The Group Relation Between the Mulliken and SlaterPauling Theories of Valence

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The Group Relation Between the Mulliken and Slater-Pauling Theories of Valence

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By means of the group theory of characters, it is shown that there is an intimate relation between Mulliken's molecular orbitals and the Slater-Pauling directed wave functions. One can pass from the former to the latter by making a simple transformation from an irreducible to a reducible representation. Consequently the same formal valence rules are usually given by either method, and one can understand generally why wave functions of the central atom which are nonbonding in Mulliken's procedure are likewise never employed in constructing Pauling's "hybridized" linear combinations.

TWO distinct viewpoints have been particularly developed in applying quantum mechanics to problems of valence,[1] namely, the Heitler-London-Pauling-Slater method of the electron pair bond, and the method of molecular orbitals used by Hund, Lennard-Jones, Mulliken, and others. The two procedures represent different approximations to the solution of a complicated secular equation. The method of molecular orbitals permits factorization into one-electron problems, but at the expense of adequate cognizance of the terms due to electron repulsion, which are too fully recognized in the H-L-P-S procedure. A characteristic feature of the latter is the "hybridization," whereby linear combinations of states of different azimuthal quantum number for the central atom are necessary in fields of, for example, tetrahedral symmetry. It was shown by the writer that in the case of carbon compounds the two theories, though superficially different, predicted similar results on geometrical arrangement.[2] It is the purpose of the present paper to show that the equivalence is general in the sense that one formulation will give the same formal stereochemical valence principles as the other. Thus it is futile to discuss whether the Mulliken or Pauling theory will give better working rules in compounds formally amenable to electron pair treatment. Both, for instance, suggest the now classic Pauling square configuration for $Ni(CN)_4^{--}$ in view of the diamagnetism of this ion. (A tetrahedral model would give paramagnetism with either method.[3]) One can only inquire which procedure involves the more reasonable hypotheses. It seems to us that in the case of the transition elements, one must probably decide in favor of the Mulliken formation as a simple qualitative description, though perhaps a poor quantitative approximation. It is difficult to believe, for instance, that the $Fe(CN)_6^{4-}$ radical has the Pauling structure $Fe^{4-}(CN)_6$, since the Fe ion certainly is unwilling to swallow four extra electrons. The conventional ionic model $Fe^{++}(CN^-)_6$, on the other hand, probably goes too far in the other direction. The Mulliken viewpoint has here the advantage of allowing an arbitrary distribution of charge between Fe and $(CN)_6$, depending on how one weights the various atomic orbitals in forming a molecular orbital as a linear combination of them. Only a limited significance should, however, be given to any purported preference between the two methods, as each represents a solution of the secular equation only under certain extreme conditions. The true wave function is in reality a combination of H-LJ-M and H-L-P-S functions, along with many ingredients intermediate between these two extremes, and so either theory is bound to have some semblance of truth. The latter functions, for instance, can be amplified

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[1] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); J. C. Slater, Phys. Rev. **38**, 1109 (1931); R. S. Mulliken, Phys. Rev. **40**, 55; **41**, 49, 751; **43**, 279 (1932–3); J. Chem. Phys. **1**, 492 (1933); **3**, 375, 506 (1935). For other references, or more detailed introduction on the methods which we compare, see J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935). Other workers besides Mulliken have contributed to the molecular orbital procedure, but we sometimes refer to the latter as Mulliken's method, since we are concerned with the application to polyatomic molecules in the light of symmetry groups, an aspect considered primarily by Mulliken.

[2] J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933).

[3] Cf. Pauling, reference 1, and J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 206, 221 (1935).

by taking linear combinations with terms representing different stages of charge transfer until finally just the right polarity is obtained.

MOLECULAR ORBITALS

We shall confine our discussion to the case where a central atom attaches n atoms arranged in some symmetrical fashion (tetrahedron, square, etc.) characteristic of a crystallographic point group.[4] Let $\psi(\Gamma)$ be a wave function of the central atom which has the proper symmetry, i.e., whose transformation scheme under the covering operations of the group is that characteristic of some irreducible representation Γ. Let ψ_i be a wave function of attached atom i. We shall assume that only one orbital state need be considered for each attached atom, and that this state is either an s state or else is symmetric (as in a $2p\sigma$ bond) about the line joining the attached to the central atom. The method of molecular orbitals in its simplest form[5] seeks to construct solutions of the form

$$\psi = \psi(\Gamma) + \Sigma_i a_i \psi_i. \tag{1}$$

The coefficients a_i must be so chosen that $\Sigma_i a_i \psi_i$ transforms in the fashion appropriate to the irreducible representation Γ. Now the important point is that bases for only certain irreducible representations can be constructed out of linear combinations of the ψ_i. To determine which, one ascertains the group characters associated with the transformation scheme, usually reducible, of the original attached wave functions ψ_i before linear combinations are taken. This step is easy, as the character χ_D for a covering operation D is simply equal to q, where q is the number of atoms left invariant by D. This result is true inasmuch as D leaves q of the atoms alone, and completely rearranges the others, so that the diagonal sum involved in the character will contain unity q times, and will have zeros for the other entries. The scheme for evaluating the characters is reminiscent of that in the group

theory of molecular vibrations employed by Wigner and by E. B. Wilson, Jr.,[6] but is simpler since we are not interested in displacements of atoms from equilibrium, and in consequence all nonvanishing entries are unity rather than some root of unity. After the characters have been found, the determination of the constituent irreducible representations proceeds in the usual way by means of the theorem that the unresolved characters must equal the sum of the primitive characters contained therein.

As an illustration, we may consider a complex containing six atoms octahedrally arranged, i.e., located at the centers of the six cube faces. Then the symmetry group is the cubic one O_h, and the characters associated with the arrangement of attached atoms are

$$\begin{array}{ccccccccccc} E & C_2 & C_4 & C_2' & C_3 & I & IC_2 & IC_4 & IC_2' & IC_3 \\ \chi = 6 & 2 & 2 & 0 & 0 & 0 & 4 & 0 & 2 & \cdot\, 0. \end{array} \tag{2}$$

Here $\chi(C_4)$, for instance, means the character for the covering operation consisting of rotation about one of the fourfold or principal cubic axes (normals to cube faces) by $2\pi/4$. Any rotation about such an axis leaves two atoms invariant, and hence $\chi(C_2) = \chi(C_4) = 2$. On the other hand, $\chi(C_2') = \chi(C_3) = 0$ since no atoms are left invariant under rotations about the twofold or secondary cubic axes (surface diagonals) or about the threefold axes (body diagonals). Inversion in the center of symmetry is denoted by I. By using tables of characters for the group O_h, one finds that the irreducible representations contained in the character scheme (2) are, in Mulliken's notation,[4]

$$A_{1g}, E_g, T_{1u}. \tag{3}$$

The irreducible representations corresponding to various kinds of central orbitals are shown below:

orbit	s	p	$d\gamma$	$d\epsilon$	f		
rep.	A_{1g}	T_{1u}	E_g	T_{2u}	$A_{2u}, T_{1u}, T_{2u}.$				(4)

The notation for the various kinds of d wave functions is that of Bethe,[7] viz.,

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[4] See R. S. Mulliken, Phys. Rev. **43**, 279 (1933) or references 6 and 7 if further background is desired on the aspects of group theory and crystallographic symmetry which we use.

[5] Called by Mulliken the LCAO ("linear combination of atomic orbitals") form. For a critique of this type of approximation see R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935). It appears to have been first suggested by Lennard-Jones.

[6] E. Wigner, Gött. Nachr., p. 133 (1930); E. B. Wilson, Jr., J. Chem. Phys. **2**, 432 (1934); Phys. Rev. **45**, 706 (1934).

[7] H. Bethe, Ann. d. Physik **3**, 165 (1929).

TABLE I.

| SYMMETRY | CENTRAL ORBITALS | | | | ATTACHED ORBITALS | |
	s	p	d	f	No.	REPRESENTATIONS
Tetrahedral (T_d)	A_1	T_2	$E(d\gamma), T_2(d\epsilon)$	A_1, T_1, T_2	4	A_1, T_2
Trigonal (D_{3h})	A_1'	A_2'', E'	A_1', E', E''	$A_1', A_2', A_2'', E', E''$	3	A_1', E'
					6	A_1', A_2'', E', E''
Tetragonal (D_{4h})	A_{1g}	A_{2u}, E_u	$A_{1g}, B_{1g}, B_{2g}, E_g$	$A_{2u}, B_{1u}, B_{2u}, 2E_u$	4	A_{1g}, B_{1g}, E_u
					8	$A_{1g}, A_{2u}, B_{1g}, B_{2u}, E_u, E_g$

$$\psi(d\gamma_1) = (1/12)^{\frac{1}{2}} f(r)(3z^2 - r^2),$$
$$\psi(d\gamma_2) = \tfrac{1}{2} f(r)(x^2 - y^2), \tag{5}$$

$$\psi(d\epsilon_1) = f(r)xy, \quad \psi(d\epsilon_2) = f(r)xz,$$
$$\psi(d\epsilon_3) = f(r)yz. \tag{6}$$

By comparison of (3) and (4) we see that is it impossible for $d\epsilon$ orbitals to form any partnerships with attached orbitals, in agreement with Mulliken's conclusion[8] that $d\gamma$ rather than $d\epsilon$ is particularly adapted to forming octahedral bonds. Mulliken's arguments were mainly of a qualitative nature. The preceding considerations enable us to formulate the situation more succinctly, as they show that the $d\epsilon$ orbitals are entirely nonbonding.

In Table I we give the irreducible representations, in Mulliken's notation, contained in the central and attached orbitals for compounds of other types of symmetry. When 3 or 4 atoms are trigonally or tetragonally attached, we have supposed that the plane of these atoms is a plane of symmetry, as in $(NO_3)^-$ or $Ni(CN)_4^{--}$. When there is no such symmetry plane, as in NH_3, the distinctions between u and g, or between primes and double primes, are to be abolished,[9] and the symmetries degenerate to C_{3v}, C_{4v} instead of D_{3h}, D_{4h}. When 6 atoms are attached in the scheme D_{3h}, or 8 in D_{4h}, they are arranged respectively at the corners of a trigonal and a square prism.

The results given in Table I are obtained by the same method as in the octahedral example. The explicit forms of the linear combinations of the attached orbitals which transform irreducibly, or in other words the values of the coefficients a_i in (1) have been tabulated by Van

Vleck and Sherman[10] in many instances, and so need not be repeated here. The a_i for the octahedral case are also given in Eqs. (2)–(7) of the following paper.

Note particularly that in the tetrahedral complexes, the $d\epsilon$ orbitals of the central atom are bonding, as there are attached orbitals of similar group properties with which they can combine, while the $d\gamma$ orbitals are nonbonding. The reverse was true of octahedral compounds—a result at first a little surprising in view of the isomorphism of the groups T_d and O_h. This reversal was also deduced by Mulliken[8] from the geometrical study of the way the central wave functions "overlap."

It will be observed that if eight atoms are attached, their full bonding power is not utilized unless one includes f wave functions for the central atom, since the representation B_{2u} is not included in s, p, or d. Now f wave functions usually have too high energy to be normally available, or else are so sequestered in the interior of the atom as to be of no value for bonding because of small overlapping. Even if eight atoms are attached at the corners of a cube, central f wave functions must be included in order to realize all possible bonding partnerships, for results always true of tetragonal symmetry surely apply to cubic symmetry, which is a special case of the latter. On the other hand, no f functions are needed for six atoms attached either octahedrally or at the corners of a trigonal prism. We thus have an indication of why it is that coordination numbers of six are common in nature, while those of eight are rare.

METHOD OF DIRECTED ELECTRON PAIRS

We now turn to the method of Pauling and Slater. Here the procedure is to use hybridized

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[8] R. S. Mulliken, Phys. Rev. 40, 55 (1932).
[9] In adapting Table I to the case C_{3v}, the following irregularity, however, is to be noted: one must replace A_1', A_1'', A_2', A_2'', respectively, by A_1, A_2, A_2, A_1 rather than by A_1, A_1, A_2, A_2 as one would guess.

[10] J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. 7, 219 (1935).

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central orbitals, i.e., linear combinations of orbitals of different azimuthal quantum number, in such a way that the resulting central wave function projects out especially in some one direction in space, and so is adapted to form an electron pair with one particular attached atom. Thus for tetrahedral compounds Pauling and Slater[1] use wave functions which are linear combinations of s and p, or alternatively as Pauling[1] shows, of s and $d\epsilon$ wave functions. For octahedral compounds, Pauling finds that $sp^3d\gamma^2$ combinations are appropriate, and $sp^2d\gamma$ for tetragonal. Hultgren[11] proves that eight atoms cannot be attached (at least symmetrically) by means of unidirectional electron pair bonds formed from s, p, and d wave functions. Incidentally, the present paper shows that sp^3d^3f functions are needed to hold eight atoms.[12] It will be noted that the wave functions involved in the Pauling unidirectional linear combinations are precisely those which are bonding in the method of molecular orbitals. For example, Pauling, like Mulliken, makes no use of $d\gamma$ orbitals for tetrahedral compounds, or of $d\epsilon$ for octahedral. Such coincidences have hitherto appeared something of a mystery, but as immediate explanation, as follows, is furnished by group theory.

In the Pauling-Slater theory, one desires the central wave functions to possess unilateral directional properties so as to be correlated with one particular attached atom. Hence the P-S central functions must have the same transformation properties as do those ψ_i of the attached atoms before linear combinations of the latter are taken. Thus the problem of finding the linear combinations of the central orbitals which exhibit the proper directional properties is simply the reverse of finding the proper linear combinations of the attached orbitals in the Mulliken procedure. The difference is only that in the P-S theory, the linear combinations are in the central rather than attached portion, and their construction corresponds to transformation from an irreducible representation to a

reducible one, of structure similar to that belonging to the original ψ_i's, rather than to the inverse transformation.[13] Clearly, the same irreducible representations are needed in the construction of a given reducible representation as those contained in the resolution of the latter into its irreducible parts. Pauling has obviously shown considerable ingenuity in constructing his wave functions without using the status in terms of group theory.

GENERALITY OF THE RESULTS

The argument underlying Table I, etc., ostensibly assumed that the molecular orbital be expressible as a linear combination of atomic orbitals, but is readily seen to be still applicable provided only that the charge cloud of any attached orbital be symmetric about the line joining the given attached atom to the central one. Hence the atomic orbitals can be of what James calls the flexible type, i.e., contain parameters which can be varied in the Ritz method, and which allow for the fact that chemical combination distorts the atomic orbitals from what they would be in the free condition. This admission of flexibility is fortunate, for it is well known that it is a bad quantitative approximation[5] to express a molecular orbital as a linear combination of undistorted atomic orbitals. The Ritz variational problem is, of course, to be of the 1 rather than n electron type, so that the generality in our analysis by means of molecular orbitals is roughly comparable with that in the Hartree method.

One thing which the preceding analysis does not do is to tell us what is the best arrangement of atoms in case the symmetry group does not uniquely determine this arrangement. For instance, by examining the overlapping of wave functions, Hultgren[11] finds that when six atoms are attached at the corners of a trigonal prism, the binding is firmest if the sides of the prism are square. This fact cannot, however, be inferred from our group theory considerations, as there are no additional elements of symmetry when the sides are square rather than rectangular.

[11] R. Hultgren, Phys. Rev. 40, 891 (1932).
[12] Similar conclusions on the type of bonds necessary to attach eight atoms have also been obtained in unpublished work of R. S. Mulliken.

[13] This transformation has been explicitly given by the writer in the case of methane (J. Chem. Phys. 1, 177 (1933)), but he did not discuss its group-theoretical significance.