http://sites.unice.fr/site/kastberg/My_Sites/Physique_Atomique/Home.html

The hydrogen atom

Introduction - The nuclear atom

- To understand matter, you have to begin by understanding the atom
- First step: the H atom (the least complex)
- After that: one gradually increases the complexity
- Keep in mind: the theory about atomic structure is based on experimental observations in spectroscopy
  - often, the experiments were made before the theory was worked out
- Atomic physics is a very instructive application of quantum mechanics

The electron

- Faraday, 1833 : electrolysis
  - electricity can be liberated by matter
- Storey, 1874 ; Helmholz 1880: Electric charge can only exist in discrete units
  - "electrons"
- J. J. Thomson : Electrons have mass and charge
  - The ratio *e*/*m* can be measured and is constant

- Millikan, 1909 : measure of the charge
    - $e \approx 1.60 \times 10^{-19}$ C
    - $\Rightarrow m \approx 9.11 \times 10^{-31}$ kg

The nuclear atom

- ≈ 1900 : Clear that an atom contain both negative and positive charges
    - But how are they distributed?

- Geiger ; Marsden ; Rutherford, ≈ 1910 : Experiments with alpha particles scattered against metallic foils
    - The Rutherford model:

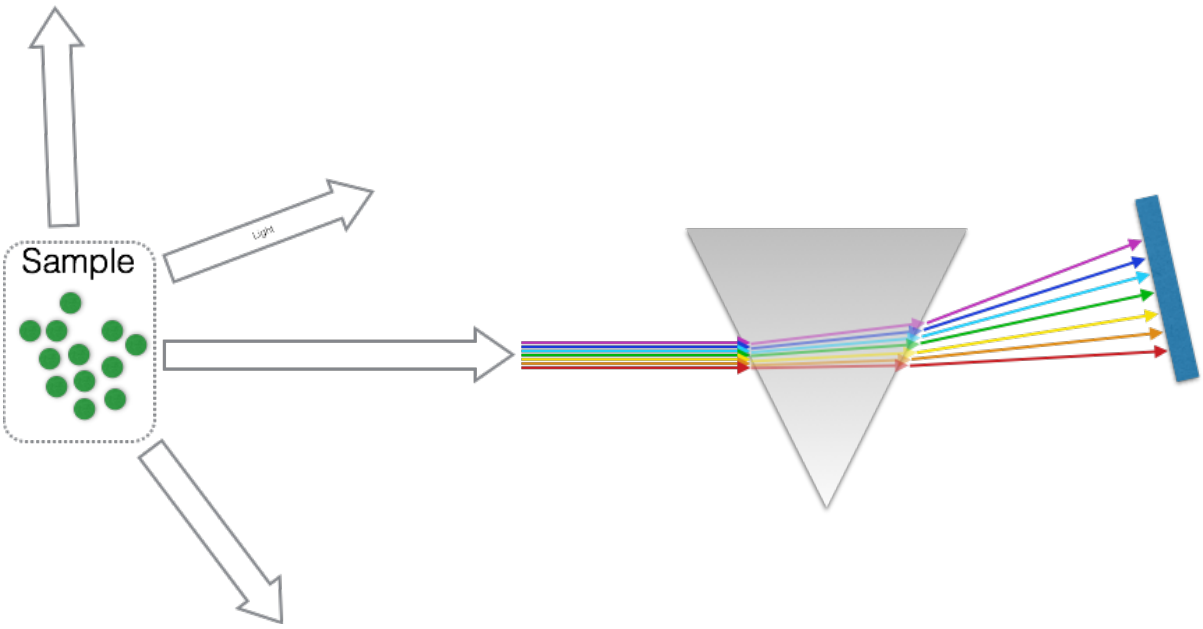
The Rutherford model

- All the positive charge of an atom, and most of its mass, is concentrated in the centre of the atom
    - "the nucleus"

- The negative charges, the electrons, orbit around this charge

The hydrogen spectrum

- What is an atomic emission spectrum?



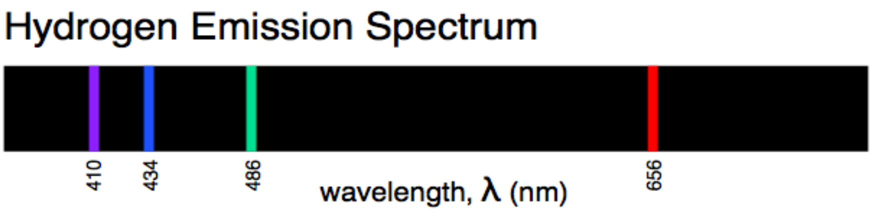
1. Take a sample of an element
2. Make it emit light (heating, discharge ….)
3. Spectrally resolve the emitted light (analysing the colours")

- The recorded spectrum is characteristic for this element
- This can be used for chemical analysis
- And it can be used in order to gain understanding of the atomic structure

hydrogen discharge

(dissociation of H_2 to H ; characteristic emission from H)

1. Distinct red light, centered around $\lambda = 656$ nm
2. A light blue component $\lambda = 486$ nm
3. A series of other weak rays, most of them in UV
4. The spectral lines seem to follow some regular order



- The inverse of the wavelength, the wave number, turns out to be more practical to use for calculation:

$$\sigma = \bar{\nu} \equiv \frac{1}{\lambda}$$

- The regularity was deciphered mathematically by Rydberg:

$$\sigma = R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$

    - R : The Rydberg constant
    - n and n' : integer numbers, $n \geq 1$, $n' > n$

Spectral series

- $n = 1$; Lyman series

$$\begin{array}{rl} n = 1\,, n' = 2 \; : & \mathrm{Ly}_\alpha \;;\; \lambda_{\mathrm{Ly}\alpha} = 121\,\mathrm{nm} \\ n = 1\,, n' = 3 \; : & \mathrm{Ly}_\beta \;;\; \lambda_{\mathrm{Ly}\beta} = 103\,\mathrm{nm} \\ n = 1\,, n' = 4 \; : & \mathrm{Ly}_\gamma \;;\; \lambda_{\mathrm{Ly}\gamma} = 97\,\mathrm{nm} \\ \ldots & \end{array}$$

- $n = 2$; Balmer series

$$\begin{array}{rl} n = 2\,, n' = 3 \; : & \mathrm{H}_\alpha \;;\; \lambda_{\mathrm{H}\alpha} = 656\,\mathrm{nm} \\ n = 2\,, n' = 4 \; : & \mathrm{H}_\beta \;;\; \lambda_{\mathrm{H}\beta} = 486\,\mathrm{nm} \\ n = 2\,, n' = 5 \; : & \mathrm{H}_\gamma \;;\; \lambda_{\mathrm{H}\gamma} = 434\,\mathrm{nm} \\ \ldots & \end{array}$$

- $n = 3$; Paschen series

$$\begin{array}{rl} n = 3\,, n' = 4 \; : & \mathrm{Pa}_\alpha \;;\; \lambda_{\mathrm{Pa}\alpha} = 1870\,\mathrm{nm} \\ \ldots & \end{array}$$

Lyman Series

n	λ(nm)
2	122
3	103
4	97.2
5	94.9
6	93.7
∞	91.1

Balmer Series

n	λ(nm)
3	656
4	486
5	434
6	410
7	397
∞	365

Paschen Series

n	λ(nm)
4	1870
5	1280
6	1090
7	1000
8	954
∞	820

Brackett Series

n	λ(nm)
5	4050
6	2630
7	2170
8	1940
9	1820
∞	1460

Pfund Series

n	λ(nm)
6	7460
7	4650
8	3740
9	3300
10	3040
∞	2280

Humphreys Series

n	λ(nm)
7	12372
8	7503
10	5129
11	4673
13	4171
∞	3282

The Bohr model

- An extension of the Rutherford model:

Assumptions:

1. The electrons orbit a heavy nucleus with positive charge
2. An electron in an orbit does not radiate - the orbit is stable
3. The angular momentum is quantified in integers of $\hbar$

$$l = n\hbar = n\frac{h}{2\pi}$$

   - This means that only certain "orbits" are allowed

4. When an atom emit (or absorb) light, an electron "jumps" from one orbit to another

   - Energy conservation then requires:

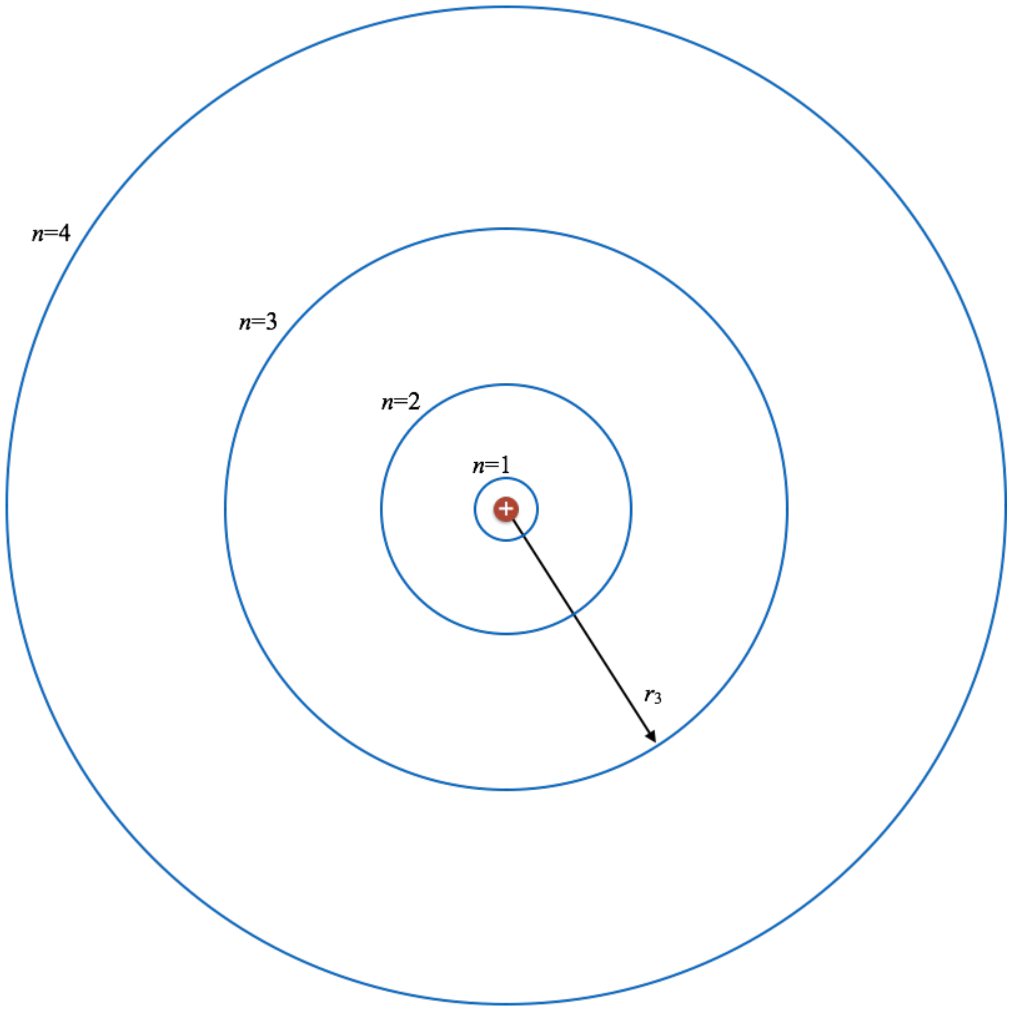
$$\lambda_{\text{light}} = \frac{c}{\nu} = \frac{c}{h\,\Delta E}$$

- Using classic mechanics and electrodynamics:
  - Total energy of an electron on an allowed orbit:

$$E = -\frac{e^2}{4\pi\varepsilon_0\, 2r}$$

    - r : the radius of the orbit
    - $r_n = a_0 n^2 \quad ; \quad n \geq 1$

- a_0 is the "Bohr radius"
- $a_0 = \dfrac{4\pi\varepsilon\,\hbar^2}{m_e\,e^2} \approx 5.292 \times 10^{-11}$ nm



- Allowed energies:

$$E_n = -\frac{e^2}{4\pi\varepsilon_0\, 2a_0}\,\frac{1}{n^2}$$

- n : "the principal quantum number"

Transitions in H, according to the Bohr model

The “spectral rays” of H

$$\sigma = \frac{1}{\lambda} \propto E_n - E_{n'}$$
$$\Rightarrow \sigma = R_\infty \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$

- R_∞ : The Rydberg constant for an infinite mass

$$hcR_\infty = \frac{e^4\, m_\mathrm{e}}{(4\pi\varepsilon_0)^2\; 2\hbar^2} \approx 13.606\,\mathrm{eV}$$

- With a different nuclear mass ($< \infty$), R has to be modified, and will be slightly different for different atomic masses (“isotope shift”)

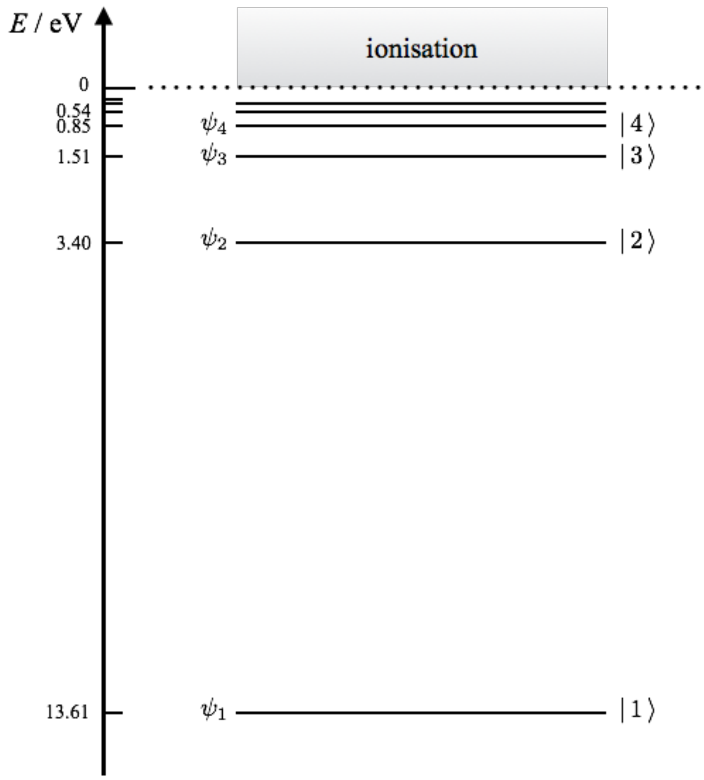
Quantum mechanics, the two-particle Hamiltonian

- Quantum mechanical approach: solve the Schrödinger equation

- The solution will give:
  - eigenstates (allowed wave functions)
  - eigenvalues of the energy (allowed energies)

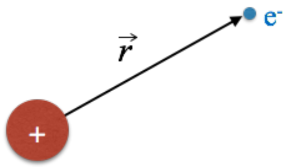
- This is "the structure of the H atom"

- The "energy levels" should be consistent with recorded spectra



- With the exact solution for the eigenstates (the wave function), in principle everything can be calculated.

The Schrödinger equation for H



- Coulomb potential:

$$V = V(r) = -\frac{Z\,e^2}{4\pi\varepsilon_0\, r}$$

- Complete two-body Hamiltonian:

$$H = \frac{(\vec{p}_{\mathrm{p}})^2}{2m_{\mathrm{p}}} + \frac{(\vec{p}_{\mathrm{e}})^2}{2m_{\mathrm{e}}} + V(|\vec{r}_{\mathrm{p}} - \vec{r}_{\mathrm{e}}|) = -\frac{\hbar^2}{2m_{\mathrm{p}}}\nabla^2_{\mathrm{p}} - \frac{\hbar^2}{2m_{\mathrm{e}}}\nabla^2_{\mathrm{e}} + V(|\vec{r}|)$$

  - substitutions:
  - $\vec{r} \equiv \vec{r}_{\mathrm{p}} - \vec{r}_{\mathrm{e}}$; relative position
  - $\vec{R} = \dfrac{m_{\mathrm{p}}\vec{r}_{\mathrm{p}} + m_{\mathrm{e}}\vec{r}_{\mathrm{e}}}{m_{\mathrm{p}} + m_{\mathrm{e}}}$; centre of mass
  - $M \equiv m_{\mathrm{p}} + m_{\mathrm{e}}$; total mass
  - $\mu = \dfrac{m_{\mathrm{p}} m_{\mathrm{e}}}{m_{\mathrm{p}} + m_{\mathrm{e}}}$; reduced mass

  - $$\Rightarrow H = \underbrace{-\frac{\hbar^2}{2M}}_{\text{(centre-of-mass motion)}}\nabla^2_R - \frac{\hbar^2}{2\mu}\nabla^2_r + V(r)$$

- In centre-of-mass coordinates:
  - $H = -\dfrac{\hbar^2}{2\mu}\nabla^2 + V(r)$
  - $\Rightarrow \left(-\dfrac{\hbar^2}{2\mu}\nabla^2 - \dfrac{Z\,e^2}{4\pi\varepsilon_0\, r}\right)\psi(\vec{r}) = E\,\psi(\vec{r})$

- and $\vec{r} = (r, \theta, \varphi)$

- The Laplacian in spherical coordinates:

$$\nabla^2 = \frac{1}{r^2}\,\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\,\vec{l}^2$$

where $\vec{l}^2 = \left\{\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right\}$

- The entire angular part is contained in $\vec{l}^2$
- $(\hbar\vec{l})^2$ is the operator for angular momentum

- We are looking for separable solutions, with one radial part and one angular part:

$$\psi(r, \theta, \varphi) = R(r)\,Y(\theta, \varphi)$$

- Substitution in the Schrödinger equation:

$$\underbrace{\frac{1}{R}\,\frac{\partial}{\partial r}\left(r^2\,\frac{\partial R}{\partial r}\right) - \frac{2\mu r^2}{\hbar^2}\,(V(r) - E)}_{r \text{ dependence}} = \underbrace{\frac{1}{Y}\,\vec{l}^2\,Y}_{\substack{\text{dependence}\\ \text{on } \theta \text{ and } \varphi}} = \text{const.}$$

$\Uparrow$

$$\begin{cases} \frac{1}{R}\,\frac{\partial}{\partial r}\left(r^2\,\frac{\partial R}{\partial r}\right) - \frac{2\mu r^2}{\hbar^2}\,(V(r) - E) = b \\ \vec{l}^2\,Y = b\,Y \end{cases}$$

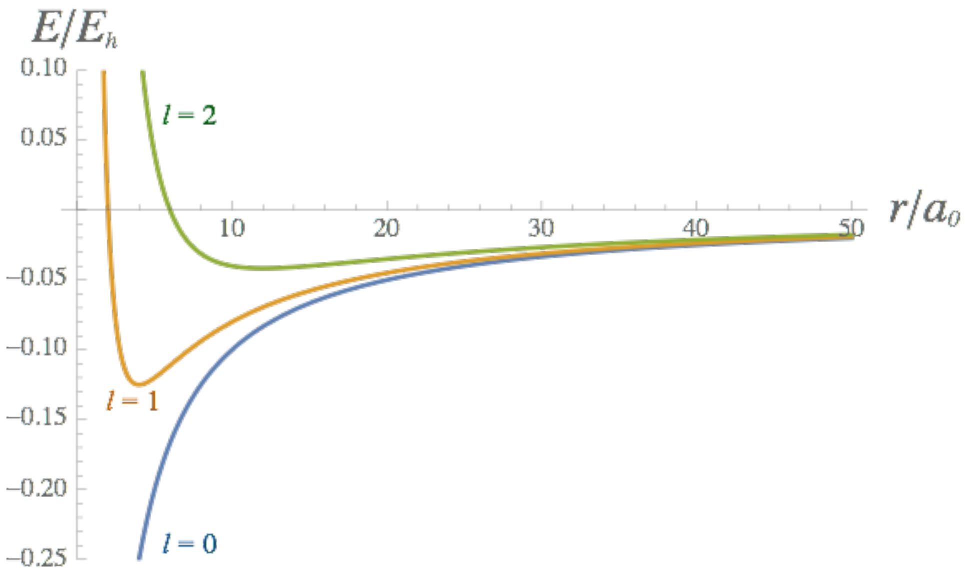
- The constant b must be an eigenvalue of the operator $\vec{l}^2$
- Therefore, we take:
- $b = l(l+1)$

The radial part of the wave function

- Introduce the substitution:

$$u(r) = r\,R(r)$$

  - $\Rightarrow \dfrac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \dfrac{2\mu}{\hbar^2}\left[E - V_{\text{eff}}(r)\right] u(r) = 0$
    - with $V_{\text{eff}}(r) \equiv \underbrace{-\dfrac{Ze^2}{4\pi\varepsilon_0\, r}}_{\text{Coulomb}} + \underbrace{\dfrac{l(l+1)\hbar^2}{2\mu r^2}}_{\text{centrifugal barrier}}$



    - For $r \to \infty \quad \Rightarrow \quad V(r) \to 0$

  - $E > 0$: oscillatory solutions
  - $\Rightarrow$ scattering states (non-bound)
  - $\Rightarrow$ continuous spectrum

- For bound states:
  - We have to have : $E < 0$
  - $E = 0$ corresponds to the ionization limit

- The solution is in the form of a series

- Quantization : $\dfrac{Ze^2}{4\pi\varepsilon_0\,\hbar}\sqrt{-\dfrac{\mu}{2E}} = n$
  - with $n = 1, 2, 3 \ldots$
  - n is "the principal quantum number"

- The energies of the bound states:

$$E_n = -\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{\mu}{\hbar^2} = -\frac{e^2}{4\pi\varepsilon_0\,a_0}\frac{\mu}{m_\mathrm{e}}\frac{Z^2}{2n^2}$$

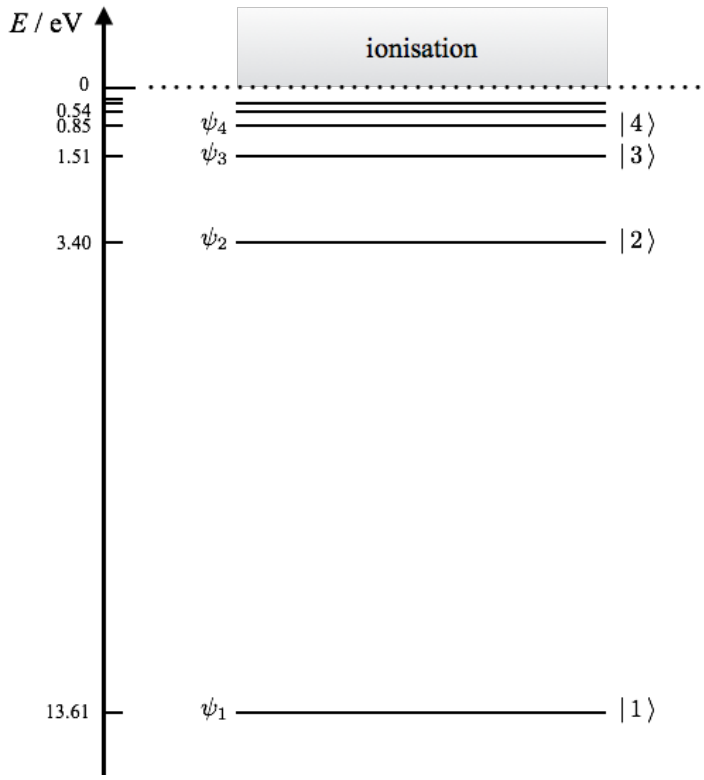
  - $\left(a_0 = \dfrac{4\pi\varepsilon_0\,\hbar^2}{m_\mathrm{e}e^2}\right)$
  - or

$$E_n = -\frac{1}{2}\mu c^2\left(\frac{Z\alpha}{n}\right)^2$$

  - $\alpha = \dfrac{e^2}{4\pi\varepsilon_0\,\hbar c}$ is the "fine-structure constant"

- $E_0 \approx -13.6\,\mathrm{ev} \quad ; \quad E_1 \approx -3.4\,\mathrm{eV}$

- Note:
  - The energy does not depend on l
  - Restriction in l : $l = 0, 1, 2, 3, \ldots, n\text{-}1$
  - The energies agree with the Bohr model



The radial wave function

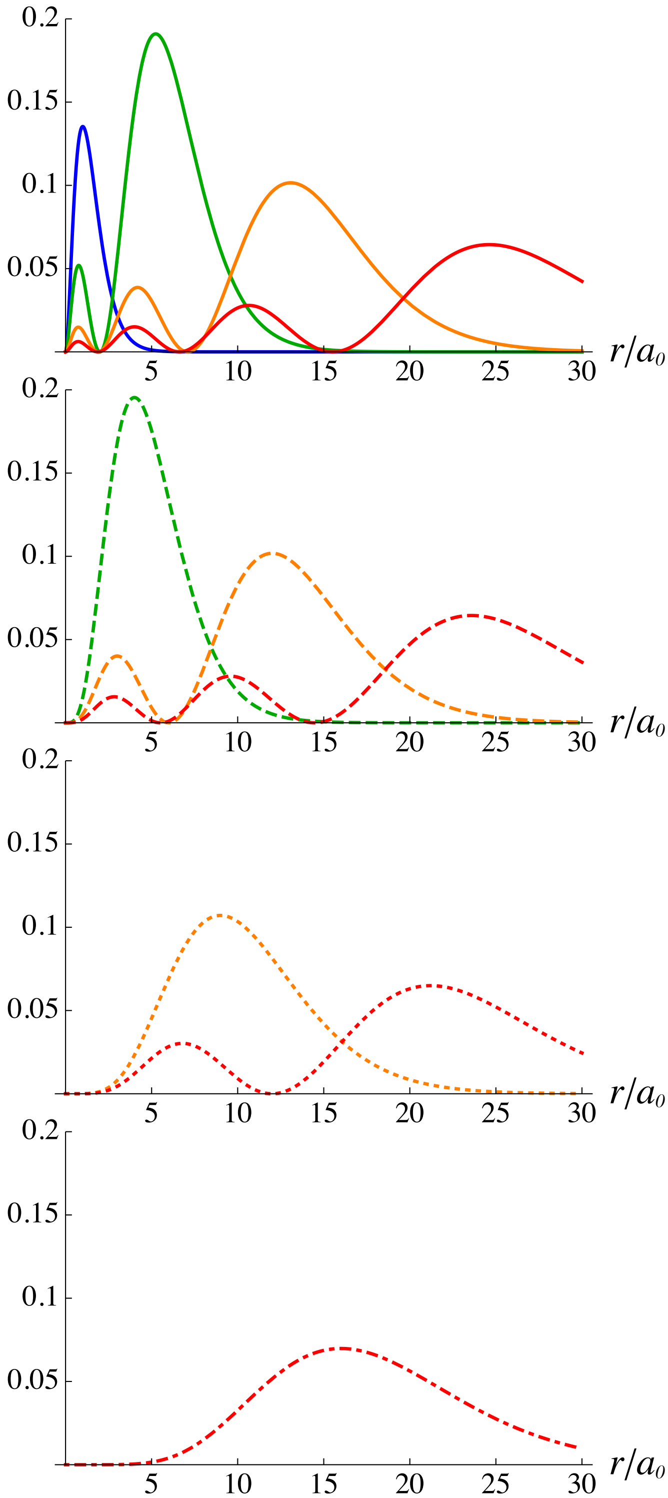
- Solutions:

$$R_{nl}(r) = -\left\{ \left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n\left[(n+1)!\right]^3} \right\}^{1/2} \mathrm{e}^{-\rho/2}\, \rho^l \, \mathrm{L}_{n+l}^{2l+1}(\rho)$$

  - with $a_\mu = a_0 \dfrac{m_\mathrm{e}}{\mu}$
  - and $\rho = \dfrac{2Z}{na_\mu}\, r$
  - L_i^j is a "Laguerre polynomial"

Charge distribution

- The probability to find the electron in the centre ($r = 0$) is finite only for $l = 0$



The angular function

$$\vec{l}^2\, Y(\theta,\varphi) = l(l+1)\, Y(\theta,\varphi)$$

- We separate variables yet again:
  - $Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)$

$$\frac{\sin\theta}{\Theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\Theta}{\partial\theta}\right) + l(l+1)\sin^2\theta = -\frac{1}{\Phi}\,\frac{\partial^2\Phi}{\partial\varphi^2} = m^2$$

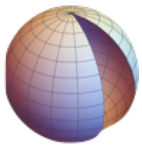
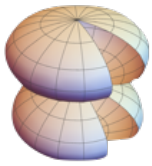
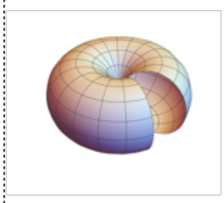
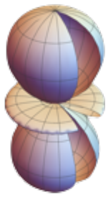
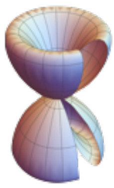
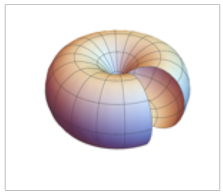
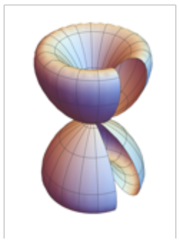
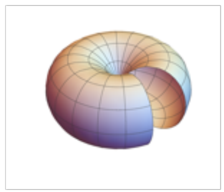
- The solution are the "spherical harmonics": Y_{lm}

$$\begin{cases} Y_{lm} & = (-1)^m \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right]^{1/2} \mathrm{P}_l^m(\cos\theta)\,\mathrm{e}^{\mathrm{i}m\varphi} \quad , \; m \geq 0 \\ Y_{l,-m} & = (-1)^m\, Y_{lm}^* \end{cases}$$

  - P_i^j are "Legendre polynomials"
  - l : quantum number for the orbital angular momentum
  - m : projection on $\hat{z}$ of l , $|m| \leq l$

- Notation convention:

$$\begin{array}{lcl} l=0 & \rightarrow & \text{s orbital} \\ l=1 & \rightarrow & \text{p orbital} \\ l=2 & \rightarrow & \text{d orbital} \\ l=3 & \rightarrow & \text{f orbital} \\ l=4 & \rightarrow & \text{g orbital} \end{array}$$

	$m = 0$	$m = \pm 1$	$m = \pm 2$	$m = \pm 3$
$l = 0$				
$l = 1$				
$l = 2$				
$l = 3$				

$$
\begin{aligned}
Y_{0,0}(\theta,\varphi) &= \tfrac{1}{2}\frac{1}{\sqrt{\pi}} \\
Y_{1,0}(\theta,\varphi) &= \tfrac{1}{2}\sqrt{\tfrac{3}{\pi}}\cos\theta \\
Y_{1,\pm 1}(\theta,\varphi) &= \mp\tfrac{1}{2}\sqrt{\tfrac{3}{2\pi}}\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\varphi} \\
Y_{2,0}(\theta,\varphi) &= \tfrac{1}{4}\sqrt{\tfrac{5}{\pi}}(3\cos^2\theta-1) \\
Y_{2,\pm 1}(\theta,\varphi) &= \mp\tfrac{1}{2}\sqrt{\tfrac{15}{2\pi}}\sin\theta\cos\theta\,\mathrm{e}^{\pm\mathrm{i}\varphi} \\
Y_{2,\pm 2}(\theta,\varphi) &= \tfrac{1}{4}\sqrt{\tfrac{15}{2\pi}}\sin^2\theta\,\mathrm{e}^{\pm 2\mathrm{i}\varphi} \\
Y_{3,0}(\theta,\varphi) &= \tfrac{1}{4}\sqrt{\tfrac{7}{\pi}}(5\cos^3\theta-3\cos\theta) \\
Y_{3,\pm 1}(\theta,\varphi) &= \mp\tfrac{1}{8}\sqrt{\tfrac{21}{\pi}}\sin\theta(5\cos^2\theta-1)\,\mathrm{e}^{\pm\mathrm{i}\varphi} \\
Y_{3,\pm 2}(\theta,\varphi) &= \tfrac{1}{4}\sqrt{\tfrac{105}{2\pi}}\sin^2\theta\cos\theta\,\mathrm{e}^{\pm 2\mathrm{i}\varphi} \\
Y_{3,\pm 3}(\theta,\varphi) &= \mp\tfrac{1}{8}\sqrt{\tfrac{35}{\pi}}\sin^3\theta\,\mathrm{e}^{\pm 3\mathrm{i}\varphi}
\end{aligned}
$$

1.2 Formulation of the Schrödinger equation for the hydrogen atom

In this initial treatment, we will make some practical approximations and simplifications. Since we are for the moment only trying to establish the general form of the hydrogenic wave functions, this will suffice. To start with, we will assume that the nucleus has zero extension. We place the origin at its position, and we ignore the centre-of-mass motion. This reduces the two-body problem to a single particle, the electron, moving in a central-field potential. To take the finite mass of the nucleus into account, we replace the electron mass with the reduced mass, μ, of the two-body problem. Moreover, we will in this chapter ignore the effect on the wave function of relativistic effects, which automatically implies that we ignore the spins of the electron and of the nucleus. This makes us ready to formulate the Hamiltonian.

The potential is the classical Coulomb interaction between two particles of opposite charges. With spherical coordinates, and with r as the radial distance of the electron from the origin, this is:

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0\, r} \,, \tag{1.1}$$

with Z being the charge state of the nucleus. The Schrödinger equation is:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\boldsymbol{r}) + V(r)\psi = E\psi(\boldsymbol{r}) \,, \tag{1.2}$$

where the Laplacian in spherical coordinates is:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \,. \tag{1.3}$$

Since the potential is purely central, the solution to (1.2) can be factorised into a radial and an angular part, $\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$. Substitution this into (1.2), the Schrödinger equation becomes:

$$\begin{aligned}\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) &- \frac{2\mu r^2}{\hbar^2}\left(-\frac{Ze^2}{4\pi\varepsilon_0\, r} - E\right)\\ &= -\frac{1}{Y(\theta,\varphi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi) \,. \end{aligned}\tag{1.4}$$

Before proceeding we will simplify the notation, by introducing atomic units, and the angular momentum operator. The motivation for using atomic units is that when performing long derivations, a large number of constants make the work cumbersome. To circumvent that, a number of constants are set to unity:

$$e = m_{\mathrm{e}} = \hbar = \frac{1}{4\pi\varepsilon_0} = 1 \; . \tag{1.5}$$

Then, units for involved physical quantities have to be adapted accordingly, whenever quantified answers are sought. A brief introduction to, and a list of, atomic units are given in appendix A. For the continuation of this book, we will use atomic units, when we do not explicitly state otherwise.

The expression within the square brackets in (1.4) is identical to the quantum mechanical operator for the square of the orbital angular momentum, $\boldsymbol{L}^2$. A more thorough discussion on angular momentum is presented in appendix C. In that appendix, it is also shown that for an angular wave function that is eigenfunction to $\boldsymbol{L}^2$, we have:

$$\boldsymbol{L}^2 Y(\theta,\varphi) = l(l+1)Y(\theta,\varphi) \; , \tag{1.6}$$

where the introduced quantum number l has to be a positive integer, or zero. In atomic units, and using (1.6) and (1.1), the Schrödinger equation can now be written as:

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) + 2Zr + 2Er^2 = -\frac{1}{Y(\theta,\varphi)}\boldsymbol{L}^2 Y(\theta,\varphi) = l(l+1) \; . \tag{1.7}$$

Here, we have set $\mu \approx m_{\mathrm{e}}$, utilising the fact that for a one-electron system, the nucleus is at least 1800 times heavier than the electron.

Equation (1.7) has to be valid for all spatial parameters, so when the radial and angular parts have been separated, both sides of (1.7) have to be constant, for a given wave function. In (1.7), we have used (1.6) and set that constant to $l(l+1)$.

We are now left with two uncoupled differential equations, which can be solved independently. The angular part of (1.7) is independent of the potential, as is the case for any kind of central potential, and the solution will be in the form of the standard spherical harmonics. The energy solely appears in the radial part of the equation, and therefor the energies will, at this level of approximation, be independent of the angular coordinates. In the following sections, we will treat the radial and angular solutions separately.

1.3 Solution of the radial equation

The radial part of (1.7) can be rewritten as:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}R(r)\right] + \left[\frac{2Z}{r} + 2E - \frac{l(l+1)}{r^2}\right]R(r) = 0 \; . \tag{1.8}$$

Equation (1.8) represents a one dimensional problem of a particle moving in an effective potential, consisting of the central Coulomb term and a centrifugal term, as shown in fig. 1.1 (for the case $Z = 1$). Positive energies will give diffusive solutions, which are relevant for scattering phenomena, but which will not be dealt with in this

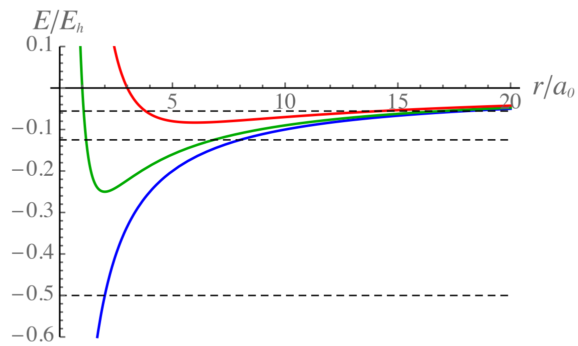


Fig. 1.1 Effective potential for the radial part of the Schrödinger equation for the hydrogen atom (1.8), with $Z = 1$, for three different values of the angular momentum quantum number: $l = 0$ (blue), $l = 1$ (green), and $l = 2$ (red). The axes are in atomic units and zero energy corresponds to an electron infinitely distant from the nucleus. The three dashed horizontal lines shows the energies of the three lowest energy eigenstates (se section 1.5.1).

chapter. In the current treatment we explicitly look for bound states, i.e., solutions for $E < 0$. In the following, we will give a very brief outline the solution. For a more thorough treatment, see appendix B and general works in the suggested further reading.

A first step is to introduce the substitution $U(r) \equiv rR(r)$. This leaves us with the equation:

$$\frac{\partial^2}{\partial r^2}U(r) + \left[\frac{2Z}{r} + 2E - \frac{l(l+1)}{r^2}\right]U(r) = 0\,. \tag{1.9}$$

Note that since we have formulated the Schrödinger equation in atomic units, the energy in (1.9) will be in E_h and r has to be given in a_0 (cf. appendix A).

The solution to (1.9) is periodical and discretized in two quantum numbers: the orbital angular momentum quantum number l (also called the azimuthal quantum number) introduced in section 1.2, and the principal quantum number n. From the solutions, we also get the following constraints for the integer quantum numbers n and l (cf. appendix B):

$$0 \le l < n\,. \tag{1.10}$$

1.3.1 Eigenstates

The eigenstates found from the solution of (1.9) are in the form of associated Laguerre polynomials (cf. appendix B):

$$U_{nl}(\rho) = -\sqrt{\frac{(n-l-1)!}{n^2\,[(n+l)!]^3}}\,\rho^{l+1}\,\mathrm{e}^{-\rho/2}\,\mathrm{L}_{n+l}^{2l+1}(\rho)\,. \tag{1.11}$$

Here, ρ is a rescaled radial parameter:

$$\rho = \frac{2Zr}{n} , \tag{1.12}$$

and equation (1.11) has been normalised such that:

$$\int_0^\infty U_{nl}^*(r) U_{nl}(r) \, \mathrm{d}r = 1 . \tag{1.13}$$

Moreover, the functions $U_{nl}(r)$ are mutually orthogonal.

Throughout this book, we will use the standard spectroscopic notation for the orbital angular momentum quantum number l, as presented in table (1.1): With this

Table 1.1 Standard letter symbols used for different values of the angular momentum quantum number l

l-quantum number	0	1	2	3	4	5	6
spectroscopic symbol	s	p	d	f	g	h	i

notation, some of the lowest order normalized radial functions, in the format $U_{nl}(r)$, are presented in (1.14), for the case $Z = 1$.

$$\begin{aligned}
U_{1\mathrm{s}} &= 2r\,\mathrm{e}^{-r} \\
U_{2\mathrm{s}} &= \frac{1}{\sqrt{2}}\, r\,\mathrm{e}^{-r/2} \left(1 - \frac{r}{2}\right) \\
U_{2\mathrm{p}} &= \frac{1}{2\sqrt{6}}\, r^2\,\mathrm{e}^{-r/2} \\
U_{3\mathrm{s}} &= \frac{2}{3\sqrt{3}}\, r\,\mathrm{e}^{-r/3} \left(1 - \frac{2r}{3} + \frac{2r^2}{27}\right) \\
U_{3\mathrm{p}} &= \frac{8}{27\sqrt{6}}\, r^2\,\mathrm{e}^{-r/3} \left(1 - \frac{r}{6}\right) \\
U_{3\mathrm{d}} &= \frac{4}{81\sqrt{30}}\, r^3\,\mathrm{e}^{-r/3} \\
U_{4\mathrm{s}} &= \frac{1}{4}\, r\,\mathrm{e}^{-r/4} \left(1 - \frac{3r}{4} + \frac{r^2}{8} - \frac{r^3}{192}\right) \\
U_{4\mathrm{p}} &= \frac{\sqrt{5}}{16\sqrt{3}}\, r^2\,\mathrm{e}^{-r/4} \left(1 - \frac{r}{4} + \frac{r^2}{80}\right) \\
U_{4\mathrm{d}} &= \frac{1}{64\sqrt{5}}\, r^3\,\mathrm{e}^{-r/4} \left(1 - \frac{r}{12}\right) \\
U_{4\mathrm{f}} &= \frac{1}{768\sqrt{35}}\, r^4\,\mathrm{e}^{-r/4} .
\end{aligned} \tag{1.14}$$

From (1.14), we can note that the wave function will be non-zero at $r = 0$ only for s-states ($l = 0$). Hence, only an s-electron, which lacks a centrifugal term, has a finit probability of being very close to the nucleus.

1.4 Solution of the angular equation

Since both the radial and the angular sides of (1.7) are equal to $l(l+1)$, for a given wave function, the angular part of the equation is:

$$-\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi)=l(l+1)\,Y(\theta,\varphi)\,. \qquad (1.15)$$

As already stated, the operator on the left side of (1.15) is the operator for the square of the orbital angular momentum (cf. appendix C) divided by $\hbar^2$, which justifies the definition of the constant as $l(l+1)$, and the eigenvalue equation in (1.6). For the projection of $\boldsymbol{L}^2$ along a quantisation axis $\hat{e}_z$, we will use the quantum number m_l (eigenvalue to L_z).

With (1.15) being in the form of the standard generator for the spherical harmonics, the solution to this differential equation is very general, and it is outlined in appendix D. The solutions are:

$$Y_{l,m_l}(\theta,\varphi)=(-1)^{(m_l+|m_l|)/2}\sqrt{\frac{(2l+1)\,(l-|m_l|)!}{4\pi\,(l+|m_l|)!}}\,P_l^{|m_l|}(\cos\theta)\,\mathrm{e}^{\mathrm{i}\varphi m_l}\,, \qquad (1.16)$$

where $P_l(\cos\theta)$ is a l'th order associated Legendre function, cf. (D.13) and (D.12). The different functions $Y_{l,m_l}(\theta,\varphi)$ are normalised and mutually orthogonal.

The explicit form of some of the lowest order solutions are:

$$
\begin{aligned}
Y_{0,0}(\theta,\varphi) &= \frac{1}{2}\frac{1}{\sqrt{\pi}} \\
Y_{1,0}(\theta,\varphi) &= \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta \\
Y_{1,\pm1}(\theta,\varphi) &= \mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\varphi} \\
Y_{2,0}(\theta,\varphi) &= \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta-1) \\
Y_{2,\pm1}(\theta,\varphi) &= \mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\,\mathrm{e}^{\pm\mathrm{i}\varphi} \\
Y_{2,\pm2}(\theta,\varphi) &= \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\,\mathrm{e}^{\pm2\mathrm{i}\varphi} \\
Y_{3,0}(\theta,\varphi) &= \frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta-3\cos\theta) \\
Y_{3,\pm1}(\theta,\varphi) &= \mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta-1)\,\mathrm{e}^{\pm\mathrm{i}\varphi} \\
Y_{3,\pm2}(\theta,\varphi) &= \frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\,\mathrm{e}^{\pm2\mathrm{i}\varphi} \\
Y_{3,\pm3}(\theta,\varphi) &= \mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\,\mathrm{e}^{\pm3\mathrm{i}\varphi}\,.
\end{aligned}
\tag{1.17}
$$

The angular probability distribution for an electron in a specific orbital can be calculated by taking the modulus squared of the spherical harmonics for the different combinations of l and m_l. The lowest orders of these, corresponding to (1.17) are depicted in fig. 1.2.

1.5 The total hydrogenic wave function

Since the total wave function is the product of $R(r)$ and $Y(\theta,\varphi)$, the complete hydrogenic wave function (from (1.11) and (1.16)) is:

$$
\begin{aligned}
\psi_{nlm_l}(r,\theta,\varphi) = (-1)^{\frac{m_l+|m_l|}{2}+1}\sqrt{\frac{(n-l-1)!\,(2l+1)(l-|m_l|)!}{4\pi n^2[(n+l)!]^3(l+|m_l|)!}} \\
\times\left(\frac{2Z}{n}\right)^{l+1} r^l\,\mathrm{e}^{-Zr/n}\,\mathrm{L}_{n+l}^{2l+1}\left(\frac{2Zr}{n}\right)\,P_l^{|m_l|}(\cos\theta)\,\mathrm{e}^{\mathrm{i}m_l\varphi}\,.
\end{aligned}
\tag{1.18}
$$

Equation (1.18) is the wave function in atomic units. This means that for any quantitative results, r must be given in a_0.

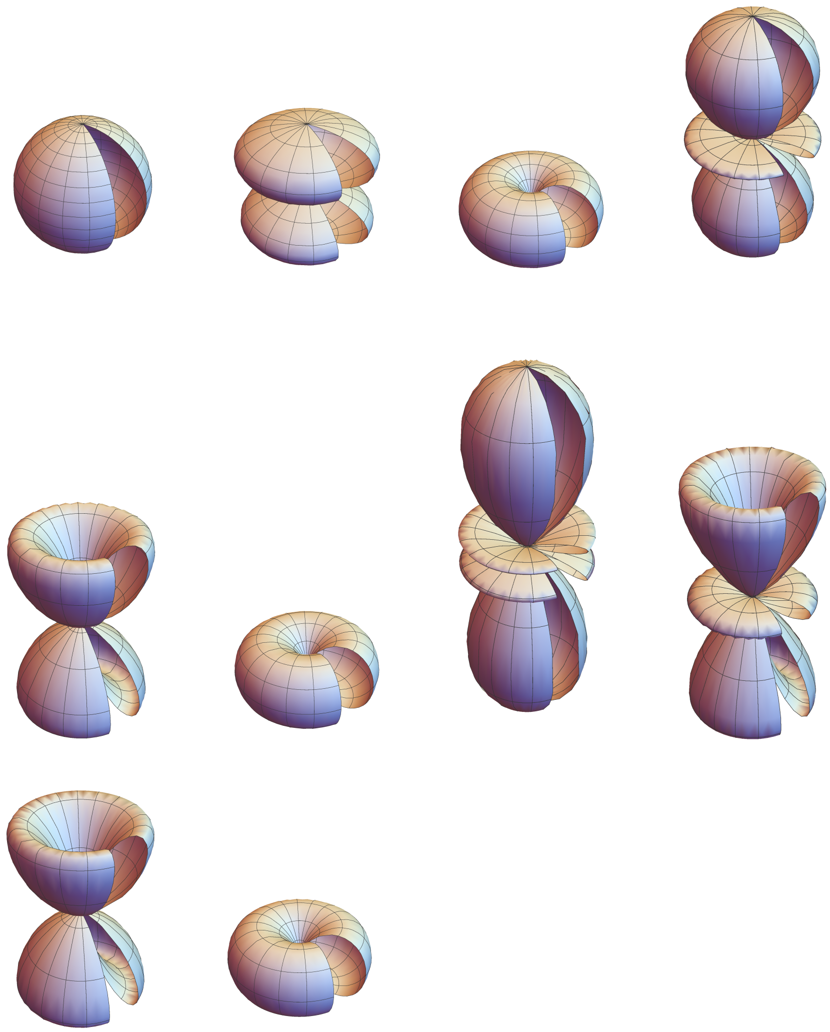


Fig. 1.2 Angular probability distribution for a one-electron atom (identical to the modulus squared of the spherical harmonics). The figures correspond to the equations in (1.17), starting fom the top left, $Y_{0,0}$, $Y_{1,0}$, $Y_{1,\pm1}$, $Y_{2,0}$, $Y_{2,\pm1}$, $Y_{2,\pm2}$, $Y_{3,0}$, $Y_{3,\pm1}$, $Y_{3,\pm2}$, and $Y_{3,\pm3}$.

1.5.1 Energy levels

The eigenenergies corresponding to the solutions in (1.18), with the ionisation limit taken as zero, are:

$$E_n = -\frac{Z^s}{2n^2} \ . \tag{1.19}$$

In SI-units this is:

$$E_n = -\frac{Z^2 m_e e^4}{2(4\pi\varepsilon_0)^2 \hbar^2 n^2} \; . \tag{1.20}$$

Thus, the energies depend only on the principal quantum number, and they are degenerate in l and m_l. For every value of l, there are $2l+1$ values of m_l, and for every value of n, there are values of l from 0 up to $n-1$. This means that the degeneracy for a certain n is:

$$D = \sum_{l=0}^{n-1}(2l+1) = 2\frac{(n+1)n}{2} + n = n^2 \; . \tag{1.21}$$

The degeneracy in m_l is obvious, since we have spherical symmetry and no external field, and this will hold true also for atoms with more electrons. The degeneracy for l in unique to hydrogenlike atoms.

The energies in (1.20) are identical with the ones found from the Bohr model, which is not surprising given that the Bohr model was adapted to fit experimental data. The energy levels have been included in the graph in fig. (1.1). This provides a graphical illustration to the constraint in (1.10). For example, for $l=1$, the centrifugal barrier inhibits energies lower than about $-0.25E_\mathrm{h}$, excluding the ground state. For the latter, $E_1 = 0.5E_\mathrm{h}$ and the potential for $l=0$ is the only one possible, and so on.

1.5.2 Radial probability distribution

The probability of finding the electron inside a spherical shell of radius r is found from:

$$\int_0^{2\pi}\int_0^{\pi} |\psi_{nlm_l}(r,\theta,\varphi)|^2 r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi$$
$$= |R_{nl}(r)|^2 r^2 \mathrm{d}r \int_0^{2\pi}\int_0^{\pi} |Y_{lm_l}(\theta,\varphi)|^2 \sin\theta \mathrm{d}\theta\mathrm{d}\varphi = |U_{nl}(r)|^2 \; , \tag{1.22}$$

where we have used the fact the the spherical harmonics are normalised. In order to calculate the radial charge density, it suffices to use the radial functions in (1.14). The probability amplitude is proportional to R^2, and this is distributed on a spherical surface of area $4\pi r^2$. Thus, the charge density in atomic units is r^2R^2, which is the square of the functions in (1.14).

In fig. 1.3, we have plotted this radial distribution for the lowest principal quantum numbers, for different l. Note that the number of anti-nodes in each distribution is given by $n-l$, and that most of the charge density is centered around the outermost anti-node. Moreover, for a given n, the maximum of the charge density lies closer to the nucleus for a larger l, even though the energy is higher.

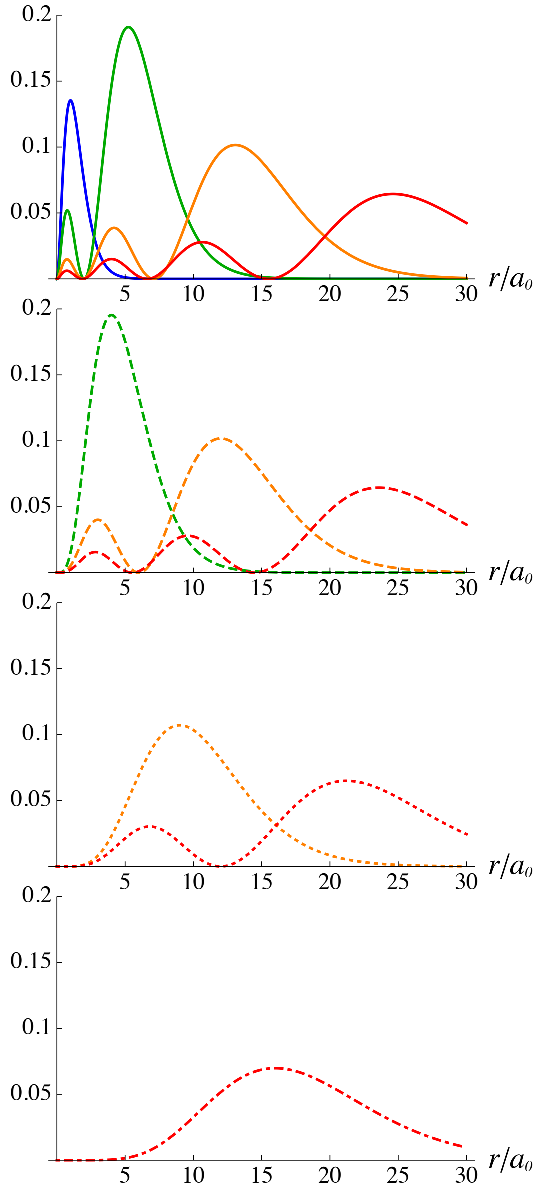


Fig. 1.3 Radial distribution of the electron charge density, corresponding to the radial wave functions in (1.14). The blue curve is for $n = 1$, the green ones for $n = 2$, the orange for $n = 3$, and the red for $n = 3$. The top graph, with full lines, are for $l = 0$, the second graph, with dashed lines, for $l = 1$, the third graph, with dotted lines, for $l = 2$, and the bottom graph, with a dash-dotted line, for $l = 3$.

Appendix B
The radial part of the hydrogenic wave function

In this appendix, we will derive the solution to the radial part of the Schrödinger equation for hydrogen, $R(r)$. We begin by the expression (1.9), derived in chapter 1.3:

$$\frac{\partial^2}{\partial r^2}U(r) + \left[\frac{2Z}{r} + 2E - \frac{l(l+1)}{r^2}\right]U(r) = 0\ . \tag{B.1}$$

This is the equation given in atomic units, and with the substitution $U(r) \equiv rR(r)$. To solve this equation, we first look at the limiting cases where $r \to 0$ and $r \to \infty$, and investigate the respective solutions, $U^{(0)}(r)$ and $U^{(\infty)}(r)$.

In the case of $r \to 0$, the terms $2Z/r$ and $2E$ in (B.1) can be neglected, and we have:

$$\frac{\partial^2}{\partial r^2}U^{(0)}(r) - \frac{l(l+1)}{r^2}U^{(0)}(r) = 0\ . \tag{B.2}$$

This equations has the two solutions $U^{(0)}(r) = r^{l+1}$ and $U^{(0)}(r) = r^{-l}$. From the definition of $U(r)$ we can se that this function must be finite also as $r \to 0$. Therefore, the latter of the two solutions above can be discarded.

We then consider the other limit, where $r \to \infty$. In this case, it is the two terms proportional to $1/r$ and $1/r^2$ that can be discarded, and we have:

$$\frac{\partial^2}{\partial r^2}U^{(\infty)}(r) + 2EU^{(\infty)}(r) = 0\ . \tag{B.3}$$

Also here we get two solutions: $U^{(\infty)}(r) = \exp(\pm\sqrt{-2E}r)$. For bound states, $E < 0$, this gives real solutions. Moreover, we cannot allow $U(r)$ to diverge, and thus we can keep only the negative exponential.

With the form of $U(r)$ determined for $r \to 0$ and $r \to \infty$, we introduce a trial solution that is a product of these limiting solutions and a polynomial function:

$$U(r) = r^{l+1}\mathrm{e}^{-\sqrt{-2E}r}(A_0 + A_1 r + A_2 r^2 + A_3 r^3 + \dots)\ . \tag{B.4}$$

This will have the correct behavior for very small and very large r. The trial solution is then substituted into (B.1), which will give us a recursion formula for the A's in (B.4):

$$A_k = -2A_{k-1}\frac{Z-(l+k)\sqrt{-2E}}{(l+k)(l+k+1)-l(l+1)}\ . \tag{B.5}$$

However, the problem with this is that when r goes to infinity, the infinite series in (B.4) increases as $\exp(2\sqrt{-2E}r)$, and thus $U(r)$ will no longer be finite.

The way to counter that is to force the series in (B.4) to break off at some point, and form a limited polynomial. This can be achieved if the numerator in (B.5) becomes zero for some k. Thus, we get a limiting condition for k when the numerator in (B.5), that is when:

$$(l+k)\sqrt{-2E} = Z\ . \tag{B.6}$$

From (B.6), we can get an expression for the energy in terms of the integers l and k, and in order to get an analogy with the Bohr model, we introduce the principal quantum number $n \equiv l+k$, and get:

$$E = -\frac{1}{2}\frac{Z^2}{n^2}\ . \tag{B.7}$$

Next step is to make the substitution:

$$\rho = \frac{2Zr}{n}\ , \tag{B.8}$$

and to rewrite (B.4) and (B.5) in terms of ρ and n. This way, $U(r)$ can be written as a Laguerre polynomial:

$$U_{nl}(\rho) = \sqrt{\frac{(n-l-1)!Z}{n^2[(n+l)!]^3}}\,\rho^{l+1}\,\mathrm{e}^{-\rho/2}\,\mathrm{L}_{n+l}^{2l+1}(\rho)\ . \tag{B.9}$$

The definition of the Laguerre polynomial in (B.9) is here:

$$\begin{aligned}\mathrm{L}_{n+l}^{2l+1}(\rho) &= B_0 + B_1\rho + B_2\rho^2 + B_3\rho^3 + \cdots + B_{n-l-1}\rho^{n-l-1}\\ B_k &= -B_{k-1}\frac{n-l-k}{(l+k)(l+k+1)-l(l+1)}\\ B_{n-l-1} &= (-1)^{n+l}\frac{(n+l)!}{(n-l-1)!}\ .\end{aligned} \tag{B.10}$$

Here, $(n-l-1)$ must be zero or positive, and thus we get a condition for l:

$$l = 0,1,2,\ldots,n-1\ . \tag{B.11}$$

Appendix C
Angular momentum

In classical mechanics, the orbital angular momentum is defined as $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$. In cartesian coordinates, the components of this vector are:

$$\begin{aligned} L_x &= yp_z - zp_y \\ L_y &= zp_x - xp_z \\ L_z &= xp_y - yp_x \,. \end{aligned} \tag{C.1}$$

Using the quantum mechanical operator forms for the linear momenta, we have:

$$\begin{aligned} L_x &= -\mathrm{i}\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \\ L_y &= -\mathrm{i}\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) \\ L_z &= -\mathrm{i}\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \,. \end{aligned} \tag{C.2}$$

This is in SI-units, and in this appendix, we will stick to this. Changing to atomic units would here simply mean discarding the factors of $\hbar$.

C.1 General angular momentum

From (C.2), we can calculate the commutators of the components of $\boldsymbol{L}$. Moreover, the resulting commutation rules are general; they will be the same for any type of angular momentum, and therfore we can write them in terms of a generalised one, $\boldsymbol{J}$:

$$\begin{aligned}[][J_x, J_y] &= \mathrm{i}\hbar J_z \\ [J_y, J_z] &= \mathrm{i}\hbar J_x \\ [J_z, J_x] &= \mathrm{i}\hbar J_y \ .\end{aligned} \tag{C.3}$$

Next, we define the ladder operators; the operators that increment (or decrement) the projection of the angular momentum of $\boldsymbol{J}$ along the $\hat{e}_z$-axis by one unit of $\hbar$:

$$\begin{aligned} J_+ &\equiv J_x + \mathrm{i}\,J_y \\ J_- &\equiv J_x - \mathrm{i}\,J_y \ ,\end{aligned} \tag{C.4}$$

and by taking the products of these raising and lowering operators, we find that they do not commute:

$$\begin{aligned} J_+J_- &= J_x^2 + J_y^2 + \hbar J_z \\ J_-J_+ &= J_x^2 + J_y^2 - \hbar J_z \\ [J_+, J_-] &= 2\hbar J_z \ .\end{aligned} \tag{C.5}$$

C.1.1 Eigenvalues

Since different cartesian components of an angular momentum never commute, the least ambiguous way in which one can be specified is by the combination of the square of its absolute value $\boldsymbol{J}^2$, and its projection along the $\hat{e}_z$-axis J_z. We have

$$\boldsymbol{J}^2 = \boldsymbol{J} \cdot \boldsymbol{J} = J_x^2 + J_y^2 + J_z^2 \ . \tag{C.6}$$

$\boldsymbol{J}^2$ commutes with J_z (as well as with J_x and J_y), and thus they have common eigenfunctions ψ_{ab}:

$$\begin{aligned} \boldsymbol{J}^2\,\psi_{ab} &= a\,\psi_{ab} \\ J_z\,\psi_{ab} &= b\,\psi_{ab} \ .\end{aligned} \tag{C.7}$$

Here a and b are the eigenvalues of the respective operators, and together a and b will also provide a unique label for the wave function. From (C.6) and (C.7), we see that:

$$(J_x^2 + J_y^2)\,\psi_{ab} = (\boldsymbol{J}^2 - J_z^2)\,\psi_{ab} = (a - b^2)\,\psi_{ab} \ , \tag{C.8}$$

and since this sum of two squares necessarily has to be positive or zero, we have the inequality:

$$a \geq b^2 \ . \tag{C.9}$$

Next, we apply the ladder operators, defined in (C.4), on ψ_{ab}. From the fact that $\boldsymbol{J}^2$ commutes with all the components of $\boldsymbol{J}$ follows that the functions $J_\pm\,\psi_{ab}$ are also eigenfunctions of $\boldsymbol{J}^2$, with the same eigenvalue a. Then we let J_z operate on $J_\pm\,\psi_{ab}$, and using the commutation relations in (C.3) we find:

$$
\begin{aligned}
J_z J_\pm \psi_{ab} &= (J_z J_x \pm \mathrm{i} J_z J_y)\psi_{ab} = [(J_x J_z + \mathrm{i}\hbar J_y) \pm \mathrm{i}(J_y J_z - \mathrm{i}\hbar J_x)]\,\psi_{ab} \\
&= [(J_x \pm \mathrm{i} J_y)(J_z \pm \hbar)]\,\psi_{ab} = (b \pm \hbar) J_\pm \psi_{ab}\,.
\end{aligned} \tag{C.10}
$$

Thus, unless $J_\pm \psi_{ab}$ is zero, it must be an eigenfunction of J_z, with eigenvalue $(b \pm \hbar)$. If we now apply $J_\pm$ repeatedly to ψ_{ab}, we find that the eigenvalues of $\boldsymbol{J}^2$ and J_z are:

$$
\begin{aligned}
\boldsymbol{J}^2 (J_\pm)^n \psi_{ab} &= a (J_\pm)^n \psi_{ab} \\
J_z (J_\pm)^n \psi_{ab} &= (b \pm n\hbar)(J_\pm)^n \psi_{ab}\,,
\end{aligned} \tag{C.11}
$$

except for the cases where $(J_\pm)^n \psi_{ab}$ is zero.

The equations (C.11) show that the ladder operators do indeed either increase or decrease the projection of the angular momentum $\boldsymbol{J}$ along the z-axis, with units of $\hbar$. They also show, that for a given eigenvalue of $\boldsymbol{J}^2$, a, there is a discrete spectrum of eigenvalues for J_z:

$$
b = \ldots, b' - 2\hbar, b' - \hbar, b', b' + \hbar, b' + 2\hbar, \ldots\,. \tag{C.12}
$$

Because of the restriction in (C.9), this spectrum must have a lower and an upper bound, set by $\pm\sqrt{a}$.

As a consequence, the eigenfunctions corresponding to these limits in the spectrum of J_z must return zero if they are acted on by an appropriate ladder operators. We have:

$$
\begin{aligned}
J_- (J_+ \psi_{ab_{\max}}) &= 0 \\
J_+ \left(J_- \psi_{ab_{\min}}\right) &= 0\,.
\end{aligned} \tag{C.13}
$$

Using (C.5), we get:

$$
\begin{aligned}
(J_x^2 + J_y^2 - \hbar J_z)\,\psi_{ab_{\max}} &= (\boldsymbol{J}^2 - J_z^2 - \hbar J_z)\,\psi_{ab_{\max}} \\
&= (a - b_{\max}^2 - \hbar b_{\max})\,\psi_{ab_{\max}} = 0 \\
(J_x^2 + J_y^2 + \hbar J_z)\,\psi_{ab_{\min}} &= (\boldsymbol{J}^2 - J_z^2 + \hbar J_z)\,\psi_{ab_{\min}} \\
&= (a - b_{\min}^2 + \hbar b_{\min})\,\psi_{ab_{\min}} = 0\,.
\end{aligned}
$$

Since the eigenfunctions $\psi_{ab_{\max}}$ and $\psi_{ab_{\min}}$, are non-zero, albeit limiting cases, we have:

$$
(a - b_{\min}^2 + \hbar b_{\min}) = (a - b_{\max}^2 - \hbar b_{\max}) = 0\,. \tag{C.14}
$$

From that we can derive:

$$
(b_{\max} + b_{\min})(\hbar + b_{\max} - b_{\min}) = 0\,. \tag{C.15}
$$

The second parenthesis above must be non-zero, and therefore the limits to the spectrum of J_z must be symmetrically placed around zero: $b_{\min} = -b_{\max}$. This together with (C.12) means that all values of b are either integers or half integers of $\hbar$. This characteristic will hold for any quantum mechanical angular momentum.

From (C.14), we can also get a condition for the eigenvalues of $\boldsymbol{J}^2$:

$$a = b_{\max}(b_{\max} + \hbar) \ . \tag{C.16}$$

Introducing the quantum numbers $j \equiv b_{\max}/\hbar$, and $m_j \equiv b/\hbar$, we have now shown that:

$$\begin{aligned} \boldsymbol{J}^2\, \psi_{jm_j} &= j(j+1)\hbar^2\, \psi_{jm_j} \\ J_z\, \psi_{jm_j} &= m_j \hbar\, \psi_{jm_j} \ . \end{aligned} \tag{C.17}$$

We end this section by computing a normalisation constant $c_\pm$ for the ladder operators. We take:

$$J_\pm\, \psi_{jm_j} = c_\pm\, \psi_{j,m_j \pm 1} \ . \tag{C.18}$$

It is convenient to express this in Dirac notation:

$$J_\pm \,|\, j, m_j \,\rangle = c_\pm \,|\, j, m_j \pm 1 \,\rangle \ . \tag{C.19}$$

We consistently assume normalised wave functions and thus, by using (C.5), we get:

$$\begin{aligned} |c_\pm|^2 &= \langle\, j, m_j \pm 1 \,|(c_\pm)^* c_\pm|\, j, m_j \pm 1 \,\rangle = \left\langle j, m_j | J_\mp J_\pm \,| j, m_j \right\rangle \\ &= \left\langle j, m_j |\, (J_x^2 + J_y^2 \mp \hbar J_z) \,| j, m_j \right\rangle = \left\langle j, m_j |\, (\boldsymbol{J}^2 - J_z^2 \mp \hbar J_z) \,| j, m_j \right\rangle \\ &= \hbar^2 \left[j(j+1) - m(m \pm 1) \right] \ . \end{aligned} \tag{C.20}$$

The phase is irrelevant so, without loss of generality, we can take:

$$c_\pm = \hbar \sqrt{j(j+1) - m(m \pm 1)} \ . \tag{C.21}$$

C.2 Orbital angular momentum

In order to get explicit expressions for the orbital angular momentum, we first chose spherical coordinates, with θ and φ respectively as the zenith and azimuthal angles:

$$\begin{cases} x = r \sin\theta \cos\varphi \\ y = r \sin\theta \sin\varphi \\ z = r \cos\theta \end{cases} , \quad \begin{cases} r &= (x^2 + y^2 + z^2)^{1/2} \\ \cos\theta &= z\,(x^2 + y^2 + z^2)^{-1/2} \\ \tan\varphi &= y/x \end{cases} . \tag{C.22}$$

From this, we can find spherical coordinate forms of the partial derivatives in (C.2):

$$
\begin{aligned}
\frac{\partial r}{\partial x} &= x\,(x^2+y^2+z^2)^{-1/2} = \frac{x}{r} = \sin\theta\cos\varphi \\
\frac{\partial r}{\partial y} &= \sin\theta\sin\varphi \\
\frac{\partial r}{\partial z} &= \cos\theta \\
\frac{\partial}{\partial x}(\cos\theta) = -\sin\theta\,\frac{\partial\theta}{\partial x} &= -zx\,(x^2+y^2+z^2)^{-3/2} = -\frac{z}{r^2}\sin\theta\cos\varphi \\
&= -\frac{\sin\theta\cos\theta\cos\varphi}{r} \\
-\sin\theta\,\frac{\partial\theta}{\partial y} &= -\frac{z}{r^2}\sin\theta\sin\varphi = -\frac{\sin\theta\cos\theta\sin\varphi}{r} \\
-\sin\theta\,\frac{\partial\theta}{\partial z} &= -\frac{z}{r^2}\cos\theta + \frac{1}{r} = \frac{\sin^2\theta}{r} \\
\frac{\partial}{\partial x}(\tan\varphi) = \frac{1}{\cos^2\varphi}\,\frac{\partial\varphi}{\partial x} &= -\frac{y}{x^2} = -\frac{\tan\varphi}{x} = -\frac{\sin\varphi}{r\sin\theta\cos^2\varphi} \\
\frac{1}{\cos^2\varphi}\,\frac{\partial\varphi}{\partial y} &= \frac{1}{x} = \frac{1}{r\sin\theta\cos\varphi} \\
\frac{\partial\varphi}{\partial z} &= 0\,,
\end{aligned}
\tag{C.23}
$$

which leads to:

$$
\begin{aligned}
\frac{\partial}{\partial x} &= \sin\theta\cos\varphi\,\frac{\partial}{\partial r} + \frac{\cos\theta\cos\varphi}{r}\,\frac{\partial}{\partial\theta} - \frac{\sin\varphi}{r\sin\theta}\,\frac{\partial}{\partial\varphi} \\
\frac{\partial}{\partial y} &= \sin\theta\sin\varphi\,\frac{\partial}{\partial r} + \frac{\cos\theta\sin\varphi}{r}\,\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{r\sin\theta}\,\frac{\partial}{\partial\varphi} \\
\frac{\partial}{\partial z} &= \cos\theta\,\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\,\frac{\partial}{\partial\theta}\ .
\end{aligned}
\tag{C.24}
$$

Combining (C.24) with (C.2), we get the operator expressions for the orbital angular momentum components:

$$
\begin{aligned}
L_x &= \mathrm{i}\hbar\left(\sin\varphi\,\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{\tan\theta}\,\frac{\partial}{\partial\varphi}\right) \\
L_y &= \mathrm{i}\hbar\left(-\cos\varphi\,\frac{\partial}{\partial\theta} + \frac{\sin\varphi}{\tan\theta}\,\frac{\partial}{\partial\varphi}\right) \\
L_z &= -\mathrm{i}\hbar\,\frac{\partial}{\partial\varphi}\ .
\end{aligned}
\tag{C.25}
$$

When we have explicit expressions for all components of $\boldsymbol{L}$, we can derive differential forms of its ladder operators:

$$L_{\pm} = \hbar\, \mathrm{e}^{\pm \mathrm{i}\varphi} \left(\pm \frac{\partial}{\partial \theta} + \mathrm{i} \frac{1}{\tan\theta} \frac{\partial}{\partial \varphi} \right) . \tag{C.26}$$

Using also (C.5), the operator for $\boldsymbol{L}^2$ becomes:

$$\begin{aligned} \boldsymbol{L}^2 &= L_x^2 + L_y^2 + L_z^2 = L_z^2 + L_- L_+ + \hbar L_z \\ &= L_z^2 + \hbar L_z - \hbar^2 \left(\frac{\partial^2}{\partial \theta^2} \frac{1}{\tan\theta} \frac{\partial}{\partial \theta} - \mathrm{i} \frac{\partial}{\partial \varphi} \frac{1}{\tan^2\theta} \frac{\partial^2}{\partial \varphi^2} \right) \\ &= -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2} \right] . \end{aligned} \tag{C.27}$$

The general properties of angular momenta, described in sect. C.1.1, are still valid, and with l and m_l as the respective quantum numbers for orbital angular momentum and its projection along $\hat{e}_z$, we have:

$$\begin{aligned} \boldsymbol{L}^2\, \psi_{lm_l} &= l(l+1)\hbar^2\, \psi_{lm_l} \\ L_z\, \psi_{lm_l} &= m_l \hbar\, \psi_{lm_l} . \end{aligned} \tag{C.28}$$

In the case of $\boldsymbol{L}$, however, we have an extra constraint. The equation for L_z in (C.25) shows that the solution to the eigenvalue equation for L_z must be of the form:

$$\psi_{lm_l}(r, \theta, \varphi) = f(r, \theta)\, \mathrm{e}^{\mathrm{i}\varphi m_l} . \tag{C.29}$$

Since this function has to be periodic, with the periodicity 2π, we have:

$$\mathrm{e}^{2\pi \mathrm{i} m_l} = 1 , \tag{C.30}$$

and thus the the projection quantum number m_l for orbital angular momentum must be a whole integer (positive or negative). As a consequence, the quantum number l also has to be a positive integer.

Appendix D
Spherical harmonics

For an atom with a single electron, the spherical harmonics are solutions to the angular part of the Schrödinger equation. This solution will be the same for any potential $V(r)$ that only depends on the radial parameter. Stated even more generally, the spherical harmonics are the angular part of the solutions to the Laplace equation:

$$\nabla^2 \psi = 0 \,. \tag{D.1}$$

In spherical coordinates, with standard definitions of the zenith and azimuthal angles, and calling the angular part of the wave function $Y(\theta,\varphi) = Y_{lm_l}$, the equation we have to solve is:

$$\begin{aligned} -\frac{1}{Y(\theta,\varphi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi) \\ = \boldsymbol{L}^2\,Y(\theta,\varphi) = l(l+1)\,Y(\theta,\varphi)\,, \end{aligned} \tag{D.2}$$

where we have used the definition of $\boldsymbol{L}^2$ used in (C.27), and we have eliminated factors of $\hbar$ by using atomic units. That is, for a bound electron, $\boldsymbol{L}^2$ corresponds to the square or the orbital angular momentum. Likewise, the quantum numbers l and m_l are the same as those used in (C.28).

The differential equation (D.2) can be integrated directly, but we shall instead take an algebraic route, which involves first separating the total angular function Y_{lm_l} into two components, a zenith function and an azimuthal function:

$$Y_{lm_l}(\theta,\varphi) = \Theta_{lm_l}(\theta)\,\Phi_{m_l}(\varphi)\,. \tag{D.3}$$

We then start with the solution that has the minimum projection of L_z (that is we set $m_l = -l$), which is $Y_{l,-l} = \Theta_{l,-l}\Phi_{-l}$. Then, we let the lowering ladder operator L_- (cf. Appendix C) act on this. This should yield zero, which in turn gives us a solvable differential equation.

From (C.26) we have:

$$L_- Y_{l,-l}(\theta,\varphi) = \mathrm{e}^{-\mathrm{i}\varphi}\left(-\frac{\partial}{\partial\theta} + \mathrm{i}\cot\theta\frac{\partial}{\partial\varphi}\right)\Theta_{l,-l}(\theta)\,\Phi_{-l}(\varphi) = 0\,. \tag{D.4}$$

In the second term within the parenthesis above, we can identify the expression for L_z from (C.25). Substituting this, we can eliminate $\Phi_{-l}(\varphi)$, as well as the initial exponential. We now have:

$$-\frac{\partial\Theta_{l,-l}}{\partial\theta} + l\cot\theta\,\Theta_{l,-l} = 0\,. \tag{D.5}$$

The solution to this is a sine function to the power of l. Then we chose an integration constant such that the zenith function becomes normalised:

$$\langle\,\Theta_{l,-l}\,|\,\Theta_{l,-l}\,\rangle = \int_0^\pi \Theta^*_{l,-l}\Theta_{l,-l}\sin\theta\,\mathrm{d}\theta = 1\,. \tag{D.6}$$

The result is:

$$\Theta_{l,-l}(\theta) = \sqrt{\frac{(2l+1)!}{2}}\,\frac{\sin^l\theta}{2^l\,l!}\,. \tag{D.7}$$

For all other functions Θ_{lm_l} we can now use the other ladder operator, the raising one. This will yield a recursion equation for the general case. We have:

$$\Theta_{l,m_l+1}\,\Phi_{m_l+1} = \sqrt{l(l+1)-m_l(m_l+1)}L_+\Theta_{l,m_l}\,\Phi_{m_l}\,, \tag{D.8}$$

where we have taken the prefactor from (C.21). Now, the azimuthal function is taken from (C.29), and as above we take the rising operator from (C.26):

$$\begin{aligned}&\Theta_{l,m_l+1}\,\mathrm{e}^{\mathrm{i}(m_l+1)\varphi}\\ &\qquad = \sqrt{l(l+1)-m_l(m_l+1)}\,\mathrm{e}^{\mathrm{i}\varphi}\left(\frac{\partial}{\partial\theta} + \mathrm{i}\cot\theta\frac{\partial}{\partial\varphi}\right)\Theta_{l,m_l}\,\mathrm{e}^{\mathrm{i}(m_l)\varphi}\,.\end{aligned} \tag{D.9}$$

Now we again identify the expression (C.25) for L_z, and we get the equation:

$$\Theta_{l,m_l+1} = \sqrt{l(l+1)-m_l(m_l+1)}\left(\frac{\partial}{\partial\theta} - m_l\cot\theta\right)\Theta_{l,m_l}\,. \tag{D.10}$$

With (D.10) and (D.7), we can get normalised zenith wave functions for any allowed combination of l and m_l. The solution is:

$$\begin{aligned}\Theta_{l,m_l}(\theta,\varphi) &= \frac{(-1)^{l+m_l}}{2^l\,l!}\sqrt{\frac{(2l+1)\,(l-m_l)!}{2\,(l+m_l)!}}\,\sin^{m_l}\theta\,\frac{\mathrm{d}^{l+m_l}}{\mathrm{d}(\cos\theta)^{l+m_l}}\,\sin^{2l}\theta\\ &= (-1)^{(m_l+|m_l|)/2}\sqrt{\frac{(2l+1)\,(l-|m_l|)!}{2\,(l+|m_l|)!}}\,P_l^{|m_l|}(\cos\theta)\,.\end{aligned} \tag{D.11}$$

In the second line of (D.11), $P_l(\cos\theta)$ is the l'th order associated Legendre function for $\cos\theta$, given by the formula:

$$P_n(x) = \frac{1}{2^n\, n!} \frac{\mathrm{d}^n}{\mathrm{d}x^n} (x^2 - 1)^n \,. \tag{D.12}$$

Including the azimuthal function from (C.29), we get the complete expression for the spherical harmonics:

$$Y_{l,m_l}(\theta,\varphi) = (-1)^{(m_l+|m_l|)/2} \sqrt{\frac{(2l+1)\,(l-|m_l|)!}{4\pi\,(l+|m_l|)!}}\, P_l^{|m_l|}(\cos\theta)\, \mathrm{e}^{\mathrm{i}\varphi m_l} \,. \tag{D.13}$$

These spherical harmonics, provide a set of orthonormal functions:

$$\langle Y_{lm_l} \,|\, Y_{l',m_l'} \rangle = \int_0^{2\pi} \int_0^{\pi} Y_{lm_l}^{*} Y_{l',m_l'} \sin\theta \,\mathrm{d}\theta \mathrm{d}\varphi = \delta_{ll'}\,\delta_{m_l m_l'} \,. \tag{D.14}$$

Interactions/Spectroscopy I

Transitions ; Fermi golden rule

- Absorption or/and emission of light is accompanied by a change in energy (state) for the atom
- Conservation of energy $\Rightarrow$ the energy difference between the two states involved must equal the photon energy
- A study of emitted/absorbed colours give information about the atomic structure : "**Spectroscopy**"

Transitions

- Is a transition, accompanied by absorption/emission of light, possible between any states?
  - According to experiments: No!
  - This cannot be explained without QM
- The absorption/emission is an interaction between the atom and light
  - governed by an interaction Hamiltionian
  - possible transitions : "allowed"
  - impossible transitions : "forbidden"

Fermi's golden rule

- "The rate (probability) for a transition induced by a specific perturbation is proportional to the modulus squared of the matrix element for the perturbation"
  - Consider a transition from state $|\,1\,\rangle$ to state $|\,2\,\rangle$
  - Assume the interaction Hamiltonian : H_{pert}
  - Transition rate :

$$A_{1\leftrightarrow 2} \propto \left| \int \psi_2^* H_{\text{pert}} \psi_1 \,\mathrm{d}V \right|^2 = |\langle\, 2\,| H_{\text{pert}} |\, 1\,\rangle|^2$$

Interaction Hamiltonian

Interaction between an atom and light

- The light (the electric field):

  $$\vec{E} = \vec{E}_0 \cos(\omega t - \vec{k}\cdot\vec{r}) = E_0\,\vec{p}\cos(\omega t - \vec{k}\cdot\vec{r})$$

  - E_0 : amplitude
  - $\vec{p}$: polarization vector
  - For an atom in an optical field:
    - $|\vec{r}| \approx 0.1\,\mathrm{nm}$
    - $\lambda \approx 500\,\mathrm{nm}$
    - $\Rightarrow \cos(\omega t - \vec{k}\cdot\vec{r}) \approx \cos\omega t$
  - $\Rightarrow \vec{E} = E_0\,\vec{p}\cos\omega t$
  - "the electric-dipole approximation"

- The atomic dipole moment (for hydrogen):

  $$\vec{D} = e\,\vec{r}$$

  - where $\vec{r}$ is an operator

- Interaction Hamiltonian (a dipole in an electric field):

  $$H_\mathrm{I} = e\,\vec{r}\cdot\vec{E}$$

- Transition rate (according to Fermi golden rule, and time averaged):

$$A_{1\leftrightarrow 2} \propto \left|\int \psi_2^* H_\mathrm{I}\psi_1\,\mathrm{d}V\right|^2 = |\langle\, 2\,|H_\mathrm{I}|\,1\,\rangle|^2 = |eE_0|^2\;\;|\langle\, 2\,|\vec{r}\cdot\vec{p}|\,1\,\rangle|^2$$

The meaning of "allowed" and "forbidden"

- Consider the matrix element : $\langle\, 2\,|\vec{r}\cdot\vec{p}|\, 1\,\rangle$
- If $\langle\, 2\,|\vec{r}\cdot\vec{p}|\, 1\,\rangle = 0$ $\Rightarrow$ the transition 1⟷2 is forbidden
- If $\langle\, 2\,|\vec{r}\cdot\vec{p}|\, 1\,\rangle \neq 0$ $\Rightarrow$ the transition 1⟷2 is allowed
  - the magnitude of $\langle\, 2\,|\vec{r}\cdot\vec{p}|\, 1\,\rangle$ gives the transition probability
- Currently, all we want to know is which transitions that are allowed and which are forbidden
- The matrix element can be divided into one radial part and one angular part:

$$\langle\, 2\,|\vec{r}\cdot\vec{p}|\, 1\,\rangle = D_{12}\, I_{\text{ang}}$$

$$D_{12} = \int_0^\infty R^*_{n_2 l_2}(r)\, r\, R_{n_1 l_1}(r)\, r^2\, \mathrm{d}^3 r$$

  - gives a characteristic rate for the transition 1⟷2
  - typically $D_{12} > 0$
- To find forbidden (allowed) transitions, we look for cases with $I_{\text{ang}} = 0$ ($I_{\text{ang}} \neq 0$)

$$I_{\text{ang}} = \int_0^{2\pi}\int_0^{\pi} Y^*_{l_2 m_2}(\theta,\varphi)\, \frac{\vec{r}\cdot\vec{p}}{r}\, Y_{l_1 m_1}(\theta,\varphi)\, \sin\theta\, \mathrm{d}\theta \mathrm{d}\varphi$$

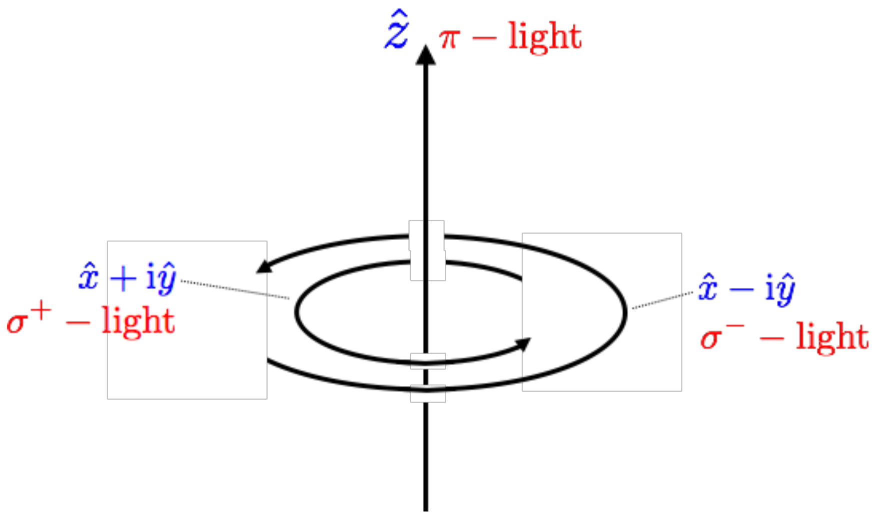
- To proceed, how can we parametrize $\vec{p}$?

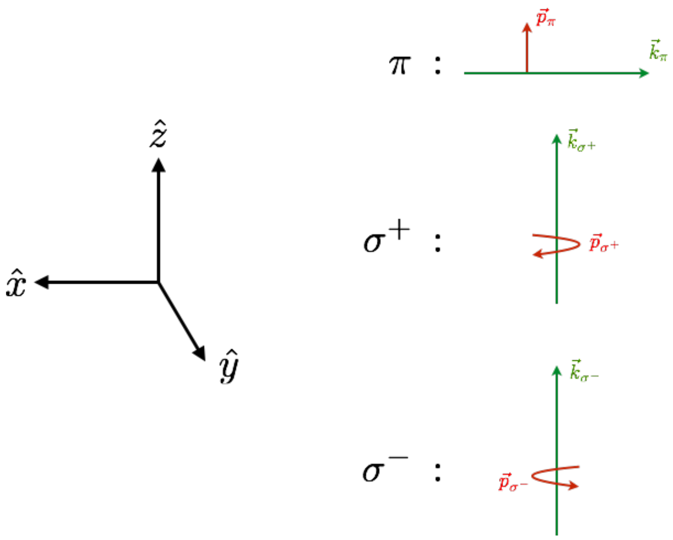
σ- and π- transitions

- We choose one preferred direction, say $\hat{z}$
- This will be our "quantization axis"
    - Angular momenta will be projected along this axis (L_z , S_z , $J_z \dots$)
- This essentially leaves us with cylindrical symmetry

Parametrising a beam of light

- A light field contains two vectors:
    - The wave vector (propagation direction) : $\vec{k}$
    - Polarisation : $\vec{p}$
    - $\vec{k} \perp \vec{p}$
- "π-light":
    - $\vec{p} \parallel \hat{z}$ (linear polarization)
    - $\vec{k} \parallel xy-$plane
- "σ⁺-light":
    - $\vec{k} \parallel \hat{z}$
    - $\vec{p} = \hat{x} + \mathrm{i}\hat{y}$ (right hand circular polarisation)
- "σ⁻-light":
    - $\vec{k} \parallel \hat{z}$
    - $\vec{p} = \hat{x} - \mathrm{i}\hat{y}$ (left hand circular polarisation)





π -transitions

- $\vec{p} = \hat{z}$; linear polarisation along $\hat{z}$
- The light propagates in the *xy*-plane

$$\frac{\vec{r}\cdot\vec{p}}{r} = (\sin\theta\cos\varphi\ ,\ \sin\theta\sin\varphi\ ,\ \cos\theta)\cdot\begin{pmatrix}0\\0\\1\end{pmatrix} = \cos\theta$$

$$I^{\pi}_{\text{ang}} = \int_0^{2\pi} \Phi^*_{m_2}\Phi_{m_1}\,\mathrm{d}\varphi\ \int_0^{\pi} \Theta^*_{l_2,m_2}\cos\theta\,\Theta_{l_1,m_1}\ \sin\theta\,\mathrm{d}\theta$$

- where : $\Phi_{m_1} = \mathrm{e}^{im_1\varphi}$, $\Phi^*_{m_2} = \mathrm{e}^{-\mathrm{i}m_2\varphi}$

- Cylindrical symmetry $\Rightarrow$ No φ dependence
  - $\Rightarrow\ I^{\pi}_{\text{ang}}(\varphi) = I^{\pi}_{\text{ang}}(\varphi+\varphi') = \mathrm{e}^{\mathrm{i}(m_1-m_2)\varphi'}\ I^{\pi}_{\text{ang}}(\varphi)$
  - (rotation around $\hat{z}$)

- So, for a π-transition to be allowed, we have to have :
  - $I^{\pi}_{\text{ang}}(\varphi) \neq 0 \quad \Rightarrow \quad m_1 = m_2$

- Selection rule for π-transitions :
  - $\Delta m = 0$

σ± -transtions

- $\vec{p} = \dfrac{1}{\sqrt{2}}(\hat{x} \pm \mathrm{i}\hat{y})$; circular polarisation
- The light propagates along $\hat{z}$

$$\frac{\vec{r}\cdot\vec{p}}{r} = (\sin\theta\cos\varphi\ ,\ \sin\theta\sin\varphi\ ,\ \cos\theta)\cdot\begin{pmatrix}\frac{1}{\sqrt{2}}\\ \pm\frac{\mathrm{i}}{\sqrt{2}}\\ 0\end{pmatrix} = \frac{1}{\sqrt{2}}\ \sin\theta\ \mathrm{e}^{\pm\mathrm{i}\varphi}$$

$$I^{\sigma^\pm}_{\text{ang}} = \int_0^{2\pi}\int_0^{\pi} Y^*_{l_2,m_2}\,\frac{1}{\sqrt{2}}\ \sin\theta\ \mathrm{e}^{\pm\mathrm{i}\varphi}\,Y_{l_1,m_1}\ \sin\theta\,\mathrm{d}\theta\mathrm{d}\varphi$$

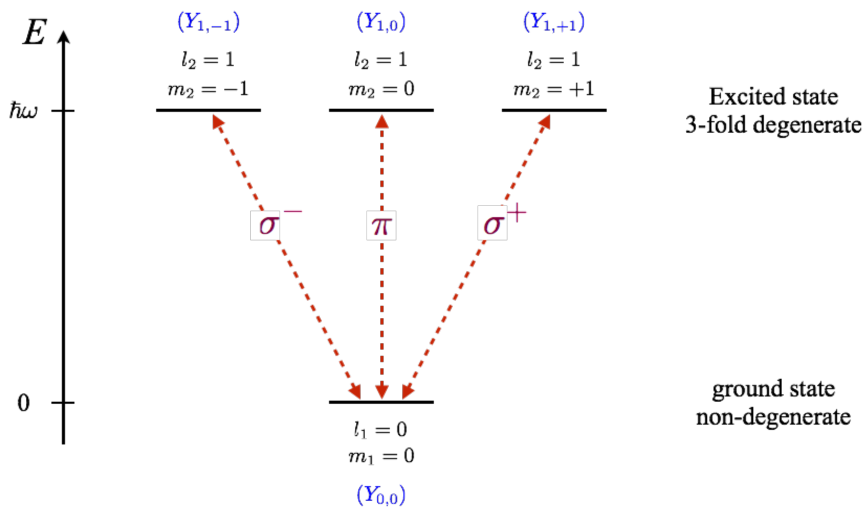
- Cylindrical symmetry $\Rightarrow$ No φ dependence

$\Rightarrow\ I^{\sigma^\pm}_{\text{ang}}(\varphi) = I^{\sigma^\pm}_{\text{ang}}(\varphi+\varphi') = \mathrm{e}^{\mathrm{i}(m_1-m_2\pm1)\varphi'}\ I^{\sigma^\pm}_{\text{ang}}(\varphi)$

- Selection rule for σ$^{\pm}$-transitions :
  - $\begin{cases} \Delta m = +1 & , \quad \sigma^{+} \\ \Delta m = -1 & , \quad \sigma^{-} \end{cases}$

Summary

- Example :
  - Transition from a $l = 0$ state to a $l = 1$ state



- These selection role can also be seen as conservation of angular momentum
  - A σ^{+}-photon carries the angular momentum $\hbar$
  - A σ^{-}-photon carries the angular momentum -$\hbar$
  - A π-photon does not carry angular momentum

Parity

- Parity transformation of a wave function,
  - $P\,:\,\vec{r}\rightarrow\ -\vec{r}$
  - $\begin{cases} x\rightarrow\ -x \\ y\rightarrow\ -y \\ z\rightarrow\ -z \end{cases}$ or $\begin{cases} r\rightarrow r \\ \theta\rightarrow\pi-\theta \\ \varphi\rightarrow\varphi+\pi \end{cases}$

- A wave function is either even or odd at a parity transformation
  - $P\,\psi=p\psi$ where $p=\pm1$
  - $(P^2\,\psi=p^2\psi=\psi)$

- Consider the angular eigenfunctions (the spherical harmonics)
  - $Y_{0,0}$: even
  - $Y_{1,m}$: odd
  - $Y_{2,m}$: even
  - $Y_{3,m}$: odd

$$P\,Y_{l,m}=(-1)^l\,Y_{l,m}$$

- How does this affect the integral I_{ang} ?

$$I_{\text{ang}}=(-1)^{l_2+l_1+1}\,I_{\text{ang}}$$

  - gives an allowed transition

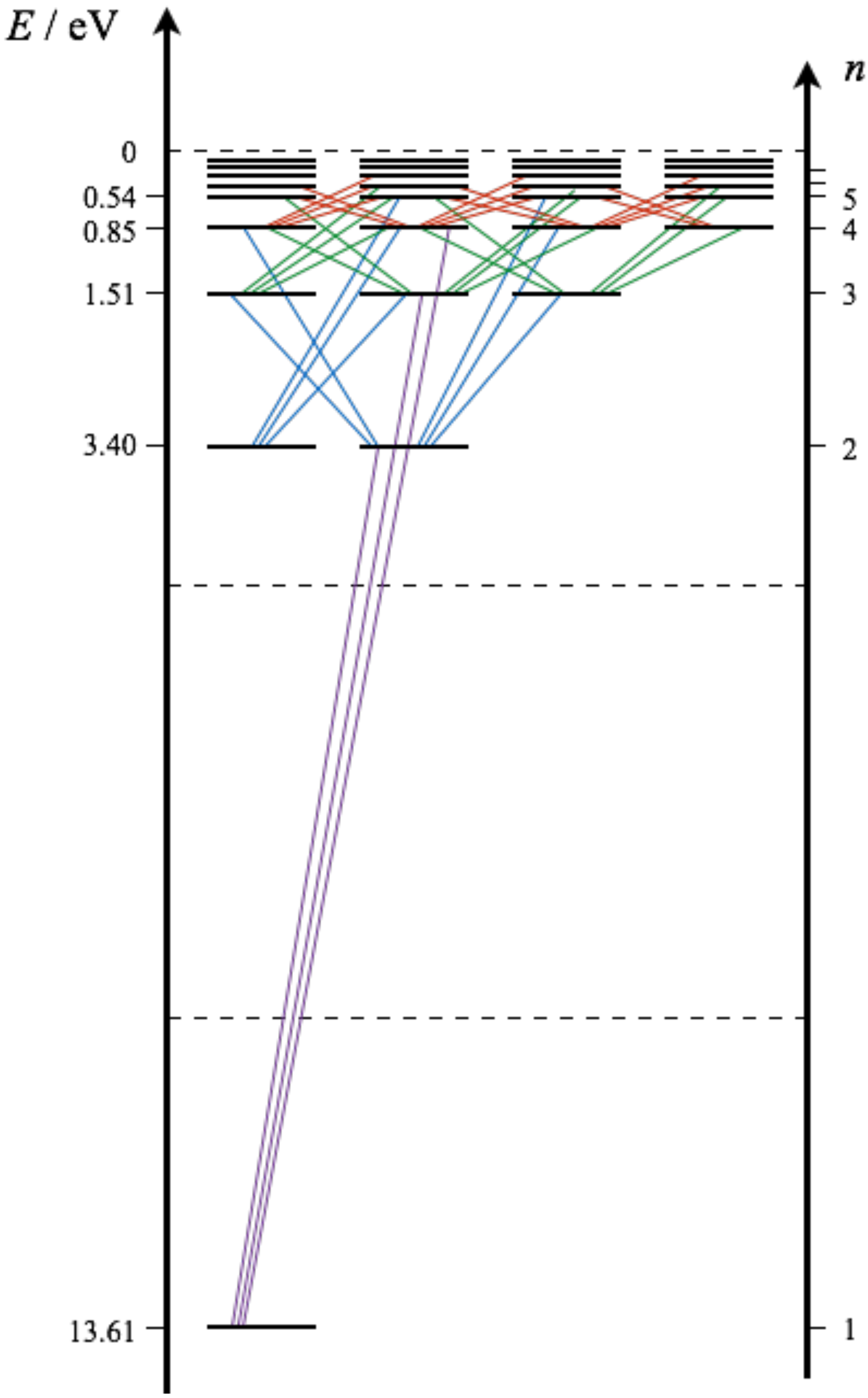
- For $I_{\text{ang}}\neq0$, (l_1+l_2) must be an odd number

- The quantum number l must change for an electric dipole transition to be allowed

Selection rules , electric dipole transitions

Summary

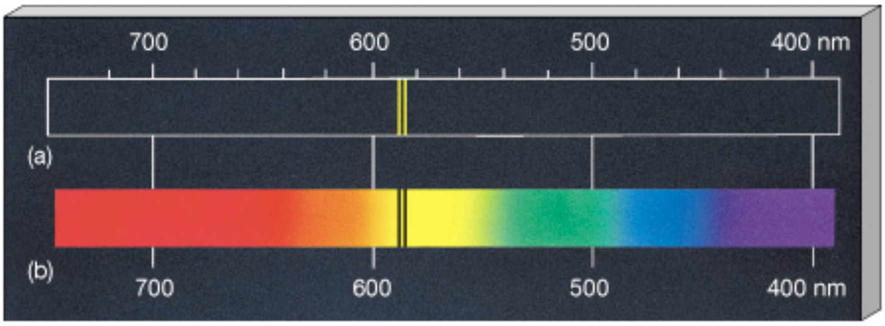
- ψ_1 and ψ_2 must have opposite parities
- $\Delta l \neq 0$
- $\Delta m = 0$ for π-transitions
- $\Delta m = \pm 1$ for $\sigma^{\pm}$-transitions


E / eV
n
0
0.54
0.85
1.51
3.40
13.61
5
4
3
2
1

Fine structure in hydrogen - relativistic effects

Electron spin ; relativistic effects

- In a spectrum from H (or from an alkali), one finds that spectral lines appears in pairs.
  - take a Na spectrum as example:



- Moreover, the rays are slightly shifted in comparison with the non-relativistic theory

- The origins of these "new" effects:
  - Electron spin
  - Relativity

Relativistic Hamiltonian

- Recall the one-electron Hmiltonian:

$$H = H_{\text{kin}} + V = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

- So far, we have treated the term $\frac{p^2}{2m}$ classically
- For a more exact solution, this has to be replaced with a relativistic version
- This gives the "Dirac equation"
    - An analytical solution is possible, but very complex
    - Instead, we treat the problem with perturbation theory

Perturbative treatment

- As a zero-order Hamiltonian, we take the non-relativistic version

- We the treat the relativistic corrections as perturbations

$$H = H_0 + H' = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + H'$$

- The corrections to the energy levels:

$$\Delta E_\psi = \langle \psi_0 | H' | \psi_0 \rangle$$

- It turns out that the relativistic corrections can be divided into three parts:

$$H' = H_{\mathrm{SO}} + H_{\mathrm{rel}} + H_{\mathrm{Darwin}}$$

  - H_{SO} : Spin-orbit interaction
  - H_{rel} : Relativistic treatment of the kinetic energy
  - H_{Darwin} : the Darwin term

  - This is consistent with the exact treatment

Relativistic treatment of the kinetic energy

$$H_{\text{rel}}$$

- Classical kinetic energy :

$$E^0_{\text{kin}} = \frac{p^2}{2m}$$

- Relativistic kinetic energy :

$$E_{\text{kin}} = \sqrt{p^2c^2 + m^2c^4} - mc^2 = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots$$

- First order correction (ignoring terms of order $\left(\frac{v}{c}\right)^4$ or higher) :

$$H_{\text{rel}} = -\frac{p^4}{8m^3c^2} = -\frac{\hbar^4}{8m^3c^2}\,\nabla^4$$

  - This does not depend on spin
  - It is diagonal in n and l

$$\Delta E_{\text{rel},nl} = -E_{n0}\,\frac{(Z\alpha)^2}{n^2}\,\left(\frac{3}{4} - \frac{4}{l+\frac{1}{2}}\right)$$

  - where $\alpha = \dfrac{e^2}{4\pi\varepsilon_0\, c^2\hbar}$
  - is the fine-structure constant
  - $\alpha^{-1} \approx 137.036$

- ΔE_{rel} is more important for small n
  - (small n $\Rightarrow$ small orbital radius
  - $\Rightarrow$ high velocity)

The Darwin term

$$H_{\text{Darwin}}$$

- Very difficult to explain ……
  - Related to the singularity at $r = 0$

$$H_{\text{Darwin}} = \frac{\pi \hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon}\right)\delta(r)$$

$$\Rightarrow \begin{cases} \Delta E_{\text{Darwin},nl} = E_{n,0}\,\frac{(Z\alpha)^2}{n} & ; \quad l = 0 \\ \Delta E_{\text{Darwin},nl} = 0 & ; \quad l \neq 0 \end{cases}$$

Spin-orbit interaction

$$H_{\mathrm{SO}}$$

- Interaction between the orbital angular momentum and the spin

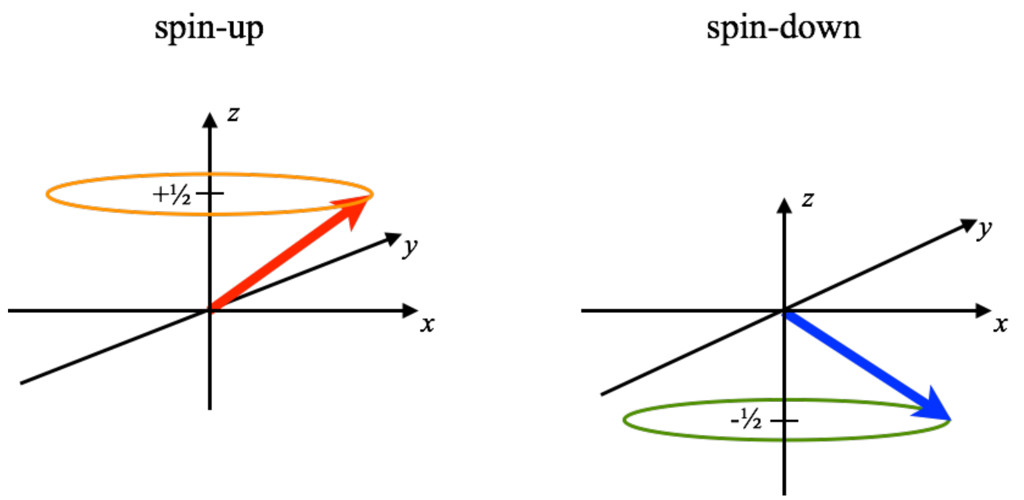
Spin

- An electron has a magnetic moment, which can be associated with a *spin*
  - Wave function : ψ_{s,m_s}
  - Vectorial representation : $|\, s\ m_s \,\rangle$

- The $|\, s\ m_s \,\rangle$ are eigenvectors to the operators:
  - $S^2 \;|\, s\ m_s \,\rangle = s(s+1)\hbar^2 \;|\, s\ m_s \,\rangle$
  - $S_z \;|\, s\ m_s \,\rangle = m_s\hbar \;|\, s\ m_s \,\rangle$

- For a single electron, we have (always):

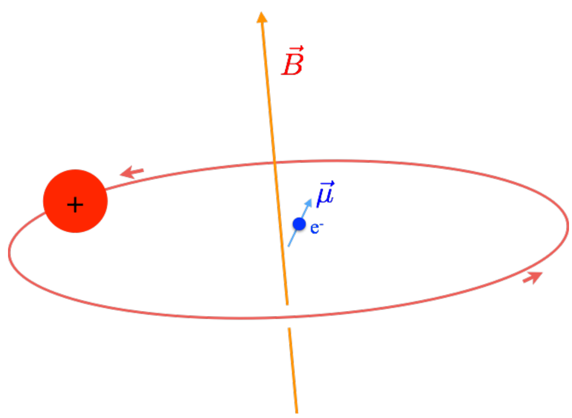
- $s = \dfrac{1}{2} \quad \Rightarrow \quad \left\langle S^2 \right\rangle = s(s+1)\hbar^2 = \dfrac{3\hbar^2}{4} = \left(\dfrac{\sqrt{3}\hbar}{2}\right)^2$
- $m_s = \pm\dfrac{1}{2} \quad \Rightarrow \quad \langle S_z \rangle = \pm\dfrac{\hbar}{2}$
  - "spin-up" and "spin-down"



- The total wave-function :
  - $\psi_{nlm_lm_s}$
  - $|\, n\, l\, m_l\, m_s \,\rangle$

Interaction between $\vec{l}$ and $\vec{s}$

- The electron has a magnetic moment : $\vec{\mu} \propto \vec{s}$
- Consider a system of reference centered at the electron
  - $\Rightarrow$ an orbiting proton (positive charge)



- An orbiting charge
  - $\Rightarrow$ induced magnetic field : $\vec{B} \propto \vec{l}$

- Interaction between $\vec{B}$ and $\vec{\mu}$

$$H_{\mathrm{SO}} = -\vec{\mu} \cdot \vec{B} \propto \underbrace{\vec{l} \cdot \vec{s}}_{\text{vectors}} \propto \underbrace{\vec{L} \cdot \vec{S}}_{\text{operators}}$$

- H_{SO} is separable in radial and angular coordinates

$$H_{\mathrm{SO}} = \xi(r)\, \vec{L} \cdot \vec{S}$$

  - where $\xi(r) = \dfrac{1}{2m^2c^2} \dfrac{1}{r} \dfrac{\mathrm{d}V}{\mathrm{d}r}$

- For example, the hydrogenic potential:

$$V = -\frac{Ze^2}{4\pi\varepsilon_0\, r} \quad \Rightarrow \quad \xi(r) = \frac{1}{2m^2c^2} \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{r^3}$$

- The energy shift due to the interaction is the expectation value of H_{SO}

$$\langle\, \psi \,|\, H_{\mathrm{SO}} \,|\, \psi \rangle = \langle\, R_{nl}(r) \,|\, \xi(r) \,|\, R_{nl}(r) \,\rangle \left\langle\, l\; m_l\; m_s \,|\, \vec{L} \cdot \vec{S} \,|\, l\; m_l\; m_s \,\right\rangle$$

$$\langle \xi(r) \rangle = \frac{1}{2m^2c^2} \frac{Ze^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r^3} \right\rangle = \frac{1}{2m^2c^2} \frac{Ze^2}{4\pi\varepsilon_0} \frac{Z^3}{a_0^3 n^3\, l(l+\frac{1}{2})(l+1)}$$

Fine structure

- For the angular part of H_{SO} :
  - we have to look for eigenvectors to $\langle \vec{L} \cdot \vec{S} \rangle$

- What about the vector : $|\, l \; m_l \; m_s \,\rangle$?
  - (eigenvector to the operators L^2 , L_z , and S_z)

- This will NOT do, since $\left[\vec{L} \cdot \vec{S} \, , \, L_z \right] \neq 0$ and $\left[\vec{L} \cdot \vec{S} \, , \, S_z \right] \neq 0$

- $\Rightarrow$ We need some other operator (and quantum number)

<u>The total angular momentum</u>

- We introduce :

$$\vec{J} = \vec{L} + \vec{S}$$

$$J^2 = L^2 + 2\,\vec{L} \cdot \vec{S} + S^2$$

$$\Rightarrow \quad \vec{L} \cdot \vec{S} = \frac{1}{2} \left(J^2 - L^2 - S^2 \right)$$

- Consider the wave functions ψ_{nljm_j} ($|\, n \; l \; j \; m_j \,\rangle$) that are eigenstates to H_0 , L^2 , J^2 and J_z :

$$\begin{aligned}
H_0 \,|\, n \; l \; j \; m_j \,\rangle &= E_0 \,|\, n \; l \; j \; m_j \,\rangle \\
L^2 \,|\, n \; l \; j \; m_j \,\rangle &= l(l+1)\hbar^2 \,|\, n \; l \; j \; m_j \,\rangle \\
J^2 \,|\, n \; l \; j \; m_j \,\rangle &= j(j+1)\hbar^2 \,|\, n \; l \; j \; m_j \,\rangle \\
J_z \,|\, n \; l \; j \; m_j \,\rangle &= m_j \hbar \,|\, n \; l \; j \; m_j \,\rangle
\end{aligned}$$

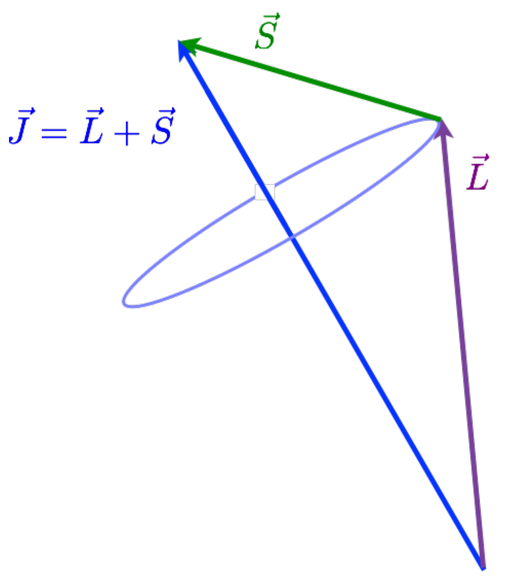
- For hydrogen, we have one single electron

$$\begin{cases} s &= \frac{1}{2} \\ m_s &= \pm\frac{1}{2} \end{cases}$$

$$\begin{cases} j = l \pm \frac{1}{2} & , \quad (l \neq 0) \\ j = \frac{1}{2} & , \quad (l = 0) \end{cases}$$

- j is a "good quantum number"
  - it makes the total Hamiltonian diagonal

- m_l and m_s are NOT good quantum numbers
  - due to the spin-orbit interaction, $\vec{L}$ and $\vec{S}$ will precess around each other
  - thus, their projections are not constant



- The sum, $\vec{J}$, IS constant

The Fine-structure energy

- Expectation value of the angular part of the hamiltonian:

$$\left\langle \vec{L}\cdot\vec{S}\right\rangle = \left\langle \frac{1}{2}\left(J^2 - L^2 - S^2\right)\right\rangle = \frac{1}{2}\left\langle\, l\; j\; m_j \,|\, J^2 - L^2 - S^2 \,|\, l\; j\; m_j \,\right\rangle$$
$$= \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

  - with $s = \frac{1}{2}$:

$$\left\langle \vec{L}\cdot\vec{S}\right\rangle = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]$$

$$\begin{aligned}\langle H_{\mathrm{SO}}\rangle &= \langle \xi(r)\rangle \left\langle \vec{L}\cdot\vec{S}\right\rangle \\ &= \frac{1}{2m^2c^2}\,\frac{Ze^2}{4\pi\varepsilon_0}\,\frac{Z^3}{a_0^3 n^3\, l(l+\frac{1}{2})(l+1)}\,\frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right] \\ &= \beta\,\frac{1}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]\end{aligned}$$

- The two possible values of m_s $(\pm\frac{1}{2})$ gives two possible values for j $(\,l + \frac{1}{2}$ and $l - \frac{1}{2}\,)$

- $\Rightarrow$ The energy level E_0 is split into a *doublet*

$$\Delta E_{\mathrm{SO}} = \left\langle H_{\mathrm{SO}}^{+}\right\rangle - \left\langle H_{\mathrm{SO}}^{-}\right\rangle = \beta\left(l + \frac{1}{2}\right)$$

Energy levels in hydrogen and spectroscopy

Spectroscopic notation

- There is a convention for how to annote quantum numbers
  - l-quantum numbers are described by a letter
  - The s-quantum number does not need description
  - The j-quantum number is given by its numerical value

- The combination of n and l (nl) is referred to as an "orbital"

- For a many-electron atom, the "electron configuration" is the list of all orbitals ($n_1 l_1, n_2 l_2, \ldots$)

- Coding for l :

$$\begin{aligned} l = 0 &\quad \rightarrow \quad \mathrm{s} \\ l = 1 &\quad \rightarrow \quad \mathrm{p} \\ l = 2 &\quad \rightarrow \quad \mathrm{d} \\ l = 3 &\quad \rightarrow \quad \mathrm{f} \\ l = 4 &\quad \rightarrow \quad \mathrm{g} \end{aligned}$$

- For a multi-electron atom, total angular momenta have to be defined.

- These are given quantum numbers with capital letters:

$\vec{L} = \vec{l}_1 + \vec{l}_2 + \ldots$ quantum numbers L and M_L

$\vec{S} = \vec{s}_1 + \vec{s}_2 + \ldots$ quantum numbers S and M_S

$\vec{J} = \vec{l}_1 + \vec{s}_1 + \vec{l}_2 + \vec{s}_2 + \ldots$ quantum numbers J and M_J

- Coding for L :

$$
\begin{aligned}
L = 0 &\quad\rightarrow\quad \mathrm{S} \\
L = 1 &\quad\rightarrow\quad \mathrm{P} \\
L = 2 &\quad\rightarrow\quad \mathrm{D} \\
L = 3 &\quad\rightarrow\quad \mathrm{F}
\end{aligned}
$$

- Coding for S (multiplicity) :

$$
\begin{aligned}
S = 0 \rightarrow (2S+1) = 1 &\quad\rightarrow\quad \text{singlet} \\
S = 1/2 \rightarrow (2S+1) = 2 &\quad\rightarrow\quad \text{doublet} \\
S = 1 \rightarrow (2S+1) = 3 &\quad\rightarrow\quad \text{triplet} \\
S = 3/2 \rightarrow (2S+1) = 4 &\quad\rightarrow\quad \text{quartet}
\end{aligned}
$$

- J is given as its number
  - (for a multi-electron atom, the definition of J is ambiguous)

- The L and S together gives the "atomic term"

$$^{2S+1}L$$

  - (examples : ^{3}S , ^{2}P , ^{4}D , ^{1}F)
  - (not always a good description)

- J is the fine structure level

$$^{2S+1}L_J$$

  - (examples : $^1S_0$, $^2P_{1/2}$)

Energy levels in hydrogen

- Ground state

$$\begin{array}{rcl} n=1 & \Rightarrow & l=0 \\ s=1/2 & \Rightarrow & j=1/2 \\ & \Rightarrow & 1\mathrm{s}\,^2\mathrm{S}_{1/2} \quad (1\text{ level}) \end{array}$$

- Excites states

- $n=2 \Rightarrow \begin{cases} l=0 \\ l=1 \end{cases}, \; s=1/2$

$$\left.\begin{array}{lcl} 2\mathrm{s} & \Rightarrow & j=1/2 \Rightarrow 2\mathrm{s}\,^2\mathrm{S}_{1/2} \\ 2\mathrm{p} & \Rightarrow & \begin{cases} j=1/2 & \Rightarrow \quad 2\mathrm{p}\,^2\mathrm{P}_{1/2} \\ j=3/2 & \Rightarrow \quad 2\mathrm{p}\,^2\mathrm{P}_{3/2} \end{cases} \end{array}\right\} \quad (3\text{ levels})$$

- $n=3 \Rightarrow \begin{cases} l=0 \\ l=1 \\ l=2 \end{cases}, \; s=1/2$

$$\left.\begin{array}{lcllll} 3\mathrm{s} & \Rightarrow & 3\mathrm{s}\,^2\mathrm{S}_{1/2} & & \\ 3\mathrm{p} & \Rightarrow & 3\mathrm{p}\,^2\mathrm{P}_{1/2} & \text{and} & 3\mathrm{p}\,^2\mathrm{P}_{3/2} \\ 3\mathrm{d} & \Rightarrow & 3\mathrm{d}\,^2\mathrm{D}_{3/2} & \text{and} & 3\mathrm{d}\,^2\mathrm{D}_{5/2} \end{array}\right\} \quad (5\text{ levels})$$

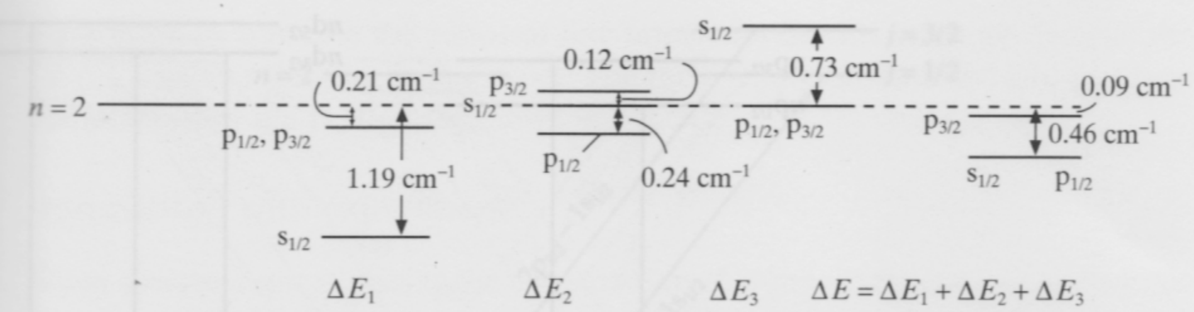


Figure 5.2 The contributions ΔE_1, ΔE_2, ΔE_3 to the splitting of the $n = 2$ level of the hydrogen atom.

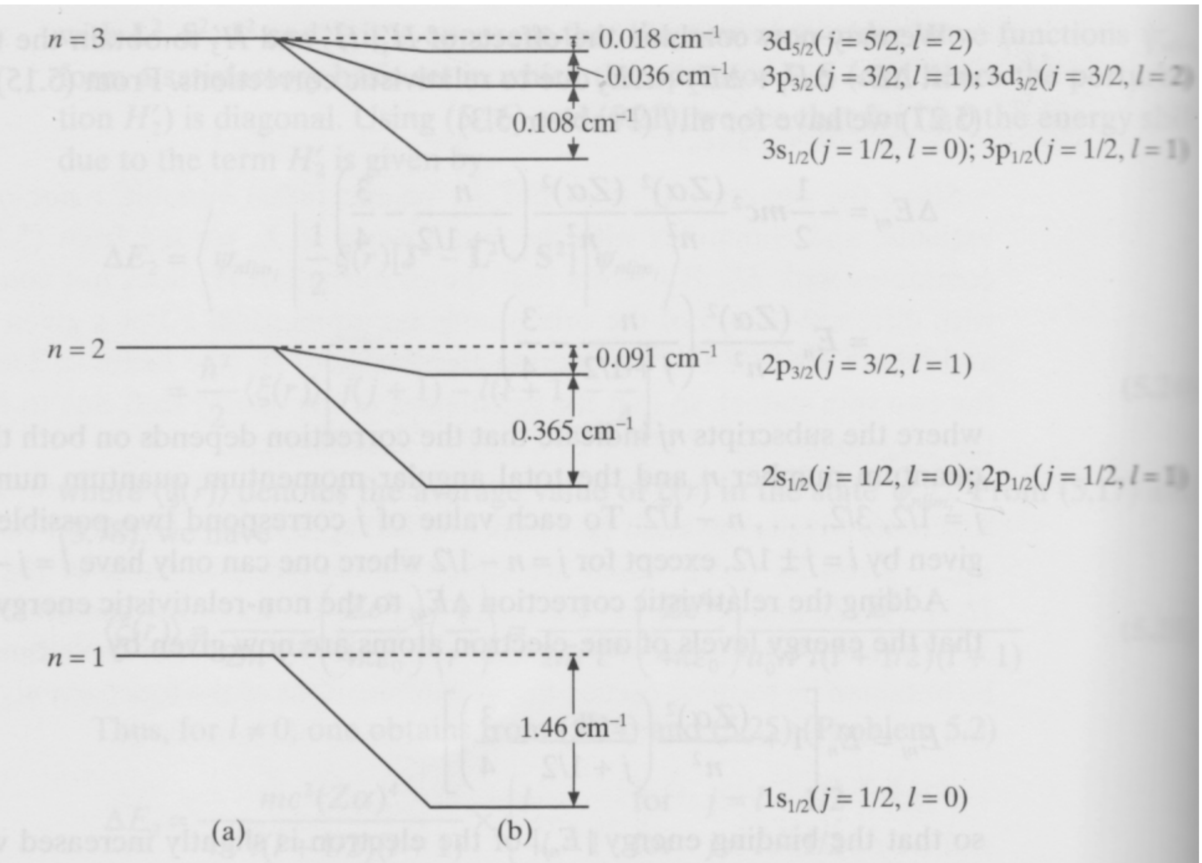


Figure 5.1 Fine structure of the hydrogen atom. The non-relativistic levels are shown on the left in column (a) and the split levels on the right in column (b), for $n = 1$, 2 and 3. For clarity, the scale in each diagram is different.

Atoms with two electrons

The Schrödinger equation for a 3-body system

- The He-atom (or an ion with two electrons)
  - Two electrons + a nucleus with charge +Ze
  - $\Rightarrow$ a 3-body problem

- Exact, analytic solutions are not possible

- We will need approximation methods
  - Perturbation theory

The Schrödinger equation

- In centre-of-mass coordinates:

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2_{r_1} - \frac{\hbar^2}{2\mu}\nabla^2_{r_2} - \frac{\hbar^2}{M}\nabla_{r_1}\cdot\nabla_{r_2} - \frac{Ze^2}{4\pi\epsilon_0\, r_1} - \frac{Ze^2}{4\pi\epsilon_0\, r_2} + \frac{e^2}{4\pi\epsilon_0\, r_{12}}\right)\psi(\vec{r_1},\vec{r_2}) = E\psi(\vec{r_1},\vec{r_2})$$

here: $r_{12} = |\vec{r_1} - \vec{r_2}|$
Simplifications: $M = \infty \quad \Rightarrow \quad \mu = m_{\rm e}$

- We introduce Atomic units

Atomic units

- Atomic units (a.u) are used to simplify calculations
  - Most constants disappear from Hamiltonians and the Schrödinger

- Starting point : the following natural constants are set to one:

$$e = m_{\mathrm{e}} = \hbar = \frac{1}{4\pi\varepsilon_0} = 1$$

- Be careful with quantitative calculations

Quantity	atomic unit	value in SI units
Charge	e	$1.602\,176\,565 \times 10^{-19}$ C
Mass	m_{e}	$9.109\,382\,91 \times 10^{-31}$ kg
Angular momentum	$\hbar$	$1.054\,571\,726 \times 10^{-34}$ J s
Length	a_0	$0.529\,177\,210\,92 \times 10^{-10}$ m
Energy	E_{h}	$4.359\,744\,34 \times 10^{-18}$ J
Time	$\hbar / E_{\mathrm{h}}$	$2.418\,884\,326\,502 \times 10^{-17}$ s
Force	E_{h} / a_0	$8.238\,722\,78 \times 10^{-8}$ N
Velocity	$c\,\alpha$	$2.187\,691\,263\,79 \times 10^{6}$ m s^{-1}
Momentum	$\hbar / a_0$	$1.992\,851\,740 \times 10^{-24}$ kg m s^{-1}
Charge density	e / a_0^3	$1.081\,202\,338 \times 10^{12}$ C m^{-3}
Electric potential	E_{h} / e	$27.211\,385\,05$ V
Electric field	$E_{\mathrm{h}} / (e\,a_0)$	$5.142\,206\,52 \times 10^{11}$ V m^{-1}
Electric dipole moment	$e\,a_0$	$8.478\,353\,26 \times 10^{-30}$ C m
Magnetic flux density	$\hbar / (e\,a_0^2)$	$2.350\,517\,464 \times 10^{5}$ T

- The 2-electron system Hamiltonian in atomic units:

$$\left(-\frac{\nabla_{r_1}^2}{2}-\frac{\nabla_{r_2}^2}{2}-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}\right)\psi(\vec{r_1},\vec{r_2})=E\psi(\vec{r_1},\vec{r_2})$$

- Consequences of the term : $\propto \dfrac{1}{r_{12}}$
  - $\psi(\vec{r_1},\vec{r_2})$ cannot be factorised
  - The exact solutions must be entangled states

Symmetry

- With two electrons, symmetry becomes important
  - Spin will matter, due to symmetry

- Total wave function: product of spatial and spin parts

$$\Psi(q_1, q_2) = \psi(\vec{r}_1, \vec{r}_2)\, \chi(\vec{s}_1, \vec{s}_2)$$

- The Hamiltonian does not depend on spin
  - the wave function can be factorised

The Pauli principle

- The total wave function for two identical fermions is antisymmetric with respect to exchange of the particles

- Two identical fermions cannot occupy the same quantum state simultaneously

- For the product function $\Psi(q_1, q_2)$, we have two options:
  - $\psi(\vec{r}_1, \vec{r}_2)$ symmetric and $\chi(\vec{s}_1, \vec{s}_2)$ anti-symmetric
  - $\psi(\vec{r}_1, \vec{r}_2)$ anti-symmetric and $\chi(\vec{s}_1, \vec{s}_2)$ symmetric

Exchange symmetry

- The exchange operator: P_{12}

$$P_{12}\, \Psi(q_1, q_2) = \Psi(q_2, q_1)$$

- A permutation of spatial coordinates:
  - if $P_{12}\,\Psi(q_1, q_2) = \lambda\Psi(q_1, q_2)$
  - $P_{12}^2\,\Psi(q_1, q_2) = \lambda^2\Psi(q_1, q_2) = \Psi(q_1, q_2)$
  - $\Rightarrow \quad \lambda = \pm 1$

Spin wave functions

- For each of the two spin functions, there are only two options
  - Spin-up or Spin-down

- We define kets in the two spin-spaces:

$$\begin{cases} |+\rangle_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \\ |-\rangle_1 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \end{cases} \qquad \begin{cases} |+\rangle_2 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 \\ |-\rangle_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 \end{cases}$$

- Compound spin function ;
  - four possibilities:

$$\begin{aligned} \chi_1(\vec{s}_1, \vec{s}_2) &: |+\rangle_1 \otimes |+\rangle_2 = |+\ +\rangle \\ \chi_2(\vec{s}_1, \vec{s}_2) &: |+\rangle_1 \otimes |-\rangle_2 = |+\ -\rangle \\ \chi_3(\vec{s}_1, \vec{s}_2) &: |-\rangle_1 \otimes |+\rangle_2 = |-\ +\rangle \\ \chi_4(\vec{s}_1, \vec{s}_2) &: |-\rangle_1 \otimes |-\rangle_2 = |-\ -\rangle \end{aligned}$$

  - (assume that the spatial functions are different, so the Pauli principle does not forbid χ_1 and χ_4)

- There are 2 problems with this basis:

- Problem 1 :
  - χ_1 and χ_4 are exchange symmetric , BUT
  - χ_2 and χ_3 are neither symmetric, nor anti-symmetric

- We need a description for the "total spin"
  - In absence of spin-spin interaction: $\left[\vec{S}_1\,,\ \vec{S}_2\right] = 0$
  - $\Rightarrow$ Logical choice : $\vec{S} \equiv \vec{S}_1 + \vec{S}_2$
  - $\Rightarrow \quad \begin{cases} S_z = S_{1z} + S_{2z} \\ S^2 = S_1^2 + S_2^2 + 2\,\vec{S}_1 \cdot \vec{S}_2 \end{cases}$
  - $\Rightarrow$ Quantum numbers S and M_S
  - The action of S^2 and S_z on $\chi_1\,,\chi_2\,,\chi_3\,,\chi_4$ can be calculated (using the Pauli spin matrices)

- Problem 2 :
  - $S_z\,|\,+\,+\,\rangle = |\,+\,+\,\rangle$
    $S^2\,|\,+\,+\,\rangle = 2\,|\,+\,+\,\rangle$
  - $S_z\,|\,+\,-\,\rangle = 0$
    $S^2\,|\,+\,-\,\rangle = |\,+\,-\,\rangle + |\,-\,+\,\rangle$
  - $S_z\,|\,-\,+\,\rangle = 0$
    $S^2\,|\,-\,+\,\rangle = |\,+\,-\,\rangle + |\,-\,+\,\rangle$
  - $S_z\,|\,-\,-\,\rangle = -|\,-\,-\,\rangle$
    $S^2\,|\,-\,-\,\rangle = 2\,|\,-\,-\,\rangle$
  - χ_2 and χ_3 are not eigenfunctions to S^2
  - $\Rightarrow$ To have a diagonal basis, where all basis functions are either symmetric or anti-symmetric at exchange, we need to replace χ_2 and χ_3

- New functions:
  - $|\,\mathrm{S}\,\rangle \propto |\,+\,-\,\rangle + |\,-\,+\,\rangle$
    $|\,\mathrm{A}\,\rangle \propto |\,+\,-\,\rangle - |\,-\,+\,\rangle$

- $\Rightarrow$ A basis of four functions: $|\, S\, M_S\, \rangle$

- 3 symmetric functions (a triplet) :
  - $\left\{ \begin{array}{lcl} |\,1,1\,\rangle & = & |\,+\,+\,\rangle \\ |\,1,0\,\rangle & = & |\,\mathrm{S}\,\rangle = \frac{1}{\sqrt{2}}\,(|\,+\,-\,\rangle + |\,-\,+\,\rangle) \\ |\,1,-1\,\rangle & = & |\,-\,-\,\rangle \end{array} \right.$

- 1 anti-symmetric function (a singlet) :
  - $|\,0,0\,\rangle = |\,\mathrm{A}\,\rangle = \dfrac{1}{\sqrt{2}}\,(|\,+\,-\,\rangle - |\,-\,+\,\rangle)$

The ground state of He

Perturbation Theory

- Assume that the interaction term can be treated as a perturbation:

$$H = H_0 + H'$$
$$H_0 = -\frac{\nabla^2_{r_1}}{2} - \frac{\nabla^2_{r_2}}{2} - \frac{Z}{r_1} - \frac{Z}{r_2}$$
$$H' = \frac{1}{r_{12}}$$

- The zero-order solution can be factorized

$$H_0\, \psi^{(0)}(\vec{r_1}, \vec{r_2}) = E_0 \psi^{(0)}(\vec{r_1}, \vec{r_2})$$
$$\psi^{(0)}(\vec{r_1}, \vec{r_2}) = \psi_1^{(0)}(\vec{r_1})\, \psi_2^{(0)}(\vec{r_2})$$
$$E_0 = E_1 + E_2$$

- The zero order ground state will be both electron is hydrogenic 1s-orbitals, with $Z = 2$

$$\psi^{(0)} = \psi_{1s}\, \psi_{1s} = (R_{1s} Y_{00})\, (R_{1s} Y_{00}) = \psi_{1s^2}$$

Identical electrons - the Pauli principle

- We have
  - $n_1 = n_2 = 1 \quad , \quad l_1 = l_2 = 0 \quad , \quad m_{l1} = m_{l2} = 0$
  - The compound spatial wave function HAS to be symmetric

- To avoid violation the Pauli principle, the two spins HAVE to be opposite

$$\Rightarrow \Psi^{(0)} = \psi_{1s^2}\ \chi_{0,0}$$
$$|\,(0)\,\rangle = |\,1s^2\,\rangle \otimes |\,0,0\,\rangle = |\,1s^2, 0\,0\,\rangle$$

$$\Rightarrow 1s^2\ {}^1S \Rightarrow 1s^2\ {}^1S$$

The energy of the ground state

- We define this as the ionization energy E_{ion}
- The zero-order energy (without the perturbation) :
  - $$E_0 = E_1 + E_2 = 2E_{1s}(Z=2) = 2\left(-Z^2 hcR_\infty\right) \approx 2\,(-54.4\,\text{eV}) \approx -109\,\text{eV}$$
- The perturbation :

$$\Delta E = \langle\, \psi_{1s^2}\,|\, H' \,|\, \psi_{1s^2}\,\rangle$$
$$H' = \frac{1}{r_{12}}$$
$$\psi_{1s^2} = \left[\left(\frac{Z}{a_m u}\right)^{3/2}\ 2e^{-\rho}\right]^2 \left[\sqrt{\frac{1}{4\pi}}\right]^2$$

$$\Rightarrow \Delta E \approx 34\,\text{eV}$$
$$\Rightarrow E(1s^2) \approx -109\,\text{eV} + 34\,\text{eV} = -75\,\text{eV}$$

- This means that *75* eV is the energy needed to remove BOTH electrons from the nucleus
  - Suppose one electron has already been removed; how much energy is needed to remove the other one?
  - $\Rightarrow$ the ionization energy of He^+

- $E_{\text{ion}}(\text{He}^+) = E_{1\text{s}}(Z=2) \approx -54.4\,\text{eV}$

- The ionization energy of He :
  $E_{\text{ion}}(\text{He}) = E(1\text{s}^2) - E_{\text{ion}}(\text{He}^+) \approx -21\,\text{eV}$

- Experimental value of the heliume ionization energy : -24.6 eV
  - The order of magnitude is right, but
  - The energy contribution from the electron-electron interaction is too great to be treated as a perturbation

Excited states of He

- One of the electrons is in the 1s-orbital
- The other in an *nl*-orbital ($n \neq 1$)

$$1\mathrm{s}nl$$

Exchange degeneracy

- We have two states with the same energy:

$$\psi_{1\mathrm{s}}(\vec{r}_1)\,\psi_{nl}(\vec{r}_2)$$

and

$$\psi_{nl}(\vec{r}_1)\,\psi_{1\mathrm{s}}(\vec{r}_2)$$

- This is the "exchange degeneracy"

Degenerate perturbation theory

- We must use superposition states
- $(H_0 + H')\;\psi = (E_0 + \Delta E)\,\psi$
  - where:
  - $\psi = \alpha\,\psi_{1\mathrm{s}}(\vec{r}_1)\,\psi_{nl}(\vec{r}_2) + \beta\,\psi_{nl}(\vec{r}_1)\,\psi_{1\mathrm{s}}(\vec{r}_2)$
  - $E_0 = E_{1\mathrm{s}} + E_{nl}$

$$H'\,\psi = \Delta E\,\psi$$

$$H' \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \Delta E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$H' = \begin{pmatrix} J & K \\ K & J \end{pmatrix}$$
$$J = \int |\psi_{1\mathrm{s}}(\vec{r}_1)|^2 \, \frac{1}{r_{12}} \, |\psi_{nl}(\vec{r}_2)|^2 \, \mathrm{d}\vec{r}_1 \, \mathrm{d}\vec{r}_2$$
$$K = \int \psi^*_{1\mathrm{s}}(\vec{r}_1)\psi^*_{nl}(\vec{r}_2)\frac{1}{r_{12}}\psi_{1\mathrm{s}}(\vec{r}_2)\psi_{nl}(\vec{r}_1) \, \mathrm{d}\vec{r}_1 \, \mathrm{d}\vec{r}_2$$

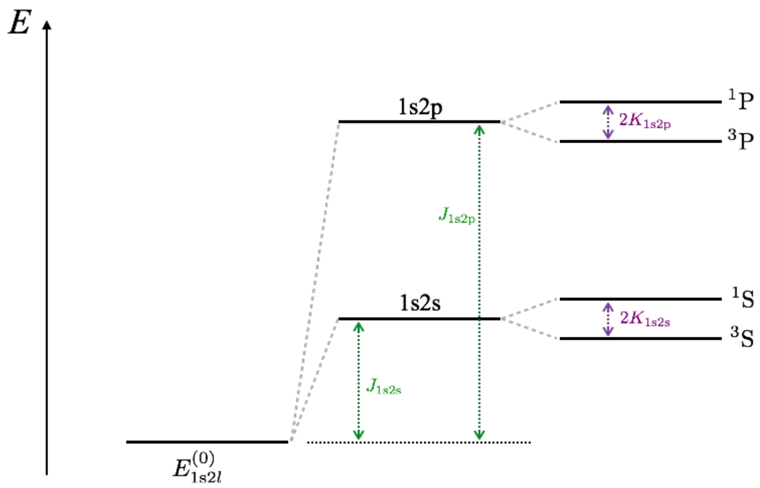
- J : the "direct integral"
  - Coulomb interaction between the two charge clouds
  - Increases energy
- K : the "exchange integral"
  - a quantum interference effect

$$\Delta E = J \pm K$$
$$E^{\pm}_{1snl} = E^0_{1snl} + J \pm K$$

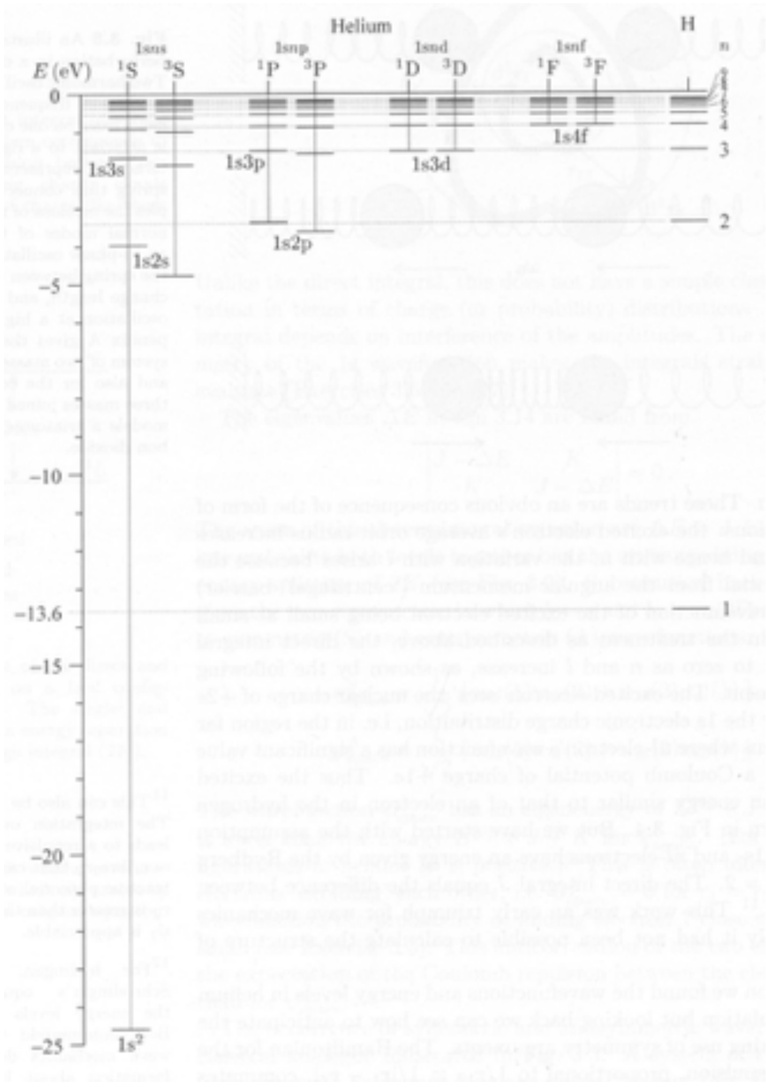
- The wave functions are symmetric or anti-symmetric :

$$\begin{cases} \psi^{(0)}_+(\vec{r}_1, \vec{r}_2) \equiv \frac{1}{\sqrt{2}} \left[\psi_{1\mathrm{s}}(\vec{r}_1) \, \psi_{nl}(\vec{r}_2) + \psi_{nl}(\vec{r}_1) \, \psi_{1\mathrm{s}}(\vec{r}_2)\right] \\ \psi^{(0)}_-(\vec{r}_1, \vec{r}_2) \equiv \frac{1}{\sqrt{2}} \left[\psi_{1\mathrm{s}}(\vec{r}_1) \, \psi_{nl}(\vec{r}_2) - \psi_{nl}(\vec{r}_1) \, \psi_{1\mathrm{s}}(\vec{r}_2)\right] \end{cases}$$

  - entangled states



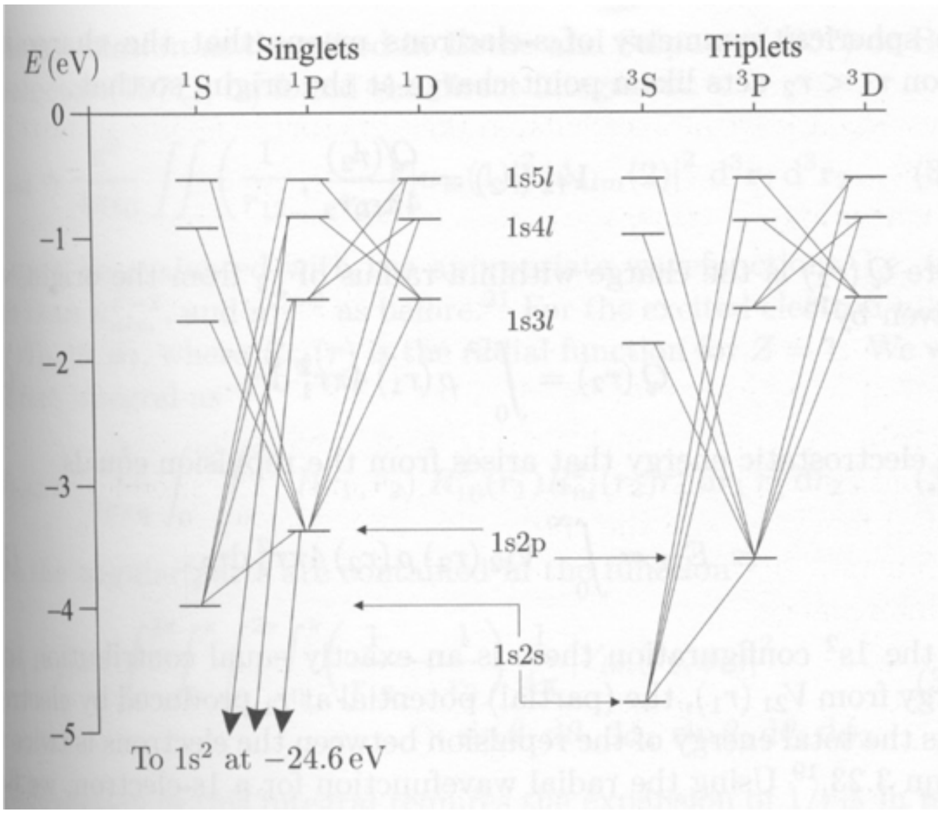
E
1s2p
1s2s
^{1}P
^{3}P
^{1}S
^{3}S
$2K_{1s2p}$
$2K_{1s2s}$
J_{1s2p}
J_{1s2s}
$E^{(0)}_{1s2l}$



Helium
H
1sns
1snp
1snd
1snf
n
E (eV)
^{1}S
^{3}S
^{1}P
^{3}P
^{1}D
^{3}D
^{1}F
^{3}F
0
-5
-10
-13.6
-15
-20
-25
1s3s
1s2s
1s3p
1s2p
1s3d
1s4f
1s^2
4
3
2
1

Transitions in He

- Selection rule for the total spin :
$$\Delta S = 0$$
- A two-electron atom will only have singlets ($S = 0$) and triplets ($S = 1$)
- There will never be transitions between a singlet and triplet



- He gives an appearance of having two separate spectra

Towards bigger atoms

The central field approximation (CFA)

- To start with, we still ignore the spin-orbit interaction
- The Schrödinger equation for the spatial part :

$$\left[\sum_{1=1}^{N}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{j>i}^{N}\frac{1}{r_{ij}}\right]\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = E\,\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

  - $3N$-dimensional differential equation
  - Not separable
  - The $1/r_{ij}$ -term is too large for a very accurate perturbation treatment

Effective potential

- A large part of the $1/r_{ij}$ -term will be radial
- On an individual valence electron, the other electrons will act like an almost spherical screening of the nuclear charge
- The effective radial part of the total potential, felt by one electron:

$$V_{\mathrm{CF}}(r) = -\frac{Z}{r} + S(r)$$

  - with $S(r)$ being the screening potential from the (N-1) other electrons

- The term $S(r)$ will include all the radial part of $\displaystyle\sum_{j>i}^{N} \frac{1}{r_{ij}}$

- The angular part of the mutual interaction term, we will treat as a perturbation

Form of V_{CF}

- Asymptotically, when $r_i \to \infty$:

  $\Rightarrow \quad r_{ij} \approx r_i$

  $$V_{\mathrm{CF}}(r) \approx -\frac{Z}{r_i} + \sum_{j=1}^{N-1} \frac{1}{r_i} = -\frac{Z-N+1}{r_i}$$

  - for a neutral atom, $Z = N$:

  $$V_{\mathrm{CF}}(r) \approx -\frac{1}{r_i}$$

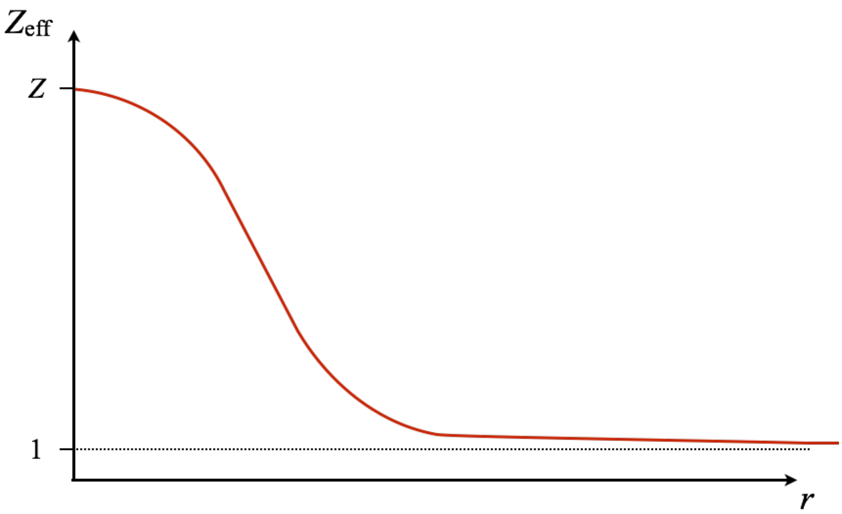
- Asymptotically, when $r_i \to 0$:

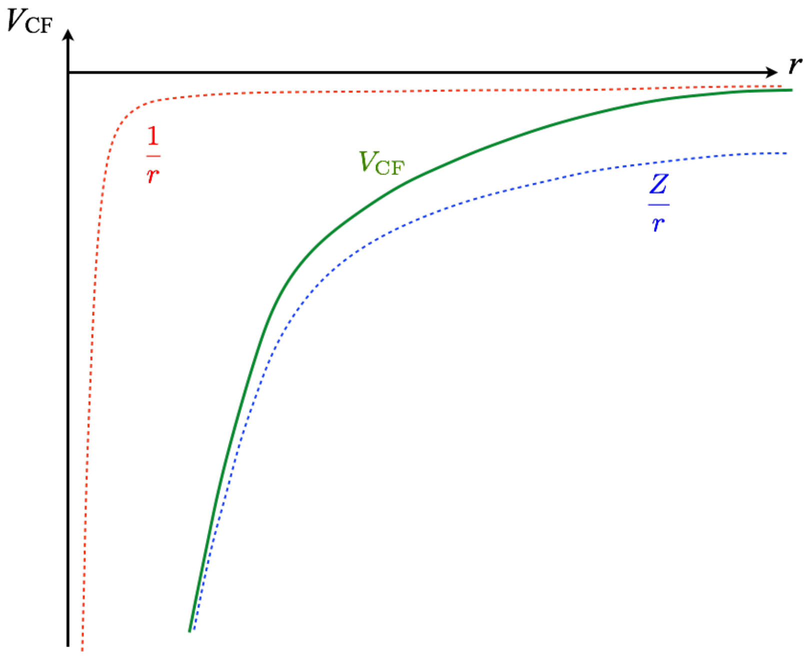
  $\Rightarrow \quad r_{ij} \approx r_j$

  $$V_{\mathrm{CF}}(r) \approx -\frac{Z}{r_i} + \left\langle \sum_{j=1}^{N-1} \frac{1}{r_j} \right\rangle \approx -\frac{Z}{r_i}$$

- In between the limits, an electron will feel an effective Z, between 1 and Z

$$V_{\mathrm{CF}}(r) = -\frac{Z_{\mathrm{eff}}(r)}{r_i}$$





- Usually, we can only guess V_{CF}, or calculate it numerically
- Nevertheless, even without knowing the exact form of V_{CF} and ψ_0, we can understand a lot of atomic structure

Perturbative treatment

- We now treat the reminder of the total Hamiltonian, the angular part of $\displaystyle\sum_{j>i}^{N}\frac{1}{r_{ij}}$, as a perturbation; H_{res}

$$H = H_{\text{CF}} + H_{\text{res}}$$

$$H = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_{r_i}^2\right) + \sum_{i=1}^{N}\left(-\frac{Z}{r_i}\right) + \sum_{j>i}^{N}\frac{1}{r_{ij}}$$

$$V_{\text{CF}}^{(\text{all})}(r) = \sum_{i=1}^{N}\left(-\frac{Z}{r}\right) + \sum_{i=1}^{N} S(r)$$

$$H_{\text{CF}} = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_{r_i}^2\right) + V_{\text{CF}}^{(\text{all})}(r_i) = \sum_{i=1}^{N} H_i$$

$$\begin{aligned}
&H_{\text{res}} = H - H_{\text{CF}} \\
&= \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_{r_i}^2\right) + \sum_{i=1}^{N}\left(-\frac{Z}{r_i}\right) + \sum_{j>i}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_{r_i}^2\right) - V_{\text{CF}}^{(\text{all})}(r_i) \\
&= \sum_{i=1}^{N}\left(-\frac{Z}{r_i}\right) + \sum_{j>i}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\left(-\frac{Z}{r_i}\right) - \sum_{i=1}^{N} S(r_i) \\
&= \sum_{j>i}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N} S(r_i)
\end{aligned}$$

zero-order wave functions, ψ_{CF}

- Schrödinger equation:

$$H_{\mathrm{CF}}\,\psi_{\mathrm{CF}} = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla^2_{r_i} + V_{\mathrm{CF}}(r_i)\right]\,\psi_{\mathrm{CF}} = E_{\mathrm{CF}}\,\psi_{\mathrm{CF}}$$

- This is a *separable* equation :

$$\psi_{\mathrm{CF}} = u_1(\vec{r}_1)\,u_2(\vec{r}_2)\,\ldots\,u_N(\vec{r}_N)$$

- This is N separate equations, of the type :

$$\left[-\frac{1}{2}\nabla^2_r + V_{\mathrm{CF}}(r)\right]\,u_{nlm_l}(\vec{r}) = E_{nl}\,u_{nlm_l}(\vec{r})$$

  - where

$$u_{nlm_l}(\vec{r}) = R_{nl}(r)\,Y_{lm_l}(\theta,\varphi)$$

- The solutions will be *similar* to the hydrogenic ones

$$n = 1, 2, 3, \ldots$$
$$l = 0, 1, \ldots, n-1$$
$$m = -l, -l+1, \ldots, l$$

- The total (zero-order) energy :

$$E_{\mathrm{CF}} = \sum_{i=1}^{N} E_{n_i l_i}$$

Electron configurations, Orbitals

- The individual one-electron wav functions will be a bit different from hydrogenic ones

- But the potential is central, and the will be close to the hydrogenic
  - Logical to use the hydrogenic notation

- Possible solutions :

$$u_{1\mathrm{s}}, u_{2\mathrm{s}}, u_{2\mathrm{p}}, u_{3\mathrm{s}}, u_{3\mathrm{p}}, \ldots$$

- We say the electrons “occupy the orbitals” :

$$1\mathrm{s}, 2\mathrm{s}, 2\mathrm{p}, 3\mathrm{s}, 3\mathrm{p}, 3\mathrm{d}, 4\mathrm{s}, 4\mathrm{p}, 4\mathrm{d}, 4\mathrm{f}, 5\mathrm{s}, \ldots$$

The Pauli principle

- Two electrons may not be in the same state:
- the set of quantum numbers, (n , l , m_l , m_s) has to be unique for every electron

- For one combination of (n , l , m_l) , there may be two electrons (m_s=+½ , m_s=-½)

- For one particular orbit (n , l), there may be $2\,(2l + 1)$ electrons

$l = 0$; "s-orbital" ; 2 electrons

$l = 1$; "p-orbital" ; 6 electrons

$l = 2$; "d-orbital" ; 10 electrons

$l = 3$; "f-orbital" ; 14 electrons

……

- For the ground sate, the electrons will gradually fill up the lowest energy orbitals

- Energy order (with lowest first) :

1s
2s
2p
3s
3p
4s
3d
4p
5s
4d
5p
6s
4f
5d
6p
7s
5f
6d
7p
8s

The periodic system

- We gradually "build up" the atom
  - "the aufbau-principle"
  - ("règle de Klechkowski")

- Electronic configuration of the ground states of the atoms:

1	H	:	$1s$	
2	He	:	$1s^2$	(full)
3	Li	:	$1s^2\ 2s$	
4	Be	:	$1s^2\ 2s^2$	(full)
5	B	:	$1s^2\ 2s^2\ 2p$	
6	C	:	$1s^2\ 2s^2\ 2p^2$	
7	N	:	$1s^2\ 2s^2\ 2p^3$	
8	O	:	$1s^2\ 2s^2\ 2p^4$	
9	F	:	$1s^2\ 2s^2\ 2p^5$	
10	Ne	:	$1s^2\ 2s^2\ 2p^6$	(full)
11	Na	:	$1s^2\ 2s^2\ 2p^6\ 3s = [Ne]\ 3s$	

…………

to form another closed subshell, are called *valence* electrons. In going from one atom having atomic number Z to the next one, with atomic number $Z+1$, the number of electrons increases by one, the $(Z+1)$ electrons occupying the lowest energy levels allowed by the exclusion principle. In this way the subshells are progressively filled. This is illustrated in Table 8.3 which gives the electron

Table 8.3 Electron configuration, term value and ionisation potential of the atoms in their ground state.

Z	*Element*		*Electronic configuration*†	*Term*†	*Ionisation potential (eV)*
1	H	hydrogen	$1s$	$^2S_{1/2}$	13.60
2	He	helium	$1s^2$	$^1S_0$	24.59
3	Li	lithium	$[\mathrm{He}]2s$	$^2S_{1/2}$	5.39
4	Be	beryllium	$[\mathrm{He}]2s^2$	$^1S_0$	9.32
5	B	boron	$[\mathrm{He}]2s^22p$	$^2P_{1/2}$	8.30
6	C	carbon	$[\mathrm{He}]2s^22p^2$	$^3P_0$	11.26
7	N	nitrogen	$[\mathrm{He}]2s^22p^3$	$^4S_{3/2}$	14.53
8	O	oxygen	$[\mathrm{He}]2s^22p^4$	$^3P_2$	13.62
9	F	fluorine	$[\mathrm{He}]2s^22p^5$	$^2P_{3/2}$	17.42
10	Ne	neon	$[\mathrm{He}]2s^22p^6$	$^1S_0$	21.56
11	Na	sodium	$[\mathrm{Ne}]3s$	$^2S_{1/2}$	5.14
12	Mg	magnesium	$[\mathrm{Ne}]3s^2$	$^1S_0$	7.65
13	Al	aluminium	$[\mathrm{Ne}]3s^23p$	$^2P_{1/2}$	5.99
14	Si	silicon	$[\mathrm{Ne}]3s^23p^2$	$^3P_0$	8.15
15	P	phosphorus	$[\mathrm{Ne}]3s^23p^3$	$^4S_{3/2}$	10.49
16	S	sulphur	$[\mathrm{Ne}]3s^23p^4$	$^3P_2$	10.36
17	Cl	chlorine	$[\mathrm{Ne}]3s^23p^5$	$^2P_{3/2}$	12.97
18	Ar	argon	$[\mathrm{Ne}]3s^23p^6$	$^1S_0$	15.76
19	K	potassium	$[\mathrm{Ar}]4s$	$^2S_{1/2}$	4.34
20	Ca	calcium	$[\mathrm{Ar}]4s^2$	$^1S_0$	6.11
21	Sc	scandium	$[\mathrm{Ar}]4s^23d$	$^2D_{3/2}$	6.54
22	Ti	titanium	$[\mathrm{Ar}]4s^23d^2$	$^3F_2$	6.82
23	V	vanadium	$[\mathrm{Ar}]4s^23d^3$	$^4F_{3/2}$	6.74
24	Cr	chromium	$[\mathrm{Ar}]4s3d^5$	$^7S_3$	6.77
25	Mn	manganese	$[\mathrm{Ar}]4s^23d^5$	$^6S_{5/2}$	7.44
26	Fe	iron	$[\mathrm{Ar}]4s^23d^6$	$^5D_4$	7.87
27	Co	cobalt	$[\mathrm{Ar}]4s^23d^7$	$^4F_{9/2}$	7.86
28	Ni	nickel	$[\mathrm{Ar}]4s^23d^8$	$^3F_4$	7.64
29	Cu	copper	$[\mathrm{Ar}]4s3d^{10}$	$^2S_{1/2}$	7.73
30	Zn	zinc	$[\mathrm{Ar}]4s^23d^{10}$	$^1S_0$	9.39
31	Ga	gallium	$[\mathrm{Ar}]4s^23d^{10}4p$	$^2P_{1/2}$	6.00
32	Ge	germanium	$[\mathrm{Ar}]4s^23d^{10}4p^2$	$^3P_0$	7.90
33	As	arsenic	$[\mathrm{Ar}]4s^23d^{10}4p^3$	$^4S_{3/2}$	9.81
34	Se	selenium	$[\mathrm{Ar}]4s^23d^{10}4p^4$	$^3P_2$	9.75
35	Br	bromine	$[\mathrm{Ar}]4s^23d^{10}4p^5$	$^2P_{3/2}$	11.81
36	Kr	krypton	$[\mathrm{Ar}]4s^23d^{10}4p^6$	$^1S_0$	14.00
37	Rb	rubidium	$[\mathrm{Kr}]5s$	$^2S_{1/2}$	4.18
38	Sr	strontium	$[\mathrm{Kr}]5s^2$	$^1S_0$	5.70
39	Y	yttrium	$[\mathrm{Kr}]5s^24d$	$^2D_{3/2}$	6.38
40	Zr	zirconium	$[\mathrm{Kr}]5s^24d^2$	$^3F_2$	6.84
41	Nb	niobium	$[\mathrm{Kr}]5s4d^4$	$^6D_{1/2}$	6.88
42	Mo	molybdenum	$[\mathrm{Kr}]5s4d^5$	$^7S_3$	7.10
43	Tc	technetium	$[\mathrm{Kr}]5s^24d^5$	$^6S_{5/2}$	7.28
44	Ru	ruthenium	$[\mathrm{Kr}]5s4d^7$	$^5F_5$	7.37
45	Rh	rhodium	$[\mathrm{Kr}]5s4d^8$	$^4F_{9/2}$	7.46
46	Pd	palladium	$[\mathrm{Kr}]4d^{10}$	$^1S_0$	8.34
47	Ag	silver	$[\mathrm{Kr}]5s4d^{10}$	$^2S_{1/2}$	7.58
48	Cd	cadmium	$[\mathrm{Kr}]5s^24d^{10}$	$^1S_0$	8.99
49	In	indium	$[\mathrm{Kr}]5s^24d^{10}5p$	$^2P_{1/2}$	5.79
50	Sn	tin	$[\mathrm{Kr}]5s^24d^{10}5p^2$	$^3P_0$	7.34
51	Sb	antimony	$[\mathrm{Kr}]5s^24d^{10}5p^3$	$^4S_{3/2}$	8.64
52	Te	tellurium	$[\mathrm{Kr}]5s^24d^{10}5p^4$	$^3P_2$	9.01
53	I	iodine	$[\mathrm{Kr}]5s^24d^{10}5p^5$	$^2P_{3/2}$	10.45
54	Xe	xenon	$[\mathrm{Kr}]5s^24d^{10}5p^6$	$^1S_0$	12.13
55	Cs	caesium	$[\mathrm{Xe}]6s$	$^2S_{1/2}$	3.89
56	Ba	barium	$[\mathrm{Xe}]6s^2$	$^1S_0$	5.21
57	La	lanthanum	$[\mathrm{Xe}]6s^25d$	$^2D_{3/2}$	5.58
58	Ce	cerium	$[\mathrm{Xe}](6s^24f5d)$	$(^1G_4)$	5.47
59	Pr	praseodymium	$[\mathrm{Xe}](6s^24f^3)$	$(^4I_{9/2})$	5.42
60	Nd	neodymium	$[\mathrm{Xe}]6s^24f^4$	$^5I_4$	5.49
61	Pm	promethium	$[\mathrm{Xe}](6s^24f^5)$	$(^6H_{5/2})$	5.55
62	Sm	samarium	$[\mathrm{Xe}]6s^24f^6$	$^7F_0$	5.63
63	Eu	europium	$[\mathrm{Xe}]6s^24f^7$	$^8S_{7/2}$	5.67
64	Gd	gadolinium	$[\mathrm{Xe}]6s^24f^75d$	$^9D_2$	6.14
65	Tb	terbium	$[\mathrm{Xe}](6s^24f^9)$	$^6H_{15/2}$	5.85
66	Dy	dysprosium	$[\mathrm{Xe}](6s^24f^{10})$	$(^5I_8)$	5.93
67	Ho	holmium	$[\mathrm{Xe}](6s^24f^{11})$	$(^4I_{15/2})$	6.02
68	Er	erbium	$[\mathrm{Xe}](6s^24f^{12})$	$(^3H_6)$	6.10
69	Tm	thulium	$[\mathrm{Xe}]6s^24f^{13}$	$^2F_{7/2}$	6.18
70	Yb	ytterbium	$[\mathrm{Xe}]6s^24f^{14}$	$^1S_0$	6.25
71	Lu	lutetium	$[\mathrm{Xe}]6s^24f^{14}5d$	$^2D_{3/2}$	5.43
72	Hf	hafnium	$[\mathrm{Xe}]6s^24f^{14}5d^2$	$^3F_2$	7.0
73	Ta	tantalum	$[\mathrm{Xe}]6s^24f^{14}5d^3$	$^4F_{3/2}$	7.89
74	W	tungsten	$[\mathrm{Xe}]6s^24f^{14}5d^4$	$^5D_0$	7.98
75	Re	rhenium	$[\mathrm{Xe}]6s^24f^{14}5d^5$	$^6S_{5/2}$	7.88
76	Os	osmium	$[\mathrm{Xe}]6s^24f^{14}5d^6$	$^5D_4$	8.7
77	Ir	iridium	$[\mathrm{Xe}]6s^24f^{14}5d^7$	$(^4F_{9/2})$	9.1
78	Pt	platinum	$[\mathrm{Xe}]6s4f^{14}5d^9$	$^3D_3$	9.0

1 **H** hydrogen $1s$																	2 **He** helium $1s^2$
3 **Li** lithium $2s$	4 **Be** beryllium $2s^2$											5 **B** boron $2p$	6 **C** carbon $2p^2$	7 **N** nitrogen $2p^3$	8 **O** oxygen $2p^4$	9 **F** fluorine $2p^5$	10 **Ne** neon $2p^6$
11 **Na** sodium $3s$	12 **Mg** magnesium $3s^2$											13 **Al** aluminium $3p$	14 **Si** silicon $3p^2$	15 **P** phosphorus $3p^3$	16 **S** sulphur $3p^4$	17 **Cl** chlorine $3p^5$	18 **Ar** argon $3p^6$
19 **K** potassium $4s$	20 **Ca** calcium $4s^2$	21 **Sc** scandium $3d\,4s^2$	22 **Ti** titanium $3d^2\,4s^2$	23 **V** vanadium $3d^3\,4s^2$	24 **Cr** chromium $3d^5\,4s$	25 **Mn** manganese $3d^5\,4s^2$	26 **Fe** iron $3d^6\,4s^2$	27 **Co** cobalt $3d^7\,4s^2$	28 **Ni** nickel $3d^8\,4s^2$	29 **Cu** copper $3d^{10}\,4s$	30 **Zn** zinc $3d^{10}\,4s^2$	31 **Ga** gallium $4p$	32 **Ge** germanium $4p^2$	33 **As** arsenic $4p^3$	34 **Se** selenium $4p^4$	35 **Br** bromine $4p^5$	36 **Kr** krypton $4p^6$
37 **Rb** rubidium $5s$	38 **Sr** strontium $5s^2$	39 **Y** yttrium $4d\,5s^2$	40 **Zr** zirconium $4d^2\,5s^2$	41 **Nb** niobium $4d^4\,5s$	42 **Mo** molybdenum $4d^5\,5s$	43 **Tc** technetium $4d^5\,5s^2$	44 **Ru** ruthenium $4d^7\,5s^1$	45 **Rh** rhodium $4d^8\,5s$	46 **Pd** palladium $4d^{10}$	47 **Ag** silver $4d^{10}\,5s$	48 **Cd** cadmium $4d^{10}\,5s^2$	49 **In** indium $5p$	50 **Sn** tin $5p^2$	51 **Sb** antimony $5p^3$	52 **Te** tellurium $5p^4$	53 **I** iodine $5p^5$	54 **Xe** xenon $5p^6$
55 **Cs** cesium $6s$	56 **Ba** barium $6s^2$	57-71 lanthanides	72 **Hf** hafnium $5d^2\,6s^2$	73 **Ta** tantalum $5d^3\,6s^2$	74 **W** tungsten $5d^4\,6s^2$	75 **Re** rhenium $5d^5\,6s^2$	76 **Os** osmium $5d^6\,6s^2$	77 **Ir** iridium $5d^7\,6s^2$	78 **Pt** platinum $5d^9\,6s$	79 **Au** gold $5d^{10}\,6s$	80 **Hg** mercury $5d^{10}\,6s^2$	81 **Tl** thallium $6p$	82 **Pb** lead $6p^2$	83 **Bi** bismuth $6p^3$	84 **Po** polonium $6p^4$	85 **At** astatine $6p^5$	86 **Rn** radon $6p^6$
87 **Fr** francium $7s$	88 **Ra** radium $7s^2$	89-103 actinides	104 **Rf** rutherfordium $6d^2\,7s^2$	105 **Db** dubnium $6d^3\,7s^2$	106 **Sg** seaborgium $6d^4\,7s^2$	107 **Bh** bohrium $6d^5\,7s^2$	108 **Hs** hassium $6d^6\,7s^2$	109 **Mt** meitnerium $6d^7\,7s^2$	110 **Ds** darmstadtium $6d^8\,7s^2$	111 **Rg** roentgenium $6d^9\,7s^2$	112 **Cn** copernicium $6d^{10}\,7s^2$	113 Uut *ununtrium* $7p$	114 **Fl** flerovium $7p^2$	115 Uup *ununpentium* $7p^3$	116 **Lv** livermorium $7p^4$	117 Uus *ununseptium* $7p^5$	118 Uuo *ununoctium* $7p^6$

57 **La** lanthanum $5d\,6s^2$	58 **Ce** cerium $4f\,5d\,6s^2$	59 **Pr** praseodymium $4f^3\,6s^2$	60 **Nd** neodymium $4f^4\,6s^2$	61 **Pm** promethium $4f^5\,6s^2$	62 **Sm** samarium $4f^6\,6s^2$	63 **Eu** europium $4f^7\,6s^2$	64 **Gd** gadolinium $4f^7\,5d\,6s^2$	65 **Tb** terbium $4f^9\,6s^2$	66 **Dy** dysprosium $4f^{10}\,6s^2$	67 **Ho** holmium $4f^{11}\,6s^2$	68 **Er** erbium $4f^{12}\,6s^2$	69 **Tm** thulium $4f^{13}\,6s^2$	70 **Yb** ytterbium $4f^{14}\,6s^2$	71 **Lu** lutetium $4f^{14}\,5d\,6s^2$
89 **Ac** actinium $6d\,7s^2$	90 **Th** thorium $6d^2\,7s^2$	91 **Pa** protactinium $5f^2\,6d\,7s^2$	92 **U** uranium $5f^3\,6d\,7s^2$	93 **Np** neptunium $5f^4\,6d\,7s^2$	94 **Pu** plutonium $5f^6\,7s^2$	95 **Am** americium $5f^7\,7s^2$	96 **Cm** curium $5f^7\,6d\,7s^2$	97 **Bk** berkelium $5f^9\,7s^2$	98 **Cf** californium $5f^{10}\,7s^2$	99 **Es** einsteinium $5f^{11}\,7s^2$	100 **Fm** fermium $5f^{12}\,7s^2$	101 **Md** mendelevium $5f^{13}\,7s^2$	102 **No** nobelium $5f^{14}\,7s^2$	103 **Lr** lawrencium $5f^{14}\,7s^2\,7p$

- Chemical properties are given by the number of valence electrons (outermost orbital)
    - alkalis
    - alkaline earths
    - ……
    - metals
    - ……
    - halogens
    - rare gases

- Optical properties are also given by the valence electrons

- Inner orbital are typically only accessible with x-rays

LS-coupling and *jj*-coupling

Spin-orbit interaction in multi-electron atoms

- We now have two effects to consider:

- 1: Interaction between $\vec{s}$ and $\vec{l}$ for every electron
    - $\vec{j} = \vec{l} + \vec{s}$

- 2: Angular part of the electrostatic interaction between the electrons
    - $\begin{cases} \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \cdots = \vec{L} \\ \vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \cdots = \vec{S} \end{cases}$

- Both these effects have to be included in a total Hamiltonian

$$H = H_{\mathrm{CF}} + H_{\mathrm{res}} + H_{\mathrm{SO}}$$

<u>The parts of the Hamiltonian</u>

- The central field Hamiltonian

$$H_{\mathrm{CF}} = \sum_{i=1}^{N} H_i = \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_{r_i}^2 + V_{\mathrm{CF}}(r_i) \right] = \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_{r_i}^2 - \frac{Z}{r_i} + S(r_i) \right]$$

   - kinetic energy of all electrons
   - Coulomb attraction to the nucleus for all electrons
   - the central (radial) part of the Coulomb repulsion between all electrons

- The residual Coulomb Hamiltonian

$$H_{\text{res}} = \sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} S(r_i)$$

  - The angular (residual) part of the Coulomb interaction between electrons
  - coupling of the angular momenta of the individual electrons

- The spin-orbit Hamiltonian

$$H_{\text{SO}} = \sum_{i=1}^{N} \xi(r_i)\, \vec{l}_i \cdot \vec{s}_i$$

  - the sum of all spin-orbit interactions

Filled shells

- For a filled orbital :
  - half of the electrons spin-up, the other half spin-down
  - ⇒ contribution to S from filled shells : zero
  - all electrons with $+m_l$ are balanced by $-m_l$
  - ⇒ contribution to L from filled shells : zero

- For the sum in H_{SO}, we only need to include the electrons outside the last closed orbital

Total angular momentum

- The interactions between electrons (angular Coulomb + spin-orbit) will couple all electronic angular momenta together

- The only thing that will stay constant is the sum of all of them

$$\vec{J} = \vec{L} + \vec{S}$$

  - where

$$\begin{cases} \vec{L} = \sum_i \vec{l}_i \\ \vec{S} = \sum_i \vec{s}_i \end{cases}$$

- A crucial point will be in which order all these momenta should be added

- That depends on in which order the perturbations are added

Ordering of the Hamiltonians

- We cannot solve the entire Hamiltonian analytically
  - perturbation theory is necessary
  - but, in which order should we take the Hamiltonians?

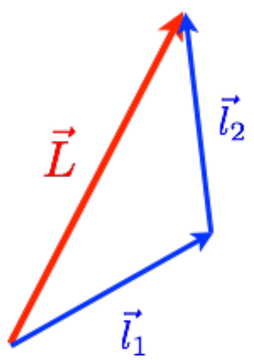
- Always true:

$$H_{\mathrm{CF}} \gg H_{\mathrm{res}} \quad \text{and} \quad H_{\mathrm{CF}} \gg H_{\mathrm{SO}}$$

- But then, there are two possibilities:
  - $H_{\mathrm{res}} > H_{\mathrm{SO}}$
  - $H_{\mathrm{SO}} > H_{\mathrm{res}}$

<u>$H_{\mathrm{res}} > H_{\mathrm{SO}}$</u>

- In this case, the interaction between the electrons is stronger than the spin-orbit interaction in each of them
  - example with a 2-electron atom:



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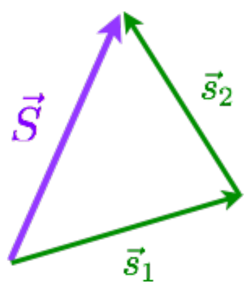
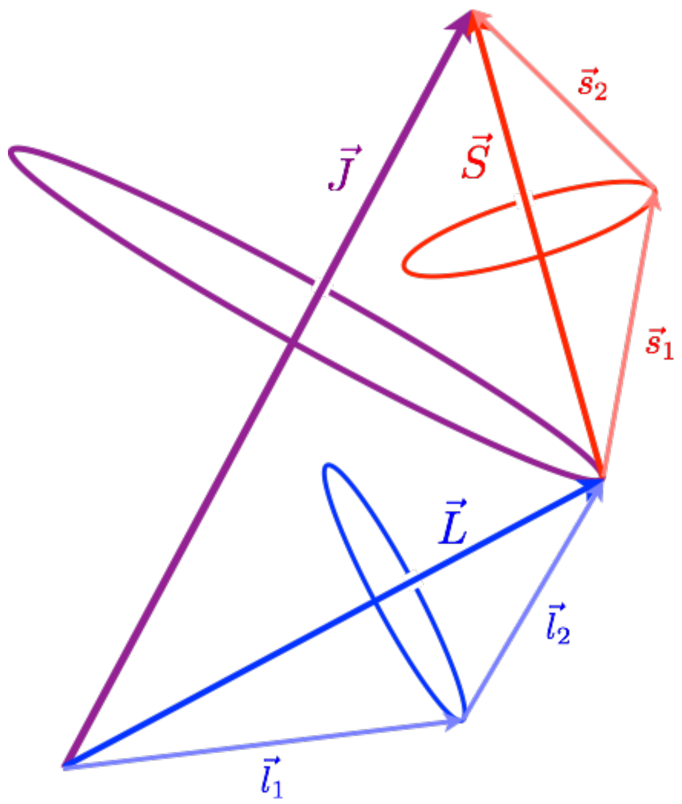


- Then, L and S couple to a total J



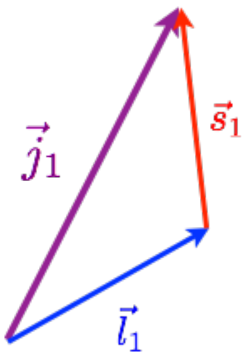
- This situation is called “*LS*-coupling”

- This approximation is valid for most atoms
  - in particular for light atoms

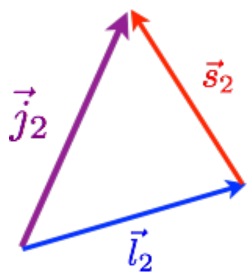
$$H_{\mathrm{SO}} > H_{\mathrm{res}}$$

- In this case, the individual coupling between the electrons, via the spin-orbit interaction, is stronger than the electrostatic interaction between them

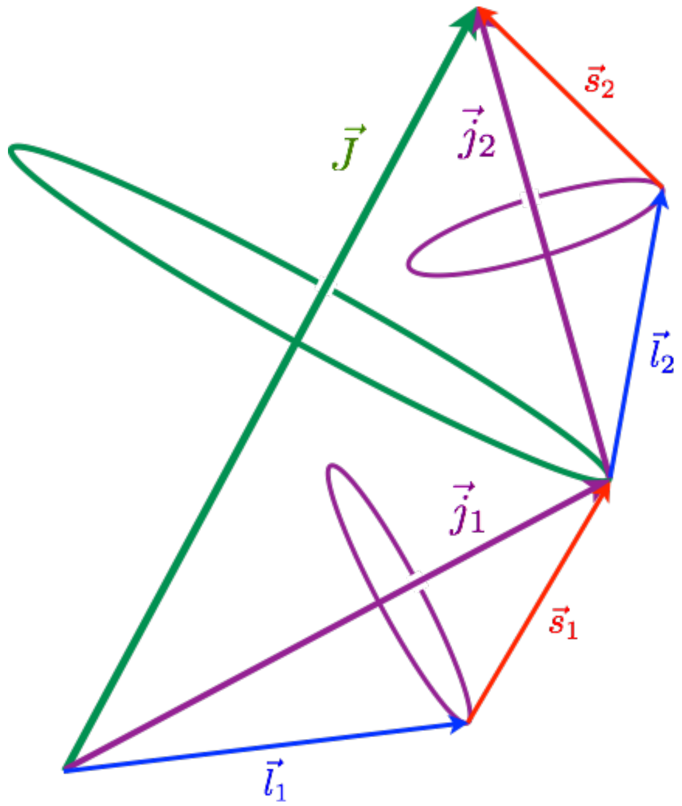
- example with a 2-electron atom:



and



- Then, j_1 and j_2 couple to a total J



- This situation is called "*jj*-coupling"
- This approximation has importance for heavy atoms
  - pure *jj*-coupling is rare
- There are often intermediate cases between *LS* and *jj*

LS-coupling

$$H = H_1 + H_{\mathrm{SO}}$$
where
$$H_1 = H_{\mathrm{CF}} + H_{\mathrm{res}}$$

- Begin with :
  - $H_{\mathrm{CF}}\,\psi_{\mathrm{CF}} = E_{\mathrm{CF}}\,\psi_{\mathrm{CF}}$
  - $\Rightarrow \quad |\,\psi_{\mathrm{CF}}\,\rangle = |\,n_1 l_1, n_2 l_2, \ldots, n_N l_N\,\rangle$
  - this gives the *electronic configuration*

- Then, calculate the fist perturbation :
  - $\langle\,\psi_{\mathrm{CF}}\,|\,H_{\mathrm{res}}\,|\,\psi_{\mathrm{CF}}\,\rangle$
  - (for the moment, we wait with the spin-orbit Hamiltonian)
  - $[\,H_{\mathrm{res}}\,,\,L\,] = [\,H_{\mathrm{res}}\,,\,S\,] = 0$
  - $\Rightarrow$ this *atomic term* can carachterised by the quantum numbers L and S
  - ${}^{2S+1}L$
  - Eigenvector : $|\,\psi_{\mathrm{CF}}\,\rangle = |\,\gamma\,L\,S\,M_L\,M_S\,\rangle$
  - (γ : the electronic configuration)
  - Degenerescence in M_L and M_S
  - $\Rightarrow\ (2L+1)(2S+1)$ degenerate states

<u>How to find L and S</u>

- Take into account :
  - Rules for addition of angular momenta
  - The Pauli principle

- For a filled shell :
  - $M_S = \sum_i m_{s_i}$ and $M_L = \sum_i m_{l_i}$
  - $\Rightarrow \quad L = S = 0$
  - no contribution from the inner shells to the global L and S
  - It is enough to consider the valence electrons

Electrons in different orbitals (non-equivalent)

- The Pauli principle is already taken into account

- As an example, take a 2-electron atom :
  - nl_1 , $n'l_2 \quad (n \neq n')$
  - $\begin{cases} L = |l_1 - l_2|, |l_1 - l_2| + 1, \ldots, l_1 + l_2 \\ S = |s_1 - s_2|, |s_1 - s_2| + 1, \ldots, s_1 + s_2 \end{cases}$
  - $(s_1 = s_2 = \frac{1}{2}) \Rightarrow S = 0$ or $S = 1$
  - (singlets and triplets)

- example 1 :
  - $l_1 = l_2 = 1 \Rightarrow$ configuration : np, n'p
  - $L = 0 \quad$ or $\quad L = 1 \quad$ or $\quad L = 2$
  - $\Rightarrow$ possible terms are :
  - ^{1}S , ^{1}P , ^{1}D , ^{3}S , ^{3}P , ^{3}D

- example 2 :
  - $l_1 = 1, l_2 = 2 \;\Rightarrow\;$ configuration : np, n'd
  - $L = 1 \quad$ or $\quad L = 2 \quad$ or $\quad L = 3$
  - $\Rightarrow$ possible terms are :
  - ^{1}P , ^{1}D , ^{1}F , ^{3}P , ^{3}D , ^{3}F

- More than 2 electrons
  - a bit more complicated

Electrons in the same orbital (equivalent electrons)

- This will normally be the case for ground state configurations

- More complicated, due to the Pauli principle

- Many states become forbidden
  - we will not cover this in detail

- Example 1 :
  - $n_1 = n_2\,,\; l_1 = l_2 = 1 \;\Rightarrow\;$ configuration : np^2
  - (the case for, for example : C, Si, Ge …..)
  - $\Rightarrow$ possible terms : ^{1}S , ^{1}D , ^{3}P
  - (other terms possible for *n*p*n*p' are forbidden due to the Pauli principle)

- Example 2 :
  - $n_1 = n_2 = n_3\,,\; l_1 = l_2 = l_3 = 1$

    $\Rightarrow$ configuration : np^3
  - (the case for, for example : N, P, As …..)
  - $\Rightarrow$ possible terms : ^{2}P , ^{2}D , ^{4}S

Electron configuration	Terms				
ns		${}^{2}S$			
ns^2	${}^{1}S$				
np , np^5		${}^{2}P$			
np^2 , np^4	${}^{1}S$, ${}^{1}D$		${}^{3}P$		
np^3		${}^{2}P$, ${}^{2}D$			
np^6	${}^{1}S$				
nd , nd^9		${}^{2}D$			
nd^2 , nd^8	${}^{1}S$, ${}^{1}D$, ${}^{1}G$		${}^{3}P$, ${}^{3}F$		
nd^3 , nd^7		${}^{2}P$, ${}^{2}D$ (2), ${}^{2}F$, ${}^{2}G$, ${}^{2}H$		${}^{4}P$, ${}^{4}F$	
nd^4 , nd^6	${}^{1}S$ (2), ${}^{1}D$ (2), ${}^{1}F$, ${}^{1}G$ (2), ${}^{1}I$		${}^{3}P$ (4), ${}^{3}D$, ${}^{3}F$ (2), ${}^{3}G$, ${}^{3}H$	${}^{5}D$	
nd^5		${}^{2}S$, ${}^{2}P$, ${}^{2}D$ (3), ${}^{2}F$ (2), ${}^{2}G$ (2), ${}^{2}H$, ${}^{2}I$		${}^{4}P$, ${}^{4}D$, ${}^{4}F$, ${}^{4}G$	${}^{6}S$
nd^{10}	${}^{1}S$				

More complicated cases

- More than two electrons
- Some equivalent and some non-equivalent electrons
- Configuration mixing ……….

Fine structure in *LS*-coupling

- Now, we add the spin-orbit term of the Hamiltonian :
  - $H = H_1 + H_{\mathrm{SO}}$

- The atomic terms have been found :
  - ${}^{2S+1}L$, corresponding to the ket :
  - $|\,\gamma\, L\, S\, M_L\, M_S\,\rangle$

- We now have to find the corrections given by:
  - $\langle\,\gamma\, L\, S\, M_L\, M_S\,|\; H_{\mathrm{SO}}\; |\,\gamma\, L\, S\, M_L\, M_S\,\rangle$

- Problem :
  - H_{SO} is not diagonal in this representation
  - ($[H_{\mathrm{SO}}\,,\, L_z] \neq 0$ and $[H_{\mathrm{SO}}\,,\, S_z] \neq 0$)

Change of basis

- We have to change to the diagonal basis :
  - $|\,\gamma\, L\, S\, J\, M_J\,\rangle$
  - (diagonalisation of H_{SO})

$$|\, L\, S\, J\, M_J\,\rangle = \sum_{M_L, M_S} C(LSJM_J; M_L M_S)\; |\,\gamma\, L\, S\, M_L\, M_S\,\rangle$$

- The coefficients $C(LSJM_J; M_L M_S)$ are the "Clebsch-Gordan coefficients"

Finding the find-structure levels

- $\vec{J} = \vec{L} + \vec{S}$
- addition of angular momenta

$$\begin{cases} J = |L-S|, |L-S|+1, \ldots, L+S \\ M_J = -J,_J +1, \ldots, J \end{cases}$$

- For every atomic term, there are $(2S+1)$ fine-structure levels
  - (or $(2L+1)$ if $L < S$)

- example 1 :
  - configuration : *n*p*n*p'

$$\begin{array}{llllll} {}^3\mathrm{D} & \Rightarrow & J = 3, 2, 1 & \Rightarrow & {}^3\mathrm{D}_1, {}^3\mathrm{D}_2, {}^3\mathrm{D}_3 \\ {}^1\mathrm{D} & \Rightarrow & J = 2 & \Rightarrow & {}^1\mathrm{D}_2 \\ {}^3\mathrm{P} & \Rightarrow & J = 2, 1, 0 & \Rightarrow & {}^3\mathrm{P}_0, {}^3\mathrm{P}_1, {}^3\mathrm{P}_2 \\ {}^1\mathrm{P} & \Rightarrow & J = 1 & \Rightarrow & {}^1\mathrm{P}_1 \\ {}^3\mathrm{S} & \Rightarrow & J = 1 & \Rightarrow & {}^3\mathrm{S}_1 \\ {}^1\mathrm{S} & \Rightarrow & J = 0 & \Rightarrow & {}^1\mathrm{S}_0 \end{array}$$

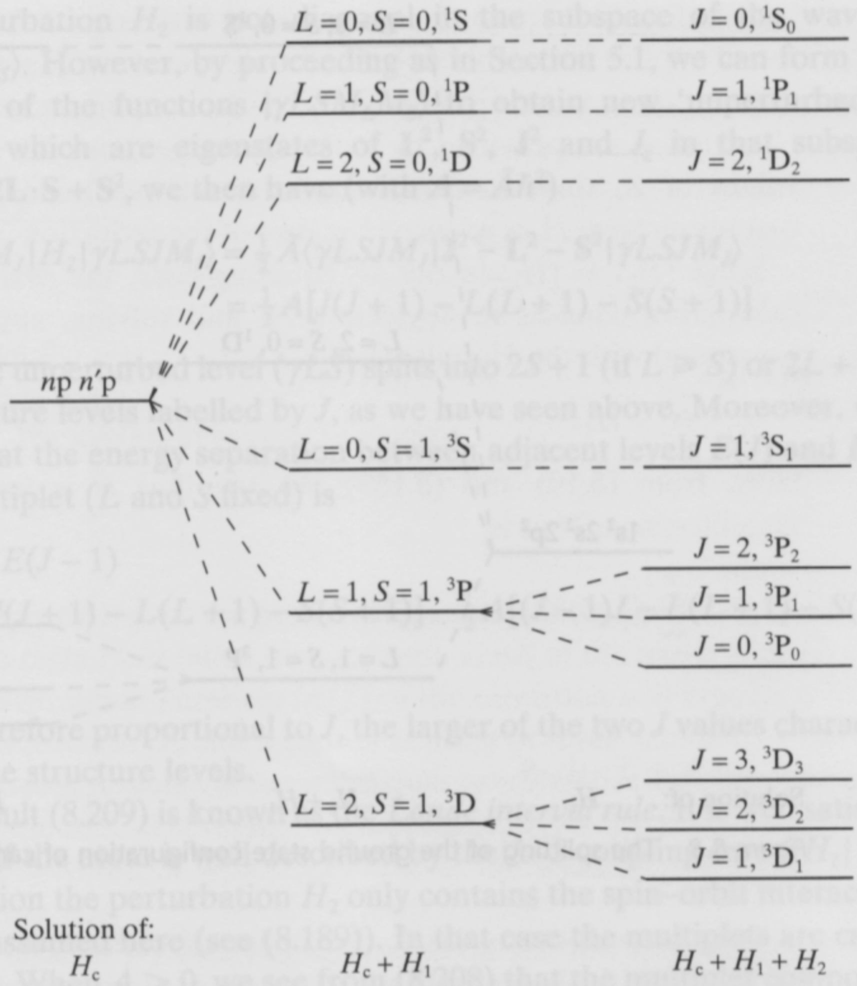


Figure 8.7 The splitting of the configuration $np\ n'p$ by the electrostatic perturbation H_1 and the spin–orbit perturbation H_2.

- example 2 :
  - configuration : $n\mathrm{p}^2$
  - $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $^1S_0$

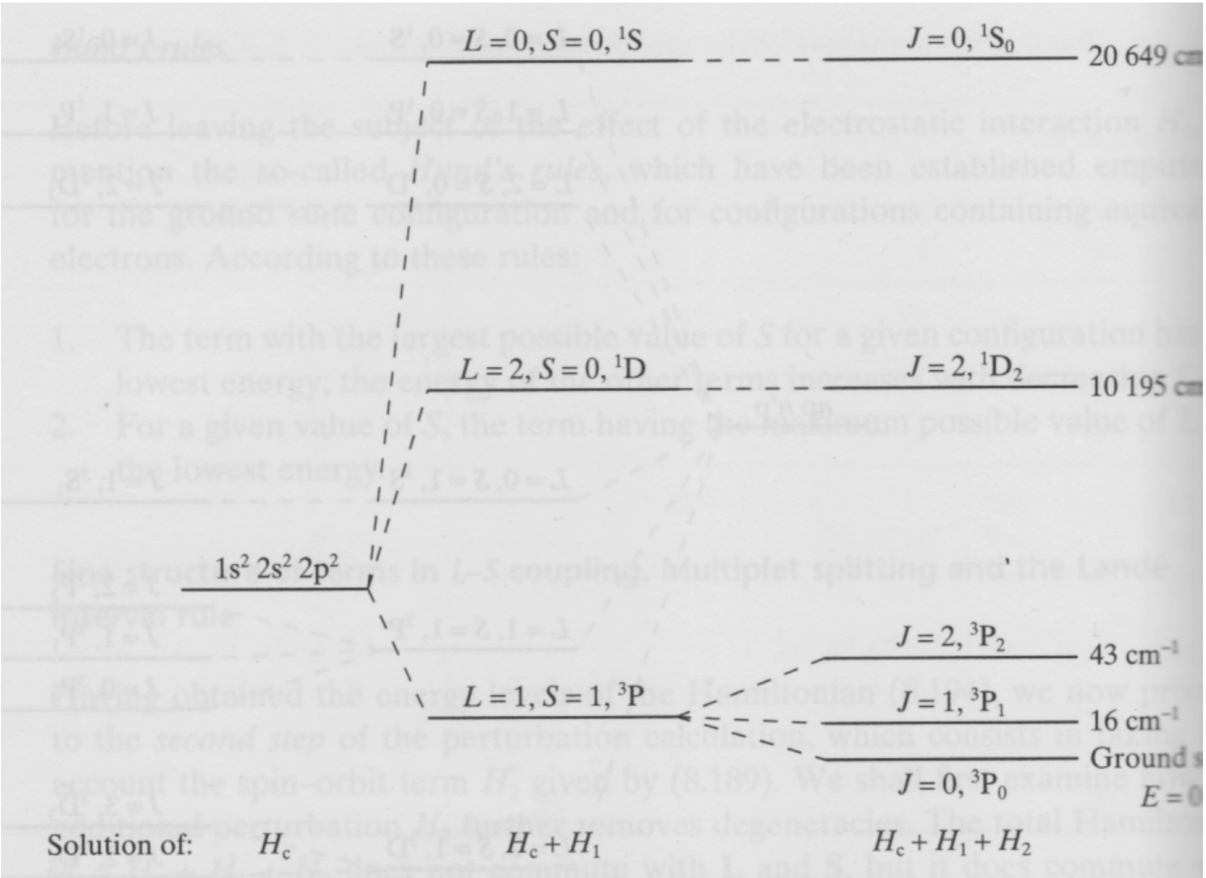


Figure 8.8 The splitting of the ground state configuration of carbon.

Spin-orbit energies

- The energy corrections due to the spin-orbit interaction, the fine-structure splitting, can be found via the Hamiltonian

$$H_{\mathrm{SO}} = \beta_{LS}\, \vec{L} \cdot \vec{S}$$

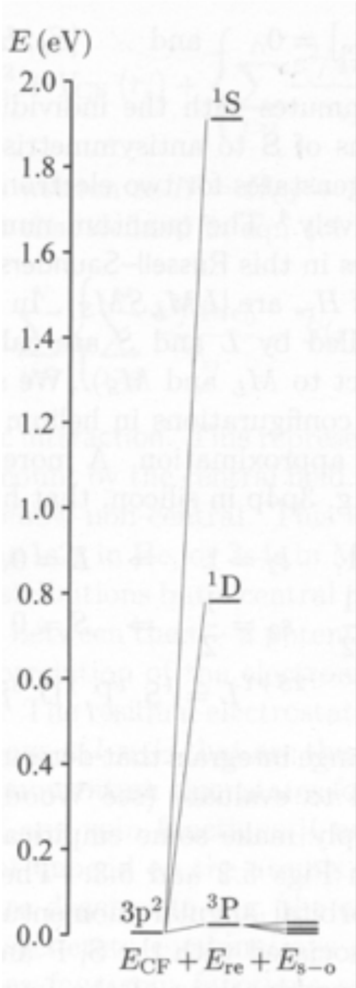
  - here, β_{LS} is a constant typical for the term $|\, \gamma\, L\, S\, \rangle$

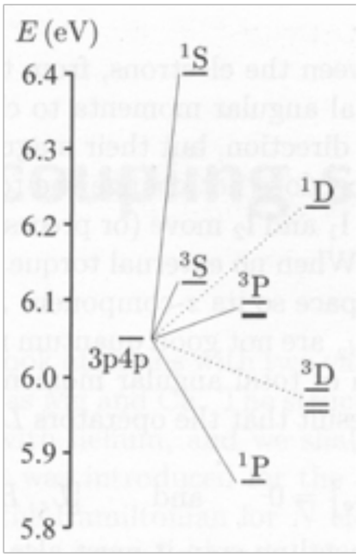
$$\begin{aligned} E_{\mathrm{SO}} &= \langle\, \gamma\, L\, S\, J\, M_J \,|\, H_{\mathrm{SO}}\, |\, \gamma\, L\, S\, J\, M_J\, \rangle \\ &= \beta_{LS}\, \langle\, L\, S\, J\, M_J \,|\, \vec{L} \cdot \vec{S}\, |\, L\, S\, J\, M_J\, \rangle \\ &= \frac{\beta_{LS}}{2}\, \langle\, L\, S\, J\, M_J \,|\, J^2 - L^2 - S^2\, |\, L\, S\, J\, M_J\, \rangle \\ &= \frac{\beta_{LS}}{2}\, [J(J+1) - L(L+1) - S(S+1)] \end{aligned}$$

- Separation between two fine-structure levels

$$\begin{aligned} E(J) \quad &- \quad E(J-1) = \\ &= \quad \frac{\beta_{LS}}{2}\, \{[J(J+1) - L(L+1) - S(S+1)] \\ &- \quad [(J-1)J - L(L+1) - S(S+1)]\} \\ &= \quad \frac{\beta_{LS}}{2}\, \left[J^2 + J - J^2 + J\right] \\ &= \quad \frac{\beta_{LS}}{2}\, J \end{aligned}$$

- “Landé’s interval rule”
  - This rule cam be used as a test of how well system can be described by LS-coupling


E (eV)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1S
1D
3p2
3P
E_CF + E_re + E_s-o


E (eV)
6.4
6.3
6.2
6.1
6.0
5.9
5.8
1S
1D
3S
3P
3p4p
3D
1P

jj-coupling

- This applies when $H_{\rm SO} > H_{\rm res}$
  - The Hamiltonians have to be applied in a different order

$$H = H_2 + H_{\rm res}$$
where
$$H_2 = H_{\rm CF} + H_{\rm SO}$$

- Remember that :
  - $H_{\rm SO} \propto Z^4$
  - $H_{\rm res} \propto Z$
  - $\Rightarrow$ *jj*-coupling will be relevant for heavy atoms

$$H_2 = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_{r_i}^2 - \frac{Z}{r_i} + S(r_i) \right) + \sum_{i=1}^{N} \xi(r_i)\, \vec{L} \cdot \vec{S}$$

- In this case, we have to begin with the SO-coupling for the individual electrons :
  - we form :
  - $\vec{j}_1 = \vec{l}_1 + \vec{s}_1 \,,\, \vec{j}_2 = \vec{l}_2 + \vec{s}_2 \;\; \ldots \,,\, \vec{j}_N = \vec{l}_N + \vec{s}_N$

- The *jj*-coupling terms, we write as a parentheses with all the *j*-values

- As an example, take a 2-electron atom :
  - $l_1 = 0, l_2 = 1 \;\Rightarrow\;$ configuration : $n\mathrm{s}, n'\mathrm{p}$
  - $\left\{ \begin{array}{l} l_1 = 0 \\ l_2 = 1 \end{array} \right. \quad \text{and} \quad \left\{ \begin{array}{l} s_1 = 1/2 \\ s_2 = 1/2 \end{array} \right.$

- $(j_i = |l_i - s_i|, |l_i - s_i| - 1, \ldots, l_i + s_i)$
- $\Rightarrow \quad j_1 = 1/2 \quad \text{and} \quad j_2 = 3/2\,,\, 1/2$
- $\Rightarrow$ Two possibilities :
- $\left(\frac{1}{2}, \frac{1}{2}\right) \quad \text{and} \quad \left(\frac{1}{2}, \frac{3}{2}\right)$

Fine-structure in *jj*-coupling

- When the terms are determined, H_{res} is added as a perturbation
  - this leads to fine-structure levels, classified by J

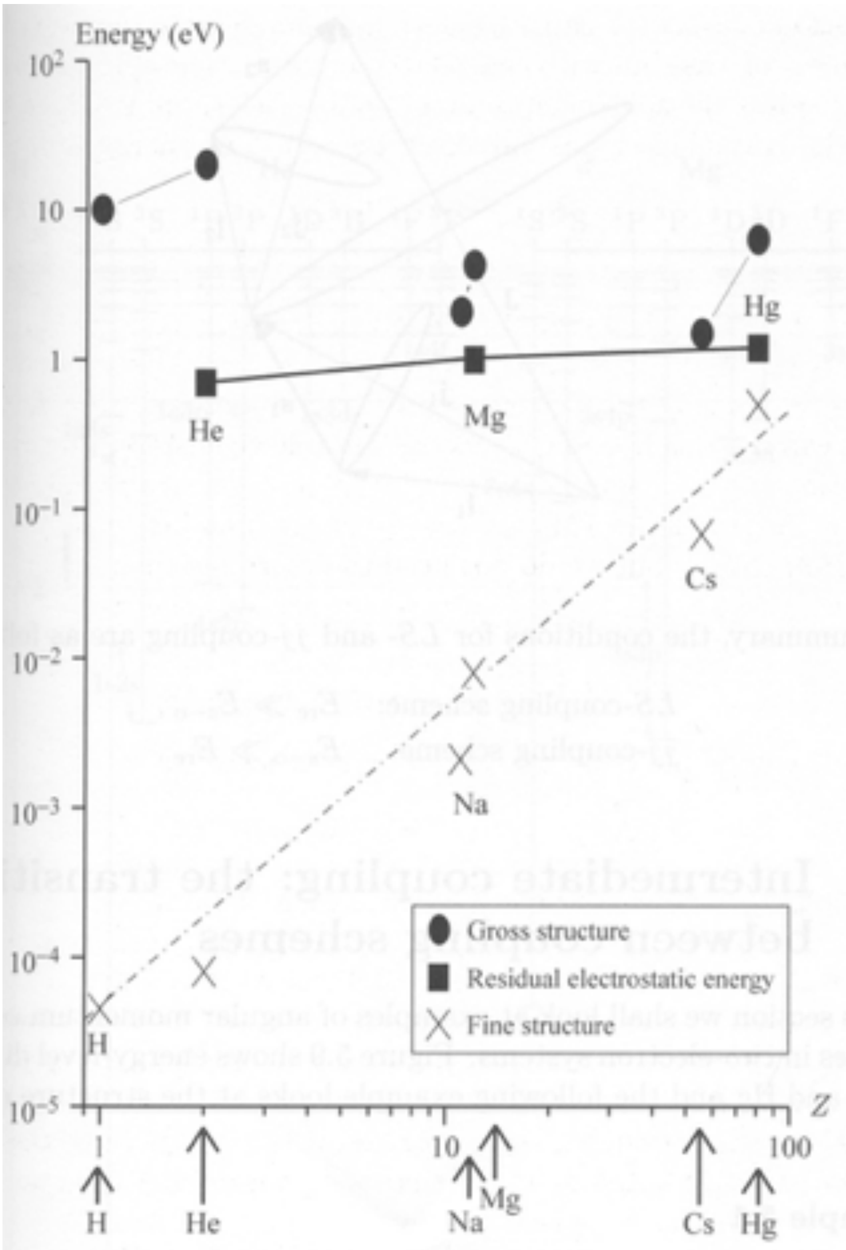
- $J = |j_1 - j_2|, |j_1 - j_2| - 1, \ldots, j_1 + j_2$

$$\left(\frac{1}{2}, \frac{1}{2}\right) \Rightarrow J = 1, 0 \Rightarrow \begin{cases} \left(\frac{1}{2}, \frac{1}{2}\right)_0 \\ \left(\frac{1}{2}, \frac{1}{2}\right)_1 \end{cases}$$

$$\left(\frac{1}{2}, \frac{3}{2}\right) \Rightarrow J = 2, 1 \Rightarrow \begin{cases} \left(\frac{1}{2}, \frac{3}{2}\right)_1 \\ \left(\frac{1}{2}, \frac{3}{2}\right)_2 \end{cases}$$

Comparison between coupling schemes

- For light atoms, *LS*-coupling dominates, since the SO-term is small
- For heavy atoms, the situation is often intermediate between *LS* and *jj*



- As example, take the isoelectronic sequence of $n\mathrm{p}^2$ atoms
  - C , Si , Ge , Sn , Pb
  - Look at the splittings in the first excites states (^{1}P and ^{3}P)
  - C has almost pure *LS*-coupling
  - Pb is well described by *jj*-coupling
  - The others are intermediate
  - This can be seen by studying spectra

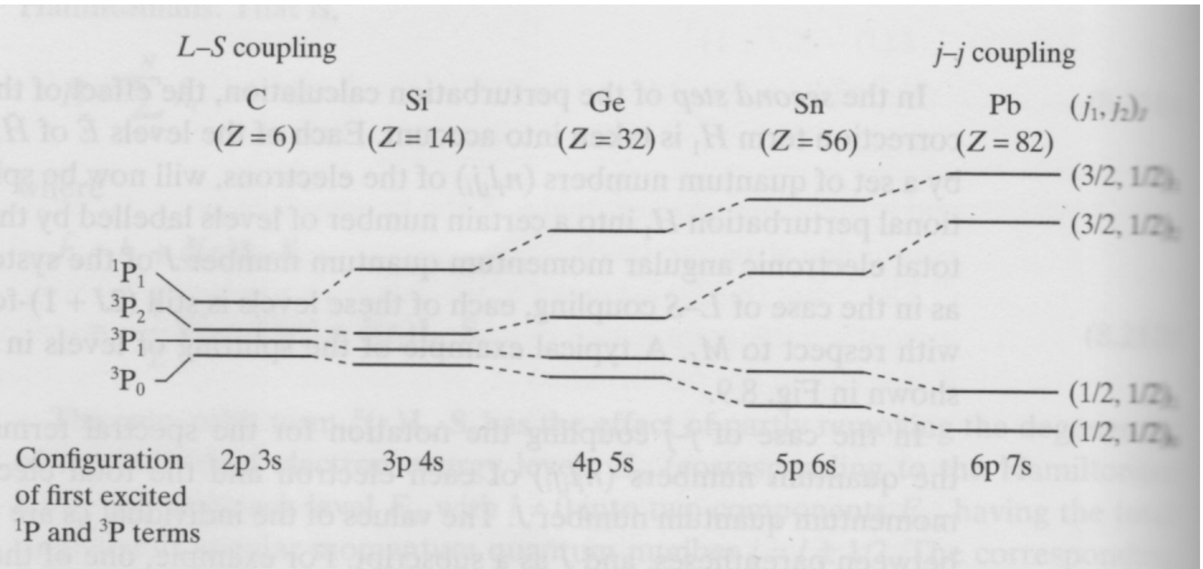


Figure 8.10 The splitting of levels in the first excited ^{1}P and ^{3}P terms of the carbon sequence

- In the case of C, the Landé rule holds

Nuclear effects

- The structure and characteristics of the nucleus has an effect on atomic structure
    - The finite mass – Isotope shift
    - The nuclear spin – Hyperfine structure
    - The finite volume and non-spherical shape – Higher order hyperfine structure

Isotope shift

- So far, we have assumed a nucleus with infinite mass

- With the finite mass taken into account, the solutions to the Schrödinger equation will be slightly different
    - The Rydberg constant will be different than R_∞

- For an atom with different isotopes (different nuclear masses), the energy levels will be slightly different
    - "Isotope shift"

Example : hydrogen and deuterium

- hydrogen : $^1\mathrm{H}$
  - nucleus : 1 proton
  - ratio : $\dfrac{M_\mathrm{T}}{M_\mathrm{nuc}} = \dfrac{M_\mathrm{nuc} + M_\mathrm{e}}{M_\mathrm{nuc}} \approx \dfrac{1837}{1836} \approx 1.000545$

- deuterium : $^2\mathrm{H}$ or $^2\mathrm{D}$
  - nucleus : 1 proton + 1 neutron
  - ratio : $\dfrac{M_\mathrm{T}}{M_\mathrm{nuc}} = \dfrac{M_\mathrm{nuc} + M_\mathrm{e}}{M_\mathrm{nuc}} \approx \dfrac{3671}{3670} \approx 1.000272$

- The spectra of $^1\mathrm{H}$ and $^2\mathrm{D}$ differ by
  - a factor 1.000545 / 1.000272 ≈ 1.00027

Hyperfine structure

- Nuclear magnetic moment :
  - the nucleus is charged
  - many nuclei (not all) have spin
  - $\Rightarrow$ magnetic moment

- Interaction between the nuclear magnetic moment and the total electronic angular momentum J
  - "hyperfine structure" (hfs)
  - (more precisely, first-order hfs, or magnetic dipole hfs)

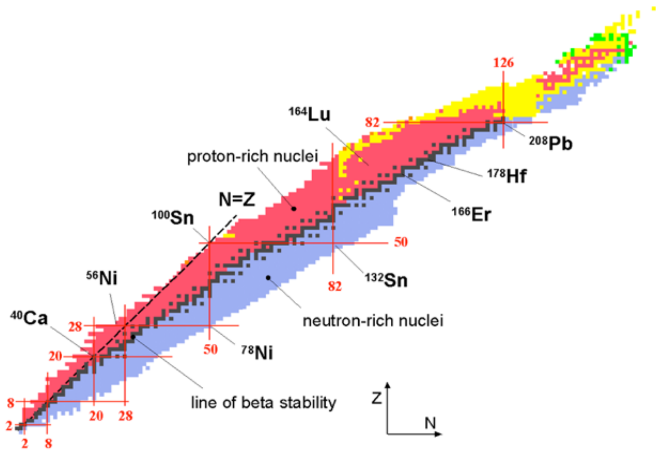
Nuclear spin

- electron : spin $\frac{1}{2}\hbar$, charge $-e$
- proton : spin $\frac{1}{2}\hbar$, charge $+e$
- neutron : spin $\frac{1}{2}\hbar$, charge 0

- A nucleus is composed of protons and neutrons

- The nuclear spin, $\vec{I}$, depends on the composition

- The nuclear spin is typically looked up in a table, or in a chart of nuclides


126
164Lu
82
208Pb
proton-rich nuclei
178Hf
N=Z
100Sn
166Er
50
56Ni
82
132Sn
40Ca
28
neutron-rich nuclei
20
50
78Ni
8
line of beta stability
Z
N
2
20 28
2 8

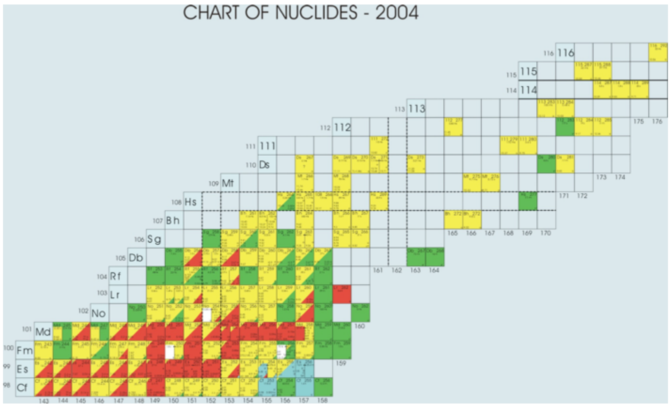
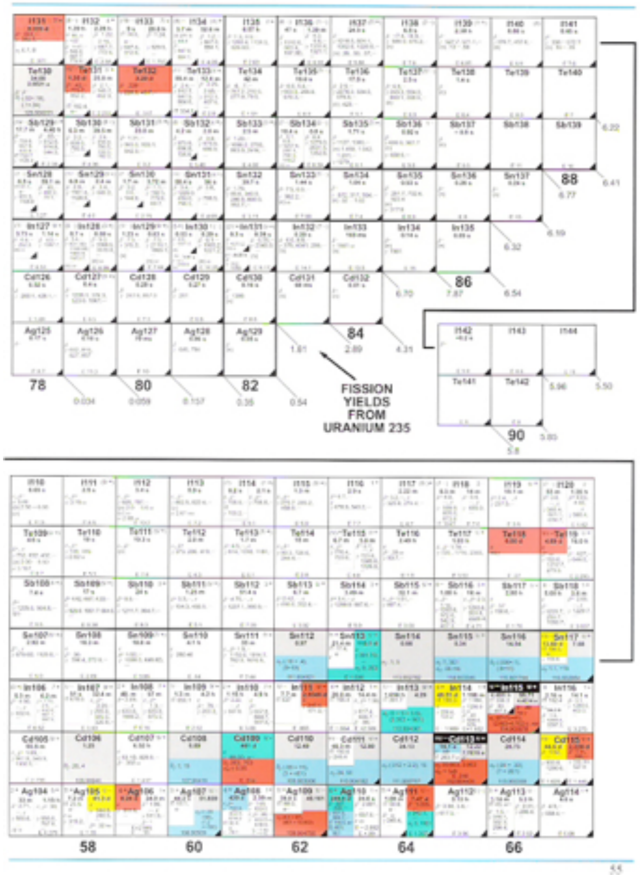


CHART OF NUCLIDES - 2004


FISSION YIELDS FROM URANIUM 235

Magnetic moment of the nucleus

$$\vec{\mu}_I = g_I \, \mu_\mathrm{N} \, \vec{I}$$

- Much smaller than the electron magnetic moment
  - μ_N : the nuclear magneton
  - $\mu_\mathrm{N} = \mu_\mathrm{B} \, \dfrac{m_\mathrm{e}}{m_\mathrm{p}} = \mu_\mathrm{B} \, \dfrac{1}{1836}$
  - ($\mu_\mathrm{B} = 9.2740154 \times 10^{-24} \, \mathrm{J \, T^{-1}}$: the Bohr magneton)
  - g_I : the nuclear gyromagnetic ratio
  - (different for different nuclei)

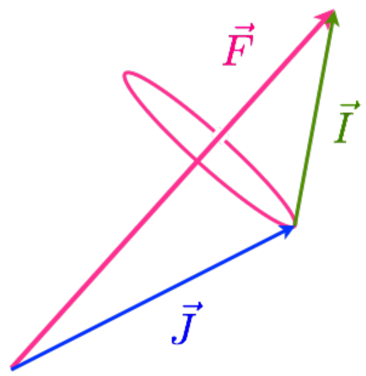
Interaction between $\vec{I}$ and $\vec{J}$

- The total electronic angular momentum $\vec{J}$ will cause an effective magnetic field at the position of the nucleus
$$\vec{B}_e \propto \vec{J}$$

- The magnetic moment of the nucleus will interact with this :
  - $H_\mathrm{hfs} = -\vec{\mu}_I \cdot \vec{B}_e = A_\mathrm{hfs} \, \vec{I} \cdot \vec{J}$
  - the hyperfine structure Hamiltonian

- A_hfs is a factor that depends on the nuclear and electronic charge distributions
  - typially, A_hfs has to be determined experimentally

- Coupling between $\vec{I}$ and $\vec{J}$
  - the sum is constant



- New quantum number for the total angular momentum, including the nucleus :
  - F et M_F
  - $\begin{cases} F = |I-J|, |I-J|-1, \ldots, I+J \\ M_F = -F, -F+1, \ldots, F \end{cases}$

- The good representation will be :
  - $|\, IJFM_F \,\rangle$
  - $\begin{cases} F^2 \,|\, IJFM_F \,\rangle & = & F(F+1) \,|\, IJFM_F \,\rangle \\ F_Z \,|\, IJFM_F \,\rangle & = & M_F \,|\, IJFM_F \,\rangle \end{cases}$

<u>Perturbation theory</u>

- H_{hfs} has smaller energy than H_{res} and H_{SO}
  - $\Rightarrow$ it can be treated as a perturbation *after* the other Hamiltonians

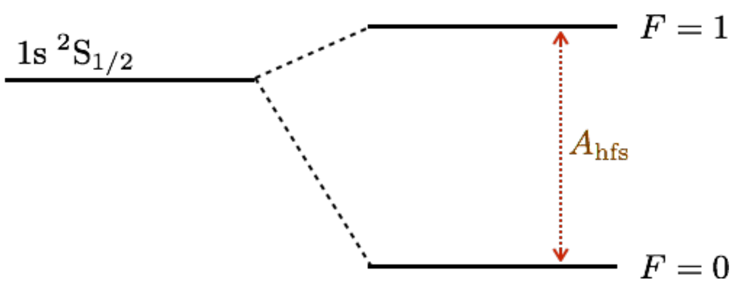
$$E_{\text{hfs}} = A_{\text{hfs}} \left\langle \vec{I} \cdot \vec{J} \right\rangle = \frac{A_{\text{hfs}}}{2} \left[F(F+1) - I(I+1) - J(J+1) \right]$$

Example ; hydrogen

- Ground state of hydrogen :
  - $1s\ ^2S_{1/2}$
  - $I = \dfrac{1}{2}$
- $\Rightarrow \quad F = 0 \quad \text{or} \quad F = 1$

$$E_{hfs} = \frac{A_{hfs}}{2}\left[F(F+1) - I(I+1) - J(J+1)\right]$$

$$\Rightarrow \begin{cases} E(F=0) = \frac{A_{hfs}}{4} \\ E(F=0) = -\frac{3A_{hfs}}{4} \end{cases}$$



- For H : $A_{hfs}(H\ ,\ 1s\ ^2S_{1/2}) \approx h \times 1.42$ GHz
  - this can be measured *very* accurately :
  - $\Delta E = A_{hfs} = h \times 1\,420\,405\,751.766\,7$ Hz
- Very important for radio astronomy
  - the “21 cm line”
- Applications in atomic clocks

Interactions/Spectroscopy II

Selection rules in *LS*-coupling

- For electric dipole transitions, the conditions for allowed transitions are :

- The parity of the two involved states *MUST* be different

One-electron transitions (change in configuration)

- $\Delta l = \pm 1$

- $\Delta m_l = 0\,,\, \pm 1$
  - depending on polarisation

Additional rules for multi-electron atoms

- $\Delta J = 0\,,\, \pm 1$
  - $J = 0 \leftrightarrow J' = 0$ forbidden

- $\Delta M_J = 0\,,\, \pm 1$
  - depending on polarisation
  - $M_J = 0 \leftrightarrow M'_J = 0$ forbidden if $J = J'$

Additional rules for *LS*-coupling

- $\Delta S = 0$
- $\Delta L = 0\,,\ \pm 1$

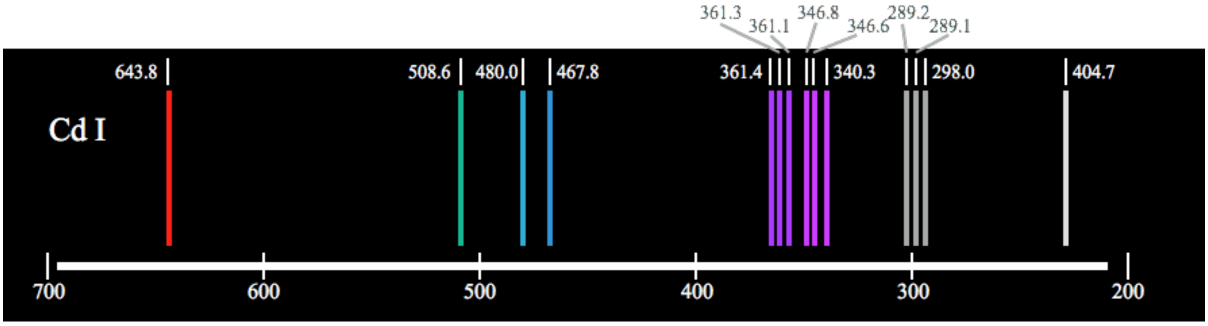
Additional rules for hyperfine strufture

- $\Delta F = 0\,,\ \pm 1$
  - $F = 0 \leftrightarrow F' = 0$ forbidden
- $\Delta M_F = 0\,,\ \pm 1$
  - depending on polarisation
  - $M_F = 0 \leftrightarrow M'_F = 0$ forbidden if $F = F'$

Analysis of spectra : example

- Knowledge of the elections rules is dispensable for analysis of spectra

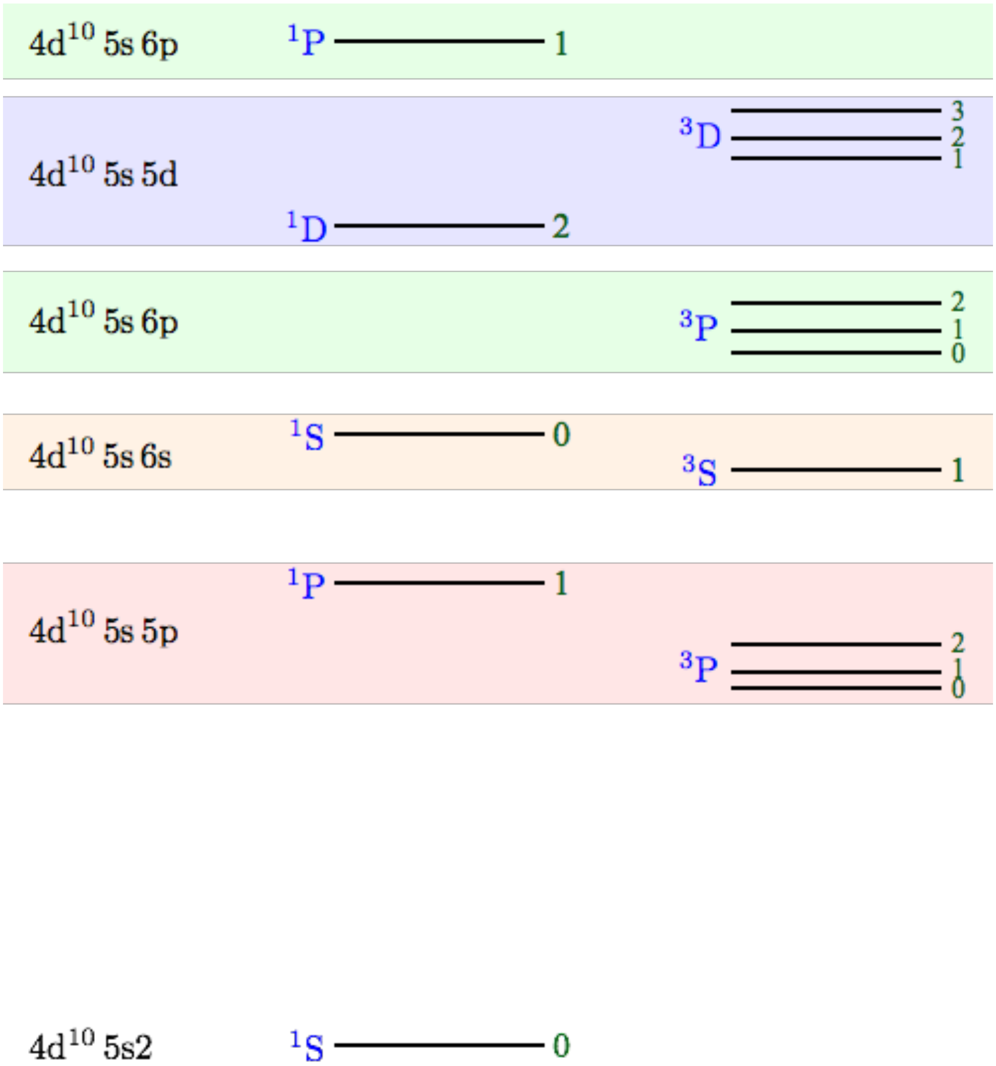
- As en example, take a part of a cadmium spectrum



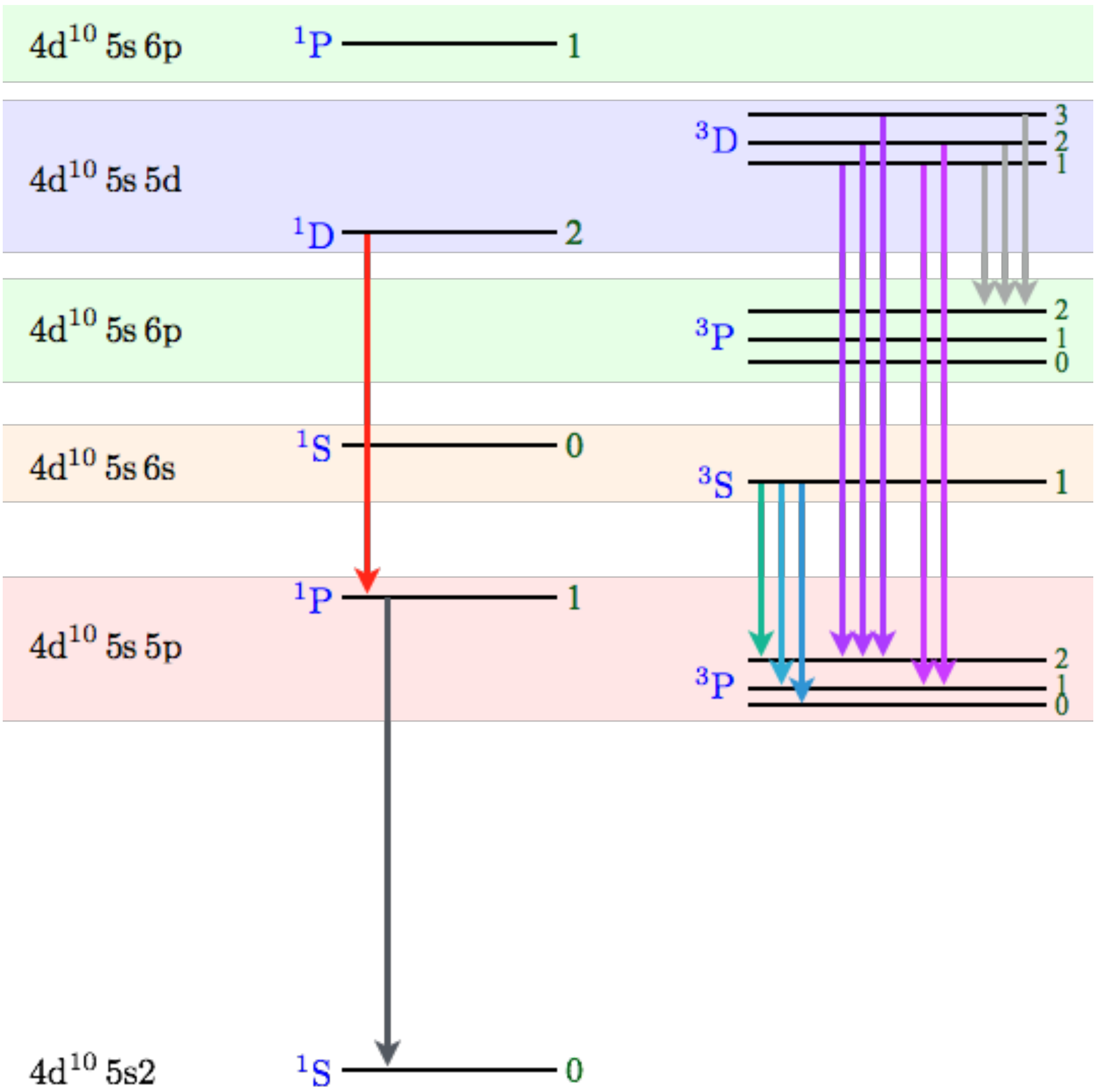
- Compare to a table of energy levels

Configuration	Term	J	Level (cm^{-1})	Reference
$4d^{10}5s^2$	^1S	0	0.000	L3466
$4d^{10}5s5p$	$^3P^\circ$	0	30 113.990	L3486
		1	30 656.087	L3486
		2	31 826.952	L3486
$4d^{10}5s5p$	$^1P^\circ$	1	43 692.384	L3486
$4d^{10}5s6s$	^3S	1	51 483.980	L3486
$4d^{10}5s6s$	^1S	0	53 310.101	L3486
$4d^{10}5s6p$	$^3P^\circ$	0	58 390.9	L3466
		1	58 461.6	L3466
		2	58 635.7	L3466
$4d^{10}5s5d$	^1D	2	59 219.734	L3486
$4d^{10}5s5d$	^3D	1	59 485.768	L3486
		2	59 497.868	L3486
		3	59 515.980	L3486
$4d^{10}5s6p$	$^1P^\circ$	1	59 907.28	L3641
$4d^{10}5s7s$	^3S	1	62 563.435	L3486
$4d^{10}5s7s$	^1S	0	63 086.896	L3486
$4d^{10}5s7p$	$^3P^\circ$	0	64 995.9	L3466
		1	65 025.5	L9542
		2	65 093.702	L3486
$4d^{10}5s6d$	^1D	2	65 134.783	L3486
$4d^{10}5s6d$	^3D	1	65 353.372	L3486
		2	65 358.881	L3486
		3	65 367.227	L3486

- The ground state is almost 3.7 eV lower than all excited states
  - 3.7 eV correspond to about 229 nm



- By applying the selection rules, we can identify the spectral lines



- For example, we can control the Landé rule by comparing lines

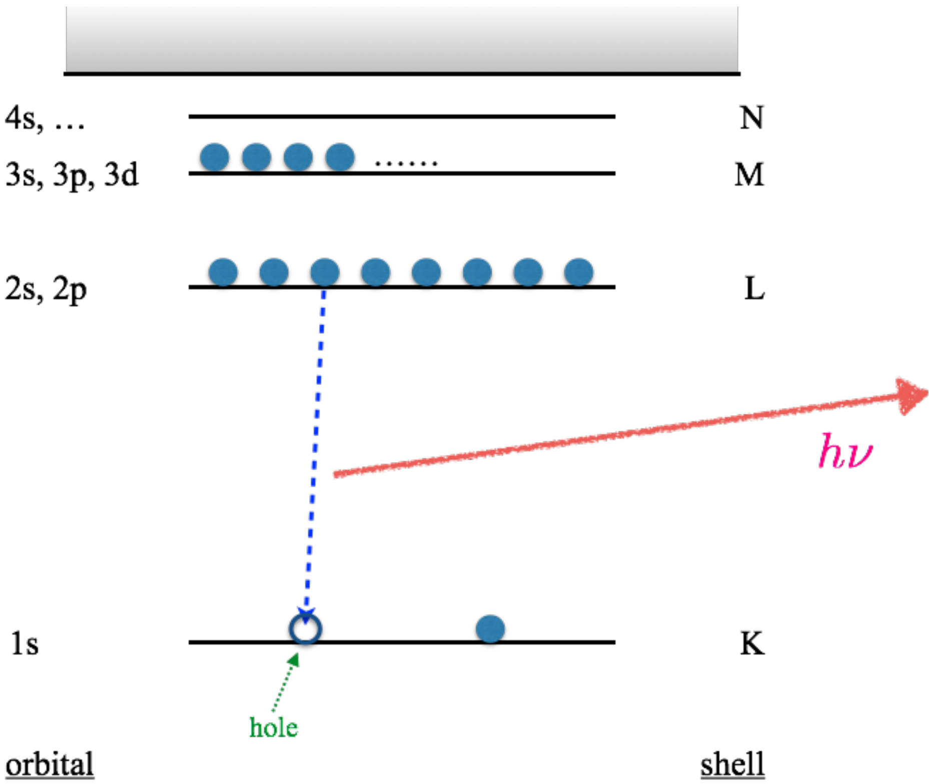
x-rays

Inner shell excitations

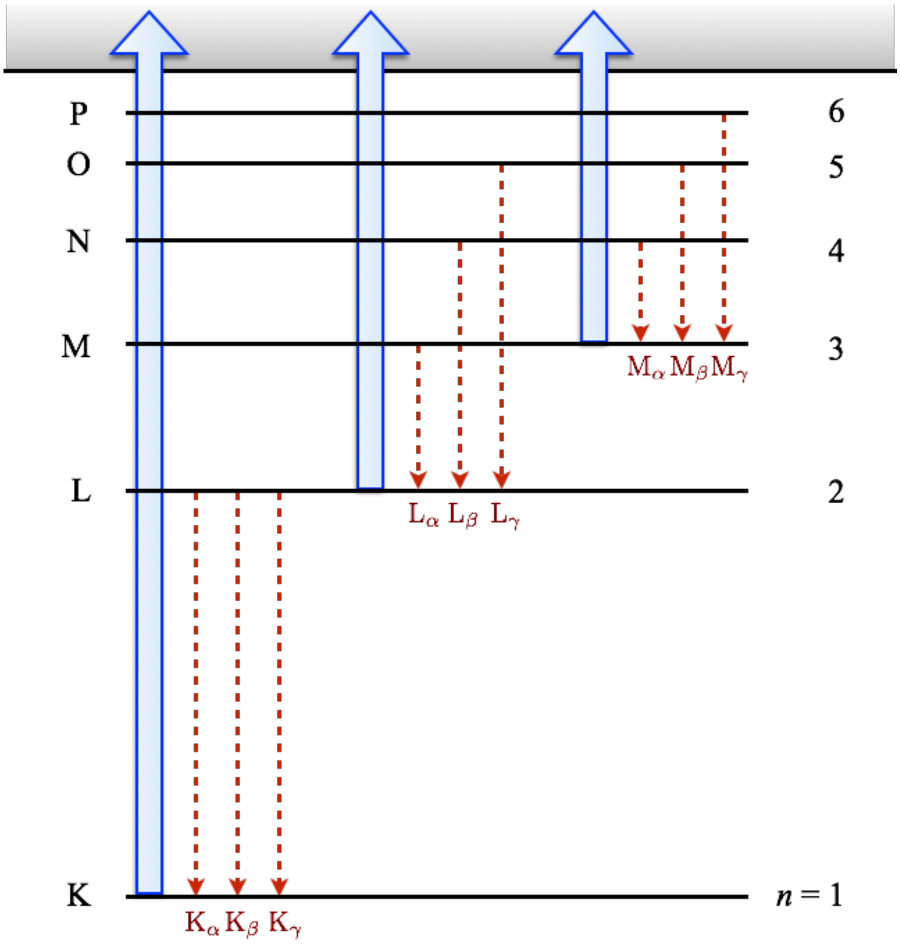
- Optical spectra (visible light)
  - excitations of valence electrons

- x-ray spectra
  - ionization of core electrons

- Suppose that an 1s-electron is ionized, for example via a collision with an energetic electron



- The valence in the inner shell will be filled by another electron
- This will result in emission of high energy radiation
- By convention, x-ray emission lines are labeled with chemical notation "for shells"



- The energy of an x-ray emission line is given by the difference in binding energies for the two involved electron shells

- These can be found via experimentally measured values (tables)

- Approximation (in atomic units) :

$$E_n \approx \frac{1}{2}\,\frac{(Z-\sigma_n)^2}{n^2}$$

  - Z : nuclear charge (atomic number)
  - n : principal quantum number
  - σ_n : screening term (depends on Z)

- Empiric values
  - $\sigma_1 \approx 1 \quad , \quad \sigma_2 \approx 7.4$
  - $\Rightarrow$ results within 10% - 20% of experimental values

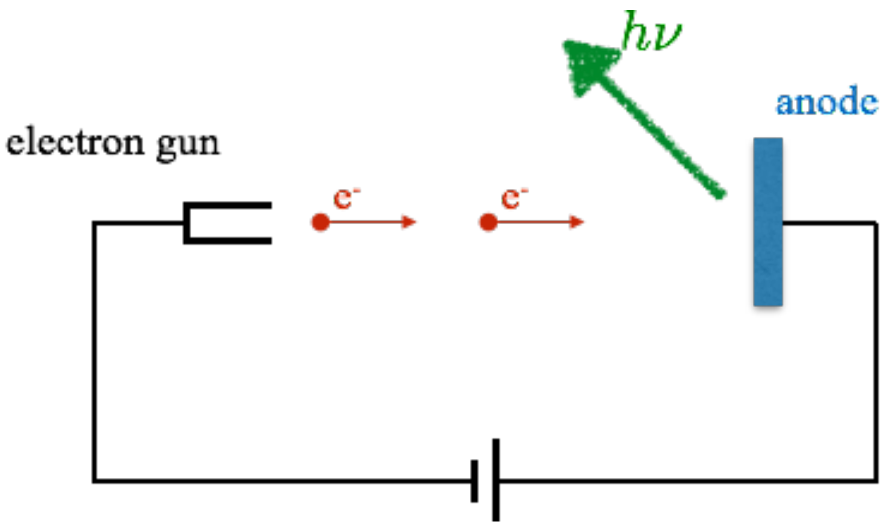
Example ; Fe

- $Z = 26$
  - $E_{1\mathrm{s}} = \frac{1}{2}\,\frac{(26-1)^2}{1^2} = 312\ \mathrm{a.u.} = 8.5\ \mathrm{keV}$
  - $E_{2\mathrm{s},2\mathrm{p}} = \frac{1}{2}\,\frac{(26-7.4)^2}{2^2} = 43\ \mathrm{a.u.} = 1.2\ \mathrm{keV}$

- $\Rightarrow\ E_{\mathrm{K}\alpha} \approx (8.5-1.2)\ \mathrm{keV} = 7.3\ \mathrm{keV}$
  - experimental value : 6.4 eV

- $\Rightarrow\ \lambda_{\mathrm{K}\alpha} \approx 170\ \mathrm{pm}$
  - experimental value : 1.94 Å

Generation of x-rays



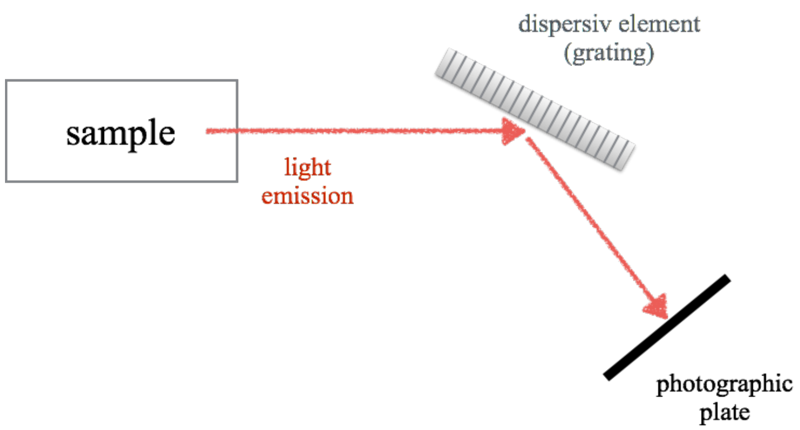
Atomic spectroscopy

- Study of the distribution of energies (or frequencies, or wavelengths)
    - $\Rightarrow$ information about the energetic structure of the atom

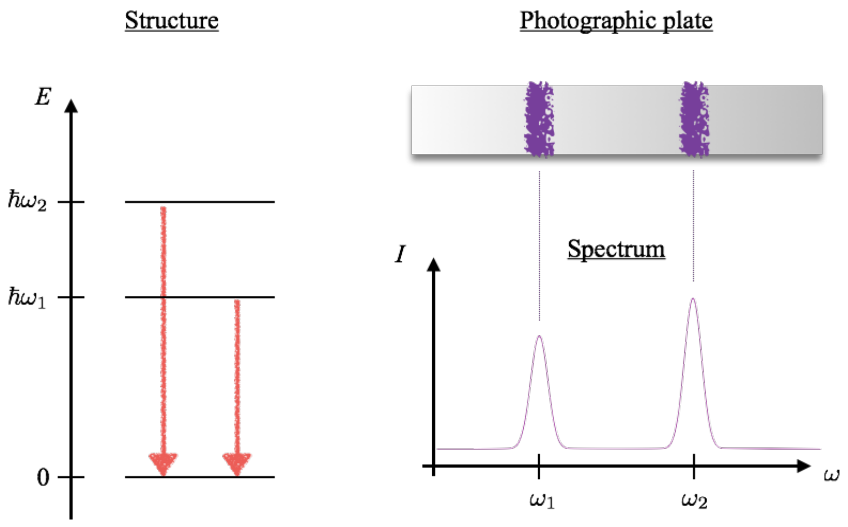
- Many types of spectroscopy. One classification is
    - Emission spectroscopy
    - Absorption spectroscopy

Emission spectroscopy

- Typical experimental setup

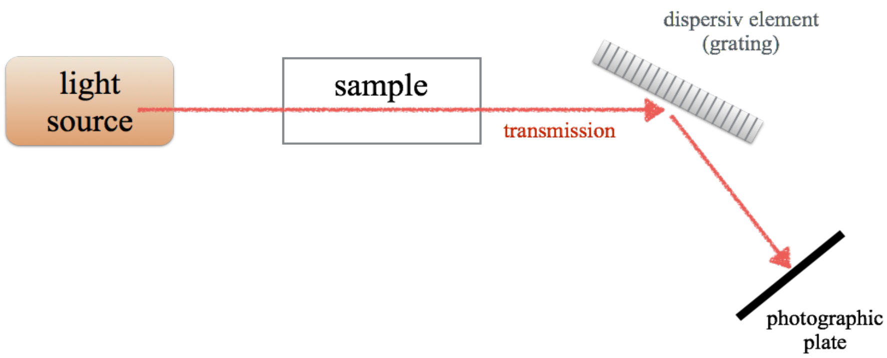


- The result reveals atomic structure :

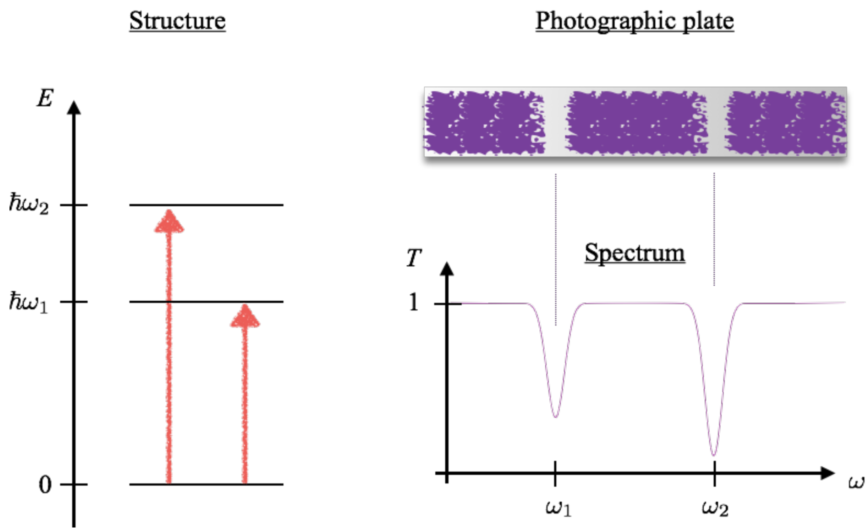


Absorption spectroscopy

- Typical experimental setup



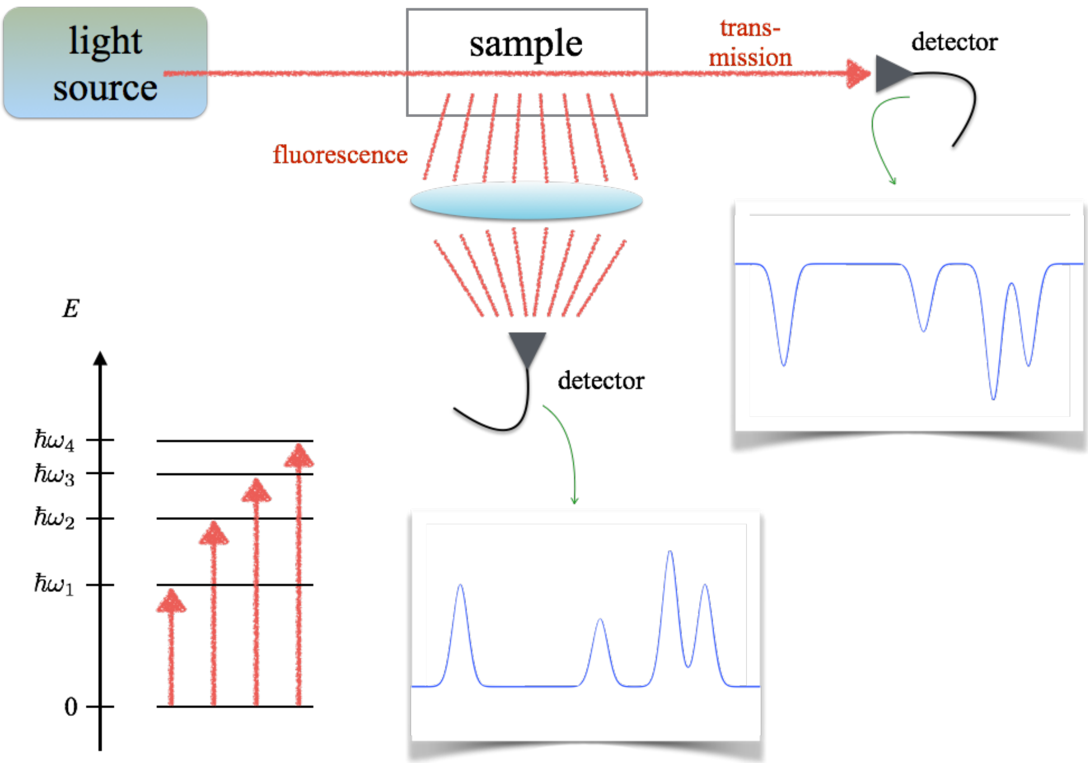
- The result reveals atomic structure :



Laser spectroscopy , selective excitation

- Laser as a light source
  - quasi-monochriomatic
  - potentially tunable

- One single, *selectable*, level can be excited



Spectral broadening

- A spectral line is never infinitely narrow

- Many different broadening mechanisms
  - different spectral widths
  - different spectral shapes

- Homogeneous broadening mechanisms
  - the broadening is present for every individual atom
  - examples : natural broadening, collisional broadening , saturation broadening

- Inhomogeneous broadening mechanisms
  - the resonance frequency is different for different atoms
  - example : Doppler broadening

Natural linewidth

- All excited states have a finite decay time (lifetime)
  - $\Rightarrow$ spectral broadening

- Can be explained in two different ways
  - with the same result

- The uncertainty principle
  - limited lifetime of the excited state : $\Delta t < \infty$
  - $\Rightarrow \quad \Delta E > 0$
  - $\left(\Delta E\, \Delta t \geq \dfrac{\hbar}{2}\right)$

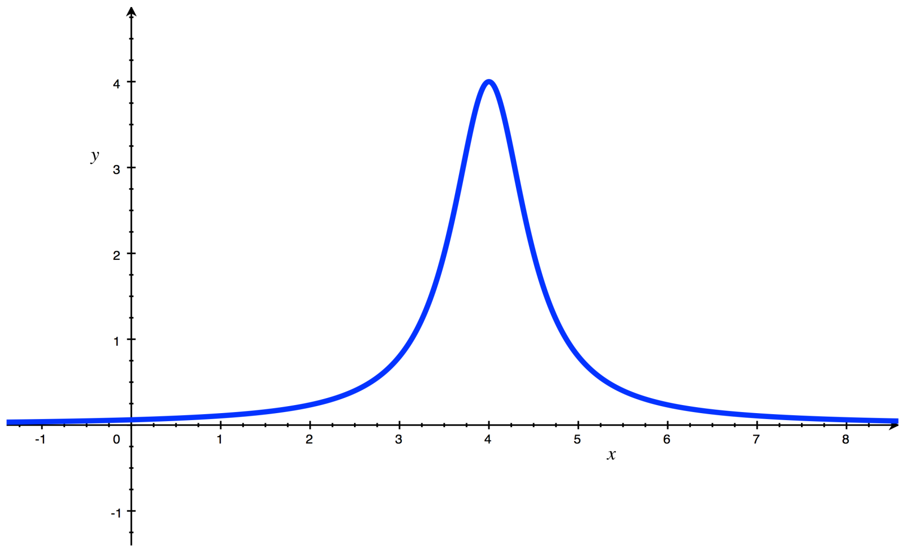
- Fourier transform
  - an oscillation that is not on for an infinite time must have a spectrum of frequencies with $\Delta\omega > 0$

- Spectral profile

$$g(\omega) = \frac{1}{\pi}\,\frac{\gamma/2}{(\omega-\omega_0)^2+\gamma/2}$$

  - γ is the spectral width
  - $\gamma = \dfrac{1}{\tau}$
- τ : the lifetime of the excited state

- Lorentzian profile



Doppler broadening

- Consider a moving atom, emitting or absorbing
  - emitted/absorbed radiation : $\omega' = \omega_0 + \vec{k} \cdot \vec{v}$

- Consider a gas of temperature T
  - $\Rightarrow$ Maxwell-Boltzmann distribution of velocities
  - $n_i(v_z)\,\mathrm{d}v_z = \dfrac{N_i}{v_\mathrm{p}\sqrt{\pi}}\,\mathrm{e}^{-\left(\frac{v_z}{v_\mathrm{p}}\right)^2}\,\mathrm{d}v_z$
  - $v_\mathrm{p} = \sqrt{\dfrac{2k_\mathrm{B}T}{m}}$: "most probable velocity"
  - N_i : number off particles in state i

- This leads to a distribution of emitted frequencies
  - $I(\omega) = I_0\,\exp\left[-\left(\dfrac{\omega-\omega_0}{\omega_0}\dfrac{c}{v_\mathrm{p}}\right)^2\right]$

- Gaussian profile