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Electronic Structures of Polyatomic Molecules and Valence. V. Molecules RX_n

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Theory. The approximate construction, for shared electrons in molecules RX_n , of molecular orbitals ("orbital" means one-electron orbital wave function) as linear combinations of atomic orbitals is discussed and illustrated by equations for RX_2 , RX_3 , RX_4 types. Properties of bonding, nonbonding, antibonding, also excited, molecular orbitals are described. *Valence* orbitals include both bonding and nonbonding types. RH_3 and H_3 orbitals are given as examples. Molecular orbitals constructed from atomic orbitals contain undetermined coefficients and implicit parameters (effective Z 's of the atomic orbitals) which make them very flexible. They are useful for a qualitative theory which can be compared with empirical, especially chemical and spectroscopic, data. They also have value in semi-quantitative calculations (Van Vleck). **Applications.** Electronic structures, ionization potentials, form and stability (at least some of these properties in each case) of the molecules CH_4 , NH_3 , H_2O , NH_4 , CH_3 , NH_2 , BeH_2 , RX_n are described and interpreted in terms of molecular orbitals. It is shown that an electronic structure $1s^2[5]^2[2p]^6$, closely related to that of the Ne atom, can be assigned to CH_4 without the least necessity or justifi-

cation for departing from the idea of the equivalence of the four C-H bonding directions. This seems in some respects more natural than the Pauling-Slater method in which four equivalent bonds are obtainable only with mixtures of $2s$ and $2p$ carbon orbitals. The structures assigned for NH_3 and H_2O are also related to that of Ne, and that for NH_4 to that of Na. The ionization potential of NH_4 is estimated as 4.5 volts, slightly greater than for the K atom. The *proton affinity* of NH_3 (energy change for $NH_3 + H^+ \rightarrow NH_4^+$) is estimated to be 9 volts. The ionization potential of CH_3 is roughly estimated as 8.5 volts, and the energy of formation of CH_4 from $CH_3 + H$ is discussed. Whether molecules RX_3 are plane or pyramidal can be considered to depend on the quantitative outcome of a conflict of different factors; three such factors are noted. The first of these gives an explanation of Zachariasen's rule. Empirical evidence is cited showing that the geometrical possibilities of forms RX_4 tend to produce stabler electron configurations than are permitted by the possible geometry of RX_3 . The ultraviolet absorption spectra of CH_4 , NH_3 , and H_2O are discussed in relation to the ionization potentials of these molecules.

A. INTRODUCTION

PAPERS I, II, III, and IV of this series were published in the *Physical Review*.¹ Paper I is a preliminary summary, correct except for a few details which are not vital, of the results to be given in II-VIII. Paper II, in which the viewpoint is strongly chemical, includes a brief critical review and comparison of theories of valence and the electronic structures of molecules. It is there pointed out that the present approach, although not stressing the idea of electron-pair bonds as does the theory of Pauling and Slater, is in some respects closer than the latter to the Lewis theory of valence, most of whose essential features are still valid as a summary and interpretation of the facts of

valence. The present viewpoint and that of Slater and Pauling illuminate the Lewis theory from more or less complementary directions. Paper III and the last part of IV are devoted to the quantum theory of C_2H_4 , which is taken as the prototype of the ordinary $C=C$ double bond; and a theory of the mechanism of the photochemical *cis-trans* conversion is suggested. The first part of IV is devoted mainly to the quantum classification of electronic states of polyatomic molecules (analogous to the classifications S , P , D , \dots , Σ , Π , Δ , \dots for atoms and diatomic molecules) with the aid of easily understood but powerful group theory methods. This classification is used as a basis for the descriptions of electronic structures in III, IV and the later papers.

B. THEORY

1. Introduction

A number of important molecules of the types RX_n , RX_mY_n , $RX_n \cdot RX_n$, $RX_lY_m \cdot RX_n$ and so

* This paper is based largely on work done during tenure of a John Simon Guggenheim Memorial Foundation Fellowship.

¹ R. S. Mulliken, *Phys. Rev.* **40**, 55; **41**, 49, 751 (1932); **43**, 279 (1933).

on can be described by using, for the valence electrons, molecular orbitals which may be called molecular *valence orbitals*. These can be constructed in zeroth approximation as linear combinations of atomic orbitals of the atoms R, X, Y, ... (method of Bloch and Hund). Only R atoms with *s* and (or) *p* valence electrons are considered in the present paper, and all atoms of any one kind X or Y near any R are assumed to be equidistant from this R and otherwise equivalent.

Only 1*s* atomic orbitals are used for the case that X or Y represent H atoms. For X or Y atoms with *p* valence electrons, e.g., halogen atoms, good molecular valence orbitals can rather obviously be obtained if in the construction of the latter an atomic orbital *pσ* is used for each X or Y atom, leaving on the latter a closed shell *pπ*⁴ of unshared atomic orbitals (cf. I of this series¹ for further discussion and examples). The axis with reference to which the atomic orbitals *pσ* and *pπ* are chosen is of course the C–X or C–Y axis. In VII of this series it will be shown that the use of the *pσ* and the exclusion of the *pπ* atomic orbitals in constructing molecular valence orbitals, although not rigorously justified, is usually a good practical approximation, but that in some cases (in particular, plane molecules RX₃) the *pπ* atomic electrons may be quite appreciably drawn into the sphere of valence activities.

In the present paper, (V), only molecules of the type RX_{*n*}, especially RH_{*n*}, are treated. In VI the types R₂X_{*n*} and RR'X_{*n*} will be considered, and in VII the types with more than one kind of substituent X, Y.

When molecular orbitals are used, as here, each must belong to some representation of the symmetry group known or assumed for the molecule (cf. IV of this series¹). The molecular orbitals given by Eqs. (1)–(7) below all conform to this requirement, as can be verified by testing (cf. IV) what happens to each under the operations of the symmetry group of the molecule in question.

2. Construction of RX_{*n*} molecular orbitals approximately from atomic orbitals

In constructing RX_{*n*} valence orbitals, the atomic valence orbitals for the *n* + 1 participating atoms are first listed. In general these are: an *s*

orbital of R, a degenerate set of three *p* orbitals of R, and a degenerate set of *n* orbitals (1*s* for H atoms, *pσ* for other X atoms) belonging one to each of the X atoms. Zeroth approximation molecular orbitals, *n* + 4 in number, are now constructed from these *n* + 4 atomic orbitals. Some, in general, are bonding, some approximately nonbonding, some antibonding; some are degenerate, some nondegenerate. As will be explained below, not all are valence orbitals.—The procedure of forming *n* + 4 zeroth approximation molecular orbitals from *n* + 4 atomic ones which are in part only *approximately* degenerate is an example of a general method discussed by Slater (cf. IV, p. 281 and reference 9, p. 1111¹).

If the number of outer *s* and *p* (valence) electrons originally possessed by R was *m*, then (*m* + *n*)/2, —or (*m* + *n* + 1)/2 if *m* + *n* is odd, —of the molecular orbitals just mentioned are occupied, in the normal state of the molecule, by the *m* + *n* valence electrons. The orbitals occupied will of course be those of lowest energy, and are what is here meant by molecular *valence orbitals*. These always include bonding orbitals, but also often some approximately nonbonding orbitals (cf. the case of NH₃, Section 14).

In molecules such as H₂O or HF, where the *s* orbital of R is obviously not appreciably concerned in the bonding, it can best be omitted from the above procedure, so that one starts with only *n* + 3 atomic orbitals. The *s* orbital of R then appears in the molecule as an atomic and therefore nonbonding type. A similar result would still be obtained, however, if the *s* R orbital were at first included as one of the *n* + 4, since it would turn out, when the linear combinations were formed, that one of them would contain this *s* orbital with a coefficient nearly unity. In such cases it is obviously sensible to leave out the *s* R orbital, but in intermediate or doubtful cases like NH₃, it should be included.

3. Excited molecular orbitals

In contrast to molecular valence orbitals, we may refer to *excited* molecular orbitals. These are orbitals which occur only in excited states of a molecule, and are important for its spectrum. Excited orbitals include, among others, the remaining (*n* + 4) – (*m* + *n* + 1)/2 molecular or-

bitals which were constructed above from the $n+4$ valence atomic orbitals. These are for the most part antibonding, with respect to *all* the R-H bonds. The occurrence and relations of the bonding, antibonding, and nonbonding orbitals formed from the $n+4$ atomic orbitals can be understood from the examples given in Eqs. (2)–(7) and from the detailed discussion of NH_3 in Section 14.

In regard to excited orbitals in general, it should be pointed out that, as in the well-known diatomic cases of He_2 and H_2 , the higher excited states, corresponding to large orbits in the Bohr theory, may be expected to form Rydberg series. Just as in the case of H_2 or He_2 , the excited electron can then be classified as ns , $n\bar{p}$, nd , \dots , with some additional subdivision of types in accordance with representations of the symmetry group of the molecule (cf. IV).

In the low excited states, where the excited electron is in a molecular orbital whose dimensions are not much greater than those of the rest of the molecule, the relations should be less simple, and much predissociation might be expected, and is found. These lower excited molecular orbitals include some for which certain antibonding forms, obtained above as a by-product in connection with the construction of valence orbitals, may be fairly good approximations.

4. X_n molecular orbitals

In constructing the $n+4$ (or $n+3$) molecular orbitals obtainable as linear combinations of atomic orbitals of the R and X valence electrons, the following procedure is convenient. First we choose axes x , y , z appropriate to the assumed symmetry of RX_n . We then note that zeroth approximation molecular orbitals which belong to representations of the assumed symmetry group can be built up only from atomic orbitals, or linear combinations of these, which are themselves representations of this group. The s atomic orbital of R always belongs to such a representation (in fact to the identical representation, usually called a_1), while the threefoldly degenerate p orbitals of R can always be so chosen as to belong to such representations. Usually the forms p_x , p_y , and p_z (i.e., $F(r)$ times $\sin \theta \cos \phi$, $\sin \theta \sin \phi$, and $\cos \theta$, respectively)

are suitable. Each of these, when R is assumed perturbed by a force-field having the assumed symmetry of RX_n , may belong to a different non-degenerate representation, or sometimes p_x , p_y together (i.e., $p\pi$) belong to a degenerate and p_z (same as $p\sigma$) to a nondegenerate representation. In certain cases, e.g., symmetry T_d as in CX_4 , the original degeneracy of the p atomic orbital is not split up at all (cf. IV, Table II¹).

From the n equivalent H atom $1s$ or X atom $p\sigma$ orbitals (cf. Section 1), we can get representations of the RX_n symmetry group *only* by forming linear combinations, n in number. These can be obtained uniquely without great difficulty, often by inspection. The resulting forms are zeroth approximation molecular orbitals of a molecule X_n (neutral or ionized) with its n X atoms arranged in accordance with the prescribed symmetry. (As will be seen in VII, however, certain other molecular orbitals built up from $p\pi$ atomic orbitals may sometimes also be important, for molecules X_n other than H_n .)

5. Molecular orbitals of X_3 and RX_3 , symmetry D_{3h}

The procedure can be made clearer by considering as an example the type RX_3 . We assume that the three X atoms form an equilateral triangle. Two cases are important, (a) R atom at the center of the triangle: symmetry D_{3h} ($D_{3h} = C_{3v}$ times σ_h); (b) R atom displaced from the center along a line perpendicular to the plane of the triangle: symmetry C_{3v} . In either case a z axis is chosen through the R atom perpendicular to the plane (cf. Fig. 1a). The x and y axes can conveniently be chosen as shown in Fig. 1a. The R atom gives orbitals s , $p\pi$, and $p\sigma$ belonging respectively to the representations a_1' , e' , and a_2'' of D_{3h} , or to a_1 , e , and a_1 of C_{3v} , as can be verified by means of Tables II, IV of IV.

Denoting the $p\sigma$ (or $1s$ if X is H) orbitals of the three X atoms by α , β , γ respectively (cf. Fig. 1a), the following three orbitals are found to be correct linear combinations.² (In the case

² J. H. Van Vleck, J. Chem. Phys. 1, 177, 219 (1933). Eqs. (1), (5)–(7) of the present paper have been obtained independently by Van Vleck (cf. reference 10 in his first paper). Van Vleck, proceeding more mathematically than here, frequently obtains results the same as or similar to those given in the present series.

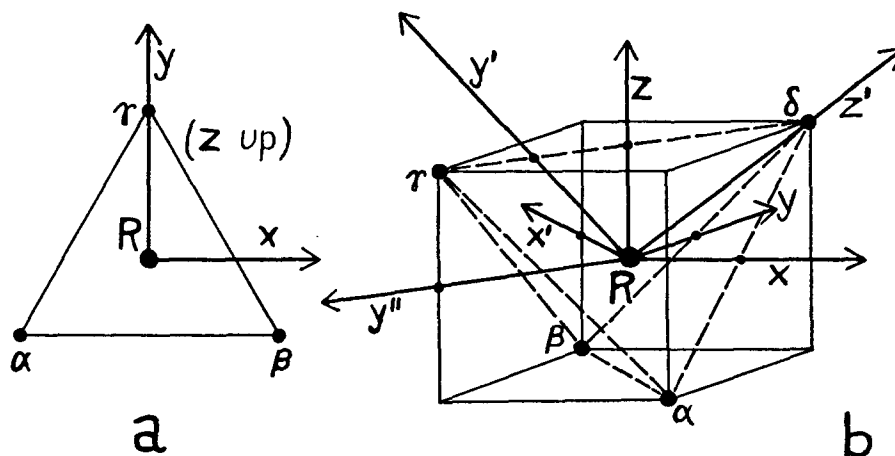


FIG. 1. (a) Arrangement of atoms and axes for RX_3 (cf. Eqs. (1)–(3)): α, β, γ are X atoms; the R atom is either in the center of the triangle (symmetry D_{3h}) or in front of it (C_{3v}) on the positive z axis, which extends toward the reader. (b) Arrangement of atoms and axes for RX_4 (symmetry T_d): $\alpha, \beta, \gamma, \delta$ are X atoms at corners of a regular tetrahedron (edges shown by dotted lines), with R in the center. Three sets of axes are shown, namely x, y, z ; x', y', z' ; x'', y'', z'' (cf. Eqs. (5)–(7)). To show these clearly, the tetrahedron is shown inscribed in a cube, and intersection of each axis with a cube edge or face is shown by a dot.

of $p\sigma$ orbitals, it is to be understood that the positive axis of each is directed toward the R atom.) The first belongs to representation a_1' of D_{3h} in case *a*, or a_1 of C_{3v} in case *b*, while the other two are equivalent and belong to the degenerate representation e' of D_{3h} or e of C_{3v} .

$$X_3 \text{ orbitals} \left\{ \begin{array}{l} a_1': (3^{-1})(\alpha + \beta + \gamma) \\ e': (2^{-1})(\alpha - \beta) \text{ and} \\ (6^{-1})(\alpha + \beta - 2\gamma), \text{ or any} \\ \text{pair of mutually orthog-} \\ \text{onal linear combinations} \\ \text{of these.} \end{array} \right\} \quad (1)$$

If we consider the three X atoms alone without R, we must use the symmetry D_{3h} , not C_{3v} ; for this, the axes of X atom $p\sigma$ orbitals must all lie in the X_3 plane, directed toward the center. Eqs. (1) then give zeroth approximation orbitals of X_3 (neutral or ionized). The a_1' type gives bonding between all three atoms. In the normal state of H_3^+ , if this has symmetry D_{3h} , the type a_1' would be occupied by two electrons giving a stable molecule. The type e' is an excited type not tending to bond all three atoms together.

Turning to RX_3 , we must combine the above X_3 orbitals with the R orbitals $s, p\pi, p\sigma$. This is simplest for symmetry D_{3h} . Following the rule that R and X_3 orbitals can be combined only if they belong to the same representation of the

desired symmetry group,—for otherwise the combination would not belong to any representation of the group,—one obtains the following RX_3 orbitals:

$$\left. \begin{array}{l} [s]a_1' = c(s) + d(\alpha + \beta + \gamma) \\ [\pi]e': \left\{ \begin{array}{l} [x] = c'(p_x) - (3^{1/2})d'(\alpha - \beta) \\ [y] = c'(p_y) - d'(\alpha + \beta - 2\gamma) \end{array} \right\} \\ [z]a_2'' = p_z \\ [s]^*a_1' = c(\alpha + \beta + \gamma) - d(s) \\ [\pi]^*e': \left\{ \begin{array}{l} [x]^* = d'(p_x) + (3^{1/2})c'(\alpha - \beta) \\ [y]^* = d'(p_y) + c'(\alpha + \beta - 2\gamma) \end{array} \right\} \end{array} \right\} \quad (2)$$

With the degenerate types $[\pi]$ and $[\pi]^*$, it is to be understood that instead of the forms given, any pair of mutually orthogonal linear combinations of them could be substituted, for instance $(2^{-1})([x] + i[y])$, $(2^{-1})([x] - i[y])$, in the case of $[\pi]$.

6. Notation and conventions

In Eqs. (2), each molecular orbital is introduced by a descriptive symbol $[s]$, $[\pi]$, or $[z]$ which suggests an orbital of the atom R to which the molecular orbital in question is more or less closely related. Following this a systematic symbol, e.g., a_1' in $[s]a_1'$, e' in $[\pi]^*e'$, is (or may be) given showing to what representa-

tion of the molecule's symmetry group the orbital belongs.

The signs in Eqs. (2) are based on the following *conventions*: the coefficients c , d , c' , d' are intrinsically positive; H atom $1s$ orbitals are always positive; the positive axis of each X atom $p\sigma$ orbital is directed toward the central atom R; each R atom s orbital is intrinsically positive in the *valence region*, i.e., the region beyond its last nodal surface where, for a valence orbital of the unexcited molecule, it overlaps X atom orbitals; for the R atom orbitals p_x , p_y , p_z , the valence regions surrounding the positive and negative x , y , or z axes are always intrinsically positive or negative, respectively. [One could, of course, choose *all* the signs just oppositely.]

7. Bonding, nonbonding and antibonding orbitals

With the conventions just given, it will be found that in $[s]$ and $[\pi]$ of Eqs. (2) the X atom orbitals α , β , γ always have the same sign as the R atom orbitals in the regions where they overlap the latter strongly. This results in a bonding effect for every such region of overlapping (cf. II, IV of this series), so that $[s]$ and $[\pi]$ are *bonding* orbitals. This refers to the interaction of R with the X's; there are also bonding and antibonding actions *between* X atoms, but these are of less importance, since the latter are considerably farther away from one another than from R.

The $[z]$ orbital here is seen to be of necessity nonbonding, because for reasons of symmetry there is no X_3 orbital with which it can combine. This conclusion, however, although correct for RH_3 , more or less loses its validity if X is not H, since for RX_3 with symmetry D_{3h} it is not a good approximation to neglect the $p\pi$ atomic orbitals of X in constructing RX_3 orbitals: cf. Section 1.

There remain the $[s]^*$ and $[\pi]^*$ orbitals, which are completely *antibonding* as regards the interaction between R and the X atoms, since the R and X orbitals overlap with opposed signs. The coefficients in $[s]^*$ and $[\pi]^*$ have been so chosen that, in zeroth approximation for very large distances of separation of X_3 from R, $[s]^*$ and $[\pi]^*$ are respectively orthogonal to $[s]$ and $[\pi]$.

8. Some general considerations; undetermined coefficients and implicit parameters in the present method

The forms given in Eqs. (2) contain undetermined coefficients which make them capable of describing molecules with various degrees of strength of bonding between R and the X atoms, and various degrees of internal polarity or of approach to polar binding. Also, the atomic orbitals used implicitly contain undetermined parameters, e.g., Z_{eff} 's, since the atomic orbitals which would give the best approximate valence orbitals would not in general be orbitals appropriate to exactly neutral atoms, but rather to something intermediate between these and orbitals of (positive or negative) ions. In describing molecules of varying degrees of internal polarity, both the parameters and the coefficients would need to be varied. For ionized molecules the zeroth approximation valence orbitals, although formally the same as for corresponding neutral molecules, must in general have different coefficients and implicit parameters.

For the relatively simple case of H_2 , this problem has been discussed by Hund.³ In H_2 the two valence electrons occupy a valence orbital which may be described as $\alpha + \beta$. One gets a much more nearly correct description of the electronic structure if one takes for α and β not ordinary $1s$ orbitals of neutral H ($Z_{eff} = 1$), but $1s$ orbitals intermediate between those of H and H^- ($Z_{eff} < 1$). Similar but more complicated effects must appear in molecules RX_n .

Because of the undetermined coefficients and implicit parameters, and because of the approximation still involved in constructing molecular orbitals from even the best possible atomic orbitals, forms such as those given in Eqs. (1)–(7) are, as they stand, only of qualitative significance. This, however, does not deprive them of power to give insight into electronic structures of molecules and a good idea of some of the energy states to be expected when the molecules are excited or ionized. Thus they furnish a qualitative theoretical framework with which empirical results can be compared and into which they can be fitted, analogous to that which has been successfully used for the quali-

³ F. Hund, *Zeits. f. Physik* **73**, 1 (1931).

tative theory of diatomic molecules and their spectra.

One can also hope in individual cases, using simplifying assumptions, to make useful more or less quantitative calculations starting with molecular orbitals. This procedure is, to be sure, not well adapted to calculations of absolute energy or energies of dissociation,³ but, as especially Van Vleck has shown,² can give good results in determining the relative energies of a molecule in different geometrical forms, so that the most stable form, and the valence angles, can be predicted.

9. Molecular orbitals of RX_3 , symmetry C_{3v}

After this brief general discussion, we return to the problem of the RX_3 orbitals, now assuming the symmetry C_{3v} . The forms for the special case RH_3 are now as follows:

$$\left. \begin{aligned} [s]a_1 &= c(s) + d(\alpha + \beta + \gamma) - g(p_z) \\ [\pi]e: &\text{as } [\pi] \text{ in Eqs. (2)} \\ [z]a_1 &= c''(p_z) - d''(\alpha + \beta + \gamma) + g''(s) \\ [\pi]^*e: &\text{as } [\pi]^* \text{ in Eqs. (2)} \\ [s]^*a_1 &= c^*(\alpha + \beta + \gamma) - d^*(s) + g^*(p_z) \end{aligned} \right\} \cdot (3)$$

In Eqs. (3), contrary to the usual conventions (Section 6), the coefficients d'' , g'' , g^* , d^* are not necessarily always positive quantities. Their signs and magnitudes depend on how far the R nucleus is from the H_3 plane, and on the nature of the atom R. If R is near the H_3 plane, d'' and all the g 's are nearly zero (cf. Eqs. (2)).

In the case of X atoms with p valence electrons, Eqs. (3) are not always very good approximations, except for $[\pi]$ and $[\pi]^*$. Modifications along the lines suggested in Section 7 for $[z]$, and in Section 1, may be needed.

10. Molecular orbitals of RX_2 , RX_4

By methods similar to those used for RX_3 , the valence orbitals for RX_2 and RX_4 given by Eqs. (4)–(7) are obtained. Other, excited, orbitals obtainable from the same atomic orbitals (cf. Sections 2, 3 above) can also be written down very easily. In the RX_4 case, for instance, where all the valence orbitals are bonding (cf. Section 6), an equal number of antibonding orbitals exists, namely one $[s]^*$ and one $[p]^*$. The orbital $[s]^*$ is obtained from $[s]$ of Eqs.

(5) by substituting d , $-c$ for c , d , while $[p]^*$ is obtained from $[p]$ by putting d' , $-c'$ for c' , d' ; these coefficients, however, are applicable only for large distances of the 4 X from the R. Actually it seems likely that atomic orbitals $3s$ and $3p$ (cf. Section 11) would be better approximations to excited orbitals of CH_4 than $[s]^*$ and $[p]^*$ would be.

In each case in Eqs. (4)–(7) the origin is taken at the R nucleus. In the RX_4 case, the positions of the axes relative to the X nuclei α , β , γ , δ are as shown in Fig. 1b.

Degenerate molecular orbitals can of course be written in an infinite variety of ways. It is of interest here to write down various forms which constitute correct zeroth approximations for distortions of the original symmetry. This is done below for the $[p]$ valence orbitals of RX_4 . They are first given, in Eqs. (5), in forms which are natural for symmetry T_d . In Eqs. (6) and (7) they are given in forms which, while still appropriate to T_d , are suitable zeroth approximations when the molecule is perturbed or its symmetry is distorted, e.g., by displacing one, or two, X atoms from their positions of equivalence with the others, in such a way as to give the lower symmetry C_{3v} or C_{2v} . As will be seen in VI and VII of this series, Eqs. (6), (7) form starting points for the consideration of derivatives RH_3X , RH_2X_2 , RX_2Y_2 , etc., and for an understanding of relations between RH_3X and RH_3 , and so on (cf. also Van Vleck's recent papers²).

Type RX_2 , symmetry C_{2v} (triangular form): see IV of this series, Eqs. (8).

$$\left. \begin{aligned} \text{Type } RX_2, D_{\infty h} \text{ (linear form; } \alpha \text{ on the} \\ \text{positive, } \beta \text{ on the negative, } y \text{ axis):} \\ [s]\sigma_g &= c(s) + d(\alpha + \beta); \\ [y]\sigma_u &= c'(p_y) + d'(\alpha - \beta) \end{aligned} \right\} \cdot (4)$$

Type RX_4 , T_d (regular tetrahedron); cf. Fig. 1b for axes x , y , z :

$$\left. \begin{aligned} [s]a_1 &= c(s) + d(\alpha + \beta + \gamma + \delta) \\ [p]t_2: &\left\{ \begin{aligned} [x] &= c'(p_x) + d'(\alpha - \beta - \gamma + \delta) \\ [y] &= c'(p_y) + d'(-\alpha + \beta - \gamma + \delta) \\ [z] &= c'(p_z) + d'(-\alpha - \beta + \gamma + \delta) \end{aligned} \right\} \end{aligned} \right\} \cdot (5)$$

Type RX_4 , T_d , zeroth approximations for C_{3v} ; cf. Fig. 1b for new axes (x' , y' , z'):

$$[p]_{t_2}' \left\{ \begin{array}{l} [x]' = (-2^{-1})([x] - [y]) \\ \quad = c'(p_{x'}) - 2^{\frac{1}{2}}d'(\alpha - \beta) \\ [y]' = (-6^{-1})([x] + [y] - 2[z]) \\ \quad = c'(p_{y'}) - (2/3)^{\frac{1}{2}}d'(\alpha + \beta - 2\gamma) \\ [z]' = (3^{-1})([x] + [y] + [z]) \\ \quad = c'(p_{z'}) - (3^{-1})d'(\alpha + \beta + \gamma - 3\delta) \end{array} \right\}. \quad (6)$$

Type RX_4 , T_d , zeroth approximations for C_{2v} ; cf. Fig. 1b for axes (x' , y'' , z):

$$[p]_{t_2}'' \left\{ \begin{array}{l} [x]' \text{ as in (6)} \\ [y]'' = (-2^{-1})([x] + [y]) \\ \quad = c'(p_{y''}) + (2^{\frac{1}{2}})d'(\gamma - \delta) \\ [z] \text{ as in (5)} \end{array} \right\}. \quad (7)$$

11. Approximation of RH_n orbitals by central-field orbitals. Comparison with electron-pair bonds

In tetrahedral molecules RX_4 , in particular CH_4 , the advantages of describing the state of the valence electrons by means of molecular orbitals are particularly obvious.^{3a} Since the symmetry of a tetrahedron approaches that of a sphere, $2s$ and $2p$ orbitals of an atom with suitably chosen nuclear charge should be rather good approximations to CH_4 molecular orbitals; probably orbitals of the O atom would do very well. (For the $1s$ electrons, C atom orbitals would of course be used.) Better still would be orbitals corresponding to the field set up by a C nucleus surrounded at a distance of about 1.1×10^{-8} cm by a thin uniform shell of positive electricity of total charge $4e$, allowance being of course made also, by the Hartree method, for the average effect on any one electron of the remaining electrons. With either of these models, the electron configuration and state of unexcited CH_4 would be described as $1s^2 2s^2 2p^6$, 1S .

To investigate the effect of the tetrahedral symmetry of CH_4 , a perturbation of the second model can be introduced which gradually concen-

trates the positive shell into four H nuclei. The group theory treatment shows that this does not alter the three-fold degeneracy of the $2p$ orbitals nor allow these to hybridize with $2s$. For according to Table II of IV (cf. note b of the table), $2s$ and $2p$ go over for tetrahedral symmetry (T_d) into examples of types a_1 and t_2 , respectively (cf. Table I of IV for the properties of these). Since these CH_4 orbitals are closely related to the unperturbed central-field orbitals $2s$ and $2p$, they may appropriately be called $[s]_{a_1}$ and $[p]_{t_2}$.—The excited orbitals of CH_4 , especially if CH_4^+ still has the symmetry of a regular tetrahedron (cf. end of Table I), should be very nearly like atomic orbitals $3s$, $3p$, \dots .

A similar approach can be made for the molecules NH_4^+ , NH_3 , H_2O , and so on, starting with s and p orbitals and applying a perturbation having the final symmetry. Except where the latter is tetrahedral, it causes the p type to split up into either two or three types, one of which in most cases can hybridize more or less with s . What happens in each case can be determined by the group theory method.

From the above approach, it appears that the relative advantages of the method of molecular orbitals are greatest as compared with the method of electron-pair bonds for molecules whose symmetry is high and so approaches that of an atom (SF_6 , CH_4 , MnO_4^- , and to a less extent NH_3 , NO_3^- , and the plane molecule $PtCl_4$), and are *least* with *diatomic* or linear molecules. Since molecular orbitals have been successfully used for diatomic molecules, they should then be all the more appropriate for more symmetrical molecules. One sees also that the use of molecular orbitals is relatively simple and natural in cases where more than one type of valence electron of a central atom is in use (e.g., s and p in CH_4 , s and d_{t_2} in MnO_4^-), and where Pauling and Slater, in forming electron-pair bonds, have used hybrid atomic orbitals (cf. Van Vleck² for a critical discussion).

C. RH_n MOLECULAR ORBITALS. APPLICATIONS

12. Electronic structures and ionization potentials of molecules RH_n

In Table I the normal state of each of several molecules RH_n is described in terms of the

^{3a} Cf. also G. Glockler, J. Am. Chem. Soc. **48**, 2021 (1926), and H. Grimm, Zeits. f. Elektrochemie **31**, 474 (1925) for a viewpoint resembling the present one.

valence orbitals given in Sections 5, 9, 10. In each case there are of course also the two K electrons $1s^2$. The type $1s$ may be regarded either as an atomic orbital or as a molecular orbital belonging to the identical representation (a_1 or a_1').

The experimentally known symmetry^{4, 5} is assumed in the cases of H_2O and CH_4 , while two possible alternative symmetries are given in those of BeH_2 and BH_3 . The molecule NH_3 is known to have a low-pyramidal form (height of pyramid about 0.38×10^{-8} cm, energy required to make it plane about 0.25 volt).⁶ Hence although the symmetry is really C_{3v} , NH_3 is so nearly plane that the corresponding symmetry D_{3h} is perhaps more important. Both cases are covered in Table I.

The normal and the predicted lowest one or two states of some ions RH_n^+ are also described in Table I, and observed ionization potentials of RH_n molecules are matched against these predicted RH_n^+ states (cf. preliminary account in I of this series). Where observed potentials are lacking, estimated values are given.

In connection with the experimental ionization potentials (the estimated values are intended to be on the same basis), it should be noticed that each of these probably corresponds approximately, in accordance with the extended Franck-Condon principle, to a process in which an electron is removed without change in the dimensions of the molecule. The adiabatic or strict minimum ionization potentials may be considerably lower in some cases. For understanding the structures of the neutral molecules RH_n , however, their non-adiabatic observed potentials are really more useful than adiabatic ones would be.

A comparison of the ionization potentials of CH_4 , NH_3 , H_2O with those of the atoms C, N, O is instructive. (HF and F would also be of interest, but data are lacking.) In order to have comparable results the change in multiplicity during ionization should be the same in all

cases, as also, so far as possible, the multiplicities themselves. In the case of all the three molecules, one starts with a singlet state 1A_1 and gets a doublet ionic state. The observed potentials are 14.4, 11.1 and 13 volts, respectively. For the atoms the best comparable figures are: C (weighted average of 1D and 1S of s^2p^2) \rightarrow $C^+(s^2p, ^2P)$, 9.8 volts; N (w. ave. 2D , 2P of s^2p^3) \rightarrow $N^+(^3P$ of s^2p^2), 11.7 volts; O (w. ave. 1D , 1S of s^2p^4) \rightarrow $O^+(w. ave. ^2D, ^2P$ of s^2p^3), 15.2 volts.

The relatively high value for CH_4 is evidently a consequence of the fact that the $[p]$ type is not split up. (The possibility,—cf. end of Table I,—that CH_4^+ has a different symmetry than CH_4 is not important for the observed ionization potential if it is non-adiabatic.) It will be noted that, judging from the ionization potential, the $[p]$ electrons in CH_4 are bound nearly as firmly as p electrons in the O atom. The low values for the other molecules RH_n , lower even than for the atoms R, are evidently consequences of the splitting up of the $[p]$ type into $[\sigma]$ and $[\pi]$ in NH_3 , or $[z]$, $[y]$, and $[x]$ in H_2O , of which the observed minimum potential corresponds to the most loosely bound type. The latter is clearly $[\sigma]$ in NH_3 , $[x]$ in H_2O .

In the case of NH_3 the argument is as follows. Assuming for simplicity that NH_3 is plane, as is nearly true, we see that only the $[s]$ and $[\pi]$ orbitals have hydrogen-bonding power, the $[z]$ orbitals being, in zeroth approximation, pure N atom orbitals (cf. Eqs. (2)). The bonding orbitals $[s]$ and $[\pi]$ are all concentrated near the plane of the four nuclei, especially in the regions between the N nucleus and the H nuclei. Brief consideration indicates that while the $[s]$ and $[\pi]$ orbitals are mainly in regions of lower potential than for a free N atom, the $[\sigma]$ orbitals are mainly in a region of relatively higher potential near the z axis, and should be less firmly bound. A similar argument applies to the $[x]$ orbitals in H_2O . These are in zeroth approximation pure O atom orbitals (cf. Eqs. (8) of IV).—It should be noted that the actual departure of normal NH_3 from planeness is enough to make the observed ionization potential, although it is strikingly low, considerably higher than would otherwise probably have been expected (cf. Table I, and note**).

NH_4 (known as an unstable substance in

⁴ Cf. R. Mecke, Zeits. f. Physik **81**, 313, 445, 465 (1933) for recent exact results.

⁵ Cf. E. Teller and L. Tisza, Zeits. f. Physik **73**, 791 (1932) for removal of last difficulties.

⁶ D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932); N. Rosen and P. M. Morse, Phys. Rev. **42**, 210 (1932); E. Fermi, Rend. Lincei **16**, 179 (1932).

large compared with the *average* value of about 4 volts per H atom for the formation of CH_4 from $\text{C}+4\text{H}$.

If, however, the CH_3^++H formed from CH_4 at 15.5 volts possess kinetic and the CH_3^+ internal energy, the above value is correspondingly lowered. If for instance the newly formed CH_3^+ had in the first moment the same shape as if it were still part of CH_4 , it would thereby possess vibrational energy of probably 1 or 2 volts as compared with CH_3^+ in equilibrium. Since it seems improbable that the products CH_3^++H produced at 15.5 volts carry away more than 2 volts energy as a result of departure from adiabatic conditions, we find that $\text{CH}_4 \rightarrow \text{CH}_3+\text{H}$ probably takes at least 5 volts.

In I it was pointed out that the energies of formation *per hydrogen atom*, in kilocalories, are about 148, 110, 87, 91 for HF , H_2O , NH_3 , CH_4 , and that the value for CH_4 is conspicuously higher than one would get by an extrapolation from the other three values.⁸ To the above series can now be added the figures (79) and 123 kcal. per H atom for $\text{C}+3\text{H} \rightarrow \text{CH}_3$ and $\text{N}^++4\text{H} \rightarrow \text{NH}_4^+$, which can be calculated assuming 5 volts for $\text{CH}_4 \rightarrow \text{CH}_3+\text{H}$ and using 9 volts for $\text{NH}_3+\text{H}^+ \rightarrow \text{NH}_4^+$. From these results and from the general chemical evidence on the high stability of molecules and ions RX_4 compared with RX_3 , one sees the importance of the *number* of centers X (the coordination number) for the stability of electron structures. Apparently, other things being equal, the arrangement of four X around an R allows the valence electrons to settle down considerably more firmly than does that of three X in either a plane or a pyramidal RX_3 . The theoretical reasons for this are not obvious. Perhaps they depend on a lessening of the average electronic repulsions in RX_4 because of the high symmetry which is possible.

The high values found in preceding paragraphs for the energies of the reactions $\text{NH}_3+\text{H}^+ \rightarrow \text{NH}_4^+$

⁸ The values for NH_3 and CH_4 may be in error by as much as 2 or 3 kcal. because of uncertainty as to the heat of dissociation of N_2 (here the value 194 kcal. was used) and as to the heat of sublimation of carbon (141 kcal. used here) and its interpretation. These uncertainties do not affect the qualitative conclusions reached here. The values here are revised as compared with R. Mecke, *Zeits. f. physik. Chemie* 7, 108 (1930).

and $\text{CH}_3+\text{H} \rightarrow \text{CH}_4$ have been seen to agree with the above conclusions. The strong tendency of NH_3 to form NH_4^+ and other complexes can also be understood from another point of view: it can be attributed directly (cf. I and II) to the resulting stabilization of the two loosely bound nonbonding $[z]$ electrons of NH_3 , which usually enter into one-sided ("semi-polar") bonds. Presumably there is a connection between the relatively low energy of formation of NH_3 from $\text{N}+3\text{H}$ and the existence in it of the loosely-bound $[z]$ electrons. It is, however, probably incorrect to attribute the former, as was done in I, simply to the fact that it contains these $[z]$ electrons.

It might be suggested that it is the greater availability of the *s* electrons for valence purposes in CH_4 than in NH_3 (cf. Section 14), rather than the geometrical possibilities, which makes CH_4 relatively so stable. The high energies of formation of NH_4^+ from NH_3 and of CH_4 from CH_3 , also the instability of BH_3 (where the availability of the *s* electrons is even greater) as against B_2H_6 , all give evidence against this.

13. RH_n absorption spectra

The observed ionization potentials of H_2O , NH_3 , CH_4 are 14.4, 11.1, 13 volts. If the lowest excited state of each of these molecules is obtainable by adding an electron in the same type of excited molecular orbital (presumably $3s$) to the molecule ion, then one might expect the frequencies at which the corresponding ultraviolet absorption spectra begin, to run roughly parallel to the ionization potentials. The energy of binding of a $3s$ orbital should probably increase slightly from CH_4 to H_2O , with an average value of about 4.5 volts (cf. NH_4 in Section 12). Such a $3s$ orbital should be large enough to be atom-like, resembling a penetrating $3s$ orbital of excited O, F, or Ne.

Actually it is true that NH_3 , with the lowest ionization potential, does show marked absorption at considerably longer wave-lengths than H_2O or CH_4 . The NH_3 absorption consists of a long series of bands of which those at longest wave-lengths ($\lambda 2360$ to $\lambda 2213$) show evidence of fine structure, while toward shorter wave-lengths the bands become diffuse, corresponding to fairly strong predissociation, at the same time in-

creasing rapidly in intensity to a very strong plateau or maximum at and below $\lambda 2000$.^{9, 10} The bands are accompanied by a continuous background. If the excited state involved is thought of as obtained by adding an excited electron to NH_3^+ (11.1 volts), then the energy of binding of this electron is about 5 volts, approximately what we expected for a $3s$ orbital. This value is obtained by taking an energy of excitation of 6.2 volts, corresponding to about $\lambda 2000$, where the absorption is strong (beginning of Franck-Condon maximum). This is the proper thing to do, since the observed ionization potential 11.1 volts probably corresponds to the beginning of fairly strong ionization (Section 12).

At one atmosphere pressure with a 15 mm path, CH_4 shows complete absorption from $\lambda 1800$ down.¹⁰ (Under the same conditions NH_3 shows complete absorption below about $\lambda 2150$.¹⁰) This continuous spectrum presumably represents a dissociation or predissociation process. The same explanation may reasonably be suggested for the strong continuous band which, beginning suddenly near $\lambda 1800$, initiates the ultraviolet absorption of H_2O vapor.¹⁰ Apparently it happens only in NH_3 that the ionization potential is low enough to permit the spectrum to begin with transitions to an excited state which is in some degree stable. The unstable states which give rise to continuous absorption can perhaps best be thought of as repulsion states of $\text{RH}_{n-1} + \text{H}$ or $\text{RH}_{n-2} + \text{H}_2$.

14. Electronic structure and form of RX_3 molecules

According to Zachariasen's rule⁷ as applied to RX_3 molecules, these are plane (D_{3h}) if the number of valence electrons is just enough so that the molecule could be thought of as built up from rare-gas-form ions (examples $\text{B}^{+3}\text{H}^-_3$ and $\text{N}^{+5}\text{O}^-_3$), but pyramidal (C_{3v}) if more

valence electrons are present (examples $\text{C}^{+3}\text{H}^-_3$, $\text{N}^{+3}\text{H}^-_3$, $\text{Cl}^{+5}\text{O}^-_3$, with one valence electron remaining on C^{+3} , two on N^{+3} , Cl^{+5}). The rule is confirmed in all observed cases,⁷ including NO_3^- , NH_3 , ClO_3^- but not yet BH_3 or CH_3 .

It is now of interest to see whether the present formulation in terms of molecular orbitals would lead one to expect such results and if so, why. Comparing the electron configurations $1s^2[s]^2[\pi]^4$ of BH_3 , $\cdots [\pi]^4[z]$ of CH_3 , and $\cdots [\pi]^4[z]^2$ of NH_3 (cf. Table I), we see that if Zachariasen's rule is applicable here, it is the $[z]$ electrons whose presence or absence determines whether RH_3 is plane or pyramidal. Similarly NO_3^- (plane) and ClO_3^- (pyramidal) differ in that the former has no $[z]$ electrons, the latter two (cf. I, VII). A good reason why $[z]$ electrons tend to make RX_3 molecules pyramidal is to be seen in the fact that they are nonbonding for the plane form (Eqs. (2)) but can be strongly bonding (d'' large in Eqs. (3)) for high-pyramid forms.

For the types $[s]$ and $[\pi]$ the possibility of strong bonding is not so obviously dependent on whether the molecule is plane or pyramidal. It appears likely, however, that strong withdrawal of the R atom from the X_3 plane might reduce the bonding power of $[\pi]$, since the R atom p_x and p_y orbitals would then overlap the H orbitals α , β , γ less. From this discussion, it would seem to be a quantitative rather than a qualitative matter whether the presence of one or even two $[z]$ electrons suffices to make a molecule pyramidal. NH_3 is, of course, known to be pyramidal, but the pyramid is rather low (about 0.38\AA high⁶), so that it would seem quite possible that NH_3^+ and CH_3 as well as BH_3 might be plane.

The idea that the decision between a plane and a pyramidal form depends entirely on an equilibrium between opposing tendencies of $[z]$ and of $[s]$ and $[\pi]$ electrons needs qualification in two respects. (1) If one writes out the complete ψ of a molecule (cf. IV), using molecular orbitals for the shared electrons, then rearranges suitably, ψ can be expressed as a linear combination of a number of ψ 's corresponding to a variety of ionic and electron-pair bond states. The former include states with R positive and one or more H's negative and others with R negative and one or more H's positive (cf. Van Vleck² for CH_4 as an example). For an essentially nonpolar molecule,

⁹ Ferrières, *Comptes Rendus* **178**, 202 (1924); G. Landsberg and A. Predwoditeff, *Zeits. f. Physik* **31**, 544 (1925); K. F. Bonhoeffer and L. Farkas, *Zeits. f. physik. Chemie* **134**, 337 (1929); V. Henri, *Leipziger Vorträge* 1931, p. 131 (S. Hirzel, Leipzig); J. K. Dixon, *Phys. Rev.* **43**, 711 (1933).

¹⁰ S. W. Leifson, *Astrophys. J.* **63**, 73 (1926). For a correction in regard to CH_4 , cf. R. Gräfin zu Dohna, *Zeits. f. Physik* **81**, 745 (1933).

there is a sort of even balance between the states with R positive and those with R negative (cf. H_2 in II, Section 13), but in general one of these sets preponderates more or less and the molecule can be called polar. In such cases, the molecule's shape evidently depends partly on polar forces. (2) So far we have neglected possible hybridization of $[s]$ and $[z]$, which for C_{3v} both belong to representation a_1 . Such hybridization cannot occur for D_{3h} and is obviously unimportant for nearly plane forms and for atoms like O, F, Cl, but should be important for high-pyramid molecules with atoms like B, C, and perhaps also N. In the limiting case of complete mixing, which might occur if the $ns-np$ energy interval were negligible compared with energy effects associated with formation of molecular from atomic valence orbitals, we should have $g=c$, $g^*=d^*$, $c''=g''$ in Eqs. (3), so that $[s]$ would be $a(s-p_z) + b(\alpha+\beta+\gamma)$. By graphically adding s and $-p_z$ and renormalizing, one sees that $s-p_z$ in a pyramidal molecule gives much stronger overlapping with $(\alpha+\beta+\gamma)$ than does s in a plane molecule ($g, g^*=0$). Hence the bonding effects of $[s]$ for a high-pyramid molecule would be much stronger than for a plane molecule. At the same time $[z]$, which (since here $c''=g''$ in Eqs. (3)) would be of the form $a'(s+p_z) + (or -)b'(\alpha+\beta+\gamma)$, would be nearly nonbonding because $s+p_z$ overlaps $(\alpha+\beta+\gamma)$ very little. [When $g=c$, ... as in the case considered here, the designations $[s]$, $[s]^*$, $[z]$ are really inappropriate, but in general, with $c>g$, $c''>g''$, ... they are not unreasonable.]

In BH_3 , it seems likely that the valence orbital $[s]$ could be of the strongly hybridized type (g nearly as large as c), so that quite possibly the molecule,—electron configuration $1s^2[s]^2[\pi]^4$,—is after all pyramidal contrary to Zachariasen's rule. In CH_3 , with configuration $1s^2[s]^2[\pi]^4[z]$, the pyramidal form also seems likely, in agreement with Zachariasen's rule. It

seems likely, however, that NH_3^+ is plane (cf. third paragraph of this section), since $s-p$ hybridization is probably negligible. If CH_3 is pyramidal, the type $[s]$ probably contains considerably more s than p_z and the type $[z]$ considerably more p_z than s . The type $[z]$ is very likely nearly nonbonding here, since it is always nonbonding for a plane RH_3 molecule and should be nearly so for the other limiting case of a pyramidal molecule with strong $s-p$ hybridization.

From the approximately known dimensions of the NH_3 molecule⁶ one can draw some conclusions about its structure. In view of the relatively high Z and low-pyramidal form, we may probably neglect hybridization of $[s]$ with $[z]$, i.e., put $g\sim 0$ and $g''\sim 0$ in Eqs. (3). Because of the relatively high Z , it is probable that $[s]$ gives only a little H-bonding (c/d large compared with $3^{\frac{1}{2}}$ in Eqs. (3)). Because the pyramid is rather low, $[z]$ cannot give very strong H-bonding (c''/d'' fairly large compared with $3^{\frac{1}{2}}$ in Eqs. (3)). This leaves the $[\pi]$ electrons as the chief bonding electrons. Defining a nonpolar bond as consisting of two strongly bonding electrons, one may estimate that the NH_3 molecule has about $2\frac{1}{2}$ such bonds (two $[\pi]$ bonds, and one-half bond divided between $[s]$ and $[z]$).

The $[\pi]$ electrons would have maximum bonding power for $c'=6^{\frac{1}{2}}d'$ in Eqs. (3); this would correspond to equal participation of N and H orbitals in $[\pi]$. Assuming this relation,—of course it can hardly be exactly true,—and assuming d/c and d''/c'' quite small, the molecular configuration $[s]^2[\pi]^4[z]^2$ would correspond in its make-up to a preponderance of N atom over H atom orbitals, i.e., NH_3 would be somewhat polar with the N negative. It may then be that the deficiency in nonpolar bonds ($2\frac{1}{2}$ instead of the three assigned by ordinary valence theory and by the Pauling-Slater model with 90° valence angles) is made up by polar forces.