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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_NH_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 chemistry[1–3] (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] 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,

$$\psi=\sum_i c_i\phi_i, \tag{1}$$

we obtain the following set of equations for the expan-

[1] W. 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.
[2] W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, J. Am. Chem. Soc. **81**, 5833 (1959).
[3] A. R. Pitochelli and M. F. Hawthorne, J. Am. Chem. Soc. **82**, 3288 (1960); J. A. Wunderlich and W. N. Lipscomb, *ibid.* **82**, 4427 (1960).
[4] W. H. Eberhardt, B. C. Crawford, and W. N. Lipscomb, J. Chem. Phys. **22**, 989 (1954).
[5] R. A. Jacobson and W. N. Lipscomb (unpublished).
[6] H. C. Longuet-Higgins and M. de V. Roberts, Proc. Roy. Soc. (London) **A230**, 110 (1955).
[7] E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, J. Chem. Phys. **35**, 1329 (1961).
[8] H. C. Longuet-Higgins and M. de V. Roberts, Proc. Roy. Soc. (London) **A224**, 336 (1954).

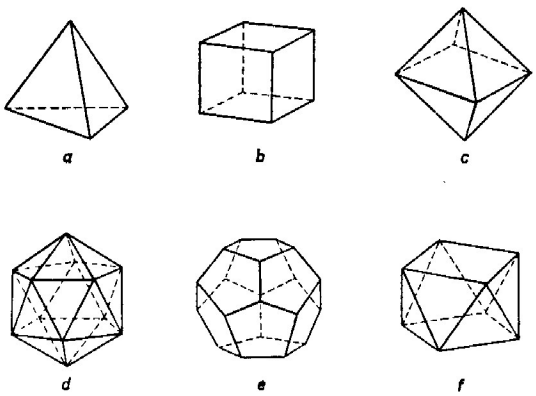

FIG. 1. a. tetrahedron, b. cube, c. octahedron, d. icosahedron, e. dodecahedron, f. archimedean antiprism. *a*, *b*, and *e* are C_NH_N possibilities.

sion coefficients:

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

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

where $M =$ number of orbitals considered

$E =$ energy

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

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

$\beta_{rs} = \int \phi_r^* H \phi_s d\tau =$ "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 may be boron (or carbon) and X may be hydrogen or chlorine.

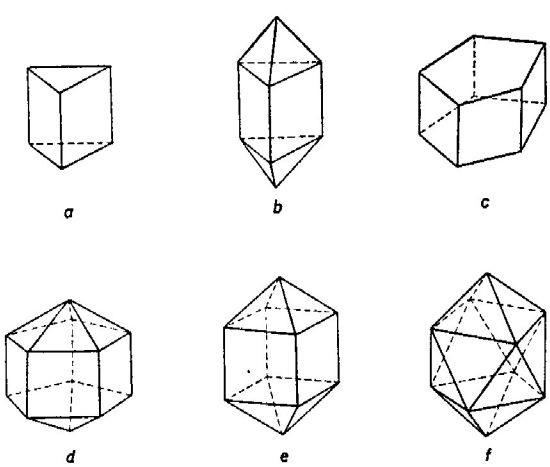

FIG. 2. a. trigonal prism, b. bicapped trigonal prism, c. pentagonal prism, d. bicapped pentagonal prism, e. bicapped cube, f. bicapped archimedean antiprism. *a*, *c* are C_NH_N possibilities.

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

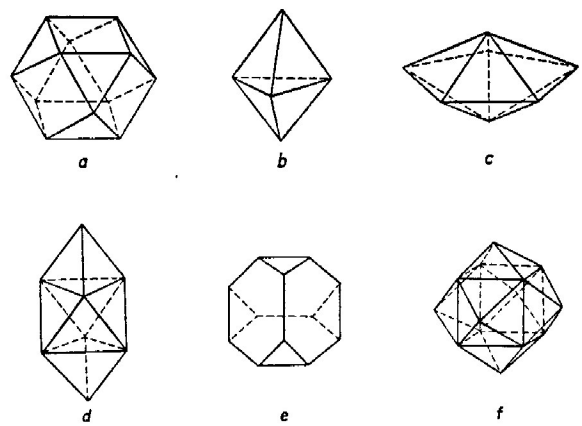

FIG. 3. a. cube-octahedron, b. trigonal bipyramid, c. pentagonal bipyramid, d. rhombic hexahedron = bicapped trigonal antiprism, e. truncated tetrahedron, f. rhombic dodecahedron = omnicapped cube. *e* is a C_NH_N possibility.

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)

$$\beta_{rs}=KS_{rs} \tag{3}$$

the set of equations reduces to

$$-xc_r+\sum_s{}' S_{rs}c_s=0 \tag{4}$$

$$-x=(\alpha-E)/(K-E), \tag{5}$$

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

$$E_i=(\alpha+Kx_i)/(1+x_i), \tag{6}$$

and

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

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

$$\boldsymbol{\phi}=\{\phi_1, \phi_2, \cdots, \phi_N\}. \tag{8}$$

The overlap matrix $\mathbf{S}$ may be expressed as the Hilbert space inner product $\boldsymbol{\phi}^+\boldsymbol{\phi}$. From this it follows that 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 S have been set equal to zero. Using Hadamard's theorem,[11] we find that the eigenvalues of $\mathbf{S}'$ are bounded as follows:

$$-(M-1)\leq\lambda_i\leq M+1, \tag{9}$$

where

$$M=\max\{\sum_l{}' \mid Sk_l' \mid\}. \tag{10}$$

Thus if $M\geq 1$ some of the eigenvalues of 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 $S\simeq 0.25$, 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:

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

where $\mathbf{R}_{ij}$ is the unit vector along the interatomic distance. All interactions are considered, and the full eigenvalue problem $(\mathbf{H}-\mathbf{ES})\mathbf{C}=0$ is solved, subject to the assumption that $\beta_{rs}=KS_{rs}$ 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 Characteristiques des Matrices* (Gauthier-Villars, Paris, 1959), Chap. 2.

TABLE I. Representations of molecular orbitals for some polyhedra.

N	Symmetry	Geometry		Representations
4	T_d	tetrahedron	$4N$	$2a_1+e+3f_2+f_1$
			out	a_1+f_2
6	O_h	octahedron	$4N$	$2a_{1g}+2e_g+3f_{1u}+f_{1c}+f_{2g}+f_{2u}$
			out	$a_{1g}+e_g+f_{1u}$
8	O_h	cube	$4N$	$2a_{1g}+2a_{2u}+e_u+e_g+f_{1g}+3f_{2g}+f_{2u}+3f_{1u}$
			out	$a_{1g}+f_{1u}+f_{2g}+a_{2u}$
12	O_h	cube-octahedron	$4N$	$2a_{1g}+a_{2g}+a_{2u}+3e_g+e_u+2f_{1g}+3f_{2g}+3f_{2u}+4f_{1u}$
			out	$a_{1g}+f_{1u}+e_g+f_{2g}+f_{2u}$
12	I_h	icosahedron	$4N$	$2a_g+3f_{1u}+f_{1g}+2f_{2u}+g_g+g_u+3h_g+h_u$
			out	$a_g+f_{1u}+h_g+f_{2u}$
10	D_{4d}	bicapped archimedean antiprism	$4N$	$5a_1+a_2+b_1+5b_2+5e_1+4e_2+5e_3$
			out	$2a_1+2b_2+e_1+e_2+e_3$

method suggested by del Re,[12] which requires only a single matrix diagonalization. When $\beta_{rs}\neq KS_{rs}$, the problem is solved by a modification of Löwdin's method,[13] requiring two matrix diagonalizations. The main time-consuming step in the calculation is the matrix diagonalization, which is carried out by Jacobi's method of two-dimensional rotations. There is provision in the program for a $g-u$ factorization when a center of symmetry is present, but otherwise no simplifications associated with molecular symmetry are introduced. It was found to be more time consuming for a computer to learn group theory than do the brute force matrix diagonalization. Approximate computation times for the solution of the $4N$ problem without a center of symmetry are 10 sec for 4 atoms, 50 sec for 8 atoms, 150 sec for 12 atoms.

To study the various physical factorizations, several subroutines are used. First sp^3 hybrids are formed at each center, with one directed axially *out* of the polyhedron center. To examine the *in-surface* separation, the $3N$ remaining orbitals are rehybridized to give an axial set of N, primarily s, and pointing *in*, and a set of $2N$ p orbitals perpendicular to the axial direction, i.e., a *surface* set. The final matrix has the form shown below.

<table>
<tr><td>out</td><td colspan="2">I</td></tr>
<tr><td rowspan="2">I</td><td>in</td><td>II</td></tr>
<tr><td>II</td><td>surface</td></tr>
</table>

[12] G. del Re, Quantum Chemistry Group, Uppsala, Tech. Note, October 20, 1958.

[13] P-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

To test the *out-in-surface* separation we first solve the $4N$ problem, then neglect the matrix elements in region I and solve the $3N$ secular equation. Finally we drop the matrix elements in region II and solve the separate *in* (N) and *surface* ($2N$) problems.

To examine the *apex-equatorial* factorization, we rotate the $3(N-2)$ orbitals of the equatorial atom set so that one orbital at each equatorial center is directed toward its apex atom. The secular equations for the equatorial set of $2(N-2)$ orbitals and for the single apical set of $\frac{1}{2}(N-2)+3$ orbitals are solved separately.

To examine the *polar-ring* factorization, sp^2 hybrids are formed for the ring atoms, with one pointing out. For the pyramidal molecules these outpointing orbitals are chosen arbitrarily in the plane of the polyhedron base (whereas otherwise they were chosen pointing out from the polyhedron center). The secular equation for the polar set of p_z ring, and apex orbitals is solved separately from that for the ring set.

Finally, provision is also made for doing the $5N$ problem, i.e., including a set of N hydrogen atoms.

B—H BONDS AND OUT-POINTING ORBITALS

The most complete version of the Hückel-type LCAO–MO calculation of the energy levels of a molecule B_NH_N yields an eigenvalue problem of degree $5N$. There are three Coulomb integrals: $\alpha(2s\text{B})$, $\alpha(2p\text{B})$, $\alpha(1s\text{H})$, and 6 types of resonance integrals: $\beta(1s\text{H},2sB)$, $\beta(1s\text{H}, 2p\text{B}, \sigma)$, $\beta(2s\text{B}, 2s\text{B})$, $\beta(2s\text{B}, 2p\text{B}, \sigma)$, $\beta(2p\text{B}, 2p\text{B}, \sigma)\beta(2p\text{B}, 2p\text{B}, \pi)$ to consider. In the polyhedra of higher symmetry considerable simplification of the eigenvalue problem may be obtained by group-theoretical methods. Thus for octahedral B_6H_6, the MO's subduce the following representations[14] of the molecu-

[14] The group-theoretical notation used is that of E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955).

TABLE II. Energy parameters.

(a) tetrahedron (T_d), B—B 1.70 A, B—H 1.21 A

5N		4N		3N	
f_2	−0.854	f_2	−0.853	f_2	−0.849
f_2	−0.792	f_1	−0.556	f_1	−0.556
a_1	−0.768	f_2	−0.093	e	0.033
f_1	−0.556	e	0.033	f_2	0.685
e	0.033	a_1	0.038	a_1	2.094
f_2	0.402	f_2	0.748		
a_1	0.753	a_1	2.159		
f_2	1.022				
a_1	2.282				

(b) Octahedron (O_h), B—B 1.73 A, B—H 1.20 A

e_g	−0.888	e_g	−0.887[a]	e_g	−0.884
f_{1u}	−0.844	f_{1u}	−0.831	f_{1u}	−0.829
e_g	−0.803	f_{1g}	−0.671	f_{1g}	−0.671
f_{1u}	−0.776	f_{2u}	−0.416	f_{2u}	−0.416
a_{1g}	−0.753	f_{1u}	−0.144	f_{2g}	0.493
f_{1g}	−0.671	e_g	−0.089	f_{1u}	1.023
f_{2u}	−0.416	a_1	0.204	a_{1g}	2.969
f_{1u}	0.337	f_{2g}	0.493		
f_g	0.493	f_{1u}	1.130		
e_g	0.652	a_{1g}	3.066		
a_{1g}	0.951				
f_{1u}	1.433				
a_{1g}	3.210				

(c) Cube (O_h), B—B 1.70 A, B—H 1.20 A

a_{2u}	−0.938	a_{2u}	−0.938	a_{2u}	−0.937
f_{2g}	−0.883	f_{2g}	−0.879	f_{2g}	−0.876
a_{2u}	−0.816	f_{1u}	−0.729	e_u	−0.729
f_{1u}	−0.806	e_u	−0.729	f_{1u}	−0.719
f_{2g}	−0.797	f_{1g}	−0.637	f_{1g}	−0.637
a_{1g}	−0.741	f_{2g}	−0.331	f_{2g}	0.064
e_u	−0.729	a_{2u}	−0.243	f_{2u}	0.096
f_{1u}	−0.684	f_{1u}	−0.028	e_g	0.893
f_{1g}	−0.637	f_{2u}	0.096	f_{1u}	1.233
f_{2g}	−0.128	f_{2g}	0.288	a_{1g}	3.127
f_{2u}	0.096	a_{1g}	0.341		
a_{2u}	0.437	e_g	0.893		
f_{1u}	0.448	f_{1u}	1.309		
f_{2g}	0.827	a_{1g}	3.243		
e_g	0.893				
a_{1g}	1.135				
f_{1u}	1.637				
a_{1g}	3.376				

(d) Cube-octahedron (O_h), B—B 1.75 A, B—H 1.20 A

e_g	−0.899	e_g	−0.892	f_{2u}	−0.885
f_{2u}	−0.891	f_{2u}	−0.887	e_g	−0.883
f_{1u}	−0.835	f_{1u}	−0.788	f_{2g}	−0.769
f_{2g}	−0.822	f_{2g}	−0.774	f_{1g}	−0.756
f_{2u}	−0.807	f_{1g}	−0.756	a_{2g}	−0.739
e_g	−0.794	a_{2g}	−0.739	f_{1u}	−0.739
f_{1g}	−0.756	e_u	−0.669	e_u	−0.669
a_{2g}	−0.739	f_{2u}	−0.540	f_{2u}	−0.483
f_{2g}	−0.733	e_g	−0.269	f_{1g}	−0.232
a_{1g}	−0.724	f_{1g}	−0.232	f_{1u}	0.361
f_{1u}	−0.677	f_{2g}	−0.177	f_{2g}	0.872
e_u	−0.669	f_{2u}	−0.159	a_{2u}	0.881
f_{2u}	−0.513	f_{1u}	0.154	e_g	0.991
f_{1g}	−0.232	f_{1u}	0.385	f_{1u}	1.754
e_g	0.249	a_{1g}	0.549	a_{1g}	3.616
f_{2g}	0.260	a_{2u}	0.811		
f_{1u}	0.331	f_{2g}	1.003		
f_{2u}	0.501	e_g	1.066		
f_{1u}	0.704	f_{1u}	1.805		
a_{2u}	0.881	a_{1g}	3.732		
e_g	1.240				
f_{2g}	1.326				
a_{1g}	1.404				
f_{1u}	2.156				
a_{1g}	3.889				

(e) Icosahedron, I_h, B—B 1.73 A, B—H 1.20 A

f_{2u}	−0.887	f_{2u}	−0.886[b]	f_{2u}	−0.886
h_g	−0.873	h_g	−0.862	h_g	−0.856
f_{1u}	−0.860	f_{1u}	−0.827	f_{1g}	−0.782
f_{2u}	−0.812	f_{1g}	−0.782	f_{1u}	−0.773
h_g	−0.783	h_u	−0.678	h_u	−0.678
f_{1g}	−0.782	g_g	−0.471	g_g	−0.471
a_g	−0.718	h_g	−0.239	g_u	0.518
f_{1u}	−0.690	f_{2u}	−0.225	h_g	0.984
h_u	−0.678	f_{1u}	0.150	f_{1u}	1.907
g_g	−0.471	g_u	0.518	a_g	4.163
h_g	0.240	a_g	0.619		
f_{2u}	0.460	h_g	1.107		
g_u	0.518	f_{1u}	1.990		
f_{1u}	0.619	a_g	4.293		
h_g	1.358				
a_g	1.485				
f_{1u}	2.370				
a_g	4.469				

(f) D_{4d} bicapped antiprism, B—B 1.74 A, B—H 1.20 A

e_2	−0.895	e_2	−0.894	e_2	−0.884
a_1	−0.875	e_3	−0.862	e_3	−0.862
e_3	−0.865	a_1	−0.859	b_2	−0.850
b_2	−0.862	b_2	−0.853	a_1	−0.812
b_2	−0.852	b_2	−0.834	b_2	−0.812
e_1	−0.851	e_1	−0.812	e_1	−0.776
e_3	−0.807	e_2	−0.754	e_3	−0.747
e_2	−0.804	a_2	−0.739	a_2	−0.739
b_2	−0.795	e_1	−0.637	e_1	−0.615
a_1	−0.786	e_2	−0.601	e_2	−0.598
e_3	−0.747	b_1	−0.590	b_1	−0.590
a_2	−0.739	e_3	−0.430	e_3	−0.327
b_2	−0.727	b_2	−0.221	e_1	0.328
e_1	−0.711	e_2	−0.198	e_2	0.756
a_1	−0.699	e_3	−0.148	e_2	0.760
e_1	−0.628	a_1	−0.120	a_1	1.004
e_2	−0.600	e_1	−0.082	e_1	1.447
b_1	−0.590	b_2	0.120	b_2	1.978
e_3	−0.363	e_1	0.379	a_1	3.877
e_1	0.197	a_1	0.489		
e_3	0.243	e_2	0.807		
e_2	0.364	e_3	0.901		
b_2	0.399	a_1	1.046		
a_1	0.446	e_1	1.584		
e_1	0.509	b_2	2.059		
b_2	0.734	a_1	3.997		
e_2	0.965				
a_1	1.095				
e_3	1.180				
a_1	1.393				
e_1	1.968				
b_2	2.375				
a_1	4.172				

[a] The energy parameters given here differ slightly from those of Longuet-Higgins and Roberts (reference 8 in text) who performed the calculation for B-B 1.72 A, Slater exponent 1.242. The latter calculations were checked with our program and an error was found in the $t_{1u}(f_{1u})$ levels, of which the authors are aware. The correct f_{1u} energy parameters are: −0.864, −0.175, 1.218.

[b] The energy parameters given here differ from those of Longuet-Higgins and Roberts (reference 6 in text) who performed the calculations for B-B 1.77 A, Slater exponent 1.271. The latter calculations were checked and found in rough agreement with the results of our program. The source of the small discrepancies here is not known.

TABLE III. Separated *in* and *surface* orbitals for some polyhedra.

tetrahedron			
surface		in	
f_1	−0.556	f_2	−0.698
e	0.033	a_1	2.094
f_2	0.534		
octahedron			
surface		in	
f_{1g}	−0.671	e_g	−0.884
f_{2u}	−0.416	f_{1u}	−0.400
f_{2g}	0.493	a_{1g}	2.969
f_{1u}	0.594		
cube			
surface		in	
e_u	−0.729	a_{2u}	−0.937
f_{1g}	−0.637	f_{2g}	−0.749
f_{2g}	−0.063	f_{1u}	0.019
f_{2u}	0.096	a_{1g}	3.127
f_{1u}	0.494		
e_g	0.893		
cube-octahedron			
surface		in	
f_{1g}	−0.756	f_{2u}	−0.848
a_{2g}	−0.739	e_g	−0.730
e_u	−0.669	f_{2g}	−0.514
f_{2u}	−0.520	f_{1u}	0.644
f_{1g}	−0.232	a_{1g}	3.616
f_{1u}	0.179		
f_{1u}	0.554		
f_{2g}	0.617		
e_g	0.838		
a_{2u}	0.881		
icosahedron			
surface		in	
f_{1g}	−0.782	f_{2u}	−0.886
h_u	−0.678	h_g	−0.666
g_g	−0.471	f_{1u}	0.609
g_u	0.518	a_g	4.163
f_{1u}	0.526		
h_g	0.794		

lar point group O_h:

$$3A_{1g}+3E_g+4F_{1u}+F_{1g}+F_{2g}+F_{2u}.$$

After group-theoretical reduction, we are left with no worse than a quartic equation to solve. Still the number of parameters is too great, and we shall seek a simpler approach.

The B—H bonds in boron hydrides and hydride ions have the characteristics of normal covalent single bonds. The bond distance is fairly constant and does not seem to depend on the bonding of the B involved, nor on the degree of electron deficiency in the molecule. We may consider the B—H bonds formed by an sp^3 orbital from the B and the hydrogen orbital consuming an electron pair, one of which is donated by the B and the other by the hydrogen atom. Once we make this step, two approaches are possible.

In the first method,[6,8] which we will call "$4N$," the H orbitals are dropped, and the eigenvalue problem of degree $4N$, involving only B orbitals, is solved. Upon examination of the resulting energy levels, one finds a set of orbitals near the nonbonding level which (1) have the correct symmetry for an outpointing set, and (2) concentrate electronic charge in the direction radially out from the polyhedron center at each atom. These "out" orbitals are then identified as those which form the B—H bonds. They interact with the set of H orbitals of the same symmetry to produce a bonding and an antibonding set. In filling the available electron slots, each boron and hydrogen is asked to contribute one electron to the bonding set, which is thus filled by $2N$ electrons. The remaining framework levels are populated in the usual fashion.

In the second method,[4] which we will call "$3N$," one orbital at each boron is prepared for bonding, i.e., we form an sp^3 hybrid directed out. We then assume that the interactions of these outpointing orbitals with the other framework orbitals are negligible, and then find by use of the methods given above that the secular equation becomes one of degree $3N$.

Now once we have removed the H orbitals, we have no *a priori* rationale for giving preference to either the $3N$ or the $4N$ scheme. The $4N$ approach has the advantage that one can work with an atomic orbital basis, whereas for $3N$ we must treat hybrids. On the other hand, the size of the matrix to be diagonalized is smaller for $3N$.

If the factorizations we have described are to have any significance, we must have a reasonable degree of coincidence between the various calculated energy level schemes. To examine this point, we have carried out the $5N$, $4N$, and $3N$ calculations for six molecules, with $\alpha(2s\mathrm{B})=\alpha(2p\mathrm{B})=\alpha(1s\mathrm{H})$. Calculations for unequal alphas give different energies, but exhibit the same kind of behavior regarding the factorizations. The molecules are the tetrahedron (T_d), octahedron (O_h), cube (O_h), bicapped archimedean antiprism (D_{4d}), cube-octahedron (O_h), icosahedron (I_h). The symmetries of the $4N$ MO's and the outpointing set are given in Table I. In Tables II(a)-II(f) we give the calculated $5N$, $4N$, and $3N$ energy levels.

It is seen that the $4N$ and $3N$ calculations are quite good approximations. In all methods, filled electronic shells are predicted for tetrahedral B_4H_4,[4] C_4H_4,[15] P_4, octahedral $B_6H_6^{-2}$,[8] cubical $B_8H_8^{-2}$, C_8H_8, D_{4d} $B_{10}H_{10}^{-2}$,[2] cubeoctahedral $B_{12}H_{12}^{-2}$,[16] icosahedral $B_{12}H_{12}^{-2}$.[6] Moreover, in each approximation the order of the significant bonding levels is preserved, while predicted electronic excitations vary. Indeed, the situation with respect to electronic transitions is analogous to that in certain heteronuclear aromatics, where there may be $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions. The B—H bond orbitals (whose energy is clearly defined only by the $5N$ calculation) are the analogs of the nonbonded orbitals, while the delocalized framework MO's are analogous to the

[15] W. N. Lipscomb, Tetrahedron Letters **18**, 20 (1959).
[16] W. N. Lipscomb and D. Britton, J. Chem. Phys. **33**, 275 (1960).

TABLE IV. Energy parameters.

(a) D_{3d} rhombic hexahedron, $N=8$, B—B 1.74 A

4N		3N		reconstructed 3N[a]		equatorial	
e_g	−0.887	e_g	−0.887	a_{2u}	−0.801	a_{2u}	−0.801
a_{1g}	−0.852	a_{2u}	−0.831	e_g	−0.795	e_g	−0.795
a_{2u}	−0.837	e_u	−0.829	a_{1g}	−0.748	a_{2g}	−0.664
e_u	−0.836	a_{2u}	−0.762	a_{2u}	−0.748	e_u	−0.618
a_{2u}	−0.819	a_{1g}	−0.736	e_g	−0.679	a_{1u}	−0.409
e_g	−0.708	e_g	−0.692	e_u	−0.679	e_g	0.287
a_{2g}	−0.664	a_{2g}	−0.664	a_{2g}	−0.664	e_u	1.004
e_u	−0.636	e_u	−0.590	e_u	−0.618	a_{1g}	2.118
e_g	−0.443	a_{1u}	−0.409	a_{1u}	−0.409		
a_{1u}	−0.409	e_g	−0.173	e_g	0.105	apex (C_{3v})	
e_u	−0.237	e_u	0.114	e_u	0.105	a_1	−0.748
a_{2u}	−0.200	e_g	0.698	e_g	0.287	e	−0.679
a_{1g}	−0.063	a_{1g}	0.830	e_u	1.004	e	0.105
a_{2u}	0.068	e_u	1.090	a_{1g}	1.896	a_1	1.896
e_g	0.153	a_{2u}	1.752	a_{2u}	1.896		
e_u	0.217	a_{1g}	3.362	a_{1g}	2.118		
a_{1g}	0.296						
e_g	0.740						
a_{1g}	0.928						
e_u	1.238						
a_{2u}	1.901						
a_{1g}	3.451						

(b) D_{4d} bicapped antiprism B—B 1.74 A

4N		3N		reconstructed 3N[a]		equatorial	
e_2	−0.894	e_2	−0.894	a_1	−0.829	e_3	−0.828
e_3	−0.862	e_3	−0.862	b_2	−0.829	b_2	−0.812
a_1	−0.859	b_2	−0.850	e_3	−0.828	e_2	−0.740
b_2	−0.853	a_1	−0.812	b_2	−0.812	a_2	−0.739
b_2	−0.834	b_2	−0.812	e_2	−0.740	e_1	−0.608
e_1	−0.812	e_1	−0.776	a_2	−0.739	b_1	−0.590
e_3	−0.754	e_3	−0.747	e_2	−0.676	e_3	−0.034
a_2	−0.739	a_2	−0.739	e_1	−0.666	e_2	0.680
e_1	−0.637	e_1	−0.615	e_3	−0.666	e_1	1.337
e_2	−0.601	e_2	−0.598	e_1	−0.608	a_1	2.528
b_1	−0.590	b_1	−0.590	b_1	−0.590		
e_3	−0.430	e_3	−0.327	e_3	−0.034		
b_2	−0.221	e_1	0.328	e_3	0.337		
e_2	−0.198	e_2	0.756	e_1	0.337	apex (C_{4v})	
e_3	−0.148	e_3	0.760	e_2	0.680	a_1	−0.829
a_1	−0.120	a_1	1.004	e_1	1.337	b_2	−0.676
e_1	−0.082	e_1	1.447	a_1	2.163	e	−0.666
b_2	0.120	b_2	1.978	b_2	2.163	e	0.337
e_1	0.379	a_1	3.877	a_1	2.528	a_1	2.163
a_1	0.489						
e_2	0.807						
e_3	0.901						
a_1	1.046						
e_1	1.584						
b_2	2.059						
a_1	3.997						

(c) D_{5d} bicapped pentagonal antiprism ($=I_h$ icosahedron), B—B 1.73 A.

4N		3N		reconstructed 3N[a]		equatorial	
f_{2u}	−0.886	f_{2u}	−0.886[b]	e_{1g}	−0.835	e_{1g}	−0.835
h_g	−0.862	h_g	−0.856	a_{1g}	−0.827	a_{1u}	−0.810
f_{1u}	−0.827	f_{1g}	−0.782	a_{2u}	−0.827	e_{2u}	−0.809
f_{1g}	−0.782	f_{1u}	−0.773	a_{1u}	−0.810	a_{2g}	−0.783
h_u	−0.678	h_u	−0.678	e_{2u}	−0.809	e_{2g}	−0.689
g_g	−0.471	g_g	−0.471	a_{2g}	−0.783	a_{2u}	−0.678
h_g	−0.239	g_u	0.518	e_{1g}	−0.718	e_{1u}	−0.636
f_{2u}	−0.225	h_g	0.984	e_{1u}	−0.718	e_{1g}	−0.243
f_{1u}	0.150	f_{1u}	1.907	e_{2g}	−0.689	e_{2u}	0.377
g_u	0.518	a_g	4.163	a_{2u}	−0.678	e_{2g}	0.957
a_g	0.619			e_{1u}	−0.636	e_{1u}	1.653
h_g	1.107			e_{2g}	−0.613	a_{1g}	2.721
f_{1u}	1.990			e_{2u}	−0.613		
a_g	4.293			e_{1g}	−0.243	apex (C_{5v})	
				e_{2u}	0.377	a_1	−0.827
				e_{1g}	0.673	e_1	−0.718
				e_{1u}	0.673	e_2	−0.613
				e_{2g}	0.957	e_1	0.673
				e_{1u}	1.653	a_1	2.143
				a_{1g}	2.143		
				a_{2u}	2.143		
				a_{1g}	2.721		

[a] *Apex* and *equatorial* levels arranged in order.
[b] The correlations from I to D_5 are: $f\rightarrow a_2+e_2$, $h\rightarrow e_1+e_2+a_1$, $f_1\rightarrow a_2+e_1$, $g\rightarrow e_1+e_2$, $a\rightarrow a_1$.

aromatic π orbitals. To preserve the analogy, we denote framework orbitals by f, f^* and the B—H bond orbitals by b, b^*. Thus the first excitation in B_4H_4, $B_6H_6^{-2}$, C_8H_8, O_h, and I_h $B_{12}H_{12}^{-2}$ is predicted as $b\rightarrow f^*$, in $B_{10}H_{10}^{-2}$ $b\rightarrow b^*$. If the $b\rightarrow f^*$ transition is symmetry allowed, it is nevertheless expected to be of low intensity since the spatial overlap of the b and f^* wavefunctions is small. Thus the spectra of these polyhedral molecules should be characterized by several weak absorptions in the near uv($b\rightarrow f^*$) followed by a strong absorption ($f\rightarrow f^*$) at higher energies. Dr. A. Kaczmarczyk of this laboratory has kindly communicated to us[17] preliminary, low-resolution uv spectral data on $B_{12}H_{12}^{-2}(I_h)$, $B_{10}H_{10}^{-2}$. Both compounds are characterized by an intense transition in the region 2000–2100 A, with no noticeable absorption at higher wavelengths. Since these spectra were taken at low concentration, further experimental study is desirable to establish if the low-intensity $b\rightarrow f^*$ transitions are indeed present.

[17] A. Kaczmarczyk (private communication).

IN-SURFACE FACTORIZATION

A further physical factorization of the $3N$ problem has been proposed.[16] One may rehybridize the 3 sp^3 hybrids at each boron so as to give an orbital (mostly $2s$) pointing "*in*" toward the polyhedron center, and two orbitals, pure $2p$, directed arbitrarily perpendicular to the axial direction, i.e., tangential to the polyhedron circumsphere. The latter set of $2N$ we call "*surface*" orbitals. One then makes the physical factorization by neglecting *in-surface* interactions, and thus factoring the $3N$ problem into one of degree N and one of degree $2N$. The levels thus obtained for 5 of the polyhedra discussed in the preceding section are given in Table III.

For the tetrahedron and octahedron there is no significant change. But for the cube, icosahedron, and cube-octahedron, the factorization has in each case produced a superfluous bonding or nonbonding f_{1u} orbital. When the interaction between *in* and *surface* orbitals is accounted for, this level becomes quite antibonding. But if we were to make predictions *entirely* on the basis of the solutions of the physically factorized

TABLE V. Energy parameters.

4N		3N		reconstructed 3N[a]		equatorial	
(a) D_{3h} bicapped trigonal prism ($N=8$), B—B 1.74A							
e''	−0.895	e''	−0.895	e''	−0.821	e''	−0.821
a_2''	−0.860	a_2''	−0.817	a_2''	−0.721	a_2''	−0.717
a_1'	−0.839	e'	−0.804	a_1'	−0.721	a_1''	−0.615
e'	−0.819	e''	−0.722	a_2''	−0.717	a_2'	−0.459
e''	−0.742	a_1'	−0.692	e''	−0.679	e'	−0.070
a_2''	−0.705	a_2''	−0.659	e'	−0.679	e''	−0.060
a_1''	−0.615	a_1''	−0.615	a_1''	−0.615	e'	0.900
e'	−0.484	a_2'	−0.459	a_2'	−0.459	a_1'	1.894
a_2'	−0.459	e''	−0.298	e'	−0.070		
e''	−0.420	e'	−0.211	e''	−0.060	apex (C_{3v})	
e''	−0.197	e'	0.338	e''	0.084	a_1	−0.721
a_2''	−0.186	e''	0.359	e'	0.084	e	−0.679
a_1'	−0.059	e'	0.991	e'	0.900	e	0.084
a_2''	0.106	a_1'	1.025	a_1'	1.894	a_1	1.910
e'	0.153	a_2''	1.706	a_2''	1.910		
a_1'	0.309	a_1'	2.993	a_1'	1.910		
e'	0.338						
e''	0.576						
e'	1.090						
a_1'	1.164						
a_2''	1.877						
a_1'	3.065						
(b) D_{4h} bicapped cube, ($N=10$), B—B 1.74 A							
b_{1u}	−0.928	b_{1u}	−0.927	b_{1u}	−0.855	b_{1u}	−0.855
a_{2u}	−0.869	e_g	−0.862	a_{2u}	−0.819	e_g	−0.813
e_g	−0.865	b_{2g}	−0.862	a_{1g}	−0.819	a_{1u}	−0.711
b_{2g}	−0.863	a_{2u}	−0.860	e_g	−0.813	a_{2u}	−0.693
a_{1g}	−0.851	a_{1g}	−0.792	a_{1u}	−0.711	a_{2g}	−0.618
e_u	−0.788	e_u	−0.745	a_{2u}	−0.693	e_u	−0.295
e_g	−0.750	e_g	−0.735	b_{1u}	−0.687	b_{2g}	−0.192
a_{2u}	−0.714	a_{1u}	−0.711	b_{2g}	−0.687	e_g	−0.182
a_{1u}	−0.711	b_{1u}	−0.711	e_g	−0.660	b_{2u}	0.113
b_{1u}	−0.711	a_{2u}	−0.685	e_u	−0.660	b_{1g}	0.871
a_{2g}	−0.618	a_{2g}	−0.618	a_{2g}	−0.618	e_u	1.193
e_u	−0.474	e_u	−0.407	e_u	−0.295	a_{1g}	2.280
e_g	−0.404	e_g	−0.394	b_{2g}	−0.192		
b_{2g}	−0.309	b_{2g}	0.079	e_g	−0.182	apex (C_{4v})	
e_g	−0.309	b_{2u}	0.113	b_{2u}	0.113	a_1	−0.819
b_{1u}	−0.230	e_u	0.463	e_g	0.312	b_2	−0.687
a_{2u}	−0.195	e_g	0.586	e_u	0.312	e	−0.660
a_{1g}	−0.110	b_{1g}	0.871	b_{1g}	0.871	e	0.312
e_u	0.012	a_{1g}	1.165	e_u	1.193	a_1	2.201
b_{2u}	0.113	e_u	1.301	a_{2u}	2.201		
a_{2u}	0.183	a_{2u}	2.005	a_{1g}	2.201		
b_{2g}	0.285	a_{1g}	3.519	a_{1g}	2.280		
a_{1g}	0.440						
e_u	0.492						
e_g	0.819						
b_{1g}	0.871						
a_{1g}	1.236						
a_{2u}	2.084						
a_{1g}	3.620						
(c) D_{5h} bicapped pentagonal prism, ($N=12$), B—B 1.74 A							
e_2''	−0.913	e_2''	−0.911	e_2''	−0.856	e_2''	−0.856
a_2''	−0.872	a_2''	−0.867	a_2''	−0.833	e_1''	−0.799
e_1''	−0.855	a_1'	−0.847	a_1'	−0.833	a_1''	−0.758
a_1'	−0.853	e_1''	−0.840	e_1''	−0.799	a_2'	−0.694
e_2'	−0.823	e_2'	−0.820	a_1''	−0.758	a_2''	−0.675
e_1'	−0.800	e_1''	−0.764	e_1''	−0.713	e_1'	−0.432
e_1''	−0.764	a_1''	−0.758	e_1'	−0.713	e_1''	−0.298
a_1''	−0.758	e_1'	−0.752	a_2'	−0.694	e_2'	−0.294
a_2''	−0.734	a_2'	−0.694	a_2''	−0.675	e_2''	0.088
a_2'	−0.694	a_2''	−0.686	e_2''	−0.620	e_2'	0.948
e_2''	−0.684	e_2''	−0.682	e_2'	−0.620	e_1'	1.480
e_1'	−0.536	e_1'	−0.535	e_1'	−0.432	a_1'	2.452
e_1''	−0.506	e_1''	−0.499	e_1''	−0.298		
e_2''	−0.311	e_2'	−0.011	e_2'	−0.294	apex (C_{5v})	
e_2'	−0.269	e_2''	0.122	e_2''	0.088	a_1	−0.833
a_1'	−0.217	e_1'	0.633	e_1''	0.660	e_1	−0.713
e_1''	−0.211	e_1''	0.894	e_1'	0.660	e_2	−0.620
a_2''	−0.201	e_2'	0.948	e_2'	0.948	e_1	0.660
e_2'	0.101	a_1'	1.136	e_1'	1.480	a_1	2.178
e_1'	0.126	e_1'	1.708	a_1'	2.178		
e_2''	0.178	a_2''	1.977	a_2''	2.178		
a_2''	0.245	a_1'	3.754	a_1'	2.452		
a_1'	0.553						
e_1'	0.637						
e_2'	1.006						
e_1''	1.050						
a_1'	1.237						
e_1'	1.769						
a_2''	2.031						
a_1'	3.870						

[a] *Apex* and *equatorial* levels arranged in order.

secular equation, we would conclude that cube-octahedral $B_{12}H_{12}^{-2}$ and cubical C_8H_8 still give closed shells, but with very small energy gaps separating highest filled and lowest unfilled levels. In the case of the icosahedron, we would be led to the erroneous prediction of the closed shell character of $B_{12}H_{12}$ with a minute gap, and the prediction of instability for the doubly negative anion.

The failure of the *in-surface* factorization does not imply that this simplification may not be used, with certain precautions, to obtain an approximate picture of the level ordering. The precaution to be observed is the following. If two levels of the same symmetry and near in energy are produced, one arising from the *in* set, the other from the *surface* set, then they will in general interact in such a way as to make one of them quite antibonding. Similar precautions must be kept in mind in judging the results of other physical factorizations considered below.

EQUATORIAL-APEX FACTORIZATION

This factorization has been used in treating the proposed $B_{10}H_{10}^{-2}$ structure[2] (D_{4d} bicapped antiprism) and in discussing icosahedral bonding.[7] The procedure applies to bicapped prisms and antiprisms where we distinguish two apex atoms from $N-2$ "*equatorial*" atoms. The following physical factorization of the $3N$ problem has been proposed by Lipscomb: Orient the three hybrids on each equatorial boron in such a manner that one orbital is directed toward the adjacent apex. Such an orbital set is illustrated in reference 7. Now separate the orbitals in three noninteracting groups: the $2(N-2)$ equatorial orbitals and two apical groups each composed of 3 apex orbitals and $\frac{1}{2}(N-2)$

orbitals pointing toward the apex. In Tables IV(a)–IV(c) and V(a)–V(c) we give the $4N$, $3N$, *apex*, *equatorial*, and "reconstructed" $3N$ (superimposed *apex* and *equatorial* energies, to facilitate comparison with $3N$) energies for the antiprism (D_{3d} bicapped trigonal antiprism, D_{4d} bicapped archimedean antiprism, D_{5d} bicapped pentagonal antiprism $= I_h$ icosahedron) and the prism (D_{3h} bicapped trigonal prism, D_{4h} bicapped cube, D_{5h} bicapped pentagonal prism) series.

TABLE VI. Energy parameters.

$4N$		$3N$		reconstructed $3N$[a]		ring	
(a) D_{3h} trigonal bipyramid ($N=5$), B—B 1.70 A							
e'	−0.865	e'	−0.863	a_2''	−0.858	e'	−0.834
a_2''	−0.858	a_2''	−0.858	e'	−0.834	a_2'	−0.556
a_1'	−0.853	a_1'	−0.823	e''	−0.649	e'	0.376
e''	−0.649	e''	−0.649	a_2'	−0.556	a_1'	1.473
a_2'	−0.556	a_2'	−0.556	e'	0.052		
e'	−0.388	e'	−0.301	a_1'	0.272	polar	
a_1'	−0.104	e''	0.335	e''	0.335	a_2''	−0.858
a_2''	−0.063	e'	0.758	e'	0.376	e''	−0.649
e'	−0.052	a_2''	1.108	a_2''	1.108	e'	0.052
a_1'	0.124	a_1'	2.567	a_1'	1.473	a_1'	0.272
e''	0.335					e''	0.335
e'	0.898					a_2''	1.108
a_2''	1.136						
a_1'	2.615						
(b) D_{4h} tetragonal bipyramid (O_h octahedron, $N=6$), B—B 1.73 A							
e_g	−0.887	b_{1g}	−0.886[b]	b_{1g}	−0.886	b_{1g}	−0.886
f_{1u}	−0.831	a_{1g}	−0.884	a_{2u}	−0.829	e_u	−0.755
f_{1g}	−0.671	a_{2u}	−0.829	e_u	−0.755	a_{2g}	−0.671
f_{2u}	−0.416	e_u	−0.819	a_{2g}	−0.671	e_u	0.421
f_{1u}	−0.144	a_{2g}	−0.671	e_g	−0.671	b_{2g}	0.493
e_g	−0.089	e_g	−0.671	b_{2u}	−0.416	a_{1g}	1.732
a_{1g}	0.204	b_{2u}	−0.416	e_u	0.089		
f_{2g}	0.493	e_u	−0.416	a_{1g}	0.400	polar	
f_{1u}	1.130	b_{2g}	0.493	e_u	0.421	a_{2u}	−0.829
a_{1g}	3.066	e_g	0.493	b_{2g}	0.493	e_g	−0.671
		e_u	0.990	e_g	0.493	b_{2u}	−0.416
		f_{1u}	1.023	a_{2u}	1.023	e_u	0.089
		a_{1g}	3.017	a_{1g}	1.732	a_{1g}	0.400
						e_g	0.493
						a_{2u}	1.023
(c) D_{5h} pentagonal bipyramid ($N=7$) B—B 1.74 A							
a_1'	−0.870	a_2''	−0.851	a_2''	−0.851	e_2'	−0.845
a_2''	−0.851	a_1'	−0.847	e_2'	−0.845	a_2'	−0.726
e_1'	−0.849	e_2'	−0.845	a_2'	−0.726	e_1'	−0.709
e_2'	−0.849	e_1'	−0.840	e_1'	−0.709	e_2'	0.494
a_2'	−0.726	a_2'	−0.726	e_1''	−0.669	e_1'	0.562
e_1''	−0.669	e_1''	−0.669	e_2''	−0.371	a_1'	1.722
e_1'	−0.553	e_1'	−0.508	e_1'	0.219		
e_2''	−0.371	e_2''	−0.371	e_2'	0.494	polar	
a_2''	−0.349	e_2'	0.494	e_1''	0.524	a_2''	−0.851
e_2'	−0.187	e_1''	0.524	e_1'	0.562	e_1''	−0.669
a_1'	−0.071	a_2''	0.740	a_1'	0.704	e_2''	−0.371
e_1'	0.020	e_1'	1.420	a_2''	0.734	e_1'	0.219
a_1'	0.275	a_1'	3.273	a_1'	1.722	e_1''	0.524
e_1''	0.524					a_1'	0.704
e_2'	0.549					a_2''	0.734
a_2''	1.084						
e_1'	1.483						
a_1'	3.311						

[a] *Ring* and *polar* orbitals arranged in order.

[b] Here orbitals lose O_h symmetry when out orbitals are removed, since the latter, in this factorization, were not chosen all equivalent. The correlations $O \to D_4$ here are $e \to b_1 + a_1$, $f_1 \to a_2 + e$, $f_2 \to b_2 + e$, $a_1 \to a_1$.

TABLE VII. Energy parameters.

$4N$		$3N$		reconstructed $3N$[b]		ring	
(a) C_{3v} trigonal pyramid (T_d tetrahedron, $N=4$), B—B 1.70 A							
f_2	−0.853	e	−0.853[a]	e	−0.834	e	−0.834
f_1	−0.556	a_1	−0.840	a_2	−0.556	a_2	−0.556
f_2	−0.093	a_2	−0.556	e	−0.495	e	0.376
e	0.033	e	−0.534	a	−0.426	a_1	1.473
a_1	0.038	e	0.029	e	0.234		
f_2	0.747	e	0.639	e	0.376	polar	
a_1	2.158	a_1	0.697	a_1	0.949	e	−0.495
		a_1	2.138	a_1	1.473	a_1	−0.426
						e	0.234
						a_1	0.949
(b) C_{4v} tetragonal pyramid ($N=5$), B—B 1.74 A							
b_1	−0.882	b_1	−0.881	b_1	−0.881	b_1	−0.881
a_1	−0.854	a_1	−0.853	e	−0.748	e	−0.748
e	−0.803	e	−0.794	b_2	−0.664	b_2	−0.664
b_2	−0.664	b_2	−0.664	e	−0.454	e	0.421
e	−0.542	e	−0.542	b_2	−0.409	a_2	0.492
b_1	−0.409	b_1	−0.409	a_1	−0.332	a_1	1.709
e	−0.152	e	0.106	e	0.368		
a_1	−0.126	a_2	0.492	e	0.421	polar	
b_1	−0.087	a_1	0.711	a_2	0.492	e	−0.454
a_1	0.130	e	0.816	a_1	0.914	b_2	−0.409
e	0.135	a_1	2.433	a_1	1.709	a_1	−0.332
a_2	0.492					e	0.368
a_1	0.803					a_1	0.914
e	0.931						
a_1	2.458						
(c) C_{5v} pentagonal pyramid ($N=6$), B—B 1.74 A							
a_1	−0.860	a_1	−0.848	e_2	−0.845	e_2	−0.845
e_2	−0.849	e_2	−0.845	a_2	−0.726	a_2	−0.726
e_1	−0.813	e_1	−0.801	e_1	−0.709	e_1	−0.709
a_2	−0.726	a_2	−0.726	e_1	−0.373	e_2	0.494
e_1	−0.592	e_1	−0.563	e_2	−0.372	e_1	0.562
e_2	−0.371	e_2	−0.371	a_1	−0.144	a_1	1.722
a_1	−0.220	e_1	0.185	e_1	0.448		
e_2	−0.187	e_2	0.494	e_2	0.494	polar	
e_1	−0.042	a_1	0.636	e_1	0.562	e_1	−0.373
a_1	0.214	e_1	1.106	a_1	0.737	e_2	−0.372
e_1	0.231	a_1	2.527	a_1	1.722	a_1	−0.144
e_2	0.549					e_1	0.448
a_1	0.842					a_1	0.737
e_1	1.173						
a_1	2.554						

[a] Here T_d symmetry is lost when out orbitals are removed. The correlations $T_d \to C_{3v}$ are $f_2 \to e + a_1$, $f_1 \to e + a_2$, $e \to e$, $a_1 \to a_1$.

[b] *Ring* and *polar* orbitals arranged in order.

On examining the closed shell possibilities from the $3N$ scheme we find $B_8H_8^{-2}$, $B_{10}H_{10}^{-2}$, $B_{12}H_{12}^{-2}$ for the antiprism series, with $B_8H_8^{+2}$ also a distinct possibility. For the prism series we have $B_8H_8^{-2}$, $B_{10}H_{10}$, $B_{12}H_{12}^{-2}$ though these would not be configurations boron would favor.

To make use of the factorization, it has been proposed that for $N=8$, 10, 12 respectively 3, 5, 7 electron pairs be assigned to the *equatorial* orbitals and 3 pairs to each *apical* set. Now the *equatorial/apical* orbital ratios were 12/12, 16/14, 20/16, while this electron assignment would give electron ratios of 6/12, 10/12, 14/12, respectively. We would expect the factorization to break down when these ratios differ considerably. Indeed it may be seen from Table IV that the fac-

TABLE VIII. Energy levels of the rhombic dodecahedron ($N=14$) for B—B=1.70 A, $\alpha(2s)=-15.36$ ev, $\alpha(2p)=-8.63$ ev, $K=-21.0$ ev.

Level	E(ev) Slater	E(ev) SCF-Slater
a_{1g}	62.79	48.52
f_{2g}	50.20	31.00
a_{2u}	31.34	35.29
e_g	30.88	24.86
f_{1g}	30.63	38.61
f_{1u}	26.07	42.10
f_{2g}	25.89	15.10
f_{2u}	21.88	30.10
f_{1u}	15.03	25.53
e_u	10.37	18.33
f_{1u}	−0.92	4.18
a_{1g}	−5.86	−4.08
f_{2g}	−6.56	−3.06
e_g	−8.35	−5.74
f_{1g}	−8.65	−5.46
a_{2u}	−10.15	−9.89
f_{1u}	−11.72	−10.98
f_{1u}	−12.52	−12.12
f_{2u}	−14.08	−13.05
a_{1g}	−15.13	−14.65
f_{2g}	−16.55	−16.84
e_g	−16.92	−17.10
f_{1u}	−18.61	−18.86
a_{1g}	−19.66	−19.78

torization fails for the $N=8$ antiprism where another *equatorial* level has come below the degenerate *apical* level. It should be noted that the factorization is somewhat better for the prism series, since the prismatic arrangement makes interactions between *equatorial* orbitals smaller with respect to the more compact antiprismatic configurations. The gaps between filled and unfilled orbitals in the prism series are correspondingly smaller.

RING-POLAR SEPARATION

This physical factorization has been devised for $N=5$, 6, 7 bipyramids and $N=4$, 5, 6 pyramids.[18] The "ring" atoms are those at the base of the pyramid or in the equatorial section of the bipyramid. Let us hybridize the orbitals of the ring so that we have 3 sp^2 hybrids at each atom in the plane of the ring, and a p_z perpendicular to that plane. The hybrids are so oriented that one of them is directed radially out from the center of the ring plane. At the apices the usual set of sp^3 hybrids is formed. We reduce the problem to degree $3N$ by removing outpointing orbitals, and then attempt the physical factorization of separating for the bipyramids the $2(N-2)$ sp^2 hybrids in the plane of the ring from the $(N-2)p_z$ orbitals combined with six apex hybrids. The latter form what we call the "*polar*" set. The planar *ring* orbitals may be considered as giving rise to $N-2$ classical covalent bonds, consuming $2(N-2)$ electrons. Indeed we may note here the empirical rule, to which we have found no exception in our calculations, that whenever a molecule (such as C_4H_4, P_4, C_8H_8) or a molecular fragment (such as the B_4, B_5, B_6 rings) can be assigned a classical non-electron-deficient single-bonded structure, the LCAO–MO calculation gives a closed shell structure with a large energy gap. The LCAO's may be transformed by a unitary transformation into a set of equivalent orbitals which closely resemble the localized saturated bonds.

The $N-2$ *polar* p_z orbitals yield the familiar aromatic ring arrangement. In a naive approach the interaction of this aromatic ring with the six apex orbitals is such that the lowest orbitals of the resultant *polar* set are an a and a doubly degenerate e. This may be seen in the last column of Tables VI(a)–VI(b) for the B_5 and B_6 bipyramids. Filling these orbitals and the above mentioned $N-2$ *ring* orbitals requires then $N+1$ electron pairs, or a $B_NH_N^{-2}$ ion is predicted. Unfortunately, the electron/orbital ratios in such a separation differ greatly, being 6/6, 8/8, 10/10 in the ring, 6/9, 6/10, 6/11 in the polar set for $N=5$, 6, 7, respectively. In the actual calculation, a totally symmetric orbital (a_1', a_{1g}) comes much too low in the *polar* set for each case studied, indeed for $N=7$ it goes below the *ring* e orbitals, leading to a prediction of a closed shell for B_7H_7, in disagreement with the clearcut prediction of $B_7H_7^{-2}$ by the $3N$ calculation.

For the B_N pyramid, there are $2(N-1)$ orbitals in the *ring* set, and $N+2$ *polar* orbitals. The results of the LCAO–MO calculations are given in Tables VII(a)–VII(c). Considerations similar to the above lead us to prediction of closed shells for B_NH_N or $B_NH_N^{-4}$. The electron/orbital ratios are 6/6, 8/8, 10/10 in the *ring*, 2/6, 2/7, 2/8 in the *polar* set, for B_NH_N, $N=4$, 5, 6, and as expected the factorization is bad, a *polar* e level coming close to the least bonding *ring* e level. The electron/orbital ratios for $B_NH_N^{-4}$ are 6/6, 6/7, 6/8 in the *polar* set, and the separation correspondingly good. However, such highly charged species are not expected to be stable. Their carborane analogs may well exist, pyramidal $C_4B_2H_6$, C_4BH_5, C_4H_4 (tetrahedrane).

It should be pointed out that for the *ring-polar* separation as for other physical factorizations discussed in this paper, judicious juggling of parameters whose relative, but not absolute, magnitudes are assumed, may lead, when coupled with correspondingly judicious caution, to worthwhile level schemes. The actual failure or success of an approximation is revealed only when numbers are substituted for the parameter symbols.

OVERLAP INTEGRALS

We now ask, "What is the best basis set to use in Eq. (1)? Shall we use atomic self-consistent field (SCF) functions, Morse-Young-Haurwitz orbitals, or Slater orbitals?" To examine this question, two calculations of the 4N type were carried out for the rhombic dodecahedron, one using Slater overlaps, the other using a mixed orbital set consisting of 2s Slater functions and 2p SCF functions for carbon. The $N=14$ polyhedron was chosen because of its symmetry (O_h)

[18] W. N. Lipscomb, Proc. Natl. Acad. Sci. U. S. 47, 1791 (1961).

and the large number of levels available for comparison. Overlaps for the mixed Slater-SCF sets are given by Mulliken[19]. The SCF $2p$ function has much greater spatial extent, and thus the overlaps are quite different, particularly at greater distances.

The energy levels of the polyhedron are given in Table VIII. The SCF calculation was checked against a previous calculation for this molecule by L. L. Lohr, who has suggested the use of these functions.[7,20] A $B_{14}H_{14}^{-2}$ species will yield a closed electronic shell. The levels of the SCF calculation agree quite well with the Slater levels, particularly for the bonding and nonbonding states, which, after all, are the only ones that matter. There is also the general trend that the SCF levels are more bonding or antibonding than their Slater counterparts, this being explained by the greater SCF overlap.

The conclusion we draw is that general predictions are not overly affected by the use of different overlap schemes. There is indeed no *a priori* reason why atomic SCF functions should be better basis orbitals for a molecular calculation. Slater orbitals are easy to handle, and will be used throughout our calculations.

[19] R. S. Mulliken, J. Chem. Phys. **19**, 900 (1951).
[20] L. L. Lohr (private communication).

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