

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. Rüdénberg and C. W. Scher, *ibid.* **21**, 1565 (1953); K. Rüdénberg 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	$(14/9)(4\pi/9)^{1/2}[Y_4^0 + (5/14)^{1/2}(Y_4^4 + Y_4^{-4})]$	$(-8/9)(4\pi/13)^{1/2}[Y_6^0 - (7/2)^{1/2}(Y_6^4 + Y_6^{-4})]$
O_h	octahedron	-6	$(-7/2)(4\pi/9)^{1/2}[Y_4^0 + (5/14)^{1/2}(Y_4^4 + Y_4^{-4})]$	$(-3/4)(4\pi/13)^{1/2}[Y_6^0 - (7/2)^{1/2}(Y_6^4 + Y_6^{-4})]$
O_h	cube	-8	$(28/9)(4\pi/9)^{1/2}[Y_4^0 + (5/14)^{1/2}(Y_4^4 + Y_4^{-4})]$	$(-16/9)(4\pi/13)^{1/2}[Y_6^0 - (7/2)^{1/2}(Y_6^4 + Y_6^{-4})]$
O_h	cube-octahedron ^b	-12	$(7/4)(4\pi/9)^{1/2}[Y_4^0 + (5/14)^{1/2}(Y_4^4 + Y_4^{-4})]$	$(39/16)(4\pi/13)^{1/2}[Y_6^0 - (7/2)^{1/2}(Y_6^4 + Y_6^{-4})]$
I_h	icosahedron	-12	...	$(-132/15)(4\pi/13)^{1/2}[Y_6^0 + (7/11)^{1/2}(Y_6^4 + Y_6^{-4})]$

^a For the tetrahedron there is also a nonvanishing V_2 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.

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

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 nonvanishing 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

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

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 Wannier⁸ and Chen⁹ 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

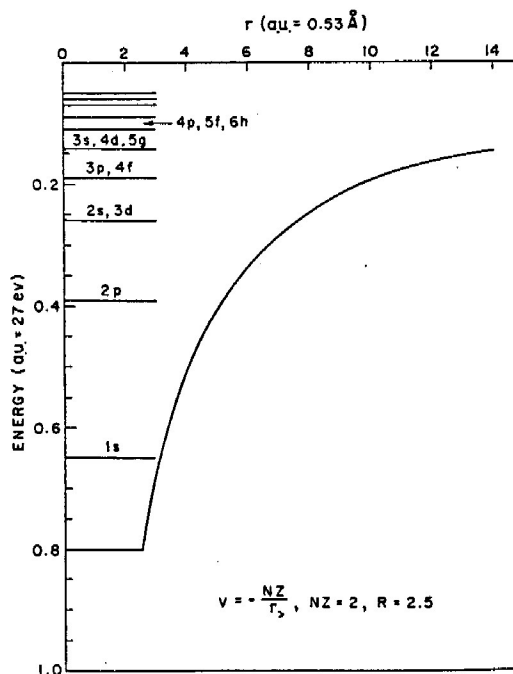


FIG. 1. The spherical potential and the energy levels given by Eq. (3).

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(<i>s</i>)	A_{1g}	A_1	A_g
1(<i>p</i>)	F_{1u}	F_2	F_{1u}
2(<i>d</i>)	$E_g + F_{2g}$	$E + F_2$	H_g
3(<i>f</i>)	$A_{2u} + F_{1u} + F_{2u}$	$A_1 + F_1 + F_2$	$F_{2u} + G_u$
4(<i>g</i>)	$A_{1g} + E_g + F_{1g} + F_{2g}$	$A_1 + E + F_1 + F_2$	$G_g + H_g$
5(<i>h</i>)	$E_u + 2F_{1u} + F_{2u}$	$E + F_1 + 2F_2$	$F_{1u} + F_{2u} + H_u$
6(<i>i</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

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

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

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

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

$$1s2p(2s3d)(3p4f)(3s4d5g)(4p5f6h)(4s5d6g7i)\dots, \quad (4)$$

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 scheme¹⁰ one would approach the problem as follows. The usual eigenvalue problem is set up, that is, we solve the set of equations

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

$$r = 1, 2, 3, \dots, N, \quad (5)$$

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

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

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 $\beta_{rs} = K S_{rs}$, 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 $\beta_{rs} = K S_{rs}$, 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

$$1s2p3d4f5g6h\dots \quad (7)$$

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).

