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THE ASSIGNMENT OF QUANTUM NUMBERS FOR ELECTRONS IN MOLECULES. I

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ABSTRACT

Quantum numbers, notation, closed shells, molecular states.—The problem of making a complete assignment of quantum numbers for the electrons in a (non-rotating) diatomic molecule is considered. A tentative assignment of such quantum numbers is made in this paper (cf. Table III) for most of the known electronic states of diatomic molecules composed of atoms of the first short period of the periodic system. The assignments are based mainly on band spectrum, and to a lesser extent on ionization potential and positive ray, data. The methods used involve the application and extension of Hund's theoretical work on the electronic states of molecules. Although the actual state of the electrons in a molecule, as contrasted with an atom, cannot ordinarily be expected to be described accurately by quantum numbers corresponding to simple mechanical quantities, such quantum numbers can nevertheless be assigned formally, with the understanding that their mechanical interpretation in the real molecule (obtainable by an adiabatic correlation) may differ markedly from that corresponding to a literal interpretation. With this understanding, a suitable *choice of quantum numbers* for a diatomic molecule appears to be one corresponding to an atom in a strong electric field, namely, quantum numbers n_τ, l_τ, σ_{l_τ}, and $s_\tau (s_\tau = 1/2$ always) for the τ'th electron, and quantum numbers s, σ_l, and σ_s for the molecule as a whole (σ_{l_τ} and σ_s represent quantized components of l_τ and s, respectively, with reference to the line joining the nuclei). These quantum numbers may be thought of as those associated with the imagined "united atom" formed by bringing the nuclei of the molecule together. A *notation* is then proposed whereby the state of each electron and of the molecule as a whole can be designated, e.g. $(1s^s)^2\ (2s^p)^2\ (2s^s)^2\ (2p^p)$, ${}^2P$ for a seven-electron molecule with $\sigma_l = 1$, $s = 1/2$; in a symbol such as $2s^p$ the superscript denotes l_τ, the main letter, σ_{l_τ}, thus $2s^p$ means that the electron in question has $n_\tau = 2$, $l_\tau = 1$, $\sigma_{l\tau} = 0$. Electrons with $\sigma_{l_\tau} = 0, 1, 2, \cdots$, are referred to as $s, p, d, \cdots$, electrons. It is shown that in a molecule it is usually natural to define a group of equivalent electrons giving a resultant $\sigma_l = 0$, $s = 0$ as a *closed shell*; in this sense, two s electrons, or four p, or $d, f, \cdots$, electrons form a closed shell. The possible *molecular states* corresponding to various electron configurations are deduced by means of the Pauli principle (cf. Table I, and Appendix).

Promoted electrons, binding energy, bonding power, and relation of molecular to atomic electron states.—As Hund has shown, some of the electrons must undergo an increase in their n values (principal quantum numbers) when atoms unite to form a molecule. Such electrons are here called *promoted electrons.* The electrons in a molecule may be classified according to their *bonding power*, positive, zero, or negative. Electrons whose presence tends to hold a molecule together, as judged by the fact that their removal from a stable molecule causes a decrease in the energy of dissociation D or an increase in the equilibrium internuclear separation r_0 may be said to have *positive bonding power*, and are identified with, or defined as, *bonding electrons.* The definitions of bonding power in terms of changes of D, and of changes of r_0, are unfortunately not in general equivalent, and we must accordingly distinguish "energy-bonding-power" and "distance-binding-power". On the whole, promoted electrons should tend to show negative energy-bonding-power, unpromoted electrons positive energy-bonding-power, but much should depend on "orbit dimensions."

Certain rules governing the relations of the electronic states of a molecule to those of its dissociation products are discussed; in addition to theoretical rules established by Hund in regard to σ_l and s values, another, presumably less strict, rule is here proposed, namely that the σ_{l_τ} values of all the atomic electrons before union should be preserved in the molecule (σ_{l_τ} *conservation rule*). Selection rules for electronic transitions are also discussed; in addition to rules given by Hund, the following are proposed: $\Delta l_\tau = \pm 1$ for intense transitions; $\Delta\sigma_{l_\tau} = 0, \pm 1$.

Results.—The key to the assignment of quantum numbers made here is found in the fact that the molecules BO, CO^+, and CN show an *inverted* ^2P state instead of the normal ^2P which should occur if this state were analogous to the ordinary ^2P states of the Na atom. The existence of such a low-lying inverted ^2P indicates that in these molecules there exists a closed shell of p electrons from which one is easily excited. It is concluded that this is a $(2p^p)^4$ shell. The identification of two other closed shells, of s electrons, very likely $(3s^p)^2$ and $(3s^s)^2$, follows; the electrons in these and the $(2p^p)^4$ shell are roughly equal in energy of binding. According to this interpretation, the electron jumps involved in the band spectra of BO, CN, CO^+, and N_2^+ are more analogous to X-ray than to optical electron transitions. From this beginning, proceeding to CO, N_2, NO, O_2, O_2^+, F_2, C_2, etc., a self-consistent assignment of quantum numbers is built up for most of the known states of the various molecules treated in this paper. The spectroscopic analogies of CN, N_2, NO, etc., to Na, Mg, Al are justified and the partial failures of these analogies, such as the chemical resemblance of CN to a halogen, are explained. Nearly all the hitherto observed ionization potentials of the molecules discussed can be accounted for by the removal of a *single* electron from one or another of the various closed shells supposed to be present. The N_2^+ band fluorescence produced by short wave length ultraviolet light (Oldenberg) is accounted for as the expected result of photo-ionization of a $3s^p$ electron. The steadily decreasing heat of dissociation in the series N_2-NO-O_2-F_2 is accounted for by the successive addition of promoted $3p^p$ electrons with strong negative bonding power. Starting from N_2, whose normal state corresponds to a ^1S configuration of closed shells, we add one $3p^p$ electron to give the ^2P normal state of NO and O_2^+, two to give the ^3S normal state of O_2, four to give a closed shell, $(3p^p)^4$, which accounts for the ^1S normal state of F_2.

In N_2 (probably also in O_2 and the other homopolar molecules, but data are too few), band systems for which $\Delta l_\tau \neq 1$ are notably lacking, thus giving support to Hund's predicted selection rule for homopolar molecules; in the analogous heteropolar molecule CO, many systems occur with $\Delta l_\tau = 0$, although they are probably weaker, as expected, than those for which $\Delta l_\tau = \pm 1$. On account of this strict selection rule in N_2, certain levels should be metastable, in particular the final level of the afterglow (α) bands of *active nitrogen*. There is evidence for the existence of a strict selection rule $\Delta s = 1$ in homopolar molecules.

INTRODUCTION

LANGMUIR,[1] in 1918, in elaborating G. N. Lewis' theory of valence,[2] suggested that the peculiar stability and inertness of the N_2 molecule might be accounted for by the following assumptions: (*a*) each N nucleus retains its two most firmly bound electrons, i.e., each atom keeps its innermost or *K* shell; (*b*) eight of the remaining ten electrons form a group of eight or "octet," i.e. an *L* shell, or complete group of two-quantum electrons, in the language of Bohr's theory; (*c*) the last two electrons form a

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[1] I. Langmuir, J. Am. Chem. Soc., **41**, 868, 1543 (1919); **42**, 274 (1920).

[2] G. N. Lewis, Valence and the Structure of Atoms and Molecules. 1923. Chemical Catalogue Company.

pair which is imprisoned in this octet and helps to stabilize the whole structure. To CO and CN^-, with the same number of electrons, Langmuir attributed similar, although of course less symmetrical, structures. The surprising stability of NO, with one more electron, Langmuir explained by a similar structure, but with three electrons imprisoned in the octet.

If the octet in these pictures really functions as an L shell, the additional electrons might be regarded as "imprisoned" valence electrons. From this point of view, the molecules CN, CO or N_2, and NO should have respectively one, two, and three valence electrons. In this, they would be exactly like the atoms Na, Mg, Al. No marked analogy is evident in chemical behavior, however. Chemically, CN resembles Cl rather than Na, as shown especially by the stability of CN^-; and N_2 resembles argon[1] rather than Mg. This is attributable to the fact that the supposed valence electrons are "imprisoned," i.e. much more firmly held than the valence electrons of Na, Mg, Al.

Nevertheless, as the writer has pointed out,[3] the band spectra of CN and a number of other "one-valence-electron" molecules (CO^+, N_2^+, BO, etc.) indicate a marked analogy between these molecules and the Na atom, in respect to the nature and arrangement of electron levels. Similarly, as Birge has shown,[4,5] the electron levels of CO and N_2 present a remarkable analogy to those of Mg. Further, as first shown by Sponer's work, the NO energy levels parallel those of the Al atom.[4,5,6]

If the suggested analogies are correct, they should be capable of expression by specifying a definite "orbit" for each electron in the molecule. For example, each electron in CN or BO should have quantum numbers the same as those of a corresponding electron in the Na atom, except that the molecules mentioned have two extra K electrons. In discussing such an assignment of quantum numbers,[7,5] the writer pointed out[7] that in the formation of such a molecule from two atoms, some of the electrons must undergo rather radical changes in their quantum numbers.

Birge and Sponer,[8] however, have obtained strong evidence that a molecule such as CO or N_2, if merely given sufficient energy of vibration, can dissociate smoothly into its atoms. This at first seemed to conflict with the conclusion stated at the end of the preceding paragraph, since in the old quantum theory there seemed to be no way in which quantum numbers could be changed except by violent agencies such as collision or light absorption. Birge and Sponer's results seemed, then, to demand a model composed of atoms with unchanged quantum numbers.[5]

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[3] R. S. Mulliken, Phys. Rev. **26,** 561 (1925).

[4] R. T. Birge, Nature, Feb. 27, 1926.

[5] R. S. Mulliken, Phys. Rev. **28,** 493–7 (1926).

[6] Cf. F. A. Jenkins, H. A. Barton and R. S. Mulliken, Phys. Rev. **30,** 150 (1927) for discussion and bibliography.

[7] R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 338 (1926).

[8] R. T. Birge and H. Sponer, Phys. Rev. **28,** 259 (1926). H. Sponer, Ergebnisse der exakten Naturwissenschaften, **6,** 75 (1927). R. T. Birge, International Critical Tables.

But Hund has now shown that, with the new quantum theory, these contradictions disappear. In fact Hund's work,[9,10,11,12] together with that of Heitler and London,[13,14] promises at last a suitable theoretical foundation for an understanding of the problems of valence and of the structure and stability of molecules. For example, Hund's work enables us to understand how a continuous transition can exist between ionic and atomic binding. Briefly, the molecule may be said to be latent in the separated atoms; in a certain sense, the molecular quantum numbers already exist before the atoms come together, but take on practical importance, at the expense of the atomic quantum numbers, only on the approach of the atoms to molecular distances.[10] This of course does not exclude the possibility that in some cases a quantum jump in the usual sense may be needed to reach the *most stable* state of the molecule.

PURPOSES

The present work represents an attempt to obtain a detailed knowledge of quantum numbers and energies of individual electrons in molecules, similar to that which we now possess in the case of atoms. The present paper is confined to the discussion of diatomic molecules composed of atoms of the first short period. Of the molecules and molecular states here discussed only a few are the stable states of chemically stable molecules. But aside from their purely theoretical interest, the numerous excited states and chemically unstable molecules discussed are indispensable in deducing the electron configurations for those special cases which correspond to stable molecules; and are also important as intermediate steps in chemical reactions.

Stability, molecular and chemical. In this connection it seems desirable to bring out a distinction not ordinarily made. Chemical stability of a molecule implies not merely that two or more atoms have united to a single stable molecule, but further, that such a molecule is stable in an assemblage of its fellows, or in a mixture with other molecules. For example, a single NO molecule is exceedingly stable with respect to N+O, but NO gas is unstable with respect to a gas composed of N_2 and O_2 molecules. The most stable state of a *single molecule* composed of specified atoms in given numbers is merely that of minimum *energy;* probably all molecules, even He_2 from normal He atoms, are capable of some stability in this sense (*molecular stability*). The most stable state of a *system of molecules* is one of ultimate statistical equilibrium, i.e., one of minimum *free energy;* this corresponds to *chemical stability*.

[9] F. Hund, Zeits. f. Physik, **36,** 657 (1926).

[10] F. Hund, Zeits f. Physik, **37,** 742 (1927).

[11] F. Hund, Zeits. f. Physik, **42,** 93 (1927).

[12] F. Hund, Zeits. f. Physik, **43,** 805 (1927).

[13] W. Heitler and F. London, Zeits f. Physik, **44,** 455 (1927). Cf. also Y. Suguira, Zeits. f. Physik, **45,**484 (1927) and S. C. Wang, Phys. Rev. **31,** 579 (1928) for further detailed calculations on H_2.

[14] W. Heitler, Zeits. f. Physik, **46,** 47 (1927), **47,** 835 (1928); F. London, Zeits. f. Physik, **46,** 455 (1927).

METHODS

Throughout the present paper, even when no specific reference is made, the essential ideas and methods are those so successfully used by Hund.[9,10,11] As compared with Hund's papers, the chief difference is in the attempt to assign individual electronic quantum numbers. This has required some additional assumptions, and it is possible that the results obtained may be far from correct. Nevertheless the writer believes that they have at least a certain degree of correspondence to the truth and that this will prove of value for the ultimate accomplishment of the objective aimed at.

Interpolation between two limiting cases, namely (*a*) two separate atoms, (*b*) the "united-atom" formed by the hypothetical process of bringing the nuclei of the separate atoms completely together, has proved valuable in arriving at conclusions about the electronic states of a diatomic molecule. For the application of the Pauli principle to determine the maximum possible number of electrons for any given set of quantum numbers the correlation with the united-atom is all-important. The possible quantum number assignments for the molecule should be obtainable from those of the united-atom by imagining the latter to be placed in a strong, non-uniform but axially symmetrical electric field, corresponding to the effect of separating the united-atom nucleus into the two nuclei which exist in the molecule. But the *energy-order* of terms corresponding to various quantum numbers may be expected to differ, often very greatly, from that appropriate to an atom in a strong electric field. For example, we shall ordinarily expect the electron distribution of the normal state of the molecule to correspond to that of some *excited* state of the united-atom, and vice versa.

Deviations from the energy-order of the united-atom are especially to be expected in the case of electrons for which an increase in the principal quantum number *n* has been forced by the formation of the molecule, but for which no correspondingly large energy changes have occurred, so that the energies lie close to those characteristic of the separated atoms. This condition should exist especially in loosely-bound molecules; and always for inner electrons which are not essentially shared by the two nuclei.

Bohr's method of determining electron configurations in atoms by imagining all electrons removed, and then returning them one by one, each to the available orbit of lowest energy, is less easily applicable to molecules on account of the difficulties in predicting binding energies for various orbit-types. But, once a body of information in regard to binding energies has been built up on the basis of spectroscopic and other facts, this method should be helpful.

Before attempting to determine the electron configurations of individual molecules, we must first consider what possibilities are to be expected theoretically. The discussion falls naturally under two heads: (1) matters in which the molecule resembles the united-atom, (2) those where the correlation is mainly with the separate atoms. Under the first head come such questions as those of notation and the nature of the quantum numbers appropriate to molecules, nature of closed shells, and of molecular states and multiplets. Under the second head come energy relations, and the question as to what particular electronic states of a molecule may be expected from the union of two atoms each in a specified state. These two groups of questions will be taken up successively in the two following sections of the paper, after which the results will be applied to specific examples.

QUANTUM NUMBERS, NOTATION, CLOSED SHELLS, AND MOLECULAR STATES

Quantum numbers. In the case of an atom, it is customary first to assign quantum numbers n, l, and s for each electron, then to fix the state of the atom as a whole by specifying how the individual l's and s's are coupled.[15] Usually most of the electrons are in "closed shells." In the present paper it will be assumed somewhat arbitrarily that each electron in a molecule, in particular the τth electron, can be characterized by four quantum numbers, n_τ, l_τ, σ_{l_τ}, and s_τ ($s_\tau = \frac{1}{2}$ always), where σ_{l_τ} corresponds to the space-quantized component of l_τ in the direction of the figure axis. In addition, the resultants σ_l, s, and σ($\sigma = \sigma_l + \sigma_s$, where σ_s is the component of s along the figure axis), must be specified,[16] these quantum numbers being applicable to the molecule as a whole, somewhat like l, s, and j in the case of the atom. This choice of quantum numbers corresponds to one of those proposed by Hund.[9] It is strictly appropriate only for the imagined case of a non-rotating molecule, but, after adding rotational and vibrational quantum numbers j and n, the proper quantum numbers for any actual case (cf. Hund's papers[9,10,11]) can be obtained by means of an adiabatic correlation.

[It should be pointed out that the quantum number σ_l as used here is identical in meaning with σ_k as used by the writer in other papers on "Band Structure and Electronic States." The notation is here changed for the sake of consistency with the use of the quantum numbers l_τ.]

Throughout the present paper, however, the molecule is to be thought of as though the nuclei were fixed, since we are not directly interested here in the effects of nuclear rotation and vibration.[16,17] In the study of electronic states and quantum numbers we shall, nevertheless, make very frequent use of information which has been gained by a study of band structure.

Just as, in atoms, the ordinary l_τ, l, s, j assignment corresponds only to an ideal limiting case, so in molecules, even with fixed nuclei, the assignment proposed is strictly appropriate only for an ideal special case. Although for atoms, the ideal case is usually (not always) closely approached,[15] the same cannot be said for molecules: rather it appears that, in molecules, no one limiting case is ordinarily approached, but that the actual condition usually

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[15] Cf. F. Hund, Linienspektren und Periodisches System der Elemente. 1927 Julius Springer.

[16] When the molecular rotation is considered, the coupling of s and σ_l may be broken down (Hund's case *b*)[9], leading to a different arrangement of the terms, in which σ_s and σ are lost.

[17] Born and Oppenheimer have shown (Ann. der Physik, **84**, 457, 1927) that this separation, in imagination, of nuclear from electronic motions, leads to no serious errors.

lies more or less in the midst of a region between several limiting cases. An adiabatic correlation can, however, always be imagined between the quantum numbers here used and others which, for a particular electron in a particular molecule, may be physically more appropriate.

In general, the quantum numbers l_τ and σ_{l_τ} must not be regarded as corresponding at all accurately to angular momenta and angular momentum components respectively. Nevertheless, the use of such quantum numbers, especially the σ_{l_τ}'s, seems to fit fairly well the behavior of the molecules studied in the present paper, and it seems likely that they represent a good compromise which is reasonably appropriate for the "average molecule."

Meaning of quantum states of electrons in new mechanics; quantum phases. In accordance with the new quantum mechanics, the assignment of independent quantum numbers for the various electrons is of course to be taken in the same qualified or figurative sense as is required for atoms. That is, each quantum state of an individual electron in such an assignment is supposed to be merely a *phase* through which *each* of the electrons of the molecule goes repeatedly. We might better speak of the quantum phases than of the quantum states of electrons.

Notation. A notation designating the "quantum numbers for each electron" will be helpful. Designations such as $1s^s$, $2s^s$, $2s^p$, $2p^p$, $3s^s$, $3s^p$, $3s^d$, $3p^p$, $3p^d$, $3d^d$, will serve this purpose. Here the number denotes n, while the main letter refers to σ_{l_τ} and the superscript letter to l_τ. If a superscript is identical with its main letter, it may be omitted if there is no danger of confusion with the atomic notation. The complete designation of the electron state of a molecule would then be given as in the following examples:

$$(1s^s)^2\,(2s^s)^2\,(2s^p)^2\,(2p^p)^4\,(3p^p),\,{}^2P;$$
$$(1s^s)^2\,(2s^s)^2\,(2s^p)^2\,(2p^p)^3\,(3s^s)^2,\,{}^2P;$$
$$(1s^s)^2\,(2s^s)^2\,(2s^p)^2\,(2p^p)^4\,(3s^s)\,(3p^d),\,{}^3P^D \text{ or } {}^1P^D$$

As in the case of atoms, abbreviations will no doubt subsequently be adopted to denote various frequently occurring configurations. The designations ${}^2P$, ${}^3P$, etc., are those already adopted previously[18] for describing the resultant state of a molecule, and are analogous to those used for atoms except that the letter (S, P, etc.) denotes the resultant value of σ_l instead of that of l. A superscript letter, as D in ${}^3P^D$, can be added to indicate the resultant l for the corresponding united-atom, if this l is known. The reason for relegating l_τ and l to superscripts and placing the emphasis on σ_{l_τ} and σ_l is that the analysis of band spectra yields directly[19] only the value of σ_l (and of s).

Closed shells and molecular states. In an atom one ordinarily speaks of two equivalent s electrons, six equivalent p electrons, ten equivalent d electrons, as forming a closed shell, the latter being defined as a completed group of equivalent electrons having $l=0$ and $s=0$. In a strong electric field, or in a molecule, the l couplings are broken down and each electron tends to ac-

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[18] Cf. R. S. Mulliken, Phys. Rev. **29**, 648–9 (1927).

[19] According to methods described in a series of papers (Phys. Rev. 1926–7) and in accordance with Hund's theoretical work.

quire a quantum number σ_{l_τ}. Considering a shell of six equivalent p electrons by way of example, two electrons now have $\sigma_{l_\tau}=0$, two have $\sigma_{l_\tau}=+1$, two have $\sigma_{l_\tau}=-1$. The two electrons with $\sigma_{l_\tau}=0$ should now have a markedly different energy than the other four, being probably more firmly bound, and are naturally set apart as forming an independent closed shell, with $\sigma_l=0$, $s=0$. The remaining four electrons should be alike in energy, since $\pm\sigma_{l_\tau}$ makes no difference in energy in an electric field; they may be regarded as forming a single closed shell, again with $\sigma_l=0$ and $s=0$. Similarly, an atomic closed shell of ten equivalent d electrons should split in the molecule into three closed shells each with $\sigma_l=0$ and $s=0$; one of these should consist of two electrons each with $\sigma_{l_\tau}=0$, another of four electrons with $\sigma_{l_\tau}=\pm 1$, the third of four electrons with $\sigma_{l_\tau}=\pm 2$.

As is well known from the work of Pauli, Hund, and others, the resultant state of an *atom* is determined exclusively by the *electrons which are not in closed shells*.[15] If *only* closed shells are present, the atom is in a ^1S state ($l=0$, $s=0$). Analogous statements are true for molecules, if we here define a closed shell as the smallest complete group of electrons having $\sigma_l=0$ and $s=0$. A molecule with a given assignment of electron states for the individual electrons may in general be as a whole in any one of several different states, depending on relative orientations among the σ_{l_τ}'s and s_τ's belonging to shells which are not closed. *E.g.*, if there is a system of closed shells plus two $3p^p$ electrons, the possible molecular states are ^1D, ^3S, and ^1S. Table I gives a summary of the possible molecular states corresponding to various electron configurations, including those likely to be met with in the molecules considered in the present paper. The occurrence of normal and inverted multiplets should probably usually be in agreement with Table I, but in this feature occasional exceptions may be expected, especially when more than one kind of electron with $\sigma_{l_\tau}>0$ is present. The method by which the results of Table I are obtained is given in an Appendix at the end of this paper.

TABLE I. *Possible molecular states for various electron configurations.*

Configuration	States	Configuration	States	Configuration	States
(As)	^2S	$(As)\,(Bp)^3$	^3P_i, ^1P	$(Ap)\,(Bd)$	^3F_n, ^3P_n, ^1F, ^1P
$(As)\,(Bs)$	^3S, ^1S	$(Ap)\,(Bp)$	^3D_n, ^3S, ^1D, ^1S	$(Ap)^2\,(Bd)$	^4D_n, ^2D_i, ^2G_n, ^2S, ^2D_n
(Ap)	^2P_n	$(Ap)^2\,(Bp)$	^4P_n, ^2P_n, ^2F_n, ^2P_i, ^2S	$(Ap)^3\,(Bd)$	^3F, ^3P_n, ^1F, ^1P
$(Ap)^2$	^3S, ^1D, ^1S	$(Ap)^3\,(Bp)$	^3D_i *or* $_z$, ^3S, ^1D, ^1S	(Ad)	^2D_n
$(Ap)^3$	^2P_i	$(Ap)^2\,(Bp)^2$	^5S, ^3S, ^1S, ^3D_z, ^3S, ^1G, ^1D, ^1S	$(Ad)^2$	^3S, ^1G, ^1S
$(As)\,(Bp)$	^3P_n, ^1P	$(Ap)^3\,(Bp)^2$	^4P_i, ^2F_n, ^2P_n, ^2P_i, ^2P_i	$(Ad)^3$	^2D_i
$(As)\,(Bp)^2$	^4S, ^2S, ^2D_z, ^2S	$(Ap)^3\,(Bp)^3$	^3D_i, ^3S, ^1D, ^1S	$(As)\,(Bd)$	^3D_n, ^1D

Notes. (*a*) Each configuration given is understood to include, in addition to the electrons specified, any number of *closed shells* such as $(Xs)^2$, $(Xp)^4$, or $(Xd)^4$. (*b*) A symbol such as As stands for *any* s electron state, as $3s^s$, $4s^d$, $3s^d$, etc.; similarly with Bp, etc. (*c*) The subscripts n and i stand for normal and inverted, and z for a very small, multiplet separation. (*d*) States corresponding to some additional configurations can be obtained by noting that the addition of a non-equivalent s electron merely alters the *multiplicity*, by ± 1.

Shells of two. The *ultimate* shell, as London has emphasized (ref. 14, p. 468) is the "*shell of two*," i.e., two electrons alike in n_τ, l_τ, and σ_{l_τ} (including the *sign* of σ_{l_τ}), but having their spins antiparallel. Such a two-shell is not necessarily a closed shell according to the ordinary meaning of the latter term. Thus for $n=2$, there are four shells-of-two: (*a*) $(2s^s)^2$, with $l=0$,

$\sigma_l=0$, $s=0$; (*b*) $(2s^p)^2$, with $\sigma_l=0$, $s=0$; (*c*) $(2p^p)^2$ with $\sigma_l=-2$, $s=0$; (*d*) $(2p^p)^2$ with $\sigma_l=+2$, $s=0$. Here (*a*) and (*b*) are closed shells in the ordinary sense for a molecule, while (*c*) and (*d*) must be taken *together* to give a molecular closed shell, with $\sigma_l=0$; (*b*) must be added to (*c*) and (*d*) to give an atomic closed *p* shell, with $l=0$.

ENERGY RELATIONS. RELATION OF MOLECULE TO SEPARATED ATOMS

Promotion of electrons. When a molecule such as CN is formed from its atoms, some of the electrons of the separated atoms must evidently suffer an increase in their n values, in order to satisfy the demands of the Pauli principle for the molecule and united-atom (the united-atom corresponding to CN is Al). An electron whose n has been increased in this way will be called a "*promoted*" electron.

Hund has shown, in terms of the new mechanics, how such a promotion comes about.[10] For the two center problem (*e.g.*, H_2^+), which is separable in elliptical coördinates (ξ, η, ϕ), the increase in n results from an increase in the quantum number n_η. In this relatively simple case, n_η is correlated with n_θ of spherical coördinates for the united atom, since if the two centers are forced together, the ellipses $\xi=$const. go over into spheres ($r=$const.) and the hyperbolas $\eta=$const. into cones ($\theta=$const.). Hence, since $l=n_\theta+n_\phi$, increase in n by promotion, in the formation of H_2^+, should be accompanied by increase in l. But in more complex molecules it seems likely from Hund's work that the correlation $n_\eta \rightarrow n_r$ may also occur; if so, l would *not* increase with n during promotion (Cf. Appendix, p. 220, for further details). At present the theory leaves us in uncertainty as to which, if either, correlation is usually preferred.

Energy relations; binding energies. The energy E of a (non-rotating, non-vibrating) molecule may conveniently be thought of as divided into (*a*) positive potential energy of repulsion of the nuclei and (*b*) negative energies ("binding energies"), of each electron in the field produced by the nuclei and other electrons. A necessary condition for the formation of a molecule is evidently that, as the distance r between the nuclei is reduced, the total binding energy (*B.E.*) of the electrons must at first *increase faster* than the nuclear energy (*N.E.*). At $r=r_0$, the two rates of increase become equal and the total energy has a minimum, while for $r<r_0$ the nuclear repulsion energy increases faster than the electronic binding energies. The energy of dissociation (D^v of Table III) is evidently given by the relation

$$D^v(=E_{r_0}-E_\infty)=[(B.E.)_{r_0}-(B.E.)_\infty]-[(N.E.)_{r_0}] \qquad (1)$$

For the formation of a reasonably stable molecule, i.e., one for which D^v is fairly large, *B.E.* must evidently increase *considerably* faster than *N.E.* over a *considerable range* of r values, as r decreases toward r_0. As a corollary, r_0 must usually be fairly small in stable molecules. The converse proposition that molecules with small r_0 necessarily have large D^v is, however, not true—

as can, for example, be seen by a comparison of the data for states X and B of CO (Table III).

Each molecular state has a different $E(r)$ curve and a different D^v. Although the $E(r)$ curves show a great variety of forms, any such curve may be characterized to a considerable extent by giving the values of r_0, ω_0 (the vibration frequency), and D^v:

$$(d^2E/dr^2)_{r_0}=(2\pi c\omega_0)^2\mu, \text{ and } D^v=\int_{r_0}^{\infty}E(r)dr.^{21}$$

For a given molecule, it is not even necessary to state r_0 and ω_0 separately, since $\omega_0 r_0^2$ has been found empirically to be approximately constant for each molecule.[22] (There is as yet no theoretical explanation for this somewhat surprising relation.)

Any $E(r)$ curve may be thought of as jointly determined by all the electrons in the molecule. Strictly speaking, we cannot divide the electronic energy into a sum of energies of individual electrons, since much of the energy is really mutual energy of different electrons. Nevertheless it is convenient to think of the, often large, changes in $E(r)$ produced by displacing a single electron from one orbit to another as being caused by changes in a $B.E.(r)$ curve of the displaced electron, corresponding to the assumed relation

$$E(r)=N.E.(r)+B.E.(r)=N.E.(r)+\sum_\tau[-B.E.(r)]_\tau \qquad (2)$$

The effect of any particular type of electron orbit on $E(r)$ may be judged by the effects, on D^v and r_0 or ω_0, of removing this electron or displacing it to another orbit. According to the results of the present investigation, as given in Table III, each occupied orbit-type has a rather specific effect on these quantities.

As the distance between the nuclei is steadily decreased, during the union of two atoms, the binding energy of any unpromoted electron may usually be expected to increase steadily, since the electron comes under the influence of a steadily increasing effective charge; the latter would reach a maximum if the nuclei were united. For a promoted electron, however, the increase in effective charge is at least partially, and often more than, offset by the direct and indirect effects of the increase in n, so that the binding energy may be either increased or decreased on union of the nuclei. This will be made clear by the following examples. (1) Suppose two normal H atoms can unite to form a 2^3S^P excited hydrogen molecule, one electron being promoted to $n=2$ (cf. "Discussion of Heitler and London's work," below). For the separate atoms, the binding energy of each electron is 13.53 volts, or a total of 27.06 volts for both. The united-atom (helium) would probably be in a 2^3P state,[10] or possibly in a 2^3S state. For present purposes it makes no difference which of these possibilities is correct. Assuming a 2^3P state, the energy of removal of the promoted electron is 3.6 volts,[20] while for the

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[20] Cf. A. Fowler, Report on series and line spectra. London, 1922. Also ref. 15.

[21] Cf. e.g. E. Condon, Phys. Rev. **28,** 1182 (1926).

[22] R. T. Birge, Phys. Rev. **25,** 240 (1925); R. Mecke, Zeits. f. Physik, **32,** 823 (1925).

subsequent removal of the other electron the energy is 54.1 volts (ionization potential of He^+). Thus while the promoted electron is more loosely bound than before union of the nuclei, the total binding energy, 57.7 volts, is over twice as great as for the separate atoms. By interpolation, similar statements are probably true for the molecule at all stages of approach of the nuclei. If it were not for the mutual repulsion of the nuclei, the two atoms should apparently unite completely to a single atom.[24] (2) If two many-electron atoms unite to form a molecule, one may expect to find that the binding energy is increased, usually at least, for all the unpromoted electrons, but that it may be either increased or decreased for the promoted electrons. Whether an increase or a decrease in binding energy occurs on promotion might be expected to depend largely on the relative shapes and sizes of the orbits in question, also on the values of n (e.g., promotion from $n=1$ to $n=2$ is energetically much more important than from 2 to 3). Roughly speaking, if $n>1$ initially, a decreased binding energy might be expected if promotion is to a non-penetrating orbit, but an increased energy if to a highly penetrating orbit.

Bonding electrons and bonding power. In chemistry, the electrons of a molecule are often thought of as divided into two classes, (*a*) "bonding" electrons, in pairs,[2] which hold the molecule together, and (*b*) "non-bonding" electrons, which do not. While the present work (cf., however, London[14]) does not indicate any such sharp division in general, it is nevertheless possible to assign, in a rough approximate way, various degrees of "*bonding power*" for various orbit-types. For this purpose, electrons whose presence in a molecule tends to make D^v large, or r_0 small, as judged by the fact that their *removal* from a stable molecule causes decrease in D^v or increase in r_0, may be said to have positive bonding power, or to be bonding electrons; and conversely. (In practise large ω_0 may be used as an alternative criterion for positive bonding power in place of small r_0, since as noted above, ω_0 varies inversely as r_0^2.) The two criteria of positive bonding power just suggested (large D^v, and small r_0 or large ω_0) are often, but unfortunately not in general, equivalent; we have for example $r_0=1.15\ A$, $D^v=11.2$ volts for state X of CO, and $r_0=1.12\ A$, $D^v=2.8$ volts (or perhaps only 0.5 volts) for state B of CO (cf. Table III). The very different $E(r)$ curves, in spite of equal r_0, in states X and B of CO, may perhaps be attributed to differences in orbit dimensions and hence in the form of the $B.E.(r)$ curve, for the electron whose orbit differs in the two cases.

To distinguish between the above two definitions of bonding power we may speak of the *energy-bonding-power* of an electron, as judged by its effect on D^v, and of its *distance-bonding-power*, as judged by its effect on r_0. Although the energy definition of bonding power is perhaps the more appropriate, it suffers from two difficulties: (*a*) in case the two molecular states to be compared give *different* dissociation products (e.g., excited atoms in the one case but not in the other), the definition is not altogether satisfactory; (*b*) the values of D^v are for the most part not known at all accurately as yet.

For these reasons the more convenient definition of bonding power is that in terms of r_0 or ω_0, ω_0 being used in practise since it is the easier to determine.

The energy-bonding-power of an electron is intimately related to the change in its binding energy during molecule formation (cf. Eqs. (1) and (2), and accompanying discussion). From this fact and the preceding discussion of *B.E.*'s of promoted and unpromoted electrons, it is evident that unpromoted electrons should on the whole show positive energy-bonding-power, and promoted electrons the reverse; and that D^v should on the whole be largest for molecules having the smallest relative number of promoted electrons. This can be applied in the following way: if D^v is markedly decreased by transfer of an electron to a certain orbit, this may be taken as evidence that the latter orbit represents a promoted condition of the electron.

Corresponding statements can, unfortunately, not be made with the same definiteness in respect to the distance-bonding-power.

Relation of orbit dimensions to energy-bonding-power and energy changes in molecule-formation. If r is the distance between the nuclei, and d is, roughly speaking, the diameter of the "electron orbit," the binding energy of an electron must obviously be a function of r/d rather than of r. Only when r_0 is small, yet large enough so that r_0/d is comparable with unity for a given electron, should we expect a large change in energy and "orbit shape" (better, in the Schrödinger ψ function) for this electron on formation of a molecule.

Except where very light atoms (H, He, Li) are present, $d/r_0 << 1$ for the K shells of the two atoms in a diatomic molecule. For example, in CN, $r_0 = 1.172$ A for the normal state, while the Bohr diameters of the K orbits of the C and N atoms respectively are about 0.24 A and 0.20 A. In the CN molecule, two of the electrons remain as $1s^s$ electrons, while two must technically be promoted, probably becoming $2s^p$ or $2s^s$ electrons. Although for the united-atom ($r = 0$) corresponding to CN the energy and other changes would be large for these electrons, they are relatively, and probably absolutely, small at the value $r = r_0 = 1.17$. Hence, as Hund puts it, it "has sense" to speak of these electrons still as K electrons (cf. ref. 10, p. 763).

For the L orbits of carbon and nitrogen, with diameters[23] of the order of $1.1 - 1.5$ A, $d/r_0 \sim 1$, and relatively if not absolutely much larger energy and other changes should occur when the atoms unite than in the case of the K orbits. If, on the other hand, we consider the formation of a CN molecule from a C atom containing a *large* orbit such as a $3d$ orbit ($d \sim 9$ A), we now have $d/r_0 >> 1$, so that, again, there should be (for this orbit) very little change in energy or other characteristics during molecule formation.

The factors of "orbit shape" and "degree of penetration" should also be important. E.g., an "elliptical" $2s^s$ orbit might be expected to show a greater increase in binding energy than a "circular" $2p^p$ orbit with its "plane" perpendicular to the internuclear axis, because the elliptical shape permits a closer approach to both nuclei, assuming equal areas for the two orbits and $r_0 \sim d$. Hence an unpromoted $2s^s$ electron might be expected to show greater

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[23] For the areas swept out, in the case of the "elliptical orbits."

energy-bonding-power than an unpromoted $2p^p$ electron. A similar difference might be expected between a $3s^s$ and a $3p^p$ electron; if, as is the case in the molecules discussed in present paper, $3s^s$ and $3p^p$ are promoted electrons, the energy-bonding-power might of course be small or negative for both, but would be expected to be much less negative for $3s^s$ than for $3p^p$. These ideas are borne out by the results given in Table III.

Promotion energies. A specific example will be helpful in introducing the convenient concept of "promotion energy." In a nitrogen molecule, there are, among others, probably two $2s^s$ electrons and two $3s^p$ electrons. In each of the two N atoms from which this N_2 molecule was formed, there were two $2s$ electrons, or a total of four $2s$ electrons, all being equally firmly bound. Suppose two of these remain unpromoted and become $2s^s$ electrons of N_2, while the other two are promoted to give the $3s^p$ electrons of N_2. We expect to find the binding energy of the $2s^s$ electrons greater than before union of the two atoms; the binding energy of the $3s^p$ electrons may, perhaps, be either greater or less than in the atoms. In any case we expect to find that the promoted, $3s^p$, electrons are less firmly bound than the unpromoted, $2s^s$, electrons. The higher energy of the $3s^p$ as compared with the $2s^s$ electrons, we shall define as the "*energy of promotion*" of these electrons. This promotion energy should ordinarily increase steadily as r decreases; of principal interest, however, of course, is the promotion energy for $r=r_0$. Although we cannot in general define the promotion energy of a promoted electron in quantitative terms as in the example given, the concept can always be used in at least a qualitative way.

Discussion of Heitler and London's work. Heitler and London have shown[13] that two normal hydrogen atoms interact in two ways: (*a*) they show attraction and form a normal hydrogen molecule (1^1S), or (*b*) they show strong repulsion in a ^3S configuration. The difference between these two cases comes about as an effect analogous to Heisenberg's quantum-mechanical "resonance." Heitler and London label the ^3S condition 1^3S and consider that it is not a true state of the molecule, and that it corresponds to an impossible state of the united-atom (helium).[24] So far as the writer can see, however, the correct designation of this state is 2^3S, in accordance with conclusions of Hund.[10,24] The repulsion of the two atoms at moderate distances is then connected with the large promotion energy required to reach 2^3S, and r_0 is merely large, but not non-existent.

Heitler and London have further concluded that a state of repulsion is a fundamental characteristic (but cf. London[25]) of any two atoms or molecules at least one of which is composed solely of electronic "shells of two" (cf. above). They cite He+He, He+H, H_2+H, etc., the normal state being meant in each case. Yet it seems obvious, from the existence of Van der Waals attractive forces in helium, that very unstable molecules must be

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[24] In their first paper, Heitler and London seem, *tacitly*, to imply that what is here called "promotion" of electrons does not exist. But in his most recent paper (Zeits. f. Physik **47,** p. p. 839, footnote), which appeared after the present paper had gone to press, Heitler accepts the (Hund) point of view stated above.

possible even in such cases.[25] In other similar cases, there is evidence that more or less stable molecules exist. Thus the low ^2S state of HgH, with a heat of dissociation of 0.4 volts, is without much doubt formed from a normal Hg and a normal H atom. Again, the ^2D state of CH, which possesses high stability ($r_0=1.11\times 10^{-8}$ cm) is probably formed from a normal H atom and a ^1D carbon atom, although the latter is composed exclusively of shells of two. These considerations, however, give no reason for disputing Heitler and London's conclusions,[13,14]—which are moreover in harmony with those of Hund,—that two molecules such as He+He or He+H should show only one mode of interaction, and that two atoms such as Li+H, H+H, Li+Li, should show just two, contrasting, modes of interaction.

Correlation of molecular quantum numbers with those of separate atoms. Hund has suggested[11] the following procedure for determining the possible states of a molecule which can be obtained by bringing together two atoms initially in specified states. Assume each atom to be placed in a strong electric field so that quantum numbers σ_l and σ_s are established ($\sigma_l=l,\ l-1, \cdots 0, \cdots -(l-1),\ -l;\ \sigma_s=s,\ s-1, \cdots -s$). Then all the possible values of σ_l and σ_s for the molecule are respectively given as algebraic sums of the σ_l and σ_s values of the two atoms. The possible s values for the molecule comprise all values lying between s_1+s_2 and s_1-s_2, inclusive, where s_1 and s_2 refer to the separate atoms;[26] i.e., the s values correspond to the possible *vector* sums of s_1 and s_2.

Consider for example a $(1s)^2(2s)^2(2p)$, ^2P boron atom and a $(1s)^2(2s)^2(2p)^4$, ^3P oxygen atom. The ^2P boron state ($l=1$, $s=\frac{1}{2}$) should give rise in a strong electric field to six components ($\sigma_l=0$, ± 1 with $\sigma_s=\pm\frac{1}{2}$), and the ^3P oxygen atom ($l=1$, $s=1$) to nine ($\sigma_l=0$, ± 1, with $\sigma_s=0$, ± 1). Some of these components fall together in pairs or threes, but this can be avoided by imagining a temporary magnetic field placed parallel to the electric axis. (Without this the σ_s values given, for $\sigma_l=0$, lack meaning; also $\pm\sigma_l$ states fall together; cf. Appendix for details). For the BO molecule formed from B(^2P) plus O(^3P), the number of strong field states formed by all possible combinations of the atoms in their various states is 6×9, or 54. This conclusion is based on Hund's principle[10,11] that in the formation of a molecule from two atoms "no state is lost." The 54 strong-field components, during withdrawal of the imagined magnetic field, group themselves into a number of molecular electronic states, as follows: three ^2S states ($\sigma_l=0$, $s=\frac{1}{2}$, $\sigma_s=\pm\frac{1}{2}$) and three ^4S states ($\sigma_l=0$, $s=1\frac{1}{2}$, $\sigma_s=\pm\frac{1}{2}$, $\pm 1\frac{1}{2}$); two ^2P ($\sigma_l=\pm 1$, $s=\frac{1}{2}$) and two ^4P ($\sigma_l=\pm 1$, $s=1\frac{1}{2}$); one ^2D and one ^4D ($\sigma_l=\pm 2$). These results have been given by Hund.[11]

We can go further than Hund in predicting the electron configuration of the molecule if we specify the individual $\sigma_{l\tau}$ value for "each electron" (or strictly, in the new quantum mechanics, of each quantum phase,—cf. above,

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[25] Possibly in some cases not, if vibration and rotation are taken into account. At the end of his second paper,[14] London refers briefly to the question of Van der Waals forces.

[26] To permit resultants other than s_1+s_2 and s_1-s_2, one must here allow the possibility of a breaking up of the original spin couplings.

p. 192) in each atom, and assume that these are all preserved in the molecule. It seems likely that this assumption (the "*detailed* σ_{l_τ} *conservation rule*") should usually if not always hold.

In order to apply this assumption, we first note that the state of each of the two *atoms*, in the imagined strong electric field before they are brought together, can be described according to the strong-field quantum numbers and notation adopted above for *molecules*. Thus the six strong-field components from $B(^2P)$ may be grouped under $(1s^s)^2(2s^s)^2(2s^p)$, $^2S^P$, with two components, corresponding to $\sigma_l=0$, $\sigma_s=\pm\frac{1}{2}$ in a magnetic field; and $(1s^s)^2(2s^s)^2(2p^p)$, $^2P^P$, with four magnetic components, corresponding to $\sigma_l=\pm 1$, $\sigma_s=\pm\frac{1}{2}$. Similarly the nine components from $O(^3P)$ fall under $(1s^s)^2(2s^s)^2(2s^p)^2(2p^p)^2$, $^3S^P$, corresponding to $\sigma_l=0$, $\sigma_s=0$, ± 1, and $(1s^s)^2(2s^s)^2(2s^p)(2p^p)^3$, $^3P^P$, corresponding to $\sigma_l=\pm 1$, $\sigma_s=0$, ± 1.

In applying the σ_{l_τ} conservation rule, it is useless to specify the n_τ and l_τ values of the electrons, since we do not in general expect these to be preserved when the molecule is formed. It is therefore sufficient to give, for each atomic strong-field state, the *total* number of s, p, or d electrons, where s, p, or d indicates $|\sigma_{l_\tau}|=0$, 1, or 2. Thus we may classify $(1s^s)^2(2s^s)^2(2s^p)$ of boron, i.e., $B(^2S^P)$, as an s^5 configuration, and $(1s^s)^2(2s^s)^2(2s^p)^2(2p^p)^2$ of oxygen, i.e., $O(^3S^P)$, as an s^6p^2. The addition of these should give a BO molecule of the $s^{11}p^2$ *configuration class*, in a ^2S or ^4S state. Similarly, $B(^2S^P)$ plus $O(^3P^P)$ should give ^2P and ^4P of the $s^{10}p^3$ class, since $O(^3P^P)$ is s^5p^3. Likewise, $B(^2P^P)$ plus $O(^3S^P)$ should give an additional ^2P and ^4P of the $s^{10}p^3$ class, while $B(^2P^P)$ plus $O(^3P^P)$ should give two ^2S, two ^4S, one ^2D, and one ^4D state of the s^9p^4 class.

A qualification in regard to the σ_{l_τ} conservation rule should be noted, as follows: if (for example) an s^4p and an s^6p^2 atom are found to give an $s^{10}p^3$ molecule, we know directly from this fact only that the *total numbers* of s and p electrons have been conserved, but not that σ_{l_τ} has been conserved for each *individual* "electron" or "quantum phase." Nevertheless it seems reasonable in most cases to infer detailed conservation of σ_{l_τ}'s as the cause of observed conservation of total numbers of s, p, $\cdots$ electrons. Such an inference will, however, in general, *not be implied* in the following discussion when reference is made to the "σ_{l_τ} conservation rule." The inference may be explicitly avoided by referring to the "*non-detailed* σ_{l_τ} *conservation rule.*"

In Table II the σ_l and s values and the σ_{l_τ} configurations obtained in a strong electric field are given, implicitly or explicitly, for the lowest energy states of the atoms of the first short period. From this information the possible σ_k and s values, and, in so far as our assumption is correct, the possibilities in respect to configuration class, can be predicted for any molecule formed from two such atoms (cf. Note 2 of Table II).

Knowing the n and l values for the atoms,[15] each configuration-class formula in Table II is sufficient to determine the *detailed* configuration for the atomic state in question, including the value and sign of each σ_{l_τ}. Consider for example $s^5p^2, {}^2S$ from $N(^2D)$. Since $N(^2D)$, in the *atomic* notation, is $(1s)^2(2s)^2(2p)^3$, the complete configuration here must, in the molecular notation, be $(1s^s)^2(2s^s)^2(2s^p)(2p^p)^2$, and since $\sigma_l=0$, the two $2p^p$ electrons must have $\sigma_{l_\tau}=+1$ and -1 respectively. Similarly s^5p^3, ^3P from $O(^3P)$ must be $(1s^s)^2(2s^s)^2(2s^p)(2p^p)^3$; and since $\sigma_l=\pm1$, two of the $2p^p$ electrons must have $\sigma_{l_\tau}=\pm1$, while the third must have $\sigma_{l_\tau}=\mp1$.

TABLE II. *Atomic configurations for a strong electric field.*

Li, ^2S:s^3, ^2S Li, ^2P: s^3, ^2S and s^2p, ^2P
Be, ^1S: s^4, ^1S Be, ^3P: s^4, ^3S and s^3p, ^3P Be, ^1P: s^4, ^1S and s^3p, ^1P
B or C$^+$, ^2P: s^5, ^2S and s^4p, ^2P
C or N$^+$, ^3P: s^5p, ^3P and s^4p^2, ^3S
^1D: s^6 (or s^4p^2?), ^1S and s^5p, ^1P and s^4p^2, ^1D
^1S: s^4p^2 (or s^6?), ^1S
N or O$^+$, ^4S: s^5p^2, ^4S
^2D: s^5p^2, ^2S and s^4p^3 (or s^6p?), ^2P and s^5p, ^{22}D
^2P: s^5p^2, ^2S and s^6p (or s^4p^3?), ^2P
O, ^3P: s^6p^2, ^3S; s^5p^3, ^3P
^1D: s^6p^2, ^1S; s^5p^3, ^1P: s^6p^2, ^1D
^1S: s^4p^4, ^1S
F, ^2P: s^5p^4, ^2S and s^6p^3, ^2P

Notes. (1) The results given in this table are obtained by methods similar to those used in the application of the Pauli principle for atomic multiplets in making the correlation between strong and vanishingly weak magnetic fields.[15] These methods are modified in a way appropriate to electric fields (cf. Table V, in the Appendix). (2) For the resulting *molecule* the following cases are important (in each case the statement made holds for *each value of s* which is possible): (*a*) if $\sigma_l=0$ for one atom, and $|\sigma_l|=q$ for the other, one molecular state with $|\sigma_l|=q$ results; (*b*) if $|\sigma_l|>0$ for both atoms, two molecular states result, each of double weight because corresponding to $\pm\sigma_l$, one with $|\sigma_l|=|(\sigma_l)_2|+|(\sigma_l)_1|$, the other with $|\sigma_l|=|(\sigma_l)_2|-|(\sigma_l)_1|$, where $(\sigma_l)_1$ and $(\sigma_l)_2$ refer to the two atoms, and $|(\sigma_l)_2|\geqq|(\sigma_l)_1|$; except that, (*c*) if $(\sigma_l)_2|-|(\sigma_l)_1|=0$, a state of double weight is replaced by *two* states of unit weight with $\sigma_l=0$; an example of (*c*) is the case of $B(^2P^P)$ plus $O(^3P^P)$, discussed above.

WORKING RULES

With the background sketched above, we are now ready to formulate a set of working rules to be used in the analysis of spectroscopic and other data for the purpose of assigning quantum numbers to electron states of actual molecules.

Ionization energies of individual electrons. Other things being equal, the energy required to remove an electron of any specified type (e.g., $3s^p$) may reasonably be expected to change regularly as the atomic number of one or both atoms is gradually altered, unless the promotion status of the electron should change. Unpromoted electrons should always, or usually, be more firmly bound in the molecule than in the atom, while promoted electrons may be either more or less firmly bound.

Multiplet separations. For the total width $\Delta\nu$ of a molecular multiplet, values are to be expected which approximate those for equally firmly bound electrons in the constituent atoms. As Mecke has shown, the molecular $\Delta\nu$, in its dependence on the atomic number Z, usually represents a compromise between the two atoms.[27] In a general way, $\Delta\nu$ may be expected to depend on Z and on an effective quantum number n^* according to the Landé formula (cf. ref. 15, p. 61). More specifically—provided the electrons concerned are fairly well shared—$\Delta\nu$ should be proportional to $(Z_a^{*2}+Z_b^{*2})/n^{*3}$, where Z^*

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[27] R. Mecke, Naturwiss. **13**, 755 (1925); Zeits. f. Physik, **36**, 795 (1926); **42**, 416–22 (1927). E. Hulthén, Nature **116**, 642 (1925).

represents the effective nuclear charge (corrected for shielding) of atom a or b. Thus in particular $\Delta\nu$ should decrease rapidly with increasing n^*.

Bonding power of electrons. Unpromoted electrons whose "orbits" are of the order of size of r_0 should show strong energy-bonding power. Electrons in large non-penetrating orbits should be as good as ionized, and should show zero energy-bonding power. Promoted electrons should show small or negative energy-bonding power unless orbit size or other conditions are very favorable.

Relation of molecule to separate atoms. The atoms into which a molecule in a given state can dissociate must be in states which have l and s values compatible with the σ_l and s values of the molecule (cf. Table II and accompanying discussion). Also, these atoms should, usually at least, be in states capable of yielding σ_{l_τ} configurations (cf. Table II) of such classes that their sum agrees with the σ_{l_τ} configuration class of the molecule. For a pair of atoms in specified electronic states a definite number of molecular states of each (σ_l, s) type can be predicted (cf. Table II), and this number cannot be exceeded; a similar but less strict rule should hold in regard to configuration classes.

Electron impact. Processes in which only one electron is removed or excited should be more probable than those involving two electrons.

Selection rules for radiation transitions. (1) Leaving out of account the selection rules for j, j_k, σ_s, etc., which determine the internal structure of bands, the only fairly strict[28] rule to be expected for ordinary molecules is $\Delta\sigma_l = 0$ or ± 1. (2) As in atoms, $\Delta s = 0$ should be greatly preferred unless the (l, s) or (σ_l, s) coupling is large (large multiplet separations). (3) For the same reasons as in atoms, jumps in which only one electron changes its quantum numbers (n_τ, l_τ, and σ_{l_τ}) should be much more common than those involving changes for two or more electrons. (4) To the extent that the l_τ's are good quantum numbers, $\Delta l_\tau = \pm 1$ should hold as for atoms; in case there is also strong coupling of l_τ's, a second electron might sometimes make a simultaneous jump such that $\Delta l_\tau = 0$ or ± 2. (5) In so far as the l_τ's are not too strongly coupled, so as to suppress the individual σ_{l_τ}'s, the latter should individually obey a selection principle $\Delta\sigma_{l_\tau} = 0$ or ± 1. The same result follows automatically from (1) and (3). (6) (Additional selection rules for symmetrical molecules.) For symmetrical molecules a strict rule should hold according to which at least one of the three transitions conceivable between three electron levels is always absent.[11] This is equivalent to (a) assigning a symmetry quantum number n_s for *each electron state* and probably, at least when rule (3) above is followed, for *each electron*, and then (b) specifying the selection rule $\Delta n_s = \pm 1, \pm 3, \cdots$. For the case of H_2^+, n_s can probably be identified with l, as Hund has shown[11]; we shall tentatively assume[29]

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[28] But in case molecular states exist where the effect of the electric axis is very small, σ_l ceases to exist, and with it the selection rule for σ_l, —cf. Hund's case d.[9]

[29] In the case of separability in elliptical coordinates, as in H_2^+, n_s is to be identified with $(n_\eta + n_\phi)$, which goes over into $(n_\theta + n_\phi) = l$ on union of the nuclei. But this particular correlation of quantum numbers in elliptical and spherical coordinates cannot be relied upon in general

that n_{s_τ} can be identified in general with l_τ. If, or when, this is true, the rule $\Delta n_{s_\tau} = \pm 1, \pm 3, \cdots$, practically coincides with a *strict* applicability of $\Delta l_\tau = \pm 1$, at least to the extent of completely cutting out $\Delta l_\tau = 0$ and ± 2.[30]

ASSIGNMENTS OF ELECTRON CONFIGURATIONS FOR KNOWN MOLECULES

Introductory. As outlined in the introduction, the writer suggested that the electronic states of certain "one-valence electron molecules" (BO, CO^+, CN, N_2^+) are analogous to those of the sodium atom. Subsequently Hund showed that the suggested analogy is entirely consistent with the possibility that each of the molecules named can dissociate directly, by increase in the vibrational quantum number, into normal or slightly excited atoms.

For each of the four molecules named, three electronic states are known; an unexcited and an excited ^2S state, and between these a ^2P state,[3,5]—except that the ^2P has not yet been observed in N_2^+. The excitation potentials of these states, and approximate values of the dissociation energies calculated by the method of Birge and Sponer,[8] are given together with other information in Table III.

The present paper originated in the attempt to explain an important defect in the analogy to sodium, namely this: that the ^2P states are *inverted* for BO, CO^+, and CN, whereas the supposedly analogous ^2P state of sodium is *normal*. This discrepancy was first demonstrated in Jenkins' analysis of the structure of the BO α bands,[31] the proof depending on the numbers of "missing lines" in the $^2P_{1\,1/2} \rightarrow {}^2S$ and $^2P_{1/2} \rightarrow {}^2S$ sub-bands. Examination of Baldet's data and photograph[32] for the λ3997 comet-tail band ($^2P \rightarrow {}^2S$) of CO^+ leaves little doubt that the same relation holds for CO^+. Unpublished work of Mr. Y. K. Roots and the writer on the red CN bands ($^2P \rightarrow {}^2S$) shows without question that the ^2P is also inverted in this case. Presumably the analogy extends also to the as yet undiscovered ^2P of N_2^+.

Interpretation of spectra, electronic quantum numbers and electron configurations: BO, CN, CO^+, N_2^+. There seems to be no possibility of accounting for an inverted ^2P state in terms of an electron configuration like that (closed shells *plus* one p electron) which gives the normal ^2P state of Na. The simplest assumption is that the inverted ^2P of BO, CO^+, and CN corresponds, like the inverted ^2P ground state of a halogen atom, to a configuration of closed shells *minus* one p electron (cf. Table I).[33] The missing p electron must in all probability be a $2p$ electron, since the number of electrons in the molecule is not large enough to give a shell of as many as three $3p$ electrons except in a highly excited state. Since the shell of six equivalent $2p$ electrons of an atom is subdivided in the molecule into two sub-shells

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(cf. pp. 194, 220), so that the assumption made here is justified only according as it is successful. *Possibly* our supposed l is merely n_s, and l itself is in general different, but unimportant.

[30] $\Delta l_\tau = \pm 3$ etc. will probably usually be weak because of rule 4 and for other reasons.

[31] F. A. Jenkins, Proc. Nat. Acad. Sci. **13**, 496 (1927).

[32] F. Baldet, Compt. Rend. **180**, 820, 1201 (1925).

[33] Other possible explanations, such as the assumption of incomplete shells of d or f, as well as of p electrons, are too improbable.

composed respectively of two $2s^p$ and four $2p^p$ electrons (cf. preceding section), it must be one of the latter which is missing in ^2P of BO.

In interpreting the three observed electron levels of BO, the fact that the combination $^2S \rightarrow {}^2P$ is much weaker[34] than $^2P \rightarrow {}^2S$ and $^2S \rightarrow {}^2S$ is also important. This indicates a strong tendency toward the validity of an additional selection principle besides $\Delta\sigma_l = 0, \pm 1$; it seems reasonable to identify this additional selection principle with the atomic rule $\Delta l_\tau = \pm 1$. This identification yields the conclusion that the united-atom quantum numbers l_τ are approximately valid in these molecules. It also follows, if we exclude as improbable the presence of any electrons with $l_\tau > 2$, that the *emission electron* has $l_\tau = 1$ in the lower ^2S state, but $l_\tau = 0$ or 2 in the ^2P and in the upper ^2S state; or else $l_\tau = 0$ or 2 in the lower state and $l_\tau = 1$ in the two upper states.

Accepting the conclusions of the preceding paragraphs, we are led, as the simplest explanation of the observed relations, to the following electron configurations for the three observed states of each molecule; lower ^2S, $(A)(ms^p)^2(2p^p)^4(ns^x)$; ^2P, $(A)(ms^p)^2(2p^p)^3(ns^x)^2$; upper ^2S, $(A)(ms^p)(2p^p)^4(ns^x)^2$. Here A is an as yet undetermined closed-shell configuration of the six most firmly bound electrons, m and n are as yet undetermined principal quantum numbers, and x is s or d. The order in which the symbols ms^p, $2p^p$, and ns^x is written is intended to conform to the relative strength of binding of these types of electrons. The assignment given satisfies the following conditions: (1) $\sigma_l = 0, 1, 0$, $s = \frac{1}{2}$, for the states ^2S, ^2P, ^2S, with $\Delta\sigma_l = 0$ or ± 1 in the observed transitions; (2) the ^2P is inverted; (3) the lower ^2S state has an outer configuration resembling that of unexcited Na; (4) $\Delta l_\tau = 1$ for the emitting electron in the strong transitions.

The energy order of the three observed molecular states then indicates the order of ionization potentials for closed shells corresponding to the three orbit-types, ms^p, $2p^p$, and ns^x. Quite as noteworthy as the existence of these three different ionization potentials is the fact that the differences are so comparatively small. Also of interest is the fact that according to the present interpretation, the transitions between the observed states are of an X-ray rather than of an optical type.

The diamagnetic ^1S normal state of CO or N_2, obtained in each case by adding an electron to the ^2S normal state of the ion, then presumably has a configuration $(A)(ms^p)^2(2p^p)^4(ns^x)^2$, composed wholly of closed shells. The absence of a ^3S state of CO or N_2 lying below the lowest ^1S state is satisfactory evidence for the assumed closed shell $(ns^x)^2$ as against $(ns^x)(ns^y)$.[35]

The configuration (A) must be either $(1s^s)^2(2s^s)^2(2s^p)^2$, $(1s^s)^2(2s^p)^2(2s^s)^2$, or $(1s^s)^2(2s^s)^2(3s^s)^2$. The first two closed shells in any case are essentially unchanged K shells of the separate atoms. One of these must, however, for

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[34] Cf. ref. 5, p. 497, footnote 43. This combination $^2S \rightarrow {}^2P$ is known to be weak in BO and CO^+, and has as yet not even been observed in CN or N_2^+.

[35] Evidence for a $(ns^x)^2$ shell in the excited states of CO^+ etc. is the fact that a large amount of energy is surely required to go from $(ns^x)^2$ to (ns^x) (ns^y) in CO and so doubtless in CO^+; for neutral CO shows *no* excited levels below 6 volts.

purposes of the Pauli principle be considered as having been promoted, doubtless to $(2s^s)^2$ or $(2s^p)^2$. The third closed shell must probably be derived from two $2s$ electrons of the separated atoms. No direct spectroscopic evidence concerning these shells appears to be available.

The ms^p electrons are doubtless either $2s^p$ or $3s^p$ electrons. The $2p^p$ electrons are probably unpromoted $2p$ electrons of the atoms. The most loosely bound, ns^x, electrons ($x=s$ or d) cannot be $2s^s$, since this shell is surely not the most loosely bound, and has been accounted for already as surely a part of (A). Most probably they are $3s^s$, or perhaps $3s^d$, electrons; or if (A) includes a group $(3s^s)^2$, they are probably either $3s^d$ or $4s^s$ electrons.

The two most likely possibilities for the normal state of CO and N_2 appear to be:

(1) $(A)(3s^p)^2(2p^p)^4(3s^s)^2$, with $(A)=(1s^s)^2(2s^p)^2(2s^s)^2$,[36]
(2) $(A)(2s^p)^2(2p^p)^4(3s^d \text{ or } 4s^s)^2$, with $(A)=(1s^s)^2(2s^s)^2(3s^s)^2$.

The fact that the ms^p shell is always more firmly bound than the $2p^p$ shell is in agreement with alternative (1) if the ms^p electrons are former $2s$ atomic electrons promoted to $3s^p$; or also with alternative (2) if they are unpromoted $2s^p$ electrons derived from $2p$, or perhaps sometimes from $2s$. The fact that the ms^p electrons always show strong positive energy-bonding-power indicates an unpromoted status and so favors the second alternative.[36a] But if this is correct, we might expect the $3s^p$ orbit, which is not yet present according to configuration (2), to be next in order of binding, or at least to be more firmly bound than the $3p^p$ and $3p^d$ orbits; whereas in the normal state of NO, with one more electron than CO, the most loosely bound electron is actually found to be in an orbit, presumably $3p^p$ or possibly $3p^d$ (see below), with $\sigma_{l_\tau}=1$. Other arguments can be given on both sides,[36a] but on the whole, alternative (1) seems the more probable, and will be assumed, tentatively, in the following discussion. It may be, or is even probable, that this special assignment is incorrect, but the unambiguous identification of A, m, n, and x is not vital to the present discussion. It is possible also that the *same* identification should not be made for *all* molecules. A definite decision in regard to these points can probably be made only with the help of many new data on band structures. It should be said, however, that the known facts about the molecules considered below offer no contradiction to the assignments involved for A, m, n, x in configuration (1).

Interpretation of ionization potentials in N_2 *and* CO. The conclusions here reached have an interesting bearing on the interpretation of ionization potential and positive ray data. In the case of CO the following ionization potentials are known: 14.2 volts, ionization begins; 16.9 volts, appearance of CO^+ comet-tail bands ($^2P\rightarrow{}^2S$); 20.0 volts, excitation of negative Des-

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[36] A likely alternative for (A) is, $(A)=(1s^s)^2\,(2s^s)^2\,(2s^p)^2$. The possibility $x=d$ instead of $x=s$ also appears not unlikely.

[36a] The fact that the $3s^p$ electrons act like unpromoted electrons is perhaps after all not inconsistent with alternative (1), for if the $2s^p$ electrons in (1) act essentially like $1s^s$ electrons, it may be that this permits the $3s^p$ electrons to act essentially like $3s^p$ electrons.

TABLE III. *Quantum number assignments.*

Molecule	Energy (volts)	State ($\Delta\nu$)	Numbers of outer electrons $2s^s$	$3s^p$	$2p^p$	$3s^s$	$3p^p$	$3s^d$	$3p^d$	Molecular Constants $r_0(A.U.)$	$\omega_0(\mathrm{cm}^{-1})$	ω_0x	Dissociation Energy (volts) D^v	D	Dissociation Probable Products	Remarks
Li$_2$	0	$\{^1S\}$	2							{2}	—	—	{1.3}	{1.3}	Li (^2S), s^3; Li (^2S), s^3	[Not known; estimated]
LiF	0	$\{^1S\}$	2	2	4					—	—	—	—	—	Li$^+$(^1S), s^2; F$^-$(^1S), s^6p^4	[Not known; estimated (see text)]
BeO	0	^1S	2	2	4		} or reverse?			1.33	1465	12.7	6.4	6.4	Uncertain (cf. text)	}BeO bands
	2.62*	^1S	2	1	4	1				1.36	1354	8.9	5.2	7.8	Uncertain (cf. text)	
C$_2$	0	^3P	2	2	3	1				1.31	1630	11.7	7.0	7.0	C(^3P), s^4p^2; C(^3P), s^5p	}Swan bands
	2.39*	^3P	2	1	3	2				1.27	1773	19.4	6.4	8.8	{C(^3P, s^4p^2; C(^1D), s^5p}	
BeF	0	$\{^2S\}$	{2	2	4	1	}			—	1253	10.2	4.8	4.8	Uncertain (cf. text)	}BeFbands
	4.10*	$\{^2P(35)\}$	{2	2	4		1}			—	1156	8.4	4.9	9.0	Uncertain (cf. text)	
B^{11}O	0	^2S	2	2	4	1				1.21	1874	11.7	9.3	9.3	B(^2P), s^4p; O(^3P), s^5p^3	$^2P\rightarrow{}^2S$ strong
	2.91*	$^2P_i(126)$	2	2	3	2				1.36	1249	10.6	4.6	7.5	B(^2P), s^5 or s^4p; O(^3P), s^5p^3 or s^6p^2	$^2S\rightarrow{}^2P$ weak
	5.30*	^2S	2	1	4	2				1.31	1270	10.1	5.0	10.3	B(^2P), s^4p; O(^3P), s^5p^3	$^2S\rightarrow{}^2S$ strong
CN	0	^2S	2	2	4	1				1.17	2056	13.8	9.5	9.5	C(^3P), s^4p^2; **N**(^4S), s^5p^2	$^2P\rightarrow{}^2S$ strong
	1.78*	$^2P_i(56)$	2	2	3	2				{1.23}	1729	13.5	6.8	8.6	C(^3P), s^5p; N(^4S), s^5p^2	$^2S\rightarrow{}^2P$ unknown
	3.18*	^2S	2	1	4	2				1.15	2144	21.3	6.7	9.9	C(^3P), s^4p^2; N(^2D), s^5p^2	$^2S\rightarrow{}^2S$ strong
N$_2$	0	$X={}^1S$	2	2	4	2				—	2345	14.4	11.7	11.7	N(^4S), s^5p^2; N(^4S), s^5p^2	Known bands,[61] $X\leftarrow\rightarrow a$, $D\rightarrow B$, $C\rightarrow B, B\rightarrow A$; also the somewhat uncertain $b\rightarrow X$ and $c\rightarrow X$ systems with initials levels probably at 12.80 and 12.88 volts respectively.
	8.18*	$A={}^3S$ (or ^3D?)	2	2	3	2	1			—	1446	13.9	3.7	11.9	N(^4S), s^5p^2; N(^2D), s^5p^2 (or N, ^4S, s^5p^2?)	
	8.50*	$a={}^1P$	2	2	4	1	1			—	1679	13.8	5.7^x	14.2^x	N(^2D), s^5p^2; N(^2D), s^4p^3	
	9.35*+	$B={}^3P_n$[70?]	2	2	4	1	1			1.21	1718	14.4	5.3	14.6	N(^2D), s^4p^3; N(^2D), s^5p^2 (or N, ^4S, s^5p^2?)	
	13.00*+	$C={}^3P_n$ [55?]	2	1	4	2	1			1.15	2019	26.0	1.6^x	14.6^x	N(^2D), s^4p^3; N(^2P), s^5p^2 (or N, ^2D, s^5p^2?)	
	14.80*	$D={}^3D$(small) or ^3S	{2	2	4	1		1(or $3d^d$?)}		—	>1718	—	>0	>14.8	—	
N$_2^+$	16.9+	^2S	2	2	4	1				1.12	2187	16.3	9.1	9.1	N$^+$(^3P), s^4p^2; N(^4S), s^5p^2	$^2P\rightarrow{}^2S$ unknown
	{17}	^2P_i	2	2	3	2				—	—	—	—	—	N$^+$(^3P), s^5p; N(^4S), s^5p^2	$^2S\rightarrow{}^2P$ unknown
	20.1*+	^2S	2	1	4	2				1.08	2392	22.8	8	11	N$^+$(^3P), s^4p^2; N(^2D), s^5p^2	$^2S\rightarrow{}^2S$ strong
	24+	^2S?	1	2	4	2				—	low?	—	—	>7	N$^+$(^3P), s^5p; N(^2D), s^4p^3	
	397*+	S?	One K electron removed							—	—	—	—	—	—	K absorption frequency, cf. Thibaud[40]
CO	0	$X={}^1S$	2	2	4	2				1.15	2155	12.7	11.2	11.2	C(^3P), s^5p or s^4p^2; O(^3P), s^5p^3 or s^6p^2	Known bands[37], $X\leftarrow\rightarrow a(10)$; $X\rightarrow a'(1)$; $X\leftarrow\rightarrow A(10{,}000)$; $X\leftarrow\rightarrow b?$ (600); $b\rightarrow a$; $X\leftarrow\rightarrow B(4000)$; $B\rightarrow A$; $X\leftarrow\rightarrow C$ (110, 000); $c\rightarrow a$; $X\leftarrow\rightarrow E(100,000)$; $X\rightarrow F(800, 000)$; $X\rightarrow G$ (7,000,000 each). The numbers in parentheses are very rough estimates of relative intensities in *absorption* (Birge, private communication). That states C and E are S states is indicated by the fact that $X\leftarrow\rightarrow C$ and $X\leftarrow\rightarrow E$ probably have P and R branches only (Birge, private communication).
	5.98*	$a={}^3P(93)$	2	2	4	1	1			—	1725	14.5	6.4	12.4	C(^3P), s^4p^2; O(^3P), s^5p^3	
	7.14*	$a'={}^3S$?	2	2	3	2	1			—	1173	9	4.6	11.9	Same as X	
	7.99*	$A={}^1P$	2	2	4	1	1			1.24	1499	17.2	4.0	12.0	Same as a	
	10.35*+	$b={}^3S$	2	2	4	1		1		—	(2214?)		small	—	C(^3P), s^4p^2 or s^5p; O(^3P), s^6p^2 or s^5p^3	
	10.73*+	$B={}^1S$	2	2	4	1		1		1.12	2132	50	2.8	13.5	{Same as b}	
	11.35*	$C={}^1S$								—	(2133)		—	—	Two excited atoms	
	11.37*+	$c={}^3P$?	{2	1	4	2	1}			—	—	—	—	—	—	
	11.46*	$E={}^1S$	{2	2	3	2			1}	—	(2134)		—	—	Two excited atoms	
	12.30*	$F={}^1P$?	2	2	3	2		1		—	1914	19.8	0.6	12.9	Two excited atoms	
	13.00*	G														
	13.12*															
	13.24*															

CO$^+$	14.2^+	^2S	2	2	4	1				1.11	2197	15.2	9.8	9.8	C$^+$(^2P), s^4p; O(^3P), s^5p^3	$^2P \rightarrow {}^2S$ strong
	16.7^{*+}	^2P_i(126)	2	2	3	2				1.25?	1550	14.1	7.1	9.6	C$^+$(^2P), s^5 or s^4p; O(^3P), s^5p^3 or s^6p^2	$^2S \rightarrow {}^2P$ weak
	19.8^{*+}	^2S	2	1	4	2				1.17	1698	24.3	3.7	9.3	C$^+$(^2P), s^4p; O(^3P), s^5p^3	$^2S \rightarrow {}^2S$ strong
NO	0	$X = {}^2P_n$(124)	2	2	4	2	1			1.15	1892	14.4	7.9	7.9	N(^4S), s^5p^2; O(^3P), s^5p^3	Known bands, $X \leftarrow\rightarrow A$ (5); $X \leftarrow\rightarrow B$(1); $X \leftarrow\rightarrow C$ (30); $X \leftarrow\rightarrow D$ (20). The numbers in parentheses give approximate intensities in absorption.[47]
	5.45^*	$A = {}^2S$	2	2	4	2		1		1.07	2352	13−	14	19.	(cf. text under NO, p. 210)	
	5.60^*	$B = {}^2P_n$(33)	2	2	4	2			1	1.42	1030	7.5	4.4	10.	N(^2D), s^5p^2; O(^3P), s^5p^3	
	6.45^*	$C = {}^2S$?	2	2	4	2(also one excited)				—	(2347)		—	—	—	
	6.58^*	D	2	2	4	2(also one excited)				—	2324	27	6.2	13.	—	
NO$^+$	9.4^+	^1S?	2	2	4	2				—	—	—	—	—	N(^4S), s^5p^2; O$^+$(^4S), s^5p^2	
	21^+	^3S?	2	2	3	2	1			—	—	—	—	—	N(^{4}(S), s^5p^2; O$^+$(^4S), s^5p^2	
	22^+	P?	2	2	4	1	1			—	—	—	—	—	N$^+$(^3P), s^4p^2; O(^3P), s^5p^3	
O$_2$	0	$X = {}^3S$	2	2	4	2	2			1.21	1565	11.4	6.65	6.65	O(^3P), s^5p^3; O(^3P), s^5p^3	Known bands, $X \rightarrow A$ (atmospheric absorption bands) and $X \leftarrow\rightarrow B$ (Schumann-Runge bands)
	1.62^*	$A = {}^1S$, ^1D?	{2	2	4	2	2}			1.23	1415	11.9	4.4	6.1	{the same}	
	6.09^*	$B = {}^3S$	2	2	4	2	1		1	1.61	708	12.4	0.96^x	7.05^x	O(^3P), s^5p^3; O(^3P), s^5p^3	
O$_2^+$	13.5^+	^2P_n(>200)	2	2	4	2	1			—	1926?	16.5	6.9	6.9	O$^+$(^4S), s^5p^2; O(^3P), s^5p^3	}Ultraviolet O$_2^+$ bands; cf. Table IV, note (b).
	{18.7^*}	^2P_n	2	2	4	2			1	—	855	13.7	1.8	6.95	O$^+$(^2D), s^5p^2; O(^3P), s^5p^3 (? see text)	
	{18.7^*}	{P?}	{2	2	3	2	2}			—	1026	11.1	2.9	{8.1}	{O$^+$(^4S); O(^3P)}	}Visible O$_2^+$ bands
	{20.8^+}	{S}	2	2	4	1	2			—	1180	17.8	2.4	{9.7}	One atom excited	
	524^*	S?	One K electron removed							—	—	—	—	—	—	K absorption frequency, cf. Thibaud.[40]
F$_2$	0	^1S	2	2	4	2	4			{1.5?	1170	10	3.1	3.1}	F(^2P), S^6P^3; F(^2P), S^6P^3	All numerical values are estimates by Birge (cf. Table IV).
	{2.9}	^1S	2	2	4	2	3		1	{ —	320	18	0.2	3.1}	F(^2P); S^6P^3; F(^2P), S^6P^3	

Notes for Table III. General: (1) References to the sources of most of the numerical data for the various molecules will be found under the discussion of these molecules in the text. Free use has also been made in preparing Table III of Birge's very valuable compilation of molecular constants in *International Critical Tables*, cf. also R. T. Birge, pp. 230–2 of the National Research Council Report on Molecular Spectra. The writer is very greatly indebted to Professor Birge for the use of the International Critical Table material before publication. (2) Material cenclosed in { } in Table III is especially uncertain or speculative.

Special Notes: (3) The values given under "Energy (volts)" are all measured upward from the lowest known state of the neutral molecule assumed as zero. In most cases the lowest known state is known to be, or else is probably, the normal state (cf. text, and ref. 3, etc., for evidence). For ionized molecules the energy is also referred to the normal state of the neutral molecule as zero. The symbol * indicates that the value given has been obtained from spectroscopic data, while + indicates that it comes from excitation potential data. When both * and + are used, the *numerical* value given is, if possible, the spectroscopic value. In some cases, in particular N$_2$ and O$_2^+$, the values given depend on both spectroscopic and excitation potential data. (4) Under "State ($\Delta\nu$)" the known or probable molecular electronic state (often preceded by an empirical designation as given by Birge) is given; and, also, in the case of multiple states, the over-all multiplet width $\Delta\nu$. The subscripts n and i in such cases as ^3P_n, ^2P_i, etc., indicate respectively a *normal* or *inverted* multiplet; if no subscript is given, evidence is lacking as to the true designation. Only in the cases of CN, BO, CO$^+$, and N$_2^+$ and the states X, A, B of CO and NO are we *certain*, from analysis of band structure, that the state designations given (such as ^2P_i, ^2S, ^1P) are correct. In all other cases, the band analysis is incomplete, and the designations given are only *probable* (strictly, the ^2P_i state of CO$^+$ is also not yet certain). The value $\Delta\nu \backsim 70$ for the B level of N$_2$ is estimated from the $B \rightarrow A$ and $D \rightarrow B$ bands, assuming $\Delta\nu \eqsim 0$ for the A and D levels; the results from the $B \rightarrow A$ and the $D \rightarrow B$ bands are in good agreement. The value $\Delta\nu \backsim 55$ then follows if the $C \rightarrow B$ bands are $^3P_n \rightarrow {}^3P_n$, as seems probable. For the a level of CO, $\Delta\nu \backsim 93$ is estimated from the $a \rightarrow X$ and the $b \rightarrow a$ bands. (5) Under "Numbers of Outer Electrons" the probable, or most plausible, number of electrons of each of the types indicated is given, in accordance with the evidence of the present paper. As has been remarked elsewhere, it is likely that some of the orbit-types are not correctly designated (e.g. "$3s^d$" should perhaps be $4s^s$). In *all* cases, it is assumed that two of the first four electrons are bound in ($1s^s$) orbits, and two in $2s^p$ orbits. *In every case*, except apparently one state of O$_2^+$ (cf. Note 8 below), *the assignments given are such as to fulfill*, so far as known, *all the requirements stated under "Working Rules."* (6) The values given under "Molecular Constants" are mainly from Birge's compilation in International Critical Tables. The values for BeF are as given by Mecke (Zeits. f. Physik, **42**, 412, 1927). (7) The dissociation energies D^v and D are for the most part from Birge and Sponer[8] or from Birge (Int. Crit. Tables). D^v refers to the (purely vibrational) energy of dissociation of the non-vibrating molecule in the stated (usually excited) electronic state, D to the *total* energy required to excite an electron (cf. second column of the table) and dissociate the molecule, starting from the normal state of the latter. *Most of the D^v values* are obtained by a linear extrapolation from the lower vibrational levels[8] (i.e. we assume $D^v = \omega_0^2/4\omega_0 x$, in cm^{-1}, the result then being converted to volts), and for this reason *are probably only very roughly correct*: cf. ref. 8, also R. Mecke, *l.c.*; in a few cases, marked x, the results were obtained by a non-linear extrapolation and are probably too small,—except in the case of O$_2$ where the result should be very accurate since the vibrational levels were followed to the point of dissociation. (8) Under "Dissociation, Probable Products" are given the results which seem most likely from the discussion in the text in Part II. The state of each atom or ion is given according to the ordinary atomic classification, then the strong-field component of this atomic state necessary to give the molecular state in question (cf. Table II) is (partially) indicated by giving its $\sigma_{l\tau}$ classification according to the system explained in the text preceding Table II. In all cases with the apparent exception of the initial ^2P state of the ultraviolet O$_2^+$ bands, and of the ^1S states of F$_2$ (cf. Part II), the molecular $\sigma_{l\tau}$ configuration appears to be obtainable in the expected way as the sum of the atomic configurations: e.g. N(^4S), s^5p^2; O(^3P), s^5p^3 gives NO(^2P), $s^{10}p^5$. For some of the N$_2$ levels, two possibilities are given in Table III for the dissociation products; the first of these corresponds to $D_x = 9.5$, the second and perhaps more probable (although indicated by "or . . . . ?") to $D_x = 11.8$ volts.

landres bands ($^2S \rightarrow {}^2S$) of CO^+.[37] According to the present interpretation, these three potentials respectively correspond to the removal of a $3s^s$, a $2p^p$, and a $3s^p$ electron from the CO molecule. Thus in the production of the known states of CO^+ by electron impact, there is no need to assume simultaneous removal of one electron and excitation of another, a process which one would perhaps expect to be relatively improbable.

In nitrogen, ionization begins at 16.9 volts, and the negative bands ($^2S \rightarrow {}^2S$) are excited at 20.0 volts[38]; probably the expected $^2P \rightarrow {}^2S$ bands fall in the infra-red, from which it would follow that the ^2P ionization potential lies not far from 17 volts.

At 24 volts in nitrogen, there is another ionization potential, according to Smyth, and Hogness and Lunn.[39] This must correspond to the removal of an electron from the shell which we have designated as $(2s^s)^2$, since the other three outer shells have already been accounted for, and since the ionization potential for the two most firmly bound shells is 397 volts (see below). Removal of this electron should give a ^2S molecule. Hogness and Lunn's work yields the information that, while N_2^+ is the primary ionic product both at 16.9 and at 24 volts, the N_2^+ ions formed below 24 volts are all of a stable character, while the 24 volt kind are decomposed, if enough opportunity is given for collisions, into N^+ and N. Probably, as Birge and Sponer suggest,[8] the 24 volt "excited N_2^+ molecule represents sufficient energy to change N_2^+ into $N^+ + N$" in collisions of the second kind.

If the selection principle $\Delta l_r = \pm 1$ is applicable, 24 volt N_2^+ ions, when collisions do not intervene, should revert in two steps to stable N_2^+, the first step (which should occur in either of two ways) giving ultraviolet bands which are as yet unknown or unclassified.

Smyth has reported a sharp increase in N^+ ions at 350 to 400 volts.[39] This may be interpreted as corresponding to the removal of an electron from one of the two inner, or *K*, shells, $(1s^s)^2$ and $(2s^p)^2$, of N_2; according to spectroscopic evidence (cf. following paragraph), this occurs at 397 volts. The formation of N^+ may have been brought about by some secondary

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[37] Cf. R. T. Birge for discussion and bibliography of CO levels (Phys. Rev. **28,** 1157, 1926). Further, J. J. Hopfield and R. T. Birge, Phys. Rev. **29,** 922*A* (1927). The values for the *a′* level are revised according to a private communication from Professor Hopfield.

Duffendack and Fox (Science, **64,** 277, 1926), and Miss A. B. Hepburn (unpublished work) find that the Baldet-Johnson or combination bands ($^2S \rightarrow {}^2P$) of CO^+ appear at 22.9 volts. These bands should however, be excited at the same potential (20.0 volts) as the $^2S \rightarrow {}^2S$ bands. Possibly the bands observed by Duffendack and Fox and by Miss Hepburn at 22.9 volts represent a new system. The 22.9 volt potential might be analogous to the 24 volt potential in N_2 (see below), and should then correspond to removal of a $(2s^s)$ electron.

[38] H. Sponer, Zeits. f. Physik, **34,** 622 (1925).

[39] H. D. Smyth, Proc. Roy. Soc. **104***A*, 121 (1923). T. R. Hogness and E. G. Lunn, Phys. Rev. **26,** 786 (1925).

G. P. Harnwell (Phys. Rev. **29,** 840, 1927) has obtained evidence that in mixtures of helium and nitrogen the action $He^+ + N_2 \rightarrow He + N_2^+$ occurs with the formation of N_2^+ ions which dissociate on collision. This result seems to prove that the 24 volt N_2 potential of Hogness and Lunn lies with certainty below 24.5 volts, the ionization potential of helium.

[40] J. Thibaud, Nature, March 3, 1928.

process; this apparently did not occur in Hogness and Lunn's apparatus, since they find no increase in N^+ at these potentials.

Far ultra-violet spectra. The fluorescent emission of the ordinary negative nitrogen bands ($^2S \rightarrow {}^2S$ of $N_2{}^+$), found by Oldenberg to result from the action of ultraviolet light of very short wave-length,[41] can now be explained as follows: a $3s^p$ electron is removed by light absorption, following which one of the outer, $3s^s$, electrons falls in to replace it, giving a line of the negative band spectrum. Again the assumption of simultaneous excitation of one electron and ionization of another is avoided.

Thibaud has recently photographed K absorption edges for N_2, O_2, and also carbon compounds. For N_2 the edge is at λ31.1, corresponding to 397 volts; and in agreement with our expectation that the energies of the promoted and unpromoted K electrons should differ very little, only a single edge is found. The results for O_2 and carbon are similar; the edges occur at 524 and 284 volts respectively. Thibaud has also obtained the $K\alpha$ line in emission for B, C, N, O; it seems likely that this "line" really represents, under suitable experimental conditions, a superposition of several *band systems* corresponding to the dropping of any one of the outer electrons of a molecule into a vacant K position.

Quantum assignments for electron levels of NO. Before considering the numerous known excited electron levels of neutral CO and N_2, it will be helpful to treat certain other molecules, beginning with NO (cf. Table III). The unexcited state of NO is a *normal* (i.e., not inverted) ^2P.[6] The energy of dissociation, as well as the value of ω_0, is lower here than for the normal state of N_2 or CO. The ionization potential (9.4 volts) is much lower than the ionization potential for the $3s^s$ shell of CO or N_2 (14.2 and 16.9 volts respectively). It is also lower than for any electron in the N or the O atom, showing that the binding energy of the most loosely bound electron has been *decreased* in the formation of NO. The NO^+ ions formed at 9.4 volts are stable in collisions.[42] All these facts point to the following conclusion: NO has the same configuration of closed shells as N_2 and CO, but the additional, last bound, electron in NO goes into a $3p^y$ orbit with large promotion energy and a pronounced negative bonding power. In particular, the presence of a *single* $3p^y$ electron accounts for the observed, normal, ^2P state.

The four known excited levels of NO (energies 5.45–6.58 volts, cf. Table III) all combine with the lowest level. Probably all correspond to excitation of the outer, $3p^y$, electron, of NO.[43]

In the initial, unquestionably also normal, ^2P state of the β bands,[6] the low values of D^V and of ω_0 ($\omega_0 = 1030$, $r_0 = 1.418\ A$) indicate that the electron has been transferred to an orbit of very large promotion energy and strong negative bonding power, probably a $3p^d$, or perhaps a $4p^p$, orbit. The fact

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[41] O. Oldenberg, Zeits. f. Physik, **38**, 370 (1926).

[42] T. R. Hogness and E. G. Lunn, Phys. Rev. **30**, 26 (1927).

[43] From energy and other considerations, it is improbable that deeper-lying electrons are excited, unless to form the group $(3p^y)^2$. This latter possibility is also improbable when the σ_l and ω_o values of the observed states are considered.

that this ^2P is normal, with a $\Delta\nu$ which is neither large nor very small ($\Delta\nu \sim 33$, as compared with $\Delta\nu \sim 124$ for the lowest, also ^2P, state), supports such designations as these. The only likely alternative would be the configuration $(A)(3s^p)^2(2p^p)^3(3s^s)^2(3p^y)^2$, to which would correspond several molecular states (^2F_i, ^2P_n, ^2P_i, ^4P_i, ^2P_n—cf. Table I), all of which, however, would be expected to have a large $\Delta\nu$ (larger than 124), arising mainly from the $(2p^p)^3$ group. Also, it seems rather probable that the displacement of a $2p^p$ electron to a $3p^y$ orbit would require more than 5.6 volts (cf. lowest states of CO and N_2 in Table III).

In the initial, ^2S, state of the γ bands,[44] ω_0 is as large ($\omega_0 = 2352$, $r_0 = 1.068$ A) as in N_2, and the heat of dissociation, although not accurately known, is very much larger than for the normal and excited ^2P states (cf. Table III). These facts indicate that one of the dissociation products has an electron in a 3-quantum orbit (as e.g., in the 12.0 volt 3 D state $(1s)^2(2s)^2(2p)^3(3d)$ of the O atom),[8] and that this electron may be present in the molecule as an *unpromoted* electron, perhaps $3s^d$, with zero or a moderate positive distance-bonding power. The initial states of the δ and ϵ bands[45, 46, 47] appear to be similar in nature to that of the γ bands; possibly the excited electron is in a $3d^d$, or in some four-quantum state.

The interpretation of the initial states of the β and γ bands, as having respectively a $3p^d$ and a $3s^d$ excited electron, conforms to the selection rule $\Delta l_r = \pm 1$ if the outer $3p^y$ electron in the normal state of NO is in a $3p^p$ state.[49]

States of NO involving the displacement of a $3s^p$, $2p^p$ or a $3s^s$ electron are apparently not known spectroscopically. Two additional ionization potentials have however been observed by Hogness and Lunn[42]: (a) $NO \rightarrow O^+ + N + \epsilon$ at 21 ± 1 volts, and (b) $NO \rightarrow N^+ + O + \epsilon$ at 22 ± 1 volts. In each case, the atom and ion are very probably in their respective normal states: dissociation of NO into normal N and O requires about 7 or 8 volts, while ionization of normal O requires 13.56, of normal N, 14.48 volts; hence the calculated potential for process (a) is about 21 volts, for process (b), about 22 volts.[8] Probably process (a) involves the removal of a $2p^p$ electron from NO, process (b), of a $3s^s$ electron; reasons for these conclusions will be given in Part II.

Electronic states of O_2^+. Although their structure has not been analyzed in detail, there can be little doubt that the ultraviolet O_2^+ bands represent a

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[44] An examination of Frl. Guillery's data (Zeits. f. Physik, **42**, 121, 1927) shows conclusively that this state can only be a ^2S state; if it were a case b ^2P or ^2D state (the latter as in CH λ4300), there would be more missing lines.

[45] Analyzed by Birge (private communication) from photographs by Leifson (Astrophys. J., **63**, 73, 1926). See also H. P. Knauss, Phys. Rev., May, 1928 (Abstract).

[46] The δ bands at least, according to recent photographs taken by Mr. W. F. C. Ferguson in this laboratory, are closely similar in apparent structure to the γ bands. Probably their initial state is ^2S.

[47] The δ and ϵ bands are more strongly absorbed than the β and γ bands; the respective absorption coefficients, as estimated from Leifson's photographs (ref. 45, Plate *IVc*), are roughly in the ratio $\gamma:\beta:\delta:\epsilon: = 5:1:40:20$.

$^2P \rightarrow {}^2P$ transition.[48] It is probable that this is completely analogous to the NO β bands, and that the final, ^2P, state ($\omega_0 = 1860$) is the lowest state of O_2^+ and has the same electron configuration as the lowest state of NO.[49]

The nature of the visible O_2^+ bands is much more uncertain. According to Frerichs[50] and Mecke,[50] they are of a complicated type, with many branches; and are unrelated to the ultraviolet bands. They show $\Delta\nu$ intervals of the order of 50 cm^{-1}; according to Mecke, each band has at least four heads with about this spacing. So far as can be seen from Frerichs' data and photographs, however, the structure is of the type characteristic of $^2S \rightarrow {}^2P$ transitions; combination relations which hold for the two strong branches make it probable that the *initial* state is the S state. If there are several heads, as Mecke indicates, the probable interpretation is $^4S \rightarrow {}^4P_i$, but the two strong branches associated with the first head do not support this; the difficulties would be greater for ^4P_n. Either $^4S \rightarrow {}^4P_i$ or $^2S \rightarrow {}^2P_n$ can be reasonably interpreted in terms of the following initial and final electron configurations: $(A)(3s^p)^2(2p^p)^4(3s^s)(3p^p)^2$, ^4S or ^2S, $\rightarrow (A)(3s^p)^2(2p^p)^3(3s^s)^2(3p^p)^2$, ^4P_i or ^2P. These possible interpretations present the difficulty, in regard to the final state, that $\Delta\nu \sim 50$ (^2P) or even $\Delta\nu \sim 150$ (^4P_i, with four heads at intervals of 50 cm^{-1}), is smaller than would be expected; for in the final state configuration the missing $2p^p$ electron, which has a smaller n^* than the $3p^p$ electron responsible for $\Delta\nu$ of the unexcited ^2P state of O_2^+ ($\Delta\nu > 200$ cm^{-1}) should be mainly responsible for $\Delta\nu$ and should give a *large* $\Delta\nu$. A possible interpretation avoiding this difficulty is $(A)(3s^p)^2(2p^p)^4(3s^s)(3p^p)^2, {}^2S \rightarrow (A)(3s^p)^2(2p^p)^4(3s^s)^2(4p^p), {}^2P_n$; this involves a double electron jump, but of legitimate type ($\Delta l_1 = 0$, $\Delta l_2 = 1$). The question can be settled only by analysis of the bands. It will be noted that *all* the interpretations suggested involve an S initial state which would be obtained from the ^3S normal state of O_2 (see below) by removal of a $3s^s$ electron.

The existing data on ionization potentials of oxygen are difficult to reconcile with one another. Lockrow[51] finds that the ultraviolet bands begin to appear at about 19.2 volts, and the visible bands at about 21 volts. Since the ultraviolet bands involve an electron jump of at least 4.73, or more probably as much as 5.2 volts,[8] this would give about 14 volts for the minimum ionization potential of O_2. (Lockrow gives 16 volts, but apparently this is unreliable.) Mackay finds ionization potentials at 12.5 and 16.1 volts, Hogness and Lunn at 13 ± 1 volts, Smyth at 15.5 volts.[52,53,54]

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[48] Cf. ref. 6, p. 174.

[49] The much larger observed doublet separation (200 cm^{-1} as compared with 92 for NO),—this represents the *difference* between the $\Delta\nu$'s of the final and initial ^2P states—is not surprising, since according to the Landé formula[15] $\Delta\nu$ increases rapidly with increased binding energy, and because the binding energy for the $3p^p$ electron must be considerably larger for O_2^+ than for NO (9.4 volts), since even for *neutral* O_2 it is 13 volts.

[50] R. Frerichs, Zeits. f. Physik, **35**, 683 (1926); R. Mecke, Zeits. f. Physik, **36**, 801 (1926).

[51] L. L. Lockrow, Astrophys. J. **63**, 205 (1926). The potential at 19.2 volts appears to be, as we should wish, that for the vibrationless initial state, according to Lockrow's data. The same appears to be true for the 21 volt potential.

[52] C. A. Mackay, Phys. Rev., **24**, 319 (1924).

We shall probably not be far wrong if we assume 13.5 volts as the lowest ionization potential, corresponding to the removal of a $3p^p$ electron from unexcited O_2 to give unexcited O_2^+. Using 5.2 volts for the electron jump in the ultraviolet bands, the excitation potential of these bands should then be 18.7 volts. This potential corresponds, according to the present interpretation, to the removal of a $3p^p$ electron from O_2 and simultaneous excitation of a second $3p^p$ electron to a $3p^d$ orbit.

Assuming Lockrow's *relative* potentials for the visible and ultraviolet bands to be correct, we then get 20.5 volts for the excitation of the visible bands, corresponding, according to the interpretation given above, to removal of a $3s^s$ electron from O_2. Since the electron jump in the visible bands corresponds to 2.0 volts, this gives 18.5 volts as the calculated potential for the *final* state of these bands. This then is the voltage required for removal of a $2p^p$ electron from O_2, if either of the first two of the three interpretations suggested above for the final state of the visible bands is correct.

If transitions occur between the final state of the visible bands and the normal state of O_2^+, the resulting bands must lie in the same spectral region as the known ultraviolet bands, for the initial energy is practically the same in both cases. Since no such bands have been found, we may conclude that they are absent, or at least very weak. A reason for this may be found in the fact that according to *any* of the electron configurations suggested above for the final state of the visible bands, the transition to the normal state would involve $\Delta l_\tau = 0$. It seems likely that Hund's characteristic selection rule for symmetrical molecules here finds expression in the *strict* exclusion of all electron jumps not conforming to the rule $\Delta l_\tau = \pm 1$. Further evidence for this same conclusion is found in the case of N_2 as discussed below.

According to Hogness and Lunn,[53] ionization of O_2 at 13 volts gives a form of O_2^+ which is stable in collisions, while at 20 volts another type of ionization sets in which gives directly $O^+ + O$; there is no evidence of unstable O_2^+ molecules which decompose on collision. Smyth[54] obtained similar results, except that he gives 15.5 and 23.0 volts, values which should presumably be corrected by about -2 volts. The 13 volt potential has already been discussed. Hogness and Lunn's 20 volt potential must be interpreted as corresponding to the formation of a state of O_2^+ whose ω_0 and heat of dissociation are very low, so that the probability is very strongly in favor, in addition to the removal of an electron, of simultaneous transfer of enough vibrational energy to produce dissociation.[8] This state of O_2^+ is presumably the initial, ^2P, state of the ultraviolet bands, since, of the known excited states of O_2^+, this one has much the lowest ω_0 and heat of dissociation. Furthermore, the potential 20.5 volts (assuming the corrections given in the third paragraph above) is almost exactly the extrapolated convergence limit of the vibrational levels associated with this state.[8]

The excited states of O_2^+ formed by the removal of a $2p^p$ electron (18.5 volts?) or a $3s^s$ electron (20.5 volts) are presumably stable even in collisions;

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[53] T. R. Hogness and E. G. Lunn, Phys. Rev., **27,** 732 (1926).

[54] H. D. Smyth, Proc. Roy. Soc., **105***A*, 116 (1924).

the proximity of these potentials to the 20.5 volt dissociation potential is probably a coincidence. Removal of a $3s^p$ electron doubtless occurs not far above 20 volts, also giving a stable form of O_2^+.

Electron configurations of O_2 and F_2. A comparison of certain band systems of NO, O_2^+, O_2 and F_2 shows a striking parallelism together with a progressive change (cf. Table IV). Although no experimental values are directly available for the F_2 absorption bands, Birge has obtained estimates of the constants for F_2 which cannot be far wrong. This is done by a systematic comparison of the analogies and progressive changes for the known bands of Cl_2-Br_2-I_2 and of O_2-S_2-Se_2-Te_2.

TABLE IV.

Molecule	Bands		Vibration frequencies				Heats of dissociation (Volts)	
	Designation	Volts	ω_0''	$\omega_0''x''$	ω_0'	$\omega_0'x'$	D''	D'
N_2	^1S		2345	14.4			11.8	
NO	$^2P \rightarrow {}^2P$	5.60	1892	14.4	1030	7.5	7.9	10?
O_2^+	$^2P \rightarrow {}^2P$	5.2?	1926?	16.5	855	13.7	6.9	6.95
O_2	$^3S \rightarrow {}^3S$	6.09	1565	11.4	708	13 −	6.65	7.05
F_2	$^1S \rightarrow {}^1S$	[2.9]	[1170]	[10]	[320]	[18 −]	[3.1]	[3.1]

Notes. (*a*)D' is the total energy required to excite and dissociate the molecule. (*b*) The values of D, ω_0'', and of the electronic energy, for O_2^+, assume that $n''=0$ of Birge and Sponer[8] is really $n''=2$ (n = vibrational quantum number). (*c*) The data for F_2 are estimated by Birge (Int. Crit. Tables).

The relations shown in Table IV may reasonably be interpreted as follows. Let us consider first the normal states. N_2 and CO have higher heats of dissociation than any other neutral diatomic molecules. Leaving out of account the four K electrons, these molecules have each six unpromoted and four promoted electrons, giving a large net bonding effect. In NO, O_2, and F_2 we have one, two and four promoted $3p^p$ electrons outside the N_2 configuration; in F_2 we have a closed shell of such electrons, giving a ^1S state. Each added $3p^p$ electron has a negative effect on the bonding, so that ω_0 and the heat of dissociation steadily fall. In F_2, with six unpromoted and eight promoted electrons, the net bonding effect has become small, and with the resulting large r_0, the entire electron configuration approaches that of two separated atoms.

Two $3p^p$ electrons as in O_2 should give a ^3S, a ^1D and a ^1S molecular state (cf. Table I), and one of these (^3S if the order of levels is as in atoms) should be the normal state of O_2. A ^3S normal state is in agreement with the magnetic behavior of O_2.[55] Also, the ultraviolet Schumann-Runge absorption and emission bands (these are the bands of Table IV)[56] have a structure which can hardly be other than $^3S \rightarrow {}^3S$.[57] The interpretation of the atmospheric

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[55] R. S. Mulliken, Phys. Rev., **28,** 505 (1926). J. H. Van Vleck, Nature, May 7, 1927; Phys. Rev., **31,** 608 (1928).

[56] Cf. Birge and Sponer, l.c. ref. 8, page 268, for bibliography and discussion.

[57] These bands, according to data of Runge (Physica, **1,** 254, 1921) consist apparently of P and R branches only. This must be interpreted in the sense that $\Delta j_k = \pm 1$ rather than

absorption bands (cf. Table III) is, however, a puzzle; these bands do not obviously correspond to any expected structure type.[58]

Granting that in the emission of the NOβ bands an electron goes from a $3p^d$ to a $3p^p$ orbit, we may reasonably assume that the same thing happens for the analogous bands of O_2^+, O_2 and F_2 in Table IV. A transition $3p^d \rightarrow 3p^p$ of the emitting electron is in harmony with the respective transitions $^2P \rightarrow {}^2P$, $^3S \rightarrow {}^3S$, $^1S \rightarrow {}^1S$ for the molecule as a whole in NO, O_2, and F_2. It also satisfies the rule $\Delta l_\tau = 1$, which apparently holds strictly for symmetrical molecules.

Molecules C_2, BeF, BeO, LiF. Turning now to molecules with *fewer* electrons than CO, CN, and the like, let us consider C_2, the emitter of the Swan bands ($^3P \rightarrow {}^3P$).[59] The final, very likely unexcited,[60] ^3P state may reasonably be interpreted as $(A)(3s^p)^2(2p^p)^3(3s^s)$, the initial ^3P state as $(A)(3s^p)(2p^p)^3(3s^s)^2$. Both should then be inverted; whether this is the case is not yet known experimentally. The "high pressure carbon bands" perhaps represent the corresponding $^1P \rightarrow {}^1P$ transition.

The normal state of BeF may be ^2S like that of BO, but the excited ^2P state, if it is such, probably has $\Delta\nu \sim 35$ as compared with 126 for BO, and can hardly be analogous to the ^2P state of BO. But the structure of these bands is as yet doubtful.

The lowest known state of BeO is ^1S, and may, together with the normal state of LiF, be $(A)(3s^p)^2(2p^p)^4$.

Excited levels and selection rules in nitrogen and carbon monoxide. The very stable molecules N_2 and CO are the only molecules, other than H_2 and He_2, for which a considerable number of electron states is known. The configuration $(A)(3s^p)^2(2p^p)^4(3s^s)^2$ of the normal states of these molecules —cf. above—precludes the occurrence of any bands in the visible and near ultraviolet analogous to those of BO, CN, CO^+ and N_2^+. Excited states of CO and N_2 must then be obtained by displacement of an electron to a higher orbit, such as one of the orbits $3p^p$, $3p^d$, and $3s^d$ which are revealed by NO. By a consideration of the promotion, bonding and energy level properties of various orbits, as deduced from the molecules already discussed, a plausible

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$\Delta j = \pm 1$ (cf. R. S. Mulliken, Phys. Rev., **30**, 138, 1927). To avoid quarter-integral quantum numbers and a rule $\Delta j_k = \pm 1/2$, alternate lines must be assumed missing. The lines which remain are however *double*, the components becoming more nearly equal in intensity with increasing j, but not by any means approaching an asymptotic equality in this respect. If we assume that the stronger doublet component is itself an unresolved double, we have here exactly the predicted structure for a $^3S \rightarrow {}^3S$ transition in a symmetrical molecule.

(Added in proof). In a recent paper (Zeits, f. Physik, **49**, 167, 1928), W. Ossenbrüggen has shown definitely that the Schumann-Runge system consists of P and R branches, with integral rotational quantum numbers (evidently j_k): $j_k' = 0, 2, 4, \cdots$, $j_k'' = 1, 3, 5, \cdots$, $\epsilon^r = Bj_k(j_k+1)$. He does not discuss the fine structure of the band lines.

[58] Possibly they involve absorption from ^3S to the expected metastable ^1D and ^1S states; this would accord with the fact that they are only moderately absorbed in the passage of sunlight through the whole thickness of the earth's atmosphere.

[59] For bibliography cf. J. D. Shea, Phys. Rev., **30**, 825 (1927) and W. E. Pretty, Proc. Phys. Soc. (London), **40**, Part 3,71 1928.

[60] According to T. Hori (Nature, July 3, 1926), the Swan bands are obtained in absorption in certain explosion spectra.

assignment of configurations has been made for a number of the excited states.[61] This assignment is given in Table III.

Hund's selection rule for symmetrical molecules, requiring that for any three electron levels not more than two electron transitions shall occur, shows no exceptions in the case of N_2. Thus none of the transitions $D \rightarrow A$, $C \rightarrow A$, $c \rightarrow a$, $b \rightarrow a$, all of which would fall in the near ultraviolet, have ever been observed. Transitions $X \rightarrow A$, $X \rightarrow C$, and $X \rightarrow D$ are not recorded in the far ultraviolet absorption or emission spectra of nitrogen, investigated by Birge and Hopfield, and Sponer.[62] Every transition mentioned is one which *should* be absent according to Hund's selection principle. The only expected transition involving known levels of N_2 which has not yet been observed is $B \rightarrow X$, which should be of low intensity on account of $\Delta s = 1$. For the known levels of N_2,[61] Hund's selection principle can apparently be expressed in the form $\Delta l_r = \pm 1$, so that it is equivalent to a sharpening of the principle which holds for the *strong* transitions in BO and CO^+ and probably CO; in regard to the theoretical justification of this form, cf. the section above on *Working Rules.*

If the assignments given in each case are correct, the same selection principle $\Delta l_r = \pm 1$ is obeyed in all the known bands of N_2^+, O_2^+, O_2, and F_2, while bands which would conflict with this rule are unknown (cf. discussion under O_2^+). The apparent absence of the "combination bands" $^2S \rightarrow {}^2P$ in N_2^+ may be ascribed to this cause.

The CO molecule possesses a richness of band systems which shows very clearly the absence of a strict selection rule like that in N_2. Transitions

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[61] Hopfield has recently reported four new systems of nitrogen bands (Abstract 89, Washington meeting Am. Phys. Soc., April, 1928; and additional details very kindly given the writer by Professor Hopfield). The electronic energies correspond approximately to 7.09 volts (0, 0 band of strong series), 7.15 volts (0, 0 of strong series), 8.14 volts (single strong band), 8.61 volts (single weak band). All the bands, except perhaps that at 8.61 volts, are so diffuse that they must be ascribed to a polyatomic form of nitrogen, or if to N_2, must involve a multiple upper level (^3P or ^3D).

The latter alternative seems very improbable, since an inter-system combination such as $^1S \rightarrow {}^3P$, starting from the ^1S normal state of N_2, should be weak (cf. $X \rightarrow a$ of CO, Table III), while three of the above four band systems are strong (about of the same intensity on Hopfield's plates as the familiar $X \rightarrow a$, probably $^1S \rightarrow {}^1P$, bands of N_2). Also, the extrapolated convergence limit of both the 7.09 and the 7.15 volt systems comes at about 9.1 volts; since, however, a ^3P or a ^3D N_2 molecule cannot dissociate into two unexcited N atoms (cf. Table II and accompanying discussion) but must give at least one excited atom, excited at least as far as the ^2D state (2.39 volts), the heat of dissociation D of N_2 cannot exceed $9.1 - 2.39 = 6.7$ volts if the bands are due to N_2. Although there is evidence, that D is lower than the value 11.4 volts given by Birge and Sponer, it seems very improbable that it is as low as 6.7 volts.

For the above and several other reasons, it seems to the writer very improbable that Hopfield's new bands are N_2 bands, in spite of the fact that Hopfield finds that they cannot be ascribed to any familiar impurity. Apparently they must be attributed to polyatomic molecules formed in the preparation of the nitrogen, which was obtained by explosion of NaN_3.

[62] Cf. H. Sponer, Proc. Nat. Acad. Sci., **13,** 100 (1927); J. J. Hopfield, and Birge and Hopfield, Phys. Rev., **29,** 356*A*, 1927. Also, Prof. Birge informs the writer that the absence of far ultraviolet N_2 bands in the spectrum of active nitrogen has again been verified in work of H. P. Knauss.

between the normal level and almost every known excited level occur. According to the assignments in Table III, the levels a, a', and A of CO are ^3P, ^3S, and ^1P and are respectively analogous to B, A, and a of N_2.

From Table III it will be seen that while the supposed analogy of CO to Mg is for the most part not very close, there still remains a good analogy between the three levels X, a, and A, and the three lowest levels, ^1S, ^3P, and ^1P of Mg. Except for the unexplained reversal of the energy order of ^3P and ^1P, a similar statement is true for levels X, B, and a of N_2.

Active nitrogen. Absence of intersystem combinations in N_2. According to the assignments here given, and the selection rule $\Delta l_r = \pm 1$, the lower vibrational levels of the lowest known excited state of N_2 (the "A" level, a ^3S or ^3D level lying at about 8.2 volts) are truly metastable.[63] For the higher vibrational levels of the A state, however, transitions should occur to vibrational levels belonging to the B electron state (^3P), which lies at 9.35 volts, and thence back to lower vibrational levels of the A state. This is in agreement with conclusions reached by various people[64] that active nitrogen contains metastable molecules which are able to transfer to other molecules amounts of energy up to but usually not much exceeding 9.4 volts. It is also in accord with Sponer's failure to obtain any far ultraviolet emission bands from active nitrogen even with exposures of sixty hours.[62]

There is, however, a difficulty: why do not a large fraction of the vibrating molecules of level A make transitions to level a which lies at 8.5 volts, and then go immediately to the normal state with emission of the known $a \rightarrow X$ bands? This transition $A \rightarrow a(^3S \text{ or } ^3D \rightarrow ^1P)$ is not excluded by the selection rule $\Delta l_r = \pm 1$, and would be expected to proceed sufficiently fast (in spite of $\Delta s = 1$) to remove effectively the metastablity of the A levels above 8.50 volts. From the evidence just cited in regard to active nitrogen, including Sponer's results, it seems clear that this does not occur. Although no theoretical reason for doing so is evident, it seems almost necessary to conclude that in symmetrical molecules such as N_2, transitions involving $\Delta s = 1$ are *strictly* ruled out.[61] This conclusion is also supported by the absence, in Sponer's work and in that of Birge and Hopfield,[62] of the transition $B \rightarrow X(^3P \rightarrow ^1S)$, which is not excluded by the $\Delta l_r = \pm 1$ rule.

[63] According to experiments of Levesley (Trans. Faraday Soc., **23,** 552, 1927), N_2 has also a critical potential at 6.3 volts. If such a level exists, it must be metastable (possibly ^3D) since no bands are known going from it to the normal state.

[64] R. T. Birge, cf. H. P. Knauss, Phys. Rev., May, 1928 (abstract). Cf. also B. Lewis, Journ. Am. Chem. Soc., **50,** 27 (1928). Okubo and Hamada, Phil. Mag. (7) **5,** 372 (1928); P. A. Constantinides, Phys. Rev. **30,** 95 (1927); J. C. McLennan, Nature, April, 1928; Ruark and co-workers (J. Opt. Soc. Am. **14,** 17, 1927) and the present writer (Phys. Rev., **26,** 28, 1925) found evidence that active nitrogen can transfer amounts of energy as large as 10 or 10.4 volts. Perhaps the limitation to 9.4 volts holds only for low pressures where the metastable molecules alone survive long enough to make collisions. At higher pressures non-metastable ^3P molecules with energies as high as 11.4 volts, and also 3-body collisions involving two N atoms, may become important.

[65] R. Mecke, Naturwiss., **13,** 698 (1925); Zeits. f. Physik, **36,** 797 (1926).

APPENDIX. DERIVATION OF RESULTS OF TABLE I

The possible molecular *states* for the various *electron configurations* of Table I can be determined by means of the Pauli principle (cf. ref. 15, p. 115). This is done by Pauli's method of imagining the atom in an external magnetic field so strong that all couplings between electrons are broken down, so that each electron can be given four quantum numbers, n, l, m_l, and m_s. In a molecule, this breaking down is partly accomplished by the intramolecular electric field. But as compared with a strong magnetic field, a strong electric field shows two peculiarities, (a) unlike the magnetic case, states differing only in the sign of σ_l do not differ in energy, (b) an electric field has no action on the electron spins, hence has no power to orient the latter, nor to break down any couplings which may exist between spins of different electrons; if $\sigma_l > 0$, however, the spin is oriented with repect to σ_l,[9] hence indirectly with respect to the electric axis. We shall temporarily assume a supplementary magnetic field parallel to the electric axis so that n, l, m_l, and m_s can be specified for each electron. We shall use m_l and m ($m = m_l + m_s$) here so long as the magnetic field is supposed present, but σ_l and σ ($\sigma_l = |m_l|$ and $\sigma = |m|$) for the undisturbed molecules. (In the body of the paper, this distinction is dropped, σ_l being used at times with a + or − sign.)

In order to determine the possible molecular states for a particular electron configuration, such as for example one composed of two electrons with $n_\tau = 2$ and specified values of l_τ and $\sigma_{l\tau}$, we first write down all the possible combinations of m_l and m_s values which are compatible with the given configuration and which also satisfy the Pauli principle. This is done in Table V for *all* the possible configurations, namely $(2s^s)^2$, $(2s^s)(2s^p)$, $(2s^p)^2$, $(2s^s)(2p^p)$, $(2s^p)(2p^p)$ and $(2p^p)^2$, which can be obtained from two 2-quantum electrons. In Table V, in the columns headed "Possible Electron States," a + sign is used to indicate the presence of an electron with $m_s = +\frac{1}{2}$, and of type (in respect to l and m_l) specified at the head of the column, while a − sign indicates the presence of an electron with $m_s = -\frac{1}{2}$. In the succeeding columns under "Resultant" are given the resultant m_l, m_s, and m values obtained by addition, and the s values (always $s \geqq |m_s|$) deduced by a consideration of the grouping of the individual components into multiplets. The resulting molecular states (single states or multiplet components as the case may be) are given in the column under "Molecular State." The superscript letters, and the column "Atomic State" are not important for present purposes; they will be explained later.

In determining s values and "molecular states" we note that on removal of the assumed magnetic field, leaving only the characteristic intramolecular axial electric field, some of the magnetic field components fall together in groups of two or three, while at the same time a coupling of individual spins to give the resultant s asserts itself. Quantum numbers whose existence depends on the magnetic field are indicated in Table V by

TABLE V. *Possible electron distributions and molecular states for two 2-quantum electrons.*

Possible Electron States				Resultant				Molecular state	Atomic state
$2s^s$	$2s^p$	$2p^p$							
$m_{l_\tau}=0$	0	+1	−1	m_l	m_s	m	s		
(+)(−)				0	0	0	0	$^1S^S$	^1S
(+)	(+)			0	(+1)	(+1)	1	$^3S^P$	^3P and ^1P
(+)	(−)			0	0	0	0 and 1	and	
(−)	(+)			0	0	0			
(−)	(−)			0	(−1)	(−1)	1	$^1S^P$	
+		+		±1	±1	±2	1	$^3P_2^P$	
−			−						
+		−		±1	0	±1	0 and 1	$^3P_1^P$ and $^1P^P$	
−			+						
−		+		±1	0	±1			
+			−						
−		−		±1	±1	±0	1	$^3P_0^P$	
+			+						
	+	+		±1	±1	±2	1	$^3P_2^P$	^3P, ^1S(?) and part of ^1D
	−		−						
	+	−		±1	0	±1	0 and 1	$^3P_1^P$ and $^1P^D$	
	−		+						
	−	+		±1	0	±1			
	+		−						
	−	−		±1	∓1	±0	1	$^3P_0^P$	
	+		+						
		(+)	(+)	0	(+1)	(+1)	1	$^3S^P$ and	
		(+)	(−)	0	0	0	0 and	$^1S^S$	
		(−)	(+)	0	0	0	1	(or $^1S^D$?)	
		(−)	(−)	0	(−1)	(−1)	1		
(+)	(−)			0	0	0	0	$^1S^D$ (or $^1S^S$?)	part of ^1D (and ^1S?)
		+−		±2	0	±2	0	$^1D^D$	
			+−						

parentheses. In more detail, the relations which exist in this process are as follows:

(a) if $\sigma_l > 0$, each pair of configurations which differ only in respect to the sign of m_l and *simultaneously* of m, falls together, giving a single molecular state. [This state has, however, a double statistical weight and is capable of splitting again into two states when the molecule rotates (σ-type doubling[66]).] In describing such a state, one uses a symbol, such as $^3P_2$ to indicate $\sigma_l=1$, $\sigma=2$, $s=1$; a quantum number σ_s may also be defined, such that $\sigma=\sigma_l+\sigma_s$; σ_s, unlike σ_l and σ, is allowed to have both positive and negative values.[67]

(b) if $\sigma_l=0$, there is nothing to orient the spins on withdrawal of the magnetic field. Consider for example a ^3S state as in Table V. This gives

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[66] Empirical relations, cf. R. S. Mulliken, Phys. Rev., **28**, 1202 (1926); **29**, 391, 637 (1927); **30**, 785 (1927); E. Hulthén, Zeits. f. Physik **46**, 349 (1927).

Theory, F. Hund[9,11]; R. de L. Kronig, Zeits. f. Physik, **46**, 814 (1928).

[67] When the nuclear rotation is considered, the coupling of σ_l and s tends to break down so that σ_s and σ lose their meaning (Hund's case *b*), but an adiabatic correlation with this case can be given.[9] Cf. F. Hund[9] and R. S. Mulliken (Phys. Rev., **29**, 637 (1927)) for discussion of the quantum numbers σ, σ_l, σ_s.

three magnetic components with $m = m_s = +1, 0$, and -1, which fall together on removal of the field, giving a single state. [This, however, has triple weight, and in the actual molecule usually splits again into three when the molecule rotates[68].]

(c) In the ^3S case just discussed, it is evident that the values $m_s = +1, 0$, and -1 may be regarded as the three possible m_s values corresponding to a resultant spin $s = 1$. As will be seen in Table V, there are (for example) four $(2s^s)(2s^p)$ strong-field configurations, three of which unite to ^3S; the fourth, with $m_s = 0$, must then evidently represent a ^1S state. Similarly in cases where $\sigma_l > 0$, the proper s values can readily be picked out, always in such a way that the resulting molecular multiplets (such as ^3P) correspond to the correct number of magnetic components.

Since it cannot be assumed that the quantum numbers here used correspond, even approximately, in general, to those actually appropriate for a particular molecule, it is desirable to see what the results of Table V mean in terms of other quantum numbers. In case the quantum numbers l_τ used here have a real physical meaning, they must have a tendency to give a resultant l, as in atoms. In an adiabatic transition to an imagined case where this tendency is realized, the individual σ_{l_τ}'s would lose their significane, but σ_l, σ_s, σ and s should persist through all stages.

One can proceed further, to the united atom. As the nuclei come nearer, the (l, s) couplings should finally become important, giving j values; in this process σ remains to the last, but σ_l and σ_s disappear, giving place to σ_j. Finally for the united atom we have only n_τ, l_τ, l, s, and j. The set of molecular states given, taken as a whole, should in the above process go over with certainty into the set of atomic states listed in the last column of Table V, so long as similar states with different values of n do not come too near. A *possible* correlation of the *individual* molecular states with the individual atomic states is that indicated in the table. This correlation corresponds to that expected for an ordinary atom on withdrawal of a strong electric field, as determined by methods such as are used in the application of the Pauli principle in atoms.[15] One cannot however expect in general to find this particular correlation in actual molecules. For example, we know that the various electric field components of a ^3P atomic state must be correlated with an equal number of components belonging to a ^3S molecular state and a ^3P molecular state. But when as here there are two ^3P atomic states, it might happen that *each* derives some components from one molecular ^3S or ^3P state, others from the other. Such a mixed correlation would be conditioned mainly by an overlapping of energy levels of different molecular states at some stage of approach of the nuclei. Such overlapping, or even complete revolution in the order of levels, may be expected if a tendency toward separability in elliptical coordinates (cf. following paragraphs) becomes dominant. Overlapping of sets of levels

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[68] Cf. F. Hund [9,11].

differing in n is often also to be expected, especially in view of the phenomenon of promotion of electrons.

Going back now to the n_τ, l_τ, σ_{l_τ}, s, σ_s assignment, we may next inquire what happens if the intramolecular electric field is so strong as to break down completely the ordinary l quantization. This condition is to be definitely expected in the case of non-penetrating orbits. Such a situation gives some degree of approach to quantization in elliptical coordinates (very close, for H_2^+). *The category of molecular states, as given in Table V, remains unchanged in elliptical coordinates.* Table V also holds for the individual field components, if we merely re-interpret the designations $2s^s$, $2s^p$, $2p^p$. In the *spherical* coordinates assumed in Table V, using the lowered quantum number values natural in the new quantum mechanics, $2s^s$ means $n_r=1$, $n_\theta=0$, $n_\phi=0$, $2s^p$ means $n_r=0$, $n_\theta=1$, $n_\phi=0$, $2p^p$ means $n_r=0$, $n_\theta=0$, $n_\phi=\pm 1$, where $n=n_r+n_\theta+|n_\phi|+1$, $n_\theta+|n_\phi|=l$, and n_ϕ means the same as m_{l_τ} of Table V. In *elliptical* coordinates, we might have $2s^s$ meaning $n_\xi=1$, $n_\eta=0$, $n_\phi=0$ and $2s^p$ meaning $n_\xi=0$, $n_\eta=1$, $n_\phi=0$, or, the meanings of $2s^s$ and $2s^p$ might be interchanged; in either case $2p^p$ surely means $n_\xi=0$, $n_\eta=0$, $n_\phi=\pm 1$. In any case, the energy order is very different than for spherical coordinates. That no uniform correspondence of n_r to n_ξ and n_θ to n_η, or vice versa, can be expected appears to follow from Hund's work, although in particular cases a definite correspondence may perhaps be predictable. So far as the theory goes at present, it appears that we may be prepared to find either or both correlations in practice, even with the possibility of opposite correlations for different electrons in the same molecule.

Results similar to those of Table V can readily be given for any desired configuration of electrons. (Results are always independent of any closed shells which may be present.) The results depend on σ_{l_τ}, not on n_τ and l_τ, e.g. two $4p^d$ or two $4p^f$ electrons give the same molecular states ^3S, ^1S, and ^1D as two $2p^p$ electrons. Two *different* electrons (e.g. $4p^d$ and $4p^f$) of course give additional possibilities (here ^3D), since the Pauli restrictions are dropped. *One* np^x ($x=p$, d, f, etc.) electron obviously gives a *normal* ^2P state only. *Three* np^p or np^x electrons probably give only an *inverted* ^2P; the reasons are given in the following paragraphs; addition of an s^x electron to such as an inverted ^2P state should yield a ^1P and an inverted ^3P state. From the results given up to this point, together with others obtained by the same methods, everything given in Table I of the text can be readily obtained.

Proof of inverted character of ^2P *from* (X) $(np^x)^3$. As Slater has pointed out,[69] the energy differences in the multiple electron levels in atoms are caused mainly by the interaction of the l of each electron with *its own s.* If there are several electrons, the interaction energy is of the form $\Sigma_\tau A_\tau l_\tau \cdot s_\tau$, l_τ and s_τ here representing the l and s *vectors* of the τ'th electron.[70] When all the electrons are equivalent, we may put $A_\tau = A$ for all. For a molecule with the type of quantum numbers here used, each term $A_\tau\, l_\tau \cdot s_\tau$ reduces

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[69] J. C. Slater, Phys. Rev., **28**, 291 (1926). Cf. also ref. 15, p. 121 *et seq.*

(noting that $s=\frac{1}{2}$) to $\frac{1}{2}A_\tau \, \sigma_{l_\tau} \cos\,(\sigma_{l_\tau}, s_\tau)$[70]. For the case of *one p* electron in a molecule, the energy is then $A/2$ for $^2P_{1\frac{1}{2}}$ and $-A/2$ for $^2P_{\frac{1}{2}}$. For the case of *three equivalent p* electrons ($\sigma_{l_\tau}=1$ for each) it will be seen by referring to Fig. 1, and performing the summation $\frac{1}{2}A\Sigma_\tau \cos\,(\sigma_{l_\tau}, s_\tau)$, that the energy is $-A/2$ for $^2P_{1\frac{1}{2}}$ and $+A/2$ for $^2P_{\frac{1}{2}}$. Fig. 1 involves the assumption that the coupling of the spins of equivalent electrons is such that the individual spins are either parallel or anti parallel to their resultant, s; since the electric field should not affect the spin coupling (cf. above), this assumption, which is valid for atoms, should be equally true for molecules.[70]

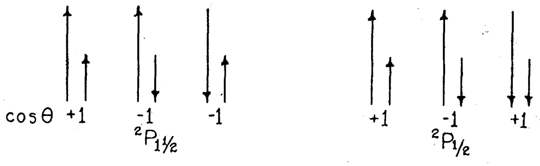

Fig. 1.

It is desirable to show that these results are independent of the assumed choice of quantum numbers. If the tendency is toward elliptical quantum numbers, σ_{l_τ} still corresponds to the average angular momentum, and nothing is changed. If the tendency is toward a coupling of l_τ's to a resultant l, the individual σ_{l_τ}'s are lost; we can determine how things are going by proceeding to the limiting case of the united atom. Here there are several possibilities, since any ns^p electrons which may be present must be considered as well as the np^p electrons. The two extreme possibilities are as follows: (1) The molecular configurations $(X)\ (ns^p)^2(np^p)^3$, ^2P and $(X)\ (ns^p)(np^p)^4$, ^2S, taken together, go over into a ^2P state of a united atom of the halogen type with, in the atomic sense, *five* equivalent p electrons; such a ^2P atomic state is always inverted.[15] (2) From an $(X)\ (np^p)^3$, ^2P molecular state without ns^p electrons, taken together with some appropriate ^2S state of the $(X)\ (ns^p)\ (np^p)^2$ type, we get a ^2P united-atom state of the same kind as in an atom with *three* equivalent p electrons, i.e. a state like the predicted low-lying metastable ^2P state of the N or O^+ atom; for such a state the doublet separation is approximately zero.[71]. Since this second limiting case will not be closely approached in the molecule, we may reasonably expect an inverted ^2P in all cases for a molecule with three equivalent np^x electrons.

In Part II of this paper, in a subsequent issue, the evidence for the "Probable Products of Dissociation" listed in Table III will be discussed, and various conclusions, arising from these and other results summarized

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[70] A revised interpretation of the cosines in Slater's formula is required according to the quantum mechanics (cf. S. Goudsmit, Phys. Rev., **31,** 946, (1928), but it seems fairly clear that these changes will not affect the qualitative conclusions stated in the text, especially since the changes required for cos $(\sigma_{l_\tau}, s_\tau)$ are probably less than for cos (l_τ, s_τ).

[71] Cf. Bowen's data on the s^2p^3 (aP) state of $\mathrm{O_{II}}$ and of $\mathrm{F_{III}}$: Phys. Rev., **29,** 243 (1927).

in Table III, will be brought out in Part II and later papers. These conclusions have to do with the changes which atomic electrons undergo in the formation of a molecule, and also bear on the problems of valence and chemical stabilities. In later papers other molecules will also be considered.

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