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Electronic Structures of Polyatomic Molecules and Valence. IV. Electronic States, Quantum Theory of the Double Bond

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The possible types of electronic states of polyatomic molecules (assuming fixed nuclei and neglecting spin fine structure) are discussed and tabulated (Table I) with the help of simple group theory methods, applying results of Bethe and Wigner. A notation for electronic states (ψ's) and molecular orbitals (ϕ's) for molecules having any type of symmetry to be found among the 32 crystal classes, is adopted; this is essentially the same as that used by Placzek for designating the vibrational states of molecules. It is shown how the possible ψ's corresponding to any given electron configuration (set of ϕ's) can be determined for any type of symmetry; for the more complicated cases, the results are tabulated (Table V). It is shown how all the *selection rules* for transitions between electronic states of molecules can be easily determined. Limitations resulting here from the application of the Franck-Condon principle are discussed. Extending work of Bethe, tables are given (Tables II–IV) showing how the various types of electronic states of atoms and of diatomic and polyatomic molecules (S, P, Σ^+, ΔA, etc.) go over into various other types of states if the symmetry of the original system is decreased. Examples are given showing how electronic wave functions (ψ's) of molecules can be constructed which conform to the possible types (Table I) allowed by the symmetry of the nuclear skeleton, and which at the same time, with Slater's method, are antisymmetrical in the electrons (cf. section 2 and Eqs. (9–12)). It is shown that for molecules having all their electrons in closed shells or electron-pair bonds, zeroth approximation ψ's which conform to the identical representation of the molecule's symmetry group (analogous to ^1S of atoms and $^1\Sigma^+$ or $^1\Sigma_g^+$ of diatomic molecules) can be built up either by using electron-pair bonds or by using molecular orbitals. The approximate construction of molecular orbitals as linear combinations of atomic orbitals, in such a way that they conform to the types allowed by the symmetry of the molecule, is discussed and illustrated (cf. Eqs. (3, 8)). Several statements made in a previous paper (III) of this series, on the quantum theory of the double bond, are here justified by the methods mentioned above, thereby also providing examples of the application of the latter. Some additional details concerning the nature of the double bond are given. Finally, it is shown that the model of the double bond given in III should according to the theory be altered somewhat for the perp. form of the molecule, in a way which offers the possibility of improved agreement with experiment.

INTRODUCTION

1. Symmetry of electronic wave functions

In I, II and III of this series[1] the use of molecular orbitals for shared electrons in describing and interpreting the electronic states of polyatomic molecules has been discussed and illustrated.[2] Discussion of further examples will be prefaced by some general considerations.—Through an oversight, the writer failed to mention in II that Hückel also[3] has been following a similar program in his work on the structure of the benzene ring, its derivatives, and certain other organic compounds. In this connection Hückel also has made a comparison of the methods of molecular orbitals and of electron-pair bonds.

For a molecule with fixed nuclei, the complete electronic wave function ψ is restricted to one of certain types which depend on the symmetry of the nuclear skeleton. In the language of group theory, ψ must conform to an irreducible representation of the symmetry group of the corresponding Schrödinger equation,—which contains a potential energy whose symmetry is that of the nuclear skeleton. Or more briefly, one may say that every ψ must belong to an irreducible

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[1] R. S. Mulliken, Phys. Rev. **40**, 55; **41**, 49, 751 (1932). Hereafter designated as I, II, III.

[2] Cf. II, also J. C. Slater, Phys. Rev. **41**, 255 (1932), for a comparison of the method of electron-pair bonds with that of molecular orbitals.

[3] E. Hückel, Zeits. f. Physik **70**, 204; **72**, 310 (1931); **76**, 628 (1932). Also it should be mentioned that the interpretation of the structure of C_6H_6 attributed in II (p. 56) exclusively to Hund had already appeared in Hückel's paper on this molecule.

representation of the symmetry group of the nuclear skeleton. Corresponding statements apply to every molecular orbital φ. In nature ψ is of course further restricted, in accordance with the Pauli principle, to forms antisymmetrical in the electrons.

In general a knowledge, for any nuclear configuration, of the different irreducible representations of its symmetry group, since these determine the forms or types to which ψ and the φ's may belong, is important in determining the number, spacing, and degree of degeneracy of molecular electronic states, and the selection rules for transitions between them, also for determining the possible states of the dissociation products of a molecule.

Like the electronic φ's and ψ's, the possible states of vibration of a (rotationless) molecule also conform to the irreducible representations of the symmetry group of the molecular skeleton (in its equilibrium or in some more symmetrical configuration).[4, 5] Finally, the *total* electronic $\times$vibrational *state*, excluding rotation, must belong to such a representation. This is strictly true even when the electronic and vibrational parts of the wave function cannot be even approximately separated.

The process of finding the irreducible representations for any given type of molecular symmetry is accomplished in an easy and instructive way (cf. section 4), by using a little group theory. The problem has already been solved, for all or most of the kinds of symmetry likely to occur in actual molecules, by Bethe[6] and Wigner.[4] The results have been applied by Wigner and by Placzek[5] to the case of nuclear vibrations, of importance especially for Raman and infrared spectra.

An important secondary problem is that of notation. It has seemed best here to adopt for classifying electronic φ's and ψ's (Table I below) essentially the same notation Placzek has used for describing vibrational states. The same notation could well be used also for the electronic φ's and ψ's of atoms in crystals (Bethe's problem[6]), and the same or a similar notation for describing the electronic$\times$vibrational states of molecules. Placzek's notation has marked advantages over the Bethe notation used in I–III of this series, in being more descriptive.

These problems will be taken up again in section 3. In section 2 the matter of building up good approximate ψ's which are antisymmetrical in the electrons will be considered.

In classifying electronic states of polyatomic molecules, complications often arise because of the existence of more than one fairly stable arrangement of the same set of nuclei. Such different arrangements as are chemically stable (chemical isomers) can when in their normal states most conveniently be treated as distinct individuals. In excited states of such molecules, the relative stabilities of different arrangements are in general altered. It may then often be advisable to regard a variety of nuclear arrangements as belonging to a single molecular species. This is of course always necessary to a greater or less degree when one considers excited molecules in which strong vibrations or internal rotations are occurring.

Even for unexcited molecules belonging to a single chemical species it is not always true that there is just a single very stable type of nuclear configuration. In C_2H_6, for example, only very weak forces[7] oppose a relative rotation of the two CH_3 groups around the $C-C$ axis. Hence in discussing the electronic structure of C_2H_6, it is perhaps best to assume only such symmetry as is common to the various forms differing by arbitrary rotations of this kind. Another less extreme example is found in NH_3, where a plane

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[4] E. Wigner, Göttinger Nachr., Math.-Phys. Klasse, p. 133 (1930). Wigner extended Bethe's results (see reference 6) to include the symmetry groups of all the 32 crystal classes.

[5] G. Placzek, article on Raman and infrared spectra, to appear soon in *Marx's Handbuch der Radiologie.* The writer is indebted to Dr. Placzek for the use of his tables before publication and for valuable discussions, also for calling his attention to reference 4. Placzek gives his tables without direct use of group theory, but they are essentially the same as the group theory results (cf. Table I below).

[6] H. Bethe (Ann. d. Physik [5], **3**, 133 (1929)) used group theory in determining the irreducible representations to which the ψ and φ's of an atom may belong when in a field of force corresponding to that produced by its neighbors in a crystal. The writer is greatly indebted to Professor J. H. Van Vleck for calling his attention to the applicability of Bethe's results to molecular electron wave functions.

[7] Cf. H. Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

form is nearly as stable as the pyramidal equilibrium forms.

2. Use of atomic and molecular orbitals to build up ψ

The complete electronic wave function ψ of a molecule can be conveniently approximated by an antisymmetrical linear combination of products of atomic or molecular one-electron wave functions, each a product of an orbital factor φ and a spin factor σ. This can be done in various ways. In any case one may start with a determinant form as follows (N is a normalizing factor):

$$U=N\begin{vmatrix}\varphi_1\sigma_1(1) & \varphi_1\sigma_1(2) & \cdots \\ \varphi_2\sigma_2(1) & \varphi_2\sigma_2(2) & \cdots \\ \cdots & \cdots & \cdots\end{vmatrix} \qquad (1)$$

This is antisymmetrical in the electrons 1, 2, 3, . . . Using a set of such U's as unperturbed functions, one can obtain the desired wave functions ψ as linear combinations of them (*general method* of Slater[8, 9]). In so doing, one includes in any linear combination only such U's as have the same M_S (resultant spin magnetic quantum number).[8] [In the case of atoms, one includes only such U's as are alike also in M_L.]

Various cases may arise. In general one has in the unperturbed system (no interactions between electrons) several U's of equal energy corresponding to a given set of φ's but various arrangements of σ's giving the same M_S (spin degeneracy), and to a variety of sets of equivalent φ's for any given spin arrangement (orbital degeneracy). In some cases (e.g., an atom or molecule built of closed shells of atomic or molecular orbitals respectively), there is no such degeneracy and a single U suffices.—In the case of any molecule, every linear combination of U's must be so chosen as to conform to an irreducible representation of the molecule's symmetry group (cf. section 1).

To get the best practical approximation (Slater's most general practical method,[10] (see also reference 9, page 1111)) one includes not only such U's as are really degenerate in the unperturbed system, but also other U's of equal M_S, etc., whose energies lie in the same neighborhood. It should be noted that the U's belonging to a really degenerate set always belong to a definite electron configuration, i.e., to a definite set of φ's (counting degenerate φ's as belonging to a single type), distributed, if there is more than one atom, with a definite set of φ's for each atom. The use of an approximation built up only from a really degenerate set of U's may therefore appropriately be referred to as the *method of the pure electron configuration.*

As applied to molecules, the method of the pure electron configuration may be specialized or approximated in various ways. The present *method of molecular orbitals* is a special form in which, following Lennard-Jones, atomic φ's (orbitals) are used for inner or unshared electrons (usually in atomic closed shells), molecular φ's for outer, shared or valence, electrons. The form used by Slater[8, 9] which for convenience will be called the "*method of atomic orbitals*," is one in which atomic φ's exclusively are used. A special case of the method of atomic orbitals, sometimes identical with it but in general representing a simpler but cruder approximation, is the Slater-Pauling *method of electron-pair bonds.* This last is applicable only to chemically saturated molecules in their normal states, i.e., to a restricted but particularly important class of molecular states.

Following a method first used by Bloch for metals[11] and later used by Hückel, Hund, and others, molecular orbitals will as a matter of convenience usually be approximated here by linear combinations of atomic orbitals, although eventually we may hope to obtain forms which are better approximations. When atomic orbitals are used in constructing molecular orbitals, the resulting ψ is in the final analysis expressed entirely in terms of atomic orbitals, but is nevertheless not in general identical with that obtained with the "method of atomic orbitals" as defined above. For excited states, to be sure, the approximate ψ's given by the two methods are very often identical: examples, $^3\Sigma_u{}^+$ and $^1\Sigma_u{}^+$ states of H_2 built up, respectively, in the atomic orbital method, from 2 H(1s) and from $H^+ + H^-(1s^2)$. For saturated molecules in their normal states, however, and whenever there is

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[8] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[9] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[10] For examples of this case cf. E. U. Condon, Phys. Rev. **36**, 1121 (1930), and other papers.

[11] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

at least one pair of electrons which form a valence bond, the two methods are never identical. Nevertheless the approximations given by the two methods can of course always be made identical if we generalize (and complicate) each, dropping their common "pure electron configuration" limitation, and form linear combinations with U's belonging to other configurations. It is still true, however, that the point of view and method of approach are different in the method of molecular orbitals than in that of atomic orbitals or of electron-pair bonds. Slater[2] has pointed out the usefulness of considering problems from both points of view.

In building up ψ's for complicated molecules according to the present method, it will often be useful to proceed in two or more stages, first assigning electron configurations composed of (atomic and) molecular orbitals for separate parts of the molecule (*radicals*), then combining these. Two courses are then open for the construction of ψ for the complete molecule. (1) One may proceed in accordance with the method of molecular orbitals, using molecular orbitals of the total molecule for those electrons which may reasonably be considered as shared by the two or more radicals, but keeping *radical orbitals* for those electrons which are shared within, but not between radicals (and of course using atomic orbitals for electrons which belong to particular atoms and are not shared at all). (2) Or one may proceed in analogy with the method of atomic orbitals, building up the final ψ entirely from orbitals of the various radicals (and atomic orbitals for the completely unshared electrons). One may form electron-pair bonds from radical orbitals if the latter are known to give bonding.

Good examples of molecules which can be built up out of radicals are C_2H_4 and its derivatives. Both procedures (1) and (2), but especially (1), will be used in section 8*d* below for building up ψ's of C_2H_4 using CH_2 orbitals. A symmetrical molecule like C_2H_4 when treated in this way is analogous to a homopolar diatomic molecule. In plane C_2H_4 the analogy is close, in perp. C_2H_4 less so in some respects. In practice (cf. the $[z]$ and $[x]$ orbitals of CH_2 used in forming C_2H_4) those radical orbitals which act as valence orbitals of a radical, forming bonding electron pairs in the complete molecule, are really often to a fairly good approximation just atomic orbitals of certain atoms between which binding chiefly occurs. Cf. the $[z]$ and $[x]$ orbitals of CH_2 used in forming the $C=C$ double bond in C_2H_4; these are not far different from C atom orbitals. Hence one need not fear that the use of the method of molecular orbitals in complex molecules necessarily means using orbitals which are spread over a large number of atoms. Even in large molecules, it will be found that one arrives at molecular orbitals which usually fade out after bridging the gap between any atom and one or more of its immediate neighbors. Especially in hydrides, however, many details of chemistry may prove to be better understandable by admitting molecular orbitals which do extend with appreciable density somewhat farther than this (cf. section 8*e* for an example; a still better example is probably B_2H_6).

2a. Method of electron-pair bonds. It will be instructive first to say something about the electron-pair bond method. In this, the ψ of a molecule with definite bonds is approximated[9] by a linear combination of the type

$$\psi = N\begin{vmatrix} \varphi_1\alpha(1) & \varphi_1\alpha(2) & \cdots \\ \varphi_2\beta(1) & \varphi_2\beta(2) & \cdots \\ \varphi_3\alpha(1) & \varphi_3\alpha(2) & \cdots \\ \varphi_4\beta(1) & \varphi_4\beta(2) & \cdots \\ \text{etc.} & \cdots & \cdots \end{vmatrix} - N\begin{vmatrix} \varphi_1\beta & \cdots \\ \varphi_2\alpha & \cdots \\ \varphi_3\alpha & \cdots \\ \varphi_4\beta & \cdots \\ \cdots & \cdots \end{vmatrix} + N\begin{vmatrix} \varphi_1\beta & \cdots \\ \varphi_2\alpha & \cdots \\ \varphi_3\beta & \cdots \\ \varphi_4\alpha & \cdots \\ \cdots & \cdots \end{vmatrix} - N\begin{vmatrix} \varphi_1\alpha & \cdots \\ \varphi_2\beta & \cdots \\ \varphi_3\beta & \cdots \\ \varphi_4\alpha & \cdots \\ \cdots & \cdots \end{vmatrix} + \text{etc.} \qquad (2)$$

The number of U's in this expression depends on the number of bonds. For H_2, with one bond, there are just two U's, each in the form of a determinant with two rows and columns, and with φ_1 and φ_2 denoting H atom 1*s* orbitals, one for atom *A*, the other for atom *B*.[9] For a molecule He_2, with no bonds, there would be only one U, with $\varphi_1=\varphi_2$, and $\varphi_3=\varphi_4$, φ_1 and φ_3 referring to a 1*s* orbital on He atom *A* or *B* respectively.

For H_2O, with two bonds and approximately a 90° angle between them, ψ would consist of four U's, with φ_1 and φ_3 representing, say, a $2p_y$

and a $2p_z$ oxygen orbital, φ_2 and φ_4 representing $1s$ orbitals of the two hydrogen atoms; each of the four determinants would also contain terms corresponding to six more electrons and to wave functions $\varphi_4\alpha$, $\varphi_5\beta$, $\varphi_6\alpha$, $\varphi_6\beta$, $\varphi_7\alpha$, and $\varphi_7\beta$, where φ_5, φ_6, φ_7 refer to oxygen $1s$, $2s$, and $2p_x$ orbitals, which do not form bonds. Similarly the Slater-Pauling model of NH_3 is approximated by using three bonds between nitrogen p_x, p_y, and p_z and hydrogen $1s$ orbitals. In every case, orbitals which are to be used in forming bonds belong to different atoms and appear with opposite spins (α and β) on the two atoms (cf. reference 9, top page 1128, for details).

In dealing with compounds of N, O, F, and their homologues, Slater and Pauling assume as a good approximation that it is only the p electrons which form the bonds. They generally use as suitable zeroth approximations atomic orbitals of the types p_x, p_y, and p_z (i.e., $f(r)$ $\sin\theta\cos\varphi$, $f(r)\sin\theta\sin\varphi$, and $f(r)\cos\theta$). For the univalent atoms such as H, Na, they, of course, use s orbitals.

For the carbon atom, Slater and Pauling use "tetrahedral" orbitals. These comprise four energetically and geometrically equivalent linear combinations[12] of $2s$ and $2p$ orbitals pointing toward the corners of a tetrahedron. Strongest binding of other atoms is then obtained if the latter are at the corners of a tetrahedron. For CH_4, the expression for ψ written down according to Eq. (2) contains sixteen U's. Each U has $\varphi_1=\varphi_2=$ carbon $1s$, $\varphi_3=\frac{1}{2}(s+p_x+p_y+p_z)$ of carbon, $\varphi_4=$ the H $1s$ which overlaps φ_3, and so on to φ_{10}.

For any saturated molecule (unshared electrons all in atomic closed shells and shared electrons all in electron-pair bonds), ψ, as well as every one of the U's, if chosen as in Eq. (2) and with atomic orbitals properly adapted to the symmetry of the molecule, can be shown to belong always to the "identical representation" of the symmetry group of the molecule, with zero spin (^1A or $^1A_1$ or $^1A_{1g}$, etc.).

The proof is as follows (cf. sections 3, 4 and Table I for necessary group theory and discussion of symmetry types). First we note that for a saturated molecule, every properly-constructed approximate U and ψ of the type found in Eq. (2) must contain for every atom one wave function for every bond which the atom forms, and for any atom which forms more than one bond of the same kind, the zeroth approximation wave functions used for these bonds must be equivalent, i.e., must transform one into another under the operations of the symmetry group (cf. e.g., the Pauling-Slater tetrahedral orbitals). [If this last condition is not met, one must in general use a linear combination of several expressions of the form of ψ in Eq. (2) in order to get a final ψ which is a representation of the symmetry group. For molecules which are not saturated, it is always necessary to form such linear combinations, by using the general form of the method of atomic orbitals, since the more special method of electron-pair bonds is not applicable.] If these conditions are fulfilled, then the effect on any U of any symmetry operation belonging to the symmetry group defined by the nuclear configuration is readily seen to be merely to permute some of the rows in its determinant (Eq. (1)), but never to eliminate any row nor to introduce any new kind of row. Every symmetry operation either leaves all φ's unchanged, or replaces some of them by other equivalent ones; it does not affect the spins (α, β). The totality of permutations produced by any operation can always be expressed in terms of a certain number of specified transpositions (exchanges) of rows. Now the value of a determinant is multiplied by -1 if an odd number, by $+1$ if an even number of transpositions of its rows is made. One now sees (1): for the totality of electrons which are in atomic closed shells, every symmetry operation produces an even number of transpositions of rows, simply because there is an even number of wave functions in the closed shells of each atom; equivalent atoms of course have equivalent closed shells; (2): the wave functions of any two electrons (one on each of two atoms) which form a bond undergo parallel transformations under any symmetry operation, and from this it is easily seen to follow that the total number of transpositions of rows resulting from the action of any symmetry operation on the bonding electron wave functions is even. Hence for a saturated molecule whose ψ is constructed as above specified, the total number of

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[12] L. Pauling, J. Am. Chem. Soc. 53, 1378 (1931).

transpositions produced in each U by any symmetry operation is even, so that each U, and ψ, is multiplied by $+1$ for every operation of its symmetry group. This behavior is that which characterizes the *identical representation* of any symmetry group; this representation has the same symmetry as the nuclear skeleton itself.

It should be noted that the result just proved holds even if the actual molecule, e.g., H_2O, does not have the ideal valence angles (90°, etc.) of Pauling and Slater, provided only that the axes for the atomic orbitals used are chosen with proper regard for the actual symmetry of the molecule. The reader can readily verify the correctness of the result of the last paragraph for the cases of H_2, He_2, H_2O, NH_3, CH_4, whose ψ's were given above, by testing what happens to each U or ψ when subjected to each operation (cf. Table I) of the appropriate symmetry group.

2b. Method of molecular orbitals. We shall assume that the symmetry of the molecule is known, empirically or perhaps from the Pauling-Slater electron-pair bond rules. In order to obtain ψ's, one inserts the proper orbitals, some atomic and molecular, into Eq. (1). A suitable linear combination of the resulting U's formed in exactly the same way as in the case[8] of an atom.

The main problem is usually that of finding suitable molecular orbitals. In the first place, these must always be representations of the symmetry group defined by the arrangement of the nuclei. For molecules in their normal states, one must furthermore usually select only *bonding* molecular orbitals. These are characterized by giving a relatively high probability density between the nuclei which they bind together. The fulfillment of this condition is assured, if one constructs the molecular orbitals approximately by taking linear combinations of atomic orbitals, by using only combinations which add between nuclei.

One can also construct a variety of antibonding and of partially bonding molecular orbitals, which should be useful mostly in describing excited or repulsive states of molecules. (Examples of antibonding orbitals: σ^*2p in N_2, cf. II; C−C antibonding orbitals $[x-x]$ in C_2H_4, —cf. III, also section 8*b* (below).)

In case degenerate (atomic or) molecular orbitals, not all in closed shells, are present in the U's of Eq. (1), one must take care to form the ψ's as linear combinations of the U's in such a way that each is a representation of the symmetry group of the molecule. The method is similar to that used for atoms[8] or diatomic molecules when degenerate orbitals are present. [Usually in the present method atomic orbitals, corresponding to unshared electrons, occur only in closed shells and so cause no trouble even if degenerate.] If only nondegenerate molecular orbitals are present, and all atomic orbitals are in closed shells, linear combinations of U's need to be taken only to remove spin degeneracy,[8] and each resultant ψ is then always a representation of the symmetry group *if the molecular orbitals are.* If all orbitals occur only in closed groups (cf. II, page 51), whether atomic or molecular, one has always the identical representation. The truth of these statements can be proved by reasoning similar to that applied to a similar matter in section 2*a*, but rather simpler. The examples to be found in section 8*d* (cf. Eqs. (9–12) should also be instructive.

2c. Construction of molecular orbitals as linear combinations of atomic orbitals. The manner in which molecular orbitals can be constructed from atomic orbitals so as to conform to definite representations of the molecular group can be seen from some examples (cf. also I, II, III, etc.). Thus, molecular orbitals of H_2^+ can be formed as sums (bonding, types σ_g, π_u, etc.) or differences (antibonding, types σ_u, π_g, etc.) of H atom orbitals, namely *const.* $(\varphi_A+\varphi_B)$ or *const.* $(\varphi_A-\varphi_B)$, where φ_A and φ_B refer to equivalent orbitals of the two H nuclei.

As a simple example of a polyatomic case, a certain bonding orbital of CH_2 (or H_2O), belonging to the identical representation a_1 of point group $\mathbf{C_{2v}}$ (cf. Tables I, Ia), and related to the carbon (or oxygen) atomic orbital $2p_z$, can be approximated as follows (cf. Eq. (8) in section 8*a* for other CH_2 or H_2O orbitals):

$$[z]=a(2p_z)+b(\alpha+\beta)+c(2s)+\cdots. \qquad (3)$$

Here α and β refer to $1s$ orbitals of two H atoms placed at equal distances from the C or O atom, while $2s$ and $2p_z$ refer to orbitals of the latter. Equality of the coefficients of α and β is necessary here in order to have the molecular orbital $[z]$ conform to a_1 of $\mathbf{C_{2v}}$, while the relative signs of a and b must be such that, in the regions where α and β strongly overlap $2p_z$, they have the same sign as the latter. In Eq. (3), c is relatively small in the case of H_2O, but larger in that of CH_2. The ratios b/a and c/a are undetermined coefficients. An antibonding orbital would be obtained if the coefficient b were taken with reversed sign; at the same time the relative magnitudes of a, b, c would be more or less changed.—It may be remarked that the symmetry type $\mathbf{C_{2v}}$ is so simple that everything can be easily seen and worked out without using group theory. For molecules of higher symmetry, however, the group theory treatment is very convenient.

In regard to the possibility of improving the approximation given by Eq. (3), by adding further terms such as $d(3s)$, $e(3p_z)$, $f(3d_z)$, the reader is referred to an illuminating discussion by Slater which is applicable here (reference 9, page 1111). In general, it is profitable only to include atomic orbitals which are fairly much alike in energy. (In the case of H_2O, even the term $c(2s)$ in Eq. (3) could probably better be dropped.) Exact equality of energy of all the orbitals, such as one has in H_2^+, is not necessary.

In Eq. (3) each of the terms $a(2p_z)$, $c(2s)$, and $b(\alpha+\beta)$, separately conforms like $[z]$ itself to representation a_1 of $\mathbf{C_{2v}}$. Such a relation is usual in cases like Eq. (3) where a molecular orbital is built up around an orbital (here $2p_z$) of a central or dominant atom. Further examples (NH_3 and CH_4 types) will be found in V. Only such orbitals of the dominant atom as conform to the final desired representation can be used, for example $2p_z$ and $2s$, but not $2p_x$ or $2p_y$, in Eq. (3).

Often the inclusion of more than one orbital of the dominant or central atom yields a hybrid orbital which gives increased overlapping with the orbitals of the other atoms and so gives stronger bonding. This fact can often be used as a guide in forming a qualitative estimate of the relative magnitudes of two coefficients such as c and a in Eq. (3). One could indeed systematically seek out the "best bonding" hybrid orbitals of the central atom, i.e., orbitals giving maximum overlapping with those of the outer atoms to be bound, as Pauling has done[12] in connection with electron-pair bonds.[13]

One has, however, in general no right to assign to two coefficients like a and c in Eq. (3) such relative values as would correspond to a BBH (best bonding hybrid). In general, if $a_B\varphi_1+c_B\varphi_2$ represents a BBH, then to get a best approximation in Eq. (3), it is correct to use the ratio c_B/a_B only if φ_1 and φ_2 are actually degenerate. If φ_1 and φ_2 are only approximately degenerate, the ratio must be less (or greater), and must approach zero (or infinity) as φ_1 and φ_2 become more unequal in energy. Clearly, however, the larger energy decrease obtainable from stronger bonding weights the scales in favor of hybrids which approximate BBH's.

In seeking approximations corresponding to valence theory, Pauling's procedure for electron-pair bonds is to use alternatively either a BBH or a simple atomic orbital according as it appears probable from chemical and other evidence that the former or the latter gives the better approximation; he does not use intermediate types. This procedure is indeed unavoidable if a *simple* approximation is to be obtained in terms of electron-pair bonds, but it is evidently at a disadvantage in this respect as compared with the present more flexible and (when desirable) more noncommittal method; and it is more subject to possible errors of judgment. The present method has even a certain advantage in having less that it must predict or decide, for this makes it better able to be guided by empirical, including spectroscopic, data. The problem of the structure of the double bond (cf. III, and section 8 below), and of the structure of NH_3, to be discussed in V, are examples of this.

APPLICATION OF GROUP THEORY

3. Objects and notation

First we might seek to determine the irreducible representations (cf. section 1) for each kind of symmetry that is possible for a polyatomic molecule. Most, at least, of the symmetry types likely to be found in actual molecules, as well,

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[13] When a hybrid $a\psi_1+c\psi_2$ of two orbitals is formed, there is of course also another one orthogonal to it, $c\psi_1-a\psi_2$. Of these two hybrid orbitals, one may be well adapted to binding in one direction, the other in another.

apparently, as a number not likely so to occur, are included among those of the 32 crystal classes. Symmetry types with n-fold axes, with $n=5$, 7, 8, or more, are not included. Table I in section 4 gives the representations for all the symmetry types of the 32 crystal classes. If the representations for other types should be needed (e.g., the ring molecule C_5H_{10} may have a five-fold axis), they can be obtained by the same methods (cf. section 4) used for the 32 crystal classes.

For each crystal class there is a symmetry group, composed of all the operations to which the crystal or molecule could be subjected without changing its appearance or aspect viewed from any fixed position.[14] Such symmetry groups are often called point groups.[14] The 32 point groups, it may be noted, correspond to a considerably smaller number of abstract groups, since many of the point groups are, when considered abstractly, identical with others.

The results, as already obtained by Bethe and Wigner (cf. section 1) but arranged somewhat differently to suit the present application, are given in Table I. The different representations of each group are designated by symbols usually the same as those used by Placzek for molecular vibrational states. As noted in section 1, this has advantages over Bethe's simple listing of representations as Γ_1, Γ_2, $\cdots$, γ_1, γ_2, $\cdots$.

Although for the symmetry group of an atom or of a diatomic or linear molecule the number of representations is infinite (s or S, P or p, D, $\cdots$; Σ^+ or σ, Σ^-, Π or (π, Δ, $\cdots$), it is finite and rather small for all the 32 point groups. For designating the representations of these, capital letters are used here for resultant electronic states (ψ's), small letters for orbitals (φ's), just as for atoms and diatomic molecules. The multiplicity of resultant states is denoted by a left-hand superscript as for atoms and diatomic molecules. No attempt will be made for the present to develop a notation for multiplet components or spin fine structure; it should be noticed that the numerical subscripts $_1$, $_2$, and $_3$ used here for certain representations belong to the *orbital* description. [Cf. Bethe[6] for a treatment of the spin structures.]

In Table I the same symbols are often used for different point groups, but each symbol has, at least in part, a rather definite significance. Thus A, B, a, b refer to nondegenerate, E, e to twofoldly degenerate, T, t to threefoldly degenerate, states or orbitals. A or a means symmetrical, B or b antisymmetrical, for a rotation of $2\pi/n$ around the (or an) n-fold principal axis. (If there is no axis, A is used.) The subscripts $_1$ and $_2$ have varying meanings; superscripts $'$ and $''$ mean symmetrical and antisymmetrical for reflection in a plane (σ_h) perpendicular to the principal axis.

Besides using general symbols such as A_1, a_2, $b_2 \cdots$ analogous to S, p, π, etc., we shall of course feel free to add more specific symbols to describe particular states or orbitals, just as we use symbols like $3p$, $2p\pi$, etc., for atoms and diatomic molecules. In particular we shall use, as already in I, II and III, a variety of symbols such as $[s]$, $[2p_x]$, $[\sigma]$, $[\pi]$, $3d_\beta$, and so on, which indicate that the molecular orbital in question is derived from, or related to, some particular type of atomic or diatomic orbital.

The objects of the following sections, insofar as group theory problems are concerned, may be summarized as follows: (1) to give all the types of electronic states (corresponding to the irreducible representations) for the 32 point groups; (2) to determine the selection rules for these; (3) to determine the nature of the resultant electronic states corresponding to any given electron configuration (e.g., $a_1^2a_2b_1e^3$); (4) to determine what happens to the orbitals and states of a molecule of given symmetry when the symmetry is altered; (5) to find what relations exist between the electronic states of a molecule and those of its (atomic or molecular) dissociation products, for various modes of dissociation. The results for (1), (2), (3), and (4) are given below; those for (5) will be considered later. For atoms and diatomic molecules the corresponding results are already well known.

4. Representations of the 32 point groups

Table I can be completely derived with the help of a limited knowledge of the theory of finite groups, not difficult to acquire in connection with a study of some of the examples

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[14] For details, cf. e.g., P. P. Ewald, *Handbuch der Physik*, Vol. 24. J. Springer, Berlin, 1927; or R. W. G. Wyckoff, *The Structure of Crystals:* The Chemical Catalog Company, New York, 1931.

given in the table. The meaning of Table I will now be explained briefly, so that it can be used without further knowledge of group theory, also the method of its derivation will be given. Table Ia shows how the symmetries of a number of molecules are distributed among various point groups.

Given a point group whose irreducible representations are desired, one first divides the symmetry elements (i.e., operations), whose total number may be called g, into a number, let us call it r, of group-theory *symmetry classes*[15] (not to be confused with crystal classes) each containing, let us say, h equivalent elements, where h varies from one class to another.[16] Every group includes the element E (identity), which always forms a class by itself, with $h=1$. An important theorem is: *the number of irreducible representations of any group equals r.* One can construct a square table of representations ($\Gamma_1, \Gamma_2, \cdots \Gamma_r$), classes ($E\equiv C_1, C_2, \cdots C_r$), and *characters* ($\chi$) as shown (also cf. Table I for specific examples).

	E	C_2	..	C_r
Γ_1	$\chi_1^{(1)}$	$\chi_2^{(1)}$	..	$\chi_r^{(1)}$
Γ_2	$\chi_1^{(2)}$	$\chi_2^{(2)}$	..	$\chi_r^{(2)}$
..	..	..	..	..
Γ_r	$\chi_1^{(r)}$	$\chi_2^{(r)}$	..	$\chi_r^{(r)}$

Any character $\chi_m^{(j)}$ describes the effect on the representation Γ_j of *any* operation of the symmetry class C_m (the notation $\Gamma_1, \cdots C_2, \cdots$ will be replaced by more specific designations in Table I). In our case the representations define the possible types of electronic wave functions ψ or φ. The representations of the 32 point groups are all either 1-, 2-, or 3-dimensional, which for φ's and ψ's means nondegenerate, twofoldly or threefoldly degenerate.

For a nondegenerate φ or ψ, belonging say to Γ_j, $\chi_m^{(j)}$ is merely a factor by which φ or ψ is multiplied when subjected to a symmetry operation of the class C_m. For a twofoldly degenerate φ or ψ, one has of course a set of two mutually orthogonal wave functions, say φ_1, φ_2. When these are subjected to any symmetry operation of the molecule's point group, each is in general transformed in such a way that one gets a new mutually orthogonal set φ_1', φ_2', where $\varphi_1'=a_{11}\varphi_1+a_{12}\varphi_2$ and $\varphi_2'=a_{21}\varphi_1+a_{22}\varphi_2$. The character χ_m for such a φ(or ψ) is merely the sum $a_{11}+a_{22}$ (i.e., the spur of the matrix of coefficients a_{ij}), taken for any operation of the class C_m. The extension to threefoldly degenerate φ's and ψ's is obvious. Important is the fact that $\chi=a_{11}+a_{22}(+a_{33})$ is independent of how one selects the original two (or three) mutually orthogonal φ's or ψ's.

For the class E, $a_{ij}=0$ except that $a_{11}=a_{22}(=a_{33})=1$, always, so that the character $\chi_1^{(j)}$ for any representation Γ_j is always equal to the number of dimensions of the latter. The following relation[16] then suffices to determine, for any group, how many of its r representations there are of each number of dimensions:

$$(\chi_1^{(1)})^2+(\chi_1^{(2)})^2+\cdots+(\chi_1^{(r)})^2=g. \qquad (4)$$

Every symmetry group has a one-dimensional representation, called the *identical representation*,[15] always symbolized by A, A_1, or A_{1g} in Table I, for which every χ is $+1$, so that any φ or ψ belonging to it has the same symmetry as the nuclear skeleton itself, as is not true of any other representation.

For most of the point groups the χ's are all integers (cf. Table I), but for a few, some of them are complex numbers. In general, φ's or ψ's belonging to different representations cannot have equal energy except in isolated special cases, and n-foldly degenerate φ's or ψ's ordinarily appear only for n-dimensional representations. But when the χ's are complex, one finds that some of the representations occur in pairs, such that the χ's of one member of a pair are conjugate complex to those of the other (cf. e.g., the groups $\mathbf{C}_3$, $\mathbf{C}_4$ in Table I). One can then readily show that the two representations of such a pair are conjugate complex to each other (φ or $\psi=A\pm Bi$); and from this it follows[4] by insertion in the Schrödinger equation (if possible magnetic interactions are neglected) that A and B, and so $A\pm Bi$, etc., are equal in energy and so should be considered as belonging to a single degenerate state.

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[15] For a convenient survey of the application of group theory to atomic and diatomic problems, cf. B. L. van der Waerden, *Die gruppentheoretische Methode in der Quantenmechanik*, J. Springer, Berlin, 1932. Also Wigner's book and Eckart's article in Rev. Mod. Phys. for atomic problems.

[16] Cf. pages 11, 76, 77 of reference 15. Placzek[5] uses a similar method without group theory.

Table I. *Irreducible representations of the 32 point groups.*

Triclinic

$\mathbf{C_1}$	E
A	1

Also $\mathbf{C_i}=\mathbf{C_1}\times i$

Monoclinic

$\mathbf{C_2}$; Co		E	C_2
	$\mathbf{C_s}$	E	$iC_2=\sigma$
A; z	A'	1	1
B; x or y	A''	1	-1

Also $\mathbf{C_{2h}}=\mathbf{C_2}\times i$

Orthorhombic

$\mathbf{V}\equiv\mathbf{D_2}$; Co		E	$C_2(z)$	$C_2(y)$	$C_2(x)$
	$\mathbf{C_{2v}}$	E	$C_2(z)$	$iC_2(y)=\sigma_v$	$iC_2(x)=\sigma_v$
A_1	A_1	1	1	1	1
B_1; z	A_2	1	1	-1	-1
B_2; y	B_1	1	-1	1	-1
B_3; x	B_2	1	-1	-1	1

Also $\mathbf{V_h}\equiv\mathbf{D_{2h}}=\mathbf{V}\times i$

Tetragonal

$\mathbf{D_4}$; Co	E	C_2	$2C_4$	$2C_2$	$2C_2'$
$\mathbf{C_{4v}}$	E	C_2	$2C_4$	$2iC_2=\sigma_v$	$2iC_2'=\sigma_d$
$\mathbf{V_d}\equiv\mathbf{D_{2d}}$	E	C_2	$2iC_4=2S_4$	$2C_2$	$2iC_2'=\sigma_d$
A_1	1	1	1	1	1
A_2; z	1	1	1	-1	-1
B_1	1	1	-1	1	-1
B_2	1	1	-1	-1	1
E; $x\pm iy$	2	-2	0	0	0

$\mathbf{C_4}$; Co	E	C_2	C_4	C_4^3
$\mathbf{S_4}$	E	C_2	S_4	S_4^3
A; z	1	1	1	1
B	1	1	-1	-1
E; $x\pm iy$	1	-1	$-i$	i
	1	-1	i	$-i$

Also $\mathbf{D_{4h}}=\mathbf{D_4}\times i$, and $\mathbf{C_{4h}}=\mathbf{C_4}\times i$

Hexagonal

$\mathbf{D_6}$; Co			E	C_2	$2C_3$	$2C_6$	$3C_2$	$3C_2'$
	$\mathbf{C_{6v}}$		E	C_2	$2C_3$	$2C_6$	$3iC_2=3\sigma_d$	$3iC_2'=3\sigma_v$
		$\mathbf{D_{3h}}$	E	$iC_2=\sigma_h$	$2C_3$	$2iC_6=2S_6$	$3C_2$	$3iC_2'=3\sigma_v$
A_1	A_1	A_1'	1	1	1	1	1	1
A_2; z	A_2	A_2'	1	1	1	1	-1	-1
B_1	B_2	A_1''	1	-1	1	-1	1	-1
B_2	B_1	A_2''	1	-1	1	-1	-1	1
E^*	E^*	E'	2	2	-1	-1	0	0
E_*^*; $x\pm iy$	E_*^*	E''	2	-2	-1	1	0	0

Also $\mathbf{D_{6h}}=\mathbf{D_6}\times i$

$\mathbf{C_6}$; Co	E	C_6	C_3	C_2	C_3^2	C_6^5
A	1	1	1	1	1	1
B	1	-1	1	-1	1	-1
E^*	1	ω^2	$-\omega$	1	ω^2	$-\omega$
	1	$-\omega$	ω^2	1	$-\omega$	ω^2
E_*^*	1	ω	ω^2	-1	$-\omega$	$-\omega^2$
	1	$-\omega^2$	$-\omega$	-1	ω^2	ω
Note: $\omega=e^{2\pi i/6}=-\omega^4$						

Also $\mathbf{C_{6h}}=\mathbf{C_6}\times i$; also $\mathbf{C_{3h}}=\mathbf{C_3}\times\sigma_h$, with states A', A'', E', E''

TABLE I. (*Continued*).

Rhombohedral

$\mathbf{D_3}$; *Co*	E	$2C_3$	$3C_2'$
$\mathbf{C_{3v}}$	E	$2C_3$	$3iC_2'=3\sigma_v$
A_1	1	1	1
A_2; z	1	1	-1
E; $x\pm iy$	2	-1	0

$\mathbf{C_3}$	E	C_3	C_3^2
A	1	1	1
E	1	ω	ω^2
	1	ω^2	ω

Note: $\omega=e^{2\pi i/3}$

Also $\mathbf{D_{3d}}=$

$\mathbf{D_3}\times i$;
$\mathbf{C_{3i}}\equiv\mathbf{S_6}=$
$\mathbf{C_3}\times i$

Cubic

$\mathbf{O}$; *Co*	E	$3C_2$ (x, y, z)	$6C_4$	$6C_2$	$8C_3$
$\mathbf{T_d}$	E	$3C_2$	$6iC_4=S_4$	$6iC_2=6\sigma_d$	$8C_3$
A_1	1	1	1	1	1
A_2	1	1	-1	-1	1
E	2	2	0	0	-1
T_1; (x, y, z)	3	-1	1	-1	0
T_2	3	-1	-1	1	0

$\mathbf{T}$	E	$3C_2$	$4C_3$	$4C_3'$
A	1	1	1	1
E	1	1	ω	ω^2
	1	1	ω^2	ω
T	3	-1	0	0

Note: $\omega=e^{2\pi i/3}$

Also $\mathbf{O_h}=\mathbf{O}\times i$;
$\mathbf{T_h}=\mathbf{T}\times i$

Besides Eq. (4), two further relations[17] can be given by means of which the characters for all the possible representations of any finite group can be completely determined. The results given in Table I have been obtained[4, 6] in this way. For the various characters of any one representation (cf. the small table above on page 287)

$$\sum_{i=1}^{r} h_i\chi_i\bar{\chi}_i=g, \tag{5}$$

where $\bar{\chi}_i$ is the complex conjugate of χ_i; and also

$$h_ih_k\chi_i\chi_k=\chi_1\sum_{l=1}^{r} c_{(ik)l}h_l\chi_l, \tag{6}$$

where the coefficients $c_{(ik)l}$ are those which appear when one takes the "product of two classes" C_i and C_k (cf. reference 15, p. 170):

$$C_iC_k=C_kC_i=\sum_{l=1}^{r} c_{(ik)l}C_l. \tag{6a}$$

In order to use Eq. (6*a*) it is of course necessary to have a multiplication table of products of classes C_iC_k (including the case $i=k$). Such tables can be constructed by obvious methods when needed, for any symmetry group (cf. reference 6).

Explanation of tables. At the top of each table are given at the left (**bold-faced type**) the point groups to which it applies, at the right (*italic type* the elements of symmetry belonging to each point group. The notations for the point groups and for the symmetry elements are essentially those of Schönflies,[14] except that in the case of certain elements (reflections and rotary-reflections) an additional designation of the form iC_n (cf. Bethe[6]), showing how the element could be obtained as the product of a pure rotation C_n and the inversion i, is given for convenience. [In some cases also a $'$ or an x, y, or z has been added to help make clear the exact operation which is meant; Ewald[14] gives complete details as to the various operations. In every case the (or a) principal axis of symmetry is called the z axis,—even in the monoclinic system, where the axis is usually called y.] The symmetry elements are arranged in symmetry classes according to group theory[17] the number preceding the symbol for any symmetry element being the *number h* of equivalent elements of this kind forming the class (if no number is given, $h=1$). The *total number g* of symmetry elements belonging to any point group can be obtained by adding the h's, e.g., $g=2$ for $\mathbf{C_2}$ and $\mathbf{C_s}$, 8 for $\mathbf{D_4}$. *In the main* and lower part of each table are given at

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[17] Cf. A. Speiser, *Die Theorie der Gruppen von endlicher Ordnung*, second edition (J. Springer, Berlin, 1927), especially Chaps. 1, 2, 11, 12; cf. p. 28 for definition of a class, pp. 174–6 for Eqs. (4)–(6*a*). For an explanation of the relations of group theory to the present problem, reference 6 is valuable (cf. also reference 4).

the left the symbols, and at the right the characters χ, of all the irreducible representations of the point groups designated at the top of the table.

Outside each table are indicated one or two point groups not included in the table, e.g., $\mathbf{D_{6h}}$ in the case of the hexagonal table. Each of these contains the same symmetry classes as for some group in the table, plus an equal number of others each generated by multiplying one of the original set by the operation i (inversion), or in one case by σ_h. For example $\mathbf{D_{6h}} = \mathbf{D_6} \times i$ has all the six classes E, C_2, $2C_3$, etc. of $\mathbf{D_6}$ plus the six classes i, iC_2, $2iC_3$, etc. Each point group $\mathbf{G} \times i$ has two irreducible representations for each one of $\mathbf{G}$. For example, corresponding to A_1, A_2, etc. of $\mathbf{D_6}$ one has for $\mathbf{D_{6h}}$ the representations A_{1g}, A_{1u}, A_{2g}, A_{2u}, etc. A_{1g} and A_{1u} have the same characters as A_1 for the symmetry classes E, C_2, $\cdots$ common to $\mathbf{D_6}$ and $\mathbf{D_{6h}}$, while the characters of A_{1g} and A_{1u} for the classes i, iC_2, etc. are respectively $+1$ and -1 times the characters of A_1 for the classes E, C_2, etc. Similar relations hold for A_{2g}, A_{2u}, and so on.

For use in connection with the determination of selection rules, the behavior of the coordinates x, y, z under the *rotational operations* of each crystal system (monoclinic, triclinic, etc.) is given in the table or tables for that system (*heading Co*, and *symmetry classes as given in first line of table*). The behavior of each coordinate, or of a pair $(x \pm iy)$ or set of three (x, y, z in the cubic system only) of coordinates which are equivalent, is given by a set of characters whose correctness the reader can easily verify. Every such set of characters is found to agree with that of some representation in the table (cf. tables). For the operation i *the character for a coordinate or set of these* is always just the negative of that for operation E, and *for any symmetry class* niC_m it *is always just the negative of that for* nC_m.

TABLE Ia. *Some probable examples of molecules having symmetries belonging to various point groups.*

$\mathbf{C_s}$: NOCl, C_2H_4 derivatives like C_2H_3Cl, C_2H_2ClBr, $C_2HClBrI$. $\mathbf{C_2}$: perp. $C_2H_2Cl_2$. $\mathbf{C_{2h}}$: plane *trans*-$C_2H_2Cl_2$. $\mathbf{C_{2v}}$: plane *cis*-$C_2H_2Cl_2$, $(Cl_2C)CH_2$, CH_2Cl_2, H_2O_2, H_2O, NO_2, SO_2, NH_2Cl, HCHO. $\mathbf{V}$: partly rotated C_2H_4. $\mathbf{V_h}$: plane C_2H_4. $\mathbf{V_d}$: perp. C_2H_4. $\mathbf{D_{4h}}$: $PtCl_4^{=}$. $\mathbf{C_{4v}}$: distorted $PtCl_4^{=}$ (Pt out of plane). $\mathbf{D_{6h}}$: C_6H_6. $\mathbf{C_{6v}}$: C_6H_6 with planes of C and H displaced. $\mathbf{D_{3h}}$: NO_3^-, O_3 (if triangular), C_2H_6 when trigonal. $\mathbf{D_3}$, $\mathbf{D_{3d}}$: rotated forms of C_2H_6. $\mathbf{C_{3v}}$: NH_3, ClO_3^-, CH_3F, PCl_5(?) $\mathbf{T_d}$: CH_4, MnO_4^-. $\mathbf{O_h}$: SF_6, $PtCl_6^{=}$.

5. Selection rules

One can easily obtain the polarization and selection rules which limit transitions between the electronic states of a molecule conforming to any point group in Table I. To do this, one makes use of the fact that the coordinates x, y, z themselves,—or combinations of equivalent coordinates, e.g., (x, y) or $(x \pm iy)$, which are analogous to degenerate φ's or ψ's,—always belong like the φ's and ψ's to definite representations of the point groups, and can be characterized by sets of χ's (cf. Table I, and last paragraph of "Explanation" following it). To find out with what states a given state with wave function ψ_i can combine, for an electric moment Q, one makes use of the expansion[16]

$$Q\psi_i = \Sigma a_{ij}\psi_j. \qquad (7)$$

Here Q is proportional in the case of one electron, for dipole transitions, to x, y, or z, or to a combination $(x+iy, x-iy)$ or (x, y, z); or if there are several electrons one replaces for example x by a sum of x's, and so on. Every transition $\psi_i \leftrightarrow \psi_j$ is allowed for which a Q can be found giving $a_{ij} \neq 0$ in Eq. (7), but it is forbidden if $a_{ij} = 0$ for all Q's. If $a_{ij} = 0$ for all but one Q, the transition is polarized accordingly. Selection rules for quadrupole and other transitions can be obtained by using suitable expressions for Q. Selection rules obtained as above, of course, apply also to vibrational[5] and electronic × vibrational transitions.

In order to determine selection rules, Eq. (7) is applied in the following way. For any ψ_i belonging to any irreducible representation of a given point group, and for a given Q, one first determines for the product $Q\psi_i$ a set of characters, by multiplying the character of ψ_i for each symmetry class by the character of Q for the same class.

Very often the resulting set of characters of $Q\psi_i$ is at once identified as belonging to one of the irreducible representations of the group; this happens whenever Q or ψ_i, or both, belong to one-dimensional representations. This means that only ψ_j's which belong to the representation thus identified have $a_{ij} \neq 0$ in Eq. (7), and only such ψ_j's can combine with ψ_i with a moment of the type Q.

Example: let Q be z and let ψ_i belong to representation B_1 of point group $\mathbf{C_{4v}}$; cf. Table I, tetragonal system. Multiplying the character-systems of z and B_1, the resulting character-system is seen to be that of B_1, since in this case z belongs to the identical representation (characters 1, 1, 1, 1, 1).[To get the correct result, one must take care to notice that the signs of the characters of z, for the operations iC_2 and iC_2', must be reversed as compared with those given in the table, since the latter apply to the operations C_2 and C_2' (cf. last paragraph of explanation under Table I). A similar precaution must be taken in other cases too.] Hence one concludes that for a z moment, states (φ's or ψ's) belonging to B_1 can combine only with other states belonging to the same representation. Similarly one finds that for electric moments $x+iy$, states of type B_1 can combine only with those of type E. One sees thus that for dipole transitions the B_1 type combines only with types B_1 and E. The reader can easily determine the selection rules for A_1, A_2, and B_2 states by the same method.

Whenever Q and ψ_i both belong to representations which are more-than-one-dimensional, the system of characters obtained for Q_i is not that of an irreducible representation. In this case one has to resolve each character of $Q\psi_i$ into a sum of characters, in such a way that the resulting (two or more) sets of characters are those of irreducible representations. Such a resolution is always possible, and the result is unique.

Example: let Q be $x\pm iy$ and let ψ_i belong to E of $\mathbf{C_{4v}}$. The character-system (4, 4, 0, 0, 0) of the product $(x\pm iy)\psi_E$ is seen to be the sum of those of the representations A_1, A_2, B_1, and B_2 of $\mathbf{C_{4v}}$. We conclude that states belonging to E can combine, for a moment $x\pm iy$, with all these four types. From the characters of $z\psi_E$ one concludes further that for a z moment, states of type E can combine only with other states of type E.

For any point group $\mathbf{G}\times i$, the types of states are the same as for group $\mathbf{G}$, except that there is one $_g$ and one $_u$ representation for each representation of group $\mathbf{G}$ (cf. "Explanation of tables" under Table I for details). It is easily shown by making use of the fact that every Q of type x, y, z or $x\pm iy$ changes sign under the operation i, that for dipole transitions one has for any group $\mathbf{G}\times i$ just the same selection rules as for the corresponding group $\mathbf{G}$, *plus the rule* $g\leftrightarrow u$ ($g\leftrightarrow g$, $u\leftrightarrow u$ forbidden). This is the same rule which holds for all systems having a center of inversion (atoms, electronic ψ of homopolar diatomic molecules, total ψ of any molecule, etc.).

5a. Franck-Condon principle. The electronic selection-polarization rules derived in section 5 hold strictly only for the case that the symmetry of the molecule belongs to the same point group in the initial and final states. (Changes of dimensions not causing a change in the point group do not, however, affect the selection rules.) The most probable transitions, according to the Franck principle, are those in which the nuclear configuration does not change its dimensions or velocities. Since even moderately large deviations from the Franck principle, which occur only with low probability, would rarely if ever cause more than a moderate break-down in the electronic selection rules, we conclude that, for any given initial state, in emission or absorption, transitions which violate the electronic selection rules belonging to the point group of this initial state should occur only with very low, usually negligible, intensity.

In the case of electronic transitions which do *not* violate the selection rules of the initial point group, the extent of deviations from the predictions of the Franck-Condon rule strictly applied, should presumably be similar to that in diatomic molecules. For an initial state without nuclear vibration or internal rotation, the application of the Franck-Condon principle shows that in many cases an electronic change may result in high-amplitude vibrations or internal rotations (cf. III for an example). These may give rise to large changes in the arrangement of the nuclei, but this makes little difference for the electronic selection rules, since according to Franck these depend mainly on what happens at the instant the light quantum is absorbed or emitted, before the nuclei have had time to move much.

If one has an initial state of high-amplitude vibration or internal rotation such that the nuclei are continually passing through a variety of configurations, one must determine what the selection rules are for each different point group whose symmetry the nuclei take on. Only such electronic selection rules as are common to all the different configurations are strict. Furthermore, if as usual there are preferred configurations in which the nuclei spend most of their time, and if these, but not intermediate, configurations, demand certain selection rules, then these rules must hold approximately.—In dealing with all such cases, one needs of course to know the rules for correlating electronic states of different point groups (cf. section 6, paragraph just before Table II, but also section 8*c*).

6. Resolution of representations of symmetry groups (atomic and molecular) into those of groups of lower symmetry

An important problem is the resolution of a reducible representation into irreducible ones.[15, 17] An example where this problem occurs, and the very simple method of solving it, have been given in section 5. Other important examples occur when, starting with a physical system having relatively high symmetry, the symmetry is altered in such a way that the new symmetry group is a subgroup of the old one, i.e., is a group containing just a part of the symmetry elements of the old group, but no new ones. Examples are: (*a*) an atom subjected to a perturbing electric field, as in a crystal[6] or as in the formation of a molecule; or imagined modified by the splitting of its nucleus to give a diatomic or polyatomic molecule; (*b*) a molecule of high symmetry distorted to one of lower symmetry, for example tetrahedral CH_4 deformed by pulling one H atom out of position.

In many cases, degenerate representations split up partly or wholly when the symmetry of a molecular system is decreased, but the total number of different irreducible representations generally decreases. The new representations can be obtained by the following method. One tests the effect of each class of symmetry elements of the *new group* on any desired representation (or specifically on a particular φ or ψ) of the old group, and writes down the resulting set of characters. If the original representation was nondegenerate, this set of characters is at once identified as belonging to a definite representation of the new group. Otherwise, one has a reducible representation which can be resolved into a sum of irreducible representations of the new group by the method stated in section 5 (second from last paragraph). The result is always unique.[15, 17] Examples are given by Bethe,[6] and in the following Tables II–IV.

In the course of the present work, it will be convenient for various purposes to have reduction tables showing how atomic→polyatomic, diatomic→polyatomic, and polyatomic→polyatomic representations of lower symmetry. Tables II–IV are not complete, but cover a number of the cases most likely to be needed. Other results can be worked out easily when needed (cf. Table II, note *c* and Table III, notes *a*, *d*, *e*). The tables with their notes are self-explanatory.

In using any table, care should be taken to be sure that the relations between the axes of the two groups with which one is concerned are the same as in the table. Otherwise the table is not applicable. In the tables, the only cases given are those where the z axes of the more and the less symmetrical group with which any table deals are coincident. Such cases are the most common in practice.

Sometimes one has two symmetry groups with some elements in common, others peculiar to each, and wishes to know in what way the representations of the one group would go over into those of the other if the symmetry were altered from the one to the other case. An *example* is the correlation of energy levels between the states of plane and "perpendicular" C_2H_4 (cf. III, and section 8*c* below). In such cases, just those symmetry elements which are common to the two groups are also possessed by the symmetry group corresponding to an arrangement of nuclei intermediate between those of the two original cases. One then reduces the representations of each of the latter in terms of those of the intermediate group, which is a sort of greatest common factor. Then one applies the usual rule for adiabatic correlations, namely that these are so made that, on the energy-level diagram, no two lines cross which denote states belonging to the same representation of the intermediate symmetry group.

Explanation of Table IV. The meaning of the tables should be clear from the following detailed interpretation of the fifth small table, headed $\mathbf{D_{4h}}\,|\,\mathbf{V_h}\ \mathbf{V_d}\ \mathbf{C_{4v}}$. This table shows what each of the ten representations of $\mathbf{D_{4h}}$ goes over into if the symmetry is reduced to $\mathbf{V_h}$, or $\mathbf{V_d}$, or $\mathbf{C_{4v}}$. For example, A_{1g}, A_{1u}, A_{2g}, etc., of $\mathbf{D_{4h}}$ go over respectively into A_{1g}, A_{1u}, B_{1g}, etc. of $\mathbf{V_h}$, or into A_1, B_1, A_2, etc. of $\mathbf{V_d}$, or into A_1, A_2, A_2, etc. of $\mathbf{C_{4v}}$. Also obviously (not in the tables) A_{1g} and A_{1u} of $\mathbf{D_{4h}}$ would go into A_1 of $\mathbf{D_4}$, and so on.

Table IV is by no means complete; other reductions when needed can easily be obtained, as were those given, by methods described in sections 6, 5. In all cases the z axes of the two groups considered are taken as coincident; otherwise different results would in general be obtained. In some cases ($\mathbf{C_{4v}}\rightarrow\mathbf{C_{2v}}$, $\mathbf{C_{6v}}\rightarrow\mathbf{C_{3v}}$) the result depends also on which of two sets of vertical planes of the larger group is identified

TABLE II. *Resolution of atomic representations into irreducible representations of molecular symmetry groups.*

Atom	$\mathbf{O_h}$	$\mathbf{T_d}$	$\mathbf{D_{6h}}$	$\mathbf{C_{3v}}$	$\mathbf{D_{4h}}$	$\mathbf{C_{2v}}$
	(all g, u)		(all g, u)		(all g, u)	
$\mathbf{S_g}$, $\mathbf{S_u}$	A_1	A_1, A_2	A_1	A_1, A_2	A_1	A_1, A_2
$\mathbf{P_g}$, $\mathbf{P_u}$	T_1	T_1, T_2	$A_2+E^*_*$	A_2+E, A_1+E	A_2+E	$A_2+B_1+B_2$, $A_1+B_1+B_2$
$\mathbf{D_g}$, $\mathbf{D_u}$	$E+T_2$	$E+T_2$, $E+T_1$	A_1+E^* $+E^*_*$	A_1+2E, A_2+2E	A_1+B_1 $+B_2+E$	$2A_1+A_2+B_1+B_2$, $A_1+2A_2+B_1+B_2$

Notes: (*a*) S_g, S_u, P_g, P_u, D_g, D_u are usually written S, S^0, P, P^0, D, D^0. (*b*) The table holds also for orbitals as follows: s behaves like S_g, p like P_u, d like D_g. (*c*) The results for $\mathbf{O_h}$, $\mathbf{D_{6h}}$, and $\mathbf{D_{4h}}$ are from reference 6, while the remaining results, and any desired results for other point groups, can be obtained from those for $\mathbf{O_h}$, $\mathbf{D_{6h}}$, and $\mathbf{D_{4h}}$ by using Tables I and IV. (*d*) Bethe[6] gives additional results, for the relations between F, G, . . . atomic states and the representations of $\mathbf{O_h}$, $\mathbf{D_{6h}}$, and $\mathbf{D_{4h}}$. (*e*) For the relations between atomic and diatomic (or linear-molecule) representations, cf. Wigner and Witmer, Zeits. f. Physik **51**, 859 (1928); or reference 15 or Mulliken, Rev. Mod. Phys. **4**, 1932 (bottom page 20).

TABLE III. *Resolution of representations of diatomic (or linear-molecule) groups* $\mathbf{C_{\infty v}}$ *and* $\mathbf{D_{\infty h}}$ *into those of some other molecular symmetry groups.*

$\mathbf{D_{\infty h}}$	$\mathbf{D_{6h}}$	$\mathbf{C_{6v}}$	$\mathbf{C_{3v}}$	$\mathbf{D_{4h}}$	$\mathbf{C_{4v}}$	$\mathbf{C_{2v}}$
$\Sigma^+{}_{g,\,u}$	A_{1g}, A_{2u}	A_1	A_1	A_{1g}, A_{2u}	A_1	A_1
$\Sigma^-{}_{g,\,u}$	A_{2g}, A_{1u}	A_2	A_2	A_{2g}, A_{1u}	A_2	A_2
$\Pi_{g,\,u}$	$E^*_{*g,\,u}$	E^*_*	E	$E_{g,\,u}$	E	B_1+B_2
$\Delta_{g,\,u}$	$E^*{}_{g,\,u}$	E^*	E	$B_{1g,\,u}+B_{2g,\,u}$	B_1+B_2	A_1+A_2
$\Phi_{g,\,u}$	$B_{1g,\,u}+B_{2g,\,u}$	B_2+B_1	A_1+A_2	$E_{g,\,u}$	E	B_1+B_2
$\Gamma_{g,\,u}$	$E^*{}_{g,\,u}$	E^*	E	$A_{1g,\,u}+A_{2g,\,u}$	A_1+A_2	A_1+A_2

Notes: (*a*) Table III holds only if the symmetry (z) axis of the diatomic case coincides with the z axis of the other case. Other results are obtained for other relations between the axes of the two cases. (*b*) Table III of course applies equally well for the corresponding small letters, e.g., $\sigma_{g,\,u}$ behave like $\Sigma^+{}_{g,\,u}$ and give a_{1g}, a_{2u}, and so on. (*c*) Table III is applicable also (dropping g's and u's) for the resolution of the representations Σ^+, Σ^-, Π, Δ, . . . of the group $\mathbf{C_{\infty v}}$ ($\mathbf{D_{\infty h}}=\mathbf{C_{\infty v}}\times i$) into representations of $\mathbf{C_{6v}}$, $\mathbf{C_{4v}}$, $\mathbf{C_{3v}}$, $\mathbf{C_{2v}}$, etc., but the representations of $\mathbf{C_{\infty v}}$ cannot, of course, be resolved into those of $\mathbf{D_{6h}}$, $\mathbf{D_{4h}}$ or other groups of type $\mathbf{G}\times i$. (*d*) Resolution, when possible, into representations of other point groups can be effected by using first Table III, then Table I. Resolution of representations of $\mathbf{C_{\infty v}}$ and $\mathbf{D_{\infty h}}$ into those of point groups belonging to the cubic system is not possible. Even and odd (g and u) representations of $\mathbf{D_{\infty h}}$ must in general be treated separately. (*e*) In constructing Table III, one needs first an auxiliary table of characters showing how the representations of $\mathbf{C_{\infty v}}$ and $\mathbf{D_{\infty h}}$ behave under various symmetry operations of the point groups. Such a table can easily be constructed by the reader by using the following relations. For the operation E, $\chi=1$ for Σ, 2 for all other states. For a rotation through any angle φ around the z axis, $\chi=1$ for all Σ states, $\chi=e^{i\Lambda\varphi}+e^{-i\Lambda\varphi}=2\cos\Lambda\varphi$ for states with $\Lambda>0$ (Π, Δ, . . . states). For reflection in any plane through the z axis, $\chi=+1$ for Σ^+, -1 for Σ^-, 0 for all other states; σ behaves like Σ^+. (Cf. Wigner and Witmer, Zeits. f. Physik **51**, 862, 1928, or reference 15, p. 40.) These results apply as well to $\mathbf{C_{\infty v}}$ as to $\mathbf{D_{\infty h}}$. For $\mathbf{D_{\infty h}}$ one needs also the following: for operation i, χ is ±1 times its value for E, according as the diatomic state is g or u; for reflection in the xy plane, which is equivalent to i times a rotation of π around the z axis, χ is equal to ±1 (depending on the sign of χ for i) times the χ for the rotation; for rotation by π around any axis perpendicular to the z axis, which is equivalent to i times reflection in any plane passing through the z axis, χ is equal to ±1 (depending on the sign of χ for i) times χ for the reflection, and so, as one easily finds, has the value $+1$ for $\Sigma^+{}_g$ and $\Sigma^-{}_u$, -1 for $\Sigma^-{}_g$ and $\Sigma^+{}_u$, 0 for all other states.

TABLE IV. *Resolution of polyatomic representations into those of groups of lower symmetry.*

$\mathbf{C_{2h}}$	$\mathbf{C_i}$	$\mathbf{C_s}$
$A_{g,u}$	$A_{g,u}$	A', A''
$B_{g,u}$	$A_{g,u}$	A'', A'

$\mathbf{V_h}$	$\mathbf{C_{2h}}$	$\mathbf{C_{2v}}$
$A_{1g,u}$	$A_{g,u}$	A_1, A_2
$B_{1g,u}$	$A_{g,u}$	A_2, A_1
$B_{2g,u}$	$B_{g,u}$	B_1, B_2
$B_{3g,u}$	$B_{g,u}$	B_2, B_1

$\mathbf{V}$	$\mathbf{C_2}$
A_1	A
B_1	A
B_2	B
B_3	B

$\mathbf{C_{2v}}$	$\mathbf{C_2}$
A_1	A
A_2	A
B_1	B
B_2	B

$\mathbf{D_{4h}}$	$\mathbf{V_h}$	$\mathbf{V_d}$	$\mathbf{C_{4v}}$
(all g, u)	(all g, u)		
A_1	A_1	A_1, B_1	A_1, A_2
A_2	B_1	A_2, B_2	A_2, A_1
B_1	A_1	B_1, A_1	B_1, B_2
B_2	B_1	B_2, A_2	B_2, B_1
E	B_2+B_3	E	E

$\mathbf{V_d}$	$\mathbf{V}$	$\mathbf{C_{2v}}$
A_1	A_1	A_1
A_2	B_1	A_2
B_1	A_1	A_2
B_2	B_1	A_1
E	B_2+B_3	B_1+B_2

$\mathbf{C_{4v}}$	$\mathbf{C_{2v}}$
A_1	A_1
A_2	A_2
B_1	A_1 or A_2
B_2	A_2 or A_1
E	B_1+B_2

$\mathbf{D_{6h}}$	$\mathbf{D_{3d}}$	$\mathbf{D_{3h}}$	$\mathbf{C_{6v}}$
(all g, u)	(all g, u)		
A_1	A_1	A_1', A_1''	A_1, A_2
A_2	A_2	A_2', A_2''	A_2, A_1
B_1	A_2	A_1'', A_1'	B_2, B_1
B_2	A_1	A_2'', A_2'	B_1, B_2
E^*	E	E', E''	E^*
E^*_*	E	E'', E'	E^*_*

$\mathbf{D_{3h}}$	$\mathbf{C_{3v}}$
A_1'	A_1
A_2'	A_2
A_1''	A_2
A_2''	A_1
E'	E
E''	E

$\mathbf{C_{6v}}$	$\mathbf{C_{3v}}$
A_1	A_1
A_2	A_2
B_2	A_2 or A_1
B_1	A_1 or A_2
E^*	E
E^*_*	E

$\mathbf{D_{3d}}$	$\mathbf{C_{2h}}$	$\mathbf{C_{3v}}$
(all g, u)	(all g, u)	
A_1	A	A_1, A_2
A_2	B	A_2, A_1
E	$A+B$	E

$\mathbf{D_3}$	$\mathbf{C_2}$
A_1	A
A_2	B
E	$A+B$

$\mathbf{C_{3v}}$	$\mathbf{C_s}$
A_1	A'
A_2	A''
E	$A'+A''$

$\mathbf{O_h}$	$\mathbf{D_{4h}}$	$\mathbf{T_d}$
(all g, u)	(all g, u)	
A_1	A_1	A_1, A_2
A_2	B_1	A_2, A_1
E	A_1+B_1	E
T_1	A_2+E	T_1, T_2
T_2	B_2+E	T_2, T_1

$\mathbf{T_d}$	$\mathbf{V_d}$	$\mathbf{C_{3v}}$
A_1	A_1	A_1
A_2	B_1	A_2
E	A_1+B_1	E
T_1	A_2+E	A_2+E
T_2	B_2+E	A_1+E

with a set of vertical planes of the smaller group; this accounts for the alternatives given in the tables.

7. Determination of possible resultant electron states for various electron configurations

An important problem is that of determining, for a given electron configuration, what are the possible electronic states. For example with a configuration $a_1^2b_2e^3$ of a molecule having the symmetry $\mathbf{C_{4v}}$, these states would be just ^3E and ^1E.

First we may consider the case that the molecule has its electrons all in different, molecular, orbitals. One forms the product, for each symmetry operation, of the characters χ for the various orbitals which are occupied, and thus gets a definite system of characters for the resultant product representation.[6, 15] This either is immediately identified as an irreducible representation of the group, defining the type of the resultant electronic state, or else it can be resolved into a sum of such representations, corresponding to several possible resultant states (cf. sections 5, 6 for the method). The resultant spin has of course all the possible values one would get for the same number of non-equivalent electrons in an atom or diatomic molecule.

Examples: (*a*) given the configuration a_2b_2 of $\mathbf{C_{4v}}$, the product representation is immediately identified as B_1, and the states are $^3B_1$ and $^1B_1$. (*b*) Given $a_2b_1e^*$ of $\mathbf{D_6}$, one gets $^4E^*_*$, $^2E^*_*$, $^2E^*_*$. (*c*) Given $e^*e^*_*$ of $\mathbf{D_6}$, one gets the product character-system 4, -4, 1, -1, 0, 0, and the states $^3B_1$, $^3B_2$, $^3E^*_*$, $^1B_1$, $^1B_2$, $^1E^*_*$.

The same method can be used if one thinks of a molecule as composed of a core plus one or more outer, perhaps valence, electrons. For example, with point group $\mathbf{C_{4v}}$, a core of type $^3B_2$ plus an outer electron of type e give states ^4E and ^2E.—The same point of view can also often be applied in determining the possible states of a united-system (molecule) in relation to the states of two part-systems (atoms or radicals) which come together. Discussion of such dissociation problems will, however, be postponed.

In a polyatomic molecule a group of $2n$ electrons occupying any n-foldly degenerate molecular orbital functions is a closed shell; it is required by the Pauli principle to have zero resultant spin, and it belongs to the identical representation of the molecule's point group, i.e., all the χ's are $+1$ (cf. fifth following paragraph for proof). The totality of electrons in closed shells composed of molecular orbitals, plus the totality of unshared electrons assigned to closed shells of atomic orbitals (assuming that no atomic closed shell has been removed *in toto* from the molecule), can always be regarded as a core, whose state always belongs to the identical representation with zero spin (cf. fifth following paragraph for proof). From the rule for getting the χ's for a product representation, it is now evident that such a core, since all its χ's are $+1$, can be disregarded in finding the nature of the resultant state of the whole molecule, in the same way that closed shells can be disregarded in the case of atoms or diatomic molecules.—It may also be noted here that, except for their spins, electrons in molecular orbitals belonging to the identical representation (a_1, a_{1g}, etc.) can also be disregarded in determining the resultant state.

Next we must consider the case where, aside from closed shells, two or more equivalent electrons are present in degenerate orbitals. (Two electrons in a nondegenerate orbital of course form a closed shell.) In case both equivalent and non-equivalent electrons are present, one of course first finds the resultant states of each of these separately, then treating the one set of electrons as a core, finds the final resultant states.

Bethe has attacked the problem by a method similar to that customary for the analogous atomic problem. He assumes the molecule, belonging to a specified point group, to be subjected to a perturbing electric field of sufficiently low symmetry so that the degenerate representations of the original group are split up. The Pauli principle can then be applied, and the nature of the allowed states for the desired case determined by resynthesizing the perturbed representations into those of the original group (cf. reference 6, pages 177–180). This method (hereafter called *method A*) is, however, not in general adequate, since the correlations by means of which one goes backward from the perturbed to the unperturbed representations do not always give unambiguous results (cf. e.g., the two alternative sets of Γ's for Bethe's g_5^2 of the tetragonal holohedral and γ_5^2 of the cubic holohedral group), although it is clear that for every set of equivalent electrons there must exist a unique set of resultant electronic states. Unique results can, however, be obtained by using method A in combination with another method (B) described below.

In the monoclinic, triclinic and orthorhombic systems of point groups, all the representations are nondegenerate, so that the present problem does not arise. In the tetragonal, hexagonal, and rhombohedral systems, we must consider cases like e^2, e^3, where e is twofoldly degenerate. In the cubic system we have e^2, e^3, also t^2, t^3, t^4, t^5, where t is threefoldly degenerate. It will be sufficient to consider just the three holohedral point groups $\mathbf{D_{4h}}$, $\mathbf{D_{6h}}$, and $\mathbf{O_h}$, for as can easily be seen, any desired results for other point groups having degenerate representations can be obtained by a process of resolution and comparison, by using Tables IV, I. (An example is given in the third following paragraph.)

Beginning with $\mathbf{D_{4h}}$, *method B* proceeds as in the following example. From Table III we note that π_u, π_g of the diatomic group $\mathbf{D_{\infty h}}$ go over, if the symmetry is reduced to $\mathbf{D_{4h}}$, into e_u, e_g. Likewise π_u^2 and π_g^2 of $\mathbf{D_{\infty h}}$ must go over, for the imaginary case of no coupling between the two electrons, into $(e_u)^2$ and $(e_g)^2$ of $\mathbf{D_{4h}}$. If now one allows some coupling between the electrons, one gets for $\mathbf{D_{\infty h}}$ the states $^3\Sigma^-{}_g$, $^1\Delta_g$, $^1\Sigma^+{}_g$ (the same for π_u^2 as for π_g^2). Since these results are independent of the strength of the coupling, these states of $\mathbf{D_{\infty h}}$ must be correlated with the states obtainable from $(e_u)^2$ and $(e_g)^2$ of $\mathbf{D_{4h}}$. Reference to Table III shows that $^3\Sigma^-{}_g$, $^1\Delta_g$, $^1\Sigma^+{}_g$ of $\mathbf{D_{\infty h}}$ go over into $^3A_{2g}$, $^1B_{1g}$, $^1B_{2g}$, and $^1A_{1g}$ of $\mathbf{D_{4h}}$, which are, then, the desired possible resultant states of the configuration $(e_u)^2$, and of $(e_g)^2$. In a similar way, since $\pi_u{}^3$ gives ${}^2\Pi_u$ and $\pi_g{}^3$ gives ${}^2\Pi_g$, one concludes that $(e_u)^3$ of $\mathbf{D_{4h}}$ gives ${}^2E_u$ and $(e_g)^3$ gives ${}^2E_g$.

In a similar way it follows, from the fact that $\pi_g{}^4$ or $\pi_u{}^4$ gives the identical representation ${}^1\Sigma^+{}_g$, that $(e_u)^4$ or $(e_g)^4$ gives ${}^1A_{1g}$. In an analogous manner, one can easily show, for any point group outside the cubic system, that a molecular closed shell always gives the identical representation of the group. For point groups of the cubic system, a different method, like that used below for such groups, gives a corresponding result.—If one regards as a core the unshared electrons which in the present method are assigned to closed shells of atomic orbitals, it follows from (1) of the proof given in section 2*a* that this core belongs to the identical representation of the molecule's point group, provided equivalent atoms have the same sets of closed shells (as they of course have in saturated molecules). Hence the totality of electrons in such atomic closed shells, together with those in closed shells of molecular orbitals, can be treated as a core which belongs to the identical representation.

If we are interested not in $\mathbf{D_{4h}}$ as above, but for example in $\mathbf{V_d}$, to which perp. C_2H_4 belongs (cf. section 8*b*), one easily finds from Table IV, by resolution of representations of $\mathbf{D_{4h}}$ into those of $\mathbf{V_d}$, that the set of states corresponding to e^2 of $\mathbf{V_d}$ is ${}^3A_2$, ${}^1B_1$, ${}^1B_2$, ${}^1A_1$, while that corresponding to e^3 is ${}^2E$.

Next considering $\mathbf{D_{6h}}$, we find from Table III that $\pi_{g,u}$ go over into $e^{*}_{*g,u}$, and $\delta_{g,u}$ into $e^*{}_{g,u}$. Matching the states of e^{*2}_{*},—either g or u,—against those of π^2, and those of e^{*2} against those of δ^2 (which are ${}^3\Sigma^-{}_g$, ${}^1\Gamma_g$, ${}^1\Sigma^+{}_g$), one finds that both e^{*2} and e^{*2}_{*} give rise to the set ${}^3A_{2g}$, ${}^1E^*{}_g$, ${}^1A_{1g}$. Similarly one finds that $e^*{}_g{}^3$ gives ${}^2E^*{}_g$, $e^{*}_{*g}{}^3$ gives ${}^2E^{*}_{*g}$, $e^*{}_u{}^3$ gives ${}^2E^*{}_u$, $e^{*}_{*u}{}^3$ gives ${}^2E^{*}_{*u}$.

For the group $\mathbf{O_h}$, method *A* gives the desired results if it is applied twice, reducing one time from $\mathbf{O_h}$ to $\mathbf{D_{4h}}$, then again from $\mathbf{O_h}$, through $\mathbf{T_d}$, to $\mathbf{C_{3v}}$. Reduction to $\mathbf{D_{4h}}$ alone, or to $\mathbf{C_{3v}}$ alone, gives ambiguous results, but when the various sets of states obtained from the two reductions are compared, it is found that there is always one and only one set of states which is common to both.

First we may consider $e_g{}^2$ and $e_u{}^2$ of $\mathbf{O_h}$. Reducing to $\mathbf{D_{4h}}$, e_g or e_u gives $a_{1g}+b_{1g}$ or $a_{1u}+b_{1u}$ (cf. Table IV). Hence $3_g{}^2$ of $\mathbf{O_h}$ corresponds to $(a_{1g}+b_{1g})^2=a_{1g}{}^2+a_{1g}b_{1g}+b_{1g}{}^2$ of $\mathbf{D_{4h}}$. The groups $a_{1g}{}^2$ and $b_{1g}{}^2$ of $\mathbf{D_{4h}}$ are closed shells (cf. Table I), so each gives ${}^1A_{1g}$, while $a_{1g}b_{1g}$ gives ${}^3B_{1g}$ and ${}^1B_{1g}$; so altogether we have $2{}^1A_{1g}+{}^3B_{1g}+{}^1B_{1g}$ of $\mathbf{D_{4h}}$. As is easily verified, $e_u{}^2$ of $\mathbf{O_h}$ gives the same result. Now going backward to states of $\mathbf{O_h}$, using Table IV, we find two possibilities: (*a*) ${}^3A_{2g}+{}^1E_g+{}^1A_{1g}$; (*b*) ${}^3A_{2g}+{}^1A_{2g}+2{}^1A_{1g}$. To decide between these, we must use the reduction to $\mathbf{C_{3v}}$.

Reducing to $\mathbf{C_{3v}}$, one first finds (Table IV) that both e_g and e_u of $\mathbf{O_h}$ go into e of $\mathbf{T_d}$ and thence into e of $\mathbf{C_{3v}}$. Hence to find either $e_g{}^2$ or $e_u{}^2$ of $\mathbf{O_h}$, we must find e^2 of $\mathbf{C_{3v}}$. Using the result obtained in a previous paragraph for $\mathbf{D}_{6h}$, that $e^*{}_g{}^2=e^*{}_u{}^2=e^{*}_{*g}{}^2=e^{*}_{*u}{}^2={}^3A_{2g}+{}^1E^*{}_g+{}^1A_{1g}$, and reducing to $\mathbf{C_{3v}}$ with the help of Table IV, we find that e^2 of $\mathbf{C_{3v}}={}^3A_2+{}^1E+{}^1A_1$. Going backward from $\mathbf{C_{3v}}$ to $\mathbf{T_d}$ and thence to $\mathbf{O_h}$ by Table 4, we find as possibilities for $e_g{}^2$ and $e_u{}^2$ of $\mathbf{O_h}$ the following: ${}^3A_{2g}+{}^1T_{2g}$; ${}^3A_{2g}+{}^1E_g+{}^1A_{1g}$, and six other sets which are obviously out of the question because each contains one or more odd (*u*) states.

One sees that the correct result is ${}^3A_{2g}+{}^1E_g+{}^1A_{1g}$, since this and only this is common to the possibilities offered by the reductions to $\mathbf{D_{4h}}$ and to $\mathbf{C_{3v}}$. The result is the same here as that given by Bethe. By similar methods one can show that $e_g{}^3$ gives ${}^2E_g$, $e_u{}^3$ gives ${}^2E_u$, for $\mathbf{O_h}$.

The results given above, and others which have been obtained for $\mathbf{O_h}$ by the method just used, are summarized in Table V. The results for $\mathbf{O_h}$ differ in part from those given by Bethe (cf. his Table XV), in that a decision is made between some alternatives left open by him. (Bethe considered that both alternatives were possible, depending on circumstances, but this seems not to be correct.)

TABLE V. *Resultant states for various numbers of equivalent electrons in molecular orbitals.*

No. Els.	e_g, e_u of $\mathbf{D_{4h}}$	e^*_g, e^*_u of $\mathbf{D_{6h}}$	e^*_{*g}, e^*_{*u} of $\mathbf{D_{6h}}$	e of $\mathbf{C_{3v}}$
1	$^2E_{g,\,u}$	$^2E^*_{g,\,u}$	$^2E^*_{*g,\,u}$	^2E
2	$^3A_{2g}+^1B_{1g}+^1B_{2g}+^1A_{1g}$	$^3A_{2g}+^1E^*_g+^1A_{1g}$	$^3A_{2g}+^1E^*_g+^1A_{1g}$	$^3A_2+^1E+^1A_1$
3	$^2E_{g,\,u}$	$^2E^*_{g,\,u}$	$^2E^*_{*g,\,u}$	^2E
4	$^1A_{1g}$	$^1A_{1g}$	$^1A_{1g}$	$^1A_1$

	e_g, e_u of $\mathbf{O_h}$	t_{1g}, t_{1u} of $\mathbf{O_h}$	t_{2g}, t_{2u} of $\mathbf{O_h}$
1	$^2E_{g,\,u}$	$^2T_{1g,\,u}$	$^2T_{2g,\,u}$
2	$^3A_{2g}+^1E_g+^1A_{1g}$	$^3T_{1g}+^1A_{1g}+^1E_g+^1T_{2g}$	$^3T_{1g}+^1A_{1g}+^1E_g+^1T_{2g}$
3	$^2E_{g,\,u}$	$^4A_{1g,\,u}+^2E_{g,\,u}+^2T_{1g,\,u}+^2T_{2g,\,u}$	$^4A_{2g,\,u}+^2E_{g,\,u}+^2T_{1g,\,u}+^2T_{2g,\,u}$
4	$^1A_{1g}$	Same as for two electrons	
5		Same as for one electron	
6		$^1A_{1g}$	$^1A_{1g}$

APPLICATION TO CH_2 AND C_2H_4

8. The molecules CH_2 and C_2H_4

In III of this series, the formation of C_2H_4 from $2CH_2$ was discussed. Several statements were made there, without proof, whose justification depends on the results of the present paper. In order to give this justification and also to illustrate the methods described above, the electronic structures of CH_2 and C_2H_4 will be considered again now. The following discussion and that in III supplement each other, and should be read together.

Applications to other molecules will be given in later papers. The basis for a number of conclusions stated in I of this series can, however, now easily be found by the reader, if he wishes, in the Tables I–IV given above.

8a. The molecule CH_2. The CH_2 molecule, assuming it to have the form of an isosceles triangle (cf. III), has the symmetry of the point group $\mathbf{C_{2v}}$ (cf. Table I). Electronic configurations of CH_2 were given in III in terms of molecular orbitals called $[s]$, $[x]$, $[y]$, $[z]$, and respectively capable of being approximated by linear combinations of $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals of the carbon atom with hydrogen $1s$ orbitals, hereafter called α and β. With the choice of x, y, z axes described in III it will be found, on testing their behavior under the symmetry operations of $\mathbf{C_{2v}}$, that carbon $2s$, $2p_x$, $2p_y$, $2p_z$ respectively belong to the representations a_1, b_1, b_2, a_1 of $\mathbf{C_{2v}}$. The linear combinations with α and β, formed in such a way that they still belong to these same representations, are

$$\left.\begin{aligned}&[s]=a(2s)+b(\alpha+\beta)+c(2p_z);\quad [x]=2p_x.\\&[y]=a'(2p_y)+b'(\alpha-\beta).\\&[z]=a''(2p_z)+b''(\alpha+\beta)+c''(2s).\end{aligned}\right\}\qquad(8)$$

The fact that $2s$ and $2p_z$ of carbon belong to the same representation allows and requires them to hybridize somewhat with each other when CH_2 is formed. Since α and β by themselves are not representations of $\mathbf{C_{2v}}$, their hybridization with the carbon orbitals, necessary to obtain bonding orbitals in CH_2, can take place freely provided the coefficients of α and β are so related that the resulting hybrids belong to representations of $\mathbf{C_{2v}}$. In the case of $[x]$, these coefficients are zero because $2p_x$ belongs to a representation b_1 which demands that the plane of the three nuclei shall be a nodal plane.

The fact that the electron configuration $1s^2[s]^2[y]^2[z]^2$ of Eq. (1) of III gives a $^1A_1$ state (called $^1\Gamma_1$ in the notation of III) is an illustration of the rule that a set of closed shells always gives the identical representation (cf. section 7). On applying the rules of section 7, one finds that $\cdots[z][x]$ in Eq. (1) of III, which is of the type $\cdots a_1b_1$, gives a $^3B_1$ and a $^1B_1$ state (called $^3\Gamma_3$ and $^1\Gamma_3$ in III), of which we may reasonably expect the $^3B_1$ to have the lower energy.

8b. Formation of C_2H_4. The normal plane form of C_2H_4 (rotation angle 0° or 180° in Fig. 2 of III) has the symmetry $\mathbf{V_h}$, the perp. form (rotation angle 90° or 270°) the symmetry $\mathbf{V_d}$, while all intermediate forms belong to $\mathbf{V}$: cf. Table I. In order to make the notation used in III conform to the revised notation of Table I, the following changes must be made: *for plane*

C_2H_4 in III (Eqs. (2, 3, 5) and elsewhere), *read* $^1A_{1g}$, $^3B_{1u}$, $^1B_{1u}$ *everywhere instead of* $^1\Gamma_{1g}$, $^3\Gamma_{4u}$, $^1\Gamma_{4u}$; *for perp.* C_2H_4 in III (Eqs. (6, 7), Fig. 1, and elsewhere), *read* $^3A_2$, $^1B_1$, $^1B_2$, $^1A_1$ *instead of* $^3\Gamma_3$, $^1\Gamma_2$, $^1\Gamma_4$, and $^1\Gamma_1$.

The orbitals $[x+x]$, and so on, of plane C_2H_4 (cf. III) have been so constructed from $[x]$, and so on, of CH_2 that they conform to representations of $\mathbf{V_h}$. As the reader can easily verify by testing the behavior of each under the symmetry operations of $\mathbf{V_h}$ (cf. Table I), the orbitals $[x+x]$, $[x-x]$, $[y+y]$, $[y-y]$, $[z+z]$ of plane C_2H_4 belong respectively to the representations b_{3u}, b_{2g}, b_{2u}, b_{3g}, a_{1g}. Any electron configuration consisting of closed shells, e.g., that in Eq. (2) or (3) of III, gives a $^1A_{1g}$ state. By applying the rule given in section 7, it is found that $\cdots[x+x][x-x]$, which is of the type $\cdots b_{3u}b_{2g}$, gives a $^3B_{1u}$ and a $^1B_{1u}$ state ($^3\Gamma_{4u}$ and $^1\Gamma_{4u}$ in the notation of III, cf. Eq. (5)).

Next we may consider perp. C_2H_4 (symmetry $\mathbf{V_d}$), and its formation from $2CH_2$, each in the state $\cdots[z][x]$, $^3B_1$ with their planes at right angles. The axes appropriate to $\mathbf{V_d}$ then are an x and a y axis whose directions make 45° angles with the x and y directions of the two CH_2, and a z axis coincident with the z axes of both. To get stable forms of perp. C_2H_4, one forms the bonding pair $[z+z]^2$ from the two $[z]$ electrons of $2CH_2$. The orbital $[z+z]$ of perp. C_2H_4, although constructed in zeroth approximation from two $[z]$ each as in Eq. (8), is not identical with $[z+z]$ of plane C_2H_4. It belongs to representation a_1 of $\mathbf{V_d}$.

Let us now denote by $[x]_A$ and $[x]_B$ the $[x]$ orbitals of the two CH_2, whose x axes, it should be remembered, are at right angles. On testing the effect of the symmetry operations of $\mathbf{V_d}$ on $[x]_A$ and $[x]_B$, one finds changes of the type

$$\begin{cases}[x]_A\rightarrow c_{AA}[x]_A+c_{AB}[x]_B\\ [x]_B\rightarrow c_{BA}[x]_A+c_{BB}[x]_B.\end{cases}$$

By writing down the sums $c_{AA}+c_{BB}$ and regarding them as characters (cf. section 4), one finds that the *pair* $[x]_A$, $[x]_B$ gives exactly the set of characters belonging to the two-dimensional representation e of $\mathbf{V_d}$. This shows that the CH_2-radical orbitals $[x]_A$, $[x]_B$, degenerate for $2CH_2$, remain so if perp. C_2H_4 is formed, and constitute suitable zeroth approximations for molecular orbitals of perp. C_2H_4.

Exactly the same situation holds for the pair of CH_2-radical orbitals $[y]_A$, $[y]_B$, and therefore the four electrons $[y]_A^2[y]_B^2$ of $2CH_2$, in spite of the fact that each of the two pairs already forms a closed shell of CH_2, all belong in perp. C_2H_4 to a single degenerate type of C_2H_4-molecule orbitals belonging to representation e, and together form a larger closed shell of type e^4. This is true even though (or even if) these electrons are not shared in any real sense by the two CH_2 radicals.

In III (cf. especially Eqs. (6, 7) and reference 6) the types $e\{[y]_B, [y]_A\}$ and $e\{[x]_A, [x]_B\}$ were called $[\pi]_y$ and $[\pi]_x$ because the relation between $[y]_B$ and $[y]_A$, or between $[x]_A$ and $[x]_B$, is rather similar to that between the two orbitals which belong to a representation π of a diatomic molecule. (One should not attach too much significance to this notation, however.) The fact that both the types $\{[x]_A, [x]_B\}$ and $\{[y]_B, [y]_A\}$ belong to the same representation e shows that there must be more or less hybridization between them. Possible consequences of some importance are discussed in section 8*e*. Until then they will for simplicity be treated as independent.

In the same way as for any degenerate pair of orbitals, one may replace $[x]_A$, $[x]_B$ of perp. C_2H_4 by any two mutually orthogonal linear combinations, for example by *const.* $\{[x]_A+[x]_B\}$ and *const.* $\{[x]_A-[x]_B\}$. (Similarly with $[y]_B$, $[y]_A$.) This is instructive when used in making comparisons with $[x+x]$ and $[x-x]$ of plane C_2H_4. (One should recall that $[x+x]$ is just an abbreviation for *const.* $\{[x]_A+[x]_B\}$.)

In plane C_2H_4, $[x+x]$ and $[x-x]$ are far apart in energy and are respectively strongly bonding and strongly antibonding, while in perp. C_2H_4 they belong to a single degenerate representation and are therefore rather obviously essentially nonbonding, as are also of course $[y+y]$ and $[y-y]$ of perp. C_2H_4 (cf. also III, beginning of paragraph containing Eq. (6)). Between plane and perp. C_2H_4 lies a continuous set of intermediate cases. Everywhere except for perp. C_2H_4, it is necessary to use orbitals of the types $[x+x]$ and $[x-x]$, which then belong to different nondegenerate representations of the appropriate point group. Just for the angles 90° and 270°, $[x+x]$ and $[x-x]$ become degenerate, and can if desired be replaced by $[x]_A$, $[x]_B$.

It is of interest to note here how the unshared-electron notation $[x][x]$ automatically becomes appropriate as the rotation angle approaches 90°, corresponding to the gradual breaking of the second bond of the double bond by twisting it. [In the case of $[y]^2[y]^2$ (cf. Eqs. (2, 6, 7) of III), the unshared-electron (CH_2-radical) notation is used for all angles, but for a different reason, namely that we have arbitrarily agreed to use it for electrons which are essentially unshared.] For perp. C_2H_4, both $[x]$ and $[y]$ orbitals may be considered as CH_2-radical or as C_2H_4-molecule orbitals with equal appropriateness.

8c. Electronic states, correlations, selection rules for C_2H_4. The problem of determining the possible electron states corresponding to an electron configuration e^2 (in particular, $[\pi]_x{}^2$ of $\mathbf{V_d}$) has been solved in section 7. The states are $^3A_2$, $^1B_1$, $^1B_2$, $^1A_1$ as stated (except for changed notation) in III (cf. Fig. 1).

Next it may be well to justify the correlations shown in Fig. 1 between the states of plane and perp. C_2H_4. This is readily done by using Table IV to see how the representations of $\mathbf{V_d}$ (perp. C_2H_4) and of $\mathbf{V_h}$ (plane C_2H_4) go over into those of $\mathbf{V}$ (intermediate angles). The results are: A_1 or B_1 of $\mathbf{V_d}$ can go (by way of A_1 of $\mathbf{V}$) into either A_{1g} or A_{1u} of $\mathbf{V_h}$, A_2 or B_2 of $\mathbf{V_d}$ (by way of B_1 of $\mathbf{V}$) into B_{1g} or B_{1u} of $\mathbf{V_h}$, while E of $\mathbf{V_d}$ splits (into B_2+B_3 of $\mathbf{V}$, which go) into B_{2g} or B_{2u} plus B_{3g} or B_{3u} of $\mathbf{V_h}$. Also, singlet→singlet, triplet→triplet. After changing the notation, Fig. 1 of III will be found consistent with these rules. One might, however, raise the question whether an adiabatic correlation scheme is appropriate to the problem considered in III (absorption of ultraviolet light followed by spontaneous relative rotation of the two halves of C_2H_4), since for such rotations the wave function cannot very well be separated into an electronic and a rotational part. Lack of separability might change the restrictions given above, except the singlet→singlet . . . rule, but, as it happens, could not effectively alter the correlations shown in Fig. 1 and so would not lead to any change in the conclusions reached in III.

The fact that a transition $^1A_{1g}\rightarrow{}^1B_{1u}$ of $\mathbf{V_h}$, identified in III (except for change of notation) with the ultraviolet absorption of C_2H_4, is allowed by the selection rules can now be verified by the method of Eq. (7); and it is seen that the electric moment is parallel to the z axis.

8d. Wave functions (ψ) and dissociation of C_2H_4. The various states of C_2H_4 have so far been described in terms of electron configurations, i.e., sets of (atomic and) molecular orbitals, but expressions have not been given for the wave functions of the molecule (cf. sections 2, 2a, 3b). It is of interest to see how approximate ψ's can be constructed (a) with C_2H_1-molecule orbitals for the valence or shared electrons, (b) with CH_2-radical orbitals as one would use atomic orbitals in the method of atomic orbitals. (The reader should refer at this point to the last two paragraphs of section 2.)

Using C_2H_4-molecule orbitals, one has for the normal state of plane C_2H_4

$$\psi=N\left|\begin{array}{lcccc} [x+x]\alpha(1) & [x+x]\alpha(2) & \cdots(3) & \cdots(4) & \\ [x+x]\beta(1) & \cdots\beta(2) & (3) & (4) & \\ [z+z]\alpha(1) & (2) & (3) & (4) & \text{etc.} \\ [z+z]\beta(1) & (2) & (3) & (4) & \\ & \text{etc.} & & & \end{array}\right| :{}^1A_{1g} \qquad (9)$$

Here "etc." refers to electrons 5 to 16, which are all in CH_2-radical or C-atom closed shells (cf. discussion of H_2O following Eq. (2)). The two excited states $^3B_{1u}$ and $^1B_{1u}$ are given, for $M_S=0$, by

$$\psi=N\left|\begin{array}{lcc} [x+x]\alpha(1) & \cdots(2) & \\ [x-x]\beta(1) & \cdots(2) & \text{etc.} \\ \multicolumn{3}{c}{\text{etc. as before}} \end{array}\right| \pm N\left|\begin{array}{lcc} [x+x]\beta(1) & \cdots(2) & \\ [x-x]\alpha(1) & \cdots(2) & \text{etc.} \\ \multicolumn{3}{c}{\text{etc. as before}} \end{array}\right| :\begin{cases} {}^3B_{1u} \\ {}^1B_{1u} \end{cases} \qquad (10)$$

Another excited state is the following:

$$\psi = N\begin{vmatrix} [x-x]\alpha(1) & \cdots(2) & \\ [x-x]\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} :{}^1A_{1g} \qquad (9')$$

The approximations (9) and (9′), which belong to the same representation, could both be improved by forming linear combinations whereby a little of (9′) is admixed with (9) and *vice versa.* That the expressions given for ψ in (9), (10), and (9′) actually belong to the representations A_{1g} and B_{1u} of $\mathbf{V_h}$ can be verified by testing the behavior of each under the symmetry operations of $\mathbf{V_h}$. The spin character of each can also be verified easily.

Expressions (9), (10), and (9′) apply also to forms of C_2H_4 intermediate between the plane and perp. forms, the states then being ${}^1A_1$ of $\mathbf{V}$ for (9) and (9′), ${}^3B_1$, ${}^1B_1$ for (10). Expression (10) still holds even for perp. C_2H_4, and the two states then prove to have exactly the symmetry properties of ${}^3A_2$ and ${}^1B_2$ of $\mathbf{V_d}$. Although expressions (9) and (9′) both conform to ${}^1A_1$ of $\mathbf{V}$, neither conforms to any representation of $\mathbf{V_d}$. Instead one must form the two linear combinations

$$(\text{Perp. } C_2H_4) \quad \psi = N\begin{vmatrix} [x+x]\alpha(1) & \cdots(2) & \\ [x+x]\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} \mp N\begin{vmatrix} [x-x]\alpha(1) & \cdots(2) & \\ [x-x]\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} : \begin{cases} {}^1B_1 \\ {}^1A_1 \end{cases} \qquad (9'')$$

Evidently the two types (9) and (9′) which differ greatly in energy and are slightly admixed for plane C_2H_4 must admix more and more as one goes from plane to perp. C_2H_4, until in the latter they are mixed in equal proportions (Eq. (9″)). This is connected with the fact, noted in an earlier paragraph, that the orbitals $[x+x]$ and $[x-x]$, although differing greatly in energy for plane C_2H_4, become degenerate for perp. C_2H_4, so that (9) and (9′) converge toward the same energy as one approaches perp. C_2H_4. The two energy curves starting approximately from (9) and (9′) of plane C_2H_4 avoid coming together, however, by interacting strongly to give the two states ${}^1A_1$ and ${}^1B_1$ of (9″). These states, together with ${}^3A_2$ and ${}^1B_2$, whose ψ's are given by Eq. (10), are of just the four types which, as we have seen in an earlier paragraph, are expected according to the group theory method when we have e^2 of $\mathbf{V_d}$, the type e here being represented by the two forms $[x+x]$, $[x-x]$.

Even more interesting results for perp. C_2H_4 are obtained by building up the ψ's using the pair of perp. C_2H_4 orbitals $[x]_A$, $[x]_B$ instead of the equivalent forms $[x+x]$, $[x-x]$. In terms of $[x]_A$, $[x]_B$,—which, it may be recalled, can also be regarded equally well as orbitals of CH_2,—the four states of perp. C_2H_4 just discussed appear as

$$\psi = N\begin{vmatrix} [x]_A\alpha(1) & \cdots(2) & \\ [x]_B\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} \pm N\begin{vmatrix} [x]_A\beta(1) & \cdots(2) & \\ [x]_B\alpha(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} : \begin{cases} {}^3A_2 \\ {}^1B_1 \end{cases} \qquad (11)$$

$$\psi = N\begin{vmatrix} [x]_A\alpha(1) & \cdots(2) & \\ [x]_A\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} \mp N\begin{vmatrix} [x]_B\alpha(1) & \cdots(2) & \\ [x]_B\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} : \begin{cases} {}^1B_2 \\ {}^1A_1 \end{cases} \qquad (12)$$

By multiplying out each of the four cases given by Eqs. (11, 12), one finds that each is identical with one of those obtained by multiplying out the expressions given by Eqs. (9″, 10). (Nothing of interest is lost if all the "etc." parts are dropped before multiplying.)

The forms of Eqs. (11) and (12) show that ${}^3A_2$ and ${}^1B_1$ tend to dissociate so as to leave one $[x]$ electron on each CH_2, but ${}^1B_2$ and ${}^1A_1$ so as to leave both on one CH_2, corresponding to $CH_2^+ + CH_2^-$. Of course the actual adiabatic dissociation processes would be mostly different.

The most probable adiabatic correlations are shown in Fig. 1 of III.

Consideration of Eqs. (9″–12) and of the integrals representing interactions between electrons in $[x+x]$ and $[x-x]$ orbitals indicates that the four states $^3A_2$, $^1B_1$, $^1B_2$, $^1A_1$ of perp. C_2H_4 lie within a moderate energy range. In this connection it should not be forgotten that the two parts of the molecule are always being held together strongly by the $[z+z]^2$ bond. Definite predictions can, however, hardly be made without careful study. The arrangement given in Fig. 1 of III seems plausible.

It will now be instructive to consider the formation of plane and perp. C_2H_4 by the method of atomic orbitals treating each CH_2 like an atom (cf. end of section 2). For simplicity we may disregard the $[z]$ electrons of CH_2, since their behavior is essentially the same as that of the 1s hydrogen electrons in the formation of H_2. The latter is to a considerable extent also true of the $[x]$ electrons of CH_2. In fact Eqs. (11) and (12) above, if we regard $[x]_A$ and $[x]_B$ as CH_2 and not as C_2H_4 orbitals, correspond exactly in form to the ψ's for the four states of H_2 ($^1\Sigma_g{}^+$, $^3\Sigma_u{}^+$, $^1\Sigma_u{}^+$, $^1\Sigma_g{}^+$) derivable from 2H(1s) and from H+H(1s^2). Eqs. (11) and (12) really apply not only for perp. C_2H_4 but also for plane and intermediate nuclear configurations, where they are the correct forms for the atomic orbital method. The forms which belong to $^3A_2$, $^1B_2$, $^3B_2$, $^1A_1$ for perp. C_2H_4 in Eqs. (11, 12) belong respectively to $^3B_1$, $^1A_1$, $^1B_1$, $^1A_1$ for intermediate and to $^3B_{1u}$, $^1A_{1g}$, $^1B_{1u}$, $^1A_{1g}$ for plane C_2H_4.

Comparing Eqs. (9, 10, 9′) with (11, 12), for plane C_2H_4, the relations and differences are exactly analogous to those between the methods of molecular and atomic orbitals as applied to the four states of H_2 mentioned above. On multiplying out the various expressions, those for the $^3B_{1u}$ and $^1B_{1u}$ states as given by the two methods are identical, while those for the two $^1A_{1g}$ states differ characteristically, but can be brought into agreement by abandoning pure electron configurations (cf. section 2) and taking suitable admixtures of the two $^1A_{1g}$ forms in each case (cf. II, section 13, after dropping the spins from the present equations). For perp. C_2H_4, the two methods become identical in all respects. All these relations are true, however, only provided we omit all but the $[x]$ electrons of CH_2 from consideration.

8e. Partial persistence of second bond in perp. C_2H_4. In an earlier paragraph it was mentioned that there must be more or less hybridization between the two e orbital types $[\pi]_x=\{[x]_A, [x]_B\}$ and $[\pi]_y=\{[y]_B, [y]_A\}$. Of these two types, it should be noted $[\pi]_y$ is presumably decidedly the lower in energy. The two resulting hybrid e types would be of the forms

$$q=\{a[y]_A+b[x]_B\},\ \{a[y]_B+b[x]_A\},\quad\text{and}$$

$$r=\{a[x]_B-b[y]_A\},\ \{a[x]_A-b[y]_B\}. \qquad (13)$$

Complete hybridization would make $a=b$, and would make the two types closely similar to the types π and π^* of O_2 (described as $(\pi+\pi)$ and $(\pi-\pi)$ in III). They would differ in zeroth approximation from π and π^* only because the $[y]$ orbitals contain contributions from hydrogen 1s and are C–H bonding (cf. Eq. (8) above).

Actually $a>b$ must hold, but it is reasonable to suppose that $a\gg b$ is not true. Then, as is obvious from its form, the lower-energy type q, which is the more closely related to $[\pi]_y$, has more or less C–C bonding power while type r has more or less C–C anti-bonding power. Since, corresponding to $[\pi]_y{}^4[\pi]_x{}^2$ for the case of no hybridization, one has q^4r^2, the result is that hybridization tends to produce a net C–C bonding effect like the O–O bonding effect of $\pi^4\pi^{*2}$ in O_2. It appears, then, that the double bond in perp. C_2H_4 is intermediate in character between the model given in III and the double bond ($\sigma^2\pi^4\pi^{*2}$) of O_2.

We now see that a 90° rotation of the two parts of a C_2H_4 molecule after all does not entirely destroy the second bond of the double bond, so that the energy difference between the normal state of plane C_2H_4 and the lowest states of perp. C_2H_4 should be less than in Fig. 1 of III. This would make the energy differences between the excited plane states and the perp. states correspondingly greater, and increase the probability of the correctness of the interpretation given in III of certain photochemical experiments.

The change in Fig. 1 just mentioned also brings it into better agreement with calculations from chemical data (cf. III, last sentence before section on *Interpretation of Photochemical Experiments*), according to which the "energy of activation" required to pass over the hill or hills of energy near 90° between *cis* and *trans* forms of ethylene derivatives is much smaller (of the order of one volt) than in Fig. 1 of III. It should be remarked, however, that it is rather uncertain how closely the chemically calculated energy of activation may be expected to correspond to the energy maximum between *cis* and *trans*.

It should further be noticed that if by hybridization the group q^4r^2 has acquired some $C-C$ bonding power, this is partly at the expense of the $C-H$ bonding power of the $[y]$ orbitals. One can see this by, for example, observing (1) that the configuration q^4r^2 with complete hybridization ($a=b$ in Eqs. (13)) corresponds to the occurrence in $2CH_2$ of only three of the $C-H$ bonding orbitals $[y]$ and three of the $C-H$ nonbonding orbitals $[x]$, as against four and two respectively if there is no hybridization; but noticing at the same time (2) that complete hybridization would result in a net gain of two $C-C$ bonding orbitals, so that on the whole the effect of hybridization could well be an appreciable lowering of the energy of the states of perp. C_2H_4 as compared with Fig. 1. That the energy decrease would be fairly large has not here been proved theoretically, but the empirical evidence on activation energies suggests that this may be the case.

A matter not yet explained is the method by which conclusions were reached as to the relative energies of binding of various molecular orbitals. (The conclusions themselves are implicit in the electron configuration formulas given in III, since the orbitals are always written in what seems their most likely order of binding energy.) Details will be postponed, but in brief, the principle used was mainly this: molecular orbitals which are strongly bonding are relatively concentrated in a relatively strong field of force, and so, other things being equal, have lower energy than those which are less strongly bonding.

Everything stated in III concerning C_2H_4 and its formation from $2CH_2$ has now been justified or improved on, except the matter of the rules for the adiabatic correlation of C_2H_4 with $2CH_2$ on dissociation. Discussion of this problem, and of the ways in which other double-bonded compounds differ from C_2H_4, will be reserved until later.

Note added in proof: In a forthcoming paper in the *Zeits. f. Physik*, dealing primarily with vibrational states of molecules, L. Tisza gives among other interesting results the representations of all possible point groups, including groups with 5-, 7-, 8-, . . . fold axes. In another forthcoming paper, E. Teller and G. Herzberg discuss in detail some of the consequences of the Franck-Condon principle, and of the interaction between electronic states and vibration, for selection rules and intensity relations in electronic bands of polyatomic molecules.[18, 19]

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[18] The writer is indebted to Dr. E. Teller in Göttingen for the opportunity of seeing the manuscripts of these papers.

[19] For earlier applications of the Franck-Condon principle to this problem, cf. G. Herzberg, Trans. Faraday Soc. **27**, 378 (1931); H. C. Urey and H. Johnston, Phys. Rev. **38**, 2131 (1931).