

REVIEWS OF MODERN PHYSICS

THE INTERPRETATION OF BAND SPECTRA

PART III. ELECTRON QUANTUM NUMBERS AND STATES OF MOLECULES AND THEIR ATOMS

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A. GENERAL SURVEY

1. Introduction

IN PART I we have seen^{115a} how data obtained from the analysis of the spectra of a diatomic molecule can be used to construct curves $U(r)$ for the energy of its various electron states as functions of the distance r between the nuclei. In Parts I and II^{115a} we have considered how the total internal energy, which is made up of $U(r)$ plus the kinetic energy of vibration and rotation, depends on the vibrational, rotational, and electronic quantum numbers. We have devoted particular attention to the relations between band structure and electronic quantum numbers.

We are therefore now in a position to interpret the structures of observed band spectra in terms of $U(r)$ curves and electronic quantum numbers. This process of analysis and interpretation has been applied in numerous papers by various investigators, so that we now have a body of information on $U(r)$ curves and electronic quantum numbers for a considerable number of diatomic molecules. Our knowledge is most complete for the He_2 molecule. It is also extensive for H_2 and many hydrides, and for molecules such as CO both of whose atoms belong in the first row of the periodic system. Figs. 35-49 summarize this information for a number of molecules. The manner in which these figures have been prepared, including a critical discussion of ways of constructing $U(r)$ curves, is given in the Appendix. A table giving numerical data and electron configuration assignments for a large number of molecular states will also be found there.

A study of the figures show several interesting relations, and raises several questions. These are all more or less connected with the problem of the assignment of quantum numbers to the individual electrons in molecules, a topic which up to this point has not been discussed in this report. An understanding of the matter will perhaps be most quickly advanced by bringing up these questions and indicating their answers briefly in connection with the discussion of a few examples. This is done in section A. More detailed explanations will be given in later sections.

Part III is largely a review of theoretical relations combined with a critical interpretation of experimental material, and is based on papers of Hund, Weizel, Herzberg, Wigner and Witmer, the writer, and others. It also contains a number of rough *Predictions* (cf. dotted lines in the figures, also section D6 and Table XVI). Some of the interpretations given here are more or less new. Another article by the writer dealing to some extent with the same material as here, but from different points of view, will be found in the December, 1931 number of *Chemical Reviews*, under the title "Bonding Power of Electrons and Valence."

In view of the length of Part III as presented here, it has seemed best to postpone the introduction of a treatment of molecules in terms of wave mechanics until these articles are revised and completed to appear in book form. The reader will find in W. Weizel's article in the *Handbuch der experimentellen Physik* (Ergänzungsband, 1931) an excellent introduction to the

quantum-mechanical theory of molecular spectra and to their analysis, as well as a complete summary and bibliography of the experimental material up to Spring, 1931. Weizel's article is really of the dimensions of an entire book. Wherever specific references to sources of experimental data are not given in this review, they can nearly always be found in Weizel's book.

2. Comparison of CH molecule with N atom. Quantum numbers of molecular electrons

Suppose we compare the observed electron states of the CH molecule (Fig. 36) with the lowest states of the isoelectronic atom nitrogen. This atom has three states whose energies are much lower than those of any others. They are the normal, 4S , state and two metastable states, 2D and 2P , which are respectively 2.39 and 3.56 volts higher. All three states belong to the electron configuration $(1s)^2(2s)^2(2p)^3$. This configuration formula means that the atom contains two $1s$ electrons, two $2s$ electrons, and three $2p$ electrons, the first mentioned ($1s$) being the most, the last mentioned ($2p$) the least firmly bound. Now suppose we imagine the nucleus of the nitrogen atom to be divided into two parts so that the atom's electron system is subjected to a strong axially symmetrical electric field, as discussed in Part IIa (cf. pp. 91-96). The three atomic states 4S , 2D , 2P would then respectively give rise to the molecular states $^4\Sigma^-$, $^2\Sigma^-$, $^2\Pi$, $^2\Delta$; $^2\Sigma^+$, $^2\Pi$. (In regard to the distinction between Σ^+ and Σ^- states, cf. Part IIc, p. 92). Comparing this list of states with the known states of the CH molecule, which would be expected to act like an N atom with divided nucleus, we find that four of the six predicted states ($^2\Sigma^-$, $^2\Pi$, $^2\Delta$, $^2\Sigma^+$) have been found. Furthermore, the absence of $^4\Sigma^-$ and a second $^2\Pi$ from the list of observed states is easily explained: (1) transitions between $^4\Sigma^-$ and the known stable states of the molecule, which are all of the doublet type ($^2\Sigma$, $^2\Pi$, $^2\Delta$) would be very weak, because of the difference in multiplicity between initial and final states; (2) the second $^2\Pi$ state is probably an unstable one (very large r_e and small D). The $^4\Sigma^-$ is probably a stable state, as indicated in Fig. 36. Further details are given in section C5.

We may now inquire as to what can be said about quantum numbers of individual electrons in the CH molecule. This inquiry can be answered by pursuing somewhat further the method used in Part IIa. In Part IIa we saw that for a sufficiently large separation of the nucleus into two parts, we get a "strong" axially symmetrical electric field which destroys J^* and gives rise to an independent precession of L^* around the axis, giving a projection M_L . Here we have Hund's case *a* if $|M_L| > 0$ and the coupling of L^* and S^* is not too weak, otherwise Hund's case *b*; $\Lambda (= |M_L|)$ and S are the characteristic quantum numbers in both cases, while in case *a* there are also Σ and $\Omega (\Omega = |\Lambda + \Sigma|)$.

We can now go one step further, to what may be called a "very strong" field (cf. Part IIa, Ref. 32). Here the action of the electric axis is so strong that even L^* is destroyed, and the I^* of each electron precesses separately around the axis, giving its own m_l . M_L and $\Lambda = |M_L|$ still exist, however, with $M_L = \Sigma m_l$, while the resultant spin S maintains its identity throughout all

stages of increasing influence of the electric axis. In addition to n and l , which are preserved unchanged, we can now assign to each separate electron a new quantum number λ , such that $\lambda = |m_l|$. In analogy to the designations Σ , Π , Δ , $\dots$ already introduced previously for $\Lambda = 0, 1, 2, \dots$, we use σ , π , δ , $\dots$ for $\lambda = 0, 1, 2, \dots$ and speak of σ , π , δ , $\dots$ electrons.

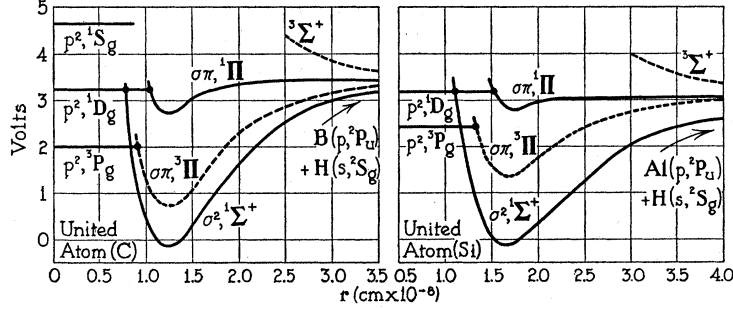


Fig. 35. $U(r)$ curves of those electron states of BH and AlH which can be derived from two unexcited atoms. Observed states, full curves; predicted states, dashed lines. Some higher-energy states of AlH, which must give an excited atom on dissociation, have been observed but are not shown here. At the left of the figures are shown the correlations of the three lowest states of BH and of AlH with the states of their united-atoms C and Si.

In terms of n , l , and λ we can now assign the following configurations to the various observed and predicted low-energy states of CH:

$$\left. \begin{aligned} &(1s)^2(2s)^2(2p\sigma)^2(2p\pi), {}^2\Pi \text{ (observed)} \\ &(1s)^2(2s)^2(2p\sigma)(2p\pi)^2, {}^4\Sigma^-, {}^2\Sigma^-, {}^2\Delta, \text{ and } {}^2\Sigma^+ \text{ (only } {}^4\Sigma^- \text{ not yet observed)} \\ &(1s)^2(2s)^2(2p\pi)^3, {}^2\Pi \text{ (not yet observed)} \end{aligned} \right\} \quad (89)$$

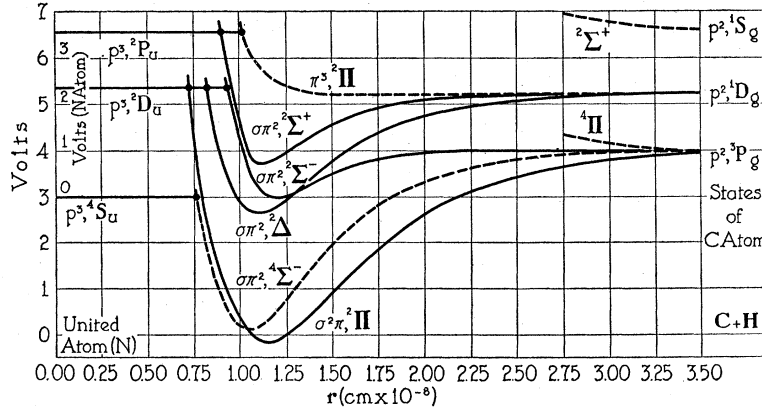


Fig. 36. $U(r)$ curves of observed states of CH and (dashed lines) of all predicted states derivable from a carbon atom with the configuration $1s^2 2s^2 2p^2$ and an unexcited H atom. Correlations of most of these states with the states of the united-atom N are shown at the left.

The three configurations given represent all that can be derived from $(1s)^2(2s)^2(2p)^3$ by assigning a λ value for each electron, since for s electrons we

necessarily have $\lambda = l = 0$, i.e., s electrons always become σ electrons, while for p electrons ($l = 1$) either $\lambda = 0$ or $\lambda = 1$ is possible.

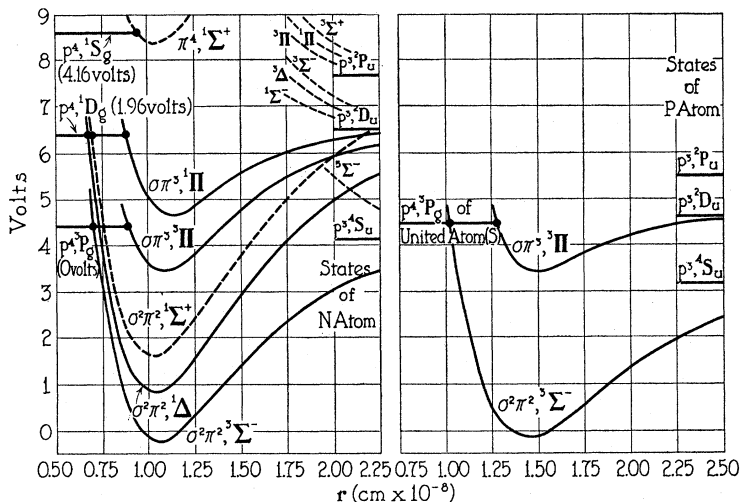


Fig. 37. $U(r)$ curves of observed states of NH and PH, and (dashed lines) of predicted states of NH derivable from lowest-energy states of the united-atom O or from unexcited H plus the lowest-energy states of the N atom. Correlations of the states shown with the states of the corresponding united-atoms O and S are given at the left. The data for the ${}^1\Pi$ and ${}^1\Delta$ curves of NH are from unpublished data of Dr. R. W. B. Pearse, which Dr. Pearse kindly communicated to the writer.

The way in which the six molecular electronic states in (89) are here distributed among the three molecular electronic configurations will be justified

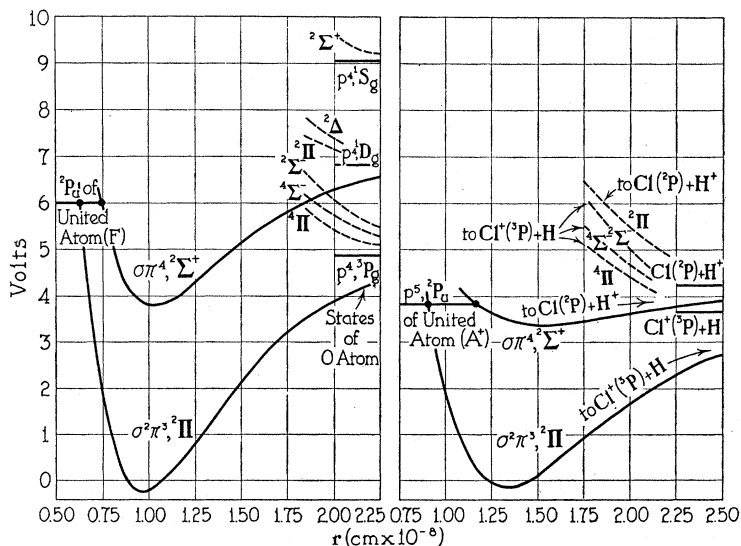


Fig. 38. $U(r)$ curves of observed states of OH and HCl^+ , of predicted states (dashed lines) of OH derivable from unexcited H plus lowest-energy states of the O atom, and of some predicted states of HCl^+ .

in section B3. It may, however, be well to emphasize at this point that the same six molecular electronic states are predicted (as can be seen from the results given in an earlier paragraph) whether one assumes a "strong field" and determines what happens to 4S , 2D , and 2P of the atom, or whether one assumes a "very strong field" and determines first the possible molecular configurations which result from the given atomic configuration, then the electron states which correspond to these molecular configurations. As a matter of fact, there is evidence that one has in CH the case of a very strong field, where the assignment of λ values is justified (cf. section C6b, discussion of NH).

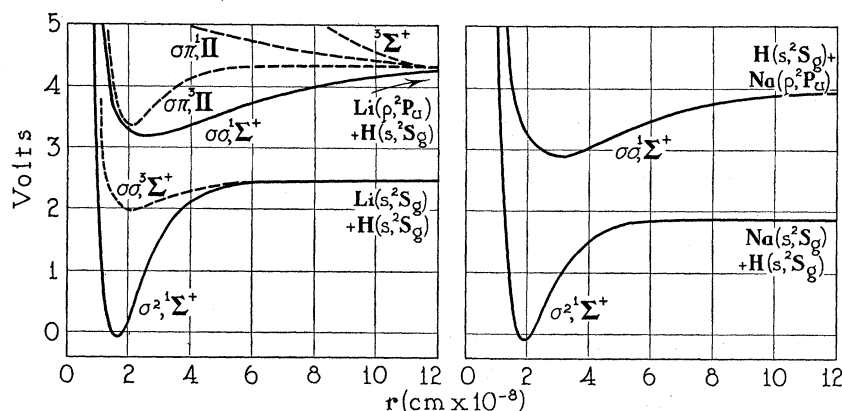


Fig. 39. $U(r)$ curves of known states of LiH and NaH, and (dashed lines) of predicted states derivable from unexcited H plus Li in its normal or first excited state.

Relations between molecular and united-atom states similar to those in CH also exist in all hydrides. Many such relations are shown in Figs. 35-40, and others can easily be worked out by the reader if he wishes.

3. Electron quantum numbers of CN, N₂, O₂ and the like

Turning now to molecules composed of two atoms both in the first row of the periodic system, it is interesting to see what electron configurations and states have been assigned. The assignments for the normal states of several such molecules are:

$$\left. \begin{aligned} \text{BO, CN, CO}^+, \text{N}_2^+ &: KK(z\sigma)^2(\gamma\sigma)^2(w\pi)^4(x\sigma)^2, {}^2\Sigma^+ \\ \text{CO, N}_2, \text{NO}^+ &: KK(z\sigma)^2(\gamma\sigma)^2(w\pi)^4(x\sigma)^2, {}^1\Sigma^+ \\ \text{NO, O}_2^+ &: KK(z\sigma)^2(\gamma\sigma)^2(x\sigma)^2(w\pi)^4(v\pi), {}^2\Pi \\ \text{O}_2 &: KK(z\sigma)^2(\gamma\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^2, {}^3\Sigma^- \end{aligned} \right\} \quad (90)$$

In all such configuration formulas, the order in which the symbols are written is the order of decreasing firmness of binding. The letters z, y, x, w, v , preceding σ or π are used merely to distinguish different kinds of σ or π electrons. They are not intended to have any sharply-defined theoretical implications. The succession of letters z, y, x, w, v , (further, u, t, r, q , if necessary) has been

assigned, however, so as to correspond approximately to the observed order of decreasing firmness of binding. The symbols KK refer to the four most firmly bound electrons in each molecule, which are for all practical purposes unchanged K electrons of the two atoms. These four electrons might also be designated by $(kz\sigma)^2(ky\sigma)^2$, the prefix k then serving to distinguish them from the somewhat analogous groups $(z\sigma)^2(y\sigma)^2$.

The symbols K , $z\sigma$, etc. have been used here instead of the more explicit symbols $1s\sigma$, $2s\sigma$, $\dots$ appropriate for hydrides and employed above for CH , because in molecules like CN , N_2 , O_2 one usually cannot assign definite n and l values approximating those of the united-atom in meaning. Formerly instead of $z\sigma$, $y\sigma$, $x\sigma$, $w\pi$, $v\pi$, $u\sigma$, the symbols $2s\sigma$, $3p\sigma$, $3s\sigma$ or $3d\sigma$, $2p\pi$, $3p\pi$ or $3d\pi$, $4f\sigma$ have usually been used. $(1s\sigma)^2(2p\sigma)^2$ has also been used instead of KK . The n and l values indicated by the old symbols really have not much meaning,

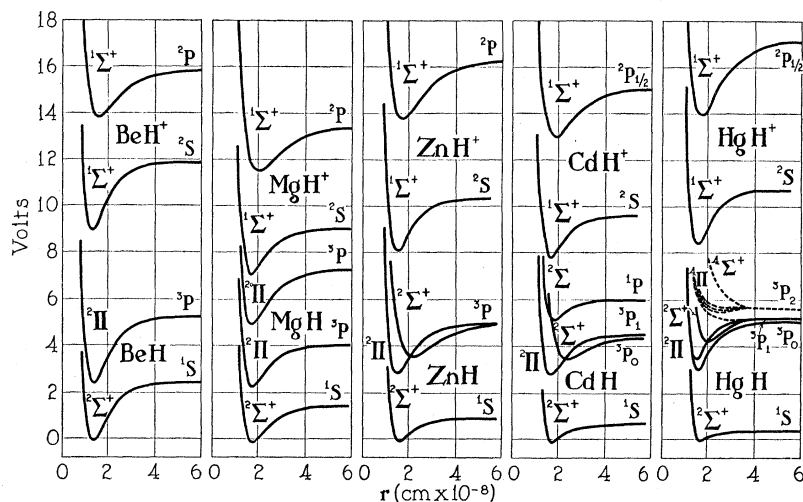


Fig. 40. $U(r)$ curves of practically all observed states of BeH , MgH , ZnH , CdH , HgH and their ions. The $^2\Pi$ states of ZnH , CdH , HgH each consist of two distinct components $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, but the separation between the two is not large enough to be worth showing except in HgH . In the case of HgH , it is possible that the $U(r)$ curves should be altered so that the upper $^2\Sigma$ state gives a 3P_0 atom, the $^2\Pi_{1/2}$ state a 3P_1 atom, as in the analogous case of CdH . In the case of HgH , curves are shown also for all the predicted states derivable from an unexcited H atom plus an Hg atom in its lowest 3P state (this of course includes 3P_0 , 3P_1 , 3P_2); dashed lines are used for predicted states not yet observed. Analogous predicted curves could be drawn for all the other molecules. It should be noted that the D values of all the states of BeH , MgH , BeH^+ , MgH^+ , ZnH^+ , CdH^+ , and HgH^+ are based on rough estimates which may be considerably in error.

however, for the molecule itself, but correspond to what one might get if the nuclei were gradually brought together. For this reason and also because the results of the correlation between molecule and united-atom are not always unambiguous, it seems better to adopt the more noncommittal symbols used here.

One might have used the symbols n and l in a sense different from that

in atoms, and corresponding to separability in elliptical coördinates, as is often done in describing the electron orbit in H_2^+ . But in most molecules the case of separability in elliptical coördinates is so poorly approximated that the results of trying to define n and l in terms of it would be ambiguous and unsatisfactory.

Another possibility would have been to use symbols $\sigma 1s, \sigma^* 1s$, where $(\sigma 1s)^2$ $(\sigma^* 1s)^2$ would correspond to $KK; \sigma 2s, \sigma^* 2s$ for $z\sigma$ and $y\sigma$ respectively; $\pi 2p$ and $\pi^* 2p$ for $w\pi$ and $v\pi$; $\sigma 2p, \sigma^* 2p$ for $x\sigma$ and $u\sigma$. Such symbols imply definite genetic relationships between the various kinds of molecular electrons and corresponding electrons of the separate atoms, indicated by the symbols $1s, 2s, 2p$ following σ or π . While the assumption of such relationships is usually in large measure justifiable (Lennard-Jones), often more so than the attempt to establish correlations with the united-atom, it is not infrequently questionable and it has seemed preferable to adopt the symbols used here. The subject of electron orbit notation in molecules will be taken up again, in detail, in section D1 (cf. also section A8).

4. Equivalent electrons and closed shells in molecules

It is convenient at this point to take up the questions of equivalent electrons, Pauli principle, and closed shells in diatomic molecules. The *Pauli principle* can here be stated for diatomic molecules as follows: *no two electrons can occupy identical orbits unless their spins are antiparallel*. If the electron orbits can be described by n, l , and m_l , where $\lambda = |m_l|$, the statement just made means that n, l , and m_l cannot all be alike for two electrons unless their spins are antiparallel. In most molecules—cf. the preceding section (3)— m_l can be specified, but quantum numbers having the usual meanings of n and l cannot. Whether two orbits alike in m_l are identical or not can, however, always be specified even if n and l cannot be given. (Two orbits differing in m_l are of course never identical.)

As in atoms, it is convenient in molecules to speak of *equivalent electrons*. In atoms, any two electrons alike in n and l are ordinarily referred to as equivalent, since in the absence of an external field, they cannot be distinguished. The maximum number of equivalent s electrons allowed by the Pauli principle is two, forming, when both present, a *closed shell*, as e.g., $(1s)^2$ or $(2s)^2$. The maximum number of equivalent p electrons is six. When this number is present, they form a closed shell, as e.g. $(2p)^6$ or $(3p)^6$. Ten equivalent d electrons, fourteen equivalent f electrons, and so on, form closed shells.

In molecules, two electrons alike in n, l , and λ (but not necessarily in m_l)—or in cases where n and l are not well-defined, alike in λ and identical in the other properties which n and l describe when they are defined—are now spoken of as *equivalent electrons*, since in the absence of an external field they cannot be distinguished. As compared with atoms, where only n and l can be distinguished, diatomic molecules have a greater variety of distinguishable orbit-types. This is because of their electric axis. For the same reason closed shells also occur in greater variety in molecules. Why molecular electrons

alike in λ but differing in m_l are considered as equivalent and not distinguishable, will be spoken of shortly.

In the case of equivalent σ electrons, the Pauli principle stated above requires that two such electrons, if present, must have their spins antiparallel, thus giving $S=0$. They thus constitute a *closed shell* of two electrons, or "*two-shell*". Examples of such closed shells are the group $(1s\sigma)^2$ in (89) and the group $(y\sigma)^2$ in (90).

When $\lambda > 0$, we have $m_l = \pm\lambda$, and we do not have a closed shell until there are two electrons with $m_l = +\lambda$ (and spins antiparallel) and two with $m_l = -\lambda$ (and spins antiparallel). This group of four electrons has $S=0$, and also has $\Lambda=0$, since $\Lambda = |M_L|$, where M_L is the sum of the m_l 's. Such a group may be referred to as a "*four-shell*". Closed shells in diatomic molecules are always either shells of two ($\lambda=0$) or of four ($\lambda>0$). Examples of four-shells are $(2p\pi)^4$ in (89), $(w\pi)^4$ in (90), and $(3d\delta)^4$.

Strictly speaking, one might regard two electrons differing in the sign of m_l as non-equivalent. One would then regard two electrons alike in other respects and both having $m_l = +\lambda$, or both with $m_l = -\lambda$, as constituting a closed shell, and it is often convenient to do so. Such two-shells have of course $S=0$, although $\Lambda=2\lambda$. But since electrons with $m_l = +\lambda$ have the same energy (for reasons which are essentially the same as those given in Part IIa, p. 93, in connection with M_L and Λ), and since it is much simpler to build up electron configurations with closed shells which always have $\Lambda=0$ as well as $S=0$, we usually deal with four-shells when $\lambda > 0$.

When all the electrons in an *atom* are in closed shells (cf. Part IIa, p. 86), the atom has $L=0$, $S=0$, and is said to be in a 1S state. Similarly when all the electrons in a molecule are in closed shells, as in the normal state of CO or N_2 —cf. (90)—we have $\Lambda=0$, $S=0$, i.e., a $^1\Sigma$ state. More precisely, this is a $^1\Sigma^+$ state or, if the two atoms are of the same element (e.g., N_2), a $^1\Sigma_g^+$ state. Since every closed shell in an atom, in particular the i^{th} , has $L_i=0$ and $S_i=0$, the resulting L and S of the atom are determined solely by those electrons which are not in closed shells. Similarly in molecules, *the resultant Λ and S are determined by those electrons which are outside closed shells*, e.g., by the $x\sigma$ electron in BO, CN, . . . , by the $v\pi$ electron in NO and O_2^+ and by the two $v\pi$ electrons in O_2 ,—cf. (90).

5. Relation of molecular electron states to electron configurations

We proceed next to a consideration of the electron states which are possible in the case of an incomplete shell. One σ electron alone gives only a $^2\Sigma^+$ state ($\lambda=\Lambda=0$). One π electron alone gives only a $^2\Pi$ state ($m_l = \pm 1$, $\lambda=\Lambda=1$). Three equivalent π electrons (π^3) also give a $^2\Pi$ state ($m_{l_1}=m_{l_2}=\pm 1$, $m_{l_3}=\mp 1$, giving $M_L=\pm 1$, hence $\Lambda=1$). In the former case (one π electron) the $^2\Pi$ state is *regular*, in the latter (π^3) it is *inverted*.¹¹⁶ Two equivalent π electrons (π^2) give three states, namely a $^1\Delta$ ($m_{l_1}=m_{l_2}=\pm 1$, giving $M_L=\pm 2$, hence $\Lambda=2$, but only $S=0$ because $m_{l_1}=m_{l_2}$), and a $^1\Sigma^+$ and a $^3\Sigma^-$ state ($m_{l_1}=+1$, $m_{l_2}=-1$, hence $\Lambda=0$, with $S=1$ as well as $S=0$ because $m_{l_1}\neq m_{l_2}$).¹¹⁷ That the $^1\Sigma$ and $^3\Sigma$ must be $^1\Sigma^+$ and $^3\Sigma^-$ can readily be shown by quantum mechanics.¹¹⁸

The possible molecular states for various other configurations of electrons can be determined in a similar way. For instance, two *nonequivalent* π electrons ($\pi\pi$) give ${}^3\Delta$, ${}^1\Delta$, ($m_{l1}=m_{l2}=\pm 1$, $S=0$ or 1), ${}^3\Sigma^-$, ${}^1\Sigma^-$, ${}^3\Sigma^+$, and ${}^1\Sigma^+$.¹¹⁹ The ${}^3\Delta$ is regular. Six π electrons in two groups of three equivalent electrons each ($\pi^3\pi^3$) give the same list of states as $\pi\pi$, although here the ${}^3\Delta$ is inverted. The states obtained by adding a σ electron to any other configuration can be determined by simply writing down all states obtainable by combining the spin of the σ electron with the previous S . For example $\sigma\sigma$ gives ${}^3\Sigma^+$ and ${}^1\Sigma^+$, $\pi^2\sigma$ gives ${}^2\Delta$, ${}^4\Sigma^-$, ${}^2\Sigma^-$, ${}^2\Sigma^+$, while $\pi\pi\sigma$ gives ${}^4\Delta$, ${}^2\Delta$, ${}^2\Delta$, ${}^4\Sigma^-$, ${}^2\Sigma^-$, ${}^2\Sigma^-$, ${}^4\Sigma^+$, ${}^2\Sigma^+$, ${}^2\Sigma^+$. The possible molecular states for a number of electron configurations are given in Table VIII.¹²⁰

TABLE VIII. Electron states corresponding to various electron configurations.

Config-uration	Electron States	Config-uration	Electron States
$\sigma\sigma$	${}^1\Sigma^+$, ${}^3\Sigma^+$	$\sigma\sigma\pi$	${}^2\Pi$, ${}^2\Pi(r?)$, ${}^4\Pi(r)$
$\sigma\pi$	${}^1\Pi$, ${}^3\Pi(r)$	$\sigma\sigma\delta$	${}^2\Delta$, ${}^2\Delta(r?)$, ${}^4\Delta(r)$
$\sigma\delta$	${}^1\Delta$, ${}^3\Delta(r)$	$\sigma\pi\pi$	${}^2\Sigma^+$, ${}^2\Sigma^+$, ${}^4\Sigma^+$, ${}^2\Sigma^-$, ${}^2\Sigma^-$, ${}^4\Sigma^-$, ${}^2\Delta$, ${}^2\Delta$, ${}^4\Delta(r)$
$\pi\pi$	${}^1\Sigma^+$, ${}^3\Sigma^+$, ${}^1\Sigma^-$, ${}^3\Sigma^-$, ${}^1\Delta$, ${}^3\Delta(r)$	$\sigma\pi\delta$	${}^2\Pi$, ${}^2\Pi$, ${}^4\Pi$, ${}^2\Phi$, ${}^2\Phi$, ${}^4\Phi(r)$
$\pi\delta$	${}^1\Pi$, ${}^3\Pi$, ${}^1\Phi$, ${}^3\Phi(r)$	$\pi\pi\pi$	${}^2\Pi$ (six), ${}^4\Pi$ (three), ${}^2\Phi$, ${}^2\Phi$, ${}^4\Phi(r)$
$\delta\delta$	${}^1\Sigma^+$, ${}^3\Sigma^+$, ${}^1\Sigma^-$, ${}^3\Sigma^-$, ${}^1\Gamma$, ${}^3\Gamma(r)$	$\pi\pi\delta$	${}^2\Sigma^+$, ${}^2\Sigma^+$, ${}^4\Sigma^+$, ${}^2\Sigma^-$, ${}^2\Sigma^-$, ${}^4\Sigma^-$, ${}^2\Delta$ (four), ${}^4\Delta$ (two), ${}^2\Gamma$, ${}^2\Gamma$, ${}^4\Gamma(r)$
$\sigma\sigma\sigma$	${}^2\Sigma^+$, ${}^2\Sigma^+$, ${}^4\Sigma^+$		
σ^2	${}^1\Sigma^+$	π^3	${}^2\Pi(i)$
π^2	${}^1\Sigma^+$, ${}^1\Delta$, ${}^3\Sigma^-$	$\pi^3\sigma$	${}^1\Pi$, ${}^3\Pi(i)$
$\pi^2\sigma$	${}^2\Sigma^+$, ${}^2\Sigma^-$, ${}^2\Delta(n)$, ${}^4\Sigma^-$	$\pi^3\pi$	${}^1\Sigma^+$, ${}^1\Sigma^-$, ${}^1\Delta$, ${}^3\Sigma^+$, ${}^3\Sigma^-$, ${}^3\Delta$
$\pi^2\pi$	${}^2\Pi(r)$, ${}^2\Pi(i)$, ${}^2\Pi(i)$, ${}^2\Phi(r)$, ${}^4\Pi(r)$	$\pi^3\delta$	${}^1\Pi$, ${}^1\Phi$, ${}^3\Pi$, ${}^3\Phi$
$\pi^2\delta$	${}^2\Sigma^+$, ${}^2\Sigma^-$, ${}^2\Delta(r)$, ${}^2\Delta(i)$, ${}^2\Gamma(r)$, ${}^4\Delta(r)$	$\pi^3\pi^2$	${}^2\Pi(i)$, ${}^2\Pi(r \text{ or } n)$, ${}^2\Pi(r)$, ${}^2\Phi(i)$, ${}^4\Pi(i)$
$\pi^2\sigma\sigma$	${}^1\Sigma^+$, ${}^1\Sigma^-$, ${}^1\Delta$, ${}^3\Sigma^+$, ${}^3\Sigma^-$, ${}^3\Sigma^-$, ${}^3\Delta(n)$, ${}^5\Sigma^-$	$\pi^3\pi^3$	${}^1\Sigma^+$, ${}^1\Sigma^-$, ${}^1\Delta$, ${}^3\Sigma^+$, ${}^3\Sigma^-$, ${}^3\Delta(i)$
$\pi^2\pi\sigma$	${}^1\Pi$, ${}^1\Pi$, ${}^1\Pi$, ${}^1\Phi$, ${}^3\Pi(r)$, ${}^3\Pi(i?)$, ${}^3\Pi(r)$, ${}^3\Pi(i)$, ${}^3\Phi(r)$, ${}^5\Pi(r)$	$\pi^3\pi^2\sigma$	${}^1\Pi$ (three), ${}^1\Phi$, ${}^3\Pi(i)$, ${}^3\Pi(r \text{ or } n?)$, ${}^3\Pi(r)$, ${}^3\Pi(i)$, ${}^3\Phi(i)$, ${}^5\Pi(i)$
$\pi^2\pi^2$	${}^1\Sigma^+$ (three), ${}^1\Sigma^-$, ${}^1\Delta$, ${}^1\Delta$, ${}^1\Gamma$, ${}^3\Sigma^+$, ${}^3\Sigma^-$, ${}^3\Sigma^-$, ${}^3\Delta(n)$, ${}^3\Delta(n)$, ${}^5\Sigma^+$	$\pi^3\pi^3\sigma$	${}^2\Sigma^+$, ${}^2\Sigma^+$, ${}^2\Sigma^-$, ${}^2\Sigma^-$, ${}^2\Delta(n)$, ${}^2\Delta(i)$, ${}^4\Sigma^+$, ${}^4\Sigma^-$, ${}^4\Delta(i)$

Notes: Where possible, the regular (r) or inverted (i) character of each multiplet state is given. In cases where no designation is given, the relations are such that it is hardly possible to make general predictions. In certain cases it can be predicted that the multiplet will be *narrow* compared with other states derived from similar electron configurations. Here the designation n (narrow) is used; in such cases, either r or i may be expected. The designations r , i , and n must not be expected to be correct for all cases without exception, especially not in cases with complicated groups of electrons. They should, however, hold in the normal coupling cases a and b , provided the magnetic interactions between the l or λ of each electron and its own spin outweigh all other magnetic interactions.

6. Dependence of energy on Λ and S for given electron configuration

First in importance, for the different states of a given electron configuration, is usually the dependence of the energy on S . Other things (electron configuration, Λ value) being equal, we may usually, as in atoms and for the same reasons, expect the *energy* to be *lower* for a *larger* than for a *smaller value* of S . For example, we may usually expect to find $\cdots m\sigma \ n\pi, {}^3\Pi$ below $m\sigma \ n\pi, {}^1\Pi$.

Now considering the dependence on Λ , for a given electron configuration, some qualitative statements and some examples can be given. In O_2 we have a configuration $\cdots \pi^2$ whose ${}^3\Sigma^-$ is the normal state of the molecule. A state

which is probably the corresponding state $^1\Sigma^+$ is 1.62 volts higher (cf. Fig. 48), and presumably the predicted $^1\Delta$ lies half-way between these (dotted curve in Fig. 48), since the quantum theory indicates that $^3\Sigma^-$, $^1\Delta$, $^1\Sigma^+$ should probably be spaced about equidistantly with $^3\Sigma^-$ lowest.¹¹⁸

Turning now to the configuration $\cdots \sigma\pi^2$, e.g. $\cdots 2p\sigma(2p\pi)^2$ in CH, we expect to find $^4\Sigma^-$ and $^2\Sigma^-$, derived from $^3\Sigma^-$ of π^2 , and $^2\Delta$ and $^2\Sigma^+$ derived from $^1\Delta$ and $^1\Sigma^+$ of π^2 . As in the case of the $^3\Pi$ and $^1\Pi$ derived from $\cdots \sigma\pi$, so here we expect the state of higher multiplicity, the $^4\Sigma^-$ of $\sigma\pi^2$, to be below the corresponding $^2\Sigma^-$. As compared with the energy order for $\cdots \pi^2$, we may for $\cdots \sigma\pi^2$ expect the relative positions of $^2\Sigma^+$, $^2\Delta$, and the *mean* of $^2\Sigma^-$ and $^4\Sigma^-$ to be about the same as those of $^1\Sigma^+$, $^1\Delta$, and $^3\Sigma^-$, while we may expect the $^2\Sigma^-$ to be displaced upwards, the $^4\Sigma^-$ downwards, by perhaps about equal amounts, from the position of their mean. In CH (Fig. 36) we have a good example of this case, except that the $^4\Sigma^-$ is not yet known. The order of the four states is $^4\Sigma^-$ (predicted), $^2\Delta$, $^2\Sigma^-$, $^2\Sigma^+$. The interval between $^2\Delta$ and $^2\Sigma^+$ is 1.07 volts (cf. Table IX). Assuming an equal interval between $^2\Delta$ and the average of $^2\Sigma^-$ and $^4\Sigma^-$, we can predict that the $^4\Sigma^-$ lies about 2.5 volts below the $^2\Delta$, with an interval of 2.9 volts between $^4\Sigma^-$ and $^2\Sigma^-$. The $^4\Sigma^-$ then probably (cf. table IX) is close above the $\cdots (2p\sigma)^2 2p\pi$, $^2\Pi$. Or it *may* lie lower and be the normal state of CH.

7. Order of binding of molecular electrons

If we compare the normal electron configuration of N_2 or CO with that which would be obtained from the corresponding united-atom Si in a strong electric field, it can be seen that there are marked differences in the electron orbits in the two cases, beyond those which would be expected from the λ subdivision of the atomic orbits caused by the presence of the electric axis. [For the Si atom the normal state is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$, 3P .] These differences may be contrasted with the fact that in CH the order of binding ($1s\sigma$, $2s\sigma$, $2p\sigma$, $2p\pi$) is the same as that in the N atom ($1s$, $2s$, $2p$). The contrast can be attributed to the fact that in the hypothetical process of dividing the Si nucleus into two equal parts to make N_2 , the resulting changes in the electric field in which each electron moves are relatively very much greater than in the process of splitting off a small fraction of the N nucleus to make CH.

In predicting the electron configuration of the normal state of an *atom*, Bohr used the following method ("Aufbauprinzip"). To the completely ionized atom, electrons are imagined added one by one, each electron being allowed to drop to the most firmly bound orbit which is available, i.e., to the available orbit of lowest energy. As successive electrons are added, successive shells become filled. The completed atom in its normal state ordinarily consists entirely of closed shells except for zero or more of the last-added electrons, which determine the values of L and S . If one knows the relative strengths of binding of the different orbits, one can specify the electron configuration and (with the help of certain additional considerations) the values of L and S for any atom in its normal state. For the lighter atoms the order of binding is $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $4p$, $3d$ $\cdots$, while for somewhat heav-

ier atoms it is $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 5s, \dots$. The shift in the relative strengths of binding of the $3d$ and other orbits with increasing atomic number, and analogous phenomena for heavier atoms, have been shown to have important consequences for the periodic table and the properties of atoms.

If would be very helpful if one could set up an *Aufbauprinzip* for determining the normal (and other) states of diatomic molecules. The relations are, however, necessarily much more complicated than in atoms, since the orbit-types are more varied and since the order of binding of the different types of orbits varies not only with the atomic numbers of the atoms, but also with the equilibrium distance r_e between the nuclei, and furthermore depends on the degree of disparity between the charges on the two nuclei. The problem will be taken up in detail in section *D1*. There is, however, a fairly definite order of binding if one limits oneself to any set of molecules which are reasonably similar in respect to the position of their atoms in the periodic table (e.g., $\text{BO}, \text{CN}, \text{CO}, \text{N}_2, \text{NO}, \text{O}_2$). The order of binding which is probably typical for the first thirteen to sixteen electrons in such molecules is that which appears in the configurations already given for them in (90).

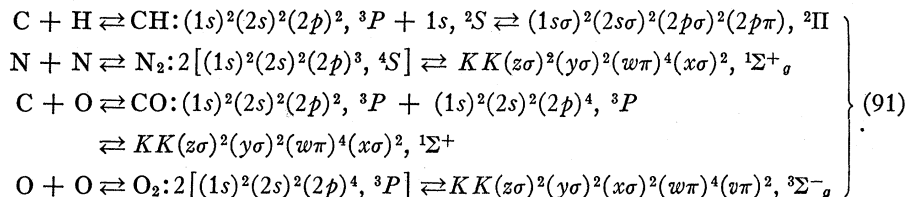
In the hydrides, on the other hand, the order of binding is essentially the same as in the corresponding united-atom, although the λ subdivision must also be considered. For a given value of n and l , the binding is firmer the smaller the value of λ . If $l - \lambda$ is large in a hydride, it may sometimes cause changes as compared with the order of binding which the n and l values alone would give: e.g. for $n = 3$ one might perhaps find the order $3s\sigma, 3d\sigma, 3p\sigma, 3p\pi, 3d\pi, 3d\delta$.

The fact that the four isoelectronic molecules $\text{BO}, \text{CN}, \text{CO}^+, \text{N}_2^+$ have the same type of normal state is an example of the truth of the statement that the order of binding of electrons is fairly definite within a set of similar molecules. The same statement applies to the molecules N_2, CO , and NO^+ , and to NO and O_2^+ . The fact that the normal state of N_2 or CO is obtained from that of N_2^+ or CO^+ , or that of NO from that of NO^+ , merely by adding one more electron in a higher orbit, without making any changes in the quantum numbers of those already present, is a further example of the applicability of the *Aufbauprinzip* in molecules. The close similarities which exist between the excited electron levels of the different members of any isoelectronic group of molecules (cf. Figs. 47, 48), should also be noticed. These give further strong evidence that the electronic structures of the molecules belonging to such a group (e.g., N_2^+ and CO^+) can be understood in terms of a molecular *Aufbauprinzip* which is largely independent of the particular atoms (e.g., $\text{N} + \text{N}^+$ or $\text{C}^+ + \text{O}$) which go to form them.

8. Electron quantum numbers of molecules and their atomic dissociation products, and the concept of promotion

A consideration of the relationship between the electron state of a molecule and the states of its component atoms on dissociation raises interesting questions. It is known, for example, that CO or N_2 or O_2 in its normal state, if its vibrational energy were steadily increased up to the point of dissocia-

tion, would give two normal atoms (C+O or N+N or O+O). Likewise CH in its low $^2\Pi$ state would give two normal atoms. This dissociation and the converse process of formation of a normal molecule from two atoms can be formulated as follows:



One sees that in the formation of such molecules, radical changes, other than merely the assignment of λ values, are in general required in the quantum numbers of some of the atomic electrons. For example in C+H there are three $1s$ and two $2p$ electrons, while in CH there are two $1s$ and three $2p$ electrons. This change can be most simply formulated by saying that the $1s$ electron of the H atom has been "*promoted*", in the formation of CH, to a $2p(\sigma)$ orbit (cf. section C5a for further details). If it were not for this promotion, there would be in the molecule too many $1s$ electrons, only two being permitted according to the Pauli principle.

The process of promotion is in one sense a discontinuous, in another a continuous one. In the simple case of a molecule containing two nuclei and one electron, as H_2^+ , the process of promotion can be followed theoretically from $r = \infty$ to $r = 0$ (cf. Fig. 45). For those orbits which are promoted, promotion, meaning an increase in certain quantum numbers, may here be regarded as taking place discontinuously at $r = \infty$. That is, the promoted orbits take on their new, *molecular*, quantum numbers at once as soon as one even *thinks* of the two parts of the molecule ($\text{H} + \text{H}^+$) as forming one system. These quantum numbers, which correspond to separation of the problem in elliptical coordinates, then remain unchanged down to $r = 0$.

But of course if r is large compared with the size of the orbit under consideration, the molecular electronic quantum numbers have no real importance as compared with the unpromoted, i.e., separated-atom, electronic quantum numbers. The criterion for promotion in the second, or continuous, sense is usually that considerable *energy changes* shall have occurred which differentiate the promoted (or more promoted) from the corresponding unpromoted (or less promoted) orbits. These take place continuously as r varies, and one may in this sense speak of different degrees of completeness of promotion. In the various electrons of various molecules, all stages of completeness can be found. In stable states of hydrides, the evidence indicates that the promotion of the H electron is nearly complete.

In many-electron molecules, the mutual effects of the electrons make it impossible in any strict sense to assign quantum numbers to the electrons which hold for all values of r . It is best not to attempt to assign quantum numbers other than λ values to electrons which are more or less half-promoted

in the energetic sense. This case exists for the *outer electrons* in molecules having nuclei not too unequal, as e.g., BO, CN, N₂, SiN, Cl₂, ICl. It is difficult or often impossible to designate these electrons according to their behavior either as $r \rightarrow 0$ or as $r \rightarrow \infty$. For these reasons it seems best to designate such electrons, as in (90) and (91), by symbols which are arbitrary except as respects λ . (In some cases, e.g., when r is large and the l 's of the separate atoms are strongly coupled to give L 's or J 's, it is not possible to assign even individual λ values.) For the *inner electrons* in such molecules, promotion is only incipient, because the equilibrium distance r_e between the nuclei is large compared with the dimensions of the orbits. These electrons are best regarded as essentially unchanged electrons of the separate atoms, and designated accordingly, e.g., by K , L , etc. in (90) and (91).

In molecules like CN, CO, N₂, the Pauli principle requires the promotion of a number, but not of all, the electrons as $r \rightarrow 0$. For example in C+O or N+N one has four $1s$, four $2s$, and six $2p$, electrons, while in the corresponding united-atom Si there cannot be more than two $1s$ and two $2s$ electrons. The two extra $1s$ and $2s$ electrons therefore must, and some of the $2p$ electrons may or must be promoted. For $r = r_e$, the energy changes in the $1s$ orbits are relatively slight and the promotion which is necessary for two of them is only incipient, because of their small dimensions. But for all the outer electrons, the energy changes are relatively large, because the dimensions of the original atomic orbits are comparable with r_e . The promotion of those outer electrons which are promoted is therefore fairly well on the way toward completion, except of course for half-inner electrons like the $2s$ electrons in F₂. Further details will be found in section D1.

9. Analogies of molecules whose atoms are homologues in the periodic system

As we have already seen, molecules with the same number of electrons, and not differing too much in the charges on their nuclei, are closely similar to one another in the order of binding of different kinds of electrons and so in respect to diagrams representing the positions of their electronic energy levels for $r = r_e$. [For $r = \infty$, these similarities largely disappear, since the electron levels are then determined by the separate atoms.] If the nuclear charges are very unequal, as in hydrides, the order of binding and arrangement of electron levels are essentially those of the atom with the same number of electrons, except for the λ and Λ subdivision.

Besides these similarities and analogies, diatomic molecules show certain homologies which parallel those that exist in series of atoms such as Li, Na, K, Rb, Cs which fall in the same column in the periodic system. These homologies are manifested in the existence of marked similarities between the energy level diagrams of such molecules as CO, CS, SiO, . . . ; or F₂, Cl₂, Br₂, I₂, ICl (cf. Fig. 42); or Li₂, Na₂, K₂ . . . (Fig. 41). Here one atom varies from one element to another in a column in the periodic system while the other remains fixed, or else *both* vary each within a given column of the periodic system. As yet the data on such series of molecules are in most cases

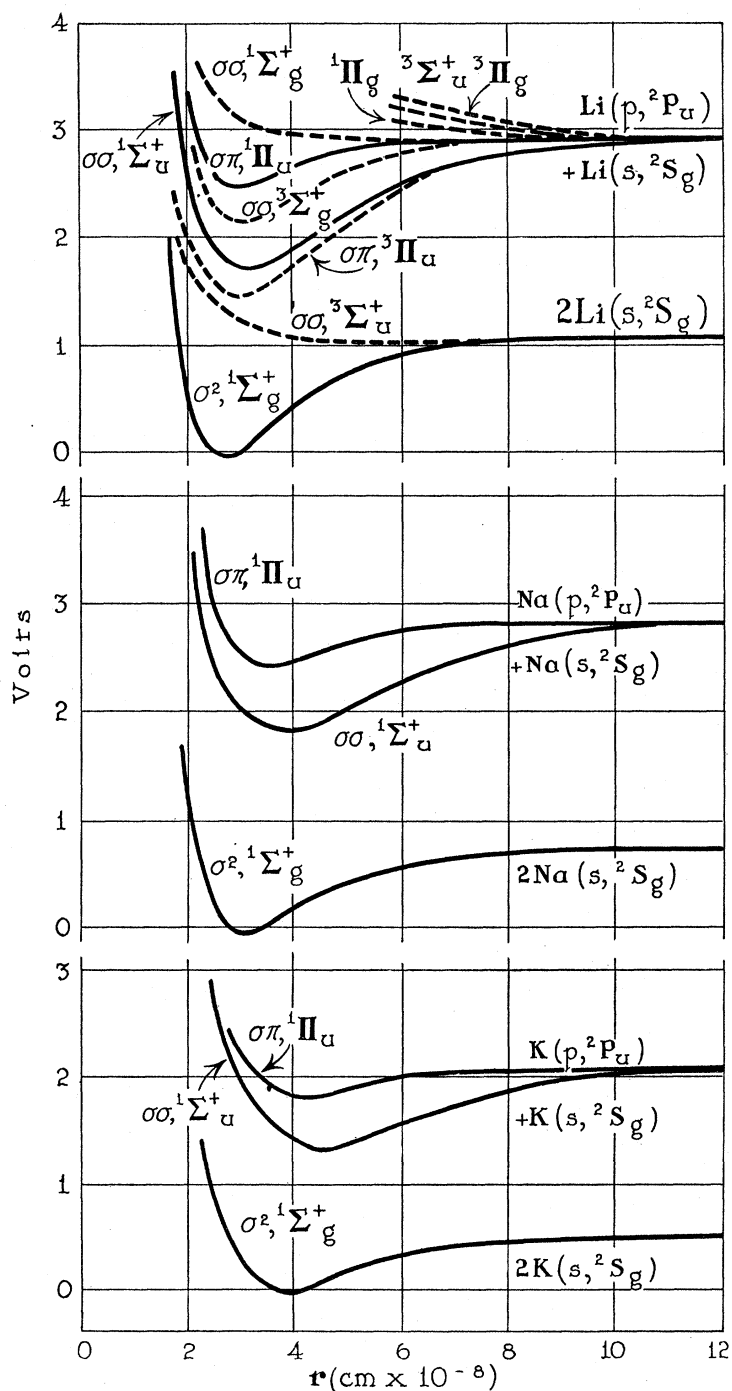


Fig. 41. $U(r)$ curves of three lowest observed electron states of Li_2 , Na_2 , and K_2 . (Other more excited states are known, but less well, and are not shown here.) In the case of Li_2 , additional predicted curves (dashed lines) are shown. These together with the curves shown for observed states represent all the electron states derivable theoretically from two unexcited atoms and from one unexcited atom plus one atom in its first excited state.

not extensive enough to show how far these similarities of homologous molecules go, except in cases like Cl_2 , Br_2 , I_2 , and Li_2 , Na_2 , K_2 , and of course the hydrides.

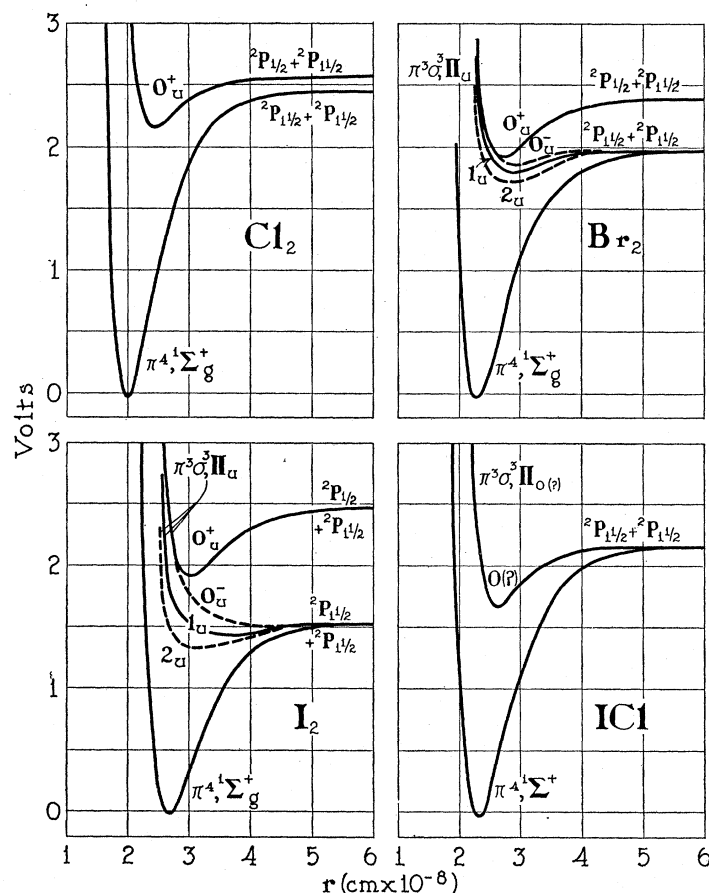
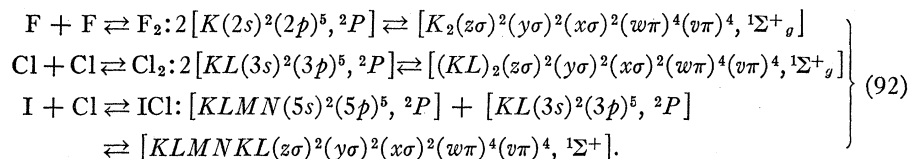


Fig. 42. $U(r)$ curves of normal and lowest excited states of the halogens. Full lines are observed states, dashed lines predicted states. Numerous additional predicted states, probably all repulsive, are derivable from normal atoms ($^2P_{1/2} + ^2P_{1/2}$) and from slightly excited atoms ($^2P_{1/2} + ^2P_{3/2}$ and $^2P_{3/2} + ^2P_{3/2}$). Cl_2 , Br_2 , and I_2 should all be analogous, ICl somewhat different, in respect to dissociation relations.

These similarities cannot be accounted for, except in hydrides or the like, by considering united-atoms. For example the united-atoms corresponding to the homologous and similar molecules F_2 and Cl_2 are respectively A (18 electrons) and Se (34 electrons), which are not at all similar. Most probably the observed similarities mean that the outer electrons of most molecules more nearly resemble electrons of the separated atoms than of the united-atom. In other words, Cl_2 resembles F_2 because $\text{Cl} + \text{Cl}$ resembles $\text{F} + \text{F}$, and in spite of the fact that Se does not resemble A.

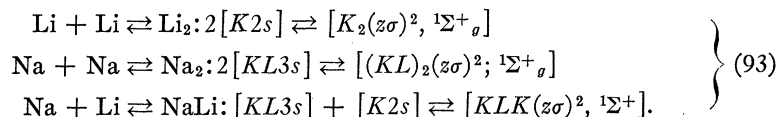
The resemblances between homologous molecules can be correctly ex-

pressed by assigning electron configurations such as the following (the symbols apply to the normal state of the molecule in each case):

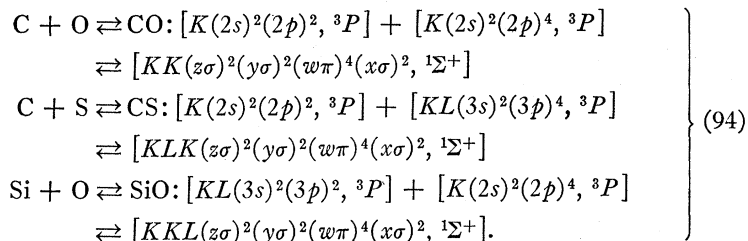


The symbols $z\sigma$, $y\sigma$, and so on, of course do not have the same meaning in all these molecules, but from the chemical and spectroscopic behavior of the molecules, are closely analogous in meaning in all. (The idea of using the same designations for analogous electron orbits with different principal quantum numbers was first suggested by Dr. W. Weizel in conversation.) If one desired, electrons corresponding to different shells L , M , N , of the separated atoms could be distinguished by writing $(lz\sigma)^2(ly\sigma)^2(lx\sigma)^2(lw\pi)^4(lv\pi)^4$ in F_2 , $(mz\sigma)^2$ and so on in Cl_2 , $(omz\sigma)^2$, $(omy\sigma)^2$, and so on, in ICl .

Similarly for the normal states of alkali molecules,



Or again,



The closest analogies of homologous molecules, chemically and spectroscopically, are those in such series as F_2 , Cl_2 , Br_2 , I_2 , ICl , and Li_2 , Na_2 , K_2 , LiNa , whose molecules are composed of univalent atoms. These molecules all have relatively small heats of dissociation. In such series as N_2 , P_2 , As_2 . . . or CO , CS , SiO , . . . , on the other hand, where the heats of dissociation are relatively large, physical and chemical evidence show that the analogies between different members are by no means close.

The contrast between the series F_2 , Cl_2 , Br_2 and the series N_2 , P_2 , As_2 can perhaps be explained as follows. F_2 , Cl_2 , Br_2 are closely analogous because r_e is large and D is small so that F_2 is very nearly $\text{F} + \text{F}$, Cl_2 very nearly $\text{Cl} + \text{Cl}$, Br_2 very nearly $\text{Br} + \text{Br}$, as already pointed out in a previous paragraph. But in N_2 , r_e is small and D large, and the molecule is far from being $\text{N} + \text{N}$, and has gone an appreciable distance on the road toward the united-atom Si . The molecule P_2 , however, perhaps is not so very far from $\text{P} + \text{P}$, and therefore differs strongly from N_2 , which is far from $\text{N} + \text{N}$. [Or else perhaps P_2 is fairly

well on the road toward its united-atom Zn, but since this is very different from the united-atom Si of $N+N$, the molecule P_2 differs strongly from N_2 .] Between P_2 and As_2 , As_2 and Sb_2 , Sb_2 and Bi_2 , the resemblances probably become increasingly closer, because the molecules become more and more like two atoms as the molecular weight increases.

Analogous explanations can be given for the properties of other series of molecules, in particular for the marked differences between molecules (N_2 , CO, NO, CO_2 , etc.) composed of atoms in the middle of the first row of the periodic system, and their heavier homologues. To make the explanation complete, we must of course give reasons why molecules such as those named have relatively small r_e and large D .

B. RELATIONS BETWEEN MOLECULE AND UNITED-ATOM

1. Introduction

Relations between electronic quantum numbers and electron states of a molecule and the corresponding "united-atom" are of direct importance mainly for the understanding of hydrogen and the hydride molecules. In most molecules, the relation to the united-atom is too remote to be of direct interest except in a few respects, relations to the separated atoms being much closer. Nevertheless, a knowledge of the relations between molecule and united-atom is needed for a thorough understanding of the nature of the electron states of molecules.

Some relations between molecule and united-atom have already been considered in Part IIa and, in terms of an example, in section A2 of Part III (comparison of CH and N). These relations, in particular as regards molecular electron configurations, will now be discussed more completely. Throughout the discussion, it should of course be borne in mind that the process of dividing a nucleus to form a molecule is possible only in imagination. If the nucleus could actually be split, the mutual repulsion of its two parts would drive them away from each other with tremendous speed. The results given in this section tacitly assume that this repulsion of the nuclei is somehow counterbalanced by external forces. All other forces exerted by nuclei and electrons are, however, assumed to exist unchanged.

2. General relations. Effect of moderate splitting of nucleus on electronic energy

Suppose we have given an atom with a specified electron configuration and in a definite state characterized by quantum numbers L , S , and J , and wish to determine the quantum numbers of the molecular states obtainable by dividing its nucleus. In addition to knowing L , S , and J , it is important to know whether the state of the atom is *even* or *odd*. An even state is one such that, if its wave-function is represented by $\psi(x_1, y_1, z_1, x_2, y_2, z_2, \dots)$, then $\psi(-x_1, -y_1, -z_1, -x_2, -y_2, -z_2, \dots) = \psi(x_1, y_1, z_1, x_2, y_2, z_2, \dots)$, while for an odd state, $\psi(-x_1, -y_1, -z_1, -x_2, -y_2, -z_2, \dots) = -\psi(x_1, y_1, z_1, x_2, y_2, z_2, \dots)$. It can be shown that the state of an atom is even or odd according as the simple sum $\sum l_r$ of the l values in its electron configuration is even or odd. Even and odd atomic states

will be distinguished here,¹²¹ when necessary, by the use of the subscripts *g* (even) or *u* (odd), e.g., ${}^2S_g, {}^2P_u$.

The changes which occur in the electron state of an atom when its nucleus is supposed divided to give a molecule may be considered as taking place in general in two stages. The first stage corresponds to the “*weak field*” case of Part IIa (Fig. 10) or to (the near-nuclei form of) the spin-coupling case *c* (cf. Part IIc, section H1). Here the atomic *L*, *S*, and *J* remain as good quantum numbers, but each atomic state of given *J* splits into a group of states having $\Omega = J, J-1, \dots, 0$ or $\frac{1}{2}$. States with $\Omega = 0$ can be classified under two types, namely the 0^+ and 0^- states of case *c* (cf. Part IIc, section H1). *One gets a 0^+ or a 0^- state according as $J + \sum l_r$ for the united-atom is even or odd.*¹²²

The change in electronic energy produced by dividing the nucleus is probably given (cf. caption of Fig. 10) by the *weak-field equation*

$$T - T_0 = \frac{1}{2}A[J(J+1) - L(L+1) - S(S+1)] + k_J r^2[3\Omega^2 - J(J+1)] + \dots, \quad (95)$$

where *r* is the distance between the nuclei, T_0 is the term value for $r=0$ and $A=0$, and k_J is a constant depending on *J*. [It should be particularly noted that the L^*, S^* interaction term $\frac{1}{2}AJ(J+1) + \dots$ on the right of Eq. (95) is also present when $r=0$; only the term $k_J r^2[3\Omega^2 - J(J+1)]$ represents the effect of dividing the nucleus. T_0 is defined corresponding to $A=0$ as well as $r=0$, and the L^*, S^* interaction term is included in Eq. (95), because this term changes when the division of the nucleus is made more pronounced (cf. Eq. 96).] The weak field case would exist if the distance between the two nuclei were very small, or if one nucleus had a much smaller charge than the other, or if the coupling of L^* and S^* were very strong.

If the division of the united nucleus is into two parts with *equal charges*, we must distinguish *even* and *odd* (*g* and *u*) electron states of the molecule. In this case, the even and odd states of the united-atom respectively become even and odd electron states of the molecule. The necessity of this can be seen from the following statements. (1) When the nucleus is divided into two parts, the *l* (and *n*) values of the electrons retain their identity and meaning at least in the first stages of the process. (2) In the case of two nuclei of equal charge the even or odd character of molecular electron states, like that of atomic states, is determined by the sum $\sum l_r$ of the *l* values of the electrons. (3) If the division of the nucleus is carried further, as in molecules like N_2 , O_2 , and F_2 , the odd or even character of each state, once established, remains unchanged.

Now suppose the effect of dividing the nucleus to be so strong as to break down the coupling of L^* and S^* which gives J^* ; then *J* disappears as a quantum number, while *L* and *S* remain. This is the “*strong field*” case of Fig. 10, corresponding to the spin-coupling cases *a* and *b* (cf. Part IIc, section H). [If the original coupling of L^* and S^* is very weak, one passes directly to strong field case *b*, practically without going through the weak field case *c* stage.] Here *L* gives rise to a set of Λ values equal to $L, L-1, \dots, 0$. When $\Lambda=0$, *we have a Σ^+ state if $L + \sum l_r$ is even, a Σ^- state if $L + \sum l_r$ is odd.*¹²³ If $\Lambda > 0$ and

the coupling of Λ and $\mathbf{S}^*$ is not negligible, we have case *a* (cf. Part IIb, p. 105), otherwise we have case *b*.

The change in electronic energy (*as compared with* $r=0$ and $A=0$) corresponding to case *a* is probably given, for not too large r , by the *strong field equation*

$$T - T_0 = k_1 r^2 [3\Lambda^2 - L(L+1)] + A\Lambda\Sigma + \dots \quad (96)$$

[In regard to the definition of T_0 and the inclusion of the $\mathbf{L}^*, \mathbf{S}^*$ interaction term, here $A\Lambda\Sigma$, cf. the remarks following Eq. (95)]. In case *b* the term $A\Lambda\Sigma$ is replaced by a small term which varies with the rotational quantum number (Part IIb, pp. 106-07).

3. Relation of molecular λ 's and Λ to atomic l and L values (pronounced splitting of nucleus)

When the united-atom is divided, the influence of the electric axis tends to cause each electron of quantum number l to assume one of the λ values given by $l, l-1, \dots, 0$. If, however, the l 's, or some of them, are coupled to give a resultant L , as we have so far assumed, these couplings must first be broken down by the influence of the electric axis. We shall refer to the case where they are thus broken down as that of a "*very strong field*," by "*field*" being meant here as always the *correction* which must be applied to the original central field of the united-atom to give the actual electric field. Ordinary molecular states always correspond to a division of the united-atom nucleus into well-separated parts, so as to produce a "*very strong field*" and give rise to definite λ values for each electron. In most molecules, the division of the united-atom is even more pronounced so that the molecule more closely resembles two *separate* atoms each in an electric field. The λ values already established then usually remain, but the n and l values of the united-atom lose their significance, while n and l values of the separate atoms tend to become important instead (cf. sections A3, A8, D1).

We have now to consider how, with a given set of l values and a given L and S for the united-atom, the possible Λ values and sets of λ values for the molecule are determined. [We could also inquire into the rules for correlating united-atom states of definite L, S and J values with molecular states of definite λ, Λ , and Ω values, but this question is of little importance. Its answer is, however, simple, and can be seen from Fig. 10, supplemented by reference to Fig. 23 and by a due regard for g and u , 0^+ and 0^- , Σ^+ and Σ^- correlation rules.]

All s electrons of the united-atom would become $s\sigma$ electrons, and every atomic closed shell $(ns)^2$ would go into a molecular closed shell $(n\sigma)^2$. For example, a $(1s)^2(2s)^2, {}^1S$, united-atom gives a $(1\sigma)^2(2\sigma)^2, {}^1\Sigma^+$ molecule, while a $(1s)^2(2s), {}^2S$ atom gives $(1\sigma)^2(2\sigma), {}^2\Sigma^+$. That these Σ states are Σ^+ rather than Σ^- follows from the fact (cf. sections A4, A5) that any number of σ electrons, or σ electrons plus closed shells of other electrons, give only Σ^+ states.

(Here and in the following paragraphs of this and the next section, the discussion assumes that the n and l values of the united-atom are preserved.

Actually, of course, this cannot be definitely expected except in molecules like hydrides where the division of the nucleus is not very pronounced. But the Λ values given here can be counted on, usually also the λ values.)

With $p, d, \dots$ electrons the relations are less simple. They can perhaps best be dealt with by considering a series of examples. We may begin with the case of an atom containing one or more closed shells of s electrons and one p electron, thus giving a 2P state, as e.g., $(1s)^2(2s)^2(2p)$, 2P . Here we know that either of the configurations $(1s\sigma)^2(2s\sigma)^22p\sigma$ or $(1s\sigma)^2(2s\sigma)^22p\pi$ may result. The former corresponds to a $^2\Sigma^+$, the latter to a $^2\Pi$ state, since here Λ is equal to λ of the one electron which is not in a closed shell, while S is equal to s of this same electron.

Next suppose we have the atomic configuration $A(ms)(np)$, where A stands for any group of closed shells, while m and n stand for two integers, which may or may not be equal. Two different atomic states, a 1P and a 3P , are associated with every such configuration. In the molecule the 1P gives $^1\Pi$ and $^1\Sigma^+$, the 3P gives $^3\Pi$ and $^3\Sigma^+$. The corresponding electron configurations are $A(ms\sigma)(np\sigma)$, giving $^1\Sigma^+$ and $^3\Sigma^+$, and $A(ms\sigma)(np\pi)$, which gives $^1\Pi$ and $^3\Pi$ (cf. Table VIII).

Now let us consider the atomic configuration $A(np)^2$, with two equivalent p electrons. Here the Pauli principle restricts the possible L and S values for the united-atom and, as we shall see, the possible Λ and S values in the molecule. For the united-atom the possible states are 3P (lowest), 1D (next), 1S (highest). The 3P gives molecular states $^3\Pi$ and $^3\Sigma^-$, the 1D gives $^1\Delta$, $^1\Pi$, and $^1\Sigma^+$, and the 1S gives $^1\Sigma^+$. Turning now to the molecular electron configurations, we see that there are three possibilities, namely $A(np\sigma)^2$, $A(np\sigma)(np\pi)$, and $A(np\pi)^2$. The configuration $A(np\sigma)^2$ gives a $^1\Sigma^+$ state, and $A(np\sigma)(np\pi)$ gives $^1\Pi$ and $^3\Pi$. $A(np\pi)^2$, as we have seen in section A5, gives a $^3\Sigma^-$, a $^1\Delta$, and $^1\Sigma^+$ state.

If we now compare the set of molecular electron states derived from the atomic states 3P , 1D , 1S that belong to $(np)^2$, and the set of states that correspond to the three electron configurations $(np\sigma)^2$, $(np\sigma)(np\pi)$, and $(np\pi)^2$ derived from $(np)^2$, we see that they are identical, as is obviously necessary if we have made no mistake. One can now give the following detailed correlations: $(np)^2$, 3P with $(np\sigma)(np\pi)$, $^3\Pi$ and $(np\pi)^2$, $^3\Sigma^-$; $(np)^2$, 1D with $(np\pi)^2$, $^1\Delta$ and $(np\sigma)(np\pi)$, $^1\Pi$ and $(np\sigma)^2$, $^1\Sigma^+$; and finally $(np)^2$, 1S with $(np\pi)^2$, $^1\Sigma^+$.

The only place where there is a possible uncertainty in the correlation is in the case of the two $^1\Sigma^+$ states, one of which is derived from 1D , the other from 1S . Here and in other similar cases, the correlation rule is that the *lowest* of two or more *atomic states* which are capable of giving rise to the kind of molecular state in question gives the lowest of the corresponding *molecular states*, the next lowest gives the next lowest, and so on.

4. Dependence of electronic energy on the λ 's

In the present example, the correlation given above was based on the supposition that $(np\sigma)^2$, $^1\Sigma^+$ is lower than $(np\pi)^2$, $^1\Sigma^+$. This is justified by the following equation,¹²⁴ which gives the change $-\hbar c(t-t_0)$ that results in the

binding energy of any electron when the united-atom is divided and the parts are separated to a distance which is still fairly small compared with the size of the original orbit:

$$t - t_0 = k_l r^2 [3\lambda^2 - l(l+1)] + \dots \quad (97)$$

This equation shows that *for a given n and l* , an electron is more firmly bound (since hct is defined as *positive energy*) *the smaller λ is*. The same qualitative behavior may also be expected for values of r so large that Eq. (97) is not valid. It has also been shown to be expected for the electrons of two *separate atoms* when they approach.

In case there is more than one electron outside closed shells,¹²⁵ Eq. (97) needs to be supplemented by terms corresponding to the energy of interaction of different electrons. In case *a* we may expect the following *very strong field* equation to hold:

$$T - T_0 = r^2 \Sigma k_l [3\lambda^2 - l(l+1)] + [f(S, \Lambda, r) - f_0(S, L)] + A\Lambda\Sigma + \dots, \quad (98)$$

where $f(S, \Lambda, r)$ is a function of r which depends on the resultant S and Λ and which has been discussed in section A6, and f_0 here refers (as in Eqs. 95, 96) to the energy for a given electron configuration and a given L and S but with the L^* , S^* interaction assumed zero. One gets a better idea of the spacing of the energy levels in the molecule if one rewrites Eq. (98) as follows:

$$T - T_{00} = r^2 \Sigma k_l [3\lambda^2 - l(l+1)] + f(S, \Lambda, r) + A\Lambda\Sigma + \dots, \quad (98a)$$

where $T_0 = T_{00} + f_0(S, L)$. T_{00} is a constant determined by the n 's and l 's of the united-atom.¹²⁵ In case *b* the term $A\Lambda\Sigma$ in Eqs. (98), (98a) is replaced by a function of the rotational quantum numbers.

Numerous examples illustrating the correctness of the dependence of T on the values of λ as given by Eqs. (97), (98) can be found in the hydrides. Here we often have pairs of states in one of which a $p\sigma$, in the other a corresponding $p\pi$ electron is present. In every case with one exception, the $p\pi$ is above the $p\sigma$, as expected. Table IX contains a summary of information regarding the electron configurations and energy differences for these examples. In comparing two states having different values of r_e , the vertical distance between the two $U(r)$ curves has been estimated for an r value usually equal to the *smaller* of the two r_e 's. The ΔE 's and r 's of the table are those obtained in this manner. It is of interest to note that the energy differences ΔE between σ and π run more or less parallel to the firmness of binding (ionization energy) of the electrons in question.

In the molecules H_2 and He_2 are examples of $\dots nd, \Sigma, \Pi, \Delta$ states where the intervals $nd\pi - nd\sigma$ and $nd\delta - nd\pi$ agree roughly with Eq. (97). For example in the $\dots 3d\sigma, \pi, \delta$ states of ortho- He_2 ($^3\Sigma, ^3\Pi, ^3\Delta$), the energy intervals in cm^{-1} are $453(^3\Delta - ^3\Pi)$ and $201(^3\Pi - ^3\Sigma)$.¹²⁶ The ratio of these is in approximate agreement with the theoretical ratio $[2^2 - 1^2]/[1^2 - 0^2] = 3:1$. The same is true of the ratio for the corresponding par- He_2 states, for which the intervals are respectively 374 and 166 cm^{-1} .¹²⁶

TABLE IX. Energy intervals ΔE corresponding to the difference between a po and a $p\pi$ electron in hydrides.

Molecule	Electronic States		r (Å)	ΔE (volts)
	Higher	Lower		
H ₂	$1s\sigma 2p\pi, {}^1\Pi$	$1s\sigma 2p\sigma, {}^1\Sigma^+$	1.07	0.92
BeH	$\dots 2p\pi, {}^2\Pi$	$\dots 2p\sigma, {}^2\Sigma^+$	1.34	2.48
MgH	$\dots 3p\pi, {}^2\Pi$	$\dots 3p\sigma, {}^2\Sigma^+$	1.70	2.37
CaH	$\dots 4p\sigma, {}^2\Sigma^+$	$\dots 4p\pi, {}^2\Pi$	1.97	-0.16
ZnH	$\dots 4p\pi, {}^2\Pi$	$\dots 4p\sigma, {}^2\Sigma^+$	1.52	2.84
CdH	$\dots 5p\pi, {}^2\Pi$	$\dots 5p\sigma, {}^2\Sigma^+$	1.68	2.75
HgH	$\dots 6p\pi, {}^2\Pi$	$\dots 6p\sigma, {}^2\Sigma^+$	1.59	3.15
BH	$\dots 2p\sigma 2p\pi, {}^1\Pi$	$\dots (2p\sigma)^2, {}^1\Sigma^+$	1.24	2.85
AlH	$\dots 3p\sigma 3p\pi, {}^1\Pi$	$\dots (3p\sigma)^2, {}^1\Sigma^+$	1.66	2.90
CH	$\dots (2p\sigma)(2p\pi)^2, {}^2\Delta$	$\dots (2p\sigma)^2(2p\pi), {}^2\Pi$	1.12	2.86
	$\dots (2p\sigma)(2p\pi)^2, {}^2\Sigma^-$	$\dots (2p\sigma)^2(2p\pi), {}^2\Pi$	1.12	3.25
	$\dots (2p\sigma)(2p\pi)^2, {}^2\Sigma^+$	$\dots (2p\sigma)^2(2p\pi), {}^2\Pi$	1.12	3.93
SiH	$\dots (3p\sigma)(3p\pi)^2, {}^2\Delta$	$\dots (3p\sigma)^2(3p\pi), {}^2\Pi$	1.53	3.00
NH	$\dots (2p\sigma)(2p\pi)^3, {}^3\Pi$	$\dots (2p\sigma)^2(2p\pi)^2, {}^3\Sigma^-$	1.08	3.67
PH	$\dots (3p\sigma)(3p\pi)^3, {}^3\Pi$	$\dots (3p\sigma)^2(3p\pi)^2, {}^3\Sigma^-$	1.45	3.6
OH	$\dots (2p\sigma)(2p\pi)^4, {}^2\Sigma^+$	$\dots (2p\sigma)^2(2p\pi)^3, {}^2\Pi$	0.98	4.06
Cl ⁺ H	$\dots (3p\sigma)(3p\pi)^4, {}^2\Sigma^+$	$\dots (3p\sigma)^2(3p\pi)^3, {}^2\Pi$	1.33	3.74

Notes: Cf. preceding text for meaning of r and ΔE . For sources of data, reference may be made to the references given in connection with Tables I and II in R. S. Mulliken and A. Christy, Phys. Rev. 38, 87 (1931).

C. RELATIONS BETWEEN MOLECULE AND SEPARATE ATOMS

1. Correlation rules: general

Suppose we have given two atoms each with a specified electron configuration and in a definite state characterized by quantum numbers L , S , and J , and wish to determine the quantum numbers of the various molecular states obtainable when the two atoms come together. This problem is more difficult than that of determining the molecular states obtained from an atom by dividing its nucleus into two parts (section B3). It is impossible to give general rules for determining the quantum numbers of the individual molecular electrons resulting from the union of two atoms in specified states; methods of determining them in special cases will be considered in sections C5a and D.

On the other hand, the molecular quantum numbers Λ and S for case a or b molecular states, as well as certain symmetry properties (g or u , Σ^+ or Σ^-), can be given with complete definiteness when the atomic L and S values and symmetries (g or u) are specified. For the occasionally occurring case c molecular states the quantum number Ω and the symmetry (g or u , 0^+ or 0^-) can be given definitely when the atomic J values and symmetries are specified. But Λ and S values corresponding to specified J values of the two atoms can rarely be unambiguously determined;¹²⁷ usually, however, such a correlation is of little interest.

Although there are no unique rules for identifying all the individual members of a set of molecular states with definite pairs of atomic states, there is one important general rule in addition to those for Λ and S which may be expected to hold. This rule is essentially identical with that given at the end of section B3 for correlating molecular and united-atom states. It may be

stated as follows: the lowest of any set of molecular states of a given type, e.g., ${}^2\Sigma^+_g$, or ${}^3\Pi_u$, or (case *c*) 0^-_u dissociates into the *lowest pair of atomic states* capable, according to the rules (99), (100), (100a), (100b) or Tables X and XI, of giving rise to a molecular state of this type, the next lowest molecular state of the given type dissociates into the next lowest suitable pair (which is sometimes the *same* pair) of atomic states, and so on. According to this rule, the nature of the dissociation products of a given molecular state depends as much on its position on an energy scale as on, say, its electron configuration.

An important point is that the above correlation rule is not always unambiguous. This is because it is not always possible to assign a molecular state to a definite type. If the coupling is intermediate between case *a* or *b* and case *c*, for instance, one cannot be sure whether the correlation with the separate atoms should be made according to molecular Λ and S values (which have no meaning in case *c*) or according to the Ω values of case *c*. Again, in defining types of molecular states, there is the possibility that the electron configuration should after all be considered, at least in respect to its λ values, which are usually pretty well defined. Thus for correlation purposes a $\cdots \pi^2, {}^1\Sigma^+_g$ state should perhaps sometimes be considered a different type than a $\cdots \sigma^2, {}^1\Sigma^+_g$ state. The *experimental* evidence on the actual correlations between atomic and molecular states is at present rather limited (cf. sections *C5* and *D*) and it is necessary to go mainly by the theory.

2. Determination of Λ and S of molecular states from L and S values: unlike atoms

First suppose we have two atoms of different elements. When these come together, each disturbs the electron system of the other by electrical forces having rotational symmetry around the line joining the two nuclei. Now if the molecule in equilibrium can be described in terms of case *a* or *b*, then regardless of what may happen in the intermediate stages of approach of the nuclei, simple and definite rules can be given connecting the possible Λ and S values of the molecule and the L and S of the two atoms. *The possible S values are*, letting $S_1 \geq S_2$, simply $S_1 + S_2, S_1 + S_2 - 1, \cdots, \cdots S_1 - S_2$. The possible Λ values or Λ states, letting $L_1 \geq L_2$, are as indicated by the following table:¹¹⁸

$$\begin{array}{l} (L_1 + L_2), (L_1 + L_2 - 1), \cdots, \Pi, \Sigma^+ \\ (L_1 + L_2 - 1), \cdots, \Pi, \Sigma^- \\ \cdots \cdots \cdots \\ (L_1 - L_2), \cdots, \Pi, \Sigma^+ \text{ or } \Sigma^- \end{array} \quad (99)$$

The Σ state in the last line is Σ^+ or Σ^- according as $L_1 + L_2 + \Sigma l_1 + \Sigma l_2$ is even or odd.

The way in which the results given in (99) may be theoretically derived can be made clear by an illustrative example. Suppose $L_1 = 2, L_2 = 1$. Then, for a given value of S , we have the following Λ values derived from various possible combinations of values M_{L_1}, M_{L_2} : $\Lambda = 3$ when M_{L_1}, M_{L_2} have the values $+2, +1$ and $-2, -1$; $\Lambda = 1$ from $+2, -1$ and $-2, +1$; $\Lambda = 2$ from $+1, +1$ and $-1, -1$; Σ^+ and Σ^- (see below) from $+1, -1$ and $-1, +1$;

$\Lambda = 1$ from 0, +1 and 0, -1; $\Lambda = 2$ from +2, 0 and -2, 0; $\Lambda = 1$ from +1, 0 and -1, 0; Σ^+ or Σ^- (see below) from 0, 0. Whenever $\Lambda > 0$, we have degenerate terms of double statistical weight, corresponding to $M_L = \pm \Lambda$; these split when the molecule rotates (Λ -type doubling). The case $\Lambda = 0$ arises whenever $M_{L_1} = M_{L_2}$. If $|M_{L_1}| > 0$, we might expect a degeneracy similar to that when $\Lambda > 0$. But actually this is removed by the interaction of the atoms even without rotation, so that we get two distinct states, one Σ^+ and one Σ^- . In case $M_{L_1} = M_{L_2} = 0$, however, we get only one state with $\Lambda = 0$, and it can be shown¹²³ that this is Σ^+ or Σ^- according as the sum $L_1 + L_2 + \Sigma_{L_1} + \Sigma_{L_2}$ is even or odd.

For convenience of reference, the different molecular states derivable from two atoms are given for all the most important cases in Table X, which is based on (99). For each molecular state given, the molecular spin takes on all the values $S_1 + S_2, S_1 + S_2 - 1, \dots, S_1 - S_2$. The results given are all equally correct if the symmetry of *both* the atoms is reversed (i.e., $g \rightarrow u$ or vice versa). If the symmetry is reversed for only *one* of the atoms, Table X is still correct for each atomic pair if one Σ^+ is replaced by a Σ^- .

TABLE X. Molecular electron states derived from specified atomic states.

Atomic States	Molecular States
$S_g + S_g$	Σ^+
$S_g + P_u$	Σ^+, Π
$S_g + D_g$	Σ^+, Π, Δ
$P_u + P_u$	$\Sigma^+(2), \Sigma^-, \Pi(2), \Delta$
$P_u + D_g$	$\Sigma^+(2), \Sigma^-, \Pi(3), \Delta(2), \Phi$
$D_g + D_g$	$\Sigma^+(3), \Sigma^-(2), \Pi(4), \Delta(3), \Phi(2), \Gamma$

Notes: The number of molecular states of each kind mentioned is given in parentheses; if no such number is given there is only one state of that kind. In case the two atoms belong to the same element, the number of molecular states is doubled: each of the states listed then occurs as a g and again as a u state.

2a. Determination of Ω values from atomic J values: unlike atoms

[This section may well be omitted by the general reader.]

If the nuclei of a molecule are rather far apart, we may often expect case c instead of case a or b (cf. Part IIc, section H). Here the molecular quantum numbers Λ and S lack meaning, but Ω is well defined. This case is expected, for large distances between the nuclei, when each atom has an L and an S greater than zero and strongly coupled to give a J . Letting L_1, S_1, J_1 and L_2, S_2, J_2 refer to the two atoms, we have J_1^* and J_2^* at first precessing more or less independently around the internuclear axis, giving quantized projections M_1 and M_2 (cf. Part IIc, p. 115). Then $\Omega = |M| = |M_1 + M_2|$ has meaning as soon as there is some coupling between M_1 and M_2 . The possible values of Ω can be conveniently summarized in the form of a table.

For *unlike atoms*, letting $J_1 \geq J_2$, the possible Ω values in case c are:¹²⁷

$$\begin{aligned}
 &J_1 + J_2, J_1 + J_2 - 1, \dots, \frac{1}{2} \text{ or } 0^+ \\
 &J_1 + J_2 - 1, \dots, \frac{1}{2} \text{ or } 0^- \\
 &\dots \dots \dots \\
 &J_1 - J_2, \dots, \frac{1}{2} \text{ or } 0^+ \text{ or } 0^-.
 \end{aligned} \tag{100}$$

If $J_1 + J_2$ is *half-integral*, the smallest Ω value is $\frac{1}{2}$. If J_1 and J_2 are *both half-integral*, the lowest Ω value is 0, and there are equally many 0^+ 's and 0^- 's. If J_1 and J_2 are *both integral* there is an odd number of 0 's and the *odd one*, which appears in the last line of the above table, is 0^+ or 0^- according as the sum $J_1 + J_2 + \Sigma l_1 + \Sigma l_2$ (where l_1 and l_2 refer to the l values of the electrons in atoms 1 and 2) is even or odd. The relations (100) can be obtained in a manner analogous to (99),—cf. paragraph following (99). For further details, and for a discussion of the correlation between the case a or b states and corresponding case c states, reference should be made to Part IIc, pp. 114–5, and to reference 127.

3. Determination of Λ , S , and symmetry of molecular states from L and S values: both atoms of same element

If the two atoms forming a molecule are alike in atomic number, the rules for Λ and S or Ω values need to be supplemented by rules for the symmetry (g or u). There is also often a doubling in the number of states derived from a given pair of atomic states. The reason for the latter can be seen by the following considerations. Suppose we first consider two *isotopic* atoms, e.g., O^{16} and O^{18} , which may form a molecule. If O^{16} is in state L_1, S_1 , O^{18} in state L_2, S_2 , then the resulting molecular states are given by (99). Next suppose O^{16} is in the state L_2, S_2 and O^{18} in the state L_1, S_1 . We then get a *second* set of molecular states corresponding to (99), since the two states $O^{16}(L_1, S_1) + O^{18}(L_2, S_2)$ and $O^{16}(L_2, S_2) + O^{18}(L_1, S_1)$, although differing imperceptibly in energy, are obviously absolutely distinct. An exception must be made to this statement, to be sure, in case the two atoms have identical quantum numbers, in which case there is only *one* set of molecular states given by (99).

The results just stated hold equally well in case both nuclei are identical (e.g., both O^{16}), as can be shown rigorously by group theory methods.¹²³ If a molecule is formed from two atoms of the same element in different states (L_1, S_1) and (L_2, S_2), the resulting molecular states are exactly the same as for two atoms of different elements, as given in (99), *except that each term of given Λ and S occurs once as a g and again once as a u state* (but cf. Part IIc, p. 157, second paragraph). It should be noted that this rule applies just as much to the case where one atom is in an ionized state (e.g., $O, {}^3P + O^+, {}^4S$) as to the case when both are neutral. This is obvious when one recalls the pair of possibilities $(O^{16}) + (O^{18})^+$ and $(O^{16})^+ + (O^{18})$.

If a molecule is formed from two atoms of the same element in the same state, i.e., L and S and all other quantum numbers the same (except of course that J and M need not be the same in both), the resulting molecular states are the single set given by (99), but approximately half the states are g , half u , in accordance with the following schemes (since $L_1 = L_2 = L$, the last line in (99) reduces to the single term Σ^+ or Σ^-):

(a) If S is even ($S = 0, 2, \dots$)

$$\left. \begin{array}{l} (2L)_g, (2L-1)_g, (2L-2)_g, \dots, \Pi_g, \Sigma_g^+ \\ (2L-1)_u, (2L-2)_u, \dots, \Pi_u, \Sigma_u^- \\ (2L-2)_g, \dots, \Pi_g, \Sigma_g^+ \\ \dots \dots \dots \Pi_u, \Sigma_u^- \\ \Sigma_g^+ \end{array} \right\} \quad (99a)$$

(b) If S is odd ($S = 1, 3, \dots$),

$$\left. \begin{array}{l} (2L)_u, (2L-1)_u, (2L-2)_u, \dots, \Pi_u, \Sigma_u^+ \\ (2L-1)_g, (2L-2)_g, \dots, \Pi_g, \Sigma_g^- \\ \dots \dots \dots \Sigma_u^+ \end{array} \right\} \quad (99b)$$

The relations (99a) and (99b) have been demonstrated by group theory methods.¹²³

For convenience of reference, the different molecular states derivable from two atoms of the same element and in the same state are given for all the most important cases in Table XI, which is based on (99a) and (99b). The symmetry (g or u) of the *atoms* does not matter here, where it is the same for both. Table X (cf. *notes* to Table X) covers the case of two atoms of the same element in different states.

TABLE XI. *Molecular electron states derived from two like atoms both in the same state.*

Atomic State	Molecular States
1S	$^1\Sigma_g^+$
2S	$^1\Sigma_g^+, ^3\Sigma_u^+$
3S	$^1\Sigma_g^+, ^3\Sigma_u^+, ^5\Sigma_g^+$
4S	$^1\Sigma_g^+, ^3\Sigma_u^+, ^5\Sigma_g^+, ^7\Sigma_u^+$
1P	$^1\Sigma_g^+(2), ^1\Sigma_u^-, ^1\Pi_g, ^1\Pi_u, ^1\Delta_g$
2P	Singlets like 1P ; then $^3\Sigma_u^+(2), ^3\Sigma_g^-, ^3\Pi_g, ^3\Pi_u, ^3\Delta_u$
3P	Singlets like 1P ; triplets like 2P ; quintets same as singlets.
1D	$^1\Sigma_g^+(3), ^1\Sigma_u^-(2), ^1\Pi_g(2), ^1\Pi_u(2), ^1\Delta_g(2), ^1\Delta_u, ^1\Phi_g, ^1\Phi_u, ^1\Gamma_g$
2D	Singlets like 1D ; then $^3\Sigma_u^+(3), ^3\Sigma_g^-(2), ^3\Pi_g(2), ^3\Pi_u(2), ^3\Delta_u(2), ^3\Delta_g, ^3\Phi_g, ^3\Phi_u, ^3\Gamma_u$.

Note: The number of states of each kind is given in parentheses; if no such number is given, there is only one state of that kind.

3a. Determination of Ω values and symmetry from atomic J values: like atoms [This section may well be omitted by the general reader.]

The rules relating Ω values to J values in the case of two atoms of the same element are analogous to those relating Λ and S values to L and S values. *If a molecule is formed from two atoms of the same element in different states* (here it is sufficient if they differ in J alone), the resulting molecular states are exactly the same as for two atoms of different elements, as given in (100), *except that each term of given Ω occurs once as a g and again once as a u state.*¹²⁷

If a molecule is formed from two atoms of the same element in the same state, i. e., L, S, J and all other quantum numbers the same (except of course that M need not be the same), the resulting molecular states are given by (100a) or (100b), as follows:¹²⁶

(a) If J is integral (number of electrons even in each atom),

$$\begin{aligned} &(2J)_g, (2J-1)_g, \dots, 0^+_g \\ &\quad (2J-1)_u, \dots, 0^-_u \\ &\dots \dots \dots \\ &\quad 0^+_g. \end{aligned} \tag{100a}$$

(b) If J is half-integral (number of electrons odd in each atom),

$$\begin{aligned} &(2J)_u, (2J-1)_u, \dots, 0^-_u \\ &\quad (2J-1)_g, \dots, 0^+_g \\ &\dots \dots \dots \\ &\quad 0^+_g. \end{aligned} \tag{100b}$$

4. Energy relations in molecule formation; bonding and anti-bonding electrons and bonding power

Although the rules stated in sections C2 and C3 give the Λ and S , or Ω , values of all the molecular states derivable from two given atomic states, they yield no information as to the electron configurations nor as to the shapes of the various $U(r)$ curves. As for the latter, usually half or more of those derived from a given pair of atoms are curves with no minimum or else only a very shallow one at very large r . In such states the atoms repel each other at all but very large distances. Such highly unstable molecular states (*repulsive states*) are, however, not without importance, not only for molecular spectra but also in such phenomena as collisions of the second kind and the pressure broadening of atomic lines. In both of the latter phenomena, it is often valuable to think in terms of incipient molecule formation.¹²⁸ Besides strongly *attractive* and strongly *repulsive states*, intermediate types are to be expected.

It is possible by quantum mechanical methods to calculate approximately the various energies of interaction of two given atoms corresponding to various molecular states. In this way the course of the $U(r)$ curves for large r values can be approximately determined. The calculations, are, however, laborious, and have been carried out for only a few relatively simple cases as yet. The calculations and results are simplest when each atom is in an S state (Heitler and London¹²⁹). According to these calculations, two He atoms in their normal state (1S) should give only a repulsive $^1\Sigma$ state. A normal He atom and a normal H atom ($^1S+^2S$) should give only a repulsive $^2\Sigma$, according to Heitler and London. On the other hand, two unexcited 2S atoms of the same or of different elements (H, Li, Na, etc.) should give an attractive $^1\Sigma$ state (the normal state of the molecule) and a repulsive $^3\Sigma$ state. Similarly two like 4S atoms should give one strongly attractive $^1\Sigma^+_g$ state, one less

strongly attractive $^3\Sigma^+_u$, and two repulsive states $^5\Sigma^+_g$ and $^7\Sigma^+_u$. Some calculations have also been made on atoms in excited S states, and in P states.

London and Heitler have attempted to generalize the results of the calculations mentioned into a quantum-mechanical valence theory corresponding to that of Lewis. This theory, however, seems not to be acceptable. For a detailed discussion of the question, and for a different approach to the problem of valence, based on a consideration of molecular electron configurations, the reader is referred to articles elsewhere.¹³⁰

Experimental band spectrum data on the $^1\Sigma$ normal states of H_2 , Li_2 , Na_2 , each of which is derived from two unexcited 2S atoms, are in good agreement with calculations made by the method of Heitler and London. The predicted repulsive $^3\Sigma$ state of H_2 derived from two normal atoms is also known. Two unexcited He atoms repel each other except at large r values, as predicted. Two 4S nitrogen atoms give the predicted very stable $^1\Sigma^+_g$ and perhaps also the less stable $^3\Sigma^+_u$ state.¹³¹ The evidence therefore indicates that the energies of interaction of atoms often can be computed fairly accurately by the method of Heitler and London.

Experimental data show, however, that it is unsafe to generalize too far from calculations made for a limited number of cases. Thus although the repulsion of two 1S unexcited atoms is found in all the rare gases as in helium, there is evidence from band spectra that two 1S atoms of Ca, or Zn, or Hg give a mildly attractive molecular state.¹³² Again, in a number of cases of a 2S atom (hydrogen) plus a 1S atom (Be, Mg, Ca, Zn, Cd, Hg, cf. Fig. 40), more or less stable molecular states are formed. The heat of dissociation, D , although not large, probably runs as high as 1.5 volts or more. If we were to generalize from the predicted repulsive behaviour of $He+H$, we should expect the normal states of all the hydrides mentioned to be repulsive states.

Although the Heitler and London method makes possible more or less quantitative predictions as to the $U(r)$ curves of molecular states, at least in simple cases, long calculations are required. Qualitative predictions can usually be made much more easily by a consideration of electron configurations of atoms and molecule. This is especially true in the prediction of unknown or uncertain $U(r)$ curves of a molecule for which at least one curve is known empirically. In the case of two normal H atoms, for example, we learn from the rules which give Table XI that a $^1\Sigma^+_g$ and a $^3\Sigma^+_u$ molecular state must result. The $U(r)$ curve of the former is known from band spectrum data (cf. Fig. 46), and by comparison with the united-atom He, it is known that this state must have the electron configuration $(1s\sigma)^2$. Now we know that the lowest-energy $^3\Sigma^+_u$ state of the united-atom, when its nuclei are slightly separated, is one with the electron configuration $(1s)(2p\sigma)$. But since the energy of the $(1s)(2p)$, 3P state of the united-atom to which this corresponds is over 20 volts above that of the $(1s)^2$, 1S normal state to which $(1s\sigma)^2$, $^1\Sigma^+_g$ corresponds, and since D for the latter is only about 4 volts, it is evident that the $U(r)$ curve of the $^3\Sigma^+_u$ state in question must rise very rapidly as r decreases. This indicates a repulsive state. The electron-configuration method thus makes the same qualitative predictions as the Heitler and London method,

and goes beyond the latter in giving a more detailed *explanation* of why the $^3\Sigma$ state is repulsive. Similar results can be obtained in other cases.

The above method of drawing conclusions as to molecular energy levels by *interpolation between united-atom and separate atoms* has been used especially by Hund. Its weakness is that besides not being quantitative, it gives no very sure indication of the course of the $U(r)$ curves for large r values. Thus for example one could not predict that the $^3\Sigma^+_u$ state of H_2 might not have a rather shallow minimum at rather large r with possibly $D=0.5$ volt. In practice, however, behavior of this sort seems not to occur, except in cases where it can be predicted on good grounds (cf. second following paragraph).

In general, we find that electrons which become *promoted* as $r \rightarrow 0$ usually tend to give repulsive $U(r)$ curves, the more so the higher the energy of the promoted condition, while unpromoted electrons tend to give attractive curves. Electrons whose promotion is only incipient at $r=r_e$, however, like the K electrons in N_2 (cf. 90, 91), of course have practically no effect on the $U(r)$ curves.

In the following, we shall use the terms *bonding* and *anti-bonding electrons* respectively for electrons which tend to make the $U(r)$ curves attractive or repulsive, and *non-bonding* electrons for those which do not affect the $U(r)$ curves. Still more generally, one may attribute to each of the electrons in a molecule a certain *bonding power*, positive or negative. Bonding electrons tend to produce stable molecules, while anti-bonding electrons have the opposite effect. Examples of bonding and anti-bonding electrons, respectively, are the $1s\sigma$ and $2p\sigma$ electrons in H_2 , just discussed. A theory of valence, at least for diatomic molecules, can be constructed in terms of bonding and anti-bonding electrons (cf. section D7 and Ref. 130).

In some cases, notably e.g., that of the $x\sigma$ electrons in molecules like N_2 , electrons which for $r=0$ would be promoted to high-energy orbits (probably $3s$ in the case of $x\sigma$), act nevertheless as bonding electrons. This behavior of the $x\sigma$ electrons can easily be accounted for as follows.¹³⁰ As $r \rightarrow \infty$ the $x\sigma$ and $w\pi$ electrons usually become $2p$ electrons of the separated atoms, i.e. $x\sigma \rightarrow \sigma 2p$, $w\pi \rightarrow \pi 2p$ (cf. section A3). It can be shown that the effect of the electric axis alone would cause $\sigma 2p$ to be more firmly bound than $\pi 2p$ electrons, in very much the same way that $2p\sigma$ electrons are more firmly bound than $2p\pi$ electrons when a united-atom is divided into two parts (cf. section B4 and Table IX). If r is sufficiently large, the lowering in energy resulting from this cause may be expected to outbalance the increase in energy corresponding to the incipient promotion, so that $x\sigma$ may be more firmly bound than $w\pi$. This is very likely the case in the normal states of O_2 and F_2 , where r_e is large. When r is smaller, however, $x\sigma$ becomes relatively less firmly bound. In N_2 , $x\sigma$ and $w\pi$ are probably about *equally* firmly bound for $r=r_e$ of the normal state. Both types are bonding electrons. In CN, $x\sigma$ is *less* firmly bound than $w\pi$ for $r=r_e$ of the normal state, as is shown by the fact that this state $\cdots (w\pi)^4 (x\sigma)^2, ^2\Sigma^+$ for $r=r_e$ has a lower energy than the state $\cdots (w\pi)^3 (x\sigma)^2, ^2\Pi$. But for larger r values, the $U(r)$ curves of these two states probably cross (cf. Fig. 47), indicating that $x\sigma$ becomes more firmly bound than $w\pi$ for large r .

5. Discussion of CH and other hydrides as examples

We have already considered the correlation of the CH molecule with the N atom (section A2). The relations with the atoms C+H are equally interesting. The three lowest states of the C atom in order of increasing energy are 3P_g , 1D_g and 1S_g , all derived from the configuration $(1s)^2(2s)^2(2p)^2$. [The possibility may also be noted that the state 5S_u of $(1s)^2(2s)(2p)^3$ has an energy not far different from these three.] It is safe to assume that all the low-energy states of CH correspond on dissociation to a $1s$, 2S_g H atom, since all excited states of the H atom have high energy. We then have according to section C2 and Table X the following results for C+H: from 3P of carbon, $^2\Sigma^-$, $^2\Pi$, $^4\Sigma^-$, $^4\Pi$; from 1D , $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$; from 1S , $^2\Sigma^+$. We need not hesitate to identify the lower of the two predicted $^2\Pi$'s, that from 3P , with $\cdots (2p\sigma)^2(2p\pi)^2$, $^2\Pi$, the lowest known state of CH. Likewise we may safely identify the predicted $^4\Sigma^-$, $^2\Sigma^-$ from 3P and the $^2\Delta$, $^2\Sigma^+$ from 1D with the three observed states and the predicted $^4\Sigma^-$ associated with $\cdots (2p\sigma)(2p\pi)^2$.

Notice that the observed states $^2\Sigma^-$, $^2\Delta$, and $^2\Sigma^+$ of $\cdots (2p\sigma)(2p\pi)^2$ form a rather narrow group whose energy is over three volts higher than that of $\cdots (2p\sigma)^2(2p\pi)^2$, $^2\Pi$. This is in agreement with Eqs. (98), (98a). As has already been shown in section A6, the not yet observed $^4\Sigma^-$ state probably lies near the observed $^2\Pi$ state.

By means of Eqs. (98), (98a) we can now predict that the state $\cdots (2p\pi)^3$, $^2\Pi$ should lie about three volts higher, for a value of r equal say to r_e of one of the other states, than say the $^2\Delta$ state of $\cdots (2p\sigma)(2p\pi)^2$. Now this experimentally unknown $^2\Pi$ state can without reasonable doubt be identified with the predicted $^2\Pi$ from 1D of carbon. In view of what we know of the $U(r)$ curves of the lower $^2\Pi$ and the other states of CH (cf. Fig. 36), it is then evident that the upper $^2\Pi$ must represent essentially a repulsive state. This gives an explanation of the fact that no bands coming from this state have been found. The form of the $U(r)$ curve of this state can be approximately predicted and is shown dotted in Fig. 36.

We have now accounted for all the molecular states derivable from 3P , 1D , and 1S except $^4\Pi$ from 3P and $^2\Sigma^+$ from 2S . Our failure to have observed these can be attributed to their being states of repulsion. From our knowledge of the relative binding energies of different orbits in the united-atom and of the way they should be modified (Eqs. 98, 98a) in the molecule, it is evident that the lowest possible $^4\Pi$ state of CH would have, for an r value near r_e of one of the known stable states, a much higher energy than even the repulsive $^2\Pi$ state discussed above. This lowest $^4\Pi$ state would probably have the electron configuration $(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)(3s\sigma)$. The predicted $^2\Sigma^+$ state derived from $C(^1S)+H$, since the known $^2\Sigma^+$ state is the only one derivable from any configuration $(2p\sigma)^2(2p\pi)^2$, must be a state having high energy, e.g. that belonging to $(1s\sigma)^2(2s\sigma)^2(2p\pi)^2(3s\sigma)$.

Relations between atomic and molecular states similar to those in CH exist in all hydrides. Many such relations are shown more or less fully in Figs. 35-40. In the figures the electron configurations, if not given, usually can easily be worked out by the reader by a consideration of the low energy states

of the united-atom and the molecular states which they must give (cf. sections A2, B3, B4) in a strong electric field. In most hydrides, except NH and its analogues, the union of the two atoms gives rise to a relatively larger proportion of repulsive states than in CH. For such molecular states, electron configurations can usually be assigned tentatively just as for attractive states (cf. the repulsive ${}^4\Pi$ and ${}^2\Sigma^+$ states of CH), but there is usually little point in so doing.

5a. Electron configurations in hydrides; promotion of electrons in formation of hydrides

It is of interest to compare the electron configurations of CH and C+H. In all the stable states of CH, as well as the unstable ${}^2\Pi$, there is one more p electron than in the C atom,—cf. (90),—while in the unstable ${}^4\Pi$ and ${}^2\Sigma^+$ states mentioned above there is one more s electron. In the states associated with $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)$ and $(1s\sigma)^2(2p\sigma)(2p\pi)^2$ we may assume that a $2p\sigma$ electron is derived by promotion (cf. section A8) from the $1s$ H electron, and in the $(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)(3s\sigma)$, ${}^4\Pi$ and $(1s\sigma)^2(2s\sigma)^2(2p\pi)^2(3s\sigma)$, ${}^2\Sigma^+$ that the $3s\sigma$ is likewise derived from the H electron by promotion. In all these cases the remaining electrons are derivable without promotion from the original $(1s)^2(2s)^2(2p)^2$ configuration of the C atom.

Dealing in a similar manner with the unstable $(1s\sigma)^2(2s\sigma)^2(2p\pi)^3$, ${}^2\Pi$ of CH, it seems necessary to conclude that one $2p\pi$ electron is a promoted $1s$ electron of hydrogen. This, however, seems strange, since a $1s$ electron with $l=0$, would be expected to give only $\lambda=0$ (e.g., $2p\sigma$ or $3s\sigma$, as above). But there is no strict theoretical rule that individual λ 's must be conserved during the formation of a diatomic molecule, so that the assumption that this ${}^2\Pi$ is derived from $\cdots(2p)^2$, 1D is perfectly possible. What happens might be thought of as follows: the two $2p$ electrons of the C atom at first tend to give $(2p\sigma)(2p\pi)$, while the H electron tends to become $3s\sigma$. This would give a ${}^2\Pi$ companion to the unstable ${}^4\Pi$. But as the atoms come nearer the tentative grouping $(2p\sigma)(3s\sigma)$ changes over to $(2p\pi)^2$, thus giving $\cdots(2p\pi)^3$, ${}^2\Pi$. Another way of expressing this would be to suppose that the ${}^2\Pi$ derived from 1D tends to start out, for r very large, with a very repulsive $U(r)$ curve corresponding to $\cdots(2p\sigma)(2p\pi)(3s\sigma)$, but that this curve if continued would cross the $U(r)$ curve corresponding to $\cdots(2p\pi)^3$, ${}^2\Pi$. But since according to quantum mechanics two curves alike in Λ , S and all other sufficiently well-defined quantum numbers do not cross, it is likely that a crossing is avoided and that the ${}^2\Pi$ from $\cdots(2p)^2$, 1D becomes $\cdots(2p\pi)^3$, ${}^2\Pi$.

In hydrides the concepts of bonding and anti-bonding electrons are not particularly useful. Electrons like $3s\sigma$ in CH promoted from $1s$ of H can, however, be called anti-bonding and those like $2p\sigma$ from $1s$ can be called bonding; $2p\sigma$ electrons derived from the C atom in CH are also bonding.

Relations similar to those in CH are found also in other hydrides. *Usually the electron configuration of any state of a diatomic hydride can be accounted for by assuming that the electrons of the heavier atom are unchanged in respect to their quantum numbers except that they take on definite λ values while the H electron is promoted to the lowest-energy kind of σ orbit which is not*

already occupied by two electrons. For example, the H electron may be supposed to become $2s\sigma$ in the normal state of LiH, $3s\sigma$ in that of NaH, $2p\sigma$ in those of BeH, BH, CH, NH, OH, FH, $3p\sigma$ in those of MgH, AlH, SiH, etc., $3d\sigma$ in normal CaH, and $4p\sigma$, $5p\sigma$, $6p\sigma$ in ZnH, CdH, and HgH. The italicized rule just given suffices for all or practically all the known stable states of diatomic hydrides. Occasionally we may expect, however, to have to assume, as in the $\cdots (2p\pi)^3$ of CH, that the H electron is promoted to a π or other orbit, or else that it and the electrons of the other atom undergo somewhat involved changes. *Strictly speaking*, the assumption that only the H electron is involved in the changes called promotion is not accurate, but for most practical purposes it is convenient and justifiable.

6. Relations between atomic and molecular multiplet separations

A comparison of the spin multiplet separations in molecular electron states with those of the constituent atoms throws a considerable amount of light on the relations between the atomic and molecular states. Especially simple relations exist in the hydrides MH, where the l 's have practically the same meaning as in the M atom (cf. section C5a) and as in the united-atom (cf. section A2).

6a. Review of theoretical multiplet equations

In general, the energy differences between members of an ordinary multiplet can be described as differences in magnetic energy corresponding to different relative orientations of orbital and spin angular momentum vectors. Usually the energy of interaction between the spin of each electron and the magnetic field of *its own* orbital motion predominates over all other magnetic interactions, and we shall so assume in the following. In atoms, and in molecules with well-defined l 's, like the hydrides, one may write¹³³ for the *total multiplet-energy* Γ ,

$$\Gamma = \Sigma \gamma_r = \Sigma a_r l_r s_r \overline{\cos(l_r^*, s_r^*)}, \quad (101)$$

where the summation is to be taken over all electrons having $l > 0$ and not in closed shells. Each coefficient a_r is a measure of the energy of interaction between l_r^* and its S^* .

For a 2P atom containing, aside from closed shells, only a p electron ($l=1$), we have

$$\Gamma = \gamma = \frac{1}{2}a[j(j+1) - l(l+1) - s(s+1)], \quad (102)$$

where for a penetrating orbit, in cm^{-1} ,

$$a \sim R\alpha^2 Z_i^2 Z_a^2 / n_a^3 l(l + \frac{1}{2})(l + 1). \quad (103)$$

Here R is the Rydberg constant, α the fine structure constant, Z_i the effective nuclear charge for the *inner* part of the orbit, Z_a that for the outer part ($Z_a=1$ for a neutral atom), and n_a is the effective principal quantum number. In general, Γ for an atom reduces to the following form, originally given by Landé:

$$\Gamma = \frac{1}{2}A[J(J+1) - L(L+1) - S(S+1)], \quad (104)$$

where A is related in a simple manner to the a 's (cf. Table XII). Eq. (102) is a special case of Eq. (104) in which $A = a$, $L = l$, $S = s$.

We shall be interested in the following mainly in *over-all multiplet widths* $\Delta\nu$. $\Delta\nu$ is simply related to A and so to the a 's. For 2P ($L=1$, $S=\frac{1}{2}$), $\Delta\nu$ (${}^2P_{1\frac{1}{2}} - {}^2P_{\frac{1}{2}}$) = $3A/2$, for 3P , $\Delta\nu$ (${}^3P_2 - {}^3P_0$) = $3A$, and so on.

For a *molecule* containing, aside from closed shells, only a single electron, Eq. (101) yields

$$\Gamma = A\Lambda\Sigma = \gamma = a\lambda\sigma. \quad (105)$$

In general for a molecule the multiplet energy is given by

$$\Gamma = A\Lambda\Sigma \quad (106)$$

Eq. (105) is a special case in which $A = a$, $\Lambda = \lambda$, $\Sigma = \sigma$. Putting $\lambda = 1$ in Eq. (105) and taking the difference correspond to $\sigma = \pm \frac{1}{2}$, one gets

$$\pi, {}^2\Pi: \Delta\nu = a = A.$$

For the case of a ${}^3\Pi$ state resulting from the presence of a σ and a π electron, one gets¹³³

$$\sigma\pi, {}^3\Pi: \Gamma = A\Lambda\Sigma = \frac{1}{2}a\Lambda\Sigma, \quad (106)$$

$$\sigma\pi, {}^3\Pi: \Delta\nu = 2A = a, \quad (107)$$

where a refers to the π electron. Similarly for states $\cdots \pi^3, {}^2\Pi$ and $\cdots \sigma\pi^3, {}^3\Pi$ one finds respectively $A = -a$ and $A = -\frac{1}{2}a$, but in both cases $\Delta\nu = -a$.

Relations expressing A and $\Delta\nu$ in terms of a are given for a number of cases in Table XII.

TABLE XII. A and $\Delta\nu$ values for P and Π states.¹³³

State	A	$\Delta\nu$	State	A	$\Delta\nu$	State	A	$\Delta\nu$
$p, {}^2P$	a	$3a/2$	$p^3, {}^2D$ or 2P	0	0	$\pi, {}^2\Pi$	a	a
$sp, {}^3P$	$a/2$	$3a/2$	$p^4, {}^3P$	$-a/2$	$-3a/2$	$\sigma\pi, {}^3\Pi$	$a/2$	a
$p^2, {}^3P$	$a/2$	$3a/2$	$sp^4, {}^2P$	$-2a/3$	$-a$	$\pi^3, {}^2\Pi$	$-a$	$-a$
$sp^2, {}^2P$	$2a/3$	a	$sp^4, {}^4P$	$-a/3$	$-4a/3$	$\sigma\pi^3, {}^3\Pi$	$-a/2$	$-a$
$sp^2, {}^4P$	$a/3$	$4a/3$	$p^5, {}^2P$	$-a$	$-3a/2$			

Notes: (1) For any atomic multiplet level, the magnetic energy is given by Eq. (104), for any molecular multiplet level (for fixed nuclei) by Eq. (106). (2) The quantity a refers to the p or π electrons, of course. (3) The results hold only for ordinary coupling relations, and neglecting interactions of the l^* of one electron with the s^* 's and l^* 's of others. (4) The results for Π states assumed that there is no coupling of l_r 's to give an L .

6b. Applications to hydrides

The above theoretical results will now be applied to an interpretation of the observed multiplet separations in hydrides. In all the *stable* hydride states known, the molecular electron configuration is in agreement with the assumption that the union of the H atom with the M atom has the following results (cf. section C5a): (1) the n and l values of the M atom's electrons are preserved, but any resultant J 's and L 's of the M atom are broken up; (2) each M electron assumes a definite λ value ($\lambda \leq l$); (3) the H electron becomes some kind of a promoted σ electron, often forming, with one of the M atom elec-

trons, a closed shell; (4) the H nucleus acts on the whole electron system like a strong external electric field. The strengths of binding and the orbits of the electrons are essentially the same as for an M atom alone, except for the effects of the establishment of the λ 's. One might then expect the coupling constants a which measure the strength of magnetic interaction between each l^* and its s^* to be nearly the same as in the atom alone, being mainly determined (cf. Eq. (103)) by l , by Z_i of the M atom, and by n_a , which measures the strength of binding. (The part of each orbit near the M nucleus, which determines Z_i , should presumably not be greatly changed by the presence of the H nucleus, unless Z_i is small.)

By means of Table XII, we can determine, for an atom M containing one or more p electrons not in closed shells, the relation between the width $\Delta\nu$ of an atomic multiplet and the coupling constant a characteristic of the p electron or electrons. Likewise for a corresponding multiplet state of a molecule MH, we can determine a from the observed $\Delta\nu$ by using Table XII. We can then compare the a values of atom M and molecule MH. Such a comparison for p electrons is made in Table XIII. It will be seen that the agreements are very good. The molecular a values are usually about 0.9 as large as the corresponding atomic a values. This is perhaps because $p\pi$ electrons are likely to be less firmly bound (larger n_a in Eq. 103) than atomic p electrons: the effect of a strong electric field on p electrons causes $p\sigma$ electrons to be more, $p\pi$ electrons to be somewhat less firmly bound (cf. Eq. (97), which is applicable to a somewhat similar situation). Also possibly the effective Z_i is decreased by the presence of the H nucleus, which tends to attract the electrons away from the M nucleus.

Discussion of an example will make clearer the nature of the relations under discussion. In the $\cdots 6s6p$, 3P state of Hg, the over-all width $\Delta\nu$ ($^3P_2 - ^3P_0$) of the triplet is 6398 cm^{-1} . Since $\Delta\nu = (3/2)a$ for any sp , 3P state, $a = 6398 \times (2/3) = 4265$ for the $6p$ electron. For the molecule HgH, the width $\Delta\nu$ ($^2\Pi_{1/2} - ^2\Pi_{3/2}$) of the $\cdots (6s\sigma)^2(6p\pi)$, $^2\Pi$ state is 3696 cm^{-1} . Since $\Delta\nu = a$ for a $\cdots \pi$, $^2\Pi$ state, we have $a = 3696$ for the $6p\pi$ electron. This is 0.89 as large as a for the same ($6p$) electron in Hg.

Mecke¹³⁴ has compared $\Delta\nu$ of $^2\Pi$ of HgH with $\Delta\nu$ of $\cdots 6p$, 2P of Au (the atom preceding Hg), and with $\Delta\nu$ of $(6s)^2(6p)$, 2P of Tl (the united-atom corresponding to HgH). For Au, $\Delta\nu = 3816$, for Tl, $\Delta\nu = 7792$. Obviously $\Delta\nu$ of HgH agrees very well with $\Delta\nu$ of Au, but this must be considered somewhat fortuitous, since $\Delta\nu = a$ for $^2\Pi$ but $\Delta\nu = (3/2)a$ for 2P . When a values are compared instead of $\Delta\nu$'s, the agreement is much closer with Hg than with Au. It is also worthy of note that a of HgH is much nearer a of Hg than a of the united-atom Tl. This is, however, what would have been expected, since the H nucleus is only on the outskirts of the outer electron orbits and therefore very far from being united with the Hg nucleus to give a Tl nucleus.

The $^3\Pi$ state of NH is interesting. Although every $^2\Pi$ molecular state in Table XIII has—as expected—a $\Delta\nu$ about $2/3$ as large as that of the 3P atomic state from which it is derived, the $^3\Pi$ state of NH has a $\Delta\nu$ many times larger than that of the $\cdots (2p\pi)^3$, 2D state from which (cf. Fig. 37) it must

TABLE XIII. Multiplet widths and a values for M atoms and MH molecules.¹³³

M	Atom			Molecule		
	State	$\Delta\nu(\text{cm}^{-1})$	$a_M(\text{cm}^{-1})$	MH	State	$a_{MH}(\text{cm}^{-1})$
Be	... $2s2p, {}^3P$	3.02	2.01	BeH	... $(2s\sigma)^2 2p\pi, {}^2\Pi(r)$	1.97
Mg	... $3s3p, {}^3P$	60.6	40.4	MgH	... $(3s\sigma)^2 3p\pi, {}^2\Pi(r)$	35
Ca	... $4s4p, {}^3P$	158.1	105.5	CaH	... $(4s\sigma)^2 4p\pi, {}^2\Pi(r)$	80
Zn	... $4s4p, {}^3P$	579	386	ZnH	... $(4s\sigma)^2 4p\pi, {}^2\Pi(r)$	341
Cd	... $5s5p, {}^3P$	1713	1142	CdH	... $(5s\sigma)^2 5p\pi, {}^2\Pi(r)$	1013
Hg	... $6s6p, {}^3P$	6398	4265	HgH	... $(6s\sigma)^2 6p\pi, {}^2\Pi(r)$	3696
C	... $(2s)^2(2p)^2, {}^3P$	42.3	28.2	CH	... $(2s\sigma)^2(2p\sigma)^2 2p\pi, {}^2\Pi(r)$	28.4
Si	... $(3s)^2(3p)^2, {}^3P$	223	149	SiH	... $(3s\sigma)^2(3p\sigma)^2 3p\pi, {}^2\Pi(r)$	143
N	... $(2s)^2(2p)^2, {}^3D$	-5	83.1	NH	... $(2s\sigma)^2(2p\sigma)(2p\pi)^2, {}^2\Pi(i)$	~60?
P	... $(3s)^2(3p)^2, {}^3D$	15	298	PH	... $(3s\sigma)^2(3p\sigma)(3p\pi)^2, {}^2\Pi(i)$	~242
O	... $(3s)^2(3p)^2, {}^3S$	297.7	149	OH	... $(2s\sigma)^2(2p\sigma)^2(2p\pi)^2, {}^2\Pi(i)$	138
Cl ⁺	... $(2s)^2(2p)^4, {}^3P$	-224	661	Cl ⁺ H	... $(3s\sigma)^2(3p\sigma)^2(3p\pi)^2, {}^2\Pi(i)$	637
	... $(3s)^2(3p)^4, {}^3P$	-992				0.98
						0.86
						0.76
						0.88
						0.89
						0.87
						1.01
						0.96
						~0.7?
						~0.8
						0.93
						0.97

be derived. Theoretically $p^3, {}^2D$ has $\Delta\nu = A = 0$ according to Table XII; the observed $\Delta\nu = -5$ in the N atom is a result of some of the small interactions of I^* 's with the s^* 's of other electrons, neglected in obtaining Table XII. The observed much larger separation in NH shows that the original couplings of the l 's of the three $2p$ electrons to give $L=2$ in the N atom have been completely broken down in NH and replaced by separate λ -quantization, as expressed by the symbol $(2p\pi)^3$. This should give $\Delta\nu = -a$; the result is unchanged when the H electron, now become $2p\sigma$, is also considered in $\cdots (2p\sigma)(2p\pi)^3, {}^3\Pi$. The observed a , which is known only roughly, agrees well with the a of a $2p$ electron in the N atom, as observed in e.g. the atomic state $\cdots (2s)^2(2p)^23s, {}^2P$ (cf. Table XIII, also Table III of reference 133).—Analogous relations are found in PH.

6c. Applications to other molecules

The existing data on molecular multiplets in other than hydride molecules refer almost exclusively to ${}^2\Pi$ states belonging to $\cdots \pi$ and $\cdots \pi^3$ configurations, and to ${}^3\Pi$ states derived from $\cdots \pi\sigma$ or $\cdots \pi^3\sigma$. Furthermore, these molecular states are in all or practically all recorded cases (cf. Figs. 47–8 for some of these) derived from atoms in low-energy 2P or 3P or other states in which outer p electrons are responsible for the multiplet separations. There seems to be no general rule which can be conveniently stated as to the relations between atomic and molecular a 's. It is usually true, however, that the molecular a agrees roughly with the a of one or the other atom, or most often with the mean of the two atomic a 's. The reader can perhaps best be left to draw his own conclusions from the following Table XIV and Figs. 47–8.

D. ELECTRON CONFIGURATIONS, ELECTRONIC STATES AND DISSOCIATION PRODUCTS IN NON-HYDRIDE MOLECULES

1. Binding scheme for electron orbits

As we have already seen in previous sections, the order of binding of the various kinds of electron orbits is essentially the same in hydrides (sections A2, B4, C5, C5a) as in the corresponding united-atoms. But in molecules like CN, N₂, NO (sections A3, A7–9), where the two atoms are alike in atomic number or nearly so, the nature of the orbits and the order of binding are very different than in the united-atoms, and often resemble those of the separated atoms.

Fig. 43 shows schematically the approximate order of binding of the electron orbits in diatomic molecules composed of two atoms of the same element.¹³⁵ Fig. 44 is a similar diagram for a molecule composed of two atoms with somewhat unequal atomic numbers. Of course in reality the binding energy of any electron depends on what other electrons are present, and on how their L and S vectors are coupled, so the figures have only an approximate meaning. The figures are based partly on theoretical considerations, but largely on empirical evidence.

The ordinates qualitatively represent binding energy, decreasing as the ordinate increases, while the abscissas represent "reduced orbit-dimensions." By the "reduced orbit-dimension" ξ of any orbit in a molecule is here meant the value of r divided by the mean diameter of the orbit (cf. second following paragraph). In most molecules, $\xi \gg 1$ for the more firmly bound, inner, electrons, $\xi > 1$ for the outer or outermost of the electron orbits which are present in the unexcited molecule, while $\xi < 1$ only for excited electrons in large orbits.

TABLE XIV. Atomic a and molecular A values (non-hydride molecules).

Atom	State	a	Molecule	State	A
Be ⁺	$p, {}^2P$	4.7	BeF	$\pi^3\sigma^2(?), {}^2\Pi(i)$	-16.5
Be	$sp, {}^3P$	2.01	MgF	${}^2\Pi$	19?
B	$p, {}^2P$	10.2	CaF	${}^2\Pi$	72
C ⁺	$p, {}^2P$	43	SrF	${}^2\Pi$	277
C	$p^2, {}^3P$	28	BaF	${}^2\Pi$	630
N	$p^2 3s$	(80)	CaCl	${}^2\Pi$	76
O ⁺	$p^2 3s$	(270)	CaBr	${}^2\Pi$	219
O	$p^4, {}^3P$	149	CaI	${}^2\Pi$	426
F	$p^5, {}^2P$	271	SrCl	${}^2\Pi$	156
Cl	$p^5, {}^2P$	587	SrBr	${}^2\Pi$	321
Br	$p^5, {}^2P$	2457	SrI	${}^2\Pi$	554
I	$p^5, {}^2P$	5067	BaCl	${}^2\Pi$	389
Mg	$sp, {}^3P$	40	BaBr	${}^2\Pi$	545
Ca	$sp, {}^3P$	106	BaI	${}^2\Pi$	756
Sr	$sp, {}^3P$	387	SnCl	${}^2\Pi$	2360
Ba	$sp, {}^3P$	832	SnCl	${}^2\Delta$	274
Cu	$p, {}^2P$	166	CN	$\pi^3\sigma^2, {}^2\Pi(i)$	-52
Tl	$p, {}^2P$	5195	BO	$\pi^3\sigma^2, {}^2\Pi(i)$	-123
Sn	$p^2, {}^3P$	2285	C ⁺ O	$\pi^3\sigma^2, {}^2\Pi(i)$	-125
			CO	$\pi^4\sigma\pi, {}^3\Pi(r)$	93
			N ₂	$\pi^4\sigma\pi, {}^3\Pi(r)$	80
			NO	$\sigma^2\pi^4\pi, {}^2\Pi(r)$	124
			NO	$\sigma^2\pi^3\pi^2, {}^2\Pi(r)$	35
			O ⁺ O	$\sigma^2\pi^4\pi, {}^2\Pi(r)$	195
			O ⁺ O	$\sigma^2\pi^3\pi^2, {}^2\Pi(r)$	8

Notes: In the Table, the symbol ${}^2\Pi(i)$ means *inverted* ${}^2\Pi(A < 0)$, while ${}^2\Pi(r)$ means regular ${}^2\Pi(A > 0)$. Most of the data on molecular multiplet separations can be found without difficulty in the recent literature (cf. e.g. W. Weizel, Handbuch der experimentellen Physik, Ergänzungsband 1931). They are by no means exact except in a few cases. In regard to BeF, cf. R. S. Mulliken, Phys. Rev. **38**, 836, 1931; CaF and SrF, cf. A. Harvey, Proc. Roy. Soc. **133A**, 336, 1931; BaF, A. Harvey and F. A. Jenkins, Phys. Rev. **37**, 1709, 1931; CN, cf. Phys. Rev. **38**, 1075, 1931; N₂, cf. S. M. Naudé, Phys. Rev. **38**, 372 (1931); O₂⁺, D. S. Stevens, Phys. Rev. **38**, 1292 (1931). The data for the chlorides, bromides and iodides of the alkaline earth metals are from R. Mecke, Zeits. f. Physik **42**, 390 (1927); since these results are not based on a detailed analysis of the spectra, they should probably be accepted with some reserve.

In determining ξ for the purpose of constructing diagrams like Figs. 43 and 44 the mean diameter of the orbit is a quantity whose estimation is not always easy. When ξ is obviously *small*, the mean diameter can be assumed the same as that which the Bohr theory gives for such an orbit in the *united-atom* ($\xi = 0$). If ξ is obviously *large*, a suitable mean diameter is evidently obtained by assuming that the orbit in question is practically the same as it would be in one of the two separated atoms ($\xi = \infty$). For intermediate values of ξ , the appropriate "mean diameter" must be taken somewhere between values corresponding to $\xi = 0$ and $\xi = \infty$.

When ξ is considerably less than unity, the orbit is obviously nearly the

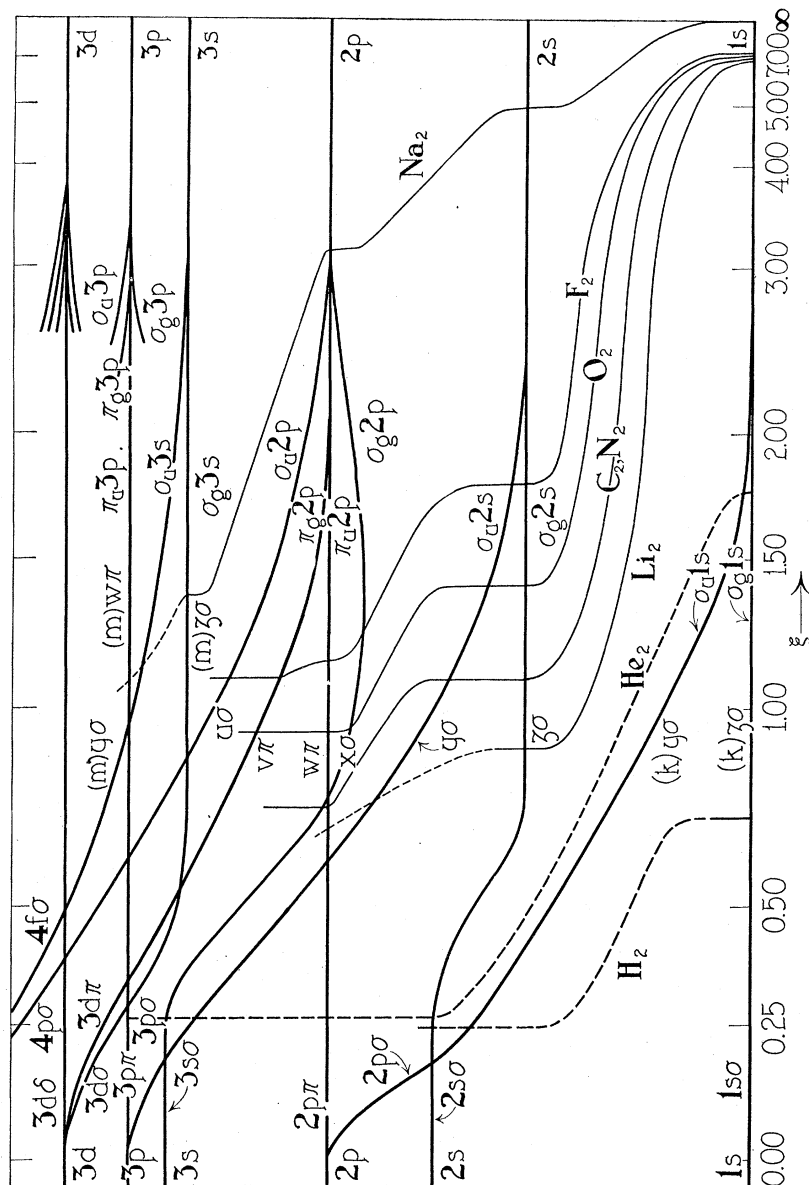


Fig. 43. Binding scheme of electron orbits for molecules whose nuclei are of the same element. Neither the abscissas ξ (distance between nuclei divided by mean diameter of electron orbit) nor the ordinates (negative energy of ionization of the electron) are plotted on a uniform scale, as will be seen from the figure. Also, from the nature of the figure, it is not possible for either ordinates or abscissas, especially the former, to have a quantitative significance. The ordinates on the right are, however, proportional to the logarithms of the binding energies of electrons in the N atom, except for the 2s level which has been arbitrarily shifted downward. Those on the left, except 2s, are proportional to a function of the logarithms of the binding energies of electrons in the Si atom, which is the united-atom corresponding to N₂. Thus the diagram is especially suited to the N₂ molecule, but is also satisfactory in a somewhat more qualitative way for other molecular states. The thin lines going upward and to the left indicate roughly for various molecules the actual ξ values of various orbitals, for stable molecular states. From these lines, the qualitative order of binding of orbit-types in each molecule can be seen, and at least a rough idea can often be obtained of the relative energy-differences between different orbit-types. (Cf. section D1 for further explanation.)

same as in the united-atom. The symbols $1s\sigma$, $2s\sigma$, $2p\sigma$, $\dots$ are then appropriate, and the order of binding is like that of the united-atom except for the λ subdivision. When $\xi > 1$, on the other hand, the orbits are more nearly like those in the separated atoms. In the union of two atoms of the same element (cf. later paragraph) each atomic s orbit can give either an even (σ_g) or an odd (σ_u) molecular orbit, of which the even one is the more firmly bound. If it is in the outer shell of the atom, it usually acts as a bonding electron while the less firmly bound σ_u electron has an anti-bonding action. Similarly each atomic p orbit can give an even or odd σ , or an even or odd π , orbit. Hence for large values of ξ , in molecules composed of two atoms of the same element,

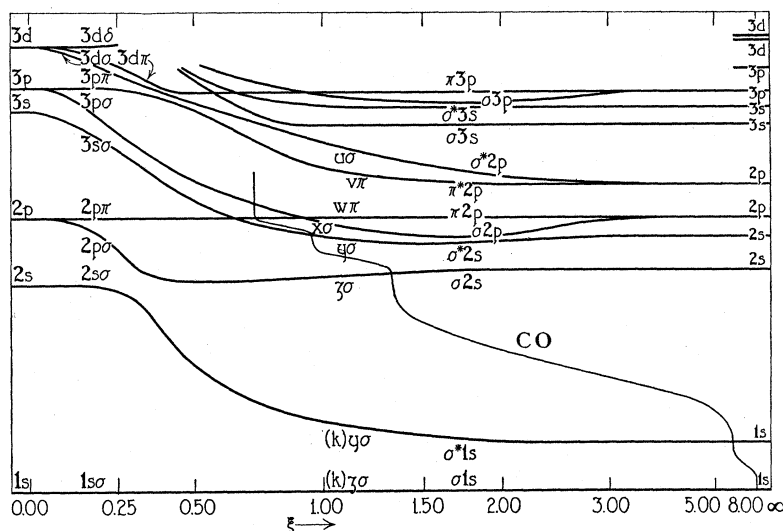


Fig. 44. Binding scheme of electron orbits for molecules with nuclei of moderately unequal charge. The figure is in most respects like Fig. 43. The ordinates on the right are proportional to the logarithms of the binding energies of electrons in the O atom (lower 1s, 2s, 2p, etc.) and in the C atom (upper 1s, 2s, 2p, etc.), those on the left correspond to the united-atom Si in the same way as in Fig. 43. The figure is qualitatively fairly correct also for other molecules composed of atoms which do not differ too much in the numbers and nature of their outer electrons.

such symbols as $\sigma_g 1s$, $\sigma_u 1s$, $\sigma_g 2s$, $\sigma_u 2s$, $\sigma_g 2p$, $\sigma_u 2p$, $\pi_u 2p$, $\pi_g 2p$ are appropriate. The types $\sigma_g 1s$, $\sigma_g 2s$, $\sigma_g 2p$, $\pi_u 2p$ are bonding electrons if derived from atomic outer-shell electrons, while the more strongly promoted types $\sigma_u 1s$, $\sigma_u 2s$, and so on, are anti-bonding. If the molecule is composed of two atoms not of the same element, the relations are similar, but the property of evenness or oddness is lacking, and the orbits corresponding to $\sigma_g 1s$, $\sigma_u 1s$, etc. may be designated $\sigma 1s$, $\sigma^* 1s$, and so on (cf. section A3). These latter designations can also be used if desired even when both atoms are of the same element.

When ξ is very large, electrons which are in closed shells in the two atoms can most conveniently be designated by letters K , L , and so on, as in (90). Such electrons are always non-bonding.

In designating electron orbits for ξ values near unity, it seems best to use the symbols $z\sigma$, $y\sigma$, and so on, introduced in section A3. In Figs. 43 and 44, to

be sure, continuous curves are given indicating the binding energy of each type of orbit such as $z\sigma$ or $y\sigma$ from $\xi=0$ to $\xi=\infty$, and these continuous curves establish definite correlations between the designations used for small, medium, and large values of ξ . It might then be thought sensible to use for all ξ values symbols determined in this way and all corresponding either to $\xi=0$ or else to $\xi=\infty$. But there are several reasons for not doing this, as follows.

(1) Symbols chosen for $\xi\sim 0$ or $\xi\sim\infty$ would usually for $\xi\sim 1$ be lacking in physical meaning (except the letters σ , π . . .), and would have a merely formal significance.

(2) The correlations are not entirely the same for molecules composed of two unlike atoms as for those of two like atoms (cf. Fig. 44 with Fig. 43). For instance, with like atoms, starting from $\xi=\infty$, we have $\sigma_u 1s$ as the second lowest orbit, and we find as ξ gets smaller, $\sigma_u 1s \rightarrow k\gamma\sigma \rightarrow 2p\sigma$. But with unlike atoms, starting with $\sigma^* 1s$, which corresponds to $\sigma_u 1s$, theory gives $\sigma^* 1s \rightarrow k\gamma\sigma \rightarrow 2s\sigma$. This is because the curves in Fig. 43 obey the following *correlation rule*: curves differing in λ can cross, but curves alike in λ can cross only if the one curve is g , the other u .

(3) The correlations given in the figures and obeying the rule just stated really cannot be relied on except when applied to the special case that there is just *one* electron in addition to closed shells. In making correlations in other cases, no strict rules can be given for the individual electrons, but only for the electron state (cf. Section C1). For example, a state which for fairly large ξ could most appropriately be described as $\cdots \pi_g \pi_u, {}^3\Sigma^+_u$ might have to be correlated for small ξ with a state most appropriately described as $\cdots \sigma_g \sigma_u, {}^3\Sigma^+_u$. Or one might for instance find the configuration $\cdots (y\sigma)(w\pi)^4(x\sigma)^2$, belonging to a ${}^2\Sigma^+_u$ state, going over as $r \rightarrow \infty$ into $(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_u 2p)$ instead of into the configuration $\cdots (\sigma_u 2s)(\pi_u 2p)^4(\sigma_g 2p)^2$ which Fig. 43 would predict. The ${}^2\Sigma^+_u$ state of N_2^+ (cf. section D7 for further details) quite possibly behaves in just this way.

In determining which of a set of states known for one value of r are to be correlated with which of a corresponding set known for another value of r , one can expect only that Λ , S , and any symmetry properties of the electron state as a whole (g or u , and $+$ or $-$ in the case of a Σ state), also Ω in case a , will be preserved if r is varied (cf. section C1.) Even Λ and S are not necessarily preserved if they are strongly coupled; in this case Ω is preserved.

An additional example may be instructive. If for large ξ one has, as in the normal state of He_2 , the state $(\sigma_g 1s)^2(\sigma_u 1s)^2, {}^1\Sigma^+_g$, one would probably expect as $\xi \rightarrow 0$ to get not $(1s)^2(2p\sigma)^2, {}^1\Sigma^+_g$ but the lower-energy state $(1s)^2(2s\sigma)^2, {}^1\Sigma^+_g$. In He_2^+ , on the other hand, with only one $\sigma_u 1s$ electron in addition to a closed shell, one *must* get $(\sigma_g 1s)^2\sigma_u 1s, {}^2\Sigma^+_u \rightarrow (1s\sigma)^2 2p\sigma, {}^2\Sigma^+_u; (1s\sigma)^2 2s\sigma, {}^2\Sigma^+_g$ is impossible because it is even.

In Figs. 43, 44, the thin lines which start vertically from the bottom of the figures show for several molecules the observed or probable order of binding of their electrons. Each thin line is drawn assuming for r a constant value representing roughly an average of the r_e values of stable states of the molecule in question. Each thin line is drawn as an unbroken line through one or more

intersections with the heavy lines corresponding to those orbits which are present in the molecule in its normal state, and is then continued as a dashed line into the region of orbits which are present only in excited states of the molecule in question. It will be noticed that the thin lines go always toward lower ξ values as they go up, corresponding to the fact that the less firmly bound orbits in any molecule are larger, hence ξ smaller since a fixed value of r is assumed for each molecule. It will also be noticed that, as the nuclear charge Z increases from molecule to molecule, ξ gets steadily larger for any given kind of electron. This is because the corresponding orbit-sizes get smaller with increasing Z , not only absolutely but also relatively to r_e . In Fig. 43 the r_e values decrease from Li_2 to N_2 , but the orbit sizes probably decrease faster, while from N_2 to F_2 the r_e 's increase and the orbit-sizes decrease.

Comparing Fig. 44 with Fig. 43, it will be noted that for a molecule with a given number of electrons, the energy differences between $\sigma 1s$ and $\sigma^* 1s$, $\sigma 2s$ and $\sigma^* 2s$, and usually also between $\sigma 2p$ and $\pi 2p$, tend to be larger if the nuclei are unequal than if they are equal. An explanation of this, evident from Fig. 44, is that corresponding energy differences usually exist even for $r = \infty$ when the nuclei are unequal, but not when they are equal.

In the case of hydrides, where the inequality of the nuclei is greatest, Fig. 44 is no longer appropriate. The binding scheme is, however, very simple in this case, as already noted ($1s\sigma$, $2s\sigma$, $2p\sigma$, etc.). Strictly speaking, there should be a different figure for every different degree of inequality between the nuclei.

In their general pattern, Figs. 43 and 44 have a rather simply describable theoretical basis, while their quantitative details are based on both theoretical and empirical evidence. The general pattern of Fig. 43 is merely that of the electron states of the one-electron molecule H_2^+ (Fig. 45), modified to take into account the main effects of the interactions between different electrons; Fig. 44 is similarly related to the diagram for a one-electron molecule with unequal nuclei. The excited electron states of H_2^+ are, to be sure, known only from theoretical calculations, but the latter can be accepted in this case as a reasonably reliable substitute for experimental data.

For $\xi = 0$, Fig. 43 represents merely the order of binding of electrons in an atom (the united-atom); for small ξ , the λ subdivision of the orbit-types appears. For $\xi = \infty$, Figs. 43 and 44 represent the order of binding in the two separated atoms, thought of as a single system; thence going backward, there appears for ξ large but not infinite the λ subdivision of the orbit-types. If the two atoms are equal, the possible energies of binding are less varied for $\xi = \infty$ (cf. Fig. 43) than if they are unequal (Fig. 44). But for $\xi < \infty$ this difference is removed by the fact that in Fig. 43 each atomic orbit-type (n, l, λ) *splits into two*, of which *one is even* (g), *one odd* (u). Correlation of the orbit-types for large ξ with those for small ξ can be effected by the rule stated previously that the orbit of given λ and symmetry which is lowest for small ξ goes into the lowest corresponding orbit for large ξ , and so on.

When two atoms unite, *each* separated-atom electron of given n and l has

in general a choice as to what λ value it will assume, and in the case of equal atoms as to whether it will become g or u . But if there is more than one such electron of given n and l , then the possible choices are more or less restricted by the Pauli principle. How this works out will be clear from the examples treated in the following sections. The examples also illustrate some other points, connected with the correlation of molecular states with the states of the separated atoms.

2. Behavior of atomic 1s electrons in formation of molecules. Pauli principle. Applications to low-energy states of H_2 , He_2 , HeH and others

If we start at $r = \infty$ with the system $H^+ + H(1s)$, the 1s electron may choose either to be of the bonding type $\sigma_g 1s$ which as $r \rightarrow 0$ goes over to " $kz\sigma$ "

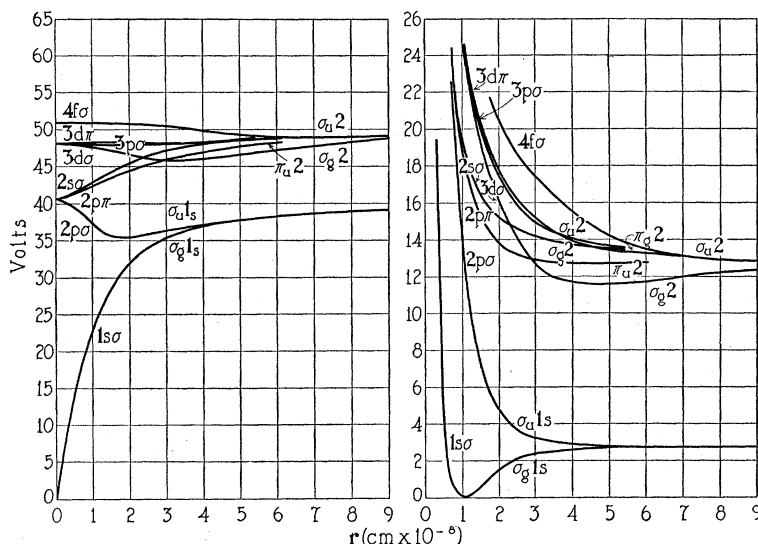


Fig. 45. (a) Electronic energies as functions of r , and (b) $U(r)$ curves, for H_2^+ molecule. The curves in Fig. 45a differ from those in 45b only in that the energy of repulsion of the nuclei (e^2/r) has been subtracted. The curves are based on quantum-mechanical calculations of Burrau and Hylleraas ($1s$ state), and Teller, except near $r=0$ where they have in part been interpolated in a plausible way.

and then to $1s\sigma$ (normal state of H_2^+) or to be of the anti-bonding type $\sigma_u 1s$, which goes over to " $k\gamma\sigma$ " and finally to $2p\sigma$. Here the Pauli principle makes no demands.

If we start at $r = \infty$ with two H nuclei and two 1s electrons there are three possibilities for the resulting H_2 molecule: $(\sigma_g 1s)^2$, $(\sigma_g 1s)(\sigma_u 1s)$, and $(\sigma_u 1s)^2$. As $r \rightarrow 0$, these become respectively $(1s\sigma)^2$, $(1s\sigma)(2p\sigma)$, and $(2p\sigma)^2$ or probably $(2s\sigma)^2$. The third of these we shall refer to hereafter as $(2p\sigma)^2$, for the sake of simplicity and because the designation is probably more nearly correct than $(2s\sigma)^2$ for the observable r values. The first and third of these, as a result of the Pauli principle, give each only one ($^1\Sigma_g^+$) molecular state, the second gives two ($^3\Sigma_u^+$ and $^1\Sigma_u^+$). The Pauli principle here does not restrict the

choice of each electron to become $\sigma_g 1s$ or $\sigma_u 1s$, but it does limit the number of molecular *states* by excluding the two conceivable ${}^3\Sigma_g^+$ states derivable one from $(\sigma_g 1s)^2$ and one from $(\sigma_u 1s)^2$.

There are, however, some other restrictions of a kind which are very common in the formation of diatomic molecules. Two unexcited H atoms, each $1s, {}^2S$, are capable according to Table XI of giving a ${}^1\Sigma_g^+$ and a ${}^3\Sigma_u^+$ state. The ${}^1\Sigma_g^+$ might be either $(1s)^2$ or $(2p\sigma)^2$ but is undoubtedly essentially the former (cf. the rule in section C1). This is the normal state of H_2 , with two bonding electrons, corresponding to an ordinary valence bond. The ${}^3\Sigma_u^+$ is evidently $(1s)(2p\sigma)$, ${}^3\Sigma_u^+$, with no valence bond (one bonding outweighed by one anti-bonding electron).

But what then becomes of the $(1s)(2p\sigma)$, ${}^1\Sigma_u^+$ and the $(2p\sigma)^2$, ${}^1\Sigma_g^+$ which are supposed also to be obtained from two H atoms with two $1s$ electrons? They can be accounted for if we use $H^+ + H^- [(1s)^2, {}^1S]$ as starting point. These give (cf. Table X, Notes), one ${}^1\Sigma_u^+$ and one ${}^1\Sigma_g^+$ state, as desired.

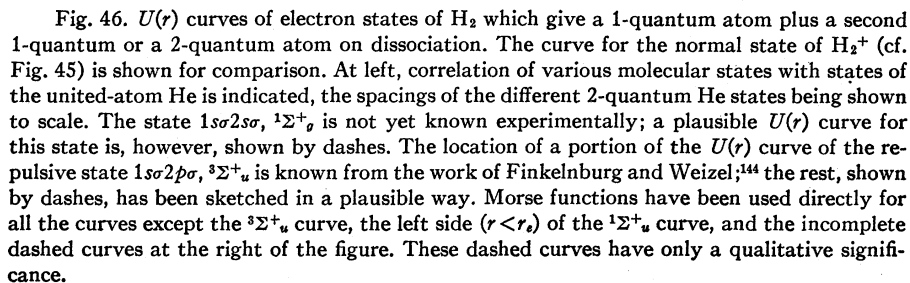
Actually, however, $(1s)(2p\sigma)$, ${}^1\Sigma_u^+$ of H_2 is not derived from $H^+ + H^-$, but instead (cf. Fig. 46), in accordance with the rule stated in section C1 and with the considerations advanced in (3) of section D1, it is derived from $H(1s) + H(2s, p)$, which is the lowest state of $H + H$ capable of giving a ${}^1\Sigma_u^+$ molecule. Similarly, $(2p\sigma)^2$, ${}^1\Sigma_g^+$ is probably derived from $H(1s) + H(?)$. These two states lost to $H^+ + H^-$ must of course be replaced by some other ${}^1\Sigma_u^+$ and ${}^1\Sigma_g^+$ states of H_2 .

If we start with $He[(1s)^2, {}^1S] + He^+[1s, {}^2S]$, the Pauli principle allows only $(\sigma_g 1s)^2(\sigma_u 1s)$, ${}^2\Sigma_u^+$ (two bonding electrons and one anti-bonding electron) and $(\sigma_g 1s)(\sigma_u 1s)^2$, ${}^2\Sigma_g^+$ (two anti-bonding electrons and one bonding electron) for the resulting molecule He_2^+ ; the configurations $(\sigma_g 1s)^3$ and $(\sigma_u 1s)^3$ are excluded. This is of course also in agreement with the demands of Table X (cf. footnote of Table X), according to which one expects one ${}^2\Sigma_u^+$ and one ${}^2\Sigma_g^+$ state.

If we start with $He[(1s)^2, {}^1S] + H[1s, {}^2S]$, we get (see Table X) only one, ${}^2\Sigma^+$, state of HeH (a repulsive state according to Heitler and London¹²⁹). This is evidently the $(\sigma 1s)^2(\sigma^* 1s)$, ${}^2\Sigma^+$ state analogous to $(\sigma_g 1s)^2(\sigma_u 1s)$, ${}^2\Sigma_u^+$ of He_2^+ . The $(\sigma 1s)(\sigma^* 1s)^2$, ${}^2\Sigma^+$ state analogous to $(\sigma_g 1s)(\sigma_u 1s)^2$, ${}^2\Sigma_g^+$ of He_2^+ can be accounted for if we start with $He^+[1s, {}^2S] + H^-[(1s)^2, {}^1S]$. Actually, however, similarly to certain states of H_2 just discussed, the $(\sigma 1s)(\sigma^* 1s)^2$ state of HeH is presumably derived from $He[(1s)^2, {}^1S] + H[2s, p]$.

Finally, if we start with $He, (1s)^2 + He, (1s)^2$, only $(\sigma_g 1s)^2(\sigma_u 1s)^2$, ${}^1\Sigma_g^+$ is allowed by the Pauli principle. This is a repulsive state because of the large energy of promotion of the two $\sigma_u 1s$ anti-bonding electrons, which outweighs the attraction produced by the two $\sigma_g 1s$ bonding electrons. It will be noticed that here *where the 1s shells are filled in both atoms, only a single molecular state consisting of closed shells is formed*. An analogous result is expected for analogous reasons whenever two atoms come together whose electrons are wholly in closed shells.

Whenever a molecule is formed from two atoms each containing a complete *K* shell, i.e., the group $(1s)^2$, we may expect in the molecule to find



$(\sigma_g 1s)^2(\sigma_u 1s)^2$ if the nuclei are alike, or $(\sigma 1s)^2(\sigma^* 1s)^2$ if they are unlike but not too greatly different in nuclear charge. Since ξ is large for these electrons in molecules containing other electrons outside, they are best regarded as essentially unchanged atomic K shells and may reasonably be designated $(K)(K)$ or KK . The two K shells of course tend to repel each other, just as in He_2 , but ξ is always so large that the repulsion energy is negligible compared with the interactions between the outer electrons of the two atoms.¹³⁶ In other words, buried K electrons are non-bonding when molecules are formed.

3. Behavior of two-quantum atomic electrons in molecule-formation. Energy-level schemes of Li_2 , BeF , BO , CN , N_2 , CO , NO , O_2 , F_2 , Ne_2

Let us consider what happens to the two-quantum electrons of the separated-atoms when a molecule is formed. In the well-understood case of $\text{H}^+ + \text{H}$ we get from $\text{H}^+ + \text{H}(2s, p)$, for large r values, the following orbit-types, with binding energy decreasing in the order named: $\sigma_g, \sigma_u, \pi_u, \pi_g, \sigma_g, \sigma_u$. For $r=0$, these respectively become $3d\sigma, 4f\sigma, 2p\pi, 3d\pi, 2s\sigma$, and $3p\sigma$ (cf. Fig. 45). It is not sensible here to distinguish between $2s$ and $2p$ orbits of the H atom, since the energy difference between them is negligible compared with the effects soon produced by the H^+ ion as it approaches.

But in most atoms, $2s$ and $2p$ differ greatly in energy, and for large r we then expect $\sigma_g 2s, \sigma_u 2s, \sigma_g 2p, \sigma_u 2p, \pi_u 2p, \pi_g 2p$ probably in the order named. In the case of unequal atoms we expect $\sigma 2s, \sigma^* 2s, \sigma 2p, \sigma^* 2p, \pi 2p, \pi^* 2p$. In either case, the orbits in the order named are alternately bonding and anti-bonding. That the $\sigma 2p$ orbits come below the $\pi 2p$ in energy is to be expected from the general rule that σ comes below π for any atomic orbit under the influence of an axially symmetrical disturbing electric field (cf. section B4).—The correlations as $r \rightarrow 0$ are shown in Figs. 43 and 44.

Empirical evidence shortly to be discussed indicates that for $r=r_e$ the order of binding of the molecular electrons derived from two-quantum atomic electrons is as follows: $z\sigma, y\sigma, x\sigma$ or $w\pi, w\pi$ or $x\sigma, v\pi, u\sigma$. Usually (cf. Figs. 43 and 44) $z\sigma$ is to be correlated with $\sigma_g 2s$ or $\sigma 2s$, $y\sigma$ with $\sigma_u 2s$ or $\sigma^* 2s$, $x\sigma$ with $\sigma_g 2p$ or $\sigma 2p$, $w\pi$ with $\pi_u 2p$ or $\pi 2p$, $v\pi$ with $\pi_g 2p$ or $\pi^* 2p$, and $u\sigma$ with $\sigma_u 2p$ or $\sigma^* 2p$. We turn now to the evidence.

The normal state of Li_2 is $(K)(K)(z\sigma)^2, {}^1\Sigma^+_g$, derived from two normal Li atoms $(K)2s, {}^2S$. Here $z\sigma$ is evidently correlated with $\sigma_g 2s$, a bonding type. Two normal Li atoms, like two H atoms, should according to theory give a ${}^3\Sigma^+_u$ state (probably repulsive) as well as a ${}^1\Sigma^+_g$. The ${}^3\Sigma^+_u$ is doubtless $(K)(K)(z\sigma)(y\sigma)$, where $z\sigma$ and $y\sigma$ are respectively even and odd and are to be correlated with $\sigma_g 2s$ and $\sigma_u 2s$. The anti-bonding action of $y\sigma$ probably outweighs the bonding action of $z\sigma$ to make the ${}^3\Sigma^+_u$ state repulsive.

Two excited states of Li_2 are known, the lower a ${}^1\Sigma^+_u$, the higher a ${}^1\Pi_u$. There cannot be much doubt that these are $(K)(K)(z\sigma)(y\sigma), {}^1\Sigma^+_u$ and $(K)(K)(z\sigma)(w\pi), {}^1\Pi_u$, respectively, and that they are derived from one normal atom and one $(K)(2p), {}^2P$ excited atom. In the ${}^1\Sigma^+_u$ state the $y\sigma$ electron must be correlated with $\sigma_u 2p$, instead of with $\sigma_u 2s$ as in the repulsive ${}^3\Sigma^+_u$ state. Exceptionally, it seems here not to have a definite anti-bonding action.

The case is like that in H_2 where the $2p\sigma$ electron in $(1s)(2p\sigma)$, $^1\Sigma_u^+$ is correlated with a 2-quantum H electron of $H+H'$ instead of with a $1s$ electron of H^++H^- (cf. section D2).

It is useful next to consider N_2 . (BeF, BO, CN will be discussed later in this section, Be_2 , B_2 , BeO and C_2 in section D6). According to calculations by the method of Heitler and London,¹²⁹ the normal state of N_2 should be a strongly attractive $^1\Sigma_g^+$ state derived from two normal atoms. These are $(1s)^2(2s)^2(2p)^3$, 4S . Experimentally,¹³⁷ N_2 has a $^1\Sigma$ normal state. The electron configuration must be composed of closed shells, since otherwise there would be excited states of low energy derived from the same configuration, of which there is no experimental evidence. The $^1\Sigma$ must then be $^1\Sigma_g^+$, since only this is possible for a set of closed shells, and two like atoms.

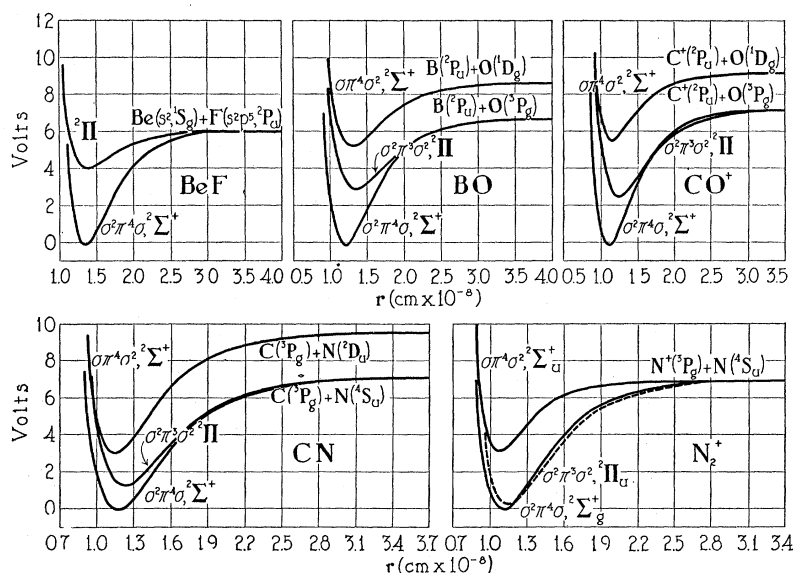


Fig. 47. $U(r)$ curves of low-energy electron states of BeF, BO, CO^+ , CN, and N_2^+ ; dashed lines represent a predicted state. The dissociation products of the observed states are not in all cases quite certain, but it is assumed in the figures that each molecular state dissociates into the lowest-energy pair of atomic states that the theory permits. The energies of dissociation are more or less uncertain in all cases. It should be noted that there are many other low-energy states of the dissociated atoms besides those shown; for example, $C(^1D) + N(^4S)$ is intermediate in energy between the two atom-pairs $C(^3P) + N(^4S)$ and $C(^3P) + N(^2D)$ shown on the diagram, while $C(^1S) + N(^4S)$ and others are close above $C(^3P) + N(^2D)$.

The nature and relative binding energies of the various closed shells in N_2 can be investigated by a consideration of the electron states of N_2^+ , and of certain other molecules with the same number of electrons. The lowest known, probably normal, state of N_2^+ is a $^2\Sigma_g^+$ state.¹³⁸ Such a state could be obtained from the $^1\Sigma_g^+$ normal state of N_2 only by removal of an even (g) σ electron; and we conclude that N_2 contains as its most loosely bound shell (or nearly so—see below) two such electrons.

About 3 volts above the normal state of N_2^+ is a $^2\Sigma^+_u$ state (cf. Fig. 47). This is known from the familiar "negative nitrogen bands", which are a $^2\Sigma^+_u \rightarrow ^2\Sigma^+_g$ transition. The most probable interpretation of the $^2\Sigma^+_u$ state is that it is obtained from normal N_2 by removing an electron from a second closed shell, which must then contain two *odd* σ electrons somewhat more firmly bound than the pair of even σ electrons. These odd σ electrons, as we shall see, correspond to the $y\sigma$ electrons already discussed in connection with Li_2 .

Further information is obtained from the known electron states of BeF, BO, CO^+ , CN (cf. Fig. 47), all of which contain thirteen electrons like N_2^+ . The lowest known, probably normal, state of each of these is a $^2\Sigma$ state, as in N_2^+ (cf. (90) in section A3). A few volts higher, as in N_2^+ , is another $^2\Sigma$ state (except perhaps in BeF, where such a state is not yet known, very likely because its energy is relatively higher than for BO and the rest). Between the two $^2\Sigma$ states is in each case an inverted $^2\Pi$ state (cf. Table XIV and section C6c for data on and discussion of the doublet separations). Reference to Table VIII shows that such a state can be accounted for most simply if the electron configuration contains three equivalent π electrons (π^3) in addition to closed shells. A consideration of all the evidence shows that this explanation is the correct one, except probably for BeF (see below). These π electrons we shall call $w\pi$. In the $^2\Sigma$ states mentioned, and in the normal state of N_2 , we must assume four of these, forming a closed shell $(w\pi)^4$.

Still more firmly bound than the two $y\sigma$ (anti-bonding), four $w\pi$ (bonding) and two $x\sigma$ (bonding) electrons in N_2 , although we have no direct experimental evidence of their presence, are presumably the two K shells (non-bonding) and two (bonding) $z\sigma$ electrons as in the normal state of the six-electron molecule Li_2 . (For a more detailed discussion of the bonding characteristics of the various electrons, cf. reference 130.)

All the evidence is in harmony with the following assignments of electron configurations:

CO and N_2 (lowest state):

$$(K)(K)(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2, ^1\Sigma^+(\text{in } N_2, ^1\Sigma^+_g)$$

BeF, BO, CN, CO^+ , N_2^+ (lowest known state of each):

$$(K)(K)(z\sigma)^2(y\sigma)^2(w\pi)^4x\sigma, ^2\Sigma^+(\text{in } N_2^+, ^2\Sigma^+_g) \quad (108)$$

BO, CN, CO^+ (second lowest state):

$$(K)(K)(z\sigma)^2(y\sigma)^2(w\pi)^3(x\sigma)^2, ^2\Pi$$

BO, CN, CO^+ , N_2^+ (third lowest state):

$$(K)(K)(z\sigma)^2(y\sigma)(w\pi)^4(x\sigma)^2, ^2\Sigma^+, (\text{in } N_2^+, ^2\Sigma^+_u).$$

[In the case of the $^2\Pi$ state of BeF, there is some doubt as to whether the electron configuration given for BO and the rest in (108) is applicable. The smallness of the doublet separation (cf. Table XIV) suggests that the $^2\Pi$ of BeF is a hybrid having largely the characteristics of a $\cdots (w\pi)^4(\cdots \pi), ^2\Pi$ state, which would be regular.]

According to these assignments, the three known states of CO^+ are respectively obtainable from the normal state of CO by removing an electron from the $x\sigma$, the $w\pi$, or the $y\sigma$, closed shell.

Presumably N_2^+ has three states similarly related to the normal states of N_2 , although one of these, the $^2\Pi$, has not yet been found. This can be explained if the $^2\Pi$ lies close to the known $^2\Sigma^+_g$ state of N_2^+ . Consideration of the series of thirteen-electron molecules BeF, BO, CN, N_2^+ indicates that this is probable: for in the first three members of this series, the interval between the lower $^2\Sigma^+$ and the $^2\Pi$ (also, incidentally, the interval between the two $^2\Sigma$ states) gets less as the nuclei become more nearly equal in charge (cf. Fig. 47). If the $^2\Pi$ in N_2^+ is $^2\Pi_u$ it can combine spectroscopically with the $^2\Sigma^+_g$ state but not with the $^2\Sigma^+_u$ state above it (cf. Part IIc, section D2, p. 96). If the $^2\Pi_u$ is very near the $^2\Sigma^+_g$ (either above or possibly below), the resulting bands would be in the infrared; this would account for the fact that they have not been detected. The absence of visible bands would also be accounted for if the $^2\Pi$ were $^2\Pi_g$ and were close to the $^2\Sigma^+_u$ state, but the trend of the $^2\Pi$ levels observed in the series BeF, BO, and CN does not support this explanation. It is also very improbable that the $^2\Pi$ combines only with the upper $^2\Sigma$ in N_2^+ in view of the fact that in BO and CN it combines far more strongly with the *lower* $^2\Sigma$. (In CO^+ , however, combination also with the upper $^2\Sigma$ seems to be fairly strong.) That the $^2\Pi$ in N_2^+ is $^2\Pi_u$ is also very probable on theoretical grounds, since in H_2^+ the most firmly bound π electrons are odd ($\pi_u 2p$).

The conclusion that N_2^+ has a $^2\Sigma^+_g$ and a $^2\Pi_u$ state of about equal energy shows that in N_2 the $w\pi$ and $x\sigma$ electrons are bound about equally firmly. In molecules with unequal nuclei, like CN, CO, BO, as we have seen, $w\pi$ electrons are distinctly more firmly bound, for $r=r_e$, than $x\sigma$ electrons. Reference should here be made to the end of section C4 for an explanation of these results. From this, it seems probable that for large r values, or better, *large ξ values*, $x\sigma$ electrons are more firmly bound than $w\pi$, but that for smaller ξ values, especially with unequal nuclei, the order is reversed.

In the molecule N_2 or CO, the four K electrons are of course far more firmly bound than the ten outer electrons. The latter are divided into four closed shells differing in binding energy by comparatively small steps. After these four, a comparatively large jump in binding energy is required to reach the next shell. This follows from the absence of any low-energy excited states of N_2 , and also from a consideration of the molecule NO. NO has a regular $^2\Pi$ normal state (cf. Fig. 48). The obvious interpretation of this fact is that one new π electron, which we shall call $v\pi$, has been added to the group of closed shells which is doubtless present in the normal state of NO^+ (cf. (90) in section A3). The ionizing potential of NO, which is approximately the binding energy of the $v\pi$ electron, is only 9.4 volts, as compared with about 16 volts for the $x\sigma$ electron in N_2 and presumably more for $x\sigma$ in NO. This fact, and the great decrease in dissociation energy for NO as compared with NO^+ or N_2 (cf. Table XVII), show that the $v\pi$ orbit-type is strongly anti-bonding.

Before continuing the discussion of NO and other molecules which in the normal state have one or more $v\pi$ electrons, it will be convenient to take up

the *excited states* of CO and N₂. Unfortunately, in spite of repeated efforts on the part of Hund, the writer, and others, it is not yet possible to assign electron configurations to these excited states with confidence. It therefore seems

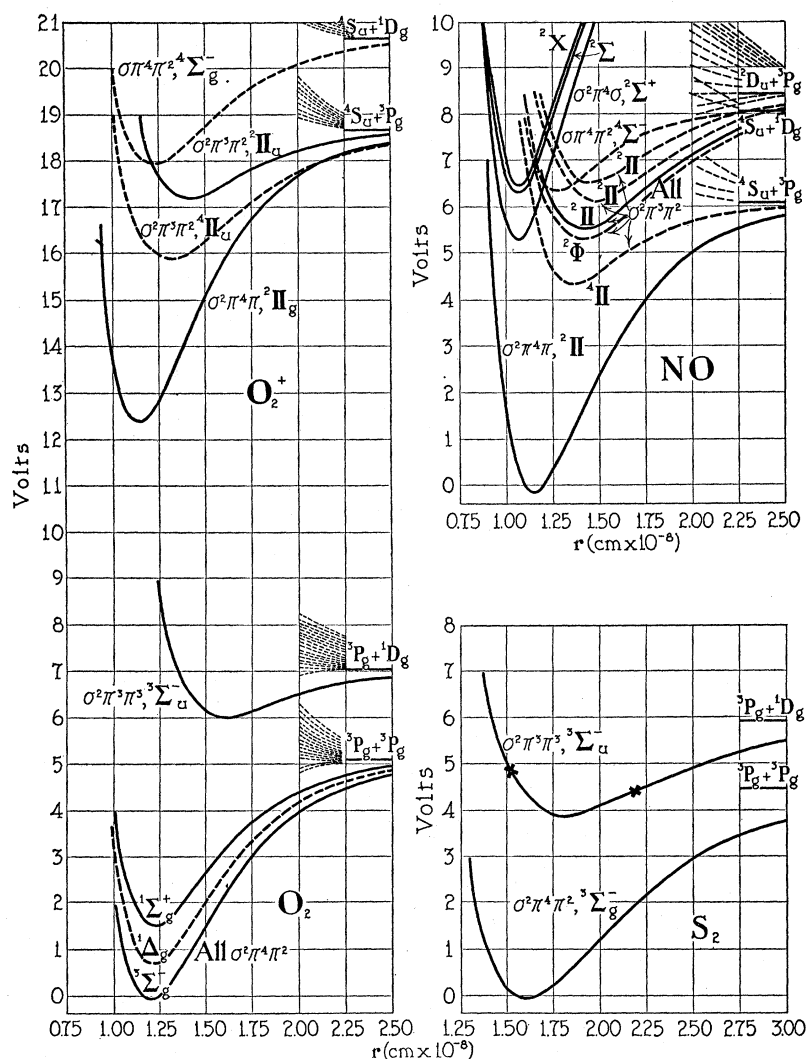


Fig. 48. $U(r)$ curves of known and (dashed lines) some predicted states of O_2 , O_2^+ , NO, and S_2 . There is a possibility that the predicted $4\Sigma^-$ and 4Π states of O_2^+ are the upper and lower states of the visible O_2^+ bands, whose structure has not yet been analyzed. Other predicted curves for O_2^+ analogous to those shown for NO could also have been drawn. The numerous predicted curves derived from $O(^3P)+O(^3P)$, $O(^3P)+O(^1D)$, $O(^4S)+O(^3P)$, $O(^4S)+O(^1D)$, $N(^4S)+O(^3P)$, $N(^4S)+O(^1D)$ and $N(^2D)+O(^3P)$ are all indicated qualitatively in the figure. Predicted curves of S_2 , which would be analogous to those of O_2 , are not shown. Two points of intersection of one,—or perhaps two,—of these predicted curves with the known $3\Sigma^-u$ curve are, however, shown by crosses. Their existence is indicated by predissociation phenomena.

best here only to give certain general rules which should govern the assignments, and to give plausible assignments for some of the best-known states.

Probably nearly all of the known excited states of N_2 and CO could be derived by displacing *one* electron from some one of the orbits normally occupied (i.e., from $x\sigma$, $w\pi$, $y\sigma$, and perhaps also from $z\sigma$) to one of the following orbits: $v\pi$, $u\sigma$ (cf. discussion of Ne_2 and F_2), and orbits derived from 3-quantum atomic orbits, of which $\sigma 3s$, $\sigma 3p$, $\sigma 3d$, $\pi 3p$, $\pi 3d$, $\delta 3d$ are the most probable. It seems likely that orbits derived from 3-quantum atomic orbits will behave more or less like the excited electron orbits in He_2 (cf. section D5), i.e., often like united-atom orbits. Another way of expressing what has just been said about excited states of CO and N_2 is that probably nearly all could be derived by adding one electron (in a $v\pi$, $u\sigma$, or atomic-3-quantum orbit) to one of the states ($^2\Sigma^+$, $^2\Pi$, $^2\Sigma^+$ discussed already, and possibly others) of CO^+ or N_2^+ .

From our knowledge of NO, O_2^+ , O_2 , and F_2 it seems clear that the $v\pi$ orbit comes next after $x\sigma$ and $w\pi$ in order of firmness of binding. Granting this, it seems highly probable that among the lowest excited states of CO and N_2 should be those obtainable by adding a $v\pi$ electron to a CO^+ or N_2^+ ion in its two lowest states $\cdots (y\sigma)^2(w\pi)^4x\sigma$, $^2\Sigma^+$ and $\cdots (y\sigma)^2(w\pi)^3(x\sigma)^2$, $^2\Pi(^2\Sigma^+_g$ and $^2\Pi_u$ in N_2^+). The following states would then be expected for N_2 :

$$\begin{aligned} &\cdots (y\sigma)^2(w\pi)^4(x\sigma)(v\pi), \ ^3\Pi_g \text{ and } ^1\Pi_g \\ &\cdots (y\sigma)^2(w\pi)^3(x\sigma)^2(v\pi), \ ^1\Sigma^-_u, \ ^3\Delta_u, \ ^3\Sigma^+_u, \ ^3\Sigma^-_u, \ ^1\Delta_u, \ ^1\Sigma^+_u. \end{aligned}$$

The same states would be expected for CO, except that no g and u labels can be assigned.

In CO one might expect the average energy of the first group to be considerably lower than that of the second, since the $^2\Sigma^+$ normal state of CO^+ is about 2.5 volts lower than the $^2\Pi$. In N_2 , however, one might expect a much smaller difference, since there is probably not much difference in energy between the normal $^2\Sigma^+$ and the $^2\Pi$ of N_2^+ . As for the energy order of the different members in each group, one would pretty definitely expect the $^3\Pi$ to be below the $^1\Pi$, probably by about two volts. In the $(w\pi)^3(v\pi)$ group, prediction is less certain, but a consideration of the wave-functions for the various states indicates¹³⁹ that the energy order would be about as given above.

The lowest known excited state of CO is a $^3\Pi$. This $^3\Pi$ (upper state of Cameron bands) and a $^1\Pi$ (upper state of fourth positive bands) are respectively 5.98 and 7.99 volts above the normal state of CO. Most probably these are the states $\cdots (w\pi)^4(x\sigma)(v\pi)$, $^3\Pi$ and $^1\Pi$. The fact that these states have considerably smaller ω_e (and presumably larger r_e) than the $^2\Sigma^+$ state of CO^+ support this assumption, since just such changes are to be expected when an anti-bonding electron is added (cf. effects of adding $v\pi$ to NO^+ and to O_2^+). The second lowest excited state of CO is what may be a $^3\Sigma$ state. It is at 7.14 volts up, and has a very low ω_e (1182 as against 2212 for the normal state of CO^+). This state may be a $^3\Sigma$ of $\cdots (w\pi)^3(x\sigma)^2(v\pi)$. The $^2\Pi$ state $\cdots (w\pi)^3(x\sigma)^2$ of CO^+ already has a rather large r_e and a small ω_e so that the very low ω_e of this $^3\Sigma$ is just what one would expect. A number of other singlet and trip-

let excited states of CO are known, but it does not seem possible as yet to assign electron configurations with any confidence. (The suggestion which has been made that some of these excited states are quintet states is improbable because it would require the excitation of two electrons, and is very improbable because of the interpretations it assumes of the structures of certain CO bands.)

Far fewer band systems and energy levels of N_2 are known than of CO. This is no doubt a result of the limitations on possible transitions imposed by the selection rule $g \longleftrightarrow u$ in N_2 . The lowest excited singlet level of N_2 whose existence has been definitely established is the upper level of the Lyman-Birge-Hopfield emission and absorption bands, at 8.50 volts above the normal state of N_2 . This has usually been interpreted as a ${}^1\Pi$ level analogous to the ${}^1\Pi$ of CO at 7.99 volts. If so, it must be ${}^1\Pi_u$, since the normal state of N_2 is ${}^1\Sigma_g$. But $\cdots (w\pi)^4(x\sigma)(v\pi)$ must give ${}^1\Pi_g$ (and ${}^3\Pi_g$), if $v\pi$ is an even $\pi(\pi_g)$ as we have so far assumed and as is theoretically necessary if it is derived from a $2p$ atomic orbit. (Atomic $2p$ is capable of giving two types of molecular π orbits, one $\pi_u 2p$, which undoubtedly becomes $w\pi$ when r gets small enough, and one $\pi_g 2p$, which presumably becomes $v\pi$.) It seems likely, then, that the N_2 level at 8.50 volts is not a ${}^1\Pi_u$ but ${}^1\Sigma^+_u$ level, very likely the predicted one corresponding to $\cdots (w\pi)^3(x\sigma)^2(v\pi)$.

The N_2 molecule has four well-known triplet levels, namely a ${}^3\Sigma$ (lower level of first positive bands), a ${}^3\Pi$ 1.17 volts higher and with $A \sim +80$ (upper level of first positive bands and lower level of second and fourth positive bands), a second ${}^3\Pi$ (upper level of second positive levels) 3.69 volts above the first, and finally a level which is probably ${}^3\Sigma$ or ${}^3\Delta$, is 5.45 volts above the lower ${}^3\Pi$, and is the upper level of the fourth positive bands. Unfortunately the positions of these triplet levels have not been accurately fixed with reference to the normal state either of N_2 or of N_2^+ . According to measurements by Sponer on the excitation potential of the second positive bands, the upper ${}^3\Pi$ is 13 volts above the normal state of the molecule. This would give 8.18 volts for the ${}^3\Sigma$. Duncan, however, finds 12 volts for the position of the upper ${}^3\Pi$.

According to Naudé's recent analysis of the first positive bands,¹³¹ these must be either ${}^3\Pi_g \rightarrow {}^3\Sigma^+_u$ or ${}^3\Pi_u \rightarrow {}^3\Sigma^-_g$, since (cf. Part IIc, section K) Naudé finds the "strong" levels in the ${}^3\Sigma$ state to be those with odd K values. It would be hard to interpret a ${}^3\Sigma^-_g$ state by means of any other electron configuration than $\cdots (w\pi)^3(x\sigma)^2(v\pi)$ with $v\pi$ of the odd type (π_u). Also the ${}^3\Pi_u$ in ${}^3\Pi_u \rightarrow {}^3\Sigma^-_g$ would most naturally be interpreted as $\cdots (w\pi)^4(x\sigma)(v\pi)$, again with $v\pi$ odd. But as we have already seen in the second preceding paragraph, there are strong theoretical objections against $v\pi$ being odd.

If we assume ${}^3\Pi_g \rightarrow {}^3\Sigma^+_u$ to be correct, the following electron configurations become plausible: $\cdots (y\sigma)^2(w\pi)^3(x\sigma)^2(v\pi)$, ${}^3\Sigma^+_u$; $\cdots (y\sigma)^2(w\pi)^4(x\sigma)(v\pi)$, ${}^3\Pi_g$; and for the upper ${}^3\Pi$, $(y\sigma)(w\pi)^4(x\sigma)^2(v\pi)$, ${}^3\Pi_u$. The energy difference 3.65 volts between the two ${}^3\Pi$ states agrees well with what according to the present interpretation is a corresponding interval in N_2^+ , namely the 3.15 volts difference between $\cdots (y\sigma)^2(w\pi)^4(x\sigma)$, ${}^2\Sigma^+_g$ and $\cdots (y\sigma)(w\pi)^4(x\sigma)^2$, ${}^2\Sigma^+_u$.

The r_e and ω_e values of the various states (and of the singlet state earlier discussed, if it is $^1\Sigma^+_u$), all support the interpretation just given. In all these excited states, r_e is considerably larger and ω_e considerably smaller than in unexcited N_2 or N_2^+ , as would be expected in view of the anti-bonding character of $v\pi$. Furthermore, r_e is largest, ω_e smallest, for the $^3\Sigma$, as might have been predicted.

Various objections can be raised against the interpretation just given. The most important is that it practically forces us to assume that the triplet levels of N_2 are all about 2 volts, or at least 1.5 volts, lower than Sponer's excitation potential data indicate. This would bring the $^3\Sigma^+_u$ level down to, say, 6.5 volts. Such a value is, however, probably not unreasonable if the singlet state of N_2 at 8.5 volts is the corresponding $^1\Sigma^+_u$. If the $^3\Sigma^+_u$ level is at 6.5 volts, the $^3\Pi_g$ level is at 7.7 volts. If these results are accepted, the $\pi^3\sigma^2\pi$, $^3\Sigma^+_u$ level of N_2 is 0.6 volts lower, the $\pi^4\sigma\pi$, $^3\Pi_g$ level 1.7 volts higher, than the corresponding level in CO; in other words $\pi^4\sigma\pi$, $^3\Pi$ is relatively 2.3 volts lower in CO than in N_2 . This is reasonable, since $\pi^4\sigma$ in CO^+ is 2.5 volts lower than $\pi^3\sigma^2$, while $\pi^4\sigma$ in N_2^+ is little if at all lower than $\pi^3\sigma^2$. It is of interest to note that the energy required to produce $\pi^3\sigma^2$ from the unexcited molecule by ionization of a π electron is almost the same in CO and N_2 .

It has just been stated without explanation that the present interpretation practically requires the energy of $^3\Sigma^+_u$ to be as low as 6.5 volts. The explanation is as follows. We know that two unexcited (4S) atoms of nitrogen must give one $^1\Sigma^+_g$ state (the normal state of N_2), one $^3\Sigma^+_u$ state, one $^5\Sigma^+_g$, and one $^7\Sigma^+_u$ (cf. Table XI). There seems to be no good reason why the $^3\Sigma^+_u$ state so predicted should not be identified with the $^3\Sigma^+_u$ state of N_2 which we have been discussing. But the known vibrational levels of the latter extend to 2.1 volts above the level $v=0$. Hence the energy of $v=0$ of $^3\Sigma^+_u$, if it dissociates into two unexcited atoms, must be at the very least 2.1 volts below the energy of dissociation D of N_2 . If D of normal N_2 is 9.4 volts, and the $^3\Sigma^+_u$ is 6.5 volts up, its D would have the not impossible value of 2.9 volts. But the weight of evidence indicates that D of normal N_2 is lower than 9.4 volts, perhaps 8.2 volts, while the excitation potential work indicates that the $^3\Sigma$ is higher than 6.5 volts up; and even the value 2.9 volts is dangerously close to the minimum possible value 2.1 volts. Further work is evidently necessary before we shall have a sure understanding of the electron configurations of the excited states of N_2 and CO.¹⁴⁰

The lowest known state of O_2^+ is a regular $^2\Pi$ state, presumably with the same electron configuration as the normal state of NO. Theoretical considerations make it practically certain that $v\pi$ in O_2 corresponds to the predicted $\pi_g 2p$, in spite of indications from certain excited levels of N_2 , already discussed, that it is odd. Neutral O_2 (Fig. 48) has a $^3\Sigma$ normal state. The structure of the atmospheric absorption bands ($^1\Sigma \leftarrow ^3\Sigma$ with only odd K values present in the $^3\Sigma$ state) shows (cf. Part IIc, section K) that their lower state is either $^3\Sigma^-_g$ or $^3\Sigma^+_u$. Since $^3\Sigma^-_g$ is what is predicted as the lowest state of a configuration $\cdots \pi^2$ (cf. Table VIII), it is doubtless the correct alternative,

and unexcited O_2 is then $\cdots (v\pi)^2, {}^3\Sigma^-_g$. Since ξ must be fairly large even for the outer orbits, we presumably have the binding order indicated by

$$\cdots (x\sigma)^2(w\pi)^4(v\pi)^2.$$

Probably ξ is so large for the orbits $z\sigma$ and $y\sigma$ in O_2 that they can definitely be correlated with $2s$ orbits of the separated atoms and that they can best be described as $\sigma_g 2s$ and $\sigma_u 2s$. For the normal state of O_2 we may then write:

$$(K)(K)(\sigma_g 2s)^2(\sigma_u 2s)^2(x\sigma)^2(w\pi)^4(v\pi)^2, {}^3\Sigma^-_g.$$

This description implies that the first two shells in O_2 are essentially unchanged atomic K shells, the next two are somewhat modified atomic $2s$ shells, while the remaining electron orbits are strongly modified as compared with their condition in the separated atoms.

Granting that the normal state of O_2 is $\cdots (v\pi)^2, {}^3\Sigma^-_g$, there should be two other stable states ${}^1\Delta_g$ and ${}^1\Sigma^+_g$ with the same electron configuration and slightly higher energy (cf. section A6). These two states should be metastable, since transitions from Δ_g or Σ^+_g to Σ^-_g would violate the usual (dipole) selection rules (Part IIc, p. 149) and since it is extremely improbable that other electron states exist, between the ${}^3\Sigma^-_g$ and the ${}^1\Delta_g$ and ${}^1\Sigma^+_g$, which would remove the metastability. Actually, however the atmospheric absorption bands probably correspond to the forbidden transition ${}^1\Sigma^+_g \leftarrow {}^3\Sigma^-_g$. The ${}^1\Sigma^+_g$ is 1.62 volts above the ${}^3\Sigma^-_g$; according to theoretical considerations,¹¹⁸ the ${}^1\Delta_g$ is probably about halfway between ${}^1\Sigma^+_g$ and ${}^3\Sigma^-_g$ (cf. Fig. 48).

Childs and Mecke¹⁴¹ have shown that the absorption intensities in the atmospheric bands of O_2 are of the order of 10^{-8} times as large as in ordinary bands. This is so weak as to represent really an extraordinarily high degree of obedience to the dipole selection rules. As a matter of fact, the observed intensity would be about right for a quadrupole transition. The observed band-lines, which, if the upper level is ${}^1\Sigma^+_g$, go only from $+$ rotational levels to $+$ rotational levels and so violate the dipole selection rules, are in agreement with the selection rules for a quadrupole transition ${}^1\Sigma^+_g \leftarrow {}^3\Sigma^-_g$. There is, however, one difficulty, namely that this would be an *intersystem* quadrupole transition and its intersystem character should almost certainly, according to the theory,¹¹⁴ reduce the intensity by a further factor of probably about 10^{-4} , making 10^{-12} altogether, as compared with the observed 10^{-8} . The most probable way out of this difficulty is to suppose that we are after all not really dealing with a quadrupole absorption, but that the observed intensity owes its existence almost entirely to disturbing effects, such as collisions between gas molecules, which tend to break down the usual selection rules and to induce an otherwise forbidden dipole transition. [In the discussion of these bands in Part IIc, section D1, p. 96, it was concluded that they are probably ${}^1\Sigma^-_u \leftarrow {}^3\Sigma^-_g$ or possibly ${}^1\Sigma^+_g \leftarrow {}^3\Sigma^-_g$. The former should, however, have a transition probability probably of the order of 10^{-4} times that of an ordinary transition, as compared with the observed 10^{-8} . (This last figure was not known when Part IIc was written.) Also, it is very diffi-

cult in terms of electron configurations to explain the existence of a ${}^1\Sigma^-_u$ state so near the ${}^3\Sigma^-_g$.]

The most important excited states of O_2^+ can probably be understood by considering the result of removing an electron from each of the various outer orbits of O_2 , just as we were able to explain the three observed states of CO^+ by considering the removal of an electron from each of the three outermost orbits in CO . If we remove a $v\pi$ electron from $\cdots (w\pi)^4(v\pi)^2$, we get the normal state of O_2^+ , $\cdots (w\pi)^4v\pi$, ${}^2\Pi_g$. If we remove a $w\pi$ electron from $\cdots (w\pi)^4(v\pi)^2$, ${}^3\Sigma^-_g$, we get $\cdots (w\pi)^3(v\pi)^2$, ${}^4\Pi_u$ or ${}^2\Pi_u$, of which the latter may reasonably be identified with the upper state of the ultraviolet O_2^+ bands. Additional states $\cdots (w\pi)^3(v\pi)^2$, ${}^2\Pi_u$ and ${}^2\Phi_u$ of O_2^+ should be obtained by removing a $w\pi$ electron from the metastable state $\cdots (w\pi)^4(v\pi)^2$, ${}^1\Delta_g$ of O_2 . From $\cdots (v\pi)^2$, ${}^1\Sigma^+_g$ of O_2 , still a third ${}^2\Pi_u$ of O_2^+ with the same electron configuration must be obtained. From $\cdots (x\sigma)^2(w\pi)^4(v\pi)^2$, ${}^3\Sigma^-_g$ by removal of one $x\sigma$ electron a ${}^4\Sigma^-_g$ and a ${}^2\Sigma^-_g$ state must be obtained. Possibly the visible O_2^+ bands represent a transition from this ${}^4\Sigma^-_g$ to the ${}^4\Pi_u$ mentioned above (cf. Fig. 48), but it has not yet been possible to analyze their structure and so determine their nature.

It may seem strange that of the three predicted ${}^2\Pi_u$ states belonging to $\cdots (w\pi)^3(v\pi)^2$, only one is known, since all three should combine with the normal state of the molecule. One plausible explanation is that while the known ${}^2\Pi_u$ is obtained by direct ionization of a ${}^3\Sigma^-_u$ molecule, the unknown ones could be obtained directly only by ionization of the metastable states ${}^1\Delta_g$ and ${}^1\Sigma^+_g$ of O_2 . Evidence that the ${}^2\Pi_u$ of O_2^+ is really related to ${}^3\Sigma^-_g$ of O_2 in the way suggested is given by the small positive A value (cf. Table XIV) of the observed ${}^2\Pi$. By a consideration of the interaction of the two groups of electrons $(w\pi)^3$ and $(v\pi)^2$, by means of the vector model, it can be shown that (1) when π^2 is constituted as in ${}^3\Sigma^-_g$, an A value much less than a of $w\pi$ or $v\pi$, but probably positive, is to be expected, while (2) when π^2 is as in ${}^1\Delta_g$, $A \sim +a$ of $w\pi$ is expected, and (3) when π^2 is as in ${}^1\Sigma^+_g$, $A \sim -a$ of $w\pi$ is expected. Probably a of $w\pi$ is not far different from a of $v\pi$, whose value is 195 according to data on the normal state of O_2^+ , which is $\cdots v\pi$, ${}^2\Pi$, with $A = a$ (cf. Table XIV). The observed $A = +8$ of ${}^2\Pi_u$ of O_2^+ is evidently in agreement with the interpretation given here.

The observed excited ${}^2\Pi$ state of NO , with $A = +35$, and the normal ${}^2\Pi$ state with $A = +124$ (upper and lower states of the NO β bands), are analogous to the two states of O_2^+ . In both NO and O_2^+ , the excited ${}^2\Pi$ has a much larger r_e and smaller ω_e and D than the normal state, in agreement with our supposition that the excited ${}^2\Pi$ contains one more anti-bonding ($v\pi$) and one less bonding ($w\pi$) electron. The bonding effects of the $w\pi$ and $v\pi$ electrons can be compared with especial directness by considering the ionization of the state $\cdots (v\pi)^2$, ${}^3\Sigma^-_g$ of O_2 . Here $r_e = 1.20$ A, $\omega_e = 1585$, $D = 5.09$ volts. On removing an anti-bonding $v\pi$ electron, giving normal O_2^+ , we find $r_e = 1.14$ A, $\omega_e = 1876$, $D = 6.15$ volts. But on removing a bonding $w\pi$ electron to get the observed ${}^2\Pi_u$ excited O_2^+ , we find $r_e = 1.41$ A, $\omega_e = 869$, $D = 1.4$ volts (cf. Fig. 48).

The $^2\Sigma^+$ initial state of the γ bands of NO has $r_e = 1.06\text{\AA}$, $\omega_e = 2375$, $D \sim 10$ volts (cf. section D7), contrasting strikingly with the $^2\Pi$ initial state of the β bands, which has almost the same energy, but $r_e = 1.43\text{\AA}$, $\omega_e = 1038$, $D = 2.9$ volts. As compared with the $^2\Pi$ normal state, with $r_e = 1.15\text{\AA}$, $\omega_e = 1906$, $D = 6.1$ volts, the upper $^2\Pi$ state shows a marked decrease, the $^2\Sigma^+$ a marked increase in stability. This indicates that in the $^2\Sigma$ state the $v\pi$ anti-bonding electron of the normal state has been replaced by a bonding electron, which must be some kind of a σ electron, probably unpromoted and derived from a 3-quantum atomic electron, since D is so high (cf. section D7). Besides the initial state of the γ bands, other excited states of NO with small r_e and large ω_e are known. Of these, at least the initial state of the δ bands appears to be $^2\Sigma$. No bands analogous to the γ and δ bands are yet known in O_2^+ . Very likely the $^2\Sigma^+$ state analogous to the upper state of the γ bands of NO is a $^2\Sigma^+_g$, and so cannot combine with the $^2\Pi_g$ normal state of O_2^+ . If so, the outer σ electron is σ_g .

We have already considered the three states $^3\Sigma^-_g$, $^1\Delta_g$, and $^1\Sigma^+_g$ of O_2 derived from $\cdots (x\sigma)^2(w\pi)^4(v\pi)^2$. The $^3\Sigma^-_g$ and $^1\Sigma^+_g$ states are rather stable states: $r_e = 1.20$ and $1.22\text{\AA}$, $\omega_e = 1585$ and 1433 , $D = 5.09$ and 3.47 volts. Now the $^3\Sigma^-_u$ upper level of the Schumann-Runge bands of O_2 is a very unstable state: $r_e = 1.60\text{\AA}$, $\omega_e = 710$, $D = 0.96$ volts. In harmony with the explanation already given of the $^2\Pi$ excited states of NO and O_2^+ , we can explain this, as first suggested by Herzberg, by assuming one less bonding electron ($w\pi$) and one more anti-bonding electron ($v\pi$) than in the normal state, i.e., $\cdots (x\sigma)^2(w\pi)^3(v\pi)^3$. Besides a $^3\Sigma^-_u$, this configuration must give rise (cf. Table VIII) to five other states: $^1\Sigma^-_u$, $^3\Delta_u$, $^3\Sigma^+_u$, $^1\Delta_u$, $^1\Sigma^+_u$. Probably most of these are unstable or have small D values, but it would not be surprising to find bands coming from one or two of them. Possibly the numerous bands which appear in absorption in oxygen at high pressures and in liquid and solid oxygen¹⁴² represent "forbidden" transitions to some of the above states, and perhaps also to $^3\Pi_g$ and $^1\Pi_g$ of $\cdots (x\sigma)(w\pi)^4(v\pi)^3$.

In F_2 there are two more electrons than in O_2 , and these are doubtless $v\pi$ like the last two electrons in O_2 . With $\cdots (v\pi)^4$ we have all shells closed again and a $^1\Sigma^+_g$ state as in N_2 , in agreement with the fact that F_2 ,—or at least its analogue Cl_2 ,—is a diamagnetic gas. (In Cl_2 the normal state is known from spectroscopic data to be $^1\Sigma$.) The normal state of F_2 may probably be described fairly well by

$$(K)(K)(\sigma_g 2s)^2(\sigma_u 2s)^2(x\sigma)^2(w\pi)^4(v\pi)^4, ^1\Sigma^+_g,$$

or possibly better by

$$(K)(K)(L_s)(L_s)(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^4, ^1\Sigma^+_g.$$

The second formulation is intended to suggest that the $2s$ electrons in F_2 may be practically the same as if the two atoms were separate, and that the remaining outer electrons are only somewhat modified $2p$ atomic electrons.

The normal state of Ne_2 is obviously, from the monatomic character of neon gas, a state of repulsion like the normal state of He_2 . Its electron con-

figuration contains two more electrons than F_2 , and these must evidently be powerfully anti-bonding. If r could be made as small as r_e of F_2 , the normal state of Ne_2 could be described as

$$(K)(K)(L_s)(L_s)(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^4(\sigma_u 2p)^2, {}^1\Sigma_g^+.$$

Actually, however, r_e , hence ξ for all electrons, is so large that the most appropriate description is simply

$$(K)(K)(L)(L), {}^1\Sigma_g^+.$$

The anti-bonding electron type $\sigma_u 2p$ which we assume in Ne_2 is also known in excited states of F_2 , at least by analogy with excited states of the other halogens (cf. section A9 and Fig. 42). The lowest excited state of F_2 is probably a ${}^3\Pi$ state which has a very large r_e and very small D , thus being practically repulsive in character (cf. section D8):

$$(K)(K)(L_s)(L_s)(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^3(\sigma_u 2p), {}^3\Pi_u.$$

4. Band spectra of heavier diatomic molecules

From Ne_2 on to Cl_2 , if we consider molecules with equal or nearly equal nuclei, we have a series of molecules more or less closely analogous to the series He_2 , Li_2 , $\dots$, CN , N_2 , $\dots$, F_2 (cf. Figs. 41, 42, 48 for $U(r)$ diagrams of some of these). In all these ξ is very large for the L as well as the K shells. Only the outer electrons, derived from $3s$ and $3p$ electrons of the separated atoms, are strongly influenced by both nuclei. From them we get a series of molecular electron types analogous to $\sigma\sigma$, $\gamma\sigma$, $x\sigma$, $w\pi$, $v\pi$, and $u\sigma$ of the molecules from Li_2 to F_2 . Because of their analogous behavior, and for the sake of simplicity, we shall describe these types, for orbits with moderate ξ values, by the same symbols $\sigma\sigma$ and so on, as already proposed in section A9. In case it should be necessary to distinguish the $\sigma\sigma$ types derived from $1-$, $2-$, and 3 -quantum atomic orbits, they can be called $kz\sigma$, $lz\sigma$, $mz\sigma$, as already suggested in section A9. For large- ξ orbits we shall use symbols such as $\sigma_g 2s$, $\sigma_g 3s$, or for closed shells and very large ξ , L_s , M_s , etc. Analogous molecules whose atoms contain $4s$ and $4p$, $5s$ and $5p$, or $6s$ and $6p$ orbits can be designated in an analogous manner (cf. (92) and (93) in section A9).

Examples are not yet known spectroscopically of diatomic molecules derived from atoms which contain d or f electrons not in closed shells. It should, however, not be very difficult to extend the notation used here to cover such cases.

Although the spectra of the higher homologues of the molecules already discussed in this section are not very well known, they will be briefly mentioned here (cf. Weizel's Handbuch article for details and references). A band system of each of the molecules MgO , CaO , SrO , and BaO is known, and may be analogous to the ${}^1\Sigma \rightarrow {}^1\Sigma$ bands of BeO . The molecules AlO , SiN and CP have ${}^2\Sigma \rightarrow {}^2\Sigma$ bands analogous to those of BO and CN ; a second system of SiN is of unidentified type. Bands of ScO , YO , and LaO are also known.

P_2 has an extensive ${}^1\Sigma \rightarrow {}^1\Sigma$ system. CS and SiO have band systems which are probably analogous to the CO fourth positive bands (${}^1\Pi \rightarrow {}^1\Sigma^+$). Bands of

TiO (${}^3\Pi \rightarrow {}^3\Pi$ and ${}^3\Sigma \rightarrow {}^3\Pi$), SnO, and PbO (${}^1\Sigma \rightarrow {}^1\Sigma?$) have also been analyzed but their interpretation in terms of electron configurations is not yet known.

PO has ${}^2\Sigma \rightarrow {}^2\Pi$ bands analogous to the γ bands of NO; bands of SbO, BiO, and VO are also known. SiF has several band systems, which are not yet well understood. SnCl has a band system which is probably ${}^2\Sigma \rightarrow {}^2\Pi$ and may be analogous to the γ bands of NO, and also has bands which are probably ${}^2\Delta \rightarrow {}^2\Pi$; possible bands of CCl and SiCl are also known.

The molecules S_2 , Se_2 , Te_2 , and SO all have a strong ultraviolet band-system which is analogous to the Schumann-Runge bands. In O_2 , it will be recalled, D is very small for the upper ${}^3\Sigma^-$, fairly large for the lower ${}^3\Sigma^-$. These and related contrasts in r_e and ω_e between the upper and the lower ${}^3\Sigma^-$ state are less pronounced in S_2 (cf. Fig. 49), and probably still less so in Se_2 , Te_2 . This is probably because with increasing principal quantum number n , both $w\pi$ and $v\pi$ electrons (cf. interpretation of ${}^3\Sigma^-_u$ state of O_2 above) become more like atomic np electrons. Similar relations are found in the halogens (cf. section D8).

Band spectra of several other classes of molecules are known, and in a few cases the electronic states involved have been determined, but no satisfactory interpretations in terms of electron configurations have been given. Such bands are those of CuO, AgO, BiCl, Zn_2 , Cd_2 , Hg_2 , the halides of Na, K, Rb, Cs, Cu, Ag, Au, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Tl, and mixed molecules composed of Na, K, Rb, Cs combined with Mg, Zn, Cd, Hg. The alkaline earth fluoride bands (also LaO bands) are presumably in part analogous to the ${}^2\Pi \rightarrow {}^2\Sigma$ band system of BeF and to the as yet undiscovered ${}^2\Sigma \rightarrow {}^2\Sigma$ bands of BeF.

5. Excited electron states and their dissociation products in H_2 , He_2 , Li_2

The electron energy level diagrams of both the molecules H_2 and He_2 (cf. Figs. 46 and 49) closely resemble in most respects the He atom diagram (cf. Fig. 46), except for the λ subdivision of the levels. The resemblance extends even to the existence of a set of singlet (par- H_2 , par- He_2) terms and one of triplet (ortho- H_2 , ortho- He_2) terms. Furthermore, every triplet term is lower in energy than the corresponding singlet term, just as in He. As in the case of the He atom, there is a large interval between the normal level and the first excited level, then other levels follow at small intervals. These lead up to the ionization level, which is relatively close above the first excited level.

In the $(1s)(nx)$, 1X or 3X excited states of the He atom ($n=2, 3, 4, \dots$, $x=s, p, d, \dots$), the binding energy T of the excited electron is, as is well known, expressible by a Rydberg term: $T=R/(n-\delta)^2$, with $|\delta| < 1$ in helium. The quantum defect δ is approximately a constant in any one series (l of excited electron fixed, and resultant spin S fixed). The term values of most of the excited states of H_2 and He_2 , measured downward from the normal states of their respective ions H_2^+ and He_2^+ , can likewise be expressed by Rydberg series. Here of course δ depends on λ as well as on l and S . Approximate δ values for a number of term-series in He, H_2 , and He_2 are listed in Table XV.

The existence of Rydberg series in the excited states of H_2 and He_2 paral-

telling those of He is not difficult to explain. In all three cases, the dimensions of the excited orbits, even for $n=2$, are large compared with those of the core. In He^+ the core consists of the nucleus and a $1s$ electron (Bohr diameter 0.53 Å). In H_2^+ it consists of the two nuclei ($r_e \sim 1.06$ Å for H_2^+) and a closely attached $1s\sigma$ electron. Since the Bohr diameter of a circular 2-quantum orbit in the field of a unit charge is 4.2 Å, it is easy to see that for an electron in an excited orbit, the field of H_2^+ is not much different from that of the corresponding united-atom He^+ , but slightly altered by the existence of an electric axis which gives the λ quantization. Similarly for excited orbits in He_2 , the field of the He_2^+ ion, with $r_e = 1.09$ Å and with the three inner electrons tightly bound in small orbits, closely resembles that of a single unit charge.

TABLE XV. Quantum defects δ for Rydberg series of He, H_2 , and He_2 .

He	δ	H_2	δ	He_2	δ
$(1s)(ns), {}^3S$ 1S	0.31 to 0.30 0.15 to 0.14	$(1s\sigma)(n\sigma), {}^3\Sigma$ ${}^1\Sigma$	(0.07) —	$\cdots n\sigma, {}^3\Sigma$ ${}^1\Sigma$	0.21 to 0.16 0.15 to 0.11
$(1s)(np), {}^3P$ 1P	0.063 to 0.068 —0.01	$(np\pi), {}^3\Pi$ ${}^1\Pi$	0.06 <0	$\cdots np\pi, {}^3\Pi$ ${}^1\Pi$	0.0726 0.035
$(1s)(nd), {}^3D$ 1D	0.003 0.002	$(nd\sigma), {}^3\Sigma$ ${}^1\Sigma$	— <0	$\cdots nd\sigma, {}^3\Sigma$ ${}^1\Sigma$	0.07 0.05
		$(nd\pi), {}^3\Pi$ ${}^1\Pi$	— <0	$\cdots nd\pi, {}^3\Pi$ ${}^1\Pi$	0.04 0.03
				$\cdots nd\delta, {}^3\Delta$ ${}^1\Delta$	—0.01 —0.02

In these excited states of H_2 and He_2 , all the molecular constants (r_e , ω_e , D , etc.) are near those of the corresponding ion H_2^+ or He_2^+ . The departures are greatest where there is a $2s\sigma$ electron. In every Rydberg series, the values of r_e , ω_e , D , etc. converge toward those of the ion as n increases.¹⁴³ These relations show that the excited electron is practically non-bonding, i.e., has very little to do with holding the molecule together. In H_2^+ the $1s\sigma$ inner electron takes care of the binding ($D \sim 2.6$ volts). When the second electron contributes to the binding, in the $(1s\sigma)^2, {}^1\Sigma^+_{g_0}$ normal state of H_2 , the binding is greatly strengthened ($D = 4.46$ volts, $r_e = 0.75$ Å.U.).

In $\text{He}_2^+[(\sigma_g 1s)^2(\sigma_u 1s), {}^2\Sigma^+_g]$, the molecule is a combination of an unexcited He and an unexcited He^+ strongly held together ($D \sim 2.6$ volts, probably) by the bonding effects of the two $\sigma_g 1s$ bonding electrons, diminished by the repulsive effect of the anti-bonding $\sigma_u 1s$ electron. When there are two $\sigma_u 1s$ electrons as well as two $\sigma_g 1s$ electrons, as in the normal state of He_2 $[(\sigma_g 1s)^2(\sigma_u 1s)^2, {}^1\Sigma^+_{g_0}]$, the repulsive forces conquer. One might ask, if two neutral $(1s)^2, {}^1S$ He atoms repel each other, why can a $(1s)^2, {}^1S$ and a $(1s)(2s), {}^3S$ atom, both neutral, attract each other, as they do, to form the state $(\sigma_g 1s)^2(\sigma_u 1s)(2s\sigma), {}^3\Sigma^+_u$ of He_2 ? In answer one may say that $1s2s, {}^3S$ of He acts like $[\text{He}^+, 1s, {}^2S](2s), {}^3S$, and that the He^+ part combines with the other He atom to form an He_2^+ core. Or one may note that in the molecule there

are two bonding electrons and only one anti-bonding electron, as in He_2^+ .

Although most of the excited states of H_2 and He_2 fall neatly in Rydberg series with small δ values, there are a few which do not. The exceptions are results of promotion. First may be mentioned the interesting $(1\sigma)(2p\sigma)$, $^3\Sigma_u^+$ repulsive state of H_2 , already considered in section D1 in the paragraph numbered (2). For this state δ is abnormally large unless we take r very small, obviously because promotion is incomplete for the larger r values.

[Parenthetically, it may be well to mention here the experimental evidence for this repulsive state of H_2 . The well-known hydrogen continuum is attrib-

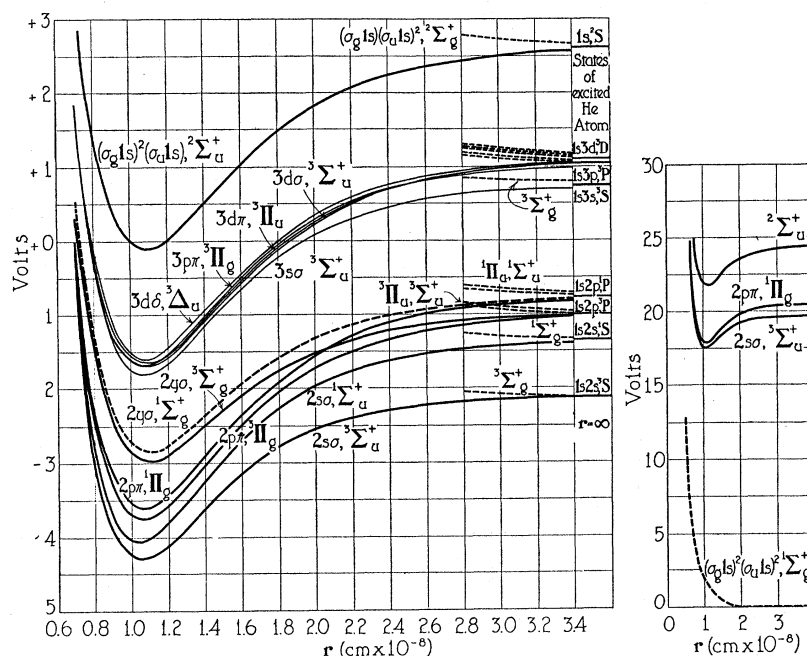


Fig. 49. Main figure: $U(r)$ curves of normal state of He_2^+ and of all observed states of He_2 with a 2- or 3-quantum excited electron, except that only the ortho- He_2 (triplet) 3-quantum states are shown. Many more states with higher values of the principal quantum number of the excited electron are also known. The figure also shows some predicted, mostly repulsive, states (dashed lines) derivable from the same dissociated atoms which probably give rise to the observed states. Fig. 49a. $U(r)$ curves of normal state of He_2 (a repulsive state) and of two typical excited states, on a smaller scale than the main figure.

uted,¹⁴⁴ mainly at least, to the transition $(1\sigma)(2s\sigma)$, $^3\Sigma_g^+ \rightarrow (1\sigma)(2p\sigma)$, $^3\Sigma_u^+$. The $U(r)$ curve of the $^3\Sigma_u^+$ state has been plotted in Fig. 46 largely on the basis of a study of the intensity distribution in the continuum as a function of exciting voltage.¹⁴⁴

The $(1\sigma)(2p\sigma)$, $^1\Sigma_u^+$ state of H_2 is also abnormal (large r_e , small ω_e , large D). This is because for medium-large r values, the $U(r)$ curve tends to follow a course similar to that of the corresponding $^3\Sigma_u^+$ state ($2p\sigma \rightarrow \sigma_u 1s$), although for large r values this tendency is lost, the molecule dissociating to give a 2-quantum atom (cf. section D1, paragraph numbered (2)). Certain

other states of H_2 are abnormal for similar reasons, e.g., the $^1\Sigma$ states with large r_e and small ω_e values for which the designations $(2p\sigma)^2$, $^1\Sigma_g^+$ and $(2p\sigma)(3p\sigma)$, $^1\Sigma_g^+$ have been suggested.¹⁴⁶

In excited He_2 matters are somewhat different than in H_2 , because of the presence of three $1s$ electrons in the atoms for $r = \infty$. The known states of He_2 all have the core $(\sigma_g 1s)^2(\sigma_u 1s)$, $^2\Sigma_u^+$, but another set of states with the core $(\sigma_g 1s)(\sigma_u 1s)^2$, $^2\Sigma_g^+$ might also be expected. But if we assume that the $\sigma_g 1s$ electron approximately balances one $\sigma_u 1s$, there remains an extra $\sigma_u 1s$ antibonding electron to make this a repulsive state, similar to the repulsive state $2p\sigma$, $^2\Sigma_u^+$ of H_2^+ . $U(r)$ curves corresponding to the $^2\Sigma_g^+$ ion and states of He_2 derived from it are indicated at the right of Fig. 49 by dashed lines. Evidence that these states really are repulsive, as assumed here, is furnished by the asymmetrical pressure broadening of certain ultraviolet atomic He lines, as interpreted by Weizel.¹²⁸

Of the known states of He_2 , those designated by $(\sigma_g 1s)^2(\sigma_u 1s)(m\gamma\sigma)$, $^3\Sigma_g^+$ are anomalous (cf. $\cdots 2\gamma\sigma$, $^3\Sigma_g^+$ and $^1\Sigma_g^+$ in Fig. 49). [The singlet states are not experimentally known, but are presumably similar to the triplets.] From the position of the energy level for $r = r_e$, it seems clear that for $2\gamma\sigma$ the electron would have $n > 2$ when $r \rightarrow 0$, and from the absence of any other known state with a $3p\sigma$ orbit, it seems probable that $2\gamma\sigma \rightarrow 3p\sigma$ as $r \rightarrow 0$. From a consideration of the Λ -type doubling in the $\cdots 2p\pi$ state,¹⁴⁶ it is probable that $2\gamma\sigma \rightarrow \sigma_u 2p \rightarrow 2p$ as $r \rightarrow \infty$. The abnormal behavior of the $2\gamma\sigma \rightarrow \sigma_u 2p$ orbit is apparently caused by the fact that a normal $2p\sigma$ excited orbit is impossible in He_2 . In He_2 , $\sigma_u 1s$ preempts the place of $2p\sigma$ ($\sigma_u 1s \rightarrow 2p\sigma$ as $r \rightarrow 0$). This forces $\sigma_u 2p$, which if it behaved like $\sigma_g 2s$, $\pi_u 2p$ and so on would become $2p\sigma$, to be promoted toward $3p\sigma$. This in turn probably forces promotion of $\sigma_u 3p$ toward $4p\sigma$, and so on.

In He_2 the energy order of most of the excited states with the core $(\sigma_g 1s)^2(\sigma_u 1s)$ and with the excited electron in various orbits is just that which one would expect if the excited electron behaves as if $\xi \sim 0$ (nearly-united-atom). (The states with the $m\gamma\sigma$ or $\sigma_u 2p$ orbit-type are exceptions). In H_2 there are for the excited electron some deviations from such an order. For $r = r_e$ the states $(1s\sigma)(2s\sigma)$ are slightly above the states $(1s\sigma)(2p\pi)$ and $(1s\sigma)(2p\sigma)$, contrary to what we expect in the united-atom. The course of the $U(r)$ curves shows, however, that as $r \rightarrow 0$, $2s\sigma$ soon crosses $2p\pi$ and afterwards $2p\sigma$ so as to assume its proper level. This behavior of $2s\sigma$ finds a satisfactory theoretical explanation in the existence of a strong tendency in H_2 toward separability in elliptical coordinates. In H_2^+ , where the separability is complete, $2s\sigma$ is always above $2p\pi$ (cf. Fig. 45).

At this point it becomes desirable to take up somewhat systematically the relations between electron configurations and states of the molecules H_2 and He_2 ,—to which Li_2 may conveniently be added,—and those of their dissociation products. First of all, of course, these relations must be in agreement with the rules of section C3 governing Λ , S , and symmetry (g or u).

In He_2 , we get from $(1s)^2 + (1s)^2$ the one state $(\sigma_g 1s)^2(\sigma_u 1s)^2$, $^1\Sigma_g^+$. From $(1s)^2$, $^1S_g + (1s)(2s)$, $^3,^1S_g$ we should get according to Table X (cf. footnote)

four states as follows: $^3,^1\Sigma^+_u$, $^3,^1\Sigma^+_g$. Two states $(\sigma_g 1s)^2(\sigma_u 1s)(2s\sigma)$, $^3,^1\Sigma^+_u$, with normal core and unpromoted outer electron, are known experimentally. The two unknown states, indicated by dashes in Fig. 49, might conceivably, according to Fig. 43, be $(\sigma_g 1s)(\sigma_u 1s)^2(2s\sigma)$, $^3,^1\Sigma^+_g$ (promoted core and unpromoted outer electron), or $(\sigma_g 1s)^2(\sigma_u 1s)(\sigma_u 2s)$, $^3,^1\Sigma^+_g$ (normal core and promoted outer electron). The empirical evidence, however suggests¹⁴⁷ that in this and in all cases of the type $(1s)^2, ^1S + (1s)(nx)$, $^3,^1X$, one gets two sets of states in both of which the nx electron is unpromoted (or promoted toward $(n+1)p\sigma$, in the special case of an np electron with $\lambda=0$). In the one (observed) set, the core is in its normal state $(\sigma_g 1s)^2(\sigma_u 1s)$, in the other set (not yet observed, dashed lines in Fig. 49), the core is in the promoted state $(\sigma_g 1s)(\sigma_u 1s)^2$. [The corresponding two sets of states with promoted outer electron can be allocated to the pair of ions $\text{He}^-[(1s)^2 nx] + \text{He}^+(1s)$, although of course they are presumably not really correlated with such ionic states (cf. discussion in section D1, paragraph numbered (2), of the states $(1s\sigma)(2p\sigma)$, $^1\Sigma^+_u$ and $(2p\sigma)^2$, $^1\Sigma^+_g$ which are allocated to $\text{H}^+ + \text{H}^-$].

In H_2 , as we have seen already, $1s+1s$ gives the two states $(1s\sigma)^2$, $^1\Sigma^+_g$ and $(1s\sigma)(2p\sigma)$, $^3\Sigma^+_u$. Next we might consider $1s+2s$; but it is not sensible to consider $2s$ and $2p$ separately, since they are practically the same in energy. Hence we shall consider them together. From $1s+(2s, p)$, i.e., $^2S_g + (^2S_g, ^2P_u)$, we should get according to Table X (cf. footnote), twelve states as follows: $^3,^1\Sigma^+_g$, $^3,^1\Sigma^+_u$, $^3,^1\Sigma^+_g$, $^3,^1\Sigma^+_u$, $^3,^1\Pi_u$, $^3,^1\Pi_g$. The empirical evidence indicates¹⁴⁷ that approximately half of these are states with an unpromoted core $(1s\sigma)$ and half with promoted core $(2p\sigma)$, but all with outer electron unpromoted, except where promotion of what would otherwise be $2p\sigma$ is forced by the existence of $2p\sigma$ promoted from $1s$. Specifically, there are probably at least five attractive states derived from $1s+(2s, p)$: $(1s\sigma)(2p\sigma)$, $^1\Sigma^+_u$; $(1s\sigma)(2s\sigma)$, $^1,^3\Sigma^+_g$; $(1s\sigma)(2p\pi)$, $^1,^3\Pi_u$. All these are shown in Fig. 46; a possible sixth state with promoted outer electron might be $(1s\sigma)(3p\sigma)$, $^3\Sigma^+_u$. Then there should be six other, probably repulsive, states with $2p\sigma$ core.—Of most of the observable stable states of H_2 , except some of those with a $p\sigma$ electron, it can probably be said that they are derived from the two atoms without promotion of their electrons.

Two unexcited Li atoms, each $(1s)^2(2s)$, 2S_g , should give according to Table XI a $^1\Sigma^+_g$ and a $^3\Sigma^+_u$, of which according to calculations by the Heitler and London method the former should be attractive, the latter repulsive (cf. section C4). The former is the known normal state $(\sigma_g 1s)^2(\sigma_u 1s)^2(z\sigma)^2$, $^1\Sigma^+_g$, with two $z\sigma$ bonding electrons. The latter has no doubt the configuration $\cdots (z\sigma)(y\sigma)$, with one $z\sigma$ bonding electron outweighed by a $y\sigma$ anti-bonding electron. Here we should have, for $\xi \sim 0 \rightarrow \xi \sim \infty$, $2s\sigma \rightarrow z\sigma \rightarrow \sigma_g 2s$, $3p\sigma \rightarrow y\sigma \rightarrow \sigma_u 2s$. Reference should be made to Fig. 41 for the $U(r)$ curves of Li_2 .

If we start with $(1s)^2(2s)$, $^2S_g + (1s)^2(2p)$, 2P_u , we should according to Table X (cf. footnote) get eight states as follows: $^1,^3\Sigma^+_u$, $^1,^3\Sigma^+_g$, $^1,^3\Pi_u$, $^1,^3\Pi_g$. Of these the $^1\Sigma^+_u$ may be identified with the empirically known $\cdots (z\sigma)(y\sigma)$, $^1\Sigma^+_u$. The $^1\Pi_u$ is evidently the known state with configuration $(z\sigma)(w\pi)$, where for $\xi \sim 0 \rightarrow \xi \sim \infty$, $2p\pi \rightarrow w\pi \rightarrow \pi 2p$. The corresponding $^3\Pi_u$ state (not known ex-

perimentally) should be a stable state with larger D than the ${}^1\Pi_u$. Of the remaining predicted states, probably all are repulsive except the ${}^1\Sigma^+_g$ and ${}^3\Sigma^+_g$. These probably have the configuration $\cdots (z\sigma)(x\sigma)$, which should give stable states, judging from the behavior of $x\sigma$ in such molecules as CN and N₂.

Some comparisons are of interest. In H₂, the configuration $(1s\sigma)(2p\sigma)$ gives a ${}^3\Sigma$ which is repulsive because it dissociates into the low-energy products $1s+1s$, and a ${}^1\Sigma$ which is attractive because it dissociates to give the high-energy products $1s+(\text{say})2p$. Similarly in Li₂, $\cdots (z\sigma)(y\sigma)$ gives a repulsive ${}^3\Sigma$ because it dissociates to $\cdots 2s+\cdots 2s$, with low energy, and an attractive ${}^1\Sigma$ because it gives $\cdots 2s+\cdots 2p$. Other similar examples are frequent among molecules.

Another instructive comparison is between $\cdots (\sigma_u 1s)(2y\sigma)$, ${}^1,{}^3\Sigma$ in He₂, and $\cdots (z\sigma)(y\sigma)$, ${}^1,{}^3\Sigma$ in Li₂. In these states of He₂, $2y\sigma$, which for $\xi \sim 0$ would become $3p\sigma$, for $\xi \sim \infty$ becomes $\sigma_u 2p$, and for $r=r_e$ is less firmly bound than $2p\pi$. In Li₂, $y\sigma \rightarrow \sigma_u 2s$ in the ${}^3\Sigma$ state, but in the ${}^1\Sigma$ state, $y\sigma \rightarrow \sigma_u 2p$ as in He₂. In both states it is more firmly bound, for r equal to r_e of the ${}^1\Pi$ state, than $2p\pi$. In other molecules with more electrons, e.g. CN, we sometimes find $y\sigma \rightarrow \sigma 2p$, sometimes $y\sigma \rightarrow \sigma 2s$, but always $y\sigma$ is more firmly bound for $r=r_e$ than $2p\pi$. When the number of electrons is larger, as in O₂ or F₂, $y\sigma$ *always* goes to $\sigma_u 2s$. [Really, however, ξ is so large for all states of O₂ or at least of F₂ that only the designation $\sigma_u 2s$ is appropriate.] Similar examples where the correlation of a given molecular electron type varies from one molecular state to another are common in cases like the above where the given electron type is not yet built into a more or less buried closed shell.

6. Energy level schemes and dissociation products of Be₂, B₂, C₂, BeO

By means of the binding scheme of Figs. 43, 44 and the Λ , S correlation rules of sections C2,3, we shall now try to interpret some of the empirical energy levels of a few molecules not yet discussed, and to make some predictions as to unknown electron states. No spectra of Be₂ or B₂ are yet known, while our knowledge of the C₂ spectrum is rather incomplete. It should be of interest to make some predictions as to the energy level schemes of these molecules. (Various people have tried this.)

According to Fig. 43, the lowest-energy state of Be₂, assuming that the line for Be₂ does not lie to the left of that given for Li₂ in the figure, must be $(K)(K)(z\sigma)^2(y\sigma)^2, {}^1\Sigma^+_g$ or $(K)(K)(\sigma_g 2s)^2(\sigma_u 2s)^2, {}^1\Sigma^+_g$. [These two descriptions of course represent the same state but for different ξ values.] The lowest-energy state of Be+Be is $2[(1s)^2(2s)^2, {}^1S]$, which according to Table XI can give just one molecular state, a ${}^1\Sigma^+_g$, which must evidently be identified with the lowest state of Be₂ just discussed. Since the molecule here contains two antibonding as well as two bonding electrons, like He₂, this state should presumably be a repulsive one. This is in agreement with Heitler and London's ideas (cf. section C4). In the analogous molecules Zn₂, Cd₂, Hg₂, however, there is evidence¹³⁰ that unstable molecules (large r_e , small D) are formed from two normal atoms, and presumably the normal state of Be₂ is of the same kind.

The first excited states of Be₂ should according to Fig. 43 be $(K)(K)(z\sigma)^2(y\sigma)(x\sigma)$, ${}^3,{}^1\Sigma^+_u$, and $(K)(K)(z\sigma)^2(y\sigma)(w\pi)$, ${}^3,{}^1\Pi$. The first excited states of

Be+Be correspond to $(1s)^2(2s)^2, {}^1S+(1s)^2(2s)(2p), {}^3, {}^1P$. From ${}^1S_g+{}^3P_u$ one expects (Table X, footnote) ${}^3\Sigma^+_g, {}^3\Sigma^+_u, {}^3\Pi_g, {}^3\Pi_u$, and from ${}^1S_g+{}^1P_u, {}^1\Sigma^+_g, {}^1\Sigma^+_u, {}^1\Pi_g, {}^1\Pi_u$. The two states $\cdots (y\sigma)(x\sigma), {}^3\Sigma^+_u$ and $\cdots (y\sigma)(w\pi), {}^3\Pi_g$ are probably moderately attractive states derived from the ${}^1S+{}^3P$ just mentioned, while the two corresponding molecular singlet states are probably attractive states derived from ${}^1S+{}^1P$.

The molecule B_2 in its lowest state should according to Fig. 43 consist of $(K)(K)(z\sigma)^2(y\sigma)^2$ (two more), where the last two electrons must be either $x\sigma$ or $w\pi$. Since B_2 should, more likely than not, fall between Li_2 and N_2 on Fig. 43, the indications are that $w\pi$ should be more firmly bound in B_2 than $x\sigma$. For the normal state one might then expect $\cdots (w\pi)^2, {}^3\Sigma^-_g$, with $\cdots (w\pi)^2, {}^1\Delta_g$ and $\cdots (w\pi)^2, {}^1\Sigma^+_g$ as low excited states (cf. section A6). But if $w\pi$ and $x\sigma$ are about equally firmly bound, $\cdots (w\pi)(x\sigma), {}^3\Pi_u$ may be the normal state instead of $\cdots (w\pi)^2, {}^3\Sigma^-_g$. In any case $\cdots (w\pi)(x\sigma), {}^1\Pi_u$ and $\cdots (x\sigma)^2, {}^1\Sigma^+_g$ should be low excited states, or if r_e is large, possibly $(x\sigma)^2, {}^1\Sigma^+_g$ may be the normal state. Various additional low excited states should exist (cf. section A5, Table VIII) in which a $y\sigma$ electron has been excited to $w\pi$ or $x\sigma$: $(K)(K)(z\sigma)^2(y\sigma)(w\pi)^3, {}^3, {}^1\Pi_g$; $(K)(K)(z\sigma)^2(y\sigma)(w\pi)^2(x\sigma)$, giving ${}^5\Sigma^-_u, {}^3\Sigma^-_u, {}^3\Sigma^-_u, {}^1\Sigma^-_u, {}^3\Delta_u, {}^1\Delta_u, {}^3\Sigma^+_u, {}^1\Sigma^+_u$; and $(K)(K)(z\sigma)^2(y\sigma)(w\pi)(x\sigma)^2, {}^3, {}^1\Pi_g$. Possibly the ${}^5\Sigma^-_u$ state included in this group is the normal state of the molecule,—in spite of the energy required to change $y\sigma$ to $x\sigma$ or $w\pi$,—because of its high multiplicity.

As for correlations with the atomic states, we note first that two normal B atoms, each $(1s)^2(2s)^22p, {}^2P_u$, must give molecular states as follows (cf. Table XI): ${}^1\Delta_g, {}^1\Pi_g, {}^1\Pi_u, {}^1\Sigma^+_g, {}^1\Sigma^-_u, {}^1\Sigma^+_g, {}^3\Delta_u, {}^3\Pi_u, {}^3\Pi_g, {}^3\Sigma^+_u, {}^3\Sigma^-_g, {}^3\Sigma^+_u$. Six of these (${}^3\Sigma^-_g, {}^1\Delta_g, {}^1\Sigma^+_g, {}^3\Pi_u, {}^1\Pi_u, {}^1\Sigma^+_g$) can be identified with the low-energy molecular states with the configurations $\cdots (w\pi)^2, \cdots (w\pi)(x\sigma)$, and $\cdots (x\sigma)^2$. Probably all these are attractive states. Five more of the states derived from two normal atoms can be identified with five out of the large list of states with one $y\sigma$ electron replaced by $x\sigma$ or $w\pi$. Probably some of these five states are mildly attractive, others mildly repulsive. The lowest excited state of the B atom is probably $(1s)^2(2s)(2p)^2, {}^4P_g$. From this plus a normal B atom a considerable number of molecular states must be derived, including the ${}^5\Sigma^-$ mentioned above.

The two best known systems of C_2 bands are a ${}^3\Pi \rightarrow {}^3\Pi$ ($\nu_e \sim 2.4$ volts) and an in all probability analogous ${}^1\Pi \rightarrow {}^1\Pi$ ($\nu_e \sim 3.2$ volts). These are most probably $(K)(K)(z\sigma)^2(y\sigma)(w\pi)^3(x\sigma)^2, {}^3, {}^1\Pi_g \rightarrow (K)(K)(z\sigma)^2(y\sigma)^2(w\pi)^3(x\sigma), {}^3, {}^1\Pi_u$. The ${}^3\Pi_u$ is probably the lowest definitely known state of C_2 , and is very likely the normal state.

The order of the lower molecular energy levels of C_2 can now be approximately predicted by means of the following assumptions, which although elaborate and perhaps seemingly arbitrary, are in the writer's opinion not likely to be much in error: (1) other things being equal, $w\pi$ is 0.3 volts more firmly bound than $x\sigma$; (2) other things being equal, $y\sigma$ is usually 2.8 volts more firmly bound than $x\sigma$; but in the case of the known intervals ${}^3\Pi - {}^3\Pi$ and ${}^1\Pi - {}^1\Pi$, we must alter the figure to 2.4 volts in the former case, 3.2 volts in

the latter, in order to be in agreement with the experimental data ; (3) other things being equal, 1.25 volts must be subtracted from the energy in the case of a triplet, or added to it in that of a singlet state (the figures are modified to 1.05 for the lower of the known Π states and 1.45 for the upper of the known Π states); except that in the special case of π^2 , we add $-0.8, 0.0, +0.8$ for the $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ states respectively (cf. section A6). The relative energies of various levels as estimated by means of these assumptions are given in Table XVI, taking the lowest energy as zero. It seems likely that these relative energies are mostly correct within a volt or two. All states derivable by varying the relative numbers of $y\sigma$, $w\pi$, and $x\sigma$ electrons are given. Other states, mostly of higher energy, could be predicted by assuming excitation of a $z\sigma$ electron or presence of a $v\pi$ electron. The estimates given in the table correspond to an r value about equal to r_e of the known states of C_2 .

TABLE XVI. Predicted approximate relative energies of some electron states of C_2 , assuming $r \sim 1.3A$.

Energy (volts)	State	Energy (volts)	State	Energy (volts)	State
0	$\sigma^2\pi^3\sigma$, $^3\Pi_u$ (lower state of Swan bands)	2.1	$\sigma^2\pi^3\sigma$, $^1\Pi_u$ (lower state of Deslandres and D'Azambuja bands)	4.8	$\sigma\pi^4\sigma$, $^1\Sigma^+_u$
0.55	$\sigma^2\pi^2\sigma^2$, $^3\Sigma^-_g$	2.15	$\sigma^2\pi^2\sigma^2$, $^1\Sigma^+_g$	5.3	$\sigma\pi^3\sigma^2$, $^1\Pi_g$ (upper state of Deslandres and D'Azambuja bands)
1.35	$\sigma^2\pi^2\sigma^2$, $^1\Delta_g$	2.3	$\sigma\pi^4\sigma$, $^3\Sigma^+_u$	7.6	$\pi^4\sigma^2$, $^1\Sigma^+_g$
2.0	$\sigma^2\pi^4$, $^1\Sigma^+_g$	2.4	$\sigma\pi^3\sigma^2$, $^3\Pi_g$ (upper state of Swan bands)		

Table XVI indicates the existence of eight states in the short energy interval 0 to 2.4 volts, of which at present we have experimental evidence only of three. It might be thought that from the large number of states given in Table XVI, many observable band systems should result. Actually most of these would be in the infrared. Besides the known $^3\Pi \rightarrow ^3\Pi$ and $^1\Pi \rightarrow ^1\Pi$ bands, probably only the following bands might be expected in the visible or ordinary ultraviolet with appreciable intensity; $\pi^4\sigma^2$, $^1\Sigma^+_g \rightarrow \sigma\pi^4\sigma$, $^1\Sigma^+_u$; $\sigma\pi^4\sigma$, $^1\Sigma^+_u \rightarrow \sigma^2\pi^4$, $^1\Sigma^+_g$ (possibly also $\pi^4\sigma^2$, $^1\Sigma^+_g \rightarrow \sigma^2\pi^3$, $^1\Pi_u$ and $\sigma\pi^4\sigma$, $^1\Sigma^+_u \rightarrow \sigma^2\pi^2\sigma^2$, $^1\Sigma^+_g$). Of course other bands involving other excited states may also occur.

The C atom has four low-energy states, namely 3P , 1D , and 1S from $(1s)^2(2s)^2(2p)^2$ and 5S from $(1s)^2(2s)(2p)^3$. From these we have ten different pairs of electron states ($^3P + ^3P$, $^3P + ^5S$, etc.) as starting points for molecular states. It would hardly be useful to make a list of these molecular states, which are very numerous. Probably the normal state and many of the other low-energy states of C_2 are derived from two 3P atoms. All the states listed in Table XVI from 0 to 2.4 volts are derivable from two 3P atoms.

According to Heitler and London's generalizations concerning valence, one would expect a $^1\Sigma^+_g$ state derived from two 5S atoms to be far lower in energy, because containing four spin valence bonds, than the state $^3\Pi_u$, probably derived from two 3P atoms and containing only one spin valence bond, which is the lowest according to Table XVI. According to the present point

of view, however, the $^1\Sigma^+$ and $^3\Pi_u$ are just alike in respect to the numbers of bonding and anti-bonding electrons which they contain, these numbers furthermore corresponding in both cases, according to the definition given in section D9, to *two* valence bonds.

The molecules BeO and BN are isoelectronic with C₂, and might be expected to be similar in their spectra. Nothing is known of a BN spectrum, but two systems of bands are known in BeO, of which one at least is a $^1\Sigma \rightarrow ^1\Sigma$ system. The values of r_e for the latter are $r_e' = 1.36 \text{ \AA}$, $r_e'' = 1.33 \text{ \AA}$. These values are only slightly larger than for the two $^3\Pi$ states of the Swan bands of C₂, indicating that BeO is nearly as stable a molecule as C₂. The $^1\Sigma \rightarrow ^1\Sigma$ bands of BeO probably correspond to $\sigma\pi^4\sigma \rightarrow \sigma^2\pi^4$. The energy interval between the two observed $^1\Sigma$ states (2.6 volts) is about the same as that predicted in Table XVI for the corresponding interval in C₂.

Turning now to the question of dissociation products, two normal atoms Be($1s^22s^2, ^1S_g$) + O(3P_g) give only a $^3\Sigma^-$ and a $^3\Pi$ state (cf. Table X). These must almost certainly be identified with the states $\sigma^2\pi^3\sigma$, $^3\Pi$ and $\sigma^2\pi^2\sigma^2$, $^3\Sigma^-$ (cf. Table XVI), but it seems probable (cf. Fig. 44) that these states are relatively higher in energy in BeO than in C₂, so that they are of low stability or possibly even repulsive. It seems likely that $\sigma^2\pi^4, ^1\Sigma^+$, the probable lower state of the observed bands, is the normal state of BeO, even though it must dissociate into excited atoms. Presumably it is derived from Be(1S_g) + O(1D_g), which is the lowest-energy pair of states capable of giving a $^1\Sigma^+$ state.

7. Dissociation product correlations in molecules composed of atoms with *K* and *L* electrons only

The relations between molecular electron states and the states of the atoms on dissociation have already been discussed for several molecules in sections D5 and D6. We shall now consider these relations for the molecules whose energy level schemes have been discussed in section D3. The close analogies which exist between the *energy levels* of the isoelectronic molecules BeF, BO, CO⁺, CN, and N₂⁺ have already been pointed out and explained. Typically, the *dissociation relations* are *different* for all the five molecules named.

Since the C atom has four low-energy states ($s^2s^2p^2, ^3P_g, ^1D_g$ and 1S_g , and $s^2sp^3, ^5S_u$) and the N atom three ($s^2s^2p^3, ^4S_u, ^2D_u, ^2P_u$), the number of molecular states derived from the twelve possible combinations of the two atoms in these various low-energy states is very large. But as usual, we may probably expect the low-energy stable states of the molecule CN all to be derived from the lowest-energy atom-pairs which are theoretically capable of giving such molecular states. Specifically, we have a $^2\Sigma^+$, a $^2\Pi$, and a second $^2\Sigma^+$ state of CN to account for. From unexcited atoms C + N ($^3P_g + ^4S_u$), six states including one $^2\Sigma^+$ and one $^2\Pi$ are derived (cf. Table X). The $^2\Sigma^+$ and $^2\Pi$ very probably correspond to the lower of the two observed $^2\Sigma^+$ states and to the observed $^2\Pi$ (cf. Fig. 47).

The upper $^2\Sigma^+$ must then be derived from excited atoms. The lowest-energy atom-pair, above $^3P + ^4S$, capable of giving a $^2\Sigma^+$ state, is C(3P_g) + N(2D_u)

or $C(^5S_u) + N(^4S_u)$. The latter would be better in harmony with the electron configuration $\cdots (z\sigma)^2(y\sigma)(w\pi)^4(x\sigma)^2$ of the upper $^2\Sigma^+$ state. For if $z\sigma \rightarrow \sigma 2s$ and $y\sigma \rightarrow \sigma^* 2s$ (also $x\sigma \rightarrow \sigma 2p$) we have three $2s$ electrons on dissociation, in agreement with $C(\cdots 2s\ 2p^3, ^5S) + N(\cdots 2s^2\ 2p^3, ^4S)$. But the argument is not conclusive, since it is possible that one of the two $x\sigma$ electrons behaves exceptionally, and becomes $\sigma^* 2s$ (cf. section D1, paragraphs beginning with that numbered (3)).

Heitler and Herzberg¹⁴⁸ concluded that the *lower* $^2\Sigma^+$ of CN gives $C(^5S) + N(^4S)$ on dissociation, and that the upper $^2\Sigma^+$ gives $^3P + ^4S$. [The $U(r)$ curves of the two $^2\Sigma^+$ states then cross.] This they took as a confirmation of the London-Heitler valence theory, according to which the energy of dissociation should be larger for a $^2\Sigma^+$ derived from $^5S + ^4S$ than one from $^3P + ^4S$, since the former would have three, the latter only two valence bonds. Their conclusion, however, was based on the assumption that the Birge and Sponer method, involving a long linear extrapolation from a set of observed vibrational levels (cf. Appendix) gives a correct value of the energy of dissociation D of the lower $^2\Sigma^+$ state. But we know from other cases (e.g. the normal states of N_2 , NO) that such linear extrapolations usually give much too high values of D . When a reasonable allowance is made for this, one gets a D value for the lower $^2\Sigma^+$ which is in accordance with the present interpretation of dissociation into unexcited atoms (cf. Fig. 47). For the upper $^2\Sigma^+$, D is approximately known from a fairly short extrapolation from the observed energy levels, and the value so obtained is in reasonable agreement with $^3P + ^2D$ as dissociation products, or equally with $^5S + ^4S$ since we do not know the exact energy of 5S . An argument in favor of the present interpretation is that it does not require the assumption of the crossing of the $U(r)$ curves of two $^2\Sigma^+$ states, which is theoretically improbable (cf. section D1, (3) *et seq.*; but cf. the $^2\Sigma^+$ state of NO discussed below).

The molecule N_2^+ is similar to CN, and the states of $N^+ + N$ are also similar to those of $C + N$. Nevertheless the correlations of atomic and molecular states are by no means identical in the two cases, since $N^+ + N$ really represents $N + N^+$ as well as $N^+ + N$ and so yields twice as many molecular states as $C + N$ (cf. section C3). The unexcited atom and ion, $N(^3P) + N(^4S)$, give twelve molecular states, including one $^2\Sigma^+_g$, one $^2\Sigma^+_u$, one $^2\Pi_u$, one $^2\Pi_g$ (cf. Table X, notes). Both the two $^2\Sigma$ states of N_2^+ as well as the predicted low $^2\Pi_u$, can theoretically be, and probably are, derived from an unexcited atom and ion (cf. Fig. 47 for data). Heitler and Herzberg's conclusion¹⁴⁸ that the lower $^2\Sigma^+$ is derived from $N(^5S) + N(^4S)$ is based, as in the analogous case of CN, on a D value obtained by the Birge and Sponer extrapolation method, which cannot be relied on.

For $B + O$ we have three or probably six low-energy states corresponding to combinations of $B(s^2s^2p, ^2P_u)$ and probably also of $B(s^2sp^2, ^4P_g)$ with $O(s^2s^2p^4, ^3P_g, ^1D_g, \text{ and } ^1S_g)$. Two normal atoms $^2P_u + ^3P_g$ give one $^2\Sigma^+$, two $^2\Sigma^-$, two $^2\Pi$, one $^2\Delta$ state and corresponding quartet states (cf. Table X). The $^2\Pi$ and the lower $^2\Sigma^+$ state of BO are probably derived from normal atoms, but the upper $^2\Sigma^+$ must then involve at least one excited atom. It is probably de-

rived from ${}^2P+{}^1D$ or from ${}^4P+{}^3P$. The former is assumed in Fig. 47. As in the case of CN, however, the probable electron configuration of the upper ${}^2\Sigma^+$ favors dissociation into ${}^4P+{}^3P$, which has only three $2s$ electrons. (The energy of 4P above 2P is not yet known.)

For CO^+ we have to consider not only the states of C^++O , which are analogous to those of $\text{B}+\text{O}$, but also those of $\text{C}+\text{O}^+$. The lowest-energy pair of dissociated states is $\text{C}^+({}^2P)+\text{O}({}^3P)$, which probably gives rise to the lower ${}^2\Sigma^+$ and to the ${}^2\Pi$ state of CO^+ , but cannot then give rise to the upper ${}^2\Sigma^+$ state. The latter is probably derived from $\text{C}^+({}^2P)+\text{O}({}^1D)$. [The energy of $\text{C}({}^3P)+\text{O}^+({}^4S)$ is 0.3 volts, and that of $\text{C}^+({}^4P)+\text{O}({}^3P)$ is 3.4 volts, higher than that of $\text{C}^+({}^2P)+\text{O}({}^1D)$.]

The two known states of BeF (${}^2\Sigma^+$ lower, and ${}^2\Pi$) can both be correlated with $\text{Be}(1s^22s^2, {}^1S_g)+\text{F}(1s^22s^22p^5, {}^2P_u)$.

Two atoms $\text{C}(1s^22s^22p^2, {}^3P_g)+\text{O}(1s^22s^22p^4, {}^3P_g)$, each atom in its normal state, should give the following set of molecular states: ${}^1\Sigma^+$, ${}^1\Sigma^+$, ${}^1\Sigma^-$, ${}^1\Pi$, ${}^1\Pi$, ${}^1\Delta$, ${}^3\Sigma^+$, ${}^3\Sigma^+$, ${}^3\Sigma^-$, ${}^3\Pi$, ${}^3\Delta$, and analogous quintet states. Of these numerous predicted states, a ${}^1\Sigma^+$ can be identified with the observed ${}^1\Sigma$ normal state of CO, while several others may be identified with the lower of the numerous observed excited states of CO. Many of the predicted states, however, including probably all the quintets, must correspond to repulsive molecular states.

In the case of $\text{N}+\text{N}$, two normal atoms (each $1s^22s^22p^3, {}^4S$) give only ${}^1\Sigma^+_g$, ${}^3\Sigma^+_u$, ${}^5\Sigma^+_g$, ${}^7\Sigma^+_u$. The first of these is the normal state of N_2 , while the second may be the lower state of the first positive nitrogen bands. The other known excited states of N_2 must give at least one excited atom on dissociation. The ${}^3\Pi$ upper level of the first positive bands, for example, doubtless gives ${}^4S+{}^2D$.

Like CN and N_2^+ , the molecules NO and O_2^+ possess analogous energy level schemes, but differ in part in the way the molecular states dissociate. Normal $\text{N}+\text{O}({}^4S_u+{}^3P_g)$ gives only one ${}^2\Pi$ state, while normal O^++O gives one ${}^2\Pi_g$ and one ${}^2\Pi_u$. NO and O_2^+ each have two known ${}^2\Pi$ states, the lower one the normal state of the molecule in each case (cf. section D3). In O_2^+ , there is practically no doubt that both ${}^2\Pi$ states (one ${}^2\Pi_g$, the other ${}^2\Pi_u$) dissociate into ${}^4S+{}^3P$; the experimental data on the vibrational energy levels strongly support this. In the case of NO, the lower ${}^2\Pi$ doubtless gives normal atoms ${}^4S+{}^3P$, but the upper probably comes from ${}^2D+{}^3P$, the lowest atomic pair capable of giving a second ${}^2\Pi$. The known vibrational levels of the upper ${}^2\Pi$, as observed in absorption, go so high as to show experimentally that this state cannot dissociate into unexcited atoms.

NO has one well-known ${}^2\Sigma^+$ state near the upper ${}^2\Pi$ state, and others a little higher. Vibrational levels of this ${}^2\Sigma^+$ state are known¹⁴⁹ up to at least $v=7$, which has an energy of about 1.96 volts above $v=0$, and a total energy of 7.4 volts above the normal state of NO. Hence it is clear that this ${}^2\Sigma^+$ state does not dissociate into unexcited atoms, since D is about 6.1 volts for the ${}^2\Pi$ normal state of NO (cf. Fig. 48). In fact a linear extrapolation from the observed vibrational levels (Birge and Sponer method) gives $D=14$ volts, indicating that on dissociation the atoms have an energy greater than that

of $^4S+^3P$ by $(14+5.4-6.1) = 13$ volts. Even when large allowance is made for the fact that D values obtained by the Birge and Sponer method are too high, it seems probable, as first suggested by Birge and Sponer, that the dissociation products include one atom in a 3-quantum state, e.g., possibly $N(\cdots 2p^3, ^4S)+O(\cdots 2p^3 3s, ^5S)$.

Unless there is an unknown $^2\Sigma^+$ state of NO below this one, which is very improbable, it is clear that the lowest $^2\Sigma^+$ state of NO is not correlated with the predicted $^2\Sigma^+$ state derivable from two normal atoms $^4S+^3P$. The $U(r)$ curve of the predicted state, which is perhaps an unstable one, must then cross that of the observed $^2\Sigma^+$ state, thus showing that exceptions are possible to the rule stated after (3), section D1.

Two unexcited O atoms (each $1s^2 2s^2 2p^4, ^3P$) give the following molecular states: $^1\Sigma^+_g, ^1\Sigma^+_g, ^1\Sigma^-_u, ^1\Pi_g, ^1\Pi_u, ^1\Delta_g, ^3\Sigma^+_u, ^3\Sigma^+_u, ^3\Sigma^-_g, ^3\Pi_g, ^3\Pi_u, ^3\Delta_u$, and quintets (cf. Table XI). The normal state of $O_2(\cdots \pi^2, ^3\Sigma^-_g)$ evidently corresponds to the $^3\Sigma^-_g$ state derived from two normal atoms. The $^1\Sigma^+_g$ and the predicted $^1\Delta_g$ state also associated with $\cdots \pi^2$ (cf. Table VIII), are no doubt also derived from $^3P+^3P$.

The $^3\Sigma^-_u$ upper level of the Schumann-Runge bands of O_2 cannot be derived from $^3P+^3P$, as Herzberg first pointed out. The lowest-energy pair of atomic states which give a $^3\Sigma^-_u$ molecular state is $^3P_g+^1D_g$, which give $^3\Sigma^+_g, ^3\Sigma^-_g$ (two), $^3\Pi_g$ (three), $^3\Delta_g$ (two), $^3\Phi_g, ^3\Sigma^+_u, ^3\Sigma^-_u$ (two), $^3\Pi_u$ (three), $^3\Delta_u$ (two), $^3\Phi_u$ (cf. Table X, notes). Probably the various predicted states of O_2 derived from $\sigma^2\pi^3\pi^3$ and from $\sigma\pi^4\pi^3$ (cf. section D3) correspond in part to $^3P+^3P$ (unexcited atoms) and in part to $^3P+^1D$.

8. Electron states and dissociation products in the halogens

The normal states of the halogens have already been discussed in sections A9 (cf. Eq. 92) and D3 (F_2 molecule). The structure of the ordinary visible absorption bands of Cl_2, Br_2 , and I_2 is identical with that of the $^1\Sigma \leftarrow ^1\Sigma$ type. The diamagnetism of Cl_2 and a systematic consideration of electron configurations (sections D3 and A9) make it extremely probable that the normal state is $^1\Sigma^+_g$. If the upper state were $^1\Sigma$, it must then be $^1\Sigma^+_u$ (cf. Part IIc, p. 149, Fig. 32).

Now it is known definitely that the upper state of the visible bands of Cl_2, Br_2 , and I_2 gives on dissociation two atoms which are unexcited, so far as their electron configurations and L and S values are concerned, although when J values are considered, one atom is excited ($\cdots p^5, ^2P_{1/2}$), the other unexcited ($\cdots p^5, ^2P_{1/2}$). [To avoid confusion, we shall speak here of an atom which is unexcited except perhaps in respect to J as an LS -normal atom; or if we wish to emphasize J , as a J -normal or a J -excited atom, as the case may be.] But according to Table XI, two like atoms in the same 2P state (J does not matter for this purpose) can give only the following states: $^1\Sigma^+_g, ^1\Sigma^+_g, ^1\Sigma^-_u, ^1\Pi_g, ^1\Pi_u, ^1\Delta_g, ^3\Sigma^+_u, ^3\Sigma^+_u, ^3\Sigma^-_g, ^3\Pi_g, ^3\Pi_u, ^3\Delta_u$. The normal state $^1\Sigma^+_g$ of each halogen molecule can be, and probably is, derived from two LS -normal atoms. The upper state of the visible bands, however, if it were $^1\Sigma^+_u$, could not be so derived. But since we know definitely that this

upper state *is* derived from two *LS*-normal atoms, it is necessary to conclude that it is not a ${}^1\Sigma_u^+$ state after all.¹⁵⁰

To escape from the dilemma into which this puts us, we note that the doublet separations in the 2P normal states of the halogens are relatively large, being larger in iodine than the energy of dissociation *D* of the upper level of the visible bands. Under these conditions, it is reasonable to expect *case c* coupling, for which Λ and S of the molecule are not defined, but Ω is (cf. Part IIc, section *H*). Referring therefore to section *C3a*, Eqs. (100b) and (100), the following *case c* molecular states are predicted: from two identical ${}^2P_{1\frac{1}{2}}$ atoms, $3_u, 2_u, 2_g, 1_u, 1_g, 1_u, 0_u^-, 0_g^+, 0_u^-, 0_g^+$; from one ${}^2P_{1\frac{1}{2}}$ and one ${}^2P_{\frac{3}{2}}$ atom of the same element, $2_g, 2_u, 1_g, 1_u, 1_g, 1_u, 0_g^+, 0_u^-, 0_g^-, 0_u^+$; from two identical ${}^2P_{\frac{3}{2}}$ atoms, $1_u, 0_u^-, 0_g^+$. The structure of the visible halogen bands can now be understood and their dissociation products accounted for, if they are a *case c* $0_u^+ \leftarrow 0_g^+$ transition. [Really the lower state 0_g^+ is much more nearly *case b'* than *case c*, but in any case, 0_g^+ of *case c* corresponds to ${}^1\Sigma_g^+$ of *case b'*.] The upper state 0_u^+ can, the theory shows, be derived *only* from ${}^2P_{1\frac{1}{2}} + {}^2P_{\frac{3}{2}}$, in agreement with its observed characteristics.

While these results are very satisfactory, it is of interest to go further, and to try to explain the 0_u^+ state in terms of electron configurations. Strictly speaking, we cannot do this with a *case c* state. But in the present case, where there is only *one* 0_u^+ state from ${}^2P + {}^2P$, we can establish an unambiguous correlation with the *case a* state which would result if we diminished *r* sufficiently. (States which are *case c* for $r = r_e$ usually would change to *case a* or *b* if *r* were artificially diminished). The only *case a* or *b* state derivable from ${}^2P + {}^2P$ of two identical atoms (cf. list above, in second paragraph), and capable of giving a 0_u^+ state on passage to *case c*, is a ${}^3\Pi_u$ state, or more specifically, the ${}^3\Pi_0$ component of a ${}^3\Pi_u$ state. Now a ${}^3\Pi_u$ state is exactly what one would expect for the first excited state of a halogen molecule, if its normal state is $\cdots (w\pi)^4, {}^1\Sigma_g^+$. By exciting a $w\pi$ electron to the $u\sigma_u$ orbit (cf. *F2* in section *D3*), one would get $\cdots (w\pi)^3 u\sigma, {}^3\Pi_u$ as the lowest excited state. From the $U(r)$ curves of the upper states of the visible halogen bands, it is evident that $u\sigma$ is much more anti-bonding even than $w\pi$.

But where are the ${}^3\Pi_1$ and ${}^3\Pi_2$ components of the ${}^3\Pi$ state? In *case c* they would become respectively 1_u and 2_u , and should probably be derived from two *J*-normal atoms (${}^2P_{1\frac{1}{2}} + {}^2P_{1\frac{1}{2}}$). There must also be a second component 0_u^- which is obtained in addition to 0_u^+ from ${}^3\Pi_0$ in *case c* (cf. Part IIc, section *H*); this 0_u^- is probably derived also from two *J*-normal atoms. The ${}^3\Pi$ state is thus split, on dissociation, 5/6 of it going to ${}^2P_{1\frac{1}{2}} + {}^2P_{1\frac{1}{2}}$, and 1/6 to ${}^2P_{1\frac{1}{2}} + {}^2P_{\frac{3}{2}}$. As a result, only the 0_u^+ part, which goes to ${}^2P_{1\frac{1}{2}} + {}^2P_{\frac{3}{2}}$, has a pronounced minimum in its $U(r)$ curve (cf. Fig. 42). Relations similar to this probably occur rather frequently in band spectra.

Recently some new infrared absorption bands of Br_2 and I_2 have been found, whose upper states have very flat minima, dissociate to give ${}^2P_{1\frac{1}{2}} + {}^2P_{1\frac{1}{2}}$, and probably correspond to the ${}^3\Pi_1$ component of the ${}^3\Pi$; the intensities of these bands are, however, surprisingly low. Transitions from the normal state of a halogen molecule to the 0_u^- part of ${}^3\Pi_0$, or to the ${}^3\Pi_2$, have

not been found; but they would be contrary to the selection rules of case *c*.

A comparison of the $U(r)$ curves of Cl_2 , Br_2 , and I_2 shows that D gets progressively less for the $^1\Sigma^+$ normal state, progressively greater for the 0^+_{u} excited state. Probably this is because the difference in binding energy between $v\pi$ and $u\sigma$ becomes smaller and smaller as both become more like atomic np electrons with increase in n (cf. discussion of O_2 , S_2 , Se_2 in section D4).

Of the mixed halogen molecules, spectra only of IBr and ICl are known. The infrared and visible absorption bands of these molecules are presumably analogous to those of Br_2 and I_2 and presumably involve a $^1\Sigma^+$ normal state, and a $^3\Pi$ first excited state or its case *c* equivalent. According to what is known of the structure of the ICl bands, it appears that the main system of visible bands corresponds to $^3\Pi_0 \leftarrow ^1\Sigma^+$ rather than merely to $0^+ \leftarrow 0^+$. [The interpretation of certain other bands at slightly shorter wave-lengths is uncertain.] Probably both 0^+ and 0^- components of $^3\Pi_0$ dissociate together into J -unexcited atoms $\text{I}(^2P_{1/2}) + \text{Cl}(^2P_{1/2})$. The not yet known $^3\Pi_1$ and $^3\Pi_2$, and the normal state $^1\Sigma^+$, probably all dissociate in the same way. With the loss of the g and u property in going from I_2 or Cl_2 to ICl , the theoretical necessity for the 0^+ component of $^3\Pi_0$ to dissociate to give one J -excited atom has disappeared. At the same time, the D of the whole $^3\Pi$ state seems to have increased, as compared with Cl_2 or I_2 (cf. Fig. 42).¹⁵⁰ It may be, however, that the main system of visible bands is $^3\Pi_1 \leftarrow ^1\Sigma^+$.

In the case of F_2 , the bands corresponding to the visible absorption bands of Cl_2 , Br_2 , and I_2 probably appear only as a continuous absorption; the $U(r)$ curve of the 0^+_{u} state of F_2 may be practically a repulsive one. A transition $^1\Sigma \rightarrow ^1\Pi$ between two excited states of F_2 is known, but its interpretation in terms of electron configurations is uncertain.

In addition to the infrared and visible absorption bands, a number of ultraviolet absorption and emission band-systems of Br_2 , I_2 , and ICl are known, but their nature and their interpretation in terms of electron configurations are uncertain.

9. Bonding power of electrons and valence

As first noted in section C4, bonding electrons tend to produce stable molecules, while anti-bonding electrons have the opposite effect. Many illustrative examples have been given in the sections between that and this. Herzberg has formulated these relations more precisely, and related them to ordinary valence theory, by suggesting that *the number of homopolar valence bonds in a molecule is equal to the difference between the number of pairs of bonding electrons and the number of pairs of anti-bonding electrons*. The numbers of bonds as given by this rule agree very well for the most part with those usually assigned by chemists, although in the case of molecules with an odd number of electrons (e.g., CN , NO) the number of bonds here comes out half-integral (cf. Table XVII).

The writer has suggested¹³⁰ that the *natural unit of valence* is a *single bonding electron*, with the *anti-bonding electron* as a *negative unit*, and that the

usual occurrence of bonding electrons in pairs is merely incidental so far as the mechanism of chemical binding is concerned. In some molecules, the ordinary rules of valence do not fit well, but the existing relations can often be understood in terms of bonding and anti-bonding electrons, or more generally, by assigning to each electron a bonding power which may, in various molecules, have any value within a continuous range.

The sharp division of all electrons into bonding and anti-bonding (and non-bonding) works well in a surprisingly large number of cases, in diatomic molecules with the exception of hydrides. (Nearly-ionic molecules are also excepted, since polar valence is assumed there.) Table XVII shows how the energies of dissociation of molecules in their normal states run parallel to the numbers of valence bonds as given by Herzberg's definition. A fuller account of the relations between atomic and molecular electron configurations and valence will be found in papers by Herzberg and by the writer.¹³⁰

TABLE XVII. *Energies of dissociation (D) and numbers of valence bonds (N).*

Mole- cule	D (volts)	No. bonds (N)	D/N	Mole- cule	D (volts)	No. bonds (N)	D/N
H ₂ ⁺	2.64	$\frac{1}{2}$	5.28	CO ⁺	(7.1)	2 $\frac{1}{2}$	(2.8)
H ₂	4.44	1	4.44	CO	(10.0)	3	(3.3)
He ₂ ⁺	[2.6]	$\frac{1}{2}$	[5.2]	N ₂	[9.1]	3	[3.0]
Li ₂	1.14	1	1.14	NO ⁺	(10.3)	3	(3.4)
C ₂	[5.5]	2	[2.7]	NO	(6.1)	2 $\frac{1}{2}$	(2.5)
BO	[6.6]	2 $\frac{1}{2}$	[2.6]	O ₂ ⁺	(6.2)	2 $\frac{1}{2}$	(2.5)
CN	[7.1]	2 $\frac{1}{2}$	[2.8]	O ₂	5.09	2	2.54
N ₂ ⁺	[6.8]	2 $\frac{1}{2}$	[2.7]	F ₂	(2.9)	1	(2.9)

Notes: Cf. Table II of Ref. 130 for discussion of probable errors of *D* values. Values in brackets are the least reliable, those in parentheses more reliable, while the remainder are the most reliable. Cf. Tables XVIII and XIX for further *D* values.

In determining *N*, $1s\sigma$ or $\sigma_g 1s$ electrons are considered bonding, $2p\sigma$ or $\sigma_u 1s$ as anti-bonding, in H₂⁺, H₂ and He₂⁺. In all the other molecules, the *K* electrons are regarded as non-bonding, while $x\sigma$ (or $\sigma 2s$), $x\sigma$ (or $\sigma 2p$), $w\pi(\pi 2p)$ are considered as bonding, $y\sigma$ (or $\sigma^* 2s$), $v\pi$ (or $\pi^* 2p$) and $u\sigma(\sigma^* 2p)$ as anti-bonding. For the electron configurations of these molecules, cf. (90) in section A3, (92) and (93) in A9, and section D3.

E. APPENDIX: CONSTRUCTION OF *U(r)* CURVES; TABULATION OF NUMERICAL DATA AND ELECTRON CONFIGURATION ASSIGNMENTS

1. Construction of *U(r)* curves

The *U(r)* curves shown in the various figures of Part III are of necessity only roughly correct. In no case do we have any method of determining quantitatively the form of the curve for *r* values far from *r_e*. But in most cases the value of *r_e* and the form of the curve in the neighborhood of *r_e* are substantially or accurately correct. This part of the curve can be drawn accurately when *r_e* and ω_e are known, from data on rotational and vibrational energy levels (cf. Part I, p. 67).

In many cases, however, *r_e* is not known, because a rotational analysis of band structures involving the given electronic level has not been made. Usually in this case ω_e is known fairly accurately from measurements on band heads (cf. Eqs. 17 and 17*a* of Part I). But often, on the other hand, *r_e* is

known from a rotational analysis, while ω_e is not known, because of a lack of a sufficient number of suitable bands. In either case, the missing quantity can be obtained as follows.

When ω_e (or r_e) is known, the corresponding r_e (or ω_e) can usually be estimated moderately accurately by means of one of the two empirical relations $r_e^2\omega_e = \text{constant}$ or $r_e^3\omega_e = \text{constant}$ (cf. Eq. (19) of Part I). The former relation is to be preferred in cases where the value of the constant can be determined for the given molecule from measured values of r_e and ω_e for another state or other states of the same molecule. In other cases, one can often assume $r_e^3\omega_e = 3000 \times 10^{-24}$ in case the molecule is composed of two atoms nearly the same in atomic weight. The value 3000×10^{-24} is an average value of $r_e^3\omega_e$ based on empirical data on many such molecules. If the atoms differ markedly in atomic weight, as in the case of hydrides, the procedure followed here has been to determine the value of $r_e^3\omega_e$ for a molecule as nearly as possible like the molecule under consideration in the atomic weights of its atoms. For example, in estimating ω_e for a state of ZnH when r_e is known, one could use for $r_e^3\omega_e$ a value obtained from values of r_e and ω_e for CuH.—In trying to estimate, say, r_e for a given molecular state, it is of course always best to use a value of $r_e^2\omega_e$ or $r_e^3\omega_e$ based on molecular states as nearly as possible like the given one in respect to r_e and ω_e .

In some cases (e.g., CH), ω_e may be estimated by means of the relation between the rotational coefficients B_e and D_e (cf. Part I, Eq. (4)), but such a value cannot usually be trusted because of the low percentage accuracy of the very small coefficient D_e . In general, a great deal of judgment has had to be used as to the most accurate way of estimating r_e and ω_e in each particular case.

The intervals E_e between the minima $U(r_e)$ of the different $U(r)$ curves of any given molecule are for the most part fairly accurately known from spectroscopic data. In some cases, however, especially when the positions of the $U(r)$ curves of an ionized molecule relative to those of the neutral molecule are involved, they are based on critical potential data. Strictly speaking, only the interval E_0 between the energy levels $v=0$ of any two electronic states is known directly from the spectrum. But when ω_e ,—and, for the greatest accuracy, also x_e ,—are known for each electronic state, the necessary small correction is easily made to get E_e from E_0 values.

The true form of the portions of the $U(r)$ curve far from $r=r_e$ is in all cases more or less uncertain. Each curve has, however, here been drawn by means of a Morse function (see below) so that the part corresponding to large r goes asymptotically to the correct energy of dissociation D as $r \rightarrow \infty$, while the part near r_e is in agreement with the empirical or estimated values of r_e and ω_e . The portion of the curve for $r < r_e$ and not very near r_e has been sketched qualitatively by extrapolating the part near r_e , or usually by assuming a Morse function.

In applying the above procedure, a large source of uncertainty is the fact that we usually do not know D at all accurately. In coping with this difficulty, a helpful fact is that,—with some reservations,¹⁵¹—as $r \rightarrow \infty$ each $U(r)$ curve

must go to an energy value corresponding to a definite electron state of each atom. This fact, taken in connection with approximate empirical evidence on D values, or with theoretical considerations (cf. Section C), often serves to fix exactly at least the *relative* positions of the different $U(r)$ curves of a molecule for $r = \infty$. An exact knowledge of D for *one* $U(r)$ curve of a molecule is then sufficient to determine exact D values for all other $U(r)$ curves for which the electron states of the dissociated atoms are known.

In the few cases where D is known accurately from spectroscopic data, it has been determined by measuring the frequency corresponding to a boundary between discrete bands and a continuous region in the spectrum (method of Franck, cf. Part I, p. 83 and reference 15). Examples where this method has been used are the ${}^3\Sigma^-_u$ excited state of O_2 from the ${}^3\Sigma^-_u \leftarrow {}^3\Sigma^-_g$ bands (cf. Fig. 49) and the ${}^3\Pi_0^+$ excited states of the halogen molecules, from the ${}^3\Pi_0^+ \leftarrow {}^1\Sigma^+_g$ bands (section D8 and Fig. 42). Knowing D accurately for these states, it has then been possible to determine it for other states by the method mentioned in the preceding paragraph.

In some cases, more or less accurate values of the D are known from chemical methods. In a few cases, values which are probably reliable have been obtained from a study of predissociation spectra. In most cases, D is directly known only roughly from the extrapolation method of Birge and Spomer. In a few cases (e.g. BeH, CH, NH) it has been necessary here to estimate D by interpolation between D values of neighboring molecules in the periodic system.

Birge and Spomer¹⁵² noted that for many electronic states, especially the normal states of molecules, the *observed* vibrational levels can be represented fairly accurately by

$$G(v) = \omega_e(v + \frac{1}{2}) - x_e\omega_e(v + \frac{1}{2})^2, \quad (109)$$

the terms in higher powers of $(v + \frac{1}{2})$ being negligible. In other cases, however, especially in excited states, the higher power terms are needed. In cases where Eq. (109) holds for the observed levels, the energy of dissociation D is easily calculated if we assume the equation to apply for all values of v . The spacing of any two adjacent vibrational levels, according to the Bohr theory, is proportional to the mean value for these two levels of the mechanical frequency of the vibration (cf. Part IIa, Eq. (23)). Evidently when this frequency reaches zero with increasing v , the molecule is at the point of dissociation. Hence if from Eq. (109) we obtain $dG(v)/dv \sim \Delta G(v)/\Delta v$ and then set it equal to zero, we shall determine a value of v , $v_{\max}$, at which dissociation is about to set in. Putting $v_{\max}$ into Eq. (109), we determine D_e in cm^{-1} . Proceeding in this way one obtains

$$(v_{\max} + \frac{1}{2}) = \omega_e/2x_e\omega_e \quad (110)$$

$$D_e = \omega_e^2/4x_e\omega_e. \quad (111)$$

The symbol D_e is used to designate the energy of dissociation measured from the bottom of the $U(r)$ curve. This is slightly larger than the ordinary energy of dissociation D_0 , which is measured from the level $v=0$.

Although in Birge and Sponer's original paper a consistent set of D values was obtained, many of them from Eq. (111) (or rather, its equivalent in the old Bohr theory, namely $D_0 = \omega_0^2/4x\omega_0$), it has since turned out that in nearly all cases where they could be checked, values from Eq. (111) are too large, often by 40 percent. Evidently Eq. (109) usually fails for large values of v .

P. M. Morse, however, noting Birge and Sponer's evidence in favor of the approximate applicability of Eq. (109) for all v values, proposed essentially the following as a suitable form for $U(r)$:⁵

$$U(r) = D_e[1 - e^{-a(r-r_e)}]^2, \quad (112)$$

where

$$a = (2\pi^2\mu c\omega_e^2/hD_e)^{1/2}, \text{ with } D_e \text{ in cm}^{-1}. \quad (113)$$

This $U(r)$ function has the property that its quantized energy values are given exactly by Eq. (109), with $x_e\omega_e$ related to D_e and ω_e by Eq. (111). Eq. (113) may therefore be written in terms of $x_e\omega_e$,

$$a = (8\pi^2\mu c x_e\omega_e/h)^{1/2}. \quad (114)$$

If in any particular case we should know that Eq. (109) holds accurately for all values of v , we could draw the complete $U(r)$ curve by means of Eqs. (112), (111), and (114) from a knowledge of the empirically determined values of ω_e , $x_e\omega_e$, and r_e . Or if we should happen to know ω_e , D_e , and r_e , we could use Eqs. (112), (113).

Morse's function is extremely useful in that it permits the construction of $U(r)$ curves which are qualitatively correct from $r=0$ to $r=\infty$, except in the region close to $r=0$, which is of no practical importance. But it is incorrect to assume that Morse's function is ever even *nearly* quantitatively correct throughout the rest of its course, unless by merest chance,—not even if Eqs. (109) and (111) should hold. It is, however, always essentially accurate close to r_e , if correct empirical values of r_e and ω_e are used in its construction. It is also of course correct for $r=\infty$ if D is known and if Eq. (113) is used to define a . At intermediate r values it merely gives a plausible interpolation and for values less than r_e a plausible extrapolation. In these regions of r , however, this is probably the best we can do in the present stage of development of the theory and of our empirical knowledge of band spectra.

If for an electron state one knows only r_e , ω_e , and D_e , one cannot easily do better in constructing its $U(r)$ curve than to use Morse's function (Eqs. (112–3)). If one knows also $x_e\omega_e$, then,—unless $x_e\omega_e$ and D_e are related as in Eq. (111), which is rarely even approximately the case,—one might approximate the true $U(r)$ curve by using Morse's function with a defined *either* as in Eq. (113) or as in Eq. (114). Of these two curves, that with Eq. (114) should presumably be the more nearly correct for r values near r_e (very close to r_e , however, the two curves are practically identical), but as $r \rightarrow \infty$, the Eq. (114) curve extrapolates to an incorrect value of D_e . Furthermore, it has been found by actual trial with several typical molecular states that the differences between the two curves near r_e do not become appreciable until r values

are reached where the incorrectness of the D_e of the Eq. (114) curve begins to become obvious. The curve using Eq. (113) and the correct value of D_e is thus evidently greatly preferable. *In constructing the $U(r)$ curves in Figs. 35–49, Eqs. (112, 113) have been used in all cases. In some cases, however (e.g., the Σ states of CH), the resulting curves have been somewhat altered for $r < r_e$ to conform better with what is known theoretically as to the necessary behavior of the curves as $r \rightarrow 0$.*

Curves shown by dashes in the figures are empirically unknown but theoretically predicted curves, for which values of r_e , ω_e , and D have been estimated by intelligent guessing.

If we have sufficient data on the coefficients of the various terms in the complete expression for the quantized energy of a molecule in a given electronic state (cf. Eqs. (3a), (4a), (5), (6) of Part I), the part of the $U(r)$ curve near $r = r_e$ can theoretically be drawn more accurately by using Kratzer's function (Eq. (1) of Part I), in the region where the latter is convergent, than by using Morse's function. Thus from α_e of Eqs. (3a) and (6) one can determine b^* of Eq. (1), and from α_e taken together with $x_e\omega_e$ (cf. Eq. (6)) one can determine c^* of Eq. (1); a^* of Eq. (1) is determined by ω_e (cf. Eq. (6)). (We are here using the revised notation α_e in place of α of Part I.) It should be especially noted that $x_e\omega_e$ alone is incapable of determining either b^* or c^* , hence by itself gives no definite information about the shape of $U(r)$. The fact that Morse's function with Eq. (114) uses $x_e\omega_e$ to determine the shape of $U(r)$ is possible only because it implicitly assumes a relation between b^* and c^* which determines both (also d^* , e^* , $\dots$) when $x_e\omega_e$ is known.¹⁵³ But there is no reason to suppose that this assumed implicit relation is the correct one. That it may sometimes be very far from correct is indicated by the fact that if $x_e\omega_e$ is negative, as sometimes happens,^{12b} its use with Eq. (114) becomes impossible.

In practice the region near r_e where Kratzer's function is convergent is so limited that in this region the $U(r)$ curve is not appreciably different from that given by Morse's function with Eq. (113).

2. Tables

Tables XVIII and XIX have the following purposes. (1) They contain a summary of the probable electron configurations for a large number of molecular states. More will be found in (92), (93), (94), and section D6. (2) They contain a number of approximate predictions as to the energy and other characteristics of a number of states not yet known experimentally. In most cases such predictions have been made only for *one* of a group of analogous molecules (e.g., for LiH in Fig. 39, and for Li₂ in Fig. 41). Analogous predictions could be made for the other analogous molecules (e.g., for NaH, Na₂ in Figs. 39, 41). (3) They contain the essential numerical constants used in drawing the $U(r)$ curves of Figs. 35–49. These constants are in part based directly on observed data, in part estimated. The estimated values are given in brackets if of relatively low reliability, in parentheses if of higher reliability. When values of r_e or ω_e are given in parentheses, this generally means that r_0 or ω_0 is

TABLE XVIII. Summary of numerical data and probable electron configurations for hydrogen, helium, and hydrides. (Notes: energies E_0 and D_0 are measured from or to the vibrational level $v=0$ of each electronic state concerned. Pr means "predicted" (not yet observed); Rep means repulsive state.)

Molecule; Fig. No.	State			Electron Config'n. (outer electrons)	Molecular Constants			Remarks
	Name	Type	E_0 (volts)		$r_e(A)$	$\omega_e(\text{cm}^{-1})$	D_0 (volts)	
H_2 (46)	A	$1\Sigma^+_g$	0	$(1s\sigma)^2$	0.74	4375	4.44	Ion. Pot. of H atom 13.54 volts
	B	$3\Sigma^+_u$	(Rep)	$(1s\sigma)(2p\sigma)$	1.28	1357	3.44	
	Pr	$3\Pi_u$	11.14	$2p\sigma$	[1.05]	[2400]	[2.86]	
	C	$3\Sigma^+_g$	11.72	$2p\pi$	0.99	2664	2.86	
H_2^+ (45, 46)	Pr	$1\Pi_u$	11.73	$2s\sigma$	1.05	2447	2.34	Ion. Pt. of He atom 24.47 volts. E_0 values for He_2 measured <i>downward</i> from level $v=0$ of normal state of He_2^+ .
		$1\Sigma^+_g$	12.24	$2p\pi$	[1.00]	[2580]	[2.33]	
		$3\Sigma^+_g$	[12.25]		1.06	2260	2.64	
		$3\Sigma^+_u$	15.34	$1s\sigma$				
He_2 (49)	2^3S	$1\Sigma^+_g$	(Rep)	$(\sigma_g 1s)^2(\sigma_u 1s)^2$	1.05	1811	[2.23]	Ion. Pt. of He atom 24.47 volts. E_0 values for He_2 measured <i>downward</i> from level $v=0$ of normal state of He_2^+ .
	2^1S	$3\Sigma^+_u$	-4.24	$(\sigma_u 1s)(2s\sigma)$	1.04	(1872)		
	2^3P	$1\Sigma^+_g$	-3.94	$(2s\sigma)$	1.06	(1773)		
	2^1P	$3\Pi_g$	-3.64	$(2p\pi)$	1.08	(1724)		
	3^3P	$1\Pi_g$	-3.51	$(2p\pi)$	1.10	(1676)		
	Pr	$3\Sigma^+_g$	-2.88	$(2p\sigma)$	[1.10]	[1676]		
	3^3S	$1\Sigma^+_g$	[-2.76]	$(2p\sigma)$	1.07	(1728)		
	3^3P	$3\Sigma^+_u$	-1.71	$(3s\sigma)$	1.08	1724		
	3^3P	$3\Pi_g$	-1.58	$(3p\pi)$	1.08	(1619)		
	3^3P	$3\Sigma^+_g$	-1.57	$(3d\sigma)$	1.08	(1639)		
	3^3P	$3\Pi_u$	-1.55	$(3d\pi)$	1.08	(1672)		
	3^3P	$3\Pi_u$	-1.49	$(3d\delta)$	1.08	(1664)		
	3^3P	$3\Sigma^+_u$	0	$(\sigma_g 1s)^2(\sigma_u 1s)$			[2.6]	
LiH (39)	Pr	$1\Sigma^+$	0	$(2s\sigma)^2$	1.60	1406	(2.47)	
	Pr	$1\Sigma^+$	[2.0]	$(2s\sigma)(2p\sigma)$	[2.1]	[450]	[0.5]	
	Pr	3Π	3.20	$(2p\sigma)$	2.53	287	(1.11)	
	Pr	1Π	[3.4]	$(2p\pi)$	[2.0]	[900]	[0.91]	
NaH (39)								
NaH (39)		$1\Sigma^+$	0	$(3s\sigma)^2$	1.88	1171	(2.25)	
		$1\Sigma^+$	2.87	$(3s\sigma)(3p\sigma)$	3.03	335	(1.47)	

TABLE XVIII. (Cont.)

Molecule; Fig. No.	State		Electron Config'n. (outer electrons)	Molecular Constants			Remarks
	Name	Type	E_0 (volts)	$r_e(A)$	$\omega_e(\text{cm}^{-1})$	D_0 (volts)	
BeH (40)		$2\Sigma^+$ 2Π	0 2.47	1.34 1.33	(2106) (2135)	[2.40] [2.75]	
BeH ⁺ (40)		$1\Sigma^+$ $1\Sigma^+$	0 4.82	1.31 1.60	2222 1477	[2.80] [1.92]	Ion. Pot. of Be atom = (9.4) volts.
MgH (40)	X A B	$2\Sigma^+$ 2Π 2Π	0 2.38 5.09	1.73 1.68 1.67	1494 1604 (1700)	[1.41] [1.74] [2.24]	
MgH ⁺ (40)		$1\Sigma^+$ $1\Sigma^+$	0 4.40	1.65 2.01	1702 1138	[1.77] [1.75]	Ion. Pot. of Mg atom = 7.62 volts.
ZnH (40)	X A B	$2\Sigma^+$ 2Π $2\Sigma^+$	0 2.89 3.61(?)	(1.61) (1.51) [2.16]	(1614) [1780] [888]	0.91 2.03 1.31(?)	
ZnH ⁺ (40)		$1\Sigma^+$ $1\Sigma^+$	0 5.73	1.51 1.71	1915 1358	[2.03] [2.33]	Ion. Pot. of Zn atom = 9.35 volts.
CdH (40)	X A B C	$2\Sigma^+$ 2Π $2\Sigma^+$ $2\Sigma^+$	0 2.81 3.50 5.25	1.75 1.66 2.38 (1.81)	1431 1748 874 [1335]	0.67 1.64 0.89 0.80	
CdH ⁺ (40)		$1\Sigma^+$ $1\Sigma^+$	0 5.27	1.66 1.86	1777 1249	[1.70] [1.90]	Ion. Pot. of Cd atom = 8.95 volts.
HgH (40)	X A B Pr Pr	$2\Sigma^+$ 2Π $2\Sigma^+$ 4Π $4\Sigma^+$	0 {3.08 3.53 4.18 (cf. Fig. 40)}	1.73 1.58 (1.97)	1433 {(2026) 2069 [1077]}	0.37 1.94 1.71 1.06	

TABLE XVIII. (Cont.)

Molecule; Fig. No.	State			Electron Config'n. (outer electrons)	Molecular Constants			Remarks
	Name	Type	E_0 (volts)		r_e (Å)	ω_e (cm ⁻¹)	D_0 (volts)	
HgH ⁺ (40)		$1\Sigma^+$ $1\Sigma^+$	0 5.44	$(6s\sigma)^2$ $(6s\sigma)(6p\sigma)$	1.59 1.69	2016 1647	[2.20] [3.11]	Ion. Pot. of Hg atom = 10.39 volts.
BH (35)	Pr	$1\Sigma^+$ 3Π 1Π	0 [0.85] 2.85	$(2s\sigma)^2(2p\sigma)^2$ $(2p\sigma)(2p\pi)$ $(2p\sigma)(2p\pi)$	1.23 [1.23] 1.22	(2230) [2230] (2275)	[3.45] [2.6] [0.6]	
AlH (35)	X Pr A	$1\Sigma^+$ 3Π 1Π	0 [1.50] 2.90	$(3s\sigma)^2(3p\sigma)^2$ $(3p\sigma)(3p\pi)$ $(3p\sigma)(3p\pi)$	1.64 [1.64] 1.64	1681 [1681] (1681)	3.06 [1.56] 0.16	D of 1Π from beginning of rotational instabil- ity.
CH (36)	X Pr A B C Pr	2Π $4\Sigma^-$ 2Δ $2\Sigma^-$ $2\Sigma^+$ 2Π	0 [0.36] 2.86 3.17 3.93 [Rep]	$(2s\sigma)^2(2p\sigma)^2(2p\pi)^2$ $(2p\sigma)(2p\pi)^2$ $(2p\sigma)(2p\pi)^2$ $(2p\sigma)(2p\pi)^2$ $(2p\sigma)(2p\pi)^2$ $(2p\pi)^3$	1.12 [1.05] (1.10) 1.17 (1.12)	[2930] [3400] [3030] [2600] [2980]	[4.0] [3.64] [2.35] [0.83] [1.28]	
NH (37)	Pr Pr	$3\Sigma^-$ 1Δ $1\Sigma^+$ 3Π 1Π $1\Sigma^+$	0 a [=1.1] [1.9] 3.67 $a+3.79$ [8.6]	$(2p\sigma)^2(2p\pi)^2$ $(2p\sigma)^2(2p\pi)^2$ $(2p\sigma)^2(2p\pi)^2$ $(2p\sigma)(2p\pi)^3$ $(2p\sigma)(2p\pi)^3$ $(2p\pi)^4$	(1.06) (1.035) [1.03] (1.08) (1.115) [1.03]	[3270] [3430] [3460] [3150] [2900] [3460]	[4.2] [5.49] [5.86] [2.92] [1.70]	Data on the 1Δ and 1Π states are from unpub- lished work of Dr. R. W. B. Pearse, kindly communicated to the writer by Dr. Pearse.
PH (37)		$3\Sigma^-$ 3Π	0 3.6	$(3p\sigma)^2(3p\pi)^2$ $(3p\sigma)(3p\pi)^3$	(1.43) (1.48)	[2600] [2420]	[3.2]	
OH (38)		2Π $2\Sigma^+$	0 4.00	$(2p\sigma)^2(2p\pi)^3$ $(2p\sigma)(2p\pi)^4$	0.97 1.01	(3660) 3183	[4.9] [2.86]	
HCl ⁺ (38)		2Π $2\Sigma^+$	0 3.47	$(3p\sigma)^2(3p\pi)^3$ $(3p\sigma)(3p\pi)^4$	1.31 1.53	2608 1603	3.63 0.74	Ion. Pot. of Cl = 12.96 volts. Dissociation of $2\Sigma^+$ into Cl + H ⁺ is assumed.

TABLE XIX. (Continued).

Molecule; Fig. No.	State			Numbers of electrons (outside of two K shells)						Molecular constants			Remarks
	Name	Type	E_0 (volts)	$z\sigma$ or σ^2s	$y\sigma$ or σ^*2s	$w\pi$ or π^2p	$x\sigma$ or σ^2p	$v\pi$ or π^*2p	$u\sigma$ or σ^*2p	r_e (Å)	ω_e (cm ⁻¹)	D_0 (volts)	
CO	X	$1\Sigma^+$	0	2	2	4	2			1.15	2167	(10.0)	Cf. section D3. D from chemical data and D of O_2
	A'	?	4.8							—	—	(5.2)	
	a	3Π	5.98	2	2	4	1	1		—	1739	(4.0)	
	a'	$3\Sigma^?$	7.14	2	2	3	2	1		—	1182	(3.9)	
	d	3Π	7.9	2	1	4	1	1	(?)	—	—	(3.1)	
N ₂	A	Π	7.99	2	2	4	1	1		1.23	1517	(2.0)	Cf. section D3.
	X	$1\Sigma^+_g$	0	2	2	4	2			1.09	2360	[9.1]	
	A	$3\Sigma^+_g?$	a	2	2	3	2	1		1.29	1460	[9.1-a?]	
	a	$1\Sigma^+_g?$	8.50	2	2	3	2	1		—	1692		
	B	3Π	a+1.17	2	2	4	1	1		1.21	1733	[10.32-a]	
NO (48)	C	3Π	a+4.82	2	1	4	2	1		1.14	2045		D from chemical data and D of O_2 and N_2 .
	D	?	a+6.62							—	—		
	X	2Π	0	2	2	4	2	1	(and one more)	1.15	1906	[6.1]	
	A	$2\Sigma^+$	5.45	2	2	4	2	2		1.06	2375	[10]	
	B	2Π	5.60	2	2	3	1	2		1.41	1038	[2.89]	
O ₂ ⁺ (48)	C	2Σ	6.45							1.07	(2401)	[9.5]	Cf. forthcoming article in Phys. Rev. in regard to E_0 and ω_e values. The D values are calculated from D of O_2 and the ion. Pots. of O (13.56 volts) and O_2 (12.5 volts).
	D		6.58							[1.06]	2351	[9.5]	
	X'	$2\Pi_g$	0	2	2	4	2	1		1.14	1876	(6.15)	
	A'	$2\Pi_u$	4.73	2	2	3	2	2		1.41	869	(1.4)	
	a'	$4\Pi_u?$	a =3.6	2	2	3	2	2	Doubt- ful	[1.31]	1037(?)	[2.6]	
O ₂ (48)	b'	$4\Sigma^-_g?$	a+2.05(?)	2	2	4	1	2		[1.22]	1198(?)	[2.5]	D estimated.
	X	$3\Sigma^-_g$	0	2	2	4	2	2		1.20	1585	5.09	
	Pr	$1\Delta_g$	[0.81]	2	2	4	2	2		[1.21]	[1509]	[4.28]	
	A	$1\Sigma^+_g$	1.62	2	2	4	2	2		1.22	1433	3.47	
	B	$3\Sigma^-_u$	6.09	2	2	3	2	3		1.60	710	0.96	
F ₂ (42)		$1\Sigma^+_g$	0	2	2	4	2	4		[1.5]?	[1150]	(2.9)	

TABLE XIX. (Continued).

Molecule; Fig. No.	State			Numbers of electrons (outside of two K shells)						Molecular constants			Remarks
	Name	Type	E_0 (volts)	$z\sigma$ or σ^2s	$y\sigma$ or σ^*2s	$w\pi$ or π^2p	$x\sigma$ or σ^2p	$v\pi$ or π^*2p	$u\sigma$ or σ^*2p	r_e (Å)	ω_e (cm ⁻¹)	D_0 (volts)	
Ne ₂	Pr	$1\Sigma^+_g$	[Rep]	2	2	4	2	4	2			0	
				$z\sigma$ or σ^*ns	$y\sigma$ or σ^*ns	$w\pi$ or πn	$x\sigma$ or σnp	$v\pi$ or π^*np	$u\sigma$ or σ^*np				
Na ₂ (41)	A	$1\Sigma^+_g$	0	2	1								D based on new data of Nusbaum and Loomis.
	B	$1\Sigma^+_u$	1.85	1	1					3.15	159	(0.76)	
	C	$1\Pi_u$	2.51	1	(σ_u^*3p)	1				3.56	116	(1.01)	
K ₂ (41)	A	$1\Sigma^+_g$	0	2	1								D based on new data of Nusbaum and Loomis.
	B	$1\Sigma^+_g$	1.44	1	1					[3.6]	93	(0.51)	
	C	$1\Pi_u$	1.90	1	(σ_u^*4p)	1				[4.2]	69	(0.67)	
Cl ₂ (42)		$1\Sigma^+_g$	0	2	2	4	2	4	4	1.98	565	2.47	
		0^+_u	2.18	2	2	4	2	3	1	2.42	261	0.40	
Br ₂ (42)	Pr	$1\Sigma^+_g$	0	2	2	4	2	4	4	2.28	324	1.96	New data by W. G. Brown of this labora- tory.
		2^+_u	(1.83)	2	2	4	2	3	1	[2.9]	(124)	(0.17)	
	Pr	0^+_u	1.93	2	2	4	2	4	4	2.67	165	0.46	
I ₂ (42)	X	$1\Sigma^+_g$	0	2	2	4	2	4	4	2.66	215	1.54	Data of W. G. Brown
	Pr	2^+_u	(1.45)	2	2	4	2	3	1	[3.7]	(45.5)	(0.10)	
	Pr	0^+_u	1.92			4	2			3.01	128	0.85	
ICl (42)		0^+_u				4	2	4	4	2.30	384	2.15	
	A	$0^+(\Pi_0)$	1.69	2	2	4	2	3	1	2.63	227	0.46	

known, and that a small correction has been estimated and applied to this to get r_e or ω_e . When the D value of one electronic state of a molecule, which we shall call the *key state*, is known, those of all other states can be calculated if we know their dissociation products and E_0 values. For each molecule, the state chosen as key state is the one whose D is considered to have the smallest (absolute) probable error; the D value of this state is given in bold-face type in the tables. By the energy of dissociation D is always meant, in this article, the quantity D_0 , i.e., the energy of dissociation of a molecule from the lowest actual vibrational level ($v=0$).

For numerical data on additional molecules or molecular states, reference may be made to Weizel's tabulation. The writer is to a large extent indebted to this and to an unpublished table by Dr. W. Jevons for the data given in Tables XVIII and XIX. Numerical data on A values of the molecular states given in Tables XVIII and XIX will be found in Tables XIII and XIV. The probable products of dissociation for most of the states given in the tables will be found in the figures.

REFERENCES

^{115a} Parts I, IIa, IIb, R. S. Mulliken, Rev. Modern Physics **2**, 60–115, 506–8 (1930); Part IIc, **3**, 90–155 (1931).

¹¹⁶ When the magnetic energy represented by $AA\Sigma$ in Eq. (98) is due¹²⁵ to a single π electron, one may write $AA\Sigma = \alpha\lambda\sigma$, where α is always positive, and σ is merely Σ for the case that the latter is the projection of the s of a single electron. When there are three equivalent π electrons, we have $m_{i_1} = m_{i_2} = \pm 1$, $m_{i_3} = \mp 1$, hence $M_L = m_{i_1} + m_{i_2} + m_{i_3} = -m_{i_1}$. Since $m_{i_1} = m_{i_2}$, the corresponding spins s_1 and s_2 are anti-parallel, and the magnetic interaction energy of m_{i_1} and s_1 , plus that of m_{i_2} and s_2 , is zero. Hence the whole magnetic energy is that of the interaction of m_{i_3} and s_3 , and is given by $\alpha_3\lambda_3\sigma_3$, where $|\sigma_3| = |m_{i_3}|$. A little consideration now shows that when Σ (defined as positive when M_L and M_S have the same sign) is positive (${}^2\Pi_{11}$), σ_3 is opposite to m_{i_3} so that the magnetic energy is negative. Hence A in $AA\Sigma$ is negative, in fact $A = -\alpha_3$, whereas for a single π electron, $A = +\alpha$. Hence π , ${}^2\Pi$ is regular, π^3 , ${}^2\Pi$ is inverted.

¹¹⁷ Since we are dealing with equivalent electrons (i.e. electrons alike in n and l), the cases $m_{i_1} = +1$, $m_{i_2} = -1$ and $m_{i_1} = -1$, $m_{i_2} = +1$ are *identical* for the Pauli principle, hence only one of them can be counted, and we get only one ${}^1\Sigma$ and one ${}^3\Sigma$ state.

¹¹⁸ Cf. F. Hund, Zeits. f. Physik **63**, 726 (1930), and E. Hückel, Zeits. f. Physik **60**, 442–3 (1930).

¹¹⁹ Here we have $S=0$ and $S=1$ for each of the two cases $m_{i_1} = +1$, $m_{i_2} = -1$ and $m_{i_1} = -1$, $m_{i_2} = +1$. These two cases are distinguishable here (unlike π^2 in Ref. 117), because the electrons are not equivalent. If there were no interaction between the electrons, the energy would be the same for the two cases, giving a Σ state with double statistical weight, but the interaction of the electrons causes this double-weight state to split, according to the new quantum mechanics, into a Σ^+ and a Σ^- state. All this holds for each of the two S values.

¹²⁰ This table is practically the same as that given by F. Hund (Zeits. f. Physik **63**, 727, 1930), except for the addition of the designations r , i and n . For the method of obtaining these results, reference may be made to R. S. Mulliken, **32**, 217–221 (1928), although the discussion given there is not very satisfactory, and does not take proper account of Σ^+ and Σ^- states. The assignment of the designations r , i , n given here is obtained by a consideration of the orientation (parallel or anti-parallel) of the m_{i_r} of each electron relative to the average projection of its spin s_r on the electric axis. In doing this, all the $\mathbf{s}^*_r$'s ($\mathbf{s}^* = [s(s+1)]^{1/2}$, cf. Part IIa, p. 86), except those which are paired off with others because of an identity of their n , l , and m_l , are supposed combined to form a resultant $\mathbf{S}^*$. The sign of the component of each $\mathbf{s}^*_r$ along $\mathbf{S}^*$ is then noted. According as this is positive or negative, the projection of $\mathbf{s}^*_r$ along the electric axis has the same or the opposite direction to the projection (M_S) of $\mathbf{S}^*$. Next one considers whether m_{i_r} and

the projection of $\mathbf{s}_r^*$ are parallel or antiparallel when M_L is parallel to M_S , i.e., when Σ is positive. Often there is only one $m_{l_r} \neq 0$ whose $\mathbf{s}_r^*$ has an average projection on the axis differing from zero. In this case, if m_{l_r} and the projection of its $\mathbf{s}_r^*$ are parallel when Σ is positive, the multiplet is regular, if they are antiparallel, it is inverted. If no $m_{l_r} \neq 0$ has a mean spin projection differing from zero, the multiplet is narrow (n), the magnetic energy then being determined by secondary factors, mainly by interactions of m_{l_r} 's with the spins of *other* electrons. If more than one electron with $m_{l_r} \neq 0$ has a mean projection of its $\mathbf{s}_r^*$ different from zero, one must sum over the effects of the different electrons. Here, if the different m_{l_r} 's differ in sign, it is impossible to decide how the result will come out unless more information is available, at least as to the relative magnitudes of the magnetic interactions of the different m_{l_r} 's with their respective $\mathbf{s}_r^*$'s.

¹²¹ According to the convention recommended by the committee on line spectrum notation, odd states are indicated by a $^\circ$, as in $^2P^\circ$, $^3S^\circ$, while even states are indicated by the absence of a distinguishing mark. In the present article, however, the symbols 2P , 3S , etc. when used without distinguishing mark are perfectly general, i.e., nothing is implied as to even or odd character. When the latter is of interest, a distinctive subscript g or u is used for each case.

¹²² The basis for this rule is similar to that for the corresponding rule applying to Σ^+ and Σ^- states (reference 123). In fact the rule for deciding between 0^+ and 0^- follows from that for deciding between Σ^+ and Σ^- if one uses the rules for correlating case c states with case a or b states (cf. Part IIc, section H1). The converse statement is equally true.

¹²³ Cf. E. Wigner and E. E. Witmer, *Zeits. f. Physik* **51**, 859 (1928) and F. Hund, *Zeits. f. Physik* **63**, 722 (1930).

¹²⁴ Cf. F. Hund, *Zeits. f. Physik* **63**, 730 (1930). Eq. (97) was obtained by E. Teller.

¹²⁵ It is easily verified that $\Sigma k[3\lambda^2 - l(l+1)] = 0$ for the electrons of any atomic closed shell. Such electrons also contribute nothing to the term $A\Lambda\Sigma$. It also seems probable that $[f(S, \Lambda, r) - f_0(S, L)] = 0$ for any atomic closed shell, if r is not too large. Hence the closed shells probably contribute nothing to $T - T_0$ in Eq. (98); or at worst, they contribute a small function of r which is independent of Λ and S , since these depend on electrons not in closed shells.

¹²⁶ Cf. W. Weizel, *Handbuch der experimentellen Physik, Ergänzungsband 1931* (Table 56).

¹²⁷ R. S. Mulliken, *Phys. Rev.* **36**, 1440-50 (1930).

¹²⁸ Cf. e.g., O. K. Rice, *Phys. Rev.* **37**, 1187 (1931); and A. Jablónski, *Zeits. f. Physik* **70**, 723 (1931); W. Weizel, *Phys. Rev.* **38**, 642 (1931).

¹²⁹ For a review of the whole subject, cf. W. Heitler, *Phys. Zeits.* **31**, 185-204 (1930), and more recent articles (cf. references given in reference 130).

¹³⁰ G. Herzberg, "Leipziger Vorträge 1931," p. 167 (S. Hirzel, Leipzig). R. S. Mulliken, *Chem. Rev.*, December (1931).

¹³¹ S. M. Naudé, *Phys. Rev.* **38**, 372 (1931); *Proc. Roy. Soc.*, 1932.

¹³² Cf. W. Weizel, *Handbuch der experimentellen Physik, Ergänzungsband, 1931*, for review and literature.

¹³³ For further particulars, cf. R. S. Mulliken, *Phys. Rev.* **33**, 742-7 (1929), and work of Goudsmit there cited.

¹³⁴ R. Mecke, *Zeits. f. Physik* **36**, 795 (1926); **42**, 417-22 (1927); E. Hulthén, *Nature* **116**, 642 (1925).

¹³⁵ Fig. 43 is essentially an elaboration of Figs. 1 and 17 of F. Hund, *Zeits. f. Physik* **63**, 719 (1930).

¹³⁶ Cf. M. Delbrück, *Ann. d. Physik* [5], **5**, 36 (1930); N. Rosen, *Phys. Rev.* **38**, 275 (1931).

¹³⁷ The diamagnetism of N_2 is nearly conclusive evidence of a $^1\Sigma$ normal state. The structure of the rotational Raman spectrum (F. Rasetti, *Zeits. f. Physik* **61**, 598, 1930) then definitely shows that the normal state is $^1\Sigma$.

¹³⁸ The lowest known state of N_2^+ is the lower state of the negative nitrogen bands, which are $^2\Sigma \rightarrow ^2\Sigma$ or, more specifically, undoubtedly $^2\Sigma^+ \rightarrow ^2\Sigma^+$, since $^2\Sigma^- \rightarrow ^2\Sigma^-$ would be absurd from the standpoint of possible electron configurations. That the lower $^2\Sigma$ is $^2\Sigma^+$, is then seen from the fact that, just as in the case of the normal state of N_2 (cf. Rasetti, Raman effect¹³⁷) the rota-

tional levels with even K , according to the way the intensities alternate in the N_2^+ bands, are "strong" levels (cf. Part IIc, section K).

¹³⁹ That $^3\Sigma^+$ should come below $^1\Sigma^+$, $^3\Delta$ below $^1\Delta$, but $^1\Sigma^-$ below $^3\Sigma^-$ for the case of two non-equivalent π electrons ($\pi\pi$) is probably to be expected, as one can see from an inspection of the wave-functions (cf. F. Hund, *Zeits. f. Physik* **63**, 726 (1930) for these). That the whole group $^1\Sigma^-$, $^3\Delta$, $^3\Sigma^+$ should come below the group $^3\Sigma^-$, $^1\Delta$, $^1\Sigma^+$ is likely, although it is possible that the two groups may overlap somewhat. A study of the wave-functions indicates that analogous results hold for the configuration $\cdots \pi^3\pi$.

¹⁴⁰ For further discussion of the electron states of N_2 and CO, and their dissociation products, cf. e.g., R. S. Mulliken, *Phys. Rev.* **32**, 186, 1928; F. Hund, *Zeits. f. Physik* **63**, 749–50 (1930).

¹⁴¹ W. H. J. Childs and R. Mecke, *Zeits. f. Physik* **68**, 344 (1931).

¹⁴² J. C. McLennan, H. D. Smith, and J. O. Wilhelm, *Trans. Roy. Soc. Canada* [3], **24**, Section III, p. 1 (1930).

¹⁴³ W. Weizel, *Handbuch der experimentellen Physik*, Ergänzungsband, 1931, Figs. 26–28.

¹⁴⁴ J. G. Winans and E. C. G. Stueckelberg, *Proc. Nat. Acad. Sci.* **14**, 867 (1928); W. Finkelburg and W. Weizel, *Zeits. f. Physik* **68**, 577 (1931).

¹⁴⁵ W. Weizel, *Zeits. f. Physik* **65**, 456 (1930).

¹⁴⁶ R. S. Mulliken and A. Christy, *Phys. Rev.* **38**, 115 (1931).

¹⁴⁷ The fact that states of He_2 with e.g., a $3d\sigma$, $3d\pi$, or $3d\delta$ electron are all stable states with about the same r_e and ω_e indicates that they all dissociate to give an atom with a 3-quantum excited electron. The $3d\delta$ electron in He_2 of course *must* give a $3d$ electron on dissociation, but it would not be surprising to find $3d\sigma$ and $3d\pi$ derived from a $2p$ (σ and π) electron of the separated atoms, by promotion. If, however, this were the case, the states with $3d\sigma$ and $3d\pi$ would be repulsive states or states with only a very flat minimum. In H_2 , evidence that states like e.g. $1s\sigma$ $3d\sigma$, $^1\Sigma$ dissociate to give a 3-quantum atom is afforded by the observed vibrational levels.

¹⁴⁸ W. Heitler and G. Herzberg, *Zeits. f. Physik* **53**, 52 (1929).

¹⁴⁹ Cf. M. Guillery, *Zeits. f. Physik* **42**, 124 (1927) and S. W. Leifson, *Astrophys. J.* **63**, 73–90 (1926).

¹⁵⁰ For details of theory, cf. R. S. Mulliken, *Phys. Rev.* **36**, 699, 1440 (1930); **37**, 1412 (1931). Infra-red bands, cf. W. G. Brown, *Phys. Rev.* **38**, 1179, 1187 (1931); R. M. Badger and D. M. Yost, *Phys. Rev.* **37**, 1548 (1931).

¹⁵¹ Strictly speaking, one cannot always expect dissociation of a molecule in a definite electron state unambiguously into two atoms in definite states; there may be only a certain *probability* of following one of two paths, e.g. dissociation into ions or into atoms. In other words, sometimes one cannot even give a definite meaning to a $U(r)$ curve, at least for the part of the curve at large r values. In highly excited states where numerous electron energy levels are close together, the $U(r)$ idea may cease altogether to be useful.

¹⁵² R. T. Birge and H. Sponer, *Phys. Rev.* **28**, 259 (1926). Cf. also reference 15 of Part I for further references.

¹⁵³ If $x_e\omega_e$ is negative, as is known to be the case in certain states of LiH and NaH, ^{15b} it is impossible to use Morse's function with a defined by Eq. (114).