

Abb. 6.20. Die zur Darstellung A_1 gehörenden Funktionen des Sauerstoffs (*oben*) und der Wasserstoffe (*unten links*) ergeben im Falle der Bindung die unten rechts gezeigte Wellenfunktion. Die Funktion $2p_z$ spielt dabei keine große Rolle. (Bzgl. des lockernden Zustands vgl. Abb. 6.21. Da die Wellenfunktion $2p_z$ wenig Einfluß hat, ist sie dort nicht aufgeführt)

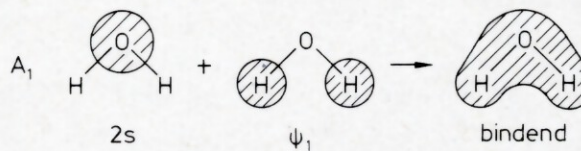
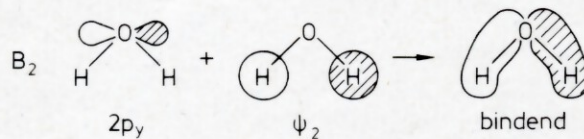
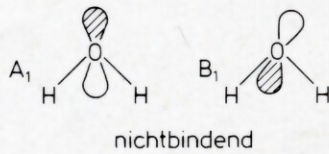
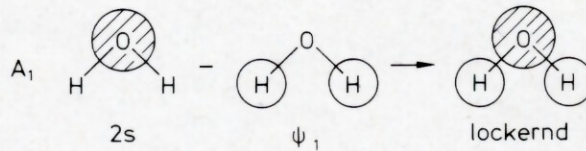
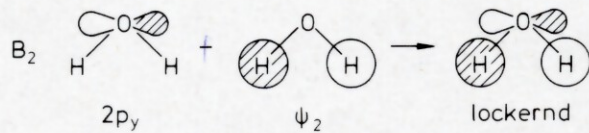
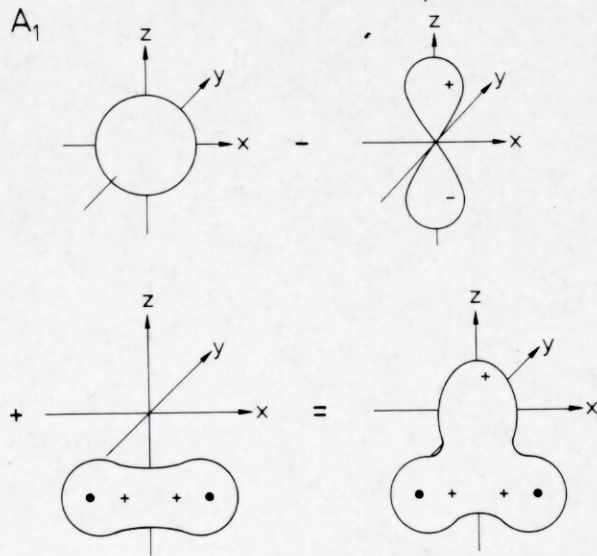


Abb. 6.21. Übersicht über die sich ergebenden H_2O Wellenfunktionen. Ihre Anordnung entspricht dem Energie-Diagramm 6.22

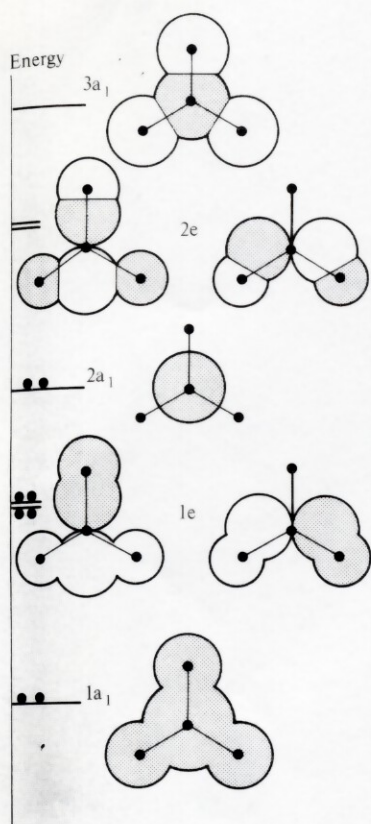


Fig. 10.17. Molecular orbitals (viewed from above) and orbital energies for NH_3 .

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(The two sets of e -orbitals are distinguished by their reflection symmetry.) The secular determinant is solved for the energy levels of the orbitals, Fig. 10.17. There are 8 electrons to accommodate, and so the configuration of the ground state is expected to be $1a_1^2 2a_1^2 1e^4, ^1A_1$. The total energy reaches a minimum when the bond angle is greater than 90° , and HF-SCF type calculations give excellent agreement with the experimental value.

10.8 Hybridization and bond angles

The direct LCAO-MO procedure applied to H_2O and NH_3 does not give much insight into the reason why the two molecules adopt their particular bond angles. This must lie in the inclusion of the $2s$ -orbital of the central atom, because when it is excluded from the basis set we revert to the description of the molecule with which we began, and that leads to predictions of 90° for each. Analysing the source of the bending is not an essential part of the calculation of molecular structure, and many publications on polyatomic molecules simply quote the energies of states and the molecular geometry without looking for deeper reasons. Nevertheless, chemists do find it useful to build up rules of thumb which let them visualize what is happening inside molecules, and they like to try to relate sophisticated accounts of molecular structure to familiar, simpler versions. How, then, can we relate bond angles to the involvement of s -orbitals in molecular orbitals, especially when those orbitals appear to spread throughout the molecule? Is there some way of thinking of the structure of the molecule in terms of *individual bonds* identifiable with links between pairs of atoms?

The answer lies in the modification of the basis set to be used in the molecular orbital description. Instead of working with the $2s$ - and the $2p$ -orbitals themselves, we can form mixtures of them called *hybrid orbitals*, and then build the LCAO molecular orbitals from them. We shall see that the hybrids point in definite directions, just like the original set of p -orbitals in our initial description of H_2O and NH_3 , and so we can see very plainly why the molecules adopt their characteristic shapes.

Consider the hybrid orbitals that may be formed from the $2s$ -, $2p_z$ -, and $2p_y$ -orbitals lying in the plane of an H_2O molecule. We shall show that from them it is possible to construct two *equivalent* hybrids pointing along the directions of the bonds and a third hybrid pointing along the exterior bisector of the bond angle, and that the composition of the hybrids depends on the bond angle. The two criteria we use are (a) the orthogonality of the three hybrids and (b) the equivalence of the two pointing along the bonding directions (so that the C_{2v} symmetry is preserved). The axes are set out in Fig. 10.18.

Consider first the combination of p_y and p_z corresponding to a p -orbital pointing along one of the bonds. Since $p_y \propto y$ and $p_z \propto z$ it follows that

$$p = p_z \cos \frac{1}{2}\theta + p_y \sin \frac{1}{2}\theta. \quad (10.8.1a)$$

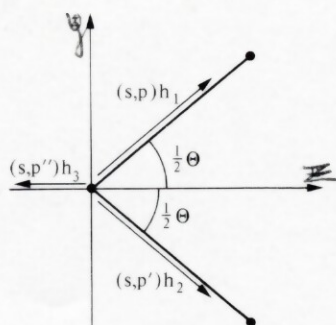


Fig. 10.18. The formation of hybrid orbitals in a C_{2v} system.

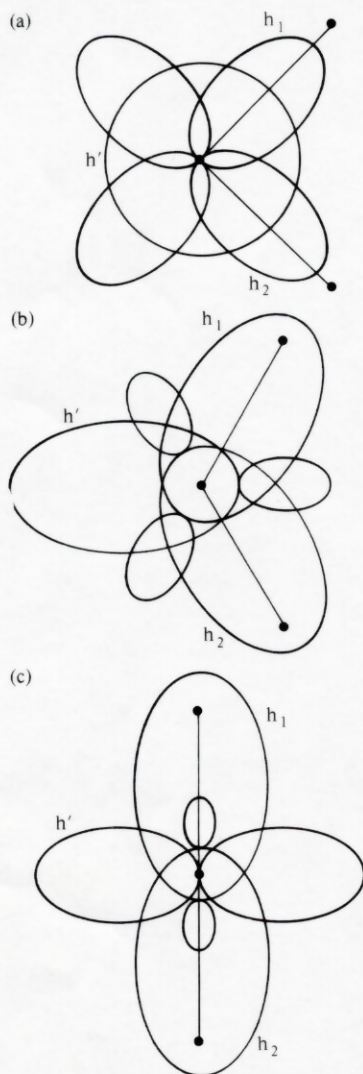


Fig. 10.19. Hybrid orbitals for $\theta =$ (a) 90° , (b) 120° , (c) 180° .

The equivalent p-orbital pointing along the other bond direction is

$$p' = p_z \cos \frac{1}{2}\theta - p_y \sin \frac{1}{2}\theta. \quad (10.8)$$

These two p-orbitals are not orthogonal (their overlap integral $\cos^2 \frac{1}{2}\theta - \sin^2 \frac{1}{2}\theta = \cos \theta$). They are made orthogonal by mixing in appropriate amount of s-character (we shall see that the proportion required is $\cos \theta$). We therefore write the two orthogonal, equivalent hybrids as

$$h_1 = as + bp, \quad h_2 = as + bp'. \quad (10.8)$$

Both hybrids should be constructed so that they are normalized unity (we have seen that this always simplifies expressions), and so require $a^2 + b^2 = 1$ (as s and p are individually normalized and mutually orthogonal). The orthogonality requirement translates into the following condition on the coefficients:

$$\begin{aligned} \int h_1 h_2 d\tau &= \int (as + bp_z \cos \frac{1}{2}\theta + bp_y \sin \frac{1}{2}\theta) \\ &\quad \times (as + bp_z \cos \frac{1}{2}\theta - bp_y \sin \frac{1}{2}\theta) d\tau \\ &= a^2 + b^2 \cos^2 \frac{1}{2}\theta - b^2 \sin^2 \frac{1}{2}\theta = a^2 + b^2 \cos \theta = 0. \end{aligned}$$

Therefore the two conditions give

$$\cos \theta = -a^2/(1-a^2), \quad \text{or} \quad a^2 = \cos \theta / (\cos \theta - 1). \quad (10.8.3)$$

As the angle changes from 90° to 180° the amount of s-character each hybrid increases from zero (pure p-orbitals when the bond angle is 90°) to 50 per cent s-character when the molecule is linear. In case of 104.45° , the experimental value for water, $a^2 = 0.20$, or 20 per cent s-character, and the hybrids are formed with $a = 0.45$ and $b = 0.89$. The third orthogonal hybrid that may be formed from the three basis orbitals is also orthogonal to the two just formed (but it is required to be equivalent to the first pair). It can be expressed in form $a's + b'p_z$, and little effort is needed to deduce that in this case

$$a'^2 = (1 + \cos \theta) / (1 - \cos \theta). \quad (10.8.4)$$

Therefore it changes from pure s when $\theta = 90^\circ$ to pure p when bonds are collinear ($\theta = 180^\circ$). The shapes of the hybrid orbitals as the angle changes are shown in Fig. 10.19: notice how their amplitudes are projected strongly into one direction. Notice too the special case $\theta = 120^\circ$ when all three hybrids are equivalent and have the composition $a^2 = \frac{1}{3}$, $b^2 = \frac{2}{3}$; these are called sp^2 -hybrids, the name reflecting s:p composition ratio.

Now consider the configuration an oxygen atom needs in order to form a molecule of bond angle θ . In general it is $2p_x^2 h'^2 h_1 h_2$. When the angle is 90° the hybrid h' is pure 2s and the pair of mutually equivalent

hybrids are pure $2p$; hence the configuration in this 'state of preparation' for bond formation, or *valence state*, to give a 90° molecule is $2s^2 2p_x^2 2p_1 2p_2$ and so overall the configuration is $2s^2 2p^4$.

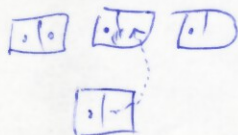
Now take the other extreme of possibilities, when the atom is in the valence state appropriate to forming a linear molecule. Since $\theta = 180^\circ$, h' is pure p_z while h_1 and h_2 are 50:50 mixtures of $2s$ and $2p_y$. The configuration is therefore $2p_x^2 2p_z^2 (2p_y^{\frac{1}{2}}, 2s^{\frac{1}{2}})(2p_y^{\frac{1}{2}}, 2s^{\frac{1}{2}})$ and so overall the configuration is $2s^2 2p^5$. The point that immediately appears is that in order to attain the valence state of a linear molecule, an electron has to be *promoted* from an s -orbital to a p -orbital. This is an energy disadvantage. When the bonds with the hydrogen atoms are formed, some of this promotion energy will be regained because Fig. 10.19 shows very clearly that as the s -character increases the distribution of amplitude increasingly favours strong overlap in the internuclear region. Therefore the strength of the resulting bond can be expected to increase as the hybridization increases the proportion of s -orbital.

Example. Find an expression for the valence configuration and extent of promotion of an $s^2 p^4$ atom needed to achieve two equivalent bonds making an angle θ .

- **Method.** Find an expression of the form $s^m p^n$ on the basis of eqns (10.8.3) and (10.8.4). The fraction of electron promoted is $n-4$.
- **Answer.** One bond hybrid is $s^{a^2} p^{b^2}$, the other is the same, and so together they account for $s^{2a^2} p^{2b^2}$ in the valence configuration. The lone pair of electrons accounts for $s^{2a'^2} p^{2b'^2}$. Another lone pair occupies p_x^2 . The overall valence configuration is therefore $s^{2a^2+2a'^2} p^{2b^2+2b'^2+2}$. Since $b^2 = 1-a^2$ and $b'^2 = 1-a'^2$ the configuration is $s^{2(a^2+a'^2)} p^{2(3-a^2-a'^2)}$. From eqns (10.8.3-4), $a^2 + a'^2 = 1/(1-\cos\theta)$, and so the valence configuration for a bond angle θ is $s^{2/(1-\cos\theta)} p^{2(2-3\cos\theta)/(1-\cos\theta)}$. The extent of promotion is $\{(2-3\cos\theta)/(1-\cos\theta)\} - 4 = 2\cos\theta/(\cos\theta - 1)$.
- **Comment.** The extent of promotion changes from 0 (at $\theta = \pi/2$) to 1 (at $\theta = \pi$), the configurations being $s^2 p^4$ and $s^1 p^5$ respectively. The *hybridization ratio* of the bond hybrids is $b^2/a^2 = -1/\cos\theta = -\sec\theta$, and so they are $sp^{-\sec\theta}$ -hybrids (e.g. sp -hybrids when $\theta = \pi$).

We can now see there is a competition. On the one hand it is energetically disadvantageous to promote the atom to its valence state. On the other hand, when it is promoted it is able to form stronger bonds on account of the improved overlap of hybrid orbitals. There is also an advantageous decrease in the electrostatic bond-bond repulsions when they move apart from 90° . It is then easy to see that there must be a compromise: there is a degree of promotion, not complete, such as to bring about the greatest net lowering of the energy of the molecule, and the molecular geometry reflects its extent. In the case of H_2O the optimum energy is obtained when there is the equivalent of 20 per cent promotion of an s -electron; in which case the hybridization corresponds to a bond angle of just over 104° .

The structure of NH_3 can be accounted for in the same way. The configuration of the unpromoted nitrogen atom is $2s^2 2p^3$. If we impose on the atom the requirement that the bonds should be built from three



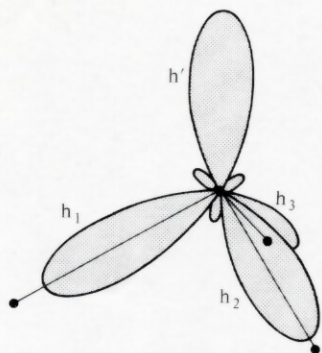


Fig. 10.20. Hybrid orbitals in NH_3 ; h_1 , h_2 , and h_3 are equivalent.

equivalent hybrid orbitals pointing towards the corners of an equilateral triangle and a fourth directed along the 3-fold axis, Fig. 10.20, then in order to achieve the valence state $h'^2h_1h_2h_3$ some degree of promotion is necessary, and it depends on the angle between the hybrids. When the molecule is flat its valence state has the configuration $2s2p^4$, corresponding to the complete promotion of an s-electron. Partial promotion of an s-electron results in the formation of hybrid orbitals forming a triangular pyramid. A fairly straightforward calculation shows that when the bond angle is 107° (the experimental angle for NH_3) the valence configuration is $2s^{1.22}2p^{3.78}$, corresponding to 78 per cent promotion. This compromise value represents the competition between promotion energy investment and bonding energy gain as a consequence both of the enhanced overlap, and of the modification of the repulsive interactions between the bonding and non-bonding electrons in the molecule (the three N—H bonds are now further apart, and so interact less strongly).

The most striking example of hybridization is the carbon atom, which in its ground state has the configuration $2s^22p^2$. In the case of methane, CH_4 , we expect four equivalent orbitals pointing towards the corners of a regular tetrahedron. This is a special case of a triangular pyramid (as in NH_3), because now all four hybrids are equivalent and the inter-bond angles are all $109.47^\circ (= \arccos(-\frac{1}{3}))$. The same techniques as before (mutual orthogonality but identical compositions) leads to the following forms of the hybrids in this special case:

$$\begin{aligned} h_1 &= s + p_x + p_y + p_z, & h_2 &= s + p_x - p_y - p_z \\ h_2 &= s - p_x + p_y - p_z, & h_3 &= s - p_x - p_y + p_z. \end{aligned} \quad (10.8.5)$$

These hybrids are illustrated in Fig. 10.21; because they consist of 1 part s-orbital to 3 parts p-orbital they are called sp^3 -hybrids.

An atom of carbon in its tetrahedral valence state has the configuration $h_1h_2h_3h_4$, and since each hybrid is $\frac{1}{4}$ s-electron and $\frac{3}{4}$ p-electron, overall this configuration is sp^3 , representing a promotion of an *entire* s-electron from the ground configuration. In the case of carbon there are special reasons why the promotion of an electron is energetically less disadvantageous than in nitrogen and oxygen. In the first place, the promotion can be regarded as taking place from an s-orbital into an *empty* p-orbital. In the case of oxygen ($2s^22p^4$) and nitrogen ($2s^22p^3$) the promoted electron has to enter an already half full orbital and suffer greater electron–electron repulsion. Therefore less promotion energy is required in carbon than in either nitrogen or oxygen. Next, *four* bonds (of enhanced strength) may be formed from the $2s2p^3$ configuration, whereas only three may be formed in the case of nitrogen or two for oxygen. Furthermore, the electrostatic repulsions between electrons in four different bonds are minimized when they adopt a tetrahedral arrangement. Therefore there is a greater gain to offset the promotion energy in the case of carbon, and it occurs readily. This accounts for the huge array of tetrahedral carbon compounds.

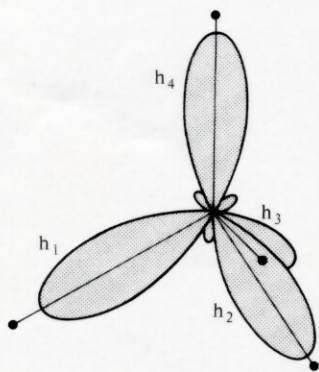


Fig. 10.21. sp^3 -hybrid orbitals; h_1 , h_2 , h_3 , and h_4 are equivalent.

When thinking about the promotion of an atom to its valence state do not think of the atom as 'undergoing' first promotion and then bonding. The two occur together: as the hydrogen atoms approach, the entire system evolves towards its state of lowest energy. Indeed, the valence state is not even a spectroscopic state. This is because the four electrons (in sp^3) have spin directions that are random with respect to each other, and the overall angular momentum of the atom is not well defined. The valence state can be regarded as a linear combination of spectroscopic states, and for the carbon atom its description is

$$\left(\frac{1}{8}\right)\{2.5^{\frac{1}{2}}(sp^3\ ^5S) + 3(p^4\ ^3P) + 3.2^{\frac{1}{2}}(sp^3\ ^3D) - 3(s^2p^2\ ^3P) - 3^{\frac{1}{2}}(p^4\ ^1D) - 2^{\frac{1}{2}}(sp^3\ ^1D) + 3^{\frac{1}{2}}(s^2p^2\ ^1D)\}.$$

Furthermore, hybridization is not a *necessary* component of the description of the structures of polyatomic molecules. The structure of the methane molecule, for instance, can be described in LCAO-MO terms using the basis functions $2s$, $2p_x$, $2p_y$, $2p_z$ on the carbon atom. It is only when we want to think in terms of the various contributions to the energy that it is sometimes convenient to use an alternative basis expressed as a linear combination of the primitive basis. The final expressions, energies, and so on, are entirely equivalent, but one form may be intuitively more appealing (and easier to analyse) than the other.

10.9 Conjugated π -systems

A special class of polyatomic molecules are those containing π -bonded atoms, especially the conjugated polyenes and aromatic molecules based on benzene. They fall into a unique class because the σ -bonds and the π -bonds can (to some extent) be discussed individually. One reason is that the electrons in π -bonds are generally less strongly bound than those in the σ -bonds, and so to some extent can be discussed separately. Another is that since π -bonds are often found in extensive planar molecules, they have symmetry properties different from the σ -bonds, and therefore span different irreducible representations of the molecular point group; as a consequence the secular equations factorize and they can be discussed separately.

The simplest π -system is that in the ethene molecule. Ethene can be regarded as the combination of two CH_2 fragments with sp^2 -hybrid bonds forming the σ -framework and the remaining p-orbitals of the carbon valence shell overlapping to form a π -bond. The maximum overlap between the two 2p-orbitals in the π -bond is achieved when the planes of the CH_2 groups are parallel. Any deviation from this conformation involves raising the energy of the molecule, and so we have a very simple explanation of the *torsional rigidity* of π -bonded molecules.

When the π -system is *conjugated* (i.e. there are p-orbitals on several neighbouring atoms capable of forming an extended system of π -orbitals, as in benzene) the simplest description of the bonding is in