

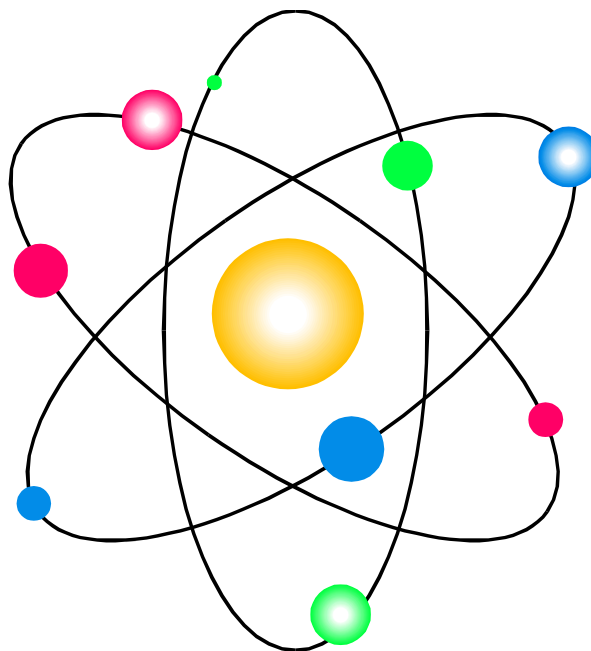
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DE PHYSIQUE QUANTIQUE

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# QUANTUM PHYSICS

## FORMULARY





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# Quantum physics

## 1. Introduction to quantum physics

### 2.

#### 1.1-Black body radiation

Planck's law for the energy distribution for the radiation of a black body is :

$$w(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}, \quad w(\lambda) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

Stefan-Boltzmann's law for the total power density can be derived from this :

$$P = A\sigma T^4$$

Wien's law for the maximum can also be derived from this :

$$T\lambda_{\max} = k_W$$

#### 1.2- The Compton effect

For the wavelength of scattered light, if light is considered to exist of particles, can be derived :

$$\lambda' = \lambda + \frac{h}{mc}(1 - \cos\theta) = \lambda + \lambda_c(1 - \cos\theta)$$

#### 1.3- Electron diffraction

Diffraction of electrons at a crystal can be explained by assuming that particles have a wave character with wavelength  $\lambda = \frac{h}{p}$ . This wavelength is called the de Broglie-wavelength.

## 3. Wave functions

The wave character of particles is described by a wavefunction  $\Psi$ . This wavefunction can be described in normal or momentum space. Both definitions are each others Fourier transform :

$$\Phi(k, t) = \frac{1}{\sqrt{h}} \int \Psi(x, t) e^{-ikx} dx \quad \text{and} \quad \Psi(x, t) = \frac{1}{\sqrt{h}} \int \Phi(k, t) e^{ikx} dk$$

These waves define a particle with group velocity  $v_g = \frac{p}{m}$  and energy  $E = \hbar\omega$ .

The wave function can be interpreted as a measure for the probability  $P$  to find a particle somewhere (Born) :  $dP = |\Psi|^2 d^3V$ . The expectation value  $\langle f \rangle$  of a quantity  $f$  of a system is given by :

$$\langle f(t) \rangle = \int \Psi^* f \Psi d^3V, \quad \langle f_p(t) \rangle = \int \Phi^* f \Phi d^3V_p$$

This is also written as  $\langle f(t) \rangle = \langle \Phi | f | \Phi \rangle$ . The normalizing condition for wave functions from this :  $\langle \Phi | \Phi \rangle = \langle \Psi | \Psi \rangle = 1$ .

## 4. Operators in quantum physics

In quantum mechanics, classical quantities are translated into operators. These operators are hermitian because their eigenvalues must be real :

$$\int \Psi_1^* A \Psi_2 d^3V = \int \Psi_2 (A \Psi_1)^* d^3V$$

When  $u_n$  is the eigenfunction of the eigenvalue equation  $A\Psi = a\Psi$  for eigenvalue  $a_n$ ,  $\Psi$  can be expanded into a basis of eigenfunctions :  $\Psi = \sum_n c_n u_n$ . If this basis is taken orthonormal,

then follows for the coefficients :  $c_n = \langle u_n | \Psi \rangle$ . If the system is in a state described by  $\Psi$ , the chance to find eigenvalue  $a_n$  when measuring  $A$  is given by  $|c_n|^2$  in the discrete part of the spectrum and  $|c_n|^2 da$  in the continuous part of the spectrum between  $a$  and  $a + da$ . The **matrix element**  $A_{ij}$  is given by :  $A_{ij} = \langle u_i | A | u_j \rangle$ .

Because  $(AB)_{ij} = \langle u_i | AB | u_j \rangle = \langle u_i | A \sum_n | u_n \rangle \langle u_n | B | u_j \rangle$  holds :  $\sum_n | u_n \rangle \langle u_n | = 1$ .

The time-dependence of an operator is given by (Heisenberg) :

$$\frac{dA}{dt} = \frac{1}{i\hbar} [A, H] + \frac{\partial A}{\partial t}$$

with  $[A, B] \equiv AB - BA$  the **commutator** of  $A$  and  $B$ . For hermitic operators the commutator is always complex. If  $[A, B] = 0$ , the operators  $A$  and  $B$  have a common set of eigenfunctions. By applying this to  $p_x$  and  $x$  follows (Ehrenfest) :

$$m \frac{d^2 \langle x \rangle_t}{dt^2} = - \left\langle \frac{dU(x)}{dx} \right\rangle$$

The first order approximation  $\langle F(x) \rangle_t \approx F(\langle x \rangle_t)$ , with  $F = -\frac{dU}{dx}$  represents the classical equation.

Before the addition of quantum mechanical operators which are a product of other operators, they should be made symmetrical : a classical product  $AB$  becomes  $\frac{1}{2}(AB + BA)$ .

## 5. The uncertainty principle

If the uncertainty  $\Delta A$  is defined as :  $(\Delta A)^2 = \langle \Psi | A_{op}^2 - \langle A \rangle^2 | \Psi \rangle = \langle A^2 \rangle - \langle A \rangle^2$  it follows :

$$\Delta A \Delta B \geq \frac{1}{2} |\langle \Psi | [A, B] | \Psi \rangle|$$

From this follows :  $\Delta E \Delta t \geq \frac{\hbar}{2}$ , and because  $[x, p_x] = i\hbar$  holds :  $\Delta x \Delta p_x \geq \frac{\hbar}{2}$  and  $\Delta L_x \Delta L_y \geq \frac{\hbar}{2} L_z$ .

## 6. The Schrödinger equation

The momentum operator is given by :  $p_{op} = -i\hbar \nabla$ . The position operator is :  $x_{op} = i\hbar \nabla_p$ . The energy operator is given by :  $E_{op} = i\hbar \frac{\partial}{\partial t}$ . The Hamiltonien of a particle with mass  $m$ ,

potential energy  $U$  and total energy  $E$  is given by :  $H = \frac{p^2}{2m} + U$ . From  $H\Psi = E\Psi$  then follows the **Schrödinger equation** :

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\Psi + U\Psi = E\Psi = i\hbar\frac{\partial\Psi}{\partial t}}$$

The linear combinaison of the solutions of this equation give the general solution. In one dimension it is :

$$\Psi(x,t) = \left( \sum + \int dE \right) c(E) u_E(x) e^{-\frac{i}{\hbar}Et}$$

The current density  $J$  is given by :  $J = \frac{\hbar}{2im}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*)$

The following conservation law holds :  $\frac{\partial P(x,t)}{\partial t} = -\nabla J(x,t)$

## 7. Parity

The parity operator in one dimension is given by  $\Pi\Psi(x) = \Psi(-x)$ . If the wave function is split in even and odd functions, it can be expanded into eigenfunctions of  $\Pi$  :

$$\Psi(x) = \underbrace{\frac{1}{2}[\Psi(x) + \Psi(-x)]}_{\text{even : } \Psi^+} + \underbrace{\frac{1}{2}[\Psi(x) - \Psi(-x)]}_{\text{odd : } \Psi^-}$$

$[\Pi, H] = 0$ . The function  $\Psi^+ = \frac{1}{2}(1 + \Pi)\Psi(x,t)$  and  $\Psi^- = \frac{1}{2}(1 - \Pi)\Psi(x,t)$  both satisfy the Schrödinger equation. Hence, parity is a conserved quantity.

## 8. The tunnel effect

The wave function of a particle in an  $\infty$  high potential step from  $x = 0$  to  $x = a$  is given by :

$$\Psi(x) = \sqrt{\frac{1}{a}} \sin kx$$

The energy levels are given by :  $E_n = n^2 \frac{\pi^2 \hbar^2}{2ma^2}$ .

If the wave function with energy  $W$  meets a potential well of  $W_0 > W$  the wave function will, unlike the classical case, be non-zero within the potential well. If 1, 2 and 3 are the area in front, within and behind the potential well, holds :

$$\Psi_1 = Ae^{ikx} + Be^{-ikx}, \quad \Psi_2 = Ce^{ik'x} + De^{-ik'x}, \quad \Psi_3 = A'e^{ikx}$$

with  $k'^2 = \frac{2m(W - W_0)}{\hbar^2}$  and  $k^2 = \frac{2mW}{\hbar^2}$ . Using the boundary conditions requiring continuity :

$\Psi$  and  $\frac{\partial\Psi}{\partial x}$  continuous at  $x = 0$  and  $x = a$  gives  $B, C$  and  $D$  and  $A'$  expressed in  $A$ .

The amplitude  $T$  of the transmitted wave is defined by  $T = \frac{|A'|^2}{|A|^2}$ .

If  $W > W_0$  and  $2a = n\lambda' = n \frac{2\pi}{k'}$  holds :  $T = 1$ .

## 9. The harmonic oscillator

For a harmonic oscillator holds :  $U = \frac{1}{2}bx^2$  and  $\omega_0^2 = \frac{b}{m}$ . The Hamiltonien  $H$  is given by :

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 = \frac{1}{2}\hbar\omega + \omega A^+ A$$

with :  $A = \sqrt{\frac{1}{2m\omega}} \left( m\omega x + \frac{ip}{\sqrt{2m\omega}} \right)$  and  $A^+ = \sqrt{\frac{1}{2m\omega}} \left( m\omega x - \frac{ip}{\sqrt{2m\omega}} \right)$

$A \neq A^+$  is non hermitic.  $[A, A^+] = \hbar$  and  $[A, H] = \hbar\omega A$ .  $A$  is a so called **raising ladder operator**,  $A^+$  a **lowering ladder operator**.  $HAu_E = (E - \hbar\omega)Au_E$ . There is an eigenfunction  $u_0$  for which holds :  $Au_0 = 0$ . The energy in this ground state is  $\frac{1}{2}\hbar\omega$  : the zero point energy. For the normalized eigenfunction follows :

$$u_n = \frac{1}{\sqrt{n!}} \left( \frac{A^+}{\sqrt{\hbar}} \right)^n u_0 \text{ with } u_0 = \left( \frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} e^{-\frac{m\omega x^2}{2\hbar}}$$

with  $E_n = \left( n + \frac{1}{2} \right) \hbar\omega$ .

## 10. Angular momentum

For the angular momentum operators  $L$  holds :  $[L_z, L^2] = [L_z, H] = [L^2, H] = 0$ . However, cyclically holds :  $[L_x, L_y] = i\hbar L_z$ . Not all components of  $L$  can be known at the same time with arbitrary accuracy. For  $L_z$  holds :

$$L_z = -i\hbar \frac{\partial}{\partial \varphi} = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

The ladder operator  $L_{\pm}$  are defined by :  $L_{\pm} = L_x \pm iL_y$ . Now holds :  $L^2 = L_+ L_- + L_z^2 - \hbar L_z$ .

Further,

$$L_{\pm} = \hbar e^{\pm i\varphi} \left( \pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right)$$

From  $[L_+, L_z] = -\hbar L_+$  follows :  $L_z(L_+ Y_l^m) = (m+1)\hbar(L_+ Y_l^m)$

From  $[L_-, L_z] = \hbar L_-$  follows :  $L_z(L_- Y_l^m) = (m-1)\hbar(L_- Y_l^m)$

From  $[L^2, L_{\pm}] = 0$  follows :  $L^2(L_{\pm} Y_l^m) = l(l+1)\hbar^2(L_{\pm} Y_l^m)$

Because  $L_x$  and  $L_y$  are hermitic (this implies  $L_{\pm}^+ = L_{\mp}$ ) and  $|L_{\pm} Y_l^m|^2 > 0$  follows :

$l(l+1) - m^2 - m \geq 0 \Rightarrow -l \leq m \leq l$ . Further follows that  $l$  has to be integral or half-integral.

Half-odd integral values give no unique solution  $\Psi$  and are therefore dismissed.



## 11. Spin

For the spin operators are defined by their commutation relations :  $[S_x, S_y] = i\hbar S_z$ . Because the spin operators do not act in the physical space  $(x, y, z)$  the uniqueness of the wave function is not a criteria here : also half odd-integer values are allowed for the spin. Because  $[L, S] = 0$  spin and angular momentum operators do not have a common set of eigenfunctions. The spin operators are given by :

$$\vec{S} = \frac{\hbar}{2} \vec{\sigma} \text{ with } \vec{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \vec{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \vec{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The eigenstates of  $S_z$  are called **spinors** :  $\chi = \alpha_+ \chi_+ + \alpha_- \chi_-$  where  $\chi_+ = (1, 0)$  represents the state with spin up  $\left(S_z = \frac{\hbar}{2}\right)$  and  $\chi_- = (0, 1)$  represents the state with spin down  $\left(S_z = -\frac{\hbar}{2}\right)$ .

Then the probability to find spin up after a measurement is given by  $|\alpha_+|^2$  and the chance to find spin down is given by  $|\alpha_-|^2$ . Of course holds  $|\alpha_+|^2 + |\alpha_-|^2 = 1$ .

The electron will have an intrinsic magnetic dipole moment  $\vec{M}$  due to its spin, given by  $\vec{M} = -g_s \frac{e\hbar}{2m} \vec{S}$  with  $g_s = 2\left(1 + \frac{\alpha}{2\pi} + \dots\right)$  the gyromagnetic ratio. In the presence of an external magnetic field this gives a potential energy  $U = -\vec{M} \cdot \vec{B}$ . The Schrödinger equation then becomes (because  $\frac{\partial \chi}{\partial x_i} \equiv 0$ ) :

$$i\hbar \frac{\partial \chi(t)}{\partial t} = g_s \frac{e\hbar}{4m} \vec{\sigma} \cdot \vec{B} \chi(t)$$

with  $\vec{\sigma} = (\vec{\sigma}_x, \vec{\sigma}_y, \vec{\sigma}_z)$ .

If  $\vec{B} = B\vec{e}_z$  there are two eigenvalues for this problem :  $\chi_{\pm}$  for  $E = \pm g_s \frac{e\hbar}{4m} B = \pm \hbar \omega$ .

So the general solution is given by  $\chi = (ae^{-i\omega t}, be^{i\omega t})$ . From this can be derived :

$$\langle S_x \rangle = \frac{\hbar}{2} \cos 2\omega t \text{ and } \langle S_y \rangle = \frac{\hbar}{2} \sin 2\omega t$$

Thus the spin precesses about the z-axis with frequency  $2\omega$ . This causes the normal Zeeman splitting of spectral lines.

The potential operator for two particles with spin  $\pm \frac{\hbar}{2}$  is given by :

$$V(r) = V_1(r) + \frac{V_2(r)}{\hbar^2} (\vec{S}_1 \cdot \vec{S}_2) = V_1(r) + \frac{V_2(r)}{2} \left[ S(S+1) - \frac{3}{2} \right]$$

This makes it possible for two states to exist :  $S = 1$  (triplet) or  $S = 0$  (singlet).

## 12. The Dirac formalism

If the operators for  $p$  and  $E$  are substituted in the relativistic equation  $E^2 = m_0^2 c^4 + p^2 c^2$ , the **Klein-Gordon** equation is found :

$$\left( \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \frac{m_0^2 c^2}{\hbar^2} \right) \Psi(\vec{x}, t) = 0$$

The operator  $\square - \frac{m_0^2 c^2}{\hbar^2}$  can be separated :

$$\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \frac{m_0^2 c^2}{\hbar^2} = \left\{ \gamma_\lambda \frac{\partial}{\partial x_\lambda} - \frac{m_0^2 c^2}{\hbar^2} \right\} \left\{ \gamma_\mu \frac{\partial}{\partial x_\mu} + \frac{m_0^2 c^2}{\hbar^2} \right\}$$

where the Dirac matrices  $\gamma$  are given by :  $\gamma_\lambda \gamma_\mu + \gamma_\mu \gamma_\lambda = 2\delta_{\lambda\mu}$ . from this it can be derived that the  $\gamma$  are hermitic  $4 \times 4$  matrices given by :

$$\gamma_k = \begin{pmatrix} 0 & -i\sigma_k \\ i\sigma_k & 0 \end{pmatrix}, \quad \gamma_4 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

With this, the Dirac equation becomes :

$$\left( \gamma_\lambda \frac{\partial}{\partial x_\lambda} + \frac{m_0^2 c^2}{\hbar^2} \right) \Psi(\vec{x}, t) = 0$$

where  $\Psi(x) = (\Psi_1(x), \Psi_2(x), \Psi_3(x), \Psi_4(x))$  is a spinor.

## 13. Atomic physics

### 12.1-/ Solutions

The solutions of the Schrödinger equation in spherical coordinates if the potential energy is a function of  $r$  alone can be written as :  $\Psi(r, \theta, \varphi) = R_{nl}(r) Y_l^m(\theta, \varphi) \chi_m$ , with :

$$Y_l^m = \frac{C_{lm}}{\sqrt{2\pi}} P_l^m(\cos \theta) e^{im\varphi}$$

For an atom or ion with one electron holds :  $R_{nl}(\rho) = C_{nl} e^{-\frac{\rho^2}{2}} L_{n-l-1}^{2l+1}(\rho)$

with  $\rho = \frac{2rZ}{na_0}$  and  $a_0 = \frac{\epsilon_0 \hbar^2}{\pi m_e e^2}$ . The  $L_l^j$  are the associated Laguerre functions and  $P_l^m$  are the associated Legendre polynomials :

$$P_l^{|m|}(x) = (1-x^2)^{\frac{m}{2}} \frac{d^{|m|}}{dx^{|m|}} \left[ (x^2-1)^l \right], \quad L_n^m(x) = \frac{(-1)^m n!}{(n-m)!} e^{-x} x^{-m} \frac{d^{n-m}}{dx^{n-m}} (e^{-x} x^n)$$

The parity of these solutions is  $(-1)^l$ . The functions are  $2 \sum_{l=0}^{n-1} (2l+1) = 2n^2$  degenerated.

### 12.2-/ Eigenvalue equations

The eigenvalue equations for an atom or ion with one electron are :

Equation	Eigenvalue	Range
$H_{op}\Psi = E\Psi$	$E_n = \frac{\mu e^4 Z^2}{8\epsilon_0^2 \hbar^2 n^2}$	$n \geq 1$
$L_{z\ op} Y_l^m = L_z Y_l^m$	$L_z = m\hbar$	$-l \leq m \leq l$
$L_{op}^2 Y_l^m = L^2 Y_l^m$	$L^2 = l(l+1)\hbar^2$	$l < n$
$S_{z\ op} \chi = S_z \chi$	$S_z = m_s \hbar$	$m_s = \pm \frac{1}{2}$
$S_{op}^2 \chi = S^2 \chi$	$S^2 = s(s+1)\hbar^2$	$s = \frac{1}{2}$

### 12.3-/ Spin-orbit interaction

The total momentum is given by  $\vec{J} = \vec{L} + \vec{S}$ . The total magnetic dipole moment of an electron is then  $\vec{M} = \vec{M}_L + \vec{M}_S = -\frac{e}{2m_e}(\vec{L} + g_s \vec{S})$  where  $g_s = 2,0023$  is the gyromagnetic ratio of the electron. Further holds :  $J^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S} = L^2 + S^2 + 2L_z S_z + L_+ S_- + L_- S_+$ .

$J$  has quantum number  $j$  with possible values  $j = l \pm \frac{1}{2}$  with  $2j+1$  possible z-components ( $m_j \in \{-j, \dots, 0, \dots, j\}$ ). If the interaction energy between  $S$  and  $L$  is small it can be stated that :

$E = E_n + E_{SL} = E_n + a\vec{S} \cdot \vec{L}$ . It can be derived that :

$$a = \frac{|E_n|Z^2\alpha^2}{\hbar^2 n l(l+1) \left(l + \frac{1}{2}\right)}$$

After a relativistic correction this becomes :

$$E = E_n + \frac{|E_n|Z^2\alpha^2}{n} \left( \frac{3}{4n} - \frac{1}{j + \frac{1}{2}} \right)$$

The ***fine structure*** in atomic spectra arises from this. With  $g_s = 2$  follows for the average

magnetic moment :  $\vec{M}_{av} = -\frac{e}{2m_e} g \hbar \vec{J}$  where  $g$  is the Landé-factor :

$$g = 1 + \frac{\vec{S} \cdot \vec{J}}{J^2} = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

For atoms with more than one electron the following limiting situations occur :

**1.  $L - S$  coupling :** for small atoms the electrostatic interaction is dominant and the state can be characterized by  $L, S, J, m_j$ .  $J \in \{|L - S|, \dots, L + S + 1, L + S\}$  and  $m_j \in \{-J, \dots, J - 1, J\}$ .

The spectroscopic notation for this interaction is :  $^{2S+1}L_J$ ,  $2S+1$  is the multiplicity of a multiplet.

**2.  $j - j$  coupling :** for larger atoms the electrostatic interaction is smaller than the  $L_i - s_i$  interaction of an electron. The state is characterized by  $j_i \dots j_n, J, m_j$  where only the  $j_i$  of the not completely filled subshells are to be taken into account.

The energy difference for larger atoms when placed in a magnetic field is :  $\Delta E = g \mu_B m_j B$  where  $g$  is the Landé factor. For a transition between two singlet states the line splits in 3

parts, for  $\Delta m_j = -1, 0, +1$ . This results in the normal Zeeman effect. At higher  $S$  the line splits up in more parts : the anomalous Zeeman effect. Interaction with the spin of the nucleus gives the hyperfine structure.

## 12.4-/ Selection rules

For the dipole transition matrix elements follows :  $p_0 \approx \left| \langle l_2, m_2 | \vec{E} \cdot \vec{r} | l_1, m_1 \rangle \right|$ . Conservation of angular momentum demands that for the transition of an electron holds that  $\Delta l = \pm 1$ .

- For an atom where  $L-S$  coupling is dominant further holds :  $\Delta S = 0$  (but not strict),  $\Delta L = 0, \pm 1$ ,  $\Delta J = 0, \pm 1$  except for  $J = 0 \rightarrow J = 0$  transition,  $\Delta m_j = 0, \pm 1$ , but  $\Delta m_j = 0$  is forbidden if  $\Delta J = 0$ .

- For an atom where  $j-j$  coupling is dominant further holds : for the jumping electron holds, except  $\Delta l = \pm 1$ , also :  $\Delta j = 0, \pm 1$ , and for all other electron :  $\Delta j = 0$ . For the total atom holds :  $\Delta J = 0, \pm 1$  but no  $J = 0 \rightarrow J = 0$  transitions and  $\Delta m_j = 0, \pm 1$ , but  $\Delta m_j = 0$  is forbidden if  $\Delta J = 0$ .

## 14. Interaction with electromagnetic fields

The Hamiltonien of an electron in a electromagnetic field is given by :

$$H = \frac{1}{2\mu} (\vec{p} + e\vec{A})^2 - eV = -\frac{\hbar^2}{2\mu} \nabla^2 + \frac{e}{2\mu} \vec{B} \cdot \vec{L} + \frac{e^2}{2\mu} A^2 - eV$$

where  $\mu$  is the reduced mass of the system. The term  $\approx A^2$  can usually be neglected, except for very strong fields or macroscopic motions. For  $\vec{B} = B\vec{e}_z$  it given by  $\frac{e^2 B^2 (x^2 + y^2)}{8\mu}$ .

When a gauge transformation  $\vec{A}' = \vec{A} - \nabla f$ ,  $V' = V + \frac{\partial f}{\partial t}$  is applied to the potentials the wave

function is also transformed according to  $\Psi' = \Psi e^{\frac{i}{\hbar} qef}$  with  $qe$  the charge of the particle. Because  $f = f(x, t)$ , this is called a **local gauge transformation**, in contrast with a **global gauge transformation** which can always be applied.

## 15. Perturbation theory

### 14.1-/ Time-independent perturbation theory

To solve the equation  $(H_0 + \lambda H_1)\Psi_n = E_n \Psi_n$  one has to find the eigenfunctions of  $H = H_0 + \lambda H_1$ . Suppose that  $\Phi_n$  is a complete set of eigenfunctions of the non-perturbed Hamiltonien  $H_0$  :  $H_0 \Phi_n = E_n^0 \Phi_n$ . Because  $\Phi_n$  is a complete set holds :

$$\Psi_n = N(\lambda) \left\{ \Phi_n + \sum_{k \neq n} c_{nk}(\lambda) \Phi_k \right\}$$

When  $c_{nk}$  and  $E_n$  are being expanded into  $\lambda$  :  $\begin{cases} c_{nk} = \lambda c_{nk}^{(1)} + \lambda^2 c_{nk}^{(2)} + \dots \\ E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{cases}$  and this put into the Schrödinger equation the result is :  $E_n^{(1)} = \langle \Phi_n | H_1 | \Phi_n \rangle$  and  $c_{nm}^{(1)} = \frac{\langle \Phi_m | H_1 | \Phi_n \rangle}{E_n^0 - E_m^0}$  if  $m \neq n$ .

The second order correction of the energy is then given by :  $E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \Phi_k | H_1 | \Phi_n \rangle|^2}{E_n^0 - E_k^0}$ . So to first order holds :  $\Psi_n = \Phi_n + \sum_{k \neq n} \frac{\langle \Phi_k | H_1 | \Phi_n \rangle}{E_n^0 - E_k^0} \Phi_k$ .

In case the levels are degenerated the above does not hold. In that case an orthogonal set eigenfunctions  $\Phi_{ni}$  is chosen for each level  $n$ , so that  $\langle \Phi_{mi} | \Phi_{nj} \rangle = \delta_{mn} \delta_{ij}$ . Now  $\Psi$  is expanded

as :  $\Psi_n = N(\lambda) \left\{ \sum_i \alpha_i \Phi_{ni} + \lambda \sum_{k \neq n} c_{nk}^{(1)} \sum_i \beta_i \Phi_{ki} + \dots \right\}$

$E_{ni} = E_{ni}^0 + \lambda E_{ni}^{(1)}$  is approximated by  $E_{ni}^0 = E_n^0$ . Substitution in the Schrödinger equation and taking dot product with  $\Phi_{ni}$  gives :  $\sum_i \alpha_i \langle \Phi_{ni} | H | \Phi_{ni} \rangle = E_n^{(1)} \alpha_j$ . Normalization requires that  $\sum_i |\alpha_i|^2 = 1$ .

## 14.2-/ Time-dependent perturbation theory

From the Schrödinger equation  $i\hbar \frac{\partial \Psi(t)}{\partial t} = (H_0 + \lambda V(t)) \Psi(t)$

and the expansion  $\Psi(t) = \sum_n c_n(t) e^{-\frac{i}{\hbar} E_n^0 t} \Phi_n$  with  $c_n(t) = \delta_{nk} + \lambda c_n^{(1)}(t) + \dots$  follows :

$$c_n^{(1)}(t) = \frac{\lambda}{i\hbar} \int_0^t \langle \Phi_n | V(t') | \Phi_k \rangle e^{\frac{i}{\hbar} (E_n^0 - E_k^0) t'} dt'$$

## 16. N-particles systems

### 15.1-/ General

Identical particles are indistinguishable. For the total wave function of a system of indistinguishable particles holds :

- Particles with a half-odd integer spin (Fermions) :  $\Psi_{total}$  must be antisymmetric w.r.t. interchange of the coordinates (spatial and spin) of each pair of particles. The Pauli principle results from this : two Fermions cannot exist in an identical state because then  $\Psi_{total} = 0$ .
- Particles with an integer spin (Bosons) :  $\Psi_{total}$  must be symmetric w.r.t. interchange of the coordinates (spatial and spin) of each pair of particles.

For a system of two electron there are 2 possibilities for the spatial wave function. When  $a$  and  $b$  are the quantum numbers of electron 1 and 2 holds :

$$\Psi_s(1,2) = \Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1) \quad , \quad \Psi_A(1,2) = \Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1)$$

Because the particles do not approach each other closely the repulsion energy at  $\Psi_A$  in this state is smaller. The following spin wave function are possible :

$$\chi_A = \frac{1}{\sqrt{2}} [\chi_+(1)\chi_-(2) - \chi_+(2)\chi_-(1)] \quad m_s = 0$$

$$\chi_S = \begin{cases} \chi_+(1)\chi_+(2) & m_s = +1 \\ \frac{1}{\sqrt{2}} [\chi_+(1)\chi_-(2) + \chi_+(2)\chi_-(1)] & m_s = 0 \\ \chi_-(1)\chi_-(2) & m_s = -1 \end{cases}$$

Because the total wave function must be antisymmetric it follows :  $\Psi_{total} = \Psi_S \chi_A$  or  $\Psi_{total} = \Psi_A \chi_S$ .

For  $N$  particles the spatial function is given by :

$$\Psi_s(1, \dots, N) = \sum \Psi(\text{all permutation of } 1 \dots N)$$

The antisymmetric wave function is given by the determinant :  $\Psi_A(1, \dots, N) = \frac{1}{\sqrt{N!}} |u_{Ei}(j)|$

## 15.2- Molecules

The wave function of atom  $a$  and  $b$  are  $\Phi_a$  and  $\Phi_b$ . If the 2 atoms approach each other there are two possibilities : the total wave function approaches the bonding function with lower total energy  $\Psi_B = \frac{1}{\sqrt{2}}(\Phi_a + \Phi_b)$  or approaches the anti-bonding function with higher energy

$\Psi_B = \frac{1}{\sqrt{2}}(\Phi_a - \Phi_b)$ . If a molecular-orbital is symmetric w.r.t. the connecting axis, like a combination of two s-orbital it is called a  $\sigma$ -orbital, otherwise a  $\pi$ -orbital, like the combination of two p-orbital along two axes.

The energy of a system is :  $E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$ .

The energy calculated with this method is always **higher** than the real energy if  $\Psi$  is only an approximation for the solution of  $H\Psi = E\Psi$ . Also, if there are more functions to be chosen, the function which gives the lowest energy is the best approximation. Applying this to the function  $\Psi = \sum c_i \Phi_i$  one finds :  $(H_{ij} - ES_{ij})c_i = 0$ . This equation has only solutions if the **secular determinant**  $|H_{ij} - ES_{ij}| = 0$ . Here  $H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$  and  $S_{ij} = \langle \Phi_i | \Phi_j \rangle$ .  $\alpha_i = H_{ii}$  is the Coulomb integral and  $\beta_{ij} = H_{ij}$  the exchange integral.  $S_{ii} = 1$  and  $S_{ij}$  is the overlap integral.

The first approximation in the molecular-orbital theory is to place both electrons of a chemical bond in the bonding orbital :  $\Psi(1,2) = \Psi_B(1)\Psi_B(2)$ . This results in a large electron density between the nuclei and therefore a repulsion. A better approximation is :

$$\Psi(1,2) = C_1 \Psi_B(1)\Psi_B(2) + C_2 \Psi_{AB}(1)\Psi_{AB}(2)$$

with  $C_1 = 1$  and  $C_2 \approx 0,6$ .

In some atoms, such as C, it is energetically more suitable to form orbitals which are linear combination of the s, p and d states. There are three ways of hybridization in C :

- SP-hybridization :  $\Psi_{sp} = \frac{1}{\sqrt{2}}(\Psi_{2s} \pm \Psi_{2p_z})$ . There are 2 hybrid orbitals which are placed on one line under  $180^\circ$ . Further the  $2p_x$  and  $2p_y$  orbitals remain.

• SP<sup>2</sup> hybridation :  $\Psi_{sp^2} = \frac{1}{\sqrt{3}}\Psi_{2s} + c_1\Psi_{2p_z} + c_2\Psi_{2p_y}$ ,

where  $(c_1, c_2) \in \left\{ \left( \sqrt{\frac{2}{3}}, 0 \right), \left( -\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{2}} \right), \left( -\frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{2}} \right) \right\}$ . The 3 SP<sup>2</sup> orbitals lay in one plane, with symmetry axes which are at an angle of 120°.

• SP<sup>3</sup> hybridation :  $\Psi_{sp^3} = \frac{1}{2}(\Psi_{2s} \pm \Psi_{2p_z} \pm \Psi_{2p_y} \pm \Psi_{2p_x})$ . The 4 SP<sup>3</sup> orbitals form a tetraheder with the symmetry axes at an angle of 109°28'.

## 17. Quantum statistics

If a system exists in a state in which one has not the disposal of the maximal amount of information about the system, it can be described by a **density matrix**  $\rho$ . If the probability that the system is in state  $\Psi_i$  is given by  $a_i$ , one can write for the expectation value  $a$  of  $A$ :

$$\langle a \rangle = \sum_i r_i \langle \Psi_i | A | \Psi_i \rangle$$

If  $\Psi$  is expanded into an orthogonal basis  $\{\Phi_k\}$  as :  $\Psi^{(i)} = \sum_k c_k^{(i)} \Phi_k$ , holds :

$$\langle A \rangle = \sum_k (A\rho)_{kk} = \text{Tr}(A\rho)$$

where  $\rho_{ik} = c_k^* c_i$ .  $\rho$  is hermitian, with  $\text{Tr}\rho = 1$ . Further holds  $\rho = \sum_i r_i |\Psi_i\rangle \langle \Psi_i|$ . The probability to find eigenvalue  $a_n$  when measuring  $A$  is given by  $\rho_{nn}$  if one uses a basis of eigenvectors of  $A$  for  $\{\Phi_k\}$ .

For the time-dependence holds (in the Schrödinger image operators are not explicitly time-dependent) :

$$i\hbar \frac{d\rho}{dt} = [H, \rho]$$

For a macroscopic system in equilibrium holds  $[H, \rho] = 0$ . If all quantum states with the same energy are equally probable :  $P_i = P(E_i)$ , one can obtain the distribution :

$$P_n(E) = \rho_{nn} = \frac{e^{-\frac{E_n}{kT}}}{Z} \text{ with the state sum } Z = \sum_n e^{-\frac{E_n}{kT}}$$

The thermodynamic quantities are related to these definitions as follows :

$$F = -kT \ln Z, \quad U = \langle H \rangle = \sum_n P_n E_n = -\frac{\partial}{\partial kT} \ln Z, \quad S = -k \sum_n P_n \ln P_n$$

For a mixed state of  $M$  orthonormal quantum states with probability  $\frac{1}{M}$  follows :

$$S = k \ln M.$$

The distribution function for the internal states for a system in thermal equilibrium is the most probable function. This function can be found by taking the maximum of the function which gives the number of states with Stirling's equation :  $\ln n! \approx n \ln n - n$ , and the conditions  $\sum_k n_k = N$  and  $\sum_k n_k W_k = W$ . For identical, indistinguishable particles which obey the Pauli principle the possible number of states is given by :

$$P = \prod_k \frac{g_k!}{n_k! (g_k - n_k)!}$$

This results in the **Fermi-Dirac statistics**. For indistinguishable particles which **do not** obey the exclusion principle the possible number of states is given by :

$$P = N! \prod_k \frac{g_k^{n_k}}{n_k!}$$

This result in the **Bose-Einstein statistics**. So the distribution function which explain how particles are distributed over the different one-particle states  $k$  which are each  $g_k$ -fold degenerate depend on the spin of the particles. They are given by :

- Fermi-Dirac statistics : half odd-integer spin.  $n_k \in \{0,1\}$ ,  $n_k = \frac{N}{Z_g} \frac{g_k}{e^{\frac{E_k - \mu}{kT}} + 1}$

with  $\ln Z_g = \sum g_k \ln \left( 1 + e^{\frac{E_k - \mu}{kT}} \right)$

- Bose-Einstein statistics : integer spin.  $n_k \in \mathbb{N}$ ,  $n_k = \frac{N}{Z_g} \frac{g_k}{e^{\frac{E_k - \mu}{kT}} - 1}$

with  $\ln Z_g = -\sum g_k \ln \left( 1 - e^{\frac{E_k - \mu}{kT}} \right)$

Here  $Z_g$  is the large-canonical state sum and  $\mu$  the chemical potential. It is found by demanding  $\sum_k n_k = N$ , and for it holds :  $\lim_{T \rightarrow 0} \mu = E_F$ , the Fermi-energy.  $N$  is the total number of particles.

The Maxwell-Boltzmann distribution can be derived from this in the limit  $E_k - \mu \gg kT$ :

$$n_k = \frac{N}{Z} e^{-\frac{E_k}{kT}} \text{ with } Z = \sum_k g_k e^{-\frac{E_k}{kT}}$$

With the Fermi-energy, the Fermi-Dirac and Bose-Einstein statistics can be written as :

- Fermi-Dirac statistics :  $n_k = \frac{g_k}{e^{\frac{E_k - E_F}{kT}} + 1}$
- Bose-Einstein statistics :  $n_k = \frac{g_k}{e^{\frac{E_k - E_F}{kT}} - 1}$

# Theory of groups

- The relation with quantum mechanics
- Applications to quantum mechanics

## 1.Introduction

### 1.1-/ Definition of a group

$G$  is a group for the operation • if :



1.  $\forall_{A,B \in G} \Rightarrow A \bullet B \in G : G$  is closed.
2.  $\forall_{A,B,C \in G} \Rightarrow (A \bullet B) \bullet C = A \bullet (B \bullet C) : G$  obeys the associative law.
3.  $\exists_{E \in G}$  so that  $\forall_{A \in G} A \bullet E = E \bullet A = A : G$  has a unit element.
4.  $\forall_{A \in G} \exists_{A^{-1} \in G}$  so that  $A \bullet A^{-1} = E$  : Each element in  $G$  has an inverse.

If also holds :

5.  $\forall_{A,B \in G} \Rightarrow A \bullet B = B \bullet A$  the group is called *Abelian or commutative*.

## 1.2-/ The Cayley table

Each element arises only once in each row and column of the Cayley or multiplication table : because  $EA_i = A_k^{-1}(A_k A_i) = A_i$  each  $A_i$  appears once. There are  $h$  position in each row and column when there are  $h$  elements in the group so each element appears only once.

## 1.3-/ Conjugated elements, subgroups and classes

$B$  is *conjugate* to  $A$  if  $\exists_{X \in G}$  such that  $B = XAX^{-1}$ . Then  $A$  is also conjugate to  $B$  because  $B = (X^{-1})A(X^{-1})^{-1}$ . If  $B$  and  $C$  are conjugate to  $A$ ,  $B$  is also conjugate with  $C$ .

A *subgroup* is a subset of  $G$  which is also a group w.r.t. the same operation.

A *conjugacy class* is the maximum collection of conjugated elements. Each group can be split up in conjugacy classes. Some theorems :

- All classes are completely disjoint.
- $E$  is a class itself : for each other element in this class would hold :  $A = XEX^{-1} = E$ .
- $E$  is the only class which is also a subgroup because all other classes have no unit element.
- In an Abelian group each element is a separate class.

The physical interpretation of classes : elements of a group are usually symmetry operations which map a symmetrical object into itself. Elements of one class are then same kind of operations. The opposite need not to be true.

## 1.4-/ Isomorfism and homomorfism : representations

Two groups are *isomorphic* if they have the same multiplication table. The mapping from group  $G_1$  to  $G_2$  so that the multiplication table remains the same is a homomorphic mapping. It need not be isomorphic.

A *representation* is a homomorphic mapping of a group of square matrices with the usual matrix multiplication as the combining operation. This is symbolized by  $\Gamma$ . The following holds :

$$\Gamma(E) = I \quad , \quad \Gamma(AB) = \Gamma(A)\Gamma(B) \quad , \quad \Gamma(A^{-1}) = [\Gamma(A)]^{-1}$$

For each group there are 3 possibilities for a representation :

1. A *faithful* representation : all matrices are different.
2. The representation  $A \rightarrow \det(\Gamma(A))$ .
3. The identical representation :  $A \rightarrow 1$ .

An *equivalent representation* is obtained by performing an unitary base transform :

$$\Gamma'(A) = S^{-1}\Gamma(A)S$$

## 1.5-/ Reducible and irreducible representations

If *the same* unitary transformation can bring all matrices of a representation  $\Gamma$  in the same block structure the representation is called *reducible* :

$$\Gamma(A) = \begin{pmatrix} \Gamma^{(1)}(A) & 0 \\ 0 & \Gamma^{(2)}(A) \end{pmatrix}$$

This is written as :  $\Gamma = \Gamma^{(1)} \oplus \Gamma^{(2)}$ . If this is not possible the representation is called *irreducible*.

The number of irreducible representations equals the number of conjugacy classes.

## 2. The fundamental orthogonality theorem

### 2.1-/ Schur's lemma

**Lemma :** Each matrix which commutes with all matrices of an irreducible representation is a constant  $\times I$ , where  $I$  is the unit matrix. The opposite is (of course) also true.

**Lemma :** if there exists a matrix  $M$  so that for two irreducible representations of group  $G$ ,  $\gamma^{(1)}(A_i)$  and  $\gamma^{(2)}(A_i)$ , holds :  $M\gamma^{(1)}(A_i) = \gamma^{(2)}(A_i)M$ , then the representations are equivalent, or  $M = 0$ .

### 2.2-/ The fundamental orthogonality theorem

For a set of unequivalent, irreducible, unitary representations holds that, if  $h$  is the number of elements of the group and  $l_i$  is the dimension of the  $i^{th}$  representation :

$$\sum_{R \in G} \Gamma_{\mu\nu}^{(i)}(R) \Gamma_{\alpha\beta}^{(j)}(R) = \frac{h}{l_i} \delta_{ij} \delta_{\mu\alpha} \delta_{\nu\beta}$$

### 2.3-/ Character

The *character* of a representation is given by the trace of the matrix and is therefore invariant for base transformations :

$$\chi^{(j)}(R) = \text{Tr}(\Gamma^{(j)}(R))$$

Also holds, with  $N_k$  the number of elements in a conjugacy class :

$$\sum_k \chi^{(i)*}(C_k) \chi^{(j)}(C_k) N_k = h \delta_{ij}$$

**Theorem :**  $\sum_{i=1}^n l_i^2 = h$

### 3. The relation with quantum mechanics

#### 3.1-/ Representation, energy levels and degeneracy

Consider a set of symmetry transformations  $\vec{x}' = R\vec{x}$  which leave the Hamiltonien  $H$  invariant. These transformations are a group. An isomorphic operation on the wave function is given by :  $P_R \Psi(\vec{x}) = \Psi(R^{-1}\vec{x})$ . This is considered an *active rotation*. These operators commute with  $H$  :  $P_R H = H P_R$  and leave the volume element unchanged :  $d(R\vec{x}) = d\vec{x}$ .

$P_R$  is the symmetry group of the physical system. It causes degeneracy : if  $\Psi_n$  is a solution of  $H\Psi_n = E_n\Psi_n$  than also holds :  $H(P_R\Psi_n) = E_n(P_R\Psi_n)$ . A degeneracy which is not the result of a symmetry is called *accidental degeneracy*.

Assume an  $l_n$ -fold degeneracy at  $E_n$  : then choose an orthonormal set  $\Psi_\nu^{(n)}$ ,  $\nu = 1, 2, \dots, l_n$ . The

function  $P_R \Psi_\nu^{(n)}$  is in the same subspace :  $P_R \Psi_\nu^{(n)} = \sum_{\kappa=1}^{l_n} \Psi_\kappa^{(n)} \Gamma_{\kappa\nu}^{(n)}(R)$  where  $\Gamma^{(n)}$  is an

*irreducible, unitary* representation of the symmetry group  $G$  of the system. Each  $n$  corresponds with another energy level. One can purely mathematical derive irreducible representations of a symmetry group and label the energy levels with a quantum number this way. A fixed choice of  $\Gamma^{(n)}(R)$  defines the base functions  $\Psi_\nu^{(n)}$ . This way one can also label each separate base function with a quantum number.

**Particle in a periodical potential** : the symmetry operation is a cyclic group : note the operator describing one translation over one unit as  $A$ . Then :  $G = \{A, A^2, A^3, \dots, A^h = E\}$ .

The group is Abelian so all irreducible representations are one-dimensional. For  $0 \leq p \leq h-1$  follows :

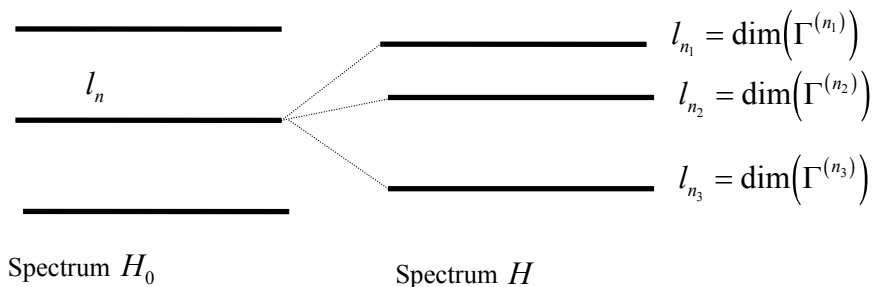
$$\Gamma^{(p)}(A^n) = e^{\frac{i}{h}np}$$

If one defines :  $k = -\frac{2\pi p}{ah} \left( \text{mod } \frac{2\pi}{a} \right)$ , so :  $P_A \Psi_p(x) = \Psi_p(x-a) = e^{\frac{2i\pi p}{h}} \Psi_p(x)$ , this gives

*Bloch's theorem* :  $\Psi_k(x) = u_k(x)e^{ikx}$ , with  $u_k(x \pm a) = u_k(x)$ .

#### 3.2-/ Breaking of degeneracy by a perturbation

Suppose the unperturbed system has Hamiltonien  $H_0$  and symmetry group  $G_0$ . The perturbed system has  $H = H_0 + V$ , and symmetry group  $G \subset G_0$ . If  $\Gamma^{(n)}(R)$  is an irreducible representation of  $G_0$ , it is also a representation of  $G$  but not all elements of  $\Gamma^{(n)}(R)$  in  $G_0$  are also in  $G$ . The representation then usually becomes *reducible* :  $\Gamma^{(n)} = \Gamma^{(n_1)} \oplus \Gamma^{(n_2)} \oplus \dots$ . The degeneracy is then (possibly partially) removed :



**Theorem :** The set of  $l_n$  degenerated eigenfunctions  $\Psi_v^{(n)}$  with energy  $E_n$  is a basis for an  $l_n$ -dimensional irreducible representation  $\Gamma^{(n)}$  of the symmetry group.

### 3.3-/ The construction of a base function

Each function  $F$  in configuration space can be decomposed into *symmetry types* :

$F = \sum_{j=1}^n \sum_{\kappa=1}^{l_j} f_{\kappa}^{(j)}$ . The following operator extracts the symmetry types :

$$\left( \frac{l_j}{h} \sum_{R \in G} \Gamma_{\kappa\kappa}^{(j)*}(R) P_R \right) F = f_{\kappa}^{(j)}$$

This is expressed as :  $f_{\kappa}^{(j)}$  is the part of  $F$  that transforms according to the  $\kappa^{th}$  row of  $\Gamma^{(j)}$ .

$F$  can also be expressed in base functions  $\Phi$  :  $F = \sum_{aj\kappa} c_{aj\kappa} \Phi_{\kappa}^{(aj)}$ . The functions  $f_{\kappa}^{(j)}$  are in

general not transformed into each other by elements of the group. However, this does happen if  $c_{aj\kappa} = c_{aj}$ .

**Theorem :** Two wavefunctions transforming according to non-equivalent unitary representation or according to different rows of an unitary irreducible representation are orthogonal :  $\langle \Phi_{\kappa}^{(i)} | \Phi_{\lambda}^{(j)} \rangle \approx \delta_{ij} \delta_{\kappa\lambda}$  and  $\langle \Phi_{\kappa}^{(i)} | \Phi_{\kappa}^{(i)} \rangle$  is independent of  $\kappa$ .

### 3.4-/ The direct product of representations

Consider a physical system existing of two subsystems. The subspace  $D^{(i)}$  of the system transforms according to  $\Gamma^{(i)}$ . Basefunctions are  $\Phi_{\kappa}^{(i)}(\vec{x}_i)$ ,  $1 \leq \kappa \leq l_i$ . Now form all  $l_1 \times l_2$  products  $\Phi_{\kappa}^{(1)}(\vec{x}_1) \Phi_{\lambda}^{(2)}(\vec{x}_2)$ . These define a space  $D^{(1)} \otimes D^{(2)}$ .

These product functions transform as :

$$P_R \left( \Phi_{\kappa}^{(1)}(\vec{x}_1) \Phi_{\lambda}^{(2)}(\vec{x}_2) \right) = \left( P_R \Phi_{\kappa}^{(1)}(\vec{x}_1) \right) \left( P_R \Phi_{\lambda}^{(2)}(\vec{x}_2) \right)$$

In general the space  $D^{(1)} \otimes D^{(2)}$  can be split up in a number of invariant subspaces :

$$\Gamma^{(1)} \otimes \Gamma^{(2)} = \sum_i n_i \Gamma^{(i)}$$

A useful tool for this reduction is that for the characters hold :

$$\chi^{(1)}(R) \chi^{(2)}(R) = \sum_i n_i \chi^{(i)}(R)$$

### 3.5-/ Clebsch-Gordan coefficients

With the reduction of the direct-product matrix w.r.t. the basis  $\Phi_{\kappa}^{(i)} \Phi_{\lambda}^{(j)}$  one uses a new basis  $\Phi_{\mu}^{(ak)}$ . These base functions lie in subspace  $D^{(ak)}$ . The unitary base transformation is given by

$$\Phi_{\mu}^{(ak)} = \sum_{\kappa\lambda} \Phi_{\kappa}^{(i)} \Phi_{\lambda}^{(j)} (i\kappa j\lambda | ak\mu)$$

and the inverse transformation by :  $\Phi_{\kappa}^{(i)} \Phi_{\lambda}^{(j)} = \sum_{ak\mu} \Phi_{\mu}^{(ak)} (ak\mu | i\kappa j\lambda)$

In essence the Clebsch-Gordan coefficients are dot products :

$$(i\kappa j\lambda | ak\mu) = \left\langle \Phi_{\kappa}^{(i)} \Phi_{\lambda}^{(j)} \middle| \Phi_{\mu}^{(k)} \right\rangle$$

### 3.6-/ Symmetric transformations of operators, irreducible tensor operators

Observables (operators) transform as follows under symmetry transformations :  $A' = P_R A P_R^{-1}$ . If a set of operators  $A_\kappa^{(j)}$  with  $0 \leq \kappa \leq l_j$  transform into each other under the transformations of  $G$  holds :

$$P_R A_\kappa^{(j)} P_R^{-1} = \sum_\nu A_\nu^{(j)} \Gamma_{\nu\kappa}^{(j)}(R)$$

If  $\Gamma^{(j)}$  is irreducible they are called *irreducible tensor operators*  $A_\kappa^{(j)}$  with components  $A_\kappa^{(j)}$ .

An operator can also be decomposed into symmetry types :  $A = \sum_{jk} a_k^{(j)}$ , with :

$$a_\kappa^{(j)} = \left( \frac{l_j}{h} \sum_{R \in G} \Gamma_{\kappa\kappa}^{(j)*}(R) \right) (P_R A P_R^{-1})$$

**Theorem :** Matrix elements  $H_{ij}$  of the operator  $H$  which is invariant under  $\forall_{A \in G}$  are 0 between states which transform according to non-equivalent irreducible unitary representations or according to different rows of such a representation. Further  $\langle \Phi_\kappa^{(i)} | H | \Phi_\kappa^{(i)} \rangle$  is independent of  $\kappa$ . For  $H = 1$  this becomes the previous theorem.

This is applied in quantum mechanics in *perturbation theory* and *variational calculus*. Here one tries to diagonalize  $H$ . Solutions can be found within each category of functions  $\Phi_\kappa^{(i)}$  with common  $i$  and  $\kappa$  :  $H$  is already diagonal in categories as a whole.

Perturbation calculus can be applied independent within each category. With variational calculus the try function can be chosen within a separate category because the exact eigenfunctions transform according to a row of an irreducible representation.

### 3.7-/ The Wigner-Eckart theorem

**Theorem :** The matrix element  $\langle \Phi_\lambda^{(i)} | A_\kappa^{(j)} | \Phi_\mu^{(k)} \rangle$  can only be  $\neq 0$  if  $\Gamma^{(j)} \otimes \Gamma^{(k)} \otimes \dots \oplus \Gamma^{(i)} \oplus \dots$

If this is the case holds (if  $\Gamma^{(i)}$  appears only once, otherwise one has to sum over  $a$ ) :

$$\boxed{\langle \Phi_\lambda^{(i)} | A_\kappa^{(j)} | \Phi_\mu^{(k)} \rangle = (i\lambda | j\kappa k\mu) \langle \Phi^{(i)} || A^{(j)} || \Psi^{(k)} \rangle}$$

This theorem can be used to determine selection rules : the probability of a dipole transition is given by ( $\vec{\varepsilon}$  is the direction of polarization of the radiation) :

$$P_D = \frac{8\pi^2 e^2 f^3 |r_{12}|^2}{3\hbar \varepsilon_0 c^3} \text{ with } r_{12} = \langle l_2 m_2 | \vec{\varepsilon} \cdot \vec{r} | l_1 m_1 \rangle$$

Further it can be used to determine intensity ratios : if there is only one value of  $a$  the ratio of the matrix elements are the Clebsch-Gordan coefficients. For more  $a$ -values relations between the intensity ratios can be stated. However, the intensity ratios are also dependent on the occupation of the atomic energy levels.

## 4. Continuous groups

Continuous groups have  $\hbar = \infty$ . However, not all groups with  $\hbar = \infty$  are continuous, e.g. the translation group of an spatially infinite periodic potential is not continuous but does have  $\hbar = \infty$ .

### 4.1-/ The 3-dimensional translation group

For the translation of wave function over a distance  $a$  holds :  $P_a \Psi(x) = \Psi(x - a)$ . Taylor expansion near  $x$  gives :

$$\Psi(x - a) = \Psi(x) - a \frac{d\Psi(x)}{dx} + \frac{1}{2} a^2 \frac{d^2\Psi(x)}{dx^2} - \dots$$

Because the momentum operator in quantum mechanics is given by :  $p_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$ , this can be written as :

$$\boxed{\Psi(x - a) = e^{-\frac{i}{\hbar} a p_x} \Psi(x)}$$

### 4.2-/ The 3-dimensional rotation group

This group is called SO(3) because a faithful representation can be constructed from orthogonal 3x3 matrices with a determinant of +1.

For an infinitesimal rotation around the  $x$ -axis holds :

$$\begin{aligned} P_{\delta\theta_x} \Psi(x, y, z) &\approx \Psi(x, y + z\delta\theta_x, z - y\delta\theta_x) \\ &= \Psi(x, y, z) + \left( z\delta\theta_x \frac{\partial}{\partial y} - y\delta\theta_x \frac{\partial}{\partial z} \right) \Psi(x, y, z) \\ &= \left( 1 - \frac{i\delta\theta_x L_x}{\hbar} \right) \Psi(x, y, z) \end{aligned}$$

Because the angular momentum operator is given by :  $L_x = \frac{\hbar}{i} \left( z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right)$

$$\text{So in an arbitrary direction holds : } \begin{cases} \text{Rotations : } P_{\alpha, \vec{n}} = e^{-\frac{i}{\hbar} \alpha (\vec{n} \cdot \vec{J})} \\ \text{Translations : } P_{a, \vec{n}} = e^{-\frac{i}{\hbar} a (\vec{n} \cdot \vec{p})} \end{cases}$$

$J_x, J_y$  and  $J_z$  are called the *generators* of the 3-dim. rotation group,  $p_x, p_y$  and  $p_z$  are called the *generators* of the 3-dim. translation group.

The commutation rules for the generators can be derived from the properties of the group for multiplications : translations are interchangeable  $\leftrightarrow p_x p_y - p_y p_x = 0$ .

Rotations are not generally interchangeable : consider a rotation around axis  $\vec{n}$  in the  $z$ -plane over an angle  $\alpha$ . Then holds :  $P_{\alpha, \vec{n}} = P_{-\theta, y} P_{\alpha, x} P_{\theta, y}$ , so :

$$e^{-\frac{i}{\hbar} \alpha (\vec{n} \cdot \vec{J})} = e^{\frac{i}{\hbar} \theta J_y} e^{-\frac{i}{\hbar} \alpha J_x} e^{-\frac{i}{\hbar} \theta J_y}$$

If  $\alpha$  and  $\theta$  are very small and are expanded to second order, and the corresponding terms are put equal with  $\vec{n} \cdot \vec{J} = J_x \cos \theta + J_z \sin \theta$ , it follows from the  $\alpha \theta$  term :  $J_x J_y - J_y J_x = i \hbar J_z$ .

### 4.3- Properties of continuous groups

The elements  $R(p_1, \dots, p_n)$  depend continuously on parameters  $p_1, \dots, p_n$ . For the translation group this are e.g.  $an_x, an_y$  and  $an_z$ . It is demanded that the multiplication and inverse of an element  $R$  depend continuously on the parameters of  $R$ .

The statement that each element arises only once in each row and column of the Cayley table holds also for continuous groups. The notion conjugacy class for continuous groups is defined equally as for discrete groups. The notion representation is fitted by demanding continuity : each matrix element depends continuously on  $p_i(R)$ .

Summation over all group elements is for continuous groups replaced by an integration. If  $f(R)$  is a function defined on  $G$ , e.g.  $\Gamma_{\alpha\beta}(R)$ , holds :

$$\int_G f(R) dR = \int \dots \int_{p_1 \dots p_n} f(R(p_1, \dots, p_n)) g(R(p_1, \dots, p_n)) dp_1 \dots dp_n$$

Here,  $g(R)$  is the *density function*.

Because of the properties of the Cayley table is demanded :  $\int f(R) dR = \int f(SR) dR$ . This fixes  $g(R)$  except for a constant factor. Define new variables  $p'$  by :  $SR(p_i) = R(p'_i)$ . If one written  $dV = dp_1 \dots dp_n$  holds :

$$g(S) = g(E) \frac{dV}{dV'}$$

Here,  $\frac{dV}{dV'}$  is the *Jacobian* :  $\frac{dV}{dV'} = \det \left( \frac{\partial p_i}{\partial p'_j} \right)$ , and  $g(E)$  is constant.

For the translation group holds :  $g(\vec{a}) = \text{constant} = g(\vec{0})$  because  $g(a\vec{n}) d\vec{a}' = g(\vec{0})$  and  $d\vec{a}' = d\vec{a}$

This leads to the fundamental orthogonality theorem :

$$\int_G \Gamma_{\mu\nu}^{(i)*}(R) \Gamma_{\alpha\beta}^{(j)}(R) dR = \frac{1}{l_i} \delta_{ij} \delta_{\mu\alpha} \delta_{\nu\beta} \int_G dR$$

*Compact groups* are groups with group volume :  $\int_G dR < \infty$ .

## 5. The group SO(3)

One can take 2 parameters for the direction of the rotational axis and one for the angle of rotation  $\varphi$ . The parameter space is a collection points  $\varphi \vec{n}$  within a sphere with radius  $\pi$ . The diametrical points on this sphere are equivalent because  $R_{\vec{n},\pi} = R_{-\vec{n},\pi}$ .

Another way to define parameters is by means of *Euler angles*. If  $\alpha, \beta$  and  $\gamma$  are the 3 Euler angles, defined as :

1- The spherical angles of axis 3 w.r.t.  $xyz$  are  $\theta, \varphi = \beta, \alpha$ . Now a rotation around axis 3 remains possible.

2- The spherical angles of the  $z$ -axis w.r.t. 123 are  $\theta, \varphi = \beta, \pi - \gamma$

then the rotation of a quantum mechanical system is described by :

$$\Psi \rightarrow e^{-\frac{i}{\hbar} \alpha J_z} e^{-\frac{i}{\hbar} \beta J_y} e^{-\frac{i}{\hbar} \gamma J_z} \Psi. \text{ So } P_R = e^{-\frac{i}{\hbar} \varepsilon(\vec{n} \cdot \vec{J})}$$

All irreducible representations of SO(3) can be constructed from the behavior of the spherical harmonics  $Y_l^m(\theta, \varphi)$  with  $-l \leq m \leq l$  and for a fixed  $l$  :

$$P_R Y_l^m(\theta, \varphi) = \sum_{m'} Y_l^{m'}(\theta, \varphi) D_{mm'}^{(l)}(R)$$

$D^{(l)}$  is an irreducible representation of dimension  $2l+1$ . The character of  $D^{(l)}$  is given by :

$$\chi^{(l)}(\alpha) = \sum_{m=-l}^{m=l} e^{im\alpha} = 1 + 2 \sum_{k=1}^l \cos k\alpha = \frac{\sin\left(l + \frac{1}{2}\right)\alpha}{\sin \frac{\alpha}{2}}$$

In the performed derivation  $\alpha$  is the rotational angle around the  $z$ -axis. This expression is valid for all rotations over an angle  $\alpha$  because the classes of  $SO(3)$  are rotations around the same angle around an axis with an arbitrary orientation.

Via the fundamental orthogonality theorem for characters one obtains the following expression for the density function (which is normalized so that  $g(0) = 1$ ) :

$$g(\alpha) = \frac{\sin^2 \frac{\alpha}{2}}{\left(\frac{\alpha}{2}\right)^2}$$

With this result one can see that the given representations of  $SO(3)$  are the only ones : the character of another representation  $\chi'$  would have to be  $\perp$  to the already found ones, so

$\chi'(\alpha) \sin^2 \frac{\alpha}{2} = 0 \forall \alpha \Rightarrow \chi'(\alpha) = 0 \forall \alpha$ . This is contradictory because the dimension of the representation is given by  $\chi'(0)$ . Because fermions have an half-odd integer spin the states  $\Psi_{S, m_S}$  with  $S = \frac{1}{2}$  and  $m_S = \pm \frac{1}{2}$  constitute a 2-dim. space which is invariant under rotations. A problem arises for rotations over  $2\pi$  :

$$\Psi_{\frac{1}{2}, m_S} \rightarrow e^{-\frac{2i\pi}{\hbar} S_z} \Psi_{\frac{1}{2}, m_S} = e^{-2i\pi m_S} \Psi_{\frac{1}{2}, m_S} = -\Psi_{\frac{1}{2}, m_S}$$

However, in  $SO(3)$  :  $R_{z, 2\pi} = E$ . So here holds  $E \rightarrow \pm \Pi$ . Because observable quantities can always be written as  $\langle \Phi | \Psi \rangle$  or  $\langle \Phi | A | \Psi \rangle$ , and are bilinear in the states, they do not change sign if the states do. If only one state changes sign the observable quantities do change.

The existence of these half-odd integer representations is connected with the topological properties of  $SO(3)$  : the group is two-fold coherent through the identification  $R_0 = R_{2\pi} = E$ .

## 6. Applications to quantum mechanics

### 6.1-/ Vector model for the addition of angular momentum

If two systems have angular momentum quantum numbers  $j_1$  and  $j_2$  the only possible values for the total angular momentum are  $J = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2|$ . This can be derived from group theory as follows : from  $\chi^{(j_1)}(\alpha) \chi^{(j_2)}(\alpha) = \sum_J n_J \chi^{(J)}(\alpha)$  follows :

$$D^{(j_1)} \otimes D^{(j_2)} = D^{(j_1+j_2)} \oplus D^{(j_1+j_2-1)} \oplus \dots \oplus D^{(j_1-j_2)}$$

The states can be characterized by quantum numbers in two ways : with  $j_1, m_1, j_2, m_2$  and with  $j_1, j_2, J, M$ . The Clebsch-Gordan coefficients, for  $SO(3)$  called the *Wigner coefficients*, can be chosen real, so :



$$\Psi_{j_1 j_2 JM} = \sum_{m_1 m_2} \Psi_{j_1 j_2 m_1 m_2} (j_1 m_1 j_2 m_2 | JM)$$

$$\Psi_{j_1 j_2 m_1 m_2} = \sum_{JM} \Psi_{j_1 j_2 JM} (j_1 m_1 j_2 m_2 | JM)$$

## 6.2-/ Irreducible tensor operators, matrix elements and selection rules

### Some examples of the behavior of operators under SO(3)

1. Suppose  $j = 0$  : this gives the identical representation with  $l_j = 1$ . This state is described by a **scalar operator**. Because  $P_R A_0^{(0)} P_R^{-1} = A_0^{(0)}$  this operator is invariant, e.g. the Hamiltonian of a free atom. Then holds :  $\langle J' M' | H | JM \rangle \approx \delta_{MM'} \delta_{JJ'}$ .

2. A **vector operator** :  $\vec{A} = (A_x, A_y, A_z)$ . The cartesian components of a vector operator transform equally as the cartesian components of  $\vec{r}$  by definition. So for rotations around the  $z$ -axis holds :

$$D(R_{\alpha,z}) = \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The transformed operator has the same matrix elements w.r.t.  $P_R \Psi$  and  $P_R \Phi$  :

$$\langle P_R \Psi | P_R A_x P_R^{-1} | P_R \Phi \rangle = \langle \Psi | A_x | \Phi \rangle \text{ and } \chi(R_{\alpha,z}) = 1 + 2 \cos \alpha$$

According to the equation for characters this means one can choose base operators which transform like  $Y_l^m(\theta, \varphi)$ . These turn out to be the spherical components :

$$A_{+1}^{(1)} = -\frac{1}{\sqrt{2}}(A_x + iA_y) \quad , \quad A_0^{(1)} = A_z \quad , \quad A_{-1}^{(1)} = \frac{1}{\sqrt{2}}(A_x - iA_y)$$

3. A **cartesian tensor of rank 2** :  $T_{ij}$  is a quantity which transforms under rotations like  $U_i V_j$ , where  $\vec{U}$  and  $\vec{V}$  are vectors. So  $T_{ij}$  transform like  $P_R T_{ij} P_R^{-1} = \sum_{kl} T_{kl} D_{ki}(R) D_{lj}(R)$ , so like

$$D^{(1)} \otimes D^{(1)} = D^{(2)} \oplus D^{(1)} \oplus D^{(0)}$$

The 9 components can be split in 3 invariant subspaces with dimension  $1(D^{(0)})$ ,  $3(D^{(1)})$  and  $5(D^{(2)})$ . The new base operators are :

I.  $\text{Tr}(T) = T_{xx} + T_{yy} + T_{zz}$ . This transforms as the scalar  $\vec{U} \cdot \vec{V}$ , so as  $D^{(0)}$ .

II. The 3 antisymmetric components  $A_z = \frac{1}{2}(T_{xy} - T_{yx})$ , etc. These transform as the vector  $\vec{U} \wedge \vec{V}$ , so as  $D^{(1)}$ .

III. The 5 independent components of the traceless, symmetric tensor  $S$  :

$$S_{ij} = \frac{1}{2}(T_{ij} + T_{ji}) - \frac{1}{3} \delta_{ij} \text{Tr}(T). \text{ These transform as } D^{(2)}.$$

### Selection rules for dipole transitions

Dipole operators transform as  $D^{(1)}$  : for an electric dipole transfer is the operator  $e\vec{r}$  for a magnetic  $\frac{e}{2m}(\vec{L} + 2\vec{S})$ . From the Wigner-Eckart theorem follows :  $\langle J' M' | A_{\kappa}^{(1)} | JM \rangle = 0$  except

$D^{(J')}$  is a part of  $D^{(1)} \otimes D^{(J)} = D^{(J+1)} \oplus D^{(J)} \oplus D^{(|J-1|)}$ .

This means that,  $J' \in \{J+1, J, |J-1|\}$  :  $J' = J$  or  $J' = J \pm 1$  except  $J' = J = 0$ .

### Landé-equation for the anomalous Zeeman splitting

According to Landé's model the interaction between a magnetic moment with an external magnetic field is determined by the projection of  $\vec{M}$  on  $\vec{J}$  because  $\vec{L}$  and  $\vec{S}$  precess fast around  $\vec{J}$ . This can also be understood from the Wigner-Eckart theorem : from this follows that the matrix elements from all vector operators show a certain proportionality. For an arbitrary operator  $\vec{A}$  follows :

$$\langle \alpha jm' | \vec{A} | \alpha jm \rangle = \frac{\langle \alpha jm | \vec{A} \cdot \vec{J} | \alpha jm \rangle}{j(j+1)\hbar^2} \langle \alpha jm' | \vec{J} | \alpha jm \rangle$$