Bonding in Octahedral Structures and Symmetric Organic Structures with Attached Phenyl Groups

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BONDING IN OCTAHEDRAL STRUCTURES AND SYMMETRIC
ORGANIC STRUCTURES WITH ATTACHED
PHENYL GROUPS

BY

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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.

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LDC
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INTRODUCTION

Before 1927, when Heitler and London\(^1\) calculated the strength of bonding in the hydrogen molecule, no fundamental explanation of the covalent bond existed. In 1931 their shared electron-pair picture was extended intuitively by Pauling\(^2\) to polyatomic molecules. Indeed in his directed valence bond theory, he assumed that localized bonds were formed, each with the character of an H-H bond. Furthermore, the direction of each bond was chosen so that valence atomic orbitals on a central atom could overlap those of the attached atoms as much as possible. (Note the use of intuition here.) Instead of using group theory, Pauling relied on elementary methods in forming possible hybridizations. Later workers have remedied this defect in his theory.

In 1930 and 1931 Born\(^3\) and Slater\(^4\) showed that antisymmetric wave functions could be employed in treating polyatomic molecules. Their procedure was essentially a generalization of the paired-electron approach of Heitler and London. Pauling\(^2\) and Van Vleck\(^5\)

\(^3\) M. Born, Zeit. f. Physik, 64, 729, 65, 718 (1930).
simplified Slater's method by breaking the complete system down into bonding electron pairs localized in bonds. This method seems to be a mathematical extension of the classical chemist's view of bonds. In treating resonating systems by this valence bond method, one superposes various canonical structures. Then the corresponding secular equation is set up and solved.

Instead of following the classical chemist, one may set up electron orbitals extending wherever needed throughout the molecule. Hund, Mulliken, Huckel, and Lennard-Jones developed such methods, which are molecular orbital procedures. Various kinds of variation functions may represent such extensive orbitals. We will base our calculations on atomic orbitals combined linearly:

\[ \psi = a_1 \phi_1 + a_2 \phi_2 + \cdots \]  

Here \( \psi \) is the molecular orbital while \( \phi_1, \phi_2, \cdots \) are atomic orbitals and the \( a \)'s are varied to obtain the best approximation to energy levels. The variation leads to the well-known secular

---


7 F. Hund, Zeits f. Physik, 51, 759 (1928); 63, 719 (1930).

8 R. S. Mulliken, Phy. Rev., 32, 186, 761 (1928); 33, 730 (1929); 41, 49, 751 (1932); 43, 279 (1933).

9 E. Huckel, Zeits f. Physik, 70, 204 (1931)

equation for linear variation functions. In referring to such use of a linear combination of valence orbitals in forming molecular orbitals, we will call it the LCAO method.

Now, group theory was first applied to quantum mechanical systems by Bethe in 1929. He pointed out that each energy level can be classified according to the irreducible representation that its eigenfunctions span. In highly symmetric molecules, one gets quite a few kinds of levels in this way. Different levels of the same kind can never cross as parameters in the system are changed; interaction between them keep them apart. We refer to this result as the non-crossing rule. Levels of different symmetries, on the other hand, can cross. Where they do, one says an accidental degeneracy exists.

We will use group theory to classify LCAO levels and to simplify the secular equation so that energy levels can be given in parametric form. Structures to be treated include those of the tantalum chloride complex ion $\text{Tal}_6\text{Cl}_{12}^{+2}$, the molybdenum chloride complex ion $\text{Mo}_6\text{Cl}_{8}^{+4}$, and the tetraphenylcyclobutadiene radical $(\text{C}_6\text{H}_5)_4\text{C}_4^\bullet$.

---

In quantum mechanics, steady states of a system are described by Schrödinger's time-free equation, which has the linear form

$$H \psi_i = (T + V) \psi_i = E_i \psi_i$$

with $\psi_i$ a wave function describing a state of the system, $E_i$ the corresponding energy, and $H$ the Hamiltonian operator consisting of a kinetic energy part $T$ and a potential energy part $V$. This operator allows for various interactions in the system through its $V$ term. Furthermore, Hamiltonian $H$ is linear in the sense that

$$H (\chi_1 + \chi_2) = H\chi_1 + H\chi_2$$

and

$$H\chi = aH\chi$$

We are ultimately concerned with consequences of the additional properties that $H$ has when a system is symmetric.

Now, a molecule or complex is said to possess symmetry if geometric operations exist which permute like nuclei. We call such processes symmetry operations and note that they include rotations, reflections, inversions. 12-14

---


When a symmetry operation acts on a given system, the Schrödinger equation is transformed; thus

\[ RH \psi_i = RE_i \psi_i \]  

(5)

where \( R \) is the mathematical operator effecting the transformation. But since in the process, the kinetic and potential energy terms in \( H \) are unchanged, operator \( R \) does not alter \( H \) and

\[ RH = HR \]  

(6)

Furthermore, the operation does not alter \( E_i \) and

\[ RE_i = E_i R \]  

(7)

Therefore, Eq. (5) rearranges to the form

\[ H(R \psi_i) = E_i (R \psi_i) \]  

(8)

and function \( R \psi_i \) is also a solution of Schrödinger's equation for the system.

If the level to which \( E_i \) belongs is not degenerate, all eigenfunctions for it are proportional to each other. Here we would have

\[ R \psi_i = c \psi_i \]  

(9)

where the most general form is a complex constant times the original eigenfunction. The new function \( R \psi_i \) needs to be normalized to the same value as \( \psi_i \) itself; the operation does not create or annihilate electrons:

\[ c^* c = 1 \]  

(10)
If the level to which $E_1$ belongs is $k$-fold degenerate, one can find $k$ (and no more) independent functions $\psi_{1l}$, $\psi_{12}$, \ldots, $\psi_{1k}$ in a certain set satisfying Eq. (2). But since the equation is linear, any linear combination of these solutions is also a solution. Consequently, when $R$ acts on one function of the set, the most general result is such a combination:

$$R \psi_{1l} = \sum_{j=1}^{k} a_{jl} \psi_{1j}$$

We suppose that each $\psi_{1j}$ is normalized to the same value (such as 1). Then the $a_{jl}$'s must obey the equation

$$\sum_{j=1}^{k} a_{jl} a_{jl} = 1$$

for $R \psi_{1l}$ to be normalized to this value.

Without loss of generality, one can consider each $a_{jl}$ as an element of a matrix. Then when the operation is applied to all $k$ functions of the degenerate set in turn, all elements of $k \times k$ matrix $A$ appear. The $k$ functions, furthermore, form a row matrix.

The reason for introducing the indices as in (11) will now be given. If $S$ is an operator effecting a transformation corresponding to another symmetry operation, we have by analogy to Eq. (11):

$$S \psi_{1j} = \sum_{m=1}^{k} b_{mj} \psi_{1m}$$

for $j = 1, 2, \ldots, k$.
But transformation $S$ may act on Eq. (11) to give

$$SR \psi_{il} = \sum_{j=1}^{k} S_{lj} \psi_{ij} = \sum_{j=1}^{k} S_{ij} \psi_{jl}$$

and since $S$ and $R$ belong to the same group, the product of $S$ and $R$ yields $T$ which also belongs to the group. Rewriting the above relationship, we have

$$T \psi_{il} = \sum_{m=1}^{k} \sum_{j=1}^{k} b_{mj} \psi_{im} = \sum_{m=1}^{k} c_{ml} \psi_{im}$$

where

$$c_{ml} = \sum_{j=1}^{k} b_{mj} a_{jl}$$

The elements $b_{mj}$ and $c_{ml}$ also form $k \times k$ matrices. Indeed with our convention, we have both

$$SR = T \quad (17)$$

and in the same order

$$ba = c \quad (18)$$

The matrices multiply according to the group multiplication table. Therefore, they are said to form a representation $\Gamma_j$ of the group.

If we use the orthonormal properties of the eigenfunctions, we can show that the representation matrices are unitary.\(^\text{15}\) Thus, Eyring, Walter, and Kimble\(^\text{16}\) make the statement "All matrices representing transformations of interest are unitary." Because


these matrices are generated by operating on the eigenfunctions $\psi_{il}$; the $\psi_{il}$ are said to form a basis for the representation.

Now, each representation of a given group can in principle be broken down into well-known irreducible representations, if it is not already one of these. Let us suppose $\Gamma_j$ obtained above to be reducible. Then $a, b, c, \ldots$ could be changed to forms

$$
\begin{pmatrix}
a' & 0 \\
0 & a''
\end{pmatrix}, \quad 
\begin{pmatrix}
b' & 0 \\
0 & b''
\end{pmatrix}, \quad 
\begin{pmatrix}
c' & 0 \\
0 & c''
\end{pmatrix}, \quad \ldots 
$$

(19)
in which $a', b', c', \ldots$ and $a'', b'', c'', \ldots$ are separately representations $\Gamma_j'$ and $\Gamma_j''$ of the group. We describe this breakdown as follows:

$$
\Gamma_j = \Gamma_j' + \Gamma_j''
$$

(20)

In these forms the column matrices

$$
\begin{pmatrix}
a_{11} \\
a_{21} \\
\vdots \\
a_{kl}
\end{pmatrix}, \quad 
\begin{pmatrix}
b_{11} \\
b_{21} \\
\vdots \\
b_{kl}
\end{pmatrix}, \quad 
\begin{pmatrix}
c_{11} \\
c_{21} \\
\vdots \\
c_{kl}
\end{pmatrix}, \quad \ldots 
$$

(21)

contain columns of either $a', b', c', \ldots$ or $a'', b'', c'', \ldots$ and zeros.

Because of these zeros, the $k$ functions $\psi_{il}'', \psi_{i2}''', \ldots$ $\psi_{ik}'''$ on which matrices (19) are based break down into two distinct sets. Thus for operation $R$, we have
\[ R \psi''_{il}' = \sum_{j=1}^{k'} a_{jl}' \psi''_{ij} \]  
(22)

where index \( l' \) is 1, 2, ..., \( k' \) and

\[ R \psi''_{il}' = \sum_{j=k+1}^{k} a_{jl}' \psi''_{ij} \]  
(23)

where index \( l' \) is \( k' + 1, \ldots k \). (In each case, all other elements of the matrix (21) are zero.)

The above process can be repeated until one has independent sets corresponding to irreducible representations. But if two such sets belong to different irreducible representations, we have a case of accidental degeneracy. As pointed out in the introduction, we would expect small changes in the parameters to destroy the degeneracy. We see this result in atomic structures. For in the hydrogen atom, ns, np, nd levels are the same. But altering the \( 1/r \) field for the electron by bringing up charge distributed as a function of \( r \) alone splits them apart. Furthermore, one may set up a ligand field that splits the np and nd levels in various ways.

On the other hand, if two such sets belonged to the same irreducible representation, it would imply that no interaction between them occurred. For in quantum mechanics, interaction between like states always causes splitting. This principle is embodied in the non-crossing rule.

Hence, representations generated by eigenfunctions having the same eigenvalue are taken to be irreducible. Note that the
dimensionality of the representation is \( k \) - the degeneracy of the level. Thus, we conclude that matrix \( \mathbf{a} \) is one of an irreducible representation \( \Gamma_i \) of the group. And we rewrite Eq. (11) in the form

\[
R \psi^i_1 = \sum_{j=1}^{k} \Gamma_i(R)_{jl} \psi^i_j
\]

(24)

where \( \Gamma_i(R)_{jl} \) is the \( jl \)th element of the matrix.

Further information on group theory can be found in Eyring, Walter, and Kimble, Margenau and Murphy, Rosenthal and Murphy, Wigner, and Streitwieser.17-21

17 Ibid., p. 172.
21 Streitwieser, op. cit., p. 63.
USING ATOMIC ORBITALS AS BASES

In our calculations the fundamental problem is how atoms combine in forming the molecules or complexes under study. Indeed, we have given a set of valence orbitals erected on various atomic cores located at known positions. The interactions between these are to be expressed as functions of interactions between independent pairs of atomic orbitals. The latter interactions appear as terms in elements of the secular equation when the variation function is a linear combination of a set of possible ψ's given by Eq. (1).

To exploit the symmetry of the over-all system, we form the variation functions so that they belong to the proper irreducible representations. Which ones are needed and how many times each appears are determined following Eyring, Walter, and Kimble. Indeed since the molecular orbitals are linear functions of the atomic orbitals, either serve equally well as basis functions - they belong to the same representation.

After this representation, based on the valence orbitals, is formed, one breaks it down into its irreducible components. In the following, we suppose that the ith irreducible representation occurs s_i times and that the dimension of Γ_i is l_i. Thus, we have s_i sets of independent eigenfunctions which form bases for Γ_i, while the degeneracy of each set is l_i.

---

Now from \( n \) different atomic orbitals one can form \( n \) independent molecular orbitals by Eq. (1). The linear relationship can be inverted so that each atomic orbital is a linear function of the molecular orbitals:

\[
\psi_i = \sum_{i} \sum_{k=1}^{S_i} \sum_{m=1}^{l_i} c_{ikm} \psi_{km}^{i}
\]  

(25)

Here \( \phi \) is an atomic orbital and \( \psi_{km}^{i} \) the molecular orbital (MO) which belongs to the \( i \)th irreducible representation of dimension \( l_i \) with the eigenvalue \( E_{ik} \). The \( m \) summation proceeds over a degenerate set of eigenfunctions belonging to each irreducible representation, while the \( k \) summation takes care of the \( s_i \) times \( \Gamma_i \) appears. Finally, summation over \( i \) allows for all irreducible components in the reducible representation.

When Eq. (25) is transformed by operation \( R \) of the group it takes on the form

\[
R \phi = \sum_{i} \sum_{k=1}^{S_i} \sum_{m=1}^{l_i} c_{ikm} R \psi_{km}^{i}
\]

But Eq. (24) reduces this to

\[
R \phi = \sum_{i} \sum_{k=1}^{S_i} \sum_{m=1}^{l_i} c_{ikm} \sum_{n=1}^{l_i} \Gamma_i(R)_{nm} \psi_{kn}^{i}
\]

Multiplying both sides by the character corresponding to \( R \) and irreducible representation \( j \), which is

\[
\chi_j(R) = \sum_{t=1}^{1} \Gamma_j(R)_{tt}
\]
and summing over all operations, we get

\[ \sum R \chi_j(R) \phi = \sum_i \sum_{k=1}^{S_i} \sum_{m=1}^{l_i} c_{ikm} \sum_{n=1}^{l_i} \sum_{t=1}^{l_i} \sum R \Gamma_j(R)_{tt} \Gamma_j(R)_{nm} \psi_{kn} \]

Finally introducing the orthogonality condition \(^{23,24}\)

\[ \sum R \Gamma_j(R)_{tt} \Gamma_j(R)_{nm} = \delta_{ij} \delta_{tn} \delta_{tm} \frac{h}{\sqrt{l_i l_j}} \]

we obtain

\[ \sum R \chi_j(R) \phi = \sum_{k=1}^{S_j} \sum_{m=1}^{l_j} c_{jkm} \sum_{n=1}^{l_j} \sum_{t=1}^{l_j} \delta_{tn} \delta_{tm} \frac{h}{l_j} \psi_{kn} \]

since the only contribution occurs when \(i = j\). Bringing in properties of the other Kronecker deltas yields

\[ \sum R \chi_j(R) \phi = \sum_{k=1}^{S_j} \sum_{t=1}^{l_j} c_{jkt} \frac{h}{l_j} \psi_{kt} \] (26)

The right side is a function belonging to the \(j\)th irreducible representation. For convenience, we normalize it

\[ \psi_j = (\text{normalization constant}) \sum R \chi_j(R) \phi \] (27)

so that if it were a suitable eigenfunction, it would satisfy Pauli's exclusion principle.

\(^{23}\text{Ibid.}, p. 181.\)

\(^{24}\text{Wigner, op. cit.}, p. 79.\)
On applying the variation theorem to our $\psi_j$, we get the secular equation

$$
\begin{vmatrix}
H_{11}-S_{11}E & H_{12}-S_{12}E & \cdots & H_{1n}-S_{1n}E \\
H_{21}-S_{21}E & H_{22}-S_{22}E & \cdots & H_{2n}-S_{2n}E \\
\vdots & \vdots & \ddots & \vdots \\
H_{n1}-S_{n1}E & H_{n2}-S_{n2}E & \cdots & H_{nn}-S_{nn}E
\end{vmatrix} = 0
$$

(28)

where $H_{jk} = \int \psi_j^* \psi_k d\gamma$ and $S_{jk} = \int \psi_j^* \psi_k d\gamma$.

The normalization introduced above makes

$$S_{jj} = 1$$

In the appendix (Eqs. A-2, A-7, A-10), we find that integrals $H_{jk}$ and $S_{jk}$ differ from zero only when $\psi_j$ and $\psi_k$ belong to the same column of the same irreducible representation.

Thus when each irreducible representation appears only once, all $H_{jk}$ and $S_{jk}$ for $j \neq k$ are zero. Furthermore, from Eq. (A-11) in the appendix we see that $H_{jj}$'s for different columns of a given representation are equal. Intuitively, the $H_{jj}$ integrals for a given level are equal because each $\psi_j$ describes the level equally well.

---

Because all these matrix elements are zero when \( s_i = 1 \) for each \( i \), the secular determinant reduces to

\[
\begin{pmatrix}
H_{11} - E & 0 & 0 & 0 & \cdots & \cdots \\
0 & H_{22} - E & 0 & 0 & \cdots & \cdots \\
0 & 0 & H_{22} - E & 0 & \cdots & \cdots \\
0 & 0 & 0 & H_{33} - E & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots & H_{33} - E & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\end{pmatrix} = 0 \quad (29)
\]

Equation (29) can also be written as

\[
\prod_j (H_{jj} - E)^{l_j} = 0 \quad (30)
\]

and the energy levels found individually. The total number of equations that are solved is equal to the number of irreducible components in the reducible representation. Also it is apparent that all we need is one of the \( l_j \) eigenfunctions to determine the energy of a level. It must be remembered that in a degenerate level we can place \( 2 l_j \) electrons, i.e. two electrons in each level with opposite spin.

Now, we are ready to investigate what happens when an irreducible representation appears more than once. For the sake of argument, we will consider an example where it appears twice.

If the irreducible representation under consideration has
degeneracy $l_j$ we can form two physically independent sets of
$l_j$ independent functions which belong to the same irreducible
representation. Each of the $l_j$ functions in each set belong to
an individual column of the representation, as shown by Eq. (A-2)
in the appendix. There will then be one function from each set
belonging to the same column of the representation. For these two
functions (which generate different eigenvalues), the $H_{jk}$, or
interaction, integral is not zero, but has a finite value. Also
since the eigenfunctions are physically independent, $S_{jk} = \delta_{jk}$,\textsuperscript{26}
the secular determinant involving the irreducible representation
appearing twice becomes

$$
\begin{vmatrix}
H_{jj} - E & 0 & & \cdots \\
0 & H_{jj} - E & & \cdots \\
& \ddots & \ddots & \ddots \\
H_{kj} & 0 & \cdots & \cdots \\
0 & H_{kj} & \cdots & \cdots \\
\end{vmatrix}
= 0 \quad (31)
$$

Both sections of the determinant are of the same dimension because
they are from the same irreducible representation. Corresponding

\textsuperscript{26} One might expect from previous arguments that when $\psi_j$ and
$\psi_k$ belong to the same column $S_{jk}$ would be different from zero.
However we have physically different eigenfunctions and normaliza-
tion to one, hence $S_{jk} = \delta_{jk}$. 

functions in the $H_{jj}$ and $H_{kk}$ integrals belong to the same column of the representation; therefore, we have the interaction integral $H_{jk}$. From the symmetry of the determinant (31) the $H_{jk}$ terms are all the same. We know that $H_{jk}$ equals $H_{kj}$ from consideration of the Hermitian properties of the Hamiltonian and the unitary nature of the representation;\(^{27}\) that is

$$
\int \psi_j^* H \psi_k \, d\tau = \int \psi_k^* H \psi_j \, d\tau \tag{32}
$$

or

$$
H_{jk} = H_{kj} \tag{33}
$$

We can rearrange the terms in Eq. (31) to obtain with the aid of (33)

$$
\begin{vmatrix}
H_{jj} - E & H_{jk} \\
H_{jk} & H_{kk} - E
\end{vmatrix}
\begin{pmatrix}
1_j \\
1_k
\end{pmatrix}
= 0 \tag{34}
$$

Equation (34) gives us the two energy levels which correspond to the irreducible representation appearing twice in the reducible representation. If the irreducible representation appears $q$ times, we will have a $q \times q$ determinant containing interaction integrals between the possible pairs of representative functions.

In applying this method, one has to be sure that $\psi_j$ and $\psi_k$ are physically independent and that they belong to the same

\(^{27}\)Fyring, Walter, and Kimble, op. cit., p. 32.
column of the representation. The first condition is clearly met when the two sets of \( \psi' \)'s are formed from independent sets of atomic orbitals. For example, one set may consist of \( s \) orbitals while the second consists of \( p \) orbitals erected on the same atoms. Otherwise, one examines orthogonal combinations of functions (26) to get representative functions in each set.

In determining whether \( \psi_j \) and \( \psi_k \) belong to the same column, we use an interaction criterion. For a given (normalized) \( \psi_j \), the function \( \psi_k \) must be a (normalized) linear combination of the functions (26) for the second set which makes \( H_{jk} \) as large as possible. One can speed up the process by (1) reasoning intuitively from plots of the wave functions and (2) using decomposition-of-representation tables. Both methods are illustrated in the next section, the first for the \( F_{1u} \) representation and the second for the \( E_g \) representation.

After the proper \( \psi' \)'s are found, one determines the integrals \( H_{jj} \) and \( H_{jk} \) in terms of the given atomic orbitals. Then Eq. (34), or its analog, is solved.

For convenience, we employ

\[
\psi_j = A \left( a_1 \Phi_1 + a_2 \Phi_2 + \cdots \right)
\]

\[
\psi_k = B \left( b_1 \Phi_1' + b_2 \Phi_2' + \cdots \right) \quad (35)
\]

where coefficients \( a_1, a_2, \ldots \) and \( b_1, b_2, \ldots \) are chosen as convenient integers while \( A \) and \( B \) effect the normalization required.
The atomic orbitals in $\psi_k$ are primed to indicate that they may be different from those in $\psi_j$. Thus in

$$H_{jj} = \int \psi_j^* H \psi_j d\tau$$  \hspace{1cm} (36)$$

we get

$$H_{jj} = A^A \int (\sum a_l^* \phi_l^*) H (\sum a_m \phi_m) d\tau$$

whence

$$H_{jj} = A^A \left[ \sum \sum a_l^* a_m \int \phi_l^* H \phi_m d\tau \right]$$  \hspace{1cm} (37)$$

Here $l$ and $m$ are summed over the same atomic orbitals as in Eq. (35). For Eq. (37) we define the following two integrals

$$\int \phi_l^* H \phi_l d\tau = H_{0l} = \text{Coulombic integral}$$  \hspace{1cm} (38)$$

and for $l \neq m$

$$\int \phi_l^* H \phi_m d\tau = H'_{lm} = \text{Resonance integral}$$  \hspace{1cm} (39)$$

Equation (39) indicates the bonding energy due to electrons resonating between atoms. Because electrons move between atoms, the region to which the electrons are confined increases, thus decreasing their kinetic energy.\(^{28}\) The average potential energy consequently decreases. Thus intuitively, the resonance integrals increase bonding energies. Until quantum mechanics was introduced, there was no way of determining the resonance energy. Classically

\(^{28}\)Duffey, op. cit., p. 79.
all that could be determined was a coulombic energy and it did not account for all the bonding energy in a molecule.

In symmetrical molecules, all the atomic orbitals in a set are the same; all the $H_{01}$ are equal and are represented by $H_0$. The $H_{lm}$'s are equal for any particular combination of neighbors. We may take $H_{1m} = \alpha$ for nearest neighbor interactions, $H_{np} = \emptyset$ for second nearest neighbor interaction, etc. until all possible combinations of interactions are labelled. Then

$$H_{jj} = A_i A_j \left[ \sum a_1^* a_1 H_0 + (\ldots + 2a_1^* a_m + \ldots) \alpha + \ldots \right]$$

Instead of multiplying Eq. (37) out by hand, we will use a multiplication table for the bracketed part as shown in Table 1.

**Table 1. Example of a Multiplication Table**

<table>
<thead>
<tr>
<th></th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$\ldots$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>$a_1^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_2$</td>
<td>$a_1^2 a_2$</td>
<td>$a_2^2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_3$</td>
<td>$a_1^2 a_3$</td>
<td>$a_2^2 a_3$</td>
<td>$a_3^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_4$</td>
<td>$a_1^2 a_4$</td>
<td>$a_2^2 a_4$</td>
<td>$a_3^2 a_4$</td>
<td>$a_4^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*We will use real functions, i.e. $a^* = a$. 
Just the coefficients are needed because the atomic orbitals used to determine a particular MO are the same. For simplicity, we just evaluate the lower half of the table since it is symmetric about the diagonal. The coefficients of the $\alpha$'s, $\beta$'s, $\gamma$'s, ... are then doubled to obtain the bracketed part of (40). Because $\psi_j$ is normalized, the coefficient of $H_0 (A^* A \sum_1 a_l^* a_l)$ in Eq. (40) must be one. This indicates that $A^* A$ is actually the reciprocal of $\sum_1 a_l^* a_l$. So upon multiplying the relationship we get from the table by $A^* A$ we have

$$H_{jj} = H_0 + \left( \ldots + 2 a_l^* a_m + \ldots \right) \alpha + \ldots \quad (41)$$

The other part of the problem is evaluating the $H_{jk}$ integrals,

$$H_{jk} = \int \psi_j^* H \psi_k d\gamma \quad (42)$$

Again a multiplication table is set up like Table 1. Across the top of the table we place the coefficients of $\psi_j$ and along the side we place the coefficients of $\psi_k$. As indicated earlier, the constituent atomic orbitals in $\psi_j$ may be different from those in $\psi_k$; therefore we must evaluate the whole table. From the table we get the relationship

$$H_{jk} = (\ldots + a_l^* b_m + \ldots) \alpha + \ldots \quad (43)$$

where $\alpha$, $\beta$, ... here denote interaction between an atomic orbital in $\psi_j$ and one in $\psi_k$. There is no coulombic integral in (43) because $a_l^* a_l$ or $b_m^* b_m$ cannot appear. To allow for $\psi_j$ and
ψ_k being normalized we have to multiply (43) by A*B. Up to now everything we have considered applies to complex functions as well as real functions. However, for the problems considered here real functions are sufficient. A person with complex functions will have to evaluate A*B for his particular problem and then multiply Eq. (43) by it. For real functions we know that

\[ A^*A = A^2 = \left( \sum_l a_l^2 \right)^{-1} \]

and similarly

\[ B^*B = B^2 = \left( \sum_m b_m^2 \right)^{-1} \]

thus

\[ AB = \left( \sum_l a_l^2 \right)^{-1/2} \left( \sum_m b_m^2 \right)^{-1/2} \]

Multiplication of Eq. (43) by AB then yields

\[ H_{jk} = \frac{\left( \ldots + a_l b_m + \ldots \right) \alpha}{\left( \sum_l a_l^2 \right)^{1/2} \left( \sum_m b_m^2 \right)^{1/2}} + \ldots \]  

(44)

We have found how to obtain MO from the irreducible representation (27), and how to determine the bonding energy levels (34). The next step is to apply the theory to some complexes and obtain their bonding levels in terms of coulombic and resonance integrals.
USE OF THE O₉ SYMMETRY GROUP

The molecular orbitals that bind octahedral B₆H₆⁻₈ together are constructed approximately from s and p valence orbitals of the boron atoms, which lie at the vertices of an octahedron. While extensive treatments of this structure are available in the literature,²⁹-³² little work has been done on other octahedral complexes, such as Ta₆Cl₁₂⁺², Ta₆Br⁺², Nb₆Cl₁₂⁺², and Mo₆Cl₈⁺⁴. The interesting thing about these is that they employ d valence orbitals as well as the s and p ones.

In all of these a metal atom is located at each vertex of the octahedron. In the complexes like Ta₆Cl₁₂⁺², a halogen is located symmetrically over each edge as in Figure I. But in the Mo₆Cl₈⁺⁴ structure, a halogen is placed over the middle of each face as in Figure II.

Each metal-halogen bond is single and localized, with the metal atom sharing a pair of electrons with the halogen. The


Figure I. The Ta₆Cl₁₂⁺² structure
Figure II. The Na$_2$Cl$_8$$^{-4}$ structure
remaining valence electrons are delocalized throughout the octahedron. Molecular orbitals describing the system are constructed from valence orbitals arranged symmetrically on each vertex as described later.

The $O_h$ character table shown in Table 2 lists all possible symmetry operations that leave the octahedron unchanged. The first column in Table 2 lists all the different irreducible representations whose components multiply as elements of the group. Singly degenerate representations are designated by $A$, doubly degenerate by $E$, and triply degenerate by $F$. Subscripts are used to label the different irreducible representations of given degeneracy. Here the numerical index distinguishes between the irreducible representations of subgroup $O$. On forming the product with $i$, the possibility of $g$ (gerade) and $u$ (ungerade) sets of basis functions for each is introduced. Under inversion a $g$ set remains unchanged while a $u$ set changes in sign.\(^{35,36}\)

The ten different operations of the $O_h$ group are as follows:

1. $E$, identity operation;
2. $C_3$, rotation of $2\pi/3$ both clockwise and counterclockwise about an axis perpendicular to two parallel faces;
3. $C_2$, rotation of $2\pi/2$ about an axis perpendicular to two parallel edges;
4. $C_4$, rotation of $2\pi/4$ both clockwise

\(^{34}\) Herzberg, op. cit., p. 123.

\(^{35}\) Ibid., p. 124.

\(^{36}\) Fyring, Walter, and Kimble, op. cit., p. 381.
Table 2. Character Table of $O_h$ Symmetry Group.

<table>
<thead>
<tr>
<th>Representation</th>
<th>E</th>
<th>$8c_3$</th>
<th>$6c_2$</th>
<th>$6c_4$</th>
<th>$3c_4^2$</th>
<th>I</th>
<th>$6s_4$</th>
<th>$8s_6$</th>
<th>$3\sigma_h$</th>
<th>$6\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{ig}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{iu}$</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{2g}$</td>
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<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{2u}$</td>
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<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E_g$</td>
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<td>0</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>-1</td>
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<td>0</td>
</tr>
<tr>
<td>$E_u$</td>
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<td>0</td>
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<td>0</td>
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<td>$F_{ig}$</td>
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<td>3</td>
<td>1</td>
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<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$F_{iu}$</td>
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<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-3</td>
<td>-1</td>
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<td>1</td>
</tr>
<tr>
<td>$F_{2g}$</td>
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<td>1</td>
<td>-1</td>
<td>-1</td>
<td>3</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$F_{2u}$</td>
<td>3</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-3</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>
and counterclockwise about a principal axis (passes through two opposite vertices); (5) $C_4^2$, rotation of $2\pi/2$ about a principal axis; (6) $I$, inversion through the center of symmetry; (7) $S_4$, $C_4$ followed by a reflection in the horizontal plane perpendicular to the principal axis; (8) $S_6$, rotation of $2\pi/6$ both clockwise and counterclockwise about a $C_3$ axis followed by a reflection in the same plane as $S_4$; (9) $\sigma_h$, reflection through a plane containing four vertices; (10) $\sigma_d$, reflection through a plane containing a principal axis and a $C_2$ axis.\(^{37}\)

\(^{37}\)These and other operations are described in Eyring, Walter, and Kimble, op. cit., p. 376.
MOLECULAR ORBITAL BONDING IN $T_6Cl_{12}^{+2}$ AND $Mo_6Cl_{18}^{+4}$ STRUCTURES

Olsen$^{38}$ based his determination of the bonding levels for the $T_6Cl_{12}^{+2}$ structure on the hybrid orbitals of Duffey.$^{39}$ In the result, each level was described by many resonance integrals, making interpretation difficult. Here we will employ simpler orbitals and obtain simpler functions since each contains fewer resonance integrals. The total number of interaction integrals will be greater, however.

The valence orbitals to be used have the following angular parts:$^{40}$

\[
s = 1
\]
\[
P_x = \sqrt{3} \sin \theta \cos \phi
\]
\[
P_y = \sqrt{3} \sin \theta \sin \phi
\]
\[
P_z = \sqrt{3} \cos \theta
\]
\[
d_{xy} = \frac{1}{2} \sqrt{15} \sin^2 \theta \sin 2\phi
\]
\[
d_{xz}^2 y^2 = \frac{1}{2} \sqrt{15} \sin^2 \theta \cos 2\phi
\]
\[
d_{xz} = \sqrt{15} \sin \theta \cos \phi \cos \phi
\]
\[
d_{yz} = \sqrt{15} \sin \theta \cos \phi \sin \phi
\]
\[
d_{xz^2 y^2} = \frac{1}{2} \sqrt{5} (3\cos^2 \theta - 1)
\]

$^{38}$David P. Olsen, Thesis to be submitted to the faculty at South Dakota State College, Brookings, S.D., 1963.


These parts are normalized to $4\pi$. The subscript on a symbol describes the nonradial variation of the orbital.

The atoms and faces of the octahedron are numbered as in Figure III. On each vertex a right handed set of axes is erected with the $xy$ axes passing over the middles of two adjacent faces and the $z$ axis pointing radially outward. Then on vertex $i$ we form the following sets of basis orbitals:

- $r_i$, hybridized from $ns$, $np_z$ and $(n-1)d^2_z - r^2$
  (this orbital is directed along the $z$ axis with the assumption that the positive lobe is directed inward);

- $t_{ij}$, directed over the middle of face $j$ and hybridized from $np_x$, $(n-1)d_{xz}$ and from $np_y$, $(n-1)d_{yz}$;

- $e_{ij}$, directed over the edge to vertex $j$ and hybridized from $np_x$, $np_y$ and $(n-1)d_{xz}$, $(n-1)d_{yz}$
  (Each combination gives us two basis orbitals, one with a positive lobe over face (or edge) $j$ and the other with a positive lobe directed over the adjacent face (or edge). In both cases the $z$ dependence is small.);

- $t_{i,jk}$ representing $(n-1)d^2_{x^2-y^2}$ with positive lobes over faces $j$ and $k$;

- $e_{i,jk}$ representing $(n-1)d_{xy}$ with positive lobes over edges $j$ and $k$
  (These orbitals are used by themselves.)

---

41 Labelling of octahedron is due to David Olsen, fellow graduate student.
Figure III. Numbering of vertices and faces for octahedron
In forming each basis orbital, one could include higher orbitals \((f, g, \ldots)\) having the same symmetry with respect to operations of the \(O_h\) group. Such inclusion would affect only the calculation of the parameters in which our results are expressed.

Now, each coordinate system is oriented so the positive \(x\) axes fall over the faces \(t_{11}, t_{21}, t_{31}, t_{47}, t_{53},\) and \(t_{68}\). The \(y\) axes are located to form a right handed system with the \(z\) axes pointing radially outward. Knowing the location of the axes will let us keep track of correct signs on basis orbitals as they are transformed.

Each of the above sets of orbitals forms the basis of a reducible representation of the group. The reducible representation itself consists of matrices expressing how the orbitals permute when acted on by the symmetry operations. To illustrate how these permutation matrices correspond to geometric operations, think of the basis orbitals as components of a vector. When such a vector is acted on by one of the permutation matrices, the order of the components is changed in the same manner as the orbitals are interchanged under the corresponding symmetry operation. The unit elements remaining on the diagonal represent the basis orbitals unchanged under the transformation. The sum of these gives the character, which is all we need to know about the matrix.\(^{42}\)

Each set of basis orbitals will be treated individually. For any irreducible representation appearing more than once we will determine the interaction integrals $H_{jk}$ in determinant (34). The radial $r_1$ orbitals will be considered in some detail so that the reader can gain some feeling for how the theory is applied.

Consider the various operations acting on the $r_1$. Under $E$ all six orbitals remain unchanged. Therefore, character 6 is placed under $E$ in Table 3. Under $C_4$ the two orbitals at the vertices lying on the principal axis chosen remain unchanged; 2 is placed under $6C_4^2$. Under $C_4^2$ the same two orbitals considered in $C_4$ remain unchanged; 2 is placed under $3C_4^2$. Under $\sigma_h$ the four orbitals in a plane perpendicular to the principal axis chosen remain unchanged; 4 is placed under $3\sigma_h^2$. Under $\sigma_d$ the same two orbitals considered in $C_4$ remain unchanged; 2 is placed under $6\sigma_d^2$. The remaining operations interchange all orbitals; 0 is placed under other operations. We designate this reducible representation $\sigma_r$.

**Table 3. Character Table for $\sigma_r$ Reducible Representation**

<table>
<thead>
<tr>
<th>$E$</th>
<th>$6C_3$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
<th>$3C_4^2$</th>
<th>$I$</th>
<th>$6S_4$</th>
<th>$8S_6$</th>
<th>$3\sigma_h$</th>
<th>$6\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
</tbody>
</table>
In Eyring, Walter, and Kimble\textsuperscript{43} we find the relationship which tells us how many times each irreducible representation occurs in the reduction of a reducible representation. We have

\[ a_j = \frac{1}{h} \sum_{R} \chi(R) \chi_j(R) \]  

(54)

where \( a_j \) is the number of times the \( j \)th irreducible representation appears, \( h \) equals the number of elements in the group, \( \chi(R) \) is the character of operation \( R \) in the reducible representation, and \( \chi_j(R) \) is the character of operation \( R \) in the \( j \)th irreducible representation. For the \( \sigma_r \) reducible representation we get

\[ \sigma_r = A_{1g} + E_g + F_{1u} \]  

(55)

We can now apply Eq. (27)

\[ \psi_j = \text{(Normalization constant)} \sum_{R} \chi_j(R) R \phi \]  

(27)

to determine our MO. As mentioned earlier, all we need is one of the \( l_j \) independent eigenfunctions to obtain the \( j \)th bonding level in parametric form. We will choose \( r_1 \) as the atomic orbital in Eq. (27) and operate on it with all operations of the group. The results of \( R \phi \) are given in Table 4. By multiplying each of the orbitals \( R \phi \) by the corresponding character and adding we have

for \( A_{1g} \)

\[ A_{1g} : (8r_1 + 8r_2 + 8r_3 + 8r_4 + 8r_5 + 8r_6) \]  

(56)

\textsuperscript{43}\textit{Ibid.}, p. 184.
Table 4. Results of Operating on $r_1$ With All Operations of the Group

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_3$</th>
<th>$C_3$</th>
<th>$C_3$</th>
<th>$C_3$</th>
<th>$C_3$</th>
<th>$C_3$</th>
<th>$C_2$</th>
<th>$C_2$</th>
<th>$C_2$</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$r_1$</td>
<td>$r_2$</td>
<td>$r_3$</td>
<td>$r_5$</td>
<td>$r_2$</td>
<td>$r_4$</td>
<td>$r_5$</td>
<td>$r_3$</td>
<td>$r_4$</td>
<td>$r_6$</td>
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</tr>
<tr>
<td>$C_2$</td>
<td>$C_4$</td>
<td>$C_4$</td>
<td>$C_4$</td>
<td>$C_4$</td>
<td>$C_4$</td>
<td>$C_4^2$</td>
<td>$C_4^2$</td>
<td>$C_4^2$</td>
<td>$I$</td>
<td>$S_4$</td>
<td>$S_4$</td>
</tr>
<tr>
<td>$r_6$</td>
<td>$r_1$</td>
<td>$r_2$</td>
<td>$r_4$</td>
<td>$r_5$</td>
<td>$r_3$</td>
<td>$r_1$</td>
<td>$r_6$</td>
<td>$r_6$</td>
<td>$r_6$</td>
<td>$r_6$</td>
<td>$r_6$</td>
</tr>
</tbody>
</table>

| $S_4$ | $S_4$ | $S_4$ | $S_6$ | $S_6$ | $S_6$ | $S_6$ | $S_6$ | $S_6$ | $S_6$ | $h$ | $h$ | $h$ |

| $r_4$ | $r_5$ | $r_3$ | $r_4$ | $r_4$ | $r_3$ | $r_2$ | $r_2$ | $r_3$ | $r_6$ | $r_1$ | $r_1$ |
| $d$ | $d$ | $d$ | $d$ | $d$ | $d$ | $d$ | $d$ | $d$ | $d$ |

Then with the normalization constant we get the eigenfunction

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

(57)

In the same manner we obtain the eigenfunctions

$$E_6 = \frac{1}{\sqrt{12}}(2r_1 - r_2 - r_3 - r_4 - r_5 + 2r_6)$$

(58)

and

$$F_{1u} = \frac{1}{\sqrt{2}}(r_1 - r_6)$$

(59)

Putting eigenfunction (57) in the multiplication table and evaluating, we obtain

$$A_{1g} = (\text{const.}) H_{11} = (6H_0 - 24\alpha - 6\beta)$$

(60)
Multiplying (60) through with $A A = 1/6$ we obtain the level

$$A_{1g}: H_0 + 4 \alpha + \beta$$

Similarly, we obtain the levels

$$E_g: H_0 - 2 \alpha + \beta$$

$$E_u: H_0 - \beta$$

where $H_0$ is the coulombic integral for the $r$'s, $\alpha$ equals the resonance integral for nearest neighbors ($r_1$ and $r_2$), and $\beta$ equals the resonance integral for second nearest neighbors ($r_1$ and $r_6$).

The $t_{ij}$ and $e_{ij}$ basis orbitals are interchangeable. For, both contain contributions from the same $p_x$, $p_y$, $d_{yz}$, and $d_{xz}$ orbitals on each vertex of the octahedron, and the same molecular orbitals can be obtained from each.

Consequently, either set of $p$-like basis orbitals gives us the same reducible representation $\sigma_p$. The resulting characters appear in Table 5.

<table>
<thead>
<tr>
<th>$E$</th>
<th>$8C_3$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
<th>$3C_4^2$</th>
<th>$I$</th>
<th>$6S_4$</th>
<th>$8S_6$</th>
<th>$3\sigma_h$</th>
<th>$6\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Particular mention should be made concerning the negative sign appearing in the $C_4^2$ character. Operation $C_4^2$ transforms the orbital $t_{11}$ into its negative. There are two such orbitals
located on each vertex of the principal axis; thus \(-4\) for the
\(C_{4h}^2\) character.

Reducible representation \(\sigma_p\) reduces to
\[
F_{1g} + F_{1u} + F_{2g} + F_{2u}
\]  
(64)

The p-type orbitals directed over the faces produce, by
themselves, the eigenfunctions

\[
\begin{align*}
F_{1u} & : \% (2t_{11}-2t_{66}+t_{21}+t_{42}-t_{24}+t_{43}+t_{31}+t_{54}+t_{32}+t_{53}) \\
F_{2g} & : \% (2t_{11}+2t_{66}+t_{21}-t_{42}+t_{24}+t_{43}+t_{31}+t_{54}+t_{32}+t_{53}) \\
F_{2u} & : \% (2t_{11}-2t_{66}-t_{21}-t_{42}+t_{24}+t_{43}+t_{31}+t_{54}+t_{32}+t_{53}) \\
F_{1g} & : \% (2t_{11}+2t_{66}-t_{21}+t_{42}-t_{24}-t_{43}+t_{31}+t_{54}-t_{32}+t_{53})
\end{align*}
\]  
(65) \(66) \(67) \(68)

where a negative sign indicates direction of the negative lobe.

Eigenfunctions (65) - (68) yield the levels

\[
\begin{align*}
F_{1u} & : H_0' + 2\delta - 2\delta + \epsilon \\
F_{2g} & : H_0' + 2\delta + 2\delta - \epsilon \\
F_{2u} & : H_0' - 2\delta + 2\delta + \epsilon \\
F_{1g} & : H_0' - 2\delta - 2\delta - \epsilon
\end{align*}
\]  
(69) \(70) \(71) \(72)

where \(H_0'\) is the coulombic integral of the p-like orbitals, \(\delta\)
equals resonance integral between nearest neighbors \((t_{11} \text{ and } t_{21})\),
\(\delta\) is the resonance integral between second nearest neighbors
\((t_{11} \text{ and } t_{24})\), and \(\epsilon\) the resonance integral between \(t_{21}\) and \(t_{42}\).

There are more resonance integrals than those mentioned, but
their resultant contribution is zero.

An alternate description of the same levels is found from
the p-like orbitals directed over the edges. From the \(e_{ij}\)
orbitals we obtain the eigenfunctions
\[ F_{1u} = \frac{1}{2}(e_{12} + e_{52} - e_{32}) \]
\[ F_{2g} = \frac{1}{2}(e_{12} + e_{41} - e_{62}) \]
\[ F_{2u} = \frac{1}{2}(e_{12} - e_{32} - e_{52} + e_{62}) \]
\[ F_{1g} = \frac{1}{2}(e_{12} + e_{41} - e_{62}) \]  

and energy levels
\[ F_{1u} = H_0 + 2 \Pi_1 + \Pi_2 \]  
\[ F_{2g} = H_0 + 2 \Sigma_1 - \Pi_2 \]  
\[ F_{2u} = H_0 - 2 \Pi_1 + \Pi_2 \]  
\[ F_{1g} = H_0 - 2 \Sigma_1 - \Pi_2 \]  

where \( \sigma_1 \) equals the resonance integral between nearest neighbors \( (e_{12} and e_{21}) \), \( \Pi_1 \) the one between \( e_{13} \) and \( e_{23} \) and \( \Pi_2 \) the one between \( e_{12} \) and \( e_{62} \). We choose the parameters \( \sigma_1, \Pi_1, \Pi_2 \) because the above orbitals are oriented with respect to each other as in conventional \( \sigma \) and \( \Pi \) bonds.

The resonance integrals in (69) - (72) are different from those in (77) - (80) because the basis orbitals are oriented differently with respect to each other. Even so, the two sets of levels are equivalent and either could be used to describe the bonding levels of \( Ta_6Cl_{12}^{+2} \) and \( Mo_6Cl_8^{+4} \) structures. In discussing bonding strengths in the conclusions, we will employ the first group of levels (69) - (72).

In interpreting the multiplication table for non-s basis orbitals, we have to consider the signs on the lobes that overlap.

\[ ^{44} \text{Duffey, op. cit., p. 159.} \]
When they are the same on the dominant one, the resonance integral is negative; when they are opposite it is positive. Now, our parameters $\alpha, \xi, \chi, \ldots$ are taken as negative. So if two basis orbitals have their positive and negative lobes next to each other, a sign change is introduced. For instance, we set the resonance integral between $t_{11}$ and $t_{53}$ equal to $-\chi$. We introduce such negative signs before we sum each kind of contribution. But if a particular MO has $t_{11}$ as one of its constituent orbitals, the table gives us $(-1)(1)(-\xi) = \xi$ for the resonance integral between $-t_{11}$ and $t_{53}$ as expected.

Up to now, everything that has been considered applies equally well to both $\text{Ta}_6\text{Cl}_{12}^{+2}$ and $\text{Mo}_6\text{Cl}_{8}^{+4}$ structures. However, in $\text{Ta}_6\text{Cl}_{12}^{+2}$ structures we employ $d_{xy}$ ($e_{i,jk}$) orbitals to bond the halogens (one over each edge) while in $\text{Mo}_6\text{Cl}_{8}^{+4}$ it is the $d_{x^2-y^2}$ ($t_{i,jk}$) orbitals which bond the halogens (one over each face). Since we neglect localized metal-halogen bonds, we are left with $t_{i,jk}$ orbitals in $\text{Ta}_6\text{Cl}_{12}^{+2}$ and $e_{i,jk}$ orbitals in $\text{Mo}_6\text{Cl}_{8}^{+4}$ for metal-metal bonding.

In $\text{Ta}_6\text{Cl}_{12}^{+2}$ structures the d orbitals represented by $t_{i,jk}$ give the reducible representation

$$\sigma_{t_{i,jk}} = A_{2u} + E_u + F_{2g}$$

from which we get the eigenfunctions

$$A_{2u}: \frac{1}{\sqrt{6}}(t_{1,13} + t_{2,15} + t_{3,17} + t_{4,37} + t_{5,55} + t_{6,57})$$

$$F_{2g}: \frac{1}{\sqrt{2}}(t_{1,13} - t_{6,57})$$

$$E_u: \frac{1}{\sqrt{12}}(2t_{1,13} - t_{2,15} - t_{3,17} - t_{4,37} - t_{5,55} + 2t_{6,57})$$
and energy levels

\[ A_{2u} : H^u + 4S - \gamma \]  
\[ F_{2g} : H^u + \gamma \]  
\[ E_u : H^u - 2S - \gamma \]

where \( H^u \) is the coulombic integral for the d orbitals, \( S \) is the resonance integral between nearest neighbors \((t_{1,13} \text{ and } t_{2,15})\) and \( \gamma \) equals the resonance integral for orbitals located on opposite vertices \((t_{1,13} \text{ and } t_{6,68})\).

For Mo\(_6\)Cl\(_8\) structures we employ the d orbitals represented by \( a_{i,jk} \) which yield the reducible representation

\[ \sum a_{i,jk} = A_{2g} + F_{2u} + E_u \]  

The irreducible representations in (88) yield the eigenfunctions

\[ E_g : 1/\sqrt{12}(e_{1,24} - e_{2,35} - e_{3,16} - e_{4,35} - e_{5,16} + 2e_{6,24}) \]  
\[ F_{2u} : 1/\sqrt{2}(e_{1,24} - e_{6,24}) \]  
\[ A_{2g} : 1/\sqrt{6}(e_{1,24} + e_{2,35} + e_{3,16} + e_{4,35} + e_{5,16} + e_{6,24}) \]

and energy levels

\[ E_g : H^u + 2\Theta + \xi \]  
\[ F_{2u} : H^u - \xi \]  
\[ A_{2g} : H^u - 4\Theta + \xi \]

where \( H^u \) is the same coulombic integral we had for the \( t_{1,13} \) orbitals, \( \Theta \) the resonance integral between \( e_{1,24} \) and \( e_{2,16} \), and \( \xi \) equals the resonance integral between \( e_{1,24} \) and \( e_{6,24} \).

Again, as in the p-type levels, there are more interaction terms, but because of the symmetry of the octahedral metal cages their resultant effect is zero.
Some of the above levels are bonding while the remaining are antibonding. The bonding levels are those whose energy is less than \( H_0 \). For example, since \( \alpha, \beta, \ldots \) are negative the level
\[
F_{1u} : H_0' + 2\gamma - 2\delta + \epsilon
\]
is bonding while the level
\[
F_{2u} : H_0' - 2\gamma + 2\delta + \epsilon
\]
is antibonding.

If all the levels, bonding and antibonding were filled, introducing the resonance would have no effect. Indeed, adding levels (61) - (63) and remembering \( E_g \) is doubly and \( F_{1u} \) is triply degenerate, we get
\[
H_0 + 4\alpha + \beta + 2H_0 - 4\alpha + 2\beta + 3H_0 - 3\beta = 6H_0
\]
or a sum of the coulombic integrals for the six radial orbitals.

A more limited result is expressed by a theorem given in Streitwieser\(^{45}\)
\[
\sum_j m_j = 0
\]
where \( m_j \) is the coefficient of the nearest-neighbor resonance integral in the \( j \)th level. However, Streitwieser gives no proof of the theorem. Our generalization is that the sum of the energies when all levels are filled equals the sum of the coulombic integrals. There is an important restriction on this theorem as it stands. The initial basis orbitals, the valence orbitals,

\(^{45}\)Streitwieser, op. cit., p. 45.
must be physically independent - that is, orthogonal. Since we are interested in results to the approximation that orbitals on different atoms are orthogonal, our results may be checked with it.

So far, we have considered each set of basis orbitals by itself. However, certain irreducible representations appear in two different sets. We must find one function from each set belonging to the same column of the common representation, for Eq. (A.10) in the appendix indicates interaction between two such functions. We may proceed by mixing the functions in one or both sets to get the largest possible interaction.

Then with the interaction term $H_{12}$ we solve determinant (34) which yields

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

(97)

where $H_{11}$ and $H_{22}$ are the levels found by considering the basis orbitals individually. Equation (97) gives us the two energy levels corresponding to the irreducible representation appearing twice.

As an aid in determining the $H_{12}$ term, we may argue intuitively from plots of functions. If the positive lobes of one MO lie next to the positive lobes of a different MO, we have interaction. However, if a positive lobe from one MO lies next to a negative lobe on another MO, a nodal surface is introduced and we have no interaction. If we take $H_{11}$ to be the lower level,
the $H_{22}$ interaction term will lower that level as far as it raises level $H_{22}$. We still retain the idea that the sum of our levels should equal the sum of the coulombic integrals. This procedure of plotting to determine correct functions is limited to the simpler functions. For more complex functions we get too many lobes on our diagrams to tell what is happening.

In either structure the $F_{lu}$ irreducible representation appears both in the radial and $p$-type orbital functions. First consider the $F_{lu}$ function from the $p$-like orbitals designated by $t_{ij}$:

$$F_{lu} : \mathcal{M}(2t_{11} - 2t_{68} + t_{42} - t_{24} + t_{43} + t_{31} + t_{54} - t_{32} - t_{53})$$  \hspace{1cm} (65)

A plot of this particular function is shown in Figure IV. Plotting the function which we obtained from the radial orbitals,

$$F_{lu} : \frac{1}{\sqrt{2}}(r_1 - r_6)$$  \hspace{1cm} (59)

on the same diagram we find nodal surfaces between lobes of $t_{ij}$ basis orbitals and $r_1$ basis orbitals. As function (59) stands we have no interaction with (65). However, if we had functions like

$$F_{lu} : \frac{1}{\sqrt{2}}(r_3 - r_5)$$  \hspace{1cm} (98)

or

$$F_{lu} : \frac{1}{\sqrt{2}}(r_2 - r_4)$$  \hspace{1cm} (99)

we would expect interaction since the positive lobes of $r_3$ and $r_2$ lie next to the positive lobes of $t_{21}$, $t_{26}$, $t_{42}$, $t_{47}$, and $t_{31}$, $t_{36}$, $t_{54}$, $t_{55}$ respectively. Functions (98) and (99) differ from (59) by a symmetry operation. Since $R \psi_j$ and $\psi_j$ both satisfy the same Schrödinger equation, functions (98) and (99) yield the same
Figure IV. Sections of principal lobes of the $F_1u$ orbital formed from the $t_{ij}$ atomic orbitals.
The simplest linear combinations are a sum and difference which yield the functions

\[ F_{lu}: \frac{1}{2}(r_2 + r_3 - r_4 - r_5) \]  \hspace{0.5cm} (100)

\[ F_{lu}: \frac{1}{2}(r_3 + r_4 - r_2 - r_5) \]  \hspace{0.5cm} (101)

These functions still give us the same \( H_{jj} \) integral as (59) because Schrödinger's equation is linear in \( \Psi \) (see Eq. 3).

Since (101) is the difference between (98) and (99), the two interactions cancel to give us zero interaction. With the integral coefficients of (100) and (65) in the multiplication table we obtain

\[ F_{lu}: \text{(const.)} H_{12} = 32\chi \]

The AB term here is \((\frac{1}{2})(\frac{1}{2})\) which yields the interaction

\[ F_{lu}: H_{12} = 4\chi \]  \hspace{0.5cm} (102)

where \( \chi \) is the resonance integral between \( t_{11} \) and \( r_2 \). The interaction term (102) has the effect of lowering level (69) and raising level (63) the same amount.

When we consider the alternate description (\( e_{ij} \) orbitals) of the \( F_{lu} \) function (73), we employ the function

\[ F_{lu}: \frac{1}{\sqrt{2}}(r_2 - r_4) \]  \hspace{0.5cm} (103)

and get

\[ F_{12}: H_{12} = 2\sqrt{2}\lambda \]  \hspace{0.5cm} (104)

where \( \lambda \) is the resonance integral between \( e_{12} \) and \( r_2 \).
In Ta$_6$Cl$_{12}^{+2}$ structures the F$_{2g}$ representation occurs in the p-type and d-type orbitals. A plot of the p-type F$_{2g}$ function (t$_{ij}$ orbitals) (66) indicates an interaction with the function

$$F_{2g} = \mathcal{K}(t_{5,35} + t_{4,37} - t_{3,17} - t_{2,15})$$

The two functions (66) and (105) yield

$$F_{2g}: H_{12} = 4 \mu$$

where $\mu$ is the resonance integral between $t_{1,13}$ and $t_{21}$.

In Mo$_6$Cl$_8^{+4}$ structures the representations E$_g$ and F$_{2u}$ appear twice. Both E$_g$ and F$_{2u}$ appear in the d orbital functions, while F$_{2u}$ appears in p-like orbital functions and E$_g$ appears in the radial orbital functions. Applying the previous argument to the F$_{2u}$ functions, we find that function (75) ($e_{ij}$ orbitals) interacts with the function

$$F_{2u}: \frac{1}{\sqrt{2}}(e_{4,35} - e_{2,35})$$

and yields the interaction

$$F_{2u}: H_{12} = 2\sqrt{2} \nu$$

where $\nu$ is the resonance integral between $e_{1,24}$ and $e_{21}$.

Because of their complexity, the E$_g$ functions do not lend themselves to the previous argument. To obtain the correct functions, we employ decomposition-of-representation tables. To better understand the use of these tables, we will discuss in some detail the reduction of the O$_h$ group shown in Table 6. 46,47

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46 Hoffman, and Gouterman, op. cit., p. 2191.

Table 6. Decomposition of Representations for Atomic Orbitals in a Ligand Field With $O_h$ Symmetry

<table>
<thead>
<tr>
<th>Atomic orbitals (l)</th>
<th>Irreducible components generated by atomic orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(s)</td>
<td>$A_{1g}$</td>
</tr>
<tr>
<td>1(p)</td>
<td>$F_{1u}$</td>
</tr>
<tr>
<td>2(d)</td>
<td>$E_g + F_{2g}$</td>
</tr>
<tr>
<td>3(f)</td>
<td>$A_{2u} + F_{1u} + F_{2u}$</td>
</tr>
<tr>
<td>4(g)</td>
<td>$A_{1g} + E_g + F_{1g} + F_{2g}$</td>
</tr>
<tr>
<td>5(h)</td>
<td>$E_u + 2F_{1u} + F_{2u}$</td>
</tr>
<tr>
<td>6(i)</td>
<td>$A_{1g} + A_{2g} + E_g + F_{1g} + 2F_{2g}$</td>
</tr>
</tbody>
</table>

In a free atom valence electrons are under the influence of a spherically symmetric electrostatic field. The d level, for example, is fivefold degenerate. Now, imposing a ligand field of $O_h$ symmetry splits this level into two different levels, one doubly and the other triply degenerate. The doubly degenerate level contains orbitals $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ while the triply degenerate one contains orbitals $d_{xy}$, $d_{yz}$, $d_{xz}$. 48,49 From Table 6 we see that the orbitals $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ generate the $E_g$ irreducible representation and the remaining orbitals generate

48 Duffey, op. cit., p. 181.
the $F_{2g}$ irreducible representation. How these levels split depends on the symmetry imposed.

In using the table, we think of each MO as being analogous to an atomic orbital in the $O_h$ field. Thus, a function generated by an $E_g$ irreducible representation should contain two nodal surfaces, i.e., be $d_{3z^2-r^2}$-like or $d_{x^2-y^2}$-like. (The MO could contain 4 or 6 nodal surfaces as $E_g$ also appears opposite $g$ and $i$ atomic orbitals in Table 6.) A similar argument holds for the $F_{2g}$ irreducible representation.

The above gives us an indication of what the functions generated by $E_g$ may be like. However, more must be said before we have criteria that can be used to determine functions we expect to belong to the same column of the same irreducible representation. We shall consider the doubly degenerate $E_g$ representation further.

We can set up two physically independent functions generated by $E_g$. One will be $d_{3z^2-r^2}$-like and the other will be $d_{x^2-y^2}$-like. Each of these two functions will belong to a particular column of the $E_g$ representation. Now for a function $\psi^i_m$ to belong to the $m$th column of the $i$th irreducible representation, it must satisfy Eq. (A.2) in the appendix

$$R \psi^i_m = \sum_{n=1}^{k} \psi^i_n \Gamma_i(R)^{nm} \quad (A.2)$$

where $\psi^i_n$ are the $k$ independent eigenfunctions which satisfy
Schrödinger's equation with eigenvalue $E_\ell$. But each of the above mentioned functions are geometrically different. So for certain operations the $d_{2z^2-r^2}$-like function is transformed differently in (A.2) than the $d_{x^2-y^2}$-like function. Thus, we have a way of distinguishing between the two functions generated by $E_g$. Next consider what happens when $E_g$ appears twice. We will have one function from each of two physically independent sets which belong to the same column; they will interact. Two such functions will have to satisfy Eq. (A.2) where $R$ and $\Gamma_i(R)$ are the same for both and have either 2, 4 or 6 nodal surfaces. Thus we may expect them to transform similarly. But to transform similarly the functions must be geometrically similar, i.e. their nodal surfaces must coincide in such a manner that they behave similarly under $R$. Thus if we can start with the two functions we get from different independent sets and form two functions whose nodal surfaces coincide, we will expect interaction. This will be one criterion our functions will have to meet. We place the further condition that to get maximum interaction these two functions must contain as many basis orbitals as possible from the corresponding set and still retain coinciding nodal surfaces. The final test to see if we do have functions which belong to the same column of the same irreducible representation will be to determine if they interact or not. For all the problems considered here the above criteria will yield interacting functions.
Now, we shall apply the above criteria to the $E_g$ representation that appears in Mo$_6$Cl$_8^{+4}$. We have the functions

$$E_g: \frac{1}{\sqrt{12}}(2r_1 - r_2 - r_3 - r_4 - r_5 + 2r_6) \quad (58)$$

$$E_g: \frac{1}{\sqrt{12}}(2e_1, 24 - e_2, 35 - e_3, 16 - e_4, 35 - e_5, 16 + 2e_6, 24) \quad (89)$$

generated by $E_g$. The first function is $d_{3z^2-r^2}$-like while the nodal surfaces in (89) form two intersecting planes with cones extending outward along the planes to the middle of edges $e_{32}, e_{25}, e_{54}$, and $e_{43}$. Thus, the functions (58) and (89) are geometrically different. We would expect no interaction; we get zero interaction. But by starting with (58), we obtain

$$E_g: \frac{1}{\sqrt{2}}(r_2 - r_3 + r_4 - r_5) \quad (109)$$

which is $d_{x^2-y^2}$-like. The two nodal planes of (109) coincide with the intersecting planes of (89). Now we have two functions which fulfill one of our criteria. Also, they are the most complete functions which we can form and still have their nodal surfaces coincide. We find that (89) and (109) yield

$$E_g: H_{12} = 2\sqrt{3} \xi \quad (110)$$

where $\xi$ is the resonance integral between $\epsilon_{1,24}$ and $r_2$. Also, both of these functions contain the number of nodal surfaces Table 6 indicates they should.

Tantalum (or niobium) atoms have five valence electrons apiece; thus on six tantalum atoms we have 30 valence electrons. Removing one for bonding each of the 12 halogens and two for producing the net plus two charge, we have 16 electrons remaining for bonding in the metallic cage. To accommodate the 16 valence
electrons, we will employ the eight bonding levels (remember the interaction terms are negative and F is triply degenerate).

\[ A_{1g} : H_0 + 4 \xi + \delta \]
\[ A_{2u} : H_0'' + 4 \xi - \eta \]
\[ F_{2g} : H_0' + 2 \xi + 2 \delta - \epsilon \]
\[ F_{1u} : H_0' + 2 \xi - 2 \delta + \epsilon \]

Both (70) and (69) are lowered by the interaction terms (106) and (102), respectively, making them more bonding. Notice that it would appear the level

\[ F_{2g} : H_0'' + \eta \]

could also be employed as a bonding level; however, the interaction term (106) lifts this level up out of reach. Again it must be pointed out that levels (61), (85), (70), and (69) apply also to complexes \( \text{Nb}_6\text{Cl}_{12}^{+2} \), \( \text{Ta}_6\text{Br}_{12}^{+2} \) and related structures.

Molybdenum atoms have six valence electrons apiece; thus on six molybdenum atoms we have 36 electrons. One valence electron is used to bond each of the eight chlorines, and four are used to produce the net plus four charge, leaving 24 electrons for Mo-Mo bonding. For the 12 orbitals needed we employ

\[ A_{1g} : H_0 + 4 \xi + \delta \]
\[ F_{2g} : H_0' + 2 \xi + 2 \delta - \epsilon \]
\[ F_{1u} : H_0' + 2 \xi - 2 \delta + \epsilon \]
\[ E_g : H_0'' + 2 \eta + \zeta \]
\[ F_{2u} : H_0'' - \zeta \]
It will be noticed that the $F_{2u}$ level has a negative sign in front of the interaction term, indicating the level is not bonding as it stands. However, the interaction term (108) is large enough to bring the level (93) down to a bonding one. Also levels (70), (69), and (92) are lowered by the interaction terms (106), (102), and (110) respectively.

If we look at the $Mo_6Cl_8^{4+}$ structure a little closer, we will notice something out of the ordinary. There are five valence electrons for each halogen and six for each molybdenum, giving $5 \times 8 + 6 \times 6 - 4 = 72$ electrons available for bonding.

There are 24 Mo-Cl bonds, three over each face, using 48 valence electrons and 12 Mo-Mo bonds, one along each edge, using 24 valence electrons. Thus, all 72 valence electrons are employed in bonds indicated by connecting lines between atoms in Figure II. This is the only possible configuration these bonds can assume between atoms. Therefore, there is no possibility of resonance between different configurations. But chemists say that unless we do have the possibility for such resonance we should not expect a molecule or complex to be peculiarly stable. For example, in benzene there are two possible arrangements for the double bonds. The fact that benzene resonates between these two configurations accounts for its exceptionally high stability. However, even without the possibility of resonance between different configurations

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$\text{Mo}_6\text{Cl}_8^{4-}$ appears to be peculiarly stable. Gould\textsuperscript{51} reports that it is unaffected when placed in aqua regia ($\text{HCl} + \text{HNO}_3$), a solvent that dissolves gold.

In both $\text{Ta}_6\text{Cl}_{12}^{2+}$ and $\text{Mo}_6\text{Cl}_8^{4-}$ structures we have neglected bonding to the halogens. Also there has been no attempt to evaluate the parameters describing the levels. Because of the similarity between the two structures, we expect the total bonding strengths to be similar. In the next section we will find an expression for the total bonding strength of each structure and will compare them.

CONCLUSIONS BASED ON OCTAHEDRAL STRUCTURES

We have obtained the bonding levels for the two octahedral structures $\text{Ta}_6\text{Cl}_{12}^{+2}$ and $\text{Mo}_6\text{Cl}_8^{+4}$. As mentioned, we may expect some similarity between these two. This similarity is evident when we compare total bonding strengths. To evaluate the total bonding strengths, we will neglect interactions between different orbitals as an approximation. This approximation is valid since the downward shift of the $F_{1u}$ levels is the same for both structures and the shift downward of $F_{2u}$ in $\text{Mo}_6\text{Cl}_8^{+4}$ is similar in magnitude to the shift of the $F_{2g}$ level in $\text{Ta}_6\text{Cl}_{12}^{+2}$. The shift downward of $E_g$ in $\text{Mo}_6\text{Cl}_8^{+4}$, for which there is no counterpart in $\text{Ta}_6\text{Cl}_{12}^{+2}$ structures, increases the stability of that complex. A schematic diagram indicating these shifts is shown in Figure V. Neglecting interactions, the bonding strength for the $\text{Ta}_6\text{Cl}_{12}^{+2}$ metallic cage is

$$E_b = 24 \gamma + 8 \xi + 8 \alpha - 2 \eta + 2 \phi = 40 \alpha'$$  \hspace{1cm} (111)$$

while for the $\text{Mo}_6\text{Cl}_8^{+4}$ cage we get

$$E_b = 24 \gamma + 8 \Theta + 8 \alpha - 2 \iota + 2 \phi = 40 \alpha'$$  \hspace{1cm} (112)$$

where $\alpha'$ is a mean resonance integral between nearest neighbors.

We have made the approximation that $\xi$, $\eta$, and $\iota$ are all about the same since they are resonance integrals between orbitals located on opposite vertices. The resonance integrals $\gamma$, $\xi$, $\alpha$, and $\phi$ are all nearest neighbor interactions and are added to give $40 \alpha'$. The hybridizations employed for the $r_i$ and $t_{ij}$ (or $e_{ij}$) are different in the $\text{Mo}_6\text{Cl}_8^{+4}$ structure from those in the $\text{Ta}_6\text{Cl}_{12}^{+2}$
Figure V. Schematic diagram of bonding and antibonding levels
structure. The orbitals used in the molybdenum complex have a smaller principal quantum number. Thus, the orbitals do not extend out from the vertices as far as those in the tantalum complex. The overlapping is less in Mo$_6$Cl$_8^{+4}$; therefore, the corresponding resonance integrals $\alpha$, $\gamma$, and $\beta$ are smaller. Part of this difference in the bonding strengths is opposed by a shift downward of the $E_g$ level for Mo$_6$Cl$_8^{+4}$. We see that the total strength of bonding in Mo$_6$Cl$_8^{+4}$ may be less than in Ta$_6$Cl$_{12}^{+2}$. (This difference is not indicated in Figure V.)

However, without these refinements the strength of metallic bonding in both complexes is the same. In the Ta$_6$Cl$_{12}^{+2}$ structures there are 16 bonding valence electrons and the bonding energy per electron is $40 \alpha'/16$ or $2\alpha'$. An earlier calculation by Duffey yielded $2 \alpha'$. In the Molybdenum complex there are 24 valence electrons employed in metallic bonding and the bonding strength per electron is $40 \alpha'/24$ or $1 3/4 \alpha'$. In both cases we have neglected differences in interactions involving the halogen atoms.

Dr. Lawrence F. Dahl and Eugene R. Corey have reported on the compound Rh$_6$(CO)$_{16}$, another octahedral complex. The compound has a rhodium atom on each vertex of an octahedron with four

---


carbonyls in a tetragonal arrangement bonded to each rhodium atom. Four of the carbonyls are located over opposite faces of the octahedron while the remaining twelve are located, two on each rhodium, to complete the tetragonal arrangement. Lawrence and Corey have stated the compound has $T_d$ symmetry, as compared to our complexes which have $O_h$ symmetry. The lower symmetry is due to the arrangement of the carbonyls on the rhodium atoms, eliminating the $C_4$ operation. As in the two structures considered here, we must employ $s, p$, and $d$ type valence orbitals in discussing the bonding levels of $\text{Rh}_6(\text{CO})_{16}$. However because of the different symmetry group, the description of bonding levels may be different. The next step in discussing octahedral complexes would be to determine the bonding levels of $\text{Rh}_6(\text{CO})_{16}$ and compare them with the $\text{Ta}_6\text{Cl}_{12}^{+2}$ and $\text{Mo}_6\text{Cl}_{18}^{+4}$ bonding levels.

It is the author’s hope that someone else working under Dr. Duffey in connection with the National Science Foundation will be able to report on the bonding levels of this new compound and compare the results with those obtained here.
PI BONDING IN TRIPHENYLCYCLOPROPENYL
AND TETRAPHENYLCYCLOBUTADIENE
STRUCTURES

Group theory is also of help in reducing the secular equation describing symmetric organic structures. In the systems under study, more than two pi orbitals having a common nodal plane bond together. All other valence orbitals on each atom interact principally with only one other orbital to form localized sigma bonds.

Each of the systems has phenyl groups attached symmetrically to a central aromatic ring. The perpendicular pi orbital on each atom of the central ring is represented by a letter a, b, c, ... locating the central core. The perpendicular pi orbital on an atom in an attached ring is designated $P_{ij}$ where $i$ is the number of the ring and $j$ the number of the central core. The labelling of each central core is given in Figures VI and VII.

Considering reflection in the plane of each system under study would contribute nothing to the results; so it is neglected. Thus, the first structure, Triphenylocyclopropenyl$^{54}$ ion or radical, is treated as a $C_{3v}$ structure. The character table used appears as Table 7.$^{55}$

$^{54}$ Streitwieser, op. cit., p. 259.

Table 7. $C_{3v}$ Character Table

<table>
<thead>
<tr>
<th>Representation</th>
<th>E</th>
<th>$2C_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

From Figure VI, we see that the $C_3(C_6H_5)_3^+$ possesses five different sets of orbitals. These are:

- $a, b, c$
- $P_{11}, P_{21}, P_{31}$
- $P_{14}, P_{24}, P_{34}$
- $P_{16}, P_{22}, P_{26}, P_{32}, P_{36}$
- $P_{13}, P_{15}, P_{23}, P_{25}, P_{33}, P_{35}$

The first three sets yield the reducible representation

$$\sigma = A_1 + E$$

from which we get the functions:

- $A_1$: $1/\sqrt{3}(a + b + c)$
- $1/\sqrt{3}(P_{11} + P_{21} + P_{31})$
- $1/\sqrt{3}(P_{14} + P_{24} + P_{34})$
- $E$: $1/\sqrt{6}(2a - b - c)$
- $1/\sqrt{6}(2P_{11} - P_{21} - P_{31})$
- $1/\sqrt{6}(2P_{14} - P_{24} - P_{34})$

and the $H_{jj}$ integrals
Figure VI. The triphenyclopropenyl structure
where $H_0$ is the coulombic integral for $p$ orbitals and $\alpha$ is the resonance integral between nearest neighbors (a and b).

The remaining two sets of orbitals yield the reducible representation

$$\sigma = A_1 + A_2 + 2E$$

from which we obtain the functions

$$A_1: \frac{1}{\sqrt{6}}(P_{12} + P_{22} + P_{32} + P_{16} + P_{26} + P_{36})$$
$$A_2: \frac{1}{\sqrt{6}}(P_{13} + P_{23} + P_{33} + P_{15} + P_{25} + P_{35})$$

$$E: \frac{1}{\sqrt{6}}(2P_{12} - P_{22} - P_{32})$$
$$\frac{1}{\sqrt{6}}(2P_{13} - P_{23} - P_{33})$$
$$\frac{1}{\sqrt{6}}(2P_{16} - P_{26} - P_{36})$$
$$\frac{1}{\sqrt{6}}(2P_{15} - P_{25} - P_{35})$$

and the $H_{ij}$ integrals

$$A_1: H_0 -- \text{twice}$$
$$A_2: H_0 -- \text{twice}$$
$$E: H_0 -- 4 \text{ times}$$
Each irreducible representation appears more than once. To determine correct levels corresponding to each representation, we must solve an \( n \times n \) determinant where \( n \) is the number of times the irreducible representation occurs. A decomposition-of-representation table will be employed to aid us in determining those functions which belong to the same column of the same representation. The decomposition for the \( C_{3v} \) group is given in Table 8.56

<table>
<thead>
<tr>
<th>Atomic orbitals</th>
<th>Irreducible components generated by the atomic orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(s)</td>
<td>( A_1 )</td>
</tr>
<tr>
<td>1(p)</td>
<td>( A_1 + E )</td>
</tr>
<tr>
<td>2(d)</td>
<td>( A_1 + 2E )</td>
</tr>
<tr>
<td>3(f)</td>
<td>( 2A_1 + A_2 + 2E )</td>
</tr>
</tbody>
</table>

Our functions have to meet three criteria. First, they must have the geometric shape indicated by Table 8. For example, \( A_1 \) must be s, p, d, or f-like. Secondly, they must behave similarly under operations of the group. Thirdly, the functions we choose must give a maximum value for \( H_{jk} \) when \( \psi_j \) and \( \psi_k \) contain orbitals which are nearest neighbors.

56 Knowing the decomposition for the \( O_h \) group given in Table 6, we can use correlation tables as given in Wilson, Decius and Cross, *Molecular Vibrations*, McGraw-Hill Book Co., Inc.: New York, 1955, pp. 333-300 to obtain the decomposition for the \( C_{3v} \) group.
Since \( A_1 \) appears five times, we have to solve a \( 5 \times 5 \) determinant. Now, functions (114) and (119) satisfy the above criteria as they stand. They are labelled as follows

\[
\psi_1 = \frac{1}{\sqrt{3}}(a + b + c) \quad (125)
\]

\[
\psi_2 = \frac{1}{\sqrt{3}}(P_{11} + P_{21} + P_{31}) \quad (126)
\]

\[
\psi_3 = \frac{1}{\sqrt{3}}(P_{12} + P_{22} + P_{32} + P_{16} + P_{26} + P_{36}) \quad (127)
\]

\[
\psi_4 = \frac{1}{\sqrt{6}}(P_{13} + P_{23} + P_{33} + P_{15} + P_{25} + P_{35}) \quad (128)
\]

\[
\psi_5 = \frac{1}{\sqrt{3}}(P_{14} + P_{24} + P_{34}) \quad (129)
\]

From the above functions we get the \( H_{jk} \) integrals

\[
H_{12} = H_{24} = \alpha \quad (130)
\]

\[
H_{23} = H_{45} = \sqrt{2}\alpha \quad (131)
\]

with all other off-diagonal terms zero because they do not involve nearest neighbors. We see here that, if any resonance integrals other than \( \alpha \) were considered, the off diagonal terms would become so numerous that the resulting determinant would become impossible to solve exactly. With interactions (130), (131), and \( H_{jj} \) integrals (116), (122), we obtain

\[
\begin{vmatrix}
A + 2\alpha & \alpha & 0 & 0 & 0 \\
\alpha & A & \sqrt{2}\alpha & 0 & 0 \\
0 & \sqrt{2}\alpha & A & \alpha & 0 \\
0 & 0 & \alpha & A & \sqrt{2}\alpha \\
0 & 0 & 0 & \sqrt{2}\alpha & A
\end{vmatrix} = 0 \quad (132)
\]

where \( A = H_0 - E \). Solving determinant (132), we have

\[
x^5 + 2x^4 - 6x^3 - 10x^2 + 7x + 8 = 0 \quad (133)
\]
where \( x = A/\alpha \). To determine the roots of Eq. (133), we employ Graeffe's root-squaring method,\(^ {57,58}\) which yields the levels

\[
A_1: \quad H_0 + 2.60929 \approx 0.58
\]

\[
H_0 - 2.04661 \approx 0.58
\]

\[
H_0 + 1.78007 \approx 0.58
\]

\[
H_0 - 1.10812 \approx 0.58
\]

\[
H_0 + 0.75515 \approx 0.58
\]

Applying the same argument to the \( A_2 \) functions, we obtain the levels

\[
A_2: \quad H_0 + \infty
\]

\[
H_0 - \infty
\]

The molecular orbitals given for \( E \) do not belong to the same column of the representation. In rearranging them so they do, we start with functions (115) as they stand and work with functions (121) until they transform in like manner. The final functions, yielding maximum \( H_{jk} \) integrals, follow:

\[
\psi_1 = 1/ \sqrt{6} (2a - b - c) \quad (141)
\]

\[
\psi_2 = 1/ \sqrt{6} (2P_{11} - P_{21} - P_{31}) \quad (142)
\]

\[
\psi_3 = 1/2 (P_{12} - P_{32} + P_{16} - P_{26}) \quad (143)
\]

\[
\psi_4 = 1/ \sqrt{12} (P_{12} - 2P_{22} + P_{32} + P_{16} + P_{26} - 2P_{36}) \quad (144)
\]


\[ \psi_5 = \frac{1}{2} \left( P_{13} - P_{33} + P_{15} - P_{25} \right) \]  
(145)

\[ \psi_6 = \frac{1}{\sqrt{12}} (P_{13} - 2P_{23} + P_{33} + P_{15} + P_{25} - 2P_{35}) \]  
(146)

\[ \psi_7 = \frac{1}{\sqrt{6}} (2P_{14} - P_{24} - P_{34}) \]  
(147)

Notice that functions \( \psi_3 \) and \( \psi_4 \), which contain like basis orbitals, are orthogonal. They must be orthogonal because we have taken \( S_{jk} = \delta_{jk} \) in determinant (34). Functions (141) - (147) yield the interaction integrals

\[ H_{12} = H_{35} = H_{46} = \alpha \]  
(148)

\[ H_{23} = H_{57} = \frac{\sqrt{6}}{2} \alpha \]  
(149)

\[ H_{24} = H_{67} = \frac{\sqrt{2}}{2} \alpha \]  
(150)

With the above interaction integrals and the \( H_{jj} \) integrals (117) and (124), we obtain the determinant

\[
\begin{vmatrix}
A - \alpha & \alpha & 0 & 0 & 0 & 0 & 0 & 0 \\
\alpha & A & \frac{\sqrt{6}}{2} \alpha & \frac{\sqrt{2}}{2} \alpha & 0 & 0 & 0 & 0 \\
0 & \frac{\sqrt{2}}{2} \alpha & A & 0 & \alpha & 0 & 0 & 0 \\
0 & \frac{\sqrt{2}}{2} \alpha & 0 & A & 0 & \alpha & 0 & 0 \\
0 & 0 & \alpha & 0 & A & 0 & \sqrt{\frac{\sqrt{6}}{6}} \alpha & \sqrt{\frac{\sqrt{2}}{2}} \alpha \\
0 & 0 & 0 & \alpha & 0 & A & \sqrt{\frac{\sqrt{6}}{6}} \alpha & \sqrt{\frac{\sqrt{2}}{2}} \alpha \\
0 & 0 & 0 & 0 & \sqrt{\frac{\sqrt{6}}{6}} \alpha & \sqrt{\frac{\sqrt{2}}{2}} \alpha & A & \sqrt{\frac{\sqrt{6}}{6}} \alpha \\
0 & 0 & 0 & 0 & 0 & \sqrt{\frac{\sqrt{6}}{6}} \alpha & \sqrt{\frac{\sqrt{2}}{2}} \alpha & A \\
\end{vmatrix}
= 0
\]  
(151)
Multiplying it out gives
\[ x^5 - x^4 - 6x^3 + 5x^2 + 7x - 4 = 0 \]  
(152)
\[ (x + 1) = 0 \]  
(153)
which yields the levels
\[
\begin{align*}
E: & \quad H_0 + \alpha \\
H_0 & = -\infty \\
H_0 - 2.13845 & \alpha \\
H_0 + 2.06408 & \alpha \\
H_0 - 1.50464 & \alpha \\
H_0 + 1.15538 & \alpha \\
H_0 - 0.50434 & \alpha 
\end{align*}
\]
(154)  
(155)  
(156)  
(157)  
(158)  
(159)  
(160)
In the sum of these levels, the various \( \alpha \) terms approximately cancel. Thus, we have a check on the validity of our levels.

Having determined the bonding levels (134), (136), (138), (139), (154), (157), and (159), we are in a position to determine the resonance energy for \( \frac{1}{2}C_6H_5^+ \). Now, the energy of a valence electron confined in a \( \pi \) bond between adjacent carbon atoms is given by Duffey\(^{59}\) to be
\[ E = H_0 + \alpha \]  
(161)
In the single charged ion, we have 18 pi electrons from 18 phenyl carbons and two from the cyclopropenyl cation. From Eq. (161) we see that these 20 valence electrons might have a total \( \pi \) electron energy of
\[ E = 20(H_0 + \alpha) = 20H_0 + 20\alpha \]  
(162)
\(^{59}\)Duffey, \textit{op. cit.}, p. 173.
But, the bonding levels yield a total energy of

$$E_b = 20H_0 + 29.17\alpha$$  \hspace{1cm} (163)

Thus, the increase in bonding due to electrons being able to leave localized regions and wander throughout the system is

$$E_{res} = 9.17\alpha$$  \hspace{1cm} (164)

This result may be off some; for Streitwieser\textsuperscript{54} quotes a better value, $9.19\alpha$. In any case, such a large resonance energy indicates a very stable structure. Indeed, it has been synthesized and found to be relatively stable.\textsuperscript{60}

The second organic structure to be considered is that of Tetraphenylcyclobutadiene (Figure VII), which has a square cyclobutadiene ring at its center and a phenyl derivative at each corner. This system is treated as a $C_{4v}$ structure. The character table used appears as Table 9.\textsuperscript{61}

As in $C_3(C_6H_5)_3^+$, we will split the atomic orbitals into the following sets: $(a,b,c,d); (P_{11}); (P_{12}, P_{16});$ and $(P_{13}, P_{15})$. Also, only nearest neighbor interactions are introduced.

The reducible representation for the first three sets is given by

$$\sigma^- = A_1 + B_2 + E$$  \hspace{1cm} (165)

\textsuperscript{60}R. Breslow and C. Yuan, \textit{J. Am. Chem. Soc.}, 80, 5991 (1958).

\textsuperscript{61}Eyring, Walter, and Kimble, \textit{op. cit.}, p. 384.
Figure VII. The tetraphenycyclobutadiene structure
Table 9. $C_{4v}$ Character Table

<table>
<thead>
<tr>
<th>Representation</th>
<th>E</th>
<th>$C_2$</th>
<th>$2C_4$</th>
<th>$2\sigma_v$</th>
<th>$2\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

whence we get the functions

\[
A_1: \frac{1}{2}(a + b + c + d) \\
\frac{1}{2}(P_{11} + P_{24} + P_{34} + P_{41}) \\
\frac{1}{2}(P_{14} + P_{21} + P_{31} + P_{44})
\]

\[
B_2: \frac{1}{2}(a - b + c - d) \\
\frac{1}{2}(P_{11} - P_{21} + P_{31} - P_{41}) \\
\frac{1}{2}(P_{14} - P_{24} + P_{34} - P_{44})
\]

\[
E: \frac{1}{\sqrt{2}}(a - c) \\
\frac{1}{\sqrt{2}}(P_{11} - P_{31}) \\
\frac{1}{\sqrt{2}}(P_{14} - P_{34})
\]

and the $H_{jj}$ integrals

\[
A_1: H_0 + 2\alpha \\
H_0 \\
H_0
\]
Here as before, parameter $\alpha$ equals nearest neighbor interaction.

From the last two sets of orbitals we get the reducible representation

$$\sigma = A_1 + A_2 + B_1 + B_2 + E$$

which gives the eigenfunctions

$$A_1: \frac{1}{\sqrt{8}} \left( P_{12} + P_{22} + P_{32} + P_{42} - P_{16} - P_{26} + P_{36} + P_{46} \right)$$

$$A_2: \frac{1}{\sqrt{8}} \left( P_{13} + P_{23} + P_{33} + P_{43} - P_{15} - P_{25} + P_{35} + P_{45} \right)$$

$$B_1: \frac{1}{\sqrt{8}} \left( P_{12} - P_{22} + P_{32} - P_{42} - P_{16} + P_{26} - P_{36} + P_{46} \right)$$

$$B_2: \frac{1}{\sqrt{8}} \left( P_{13} + P_{23} + P_{33} + P_{43} - P_{15} - P_{25} + P_{35} + P_{45} \right)$$

$$E: \frac{1}{\sqrt{2}} \left( P_{12} - P_{32} \right)$$

$$\frac{1}{\sqrt{2}} \left( P_{13} - P_{33} \right)$$

$$\frac{1}{\sqrt{2}} \left( P_{15} - P_{35} \right)$$
Each of the above functions yields a $H_{ij}$ integral of $H_0$:

\begin{align*}
A_1 &: H_0 \quad \text{twice} \\
A_2 &: H_0 \quad \text{twice} \\
B_1 &: H_0 \quad \text{twice} \\
B_2 &: H_0 \quad \text{twice} \\
E &: H_0 \quad 4 \text{ times}
\end{align*}

Each irreducible representation appears more than once. To determine correct levels, we will employ the decomposition-of-representation table for the $C_{4v}$ group.

Table 10. Decomposition of Representations for $C_{4v}$ Group

<table>
<thead>
<tr>
<th>Atomic orbitals</th>
<th>Irreducible components generated by atomic orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(s)</td>
<td>$A_1$</td>
</tr>
<tr>
<td>1(p)</td>
<td>$A_1 + E$</td>
</tr>
<tr>
<td>2(d)</td>
<td>$A_1 + B_1 + B_2 + E$</td>
</tr>
<tr>
<td>3(f)</td>
<td>$A_1 + B_1 + B_2 + 2E$</td>
</tr>
</tbody>
</table>

Our functions are to be formulated so that they satisfy the same criteria as before. The functions generated by $A_1$, $A_2$, $B_1$, and $B_2$ as they stand satisfy the three criteria and yield the levels

\begin{align*}
A_1 &: H_0 + 2.60929 \alpha \\
H_0 - 2.04661 \alpha \\
H_0 + 1.78007 \alpha
\end{align*}
\[
\begin{align*}
H_0 &= 1.10812 \alpha \\
H_0 &= 0.75515 \alpha \\
A_2: \quad H_0 &= \alpha \\
&\quad H_0 = -\alpha \\
B_1: \quad H_0 &= \alpha \\
&\quad H_0 = -\alpha \\
B_2: \quad H_0 &= 2.60929 \alpha \\
&\quad H_0 = 2.04661 \alpha \\
&\quad H_0 = 1.78007 \alpha \\
&\quad H_0 = 1.10812 \alpha \\
&\quad H_0 = 0.75515 \alpha
\end{align*}
\]

The functions generated by \( E \), (168) and (177), must be altered before they are satisfactory. We will form \( p \)-like functions with coinciding nodal planes. Also, the functions must be orthogonal. We find the following functions which satisfy our criteria:

\[
\begin{align*}
\psi_1 &= \frac{1}{2}(a - b - c + d) \\
\psi_2 &= \frac{1}{2}(P_{11} - P_{21} - P_{31} + P_{41}) \\
\psi_3 &= \frac{1}{2}(-P_{22} + P_{42} + P_{16} - P_{36}) \\
\psi_4 &= \frac{1}{2}(P_{12} - P_{32} - P_{26} + P_{46}) \\
\psi_5 &= \frac{1}{2}(-P_{23} + P_{43} + P_{15} - P_{35}) \\
\psi_6 &= \frac{1}{2}(P_{13} - P_{33} - P_{25} + P_{45}) \\
\psi_7 &= \frac{1}{2}(P_{14} - P_{24} - P_{34} + P_{44})
\end{align*}
\]

The \( H_{jj} \) integrals are still given by (171) and (182). From the above functions we obtain the interaction terms.
\[ H_{12} = H_{23} = H_{24} = H_{35} = H_{46} = H_{57} = H_{67} = \alpha \]  

(204)

which with (171) and (182) yields

\[
\begin{pmatrix}
A & \lambda & 0 & 0 & 0 & 0 & 0 \\
\lambda & A & \lambda & 0 & 0 & 0 & 0 \\
0 & \lambda & A & 0 & \lambda & 0 & 0 \\
0 & \lambda & 0 & A & 0 & \lambda & 0 \\
0 & 0 & \lambda & 0 & A & 0 \\
0 & 0 & 0 & \lambda & 0 & A \\
0 & 0 & 0 & 0 & \lambda & A \\
\end{pmatrix} = 0
\]

(205)

Solving (205) we get

\[ (A)(A + \alpha)(A - \alpha)(A^4 - 6\alpha^2 + 7\alpha^4) = 0 \]

(206)

from which we get the levels

\[
\begin{align*}
E: & \\
H_0 & \\
H_0 + \alpha & \\
H_0 - \alpha & \\
H_0 + \sqrt{3 + \sqrt{2}\alpha} & = H_0 + 2.10100\alpha \\
H_0 - \sqrt{3 + \sqrt{2}\alpha} & = H_0 - 2.10100\alpha \\
H_0 + \sqrt{3 - \sqrt{2}\alpha} & = H_0 + 1.25928\alpha \\
H_0 - \sqrt{3 - \sqrt{2}\alpha} & = H_0 - 1.25928\alpha
\end{align*}
\]

(207)

(208)

(209)

(210)

(211)

(212)

(213)

Summing our levels, we get a sum of the coulombic integrals.

This is consistent with the theorem expressed by Eq. (96). A more restrictive form of this theorem is given in Daudel, Lefebver, and Moser. They state that if an organic molecule or complex is

---

alternate (all rings contain an even number of vertices) the levels should appear in pairs, i.e., for every orbital of energy

\[ E_j = H_0 + m_j \alpha \]  

(214)

there is another level of energy

\[ E_j' = H_0 - m_j \alpha \]  

(215)

Also there should be one level where \( m_j = 0 \). Now, the tetraphenyl-cyclobutadiene structure, which is alternate, has levels (183) - (196) and (208) - (213) which appear in pairs, while (207) is just \( H_0 \). Thus, we have reason to believe our levels are correct.

We find 13 bonding orbitals, which would hold 26 valence electrons. But in the molecule 28 valence electrons would be used. Thus, the ion \( C_4(C_6H_5)_4^{+2} \) would tend to form whenever possible. If its electrons were localized in single \( \pi \) bonds, their energy would be

\[ E = 26(H_0 + \alpha) = 26H_0 + 26\alpha \]  

(216)

But the total energy of the delocalized electrons is

\[ E_0 = 26H_0 + 38.13\alpha \]  

(217)

Thus, the resonance energy is

\[ E_{\text{res}} = 12.13\alpha \]  

(218)

Hence, the tetraphenylcyclobutadiene ion should be relatively stable.

Introductory work was also done on pentaphenylcyclopentadienyl (see Figure VIII). \(^63\) This complex has \( C_{5v} \) symmetry, for which the character table is shown in Table 11. \(^64\)

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\(^63\) Streitwieser, op. cit., p. 273.

\(^64\) Byring, Walter, and Kimble, op. cit., p. 384.
Figure VIII. The pentaphenylcyclopentadienyl structure
The basis orbitals divide into the following sets: \((a, b, c, d, e); (P_{11}); (P_{14}); (P_{12}, P_{16}); \) and \((P_{13}, P_{15})\). For each of the first three sets we obtain the reducible representation

\[
\sigma = A_1 + E_1 + E_2
\]

For each of the remaining two sets we get

\[
\sigma = A_1 + A_2 + 2E_1 + 2E_2
\]

A decomposition-of-representation table is not available for the \(C_{5v}\) group. Thus, we tried to form functions that would transform similarly and that would give us a finite value for \(H_{jk}\) when \(\psi_j\) and \(\psi_k\) contain nearest neighbors. The functions generated by \(A_1\) and \(A_2\) can be used directly since they satisfy the two remaining criteria. They include the expressions

\[
A_1: 1/\sqrt{5}(a + b + c + d + e)\\
1/\sqrt{5}(P_{11} + P_{21} + P_{31} + P_{41} + P_{51})\\
1/\sqrt{5}(P_{14} + P_{24} + P_{34} + P_{44} + P_{54})
\]
\[
\begin{align*}
1/ \sqrt{10}(P_{12} + P_{22} + P_{32} + P_{42} + P_{52} + P_{16} + P_{26} + P_{36} + P_{46} + P_{56}) \\
1/ \sqrt{10}(P_{13} + P_{23} + P_{33} + P_{43} + P_{53} + P_{15} + P_{25} + P_{35} + P_{45} + P_{55}) \\
A_2: \quad 1/ \sqrt{10}(P_{12} + P_{22} + P_{32} + P_{42} + P_{52} - P_{16} - P_{26} - P_{36} - P_{46} - P_{56}) \\
1/ \sqrt{10}(P_{13} + P_{23} + P_{33} + P_{43} + P_{53} - P_{15} - P_{25} - P_{35} - P_{45} - P_{55})
\end{align*}
\]

which yield the levels

\[
\begin{align*}
A_1: & \quad H_0 + 2.60929 \alpha \\
& \quad H_0 - 2.04661 \alpha \\
& \quad H_0 + 1.78007 \alpha \\
& \quad H_0 - 1.10812 \alpha \\
& \quad H_0 + 0.75515 \alpha \\
A_2: & \quad H_0 + \alpha \\
& \quad H_0 - \alpha 
\end{align*}
\]

The functions generated for $E_1$ and $E_2$ do not give nonzero $H_{jk}$ integrals. Thus, we must operate on the functions until we do get mixed ones having the greatest possible $H_{jk}$ integrals. But we run into a problem; the simple functions that give us finite $H_{jk}$ integrals apparently do not transform similarly. However, the following functions are the best ones we could find:

\[
\begin{align*}
1/ \sqrt{10}(2a + rb - sc - sd + re) \\
1/ \sqrt{10}(2P_{11} + rP_{21} - sP_{31} - sP_{41} + rP_{51}) \\
1/ \sqrt{10}(2P_{12} + rP_{22} - sP_{32} - sP_{42} + rP_{52}) \\
1/ \sqrt{10}(2P_{16} + rP_{26} - sP_{36} - sP_{46} + rP_{56}) \\
1/ \sqrt{10}(2P_{13} + rP_{23} - sP_{33} - sP_{43} + rP_{53}) \\
1/ \sqrt{10}(2P_{15} + rP_{25} - sP_{35} - sP_{45} + rP_{55})
\end{align*}
\]
Here \( r = \frac{\sqrt{5} - 1}{2} \) and \( s = \frac{\sqrt{5} + 1}{2} \) for \( E_1 \) while \( r = -\frac{\sqrt{5} + 1}{2} \) and \( s = -\frac{\sqrt{5} - 1}{2} \) for \( E_2 \). From the functions (230) we obtain the integrals

\[
\begin{align*}
H_{jj} &= H_0 \\
H_{11} &= H_0 + q\alpha \\
H_{12} &= H_{23} = H_{24} = H_{35} = H_{46} = H_{57} = H_{67} = \alpha
\end{align*}
\]

which when substituted into determinant (34) gives us the levels

\[
\begin{align*}
H_0 + \alpha \\
H_0 - \alpha
\end{align*}
\]

and the polynomial

\[
A^5 + q\alpha A^4 - 6\alpha A^3 + 5q\alpha A^2 + 7\alpha A - 4q = 0
\]

for both \( E_1 \) and \( E_2 \).

Perhaps because of the nature of the roots, the root-squaring method was not effective in solving Eq. (236).

It is the author's hope that it will be possible for someone else in connection with the NSF research program to find better functions and a solution to this problem.


Mulliken, R. S., *Phys. Rev.*, 32, 186, 761 (1928); 33, 730 (1929); 41, 49, 751 (1932); 43, 279 (1933).


Here certain useful conditions that must be met by independent eigenfunctions which form the basis of an irreducible representation will be derived.

Start with Eq. (24) in the form

$$R \psi_i^1 = \sum_{j=1}^{k} \psi_j^i \Gamma_i^j (R)_{jl} \quad i = 1, 2, \ldots k \quad (A.1)$$

which shows how the eigenfunctions transform. Now, the complete matrix equation is

$$R(\psi_1^i \ldots \psi_j^i \ldots \psi_k^i) = (\psi_1^i \ldots \psi_j^i \ldots \psi_k^i) \begin{pmatrix} \Gamma_i^1 (R)_{11} \ldots \Gamma_i^1 (R)_{1j} \ldots \Gamma_i^1 (R)_{1k} \\ \vdots \\ \vdots \\ \vdots \\ \Gamma_i^j (R)_{j1} \ldots \Gamma_i^j (R)_{jj} \ldots \Gamma_i^j (R)_{jk} \\ \vdots \\ \vdots \\ \Gamma_i^k (R)_{kl} \ldots \Gamma_i^k (R)_{kk} \end{pmatrix}$$

or

$$(R \psi_1^i \ldots R \psi_j^i \ldots R \psi_k^i) = \left[ \psi_1^i \Gamma_1^i (R)_{1j} + \cdots + \psi_j^i \Gamma_j^i (R)_{1j} + \cdots + \psi_k^i \Gamma_k^i (R)_{1j} \right]$$

$$\ldots \left[ \psi_1^i \Gamma_1^i (R)_{1k} + \cdots + \psi_j^i \Gamma_j^i (R)_{1k} + \cdots + \psi_k^i \Gamma_k^i (R)_{1k} \right] \ldots \quad (A.2)$$

One says that $\psi_1^i$ belongs to the $i$th column of the $i$th irreducible representation. The remaining $\psi_1^i$'s are called partner functions of $\psi_1^i$. The partner functions also satisfy a relationship like (A.1)

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and are said to belong to the remaining columns of the $i$th irreducible representation.

We will show that two functions $\psi_i^1$ and $\phi_i^1$, which belong to two different irreducible representations or to two different columns of the same representation are (mathematically) orthogonal. Then in a similar manner, we will show that the integral

$$\int \psi_i^1 \phi_i^1 \, d\tau$$

equals zero unless the eigenfunctions belong to the same column of the same irreducible representation.

We have for the functions, in terms of their irreducible representations

$$R\psi_i^1 = \sum_{j=1}^{k} \Gamma_i^1(R)_{j1} \psi_j$$

$$R\phi_i^{1'} = \sum_{j=1}^{k'} \Gamma_i^{1'}(R)_{j1'} \phi_j$$

To determine if the two functions are orthogonal, we will evaluate the scalar product; for two functions are orthogonal if their scalar product is zero. From Wigner we find that the Hermitian scalar product of two real eigenfunctions to be defined as

$$\langle \psi_i^1, \phi_i^{1'} \rangle = \int \overline{\psi_i^1} \phi_i^{1'} \, d\tau$$

A unitary transformation leaves the Hermitian scalar product unchanged.

---

thus
\[ (\psi^i_1, \phi^{i'}_1) = (R \psi^i_1, R \phi^{i'}_1) = \int_{-\infty}^{\infty} R \psi^i_1 R \phi^{i'}_1 \, d\gamma \]
where \( R \) is a unitary transformation. Then from (A.3), we have
\[ (\psi^i_1, \phi^{i'}_1) = \sum_{j=1}^{k} \langle R \rangle_{ij} \psi^i_j \sum_{j'=1}^{k'} \langle R' \rangle_{i'j'} \phi^{i'}_j \, d\gamma \quad (A.5) \]
Our \( \Gamma \)'s are transformation matrices and do not depend on a particular space; so
\[ (\psi^i_1, \phi^{i'}_1) = \sum_{j=1}^{k} \langle R \rangle_{ij} \sum_{j'=1}^{k'} \langle R' \rangle_{i'j'} \int_{-\infty}^{\infty} \psi^i_j \phi^{i'}_j \, d\gamma \quad (A.6) \]
Summing over all operations and using the orthogonality condition \(^{69}\) for our \( \Gamma \)'s, we have
\[ \sum_{R} \langle R \rangle_{ij} \delta_{ij} \delta_{jj'} \delta_{ll'} \sum_{j=1}^{k} \int_{-\infty}^{\infty} \psi^i_j \phi^{i'}_j \, d\gamma \quad (A.6) \]
where \( h \) is the number of symmetry operations corresponding to the system. The right hand side of (A.6) is different from zero only when \( j = j' \). With \( j = j' \) both representations (\( \Gamma_i \) and \( \Gamma_{i'} \)) will have the same dimension \( k \) (assume \( j' > j \)). Since the scalar product on the left is independent of \( R \), summing over the \( h \) operations and dividing by \( h \) leaves
\[ (\psi^i_1, \phi^{i'}_1) = \delta_{ii} \delta_{ll'} \frac{1}{k} \sum_{j=1}^{k} \int_{-\infty}^{\infty} \psi^i_j \phi^{i'}_j \, d\gamma \quad (A.7) \]
If \( i \neq i' \), the two eigenfunctions do not belong to the same irreducible representation. If \( l \neq l' \), the two eigenfunctions do not belong to the

\(^{69}\)Ibid., p. 79.
same column of the same irreducible representation. In either case, we pick two physically different eigenfunctions. Hence, the two eigenfunctions that belong to a level infinitely degenerate \( (k = 3) \) are necessarily orthogonal, whether they belong to the same column or not. However, one could pick eigenfunctions that are not identical to \( \psi \) of the \( H \), integral to determine \( S \), physically different and retain the overlap integrals \( S \) in our secular determinant.

Next consider the integral
\[
\int_{-\infty}^{\infty} \psi_i^H \phi_i^1 \, d\tau
\]
(A.8)
following a similar procedure as used to obtain Eq. (A.7). We recall that operation \( R \) leaves \( H \) unchanged. Also, \( R \psi \) and \( \psi \) satisfy the same Schrödinger equation. Therefore,
\[
\int_{-\infty}^{\infty} \psi_i^H \phi_i^1 \, d\tau = \int_{-\infty}^{\infty} R \psi_i^H R \phi_i^1 \, d\tau
\]
replacing \( R \psi \) and \( R \phi \) with expression (A.3), summing over \( R \), and applying the orthogonality condition, yields
\[
\int_{-\infty}^{\infty} \psi_i^H \phi_i^1 \, d\tau = \sum_{j=1}^{K} \frac{1}{K} \delta_{i1} \delta_{11} \int_{-\infty}^{\infty} \psi_j^H \phi_j^1 \, d\tau
\]
(A.9)
But, we are interested in eigenfunctions that are a basis for the same irreducible representation. Setting \( i = i' \) gives
\[
\int_{-\infty}^{\infty} \psi_i^H \phi_i^1 \, d\tau = \frac{1}{K} \delta_{i1} \sum_{j=1}^{K} \int_{-\infty}^{\infty} \psi_j^H \phi_j^1 \, d\tau
\]
(A.10)
Hence, the integral \( H_{11} \) is zero unless the two eigenfunctions \( \psi_1^i \), \( \phi_1^i \) belong to the same column of the same irreducible representation.

Finally, notice that the summation on the right of Eq. (A.10) does not depend on \( l \). Therefore,
Equation (A.11) shows that if a level is triply degenerate \((k = 3)\) it does not make any difference which of the three independent eigen-functions we use to form the \(H_{jj}\) integral in determinant \(3^4\).