Computational Quantum Physics

— Lecture notes —

SS 2020

http://www.atomic-theory.uni-jena.de/
→ Teaching → Computational Quantum Physics

(Notes and additional material)

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0. Preliminary remarks

0.1. Schedule and agreements

Lecture period:	14. 4. 2018 – 17. 07. 2020
Lecture:	Fr 12 – 14, Max-Wien-Platz (Physik, SR 1)
Tutorial:	Fr 14 – 16, Computerpool, Physik (PAF)
Language:	German / English ??
ECTS points:	4 (inclusive the tasks and exam).
Exam:	Tasks (40 %), oral exam or a home task including some moderate programming.
Requirements for exam:	*Modulanmeldung* within the first 6 weeks; at least 50 % of the points from tutorials.
Home work:	Some discussion/collaboration on homework problems is encouraged; however, everyone should be able and turn in his/her written programs independently.
A few questions ahead:	Who has experience with programming ?? Which languages ?? ... Julia ?? Who makes regularly use of Maple oder Mathematica ?? Who has used the PAF computer pool before ??

0.2. Further reading

- K. Blum: *Density Matrix Theory and Applications: Physics of Atoms and Molecules* (Plenum Press, New York, 1981, 1996).
- H. Friedrich: *Theoretical Atomic Physics* (Springer, 3rd edition, 2003).
- W. R. Johnson: *Atomic Structure Theory: Lectures on Atomic Physics* (Springer, Berlin, 2007).
- W. H. Press et al.: *Numerical Recipes: The Art of Scientific Computing* (Cambridge University Press, Cambridge, 2007).
- For Maple, moreover, you can find much material in the web: `http://www.maplesoft.com/applications/`
- J. Bezanson, S. Karpinski, V. B. Shah and A. Edelman: Julia: A Fast Dynamic Language for Technical Computing (2012).
- http://julialang.org/

1. Computational physics & quantum mechanics: An overview

1.1. Scientific computing in ‘physics’

Modelling physical systems by using computers:

- Many systems of equations (especially for many-particle quantum systems) that cannot be ‘solved’ analytically; numerical simulations of physical systems in space and time.
- Computational physics is often considered as a third ‘pillar’ of physics.
- Many subfields of physics make heavily use of computations (dynamics of solar systems, galaxies, etc.; fluid dynamics & turbulence; molecular dynamics of fluids & gases; solving Maxwell’s equations; statistical mechanics of polymers; magnetic systems, ...)
- Most of you will need to do some computational work, especially also in theoretical physics.
- Recommendation: Gain some proficiency in scientific computing.

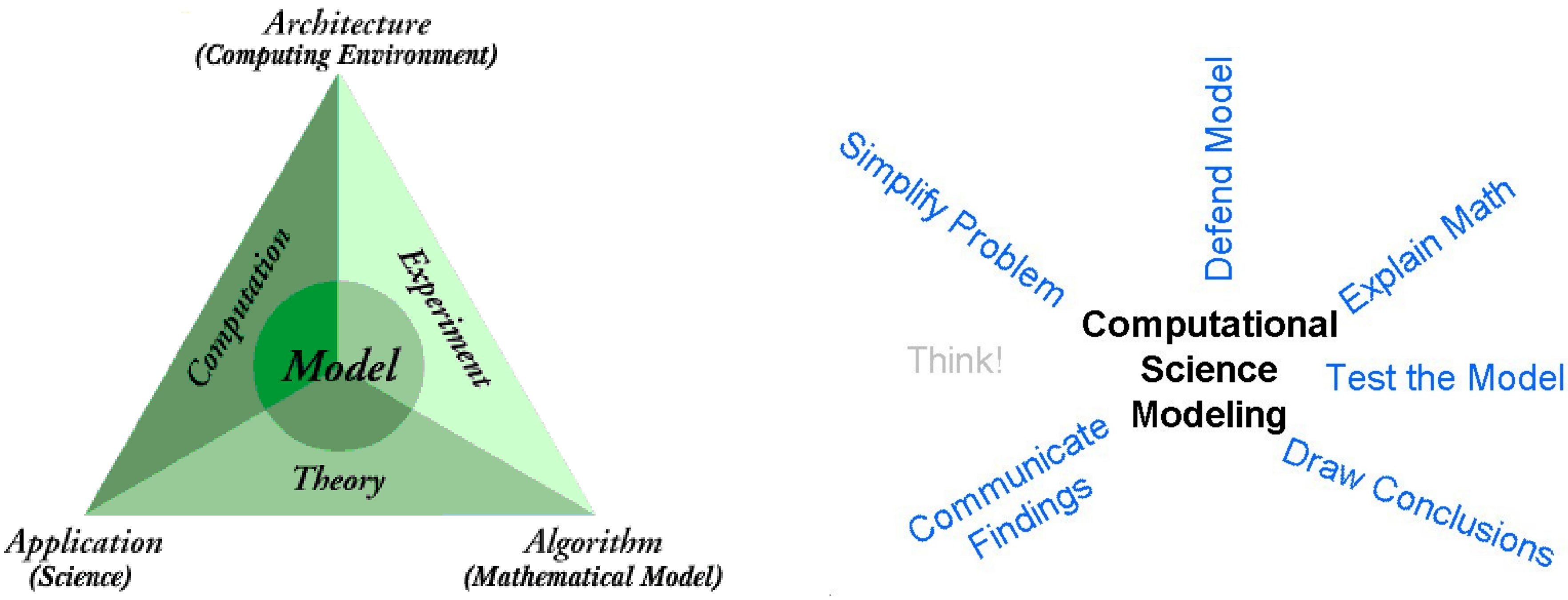


Figure 1.1.: Left: Interplay of experiment, theory and computations in science (taken from www.shodor.org/chemviz/overview). Right: Abilities to be trained in order to make use of this interplay (from www.ncsec.org/cadre2/)

1.2. Modern fields of (theoretical) quantum physics

Well-established fields of quantum physics:

- ➢ Quantum field theory (QFT: QED, QCD, string theory).
- ➢ Quantum many-body theory (nuclear structure, electronic structures of atoms and molecules, quantum chemistry).
- ➢ Quantum scattering & collision theory (nuclear reactions, atom-ion and atom-molecule collisions, electron-atom and

electron-molecule collisions, etc.).

- Solid-state theory (band structures, density functional theory, magnetism, spin chains, ...).
- Quantum optics (Rabi oscillations, field amplitudes, EIT, coherent states, ...).

Recently emerging fields:

- Quantum control theory.
- Quantum engineering (generation, tomography and use of quantum states, ...).
- Quantum information theory and processing.
- Light-matter interactions with single photons and twisted light (cavity-QED, ...).
- Metamaterials (negative refraction indices, ...).
- Electron transfer theory and photosynthesis in complex molecules.
- Parity non-conservation and electric-dipole moments.
- Ultra-cold atoms and molecules (Bose-Einstein condensation, astro chemistry, ...).
- Strong-field electron dynamics.
- ...

1.3. Programming languages in physics

1.3.a. Programming languages used in physics

- It is almost impossible to ‘overview’ all the computational languages and tools, presently available.
- Languages for doing numerics: Fortran 77/90/2008, Pascal, C, C++, Julia, ...
- Languages for scripting: python, perl, R, ...
- Computeralgebra & symbolic computations: Reduce, Maple, Mathematica, ...

High-level programming (HLP) languages; properties:

- In computer science, a programming language with strong abstraction from the details of the computer.
- HLP languages may use natural language elements or may automate (or even hide entirely) significant areas of computing systems (e.g. memory management).
- They simplify the development a programs; good readability.
- Amount of abstraction decides how “high-level” a programming language really is.
- A HLP language must always be translated into machine language by a compiler or interpreter.

The Fortran 90/2008 programming language:

- Fortran has evolved since the early days of computing (formula translation); it was introduced in 1957 and remains in many scientific computing environments the language of choice.
- Fortran 90/2008 is a quite modern programming language.
- Many useful features for scientific (numerical) computing (dynamic allocation; derived data types; modules, kind parameters, recursive subroutines, pointers, manipulation of entire arrays, ...);

- Widely used language in computational science ... but also still in engineering, etc.
- Simple control of different data types and accuracy of computations;
- Many intrinsice functions and protection of code; also intrinsic feature for parallelization.
- Object-oriented features: Abstract data types – Polymorphism – Hidden code; it misses inheritance.
- Relatively easy to learn;
- Many commercial and open-source compilers available; gfortran; free open source Fortran 90/95/2003/2008 compiler;
- Disadvantages: Case insensitive; different tricks still possible; not very strict, ...
- Enforce declarations with the implicit none statement; this help avoid a large fraction of all programming errors.

Some reasons for using C++:

- C++ is now one of the dominating language in Unix and Windows environments.
- It is widely available and is the language of choice for system programmers.
- C++ is very widespread for developments of non-numerical software; the C++ syntax has inspired lots of popular languages, such as Perl, Python, Java and Julia.
- Complex variables, one of Fortran's strongholds, can now also be defined in the new ANSI C++ standard.
- C++ is an object-oriented language, in contrast to C and Fortran, i.e. it supports three fundamental ideas: namely objects, class hierarchies and polymorphism.

Julia – A fresh approach to technical computing:

- Faster than other scripting languages ... as fast as C/Fortran.
- Supports rapid code development like with Python/MATLAB/R.

- Just-In-Time (JIT) compilation.
- Built-in documentation; ? gets you to the documentation for a type, function, etc.
- Julia stands for the combination of productivity and performance through a careful language design and carefully chosen technologies.
- Multiple dispatch: refers to the dynamically selected implementation and to the concept of running the right code at the right time.
- Julia's type system: ... supports an agressive code specializiation against run-time types.

1.3.b. Good coding practices

- Keep the code simple ... and always well readable.
- Use a proper set of name conventions ... and maintain them uniformly throughout.
- Provide a brief description of what a variable is for and what a block of code is doing; don't be extensive and don't comment obvious issues.
- Correct errors as they occur.
- Portability.
- The size of a program has a very significant effect on error rates, programmer productivity, and the amount of management needed.
- Physical models: In general, better physics is more important than better computer science.
- Visualization: Visualization of large data sets is essential for debugging, problem generation and analysis of results.
- Quality tests: If a code is not verified and validated by proper examples, the users will not believe and see its connection to reality.

- McConnell's advice: "Every programming language has strengths and weaknesses. Be aware of the specific strengths and weaknesses of the language you're using."

A personal view [cf. Hoare (2002)]:

- Readability of the code; save your (and other people's) time with regard to mis-assignments and tricks.
- Simplicity of use.
- Keep programs modular.
- Ruggedness (difficult to misuse, kind to errors); stop when certain errors are not 'treated' internally.
- Clear, accurate, and precise user documentation.
- Reliability – efficiency – portability – parallelism.

1.4. Computer-algebra systems (CAS)

Symbolic computations:

- Computer Algebra studies the algorithms for Symbolic Computations in which one computes with symbols, rather than with numbers.
- In physics, we are mainly concerned with the practical aspects of how to use Symbolic Computations in order to solve practical mathematical problems (from QM).
- In CAS, the numbers are not limited to the hardware integers or floating-point numbers but can be made up of symbols, such as π, $\sqrt{2}$ or contineous fractions.
- CAS are essentially equation crunchers (in analogy with the number crunching algorithms of numerical analysis).
- Integration is one of the highlights of general-purpose CAS.

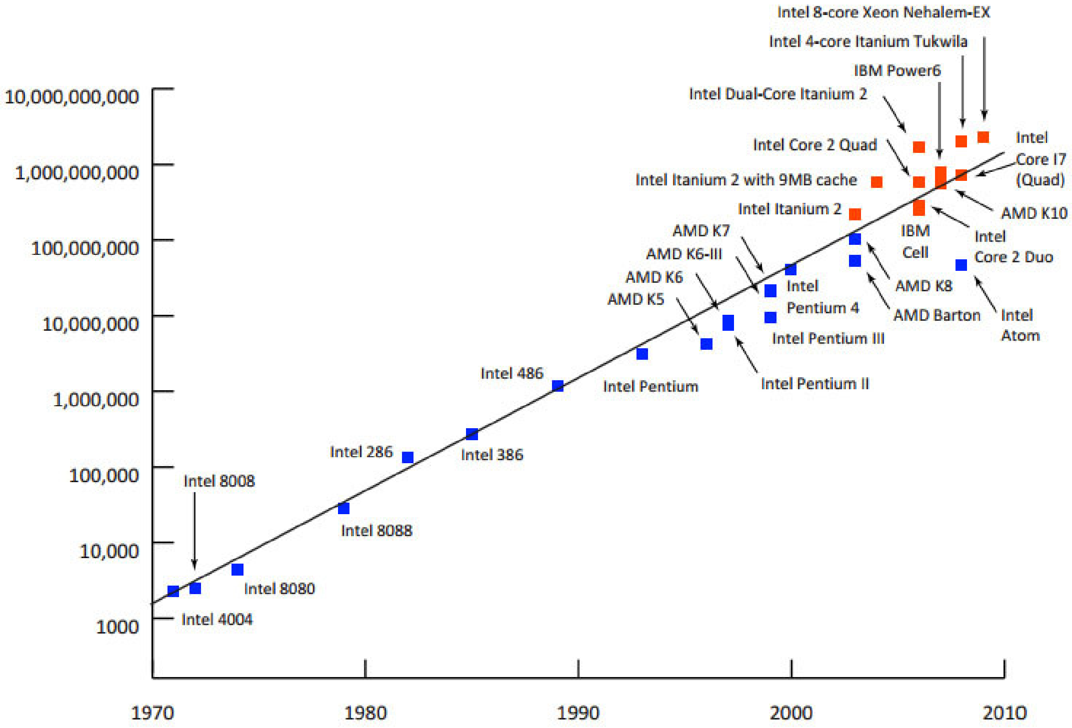


Figure 1.2.: Moore's law in term of transitors as realized on individual processor ships (from wrapidconsultingusa.com/wp-content/).

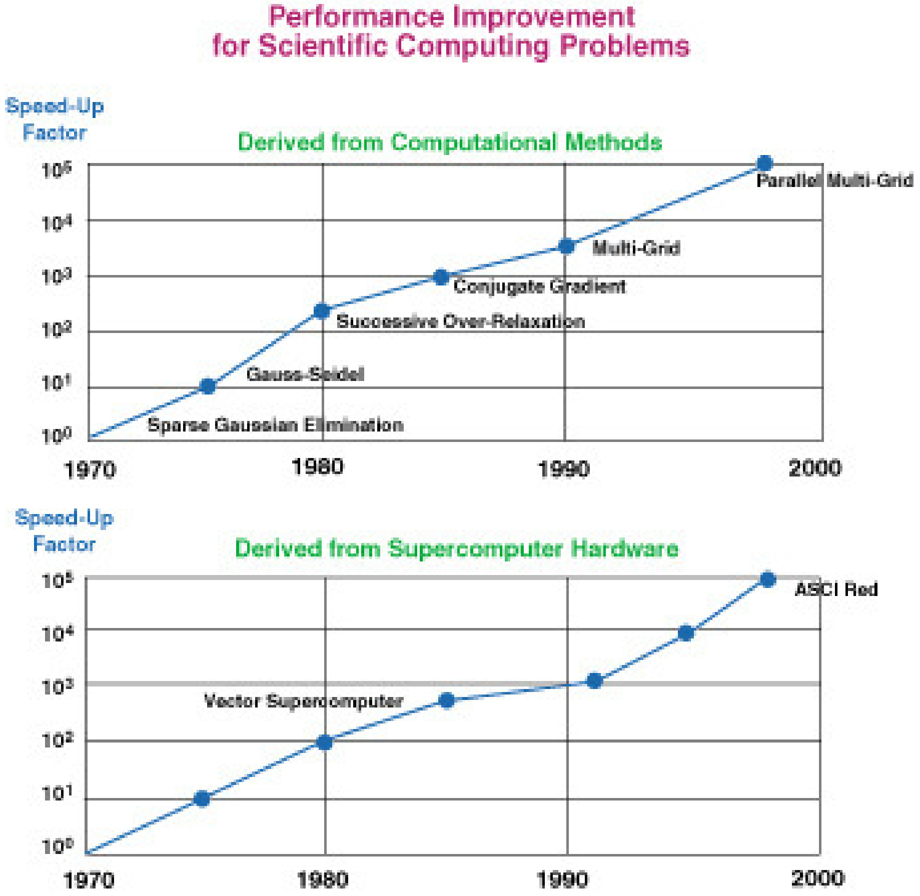


Figure 1.3.: Moore's law in term of the speed-up factor as derived from the computational methods (top panel) and the hardware of supercomputers (lower panel).

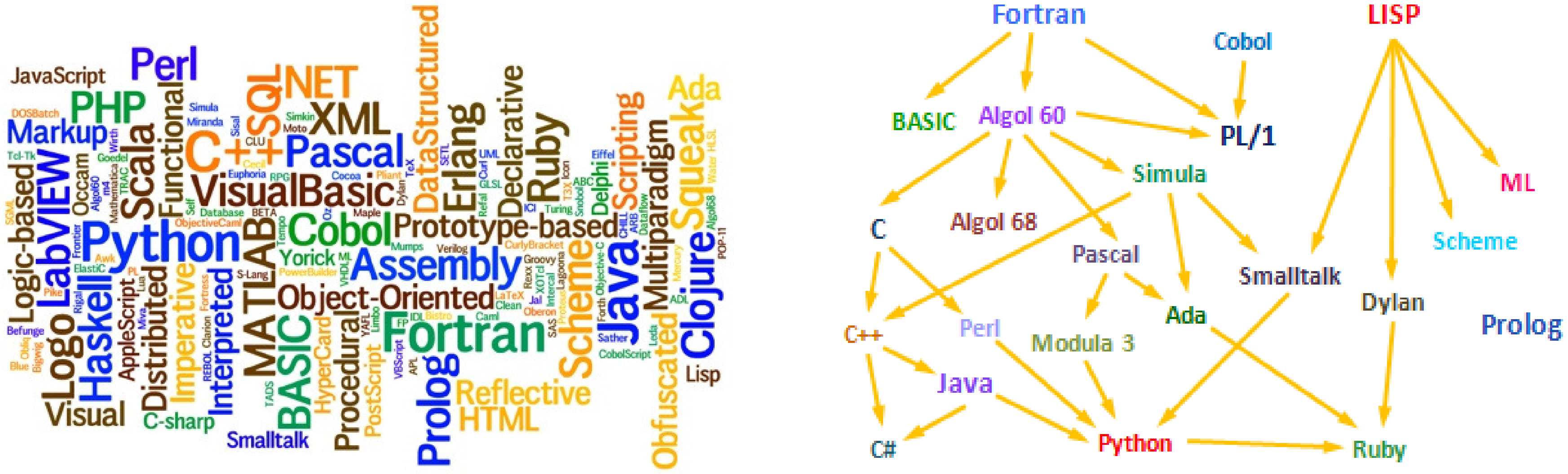


Figure 1.4.: Left: Collection of different languages, indicating the popularity (taken from blog.startapp.com/wp-content/). Right: Historical dependence of some languages (from xrds.acm.org/images)

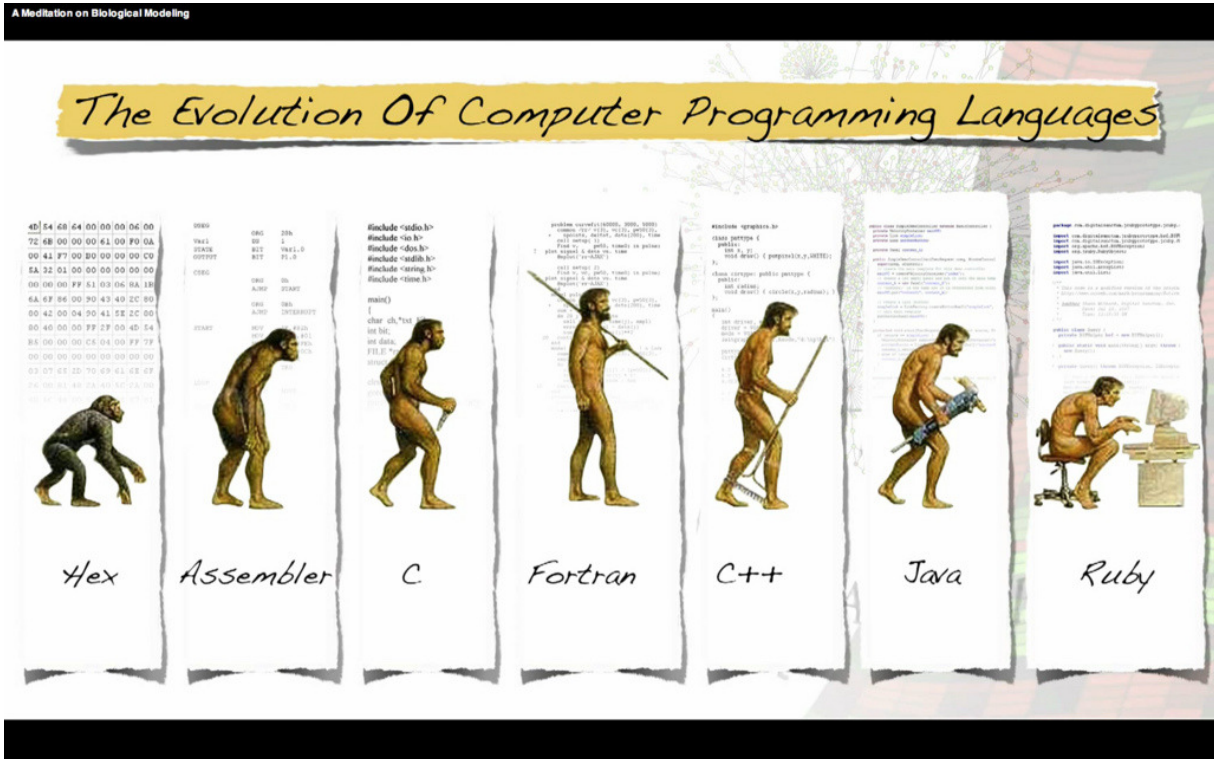


Figure 1.5.: The Evolution of Computer Programming Languages (from: ganeshkamath89.blogspot.com).

2. Julia & Maple: Some first tutorials

2.1. What is Julia standing for ??

- Julia stands for the combination of productivity and performance through a careful language design and carefully chosen technologies; it never forces the user to resort to C or Fortran for fast computations.
- Julia's design allows for gradual learning of modern concepts in scientific computing; from a manner familiar to many users and towards well-structured and high-performance code.
- High-level languages: Most traditional high-level languages are hampered by the overhead from the interpretor and which typically results into more run-time processing that are strictly necessary. One of these hindrances is (missing) type information, and which then results in the request for supporting vectorization.
- Julia is a 'verb'-based language in contrast to most object-oriented 'noun'-based language, in which the generic functions play a more important role than the datatypes.
- Code selection: Julia name space allows the use of the same vocabulary in different circumstances, and which makes programs easier to read.
- Multiple dispatch: refers to the dynamically selected implementation and to the concept of running the right code at the right time. This is achieved by overloading by multiple-argument function, a very powerful abstraction. Multiple dispatch makes it easier to structure the programs close to the underlying science.

- Instead of encapsulating methods inside classes, Julia's multiple dispatch is a paradigm in wich methods are defined on combinations of data types (classes). Julia shows that this is remarkably well-suited for numerical computing.
- Code re-use: In good language design, on should be able to write a general implementation and, as long as the necessary operations are available, the code should just work.
- Julia's type system: Julia's expressive type system that allows optional type annotations; this type system supports an agressive code specializiation against run-time types. Over a large extent, however, Julia code can be used without any mentioning of types (in contrast to C and Fortran); this is achieved by data-flow interference.
- Parallelization: One of the central motivation to built Julia was the design of a parallel computing language.
- Performance: There are helpful macros, such as @timing function_call(parameters) or @benchmark function_call(parameters) to analyze the performance of the program and to find (and resolve) bottlenecks.
- LAPACK: All of LAPACK is available in Julia, not just the most common functions. LAPACK wrappers are fully implemented by 'ccall' and can be called directly from the Julia prompt.
- Macros: A macro is a function that runs at parse time. It takes symbolic expressions in and returns transformed expressions out, which are inserted into the code for later compilation. The output of macros is often 'inlined' into the code.

2.2. What is Maple standing for ?

Maple's internal set-up and organization:

- Maple consists of four parts: kernel, interface, library, and share library.
- While, for efficiency reasons, most kernel routines are written in C, the procedures in the library are written in the language of Maple and can be viewed: `interface(verboseproc=3);` and, for example, `print(factor);`

- A strong features of Maple is their worksheet: This can be seen a regular text document that is enhanced with computational features like a spreadsheet, or with layers and links like hypertext.
- A worksheet can be organized in sections and subsections as we would structure a technical report (see insert menu).
- An execution group in Maple is a sequence of instructions to be executed as one (similar like a paragraph).
- After loading, the worksheet is considered as plain text. We must execute the instructions (via Execute from the edit menu) to give values to the variables; the execution of an entire worksheet is analogue to running a program.
- Maple has many composite data types and a seemingly huge number of commands; each command can be considered also as part of the language that enables one to built up commands at higher complexity.
- Maple is organized in packages; instead of loading an entire package, one can always use the long form, e.g., `plots[display](...)` when only the display command from the plots package is needed.
- The internal work and memory management of Maple can be affected by `interface()`.
- There is a large library of user contributions, available online at the Maple Application Center http://www.mapleapps.com.

2.2.a. Getting started

Web link (Some useful Maple tutorials:):

- A first Maple tutorial from the University of New South Wales (Australia): www.maths.unsw.edu.au/sites/default/files/maplenotes.pdf
- Basic worksheets can be find at: www.peterstone.name/Maplepgs/intro.html
- Maple's Applications Center: www.maplesoft.com/applications/index.aspx/

2.2.b. Packages for Maple

Libraries & toolboxes

- There are about 120 packages and toolboxes that belong to Maple's standard distribution; among them you can find:
- ArrayTools – tools used for low level manipulation of Matrices, Vectors, and Arrays.
- CodeGeneration – tools for translating Maple code to other languages.
- CurveFitting – commands that support curve-fitting.
- eBookTools – tools to convert Maple worksheets into a book using DocBook.
- GraphTheory – routines for creating, drawing, manipulating, and testing graphs.
- Maplets – tools to create graphical user interfaces for Maple.
- Matlab – commands to facilitate a Matlab Link.
- PDEtools – tools for solving partial differential equations.
- Physics – a package implementing the standard mathematical physics computational objects and their operations.
- plots – commands for displaying graphical representations.
- ScientificConstants – access to physical const. and Periodic Table Element properties.
- Student – collection of packages covering undergraduate mathematics courses.
- Units – commands for converting values between units, and environments for performing calculations with units.
- VectorCalculus – commands for performing multivariate and vector calculus operations.

2.3. Tasks

See tutorials.

2.4. Atomic theory and computations in a nut-shell

2.4.a. 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 basically the same phase, frequency, polarization, and direction of propagation as the incident photons.
- Photoionization: ... release of free electrons.
- Rayleigh and Compton scattering: ... Elastic and inelastic scattering of X-rays and gamma rays by atoms and molecules.
- Thomson scattering: ... elastic scattering of electromagnetic radiation by a free charged particle (electrons, muons, ions); low-energy limit of Compton scattering.
- Multi-photon excitation, ionization and decay: ... non-linear electron-photon interaction.
- Autoionization: ... nonradiative electron emission from (inner-shell) excited atoms.
- Electron-impact excitation & ionization: ... excited and ionized atoms; occurs frequently in astro-physical and laboratory plasmas.
- Elastic & inelastic electron scattering: ... reveals electronic structure of atoms and ions; important for plasma physics.
- Pair production: ... creation of particles and antiparticles from the internal of light with matter (electron-positron pairs).

- Delbrück scattering: ... deflection of high-energy photons in the Coulomb field of atomic nuclei; a consequence of vacuum polarization.
- ...
- In practice, the distinction and discussion of different atomic and electron-photon interaction processes also depends on the particular community/spectroscopy.

2.4.b. Atomic theory

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

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

Atomic theory is a great playground, indeed.

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

Theoretical models:

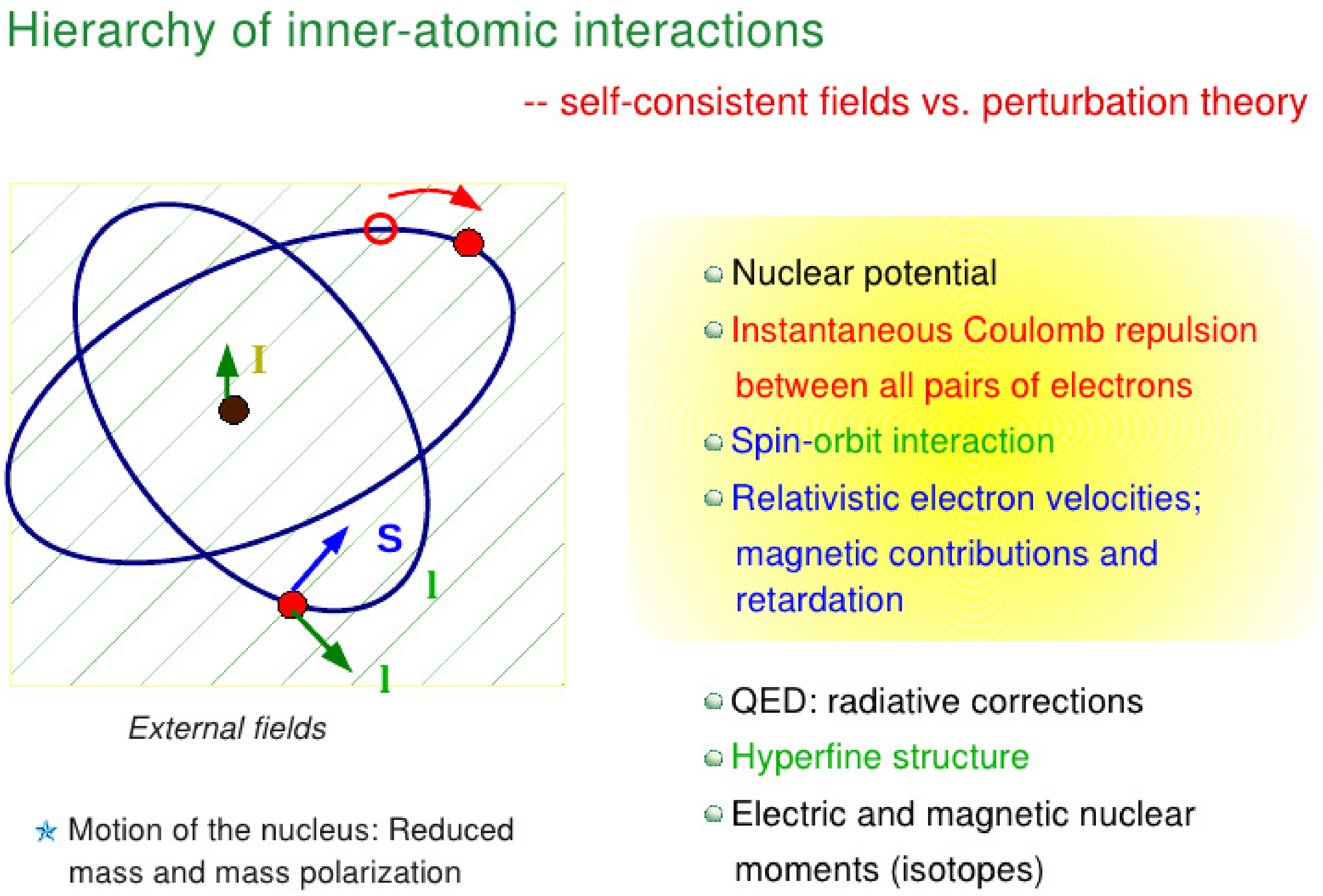
- ➢ Electronic structure of atoms and ions: is described quantum mechanically in terms of wave functions, energy levels, ground-state densities, etc., and is usually based on some atomic (many-electron) Hamiltonian.
- ➢ Interaction of atoms with the radiation field: While the matter is treated quantum-mechanically, the radiation is — more often than not (> 99 % of all case studies) — described as a classical field.
- ➢ This semi-classical treatment is suitable for a very large class of problems, sometimes by incorporating 'ad-hoc' quantum effects of the em field (for instance, spontaneous emission).
- ➢ Full quantum treatment: of the radiation field is very rare in atomic and plasma physics and requires to use quantum-field theoretical techniques; for example, atomic quantum electrodynamics (QED).

Combination of different (theoretical) techniques:

- ➢ Special functions from mathematical physics (spherical harmonics, Gaussian, Legendre- and Laguerre polynomials, Whittacker 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.

2.5. Need of (accurate) atomic theory and data

- Astro physics: Analysis and interpretation of optical and x-ray spectra.
- Plasma physics: Diagnostics and dynamics of plasma; astro-physical, fusion or laboratory plasma.
- EUV lithography: Development of UV/EUV light sources and lithograhpic techniques (13.5 nm).
- Atomic clocks: Design of new frequency standards; requires accurate data on hyperfine structures, atomic polarizibilities, light shift, blackbody radiation, etc.
- Search for super-heavy elements: beyond fermium ($Z = 104$); ‘island of stability’; better understanding of nuclear structures and stabilities.
- Nuclear physics: Accurate hyperfine structures and isotope shifts to determine nuclear parameters; formation of the medium and heavy elements.
- Surface & environmental physics: Attenuation, autoionization and light scattering.
- X-ray science: Ion recombination and photon emission; multi-photon processes; development of x-ray lasers; high-harmonic generation (HHG).
- Fundamental physics: Study of parity-nonconserving interactions; electric-dipole moments of neutrons, electrons and atoms; ‘new physics’ that goes beyond the standard model.
- Quantum theory: ‘complete’ experiments; understanding the frame and boundaries of quantum mechanics ?
- ...



Hierarchy of inner-atomic interactions

-- self-consistent fields vs. perturbation theory

- 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)

External fields

☆ Motion of the nucleus: Reduced mass and mass polarization

Figure 2.1.: Atomic interactions that need to be considered for a quantitative description/prediction of atoms.

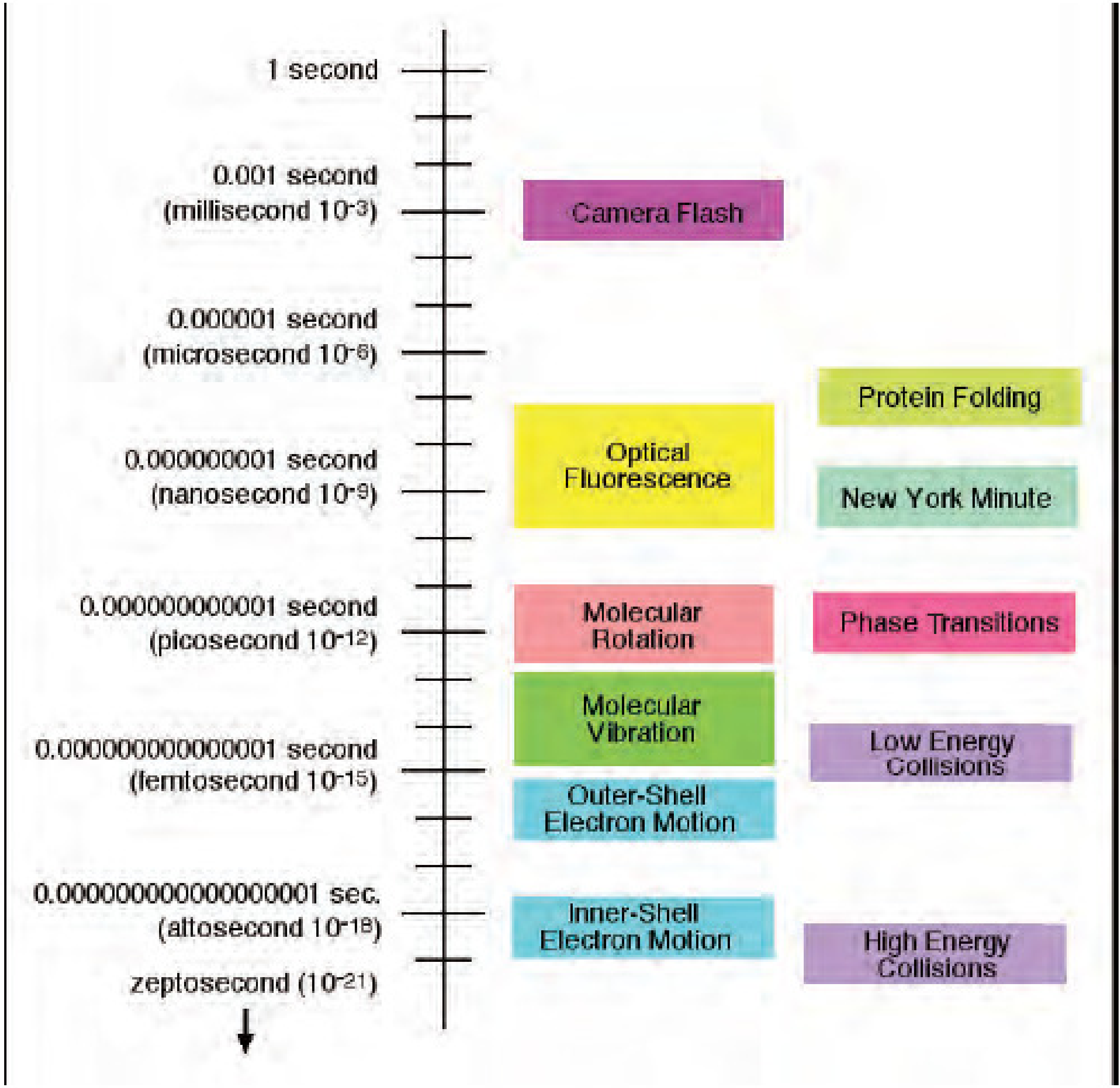


Figure 2.2.: Characteristic time scales of atomic and molecular otions; taken from: *Controlling the Quantum World*, page 99.

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

3.1. 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 $10^{-11}...10^{-13}$.

3.1.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.

- 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':

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

- Final form makes use of relative coordinates:

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

- 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: $V \;=\; V(r) \;=\; -\frac{Ze^2}{4\pi\epsilon_0 r} \;=\; -\frac{\alpha\hbar c Z}{r}$

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

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

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

- 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 $\psi = \psi(\mathbf{r})$.

3.1.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: $1\ \mathrm{a}_0 = 0.5291 \cdot 10^{-10}$ m
- ➢ Energies in Hartree units: 1 Hartree $= 27.211$ eV $= 4.359 \cdot 10^{-18}$ J
- ➢ Time: 1 a.u. $= 2.418 \cdot 10^{-17}$ s
- ➢ Velocity: 1 a.u. $= 2.187 \cdot 10^{6}$ m/s

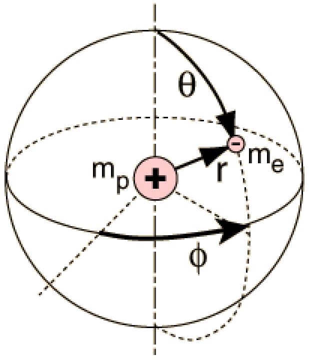
3.2. Nonrelativistic theory: A short reminder

3.2.a. Schrödinger equation for hydrogenic atoms

Solving the SE in a nutshell:

- ➢ Correspondence principle:

$$\text{classical mechanics} \quad \Longrightarrow \quad \begin{array}{c} \mathbf{r} \longrightarrow \hat{\mathbf{r}} \\[1em] \mathbf{p}_r \longrightarrow -i\hbar\,\frac{\partial}{\partial\,\mathbf{r}} \\[1em] E \longrightarrow i\hbar\,\frac{\partial}{\partial\,t} \end{array} \quad \Longrightarrow \quad \text{quantum mechanics}$$



hyperphysics.phy-astr.gsu.edu

- 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 $\lambda,\ \beta^2$

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

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

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

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

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

- 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:

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

- 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.

3.2.b. Spherical harmonics

Building blocks of atomic physics:

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

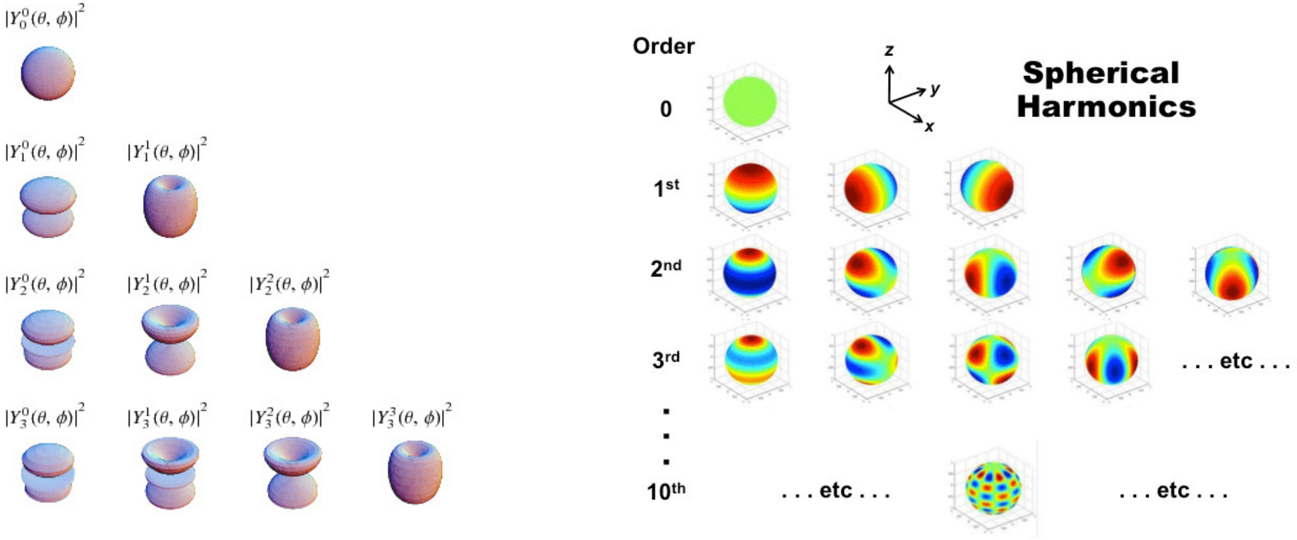


Figure 3.1.: Left: There are many different representations of the spherical harmonics, in which one displays the modulus, real or imaginary parts of these functions, or changes in the (complex) phase; from: mathworld.wolfram.com. Right: from http://mri-q.com/uploads.

- Explicit representation in coordinate space:

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

$$Y_{10}(\vartheta,\varphi) \;=\; \sqrt{\frac{3}{4\pi}}\,\cos\vartheta, \qquad Y_{1,\pm1}(\vartheta,\varphi) \;=\; \mp\sqrt{\frac{3}{8\pi}}\,\sin\vartheta\, e^{\pm i\varphi}$$

$$Y_{20}(\vartheta,\varphi) \;=\; \frac{1}{4}\sqrt{\frac{5}{\pi}}\,\left(3\cos^2\vartheta \;-\; 1\right), \qquad Y_{2,\pm1}(\vartheta,\varphi) \;=\; \mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\,\sin\vartheta\cos\vartheta\, e^{\pm i\varphi}, \qquad Y_{2,\pm2}(\vartheta,\varphi) \;=\; \frac{1}{2}\sqrt{\frac{15}{2\pi}}\,\sin^2\vartheta\, e^{\pm 2i\varphi}$$

- Make use of properties, whenever possible:

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

- Wigner 3-j symbols:

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

$$\langle Y_{l_1m_1}\,|Y_{l_2m_2}|\,Y_{l_3m_3}\rangle \;=\; \sqrt{\frac{(2l_1+1)\,(2l_2+1)\,(2l_3+1)}{4\pi}}\,\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}\,\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

- 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

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

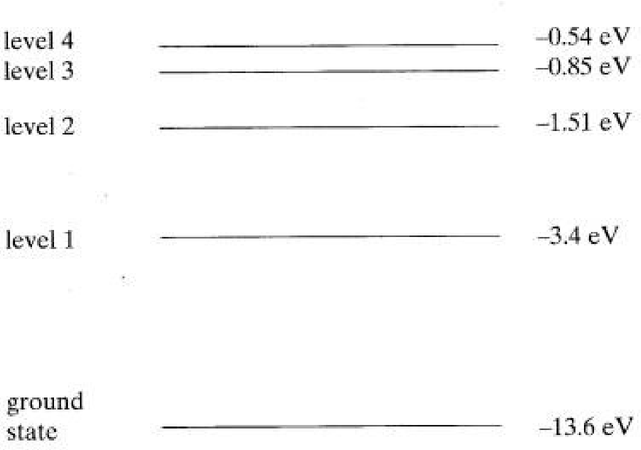
- Unsöld's theorem: ... for $\mathbf{x} \;=\; \mathbf{y}$ (see below).

3.2.c. Complete set of commutable operators

Reminder:

- ➢ A set of operators A_i $(i = 1, ..., n)$ 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: $[H, \mathbf{l}^2] = [H, l_z] = [\mathbf{l}^2, l_z] = 0$.

3.2.d. Energies and quantum numbers



From: sciwebhop.net

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

- ➢ Are classified by three quantum numbers
  - principal quantum number: $n = 1, 2, 3, ...$
  - orbital angular momentum quantum number: $l = 0, 1, 2, ...$
  - magnetic quantum number: $m = -l, -l+1, ..., l$
- ➢ Eigen energies: ... degenerate in l and m

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

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

3.2.e. Radial equation

Radial orbitals:

- ➢ Radial equation:

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

- ➢ 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.

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

- ➢ The functions $L^p_q(x)$ 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: $P(r \to 0) = A\,r^{l+1}; \quad P(r \to \infty) = B\,e^{-\alpha r}$
  - Choose a proper (numerical) grid: $\{r_1,\,r_2,\,...,\,r_N;\;\; r_i \le r_{i+1}\}$.
  - Take initial values $P(r_1)$, $P(r_2)$ due to the near-zero behavior $P(r \to 0) \sim r^{l+1}$.

- 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

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

- Frequently utilized atomic basis sets: (tempered functions)
  - i) Slater functions (STO): $g_i(r) \;=\; A_i \, r^{l+1} \, e^{-\alpha_i \, r}, \quad i \;=\; 1, ..., N$
  - ii) Gaussian functions (GTO): $g_i(r) \;=\; B_i \, r^{l+1} \, e^{-\alpha_i \, r^2}, \quad i \;=\; 1, ..., N$

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

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

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

$$\langle \psi_{n\ell m} \,|\, \psi_{n'\ell'm'} \rangle \;\equiv\; \langle n\ell m \,|\, n'\ell'm' \rangle \;=\; \int d^3r \;\; \psi^*_{n\ell m} \;\; \psi_{n'\ell'm'} \;=\; \delta_{nn'} \, \delta_{\ell\ell'} \, \delta_{mm'}$$

$$= \int_0^\infty dr \; r^2 \, R^*_{nl}(r) \, R_{n'l'}(r) \int_0^\pi d\vartheta \; \sin\vartheta \; \Theta^*_{lm} \, \Theta_{l'm'} \int_0^{2\pi} d\varphi \; \Phi^*_m \, \Phi_{m'}$$

$$\langle r^k \rangle \;=\; \int_0^\infty dr \, r^2 \, R^*_{nl}(r) \, r^k \, R_{n'l'}(r); \qquad \langle r \rangle_{l=n-1} \;=\; n^2 \left(1 \;+\; \frac{1}{2n} \right) \frac{a_0}{Z}; \qquad \langle r^{-1} \rangle \;=\; \frac{1}{n^2} \left(\frac{Z}{a_0} \right); \quad \ldots$$

3.2.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; $\boldsymbol{\mu} \sim \mathbf{l}, \mathbf{s}$.

  Inhomogenoues field (and magnetic moment μ_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 cm^{-1}.

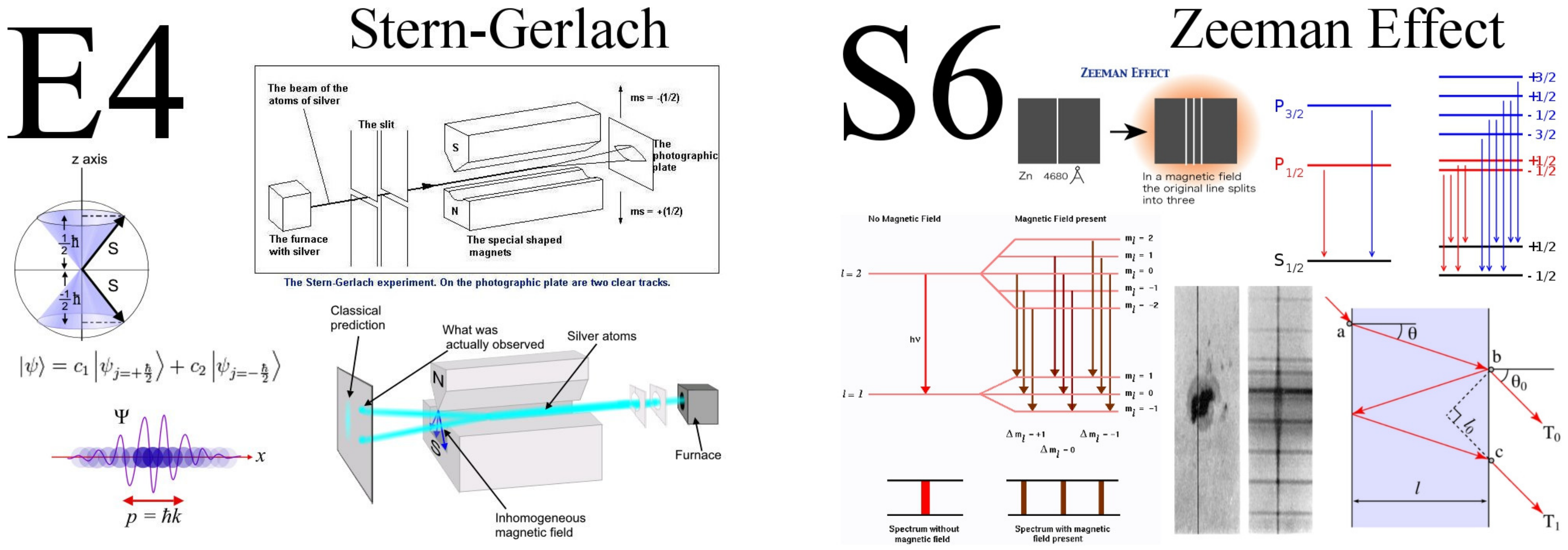


Figure 3.2.: Left: From: http://pages.physics.cornell.edu/ Right: Normal Zeeman effect: splitting of a spectral line into several components in the presence of a static magnetic field. Anamalous Zeeman effect: There are a lot of observations that cannot be explained alone in terms of the magnetic and 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 $m_s = \pm 1/2$:

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

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

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

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

- Pauli matrices: Spin operator can be written as

$$\mathbf{s} \;=\; \frac{\hbar}{2}\boldsymbol{\sigma} \;=\; \frac{\hbar}{2}\left(\sigma_x\,\mathbf{e}_x + \sigma_y\,\mathbf{e}_y + \sigma_z\,\mathbf{e}_z\right)$$

$$\sigma_x \;=\; \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \qquad \sigma_y \;=\; \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \qquad \sigma_z \;=\; \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$[\sigma_i, \sigma_k] \;=\; 2i\,\epsilon_{ikm}\,\sigma_m; \qquad \{\sigma_i, \sigma_k\} \;=\; 0.$$

- Schrödinger operators: are diagonal in this representation; within Pauli's wave mechanics, all operators are 2 × 2 matrices.

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

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

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

➢ In Pauli representation, we have

$$(j_z)_{\,\mathrm{Pauli}} \;=\; (l_z)_{\,\mathrm{Pauli}} + \frac{\hbar}{2}\,\sigma_z \;=\; \begin{pmatrix} l_z + \frac{\hbar}{2} & 0 \\ 0 & l_z - \frac{\hbar}{2} \end{pmatrix} \qquad \left(\mathbf{j}^2\right)_{\,\mathrm{Pauli}} \;=\; \begin{pmatrix} \mathbf{l}^2 + \hbar\, l_z + \frac{3}{4}\,\hbar^2 & \hbar\,(l_x - i l_y) \\ \hbar\,(l_x + i l_y) & \mathbf{l}^2 - \hbar\, l_z + \frac{3}{4}\,\hbar^2 \end{pmatrix}.$$

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

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

3.2.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 ℓ

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

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

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

$$\Delta E''_n = -\frac{\alpha^2\, Z^2}{n^2}\, E_n\, \frac{n}{\ell(\ell + 1/2)(\ell + 1)}\, < \mathbf{l} \cdot \mathbf{s} > \qquad \ell \neq 0$$

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

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

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

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

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

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

3.3. Relativistic theory: Dirac's equation

3.3.a. Relativistic Hamiltonians and wave equations

Different Hamiltonian operators:

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

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

- Question: How to transform this expression with $\mathbf{p} \rightarrow -i\hbar\,\frac{\partial}{\partial\mathbf{r}}$ into a useful Hamiltonian ?
- Expansions in powers $1/m^2c^2$: ... 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 $\mathbf{p} \;=\; -i\hbar\,\frac{\partial}{\partial\mathbf{r}}, \quad e\phi \;=\; V \;\neq\; V(t)$

$$(\mathbf{p}+e\mathbf{A})\,(\mathbf{p}+e\mathbf{A}) \;=\; \mathbf{p}^2 \;+\; e\,(\mathbf{p}\cdot\mathbf{A} \;+\; \mathbf{A}\cdot\mathbf{p}) \;+\; e^2\mathbf{A}^2 \;=\; \left(\frac{E \;-\; e\phi}{c}\right)^2 \;-\; m^2c^2$$

$$\left[-\hbar^2\,\boldsymbol{\nabla}^2 \;-\; i\hbar e\,(\boldsymbol{\nabla}\cdot\mathbf{A} \;+\; \mathbf{A}\cdot\boldsymbol{\nabla}) \;+\; e^2\mathbf{A}^2\right]\,\psi \;=\; \left[\frac{(E \;-\; V)^2}{c^2} \;-\; m^2c^2\right]\,\psi$$

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

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

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

$$H = c\sqrt{m^2c^2 + (\mathbf{p} + e\mathbf{A})\,(\mathbf{p} + e\mathbf{A})} + V = c\sqrt{m^2c^2 + (p_x + eA_x)^2 + (p_y + eA_y)^2 + (p_z + eA_z)^2} + V$$

$$= c\sqrt{[\beta\, mc + \alpha \cdot (\mathbf{p} + e\mathbf{A})]^2} + V$$

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

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

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

- Dirac matrices and spinors:
  - $\alpha_m,\ \beta$ cannot be numbers nor 2×2 matrices;
  - simplest constants are 4×4 matrices;
  - most common represenation are called Dirac matrices (see below).
  - since H_{D} is a 4×4 matrix, the wave functions ψ (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

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

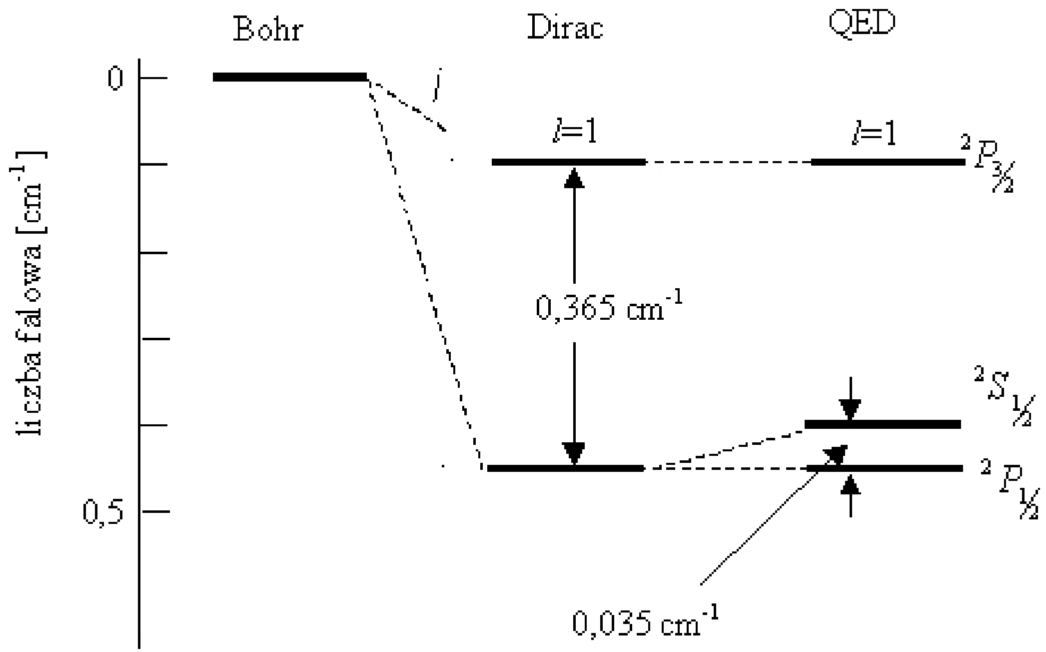


Figure 3.3.: The subtle Lamb shift of the $n = 2$ levels in hydrogen according to Bohr's and Dirac's theory and together with the QED predictions. In particular, the Lamb shift removes the degeneration due to quantum number j; from: Haken and Wolf, Atomic Physics (Springer, 1996).

3.3.b. Dirac's Hamiltonian

Properties of Dirac spinors and operators:

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

$$i\hbar \frac{\partial \psi(\mathbf{r},t)}{\partial t} = \left(\underbrace{-i\hbar c\, \boldsymbol{\alpha} \cdot \boldsymbol{\nabla}}_{\text{kinetic energy term } \mathbf{p} = -i\hbar \frac{\partial}{\partial \mathbf{r}}} + \underbrace{mc^2\, \alpha_0}_{\text{rest mass term}} \right) \psi(\mathbf{r},t)\,.$$

- Dirac matrices: ... $\boldsymbol{\alpha}$ and α_0 are 4×4 matrices ...

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

- Wave functions are 4-spinors:

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

- 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 4×4 matrices

$$(x)_{\,\mathrm{Dirac}} \;=\; \begin{pmatrix} x & 0 & 0 & 0 \\ 0 & x & 0 & 0 \\ 0 & 0 & x & 0 \\ 0 & 0 & 0 & x \end{pmatrix}, \qquad (l_z)_{\,\mathrm{Dirac}} \;=\; \begin{pmatrix} l_z & 0 & 0 & 0 \\ 0 & l_z & 0 & 0 \\ 0 & 0 & l_z & 0 \\ 0 & 0 & 0 & l_z \end{pmatrix}$$

- Alternative form of Dirac equation: ... because of $H_{\mathrm{D}} \, \psi \;=\; E \, \psi$ and $H_+ \psi \;=\; (-H_{\mathrm{D}} + 2V) \, \psi$, and with

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

$$\begin{aligned}
H_{+}\,H_{\mathrm{D}}\,\psi &= E\,(-E + 2V)\,\psi \\
\left[\boldsymbol{\alpha}\cdot(\mathbf{p} + e\mathbf{A})\,\boldsymbol{\alpha}\cdot(\mathbf{p} + e\mathbf{A}) - \frac{\boldsymbol{\alpha}}{c}\,(\mathbf{p}V - V\mathbf{p})\right]\psi &= \left[\left(\frac{E-V}{c}\right)^2 - m^2c^2\right]\psi \\
\boldsymbol{\alpha}\cdot(\mathbf{p} + e\mathbf{A})\,\boldsymbol{\alpha}\cdot(\mathbf{p} + e\mathbf{A}) &= \mathbf{p}^2 + e(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{P}) + e^2\,\mathbf{A}^2 + \hbar e\,\boldsymbol{\sigma}_D\cdot\mathbf{B} \\
-\frac{\boldsymbol{\alpha}}{c}\,(\mathbf{p}V - V\mathbf{p}) &= \frac{i\hbar e}{c}\,\boldsymbol{\alpha}\cdot\mathbf{E} \\
\boldsymbol{\sigma}_D &= \begin{pmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{pmatrix}\mathbf{e}_x + \begin{pmatrix} \sigma_y & 0 \\ 0 & \sigma_y \end{pmatrix}\mathbf{e}_y + \ldots
\end{aligned}$$

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

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

➢ Spin contributions to the Dirac equation:

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

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

Plane-wave solutions for free particles:

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

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

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

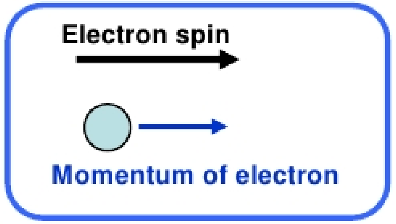
$$\begin{pmatrix} mc^2 & 0 & pc & 0 \\ 0 & mc^2 & 0 & -pc \\ pc & 0 & -mc^2 & 0 \\ 0 & -pc & 0 & -mc^2 \end{pmatrix} w(p) \;=\; E\, w(p) \;.$$

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

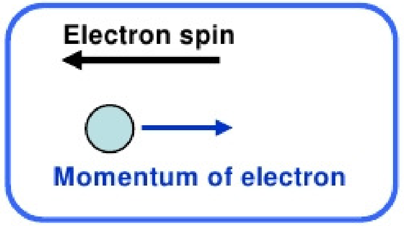
$$E_+(p) \;=\; \sqrt{(mc^2)^2 \,+\, (pc)^2}\;; \qquad\qquad E_-(p) \;=\; -\sqrt{(mc^2)^2 \,+\, (pc)^2}$$

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

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



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

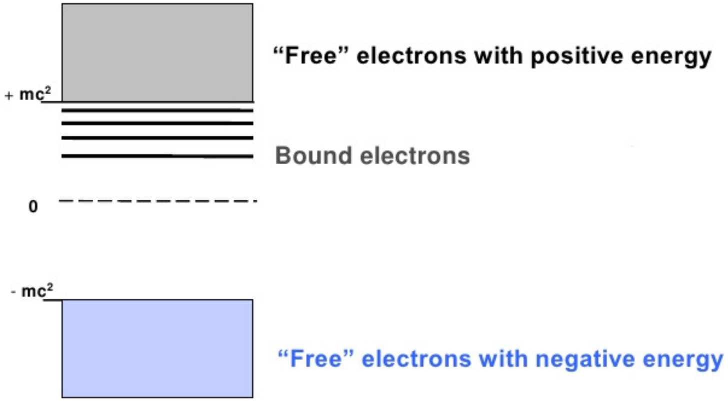


Helicity −1; $w_{-1/2}$.

3.3.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.



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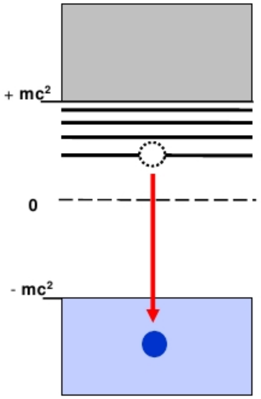

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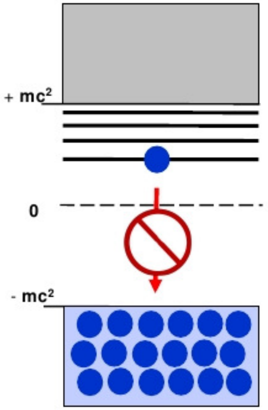

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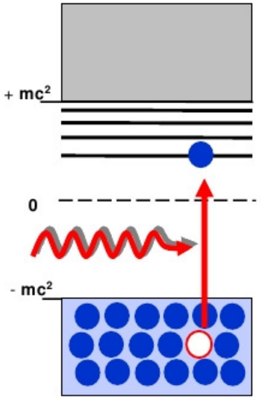

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Concept of “Dirac sea” (Dirac, 1930):

- 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

3.3.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:

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

- 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: $[H_\mathrm{D},\, \mathbf{j}^2] = [H_\mathrm{D},\, j_z] = [\mathbf{j}^2,\, j_z] = 0$, with

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

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

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

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

$$\begin{aligned} \mathbf{j}^2\, \psi(\mathbf{r}) &= \hbar^2\, j(j+1)\, \psi(\mathbf{r}) && \text{half integer} \\ j_z\, \psi(\mathbf{r}) &= \hbar\, m_j\, \psi(\mathbf{r}) \\ k\, \psi(\mathbf{r}) &= \hbar\, \kappa\, \psi(\mathbf{r}) \qquad \kappa = \pm\,(j+1/2) = \pm 1,\, \pm 2,\, \ldots && \text{integer} \end{aligned}$$

- Relativistic angular momentum quantum number κ: ... 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 $V(r)$.

3.3.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

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

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

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

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

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

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

- Bound solutions for $E < mc^2$: ... linear combinations of the confluent-hypergeometric function.
- Sommerfeld's fine-structure formula: ... eigenvalues of radial equations

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

3.3.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.

$$P_{n\kappa}(r) = N^L_{n\kappa}\, r\,(2qr)^{s-1}\, e^{-qr} \left[-n'\, F(-n'+1, 2s+1; 2qr) - \left(\kappa - \frac{\alpha Z}{q\lambda_c}\right) F(-n', 2s+1; 2qr) \right]$$

$$Q_{n\kappa}(r) = N^S_{n\kappa}\, r\,(2qr)^{s-1}\, e^{-qr} \left[n'\, F(-n'+1, 2s+1; 2qr) - \left(\kappa - \frac{\alpha Z}{q\lambda_c}\right) F(-n', 2s+1; 2qr) \right]$$

$$n' = n - |\kappa|, \qquad s = \sqrt{\kappa^2 - (\alpha Z)^2} \qquad q = \frac{\sqrt{1 - W^2_{n\kappa}}}{\lambda_c} = \frac{\alpha Z}{\lambda_c\, \left[(\alpha Z)^2 + (n'+s)^2\right]^{1/2}}$$

$$N^L_{n\kappa} = \frac{\sqrt{2} q^{5/2} \lambda_c}{\Gamma(2s+1)} \left[\frac{\Gamma(2s+n'+1)\,(1+W_{n\kappa})}{n'!\,(\alpha Z)\,(\alpha Z - \kappa q \lambda_c)} \right]^{1/2} \qquad N^S_{n\kappa} = -N^L_{n\kappa} \left(\frac{1 - W_{n\kappa}}{1 + W_{n\kappa}} \right)^{1/2}$$

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

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

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

3.4. Beyond Dirac's theory

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

3.4.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 energyotime 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.

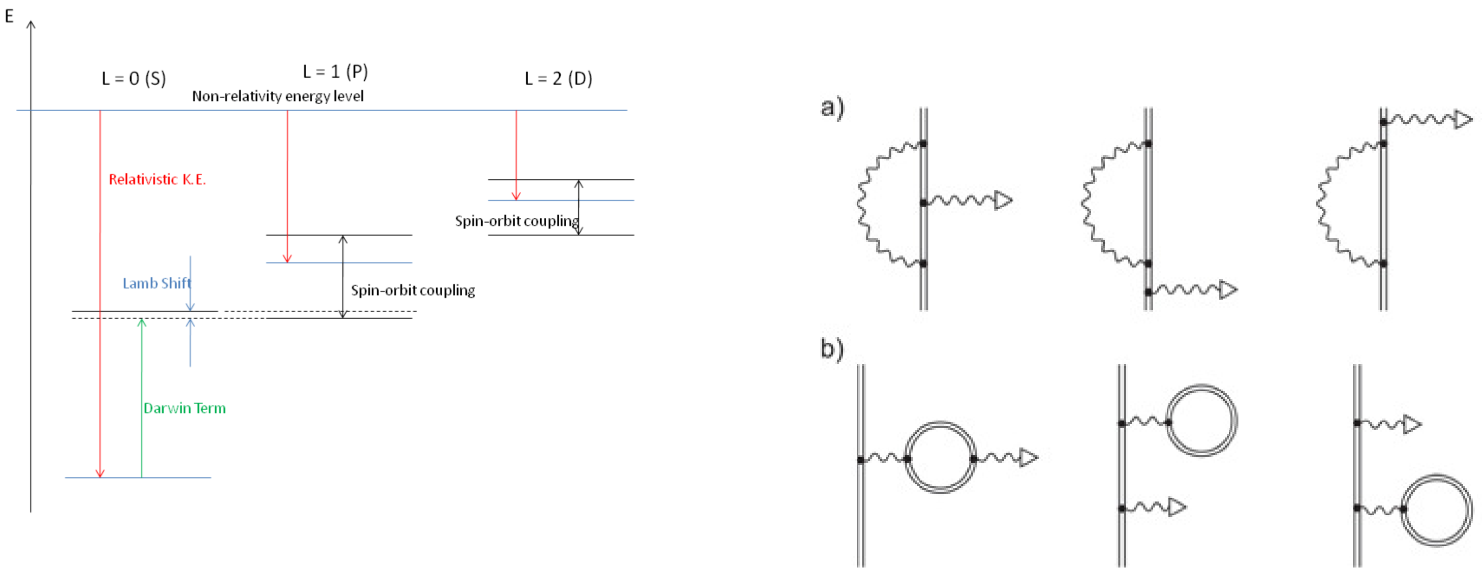


Figure 3.4.: Left: Relativistic level shifts for hydrogen-like ions; from: http://en.wikipedia.org/wiki/ Right: Feynman diagrams of the bound electron in first order of the fine structure constant α. (a) Self energy, (b) vacuum polarization. The double line represents the bound state electron propagator and contains the interaction between electron and the binding field to all orders of α; from http://iopscience.iop.org/1402-4896/89/9/098004.

3.5. Hydrogenic atoms in constant external fields

(Normal) Zeeman effect:

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

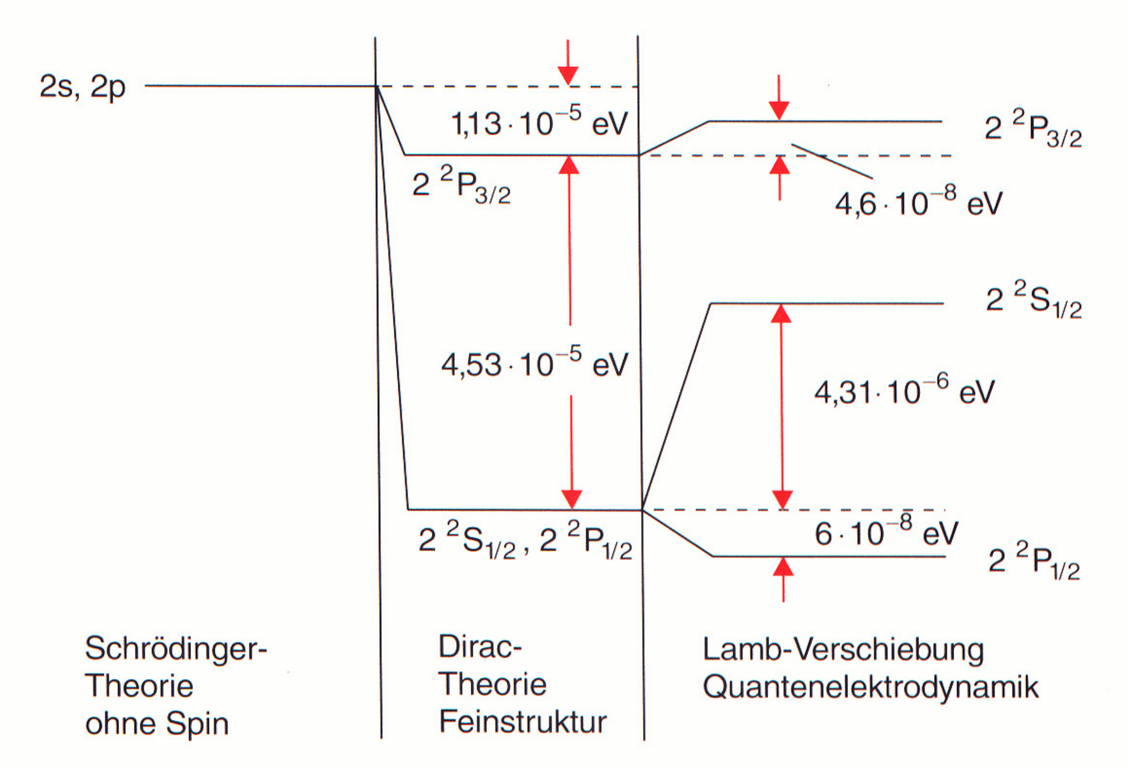


Figure 3.5.: Accurate Lamb-shift calculations for atomic hydrogen.

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

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

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

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

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

$$|H'_{ik} \; - \; \Delta E \, \delta_{ik}| \;=\; \left| \underbrace{\langle nl'm_l' \, | H' | \, nlm_l \rangle}_{\mu_B \, B \, m_\ell \, \delta_{ll'} \delta_{m_l m_l'}} - \Delta \, E \; \underbrace{\langle nl'm_l' \, | \, nlm_l \rangle}_{\delta_{ll'} \delta_{m_l m_l'}} \right| \;=\; 0$$

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

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

  $\hbar\omega_L \;=\; \mu_B \, B$ $\qquad$ ω_L ... 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: $\mathbf{E} \;=\; E \, \mathbf{e}_z \;=\; (0, 0, E) \;=\; -\mathrm{grad}\varphi$:

$$H' \;=\; -e \, E \, z \;=\; -e \, E \, r \; \cos \vartheta , \qquad\qquad | \, \langle n', l', m_l' \, | H' | \, n, l, m_l \rangle \; - \; \Delta E \, \delta_{ll'} \, \delta_{m_l m_l'} | \;=\; 0$$

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

$$= \; -eE \int_0^\infty dr \, r^3 \, R^*_{n\ell'} \, R_{n\ell} \int_0^\pi \int_0^{2\pi} d\varphi d\vartheta \sin \vartheta \; Y^*_{\ell' m_\ell'} \cos \vartheta Y_{\ell m_\ell}$$

$$= \; -eE \left[\sqrt{\frac{(\ell - m_\ell + 1)(\ell + m_\ell + 1)}{(2\ell + 1)(2\ell + 3)}} \int_0^\infty dr \, r^3 \, R^*_{n,\ell+1} R_{n\ell} \; + \; \sqrt{\frac{(\ell - m_\ell)(\ell + m_\ell)}{(2\ell - 1)(2\ell + 1)}} \int_0^\infty dr \, r^3 \, R^*_{n,\ell-1} R_{n\ell} \right] \; \delta_{m_\ell m_\ell'} .$$

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

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

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

- 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 $g(\text{electron}) = 2$

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

$$= \mu_B\,B\,\frac{j+1/2}{\ell+1/2}\,m_j \qquad j = \ell \pm 1/2$$

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

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

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

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

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

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

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

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

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

3.6. Exotic (hydrogenic) atoms

Pionic atoms:

- Pions (π^+, π^-): ... 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: $\pi^- + p \longrightarrow n$; $\pi^+ + n \longrightarrow p$. ... 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: $p + p \longrightarrow p + p + \pi^+ + \pi^-$ and $\pi^- \longrightarrow \mu^- + \nu_\mu$
- 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.

3.7. Tasks

See tutorials.

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 $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$

$$H\,\psi \;=\; (H_1 \,+\, H_2 \,+\, H')\,\psi \;=\; E\,\psi \;=\; \left(-\frac{\boldsymbol{\nabla}_1^2}{2} + V_{\rm nuc}(\mathbf{r}_1) - \frac{\boldsymbol{\nabla}_2^2}{2} + V_{\rm nuc}(\mathbf{r}_2) + \frac{1}{r_{12}} \right) \psi$$

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

- Suppose

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

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

$$\psi_o = c_1\, u_{ab} + c_2\, u_{ba} \qquad\qquad \psi_o^{'} = c_3\, u_{ab} + c_4\, u_{ba}$$

- Time-independent perturbation theory for H':

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

$$K = \int d\tau_1\, d\tau_2\, \frac{u_{ab}(1,2)\, u_{ba}(1,2)}{r_{12}} \qquad \text{exchange term}$$

- Which linear combinations $(c_1,\, ...,\, c_4)$ 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:

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

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

- Ground state $a = b = (n\ell\, m_\ell) = (1\, s\, 0)$:

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

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

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

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

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

- Excited states $a \neq b$

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

- Large n and ℓ: ... exchange integral K becomes negligible

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

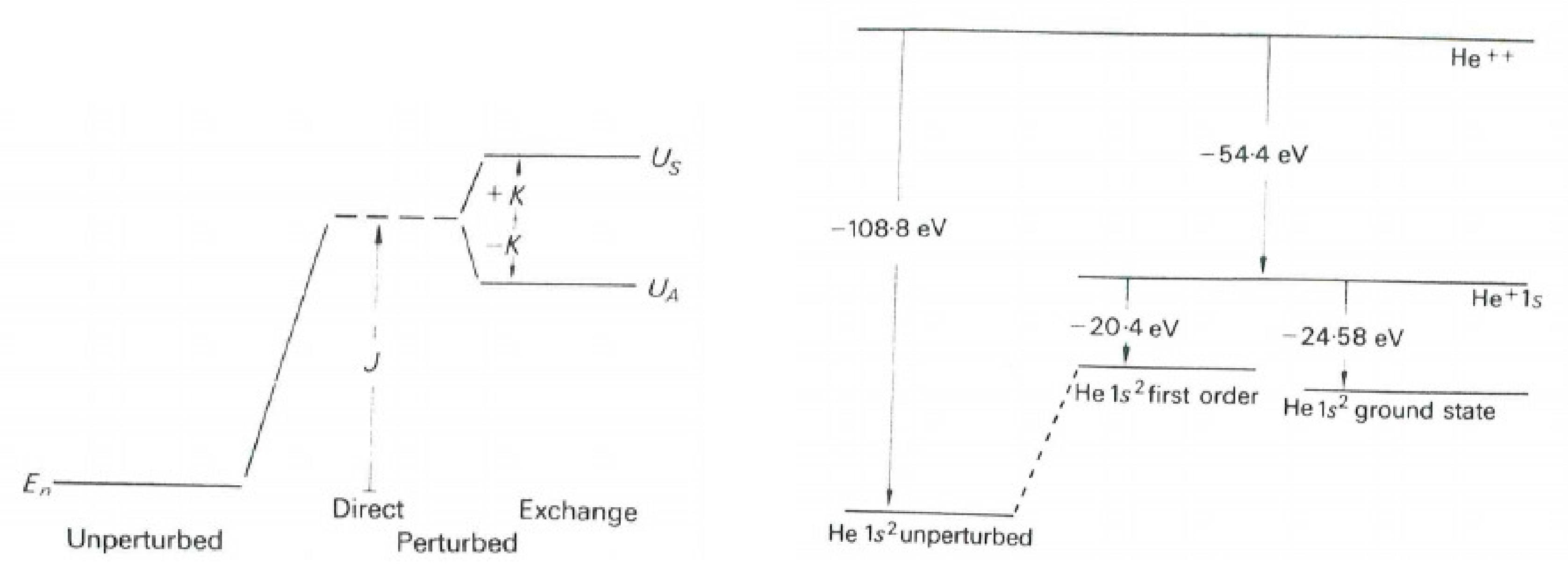


Figure 4.1.: Left: Schematic energy levels for the excited states of helium, showing the effect of the direct and exchange term. Right: Energy levels of helium relative to the singly and doubly-charged ion.

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

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

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

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	
χ_s:	$\chi_+(1)\,\chi_+(2)$	1	$+1$	symmetric
	$\frac{1}{\sqrt{2}}\,(\chi_+(1)\,\chi_-(2)\;+\;\chi_-(1)\,\chi_+(2))$		0	
	$\chi_-(1)\,\chi_-(2)$		$+1$	
χ_a:	$\frac{1}{\sqrt{2}}\,(\chi_+(1)\,\chi_-(2)\;-\;\chi_-(1)\,\chi_+(2))$	0	0	anti-symmetric

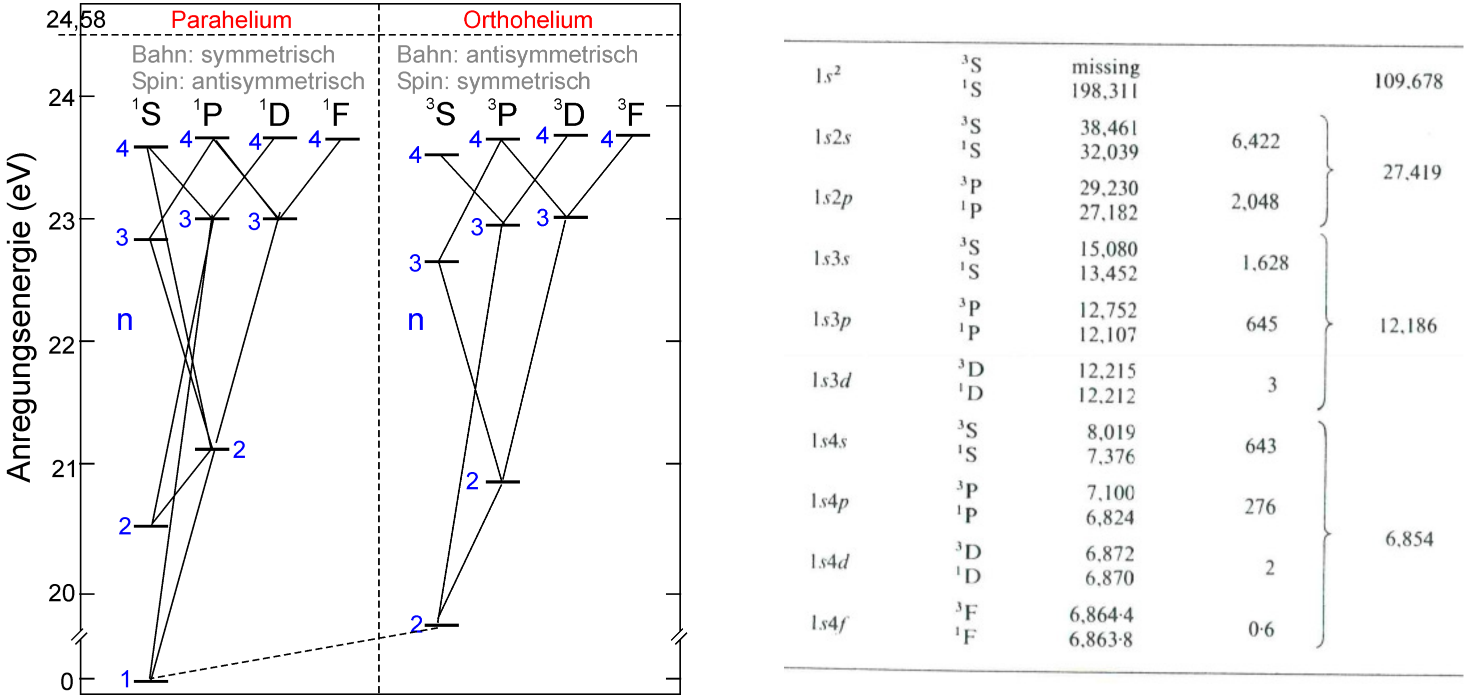
- Total wave functions:

$$\underbrace{\psi_s\,\chi_s,\ \ \psi_a\,\chi_a}_{\text{totally symmetric}} \quad \text{... not possible}\;, \qquad\qquad \underbrace{\psi_s\,\chi_a,\ \ \psi_a\,\chi_s}_{\text{totally antisymmetric}} \quad \text{... possible}$$

- 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).

➢ 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	27,419
$1s2p$	^3P ^1P	29,230 27,182	2,048	
$1s3s$	^3S ^1S	15,080 13,452	1,628	12,186
$1s3p$	^3P ^1P	12,752 12,107	645	
$1s3d$	^3D ^1D	12,215 12,212	3	
$1s4s$	^3S ^1S	8,019 7,376	643	6,854
$1s4p$	^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.

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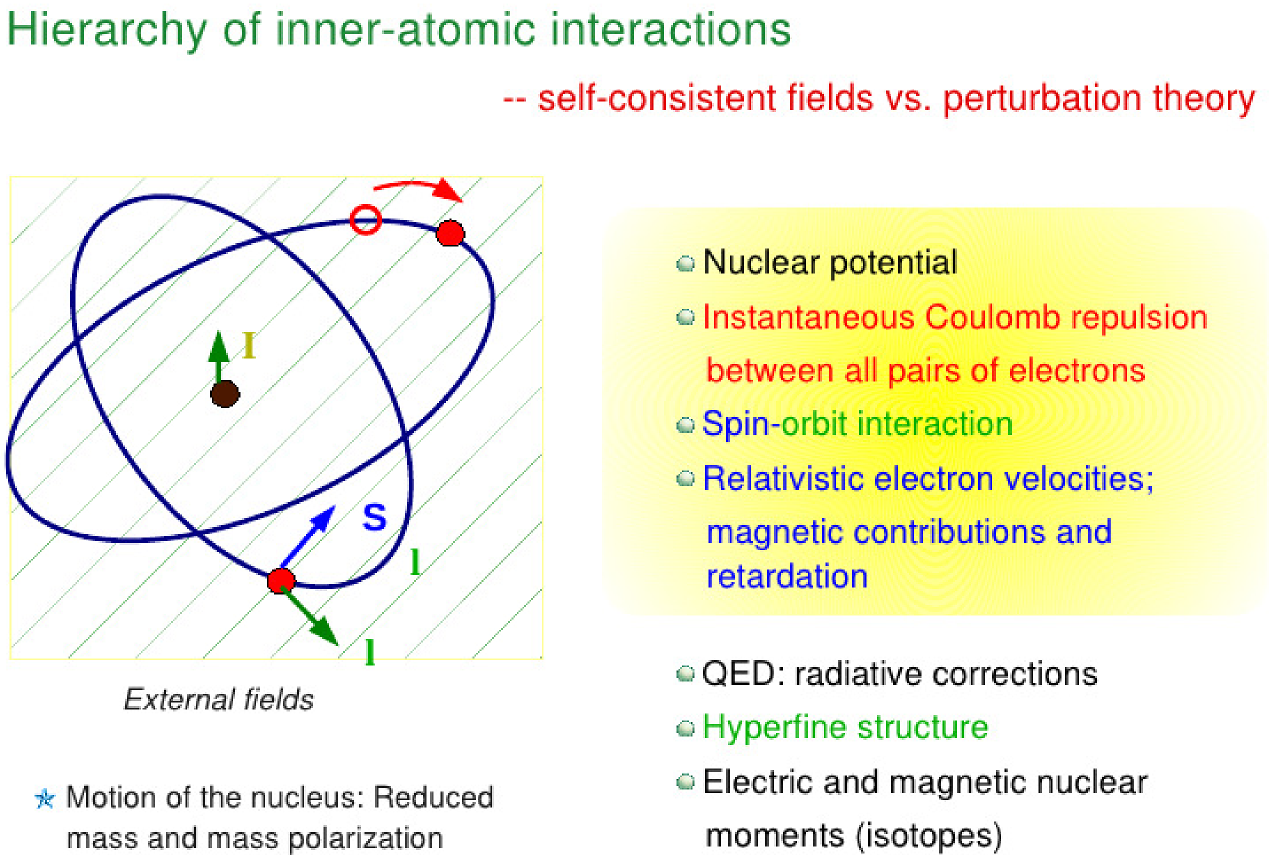
4.2. Interaction and couplings in many-electron atoms

4.2.a. Hierarchy of atomic interactions



Hierarchy of inner-atomic interactions

-- self-consistent fields vs. perturbation theory

External fields

- 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)

☆ Motion of the nucleus: Reduced mass and mass polarization

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:

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

  - 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 $V_{nuc}(r)$

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

4.2.c. Interelectronic interactions

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

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

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

➢ Spin-orbit interaction:

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

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

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

➢ 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:

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

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

- Atomic units: ... reminder

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

4.3. Interaction-induced shifts in atoms and ions

4.3.a. Isotope shifts

Isotopic effects:

- Isotopic volume effect: $r_N \sim A^{1/3}$ ⇝ change in the nuclear potential.
- Reduced mass: $\mu = \frac{m\,M}{m+M}$ ⇝ 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

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

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

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 τ of all excited states, often pressure-dependent.

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

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

➢ Intensity distribution (Lorentz profile): σ ... wave number (transition energy); Γ ... 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

$$H_C \;\equiv\; H^{\,\mathrm{(Coulomb)}} \;=\; \sum \mathrm{one-particle\ operators} \;+\; \begin{matrix}\mathrm{electrostatic} \\ \mathrm{Coulomb\ repulsion}\end{matrix} \;+\; \ldots$$

$$= \; H_{\,kin} \;+\; H_{\,nuc} \;+\; H_{\,e-e} \;+$$

$$= \; -\sum_i \frac{\nabla_i^2}{2} \;-\; \sum_i \frac{Z}{r_i} \;+\; \sum_{i<j} \frac{1}{r_{ij}} \qquad\qquad r_{ij} \;=\; |\mathbf{r}_i \;-\; \mathbf{r}_j|$$

- 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 soluations to the many-electron SE

$$H_{\,C}\;\; \psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \sigma_1, \sigma_2, ..., \sigma_N) \;=\; E\;\psi(...)$$

- 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

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

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

4.5.b. Product functions and Slater determinants

- Product functions: $H_{\rm o}$ has one-particle character

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

- ➢ 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

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

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

$$\langle \psi \,|\, \psi' \rangle \;=\; \frac{1}{N!} \sum_{PP'} (-1)^{P+P'} \; \langle \phi_1(k_1)\, \phi_2(k_2) \,...\phi_N(k_N) \,|\, \phi'_1(k'_1)\, \phi'_2(k'_2) \,...\phi'_N(k'_N) \rangle$$

$$\;=\; \frac{1}{N!} \sum_P (-1)^{2P} \, \delta_{\psi\psi'} \;=\; \delta_{\psi\psi'}.$$

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

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

- ➢ Classification of many-electron quantum states: ... require generally $4\,N$ 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_ℓ, m_s)
- Subshell: $(n\ell)^w$; ... set of (maximal) $q = 2\,(2\ell + 1)$ equivalent electrons form a subshell
- Electron configuration:

$$(n_1\ell_1)^{q_1}\,(n_2\ell_2)^{q_2}\;\ldots\;(n_r\ell_r)^{q_r} \qquad 0 \le q_i \le 2(2\ell_i + 1) \qquad \sum_{i=1}^{r} q_i = N$$

- 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

$$\rho_{\,subshell} = e\,\frac{1}{r^2}\,|P_{n\ell}|^2 \sum_{m=-\ell}^{\ell} \sum_{m_s} |Y_{\ell m}|^2\,|\chi_{m_s}|^2 = \frac{2\,(2\ell + 1)}{4\pi\,r^2}\,|P_{n\ell}|^2$$

... basis of atomic shell model

- Atomic shell model: ... central-field model (approximation); theoretical basis for the periodic table of elements
- Rydberg series (of configurations): ... $2p^5 3p,\quad 2p^5 4p,\quad 2p^5 5p,\ \ldots$
- Aufbau principle: ... successive filling of electron shells $(n\ell)$

- ➢ 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 $\rightsquigarrow$ transition metals.

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

    $4d$ ... paladium group $Z = 39, ..., 46$

    $5d$ ... platinum group $Z = 71, ..., 78$
  - nf-shells are filled 'afterwards' ($4f$ ... lanthanides, $5f$ ... actinides);
  - filled and half-filled shells are particular stable.

Blackboard example (Low-lying electron configurations of light elements):

Blackboard example (Alkali atoms):

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4.5.d. Thomas-Fermi model

Brief outline of Thomas-Fermi theory:

- ➢ Thomas-Fermi model: ... electrons form Fermi gas (Fermi-Dirac statistic); electron density $\longrightarrow$ 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)

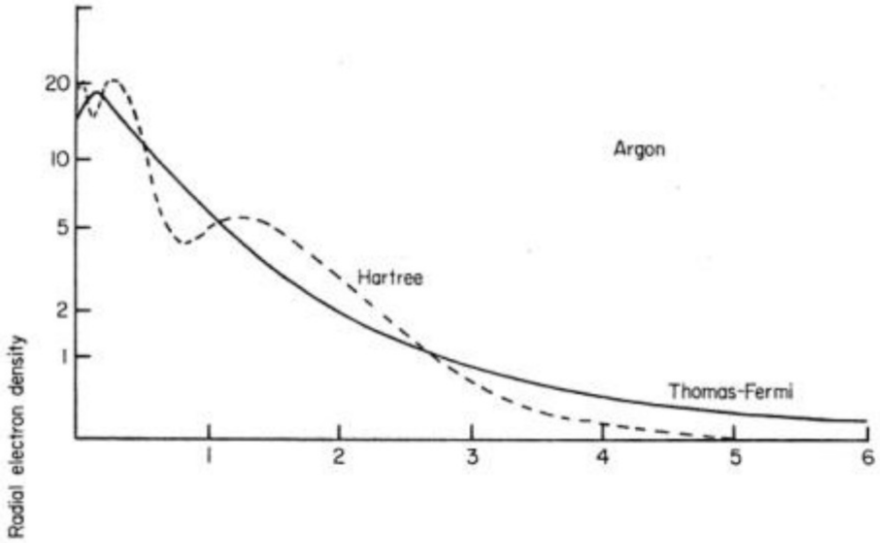


Figure 4.4.: Comparison between the Thomas-Fermi electron densities (from which the potential is derived) and a more accurate quantum-mechanical Hartree density, obtained in the independent-electron approximation. From http://www.virginia.edu/ep/Interactions/.

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

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

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

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

- 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, $H \approx H_o + H'$:

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

- Vector model of angular momentum: $[H, l_{i\,z}] \neq 0$:
- Sets of commutable operators:

$$\left\{H, \mathbf{L}^2, L_z, \mathbf{S}^2, S_z\right\} \qquad \text{...} \quad LS \text{ coupling scheme}$$

$$\left\{H, \mathbf{L}^2, \mathbf{S}^2, \mathbf{J}^2, J_z\right\} \qquad \text{...} \quad LSJ \text{ coupling scheme}$$

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

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

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

$\left\{H,\, \mathbf{J}^2,\, J_z\right\}$ ... jj coupling scheme

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

Blackboard example (Classification of an (effective) two-particle systems):

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

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

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

- ➢ In this approximation, H is diagonal with regard to coupled states of the kind:
  - (...) $LS\, M_L M_S$ or
  - (..) $LS\, J M_J$,
  - 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

Blackboard example (p^2 configuration):

LS terms of equivalent electrons:

- In general: ℓ^2 configuration $\longrightarrow$ allowed terms with even $L + S$.
- Use group theoretical methods to determine the terms and levels of complex ℓ^w configurations, or even for several open shells: $\ell_1^{w_1}\, \ell_2^{w_2}\, \ldots$.
- 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:

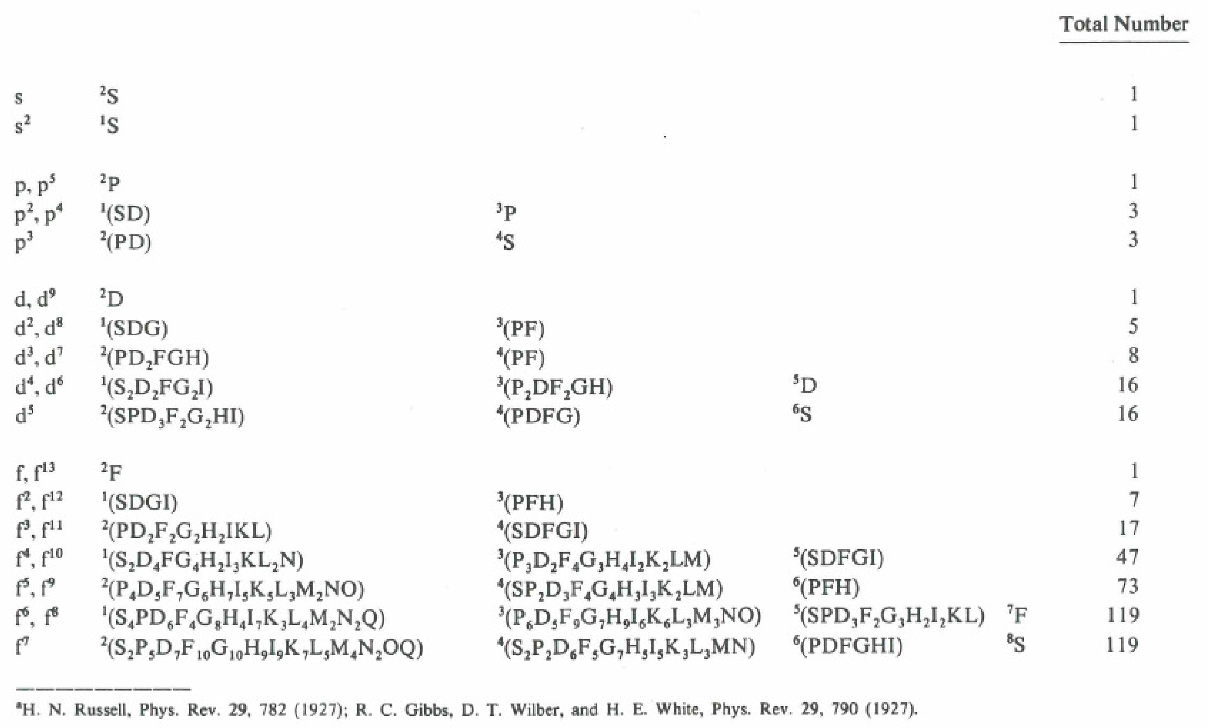
- Vector model ... to determine all possible L and S.

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

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

- Coupling sequence:

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



					Total Number
s	^2S				1
s^2	^1S				1
p, p^5	^2P				1
p^2, p^4	$^1(SD)$	^3P			3
p^3	$^2(PD)$	^4S			3
d, d^9	^2D				1
d^2, d^8	$^1(SDG)$	$^3(PF)$			5
d^3, d^7	$^2(PD_2FGH)$	$^4(PF)$			8
d^4, d^6	$^1(S_2D_2FG_2I)$	$^3(P_2DF_2GH)$	^5D		16
d^5	$^2(SPD_3F_2G_2HI)$	$^4(PDFG)$	^6S		16
f, f^{13}	^2F				1
f^2, f^{12}	$^1(SDGI)$	$^3(PFH)$			7
f^3, f^{11}	$^2(PD_2F_2G_2H_2IKL)$	$^4(SDFGI)$			17
f^4, f^{10}	$^1(S_2D_4FG_4H_2I_3KL_2N)$	$^3(P_3D_2F_4G_3H_4I_2K_2LM)$	$^5(SDFGI)$		47
f^5, f^9	$^2(P_4D_5F_7G_6H_7I_5K_5L_3M_2NO)$	$^4(SP_2D_3F_4G_4H_3I_3K_2LM)$	$^6(PFH)$		73
f^6, f^8	$^1(S_4PD_6F_4G_8H_4I_7K_3L_4M_2N_2Q)$	$^3(P_6D_5F_9G_7H_9I_6K_6L_3M_3NO)$	$^5(SPD_3F_2G_3H_2I_2KL)$	^7F	119
f^7	$^2(S_2P_5D_7F_{10}G_{10}H_9I_9K_7L_5M_4N_2OQ)$	$^4(S_2P_2D_6F_5G_7H_5I_5K_3L_3MN)$	$^6(PDFGHI)$	^8S	119

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[a] 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: α_i ... additional quantum numbers, if necessary

$$\{[((\ell_1^{w_1}\alpha_1\, L_1S_1,\ \ell_2^{w_2}\alpha_2\, L_2S_2)\ L_{12}\, S_{12},\ (...))\ ...]\ L_q\, S_q\}\ \ JM$$

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

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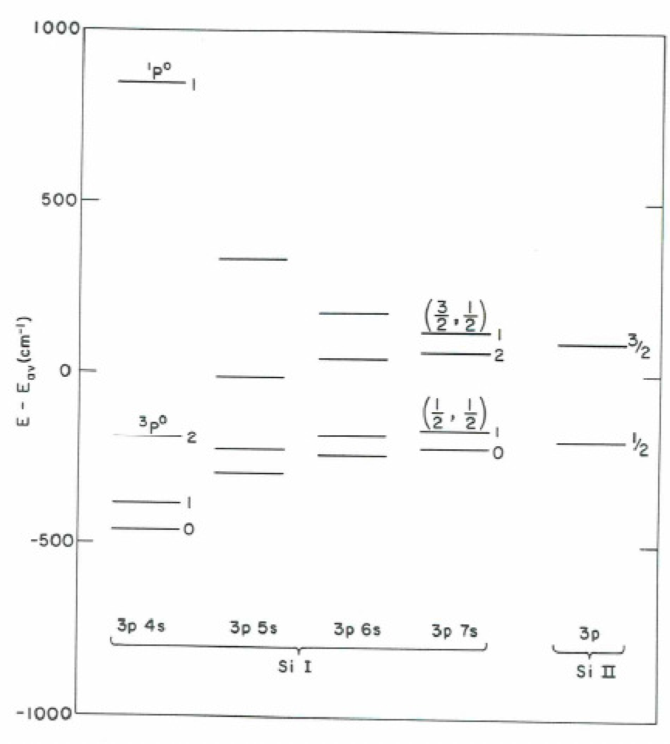

Figure 4.6.: The observed energy level structure for the four lowest $3pns$ comfigurations of Si I and together with the Si II configuration, relative to the respective centers of gravity. The figure shows a rapid change from *LS* to pair-coupling conditions.

Blackboard example ($d^2\,p^2$ configuration):

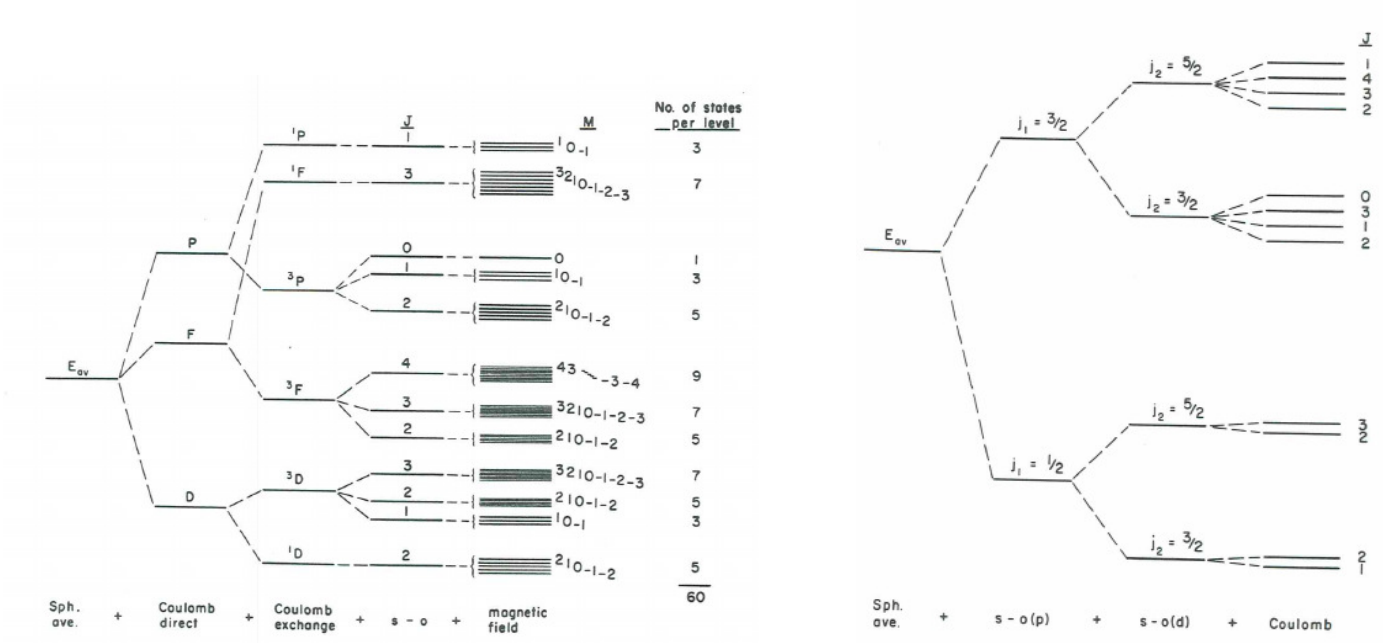

Figure 4.7.: Left: Energy level structure of a pd electron configuration under LS coupling conditions; it starts from the central-field averaged energy and takes different contributions into account. Right: The same but under jj coupling conditions; the two quite strong spin-orbit interactions of the 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: $H_{\rm SO} \gg H_{rest}(e-e)$

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

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

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

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

ℓ	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

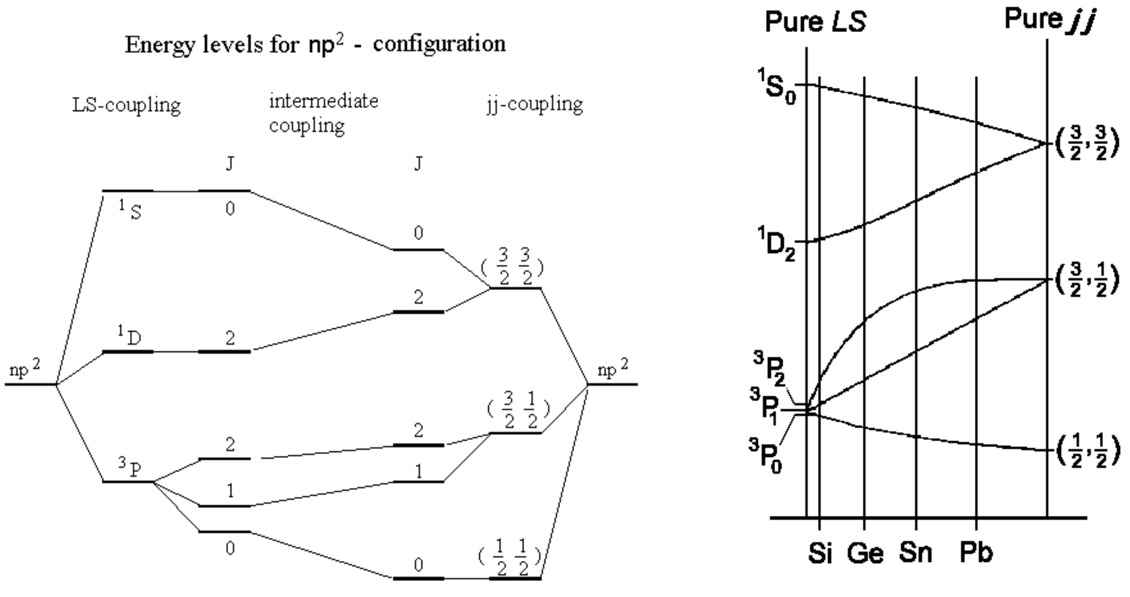

Figure 4.8.: Energies for the np^2 configuration and change in the coupling scheme for various elements homolog to atomic silicon.

4.6.e. Intermediate coupling. The matrix method

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

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

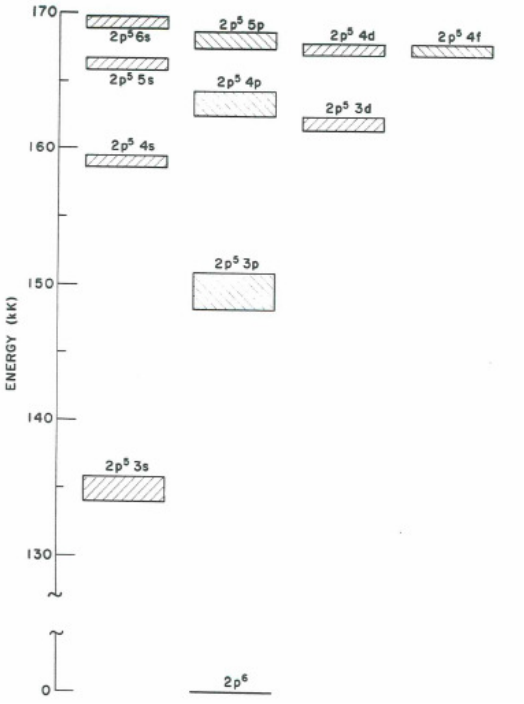

Figure 4.9.: Block diagram of the lowest configurations of Ne I. For each configuration, the levels lay within a limited range of energies as it is shwon by the shadowed blocks. There is one level for $2p^6$, 4 levels of ps configurations, 10 levels for p^5p' configurations and 12 levels for p^5d and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

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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: $F = \sum_i^N f(\mathbf{x}_i)$ ⇝ symmetric in $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$.
- ➢ Two-particle operators: $G = \sum_{i<j}^N g(\mathbf{x}_i, \mathbf{x}_j)$ ⇝ symmetric in all pairs of electron coordinates.

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

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

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

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

➢ Matrix elements of symmetric two-particle operators:

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

Simplified notations for determinants and matrix elements:

- Slater determinant: $|\alpha\rangle$ ... Slater determinant $|\{a, b, ..., n\}\rangle$, ordered set of one-particle functions
- Occupied vs. virtual orbitals: ... we need to distinguish in $|\alpha\rangle$
  - occupied orbitals (one-particle functions): $a, b, ...$
  - virtual orbitals (which do not occur in $|\alpha\rangle$): $r, s, ...$

  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:

$$\langle \alpha \,|\, F \,|\, \alpha \rangle \;=\; \sum_a^{\text{occ}} \langle a \,|\, f \,|\, a \rangle$$

$$\langle \alpha \,|\, G \,|\, \alpha \rangle \;=\; \sum_{a<b}^{\text{occ}} \left(\langle ab \,|\, g \,|\, ab \rangle \;-\; \langle ba \,|\, g \,|\, ab \rangle \right) \;=\; \frac{1}{2} \sum_{ab}^{\text{occ}} \left(\langle ab \,|\, g \,|\, ab \rangle \;-\; \langle ba \,|\, g \,|\, ab \rangle \right)$$

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

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

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

- ➢ ME between determinant which differ by two orbitals:

$$\begin{aligned}\langle \alpha_{ab}^{rs} \,|\, F \,|\, \alpha \rangle &= 0 \\ \langle \alpha_{ab}^{rs} \,|\, G \,|\, \alpha \rangle &= \langle rs \,|\, g \,|\, ab \rangle \;-\; \langle sr \,|\, g \,|\, ab \rangle\end{aligned}$$

- ➢ All other ME vanish identically.
- ➢ Feynman-Goldstone diagrams: ... graphical representation of matrix elements and operators;
  ➥ MBPT ... many-body perturbation theory.

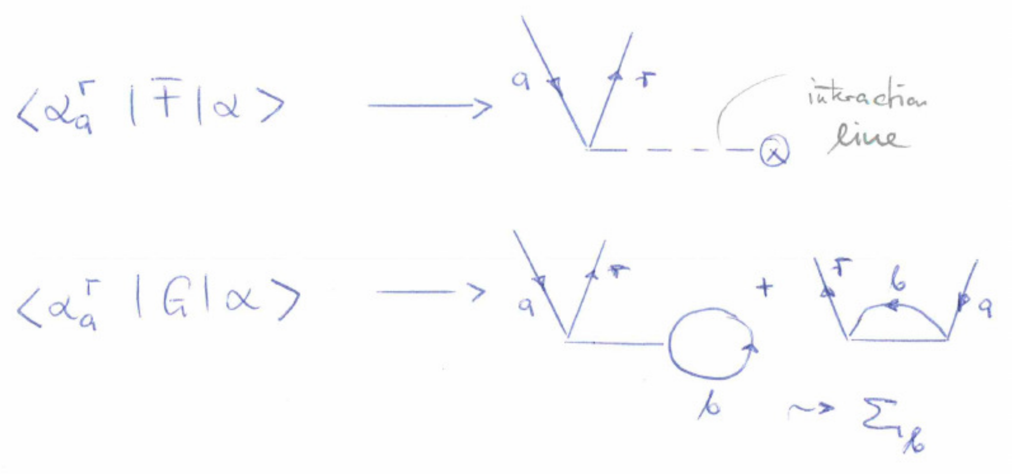


Figure 4.10.: Selected Feynman-Goldstone diagrams to represent matrix elements and wave operators.

Blackboard example (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):

$$\text{Starting potential} \quad \longrightarrow \quad \underbrace{\text{Calculate 1} - \text{p functions} \quad \longrightarrow \quad \text{Calculate new potential}}_{\longleftarrow \text{ perform iteration}}$$

- 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 $|\alpha\rangle$

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

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

$$\langle E \rangle \qquad \text{... stationary with respect to small changes in the orbitals}$$

$$|a\rangle \longrightarrow |a\rangle + \eta\,|r\rangle \qquad \eta \text{ ... real}$$

$$|\alpha\rangle \longrightarrow |\alpha\rangle + \eta\,|\alpha_a^r\rangle$$

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

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

- 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:

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

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

- Hartree-Fock potential:

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

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

$$\langle r \,| h_{\mathrm{H}F} |\, a \rangle \;=\; 0 \qquad\qquad \text{a ... occupied;} \qquad \text{r ... virtual orbitals}$$

$$h_{\mathrm{H}F}\; |a\rangle \;=\; \sum_i^{\mathrm{all}} |i\rangle \, \langle i \,| h_{\mathrm{H}F} |\, a \rangle \;=\; \sum_b^{\mathrm{occ}} |b\rangle \, \langle b \,| h_{\mathrm{H}F} |\, a \rangle$$

- ➢ Properties of $u_{\mathrm{H}F}$
  - $h_{\mathrm{H}F}$ is hermitian
  - invariant with regard to unitary transformations; it can hence be written in a diagonal form.

- ➢ Normal form of the Hartree-Fock equations:

$$h_{\mathrm{H}F}\; |a'\rangle \;=\; \left(-\frac{\boldsymbol{\nabla}^2}{2} \;-\; \frac{Z}{r} \;+\; u_{\mathrm{H}F} \right) |a'\rangle \;=\; \varepsilon_a' \; |a'\rangle$$

- ➢ Binding energy:

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

- ➢ Ionisation energies: ... means to 'take out' an electron a

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

- ➢ 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

$$h_o\,\phi_k \;=\; \left(-\frac{\nabla^2}{2} \;-\; \frac{Z}{r} \;+\; u(r)\right) \;=\; \varepsilon_k\,\phi_k \qquad\qquad \phi_k \;=\; \frac{P_k(r)}{r}\, Y_{\ell_k m_{\ell_k}}(\vartheta,\varphi)\, \chi_{m_{s_k}}(\sigma)$$

➢ Radial equation:

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

➢ Boundary conditions:

$$P(r\rightarrow 0) \;=\; 0 \qquad \Longleftrightarrow \qquad \frac{P(r)}{r} \;\longrightarrow_{\,r\rightarrow 0}\; \text{finite}$$

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

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

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.

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

$a \equiv (n_a, \ell_a),\ b$	... 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:

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

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

$$R^k(abcd) = \int_0^\infty \int_0^\infty dr\, ds\; P_a(r)\, P_b(r)\, \frac{r_<^k}{r_>^{k+1}}\, P_c(s)\, P_d(s) \qquad r_< = \min(r,s), \qquad r_> = \max(r,s)$$

$$= \int_0^\infty dr \int_0^r ds\; [P_a P_b]_r\, \frac{s^k}{r^{k+1}}\, [P_c P_d]_s + \int_0^\infty dr \int_r^\infty ds\; [P_a P_b]_r\, \frac{r^k}{s^{k+1}}\, [P_c P_d]_s$$

$$F^k(a,b) = R^k(aabb); \qquad G^k(a,b) = R^k(abab).$$

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

$$\frac{1}{r_{12}} = r_1^2 + r_2^2 - 2 r_1 r_2 \cos\omega = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}}\, P_k(\cos\omega) = \sum_{k=0}^{\infty} \frac{4\pi}{k+1}\, \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{k} Y_{kq}(\vartheta_1,\varphi_1)\, Y_{kq}^*(\vartheta_2,\varphi_2)$$

$$r_< = \min(r_1,r_2), \qquad r_> = \max(r_1,r_2).$$

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

$$\delta\,\langle E \rangle = \delta\, E_{\text{av}} = 0, \qquad N_{n\ell,n'\ell} = \int_0^\infty dr\, P_{n\ell}^*(r)\, P_{n'\ell}(r) = \delta_{nn'} \qquad \text{or} \quad \text{equivalent}$$

$$\delta_{\{P_a\}} \left[E_{\text{av}} - \sum_a q_a\, \lambda_{aa}\, N_{aa} - \sum_{a \neq b} \delta_{\ell_a,\ell_b}\, q_a\, q_b\, \lambda_{ab}\, N_{ab} \right] = 0$$

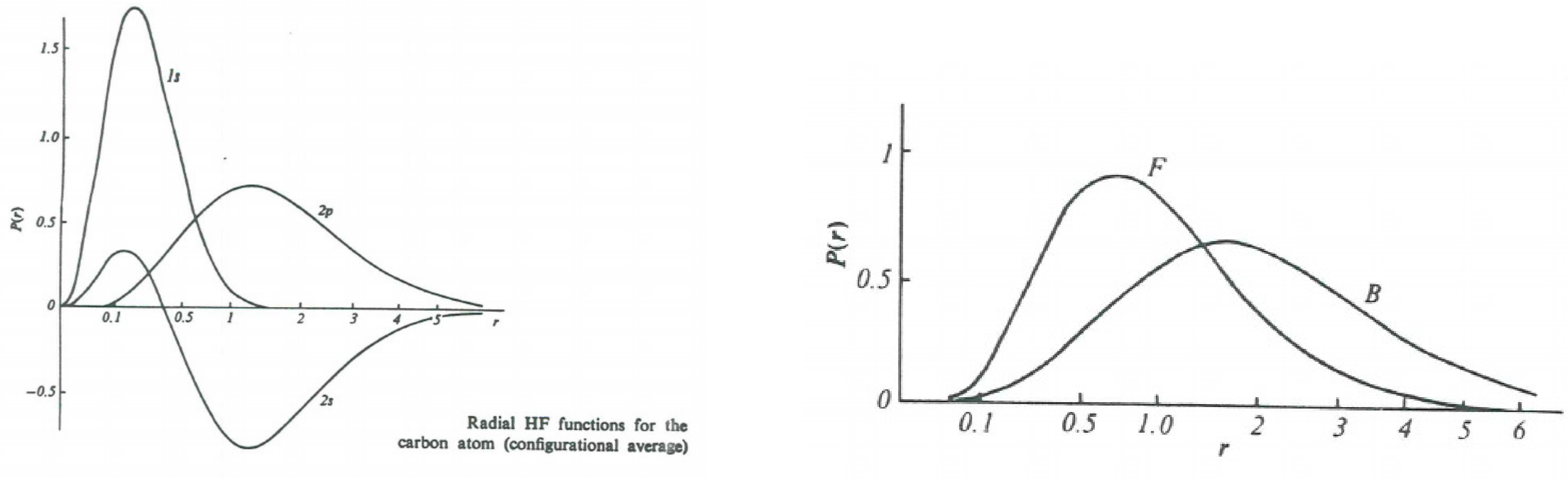


Figure 4.11.: (Radial Hartree-Fock functions for carbon (left) as well as for the $2p$ electrons of boron and fluorine (right).

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

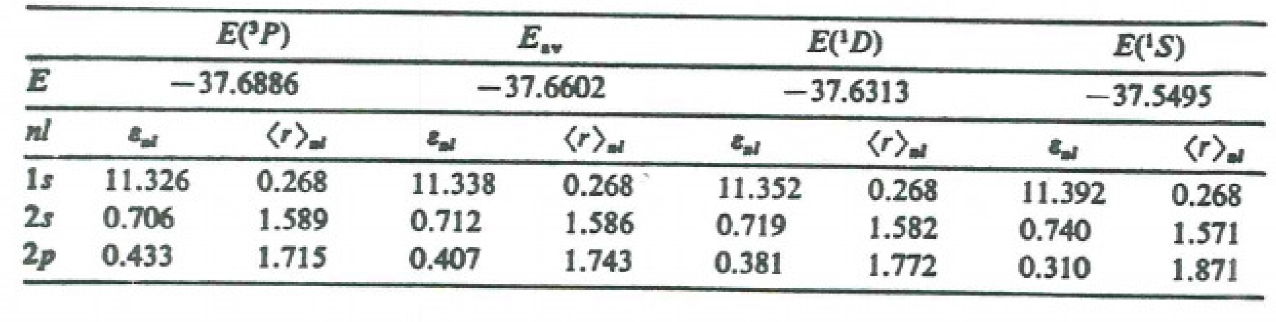
$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell_a(\ell_a+1)}{2\,r^2} - \frac{Z}{r} \right] P_a(r) + \sum_{b,k} q_b \left[c(abk)\,\frac{Y^k(bb;r)}{r}\,P_a(r) + d(abk)\,\frac{Y^k(ab;r)}{r}\,P_b(r) \right]$$

$$= \varepsilon_a\,P_a(r) + \sum_{b\neq a} q_b\,\varepsilon_{ab}\,P_b(r)$$

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

$$\epsilon_a = \lambda_{aa} \qquad \text{... one − electron eigenvalues}$$

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



	$E(^3P)$		E_{av}		$E(^1D)$		$E(^1S)$	
E	-37.6886		-37.6602		-37.6313		-37.5495	
nl	ε_{nl}	$\langle r\rangle_{nl}$	ε_{nl}	$\langle r\rangle_{nl}$	ε_{nl}	$\langle r\rangle_{nl}$	ε_{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

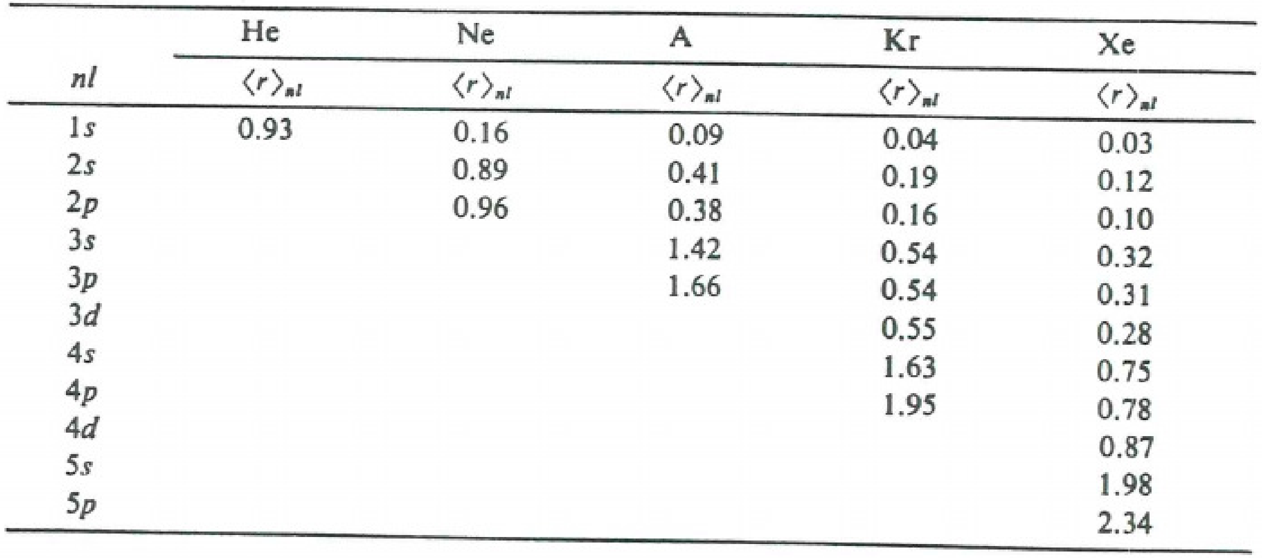
4.8.a. Configuration interaction theory (CI, matrix method)

CI method:

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

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

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



	He	Ne	A	Kr	Xe
nl	$\langle r \rangle_{nl}$	$\langle r \rangle_{nl}$	$\langle r \rangle_{nl}$	$\langle r \rangle_{nl}$	$\langle r \rangle_{nl}$
1s	0.93	0.16	0.09	0.04	0.03
2s		0.89	0.41	0.19	0.12
2p		0.96	0.38	0.16	0.10
3s			1.42	0.54	0.32
3p			1.66	0.54	0.31
3d				0.55	0.28
4s				1.63	0.75
4p				1.95	0.78
4d					0.87
5s					1.98
5p					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: $H\,\Psi_k \;=\; E_k\,\Psi_k : \quad H_{ji} \;=\; \langle \Phi_j\,|H|\,\Phi_i \rangle \quad ... \quad$ matrix elements of H.

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

- ➢ Secular equation: $|H \;-\; E\,I| \;=\; 0\,;$ with hermitian matrix $(H_{ik} \;=\; H^*_{ki})$.
- ➢ Representation of wave function: $C \;=\; (c_{ik})$ with $H_{\rm diag} \;=\; C^{-1}\,H\,C$

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

MCHF method:

➢ Comparison HF *versus* MCHF:

Hartree-Fock method		MCDF method
$\lvert\alpha\rangle$	$\longrightarrow$	$\lvert\alpha(k)\rangle \; = \; \sum_i c_{ik} \; \lvert\alpha_i\rangle$
* single determinant		* superposition of determinants
* variation of (radial) orbital functions		* 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

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

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

➢ 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 Schödinger equation as the number of basis functions is increased.

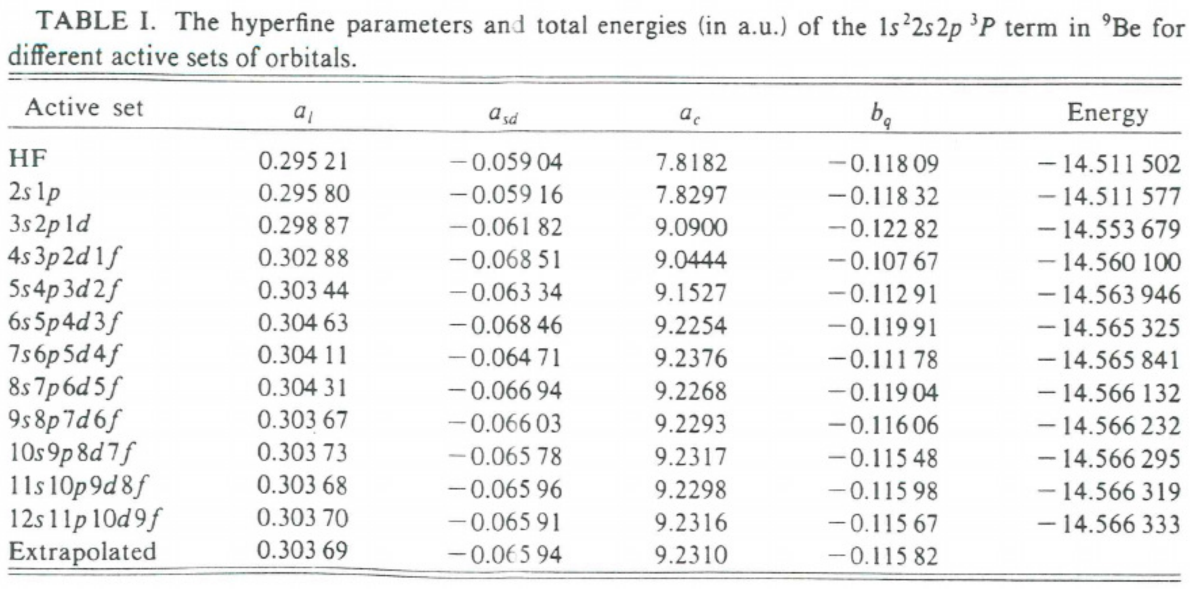


TABLE I. The hyperfine parameters and total energies (in a.u.) of the $1s^22s2p\ ^3P$ term in ^{9}Be for different active sets of orbitals.

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

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

- Ansatz: m ... summation over a complete set of many-particle states.

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + ...; \qquad \phi_n = \phi_n^{(0)} + \phi_n^{(1)} + ...$$

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

  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

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

- Slater determinants: Φ_a built from one-electron functions ϕ_k : $h_o \phi_k = \varepsilon \phi_k$.
- Goal: Solutions of the SE $H \Psi_a = E_a \Psi_a$ for a finite number $a = 1, ..., d$ of atomic states.
- Model space: $\mathcal{M} = \text{span}\{\Phi_a, a = 1, ..., d\}$; in contrast to the (complementary) space orthogonal $\mathcal{Q}$.
- Projection operator: ... commute with H_o; if Φ_a is known, Φ_a^o is just the projection of the exact solution upon the model space.

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

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

- Wave operator (Möller, 1945): ... however, Ω and P are not *inverse* operators.

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

- Generalized Bloch equation: ... intermediate normalization:

$$\langle \Phi_a \,|\, \Phi_a^o \rangle \;=\; \langle \Phi_a^o \,|\, \Phi_a^o \rangle \;=\; 1 \quad \Longleftrightarrow \quad P \;=\; P\,\Omega\,P$$

$$\cdot\,\Omega P| \qquad\qquad \Omega P\, H_o\, \Psi^a \;+\; \Omega P\, V\, \Psi_a \;=\; E_a\, \Omega\, P\, \Psi_a$$

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

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

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

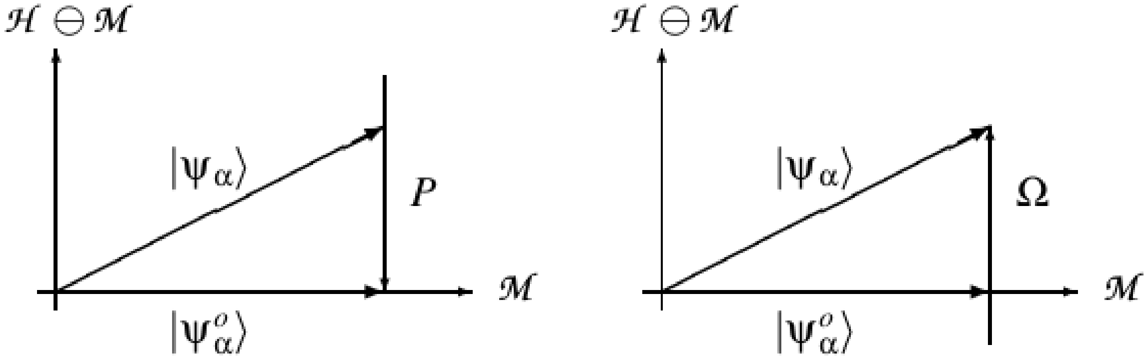


Figure 4.15.: Simplified representation of the operators P and Ω in IN. The projector P transforms a d-dimensional space $\{\Phi_a,\; a \,=\, 1, ..., d\}$ of the Hilbert space into the model space $\mathcal{M}$ of the same dimension. The wave operator Ω reverses this transformation. Note, however, that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

- For the states of interest $\{ \Phi_a, \; a = 1, ..., d \}$, 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 Ω.

Order-by-order perturbation expansions:

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

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

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

$$\vdots$$

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

- 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.

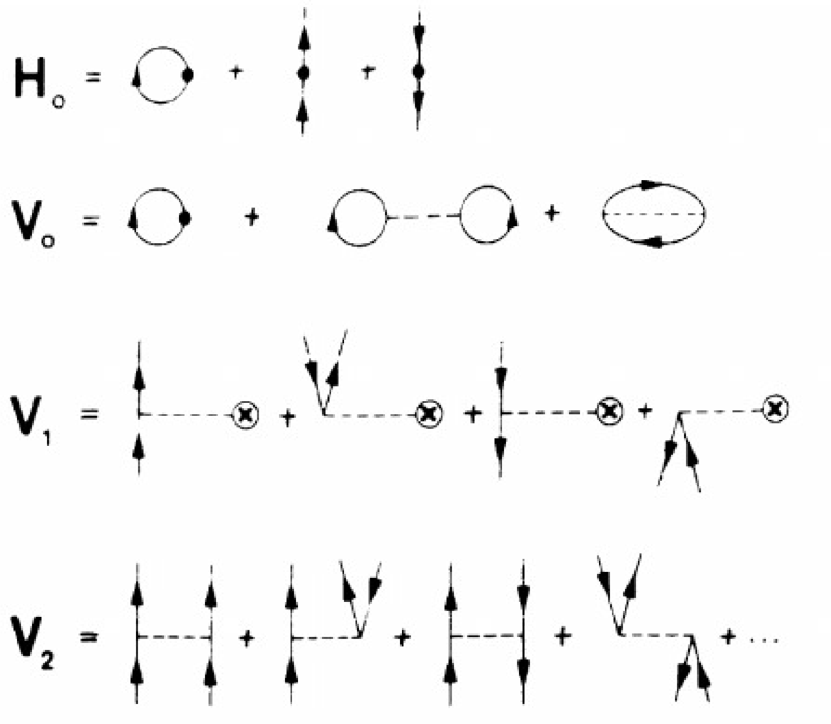


Figure 4.16.: Grafical representation of the unperturbed Hamiltonian operator H_o and the perturbation V, written in normal form [cf. Eqs. (4.31-4.35) in Lindgren (1978).

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

Relativistic Hamilton operator:

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

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

- Dirac-Fock method: ... again, use single Slater determinant, but for $\{\psi_{\mathrm{D},i}\}$
- Dirac-Coulomb Hamiltonian: ... built-up from the one-particle Dirac Hamiltonian

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

$$h_\mathrm{D}(i) = c\,\boldsymbol{\alpha}_i\cdot\mathbf{p}_i + (\beta_i - 1)\,c^2 - \frac{Z}{r_i}, \qquad b(i,j) = \frac{\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j}{r_{ij}} + (\boldsymbol{\alpha}_i\cdot\boldsymbol{\nabla}_i)\,(\boldsymbol{\alpha}_j\cdot\boldsymbol{\nabla}_j)\,\frac{\cos(\omega\, r_{ij} - 1)}{\omega^2\, r_{ij}}.$$

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

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

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

4.9. Tasks

See tutorials.

5. Angular momentum (AM) in quantum physics

5.1. Angular momentum operators

Commutation relation & eigenfunctions:

$$
\begin{aligned}
[l_i,\, l_j] &= i\hbar\, \epsilon_{ijk}\, l_k \\
\mathbf{l}^2\, Y_{lm} &= \hbar^2\, \ell(\ell+1)\, Y_{lm} & \ell &= 0, 1, 2, \ldots & &\text{orbital angular momentum QN} \\
l_z\, Y_{lm} &= m\, \hbar\, Y_{lm} & m &= -\ell, -\ell+1, \ldots, \ell & &\text{magnetic QN}
\end{aligned}
$$

5.1.a. Algebraic definition of angular momentum

Definition of AM operators by their commutators:

- ➢ Commutators of cartesian components:

$$[j_i,\, j_j] = i\hbar\, \epsilon_{ijk}\, j_k\ , \qquad \ldots \text{ defines an algebra for all (half}-\text{)integer values } j \geq 0$$

- Ladder operators: $j_\pm = j_x \pm i\, j_y\,, \quad \mathbf{j}^2 = j_x^2 + j_y^2 + j_z^2$

$$[j_i,\, \mathbf{j}^2] = 0 \qquad (i = 1,2,3)$$

$$[j_+,\, j_-] = 2\,\hbar\, j_z, \qquad [j_z,\, j_\pm] = \pm\,\hbar\, j_\pm, \qquad [j_\pm,\, \mathbf{j}^2] = 0$$

- Ladder operators $j_\pm$ are non-hermitian and related to each other by: $j_+ = j_-^+$

$$j_\pm\, |jm\rangle = N_\pm\, |j, m \pm 1\rangle\,, \qquad N_\pm(j,m) = \hbar\sqrt{j(j+1) - m(m\pm 1)}$$

- Derivation:

$$\mathbf{j}^2\, u_{\lambda\, m} = \hbar^2\, \lambda\, u_{\lambda\, m} \qquad j_z\, u_{\lambda\, m} = \hbar\, m\, u_{\lambda\, m}$$

$$j_\pm\, u_{\lambda\, m} = N_\pm(\lambda, m)\, u_{\lambda,\, m\pm 1}$$

$$N_+(\lambda, m) = N_-^*(\lambda, m+1) \equiv N(\lambda,\, m) \qquad \rightsquigarrow \qquad |N(\lambda, m)|^2 = \hbar^2\,[j(j+1) - m(m+1)]$$

- Condon-Shortley phase convention: $N(\lambda, m) = \hbar\sqrt{j(j+1) - m(m+1)}\,.$
- Possible values: ... $j \geq 0$

$$m = j, j-1, j-2, ..., -j, \qquad j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, ... \qquad \lambda = j\,(j+1)$$

5.1.b. Matrix representation of angular momentum operators

- Matrix representation of $\mathbf{j}^2$ and $j_\pm$:

$$\left\langle u_{jm} \,|\, \mathbf{j}^2 \, u_{jm'} \right\rangle \;=\; \hbar^2 \, j(j+1) \, \delta_{mm'} \qquad\qquad \langle u_{jm} \,|\, j_z \, u_{jm'} \rangle \;=\; \hbar \, \delta_{mm'}$$

$$\langle u_{jm} \,|\, j_\pm \, u_{jm'} \rangle \;=\; \hbar \sqrt{j(j+1) \;-\; m(m \pm 1)} \, \delta_{m,m'\pm 1}$$

- Matrix representation of cartesian components j_x, j_y and j_z:

$$\langle u_{jm} \,|\, j_x \, u_{jm'} \rangle \;=\; \frac{\hbar}{2} \left[\sqrt{j(j+1) \;-\; m(m-1)} \;\; \delta_{m,m'+1} \;+\; \sqrt{j(j+1) \;-\; m(m+1)} \;\; \delta_{m,m'-1} \right]$$

$$\langle u_{jm} \,|\, j_y \, u_{jm'} \rangle \;=\; \frac{\hbar}{2i} \left[\sqrt{j(j+1) \;-\; m(m-1)} \;\; \delta_{m,m'+1} \;-\; \sqrt{j(j+1) \;-\; m(m+1)} \;\; \delta_{m,m'-1} \right] .$$

- Example (Spin-1/2 systems): For $m \;=\; (+1/2, \, -1/2)$, we find the matrix representation

$$(j_{x;\, mm'}) \;\equiv\; j_x \;=\; \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \qquad j_y \;=\; \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} , \qquad j_z \;=\; \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$j_+ \;=\; \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} , \qquad j_- \;=\; \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} , \qquad \mathbf{j}^2 \;=\; \hbar^2 \, \frac{3}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

- Example (Spin-1 systems): With $m \;=\; +1, 0, -1$, one obtains (prove !)

$$j_x \;=\; \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} , \qquad j_y \;=\; \frac{i\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} , \qquad j_z \;=\; \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} .$$

5.1.c. Algebra of Pauli matrices

➢ Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad \sigma_o = I_{2x2} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

➢ Important relations:

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \sigma_o^2 = \sigma_o \,, \qquad [\sigma_i, \sigma_j] = 2i\, \epsilon_{ijk}\, \sigma_k$$

$$\{\sigma_i, \sigma_j\} = 2\delta_{ij}\, \sigma_o \,, \qquad \sigma_i \sigma_j = \delta_{ij}\, \sigma_o + i\, \epsilon_{ijk}\, \sigma_k$$

➢ Linear independence of the Pauli matrices: ... only holds iff $a_o = a_1 = a_2 = a_3 = 0\,.$

$$a_o\, \sigma_o + a_1\, \sigma_1 + a_2\, \sigma_2 + a_3\, \sigma_3 = 0$$

➢ Basis for arbitrary 2×2 matrices:

$$A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} = a_o\, \sigma_o + a_1\, \sigma_1 + a_2\, \sigma_2 + a_3\, \sigma_3 = \sum_i a_i\, \sigma_i$$

$$a_0 = \frac{1}{2}\,(a_{11} + a_{22})\,, \qquad a_1 = \frac{1}{2}\,\mathrm{Tr}\,(\sigma_x\, A)\,, \qquad a_2 = \frac{1}{2}\,\mathrm{Tr}\,(\sigma_y\, A)\,, \qquad a_3 = \frac{1}{2}\,\mathrm{Tr}\,(\sigma_z\, A)$$

$$a_i = \frac{1}{2}\,\mathrm{Tr}\,(\sigma_i\, A)\,, \qquad (\mathbf{a} \cdot \boldsymbol{\sigma})\,(\mathbf{b} \cdot \boldsymbol{\sigma}) = \mathbf{a} \cdot \mathbf{b} + i\, \boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b})\,, \qquad (\mathbf{a} \cdot \boldsymbol{\sigma})^2 = a^2\,.$$

5.2. Coupling of angular momenta

5.2.a. AM of spin-1/2 particles. Electrons, ...

Electrons, protons, etc.

➢ Hilbert space: ... product of position space and spin space

$$|\mathbf{r},\, \pm\rangle \;=\; |\mathbf{r}\rangle \,\otimes\, |\uparrow, \downarrow\rangle\,; \qquad\qquad \mathcal{H} \;=\; \{|\mathbf{r},\, \pm\rangle\} \;=\; \mathcal{H}_p \otimes \mathcal{H}_2$$

➢ AM operators:

$$\mathbf{j} \;=\; \mathbf{l} \otimes \mathbf{1} \;+\; \mathbf{1} \otimes \mathbf{s} \;=\; \mathbf{l} \;+\; \mathbf{s}\,, \qquad [l_i,\, l_j] \;=\; i\hbar\, \epsilon_{ijk}\, l_k\,, \qquad [s_i,\, s_j] \;=\; i\hbar\, \epsilon_{ijk}\, s_k\,, \qquad [l_i,\, s_j] \;=\; 0\,.$$

➢ Rotation operator in product space: ... with unit vector **n** along the rotation axis

$$U_R(\mathbf{n}, \vartheta) \;=\; \exp\left(\frac{-i\, \mathbf{j} \cdot \mathbf{n}\, \vartheta}{\hbar}\right) \;=\; \exp\left(\frac{-i\, \mathbf{l} \cdot \mathbf{n}\, \vartheta}{\hbar}\right)\, \exp\left(\frac{-i\, \mathbf{s} \cdot \mathbf{n}\, \vartheta}{\hbar}\right)\,.$$

➢ Wave functions in product space: ... superposition of two spin components

$$\psi(\mathbf{r}, \sigma) \;=\; \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix} \;=\; \psi_\uparrow(\mathbf{r})\, |\uparrow\rangle \;+\; \psi_\downarrow(\mathbf{r})\, |\downarrow\rangle \;=\; \underbrace{\psi_0\, |0\rangle \;+\; \psi_1\, |1\rangle}_{\text{QIP}} \;=\; \underbrace{\psi_\alpha\, |\alpha\rangle \;+\; \psi_\beta\, |\beta\rangle}_{\text{quantum chemistry}}\,.$$

- ➢ Product or uncoupled basis: ... product states of composite system, diagonal in $\{\mathbf{l}^2, l_z, \mathbf{s}^2, s_z\}$

$$|\ell, s, m_\ell, m_s\rangle \;=\; |\ell, m_\ell\rangle\, |s, m_s\rangle \;=\; |\ell s\, m_\ell m_s\rangle$$

$$\mathbf{l}^2 \; |\ell\, m_\ell\rangle \;=\; \ell(\ell+1)\,\hbar^2 \; |\ell\, m_\ell\rangle \;, \qquad l_z \; |\ell\, m_\ell\rangle \;=\; m_\ell\,\hbar \; |\ell\, m_\ell\rangle$$

$$\mathbf{s}^2 \; |s\, m_s\rangle \;=\; s(s+1)\,\hbar^2 \; |s\, m_s\rangle \;, \qquad s_z \; |s\, m_s\rangle \;=\; m_s\,\hbar \; |s\, m_s\rangle$$

- ➢ Different sets of commuting operators: $\{\mathbf{l}^2, l_z, \mathbf{s}^2, s_z\}$ or $\{\mathbf{l}^2, \mathbf{s}^2, \mathbf{j}^2, j_z\}$
- ➢ Coupled basis: ... $|\ell s\, j m_j\rangle$ with eigenvalue equations from above.

$$\mathbf{l}^2 \; |\ell s\, j m_j\rangle \;=\; l(l+1)\,\hbar^2 \; |\ell s\, j m_j\rangle \;, \qquad \mathbf{j}^2 \; |\ell s\, j m_j\rangle \;=\; j(j+1)\,\hbar \; |\ell s\, j m_j\rangle$$

$$\mathbf{s}^2 \; |\ell s\, j m_j\rangle \;=\; \frac{3}{4}\hbar^2 \; |\ell s\, j m_j\rangle \;, \qquad j_z \; |\ell s\, j m_j\rangle \;=\; m_j\,\hbar \; |\ell s\, j m_j\rangle$$

5.2.b. Coupling of two angular momenta (AM)

Uncoupled *vs.* coupled basis states:

- ➢ Uncoupled basis: $\{\mathbf{j}_1^2,\, j_{1z},\, \mathbf{j}_2^2,\, j_{2z}\}$ with the product basis $|j_1 m_1, j_2 m_2\rangle$

$$\mathbf{j}_1^2 \; |j_1 m_1, j_2 m_2\rangle \;=\; j_1(j_1+1)\,\hbar^2 \; |j_1 m_1, j_2 m_2\rangle \,, \qquad j_{1z} \; |j_1 m_1, j_2 m_2\rangle \;=\; m_1\,\hbar \; |j_1 m_1, j_2 m_2\rangle$$

- Product space: ... built from a complete set of $(2j_1+1)\,(2j_2+1)$ product functions

$$\dim(\mathfrak{h}_{j_1,j_2}) \;=\; \dim(\mathfrak{h}_{j_1})\cdot\dim(\mathfrak{h}_{j_2}) \;=\; (2j_1+1)\,(2j_2+1), \qquad \mathfrak{h}_{j_1,j_2} \;=\; \mathfrak{h}_{j_1}\otimes\mathfrak{h}_{j_2}$$

$$\sum_{m_1=-j_1}^{j_1}\;\sum_{m_2=-j_2}^{j_2} |j_1m_1, j_2m_2\rangle\,\langle j_1m_1, j_2m_2| \;=\; 1$$

$$\langle j_1m_1, j_2m_2\,|\,j_1'm_1', j_2'm_2'\rangle \;=\; \delta_{j_1,j_1'}\,\delta_{j_2,j_2'}\,\delta_{m_1,m_1'}\,\delta_{m_2,m_2'}$$

Clebsch-Gordan expansion:

- Clebsch-Gordan coefficients $\equiv\; \langle j_1m_1, j_2m_2\,|\,jm_j\rangle \;=\; C^{jm}_{j_1m_1,\,j_2m_2} \;=\; C(j_1j_2j;m_1m_2m):$

$$|j_1j_2\,jm_j\rangle \;=\; \sum_{m_1=-j_1}^{j_1}\;\sum_{m_2=-j_2}^{j_2} |j_1m_1j_2m_2\rangle\;\langle j_1m_1, j_2m_2\,|\,j_1j_2\,jm_j\rangle$$

$$|j_1m_1j_2m_2\rangle \;=\; \sum_{j=|j_1-j_2|}^{j_1+j_2}\;\sum_{m_j=-j}^{j} |j_1j_2\,jm_j\rangle\;\langle j_1j_2\,jm_j\,|\,j_1m_1, j_2m_2\rangle$$

- Group theory: ... tensor product $\mathfrak{h}_{j_1}$ and $\mathfrak{h}_{j_2}$ leads to a 'sum' of irreducible representations of AM

$$\mathfrak{h}_{j_1}\otimes\mathfrak{h}_{j_2} \;=\; \mathfrak{h}_{j_1+j_2}\,\oplus\,\mathfrak{h}_{j_1+j_2-1}\,\oplus\,\ldots\,\oplus\,\mathfrak{h}_{|j_1-j_2|}.$$

Example (Irreducible representations of coupled angular momenta):

1) $\ell_1 = 1,\ \ell_2 = 2;\quad L = 1,2,3:\qquad \mathbf{3} \otimes \mathbf{5} \;=\; \mathbf{3} \oplus \mathbf{5} \oplus \mathbf{7};\qquad (p+d)$ electrons $\rightsquigarrow\ P + D + F$
2) $L_1 = 2,\ L_2 = 3;\quad L = 1,2,3,4,5:\qquad \mathbf{5} \otimes \mathbf{7} \;=\; \mathbf{3} \oplus \mathbf{5} \oplus \mathbf{7} \oplus \mathbf{9} \oplus \mathbf{11}$
3) $\ell = 2,\ s = 1/2;\quad J = 3/2, 5/2:\qquad \mathbf{5} \otimes \mathbf{2} \;=\; \mathbf{4} \oplus \mathbf{6};\qquad (d+1/2) \rightsquigarrow d_{3/2} + d_{5/2}$
4) $j_1 = 1/2,\ j_2 = 3/2,\ j_3 = 1/2;\quad J = 1/2,\ 3/2,\ 3/2,\ 5/2:\quad \mathbf{2} \otimes \mathbf{4} \otimes \mathbf{2} \;=\; \mathbf{2} \oplus \mathbf{4} \oplus \mathbf{4} \oplus \mathbf{6};$ indep. coupling seq.

Successive coupling; can be generalized to arbitrarely large No. of angular momenta.

5.2.c. Properties of Clebsch-Gordan (CG) coefficients

- ➢ $\langle j_1 m_1, j_2 m_2 \,|\, j, m_j \rangle \;=\; 0$ ... unless $m_1 \,+\, m_2 \;=\; m_j.$
- ➢ $\underbrace{\langle j_1 m_1, j_2 m_2 \,|\, jm \rangle}_{standard\ form} \;=\; \langle jm \,|\, j_1 m_1, j_2 m_2 \rangle$ ... real.
- ➢ Triangular rule: CG coefficients vanish unless $|j_1 \,-\, j_2| \;\leq\; j \;\leq\; j_1 \,+\, j_2$
- ➢ Magnetic quantum numbers: $-j \;\leq\; m_j \;\leq\; j \qquad \forall\, j\,.$

- Orthogonality and sum rules:

$$\sum_{m_1,m_2} \langle j_1 m_1, j_2 m_2 \,|\, jm \rangle^2 \;=\; 1 \qquad\qquad \Longleftrightarrow \qquad\qquad \sum_{j,m} \langle j_1 m_1, j_2 m_2 \,|\, jm \rangle^2 \;=\; 1$$

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} \; \sum_{m_j=-j}^{j} \langle j_1 m_1, j_2 m_2 \,|\, j m_j \rangle \, \langle j_1 m_1', j_2 m_2' \,|\, j m_j \rangle \;=\; \delta_{m_1,m_1'} \, \delta_{m_2,m_2'}$$

$$\sum_{m_1,m_2} \langle j_1 m_1, j_2 m_2 \,|\, jm \rangle \, \langle j_1 m_1, j_2 m_2 \,|\, j'm' \rangle \;=\; \delta_{jj'} \, \delta_{mm'}$$

- Related to the Wigner 3–j symbols:

$$\langle j_1 m_1, j_2 m_2 \,|\, jm \rangle \;=\; (-1)^{j_1-j_2+m} \sqrt{2j+1} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} .$$

5.2.d. Calculation of Clebsch-Gordan coefficients

- Recursion relations:

$$j_\pm \, |j_1 j_2, j m_j\rangle \;=\; (j_{1,\pm} \,+\, j_{2,\pm}) \, |j_1 j_2, j m_j\rangle \;=\; \sum_{m_1', m_2'} (j_{1,\pm} \,+\, j_{2,\pm}) \, |j_1 m_1', j_2, m_2'\rangle \, \langle j_1 m_1' j_2, m_2' \,|\, j_1 j_2, j m_j\rangle$$

$$\begin{aligned}
&\sqrt{(j-m)(j+m+1)} \; \langle j_1 m_1, j_2 m_2 \,|\, j, m+1\rangle \\
&\qquad = \sqrt{(j_1 - m_1 + 1)(j_1 + m_1)} \; \langle j_1, m_1 - 1, j_2 m_2 \,|\, jm\rangle \;+\; \sqrt{(j_2 - m_2 + 1)(j_2 + m_2)} \; \langle j_1 m_1, j_2, m_2 - 1 \,|\, jm\rangle
\end{aligned}$$

$$\begin{aligned}
&\sqrt{(j+m)(j-m+1)} \; \langle j_1 m_1, j_2 m_2 \,|\, j, m-1\rangle \\
&\qquad = \sqrt{(j_1 + m_1 + 1)(j_1 - m_1)} \; \langle j_1, m_1 + 1, j_2 m_2 \,|\, jm\rangle \;+\; \sqrt{(j_2 + m_2 + 1)(j_2 - m_2)} \; \langle j_1 m_1, j_2, m_2 + 1 \,|\, jm\rangle \; .
\end{aligned}$$

- Racah's formula:
- Computer-algebra or program libraries:
- Tables and books:

5.2.e. Coupling of three and more angular momenta; re-coupling coefficients

Coupling of three angular momenta:

- Three particles with AM operators $\mathbf{j}_1, \mathbf{j}_2, \mathbf{j}_3$ and eigenfunctions: $\{|j_1 m_1\rangle \, , \; |j_2 m_2\rangle \, , \; |j_3 m_3\rangle\}$

i) Coupling sequence $(\mathbf{j}_1 + \mathbf{j}_2) + \mathbf{j}_3$: $\quad \mathbf{j}_1 + \mathbf{j}_2 = \mathbf{J}_{12}$ and $\mathbf{J}_{12} + \mathbf{j}_3 = \mathbf{J}$

$$|(j_1, j_2)\, J_{12},\; j_3 :\; JM\rangle \;=\; \sum_{m_1,m_2,m_3} \sum_{M_{12}} |j_1 m_1,\; j_2 m_2,\; j_3 m_3\rangle\, \langle j_1 m_1,\; j_2 m_2 \,|\, J_{12} M_{12}\rangle\, \langle J_{12} M_{12},\; j_3 m_3 \,|\, JM\rangle$$

uncoupled basis $|j_1 m_1,\; j_2 m_2,\; j_3 m_3\rangle \;\equiv\; |j_1 m_1\rangle\, |j_2 m_2\rangle\, |j_3 m_3\rangle$

ii) Coupling sequence $\mathbf{j}_1 + (\mathbf{j}_2 + \mathbf{j}_3)$: $\quad \mathbf{j}_2 + \mathbf{j}_3 = \mathbf{J}_{23}$ and $\mathbf{j}_1 + \mathbf{J}_{23} = \mathbf{J}$

$$|j_1,\; (j_2, j_3)\, J_{23} :\; JM\rangle \;=\; \sum_{m_1,m_2,m_3} \sum_{M_{23}} |j_1 m_1,\; j_2 m_2,\; j_3 m_3\rangle\, \langle j_2 m_2,\; j_3 m_3 \,|\, J_{23} M_{23}\rangle\, \langle j_1 m_1,\; J_{23} M_{23}, \,|\, JM\rangle$$

➢ Re-coupling coefficient: ... form a unitary matrix.

$$|j_1\, (j_2, j_3)\, J_{23} :\; JM\rangle \;=\; \sum_{J_{12}} |(j_1, j_2)\, J_{12}\, j_3 :\; JM\rangle\, \langle (j_1, j_2)\, J_{12},\; j_3 :\; JM \,|\, j_1,\; (j_2, j_3)\, J_{23} :\; JM\rangle$$

Calculation of recoupling coefficients:

➢ Explicit expansion in terms of CG coefficients:

$$\langle (j_1, j_2)\, J_{12}\, j_3 :\; JM \,|\, j_1\, (j_2, j_3)\, J_{23} :\; JM\rangle$$

$$= \sum_{M_{12},M_{23}} \sum_{m_1,m_2,m_3} \langle j_1 m_1,\; j_2 m_2 \,|\, J_{12} M_{12}\rangle\, \langle j_2 m_2,\; j_3 m_3 \,|\, J_{23} M_{23}\rangle\, \langle j_1 m_1,\; J_{23} M_{23}, \,|\, JM\rangle\, \langle J_{12} M_{12},\; j_3 m_3 \,|\, JM\rangle$$

$$= \sum_{m_1,M_{12}} \langle j_1 m_1,\; j_2, M_{12} - m_1 \,|\, J_{12} M_{12}\rangle\, \langle j_2, M_{12} - m_1,\; j_3, M - M_{12} \,|\, J_{23}, M - m_1\rangle$$

$$\times\; \langle j_1 m_1,\; J_{23}, M - m_1 \,|\, JM\rangle\, \langle J_{12} M_{12},\; j_3, M - M_{12} \,|\, JM\rangle$$

Wigner 6–j symbols:

- Defined from the re-coupling of three angular momenta:

$$\begin{Bmatrix} j_1 & j_2 & J_{12} \\ j_3 & J & J_{23} \end{Bmatrix} \;=\; (-1)^{j_1+j_2+j_3+J} \; [(2J_{12}+1)(2J_{23}+1)]^{-1/2} \; \langle (j_1, j_2)\, J_{12}\, j_3 : \; JM \,|\, j_1\, (j_2, j_3)\, J_{23} : \; JM \rangle \, .$$

- Non-zero only, if all triangular rules are fullfilled:

$$\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix} \neq 0 \qquad \Longleftrightarrow \qquad \delta(a,b,c) \;=\; \delta(a,e,f) \;=\; \delta(d,b,f) \;=\; \delta(d,e,c) \;=\; 1$$

Coupling of four angular momenta:

- Four particles with AM operators $\mathbf{j}_1,\, \mathbf{j}_2,\, \mathbf{j}_3,\, \mathbf{j}_4$ and eigenfunctions: $\{|j_1 m_1\rangle\, ,\, |j_2 m_2\rangle\, ,\, |j_3 m_3\rangle\, ,\, |j_4 m_4\rangle\}$
- Two coupling sequences:

$$\mathbf{j}_1 + \mathbf{j}_2 \;=\; \mathbf{J}_{12} \;\; \text{and} \;\; \mathbf{j}_3 + \mathbf{j}_4 \;=\; \mathbf{J}_{34} \;\; \text{and} \;\; \mathbf{J}_{12} + \mathbf{J}_{34} \;=\; \mathbf{J} \qquad \Longrightarrow \qquad |(j_1, j_2)\, J_{12},\; (j_3, j_4)\, J_{34} : JM\rangle$$

$$\mathbf{j}_1 + \mathbf{j}_3 \;=\; \mathbf{J}_{13} \;\; \text{and} \;\; \mathbf{j}_2 + \mathbf{j}_4 \;=\; \mathbf{J}_{24} \;\; \text{and} \;\; \mathbf{J}_{13} + \mathbf{J}_{24} \;=\; \mathbf{J} \qquad \Longrightarrow \qquad |(j_1, j_3)\, J_{13},\; (j_2, j_4)\, J_{24} : JM\rangle$$

- Re-coupling coefficients: ... appear again naturally as Fourier coefficients

$$|(j_1, j_2)\, J_{12}\, (j_3, j_4)\, J_{34} : JM\rangle \;=\; \sum |(j_1, j_3)\, J_{13}\, (j_2, j_4)\, J_{24} : JM\rangle \; \langle (j_1, j_3)\, J_{13}\, (j_2, j_4)\, J_{24} : JM \,|\, (j_1, j_2)\, J_{12}\, (j_3, j_4)\, J_{34} : JM\rangle$$

Example (LS vs. jj-coupling:): The 9–j symbols appear frequently in atomic structure theory in transformations between LS- to jj-coupled functions

$$|(\ell_1, s_1)\, j_1\, (\ell_2, s_2)\, j_2 : JM\rangle \;=\; \sum_{LS} [j_1,\, j_2,\, L,\, S]^{1/2} \begin{Bmatrix} \ell_1 & s_1 & j_1 \\ \ell_2 & s_2 & j_2 \\ L & S & J \end{Bmatrix} |(\ell_1, \ell_2)\, L,\, (s_1, s_2)\, S : JM\rangle$$

5.3. Rotations of states and operators

➢ Transform states and operators: ... from unrotated to rotated coordinate frame; $\Sigma\,(x, y, z) \longrightarrow \Sigma'\,(x', y', z')$

$$R_{\mathbf{n}}(\chi) \;=\; \exp\left(-i\chi\, \mathbf{n}\cdot\mathbf{J}\right), \qquad\qquad |jm\rangle' \;=\; R_{\mathbf{n}}(\xi)\; |jm\rangle \;=\; R(\varphi, \vartheta, \chi)\;\; |jm\rangle$$

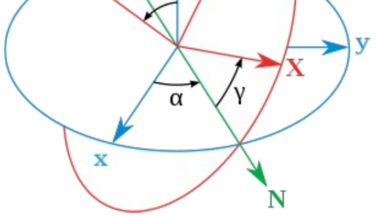
➢ Different views of rotations:

- Active view: Rotation of the quantum mechanical system.
- Passive view: Rotation of the coordinates in counter-direction.

5.3.a. Definition of Euler angles

➢ Rotations:

1. Rotate counterclockwise by angle φ around z-axis
2. Rotate (counterclockwise) by angle ϑ around new y'-axis



3. Rotate (counterclockwise) by angle χ around new z''-axis

- Mathematically:

$$\begin{aligned} R(\varphi,\vartheta,\chi) &= \exp\left(-i\chi\, \mathbf{n}_\chi \cdot \mathbf{J}\right) \cdot \exp\left(-i\vartheta\, \mathbf{n}_\vartheta \cdot \mathbf{J}\right) \cdot \exp\left(-i\varphi\, \mathbf{n}_\varphi \cdot \mathbf{J}\right) \\ &= \exp\left(-i\chi\, J_{z''}\right) \cdot \exp\left(-i\vartheta\, J_{y'}\right) \cdot \exp\left(-i\varphi\, J_z\right) \end{aligned}$$

- Transformation of operators: $A' = U\,A\,U^{-1}$ general rule for any (unitary) rotation, … and which is applied to the operators $\exp\left(-i\vartheta\, J_{y'}\right)$, $\exp\left(-i\chi\, J_{z''}\right)$

$$\left.\begin{aligned} \exp\left(-i\vartheta\, J_{y'}\right) &= \exp\left(-i\varphi\, J_z\right) \cdot \exp\left(-i\vartheta\, J_y\right) \cdot \exp\left(i\varphi\, J_z\right) \\ \exp\left(-i\chi\, J_{z''}\right) &= \exp\left(-i\vartheta\, J_{y'}\right) \cdot \exp\left(-i\chi\, J_z\right) \cdot \exp\left(i\vartheta\, J_{y'}\right) \\ \exp\left(-i\chi\, J_z\right) &= \exp\left(-i\varphi\, J_z\right) \cdot \exp\left(-i\chi\, J_z\right) \cdot \exp\left(i\phi\, J_z\right) \\ R(\varphi,\vartheta,\chi) &= \exp\left(-i\varphi\, J_z\right) \cdot \exp\left(-i\vartheta\, J_y\right) \cdot \exp\left(-i\chi\, J_z\right) \end{aligned}\right\}$$

Important result !

All these operators are now defined in the same unrotated coordinate system.

- Resume: A rotation by the Euler angles is equivalent to a rotation with the angle χ around z-axis, followed by a rotation with the angle ϑ around y-axis, and followed by a rotation with the angle φ around z-axis.

5.3.b. Wigner's rotation matrix

- Wigner's rotation matrix: ... matrix elements of rotation operator; rotation of eigenfunctions:

$$\underbrace{|jm\rangle'}_{\text{rotated coord.}} = R(\varphi,\vartheta,\chi)\ \underbrace{|jm\rangle}_{\text{unrotated coord.}} = \sum_{m'} |jm'\rangle\ \langle jm'\,|R(\varphi,\vartheta,\chi)|\,jm\rangle = \sum_{m'} D^j_{m'm}(\varphi,\vartheta,\chi)\ |jm'\rangle$$

$$\begin{aligned} D^j_{m'm}(\varphi,\vartheta,\chi) &\equiv \langle jm'\,|R(\varphi,\vartheta,\chi)|\,jm\rangle = \langle jm'\,|\exp\left(-i\varphi\,J_z\right)\cdot\exp\left(-i\vartheta\,J_y\right)\cdot\exp\left(-i\chi\,J_z\right)|\,jm\rangle \\ &= e^{-i\varphi\,m'}\cdot d^j_{m'm}(\vartheta)\cdot e^{-i\chi\,m} \end{aligned}$$

- Wigner's small d-matrices:

$$d^j_{m'm}(\vartheta) = \langle jm'\,|\exp\left(-i\vartheta\,J_y\right)|\,jm\rangle$$

Example (Wigner's small $d^{1/2}_{m'm}(\vartheta)$ matrix): For systems with $J = 1/2$, $\exp\left(-i\vartheta\,J_y\right) \to \exp\left(-i\vartheta\,\frac{\sigma_y}{2}\right)$

$$\begin{aligned} \exp\left(-i\vartheta\,\frac{\sigma_y}{2}\right) &= \exp\left[-i\frac{\vartheta}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\right] = I + \frac{\vartheta}{2}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} + \frac{1}{2!}\left(\frac{\vartheta}{2}\right)^2\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}^2 + \ldots \\ &= \left[1 - \frac{1}{2!}\left(\frac{\vartheta}{2}\right)^2 + \ldots\right]\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \left[\frac{\vartheta}{2} - \frac{1}{3!}\left(\frac{\vartheta}{2}\right)^3 + \ldots\right]\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = \cos\frac{\vartheta}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \sin\frac{\vartheta}{2}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \\ &= \begin{pmatrix} \cos\frac{\vartheta}{2} & -\sin\frac{\vartheta}{2} \\ \sin\frac{\vartheta}{2} & \cos\frac{\vartheta}{2} \end{pmatrix} \qquad \text{w.r.t. eigenvectors} \quad |1/2,\,1/2\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix},\ \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{aligned}$$

$$\text{Especially :} \quad \rightsquigarrow \qquad d^{1/2}_{1/2,1/2} = d^{1/2}_{-1/2,-1/2} = \cos\frac{\vartheta}{2}$$

Properties of the rotation matrices:

- Product of two D matrices: ... with the same arguments

$$|j_1 m_1\rangle' \, |j_2 m_2\rangle' \;=\; \sum_{JM} |JM\rangle' \, \langle j_1 m_1, j_2 m_2 \,|\, JM\rangle$$

$$\sum_{m_1', m_2'} D^j_{m_1', m_1}(\varphi, \vartheta, \chi)\, D^j_{m_2', m_2}(\varphi, \vartheta, \chi)\; |j_1 m_1\rangle' \, |j_2 m_2\rangle' \;=\; \sum_{JMM'} |JM\rangle'' \, D^J_{M', M}(\varphi, \vartheta, \chi)\, \langle j_1 m_1, j_2 m_2 \,|\, JM\rangle$$

$$D^j_{m_1'', m_1}(\varphi, \vartheta, \chi)\, D^j_{m_2'', m_2}(\varphi, \vartheta, \chi) \;=\; \sum_{JMM'} D^J_{M', M}(\varphi, \vartheta, \chi)\; \langle j_1 m_1'', j_2 m_2'' \,|\, JM'\rangle \; \langle j_1 m_1, j_2 m_2 \,|\, JM\rangle$$

- Relation to spherical harmonics:

$$D^L_{M,0}(\varphi, \vartheta, \chi) \;=\; \sqrt{\frac{4\pi}{2L+1}}\, Y^*_{LM}(\vartheta, \varphi) \;\neq\; f(\chi)$$

$$D^L_{0,0}(\varphi, \vartheta, \chi) \;=\; P_L(\cos\vartheta) \;\neq\; f(\varphi, \chi), \qquad\qquad D^0_{0,0}(\varphi, \vartheta, \chi) \;=\; 1$$

Example (Classical interpretation of the D-matrix): In the classical vector model, the angular momentum describes a vector with length $\sqrt{j(j+1)}$ and projection m that precesses around the quantization axis.

If we rotate the coordinates, the probability to find this vector with projection m' w.r.t. to the z'-axis is:

$$P \;=\; |\, \langle (jm)' \,|\, jm\rangle \,|^2 \;=\; |\, \left\langle jm' \left| R^+ \right| jm \right\rangle |^2 \;=\; |D^j_{mm'}(\varphi, \vartheta, \chi)|^2 \;=\; |\, d^j_{mm'}(\vartheta)\,|^2$$

5.4. Expressions from Racah's algebra

5.4.a. Wigner n–j symbols

Wigner n–j symbols:

- ➢ Wigner 3–j symbols obey a high symmetry.
- ➢ Racah's expression (1942): ... non-zero value only if the arguments of all factorials are non-negative integers.

$$\begin{aligned}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} &= \delta_{m_1+m_2+m_3,0}\,(-1)^{j_1-j_2-m_3}\;\Delta(j_1,j_2,j_3) \\ &\times\;\left[(j_1-m_1)!\,(j_1+m_1)!\,(j_2-m_2)!\,(j_2+m_2)!\,(j_3-m_3)!\,(j_3+m_3)!\right]^{1/2} \\ &\times\;\sum_l \left[\frac{(-1)^l}{l!\,(j_1+j_2-j_3-l)!\,(j_1-m_1-l)!\,(j_2+m_2-l)!\,(j_3-j_2+m_1+l)!\,(j_3-j_1-m_2+l)!}\right]\end{aligned}$$

$$\Delta(a,b,c) = \left[\frac{(a+b-c)!\,(a-b+c)!\,(-a+b+c)!}{(a+b+c+1)!}\right]^{1/2}$$

- ➢ Symmetry of Wigner 3–j symbols: ... exchange of any two (columns of) angular momenta

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} = (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} = (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \qquad \text{12 classical symmetries}$$

- ➢ Recursion relations for the Wigner3–j symbols: with $J = j_1 + j_2 + j_3$; 4 kinds or recursion in totel.

(i) Halfstep-recursion: ... decreases two j-values by 1/2:

$$[(J+1)(J-2j_1)]^{1/2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

$$= [(j_2+m_2)(j_3-m_3)]^{1/2} \begin{pmatrix} j_1 & j_2-1/2 & j_3-1/2 \\ m_1 & m_2-1/2 & m_3+1/2 \end{pmatrix} - [(j_2-m_2)(j_3+m_3)]^{1/2} \begin{pmatrix} j_1 & j_2-1/2 & j_3-1/2 \\ m_1 & m_2+1/2 & m_3-1/2 \end{pmatrix}.$$

(ii) Recursion due to Louck (1958): ... another 1/2-step recursion

$$(j_2+m_2)^{1/2}\,(2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_2-m_3 & -m_2 & m_3 \end{pmatrix}$$

$$= -\,[(J-2j_1)(J+1)(j_3+m_3)]^{1/2} \begin{pmatrix} j_1 & j_2-1/2 & j_3-1/2 \\ m_2-m_3 & -m_2+1/2 & m_3-1/2 \end{pmatrix}$$

$$-\,[(J-2j_3)(J-2j_2+1)(J+1)(j_3-m_3+1)]^{1/2} \begin{pmatrix} j_1 & j_2-1/2 & j_3+1/2 \\ m_2-m_3 & -m_2+1/2 & m_3-1/2 \end{pmatrix}.$$

Wigner 6–j and 9–j symbols:

- Wigner 6–j: ... recoupling of three angular momenta.
- Symmetry of the Wigner 6–j symbols: ... 24 symmetric forms
- Wigner 9–j: ... recoupling of four angular momenta; zero unless the arguments in each row and column satisfy the triangular relation.

- Symmetry of the Wigner 9–j symbols: ... 72 symmetric forms

$$\begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{Bmatrix} = \sum_j (-1)^{2j} \begin{Bmatrix} j_{11} & j_{21} & j_{31} \\ j_{32} & j_{33} & j \end{Bmatrix} \begin{Bmatrix} j_{12} & j_{22} & j_{32} \\ j_{21} & j & j_{23} \end{Bmatrix} \begin{Bmatrix} j_{13} & j_{23} & j_{33} \\ j & j_{11} & j_{12} \end{Bmatrix} .$$

5.4.b. Sum rules of the Wigner n–j symbols

- Sum rules for one 3–j symbol: ... with $[a, b, ...] = (2a+1)(2b+1)...$; Varshalovich *et al.* (1988, eq. 12.1.2) ≡ Var(12.1.2)

$$\sum_m (-1)^{j-m} \begin{pmatrix} j & j & j' \\ m & -m & m' \end{pmatrix} = [j]^{1/2}\, \delta_{m'0}\, \delta_{j'0}$$

- Sum rules for one 6–j symbol: ... Var(12.2.3–4).

$$\sum_X [X] \begin{Bmatrix} a & b & X \\ a & b & c \end{Bmatrix} = (-1)^{2c}\, \delta(a, b, c), \qquad \sum_X (-1)^{a+b+X}\, [X] \begin{Bmatrix} a & b & X \\ b & a & c \end{Bmatrix} = [a, b]^{1/2}\, \delta_{c0}$$

- Sum rules for two 3–j symbols: ... orthogonality

$$\sum_{j_3, m_3} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta(m_1, m_1')\, \delta(m_2, m_2')$$

$$\sum_{m_1, m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \frac{\delta(j_3, j_3')\, \delta(m_3, m_3')}{(2j_3+1)}\, \delta(j_1, j_2, j_3)$$

- Sum rules for two 3–j symbols & one 6–j symbol: ... Var(12.1.5).

$$\sum_{l_3,n_3} (-1)^{j_3+l_3+m_1+n_1}\ [l_3] \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix} \begin{pmatrix} l_1 & j_2 & l_3 \\ n_1 & m_2 & n_3 \end{pmatrix} \begin{pmatrix} j_1 & l_2 & l_3 \\ m_1 & n_2 & -n_3 \end{pmatrix} = \sum_{m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & j_3 \\ n_1 & n_2 & -m_3 \end{pmatrix}$$

- Sum rules for three 6–j symbols: ... from Biedenharn and Elliot; with $R = a+b+c+d+e+f+p+q+r$

$$\sum_{X} (-1)^{R+X}\ [X] \begin{Bmatrix} a & b & X \\ c & d & p \end{Bmatrix} \begin{Bmatrix} c & d & X \\ e & f & q \end{Bmatrix} \begin{Bmatrix} e & f & X \\ b & a & r \end{Bmatrix} = \begin{Bmatrix} p & q & r \\ e & a & d \end{Bmatrix} \begin{Bmatrix} p & q & r \\ f & b & c \end{Bmatrix}$$

- Sum rules for one 6–j symbol & three 9–j symbols: ... Var(12.2.44)

$$\sum_{XYZ} [X,Y,Z] \begin{Bmatrix} a & b & X \\ c & d & Y \\ t & s & r \end{Bmatrix} \begin{Bmatrix} a & b & X \\ h & j & q \\ e & f & Z \end{Bmatrix} \begin{Bmatrix} k & l & p \\ c & d & Y \\ e & f & Z \end{Bmatrix} \begin{Bmatrix} p & q & r \\ X & Y & Z \end{Bmatrix} = \begin{Bmatrix} k & l & p \\ h & j & q \\ t & s & r \end{Bmatrix} \begin{Bmatrix} k & h & t \\ a & c & e \end{Bmatrix} \begin{Bmatrix} l & j & s \\ b & d & f \end{Bmatrix}$$

5.4.c. Other symbols and functions from the theory of AM

Symbol	Designation
$W(abcd;ef)$	Racah's W coefficient
$d^{j}_{mm'}(\beta)$	Wigner $d^{j}_{mm'}(\beta)$ rotation matrix
$D^{j}_{mm'}(\alpha,\beta,\gamma)$	Wigner's $D-$function
$U^{j}_{mm'}(\omega;\Theta,\Phi)$	Rotation matrix $U(\omega)$
$Y_{lm}(\vartheta,\varphi)$	Spherical harmonic
$\{\mathbf{Y}_{l_1}(\vartheta_1,\varphi_1)\otimes\mathbf{Y}_{l_2}(\vartheta_2,\varphi_2)\}_{LM}$	Bipolar spherical harmonic
$\big\{\mathbf{Y}_{l_1}(\vartheta_1,\varphi_1)\otimes\{\mathbf{Y}_{l_2}(\vartheta_2,\varphi_2)\otimes\mathbf{Y}_{l_3}(\vartheta_3,\varphi_3)\}_{l_{23}}\big\}_{LM}$	Tripolar spherical harmonic
$\mathbf{Y}^{l}_{jm}(\vartheta,\varphi)$	Vector spherical harmonic
$\Omega^{l}_{jm}(\vartheta,\varphi)$	Spinor spherical harmonic
$Y^{ls}_{jm}(\vartheta,\varphi)$	Tensor spherical harmonic
$\langle l_a m_a \,\vert l_b m_b\vert\, l_c m_c\rangle$	Gaunt coefficient
$C^{k}(l_a,m_a;l_b,m_b)$	Condon–Shortley coefficient
$\mathbf{H}_{l,\{\mu\}}$ †	Hyperspherical harmonic
$\big(\gamma\ \alpha Q\Gamma\,\vert\vert\vert\, a^{(q\gamma)}\,\vert\vert\vert\,\gamma\ \alpha' Q'\Gamma'\big)$	Reduced coefficient of fractional parentage
...	

Further remarks on the quantities above:

- Spherical harmonics: The $Y_{lm}(\theta,\phi)$ functions form a complete and orthonormal set on the unit sphere, and are therefore widely used in classical and quantum physics; the spherical harmonics frequently appear in the representation of wave functions for a wide range of physical systems, in the evaluation of the corresponding (quantum) matrix elements, and at many places elsewhere.

- Bipolar and tripolar spherical harmonics: When defined as *irreducible tensors*, linear combinations of products of p spherical harmonics often form a convenient basis to represent (distribution) functions in physics which depend on p vector directions. For this purpose, for instance, the *bipolar spherical harmonics* are defined as the irreducible tensor product of two spherical harmonics with different arguments (Varshalovich *et al.*, 1988)

$$\{\mathbf{Y}_{l_1}(\vartheta_1, \varphi_1) \otimes \mathbf{Y}_{l_2}(\vartheta_2, \varphi_2)\}_{LM} \;=\; \sum_{m_1 m_2} \langle l_1 m_1,\, l_2 m_2 \,|\, LM \rangle \; Y_{l_1 m_1}(\vartheta_1, \varphi_1)\, Y_{l_2 m_2}(\vartheta_2, \varphi_2)\;.$$

For different $l_1,\; l_2,\; L,$ and M, the bipolar harmonics form a complete and orthonormal set

$$\int\!\!\int d\Omega_1 d\Omega_2 \; \{\mathbf{Y}_{l_1}(\Omega_1) \otimes \mathbf{Y}_{l_2}(\Omega_2)\}^*_{LM} \; \left\{\mathbf{Y}_{l'_1}(\Omega_1) \cdot\cdot \mathbf{Y}_{l'_2}(\Omega_2)\right\}_{L'M'} \;=\; \delta_{l_1 l'_1}\, \delta_{l_2 l'_2}\, \delta_{LL'}\, \delta_{MM'}$$

of functions which depend on two unit vectors, say, $\mathbf{n_1}$ and $\mathbf{n_2}$, respectively. A similar definition also applies for the *tripolar spherical harmonic*

$$\begin{aligned} &\left\{\mathbf{Y}_{l_1}(\vartheta_1, \varphi_1) \otimes \{\mathbf{Y}_{l_2}(\vartheta_2, \varphi_2) \otimes \mathbf{Y}_{l_3}(\vartheta_3, \varphi_3)\}_{l_{23}}\right\}_{LM} \\ &\quad = \sum_{m_1, m_2, m_3, m_{23}} \langle l_1 m_1,\, l_{23} m_{23} \,|\, LM \rangle \; \langle l_2 m_2,\, l_3 m_3 \,|\, l_{23} m_{23} \rangle \; Y_{l_1 m_1}(\vartheta_1, \varphi_1)\, Y_{l_2 m_2}(\vartheta_2, \varphi_2)\, Y_{l_2 m_2}(\vartheta_3, \varphi_3)\;, \end{aligned}$$

where, however, different coupling sequences are possible and have to be taken into account in applications.

- Tensor spherical harmonics: Following the standard coupling of two angular momenta, the tensor spherical harmonics are constructed as the product of the spherical harmonics $Y_{lm}(\vartheta, \varphi)$ (eigenfunctions of $\mathbf{l}^2$ and l_z) and the spin function χ_{sm} (eigenfunctions of $\mathbf{s}^2$ and s_z)

$$Y^{ls}_{jm}(\vartheta, \varphi) \;\equiv\; \{\mathbf{Y}_l \otimes \chi_s\}_{jm} \;=\; \sum_{m_l, m_s} Y_{l m_l}(\vartheta, \varphi)\, \chi_{s m_s} \; \langle l m_l,\;\; s m_s \,|\, jm \rangle$$

so that a irreducible tensor of rank j is obtained. While the l quantum number always occurs as a (nonnegative) integer, the indices j and s are both either integers or half-integers. For given j and s, the (orbital) angular momentum l can take the values $|j-s|,\; |j-s|+1,\; ...,\; j+s$; the allowed values of m are $-j,\; -j+1,\; ...,\; j$. Similar to the spherical harmonics, which form a complete set of functions on the unit sphere, the tensor spherical harmonics $Y^{ls}_{jm}(\vartheta, \varphi)$ form a complete and orthonormal set of functions for the expansion of rank s spinors with the domain of arguments $0 \,\le\, \vartheta \,\le\, \pi,\; 0 \,\le\, \varphi \,\le\, 2\pi$.

According to different definitions of the spin functions such as in a cartesian, spherical, or helicity basis representation, different components of the tensor spherical harmonics need to be distinguished.

- Spinor spherical harmonics: For the case $s = 1/2$, the tensor harmonics are also called spinor spherical harmonics

$$\Omega^{l}_{jm}(\vartheta, \varphi) \;\; \equiv \;\; Y^{l\frac{1}{2}}_{jm}(\vartheta, \varphi)$$

which are eigenfunctions of the operators $\mathbf{j}^2$, j_z, $\mathbf{l}^2$ and $\mathbf{s}^2$, where $\mathbf{s}$ is assumed to be the spin operator for $s = 1/2$. As for the tensor spherical harmonics, a number of different components need to be distinguished, including contravariant and covariant tensor components.

- Vector spherical harmonics: The other *special* case of tensor spherical harmonics are those for spin $s = 1$, i.e. the vector spherical harmonics

$$\mathbf{Y}^{l}_{jm}(\vartheta, \varphi) \;\; \equiv \;\; Y^{l1}_{jm}(\vartheta, \varphi) \, .$$

A large deal of representations, integrals, and algebraic relations are known for the vector sphercial harmonics which play an crucial role, for instance, in the quantum theory of light and in laser-matter interactions.

5.4.d. Tools for dealing with Racah expressions

- Structure of a Racah expression: ... as they typically appear in Racah's algebra.

$$\mathrm{Racahexpr} \;\; := \;\; \sum_{j_1, j_2, l_1, \ldots} (-1)^{2j_1 - j_2 + \ldots} \; j_1^{3/2} \; [j_2] \ldots \begin{pmatrix} \cdot & \cdot & j_1 \\ \cdot & \cdot & \cdot \end{pmatrix} \begin{pmatrix} j_1 & j_2 & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix} \begin{Bmatrix} \cdot & j_3 & \cdot \\ j_1 & \cdot & \cdot \\ J & \cdot & j_2 \end{Bmatrix} \ldots$$

$$\times \int d\Omega_1 \, Y_{l_1 m_1}(\Omega_1) \, Y_{l_2 m_2}(\Omega_2) \int d\beta \; d^{j_3}_{p_3 q_3}(\beta) \; d^{j_4}_{p_4 q_4}(\beta') \; \ldots$$

5.5. Irreducible tensor operators. Wigner-Eckardt theorem

5.5.a. Irreducible tensor operators

Reminder & definition:

- Transformation of irreducible tensor operator (components):

$$
\begin{aligned}
|jm\rangle' &= \sum_{m'} D^{j}_{m'm}(\varphi,\vartheta,\chi)\; |jm'\rangle && \text{rotation of eigenstate} \\
T^{'} &= R_{\mathbf{n}}(\beta)\, T\, R_{\mathbf{n}}^{-1}(\beta) && \text{rotation of general operator} \\
T^{'}_{kq} &:= \sum_{q'} D^{k}_{q'q}(\varphi,\vartheta,\chi)\, T_{kq'}
\end{aligned}
$$

- An irreducible tensor operator is a set of $2k+1$ functions (tensor components) that transform like the spherical harmonics above.

Example (Spherical scalar operators, T_{00}): ... just single component, invariant under rotations.

$$T^{'}_{00} = \underbrace{D^{0}_{00}(\varphi,\vartheta,\chi)}_{1}\, T_{00} = T_{00}$$

Example (Spherical vector operators, T_{1q} :): $q = 0, \pm 1$ ... three vector components.

$$T^{'}_{1\,q} = \sum_{q'} D^{1}_{q'q}(\varphi,\vartheta,\chi)\, T_{1\,q'}$$

Every cartesian vector $\mathbf{A} = (A_x, A_y, A_z)$ can be re-written as spherical tensor of rank one with irreducible components

$$T_{11} = -\frac{A_x + iA_y}{\sqrt{2}}, \qquad T_{10} = A_z, \qquad T_{1,-1} = \frac{A_x - iA_y}{\sqrt{2}} \qquad \text{since}$$

$$T_{1q} = |\mathbf{A}| \sqrt{\frac{4\pi}{3}} \cdot Y_{1q}(\vartheta, \varphi), \qquad \left(Y_{\ell m}(\bar{\vartheta}, \bar{\varphi})\right)' = \sum_{m'} D^{\ell}_{m'm}(\varphi, \vartheta, \chi) \; Y_{\ell m}(\bar{\vartheta}, \bar{\varphi}).$$

5.5.b. Wigner-Eckart theorem

ME of irreducible tensor operators:

- States of well-defined AM: $|aJ_aM_a\rangle$, $|bJ_bM_b\rangle$, a, b ... all QN that are required to specify the state uniquely.
- Quantum transition amplitudes:

$$\langle aJ_aM_a \,|\, T_{KQ} \,|\, bJ_bM_b\rangle = \left(\langle aJ_aM_a \,|\, T_{KQ} \,|\, bJ_bM_b\rangle\right)'^{\text{ ... rotated}} \equiv M \qquad \text{... invariant}$$

$$= \sum_{m_a m_b q} D^{J_a\,*}_{m_a M_a}(\varphi, \vartheta, \chi)\, D^{K}_{qQ}(\varphi, \vartheta, \chi)\, D^{J_b}_{m_b M_b}(\varphi, \vartheta, \chi) \;\langle aJ_am_a \,|\, T_{Kq} \,|\, bJ_bm_b\rangle \qquad \text{... product of 2 D}'\text{s}$$

$$= \sum_{bJ_bM_b} D^{J_a\,*}_{m_a M_a}(\varphi, \vartheta, \chi) \sum_{prL} \langle J_bm_b, Kq \,|\, Lp\rangle \;\langle J_bM_b, KQ \,|\, Lr\rangle \; D^{L}_{pr}(\varphi, \vartheta, \chi) \;\langle aJ_am_a \,|\, T_{Kq} \,|\, bJ_bm_b\rangle$$

Wigner-Eckart theorem & reduced ME:

- Wigner-Eckart theorem: Definition of reduced ME:

$$\langle a J_a \,\|\, T_K \,\|\, b J_b \rangle \;:=\; \frac{1}{\sqrt{2J+1}} \sum_{m_a m_b q} \langle J_b m_b, K q \,|\, J_a m_a \rangle \; \langle a J_a m_a \,|\, T_{Kq} \,|\, b J_b m_b \rangle$$

$$\langle a J_a M_a \,|\, T_{KQ} \,|\, b J_b M_b \rangle \;=\; \frac{1}{\sqrt{2J+1}} \langle J_b M_b, K Q \,|\, J_a M_a \rangle \; \langle a J_a \,\|\, T_K \,\|\, b J_b \rangle$$

  Wigner-Eckardt theorem shows that the matrix element $\langle a J_a \,\|\, T_K \,\|\, b J_b \rangle$ can always be factorized into a Clebsch-Gordan coefficient (the geometrical part) and a reduced matrix element $\langle a J_a \,\|\, T_K \,\|\, b J_b \rangle$ which does not depend on the magnetic QN M_a, M_b, Q

- Wigner-Eckart decomposition of ME = radial × effective interaction part.

Blackboard example (Eletric-dipole ME:):

5.6. Problems

See problems.

6. Interactions of atoms in weak (light) fields

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

6.1. Radiative transitions

6.1.a. Einstein's A and B coefficients

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

Spectral energy density:

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

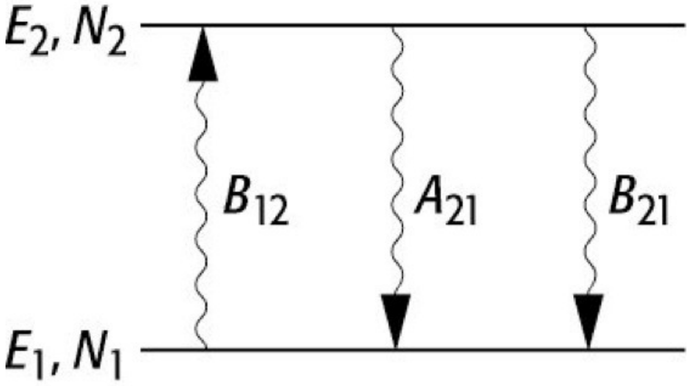


Figure 6.1.: Model of the induced and spontaneous processes.

Einstein's argumentation and coefficients:

- Einstein's rate equation:

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

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

- No field, $\rho(\omega) = 0$:

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

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

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

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

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

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

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

- Generalized field-free case:

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

- Ratio $A_{ji} : B_{ji} : B_{ij}$:

Thermal equilibrium:

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

Planck's black-body radiation

➢ Power density radiation law is a product of three quantities

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

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

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

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

➢ Spontaneous emission increases rapidly with the frequency of the modes.

Some additions:

➢ Mean occupation number of mode ω also describes the ratio of the induced and sponteneous emission probabilities

$$\langle n_{ij}\rangle = \frac{B_{21}W(\omega)}{A_{21}} = \frac{P_{21}^{induced}}{P_{21}^{spontaneous}}$$

➢ Lamps at thermodynamical equilibrium and typical temperatures: $\langle n\rangle \ll 1$.

Lasers, far away from thermodynamical equilibrium: $\langle n\rangle \gtrsim 1$.

Line-width contributions in atomic spectroscopy

- For a time-dependent function $\psi(t) \propto e^{-\frac{\Gamma t}{2}} \cos(\omega_o t)$ with damping constant $\Gamma = 1/\tau$ and lifetime τ, the Fourier transform is given by

$$\phi(\omega) \propto \frac{\frac{\Gamma}{4}}{(\omega - \omega_o)^2 + \frac{\Gamma}{4}} \qquad \text{Lorentz shape}$$

- Natural linewidth: Energy uncertainty $\Delta E = \hbar\omega = \hbar/\tau$ of an excited level due to its finite lifetime; the natural widths gives rise to a Lorentzian line shape.

- Doppler width: Relative frequency shift due to the thermic motion in the direction towards the detector $\frac{\Delta\omega}{\omega} = \frac{v_z}{c}$; the Doppler shift leads to a Gaussian line shape.

  For isotopes with mass number A, the Doppler widths is given by

$$\frac{\Delta\omega}{\omega} = 7 \cdot 10^{-7} \left(\frac{T[K]}{A}\right)^{1/2} .$$

- Collisional broadening: Shift in the transition frequency due to the interaction with other atoms in the gas; extrapolation of linewiths towards *zero* pressure; line forms still Lorentzian with line widths $\Delta\omega = 1/\tau_{\text{coll}}$, with the mean collision time τ_{coll}.

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

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

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

6.1.b. Transition amplitudes and probabilities

$$\begin{array}{ccc} \text{radiation field} & \text{atom -- field interaction} & \text{atomic structure} \\ (\text{time -- dependent}) & \Longleftrightarrow & \text{and motion} \end{array}$$

Time-dependent perturbation theory:

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

Limitations of the semi-classical description:

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

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

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

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

$$\mathbf{B} = \mathrm{rot}\,\mathbf{A}$$

$$(\phi, \mathbf{A}) \quad ...\ 4 - \text{comp. vector potential}$$

$$= \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{e}{2m}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2}{2m}\mathbf{A}^2 - e\phi$$

$$= H_{\text{atom}} + H_{\text{atom}-\text{field interaction}}$$

$$= H_o + H'$$

Special case: Superposition of plane waves

$$\phi = 0$$

$$\mathbf{A} = \mathbf{A}_-\,e^{i\,(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \mathbf{A}_+\,e^{i\,(\mathbf{k}\cdot\mathbf{r}+\omega t)}$$

$$\mathrm{div}\,\mathbf{A} = 0 \qquad \text{Coulomb gauge;} \qquad [\mathbf{p},\,\mathbf{A}] = 0$$

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

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

Reminder on time-dependent perturbation theory:

- ➣ Ansatz:

$$\Psi(t) \;=\; \sum_n c_n(t)\,\psi_n(\mathbf{r})\,e^{-\frac{i}{\hbar}E_n t}$$

$$H_o\,\psi_n(\mathbf{r}) \;=\; E_n\,\psi_n(\mathbf{r}) \qquad \text{stationary states of the atom}$$

- ➣ Atom at $t = 0$ in initial state $|i\rangle$:

$$c_i(t=0) \;=\; 1\,, \qquad c_{n\neq i}(t=0) \;=\; 0$$

Absorption probability:

- ➣ Fermi's Golden rule gives rise to

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

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

- ➣ Non-degenerate case: $B_{ij} \;=\; B_{ji}$ (microscopic reversible)
- ➣ Many-electron atoms:

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

6.2. Electric-dipole interactions and higher multipoles

6.2.a. Electric-dipole approximation

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

➥ visible light: $\lambda \approx 500$ nm ... 1000-10000 atomic radii

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

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

Evaluation of the Einstein A coefficients:

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

$$\langle j\,|p_x|\,i\rangle = \langle j\,|m\dot{x}|\,i\rangle = \frac{im}{\hbar}\,\langle j\,|\,[H_o,\,x]\,|\,i\rangle$$

$$\left\langle j \left| \frac{e}{m}\,p_x \right| i \right\rangle = \frac{i}{\hbar}\,(E_j - E_i)\,\langle j\,|\,e\,x\,|\,i\rangle$$

$$B_{ij} = \frac{\pi}{\epsilon_o\,\hbar^2}\,|\langle j\,|\,e\,x\,|\,i\rangle|^2 \qquad \text{x} - \text{polarization}$$

$$= \frac{1}{3}\cdot\frac{\pi}{\epsilon_o\,\hbar^2}\,|\langle j\,|e\,\mathbf{r}|\,i\rangle|^2 \qquad \text{unpolarized}$$

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

- Spontaneous decay for non-degenerate levels:

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

- Especially, optical transitions: $A \;\sim\; 10^8/s$ or $\tau \;=\; \frac{1}{A} \;=\; 10^{-8}\,s$

spontaneous decay dominates

Radio frequencies: Spontaneous decay negligible, since $A \;\sim\; \omega^3$.

- Spontaneous decay for degenerate levels $|jm\rangle$:

$$A_{ji} \;=\; \frac{1}{3}\,\frac{\omega_{ij}^3}{\pi\,c^3\,\epsilon_o\hbar}\;\sum_{m_i}\;|\langle jm_j\,|\,e\mathbf{r}\,|\,im_i\rangle|^2 \qquad \neq\; f(m_j)$$

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

Alternative representation of the Einstein A coefficients:

- Line strength: is more symmetric

$$S_{ji} \;=\; S_{ij} \;=\; \sum_{m_i,m_j}|\langle jm_j\,|\,e\mathbf{r}\,|\,im_i\rangle|^2$$

$$A_{ji} \;=\; \frac{1}{3}\,\frac{\omega_{ij}^3}{\pi\,c^3\,\epsilon_o\,\hbar}\;\frac{S_{ji}}{g_j}$$

➢ Oscillator strength:

$$\begin{aligned} A_{ji} &= \frac{1}{2\pi\epsilon_o}\,\frac{e^2\,\omega_{ij}^2}{mc^3}\,f_{ji} \\ f_{ji} &= -\,\frac{2}{3}\,\frac{m\hbar\,\omega_{ij}}{e^2\,\hbar^2}\,\frac{S_{ji}}{g_j} \\ f_{ij} &= -\,\frac{g_j}{g_i}\,f_{ji} \end{aligned}$$

➢ Sum rule:

$$\sum_{i<j,\;k>j} (\underset{<\,0}{f_{ji}} \quad + \quad \underset{>\,0}{f_{jk}}) \;=\; N \qquad \text{... number of electrons}$$

6.2.b. Selection rules and discussion

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

Electron temperature T_e:

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

- $T_e \approx 10^4\ K \quad \rightsquigarrow \quad kT_e \sim 1$ eV
- $T_e \approx 300\ K \quad \rightsquigarrow \quad kT_e \sim 1/40$ eV

- $T_e \;\rightarrow\; \infty$

Selection rules for bound-bound transitions:

➢ Matrix elements between bound states: $\langle j m_j \,|\, e\mathbf{r} \,|\, i m_i \rangle$

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

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

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

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

➢ The electric-dipole operator is a rank-1 operator.

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

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

(i) Calculation of intensities ⇝ evaluation of radial integrals.

(ii) Angular part of the intensity that can be obtained analytically within the central-field approximation; this is true even for many-electron atoms.

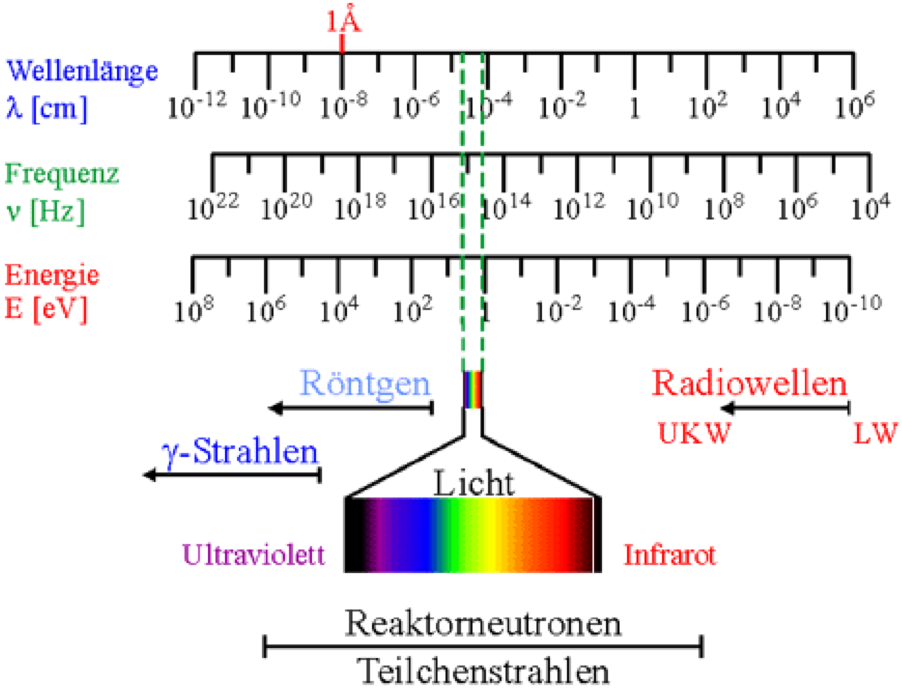


Figure 6.2.: The visible light covers only a very restricted range of the entire electromagnetic spectrum, which is shown here over a range 18 decades. From www.helmholtz-berlin.de

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

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

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

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

$$\boldsymbol{\mu} \;=\; \frac{e\,\hbar}{2m}\,\mathbf{l} \;=\; \mu_{\mathrm{B}}\,\mathbf{l}$$ ... magnetic moment of electron

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

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

Intensity ratio for hydrogen-like wave functions:

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

6.2.d. Dipole transitions in many-electron atoms

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

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

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

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

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

spherical components of the (many-electron) dipole operator

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

Spherical tensor operators:

- ➢ Decomposition of all operators into tensor components that transform like the spherical harmonics, and for which the evaluation of the (many-electron) matrix elements is much simpler.
- ➢ Such tensor operators are based on the representation of $\mathbf{r} = x\,\mathbf{e}_x + y\,\mathbf{e}_y + z\,\mathbf{e}_z$ into spherical unit vectors

$$\mathbf{r} = r_1\,\mathbf{e}_1 + r_0\,\mathbf{e}_0 + r_{-1}\,\mathbf{e}_{-1} \qquad \left[\begin{array}{lcl} \mathbf{e}_0 & = & \mathbf{e}_z \\ \mathbf{e}_{\pm 1} & = & \frac{1}{\sqrt{2}}\,(\mathbf{e}_x \pm i\mathbf{e}_y) \end{array} \right]$$

- ➢ The use of the (known) symmetries of wave functions and of spherical tensors is often referred to as applying the techniques of Racah's algebra.
- ➢ Mathematically, this formalism can be built purely algebraically upon the commutators of the components of the angular momentum operator.

Gauge forms of the transition probabilities:

- The dipole matrix element can be re-written by means of various operator identities; for example:

$$[\mathbf{r}_j,\, H] \;=\; \frac{1}{2m}\,[\mathbf{r}_j,\, \mathbf{p}_j^2] \;=\; \frac{ih}{m}\,\mathbf{p}_j \qquad\qquad \forall\, j$$

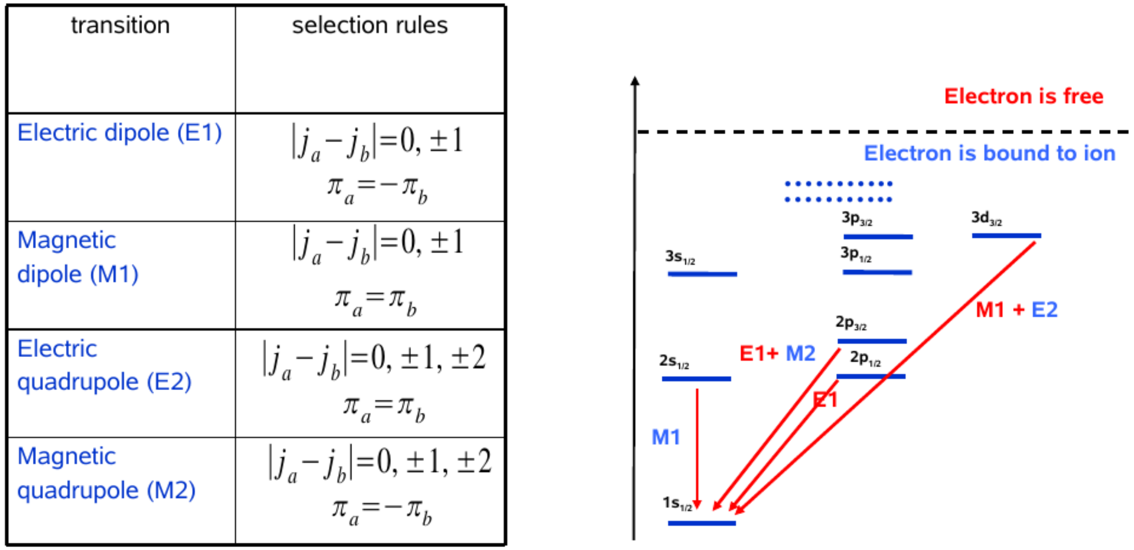
$$\langle \psi' \,|[\mathbf{r}_j,\, H]|\, \psi\rangle \;=\; (E \,-\, E')\; \langle \psi' \,|\, \mathbf{r}_j |\, \psi\rangle \;=\; \frac{ih}{m}\; \langle \psi' \,|\, \mathbf{p}_j |\, \psi\rangle \;.$$

- Length gauge: $\langle \gamma' J' M' \,|\, \sum_i \,\mathbf{r}_i \,|\, \gamma J M\rangle$
- Velocity gauge: $\frac{2}{E - E'}\; \langle \gamma' J' M' \,|\, \sum_i \,\boldsymbol{\nabla}_i \,|\, \gamma J M\rangle$
- Acceleration gauge: $\frac{2}{(E - E')^2}\; \langle \gamma' J' M' \,|\, \sum_i \,\boldsymbol{\nabla}_i\, V(r_i) \,|\, \gamma J M\rangle$

Selection rules for electric-dipole radiation:

- $\Delta J \;=\; J' \,-\, J \;=\; 0,\, \pm 1$ ... and where $J \;=\; J' \;=\; 0$ is forbidden;
- $\Delta M \;=\; 0,\, \pm 1$ ... vector character of the electric-dipole operator.
- ψ and ψ' must differ in their parity.
- These three selection rules above are quite general; in the non-relativistic limit of pure LS-coupling, two further rules apply in addition:

$$\Delta L \;=\; 0,\, \pm 1 \quad \text{(but not} \quad L \;=\; L' \;=\; 0) \qquad\qquad \Delta S \;=\; 0\,.$$



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

Figure 6.3.: Left: Selection rules for higher multipole transitions, and where $\pi_{a,b}$ refer to the parities of the initial and final states. Although the notation refers here for one-electron atoms, the same rules also apply for many-electron atoms and ions. Right: Selective multipole transitions are shown for hydrogen-like ions.

6.2.e. Multipol expansions of the radiation field

Multipoles radiation

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

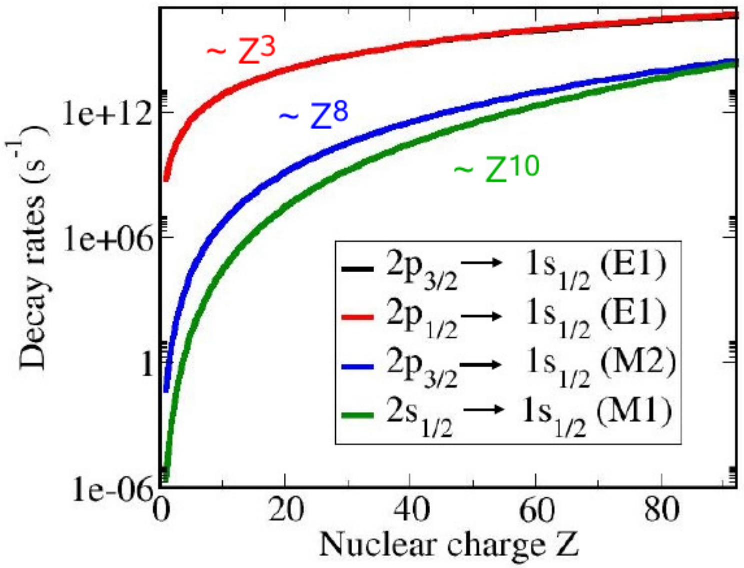


Figure 6.4.: Decay rates and scaling of the high multipole transitions with the nuclear charge, Z, for hydrogen-like ions.

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

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

- Selection rules:

$$\begin{array}{rcll} |J_a - J_b| \le & L & \le J_a + J_b & \delta(J_a, L, J_b) \\ \pi & = & (-1)^L & \text{electric multipoles} \\ \pi & = & (-1)^{L+1} & \text{magnetic multipoles} \end{array}$$

- For low-Z, all high(er) multipole transition are negligible compared to the leading electric dipole (E1) term.
- For heavy and superheavy elements, the high multipoles become rapidly important with nuclear charge Z.

6.3. Photo excitation and photo emission processes

6.3.a. Photo excitation and fluorescence

- Notation: $\hbar\omega + A \longrightarrow A^* \longrightarrow A^{*'} + \hbar\omega'$.
- Photoexcitation is often discussed together with photoionization or even photofragmentation (for molecules).
- Fluorescence: spontaneous photon emission that results in some lower-lying level of the atoms or ions.

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

- Left- and right-circular light are often called also $\sigma^\pm$ light, in contrast to the linear-polarized π-light.
- If the atom is aligned along the z-axis (quantization axis), the π-light is emitted in the $x - y$ plane, oscillates predominantly along the z-axis and combines substates with $\Delta\, m = 0$.

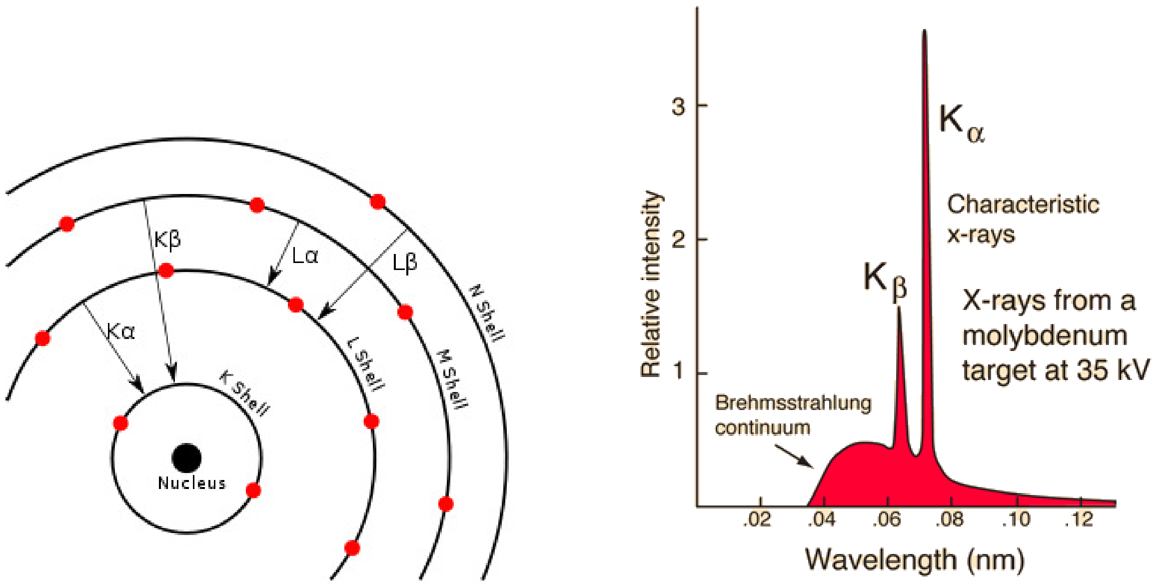


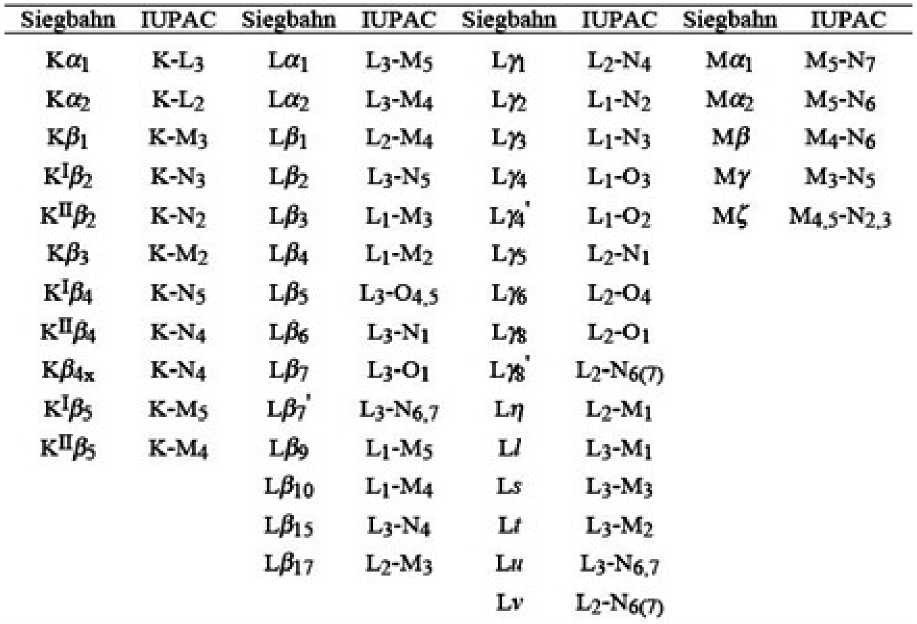
Figure 6.5.: Left: Characteristic x-rays are emitted from heavy elements when their electrons make transitions between the lower atomic energy levels. Right: The characteristic $\mathrm{K}_{\alpha,\beta}$ x-ray emission appears as two sharp peaks in the photon spectra following the production of a vacancy in the K-shell ($n = 1$). The background in the emitted x-ray spectra arises from Compton and bremsstrahlung radiation. From en.wikipedia.org/wiki and

6.3.b. Characteristic x-ray radiation

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

- X-ray fluorescence following electron impact:

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



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

Figure 6.6.: While the x-ray (analytical) community still largely uses the so-called Siegbahn notation, the IUPAC notation is consistent with the notation used for Auger electron spectroscopy, though the latter one is slightly more cumbersome. From nau.edu/cefns/labs.

- Mosley's law: The energies of the characteristic radiation and of the absorption edges follow (very) approximately Balmer's rule:

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

where $Z_{\text{eff}} = Z - S$, and with the screening number S.

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

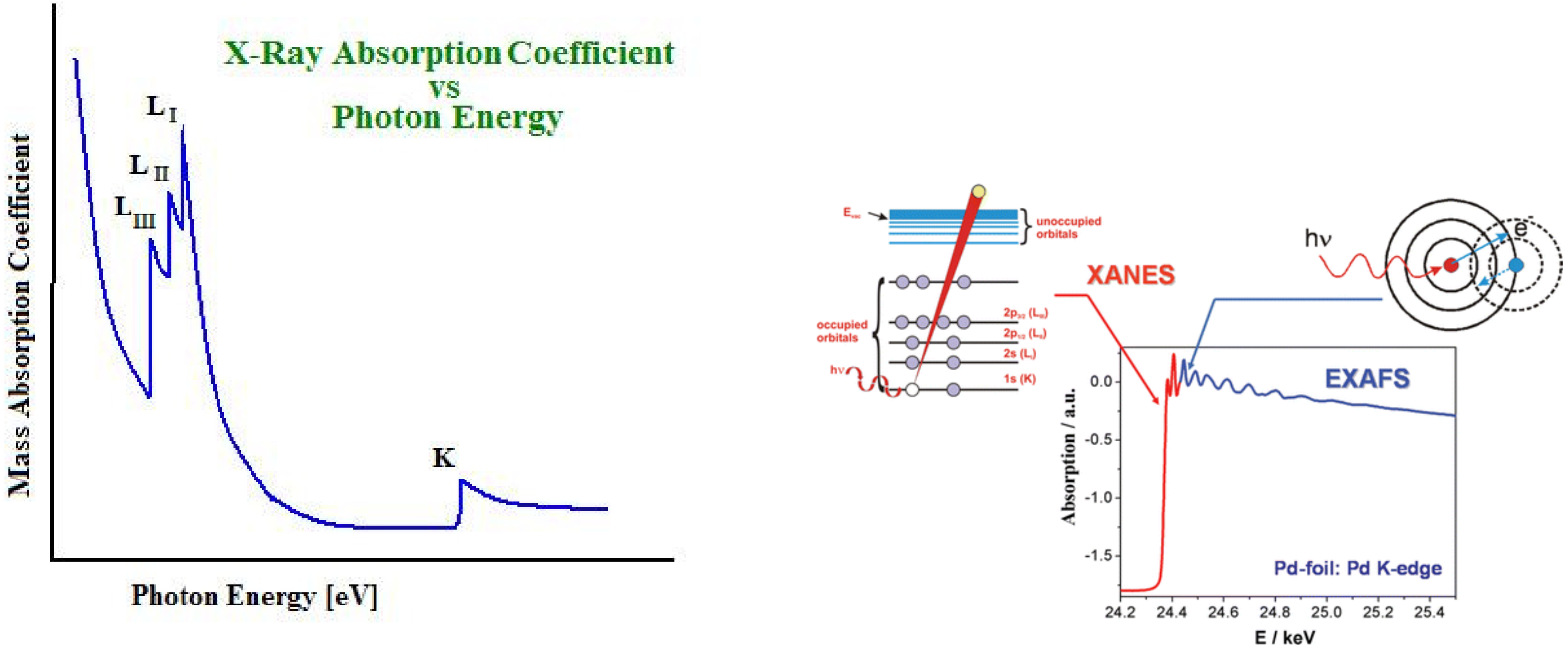


Figure 6.7.: Left: Edges in the x-ray absorption coefficients as function of the photon energy. Right: Principle of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. From chemwiki.ucdavis.edu and pubs.rsc.org

6.3.c. Characteristic x-ray absorption

➢ Beer's law: $\frac{dN}{N} = -\sigma_a \, n \, dx$ with number density n;

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

n ... the number of atoms per cm^3 of the material (atomic density).

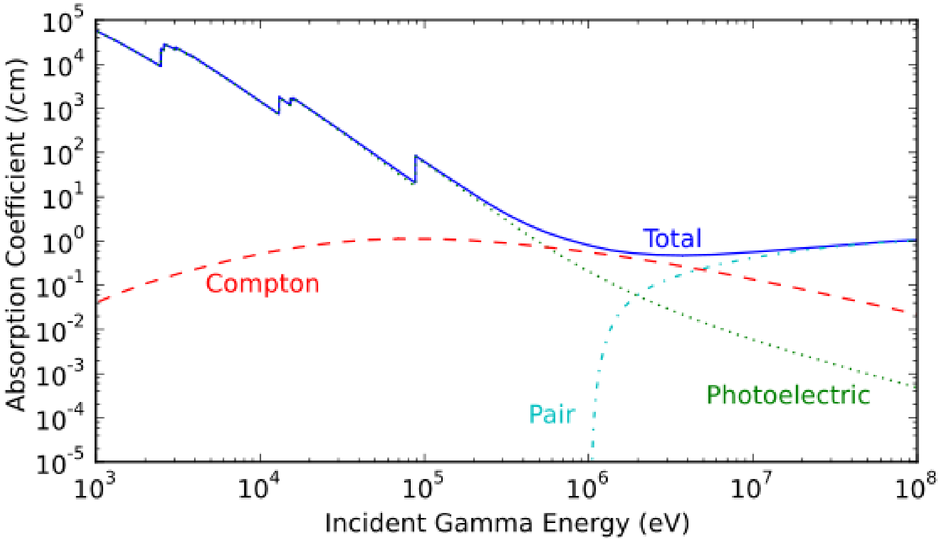


Figure 6.8.: The total (x-ray) absorption coefficient as function of the photon energy, and up to very high γ energies. The figure displays the relative importance of the three major effects, the photoionization, Compton and pair-creation process. Above 5 MeV, pair production starts to dominate the photoabsorption of matter.

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

- Note that the 'edges' are often displayed as function of the wavelength ... which leads to a virtual 'mirror' image of the figure at some vertical line.

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

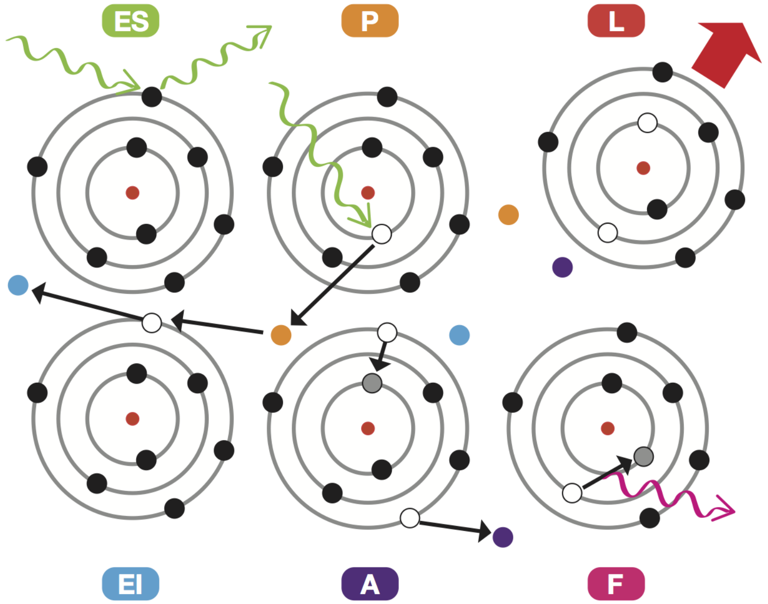


Figure 6.9.: Comparison of different ionization and subsequent decay processes in atoms.

6.3.d. Rayleigh and Compton scattering

➢ Rayleigh: elastic scattering of high-energetic photons

$$\hbar\omega \;+\; A \;\longrightarrow\; A \;+\; \hbar\omega$$

➢ Compton: inelastic scattering of high-energetic photons with a simultaneous atomic excitation/de-excigtation

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

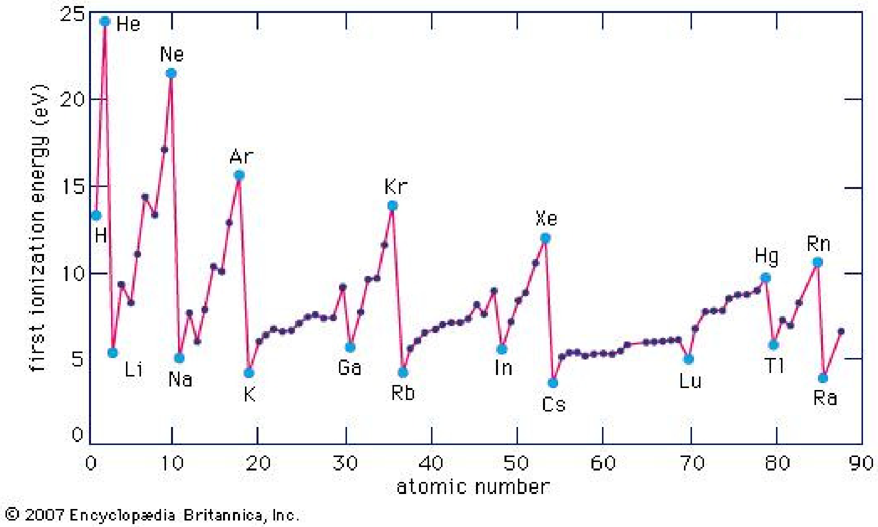


Figure 6.10.: First ionization potential as function of the nuclear charge of elements. From: www1.aps.anl.gov.

6.3.e. Bremsstrahlung

- ➢ $e^-(E_e) \; + \; A \;\longrightarrow\; e^-(E_e') \; + \; A \; + \; \hbar\omega, \qquad \hbar\omega \;=\; E_e - E_e'$ ... energy conservation.
- ➢ Maximal loss of kinetic energy of the electron, $E_{\max} \;=\; eU$ leads to a minimum wave lengths

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

- ➢ Examples: $U \;=\; 10\text{ kV} \quad \rightsquigarrow \; \lambda \;\sim\; 1\;\text{Å};$

  $U \;=\; 100\text{ kV} \quad \rightsquigarrow \; \lambda \;\sim\; 0.1\;\text{Å}.$
- ➢ Continuation of the radiative recombination (RR) process if the 'capture' occurs into the continuum of the ions.

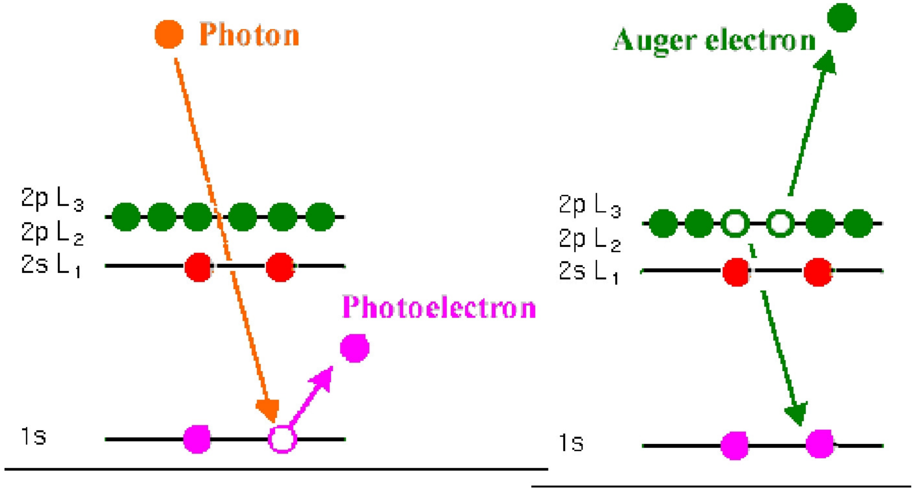


Figure 6.11.: Schematic diagram for the XPS emission process (left). An incoming photon causes the ejection of a photoelectron. The subsequent relaxation process (right) leads to the emission of an Auger KLL electron; from http://www.vub.ac.be/

6.3.f. Radiative electron capture (REC)

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

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

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

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

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

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

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

- ➢ Simultaneous absorption or emission of two photons:

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

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

- ➢ Atomic transition rate depends quadratically on the light intensity: $A_{\text{absorption}} \sim I^2$.
- ➢ Different selection rules for TPA than for one-photon absorption.
- ➢ Examples:
  - Helium-like ions: $1s2s\ ^1S_0 \rightarrow 1s^2\ ^1S_0$ decay by E1E1 + M1M1 + E2E2 + ... emission; the E1E1 channel clearly dominates by several orders of magnitude.
  - Beryllium-like ions: $1s^2 2s2p\ ^3P_0 \rightarrow 1s^2 2s^2\ ^1S_0$ decay by E1M1 + E2M2 + 3E1 + ... emission; the $^3P_0$ level is the lowest excited level and has extreme long lifetimes up to many thousands of years near to the neutral end of the sequence.
- ➢ Scaling with nuclear charge: $A_{if} \propto Z^{-6}$

6.4. Atomic photoionization

Photoionization with subsequent Auger electron emission (autoionization):

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

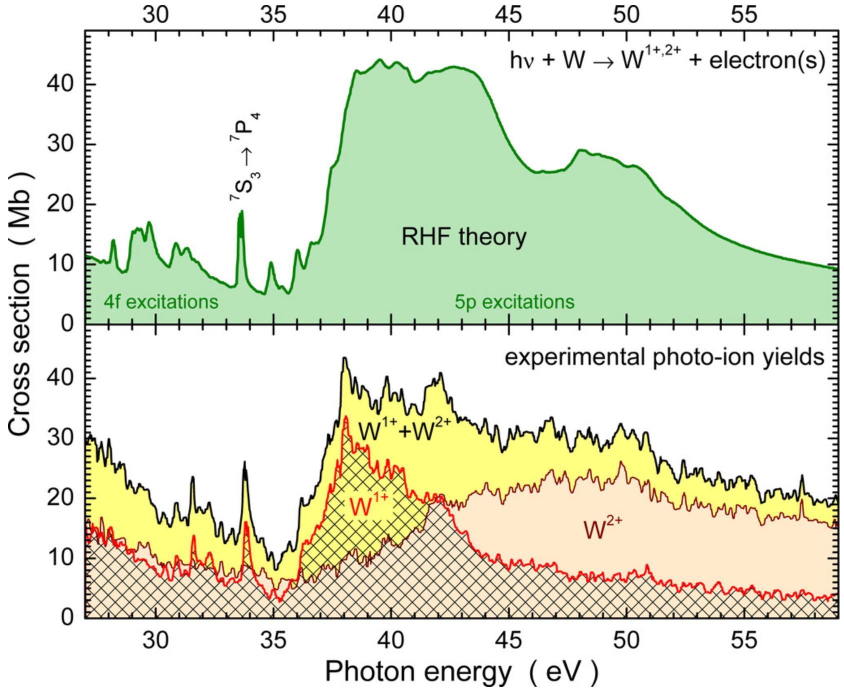


Figure 6.12.: Cross sections for the photoionization of neutral W (tungsten) atoms. The upper panel shows the result of relativistic Hartree-Fock (RHF) calculations for the photoabsorption by neutral tungsten. The tungsten atoms are brought into the gas phase by evaporating tungsten at 3200 K. From www.mdpi.com.

6.4.a. Photoionization amplitudes and transition amplitudes

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

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

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

- Cross section for the photoionization of an atom that undergoes the transition from $|i\rangle \rightarrow |f\rangle$:

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

where $P(\omega)$ is the ionization probability per atom and time unit as function of the photon frequency.

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

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

- Transition probability:

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

and where k_f is the asymptotic momentum of the free electron.

- Density of states:

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

- Total transition probability:

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

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

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

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

δ_ℓ ... non – Coulomb phase shift

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

- Summation over k_f:

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

$\frac{2}{\pi}$ ... is the normalization factor of free electrons in the momentum scale.

6.4.b. Cross section and angular distribution

- The (induced) photo excitation and ionization is usually described by means of cross sections; it can be expressed in different gauge forms (of the transition operator) and as integral over energy or momentum domains.

$$\sigma_{if}(\omega) \;=\; \int dk_f \, \frac{8\pi\,\omega}{k_f\,c} \; \delta\left(k_f \;-\; (2\omega \;-\; 2I_f)^{1/2}\right) \; \left|\langle f \,| Z_{\rm op} |\, i \rangle\right|^2$$

$$Z_{\rm op} \;=\; \sum_{k=1}^{N} z_i \qquad\qquad \text{length gauge}$$

$$\;=\; \sum_{k=1}^{N} \frac{\partial}{\partial z_i} \qquad\qquad \text{velocity gauge,} \qquad [\mathbf{r},\, H] \;=\; i\mathbf{p}$$

- This cross section can be expressed also as imaginary part of the frequency-dependent dipole polarizibility $\alpha_{\rm pol}(\omega)$

$$\sigma(\omega) \;=\; \frac{4\pi\,\omega}{c} \, \Im \left[\alpha_{\rm pol}(\omega)\right]$$

- For many-electron systems, the symmetry of the wave functions should be clearly indicated in the transition amplitudes

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

- Differential cross section for the photoionization of an electron from the k-th subshell by linear-polarized photons

$$\frac{d\sigma_k}{d\Omega} \;=\; \frac{\sigma_k}{4\pi} \left[1 \;+\; \beta_{2,k}\, P_2(\cos\vartheta)\right]$$

σ_k ... total subshell cross section

$\beta_{2,k}$ ... asymmetry parameter that contains all dynamical information.

- Differential cross section for unpolarized photons

$$\frac{d\sigma_k}{d\Omega} \;=\; \frac{\sigma_k}{4\pi} \left[1 - \beta_{2,k}\, P_2(\cos\vartheta)\right] \;.$$

- For open-shell atoms $(L \neq 0 \text{ or } S \neq 0)$, the initial alignment or polarization of the atoms need to be taken into account in addition:

$$A\,(L_i S_i\, J_i P_i) \;+\; \hbar\omega_1\,(E1) \;\longrightarrow\; A^+\,(L_f S_f\, J_f P_f) \;+\; e^-\left(\ell s j,\, \pi = (-1)^\ell\right) \;.$$

6.4.c. Shake-up and shake-off processes; direct double photoionization

- Photoionization with excitation and direct double photoionization:

$$\hbar\omega \;+\; A \;\longrightarrow\; A^{+*} \;+\; e_p^- \qquad \longrightarrow\; A^{++} \;+\; e_p^- \;+\; e_A^-$$

ionization – excitation with subs. Auger

$$\longrightarrow\; A^{++} \;+\; 2\,e_p^- \qquad \text{direct double ionization}$$

$$\longrightarrow\; A^{*} \qquad \longrightarrow\; A^{++} \;+\; 2\,e_A^-$$

excitation with Auger with shake – off

$$\longrightarrow\; A^{*} \qquad \longrightarrow\; A^{+*} \;+\; e_A^- \qquad \longrightarrow\; A^{++} \;+\; 2\,e_A^-$$

excitation with two – step Auger

- Transition amplitude: ... with the transition operator in one of the gauges from above, for instance, in length or velocity gauge

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

6.5. Non-radiative transitions: Auger transitions and autoionization

- Single- or two-step Auger decay:

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

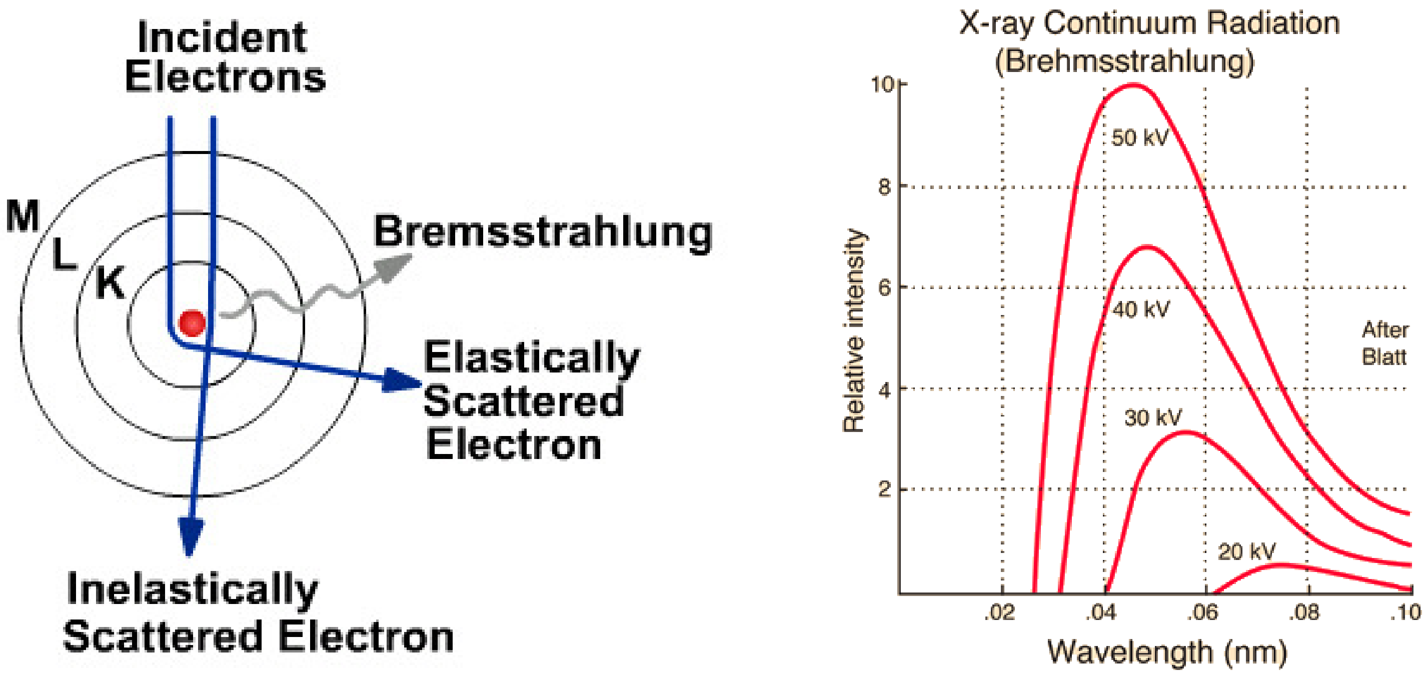


Figure 6.13.: Left: Different elastic and inelastic electron scattering processes on atoms, including bremsstrahlung. Right: Bremsstrahlung is characterized by a continuous distribution of radiation that is shifted towards higher photon energies and becomes more intense with increasing electron energy. From: www.nde-ed.org/EducationResources and hyperphysics.phy-astr.gsu.edu.

- Examples: K–LL, K–LM, L–MM, L_3–M_1M_{23}, ...
- Especially: Coster-Kronig transitions L–LM, M–MN, ...
  super-Coster-Kronig transitions L-LL, L_1-L_2L_3, M–MM, ...
- For an autoionization, the excited atom $A^{q+,*}$ must lay energetically in the continuum of the next higher charge state.

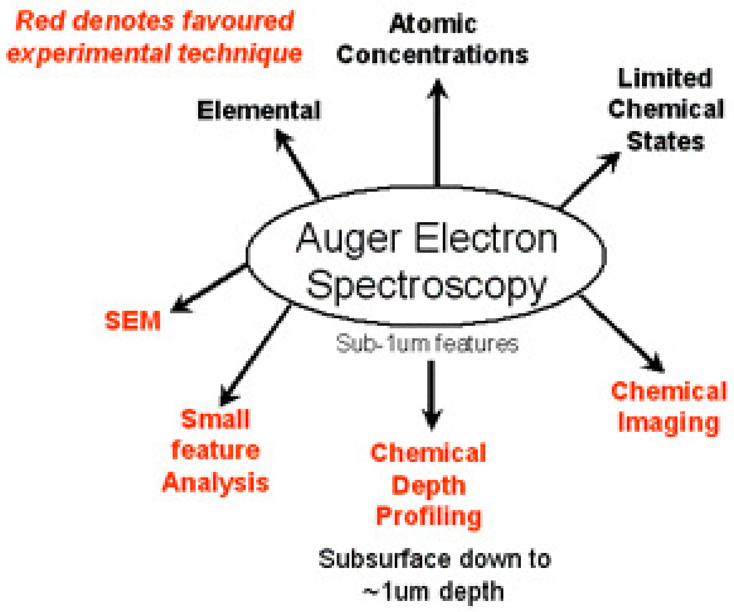


Figure 6.14.: Information that is available from Auger electron spectroscopy. From www.lpdlabservices.co.uk

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

$$E_{\rm kin} \;=\; E_i(N) \;-\; E_f(N-1)\,.$$

- ➢ Autoionization: (Low-energy) emission of valence electrons.
  Auger decay: (High-energetic) electron emission after decay of an inner-shell hole.
- ➢ Autoionization and Auger decay are very similar in their theoretical treatment; they are both described by the Auger

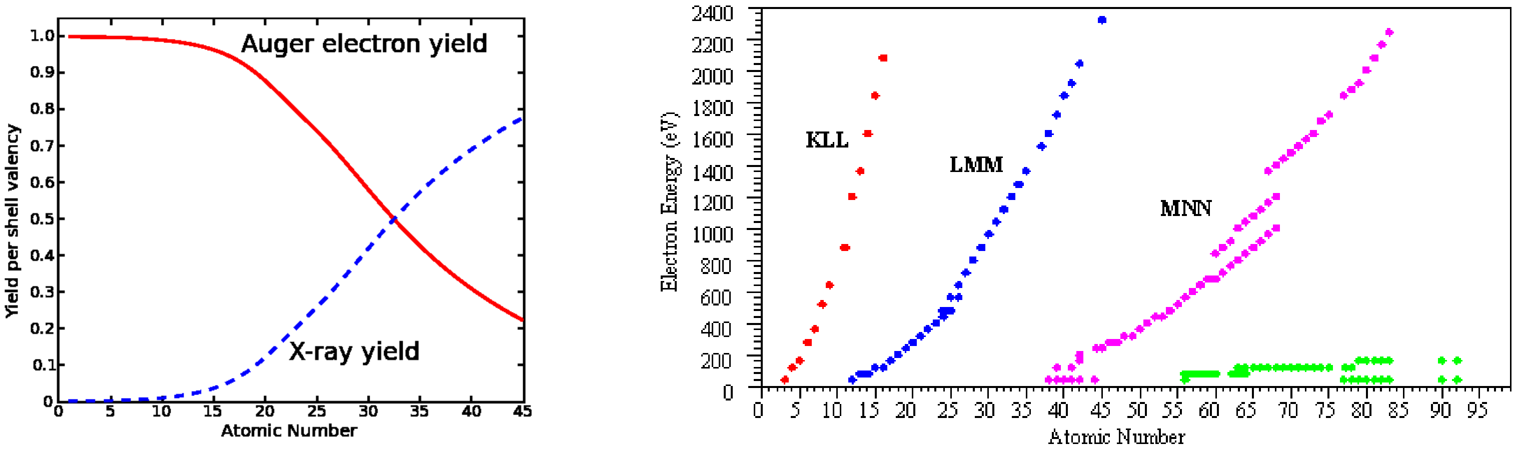


Figure 6.15.: Left: Comparison of Auger yield and fluorescence yield as a function of atomic number. Right: Auger characteristic energies. From and commons.wikimedia.org and www.semitracks.com.

(autoionization) rate

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

➢ Selection rules for Auger transitions:

$$\Delta J = \Delta M = 0 \qquad \text{(strict, since caused by inner interactions)}$$

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

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

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

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

➢ Excitation and subsequent decay of a neutral atom:

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

➢ Auger vs. fluorescence yield:

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

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

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

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

6.6. Beyond single-photon or single-electron transitions

Weak processes with several photons and/or electrons:

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

$$\begin{aligned} A^* &\longrightarrow A + \hbar\omega_1 + \hbar\omega_2 \\ \Delta E &= \hbar\omega_1 + \hbar\omega_2 = E(A^*) - E(A)\,. \end{aligned}$$

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

  Hyperfine quenching: The coupling of the total electronic angular momentum J with the nuclear spin I to a total angular momentum F can lead to single-photon transitions with a much higher rate and which often also dominates the lifetime of the states.

- Radiative Auger decay: $A^{++*} \longrightarrow A^{++} + \hbar\omega + e^-_A$
- Two-photon double ionization: $2\hbar\omega + A^{+*} \longrightarrow A^{++} + e^-_{p,1}(E_1) + e^-_{p,2}(E_2)$
- Two-color single ionization: $\hbar\omega_1 + \hbar\omega_2 + A \longrightarrow A^+ + e^-_p$
- Two-color double ionization: $\hbar\omega_1 + \hbar\omega_2 + A \longrightarrow A^{++} + e^-_{p,1}(E_1) + e^-_{p,2}(E_2)$
- Multi-photon ionization: $n \cdot \hbar\omega + A \rightarrow A^+ + e^-_p$