  (prove it !)

$$[H, \mathbf{j}^2] = [H, j_z] = [\mathbf{j}^2, j_z] = [\mathbf{j}^2, \mathbf{l}^2] = [\mathbf{l}^2, j_z] = 0.$$

## 2.2.h. Fine structure: Relativistic interaction terms

### Three (widely-known) terms:

- Dirac equation: ... leads to a partial splitting of the degenerate levels; expansion in  $v/c$  and with terms up to  $(v/c)^2$
- Relativistic mass term: ... spin-independent level shift that depends on  $n$  and  $\ell$

$$H' = -\frac{1}{2mc^2} (E_n - V(r))^2, \quad \Delta E'_n = -\frac{\alpha^2 Z^2}{n^2} E_n \left( \frac{3}{4} - \frac{n}{\ell + 1/2} \right)$$

## 2. Review of one-electron atoms (hydrogen-like)

➤ Spin-orbit couplings term: ... level splitting due to the expectation value

$$H'' = -\frac{\hbar^2}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr} \langle \mathbf{l} \cdot \mathbf{s} \rangle = \frac{\hbar^2 Z^2 e^2}{8\pi\epsilon_0 m^2 c^2} \frac{\langle \mathbf{l} \cdot \mathbf{s} \rangle}{r^3}$$

$$\Delta E_n'' = -\frac{\alpha^2 Z^2}{n^2} E_n \frac{n}{\ell(\ell+1/2)(\ell+1)} \langle \mathbf{l} \cdot \mathbf{s} \rangle \quad \ell \neq 0$$

➤ Darwin term: ... pure relativistic origin; due to behaviour of electron for  $r \rightarrow 0$  (nuclear potential).

$$H''' = -\frac{\hbar^2}{4m^2 c^2} e \mathbf{E} \cdot \boldsymbol{\nabla} \quad \Delta E_n''' = \frac{\pi\hbar^2}{2m^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} |\psi(0)|^2 \quad \text{only for } \ell = 0$$

➤ Fine structure splitting: ... total level shift and splitting

$$\Delta E = \Delta E' + \Delta E'' + \Delta E'''$$

$$\Delta E_{nj} = -\frac{\alpha^2 Z^2}{n^2} E_n \left( \frac{3}{4} - \frac{n}{j+1/2} \right) = \alpha^2 \frac{m}{2\hbar^2} \frac{e^2}{(4\pi\epsilon_0)^2} \frac{Z^4}{n^4} \left( \frac{3}{4} - \frac{n}{j+1/2} \right) \sim Z^4$$

$$\Delta E_{nj} \sim Z^4; \quad \Delta E_{nj} - \Delta E_{nj'} \sim n^{-3}$$

## 2.3. Relativistic theory: Dirac's equation

### 2.3.a. Relativistic Hamiltonians and wave equations

#### Different Hamiltonian operators:

- Hamiltonian function: ... of a relativistic electron in an electro-magnetic field

$$H = \underbrace{c \sqrt{m^2 c^2 + (\mathbf{p} + e\mathbf{A})(\mathbf{p} + e\mathbf{A})}}_{\text{rest and kinetic energy}} - e\phi \underset{\mathbf{A} \neq \mathbf{A}(t), \phi \neq \phi(t)}{=} E.$$

- Question: How to transform this expression with  $\mathbf{p} \rightarrow -i\hbar \frac{\partial}{\partial \mathbf{r}}$  into a useful Hamiltonian ?
- Expansions in powers  $1/m^2 c^2$ : ... possible but difficult.
- Klein-Gordan equation: Use of the quadratic form gives rise to a wave equation for massive spin-0 particles.
- Relativistic Schrödinger equation ... quadratic form of the Hamiltonian function; together with  
 $\mathbf{p} = -i\hbar \frac{\partial}{\partial \mathbf{r}}, \quad e\phi = V \neq V(t)$

$$\begin{aligned} (\mathbf{p} + e\mathbf{A})(\mathbf{p} + e\mathbf{A}) &= \mathbf{p}^2 + e(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + e^2 \mathbf{A}^2 = \left( \frac{E - e\phi}{c} \right)^2 - m^2 c^2 \\ [-\hbar^2 \nabla^2 - i\hbar e(\nabla \cdot \mathbf{A} + \mathbf{A} \cdot \nabla) + e^2 \mathbf{A}^2] \psi &= \left[ \frac{(E - V)^2}{c^2} - m^2 c^2 \right] \psi \end{aligned}$$

- Especially for hydrogen-like atoms:  $\mathbf{A} = 0$  and  $V = -\frac{\alpha \hbar Z}{r}$  ()

$$-\hbar^2 \nabla^2 \psi = \left[ \left( \frac{E}{c} - \frac{\alpha \hbar Z}{r} \right)^2 - m^2 c^2 \right] \psi$$

## 2. Review of one-electron atoms (hydrogen-like)

➤ Dirac's Hamiltonian: ... with Dirac's assumption:  $\beta, \alpha = (\alpha_x, \alpha_y, \alpha_z)$  are constants.

$$\begin{aligned} H &= c \sqrt{m^2c^2 + (\mathbf{p} + e\mathbf{A})(\mathbf{p} + e\mathbf{A})} + V = c \sqrt{m^2c^2 + (p_x + eA_x)^2 + (p_y + eA_y)^2 + (p_z + eA_z)^2} + V \\ &= c \sqrt{[\beta mc + \alpha \cdot (\mathbf{p} + e\mathbf{A})]^2} + V \end{aligned}$$

➤ Two mathematically equivalent operators: ... the root remains the same for  $(\alpha, \beta) \rightarrow (-\alpha, -\beta)$

$$H_+ = \beta mc^2 + c\boldsymbol{\alpha}(\mathbf{p} + e\mathbf{A}) + V = -H_- + 2V$$

$$H_- = -\beta mc^2 - c\boldsymbol{\alpha}(\mathbf{p} + e\mathbf{A}) + V = H_D = -\beta mc^2 - c\boldsymbol{\alpha}(-i\hbar\nabla + e\mathbf{A}) + V$$

➤ Dirac matrices and spinors:

- $\alpha_m, \beta$  cannot be numbers nor  $2 \times 2$  matrices;
- simplest constants are  $4 \times 4$  matrices;
- most common representation are called Dirac matrices (see below).
- since  $H_D$  is a  $4 \times 4$  matrix, the wave functions  $\psi$  (in  $H\psi = E\psi$ ) must have 4 columns.

➤ Relativistic equation for motion of an electron in the central field of the nucleus:

➤ Time-dependent Dirac equation: ... (correct) wave equation for all spin-1/2 particles

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = H_D(\mathbf{r}, t).$$

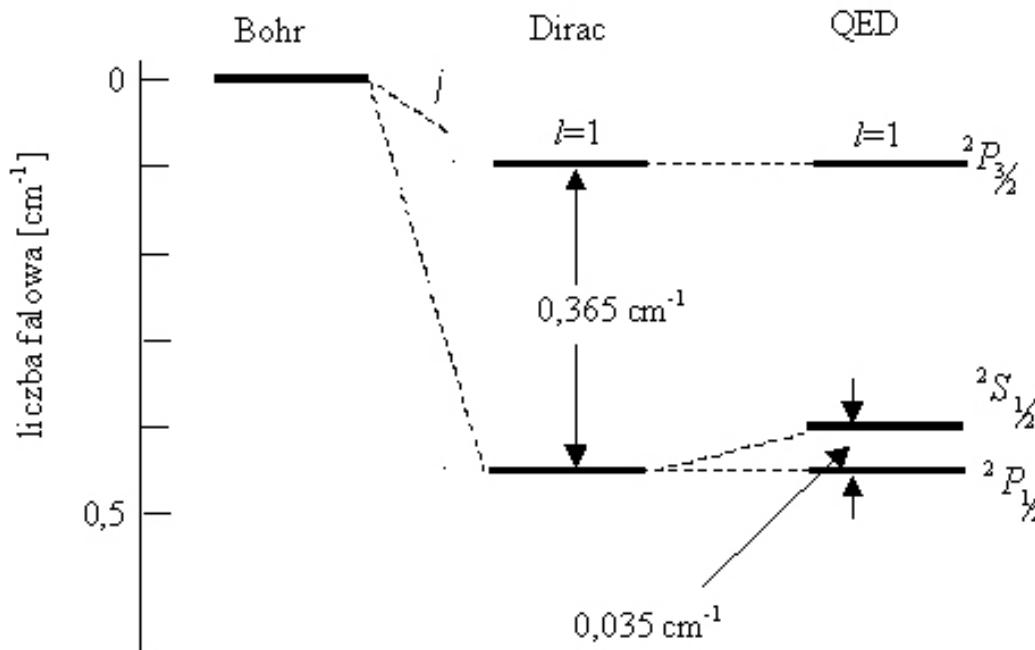


Figure 2.3.: The subtle Lamb shift of the  $n = 2$  levels in hydrogen according to Bohr's and Dirac's theory and together with the QED predictions. In particular, the Lamb shift removes the degeneration due to quantum number  $j$ ; from: Haken and Wolf, Atomic Physics (Springer, 1996).

### 2.3.b. Dirac's Hamiltonian

#### Properties of Dirac spinors and operators:

➤ Time-dependent Dirac equation: ... relativistic covariant; for free electrons

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \left( \underbrace{-i\hbar c \boldsymbol{\alpha} \cdot \nabla}_{\text{kinetic energy term } \mathbf{p} = -i\hbar \frac{\partial}{\partial \mathbf{r}}} + \underbrace{mc^2 \boldsymbol{\alpha}_0}_{\text{rest mass term}} \right) \psi(\mathbf{r}, t).$$

## 2. Review of one-electron atoms (hydrogen-like)

➤ Dirac matrices: ...  $\alpha$  and  $\alpha_0$  are  $4 \times 4$  matrices ...

$$\alpha = (\alpha_x, \alpha_y, \alpha_z) = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad \alpha_0 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

➤ Wave functions are 4-spinors:

$$\psi(\mathbf{r}, t) = \begin{pmatrix} \phi_1(\mathbf{r}, t) \\ \phi_2(\mathbf{r}, t) \\ \phi_3(\mathbf{r}, t) \\ \phi_4(\mathbf{r}, t) \end{pmatrix}, \quad \psi^*(\mathbf{r}, t) = (\phi_1^*(\mathbf{r}, t), \dots)$$

➤ Normalization:

$$1 = \langle \psi(\mathbf{r}, t) | \psi(\mathbf{r}, t) \rangle = \int dV \psi^* \psi = \int dV [\phi_1^* \phi_1 + \phi_2^* \phi_2 + \phi_3^* \phi_3 + \phi_4^* \phi_4]$$

➤ Dirac operator: ... all operators are generally  $4 \times 4$  matrices

$$(x)_{\text{Dirac}} = \begin{pmatrix} x & 0 & 0 & 0 \\ 0 & x & 0 & 0 \\ 0 & 0 & x & 0 \\ 0 & 0 & 0 & x \end{pmatrix}, \quad (l_z)_{\text{Dirac}} = \begin{pmatrix} l_z & 0 & 0 & 0 \\ 0 & l_z & 0 & 0 \\ 0 & 0 & l_z & 0 \\ 0 & 0 & 0 & l_z \end{pmatrix}$$

➤ Alternative form of Dirac equation: ... because of  $H_D \psi = E \psi$  and  $H_+ \psi = (-H_D + 2V) \psi$ , and with

$$V = -e\phi, \mathbf{E} = -\nabla\phi, \mathbf{B} = \nabla \times \mathbf{A}$$

$$H_+ H_D \psi = E(-E + 2V) \psi$$

$$\left[ \boldsymbol{\alpha} \cdot (\mathbf{p} + e\mathbf{A}) \boldsymbol{\alpha} \cdot (\mathbf{p} + e\mathbf{A}) - \frac{\boldsymbol{\alpha}}{c} (\mathbf{p}V - V\mathbf{p}) \right] \psi = \left[ \left( \frac{E - V}{c} \right)^2 - m^2 c^2 \right] \psi$$

$$\boldsymbol{\alpha} \cdot (\mathbf{p} + e\mathbf{A}) \boldsymbol{\alpha} \cdot (\mathbf{p} + e\mathbf{A}) = \mathbf{p}^2 + e(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{P}) + e^2 \mathbf{A}^2 + \hbar e \boldsymbol{\sigma}_D \cdot \mathbf{B}$$

$$-\frac{\boldsymbol{\alpha}}{c} (\mathbf{p}V - V\mathbf{p}) = \frac{i\hbar e}{c} \boldsymbol{\alpha} \cdot \mathbf{E}$$

$$\boldsymbol{\sigma}_D = \begin{pmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{pmatrix} \mathbf{e}_x + \begin{pmatrix} \sigma_y & 0 \\ 0 & \sigma_y \end{pmatrix} \mathbf{e}_y + \dots$$

➤ Alternative form of Dirac equation: This equation can be re-written with  $\mathbf{p} = -i\hbar\nabla$ ; two additional terms

$$\left[ \mathbf{p}^2 + e(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{P}) + e^2 \mathbf{A}^2 + \hbar e \boldsymbol{\sigma}_D \cdot \mathbf{B} + \frac{i\hbar e}{c} \boldsymbol{\alpha} \cdot \mathbf{E} \right] \psi = \left[ \left( \frac{E - V}{c} \right)^2 - m^2 c^2 \right] \psi$$

➤ Spin contributions to the Dirac equation:

- magnetic spin moment:  $-\frac{\hbar e}{2m} \boldsymbol{\sigma}_D$
- electrical moment:  $-\frac{i\hbar e}{2mc} \boldsymbol{\alpha}$

2. Review of one-electron atoms (hydrogen-like)

### 2.3.c. Plane-wave solutions for the time-independent Dirac equation

#### Plane-wave solutions for free particles:

- Time-independent Dirac equation for free particles: ... separation of time; first-order differential equation

$$(-i\hbar c \boldsymbol{\alpha} \cdot \nabla + mc^2 \boldsymbol{\alpha}_0) \psi(\mathbf{r}) = E \psi(\mathbf{r}).$$

- Plane-wave ansatz (solutions): ...  $\psi_p(\mathbf{r}) = w(p) \exp(ipz/\hbar)$ ; for the motion along the  $z$ -axis (quantization axis).

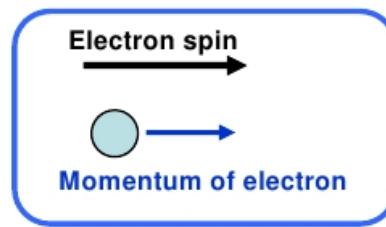
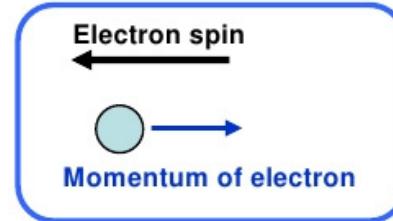
$$\begin{pmatrix} mc^2 & 0 & pc & 0 \\ 0 & mc^2 & 0 & -pc \\ pc & 0 & -mc^2 & 0 \\ 0 & -pc & 0 & -mc^2 \end{pmatrix} w(p) = E w(p).$$

- Solutions with negative energy — h'm ?? ... Two solutions can be found from the characteristic polynomial:

$$E_+(p) = \sqrt{(mc^2)^2 + (pc)^2}; \quad E_-(p) = -\sqrt{(mc^2)^2 + (pc)^2}$$

- Bi-spinors: ... for each energy, there are two (degenerate) wave functions according to the two spin directions (parallel & anti-parallel) to  $z$ -axis.

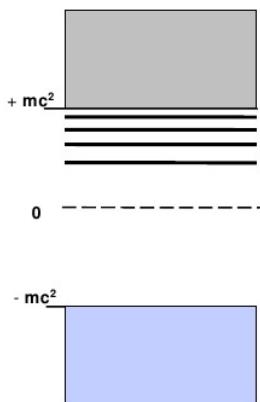
$$w_{+1/2} = N \begin{pmatrix} 1 \\ 0 \\ \frac{cp}{E_+ + mc^2} \\ 0 \end{pmatrix}, \quad w_{-1/2} = N \begin{pmatrix} 0 \\ 1 \\ 0 \\ \frac{-cp}{E_+ + mc^2} \end{pmatrix} \quad w_{m_s} = N \begin{pmatrix} \chi_{m_s} \\ \frac{cp \sigma_z}{E_+ + mc^2} \chi_{m_s} \end{pmatrix}$$

Helicity +1;  $w_{+1/2}$ .Helicity -1;  $w_{-1/2}$ .

### 2.3.d. Dirac spectrum: Antiparticles

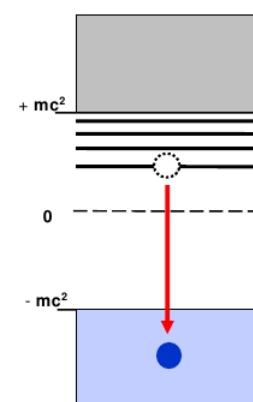
Energy of free particles  $E(p) = \pm \sqrt{(mc^2)^2 + (pc)^2}$ :

- Particles with positive energy:  $E_+(p) \geq mc^2$
- Particles with negative energy:  $E_-(p) \leq -mc^2$
- Ground state of atoms (should) becomes apparently unstable.

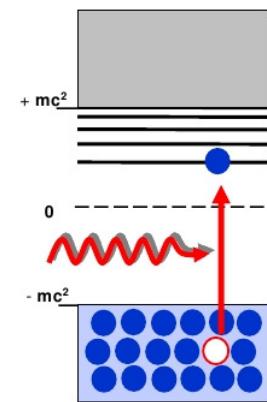
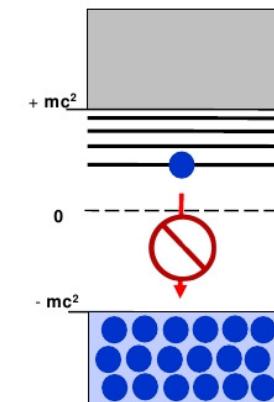


“Free” electrons with positive energy

Bound electrons



“Free” electrons with negative energy



## 2. Review of one-electron atoms (hydrogen-like)

### Concept of “Dirac sea” (Dirac, 1930):

- Dirac sea: ... proposed model for vacuum as infinite sea of particles with negative energy.
- Stability of electrons: ... due to the Pauli principle
- Positrons: ... hole in the Dirac sea; appears to an electric field like a positively-charged particle

### 2.3.e. Constants of motion in a central field

#### Commutable operators for the Dirac Hamiltonian:

- Time-independent Dirac equation: ... for a particle in a central field:

$$(-i\hbar c \boldsymbol{\alpha} \cdot \nabla + mc^2 \alpha_0 + V(\mathbf{r})) \psi(\mathbf{r}) = E \psi(\mathbf{r}).$$

- Complete set in non-relativistic theory: ... either  $\{H, \mathbf{l}^2, l_z, s_z\}$  or  $\{H, \mathbf{l}^2, \mathbf{j}^2, j_z\}$ ;

- Complete set for Dirac particles:  $[H_D, \mathbf{j}^2] = [H_D, j_z] = [\mathbf{j}^2, j_z] = 0$ , with

$$\mathbf{j}^2 = j_x^2 + j_y^2 + j_z^2 = \left( \mathbf{l} + \frac{\hbar}{2} \boldsymbol{\sigma}_D \right) \cdot \left( \mathbf{l} + \frac{\hbar}{2} \boldsymbol{\sigma}_D \right), \quad j_z = \left( l_z + \frac{\hbar}{2} \sigma_{D,z} \right)$$

- Dirac operator  $k = \alpha_0 (\mathbf{l} \cdot \boldsymbol{\sigma}_D + \hbar)$  :  $[H_D, \mathbf{l}^2] \neq 0$ ; only

$$[H_D, k] = [\mathbf{j}^2, k] = [j_z, k] = 0.$$

➤ Complete set for Dirac operator with central field  $V(r)$ :  $\{H_D, k, \mathbf{j}^2, j_z\}$

$$\mathbf{j}^2 \psi(\mathbf{r}) = \hbar^2 j(j+1) \psi(\mathbf{r}) \quad \text{half integer}$$

$$j_z \psi(\mathbf{r}) = \hbar m_j \psi(\mathbf{r})$$

$$k \psi(\mathbf{r}) = \hbar \kappa \psi(\mathbf{r}) \quad \kappa = \pm (j + 1/2) = \pm 1, \pm 2, \dots \quad \text{integer}$$

➤ Relativistic angular momentum quantum number  $\kappa$ : ... defines the quantum number  $j$  uniquely.

➤ Simultaneous eigenfunctions for  $k, \mathbf{j}^2, j_z$ : ... similar also for  $\psi_{\kappa=-(j+1/2), m_j}(\mathbf{r})$

$$\psi_{\kappa=j+1/2, m_j}(\mathbf{r}) = \begin{pmatrix} \sqrt{\kappa + m_j - 1/2} & P_\kappa(r) Y_{\kappa-1, m_j-1/2}(\theta, \phi) \\ \sqrt{\kappa - m_j - 1/2} & P_\kappa(r) Y_{\kappa-1, m_j+1/2}(\theta, \phi) \\ \sqrt{\kappa - m_j + 1/2} & Q_\kappa(r) Y_{\kappa, m_j-1/2}(\theta, \phi) \\ -\sqrt{\kappa + m_j + 1/2} & Q_\kappa(r) Y_{\kappa, m_j+1/2}(\theta, \phi) \end{pmatrix}$$

➤ Radial functions  $P_\kappa(r)$  and  $Q_\kappa(r)$ : in general different and depend on the shape of the (radial) potential  $V(r)$ .

### 2.3.f. Solutions for the time-independent Dirac equation with a Coulomb potential $V(r) \simeq -Z/r$

#### Coulomb potential

➤ Hydrogen-like ions: ... for an electron in a Coulomb field

$$H_D \psi(\mathbf{r}) = \left( -i\hbar c \boldsymbol{\alpha} \cdot \nabla + mc^2 \alpha_0 + \frac{\alpha \hbar c Z}{r} \right) \psi(\mathbf{r}) = E \psi(\mathbf{r}).$$

2. Review of one-electron atoms (hydrogen-like)

➤ Radial functions  $P_\kappa(r)$  and  $Q_\kappa(r)$ :

$$\psi(\mathbf{r}) = \psi_{\kappa=\pm(j+1/2), m_j} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \quad \text{or} \quad \psi(\mathbf{r}) = \psi_{\kappa=\pm(j+1/2), m_j} = \begin{pmatrix} P_\kappa \Omega_{\kappa m} \\ i Q_\kappa \Omega_{-\kappa m} \end{pmatrix}$$

➤ Spherical Dirac spinors  $\Omega_{\kappa m}(\vartheta, \varphi)$ : ... radial equations; the same for using  $\psi_{\kappa=+(j+1/2), m_j}$  and  $\psi_{\kappa=-(j+1/2), m_j}$

$$\left( B + \frac{\gamma}{r} \right) \frac{P_\kappa(r)}{\sqrt{2\kappa+1}} - i \left( \frac{d}{dr} + \frac{\kappa+1}{r} \right) \frac{Q_\kappa(r)}{\sqrt{2\kappa-1}} = 0, \quad A = \frac{mc^2 - E}{\hbar c}$$

$$i \left( A - \frac{\gamma}{r} \right) \frac{Q_\kappa(r)}{\sqrt{2\kappa-1}} - \left( \frac{d}{dr} - \frac{\kappa-1}{r} \right) \frac{P_\kappa(r)}{\sqrt{2\kappa+1}} = 0, \quad B = \frac{mc^2 + E}{\hbar c}; \quad \gamma = \alpha Z$$

➤ Bound solutions for  $E < mc^2$ : ... linear combinations of the confluent-hypergeometric function.

➤ Sommerfeld's fine-structure formula: ... eigenvalues of radial equations

$$E - mc^2 = -mc^2 \left\{ 1 - \left[ 1 + \frac{\alpha^2 Z^2}{(n_r + \sqrt{\kappa^2 - \alpha^2 Z^2})} \right]^{-1/2} \right\}$$

## 2.3.g. Bound-state solutions in a central field

### Hydrogenic wave functions for a point nucleus:

➤ Discrete spectrum:  $P_{n\kappa}(r)$  and  $Q_{n\kappa}(r)$  are also called large and small component.

$$\begin{aligned} P_{n\kappa}(r) &= N_{n\kappa}^L r (2qr)^{s-1} e^{-qr} \left[ -n' F(-n'+1, 2s+1; 2qr) - \left( \kappa - \frac{\alpha Z}{q\lambda_c} \right) F(-n', 2s+1; 2qr) \right] \\ Q_{n\kappa}(r) &= N_{n\kappa}^S r (2qr)^{s-1} e^{-qr} \left[ n' F(-n'+1, 2s+1; 2qr) - \left( \kappa - \frac{\alpha Z}{q\lambda_c} \right) F(-n', 2s+1; 2qr) \right] \\ n' &= n - |\kappa|, \quad s = \sqrt{\kappa^2 - (\alpha Z)^2} \quad q = \frac{\sqrt{1 - W_{n\kappa}^2}}{\lambda_c} = \frac{\alpha Z}{\lambda_c [(\alpha Z)^2 + (n' + s)^2]^{1/2}} \\ N_{n\kappa}^L &= \frac{\sqrt{2}q^{5/2}\lambda_c}{\Gamma(2s+1)} \left[ \frac{\Gamma(2s+n'+1)(1+W_{n\kappa})}{n'!(\alpha Z)(\alpha Z - \kappa q\lambda_c)} \right]^{1/2} \quad N_{n\kappa}^S = -N_{n\kappa}^L \left( \frac{1-W_{n\kappa}}{1+W_{n\kappa}} \right)^{1/2} \end{aligned}$$

➤ Especially, the  $|1s_{1/2}, \pm 1/2\rangle$  ground-state of hydrogen: ... with  $\bar{s} = \sqrt{1 - (\alpha Z)^2}$

$$\psi_{(1s,1/2,+1/2)}(r, \vartheta, \varphi) = \frac{1}{\sqrt{4\pi} r} \begin{pmatrix} P_{1s}(r) \\ 0 \\ -i Q_{1s}(r) \cos \vartheta \\ -i Q_{1s}(r) \sin \vartheta e^{i\varphi} \end{pmatrix}, \quad \psi_{(1s,1/2,-1/2)}(r, \vartheta, \varphi) = \frac{1}{\sqrt{4\pi} r} \begin{pmatrix} 0 \\ P_{1s}(r) \\ -i Q_{1s}(r) \sin \vartheta e^{-i\varphi} \\ -i Q_{1s}(r) \cos \vartheta \end{pmatrix}$$

$$P_{1s}(r) = \frac{(2Z)^{\bar{s}+1/2}}{[2\Gamma(2\bar{s}+1)]^{1/2}} (1+\bar{s})^{1/2} r^{\bar{s}-1} e^{-Zr},$$

$$Q_{1s}(r) = -\frac{1-\bar{s}^{1/2}}{1+\bar{s}} \frac{(2Z)^{\bar{s}+1/2}}{[2\Gamma(2\bar{s}+1)]^{1/2}} (1+\bar{s})^{1/2} r^{\bar{s}-1} e^{-Zr}$$

## 2.4. Beyond Dirac's theory

### 2.4.a. Fine-structure of hydrogenic ions: From Schrödinger's equation towards QED

### 2.4.b. QED: Interactions with a quantized photon field

#### Dominant QED corrections:

##### ➤ Vacuum polarization (VP):

- The quantum vacuum between interacting particles is not simply empty space but contains virtual particle-antiparticle pairs (leptons or quarks and gluons).
- These pairs are created out of the vacuum due to the energy constrained in time by the **energytime version of the Heisenberg uncertainty principle**.
- VP typically lowers the binding of the electrons (screening of nuclear charge).

##### ➤ Self energy:

- **Electrostatics:** The self-energy of a given charge distribution refers to the energy required to bring the individual charges together from infinity (initially non-interacting constituents).
- Frankly speaking, the self-energy is the energy of a particle due to its own response upon the environment.
- Mathematically, this energy is equal to the so-called on-the-mass-shell value of the **proper self-energy operator (or proper mass operator) in the momentum-energy representation**.

##### ➤ Feynman diagrams: graphical representation of the interaction; each Feynman diagram can be readily expressed in its algebraic form by applying more or less simple rules.

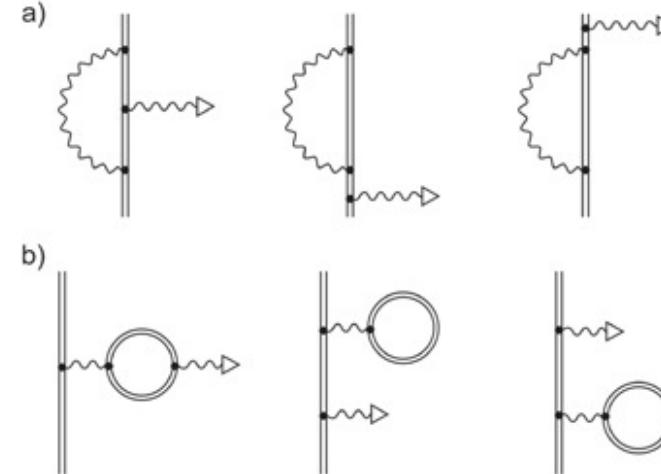
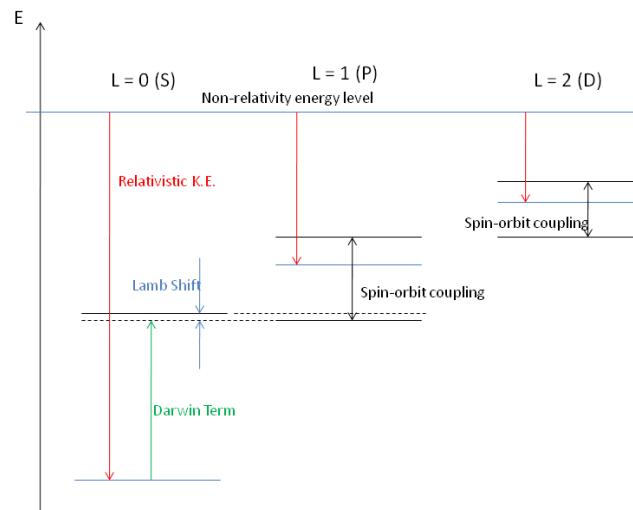


Figure 2.4.: Left: Relativistic level shifts for hydrogen-like ions; from: <http://en.wikipedia.org/wiki/> Right: Feynman diagrams of the bound electron in first order of the fine structure constant  $\alpha$ . (a) Self energy, (b) vacuum polarization. The double line represents the bound state electron propagator and contains the interaction between electron and the binding field to all orders of  $\alpha$ ; from <http://iopscience.iop.org/1402-4896/89/9/098004>.

## 2.5. Hydrogenic atoms in constant external fields

### (Normal) Zeeman effect:

➤ Hamiltonian:  $H = \frac{1}{2m}(\mathbf{p} + e\mathbf{A})(\mathbf{p} + e\mathbf{A}) - e\phi$ .

## 2. Review of one-electron atoms (hydrogen-like)

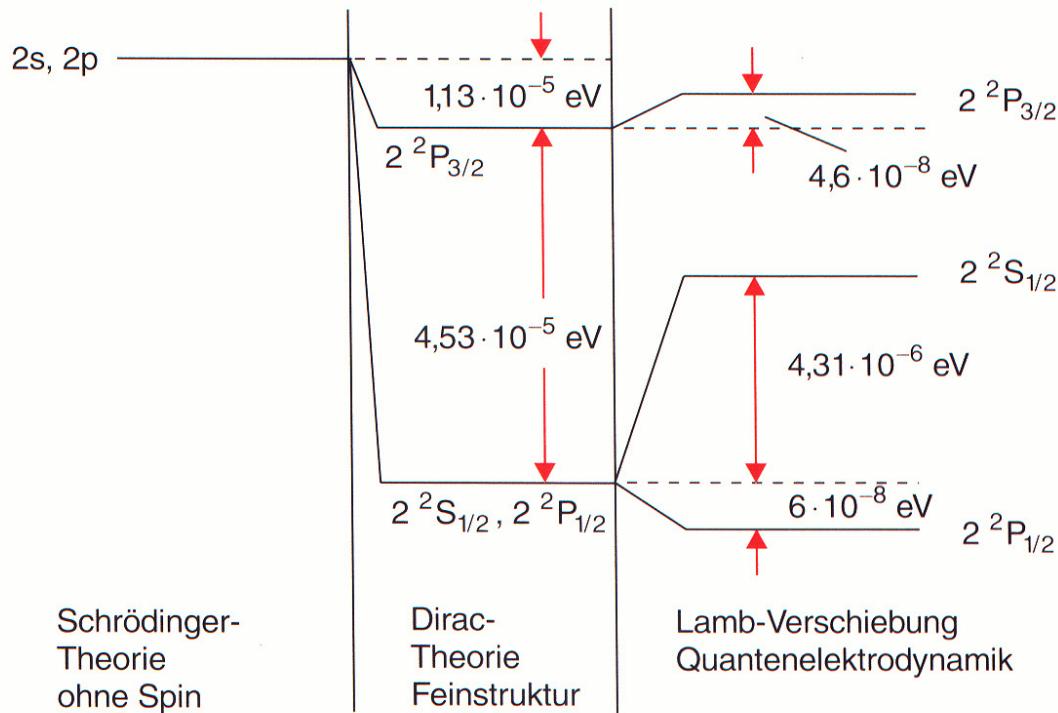


Figure 2.5.: Accurate Lamb-shift calculations for atomic hydrogen.

➤ Constant magnetic field in  $z$ -direction:  $\mathbf{B} = B \mathbf{e}_z = (0, 0, B)$ :

$$\mathbf{A} = \left( -\frac{1}{2}By, \frac{1}{2}Bx, 0 \right), \quad \text{div } \mathbf{A} = 0$$

$$H = H_o + H' = \frac{\mathbf{p}^2}{2m} - \frac{\alpha c \hbar Z}{r} + \frac{e}{m} \mathbf{A} \cdot \mathbf{p} + \frac{e^2 \mathbf{A}^2}{2m} \quad \text{weak field}$$

$$H' = -\frac{i \hbar e}{m} \mathbf{A} \cdot \nabla = -i \mu_B B \frac{\partial}{\partial \varphi} \quad \mu_B \dots \text{Bohr magneton}$$

- Secular equation: ... energy shifts from time-independent (perturbation) theory

$$|H'_{ik} - \Delta E \delta_{ik}| = \left| \underbrace{\langle nl'm'_l | H' | nlm_l \rangle}_{\mu_B B m_e \delta_{ll'} \delta_{m_lm'_l}} - \Delta E \underbrace{\langle nl'm'_l | nlm_l \rangle}_{\delta_{ll'} \delta_{m_lm'_l}} \right| = 0$$

$$\Delta E_{m_l} = \mu_B B m_l, \quad E_{n,l,m_l} = E_n^{(0)} + \mu_B B m_l$$

Every degenerate level  $E_n^{(0)}$  splits into  $(2l+1)$  sublevels levels.

- Line splitting & Lamor frequency: ... for a given transition  $\hbar\omega = E_{n',l',m'_l} - E_{n,l,m_l} = E_{n'} - E_n + \mu_B B(m'_l - m_l)$   
i.e., because of  $\Delta m_l = 0, \pm 1$ , every line just split into three lines which are shifted to each other by

$$\hbar\omega_L = \mu_B B \quad \omega_L \dots \text{Lamor frequency.}$$

- Gyromagnetic ratio:  $\frac{\mu_z}{l_z} = -\frac{e}{2m}$  refers to the ratio between magnetic moment and orbital angular momentum.

### Stark effect:

- Constant electric field in  $z$ -direction:  $\mathbf{E} = E \mathbf{e}_z = (0, 0, E) = -\text{grad}\varphi$ :

$$H' = -eEz = -eEr \cos\vartheta, \quad |\langle n', l', m'_l | H' | n, l, m_l \rangle - \Delta E \delta_{ll'} \delta_{m_lm'_l}| = 0$$

$$\langle n', l', m'_l | -eEr \cos\vartheta | n, l, m_l \rangle$$

$$\begin{aligned} &= -eE \int_0^\infty dr r^3 R_{n'l'}^* R_{nl} \int_0^\pi \int_0^{2\pi} d\varphi d\vartheta \sin\vartheta Y_{l'm'_l}^* \cos\vartheta Y_{lm_l} \\ &= -eE \left[ \sqrt{\frac{(\ell - m_\ell + 1)(\ell + m_\ell + 1)}{(2\ell + 1)(2\ell + 3)}} \int_0^\infty dr r^3 R_{n,\ell+1}^* R_{n\ell} + \sqrt{\frac{(\ell - m_\ell)(\ell + m_\ell)}{(2\ell - 1)(2\ell + 1)}} \int_0^\infty dr r^3 R_{n,\ell-1}^* R_{n\ell} \right] \delta_{m_\ell m'_l}. \end{aligned}$$

## 2. Review of one-electron atoms (hydrogen-like)

### Anomalous Zeeman & Paschen-Back effect:

➤ Spin & orbital momentum: with  $\mathbf{B} = B \mathbf{e}_z$

$$H' = -(\mathbf{M} + \mathbf{M}_s) \cdot \mathbf{B} = -(M_z + M_{sz}) \cdot B = \frac{eB}{2m} (l_z + g s_z) = \frac{eB}{2m} (j_z + (g-1) s_z)$$

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

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

### A) Anomalous Zeeman effect for $H' \ll H^{\text{so}}$ :

➤ Pauli's formalism: ... because of spin

$$(H')_{\text{Pauli}} = \frac{eB}{2m} \left[ (j_z)_{\text{Pauli}} + (g-1) \frac{\hbar}{2} \sigma_z \right].$$

➤ Consider perturbation  $H'$  independently for each degenerate spin-orbit state  $|njm_j\rangle$ ,  $j = \ell \pm 1/2$  and with  $g(\text{electron}) = 2$

$$\begin{aligned} \Delta E' &= \langle njm_j | (H')_{\text{Pauli}} | njm_j \rangle = \begin{cases} \mu_B B \frac{2\ell+g}{2\ell+1} m_j & j = \ell + 1/2 \\ \mu_B B \frac{2\ell+2-g}{2\ell+1} m_j & j = \ell - 1/2 \end{cases} \\ &= \mu_B B \frac{j+1/2}{\ell+1/2} m_j \quad j = \ell \pm 1/2 \end{aligned}$$

➤ Lande's factor  $g_L = \frac{j+1/2}{\ell+1/2}$ : ... for given  $\ell$ , levels with  $j = \ell + 1/2$  are stronger shifted.

**B) Paschen-Back effect for  $H' \gg H^{\text{so}}$ :**

➤ Pauli's formalism: ... calculate the splitting of  $H'$  independently for  $|n\ell m_\ell m_s = \pm 1/2\rangle$  states

$$\psi_{n\ell m_\ell + 1/2} = \begin{pmatrix} \psi_{n\ell m_\ell} \\ 0 \end{pmatrix}; \quad \psi_{n\ell m_\ell - 1/2} = \begin{pmatrix} 0 \\ \psi_{n\ell m_\ell} \end{pmatrix}$$

$$(H')_{\text{Pauli}} = \frac{eB}{2m} [(l_z)_{\text{Pauli}} + 2(s_z)_{\text{Pauli}}], \quad \Delta E' = \mu_B B (m_\ell + 2m_s) \quad m_s = \pm 1/2$$

i.e. for  $\ell \neq 0$ , there are  $2\ell + 3$  levels

$$E = E_n + \mu_B B (m_\ell + 2m_s) = E_{n,m_\ell}^{(\text{Normal-Zeeman})} + \mu_B B \cdot 2m_s.$$

➤ Transition within two levels: same splitting into 3 lines as for the normal Zeeman effect

$$\hbar\omega = E_{n'} - E_n + \mu_B B [(m'_\ell + 2m'_s) - (m_\ell + 2m_s)] = \hbar\omega_o + \hbar\omega_L (\Delta m_\ell + 2\Delta m_s)$$

## 2.6. Exotic (hydrogenic) atoms

### Pionic atoms:

- Pions ( $\pi^+$ ,  $\pi^-$ ): ... spin-0 mesons that obey Klein-Gordan equation .
- Pion production: ... by inelastic proton scattering  $p + p \implies p + p + \pi^+ + \pi^-$
- Strong interaction with the nucleus: ... capture by the nucleus:  $\pi^- + p \rightarrow n$ ;  $\pi^+ + n \rightarrow p$ . ... broadening of all lines.
- Short lifetimes:  $\tau(\pi^-) \sim 10^{-8} s \longleftrightarrow$  large level widths (due to strong interactions).
- No spin-orbit splitting but standard  $nl$  classification similar to the non-relativistic H-atom.

### Muonic atoms:

- Spin-1/2 particles like electrons but with mass,  $m_\mu \approx 207 m_e$ : ... described by Dirac equation.
- Muon production:  $p + p \rightarrow p + p + \pi^+ + \pi^-$  and  $\pi^- \rightarrow \mu^- + \nu_\mu$
- Muon are typically captured into some high excited level:
- Recoil effects: reduced mass of the muons
- Strongly enhanced QED effects: ... because of the small radii of the muonic orbits.

## 2.7. Tasks

See tutorials.

### **3. AMO Science in the 21<sup>st</sup> century**

#### **Potential and grand challenges for AMO Science** (from ‘Controlling the Quantum World’):

- **Quantum metrology:** New methods to measure the nature of space and time with extremely high precision; this field has emerged within the last decade from a convergence of technologies in the control of the coherence of ultrafast lasers and ultracold atoms. Promises new research opportunities.
- **Ultracold AMO physics:** A spectacular new (AMO) research area of the past (three) decades which led to the development of coherent quantum gases. This new field promises to resolve important fundamental problems in condensed matter science and plasma physics, with many interdisciplinary relations.
- **High-intensity and short-wavelength sources:** such as new x-ray free-electron lasers or HHG promise significant advances in AMO science, condensed matter physics and materials research, chemistry, medicine, and others.
- **Ultrafast quantum control:** will unveil the internal motion of atoms within molecules, or of electrons within atoms, to a degree thought impossible only a decade ago. This field gives rise to a sparking revolution in the imaging and coherent control of quantum processes; is expected to become to one of the most fruitful new areas of AMO science in the next 10 years or so.
- **Quantum engineering:** on the nanoscale of tens to hundreds of atomic diameters has led to new opportunities for atom-by-atom control of quantum structures using the techniques of AMO science.

### 3. AMO Science in the 21<sup>st</sup> century

- **Quantum information:** is a rapidly growing research area in AMO science with great **potential applications in data security and encryption**. Multiple approaches to quantum computing and communication are likely to be fruitful in the coming decade. Current topics include: Realization of quantum information processing; models of quantum computations and simulations; ect.
- **Quantum imaging:** new sub-field of quantum optics; exploits quantum correlations (entanglement of em field) to image objects with a resolution beyond what is possible in classical optics.

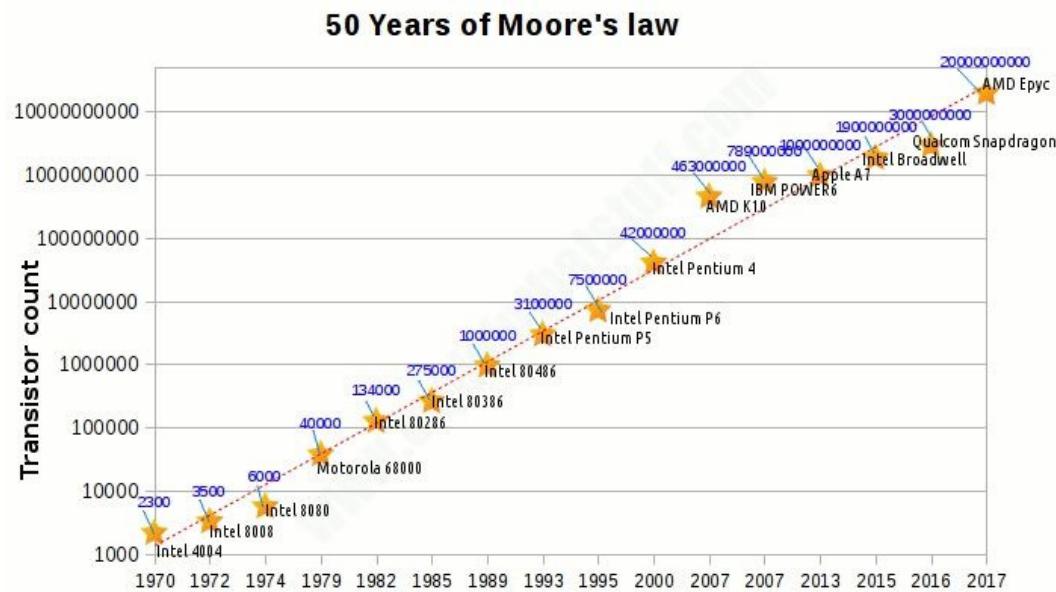
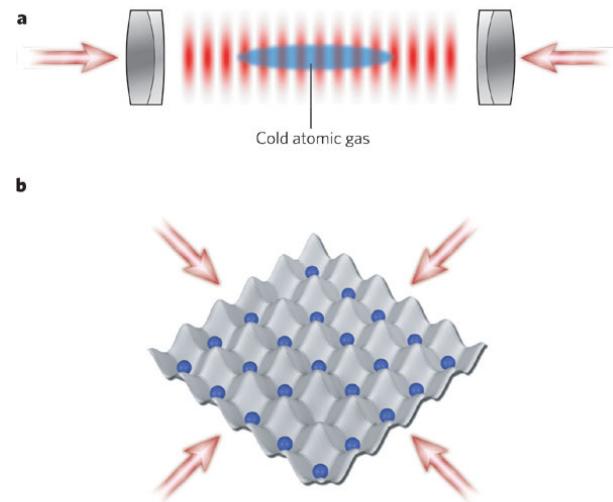


Figure 3.1.: Left: Formation of an optical lattice; from I. Bloch, Nature 453, 1016 (2008). Right: 50 years Moores law.

## Present questions to AMO science:

- What are the undiscovered laws of physics that lie beyond our current understanding of the physical world ? What is the deeper nature of space, time, matter, and energy ?
  
- Is there an atomic dipole moment ? ➔ Help explore the physics beyond the standard model by using techniques from AMO physics.
  
- How can one improve the measurement precision in order to become sensitive to very weak magnetic fields, such as of the brain or heart ? ➔ New diagnostic tools for various diseases.
  
- How can one detect gravitational waves and anomalies, such as hostile underground structures and tunnels ? ➔ Matter-wave interferometers.
  
- Can ultra-cold gases be used to mimic and explore the interactions in periodic structures of solid crystals.  
Do they provide us with some useful quantum simulators ?
  
- Biological imaging ? Can free-electron lasers help us to explore the structure and dynamics of proteins and biomolecules ? ➔ Freezing the motion of electrons as they move about the molecule requires sub-femtosecond, or even attosecond, laser pulses.
  
- How can intense lasers be utilized to create directed beams of electrons, positrons or neutrons for medical and material diagnostics ?
  
- Is it possible to use laser-induced fusion in large-scale power plants ?
  
- Can we use lasers to control the outcome of selected chemical reactions ?  
➔ Such control technologies may ultimately lead to powerful tools for creating new molecules and materials tailored for applications in health care, nanoscience, environmental science, and energy.

### 3. AMO Science in the 21<sup>st</sup> century

- What comes beyond Moore's law ? ➔ Should quantum computers be realized at all in the future, they would be more different from today's high-speed digital computers than those machines are from the ancient abacus.

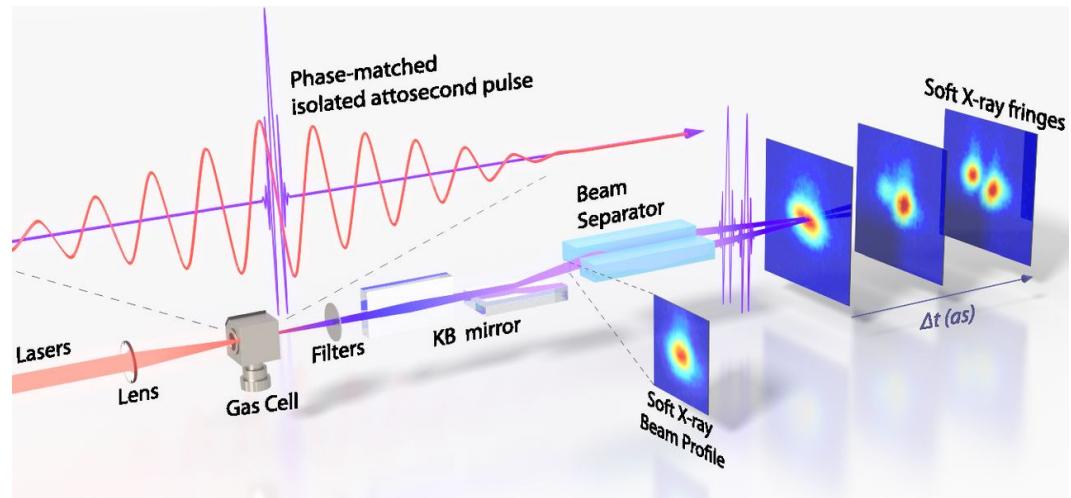
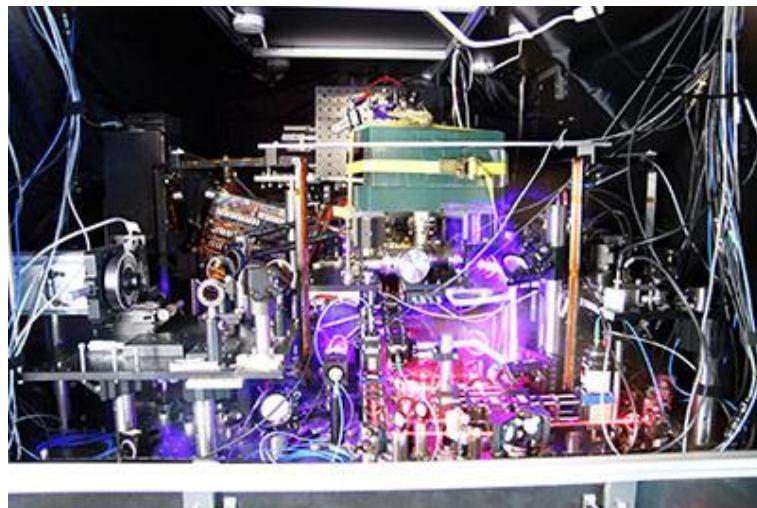


Figure 3.2.: Left: From: Strontium clock at JILA; from <https://jila.colorado.edu/yelabs/research/> Right: From <https://www.pnas.org/content/111/23/E2361>

## 3.1. AMO Science and the basic laws of Nature

### Search for atomic EDM:

- Permanent electric-dipole moment (EDM): ... of electrons or atoms
- Supersymmetry: ... predicts a tiny offset between the mass and electric charge centers of electrons, neutrons, ... along the spin axis of these particles, the EDM; it would mean the violation of time reversal ( $t$ ) invariance.

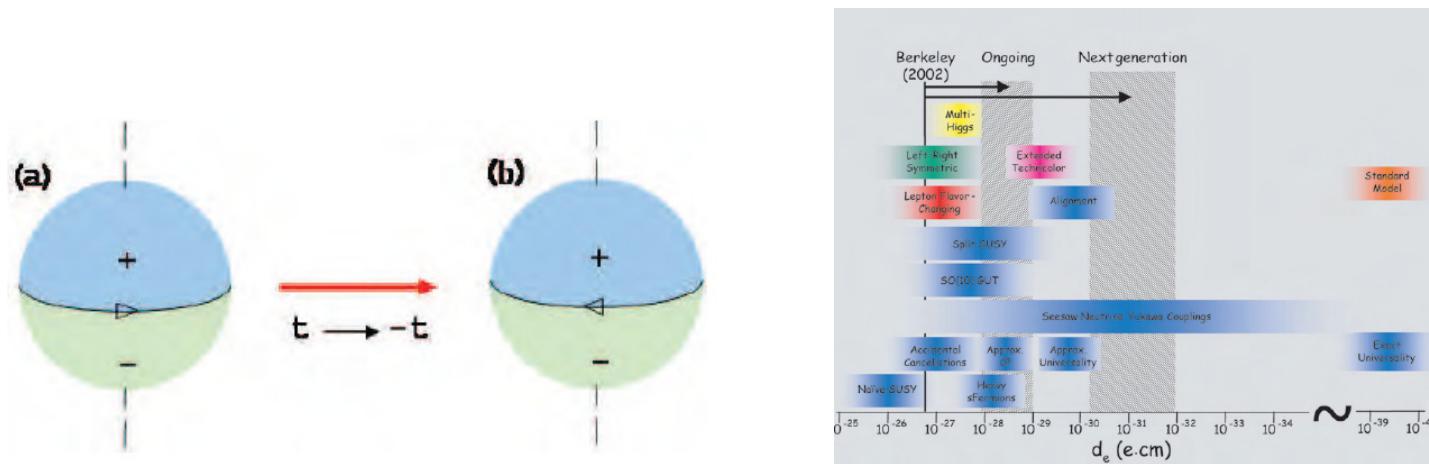


Figure 3.3.: Left: An electric dipole moment (EDM) of an atom (left) is a permanent separation between the centers of positive and negative charge along the axis of spin. Under time reversal (right), the spin direction is reversed but the charge separation is not. An observed EDM would have to be caused by forces that violate time reversal symmetry; taken from: *Controlling the Quantum World*, page 32. Right: Scientific impact of current and next-generation electron EDM measurements. It is anticipated that next-generation measurements will reach the  $10^{-31}$  e-cm level, equivalent to a dipole consisting of a positive and negative electronic charge separated by only  $10^{-31}$  cm, which will test large classes of supersymmetric (SUSY) theories. Ongoing measurements of an atomic EDM due to nuclear spin and the EDM of the neutron have similar sensitivity to different SUSY parameters. Thus, atomic EDM experiments will be probing SUSY and other theories on a broad front. SOURCE: D. DeMille, Yale University; taken from: *Controlling the Quantum World*, page 33.

- **Time-reversal violating forces:** also appear in the (conventional) Standard Model of elementary particle interactions but cause an EDM far too small to be observable by any presently envisioned experiment; therefore, any measurement of an electron/atomic EDM would mean **new physics beyond the standard model**.
- **New interactions:** ... required to overcome several ‘gaps’ of the standard model, for example, the preponderance of matter over antimatter.

### 3. AMO Science in the 21<sup>st</sup> century

#### Test of CPT theorem:

- Violation of CPT theorem: violations of the so-called charge, parity, and time reversal (CPT) symmetry ?
- Atomic QED: ... understanding the forces with high precision; existence of quantum vacuum
- Atomic parity violation experiments: ... valuable information for particle physics; cesium measurements
- Antihydrogen in the laboratory: ... one of the most exact CPT tests

#### Time variations of $\alpha$ :

- Fine-structure constant  $\alpha = e^2/\hbar c$ : ... dimensionless constants of three fundamental constants; does spatial and temporal variations of  $\alpha$  exist ?
- Search for variations of  $\alpha$ : ... different atomic transitions depend differently on  $\alpha$
- No evidence for changes  $> 10^{-16}/a$ : ... from spectroscopic data presently provide

#### AMO physics & multimessenger astronomy:

- Laws of physics: ... across very large distances ? ... from the earliest moments on ?
- Astrophysical observation: ... requires AMO spectroscopy and collision studies in the lab
- Dark energy: ... precision spectroscopy, based on accurate atomic data. **Existence of dark energy poses a challenge to the Standard Model of particle physics.**
- Molecular hydrogen formation: ... understanding the early universe and galaxy formation

- Life at other planetary systems: ... spectroscopy of organic molecules; AMO physics provides the necessary backbone to this work
- Numerical methods & computer codes: ... to calculate energy levels, wavefunctions and spectral line strengths.

## 3.2. Extreme light sources: Development and applications

### Brilliant bursts of x-ray beams:

- Bright & directed x-ray beams: ... laser-like; can be focused to the size of a virus;
- Observe motion of electrons;
- Extreme strobes: ... direct view on the electronic and structural changes of nanostructures and biomolecules.

### Table-top x-ray sources:

- Atomic plasmas as lasing medium: laser-induced plasma to generate highly monochromatic and directed laser beams at wavelengths from 11 to 47 nm.
- Next-generation micro-lithography: ... good for industrial applications
- High-harmonics generation: ... high harmonics of the fundamental laser are emitted as coherent, laser-like beams at short wavelengths.
- Table-top extreme x-ray sources: ... bring the source to the application; probe of materials

### Free-electron lasers (FEL):

- Properties of x-ray lasers: ... short wavelength, short pulses, high pulse intensity.
- XFEL sources: ... much shorter and more brilliant x-ray pulses than all other x-ray sources.
- Structural dynamics: ... in materials and chemical/biological systems.
- LCLS x-ray laser (Stanford): ... first x-ray source with similar extreme focused powers as high-powered lasers
- Hollow atoms and ions: ... store large amounts of potential energy and represent extreme matter in a truly exotic form.

### Imaging of biomolecules:

- Short x-ray bursts: ... tens to hundreds of femtoseconds of brilliant x-ray light
- High brilliance per pulse (  $10^{12}$  photons): ... generate x-ray diffraction pattern of individual (macro-) molecule; biomolecules that cannot be crystallized
- Radiation damage: ... understanding the fundamental mechanisms of damage at high intensities.
- Input from theory: ... molecular dynamics simulations

### Extreme states of matter:

- Relativistic plasma: ... electrons and ions are accelerate to relativistic velocities
- Particle accelerators: ... are table-top devices realistic that can accelerate electrons to GeV energies within a few cm ?

- Petawatt lasers: ... high-energy-density states of matter.
- Laser-induced fusion: Ignition of an imploded fusion pellet by externally heating the fusion fuel.
- High energy density (HeD) plasmas: exist in nuclear explosions, neutron stars, white dwarfs, ...
- Schwinger (critical field) limit at  $3 \times 10^{18}$  V/m: electron-positron pairs can be spontaneously generated from the vacuum; corresponds to  $10^{29}$  W/cm<sup>2</sup>.

### 3.3. Quantum information with light and atoms

#### Quantum processors:

- Do they will exist and for what they can be applied ?
- Quantum information science: ... far-reaching relevance to economic growth, secure communication as well as number-crunching in the 21<sup>st</sup> century.
- Quantum parallelism: ... designing proper quantum algorithms; Shor's quantum algorithm for factoring (prime numbers)
- Quantum simulations: are computations using (many) qubits of one system type that can be initialized and controlled in the laboratory in order to simulate an equal number of qubits of another type that cannot be easily controlled.

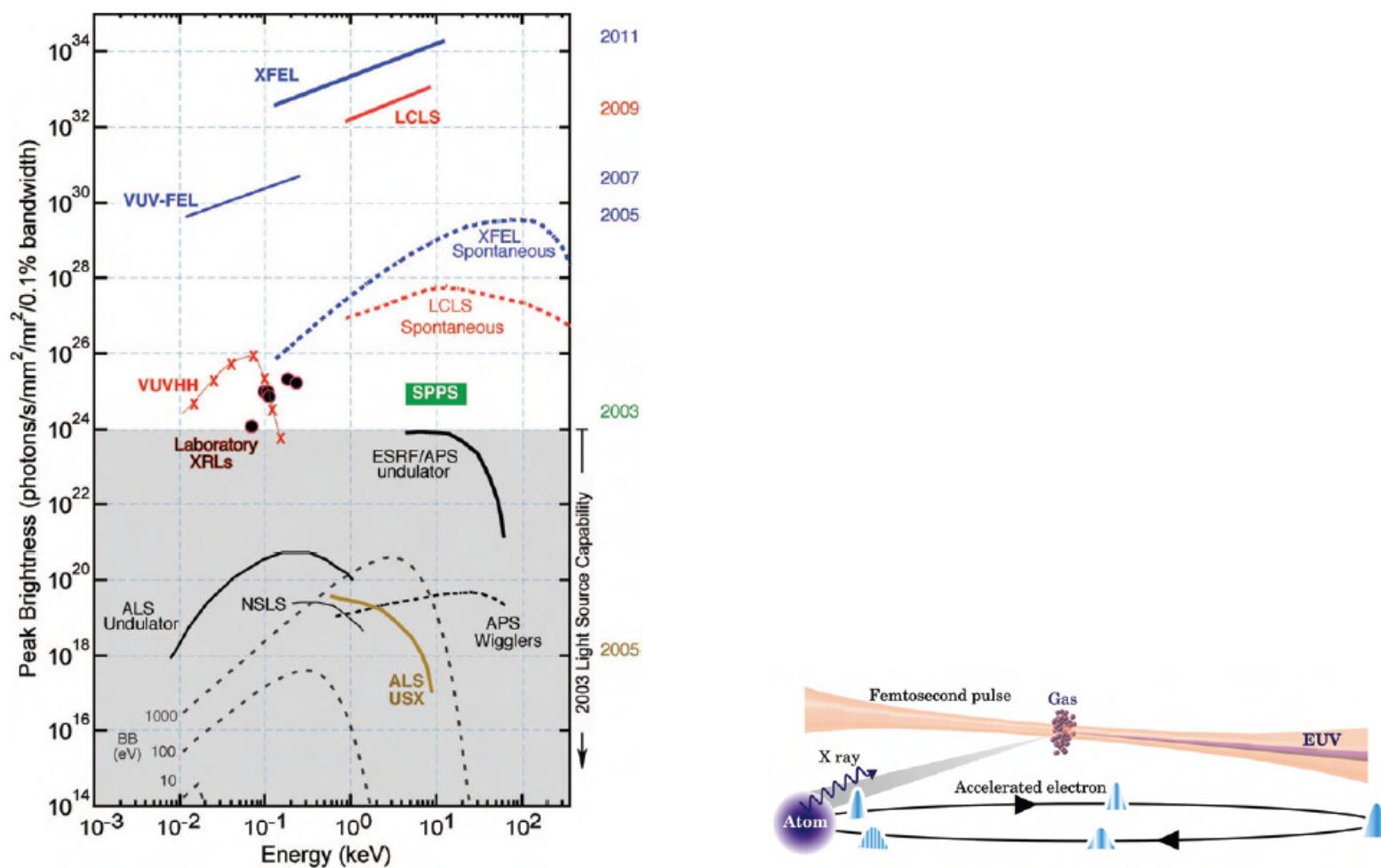


Figure 3.4.: Left: Brightness comparison between current and future sources of x rays generated in laboratory x-ray lasers or at accelerators; taken from: *Controlling the Quantum World*, page 76. Right: Simple and quantum pictures of high-harmonic generation. Top: An electron is stripped from an atom, gains energy, and releases this energy as a soft x-ray photon when it recombines with an ion. Bottom: Two-dimensional quantum wave of an electron is gradually stripped from an atom by an intense laser. Fast changes in this quantum wave lead to the generation of high harmonics of the laser. Reprinted with permission from H.C. Kapteyn, M.M. Murnane, and I.P. Christov, 2005, Extreme nonlinear optics: Coherent x-rays from lasers, Physics Today 58. Copyright 2005, American Institute of Physics.; taken from: *Controlling the Quantum World*, page 79..

### 3. AMO Science in the 21<sup>st</sup> century

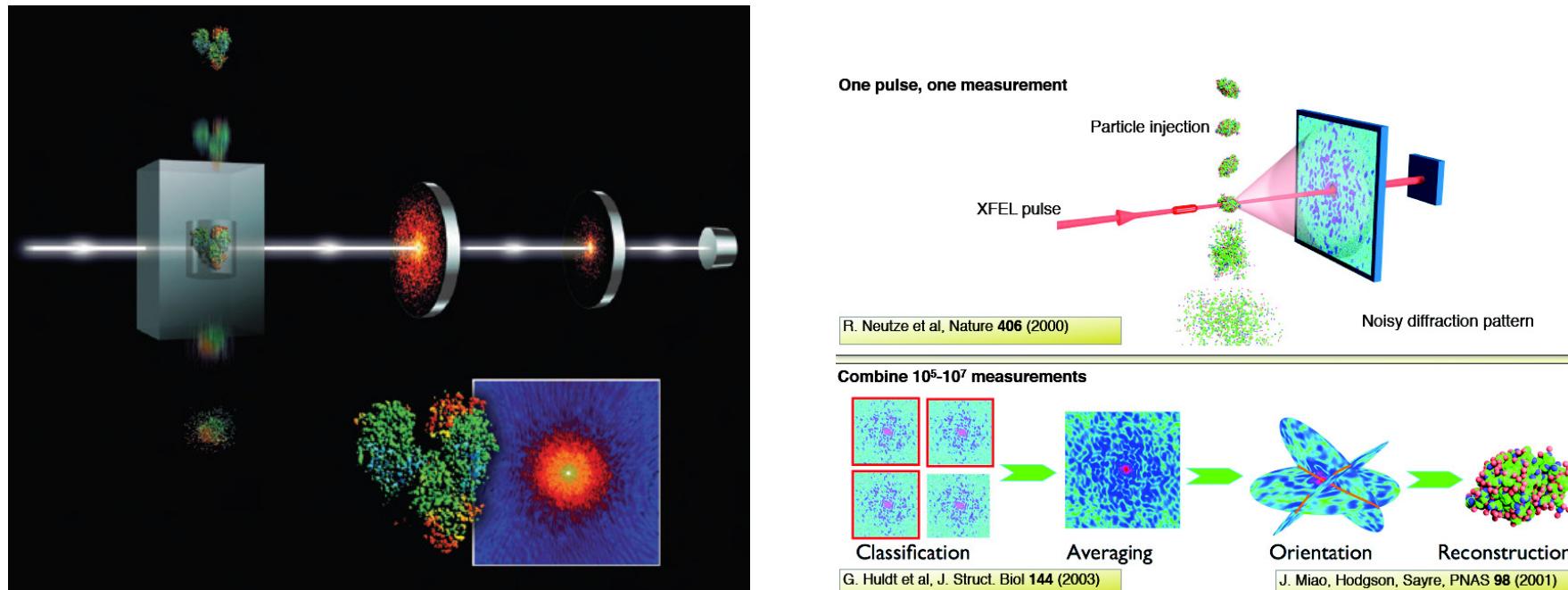


Figure 3.5.: Left: Single-molecule diffraction by an x-ray laser. Individual biological molecules fall through the x-ray beam, one at a time, and are imaged by x-ray diffraction. **So far, it remains a previous and current dream !** An example of the image is shown in the inset. H. Chapman, Lawrence Livermore National Laboratory.; taken from: *Controlling the Quantum World*, page 82. Right: X-ray free-electron lasers may enable atomic resolution imaging of biological macromolecules; from Henry Chapman, talk (2007)..

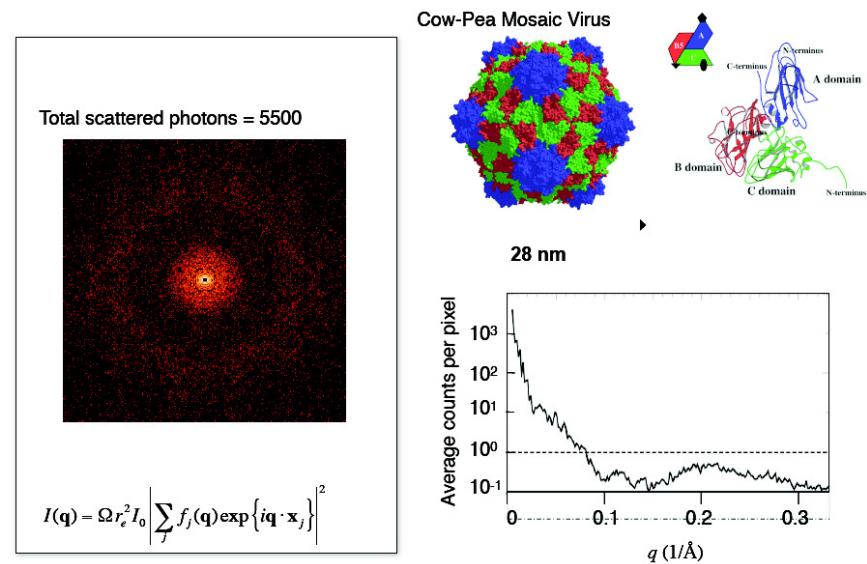
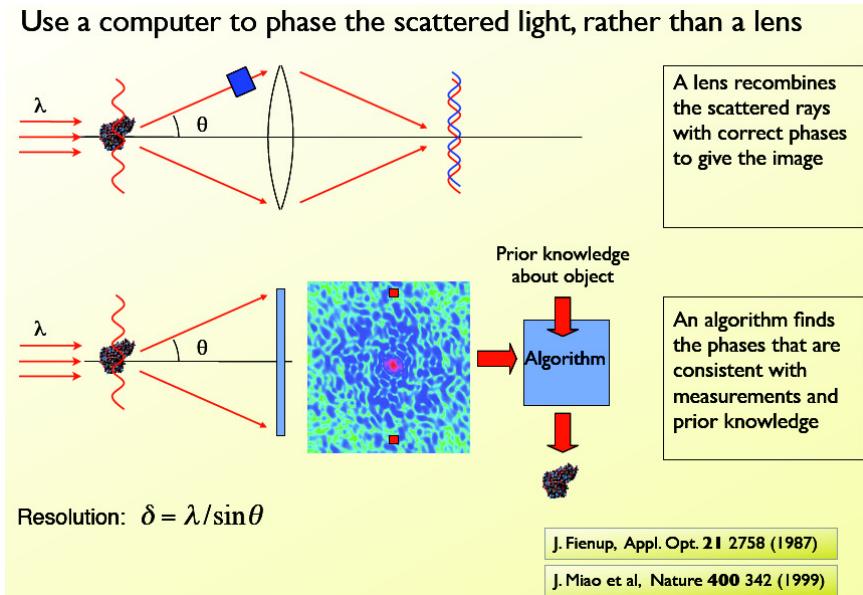


Figure 3.6.: Left: Coherent diffractive imaging is lensless; from Henry Chapman, talk (2007). Right: Diffraction images from single particles will be very weak; from Henry Chapman, talk (2007).



## 4. Atomic many-electron systems

### 4.1. Two-electron (helium-like) atoms and ions

#### 4.1.a. Coulomb vs. exchange interaction

##### Atomic Hamiltonian:

➢ Hamiltonian: ... invariant with regard to exchange  $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$

$$H \psi = (H_1 + H_2 + H') \psi = E \psi = \left( -\frac{\nabla_1^2}{2} + V_{\text{nuc}}(\mathbf{r}_1) - \frac{\nabla_2^2}{2} + V_{\text{nuc}}(\mathbf{r}_2) + \frac{1}{r_{12}} \right) \psi$$

Since there occurs no spin in the Hamiltonian, it can be omitted also in the wave functions.

➢ Suppose

$$H' \ll (H_1 + H_2) \iff \begin{cases} (H_1 + H_2) \psi_o = E_o \psi_o \\ \psi_o = u_{n_1 \ell_1 m_{\ell_1}}(\mathbf{r}_1) u_{n_2 \ell_2 m_{\ell_2}}(\mathbf{r}_2) = u_a(1) u_b(2) = u_{ab}(1, 2) = u_{ab} \\ E_o = E_{u_a} + E_{u_b} = E_a + E_b & a \neq b \end{cases}$$

#### 4. Atomic many-electron systems

➤ Indistinguishability: ... degenerate with regard to an exchange of the electron coordinates (**exchange degeneracy**);

$$\psi_o = c_1 u_{ab} + c_2 u_{ba} \quad \psi'_o = c_3 u_{ab} + c_4 u_{ba}$$

➤ Time-independent perturbation theory for  $H'$ :

$$\begin{pmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{pmatrix} = \begin{pmatrix} J & K \\ K & J \end{pmatrix} \quad \begin{aligned} J &= \int d\tau_1 d\tau_2 \frac{\rho_a(1) \rho_b(2)}{r_{12}} = \int d\tau_1 d\tau_2 \frac{\rho_a(2) \rho_b(1)}{r_{12}} && \text{direct term} \\ K &= \int d\tau_1 d\tau_2 \frac{u_{ab}(1,2) u_{ba}(1,2)}{r_{12}} && \text{exchange term} \end{aligned}$$

➤ Which linear combinations  $(c_1, \dots, c_4)$  make also  $H'$  diagonal ??

$$\begin{pmatrix} J & K \\ K & J \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \Delta E \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

a) Trivial solution:  $c_1 = c_2 = 0$ .

b) Solution of the secular equation:

$$\begin{vmatrix} J - \Delta E & K \\ K & J - \Delta E \end{vmatrix} = 0 \iff \Delta E = J \pm K \quad \begin{cases} \psi_s = \frac{1}{\sqrt{2}} (u_{ab} + u_{ba}) & \text{symmetric} \\ \psi_a = \frac{1}{\sqrt{2}} (u_{ab} - u_{ba}) & \text{antisymmetric} \end{cases}$$

### 4.1.b. Ground and (low-lying) excited states of helium

➤ Ground state  $a = b = (n\ell m_\ell) = (1s0)$ :

$$\psi_a \equiv 0; \quad \psi_s = u_{1s}(1) u_{1s}(2)$$

$$E(1s^2) = 2E(1s) = -2 \frac{Z^2}{n^2} = -4 \text{ Hartree} = -108 \text{ eV}$$

$$\Delta E(1s^2) = \left\langle \frac{1}{r_{12}} \right\rangle = \frac{5}{8} Z \text{ Hartree} \approx 34 \text{ eV}$$

Total binding energy for (removing one)  $1s$  electron:

$$E_b = E(1s) + \Delta E(1s^2) \approx -20.4 \text{ eV} \quad \text{perturbative}, \quad E_b = -24.580 \text{ eV} \quad \text{variational}$$

➤ Excited states  $a \neq b$

$$E = E_a + E_b + J \pm K, \quad J = \left\langle 1s, nl \left| \frac{1}{r_{12}} \right| 1s, nl \right\rangle, \quad K = \left\langle 1s, nl \left| \frac{1}{r_{12}} \right| nl, 1s \right\rangle$$

➤ Large  $n$  and  $\ell$ : ... exchange integral  $K$  becomes negligible

$$H \approx -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{(Z-1)}{r_2}$$

#### 4. Atomic many-electron systems

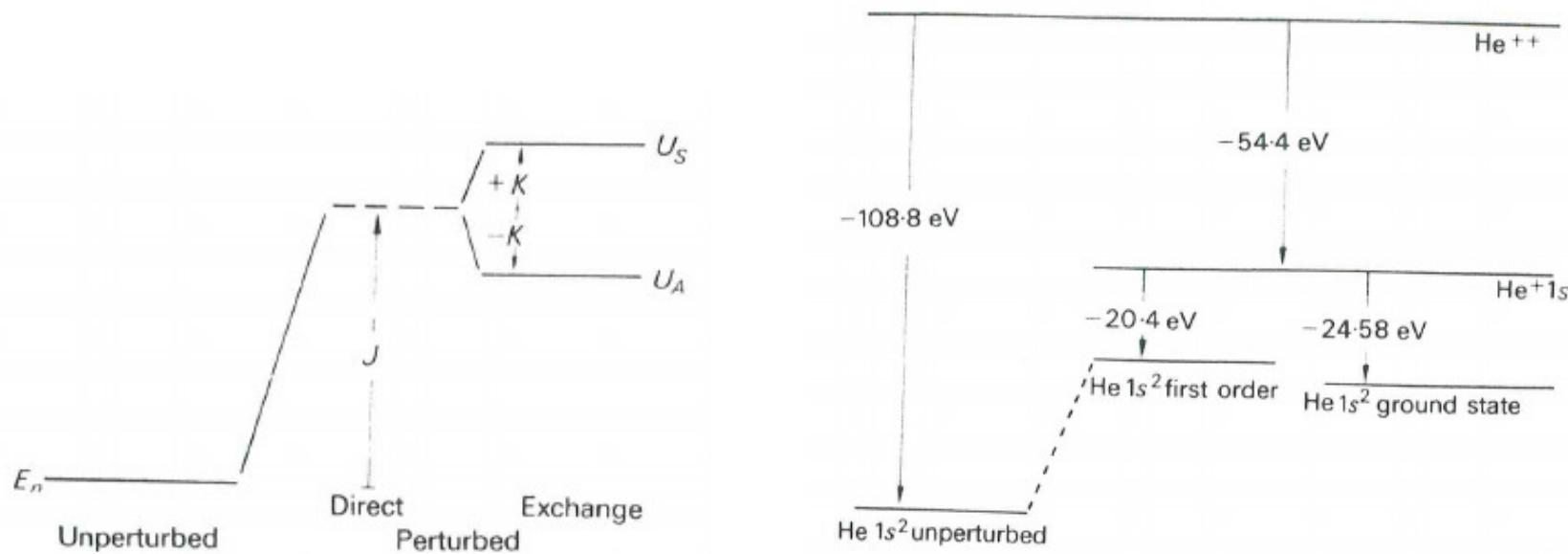


Figure 4.1.: Left: Schematic energy levels for the excited states of helium, showing the effect of the direct and exchange term. Right: Energy levels of helium relative to the singly and doubly-charged ion.

➤ **Constants of motion:** ... complete set of operators

$$\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2, \quad L_z = l_{1z} + l_{2z}$$

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2, \quad S_z = s_{1z} + s_{2z}, \quad \{H, P_{12}, \mathbf{L}^2, L_z, \mathbf{S}^2, S_z\}.$$

### 4.1.c. Spin functions and Pauli principle

#### (Non-relativistic) Spin-orbital functions:

- One-electron orbitals: ... product functions

$$\phi(1) = u_{n\ell m_\ell}(1) \chi_{m_s}(1) = \frac{1}{r} P_{n\ell}(r) Y_{\ell m_\ell}(\vartheta, \varphi) \chi_{m_s}(\sigma)$$

- Two-electron spin functions:  $\chi_{m_{s1}}(1) \chi_{m_{s2}}(2)$

Function	$S$	$M_S$	
$\chi_+(1) \chi_+(2)$		+1	
$\chi_s:$	$\frac{1}{\sqrt{2}} (\chi_+(1) \chi_-(2) + \chi_-(1) \chi_+(2))$	1	0
	$\chi_-(1) \chi_-(2)$		+1
$\chi_a:$	$\frac{1}{\sqrt{2}} (\chi_+(1) \chi_-(2) - \chi_-(1) \chi_+(2))$	0	0
			anti-symmetric

- Total wave functions:

$\underbrace{\psi_s \chi_s}_{\text{totally symmetric}}, \underbrace{\psi_a \chi_a}_{\dots \text{not possible}}$ ,

$\underbrace{\psi_s \chi_a}_{\text{totally antisymmetric}}, \underbrace{\psi_a \chi_s}_{\dots \text{possible}}$

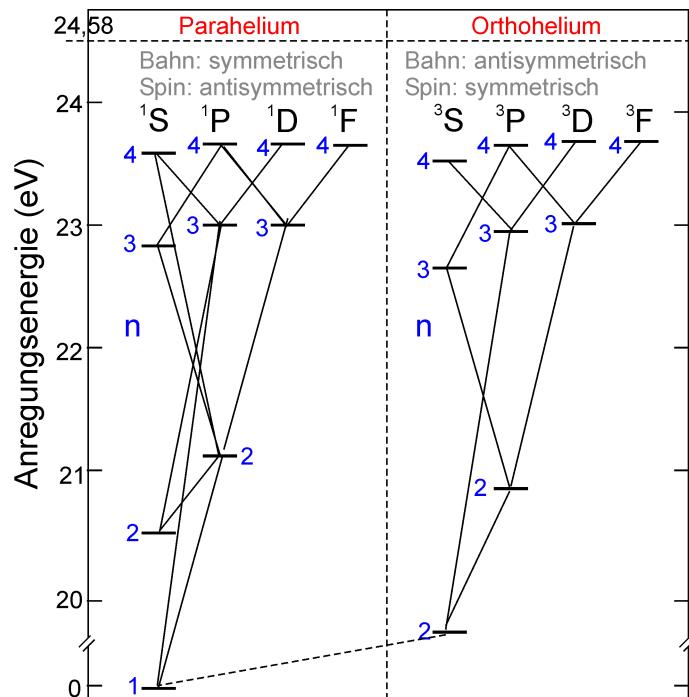
- Pauli principle: Fermionic (electronic) wave functions are totally antisymmetric with regard to an exchange of particle coordinates.      OR:

Two one-electron wave functions cannot agree in all quantum numbers (for their space and spin motion).

#### 4. Atomic many-electron systems

➤ Especially helium:

- $\psi_s \chi_a$  singulet ... para helium
- $\psi_a \chi_s$  triplet ... ortho helium



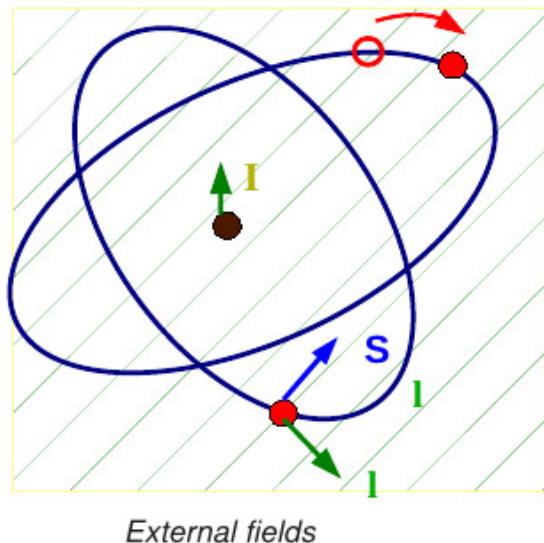
$1s^2$	$^3S$ $^1S$	missing 198,311	109.678
$1s2s$	$^3S$ $^1S$	38,461 32,039	6,422
$1s2p$	$^3P$ $^1P$	29,230 27,182	2,048
$1s3s$	$^3S$ $^1S$	15,080 13,452	1,628
$1s3p$	$^3P$ $^1P$	12,752 12,107	645
$1s3d$	$^3D$ $^1D$	12,215 12,212	3
$1s4s$	$^3S$ $^1S$	8,019 7,376	643
$1s4p$	$^3P$ $^1P$	7,100 6,824	276
$1s4d$	$^3D$ $^1D$	6,872 6,870	2
$1s4f$	$^3F$ $^1F$	6,864.4 6,863.8	0.6

Figure 4.2.: Left:  $LS$  terms for para and ortho helium; from: <http://www.ipf.uni-stuttgart.de/lehre/>. Right: Energy levels in helium.

## 4.2. Interaction and couplings in many-electron atoms

### 4.2.a. Hierarchy of atomic interactions

#### Hierarchy of inner-atomic interactions -- self-consistent fields vs. perturbation theory



- ★ 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 4.3.: Atomic interactions that need to be considered for a quantitative description/prediction of atoms.

**4.2.b. Nuclear potential**Nuclear models:

➤ General:

$$V_{nuc}(r) = e \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} .$$

➤ Point nucleus:  $V_{nuc}(r) = -\frac{Z}{r} .$

➤ Homogeneously extended nucleus:

$$V_{nuc}(r) = \begin{cases} -\frac{Ze^2}{2R} \left(3 - \frac{r^2}{R^2}\right) & r \leq R \\ -\frac{Z}{r} & r > R \end{cases}$$

- Light atoms:  $R \approx 1.2 \cdot A^{1/3}$  fm.

- Heavy elements: Radii are taken from electron-nucleus scattering experiments.

➤ Fermi distribution of the nuclear charge: ... no closed form for  $V_{nuc}(r)$

$$\rho(r) = \frac{\rho_0}{1 + \exp\left(\frac{r-R}{d}\right)}, \quad d = 1.039 \cdot 10^5$$

### 4.2.c. Interelectronic interactions

➤ Coulomb interaction between pairs of electrons: ... instantaneous (Coulomb) repulsion

$$v_{ij}^{(\text{Coulomb})} = \frac{e^2}{4\pi \epsilon_0 r_{ij}}; \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$$

- dominant Coulomb repulsion
- 'origin' of electronic correlations
- Breit interaction

➤ Spin-orbit interaction:

$$H_{so} \sim \frac{1}{r} \frac{dV}{dr} \mathbf{l} \cdot \mathbf{s} \quad \rightarrow \quad \sum_i \frac{1}{r_i} \frac{dV}{dr_i} \mathbf{l}_i \cdot \mathbf{s}_i$$

➤ Breit interaction: ... relativistic corrections to the e-e interaction

$$v_{ij}^{Breit} = -\frac{1}{2r_{ij}} \left[ \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right] \quad \dots \text{long-wavelength approximation}$$

➤ Expansion in  $v^2/c^2$ : ... gives rise to several terms in the non-relativistic limit.

- orbit-orbit interaction  $H_{oo}$
- spin-spin interaction  $H_{ss}$
- spin-other-orbit interaction  $H_{soo}$

➤ Total e-e interaction:  $v_{ij} = v_{ij}^{(\text{Coulomb})} + v_{ij}^{(\text{Breit})}$

### 4.2.d. Hyperfine interaction

➤ Interaction of the magnetic moments of the electron(s) with the magnetic moment of the nucleus:

$$\boldsymbol{\mu}_e = \frac{e}{2m} (\mathbf{l} + g \mathbf{s}) \quad \mu_B = \frac{e\hbar}{2m_e} \quad \dots \text{Bohr magneton}$$

$$\boldsymbol{\mu}_{\text{nuc}} = g_I \mu_N \mathbf{I}_{\text{nuc}} \quad \mu_N = \frac{e\hbar}{2m_p} \quad \dots \text{nuclear magnet}$$

➤ Atomic units: ... reminder

$$m_e = \hbar = \frac{e^2}{4\pi\epsilon_0} \equiv 1$$

## 4.3. Interaction-induced shifts in atoms and ions

### 4.3.a. Isotope shifts

#### Isotopic effects:

➤ Isotopic volume effect:  $r_N \sim A^{1/3}$   $\rightsquigarrow$  change in the nuclear potential.

➤ Reduced mass:  $\mu = \frac{mM}{m+M}$   $\rightsquigarrow$  change in atomic units.

➤ Picture of the nucleus: ... different charge and magnetization distribution inside the nucleus (nuclear structure).

➤ Hamiltonian: normal mass shift (Bohr) + specific mass shift; mathematical treatment

$$H_{Atom} \longrightarrow H_{Atom} + \frac{\mathbf{P}^2}{2M} \quad \mathbf{P} \dots \text{momentum of nucleus}$$

$$\frac{\mathbf{P}^2}{2M} = \frac{(-\sum_i \mathbf{p}_i)^2}{2M} = \frac{1}{2M} \sum_i \mathbf{p}_i^2 + \frac{1}{2M} \sum_{i < j} (\mathbf{p}_i \cdot \mathbf{p}_j)$$

### 4.3.b. Natural line widths

➤ Excited atomic states are generally not stable because of the

- spontaneous emission
- collisional de-excitation
- electron-electron interaction, if embedded into the continuum of the next higher charge state of the atom.  
~~ finite lifetime  $\tau$  of all excited states, often pressure-dependent.

➤ Heisenberg's principle:  $\Delta E \simeq \frac{\hbar}{\tau}$

$$\text{optical transitions : } \tau \sim 10^{-8} \text{ s} \longrightarrow \Delta E \sim 5 \cdot 10^{-4} \text{ cm}^{-1} .$$

➤ Intensity distribution (Lorentz profile):  $\sigma$  ... wave number (transition energy);  $\Gamma$  ... line widths

$$I(\sigma) = \frac{\Gamma/\pi}{(\sigma - \sigma_o)^2 + \Gamma^2} .$$

## 4.4. Atomic many-body hamiltonians

- Many-electron Hamiltonian: ... sum over all pairs of electrons

$$\begin{aligned}
 H_C &\equiv H^{(\text{Coulomb})} = \sum \text{one-particle operators} + \frac{\text{electrostatic}}{\text{Coulomb repulsion}} + \dots \\
 &= H_{kin} + H_{nuc} + H_{e-e} + \\
 &= -\sum_i \frac{\nabla_i^2}{2} - \sum_i \frac{Z}{r_i} + \sum_{i < j} \frac{1}{r_{ij}} \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|
 \end{aligned}$$

- Relativistic corrections to e-e interaction and HFS splitting: ... typically rather small; treated perturbatively.
- Spin-orbit interaction:

$$H_{C-so} = H_C + \sum_i \xi_i(r_i) (\mathbf{l}_i \cdot \mathbf{s}_i)$$

- Atomic structure theory: Find approximate solutions to the many-electron SE

$$H_C \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) = E \psi(\dots)$$

- The spin-orbit interaction must usually be included into the self-consistent treatment and may change the calculated level structure and spectra qualitatively.

## 4.5. Central-field approximations

### 4.5.a. The central-field model

➤ Coulomb Hamiltonian: can be written in different forms; choose  $u(r_i)$  appropriately

$$H_C = \sum_i \left( -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}}$$

$$H_C = H_o + H' = \sum_i \left( -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + u(r_i) \right) + \sum_{i < j} \frac{1}{r_{ij}} - \sum_i u(r_i).$$

➤ Independent-particle model (IPM): ... each electron moves independent

Hope:  $H_o \gg H'$ , i.e.  $H'$  can be treated later by perturbation theory.

➤ Spin-orbitals: ... one-electron functions

$$\phi_k(\mathbf{r}, \sigma) = \frac{1}{r} P_{n_k \ell_k}(r) Y_{\ell_k m_k}(\vartheta, \varphi) \chi_{m_{s_k}}(\sigma) = |n_k \ell_k m_{\ell_k}, m_{s_k}\rangle$$

$$\langle \phi_k | \phi_p \rangle = \langle n_k \ell_k m_{\ell_k}, m_{s_k} | n_p \ell_p m_{\ell_p}, m_{s_p} \rangle = \delta_{kp} = \delta_{n_k n_p} \delta_{\ell_k \ell_p} \delta_{m_{\ell_k} m_{\ell_p}} \delta_{m_{s_k} m_{s_p}}.$$

### 4.5.b. Product functions and Slater determinants

➤ Product functions:  $H_o$  has one-particle character

$$\psi = \phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) \dots \phi_N(\mathbf{x}_N), \quad \mathbf{x} = (\mathbf{r}, \sigma).$$

#### 4. Atomic many-electron systems

➤ Symmetry requests: ... solutions must be totally antisymmetric.

- Pauli principle: No two electrons may agree in all quantum numbers,  $n l, m_l, m_s$
- $[H, P_{ij}] = 0$  for all  $i \neq j$ .

➤ Slater determinants: ...  $N!$  terms

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \dots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \dots & \phi_2(N) \\ \dots & & & \\ \phi_N(1) & \phi_N(2) & \dots & \phi_N(N) \end{vmatrix} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \phi_1(k_1) \phi_2(k_2) \dots \phi_N(k_N)$$

➤  $H_o$  and  $\{P_{ij}, i \neq j\}$  do NOT describe a complete set of operators: ... solutions are more complicated

➤ Norm:

$$\begin{aligned} \langle \psi | \psi' \rangle &= \frac{1}{N!} \sum_{PP'} (-1)^{P+P'} \langle \phi_1(k_1) \phi_2(k_2) \dots \phi_N(k_N) | \phi'_1(k'_1) \phi'_2(k'_2) \dots \phi'_N(k'_N) \rangle \\ &= \frac{1}{N!} \sum_P (-1)^{2P} \delta_{\psi\psi'} = \delta_{\psi\psi'}. \end{aligned}$$

➤ Total angular momentum: ... solutions to  $H$  (or  $H_o$ ) can be classified due to  $J, M$  quantum numbers

$$[H, \mathbf{J}^2] = [H, J_z] = 0; \quad \mathbf{J} = \sum_{i=1}^N (\mathbf{l}_i + \mathbf{s}_i)$$

➤ Classification of many-electron quantum states: ... require generally  $4N$  quantum numbers.

### 4.5.c. Equivalent electrons. Electron configurations and the PSE

- Equivalent electrons (orbitals):  $\phi_k(\mathbf{r}, \sigma); k = (n \ell m_\ell, m_s)$  degenerate in  $(m_\ell, m_s)$
- Subshell:  $(n\ell)^w$ ; ... set of (maximal)  $q = 2(2\ell + 1)$  equivalent electrons form a subshell
- Electron configuration:

$$(n_1\ell_1)^{q_1} (n_2\ell_2)^{q_2} \dots (n_r\ell_r)^{q_r} \quad 0 \leq q_i \leq 2(2\ell_i + 1) \quad \sum_{i=1}^r q_i = N$$

- Shell notations in atomic spectroscopy:

K-shell:	$n = 1$	$(1s)$	$N_{\max} = 2$
L	$n = 2$	$(2s + 2p)$	$N_{\max} = 8$
M	$n = 3$	$(3s + 3p + 3d)$	$N_{\max} = 18$
N	$n = 4$	$(4s + 4p + 4d + 4f)$	$N_{\max} = 32$
O	$n = 5$	$(5s + 5p + 5d + 5f + 5g)$	$N_{\max} = 50$

- Unsöld's theorem: ... total charge density of a filled subshell is **spherical symmetric**

$$\rho_{subshell} = e \frac{1}{r^2} |P_{n\ell}|^2 \sum_{m=-\ell}^{\ell} \sum_{m_s} |Y_{\ell m}|^2 |\chi_{m_s}|^2 = \frac{2(2\ell + 1)}{4\pi r^2} |P_{n\ell}|^2 \quad \dots \text{basis of atomic shell model}$$

- Atomic shell model: ... central-field model (approximation); theoretical basis for the periodic table of elements
- Rydberg series (of configurations): ...  $2p^53p, 2p^54p, 2p^55p, \dots$
- Aufbau principle: ... successive filling of electron shells ( $n\ell$ )

#### 4. Atomic many-electron systems

➤ Deviations from the aufbau principle: ... occur already for  $Z \gtrsim 18$  (argon)

- $(n+1)s$  and  $(n+1)p$  are often filled before the  $nd$  shell ↗ transition metals.

$3d$  ... iron group  $Z = 21, \dots, 28$

$4d$  ... palladium group  $Z = 39, \dots, 46$

$5d$  ... platinum group  $Z = 71, \dots, 78$

- $nf$ -shells are filled 'afterwards' ( $4f$  ... lanthanides,  $5f$  ... actinides);

- filled and half-filled shells are particularly stable.

**Tafelbeispiel (Low-lying electron configurations of light elements):**

**Tafelbeispiel (Alkali atoms):**

#### 4.5.d. Thomas-Fermi model

**Brief outline of Thomas-Fermi theory:**

- Thomas-Fermi model: ... electrons form Fermi gas (Fermi-Dirac statistic); electron density → electrostatic potential
- Phase space volume of electrons:  $\frac{4\pi}{3} p^3 dV$
- Pauli's principle: max. 2 electrons / ( $h^3 \times$  phase space volume)

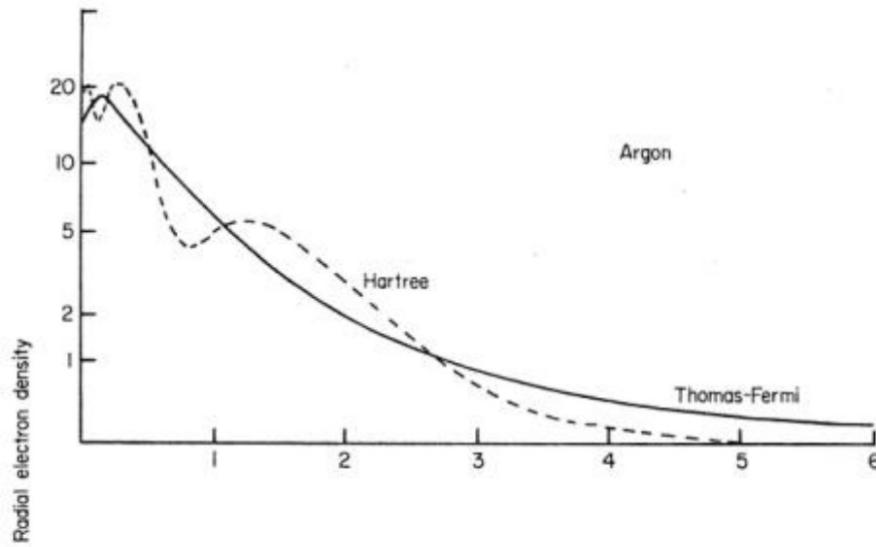


Figure 4.4.: Comparison between the Thomas-Fermi electron densities (from which the potential is derived) and a more accurate quantum-mechanical Hartree density, obtained in the independent-electron approximation. From <http://www.virginia.edu/ep/Interactions/>.

➤ Maximum electron number with  $p \leq p_o$  per unit volume (at zero temperature):

$$n = \frac{2}{h^3} \frac{4\pi}{3} p_o^3 = \frac{8\pi}{3 h^3} (2mT_o)^{2/3}, \quad T \dots \text{kinetic energy (density)}$$

➤ Bound electrons:  $T - e\phi \leq 0 \rightsquigarrow T_o = T_{\max} = e\phi$

➤ Charge density:  $\rho = -e n = -\frac{8\pi}{3 h^3} e (2me\phi)^{3/2}$

## 4.6. Coupling schemes

### 4.6.a. Term splitting in electron configurations

#### Common set of (hermitian) operators:

➤ Rest interactions: ... removes partially the de-generacy of the central-field solutions.

$$H' = \sum_{i < j} \frac{1}{r_{ij}} - \sum_i u(r_i), \quad H'' = \sum_i \xi_i(r_i) (\mathbf{l}_i \cdot \mathbf{s}_i) \quad \dots \text{spin-orbit interaction}$$

➤ Two approaches to obtain the level splitting:

(i) Calculation and diagonalization of the submatrices to  $H_o + H' + H''$ .

(ii) Form linear combinations of determinants (from a given configuration) which are diagonal w.r.t.  $H'$  and/or  $H''$

➤ Light atoms,  $H \approx H_o + H'$ :

$$[H, \mathbf{L}^2] = [H, L_z] = [H, \mathbf{S}^2] = [H, S_z] = 0; \quad [H, \mathbf{J}^2] = [H, J_z] = 0$$

➤ Vector model of angular momentum:  $[H, l_{iz}] \neq 0$ :

➤ Sets of commutable operators:

$$\{H, \mathbf{L}^2, L_z, \mathbf{S}^2, S_z\} \quad \dots \text{LS coupling scheme}$$

$$\{H, \mathbf{L}^2, \mathbf{S}^2, \mathbf{J}^2, J_z\} \quad \dots \text{LSJ coupling scheme}$$

➤ (Very) Heavy atoms ( $Z \gtrsim 90$ ),  $H \approx H_o + H''$ : ...  $H_{SO} \gg H_{rest}(e - e)$ .

$$[H, \mathbf{j}_i^2] = [H, j_{iz}] = [H, \mathbf{l}_i^2] = 0; \quad [H, \mathbf{J}^2] = [H, J_z] = 0$$

Sets of commutable operators:  $[H, X] \neq 0 \quad \forall \quad \{X, X = \mathbf{L}^2, L_z, \mathbf{S}^2, S_z\}$ .

$$\{H, \mathbf{J}^2, J_z\} \quad \dots \quad jj \text{ coupling scheme}$$

➤ ... possible;  $jl$ -coupling or  $jK$ -coupling

**Tafelbeispiel (Classification of an (effective) two-particle systems):**

#### 4.6.b. LS-coupling (Russel-Saunders)

➤ LS-coupling approach:  $H_{so} \ll H_{rest}(e - e)$

$$H \approx H_o + \sum_{i < j} \frac{1}{r_{ij}} - \sum_i u(r_i).$$

➤ In this approximation,  $H$  is diagonal with regard to coupled states of the kind:

- (...)  $LS M_L M_S$  or
- (..)  $LS JM_J$ ,
- while states with different  $M_L$  and  $M_S$  are obviously degenerate.

➤ LS term: Set of all  $(2L + 1)(2S + 1) = \sum_{|L-S|}^{L+S} (2J + 1)$  states

➤ Level  $|\alpha LSJP\rangle$ : ... is specified by  $LSJ$  and parity

**Tafelbeispiel ( $p^2$  configuration):**

**LS terms of equivalent electrons:**

- In general:     $\ell^2$  configuration     $\longrightarrow$     allowed terms with even  $L + S$ .
- Use group theoretical methods to determine the terms and levels of complex  $\ell^w$  configurations, or even for several open shells:     $\ell_1^{w_1} \ell_2^{w_2} \dots$ .
- For all electron configurations with a single open shell, the allowed  $LS$  terms are determined by this shell alone.

**4.6.c. LS-coupling of several open shells**

**Coupling sequence and notations:**

- Vector model ... to determine all possible  $L$  and  $S$ .

$$\mathbf{L} = [(\mathbf{L}_1 + \mathbf{L}_2) + \mathbf{L}_3] + \dots = [\mathbf{L}_1 + (\mathbf{L}_2 + \mathbf{L}_3)] + \dots$$

$$\mathbf{S} = [(\mathbf{S}_1 + \mathbf{S}_2) + \mathbf{S}_3] + \dots$$

- Coupling sequence:

$$\{[(L_1, L_2) \ L_{12}, L_3) \ L_{123} \dots] \ L_q, [(S_1, S_2) \ S_{12}, S_3) \ S_{123} \dots] \ S_q\} \ JM$$

				<u>Total Number</u>	
s	<sup>2</sup> S			1	
s <sup>2</sup>	<sup>1</sup> S			1	
p, p <sup>5</sup>	<sup>2</sup> P			1	
p <sup>2</sup> , p <sup>4</sup>	<sup>1</sup> (SD)	<sup>3</sup> P		3	
p <sup>3</sup>	<sup>2</sup> (PD)	<sup>4</sup> S		3	
d, d <sup>9</sup>	<sup>2</sup> D			1	
d <sup>2</sup> , d <sup>8</sup>	<sup>1</sup> (SDG)	<sup>3</sup> (PF)		5	
d <sup>3</sup> , d <sup>7</sup>	<sup>2</sup> (PD <sub>2</sub> FGH)	<sup>4</sup> (PF)		8	
d <sup>4</sup> , d <sup>6</sup>	<sup>1</sup> (S <sub>2</sub> D <sub>2</sub> FG <sub>2</sub> I)	<sup>3</sup> (P <sub>2</sub> DF <sub>2</sub> GH)	<sup>5</sup> D	16	
d <sup>5</sup>	<sup>2</sup> (SPD <sub>3</sub> F <sub>2</sub> G <sub>2</sub> HI)	<sup>4</sup> (PDFG)	<sup>6</sup> S	16	
f, f <sup>13</sup>	<sup>2</sup> F			1	
f <sup>2</sup> , f <sup>12</sup>	<sup>1</sup> (SDGI)	<sup>3</sup> (PFH)		7	
f <sup>3</sup> , f <sup>11</sup>	<sup>2</sup> (PD <sub>2</sub> F <sub>2</sub> G <sub>2</sub> H <sub>2</sub> IKL)	<sup>4</sup> (SDFGI)		17	
f <sup>4</sup> , f <sup>10</sup>	<sup>1</sup> (S <sub>2</sub> D <sub>4</sub> FG <sub>4</sub> H <sub>2</sub> I <sub>3</sub> KL <sub>2</sub> N)	<sup>3</sup> (P <sub>3</sub> D <sub>2</sub> F <sub>4</sub> G <sub>3</sub> H <sub>4</sub> I <sub>2</sub> K <sub>2</sub> LM)	<sup>5</sup> (SDFGI)	47	
f <sup>5</sup> , f <sup>9</sup>	<sup>2</sup> (P <sub>4</sub> D <sub>5</sub> F <sub>7</sub> G <sub>6</sub> H <sub>7</sub> I <sub>5</sub> K <sub>5</sub> L <sub>3</sub> M <sub>2</sub> NO)	<sup>4</sup> (SP <sub>2</sub> D <sub>3</sub> F <sub>4</sub> G <sub>4</sub> H <sub>3</sub> I <sub>3</sub> K <sub>2</sub> LM)	<sup>6</sup> (PFH)	73	
f <sup>6</sup> , f <sup>8</sup>	<sup>1</sup> (S <sub>4</sub> PD <sub>6</sub> F <sub>4</sub> G <sub>8</sub> H <sub>4</sub> I <sub>1</sub> K <sub>3</sub> L <sub>4</sub> M <sub>2</sub> N <sub>2</sub> Q)	<sup>3</sup> (P <sub>6</sub> D <sub>3</sub> F <sub>9</sub> G <sub>7</sub> H <sub>9</sub> I <sub>6</sub> K <sub>6</sub> L <sub>3</sub> M <sub>3</sub> NO)	<sup>5</sup> (SPD <sub>3</sub> F <sub>2</sub> G <sub>3</sub> H <sub>2</sub> I <sub>2</sub> KL)	<sup>7</sup> F	119
f <sup>7</sup>	<sup>2</sup> (S <sub>2</sub> P <sub>5</sub> D <sub>7</sub> F <sub>10</sub> G <sub>10</sub> H <sub>9</sub> I <sub>9</sub> K <sub>7</sub> L <sub>5</sub> M <sub>4</sub> N <sub>2</sub> OQ)	<sup>4</sup> (S <sub>2</sub> P <sub>2</sub> D <sub>6</sub> F <sub>5</sub> G <sub>7</sub> H <sub>5</sub> I <sub>5</sub> K <sub>3</sub> L <sub>3</sub> MN)	<sup>6</sup> (PDFGHI)	<sup>8</sup> S	119

<sup>a</sup>H. N. Russell, Phys. Rev. 29, 782 (1927); R. C. Gibbs, D. T. Wilber, and H. E. White, Phys. Rev. 29, 790 (1927).

Figure 4.5.: Possible LS terms for  $s^w$ ,  $p^w$ ,  $d^w$ ,  $f^w$ , configurations; the subscripts to the total L values here refer to the number of different LS terms that need be distinguished by some additional quantum number(s). See table for references.

➤ Compact notation:  $\alpha_i \dots$  additional quantum numbers, if necessary

$$\{ [((\ell_1^{w_1} \alpha_1 L_1 S_1, \ell_2^{w_2} \alpha_2 L_2 S_2) L_{12} S_{12}, (\dots)) \dots] L_q S_q \} JM$$

➤ Number of LS terms ... independent of the coupling sequence

#### 4. Atomic many-electron systems

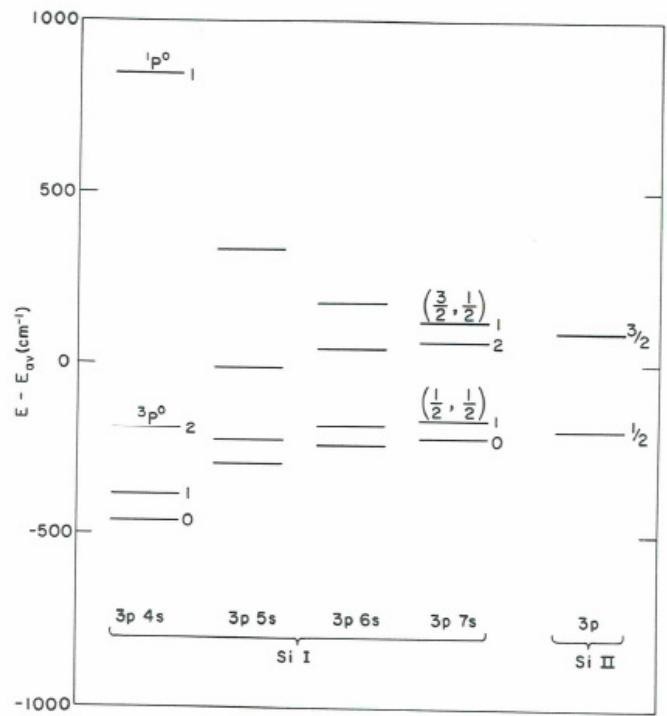


Figure 4.6.: The observed energy level structure for the four lowest  $3pns$  configurations of Si I and together with the Si II configuration, relative to the respective centers of gravity. The figure shows a rapid change from  $LS$  to pair-coupling conditions.

**Tafelbeispiel ( $d^2 p^2$  configuration):**

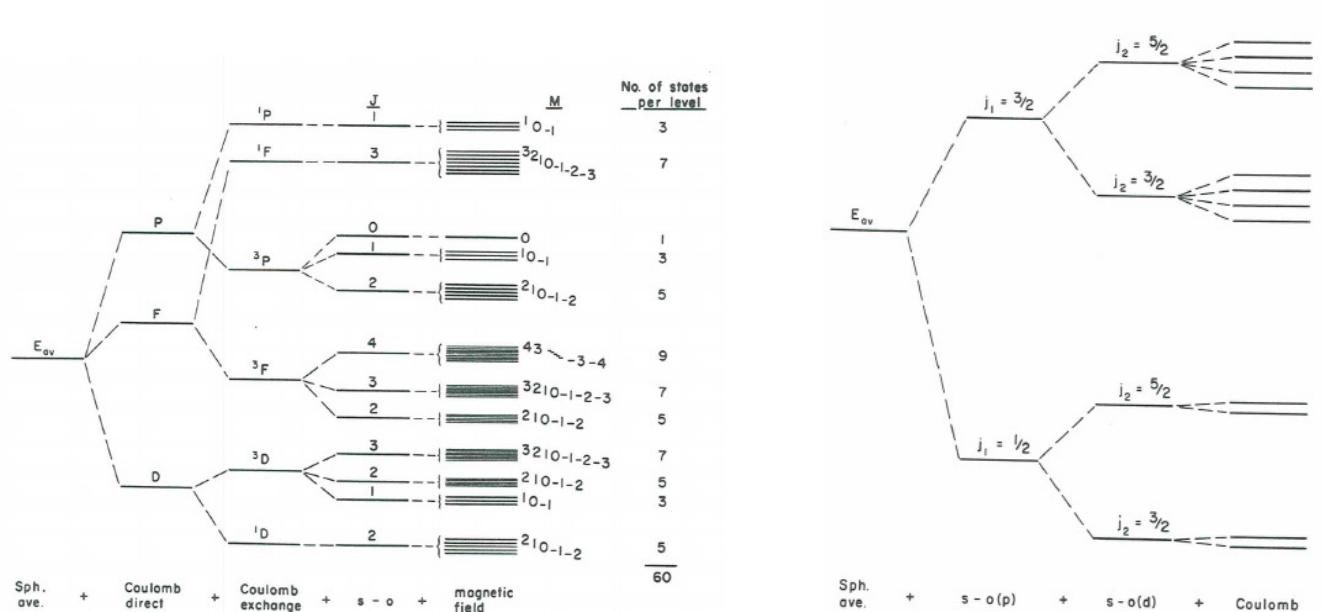


Figure 4.7.: Left: Energy level structure of a *pd* electron configuration under *LS* coupling conditions; it starts from the central-field averaged energy and takes different contributions into account. Right: The same but under *jj* coupling conditions; the two quite strong spin-orbit interactions of the *p* and *d* electrons result into four different energies due to the pairs ( $j_1, j_2$ ) of the two electrons.

#### 4.6.d. *jj*-coupling

➤ *jj*-coupling approach:  $H_{SO} \gg H_{rest}(e - e)$

$$\mathbf{J} = \sum_i \mathbf{j}_i = \sum_i (\mathbf{l}_i + \mathbf{s}_i)$$

#### 4. Atomic many-electron systems

➤ Level  $|\alpha LSJP\rangle$  : ... all  $(2J + 1)$  degenerate states; specified by  $LSJ$  and parity

$$^{2S+1}L_J \quad \longrightarrow \quad (j_1, j_2, \dots)_J$$

Allowed  $jj$ -terms for equivalent electrons can be derived quite similarly to the  $LS$  case.

	$\ell$	$j$	$w$	$J$
$s, p$	$1/2$	0, 2	0	
		1	1/2	
$p, d$	$3/2$	0, 4	0	
		1, 3	3/2	
		2	0, 2	
$d, f$	$5/2$	0, 6	0	
		1, 5	5/2	
		2, 4	0, 2, 4	
		3	3/2, 5/2, 9/2	
$f, g$	$7/2$	0, 8	0	
		1, 7	7/2	
		2, 6	0, 2, 4, 6	
		3, 5	3/2, 5/2, 7/2, 9/2, 11/2, 15/2	
		4	0, 2, 2, 4, 4, 5, 6, 8	

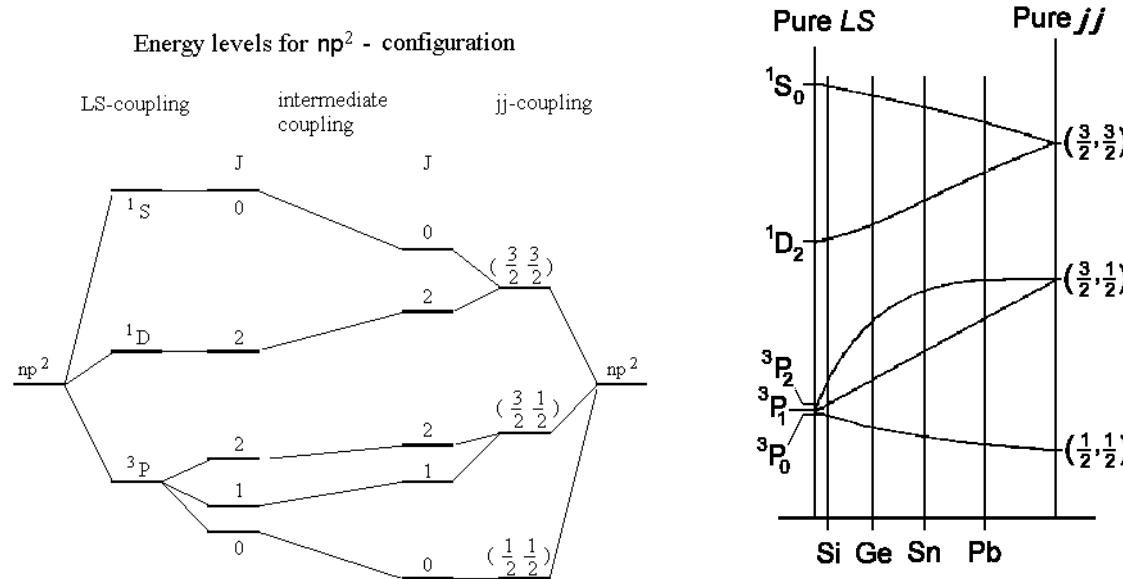


Figure 4.8.: Energies for the  $np^2$  configuration and change in the coupling scheme for various elements homolog to atomic silicon.

#### 4.6.e. Intermediate coupling. The matrix method

- Intermediate coupling approach:  $H' + H'' = H_{rest}(e - e) + H_{SO}$ ; total rest interaction is not diagonal in any (geometrically fixed) coupling scheme.
- Common set of operators:

$$[H, \mathbf{J}^2] = [H, J_z] = [H, P] = 0,$$

#### 4. Atomic many-electron systems

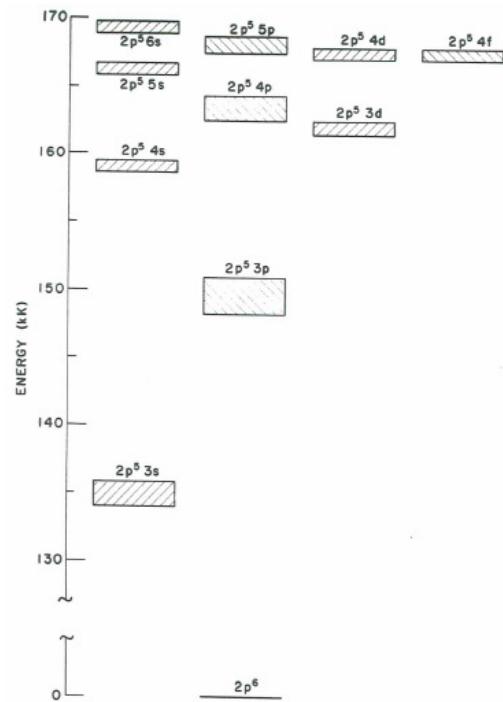


Figure 4.9.: Block diagram of the lowest configurations of Ne I. For each configuration, the levels lay within a limited range of energies as it is shown by the shadowed blocks. There is one level for  $2p^6$ , 4 levels of  $ps$  configurations, 10 levels for  $p^5p'$  configurations and 12 levels for  $p^5d$  and  $p^5f$  configurations, respectively.

## 4.7. Hartree-Fock theory: Electronic motion in a self-consistent field

### 4.7.a. Matrix elements (ME) of symmetric operators with Slater determinants

#### Many-electron matrix elements in atomic theory:

➤ Hamiltonian:

$$H_C = \sum_i \left( -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}}$$

➤ One-particle operators:  $F = \sum_i^N f(\mathbf{x}_i)$   $\rightsquigarrow$  symmetric in  $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$ .

➤ Two-particle operators:  $G = \sum_{i < j}^N g(\mathbf{x}_i, \mathbf{x}_j)$   $\rightsquigarrow$  symmetric in all pairs of electron coordinates.

#### 4. Atomic many-electron systems

➤ Matrix elements of one-particle operators  $F = \sum_i^N f(\mathbf{r}_i)$ : ... because of symmetry  $\langle \psi' | f(\mathbf{r}_i) | \psi \rangle = \langle \psi' | f(\mathbf{r}_j) | \psi \rangle$

$$\langle \psi' | F | \psi \rangle = N \langle \psi' | f(\mathbf{r}_1) | \psi \rangle = \frac{N}{N!} \sum_{PP'} (-1)^{P+P'} \langle \phi_{k_1}(1) \phi_{k_2}(2) \dots | f(\mathbf{r}_1) | \phi_{k'_1}(1) \phi_{k'_2}(2) \dots \rangle$$

$$= \begin{cases} \sum_i \langle i | f(\mathbf{r}) | i \rangle & \text{if } \psi' = \psi \text{ and } \psi = \{a, b, c, \dots\} \\ \pm \langle a' | f(\mathbf{r}) | a \rangle & \text{if } \psi' = \{a', b, c, \dots\} \text{ and } \psi = \{a, b, c, \dots\} \\ 0 & \text{else; i.e. if two or more orbitals differ} \\ & \psi' = \{a', b', c, \dots\} \text{ and } \psi = \{a, b, c, \dots\} \end{cases}$$

$$\langle \psi' | F | \psi \rangle = \begin{cases} \sum_i \langle i | f | i \rangle & \text{all diagonal ME} \\ \langle a' | f(\mathbf{r}) | a \rangle & \text{ME which differ in just one orbital: } a' \neq a \\ 0 & \text{else.} \end{cases}$$

➤ Matrix elements of symmetric two-particle operators:

$$\langle \psi' | G | \psi \rangle = \begin{cases} \sum_{i < j} (\langle ij | g | ij \rangle - \langle ji | g | ij \rangle) & \text{all diagonal ME} \\ \sum_i (\langle ia' | g | ia \rangle - \langle a'i | g | ia \rangle) & \text{ME which just differ in one orbital: } a' \neq a \\ (\langle a'b' | g | ab \rangle - \langle a'b' | g | ab \rangle) & \text{ME which differ in two orbitals: } a' \neq a, b' \neq b \\ 0 & \text{else, i.e. if more than two orbitals differ} \end{cases}$$

### Simplified notations for determinants and matrix elements:

➤ Slater determinant:  $|\alpha\rangle \dots$  Slater determinant  $|\{a, b, \dots, n\}\rangle$ , ordered set of one-particle functions

➤ Occupied vs. virtual orbitals: ... we need to distinguish in  $|\alpha\rangle$

- occupied orbitals (one-particle functions):  $a, b, \dots$
- virtual orbitals (which do not occur in  $|\alpha\rangle$ ):  $r, s, \dots$

Then,  $|\alpha_a^r\rangle$  refers to a Slater determinant, where the occupied orbital  $a \rightarrow r$  is replaced by the virtual orbital  $r$ ; analogue for  $|\alpha_{ab}^{rs}\rangle$ .

➤ Diagonal ME:

$$\begin{aligned}\langle \alpha | F | \alpha \rangle &= \sum_a^{\text{occ}} \langle a | f | a \rangle \\ \langle \alpha | G | \alpha \rangle &= \sum_{a < b}^{\text{occ}} (\langle ab | g | ab \rangle - \langle ba | g | ab \rangle) = \frac{1}{2} \sum_{ab}^{\text{occ}} (\langle ab | g | ab \rangle - \langle ba | g | ab \rangle)\end{aligned}$$

➤ ME between determinant which differ by one (1-particle) orbital

$$\langle \alpha_a^r | F | \alpha \rangle = \langle r | f | a \rangle$$

$$\langle \alpha_a^r | G | \alpha \rangle = \sum_b^{\text{occ}} (\langle rb | g | ab \rangle - \langle br | g | ab \rangle)$$

#### 4. Atomic many-electron systems

➤ ME between determinant which differ by two orbitals:

$$\langle \alpha_{ab}^{rs} | F | \alpha \rangle = 0$$

$$\langle \alpha_{ab}^{rs} | G | \alpha \rangle = \langle rs | g | ab \rangle - \langle sr | g | ab \rangle$$

➤ All other ME vanish identically.

➤ Feynman-Goldstone diagrams: ... graphical representation of matrix elements and operators;

➡ MBPT ... many-body perturbation theory.

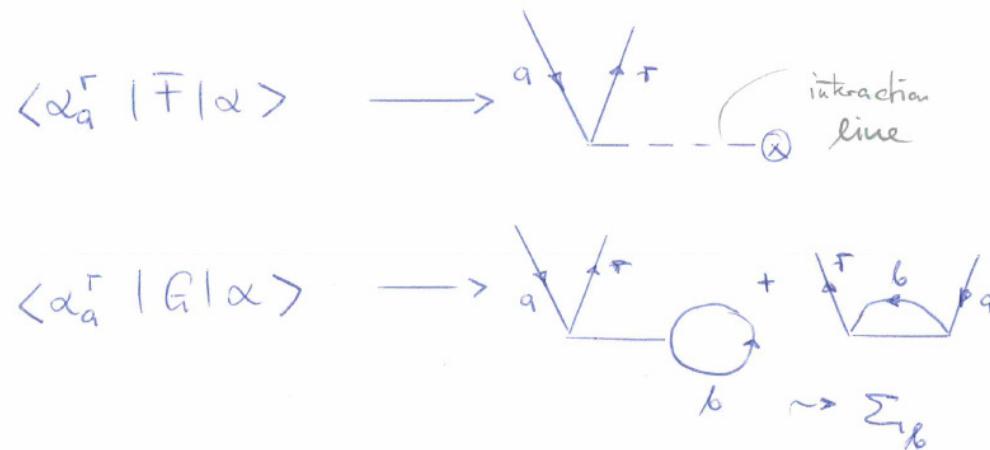


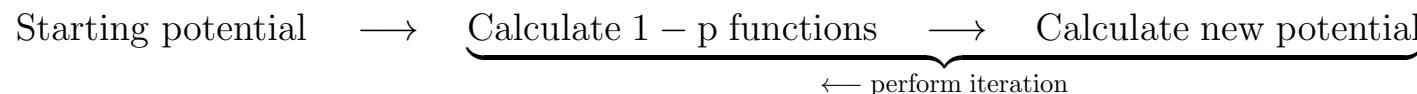
Figure 4.10.: Selected Feynman-Goldstone diagrams to represent matrix elements and wave operators.

**Tafelbeispiel (Feynman-Goldstone diagrams):**

## 4.7.b. Self-consistent-field (SCF) calculations

### Hartree-Fock method:

- Central-field model:  $\sum_i u(r_i)$
- Question: Is there an optimal choice of  $u(r_i)$  or  $u(\mathbf{r}_i)$  ?
- Self-consistent field (SCF-field):



- Hartree-Fock equations: ... mathematical formulation of this SCF scheme

## 4.7.c. Abstract Hartree-Fock equations

### Hartree-Fock method:

- Expectation value of the total energy: ... with respect to a single Slater determinant  $|\alpha\rangle$

$$\langle E \rangle = \langle \alpha | H | \alpha \rangle = \left\langle \alpha \left| \sum_{i=1}^N \left( -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}} \right| \alpha \right\rangle$$

#### 4. Atomic many-electron systems

(Variational) Minimization of the expectation value: ... with regard to variations of the orbital functions

$\langle E \rangle$  ... stationary with respect to small changes in the orbitals

$$|a\rangle \rightarrow |a\rangle + \eta |r\rangle \quad \eta \dots \text{real}$$

$$|\alpha\rangle \rightarrow |\alpha\rangle + \eta |\alpha_a^r\rangle$$

$$\langle E \rangle \rightarrow \langle E \rangle + \eta (\langle \alpha_a^r | H | \alpha \rangle + \langle \alpha | H | \alpha_a^r \rangle) + \mathcal{O}(\eta^2)$$

$$\langle \alpha_a^r | H | \alpha \rangle = 0 \quad \text{for all pairs } a, r \quad \text{Hartree – Fock condition}$$

➤ **Brillouin's theorem:** In the Hartree-Fock approximation, non-diagonal matrix elements must vanish for all those determinants which just differ by a single one-electron orbital.

Or shorter: One-particle excitations do not contribute to the Hartree-Fock energy.

➤ Explicit form of the HF condition:

$$\left\langle r \left| -\frac{\nabla^2}{2} - \frac{Z}{r} \right| a \right\rangle + \sum_b^{occ} \left( \left\langle rb \left| \frac{1}{r_{12}} \right| ab \right\rangle - \left\langle br \left| \frac{1}{r_{12}} \right| ab \right\rangle \right) = 0 =: \langle r | h_{HF} | a \rangle$$

➤ Hartree-Fock operator:  $h_{HF} = -\frac{\nabla^2}{2} - \frac{Z}{r} + u_{HF}$

➤ Hartree-Fock potential:

$$\langle i | u_{HF} | j \rangle = \sum_b^{occ} \left( \left\langle ib \left| \frac{1}{r_{12}} \right| jb \right\rangle - \left\langle bi \left| \frac{1}{r_{12}} \right| jb \right\rangle \right) \equiv \sum_b^{occ} \langle ib || jb \rangle; \quad \langle ij || kl \rangle = \left\langle ij \left| \frac{1}{r_{12}} \right| kl \right\rangle - \left\langle ji \left| \frac{1}{r_{12}} \right| kl \right\rangle.$$

➤ Acting with HF-operator on an occupied orbital only produces (a linear combination of) other occupied orbitals because:

$$\langle r | h_{HF} | a \rangle = 0 \quad \text{a ... occupied; r ... virtual orbitals}$$

$$h_{HF} |a\rangle = \sum_i^{\text{all}} |i\rangle \langle i | h_{HF} | a \rangle = \sum_b^{\text{occ}} |b\rangle \langle b | h_{HF} | a \rangle$$

➤ Properties of  $u_{HF}$

- $h_{HF}$  is hermitian
- invariant with regard to unitary transformations; it can hence be written in a diagonal form.

➤ Normal form of the Hartree-Fock equations:

$$h_{HF} |a'\rangle = \left( -\frac{\nabla^2}{2} - \frac{Z}{r} + u_{HF} \right) |a'\rangle = \varepsilon'_a |a'\rangle$$

➤ Binding energy:

$$\langle E(N) \rangle = \sum_b^{\text{occ}} \left\langle b \left| -\frac{\nabla^2}{2} - \frac{Z}{r} \right| b \right\rangle + \frac{1}{2} \sum_{bc} \langle bc || bc \rangle$$

➤ Ionisation energies: ... means to 'take out' an electron  $a$

$$\langle E(N) \rangle - \langle E(N-1) \rangle_a = \left\langle a \left| -\frac{\nabla^2}{2} - \frac{Z}{r} \right| a \right\rangle + \sum_b \langle ab || ab \rangle = \langle a | h_{HF} | a \rangle = \varepsilon_a$$

➤ Koopman's theorem: In the HF approximation, the ionization (binding) energy for releasing an electron  $a$  is equivalent to the (negative) one-electron HF energy of the electron  $a$ .

**4.7.d. Restricted Hartree-Fock method: SCF equations for central-field potentials**Hartree-Fock method:

- Central-field model:  $H_o = \sum_i^N h_o(i)$ ; only the radial functions are varied

$$h_o \phi_k = \left( -\frac{\nabla^2}{2} - \frac{Z}{r} + u(r) \right) \phi_k = \varepsilon_k \phi_k$$

$$\phi_k = \frac{P_k(r)}{r} Y_{\ell_k m_{\ell_k}}(\vartheta, \varphi) \chi_{m_{s_k}}(\sigma)$$

- Radial equation:

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} - \frac{Z}{r} + u(r) \right] P(r) = \varepsilon P(r); \quad \int dV |\phi|^2 = \int_0^\infty dr P^2(r) \quad \dots \text{normalizable}$$

- Boundary conditions:

$$P(r \rightarrow 0) = 0 \iff \frac{P(r)}{r} \xrightarrow{r \rightarrow 0} \text{finite}$$

- Classification of  $P_{nl}(r)$  by  $n$  and  $l$ : ... still possible;  $\nu$  ... number of knots

$$n = \nu + l + 1, \quad \varepsilon = \varepsilon(n, \ell) = \varepsilon_{n\ell}.$$

### Restricted Hartree-Fock equations:

- Closed-shell atoms: ... HF equations represent a set of coupled one-particle (integro-differential) equations.
- Open-shell atoms: Derivation requires an additional averaging over the magnetic quantum numbers.

$$E_{av} = \langle E \rangle_{av} = \sum_a q_a I_a + \frac{1}{2} \sum_{ab,k} q_a q_b [c(abk) F^k(a,b) + d(abk) G^k(a,b)]$$

$a \equiv (n_a, \ell_a)$ ,  $b$  ... runs over all occupied subshells

$q_a$  ... occupation of the subshell  $(n_a \ell_a)^{q_a}$

$c(ab, k)$ ,  $d(ab, k)$  ... constants for some given shell structure

- One-particle kinetic and potential energy:

$$I(a) = \int_0^\infty dr P_a(r) \left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} - \frac{Z}{r} \right] P_a(r) .$$

#### 4. Atomic many-electron systems

➤ **Slater integrals:** ... radial intergrals  $F^k(a, b)$  and  $G^k(a, b)$  are special forms of

$$\begin{aligned} R^k(abcd) &= \int_0^\infty \int_0^\infty dr ds P_a(r) P_b(r) \frac{r_-^k}{r_+^{k+1}} P_c(s) P_d(s) \quad r_- = \min(r, s), \quad r_+ = \max(r, s) \\ &= \int_0^\infty dr \int_0^r ds [P_a P_b]_r \frac{s^k}{r^{k+1}} [P_c P_d]_s + \int_0^\infty dr \int_r^\infty ds [P_a P_b]_r \frac{r^k}{s^{k+1}} [P_c P_d]_s \\ F^k(a, b) &= R^k(aabb); \quad G^k(a, b) = R^k(abab). \end{aligned}$$

➤ The integrals to the e-e interaction are based on an expansion:

$$\begin{aligned} \frac{1}{r_{12}} &= r_1^2 + r_2^2 - 2r_1 r_2 \cos \omega = \sum_{k=0}^{\infty} \frac{r_-^k}{r_+^{k+1}} P_k(\cos \omega) = \sum_{k=0}^{\infty} \frac{4\pi}{k+1} \frac{r_-^k}{r_+^{k+1}} \sum_{q=-k}^k Y_{kq}(\vartheta_1, \varphi_1) Y_{kq}^*(\vartheta_2, \varphi_2) \\ r_- &= \min(r_1, r_2), \quad r_+ = \max(r_1, r_2). \end{aligned}$$

➤ **(Restricted) Hartree-Fock method:** ... variational principle of the total energy; w.r.t.  $\delta P_a(r)$

$$\begin{aligned} \delta \langle E \rangle &= \delta E_{av} = 0, & N_{n\ell, n'\ell} &= \int_0^\infty dr P_{n\ell}^*(r) P_{n'\ell}(r) = \delta_{nn'} & \text{or equivalent} \\ \delta_{\{P_a\}} \left[ E_{av} - \sum_a q_a \lambda_{aa} N_{aa} - \sum_{a \neq b} \delta_{\ell_a, \ell_b} q_a q_b \lambda_{ab} N_{ab} \right] &= 0 \end{aligned}$$

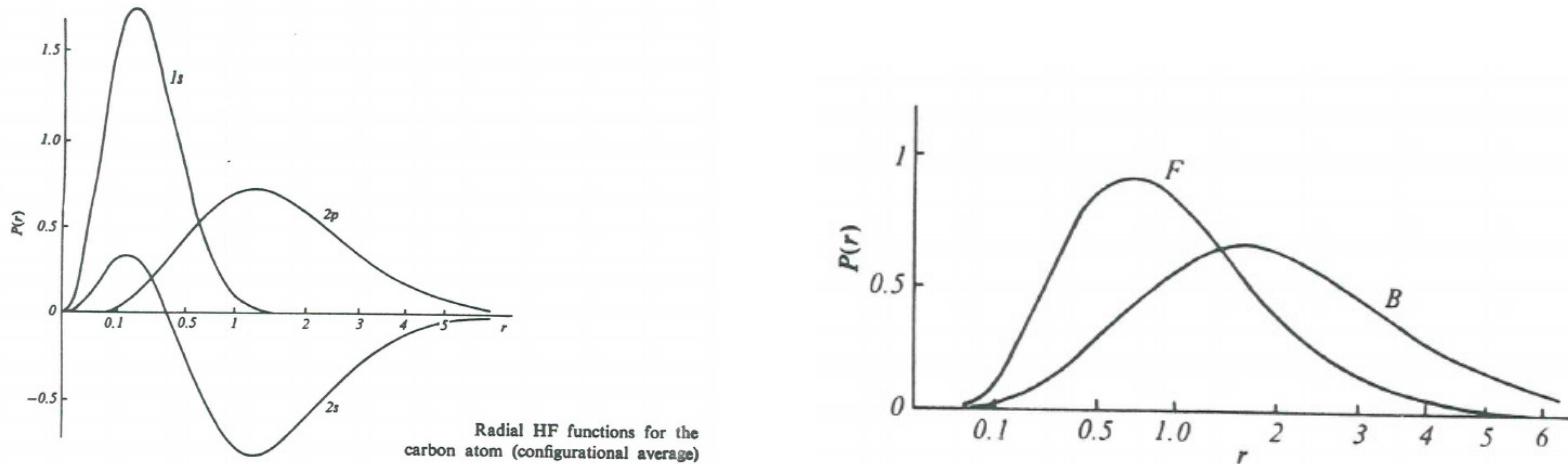


Figure 4.11.: (Radial Hartree-Fock functions for carbon (left) as well as for the  $2p$  electrons of boron and fluorine (right)).

➤ **Restricted HF equations:** ... set of linear and coupled integro-differential equations

$$\begin{aligned} \left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell_a(\ell_a + 1)}{2r^2} - \frac{Z}{r} \right] P_a(r) + \sum_{b,k} q_b \left[ c(abk) \frac{Y^k(bb; r)}{r} P_a(r) + d(abk) \frac{Y^k(ab; r)}{r} P_b(r) \right] \\ = \varepsilon_a P_a(r) + \sum_{b \neq a} q_b \varepsilon_{ab} P_b(r) \end{aligned}$$

with :  $Y^k(ab, r) = r \int_0^\infty ds \frac{r_s^k}{r_{>}^{k+1}} P_a(s) P_b(s)$

$$\epsilon_a = \lambda_{aa} \quad \dots \text{one-electron eigenvalues}$$

$$\epsilon_{ab} = \frac{1}{2} \delta(\ell_a, \ell_b) (\lambda_{ab} + \lambda_{ba})$$

$E(^3P)$			$E_{av}$		$E(^1D)$		$E(^1S)$	
$E$	-37.6886		-37.6602		-37.6313		-37.5495	
$nl$	$\varepsilon_{nl}$	$\langle r \rangle_{nl}$						
1s	11.326	0.268	11.338	0.268	11.352	0.268	11.392	0.268
2s	0.706	1.589	0.712	1.586	0.719	1.582	0.740	1.571
2p	0.433	1.715	0.407	1.743	0.381	1.772	0.310	1.871

Figure 4.12.: Total energies, orbital eigenvalues and expectation values of  $r$  from Hartree-Fock calculations for the  $1s^2 2s^2 2p^2$  configuration of carbon (taken from Lindgren and Morrison, 1986).

## 4.8. Beyond Hartree-Fock theory: Electron-electron correlations

### 4.8.a. Configuration interaction theory (CI, matrix method)

#### CI method:

➢ (Fourier) expansion of the unknown solution  $\Psi$ : ... with regard to a (complete) set of basis functions  $\{\Phi_i\}$ :

$$|\Psi_k\rangle = \sum_i c_{ik} |\Phi_i\rangle, \quad \langle \Phi_i | \Phi_j \rangle = \delta_{ij}.$$

➢ Truncation of the basis: ... in practice, the infinitely large basis must always be truncated,  $i = 1, \dots, M$

<b>He</b>	<b>Ne</b>	<b>A</b>	<b>Kr</b>	<b>Xe</b>
<b><i>n</i>l</b>	$\langle r \rangle_{nl}$	$\langle r \rangle_{nl}$	$\langle r \rangle_{nl}$	$\langle r \rangle_{nl}$
1s	0.93	0.16	0.09	0.04
2s		0.89	0.41	0.19
2p		0.96	0.38	0.16
3s			1.42	0.54
3p			1.66	0.54
3d				0.55
4s				1.63
4p				1.95
4d				
5s				
5p				0.87
				1.98
				2.34

Figure 4.13.: Expectation values of  $r$  from Hartree-Fock calculations for noble gas atoms (taken from Lindgren and Morrison, 1986).

➤ Substitution into SE:  $H \Psi_k = E_k \Psi_k : H_{ji} = \langle \Phi_j | H | \Phi_i \rangle \dots$  matrix elements of  $H$ .

$$\sum_i^M H c_{ik} |\Phi_i\rangle = E_k \sum_i^M c_{ik} |\Phi_i\rangle \quad | \cdot \langle \Phi_j |, \quad j = 1, \dots, M \quad \iff \quad \sum_i^M H_{ji} c_{ik} = E_k c_{jk} \quad \forall j.$$

➤ Secular equation:  $|H - EI| = 0$ ; with hermitian matrix ( $H_{ik} = H_{ki}^*$ ).

➤ Representation of wave function:  $C = (c_{ik})$  with  $H_{\text{diag}} = C^{-1} H C$

## 4.8.b. Multiconfiguration Hartree-Fock (MCHF) theory

### MCHF method:

➤ Comparison HF *versus* MCHF:

Hartree-Fock method

$$|\alpha\rangle \longrightarrow$$

\* single determinant

\* variation of (radial) orbital functions

MCDF method

$$|\alpha(k)\rangle = \sum_i c_{ik} |\alpha_i\rangle$$

\* superposition of determinants

\* variation of (radial) orbital and expansion coefficients  $\{c_{ik}\}$ .

➤ Steps in deriving the MCDF equations: ... Variation of the expectation value (energy functional) and secular equation

$$\langle E \rangle = \langle \alpha(k) | H | \alpha(k) \rangle, \quad \langle \alpha_i | \alpha_j \rangle = \delta_{ij} \quad \text{or} \quad \langle a | b \rangle = \delta_{ab}$$

$$|H - E_k^{(n)} I| = 0 \quad \text{iteration of the coupled equations}$$

➤ Hylleras-Undheim theorem: The eigenvalues  $E_k^{(n+1)} \leq E_k^{(n)}$  of the Hamiltonian matrix converge monotonically from above to the exact energies of the Schrödinger equation as the number of basis functions is increased.

TABLE I. The hyperfine parameters and total energies (in a.u.) of the  $1s^2 2s 2p\ ^3P$  term in  ${}^9\text{Be}$  for different active sets of orbitals.

Active set	$a_l$	$a_{sd}$	$a_c$	$b_q$	Energy
HF	0.295 21	-0.059 04	7.8182	-0.118 09	-14.511 502
$2s1p$	0.295 80	-0.059 16	7.8297	-0.118 32	-14.511 577
$3s2p1d$	0.298 87	-0.061 82	9.0900	-0.122 82	-14.553 679
$4s3p2d1f$	0.302 88	-0.068 51	9.0444	-0.107 67	-14.560 100
$5s4p3d2f$	0.303 44	-0.063 34	9.1527	-0.112 91	-14.563 946
$6s5p4d3f$	0.304 63	-0.068 46	9.2254	-0.119 91	-14.565 325
$7s6p5d4f$	0.304 11	-0.064 71	9.2376	-0.111 78	-14.565 841
$8s7p6d5f$	0.304 31	-0.066 94	9.2268	-0.119 04	-14.566 132
$9s8p7d6f$	0.303 67	-0.066 03	9.2293	-0.116 06	-14.566 232
$10s9p8d7f$	0.303 73	-0.065 78	9.2317	-0.115 48	-14.566 295
$11s10p9d8f$	0.303 68	-0.065 96	9.2298	-0.115 98	-14.566 319
$12s11p10d9f$	0.303 70	-0.065 91	9.2316	-0.115 67	-14.566 333
Extrapolated	0.303 69	-0.065 94	9.2310	-0.115 82	

Figure 4.14.: From Jönsson and Froese Fischer, Phys. Rev. A48 (1993).

#### 4.8.c. Elements of many-body perturbation theory (MBPT)

##### MBPT method:

➤ Decomposition of the Hamiltonian operator: ... solutions to  $H_o$  are known

$$H = H_o + V, \quad H_o \phi_n^{(0)} = E_n^{(0)} \phi_n^{(0)}, \quad V_{mn} = \langle \phi_m^{(0)} | V | \phi_n^{(0)} \rangle,$$

#### 4. Atomic many-electron systems

➤ Ansatz:  $m \dots$  summation over a complete set of many-particle states.

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots; \quad \phi_n = \phi_n^{(0)} + \phi_n^{(1)} + \dots$$

$$E_n^{(1)} = V_{mn}, \quad E_n^{(2)} = \sum_m \frac{V_{nm} V_{mn}}{E_n^{(0)} - E_m^{(0)}}, \quad \phi_n^{(1)} = \sum_m \frac{|\phi_m^{(0)}\rangle V_{mn}}{E_n^{(0)} - E_m^{(0)}}$$

Not so easy applicable to many-electron system because of complications with book-keeping and the degeneracy of the zero-order solutions.

➤ Basic steps of MBPT: ... assume again decomposition

$$H = H_o + V, \quad H_o = \sum_i h_o(\mathbf{r}_i), \quad H_o \Phi_a = E_a^{(o)} \Phi_a, \quad \langle \Phi_a | \Phi_b \rangle = \delta_{ab}$$

➤ Slater determinants:  $\Phi_a$  built from one-electron functions  $\phi_k$ :  $h_o \phi_k = \varepsilon \phi_k$ .

➤ Goal: Solutions of the SE  $H \Psi_a = E_a \Psi_a$  for a finite number  $a = 1, \dots, d$  of atomic states.

➤ Model space:  $\mathcal{M} = \text{span}\{\Phi_a, a = 1, \dots, d\}$ ; in contrast to the (complementary) space orthogonal  $\mathcal{Q}$ .

➤ Projection operator: ... commute with  $H_o$ ; if  $\Phi_a$  is known,  $\Phi_a^o$  is just the projection of the exact solution upon the model space.

$$P = \sum_{a \in \mathcal{M}} |\Phi_a\rangle \langle \Phi_a|, \quad Q = 1 - P = \sum_{r \notin \mathcal{M}} |\Phi_r\rangle \langle \Phi_r|$$

$$P = P^+ = P^2, \quad PQ = QP = 0, \quad [P, H_o] = [Q, H_o] = 0, \quad \Phi_a^o = P \Phi_a$$

➤ Wave operator (Möller, 1945): ... however,  $\Omega$  and  $P$  are not *inverse* operators.

$$\Phi_a = \Omega \Phi_a^o$$

➤ Generalized Bloch equation: ... intermediate normalization:

$$\langle \Phi_a | \Phi_a^o \rangle = \langle \Phi_a^o | \Phi_a^o \rangle = 1 \iff P = P \Omega P$$

$$\cdot \Omega P | \quad \Omega P H_o \Psi^a + \Omega P V \Psi_a = E_a \Omega P \Psi_a$$

$$- H_o \Omega P \Psi_a + V \Omega P \Psi_a = E_a \Omega P \Psi_a$$

$$(\Omega H_o - H_o \Omega) P \Psi_a + (\Omega P V \Omega P - V \Omega P) \Psi_a = 0 \quad \forall a = 1, \dots, d$$

$$[\Omega, H_o] P = (V \Omega - \Omega P V \Omega) P$$

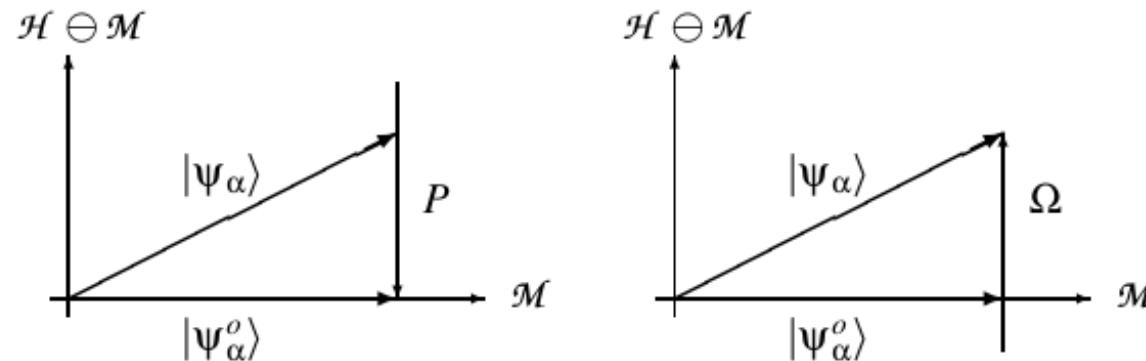


Figure 4.15.: Simplified representation of the operators  $P$  and  $\Omega$  in IN. The projector  $P$  transforms a  $d$ -dimensional space  $\{\Phi_a, a = 1, \dots, d\}$  of the Hilbert space into the model space  $\mathcal{M}$  of the same dimension. The wave operator  $\Omega$  reverses this transformation. Note, however, that  $P$  and  $\Omega$  are **not inverse operators**.

#### 4. Atomic many-electron systems

- For the states of interest  $\{\Phi_a, a = 1, \dots, d\}$ , this equation is completely equivalent to Schrödinger's equation.  
Instead an equation for the wave function, we now have an (operator) equation for the wave operator  $\Omega$ .

#### Order-by-order perturbation expansions:

- Expansion of the wave operator:  $\Omega = 1 + \Omega^{(1)} + \Omega^{(2)} + \dots$  gives rise to

$$[\Omega^{(1)}, H_o] P = Q V P$$

$$[\Omega^{(2)}, H_o] P = Q V \Omega^{(1)} P - \Omega^{(1)} V P$$

⋮

$$[\Omega^{(n)}, H_o] P = Q V \Omega^{(n-1)} P - \sum_m^{n-1} \Omega^{(n-m)} V \Omega^{(m-1)} P$$

- Second quantization: ... use ansatz to determine the coefficients  $x_j^{i(1)}$  and  $x_{kl}^{ij(1)}$

$$\Omega^{(1)} = \sum_{ij} a_i^+ a_j x_j^{i(1)} + \sum_{ijkl} a_i^+ a_j^+ a_k a_l x_{kl}^{ij(1)}$$

- Feynman-Goldstone diagrams: ... graphical representation and handling of these equations.

$$\begin{aligned}
 H_o &= \text{(Diagram of two electrons in opposite spin states)} + \text{(Diagram of two electrons in same spin state)} \\
 V_o &= \text{(Diagram of two electrons in opposite spin states)} + \text{(Diagram of two electrons in same spin state)} + \text{(Diagram of two electrons in same spin state with exchange)} \\
 V_1 &= \text{(Diagram of two electrons in opposite spin states)} + \text{(Diagram of two electrons in same spin state)} + \text{(Diagram of two electrons in same spin state with exchange)} + \text{(Diagram of two electrons in same spin state with exchange)} \\
 V_2 &= \text{(Diagram of two electrons in opposite spin states)} + \text{(Diagram of two electrons in same spin state)} + \text{(Diagram of two electrons in same spin state with exchange)} + \text{(Diagram of two electrons in same spin state with exchange)} + \dots
 \end{aligned}$$

The figure shows the graphical representation of the unperturbed Hamiltonian operator  $H_o$  and the perturbation  $V$  in normal form.   
 $H_o$  consists of two diagrams: one showing two electrons in opposite spin states (one up, one down) and another showing two electrons in the same spin state (both up or both down).   
 $V_o$  consists of three diagrams: two showing two electrons in opposite spin states and one showing two electrons in the same spin state with exchange.   
 $V_1$  consists of four diagrams: two showing two electrons in opposite spin states and two showing two electrons in the same spin state with exchange.   
 $V_2$  consists of five diagrams: two showing two electrons in opposite spin states and three showing two electrons in the same spin state with exchange.

Figure 4.16.: Grafical representation of the unperturbed Hamiltonian operator  $H_o$  and the perturbation  $V$ , written in [normal form](#) [cf. Eqs. (4.31-4.35) in Lindgren (1978)].

#### 4.8.d. Relativistic corrections to the HF method: Dirac-Fock

##### Relativistic Hamilton operator:

➤ One-particle Dirac Hamiltonian, Dirac matrices and Dirac spinors:

$$h = -\frac{\nabla^2}{2} - \frac{Z}{r} \quad \longrightarrow \quad h_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)c^2 - \frac{Z}{r}, \quad \phi \quad \longrightarrow \quad \psi_D = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}.$$

➤ Dirac-Fock method: ... again, use single Slater determinant, but for  $\{\psi_{D,i}\}$

➤ Dirac-Coulomb Hamiltonian: ... built-up from the one-particle Dirac Hamiltonian

$$H = \sum_{i=1}^N h_D(i) + \sum_{i < j} \frac{1}{r_{ij}} + b(i,j) = H_{DC}$$

$$h_D(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 - \frac{Z}{r_i}, \quad b(i,j) = \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} + (\boldsymbol{\alpha}_i \cdot \nabla_i) (\boldsymbol{\alpha}_j \cdot \nabla_j) \frac{\cos(\omega r_{ij} - 1)}{\omega^2 r_{ij}}.$$

➤ Frequency-dependent Breit interaction  $b^o(i,j)$ :

$$b^o(i,j) = -\frac{1}{2r_{ij}} \left[ \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right],$$

➤ Exact description of relativistic many-electron atoms requires a QED treatment; practically, however, this is quite unfeasible.

## 4.9. Tasks

See tutorials.