

8.5 HYBRID ORBITALS

The MO approach to σ bonding in AB_n molecules is widely regarded as the most generally useful one for two reasons. First, it is rigorous with regard to orbitals and MOs. Second, within the symmetry properties of both the basis orbitals and MOs, the accuracy of the results can be taken to any level desired if sufficiently elaborate computations are done.

Analysis might seem at odds with the obvious fact that in molecules such as CH_4 or SF_6 , all of the σ bonds are equivalent. Actually, there is no inconsistency. In all of the filled MOs (e.g., the A_1 and T_2 MOs in CH_4), all the bonds will be evident. The presence of electrons in nonequivalent MOs is also experimentally verifiable by the technique of photoelectron spectroscopy.

On the other hand, the results of an MO analysis might seem at odds with the obvious fact that in molecules such as CH_4 or SF_6 , all of the σ bonds are equivalent. Actually, there is no inconsistency. In all of the filled MOs (e.g., the A_1 and T_2 MOs in CH_4), all the bonds will be evident. The presence of electrons in nonequivalent MOs is also experimentally verifiable 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 appropriate to the A_1 and T_2 MOs.

Long before it was possible to perform MO calculations or even the simplest molecules, the equivalence of the bonds led to the development of a different conception of the bonding in AB_n 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-

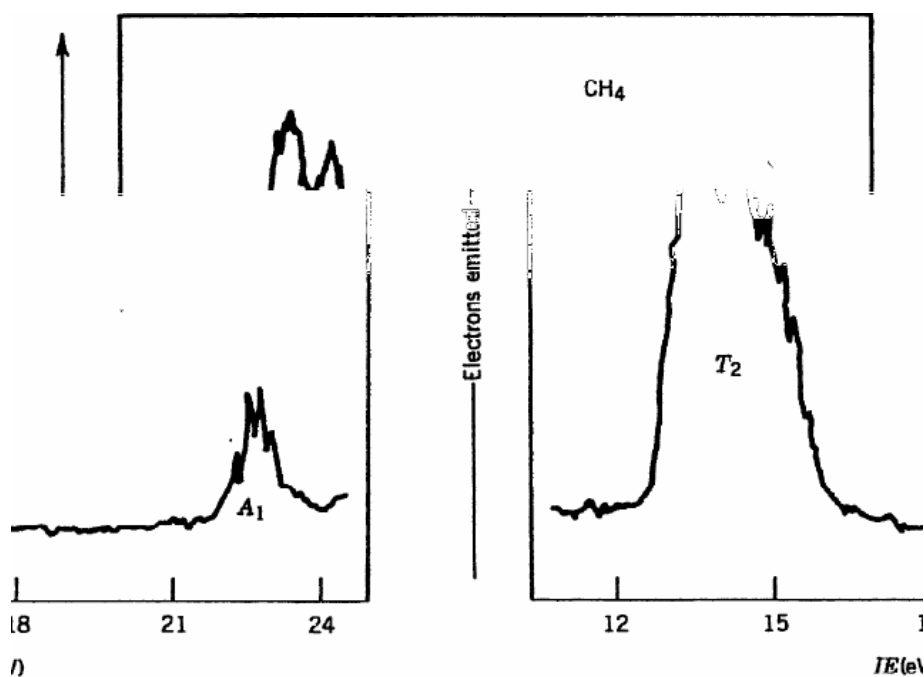


Figure 8.8 The photoelectron spectrum of CH_4 . Adapted by permission from A. W. Potts and W. C. Price, *Proc. R. Soc. London*, A326, 165 (1972). The T_2 ionization (~ 14 eV) is more intense than the A_1 ionization (~ 23 eV) partly because of the 3:1 ratio of populations. It is much broader because of a Jahn–Teller effect.

appropriate to explain and illustrate it. To do so, let us take the case of a trigonal planar AB_3 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 σ 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 Φ_1 , Φ_2 , and Φ_3 , (Fig. 8.9) will be expressed in terms of the atomic s , p_x , and p_y orbitals by the following set of equations:

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

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

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

The problem now is to evaluate the coefficients c_{ij} and the procedure for

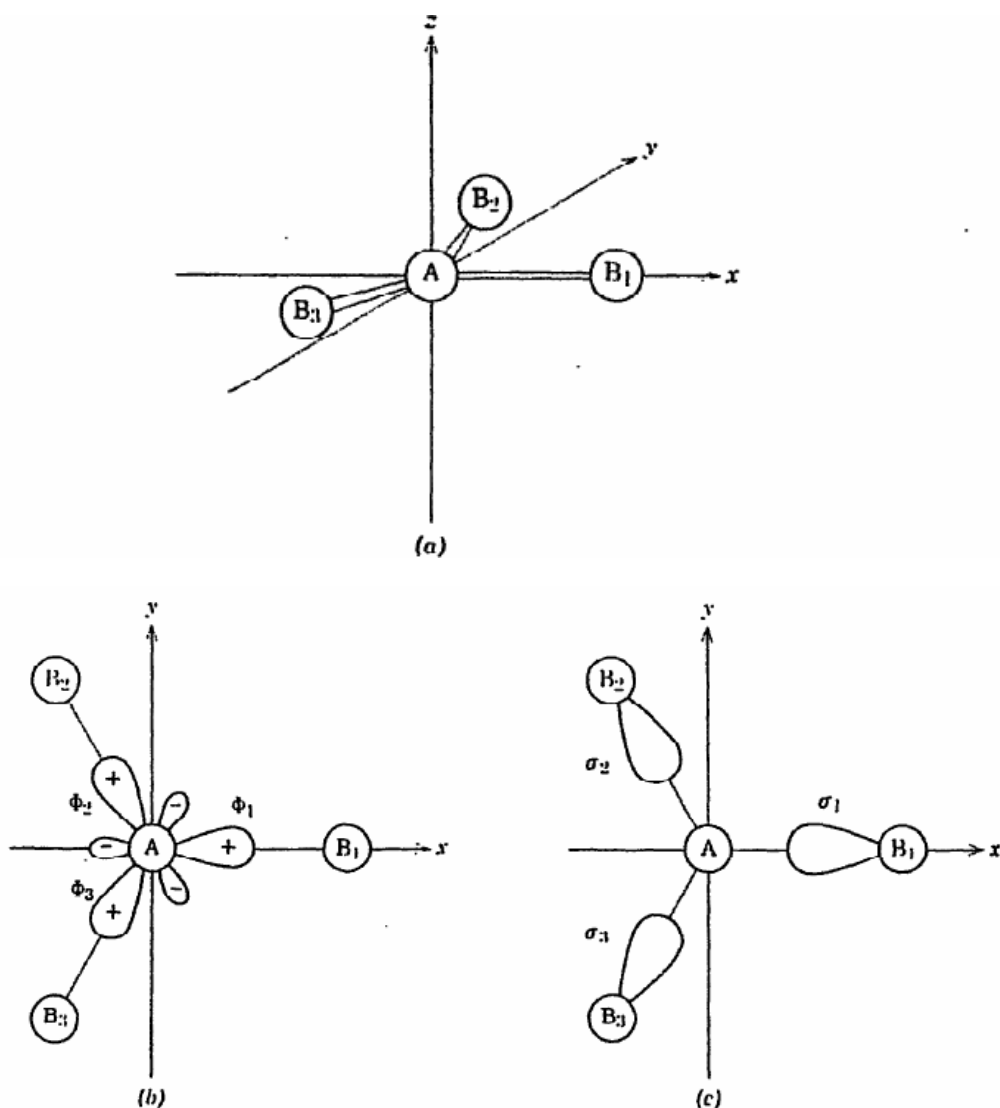


Figure 8.9 (a) Orientation of AB₃ molecule in Cartesian coordinate system. (b) Set of equivalent hybrid orbitals, Φ_1 , Φ_2 , Φ_3 . (c) Set of equivalent σ orbitals on pendent atoms, σ_1 , σ_2 , σ_3 .

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

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

$$\begin{bmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2} \\ 1/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{2} \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \end{bmatrix} = \begin{bmatrix} (1/\sqrt{3})s + (2/\sqrt{6})p_x \\ (1/\sqrt{3})s - (1/\sqrt{6})p_x + (1/\sqrt{2})p_y \\ (1/\sqrt{3})s - (1/\sqrt{6})p_x - (1/\sqrt{2})p_y \end{bmatrix} = \begin{bmatrix} \Phi_1 \\ \Phi_2 \\ \Phi_3 \end{bmatrix}$$

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_n molecules for which hybrid orbitals on atom A are often wanted. The results for these are summarized below.

AB_4 , 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.

AB₆, 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.

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