

### 3 Principles of Structure and Symmetry

In this chapter we begin with the quantum mechanical description of the hydrogen atom and the transition from atomic to molecular orbitals. We continue with the harmonic oscillator and rigid rotor., Then the splitting of the electron energy levels will be explained without the aid of quantum mechanics. Finally, the use of group theory for the examination of molecular symmetry will be demonstrated.

#### 3.1 The Results of Quantum Mechanics

##### 3.1.1 The Road to the Calculation of the Hydrogen Atom

In 1900, Max Planck presented the relationship between the energy  $E$  and the frequency  $\nu$  of the microscopic oscillators in a black body as

$$E = n h \nu. \quad (3.01)$$

$n$  is a natural number and  $h$  is the Planck constant, which was later named after him. In 1913, the quantization of the energy followed the quantization of the orbital angular momentum of the electron. Niels Bohr postulated in his atomic model that the electrons follow circular orbits around the nucleus with an angular momentum of  $p = n \hbar = n h/2\pi$ . The radius is  $r_n = a n^2$ , with  $a = 4\pi\epsilon_0 \hbar^2/Zm_r e^2$ , which is the orbital radius for  $n = 1$ , and  $Z$  represents the atomic number. The atomic constant known as the Bohr radius of the hydrogen atom is defined as  $a_0 = 4\pi\epsilon_0 \hbar^2/m_e e^2 \approx 0,529 \times 10^{-10}$  m. This number contains the following physical constants: dielectric constant, Planck constant/ $2\pi$ , the rest mass of the electron, and the electric charge. Bohr further postulated that the electrons in these states do not emit energy according to the laws of classical electrodynamics. The transition from a higher energy level  $n'$  to a lower level  $n''$  should however emit the classically calculated difference  $\Delta E$  in the form of a photon with the energy  $h\nu$ :

$$\Delta E = \frac{m_r e^4}{8h^2 \epsilon_0^2} \left( \frac{1}{n''^2} - \frac{1}{n'^2} \right) = h\nu. \quad (3.02)$$

The reduced mass  $m_r$  of an electron-nucleus pair is  $m_r = m_e m_{\text{nucleus}}/(m_e + m_{\text{nucleus}})$ . Janne Robert Rydberg found in 1889 that the wave number  $\tilde{\nu}$  (the reciprocal of the wavelength measured in units of  $\text{cm}^{-1}$ ) can be written as a difference of terms in a way analogous to equ. (3.02). The constant factor is calculated in an analogous equation for wave numbers and is called the Rydberg constant  $R$ .  $R_\infty$  denotes the constant for  $m_r = m_e$ , what is correct for a hypothetical nucleus with infinite mass. For the real nuclei, a correction factor of  $1 + m_e/m_{\text{nucleus}}$  must be taken into consideration:

$$R_\infty = \frac{m_e e^4}{8h^3 \epsilon_0^2 c_0} \approx 1,09737315 \times 10^7 \text{ m}^{-1} \quad \text{and} \quad R = \frac{R_\infty}{1 + \frac{m_e}{m_{\text{Kem}}}}. \quad (3.03)$$

If we set  $m_{\text{nucleus}}$  equal to the rest mass of a proton, we get  $R_H$ , which has been measured from the spectrum of hydrogen to be  $109677,58 \text{ cm}^{-1}$ .

The particle-wave duality of material has been a topic of fundamental discussions for centuries. Newton's theory that light has a pure corpuscular nature was dominant for a long time. The wave nature of light first won acceptance among physicists in the 19<sup>th</sup> century. The particle nature was not, however, forgotten. In 1906, Einstein used it to explain the photoelectric effect. Louis Victor Prince de Broglie generalized the wave nature in 1924. He proposed that all particles with momentum  $p$  have a wavelength  $\lambda$  given by the equation  $p = h/\lambda$ . In 1926 Max Born came to a compromise that still has validity today. He gave the wave function  $\psi(x,y,z,t)$ , which describes the amplitude of a wave as a function of position and time, a fundamentally statistical meaning. The particle is not at a particular point  $(x,y,z)$  at time  $t$ . Rather the product  $\psi\psi^*$  of the wave function  $\psi$  with its complex conjugate  $\psi^*$  tells us the probability that a particle will be found at time  $t$  at the location  $(x,y,z)$ . The wave function thus defined is an important part of Erwin Schrödinger's 1926 wave equation. The time independent Schrödinger equation is

$$\mathcal{H}\psi = E\psi. \quad (3.04)$$

This eigenvalue equation only has normalizable solutions  $\psi$  for certain eigenvalues of energy  $E$ . The solutions are called eigenfunctions.  $E$  can be considered as a numerical factor. It stands for the ensemble of the discrete eigenvalues of a quantum mechanical system that can be observed. The operator  $\mathcal{H}$  denotes a mathematical operation which has to be applied to the wave function. The simplest example is a non-interacting particle of mass  $m$  that moves in the  $x$ -direction along a potential  $V$  and the operation is a double differentiation of the wave function  $\psi$ :

$$\mathcal{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x). \quad (3.05)$$

The fundamental operator of quantum mechanics  $\mathcal{H}$  is named after William Rowan Hamilton, and is called the hamiltonian (Hamiltonian operator). Hamilton described classical mechanics in way that served Schrödinger about hundred years later as a basis for his wave mechanics. For simplicity, we present the hamiltonian along with other operators without the recommended hat. The three dimensional representation of the hamiltonian is:

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x) \quad (3.06)$$

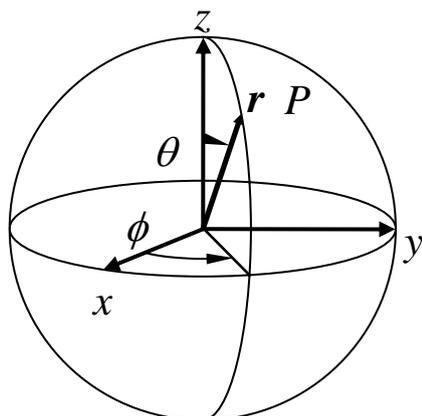
The operator  $\nabla^2$  (Nabla-squared) is called the Laplace operator or laplacian, and is named after Pierre Simon Laplace. It is often written as  $\Delta$ , and is explicitly written out in Cartesian coordinates as

$$\Delta = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (3.07)$$

and in spherical coordinates as

$$\Delta = \nabla^2 = \frac{1}{r^2 \sin \theta} \left[ \sin \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (3.08)$$

$r$  is the distance to the origin, which we will place inside the nucleus. Figure 3.1 shows a sphere of radius  $r$ . The vector  $\mathbf{r}$  connects the origin in the middle of the sphere with a point  $P$  on the surface. In polar coordinates, the point is given by  $P(r, \theta, \phi)$ , and in Cartesian coordinates by  $P(x, y, z)$ .



**Fig. 3.1** Polar coordinates. The range of the angles is  $0 \leq \theta \leq \pi$  and  $0 \leq \phi < 2\pi$ .

To convert between  $P(r, \theta, \phi)$  and  $P(x, y, z)$ , one can use the following equations:

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta. \quad (3.09)$$

The solution of the time dependent Schrödinger equation describes the temporal development of the system:

$$\mathcal{H} \psi = i \hbar \frac{\partial \psi}{\partial t}. \quad (3.10)$$

We have now arrived at the hydrogen atom, where an electron with the reduced mass  $m_r$  and charge  $-e$  moves in the electric field of a nucleus with charge  $e$ . The Coulomb potential contains  $r$  as the distance between the charges, and the hamiltonian becomes

$$\mathcal{H} = -\frac{\hbar^2}{2m_r} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}. \quad (4.11)$$

The laplacian in polar coordinates, equ. (4.08), which appears complicated in comparison to its Cartesian representation, equ. (4.07), greatly simplifies the problem for spherically symmetrical charge distributions. A good approach to the problem is to introduce a wave function that is composed of products of well known radial and spherical functions. The wave function then looks like

$$\psi(r, \theta, \phi) = R_{n\ell}(r) N_{\ell|m|} P_{\ell}^{|m|}(\theta) e^{im\phi} = R_{n\ell}(r) Y_{\ell m}(\theta, \phi). \quad (3.12)$$

We will begin with the physical explanation of the radial component  $R$  of this equation.  $n$  represents the principal quantum number,  $\ell$  is the orbital quantum number for which  $\ell < n$ , and  $m$  (actually  $m_{\ell}$  with  $\ell \leq m \leq \ell$ ) is the magnetic quantum number which is also known as the orientational quantum number (orientation of the orbital angular momentum with respect to the direction of any magnetic or electric external field). For the radial wave function  $R_{n\ell}(r)$ , the radius  $r$  is often replaced by the dimensionless quantity  $\rho = r/a_0$ , where  $a_0$  is the Bohr radius of the hydrogen atom. For hydrogen-like nuclei with atomic charge  $Z$ ,  $a_0$  has to be replaced with  $a_0/Z$ . In the first three shells ( $n = 1, 2, 3$ ),  $R(\rho)$  becomes

$$\begin{aligned} R_{10} &= \frac{1}{\sqrt{a_0^3}} 2e^{-\rho}, R_{20} = \frac{1}{\sqrt{8a_0^3}} (2 - \rho)e^{-\frac{\rho}{2}}, R_{21} = \frac{1}{\sqrt{24a_0^3}} \rho e^{-\frac{\rho}{2}} \\ R_{30} &= \frac{1}{\sqrt{243a_0^3}} (6 - 6\rho + \rho^2)e^{-\frac{\rho}{2}}, R_{31} = \frac{1}{\sqrt{486a_0^3}} (4 - \rho)\rho e^{-\frac{\rho}{2}}, R_{32} = \frac{1}{\sqrt{2430a_0^3}} \rho^2 e^{-\frac{\rho}{2}}. \end{aligned} \quad (3.13)$$

The radial wave functions go exponentially toward zero as  $\rho$  increases. They can, however, be zero or even negative, as one can easily see in  $R_{20}$  for  $\rho = 2$  and  $\rho > 2$ . The probability of finding an electron in the radial direction is determined from the quantity  $4\pi\rho^2 R_{n\ell}^2$ .

The  $N_{\ell|m|}$  in equ. (3.12) is a normalization factor. The  $\theta$  dependent function  $P_{\ell}^{/m|}(\cos\theta)$  represents for  $m = 0$  the Legendre polynomials, named after Adrien Marie Legendre. When  $m \neq 0$ , they are called the Legendre associated functions of degree  $\ell$  and order  $|m|$ . On the right side of equ. (3.12), the Laplace spherical function  $Y_{\ell m}(\theta, \phi) = N_{\ell|m|} P_{\ell}^{/m|}(\cos\theta) \exp(im\phi)$  is used. The functions for  $\ell = 0, 1$  and  $2$  are given in equ. (3.11). In consideration of further necessary transformations, we have written the Cartesian coordinate versions of the equations in equ. (3.14) as well. With the equations in equ. (3.09) and the relation  $\exp(i\phi) = \cos\phi + i \sin\phi$ , we become  $Y_{\ell m}(x/r, y/r, z/r)$  from the representation of  $Y_{\ell m}(\theta, \phi)$ :

$$\begin{aligned} Y_{00} &= \frac{1}{\sqrt{4\pi}}, & Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r}, \\ Y_{1\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi} = \mp \sqrt{\frac{3}{8\pi}} \frac{x \pm iy}{r}, & Y_{20} &= \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1) = \sqrt{\frac{5}{16\pi}} \frac{3z^2 - r^2}{r^2}, \\ Y_{2\pm 1} &= \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{\pm i\phi} = \mp \sqrt{\frac{15}{8\pi}} \frac{(x \pm iy)z}{r^2}, & Y_{2\pm 2} &= \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{\pm 2i\phi} = \sqrt{\frac{15}{32\pi}} \left(\frac{x \pm iy}{r}\right)^2. \end{aligned} \quad (3.14)$$

We are now faced with the problem of finding a spatial representation of the wave function  $\psi(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$  for selected quantum numbers  $n, \ell$  and  $m$ . The first hurdle is the complex factor in the spherical function for  $m > 0$ . One result of quantum mechanics is that in the absence of an external field, the functions  $Y_{\ell m}$  have  $\ell$ -fold degeneracy. In other words:  $\ell$  functions  $Y_{\ell m}$  have the same energy eigenvalue. A further result of quantum mechanics is that linear combinations of degenerate functions are also solutions of the Schrödinger equation. We can immediately see in equ. (3.14) that through the addition or subtraction of functions with opposite signs of  $m$ , we can cancel the imaginary or real component. The combinations

$$\psi_{2p_x} = \frac{1}{\sqrt{2}} (-\psi_{2p,1} + \psi_{2p,-1}) \quad \text{und} \quad \psi_{2p_y} = \frac{i}{\sqrt{2}} (\psi_{2p,1} + \psi_{2p,-1}) \quad (3.15)$$

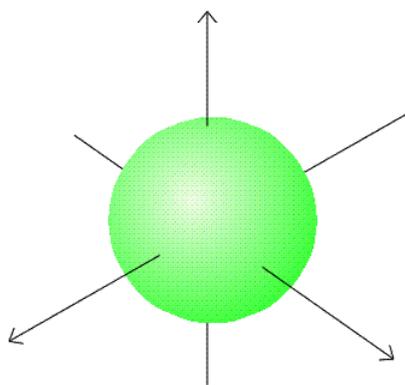
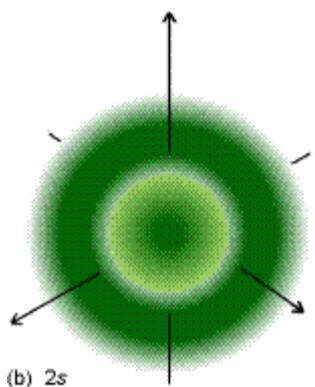
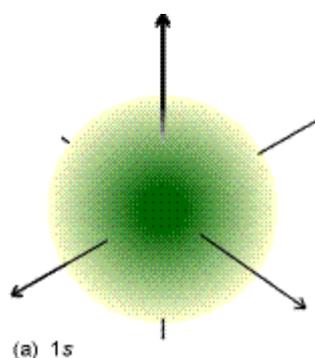
are real valued functions. The functions with  $m = 0$  are in any case real, cf. equ. (3.14). By indexing the real functions, we have peaked ahead to section 3.2: Functions that belong to the orbital quantum number  $\ell = 0, 1$  and  $2$ , we index with s, p and d, respectively. The index 2p stands therefore for  $n = 2$  and  $\ell = 1$ . The third place in the index holds the coordinate(s) which the wave function depends on. If we put the respective functions from the right side of equ. (3.14) into the sum or difference of two wave functions with parity values of  $m$ , for example in equ. (3.15), we immediately recognize the coordinates  $x, y$  or  $z$  when  $\ell = 1$ , or  $z^2, xz, yz, x^2 - y^2$  or  $xy$  when  $\ell = 2$ :

$$\begin{aligned} \psi_{1s} &= \sqrt{\frac{1}{4\pi}} R_{10}, & \psi_{2p_x} &= \sqrt{\frac{3}{4\pi}} R_{21} \frac{x}{r}, & \psi_{2p_y} &= \sqrt{\frac{3}{4\pi}} R_{21} \frac{y}{r}, & \psi_{2p_z} &= \sqrt{\frac{3}{4\pi}} R_{21} \frac{z}{r}, \\ \psi_{3d_{z^2}} &= \sqrt{\frac{5}{4\pi}} R_{30} \frac{3z^2 - r^2}{2r^2}, & \psi_{3d_{zx}} &= \sqrt{\frac{15}{4\pi}} R_{31} \frac{zx}{r^2}, & \psi_{3d_{yz}} &= \sqrt{\frac{15}{4\pi}} R_{31} \frac{yz}{r^2}, \\ \psi_{3d_{x^2-y^2}} &= \sqrt{\frac{15}{4\pi}} R_{32} \frac{x^2 - y^2}{2r^2}, & \psi_{3d_{xy}} &= \sqrt{\frac{15}{4\pi}} R_{32} \frac{xy}{r^2}. \end{aligned} \quad (3.16)$$

The equations in equ. (3.16) help us find surfaces on which the function's value is zero. To illustrate such surfaces, consider for example 2p<sub>x</sub> with  $x = 0$  and any  $y$  or  $z$ , or 3d<sub>z<sup>2</sup></sub> with  $z = \pm 3^{-1/2} r$  and any  $x$  or  $y$ , or 3d<sub>xz</sub> with  $x = 0$  and any  $y$  or  $z$ , or  $z = 0$  and any  $y$  or  $x$ .

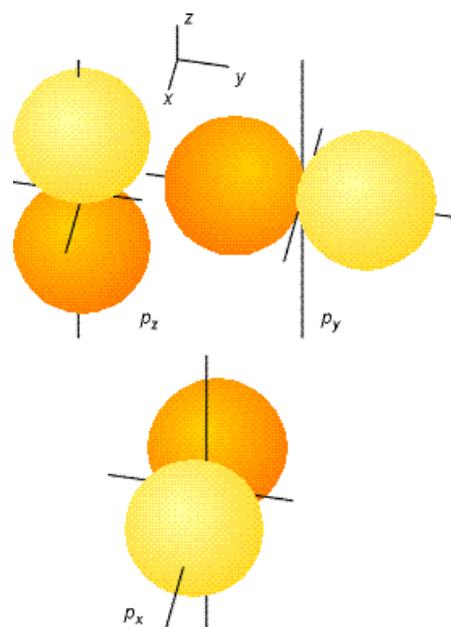
The equations (3.12), (3.13) and (3.16) now allow us to construct a 3-dimensional depiction of the wave functions for  $n = 1, 2$  and 3. Let's begin with the spherical s-orbitals. 1s has no radial zero points, 2s has one, and 3s has two. We will depict a cross-section of the orbitals (for example  $z = 0$ ), where the darkness of the shades of gray in Fig. 3.2 increases with the value of the wave function. One problem of this presentation becomes apparent with the 3s-orbital: According to equ. (3.13), the middle ring has a negative value of the wave, while all the other rings have positive values. The difference of signs can't be seen using this method.

A simpler method is necessary for the more complicated p and d orbitals. We divide space into the smallest possible regions with a 90% probability of containing the electron. The rest of space only has 10% of the electron density. In three dimensions, we draw the surface areas of these volumes, or in two dimensions the boundary lines. Only the 1s-Orbital is portrayable with only one closed region. We will also label the separated regions with the sign of the wave function in those regions. The simplest p-orbitals are the 2p-orbitals, and the simplest d-orbitals are the 3d-orbitals. Fig. 3.4 shows the 3-dimensional portrayal of these orbitals.



**Fig. 3.2** The s-orbitals of the hydrogen atom, left 1s, lower left 2s. The values of the radial wave function are represented by different colors (or shades of gray). Below at right is an s-orbital showing the 90% (taken from Atkins, 6<sup>th</sup> ed., Fig. 13.11+13.12).

**Fig. 3.3** (at right) The 2p orbitals of the hydrogen atom. The nodal planes go through the nucleus. Yellow and orange (or light and dark) areas describe different signs of the wave function. (taken from Atkins, 6<sup>th</sup> ed., Fig.13.17).



For visualization of the atomic orbitals of hydrogen, refer to:  
<http://www.orbitals.com/orb/ov.htm> and  
<http://www-wilson.ucsd.edu/education/pchem/qm/orbvisual.html>

The previous equations are only true for the hydrogen atom, and have to be slightly modified for hydrogen-like atoms, and atoms with a single electron in the outer shell. A description of the splitting of the electron energy levels for multi-electron systems and linear molecules is done in chapter 3.2, without an explanation of the quantum mechanical basis.

### 3.1.2 From Atomic to Molecular Orbitals

The simplest molecule to calculate is the hydrogen molecular ion, which is composed of one electron and two nuclei of one proton each. But even the treatment of this three body problem is so difficult, that we will first introduce an approximation that considers atomic states to be independent of electron states. This simplification, which is known as the Born-Oppenheimer-approximation, is justified because the nuclei, which are very heavy in comparison to the electron, hardly react to a change of the electron state. With this approximation, the problem is reduced to the one-particle Schrödinger equation of an electron in the potential of nuclei A and B with the distance  $R$ . The potential that the electron feels can thus be replaced by

$$V = -\frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_A} + \frac{1}{r_B} \right). \quad (3.17)$$

In the hamiltonian appears the electron mass  $m_e$ , which is assumed to be infinitesimal in comparison to the nuclear masses:

$$\mathcal{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_A} + \frac{1}{r_B} \right). \quad (3.18)$$

By comparing equ. (3.18) with equ. (3.11) it is important to note that the total energy  $E$  is composed of the eigenvalue of the Schrödinger equation and the repulsion of the nuclei:

$$V_{\text{nuclear repulsion}} = \frac{e^2}{4\pi\epsilon_0 R} \quad (3.19)$$

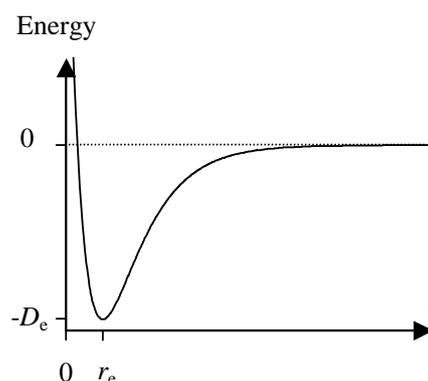
Let us now make the assumption that the electron is near the nucleus A (or B). In that case we can disregard the term  $1/r_B$  (or  $1/r_A$ ), because  $r_A \ll r_B$  (or  $r_B \ll r_A$ ), and equ. (3.18), like equ. (3.11), describes the atomic orbitals. Accordingly, the wave function of an electron near a nucleus in a molecular ion should be described by the overlapping of two atomic orbitals:

$$\begin{aligned} \psi &= N[\psi_{1s}(A) + \psi_{1s}(B)] \text{ and} \\ \psi^2 &= N^2 \left[ \{\psi_{1s}(A)\}^2 + \{\psi_{1s}(B)\}^2 + 2\psi_{1s}(A)\psi_{1s}(B) \right] \text{ where} \\ \int \psi^2 d\tau &= 1 \quad \text{and} \quad S = \int \psi_{1s}(A)\psi_{1s}(B) d\tau = \frac{1}{2N^2} - 1. \end{aligned} \quad (3.20)$$

The normalization factor  $N$  ensures the usual normalization condition  $\int \psi^2 d\tau = 1$  in relation to the molecular orbital.  $S$  refers to the overlap integral. equ. (3.20) is a linear combination of atomic orbitals. (**L**inear **C**ombination of **A**tomical **O**rbitals = LCAO). Although the s-orbitals have a spherical symmetry, the molecular orbital defined in equ. (3.20) has only a rotational symmetry about the axis connecting the nuclei. Such rotationally symmetric electron densities are generally referred to as  $\sigma$ -orbitals (see chapter 3.2), and specifically the state in equ. (3.20) is the  $1s\sigma$ -orbital.

Bonding orbitals are states whose population with a single electron leads to a reduction of the total energy  $E$  of the molecule. If we consider the dependency of this energy on the distance  $r$  between the nuclei of a diatomic molecule, the energy decreases from a fixed value at  $r = \infty$  and  $E = 0$  (convention for the energy scale) to a minimum at  $r = r_e$  and  $E = -D_e$  (see Fig. 3.4). The reason for this reduction is the increase in the electron density in the internuclear region resulting from the increasing overlapping of the atomic orbitals. At the minimum, this effect is compensated by the repulsion of the two nuclei. With the LCAO-approximation for  $\text{H}_2^+$ , the equilibrium bond length  $r_e = 130$  pm and the spectroscopic dissociation energy is calculated to be  $D_e = 1,77$  eV. The experimentally determined values are  $r_e = 106$  pm and  $D_e = 2,6$  eV. This shows that the LCAO methods for the calculation of molecular orbitals fail to give exact values even for the simplest example. That does not, however, affect their usefulness for a qualitative description of molecular orbitals.

**Fig. 3.4** Potential curve of a diatomic molecule. The distance between the nuclei at the minimum is referred to by  $r_e$  and the minimum of the energy is  $D_e$  below the value 0 for the dissociated molecule ( $r = \infty$ ).



An antibonding orbital is created when the 1s atomic orbitals are subtracted rather than added:

$$\begin{aligned} \psi' &= N[\psi_{1s}(A) - \psi_{1s}(B)] \text{ and} \\ \psi'^2 &= N^2[\{\psi_{1s}(A)\}^2 + \{\psi_{1s}(B)\}^2 - 2\psi_{1s}(A)\psi_{1s}(B)] \end{aligned} \quad (3.21)$$

The term in the lower right of equ. (3.21) reduces the electron density between the nuclei and raises the total energy compared to the separated atoms. That orbital is referred to with  $1s\sigma^*$ , where  $\sigma$  again refers to the rotational symmetry. All antibonding orbitals sport an asterisk. We will consider molecules composed of two identical atoms from the 2nd period for the further description of molecular orbitals. The same considerations that we used for  $\text{H}_2^+$  are valid for  $2s\sigma$  and  $2s\sigma^*$ . However, we now also have the 2p orbitals that we label  $2p_x$ ,  $2p_y$  and  $2p_z$  in accordance with equ. (3.15). The  $z$ -direction points along the bonding direction in a diatomic molecule. Because of the rotational symmetry of a diatomic molecule, the combinations of the  $2p_x$  orbitals should not be differentiable from the combinations of the  $2p_y$  orbitals, but should be different than the  $2p_z$  orbitals:  $2p_{x,y} + 2p_{x,y}$  gives  $2p_{x,y}\pi$ ,  $2p_{x,y} - 2p_{x,y}$  gives  $2p_{x,y}\pi^*$ ,  $2p_z + 2p_z$  gives  $2p\sigma^*$  and  $2p_z - 2p_z$  gives  $2p\sigma$ . The  $\pi$  orbitals have a nodal plane through the molecular connection axis in the  $z$  direction.

In the upper shells there are, in general, non-bonding orbitals in addition to the bonding and antibonding orbitals. These orbitals have no influence on the total energy of the molecule. If d-electrons in the third or higher period are involved, we are dealing with  $\delta$  orbitals (see chapter 3.2).

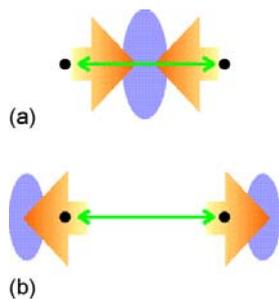


Fig. 14.22 taken from Atkins 6E: A partial explanation of the origin of bonding and antibonding effects. (a) In a bonding orbital, the nuclei are attracted to the accumulation of electron density in the internuclear region. (b) In an antibonding orbital, the nuclei are attracted to an accumulation of electron density outside the internuclear region.

Fig. 14.23 taken from Atkins 6E: A molecular orbital energy level diagram for orbitals constructed from the overlap of H1s orbitals; the separation of the levels corresponds to that found at the equilibrium bond length. The ground electronic configuration of H<sub>2</sub> is obtained by accommodating the two electrons in the lowest available orbital (the bonding orbital).

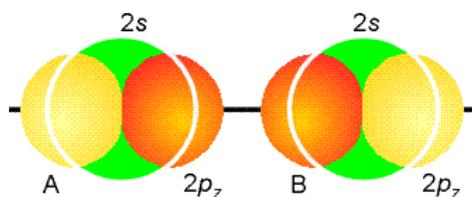
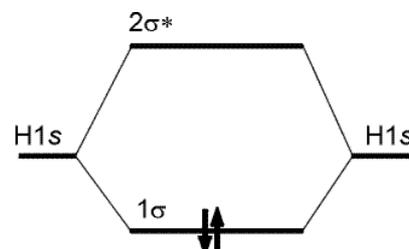


Fig. 14.25 taken from Atkins 6E: According to molecular orbital theory,  $\sigma$  orbitals are built from all orbitals that have the appropriate symmetry. In homonuclear diatomic molecules of Period 2, that means that two  $2s$  and two  $2p_z$  orbitals should be used. From these four orbitals, four molecular orbitals can be built.

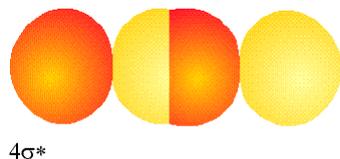


Fig. 14.26 taken from Atkins 6E: A representation of the composition of bonding and antibonding  $\sigma$  orbitals built from the overlap of  $p$  orbitals. These illustrations are schematic.

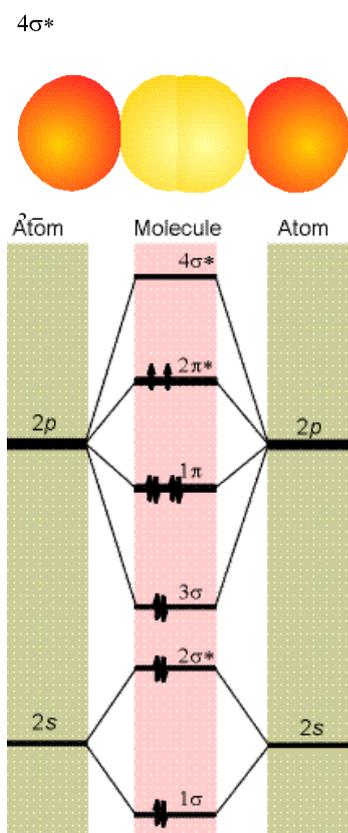


Fig. 14.29 taken from Atkins 6E: The molecular orbital energy level diagram for homonuclear diatomic molecules. As remarked in the text, this diagram should be used for O<sub>2</sub> and F<sub>2</sub>.

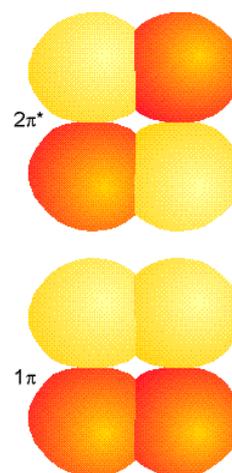


Fig. 14.27 taken from Atkins 6E: A schematic representation of the structure of  $\pi$  bonding and antibonding molecular orbitals.

Fig. 3.5 A few molecular orbitals and orbital energies from P. Atkins: Physical Chemistry, 6th ed.

### 3.1.3 The Harmonic Oscillator

A particle undergoes a harmonic oscillation in the  $x$ -direction, if the force  $F$  and potential  $V$  on it are described by

$$F = -fx \quad \text{and} \quad V = \frac{1}{2}fx^2. \quad (3.22)$$

$f$  represents the force constant. Putting this potential into the Schrödinger equation, see equ. (3.04) and equ. (3.05), leads to the Weber differential equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2}fx^2\psi = E\psi \Rightarrow \frac{\partial^2 \psi}{\partial y^2} + (\varepsilon - y^2)\psi = 0. \quad (3.23)$$

The Substitutions that led to the Weber equation in equ. (3.23) are

$$y = \frac{x\sqrt{mf}}{\sqrt{\hbar}} \quad \text{and} \quad \varepsilon = \frac{2E}{\hbar} \sqrt{\frac{m}{f}}. \quad (3.24)$$

$\varepsilon$  can be rewritten as  $\varepsilon = \frac{E}{\frac{1}{2}\hbar\omega}$ , if we make use of  $\omega = \sqrt{\frac{f}{m}}$  as the classical angular frequency of the harmonic oscillator. Although the harmonic oscillator is described by the motion of a single particle in a force field, the simplest example in spectroscopy is the motion of two atoms of a diatomic molecule around the common center of mass. In this case we have to replace the mass  $m$  in equ. (3.23) with the reduced mass  $m_r$ , and note that  $x = r - r_e$  represents the displacement of the interatomic distance  $r$  relative to the equilibrium distance.

A solution to the Schrödinger equation (3.23) can be found with  $\psi = H \exp(-y^2/2)$ . It results the hermitic differential equation, with its (for mathematicians) well-known solutions:

$$\frac{\partial^2 H}{\partial y^2} - 2y \frac{\partial H}{\partial y} + (\varepsilon - 1)H = 0. \quad (3.25)$$

If we select  $H(y)$  as a polynomial,  $\psi$  falls to zero for large  $y$ . Finite solutions of this differential equation exist only for  $\varepsilon = 2v + 1$  where  $v = 0, 1, 2, \dots$ . This leads to

$$E_v = (2v + 1) \frac{1}{2} \hbar \omega. \quad (3.26)$$

The corresponding wave functions are shown in Fig. 3.6. They are calculated from

$$\psi_v = N_v H_v(y) \exp(-y^2/2). \quad (3.27)$$

$N_v = [(\hbar\pi/m\omega)^{1/2} 2^v v!]^{-1/2}$  is a normalization factor for the benefit of the integral  $\int \psi^2 dy = 1$ . The hermitic polynomials are 1,  $2y$ ,  $4y^2 - 2$ ,  $8y^3 - 12y$  and  $16y^4 - 48y^2 + 12$  where  $v = 0, 1, 2, 3$  and 4. The general equation for the calculation of this polynomial is

$$H_v(y) = (-1)^v e^{y^2} \left( \frac{\partial}{\partial y} \right)^v e^{-y^2}. \quad (3.28)$$

The integral  $\int \psi(v) \psi(v') dy$  disappears by replacing two different wave functions for  $v$  and  $v'$  in  $\int \psi(v) \psi(v') dy$ , as is necessary for orthogonal wave functions.

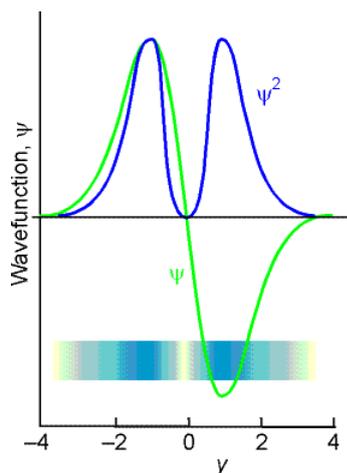


Fig. 12.18 taken from Atkins 6<sup>th</sup> ed.: The normalized wave function and probability distribution (shown also by shading) for the first excited state of a harmonic oscillator.

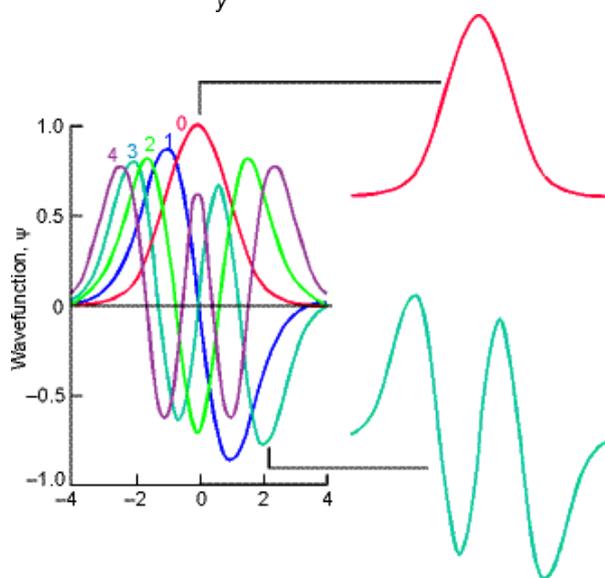
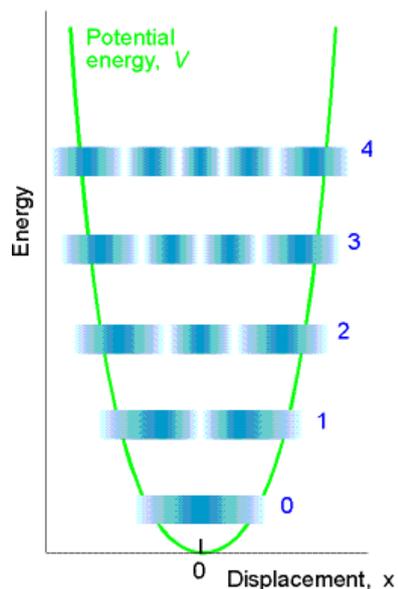


Fig. 12.19 taken from Atkins 6<sup>th</sup> ed.: The normalized wave functions for the first five states of a harmonic oscillator. Even values of  $v$  are black; odd values are green. Note that the number of nodes is equal to  $v$  and that alternate wave functions are symmetric or antisymmetric about  $y = 0$  (zero displacement).

Fig. 12.20 taken from Atkins 6<sup>th</sup> ed.: The probability distributions for the first five states of a harmonic oscillator represented by the density of shading. Note how the regions of highest probability (the regions of densest shading) move towards the turning points of the classical motion as  $v$  increases.



**Fig. 3.6** The wave function  $\psi$  and probability density  $\psi^2$  of the harmonic oscillator, from Atkins: Physical Chemistry, 6th ed.

### 3.1.4 The Rigid Rotor

Let us now consider two special cases of rotation: the diatomic or linear molecule and a molecule with a rotationally symmetric tensor of inertia. Spherical coordinates are convenient for the description of the rigid rotor, because the radius  $r$  has a constant value. In a linear rotor, we can ignore the rotation around the molecular axis because of the very small inertial moment. The axis of rotation orients itself perpendicular to the molecular axis due to the centrifugal force, i.e.  $\theta = \pi/2$  is a constant value. For the calculation of the wave function and energy eigenvalues, we use the Schrödinger equation, equ. (3.04) and equ. (3.06), though the potential  $V$  is zero. The Laplace operator, equ. (3.08), is simplified by the fact that the derivatives relative to  $r$  (and  $\theta$  in linear molecules) are zero. The result for a diatomic molecule with the reduced mass  $m_r$ , the radius of gyration  $r$ , and the moment of inertia  $I = m_r r^2$  perpendicular to the molecular axis is

$$\mathcal{H}\psi = -\frac{\hbar^2}{2m_r r^2} \frac{\partial^2 \psi}{\partial \phi^2} = E\psi. \quad (3.29)$$

That leads to the differential equation

$$\frac{\partial^2 \psi}{\partial \phi^2} = -\frac{2IE}{\hbar^2} \psi \quad (3.30)$$

with the solutions

$$\psi_J = \sqrt{\frac{1}{2\pi}} \exp(iJ\phi) \quad \text{where} \quad J = \pm \frac{\sqrt{2IE}}{\hbar}. \quad (3.31)$$

The quantity  $J$  with the cyclic boundary condition

$$\sqrt{\frac{1}{2\pi}} \exp(iJ\phi) = \psi_J(\phi) = \psi_J(\phi + 2\pi) = \sqrt{\frac{1}{2\pi}} \exp(iJ[\phi + 2\pi]) \quad (3.32)$$

is reduced to the values

$$J = 0, \pm 1, \pm 2, \dots \quad (3.33)$$

$J$  is the rotational quantum number. The energy values follow as

$$E = \frac{J^2 \hbar^2}{2I}. \quad (3.34)$$

Unfortunately, this simple derivation fails to explain experimental results. The reason is that we arbitrarily fixed the axis of rotation, even though all axes perpendicular to the molecular axis are equally probable. An agreement of the theory with the rotational spectra of linear molecules is reached when  $J^2$  is replaced by  $J(J+1)$ .

For the consideration of rotationally symmetric non-linear molecules, we make no restriction to the direction of the axis of rotation, and define the rotationally symmetric tensor of inertia through the moment of inertia parallel to the axis of symmetry  $I_{\parallel} = I_z = I_A$ , and the moment of inertia perpendicular to the axis of symmetry  $I_{\perp} = I_x = I_y = I_B$ .

The Laplace operator in equ. (3.08) is reduced by the term containing the derivation with respect to  $r$ . For that reason, the wave function does not contain the radial component that represents the wave function of the electron in equ. (3.12). The spherical functions, now with their  $\theta$  and  $\phi$  dependent components, describe the rotation of the molecule around arbitrary axes, see equ. (3.14). Putting these functions into the potential-free hamiltonian gives us the following eigenvalues as a function of the quantum numbers:

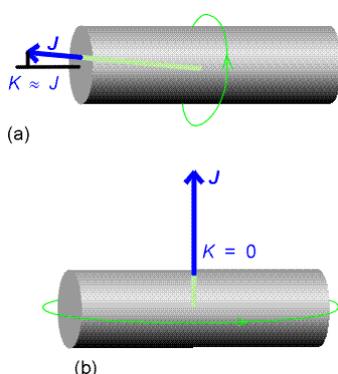
$$E_{\text{Rot}} = \frac{\hbar^2}{2I_B} [J(J+1) - K^2] + \frac{\hbar^2}{2I_A} K^2, \quad 0 \leq K \leq J. \quad (3.35)$$

The rotational quantum number  $J$  stands for the orbital quantum number  $\ell$ , which can only be zero or a positive whole number. A change of the direction of rotation is reached by the addition of  $180^\circ$  to  $\theta$ , as in the above rotation in a plane.

The magnetic quantum number  $m$ , for which  $-\ell \leq m \leq \ell$  is true for electrons, is replaced here by  $k$ . The convention  $K = |k|$  is often used. Since the  $K$  in equ. (3.35) only appears to the second power, we could also use  $k$  instead. When  $K = 0$ , we have an axis of rotation perpendicular to the molecular axis of symmetry. This results in an expression which is analogous to equ. (3.34), provided that  $J^2$  is replaced by  $J(J+1)$ . When  $K = J$ , and  $J \gg 1$ , the second term in equ. (3.35) is dominant. The axis of rotation is almost parallel to the axis of symmetry.

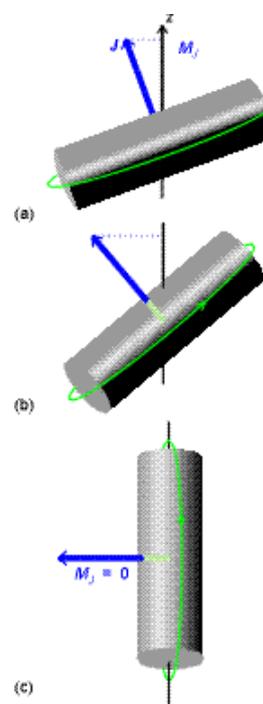


The rotational energy levels of a linear or spherical rotor. Note that the energy separation between neighbouring levels increases as  $J$  increases.



The significance of the quantum number  $K$ . (a) When  $|K|$  is close to its maximum value,  $J$ , most of the molecular rotation is around the principal axis. (b) When  $K = 0$  the molecule has no angular momentum about its principal axis: it is undergoing end-over-end rotation.

**Figures 16.17-16.19**  
taken from Atkins 6<sup>th</sup> ed.



The significance of the quantum number  $MJ$ . All three Figures correspond to a state where  $K = 0$

### 3.2 Splitting the Electron Energy Levels

Now that we have discussed the eigenfunctions of the hydrogen atom in chapter 3.1.1 and the transition from atomic to molecular orbitals in chapter 3.1.2., we turn to eigenvalues without further use of quantum mechanics. By using the Rydberg constant for the hydrogen atom  $R_H$ , see equ. (3.03) and subsequent equations, the eigenvalues are

$$E_{n\ell m} = -\frac{hc_0 R_H}{n^2}. \quad (3.50)$$

The energy eigenvalues only depend on the principal quantum number  $n$  and not on the orbital quantum number  $\ell$  or the magnetic quantum number  $m$ . This is only true, if we ignore the rather small splittings caused by relativistic and quantum electrodynamic effects. In general for these quantum numbers the following inequality holds:

$$|m| \leq \ell \leq n - 1. \quad (3.51)$$

For the transitions between different triplets of quantum numbers, which would give us the discrete frequencies of the hydrogen atom according to equ. (3.02), we have to consider the selection rules for the transitions. These tell us which transitions are allowed. While the principal quantum number  $n$  can arbitrarily change its value, we use of the following selection rules for the change in the orbital quantum number  $\ell$  and the magnetic quantum number  $m$ :

$$\Delta\ell = \pm 1 \quad \text{and} \quad \Delta m = 0, \pm 1. \quad (3.52)$$

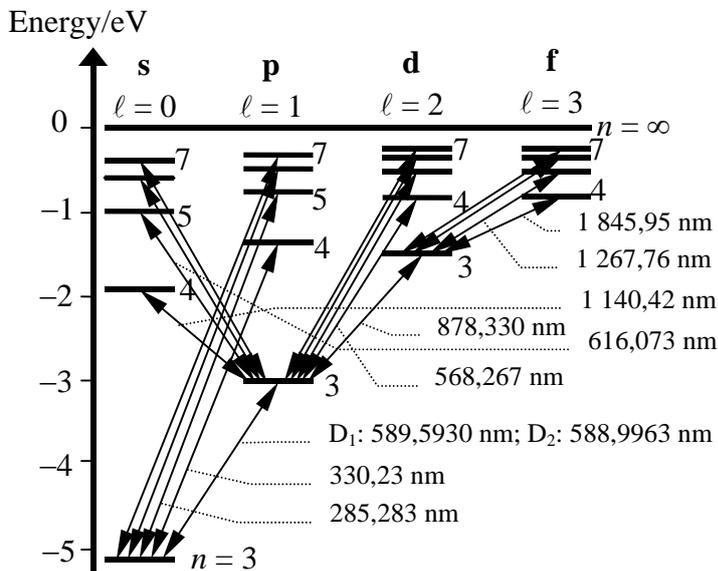
That all transitions with  $\Delta\ell \neq \pm 1$  are forbidden results from the theorem of the conservation of angular momentum. A photon has spin one, which means that it has the angular momentum  $1 \cdot \hbar$ . If a photon is created (emitted) or destroyed (absorbed), the orbital quantum number of the electron changes by one.

Let us now consider the outermost electron of an alkali atom, which is often referred to as the valence electron. The difference between this situation and a hydrogen atom are due in part to the larger atomic number  $Z$  of the alkali atom and in part to the shielding of the electric field of the nucleus by the inner electrons. The nuclear charge, which is increased by the factor  $Z$ , acts without shielding on space elements of the electric charge very close to the nucleus. If the valence electron were far away from the inner electrons, the nuclear charge would look like a single elementary charge to it, because of shielding by the other electrons. When we look closer at the radial charge distribution of the s electrons in higher orbits, such as  $R_{20}$  and  $R_{30}$  in equ. (3.13), it is easy to see that they have a non zero charge density at the nucleus ( $\rho = 0$ ). The radial charge distribution in equation (3.13) also shows that as we move from the s electrons ( $R_{20}$  and  $R_{30}$ ), to the p electrons ( $R_{21}$  and  $R_{31}$ ) and to the d electrons ( $R_{32}$ ), the centers of charge move outward. That means that the shielding effect of the inner electrons is weakest for an s electron and strongest for a d electron. It also follows that the energy values at the same principal quantum number are smallest for s electrons ( $s < p < d$ ). These effects are taken into account by using an effective principal quantum number  $n_{\text{eff}}(n, \ell)$  or with the quantum defect  $\Delta(n, \ell)$ . For example, the energy terms of the sodium atom are given by

$$E_{n\ell} = -\frac{R_{\text{Na}} hc_0}{n_{\text{eff}}^2} = -\frac{R_{\text{Na}} hc_0}{(n - \Delta)^2}. \quad (3.53)$$

The quantum defect  $\Delta$  increases as one moves from lithium to cesium in the alkaline group, but decreases with increasing orbital quantum number  $\ell$ . It doesn't depend much on the

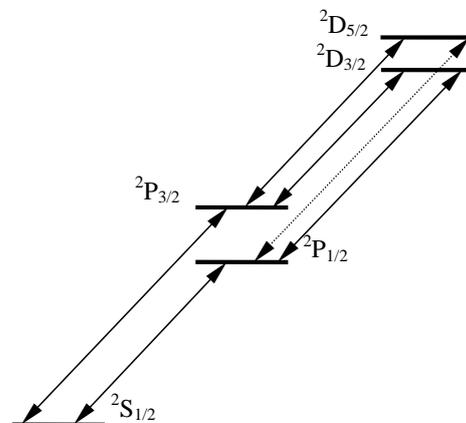
principal quantum number  $n$ , as can be seen in the following values taken from the quantum defect for sodium  $\Delta(n, \ell)$ : 1,37 (3, 0), 1,36 (4, 0), 1,35 (5, 0), 0,88 (3, 1), 0,87 (4, 1), 0,86 (5, 1), 0,010 (3, 2), 0,011 (4, 2), 0,013 (5, 2), 0,000 (4, 3) and  $-0,001$  (5, 3).



**Fig. 3.7** Term figure and spectral series of the sodium atom. All terms with  $n > 7$  have been left out. The wavelength of the transitions is only shown for the lowest levels of each series. The common lowest level of the principal series (p series) is the ground state of the valence electron  $n = 3$ ,  $\ell = 0$ ,  $E = -5,12$  eV. The s and d series start from the state  $n = 3$  and  $\ell = 1$ . The upper levels of the s, p, d, and f transitions belong to  $\ell = 0, 1, 2$  and  $3$ , respectively.

The terms in Fig. 3.7 can be calculated by equ. (3.53) and the quantum defects  $\Delta(n, \ell)$  given above. The transitions obey the selection rule equ. (3.52). The levels with the same  $\ell$  (all the levels in the same column) have spectral series assigned to them. These series are labeled with s, p, d and f. This generally applicable notation comes from the abbreviations for sharp, principal, diffuse and fundamental. The principal series (main branch) contains all transitions between states with  $\ell = 1$  and the ground state. Since the ground state is almost exclusively the occupied state at room temperature, the principal series dominates the absorption spectra. Two subordinate series (side branch) starting at states  $\ell = 0$  and  $\ell = 2$  have the level  $\ell = 1$  in common as lowest level. They appear in the emission spectrum as sharp and diffuse subordinate series. The latter subordinate series becomes diffuse because of another fine structure shown in Fig. 3.8. Transitions from states with  $\ell = 3$  and the lowest state of  $\ell = 2$  belong to the Bergmann series (fundamental series), which was historically and wrongly given a fundamental meaning for the atomic structure.

**Fig. 3.8** Fine-structure splitting of the alkali atoms. The energy difference of the splitting due to the different total orbital angular momenta is exaggerated in this figure.  $P \leftrightarrow D$  contains a forbidden transition shown with a dotted line alongside the line triple of the diffuse subordinate series.



Using this notation for the spectral series, an electron is called an s-electron, p-electron, d-electron or f-electron, if it has the orbital quantum number  $\ell = 0, 1, 2$  or  $3$ , respectively. For  $\ell = 4, 5, 6$  etc..., the notation is continued alphabetically as g, h, i etc.

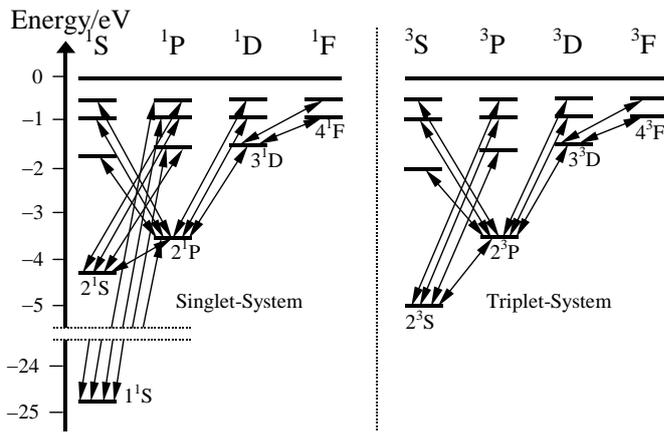
In the multi-electron systems which we will treat later, the orbital quantum numbers of the individual electrons add to a total orbital quantum number  $L$ . The states  $L$  are labeled with S, P, D and F for  $L = 0, 1, 2$  and  $3$  in analogy to the single electron case.

The term “spin” is used to label the intrinsic angular momentum of electrons and nuclei. In the Stern-Gerlach experiment it was shown that electrons with the spin  $|s| = 1/2$  have the spin quantum number  $s = 1/2$ . (The spin  $s$  that we introduce here and the total spin  $S$  which will be introduced later should not be confused with the term notation symbols  $s$  and  $S$  of the previous section.) By adding the orbital angular momentum and spin we get the total angular momentum  $\mathbf{j} = \ell + s$  for a single electron. The direction between the vectors is set for optical transitions by the quantum mechanical selection rule for the total angular momentum quantum number  $\Delta j = 0, \pm 1$ . This only allows a parallel or antiparallel orientation between spin and orbital angular momentum, with  $j = \ell \pm 1/2$ . For this reason, all energy terms except for those with  $\ell = 0$  split into two levels. This so-called fine-structure splitting which follows from the interaction of orbital and spin moments in atomic fields decreases with increasing  $n$  and  $\ell$ . All spectral lines which are determined by an s state and another state split into a doublet. This is true for the principal series and the sharp subordinate series (sharp side branch). For the splitting of the D lines of the sodium spectrum, the two wavelengths can be seen in Fig. 3.7. In the diffuse side branch, both contributing levels are split, and there are, in principle, four possible transitions. One of those is forbidden. A triplet remains, though the transition with  $\Delta j = 0$  has a relatively low intensity, since  $\ell$  and  $s$  have to change at the same time, see Fig. 3.8.

By using capital letters to symbolize the states in multiple-electron systems, we differentiate them from the symbols for the electrons, for example 2p when  $n = 2$  and  $\ell = 1$ . In a single electron system, the designation  $2^2P_{3/2}$  (read two doublet P three halves) tells us that  $n = 2$ ,  $(2s + 1) = (2S + 1) = 2$ ,  $\ell = L = 1$  and  $j = J = 3/2$ .

Multiple electrons couple in different ways. In very heavy atoms, the spin-orbit interaction of the individual electrons is much stronger than the interaction with the orbital momenta (or spin momenta) of nearby electrons. The total angular momentum  $J$  of the system is composed of the sum of the total angular momenta  $j$  of the individual electrons, and we speak of *jj*-coupling. Although we can see an intensive intercombination line at 254,7 nm in high-pressure mercury lamps, which shows us a property of *jj*-coupling, we can still see the *LS*-coupling which is typical of lighter atoms.

In light atoms there is a prohibition of intercombinations between singlet and triplet terms. The spin-orbit interaction of individual electrons is smaller than the coupling of the orbital momenta or spin momenta with neighboring electrons. The total orbital momentum of the system is given by the sum of  $L$  and  $S$ . Here we speak of *LS*-coupling, which is also called Russell Saunders-coupling after Henry Norris Russell and Frederick Albert Saunders who in 1925 discovered it in alkaline earth spectra.



**Fig. 3.9** Helium singlet and triplet. The  $1^1S$ -state has the energy  $-24,77$  eV, while the  $2^3S$ -state has  $-5,00$  eV. The transitions shown here apply to one electron, if the other remains in the  $1s$  state.

Fig. 3.9 shows the singlet and triplet terms of the helium atom for  $1 \leq n \leq 5$ . The triplet splitting has been left out in this figure. In the triplet state, the electron spins add to a total spin of one with three possible values in an inner magnet field connected with the total angular momentum. They are  $(1, 0, -1)$ . The spectrum with the most intense transitions lies in the infrared and visible region. The singlet state has oppositely aligned electron spins with a total spin of zero. The most intense transitions between the singlet terms lie in the ultraviolet region. In the transition of an electron between a singlet and triplet state, the spin has to change. Such transitions are forbidden and therefore occur very rarely. Due to the non-observable intercombination, helium spectroscopically behaves as if it were two distinct species, and early spectroscopists actually thought of helium as consisting of "parahelium" (now known to be  $S = 0$ ) and "orthohelium" ( $S = 1$ ).

For light atoms with a resulting orbital momentum  $L$ , a resulting spin  $S$ , and a resulting total angular momentum  $J$ , where  $i$  is the running index for the electrons, it holds in general:

$$\begin{aligned}
 L &= \sum_i \ell_i \quad \text{mit } \Delta L = \pm 1, \\
 S &= \sum_i s_i \quad \text{und} \\
 J &= L + S \quad \text{mit } \Delta J = \pm 1 \text{ oder } \Delta J = 0 \text{ f\"ur } J \neq 0.
 \end{aligned} \tag{3.54}$$

Equations (3.54) contains sums of vectors, without saying anything about the directions of the vectors to be added. For this reason we don't use them in the calculation of the sums. The fact that the orbital angular momenta of the individual electrons  $\ell_i$  precess around the total orbital angular momentum  $L$  helps us out of this difficulty. This lets us replace the vector addition of  $\ell_i$  by the addition of the related magnetic quantum numbers. With  $m_i^\ell = \ell_i, \ell_i - 1, \dots, -\ell_i$  we label the  $2\ell_i + 1$  magnetic quantum numbers of the orbital angular momentum of the electron  $i$ . We have to introduce the superscript  $\ell$  of the magnetic quantum numbers of the orbital angular momentum, because we are trying to express a similar concept for the intrinsic angular momentum. In the total spin, we replace the sum of the individual spins in equ. (3.54) by the sum of the magnetic quantum numbers of the spins  $m_i^s = +\frac{1}{2}$  or  $-\frac{1}{2}$ .

The multiplicity of the terms (singlet, doublet, triplet, etc.) is  $2S + 1$ . We can describe them in an analogous way:  $S$  precesses around the direction of  $J$  (the same applies to  $L$ ). From that we get  $M^S = S, S - 1, \dots, -S$  as the magnetic quantum numbers of the total spin. These produce the  $2S + 1$  time multiplicity of the terms. This is valid when  $L \geq S$ , otherwise the multiplicity is only  $2L + 1$ . Which multiplicity exists by which electron configuration can be determined by the total number of electrons  $N$  in the outer shell. The resulting spin for  $N$  electrons with the spin  $s = \frac{1}{2}$  can have the maximum value of  $N/2$  but can also take on lesser values by whole positive numbers. Thereby we have a maximum multiplicity of  $2S + 1 = N + 1$ , and smaller

positive values by two can also occur. That means doublet for alkali atoms, triplet and singlet for two electron atoms, quartet and doublet for three electron atoms, etc. The total spin of the electrons in a shell increases with an increasing number of electrons until the shell is half full. Afterwards it sinks back down to zero for a full shell. This result can be extracted from Linus Pauling's 1925 exclusion principle: no more than two electrons can occupy one orbital, and, if two electrons are in an orbital, their spins must be paired (positive and negative). In other words, two electrons of a quantum mechanical system are not allowed to have all the same quantum numbers.

The ground state of atoms can be determined using the in 1927 empirically discovered rule of Friedrich Hund. Consider the electrons in the outer shell (or in the outer non-closed electron shells of transition metals). The term with the largest possible value of  $S$  for the given electron number and the largest  $L$  for this  $S$  has the lowest energy. This determines  $S$  and  $L$ . For the total angular momentum we have  $J = L - S$  for a less than half full subshell,  $J = S$  for a half full subshell, for which  $L = 0$ , and  $J = L + S$  for a more than half full subshell. For the ground state the vector sums in equ. (3.54) simplify to the scalar sums:

$$S = \text{Max} \left( \sum_i m_i^s \right),$$

$$L = \text{Max} \left( \sum_i m_i^l \right) \text{ considering maximum } S \quad (3.55)$$

depending if the  $\frac{\text{Number of electrons in shell}}{\text{Number of states in shell}} < \frac{1}{2}, = \frac{1}{2}$  or  $> \frac{1}{2}$

$$J = L - S, J = S \text{ or } J = L + S.$$

For the ground states in Tab. 3.1, the  $2S + 1$  multiplicities are given as leading indices, the letters S, P, D, F, G, H, I, K, L represent the total orbital angular momentum  $L = 0, 1, 2, 3, 4, 5, 6, 7, 8$  and as follow up index the total angular momentum  $J$ . To illustrate Hund's rule, we will determine the ground state for two examples from the given occupation of the electron levels given in Tab. 3.1.:

In sulfur, the shells up to 3s are completely occupied. The 3p shell contains four electrons. Since a p shell can contain a maximum of six electrons with  $m^l = 1, 0, -1$  and  $m^s = 1/2, -1/2$ , we can reach a maximum total spin with three electrons with the quantum number  $m^s = 1/2$ . The fourth electron has to have a spin of  $m^s = -1/2$ , and the total spin therefore becomes  $S = 1$ . For the multiplicity we get  $2S + 1 = 3$  (triplet and singlet terms). If we try to optimize the total orbital angular momentum with this determination of the spin, we get as a sum of the total orbital angular momentum  $L = 1$  (a P term) from the magnetic quantum numbers of the orbital angular momentum of the four electrons with  $m^l = 1, 0, -1, 1$ . Since the four electrons fill the shell up more than half way, occupation is  $J = L + S = 2$ . The ground state of sulfur atoms is therefore  $^3P_2$ .

As a further example let us consider uranium. The shells up to 5d and the shells 6s, 6p and 7s are completely occupied. There are 3 electrons in the 5f shell, and one in the 6d shell. All of these can have a positive magnetic quantum number of spin, which gives us  $S = 2$  and a multiplicity of 5. The maximum magnetic quantum numbers of the orbital angular momentum are thus  $m^l = 3, 2, 1$  for the 5f electrons and  $m^l = 2$  for the 6d electron. That gives us for  $L = 8$  an L state. Remember that states are written using straight letters and the quantum numbers written in italics. Because the shells are less than half filled,  $J = L - S = 6$ . The ground state of the uranium atom is therefore  $^5L_6$ .

1	H	${}^2S_{1/2}$	$1s^1$	36	Kr	${}^1S_0$	$(4s)4p^6$	71	Lu	${}^2D_{3/2}$	$(5p)5d^16s^2$
2	He	${}^1S_0$	$1s^2$	37	Rb	${}^2S_{1/2}$	$(4p)5s^1$	72	Hf	${}^3F_2$	$(5p)5d^26s^2$
3	Li	${}^2S_{1/2}$	$(1s)2s^1$	38	Sr	${}^1S_0$	$(4p)5s^2$	73	Ta	${}^4F_{3/2}$	$(5p)5d^36s^2$
4	Be	${}^1S_0$	$(1s)2s^2$	39	Y	${}^2D_{3/2}$	$(4p)4d^15s^2$	74	W	${}^5D_0$	$(5p)5d^46s^2$
5	B	${}^2P_{1/2}$	$(2s)2p^1$	40	Zr	${}^3F_3$	$(4p)4d^25s^2$	75	Re	${}^6S_{5/2}$	$(5p)5d^56s^2$
6	C	${}^3P_0$	$(2s)2p^2$	41	Nb	${}^6D_{1/2}$	$(4p)4d^45s^1$	76	Os	${}^5D_4$	$(5p)5d^66s^2$
7	N	${}^4S_{3/2}$	$(2s)2p^3$	42	Mo	${}^7S_3$	$(4p)4d^55s^1$	77	Ir	${}^4F_{9/2}$	$(5p)5d^76s^2$
8	O	${}^3P_2$	$(2s)2p^4$	43	Tc	${}^6S_{5/2}$	$(4p)4d^55s^2$	78	Pt	${}^3D_3$	$(5p)5d^96s^1$
9	F	${}^2P_{3/2}$	$(2s)2p^5$	44	Ru	${}^5F_5$	$(4p)4d^75s^1$	79	Au	${}^2S_{1/2}$	$(5d)6s^1$
10	Ne	${}^1S_0$	$(2s)2p^6$	45	Rh	${}^4F_{9/2}$	$(4p)4d^85s^1$	80	Hg	${}^1S_0$	$(5d)6s^2$
11	Na	${}^2S_{1/2}$	$(2p)3s^1$	46	Pd	${}^1S_0$	$(4p)4d^{10}$	81	Tl	${}^2P_{1/2}^{\circ}$	$(5d)6s^26p^1$
12	Mg	${}^1S_0$	$(2p)3s^2$	47	Ag	${}^2S_{1/2}$	$(4d)5s^1$	82	Pb	${}^3P_0$	$(5d)6s^26p^2$
13	Al	${}^2P_{1/2}$	$(3s)3p^1$	48	Cd	${}^1S_0$	$(4d)5s^2$	83	Bi	${}^4S_{3/2}^{\circ}$	$(5d)6s^26p^3$
14	Si	${}^3P_0$	$(3s)3p^2$	49	In	${}^2P_{1/2}$	$(4d)5s^25p^1$	84	Po	${}^3P_2$	$(5d)6s^26p^4$
15	P	${}^4S_{3/2}$	$(3s)3p^3$	50	Sn	${}^3P_0$	$(4d)5s^25p^2$	85	At	${}^2P_{3/2}^{\circ}$	$(5d)6s^26p^5$
16	S	${}^3P_2$	$(3s)3p^4$	51	Sb	${}^4S_{3/2}$	$(4d)5s^25p^3$	86	Rn	${}^1S_0$	$(5d)6s^26p^6$
17	Cl	${}^2P_{3/2}$	$(3s)3p^5$	52	Te	${}^3P_2$	$(4d)5s^25p^4$	87	Fr	${}^2S_{1/2}$	$(5d)6s^26p^67s^1$
18	Ar	${}^1S_0$	$(3s)3p^6$	53	I	${}^2P_{3/2}^{\circ}$	$(4d)5s^25p^5$	88	Ra	${}^1S_0$	$(5d)6s^26p^67s^2$
19	K	${}^2S_{1/2}$	$(3p)4s^1$	54	Xe	${}^1S_0$	$(4d)5s^25p^6$	89	Ac	${}^2D_{3/2}$	$(5d)6s^26p^66d^17s^2$
20	Ca	${}^1S_0$	$(3p)4s^2$	55	Cs	${}^2S_{1/2}$	$(4d)5s^25p^66s^1$	90	Th	${}^3F_2$	$(5d)6s^26p^66d^27s^2$
21	Sc	${}^2D_{3/2}$	$(3p)3d^14s^2$	56	Ba	${}^1S_0$	$(4d)5s^25p^66s^2$	91	Pa	${}^4K_{11/2}$	$(5d)5f^26s^26p^66d^17s^2$
22	Ti	${}^3F_2$	$(3p)3d^24s^2$	57	La	${}^2D_{3/2}$	$(4d)5s^25p^65d^16s^2$	92	U	${}^5L_6^{\circ}$	$(5d)5f^36s^26p^66d^17s^2$
23	V	${}^4F_{3/2}$	$(3p)3d^34s^2$	58	Ce	${}^1G_4^{\circ}$	$(4d)4f^15s^25p^65d^16s^2$	93	Np	${}^6L_{11/2}$	$(5d)5f^46s^26p^66d^17s^2$
24	Cr	${}^7S_3$	$(3p)3d^54s^1$	59	Pr	${}^4I_{9/2}$	$(4d)4f^35s^25p^66s^2$	94	Pu	${}^7F_0$	$(5d)5f^66s^26p^67s^2$
25	Mn	${}^6S_{5/2}$	$(3p)3d^54s^2$	60	Nd	${}^5I_4$	$(4d)4f^45s^25p^66s^2$	95	Am	${}^8S_{7/2}^{\circ}$	$(5d)5f^76s^26p^67s^2$
26	Fe	${}^5D_4$	$(3p)3d^64s^2$	61	Pm	${}^6H_{5/2}^{\circ}$	$(4d)4f^55s^25p^66s^2$	96	Cm	${}^9D_2$	$(5d)5f^76s^26p^66d^17s^2$
27	Co	${}^4F_{9/2}$	$(3p)3d^74s^2$	62	Sm	${}^7F_0$	$(4d)4f^65s^25p^66s^2$	97	Bk	${}^6H_{15/2}^{\circ}$	$(5d)5f^96s^26p^67s^2$
28	Ni	${}^3F_4$	$(3p)3d^84s^2$	63	Eu	${}^8S_{7/2}^{\circ}$	$(4d)4f^75s^25p^66s^2$	98	Cf	${}^5I_8$	$(5d)5f^{10}6s^26p^67s^2$
29	Cu	${}^2S_{1/2}$	$(3p)3d^{10}4s^1$	64	Gd	${}^9D_2$	$(4d)4f^75s^25p^65d^16s^2$	99	Es	${}^4I_{15/2}^{\circ}$	$(5d)5f^{11}6s^26p^67s^2$
30	Zn	${}^1S_0$	$(3p)3d^{10}4s^2$	65	Tb	${}^6H_{15/2}^{\circ}$	$(4d)4f^95s^25p^66s^2$	100	Fm	${}^3H_6$	$(5d)5f^{12}6s^26p^67s^2$
31	Ga	${}^2P_{1/2}$	$(4s)4p^1$	66	Dy	${}^5I_8$	$(4d)4f^{10}5s^25p^66s^2$	101	Md	${}^2F_{3/2}^{\circ}$	$(5d)5f^{13}6s^26p^67s^2$
32	Ge	${}^3P_0$	$(4s)4p^2$	67	Ho	${}^4I_{15/2}^{\circ}$	$(4d)4f^{11}5s^25p^66s^2$	102	No	${}^1S_0$	$(6p)7s^2$
33	As	${}^4S_{3/2}$	$(4s)4p^3$	68	Er	${}^3H_6$	$(4d)4f^{12}5s^25p^66s^2$	103	Lr	${}^2D_{3/2}$	$(6p)6d^17s^2$
34	Se	${}^3P_2$	$(4s)4p^4$	69	Tm	${}^2F_{7/2}^{\circ}$	$(4d)4f^{13}5s^25p^66s^2$	104	-	${}^3F_2$	$(6p)6d^27s^2$
35	Br	${}^2P_{3/2}$	$(4s)4p^5$	70	Yb	${}^1S_0$	$(5p)6s^2$				

**Tab. 3.1** Atomic number, atom, the ground state and the occupation of the electron levels in the ground state. The electron shells are written in the order 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f, 6s, 6p, 6d and 7s. The last filled element of this series is written in parenthesis in front of the other shells. The superscript contains the number of electrons in each shell.

Linear molecules have an axially symmetric electric field around the axis connecting the nuclei. This axis is therefore most significant for a space quantization of the orbital angular momentum. Besides the principal quantum number  $n$  and the orbital angular momentum quantum number  $\ell$ , the electron is indicated by the magnetic quantum number  $\lambda$ . The absolute value of the orbital angular momentum along the axis connecting the nuclei is therefore

$$|\lambda| = \lambda \hbar \quad \text{where} \quad \lambda = \ell, \ell - 1, \dots -\ell \quad \text{and} \quad |\lambda| \leq \ell \leq n - 1, \quad (3.56)$$

where both positive and negative  $\lambda$  values have in general the same energy. Such degeneracy can be removed by for example molecular rotation. When  $\ell = 0, 1, 2, 3, \dots$  we again have s, p, d, f, ..., and for  $\lambda = 0, 1, 2, 3, \dots$  we use the lower case Greek letters  $\sigma, \pi, \delta, \phi, \dots$ . The  $\pi$  electron therefore has the quantum numbers  $\ell = 1$  and  $\lambda = 1$ .

For the electrons in the outer shell of a molecule we only have a weak  $\ell\ell$ ,  $ss$  or  $jj$  coupling in contrast to the inner shells or atomic systems. The precession of the individual orbital momenta around the axis connecting the nuclei produces a  $\lambda\lambda$  coupling. The components  $\lambda$  add, and the vector addition becomes

$$\Lambda = \sum_i \ell_i \quad \text{and} \quad |\Lambda| = \hbar \quad \text{with} \quad \Delta = 0, \pm 1, \quad (3.57)$$

which can again be replaced by the addition of the magnetic quantum numbers  $\lambda$ . When  $\Lambda = 0, 1, 2, 3, \dots$ , we use the capital Greek letters  $\Sigma, \Pi, \Delta, \Phi, \dots$  as term symbols.

The spins are added as vectors, as with atoms, cf. equ. (3.54), to a total spin  $S$ . The total spin vector  $S$  precesses around  $\Lambda$  and the related components of  $S$  in the direction of  $\Lambda$  are described by the magnetic quantum numbers  $\Sigma = S, S - 1, \dots, -S$ . Again we must take care not to confuse the magnetic quantum numbers  $\Sigma$  with the state  $\Sigma$ . The resulting angular momentum is  $\Omega = \Lambda + \Sigma$ . Every term belonging to a value of  $\Lambda$  splits  $2S + 1$  times (when  $\Lambda < S$  only  $2\Lambda + 1$  times).  $\Omega$  is not, however, the total angular momentum of the molecule. The deciding contribution to the total angular momentum comes from the molecular rotation.

As an example let us look at the notation for the ground state of the hydrogen molecule  $\text{H}_2$ :  $(1s\sigma)^2 \ ^1\Sigma_0$ . This means  $n = 1$  for  $s\sigma$  electrons, 2 electrons, singlet due to  $S = 0$ ,  $\Sigma$ -state due to  $\Lambda = 0$ ,  $\Omega = 0$ .

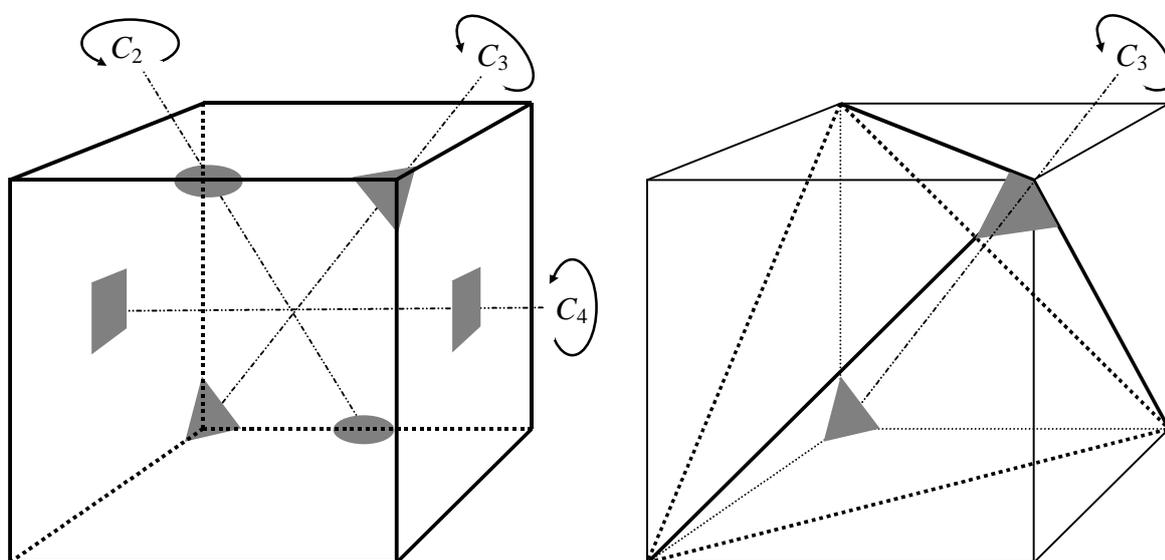
For non-linear molecules, the states are often denoted with the letters a, b, ... or A, B, ..., which rest upon the irreducible representations which we will describe in the following chapter.

### 3.3 A Few Applications of Group Theory

The systematic mathematical treatment of symmetry is called group theory. In the sciences, this theory is the basis for the detailed study of symmetry properties and shows often a simple way for obtaining useful conclusions. Even if one doesn't know the mathematical definition of a group, one can apply easily understood rules of group theory to make useful conclusions about the properties of the symmetry of a given system. In this chapter, we will present the most important foundations for a few simple applications of group theory in spectroscopy.

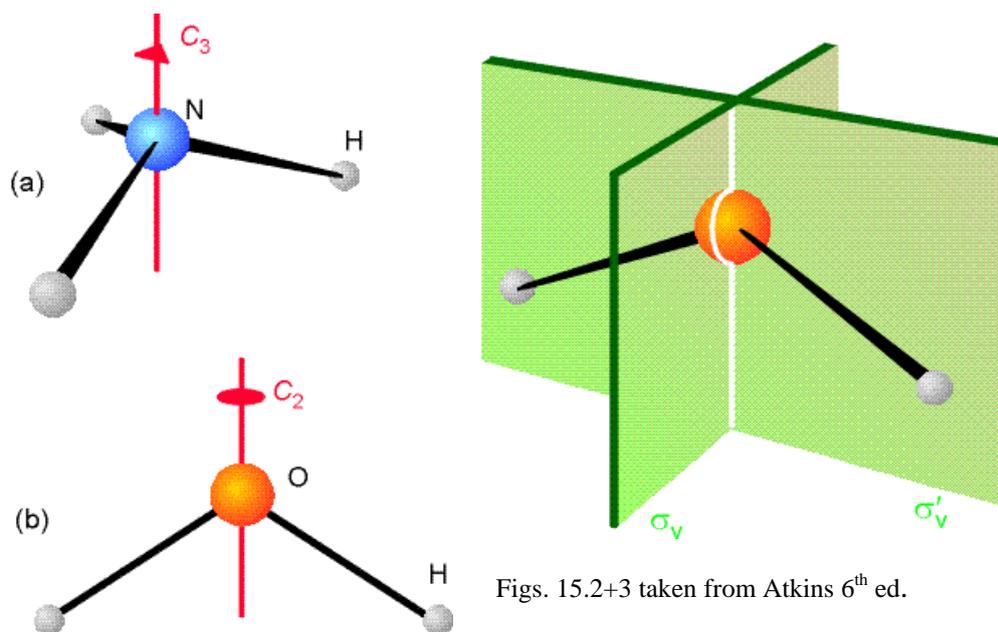
#### 3.3.1 Point Groups

A symmetry operation changes coordinates in such a way, that the appearance of a shape in space remains the same. The shape could be a geometrical figure such as a cube or a tetrahedron, as shown in Fig. 3.10. Rotations around the shown axes belong to the symmetry operations that transform cubes and tetrahedrons into themselves.



**Fig. 3.10** Symmetry properties of figures with cubic symmetry what means more than one main axis of rotation. At left a cube and at right a tetrahedron enclosed by the cube. The main axes of rotation of the cube are three  $C_4$  axes, in the case of the tetrahedron there are four  $C_3$  axes. There is only one of each type portrayed in the figure.

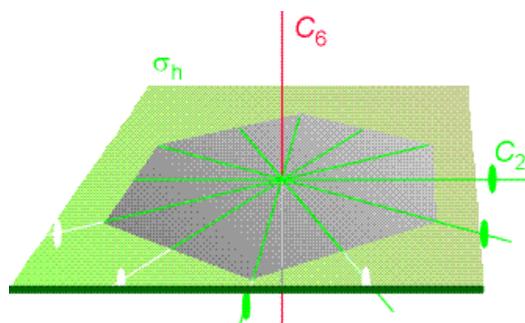
To examine the symmetry properties of orbitals, molecules consisting of atoms, or the building blocks of crystals, we need the tools that we will develop with the example of symmetry operations on molecules. With a rotation around an axis of symmetry, the ammonia and water molecules can both exchange their hydrogen atoms in such a way that the orientation and shape of the molecules after the rotation are the same as they were before. Different atoms of a single type, in this case hydrogen atoms, cannot be distinguished in a symmetry operation.

Figs. 15.2+3 taken from Atkins 6<sup>th</sup> ed.

It is clear that in water there are two (vertical) planes of reflection which lie parallel to the axis of rotation. These are appropriate for symmetry operations.

Two symmetry operations are sufficient to describe all necessary symmetry operations. These two are rotation by  $2\pi/n$  around an axis, and reflection in a plane. To avoid a product of operators when performing one symmetry operation, we use in addition to rotation and reflection further operators which transform molecules and crystal building blocks into themselves. These operators fulfill the requirements (in each point group), that we associate with the mathematical definition of a group: by combining two operations we get an operation that belongs to the same group. All the symmetry operations together build:

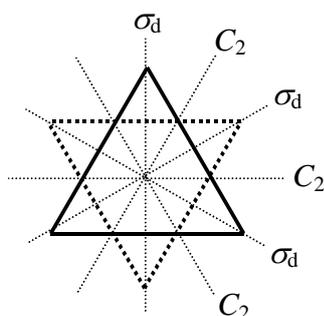
$C_n$	Rotation through the angle $2\pi/n$ ,
$\sigma$	Reflection about a symmetry plane,
$S_n$	Rotary reflection,
$i$	Inversion at a center of symmetry,
$E$	The neutral element.



A rotation by  $2\pi/n$  considers the number  $n$  of identical positions in a rotation of  $360^\circ$  ( $n$ -fold axis of symmetry). The most common is a twofold axis of symmetry. This means that a rotation through  $180^\circ$  will transform the molecule into itself. If a group contains several  $C_n$  axes with different fold axes of symmetry, the axis with the highest value of  $n$  is called the principal axis of symmetry, and is commonly taken as the  $z$  axis.

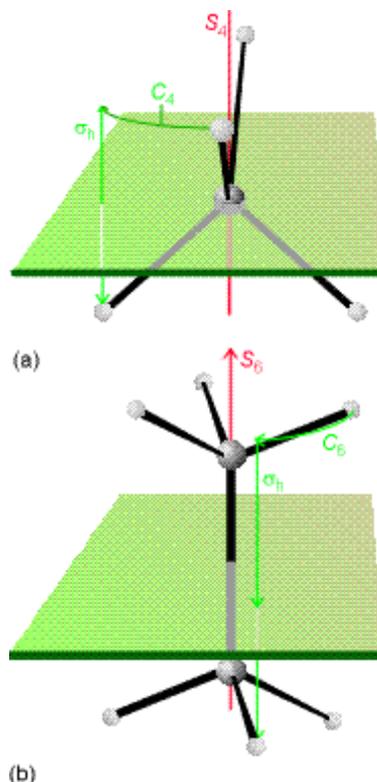
Fig. 15.9 taken from Atkins 6<sup>th</sup> ed.: A molecule with a mirror plane perpendicular to a  $C_n$  axis, and with  $n$  twofold axes in the plane, belongs to the group  $D_{nh}$ .

If a reflection  $\sigma$  is perpendicular to the principal axis of symmetry, it is called a horizontal reflection and is labeled  $\sigma_h$ . If the principal axis of symmetry lies in the plane of reflection, it is called a vertical reflection  $\sigma_v$ . If a vertical plane of reflection also halves the angle between two  $C_2$  axes, it is called a dihedral plane, and is labeled  $\sigma_d$ . Vertical and horizontal planes of reflection are shown in the figures on the previous page (Atkins 6<sup>th</sup> ed. 15.2, 15.3 and 15.9) and this page (Atkins 6<sup>th</sup> ed. 15.6). Dihedral planes exist in ethanol, where both  $\text{CH}_3$  groups lie exactly on spaces (point group  $D_{3d}$ ). Fig. 3.11 shows a representation of the ethanol molecule with the C-C bonding direction perpendicular to the drawing plane.



**Fig. 3.11** The  $C_2$ -axes and  $\sigma_d$ -planes of an ethanol molecule, whose atoms are lying before and behind the drawing plane. Hydrogen atoms are located at the points of the triangle. The  $\text{CH}_3$ -group in the background is drawn with a dotted line. The second carbon atom is behind the first, in the center of the triangles. The  $C_2$ -axes are lying in the drawing plane.

At right Fig. 15.6 taken from Atkins 6<sup>th</sup> ed.: (a). A  $\text{CH}_4$  molecule has a fourfold improper rotation axis ( $S_4$ ): the molecule is indistinguishable after a  $90^\circ$  rotation followed by a reflection across the horizontal plane, but neither operation alone is a symmetry operation. (b) The staggered form of ethane has an  $S_6$  axis composed of a  $60^\circ$  rotation followed by a reflection.



A rotary reflection  $S_n$  contains two operations: a rotation through the angle  $2\pi/n$  followed by a reflection in a plane perpendicular to the axis of rotation.

An inversion occurs when the molecule is transformed into itself after changing the signs on all coordinates (the center of inversion is placed at the origin). This happens in the benzene molecule, which has a center of inversion in the middle of the ring. The inversion operation can be considered to be a combination of rotation and reflection with  $S_2$ .

The identity element  $E$  transforms every atom and therefore every molecule into itself. It is the only element in the  $C_1$  group that can, for example, be assigned to the molecule fluorine-chlorine-bromine-iodine-methane.

Since all symmetry operations on finite molecules conserve a point (not necessarily an atom), the symmetry groups of molecules are called point groups. Two notations for point groups are in use: for molecules, the most common notation is that of Schönflies, which uses capital letters ( $C$ ,  $D$ ,  $S$ ,  $T$ ,  $O$ ) and subscripts (where the number refers to the folds of the rotation and the lower case letters v, h, and d refer to the type of reflection plane). The international system (or Hermann Mauguin system) is used primarily for crystals. 32 molecular symmetry point groups combined with translations give us 230 possible space groups for crystals.

**Tab. 3.2** Notation for the crystallographic point groups. In the international system, the numbers 1, 2, 3, 4 or 6 indicate the presence of an 1-, 2-, 3-, 4- or 6-fold axis of rotation,  $m$  refers to a plane of reflection. A forwards slash / indicates that the plane of reflection is perpendicular to the axis of rotation. It is important to differentiate between symmetry elements of the same type, but of different classes, for example in  $4/mmm$ , where three different classes of reflection plane exist ( $\sigma_v$ ,  $\sigma_h$  and  $\sigma_d$ ). A line over the number shows that this element is combined with an inversion.

$C_i$	$\bar{1}$								
$C_s$	$m$								
$C_1$	1	$C_2$	2	$C_3$	3	$C_4$	4	$C_6$	6
		$C_{2v}$	$2mm$	$C_{3v}$	$3m$	$C_{4v}$	$4mm$	$C_{6v}$	$6mm$
		$C_{2h}$	$2/m$	$C_{3h}$	$\bar{6}$	$C_{4h}$	$4/m$	$C_{6h}$	$6/m$
		$D_2$	222	$D_3$	32	$D_4$	422	$D_6$	622
		$D_{2h}$	$mmm$	$D_{3h}$	$\bar{6}2m$	$D_{4h}$	$4/mmm$	$D_{6h}$	$6/mmm$
		$D_{2d}$	$\bar{4}2m$	$D_{3d}$	$\bar{3}m$	$S_4$	$\bar{4}$	$S_6$	$\bar{3}$
$T$	23	$T_d$	$\bar{4}3m$	$T_h$	$m\bar{3}$				
$O$	432	$O_h$	$m\bar{3}m$						

We can define a symmetry group as follows:

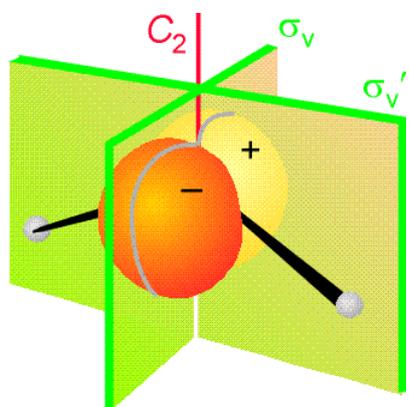
- The symmetry group of a molecule contains all the symmetry operations that transform the molecule into itself.
- The number of elements in a symmetry group determines its order. Each element of the group only appears in one class (for example  $C_3$ ,  $\sigma_v$ ). The number of classes in a group gives us the number of types of symmetry described by a character.
- The character is the type of a matrix, in this case the characters are the types of the irreducible matrix representations of a point group. The number of irreducible representations (also called symmetries) is the number of classes in a group. The character tells us whether the type of symmetry with respect to the class of a symmetry operation is symmetric (+1), antisymmetric (-1) or degenerate (0,  $\pm 2, \dots$ ). Antisymmetric means that a coordinate changes its sign after the operation that transforms the coordinate.
- The symmetry types are labeled in the form  $A_{g1}$ . Thereby:  
 A and B are symmetric or antisymmetric relative to  $C_n$  max, respectively.  
 E and T are twofold or threefold degenerate, respectively, and  
 g and u are symmetric or antisymmetric with respect to an inversion  $i$ .

### 3.3.2 The Bridge to Applications

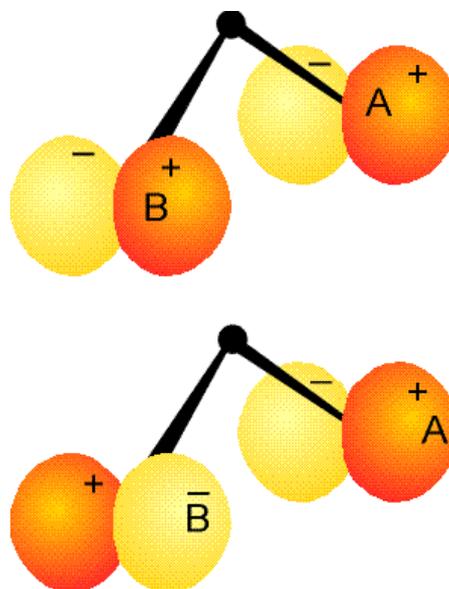
**Tab. 3.3** The character table of the group  $C_{2v}$

$C_{2v}, 2mm$	$E$	$C_2$	$\sigma(xz)_v$	$\sigma'(yz)_v$		
$A_1$	1	1	1	1	$z$	$z^2, y^2, x^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

Table 3.3 shows the character table for the group  $C_{2v}$ , which describes the properties of the  $H_2O$  and  $SO_2$  molecules, among others. This determines the properties of the orbital of the central atom, the molecular orbital composed of atomic orbitals, the symmetric and antisymmetric valence vibrations, and the translation and rotation. The  $C_2$  axis of the molecule, which lies in the  $y$ - $z$  plane, points in the  $z$  direction.

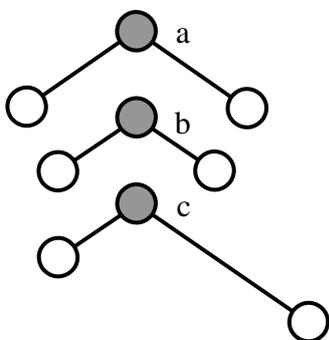


Figs 15.24 and 15.22 taken from Atkins 6<sup>th</sup> ed.



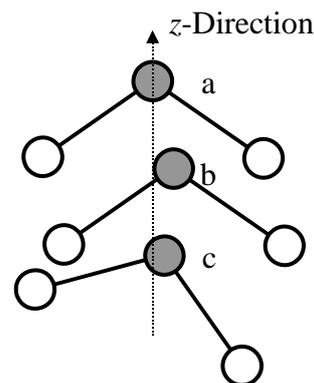
By taking the sign on the wave function  $\psi$  into account, we can determine that the  $p_x$  orbital of the central atom is of symmetry type  $B_1$ , and the LCAO orbital  $\psi = \psi_A - \psi_B$  is of symmetry type  $A_2$ . This LCAO orbital is composed of the two  $p_x$  orbitals from the oxygen atoms in  $SO_2$ .

For the symmetric and antisymmetric valence vibrations, let us consider Fig. 3.12. The equilibrium position of Fig. 3.12a belongs to the symmetry type  $A_1$ . The extension in the symmetrical vibration, Fig. 3.12b, also belongs to  $A_1$ . The antisymmetric vibration of Fig. 3.12c, however, belongs to the symmetry type  $B_2$ .



**Fig. 3.12** (at left) Pictures of a tri-atomic molecule of group  $C_{2v}$  during valence vibrations. (a) represents the equilibrium position, (b) symmetrical extension, and (c) extension during antisymmetric vibration.

**Fig. 3.13** (at right) Translation of a tri-atomic molecule of group  $C_{2v}$  with translation in the  $y$ -direction and rotation around the  $x$ -axis. (a) represents the original state, (b) the displacement, and (c) the rotation.



The equilibrium position in Fig. 3.12a always belongs to the symmetry type  $A_1$ . The translation in the  $y$ -direction (Fig. 3.13b), can only be transformed into itself by a reflection in the  $x$ - $z$  plane. All other symmetry operations change the sign of the translation. We have an analogous situation for rotation around the  $x$ -axis in Fig. 3.13c. Therefore  $y$ -translation and  $x$ -rotation belong to the symmetry type  $B_2$ , as is shown in the character table of Tab. 3.3.

The intensity of a spectral line (absorption, emission, non-Raman) is proportional to the square of the dipole moment of the transition from state 2 to state 1, as shown in chapter 3.6, equ. (3.100),

$$M_{21} = q \int \psi_2^* \hat{r} \psi_1 d\tau, \quad (3.62)$$

where  $\psi_1$  is the wave function of the state 1 and  $\psi_2^*$  is the complex conjugated wave function of state 2.  $q \hat{r}$  is the vector operator of the dipole moment. The dipole operator is thus the translation operator multiplied by the charge  $q$ . Symmetry considerations can not determine the value of  $M_{21}$ , they can however tell us whether the integral and dipole moment of the transition is zero. This gives us spectroscopic selection rules which tell us whether a given transition is allowed. Allowed transitions in equ. (3.62) have an integral whose symmetry type is  $A_1$ ,  $A_g$  or  $A_{g1}$ . That are symmetry types where all characters equals plus one.

To determine the symmetry type of the integral in equ. (3.62), multiply the symmetry types of the wave functions with the symmetry type of the translation. The convention for building the product of three symmetry types ( $X$ ,  $Y$  and  $Z$ ) of three classes is:

$$X(x_1, x_2, x_3) \times Y(y_1, y_2, y_3) \times Z(z_1, z_2, z_3) = (x_1y_1z_1, x_2y_2z_2, x_3y_3z_3) \quad (3.63)$$

We can see from equ. (3.63) that the totally symmetric symmetry types  $A_1$ ,  $A_g$  and  $A_{g1}$ , which only contain the values 1, represent the one-element of this multiplication.

As an example let us consider the transition of an electron from an  $a_1$  to a  $b_1$  orbital of the hydrogen molecule in the  $C_{2v}$  group. Don't forget that the orbitals in molecules with more than two atoms are labeled by the symmetry type to which they belong. The  $a_1$  electron belongs to the symmetry type  $A_1$ , which represents the one-element of the multiplication. For this reason it is necessary that the product of the electron  $b_1$  of type  $B_1$  with the type of the translation results in  $A_1$ , so that the product over all three types also results in  $A_1$ . It is easy to see that that is only possible if the translation also belongs to type  $B_1$ . The character table for  $C_{2v}$  (Tab. 3.3), shows that the  $x$ -translation belongs to type  $B_1$ . Thus, a transition from an  $a_1$  to a  $b_1$  orbital of the hydrogen molecule is allowed.

In general it holds for the symmetry properties of orbitals:

- The type of symmetry of the total state is equal to the product of the types of symmetry of the individual electrons.
- The type of symmetry of the electron is the same as the type of symmetry of the orbital in which the electron is located.
- If two electrons are in one orbital, their only difference is in their spin. The product of the types of symmetry of these paired electrons gives the total symmetric type, the one-element of multiplication. For the type of symmetry of the total state, we only need consider the outer non-filled orbitals.

Equation (3.62) is not valid for Raman transitions. Although the electric dipole moment has the type of symmetry of a translation, the polarization tensor, which is important for Raman transitions, transforms as the dyadic tensor product of identical vectors. The product contains the tensor elements  $x_i x_j$ , which means  $x^2$ ,  $y^2$ ,  $z^2$ ,  $xy$ ,  $xz$  and  $yz$ . To see this, consider the following representation:

$$\text{from } \mu_j^{\text{induced}} = \alpha_{ij} E_i = e \Delta x_j \quad \text{with} \quad E_i = -\frac{\Delta U}{\Delta x_i} \quad \text{follows} \quad \alpha_{ij} = -e \frac{\Delta x_i \Delta x_j}{\Delta U}. \quad (3.64)$$

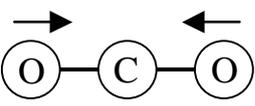
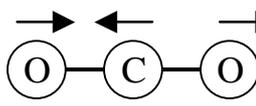
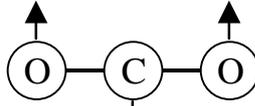
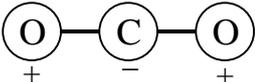
### 4.3.3 Symmetry Considerations for of Normal Modes

Before we demonstrate how to treat the excitation of normal modes using group theory, we have to define normal coordinates and normal modes of multi-atomic molecules. It is easy for diatomic molecules (see chapter 3.1.3): there is only one vibration and the normal coordinate is parallel to the bonding direction. In general it is possible to clarify the normal coordinates and normal modes for multi-atomic molecules ( $N$ -atomic molecules) with the following rules:

- There are  $3N-6$  normal oscillations for non linear molecules without free inner rotation. If there are degenerate vibrations, these are counted multiple times. Let us clarify this using the example of the doubly degenerate bending vibration in the  $\text{CO}_2$  molecule. Here we have one vibrational frequency which relates to two vibrations. If the molecule is linear, we have  $3N-5$  normal modes, and every free inner rotation reduces the number of vibrations by one. The number of normal coordinates is always the same as the number of normal modes.
- In equilibrium, all normal coordinates are zero. Note that this “equilibrium” is a classical description in which all oscillations are frozen at zero Kelvin. One can also imagine the vibrating atoms to be masses connected by springs, in which “equilibrium” is the state where the system is at rest. Equilibrium is a useful description, but it doesn’t exist, even in the lowest energy state, as shown in chapter 3.1.3.
- If the atoms are moved from their equilibrium position in the direction of a normal coordinate, only the related normal mode is excited.

As an example, consider the vibrations of the  $\text{CO}_2$  molecule. It is linear, and therefore has  $3N - 5 = 4$  vibrations: the symmetric ( $\tilde{\nu}_s = 1340 \text{ cm}^{-1}$ ) and anti-symmetric ( $\tilde{\nu}_{as} = 2349 \text{ cm}^{-1}$ ) valence vibrations and two deformation vibrations with a wave number of  $\tilde{\nu}_\delta = 667 \text{ cm}^{-1}$ .

**Tab. 3.4** Visualization of the four normal coordinates of the oscillations of  $\text{CO}_2$ .

			
$\alpha = \alpha_0 \cos \omega_s t$ $z_1^s = z_1^0 + \alpha$ $z_2^s = z_2^0$ $z_3^s = z_3^0 - \alpha$ $x_i = y_i = 0$	$\beta = \beta_0 \cos \omega_{as} t$ $z_1^{as} = z_1^0 + \beta$ $z_2^{as} = z_2^0 - c\beta$ $z_3^{as} = z_3^0 + \beta$ $x_i = y_i = 0$	$\gamma = \gamma_0 \cos \omega_{\delta(y)} t$ $y_1^{\delta(y)} = \gamma$ $y_2^{\delta(y)} = -c\gamma$ $y_3^{\delta(y)} = \gamma$ $z_i = z_i^0, x_i = 0$	$\mathcal{G} = \mathcal{G}_0 \cos \omega_{\delta(x)} t$ $x_1^{\delta(x)} = \mathcal{G}$ $x_2^{\delta(x)} = -c\mathcal{G}$ $x_3^{\delta(x)} = \mathcal{G}$ $z_i = z_i^0, y_i = 0$

The molecular axis lies in the  $z$ -direction in Tab. 3.4, the  $y$ -direction points upwards, and the  $x$ -direction into the page. Starting at the left, the  $x$  and  $y$  components in the symmetric vibration with the angular frequency  $\omega_s$  are zero. In the anti-symmetric vibration  $\omega_{as}$ , the  $x$  and  $y$  components are also zero. In the third figure on the top of Tab. 3.4, which shows a bending vibration  $\omega_{\delta(y)}$ , the  $x$  and  $z$  components are zero. The last figure shows a bending vibration  $\omega_{\delta(x)}$  into the page, the  $y$  and  $z$  components are zero. The coordinates relating to the atoms O, C, O were denoted by the indexes 1, 2, and 3, respectively. The coordinates in the equilibrium state get the superscript 0, and the coordinates for the symmetric vibration, anti-symmetric vibration, and the two bending vibrations get the subscripts s, as,  $\delta(y)$ ,  $\delta(x)$ , respectively. The time-dependencies of the four vibrations (vibrational amplitude with the subscript 0) are

also shown in Tab. 3.4. The proportionality factor  $c$  in Tab. 3.4 stands for the displacement of the coordinates of the carbon atom, which is determined by the condition of the preservation of the center of mass for the three vibrational types with the indices as,  $\delta(y)$ ,  $\delta(x)$ . For example, if for the asymmetric vibration (as) the equation for the preservation of the center of mass is  $2\beta m_O - c\beta m_C = 0$ , where  $m_O$  and  $m_C$  stand for the masses of the oxygen atom and the carbon atom, respectively, we get from the well known relation of the masses of carbon and oxygen (approximated by 16/12) a value  $c = 8/3$ .

Using the Tab. 3.4 we can make the following statement: the symmetric normal mode (s) has the normal coordinate  $\alpha$ , and the anti-symmetric normal mode (as) has the normal coordinate  $\beta$ . The normal coordinates  $\gamma$  and  $\varrho$ , which are perpendicular, belong to the two bending vibrations  $\delta(y)$  and  $\delta(x)$ . In this case we have a degenerate normal mode. That means that both vibrations  $\delta(y)$  and  $\delta(x)$  have the same angular frequency  $\omega_\delta$ . This is certainly possible, but does not necessarily follow from the above considerations.

With the insights gained from equ. (3.64), and the symmetry properties of normal coordinates and normal modes, we come to the following procedure:

- Use the character table and consider the symmetry properties of the integral  $\int \psi_2^* x_i \psi_1 d\tau$  (absorption spectra) and  $\int \psi_2^* x_i x_j \psi_1 d\tau$  (Raman scattering). The integral, in the first case the dipole moment of the transition, equ. (3.63), is non-zero if it is totally symmetric, i.e. the product of the three types of symmetry of  $\psi_2^* x_i \psi_1$  and  $\psi_2^* x_i x_j \psi_1$  give (or contain, if the type of symmetry has an order greater than one) the type of symmetry  $A_1$ ,  $A_g$  or  $A_{1g}$ . If  $\psi_1$  is the ground state and corresponds therefore to the symmetry type of the type of symmetry  $A_1$ ,  $A_g$  or  $A_{1g}$ , the integral is then non-zero, when  $x_i$  (or  $x_i x_j$ ) is of the same type of symmetry as  $\psi_2$ .
- The following theorem is called the Wigner-Theorem: If a system contains a certain group of symmetry operations, then every physically observable quantity of this system must also contain the same symmetry. That is why a harmonic vibration with any  $\nu''$  is assigned the same type of symmetry as its normal coordinate. The even wavefunctions of the harmonic oscillator are symmetric, and the odd are antisymmetric with respect to the normal coordinate. If a translation is transformed with the same type of symmetry as a normal coordinate ( $x$ ,  $y$ ,  $z$ , are odd functions), then the translation is anti-symmetric with respect to the normal coordinate, and the integral is totally symmetric because of  $\Delta\nu = 1$ .
- The symmetry considerations are often replaced by the following simple rules:  

$$\frac{d\mu}{dq} \neq 0 \Rightarrow \text{IR active}, \quad \frac{d\alpha}{dq} \neq 0 \Rightarrow \text{Raman active},$$
 where the consideration for each vibration and their normal coordinates  $q$  must be done individually.
- The dimension of the vibrational subspace of a type of symmetry is given by the sum of the proper and improper vibrations ( $\sum_i \text{Dim}\{U_i\} = 3N$ ). After the subtraction of the translation(s) and rotation(s), we get the number of proper vibrations, after further consideration of the degeneracy of the number of basic vibrations

### Calculation of the dimension of the vibrational subspace

$$\text{Dim}\{U_i\} = \frac{h_i}{h} \sum_k h_k \text{trace}(k) \chi_{ik} \quad (3.65)$$

- $\chi_{ik}$  is the value of the character table for the  $i$ -th representation and the  $k$ -th class,  
 $h_i \equiv \chi_{i1}$  is the dimension of the  $i$ -th representation (= 1 for A, B; 2 for E; 3 for T),  
 $h_k$  is the order of the  $k$ -th class (the number in front of the class label in the character table corresponds to the number of elements in the class) and  
 $h = \sum_k h_k$  is the order of the group (number of elements in a molecular point group)

The vector  $\text{trace}(k)$  consists of traces of all classes. It can be determined in the following way: choose 3N Cartesian coordinates ( $x, y, z$  for each atom) and check how many of the coordinates which are transformed into themselves after the symmetry operation in class ( $k$ ) retain their sign (+) or change their sign (-).  $\text{Trace}(k)$  is then the sum of the signed invariant coordinates.

A more comfortable way is to determine the number of atoms  $n(k)$  which have retained their locations after an operation of class  $k$  and build:

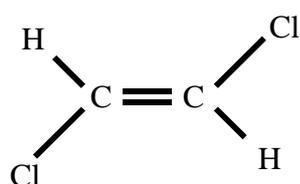
$$\text{trace}(k) = n(k) \times \alpha(k) \quad (3.66)$$

with the table

$k$	$E$	$\sigma$	$C_2$	$C_3$	$C_4$	$C_6$	$i$	$S_3$	$S_4$	$S_6$	$C(\beta)$	$S(\beta)$
$\alpha(k)$	3	1	-1	0	1	2	-3	-2	-1	0	$1+2\cos\beta$	$-1+2\cos\beta$

#### Example 1:

If the molecule trans-dichloro ethylene is lying in the  $x$ - $y$ -plane, we have the following symmetry elements:



- 2-fold axis of revolution in the  $z$ -direction  $C_2$   
 horizontal  $x$ - $y$  plane of reflection  $\sigma_h$   
 center of inversion  $i$

These symmetry operation together with the identity element  $E$  build the group  $C_{2h}$ , for which we can find published character tables that correspond to the outlined part of the following table:

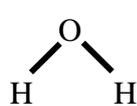
$C_{2h}$ $2/m$	$E$	$C_2$	$i$	$\sigma_h$			$\text{Dim}\{U_i\}$	proper vibrations	excitation / polarization
$A_g$	1	1	1	1	$R_z$	$x^2, y^2, z^2, x, y$	6	5	Raman-active, polariz.
$B_g$	1	-1	1	-1	$R_x, R_y$	$xz, yz$	3	1	Raman-act., depolar.
$A_u$	1	1	-1	-1	$z$		3	2	IR-active
$B_u$	1	-1	-1	1	$x, y$		6	4	IR-active
trace	18	0	0	6			$\Sigma=18$	$\Sigma=12$	

From the second to the fifth column, the lowest line contains the trace of the representation, which apparently doesn't only depend on the properties of the group, but also on the number  $N$  of atoms in the molecule, see equ. (3.66). For this group, we have  $h_i \equiv 1$ ,  $h_k \equiv 1$ ,  $h = 4$ . This gives from equ. (3.65) us  $\text{Dim}\{U_i\} = (1/4) \sum_k \text{trace}(k) \chi_{ik}$  in the eighth column as the dimension of the vibrational subspace. The sum of the dimensions is  $3N$  as expected. In every irreducible representation (row) we get the number of proper vibrations by subtracting the translations and rotations contained in the same line from the dimension of the vibrational subspace. The sum of all the proper vibrations of a non-linear molecule with free inner rotations is  $3N - 6$ . The last column contains information about the excitement according to the previously explained rules. For example: Five vibrations in the symmetry group  $A_g$  are Raman-active, since the elements  $x^2, y^2, z^2, xy$  in this group are transformed. We will consider the polarization of the Raman vibrations at the end of this chapter.

In molecules with a center of symmetry there is an alternative ban which says that the optically active vibrations of an irreducible representation are either IR-active or Raman-active. (As will be shown in example 3, they can't actually be optically active at all.) One can see from the character table of  $C_{2h}$  (see example 1 above), or from any other group with the class  $i$ , that elements of a translation ( $x, y, z$ ) never appear together in an irreducible representation with the elements of a dyadic tensor product of identical vectors ( $x^2, y^2, z^2, xy, xz, yz$ ). From that we also can see that the vibrations of  $A_g$  and  $A_{1g}$  are always Raman active.

### Example 2:

If we place the  $H_2O$  molecule in the  $x$ - $z$  plane, we get the following symmetry elements:



2-fold axis of revolution in the  $z$ -direction  $C_2$  in  $z$ -direction  
 vertical  $x$ - $z$ -plane of reflection  $\sigma_v = \sigma(xz)$   
 vertical  $y$ - $z$ - plane of reflection  $\sigma'_v = \sigma(yz)$

These elements together with  $E$  build the group  $C_{2v}$ , in the outlined part of the character table:

$C_{2v}$ $2mm$	$E$	$C_2$	$\sigma(xz)_v$	$\sigma'(yz)_v$			$\text{Dim}\{U_i\}$	proper vibrations	excitation/polarization
$A_1$	1	1	1	1	$z$	$z^2, y^2, x^2$	3	2	IR+Raman polar.
$A_2$	1	1	-1	-1	$R_z$	$xy$	1	0	
$B_1$	1	-1	1	-1	$x, R_y$	$xz$	3	1	IR+Raman depol.
$B_2$	1	-1	-1	1	$y, R_x$	$yz$	2	0	
trace	9	-1	3	1			$\Sigma=9$	$\Sigma=3$	

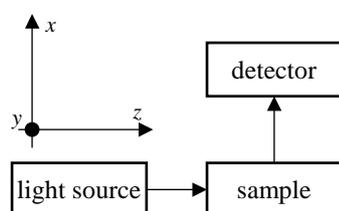
The trace is calculated analogously to example 1. Since the water molecule contains three atoms, the sum of the dimension of the vibrational subspace is 9, and the sum of the proper vibrations is 3.

**Example 3:**

The ethane molecule with the C-C-bonding in z-direction perpendicular to the drawing plane is shown in Fig. 3.11. The symmetry elements are  $C_2$ ,  $C_3$ ,  $\sigma_d$ ,  $i$  and the rotary reflection  $S_6$ . Together with  $E$  we have the group  $D_{3d}$  in the outlined character table:

$D_{3d}$ $\bar{3}m$	$E$	$2C_3$	$3C_2$	$i$	$2S_6$	$3\sigma_d$		$\text{Dim}\{U_i\}$	proper vibrations	excitation / polarization
$A_{1g}$	1	1	1	1	1	1	$x^2+y^2, z^2$	3	3	Raman, polariz.
$A_{2g}$	1	1	-1	1	1	-1	$R_z$	1	0	
$E_g$	2	-1	0	2	-1	0	$(R_x, R_y)$ $(x^2-y^2, xy, xz, yz)$	8	6	Raman, depolar.
$A_{1u}$	1	1	1	-1	-1	-1		1	1	non active
$A_{2u}$	1	1	-1	-1	-1	1	$z$	3	2	IR-active
$E_u$	2	-1	0	-2	1	0	$(x, y)$	8	6	IR-active
Ttype	24	0	0	0	0	4		$\Sigma=24$	$\Sigma=18$	

During the calculation of the dimension of the vibration subspace, we have to consider that  $h = 12$  and that not only  $h_i$  but also  $h_k$  assume more than just the value 1. The internal rotation around the C-C bonding axis has not been considered here. The examples 1-3 have shown that symmetry considerations make possible the division of the normal modes into IR-active, Raman-active, and non-active. Using the character table, one can also make experimentally measurable statements about the degree of depolarisation of the Raman scattering, as shown in chapter 3.3.3. Thereby we have a further aid for the allocation of the lines in the Raman spectrum to normal modes.

**3.3.3 Polarization of the Raman-Scattering**

In a scattering experiment, light sent from a source in  $z$ -direction creates a transversal wave oscillating in the  $x$ - $y$  plane. The light scattered by the sample in the  $x$ -direction only oscillates in the  $y$ -direction. It is therefore linearly polarized in the  $y$ - $z$ -plane perpendicular to the scattering direction.

If the polarizability  $\mathbf{P}$  of a molecule is isotropic ( $\alpha^I = \alpha_{xx} = \alpha_{yy} = \alpha_{zz}$ , z. B. for  $\text{CH}_4$ ), the direction of the induced dipole moment corresponds to the direction of the incoming electric wave  $\mathbf{E}$ , and the scattered light is linearly polarized. If the polarizability  $\alpha_{ij}$  is described by an anisotropic tensor, then  $\mathbf{P}$  is only parallel to  $\mathbf{E}$  if  $\mathbf{E}$  is parallel to the principal axis of  $\alpha_{ij}$  in a monocrystal. In different orientations of the monocrystal and also in liquids and vapors, the light scattered at a right angle is not fully polarized.

The degree of depolarization  $p_n$  of a normal mode  $n$  is defined as the relation of the intensity  $I_{\text{perpendicular}}$  of the light scattered and polarized in the  $x$ - $z$ -plane (perpendicular to the  $x$ - $y$ -plane) to the intensity  $I_{\text{parallel}}$  of the light scattered and polarized in the  $x$ - $y$ -plane. For unpolarized incoming light, see Max Born: Optik P.381:

$$p_n = \frac{I_{\text{perpendicular}}}{I_{\text{parallel}}} = \frac{2\Omega}{\Omega_0 + \frac{7}{3}\Omega} \quad (3.67)$$

The valid polarization tensor for the vibrational Raman Effect is given by the square of the isotropic part (type of  $\alpha_{ij}$ ) with

$$\Omega_0 = \left( \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \right)^2 \quad (3.68)$$

an anisotropy parameter

$$\Omega = \frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yx}^2 + \alpha_{zx}^2)}{30} \quad (3.69)$$

see Max Born: Optik p.399.  $\Omega_0$  and  $\Omega$  are invariant with respect to a coordinate transformation. The matrix elements  $\alpha_{ij}$  transform as  $x_i x_j$ , see equ. (3.64). If the type of symmetry, to which a normal mode belongs, contains none of the quantities  $x^2, y^2, z^2$ , then the isotropic part is not excited (no contribution to  $\Omega_0$ ), and from equ. (3.67) we get a degree of depolarization of 6/7. That is the maximum depolarization. Only the representations  $A_{1g}$  or  $A_1$  can contain all the quadratic tensor elements, so that the Raman line is completely polarized. In isotropic molecules, the depolarization is zero. Everything else lies in between.

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