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GROUP THEORETICAL INVESTIGATION OF OCTAHEDRAL  
AND CUBOCTAHEDRAL BONDING 3

BY

DAVID PECKHAM OLSEN

A thesis submitted  
in partial fulfillment of the requirements for the  
degree Master of Science, Department of  
Physics, South Dakota State  
College of Agriculture  
and Mechanic Arts

August, 1963

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**GROUP THEORETICAL INVESTIGATION OF OCTAHEDRAL**

**AND CUBOCTAHEDRAL BONDING**

This thesis is approved as a creditable, independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser

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Head of the Major Department

2441 R

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DPO



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## INTRODUCTION

The behavior of electrons in molecules is governed by quantum mechanical laws - insofar as we can tell. A quantitative check has proved impossible for all except the most simple systems, such as the  $H_2^+$  and  $H_2$  molecules. Generally, severe approximations have to be made.

The procedure that is supported by spectral measurements is the molecular orbital method. Indeed, energy levels of many systems can be classified in molecular orbital configurations, while a similar explanation is not possible in terms of a valence-bond or hybridization description.

In the work reported here, group theoretical methods have been used to obtain symmetry orbitals that are molecular orbital candidates. The symmetric structures considered include an octahedral  $B_6$  cage, octahedral  $Ta_6C_{12}^{+2}$ , and a cuboctahedral  $B_{12}$  cage. The biggest problem arose in combining the symmetry orbitals from multiply occurring irreducible representations to get functions belonging to the same column. Finally, energy levels were found and expressed in parametric form.

## GROUP THEORY AND SCHRÖDINGER'S EQUATION

We are to consider the energy levels of electrons moving among nuclei placed symmetrically in space. The symmetry causes certain levels to be degenerate. It also simplifies calculations by reducing many matrix elements in the secular equation to zero. Thus, a generally very complicated problem in solving Schrödinger's equation approximately is made tractable.

The following discussion would apply to other symmetric problems; thus it is couched in general terms.

First, we recognize that the operations which interchange like particles of a system form a mathematical group. Background material on group theory is readily available.<sup>1-6</sup> The operations that need to be considered include rotations, reflections, and inversions.

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<sup>1</sup>Birkhoff and MacLane, A Survey of Modern Algebra, The MacMillan Company: New York, 1953.

<sup>2</sup>Eyring, Walter, and Kimball, Quantum Chemistry, John Wiley and Sons, Inc: New York, 1944.

<sup>3</sup>Brian Higman, Applied Group-Theoretic and Matrix Methods, Oxford at the Clarendon Press: London, 1955.

<sup>4</sup>J. S. Lomont, Applications of Finite Groups, Academic Press, Inc.: New York, 1959.

<sup>5</sup>Margenau and Murphy, The Mathematics of Physics and Chemistry, D. Van Nostrand Company, Inc.: Princeton, 1956.

<sup>6</sup>Eugene P. Wigner, Group Theory, Academic Press, Inc.: New York, 1959.

Secondly, we recall the fundamental postulate that particles of the same kind are indistinguishable. Since the operations of the group merely exchange like particles, they must leave fundamental mathematical forms unchanged.

In quantum mechanics the fundamental form is the linear Hamiltonian operator  $H$ . From it, we form the time-independent Schrödinger equation

$$H \psi_i = E \psi_i \quad (1)$$

where  $E$  is an  $f$ -fold degenerate energy level and  $\psi_i$  one of the  $f$  linearly independent eigenfunctions corresponding to it.

Now, any operation  $R$  of the group must not alter  $H$ ; therefore  $R$  and  $H$  commute. Furthermore,  $E$  being a constant,  $R$  commutes with  $E$ . So when Eq. (1) is acted on by  $R$ , the result

$$RH \psi_i = RE \psi_i$$

rearranges to

$$HR \psi_i = ER \psi_i \quad (2)$$

Thus, the new function  $R \psi_i$  is also a solution of the given Schrödinger equation. Because Eq. (1) is linear in the  $\psi$ 's, the most general solution is a linear combination of the  $f$  linearly independent eigenfunctions  $\psi_1, \psi_2, \dots, \psi_f$ . Hence, the transformed function  $R \psi_i$  has the form

$$R \psi_i = \sum_{k=1}^f D(R)_{ki} \psi_k \quad (3)$$

where the coefficients of the  $\psi_k$ , denoted by  $D(R)_{ki}$ , may be complex.

The  $\psi_k$  are assumed to be normalized. For the  $R\psi_i$  to be normalized, the  $D(R)_{ki}$  must satisfy the normalization condition

$$\sum_{k=1}^f D(R)_{ki}^* D(R)_{ki} = 1 \quad (4)$$

If  $S$  is another symmetry operation included in the symmetry group of the Hamiltonian, proceeding as above gives a similar form

$$S\psi_k = \sum_{l=1}^f D(S)_{lk} \psi_l \quad (5)$$

where the coefficients  $D(S)_{lk}$  satisfy the normalization condition.

Since  $S$  is a linear operator and the  $D(R)_{ki}$  are constants, we obtain

$$SR\psi_i = S \sum_{k=1}^f D(R)_{ki} \psi_k = \sum_{k=1}^f \sum_{l=1}^f D(S)_{lk} D(R)_{ki} \psi_l \quad (6)$$

upon applying  $S$  to both sides of Eq. (3). By the definition of a group, the product  $SR$  is also a symmetry operation included in the group. If  $P$  is that symmetry operation, then Eq. (6) must be the same as the equation

$$P\psi_i = \sum_{l=1}^f D(P)_{li} \psi_l \quad (7)$$

which leads to the result

$$D(P)_{li} = \sum_{k=1}^f D(S)_{lk} D(R)_{ki} \quad (8)$$

Equation (8) is the definition of matrix multiplication and in matrix notation it becomes

$$D(P) = D(S)D(R) \quad (9)$$



The matrix  $D(R)$  is formed from the coefficients  $D(R)_{ki}$  of Eq. (3), which determines the  $i$ th column of  $D(R)$ . One gets the other  $(f-1)$  columns from Eq. (3) by letting the subscript  $i$  take on the values  $1, 2, \dots, i-1, i+1, \dots, f$ . In this way, an  $f \times f$  matrix representation  $D(R)$  of the symmetry operation  $R$  is obtained. In the same manner, one finds an  $f \times f$  matrix for each symmetry operation in the group. The set of matrices so formed is said to be an  $f$ -dimensional representation of the group because the matrices multiply in the same order as the operations of the group.

The set of  $f$  linearly independent eigenfunctions forms a basis for the representation since the representation is obtained by operating on the  $f$  eigenfunctions with the operations of the group. That is, the eigenfunctions belonging to a given energy eigenvalue generate a representation of the symmetry group of the Hamiltonian. Wigner<sup>7</sup> shows that if the basis functions are mutually orthogonal then the representation will be by unitary matrices. The importance of the unitary property of the matrix representation is that it leaves the scalar product of two functions invariant under the operations of the group.

In general, the representation one generates by operating on the set of eigenfunctions corresponding to a single eigenvalue  $E$  may be either reducible or irreducible. If the representation is reducible,

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<sup>7</sup>Ibid., p. 111.

distinct sets of linear combinations of the eigenfunctions providing the basis for the reducible representation can be formed. Each set will form the basis for one of the irreducible components of the reducible representation. The eigenvalues to which each new set corresponds all give the same energy  $E$ ; but each set of eigenfunctions behaves differently under the operations of the group. The sets are said to be accidentally degenerate.

Accidental degeneracy is postulated when the valence orbitals of an atom are hybridized to form bond orbitals.<sup>8</sup> One assumes that all valence electrons in the atom have the same energy. The proper linear combination of valence orbitals to form a hybrid orbital is found by group theoretical methods.<sup>9</sup> But, the valence orbitals contained in the hybrid orbital behave differently under symmetry operations of the group. Consequently, each set of valence orbitals of a different symmetry type will form the basis for a different irreducible representation. In the absence of accidental degeneracy, the representation formed by the set of eigenfunctions of a single energy level is irreducible.

We can obtain a representation of a group from an arbitrary function  $\phi$  by applying the  $\underline{h}$  operations of the group to  $\phi$ . The result of these operations is a set of  $\underline{h}$  functions  $R\phi, S\phi, \dots$ .

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<sup>8</sup>George H. Duffey, Physical Chemistry, McGraw-Hill Book Company, Inc.: New York, 1962, pp. 147-163.

<sup>9</sup>Eyring, Walter, and Kimball, op. cit., pp. 227-231.

which are denoted as  $\phi_1, \phi_2, \dots, \phi_h$ . These  $h$  functions may not be linearly independent; however, we can choose from them  $h'$  functions,  $\phi_1, \phi_2, \dots, \phi_{h'}$ , that are linearly independent where  $R\phi = \phi_1, S\phi = \phi_2, \dots$ , etc. The new set of  $h'$  functions form a basis for a representation of the group. For instance, the operation  $S$  applied to  $\phi_1$  yields

$$S\phi_1 = SR\phi = P\phi \quad (10)$$

The result  $P\phi$  belongs to the original set of  $h$  functions; so it is one of the  $h'$  functions or a linear combination of them such as

$$S\phi_i = \sum_{k=1}^{h'} \Delta(S)_{ki} \phi_k \quad (11)$$

The coefficients  $\Delta(S)_{ki}$  form a matrix  $\Delta(S)$  which is a reducible representation of the operation  $S$  (compare with Eq. (3)). Matrix representations of the remaining operations are obtained in the same manner. The arbitrary function  $\phi$  can be written as a sum of its components in the various columns of the reducible representation for which it is a base. Thus, we have

$$\phi = \sum_j \sum_{k=1}^{l_j} \phi_k^j \quad (12)$$

where  $\phi_k^j$  belongs to the  $k$ th column of the  $j$ th irreducible representation of the reducible one. By Eq. (3), functions  $\phi_k^j$  satisfy the relationship

$$R\phi_k^j = \sum_{l=1}^{l_j} D^j(R)_{lk} \phi_l^j \quad (13)$$

where the matrix  $D^j(R)$  belongs to the  $j$ th irreducible representation. Multiplying both sides of Eq. (13) by  $D^i(R)_{mn}^*$  and summing over all operations of the group yields

$$\begin{aligned} \sum_R D^i(R)_{mn}^* \phi_k^j &= \sum_{l=1}^{l_j} \left( \sum_R D^i(R)_{mn}^* D^j(R)_{lk} \right) \phi_l^j \\ &= \frac{h}{l_j} \phi_m^j \delta_{nk} \delta_{ij} \end{aligned} \quad (14)$$

where  $h$  is the order of the group and  $l_j$  is the dimension of the  $j$ th irreducible representation. For  $n = m$ ,  $i = j$ , and  $m = k$  we get

$$\sum_R D^j(R)_{kk}^* \phi_k^j = \frac{h}{l_j} \phi_k^j \quad (15)$$

Eq. (15) is the necessary and sufficient condition that  $\phi_k^j$  belongs to the  $k$ th column of the  $j$ th irreducible representation.<sup>10</sup> On setting  $n = k$  and  $i = j$  in Eq. (14), we obtain

$$\sum_R D^j(R)_{mk}^* \phi_k^j = \frac{h}{l_j} \phi_m^j \quad (16)$$

From Eq. (12) we can find the  $(l_j - 1)$  partners of  $\phi_k^j$ . The resulting set of  $l_j$  functions satisfy Eq. (13) and will form the basis for the  $j$ th irreducible representation.

Given the function  $\phi$ , we can obtain the  $\phi_k^j$  appearing in Eq. (12) from the following considerations. Setting  $n = m$  in Eq. (14) gives

$$\sum_R D^i(R)_{mm}^* \phi_k^j = \frac{h}{l_j} \phi_m^j \delta_{mk} \delta_{ij} \quad (17)$$

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<sup>10</sup>Wigner, op. cit., p. 112.

or

$$P_m^i \phi_k^j = \phi_m^j \delta_{mk} \delta_{ij} \quad (18)$$

where

$$P_m^i = \frac{1_i}{h} \sum_R D^i(R)_{mm} R \quad (19)$$

The  $P_m^i$  of Eq. (19) is called a projection operator. The application of  $P_m^i$  to some function is similar to the product  $\underline{i} \cdot \underline{v}$  where  $\underline{i}$  is the unit vector in the  $\underline{x}$ -direction and  $\underline{v}$  is an arbitrary vector. The result of taking the scalar product of  $\underline{i}$  with  $\underline{v}$  is that one obtains the component of  $\underline{v}$  which lies in the  $\underline{x}$ -direction. If we now apply  $P_m^i$  to both sides of Eq. (12), we get

$$\phi_m^i = \frac{1_i}{h} \sum_R D^i(R)_{mm} R \phi = P_m^i \phi \quad (20)$$

Equation (20) expresses the fact that, given an arbitrary function  $\phi$ , one can obtain from it a function  $\phi_m^i$  which belongs to the  $\underline{m}$ th column of the  $\underline{i}$ th irreducible representation of a group.

Use of the operator  $P_m^i$  defined in Eq. (19) depends on a complete knowledge of the diagonal elements  $D^i(R)_{mm}$  of the  $\underline{i}$ th irreducible representation. To get an expression free of this restriction, we sum over  $\underline{m}$  on both sides of Eq. (20):

$$\sum_{m=1}^{1_i} \phi_m^i = \frac{1_i}{h} \sum_R \chi^i(R) R \quad (21)$$

Here  $\chi^i(R)$  is the character of operation  $R$  in the  $\underline{i}$ th irreducible representation. Function  $\psi^i$  is said to belong to the  $\underline{i}$ th irreducible representation if it can be written as a sum of functions belonging to

the various columns of that representation:

$$\psi^i = \sum_{m=1}^{l_i} \phi_m^i \quad (22)$$

We have from Eq. (21)

$$\psi^i = \frac{l_i}{h} \sum_R \chi^i(R) R \phi \quad (23)$$

or

$$\psi^i = P^i \phi \quad (24)$$

Here projection operator

$$P^i = \frac{l_i}{h} \sum_R \chi^i(R) R \quad (25)$$

produces the function  $\psi^i$  belonging to the  $i$ th irreducible representation from the arbitrary function  $\phi$ .

Classification of functions as belonging to a particular column of an irreducible representation or to different irreducible representations leads to orthogonality conditions for the functions. Letting  $\psi_k^j$  be a function belonging to the  $k$ th column of the  $j$ th irreducible representation and  $\phi_n^i$  be a function belonging to the  $n$ th column of the  $i$ th irreducible representation, the orthogonality relations

$$\int \psi_k^j \phi_n^i d\tau = \frac{1}{\sqrt{l_j l_i}} \delta_{ji} \delta_{kn} \sum_s \int \psi_s^j \phi_s^i d\tau \quad (26)$$

hold.<sup>11</sup> Now, the right side of Eq. (26) vanishes when  $j \neq i$  or  $k \neq n$ , indicating that the two functions are orthogonal if they belong to

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<sup>11</sup>Ibid., p. 115.

different irreducible representations or if they each belong to different columns of the same irreducible representation.

If  $i = j$  and  $n = k$ , then Eq. (26) becomes

$$\int \psi_k^j \phi_k^j d\tau = \frac{1}{l_j} \sum_{s=1}^{l_j} \int \psi_s^j \phi_s^j d\tau \quad (27)$$

The right side of Eq. (27) will be the same no matter what value of  $k$  is chosen on the left side; so we have

$$\int \psi_1^j \phi_1^j d\tau = \int \psi_2^j \phi_2^j d\tau = \dots = \int \psi_{l_j}^j \phi_{l_j}^j d\tau \quad (28)$$

That is, the value of the scalar product of two eigenfunctions from a given irreducible representation is independent of the column from which the two functions come as long as it is the same column.

The orthogonality relations also apply to integrals of the form  $\int \psi H \phi d\tau$  if the operator  $H$  is invariant under all operations of the group.<sup>12</sup> The Hamiltonian  $H$  satisfies this condition because its symmetry defines the Schrödinger group. We then have

$$\int \psi_k^j H \phi_n^i d\tau = \frac{h}{l_j l_i} \delta_{ji} \delta_{kn} \sum_{s=1}^{l_j} \int \psi_s^j H \phi_s^i d\tau \quad (29)$$

where the right side vanishes for  $j \neq i$  or  $k \neq n$ . When  $i = j$  and  $n = k$ , the value of the integral on the left is independent of which value the subscript  $s$  assumes. Equation (29) holds for any operator invariant under the operations of the group.

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<sup>12</sup>Ibid., pp. 115-116.

For complicated quantum mechanical systems one may obtain approximations to the energy levels of the system by solving a secular determinant.<sup>13</sup> Thus, the allowed energy levels are given by the roots  $E$  of the equation

$$\det |H_{ij} - S_{ij}E| = 0 \quad (30)$$

where

$$H_{ij} = \int \psi_i^* H \phi_j d\tau \quad (31)$$

and

$$S_{ij} = \int \psi_i^* \psi_j d\tau \quad (32)$$

Factoring the secular determinant is quite difficult in general.

However, the elements of the determinant have the same form as those given by Eqs. (26) and (29). So these equations, called orthogonality conditions, may be used to simplify Eq. (30) as long as the  $\psi$ 's are formed according to Eq. (20).

Consider  $n$  linearly independent basis functions in terms of which the eigenfunctions are to be obtained. The secular equation formed from the  $n$  functions is  $n$ -dimensional. Also, suppose the reducible representation  $\Gamma$  generated by the basis functions decomposes into irreducible components  $\Gamma^1, \Gamma^2, \dots, \Gamma^s$  of dimensions  $l_1, l_2, \dots, l_s$ , respectively. The decomposition of  $\Gamma$  is represented symbolically as the sum

$$\Gamma = a_1 \Gamma^1 + a_2 \Gamma^2 + \dots + a_s \Gamma^s \quad (33)$$

---

<sup>13</sup>Duffey, op. cit., pp. 164-166.



where the  $a$ 's are integers denoting how many times a given irreducible representation occurs in the reducible one. We consider two situations which occur in the decomposition of  $\Gamma$ : (1) All irreducible representations occur only once. (2) One or more irreducible representations occur more than once.

Given situation (1) with the eigenfunctions formed according to Eq. (20), Eqs. (26) and (29) are valid and the secular determinant reduces to the form

$$\begin{vmatrix} H_{11}-E & 0 & 0 & \dots & 0 \\ 0 & H_{22}-E & 0 & \dots & 0 \\ 0 & 0 & H_{22}-E & \dots & 0 \\ \cdot & \cdot & \cdot & \dots & \cdot \\ 0 & 0 & 0 & \dots & H_{ss}-E \end{vmatrix} = 0 \quad (34)$$

which is simply the product of the diagonal elements

$$\prod_j (H_{jj} - E)^{l_j} = 0 \quad (35)$$

Here  $l_j$  is the dimension of the  $j$ th irreducible representation. Thus, the energy levels can be found individually. We also note that, if an  $l_j$  dimensional representation occurs only once, one can find the energy for that level from a function formed according to Eq. (23). Such a function is a linear combination of the  $l_j$  basis functions of Eq. (20); hence we obtain the same energy by using it.

Now consider situation (2) and suppose that an irreducible representation of dimension  $l_j$  appears  $a_j$  times, where  $a_j$  is greater than one. In such a case,  $a_j$  independent complete sets of  $l_j$

eigenfunctions forms the basis for the same irreducible representation. Each set, however, belongs to a different energy eigenvalue. As an example, suppose  $a_j$  is two. Then two physically independent<sup>14</sup> sets of  $l_j$  independent eigenfunctions belonging to the same irreducible representation can be formed. As shown by Eq. (29), the integral  $H_{jk}$  is not zero when the function  $\psi_j$  from one set and the function  $\psi_k$  from the other set belong to the same column of the same irreducible representation. Furthermore, the physical independence of the two sets gives  $S_{jk} = \delta_{jk}$  (see footnote 14). The secular determinant for this situation becomes

$$\begin{vmatrix}
 H_{jj}-E & 0 & & & \\
 0 & H_{jj}-E & & & \\
 & & \ddots & & \\
 & & & \ddots & \\
 & & & & \ddots \\
 H_{kj} & 0 & & & \\
 0 & H_{kj} & & & \\
 & & \ddots & & \\
 & & & \ddots & \\
 & & & & \ddots
 \end{vmatrix}
 = 0 \quad (36)$$

Now, rows and columns are rearranged to obtain the factors

$$\begin{vmatrix}
 H_{jj}-E & H_{jk} \\
 H_{jk} & H_{kk}-E
 \end{vmatrix}
 l_j = 0 \quad (37)$$

<sup>14</sup>Physical independence means that the eigenfunctions of one set are orthogonal to those in the other set because each set corresponds to a different eigenvalue. Hence, the integral  $S_{jk} = \delta_{jk}$ .

from which two energy eigenvalues can be found. Here we have used the Hermitian properties of the Hamiltonian<sup>15</sup> to write

$$H_{jk} = H_{kj} \quad (38)$$

The integral  $H_{jk}$  is called an interaction integral since its effect is to split the energy levels corresponding to the multiply occurring irreducible representation. By induction, an irreducible representation occurring  $a_j$  times produces an  $a_j$ -dimensional secular determinant. In each case, Eqs. (28) and (29) imply that we need only one function from each of the  $a_j$  independent sets forming bases for the irreducible representation.

Applying this method depends on some procedure for ensuring that  $\psi_j$  and  $\psi_k$  belong to exactly the same column of the irreducible representation. The procedure is guided by intuition to a great extent. For this reason, its development is postponed until the difficulty arises in a specific problem.

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<sup>15</sup>Wigner, op. cit., pp. 36-37.

## THE LCAO MOLECULAR ORBITAL METHOD

Each stationary state of a molecular system is described by a wave function  $\Psi$  which is a solution of the time-independent Schrödinger equation (1). The wave function  $\Psi$  is a function of spin and space coordinates of the particles, nuclei and electrons, making up the molecule. However, the appearance of nucleus-nucleus and electron-electron repulsion terms in the Hamiltonian operator for the system precludes the possibility of exact solution. So various schemes for obtaining approximate solutions have been developed.

Invariably, the first approximation made is a separation of the Hamiltonian into nuclear and electronic parts. The separation is effected by approximating  $\Psi$  as a product of a nuclear wave function  $\Psi_n$  and an electronic one  $\Psi_e$ . That is,

$$\Psi = \Psi_n \Psi_e \quad (39)$$

where  $\Psi_n$  is a function of the spin and space coordinates of the  $N$  nuclei only and  $\Psi_e$  is a function of the space and spin coordinates of the  $n$  electrons. The positions of the nuclei also enter into  $\Psi_e$  as parameters. This approximation, called the Born-Oppenheimer approximation,<sup>16</sup> reduces the problem to that of finding the wave function and corresponding energy levels of  $n$  electrons in the field of  $N$  fixed nuclei.

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<sup>16</sup>J. C. Slater, Quantum Theory of Molecules and Solids, Vol. I, McGraw-Hill Book Company, Inc.: New York, 1963.

In the resulting electronic Hamiltonian, electron-electron repulsion terms cause difficulty. To circumvent this, we assume that the single electronic wave function  $\Psi_e$  can be written as the product of n one-electron wave functions  $\psi(\underline{x}_i)$ :<sup>17</sup>

$$\Psi_e = \psi_1(\underline{x}_1) \psi(\underline{x}_2) \dots \psi(\underline{x}_n) \quad (40)$$

Here  $\underline{x}_i$  contains the position and spin coordinates of the ith electron. The antisymmetry of a wave function describing spin one-half particles can be accounted for by writing the total electronic wave functions as a Slater determinant<sup>18</sup> of the filled one-electron wave functions.

The one-electron wave functions may be obtained from the molecular orbital (MO) method developed by Mulliken,<sup>19</sup> Hund,<sup>20</sup> Lennard-Jones,<sup>21</sup> and Hückel.<sup>22</sup> The fundamental idea behind the MO method is that the valence electrons belong to the molecule as a whole. In this approximation we set up electron orbitals which may extend throughout the entire molecule. These electron orbitals are called molecular orbitals.

<sup>17</sup> Such an assumption is quite drastic since it neglects that part of the mutual interaction of the electrons which does not have the symmetry of the nuclei. Much effort has been expended to reintroduce these "electron correlation" effects. See P. O. Löwdin, Advances in Chemical Physics, Vol. II, Interscience Publishers, Inc.: New York, 1958.

<sup>18</sup> Eyring, Walter, and Kimball, op. cit., p. 232.

<sup>19</sup> R. S. Mulliken, Phys. Rev., 32, 186, 761 (1928); 33, 730 (1929); 40, 55 (1932); 41, 49, 751 (1932); 43, 279 (1933).

<sup>20</sup> F. Hund, Z. Physik, 51, 759 (1928); 63, 719 (1930).

<sup>21</sup> J. E. Lennard-Jones, Trans. Faraday Soc., 25, 668 (1929).

<sup>22</sup> E. Hückel, Z. Physik, 70, 204 (1931).

The particular MO method to be considered here is the linear combination of atomic orbitals (LCAO-MO) method. As the name implies, we set up a variation function of the form

$$\psi = c_1 \phi_1 + c_2 \phi_2 + \dots + c_N \phi_N \quad (41)$$

where  $\psi$  is the molecular orbital and the  $\phi_1, \phi_2, \dots, \phi_N$  may be atomic orbitals or appropriate hybrid orbitals. The subscript  $i$  on the function  $\phi_i$  indicates that the function is an atomic orbital (or hybrid orbital) based on the  $i$ th atom. The  $c$ 's are constants which must satisfy the relation

$$\sum_{i=1}^N c_i^* c_i = 1 \quad (42)$$

if the  $\psi$ 's are to be normalized.

The use of molecular symmetry allows us to find some molecular orbitals of Eq. (41) directly, without resorting to the variation method. The proper choice leads to an automatic factoring of the secular equation.

A symmetry operation of the group interchanges  $N$  equivalent atoms or atomic orbitals based on those atoms. Hence, the operation is equivalent to a permutation of  $N$  like objects. As such, each symmetry operation can be represented by an  $N$ -dimensional permutation matrix. We conclude that the  $N$  equivalent atomic orbitals generate a set of  $N$ -dimensional permutation matrices which form a reducible representation  $\Gamma$  of the group.

Since the molecular orbitals are linear combinations of the atomic orbitals, the entire set of molecular orbitals generates a representation of the group which is equivalent to  $\Gamma$ . The equivalence of the two representations means that they have the same character system.<sup>23</sup> The character system for  $\Gamma$  is obtained simply by summing up the diagonal elements of each permutation matrix. The number of times  $a_i$  the  $i$ th irreducible representation appears in the reducible one  $\Gamma$  is given by the relation<sup>24</sup>

$$a_i = \frac{1}{h} \sum_R \chi(R) \chi^i(R) \quad (43)$$

Here  $h$  is the order of the group,  $\chi(R)$  is the character of symmetry operation  $R$  in the reducible representation, and  $\chi^i(R)$  is the character of  $R$  in the  $i$ th irreducible representation.

As indicated before, it is not necessary to find a complete set of eigenfunctions for a given energy value  $E$ . In fact, the application of the projection operator  $P^i$  of Eq. (25) to an atomic orbital yields

$$\begin{aligned} \psi^i &= c P^i \phi \\ &= c \sum_R \chi^i(R) R \phi \end{aligned} \quad (44)$$

where  $\phi$  is an atomic orbital and  $c$  is a normalization constant. By Eq. (22),  $\psi^i$  is a linear combination of the functions  $\phi_m^i$  which form

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<sup>23</sup>Eyring, Walter, and Kimball, op. cit., p. 183.

<sup>24</sup>Ibid., p. 184.



a complete set of basis functions for the  $i$ th irreducible representation. The  $\phi_m^i$  are linear combinations of the atomic orbitals of the form of Eq. (41). They are molecular orbitals. Since the  $\psi^i$  are linear combinations of the  $\phi_m^i$ , the  $\psi^i$  are also molecular orbitals yielding the same energy value  $E$ .

Again we point out that the use of Eq. (44) relies only on a knowledge of the character systems of the various irreducible representations appearing in the appropriate group. This fact is especially helpful since character tables for numerous symmetry groups are available.<sup>25-27</sup>

The energy levels for irreducible representations appearing once are found from the expression

$$E_i = \int \psi^{i*} H \psi^i d\tau \quad (45)$$

Here  $\psi^i$  is a normalized molecular orbital obtained from Eq. (44) and  $E_i$  is the energy level corresponding to the  $i$ th irreducible representation. For ease of manipulation, we write

$$\psi^i = C(c_1 \phi_1 + c_2 \phi_2 + \dots + c_N \phi_N) \quad (46)$$

where  $c_1, c_2, \dots, c_N$  are chosen as integers and the constant  $C$  produces the required normalization. Equation (45) becomes

<sup>25</sup>Ibid., pp. 383-388.

<sup>26</sup>Gerhard Herzberg, Molecular Spectra and Molecular Structure, D. Van Nostrand Company, Inc.: New York, 1945.

<sup>27</sup>Wilson, Decius, and Cross, Molecular Vibrations, McGraw-Hill Book Company, Inc.: New York, 1955.



$$E_i = C^* C \int \left( \sum_{k=1}^N c_k^* \phi_k^* \right) H \left( \sum_{m=1}^N c_m \phi_m \right) d\tau$$

or

$$E_i = C^* C \sum_{k=1}^N \sum_{m=1}^N c_k^* c_m \int \phi_k^* H \phi_m d\tau \quad (47)$$

Appearing in Eq. (47) are the two integrals:

$$H_0 = \int \phi_k^* H \phi_k d\tau \quad (48)$$

and for  $k \neq m$

$$H_{km} = \int \phi_k^* H \phi_m d\tau \quad (49)$$

The integral  $H_0$  is called the Coulombic integral; it gives the average energy of an electron in an atomic orbital  $\phi$ . The  $H_{km}$  is called an exchange or resonance integral; it indicates the energy depression due to the delocalization of an electron between two nuclei.

When all of the atomic orbitals appearing in  $\psi_i$  are the same, the  $H_0$  are all equal. But the exchange integrals are different for different combinations of neighboring orbitals. The different types of exchange integrals, such as nearest neighbor, second nearest neighbor, etc., are denoted by the Greek letters  $\alpha$ ,  $\beta$ , . . ., respectively. The energy value of Eq. (47) is then written in the parametric form

$$E_i = H_0 + a\alpha + b\beta + \dots \quad (50)$$

Here the constant  $a$  is the sum of the coefficients of all  $\alpha$  terms appearing in Eq. (47),  $b$  is the sum of the coefficients of all  $\beta$  terms, and so forth. No attempt was made to evaluate the  $H_0$ ,  $\alpha$ ,  $\beta$ , . . ., terms appearing in Eq. (50).

To obtain the energy levels corresponding to an irreducible representation appearing  $a_i$  times, we must find  $a_i$  functions which are physically independent and which all belong to the same column of the irreducible representation. The method for determining these two conditions is developed later.

# MOLECULAR ORBITAL BONDING IN THE $\text{Ta}_6\text{Cl}_{12}^{+2}$ STRUCTURE

The octahedral structure for  $\text{Ta}_6\text{Cl}_{12}^{+2}$ ,  $\text{Ta}_6\text{Br}_{12}^{+2}$ , and  $\text{Nb}_6\text{Cl}_{12}^{+2}$  was proposed by Vaughan, Sturdivant, and Pauling<sup>28,29</sup> to explain their x-ray diffraction data. In the structure a metal atom is located at each vertex of the octahedron and halogen atom over the middle of each edge as in Figure I.

In discussing the structure, Duffey<sup>30</sup> supposed that hybrid orbitals from neighboring metal atoms meet over the atom of each face. When each such set of three overlapping orbitals was considered independent, the right number of bonding orbitals was obtained. Here interactions between the different faces are taken into account and the results are expressed parametrically.

The treatment to follow is mathematically the same for all three ions mentioned. Each tantalum atom or niobium atom has five valence electrons and each offers similar orbitals for hybridization.<sup>31</sup> We shall make reference only to the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  ion, keeping in mind the treatment applies equally well to the other two ions.

The symmetry operations which leave the ion unchanged form the

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<sup>28</sup>P. A. Vaughan, J. H. Sturdivant, and L. Pauling, J. Am. Chem. Soc., 72, 5477 (1950).

<sup>29</sup>L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press: Ithaca, New York, 1960.

<sup>30</sup>G. H. Duffey, J. Chem. Phys., 19, 963 (1951).

<sup>31</sup>Pauling, op. cit., pp. 50-51.

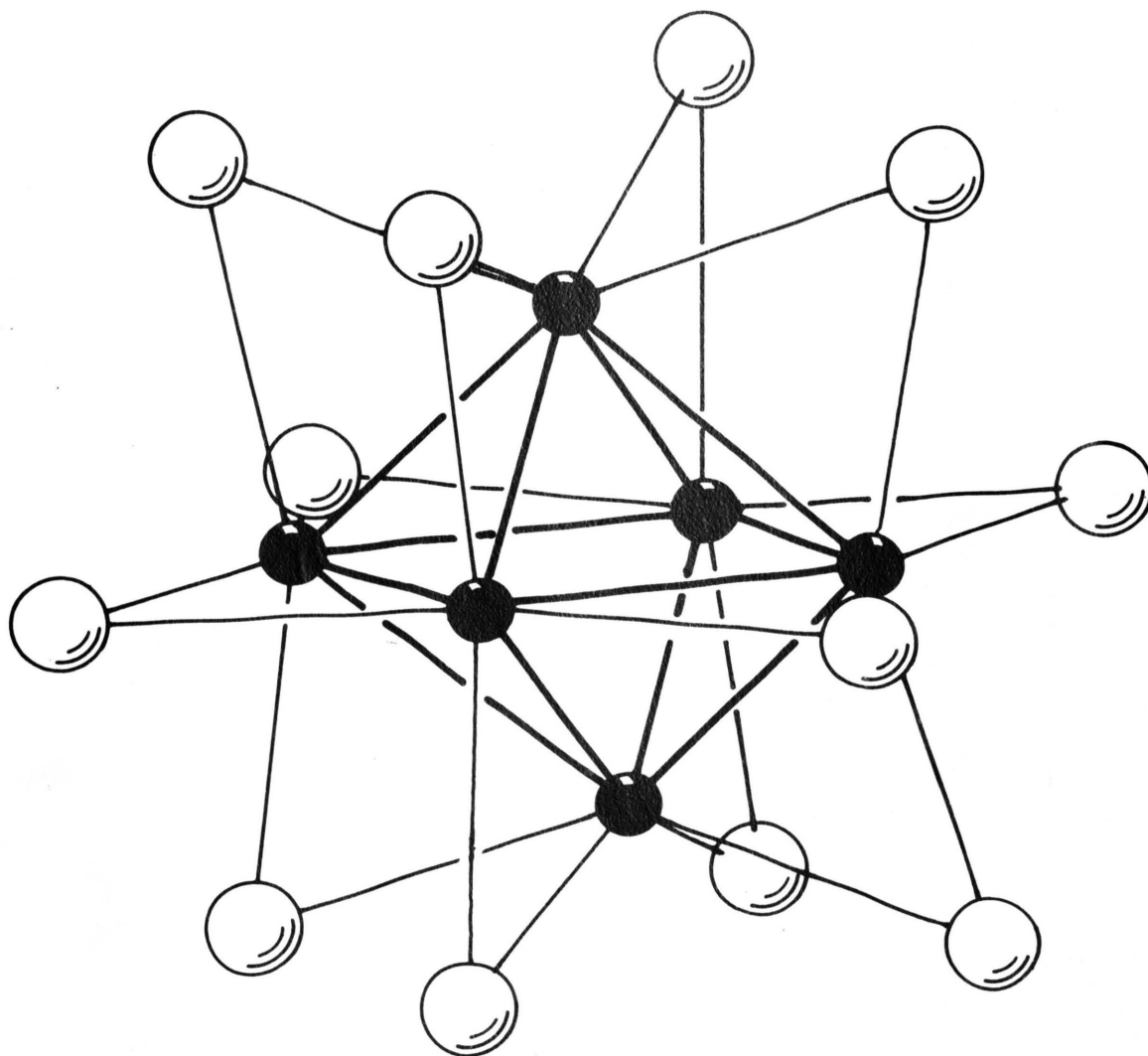


Figure I. The  $\text{Ta}_6\text{Cl}_{12}^{+2}$  structure (Due to L. Crossman)

$O_h$  symmetry group. The  $O_h$  group consists of 48 operations divided among ten classes. These symmetry operations are explained elsewhere.<sup>32</sup>

The character table for the  $O_h$  group, taken from Herzberg,<sup>33</sup> is shown in Table 1. Listed on the first ten lines are the irreducible representations of the group and their corresponding character systems. Reducible representations and their corresponding character systems used in this work are given on the following lines.

The symbols in the first column of Table 1 indicate the particular representation. Irreducible ones are denoted by capital letters with the following meaning: an A designates a singly degenerate representation, an E a doubly degenerate one, and F a triply degenerate one. Representations which are symmetric under the operation I are given the subscript g (gerade) and those which are antisymmetric with respect to I take the subscript u (ungerade). The symbol  $\Gamma$  refers to a reducible representation of the group. The subscript on the  $\Gamma$ 's refer to particular reducible representations which will take on more meaning in the discussion to follow.

About each tantalum atom the 5d, 6s, and 6p valence orbitals are hybridized to yield the distorted square antiprism arrangement of Duffey.<sup>34</sup> The bond orbitals of this arrangement are given by the functions

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<sup>32</sup>Herzberg, op. cit.

<sup>33</sup>Ibid., p. 123.

<sup>34</sup>Duffey, op. cit.

Table 1. Character Table of  $O_h$  Group

Representation	E	$8C_3$	$6C_2$	$6C_4$	$3C_4^2$	I	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$A_{1g}$	1	1	1	1	1	1	1	1	1	1
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1
$A_{2g}$	1	1	-1	-1	1	1	-1	1	1	-1
$A_{2u}$	1	1	-1	-1	1	-1	1	-1	-1	1
$E_g$	2	-1	0	0	2	2	0	-1	2	0
$E_u$	2	-1	0	0	2	-2	0	1	2	0
$F_{1g}$	3	0	-1	1	-1	3	1	0	-1	-1
$F_{1u}$	3	0	-1	1	-1	-3	-1	0	1	1
$F_{2g}$	3	0	1	-1	-1	3	-1	0	-1	1
$F_{2u}$	3	0	1	-1	-1	-3	1	0	1	-1
$\Gamma_t$	24	0	0	0	0	0	0	0	0	4
$\Gamma_r$	6	0	0	2	2	0	0	0	4	2
$\Gamma_p$	12	0	0	0	-4	0	0	0	0	0

$$\psi_1 = \sqrt{\frac{1}{8}}S + \sqrt{\frac{1}{8}}Ap_z + \sqrt{\frac{1}{2}}Cp_x - \sqrt{\frac{1}{8}}Bd_{3z^2-r^2} + \frac{1}{2}d_{x^2-y^2} + \sqrt{\frac{1}{2}}Dd_{xz} \quad (51)$$

$$\psi_2 = \sqrt{\frac{1}{8}}S + \sqrt{\frac{1}{8}}Ap_z + \sqrt{\frac{1}{2}}Cp_y - \sqrt{\frac{1}{8}}Bd_{3z^2-r^2} - \frac{1}{2}d_{x^2-y^2} + \sqrt{\frac{1}{2}}Dd_{yz} \quad (52)$$

$$\psi_3 = \sqrt{\frac{1}{8}}S + \sqrt{\frac{1}{8}}Ap_z - \sqrt{\frac{1}{2}}Cp_x - \sqrt{\frac{1}{8}}Bd_{3z^2-r^2} + \frac{1}{2}d_{x^2-y^2} - \sqrt{\frac{1}{2}}Dd_{xz} \quad (53)$$

$$\psi_4 = \sqrt{\frac{1}{8}}S + \sqrt{\frac{1}{8}}Ap_z - \sqrt{\frac{1}{2}}Cp_y - \sqrt{\frac{1}{8}}Bd_{3z^2-r^2} - \frac{1}{2}d_{x^2-y^2} - \sqrt{\frac{1}{2}}Dd_{yz} \quad (54)$$

$$\begin{aligned} \psi_5 = & \sqrt{\frac{1}{8}}S - \sqrt{\frac{1}{8}}Ap_z + \frac{1}{2}Dp_x + \frac{1}{2}Dp_y + \sqrt{\frac{1}{8}}Bd_{3z^2-r^2} \\ & + \frac{1}{2}d_{xy} - \frac{1}{2}Cd_{xz} - \frac{1}{2}Cd_{yz} \end{aligned} \quad (55)$$

$$\begin{aligned} \psi_6 = & \sqrt{\frac{1}{8}}S - \sqrt{\frac{1}{8}}Ap_z - \frac{1}{2}Dp_x + \frac{1}{2}Dp_y + \sqrt{\frac{1}{8}}Bd_{3z^2-r^2} \\ & - \frac{1}{2}d_{xy} + \frac{1}{2}Cd_{xz} - \frac{1}{2}Cd_{yz} \end{aligned} \quad (56)$$

$$\begin{aligned} \psi_7 = & \sqrt{\frac{1}{8}}S - \sqrt{\frac{1}{8}}Ap_z - \frac{1}{2}Dp_x - \frac{1}{2}Dp_y + \sqrt{\frac{1}{8}}Bd_{3z^2-r^2} \\ & + \frac{1}{2}d_{xy} + \frac{1}{2}Cd_{xz} + \frac{1}{2}Cd_{yz} \end{aligned} \quad (57)$$

$$\begin{aligned} \psi_8 = & \sqrt{\frac{1}{8}}S - \sqrt{\frac{1}{8}}Ap_z + \frac{1}{2}Dp_x - \frac{1}{2}Dp_y + \sqrt{\frac{1}{8}}Bd_{3z^2-r^2} \\ & - \frac{1}{2}d_{xy} - \frac{1}{2}Cd_{xz} + \frac{1}{2}Cd_{yz} \end{aligned} \quad (58)$$

$$\psi_9 = Bp_z + Ad_z \quad (59)$$

Here

$$A = \cos \beta, \quad B = \sin \beta, \quad C = \cos \alpha, \quad D = \sin \alpha$$

are constants (with  $\alpha$  and  $\beta$  as parameters) which effect normalization of the functions. The angular parts of the valence orbitals s, p, and

d, normalized to  $4\pi$ , are defined by the equations<sup>35</sup>

$$s = 1 \quad (60)$$

$$p_x = \sqrt{3} \sin \theta \cos \phi \quad (61)$$

$$p_y = \sqrt{3} \sin \theta \sin \phi \quad (62)$$

$$p_z = \sqrt{3} \cos \theta \quad (63)$$

$$d_{xy} = \frac{1}{2} \sqrt{15} \sin^2 \theta \sin 2\phi \quad (64)$$

$$d_{x^2-y^2} = \frac{1}{2} \sqrt{15} \sin^2 \theta \cos 2\phi \quad (65)$$

$$d_{xz} = \sqrt{15} \sin \theta \cos \theta \cos \phi \quad (66)$$

$$d_{yz} = \sqrt{15} \sin \theta \cos \theta \sin \phi \quad (67)$$

$$d_{3z^2-r^2} = \frac{1}{2} \sqrt{5} (3\cos^2 \theta - 1) \quad (68)$$

where  $\theta$  and  $\phi$  are the usual polar coordinates.

The atoms and faces of the octahedron are labeled as in Figure II. On each atom the hybrid orbitals are oriented symmetrically so that  $\psi_1$ ,  $\psi_2$ ,  $\psi_3$ , and  $\psi_4$  extend over the edges of the octahedron. This set of equivalent orbitals is employed to form localized bonds with neighboring halogen atoms. Functions  $\psi_5$ ,  $\psi_6$ ,  $\psi_7$ , and  $\psi_8$  compose another set of equivalent orbitals. They point out over adjacent faces to form delocalized bonds within the octahedral cage. In Figure III, these bond orbitals are represented by vectors. (The orbitals on atoms 5 and 6 are omitted from the figure.) Each vector representing an orbital on a given atom meets the radius vector

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<sup>35</sup>George H. Duffey, Physical Chemistry, McGraw-Hill Book Company, Inc.: New York, 1962, p. 152.



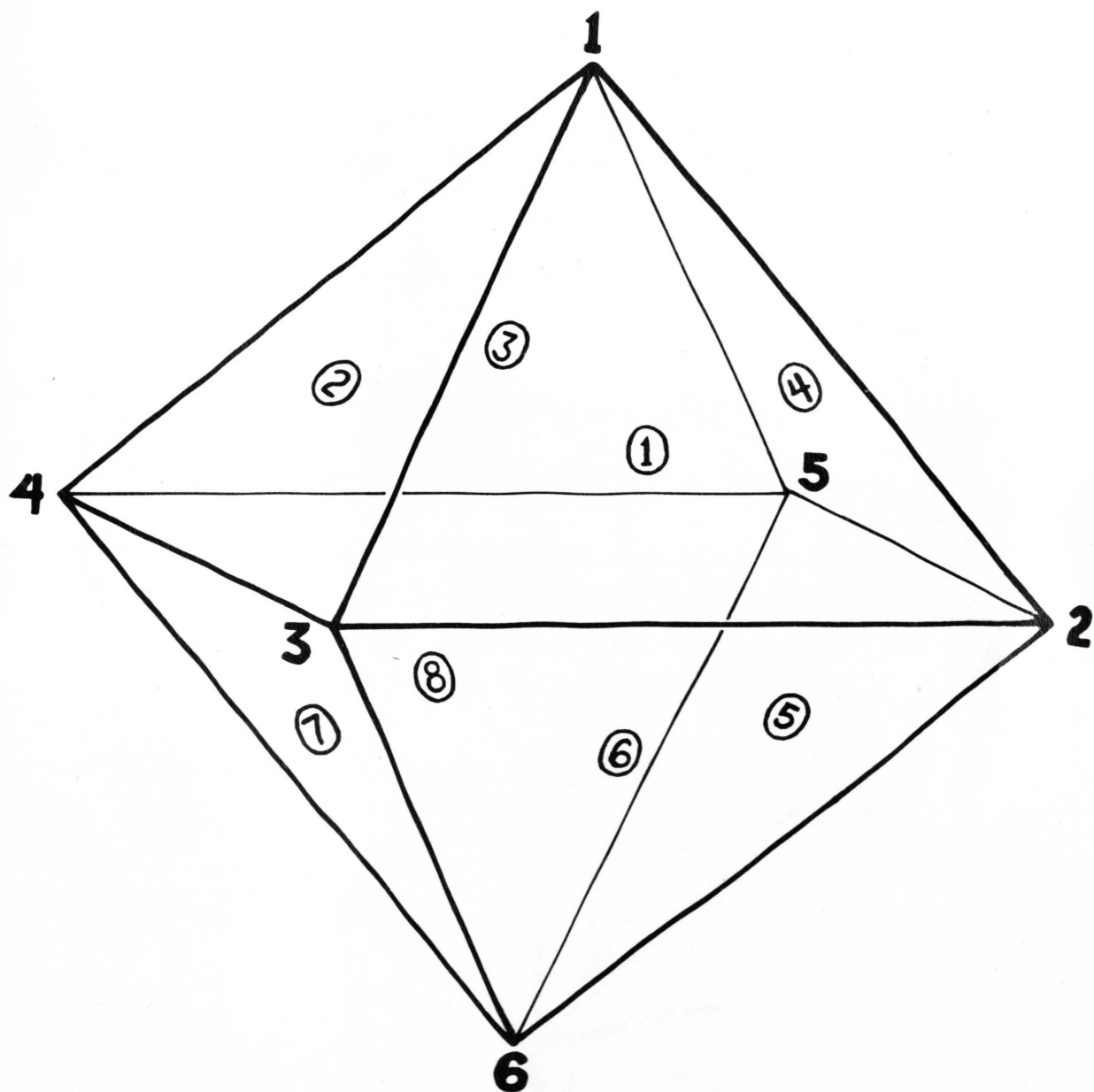


Figure II. Numbering of vertices and faces of octahedron

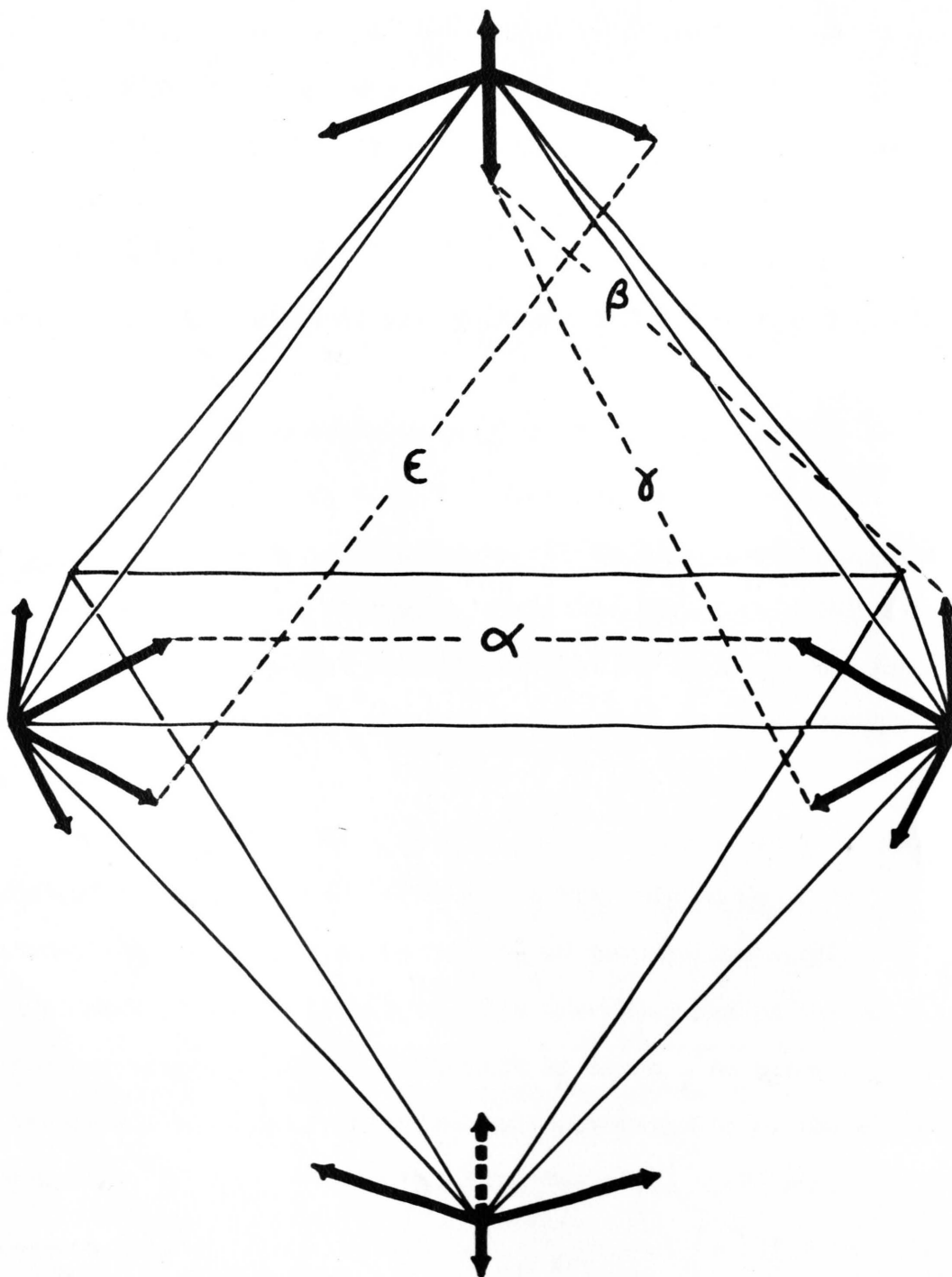


Figure III. Orientation of bond orbitals and labelling of resonance integrals in  $\text{TaCl}_6^{+2}$  structure

drawn through that atom at the same angle and extends symmetrically out over the neighboring face.

Finally, a bond orbital  $\psi_9$  points radially outward from each tantalum atom. Each radial orbital may be used for bonding additional atoms, or groups of atoms, to the structure. In the absence of such bonding, the radial orbitals are available for delocalized bonding in the octahedral structure.

Since concern is directed toward delocalized bonding, only the last two sets are considered in the molecular orbital scheme.

Each bond orbital in the second set is designated by a symbol  $t_{ij}$ , where  $i$  denotes the atom upon which the orbital is based and  $j$  denotes the face over which the valence orbital extends. The radial orbitals are denoted by  $r_i$ , where  $i$  denotes the atom upon which the atom is based.

The set of functions  $t_{ij}$  forms the basis of a reducible representation of the group. As mentioned in the section on molecular orbitals, the representation is made up of permutation matrices<sup>36</sup> which permute equivalent orbitals. The character system for the reducible representation  $\Gamma_t$  generated by the  $t_{ij}$  is given in Table 1. The number of times an irreducible representation of the group appears in  $\Gamma_t$  is obtained by applying Eq. (43), which yields

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<sup>36</sup>In a strict sense, these are pseudopermutation matrices since the unit elements are not all positive.

$$\Gamma_t = A_{1g} + A_{2u} + E_g + E_u + F_{1g} + 2F_{1u} + 2F_{2g} + F_{2u} \quad (69)$$

The decomposition of  $\Gamma_t$  into its irreducible representations gives information about the number of energy levels one would expect. From Eq. (69), for instance, we see that two singly degenerate levels,  $A_{1g}$  and  $A_{2u}$ , occur once each. Two doubly degenerate levels,  $E_g$  and  $E_u$ , occur once each. The triply degenerate levels,  $F_{1u}$  and  $F_{2g}$ , occur only once each, while  $F_{1g}$  and  $F_{2g}$  appear two times. Thus, we expect ten energy levels ranging from nondegenerate to triply degenerate ones.

As mentioned before, only one molecular orbital need be found for each irreducible representation appearing but once in expression (69). The molecular orbital belonging to  $A_{1g}$  is found by applying the projection operator of Eq. (44) in the form

$$cP^{A_{1g}} = c \sum_R \chi_{A_{1g}}^{(R)} R \quad (70)$$

to bond orbital  $t_{11}$ . The result is the normalized eigenfunction.

$$A_{1g}: \frac{1}{\sqrt{24}} (t_{11} + t_{12} + t_{13} + t_{14} + t_{21} + t_{24} + t_{25} + t_{26} + t_{31} + t_{32} + t_{36} + t_{37} + t_{42} + t_{43} + t_{47} + t_{48} + t_{53} + t_{54} + t_{55} + t_{58} + t_{65} + t_{66} + t_{67} + t_{68}) \quad (71)$$

In a similar manner the eigenfunctions corresponding to the other singly appearing irreducible representations are found. We obtain

$$A_{2u}: \frac{1}{\sqrt{24}} (t_{11} - t_{12} + t_{13} - t_{14} + t_{21} - t_{24} + t_{25} - t_{26} + t_{31} - t_{36} + t_{37} - t_{32} - t_{42} + t_{47} - t_{48} + t_{43} + t_{53} - t_{58} + t_{55} - t_{54} + t_{65} - t_{66} + t_{67} - t_{68}) \quad (72)$$

$$E_g: \frac{1}{\sqrt{48}} (2t_{11} + 2t_{12} + 2t_{13} + 2t_{14} - t_{21} - t_{24} - t_{25} - t_{26} - t_{31} - t_{36} - t_{37} - t_{32} - t_{42} - t_{47} - t_{48} - t_{43} - t_{53} - t_{58} - t_{55} - t_{54} + 2t_{65} + 2t_{66} + 2t_{67} + 2t_{68}) \quad (73)$$

$$E_u: \frac{1}{\sqrt{48}} (2t_{11} - 2t_{12} + 2t_{13} - 2t_{14} - t_{21} + t_{24} - t_{25} + t_{26} - t_{31} + t_{36} - t_{37} + t_{32} + t_{42} - t_{47} + t_{48} - t_{43} - t_{53} + t_{58} - t_{55} + t_{54} + 2t_{65} - 2t_{66} + 2t_{67} - 2t_{68}) \quad (74)$$

$$F_{1g}: \frac{1}{\sqrt{32}} (2t_{11} - 2t_{13} - t_{21} - t_{24} + t_{25} + t_{26} - t_{31} + t_{36} + t_{37} - t_{32} + t_{42} - t_{47} - t_{48} + t_{43} + t_{53} - t_{58} - t_{55} + t_{54} - 2t_{66} + 2t_{68}) \quad (75)$$

$$F_{2u}: \frac{1}{\sqrt{32}} (2t_{11} - 2t_{13} - t_{21} + t_{24} + t_{25} - t_{26} - t_{31} - t_{36} + t_{37} + t_{32} - t_{42} - t_{47} + t_{48} + t_{43} + t_{53} + t_{58} - t_{55} - t_{54} + 2t_{66} - 2t_{68}) \quad (76)$$

The energy  $E_i$  corresponding to an irreducible representation is obtained by using the eigenfunction from that representation in Eq. (49). In parametric form, the results are

$$A_{1g}: H_0 + 2\alpha + 2\beta + 4\gamma + 4\delta + 2\epsilon + 2f + 2\eta + \theta \quad (77)$$

$$A_{2u}: H_0 + 2\alpha - 2\beta - 4\gamma + 4\delta + 2\epsilon - 2f + 2\eta - \theta \quad (78)$$

$$E_g: H_0 - \alpha - \beta - 2\gamma - 2\delta - \epsilon - f + 2\eta + \theta \quad (79)$$

$$E_u: H_0 - \alpha + \beta + 2\gamma - 2\delta - \epsilon + f + 2\eta - \theta \quad (80)$$

$$F_{1g}: H_0 - \alpha - \beta + 2\gamma + 2\delta - \epsilon - f - \theta \quad (81)$$

$$F_{2u}: H_0 - \alpha + \beta - 2\gamma + 2\delta - \epsilon + f + \theta \quad (82)$$

Here  $H_0$  is the coulomb integral and  $\alpha$  is represented by the resonance integral between  $t_{11}$  and  $t_{21}$ ,  $\beta$  between  $t_{11}$  and  $t_{24}$ ,  $\gamma$  between  $t_{11}$  and  $t_{26}$ ,  $\delta$  between  $t_{11}$  and  $t_{47}$ ,  $f$  between  $t_{11}$  and  $t_{48}$ ,  $\eta$  between  $t_{11}$  and  $t_{65}$ , and  $\theta$  between  $t_{11}$  and  $t_{66}$ . In Figures III and IV the different combinations are represented pictorially.

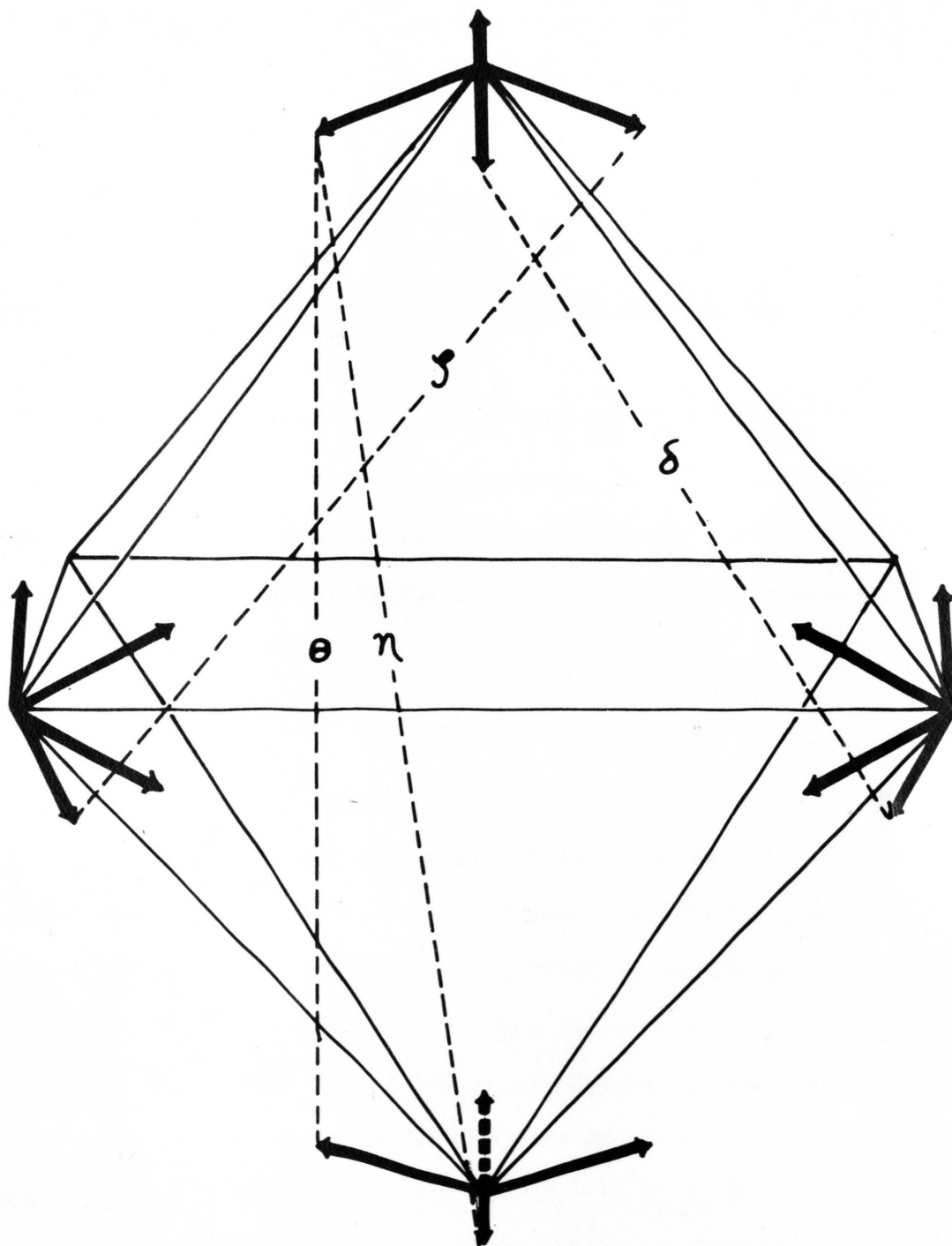


Figure IV. Remaining resonance integrals for the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  structure



Now, representation  $F_{2g}$  appears twice in the decomposition of  $\Gamma_t$ . Thus, two independent sets of basis functions belong to  $F_{2g}$  and the method used before to obtain the energy levels does not apply. Indeed, a two dimensional secular equation must be solved. Furthermore, the two functions used in forming the secular equation must belong to the same column of the same irreducible representation. How to find these will now be discussed.

A systematic method is based on the noncrossing rule,<sup>37,38</sup> which states that energy levels corresponding to molecular orbitals of the same symmetry type cannot cross as internuclear distances are varied. The terms responsible for noncrossing are the interaction terms of Eq. (30). Solving determinant (30) yields

$$E = \frac{1}{2} (H_{11} + H_{22}) \pm \frac{1}{4} [(H_{11} - H_{22})^2 + H_{12}^2]^{\frac{1}{2}} \quad (83)$$

where  $H_{11}$  is obtained by using a molecular orbital from one set in Eq. (45) and  $H_{22}$  by using a molecular orbital from the other set which belongs to the same column as the first one. The two independent molecular orbitals may be obtained by setting up an analogy between molecular orbitals and atomic valence orbitals.

Thus, we consider the effect on orbitals when the governing potential is changed from spherical to octahedral symmetry. In the

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<sup>37</sup>Eyring, Walter, and Kimball, op. cit., pp. 207-208.

<sup>38</sup>Coulson and Lewis, Quantum Theory, Vol. II, ed. D. R. Bates, Academic Press Inc.: New York, 1962, p. 204.

spherically symmetric field, the s level is nondegenerate, the p level is threefold degenerate, the d level is fivefold degenerate, and so on. If an octahedral potential is imposed on it, some of the degenerate levels split.<sup>39</sup> For instance, the fivefold degenerate d level is split into two levels, one doubly degenerate and the other triply degenerate. The two new levels have different energies and dimensions. Hence they correspond to different irreducible representations. The doubly degenerate set consists of the two valence orbitals  $d_{3z^2-r^2}$  and  $d_{x^2-y^2}$ . These two orbitals provide the basis for  $E_g$  of the  $O_h$  group, while the functions  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  belonging to the triply degenerate level form the basis for  $F_{2g}$  of  $O_h$ . The splitting is indicated in Table 2.<sup>40</sup> The first column lists the basis functions for the irreducible representations of the  $O_h$  group lying in the same row and in the right hand column.

If we now assume that each molecular orbital of an octahedral structure is analogous to a valence orbital of an atom in an octahedral potential, then the molecular orbitals form bases for the corresponding irreducible representations of the  $O_h$  group. Hence, two independent molecular orbitals which generate  $E_g$  should have the angular appearance of the atomic orbitals which generate  $E_g$ . One of the

<sup>39</sup>C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Company, Inc.: New York, 1962, pp. 57-97.

<sup>40</sup>R. Hoffman and M. Gouterman, J. Chem. Phys., 36, 2189 (1962).



Table 2. Reduction of Spherical Symmetry to  $O_h$  Symmetry

Atomic orbitals l	Irreducible representations of $O_h$ group generated by atomic orbitals
0(s)	$A_{1g}$
1(p)	$F_{1u}$
2(d)	$E_g + F_{2g}$
3(f)	$A_{2u} + F_{1u} + F_{2u}$
4(g)	$A_{1g} + E_g + F_{1g} + F_{2g}$
5(h)	$E_u + 2F_{1u} + F_{2u}$
6(i)	$A_{1g} + A_{2g} + E_g + F_{1g} + 2F_{2g}$

molecular orbitals has two cones as nodal surfaces and is  $d_{3z^2-r^2}$ -like while the other has two nodal planes and is  $d_{x^2-y^2}$ -like. The nodal surfaces of the two molecular orbitals are aligned in the same way as they are for the single atom. One molecular orbital then belongs to one column of  $E_g$ , while the other molecular orbital belongs to the other column.

Applying these ideas to the doubly occurring representation  $F_{2g}$ , we note from Table 2 that a set of d-like molecular orbitals will provide the basis for  $F_{2g}$  as will a set of g-like molecular orbitals. A set of i-like ones is also possible, but we confine ourselves first to those orbitals having lower energies. Considering only p-like and g-like orbitals, we have three possibilities for the two orbitals we

seek. (1) Two physically independent sets of p-like orbitals exist. We then obtain a p-like orbital from each set and align the nodal planes so they coincide. The coincidence of nodal planes is only an indication that the two orbitals belong to the same column; the orbitals must also be independent, orthogonal, and must give maximum interaction. (2) One set consists of p-like orbitals and the other set of g-like orbitals. Again, nodal surfaces must be aligned, independence and orthogonality checked, and interaction tested. (3) Two physically independent sets of g-like orbitals exist. The orbitals are checked as in possibilities (1) and (2).

We start with possibility (1) since the functions should contain as few nodal surfaces as possible to ensure low energy. Also, lobes of the same sign need to be near each other for the interaction integral to be large. In any case, one tests the orbitals to see whether or not they give maximum interaction. For all problems presented here the above method has been successful.

We now obtain molecular orbitals corresponding to  $F_{2g}$ . Applying Eq. (44) to bond orbital  $t_{11}$  yields the function

$$F_{2g} = \frac{1}{8} (4t_{11} - 2t_{12} - 2t_{14} + t_{21} + t_{24} - t_{25} - t_{26} + t_{31} - t_{37} + t_{32} - t_{42} + t_{47} \\ + t_{48} - t_{43} - t_{53} + t_{58} + t_{55} - t_{54} - 2t_{65} - 2t_{67} + 4t_{66}) \quad (84)$$

By itself, function (84) exhibits little d-like or g-like quality. So we operate similarly on  $t_{12}$  to obtain another function

$$F_{2g}: \frac{1}{8} (-2t_{11} + 4t_{12} - t_{13} - t_{21} - t_{24} + t_{25} + t_{26} + t_{31} - t_{36} - t_{37} + t_{32} + t_{42} - t_{47} - t_{48} + t_{43} - t_{53} + t_{58} + t_{55} - t_{54} + 4t_{65} - 2t_{66} - 2t_{68}) \quad (85)$$

The sum of (84) and (85) yields

$$F_{2g}: \frac{1}{\sqrt{12}} (t_{11} + t_{12} - t_{13} - t_{14} + t_{31} - t_{36} - t_{37} + t_{32} - t_{53} + t_{58} + t_{55} - t_{54} + t_{65} - t_{66} - t_{67} + t_{68}) \quad (86)$$

Function (86) is a d-like orbital as shown by its plot in Figure Va. One nodal plane contains vertices 2, 3, 4, and 5 while the other passes through 1, 2, 4, and 6. Having obtained one d-like orbital, we now proceed to find either another d-like or a g-like with coincident planes. We are aided in this search by plots of possible functions which are similar to those of Figure V.

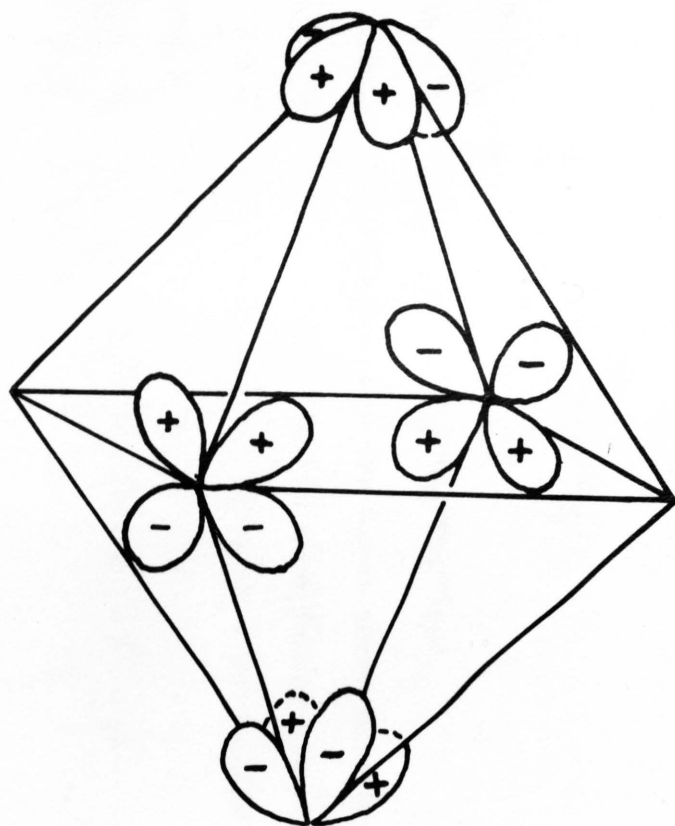
Proceeding in a similar manner, we obtain the function

$$F_{2g}: \frac{1}{\sqrt{8}} (t_{21} - t_{24} + t_{25} - t_{26} + t_{42} - t_{47} + t_{48} - t_{43}) \quad (87)$$

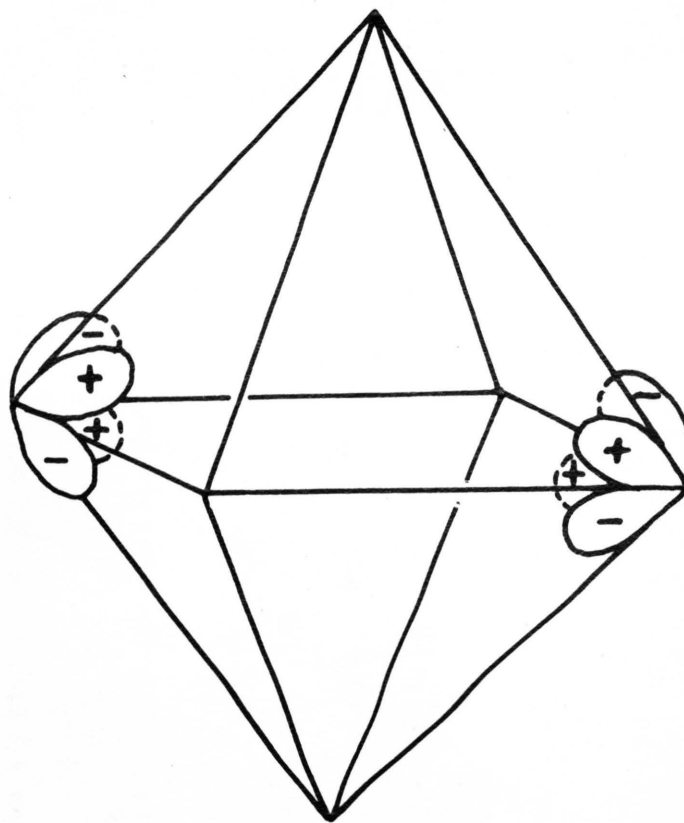
which is also d-like. This function is plotted in Figure Vb. Function (87) has one nodal plane passing through vertices 2, 3, 4, and 5 while the other contains vertices 1, 2, 4, and 6. Hence, the nodal surfaces of (87) coincide with those of (86). The two d-like functions are independent, as can be seen from the plots. They are also orthogonal.

One might suppose that functions (86) and (87) could be added to obtain a d-like orbital and subtracted to yield a g-like orbital. However, the functions so obtained are not orthogonal. Hence, they violate the orthogonality requirement.

*ignore*



(a)



(b)

Figure V. Hybrid lobes contained in (a) molecular orbital (86) and (b) molecular orbital (87) corresponding to representation  $F_{2g}$

The energy corresponding to orbital (86) is obtained from Eq.

(45). We get

$$F_{2g}: H_0 + \alpha + \beta - 2\gamma - 2\delta + \epsilon + f - \theta \quad (88)$$

where the symbols have the same meaning as before. Similarly, the energy for orbital (87) is obtained. We have

$$F_{2g}: H_0 - 2\eta + \theta \quad (89)$$

The interaction term  $H_{12}$  between orbitals (86) and (87) becomes

$$F_{2g}: H_{12} = \sqrt{2}\alpha - \sqrt{2}\beta - \sqrt{2}\epsilon + \sqrt{2}f \quad (90)$$

Expression (90) lowers energy level (88) and raises energy level (89) by the same amount.

Representation  $F_{1u}$  also appears twice in the decomposition of

$\Gamma_t$ . Applying the method above, we obtain

$$F_{1u}: \frac{1}{4} (t_{11} - t_{12} - t_{13} + t_{14} + t_{31} + t_{36} - t_{37} - t_{32} - t_{53} - t_{58} \\ + t_{55} + t_{54} + t_{65} + t_{66} - t_{67} - t_{68}) \quad (91)$$

and

$$F_{1u}: \frac{1}{\sqrt{8}} (t_{21} + t_{24} + t_{26} + t_{27} - t_{42} - t_{47} - t_{48} - t_{43}) \quad (92)$$

Orbital (91) is p-like with the nodal plane passing through vertices 1, 3, 5, and 6. Orbital (92) is also p-like with a nodal surface coinciding with that of orbital (91). The corresponding energy levels have the form

$$F_{1u}: H_0 + \alpha - \beta + 2\gamma - 2\delta + \epsilon - f + \theta \quad (93)$$

$$: H_0 - 2\eta - \theta \quad (94)$$



The interaction term between orbitals (91) and (92) becomes

$$F_{1u}: H_{12} = \sqrt{2}\alpha + \sqrt{2}\beta - \sqrt{2}\epsilon - \sqrt{2}\gamma \quad (95)$$

This term lowers energy level (93) and raises level (94).

Now, each inwardly pointing hybrid atomic orbital,  $\psi_5$ ,  $\psi_6$ ,  $\psi_7$ , or  $\psi_8$  of Eqs. (55) - (58), has cross sections as shown in Figures VI and VII. From these we see that the overlaps causing the resonance integrals  $\beta$ ,  $\gamma$ ,  $\eta$ , and  $\zeta$  are small. Also, the overlap of  $\theta$  seems to be much greater than that of  $\delta$  and the overlap of  $\delta$  greater than that of  $\epsilon$ .

For the purpose of an estimate we take

$$\theta \approx \frac{1}{4}\alpha \quad (96)$$

and

$$\delta \approx \epsilon \approx 0 \approx \zeta \approx \eta \approx \gamma \approx \beta \quad (97)$$

whence the bonding levels are

$$A_{1g}: H_0 + 2.25\alpha \quad (98)$$

$$F_{1u}: H_0 + 2.10\alpha \quad (99)$$

$$F_{2g}: H_0 + 2.00\alpha \quad (100)$$

$$A_{2u}: H_0 + 1.75\alpha \quad (101)$$

In this estimate, all other energy levels are antibonding. The Pauli exclusion principle allows us to have two electrons in each level.

Thus, we place two electrons into each of the non-degenerate levels  $A_{1g}$  and  $A_{2u}$  and six electrons into each triply degenerate level  $F_{1u}$  and  $F_{2g}$ . We have used 16 electrons in filling the bonding levels -

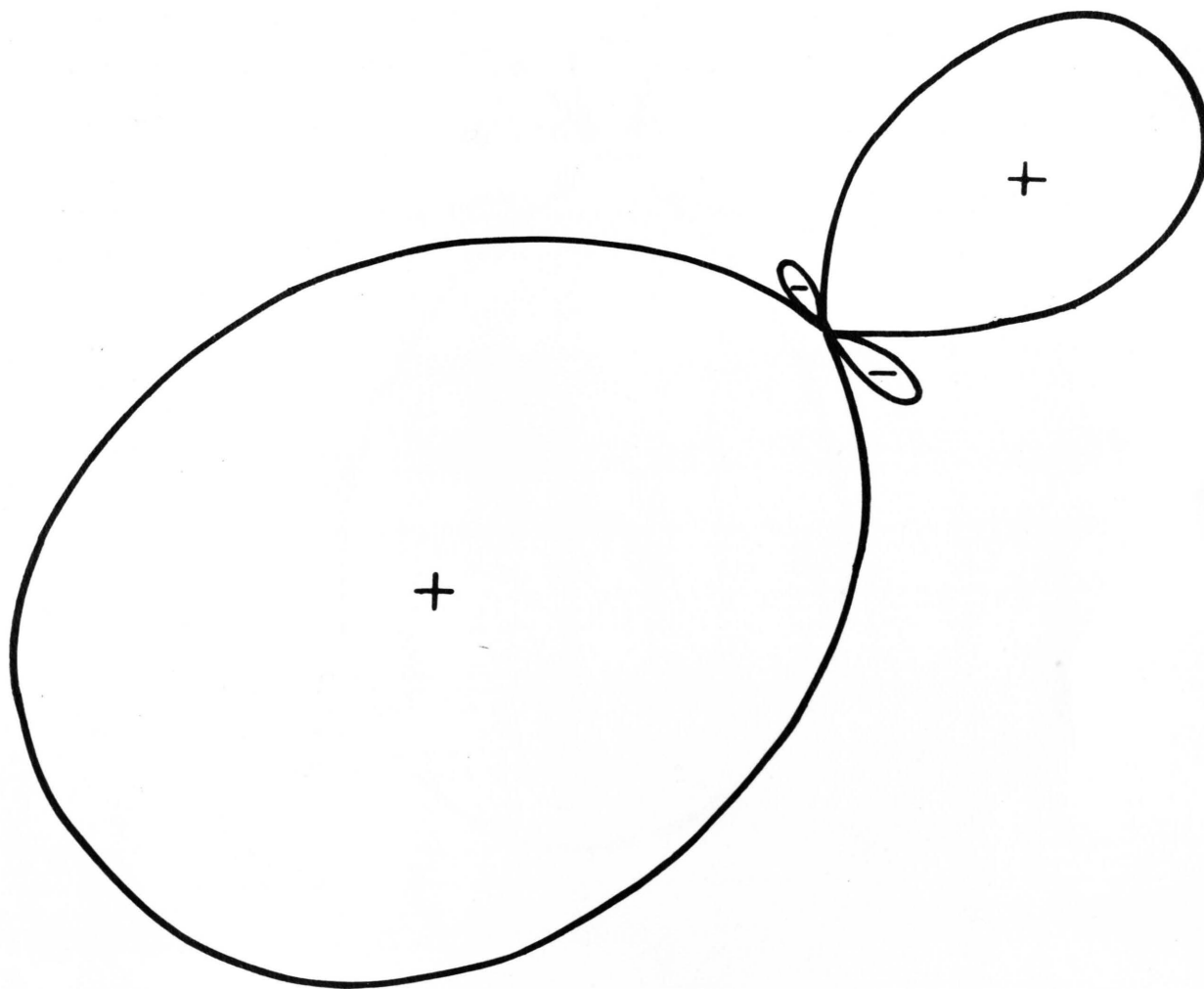


Figure VI. Cross section of Ta valence orbital through plane cutting octahedron and opposite triangular faces in two. Large lobe, small lobe, and side band are bisected by this plane.

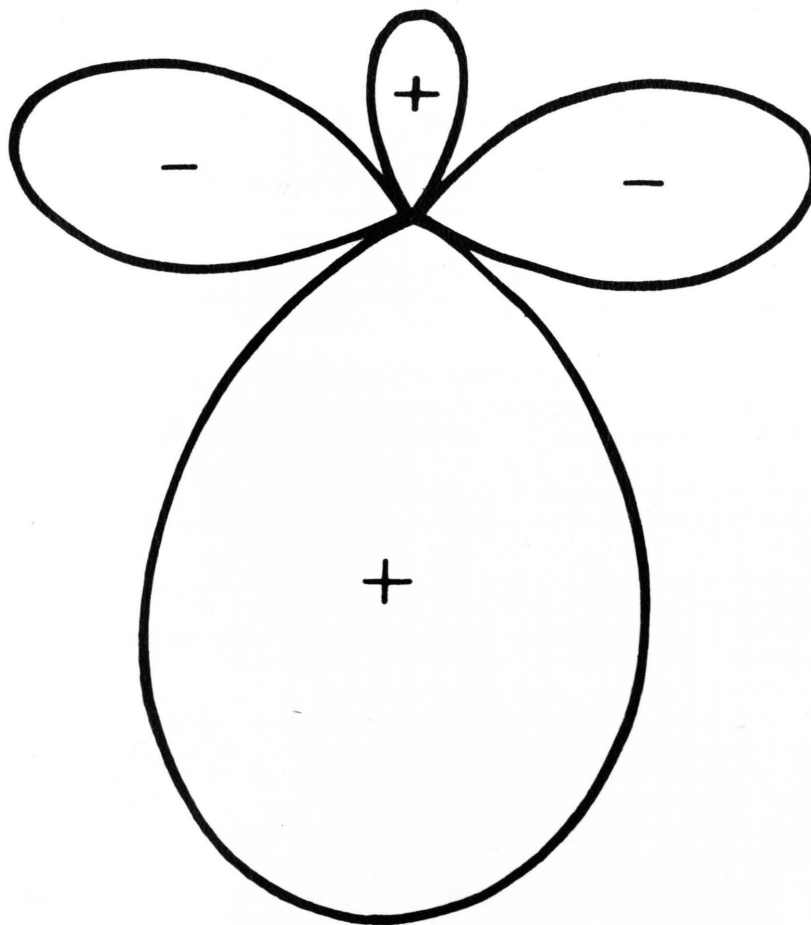


Figure VII. Cross section of Ta valence orbital through plane that is perpendicular to radius vector drawn from the center to Ta nucleus. Large lobe is mostly below this plane, small lobe mostly above.



two for each face as used in the simpler and rougher treatment of Duffey.<sup>41</sup>

Each tantalum atom has five valence electrons; so for six tantalum atoms we have 30 valence electrons. Removing one for binding each chlorine atom and two for producing the net charge, we have left 16 electrons, which is just the number that occupy the bonding levels (98) - (100).

Now, the hybrid orbitals  $\psi_9$  may also take part in the delocalized bonding. Thus, we obtain the reducible representation  $\Gamma_r$  for the radial orbitals. Representation  $\Gamma_r$  is listed in Table 1. It decomposes into

$$\Gamma_r = A_{1g} + E_g + F_{1u} \quad (102)$$

Applying Eq. (44) we obtain the molecular orbitals

$$A_{1g}: \frac{1}{\sqrt{6}} (r_1 + r_2 + r_3 + r_4 + r_5 + r_6) \quad (103)$$

$$E_g: \frac{1}{\sqrt{12}} (2r_1 - r_2 - r_3 - r_4 - r_5 + r_6) \quad (104)$$

$$F_{1u}: \frac{1}{\sqrt{12}} (r_1 - r_6) \quad (105)$$

where  $r_i$  is the hybrid  $\psi_9$  directed radially outward from the  $i$ th vertex of the octahedron. Neglecting interaction with square antiprism combinations of the same symmetries, we find that only  $A_{1g}$  is bonding, with the energy

$$A_{1g}: H_0 + 4\alpha' + \beta' \quad (106)$$

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<sup>41</sup>G. H. Duffey, J. Chem. Phys., 19, 963 (1951).

Here  $\alpha'$  is the resonance integral between  $r_1$  and  $r_2$  while  $\beta'$  is the one between  $r_1$  and  $r_6$ . These integrals are small because the  $\psi_9$ 's are directed away from the center of the octahedron. Thus, this level is probably well above levels (98) - (101).

Instead of using the hybrid orbitals used here, Crossman<sup>42,43</sup> has employed different combinations of s, p, and d atomic orbitals as basis orbitals. In his result, each level is described by fewer resonance integrals, making interpretation easier. However, the number of bonding levels is the same as we have found here.

The octahedral structure has  $O_h$  symmetry so that Table 1 is

The octahedral structure has  $O_h$  symmetry so that Table 1 is

44. S. S. Lipscomb and D. E. Mann, *J. Chem. Phys.*, 33, 475 (1960).

<sup>42</sup>L. D. Crossman, M. S. Thesis, South Dakota State College, 1963.

<sup>43</sup>Crossman, Olsen, and Duffey, *J. Chem. Phys.*, 38, 73 (1963).

## INTERACTION BETWEEN ORBITALS OF THE SAME SYMMETRY

## TYPE IN THE CUBOCTAHEDRAL STRUCTURE

The electronic structure of the cuboctahedron has been discussed by Lipscomb and Britton,<sup>44</sup> and by Cannon and Duffey.<sup>45,46</sup> The first two authors have used the variation method, while the second two have used group theory to find the necessary wave functions. However, the last result neglects interaction among molecular orbitals of the same symmetry type. The interaction will now be accounted for.

Bonding in the cuboctahedral structure is among 12 atoms located at the vertices as shown in Figure VIII. About each atom  $s$ ,  $p_x$ ,  $p_y$ , and  $p_z$  atomic valence orbitals take part in the bonding. The valence orbitals are arranged about a given atom so that the  $p_x$  orbital is tangent to a sphere circumscribing the cuboctahedron and pointed over the center of an adjacent triangular face, the  $p_y$  orbital tangent to the sphere and pointing over the center of an adjacent square face, and the  $p_z$  orbital pointing radially outward. The  $s$  and  $p_z$  orbitals are hybridized to form an orbital directed toward the center of the cuboctahedron.

The cuboctahedral structure has  $O_h$  symmetry so that Table 1 is

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<sup>44</sup>W. N. Lipscomb and D. Britton, J. Chem. Phys., 33, 275 (1960).

<sup>45</sup>J. R. Cannon and G. H. Duffey, J. Chem. Phys., 35, 1657 (1961).

<sup>46</sup>J. R. Cannon, M. S. Thesis, South Dakota State College, 1961.

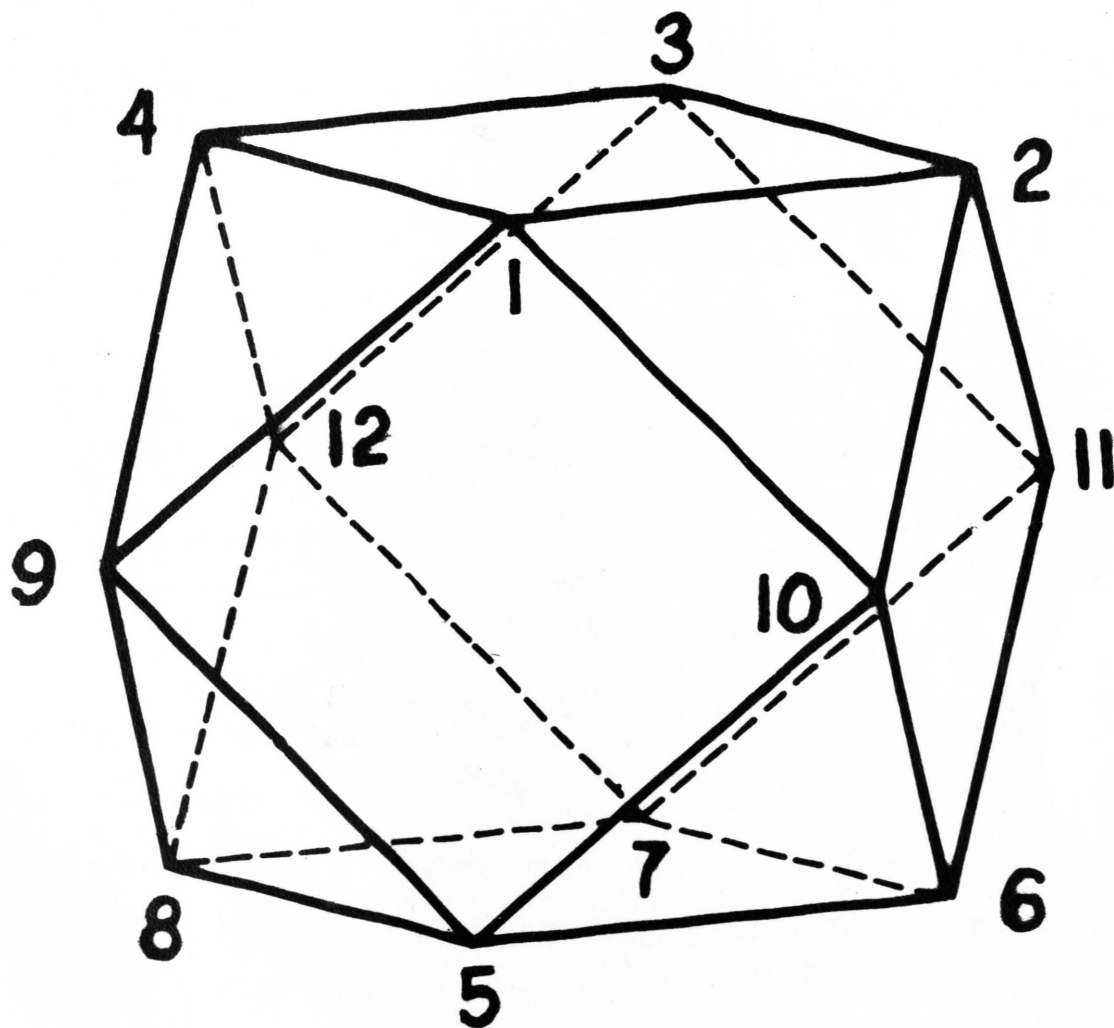


Figure VIII. Numbering of vertices of cuboctahedron

still used. The reducible representations generated by the three sets of basis orbitals  $sp_z$ ,  $p_x$ , and  $p_y$  decompose into the irreducible components<sup>47</sup>

$$sp_z: A_{1g} + E_g + F_{1u} + F_{2g} + F_{2u} \quad (107)$$

$$p_x: A_{2u} + E_u + F_{1g} + F_{1u} + F_{2g} \quad (108)$$

$$p_y: A_{2g} + E_g + F_{1g} + F_{1u} + F_{2u} \quad (109)$$

We note that  $E_g$  appears twice,  $F_{1g}$  twice,  $F_{1u}$  three times,  $F_{2g}$  twice and  $F_{2u}$  twice.

First, we consider the molecular orbitals belonging to  $E_g$ . We have two sets; one set of molecular orbitals is composed of linear combinations of  $sp_z$  hybrids while the other set is composed of linear combinations of  $p_y$  orbitals. From Table 2 we see that the molecular orbitals belonging to  $E_g$  may be d-like or g-like. Applying the interaction method as before we find the two molecular orbitals

$$E_g: \frac{1}{\sqrt{24}} (r_1 + r_2 + r_3 + r_4 + r_5 + r_6 + r_7 + r_8 - 2r_9 - 2r_{10} - 2r_{11} - 2r_{12}) \quad (110)$$

$$E_g: \frac{1}{\sqrt{8}} (s_1 - s_2 + s_3 - s_4 + s_5 - s_6 + s_7 - s_8) \quad (111)$$

Here  $r_i$  denotes the  $sp_z$  hybrid and  $s_i$  the  $p_y$  orbital based on the  $i$ th atom. Both molecular orbitals are  $d_{3z^2-r^2}$ -like with their nodal cones oriented so they coincide.

Molecular orbitals (110) and (111) yield the energy levels

$$E_g: H_0 - 2\alpha + 2\beta - 2\gamma + \delta \quad (112)$$

$$E_g: H_0 + 2\epsilon + 2\kappa + 2\lambda - \mu \quad (113)$$

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<sup>47</sup> Ibid.

where  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  represent resonance integrals between nearest, second nearest, third nearest, and fourth nearest neighboring  $sp_z$  orbitals, respectively. The resonance integrals between  $p_y$  orbitals are denoted by  $\epsilon$ ,  $\eta$ ,  $\lambda$ , and  $\mu$ . The interaction integral  $H_{rs}$  between levels (112) and (113) has the form

$$H_{rs} = 2\sqrt{3}\rho - 2\sqrt{3}\tau \quad (114)$$

where  $\rho$  denotes a nearest neighbor resonance integral between  $sp_z$  and  $p_y$  orbitals and  $\tau$  represents a third nearest neighbor resonance integral. The  $H_{rs}$  term raises level (112) and lowers level (113) by the same amount. Hence, level (113) remains bonding while level (112) remains antibonding. (The energies are roots of Eq. (37)).

Representation  $F_{1g}$  also appears twice; once for  $p_x$  orbitals and once for  $p_y$  orbitals. According to Table 2 the molecular orbitals forming the basis for  $F_{1g}$  are g-like or i-like. Proceeding as before, we obtain

$$F_{1g}: \frac{1}{\sqrt{8}} (t_1 - t_3 + t_5 - t_7 - t_9 - t_{10} + t_{11} + t_{12}) \quad (115)$$

$$F_{1g}: \frac{1}{2} (-s_4 - s_6 + s_8 + s_{10}) \quad (116)$$

where  $t_i$  represents the  $p_x$  orbital based on the  $i$ th atom. Here each molecular orbital is g-like and contains four nodal planes.

The eigenvalues corresponding to these molecular orbitals are

$$F_{1g}: H_0 - 2\epsilon - 2\eta - \theta \quad (117)$$

$$F_{1g}: H_0 - 2\eta - \mu \quad (118)$$

where  $\epsilon$ ,  $\eta$ , and  $\theta$  represent resonance integrals between nearest, third nearest, and fourth nearest neighbor  $p_x$  orbitals. The interaction



term  $H_{ts}$  obtained from functions (115) and (116) is given by

$$H_{ts} = -2\sqrt{2}\nu - 2\sqrt{2}\xi \quad (119)$$

Here  $\nu$  is a nearest and  $\xi$  a third nearest neighbor resonance integral between  $p_x$  and  $p_y$  orbitals.

Level (118) lies below level (117) since  $K$  is smaller than  $\epsilon$  and  $\mu$  is about the same as  $\theta$ . Hence,  $H_{ts}$  will lower (118) and raise (117). The splitting is not enough to make (118) a bonding level.

Representation  $F_{2g}$  appears once for  $sp_z$  orbitals and once for  $p_x$  orbitals. The molecular orbitals corresponding to  $F_{2g}$  are

$$F_{2g}: \frac{1}{2}(r_2 - r_4 - r_6 + r_8) \quad (120)$$

$$F_{2g}: \frac{1}{\sqrt{8}}(t_1 - t_3 + t_5 - t_7 + t_9 + t_{10} - t_{11} - t_{12}) \quad (121)$$

Molecular orbitals (120) and (121) are both d-like, as we expect from Table 2.

From the two molecular orbitals we obtain the corresponding energy levels

$$F_{2g}: H_0 - 2\beta + \delta \quad (122)$$

$$F_{2g}: H_0 + 2\epsilon + 2\eta - \theta \quad (123)$$

The interaction term  $H_{rt}$  has the form

$$H_{rt} = 2\sqrt{2}\nu - 2\sqrt{2}\omega \quad (124)$$

where  $\nu$  is a nearest neighbor and  $\omega$  a third nearest neighbor resonance integral between  $sp_z$  and  $p_x$  orbitals. Interaction integral  $H_{rt}$  lowers the bonding level (123) and raises the antibonding level (122).

For the doubly occurring representation  $F_{2u}$ , we obtain the two molecular orbitals

$$F_{2u}: \frac{1}{\sqrt{8}} (r_1 - r_2 + r_3 - r_4 - r_5 + r_6 - r_7 + r_8) \quad (125)$$

$$F_{2u}: \frac{1}{\sqrt{8}} (s_1 + s_2 + s_3 + s_4 - s_5 - s_6 - s_7 - s_8) \quad (126)$$

A plot of (125) shows it to be f-like with three mutually perpendicular nodal planes. Molecular orbital (126) is h-like, having two cones and three planes as nodal surfaces.

The energy levels for the two molecular orbitals (125) and (126) are

$$F_{2u}: H_o - 2\alpha + 2\delta - \delta \quad (127)$$

$$F_{2u}: H_o - 2\epsilon + 2\lambda + \mu \quad (128)$$

The interaction integral  $H_{rs}$  between the two energy levels is given by

$$H_{rs} = -2\rho + 2\sigma - 2\tau \quad (129)$$

Here  $\rho$  and  $\tau$  are the same as before while  $\sigma$  denotes a resonance integral between second nearest neighbor  $sp_z$  and  $p_y$  orbitals.

Energy level (128) lies slightly lower than level (127); hence (128) will split downward while (127) is split upward. In  $H_{rs}$ ,  $\rho$  and  $\sigma$  are approximately the same in value while  $\tau$  is small in comparison. So the interaction term  $H_{rs}$  will be small and the two energy levels will not split much. We then expect them to retain their antibonding nature.

Since  $F_{1u}$  occurs three times, a third order secular determinant must be solved. The determinant has the form



$$\begin{vmatrix} H_{rr}-E & H_{rs} & H_{rt} \\ H_{rs} & H_{ss}-E & H_{st} \\ H_{rt} & H_{st} & H_{tt}-E \end{vmatrix} = 0 \quad (130)$$

The integrals  $H_{rr}$ ,  $H_{ss}$ ,  $H_{tt}$ ,  $H_{rs}$ ,  $H_{rt}$ , and  $H_{st}$  will now be found by the same method used before.

According to Table 2, the molecular orbitals which provide the base for  $F_{lu}$  may be p-like, f-like, or h-like. Indeed, we find the functions

$$F_{lu}: \frac{1}{\sqrt{8}} (r_2 - r_4 + r_6 - r_8 - r_9 + r_{10} + r_{11} - r_{12}) \quad (131)$$

$$F_{lu}: \frac{1}{\sqrt{8}} (-s_2 + s_4 - s_6 + s_8 - s_9 + s_{10} + s_{11} - s_{12}) \quad (132)$$

$$F_{lu}: \frac{1}{2} (t_1 - t_3 - t_5 + t_7) \quad (133)$$

Here molecular orbital (131) is p-like with a nodal plane passing through vertices 1, 3, 5, and 7. Molecular orbital (132) is f-like with a nodal plane passing through vertices 1, 3, 5, and 7 and two cones lying along an axis perpendicular to the plane. Function (133) has one nodal plane passing through vertices 1, 3, 5, and 7, hence it is p-like.

The three molecular orbitals individually yield the corresponding energy levels

$$F_{lu}: H_{rr} = H_0 + 2\alpha - 2\delta - \delta \quad (134)$$

$$F_{lu}: H_{ss} = H_0 \quad (135)$$

$$F_{lu}: H_{tt} = H_0 + 2\epsilon - 2\gamma + \mu \quad (136)$$

Also from the molecular orbitals (131), (132), and (133), we obtain the interaction integrals

$$H_{rs} = -2\rho - 2\sigma - 2\tau \quad (137)$$

$$H_{rt} = 2\sqrt{2}\nu + 2\sqrt{2}\xi \quad (138)$$

$$H_{st} = 2\sqrt{2}\nu - 2\sqrt{2}\omega \quad (139)$$

The interaction will raise nonbonding level (135) into an antibonding level. The splitting of levels (134) and (135) will depend upon the values of the resonance integrals contained in each. However, level (136) lies lower than level (134) since  $\epsilon$  and  $\alpha$  are approximately the same, as are  $\lambda$  and  $\delta$ , while  $\mu$  is smaller than  $\delta$ . Hence, level (136) can be expected to shift to a lower energy value.

The inclusion of interaction between symmetry orbitals in the cuboctahedral structure has not appreciably altered the conclusions drawn by Cannon. The same number of bonding levels is retained while the nonbonding level of  $F_{1u}$  is shifted by interaction into an antibonding level. Even so, accounting for interaction makes the results more complete.

For hybrid orbitals which point toward the center of the octahedron, the  $p_x$  and  $p_y$  orbitals are arranged so that they are tangent to a sphere which circumscribes the octahedron and are directed out over the centers of adjacent triangular faces. Using the numbering of Figure 10, we denote by  $\sigma_1$  the  $sp_3$  hybrid located on the

MOLECULAR ORBITAL BONDING IN THE  $B_6$  STRUCTURE

Another problem of interest involves bonding in the octahedral  $B_6$  cage. Here bonding takes place among six boron atoms located symmetrically on the vertices of an octahedron. Eberhardt, Crawford, and Lipscomb<sup>48</sup> treat this arrangement; but they have used the variation method which involves making approximations in order to solve the resulting sixth order secular determinant. Also, they have made an error concerning the interaction integral for the doubly occurring  $F_{1u}$  representation.

The use of group theory, however, avoids the sixth order determinant. Thus, we are able to include all the resonance integrals, without making approximations. Furthermore, the use of the interaction method devised previously enables us to find the correct interaction integral for  $F_{1u}$ .

About each boron atom the  $s$ ,  $p_x$ ,  $p_y$ , and  $p_z$  atomic valence orbitals are available to form molecular orbitals. The  $s$  and  $p_z$  orbitals are combined to form hybrid orbitals which point inward toward the center of the octahedron. The  $p_x$  and  $p_y$  orbitals are arranged so that they are tangent to a sphere which circumscribes the octahedron and are directed out over the centers of adjacent triangular faces. Using the numbering of Figure II, we denote by  $r_1$  the  $sp_z$  hybrid located on the

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<sup>48</sup>W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, J. Chem. Phys., 22, 989 (1954).

$i$ th atom and by  $t_{ij}$  the  $p_x$  or  $p_y$  orbital based on the  $i$ th atom with its positive lobe directed toward the center of the  $j$ th triangular face.

The reducible representation  $\Gamma_r$  obtained by applying the symmetry operations of the  $O_h$  group to the  $sp_z$  hybrids has the character system given by Table 1. Representation  $\Gamma_r$  decomposes into

$$\Gamma_r = A_{1g} + E_g + F_{1u} \quad (140)$$

This decomposition is exactly what we obtained before in the  $Ta_6Cl_{12}^{+2}$  octahedron when using  $sp_z$  hybrids which point radially outward. We expect this since the set of outward pointing hybrids behaves the same as the inward directed set of  $sp_z$  hybrids. Hence, we use the same set of molecular orbitals as before except now  $r_i$  refers to an  $sp_z$  hybrid pointing radially inward. The molecular orbitals are given by

$$A_{1g}: \frac{1}{\sqrt{6}} (r_1 + r_2 + r_3 + r_4 + r_5 + r_6) \quad (141)$$

$$E_g: \frac{1}{\sqrt{12}} (2r_1 - r_2 - r_3 - r_4 - r_5 + 2r_6) \quad (142)$$

$$F_{1u}: \frac{1}{\sqrt{2}} (r_1 - r_6) \quad (143)$$

The corresponding energies have the parametric form

$$A_{1g}: H_o + 4\alpha + \beta \quad (144)$$

$$E_g: H_o - 2\alpha + \beta \quad (145)$$

$$F_{1u}: H_o - \beta \quad (146)$$

which is the same result obtained for  $Ta_6Cl_{12}^{+2}$ . Here, however, resonance integrals  $\alpha$  and  $\beta$  will have larger absolute values because the  $sp_z$  hybrids point radially inward rather than outward.

The set of 24 equivalent p orbitals generates the reducible representation  $\Gamma_p$ . The character system for  $\Gamma_p$  is given in Table 1. The representation decomposes into

$$\Gamma_p = F_{1g} + F_{2g} + F_{1u} + F_{2u} \quad (147)$$

Applying Eq. (44) to a p orbital yields the eigenfunctions

$$F_{1g}: \frac{1}{4} (2t_{11} - t_{21} - t_{24} - t_{31} - t_{32} + t_{42} + t_{43} + t_{53} + t_{54} + 2t_{68}) \quad (148)$$

$$F_{2g}: \frac{1}{4} (2t_{11} + t_{21} + t_{24} + t_{31} + t_{32} - t_{42} - t_{43} - t_{53} - t_{54} + 2t_{68}) \quad (149)$$

$$F_{1u}: \frac{1}{4} (2t_{11} + t_{21} - t_{24} + t_{31} - t_{32} + t_{42} - t_{43} - t_{53} + t_{54} - 2t_{68}) \quad (150)$$

$$F_{2u}: \frac{1}{4} (2t_{11} - t_{21} + t_{24} - t_{31} + t_{32} - t_{42} + t_{43} + t_{53} - t_{54} - 2t_{68}) \quad (151)$$

These eigenfunctions yield the four corresponding energy levels

$$F_{1g}: H_0 - 2\delta - 2\epsilon - \epsilon \quad (152)$$

$$F_{2g}: H_0 + 2\delta + 2\epsilon - \epsilon \quad (153)$$

$$F_{1u}: H_0 + 2\delta - 2\epsilon + \epsilon \quad (154)$$

$$F_{2u}: H_0 - 2\delta + 2\epsilon + \epsilon \quad (155)$$

Here  $\delta$  is the resonance integral between  $t_{11}$  and  $t_{21}$ ,  $\delta$  between  $t_{11}$  and  $t_{24}$ , and  $\epsilon$  between  $t_{21}$  and  $t_{42}$ .

Now,  $F_{1u}$  appears once in  $\Gamma_r$  and once in  $\Gamma_p$ . We then have interaction between molecular orbitals (143) and (150). According to Table 2 the molecular orbitals forming the base for  $F_{1u}$  should be p-like or f-like. Indeed, a plot of (143) shows it to be p-like with a single nodal plane passing through vertices 2, 3, 4, and 5 of the octahedron. Molecular orbital (150) is f-like, having two nodal cones lying along an axis perpendicular to a nodal plane which passes through vertices 1 and 6 and bisects edges 2-5 and 3-4.



The nodal planes of (143) and (150) do not coincide so they are not from the same column. As discussed before, function  $R \psi$  is a solution of Schrödinger's equation if  $\psi$  is. Here  $R$  is a symmetry operation. Hence, operating on function (143) with the rotation  $C_4$  about an axis through vertices 2 and 4 yields

$$F_{1u}: \frac{1}{\sqrt{2}} (r_3 - r_5) \quad (156)$$

This function is also p-like with a nodal plane cutting vertices 1, 2, 4, and 6. Evidently, Eberhardt, Crawford, Jr., and Lipscomb have used functions (150) and (156) to obtain the interaction term

$$H_{rt} = 2 \sqrt{2} \Theta \quad (157)$$

where  $\Theta$  is a resonance integral between  $r_1$  and  $t_{11}$ . But this is not correct because the nodal planes of (150) and (156) still do not coincide. Another function like (156) can be obtained from it by applying  $C_4$  operation about an axis through vertices 1 and 6. The operation yields

$$F_{1u}: \frac{1}{\sqrt{2}} (r_2 - r_4) \quad (158)$$

The sum of (156) and (158) is also a solution of the linear Schrödinger's equation yielding the energy value (146). We have the function

$$F_{1u}: \frac{1}{2} (r_2 + r_3 - r_4 - r_5) \quad (159)$$

which is p-like with the nodal plane passing through vertices 1 and 2 and bisecting edges 2-5 and 3-4. This nodal plane coincides with that of the f-like molecular orbital. Therefore, molecular orbitals (150) and (159) belong to the same column of irreducible representation  $F_{1u}$ .

The interaction integral between (150) and (159) is

$$H_{rt} = 4\Theta \quad (160)$$

which is larger than that given by Eq. (157). This result fits in better with the interaction method developed previously.

Interaction integral  $H_{rt}$  raises antibonding level (146) and lowers bonding level (154) by the same amount. Thus, we still retain the same number of bonding and antibonding levels found in the more approximate treatment. The result we have obtained is more complete, however. It also illustrates the need for the interaction method to choose the correct molecular orbitals.

We now have the bonding levels

$$A_{1g}: H_0 + 4\alpha + \beta \quad (144)$$

$$F_{2g}: H_0 + 2\delta + 2\delta - \epsilon \quad (153)$$

$$F_{1u}: H_0 + 2\delta - 2\delta + \epsilon \quad (154)$$

where (154) will be lowered by the interaction term (160) making it more bonding. The bonding levels are then filled in the manner discussed by Eberhardt, Crawford, and Lipscomb.

## CONCLUSIONS

Molecular orbitals for the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  structure have been obtained. Energy levels for these orbitals were found and presented in parametric form. The use of distorted square antiprism hybrid orbitals caused many resonance integrals to appear in the energy expressions. It was concluded that the results of Crossman allow easier interpretation since fewer resonance integrals are involved in the energy levels. However, both treatments yield the same number of bonding levels.

The method used to treat multiply occurring representations in the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  structure has been employed to complete the results of Cannon for molecular orbital bonding in the cuboctahedral structure. The inclusion of interaction did not alter the previous conclusions, as the same number of bonding levels was obtained. Times might arise, though, when the interaction would alter this number; so it is desirable to have the interaction terms included in the over-all picture.

The molecular orbital method was also applied to the octahedral  $\text{B}_6$  cage. Molecular orbitals and energy levels were obtained. The results were more detailed than the results of Eberhardt, Crawford, and Lipscomb, but the conclusions of those authors were unchanged. However, the interaction method applied to the doubly occurring  $F_{1u}$  representation produced a larger interaction integral than was obtained in the earlier and simpler treatment.

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