

PC IV: MOLECULAR SPECTROSCOPY /

Molekülspektroskopie

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Prof. Karl-Heinz Gericke

Summer Semester: from April 2, 2009 till July 10, 2009

Lectures: Thursday 8:00 – 9:30 (PK11.2)

Friday 11:30 – 12:15 (PK11.2)

Exercises: Friday 12:15 – 13:00 (PK11.2)

What is Spectroscopy?

The study of molecular structure and dynamics through the absorption, emission, and scattering of light

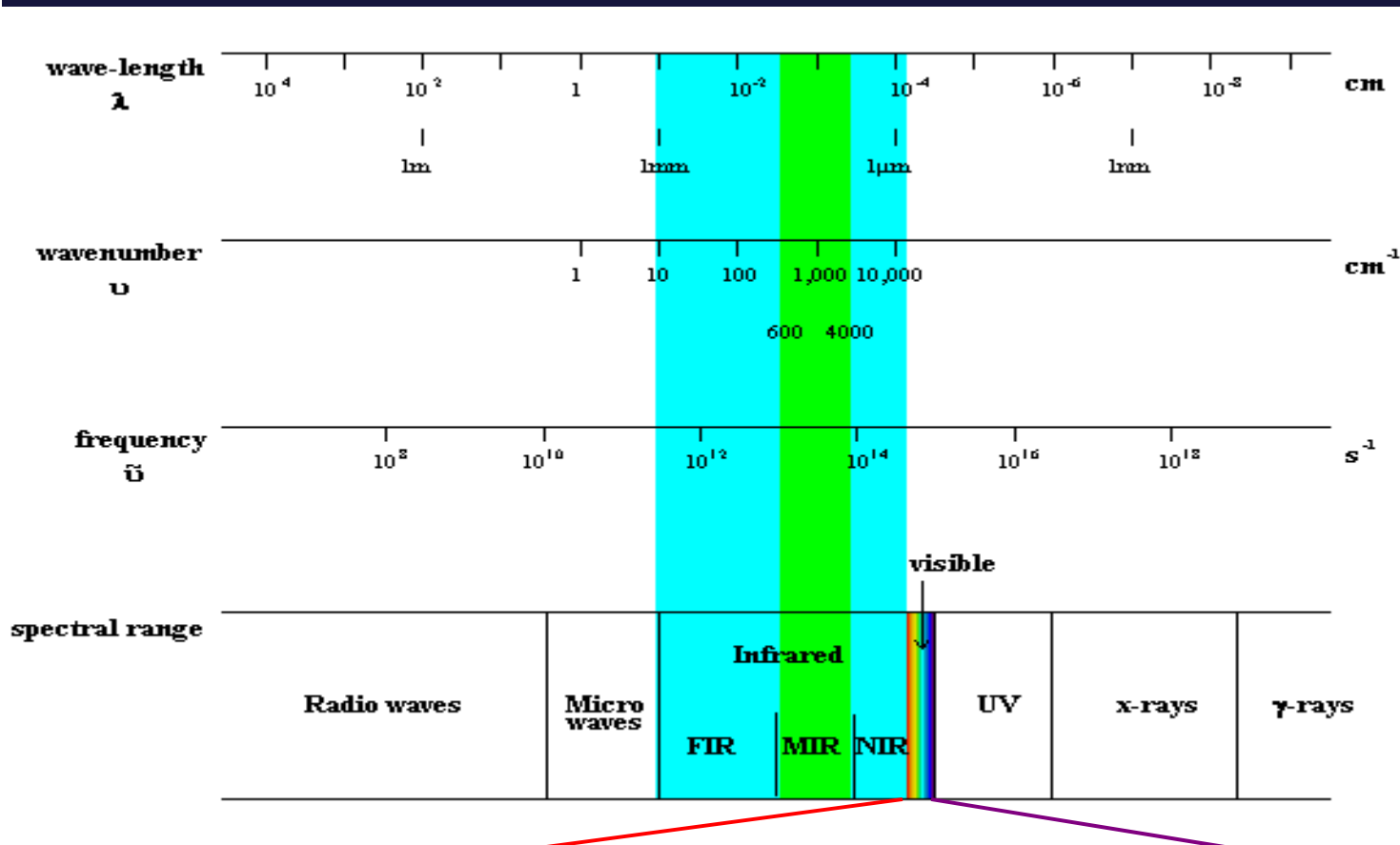
URL Internet Skript

Vorlesung: <http://www.pci.tu-bs.de/aggericke/PC4>
Englisch: <http://www.pci.tu-bs.de/aggericke/PC4e/>
Download: <http://www.pci.tu-bs.de/aggericke/PC4e/download/>
Exercises: <http://www.pci.tu-bs.de/aggericke/PC4e/exercises/>

List of References

- Banwell, Colin N. McCash, Elaine M., "Fundamentals of Molecular Spectroscopy", Tata McGraw Hill, ISBN: 0074620258
- Haken / Wolf, "Molekülphysik und Quantenchemie", Springer, ISBN: 3-540-5
- P. W. Atkins, "Physical Chemistry", or "Physikalische Chemie"
- Kettle, "Symmetrie und Struktur", Teubner Taschenbuch
- W. Kutzelnigg, "Einführung in die Theoretische Chemie", Band I, II, Verlag Chemie, ISBN: 3-527-25719-9
- R. McWeeny, "Coulsons Chemische Bindung", S.Hirtzel-Verlag Stuttgart, ISBN: 3-7776-0383-x
- B. Webster, "Chemical Bonding Theory", Blackwell Scientific Publications, ISBN: 0-632-01619-1 (-01621-3)
- D. A. Quarrie, "Quantum Chemistry", Oxford University Press
- G. Wedler, "Lehrbuch der Physikalischen Chemie", 4. Auflage, VCH, 1997, ISBN: 3-527-29481-3
- G. Herzberg, "Molecular Spectra and Molecular Structure", V. I, II, III, Princeton

Spectrum of Electromagnetic Waves



$$n = c/\lambda \text{ (Hz)}$$

Spectral Areas



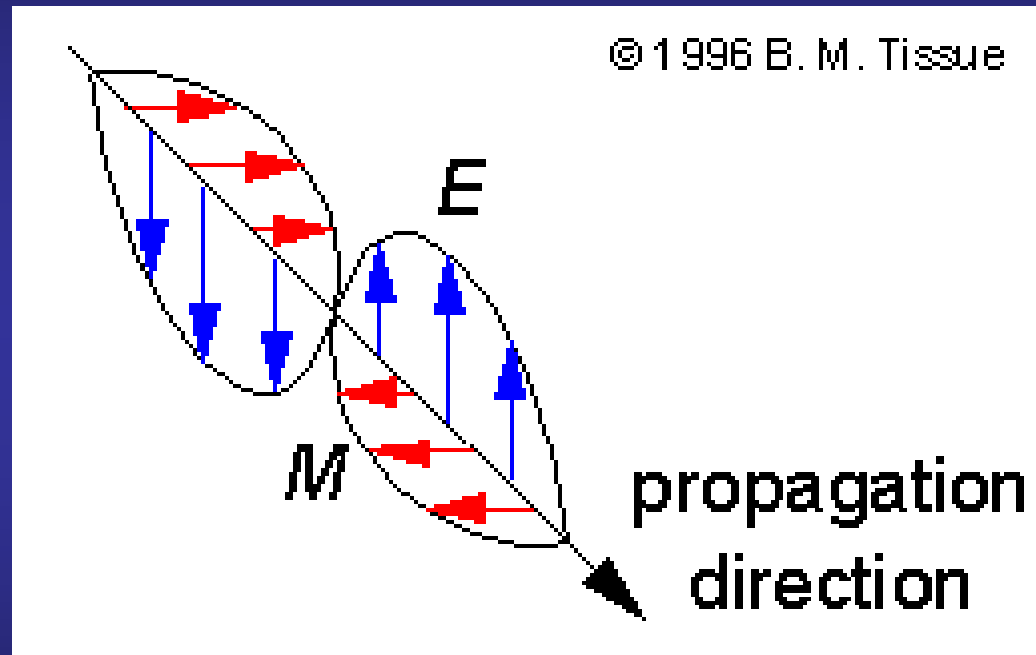
Wavelength, nm

Visible Light

Electromagnetic Spectrum

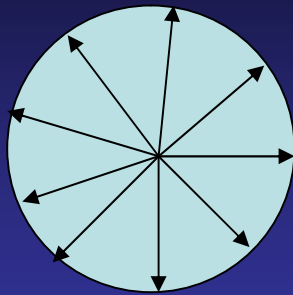
Type of Radiation	Frequency Range (Hz)	Wavelength Range	Type of Transition
gamma-rays	10^{20} - 10^{24}	<1 pm	nuclear
X-rays	10^{17} - 10^{20}	1 nm-1 pm	inner electron
ultraviolet	10^{15} - 10^{17}	400 nm-1 nm	outer electron
visible	4 - 7.5×10^{14}	750 nm-400 nm	outer electron
near-infrared	1×10^{14} - 4×10^{14}	2.5 μ m-750 nm	outer electron molecular vibrations
infrared	10^{13} - 10^{14}	25 μ m-2.5 μ m	molecular vibrations
microwaves	3×10^{11} - 10^{13}	1 mm-25 μ m	molecular rotations, electron spin flips, EPR
radio waves	< 3×10^{11}	>1 mm	nuclear spin flips, NMR

Electromagnetic Radiation



Light Polarization

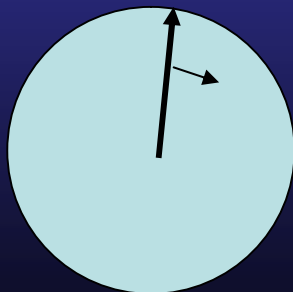
E



Unpolarized light

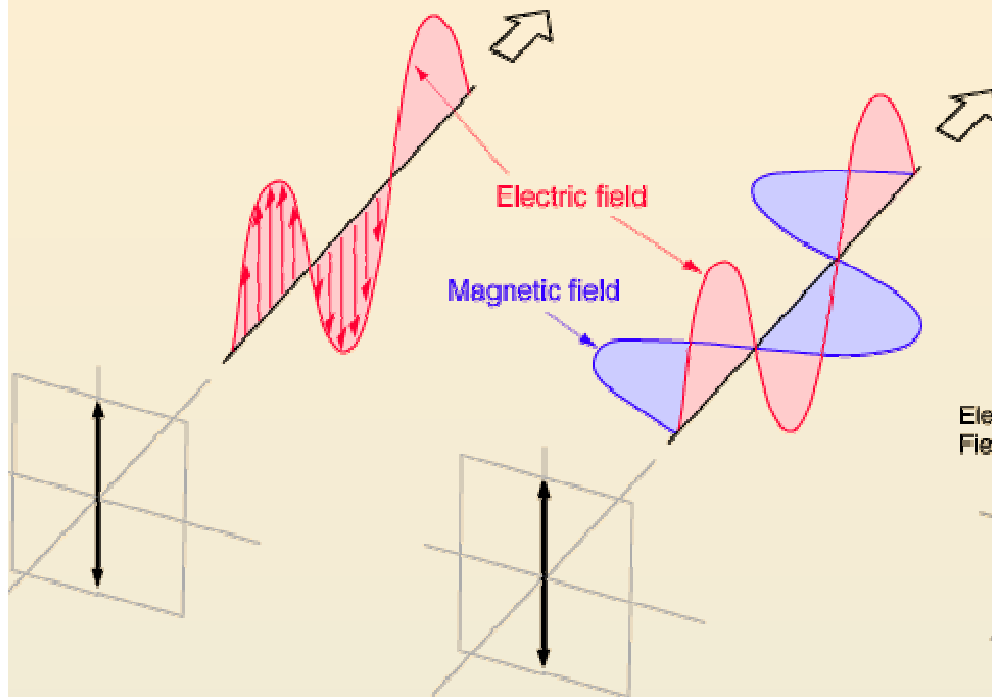


Linearly polarized light



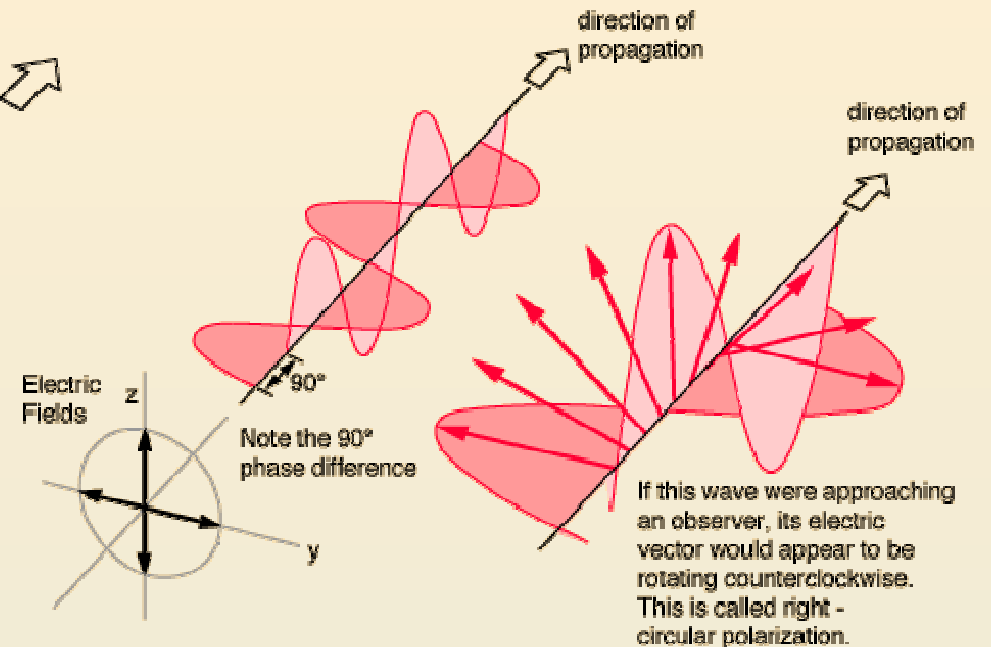
Circularly polarized light

Linear Polarization



A plane electromagnetic wave is said to be linearly polarized. The transverse electric field wave is accompanied by a magnetic field wave as illustrated.

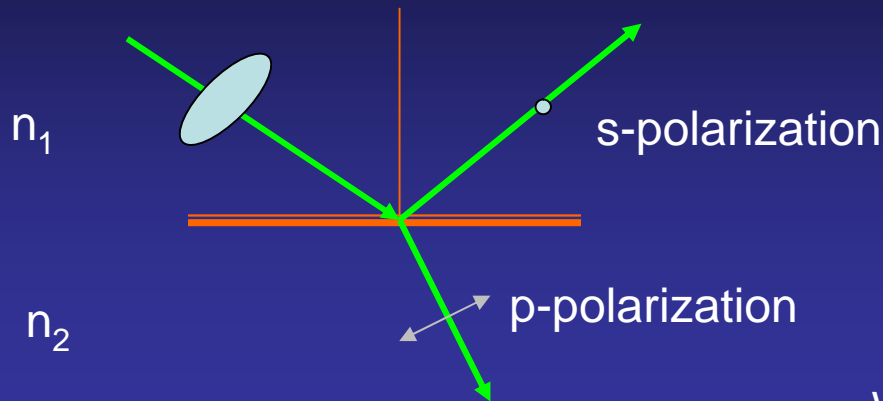
Circular Polarization



Circularly polarized light consists of two perpendicular electromagnetic plane waves of equal amplitude and 90° difference in phase. The light illustrated is right-circularly polarized.

How to produce polarized light ?

1. Reflection from a surface, or refraction through a plate



Brewster's angle:

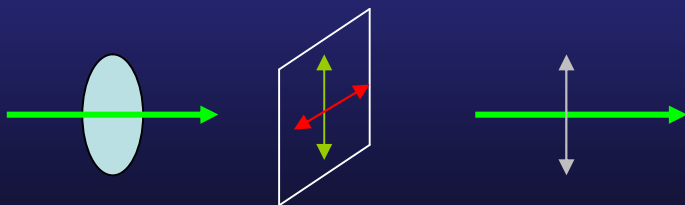
$$\theta_B = \arctan\left(\frac{n_2}{n_1}\right)$$

where n_1 and n_2 are refraction indices

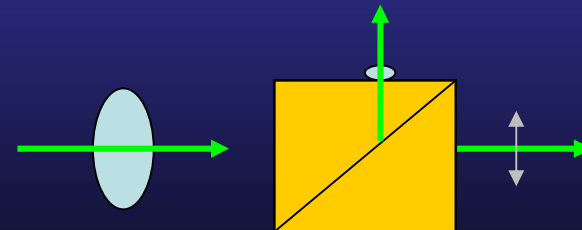
For the pair air ($n_1=1$) – glass ($n_2= 1,5$) for visible light $\theta_B \approx 56^\circ$.

Stack of glass plates can be used as a polarizer for transmitted light.

2. Dichroic polaroids (thin films)

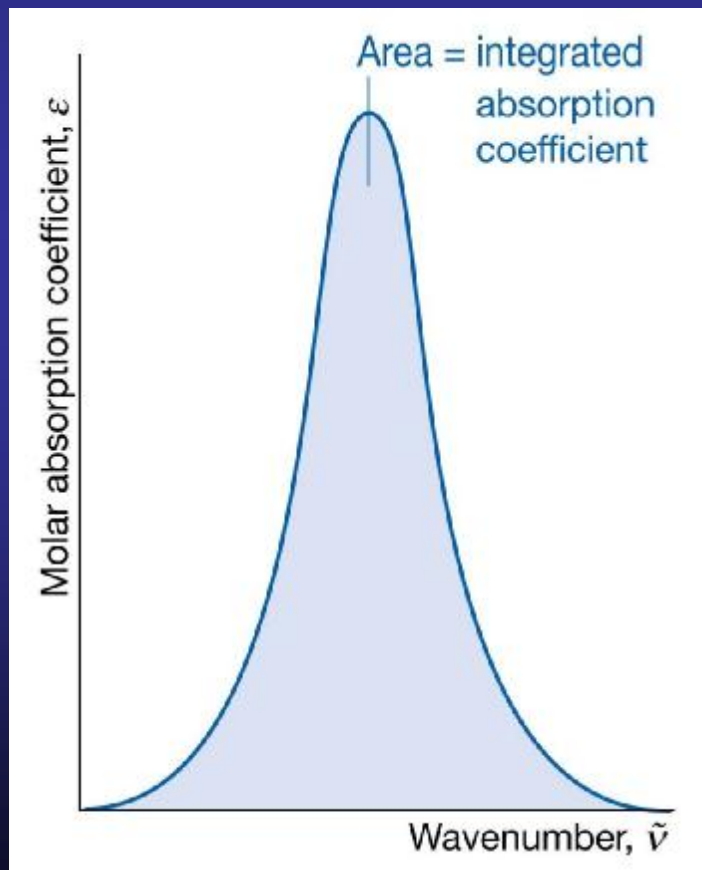


3. Crystal polarizers (Glan Prism)

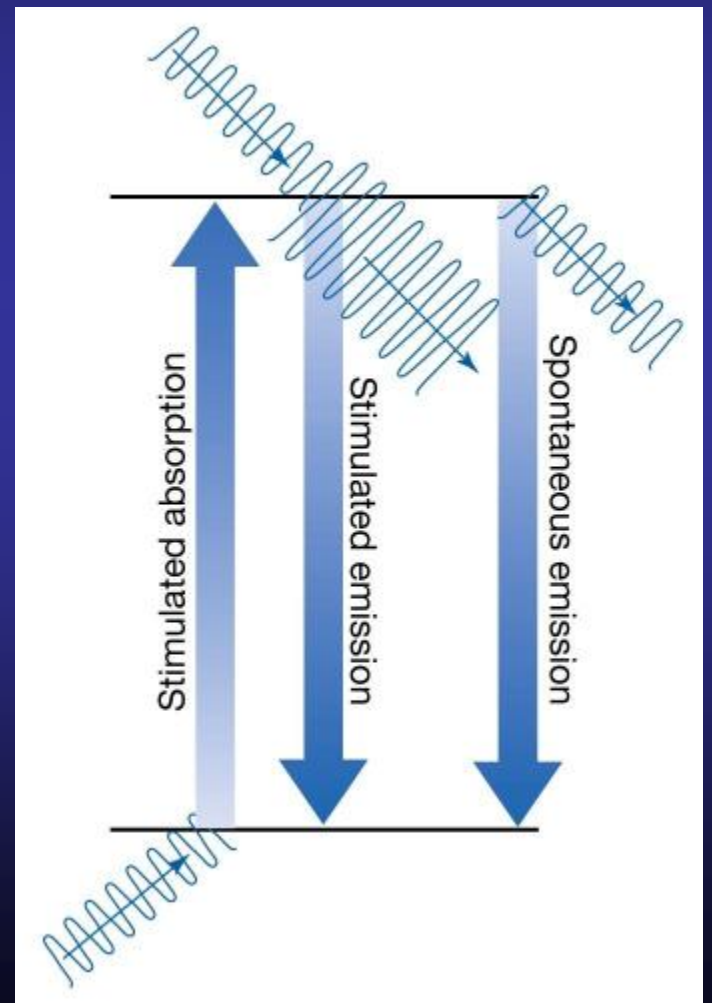


Optical transitions occurring due to the radiation-matter interaction

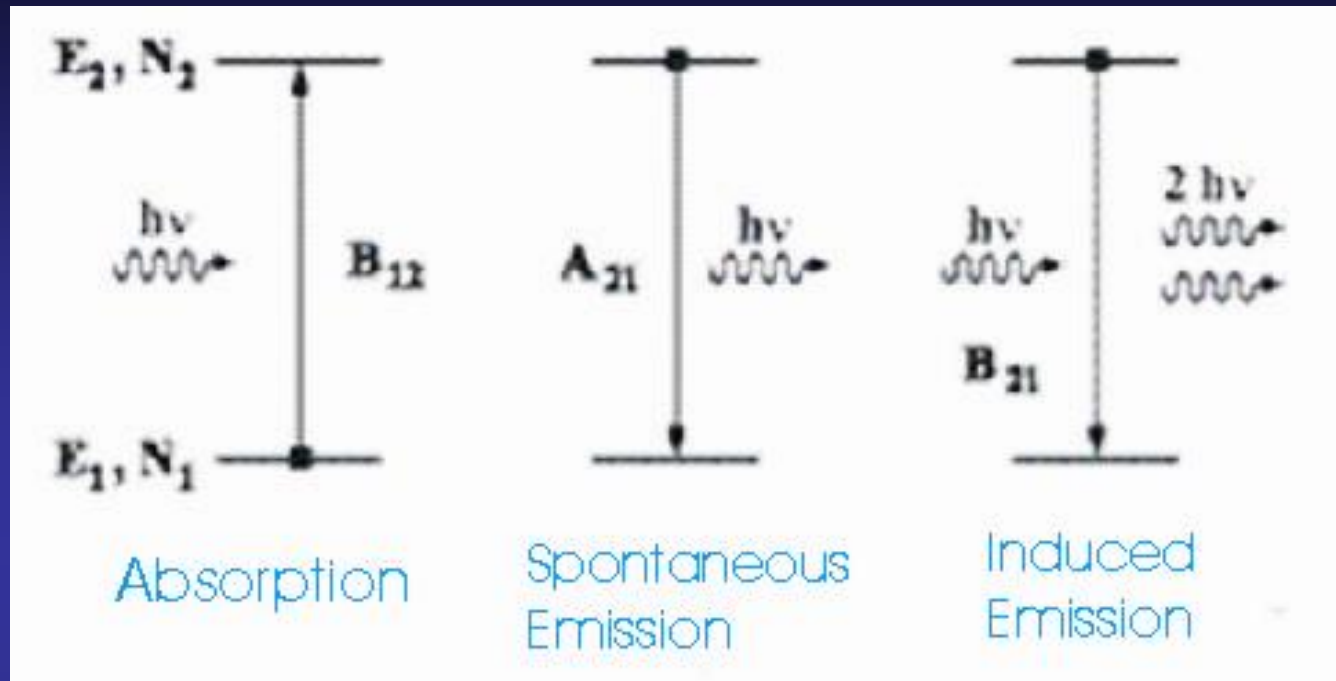
The integration absorption coefficient



Transitions



Einstein Coefficients



$$\frac{dN_2}{dt} = B_{12} \cdot u(n) \cdot N_1 \quad \frac{dN_2}{dt} = -A_{21} N_2 \quad \frac{dN_2}{dt} = -B_{21} \cdot u(n) \cdot N_2$$

$$B_{21} / B_{12} = g_2 / g_1$$

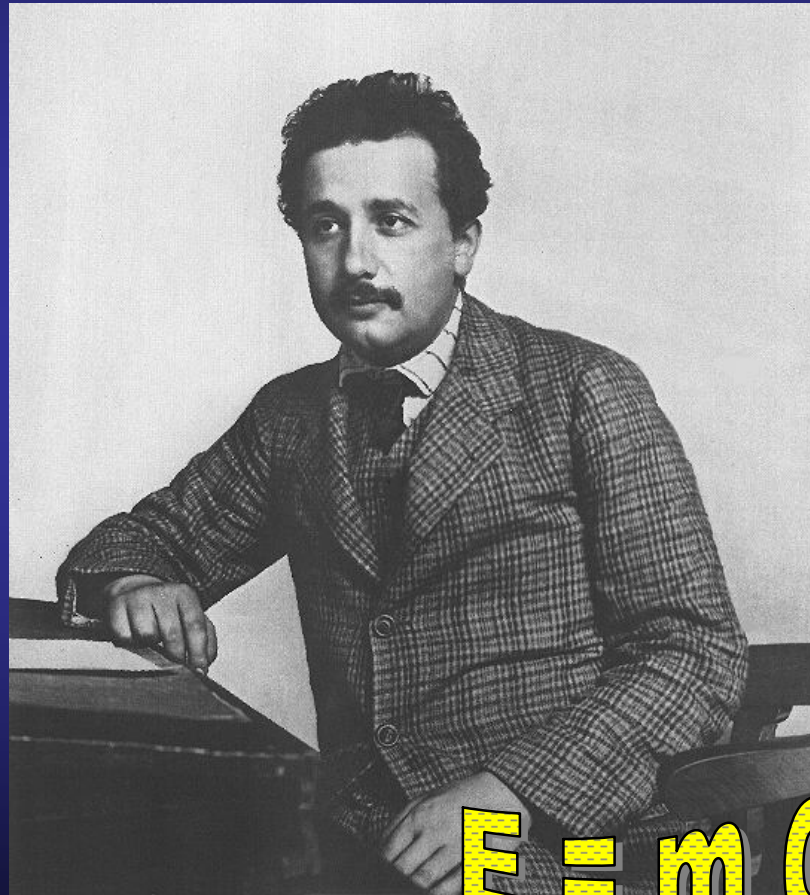
$$A_{21} / B_{12} = 8\pi h n^3 / c^3$$

Albert Einstein

* 14. März 1879 in Ulm, Württemberg
+ 18. April 1955 in Princeton, New Jersey, USA
Nobel Prize 1921 für Photoeffekt



He developed the Theory of Photoeffect, the Theory of Light Absorption my Matter, the Special Relativistic Theory, and the General Ralativistic Theory.



$$E = mc^2$$

Albert Einstein



Lambert-Beer Law

Transmittance of the sample::

$$T = I / I_0 \quad T = e^{-sNl} = e^{-\alpha},$$

where s [cm^2] is an absorption cross section, N [cm^{-3}] is a concentration, and l [cm] is a sample length.

The form which widely used in laboratory practice:

$$T = 10^{-\epsilon c l},$$

where ϵ [$\text{L mol}^{-1} \text{cm}^{-1}$] is the extinction coefficient and c [mol L^{-1}] is the molar concentration:

$$C = \frac{\text{Number of molecules}}{N_A V} = \frac{N}{N_A}$$

N_A is Avogadro number, $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$

Low Optical Density Approximation

In case if the exponent factor $a = s N l$ is small compared to unity, $a \ll 1$, the exponential function can be expanded over a . Keeping in this expansion only first two terms one comes to the important for practice particular case called **low optical density** of the sample:

$$I = I_0(1 - s N l)$$

Integrating the cross section $s = s(n)$ over the light frequency n within the absorption peak, one obtains the integrated cross section $\langle s(n) \rangle$:

$$\langle s \rangle = \int s(n) dn = B_{12} \frac{h n_0}{c}$$

where B_{12} is the Einstein absorption coefficient and n_0 is the center of the molecular absorption line. Thus, the Einstein coefficient B_{12} can be directly determined from experiment.

Spectral Line Shape

Uncertainty relation for energy:

$$\Delta E \approx \frac{\hbar}{t}$$

Two main processes which are responsible to the finite lifetime of excited states:

1. Spontaneous decay which is proportional to the corresponding Einstein coefficient A_{nm} . The intensity of the spontaneous decay is proportional to the square of the matrix element of the interaction of the molecule with electromagnetic modes of vacuum.

2. Interaction between the molecular quantum states and other particles and fields. In the gas phase, this interaction is mostly inelastic collisions with surrounding particles. In the condensed matter there can be interaction with phonons (vibration of the surrounding lattice).

The corresponding line has the Lorentz shape:

$$I(\nu) = \frac{1}{P} \frac{\frac{g}{2}}{(\nu - \nu_0)^2 + \left(\frac{g}{2}\right)^2}$$

where $\gamma = 1/2\pi\tau$ is the decay rate

and $\Delta\nu_L = \gamma$

Homogeneous (Lorentz) Broadening

	Condition	Δn_L (Hz)	Δn_L (cm ⁻¹)
Natural lifetimes	Gas phase, electronic transitions	$\sim 10^7$	$\sim 10^{-4}$
Natural lifetimes	Gas phase, rotational transitions	$\sim 10^{-4}$	$\sim 10^{-15}$
Collisional lifetimes	Gas, atmospheric pressure	$\sim 10^9$	$\sim 10^{-2}$
Collisional lifetimes	Liquid, electronic transitions	$\sim 10^{12}$	$\sim 10^1$

Inhomogeneous Broadening

The **Doppler effect** results in the shift of the light frequency when a light source is moving toward or away (+/-) from an observer. When the source emits radiation with a frequency ν_0 and moves with a velocity v , the observer detects the light frequency:

$$\nu = \nu_0 \left(1 \pm \frac{v_z}{c} \right)$$

Molecules in a gas move chaotically in all directions. In case of thermal equilibrium, the distribution of the molecular velocities along the line of detection (z axis) is known as the (1-dimensional) **Maxwell-Boltzmann distribution**:

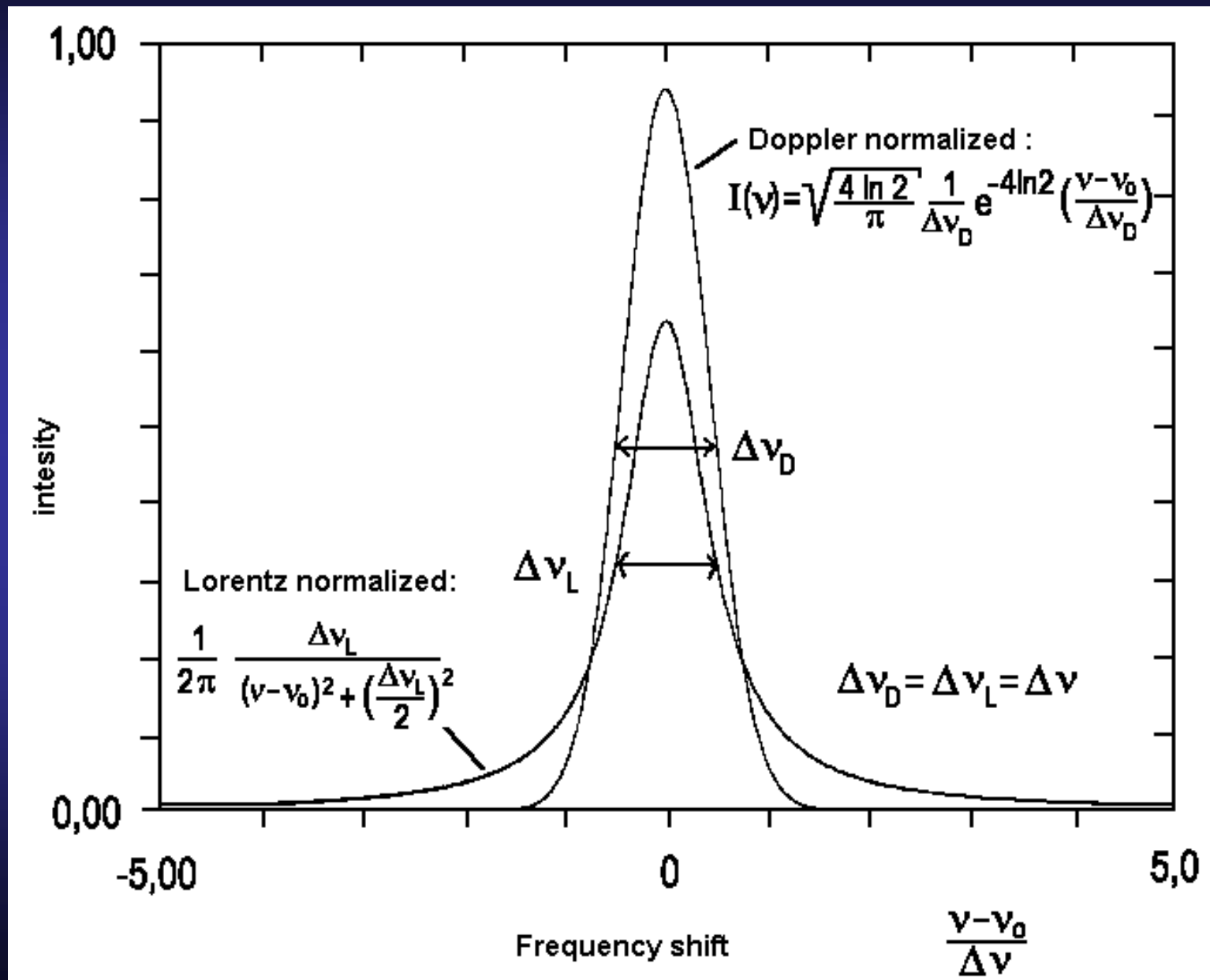
$$f(v_z) = \sqrt{\frac{m}{2\pi kT}} \exp\left[-\frac{m v_z^2}{2kT}\right]$$

The observer detects the corresponding **Doppler-broadened spectral line profile**:

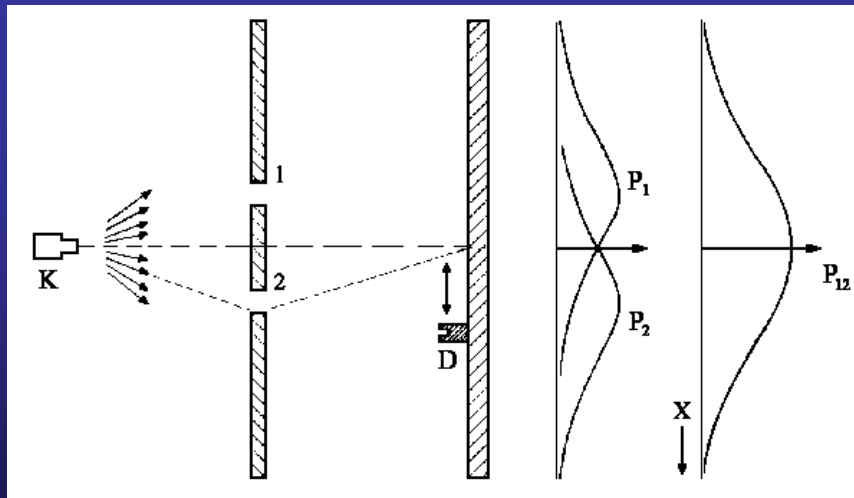
$$I(\nu) = \sqrt{\frac{4 \ln 2}{\pi}} \frac{1}{\Delta\nu_D} \exp\left[-4 \ln 2 \frac{(\nu - \nu_0)^2}{\Delta\nu_D^2}\right] \quad \text{where} \quad \Delta\nu_D = \frac{2\nu_0}{c} \sqrt{\frac{2 \ln 2 kT}{m}}$$

For transitions which belong to the visible or near-UV spectral range the **Doppler width** is typically within **one GHz** at temperature around 300 K. For this spectral range the **Doppler line broadening** is usually much larger than the lifetime (Lorentz-type) broadening.

Lorentz and Doppler Line Shapes



Experiment with particles



$$P_{12} = P_1 + P_2$$

de Broglie: a Particle is a Wave



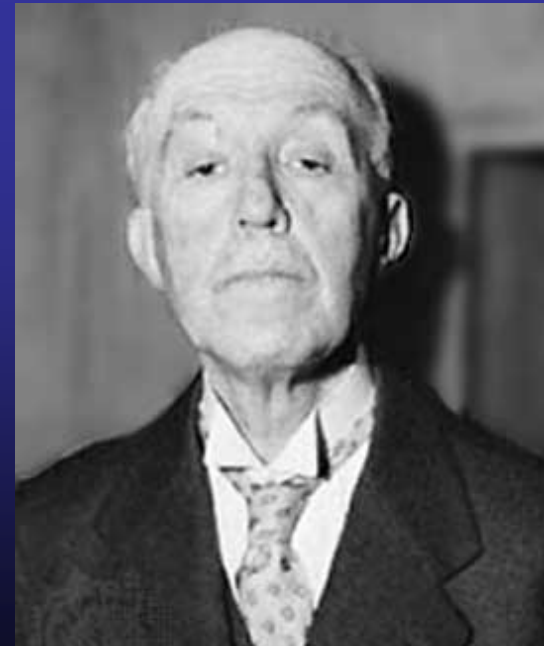
De Broglie's Dissertation "Recherches sur la théorie des quanta" in 1924 at the first time gave a relationship between a particle mass m , its velocity v , and the corresponding wavelength λ :

$$\text{Wavelength: } \lambda = \frac{h}{mv}$$

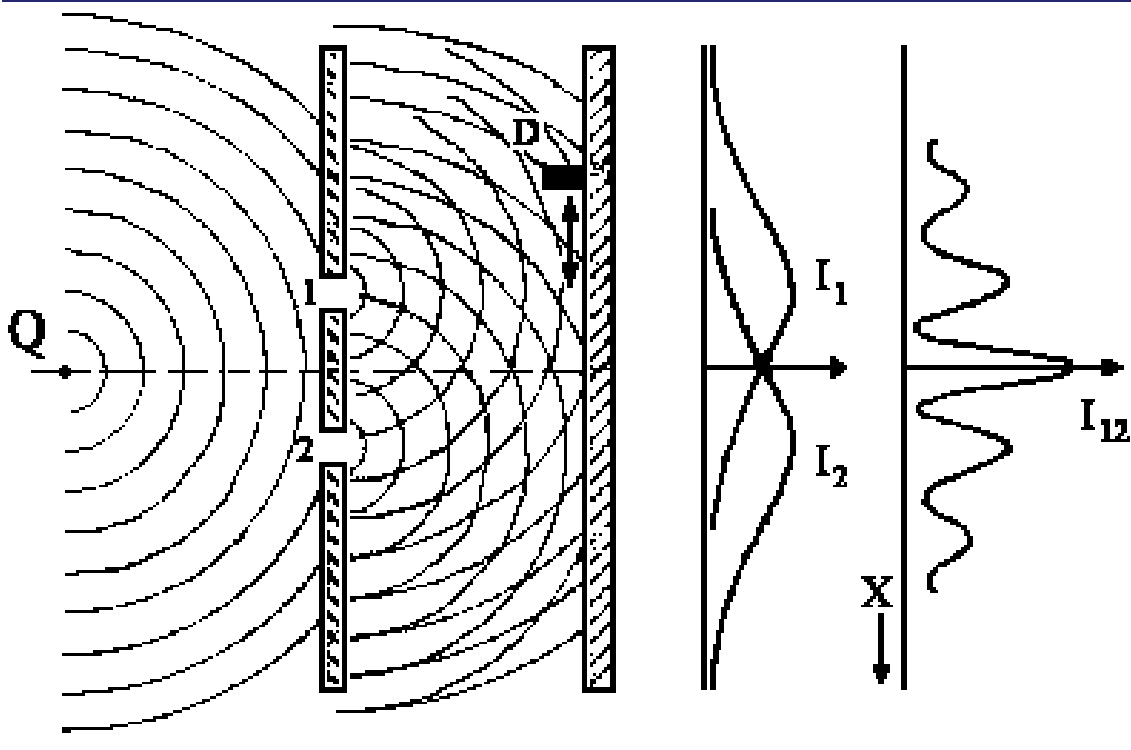
**Louis Victor Pierre Raymond
duc de Broglie**

* 15. Aug. 1892 in Dieppe, France
+ 19. März 1987 in Paris, France

Nobelpreis 1929



Interference of Matter Waves



$$\phi = A e^{-i\omega t + ikx}$$

$$\omega = 2\pi E/\hbar: \quad \text{Frequency}$$

$$\mathbf{k} = 2\pi/\lambda = \mathbf{p}/\hbar: \quad \text{Wavevector}$$

Probability to detect the particle

$$I = |\phi|^2$$

$$f = f_1 + f_2$$

$$I = |f_1 + f_2|^2$$

$$I = I_1 + I_2 + 2(I_1 I_2)^{1/2} \cdot \cos D\phi$$

where $\Delta\phi$ is the phase difference

The Schrödinger Equation

Time-independent Schrödinger Equation:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right] y(\mathbf{x}) = E y(\mathbf{x}) \quad (1 \text{ dimension})$$

$$\left[-\frac{\hbar^2}{2m} \Delta + V(x,y,z)\right] y(\mathbf{x},\mathbf{y},\mathbf{z}) = E y(\mathbf{x},\mathbf{y},\mathbf{z}) \quad (3 \text{ dimensions})$$

where Δ is the Laplace operator: $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Time-dependent Schrödinger Equation:

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V\right] y(\mathbf{x},t) = i\hbar \frac{\partial}{\partial t} y(\mathbf{x},t)$$

Normalization of the wave function:

$$\int_{-\infty}^{+\infty} |y(x,y,z)|^2 dx dy dz = 1$$

Calculation of the Probability Amplitude (Wavefunction)

1) Matrix algebra

Werner Heisenberg
Nobelpreis 1932

* 5. Dez. 1901
+ 1. Feb. 1976

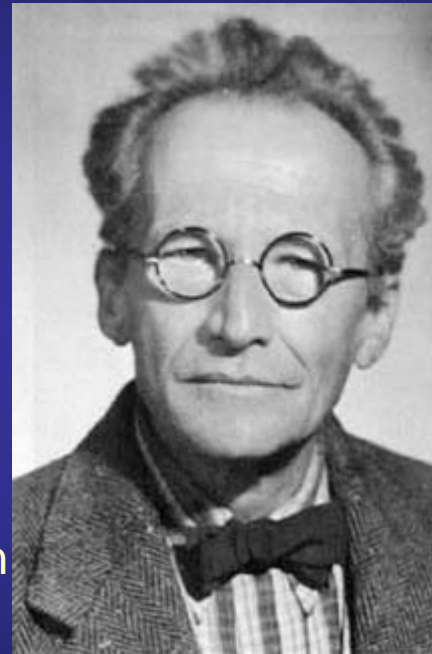


There are three mathematically equivalent ways for calculating the probability amplitude:

2) Differential equation, DGL

Erwin Schrödinger
Nobelpreis 1933

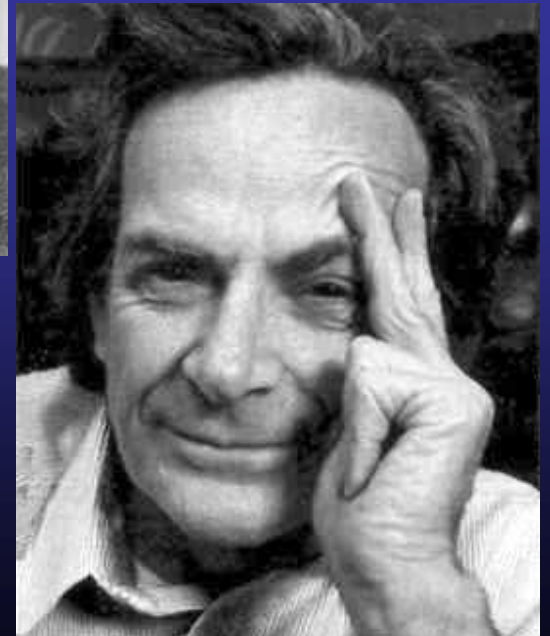
* 12. Aug. 1887 in Erdberg, Wien
+ 4. Jan. 1961 in Wien



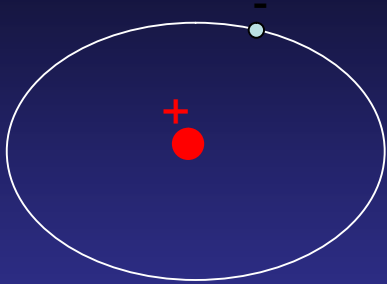
3) Trajectory integrals

Richard Feynman;
Nobelpreis 1965

* 11. Mai 1918 in Far Rockaway, New York
+ 15. Feb. 1988 in Los Angeles



Hydrogen Atom

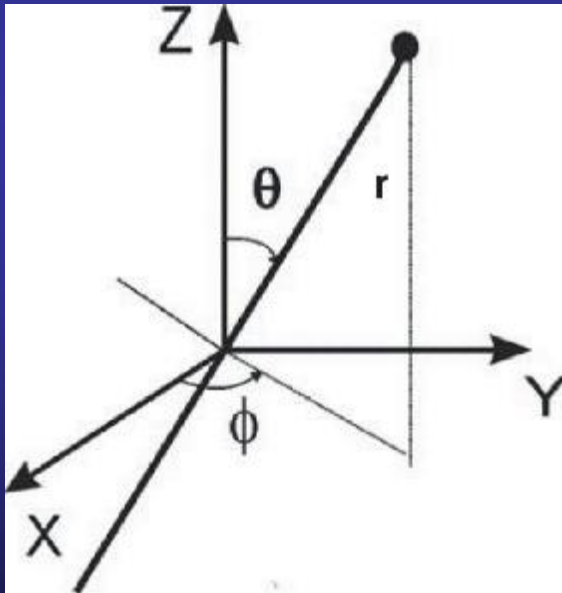


Hamiltonian

$$H y_k = E_k y_k$$

$$H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{Z e^2}{4\pi \epsilon_0 r}$$

Polar coordinates



$$\nabla_e^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \nabla_e^2 = \frac{1}{r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) + \Lambda^2(q, f)$$

$$\Lambda^2(q, f) = \frac{1}{\sin^2 q} \frac{\partial^2}{\partial q^2} + \frac{1}{\sin q} \frac{\partial}{\partial q} \sin q \frac{\partial}{\partial q}$$

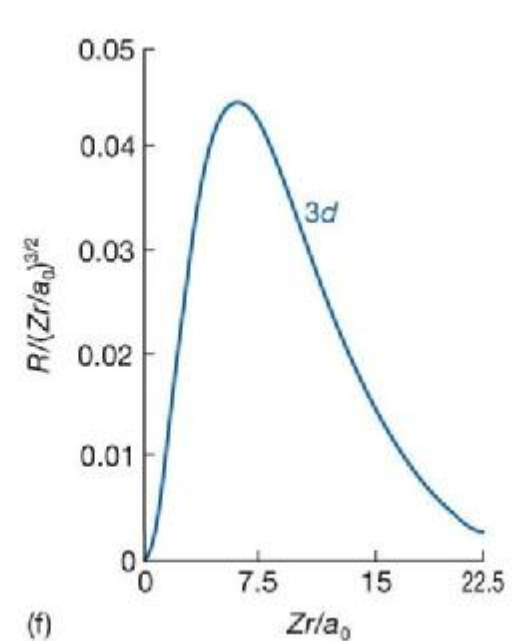
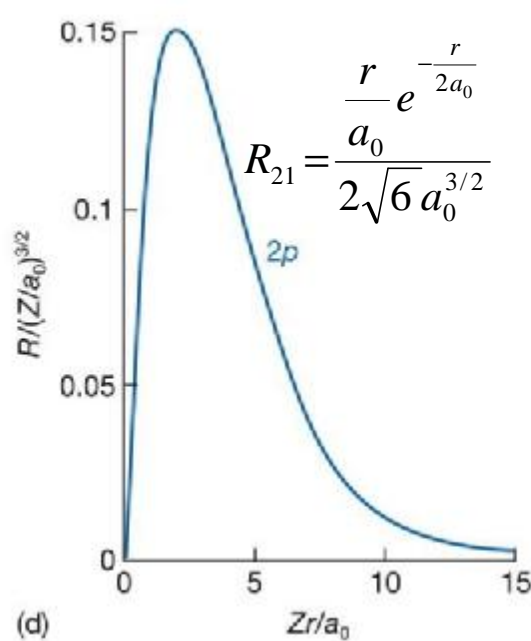
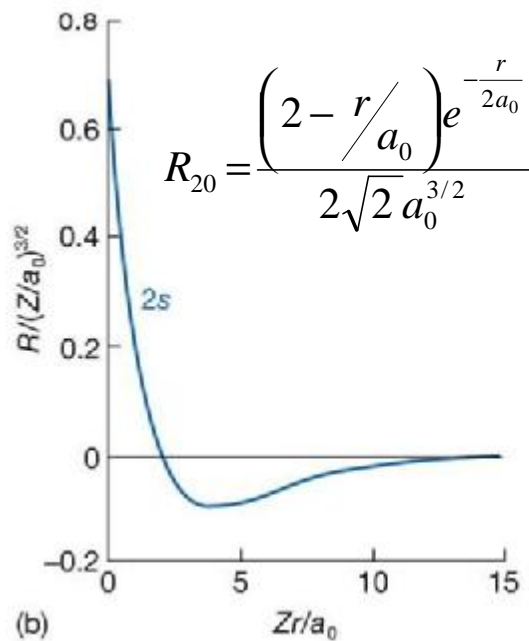
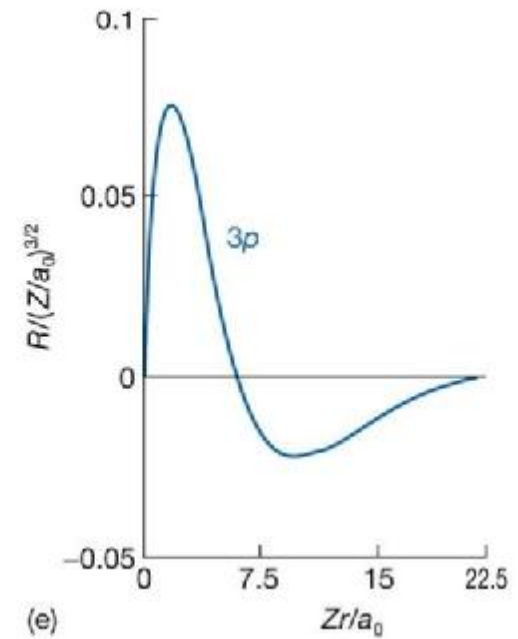
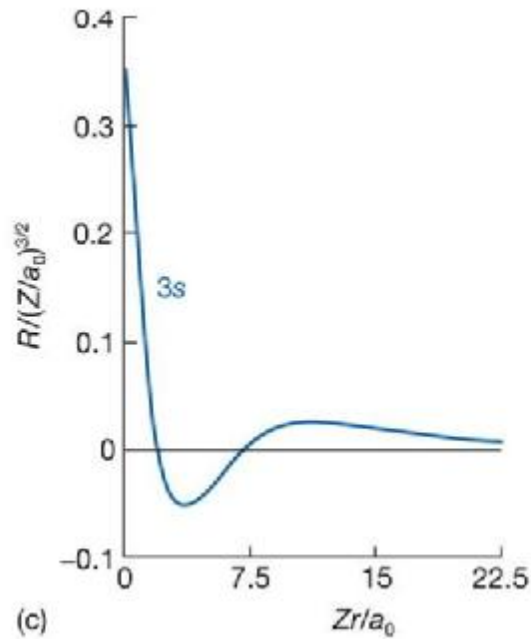
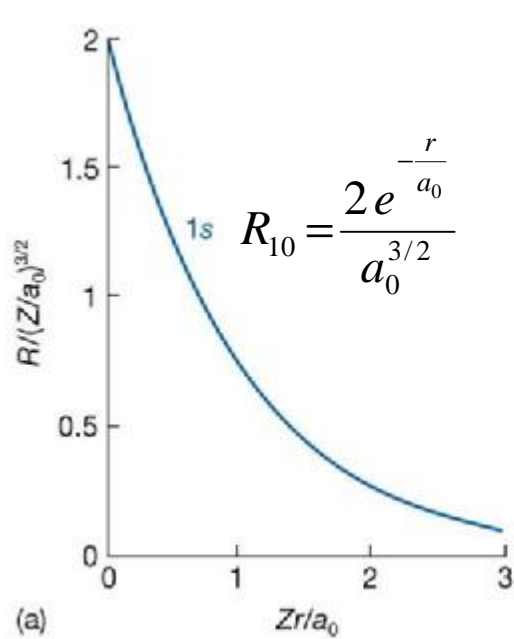
Wavefunctions

$$y_k(r, q, f) \quad \text{where } k \equiv n, l, s, m_l, m_s$$

$$y_k(r, q, f) = R_{nl}(r) Y_{lm_l}(q, f) c_{sm_s}$$

R_{nl} are Associated Laguerre Polynomials and Y_{lm} are Spherical Harmonics

Hydrogen Atom Wavefunctions: Radial Part



Spherical Harmonics $l = 0, 1, 2, 3, 4$

$$Y_{l,m}(\theta, \phi) = P_l^m(\cos \theta) \cdot f_m(\phi) \quad f_m(j) = 1/(2\pi)^{1/2} e^{im\phi}$$

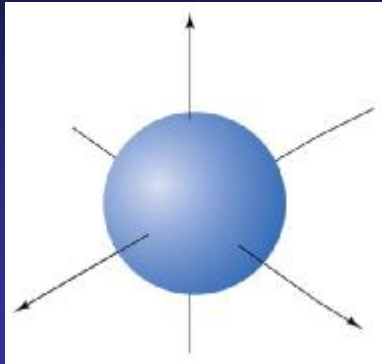
Electron	l	m	$Y_{l,m}(\theta, \phi)$	$ Y_{l,m} ^2$
s	0	0	$1/(4\pi)^{1/2}$	$1/4\pi$
p	1	± 1	$\mp (3/8\pi)^{1/2} \sin \theta e^{\pm i\phi}$	$3/8\pi \sin^2 \theta$
	1	0	$(3/4\pi)^{1/2} \cos \theta$	$3/4\pi \cos^2 \theta$
d	2	± 2	$(15/32\pi)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$	$15/32\pi \sin^4 \theta$
	2	± 1	$\mp (15/8\pi)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}$	$15/8\pi \sin^2 \theta \cos^2 \theta$
	2	0	$(5/16\pi)^{1/2} (3\cos^2 \theta - 1)$	$5/16\pi (3\cos^2 \theta - 1)^2$
f	3	± 3	$\mp (35/64\pi)^{1/2} \sin^3 \theta e^{\pm 3i\phi}$	$35/64\pi \sin^6 \theta$
	3	± 2	$(105/32\pi)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$	$105/32\pi \sin^4 \theta \cos^2 \theta$
	3	± 1	$\mp (21/64\pi)^{1/2} \sin \theta (5\cos^2 \theta - 1) e^{\pm i\phi}$	$21/64\pi \sin^2 \theta (5\cos^2 \theta - 1)^2$
	3	0	$(7/16\pi)^{1/2} (5\cos^3 \theta - 3\cos \theta)$	$7/16\pi (5\cos^3 \theta - 3\cos \theta)^2$
g	4	± 4	$(315/512\pi)^{1/2} \sin^4 \theta e^{\pm 4i\phi}$	$315/512\pi \sin^8 \theta$
	4	± 3	$\mp (315/64\pi)^{1/2} \sin^3 \theta \cos \theta e^{\pm 3i\phi}$	$315/64\pi \sin^6 \theta \cos^2 \theta$
	4	± 2	$(225/660\pi)^{1/2} \sin^2 \theta (7\cos^2 \theta - 1) e^{\pm 2i\phi}$	$225/660\pi \sin^4 \theta (7\cos^3 \theta - 1)^2$
	4	± 1	$\mp (225/320\pi)^{1/2} \sin \theta (7\cos^3 \theta - 3\cos \theta) e^{\pm i\phi}$	$225/320\pi \sin^2 \theta (7\cos^3 \theta - 3\cos \theta)^2$
	4	0	$(9/256\pi)^{1/2} (35\cos^4 \theta - 30\cos^2 \theta + 3)$	$9/256\pi (35\cos^4 \theta - 30\cos^2 \theta + 3)^2$

Real wave functions (linear combinations)

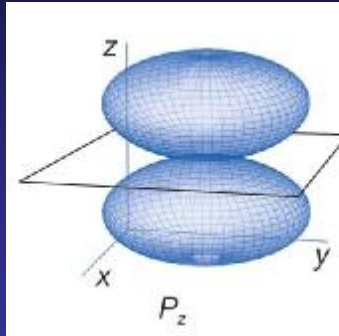
l	$ m_l $	Wave Functions
0	0	$s = 1/(4\rho)^{1/2}$
1	0	$p_z = Y_{10} = (3/4\pi)^{1/2} \cos\theta$
	1	$p_x = -1/\sqrt{2} (Y_{11} - Y_{1-1}) = (3/4\pi)^{1/2} \sin\theta \cos f$
	1	$p_y = i/\sqrt{2} (Y_{11} + Y_{1-1}) = (3/4\pi)^{1/2} \sin\theta \sin f$
2	0	$d_{3z^2-r^2} = Y_{20} = (5/16\pi)^{1/2} (3 \cos^2\theta - 1)$
	1	$d_{xz} = -1/\sqrt{2} (Y_{21} - Y_{2-1}) = (15/4\pi)^{1/2} \sin\theta \cos\theta \cos f$
	1	$d_{yz} = i/\sqrt{2} (Y_{21} + Y_{2-1}) = (15/4\pi)^{1/2} \sin\theta \cos\theta \sin f$
	2	$d_{x^2-y^2} = 1/\sqrt{2} (Y_{22} + Y_{2-2}) = (15/16\pi)^{1/2} \sin^2\theta \cos 2f$
	2	$d_{xy} = -i/\sqrt{2} (Y_{22} - Y_{2-2}) = (15/16\pi)^{1/2} \sin^2\theta \sin 2f$

Hydrogen Atom Wavefunctions: Angular Part

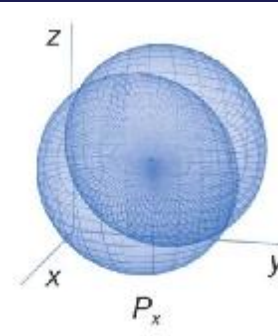
s orbital:
 $l = 0 \ m = 0$



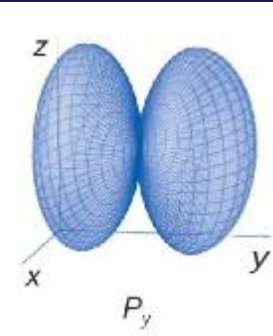
p_z orbital:
 $l = 1 \ m = 0$



p_x orbital
 $l = 1 \ m = \pm 1$

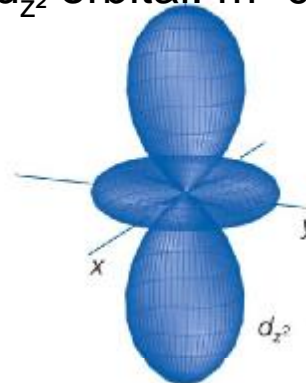


p_y orbital

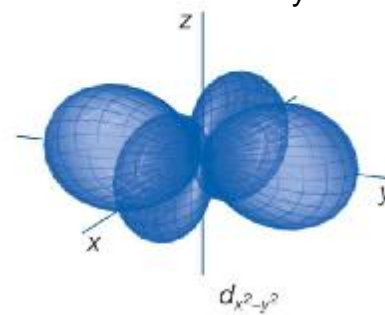


$l = 2$

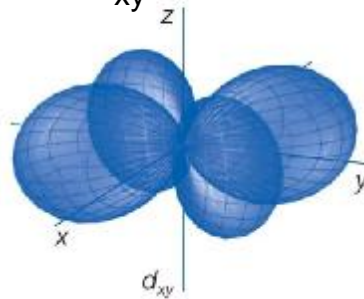
d_{z^2} orbital: $m=0$



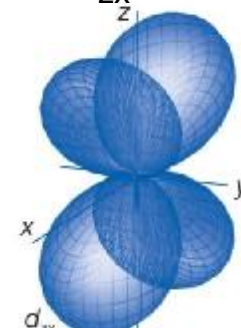
$d_{x^2-y^2}$ orbital



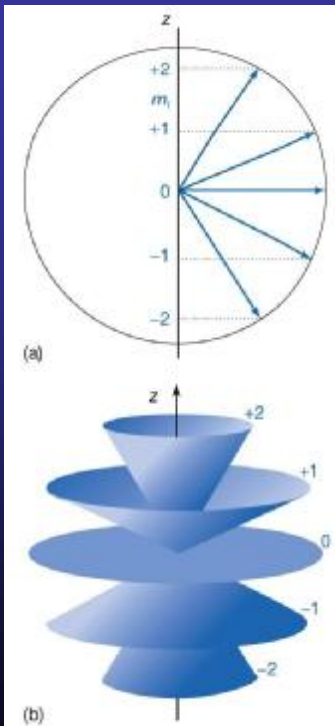
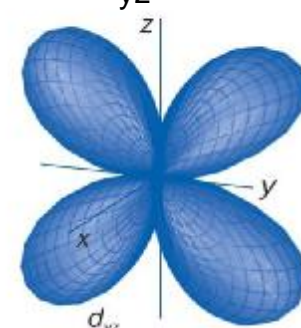
d_{xy} orbital



d_{zx} orbital



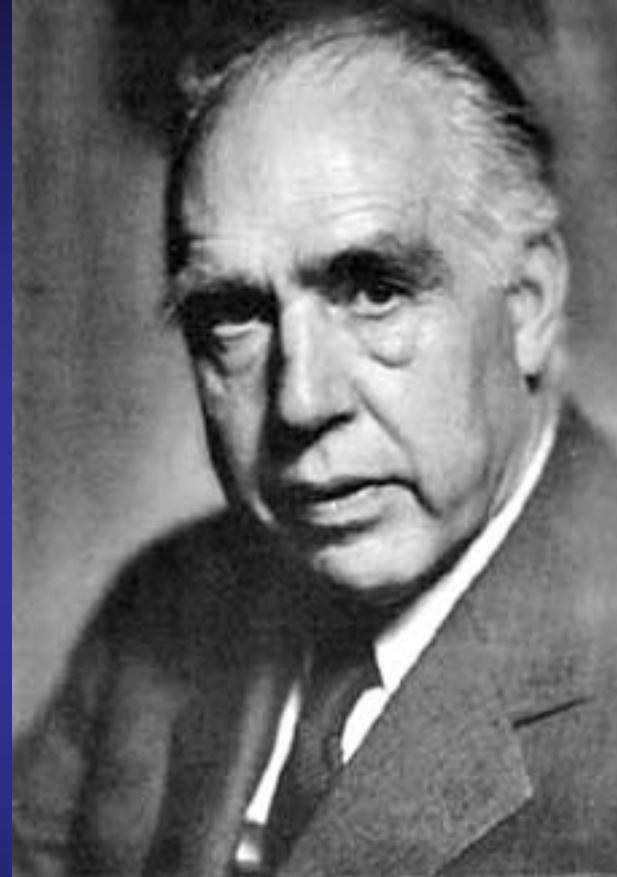
d_{yz} orbital



Niels Henrik David Bohr

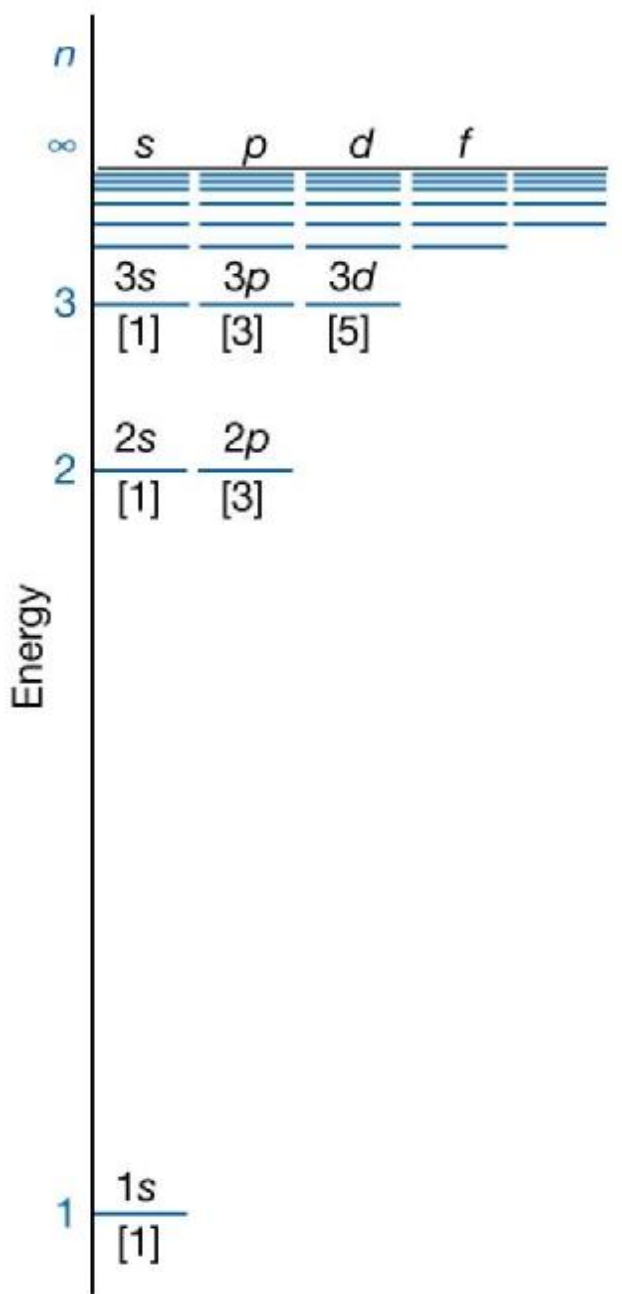


* 7. Okt. 1885 in Kopenhagen,
+ 18. Nov. 1962 in Kopenhagen



Nobelpreis 1965

Hydrogen Atom Energy Levels



$$E_{nl} = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_0 n^2} \quad n=1, 2, 3, \mathbf{K}$$

ϵ_0 is the Vacuum permittivity; $\epsilon_0 = 8.854 \cdot 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
 e is the Elementary charge; $e = 1.602 \cdot 10^{-19} \text{ C}$
 a_0 is the Bohr radius; $a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2 = 5.292 \cdot 10^{-11} \text{ m}$

Selection rules for radiative transitions:

$$l'' - l' = \pm 1, \quad m_l'' - m_l' = 0, \pm 1$$

$$s'' - s' = 0, \quad m_s'' - m_s' = 0$$

Spin-orbital interaction in Hydrogen atom

Electron orbital magnetic moment:

$$\mathbf{m}_l = -m_B \frac{\mathbf{l}}{\hbar}$$

z-projection:

$$m_{lZ} = -m_B m_l$$

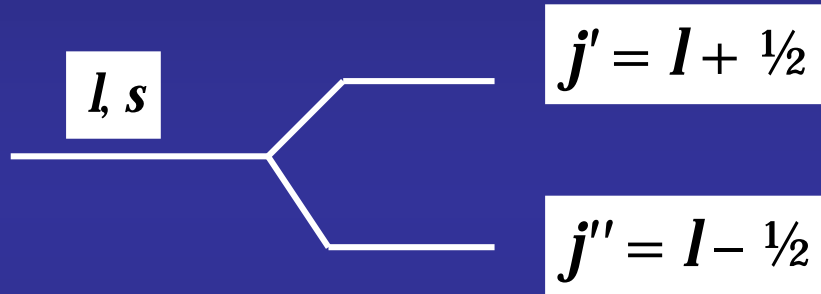
Electron spin magnetic moment:

$$\mathbf{m}_s = -2m_B \frac{\mathbf{s}}{\hbar}$$

z-projection:

$$m_{sZ} = -2m_B m_s$$

$$\mathbf{j} = \mathbf{l} + \mathbf{s}$$



where μ_B is the Bohr magneton:

$$m_B = \frac{e\hbar}{2m_e} = 9,27 \cdot 10^{-24} \frac{J}{T}$$

$$\Delta E_{j''j'} = \frac{a^2 Z^4}{n^3 l(l+1)} \frac{1}{2} \frac{m_e e^4}{\hbar^2}$$

$\alpha \approx 1/137$ - fine structure constant

For $n = 2, 3$ и 4 $\Delta E_{j''j'} = 0,36, 0,12, 0,044$ cm⁻¹

Selection rules for radiative transitions:

$$j'' - j' = 0, \pm 1, \quad m_{j''} - m_{j'} = 0, \pm 1$$

Multi-electron atoms

1. Each electron moves in the field of **atomic nucleus** and all **other electrons**. This field is named the **Self-Consistent Field**. The Self-Consistent field is spherically symmetric, however it is not a **Coulomb field**. The corresponding Schrödinger equation cannot be solved analytically. Approximate wave functions and atomic energy levels for each electron can be obtained by computing the set of **Hartree-Fock** differential equations.
2. The obtained one-electron energy levels depend on the quantum numbers n и l . These energy levels are filled by all electrons which form the electron configuration of an atom. The filling of the energy levels is performed following the **Pauli Principle**:

Two electrons cannot simultaneously occupy the state with the same quantum numbers

Therefore, each **s-state** ($l = 0$) can be populated with no more than **two** electrons, each **p-state** ($l = 1$) can be populated with no more than **six** electrons, each **d-state** ($l = 2$) can be populated with no more than **ten** electrons and so on.

3. The quantum numbers which describe a quantum state of the whole multielectron atom can be obtained by summation the moments of individual electrons using the quantum mechanical rules:

L – total orbital angular momentum of the atom, **M_L** – projection of **L** onto the direction **Z**

S – total electron spin, **M_S** – projection of **S** onto the direction **Z**

J – total electron angular momentum, **$J = L + S$** . **M_J** – projection of **J** onto the direction **Z** .

$P = (-1)^{\sum l_i} = \pm 1$ – atomic parity.

Wolfgang Ernst Pauli



Nobelpreis 1945



* 25. April 1900 in Wien
+ 15. Dez. 1958 in Zürich

The nomenclature of the energy levels (terms) in multielectron atoms in the LS approximation.

$$2S+1 L_J^o \quad \text{- odd states}$$

$$2S+1 L_J \quad \text{- even states}$$

$$L = 0 \longrightarrow \text{S -state}$$

$$L = 1 \longrightarrow \text{P -state}$$

$$L = 2 \longrightarrow \text{D -state}$$

$$S = 0 \longrightarrow \text{Singlet state}$$

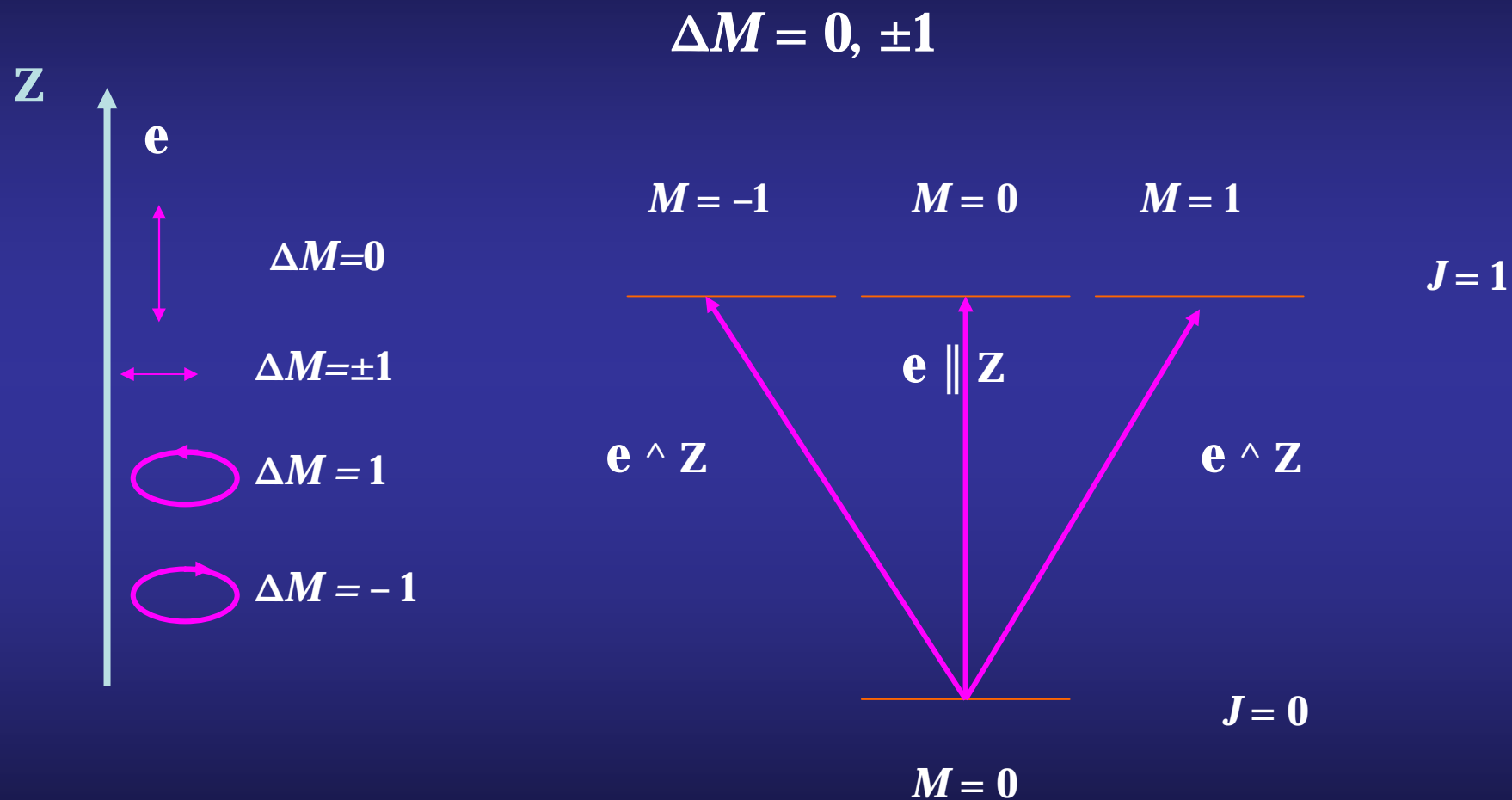
$$S = 1 \longrightarrow \text{Triplet state}$$

Selection rules for radiative transitions in multielectron atoms

$L - L'$	$M_L - M_L'$	$S - S'$	$M_S - M_S'$	$J - J'$	$M_J - M_J'$	P
$0, \pm 1$	$0, \pm 1$	0	0	$0, \pm 1$	$0, \pm 1$	$+\leftrightarrow -$

$$J + J' \geq 1!$$

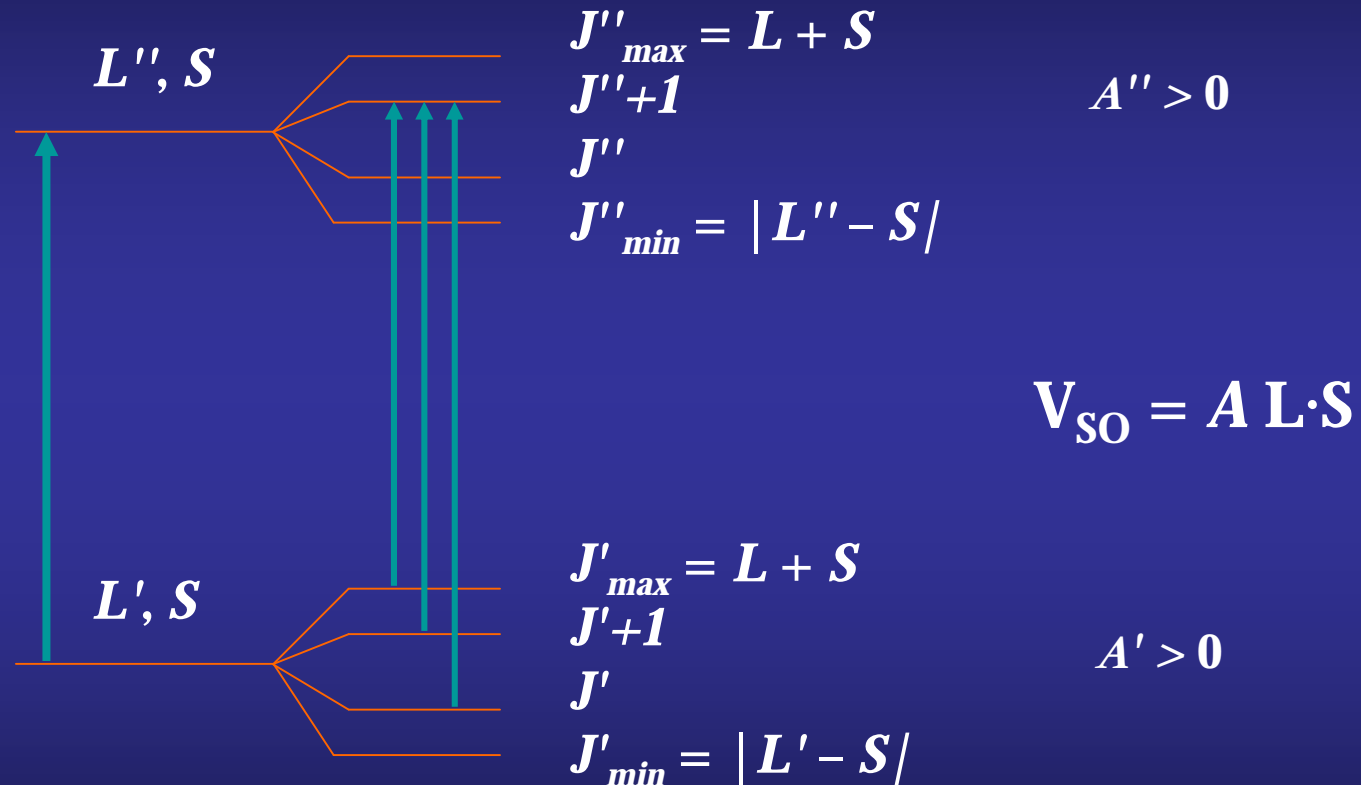
Physical meaning of the selection rules for the quantum number M



In the absence of external fields all M -sublevels at fixed J -value are degenerated!

The fine structure of spectral lines

The fine structure is a result of the spin-orbit interaction

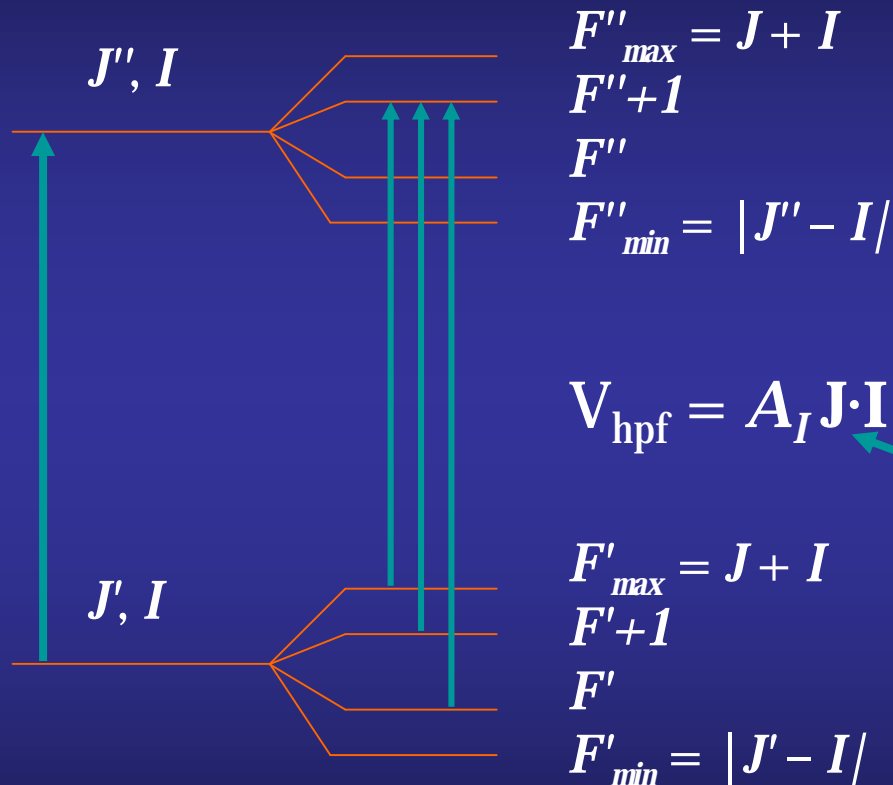


$$E_J = \frac{1}{2} A [J(J+1) - S(S+1) - L(L+1)] \rightarrow \Delta E_{J, J-1} = A J$$

This is the Lande interval rule

The hyperfine structure of spectral lines

The hyperfine structure of spectral lines is a results of interaction between the dipole and quadrupole moments of nuclei with electrons



Nuclear magnetic dipole moment
 $\mu = \mu_n g_I \mathbf{I}$
 g_I is the nuclear gyromagnetic ratio
 μ_n is the nuclear magneton

Nuclear electric quadrupole moment

$$Q_{\alpha\beta} = \sum_i e_i (3r_{i\alpha} r_{i\beta} - \delta_{\alpha\beta} r_i^2)$$

$$Q = \langle \gamma \mathbf{I} M_I | Q_{ZZ} | \gamma \mathbf{I} M_I \rangle_{M=I}$$

$$W = W_m + W_Q = -mH(0) + \frac{e}{6} \sum_{a,b} Q_{ab} \frac{\partial^2 j}{\partial x_a \partial x_b}$$

$$E_F = \frac{1}{2} A_I [F(F+1) - J(J+1) - I(I+1)] \rightarrow \Delta E_{F, F-1} = A_I F \quad \mathbf{F} = \mathbf{J} + \mathbf{I}$$

Lande interval rule

A little-bit of quantum mechanics: Perturbation theory for nondegenerate quantum states

The exact solution for the non-perturbed quantum problem is known:

$$H_0 \psi_n^{(0)} = E^{(0)} \psi_n^{(0)}$$

where $\psi_n^{(0)}$ is the non-perturbed wave function

The full Hamiltonian: $H = H_0 + V$, where $H_0 \gg V$

We seek for an approximate solution for the full Hamiltonian H :

$$(H_0 + V) \psi = E \psi$$

1. The perturbed wave function is presented as an expansion over the unperturbed wave functions
2. This expansion is substituted into the Schrödinger equation for the full Hamiltonian
3. The obtained expression is multiplied from the left by $Y_k^{(0)}(q)$ and integrated over all coordinates q .
4. Using the orthogonality of the wave function, we obtain the first approximation correction for the k – level energy:

$$y(q) = \sum_n c_n y_n^{(0)}(q)$$

$$E_k^{(1)} = \int y_k^{(0)*}(q) V y_k^{(0)}(q) dq = \langle y_k^{(0)} | V | y_k^{(0)} \rangle$$

The perturbation theory for non-degenerate quantum states: Second-order approximation

5. Substituting the obtained first-order solution again the Schrödinger equation we can get the expression for the second-order correction to the k – th level energy:

$$E_k^{(2)} = \sum_m \frac{\langle k | V | m \rangle \langle m | V | k \rangle}{E_k - E_m}, \quad m \neq k$$

In general, $E_k = E_k^{(0)} + E_k^{(1)} + E_k^{(2)} + \dots$

The perturbation theory for degenerate quantum states

$$\text{The Hamiltonian: } H = H_0 + V$$

The exact solution for the non-perturbed wave function is:

$$H_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$$

where $E_n^{(0)} = E_{n'}$

We seek for an approximate solution for the full Hamiltonian H :

$$(H_0 + V) \psi = E \psi$$

1. The wave function in the zero approximation $\Psi^{(0)}(q)$ is sought as an expansion over the wave functions $\Psi_n^{(0)}(q)$

2. This expansion is substituted to the Schrödinger equation for the full Hamiltonian

$$\Psi^{(0)}(q) = \sum_n c_n^{(0)} \Psi_n^{(0)}(q)$$

3. The obtained expression is multiplied from the right on $\Psi_n^{(0)}(q)$ and integrated over all coordinates q .

4. The solution of the obtained set of algebraic equations gives the energy corrections of the 1st approximation E_n and the expansion coefficients $c_n^{(0)}$.

The perturbation theory for degenerate quantum states

The set of N linear equations for determination of the expansion coefficients $c_n^{(0)}$ and the energy corrections E_n

$$\sum_{n'} \left(\langle n | V | n' \rangle - d_{n,n'} E_n \right) c_{n'}^{(0)} = 0$$

This determinant must be equal to zero which allows for determination of the 1st approximation energy corrections E_n .

The determinant is equivalent to the N^{th} -order algebraic equation on the variable E , which is called Secular Equation

$$\begin{vmatrix} V_{11} - E & V_{12} & \mathbf{L} & V_{1N} \\ V_{21} & V_{22} - E & \mathbf{L} & V_{2N} \\ \mathbf{L} & \mathbf{L} & \mathbf{L} & \mathbf{L} \\ V_{N1} & V_{N2} & \mathbf{L} & V_{NN} - E \end{vmatrix} = 0$$

An atom in an external electric field: Stark effect

$$W_E = -E D = e E \sum_i r_i$$

$$\Delta E_{gJM} = -E \langle gJM | D_Z | gJM \rangle + E^2 \sum_{g'J'} \frac{\langle gJM | D_Z | g'J'M \rangle \langle g'J'M | D_Z | gJM \rangle}{E_{gJ} - E_{g'J'}}$$

0

$$\Delta E_{\gamma JM} = E^2 [A_{\gamma J} + B_{\gamma J} M^2]$$

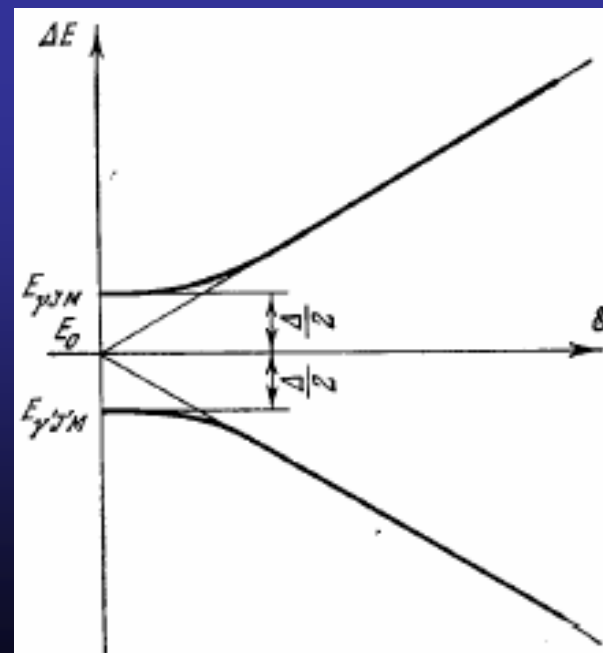
After applying a homogeneous external electric field, the energy level $|\gamma JM\rangle$ is splitted into the components which refer to the quantum numbers:

$$|M| = J, J-1, \dots,$$

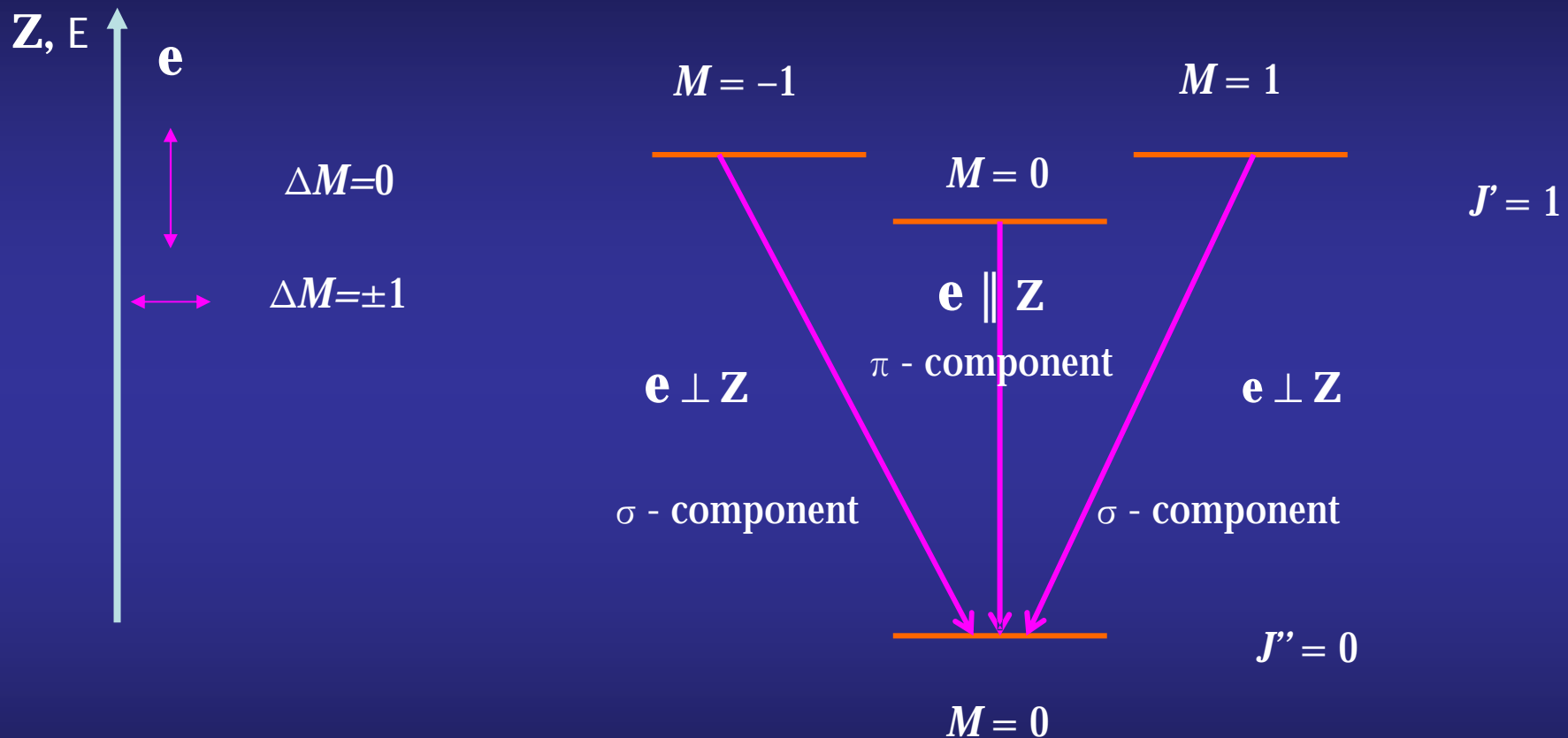
In case of strong electric field when the Stark shifts are comparable with the initial splitting between the energy levels $|\gamma J\rangle$, $|\gamma' J'\rangle$, the expression for the total energy splitting is written as:

$$\Delta E_{1,2} = \pm \sqrt{\left(\frac{\Delta}{2}\right)^2 + E^2 |\langle gJM | D_Z | g'J'M \rangle|^2}$$

Thus, for large fields the initially quadratic Stark effect becomes linear.



Fluorescence polarization due to the Stark effect



Observing the fluorescence from the state $J' = 1$ to the state $J'' = 0$ along the electric field direction, one can see **a single** spectral line (σ - component), while observing the fluorescence perpendicular to the electric field direction, one can see **two** close spectral lines (σ - and π - components).

An atom in an external magnetic field: Zeeman effect

$$W_B = - \mu B$$

$\mu = - \mu_B g J$, where $m_B = \frac{e h}{2 m_e}$ is the Bohr magneton, $\mu_B \approx 9,2732 \times 10^{-24}$ Joule/Tesla and g is the gyromagnetic ratio

$$E_B = \langle W_B \rangle = g \mu_B B M$$

Therefore, after applying of an external magnetic field the energy level $|\gamma J M\rangle$ splits into $2J+1$ components which refer to the quantum numbers:

$$M = J, J-1, \dots, -J$$

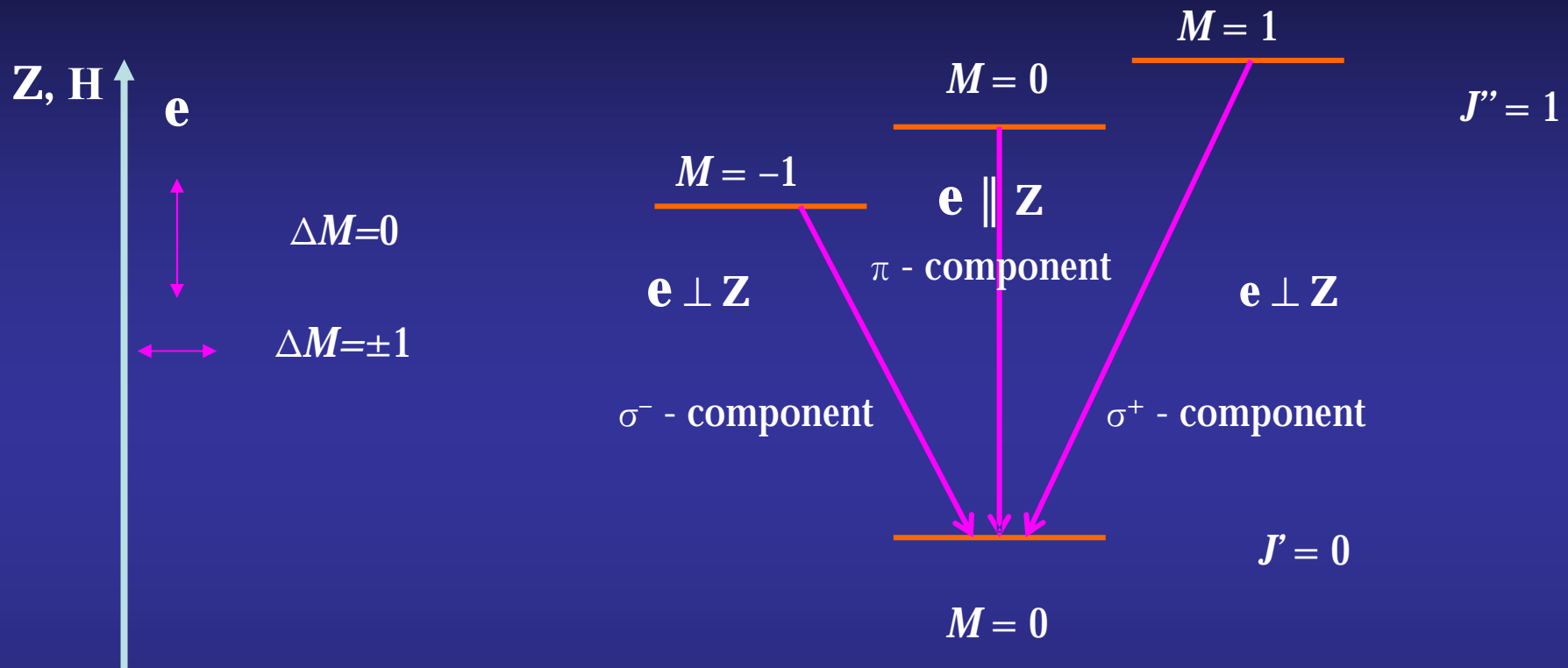
In case of the LS-coupling

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

In case of a pure **orbital** angular momentum ($J=L, S=0$), $g = 1$

In case of a pure **spin** angular momentum ($J=S, L=0$), $g = 2$

Fluorescence polarization due to the Zeeman effect



Observation the fluorescence from the excited state $J'=1$ to the ground state $J''=0$ along the magnetic field shows a spectral line consisting of **two** components (σ^+ and σ^-), Observation along the direction perpendicular to the magnetic field shows a spectral line consisting of **three** components (σ^+ , σ^- and π).

Radiation transitions

Quantization of the electromagnetic field

$$\mathbf{W}_{field} = \mathbf{h}\omega \left(n_{kr} + \frac{1}{2} \right)$$

According to the Quantum Electrodynamics, the probability of radiation transition can be presented in the form:

$$dW_{em} = \frac{e^2 \omega}{2p \mathbf{h} c^3 m^2} \left| \langle gJM | \mathbf{e}_{kr} \mathbf{p} e^{i\mathbf{k}\mathbf{r}} | g'J'M' \rangle \right|^2 (\bar{n}_{kr} + 1) dO$$
$$dW_{ab} = \frac{e^2 \omega}{2p \mathbf{h} c^3 m^2} \left| \langle gJM | \mathbf{e}_{kr} \mathbf{p} e^{-i\mathbf{k}\mathbf{r}} | g'J'M' \rangle \right|^2 \bar{n}_{kr} dO$$

Expanding the exponent over the powers of kr , one can obtain particular expressions for multipole radiation. The **first** term of the expansion (it's **1**), $e^{i\mathbf{k}\mathbf{r}} = 1 + i\mathbf{k}\mathbf{r} + \dots$, describes the electric dipole emission and absorption.

Multipole emission and absorption

Electric dipole emission and absorption

$$dW_{DE}^{sp} = \frac{w^3}{2p\hbar c^3} \left| \langle gJM | \mathbf{e}_{kr} \cdot \mathbf{D} | g'J'M' \rangle \right|^2 dO$$

$$dW_{DE}^{ind} = \frac{4p^2}{\hbar^2 c} \left| \langle gJM | \mathbf{e}_{kr} \cdot \mathbf{D} | g'J'M' \rangle \right|^2 I_w dO$$

$$\mathbf{D} = e \sum_i \mathbf{r}_i$$

Selection rules:

$$\Delta J = 0, \pm 1$$

$$\Delta M_J = 0, \pm 1$$

$$\Delta P \neq 0 \quad (+ \leftrightarrow -)$$

Magnetic dipole emission and absorption

$$dW_{DM}^{sp} = \frac{w^3}{2p\hbar c^3} \left| \langle gJM | \hat{\mathbf{m}}_{kr} \cdot \mathbf{M} | g'J'M' \rangle \right|^2 dO$$

$$dW_{DM}^{ind} = \frac{4p^2}{\hbar^2 c} \left| \langle gJM | \hat{\mathbf{m}}_{kr} \cdot \mathbf{M} | g'J'M' \rangle \right|^2 I_w dO$$

$$\mathbf{M} = -\frac{e\hbar}{2mc} \sum_i (\mathbf{l}_i + 2\mathbf{s}_i)$$

Selection rules:

$$\Delta J = 0, \pm 1$$

$$\Delta M_J = 0, \pm 1$$

$$\Delta P = 0 \quad (+ \leftrightarrow + \text{ or } - \leftrightarrow -)$$

A link between theoretical and experimental quantities

Provided only emission, but no other processes like collisions with other particles or internal conversions occur, a measurement of the fluorescence lifetime τ directly yields the transition probability A_{mn} which gives you also B_{mn} :

$$A_{mn} = 1/\tau$$

$$\frac{A_{mn}}{B_{mn}} = \frac{8\pi\hbar\nu^3}{c^3}$$

From theory the quantity $R_{mn} = \int \phi_m^* \vec{r} \phi_n dV$ is calculated, which is linked to A_{mn} :

$$A_{mn} = \frac{8\pi^2 e^2}{3\hbar\epsilon_0 c^3} \cdot \nu_{mn}^3 |R_{mn}|^2$$

Here follows the relationships between the integrated absorption cross section σ_o , the Einstein coefficient B_{mn} , the quantity R_{mn} , and the oscillator strength f :

$$\sigma_o = B_{mn} \cdot \frac{h\nu}{c} = \frac{\pi e^2 \nu}{3\epsilon_0 \hbar c} \cdot |R_{mn}|^2 = \frac{e^2}{4\epsilon_0 c m_e} \cdot f_{mn}$$

$$B_{mn} = \frac{c}{h\nu} \cdot \sigma_o = \frac{e^2}{6\epsilon_0 \hbar^2} \cdot |R_{mn}|^2 = \frac{e^2}{4\epsilon_0 h\nu m_e} \cdot f_{mn}$$

$$|R_{mn}|^2 = \frac{3\epsilon_0 \hbar c}{\pi e^2 \nu} \cdot \sigma_o = \frac{6\epsilon_0 \hbar^2}{e^2} \cdot B_{mn} = \frac{3\hbar}{4\pi\nu m_e} \cdot f_{mn}$$

$$f_{mn} = \frac{4\epsilon_0 c m_e}{e^2} \cdot \sigma_o = \frac{4\epsilon_0 h\nu m_e}{e^2} \cdot B_{mn} = \frac{4\pi\nu m_e}{3\hbar} \cdot |R_{mn}|^2$$