5   The Theory of Chemical Bonds

5.1   Heteropolar and Homopolar Bonding

The heteropolar bond of a molecule, for example the salt molecule NaCl, cf. Fig. 5.1, can be explained using electrostatics. When the Na atom gets close to the Cl atom, the transfer of an electron from Na to Cl results in a reduction of the total energy, and the ions are held together by an electrostatic bond. The electron transfer and potential difference of the cations with respect to the neutral atoms can only be explained with quantum mechanics.
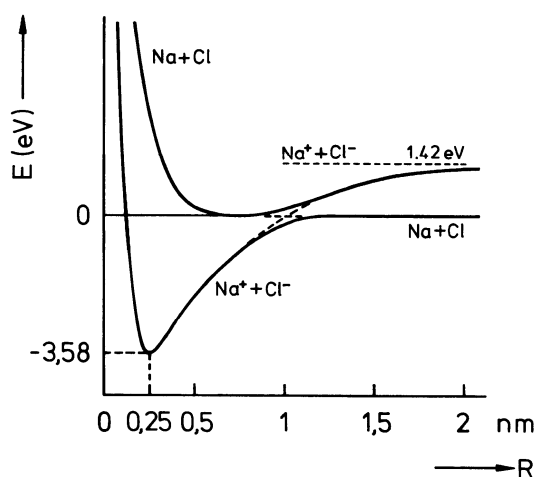

Fig. 5.1 Potential energy E for the ionic and covalent bonds of a chlorine atom with a sodium atom (vapor state) as a function of the distance between the nuclei R, from Fig. 1.2 Haken and Wolf

In homopolar bonding, there is no transfer of charge. The simplest example is the hydrogen molecule H_2. The most important characteristics of this bond can be clarified with the H_2^+ ion, which has already been dealt with in chapter 4.1.2. As a refresher, we begin with equations 4.16-17 from chapter 4, here equations 1-2.

5.2   The Hydrogen Molecular Ion H_2^+

In a molecular ion, the wave function of an electron near the nuclei A and B, can be described by the overlapping of two atomic orbitals:

$$\psi = N[\psi_{1s}(A) + \psi_{1s}(B)] \quad \text{and}$$

$$\psi^2 = N^2\left[\{\psi_{1s}(A)\}^2 + \{\psi_{1s}(B)\}^2 + 2\psi_{1s}(A)\psi_{1s}(B)\right] \quad \text{where} \tag{5.01}$$

$$\int \psi^2 d\tau = 1 \quad \text{and} \quad S = \int \psi_{1s}(A)\psi_{1s}(B)\,d\tau = \frac{1}{2N^2} - 1.$$

The normalization factor N guarantees the usual normalization condition for probability waves: $\int \psi^2 d\tau = 1$, as applied to molecular orbitals. S refers to the so-called overlap integral. Equation (5.01) is a *Linear Combination of Atomic Orbitals* = LCAO. Although the s-orbitals have a spherical symmetry, the molecular orbital of equ.(5.01) only has rotational symmetry with respect to the bonding axis. Rotationally symmetric electron densities are generally called σ-orbitals, and the complete label for the state in equ.(5.01) is the 1sσ-Orbital.
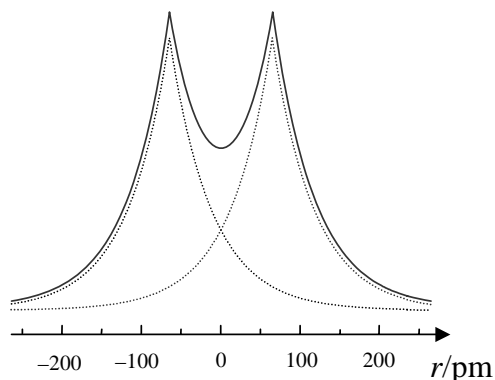
Fig. 5.2 The symmetric wave functions of the H_2^+ ion according to equ.(5.01). The dotted lines show the atomic orbitals, the solid curve show the wave function of the LCAO orbital along the nuclear bonding axis.

Figure 5.2 uses the radial dependency $\psi \approx \exp(-r/a_0)$ with $a_0 \approx 53$ pm, cf. chapter 4.1.1, for the wave function of the atomic orbitals. During the calculation of the eigenvalues of the Schrödinger equation with equ. 4.15, we get integrals which contain the square of the wave function of an atomic orbital ($\int \psi_1 * \mathcal{H} \psi_1 d\tau$). These integral represent the Coulomb interaction energy between the electron density and nuclear charge. Other exchange integrals ($\int \psi_1 * \mathcal{H} \psi_2 d\tau$) contain the product of the wave function of both atomic orbitals and characterize the quantum mechanical effect that an electron is partially in both states at the same time. This exchange integral creates the bonding effect.

A plausible explanation instead of the quantum mechanical derivation and numerical calculation is possible with the help of Fig. 5.2: For the LCAO state in Fig. 5.2, the probability of finding an electron between the nuclei is rather large (one builds the square of the wave function). The electron charge between the nuclei experiences an attractive force from both nuclei, which leads to a reduction of the potential energy of the system.

When speaking of bonding orbitals, we mean two states whose occupation by an electron leads to a reduction in the total energy E of the molecule. If the 1s atomic orbitals are subtracted rather than added, we have an antibonding orbital:

$$\psi' = N[\psi_{1s}(A) - \psi_{1s}(B)] \text{ and}$$
$$\psi'^2 = N^2 \left[\{\psi_{1s}(A)\}^2 + \{\psi_{1s}(B)\}^2 - 2\psi_{1s}(A)\psi_{1s}(B) \right] \tag{5.02}$$

The term on the right in equ.(5.02) reduces the electron density between the nuclei and raises the total energy in comparison to the separated atoms. Such orbitals are labeled by $1s\sigma*$, where the σ refers to the rotational symmetry. All antibonding orbitals are labeled with an asterisk (*). It is easy to create a visual portrayal by making the atomic orbital on the right in Fig. 5.2 (dotted line) negative and again building the sum. The square of this antibonding orbital shows a low charge density between the nuclei and therefore a increase in the total energy.

In chapter 4.1.2, we referred to the poor correlation between the predictions of the LCAO model and experimental results, for example $D_e(\text{LCAO}) = 1,77$ eV and $D_e(\text{experiment}) = 2,6$ eV. An improvement is reached by variation of the atomic orbitals. If we use for the radial dependency $\psi \approx \exp(-r/a)$ and vary a, instead of $\psi \approx \exp(-r/a_0)$, we get with $a = a_0/1,24$ a good correlation.

5.3   The Hydrogen Molecule H_2

5.3.1   Variation Principle and the Method of Heitler-London

The general (and mathematically verifiable) statement of the variation principle is that the exact solution of the Schrödinger equation leads to eigenvalues with the lowest energy. It is therefore possible to approach an exact solution of the Schrödinger equation by varying the wave function with the intention of minimizing the energy. This principle allows the complicated calculation of the wave function of the hydrogen molecule.

The method of Heitler-London uses additionally the spin functions of both electrons (which are unaffected by the hamiltonian) and thereby leads to a bound odd wave function with parallel spin ψ_u (antisymmetric and odd with respect to the exchange of the spatial coordinates of the electrons), and to a bound even wave function ψ_e with antiparallel spin. We have:

$$\Psi_{e,\,u} = \psi_A(1)\ \psi_B(2) \pm \psi_A(2)\ \psi_B(1). \tag{5.03}$$

The numbers (1) and (2) tell us what electron the wave function is referring to. For these wave functions, the integrals

$$E = \frac{\int \psi * \mathcal{H} \,\psi \, d\tau}{\int \psi * \psi \, d\tau} \tag{5.04}$$

are analytically determined and numerically calculated. The results are portrayed in Fig. 5.3 (ψ_u is ↑↑ and ψ_g is ↓↑).
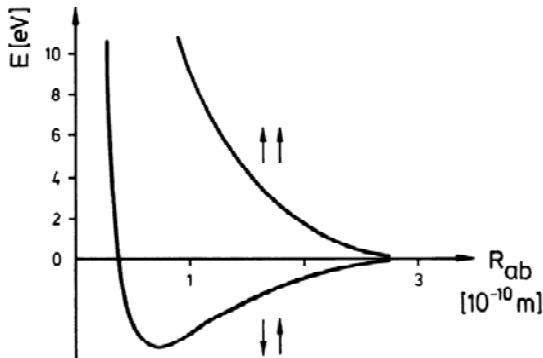

Fig. 5.3 Binding energy of the hydrogen molecule as a function of the nuclear distance R_{ab}, with consideration of the repulsive coulomb energy between the nuclei. In the lower curve, the electron spins are antiparallel, in the upper curve they are parallel. Taken from Fig. 4.12 Haken and Wolf.

The energy minimum comes from the exchange integrals ($\int \psi_1 * \mathcal{H} \,\psi_2 d\tau$), as already shown with the hydrogen molecular ion. The correlation between this calculation ($D_e = 3{,}14$ eV) and experiment ($D_e = 4{,}48$ eV) is also unsatisfactory, since we did not yet consider the effect of the hydrogen bond.

5.3.2   Hydrogen Bonds According to Hund-Mulliken-Bloch

The method of Heitler-London makes no use of the atomic orbitals. Still, by using a linear combination of atomic orbitals (LCAO) for the calculation of the molecular orbitals (MO) of the hydrogen molecule (the procedure of Hund-Mulliken-Bloch), we get poorer results than we would by using the procedure of Heitler-London. We start with the LCAO procedure of equ.(5.01) and put in the electrons of the state described in equ.(5.01), one after the other. An approach to the solution for the hamiltonian which describes the state of both electron is

$$\Psi(1, 2) = \psi(1)\ \psi(2) \times \text{spin function } (1, 2). \tag{5.05}$$

We will use the convention from magnetic resonance of labelling with α the spin state (magnetic quantum number) $m = +\frac{1}{2}$ of an electron (or nuclear) spin $s = \frac{1}{2}$, and the state $m = -\frac{1}{2}$ with β. If we use the result of the considerations of Heitler-London, where only antiparallel spins ($\alpha\beta$) play a part in the bonding, we can use an antisymmetric function

$$\text{spin function} = \frac{1}{\sqrt{2}}\ [\alpha(1)\beta(2) - \alpha(2)\beta(1)]. \tag{5.06}$$

This procedure gives us poorer results than Heitler-London for the hydrogen molecule, but it is applicable to more complicated molecules.

5.3.3   Covalent-Ionic Resonance and the Generalized Approach for H₂

Heitler-London introduced a covalent wave function which has one electron at each of the nuclei:

$$\Psi_{\text{covalent}} = N\ [\psi_A(1)\ \psi_B(2) + \psi_A(2)\ \psi_B(1)]. \tag{5.07}$$

N is the normalization factor. The probability that both electrons are at the nucleus A or B is $\psi_A(1)\ \psi_A(2)$ or $\psi_B(1)\ \psi_B(2)$. Both states correspond to ion pairs, since in both cases we have two electrons at one nucleus, and none at the other. They are also clearly energetically degenerate. The symmetric linear combination is a purely ionic bond due to the statement in quantum mechanics that linear combinations of degenerate function are also solutions of the Schrödinger equation:

$$\Psi_{\text{ionic}} = N'\ [\psi_A(1)\ \psi_A(2) + \psi_B(1)\ \psi_B(2)]. \tag{5.08}$$

In nature we see neither purely covalent nor purely ionic bonds, although one or the other bond type can be dominant. With the variable parameter c, we aim for a minimum of the expectation value of the energy of a wave function that is a linear combination of equations (5.07) and (5.08):

$$\Psi = \Psi_{\text{covalent}} + c\ \Psi_{\text{ionic}}. \tag{9}$$

Haken and Wolf use a modified Heitler-London-approach, in which an extra part is added to the wave function ψ_A localized at nucleus A, which comes from the wave function of the atom B. ψ_A is replaced by $\psi_A + d\psi_B$, where $0 \leq d \leq 1$. ψ_B is replaced analogously. We then get

$$\Psi_g(1, 2) = [\psi_A(1)+d\psi_B(1)]\ [\psi_B(2)+d\psi_A(2)] + [\psi_A(2)+d\psi_B(2)]\ [\psi_B(1)+d\psi_A(1)] \tag{5.10}$$
$$= (1+d^2)\ [\psi_A(1)\ \psi_B(2) + \psi_A(2)\ \psi_B(1)] + 2d\ [\psi_A(1)\ \psi_A(2) + \psi_B(1)\ \psi_B(2)].$$

For $d = 0$, equ.(5.10) gives us the result of Heitler-London, for $d = 1$ the approach of Hund-Mulliken-Bloch, and for $c = 2d/(1+d^2)$ the covalent-ionic resonance of equ (5.09).

5.4   Hybridization

Hybridization refers to the mixing of atomic orbitals to produce hybrid orbitals, which occur in many bonds. The total energy of the molecule is reduced. This type of bond is common in organic chemistry, since it is typical of carbon bonds.

In the ground state, the carbon atom has the electronic configuration $1s^2 2s^2 2p_x 2p_y$, which should be bivalent due to the two unpaired electrons. A 2s electron is raised by promotion into the $2p_z$ state, which lies about 4 eV higher. This gives us the state $1s^2 2s 2p_x 2p_y 2p_z$. The four unpaired electrons can take part in four bonds. This leads to a significant reduction of the total energy, which more than compensates for the 4 eV required for the promotion of the 2s electron into the $2p_z$ state.

From the state $1s^2 2s 2p_x 2p_y 2p_z$ we would expect three equally energetic perpendicular bonds and one weaker bond from the 2s electron. This contradicts the four equal tetrahedrally coordinated bonds which we see for example in the methane molecule. To overcome this problem, Pauling and Slater showed that four linear combinations of 2s, $2p_x$, $2p_y$ and $2p_z$ lead to four equal sp^3 hybrid orbitals:

$$\psi_1 = \frac{1}{2}\left(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z}\right),$$
$$\psi_2 = \frac{1}{2}\left(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z}\right),$$
$$\psi_3 = \frac{1}{2}\left(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z}\right),$$
$$\psi_4 = \frac{1}{2}\left(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z}\right). \tag{5.11}$$

From equation (4.13) in chapter 4, we see that the variables x/r, y/r and z/r appear in the wave functions ψ_{2px}, ψ_{2py} and ψ_{2pz}. From Fig. 4.10, we can see on the right side that a tetrahedron is build by the occupation diagonally adjacent corners of a cube (exchange of two signs). From equ.(5.11) we can see that the wave function differ from each other by the exchange of two signs of p-orbitals. The four wave functions ψ_1-ψ_4 in equ.(5.11) span the tetrahedron that we expect for the bonds of the carbon atom. The (non-geometric) orthogonality of the functions ψ_1-ψ_4 can be easily shown by calculation of the integrals $\int \psi_i^* \psi_j d\tau$, where we refer to the orthogonality of the wave functions for 2s, $2p_x$, $2p_y$ and $2p_z$.

When the four wave functions of equ.(5.11) each build a corner of the carbon tetrahedron, we can build the methane molecule using the LCAO method by saying that every corner of the carbon tetrahedron is bound to a hydrogen atom. For example: for the bond in the corner with the number 1, we have:

$$\psi_1 = \psi_{C1} + c\,\psi_{H1}, \tag{5.12}$$

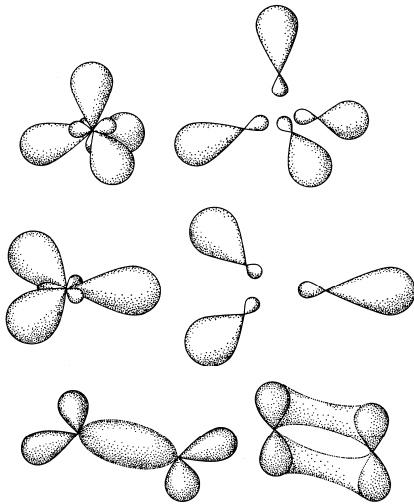where the constant c is determined using a variation method.

Fig. 5.4. Density distributions of electrons in the tetragonal (top) and trigonal (middle) hybridisation of carbon in a single bond. In the top and middle on the right, the parts are drawn separately (explosion representation). On the bottom, the hybridizations of ethylene are shown. The figure on the left shows the sp^2 parts, which are each composed of three electrons, while in the figure on the right, the fourth electrons from the p$_z$-orbitals build a second carbon bridge. Taken from Fig. 4.15-17 Haken and Wolf

Beside the sp^3 hybridization, we have still other hybridizations of the carbon atom, for example the sp^2-hybridization, cf. Fig. 4 middle, which has the orthogonal wave functions

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

$$\psi_2 = \sqrt{\frac{1}{3}}\left(\psi_s - \sqrt{\frac{1}{2}}\,\psi_{p_x} + \sqrt{\frac{3}{2}}\,\psi_{p_y}\right), \tag{5.13}$$

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

These build a simultaneous triangle in the *x-y* plane. These wave functions do not involve the p$_z$-orbital, which takes part in bonds independent of the sp^2-orbitals. In the ethene molecule, both of the carbon atoms each have two hydrogen atoms in an sp^2 configuration, and the third sp^2 orbital serves as a bridge between the carbon atoms. On the other hand, the two p$_z$-electrons of both carbon atoms form another bond through a linear combination, which leads to a double bond between the carbon atoms, cf. Fig. 5.4 bottom.

5.5   Benzen, Parity of Ethene, and the Hückel Method for Butadiene

We will use the symmetry operation C$_6$ on benzene, and consider the atomic orbitals 2p$_z$. From equation (4.13) of chapter 4 we see that the variables z/r appear in the wave function of the atomic orbital ψ_{2pz}. From that we conclude that a rotation around the z-axis has no effect on the wave function:

$$C_6\psi_{2pz} = \psi_{2pz.} \tag{5.14}$$

The same is true for the hamiltonian, which has the same effect on all symmetric bonds:

$$C_6\mathcal{H}(r) = \mathcal{H}(r). \tag{5.15}$$

If we multiply the C_6-operator from the left with the Schrödinger equation, we get

$$C_6\,\mathcal{H}(r)\,\psi(r) = C_6\,E\,\psi(r) \quad \rightarrow \quad \mathcal{H}(r)\,C_6\psi(r) = C_6\,E\,\psi(r). \tag{5.16}$$

Comparison of these two equations (5.16) gives us:

$$C_6\,\mathcal{H}(r) - \mathcal{H}(r)\,C_6 = [C_6,\mathcal{H}(r)] = 0. \tag{5.17}$$

Since the commutator is zero, the rotational operator and the hamiltonian commute.

Supposed there is no energy degeneration, the wave function should only be changed by a constant factor λ after a rotation operation:

$$C_6 \ \psi(r) = \lambda \ \psi(r). \tag{5.18}$$

λ can be determined by taking advantage of the property that after six C_6 operations, we have the complete identity

$$(C_6)^6 = \lambda^6 = 1 \tag{5.19}$$

The six solutions of this equation are given by

$$\lambda = \exp(2\pi i k/6) \quad \text{with } k = 0, 1, 2, 3, 4, 5 \tag{5.20}$$

Now let us again make use of the condition that the state of a degenerate system is given by a linear combination of wave functions of a single energy eigenvalue. From the atomic orbitals ψ_1 to ψ_6 we get the molecular orbital

$$\psi = c_1 \psi_1 + c_2 \psi_2 + \ldots + c_6 \psi_6. \tag{5.21}$$

The use of the operation C_6 gives:

$$C_6 \psi = \lambda(c_1 \psi_1 + c_2 \psi_2 + \ldots + c_6 \psi_6) = c_1 \psi_6 + c_2 \psi_1 + \ldots + c_6 \psi_5. \tag{5.22}$$

Since the wave functions are an orthogonal set of functions which are linearly independent, the coefficients in the middle on the right side of equ.(5.22) have to be the same. We get $c_1 = \lambda c_6, \ldots, c_2 = \lambda c_1$. Multiple use ($j$-times) of the procedure in (5.22) gives $c_k = \lambda^j c_{k-j}$. With equ.(5.20) we arrive at the wave function of the π-electrons of the benzene molecule, which still needs to be normalized,

$$\psi \approx \sum_{j=1}^{6} \psi_j \exp(2\pi i \, kj / 6) \ . \tag{5.23}$$

Parity can be demonstrated on the wave function of ethene:
For the operations of inversion and reflection, double application gives the complete identity:

$$\psi(r) = \lambda^2 \ \psi(r) \ \rightarrow \ \lambda = \pm 1. \tag{5.24}$$

From that we get for inversion

$$\psi(-r) = \pm \psi(r). \tag{5.25}$$

The upper sign refers to even parity, the lower to odd parity. With the double bond of ethene lying in the z-direction and the variables z/r in the wave functions of the atomic orbitals ψ_{2p_z} we get

$$\psi_1(r) = -\psi(r - R_{AB}/2) \quad \text{and} \quad \psi_2(r) = -\psi(r + R_{AB}/2), \tag{5.26}$$

where the following parities for the atomic wave function ψ_1 and ψ_2 are valid:

$$\psi_1(-r) = -\psi_2(r) \quad \text{and} \quad \psi_2(-r) = -\psi_1(r). \tag{5.27}$$

For the construction of the MO we build the linear combination

$$\psi(r) = c_1 \psi_1(r) + c_2 \psi_2(r). \tag{5.28}$$

Equation (5.28) put into equ.(5.27) together with equ.(5.25) gives

$$c_1 \psi_1(-r) + c_2 \psi_2(-r) = -c_1 \psi_2(r) - c_2 \psi_1(r) = \pm c_1 \psi_1(r) \pm c_2 \psi_2(r). \tag{5.29}$$

From that we conclude that $c_1 = \pm c_2$ for even and odd parity, and equ.(5.24) gives us

$$\psi(r) = c\,\psi_1(r) \pm c\,\psi_2(r), \tag{5.30}$$

where the even parity represents a bonding orbital and the odd parity and antibonding orbital.

The explanation of the **secular determinant**, cf. equ.(5.33), is a prerequisite for the understanding of the Hückel approximation. For this we will us the LCAO approach with only 3 atomic orbitals:

$$\psi = c_1\,\psi(1) + c_2\,\psi(2) + c_3\,\psi(3). \tag{5.31}$$

The determination of the coefficients is done by simultaneously solving three secular equations of the form

$$
\begin{aligned}
(\alpha_1 - E)\,c_1 + (\beta_{12} - ES_{12})\,c_2 + (\beta_{13} - ES_{13})\,c_3 &= 0 \\
(\beta_{21} - ES_{21})\,c_1 + (\alpha_2 - E)\,c_2 + (\beta_{23} - ES_{23})\,c_3 &= 0 \\
(\beta_{31} - ES_{31})\,c_1 + (\beta_{32} - ES_{32})\,c_2 + (\alpha_3 - E)\,c_3 &= 0
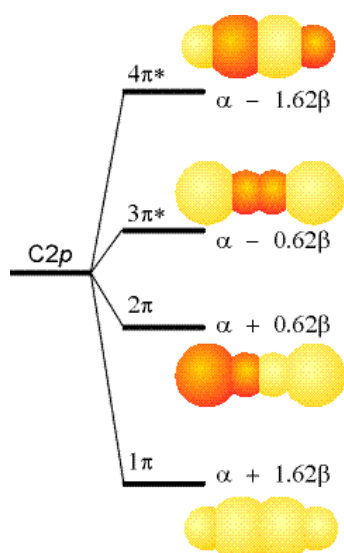\end{aligned}
\tag{5.32}
$$

The parameters α_i represent the coulomb interactions ($\int \psi_i{}^* \mathcal{H}\,\psi_i\,\mathrm{d}\tau$), β_{ij} labels the exchange interactions ($\int \psi_i{}^* \mathcal{H}\,\psi_j\,\mathrm{d}\tau$), and S_{ij} refers to the overlap integrals ($\int \psi_i{}^* \psi_j\,\mathrm{d}\tau$). The solution of these equations is the same as the solution of the secular determinant, with which we can also determine the energy eigenvalues:

$$
\begin{vmatrix}
\alpha_1 - E & \beta_{12} - ES_{12} & \beta_{13} - ES_{13} \\
\beta_{21} - ES_{21} & \alpha_2 - E & \beta_{23} - ES_{23} \\
\beta_{31} - ES_{31} & \beta_{32} - ES_{32} & \alpha_3 - E
\end{vmatrix} = 0 .
\tag{5.33}
$$

In the **Hückel approximation**, the overlap integrals S_{ij} are set to zero. The exchange integrals ($\int \psi_i{}^* \mathcal{H}\,\psi_j\,\mathrm{d}\tau$) are equal to a constant parameter β, or zero, depending on whether the atoms are consecutive or non-consecutive. For the secular determinant, all the elements of the principal diagonal are $\alpha - E$, for concecutively numbered chain molecules are the elements of the side diagonals β and all other elements are zero. We used this Hückel-Approximation implicitly in benzene and ethene.

In **butadiene**, there is a single bond between the carbon atoms in the middle, and a double bond between each of the outermost carbon atoms. The four $2p_z$-orbitals of the four carbon atoms are perpendicular to the plane of the carbon atoms and create the π-electron system. The use of the Hückel approximation gives us a determinant of the fourth order where the elements of the principal diagonal are $\alpha - E$, the elements of the two side diagonals are β, and all other elements are zero. Working out the determinant, we get

$$(\alpha - E)^4 - 3(\alpha - E)^2 \beta^2 + \beta^4 = 0. \tag{5.34}$$

4π*

α − 1.62β

3π*

C2p

α − 0.62β

2π

α + 0.62β

The polynomial of the fourth degree can be written in the form of a quadratic equation $x^2 - 3x + 1 = 0$ by substituting $x = (\alpha - E)^2/\beta^2$. This gives us $x = 0{,}38$ and $2{,}62$ as solutions. From that we determine the energies of the four MO's: $E = \alpha \pm 0{,}62\beta$ and $E = \alpha \pm 1{,}62\beta$. The four carbon atoms occupy the two lowest orbitals.

Fig. 5.5 The Hückel MO energy levels of butadiene, and its four molecular orbitals. The four π electrons are delocalized and come from the four carbon atoms. They occupy the two lower orbitals, labeled with 1π and 2π. Taken from Fig. 14.42 Atkins. 6th ed., CD version.

1π

α + 1.62β

5.6   General Approches to the Multielectron Problem (Quantum Chemistry)

The model of Heitler-London, presented in chapter 5.3.1 is the basis for the valence bonding theory (VB), which considers electron pairs to be the basic unit of special individual bonds (in the H_2-molecule there is only one). The theory of molecular orbitals (MO) of Hund-Mulliken-Bloch is the second common theory of chemical bonds, previously discussed in chapter 5.3.2. It assumes that an electrons can *not* be ordered into a special bond. There are especially simple examples of this in chapter 5.4 and 5.5.

For a general description we assume N electrons with the coordinates r_j, $j = 1, ..., N$, in a coulomb field of M nuclei with the (invariable) coordinate R_K, $K = 1, ..., M$, and the atomic number Z_K, and with further coulomb interactions of the electrons with each other. For the electron with the coordinate r_j we get for the interaction with the nucleus the potential

$$V(r_j) = -\sum_{K=1}^{M} \frac{Z_K e^2}{4\pi\varepsilon_0 |R_K - r_j|} . \tag{5.35}$$

The interaction energy of all the electrons with each other is

$$\mathcal{H}_{\text{Elektron-Elektron}} = \sum_{j<j'} \frac{e^2}{4\pi\varepsilon_0 |r_j - r_{j'}|} . \tag{5.36}$$

The hamiltonian of the total system is

$$\mathcal{H} = \sum_{j=1}^{N} -\frac{\hbar^2}{2m_0}\Delta_j + V(r_j) + \mathcal{H}_{\text{Elektron-Elektron}} . \tag{5.37}$$

In the Schrödinger equation

$$\mathcal{H}\Psi(r_1, ..., r_N) = E\,\Psi(r_1, ..., r_N) \tag{5.38}$$

the wave functions also depend on the spin, even though the hamiltonian does not explicitly contain the spin. Already for two electron of the hydrogen molecule, the problem could not be solved exactly, we therefore need methods of approximation.

An approximation for the wanted wave function, which should give us the lowest energy, is given by the Slater determinant

$$\psi(r_1, ..., r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) \dots \varphi_N(1) \\ \varphi_1(2) & \varphi_2(2) \dots \varphi_N(2) \\ \vdots \\ \varphi_1(N) & \varphi_2(N) \dots \varphi_N(N) \end{vmatrix}. \tag{5.39}$$

$\varphi_k(j)$ is the single particle wave function, in which k stands for a certain combination of the quantum numbers (including spin). According to the Pauli principle, k runs from 1 to N. The variable j contains the appropriate spin variable of the state in addition to r_j, which can assume the values α and β.

The expectation value of the energy is given by

$$E = \int \psi^* \mathcal{H} \psi \, d\tau_1 \dots d\tau_N, \tag{5.40}$$

where the integration over τ_j also contains the spin variables. The calculation of the integral can be seen on pages 465-469 of Haken and Wolf, we get:

$$E = \sum_k E_{k,k} + \sum_{k<k'} (V_{kk',kk'} - V_{kk',k'k}) \tag{5.41}$$

with $E_{k,k} = \int \varphi_k^* \mathcal{H} \varphi_k \, d\tau_k$. The spin part gives no contribution to the expectation value $E_{k,k}$ of the hamiltonian of a single electron in the quantum state k. For the two other terms, consider the two electrons 1 and 2. The term

$$V_{kk',kk'} = \iint \varphi_k^*(1) \varphi_{k'}^*(2) \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} \varphi_k(1) \varphi_{k'}(2) \, d\tau_1 d\tau_2 \tag{5.42}$$

gives us the coulomb interaction energy of electron 1 in the state k with electron 2 in the state k'. In the following integral, both electrons are in both states:

$$V_{kk',k'k} = \iint \varphi_k^*(1) \varphi_{k'}^*(2) \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} \varphi_{k'}(1) \varphi_k(2) \, d\tau_1 d\tau_2 \tag{5.43}$$

Equation (5.43) is the potential of the so-called Coulomb exchange interaction. As we can see in equ.(5.43), the exchange interaction is zero when the wave function of the two electrons do not overlap. A further simple conclusion from equ.(5.43) is that an exchange interaction only occurs between electrons with the same spin. As proof, we put in $\varphi = \varphi' \varphi''$ for the wave function, where φ'' only contains the spin part, upon which the hamiltonian has no effect. Then we can pull out the two integrals $\int \varphi_k^*(1) \varphi_{k'}(1) \, d\tau_1 \times \int \varphi_k^*(2) \varphi_{k'}(2) \, d\tau_2$ in equ.(5.39) as a factor. Since only two spin wave functions exist, and these are orthogonal to each other, the factor is only different from zero, when k and k' belong to the same spin.

Warning: Coulomb and exchange integral in equations (5.42) and (5.43) refer to the interaction of the electrons between themselves and therefore have a different meaning than the equations (5.32) and (5.34), which refer to the interaction of electrons with nuclei.

A procedure named after Hartree-Fock starts with the assumption that an *N*-electron wave function Ψ is described by the Slater determinant (5.39), where the functions φ_I are orthonormalized and the wave function Ψ gives an energy minimum. The method was introduced by Douglas Hartree and later modified by Vladimir Fock, in order to take the Pauli principle into consideration. It was introduced before computers were available for numerical calculations, and was the basis for the numerical methods of quantum chemistry for the calculation of molecules.

Equations (5.35) to (5.43) are equally true for atoms. Let us consider as an example the sodium atom. These are the steps we shall follow:

- Approach for the hydrogen like orbitals: $1s^2 2s^2 2p^6 3s^1$,

- Exclusive consideration of the 3s electrons according to equ.(5.37),

- Numerical solution of the Schrödinger-equation leads to a new ψ_{3s} with lower energy,

- Now consider one of the 2p-orbitals under the influence of the other orbitals including the improved ψ_{3s}-orbitals according to equ.(5.37),

- The numerical solution of the Schrödinger-equation leads to a new ψ_{2p} with lower energy,

- etc.

This procedure is started again after the numerical calculation of all orbitals, and repeated until the orbitals and calculated energies of further repetitions do not get any better. The orbitals are then self consistent. That is the reason that the procedure is called the *self-consistent-field* (SCF) calculation.

Semi-empirical techniques combine empirical data with quantum chemical calculations. We could, for example, calculate small molecules using the LCAO procedure and get wave functions and energies as function of the coulomb integrals and exchange integrals. We could then approximate these energies from the ionization energies. The number of necessary parameters is often more than the number of experimentally measurable ones. We thus end up with free parameters, which have brought this method into disrepute.

Ab initio **techniques** calculate all integrals with numerical quantum mechanical methods and deliver exact solutions, if there is a sufficiently good and large basic set of Slater orbitals (spherical functions) or Gauss orbitals (Cartesian coordinates) available. Quantum chemists have calculated molecular systems containing much more than 10 atoms with the help of super computers.