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# ELECTRONIC STRUCTURES OF POLYATOMIC MOLECULES AND VALENCE

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## Abstract

The electronic structures of a number of molecules and ions ($H_2O$, $NH_3$, $CH_4$, $CF_4$, $CI_4$, $ClO_4^-$, $SO_4^=$, $ClO_3^-$, $SO_3^=$, $CO_2$, and others) are briefly described in terms of one-electron wave functions; other molecular types are easily described in a similar way, and will be discussed in later detailed papers. Many valence phenomena can be understood using these wave functions and a simple rule based on the Pauli principle.

The electronic structures of polyatomic molecules can probably best be understood by expressing them in terms of one-electron wave functions. The forms of these are conditioned by the symmetry of the molecule, which is that given by the arrangement of the nuclei.

Following are the electron configurations of a number of simple hydrides with ten electrons: HF, $OH^-$, $1s^2\ 2s^2\ 2p\sigma^2\ 2p\pi^4$; $H_2O$, $NH_2^-$, $1s^2\ 2s^2\ 2pa^2\ 2pb^2\ 2pc^2$; $H_3O^+$, $NH_3$, $1s^2\ 2s^2\ 2p[\pi]^4\ 2p[\sigma]^2$; $NH_4^+$, $CH_4$, $1s^2\ 2s^2\ 2p^6$. The order in which the symbols are written is that of decreasing firmness of binding. The $2s$ and $2p$ types, more or less modified, of course, always remain distinct; the $2p$ type does not split up in the case of regular tetrahedral symmetry ($CH_4$), splits into two types $\sigma$ and $\pi$ in linear molecules (HF) or into a different but somewhat related pair of types $[\pi]$ and $[\sigma]$ in molecules having the symmetry of a trigonal pyramid ($NH_3$), and splits into three types when the symmetry is that of an isosceles triangle ($H_2O$). The amount of splitting corresponding to each kind of molecular symmetry can be easily determined by group theory methods.[1] The results just stated are based on the kinds of symmetry empirically known for the nuclear configurations in $H_2O$, $NH_3$, and $CH_4$.

Empirical data on the energy of formation of each of the molecules HF, $H_2O$, $NH_3$, $CH_4$ from their atoms indicate that the tetrahedral arrangement of the hydrogen nuclei, combined with the one-electron wave functions adapted thereto, gives a relatively high stability: the energies of formation *per hydrogen atom*, in kilocalories, are about 148, 110, 87, and 91 for HF, $H_2O$, $NH_3$, $CH_4$. The value for $CH_4$ is higher than one would get by an extrapolation from the other values. A theoretical reason for this may probably be found in the form of the wave functions. In $CH_4$ the four H nuclei are embedded in the wave functions of the six equivalent modified-$2p$ wave functions and to a somewhat less extent in those of the two $2s$ wave functions. All these wave functions, of course, correspond to "representations of the tetrahedral group", i.e., have symmetries of a tetrahedral type. The present

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[1] Cf. H. Bethe, Ann. d. Physik [5], **3**, 133 (1929).

explanation of the structure and stability of $CH_4$ in terms of one-electron wave functions seems at first sight not closely related to that given by Pauling[2] and Slater.[3] The zeroth order wave functions which they use do indeed indicate that tetrahedral symmetry should give high stability, but it seems doubtful whether their wave functions are the most appropriate ones (cf. note added in proof, below).

With the triangular pyramid arrangement as in $NH_3$, the three H nuclei are embedded in the four $2p[\pi]$ and to a lesser degree in the two $2s$ wave functions. But the two $2p[\sigma]$ electrons in $NH_3$ avoid the region of the H nuclei, and as a result are relatively loosely bound and reduce the energy of formation of the molecule. Direct evidence of these electrons in $NH_3$ is given by the low ionization potential of this molecule, which is 11.1 volts. $CH_4$, on the other hand, has an ionization potential of 14.5 volts. One may predict roughly that ionization of a $2p[\pi]$ electron of $NH_3$ would take 15 volts, and of a $2s$ electron 23 volts in $CH_4$ and 25 volts in $NH_3$. Many features of the chemical behavior of $NH_3$, e.g., the formation of $NH_4^+$, $BCl_3 \cdot NH_3$, $Cu^{++}(NH_3)_4$, are reasonably interpreted as conditioned by the stabilization of the two loosely bound $2p[\sigma]$ electrons of $NH_3$ under the influence of an additional nucleus, giving relations somewhat closely related to those for tetrahedral symmetry.

For the ionization potentials of $H_2O$ the following rough estimates may be given: $2pc$, 13.2 volts (*observed*); $2pb$, $2pa$, 16 and 17 volts; $2s$, 30 volts. The $2pc$ type in $H_2O$ is relatively loosely bound like the $2p[\sigma]$ in $NH_3$.

Among the molecules or "radicals" related to the foregoing, but containing fewer electrons, there is interesting experimental evidence concerning $CH_4^+$, $CH_3$, $CH_3^+$. The energy of dissociation of $CH_4$ into $CH_3+H$ is perhaps roughly 120 kilocalories, or at any rate much more than the average value 91 kcal per H atom for $C+4H \rightarrow CH_4$. Probably the $CH_3$ radical is pyramidal like $NH_3$, with an electron configuration $1s^2\ 2s^2\ 2p[\pi]^4\ 2p[\sigma]$, the $2p[\sigma]$ electron making it relatively unstable. Taking 5.2 volts (120 kcal) for $CH_4 \rightarrow CH_3+H$, and using the result of Hogness and Kvalnes[4] that $CH_3^+$ ions are produced from $CH_4$ at 15.5 volts ($CH_4 \rightarrow CH_3^+ + H + \epsilon$), while $CH_4^+$ ions are produced at 14.5 volts, one gets 10.3 volts for the ionization potential of $CH_3$, a result in harmony with the above interpretation. When $CH_3$ molecules unite with other atoms or radicals, as in $C_2H_6$ or $CH_3Cl$, the loosely bound $2p[\sigma]$ electron becomes firmly bound by being shared with another nucleus which at the same time shares an electron with the $CH_3$ radical. Thus there is formed an "electron-pair bond". The stabilization of the $2p[\sigma]$ electron here is similar in nature to that effected when $NH_3$ forms $NH_4^+$ or unites with $BCl_3$, although in terms of conventional valence theory the two latter processes are quite different from the present one.

More complicated molecules can be treated by extending the methods used above. The following additional *valence rule*, with which the preceding

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[2] L. Pauling, J. Am. Chem. Soc. **53,** 1367, 3225 (1931).

[3] J. C. Slater, Phys. Rev. **37,** 481; **38,** 325, 1109 (1931).

[4] Phys. Rev. **32,** 942 (1928).

results also are in harmony, is needed: Every nucleus in a molecule tends to be surrounded by an electron density distribution corresponding to some stable electron configuration having a total charge approximately equal to or somewhat exceeding the charge of the nucleus; the electron density distribution as a whole, and the individual wave functions, have symmetries adapted to the configuration of nuclei surrounding the given nucleus. By "stable configuration" is meant a set of wave functions completely occupied by electrons (i.e., a set of closed shells) and of such type that further electrons could go only into wave functions of distinctly higher energy,—usually of higher quantum number, from the point of view of the central nucleus. The truth of the first part of the rule follows at once from the fact that for the electrons in the neighborhood of every nucleus in a molecule the Pauli exclusion principle makes effectively nearly the same requirements as for electrons in an isolated atom.

This simple rule, together with the energy-decrease which is normal when a bonding electronic wave function is brought near an incomplete atom, suffices to give a qualitative explanation of molecule-formation and of the ordinary numerical aspects of valence (combining ratios), and covers polar and non-polar valence under a single viewpoint. The first part of the rule is in most respects merely a somewhat generalized re-statement in present-day quantum language of the familiar rules of Lewis and Langmuir (cf. especially the "octet"-forming tendency emphasized by these authors). Essentially this same principle has been used earlier by Dunkel[5] and others and still earlier but rather less definitely by Knorr.[6] Dunkel's results on electron configurations in polyatomic molecules are more or less similar to and in some cases the same as those obtained here. Knorr's results on valence phenomena are also in many respects similar to the present.

The principal novelty in the present viewpoint in regard to molecular structure, aside from the consideration of the effect of the symmetry of the molecule on the wave functions, consists in the following: in general no attempt is made to treat the molecule as *consisting of* atoms or ions. Attempts to regard a molecule as consisting of specific atomic or ionic units held together by discrete numbers of bonding electrons or electron-pairs are considered as more or less meaningless, except as an approximation in special cases, or as a method of calculation. It is believed that the main physical content of the assumption that a molecule consists of specified atoms or ions, or even of a quantum-mechanical hybrid of several different sets of these, could better be expressed in terms of electric moments. A molecule is here regarded as a set of *nuclei*, around each of which is grouped an electron configuration closely similar to that of a free atom in an external field, except that the outer parts of the electron configurations surrounding each nucleus usually belong, in part, jointly to two or more nuclei. The electron configuration surrounding each nucleus can be described to a good approximation *with reference to that nucleus* in terms of its own set of electronic quantum

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[5] Dunkel, Zeits. f. phys. Chem. [*B*] **7**, 81; **10**, 434 (1930).

[6] Knorr, Zeits. f. anorgan. Allgem. Chem. **129**, 109 (1923).

numbers or one-electron wave functions. In the case of shared electrons, the same wave functions may be given quite different approximate formulations or descriptions from the points of view of different nuclei. The procedure just outlined is useful for a qualitative understanding of many features of chemical valence, especially combining ratios and valence saturation. A more accurate and detailed method of dealing with shared electrons is to make use of one-electron wave functions whose effective domains embrace more than one atom.

The molecules $CF_4$ and $CI_4$ will serve as illustrations of both methods. Presumably the arrangement of the nuclei is tetrahedral as in methane. First let us consider $CF_4$. The electrons immediately surrounding the carbon nucleus in all probability constitute, from the latter's point of view, a set of closed shells $1s^2\ 2s^2\ 2p^6$, the one-electron wave functions being much like those in methane. Other electrons in the molecule, namely, those specially attached to the fluorine atoms, perhaps function from the point of view of the carbon nucleus as 3- or 4- quantum electrons. Their connection with the carbon nucleus is, at any rate, very remote.

Now considering the electron configuration from the point of view of a fluorine nucleus, the electrons immediately surrounding the latter undoubtedly constitute a set of closed shells $1s^2\ 2s^2\ 2p^6$, while other electrons are too distant to be of much importance. From the point of view of the electrons near one F nucleus, the rest of the molecule (approximately $CF_3$) sets up a field of force which is nearly symmetrical around the F-C axis, although strictly speaking it has symmetry like that in $NH_3$ or better, as in $CH_3F$. This field causes a splitting of the $2p^6$ group of the F nucleus in question into $2p[\sigma]^2\ 2p[\pi]^4$, of which $2p[\sigma]^2$ is shared with the C nucleus. In fact the four pairs $2p[\sigma]^2$ belonging to the four fluorine nuclei are all shared by the carbon nucleus, which regards these same electrons as constituting its own outer shell $2s^2\ 2p^6$.

The complete molecule may now be approximately described as consisting of $1s^2$ close to the C nucleus, $1s^2 2s^2 2p[\pi]^4$ near each F nucleus, and eight shared wave functions. (Strictly speaking, the fluorine types $1s$, $2s$, $2p[\pi]$ each split up as a result of "resonance" interactions, but for most purposes this effect can be neglected.) *Each* of the shared wave functions surrounds the C nucleus and reaches out to and around each F nucleus. Two of them correspond approximately to a linear combination consisting to the extent of perhaps about 50 percent of a tetrahedralized but uncombined $2s$ carbon wave function plus $12\frac{1}{2}$ percent each of four uncombined $2p[\sigma]$ fluorine wave functions. The other six consist of similar combinations of tetrahedralized uncombined carbon $2p$ plus uncombined $2p[\sigma]$ of the four F atoms, probably with the latter predominant, corresponding to the strong tendency of the F to be $F^-$. The resulting wave functions are largely concentrated in the regions between the C and the F nuclei and so are acceptable to the various nuclei as parts of their outer shells, at the same time being very effective in producing chemical binding; only a small fraction of the density is behind the F nuclei or (in the $2s$ type) too close to the C nucleus to be effective. Although eight electrons, of two types, take part in the binding of each F atom, only about two of these on the average are in action at any one instant between the C and any one F. It is these two electrons which, in spite of the fact that they belong to *two types* different in energy and one contributing about $\frac{1}{2}$ electron and the other $1\frac{1}{2}$ electrons on the average, are regarded by the F nucleus as fairly satisfactorily representing its shell of two $2p[\sigma^4$ electrons.

In the molecule $CI_4$, the much weaker electron affinity of the I atom very likely has the following results: (1) two of the shared wave functions are such as might be formed from say possibly 88 percent of carbon $2s$ and only 3 percent each of the iodine $5p[\sigma]$'s, i.e., the carbon nucleus shares its $2s$ electrons very little; (2) the other six shared wave functions are such as might be formed from say possibly 50 percent of carbon $2p$. Thus the four halogen atoms in $CI_4$ are held practically by about six electrons, instead of by about eight as in $CF_4$. This causes $CI_4$ to be chemically relatively unstable.

The electronic structure of such groups as $BF_4^-$, $SO_4^=$, $ClO_4^-$ is doubtless of the same type as that of $CF_4$ and $CI_4$. Each O nucleus in $SO_4^=$ and $ClO_4^-$ shares two electrons which from its point of view are $2p[\sigma]$, these eight electrons functioning at the same time as (tetrahedralized) $3s^23p^6$ for the S or Cl atom. In the groups $SO_3^=$ and $ClO_3^-$ only six electrons of the expected shell $3s^23p^6$ of the central nucleus can be shared, otherwise the 2-quantum oxygen shells would be more than filled. Now $SO_3^=$ and $ClO_3^-$ have a pyramidal structure,[7] hence the group $3p^6$ must be subdivided into $3p[\pi]^43p[\sigma]^2$, with the $[\sigma]$ type less firmly bound than the $[\pi]$ (cf. discussion of $NH_3$ above). Doubtless the two $3p[\sigma]$ electrons, whose wave functions avoid the vicinity of the O nuclei, are the unshared ones, while $3s^23p[\pi]^4$ describes the shared electrons from the viewpoint of the central nucleus. From the viewpoint of the O nuclei, these same six electrons function as three pairs of $2p[\sigma]$ electrons, one pair for each O nucleus. The existence of the unshared $3p[\sigma]$ electrons is in harmony with conclusions of Zachariasen.[7]

The electronic structures of many other types of molecules can be described with some confidence by proceeding according to the methods illustrated above. These will be discussed in forthcoming more detailed publications. A beginning has been made for some of these in a recent article.[8] Other authors, especially Hund and Herzberg, have also been attacking the problem from more or less similar viewpoints. One more example, that of the $CO_2$ molecule, will be given here. This illustrates particularly well the uselessness of trying to decide whether molecules are composed of atoms or ions and in what states. The examples already given also illustrate the same point, but are more complicated.

It is now generally accepted that $CO_2$ is a linear molecule. Hence its electrons can be classified, like those of a diatomic molecule, as $\sigma$, $\pi$, $\delta$ . . . . Since $CO_2$ is diamagnetic, its normal state in all probability has a configuration of closed shells. Consideration of available evidence makes it probable that there are *two* closed shells ($\pi^4$) of $\pi$ electrons. Hence the complete electron

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[7] Cf. W. H. Zachariasen, J. Am. Chem. Soc. **53,** 2123 (1931).

[8] R. S. Mulliken, Chem. Reviews **9,** 347 (1931).

configuration is of the type $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4$.Consideration of the available evidence, and application of the valence rule stated above, according to which each nucleus tends to be surrounded by what from its point of view is a closed shell, leads to a rather definite description of the wave functions. They may be approximately described by writing the electron configuration as follows:

$$(1s)^2{}_{\mathrm{O}}(1s)^2{}_{\mathrm{O}}(1s)^2{}_{\mathrm{C}}(2s)^2{}_{\mathrm{O}}(2s)^2{}_{\mathrm{O}}(\sigma)^2{}_{\mathrm{C-O}}(\sigma)^2{}_{\mathrm{C-O}}(\pi 2p)^4{}_{\mathrm{C-O}}(\pi^* 2p)^4{}_{\mathrm{O}}.$$

The first six electrons are essentially $1s$ electrons of the O and C atoms, the next four,—which might also be written $(\sigma 2s)^2(\sigma^* 2s)^2$,—are slightly modified oxygen $2s$ electrons. All these are non-bonding electrons or nearly so (strictly, $\sigma 2s$ are somewhat bonding, $\sigma^* 2s$ somewhat anti-bonding). Next come eight bonding electrons (four $\sigma$ and four $\pi$), enough to give two bonding pairs between the C and each O, in agreement with conventional valence theory. Finally there are four non-bonding (or slightly anti-bonding) $\pi$ electrons which remain near the O nuclei. The two pairs of $\sigma$ bonding electrons have wave functions which are concentrated mainly around the C nucleus and, especially, between the C and the O nuclei, while the $\pi$ bonding electrons are concentrated mainly between the C and the two O's, half on the side of each O. From the point of view of the carbon nucleus the two $\sigma^2$ pairs represent $2s^2 2p\sigma^2$ while the $\pi^4$ group represents $2p\pi^4$, so that the carbon nucleus has a complete $L$ shell. From the point of view of either O nucleus, about *half* of the electron density represented by the bonding electrons $\sigma^2\sigma^2\pi^4$ is near enough to it to count as belonging to its $L$ shell, and counts as $2p\sigma^2 2p\pi^2$. The additional $2p\pi^2$ necessary to complete the $L$ shell is represented by that half of the electron density corresponding to $(\pi^* 2p)^4$ which is near the nucleus in question. This picture of the wave functions is exactly what one would get by pushing two $O^{=}$ ions up against a $C^{++++}$ ion, but it is equally what one would expect from $2O^{-}+C^{++}$, or $2O^{+}+C^{=}$, or $2O+C$. Nevertheless it is foolish to try to think of the molecule as consisting of any one of these sets of ions or atoms.

The writer is indebted to Professors C. Eckart and J. H. Van Vleck for helpful suggestions.

*Added in Proof.* Further consideration indicates that the present method gives results which are usually essentially in agreement with those of Pauling and Slater, but that it goes considerably farther. Hund also has developed the method of molecular one-electron wave functions and has obtained important results.[9] He has not, however, as yet paid much attention to the matter of finding wave functions having the proper symmetry with respect to the nuclear configurations. Recently[10] he has expressed the conclusion that the Pauling and Slater method of electron-pair "localized bonding" is a poorer approximation than a method like the present one, but nevertheless a very valuable approximation corresponding rather well to the conventional electron-paid bond theory of homopolar valence. In the writer's opinion, the present method gives the possibility of going behind conventional valence theory

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[9] F. Hund, Zeits. f. Physik **73,** 1 (1931).

[10] F. Hund, Zeits. f. Physik **73,** 565 (1932).

and understanding both the rules and the exceptions together, and furthermore is well adapted to intermediate cases, e.g., cases on the border-line between homopolar and heteropolar valence. The present method also goes beyond that of Slater and Pauling in its ability to deal with spectroscopic terms and ionization potentials.

In the case of molecules like $NH_3$ and $ClO_3^-$ having the symmetry of a trigonal pyramid, the wave functions above called $s$ and $p[\sigma]$ both belong to the same representation of the symmetry-group. [This particular symmetry-group has not been considered by Bethe.] A consequence, overlooked in the discussion given above, is that the true molecular wave functions must correspond to (perturbed) linear combinations of $s$ and $p[\sigma]$. If one should take equal parts of $s$ and $p[\sigma]$, the resulting zeroth approximation wave functions may be written as $(s-p[\sigma])$, concentrated largely on the opposite side of the N or Cl nucleus from the three H or O nuclei, and $(s+p[\sigma])$, concentrated near the plane of the three H or O nuclei. The $(s+p[\sigma])$ type is well suited to share with the $p[\pi]$ type in binding the three H or O nuclei, while the $(s-p[\sigma])$ type avoids the neighborhood of all the nuclei, and agrees well with Zachariasen's conclusions as to the unshared pair of electrons in $ClO_3^-$ and similar molecules.[7] This unshared type is, however, extremely well suited to the formation of a new bond with an additional atom to form a structure of approximate or exact tetrahedral symmetry, e.g., $ClO_4^-$ from $ClO_3^-$ or $CH_3Cl$ from $CH_3$.

Actually, of course, because of the difference in energy between $s$ and $p$ in the unperturbed central atom, one must expect instead of $(s+p[\sigma])$ and $(s-p[\sigma])$, types intermediate between the former and $s$, and between the latter and $p[\sigma]$. The actual wave functions in order of energy, in say $NH_3$ or $CH_3$, can perhaps be fairly well described as (*a*) $1s$; (*b*) $2s[\sigma]$ obtained as a linear combination of $2s$ of the central atom, $1s$ of the three H atoms, and a lesser proportion of $2p[\sigma]$ of the central atom, with the $1s$ wave functions so introduced as to conform to the proper representation of the symmetry group; (*c*) $2p[\pi]$ composed of $2p\pi$ of the central atom mixed with $1s$ of the H atoms; (*d*) $2p[\sigma]$ consisting mainly of $2p\sigma$ of the central atom, a smaller proportion of $2s$, and a small proportion of $1s$ of the H atoms.

In molecules like $NO_3^-$, $CO_3^=$, and presumably $SO_3$, with a plane arrangement of the nuclei,[7] the wave functions correspond to representations of the trigonal symmetry-group, which are the same as those of the hexagonal group.[1] Here, from the standpoint of the central atom, the types $s$, $p[\pi]$ and $p[\sigma]$ are possible. Of these $p[\pi]$ is well suited to bonding and $s$ is moderately so, while $p[\sigma]$ avoids the plane of the nuclei. In this case $s$ and $p[\sigma]$ belong to different representations and so cannot hybridize as in $NH_3$ and $SO_3^=$ to form a stronger bonding type. Assuming two shared electrons per O atom, the central atom has the incomplete (but diamagnetic) shell $s^2p[\pi]^4$, the $p[\sigma]$ wave function being unoccupied. From the point of view of an O nucleus, the two electrons which it shares are $p[\sigma]$,—this must not be confused with the central-atom-viewpoint kind of $p[\sigma]$,—while its unshared electrons are $1s^22s^22p[\pi]^4$ (cf. discussion of $CF_4$, above). Possibly the twelve

$p[\pi]$ electrons of the three O atoms interact in such a way as to be available for partial sharing with the central atom, so that in effect two of their number, on the average, function as $p[\sigma]$ electrons of the central atom and so after all complete the latter's otherwise incomplete $p$ shell.

Many other interesting results can be obtained. In the case of atoms with $d$ electrons, these closely parallel the results of Pauling,[2] even to the explanation of diamagnetic and paramagnetic susceptibilities. For example, the square arrangement and diamagnetism of $PtCl_4^=$ and the octahedral arrangement and diamagnetism of $PtCl_4^=$ can be easily predicted or understood. These results are based on Bethe's work[1] showing that $d$ wave functions split into two types $d_\epsilon$ (3-fold orbital degeneracy) and $d_\gamma$ (2-fold degeneracy) in a field of octahedral or tetrahedral symmetry; $d_\epsilon$ and $d_\gamma$ are of forms which appear to be respectively specially adapted to bond-formation with tetrahedral and octahedral symmetry. The tetrahedral ions $CrO_4^=$ and $MnO_4^-$ are tentatively interpreted as having shared central-atom configurations $3d_\epsilon{}^6 4s^2$, thus being closely analogous to $SO_4^=$ and $ClO_4^-$ with $3s^2 3p^6$. This interpretation appears more plausible than Pauling's, which involves a hybrid of $3d$, $4s$, and $4p$ electrons. $SF_6$ is interpreted as being octahedral with $3s^2 3p^6 3d_\gamma{}^4$ around the $S$ core. Further details will be given later.