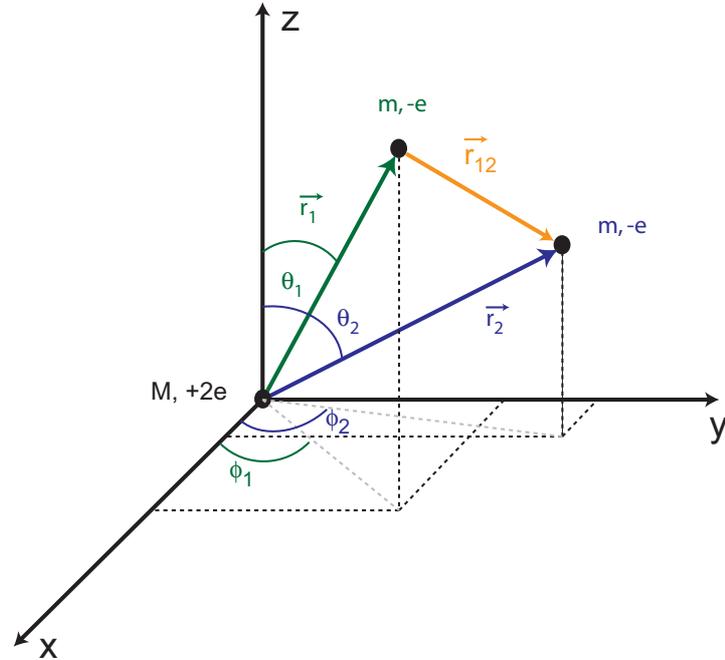


## 11 Two and many electron atoms

### 11.1 Helium



**Abbildung 11.1.** Helium atom with two electrons 1 and 2 at positions  $r_1$  and  $r_2$ .

The partial differential equation of a three particle system is not solvable. In Helium we have one nucleus and two electrons and the SE is given by

$$\left[ -\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right] \psi_E(\vec{r}_1, \vec{r}_2) = E\psi_E(\vec{r}_1, \vec{r}_2). \quad (11.1)$$

Because of the presence of the electron-electron interaction term  $1/r_{12}$  this equation is not separable, so that an eigenfunction  $\psi(\vec{r}_1, \vec{r}_2)$  of (11.1) cannot be written in the form of a single product of one-electron wave functions. The wave functions are said to be entangled. We remark that the equation (11.1) is unchanged when the coordinates of the two electrons are interchanged ( $\vec{r}_1 \leftrightarrow \vec{r}_2$ ). Thus, if we denote by  $P_{12}$  an interchange operator that permutes the spatial coordinates of the two electrons, the wave functions

$$P_{12}\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1) \quad (11.2)$$

satisfy the same SE. If both functions solve the same SE with non degenerate

eigenvalues  $E$  the functions can only differ by a factor  $\lambda$ .

$$P_{12}\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1) = \lambda\psi(\vec{r}_1, \vec{r}_2) \quad (11.3)$$

$$P_{12}^2\psi(\vec{r}_1, \vec{r}_2) = \lambda^2\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1, \vec{r}_2) \quad (11.4)$$

$$\psi(\vec{r}_2, \vec{r}_1) = \pm\psi(\vec{r}_1, \vec{r}_2) \quad (11.5)$$

Moreover, both functions  $\psi(\vec{r}_1, \vec{r}_2)$  and  $\vec{r}_2, \psi(\vec{r}_1)$  must be continuous, single-valued and bounded. The eigenvalues of  $P_{12}$  are  $\pm 1$ . The eigenfunctions are *space-symmetric*  $\psi_+(\vec{r}_1, \vec{r}_2)$  ( $\lambda = 1$ ) or *space-antisymmetric*  $\psi_-(\vec{r}_1, \vec{r}_2)$  ( $\lambda = -1$ ). States described by space-symmetric wave functions are called *para* states; those corresponding to space-antisymmetric wave functions are known as *ortho* states. For the parity operator we have

$$[H_0, P_{12}] = 0 \quad (11.6)$$

and the quantum number of the parity operator (+1, -1) are good quantum numbers describing the space-symmetry of the wave function.

Experimentally we can acquire information on Helium atoms by ionizing the Helium atom.

- 24.6 eV : Ionization of the first electron
- 54.4 eV : Ionization of the second electron
- 79.0 eV : Sum of both, total energy of both electrons

The energy of 54.4 eV is known, since we already solved the SE for atoms like  $\text{He}^+$  to be

$$E_1 = -\frac{Z^2}{1^2} \frac{\hbar^2}{2ma_0^2} = -4 \frac{\hbar^2}{2ma_0^2} = -4 \times 13.6 \text{ eV} = -54.4 \text{ eV} \quad (11.7)$$

The smaller binding energy of the first released electron is due to the shielding effect of the remaining inner electron. If we take  $\frac{e^2}{4\pi\epsilon_0 r_{12}}$  as a perturbation  $H'$  we can apply perturbation theory. The energy without the electron-electron interaction term is

$$H_0 = -\frac{\hbar^2}{2m} \Delta_1 - \frac{\hbar^2}{2m} \Delta_2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} = -108.8 \text{ eV}. \quad (11.8)$$

The difference between -79 eV and 108.8 eV is not small so that we can expect the result of the perturbation theory not to be very precise. The unperturbed Hamiltonian is

$$H_0 = H_1 + H_2 = \sum_{i=1}^2 -\frac{\hbar^2}{2m} \Delta_i - \frac{2e^2}{4\pi\epsilon_0 r_i}. \quad (11.9)$$

Equation (11.9) is the sum of two one-electron hydrogenic Hamiltonians. For such a decoupled Hamiltonian we can write the wave function  $\psi(\vec{r}_1, \vec{r}_2)$  in the form of single products of hydrogenic wave functions

$$\psi^{(0)}(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2). \quad (11.10)$$

Where we abbreviated  $a = n_1\ell_1m_1$  and  $b = n_2\ell_2m_2$ . The corresponding discrete energies being given by

$$H_0\psi^{(0)}(\vec{r}_1, \vec{r}_2) = H_0\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \quad (11.11)$$

$$= (H_1 + H_2)\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \quad (11.12)$$

$$= \psi_b(\vec{r}_2)H_1\psi_a(\vec{r}_1) + \psi_a(\vec{r}_1)H_2\psi_b(\vec{r}_2) \quad (11.13)$$

$$= \psi_b(\vec{r}_2)E_a\psi_a(\vec{r}_1) + \psi_a(\vec{r}_1)E_b\psi_b(\vec{r}_2) \quad (11.14)$$

$$= (E_a + E_b)\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) = E\psi^{(0)}(\vec{r}_1, \vec{r}_2). \quad (11.15)$$

In general for  $N$  'uncoupled' electrons we have  $N$  single electron Hamiltonians

$$H_0 = \sum_i^N H_i \quad (11.16)$$

$$H_i\psi_{a_i}(\vec{r}_i) = E_{a_i}\psi_{a_i}(\vec{r}_i) \quad (11.17)$$

$$\psi = \prod_i^N \psi_{a_i}(\vec{r}_i) \quad (11.18)$$

$$E = \sum_i E_{a_i} \quad (11.19)$$

$$E_0 = -4 \left( \frac{\hbar^2}{2ma_0^2} \right) \left[ \frac{1}{n_1^2} + \frac{1}{n_2^2} + \dots \right]. \quad (11.20)$$

Using this approximation we find  $E_0$  to be  $E_0 = -108.0\text{eV}$ . We still have to take into account the symmetry of the wave function and the electron-electron interaction term. For the electron-electron interaction term we find in first order perturbation theory

$$\Delta E = \int \int \psi_a^*(\vec{r}_1)\psi_b^*(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (11.21)$$

$$= \frac{e^2}{4\pi\epsilon_0} \int \int |\psi_a(\vec{r}_1)|^2 \frac{1}{|\vec{r}_2 - \vec{r}_1|} |\psi_b(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 \quad (11.22)$$

$$\equiv J \quad (11.23)$$

The integral  $J$  is called the Coulomb integral describing the electrostatic interaction energy of two overlapping distributions of charge density  $\rho_{n_1}(\vec{r}_1)$  and  $\rho_{n_2}(\vec{r}_2)$ . With the definition of charge densities we can rewrite the Coulomb

integral

$$\varrho_{n_i}(\vec{r}_i) = -e|\psi_{n_i}(\vec{r}_i)|^2 \quad (11.24)$$

$$J_{n_1 n_2} = \frac{1}{4\pi\epsilon_0} \int \int \frac{\varrho_{n_1}(\vec{r}_1)\varrho_{n_2}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2. \quad (11.25)$$

Now, we evaluate  $J_{1s1s}$  for the unperturbed wave functions to get the energy correction  $\Delta E$ . With

$$\psi_{1s}(\vec{r}_i) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr_i/a_0} \quad (11.26)$$

$$\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1} \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} Y_{\ell m}^*(\vartheta_1, \varphi_1) Y_{\ell m}(\vartheta_2, \varphi_2) \quad (11.27)$$

where in equation (11.27)  $r_{<}$  is the smaller  $r$  of the two radial distances  $r_1$  and  $r_2$ , whereas  $r_{>}$  is the bigger  $r$  of the two radial distances  $r_1$  and  $r_2$ , we have

$$J = \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int \int e^{-2\frac{Z(r_1+r_2)}{a_0}} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{2\ell+1} \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} \times \\ Y_{\ell m}^*(\vartheta_1, \varphi_1) Y_{\ell m}(\vartheta_2, \varphi_2) r_1^2 r_2^2 dr_1 dr_2 d\cos\vartheta_1 d\cos\vartheta_2 d\varphi_1 d\varphi_2 \quad (11.28)$$

All values for  $\ell \neq 0$  and  $m \neq 0$  vanish, because of the orthornormality condition of the spherical harmonics and we have

$$J = \frac{e^2}{4\pi\epsilon_0} (4\pi)^2 \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int_0^{\infty} \int_0^{\infty} e^{-2\frac{Zr_1}{a_0}} e^{-2\frac{Zr_2}{a_0}} \frac{r_1^2 r_2^2}{r_{>}} dr_1 dr_2 \quad (11.29)$$

$$= \frac{e^2}{4\pi\epsilon_0} (4\pi)^2 \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int_0^{\infty} r_2^2 e^{-2\frac{Z(r_2)}{a_0}} \underbrace{\left[ \int_0^{r_2} \frac{r_1^2 e^{-2\frac{Z(r_1)}{a_0}}}{r_2} dr_1 + \int_{r_2}^{\infty} \frac{r_1^2}{r_1} e^{-2\frac{Z(r_1)}{a_0}} dr_1 \right]}_{\frac{5a_0^5}{2^7 Z^5}} dr_2 \quad (11.30)$$

$$= \frac{5}{8} \frac{e^2}{4\pi\epsilon_0} \frac{Z}{a_0} = 34.0 \text{ eV}. \quad (11.31)$$

Thus the energy is

$$E_{He} = 2E_{1s} + J = -108.8 + 34.0 = -74.8 \text{ eV}. \quad (11.32)$$

This is close to the experimentally measured energy of  $-79.0 \text{ eV}$  and is only 5% off.

## 11.2 Excited states of helium

If one of the two electrons in helium is not in its ground state but in a higher orbital, we find the energy of the excited state in zero order perturbation to be

$$E_{1,n}^{(0)} = -Z^2 13.6 \text{ eV} \left( 1 + \frac{1}{n^2} \right). \quad (11.33)$$

The energy levels corresponding to the wave functions are degenerate in  $\ell$  and  $m$  and also exhibit the *exchange degeneracy*. Upon exchanging the electrons 1 and 2 we find the same energy for the two wave functions  $\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$  and  $\psi_a(\vec{r}_2)\psi_b(\vec{r}_1)$ . We can solve this problem in two ways:

With perturbation theory on degenerate levels we have to solve

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0. \quad (11.34)$$

with

$$H_{ij} = \langle i|H|j \rangle \quad (11.35)$$

$$S_{ij} = \langle i|j \rangle \quad (11.36)$$

$$i = \psi_1 = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \quad (11.37)$$

$$j = \psi_2 = \psi_a(\vec{r}_2)\psi_b(\vec{r}_1). \quad (11.38)$$

Evaluating of equation (11.34) leads to

$$H_{11} = H_{22} = E_a + E_b + J_{ab} \quad (11.39)$$

$$S_{11} = S_{22} = 1 \quad (11.40)$$

$$S_{12} = S_{21} = 0 \quad (11.41)$$

$$H_{12} = H_{21} = \kappa_{ab} \quad (11.42)$$

$$\kappa_{ab} = \int \int \psi_a^*(\vec{r}_1)\psi_b^*(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \psi_a(\vec{r}_2)\psi_b(\vec{r}_1) d\vec{r}_1 d\vec{r}_2. \quad (11.43)$$

The integral  $\kappa_{ab}$  in equation (11.43) is called *exchange integral* and is a pure quantum mechanical effect of two particles that cannot be distinguished. The exchange integral can also be represented by the exchange charge density

$$\varrho_{ab}(\vec{r}_i) = -e\psi_a^*(\vec{r}_1)\psi_b(\vec{r}_1). \quad (11.44)$$

The exchange integral is a measure of the overlap of the wave functions  $\psi_a(\vec{r}_1)$  and  $\psi_b(\vec{r}_1)$ . If the overlap vanishes there is no exchange degeneracy and the integral is zero ( $\kappa_{ab} = 0$ ). With the relations above we can solve equation (11.34)

$$\begin{vmatrix} E_a + E_b + J_{ab} - E & \kappa_{ab} \\ \kappa_{ab} & E_a + E_b + J_{ab} - E \end{vmatrix} = 0. \quad (11.45)$$

$$E_{\pm} = E_a + E_b + J_{ab} \pm \kappa_{ab}. \quad (11.46)$$

So the energy levels are split by the exchange energy  $\kappa_{ab}$  with the normalized wave functions given by

$$\psi_{\pm} = \frac{1}{\sqrt{2}} [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)]. \quad (11.47)$$

An alternative approach is conclude from the application of the parity operator that the wave functions have to be space-symmetric or space-antisymmetric.

$$\begin{aligned} \psi_s(\vec{r}_1, \vec{r}_2) &= \psi_+(\vec{r}_1, \vec{r}_2) \\ &= \frac{1}{\sqrt{2}} [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)] \quad (Para) \end{aligned} \quad (11.48)$$

$$\begin{aligned} \psi_{as}(\vec{r}_1, \vec{r}_2) &= \psi_-(\vec{r}_1, \vec{r}_2) \\ &= \frac{1}{\sqrt{2}} [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)] \quad (Ortho) \end{aligned} \quad (11.49)$$

Without any calculations we conclude that

$$\langle +|H'|-\rangle = \langle +|\frac{e^2}{4\pi\epsilon_0 r_{12}}|-\rangle = 0 = \int \psi_s^* H' \psi_{as} d\vec{r}_1 d\vec{r}_2. \quad (11.50)$$

In the basis of  $\psi_s$  and  $\psi_{as}$  the perturbation  $H'$  is already diagonal.

$$\Delta E_+ = \langle \psi_s | H' | \psi_s \rangle \quad (11.51)$$

$$\Delta E_- = \langle \psi_{as} | H' | \psi_{as} \rangle \quad (11.52)$$

$$\begin{aligned} \Delta E_{\pm} &= \frac{1}{2} \int \{ \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1) \}^* \frac{e^2}{4\pi\epsilon_0 r_{12}} \times \\ &\quad \{ \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\psi_b(\vec{r}_1) \} d\vec{r}_1 d\vec{r}_2 \end{aligned} \quad (11.53)$$

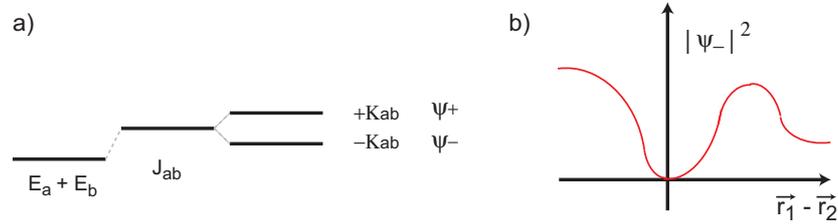
$$\begin{aligned} &= \frac{1}{2} \int |\psi_a(\vec{r}_1)|^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} |\psi_b(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 \\ &+ \frac{1}{2} \int |\psi_a(\vec{r}_2)|^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} |\psi_b(\vec{r}_1)|^2 d\vec{r}_1 d\vec{r}_2 \\ &\pm \frac{1}{2} \int \psi_a^*(\vec{r}_1)\psi_a(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \psi_b^*(\vec{r}_2)\psi_b(\vec{r}_1) d\vec{r}_1 d\vec{r}_2 \\ &\pm \frac{1}{2} \int \psi_a^*(\vec{r}_2)\psi_a(\vec{r}_1) \frac{e^2}{4\pi\epsilon_0 r_{12}} \psi_b^*(\vec{r}_1)\psi_b(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \end{aligned} \quad (11.54)$$

The first two and the last two integrals in equation (11.54) are equal so that  $\Delta E_{\pm}$  becomes

$$\Delta E_{\pm} = \underbrace{\int |\psi_a(\vec{r}_1)|^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} |\psi_b(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2}_{J_{ab}} \pm \underbrace{\int \psi_a^*(\vec{r}_2) \psi_a(\vec{r}_1) \frac{e^2}{4\pi\epsilon_0 r_{12}} \psi_b^*(\vec{r}_1) \psi_b(\vec{r}_2) d\vec{r}_1 d\vec{r}_2}_{\kappa_{ab}} \quad (11.55)$$

$$\Delta E_{\pm} = J_{ab} \pm \kappa_{ab} \quad (11.56)$$

The twofold degenerated levels are shifted ( $J_{ab}$ ) and split by the energy spacing of  $2\kappa_{ab}$ , which is a result of the electron-electron interaction. The energy levels of



**Abbildung 11.2.** a) Shifting and splitting of the energy levels due to electrostatic interaction ( $J_{ab}$ ) and exchange interaction ( $\kappa_{ab}$ ). b) Probability of finding two electrons of the antisymmetric wave function at the same position. The probability is zero for  $r_{12} = 0$ ; this is called Fermi-hole.

the antisymmetric wave functions  $\psi_-$  exhibit higher negative energies ( $E_a + E_b + J_{ab} - \kappa_{ab}$ ), because the electrons omit the same space and therefore the repulsion is smaller. The values of  $J_{ab}$  and  $\kappa_{ab}$  are always positive. In the ground state with  $a = b$  the antisymmetric wave function is constant zero, so that the wave function of the ground state is space-symmetric  $\psi_+$  with energy  $E = 2E_a + J_{aa}$ . Excited states can be either space-symmetric or space-antisymmetric and there are no allowed optical transitions in the dipole approximation between para ( $\psi_+$ ) and ortho ( $\psi_-$ ) states.

$$\langle \vec{\mu}_{s,as} \rangle = -e \int \underbrace{\psi_s(\vec{r}_1, \vec{r}_2)}_+ \underbrace{[\vec{r}_1 + \vec{r}_2]}_+ \underbrace{\psi_{as}(\vec{r}_1, \vec{r}_2)}_- d\vec{r}_1 d\vec{r}_2 = 0 \quad (11.57)$$

Optical transitions between  $\psi_-$  and  $\psi_+$  are forbidden (exception: strong LS coupling, intercombination lines). Ortho helium cannot be transferred to para helium by light absorption (behave like different atoms).

### 11.3 Indistinguishable particles

Two particles are said to be *identical* when they cannot be distinguished by means of any intrinsic property. While in classical physics the particles can be

distinguished by their paths of sharp trajectories, this is not possible in quantum mechanics, if the particles are found in the same regions of space such as their interaction region. Let us consider a quantum mechanical system of  $N$  identical particles. The Hamiltonian and all observables corresponding to this system must be symmetric with respect to any interchange of the space and spin coordinates of the particles ( $i$  and  $j$ ), defined by the parity operator  $P_{ij}$ .

$$[P_{ij}, H] = 0. \quad (11.58)$$

Note, if there are more than  $N = 2$  particles we have  $N!$  permutations and  $P$  do *not* commute among themselves ( $P_{ij}, P_{jk}$ ). There are *two* exceptional states which are eigenstates of  $H$  and of the  $N!$  permutation operators  $P$ , the totally symmetric state  $\psi_s(q_1, \dots, 1_N)$  and the totally antisymmetric state  $\psi_{as}(q_1, \dots, 1_N)$

$$P\psi_s(q_1, \dots, 1_N) = \psi_s(q_1, \dots, 1_N) \quad (11.59)$$

$$P\psi_{as}(q_1, \dots, 1_N) = \psi_{as}(q_1, \dots, 1_N) \times \begin{cases} 1, & \text{even permut.} \\ -1, & \text{odd permut.} \end{cases} \quad (11.60)$$

Note, equation (11.58) implies that  $P$  is a constant of the motion so that the system of identical particles represented by  $\psi_s$  or  $\psi_{as}$  will keep that symmetry at all times. To our present knowledge of particles occurring in nature, the two types of states  $\psi_s$  and  $\psi_{as}$  are thought to be sufficient to describe all systems of identical bosons and identical fermions, respectively. This is called the symmetrization postulate. Bosons (mesons, photons) are particles of zero or integer spin, described by totally symmetric wave functions and obey Bose-Einstein statistics. Fermions are particles having half-odd integer spin (electrons, protons, neutrino) and are described by totally antisymmetric wave functions. They satisfy Fermi-Dirac statistics.

## 11.4 Wave functions of helium

The correct wave function describing the electrons in the helium atom has to be a totally antisymmetric wave function, since the electrons are fermions. In the case of negligible spin-orbit coupling the Hamiltonian has no terms coupling space coordinates and spin coordinates resulting in a product type wave function

$$\psi(\vec{r}_1, m_{s_1}; \vec{r}_2, m_{s_2}) = \psi(\vec{r}_1, \vec{r}_2)\chi(m_{s_1}, m_{s_2}) \quad (11.61)$$

which has to be antisymmetric by interchanging all coordinates of two electrons. There are two possibilities to fulfil this condition

$$\psi_-(\vec{r}_1, m_{s_1}; \vec{r}_2, m_{s_2}) = \begin{cases} \psi_+(\vec{r}_1, \vec{r}_2)\chi_-(m_{s_1}, m_{s_2}) \\ \psi_-(\vec{r}_1, \vec{r}_2)\chi_+(m_{s_1}, m_{s_2}) \end{cases} \quad (11.62)$$

Also the spin wave function  $\chi(m_{s_1}, m_{s_2})$  can be written in the product form, (in the absence of spin-spin coupling) with four different combinations

$$\chi(m_{s_1}, m_{s_2}) = \chi(m_{s_1})\chi(m_{s_2}) \quad (11.63)$$

$$\chi_1(1, 2) = \alpha(1)\alpha(2) \quad \uparrow\uparrow \quad (11.64)$$

$$\chi_2(1, 2) = \alpha(1)\beta(2) \quad \uparrow\downarrow \quad (11.65)$$

$$\chi_3(1, 2) = \beta(1)\alpha(2) \quad \downarrow\uparrow \quad (11.66)$$

$$\chi_4(1, 2) = \beta(1)\beta(2) \quad \downarrow\downarrow \quad (11.67)$$

These four combinations are not symmetrized but upon introducing the total Spin operator  $\vec{S} = \vec{S}_1 + \vec{S}_2$  we can achieve a symmetrized new basis by linear combination of these four wave functions, that are eigenfunctions of  $\vec{S}^2$ ,  $\vec{S}_z$ ,  $\vec{S}_1^2$ ,  $\vec{S}_2^2$  and  $P_{12}$ .

$$\chi_{1,1}(1, 2) = \alpha(1)\alpha(2) \quad \uparrow\uparrow \quad (11.68)$$

$$\chi_{1,0}(1, 2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \quad \uparrow\downarrow + \downarrow\uparrow \quad (11.69)$$

$$\chi_{1,-1}(1, 2) = \beta(1)\beta(2) \quad \downarrow\downarrow \quad (11.70)$$

$$\chi_{0,0}(1, 2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad \uparrow\downarrow - \downarrow\uparrow \quad (11.71)$$

The indices in  $\chi_{S,m_s}$  are the quantum numbers of  $\vec{S}^2$  and  $\vec{S}_z$ . The three functions  $\{\chi_{1,1}, \chi_{1,0}, \chi_{1,-1}\}$  have a total spin of  $S = 1$  and magnetic spin quantum numbers of  $m_s = 1, 0, -1$ . These three spin wave functions represent the symmetric spin wave functions, with total **spin**  $S = 1$  and belong to **Spin Triplet** states. The other spin wave function  $\chi_{0,0}$  is the antisymmetric spin wave function with total **spin**  $S = 0$  and belong to **Spin Singlet** states. Hence the correct wave functions are

$$\psi_+(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (11.72)$$

for para or singlet states ( $|\vec{S}| = 0$ , spins antiparallel or zero) or

$$\psi_-(\vec{r}_1, \vec{r}_2) \times \left\{ \begin{array}{c} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \beta(1)\beta(2) \end{array} \right\} \quad (11.73)$$

for ortho or triplet states ( $|\vec{S}| \neq 0$ ). The Pauli principle says that there are no two identical particles (fermions) with the same quantum numbers. Therefore, we have a correlation between the electrons resulting in specific allowed combinations of spin and space wave functions. The ground state of helium has a symmetric space wave function and consequently an antisymmetric spin function so that the

ground state of helium is a singlet state. The excited states of helium  $(10)(n\ell)$  are split by

$$E_{10,n\ell}^{\pm} = E_{10} + E_{n\ell} + J_{10,n\ell} \pm \kappa_{10,n\ell} \quad (11.74)$$

$$J_{10,n\ell} = \int_0^{\infty} R_{n\ell}^2(r_2)r_2^2 \int_0^{\infty} R_{10}^2(r_1)\frac{r_1^2}{r_{>}} dr_1 dr_2 \quad (11.75)$$

$$\kappa_{10,n\ell} = \frac{1}{2\ell + 1} \int_0^{\infty} R_{10}(r_2)R_{n\ell}(r_2)r_2^2 \int_0^{\infty} R_{10}(r_1)R_{n\ell}(r_1)\frac{r_1^2 r_{\leq}^{\ell}}{r_{>}^{\ell+1}} dr_1 dr_2 \quad (11.76)$$

with para-He (+) and ortho-He (-). The triplet states are energetically lower than the singlet states, due to the reduced electron-electron repulsion. The triplet state  $(1s)(2s)$  is metastable, since relaxation to  $(1s)^2$  is not possible upon light emission (intercombination lines are forbidden). Excitation of triplet states is possible upon collisions of atoms, spin-orbit coupling (which is very weak for helium) and magnetic dipole transitions. Interaction with an electromagnetic field in the dipole approximation do not result in changing the total electron spin, because for such interactions it is

$$\Delta S = 0 \quad (11.77)$$

and the transition is spin forbidden. Both integrals (11.75, 11.76) depend explicitly on the quantum number  $\ell$ . Thus, degeneracy in  $m_{\ell}$  is still present but not in  $\ell$ . For a given  $n$  the Coulomb interaction  $J_{10,n\ell}$  increases with increasing  $\ell$ . This can be explained with bigger Coulomb repulsion upon decreasing  $\langle r_{n\ell} \rangle$  with increasing  $\ell$ .

$$\vec{S} = \vec{S}_1 + \vec{S}_2 \quad (11.78)$$

$$\vec{S}^2 = \vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1 \cdot \vec{S}_2 \quad (11.79)$$

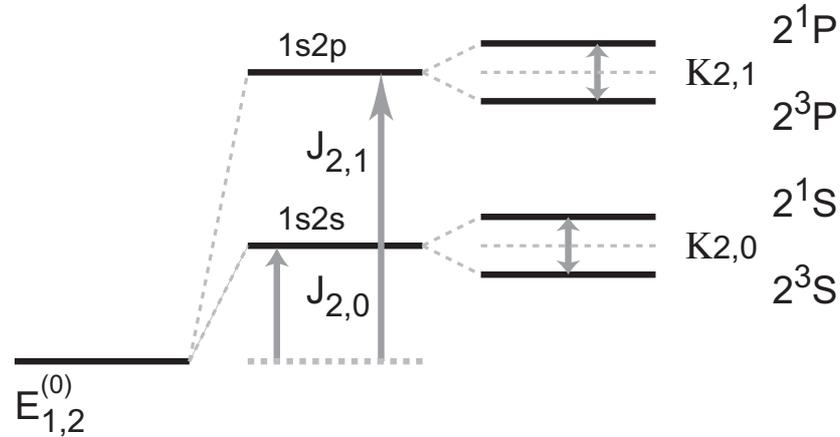
$$(\vec{S}_1 \cdot \vec{S}_2)\chi_{sm_s} = \frac{\hbar^2}{2} \left[ s(s+1) - \frac{3}{2} \right] \chi_{sm_s} \quad (11.80)$$

$$E_{10,n\ell}^{\pm} = E_{10} + E_{n\ell} + J_{10,n\ell} - \frac{1}{2} \left\{ 1 + 4 \frac{\vec{S}_1 \cdot \vec{S}_2}{\hbar^2} \right\} \kappa_{10,n\ell} \quad (11.81)$$

The energy splitting in equation (11.81) can be interpreted as an additional force called *exchange force*. The sign of the exchange force depend on the orientation of the spins, and the strengths of the force is sufficient to orient neighboring spins (ferromagnetism). The naming of the different states are as follows

$$n^{2S+1}L_J \quad (11.82)$$

$n$  is the principal quantum number;  $S$  is the total spin quantum number (for helium 0 and 1);  $L$  is the total orbital angular momentum quantum number (S, P, D, F, ...);  $J$  is the total angular momentum quantum number.



**Abbildung 11.3.** The splitting of the unperturbed helium level for  $n = 2$  by the Coulomb integrals and the exchange integrals.

## 11.5 Slater determinant

The total wave function is antisymmetric upon exchange of all coordinates of two electrons. If there are  $N$  independent electrons the wave function can be written as a product of  $N$  single electron wave functions  $\phi_i$ . To fulfil the symmetry conditions of the wave function, the wave function can be written as a sum of Slater determinants

$$\psi_{as}(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \dots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \dots & \phi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \dots & \phi_N(N) \end{vmatrix}. \quad (11.83)$$

Using the formalism of the Slater determinant, we can write the ground state wave function of helium:

$$\phi_1(1) = 1s(1)\alpha(1) \quad (11.84)$$

$$\phi_1(2) = 1s(2)\alpha(2) \quad (11.85)$$

$$\phi_2(1) = 1s(1)\beta(1) \quad (11.86)$$

$$\phi_2(2) = 1s(2)\beta(2) \quad (11.87)$$

$$\psi_{as}(1, 2, \dots, N) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) \\ 1s(1)\beta(1) & 1s(2)\beta(2) \end{vmatrix} \quad (11.88)$$

$$= \frac{1}{\sqrt{2}} \left( \underbrace{1s(1)1s(2)}_{+} [\underbrace{\alpha(1)\beta(2) - \alpha(2)\beta(1)}_{-}] \right) \quad (11.89)$$

- The Slater determinant and sums of Slater determinants give always antisymmetric wave functions

- Upon exchange of two rows or two columns, which correspond to exchange of all coordinates of two electrons  $P_{ij}$ , the Slater determinant change its sign.
- If the quantum numbers of two electrons are the same, two rows are equivalent and the Slater determinant is zero. That correspond to the Pauli exclusion principle that no two electrons in a system can have the same quantum numbers.

## 11.6 Many electron atoms

The SE for atoms with  $N$  electrons is

$$E\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \left[ -\sum_i^N \frac{\hbar^2}{2m} \Delta_i - \sum_i^N \frac{Ze^2}{4\pi\epsilon_0 r_i} + \frac{e^2}{4\pi\epsilon_0} \sum_i^N \sum_{\substack{j \\ i < j}}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \right] \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N). \quad (11.90)$$

With increasing  $Z$  the electron-electron repulsion becomes stronger and stronger and cannot be treated as a perturbation with respect to the electron-nucleus interaction. For  $N$  electrons we have  $1/2N(N-1)$  electron-electron interaction terms. Hartree (1928) used the averaged electron-electron interaction, which is for the  $j^{\text{th}}$  electron

$$Q_j(\vec{r}_j) = -e|\phi_j(\vec{r}_j)|^2. \quad (11.91)$$

and postulated a SE for single electron wave functions to be

$$\epsilon_i \phi_i(\vec{r}_i) = \left[ -\sum_i^N \frac{\hbar^2}{2m} \Delta_i - \sum_i^N \frac{Ze^2}{4\pi\epsilon_0 r_i} - e \sum_{j \neq i} V_j(\vec{r}_i) \right] \phi_i(\vec{r}_i) \quad (11.92)$$

$$V_j(\vec{r}_i) = -\frac{e}{4\pi\epsilon_0} \int \frac{|\phi_j(\vec{r}_j)|^2}{|\vec{r}_i - \vec{r}_j|} d\vec{r}_j. \quad (11.93)$$

The Hartree-Fock equations add an exchange term to the Hartree equation.

$$\begin{aligned} \epsilon_i \phi_i(\vec{r}_i) = & \left[ -\sum_i^N \frac{\hbar^2}{2m} \Delta_i - \sum_i^N \frac{Ze^2}{4\pi\epsilon_0 r_i} + \frac{e^2}{4\pi\epsilon_0} \sum_{j \neq i} \int \frac{|\phi_j(\vec{r}_j)|^2}{|\vec{r}_i - \vec{r}_j|} d\vec{r}_j \right] \phi_i(\vec{r}_i) \\ & - \frac{e^2}{4\pi\epsilon_0} \sum_{j \neq i} \left\{ \int \frac{\phi_j^*(\vec{r}_j) \phi_i(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} d\vec{r}_j \right\} \phi_j(\vec{r}_i). \end{aligned} \quad (11.94)$$

Solutions to the Hartree equations are found iteratively. One starts with zero order single electron wave functions and potentials, calculates the energies, sort

the energies obeying the Pauli principle and determine the averaged potential for the  $i^{\text{th}}$  electron. With the help of the new potential one calculates the new wave function. If this wave function is the same wave function as before the calculation is finished. If the wave function has changed, it is used for sorting the energies and so on. The solution is called a self-consistent solution. From the calculated energies one can determine the configurations with the lowest energies and fill up the orbitals with electrons. This gives the building up of atoms. Since there is no  $\ell$  degeneracy due to the Coulomb and exchange integral and the energy increases with increasing  $\ell$  the orbitals are filled up in the following order:

$$1s, 2s, 2p, 3s, 3p, \underline{4s}, 3d, 4p, \underline{5s}, \underline{4d}, 5p, \underline{6s}, 4f, 5d, 6p, \underline{7s}, 5f, 6d, 7p \quad (11.95)$$

The underlined states have similar energies and lead to complex transition spectra. Note,  $E_{4s} < E_{3d}$  due to the higher probability density of 4s electrons at  $r = 0$  than for 3d electrons, leading to an effectively increased nucleic charge for 4s electrons compared to 3d electrons (but  $\langle r \rangle_{3d} < \langle r \rangle_{4s}$ ). The wave functions of many electron atoms are similar to single-electron wave functions with the same  $Y(\vartheta, \varphi)$ , but with changed  $R_{n\ell}$ . The quantum numbers are the same  $n, \ell, m_\ell, m_s$ . Electrons with the same quantum numbers  $n$  and  $\ell$  belong to the same subshell ( $n\ell$ ). Those electrons are called equivalent electrons. Due to the Pauli exclusion principle there are maximally  $2(2\ell + 1)$  electrons per ( $n\ell$ ) subshell.

$$s \quad p \quad d \quad f \quad g \quad (11.96)$$

$$\ell = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad (11.97)$$

$$2\ell + 1 = 1 \quad 3 \quad 5 \quad 7 \quad 9 \quad (11.98)$$

$$\delta_i = 2(2\ell + 1) = 2 \quad 6 \quad 10 \quad 14 \quad 18 \quad (11.99)$$

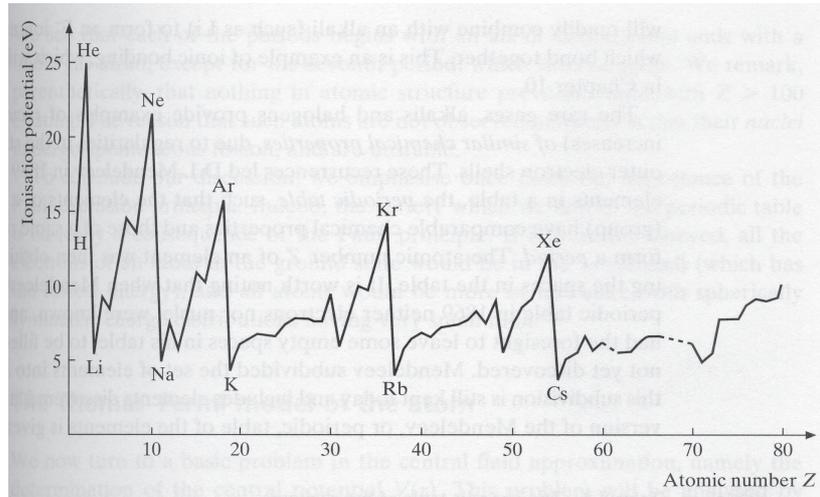
The degeneracy  $d_i$  is given by

$$d_i = \frac{\delta_i!}{\nu_i!(\delta_i - \nu_i)!} \quad (11.100)$$

the possible positions and the number of identical electrons. For example two electrons ( $\nu_i$ ) in a ( $2p$ ) subshell have degeneracy 15.

$$d_i = \frac{6!}{2!4!} = 15. \quad (11.101)$$

Now, we can build up the many electron atoms by filling up the subshells according to their energies and obeying the Pauli exclusion principle. Electrons in an open shell have the highest energy and are most weakly bound. They are called valence electrons. Closed shells exhibit a total orbital angular momentum  $\vec{L}$  and total spin angular momentum  $\vec{S}$  of zero. In the many electron atom nomenclature closed shells are described by  $^1S_0$  ( $L = 0, S = 0, J = 0$ ). They have a radial



**Abbildung 11.4.** Ionization potential for neutral atoms as a function of nucleic charge  $Z$ .

symmetric charge distribution and are chemically inert (noble gases: He, Ne, Ar, Kr, Xe). Alkali atoms with one valence electron in the  $s$ -orbital have low binding energy, low ionization energy, increased volume and are chemical reactive. We see that the degeneracy is high in  $m_l$  and  $m_s$ . In the case of **non equivalent electrons** in different subshells the Pauli exclusion principle is fulfilled and we find for two electrons

$$l = |\ell_1 - \ell_2|, |\ell_1 - \ell_2| + 1, \dots, \ell_1 + \ell_2 \quad (11.102)$$

$$s = |s_1 - s_2|, |s_1 - s_2| + 1, \dots, s_1 + s_2. \quad (11.103)$$

For example  $(np)(n'p)$  gives 6 different terms

$$\ell_1 = \ell_2 = 1 \quad (11.104)$$

$$s_1 = s_2 = \frac{1}{2} \quad (11.105)$$

$$L = 0, 1, 2 \quad (11.106)$$

$$S = 0, 1 \quad (11.107)$$

$$\Rightarrow {}^1S, {}^1P, {}^1D, {}^3S, {}^3P, {}^3D \quad (11.108)$$

For example  $(np)(n'd)$  gives also 6 different terms

$$\ell_1 = 1, \ell_2 = 2 \quad (11.109)$$

$$s_1 = s_2 = \frac{1}{2} \quad (11.110)$$

$$L = 1, 2, 3 \quad (11.111)$$

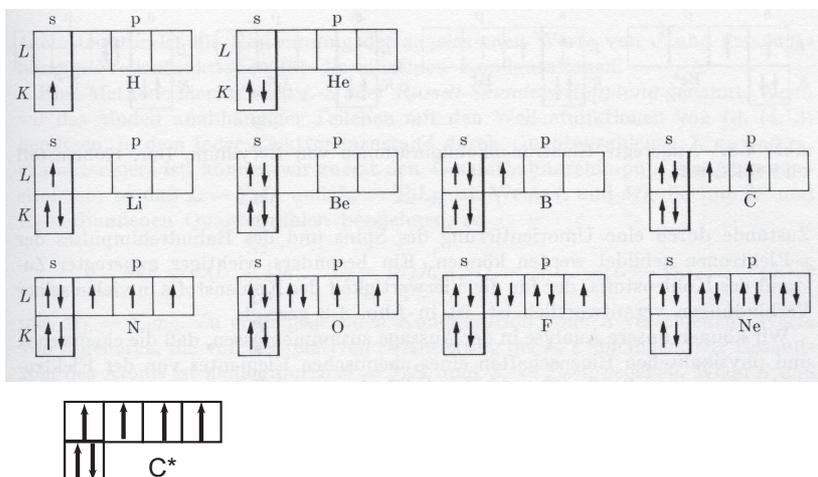
$$S = 0, 1 \quad (11.112)$$

$$\Rightarrow {}^1P, {}^1D, {}^1F, {}^3P, {}^3D, {}^3F \quad (11.113)$$

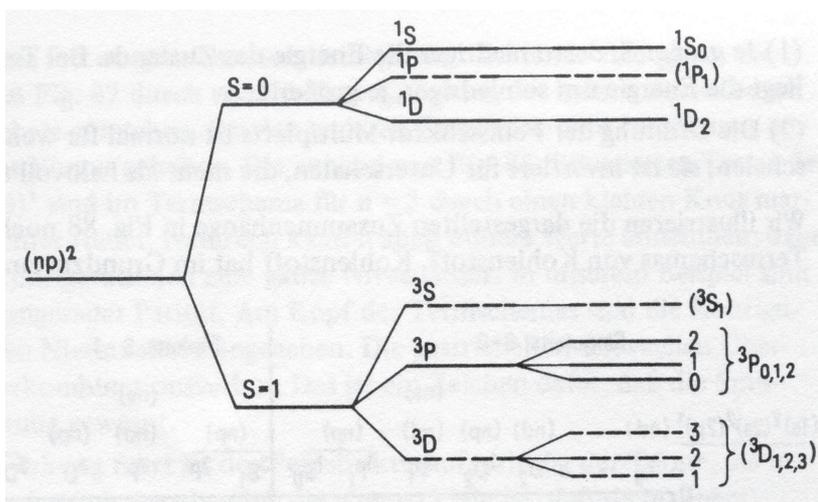
For three electrons this process has to be extended stepwise.

Z	Symbol	Grund-zustand	Grund-zustandskon-figuration	Ionisations-energie, eV	Z	Symbol	Grund-zustand	Grund-zustandskon-figuration	Ionisations-energie, eV
1	H	$2S$	$1s$	13.595	52	Te	$3P_2$	$4d^{10} 5s^2 5p^4$	9.01
2	He	$1S$	$1s^2$	24.581	53	I	$2P_{3/2}$	$4d^{10} 5s^2 5p^5$	10.454
3	Li	$2S$	[He] $2s$	5.390	54	Xe	$1S$	$4d^{10} 5s^2 5p^6$	12.127
4	Be	$1S$	$2s^2$	9.320	55	Cs	$2S$	[Xe] $6s$	3.893
5	B	$2P_{1/2}$	$2s^2 2p$	8.296	56	Ba	$1S$	$6s^2$	5.210
6	C	$3P_0$	$2s^2 2p^2$	11.256	57	La	$2D_{3/2}$	$5d 6s^2$	5.61
7	N	$4S$	$2s^2 2p^3$	14.545	58	Ce	$1G_4$	$4f 5d 6s^2$	6.54
8	O	$3P_2$	$2s^2 2p^4$	13.614	59	Pr	$4I_{9/2}$	$4f^3 6s^2$	5.48
9	F	$2P_{3/2}$	$2s^2 2p^5$	17.418	60	Nd	$5I_4$	$4f^4 6s^2$	5.51
10	Ne	$1S$	$2s^2 2p^6$	21.559	61	Pm	$6H_{5/2}$	$4f^5 6s^2$	
11	Na	$2S$	[Ne] $3s$	5.138	62	Fm	$7F_0$	$4f^6 6s^2$	5.6
12	Mg	$1S$	$3s^2$	7.644	63	Eu	$8S$	$4f^7 6s^2$	5.67
13	Al	$2P_{1/2}$	$3s^2 3p$	5.984	64	Gd	$9D_2$	$4f^7 5d 6s^2$	6.16
14	Si	$3P_0$	$3s^2 3p^2$	8.149	65	Tb	$6H_{15/2}$	$4f^9 6s^2$	6.74
15	P	$4S$	$3s^2 3p^3$	10.484	66	Dy	$5I_8$	$4f^{10} 6s^2$	6.82
16	S	$3P_2$	$3s^2 3p^4$	10.357	67	Ho	$4I_{15/2}$	$4f^{11} 6s^2$	
17	Cl	$2P_{3/2}$	$3s^2 3p^5$	13.01	68	Er	$3H_6$	$4f^{12} 6s^2$	
18	Ar	$1S$	$3s^2 3p^6$	15.755	69	Tm	$2F_{7/2}$	$4f^{13} 6s^2$	
19	K	$2S$	[Ar] $4s$	4.339	70	Yb	$1S$	$4f^{14} 6s^2$	6.22
20	Ca	$1S$	$4s^2$	6.111	71	Lu	$2D_{3/2}$	$4f^{14} 5d 6s^2$	6.15
21	Sc	$2D_{3/2}$	$3d 4s^2$	6.54	72	Hf	$3F_2$	$4f^{14} 5d^2 6s^2$	7.0
22	Ti	$3F_2$	$3d^2 4s^2$	6.83	73	Ta	$4F_{3/2}$	$4f^{14} 5d^3 6s^2$	7.88
23	V	$4F_{3/2}$	$3d^3 4s^2$	6.74	74	W	$5D_0$	$4f^{14} 5d^4 6s^2$	7.98
24	Cr	$7S$	$3d^5 4s$	6.764	75	Re	$6S$	$4f^{14} 5d^5 6s^2$	7.87
25	Mn	$6S$	$3d^5 4s^2$	7.432	76	Os	$5D_4$	$4f^{14} 5d^6 6s^2$	8.7
26	Fe	$5D_4$	$3d^6 4s^2$	7.87	77	Ir	$4F_{9/2}$	$4f^{14} 5d^7 6s^2$	9.2
27	Co	$4F_{9/2}$	$3d^7 4s^2$	7.86	78	Pt	$3D_3$	$4f^{14} 5d^8 6s^2$	8.88
28	Ni	$3F_4$	$3d^8 4s^2$	7.633	79	Au	$2S$	[Xe, $4f^{14} 5d^{10}$ ] $6s$	9.22
29	Cu	$2S$	$3d^{10} 4s$	7.724	80	Hg	$1S$	$6s^2$	10.434
30	Zn	$1S$	$3d^{10} 4s^2$	9.391	81	Tl	$2P_{1/2}$	$6s^2 6p$	6.106
31	Ga	$2P_{1/2}$	$3d^{10} 4s^2 4p$	6.00	82	Pb	$3P_0$	$6s^2 6p^2$	7.415
32	Ge	$3P_0$	$3d^{10} 4s^2 4p^2$	7.88	83	Bi	$4S$	$6s^2 6p^3$	7.287
33	As	$4S$	$3d^{10} 4s^2 4p^3$	9.81	84	Po	$3P_2$	$6s^2 6p^4$	8.43
34	Se	$3P_2$	$3d^{10} 4s^2 4p^4$	9.75	85	At	$2P_{3/2}$	$6s^2 6p^5$	
35	Br	$2P_{3/2}$	$3d^{10} 4s^2 4p^5$	11.84	86	Rn	$1S$	$6s^2 6p^6$	10.745
36	Kr	$1S$	$3d^{10} 4s^2 4p^6$	13.996	87	Fr	$2S$	[Rn] $7s$	
37	Rb	$2S$	[Kr] $5s$	4.176	88	Ra	$1S$	$7s^2$	5.277
38	Sr	$1S$	$5s^2$	5.692	89	Ac	$2D_{3/2}$	$6d 7s^2$	6.9
39	Y	$2D_{3/2}$	$4d 5s^2$	6.377	90	Th	$3F_2$	$6d^2 7s^2$	
40	Zr	$3F_2$	$4d^2 5s^2$	6.835	91	Pa	$4K_{11/2}$	$5f^2 6d 7s^2$	
41	Nb	$6D_{1/2}$	$4d^4 5s$	6.881	92	U	$5L_6$	$5f^3 6d 7s^2$	4.0
42	Mo	$7S$	$4d^5 5s$	7.10	93	Np	$6L_{11/2}$	$5f^4 6d 7s^2$	
43	Tc	$6S$	$4d^5 5s^2$	7.228	94	Pu	$7F_0$	$5f^6 7s^2$	
44	Ru	$5F_5$	$4d^7 5s$	7.365	95	Am	$8S$	$5f^7 7s^2$	
45	Rh	$4F_{9/2}$	$4d^8 5s$	7.461	96	Cm	$9D_2$	$5f^7 6d 7s^2$	
46	Pd	$1S$	$4d^{10}$	8.33	97	Bk		$(5f^8 6d 7s^2)$	
47	Ag	$2S$	$4d^{10} 5s$	7.574	98	Cf		$(5f^9 6d 7s^2)$	
48	Cd	$1S$	$4d^{10} 5s^2$	8.991	99	E		$(5f^{10} 6d 7s^2)$	
49	In	$2P_{1/2}$	$4d^{10} 5s^2 5p$	5.785	100	Fm		$(5f^{11} 6d 7s^2)$	
50	Sn	$3P_0$	$4d^{10} 5s^2 5p^2$	7.342	101	Mv			
51	Sb	$4S$	$4d^{10} 5s^2 5p^3$	8.639	102	No			
					103	Lw			

Abbildung 11.5. Electronic configuration of the atoms and ionization energies.



**Abbildung 11.6.** Electronic configuration of the ground state of atoms with the spin orientations according to Hund's rules.  $C^*$  is the excited state of carbon leading to  $sp^3$  hybridization.



**Abbildung 11.7.** Coupling of two equivalent p-electrons. The dotted lines correspond to energy levels which are forbidden by the Pauli exclusion principle.

In the case of equivalent electrons in the same subshell the Pauli exclusion principle forbid two electrons to have the same quantum numbers. Also combinations of two electrons with quantum numbers are forbidden if they are identical upon electron exchange. For example  $(np)^2$  (Fig. 11.6) gives 3 different terms

$$\ell_1 = \ell_2 = 1 \quad (11.114)$$

$$s_1 = s_2 = \frac{1}{2} \quad (11.115)$$

$$L = 0, 1, 2 \quad (11.116)$$

$$S = 0, 1 \quad (11.117)$$

$$\Rightarrow {}^1S, {}^1D, {}^3P \quad (11.118)$$

The terms of  ${}^1P$ ,  ${}^3S$ , and  ${}^3D$  are not allowed due to Pauli exclusion principle. The forbidden  ${}^3D$  state would have two electrons with the same spin quantum number in the same orbital  $m_\ell = \pm 1$ . Furthermore, the total wavefunction, i.e. the product of the spatial wavefunction and spin wavefunction has to be antisymmetric. In the case of odd numbers for the total angular momentum ( $L = 1, 3, 5, \dots$ ) the spatial wavefunction is antisymmetric upon electron exchange. Singlet spin states have antisymmetric spin wavefunctions and triplet states symmetric spin functions upon electron exchange. Thus, the state  ${}^1P$  would have a symmetric electron wavefunction and consequently is forbidden. Due to the Coulomb interaction and exchange force the levels split. The Hund's rules establish empirically the ground state configuration.

- 1 The term with the largest possible value of  $S$  for a given configuration has the lowest energy; the energy of the other terms increases with decreasing  $S$ .
- 2 For a given value of  $S$ , the term having the maximum possible value of  $L$  has the lowest energy.

Explanation for the Hund's rules are the following (Fig. 11.6): If the spin quantum number is maximal, the spins are parallel and the electrons have to occupy different orbitals, reducing the Coulomb repulsion. In addition, parallel spins are favored because of the exchange force. For a given quantum number  $S$  maximal quantum numbers of  $L$  provide the lowest energies. This is because of the reduced Coulomb repulsion in orbitals with high  $L$  and therefore higher averaged electron-electron distance.

Introducing spin-orbit coupling result in splitting of  $2j + 1$  degenerated levels. This is shown in Fig. (11.6) where the  ${}^3P_1$  level split in three sublevels. Using the

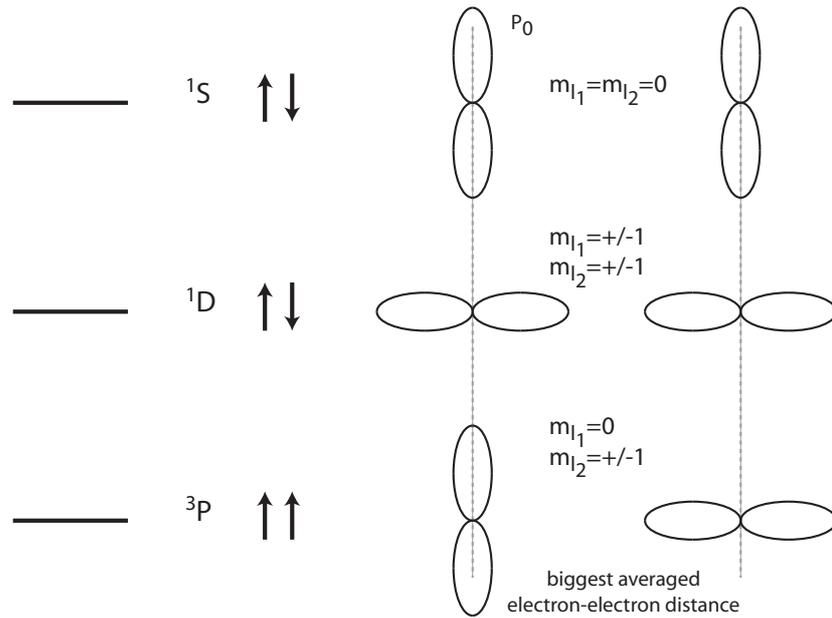


Abbildung 11.8. .

quantum numbers of the hydrogen wave function  $\ell, s, j, m_j$  we find

$$\left\langle \sum_k \xi(r_k) \vec{L}_k \cdot \vec{S}_k \right\rangle = A \langle \ell s j m_j | \vec{L}_i \cdot \vec{S}_i | \ell s j m_j \rangle \quad (11.119)$$

$$= \frac{A}{2} \langle \ell s j m_j | \vec{J}^2 - \vec{L}^2 - \vec{S}^2 | \ell s j m_j \rangle \quad (11.120)$$

$$= \frac{A}{2} \{ j(j+1) - \ell(\ell+1) - s(s+1) \} \quad (11.121)$$

$$\Rightarrow E(j) - E(j-1) = Aj \quad (11.122)$$

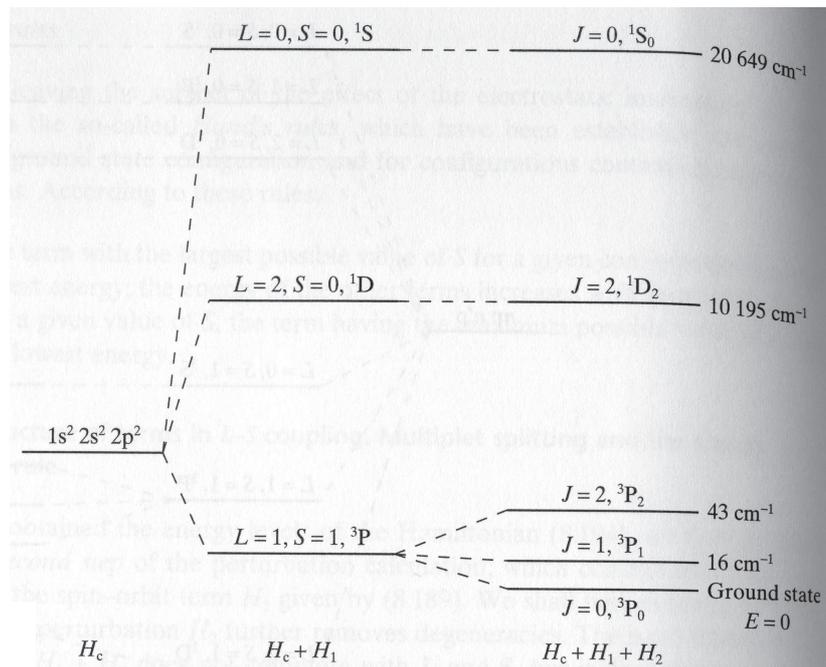
Equation (11.122) is called *Landé interval rule* and is well satisfied experimentally if the atom is well described by the L-S coupling case (only coupling and weak). One finds

$A > 0$ : Open subshell is less than half full. The lowest value of  $j$  exhibits the lowest energy.

$A < 0$ : Open subshell is more than half full. The highest value of  $j$  exhibits the lowest energy.

The strength of Spin-orbit coupling is proportional to  $Z^4$ , so that weak spin-orbit coupling holds for  $Z \leq 40$ .

If spin-orbit coupling is dominant the total angular momentum couples for each



**Abbildung 11.9.** The splitting of the ground state configuration of carbon due to spin-orbit coupling.

individual electron  $i$

$$\vec{J}_i = \vec{L}_i + \vec{S}_i. \quad (11.123)$$

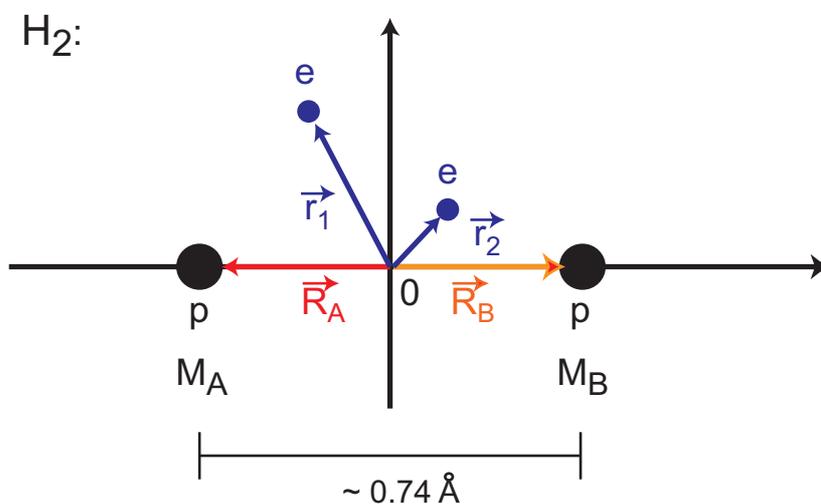
This is called *j-j-coupling*. Since closed shells have  $\vec{L} = \vec{S} = 0$  only valence electrons are relevant. Pure j-j-coupling is rarely found and most atoms show intermediate coupling schemes.

## 12 Molecules

Molecules consist of several atoms bound together. In addition to the atomic interactions, interactions between the electrons and nuclei of the atoms (for example  $A$  and  $B$ ) have to be taken into account. The forces resulting from electron-electron interaction and electron-nuclei interactions are comparable, but the masses of the nuclei  $M$  are much bigger than those of the electrons  $m$

$$\frac{m}{M} \approx 10^{-3} \dots 10^{-5}. \quad (12.1)$$

Therefore, the velocities of the nuclei are much smaller than that of the electrons and the kinetic energy of the nuclei is much smaller than that of the electrons. Thus, the electrons can adapt nearly instantaneously to the positions of the nuclei and the movement of electrons and nuclei can be separated. As long as this assumption holds we can use the product solution method to uncouple the movement of the electrons from the nuclei. Typical bond lengths of molecules



**Abbildung 12.1.** Hydrogen molecule ( $H_2$ ) and coordinates of the two electrons and nucleic protons. The center of mass is indicated as 0.

are in the range of Angstroms. The diatomic distance in the hydrogen and oxygen molecule ( $H_2$ ,  $O_2$ ) was measured by neutron diffraction to be  $\approx 0.74 \text{ \AA}$  and  $\approx 1.21 \text{ \AA}$ , respectively. In Fig. (12) the coordinates of the individual particles are

given. We can write them in the following form (here diatomic molecule)

$$\vec{R} = \vec{R}_B - \vec{R}_A \quad (12.2)$$

$$\mu = \frac{M_A M_B}{M_A + M_B} \quad (12.3)$$

$$T_N = -\frac{\hbar^2}{2\mu} \nabla_{\vec{R}}^2 \quad (12.4)$$

$$T_e = \sum_{i=1}^N -\frac{\hbar^2}{2m} \nabla_{\vec{r}_i}^2 \quad (12.5)$$

$$V(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) = \frac{e^2}{4\pi\epsilon_0} \left( -\sum_{i=1}^N \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} - \sum_{i=1}^N \frac{Z_B}{|\vec{r}_i - \vec{R}_B|} \right) + \sum_{\substack{i,j=1 \\ i>j}}^N \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R} \quad (12.6)$$

With this abbreviations the SE is given by

$$[T_N + T_e + V] \psi(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) = E \psi(\vec{R}; \vec{r}_1, \dots, \vec{r}_N). \quad (12.7)$$

In order to get an impression of the energy scales we estimate the binding energy of the electrons by choosing their wavelengths of the order of the internuclear distance

$$p \approx \frac{\hbar}{R} \quad (12.8)$$

$$E_e \approx \frac{p^2}{2m} \approx \frac{\hbar^2}{mR^2} \quad \text{some eV} \quad (12.9)$$

$$E_v = \hbar\omega_0 \left(v + \frac{1}{2}\right) = \hbar \sqrt{\frac{k}{\mu}} \left(v + \frac{1}{2}\right). \quad (12.10)$$

To dissociate a molecule one has to overcome the binding energy of the electrons or tear the atoms apart by the additional distance of  $R$ . With these assumptions we find

$$kR^2 \approx E_e, \quad \text{H.O.} \quad (12.11)$$

$$E_v \approx \hbar \sqrt{\frac{k}{\mu}} \approx \hbar \sqrt{\frac{E_e}{\mu R^2}} \quad (12.12)$$

$$\stackrel{(12.9)}{\approx} \hbar \sqrt{\frac{mE_e^2}{\mu\hbar^2}} \quad (12.13)$$

$$\approx E_e \sqrt{\frac{m}{\mu}} \approx 10^{-2} \times E_e. \quad (12.14)$$

Thus, the vibrational energies are about 0.1 eV and lie in the infrared spectral region. For example the vibrational energy of the diatomic molecule  $HCl$  is

$$\bar{\nu}_0 = \frac{\nu_0}{c_0} \approx 2990 \text{ cm}^{-1} = \frac{1}{\lambda_{[\text{cm}]}}. \quad (12.15)$$

We estimate the rotational energy of a molecule by taking the Hamiltonian of a rigid rotor with the moment of inertia  $I$ ,  $I = mR_0^2$ , that is

$$H = \frac{\vec{L}_N^2}{2I} = \frac{\vec{N}^2}{2I} \quad (12.16)$$

where  $m$  is the mass of the particle (point mass) fixed at the distance  $R_0$  to the axis of rotation. The eigenfunctions are proportional to the spherical harmonics  $\bar{Y}_{KM_K}(\Theta, \Phi)$  of the nucleic coordinates and the energy eigenvalues are

$$E_r = \frac{\hbar^2}{2I} J(J+1) = \frac{\hbar^2}{2\mu R^2} J(J+1). \quad (12.17)$$

The operator  $\vec{N}$  is the angular momentum operator of the nuclei with

$$\vec{N}^2 = -\hbar^2 \left[ \frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \left( \sin \Theta \frac{\partial}{\partial \Theta} \right) + \frac{1}{\sin^2 \Theta} \frac{\partial^2}{\partial \Phi^2} \right] \quad (12.18)$$

$$E_r = \langle \psi | \vec{N}^2 | \psi \rangle = \hbar^2 \frac{J(J+1)}{2\mu R^2} \quad (12.19)$$

$$\approx \frac{\hbar^2}{2\mu R^2} \approx \frac{m}{\mu} E_e \quad (12.20)$$

$$\approx 10^{-4} \times E_e. \quad (12.21)$$

The rotational energies are in the range of 0.001 eV or in the far infrared / microwave spectral region  $1 \dots 10^2 \text{ cm}^{-1}$ . Therefore the contribution of the rotational energies are negligible in comparison to the electronic and vibrational contributions to the total energy. After estimation of the relative contributions to the total energy we see that the movements of the nuclei are much slower than that of the electrons. For every nucleic geometry the electrons have enough time to adopt to the actual situation and we solve the SE for the electrons for every fixed and for the electrons static geometry of nuclei ( $\vec{R}$  fixed).

$$\begin{aligned} [T_e + V(\vec{R}; \vec{r}_1, \dots, \vec{r}_N)] \Phi_q(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) &= E_q(\vec{R}) \Phi_q(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) \\ H_e \Phi_q(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) &= E_q(\vec{R}) \Phi_q(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) \\ H_e \Phi_q &= E_q(\vec{R}) \Phi_q \end{aligned} \quad (12.22)$$

$H_e$  in equation (12.22) is called the electronic Hamiltonian of the *electronic wave equation* with  $\Phi_q$  being the electronic wave functions. The electronic wave functions and electronic energies depend on the parameter  $\vec{R}$  for every state described

by the quantum numbers  $q$ . The wave functions  $\{\Phi_q(\vec{R}; \vec{r})\}$  form a complete and orthonormal set of functions:

$$\int \Phi_s^*(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) \Phi_q(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1, \dots, d\vec{r}_N = \delta_{s,q}. \quad (12.23)$$

Therefore, the exact total wave function  $\psi(\vec{R}; \vec{r}_1, \dots, \vec{r}_N)$  can be expanded for every  $\vec{R}$  with the help of the electronic wave functions  $\{\Phi_q(\vec{R}; \vec{r})\}$

$$\psi(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) = \sum_q F_q(\vec{R}) \Phi_q(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) \quad (12.24)$$

with the coefficients  $F_q(\vec{R})$  representing the nuclear motion (vibration and rotation) when the electronic system is in the state  $q$ . Inserting equation (12.24) into (12.7)

$$\left[ T_N + T_e + V(\vec{R}; \vec{r}) \right] \sum_q F_q(\vec{R}) \Phi_q(\vec{R}; \vec{r}) = E \sum_q F_q(\vec{R}) \Phi_q(\vec{R}; \vec{r}) \quad (12.25)$$

and multiplying with  $\int \Phi_s^* \dots d\vec{r}_1, \dots, d\vec{r}_N$  we find

$$\sum_q \int \Phi_s^*(\vec{R}; \vec{r}) \left[ T_N + T_e + V(\vec{R}; \vec{r}) - E \right] F_q(\vec{R}) \Phi_q(\vec{R}; \vec{r}) d\vec{r}_1, \dots, d\vec{r}_N = 0 \quad (12.26)$$

$$0 = \sum_q \langle \Phi_s | T_N + T_e + V(\vec{R}; \vec{r}) - E | \Phi_q \rangle F_q(\vec{R}) \quad (12.27)$$

$$= \sum_q \langle \Phi_s | T_N + H_e - E | \Phi_q \rangle F_q(\vec{R}) \quad (12.28)$$

$$= \sum_q \langle \Phi_s | T_N + E_q(\vec{R}) - E | \Phi_q \rangle F_q(\vec{R}) \quad (12.29)$$

$$= \sum_q \langle \Phi_s | -\frac{\hbar^2}{2\mu} \left[ \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) - \frac{\vec{N}^2}{\hbar^2 R^2} \right] | \Phi_q \rangle F_q(\vec{R}) + [E_s(\vec{R}) - E] F_s(\vec{R}). \quad (12.30)$$

In equation (12.30) we used the orthonormality of  $\{\Phi_q(\vec{R}; \vec{r})\}$  and the fact that  $E_q(\vec{R})$  only depends on  $\vec{R}$  and  $E$  is eigenvalue of the total wave function  $\psi(\vec{R}; \vec{r}_1, \dots, \vec{r}_N)$ . The set of coupled equations (12.30) is exact and equivalent to the full SE (12.7). The *Born-Oppenheimer* (BO) or *adiabatic approximation*

will now be introduced. Since  $\Phi_q$  varies slowly with respect to  $R$ ,  $\Theta$  and  $\Phi$  the following relation holds

$$\left| \frac{\partial \Phi_q}{\partial R} \right| \ll \left| \frac{\partial F_q}{\partial R} \right| \quad (12.31)$$

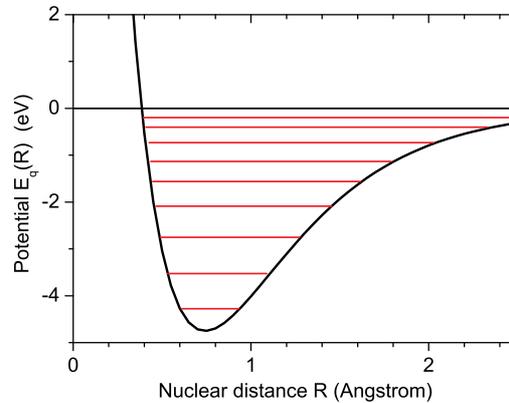
$$\Rightarrow \sum_q \langle \Phi_s | T_N | \Phi_q \rangle F_q(\vec{R}) \approx \sum_q \langle \Phi_s | \Phi_q \rangle T_N F_q(\vec{R}) \quad (12.32)$$

$$\forall s: \left[ -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \underbrace{\frac{\langle \Phi_s | \vec{N}^2 | \Phi_q \rangle}{2\mu R^2}}_{\sim E_{rot}} + E_s(R) - E \right] F_s(\vec{R}) = 0. \quad (12.33)$$

Equation (12.33) is the *nuclear wave equation*. Since  $E_{rot}$  is negligible small the nuclear wave equation simplifies to

$$\left[ -\frac{\hbar^2}{2\mu} \vec{\nabla}_R^2 + E_s(\vec{R}) \right] F_s(\vec{R}) = E F_s(\vec{R}), \quad \forall s \quad (12.34)$$

In the BO approximation first the electronic wave equation (12.22) with the wave functions  $\{\Phi_q(\vec{R}; \vec{r})\}$  are solved for parametric values of  $\vec{R}$  to find the energies  $E_q(\vec{R})$ . With the electronic energies  $E_q(\vec{R})$  we can solve the nuclear wave equa-



**Abbildung 12.2.** Energy eigenvalue of the electronic wave function  $E_q$  plays the role of a potential for the nuclear wave function. Red horizontal lines indicate the energy eigenvalues of the nuclear vibrational energies. For different quantum numbers  $q$  the potentials are different.

tion (12.33) to get the wave functions  $F_s(\vec{R})$ , where the energy functions  $E_s(\vec{R})$  play the role of a potential. The total wave functions  $\psi_s$  in the BO approximation has the product form

$$\psi_s(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) = F_s(\vec{R}) \Phi_s(\vec{R}; \vec{r}_1, \dots, \vec{r}_N). \quad (12.35)$$

For every nuclear coordinate  $\vec{R}$  the electron probability density  $|\Phi_q(\vec{R}; \vec{r})|^2$  is different and the equations (12.22) and (12.34) have to be solved. The nuclei move in the potential given by the eigenvalues of the electronic wave equation  $E_s(\vec{R})$ .

## 12.1 Diatomic molecules

The electronic wave equation (12.22), in which only the Coulomb interactions are taken into account, is solved for diatomic molecules by using a system of coordinates  $\overline{OX}$ ,  $\overline{OY}$ ,  $\overline{OZ}$  which is fixed with respect to the molecule. The  $\overline{Z}$  axis is chosen along the internuclear axis from B to A. The origin  $O$  is the center of mass and the spherical coordinates are  $R$ ,  $\Theta$  and  $\Phi$ . This is called the *body-fixed* or *molecular* frame. The position vector  $\vec{r}_i$  of an electron is the same in the space-fixed and body-fixed frames, but the components of  $\vec{r}_i$  are different in each frame. We will label the components of  $\vec{r}_i$  by  $x_i$ ,  $y_i$ , and  $z_i$  in the space-fixed frame and by  $\bar{x}_i$ ,  $\bar{y}_i$ , and  $\bar{z}_i$  in the body-fixed frame. The eigenvalues  $E_s(R)$  are independent of the frame of reference.

$$\bar{x}_i = \cos \Theta \cos \Phi x_i + \cos \Theta \sin \Phi y_i - \sin \Theta z_i \quad (12.36)$$

$$\bar{y}_i = -\sin \Phi x_i + \cos \Phi y_i \quad (12.37)$$

$$\bar{z}_i = \sin \Theta \cos \Phi x_i + \sin \Theta \sin \Phi y_i + \cos \Theta z_i \quad (12.38)$$

The different frames of reference can be brought to coincidence by a rotation through an angle  $\phi$  about the  $OZ$  axis and rotation about  $OY'$  axis through an angle  $\Theta$ . We find that

$$\frac{\partial \Phi_q}{\partial \Phi} = -\frac{i}{\hbar} L_{\bar{y}} \Phi_q \quad (12.39)$$

$$\frac{\partial \Phi_q}{\partial \Theta} = \left[ -\frac{i}{\hbar} \cos \Theta L_{\bar{z}} + \frac{i}{\hbar} \sin \Theta L_{\bar{x}} \right] \Phi_q \quad (12.40)$$

$$L_{\bar{z}} = -i\hbar \sum_{i=1}^N \left( \bar{x}_i \frac{\partial}{\partial \bar{y}_i} - \bar{y}_i \frac{\partial}{\partial \bar{x}_i} \right) \quad (12.41)$$

## 12.2 Symmetry properties

In the electronic wave equation the three components of the total electronic orbital angular momentum  $\vec{L}$  commute with the Hamiltonian (11.90) of a many electron atom as well as  $\vec{L}^2$ . Thus, we have the good quantum numbers  $L$  and  $M_L$ . The fact that  $L$  is approximately a good quantum number is used in the classification of atomic energy levels and terms (e.g.  $^3P_2$ ). In contrast the internuclear axis of diatomic molecule picks out a single direction in space. If we choose this direction as the  $\bar{z}$  axis, then the operator  $L_{\bar{z}}$  commutes with  $H_e$ , but not  $L_{\bar{x}}$ ,  $L_{\bar{y}}$ , and  $\vec{L}^2$ . Since the electronic molecular Hamiltonian  $H_e$  is invariant under

rotations about the internuclear line or  $\bar{z}$  axis, but not about  $\bar{x}$  or  $\bar{y}$  axis, only  $L_{\bar{z}}$  commutes with the Hamiltonian. Therefore, simultaneous eigenfunctions of  $H_e$  and  $L_{\bar{z}}$  can construct the electronic eigenfunctions  $\Phi_s$  of a diatomic molecule and it is

$$L_{\bar{z}} = M_L \hbar \Phi_s, \quad M_L = 0, \pm 1, \pm 2, \dots \quad (12.42)$$

$$= \pm \Lambda \hbar \Phi_s, \quad \Lambda = 0, 1, 2, \dots \quad (12.43)$$

where  $\Lambda = |M_L|$  is the projection of the total electronic orbital angular momentum on the internuclear axis. The azimuthal part of the  $\Phi_s$  is therefore given by

$$\Phi_s \propto \frac{1}{\sqrt{2\pi}} e^{\pm i\Lambda\Phi}. \quad (12.44)$$

By analogy with the spectroscopic notation S,P,D,F,... used for many electron atoms having the quantum number  $L$  the quantum number  $\Lambda$  is used for diatomic molecules

Value of $\Lambda$	0	1	2	3	...	
	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$		(12.45)
Code letter	$\Sigma$	$\Pi$	$\Delta$	$\Phi$	...	

To describe transitions or the state characterized by individual electrons we use the quantum number  $\lambda = |m_\ell|$  and the analogue notation

Value of $\lambda$	0	1	2	3	...	
	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$		(12.46)
Code letter	$\sigma$	$\pi$	$\delta$	$\phi$	...	

The electronic Hamiltonian  $H$  (without interaction to the nuclei) of a diatomic molecule is invariant under reflections in all planes containing the internuclear line, for example the  $\bar{X}\bar{Z}$  plane. If this operation  $\bar{y}_i \rightarrow -\bar{y}_i$  is described by the operator  $A_{\bar{y}}$  then

$$[A_{\bar{y}}, H_e] = 0 \quad (12.47)$$

$$L_{\bar{z}} = -i\hbar \sum_{i=1}^N \left( \bar{x}_i \frac{\partial}{\partial \bar{y}_i} - \bar{y}_i \frac{\partial}{\partial \bar{x}_i} \right), \quad N \text{ electrons} \quad (12.48)$$

$$A_{\bar{y}} L_{\bar{z}} = -L_{\bar{z}} A_{\bar{y}} \quad (12.49)$$

If  $\Lambda \neq 0$  (the  $\Pi$ ,  $\Delta$ ,  $\Phi$  ... terms) the operator  $A_{\bar{y}}$  acting on the wave function with eigenvalue  $\Lambda\hbar$  of  $L_{\bar{z}}$  converts the wave function into another one with eigenvalue  $-\Lambda\hbar$ . Both eigenfunctions have the same energy, because  $A_{\bar{y}}$  commutes with  $H_e$ , and are doubly degenerate.

If we consider the case  $\Lambda = 0$  we have  $\Sigma$  states, that are non-degenerate and

simultaneous eigenfunction of  $H_e$ ,  $L_{\bar{z}}$ , and  $A_{\bar{y}}$  can be constructed. The eigenvalues of  $A_{\bar{y}}$  are  $\pm 1$  and thus the  $\Sigma$  states of diatomic molecules are specified by  $\Sigma^+$  and  $\Sigma^-$  for states left unchanged or changed upon reflection in a plane containing the nuclei, respectively. In the special case of *homonuclear* diatomic molecules (such as  $H_2$ ,  $O_2$ ,  $N_2$ , etc.) there is an extra symmetry upon reflecting the coordinates of all electrons with respect to the origin  $\vec{r}_i \rightarrow -\vec{r}_i$ , because of the center of symmetry of this molecule. This operator commutes with  $L_{\bar{z}}$  and the electronic wave functions split into two sets, those that are even and do not change and those that are odd and change its sign. The even electronic wave functions are denoted by a subscript  $g$  called *gerade* states, the odd electronic wave functions denoted by a subscript  $u$  called *ungerade* states. For homonuclear diatomic molecules we have the following states

$$\Sigma_g^+, \Sigma_u^+, \Sigma_g^-, \Sigma_u^-, \Pi_g, \Pi_u, \dots \quad (12.50)$$

Exchanging the nuclear coordinates  $\vec{R} \rightarrow -\vec{R}$  is the same operation as first rotating the molecule as a whole through  $180^\circ$  about the  $\bar{Y}$  axis, followed by the operations  $\bar{y}_i \rightarrow -\bar{y}_i$  and  $\vec{r}_i \rightarrow -\vec{r}_i$ . If we denote the resultant spin of the individual electron spins by  $\vec{S}$  with the usual eigenvalues of  $\vec{S}^2$  to be  $\hbar^2 S(S+1)$  we characterize the molecule by its multiplicity  $(2S+1)$  as a left superscript. The term symbol is written

$${}^{2S+1}\Lambda, \quad \text{for } \Lambda = 0, 1, 2, \dots \quad (12.51)$$

$${}^3\Delta, \quad \Lambda = 2, S = 1 \quad (12.52)$$

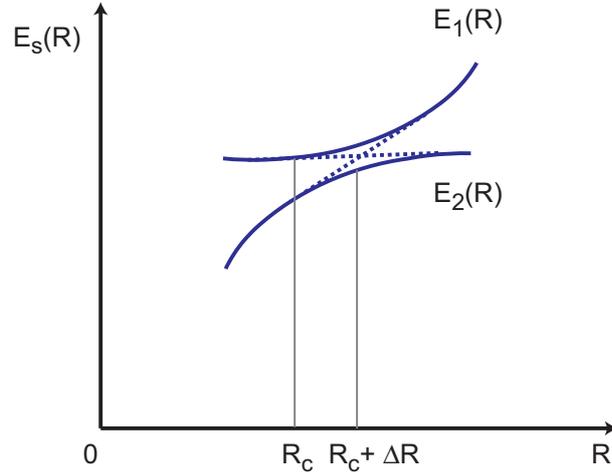
The ground state of a molecule is often labeled by the symbol  $X$  and since the ground state has very often maximum symmetry in diatomic molecules it is then denoted by  $X^1\Sigma_g^+$ . Excited states of the same multiplicity as the ground state are usually distinguished by the upper case letters  $A, B, C, \dots$  and those of different multiplicity by lower case letters  $a, b, c, \dots$

Hyperfine structure interactions due to coupling to the nuclear spins and the orbital motion and spin of the electrons are usually small and can be neglected. However, symmetry effects related to the spin of the nuclei have an important influence on the structure of the wave functions especially if the molecule consist of identical nuclei.

### 12.3 Neumann-Wigner non-crossing rule

For every electronic eigenfunction  $\Phi_s$  of the molecule there is a multidimensional potential  $E_s(\vec{R})$ , which depends on the internuclear vector  $\vec{R}$ . We want to know how these potential curves changes as  $R$  varies, and if is it possible that two

potential curves intersect. If we suppose we have two different electronic potential curves  $E_1(R)$  and  $E_2(R)$  as depicted in Fig. 12.3 that are close but distinct at the internuclear distance  $R_c$ . The energies  $E_1^{(0)}$  and  $E_2^{(0)}$  are eigenvalues of the electronic Hamiltonian  $H_0 = H_e(R_c)$ . The corresponding orthonormal electronic eigenfunctions are  $\Phi_1^{(0)}$  and  $\Phi_2^{(0)}$ . If we modify the internuclear distance  $R_c$  to



**Abbildung 12.3.** Angular momentum of a diatomic molecule with no coupling between the electronic and nuclear orbital motion and without spin coupling.

$R_c + \Delta R$  with small  $\Delta R$ , we can treat the new situation as a perturbation to the electronic Hamiltonian

$$H_e(R_c + \Delta R) = H_e(R) + H' = H_0 + H' \quad (12.53)$$

$$H' = \Delta R \frac{\partial H_0}{\partial R_c} \quad (12.54)$$

$$H'_{ij} = \langle \Phi_i^{(0)} | H' | \Phi_j^{(0)} \rangle, \quad i, j = 1, 2. \quad (12.55)$$

If we have a degenerate case with degeneracy of  $N$  and  $N$  wave functions  $\psi_{ku}^{(0)}$  we have to solve the following determinant to obtain a non-trivial solution.

$$\det |\langle \psi_{ku}^{(0)} | H' | \psi_{ks}^{(0)} \rangle - E_{kr}^{(1)} \delta_{us}| = 0, \quad (r, s, u = 1, 2, \dots, N) \quad (12.56)$$

Solving the determinant yields  $N$  real roots  $E_{k1}^{(1)}, E_{k2}^{(1)}, \dots, E_{kN}^{(1)}$ . If all these roots are distinct the degeneracy is completely removed to first order in the perturbation. Here, we have  $N = 2$  and we have to solve the determinant at the position where the curves should cross, that is at  $R_c + \Delta R$  and  $H_0 + H'$ . It is  $\langle \Phi_i^{(0)} | H_0 | \Phi_j^{(0)} \rangle = E_i^{(0)} \delta_{ij}$ , and we have the determinant

$$\begin{vmatrix} \langle \Phi_1^{(0)} | H_0 + H' | \Phi_1^{(0)} \rangle - E & \langle \Phi_1^{(0)} | H' | \Phi_2^{(0)} \rangle \\ \langle \Phi_2^{(0)} | H' | \Phi_1^{(0)} \rangle & \langle \Phi_2^{(0)} | H_0 + H' | \Phi_2^{(0)} \rangle - E \end{vmatrix} = 0. \quad (12.57)$$

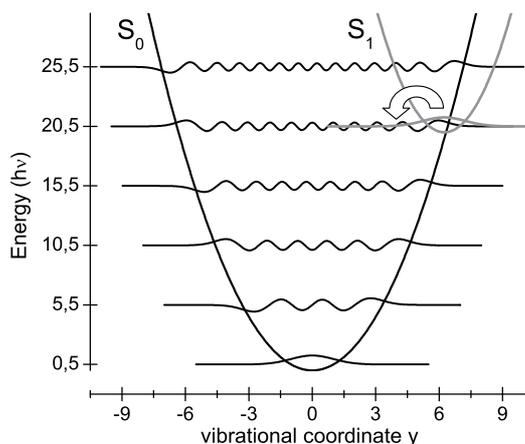
The potentials  $E_1(R)$  and  $E_2(R)$  are equal at position  $R_c + \Delta R$  if the two equations are simultaneously satisfied

$$E_1^{(0)} - E_2^{(0)} + H'_{11} - H'_{22} = 0, \quad \text{same energies for 1 and 2} \quad (12.58)$$

$$H'_{12} = 0. \quad (12.59)$$

The last term follows from solving the determinant with two identical energy values  $E$ , so that the potentials can cross. We have to distinguish two cases:

- The matrix element  $H'_{12}$  is zero. That is the case if the two functions  $\Phi_1^{(0)}$  and  $\Phi_2^{(0)}$  have different symmetries (for example having different values of  $\Lambda$ ). Then it is possible to find a certain value  $\Delta R$  where the energies are the same  $E_1(R_c + \Delta R) = E_2(R_c + \Delta R)$ .
- If  $\Phi_1^{(0)}$  and  $\Phi_2^{(0)}$  have the same symmetry, then  $H'_{12}$  will in general be non-zero. In almost all cases it is impossible to find a single value  $\Delta R$  for which the two conditions are satisfied simultaneously. Thus in general *two electronic curves belonging to the same symmetry species cannot cross*. This is called the non-crossing rule of von Neumann and Wigner.



**Abbildung 12.4.** Energy relaxation via internal conversion (IC). If two potentials have different symmetries, they can cross. This is naturally the case for singlet and triplet potentials. However, if some coupling exists between two potentials  $S_0$  and  $S_1$  for example by vibrational coupling, the population of the level  $S_1$  can relax via internal conversion (IC) to the  $S_0$  state. In this case the IC increases with increasing overlap (and mixing due to coupling) of the vibrational wave functions in the two potentials.

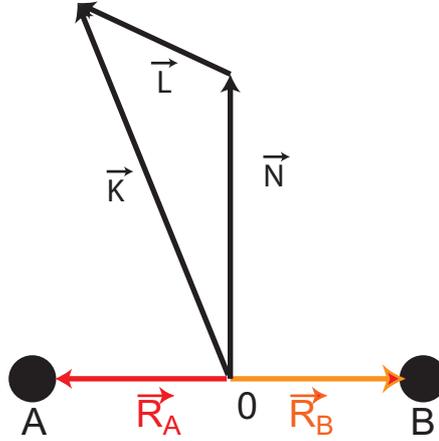
## 12.4 Rotation and vibration of diatomic molecules

In the nuclear wave equation (12.33) the first term describes the kinetic energy due to radial motion (we are in the center of mass coordinate system) and the second

term is the kinetic energy due to rotational motion.  $E_s(R)$  acts as an effective potential. The orbital angular momentum  $\vec{N}$  of the nuclei A and B (diatomic molecule) can be expressed by the total orbital angular momentum  $\vec{K}$ , and the orbital angular momentum of the electrons

$$\vec{N} = \vec{K} - \vec{L}. \quad (12.60)$$

The orbital angular momentum is given by  $\vec{N} = \vec{R} \times \vec{P}$ , where  $\vec{P}$  is the operator for the relative linear momentum of A and B and  $\vec{R}$  the internuclear position vector. It follows that  $\vec{R} \cdot \vec{N} = 0$  and that the components of the electronic orbital angular momentum  $\vec{L}$  and the total orbital angular momentum  $\vec{K}$  along AB, which we define as the z-axis are equal  $L_{\bar{z}} = K_{\bar{z}}$ .



**Abbildung 12.5.** Angular momentum of a diatomic molecule with no coupling between the electronic and nuclear orbital motion and without spin coupling.

$$K_{\bar{z}} = \vec{K} \cdot \vec{R} = L_{\bar{z}}. \quad (12.61)$$

For an isolated molecule with negligible spin-dependent coupling and no coupling between electronic and nuclear orbital motion the wave function  $\psi_s$  must be a simultaneous eigenfunction of  $\vec{K}^2$  and  $K_z$ , where  $K_z$  is the component of  $K$  along the  $OZ$  ( $OA$ ,  $OB$ ) space-fixed axis. Thus we have that

$$\vec{K}^2 \psi_s = K(K+1)\hbar^2 \psi_s \quad (12.62)$$

where the rotational quantum number  $K$  is a positive integer or zero, and  $-K \leq M_K \leq K$ :

$$K_z \psi_s = M_K \hbar \psi_s. \quad (12.63)$$

In addition equations (12.42, 12.43) show that  $\psi_s$  is an eigenfunction of  $L_{\bar{z}}$

$$L_{\bar{z}} \psi_s = F_s(\vec{R}) L_{\bar{z}} \Phi_s = \pm \hbar \Lambda \psi_s \quad (12.64)$$

$$K_{\bar{z}} \psi_s = \pm \hbar \Lambda \psi_s \quad (12.65)$$

and because of equation (12.61)  $\psi_s$  must also be an eigenfunction of  $K_{\bar{z}}$ . The possible values of the quantum number  $K$  are (see Fig. 12.4)

$$|\vec{K}| \geq K_{\bar{z}} \quad (12.66)$$

$$K = \Lambda, \Lambda + 1, \Lambda + 2, \dots \quad (12.67)$$

Now we show the rotational kinetic energy term is given by

$$\begin{aligned} \frac{1}{2\mu R^2} \langle \Phi_s | \vec{N}^2 | \Phi_s \rangle F_s(\vec{R}) &= \frac{1}{2\mu R^2} \langle \Phi_s | \vec{K}^2 + \vec{L}^2 - 2\vec{K} \cdot \vec{L} | \Phi_s \rangle F_s(\vec{R}) \\ &= \frac{1}{2\mu R^2} \langle \Phi_s | \vec{K}^2 + L_{\bar{z}}^2 - 2\vec{K} \cdot \vec{L} + L_{\bar{x}}^2 + L_{\bar{y}}^2 | \Phi_s \rangle F_s(\vec{R}) \\ &= \frac{\hbar^2}{2\mu R^2} [K(K+1) - \Lambda^2] F_s(\vec{R}) \\ &\quad - \frac{1}{2\mu R^2} \langle \Phi_s | L_{\bar{x}}^2 + L_{\bar{y}}^2 + 2N_{\bar{x}}L_{\bar{x}} + 2N_{\bar{y}}L_{\bar{y}} | \Phi_s \rangle F_s(\vec{R}) \end{aligned} \quad (12.68)$$

Here we used the fact that  $\Phi_s$  are orthonormal eigenfunctions and eigenstates of  $\vec{L}_{\bar{z}}$ . Because of the axial symmetry around the  $\bar{z}$  axis the expectation values  $\langle L_{\bar{y}} \rangle$ , and  $\langle L_{\bar{x}} \rangle$  are zero. The relative motion of nuclei can now be expressed as

$$0 = -\frac{\hbar^2}{2\mu} \left[ \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) - \frac{K(K+1)}{R^2} \right] F_s(\vec{R}) + [E'_s(R) - E] F_s(\vec{R}) \quad (12.69)$$

$$E'_s(R) = E_s(R) - \frac{\Lambda^2 \hbar^2}{2\mu R^2} - \frac{1}{2\mu R^2} \langle \Phi_s | L_{\bar{x}}^2 + L_{\bar{y}}^2 | \Phi_s \rangle \quad (12.70)$$

The energy  $E'_s(R)$  acts as an effective potential for the wave function  $F_s(\vec{R})$  and depends only on the electronic states. Since the last two terms are much smaller than the first one, due to the greater mass of  $\mu$  with respect to  $m$  we use the approximation

$$E'_s(R) = E_s(R). \quad (12.71)$$

The wave function for the nuclear motion  $F_s(\vec{R})$  can be expressed in terms of the product of a radial function  $\mathfrak{F}_{svK}(R)$  and an angular function  $\bar{Y}_{\Lambda K M_K}(\Theta, \Phi)$

$$F_s(\vec{R}) = \frac{1}{R} \mathfrak{F}_{svK}(R) \bar{Y}_{\Lambda K M_K}(\Theta, \Phi). \quad (12.72)$$

The quantum number  $v$  is called *vibrational quantum number* and assigns different solutions of equation (12.69) and is related to molecular vibrations. For a given electronic state  $s$  the different states called *rovibronic states* are labeled

by the rotational quantum number  $K$  and the vibrational quantum number  $v$ . The angular function  $\bar{Y}_{\Lambda K M_K}(\Theta, \Phi)$  are eigenfunctions of  $\bar{K}^2$  and  $K_z$  for a given  $\Lambda$ . For  $\Sigma$  states ( $\Lambda = 0$ ) it is  $\bar{K} = \bar{N}$  and the angular functions reduce to the spherical harmonics  $Y_{KM_K}(\Theta, \Phi)$ .

$$\begin{aligned} \bar{Y}_{\Lambda K M_K}(\Theta, \Phi) &= N_{\Lambda K M_K} \times e^{iM_K\Phi} (1 - \cos \Theta)^{(\Lambda - M_K)/2} (1 + \cos \Theta)^{-(\Lambda + M_K)/2} \\ &\times \left[ \left( \frac{\partial}{\partial \cos \Theta} \right)^{(K - M_K)} \{ (1 - \cos \Theta)^{K - \Lambda} (1 + \cos \Theta)^{K + \Lambda} \} \right] \end{aligned} \quad (12.73)$$

$$N_{\Lambda K M_K} = (-1)^K \frac{1}{\sqrt{2\pi}} \sqrt{\frac{(2K + 1)(k + M_K)!}{2^{2K+1}(K + \Lambda)!(K - \Lambda)!(K - M_K)!}} \quad (12.74)$$

Inserting equation (12.72) into equation (12.69) and dividing by the angular functions we obtain the radial equation for the nuclei

$$0 = \left[ -\frac{\hbar^2}{2\mu} \left( \frac{d^2}{dR^2} - \frac{K(K+1)}{R^2} \right) + E_s(R) - E_{svK} \right] \mathfrak{F}_{svK}(R) \quad (12.75)$$

$$E_s(R) = E_s(R_0) + (R - R_0) \left. \frac{dE_s}{dR} \right|_{R=R_0} + \frac{1}{2} (R - R_0)^2 \left. \frac{d^2E_s}{dR^2} \right|_{R=R_0} + \dots \quad (12.76)$$

Since  $E_s(R)$  has a minimum at  $R = R_0$  the second term on the right hand side of equation (12.76) vanishes. Neglecting the third and higher order terms we get the parabolic approximation that correspond to the harmonic oscillator

$$E_s(R) = E_s(R_0) + \frac{1}{2} k_s (R - R_0)^2 \quad (12.77)$$

$$k_s = \left. \frac{1}{2} \frac{d^2E_s}{dR^2} \right|_{R=R_0} \quad (12.78)$$

Inserting equation (12.77) into (12.75) we find an eigenvalue equation of the vibrational energy  $E_v$

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2} k_s (R - R_0)^2 - E_v \right] \psi_v = 0. \quad (12.79)$$

This is the same eigenvalue equation than for the harmonic oscillator and we find the same eigenfunctions as in the case of the harmonic oscillator and eigenvalues given by

$$E_v = \hbar\omega_0 \left( v + \frac{1}{2} \right) = h\nu_0 \left( v + \frac{1}{2} \right), \quad v = 0, 1, 2, \dots \quad (12.80)$$

with  $\omega_0 = (k_s/\mu)^{1/2}$ . Additionally, we can simplify equation (12.75) by approximating the internuclear distance  $R$  by  $R_0$ , that result in an expression for the

rotational energy  $E_r$

$$E_r = \frac{\hbar^2}{2\mu R_0^2} K(K+1) = \frac{\hbar^2}{2I_0} K(K+1) \equiv BK(K+1), \quad K = \Lambda, \Lambda+1, \dots \quad (12.81)$$

$I_0$  is the moment of inertia of the molecule for an equilibrium distance  $R_0$  and reduced mass  $\mu$ . The constant  $B$  describing molecular properties is called *rotational constant*. The equilibrium distance and hence  $B$  depends on the electronic state  $s$ . The total energy  $E_{svK}$  is the sum of the individual energies

$$E_{svK} = E_s(R_0) + E_v + E_r. \quad (12.82)$$

For allowed pure rotational transitions the permanent electric dipole moment has to be non-zero. In the dipole approximation the selection rules are for pure rotational transitions

$$\Delta K = \pm 1 \quad (12.83)$$

$$\Delta M_K = 0, \pm 1. \quad (12.84)$$

Note, the energy of the molecule cannot depend on  $M_K$  in the absence of external fields and with no preferred direction in space. The energy is twofold degenerated for  $\Lambda \neq 0$  with degeneracy  $2(2K+1)$  and for  $\Sigma$  states with  $\Lambda = 0$  we find degeneracy of the energy levels of  $2K+1$ . The levels split in the presence of an electric field (Stark effect).

In the representation of the principal axis system of a rigid body the kinetic energy of a rotating body is

$$E_r = \frac{1}{2I_a} K_a^2 + \frac{1}{2I_b} K_b^2 + \frac{1}{2I_c} K_c^2 \quad (12.85)$$

$$\vec{K}^2 = K_a^2 + K_b^2 + K_c^2 \quad (12.86)$$

where  $I_a$ ,  $I_b$ , and  $I_c$  are the principal moments of inertia about axis  $a$ ,  $b$ , and  $c$  with its components of the angular momentum  $K_a$ ,  $K_b$ , and  $K_c$  about the axis. Diatomic molecules are axially symmetric about the internuclear line, with  $I_a = I_b$ ,  $I_c = I_z$ , and  $K_c = K_z$ . The system is called *symmetrical top* molecule

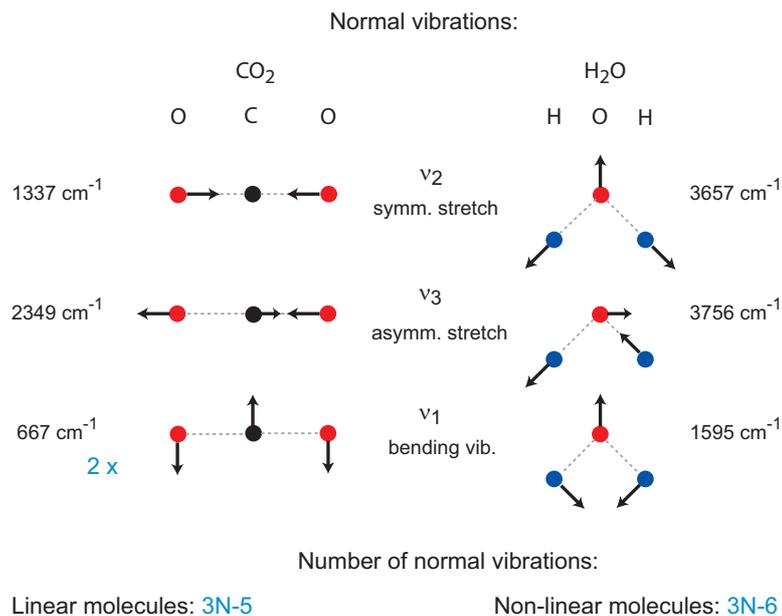
$$E_r = \frac{1}{2I_a} (K_a^2 + K_b^2) + \frac{1}{2I_c} K_c^2 \quad (12.87)$$

$$E_r = \frac{1}{2I_a} K(K+1) + \left( \frac{1}{2I_c} - \frac{1}{2I_a} \right) \Lambda^2 \hbar^2, \quad K = \Lambda, \Lambda+1, \dots \quad (12.88)$$

The rotational energy in equation (12.88) consist of two terms. The first term has a rotational axis that goes through the center of mass with  $I_a = \mu R_0^2$  and depend

on  $K(K + 1)$ . The second term depends on the moment of inertia  $I_c$  and on the eigenvalue of the electronic state  $\Lambda^2 \hbar^2$ . If we include the second term in the electronic energy  $E_s(R_0)$  we get the same description of the rotational energy as in equation (12.81).

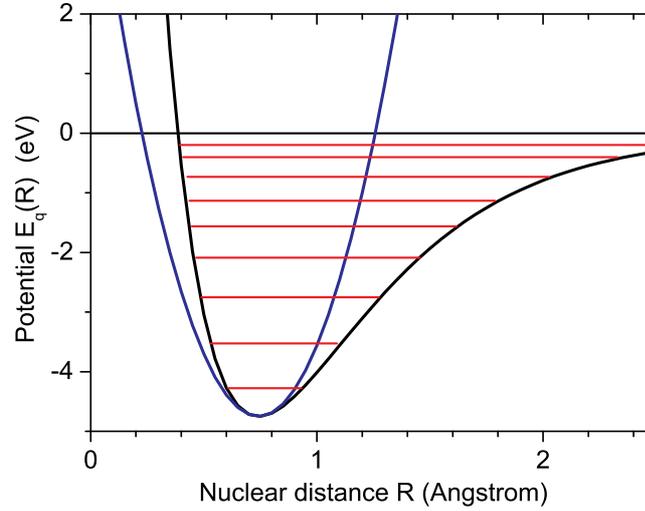
The approximation of the harmonic oscillator potential is only accurate in the vicinity of the equilibrium internuclear distance  $R_0$ . Using this potential we immediately find the eigenfunctions, which is more difficult for real potentials. In the harmonic approximation one can identify  $3N - 5$  normal vibrations for linear molecules and  $3N - 6$  normal vibrations for non-linear molecules.  $N$  denotes the number of atoms (see Fig. 12.4). For a linear molecule like carbon dioxide the potential for small oscillations around the equilibrium position by an asymmetric stretching will be  $V = \frac{1}{2}k(\Delta x_1 - \Delta x_2)^2 + \frac{1}{2}k(\Delta x_2 - \Delta x_3)^2$ , with  $x_i$  are the coordinates for the three atoms along the internuclear axis. Solving the linear equations of the atomic coordinates result in normal coordinates describing normal vibrations. The HO potential underestimates the real potential for smaller  $R$  and is



**Abbildung 12.6.** Normal modes of carbon dioxide and water.

far to strong for large internuclear distances  $R$ . A much better description of the electronic potential for the nuclear vibration is given by (see Fig. 12.4)

$$\begin{aligned}
 E_s(R) &= E_s(\infty) + V_M(R) = E_s(\infty) + D_e [e^{-2\alpha(R-R_0)} - 2e^{-\alpha(R-R_0)}] \quad (12.89) \\
 V_M(R) &= D_e[-1 + \alpha^2(R - R_0)^2 + \dots]. \quad (12.90)
 \end{aligned}$$



**Abbildung 12.7.** Comparison between the harmonic oscillator potential (blue) and the much more realistic Morse potential.

The terms  $R_0$ ,  $D_e$ , and  $\alpha$  are positive constants and are properties of the molecules. Upon expanding  $V_M(R)$  we find by comparison of the coefficients

$$D_e\alpha^2 = \frac{1}{2}k_s; \quad \alpha = \omega_0\sqrt{\frac{\mu}{2D_e}} \quad (12.91)$$

and the energies

$$E_v = \hbar\omega_0 \left[ \left( v + \frac{1}{2} \right) - \beta \left( v + \frac{1}{2} \right)^2 \right] \quad (12.92)$$

$$\beta\omega_0 = \frac{\hbar\omega_0^2}{4D_e} \quad (12.93)$$

$$\beta = \chi_e = \ll 1 \quad (12.94)$$

$$D_0 = D_e - \frac{\hbar\omega_0}{2}. \quad (12.95)$$

The quantity  $\beta\omega_0$  is known as the *anharmonicity constant* and the *dissociation energy* of the molecule (from the vibrational ground state at  $T = 0\text{K}$ ) is given by  $D_0$ . A deficiency of the Morse potential is that it is finite at  $R = 0$ , in contrast to the true interaction  $V(R)$  which is infinite at the origin. Another defect is that the potential falls off exponentially at large  $R$  instead of showing the  $R^{-6}$  fall-off due to van der Waals interaction between two neutral atoms which are far apart. The wave functions of the Morse potential  $\Psi_{j,v}$  are given by

Molecule	$R_0(\text{\AA})$	$D_0$ (eV)	$\bar{\nu}_{0 \rightarrow 1}$ ( $\text{cm}^{-1}$ )	$B/(hc)$ ( $\text{cm}^{-1}$ )	$10^{30}  D $ (Cm)
$H_2$	0.742	4.5	4159.2	60.8	-
$O_2$	1.21	5.15	1556.3	1.45	-
$Cl_2$	1.99	2.51	565.9	0.244	-
$N_2$	1.09	9.83	2330.7	2.01	-
$CO$	1.13	11.13	2143.3	1.93	0.40
$NO$	1.15	6.5	1876	1.70	0.50
$HCl$	1.28	4.46	2885.6	10.6	3.53
$NaCl$	2.36	4.24	378	0.190	28.1

**Tabelle 12.1.** Equilibrium distance  $R_0$ , dissociation energy  $D_0$ , fundamental vibrational frequency  $\bar{\nu}_0 = \nu_0/c$ , rotational constant  $B$  and the magnitude of the electric dipole moment in debyes (1 debye =  $3.36 \times 10^{-30}$  Cm).

$$z = ke^{-\alpha[R-R_0]} \quad (12.96)$$

$$k = \sqrt{\frac{8\mu D_e}{\alpha^2 \hbar^2}} \quad (12.97)$$

$$A_v = \sqrt{v!(k-2v-1)\Gamma(k-v)} \quad (12.98)$$

$$\Psi_v = \sqrt{\alpha} A_v e^{-z/2} \sum_{s=0}^v \frac{(-1)^s z^{\frac{k-2s-1}{2}}}{s!(v-s)!\Gamma(k-v-s)} \quad (12.99)$$

$$v_{Max} = \frac{1}{2\beta} - \frac{1}{2}. \quad (12.100)$$

$$1 \text{ eV} = 8065.48 \text{ cm}^{-1} \quad (12.101)$$

$$= 1.60219 \times 10^{-19} \text{ J} \quad (12.102)$$

$$1 \text{ cm}^{-1} = 1.98648 \times 10^{-23} \text{ J} \quad (12.103)$$

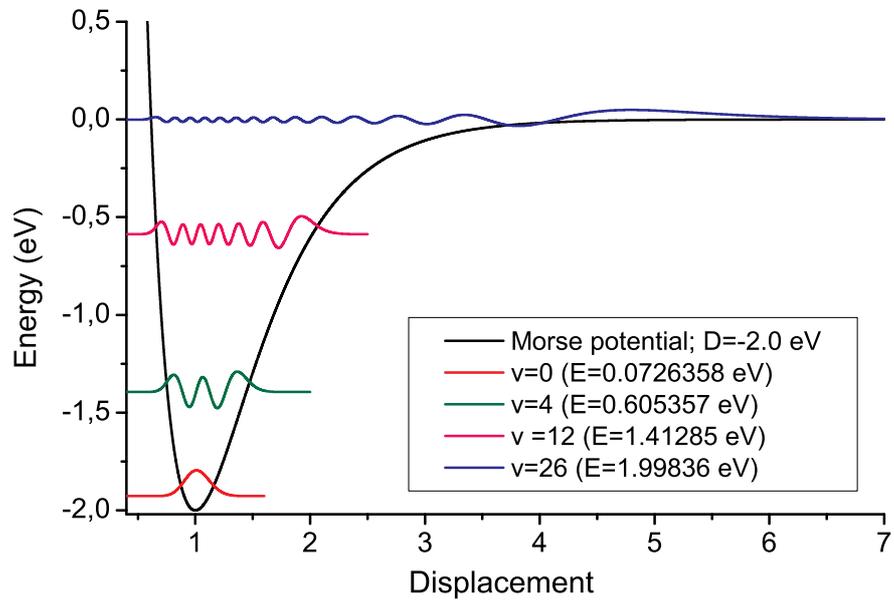


Abbildung 12.8. Morse Potential with some selected eigenfunctions of the Morse potential.

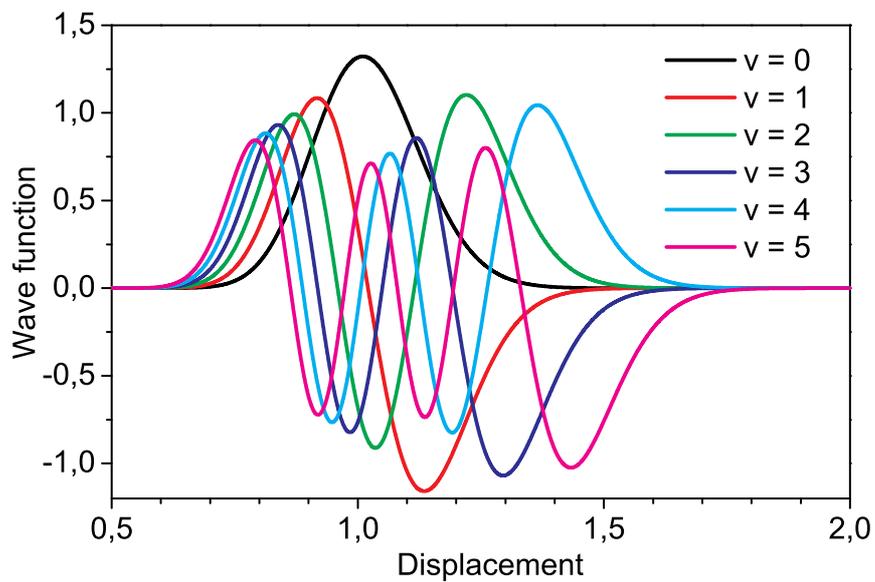
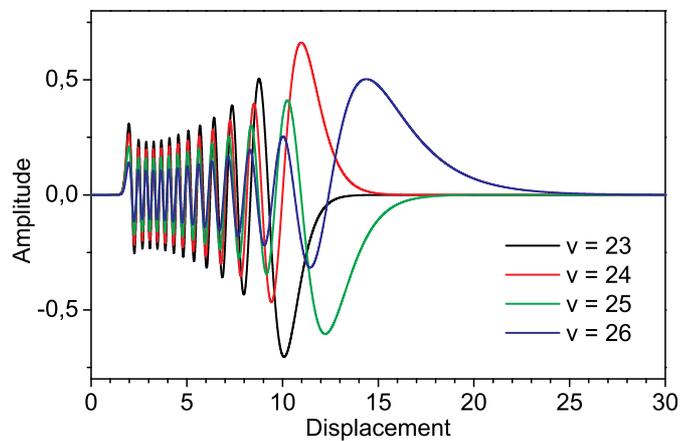
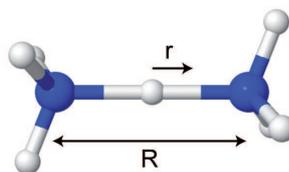
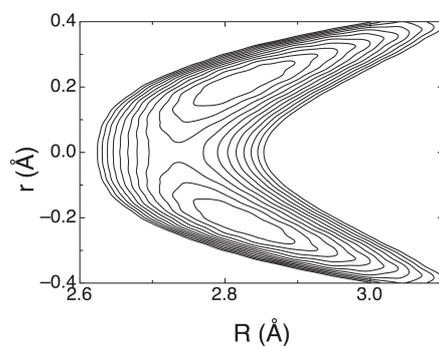


Abbildung 12.9. Asymmetric shift of the probability of the eigenfunctions of the Morse potential to larger nuclear distances (displacement) upon going from  $v = 0$  to  $v = 5$ .



**Abbildung 12.10.** Enhancement of the wave function amplitude at larger displacement for high vibrational excitations near the dissociation limit.



**Abbildung 12.11.** Explicitly calculated dependence of the N-H stretching vibration of a  $NH_3NH_4^+$  complex with the hydrogen bonding stretching.

### 12.4.1 Centrifugal distortion or rotation-vibration coupling

The rotational energy  $E_r$  was approximated by the simple 'rigid rotator' expression with a fixed internuclear distance at the equilibrium distance  $R_0$  leading to a decoupling of vibrational and rotational motions. Without this approximation we get a refined equation

$$0 = \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_{eff}(R) - E_{svK} \right] \mathfrak{F}_{svK}(R) \quad (12.104)$$

$$V_{eff}(R) = V_M(R) + \frac{\hbar^2}{2\mu} \frac{K(K+1)}{R^2}, \quad K = \Lambda, \Lambda + 1, \dots \quad (12.105)$$

$$V_{eff}(R) = V_0 + \frac{1}{2} \bar{k}_s (R - R_1)^2 + c_1 (R - R_1)^3 + c_2 (R - R_1)^4 \quad (12.106)$$

In equation (12.106) we expanded  $V_{eff}(R)$  to the fourth order about its minimum  $V_0$  at  $R = R_1$ . Due to the fact that  $R$  is no longer a constant with  $R = R_0$  we find a new equilibrium position at  $R_1$ . The new equilibrium position  $R_1$  coincides only with  $R_0$  if  $K = 0$ . If we use the simple approximation of  $c_1 = c_2 = 0$  and  $\bar{k}_s = k_s$  in equation (??) we find the new equilibrium position to be

$$R_1 \cong R_0 + \frac{\hbar^2}{2\mu} \frac{K(K+1)}{\alpha^2 R_0^3 D_e}. \quad (12.107)$$

The new energy eigenvalues can be calculated by treating the coefficients  $c_1$  and  $c_2$  as perturbations. The energy eigenvalues are given to second order by

$$E_{svK} = -D_e + \hbar\omega_0 \left[ \left( v + \frac{1}{2} \right) - \beta \left( v + \frac{1}{2} \right)^2 \right] + \frac{\hbar^2}{2\mu R_0^2} K(K+1) \\ - \underbrace{a \left( v + \frac{1}{2} \right) K(K+1)}_{\text{rotation-vibration coupling}} - \underbrace{\frac{bK^2(K+1)^2}{2\mu R_0^2}}_{\text{stretching correction to the rigid rotator}} \quad (12.108)$$

$$a = \frac{3\hbar^3 \omega_0}{4\mu \alpha R_0^3 D_e} \left( 1 - \frac{1}{\alpha R_0} \right) \quad (12.109)$$

$$b = \frac{\hbar^4}{4\mu^2 \alpha^2 R_0^6 D_e}, \quad \text{stretching constant.} \quad (12.110)$$

In contrast to molecular vibrations in the condensed phase (liquid, solid phase) excitations of molecular vibrations in the gas phase are coupled to rotational transitions. If we assume excitation from the vibrational levels  $v \rightarrow v'$  and rotational levels  $K \rightarrow K'$  and no rotation-vibration coupling we find the following energy differences:

$$E_2 - E_1 = hc\bar{\nu} \left( v' + \frac{1}{2} \right) + B' K'(K'+1) - hc\bar{\nu} \left( v + \frac{1}{2} \right) - BK(K+1) \quad (12.111)$$

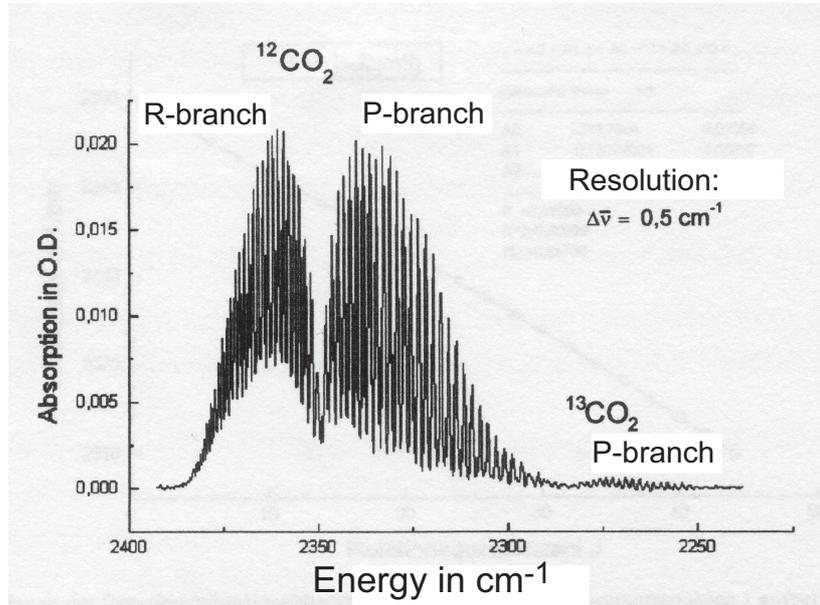
$$\overset{K' \cong K-1}{\Rightarrow} \Delta E = hc\bar{\nu} - K(B'+B) + K^2(B'-B) \quad (12.112)$$

The rotational constants  $B$  and  $B'$  are distinct for the different vibrational quantum numbers  $v$  and  $v'$ . From the measurement of the spectral positions of the absorption peaks one can determine the changes of the rotational constants and thus the averaged internuclear distance for simple molecules. In the case of the linear triatomic  $^{12}\text{CO}_2$  molecule the internuclear distance between the oxygen and carbon atom is given by  $R_{\text{C=O}} = 1.1588 \times 10^{-8}$  cm.

The total wave function  $\psi$  is given by

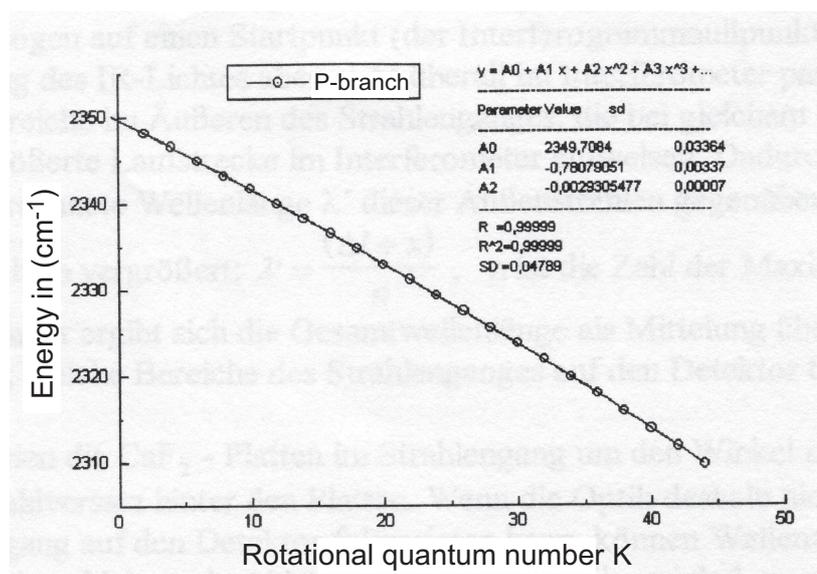
$$\Psi = \psi\chi_N = \Phi_s\chi_{SM_s} \frac{1}{R} \mathfrak{F}_{svK}(R) \bar{Y}_{\Lambda KM_K}(\Theta, \Phi) \chi_N. \quad (12.113)$$

In equation (12.113)  $\Phi_s$  is the spatial part of the electronic wave function,  $\chi_{SM_s}$  is



**Abbildung 12.12.** Rotation-Vibration spectrum of  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$ . There are two rotational transition branches R ( $J \rightarrow J+1$ ) and P ( $J \rightarrow J-1$ ) coupled to the vibrational transition  $v = 0 \rightarrow 1$ . The dip in the middle of the two branches is related to the energy difference  $\Delta\bar{\nu} = \bar{\nu}_1 - \bar{\nu}_0 = 2349 \text{ cm}^{-1}$  of a vibrational transition of  $^{12}\text{CO}_2$ . The analogue energy for  $^{13}\text{CO}_2$  has a value of  $2282 \text{ cm}^{-1}$ .

the spin function of the electrons, and  $\mathfrak{F}_{svK}(R)$  and  $\bar{Y}_{\Lambda KM_K}(\Theta, \Phi)$  are the nuclear vibrational and rotational wave functions, respectively. The function  $\chi_N$  is the nuclear spin function. The function  $\Phi_s$  is even or odd under the transformation  $\vec{R} \rightarrow -\vec{R}$ . For example for  $\Lambda = 0$  the  $\Sigma_g^+$  and  $\Sigma_u^-$  states are even while the  $\Sigma_u^+$  and  $\Sigma_g^-$  states are odd. The function  $\chi_{SM_s}$  is unaffected upon  $\vec{R} \rightarrow -\vec{R}$ . The vibrational wave function  $\mathfrak{F}_{svK}(R)$  depends only on the magnitude  $R$  of the vector  $\vec{R}$  and is unaltered when  $\vec{R} \rightarrow -\vec{R}$ . The rotational wave function  $\bar{Y}_{\Lambda KM_K}(\Theta, \Phi)$



**Abbildung 12.13.** Spectral positions of the rotation-vibration absorption maxima as a function of  $K$ . The solid line is a polynomial fit to second order with coefficients:  $A_0 = 2349.71 \pm 0.04$ ,  $A_1 = -0.781 \pm 0.004$ ,  $A_2 = -0.00293 \pm 0.00007$ .

is either even (for  $K = 0, 2, 4, \dots$ ) or odd (for  $K = 1, 3, 4, \dots$ ) under the transformation  $\vec{R} \rightarrow -\vec{R}$ . The overall symmetrical (S) or antisymmetrical (A) character of the function  $\psi$  is given as follows:

$$\begin{array}{cc}
 & \begin{array}{cccc}
 g^+ & g^- & u^+ & u^-
 \end{array} \\
 \begin{array}{c}
 K \text{ even} \\
 K \text{ odd}
 \end{array} & \begin{array}{cccc}
 S & A & A & S \\
 A & S & S & A
 \end{array}
 \end{array} \quad (12.114)$$

The nuclear spin function  $\chi_N$  can be symmetric or antisymmetric with respect to the interchange of the nuclei. For example  $^{16}\text{O}_2$ :

- $^{16}\text{O}_2$  has two spinless nuclei;  $I_N = 0$
- $\chi_N$  is a constant and trivially symmetric in the interchange of the nuclei.
- The total wave function  $\Psi$  has to be symmetric (Boson)
- $\Psi, \chi_N, \psi$  have to be symmetric
- If the electronic state is even ( $g^+, u^-$ ), only even  $K$  are allowed and if the electronic state is odd ( $g^-, u^+$ ), only odd  $K$  are allowed
- The electronic ground state of  $\text{O}_2$  is a  $^3\Sigma_g^-$  state
- Only odd rotational quantum numbers  $K$  are allowed. The ground state of the  $^{16}\text{O}_2$  molecule is given by  $K = 1$ .

The same effect is observed in  $CO_2$  which has a ground state  $^1\Sigma_g^+$  and therefore only even rotational quantum numbers  $K$  are allowed ( $\Delta K = \pm 2$ ). This results in reduced numbers of vibration-rotation transitions. If the symmetry is reduced  $^{16}O = C = ^{18}O$  all vibration-rotation transitions can be observed.

The degeneracy of rotational levels is  $(2K + 1)$  (for  $\Sigma$  states), and the relative population ratios are given by

$$\frac{N_K}{N_0} = \frac{g_K}{g_0} e^{-(E_K - E_0)/(k_B T)} = (2K + 1) e^{-BhcK(K+1)/(k_B T)}. \quad (12.115)$$

Since the rotational energies are small compared to the room temperature

$$k_B T_{T=293K} \approx \frac{1}{40} \text{ eV} \approx 204 \text{ cm}^{-1} \quad (12.116)$$

we can expect population of higher rotational levels at room temperature. The rotational level with the highest population  $K_{max}$  is given by

$$K_{max} = \sqrt{\frac{k_B T}{2hcB}} - \frac{1}{2}. \quad (12.117)$$

That the population varies for different rotational quantum numbers  $K$  is visible in Fig. 12.4.1. In this figure the rovibronic absorption spectrum of the triatomic linear molecule  $^{12}CO_2$  is presented. The vibration that is excited is the asymmetric stretching vibration which is infrared active and Raman inactive. Changing the vibrational quantum number  $v_{as}$  of the asymmetric stretching vibration is always connected with changing the rotational quantum number  $K$ . This is due to the fact that changing the average bond length by going to higher or lower vibrational quantum numbers changes the moment of inertia and therefore the rotational quantum number ( $\Delta K \pm 1$ ). Excitation of the bending vibrations of  $^{12}CO_2$  changes only the rotational quantum number for rotations with rotation axis perpendicular to the bending vibration plane ( $\Delta K \pm 1$ ). Rotations parallel to the bending vibration plane do not change  $K$  and lead to the so called  $Q$ -branch with  $\Delta K = 0$ .

In general the expectation value of the transition dipole moment (dipole appro-

ximation) is given by

$$\begin{aligned} \langle \vec{\mu}_T \rangle &= \iint \bar{Y}_{\Lambda K' M_{K'}}^* \Phi_f^*(\vec{R}, \vec{r}') \mathfrak{F}_{fv'K'}(R) \left[ -e \sum_{i=1}^N \vec{r}_i + e \sum_{j=1}^M Z_j \vec{R}_j \right] \\ &\times \bar{Y}_{\Lambda K M_K} \Phi_i(\vec{R}, \vec{r}') \mathfrak{F}_{ivK}(R) d \cos \Theta d\Phi \end{aligned} \quad (12.118)$$

$$= \iint \bar{Y}_{\Lambda K' M_{K'}}^* \vec{\mu}_{i \rightarrow f, v \rightarrow v'} \bar{Y}_{\Lambda K M_K} d \cos \Theta d\Phi \quad (12.119)$$

$$\stackrel{i=f, v=v'}{=} \iint \bar{Y}_{\Lambda K' M_{K'}}^* \vec{\mu}_{perm} \bar{Y}_{\Lambda K M_K} d \cos \Theta d\Phi. \quad (12.120)$$

In equation 12.120 the term  $\vec{\mu}_{perm}$  is the permanent dipole moment of a molecule. *HCl* has a permanent dipole moment in contrast to homonuclear diatomic molecules such as *H<sub>2</sub>* or *N<sub>2</sub>*. Molecules with zero permanent dipole moment have no infrared active rotational transitions. For molecules with non vanishing permanent dipole moment the selection rules for pure rotational transitions are in analogy to the electronically transitions of atoms (dipole approximation):

$$\Delta K = \pm 1 \quad (12.121)$$

$$\Delta M_K = 0, \pm 1 \quad (12.122)$$

### 12.4.2 Electronic spin and Hund's cases

The most important magnetic interaction in molecules is the coupling of electronic spin  $\vec{S}$  and the electronic orbital angular momentum  $\vec{L}$ . If the nuclear spins are ignored, the total angular momentum operator  $\vec{J}$  for a diatomic molecule is given by

$$\vec{J} = \vec{L} + \vec{N} + \vec{S} = \vec{K} + \vec{S} \quad (12.123)$$

where  $\vec{N}$  is in a direction orthogonal to the internuclear line. In the case of  $|\Delta E| \gg |A| \gg B$  that is the electrostatic interaction is much larger than the spin-orbit interaction which is in turn larger than the rotational energy. An example is given by the *A<sup>2</sup>Π* term of *CO<sup>+</sup>*. In the electronic ground state *X<sup>2</sup>Σ<sup>+</sup>* it is found that  $|\Delta E| = 20733 \text{ cm}^{-1}$ , the spin-orbit constant is  $A = -117 \text{ cm}^{-1}$  and the rotational constant is  $B = 1.6 \text{ cm}^{-1}$ . The electrostatic interaction has axial symmetry and this causes  $\vec{L}$  to precess about the internuclear axis, and therefore  $L_{\bar{z}} = \pm \Lambda \hbar$  and  $\langle L_{\bar{x}} \rangle = \langle L_{\bar{y}} \rangle = 0$ . Since in this case the rotation of the molecule is slow, and the spin-orbit interaction is large compared with the rotational energy, the spin angular momentum  $\vec{S}$  will also tend to precess about the internuclear axis. Thus, simultaneous eigenfunctions of  $\vec{S}^2$  and  $S_{\bar{z}}$  can be found with eigenvalues of  $S(S+1)\hbar^2$  and  $\Sigma \hbar$ , respectively. Since  $N_{\bar{z}} = 0$  it is

$$J_{\bar{z}} = L_{\bar{z}} + S_{\bar{z}} \quad (12.124)$$

$$\Omega = \pm \Lambda + \Sigma \quad (12.125)$$

where  $\Omega\hbar$  are the eigenvalues of  $J_z$  and the quantum number  $\Sigma$  can take the  $(2S + 1)$  values  $-S, -S + 1, \dots, S$ . The quantum numbers  $\Lambda$  and  $\Sigma$  are the projections of  $\vec{L}$  and  $\vec{S}$  on the internuclear line. The additional L-S coupling leads to an energy given by

$$\Delta E = A\Lambda\Sigma. \quad (12.126)$$

For a given number  $\Lambda$  the energy levels split into  $(2S + 1)$  multiplet components, which are equally spaced in energy by the factor  $A$ . For example if  $\Lambda = 1$  and  $S = 1$ , we have  $\Omega = 0, 1, 2$  and  ${}^3\Pi_0, {}^3\Pi_1$ , and  ${}^3\Pi_2$ . Since  $\vec{N}^2$  is now given by

$$\vec{N} = \vec{J} - \Omega\hbar\vec{R} = \vec{J} - \vec{\Omega} \quad (12.127)$$

and we can rewrite the rotational energy by

$$E'_r = B[J(J + 1) - \underbrace{\Omega^2}_{\text{depends on the electronic state}}] \quad (12.128)$$

$$E_r = B[J(J + 1)], \quad J = \Omega, \Omega + 1, \dots \quad (12.129)$$

Since  $|\vec{J}| \geq J_z$  and  $J \geq \Omega$  this can be used to determine an unknown quantum number  $\Omega$  by missing spectral lines with lower values of  $J$ .

## 12.5 LCAO: Linear combination of atomic orbitals

To determine the orbitals of molecules we start with linear combinations of single electron atomic orbitals. This approach simplifies wave function optimization with variational methods (Rayleigh-Ritz). We define a test function  $\psi_{test}$

$$\psi_{test} \equiv \psi = \sum_j c_j \varphi_j \quad (12.130)$$

constructed by a complete basis set of single electron atomic orbitals  $\{\varphi_i\}$ . We have to minimize

$$\epsilon = \frac{\int \psi^* H \psi dV}{\int \psi^* \psi dV} = \frac{\int \sum_i c_i^* \varphi_i^* H \sum_j c_j \varphi_j dV}{\int \sum_i c_i^* \varphi_i^* \sum_j c_j \varphi_j dV} \quad (12.131)$$

$$= \frac{\sum_i \sum_j c_i^* c_j H_{ij}}{\sum_i \sum_j c_i^* c_j S_{ij}} \quad (12.132)$$

with the following integrals

$$H_{ij} = \int \varphi_i^* H \varphi_j dV \quad (12.133)$$

$$S_{ij} = \int \varphi_i^* \varphi_j dV, \quad \text{overlap integrals for } i \neq j. \quad (12.134)$$

To minimize (or maximize)  $\epsilon$  we have to fulfil the equations

$$\forall i \quad \frac{\partial \epsilon}{\partial c_i} = \frac{\partial \epsilon}{\partial c_i^*} = 0 \quad (12.135)$$

Using equation (??) together with equation (12.132) we have

$$\sum_i \sum_j c_i^* c_j H_{ij} = \epsilon \sum_i \sum_j c_i^* c_j S_{ij} \quad (12.136)$$

$$\frac{\partial}{\partial c_i^*}, \frac{\partial \epsilon}{\partial c_i^*} = 0 \Rightarrow \sum_j H_{ij} c_j = \epsilon \sum_j S_{ij} c_j \quad (12.137)$$

$$\sum_j (H_{ij} - \epsilon S_{ij}) c_j = 0 \quad (12.138)$$

$$\det |H_{ij} - \epsilon S_{ij}| = 0 \quad (12.139)$$

Equation (12.138) is a homogeneous system of linear equations (for all  $i$ 's). We have to solve it in a non-trivial way to determine the coefficients  $\{c_j\}$  and build the optimized eigenfunction of the molecular orbital. Thus, the determinant in equation (12.139) has to vanish. As a result we obtain solutions of  $\epsilon_\alpha$ , which have to be inserted into equation (12.138) to determine the coefficients  $\{c_j^\alpha\}$ .

In the case of the  $H_2^+$  **molecule** we choose the normalized 1s atomic orbitals (AO)  $\varphi_1$  and  $\varphi_2$  which are centered around the protons A and B (see Fig. 12.5).

$$\varphi_1 = \varphi_{1s}(A) = \varphi_1(r_A) = \sqrt{\frac{1}{a_0\pi}} e^{-r_A/a_0} \quad (12.140)$$

$$\varphi_2 = \varphi_{1s}(B) = \varphi_2(r_B) = \sqrt{\frac{1}{a_0\pi}} e^{-r_B/a_0} \quad (12.141)$$

$$r_A = |\vec{r} - \vec{R}_A|; \quad r_B = |\vec{r} - \vec{R}_B| \quad (12.142)$$

$$\vec{r}_A = \vec{r} - \vec{R}/2; \quad \vec{r}_B = \vec{r} + \vec{R}/2 \quad (12.143)$$

Since  $\varphi_1$  and  $\varphi_2$  are normalized we have  $S_{11} = S_{22} = 1$ , we find the overlap integral  $S(R)$  to be

$$S(R) = S_{12}(R) = \int \varphi_1^*(r_A) \varphi_2(r_B) d\vec{r} = \left(1 + \frac{R}{a_0} + \frac{1}{3} \left(\frac{R}{a_0}\right)^2\right) e^{-R/a_0} \quad (12.144)$$

The overlap integral is a two center integral and can be solved using confocal elliptical coordinates. The matrix elements  $H_{ij}$  are determined by using the fact

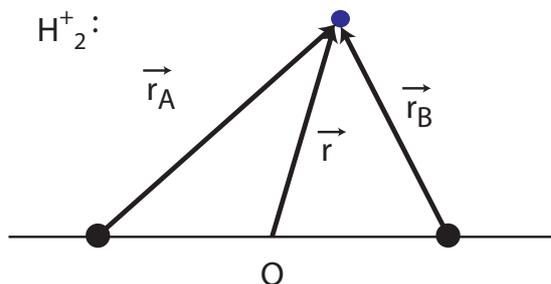


Abbildung 12.14. Coordinate system for the molecular ion  $H_2^+$ .

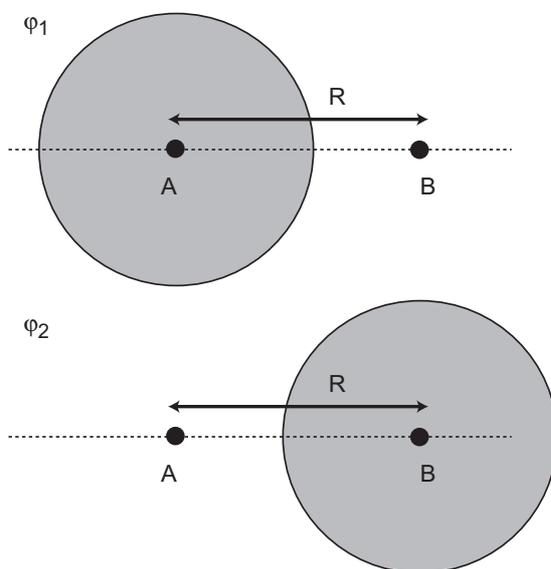


Abbildung 12.15. .

that  $\varphi_1$  and  $\varphi_2$  are eigenfunctions of the hydrogen atoms A and B.

$$H_{el} = H_A + H_B + \frac{e^2}{4\pi\epsilon_0 R} \quad (12.145)$$

$$= -\frac{\hbar^2}{2m} \nabla_{\vec{r}_A}^2 - \frac{\hbar^2}{2m} \nabla_{\vec{r}_B}^2 - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{R}_A|} - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{R}_B|} + \frac{e^2}{4\pi\epsilon_0 R} \quad (12.146)$$

We can directly evaluate the matrix elements

$$H_{11} = \int \varphi_1^*(r_A) H_{el} \varphi_1(r_A) d\vec{r} \quad (12.147)$$

$$\begin{aligned} &= \int \varphi_1^*(r_A) H_A \varphi_1(r_A) d\vec{r} - \int \varphi_1^*(r_A) \frac{e^2}{4\pi\epsilon_0 r_B} \varphi_1(r_A) d\vec{r} + \frac{e^2}{4\pi\epsilon_0 R} \\ &= E_{1s} + \frac{e^2}{4\pi\epsilon_0 R} - \underbrace{\int \varphi_1^*(r_A) \frac{e^2}{4\pi\epsilon_0 r_B} \varphi_1(r_A) d\vec{r}}_{\text{Coulomb integral } J} \end{aligned} \quad (12.148)$$

$$= E_{1s} + \frac{e^2}{4\pi\epsilon_0 R} - J. \quad (12.149)$$

The integral  $J$  in equation (12.149) describes the electrostatic attraction of  $-e|\varphi_1|^2$  from the nucleus  $A$  on the nucleic charge of the atom  $B$ . The Coulomb integral is positive ( $(\int e^2|\varphi_1|^2 d\vec{r})$ ). Since the system is symmetric under exchange of nuclei  $A$  and  $B$  the matrix elements  $H_{11} = H_{22}$  are identical. The overlap integrals are given by

$$H_{12} = \int \varphi_1^*(r_A) H_{el} \varphi_2(r_B) d\vec{r} \quad (12.150)$$

$$= \int \varphi_1^*(r_A) \left[ -\frac{e^2}{4\pi\epsilon_0 r_A} + \frac{e^2}{4\pi\epsilon_0 R} + \underbrace{H_B}_{E_{1s}\varphi_2(r_B)} \right] \varphi_2(r_B) d\vec{r} \quad (12.151)$$

$$= \left( E_{1s} + \frac{e^2}{4\pi\epsilon_0 R} \right) S - \underbrace{\int \varphi_1^*(r_A) \frac{e^2}{4\pi\epsilon_0 r_A} \varphi_2(r_B) d\vec{r}}_{\text{overlap integral } K} \quad (12.152)$$

$$= \left( E_{1s} + \frac{e^2}{4\pi\epsilon_0 R} \right) S(R) - K. \quad (12.153)$$

The overlap integral  $K$  describes the electronic overlap probability density  $-e\varphi_1^*(r_A)\varphi_2(r_B)$  which interacts with the nucleic charge of atom  $A$ . Due to symmetry reasons it has to be  $H_{12} = H_{21}$ . The term  $K$  in equation (12.153) is without classical interpretation, but represents the term that is responsible for the binding of different atoms. Now we have to solve the determinant:

$$\begin{vmatrix} H_{11} - \epsilon & H_{12} - \epsilon S \\ H_{21} - \epsilon S & H_{22} - \epsilon \end{vmatrix} = 0. \quad (12.154)$$

This leads to a quadratic equation with solutions for the energies

$$\epsilon_+ = \frac{H_{11} + H_{12}}{1 + S} \quad (12.155)$$

$$\epsilon_- = \frac{H_{11} - H_{12}}{1 - S}. \quad (12.156)$$

Inserting the solutions into the system of equations we have the coefficients

$$c_1^+ = c_2^+ = \frac{1}{\sqrt{2(1+S(R))}} \quad (12.157)$$

$$c_1^- = -c_2^- = \frac{1}{\sqrt{2(1-S(R))}} \quad (12.158)$$

and can build the eigenfunctions  $\psi_+$  and  $\psi_-$

$$\psi_+ = \frac{1}{\sqrt{2(1+S(R))}} [\varphi_{1s}(A) + \varphi_{1s}(B)] \quad (12.159)$$

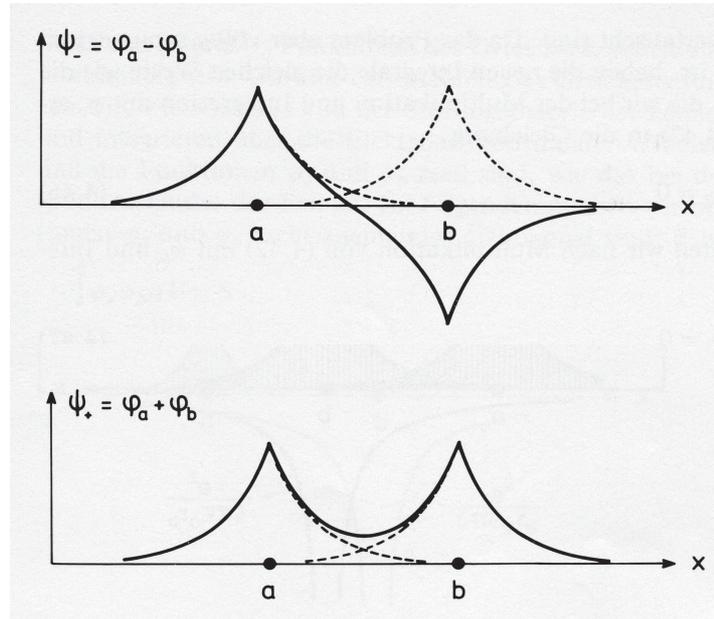
$$\psi_- = \frac{1}{\sqrt{2(1-S(R))}} [\varphi_{1s}(A) - \varphi_{1s}(B)] \quad (12.160)$$

$$(12.161)$$

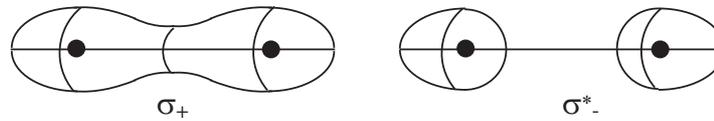
The eigenfunctions  $\psi_+$  and  $\psi_-$  given in equations (12.159) and (12.160), respectively, are *gerade* and *ungerade* functions under the inversion operation  $\vec{r} \rightarrow -\vec{r}$  and represent the molecular orbitals for  $H_2^+$ . The wave function  $\psi_+$  is the binding wave function and exhibit an increased electron density between the two nuclei  $A$  and  $B$  (see Fig. 12.5), whereas the wave function  $\psi_-$  exhibits a knot at the center of inversion symmetry and a strongly reduced electron density between the two nuclei. The electron density is given by

$$e|\psi_{\pm}|^2 = \frac{-e}{2(1 \pm S)} [\varphi_{1s}^*(A) \pm \varphi_{1s}^*(B)] [\varphi_{1s}(A) \pm \varphi_{1s}(B)] \quad (12.162)$$

$$= \frac{-e}{2(1 \pm S)} [|\varphi_{1s}(A)|^2 + |\varphi_{1s}(B)|^2] \pm \frac{[\varphi_{1s}^*(A)\varphi_{1s}(B) + \varphi_{1s}^*(B)\varphi_{1s}(A)]}{2(1 \pm S)} \quad (12.163)$$



**Abbildung 12.16.** Orbital wave functions of the hydrogen ion. The wave functions  $\psi_+$  and  $\psi_-$  represent the binding and antibinding orbitals of the hydrogen ion. The binding orbital exhibits increased electron density between the nuclei, while the antibinding orbital shows reduced electron density between the nuclei.



**Abbildung 12.17.** The binding and antibinding molecular orbitals of the hydrogen ion has axial symmetry.

The two energies of the molecular orbitals are given by

$$\epsilon_+(R) = \frac{H_{11} + H_{12}}{1 + S(R)} \quad (12.164)$$

$$= \frac{E_{1s} + \frac{e^2}{4\pi\epsilon_0 R} - J(R) + \left(E_{1s} + \frac{e^2}{4\pi\epsilon_0 R}\right) S(R) - K(R)}{1 + S(R)} \quad (12.165)$$

$$= E_{1s} + \frac{e^2}{4\pi\epsilon_0 R} - \frac{J(R) + K(R)}{1 + S(R)} \quad (12.166)$$

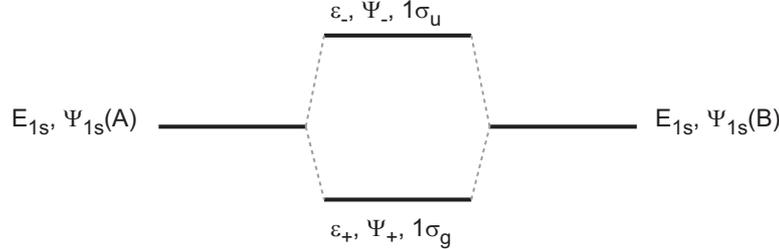
$$\epsilon_-(R) = \frac{H_{11} - H_{12}}{1 - S(R)} = E_{1s} + \frac{e^2}{4\pi\epsilon_0 R} - \frac{J(R) - K(R)}{1 - S(R)} \quad (12.167)$$

$$S(R) = \left\{ 1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2} \right\} e^{-R/a_0} \quad (12.168)$$

$$J(R) = \frac{e^2}{4\pi\epsilon_0 R} \left\{ 1 - \left( 1 + \frac{R}{a_0} \right) e^{-2R/a_0} \right\} \quad (12.169)$$

$$K(R) = \frac{e^2}{4\pi\epsilon_0 a_0} \left\{ 1 + \frac{R}{a_0} \right\} e^{-R/a_0}. \quad (12.170)$$

The integrals  $J(R)$ ,  $K(R)$ , and  $S(R)$  were solved by the use of confocal elliptical coordinates. The molecular ground state is connected with the wave function  $\psi_+$  (binding state). To compare these energies with the dissociation energy  $D_e$  one



**Abbildung 12.18.** Energy splitting of the molecular orbital states.

has to calculate the full dependence of  $\epsilon_+(R)$  of the internuclear distance  $R$ . The equilibrium distance  $R_0$  is calculated to be  $R_0 = 1.32 \text{ \AA}$  and the dissociation energy is calculated to be  $D_e = E_{1s} - \epsilon_+ = 1.77 \text{ eV}$ . The experimental values are  $R_0 = 1.06 \text{ \AA}$  and  $D_e = 2.79 \text{ eV}$ . The discrepancy is due to the fact that for  $R = 0$  the charge at the origin is 2, comparable to the helium atom. But in the case of the helium atom we saw, that the effective charge is less than 2. The next step is to optimize the molecular orbitals with varied nuclear charge ( $e^{-Z^*r/a_0}$ ). Up to now we considered only homonuclear diatomic molecules where the covalent bonding is strong. In general  $H_{11} \neq H_{22}$  and if we set  $S(R) = 0$  we find for heteronuclear diatomic molecules:

$$0 = (H_{11} - \epsilon)(H_{22} - \epsilon) - H_{12}H_{21} \quad (12.171)$$

$$H_{21} = H_{12}^*; |H_{12}|^2 = A^2 > 0 \quad (12.172)$$

$$0 = (H_{11} - \epsilon)(H_{22} - \epsilon) - |H_{12}|^2 \quad (12.173)$$

$$\epsilon_{\pm} = \frac{H_{11} + H_{22}}{2} \pm \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + A^2} \quad (12.174)$$

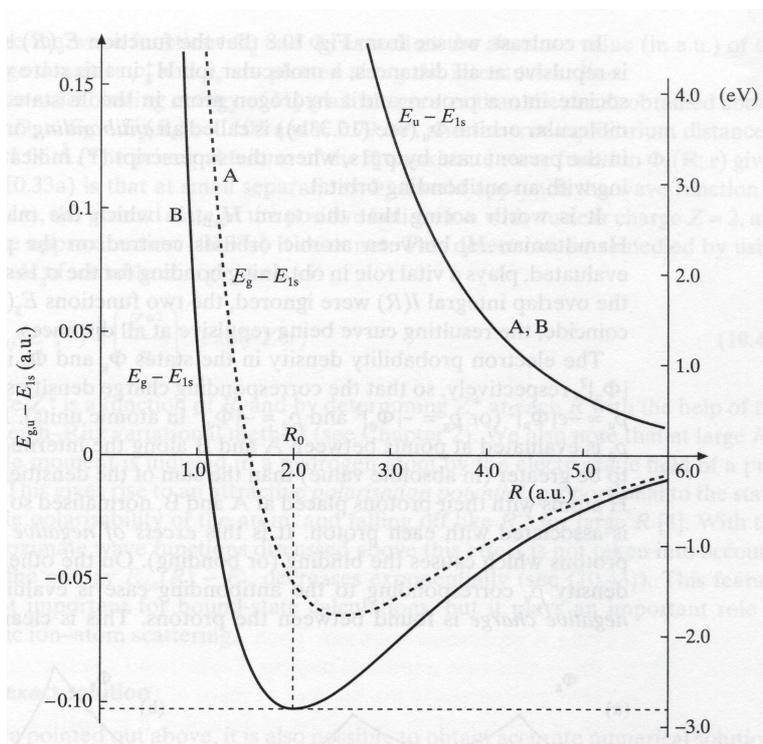
$$= \frac{H_{11} + H_{22}}{2} \pm \frac{H_{11} - H_{22}}{2} \sqrt{1 + \frac{4A^2}{(H_{11} - H_{22})^2}} \quad (12.175)$$

For many heteronuclear molecules it is  $|H_{11} - H_{22}| \gg A$  so that we can expand the square root and get

$$\epsilon_- = H_{11} + \frac{A^2}{H_{11} - H_{22}} \quad (12.176)$$

$$\epsilon_+ = H_{22} - \frac{A^2}{H_{11} - H_{22}} \quad (12.177)$$

The lowering of the lowest energy level is now given by the term



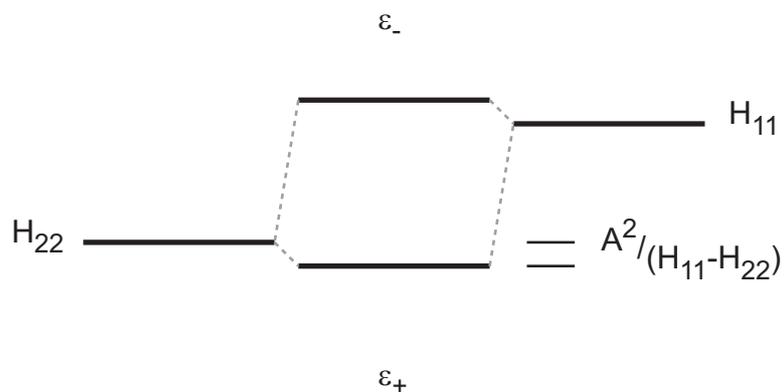
**Abbildung 12.19.** The lowest electronic energy curves of  $H_2^+$ . The curves labeled A show the calculated wave functions using LCAO, while the curves labeled B show the exact solutions.

$$\frac{A^2}{H_{11} - H_{22}} \propto H_{12} \left( \frac{H_{12}^*}{H_{11} - H_{22}} \right) \ll H_{12} \quad (12.178)$$

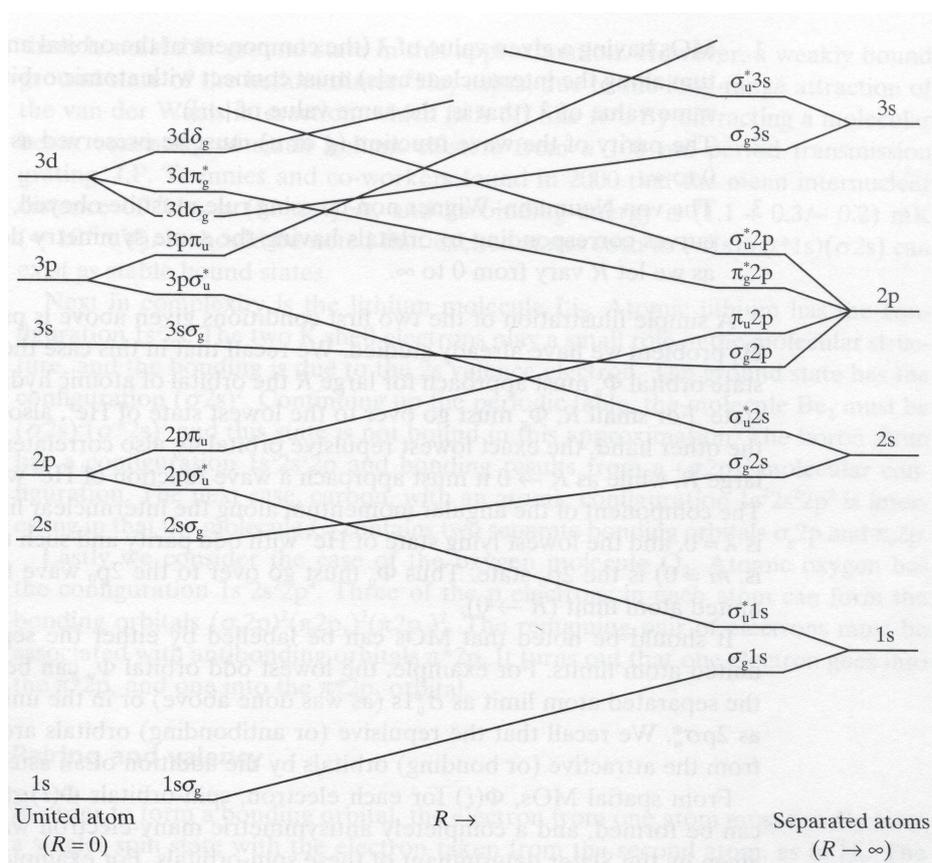
$$\left( \frac{c_1}{c_2} \right)_- \propto \frac{H_{12}}{\epsilon_- - H_{11}} = \frac{H_{11} - H_{22}}{H_{12}} \gg 1 \quad (12.179)$$

$$\left( \frac{c_1}{c_2} \right)_+ \propto \frac{H_{12}}{\epsilon_+ - H_{11}} \sim \frac{H_{12}}{H_{22} - H_{11}} \ll 1 \quad (12.180)$$

In the case of heteronuclear bindings the binding is strong if the interacting atomic orbitals are similar and  $H_{11} \approx H_{22}$ . If this is not the case, the ratios of coefficients for  $\psi_+$  and  $\psi_-$  is very different, meaning the molecular orbitals are poorly mixed ( $\psi_+ \sim \varphi_1$  and  $\psi_- \sim \varphi_2$ ).



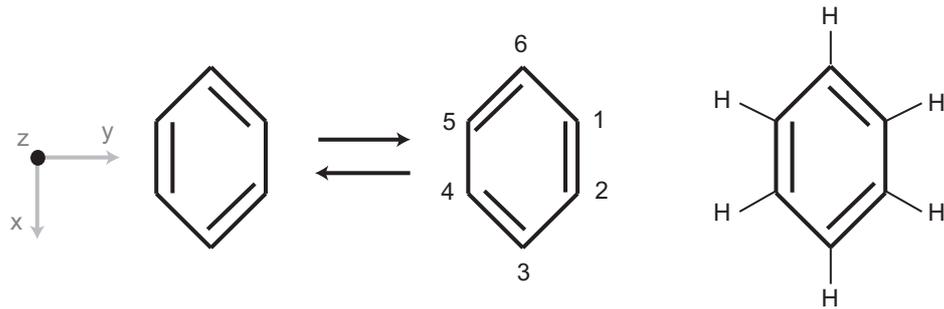
**Abbildung 12.20.** Energy splitting of the molecular orbital states of heteronuclear diatomic molecules.



**Abbildung 12.21.** Correlation diagram between united atom and separated atom states for homonuclear diatomic molecules. The energy spacings are arbitrary and the actual energies vary from molecule to molecule. The diagonal lines sketch only trends and for a specific distance  $R$  the actual energies have to be calculated.

## 12.6 Benzene: Application of the LCAO-MO method

In molecules with more than two ( $H_2^+$ ) identical atoms the symmetry is higher. In the case of benzene  $C_6H_6$  we find six identical atoms with six single bonds ( $\sigma$ ) between the carbon atoms  $C$  and the hydrogen atoms  $H$  and six bonds between the carbon atoms. This is due to  $sp^2$  hybridization. One  $p_z$  atomic orbital per carbon atom remains and is responsible for double bonds between the carbons. The molecule does not change under rotation about the  $z$ -axis (see Fig. 12.6) by  $60^\circ$ . Thus it has  $C_6$  symmetry. Due to the fact that all atoms are identical, the



**Abbildung 12.22.** 'Resonance structure' of benzene. The 6 carbon atoms are equivalent and the molecule has  $C_6$  symmetry. The  $z$ -axis is directed perpendicular out of the paper plane.

picture of a 'resonance structure' as presented in Fig. 12.6 has to be wrong. The molecular orbital wave functions are given by

$$\psi = \sum_i c_i \phi_i \quad (12.181)$$

with equal coefficients  $|c_i|$ . The probability to find an electron at the atom  $i$  does not depend on  $i$  and the electron is called delocalized. There are six electrons from the six  $p_z$  orbitals, which are delocalized. To determine the coefficients we use the symmetry property  $C_6$  of the system. Assume a  $p_z$  atomic orbital  $\phi(\vec{r})$  centered at the origin of the molecule. The atomic orbital centered at the atom  $i$  at  $\vec{R}_j$  is given by

$$\phi_j(\vec{r}) = \phi(\vec{r} - \vec{R}_j). \quad (12.182)$$

If  $H$  is the Hamilton operator describing the delocalized electrons, the operator commutes with  $R_{60}$ :

$$[H, R_{60}] = 0 \quad (12.183)$$

and both operators share the same eigenfunctions. The eigenvalues  $\lambda$  are

$$R_{60}\psi(\vec{r}) \equiv \psi(R_{60}\vec{r}) = \lambda\psi(\vec{r}) \quad (12.184)$$

$$\lambda^6 = 1 \quad (12.185)$$

$$\lambda_k = e^{i\frac{2\pi}{6}k}, \quad k = 0, \pm 1, \pm 2. \quad (12.186)$$

If we let  $R_{60}$  operate on  $\psi$  we find

$$\begin{aligned} R_{60}\psi(\vec{r}) &= R_{60} \sum_j c_j \phi_j(\vec{r} - \vec{R}_j) = \sum_j c_j R_{60} \phi_j(\vec{r} - \vec{R}_j) \\ &= \sum_j c_j \phi_{j-1}(\vec{r} - \vec{R}_{j-1}) \end{aligned} \quad (12.187)$$

$$= \lambda \psi \quad (12.188)$$

$$= e^{i\frac{2\pi}{6}k} \sum_j c_j \phi_j(\vec{r} - \vec{R}_j) \quad (12.189)$$

$$\Rightarrow \sum_j c_j \phi_{j-1} = e^{i\frac{2\pi}{6}k} \sum_j c_j \phi_j \quad (12.190)$$

$$\stackrel{j-1=m}{\Rightarrow} \sum_m c_{m+1} \phi_m = e^{i\frac{2\pi}{6}k} \sum_m c_m \phi_m, \quad \phi_m \text{ linear independent} \quad (12.191)$$

$$c_{m+1} = e^{i\frac{2\pi}{6}k} c_m \quad (12.192)$$

$$c_{m+6} = c_m. \quad (12.193)$$

The solution is

$$c_j^{(k)} = e^{i\frac{2\pi}{6}kj} c_0^{(k)} \quad (12.194)$$

$$|c_j^{(k)}| = |c_0^{(k)}|. \quad (12.195)$$

The probability to find an electron in the status  $k$  at the  $j^{\text{th}}$  carbon atom is proportional to  $\propto |c_j^{(k)}|^2$ . Since this probability is the same for every  $j$  the wave function has to be symmetric in  $j$  and is given by

$$\psi_k = \sum_{j=1}^6 c_j^{(k)} \phi_j(\vec{r} - \vec{R}_j) = c_0^{(k)} \sum_{j=1}^6 e^{i\frac{2\pi}{6}kj} \phi_j(\vec{r} - \vec{R}_j). \quad (12.196)$$

The coefficient  $c_0^{(k)}$  in equation 12.196 is the normalization coefficient (for example  $1/\sqrt{6}$ ) and we can now solve the system of equations

$$(H_{ij} - \epsilon_k S_{ij}) c_j^{(k)} = 0 \quad (12.197)$$

and calculate the eigenenergies. We can set

$$H_{i,i} = \alpha \quad (12.198)$$

which is independent of  $i$  and set

$$H_{i,i\pm 1} = \beta \quad (12.199)$$

which is the resonance integral and does not depend on  $i$  and is cyclic  $i-1 = i+5$ .

In the Hückel method the following approximations are made:

- Only the nearest neighbor interactions are not zero

$$H_{ij} \neq 0, \quad j = i \pm 1$$

- Overlap with the neighboring atoms are neglected

$$S_{ij} = \delta_{ij}$$

Inserting the coefficients into equations 12.197 we find with the Hückel method

$$0 = \underbrace{(H_{11} - \epsilon_k S_{11})}_{\alpha} c_1^{(k)} + \underbrace{(H_{12} - \epsilon_k S_{12})}_{\beta} c_2^{(k)} + \underbrace{\dots}_{=0} + \underbrace{(H_{16} - \epsilon_k S_{16})}_{\beta} c_6^{(k)} \quad (12.200)$$

$$0 = (\alpha - \epsilon_k) e^{i\frac{2\pi}{6}k} + \beta e^{i\frac{2\pi}{6}k^2} + \beta e^{i\frac{2\pi}{6}k6} \quad (12.201)$$

$$0 = (\alpha - \epsilon_k) + \beta \left( e^{i\frac{2\pi}{6}k} + e^{-i\frac{2\pi}{6}k} \right) \quad (12.202)$$

$$\epsilon_k = \alpha + 2\beta \cos\left(\frac{2\pi k}{6}\right), \quad k = 0, \pm 1, \pm 2. \quad (12.203)$$

The terms  $\alpha = \langle i|H|i \rangle$  and  $\beta = \langle i|H|i \pm 1 \rangle$  are negative and  $\beta$  is the interaction between the nearest neighbors which result in a stabilizing interaction. The lowest energy term is  $\epsilon_0 = \alpha + 2\beta$ , which is the ground state of benzene. According to Pauli's principle we can fill up the ground state with two electrons of opposite spin and go on with the second next lowest state and so on. Since we can fill up the states with 6  $p_z$  electrons the total ground state energy is (in the Hückel approximation without electron-electron interaction S)

$$E_{ges} = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta \quad (12.204)$$

$$\epsilon_0 = \alpha + 2\beta \quad (12.205)$$

$$\epsilon_1 = \alpha + \beta \quad (12.206)$$

$$\epsilon_2 = \alpha - \beta \quad (12.207)$$

$$\epsilon_3 = \alpha - 2\beta. \quad (12.208)$$

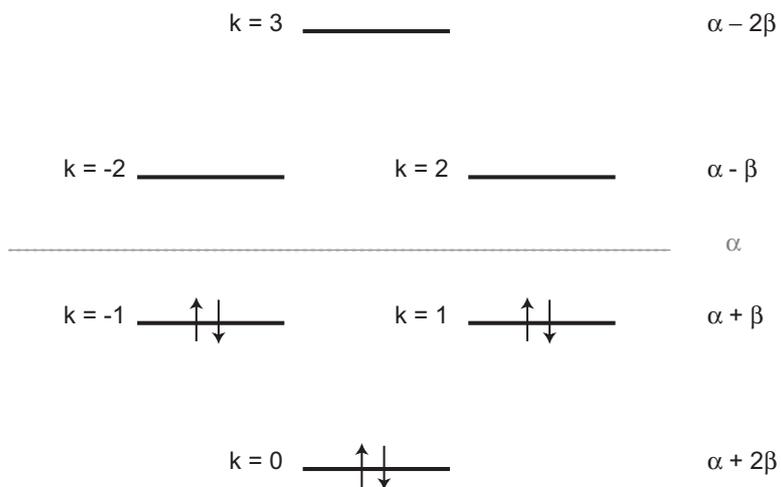
The total energy of the six delocalized electrons is  $E_{ges} = 6\alpha + 8\beta$ , which is  $2\beta$  lower than the total energy for three localized double bonds with  $E = 6\alpha + 6\beta$  (within the Hückel approximations). Therefore, the stabilizing of the delocalization of the electrons is  $2\beta$ . The wave functions  $\psi_k$  are given without normalization

$$\psi_0 = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 \quad (12.209)$$

$$\psi_{\pm 1} = e^{\pm i\pi/3} \phi_1 + e^{\pm i2\pi/3} \phi_2 + e^{\pm i\pi} \phi_3 + e^{\pm i4\pi/3} \phi_4 + e^{\pm i5\pi/3} \phi_5 + e^{\pm i6\pi/3} \phi_6 \quad (12.210)$$

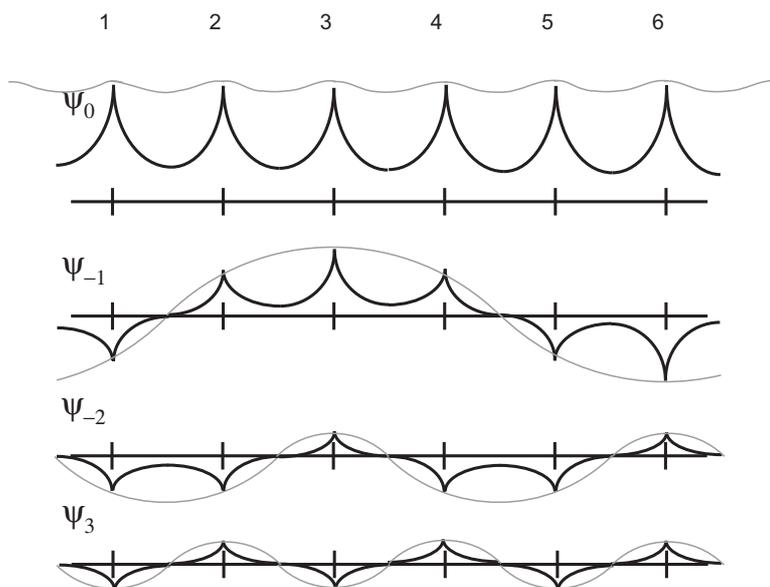
$$\psi_{\pm 2} = e^{\pm i2\pi/3} \phi_1 + e^{\pm i4\pi/3} \phi_2 + e^{\pm i2\pi} \phi_3 + e^{\pm i8\pi/3} \phi_4 + e^{\pm i10\pi/3} \phi_5 + e^{\pm i12\pi/3} \phi_6 \quad (12.211)$$

$$\psi_3 = -\phi_1 + \phi_2 - \phi_3 + \phi_4 - \phi_5 + \phi_6 \quad (12.212)$$

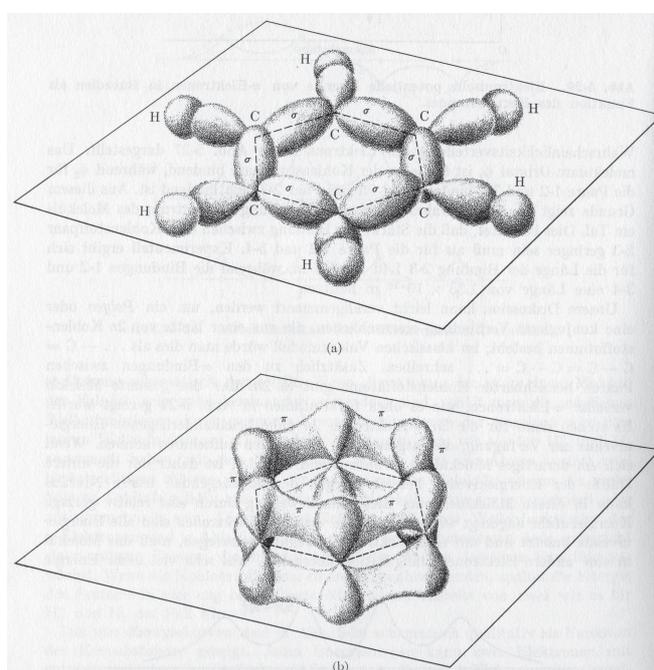


**Abbildung 12.23.** Energy eigenvalues of the benzene molecule calculated with Hückel method.

The wave function  $\psi_0$  has zero knots,  $\psi_{\pm 1}$  has one knot line,  $\psi_{\pm 2}$  has two knot lines, and  $\psi_3$  has three knot lines going through the molecule.



**Abbildung 12.24.** Qualitative representation of the benzene wave functions with increasing number of knots along the benzene ring.



**Abbildung 12.25.** Molecular orbitals of benzene forming single bonds (a) and double bonds (b).

## 12.7 Hybridization, structure of polyatomic molecules

Atomic orbital wave functions represent solutions of the SE. A linear superposition of solutions is again a solution of the SE. Molecular orbitals can be built of superpositions of atomic orbitals resulting in binding and antibinding orbitals (Fig. 12.7). For example upon excitation of an electron of the s-orbital of a carbon

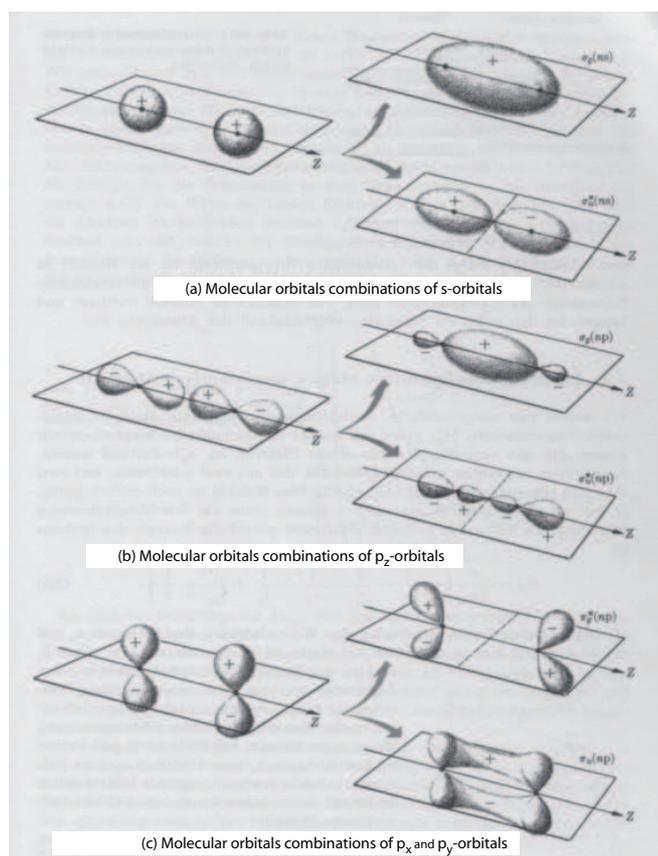


Abbildung 12.26.

atom  $((1s)^2(2s)^2(2p)^2)$  to the excited state  $((1s)^2(2s)(2p)^3)$ , we get one electron in the  $2s$ ,  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbital, and we can form a linear superposition of several wave functions (Fig. 12.7). This is called hybridization. Hybridization of an s-orbital and an  $p_z$ -orbital leads to digonal hybridization with MO wave functions  $\psi_+$  and  $\psi_-$  (Fig. 12.7). These two functions give rise to two  $\sigma$  bonds in opposite directions along the z-axis. Ethine is an example for sp-hybridization (Fig. 12.7).

$$\psi_+ = \frac{1}{N_+}(\psi_s + \psi_{p_z}) \quad (12.213)$$

$$\psi_- = \frac{1}{N_-}(\psi_s - \psi_{p_z}) \quad (12.214)$$

$$(12.215)$$

Hybridization of an s-orbital and two p-orbitals is called  $sp^2$  hybridization. This

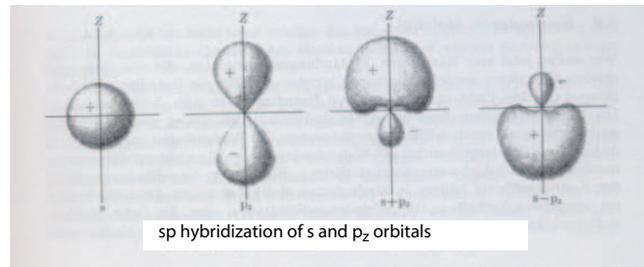


Abbildung 12.27.

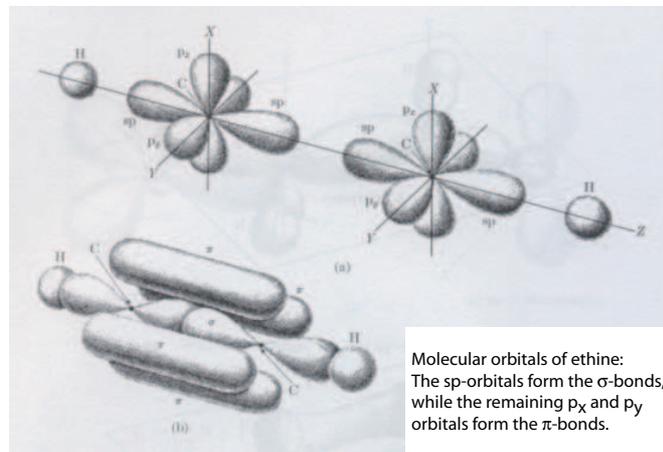


Abbildung 12.28.

type of hybridization is responsible for the molecular structure of ethylene (Fig. 12.7, Fig. 12.7). The angle between the three  $\sigma$ -bonds, which lie within one plane is  $120^\circ$ .

$$\psi_1 = \frac{1}{\sqrt{3}} \left( \psi_s + \sqrt{2}\psi_{p_x} \right) \quad (12.216)$$

$$\psi_2 = \frac{1}{\sqrt{3}} \left( \psi_s + \sqrt{\frac{3}{2}}\psi_{p_y} - \frac{1}{\sqrt{2}}\psi_{p_x} \right) \quad (12.217)$$

$$\psi_3 = \frac{1}{\sqrt{3}} \left( \psi_s - \sqrt{\frac{3}{2}}\psi_{p_y} - \frac{1}{\sqrt{2}}\psi_{p_x} \right) \quad (12.218)$$

$$(12.219)$$

Hybridization of an s-orbital and three p-orbitals is called  $sp^3$  hybridization. This type of hybridization is responsible for the molecular structure of methane (Fig. 12.7). The four new wave functions called hybrid orbitals are equivalent and

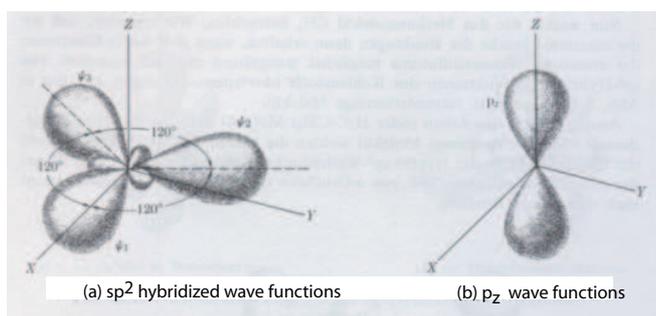


Abbildung 12.29.

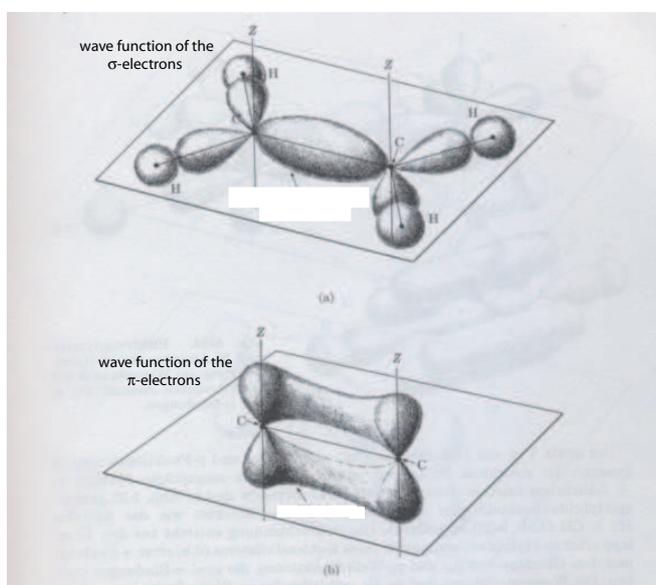


Abbildung 12.30.

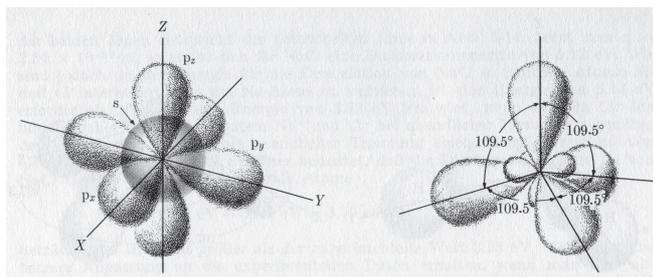
orthonormal (in the sense of the scalar product) and point in the four different directions of a tetrahedra:  $(1,1,1)$ ,  $(1,-1,-1)$ ,  $(-1,1,-1)$ , and  $(-1,-1,1)$ . The four unpaired electrons occupy the wave functions  $\psi_1, \dots, \psi_4$  with parallel spins (Hund's rule) and experience a reduced Coulomb repulsion because of reduced overlap of the wave functions. The resulting angle between the main directions of the wave functions is  $109.47^\circ$ . For the directions we can write

$$\psi_1 \propto \vec{r}_1 = x + y + z \quad (12.220)$$

$$\psi_2 \propto \vec{r}_2 = -x - y + z \quad (12.221)$$

$$\cos \theta = \frac{\vec{r}_1 \cdot \vec{r}_2}{\sqrt{(\vec{r}_1)^2(\vec{r}_2)^2}} \quad (12.222)$$

$$= \frac{-1 - 1 + 1}{\sqrt{3}\sqrt{3}} = -\frac{1}{3} = 109.47^\circ. \quad (12.223)$$



**Abbildung 12.31.** Atomic wave functions of the carbon atom (left) and its hybridized wave functions (right). The angle between the main directions of the wave functions is  $109.47^\circ$ .

In the methane molecule ( $\text{CH}_4$ ) the four molecular orbitals responsible for the four single bonds between the carbon and the four hydrogen atoms are given by the hybrid wave functions  $\psi_i$  and the hydrogen wave functions  $\varphi_i$  (see Fig. 12.7)

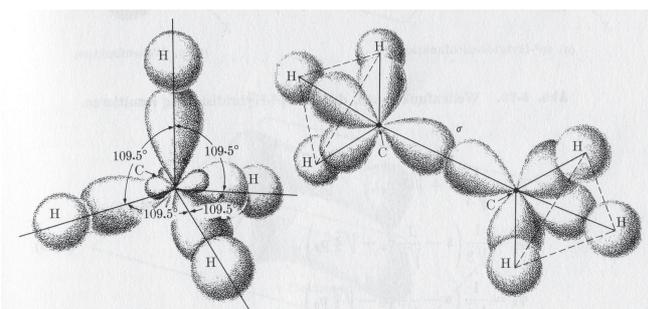
$$\Psi_1 = \frac{1}{\sqrt{a^2 + b^2}} (a\varphi_1 + b\psi_1) \quad (12.224)$$

$$\Psi_2 = \frac{1}{\sqrt{a^2 + b^2}} (a\varphi_2 + b\psi_2) \quad (12.225)$$

$$\Psi_3 = \frac{1}{\sqrt{a^2 + b^2}} (a\varphi_3 + b\psi_3) \quad (12.226)$$

$$\Psi_4 = \frac{1}{\sqrt{a^2 + b^2}} (a\varphi_4 + b\psi_4). \quad (12.227)$$

Hybridization result in strongly increased electron overlap and therefore in stron-



**Abbildung 12.32.** Hybridized wave functions and molecular orbitals of the methane molecule (left) and ethane molecule (right).

ger chemical bonds.

## 12.8 Van der Waals interaction

## 12.9 Electronic transitions in molecules

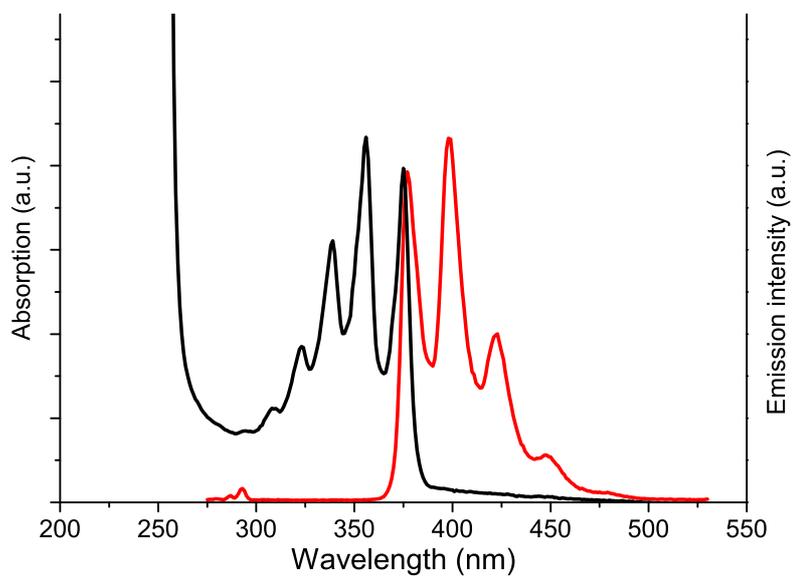
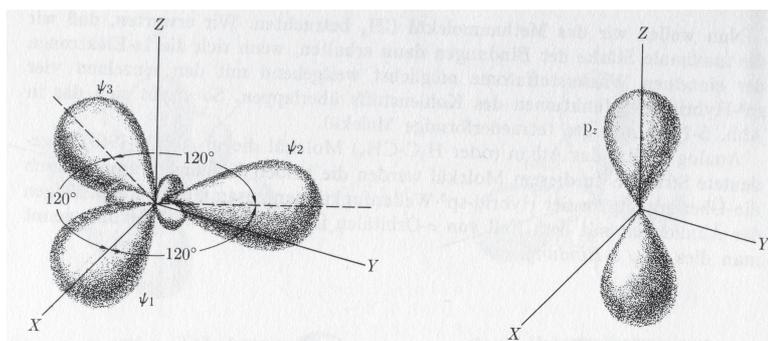
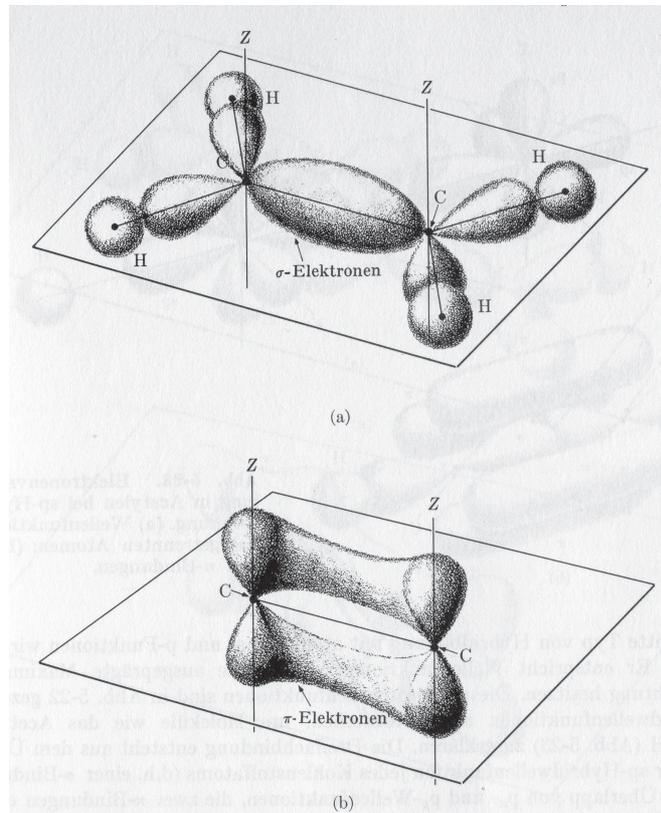


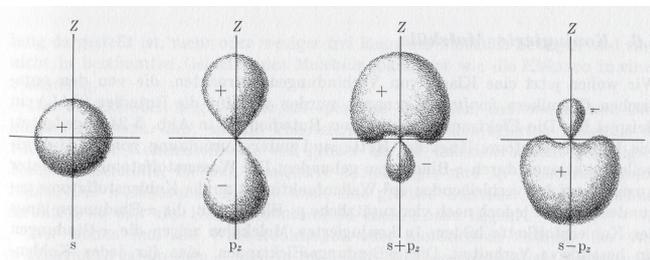
Abbildung 12.33. .



**Abbildung 12.34.** Hybridized wave functions with  $sp^2$  hybridization and angle of  $120^\circ$  between the orbitals (left). The remaining  $p_z$  orbital (right).



**Abbildung 12.35.** Hybridized wave functions ( $sp^2$ ) and molecular orbitals of the ethylene molecule (upper panel). The remaining two  $p_z$  orbital perpendicular to the  $\sigma$  bonds form a double bond (lower panel).



**Abbildung 12.36.** Hybridized wave functions ( $sp$ ). The remaining two  $p_y$  and two  $p_z$  orbitals lead to two  $\pi$  bonds perpendicular to the  $\sigma$  bond. The molecules can form triple bonds (e.g. ethine).

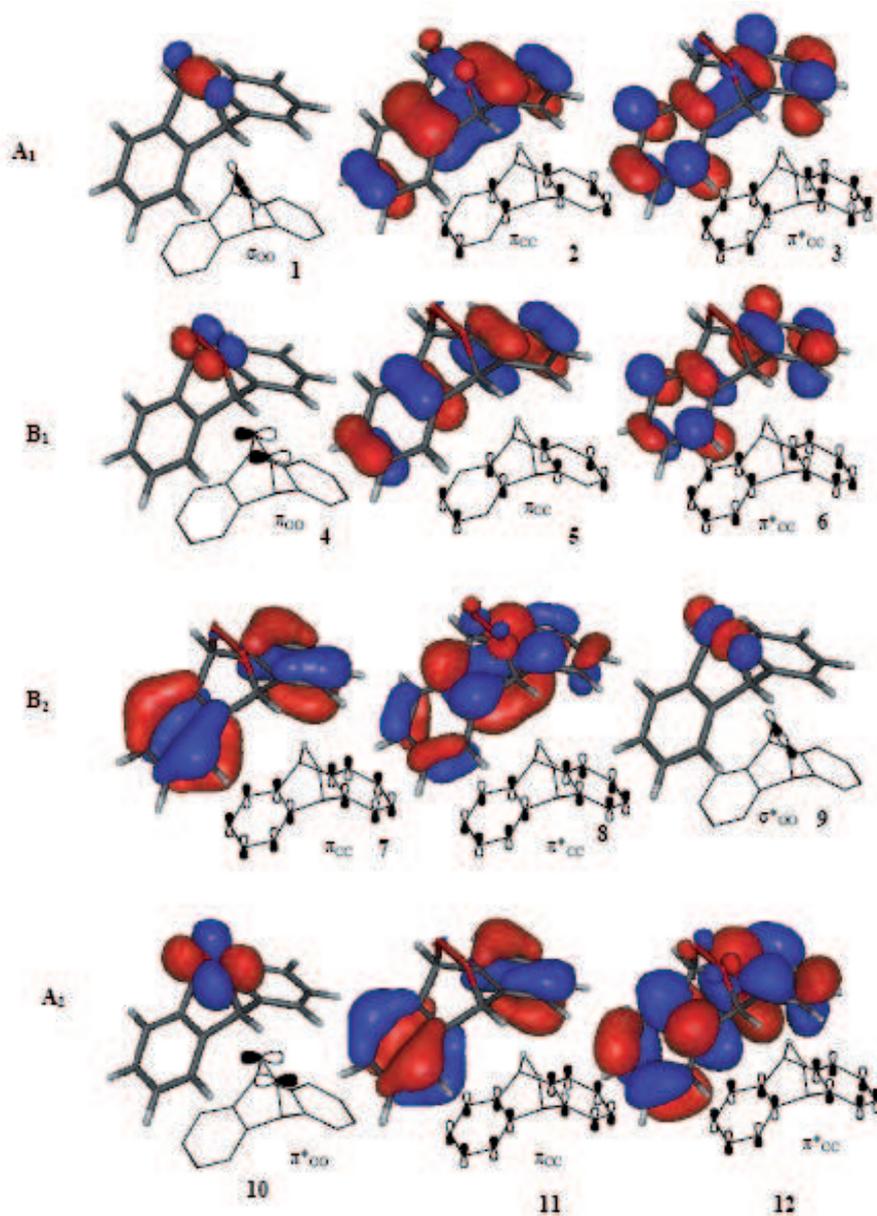


Abbildung 12.37. .