## 8.5 HYBRID ORBITALS

The MO approach to  $\sigma$  bonding in AB, molecules is widely regarded as the ment consellence ful nagles two species Eist it is riverous sitt same down

s-and MOs-Second within the symmetry properties of both the basis orbita accuracy of the results can elaborate computations are

this symmetry-based framework, the numerical then be taken to any level desired if sufficiently done.

sis might seem at odds with r SF<sub>6</sub> all of the  $\sigma$  bonds are f the electron density in the r all of the filled MOs (e.g., If the bonds will be evident. it bonds are a result of the so experimentally verifiable

On the other hand, the results of an MO analy the obvious fact that in molecules such as CH4 o equivalent. Actually, there is no inconsistency. I molecule is computed from the wave functions fo the  $A_1$  and  $T_2$  MOs in CH<sub>4</sub>) the equivalence of a At the same time, the fact that these equivalen presence of electrons in nonequivalent MOs is al by the technique of photoelectron spectroscopy.

If all the valence shell electrons of methane (i.e., all but the carbon 1s electrons) were equivalent, the photoionization spectrum of methane would show only one peak. In fact, as seen in Figure 8.8, it shows two, which have energies and intensities annropriate to the A and T. MOs.

Fore before it was possible to perform MO catellations on even the simplest molecules, the equivalence of the bonds led to the development of a different conception of the bonding in AB, molecules, in which nonequivalent AOs on the central atom are combined into hybrid orbitals. These hybrid orbitals provide a set of equivalent lobes directed at the set (or subset) of symmetry equivalent B atoms. It is therefore obvious that all A—B bonds to all equivalent B atoms will be equivalent.

In spite of the advances in computational chemistry, which have made the MO approach highly feasible and widely used, the hybridization approach is still of value and interest. Moreover, it too has a firm foundation in the symmetry properties of the molecule. It is therefore worthwhile and appro-

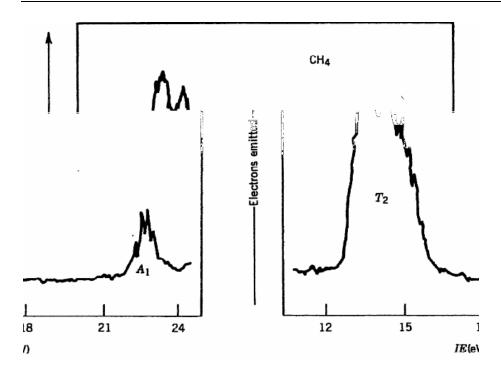


Figure 8.8 The photoelectron spectrum of CH<sub>4</sub>. Adapted by permission from A. W. Potts and W. C. Price, *Proc. R. Soc. London*, A326, 165 (1972). The  $T_2$  ionization ( $\sim$ 14 eV) is more intense than the  $A_1$  ionization ( $\sim$ 23 eV) partly because of the 3:1 ratio of populations. It is much broader because of a Jahn-Teller effect.

priate to explain and illustrate it. To do so, let us take the case of a trigonal planar AB<sub>3</sub> molecule of  $D_{3h}$  symmetry.

To determine how to form a set of trigonally directed hybrid orbitals, we begin in exactly the same way as we did in the MO treatment. We use the three  $\sigma$  bonds as a basis for a representation, reduce this representation and obtain the results on page 219. However, we now employ these results differently. We conclude that the s orbital may be combined with two of the p orbitals to form three equivalent lobes projecting from the central atom A toward the B atoms. We find the algebraic expressions for those combinations by the following procedure.

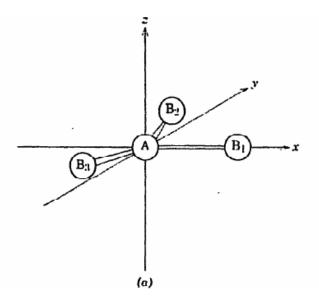
The hybrid orbitals, which we may designate as  $\Phi_1$ ,  $\Phi_2$ , and  $\Phi_3$ , (Fig. 8.9) will be expressed in terms of the atomic s,  $p_s$ , and  $p_s$  orbitals by the following set of equations:

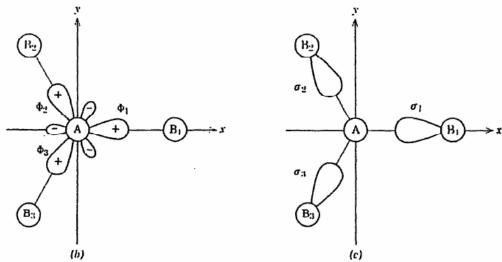
$$\Phi_1 = c_{11}s + c_{12}p_x + c_{13}p_y$$

$$\Phi_2 = c_{21}s + c_{22}p_x + c_{23}p_y$$

$$\Phi_3 = c_{31}s + c_{32}p_x + c_{33}p_y$$

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**Figure 8.9** (a) Orientation of AB<sub>3</sub> molecule in Cartesian coordinate system. (b) Set of equivalent hybrid orbitals,  $\Phi_1$ ,  $\Phi_2$ ,  $\Phi_3$ . (c) Set of equivalent  $\sigma$  orbitals on pendent atoms,  $\sigma_1$ ,  $\sigma_2$ ,  $\sigma_3$ .

doing so is as follows. The set of coefficients we seek forms a matrix, and the above set of equations can be written in matrix form:

$$\begin{bmatrix} \Phi_1 \\ \Phi_2 \\ \Phi_3 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \end{bmatrix}$$

This matrix tells us how to take a set of atomic wave functions, each belonging to a particular irreducible representation and listed in a specified order, and combine them into a set of three equivalent functions. It should evidently be

possible to carry out the inverse transformation and to express it in matrix form, namely,

$$\begin{bmatrix} s \\ p_x \\ p_y \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \end{bmatrix} \begin{bmatrix} \Phi_1 \\ \Phi_2 \\ \Phi_3 \end{bmatrix}$$

where the  $\mathcal{D}$  matrix is the inverse of the  $\mathcal{E}$  matrix. Thus, one way to determine the elements of the  $\mathcal{E}$  matrix would be to have the  $\mathcal{D}$  matrix and take its inverse. This is a very simple process because the inverse of an orthogonal matrix is the transpose. Thus, we can obtain the  $\mathcal{L}$  matrix easily if we know how to obtain the  $\mathcal{L}$  matrix. A little reflection will show that we already know how to obtain the  $\mathcal{L}$  matrix. The  $\mathcal{L}$  matrix describes the transformation of a set of three equivalent basis functions into a set of linear combinations having the symmetry of the AOs, which, in turn, have symmetry corresponding to certain irreducible representations of the molecular symmetry group.

n operators generate such symmetry-adapted linear cients of which are the elements of the desired matrix. ection operator technique to transform a set of equivthe hybrid orbitals on the central atom or the  $\sigma$  orbitals—into SALCs we obtain a set of coefficients which  $\kappa$ . We can now state and illustrate the three steps in for forming hybrid orbitals.

As we know, projectio combinations, the coeffi Thus, if we use the projulent σ orbitals—either on the pendent atomsconstitute the \$\mathcal{L}\$ matrix a systematic procedure

1. Form SALCs from the set of equivalent orbitals on the pendent atoms. As noted above and emphasized in Figure 8.9, we could use either the hybrid orbitals on atom A or the  $\sigma$  orbitals on the B atoms, since their symmetry properties are the same. We choose the orbitals on the pendent atoms because the application of projection operators to these is exactly as previously explained in Chapter 6. The results obtained are

$$\psi_{1}(A'_{1}) = \frac{1}{\sqrt{3}} (\sigma_{1} + \sigma_{2} + \sigma_{3})$$

$$\psi_{2}(E'_{a}) = \frac{1}{\sqrt{6}} (2\sigma_{1} - \sigma_{2} - \sigma_{3})$$

$$\psi_{3}(E'_{b}) = \frac{1}{\sqrt{2}} (\sigma_{2} - \sigma_{3})$$

2. The matrix of the coefficients is written and its inverse taken. The matrix

$$\begin{bmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \end{bmatrix}$$

and the inverse of this matrix (its transpose) is

$$\begin{bmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0\\ 1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2}\\ 1/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{2} \end{bmatrix}$$

3. The matrix so obtained is applied to a column vector of the AOs (in the correct order of the representations to which they belong) to generate the hybrids. We therefore write

$$\begin{bmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2} \\ 1/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{2} \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \end{bmatrix}$$

$$= \begin{bmatrix} (1/\sqrt{3}) s + (2/\sqrt{6}) p_x \\ (1/\sqrt{3}) s - (1/\sqrt{6}) p_x + (1/\sqrt{2}) p_y \\ (1/\sqrt{3}) s - (1/\sqrt{6}) p_x - (1/\sqrt{2}) p_y \end{bmatrix} = \Phi_1$$

$$= \Phi_2$$

$$= \Phi_3$$

These hybrid orbitals are commonly designated  $sp^2$  hybrids, it being understood that the explicit form of mixing is that shown above. In a very similar way  $sp^3$  hybrids give rise to four equivalent orbitals directed to the vertices of a tetrahedron. The explicit forms here can be written virtually by inspection. With the coordinate system in Figure 8.2 and the hybrids numbered as are the vectors  $\mathbf{r}_i$ , we can write

$$\Phi_{1} = \frac{1}{2} (s + p_{x} + p_{y} + p_{z})$$

$$\Phi_{2} = \frac{1}{2} (s - p_{x} + p_{y} - p_{z})$$

$$\Phi_{3} = \frac{1}{2} (s + p_{x} - p_{y} - p_{z})$$

$$\Phi_{4} = \frac{1}{2} (s - p_{x} - p_{y} + p_{z})$$

## Hybrid Orbitals in Other Important Cases

There are several other symmetries of AB, molecules for which hybrid orbitals on atom A are often wanted. The results for these are summarized below.

**AB<sub>4</sub>, planar.** We require  $A_{1g} + B_{1g} + E_u$  atomic orbitals. The two possible combinations are  $d_{z^2} + d_{x^2-y^2} + p_x + p_y$  and  $s + d_{x^2-y^2} + p_x + p_y$ . The latter is usually chosen and designated briefly as  $dsp^2$  hybridization. However, not just any choice of d or p orbitals is implied, but rather only the specific one just mentioned.

 $AB_5$ , trigonal bipyramidal. We require AOs corresponding to  $2A_1' + A_2'' + E'$  (of group  $D_{3h}$ ). There are two possible  $A_1'$  orbitals  $(s, d_{z^2})$ , one  $A_2''$  orbital  $(p_z)$  and two choices for the E'' orbitals,  $(p_x, p_y)$  or  $(d_{xy}, d_{x^2-y^2})$ . We can have either  $dsp^3$  or  $d^3sp$  hybrids.

 $AB_6$ , Octahedral. This is perhaps the best known case, where the  $A_{1g} + E_g + T_{1u}$  set of orbitals is made up of s,  $(d_{z^2}, d_{x^2-y^2})$  and  $(p_x, p_y, p_z)$  and  $d^2sp^3$  hybrids are often cited in the chemical literature.