(4-23) and ϕ_3 to $-\sqrt{\frac{3}{2}}\phi_2 - \frac{1}{2}\phi_3$ (4-24). Degenerate orbitals must always therefore be treated as a pair and never individually.

4-23

4-24

(ii) Although the symmetry operation does not transform each degenerate orbital into itself or minus itself, the new orbital has the same energy as the starting one. In effect, if ϕ_i and ϕ_j are two functions of the same energy then all normalized linear combinations of the type $\lambda\phi_i + \mu\phi_j$ are equally good functions with the same energy (see Section 2.1.2c).

(iii) This leads us to conclude that the degenerate orbitals which we obtained for systems such as square planar H_4 (Figure 4.1) and triangular H_3 (Figure 4.5) represent just one solution out of a whole host of possibilities. In general one can replace such pairs of orbitals with a pair of linear combinations of the form

$$\phi_i' = \phi_i \cos\theta + \phi_j \sin\theta$$
$$\phi_j' = -\phi_i \sin\theta + \phi_j \cos\theta$$

We can easily show that the MOs ϕ_i' and ϕ_j' are normalized and orthogonal just like ϕ_i and ϕ_j themselves. In the cases of square planar H_4 (4-21 and 4-22) and triangular H_3 (4-23 and 4-24) described above, rotation about the C_4 or C_3 axis respectively transforms the initial pair of degenerate orbitals into an exactly equivalent pair which may be derived by using $\theta = \pi/2$ and $2\pi/3$ respectively in these formulae.
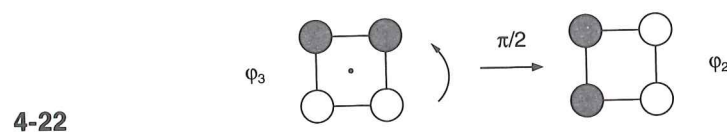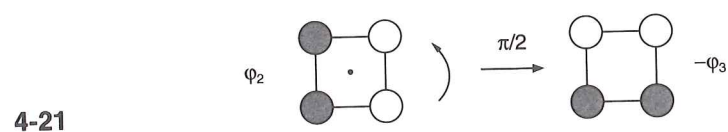
APPENDIX

Degenerate orbitals

In several of our model systems, including square H_4 and triangular H_3, some of the orbitals are degenerate, i.e., they have the same energy. We find degenerate orbitals such as these in geometries where there is a rotation axis of order higher than two. Obviously the triangle and the square have axes of order three and four respectively. Besides their energetic degeneracy these MOs have a number of other characteristics.

(i) As a result of a symmetry operation an MO is usually transformed into itself (symmetric) or into minus itself (antisymmetric). So for H_4 a rotation of $2\pi/4 = \pi/2$ around the z axis (this is the four-fold rotation axis perpendicular to the plane of the molecule) transforms ϕ_1 into ϕ_1 (4-19) and ϕ_4 into $-\phi_4$ (4-20). The situation
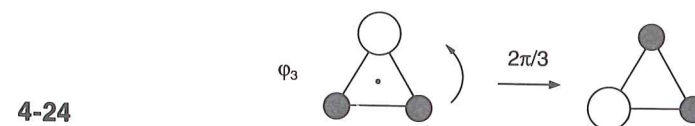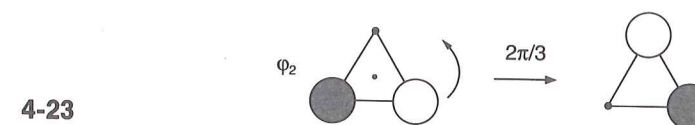
4-19

4-20
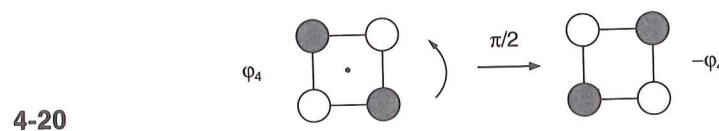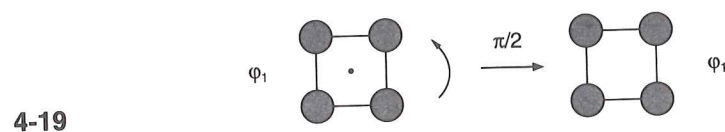
is different for the degenerate orbitals ϕ_2 and ϕ_3. They are transformed into each other, namely $\phi_2 \rightarrow -\phi_3$ (4-21) and $\phi_3 \rightarrow \phi_2$ (4-22). The same holds for p_x and p_y orbitals located at the center of the square ($p_x \rightarrow p_y$ and $p_y \rightarrow -p_x$). In a very

4-21

4-22

general way certain symmetry operations transform degenerate MOs into linear combinations of the starting functions. Taking, for example, triangular H_3, one can show that a rotation of $2\pi/3$ around the z axis (C_3) takes ϕ_2 to $-\frac{1}{2}\phi_2 + \sqrt{\frac{3}{2}}\phi_3$

5   Interactions between two fragment orbitals: linear AH_2, trigonal AH_3 and tetrahedral AH_4

When combined with symmetry ideas the fragment orbital method leads to the determination of the molecular orbital diagrams of many simple molecules. In this chapter we will study some molecules which have orbital diagrams which may be assembled by the interaction of pairs of orbitals, one from each fragment. We will derive the level structures of linear AH_2, trigonal planar AH_3 and tetrahedral AH_4 molecules (5-1) in which A is an element from the second or third row of the periodic
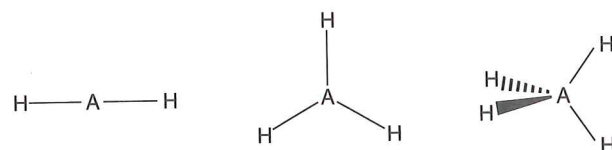
5-1

table. We assume that all the A—H distances are equal and only use the valence orbitals on the atoms concerned. These are thus the $1s$ orbitals on the hydrogen atoms and the ns and np orbitals ($n = 2$ or 3) for the A atoms. The core orbitals are ignored. As we have noted earlier since they lie very deep in energy and their overlap integrals with other orbitals is tiny, their influence on bond formation is negligible.

A vital aspect of our analysis concerns the symmetry properties of the orbitals concerned. We will gradually introduce the symmetry labels for orbitals of various types as the chapter progresses. Although these formally come from group theory, as we will see, no knowledge of the mathematics behind them is needed.

The molecules to be studied (5-1) have the common property of being able to be decomposed into the two fragments, A and H_n (H_2, triangular H_3 and tetrahedral H_4) whose orbitals we have already described in Chapter 4. In each case the MOs will be generated by allowing the interaction of pairs of orbitals which have the same symmetry properties. These, as we saw in Chapter 3 are the only pairs of orbitals which have a non-zero overlap integral. If the principle itself is simple, its application sometimes poses problems when some of the fragment orbitals are degenerate as in triangular H_3 and tetrahedral H_4. It turns out that the use of one or two symmetry planes is not sufficient to completely characterize the orbital symmetry. This is a

consequence of the rather simple approach to the molecular orbital problem used in this book, but we will be able to make analogies between the symmetry properties of the central atom orbitals and the molecular orbitals of the H_n fragments to produce a readily understandable picture.

5.1. Linear AH_2 molecules

We divide the molecule into two fragments; a pair of non-bonded atoms $H_a \ldots H_b$ which give rise to the orbitals σ_{H_2} (bonding) and $\sigma_{H_2}^*$ (antibonding), and a central atom A on which we keep the valence orbitals s, p_x, p_y and p_z. The internuclear axis is chosen as z. (Although ns orbitals ($n \geq 2$) have radial nodes as shown in 2-6 for the $2s$ function, we shall ignore these in generating our orbital diagrams. Only the overlap with the outermost part of the orbital is chemically important at normal internuclear distances.)

### 5.1.1. Symmetry properties of the fragment orbitals

Consider the collection of symmetry elements the two fragments have in common. This is effectively the collection of symmetry operations for the linear AH_2 molecule. There are an infinite number of these. For example all planes which contain the z-axis are planes of symmetry for the two fragments (5-2). In the same way a rotation of any
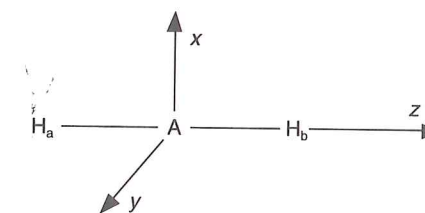
5-2

angle around z leaves the positions of the nuclei unchanged. Other elements of symmetry include the xy plane perpendicular to z and containing the atom A, the inversion center, i, located at A, etc. A general treatment of the symmetry problem would study the behavior of the orbitals as a result of all of these symmetry operations but we will content ourselves here by making a judicious selection of just one symmetry element which will allow us to provide a symmetry classification good enough to be able to decide which pairs of orbitals may interact via non-zero values of their overlap integral.

The p_x orbital on A (5-3) is antisymmetric (A) with respect to the yz plane, a nodal plane of this orbital. Contrarily the orbitals σ_{H_2} and $\sigma_{H_2}^*$ are symmetric (S) with

**5-3** p_x (A) σ_{H_2} (S) $\sigma_{H_2}^*$ (S)
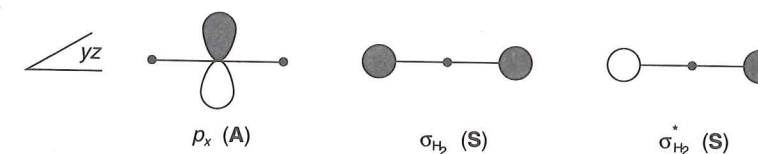
respect to this plane. Thus there is no interaction between this p orbital and these two hydrogen located orbitals since the overlap integral is zero by symmetry. In the same way their behavior with respect to reflection in the xz plane shows that the p_y orbital (A) may interact (5-4) with neither σ_{H_2} nor $\sigma_{H_2}^*$ (S). This result was discussed

5-4 p_y (A) σ_{H_2} (S) $\sigma_{H_2}^*$ (S)
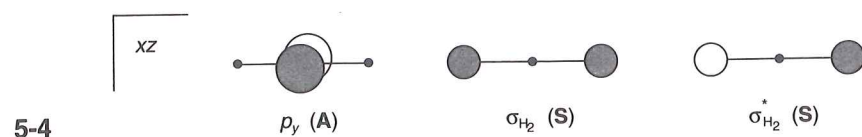
in Section 3.4.4a; the overlap between a p orbital and an s orbital lying in its nodal plane is zero.

We need now to consider the possible interaction between the s and p_z orbitals on the central atom and the σ_{H_2} and $\sigma_{H_2}^*$ orbitals on $H_a \ldots H_b$. For these we will make use of the xy plane. It is clear to see (5-5) that both s and σ_{H_2} are symmetric

5-5 s (S) σ_{H_2} (S) p_z (A) $\sigma_{H_2}^*$ (A)
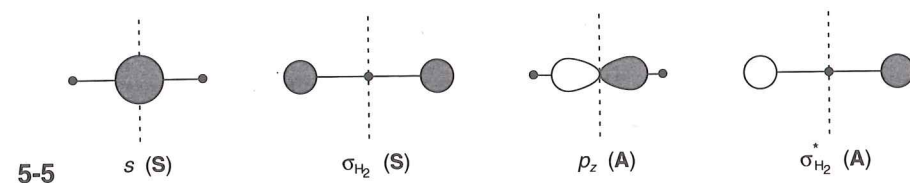
with respect to this plane, but p_z and $\sigma_{H_2}^*$ are both antisymmetric (A). It is simple to show that the overlap integrals associated with these interactions are non-zero. In each case (5-6 and 5-7) the overlap integral of the central atom orbital with each of the hydrogen atoms is positive, so that the total overlap integral is different from zero.

5-6 $S \neq 0$ 5-7 $S \neq 0$

The construction of the molecular orbital diagram for the linear AH_2 molecule thus consists of two pairs of interactions between two fragment orbitals (5-8). The positions of the AO energy levels depend of course on the nature of A but those shown will be sufficient for our needs. This interaction scheme though applies to any linear AH_2 molecule.

5-8
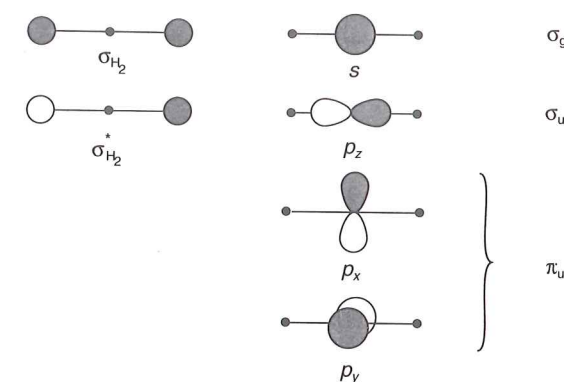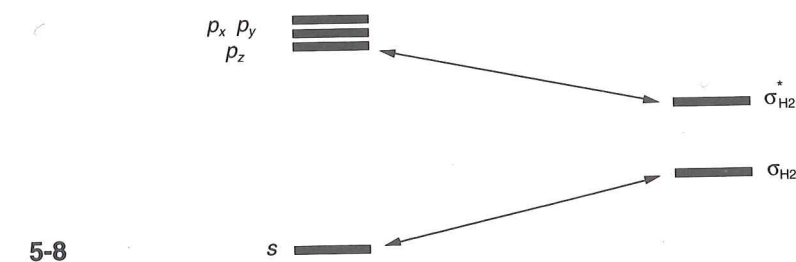
5-9

5-9 shows a common labeling scheme for the set of orbitals under consideration, using the conventions of group theory. The orbitals σ_{H_2}, $\sigma_{H_2}^*$, s and p_z are all symmetric with respect to rotation about the z-axis, that is to say they remain unchanged as a result of any rotation about this axis. They are each labeled by σ. The σ_{H_2} and s orbitals are symmetric with respect to inversion and are thus labeled σ_g; the $\sigma_{H_2}^*$ and p_z orbitals are antisymmetric with respect to inversion and are thus labeled σ_u. The pair of orbitals p_x, p_y are not symmetric with respect to rotation about z and are antisymmetric with respect to inversion. They are labeled as π_u.

5.1.2. MOs for linear AH_2 molecules

The construction of the interaction diagram relies both on the symmetry properties of the fragment orbitals and their relative energies. In the linear AH_2 molecule the hydrogen atoms are far apart. Accordingly since the overlap integral between the two $1s$ orbitals is small the energies of the σ_{H_2} and $\sigma_{H_2}^*$ orbitals are similar and close to that of the energy of an isolated hydrogen $1s$ orbital. The σ_{H_2} orbital (bonding) lies a little lower in energy than $\sigma_{H_2}^*$ (antibonding). The energies of the s and p orbitals depend upon the nature of A. The more electronegative A, the deeper these levels lie. The values used in Figure 5.1 are those appropriate for beryllium ($\varepsilon_{2s} = -9.4$ eV; $\varepsilon_{2p} = -6.0$ eV).

The molecular orbital diagram is assembled simply by pairing up those orbitals on the two framents with the same symmetry. Thus the s and σ_{H_2} orbitals (σ_g) interact to give bonding ($1\sigma_g$) and antibonding ($2\sigma_g$) orbitals. In the same way interaction between p_z and $\sigma_{H_2}^*(\sigma_u)$ leads to a bonding ($1\sigma_u$) and antibonding ($2\sigma_u$) pair. The p_x and p_y orbitals are not changed in energy since they do not find a symmetry matched with the $H_a \ldots H_b$ fragment. They become the degenerate, π_u MOs of the molecule. We still call them molecular orbitals even though they are localized on one atomic center.

The molecular orbitals thus fall into three groups (5-10).

(i) Two MOs bonding between the central atom and the hydrogen atoms, built from the in-phase combination of the fragment orbital pairs s and σ_{H_2}, and p_z and $\sigma_{H_2}^*$. Of these orbitals the lowest, $1\sigma_g$, is that derived from the fragment orbital which lies lowest in energy.
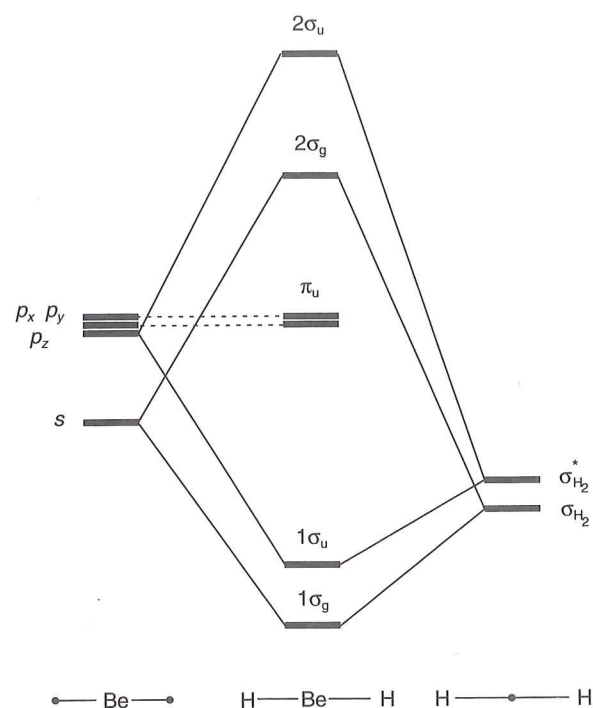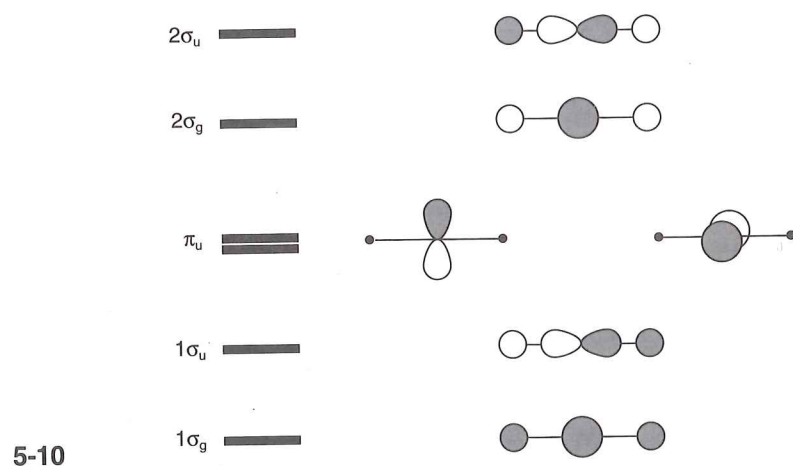
Figure 5.1. Construction of the MOs of a linear AH_2 molecule. (The relative AO energies are appropriate for A = Be.)


(ii) Two MOs, antibonding between the central atom and the hydrogen atoms ($2\sigma_g$ and $2\sigma_u$) built from the out-of-phase combinations of these same fragment orbitals.

(iii) Between these two groups, two degenerate MOs completely localized on the central atom, and therefore with no contribution from the hydrogen atom orbitals. Such orbitals are called nonbonding orbitals.

Although the details of the molecular orbital diagram depend upon the nature of the central atom, this general description in terms of two bonding, two nonbonding and two antibonding orbitals is a general one, applicable to all linear AH_2 molecules.

5.1.3. Application to BeH_2

BeH_2 is a linear triatomic molecule which has four valence electrons. In its electronic ground state the lowest two orbitals, $1\sigma_g$ and $1\sigma_u$ are therefore doubly occupied to give the configuration $1\sigma_g^2 1\sigma_u^2$ (**5-11**). These two orbitals are bonding between the

5-11
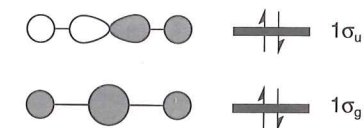
central atom and the hydrogens. With two bonding pairs of electrons we should expect two Be—H bonds as indeed indicated by the Lewis structure H—Be—H. Notice however, that it is not possible to identify one doubly occupied bonding orbital with one Be—H bond, and the other with the second Be—H bond. Each bonding MO is equally associated with both Be—H bonds. The one $2p$ ($2p_z$) and one $2s$ orbital on beryllium are then equally associated with each Be—H linkage in the bonding orbitals in which they are involved. We say that these orbitals and the electrons in them are *delocalized* over the whole molecule in contrast to the localized viewpoint of the Lewis structure.

The pattern of ionization energies for BeH_2 leads to some further insight into this delocalized view of the bonding problem. From Figure 5.1 it is clear that the ionization energy depends upon the origin of the ejected electron. The ionization energy from the $1\sigma_g$ orbital is larger than that from $1\sigma_u$. From the Lewis viewpoint one might have expected just a single ionization energy. Thus, although the two Be—H bonds are equivalent in every way the molecular orbitals which describe them are not. Later in the Appendix to Chapter 8 we will show an interesting connection between the two viewpoints.

5.2. Trigonal planar molecules

The natural fragmentation of the AH_3 molecule, where the angles between the A—H bonds are $120°$, is into a central A atom and a collection of three H atoms at the corners of an equilateral triangle. We described the energy levels of such an H_3 unit in the previous chapter. The levels of the A atom to be used are just the valence s and p orbitals.

### 5.2.1. Symmetry properties of the fragment orbitals

The two fragments, A and H_3 have many symmetry elements in common, among them (**5-12**) the molecular plane (xy), three two-fold rotation axes (x being one of them) collinear with the A—H bonds, three symmetry planes perpendicular to the
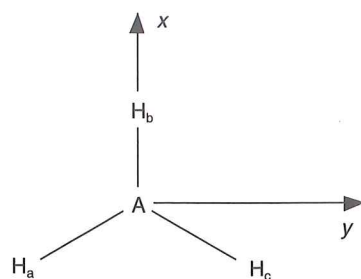
5-12

mirror plane and containing an A—H bond (xz for example) and the z-axis which is a three-fold rotation axis. From all of these symmetry elements we will only keep the molecular plane (xy) and the xz plane in order to characterize the symmetry of the molecular orbitals. In doing this we 'reduce' the symmetry of the system (since the number of symmetry elements has decreased) but as we will see this new set will be sufficient for our needs.

All of our fragment orbitals will be either symmetric (S) or antisymmetric (A) with respect to reflection in these planes of symmetry. So there is just one AS orbital (p_z) which is antisymmetric with respect to xy but symmetric with respect to xz (**5-13**)
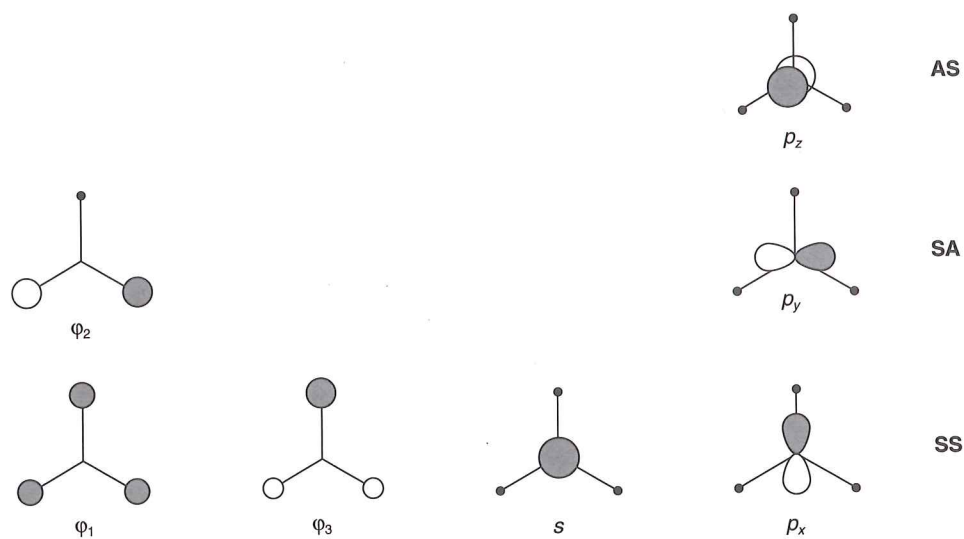
5-13

two SA orbitals (ϕ_2 and p_y) and four SS orbitals (ϕ_1, ϕ_3, s and p_x). This preliminary analysis allows us to separate the fragment orbitals into three groups (**5-13**). Orbitals in one group may not interact with orbitals from another since their symmetry properties with respect to one or other of the planes xy or xz are different. One can conclude therefore that the p_z orbital, the only orbital of **AS** symmetry, cannot take part in any interaction. We now have to determine whether the overlaps between

orbitals from within the same group are different from zero. In effect, if it turns out that a pair of orbitals have different behavior with respect to a symmetry element ignored in the simple treatment, then the overlap is of course zero. The overlap between the orbitals ϕ_2 and p_y (AS) is non-zero since the contributions from p_y–$1s_H$ overlap are both of the same sign (**5-14**). But now consider the case of four orbitals of SS symmetry. For the pairs (s, ϕ_1) and (p_x, ϕ_3) the overlaps involved are different from zero since all the contributions between the central orbital and each of the $1s_H$ orbitals are of the same sign (**5-15** and **5-16**). However, consider the overlap integrals between s and ϕ_3 and between p_x and ϕ_1. The first of these (**5-17**) is made up of a positive contribution from s and $1s_b$ and two negative contributions from s and $1s_a$ and $1s_c$. Since the coefficient of $1s_b$ is twice as large, in an absolute sense, than the coefficients of $1s_a$ and $1s_c$ (see Section 4.1.5) the total overlap integral is identically zero. A similar situation holds (**5-18**) for the overlap between p_x and ϕ_1. The three
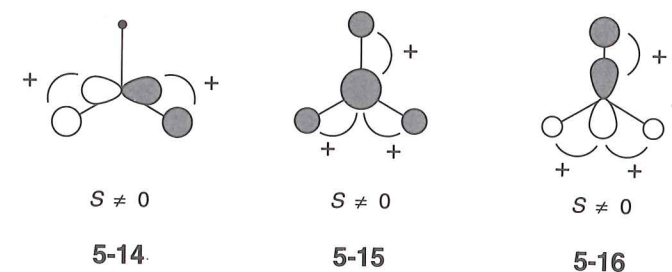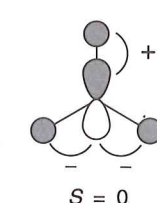

**5-14**   **5-15**   **5-16**
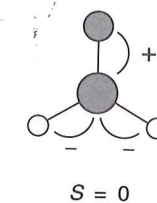
5-17   **5-18**

coefficients on the hydrogen atoms are equal in ϕ_1 but the overlap integral with p_x varies as the cosine of the angle the A—H bond makes with the x-axis (see Section 3.4.3). Thus there is one positive overlap (where this angle is zero) and two negative overlaps (where this angle is $\pm 120°$). Thus the total overlap integral is proportional to $\cos(0°) + \cos(120°) + \cos(-120°) = 1 - \frac{1}{2} - \frac{1}{2} = 0$.

We should point out at this stage that the zero overlap integral between orbitals of the 'same symmetry' (SS) is a consequence of the reduction in symmetry we used to make this problem tractable. The two pairs of orbitals, (s, ϕ_1) and (p_x, ϕ_3) do in fact have different symmetry if all of the symmetry elements are used.

In order to construct a molecular orbital diagram for the AH_3 molecule we use the same technique employed for the linear AH_2 system, namely only fragment orbitals with non-zero overlap may interact. This reduces the orbital problem to one

of interactions between the three pairs of orbitals, s and ϕ_1, p_y and ϕ_2 and p_x and ϕ_3 as shown in **5-19**. The p_z orbital is not involved in any interaction. The actual
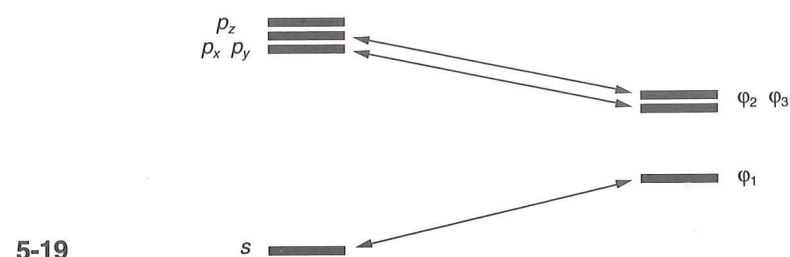
5-19

form of the diagram will vary from one AH_3 molecule to another since the energies of the central atom s and p orbitals depend upon the identity of A, but the interactions shown are the same irrespective of the identity of the system.

As described before for the AH_2 molecule we usually attach group theoretical labels to describe the orbitals of the fragment. The s orbital is labeled a'_1. Here, a describes a non-degenerate level, just as σ did in the linear molecule, and the single prime a function symmetric with respect to reflection in the plane perpendicular to the three-fold axis (z). The p_z orbital is labeled a''_2, antisymmetric with respect to reflection. The pairs of degenerate levels carry an e label, just like the label π in linear molecules. Both p_x, p_y and ϕ_2, ϕ_3 are labeled e' (**5-20**) although we will want to distinguish e'_x (p_x and ϕ_3) and e'_y (p_y and ϕ_2).
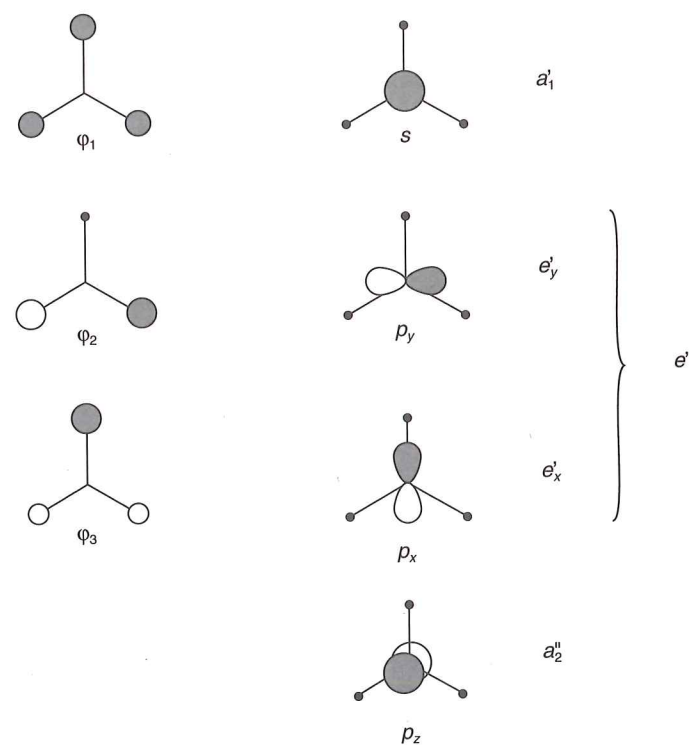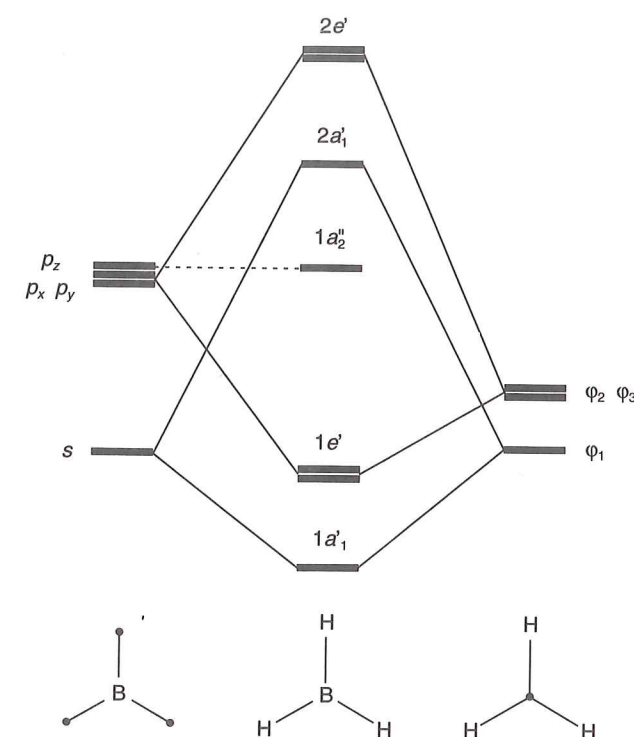

5-20

Figure 5.2. Construction of the MOs of a trigonal planar AH_3 molecule. (The relative AO energies are appropriate for A = B).

5.2.2. MOs of trigonal planar AH_3

The fragment orbital interaction diagram of Figure 5.2 corresponds to that for BH_3 where $\varepsilon_{2s} = -14.7$ eV and $\varepsilon_{2p} = -5.7$ eV. The energies of the H_3 fragment orbitals straddle the energy of an isolated $1s_H$ orbital, since ϕ_1 (bonding) lies a little below and ϕ_2 and ϕ_3 (antibonding) a little above. Their splitting is small since the interaction between the hydrogen $1s$ orbitals is small as a result of the large H—H separation. First of all we readily see that the p_z orbital ($1a''_2$) is unchanged in energy. The orbitals ϕ_1 and $2s$, both of a'_1 symmetry, interact to give a bonding orbital ($1a'_1$) and an antibonding orbital ($2a'_1$). Similarly the orbital pairs, ϕ_3 and p_x (e'_x), and ϕ_2 and p_y (e'_y) interact to give a bonding pair ($1e'_x$ and $1e'_y$) and an antibonding pair ($2e'_x$ and $2e'_y$). The orbitals $1e'_x$ and $1e'_y$ are degenerate, as are $2e'_x$ and $2e'_y$; as shown in exercise 5.1, since the overlap integrals associated with the x and y partners of a degenerate pair are equal the resultant molecular orbitals are degenerate. The origin of this degeneracy comes just as in triangular H_3 from the presence of a three-fold rotation axis in the molecule.

The MOs of trigonal planar molecules thus divide into three groups (**5-21**).

(i) Three MOs bonding between the central atom and the hydrogen atoms. These are $1a'_1$, $1e'_x$ and $1e'_y$, in-phase combinations of the fragment orbitals (ϕ_1, s),

5-21
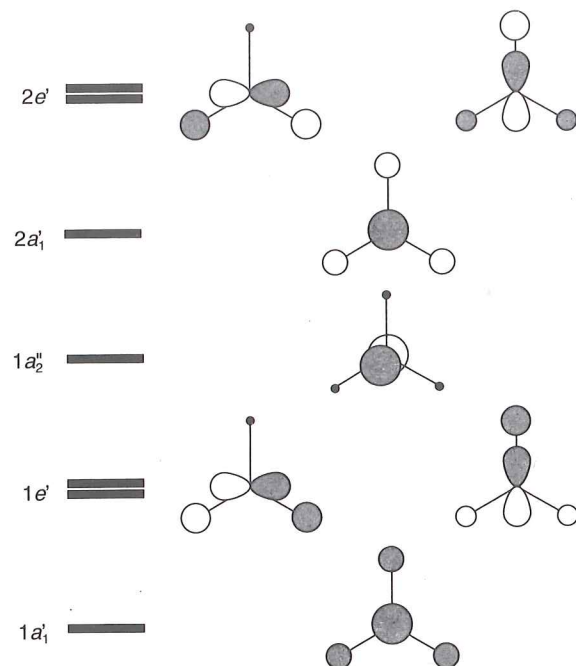
(ϕ_2, p_y) and (ϕ_3, p_x) respectively. The deepest lying orbital, $1a_1'$ is the one that comes via interaction of the deepest lying fragment orbitals.

(ii) Three MOs antibonding between the central atom and the hydrogen atoms. These are $2a_1'$, $2e_x'$ and $2e_y'$ and are the out-of-phase combinations of the fragment orbitals.

(iii) Between these two groups there is a non-bonding orbital ($1a_2''$), completely localized on the central atom without any hydrogen atom contribution.

5.2.3. Application to the electronic structure of BH₃

BH₃ is a short-lived molecule, rapidly dimerizing to give B_2H_6, although many of the reactions of the latter may be understood via an equilibrium between the two but lying very much in favor of the dimer. It is a trigonal planar molecule with six valence electrons. In its electronic ground state the three lowest energy levels are doubly occupied to give (**5-22**) $1a_1'^2 \, 1e_x'^2 \, 1e_y'^2$. These three orbitals are bonding between the central atom and the hydrogen atoms thus providing a connection to the Lewis structure with three B—H bonds each made up of two electrons. However, as before for AH₂, although it is not possible to identify the two electrons in one particular MO with a particular B—H bond, the *collection* of three doubly occupied bonding orbitals gives rise to three chemical bonds. Obviously in $1a_1'$ each of the hydrogen atoms are bonded equally to the central atom since the corresponding overlap integrals are equal. The situation is more complex in the $1e'$ pair. $1e_y'$ is only bonding between the boron atom and two of the hydrogen atoms (H_a and H_c) since the coefficient on H_b is zero. Contrariwise the $1e_x'$ orbital is largely bonding between boron and H_b. In this orbital the coefficient on H_b is twice as large as those on H_a
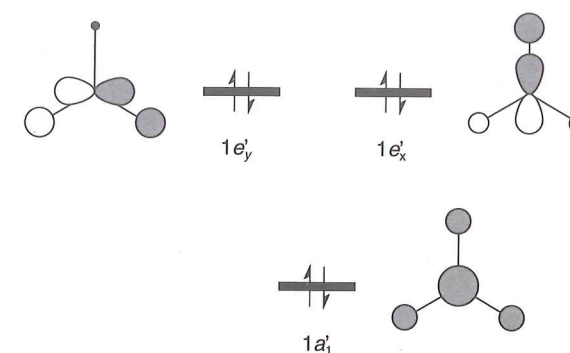
5-22

and H_c. In addition the $2p_x$ orbital points directly at H_b and so its overlap will be larger than with H_a or H_c. In fact if one considers the orbitals $1e_x'$ and $1e_y'$ as a pair one can show that they lead to equal bonding character between the central atom and each of the hydrogen atoms. Thus consideration of the trio of doubly occupied bonding orbitals leads to the conclusion that the three B—H bonds are equivalent in every way. However the three molecular orbitals which lead to this picture are not energetically equivalent (**5-22**). It is easier to eject an electron from the $1e'$ level than it is from the $1a_1'$ level. There are then two different ionization energies for the molecule which depend upon the origin of the ionized electron. We must once again clearly recognize the equivalence of three B—H bonds which arise via the occupation of three clearly non-equivalent orbitals.

A final point merits mention. The lowest unoccupied orbital in BH₃ is a non-bonding p orbital ($1a_2''$). This orbital, vacant and low in energy, is susceptible to donation by a pair of electrons. If this electron pair is associated with an H⁻ ion such that $BH_3 + H^- \rightarrow BH_4^-$, then we can readily see the origin of the Lewis acid properties of such a species.

5.3. Tetrahedral AH₄ molecules

The natural decomposition for a tetrahedral AH₄ molecule is into a central A atom and a tetrahedron of hydrogen atoms. The levels of the latter, a tetrahedral H₄ unit were studied in the previous chapter. The fragment orbitals for the atom A are just its valence s and p orbitals.

### 5.3.1. Symmetry properties of the fragment orbitals

The fragments A and H₄ have many symmetry elements in common, among them (**5-23**) six planes of symmetry containing two A—H bonds (xz and xy are two
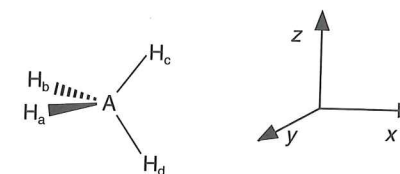
5-23

examples), three C_2 axes which bisect opposite pairs of H—A—H angles (x for example) and four C_3 axes collinear with the A—H bonds. As before we will just retain two planes (xz and xy) in order to distinguish between the orbitals concerned.

There are two SA orbitals (ϕ_4 and p_z) symmetric with respect to xz and antisymmetric with respect to xy, two AS orbitals (ϕ_3 and p_y) and four SS orbitals (ϕ_1, ϕ_2, s and p_x) as shown in 5-24. The fragment orbitals thus separate into three
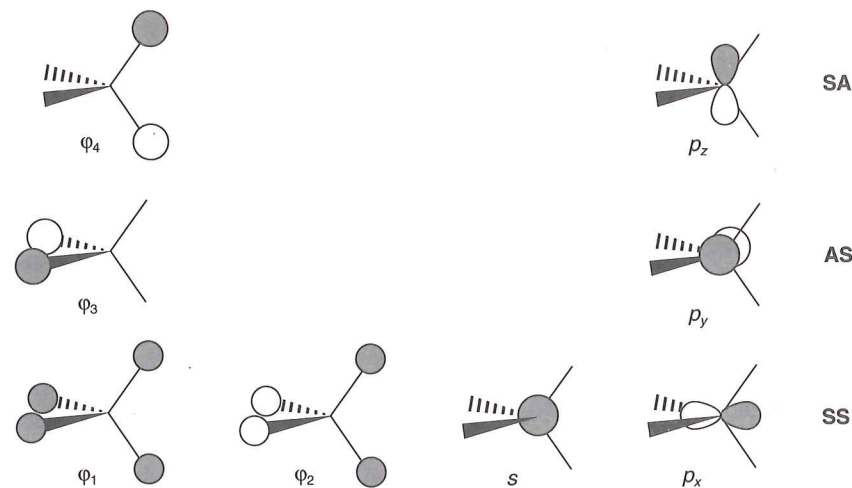

5-24

groups. Recall that orbitals belonging to different groups may not interact, but we still have to look carefully at the overlaps between orbitals within each group. We can see that overlap between the p_z and ϕ_4 orbitals is non-zero since the individual overlaps between p_z and $1s_H$ orbitals are of the same sign (5-25). The same is true for p_y and ϕ_3 (5-26). For the orbitals of SS symmetry we need to consider the two pairs (s, ϕ_1) and (p_x, ϕ_2). In each case since all of the individual overlaps between $1s_H$ orbitals and the central atom orbital are of the same sign (5-27 and 5-28) the total overlap integral is non-zero and the orbitals within each pair may interact. This is not the case for the overlap between (s and ϕ_2) and (p_x and ϕ_1). Just as we showed for the related AH$_3$ case, the overlap integrals between these pairs are identically zero (5-29 and 5-30). In both cases the two positive overlap integrals are exactly cancelled by the two negative overlap integrals. Also, as in AH$_3$, these zero overlap integrals between orbitals of the 'same symmetry' come about because of the reduction of the tetrahedral symmetry to just the two planes xz and yz. Use of the full symmetry removes this problem. In conclusion, just as in all of the preceding examples, only the orbitals of the same symmetry, with non-zero overlap may interact.

The construction of the molecular orbital diagram for tetrahedral AH$_4$ thus reduces to a question of the four pairs of interactions of 5-31, the variation from one molecule to another being set by the central atom s and p orbital energies dependent upon the identity of A. We will use in what follows the group theoretical labels for these orbitals (5-32). Both s and ϕ_1 are of a_1 symmetry and the trios (p_x, p_y, p_z) and (ϕ_2, ϕ_3, ϕ_4)

5-25   5-26   5-27
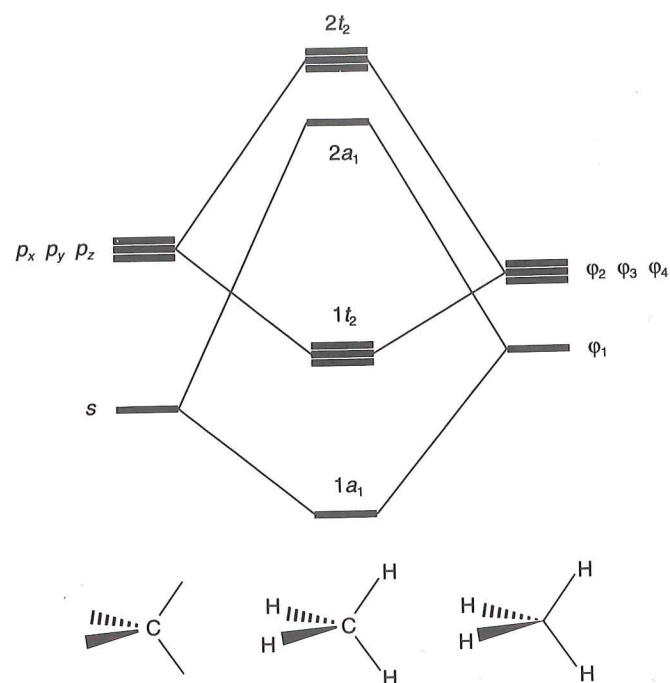
5-28   5-29   5-30
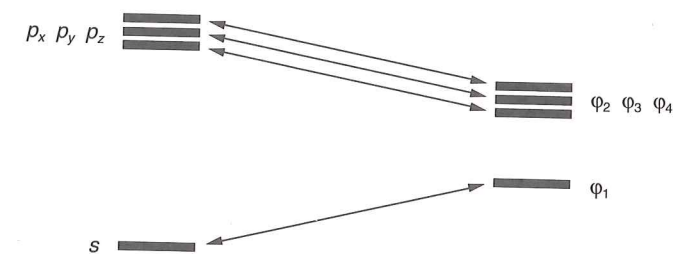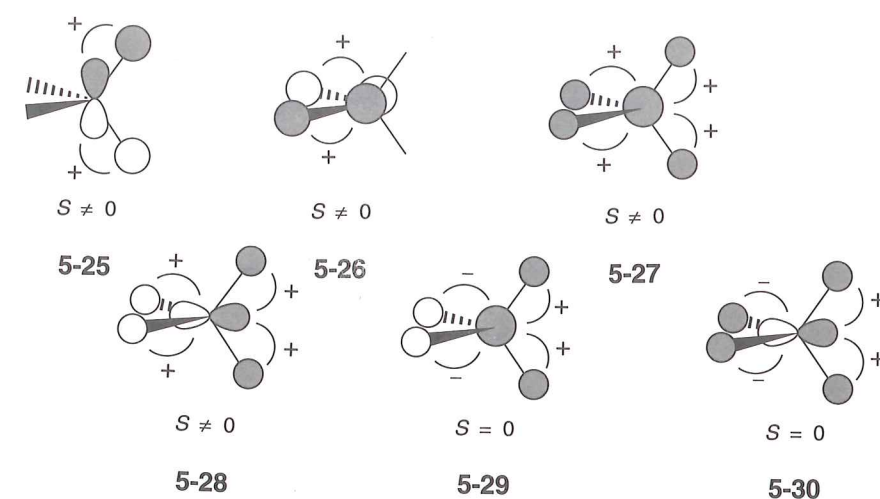
5-31
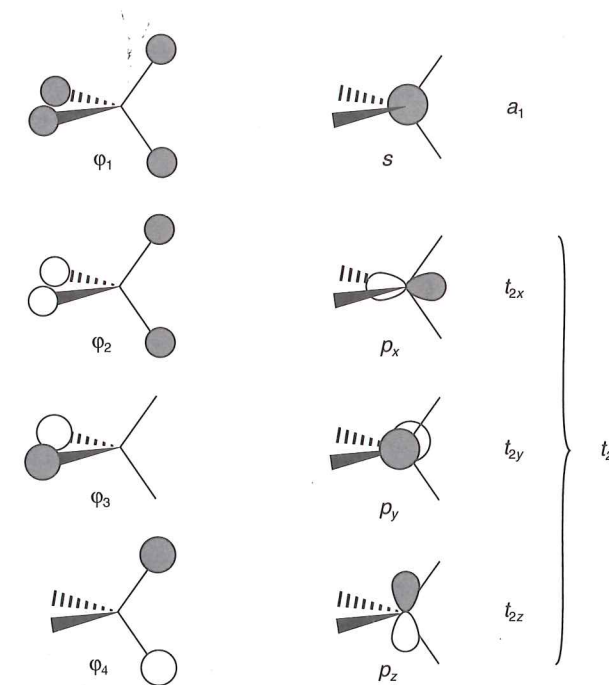
5-32

Figure 5.3. Construction of the MOs of a tetrahedral AH_4 molecule. (The relative AO energies are appropriate for A = C).

are of t_2 symmetry. (The label t is used for triply degenerate levels.) We may distinguish t_{2x} (p_x and ϕ_2), t_{2y} (p_y and ϕ_3) and t_{2z} (p_z and ϕ_4). Notice that here (and in the AH_3 molecule too) there is no center of symmetry unlike the situation in linear AH_2. Accordingly the subscript g or u which described the behavior with respect to inversion is inappropriate here.

5.3.2. MOs of tetrahedral AH_4 molecules

The fragment orbital interaction diagram of Figure 5.3 corresponds to the case of CH_4 where $\varepsilon_{2s} = -19.4$ eV and $\varepsilon_{2p} = -10.7$ eV. The H_4 fragment levels lie just below (ϕ_1 is H—H bonding) and just above (ϕ_2, ϕ_3 and ϕ_4 are H—H antibonding) the energy of an isolated $1s_H$ orbital (-13.6 eV). The orbitals ϕ_1 and s (a_1) interact to give bonding ($1a_1$) and antibonding ($2a_1$) partners. Interaction between ϕ_2 and p_x, between ϕ_3 and p_y and between ϕ_4 and p_z leads to the formation of three bonding MOs, $1t_2$ ($1t_{2x}$, $1t_{2y}$, $1t_{2z}$) and three antibonding MOs $2t_2$ ($2t_{2x}$, $2t_{2y}$, $2t_{2z}$). The set of $1t_2$ levels is degenerate, as is the set $2t_2$. As shown in exercise 5.2 the pairwise overlap integrals between orbitals of each degenerate set, ϕ_2, ϕ_3 and ϕ_4 on H_4 with respectively p_x, p_y and p_z on A, are equal. This triple degeneracy comes about because of the high symmetry of the tetrahedral molecule.

The molecular orbitals of tetrahedral AH_4 molecules divide into two sets (5-33).
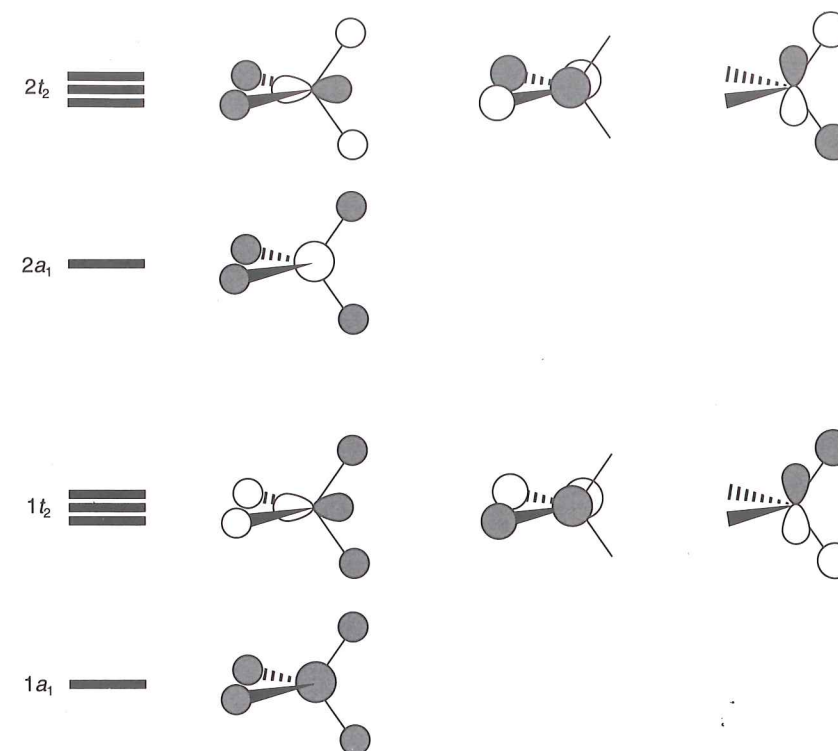
5-33

(i) Four MOs bonding between the central atom and the hydrogens. These are $1a_1$, $1t_{2x}$, $1t_{2y}$, $1t_{2z}$, in-phase combinations of the fragment orbitals (ϕ_1, s), (ϕ_2, p_x), (ϕ_3, p_y) and (ϕ_4, p_z) respectively. The deepest lying orbital, $1a_1$, arises via interaction with the deepest lying fragment orbitals. (The three $1t_2$ orbitals are degenerate.)

(ii) Four MOs antibonding between the central atom and the hydrogens. These are $2a_1$, $2t_{2x}$, $2t_{2y}$ and $2t_{2z}$ out-of-phase combinations of the same fragment orbitals. (The three $2t_2$ orbitals are degenerate.)

5.3.3. Application to the electronic structure of CH_4

In the methane molecule, with a total of eight valence electrons, the lowest four molecular orbitals are doubly occupied in the electronic ground state to give the electronic configuration $1a_1^2 1t_{2x}^2 1t_{2y}^2 1t_{2z}^2$ or $1a_1^2 1t_2^6$ as in 5-34. These four occupied bonding orbitals correspond to the four C—H bonds of the Lewis structure. The central atom uses one s and three p orbitals to form these bonds. Just as in our earlier AH_2 and AH_3 examples it is not possible to make a one-to-one correspondence between a single delocalized molecular orbital and a particular C—H bond. In the $1a_1$ orbital the bonding character is the same between the central atom and each of the hydrogens since the hydrogen coefficients are all equal. The same is true for the $1t_{2x}$ orbital. Here all of the coefficients are equal in absolute magnitude and each of the A—H bonds make the same angle (one half of the 'tetrahedral' angle, $109.5°/2$)

$1t_{2x}$ $1t_{2y}$ $1t_{2z}$

$1a_1$
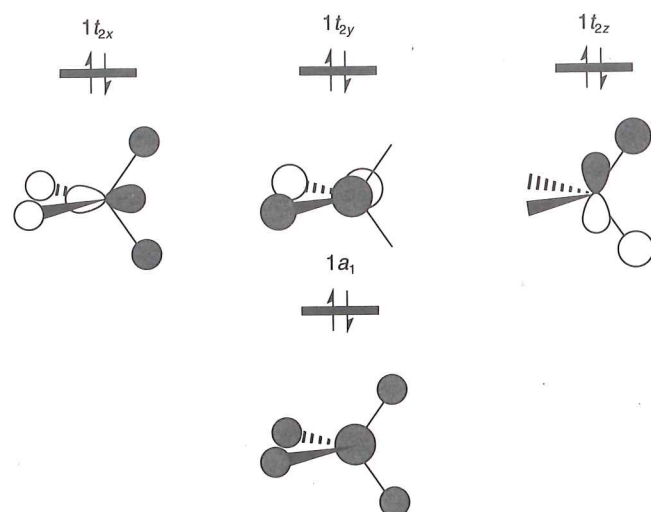
5-34

with the axis (x) of the p_x orbital. On the other hand the $1t_{2y}$ orbital is bonding only between carbon and H_a and H_b, and the $1t_{2z}$ orbital is bonding in the same way between carbon and H_c and H_d. It is the collection of four occupied MOs taken together which lead to four equivalent C—H bonds.

Finally, all of the occupied MOs are not of the same energy, $1a_1$ lying deeper than $1t_2$. This prediction from molecular orbital theory is confirmed experimentally via the photoelectron spectrum. There are two ionization energies which differ by about 10 eV. To conclude, just as in the earlier examples it is necessary to distinguish between the equivalence of the four C—H bonds and the non-equivalence of the four occupied molecular orbitals (split into the two sets $1a_1$ and $1t_2$).

EXERCISES

**5-1** *Overlap integrals between fragment orbitals in AH_3*

We will consider the orbitals ϕ_2 and ϕ_3 on the triangular H_3 unit and the p_x and p_y orbitals on the A atom which lead to the levels of the trigonal planar AH_3 molecule. The values of the coefficients in the orbitals ϕ_i are those that were calculated by including the overlaps between the $1s_H$ orbitals in Section 4.1.5b. S is the overlap integral between two $1s_H$ orbitals.


$\frac{1}{\sqrt{2(1-S)}}$ $\frac{1}{\sqrt{2(1-S)}}$ $\frac{2}{\sqrt{6(1-S)}}$ $-\frac{1}{\sqrt{6(1-S)}}$ $-\frac{1}{\sqrt{6(1-S)}}$

φ_2 φ_3 p_y p_x
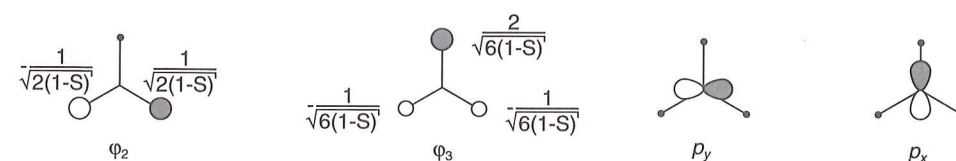
Show that the overlap integrals $S_2 = \langle \phi_2 \mid p_y \rangle$ and $S_3 = \langle \phi_3 \mid p_x \rangle$ are equal. (Call S_0 the overlap integral between a p orbital and a $1s_H$ orbital lying along the p orbital axis at a distance $d = $ A—H.)

5.2 *Overlap integrals between fragment orbitals in AH_4*

Show in the same way that the overlap integrals between the pairs of fragment orbitals $S_2 = \langle \phi_2 \mid p_x \rangle$, $S_3 = \langle \phi_3 \mid p_y \rangle$ and $S_4 = \langle \phi_4 \mid p_z \rangle$ in tetrahedral AH_4 molecules are equal. The values of the coefficients in the orbitals ϕ_i are those that were calculated in the exercise 4.1. Note that the angle between the bonds in a tetrahedron (α) is 109.5° and verify that $\cos(\alpha/2) = 1/\sqrt{3}$.

φ_2 φ_3 φ_4

p_x p_y p_z
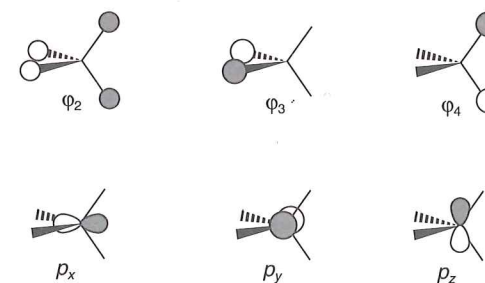
5.3 *Star-shaped H_4*

Construct the molecular orbitals of star-shaped H_4 starting from the two fragments, triangular H_3 and a single central H atom.
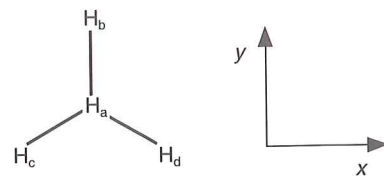
(i) Give the symmetry properties of the fragment orbitals with respect to the yz plane. Deduce immediately the form of one of the MOs of star-shaped H_4.

(ii) Analyze the overlap integrals between the symmetric orbitals of the two fragments and derive a second MO.

(iii) Construct a complete molecular orbital diagram given the fact that the highest MO is non-degenerate. Give the form of all of the MOs.

5.4   Trigonal bipyramidal H_5

Construct the energy level diagram of trigonal bipyramidal H_5. The atoms H_d and H_e lie along the z-axis and H_a, H_b and H_c lie at the vertices of a trigonal plane. Make all of the distances of these hydrogen atoms to the origin equal and construct the MOs of this system from the two fragments, triangular H_3 ($H_a H_b H_c$) and linear H_2 ($H_d \ldots H_e$) units.
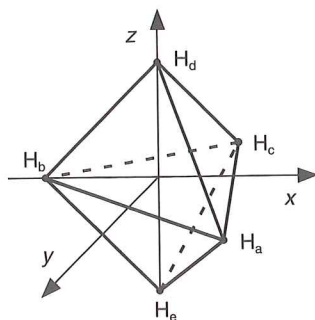
(i) Describe the relative energies of the fragment orbitals, taking into account the distances between the hydrogen atoms.

(ii) Use the xy plane of symmetry to find one of the MOs of H_5.

(iii) Use the xz plane to determine a second MO.

(iv) Analyze the overlap integrals between the orbital pairs symmetric with respect to reflection in both of these planes. Hence determine a third MO of H_5.

(v) Construct the complete orbital interaction diagram, given the fact that the highest energy orbital is non-degenerate. Give the form of each MO.

5.5   Analogy between the orbitals of square planar H_4 and those of a central A atom (*see* Appendix)

Decompose a square planar AH_4 molecular into the two fragments, A and square planar H_4.
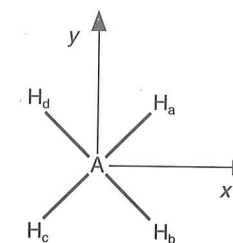
(i) Establish the orbital analogy between the MOs of square planar H_4 (ϕ_1–ϕ_4 of Section 4.1.1) and the AOs (s, p_x, p_y, p_z) of the central A atom.

(ii) Do the same but for the case where the four hydrogen atoms lie along the axes x and y. In this case use the H_4 fragment orbitals determined in exercise 4.4.