

Theory of Polyhedral Molecules. I. Physical Factorizations of the Secular Equation

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An LCAO-MO systematization of polyhedral molecules such as $B_N H_N$ is undertaken. Peculiarities of polyhedral systems, such as inapplicability of nearest-neighbor assumption and increased number of parameters are discussed within the framework of a Hückel type of theory. It is found that inclusion of hydrogen atoms does not affect predictions of closed shells, but is important in determining electronic transitions. Various physical factorizations of the secular equations, such as the in-surface, apex-equatorial, and ring-polar separations are critically examined. A computer program for calculations on molecules of up to 15 atoms is described and used to obtain the energy levels of a variety of polyhedral molecules.

INTRODUCTION

POLYHEDRAL molecules and ions represent a class of molecular and ionic species for which arguments based upon symmetry considerations may be expected to yield interesting results. Degeneracies in the one-electron approximation to molecular orbital descriptions often give rise to relatively large gaps in the energy level scheme, and hence relatively complex molecules may be described with some greater degree of success than is possible in molecules of lower symmetry. Such polyhedral species are prominent in boron chemistry¹⁻³ (B_4Cl_4 , B_8Cl_8 , $B_{10}H_{10}^{-2}$, $B_{12}H_{12}^{-2}$) and in intermetallic complexes and crystals. Saturated analogs are expected in carbon chemistry (tetrahedrane C_4H_4 , cubane C_8H_8 , dodecahedrane $C_{20}H_{20}$, etc.) and some arise in carbon-boron chemistry (the carboranes). Inorganic molecules may also form compact polyhedral structures (P_4 , As_4 , etc.). Some of the polyhedra discussed in this paper are shown in Figs. 1-3.

Molecular orbital descriptions have been given to the known B_4Cl_4 , B_8Cl_8 , $B_{10}H_{10}^{-2}$, $B_{12}H_{12}^{-2}$ species,^{2,4-6}

¹W. N. Lipscomb, "Recent studies of the boron hydrides," in *Advances in Inorganic Chemistry and Radiochemistry* (Academic Press Inc., New York, 1959), Vol. I, p. 117.

²W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *J. Am. Chem. Soc.* **81**, 5833 (1959).

³A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.* **82**, 3288 (1960); J. A. Wunderlich and W. N. Lipscomb, *ibid.* **82**, 4427 (1960).

⁴W. H. Eberhardt, B. C. Crawford, and W. N. Lipscomb, *J. Chem. Phys.* **22**, 989 (1954).

⁵R. A. Jacobson and W. N. Lipscomb (unpublished).

⁶H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc. (London)* **A230**, 110 (1955).

and to^{7,8} $B_5H_5^{-2}$, $B_6H_6^{-2}$ and other species, in varying degrees of approximation. Our purpose here is to explore the nature of some of these approximate theories. In the first paper we investigate approximations, made for convenience in handling the secular determinants arising from linear combinations of molecular orbitals (LCAO). In the second paper, a crystal-field model is compared with the LCAO calculations, with, surprisingly, a resultant improvement in the assumptions of both types of orbital descriptions. In the third paper we give atomic charges, bond orders, and reactivity parameters for some carboranes. In the fourth contribution we present the results of a systematic survey of energy levels for a much larger variety of polyhedral species than has heretofore been investigated, having been encouraged by recent experimental developments along these lines in boron and carbon chemistry.

LCAO-MO EQUATIONS

If we consider a molecular orbital ψ built up as a linear combination of atomic orbitals ϕ ,

$$\psi = \sum_i c_i \phi_i, \quad (1)$$

we obtain the following set of equations for the expansion

⁷E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.* **35**, 1329 (1961).

⁸H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc. (London)* **A224**, 336 (1954).

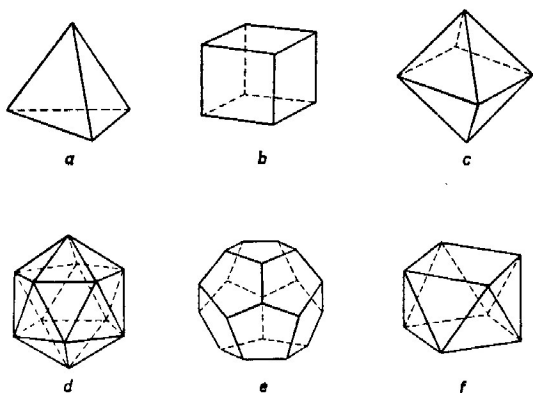


FIG. 1. a. tetrahedron, b. cube, c. octahedron, d. icosahedron, e. dodecahedron, f. archimedean antiprism. a, b, and e are C_NH_N possibilities.

sion coefficients:

$$(\alpha_r - ES_{rr})c_r + \sum'_s (\beta_{rs} - ES_{rs})c_s = 0$$

$$r = 1, 2, 3, \dots, M, \quad (2)$$

where M = number of orbitals considered

E = energy

$$S_{rs} = \int \phi_r^* \phi_s d\tau = \text{overlap}$$

$$\alpha_r = \int \phi_r^* H \phi_r d\tau = \text{"Coulomb integral"}$$

$$\beta_{rs} = \int \phi_r^* H \phi_s d\tau = \text{"resonance integral."}$$

H is the ubiquitous Hückel Hamiltonian, whose explicit form is hardly ever specified in the semiempirical theory. In the following, we will concern ourselves with polyhedral molecules of the formula B_NX_N , where B

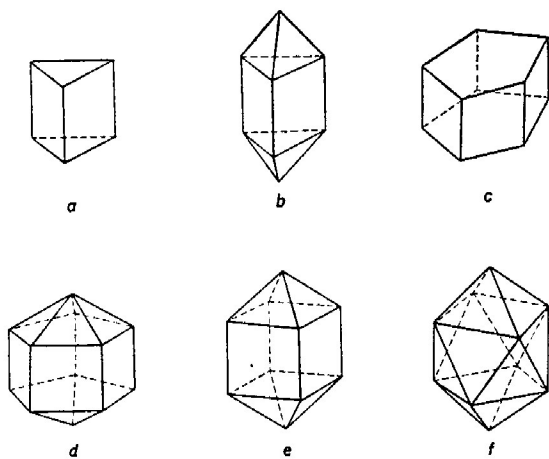


FIG. 2. a. trigonal prism, b. bicapped trigonal prism, c. pentagonal prism, d. bicapped pentagonal prism, e. bicapped cube, f. bicapped archimedean antiprism. a, c are C_NH_N possibilities.

may be boron (or carbon) and X may be hydrogen or chlorine.

The simplest Hückel type of treatment of these molecules differs considerably from the corresponding calculations on aromatic systems. The polyhedral frameworks are inherently three dimensional. No symmetry factorization of the σ - π type is possible, though various other physical factorizations will be discussed below. Thus the number of orbitals considered is greater for polyhedral molecules. In general, we are forced to examine the interaction of 4 orbitals on each boron (one $2s$ and three $2p$) with one orbital on each hydrogen. The secular equation is thus of degree $5N$. If we factor out the B-H bonds, we are still left with a diagonalization of a $3N$ by $3N$ matrix.

Moreover, as we will show in the next section, the equally ubiquitous tight binding assumption of aromatic theory, i.e., the neglect of all but nearest-neigh-

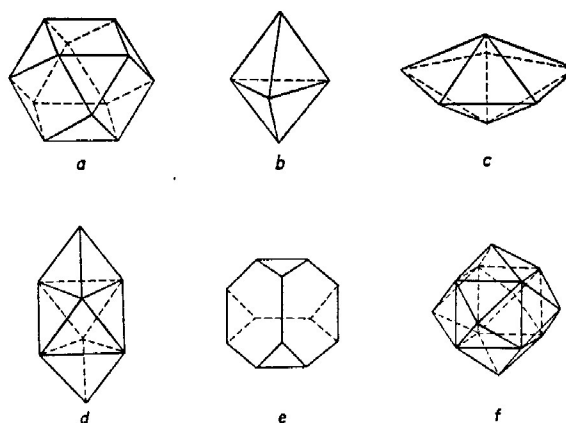


FIG. 3. a. cube-octahedron, b. trigonal bipyramid, c. pentagonal bipyramid, d. rhombic hexahedron = bicapped trigonal antiprism, e. truncated tetrahedron, f. rhombic dodecahedron = omnicailed cube. e is a C_NH_N possibility.

bor interactions in the Hamiltonian matrix, is inapplicable to boron polyhedra. All interactions must be evaluated.

Still another difference is that, whereas there is only one Coulomb integral in the π -electron theory of homonuclear aromatics, for polyhedral molecules we are obliged to consider in the homonuclear case a $2s$ and a $2p$ Coulomb integral. In most previous treatments these have been set equal, an assumption which is not justifiable, but which reduces the number of parameters and therefore is habit forming. Arguments for setting $\alpha(2s)$ and $\alpha(2p)$ unequal will be presented in subsequent communications.⁹ Since our main purpose in this paper is to examine critically various physical factorizations of the secular equation, we shall retain here the assumption of equal Coulomb integrals, in order to facilitate intercomparison of our results with those already in the literature. We shall also use a

⁹ R. Hoffmann and M. P. Gouterman 36, 2189 (1962) following paper; R. Hoffmann and W. N. Lipscomb (to be published).

Slater orbital basis (exponent 1.30 for B), though in a subsequent section we examine the consequences of using a different orbital basis. If the resonance integral is taken to be proportional to the overlap (perhaps a better assumption would be to take a different proportionality constant for each overlap type)

$$\beta_{rs} = K S_{rs} \quad (3)$$

the set of equations reduces to

$$-x c_r + \sum'_s S_{rs} c_s = 0 \quad (4)$$

$$-x = (\alpha - E)/(K - E), \quad (5)$$

where we have chosen $S_{rr} = 1$, $\alpha(2s) = \alpha(2p)$. The energy parameters are the eigenvalues of the off-diagonal overlap matrix $\mathbf{S} - \mathbf{1}$, and must all be greater than -1 . From (5) we obtain

$$E_i = (\alpha + K x_i)/(1 + x_i), \quad (6)$$

and

$$E_i - E_j = (x_i - x_j)(K - \alpha)/(1 + x_i)(1 + x_j). \quad (7)$$

Thus the order of energy levels is preserved for all K and α (K must be taken greater than α) and we may work directly with the energy parameters x_i thus postponing a choice of K and α . The method outlined above was first introduced for boron polyhedra by Longuet-Higgins and Roberts.^{6,8}

NEAREST-NEIGHBOR ASSUMPTION FOR BORON POLYHEDRA

Neglect of all but nearest-neighbor interactions in the Hamiltonian matrix is an *idée fixe* of the LCAO-MO Hückel method for aromatics. It is perhaps not widely recognized that its feasibility is merely due to the relatively small magnitude of the p - p π overlap for two carbons a reasonable distance apart. As has been pointed out by Ruedenberg,¹⁰ the tight binding approximation would fail, if this overlap, which we will call S , would exceed $\frac{1}{3}$. Consider a basis set of normalized atomic orbitals

$$\phi = \{\phi_1, \phi_2, \dots, \phi_N\}. \quad (8)$$

The overlap matrix \mathbf{S} may be expressed as the Hilbert space inner product $\phi^+ \phi$. From this it follows that \mathbf{S} is positive definite and therefore its eigenvalues are all greater than zero. Now we inquire about the eigenvalues of \mathbf{S}' , a modification of \mathbf{S} in which some of the off-diagonal elements of \mathbf{S} have been set equal to zero. Using Hadamard's theorem,¹¹ we find that the eigenvalues of \mathbf{S}' are bounded as follows:

$$-(M-1) \leq \lambda_i \leq M+1, \quad (9)$$

where

$$M = \max\left\{\sum'_i |S_{ki}|\right\}. \quad (10)$$

Thus if $M \geq 1$ some of the eigenvalues of \mathbf{S}' may be negative or zero; this in turn would imply linear dependence of the basis set and would lead to an incorrect energy level scheme. To ensure consistency in the theory we must have $M < 1$. The maximum number of nearest neighbors in aromatics is 3, which leads to Ruedenberg's criterion that S must be less than $\frac{1}{3}$. Since $S \approx 0.25$, this is satisfied. When we turn to boron polyhedra, the maximum number of nearest neighbors is 4 or 5, moreover there is more than one orbital on each center. Even if we were to consider only one non-vanishing interaction with each center, we would still have to require that S be $< \frac{1}{4}, \frac{1}{5}$, respectively, whereas S actually is over 0.30. Indeed, calculations with a nearest neighbor assumption for the octahedron and cube lead to negative eigenvalues of the overlap matrix and confirm the theoretical conclusion that for B polyhedra the assumption of only nearest-neighbor interactions leads to inconsistencies: all interactions in the polyhedron must be accounted for.

COMPUTATION

A program for LCAO-MO calculations on polyhedral molecules has been written for the IBM 7090 computer. The overlap matrix for a single s and three p orbitals on each of up to 15 arbitrarily situated atoms is set up. Since the p orbitals transform as vectors, the coefficients (each to be multiplied by the proper overlap) of the various interactions between orbitals on the atoms i and j may be written down as:

$$\begin{aligned} C(s_i, s_j) &= 1, \\ C(s_i, p_j; \sigma) &= -\mathbf{R}_{ij} \cdot \mathbf{P}_j, \\ C(p_i, p_j; \sigma) &= -(\mathbf{R}_{ij} \cdot \mathbf{P}_i)(\mathbf{R}_{ij} \cdot \mathbf{P}_j), \\ C(p_i, p_j; \pi) &= [\mathbf{P}_i - (\mathbf{R}_{ij} \cdot \mathbf{P}_i)\mathbf{R}_{ij}] \cdot [\mathbf{P}_j - (\mathbf{R}_{ij} \cdot \mathbf{P}_j)\mathbf{R}_{ij}] \\ &= \mathbf{P}_i \cdot \mathbf{P}_j - (\mathbf{R}_{ij} \cdot \mathbf{P}_i)(\mathbf{R}_{ij} \cdot \mathbf{P}_j), \\ \mathbf{P}_i &= \hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}} \text{ Cartesian unit vectors,} \end{aligned} \quad (11)$$

where \mathbf{R}_{ij} is the unit vector along the interatomic distance. All interactions are considered, and the full eigenvalue problem $(\mathbf{H} - \mathbf{E}\mathbf{S})\mathbf{C} = 0$ is solved, subject to the assumption that $\beta_{rs} = K S_{rs}$ for atomic orbitals. The input parameters are:

- (1) Coordinates of the atoms.
- (2) S and p Coulomb integrals. Provision is made for putting a different s and p Coulomb integral at each center.
- (3) The parameter K .
- (4) An overlap scheme. This may be a subroutine which uses Slater $2s$ and $2p$ overlaps, as was done throughout the calculations in this paper; or SCF overlaps may be read in.

The eigenvalue problem is set up in an AO basis and the energies and molecular orbitals obtained by a

¹⁰ K. Ruedenberg, J. Chem. Phys. **34**, 1884 (1961).

¹¹ See M. Parodi, *La Localisation des Valeurs Caractéristiques des Matrices* (Gauthier-Villars, Paris, 1959), Chap. 2.

