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A Modification of the Lewis-Langmuir Octet Rule

BY J. W. LINNETT¹

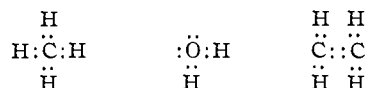
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The object of this paper is to propose that the Lewis-Langmuir octet should be treated as a *Double-Quartet* of electrons, rather than as four pairs. The consequences of this change of viewpoint have been examined for a broad variety of examples, and it has been demonstrated that, as a result, certain observations can be understood more readily than before. The form of the wave function derived according to this hypothesis is also discussed.

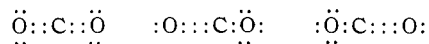
Introduction

In 1916 Lewis^{2a} proposed electronic formulae based on the "group of eight" which was later described more tersely by Langmuir^{2b} as the *octet*. Lewis also stressed the importance of "the pairing of electrons." This showed itself in the "group of two" which was encountered in compounds of hydrogen and in the pair of electrons which constituted a single covalent bond. Lewis was unable to explain the stability of molecules (or radicals) like nitric oxide and stated that the cause of this was "not yet understood."³ Pauling later accounted for the stability of these compounds and others by introducing the concept of resonance⁴; he also proposed the existence of the one and three-electron bonds. Nowadays other quite stable free radicals such as diphenyl-picryl-hydrazyl are known. In this paper, a hypothesis will be proposed which will account for the high stability of these radicals, and it will be suggested that this hypothesis is also applicable to some molecules which contain an even number of electrons. Most of the substances dealt with in this paper will be ones which contain only hydrogen and elements of the First Short Period.

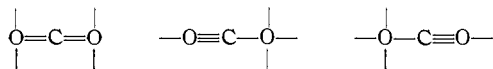
All the formulae proposed by Lewis contained electron pairs; sometimes shared, sometimes unshared (lone). For example



When resonance was proposed and accepted as an important part of valence-bond theory, the concept of the electron-pair was retained, and it was supposed that better descriptions could be given of certain molecules' electronic structures by a combination of canonical structures of the type proposed by Lewis. For instance carbon dioxide was represented by a resonance mixture of



which was more usually written as



That is, all the contributing structures were made up of electron pairs. It is one of the main purposes

of this paper to suggest that the importance of the pairing of electrons has been overemphasized.

Lewis's proposal of the octet preceded the concept of electron spin together with its many consequences, but now it is accepted that the stable octet is made up of four electrons of one spin and four of the other. In this paper it is proposed that the octet should be applied to structures on this basis. That is, it should be treated as two groups of four rather than as four pairs, as was done by Lewis (moreover this has continued to be an integral part of the octet and valence-bond theory ever since and wave-functions are constructed using it). Further it will be supposed, as theory would suggest, that each group of four electrons will tend to have a disposition round the nucleus which is approximately that of the corners of a regular tetrahedron.⁵ In many molecules, such as CH₄, H₂O, aliphatic hydrocarbons and their simple derivatives, etc., the two groups of four are similarly disposed round each nucleus, and the two descriptions (two-quartets or four-pairs) then become identical. There are other molecules and stable radicals in which it appears that the treatment in terms of, or partly in terms of, the *double-quartet* is alone satisfactory. Therefore the double-quartet treatment has a wider applicability than has the four-pairs treatment.

This change of emphasis in treating the octet is consistent with present day views regarding the behavior of electrons in atoms and molecules.⁶ The application of the Pauli Principle, in its wave mechanical form, leads to the qualitative conclusion that electrons with the same spin tend to keep apart while those having opposed spins have a tendency to come together. Phenomena associated with the *mutual* spatial distribution of electrons are usually referred to as correlation effects. The above, which are connected with spin, may be referred to as *spin correlation effects*. However, all electrons have, in addition, a general tendency to keep apart because they are all negatively charged. This is often referred to as *charge correlation*. Therefore, electrons having the same spin tend to keep apart both because of their like charge and because of spin correlation. As a consequence a group of four electrons, occupying one *s*-orbital and three *p*-orbitals, and having roughly similar radial distri-

(1) On leave from the Inorganic Chemistry Laboratory, Oxford University, England.

(2) (a) G. N. Lewis, *J. Amer. Chem. Soc.*, **38**, 762 (1916). (b) I. Langmuir, *ibid.*, **38**, 2221 (1916).

(3) G. N. Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, N. Y., 1923.

(4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939.

(5) H. K. Zimmermann and P. Van Rysselberghe, *J. Chem. Phys.*, **17**, 598 (1949); J. W. Linnett and A. J. Poe, *Trans. Faraday Soc.*, **47**, 1033 (1951); R. Daudel and C. Vroelant, *Compt. rend.*, **236**, 78 (1953); C. E. Mellish and J. W. Linnett, *Trans. Faraday Soc.*, **50**, 657, 665 (1954).

(6) P. G. Dickens and J. W. Linnett, *Quart. Rev. Chem. Soc.*, **11**, 291 (1957); J. W. Linnett, "Wave Mechanics and Valency," Methuen, 1960.

butions, have a high tendency to adopt a tetrahedral configuration.⁵ On the other hand, for electrons of opposed spins, spin and charge correlation produce opposing tendencies, the former bringing the electrons together and the latter keeping them apart. Hence, to regard the octet as two groups of four electrons would seem to be preferable; the quartets being strongly correlated within the group, but the two groups being loosely correlated the one with the other.

There are two potential advantages to be obtained from any change in the formulation of molecular structures. These are: (i) the provision of a simple and satisfactory explanation of the stability of compounds, the existence of which cannot otherwise be so readily understood; and (ii) the provision of a more simple scheme for obtaining good approximations to molecular wave functions. As regards (ii), valence-bond theory provides functions which can be improved by applying the procedure of resonance. Molecular orbital theory operates in the same way with the help of configuration interaction. However, both methods become unsatisfactory if a good representation is only achieved by the combination of a large number of structures. If the present hypothesis could provide a better representation with fewer resonating forms, then the method would be a profitable one. It will be shown that it does lead to functions intermediate between those of simple valence-bond and molecular orbital theory, and so it is likely that it may be successful as regards (ii). It will be shown that it is also successful under (i) both as regards molecular structures and also in explaining the course of certain reactions. Both aspects will be referred to in this paper but more space will be devoted to (i) than to (ii).

Summary of Hypothesis and its Basis.—The following summarize the basic guiding rules, derived from the above general considerations, that will be applied, in the pages that follow, to several particular molecules and ions:

(A) The octet of electrons is to be regarded as two sets of four, one set being made up of the electrons having one spin quantum number (*e.g.* $+1/2$) and the other having the other spin quantum number (*e.g.* $-1/2$).

(B) Because of the effects of like charge (electrostatic repulsion) and like spin (spin correlation) each set of four will have a high probability of being arranged in an approximately regular tetrahedral pattern round its nucleus. It is further postulated that the two sets of four round a given nucleus, which individually have an approximately tetrahedral arrangement, can be treated as essentially uncorrelated spatially relative to one another. As stated above, this is because of the opposing effects of electrostatic repulsion which tends to keep all electrons apart and of the Pauli Principle effect that electrons having opposite spins have a tendency to come together. There is a supposition, therefore, that these two opposing effects do, to some extent, cancel one another as far as the spatial correlation of the two tetrahedral sets is concerned.

(C) As a corollary of (B), electrons of one spin set which are participating in a double bond will

have a high probability of being disposed near the vertices of two tetrahedra (one round each nucleus) which have an edge in common between the two nuclei (*i.e.* two shared electrons). Similarly those participating in a triple bond may be visualized in terms of the combination of two tetrahedral distributions having a face in common between the two nuclei; the three electrons at the corners of this common face having a triangular distribution round the internuclear axis.

(D) Since electrons repel one another it follows that, if the two tetrahedral spin sets round a nucleus assume different dispositions, the energy will be lower than if they are close to one another (providing, of course, no other features more seriously unsatisfactory energetically are involved). The reason for this is that the mean interelectron repulsion energy is reduced. For instance, if the adoption of spatially separated dispositions by the two spin sets can be achieved with no reduction in the number of electrons in regions of space influenced by two nuclei (*i.e.* bond regions), then a structure involving two separated dispositions will have a lower energy than one having identically disposed spin sets and the same number of electrons in bond regions (*cf.* O_2 , CO_2 and others later). This will take place, as stated above, because the interelectron repulsion energy will be thereby reduced while the bonding energy is maintained. On the other hand, in CH_4 , H_2O , etc., it is *only* possible to put two electrons into each bond region if the two spin sets adopt essentially the same spatial dispositions, so that this must occur in spite of some resulting increase in the inter-electron repulsion energy. Hence, for such molecules and ions, the disposition of the two tetrahedral sets, produces four electron pairs tetrahedrally disposed, and this is the type of electron configuration found in many compounds. It is, of course, the only type of distribution allowed by the Lewis-Langmuir form of the octet rule (four pairs).

(E) The two spin sets of electrons will each tend to adopt a regular tetrahedral configuration, and any deviation from this will involve an increase of energy. Therefore, if, in a polyatomic molecule, the two spin sets have different dispositions, which correspond ideally to somewhat different nuclear arrangements (*e.g.* somewhat different inter-bond angles) the tetrahedral configurations will be distorted to accommodate an intermediate nuclear arrangement, but these distortions will result in an increase of energy (*cf.* NO_2 and others later).

It will be seen that the above rules are derived naturally and directly from the two simple basic concepts: (a) that, because all electrons are negatively charged, they tend to keep apart, and configurations in which they come close to one another will have a high energy and (b) that, as a result of so-called spin correlation effects (*i.e.* the Pauli Principle in its quantum mechanical form) electrons having the same spin tend to keep apart, while those having opposite spins tend to come together. These are two well established features of electron behavior, so that the above rules are derived from what must be regarded as the fundamental properties of electrons.

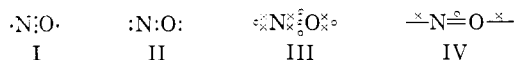
In addition to the above, simple formal charges, which have been frequently employed by others, will be used in the following way:

(F) The formal charge of an atom in a molecule is calculated by supposing that each lone electron contributes its full charge to the atom with which it is associated, and each shared electron contributes half its charge to each of the bonded atoms. Experience suggests that a formal positive charge on a fluorine atom is improbable, presumably because it leads to a high energy while the atom readily assumes a formal negative charge up to -1 (e.g. F^-). An oxygen atom can assume formal charges between $+1$ and -1 (e.g. H_3O^+ and OH^-). A nitrogen atom can readily assume a positive formal charge up to $+1$ (e.g. NH_4^+) but does not so readily assume a negative charge (NH_2^-).

The object of this paper is therefore to show, by means of a variety of examples, that these concepts, which take into account the basic properties of electrons, can be applied with reasonable simplicity and considerable success to a number of molecules by continuing to make use of the Lewis-Langmuir octet rule but modifying it so that the octet is regarded as a double-quartet.

Applications.—To begin with some applications of the first type ((i) earlier) will be described. Then it will be shown that, in a particular example, the wave function written on the basis of the present hypothesis is a reasonable intermediate between the simple valence-bond and molecular orbital functions, which is likely to be an improvement on either. Then some further applications of the first type will be presented.

Diatomic Molecules and Ions.—Molecules such as F_2 and N_2 and ions such as CN^- would be described in a similar manner by the Lewis four-pairs and by the double-quartet representations. However NO, which could not be satisfactorily described by Lewis, can be understood on the basis of the present hypothesis.⁷ The five electrons of one spin adopt the pattern shown in I and the six of the other that are shown in II. The combination of these may be indicated by III or IV. In these each atom has an octet, or double-quartet, of electrons. In II, the electrons of one spin are represented by circles and those of the other by crosses. In IV, two electrons, one of each spin

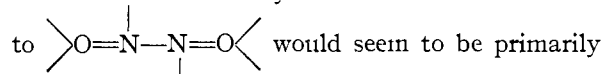


represented^{7a} by single electrons of one spin by o and single electrons of the other by x. The bond length and force constant of NO are consistent with the structure III (or IV) because they have values which are intermediate between those expected for conventional double and triple

(7) M. Green and J. W. Linnett, *J. Chem. Soc.*, 4959 (1960).

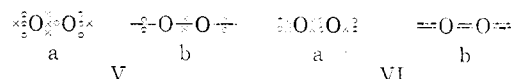
(7a) This line represents two electrons, one of each spin; it does not necessarily represent two electrons localized in the same region of space. In $CH_2=CH_2$, because the electrons of both spinsets adopt the same pattern, the two electrons in C-C do occupy the same region, but in NO (IV) the three bonding electrons of one spin-set adopt a different pattern from the two electrons of the other. That is the lines— are used more for counting electrons than for indicating the spatial distribution. A reader must examine each formula he encounters to see which is involved.

bonds.⁸ The stability of NO to dimerization



due to the fact that there is no net gain in the number of bonds in the process. Moreover, the bonds in the dimer would involve two formally coincident sets of electrons of opposed spins (*i.e.* the two spin-sets would be identical), whereas in the monomer there is a gain in stability because the electrons of one spin do not adopt the same spatial pattern as the electrons of the other spin and, as a result, the mean electron-electron repulsion energy is reduced (Rule D). This favors $2NO$ relative to the dimer energetically (*i.e.* "electron pairing" is here a disadvantage, *cf.* O_2 below).

According to the present hypothesis, the oxygen molecule might adopt the electronic structure V (a or b) or VI (a or b), both of which have four electrons concentrated in the bond region. Struc-



ture V is, in fact, that of the ground state, whereas VI, the structure of the conventional double bond, is that of an excited state.⁸ The reason why V is more stable than VI is that, in V, the electrons are separated, on an average, more widely than they are in VI; in the bond region the three electrons of one spin tend to adopt a triangular arrangement⁹ (the triangle being the common face of the tetrahedra formed by the quartets round each nucleus (Rule C)) while the other electron tends to be on the inter-nuclear axis (the electrons having this spin tend to be located near the apices of two tetrahedra having a common apex between the two nuclei). Thus this hypothesis gives a natural explanation as to why V is more stable than VI (Rule D). It is a natural "valence-bond" explanation in the sense that it is based on the Lewis-Langmuir Octet, whereas it is usually maintained that the ability to account, in easily comprehended basic terms, for the paramagnetism of O_2 is an instance of the superiority of the molecular orbital treatment over the valence-bond treatment. It is worth remarking that, both the molecular orbital explanation and the present one ascribe the reason for the paramagnetic ground state to the same cause (as they should); that is to the effects of spin correlation and the reduction in inter-electron repulsion energy by unpairing electrons. The alternate structures introduced by the present hypothesis are thought to have particular importance relative to the conventional ones because they increase the separation of electrons and hence reduce the inter-electron repulsion energy (*cf.* $2NO$ and N_2O_2 earlier).

The first two excited states of O_2 are $^1\Delta$ and $^1\Sigma$ being 22.6 and 37.7 kcal per g. atom above the $^3\Sigma$ ground state, respectively.¹⁰ Both of these

(8) J. W. Linnett, *J. Chem. Soc.*, 275 (1956).

(9) J. E. Lennard-Jones and G. G. Hall, *Proc. Roy. Soc. (London)*, **A205**, 357 (1951); J. A. Pople, *Quart. Rev. Chem. Soc.*, **11**, 273 (1957).

(10) G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," Van Nostrand Co., New York, N. Y., 1950.

may be represented by VI. However, in the $^1\Delta$ state, the electrons having opposed spins exert no azimuthal spin correlation on one another, whereas in the $^1\Sigma$ state, the sets of electrons of opposed spins tend to be coincident, insofar as the effects of spin correlation are concerned.⁸ This is the reason why the $^1\Delta$ state has a lower energy than the $^1\Sigma$ state. However, it means that the electron configuration of the $^1\Sigma$ state is more similar to that of the conventional double bond. Therefore it appears that the $^3\Sigma$ state is more stable than the conventional double bond (*i.e.* VI) by about 35-40 kcal. per g. atom. Because all these states have four electrons in the bond region, the bond lengths are approximately equal: $^3\Sigma$: 1.207; $^1\Delta$: 1.216; $^1\Sigma$: 1.227 Å.¹⁰

The double-quartet hypothesis has explained naturally the paramagnetism of the ground state of molecular oxygen. Will it explain why N_2 and F_2 are not paramagnetic in their ground states? For N_2 to be paramagnetic and involve a bond as strong as the conventional triple bond (VII), the structure would have to be that shown in VIII for this also has six electrons in the bond region. But such a structure is not possible because it

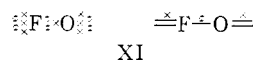


would involve the group of four bonding electrons of one spin all being on one side of the nucleus. This would require such a serious departure from the tetrahedral pattern that it is not possible (*i.e.* only possible with an excessive increase in the energy of the system). Therefore VIII is not a low energy configuration, and VII, which is diamagnetic, is the ground state. Similarly for F_2 to be both paramagnetic and involve a pair of electrons in the bond region, the structure would have to be IX. This would cause, with tetrahedral



quartets, an excessive van der Waals repulsion between electrons of the two independent quartets. This will operate against IX relative to the diamagnetic X.

Since NO exists with the structure III, it would be expected that FO would exist with the structure XI. This is not, in fact, known. F_2O_2 , which is stable at low temperatures, decomposes just above its boiling point to F_2 and O_2 .¹¹ On the other hand,



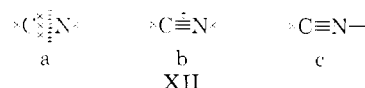
paramagnetic O_2^- , which presumably has the electronic pattern of XI, is known in crystalline KO_2 and the bond length (1.28 Å.) is intermediate between that in O_2 (1.207) and O_2^{2-} (1.49 Å.).¹² For FO, structure XI places formal charges of $+1/2$ and

(11) H. Remy, "Treatise on Inorganic Chemistry," Elsevier Publishing Co., Amsterdam, 1956, p. 801.

(12) L. E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication No. 11, Chem. Soc., London, 1958 (most bond lengths used in this paper are taken from this source).

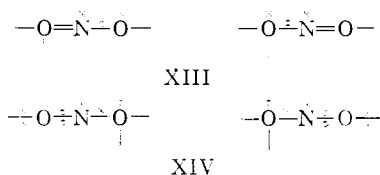
$-1/2$ on the fluorine and oxygen atoms respectively. A fluorine atom does not readily assume a positive charge (H_2F^+ is certainly much less stable than F^- , whereas both H_3O^+ and OH^- are known (Rule F)). This may explain why OF has not been observed whereas O_2^- is reasonably stable since, in the latter, both atoms carry formal negative charges of $-1/2$ (*cf.* discussion by Green and Linnett, *ref.* 7).

By a similar argument, the existence of NO, formed by elements of the First Short Period from adjacent groups in the Periodic Table, might suggest that CN would be equally stable. However, if, for CN, there were to be no net gain in the number of bonding electrons on dimerization to $N\equiv C-C\equiv N$, the electronic structure would have to be XII a or b, which is permitted on the simple double-quartet hypothesis but would not be satis-



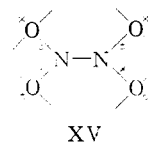
factory for the same reason that VIII could not be allowed for N_2 . The most important structure will be XIIc which places zero formal charges on each atom.

Triatomic Molecules and Ions.—The molecule NO_2 contains an odd number of electrons. Its structure may be represented by resonance between the following pairs (XIII and XIV) of struc-

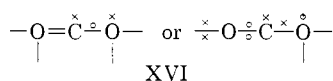


tures. In all four of these each atom possesses a double-quartet of electrons, so that they all satisfy the present hypothesis. The second pair of structures (XIV) is, however, likely to be more important than the first pair (XIII) because they produce a greater average separation of the electrons. However, all four structures have one unsatisfactory feature in that the 8 electrons of one spin favour a linear arrangement of the nuclei (*cf.* CO_2 with 16 electrons) while the nine electrons having the other spin favor the molecule being bent (*cf.* O_3 with 18 electrons). This may result in the molecule being less stable than would otherwise be expected and help to explain why NO_2 dimerizes weakly to O_2N-NO_2 (whereas NO does not dimerize

to $=O=N-N=O=$) even though there is no net gain in the number of bonding electrons (Rule E).⁷ An additional factor is that N_2O_4 would be expected to have primarily the structure XV. In this there is only one fully coincident pair (in

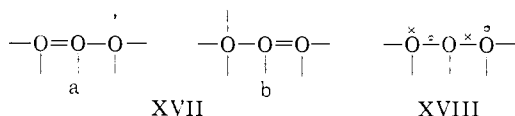


the NN bond). Therefore, though the number of bonds is not increased compared with 2 NO₂, the electronic structure is more stable because both sets of electrons favor approximately the same shape. Also there is not a great increase in the number of coincident electron pairs in N₂O₄ compared with 2 NO₂. In this, the dimerization of NO₂ is quite different from the equivalent dimerization of NO. The instability of 2 CO₂⁻ relative to C₂O₄²⁻ (isoelectronic system) may be due to the fact that, in XVI, there is a formal charge of -1/2 on the carbon atom which does not easily assume such an excess of electrons, and also there are



similar charges on adjacent atoms (-1/2 on both C and O).⁷ A structure analogous to XV for C₂O₄²⁻ does not have any of these unsatisfactory features and in fact appears, *a priori*, to be very satisfactory because it divides the negative charge equally between the four oxygen atoms.

The ozone molecule is usually represented as a resonance hybrid of the pair of structures, XVII. According to the present hypothesis, XVIII



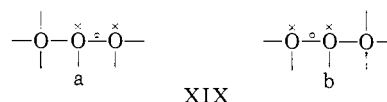
should be considered for the ground state, since, in this structure, each atom has the appropriate double-quartet. Moreover, both spin sets of nine electrons would favor the molecule being bent. The bond length in ozone (1.28 Å) is intermediate between that of a double (1.21) and that of a single bond (1.49 Å). This bond length (1.28) is identical with that in O₂⁻ which is to be expected, since in both species there are supposed to be three-electron bonds (here the phrase "three-electron bond" is used in the sense that there are three electrons binding the two atoms together; and not in the sense used by Pauling⁴). Ozone is an endothermic substance with respect to diatomic oxygen in the ground state (Δ*H* equals +34 kcal.), but with respect to ¹Σ O₂, supposed to contain a conventional double bond, it is exothermic (Δ*H* equals -23 kcal.).^{13a} This is here interpreted as resulting from a separation of the close (*i.e.* "coincident" pairs of electrons^{13b} (*cf.* ground states of O₂ and NO (Rule D)).

The substitution of XVIII for the two structures XVII does constitute a change because XVII a and b give a high probability to configurations in which two electrons are in one bond and four in the other, and vice versa, whereas XVIII gives a high probability to configurations in which there are three electrons simultaneously in both bond regions. Resonance between XVII a and b can result in the mean electron density in each bond region being

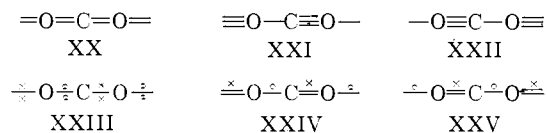
(13) (a) Selected values of Chemical Thermodynamic Properties, Circular 500 of Natl. Bur. of Standards, 1952. (b) In this context the words "close-pair" and "coincident pair" are used to mean that there are two electrons having opposite spins localized mainly in the same restricted region of space.

three, but it gives a different measure of the instantaneous configurations from that denoted by XVIII, and hence inter-electron effects will be different for the conventional resonance hybrid (XVII a and b) from what they would be for XVIII. Since XVIII would appear to reduce inter-electron repulsion compared with XVII, it is likely that XVIII will provide a more satisfactory description of the ground state than will a resonance hybrid of XVII a and b (see later).

The ozonide ion O₃⁻, found in KO₃, can be formulated as a resonance hybrid of XIX a and b. It is then similar to NO₂.



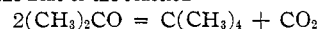
The most stable triatomic species involving elements of the First Short Period are those having sixteen valency shell electrons. Of these CO₂ is the most common and will be used to illustrate the application of the present ideas to these molecules and ions. The CO₂ molecule is usually described as a resonance hybrid of XX, XXI and XXII. There would now be added XXIII, XXIV and XXV. Of these XXIII is likely to have, theoretically,



the lowest energy, and to be the most important member of a resonating group of structures, because, in it, the electrons tend to be more widely separated than in the others (*cf.* O₂). Further the formal charges on each of the atoms is zero in XXIII (as they are in XX). On this basis, the lowering of the energy in the CO₂ molecule relative to that to be expected for the molecule containing two conventional double bonds (XX) is probably to be ascribed, at any rate in large part, to the lower energy of XXIII relative to that of XX (*i.e.* to a reduction in inter-electron repulsion energy in XXIII relative to XX (Rule D)). The experimental stabilization energy relative to XX may be taken to be 30 kcal. per mole,¹⁴ and it is significant that this is the same order of magnitude as was deduced for the stabilization of O₂ (V) relative to the double bonded ¹Σ state (VI). This is not inconsistent with the proposal that the effect occurring in these two molecules is the same.

The CO bond length in CO₂ is 1.16 Å. Bond lengths in H₂CO, (CH₃)₂CO, F₂CO, FHCO, Cl₂CO and Br₂CO are 1.23, 1.23, 1.17, 1.19, 1.17 and 1.13 Å., respectively.¹² It is clear that the CO double-bond length is greatly affected by the

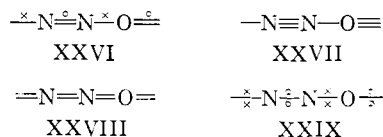
(14) This is the heat of the reaction



and corresponds to changing two ketonic CO bonds to the two CO bonds in CO₂ (N. A. Lange, "Handbook of Chemistry," Handbook Publishers Inc., 1956). It is assumed that the CH and CC bonds remain approximately unchanged. The heats of the corresponding reactions of Cl₂CO, Br₂CO, H₂CO and CH₃CHO are different from the above, but it seems likely that the assumption of the constancy of the other bonds is much less likely to be true in these other cases than in the reaction involving acetone.

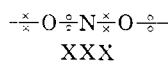
nature of the other atoms attached to the carbon. However, the CO bond length in CO₂ lies in the range covered by the other CO bonds. This would be expected since it is also a four-electron bond.

For N₂O the four structures that might be important are XXVI, XXVII, XXVIII and XXIX (the other two of the set of six for CO₂ are eliminated because of excessive formal charges on the end nitrogen atom (Rule F)). These involve the



following formal charge distributions: XXVI: -1/2, +1, -1/2; XXVII: 0, +1, -1; XXVIII: -1, +1, 0; and XIX: -1, +1, 0. The first and last structures achieve the separation of electron pairs as the two spin-sets have different spatial distributions. This will tend to favour the contributions of XXVI and XXIX. Of these XXVI will be more important than XXIX because the charge distribution is more suitable; a nitrogen atom does not easily assume a charge of -1 (*cf.* NH₂⁻ as compared with NH₄⁺ (Rule F)). Of XXVII and XXVIII, the former is likely to be the more important. Therefore, the order of importance of the structures will probably be XXVI > XXIX > XXVII > XXVIII; or perhaps XXVI > XXIX ~ XXVII > XXVIII. The bond lengths are most consistent with XXVI being the most important structure, with a small contribution from XXIX. They are NN: 1.13 Å (*cf.* N₂, 1.095; N₂⁺, 1.12; N₂F₂, 1.25) and NO: 1.19 (*cf.* NO⁺, 1.06; NO, 1.15; NO₂, 1.20). The NN bond is therefore just a little longer than the five electron bond in N₂⁺ and the NO bond a little shorter than the NO bond in NO₂, which is a resonance between equal contributions of bonds involving three and four electrons (resonance involving XIII and XIV). However, it appears that a good representation is probably given by the single structure XXVI.

The other isoelectronic species (N₃⁻, CN₂²⁻, NO₂⁺ and NCO⁻) can be discussed in similar terms. In NO₂⁺, the most important structure is likely to be XXX, as in CO₂.

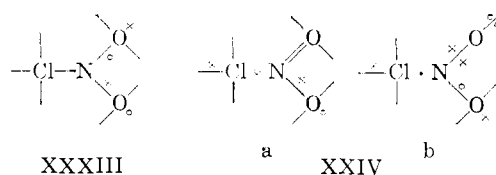


The nitrosyl halides would have been expected to have the structure XXXI. However the bond lengths indicate that this does not provide anything like a true representation. They are:



BrNO: NBr, 2.14 Å.; NO, 1.15 (*cf.* 1.15 in NO and in NO₂⁺); ClNO: NCl, 1.95 (*cf.* 1.76 in NHCl₂, 1.77 in NH₂Cl and 1.79 in ClNO₂), and NO, 1.14; FNO: NF, 1.52 (*cf.* 1.37 in NF₃, 1.44 in FNNF and 1.35 in FNO₂) and NO, 1.13. These lengths do suggest that the NX bond is significantly longer

than an ordinary single bond, and hence the structure of these halides may be better represented by XXXII (or there might be some resonance of XXXI and XXXII). It is somewhat unexpected that this should be so, particularly as the length of the NCl bond in ClNO₂ is almost the same as in NHCl₂, and also the NF bond is virtually the same in FNO₂ (1.35) as in NF₃ (1.37).¹² Probably XXXII is important relative to XXXI, (which has the same total bond order), because it allows the separation of the electron pairs, and hence a reduction in inter-electron repulsion energy, but does not involve an unsuitable charge distribution (-1/2, 0, +1/2). In ClNO₂ the corresponding structures would be XXXIII and XXXIV (a or b). Inter-electron repulsion effects would



favor XXXIII and XXXIVb. However, in XXXIII, both spin sets of electrons favor the same shape, whereas in XXXIVb they do not (*i.e.* ONO, linear and bent). This is analogous to the difference observed in the dimerization of NO and NO₂ and explains why XXXIII is the important structure and the NCl bond is a normal two-electron bond in ClNO₂ whereas it is not in ClNO.

Johnston and Bertin have examined the electronic spectrum of FNO.¹⁵ (I am most grateful to Prof. H. S. Johnston for drawing my attention to the following, together with the proposed interpretation). They show that the experimental results require that, in the excited state, one of the bonds be shorter and the other longer than in the ground state. They suggested in their paper that, if the ground state bond orders were 1 and 2 for NF and NO, respectively, those in the excited state might be 1.5 or 1.25 (for NF) and 1.5 or 1.75 (for NO). On the hypothesis proposed here, the ground state would be regarded as XXXII, and hence the excited state would probably be XXXI. On this basis the NF bond order would increase from a half to one on excitation, and the NO bond order would decrease from 2 1/2 to 2. This would fit the type and magnitude of the bond order changes required by the spectrum observed by Johnston and Bertin. Moreover, it is qualitatively in agreement with the increase in the NF vibration frequency from 766 to 1086 cm.⁻¹ on excitation and the decrease in the NO vibration frequency from 1844 to 1450 cm.⁻¹, though as the frequencies come closer together it is less reasonable to treat them as bond frequencies.

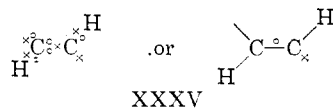
The excited state of acetylene, observed by Ingold and King,¹⁶ has been described in terms somewhat similar to those presented here, though, in this excited state, the carbon atoms are no longer associated with octets.¹⁷ Using the present

(15) H. S. Johnston and H. J. Bertin, Jr., *J. Mol. Spectroscopy*, **3**, 683 (1959).

(16) C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702, 2704, 2708, 2725, 2745 (1953).

(17) J. W. Linnett, *Canadian J. of Chem.*, **36**, 24 (1958).

symbolism, the excited state would be represented by XXXV resonating with its inverted form. As may be seen from the original paper,¹⁷ which also discusses HCO and NH₂, XXXV explains why,



in this state, the acetylene molecule is non-linear, and why the central CC bond has the same length as in benzene.

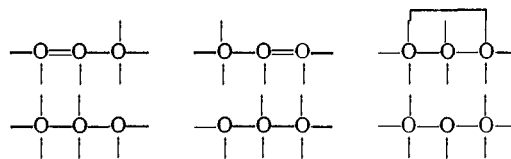
Form of the Wave Function.—It is important to be sure that the present hypothesis does provide a different representation from either a simple valence-bond treatment or a molecular orbital one which gives the wave function in its antisymmetrized (determinantal) form (see earlier). The π -electron system of ozone will be used as a test example.

The simplest valence-bond method would treat the ozone molecule as a resonating hybrid of XVII a and b, and if the atoms are labelled X, Y and Z, the wave function of the four electron π -system would contain terms of the following two types: $p_x p_x p_y p_z$ and $p_x p_y p_z p_z$, a Heitler-London expression being used for the pair-bonds. The antisymmetrized molecular orbital expression (LC-AO approximation) would contain terms of the following types: $p_x p_x p_y p_z$, $p_x p_y p_y p_z$, $p_x p_y p_z p_z$, $p_x p_x p_z p_z$, $p_x p_x p_y p_y$ and $p_y p_y p_z p_z$, (*i.e.* all possible combinations allowed by the Pauli Principle).

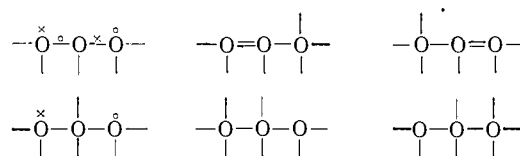
The present hypothesis would use a wave function based on XVII. It would contain terms of the following types: $p_x p_x p_y p_z$, $p_x p_y p_z p_z$, $p_x p_y p_y p_z$ and $p_x p_x p_z p_z$, presuming that bond orbitals of the type ($a p_x + b p_y$) were used. It will be seen that the first two terms are those occurring in the simple valence-bond expression, whereas the last two terms listed for the molecular orbital expression are missing. It may be said therefore that, at this level of approximation, the hypothesis provides a representation intermediate between the simple valence-bond and simple molecular orbital methods. The former restricts the electron distribution more than does the present hypothesis, whereas, as is well known, the molecular orbital method allows the electrons too great a "freedom of movement." This intermediate character of the present hypothesis is one of its most encouraging features. Also the nature of the intermediate is encouraging since the extra term-types that have been included as compared with the valence-bond set (Heitler-London) are just those that would have been expected from an *a priori* argument, while those that have been excluded from the molecular orbital set are those which place electron pairs on adjacent atoms.

Because there are three p-orbitals under consideration (p_x , p_y and p_z) and four electrons have to be accommodated in π -orbitals derived from them, there must be six singlet molecular states, which are to be regarded as arising from atomic states using only these orbitals. Simple valence-bond theory describes these basic set of six covalent

structures



A resonance treatment, using Heitler-London type functions, can be carried out with these six structures which will lead to the wave functions of the ground state and of five excited states. An LC-AO molecular orbital treatment, using the three molecular orbitals derived from the same three atomic orbitals, will lead, with configuration interaction, to precisely the same results for these six states as did the valence bond method with resonance, though it will start from a different basic set of six structures. The present hypothesis would begin with a still further basic set of six structures though, with resonance, it also leads, at the same level of approximation, to the same result as the others. It is hoped, however, that it might provide a better starting set so that less resonance would be necessary, and, in particular, that XVIII might prove to be a good approximation for the ground state, which could then be represented reasonably by a single structure (*i.e.* no resonance). The set of six basic structures that might be used are



though other alternatives are possible. Since the main concern of this paper is with ground states, a more careful examination will be given elsewhere to the best way of choosing the basic set of formulae.

Some Other Simple Molecules and Ions.—The HF₂⁻ ion can also be discussed as a four electron system. Pimentel outlined the simple molecular orbital treatment¹⁸ using the orbitals ($as + bp_z' - bp_z''$)—bonding—and ($p_z' + p_z''$)—anti-bonding—where s represents the 1s orbital on the H atom and p_z' and p_z'' the relevant 2p orbitals on the fluorine atoms, z being the nuclear axis. The final molecular orbital wave function produces terms of the types: $sp_z' p_z'' p_z''$, $sp_z'' p_z' p_z'$, $ssp_z' p_z''$, $p_z' p_z' p_z'' p_z''$, $ssp_z' p_z'$ and $ssp_z'' p_z''$. The simple valence-bond approach treats the ion as a resonance hybrid of FH F⁻ and F⁻ HF. Using Heitler-London (H-L) functions, the wave function would include terms of the type $sp_z' p_z'' p_z''$ and $sp_z'' p_z' p_z'$. If a valence-bond representation using bond orbitals (*i.e.* as $+ bp_z$) were employed, the terms $ssp_z' p_z'$, $ssp_z'' p_z''$ and $p_z' p_z' p_z'' p_z''$ would be added to these. That is, compared with the molecular orbital set, only $ssp_z' p_z''$ would be excluded.

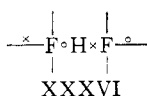
The double-quartet (D-Q) hypothesis would modify the valence-bond treatment writing the most important structure as XXXVI. This would lead (with bond orbitals (B-O) of the form $as + bp_z$) to a wave function made up of terms of the type

(18) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

$sp_z'p_z''p_z'''$, $sp_z''p_z'p_z'''$, $p_z'p_z'p_z''p_z'''$ and $ssp_z'p_z'''$. These are the first four of the molecular orbital (M-O) set. The orbital combinations that are included by the various treatments are summarized for comparison in Table I.

TABLE I
LISTING TERMS INCLUDED AND NOT INCLUDED BY THE
VARIOUS TREATMENTS

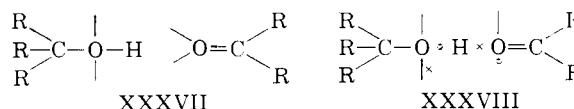
Type of treatment	(1) $sp_z'p_z''p_z'''$ (FH ⁻ F ⁻)	(2) $ssp_z'p_z'''$ (FH ⁻ F ⁻)	(3) $p_z'p_z'p_z''p_z'''$ (F ⁻ H ⁺ F ⁻)	(4) $ssp_z'p_z'''$ and $sp_z''p_z'p_z'''$ (F ⁻ H ⁺ F ⁺)
M-O	Yes	Yes	Yes	Yes
V-B (H-L)	Yes	No	No	No
V-B (B-O)	Yes	No	Yes	Yes
D-Q (B-O)	Yes	Yes	Yes	No



In order to decide the likely relative importance of the orbital combinations listed in Table I, it is necessary to estimate the order of the "energies" associated with them. This can be done, with sufficient accuracy for the present purpose (which is to examine the trend) by considering the ionization potentials of the separate atoms (or ions) and then the effect of bringing the atoms (or ions) together. The ionization potentials will be taken to be: H: $13\frac{1}{2}$; H⁻: 1; F: $17\frac{1}{2}$; F⁻: 4 eV. The first two structures are of the type FH⁻F⁻ and the sum of the ionization potentials for the four electrons (thereby reducing the system to F⁺H⁺F⁺) is $52\frac{1}{2}$ eV. The structure in the second column of the Table is FH⁻F and the corresponding sum is $49\frac{1}{2}$ eV. That in the third column corresponds to F⁻H⁺F⁻ and the sum is 43 eV, while the last pair corresponds to structures of the type F⁻H⁺F⁺ and the sum of the ionization potentials is 36 eV. Moreover, the effect of bringing the system together as F⁻H⁺F⁺ is clearly unsatisfactory because of the charge distribution and the consequent electrostatic effects. On the other hand, in all the other three structures there will be some lowering of the energy on bringing the parts of the system together. For instance, the energy to remove an electron from H in (1) will be increased by the presence of the neighbouring F, and the combination of the two equivalent structures will increase the electron probability in the inter-nuclear region with a consequent lowering of the energy. Also in FH⁻F, the electrons on H⁻ will be more tightly bound because of the neighboring fluorine atoms, and in F⁻H⁺F⁻, the electrons on the fluoride ions will be more tightly bound because of the presence of the proton. It would therefore seem that the order of importance of the structures is likely to be (1) > (2) > (3) >> (4), the last being probably very unimportant. Therefore the molecular orbital method is at fault in including the structures under (4) while the valence-bond (Heitler-London) is probably over-restrictive in including only the structures under (1). If the valence-bond method is modified by using bond-orbitals, the wrong structures are added, since those under (4) are included while that under (2) is not. The present double-

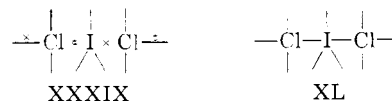
quartet approach clearly provides a means of including the correct additional structures and, in particular, it excludes the structures under (4). Therefore it would appear that the wave function derived from the double-quartet hypothesis might provide a satisfactory description, since it is known that the Heitler-London function limits the range of electron configurations too severely. This means that XXXVI may provide the best simple diagrammatic representation of HF₂⁻; moreover, it divides the negative charge equally between the two fluorine atoms.

On this basis, a hydrogen bond between a hydroxyl group and a carbonyl group might be represented as a resonance mixture of XXXVII and XXXVIII, and the latter type of structure might provide the best simple representation of the transition state in reactions involving the donation of



a proton.

Pimentel¹⁸ has also pointed out that the ions such as ICl₂⁻ can be treated on a molecular orbital basis without making use of the d-orbitals of the iodine atom. In an analogous manner this would involve describing the above ion (and similar ones also) by XXXIX, rather than, as is more usually done as XL. Formally, XL places all the negative



charge on the iodine atom and none on the chlorine atoms. This cannot be true. XXXIX divides the negative charge equally between the chlorine atoms, leaving the iodine atom formally neutral, and this is more reasonable. Moreover, Cornwell and Yamasaki¹⁹ have deduced from their nuclear quadrupole coupling results that there is "a negative charge on each chlorine atom of roughly half that of an electron". This is exactly the charge distribution of XXXIX. On the other hand the ICl bond length in ICl₂⁻ is 2.36, as against 2.32 Å, in ICl.¹² Admittedly there is an increase from ICl to ICl₂⁻, but a greater alteration would have been expected for a change from a two to a one-electron bond (by analogy with ClNO and ClNH₂). However, it is possible that the behavior of bond lengths may be different for iodine having a high atomic number than for nitrogen having fewer electrons. In a second paper, Yamasaki and Cornwell¹⁹ have concluded, from the iodine nuclear quadrupole coupling results, that the iodine atom in ICl₂⁻ is similar to that in ICl, and hence that the d-orbitals of the iodine atom are not employed in ICl₂⁻. This is again consistent with XXXIX.

In I₃⁻, the II bond lengths are certainly markedly greater than in I₂ (2.66). In CsI₃, the ion is unsymmetrical, the bond lengths being 2.83 and 3.035. It would seem therefore that a structure of the

(19) R. S. Yamasaki and C. D. Cornwell, *J. Chem. Phys.*, **27**, 1060 (1957); **30**, 1265 (1959); cf. P. J. Bray, *ibid.*, **23**, 703 (1955).

type of XXXIX would not be at all inappropriate for I_3^- . The lack of symmetry may be imposed by the crystal forces.

Other inter-halogen compounds (*e.g.* ICl_4^- and I_2Cl_6) and substances such as PF_5 can be treated along similar lines, but the way in which these molecules should be described is, at the present time, more problematical. Therefore the discussion of these molecules will be deferred till later.

Benzene.—The molecule of benzene cannot be represented by a single Lewis-type formula and so, on valence-bond theory, it has been described as a resonance hybrid; in the most simple of these descriptions, as a mixture of the two Kekule structures. On the double-quartet hypothesis, a more important structure would be XLI. In this each



XLI

carbon atom has around it four electrons of each spin (*i.e.* a double quartet). Moreover, as for the two Kekule forms, all six electrons of the "aromatic sextet" are in bond orbitals; therefore XLI will correspond to a lower energy than does a Kekule structure because inter-electron repulsion is reduced. It is clear from the discussion of ozone that XLI constitutes a changed interpretation of the structure of the ground state of benzene, and XLI alone might be more successful than just two Kekule structures or a resonance hybrid of these with Dewar forms.

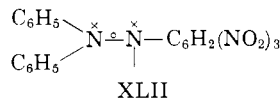
If XLI provides a good representation of the ground state of benzene, then the stabilisation energy of benzene must be due in considerable part to the lower energy of XLI relative to a Kekule structure. According to Craig²⁰ the stabilization energy of benzene relative to that expected for a Kekule structure is 36 kcal. per g. mole. It is interesting that this is about the same as that observed for O_2 and CO_2 . In O_2 , 12 valency shell electrons are involved; in CO_2 , 16; and in benzene there are 18 in the carbon ring system (the 6 pairs in the CH bonds are "coincident" in XLI as well as in a Kekule structure). The approximate energy lowerings achieved in the three molecules by separating electron pairs are 38, 30 and 36 kcal. per g. mole, respectively. Since the separation of the pairs is not precisely the same in the three molecules, but only roughly comparable, these figures are consistent with the hypothesis that the same effect is occurring in each molecule. The heat of formation of O_3 from O_2 in the Σ state is -23 kcal. per g. mole. This is also about the same, and the same type of effect is supposedly involved with approximately the same number of electrons (16, since one pair is coincident in XVIII).

Organic Free Radicals.—The high stability of some organic free radicals can be accounted for on the double-quartet hypothesis. For example, α, α -diphenyl- β -picryl hydrazyl is a stable substance²¹ showing no tendency to dimerize even though it is a free radical and paramagnetic. Its stability can

(20) D. P. Craig, "Non-Benzenoid Aromatic Compounds," ed. D. Ginsburg, Interscience Publishing Co., New York, N. Y., 1959.

(21) W. A. Waters, "Free Radicals," Oxford, 1948, Chapter IV.

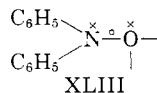
be accounted for by the formula XLII. Dimerization would then produce no increase in the total



XLII

number of bonds but would increase the number of coincident pairs (*cf.* NO). Also diphenyl-picrylhydrazyl does not react with nitric oxide for the same reason, and this is also consistent with XLII. Electron spin resonance measurements show that the odd electron spin densities at the two nitrogen atoms are approximately equal.²²

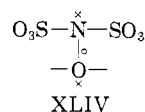
Diphenylhydroxylamine is oxidized by silver oxide to diphenyl nitric oxide which is monomeric in ether.²¹ Both di-*para*-nitrophenyl and di-*para*-anisyl nitric oxide are paramagnetic. The formula of the diphenyl compound would be expected to be XLIII, and therefore it does not dimerize for the same reason as NO and diphenyl-



XLIII

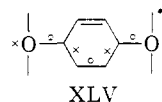
picryl-hydrazyl. It reacts with NO to give $(C_6H_5)_2N-NO_2$ by a rearrangement, and further products containing the nitro group are formed from this by subsequent reactions. The high stability of the nitro group (see earlier explanation) may explain why this reaction takes place.

Another stable odd-electron species of a similar type is the peroxyamine disulfonate ion $((SO_3)_2NO)^{2-}$. Electron spin resonance measurements have shown that this has some, but not all, of the spin density on the nitrogen atom,²³ and it is likely that the structure is XLIV, which accounts for the observation that dimerization does not take place (*cf.* diphenyl nitric oxide).



XLIV

The semi-quinones, which are stable in strongly alkaline solutions,²¹ also contain an odd number of electrons in the molecule (or ion). The formula of the negative ion of *para*-benzo-semiquinone can be written as a resonance hybrid of XLV and its mirror image. Consequently the semiquinone



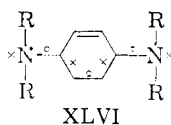
XLV

shows considerable stability both to polymerization and to disproportionation to hydroquinone and quinone, because in neither process would there be any increase in the total number of bonds, but there would be an increase in the number of coincident

(22) C. A. Hutchison, R. C. Pastor and A. G. Kowalsky, *J. Chem. Phys.*, **20**, 534 (1952); C. Kikuchi and V. W. Cohen, *Phys. Rev.*, **93**, 394 (1954).

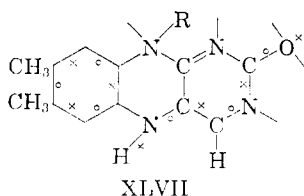
(23) S. I. Weissmann and D. Banfil, *J. Am. Chem. Soc.*, **75**, 2534 (1953).

electron pairs. The stability of Wurster's blue salts may be accounted for by a similar structure (XLVI). For this compound and the semi-



quinone the above structures (XLV and XLVI) divide the ionic charge equally between the two oxygen or nitrogen atoms respectively. This would tend to favor the stability. Wurster's salts are only stable in the pH range 3.5 to 6, presumably because the symmetry of the ion is an important factor (*cf.* the semiquinone).

The ability of riboflavin to add on two hydrogen atoms in successive and distinct stages,²⁴ the intermediate having some stability, can be explained in similar terms using structures analogous to XLV and XLVI. On this hypothesis, the intermediate would be assigned the structure XLVII, together with similar resonance forms. Alternatively,



the hydrogen atom might be added to the oxygen atom, though XLVII disposes the charges more reasonably. In this formulation the increase in the gross number of bonds in the riboflavin molecule is a half at the first stage and a half at the second. This means that the oxidation process can take place in two easier stages such that the change in energy is divided between each.

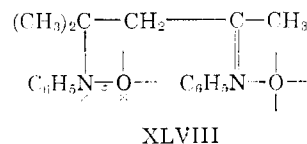
Bijl, Kainer and Rose-Innes²⁵ have shown that several molecular compounds analogous to those formed by chloranil and *para*-dimethyl-amino-benzene are paramagnetic. Presumably an electron transfer occurs and free radical ions of the semiquinone and Wurster's blue types (XLV and XLVI) are formed. This would occur with no change in the total number of species. Favoring the electron transfer will be the reduction, in the ions, of inter-electron repulsion because of the separation of electron pairs. Opposing the electron transfer will be the separation of positive and negative charges onto the two ions. This latter effect will be dependent on the ability of the diamine to lose an electron and of the quinone to accept one. It is found that the extent to which the transfer occurs is dependent on just these factors.²⁵ Moreover, the above interpretation, which postulates two opposing factors, accounts for the observation that, with some pairs of substances, electron transfer occurs, while with others it does not.

(24) R. J. Williams, R. E. Fakin, E. Beerstecher and W. Shive, "Biochemistry of B Vitamins," Reinhold Publishing Corp., New York, N. Y., 1950, p. 146.

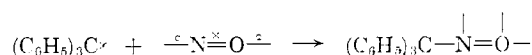
(25) D. Bijl, H. Kainer and A. C. Rose-Innes, *J. Chem. Phys.*, **30**, 765 (1959).

Eley and Inokuchi have shown that some of these molecular compounds are semi-conductors which implies that electron transfer between the species is fairly easy (*ref.* 25).

Banfield and Kenyon prepared a stable paramagnetic compound from acetone and phenylhydroxylamine.²⁶ This can be given the formula XLVIII. Again the double-quartet hypothesis accounts for the stability.

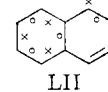
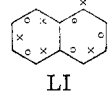
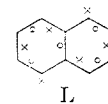
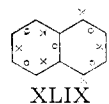


The formula of certain organic free radicals such as triphenyl-methyl would not be modified by the present hypothesis, and their stability must be ascribed to resonance and the delocalization of the odd electron between several carbon atoms. However, triphenyl-methyl combines instantaneously with nitric oxide, whereas diphenyl-picryl-hydrazyl does not react at all. This is to be expected because the reaction does lead to an increase of one



in the total number of electrons participating in bonding, whereas the addition of nitric oxide to the diphenyl-picryl-hydrazyl radical would not increase the number of bonding electrons but would increase inter-electron repulsion.

When certain aromatic compounds in solution in tetrahydro-furan or dimethoxyethane are treated with alkali metals, aromatic negative ions are formed.²⁷ For instance naphthalene, C_{10}H_8 , forms the ion $\text{C}_{10}\text{H}_8^-$. On the double-quartet hypothesis important contributing structures for this ion would be XLIX, L and LI, together with the mirror image forms of analogous structures; though



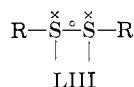
structures such as LII might also be significant. On the presumption that structures like these are important contributors to the resonance hybrids, it would be expected that there would be greater spin density at the α than the β -positions. From the experimental data and molecular orbital calculations it is believed that this is the case.²⁸ The exact ratio for the two positions will depend on the relative importance of the different structures. A similar approach is also qualitatively satisfactory for other aromatic ions.

(26) F. H. Banfield and J. Kenyon, *J. Chem. Soc.*, 1612 (1926); J. Kenyon and S. Sugden, *ibid.*, 170 (1932).

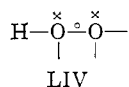
(27) T. L. Chu, D. E. Paul, J. Townsend and S. I. Weissmann, *J. Phys. Chem.*, **67**, 504 (1953); *J. Chem. Phys.*, **21**, 2227 (1953).

(28) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworths, 1958, p. 143.

Various Other Examples.—Gordy, Ard and Shields²⁹ observed that, when sulfur-containing proteins and polypeptides were subjected to radiation, a particular electron spin resonance signal always appears. They ascribed this to the localization of the odd electron in the region of the sulfur-sulfur bond with the formation of a three-electron bond (they used the phrase in the Pauling sense, but it is also a three-electron bond in the sense of this paper). This occurs because it is only in this way that an increase in total or gross bond order can be achieved in the radical. The species would be represented by LVIII on the double-quartet scheme.

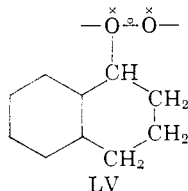


In the hydrogen-oxygen reaction it is now established that HO₂ is an important and relatively stable intermediate. This is the acid conjugate with O₂⁻ (see earlier) and would therefore be assigned the structure LIV. The pattern of the spatial distribution of the two spin sets is such



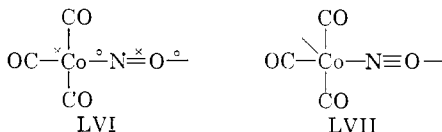
that, with tetrahedral configurations for both, two electrons would be suitably placed to bind the proton. This structure also accounts for the mass spectrometric observation³⁰ that the OO bond in HO₂ is intermediate in energy content between a single and a double bond.

The same type of structure may be used to describe similar intermediates which are formed during the production of organic peroxides. In the case of the formation of tetralin hydroperoxide, the intermediate would be LV, so that the change



from the OO double bond to the single bond would then occur in two stages (*cf.* riboflavin).

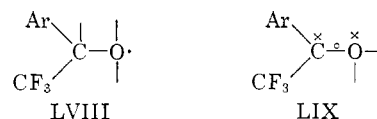
As a further example from inorganic chemistry, the structure of Co(CO)₃NO would be formulated as LVI (in this diagram, 8 electrons of the valency



shell of the cobalt atom are not indicated). This gives to the cobalt atom a shell of eighteen electrons. It also explains the shortness of the CoN bond (1.76 Å as against 1.95 to 1.99 in ammine and nitrite complexes).¹² In 1937, the NO bond length

was said to be 1.10 ± 0.04 , which indicates that it may be a little shorter than in nitric oxide. This suggests that there may be a small contribution from the structure LVII, though this would be expected to be negligible, or almost so, because the bond arrangement places formal charges of +1 on both the nitrogen and oxygen atoms. Other nitrosyl compounds can be represented in a similar manner (in Fe(CO)₂(NO)₂, the NO bond length was given in 1937 as 1.12 ± 0.03).¹² Orgel³¹ has pointed out that the structure of complexes (*e.g.* those of cupric) showing the Jahn-Teller effect can be represented in terms of three-electron bonds.

Ross Stewart and van der Linden³² have suggested that the radical LVIII may be an intermediate in the oxidation of the corresponding secondary alcohol with potassium permanganate. On the double-quartet hypothesis, this species would be written as LIX. On this basis the two stages



postulated by Ross Stewart and van der Linden would involve the intermediate having only half

a bond less than the reactant $\left(\begin{array}{l} \text{Ar} \\ \text{CF}_3 \end{array} \right) \text{CH} - \text{O}^-$ and product (the ketone), whereas their formulation (LVIII) would involve it having two fewer bonding electrons (*cf.* riboflavin). However, the intermediate is still likely to have a low stability because the carbon atom carries a formal charge of $-1/2$ (see earlier), and therefore it would be anticipated that it would be oxidized rapidly by permanganate to the final ketone.

Conclusion.—In this paper it has been proposed that the Lewis-Langmuir Octet should be regarded as a double-quartet rather than as four pairs. The consequences of this hypothesis have been pursued in a qualitative way over a wide range of examples. It has been demonstrated that the hypothesis is capable of broad and useful application in many branches of chemistry. A number of the topics that have been mentioned here, as well as others, will be examined in more quantum mechanical detail and more quantitatively along the lines outlined in the section entitled, "The form of the wave function," to be published subsequently.

This paper was written during a period of leave spent at the University of California. I wish to thank the University of Oxford for granting me this leave, and the Chemistry Department of the University of California for the welcome it gave me. I am most grateful to the many members of the staff of that department for their friendly advice and encouragement. I also wish to thank the Astor Foundation for the Cherwell Memorial Fellowship which I held during this time.

(29) W. Gordy, W. B. Ard and H. Shields, *Proc. Natl. Acad. Sci. U. S.*, **41**, 983 (1955).

(30) A. J. B. Robertson, *Trans. Faraday Soc.*, **48**, 228 (1952); S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **23**, 1364 (1955).

(31) L. E. Orgel, Reports of the Solvay Conference, Brussels, 1956, p. 289.

(32) Ross Stewart and van der Linden, *Discussions Faraday Soc.*, **29**, 211 (1960).