Theory of Polyhedral Molecules. II. A Crystal Field Model

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A crystal field model is developed for finding the molecular orbitals of polyhedra of identical atoms. The valence electrons are taken as moving in a one-electron crystal field set up by an effective nuclear charge centered at each atom. The field is expanded in spherical harmonics. Zeroth-order solutions are found from the spherically symmetric term, while higher terms are treated as a first-order crystal field perturbation. Polyhedra of hydrogen and of boron or carbon are considered. For the latter special attention is given to the identification of out-pointing orbitals, i.e., the orbitals used in bonding. Comparison is made between crystal field and LCAO energy levels. It is shown that they become more alike when, in the latter, $\alpha(2s)$ is made much lower than $\alpha(2p)$.

I. INTRODUCTION

WE will concern ourselves in this contribution with the energy levels of highly symmetrical polyhedral molecules. The symmetries considered are T_d, O_h, I_h.[1] Known molecules of T_d symmetry are P_4, As_4, and the framework is found in B_4Cl_4. O_h symmetry is possessed by the B_6^{-2} unit in molecules such as CaB_6,[2] and the cube–octahedral B_{12}^{-2} unit in uranium and zirconium borides.[3] The I_h symmetry has been realized for the first time in the $B_{12}H_{12}^{-2}$ ion.[4] There are also the hypothetical polyhedral alkanes C_4H_4 (T_d-tetrahedrane), C_8H_8 (O_h-cubane), $C_{20}H_{20}$ (I_h-dodecahedrane).

The LCAO-MO calculations for these polyhedral systems are fairly complex and the aim of this work has been the search for a scheme by which one could easily obtain the sequence of orbital energy levels of such compounds. Such a scheme should be utilizable for the simplest predictions, i.e., for judging when a closed electronic shell was realized and which electronic transitions were probable. We have been encouraged and guided in our treatment by the simple yet quite successful application of the free electron model to conjugated systems.[5,6]

We shall confine the discussion of this paper to the case of identical nuclei arranged as a highly symmetrical polyhedron. Although there are few such polyhedra that are stable in themselves (e.g., P_4), stability is obtained through bonding with hydrogen or other atoms (e.g., B_4Cl_4, $B_{12}H_{12}^{-2}$). In $B_{12}H_{12}^{-2}$, for example, the BH bonds are formed from the so-called *outpointing* orbitals of the B_{12} polyhedron. Hence the identification

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

[2] L. Pauling and S. Weinbaum, Z. Krist. 87, 181 (1934).

[3] W. N. Lipscomb and D. Britton, J. Chem. Phys. 33, 275 (1960).

[4] A. R. Pitochelli and M. F. Hawthorne, J. Am. Chem. Soc. 82, 3228 (1960). J. A. Wunderlich and W. N. Lipscomb, *ibid.* 82, 4427 (1960).

[5] N. S. Bayliss, J. Chem. Phys. 16, 287 (1948); Quart. Revs. 6, 319 (1952); H. Kuhn, J. Chem. Phys. 16, 840 (1948); Chimia 9, 237 (1955); W. T. Simpson, J. Chem. Phys. 16, 1124 (1948); K. Rüdenberg and C. W. Scher, *ibid.* 21, 1565 (1953); K. Rüdenberg and R. G. Parr, *ibid.* 19, 1268 (1951); J. R. Platt, J. Chem. Phys. 17, 484 (1949); *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, to be published).

[6] The first steps toward a free electron theory for boron compounds have been made by G. C. Pimentel and K. S. Pitzer, J. Chem. Phys. 17, 882 (1949); N. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, J. Chem. Phys. 22, 989 (1954).

TABLE I. Nonvanishing angular coefficients in the expansion of the nuclear-electronic attraction.

Symmetry	Geometry	V_0/Z	V_4/Z	V_6/Z
T_d	tetrahedron[a]	-4	$(14/9)(4\pi/9)^{\frac{1}{2}}[Y_4^0+(5/14)^{\frac{1}{2}}(Y_4^4+Y_4^{-4})]$	$(-8/9)(4\pi/13)^{\frac{1}{2}}[Y_6^0-(7/2)^{\frac{1}{2}}(Y_6^4+Y_6^{-4})]$
O_h	octahedron	-6	$(-7/2)(4\pi/9)^{\frac{1}{2}}[Y_4^0+(5/14)^{\frac{1}{2}}(Y_4^4+Y_4^{-4})]$	$(-3/4)(4\pi/13)^{\frac{1}{2}}[Y_6^0-(7/2)^{\frac{1}{2}}(Y_6^4+Y_6^{-4})]$
O_h	cube	-8	$(28/9)(4\pi/9)^{\frac{1}{2}}[Y_4^0+(5/14)^{\frac{1}{2}}(Y_4^4+Y_4^{-4})]$	$(-16/9)(4\pi/13)^{\frac{1}{2}}[Y_6^0-(7/2)^{\frac{1}{2}}(Y_6^4+Y_6^{-4})]$
O_h	cube-octahedron[b]	-12	$(7/4)(4\pi/9)^{\frac{1}{2}}[Y_4^0+(5/14)^{\frac{1}{2}}(Y_4^4+Y_4^{-4})]$	$(39/16)(4\pi/13)^{\frac{1}{2}}[Y_6^0-(7/2)^{\frac{1}{2}}(Y_6^4+Y_6^{-4})]$
I_h	icosahedron	-12	$\cdots$	$(-132/15)(4\pi/13)^{\frac{1}{2}}[Y_6^0+(7/11)^{\frac{1}{2}}(Y_6^5+Y_6^{-5})]$

[a] For the tetrahedron there is also a nonvanishing V_3 which does not contribute to the crystal field splitting in first order.

[b] The cube-octahedron may be constructed by connecting the midpoints of the edges of a cube or an octahedron.

of such orbitals is of great importance in discussing stability. In the next section we present a crystal field model for polyhedra of identical nuclei. We then show how the crystal field molecular orbitals (CF-MO's) correlate to the LCAO-MO's for polyhedra of hydrogen atoms. We conclude with the more interesting case of polyhedra of boron or carbon atoms and the problem of identifying outpointing orbitals.

II. CRYSTAL FIELD MODEL

The Coulomb interactions between an electron i and a set of N nuclei g may be expanded in a series of normalized spherical harmonics.

$$-\sum_{g=1}^{N}\frac{Z_g}{r_{ig}}=-\sum_{g=1}^{N}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}Z_g\frac{4\pi}{2l+1}\frac{r_{i<}^{l}}{r_{i>}^{l+1}}Y_l^m(\theta_i,\phi_i)$$

$$\cdot Y_l^{-m}(\theta_g,\phi_g)=\sum_l V\frac{r_{i<}^{l}}{r_{i>}^{l+1}}. \quad (1)$$

For the case of highly symmetrical polyhedra of nuclei with identical charges Z this Laplace expansion becomes quite simple. In Table I we list the first few non-vanishing terms in these expansions for the tetrahedron, cube, octahedron, cube-octahedron, and icosahedron.

Our crystal field model for polyhedra of identical nuclei considers each valence electron as moving in a one-electron field set up by an effective nuclear charge Z located at each nucleus. This field can be thought of as arising from the true nuclear charges shielded both by the inner shell electrons and the other valence electrons. Hence in adjusting Z (our only parameter) we partially take into account electron interaction, which will not be considered explicitly.

Approximate wave functions for this crystal field Hamiltonian will be obtained in two steps. First we solve the one-electron problem retaining only the first, spherically symmetric term of the Laplace expansion. Thus the one-electron zeroth-order Hamiltonian is

$$H_i^0=-\tfrac{1}{2}\nabla_i^2-(NZ/r_{i>}), \quad (2)$$

where $r_{i>}=R$ for $r_i<R$ and $r_{i>}=r_i$ for $r_i>R$, N is the number of atoms, and Z is the effective nuclear charge. From this Hamiltonian we obtain a set of zeroth-order energy levels and molecular orbitals which will have

the form $\psi_{nlm}(\mathbf{r}_i)=Y_l^m(\theta_i,\phi_i)R_{nl}(r_i)$. The second step of our treatment introduces the higher spherical harmonics given in Table I as a first-order perturbation that lifts the degeneracy in the quantum number l for functions of a given n. (In Appendix I we discuss the validity of this approximation.) This procedure enables us to use the full apparatus of the crystal field theory for evaluating matrix elements.[7]

To carry out step one, we refer back to the work of Wannier[8] and Chen[9] who studied in detail the eigenfunctions of the zeroth-order Hamiltonian (2). A numerical matching of spherical Bessel functions and confluent hypergeometric functions for each R is necessary to obtain exact eigenvalues. However, one of
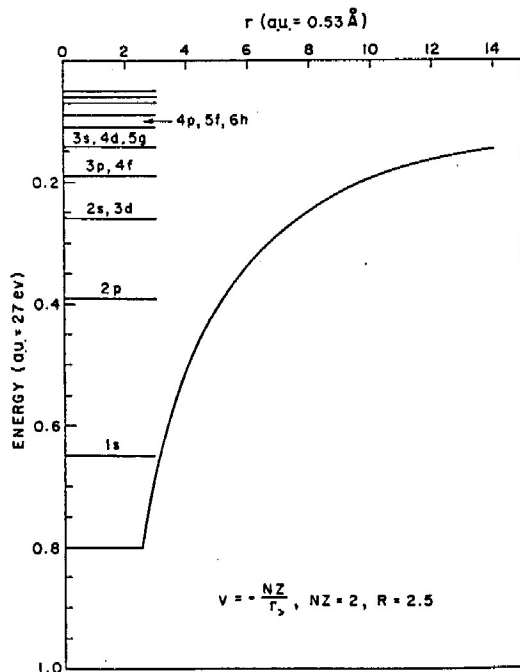

FIG. 1. The spherical potential and the energy levels given by Eq. (3).

[7] See for example: J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, New York, 1961).

[8] G. H. Wannier, Phys. Rev. **64**, 359 (1943).

[9] T. C. Chen, J. Chem. Phys. **29**, 347, 356 (1958), where a one-center model for the cyclic polyenes is discussed.

TABLE II. The reduction of spherical symmetry to T_d, O_h, I_h.

l	O_h	T_d	I_h
$0(s)$	A_{1g}	A_1	A_g
$1(p)$	F_{1u}	F_2	F_{1u}
$2(d)$	$E_g + F_{2g}$	$E + F_2$	H_g
$3(f)$	$A_{2u} + F_{1u} + F_{2u}$	$A_1 + F_1 + F_2$	$F_{2u} + G_u$
$4(g)$	$A_{1g} + E_g + F_{1g} + F_{2g}$	$A_1 + E + F_1 + F_2$	$G_g + H_g$
$5(h)$	$E_u + 2F_{1u} + F_{2u}$	$E + F_1 + 2F_2$	$F_{1u} + F_{2u} + H_u$
$6(i)$	$A_{1g} + A_{2g} + E_g + F_{1g} + 2F_{2g}$	$A_1 + A_2 + E + F_1 + 2F_2$	$A_{1g} + F_{1g} + G_g + H_g$

Wannier's explicit limiting formulas is accurate to about 15% or better for the parameter range considered by us, and this will suffice for the qualitative predictions we seek. In the case of large $(8NRZ)^{\frac{1}{2}}$ the eigenvalues of the Hamiltonian (2) are approximated by

$$E_i \approx \frac{-(NZ)^2}{2[n - (2l+1)/4 - (2NRZ)^{\frac{1}{2}}/\pi]} \qquad (3)$$

$$n = 1, 2, 3, \cdots,$$

$$l = 0, 1, 2, \cdots, n-1,$$

where n and l are the usual spherical quantum numbers. In united atom notation, the "magic scheme" for this potential has the energy levels in order of increasing energy as

$$1s2p(2s3d)(3p4f)(3s4d5g)(4p5f6h)(4s5d6g7i)\cdots, \qquad (4)$$

where approximately degenerate levels are grouped in parentheses. Figure 1 shows the zeroth-order potential well and the energy levels as obtained from (3) for $NZ = 2$ and $R = 2.5$ a.u.

The second step of our model, the introduction of the first-order energy splittings by the higher spherical harmonics of the crystal field, will only be carried out qualitatively. The splittings that occur can be determined group theoretically. Thus, for example, the five d orbitals ($l = 2$) in a polyhedron of O_h symmetry split into two groups of three and two degenerate orbitals f_{2g} and e_g, respectively; f orbitals ($l = 3$) in I_h split into two groups of three and four f_{2u} and g_u. The crystal field splittings for l up to 6 and T_d, O_h, and I_h crystal fields are given in Table II. It would be nice if the order of the energies of the split levels were given by a simple rule. Unfortunately this is not so. The order of the splitting may differ between polyhedra of the same symmetry. Thus for d orbitals in O_h symmetry f_{2g} has lower energy than e_g in the cube and cube-octahedron, but higher energy in the octahedron. Moreover, for $l \geq 3$ in T_d and O_h and $l \geq 4$ in I_h, the order of the splitting will depend on the radial functions $R_{nl}(r)$, since it is necessary to know the relative magnitudes of two or more crystal field terms V_l.

Since we are seeking only qualitative results, we shall not attempt to determine the ordering in such cases.

III. SIMPLE CASE. HYDROGEN ATOMS

As a simple illustration of our procedure we will consider the energy levels of a set of hydrogen atoms located at the vertices of some polyhedron. In the Hückel-type LCAO-MO scheme[10] one would approach the problem as follows. The usual eigenvalue problem is set up, that is, we solve the set of equations

$$(\alpha_r - E)C_r + \sum_s{}'(\beta_{rs} - ES_{rs})C_s = 0$$

$$r = 1, 2, 3, \cdots, N, \qquad (5)$$

where the c_r are the coefficients of the rth $1s$ orbital in the molecular orbital; i.e.,

$$\psi(\mathbf{r}_i) = \sum_{r=1}^N C_r \phi_r(\mathbf{r}_i). \qquad (6)$$

Here α_r and β_{rs} are the usual "Coulomb" and "resonance" integrals. One then proceeds to make some assumption about the resonance integrals. One common assumption sets equal to zero non-nearest neighbor interactions. A somewhat better assumption sets $\beta_{rs} = KS_{rs}$, where K is a constant. The secular equation is of degree N; however, the high symmetry enables one to write down easily symmetry orbitals and reduce the complexity of the problem. In Table III we give the ordering of such LCAO-MO levels, calculated with the above-mentioned assumption of $\beta_{rs} = KS_{rs}$, for some common and not so common polyhedral configurations.

To approximate a polyhedron of hydrogen atoms by the crystal-field model, we begin by taking only the radially nodeless orbitals from the ordering (4). We reject radially noded orbitals since the LCAO orbitals have only angular nodes. Thus the zeroth-order crystal field orbitals are

$$1s2p3d4f5g6h\cdots. \qquad (7)$$

We then use the reduction properties of Table II to find

[10] See for example, B. H. Chirgwin and C. A. Coulson, Proc. Roy. Soc. (London) A201, 196 (1950).

TABLE III. Representations and orbitals for polyhedra of hydrogen atoms.

N	Symmetry	Geometry	Representations	CF-MO[a] 1s	2p	3d	4f	5g	6h	LCAO-MO[a]
4	T_d	tetrahedron	A_1+F_2	a_1	f_2					a_1f_2
6	O_h	octahedron	$A_{1g}+F_{1u}+E_g$	a_{1g}	f_{1u}	e_g				$a_{1g}f_{1u}e_g$
8	O_h	cube	$A_{1g}+A_{2u}+F_{1u}+F_{2g}$	a_{1g}	f_{1u}	f_{2g}	a_{2u}			$a_{1g}f_{1u}f_{2g}a_{2u}$
12	O_h	cube-octahedron	$A_{1g}+E_g+F_{1u}+F_{2g}+F_{2u}$	a_{1g}	f_{1u}	$f_{2g}e_g$	f_{2u}			$a_{1g}f_{1u}f_{2g}e_gf_{2u}$
12	I_h	icosahedron	$A_g+F_{1u}+F_{2u}+H_g$	a_g	f_{1u}	h_g	f_{2u}			$a_gf_{1u}h_gf_{2u}$
10	T_d	adamantane type[b]	$2A_1+E+2F_2$	a_1	f_2	ef_2	a_1			$a_1f_2ef_2a_1$
12	T_d	truncated tetrah. type[e]	$A_1+E+F_1+2F_2$	a_1	f_2	ef_2	f_1			$a_1f_2ef_2f_1$
14	O_h	rhombic dodecah. type[d]	$2A_{1g}+A_{2u}+E_g+2F_{1u}+F_{2u}$	a_{1g}	f_{1u}	e_gf_{2g}	$a_{2u}f_{1u}{}^f$	a_{1g}		$a_{1g}f_{1u}f_{2g}e_ga_{2u}f_{1u}a_{1g}$
20	I_h	dodecahedron	$A_g+F_{1u}+F_{2u}+G_g+G_u+H_g$	a_g	f_{1u}	h_g	g_uf_{2u}	g_g		$a_gf_{1u}h_gg_uf_{2u}g_g$
24	O_h	truncated cube[e]	$2A_{1g}+A_{2u}+E_g+E_u+F_{1g}+F_{1u}+2F_{1u}+2F_{2g}+F_{2u}$	a_{1g}	f_{1u}	$e_gf_{2g}{}^f$	$a_{2u}f_{1u}f_{2u}{}^f$	$f_{1u}f_{2g}{}^f$	e_u	$a_{1g}f_{1u}f_{2g}e_ga_{2u}f_{2u}f_{1u}f_{2g}f_{1u}e_u$

[a] Energy increases to the right.
[b] A distortion of the adamantane ($C_{10}H_{16}$) geometry; vertices at $(\pm1, 0, 0)$, $(0, \pm1, 0)$, $(0, 0, \pm1)$, (a, a, a), $(a, -a, -a)$, $(-a, a, -a)$, $(-a, -a, a)$: $a=\sqrt{3}$.
[c] Vertices at $(1, 1, 3)$, $(-1, -1, 3)$, $(1, -1, -3)$, $(-1, 1, -3)$, $(1, 3, 1)$, $(-1, -3, 1)$, $(1, -3, -1)$, $(-1, 3, -1)$, $(3, 1, 1)$, $(-3, -1, 1)$, $(3, -1, -1)$, $(-3, 1, -1)$.
[d] Distortion of rhombic dodecahedron; vertices at $(\pm1, \pm1, \pm1)$, $(\pm\sqrt{3}, 0, 0)$, $(0, \pm\sqrt{3}, 0)$, $(0, 0, \pm\sqrt{3})$.
[e] Polyhedron with vertices at $(\pm3, \pm1, \pm1)$, $(\pm1, \pm3, \pm1)$, $(\pm1, \pm1, \pm3)$.
[f] Order of crystal-field splitting undetermined within spherical level.

the first-order splitting introduced by the crystal field. Finally we choose from the infinite set of CF-MO's, the N lowest energy orbitals that yield the same representations as the LCAO-MO's.

Consider, as a simple example, the octahedron. The order of LCAO-MO's constructed from $1s$ orbitals is a_{1g}, f_{1u}, e_g. The crystal-field orbitals are $1s(a_{1g})$, $2p(f_{1u})$, $3d(e_g, f_{2g})$, etc. We choose the six lowest CF levels of a_{1g}, f_{1u}, e_g and find that they are in the same order as the LCAO levels. A comparison of the CF and LCAO order for the orbital energy levels of various hydrogen polyhedra is given in Table III. The agreement between the two is seen to be excellent.

It should be noted that the conclusions of this section should apply not only to $1s$ orbitals but to any set of orbitals which transform in the same manner as $1s$ orbitals and which interact in such a way that the energy of interaction is some uniformly decreasing function of the separation. For instance, a set of sp^3 hybrids directed radially *in* or *out* at polyhedral vertices sufficiently removed from each other (as in any actual molecular configuration) will give a set of levels in the same order as they are listed in Table III.

IV. POLYHEDRA OF BORON OR CARBON ATOMS

For polyhedra of boron or carbon atoms an LCAO-MO calculation proceeds as in (5) and (6) except that now each atom contributes four orbitals; one $2s$ and three $2p$. Usually the assumptions are made that $\beta_{rs} = KS_{rs}$ and that $\alpha(2s) = \alpha(2p)$.[11] The representations generated by the $4N$ orbitals for the tetrahedron, octahedron, cube, cube-octahedron, and icosahedron are given in Table IV. The high symmetry of these configurations allows reduction of the secular equation to at most a cubic or quartic equation. The ordering of the LCAO-MO energies determined under these assumptions is given in Table V.

Now since the boron or carbon polyhedra are not generally stable in themselves, it is necessary to consider how the LCAO-MO's enter into bonding. When the solutions to the secular equations are examined, a set of orbitals is found with energies near the nonbonding level, with charge concentrated in the radial direction *out* from the polyhedron center, and

TABLE IV. Representations generated by a $2s$ and three $2p$ orbitals.

tetrahedron	$2A_1+E+F_1+3F_2$
octahedron	$2A_{1g}+2E_g+F_{1g}+3F_{1u}+F_{2g}+F_{2u}$
cube	$2A_{1g}+2A_{2u}+E_u+E_g+F_{1g}+3F_{1u}+F_{2u}+3F_{2g}$
cube-octahedron	$2A_{1g}+A_{2g}+A_{2u}+3E_g+E_u+2F_{1g}+4F_{1u}+$ $3F_{2g}+3F_{2u}$
icosahedron	$2A_g+3F_{1u}+F_{1g}+2F_{2u}+G_g+G_u+3H_g+H_u$

[11] H. C. Longuet Higgins and M. deV. Roberts, Proc. Roy. Soc. (London) A224, 336 (1954); A230, 110 (1955).

TABLE V. Comparison of CF[a] and LCAO levels for polyhedra of boron or carbon.

Polyhedron		Bracketed $(1s)\ (2p)\ (2s3d)\ (3p4f)\ (4d5g)\ (5f6h)\ (6g7i)$
tetrahedron	CF	$(a_1)\ (f_2)\ (\mathbf{a_1}f_2e)\ (\mathbf{f_2}{}^c f_1)$
B—B 1.70 A[b]	LCAO	$a_1 f_2 \mathbf{a_1} e \mathbf{f_2} f_1 f_2$
octahedron	CF	$(a_{1g})\ (f_{1u})\ (\mathbf{a_{1g}}e_g f_{2g})\ (\mathbf{f_{1u}}f_{2u}f_{1u})\ (e_g{}^c f_{1g})$
B—B 1.73 A	LCAO	$a_{1g} f_{1u} f_{2g} \mathbf{a_{1g}} e_g f_{1u} f_{2u} f_{1g} f_{1u} e_g$
cube	CF	$(a_{1g})\ (f_{1u})\ (\mathbf{a_{1g}}f_{2g}e_g)\ (\mathbf{f_{1u}}a_{2u}f_{2u}f_{1u})\ (f_{2g}f_{1g}f_{2g})\ (\mathbf{a_{2u}}{}^c e_u)$
B—B 1.70 A	LCAO	$a_{1g} f_{1u} e_g \mathbf{a_{1g}} f_{2g} f_{2u} f_{1u} a_{2u} f_{2g} f_{1g} e_u f_{1u} f_{2g} a_{2u}$
cube–octahedron	CF	$(a_{1g})\ (f_{1u})\ (\mathbf{a_{1g}}f_{2g}e_g)\ (\mathbf{f_{1u}}a_{2u}f_{2u}f_{1u})\ (f_{2g}e_g f_{1g}f_{2g}e_g)\ (\mathbf{f_{2u}}{}^c f_{1u}e_u f_{2u})\ (a_{2g}f_{1g})$
B—B 1.75 A	LCAO	$a_{1g} f_{1u} e_g f_{2g} a_{2u} \mathbf{a_{1g}} f_{1u} f_{1u} f_{2u} f_{2g} f_{1g} e_g f_{2u} e_u a_{2g} f_{1g} f_{2g} f_{1u} f_{2u} e_g$
icosahedron	CF	$(a_g)\ (f_{1u})\ (\mathbf{a_{1g}}h_g)\ (\mathbf{f_{1u}}f_{2u}g_u)\ (\mathbf{h_g}g_g h_g)\ (\mathbf{f_{2u}}{}^c f_{1u}h_u)\ (f_{1g})$
B—B 1.73 A	LCAO	$a_g f_{1u} h_g \mathbf{a_g} g_u f_{1u} f_{2u} \mathbf{h_g} g_g h_u f_{1g} f_{1u} h_g f_{2u}$

[a] Order of energy levels within groups which are degenerate under the spherical potential is given, when determined, with energy increasing to the right.

[b] Distance used for LCAO calculation.

[c] Noded CF orbital with unnoded orbital of same symmetry, the latter better resembling LCAO level.

with correct symmetry for an outpointing set (i.e., the same as that given in Table III for a set of s orbitals). These *out* orbitals are then taken as interacting with the ligand orbitals to form bonding and antibonding pairs. The boron (or carbon) polyhedra donate one electron to each bonding orbital as do the ligands. These orbitals are thus removed from consideration when closed shell properties or transitions are determined. The *out* orbitals are shown in Table V in boldface.

To approximate boron or carbon atom polyhedra by the crystal field model, we choose from the spherical crystal field ordering (4) the nodeless *and* the singly noded orbitals, here introduced by the $2p$ radial atomic

orbitals. Thus the zeroth-order crystal field orbitals are

$$1s2p(\mathbf{2s3d})\ (\mathbf{3p4f})\ (\mathbf{4d5g})\ (\mathbf{5f6h})\ (\mathbf{6g7i}),\ \cdots,\qquad (8)$$

where the singly noded functions are in boldface. Again using the reduction properties of Table II, we can determine the first-order splitting introduced by the crystal field. From the infinite set of CF-MO's we choose the $4N$ orbitals lowest in energy that yield the same representations as the LCAO-MO's. Table V gives the CF-MO ordering of energy levels. Agreement with the LCAO scheme is seen to be generally rather good, but discrepancies occur.

One final step is necessary before the CF-MO's for boron or carbon polyhedra can be used for predicting molecular properties: the set of outpointing orbitals that enter in bonding must be identified. We shall choose these as the N lowest energy orbitals with the proper symmetry from the set of *singly noded* orbitals. This choice is indicated by boldface in Table V. Agreement between this set and that found by the LCAO
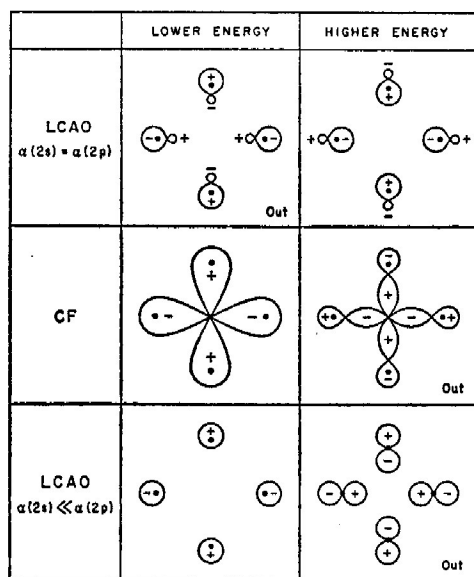

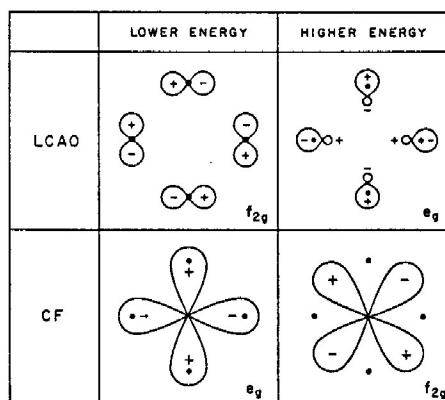FIG. 2. Sketch of possible *out* orbitals for LCAO model and CF model for the octahedron.

FIG. 3. Sketch of singly noded CF d orbitals in octahedron and the corresponding LCAO orbitals.

TABLE VI. LCAO levels for $\alpha(2s) = -25.1$ ev, $\alpha(2p) = -8.63$ ev, $K = -30$ ev.

| cube | $a_{1g}f_{1u}f_{2g}e_{g}a_{1g}a_{2u}f_{2u}f_{1u}f_{2g}f_{1u}f_{1g}e_{u}f_{2g}a_{2u}$ |
| octahedron | $a_{1g}f_{1u}e_{g}a_{1g}f_{2g}f_{1u}f_{2u}f_{1g}f_{1u}e_{g}$ |

method always fails for one CF-MO, indicated in the table by an asterisk. For asterisked orbitals identified as *out* there is always an unnoded orbital of the same symmetry at lower energy that more closely identifies with the *out* orbitals of the LCAO scheme.

An investigation of the discrepancies between the LCAO and CF *out* orbitals is very instructive. In Fig. 2 we show one member of the two e_g orbital pairs on which there is disagreement. In the LCAO-MO scheme the outpointing e_g orbital has lower energy due to less negative overlap. In the CF model the orbital with more nodes is taken as *out*. However, the LCAO identification can be reversed if we no longer set $\alpha(2s) = \alpha(2p)$, but instead set $\alpha(2s) \ll \alpha(2p)$. The lower energy orbital thus becomes nearly pure $2s$ in character as shown in Fig. 3 and *out* character must be attributed to the higher energy orbital in agreement with the CF assignment.

Certain other discrepancies between the CF and LCAO order occur in Table V. A common discrepancy is well illustrated in the octahedron where the CF d orbitals split with e_g at lower energy than f_{2g}, while the corresponding LCAO-MO's are in reverse order. The orbitals are illustrated in Fig. 3, and the reason for the discrepancy is apparent. The LCAO model makes e_g higher because of negative overlap, while the CF model puts it lower as it is centered at the positive nuclei. Again, it can be seen from Fig. 4 the LCAO scheme can be made to correspond to the CF scheme if we make $\alpha(2s) \ll \alpha(2p)$. In Table VI we give the energy-level order obtained from an LCAO-MO calculation for the cube and the octahedron with $\alpha(2p) = -8.3$ ev and $\alpha(2s) = -25.1$ ev. (These are the first and second atomic ionization potentials of B.) The disagreement between the order of e_g and f_{2g} is removed.

Both discrepancies between the LCAO and CF energy levels discussed above tend to be removed by setting $\alpha(2s) \ll \alpha(2p)$ in the LCAO calculations. Theoretically the assumption of equality cannot be justified and if applied to B_2 leads to very incorrect results.[12] Although detailed calculations in several polyhedra have shown that energy levels are not overly sensitive to this assumption,[13] the comparison with the CF model in Fig. 3 shows that the LCAO results with $\alpha(2s) = \alpha(2p)$ are not physically reasonable, and *it seems best to us that the assumption of equality not be used.*

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[12] M. Gouterman and S. Senturia (unpublished).
[13] R. Hoffmann (to be published).

DISCUSSION

Several points should be stressed about the crystal-field model developed in this paper.

(a) The theory requires only one parameter Z.

(b) The levels converge in a reasonable Rydberg series to the continuum.

(c) The correspondences between the CF levels and the LCAO levels give a good insight into the reason for the ordering of the latter. For example, many calculations yield a series of lowest orbitals corresponding to $1s$, $2p$, $(2s3d)$, the first levels of the spherically symmetric crystal-field term.

(d) Many discrepancies between the CF and LCAO models can be traced back to the LCAO assumption that $\alpha(2s) = \alpha(2p)$. The discrepancies tend to be reduced when $\alpha(2s)$ is made more negative. In the case of the splitting of d orbitals, the CF results show that it is indeed better to make $\alpha(2s)$ lower; however, in the identification of *out* orbitals the CF model may overemphasize this feature.

We would like to thank Professor W. N. Lipscomb for many valuable discussions, and the Shell Foundation for a fellowship to one of us (R. H.).

APPENDIX I: ORDERS OF MAGNITUDE

Figure 1 shows the spherical potential for a figure with $NZ = 2$ and $R = 2.5$ a.u. This corresponds to an octahedron with a side of 1.85 A. For a boron octahedron the $(2s, 3d)$ spherical potential levels will be the top filled. It may be seen from Fig. 1 that this level has an ionization potential of 0.26 a.u.~ 7 ev, which is a reasonable value. We can conclude that effective charges will be on the order of magnitude of 0.3.

We may next inquire whether such an effective charge produces a crystal-field splitting small compared
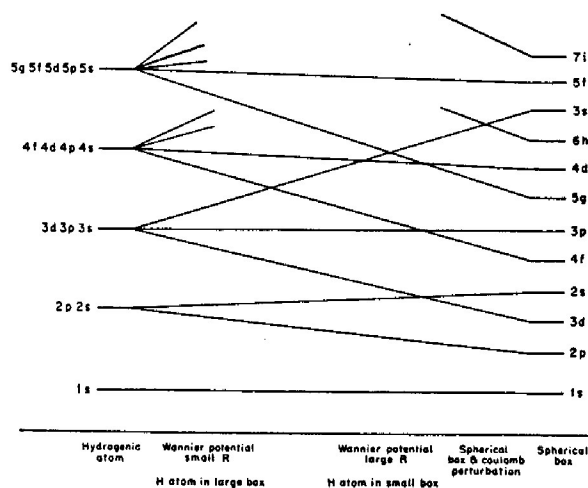

FIG. 4. "Correlation" diagram for various spherical potentials. The energy levels of a hydrogen atom in a box have been computed by S. R. DeGroot and C. A. Ten Seldam, Physica **12**, 669 (1946).

to the zeroth-order spacings of the spherical potential. Evaluation of this splitting would require knowledge of the radial wave functions. However, suppose we use as a crude wave functions the solutions to a spherical box, which are well-known Bessel functions. The octahedral splitting turns out to be 1.26 Z/P, where P is the size of the box.[14] From the rate of falloff of the Coulomb potential in Fig. 1, a reasonable size of the box for the d orbital would seem to be 8 a.u. Taking $Z=0.3$ we have a crystal field splitting of roughly 0.05 a.u.~1.3 ev. The separation to the next spherical potential level is about 0.07 a.u.~1.9 ev. Thus the crystal-field splitting may just about cause levels from distinct spherical potential shells to overlap, and an exact quantitative use of the model would have to be carried out very carefully. It may be that rather than such a refinement of the model with effective Z, a full SCF calculation with the atomic Z and including electron interaction could be carried out using some convenient basis set of radial orbitals.

APPENDIX II. OTHER FREE ELECTRON MODELS

1. Spherical Box

The potential well of Fig. 1 may be approximated by a spherical box. The solutions to the radial equation are the spherical Bessel functions $j_l(kr)$[15] and the eigenvalues may be obtained from requiring these to vanish at some radius $P \geq R$, which then becomes another parameter of the theory. The spherical energy level ordering engendered by this potential is

$$1s2p3d2s4f3p5g4d6h3s5f7i, \cdots.$$

This magic scheme does not differ greatly from that discussed in detail in our paper. It has the advantage of well-known analytic wave functions, for which all radial integrals may be done with relative ease. The predictions do not match the LCAO-MO levels quite as well, even when a perturbation of the form $-(C/r)$ is added in an attempt to account for the non-Coulombic features of the box walls. The "correlation" diagram of

Fig. 4 (no real correlation can be made along the entire horizontal axis) summarizes the various spherical schemes.

We could also use spherical box wave functions, but require that $d/dr(r^2 j_l^2) = 0$ at $r = R$, i.e., that the electron density be a maximum at the position of the nuclei. This gives again almost the same shell structure as the box model, but with levels further apart. Since a box normalization would have to be used, the simplicity of the wave functions is lost.

The spherical box does not, of course, yield the convergence to a continuum and Rydberg series of the Wannier potential.

2. Perimeter Model

A three dimensional spherical rotator gives the level order

$$spdfgh \cdots$$

with eigenvalues proportional to $l(l+1)$. The scheme is good for hydrogen atoms, but fails for other molecules.

3. Shell Model

Here we have a spherical shell instead of a box. The analysis is more complicated but the general result is that as the shell is made thinner, the levels with one or more radial nodes are pushed up very quickly. To preserve the $2s$ level in about the same position it occupies in the spherical box would require a ratio of outer to inner radius large enough so that the fixing of a node at the inner shell would be artificial.

4. Cubical Box

It is interesting to compare the energy levels of an electron in a cubical box with those of a spherical potential plus a cubical crystal-field perturbation. The cubical box levels are given by Pauling and Wilson[16] and they do not match the LCAO-MO levels for a cube very well. No doubly degenerate e levels arise and the box gives degeneracies higher than those actually present.

[14] R. Hoffman (unpublished results).

[15] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953).

[16] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935) p. 99.