Atomic Theory

— Lecture script —

SS 2015

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

(Script and additional material)

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0. Preliminary remarks

0.1. Schedule and agreements

Lecture period:	13. 4. – 17. 7. 2015
Lecture:	We 12 – 14, Max-Wien-Platz (Physik, SR 1)
Tutorial:	Thu 10 – 12, every 2nd week, to be agreed
Language:	German / English ??
ECTS points:	4 (inclusive the tasks and exam).
Exam:	Tasks (40 %), oral or written exam.
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:	How much have you heart about atomic theory so far ?? Who makes regularly use of Maple oder Mathematica ?? ...

0.2. Further reading

➢ K. Blum: *Density Matrix Theory and Applications: Physics of Atoms and Molecules* (Plenum Press, New York, 1981, 1996).

➢ B. H. Brandsen and C. J. Joachain: *Physics of Atoms and Molecules* (Benjamin Cummings, 2nd Edition, 2003).

➢ R. D. Cowan: *Theory of Atomic Struture and Spectra* (Los Alamos Series, 1983).

➢ W. R. Johnson: *Atomic Structure Theory: Lectures on Atomic Physics* (Springer, Berlin, 2007).

➢ J. Foot: *Atomic Physics* (Oxford Master Series, Oxford University Press, 2005).

➢ H. Friedrich: *Theoretical Atomic Physics* (Springer, 3rd edition, 2003).

➢ M. Metcalf, J. Reid and M. Cohen: *Fortran 95/2003 Explained: Numerical Mathematics and Scientific Computation* (Oxford University Press, Oxford, 2007).

➢ G. K. Woodgate: *Elementary Atomic Structure* (Oxford University Press, 2nd Edition, 1983).

0. Preliminary remarks

➢ *Controlling the Quantum World: The Science of Atoms, Molecules and Photons* (The National Academy Press, Washington, 2007).

Additional texts: ... (Blackboard)

1. Atomic theory: A short overview

1.1. Atomic spectroscopy: Structure & collisions

Atomic processes & interactions:

➢ Spontaneous emission/fluorescence: occurs without an ambient electromagnetic field; related also to absorption, and it shows the deep quantum nature of atoms and light.

➢ Stimulated emission: from excited atoms leads to photons with basically the same phase, frequency, polarization, and direction of propagation as the incident photons.

➢ Photoionization: results in free electrons.

➢ Rayleigh and Compton scattering: Elastic and inelastic scattering of X-rays and gamma rays by atoms and molecules. Compton scattering often leads to an decrease in the photon energy but a energy transfer from matter to the photon can also be observed under certain circumstances (inverse Compton scattering).

➢ Thomson scattering: elastic scattering of electromagnetic radiation by a free charged particle (electrons, muons, ions); low-energy limit of Compton scattering.

➢ Multi-photon excitation, ionization and decay: shows the non-linear electron-photon interaction and is presently a very active field of research.

➢ Autoionization: Nonradiative electron emission from (inner-shell) excited atoms.

➢ Electron-impact excitation & ionization: results in excited and ionized atoms and occurs frequently in astro-physical and laboratory plasmas.

➢ Elastic & inelastic electron scattering: reveals the electronic structure of atoms and ions; it is important for plasma physics.

➢ Pair production: creation of an elementary particle and its antiparticle from light (electron-positron pairs); pairs from the vacuum.

➢ Delbrück scattering: the deflection of high-energy photons in the Coulomb field of atomic nuclei as a consequence of vacuum polarization.

➢ ...

➢ In practice, the distinction and discussion of different atomic and electron-photon interaction processes also depends on the particular community/spectroscopy.

1.2. Atomic theory

Covers a very wide range of many-body methods and techniques, from the simple shell model of the atom to various semi-empirical method to mean-field approaches ... and up to ab-initio and quantum-field theories. The aim of ab-initio atomic structure and collision theory is to describe the (electronic) level structure, properties and dynamical behaviour on the basis of the (many-electron) Schrödinger equation or by applying even field-theoretical techniques. — In short, the knowledge of the fundamental constants of Nature, the basic equations, and a bundle of proper approximation techniques will be enough to predict the energies and properties of ions, atoms and molecules with spectroscopic accuracy or even better.

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

Atomic theory is a great playground, indeed.

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

Hierarchy of inner-atomic interactions

-- self-consistent fields vs. perturbation theory
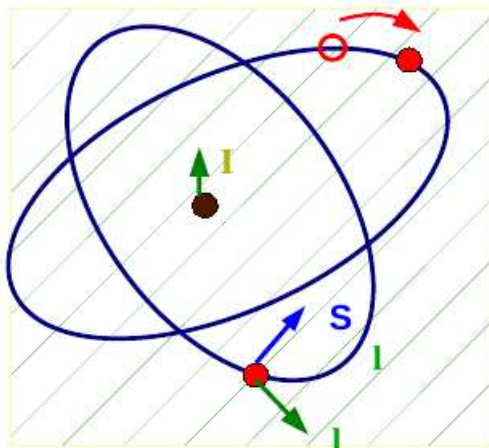
External fields

* Motion of the nucleus: Reduced mass and mass polarization

- Nuclear potential
- Instantaneous Coulomb repulsion between all pairs of electrons
- Spin-orbit interaction
- Relativistic electron velocities; magnetic contributions and retardation

- QED: radiative corrections
- Hyperfine structure
- Electric and magnetic nuclear moments (isotopes)

Figure 1.1.: Atomic interactions that need to be considered for a quantitative description/prediction of atoms.
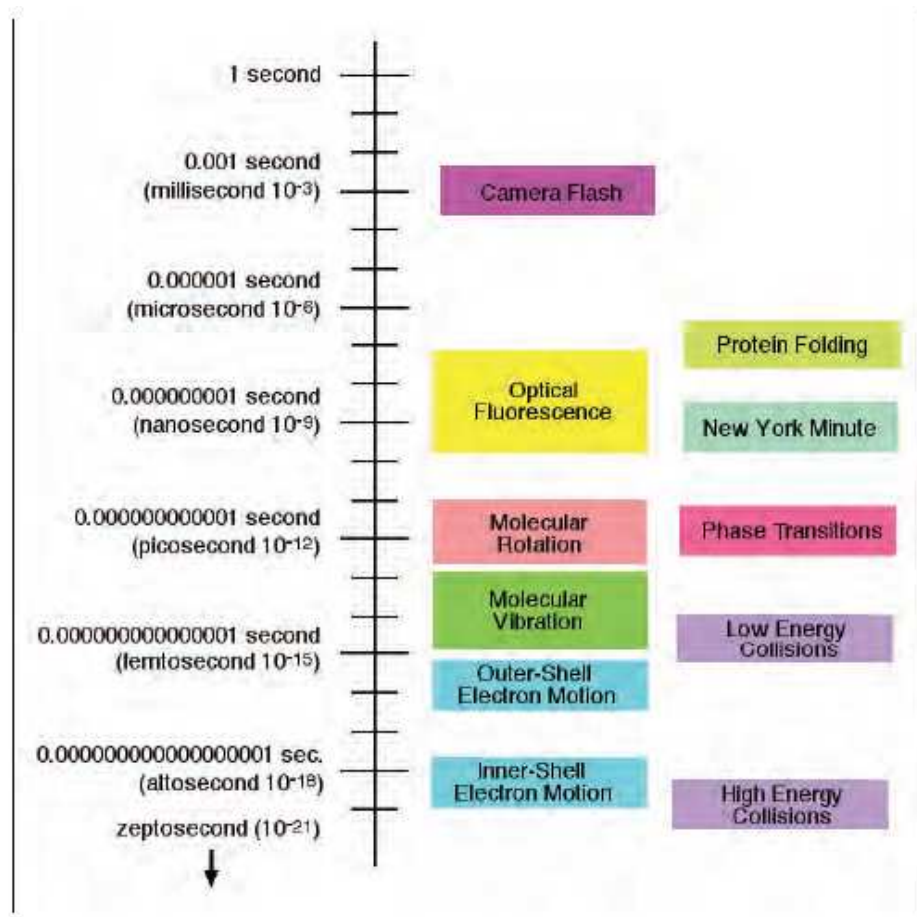
Figure 1.2.: Characteristic time scales of atomic and molecular motions; taken from: *Controlling the Quantum World*, page 99.

Theoretical models:

➤ Electronic structure of atoms and ions: is described quantum mechanically in terms of wave functions, energy levels, ground-state densities, etc., and is usually based on some atomic (many-electron) Hamiltonian.

➤ Interaction of atoms with the radiation field: While the matter is treated quantum-mechanically, the radiation is — more often than not (> 99 % of all case studies) — described as a classical field (upon which the quantum system does not couple back).

➤ This semi-classical treatment is suitable for a very large class of problems, sometimes by including quantum effects of the field in some 'ad-hoc' manner (for instance, spontaneous emission).

➤ Full quantum treatment: of the radiation field is very rare in atomic and plasma physics and requires to use quantum-field theoretical techniques; for example, atomic quantum electrodynamics (QED). QED is important for problems with definite photon statistics or in cavities in order to describe single-photon-single-atom interactions.

Combination of different (theoretical) techniques:

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

➤ Green's functions.

➤ Advanced computational techniques (object-oriented; computer algebra; high-performance computing).

1.3. Applications of atomic theory

1.3.a. Need of (accurate) atomic theory and data

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

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

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

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

➤ Search for super-heavy elements: beyond fermium ($Z = 100$); 'island of stability'; better understanding of nuclear structures and stabilities.

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

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

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

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

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

➤ ...

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

➤ High power short-pulse lasers with peak powers at the Terawatt or even Petawatt level enables one to reach focal intensities of $10^{18} - 10^{23}$ W/cm^2. These lasers are able also to produce a variety of secondary radiation, from relativistic electrons and multi-MeV/nucleon ions to high energetic x-rays and gamma-rays.

➤ Applications: The development of this novel tool of particle acceleration is presently explored in many different labs, and includes studies in fundamental and high-field physics as well as on medical technologies for diagnostics and tumor therapy.

➤ Extreme Light Infrastructure (ELI): a new EU-funded large-scale research infrastructure in which one (out of four) pillar is exclusively devoted to nuclear physics based on high intensity lasers. The aim is to push the limits of laser intensity three orders towards 10^{24} W/cm^2.

➤ This ELI project, a collaboration of 13 European countries, comprises three branches:
- Ultra High Field Science to explore laser-matter interactions in an energy range where relativistic laws could stop to be valid;
- Attosecond Laser Science to conduct temporal investigations of the electron dynamics in atoms, molecules, plasmas and solids at the attosecond scale;
- High Energy Beam Science.
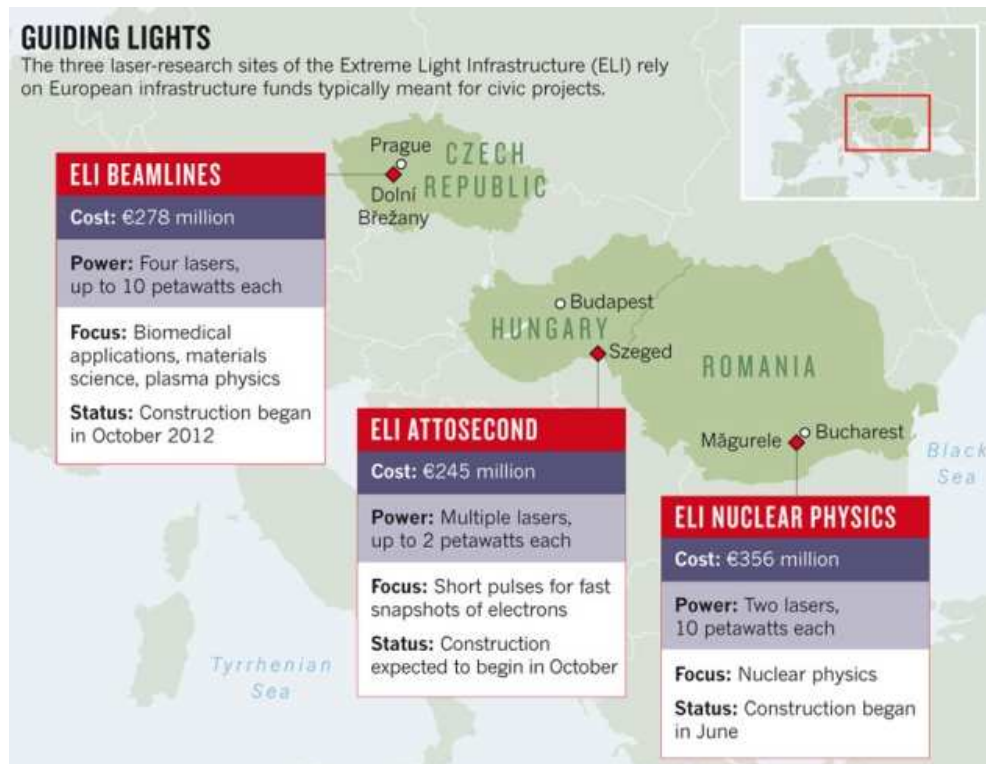
Figure 1.3.: Status of the ELI project 2014 (from: http://www.nature.com).

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

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

➤ One of the simplest quantum systems that can be solved analytically, both for the (non-relativistic) Schrödinger as well as the (relativistic) Dirac equation.

➤ Basis of the atomic shell model: Electronic wave functions are constructed as 'products' of some radial function *times* spherical harmonics, or linear combination of that.

➤ The shell model has large impact for the understanding of most atomic processes: the motion of electrons in all atoms basically follows those in hydrogen, although for some modified (screened) potential. The shell model is closely related also to the Hartree-Fock theory of atoms and molecules.

➤ 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 $10^{-11}...10^{-13}$.

2.2. Separation of the center-of-mass motion

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

For every closed system of interacting particles, one can de-couple the center-of-mass motion from the relative motion (see classical mechanics); the total energy of the system is then just the sum of energies associated with these two — independent — motions.

While this separation is conceptually rather difficult within the relativistic theory, we can typically use a nonrelativistic treatment owing to the (large) mass ratio $m_p/m_e \approx 1836$.

Hamiltonian functions of 'nucleus + electron':

$$H = K + V = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + V(\mathbf{r}_1, \mathbf{r}_2)$$

$$= \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}_r^2}{2\mu} + V(\mathbf{x}_r) \qquad \text{if} \qquad V = V(\mathbf{x}_1 - \mathbf{x}_2)$$

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

The last line is obtained by using the relative coordinates with $M = m_1 + m_2$:

$$\mathbf{x}_1, \quad \mathbf{x}_2 \qquad \qquad \mathbf{r}_r = \mathbf{r}_2 - \mathbf{r}_1; \qquad \mathbf{p}_r = \mu\,\dot{\mathbf{r}}_r; \qquad \mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

$$\mathbf{p}_1, \quad \mathbf{p}_2 \qquad \Longrightarrow \qquad \mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}; \qquad \mathbf{P} = M\,\dot{\mathbf{R}}$$

This results in a separation of the Hamilton function into two parts:

(i) a trivial part $\frac{\mathbf{P}^2}{2M}$ and   (ii) the Hamiltonian function for the relative coordinates.

Separation ansatz:

$$\Psi(\mathbf{R}, \mathbf{r}_r) = S(\mathbf{R})\,\psi(\mathbf{r}_r)$$

and a symmetric potential: $\qquad V = V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{\alpha\hbar cZ}{r}$

gives rise to (see tutorial):

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

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

$$(2.1)$$

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

The second equation is the Schrödinger equation (SE) for the relative motion of the electron and nucleus with regard to the center of mass. The center-of-mass of the atom moves like a free particle of mass $M = m_1 + m_2$ and total (kinetic) energy W (first equation).

Owing to the large mass ratio $m_p/m_e \approx 1836$, one often simply says that Eq. (2.1) describes the motion of the electron; this corresponds to an nucleus of infinite mass.

Agreement: We usually assume $\mu \approx m_{\text{electron}}$ and $\mathbf{r}_r \approx \mathbf{r}_{\text{electron}} \equiv \mathbf{r}$, and simply call Eq. (2.1) the SE of the electron with $\psi = \psi(\mathbf{r})$.

2.3. Nonrelativistic theory: A short reminder

2.3.a. Atomic units

The use of SI units can be rather tedious in writing down the equations, cf. Eq. (2.1). In atomic theory, therefore, one defines (quite arbitrarely):

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

This re-definition simplifies (almost) all equations considerably and defines the atomic units (.a.u.) in which all other quantities then appear. For example

<u>Atomic units:</u>   ... (Blackboard)

2.3.b. Schrödinger equation for hydrogenic atoms
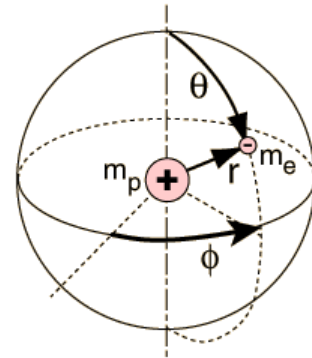
hyperphysics.phy-astr.gsu.edu

Correspondence principle:

$$\mathbf{r} \longrightarrow \hat{\mathbf{r}}$$

Classical mechanics $\implies$ $\mathbf{p}_r \longrightarrow -i\hbar \frac{\partial}{\partial \mathbf{r}}$ $\implies$ Quantum mechanics

$$E \longrightarrow i\hbar \frac{\partial}{\partial t}$$

<u>Steps of the separation:</u>

➢ Separation of center-of-mass motion (see above).

➢ Separation of relative motion with

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

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

➢ A subsequent separation procedure results in three independent ODE's and two separation constants:

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

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

$$\frac{d^2\,\Phi}{d\varphi^2} + \beta^2\, \Phi(\varphi) = 0\,,$$

and where the latter two equations can be written also:

$$\mathbf{l}^2\, Y(\vartheta, \varphi) = \lambda\,\hbar^2\, Y(\vartheta, \varphi)\,.$$

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In atomic units, Eq. (2.1) then simplifies to: ... (Blackboard)

Problem (Angular momentum operator):

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} = -i\hbar \left(\mathbf{r} \times \boldsymbol{\nabla} \right)$$

a) Prove that the Cartesian components of this operators reads as:

$$l_x = i\hbar \left(\sin \phi \frac{\partial}{\partial \vartheta} + \cot \vartheta \cos \varphi \frac{\partial}{\partial \varphi} \right)$$

$$l_y = i\hbar \left(-\cos \varphi \frac{\partial}{\partial \vartheta} + \cot \vartheta \sin \varphi \frac{\partial}{\partial \varphi} \right)$$

$$l_z = -i\hbar \frac{\partial}{\partial \varphi}$$

b) Show that $\mathbf{l}^2 = l_x^2 + l_y^2 + l_z^2$ coincides with the expression for $\mathbf{l}^2$ in Eq. (??).

Problem (Commutation relations of l): Prove the two commutation relations

a) $[H, \mathbf{l}^2] = 0,$ $[H, l_z] = 0,$

b) $[l_x, l_y] = i\hbar l_z,$ $[l_y, l_z] = i\hbar l_x,$ $[l_z, l_x] = i\hbar l_y$

2.3.c. Spherical harmomics: A short account

➤ The spherical harmomics $Y_{lm}(\vartheta, \varphi)$ are very important for atomic physics owing to their properties.

➤ Eigenfunctions of $\mathbf{l}^2$ and l_z.

➤ Explicit representation in coordinate space:

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

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

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

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

$|Y_0^0(\theta, \phi)|^2$

$|Y_1^0(\theta, \phi)|^2$ $\quad$ $|Y_1^1(\theta, \phi)|^2$

$|Y_2^0(\theta, \phi)|^2$ $\quad$ $|Y_2^1(\theta, \phi)|^2$ $\quad$ $|Y_2^2(\theta, \phi)|^2$

$|Y_3^0(\theta, \phi)|^2$ $\quad$ $|Y_3^1(\theta, \phi)|^2$ $\quad$ $|Y_3^2(\theta, \phi)|^2$ $\quad$ $|Y_3^3(\theta, \phi)|^2$
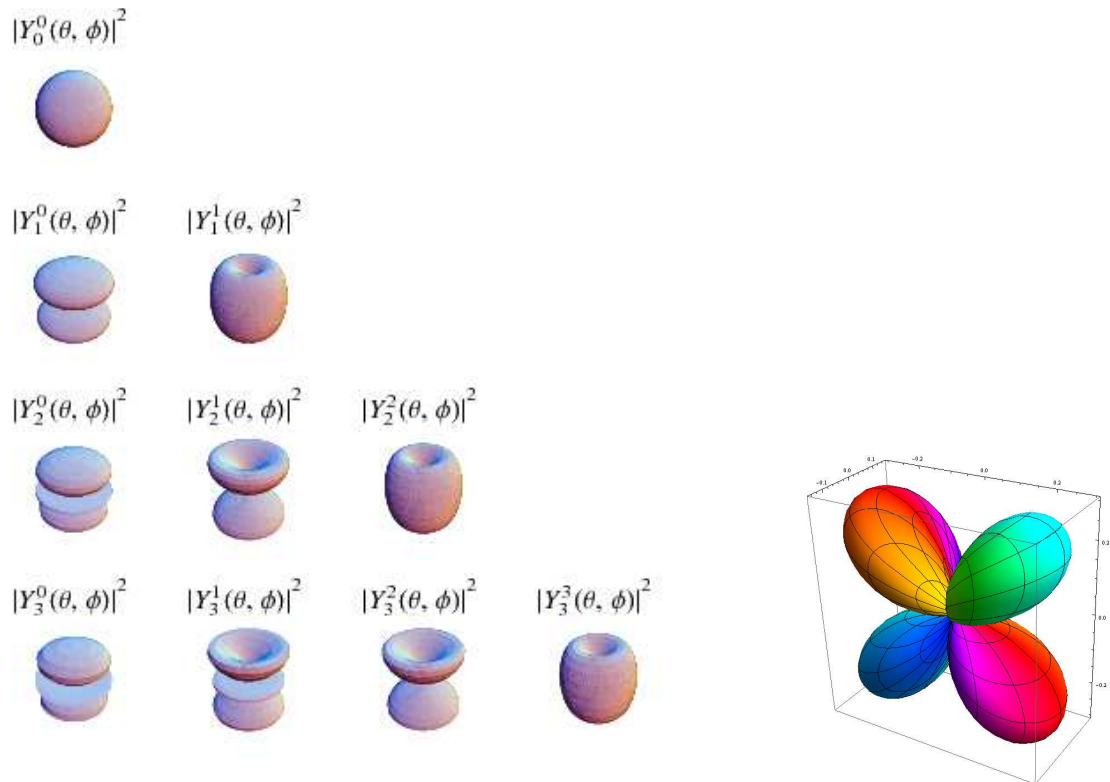
Figure 2.1.: There are many different representations of the spherical harmonics to display the modulus, real or imaginary parts of these functions, or changes in the (complex) phase; spherical plot of the function Y_{21} using Mathematica (rhs). From: mathworld.wolfram.com
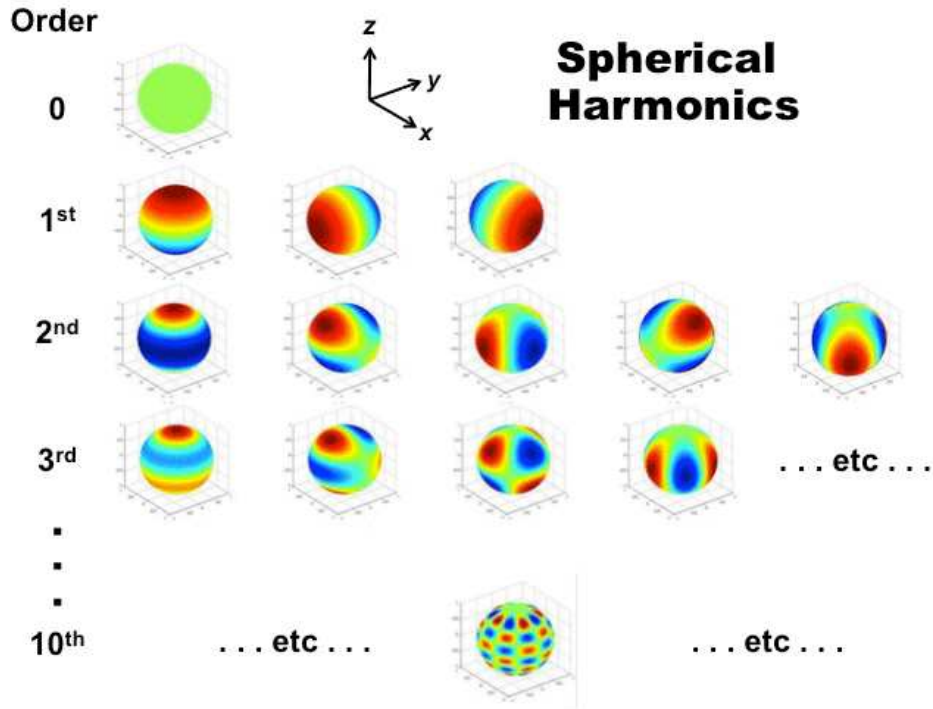
Figure 2.2.: Spherical harmonics of different orders. Order 0 is a constant value. Order 1 contains simple linear harmonics, here principally directed and labeled in the Cartesian coordinate system as Z, Y, and X respectively. The 2nd Order has five harmonics, called Z^2, ZX, $X^2 - Y^2$, ZY, and XY; from http://mri-q.com/uploads.

➤ If possible, however, one should always make use of the properties of these functions (instead of any explicit representation)

$$\langle Y_{lm} \mid Y_{l'm'} \rangle \quad = \quad \delta_{ll'}\, \delta_{mm'}$$

$$Y_{lm}^{*}(\vartheta, \varphi) \quad = \quad (-1)^m\, Y_{l,-m}(\vartheta, \varphi)$$

$$Y_{lm}(\pi - \vartheta, \pi + \varphi) \quad = \quad (-1)^l\, Y_{lm}(\vartheta, \varphi)$$

➤ Nowadays, the (properties of the) spherical harmonics can be easily utilized and evaluated by means of computer algebra tools; cf. MATHEMATICA, MAPLE.

➤ The spherical harmomics are closely related to many other functions from mathematical physics, such as the Legendre polynomials, Gegenbauer polynomials, vector and spinor spherical harmonics, Wigner rotation matrices, and several others.

➤ A few more (exotic) relations: ...

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

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

➤ Addition theorem: For two unit vectors $\mathbf{x} = \mathbf{x}(\vartheta, \varphi)$ and $\mathbf{y} = \mathbf{y}(\vartheta', \varphi')$, the spherical harmonics fulfill the relation

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

where P_l denotes the Legendre polynomial of order l, and which gives for $\mathbf{x} = \mathbf{y}$ rise to Unsöld's theorem (see below).

➤ See Wikipedia for a larger number of additional relations and the use of sphercial harmomnics in many different fields of physics.

2.3.d. Note: Complete set of commutable operators

A set of operators A_i $(i = 1, ..., n)$ is called complete, if no additional (linear-independent) operator exist which commutes with the A_i.

A complete set of operators has a simultaneous set of eigenfunctions which is not degenerate.

Example (H-atom): H, $\mathbf{l}^2$ and l_z are a complete set:

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

2.3.e. Energies and quantum numbers

level 4	————————	–0.54 eV
level 3	————————	–0.85 eV
level 2	————————	–1.51 eV
level 1	————————	–3.4 eV
ground state	————————	–13.6 eV

From: sciwebhop.net

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

2.3.f. Radial equation

We saw that the Schrödinger equation (2.1) can be solved by separating the variables using ansatz $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$. This leads to the (so-called) radial equation

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

$$\frac{d}{dr}\left(r^2 \frac{dR(r)}{dr}\right) + \left[2r^2\left(E + \frac{Z}{r}\right) - \lambda\right] = 0 \qquad (2.2)$$

Instead of the radial function $R(r)$, one often works with $P(r) = r\,R(r)$ which help simplify the radial equation. The functions $P(r)$ are often called the radial orbital functions or briefly the radial orbitals.

How to find solutions for $R(r)$ in Eq. (2.2) ??   ... (Blackboard)

2.3.g. Numerical vs. algebraic solutions to the radial equation

Numerical solutions

Direct integration: see the Runge-Kutta method or various improved integration schemes, so-called preditor-corrector methods (from the mathematical approximation theory).

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

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

Algebraic solutions

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

For a given set of linear-independent and for $N \to \infty$ complete set of basis functions $\{g_i(r),\ i = 1, ..., N\}$, the radial Schrödinger equation can be transformed into an equivalent algebraic eigenvalue problem

$$\sum_i \int dr\, g_k(r)\left\{-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + V(r)\right]\right\} g_i(r)\,X_i$$

$$= E\sum_i \underbrace{\int dr\,g_k(r)\,g_i(r)}_{S_{ki}\ ...\ \text{overlap matrix}} \qquad \text{for all}\quad k = 1, ..., N.$$

Choice of basis functions: ... (Blackboard)

Normalization and expectation values: $\bar{A} = \langle A \rangle = \langle \psi | A | \psi \rangle$

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

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

$$\langle r^k \rangle = \int_0^\infty dr \, r^2 \, R^*_{nl}(r) \, r^k \, R_{n'l'}(r)$$

$$\langle r \rangle_{l=n-1} = n^2 \left(1 + \frac{1}{2n} \right) \frac{a_0}{Z}$$

$$\langle r^{-1} \rangle = \frac{1}{n^2} \left(\frac{Z}{a_0} \right)$$

Figure 2.3.: From: http://pages.physics.cornell.edu/
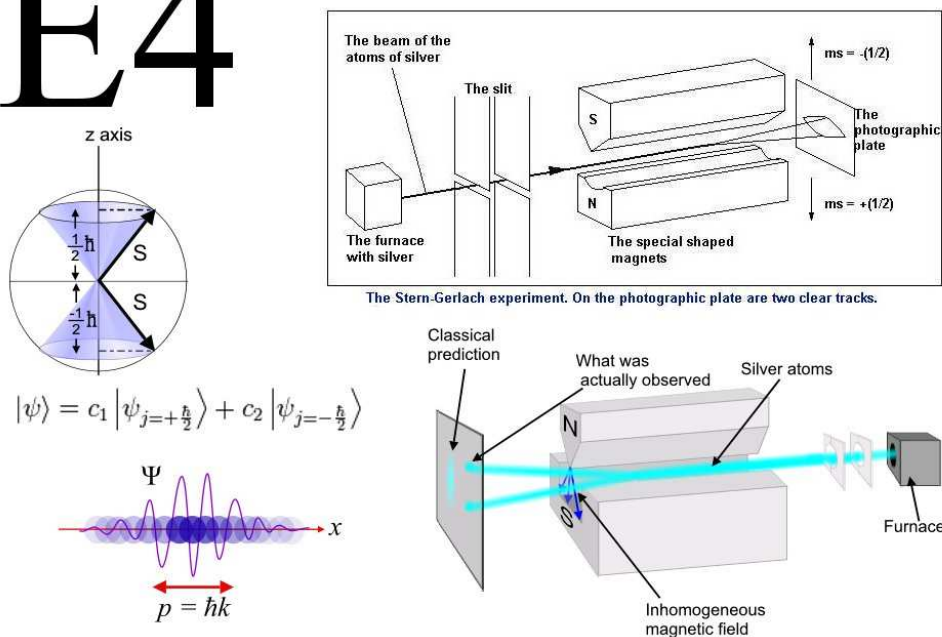
2.3.h. Pauli's wave mechanics: Fine structure

While all solutions $\psi(\mathbf{r}) = R_{nl}(r) \, Y_{lm}(\theta, \phi)$ with given n are degenerate within the non-relativistic theory, more detailed observations show a line and level splitting which cannot
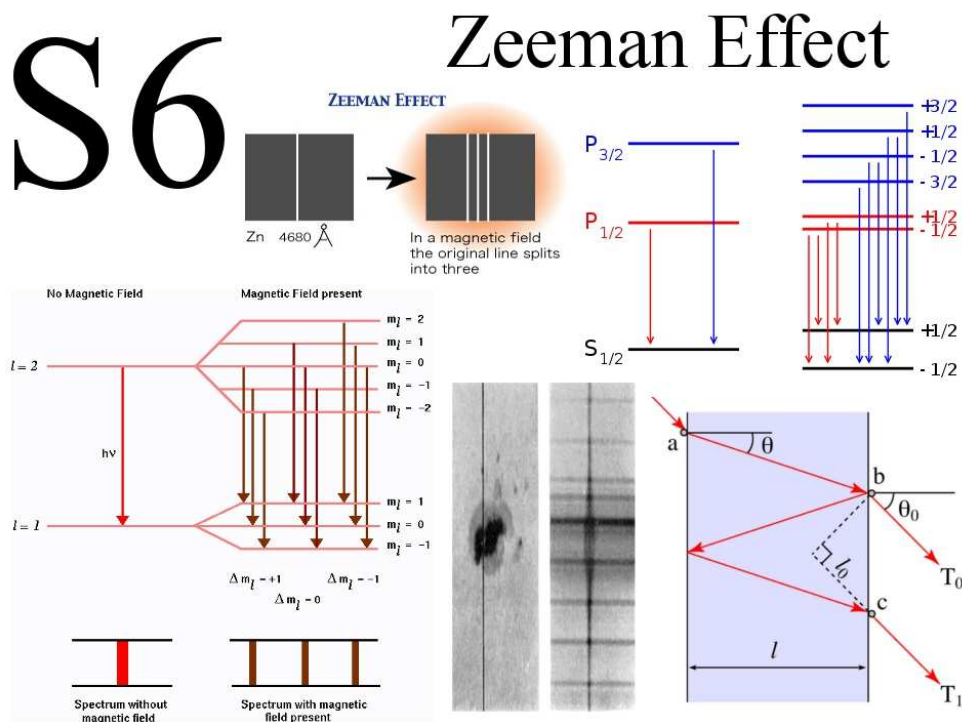
Figure 2.4.: Normal Zeeman effect: splitting of a spectral line into several components in the presence of a static magnetic field. However, there are a lot of observations that cannot be explained alone in terms of the magnetic and angular momentum quantum numbers and are called the 'Anamalous' Zeeman effect. From: http://pages.physics.cornell.edu/

be explained without the spin of the electron(s).

These observations suggested to postulate a further quantum number, the electron spin, with just two space projections (Uhlenbeck and Goudsmit, 1925). This is called the magnetic spin quantum number m_s.

Observations that suggest an electron spin, $s = 1/2$:   ... (Blackboard)

Spin & spin operators: ... (Blackboard)

Spin is a pure quantum concept:

➤ Without classical counterpart; especially, there is no 'classical limit' $s \to \infty$. Within Pauli's wave mechanics, all operators are 2×2 matrices.

➤ There is a magnetic moment associated to the spin which gives rise to the interaction of (free) electrons with the magnetic field; cf. gyromagnetic factor of the electron $g = 2.002... \approx 2$ (Dirac theory).

➤ For the hydrogen atom and without spin-orbit interactions (i.e. in the pure non-relativistic limit), the SE has some trivial, two-compoment solutions

$$\psi(\mathbf{x}) \equiv \psi(\mathbf{r}, \sigma) = \psi_{nlm}(\mathbf{r}) \, \chi_{m_s}$$

which factorize into a spatial and spin part.

Blackboard example (Matrix elements and variance of spin operator):

Problem (Eigen states of electron along x-axis): Find the eigen states of a (spin-1/2) electron along the x-axis !

2.3.i. Vector model: Constants of motion in a central field

If we accept the spin as an additional degree of freedom, we need 4 quantum numbers in total to classify the motion of an electron in a central-field potential.

The vector model provides a (simple) geometrical picture, without two much importance however, which displays the precession of the total angular momentum around the quantization axis:

$$|j_1 - j_2| \leq j \leq |j_1 + j_2|$$

Complete set of quantum numbers: ... (Blackboard)

2.3.j. Fine structure: Relativistic interaction terms

The correct behaviour of the hydrogen atom follows from the solution of the Dirac equation (see below) and leads to a partial splitting of the degenerate levels; the rather weak splitting for light and medium elements can be described however in good approximation perturbatively by expanding the Dirac operator in v/c and by including only terms up to $(v/c)^2$.

Three (widely-known) terms   ... (Blackboard)

Total level shift and splitting

➤ Fine structure splitting:

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

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

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

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

➤ $E_n(j = \ell + 1/2) = E_n(j = \ell' - 1/2)$

➤ Fine structure shifts are independent of orbital angular momentum quantum number ℓ (although the individual terms do depend).

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

➤ Fine structure constant ($\alpha^2 \simeq 5 \cdot 10^{-5}$) determines the relative splitting with regard to E_n.

➤ While all three terms are comparable for hydrogenic ions, the spin-orbit term clearly dominates in many-electron atoms and ions. The relativistic mass correction and the Darwin term are often negligible.

➤ Selection rule for electric-dipole transitions: $\Delta j = 0, \pm 1$.

2.4. Relativistic theory: Dirac's equation

2.4.a. Relativistic Hamiltonians and wave equations

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

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

Question: How can we transform this expression by the correspondence principle $\mathbf{p} \rightarrow -i\hbar\,\frac{\partial}{\partial \mathbf{r}}$ into a useful Hamiltonian ?

Different approaches: ... (Blackboard)
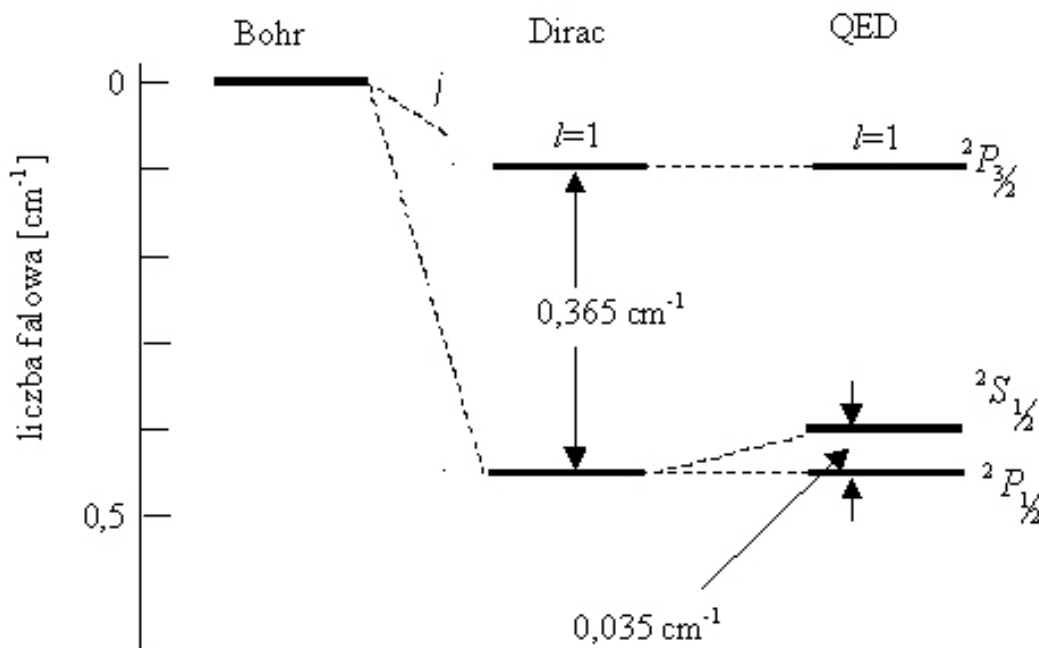
Figure 2.5.: The subtle Lamb shift of the $n = 2$ levels in hydrogen according to Bohr's and Dirac's theory and together with the QED predictions. In particular, the Lamb shift removes the degeneration due to quantum number j; from: Haken and Wolf, Atomic Physics (Springer, 1996).

Dirac equation ... (Blackboard)

2.4.b. Dirac's Hamiltonian

➤ Time-dependent (and relativistic covariant) Dirac equation for a free electron reads as:

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

<div align="center">kinetic energy term   rest mass term</div>

$$\mathbf{p} \;=\; -i\hbar\,\tfrac{\partial}{\partial\mathbf{r}}$$

➤ Fulfills relativistic energy-momentum relation only if ... $\boldsymbol{\alpha}$ 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:

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

Properties of Dirac spinors and operators: ... (Blackboard)

2.4.c. Plane-wave solutions to the time-independent Dirac equation for free particles

➤ Separation of time gives rise to the time-independent Dirac equation for a free particle:

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

➤ First-order differential equation (in contrast to the Schrödinger equation).

➤ Ansatz for plane waves (solutions) for the motion along the $z-$axis (quantization axis):

$$\psi_p(\mathbf{r}) \;=\; w(p)\,\exp(ipz/\hbar)$$

transforms the time-independent Dirac equation into a standard eigenvalue problem:

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

➤ Two solutions can be found from the characteristic polynomial:

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

<div align="right">Solutions with negative energy — h'm ??</div>

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

➤ For each energy, there are two (degenerate) wave functions according to the two spin directions, in parallel and anti-parallel to the $z-$axis.

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

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

Free-electron wavefunction (plane wave solution) can be written as bi-spinor.
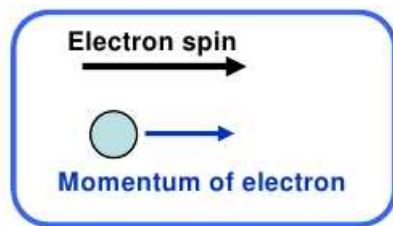
Helicity +1; $w_{+1/2}$.
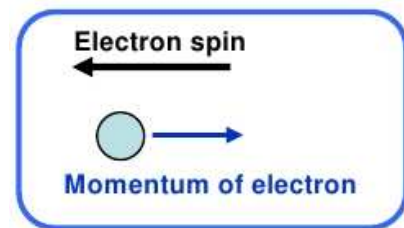
Helicity –1; $w_{-1/2}$.

2.4.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: $E_-(p) \;\leq\; -mc^2$
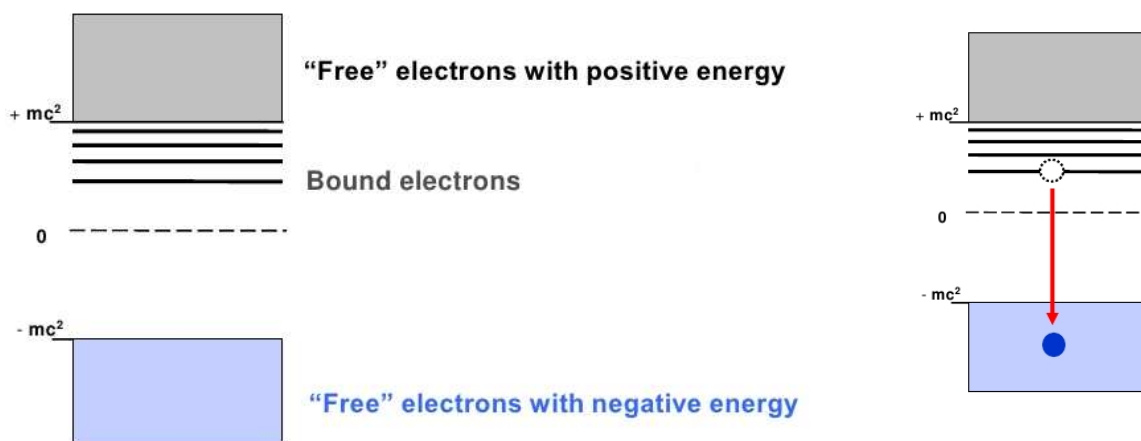
➡ The ground state of atoms becomes unstable.

Concept of the "Dirac sea"   ... (Blackboard)
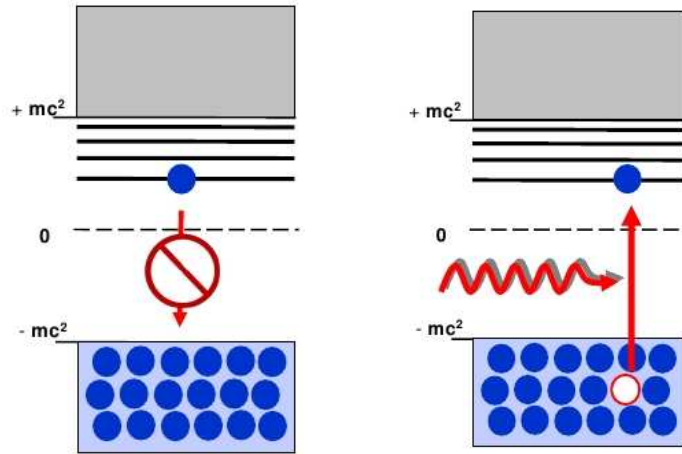
Figure 2.6.: Dirac sea: A 'filled' sea forbids that electrons with positive energy can decay into the 'sea', while 'holes' in the sea have opposite charge and represent the anti-particles.

Problem (Creation of holes in the Dirac sea): How much energy is required to create an electron-positron pair in the field of an calcium nucleus (Z=20) if the electron is captured into the $1s$ ground state of the ion. (Hint: Use the non-relativistic formula for the bound-state energies, $E_n = -Z^2/2n^2$ [a.u.].)

2.4.e. Constants of motion in a central field

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

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

<u>Remember:</u> In the non-relativistic theory, we can use either $\{H,\, \mathbf{l}^2,\, l_z,\, s_z\}$ or $\{H,\, \mathbf{l}^2,\, \mathbf{j}^2,\, j_z\}$ as complete set of commutable operators in order to classify the solutions of the SE.

Commutable operators for the Dirac Hamiltonian

➤ Analogue to the Pauli theory, we find $\quad [H_{\mathrm{D}},\, \mathbf{j}^2] = [H_{\mathrm{D}},\, j_z] = [\mathbf{j}^2,\, j_z] = 0$ with

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

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

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

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

➤ For a central field $V(r)$:   Complete set of commutable operators $\{H_\mathrm{D}, k, \mathbf{j}^2, j_z\}$
with eigenvalue equations:

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

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

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

κ is called the relativistic angular momentum quantum number, and it defines the quantum number j uniquely. Therefore, the two quantum numbers (κ, m_j) are suitable to classify the spin-angular dependence of the solutions in every central field.

➤ Simultaneous eigenfunctions for k, $\mathbf{j}^2$, j_z:

$$\psi_{\kappa=j+1/2,m_j}(\mathbf{r}) \;=\; \begin{pmatrix} \sqrt{\kappa+m_j-1/2}\;\; P_\kappa(r)\,Y_{\kappa-1,m_j-1/2}(\theta,\phi) \\[4pt] \sqrt{\kappa-m_j-1/2}\;\; P_\kappa(r)\,Y_{\kappa-1,m_j+1/2}(\theta,\phi) \\[4pt] \sqrt{\kappa-m_j+1/2}\;\; Q_\kappa(r)\,Y_{\kappa,m_j-1/2}(\theta,\phi) \\[4pt] -\sqrt{\kappa+m_j+1/2}\;\; Q_\kappa(r)\,Y_{\kappa,m_j+1/2}(\theta,\phi) \end{pmatrix}$$

and similar for $\psi_{\kappa=-(j+1/2),m_j}(\mathbf{r})$.

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

Problem (Dirac operator):   Evaluate the (4×4) representation of the Dirac operator

$$k \;=\; \alpha_0\,(\mathbf{l}\cdot\boldsymbol{\sigma}_\mathrm{D} + \hbar) \qquad \text{with} \qquad \sigma_{\mathrm{D},i} \;=\; \begin{pmatrix} \sigma_i & 0 \\ 0 & \sigma_i \end{pmatrix}.$$

2.4.f. Solutions of the Dirac equation for a Coulomb potential $V(r) \simeq -Z/r$

Time-independent Dirac equation for an electron in the Coulomb field (hydrogen-like ions) reads as:

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

➤ Results in a coupled system of four (first-order) equations for the (four) components of

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

➤ two coupled first-order odg for the radial functions $P_\kappa(r)$ and $Q_\kappa(r)$:

$$\psi(\mathbf{r}) \;=\; \psi_{\kappa \,=\, \pm(j+1/2),\, m_j} \;=\; \begin{pmatrix} P_\kappa\, \Omega_{\kappa m} \\ iQ_\kappa\, \Omega_{-\kappa m} \end{pmatrix}$$

where the $\Omega_{\kappa m}(\vartheta, \varphi)$ are the so-called (spherical) Dirac spinors. In this representation, the radial equations are given by:

$$\left(B + \frac{\gamma}{r}\right) \frac{P_\kappa(r)}{\sqrt{2\kappa+1}} \;-\; i\left(\frac{d}{dr} + \frac{\kappa+1}{r}\right) \frac{Q_\kappa(r)}{\sqrt{2\kappa-1}} \;=\; 0$$

$$i\left(A - \frac{\gamma}{r}\right) \frac{Q_\kappa(r)}{\sqrt{2\kappa-1}} \;-\; \left(\frac{d}{dr} - \frac{\kappa-1}{r}\right) \frac{Q_\kappa(r)}{\sqrt{2\kappa+1}} \;=\; 0$$

$$A \;=\; \frac{mc^2 - E}{\hbar c}; \qquad B \;=\; \frac{mc^2 + E}{\hbar c}; \qquad \gamma \;=\; \alpha Z$$

They are the same for using $\psi_{\kappa \,=\, +(j+1/2),\, m_j}$ and $\psi_{\kappa \,=\, -(j+1/2),\, m_j}$ above.

➤ The bound solutions to these coupled equations for $E < mc^2$ are linear combinations of the confluent hypergeometric function. — H'm, ... these functions are rather unpleasant to deal with but have been discussed extensively in the literature; cf. below

➤ The corresponding eigenvalues are:

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

Sommerfeld's fine-structure formula.

This formula describes the spectrum completely for all hydrogen-like ions apart from the Lamb shift (QED corrections).

2.4.g. Bound-state solutions in a central field

Discrete spectrum: The radial functions $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ from above are often called the large and small components and can be expressed in a Coulomb potential by the confluent hypergeometric function $F(\alpha, \beta; x)$ as (cf. Eichler & Meyerhof 1995, Eq. 4.98–4.99)

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

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

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

with

$$n' = n - |\kappa|, \qquad s = \sqrt{\kappa^2 - (\alpha Z)^2}$$

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

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

$$N_{n\kappa}^S = -N_{n\kappa}^L \left(\frac{1 - W_{n\kappa}}{1 + W_{n\kappa}} \right)^{1/2}$$

Especially, the $\left| 1s_{1/2}, \pm 1/2 \right\rangle$ ground-state of hydrogen:

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

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

with

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

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

and $\bar{s} = \sqrt{1 - (\alpha Z)^2}$. Since for $|\kappa| = 1$ one has $\bar{s} < 1$, a mild singularity appears at the origin in the wavefunctions for $s_{1/2}$ and $p_{1/2}$ states. For the radial components of the lowest few states, i.e. $1s_{1/2}$, $2s_{1/2}$, $2p_{1/2}$, $2p_{3/2}$, Eichler & Meyerhof (1995, Eq. 4.103 and Table 4.4) give also their form explicitly.

In some cases it is more suitable to use the representation of the bound electron wavefunctions as proposed by Rose (1961). According to his text, the wave function with quantum numbers n, κ is given by

$$P_{n_b \kappa_b}(r) = r\, N_b\, e^{-qr} (qr)^{s-1} \sum_{k=0}^{n'} cb, k^+ (qr)^k$$

$$Q_{n_b \kappa_b}(r) = r\, N_b\, e^{-qr} (qr)^{s-1} \sum_{k=0}^{n'} cb, k^- (qr)^k$$

where

$$N_b = \frac{2^s\, q^2}{\Gamma\,(2s+1)} \left(\frac{\Gamma\,(2s+n'+1)}{qn'!\,[(\alpha Z/q - \kappa)^2 + n'(2s+n')]} \right)^{1/2}$$

$$cb,k^\pm = \left(1 \pm \sqrt{1-q^2}\right)^{1/2} \frac{(-n')_k\, 2^k}{k!\,(2s+1)_k}\, [(k-n') \pm (\alpha Z/q - \kappa)]$$

Such an representation is very useful for the calculation of different matrix elements that includes the functions from the contineous spectrum .

Well, some people can and enjoy handle such functions for evaluating matrix elements, etc.

2.5. Beyond Dirac's theory
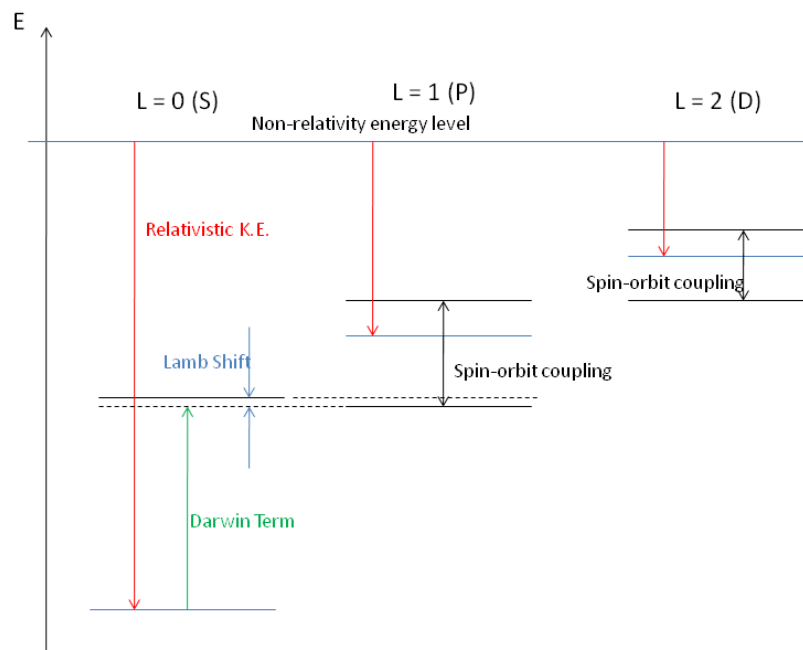
Figure 2.7.: Relativistic level shifts for hydrogen-like ions; from: http://en.wikipedia.org/wiki/ .

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

2.5.b. QED: Interactions with a quantized photon field

Dominant QED corrections:

2. *Review of one-electron atoms (hydrogen-like)*
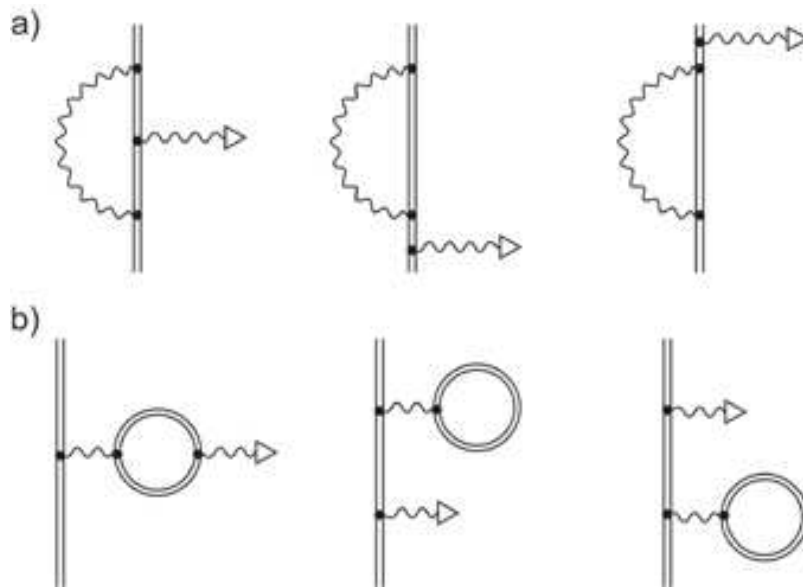
Figure 2.8.: Feynman diagrams of the bound electron in first order of the fine structure constant α. (a) Self energy, (b) vacuum polarization. The double line represents the bound state electron propagator and contains the interaction between electron and the binding field to all orders of α; from http://iopscience.iop.org/1402-4896/89/9/098004.

➢ Vacuum polarization (VP): virtual electron-positron pairs are produced that modify the nuclear potential.

  • 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 energy-time version of the Heisenberg uncertainty principle.

  • The VP typically lowers the binding of the electrons.

➢ Self energy: represents the contribution to the particle's energy or effective mass due to interactions between the particle and the system it is part of.

  • In 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 particular due to the changes that itself causes in its environment.

  • Mathematically, this energy is equal to the so-called on-the-mass-shell value of the proper self-energy operator (or proper mass operator) in the momentum-energy representation.

➢ Feynman diagrams: graphical representation of the interaction; each Feynman diagram can be readily expressed in its algebraic form by applying more or less simple rules.
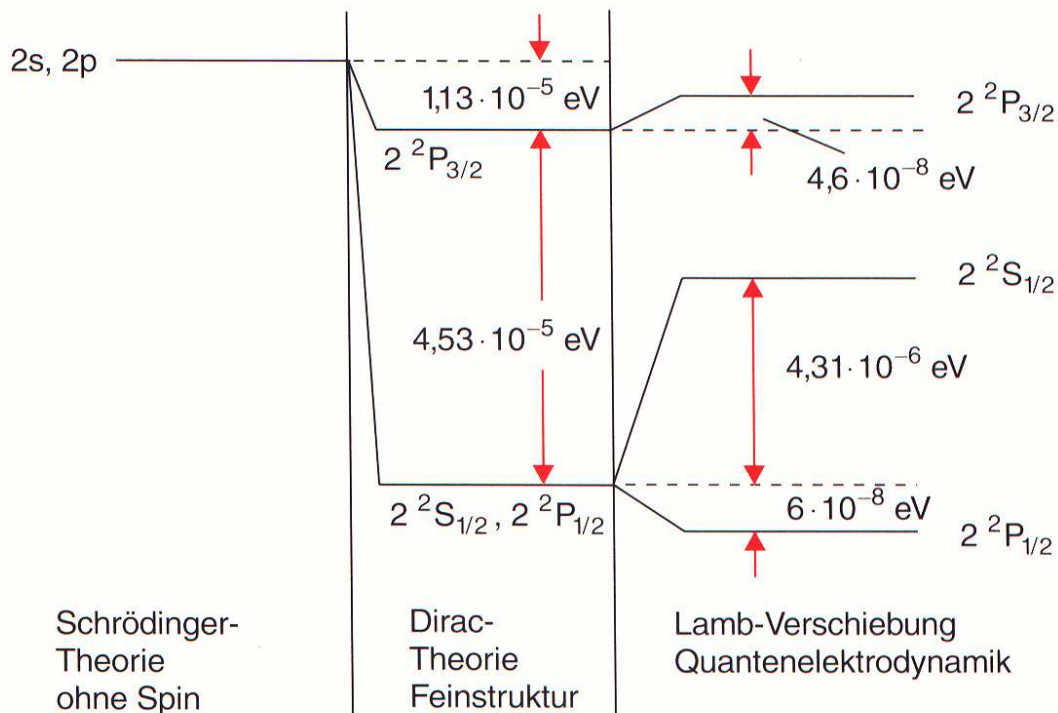
Figure 2.9.: Accurate Lamb-shift calculations for atomic hydrogen.

2.6. Hydrogenic atoms in constant external fields

In constant external fields, the observed atomic spectra often depend quite sensitively on the interplay of the level splittings that arises due to the field strength and (inner-atomic) spin-orbit interactions. This interplay gives rise to a number of (well-explored) effects.

Usually, the level splitting in external fields is treated perturbatively by studying the

Hamiltonian: $H = H_o + H'$.

(Normal) Zeeman effect: ... (Blackboard)

Stark effect: ... (Blackboard)

Anomalous Zeeman & Paschen-Back effect: ... (Blackboard)

2.7. Exotic 'hydrogenic' atoms

Instead of electron, an atomic nucleus (charge) can capture also negatively charged particles, at least for some time.

Pionic atoms:

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

➤ Pions (π^+, π^-) are spin-0 mesons that obey to the electromagnetic and strong interactions and which follow the Klein-Gordan equation.

➤ Produced by inelastic proton scattering:

$$p + p \implies p + p + \pi^+ + \pi^-$$
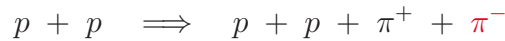
can be captured by nuclei/atoms under the emission of Auger electrons.

After the production, the pions are decellerated and deflected upon some atomic target.

➤ Strong interaction with the nucleus can lead to the capture by the nucleus:

$$\pi^- + p \longrightarrow n; \qquad \pi^+ + n \longrightarrow p$$

Therefore, the strong-interaction potential has imaginary part, $V = V_{real} + V_{imag}$, and this leads to a 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, $m_\mu \approx 207\,m_e$;
they are also described by the Dirac equation.

➤ $p + p \longrightarrow p + p + \pi^+ + \pi^-$ and $\pi^- \longrightarrow \mu^- + \nu_\mu$

➤ Muons are typically captured into some high excited level. The muonic atoms decay then radiatively (via characteristic x-ray emission) or non-radiatively in several steps towards the ground state.

➤ Relativistic solutions only apply for (very) heavy nuclei; the reduced mass of the muons lead to recoil effects which can be analysed experimentally.

➤ Strongly enhanced QED effects because of the small radii of the muonic orbits.

3. AMO Science in the 21st century

Potential and grand challenges for AMO Science (from 'Controlling the Quantum World'):

➢ Quantum metrology: New methods to measure the nature of space and time with extremely high precision; this field has emerged within the last decade from a convergence of technologies in the control of the coherence of ultrafast lasers and ultracold atoms. Promises new research opportunities.

➢ Ultracold AMO physics is a spectacular new (AMO) research area of the past (two) decades which led to the development of coherent quantum gases. This new field promises to resolve important fundamental problems in condensed matter science and plasma physics, with many interdisciplinary relations.

➢ High-intensity and short-wavelength sources such as new x-ray free-electron lasers promise significant advances in AMO science, condensed matter physics and materials research, chemistry, medicine, and others.

➢ Ultrafast quantum control will unveil the internal motion of atoms within molecules, and of electrons within atoms, to a degree thought impossible only a decade ago. This field gives rise to a sparking revolution in the imaging and coherent control of quantum processes; is expected to become to one of the most fruitful new areas of AMO science in the next 10 years or so.

➢ Quantum engineering on the nanoscale of tens to hundreds of atomic diameters has led to new opportunities for atom-by-atom control of quantum structures using the techniques of AMO science.

➢ Quantum information is a rapidly growing research area in AMO science with great potential applications in data security and encryption. Multiple approaches to quantum computing and communication are likely to be fruitful in the coming decade. Current topics include: Realization of quantum information processing; models of quantum computations and simulations; ect.

Web link (ultra-cold physics):

➢ 'As cold as it gets'; www.youtube.com/watch?v=fnqAwtorUTE
➢ 'Light Stopper'; www.youtube.com/watch?v=F5uF1qx7mT0&NR=1
➢ www.youtube.com/watch?v=Mgyp94TZdqQ
➢ www.youtube.com/watch?v=iDBZ3bwGseE

Present questions to AMO science:

➢ What are the undiscovered laws of physics that lie beyond our current understanding of the physical world ? What is the nature of space, time, matter, and energy ?
Is there an atomic dipole moment ?   ➥ Help explore the physics beyond the standard model by using techniques from AMO physics.

➢ How can one improve the measurement precision to become sensitive to very weak magnetic fields, such as of the brain or heart ?   ➥ New diagnostic tools for various diseases.

➢ How can one detect gravitational waves and anomalies, such as hostile underground structures and tunnels ?   ➥ Matter-wave interferometers.

➢ Can ultra-cold gases be used to mimic and explore the interactions in periodic structures of solid crystals. Do they provide us with some useful quantum simulators ?

➢ Biological imaging ? Can free-electron lasers help us to explore the structure and dynamics of proteins and biomolecules ?   ➥ Freezing the motion of electrons as they move about the molecule requires subfemtosecond, or attosecond, laser pulses.

➢ How can intense laser be utilized to create directed beams of electrons, positrons, or neutrons for medical and material diagnostics ?

➢ Is it possible to use laser-induced fusion in large-scale power plants ?

➢ Can we use lasers to control the outcome of selected chemical reactions ?
➥ Such control technologies may ultimately lead to powerful tools for creating new molecules and materials tailored for applications in health care, nanoscience, environmental science, and energy.

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

3.1. AMO Science and the basic laws of Nature

Search for atomic EDM's:

➢ For example, AMO scientists aim at measuring subtle new effects due to a possible permanent electric dipole moment (EDM) of an electron or an atom, which — if it really exists — would require a dramatic extension of our theory of elementary particles.

➢ The theory of supersymmetry predicts that electrons and nuclei in atoms should possess a tiny offset between their mass and electric charge centers along the spin axis of these particles, the EDM. If it really exist, it would mean the violation of time reversal (t) invariance.

➢ Time-reversal violating forces also appear in the (conventional) Standard Model of elementary particle interactions but cause an EDM far too small to be observable by any presently envisioned experiment; therefore, any measurement of an electron/atomic EDM would mean new physics beyond the standard model.
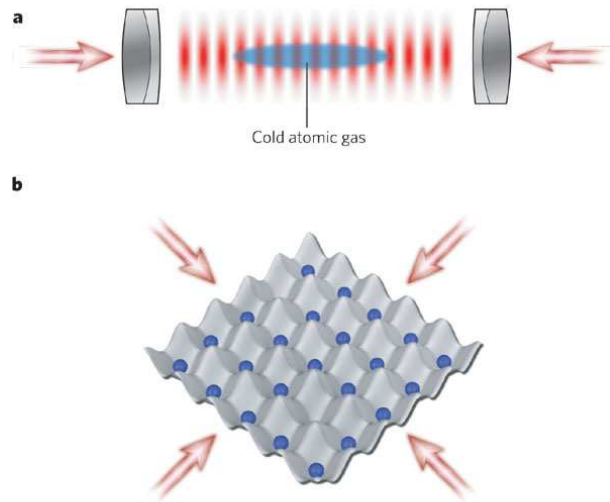
Figure 3.1.: Formation of an optical lattice; from I. Bloch, Nature 453, 1016 (2008).

➤ New 'interactions' are required to overcome several 'gaps' of the standard model, for example, the preponderance of matter over antimatter.

➤ Figure 3.3 shows the ranges of some of the current predictions for EDMs which arise from various dynamical models that extend the Standard Model of particle physics.

➤ Atomic physics can measure very tiny frequency shifts of smaller than a nanohertz, i.e. less than one complete spin precession in 30 years. This may help to unveil such interactions.

➤ Supersymmetric particles are hoped to be found eventually in high-energy experiments, such as the Large Hadron Collider (LHC). But atomic EDM experiments are also well positioned to discover supersymmetric particles if they do indeed exist.

Test of CPT theorem:

➤ Atomic physics experiments can also search for violations of the so-called charge, parity, and time reversal (CPT) symmetry. Together, these symmetries state that matter and antimatter particles should have exactly the same mass and the same magnetism. These symmetries are fundamental pillars of modern physics and, hence, must be tested precisely.

➤ The study of atoms can tell us about forces that are normally explored at high-energy accelerators or large underground labs. Close to an electron, namely, the electron envelops itself in a tiny cloud of emitted and reabsorbed virtual particles ... not only photons but also heavier particles studied at high-energy accelerators. The existence of these tiny clouds shows up in highly sensitive measurements of energy levels and other atomic properties.

➤ In fact, atomic experiments have already shown how the small virtual clouds around each electron may yield valuable information for particle physics. For example, the
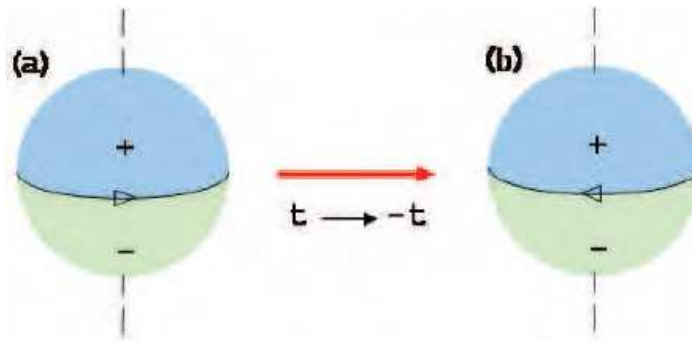
Figure 3.2.: An electric dipole moment (EDM) of an atom (left) is a permanent separation between the centers of positive and negative charge along the axis of spin. Under time reversal (right), the spin direction is reversed but the charge separation is not. An observed EDM would have to be caused by forces that violate time reversal symmetry; taken from: *Controlling the Quantum World*, page 32.

90 GeV Z^0 boson which distinguishes left from right (and violates parity) causes an isolated atom to absorb right-handed, circularly polarized photons at a slightly different rate than left-handed photons. — Present measurements in the cesium atom are so precise and agree so well with the Standard Model that any proposed heavier version of this Z^0 gauge boson must be at least eight times heavier, if such particles exists at all.

➤ One of the most exact CPT tests is expected from the creation of antihydrogen in the laboratory. By comparing the spectral energies of antihydrogen atoms and ordinary hydrogen atoms, one can search for effects due to possible CPT violations.

Time variations of α:

➤ The fine-structure constant $\alpha = e^2/\hbar c$ is a dimensionless constants of three fundamental constants. Indeed, recent 'unifying' theories suggest the possibility of spatial and temporal variations of α and other physical 'constants'.

➤ Atomic physics may help to explore such variations because different atomic transitions depend differently on α ➡ One need therefore to compare the rates of different atomic clocks over long periods of time to place bounds on local change of α with time.

➤ Spectroscopic data presently provide so far no evidence that the value of α has changed as the universe expanded (at least, with an averate rate $> 10^{-16}/a$; if such changes would be confirmed, our understanding of QED and its relation to the structure of spacetime would need to be revised.

AMO physics & astronomy:

➤ Light from distant stars and galaxies exhibits characteristic spectral features as predicted accurately by atomic theory. This provides evidence that the laws of physics apply across very large distances of the universe and from the earliest moments on.
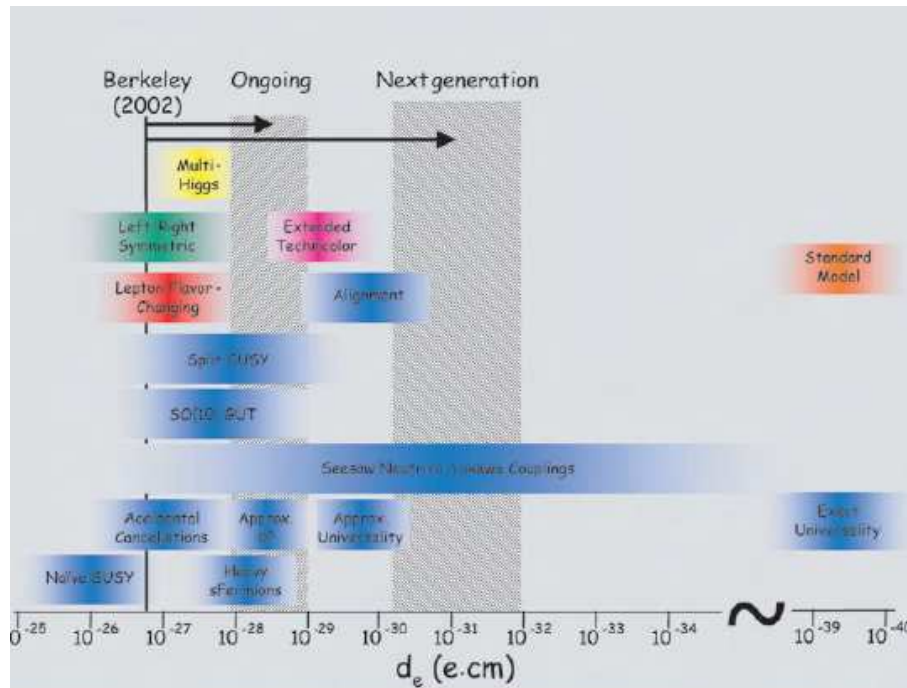
Figure 3.3.: Scientific impact of current and next-generation electron EDM measurements. It is anticipated that next-generation measurements will reach the 10^{-31} e-cm level, equivalent to a dipole consisting of a positive and negative electronic charge separated by only 10^{-31} cm, which will test large classes of supersymmetric (SUSY) theories. Ongoing measurements of an atomic EDM due to nuclear spin and the EDM of the neutron have similar sensitivity to different SUSY parameters. Thus, atomic EDM experiments will be probing SUSY and other theories on a broad front. SOURCE: D. DeMille, Yale University; taken from: *Controlling the Quantum World*, page 33.

➢ To address and interprete many astrophysical observation, AMO spectroscopy and collision studies in the lab need to be carried out, involving atoms, ions, molecules, and electrons. Moreover, theoretical calculations provide essential input to the models used in the interpretation of astronomical observations.

➢ Precision spectroscopy played an important role in the recent discovery that the expansion of the universe is accelerating rather than decelerating, as it was expected for a long time; this lead to the notion of dark energy whose nature is not at all understood. ➥ Existence of dark energy poses a challenge to the Standard Model of particle physics.

➢ Molecules can efficiently lose energy and allow a gas to cool under gravitational collapse, the first step in star formation; the study of molecular hydrogen formation in the early universe is an active area of study in AMO physics.

➢ Spectroscopy is the tool to search for life in other planetary systems; AMO physics provides the necessary backbone to this work.

➢ Atomic and molecular theorists have developed powerful numerical methods and extensive computer codes to calculate energy levels, wavefunctions, and spectral line strengths.

3.2. Extreme light sources: Development and applications
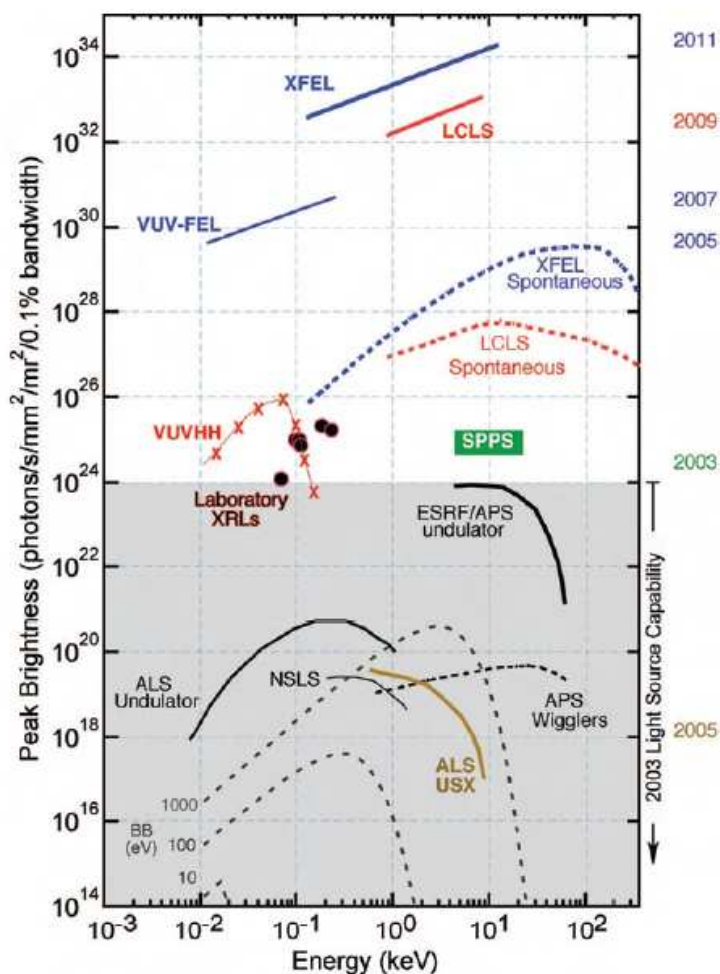
Figure 3.4.: Brightness comparison between current and future sources of x rays generated in laboratory x-ray lasers or at accelerators; taken from: *Controlling the Quantum World*, page 76.

New advances in AMO physics are creating brilliant bursts of x-ray beams:

➤ Laser-like bright, directed x-ray beams that can be focused to the size of a virus;

➤ fast and bright enough to capture the fleeting motion of electrons within atoms and molecules;

➤ 'extreme strobes' that may provide a direct view on the electronic and structural changes that govern biology and nanoscience at the molecular level.

Table-top x-ray sources:

➤ Use of ionized atomic plasmas as the lasing medium to generate highly monochromatic and directed laser beams at wavelengths from 11 to 47 nm.

➤ These light sources may be used for next-generation micro-lithography, where the energy needs to be absorbed in a very precise nanopattern or in a very thin layer; good
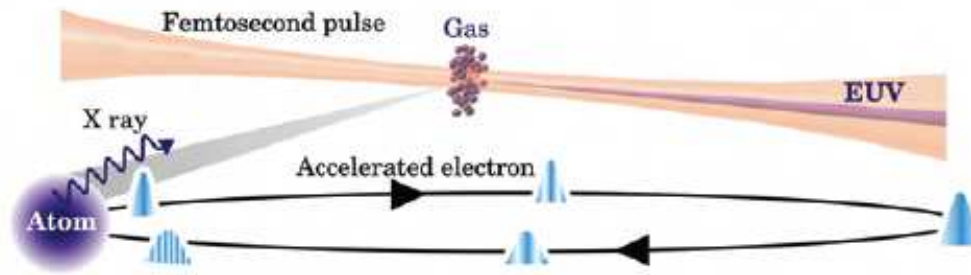
Figure 3.5.: Simple and quantum pictures of high-harmonic generation. Top: An electron is stripped from an atom, gains energy, and releases this energy as a soft x-ray photon when it recombines with an ion. Bottom: Two-dimensional quantum wave of an electron is gradually stripped from an atom by an intense laser. Fast changes in this quantum wave lead to the generation of high harmonics of the laser. Reprinted with permission from H.C. Kapteyn, M.M. Murnane, and I.P. Christov, 2005, Extreme nonlinear optics: Coherent x-rays from lasers, Physics Today 58. Copyright 2005, American Institute of Physics.; taken from: *Controlling the Quantum World*, page 79.

for industrial applications because of their relatively low cost.

➤ High-harmonics generation: Focusing an intense femtosecond laser into a gas, the electrons in the gas atoms are driven so nonlinearly that high harmonics of the fundamental laser are emitted as coherent, laser-like beams at short wavelengths. Photon energies from the ultraviolet to keV.

➤ Instead of two or three laser photons that are added together in traditional nonlinear optics, high-harmonic generation combines tens to hundreds of visible laser photons together, to generate laserlike beams with photon energies up to the keV regime.

➤ HHG can be used also to create x-ray beams with ultrashort, sub-femtosecond (or attosecond) durations.

➤ Although high-harmonic generation is often explained as an extreme version of nonlinear optics, this process of stripping away electrons from an atom is a real quantum phenomenon and is deeply affected by the quantum wave nature of the electrons as they move under the influence of the laser.

➤ Table-top extreme x-ray sources bring the source to the application, i.e. they enable the widespread use of next-generation microscopes and spectroscopy to probe materials with unprecedented spatial and temporal resolution.

Free-electron lasers (FEL):

➤ XFEL sources use linear electron accelerators in order to produce much shorter and more brilliant x-ray pulses than all other x-ray sources. These extreme x-ray laser sources take advantage of true laser amplification to generate coherent beams that are exquisitely directed and focusable.

➤ Their promise is to open up a completely new realm of x-ray science, enabling a new era of single biomolecular and nanostructure determination as well as the ability to study structural dynamics in materials and chemical/biological systems.

➤ The present-day synchrotrons, in contrast, have relatively long pulse durations, ranging from tens to hundreds of picoseconds. Moreover, there are a relatively small number of coherent photons in the hard x-ray regime.

➤ The LCLS x-ray laser (Stanford) beam is the first x-ray source that generates a similar extreme focused powers as they can be accessed by current generation of high-powered lasers; unusual physical phenomena are expected that have not previously been studied or even observed.

➤ Three remarkable properties of x-ray lasers: Short wavelength, short pulses, and high pulse intensity. This allows to remove the inner shell electrons rather than the valence electrons.

➤ Creation of 'hollow atoms and ions' (species with two or more electrons from inner shells); such atoms store enormous amounts of potential energy and represent extreme matter in a truly exotic form.

➤ Similarly, two-photon ionization in the x-ray domain will be a major milestone in this field.

Web link (high-intense lasers):

➤ 'Laser fusion gets HiPERactive' (interview with M. Dunne)
physicsworld.com/cws/article/multimedia/41169

➤ 'Taking the pulse of the Vulcan laser'
physicsworld.com/cws/article/multimedia/41170

Imaging of biomolecules:

➤ Since XFEL produce very short bursts (tens to hundreds of femtoseconds of brilliant x-ray light, they might be used to explore the movement of the atoms making up the biomolecule and eventually to capture perhaps the molecular structure before the molecule explodes as a result of the bright x-ray flash.

➤ For extremely short x-ray laser pulses (tens of femtoseconds or less) with sufficient brilliance per pulse (10^{12} photons) are used, then an individual x-ray diffraction pattern could be recorded from the macromolecule in the gas phase before radiation damage manifests itself and ultimately destroys the molecule by literally blowing it apart.
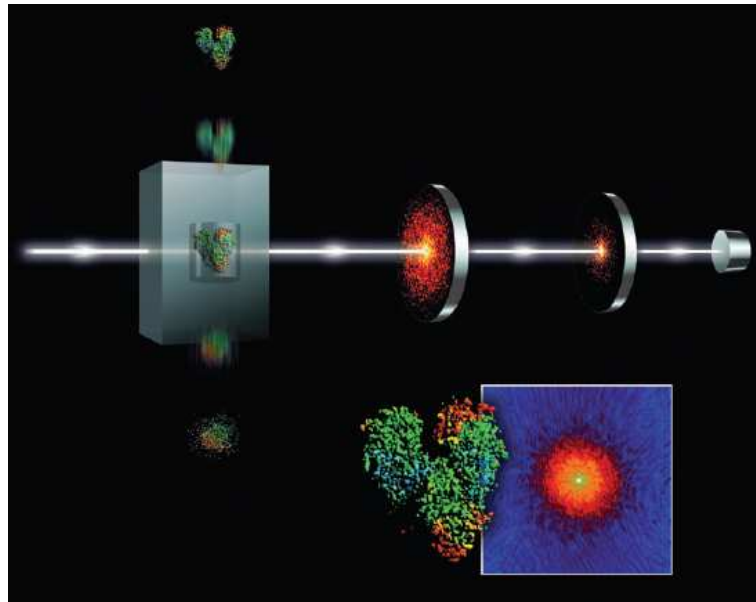
Figure 3.6.: Single-molecule diffraction by an x-ray laser. Individual biological molecules fall through the x-ray beam, one at a time, and are imaged by x-ray diffraction. So far the previous and current dream ! An example of the image is shown in the inset. H. Chapman, Lawrence Livermore National Laboratory.; taken from: *Controlling the Quantum World*, page 82.

➢ Such studies might include biomolecules that are difficult or impossible to crystallize, for example, membrane-bound proteins or even larger molecular machines responsible for many aspects of cellular function.

➢ In practice, however, even the fundamental mechanisms of damage at such high intensities are not well understood and are related to basic questions in AMO physics: Are there important new nonlinear damage mechanisms ?

➢ Requires input from theory: Molecular dynamics simulations are needed to study how the biomolecules behave under these high-vacuum conditions and how the water structure on their surfaces or other structural elements are affected.

Extreme states of matter:

➢ For high enough laser pulse energies, the electrons and ions are accelerate to relativistic velocities close to the speed of light;

➢ Can one design tabletop particle accelerators that can accelerate electrons to GeV energies within a few cm ? (Compare with the 28 km size of the LHC.)

➢ Lasers with a peak power of larger than 1 PW = 10^{15} W are currently constructed in the US, Japan, Britain, France, and Germany. Lasers with 100 times larger peak power (10^{17} W) might be possible in the coming decade. These high-power lasers open up new scientific opportunities to understand, control, and use high-energy-density states of matter.

➢ Laser-induced fusion: Ignition of an imploded fusion pellet by externally heating the fusion fuel.
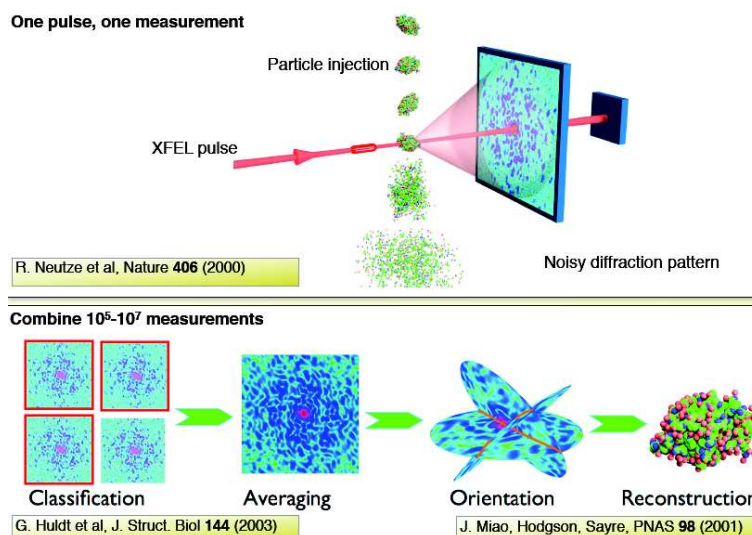
Figure 3.7.: X-ray free-electron lasers may enable atomic resolution imaging of biological macromolecules; from Henry Chapman, talk (2007).

➢ High energy density (HeD) plasmas: exist in nuclear explosions, neutron stars, white dwarfs, or in plasmas that might be controlled to produce energy from nuclear fusion; challenge to develope proper conceptual models in theory.

➢ Schwinger (critical field) limit at 3×10^{18} V/m: At this field strength, the vacuum becomes unstable and QED predicts that electron-positron pairs can be spontaneously generated from the vacuum. The laser intensity required to reach the Schwinger critical field is around 10^{29} W/cm^2. Such high laser intensities are several orders of magnitude beyond the current state of the art.

Web link (total internal reflection):

➢ www.youtube.com/watch?v=5BPC9fWqkDw

3.3. Quantum information with light and atoms

Quantum information science may have profound and far-reaching relevance to economic growth, secure communication as well as number-crunching in the 21st century. The quantum hardware now found in atomic, molecular, and optical (AMO) systems is seen as a key for realizing future quantum devices.
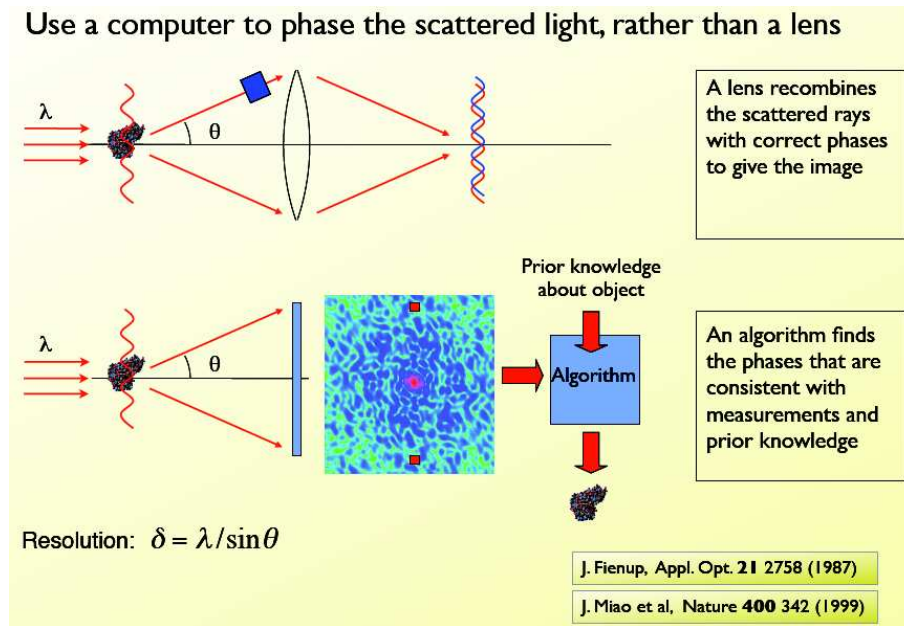
Figure 3.8.: Coherent diffractive imaging is lensless; from Henry Chapman, talk (2007).

What to do with (potential) 'quantum processors ?

➤ Quantum parallelism: N quantum bits cannot only store a superposition of all 2^N binary numbers but also process them simultaneously. One can benefit from this behaviour by designing proper quantum algorithms.

➤ Shor's quantum algorithm for factoring (prime numbers) would factor large numbers exponentially faster than any known classical algorithm. Indeed, factoring a number with 300 digits would require near-perfect control of at least 10^9 near-perfect quantum logic gates, the analog of classical Boolean operations.

➤ Quantum simulations are computations using (many) qubits of one system type that can be initialized and controlled in the laboratory in order to simulate an equal number of qubits of another type that cannot be easily controlled.
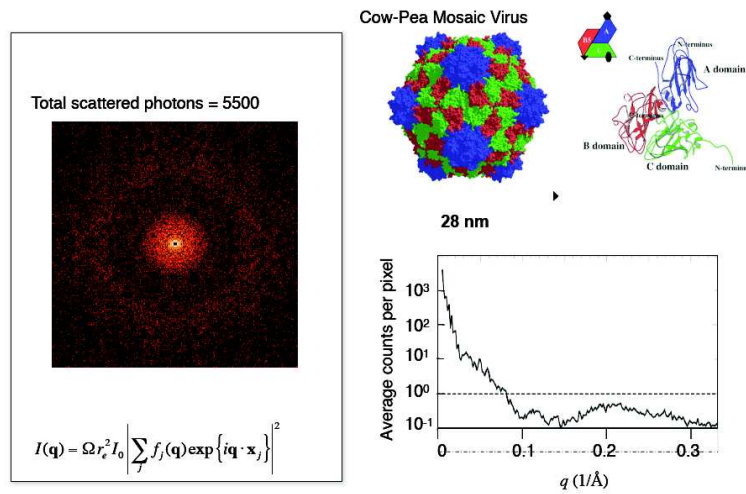
Figure 3.9.: Diffraction images from single particles will be very weak; from Henry Chapman, talk (2007).

4. Atomic many-electron systems

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

4.1.a. Coulomb vs. exchange interaction

$$
\begin{aligned}
H \, \psi \; &= \; (H_1 \; + \; H_2 \; + \; H') \, \psi \; = \; E \, \psi \\[2mm]
&= \; \left(-\frac{\boldsymbol{\nabla}_1^2}{2} \; + \; V_{\mathrm{nuc}}(\mathbf{r}_1) \; - \; \frac{\boldsymbol{\nabla}_2^2}{2} \; + \; V_{\mathrm{nuc}}(\mathbf{r}_2) \; + \; \frac{1}{r_{12}} \right) \psi
\end{aligned}
$$

Hamiltonian is invariant with regard to exchange $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$

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

Suppose $H' \ll (H_1 \; + \; H_2)$, and with

$$
\Longleftarrow \quad
\begin{cases}
(H_1 \; + \; H_2) \, \psi_o \; = \; E_o \, \psi_o \\[2mm]
\psi_o \; = \; u_{n_1 \ell_1 m_{\ell_1}}(\mathbf{r}_1) \, u_{n_2 \ell_2 m_{\ell_2}}(\mathbf{r}_2) \; = \; u_a(1) \, u_b(2) \; = \; u_{ab} \\[2mm]
E_o \; = \; E_{u_1} \; + \; E_{u_2} \; = \; E_a \; + \; E_b \qquad a \neq b
\end{cases}
$$

Indistinguishability: Helium atoms are degenerate with regard to an exchange of the electron coordinates (exchange degeneracy); therefore, a better representation for overlapping charge clouds is

$$
\psi_o \; = \; c_1 \, u_{ab} \; + \; c_2 \, u_{ba}
$$

$$
\psi_o' \; = \; c_3 \, u_{ab} \; + \; c_4 \, u_{ba}
$$

Application of time-independent perturbation theory for H' in this two-dimensional basis gives the matrix

$$
\begin{pmatrix} H_{11}' & H_{12}' \\ H_{21}' & H_{22}' \end{pmatrix} \; = \; \begin{pmatrix} J & K \\ K & J \end{pmatrix}
$$

$$
J \; = \; \int d\tau_1 \, d\tau_2 \, \frac{\rho_a(1)\,\rho_b(2)}{r_{12}} \; = \; \int d\tau_1 \, d\tau_2 \, \frac{\rho_a(2)\,\rho_b(1)}{r_{12}} \qquad \text{direct term}
$$

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

4. Atomic many-electron systems

The two functions ψ_o, ψ'_o are always degenerate with regard to $(H_1 + H_2)$.

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

$$\begin{vmatrix} J - \Delta E & K \\ K & J - \Delta E \end{vmatrix} = 0 \qquad \Longleftrightarrow \qquad \Delta E = J \pm K .$$

ΔE is the energy shift which need to be added to $E_o = E_a + E_b$, and which removes the degeneracy: $E = E_o \pm \Delta E$. The corresponding eigenfunctions are

$$\psi_s = \frac{1}{\sqrt{2}} (u_{ab} + u_{ba}), \qquad \psi_s = \frac{1}{\sqrt{2}} (u_{ab} - u_{ba}) .$$

For these functions, we have (prove it !)

$$\int d\tau \; \psi_s^*(1,2) \frac{1}{r_{12}} \psi_a^*(1,2) = 0 .$$

(Symmetry-) classification of many-particle states: In general, the degeneracy of the wave functions with regard to the exchange of electron coordinates follows directly from the permutation symmetry of the wave functions.

Permutation operator:

$$P_{ij} \, \psi(\mathbf{r}_1, ..., \mathbf{r}_i, \mathbf{r}_j, ...) = \pm \psi(\mathbf{r}_1, ..., \mathbf{r}_j, \mathbf{r}_i, ...)$$

$$P_{ij}^2 \, \psi = \psi \qquad \text{for all functions}$$

with eigenvalue ± 1 ; the permutation operator commutes with all (internal) interactions of H

$$[H, \, P_{ij}] = 0 \qquad \forall \, i \neq j$$

The $\{P_{ij}\}$ are constants of the motion, and all eigenfunctions to H must be either symmetric or antisymmetric with regard to the exchange of electron coordinates.

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

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

$$\psi_a \equiv 0$$

$$\psi_s = u_{1s}(1)\,u_{1s}(2)$$

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

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

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

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

$$= -24.580\,\text{eV} \qquad\qquad\qquad \text{variational}$$

Excited states $a \neq b$

$$E = E_a + E_b + J \pm K$$

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

Large n and ℓ: Exchange integral K becomes negligible

$$H \approx -\frac{\mathbf{\nabla}_1^2}{2} - \frac{\mathbf{\nabla}_2^2}{2} - \frac{Z}{r_1} - \frac{(Z-1)}{r_2}$$

Constants of motion   **... if we neglect the spin-orbit interaction**

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

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2\,, \qquad S_z = s_{1z} + s_{2z}$$

$$\left\{ H,\, P_{12},\, \mathbf{L}^2,\, L_z,\, \mathbf{S}^2,\, S_z \right\}$$

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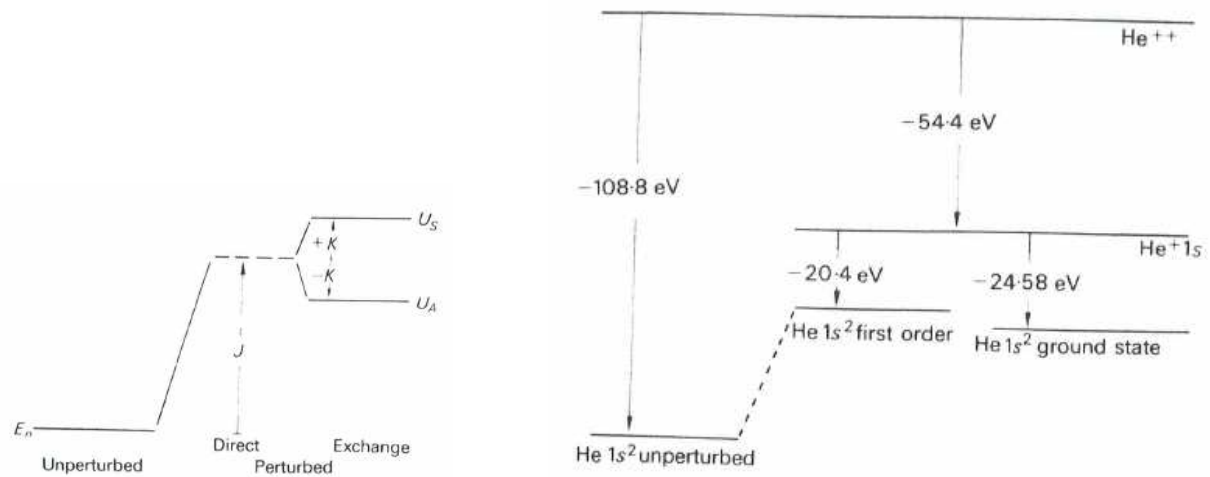
Figure 4.1.: Left: Schematic energy levels for the excited states of helium, showing the effect of the direct and exchange term. Right: Energy levels of helium relative to the singly and doubly-charged ion.

4.1.c. Spin functions and Pauli principle

Without spin-orbit interactions, all one-electron wave functions are separable

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

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

	Function	S	M_S	
	$\chi_+(1)\,\chi_+(2)$		$+1$	
χ_s:	$\frac{1}{\sqrt{2}}\,(\chi_+(1)\,\chi_-(2)\,+\,\chi_-(1)\,\chi_+(2))$	1	0	symmetric
	$\chi_-(1)\,\chi_-(2)$		$+1$	
χ_a:	$\frac{1}{\sqrt{2}}\,(\chi_+(1)\,\chi_-(2)\,-\,\chi_-(1)\,\chi_+(2))$	0	0	antisymmetric

Total wave functions:

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

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

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

- $\psi_s\,\chi_a \qquad$ singulet $\quad$ ... $\quad$ para helium
- $\psi_a\,\chi_s \qquad$ triplet $\quad$ ... $\quad$ 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	
$1s3p$	³P ¹P	12,752 12,107	645	12,186
$1s3d$	³D ¹D	12,215 12,212	3	
$1s4s$	³S ¹S	8,019 7,376	643	
$1s4p$	³P ¹P	7,100 6,824	276	6,854
$1s4d$	³D ¹D	6,872 6,870	2	
$1s4f$	³F ¹F	6,864·4 6,863·8	0·6	
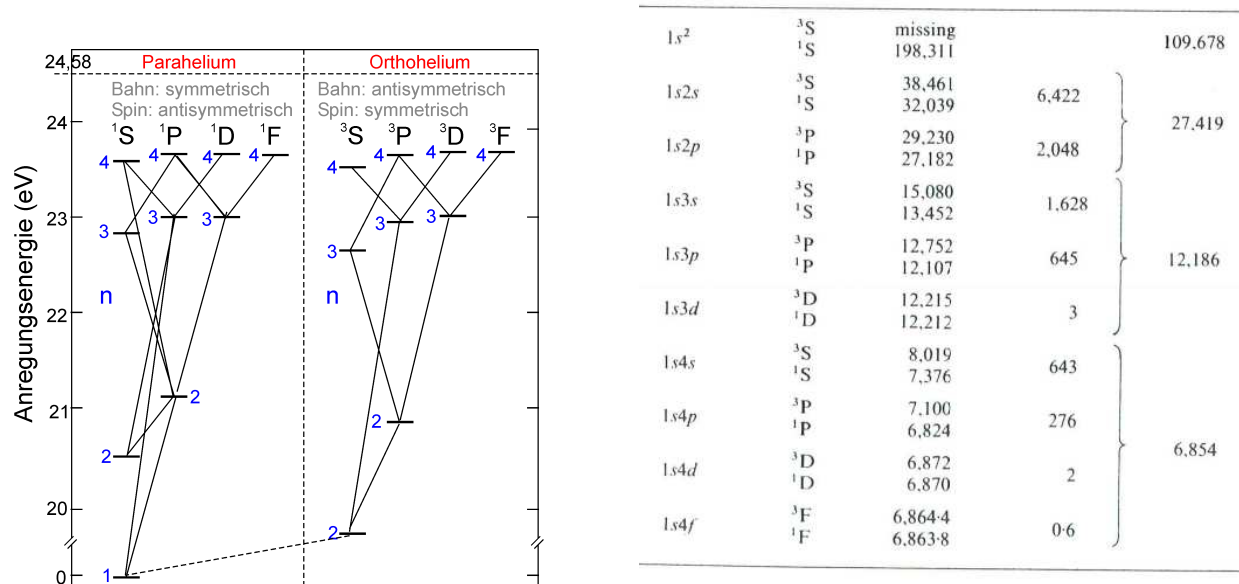
Figure 4.2.: Left: *LS* terms for para and ortho helium; from: http://www.ipf.uni-stuttgart.de/lehre/.
Right: Energy levels in helium.

4.2. Interaction and couplings in many-electron atoms

4.2.a. Hierarchy of atomic interactions

4.2.b. Nuclear potential

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

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

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

- Light atoms: $R \approx 1.2 \cdot A^{1/3}$ fm.
- Heavy elements: Radii are taken from electron-nucleus scattering experiments.

➤ Fermi distribution of the nuclear charge:
$$\rho(r) = \frac{\rho_o}{1 + \exp\left(\frac{r-R}{d}\right)}, \qquad d = 1.039 \cdot 10^5$$

Potential cannot be represented in a simple closed form; numerical solutions or expressed as superposition of Gaussian-type functions.

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

4.2.c. Coulomb interaction between pairs of electrons

For light and medium-heavy elements, there occurs an instantaneous (Coulomb) repulsion between each pair of electrons

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

- This e-e interaction is 'origin' of the eletronic correlations.
- In addition, there occurs a (so-called) Breit interaction in the relativistic description of the electronic structure of atoms and ions; see below.

4.2.d. Spin-orbit interaction

A spin-orbit coupling term

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

need to be treated for each electron i separately; computational simpler than e-e interaction since each term only depends on a single electron coordinate.

4.2.e. Relativistic corrections to the e-e interaction

➤ Current-current interactions (magnetic interactions) and retardation effects give rise to the (so-called) 'Breit interactions'

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

Breit interaction in the long-wavelength approximation

➤ Retardation of the interaction because the 'action' travels only with the speed of light.

➤ Expansion of the Breit interaction in v^2/c^2 gives rise to several terms in the non-relativistic limit; interaction of different magnetic moments as associated with the electronic motion:

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

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

4.2.f. Hyperfine interaction

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

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

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

Rather weak interaction; in light elements, HFS is typically so small that the individual hyperfine lines overlap with each other. A separate HFS line structure typically appears only in medium and heavy elements.

4.2.g. Atomic units

As for the hydrogenic systems, the theoretical treatment is often considerably simplified if we set (see above)

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

4.3. Interaction-induced shifts in atoms and ions

4.3.a. Isotopic effects

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

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

➢ Different charge and magnetization distribution inside the nucleus (nuclear structure)
➟ 'nuclear picture' of the nucleus.
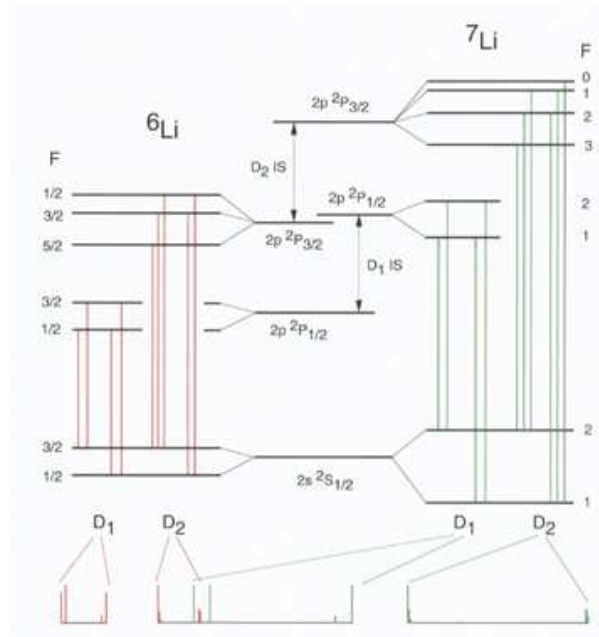
Figure 4.4.: High-precision measurements of the D1 and D2 transition lines of two stable isotopes of lithium allow a separation of individual hyperfine components and small isotope shifts; from http://www.nist.gov/.

Mathematical treatment: ... (Blackboard)

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 the state is 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 : $\tau \sim 10^{-8}\ s$ $\longrightarrow$ $\Delta E \sim 5 \cdot 10^{-4}\ \mathrm{cm}^{-1}$.
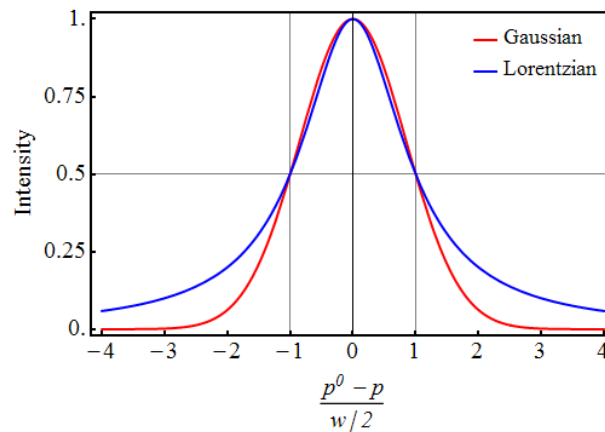
Figure 4.5.: Comparison of Gaussian (red) and Lorentzian (blue) standardized line shapes. The HWHM (w/2) is 1.; from http://en.wikipedia.org/wiki/ .

Intensity distribution (Lorentz profile):

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

- σ ... wave number (transition energy)
- Γ ... line widths

4.4. Atomic many-body hamiltonians

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

... sum over all pairs of electrons

➤ Relativistic corrections in the e-e interaction and HFS splitting are typically rather small and can be treated perturbatively.

➤ Quite sizeable corrections arises from the spin-orbit interaction

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

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

Atomic structure theory: Find approximate soluations to the many-electron Schrödinger equation

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

4.5. Central-field approximations

4.5.a. The central-field model

The (so-called) Coulomb Hamiltonian can be written in different forms:

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

$$
\begin{aligned}
H_C \;=&\; H_o \,+\, H' \\
=&\; \sum_i \left(-\frac{\mathbf{\nabla}_i^2}{2} - \frac{Z}{r_i} + u(r_i) \right) + \sum_{i<j} \frac{1}{r_{ij}} - \sum_i u(r_i) \,,
\end{aligned}
$$

and choose $u(r_i)$ such that the repulsion with the $N-1$ other electrons, when averaged over time, is well described.

Independent-particle model (IPM):   Each electron moves independent of all other electrons in the central field of the nucleus and the $N-1$ remaining electrons.

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

Solutions to H_o are product functions of the one-electron orbital functions

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

spin-orbitals; one-electron functions

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

4.5.b. Product functions and Slater determinants

Since H_o has one-particle character, each product function

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

is solution for H_o. In addition, however, we need to consider:

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

Simplest form of antisymmetric solutions are Slater determinants:

$$\psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(1) & \phi_1(2) & ... & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & ... & \phi_2(N) \\ ... & & & \\ \phi_N(1) & \phi_N(2) & ... & \phi_N(N) \end{vmatrix}$$

$$= \frac{1}{\sqrt{N!}}\sum_P (-1)^P\,\phi_1(k_1)\,\phi_2(k_2)\,...\phi_N(k_N)$$

$N!$ terms; this form is nevertheless quite simple for practical computations.

Remark: There are (much) more complicated functions ψ possible which fulfill the two requirements from above since H_o and $\{P_{ij},\ i \neq j\}$ do NOT describe a complete set of operators.

Norm:

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

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

For free atoms, however, also

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

i.e. solutions to H (or H_o) can be classified due to J, M quantum numbers, while determinants are in general NO eigenfunctions for $\mathbf{J}^2$, only to J_z with eigenwert $M = \sum_i (m_{\ell_i} + m_{s_i})$.

The complete classification of the many-electron quantum states require further quantum numbers; usually $4\,N$ quantum numbers.

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

Electron orbitals: $\qquad \phi_k(\mathbf{r}, \sigma)\,; \qquad k = (n\,\ell\,m_\ell, m_s)$

➥ all functions with equal quantum numbers $(n\ell)$ but different (m_ℓ, m_s) are degenerate in any central-field potential. They are called equivalent electron orbitals or short equivalent electrons.

Set of (maximal) $q = 2\,(2\ell + 1)$ equivalent electrons form a subshell: $\qquad (n\ell)^w$

Electron configuration:

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

does not describe a particular quantum state but rather a set of determinants which only differ in the magnetic quantum numbers and which are degenerate with respect to H_o. An electron configuration also represents some particular sub-space of the many-electron Hilbert space.

Shell notations in spectroscopy:

K-shell:	$n = 1$	$(1s)$
L	$n = 2$	$(2s + 2p)$
M	$n = 3$	$(3s + 3p + 3d)$
N	$n = 4$	$(4s + 4p + 4d + 4f)$
O	$n = 5$	$(5s + 5p + 5d + 5f + 5g)$

Atomic shell model:

Total charge density of a filled subshell is spherical symmetric since

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

i.e. the equivalent electrons of a filled subshell form indeed a spherical symmetric shell (Unsöld's theorem).

Central-field model (approximation) is the theoretical basis for the periodic table of elements

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

Rydberg series (of configurations): $\qquad 2p^5 3p,\; 2p^5 4p,\; 2p^5 5p,\; ...$

The fully occupied core is typically omitted from the notation.

Aufbau principle: Electron shells $(n\ell)$ are filled successively due to their energy, from shells with large binding energies to those with lower energy. In practice, deviation from

this principle occur already for $Z \gtrsim 18$ (argon)
- $(n+1)s$ and $(n+1)p$ are often filled before the nd shell ⤳ transition metals.

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

$4d$ ... 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 (Alkali atoms):
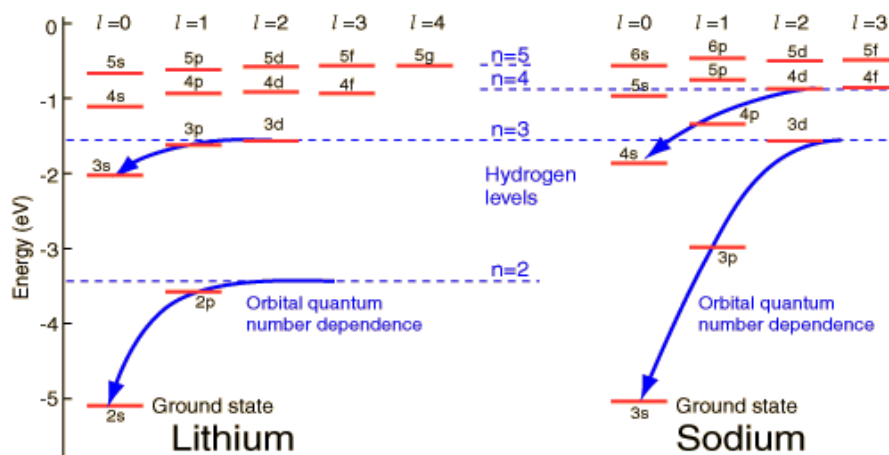
Figure 4.6.: For alkali atoms, a rather strong orbital angular momentum dependence if found for the low-lying energy levels; from http://hyperphysics.phy-astr.gsu.edu.

4.5.d. Thomas-Fermi potential

Thomas-Fermi model: Electrons form a Fermi gas (Fermi-Dirac statistic)

electron density $\longrightarrow$ electrostatic potential

Thomas-Fermi equation: ... (Blackboard)

Gives rise to Thomas-Fermi equation

$$\frac{d^2\chi}{dx^2} = x^{-1/2}\chi^{3/2}$$
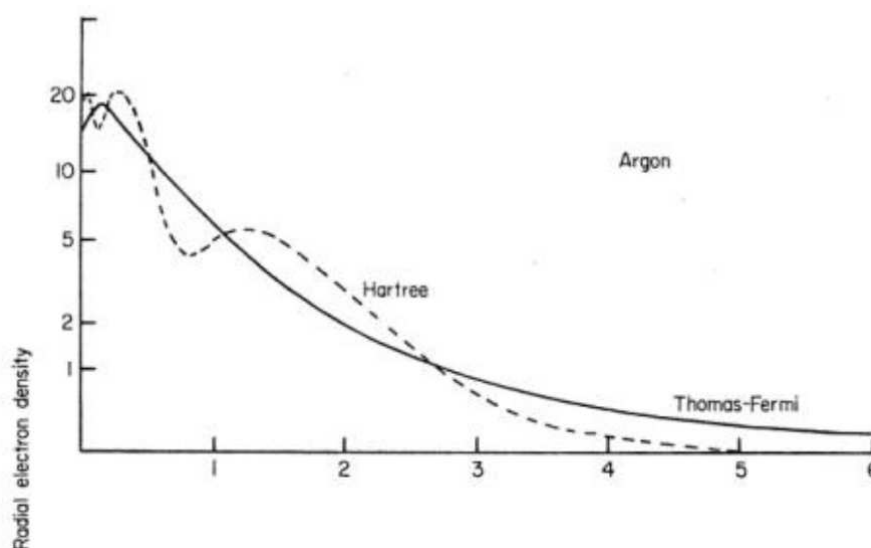
Figure 4.7.: Comparison between the Thomas-Fermi electron densities (from which the potential can be derived) and more accurate quantum-mechanical Hartree densities, obtained in the independent-electron approximation.; from http://www.virginia.edu/ep/Interactions/.

Universal equation for all atoms (within the TF model) which can be solved numerically; $\chi(r)$ describes the screening of the nuclear charge and b a weak Z-dependent scaling factor.

- For $r \sim a_o$, we have $\quad -\frac{Z}{r} < V^{\text{TF}}(r) < -\frac{1}{r}$.

- Correct for $r \to 0$: $\quad\quad V(r) \to -\frac{Z}{r}$.

- Incorrect for $r \to \infty$: $\quad V(r)$ goes to quickly to zero since it includes all the electrons in the consideration; improvements of this behaviour is possible.

- Although the TF model is a statistical one, it also describes small atoms surprising well; it is often used to start an SCF iteration.

4.6. Coupling schemes

4.6.a. Term splitting in electron configurations

Rest interaction:

$$H' = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i u(r_i)$$

$$H'' = \sum_i \xi_i(r_i) \; (\mathbf{l} \cdot \mathbf{s}) \quad\quad\quad\quad \text{spin} - \text{orbit interaction}$$

... removes the de-generacy of the central-field solutions.

Two approaches to obtain the level splitting:

- Calculation and diagonalization of the submatrices to $H_o + H' + H''$.
- Form linear combinations of the determinants (of a given configuration) for which H' and/or H'' are diagonal; use of the known constants of motion.

Constants of motion: ... (Blackboard)

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

LS-coupling approach: For light atoms ($Z \lesssim 20$), the spin-orbit interaction is usually negligible when compared with the remaining electron-electron interaction, i.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; their energy only depends on L and S.

Level: is specified by LSJ and parity

Blackboard example (p^2 configuration):

LS terms of equivalent electrons: ... (Blackboard)

4.6.c. LS-coupling of open shells

For two or several open shells, we must couple the total orbital and spin momenta of the individual shells:

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

       ..., i.e. apply the vector model to determine all possible L and S .

Coupling sequence:

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

Compact notation:

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

					Total Number
s	²S				1
s²	¹S				1
p, p⁵	²P				1
p², p⁴	¹(SD)	³P			3
p³	²(PD)	⁴S			3
d, d⁹	²D				1
d², d⁸	¹(SDG)	³(PF)			5
d³, d⁷	²(PD₂FGH)	⁴(PF)			8
d⁴, d⁶	¹(S₂D₂FG₂I)	³(P₂DF₂GH)	⁵D		16
d⁵	²(SPD₃F₂G₂HI)	⁴(PDFG)	⁶S		16
f, f¹³	²F				1
f², f¹²	¹(SDGI)	³(PFH)			7
f³, f¹¹	²(PD₂F₂G₂H₂IKL)	⁴(SDFGI)			17
f⁴, f¹⁰	¹(S₂D₄FG₄H₂I₃KL₂N)	³(P₃D₂F₄G₃H₄I₂K₂LM)	⁵(SDFGI)		47
f⁵, f⁹	²(P₄D₅F₇G₆H₇I₅K₅L₃M₂NO)	⁴(SP₂D₃F₄G₄H₃I₃K₂LM)	⁶(PFH)		73
f⁶, f⁸	¹(S₄PD₆F₄G₈H₄I₇K₃L₄M₂N₂Q)	³(P₆D₅F₉G₇H₉I₆K₆L₃M₃NO)	⁵(SPD₃F₂G₃H₂I₂KL) ⁷F		119
f⁷	²(S₂P₅D₇F₁₀G₁₀H₉I₉K₇L₅M₄N₂OQ)	⁴(S₂P₂D₆F₇G₇H₅I₅K₃L₃MN)	⁶(PDFGHI) ⁸S		119

*H. N. Russell, Phys. Rev. 29, 782 (1927); R. C. Gibbs, D. T. Wilber, and H. E. White, Phys. Rev. 29, 790 (1927).

Figure 4.8.: 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 that need be distinguished by some additional quantum number(s). See table for references.

There are no further restrictions due to the Pauli principle. The number of LS terms is of course independent of the coupling sequence.

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

4.6.d. jj-coupling

jj-coupling approach: Applies approximately for the heavy elements ($Z \gtrsim 90$), for which we have $H_{\mathrm{SO}} \gg H_{rest}(e-e)$.

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

The set of all $(2J+1)$ degenerate states is equivalent here to a Level (as specified by LSJ and parity).

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

A number of further coupling schemes have been discussed in the literature but are less important in practice.
.
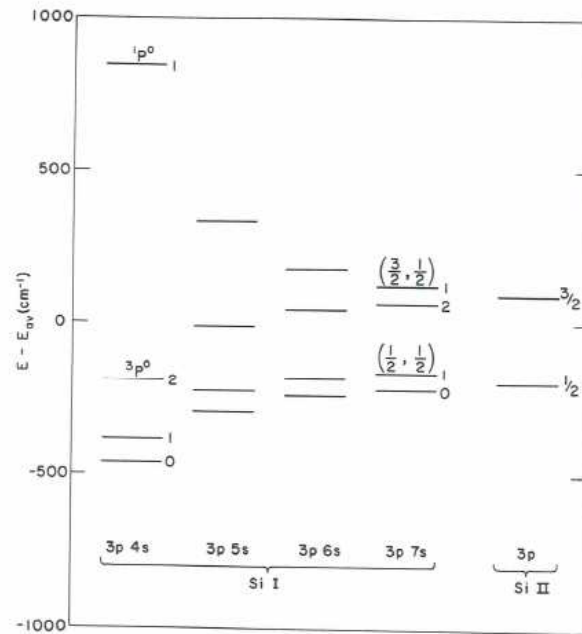
Figure 4.9.: The observed energy level structure for the four lowest $3pns$ comfigurations of Si I and together with the Si II configuration, relative to the respective centers of gravity. The figure shows a rapid change from LS to pair-coupling conditions.

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

4.6.e. Intermediate coupling. The matrix method

The total rest interaction $H' + H'' = H_{rest}(e-e) + H_{SO}$ is not diagonal in any (geometrically fixed) coupling scheme. In general, we only have

$$[H, \mathbf{J}^2] = [H, J_z] = [H, P] = 0,$$
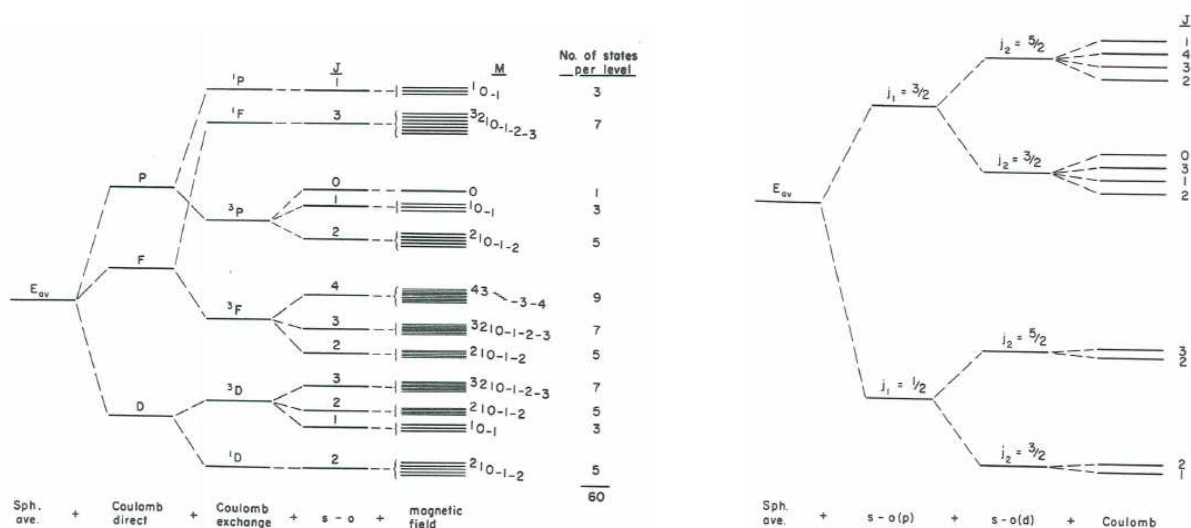
Figure 4.10.: Left: Energy level structure of a pd configuration under LS coupling conditions; it starts from the central-field averaged energy and takes different contributions into account. Right: The same but under jj coupling conditions; the two quite strong spin-orbit interactions result into four different energies due to the pairs (j_1, j_2) of the two electrons.

		p^2	
d^2	^1S	^3P	^1D
^1S	^1S	^3P	^1D
^3P	^3P	$^{1,3,5}SPD$	^3PDF
^1D	^1D	^3PDF	^1SPDFG
^3F	^3F	$^{1,3,5}DFG$	^3PDFGH
^1G	^1G	^3FGH	^1DFGHI

Figure 4.11.: Possible LS terms of the $d^2\, p^2$ configuration.

i.e., only the total angular momentum $\mathbf{J}^2$ and J_z as well as the total parity are (strictly) conserved in free atoms.

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

4.7.a. Matrix elements of symmetric operators with Slater determinants

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

Most operators in atomic theory consist of:

➢ One-particle operators: $\quad F = \sum_i^N f(\mathbf{x}_i) \qquad$ ➥ symmetric in $(\mathbf{r}_i, \sigma_i)$.
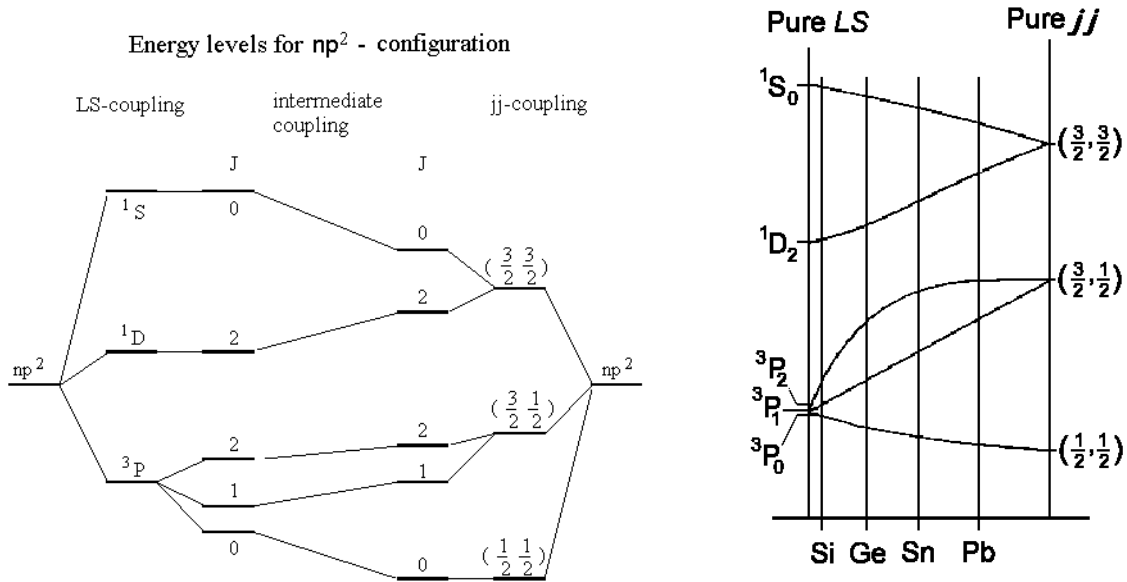
Figure 4.12.: Energies for the np^2 configuration and change in the coupling scheme for various elements homolog to atomic silicon.

➤ 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 $F = \sum_i^N f(\mathbf{r}_i)$

Owing to the symmetry $\langle \psi' | f(\mathbf{r}_i) | \psi \rangle = \langle \psi' | f(\mathbf{r}_j) | \psi \rangle$, we find:

$$
\begin{aligned}
\langle \psi' | F | \psi \rangle &= N \, \langle \psi' | f(\mathbf{r}_1) | \psi \rangle \\[2mm]
&= \frac{N}{N!} \sum_{PP'} (-1)^{P+P'} \, \langle \phi_{k_1}(1)\, \phi_{k_2}(2) \,...\, | f(\mathbf{r}_1) |\, \phi_{k_1'}(1)\, \phi_{k_2'}(2) \,... \rangle \\[2mm]
&= \begin{cases}
\sum_i \langle i | f(\mathbf{r}) | i \rangle & \text{if } \psi' = \psi \text{ and } \psi = \{a, b, c, ...\} \\[2mm]
\pm \langle a' | f(\mathbf{r}) | a \rangle & \text{if } \psi' = \{a', b, c, ...\} \text{ and } \psi = \{a, b, c, ...\} \\[2mm]
0 & \text{else; i.e. if two or more orbitals differ} \\
& \psi' = \{a', b', c, ...\} \text{ and } \psi = \{a, b, c, ...\}
\end{cases}
\end{aligned}
$$

That is

$$
\langle \psi' | F | \psi \rangle = \begin{cases}
\sum_i \langle i | f | i \rangle & \text{all diagonal ME} \\[2mm]
\langle a' | f(\mathbf{r}) | a \rangle & \text{ME which differ in just one orbital } a' \neq a \\[2mm]
0 & \text{else}
\end{cases}
$$

67
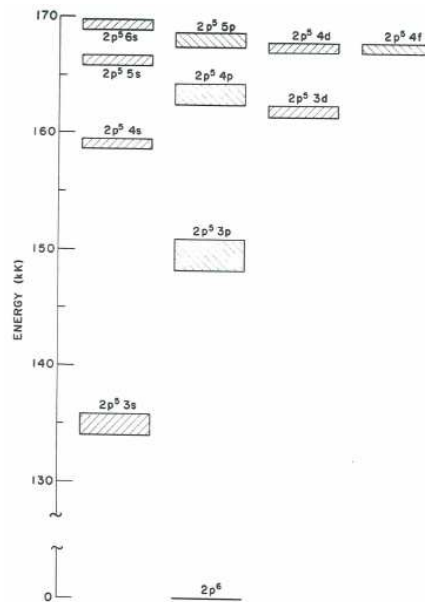
Figure 4.13.: Block diagram of the lowest configurations of Ne I. For each configuration, the levels lay within a limited range of energies as it is shwon by the shadowed blocks. There is one level for $2p^6$, 4 levels of ps configurations, 10 levels for p^5p' configurations and 12 levels for p^5d and p^5f configurations, respectively.

Matrix elements of symmetric two-particle operators

Similar discussion lead to

$$
\langle \psi' \,|G|\, \psi \rangle \;=\;
\begin{cases}
\sum_{i<j} \left(\langle ij \,|\, g \,|\, ij \rangle \;-\; \langle ji \,|\, g \,|\, ij \rangle \right) & \text{all diagonal ME} \\[2ex]
\sum_{i} \left(\langle ia' \,|\, g \,|\, ia \rangle \;-\; \langle a'i \,|\, g \,|\, ia \rangle \right) & \text{ME which just differ in} \\
 & \text{one orbital } a' \neq a \\[2ex]
\left(\langle a'b' \,|\, g \,|\, ab \rangle \;-\; \langle a'b' \,|\, g \,|\, ab \rangle \right) & \text{ME which differ in} \\
 & \text{two orbitals } a' \neq a,\; b' \neq b \\[2ex]
0 & \text{else, i.e. for more than} \\
 & \text{two differences}
\end{cases}
$$

Simplified notation

$|\alpha\rangle$ ... Slater determinant $|\{a, b, ..., n\}\rangle$

ordered set of one-particle functions, i.e. quantum numbers

Moreover, 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 $a \to r$ is replaced by a virtual orbital (r); analogue for $|\alpha_{ab}^{rs}\rangle$.

Simplified notations for matrix elements

➤ Diagonal ME

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

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

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

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

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

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

➤ ME between determinant which differ by two orbitals

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

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

➤ All other ME vanish identically.

Feynman-Goldstone diagrams

Matrix elements can be represented also in terms of diagrams; such graphical methods are very important for studying complex atoms and molecules. ➥ MBPT   ... many-body perturbation theory.
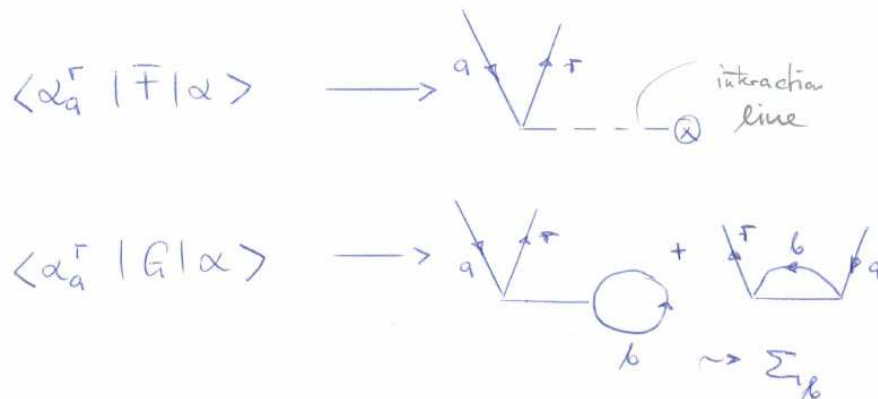

Figure 4.14.: Selected Feynman-Goldstone diagrams to represent matrix elements and wave operators.

Blackboard example (Feynman-Goldstone diagrams):

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

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):

Starting potential $\longrightarrow$ $\underbrace{\text{Calculate } 1-\text{p functions}}$ $\longrightarrow$ Calculate new potential
$\hspace{8cm} \longleftarrow perform\ iteration$

Mathematical formulation of this SCF scheme, and which takes into account also the Pauli principle, leads us to the Hartree-Fock equations.

4.7.c. Abstract Hartree-Fock equations

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

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

The optimal approximation for the (ground state) $|\alpha\rangle$ is obtained from the (variational) minimization of the expectation value with regard to variations of the orbital functions, i.e.:

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

$|a\rangle \;\longrightarrow\; |a\rangle \,+\, \eta\,|r\rangle$ η ... real

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

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

$\langle\alpha_a^r\,|H|\,\alpha\rangle \;=\; 0$ for all pairs a, r Hartree $-$ Fock condition

Brillouin's theorem: In the Hartree-Fock approximation, the 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.

Hartree-Fock method in more detail   ... (Blackboard)

Koopman's theorem: In the HF approximation, the ionization energy for releasing an electron a is equivalent to the (negative) one-electron HF energy of the electron a. In this approximation, no relaxation of the $N-1$ other electrons is taken into account.

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

Central-field model: $\qquad H_o = \sum_i^n h_o(i)$

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

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

I.e. only the radial functions are NOT YET fixed and are allowed to vary.

Orbital functions must be solutions of the radial equation

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2\,r^2} - \frac{Z}{r} + u(r) \right] P(r) = \epsilon \, P(r)$$

with the boundary conditions:

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

$$\int dV \, |\phi|^2 = \int_0^\infty dr \, P^2(r) \qquad \text{... must be normalizable}$$

Classification of $P_{nl}(r)$ by n and l is still possible:

$$n = \nu + \ell + 1 \qquad\qquad \nu \text{ ... number of knots}$$

$$\epsilon = \epsilon(n, \ell) = \epsilon_{n\ell}$$

Form of the restricted Hartree-Fock equations: $\qquad$ ... (Blackboard)

(Restricted) Hartree-Fock method: Ritz variational principle of the total energy

$$\delta \, \langle E \rangle = \delta \, E_{\text{av}} = 0$$

with additional condition

$$N_{n\ell,n'\ell} = \int_0^\infty dr \, P_{n\ell}^*(r) \, P_{n'\ell}(r) = \delta_{nn'}$$

or equivalent:

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

for all variations $\delta P_a(r)$ with the given boundary conditions from above, and where E_{av} refers to the expression for the configuration-averaged energy.
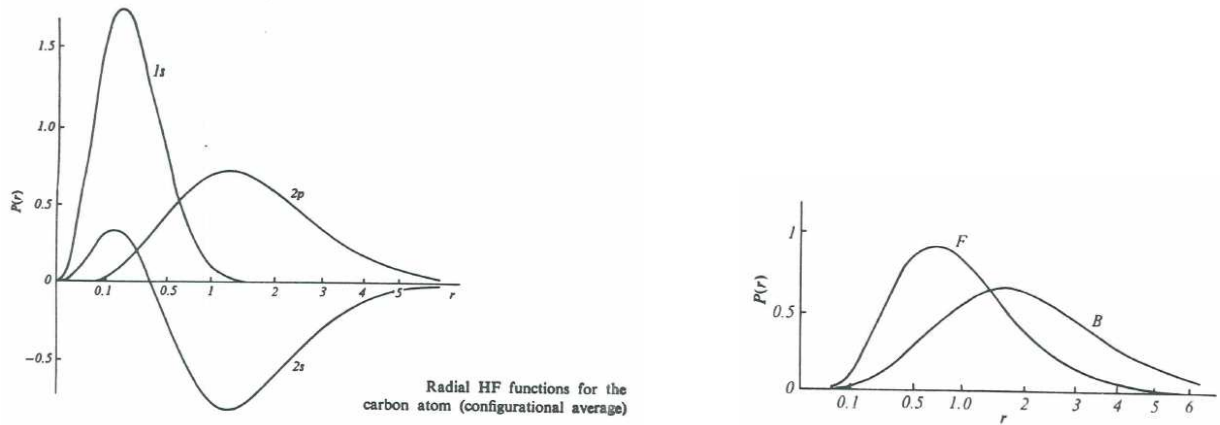
Figure 4.15.: (Radial Hartree-Fock functions for carbon (left) as well as for the $2p$ electrons of boron and fluorine (right).

Then, the restricted HF equations read as:

$$
\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell_a(\ell_a+1)}{2\,r^2} - \frac{Z}{r} \right] P_a(r)
$$

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

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

where

$$
\epsilon_a = \lambda_{aa} \qquad\qquad \mathrm{one-electron\ eigenvalues}
$$

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

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

Set of linear and coupled integro-differential equations which have to be solved iteratively.

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

4.8.a. Configuration interaction theory (matrix method)

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

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

E	E(^{3}P)		E$_{av}$		E(^{1}D)		E(^{1}S)	
	−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 4.16.: 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).

nl	He $\langle r \rangle_{nl}$	Ne $\langle r \rangle_{nl}$	A $\langle r \rangle_{nl}$	Kr $\langle r \rangle_{nl}$	Xe $\langle r \rangle_{nl}$
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 4.17.: Expectation values of r from Hartree-Fock calculations for noble gas atoms (taken from Lindgren and Morrison, 1986).

In practice, the infinitely large basis must always be truncated, $i = 1, ..., M$: Substitution into the Schrödinger $H \Psi_k = E_k \Psi_k$ equation gives rise to:

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

$$\sum_i^M H_{ji} c_{ik} = E_k c_{jk} \qquad \forall j$$

$$H_{ji} = \langle \Phi_j | H | \Phi_i \rangle \quad ... \quad \text{matrix elements of } H.$$

The matrix method result into a homogenous equation with hermitian matrix ($H_{ik} = H_{ki}^*$) and, in atomic structure theory, into a real-symmetric matrix with non-trivial solutions for

$$|H - E I| = 0,$$

the so-called secular equation.

Solutions are the zeros of the characteristic polynomial and are obtained by diagonalization of the Hamiltonian matrix.

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

Hartree-Fock method

MCDF method

$$|\alpha\rangle \qquad \longrightarrow \qquad |\alpha(k)\rangle \; = \; \sum_i c_{ik} \, |\alpha_i\rangle$$

* single determinant

* superposition of determinants

* variation of (radial) orbital functions

* variation of (radial) orbital <u>and</u> the expansion coefficients $\{c_{ik}\}$.

Steps in deriving the MCDF equations   ... (Blackboard)

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 $1s^2 2s 2p \ ^3P$ 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	$-0.118\,09$	$-14.511\,502$
$2s\,1p$	0.295 80	$-0.059\,16$	7.8297	$-0.118\,32$	$-14.511\,577$
$3s\,2p\,1d$	0.298 87	$-0.061\,82$	9.0900	$-0.122\,82$	$-14.553\,679$
$4s\,3p\,2d\,1f$	0.302 88	$-0.068\,51$	9.0444	$-0.107\,67$	$-14.560\,100$
$5s\,4p\,3d\,2f$	0.303 44	$-0.063\,34$	9.1527	$-0.112\,91$	$-14.563\,946$
$6s\,5p\,4d\,3f$	0.304 63	$-0.068\,46$	9.2254	$-0.119\,91$	$-14.565\,325$
$7s\,6p\,5d\,4f$	0.304 11	$-0.064\,71$	9.2376	$-0.111\,78$	$-14.565\,841$
$8s\,7p\,6d\,5f$	0.304 31	$-0.066\,94$	9.2268	$-0.119\,04$	$-14.566\,132$
$9s\,8p\,7d\,6f$	0.303 67	$-0.066\,03$	9.2293	$-0.116\,06$	$-14.566\,232$
$10s\,9p\,8d\,7f$	0.303 73	$-0.065\,78$	9.2317	$-0.115\,48$	$-14.566\,295$
$11s\,10p\,9d\,8f$	0.303 68	$-0.065\,96$	9.2298	$-0.115\,98$	$-14.566\,319$
$12s\,11p\,10d\,9f$	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 4.18.: From Jönsson and Froese Fischer, Phys. Rev. A48 (1993).

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

Standard perturbation theory starts from a suitable decomposition of the Hamiltonian operator

$$H \;=\; H_o + V$$

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

and where solutions to H_o are supposed to be known.

Ansatz:

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} +$$

$$\phi_n = \phi_n^{(0)} + \phi_n^{(1)} +$$

for which we find easily:

$$E_n^{(1)} = V_{mn}$$

$$E_n^{(2)} = \sum_m \frac{V_{nm} V_{mn}}{E_n^{(0)} - E_m^{(0)}}$$

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

m ... sum over a complete set of many-particle states.

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

➤ We assume the decomposition

$$H = H_o + V , \qquad H_o = \sum_i h_o(\mathbf{r}_i)$$

$$H_o \Phi^a = H_o^a \Phi^a , \qquad \left\langle \Phi^a \mid \Phi^b \right\rangle = \delta_{ab}$$

➤ with Slater determinants Φ^a built from one-electron functions $\phi_k : h_o \phi_k = \epsilon \phi_k$.

➤ Goal: Solutions of the SE $H \Psi^a = E^a \Psi^a$ for a finite number $a = 1, ..., d$ of atomic states.

➤ Model space: $\quad \mathcal{M} = \text{span}\{\Phi^a, a = 1, ..., d\}$

All other solutions Φ^r of H_o with $\Phi^r \notin \mathcal{M}$ lay in the (complementary) space orthogonal to $\mathcal{M}$.

➤ Projection operator:

$$P = \sum_{a \in \mathcal{M}} |\Phi^a\rangle \langle \Phi^a|$$

$$Q = 1 - P = \sum_{r \notin \mathcal{M}} |\Phi^a\rangle \langle \Phi^a|$$

$$P = P^+ = P^2, \qquad PQ = QP = 0$$

$$[P, H_o] \;=\; [Q, H_o] \;=\; 0$$

$$\Phi_o^a \;=\; P\,\Phi^a$$

Projection operators commute with H_o.

If Φ^a is known, Φ_o^a is just the projection of the exact solution upon the model space.

➤ Wave operator: (Möller, 1945)

$$\Phi^a \;=\; \Omega\,\Phi_o^a$$

Note: Ω and P are not *inverse* operators.

➤ Intermediate normalization:

$$\langle \Phi^a \,|\, \Phi_o^a \rangle \;=\; \langle \Phi_o^a \,|\, \Phi_o^a \rangle \;=\; 1 \quad \Longleftrightarrow \quad P \;=\; P\Omega P \,.$$

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

$$-\,H_o\,\Omega P\,\Psi^a \;+\; V\,\Omega P\,\Psi^a \;=\; E^a\,\Omega P\,\Psi^a$$

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

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

Generalized Bloch equation.

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.
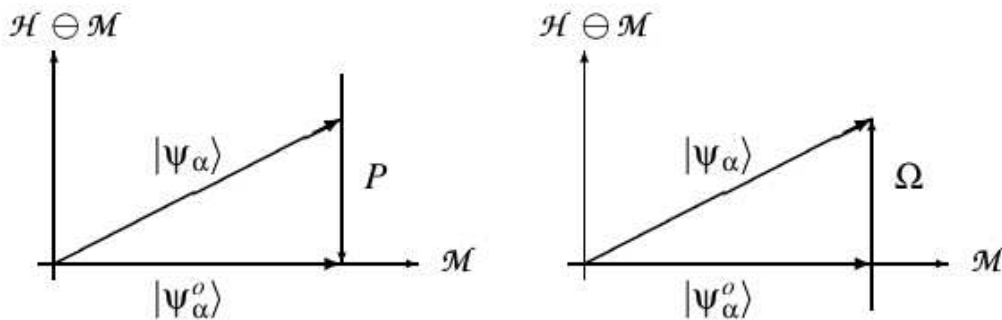
Figure 4.19.: Simplified representation of the operators P and Ω in IN. The projector P transforms a d-dimensional space $\{\Phi^a,\; a \;=\; 1,...,d\}$ of the Hilbert space into the model space $\mathcal{M}$ of the same dimension. The wave operator Ω reverses this transformation. Note, however, that P and Ω are not inverse operators.

Order-by-order perturbation expansions: ... (Blackboard)
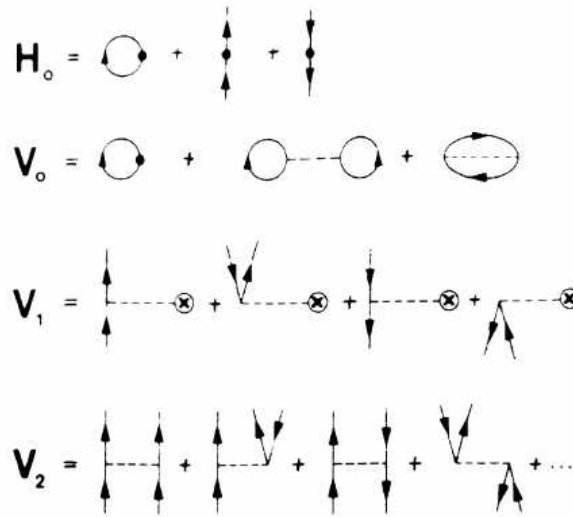
Figure 4.20.: Grafical representation of the unperturbed Hamiltonian operator H_o and the perturbation V, written in normal form [cf. Eqs. (4.31-4.35) in Lindgren (1978).

4.8.d. Relativistic corrections to the HF method

The most simple and straightforward extension starts from the replacements

$$h = -\frac{\nabla^2}{2} - \frac{Z}{r} \qquad \longrightarrow \qquad h_{\mathrm{D}} = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)\,c^2 - \frac{Z}{r}$$

$$\phi \qquad \longrightarrow \qquad \psi_{\mathrm{D}} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix},$$

i.e., the use of one-particle Dirac Hamiltonian, Dirac matrices and Dirac spinors.

Therefore, we need to construct the determinants, the solutions to the central-field Hamiltonian, from four-component Dirac spinors. This is known as Dirac-Fock method; it contains the same abstract (HF) equations as above and also incorporates completely the spin-orbit interaction due to the one-particle Dirac Hamiltonian.

Relativistic Hamilton operator: ... (Blackboard)

5. Angular momentum (AM) in quantum physics

5.1. Angular momentum operators

Commutation relation & eigenfunctions:

$$[l_i,\, l_j] \;=\; i\hbar\,\epsilon_{ijk}\,l_k$$

$$\mathbf{l}^2\,Y_{lm} \;=\; \hbar^2\,\ell(\ell+1)\,Y_{lm} \qquad \ell \;=\; 0,1,2,... \qquad\qquad \text{orbital angular momentum QN}$$

$$l_z\,Y_{lm} \;=\; m\,\hbar\,Y_{lm} \qquad\qquad m \;=\; -\ell, -\ell+1, ..., \ell \qquad\qquad \text{magnetic QN}$$

The eigenfunctions Y_{lm} are called the spherical harmonics, and $\hbar$ is often omitted (if all angular momenta are taken in units of $\hbar$).

5.1.a. Algebraic definition of angular momentum

Definition by commutator:

➢ In the algebraic method of angular momentum (AM) theory, one defines the commutators of the cartesian components by:

$$[j_i,\, j_j] \;=\; i\hbar\,\epsilon_{ijk}\,j_k\ ,$$

with the consequence that the eigenvalues include all (non-negative) integer and half-integer values, such as the spin-1/2 systems.

➢ From this definition, one then obtains:

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

$$[j_+,\, j_-] \;=\; 2\,\hbar\,j_z$$

$$[j_z,\, j_\pm] \;=\; \pm\,\hbar\,j_\pm$$

$$[j_\pm,\, \mathbf{j}^2] \;=\; 0$$

with $\mathbf{j}^2 \;=\; j_x^2 + j_y^2 + j_z^2$ and $j_\pm \;=\; j_x \pm i\,j_y$.

➢ Since j_x, j_y, j_z are observables and hermitian, also the operators $\mathbf{j}^2$, $j_\pm$ are hermitian and related to each other by: $j_+ \;=\; j_-^\dagger$.

➢ j_+ is called the raising operator and j_- is the lowering operator, and together briefly the ladder operators.

5. Angular momentum (AM) in quantum physics

➤ The algebraic method considers the eigenvalue equations

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

$$j_z \, u_{\lambda m} = \hbar \, m \, u_{\lambda m}$$

and determines conditions for λ and m by using the ladder operators, commutation relations and orthogonality of the eigenfunctions.

For example, one obtains with

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

$$N_+(\lambda, m) = N_-^*(\lambda, m+1) \equiv N(\lambda m)$$

$$|N(\lambda, m)|^2 = \hbar^2 \, [j(j+1) - m(m+1)]$$

➤ Condon-Shortley phase convention: $\quad N(\lambda, m) = \hbar \, \sqrt{j(j+1) - m(m+1)}$.

➤ The possible values of m are $m = j, j-1, j-2, ..., -j$, and with $j >= 0$, this means

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, ...$$

$$\lambda = j(j+1)$$

➤ Eigenvalue equations:

$$\mathbf{j}^2 \, u_{jm} = \hbar^2 \, j(j+1) \, u_{jm}$$

$$j_z \, u_{jm} = \hbar \, m \, u_{jm}$$

Problem (Commutation relations of AM operators): Derive the commutation relations

$$[j_i, \mathbf{j}^2] = 0 \quad (i = 1, 2, 3), \qquad [j_+, j_-] = 2\,\hbar\,j_z,$$

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

from

$$[j_i, j_j] = i\hbar\,\epsilon_{ijk}\,j_k\;,$$

5.1.b. Matrix representation of angular momentum operators

We wish to construct a matrix representation of the cartesian components j_x, j_y and j_z of the angular momentum operator $\mathbf{j} = j_x\,\mathbf{e}_x + j_y\,\mathbf{e}_y + j_z\,\mathbf{e}_z$.
We can form the matrix elements:

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

$$\langle u_{jm} \,|\, j_z \, u_{jm'} \rangle = \hbar \, \delta_{mm'}$$

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

and with $j_\pm = j_x \pm i\, j_y$

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

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

Example (Spin-1/2 systems): For spin-1/2 systems, we have $m = \pm 1/2$ and this gives rise to the matrix representations

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

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

Blackboard example (Spin-1 systems):

5.1.c. Algebra of Pauli matrices

Because of the significance of spin-1/2 particles and systems, the matrix representation of the angular momentum operators (apart from the factor $\hbar/2$) are known also as Pauli matrices, and together with σ_o :

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

These Pauli matrices obey several important relations:

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \sigma_o$$

$$[\sigma_i, \sigma_j] = 2i\, \epsilon_{ijk}\, \sigma_k$$

$$\{\sigma_i, \sigma_j\} = 2\delta_{ij}\, \sigma_o$$

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

Linear independence of the Pauli matrices:

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

only holds iff $a_o = a_1 = a_2 = a_3 = 0$. This completeness of the Pauli matrices means that they form a basis for arbitrary 2×2 matrices:

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

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

$$a_i = \frac{1}{2} \operatorname{Tr} (\sigma_i A)$$

$$(\mathbf{a} \cdot \boldsymbol{\sigma}) (\mathbf{b} \cdot \boldsymbol{\sigma}) = \mathbf{a} \cdot \mathbf{b} + i \boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b}), \qquad (\mathbf{a} \cdot \boldsymbol{\sigma})^2 = a^2 .$$

5.2. Coupling of angular momenta

5.2.a. Example: Angular momentum of electrons (spin-1/2 particles)

Let us consider an electron (spin-1/2 particle) with spatial coordinate $\mathbf{r}$ and spin projection $m_s = \pm 1/2$.

Hilbert space: Product of the position space $\mathbf{r}$ and the spin space

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

Rotation operator: still given by $\exp\left(\frac{-i \mathbf{j} \cdot \mathbf{n} \vartheta}{\hbar}\right)$ with

$$\mathbf{j} = \mathbf{l} \otimes \mathbf{1} + \mathbf{1} \otimes \mathbf{s} = \mathbf{l} + \mathbf{s} \qquad \text{and}$$

$$[l_i, l_j] = i\hbar \, \epsilon_{ijk} \, l_k, \qquad [s_i, s_j] = i\hbar \, \epsilon_{ijk} \, s_k, \qquad [l_i, s_j] = 0,$$

and where $\mathbf{n}$ is a unit vector along the rotation axis. This gives rise to the rotation operator in the product space

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

Wave functions in product space: Superposition of two spin components

$$\psi(\mathbf{r}, \sigma) = \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix} = \psi_\uparrow(\mathbf{r}) |\uparrow\rangle + \psi_\downarrow(\mathbf{r}) |\downarrow\rangle .$$

Operators and product states of composite system: $\{\mathbf{l}^2, l_z, \mathbf{s}^2, s_z\}$

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

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

$$l_z \, |\ell, m_\ell\rangle \;=\; m_\ell\,\hbar\, |\ell, m_\ell\rangle$$

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

$$s_z \, |s, m_s\rangle \;=\; m_s\,\hbar\, |s, m_s\rangle$$

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

Spin-orbital motion of electrons can be described by different sets of commuting operators $\{\mathbf{l}^2, l_z, \mathbf{s}^2, s_z\}$ and $\{\mathbf{l}^2, \mathbf{s}^2, \mathbf{j}^2, j_z\}$ and with the well-known commutators from above.

<u>**Useful bases:**</u>

➤ Coupled basis: $|\ell, s, j, m_j\rangle$ with eigenvalue equations from above.

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

$$l_z \, |\ell, s, j, m_j\rangle \;=\; m_\ell\,\hbar\, |\ell, s, m_\ell, m_s\rangle$$

More general: $\{\mathbf{j}_1^2,\, j_{1z},\, \mathbf{j}_2^2,\, j_{2z}\}$ and $|j_1, m_1, j_2, m_2\rangle$ with analogue commutation and eigenvalue equations

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

$$j_{1z} \, |j_1, m_1, j_2, m_2\rangle \;=\; m_1\,\hbar\, |j_1, m_1, j_2, m_2\rangle$$

and similar for $\mathbf{j}_2$, j_{2z}; these eigenvectors form a complete set

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

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

The product space of operators $\mathbf{j}_1$, $\mathbf{j}_2$ has dimension: $(2j_1+1)\,(2j_2+1)$

➤ Coupled basis: $|j_1, j_2, j, m_j\rangle$ with the same eigenvalue equations for $\mathbf{j}_1$, $\mathbf{j}_2$ and

$$\mathbf{j}^2 \, |j_1, j_2, j, m_j\rangle \;=\; j(j+1)\,\hbar^2\, |j_1, j_2, j, m_j\rangle$$

$$j_z \, |j_1, j_2, j, m_j\rangle \;=\; m_j\,\hbar\, |j_1, j_2, j, m_j\rangle$$

These functions are also complete:

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} \sum_{m_j=-j}^{j} |j_1, j_2, j, m_j\rangle \langle j_1, j_2, j, m_j| \;=\; 1$$

$$\langle j_1, j_2, j, m_j \,|\, j_1', j_2', j', m_j'\rangle \;=\; \delta_{j_1,j_1'}\, \delta_{j_2,j_2'}\, \delta_{j,j'}\, \delta_{m_j,m_j'}\,.$$

Clebsch-Gordan expansion: The functions of the uncoupled and coupled bases can be easily transformed into each other:

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

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

These expansions coefficients are called the Clebsch-Gordan coefficients

$$\langle j_1, m_1, j_2, m_2 \,|\, j_1, j_2, j, m_j\rangle \;\equiv\; \langle j_1, m_1, j_2, m_2 \,|\, j, m_j\rangle \;;$$

these coefficients freqently appear in the description of multi-qubit and quantum many-particle systems and elsewhere.

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

Although the Clebsch-Gordan coefficients need to be calculated in many cases, one often wishes to just use their properties in order to understand the behaviour of physical systems, at least qualitatively.

➢ The CG coefficients $\langle j_1, m_1, j_2, m_2 \,|\, j, m_j\rangle \;=\; 0$, unless $m_j \;=\; m_1 + m_2$.

➢ By convention, the CG coefficients are taken to be real:

$$\langle j_1, m_1, j_2, m_2 \,|\, j, m_j\rangle \;=\; \langle j, m_j \,|\, j_1, m_1, j_2, m_2\rangle\,.$$

➢ The CG coefficients vanish unless $|j_1 - j_2| \;\leq\; j \;\leq\; j_1 + j_2$ (triangular rule)

Indeed, one can show:

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} \;=\; (2j_1 + 1)\,(2j_2 + 1)$$

for all integer and half-integer values of j_1, j_2.

➢ For each j, the values of m_j are: $-j \;\leq\; m_j \;\leq\; j$.

➤ The CG coefficients obey a large number of sum rules; for example:

$$\sum_{m_1,m_2} \langle j_1, m_1, j_2, m_2 \,|\, j, m_j\rangle^2 \;=\; 1$$

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

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

➤ The CG coefficients are closely related to the (so-called) Wigner 3–j symbols which obey higher symmetries:

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

Problem (Clebsch-Gordan coefficients): Show the that Clebsch-Gordan coefficients are *zero* unless $m = m_1 + m_2$.

5.2.d. Calculation of Clebsch-Gordan coefficients

➤ Recursion relations: The CG coefficients are 1 for $m_1 = j_1$, $m_2 = j_2$, $m_j = j_1+j_2$ and $m_1 = -j_1$, $m_2 = -j_2$, $m_j = -j_1 - j_2$; this can be used together with the properties of the $j_\pm$ operators

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

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

to find the recursion relations

$$\sqrt{(j-m)(j+m+1)}\ \langle j_1, m_1, j_2, m_2 \,|\, j, m+1\rangle$$

$$= \sqrt{(j_1 - m_1 + 1)(j_1 + m_1)}\ \langle j_1, m_1 - 1, j_2, m_2 \,|\, j, m\rangle$$

$$+ \sqrt{(j_2 - m_2 + 1)(j_2 + m_2)}\ \langle j_1, m_1, j_2, m_2 - 1 \,|\, j, m\rangle$$

$$\sqrt{(j+m)(j-m+1)}\ \langle j_1, m_1, j_2, m_2 \,|\, j, m-1\rangle$$

$$= \sqrt{(j_1 + m_1 + 1)(j_1 - m_1)}\ \langle j_1, m_1 + 1, j_2, m_2 \,|\, j, m\rangle$$

$$+ \sqrt{(j_2 + m_2 + 1)(j_2 - m_2)}\ \langle j_1, m_1, j_2, m_2 + 1 \,|\, j, m\rangle .$$

➤ Use of Racah's formula.

➤ Use computer-algebra or program libraries.

➤ Look up tables and books; there are extensive tabulations available from the past.

5.3. Wigner n–j symbols

5.3.a. Wigner 3–j symbols

Instead of the Clebsch-Gordan coefficients, one often uses the (so-called) Wigner n–j symbols which obey a higher symmetry. To this end, let us introduce the Δ symbol by

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

Then, the numerical value of a Wigner 3–j symbol is calculated by the expression due to Racah from 1942:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \;=\; \delta_{m_1+m_2+m_3,0}\,(-1)^{j_1-j_2-m_3}\,\Delta(j_1,j_2,j_3)$$

$$\times\, [(j_1-m_1)!\,(j_1+m_1)!\,(j_2-m_2)!\,(j_2+m_2)!\,(j_3-m_3)!\,(j_3+m_3)!]^{1/2}$$

$$\times\, \sum_l \left[\frac{(-1)^l}{l!\,(j_1+j_2-j_3-l)!\,(j_1-m_1-l)!\,(j_2+m_2-l)!} \right.$$

$$\left. \times\, \frac{1}{(j_3-j_2+m_1+l)!\,(j_3-j_1-m_2+l)!} \right].$$

This expression has a non-zero value only if the arguments of all factorials are non-negative integers.

Symmetries of the Wigner 3–j symbols: under the exchange of two (columns of) angular momenta

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix}$$

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

Moreover, an analogue phase factor occurs for

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

Recursion relations for the Wigner 3–j symbols: are listed by Rotenberg *et al.* (1959), eqs. (1.45)–(1.48). If we assume $J = j_1 + j_2 + j_3$ in this subsection, we find for example:

One recursion relation decreases two j-values by $1/2$ [halfstep]-recursion:

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

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

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

From Louck (1958) is the following $1/2$-step recursion relation [Louck]-recursion:

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

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

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

5.3.b. Wigner 6–j and 9–j symbols

Apart from the Wigner 3–j symbols, one can define Wigner 6–j and 9–j symbols, which also obey high symmetries. For example, the 9–j symbols with given numeric arguments can be calculated by means of a known sum rule over three Wigner 6–j symbols

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

From the symmetry properties of the Wigner 6–j symbols (not shown here), one would see that the 9–j symbol is zero unless the arguments in each row and column satisfy the triangular relation.

5.3.c. Sum rules of the Wigner n–j symbols

The Wigner n–j symbols obey a very large number of sum rules which can be utilized to enourmoulsy simplify the spin-angular integration in the treatment of most quantum many-particle systems with some kind of rotational symmetry. An extensive list of such sum rules are provided in the monograph of Varshalovich *et al.* (1988) to which we here refer just for a few examples.

Sum rules for one 3–j symbol

Varshalovich *et al.* (1988), eq. (12.1.2) give one sum rule with one 3–j symbol.

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

and with $[a, b, ...] = (2a+1)(2b+1)... \, .$

5. Angular momentum (AM) in quantum physics

Sum rules for one $6-j$ symbol

Rotenberg *et al.* (1959), eqs. (2.9–10) give sum rules with one $6-j$ symbol. A more general form is given by Varshalovich *et al.* (1988), eqs. (12.2.3–4).

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

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

Sum rules for two $3-j$ symbols

Two orthogonality relations for $3-j$ symbols are given by Rotenberg *et al.* (1959), eqs. (1.13–14). The same rules are given by Varshalovich *et al.* (1988), eqs. (12.1.3–4).

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

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

Sum rules for two $3-j$ symbols and one $6-j$ symbol

One such rule is given by Rotenberg *et al.* (1959), eq. (2.19). The same rule is shown by Varshalovich *et al.* (1988), eq. (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

There is a sum rule for three $6-j$ symbols from Biedenharn and Elliot [see Rotenberg *et al.* (1959), eq. (2.8)]. The same rule is given by Varshalovich *et al.* (1988), eq. (12.2.18).

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

$$= \begin{Bmatrix} p & q & r \\ e & a & d \end{Bmatrix} \begin{Bmatrix} p & q & r \\ f & b & c \end{Bmatrix}$$

where $R = a + b + c + d + e + f + p + q + r$.

Figure 5.1.: Structure of a Racah expression, i.e. typical expressions which appear in Racah's algebra.

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

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

Sum rules for one $6-j$ symbol and three $9-j$ symbols

Varshalovich *et al.* (1988), eq. (12.2.44) gives a sum rule for one $6-j$ symbol and three $9-j$ symbols.

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

$$
= \begin{Bmatrix} k & l & p \\ h & j & q \\ t & s & r \end{Bmatrix}
\begin{Bmatrix} k & h & t \\ a & c & e \end{Bmatrix}
\begin{Bmatrix} l & j & s \\ b & d & f \end{Bmatrix}
$$

5.4. The RACAH program in Maple

In atomic and nuclear structure theory, the evaluation and spin-angular integration of many-particle matrix elements is typically based on standard quantities like the matrix elements of the unit tensor, the (reduced) coefficients of fractional parentage as well as a number of other reduced matrix elements concerning various products of creation and annihilation operators. These quantities arise very frequently both in configuration interaction approaches and the derivation of perturbation expansions for many-particle systems using symmetry-adapted configuration state functions.

In the framework of the RACAH program (Fritzsche 1997; Fritzsche *et al.* 1998), we provide a set of procedures for the manipulation and computation of such standard quantities in atomic theory. This (so-called) RACAH program is designed for interactive work and appropriate for almost any complexity of expressions from Racah algebra. In Figure 5.3.c, we display the typical structure of such expressions to which we refer as *Racah expressions.*

5.4.a. Presently supported symbols and functions in the RACAH program

The following symbols and quantities from the theories of angular momentum and irreducible tensor operators are known to the RACAH program.

Symbol	Designation	RACAH program
$\begin{pmatrix} a & b & c \\ m_a & m_b & m_c \end{pmatrix}$	Wigner 3–j symbol	Racah_w3j()
$\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$	Wigner 6–j symbol	Racah_w6j()
$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix}$	Wigner 9–j symbol	Racah_w9j()
$\langle a\, m_a,\ b\, m_b\, |\, c\, m_c \rangle$	Clebsch–Gordan coefficient	Racah_ClebschGordan()
$W(abcd; ef)$	Racah's W coefficient	Racah_Wcoefficient()
$d^j_{mm'}(\beta)$	Wigner $d^j_{mm'}(\beta)$ rotation matrix	Racah_dmatrix()
$D^j_{mm'}(\alpha, \beta, \gamma)$	Wigner's $D-$function	Racah_Dmatrix()
$U^j_{mm'}(\omega; \Theta, \Phi)$	Rotation matrix $U(\omega)$	Racah_Umatrix()
$Y_{lm}(\vartheta, \varphi)$	Spherical harmonic	Racah_Ylm()
$\{\mathbf{Y}_{l_1}(\vartheta_1, \varphi_1) \cdot\cdot \mathbf{Y}_{l_2}(\vartheta_2, \varphi_2)\}_{LM}$	Bipolar spherical harmonic	Racah_bipolarY()
$\{\mathbf{Y}_{l_1}(\vartheta_1, \varphi_1) \cdot\cdot \{\mathbf{Y}_{l_2}(\vartheta_2, \varphi_2) \cdot\cdot \mathbf{Y}_{l_3}(\vartheta_3, \varphi_3)\}_{l_{23}} \}_{LM}$	Tripolar spherical harmonic	Racah_tripolarY()
$\mathbf{Y}^l_{jm}(\vartheta, \varphi)$	Vector spherical harmonic	Racah_vectorY()
$\Omega^l_{jm}(\vartheta, \varphi)$	Spinor spherical harmonic	Racah_spinorY()
$Y^{ls}_{jm}(\vartheta, \varphi)$	Tensor spherical harmonic	Racah_tensorY()
$\langle l_a m_a\, |l_b m_b|\, l_c m_c \rangle$	Gaunt coefficient	Racah_Gaunt()
$C^k(l_a, m_a; l_b, m_b)$	Condon–Shortley coefficient	Racah_CondonShortley()
$\mathbf{H}_{l,\{\mu\}}$ †	Hyperspherical harmonic	Racah_hypersphericalY()
$\left(\gamma\, \alpha Q\Gamma\, |||\, a^{(q\gamma)}\, |||\, \gamma\, \alpha'Q'\Gamma' \right)$	Reduced coefficient of fractional parentage	Racah_cfp()

...

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

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

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*

$$\left\{\mathbf{Y}_{l_1}(\vartheta_1, \varphi_1) \otimes \{\mathbf{Y}_{l_2}(\vartheta_2, \varphi_2) \otimes \mathbf{Y}_{l_3}(\vartheta_3, \varphi_3)\}_{l_{23}}\right\}_{LM}$$

$$= \sum_{m_1, m_2, m_3, m_{23}} \langle l_1 m_1, l_{23} m_{23} \,|\, LM \rangle \, \langle l_2 m_2, l_3 m_3 \,|\, l_{23} m_{23} \rangle$$

$$Y_{l_1 m_1}(\vartheta_1, \varphi_1) \, Y_{l_2 m_2}(\vartheta_2, \varphi_2) \, Y_{l_2 m_2}(\vartheta_3, \varphi_3) \,.$$

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)

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

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 $0 \leq \vartheta \leq \pi$, $0 \leq \varphi \leq 2\pi$.

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 the current (hop) topic of laser-matter interactions.