# THE ASSIGNMENT OF QUANTUM NUMBERS FOR ELECTRONS IN MOLECULES. III. DIATOMIC HYDRIDES*

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## Abstract

The known electronic states of diatomic hydride molecules (MH) are derivable from unexcited H plus familiar low-energy states of M atoms (Hund, Hulthén, Mecke, Mulliken: cf. Table I). Observed states, and especially observed $\Delta\nu$ intervals in $^2\Pi$ or $^3\Pi$ states of such MH molecules (cf. Table III), indicate that the effects of the H on the M atom are confined essentially to the following: (1) the couplings, when present, between $l_\tau$ vectors of M atom outer electrons to give a resultant $l$ are completely broken down by the field of the H nucleus; the M atom orbits are otherwise scarcely changed, except for slight shielding or similar effects produced by the H electron and nucleus; the usual $l_\tau$ selection rules are, however, abolished; (2) the uncoupled vectors $l_\tau$ are separately space-quantized with reference to the electric axis, giving component quantum numbers $i_{l_\tau}$; (3) the electron of the H atom ($i_{l_\tau}=0$) is promoted and takes its place with the M electrons, sometimes becoming equivalent to one of them giving a new closed shell (of two electrons); the H nucleus, however, stays on the outside edge of the M electron cloud, so that the hydrides should in general be strongly polar, in agreement with Mecke's conclusions: (4) the original couplings of $s_\tau$ vectors are often broken down by the advent of the H electron spin; always, the latter alters the original multiplicity by one unit. In Table II and the related discussion, data are presented as evidence that molecular stability is primarily a matter of promotion energy, rather than of *valence bonds* in the sense of Lewis or London. In connection with Table III, a simple explanation is given of observed *multiplet widths* $\Delta\nu$ in $^2\Pi$ and $^3\Pi$ states of MH molecules in terms of $\Delta\nu$ values of corresponding M atoms in states resulting from dissociation of MH. Usually $\Delta\nu_{\mathrm{MH}}/\Delta\nu_{\mathrm{M}}$ is a little under 2/3; the factor 2/3 is that expected, according to theory, from the space-quantization of $l_\tau$'s to give $i_{l_\tau}$'s.

## Introduction

SINCE the publication of the first two papers[1,2] of this series, Hund has published a paper[3] dealing with similar subject matter, and has arrived at, for the most part, similar conclusions. In addition to the molecules already dealt with by the present writer, Hund has discussed others, including diatomic hydrides and polyatomic molecules.

In his discussion of diatomic hydride molecules, Hund has shown that the observed lowest states and transitions are in excellent agreement with those

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* Paper presented at 1928 Annual meeting of American Physical Society (cf. Phys. Rev. **33,** 285 (1929)).

[1] R. S. Mulliken, Phys. Rev. **32,** 186–222 (1928): I.

[2] R. S. Mulliken, Phys. Rev. **32,** 761–772 (1928): II. Cf. also W. Heitler and G. Herzberg, Zeits. f. Physik **53,** 52 (1929).

[3] F. Hund, Zeits. f. Physik **51,** 759 (1928). Cf. also, E. Wigner and E. E. Witmer, Zeits. f. Physik **51,** 859 (1928). Hund gives theoretical justification for several relations (e.g., selection rules) which were assumed by the writer. Hund discusses some topics (e.g., hydride molecules) which the writer had expected to treat in later papers of this series; these will therefore be somewhat differently treated than was originally intended.

which can be predicted on the simple assumption that the hydride molecule (e.g., CH) is equivalent to the corresponding united atom (e.g., N) in a strong electric field.[4]

In the present paper, a systematic survey is made of existing band spectrum data on energy levels of diatomic hydrides, and these data are interpreted in terms of theory. Especial attention is given to the relation between multiplet separations in atoms (M) and their hydrides (MH).

## NOTATION

In his recent paper, Hund has proposed a new notation for molecular electron configurations and states;[3] Wigner and Witmer have also used a similar notation.[3] The advantages of this notation over that hitherto used are so great that it seems best to adopt it at once. Hund uses the symbols $s, p, d, f, \cdots$ and $S, P, D, F, \cdots$, to denote $l_r$ and $l$ values, respectively, as is customary for atoms. He uses symbols $\sigma, \pi, \delta, \phi, \cdots, \Sigma, \Pi, \Delta, \Phi, \cdots$, to denote $i_{l_r}$ values and $i_l$ values respectively. (Hund's $i$, $i_l$, $i_{l_r}$, $i_s$, are here adopted in place of the writer's $\sigma$, $\sigma_l$ or $\sigma_k$, $\sigma_{l_r}$ or $\sigma_{k_r}$, $\sigma_s$, because of Hund's use of the symbol $\sigma$ to denote $i_{l_r}=0$.) For the complete specification of a molecular state, Hund uses formulas such as $1s\sigma^2 2s\sigma^2 2p\sigma 2p\pi^2\ {}^2\Delta$. The corresponding formula in the writer's notation[1] is $(1s^s)^2(2s^s)^2(2s^p)(2p^p)^2$, ${}^2D$.

As an example of the use of the new notation, Table II of I (p. 201) would now read in part (for the O atom) as follows:

$$\begin{aligned} \mathrm{O},\ {}^3P&:\sigma^6\pi^2\ {}^3\Sigma\ ;\ \sigma^5\pi^3\ {}^3\Pi \\ {}^1D&:\sigma^6\pi^2\ {}^1\Sigma\ ;\ \sigma^5\pi^3\ {}^1\Pi\ ;\ \sigma^6\pi^2\ {}^1\Delta \\ {}^1S&:\sigma^4\pi^4\ {}^1\Sigma. \end{aligned}$$

Corresponding changes, e.g. of such symbols as $s^5p^3$ to $\sigma^5\pi^3$, would be made under the heading "Dissociation, Probable Products" in Table III of I.

## FORMATION OF MH MOLECULES FROM M+H; QUANTUM NUMBERS, PROMOTION, AND CLOSED SHELLS; ENERGY RELATIONS; VALENCE

*General principles.* As Hund has pointed out, the effect of one atom on the electrons of another is essentially a Stark effect,[5] plus certain other effects,—in particular, promotion of electrons. Since we are now interested in MH molecules, let us consider specifically the effects of an H atom on an M atom.[6] These may in thought be divided into, (*a*) effects of the electric field of the H nucleus, modified by that of its electron; (*b*) the effect of the H electron and its spin, taking into account the Pauli exclusion principle.

In the intensity of effects (a), four stages are conceivable.[5] (1) The M atom electron orbits, and the various couplings of M atom electrons with

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[4] This is Hund's "Case 3*b*:" cf. his Tables 2*b* and 3 (his Case 3*a* corresponds to the united-atom in a *weak* electric field). The writer's Table II in ref. 1 (p. 201 and discussion, foot of p. 200) embodies the same results.

[5] F. Hund, Zeits. f. Physik **36**, 659–60 (1926).

[6] For all the molecules and molecular states treated in the present paper, we may safely assume that the H atom before union is in its normal state.

one another, might remain unchanged, so that we should have merely a space-quantization of $j$ of the M atom with reference to the electric axis, giving a new quantum number $i$ for the atom as a whole. (2) The coupling between $l$ and $s$ of the M atom might be broken down, and $l$ and $s$ be separately space-quantized to give quantum numbers $i_l$ and $i_s$. Different values of $i_s$, for fixed $l$, $s$, and $i_l$, give a multiplet. For example, suppose $i_l=1$, $i_s=\pm 1/2$. This, in the molecular notation which is obviously appropriate for an atom in a strong electric field, is a $^2\Pi$ state ($^2\Pi_{1/2}$, with $i=1/2$, and $^2\Pi_{3/2}$, with $i=3/2$). (3) The coupling, if present, between individual $l_\tau$'s to give $l$ might be broken down, so that each $l_\tau$ would be individually quantized to give an $i_{l_\tau}$ whose value could be indicated by the molecular notation ($\sigma$, $\pi$ $\delta$, $\cdots$, for $i_{l_\tau}=0, 1, 2, \cdots$), while $\Sigma i_{l_\tau}=i_l$; $s$ would give $i_s$, and $i=i_l+i_s$, as before. In this stage, the individual $l_\tau$'s still retain a good meaning, and the corresponding "orbits" are essentially the same as in the original M atom. (4) The field of the H nucleus might act so strongly as to destroy the $l_\tau$ quantization completely, as in the linear Stark effect for the hydrogen atom. Quantum numbers $i_{l_\tau}$, $i_l$, $i_s$ and $i$ would still exist.—The couplings of the $s_\tau$'s of the M atom, giving a resultant $s$, should not at any stage be broken down by the electric field of the H atom; but they are often broken down by the incidence of an interaction with the $s_\tau$ of the H electron.

Although the actuality can hardly correspond exactly to any one of the above stages,[1,3] it appears that stage 3 is approximated in practice, for the outer electrons. Even where this is not true, the state of any molecule can be described in terms of quantum numbers appropriate to stage 3.[1] (Inner electrons probably are in a condition nearer stage 1 or 2, but since they are in closed shells, each such shell giving $i_l=i_s=i=0$ for all stages, this does not matter.)

Let us now consider the part which the electron of the H atom plays, aside from the effects of its electric field, in the MH molecule. In the free H atom before union, this electron is in a $1s$ orbit[6] or, if we think of it as under the influence of the field of the M atom, in a $1s\sigma$ orbit. Since in most atoms there is a closed shell of two $1s$ electrons, this H electron must be promoted,[7] and must go to some $\sigma$ orbit[8] belonging to an electron shell which is not yet closed in the M atom. We shall in the following assume as a *promotion rule* that the H electron is promoted in every instance to the *lowest available* $\sigma$ orbit. In case one M electron is already present in such an orbit, it and the H electron now form a closed shell-of-two, the spin of the H electron becoming coupled with that of the M electron to give a zero resultant spin. This process often involves the breaking up of a previously existing coupling of the $s_\tau$'s of the outer M electrons.[9] In any case, the

[7] One might instead conceivably suppose that one of the $1s$ electrons of the M atom is promoted, but such an attempted distinction would in the end be meaningless (cf. also ref. 9).

[8] The promotion process probably usually if not always leaves $i_{l_\tau}$ unchanged for both the M and the H electrons ($i_{l_\tau}$ conservation rule, cf. I, p. 200): e.g., a $\sigma^5\pi$ carbon atom in all probability becomes a $\sigma^6\pi$ CH molecule (cf. I, p. 200–1).

[9] It seems probable, however, that $s_\tau$ couplings of M electrons which already exist in closed shells cannot be broken up by the H electron. Further, it would seem from Heitler and Lon-

addition of the H electron spin changes the multiplicity by $\pm 1$, e.g., a $^2\Pi$ state of an M atom gives a $^1\Pi$ and a $^3\Pi$ state of the MH molecule.—There appears to be as yet no definite theoretical basis for the above promotion rule, but it finds no contradiction in the empirical data.[9,11]

*Application to* CH *molecule as an example.* The general principles just reviewed will be made clearer by application to an example. Let us consider what may be expected to happen to the electron distribution of a carbon atom, in its $1s^22s^22p^2\ ^3P$ normal state, when an H atom approaches. If we at first neglect the effects of the hydrogen electron and its spin, we have merely the effects of the electric field of the H nucleus. On sufficiently close approach of the H atom, the coupling between the $l_\tau$ vectors of the two $2p$ electrons to give the resultant $l=1$ should be broken down and the $l_\tau$ vectors should be separately space-quantized, each giving an $i_{l_\tau}$. Two strong-field states should result, which may be symbolized as follows (cf. pp. 200–201 and Table II of I)[1]: $1s\sigma^2 2s\sigma^2 2p\sigma 2p\pi\ ^3\Pi$ and $1s\sigma^2 2s\sigma^2 2p\pi^2\ ^3\Sigma$.

We have now to consider the fact that the H nucleus was accompanied by a $1s$ electron, which must be promoted to some $\sigma$ orbit, of which the lowest available is the $2p\sigma$ orbit. For this orbit, the promotion energy should be comparatively small, or even negative, since the binding energy for a $2p$ orbit in a carbon atom is approximately the same as for the $1s$ orbit in a hydrogen atom.[12,13] If the H electron *does* go into a $2p\sigma$ orbit, we obtain from the $^3\Sigma$ state of the atom both a $^2\Sigma$ and a $^4\Sigma$ state of the molecule, each with the configuration $1s\sigma^2 2s\sigma^2 2p\sigma 2p\pi^2$. Similarly from the $^3\Pi$ state of the atom we obtain a $1s\sigma^2 2s\sigma^2 2p\sigma^2 2p\pi\ ^2\Pi$ state of CH. Corresponding to the small promotion energy for $1s\sigma \rightarrow 2p\sigma$, these three states of CH ($^2\Sigma$, $^4\Sigma$, $^2\Pi$) should have comparatively large energies of dissociation, i.e., they should be relatively *stable* states.

In addition to a $^2\Pi$ state, the $^3\Pi$ state of the atom must yield also a $^4\Pi$ state of CH. Such a state is not possible with the same electron configuration as the corresponding $^2\Pi$ state, because of the closed shell $2p\sigma^2$ in the

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don's work[10] that if two M electrons are coupled so as to give $s=0$, even if they do not form a closed shell, the H electron spin cannot enter into interaction with either of them; such a case would constitute an exception to the above promotion rule. For example, in the case of a $1s\sigma^2 2s\sigma^2 2p\sigma 2p\pi\ ^1\Pi$ state of a C atom, the H electron could not, according to this principle, be promoted to a $2p\sigma$ orbit, but would have to go to $3s\sigma$. But this promotion to $3s\sigma$ would in this instance be necessary anyway, since the $1s\sigma^2 2s\sigma^2 2p\sigma 2p\pi\ ^3\Pi$ state of the C atom lies below the $^1\Pi$ state and thus uses up the possibility of promotion of the H electron to a $2p\sigma$ orbit to give a $\cdots 2p\sigma^2 2p\pi\ ^2\Pi$ state.

[10] W. Heitler and F. London, Zeits. f. Physik **44,** 455 (1927); F. London, Zeits. f. Physik **46,** 455 and **50,** 24, 437 (1928); W. Heitler, Zeits. f. Physik **46,** 47 (1927); **47,** 835 and **51,** 805, (1928).

[11] For homopolar molecules, including $H_2$, such a rule is not true,[3] but it may still be essentially true for heteropolar molecules such as MH.

[12] Cf. discussion of binding energies and promotion energies in I, pp. 194–8.

[13] The lowest ionization potential of a $^3P$ carbon atom (removal of a $2p$ electron to give a $^2P$ ion of $C^+$) is 11.3 volts (cf. I. S. Bowen, Phys. Rev. **29,** 240 (1927)), as compared with 13.54 volts for the $1s$ hydrogen orbit. For the normal states of the N and O atoms, the lowest ionization potentials are respectively 14.49 and 13.56 volts.

latter. The hydrogen electron must therefore be promoted to a higher orbit, most likely a $3s\sigma$ orbit, giving a state such as $1s\sigma^2 2s\sigma^2 2p\sigma 2p\pi 3s\sigma\ ^4\Pi$. Since the binding energy for a 3-quantum orbit in a carbon or nitrogen atom is only about 4 volts,[14] as compared with 13.54 volts for a $1s$ electron in a H atom, it is evident that for this $^4\Pi$ state the promotion energy for the H electron is large. Hence we may expect this state of CH to be much less stable than the three states above mentioned.

This example illustrates how one may expect to make deductions in regard to the stability of molecular states by a consideration of promotion energies.[23] Large promotion energy means low stability. Although no sharp division between stable and unstable molecular states is to be expected in general, a rough classification on this basis should often be feasible.

Not far above the $1s^2 2s^2 2p^2\ ^3P$ normal state of the carbon atom there exist a $^1D$ and a $^1S$ state with the same electron configuration. The $^1D$ state should give three strong-field states, and the $^1S$ state one such state, as follows: $A 2p\sigma^2\ ^1\Sigma$, $A 2p\sigma 2p\pi\ ^1\Pi$, $A 2p\pi^2\ ^1\Delta$, and $A 2p\pi^2\ ^1\Sigma$, where $A$ means $1s\sigma^2 2s\sigma^2$. The most likely configurations for the four resulting states of CH are: $A 2p\sigma^2 3s\sigma\ ^2\Sigma$; $A 2p\sigma 2p\pi 3s\sigma\ ^2\Pi$; $A 2p\sigma 2p\pi^2\ ^2\Delta$; $A 2p\sigma 2p\pi^2\ ^2\Sigma$, the last two being presumably stable and the first two unstable.

Of the five stable low-energy states $^2\Pi$, $^4\Sigma$, $^2\Sigma$, $^2\Delta$, $^2\Sigma$ of the CH molecule just shown to be derivable from the three low-energy states $^3P$, $^1D$, and $^1S$ of the carbon atom, three ($^2\Pi$, $^2\Delta$, $^2\Sigma$) can be definitely identified with known states as observed in band spectra.[15,3]

Other stable states of CH, but on the whole of higher energy, are derivable (together with additional unstable states) from the various $1s^2 2s 2p^3$ states ($^5S$, $^3D$, $^3P$, $^3S$, $^1D$, $^1P$) of the carbon atom. Likewise from other excited states of the carbon atom, e.g., the $1s^2 2s^2 2p 3s$ states ($^3P$ and $^1P$), excited states of CH, of both the stable and the unstable type, are derivable.

*Atoms, hydrides, and united-atoms.* The same set of five stable states of the CH molecule which is derived by considering the addition of an H electron to the various $s^2p^2$ states of the carbon atom can be derived by considering the converse process of splitting the nucleus of the corresponding united-atom (nitrogen), starting from the $s^2p^3$ states of the latter ($^4S$, $^2D$, $^2P$): cf. Fig. 1 of Hund's paper.[3] (The various ways of splitting the $s^2p^3$ N atom give, however, one additional state of CH, a $^2\Pi_i$ state which would go over into H plus the $sp^3\ ^3P$ state of carbon.) Similar relations hold for other atoms. In general, *the stable low-energy states of any* MH *molecule are all derivable from the low-energy states of the* M *atom and go over into the low-energy states of the corresponding united-atom.*

In Table I tentative quantum number assignments, based on the methods discussed above, are given for all the recorded states of diatomic hydrides (except hydrogen halides[2]), together with $r_0$, $\omega_0$, and energy data, and in each case the most likely state of the M atom on dissociation. Perhaps the most striking fact brought out by the table is the incompleteness of the data,

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[14] Cf. L. A. Turner, Phys. Rev. **32**, 728 (1928).

[15] R. S. Mulliken, Phys. Rev. **30**, 785 (1927).

especially in respect to $D^v$ and $D$ values. Some conclusions of interest can, however, be reached. These can best be discussed after and in connection with a consideration of individual molecules.

*Copper, silver, gold, hydrides.* The $\cdots 4s\ {}^2S$ normal state of the Cu atom would be expected, on union with a normal H atom, to give a stable $4s\sigma^2\ {}^1\Sigma$ and a less stable or unstable $4s\sigma 4p\sigma\ {}^3\Sigma$ molecular state. The fact that the observed normal state of CuH is ${}^1\Sigma$ is good evidence that the promotion of the H electron is to the *lowest available* $\sigma$ orbit ($4s\sigma$); if it were to any other ($nx\sigma$) orbit, we should expect $(4s\sigma)(nx\sigma)$, ${}^3\Sigma$ and ${}^1\Sigma$, with the ${}^3\Sigma$ below the ${}^1\Sigma$. Corresponding statements hold for AgH and AuH.

Assuming that the lowest ${}^1\Sigma$ state of CuH is derived from the normal ${}^2\Sigma$ atom, the first *excited* ${}^1\Sigma$ state may reasonably be correlated with the low ${}^2D'$ state of the atom—which should give rise to one ${}^1\Sigma$ state of CuH. The empirical $D-D_0$ (1.75 volts) for the observed excited ${}^1\Sigma$ state agrees within reasonable limits of error, as is necessary if this explanation is correct, with the energy (1.38 or 1.64 volts for ${}^2D_{5/2}$ or ${}^2D_{3/2}$)[16] of the ${}^2D'$ atom. In AuH, the first excited ${}^1\Sigma$ state shows characteristics (cf. the $r_0$ and $\omega_0$ values) resembling those of the corresponding state of CuH, and it seems probable that this state of AuH should be correlated with the low ${}^2D'$ state of the Au atom. The empirical $D-D_0$ value, however ($-0.18$), agrees badly with the energies (1.13) and 2.17)[16] of the ${}^2D'$ levels. This probably means that the extrapolated $D$ values (method of Birge and Sponer), used in getting $D-D_0$, are unreliable to this extent, since there seems to be no other more reasonable correlation of the atomic and molecular levels.[17] In AgH, the excited ${}^1\Sigma$ state has different characteristics than the just-discussed states of CuH and AuH (cf. e.g., the $r_0$ values); also, the ${}^2D'$ state of Ag is not yet known, and is generally believed to be of high energy; the derived ${}^1\Sigma$ state of AgH is then probably still undiscovered.

Aside from the ${}^2D'$ levels of Cu and Au, the first excited state of Cu, Ag, and Au is a ${}^2P$ level, which should give rise to a stable hydride level of each of the types ${}^1\Sigma$, ${}^1\Pi$, ${}^3\Sigma$, ${}^3\Pi$. The ${}^1\Pi$ level of CuH, and the highest observed ${}^1\Sigma$ level of AgH and of AuH, appear to correspond reasonably well, so far as data are available, to members of this group.

*Hydrides of bivalent metals.* The normal ${}^1S$ state of the Hg atom should give rise to a ${}^2\Sigma$ state of HgH, the first excited group of states of Hg (${}^3P_{012}$ and ${}^1P$) to two ${}^2\Sigma$, two ${}^2\Pi$, and a ${}^4\Sigma$ and a ${}^4\Pi$ state. The lowest known, doubtless normal, state of HgH is a very unstable ${}^2\Sigma$ state ($D^v=0.369$ volts, known with unusual accuracy). About 3 volts above this is a ${}^2\Pi$ state of rather high stability ($D^v\sim 3$ volts); above this is a ${}^2\Sigma$ state of large $r_0$, larger even than for the lower ${}^2\Sigma$. The lower ${}^2\Sigma$ state is almost certainly to be

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[16] There appears to be as yet no good theoretical basis for deciding how, in the case of doublet or triplet atomic levels, the corresponding molecular levels should be correlated with the different sub-levels of the atomic multiple level.

[17] A *slightly* better agreement in respect to $D-D_0$ results if the lowest ${}^1\Sigma$ level is assumed derived from the ${}^2D_{5/2}$ atom, the second ${}^1\Sigma$ from the normal ${}^2S$ atom; but this does not seem very reasonable, especially in view of the analogy to CuH.

correlated with the normal $^1S$ state of Hg.[18] The $^2\Pi$ state is probably to be correlated with the just-mentioned $^3P$ (or perhaps $^1P$) state of the atom[16,18]; the $D-D_0$ values are in reasonable agreement with this. The upper $^2\Sigma$ state is perhaps derived like the $^2\Pi$ state from the $^3P$ (or perhaps $^1P$) atom; if from the $^3P$, it must have $D^v \sim 1$ volt.

In the formation of the normal $^2\Sigma$ state of HgH as above, the H electron has to be promoted probably to a $6p\sigma$ orbit, since the $6s\sigma$ shell is closed in Hg $^1S$. In the formation HgH $^2\Pi$, however, there is available a vacancy in the $6s\sigma$ shell, because of the previous excitation of one $6s$ electron to $6p$ in the $^3P$ state of Hg, and into this vacancy the H electron can drop. The lesser promotion energy of the H electron in the $^2\Pi$ state then accounts for the greater stability of the molecule in this as compared with the normal $^2\Sigma$ state.—If the higher $^2\Sigma$ level is derived from Hg $^3P$, we have again promotion of the H electron to a $6p\sigma$ orbit, with resulting low stability.

The CdH, ZnH, MgH, and probably the BeH states are analogous to those of HgH, but the data are less complete,[18a] except for MgH. If, however, the $r_0$ values may be taken as an indication, there is a steady increase in the relative stability of the $^2\Sigma$ normal state as compared with the $^2\Pi$ excited state as the atomic weight decreases. This indication is confirmed in the case of MgH, where $D^v$ has practically the same value for the low $^2\Sigma$ and the first $^2\Pi$ state.[18a]

The two lowest states of CaH are analogous to those of MgH and HgH, while (as first suggested by Hund) the second $^2\Sigma$ state is probably derived from the lowest $^3D$ level, which is especially low in Ca and its homologues as contrasted with the metals just discussed.

*Electron sharing, polarization, and $r_0$ values in* MH *molecules.* A comparison of the various bivalent metals, in respect to $r_0$ values of the $^2\Sigma$ normal and $^2\Pi$ states of their hydrides on the one hand, and in respect to the energy-scale of the M atom on the other hand (e.g., size of the interval $1^1S$–$2^3P$, or of the $1^1S$ term itself [=ionization potential]), shows that the larger the atomic energy scale, the smaller are the $r_0$ values, and also the greater is the *difference* in $r_0$ between the $^2\Sigma$ and the $^2\Pi$ states. At two extremes in both respects are Ca ($r_0=2.01$ for $^2\Sigma$, 2.04 for $^2\Pi$) and Hg ($r_0=1.76$ for $^2\Sigma$, 1.59 for $^2\Pi$). These relations are even more striking if allowance is made for the observed tendency, other things being equal, for $r_0$ to increase with increasing atomic number (cf. e.g., ZnH and CdH). The observed variation of $r_0$ with the ionization potential and atomic number closely corresponds to, and is presumably determined by, the variation in atomic radius with these two factors as given by the quantum theory. A precisely analogous parallelism between $r_0$ and atomic radius occurs in the series CuH, AgH, AuH (cf. Table I) and in other cases.[19]

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[18] Since the minimum (i.e., $r=r_0$) of the $E(r)$ curve for the $^2\Pi$ state lies about 3 volts above the maximum (i.e., $r=\infty$,—dissociation) of the $E(r)$ curve of the $^2\Sigma$ state, the $^2\Sigma$ state must unquestionably derive from a considerably lower atomic level than does the $^2\Pi$ state. This level can hardly be other than the normal $^1S$ level.

[18a] *Added in proof.* But new data of Hulthén (forthcoming letter to Nature) give $D^v$ values as follows for the $^2\Sigma$ normal states of MgH, ZnH, CdH, CaH respectfully: 0.5, 0.8, 0.7, 0.4 volts.

[19] Cf. R. Mecke (Zeits. f. Physik **42**, 393–5, 1927) for a further discussion of the parallelism of $r_0$ values and atomic radii.

The comparatively high stability[18a] of the normal $^2\Sigma$ state in MgH and CaH as compared with its very low stability in HgH probably means that, although the H electron has undergone an analogous promotion in all cases, it penetrates, in Mg and Ca, the relatively diffuse outer region of the atom and thus gains in binding energy enough to make up for the energy of promotion, while in the case of the more compact Hg atom it hardly penetrates at all.[20] In the case of the $^2\Pi$ states, however, the difference between, say, MgH and HgH, is much less marked (cf. the $D^v$ values in Table I), because in both cases the promoted electron penetrates the M atom by going into a vacancy in the outer shell of the metal atom.

From what has preceded it appears that, in the union of an M and an H atom, the H nucleus always stops just short of seriously penetrating the region occupied by the M atom electrons,—doubtless because if it *did* penetrate it would be strongly repelled. But its electron, being attracted by the M nucleus, may to a considerable extent penetrate the region of the M outer electrons, especially if their orbits are large or if the H electron is promoted to a type of orbit already present in the M atom. When the H electron does so penetrate, as, e.g., in CaH or $^2\Pi$ excited HgH, it must more or less leave the H nucleus behind, making the molecule strongly polar. (Nevertheless the H electron tends to drag the H nucleus after it to some extent, so that with increasing penetration of the H electron, $r_0$ tends to decrease.) When the H electron does *not* penetrate, it should remain rather closely attached to the H nucleus, and the molecule should be almost lacking in polarity (normal HgH). Evidence that most diatomic hydrides are polar (exception, normal HgH) has been given by Mecke.[20]

*Aluminum hydride.* In AlH we have the interesting case of two molecular states both in all probability derived from the normal $^2P$ state of the Al atom. These molecular states differ in that the $3p$ electron of the atom becomes a $3p\pi$ electron in the upper ($^1\Pi$) molecular state, but a $3p\sigma$ electron in the lower ($^1\Sigma$). The energy difference between these levels (2.9 volts) gives a good idea of the considerable intensity of the effect of the H atom on the Al atom, and shows the importance of $i_{l_\tau}$. It is of interest that these two states are observed even at hydrogen pressures of one atmosphere, while the upper $^1\Sigma$ state is found only at low pressures. A reasonable explanation is that the latter state can be formed only from excited Al atoms (cf. Table I), which, when the pressure is too high, are deactivated by collisions before they have time to form AlH; while the two former states require only unexcited atoms.

CH, NH, *and* OH. The CH levels, and their correlation with the levels of the C and N atoms, have already been discussed. For NH the following stable low levels are derivable from the three low $s^2p^3$ states ($^4S$, $^2D$, $^2P$)of

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[20] In the paper just cited,[19] Mecke concludes from a study of potential energy curves based on $r_0$, $\omega_0$, and similar data, that most of the hydrides (exception, HgH) are of a polar character and that the H atom "gives up its electron to the binding." This supports the present idea that the H electron is promoted to an orbit which is fairly well a part of the electron system of the M atom except in unstable states like the lower $^2\Sigma$ of HgH.

TABLE I. *Quantum number assignments and dissociation products.*[18a]

| | Molecule MH | | | | | | | | | | Atom M | | | Molecule |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M | Energy (volts) | $r_0$ (A.U.) | $\omega_0$ (cm$^{-1}$) | $\omega_0 x$ (cm$^{-1}$) | $D^v$ (volts) | $D$ (volts) | $D-D_0$ (volts) | State | Likely configuration (outer electrons) | H electron | State | Energy (volts) | Ioniz. Pot'l. | Known Transitions |
| Cu | 0 | 1.471 | 1903.7 | 37.36 | 3.02 | 3.02 | 0 | $^1\Sigma$ | $3d^{10}4s\sigma^2$ | $4s\sigma$ | $^2\Sigma$,from $4s\,^2S$ | 0 | 7.69 | |
| | 2.88 | 1.582 | 1655.7 | 44.63 | 1.89 | 4.77 | 1.75 | $^1\Sigma$ | $3d\sigma d\pi^4 d\delta^4 4s\sigma^2 4p\sigma$ | $4p\sigma$ | $^2\Sigma,3d^9 4s^2\,^2D_i$ | 1.38, 1.64 | | $^1\Sigma \leftarrow\rightarrow {}^1\Sigma$ |
| | 5.51 | 1.50 | | | $z$ | $5.51+z$ | $2.49+z$ | $^1\Pi$ | $3d^{10}4s\sigma 4p\pi$ | $4s\sigma$ | $^2\Pi_n,4p\,^2P_n$ | 3.76, 3.80 | | $^1\Pi \leftarrow {}^1\Sigma$ |
| Ag | 0 | 1.630 | (1690) | | | | | $^1\Sigma$ | $4d^{10}5s\sigma^2$ | $5s\sigma$ | $^2\Sigma,5s\,^2S$ | 0 | 7.55 | |
| | 3.69 | 1.665 | (1490) | | | | | $^1\Sigma$ | $4d^{10}5s\sigma 5p\sigma$ | $5s\sigma$ | $^2\Sigma,5p\,^2P_n$ | 3.64, 3.76 | | $^1\Sigma \leftarrow\rightarrow {}^1\Sigma$ |
| Au | 0 | 1.54 | 2249.4 | 34.0 | 4.59 | 4.59 | 0 | $^1\Sigma$ | $5d^{10}6s\sigma^2$ | $6s\sigma$ | $^2\Sigma,6s\,^2S$ | 0 | 9.2 | |
| | 3.37 | 1.69 | 1630 | 79 | 1.04 | 4.41 | −0.18 | $^1\Sigma$ | $5d\sigma d\pi^4 d\delta^4 6s\sigma^2 6p\sigma$ | $6p\sigma$ | $^2\Sigma,5d^9 6s^2\,^2D_i$ | 1.13, 2.17 | | $^1\Sigma \leftarrow\rightarrow {}^1\Sigma$ |
| | 4.72 | 1.71 | (1548) | | $z$ | $4.72+z$ | $0.13+z$ | $^1\Sigma$ | $5d^{10}6s\sigma 6p\sigma$ | $6s\sigma$ | $^3\Sigma,6p\,^2P_n$ | 4.60, 5.08 | | $^1\Sigma \leftarrow {}^1\Sigma$ |
| Be | 0? | 1.35 | [2026] | — | $x$ | $x$? | 0? | $^2\Sigma$ | $2s\sigma^2 2p\sigma$ | $2p\sigma$ | $^1\Sigma,2s^2\,^1S$ | 0 | 9.4 | $^2\Pi \rightarrow {}^2\Sigma$ |
| | 2.48? | 1.34 | [2053] | — | $y$ | $2.48+y$? | $2.48+y-x$? | $^2\Pi$ | $2s\sigma^2 2p\pi$ | $2s\sigma$ | $^1\Pi,2s2p\,^3P$ | 2.9 | | |
| Mg | 0 | 1.74 | 1462.2 | 31.25 | 2.12 | 2.12 | 0 | $^2\Sigma$ | $3s\sigma^2 3p\sigma$ | $3p\sigma$ | $^1\Sigma,3s^2\,^1S$ | 0 | 7.62 | |
| | 2.38 | 1.70 | 1568.7 | 34.75 | 2.18 | 4.56 | 2.44 | $^2\Pi_n$ | $3s\sigma^2 3p\pi$ | $3s\sigma$ | $^3,\Pi 3s3p\,^3P$ | 2.70 | | $^2\Pi \leftarrow\rightarrow {}^2\Sigma$ |
| | 5.09 | 1.70 | (1622) | | $z$ | $5.09+z$ | $2.97+z$ | $^2\Pi$ | $3s\sigma^2 4p\pi$ | $3s\sigma$ | $^3\Pi,3s4p\,^3P$ | 5.91 | | $^2\Pi \rightarrow {}^2\Sigma$ |
| Zn | 0 | 1.608 | (1552) | | $x$ | $x$ | 0 | $^2\Sigma$ | $4s\sigma^2 4p\sigma$ | $4p\sigma$ | $^1\Sigma,4s^2\,^1S$ | 0 | 9.35 | |
| | 2.87, 2.91 | 1.522 | | | $y$ | $2.89+y$ | $2.89+y-x$ | $^2\Pi_n$ | $4s\sigma^2 4p\pi$ | $4s\sigma$ | $^3\Pi,4s4p\,^3P$ | 3.98, 4.01, 4.06 | | $^2\Pi \rightarrow {}^2\Sigma$ |
| Cd | 0 | 1.776 | (1374) | | $x$ | $x$ | 0 | $^2\Sigma$ | $5s\sigma^2 5p\sigma$ | $5p\sigma$ | $^1\Sigma,5s^2\,^1S$ | 0 | 8.95 | |
| | 2 75,2.88 | 1.674 | | | $y$ | $2.81+y$ | $2.81+y-x$ | $^2\Pi_n$ | $5s\sigma^2 5p\pi$ | $5s\sigma$ | $^3\Pi,5s5p\,^3P$ | 3.72, 3.78, 3.93 | | $^2\Pi \rightarrow {}^2\Sigma$ |

| | Molecule MH | | | | | | | | | | Atom M | | | Molecule |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M | Energy (volts) | $r_o$(A.U) | $\omega_o$(cm$^{-1}$) | $\omega_o x$(cm$^{-1}$) | $D^v$ (volts) | $D$ (volts) | $D-D_o$ (volts) | State | Likey configuration (outer electrons) | H electron | State | Energy (volts) | Ioniz. Pot'l. | Known Transitions |
| Hg | 0 | 1.763 | 1308 | 104 | 0.369 | 0.369 | 0 | $^2\Sigma$ | $6s\sigma^2 6p\sigma$ | $6p\sigma$ | $^1\Sigma, 6s^2\ ^1S$ | 0 | 10.39 | |
| | 3.08 | 1.593 | (1938.7) | | $y$ | 3.08+$y$ | 2.71+$y$ | $^2\Pi_n$ | $6s\sigma^2 6p\pi$ | $6s\sigma$ | $^3\Pi, 6s6p\ ^3P$ | 4.65, | | $^2\Pi \rightarrow\ ^2\Sigma$ |
| | 3.56 | | 2025.7 | 43.8 | 2.90 | 6.46 | 6.09 | | | | | 4.87, | | |
| | 4.18 | 2.02 | [<1940] | — | $z$ | 4.18+$z$ | 3.81+$z$ | $^2\Sigma$ | $6s\sigma 6p\sigma^2$ | $6p\sigma$ | $^3\Sigma, 6s6p\ ^3P$(?) | 5.44 | | $^2\Sigma \rightarrow\ ^2\Sigma$ |
| | 0 | 2.01 | [$\omega_N$] | — | | | | $^2\Sigma$ | $4s\sigma^2 4p\sigma$ | $4p\sigma$ | $^1\Sigma, 4s^2\ ^1S$ | 0 | 6.08 | |
| | 1.78, 1.79 | 2.04 | [$>\omega_N$] | — | | | | $^2\Pi_n$ | $4s\sigma^2 4p\pi$ | $4s\sigma$ | $^3\Pi, 4s4p\ ^3P$ | 1.88 | | $^2\Pi \rightarrow\ ^2\Sigma$ |
| | 1.94 | 1.97 | [$<\omega_N$] | — | | | | $^2\Sigma$ | $4s\sigma^2 3d\sigma$ | $4s\sigma$ | $^3\Sigma, 4s3d\ ^3D$ | 2.51 | | $^2\Sigma \rightarrow\ ^2\Sigma$ |
| | 3.50 | 1.86 | [$>\omega_N$] | | | | | $^2\Sigma$ | $4s\sigma^2 5s\sigma$ | $4s\sigma$ | $^3\Sigma, 4s5s\ ^3S$ | 3.89 | | $^2\Sigma \rightarrow\ ^2\Sigma$ |
| Al | 0 | 1.658 | (1625) | | $y$+2.90 | $y$+2.90 | 0 | $^1\Sigma$ | $3s\sigma^2 3p\sigma^2$ | $3p\sigma$ | $^2\Sigma, 3p\ ^2P$ | 0 | 5.95– | $^1\Pi \leftarrow\rightarrow {}^1\Sigma$ |
| | 2.90 | 1.690 | (1082) | | $y$ | $y$+2.90 | 0 | $^1\Pi$ | $3s\sigma^2 3p\sigma 3p\pi$ | $3p\sigma$ | $^2\Pi, 3p\ ^2P$ | | 5.96 | $^1\Sigma \rightarrow\ ^1\Sigma$ |
| | 5.51 | 1.65 | (1326) | | | | | $^1\Sigma$ | $3s\sigma^2 3p\sigma 4s\sigma$? | $3p\sigma$ | $^2\Sigma, 4s\ ^2S$ | 3.12 | | $^1\Sigma \rightarrow\ ^1\Pi$ (weak) |
| C | 0 | 1.13 | (2806) | | | | | $^2\Pi_n$ | $2s\sigma^2 2p\sigma^2 2p\pi$ | $2p\sigma$ | $^3\Pi, 2s^2 2p^2\ ^3P$ | 0 | 11.28 | |
| | 2.86 | 1.11 | (2851) | | | | | $^2\Delta_i$ | $2s\sigma^2 2p\sigma 2p\pi^2$ | $2p\sigma$ | $^1\Delta, 2s^2 2p^2\ ^1D$ | 1.20 | | $^2\Delta \rightarrow\ ^2\Pi$ |
| | 3.18 | 1.20 | (<2806) | | | | | $^2\Sigma$ | $2s\sigma^2 2p\sigma 2p\pi^2$ | $2p\sigma$ | $^3\Sigma, 2s^2 2p^2\ ^3P$ or | 0 or | | $^2\Sigma \rightarrow\ ^2\Pi$ |
| | | | | | | | | | | | $^1\Sigma, 2s^2 2p^2\ ^1S$ (or $^1D$?) | 2.61 [or 1.20?] | | |
| N | 0 | 1.08 | | | | | | $^3\Sigma$ | $2s\sigma^2 2p\sigma^2 2p\pi^2$ | $2p\sigma$ | $^4\Sigma, 2s^2 2p^3\ ^4S$ | 0 | 14.49 | |
| | 3.67 | 1.08+ | | | | | | $^3\Pi$ | $2s\sigma^2 2p\sigma 2p\pi^3$ | $2p\sigma$ | $^2\Pi_i, 2s^2 2p^3, ^2P$ or $^2D$? | 3.56 or 2.39 | | $^3\Pi \rightarrow\ ^3\Sigma$ |
| O | 0 | 0.979 | (3568.4) | | 5.4 | 5.4 | 0 | $^2\Pi_i$ | $2s\sigma^2 2p\sigma^2 2p\pi^3$ | $2p\sigma$ | $^3\Pi_i, 2s^2 2p^4\ ^3P$ | 0 | 13.56 | |
| | 4.00 | 1.022 | 3084.7 | 97.8 | 3.0 | 7.0 | 1.6 | $^2\Sigma$ | $2s\sigma^2 2p\sigma 2p\pi^4$ | $2p\sigma$ | $^1\Sigma, 2s^2 2p^4\ ^1S$ (or $^1D$?) | [4.2] (or [2.0]?) | | $^2\Sigma \leftarrow\rightarrow {}^2\Pi$ |

*Notes for Table I.* (1) The energy and ionization potential values for atoms have been obtained from the known spectroscopic data (cf. A. Fowler, Series in Line Spectra, and W. Grotrian, Graphische Darstellung der Spektren). (2) For the molecules, the "energy (volts)" is with reference to the lowest known level, which is probably in all or nearly all cases actually the lowest level; in many cases (cf. "Known Transitions") bands arising from this level have been observed in absorption. The data on observed bands, energy levels, and $r_0$, $\omega_0$, and $\omega_0 x$ values are in many cases from Birge's compilation in International Critical Tables (cf. also Birge, pp. 230–2 of Report on Molecular Spectra). Additional data have been obtained from original sources as follows: $^1\Pi \leftarrow {}^1\Sigma$ of CuH, H. Stücklen, Zeits. f. Physik, **35**, 562, 1925, as re-interpreted by E. Hulthén (private communication); BeH, W. W. Watson, Phys. Rev. **32**, 600, 1928; HgH, E. Hulthén, Zeits. f. Physik, **50**, 319, 1928; AlH, E. Bengttson, Zeits. f. Physik, **51**, 889, 1928 and E. Bengttson and E. Hulthén, Zeits. f. Physik, **52**, 275, 1928; the upper $^1\Sigma$ level of AlH is obtained only if a low pressure (of hydrogen) is used, while the $^1\Pi$ level can be obtained even with high pressure; observation of MgH bands in absorption, cf. S. Barratt, Proc. Roy. Soc. **109A**, 194 (1925); CuH, AgH, AuH AlH, OH bands in absorption, cf. E. Hulthén and R. V. Zumstein, Phys. Rev. **28**, 13 (1926). (3) The $D^v$ and $D$ values are computed by the method of Birge and Sponer from $\omega_0$ and $\omega_0 x$ data (cf. note 7 of Table III of I), except the value for the $^2\Pi$ level of OH, which is from chemical data (K. Bonhoeffer and H. Reichardt, Zeits. Phys. Chem. **139**, 92, 1928). The value $D-D_0$ is (within the large experimental error of the $D$ values) a measure of the energy of excitation of the M atom after dissociation, assuming zero excitation for the M atom formed by dissociation of the *unexcited* molecule. (4) The molecular "state" is that determined by analysis of the bands. This is in practically all cases certainly correct. (Watson has, however, suggested that the two upper $^2\Sigma$ levels of BeH may be $^1\Sigma$ levels of BeH$^+$, and there is no proof to the contrary, since the expected rotational doubling (if present) is too small to have been observed.) (5) Under "H electron" is given the promoted orbit of the (initially $1s$) H electron which must be assumed in order, starting from the state of the atom M specified in the fourth-from-last column, to get the "likely configuration" and state given for the molecule MH.—Added in proof: (1), for data on C atom, cf. A. Fowler and E. W. H. Selwyn, Proc. Roy. Soc. **118***A*, 34 (1928); (2), for data on upper $^2\Pi$ level of MgH, cf. R. W. B. Pearse, Proc. Roy. Soc. **122***A*, 442 (1929); Pearse also mentions an additional system ($^2\Sigma \rightarrow {}^2\Sigma$?) in course of analysis.

the N atom; all of these would go over into the $s^2p^4\ {}^1D$ and ${}^3P_i$ states of the O atom: $\sigma^2\pi^2\ {}^3\Sigma$ from ${}^4S$ of nitrogen and going over into ${}^3P_i$ of oxygen; $\sigma^2\pi^2\ {}^1\Delta$ and ${}^1\Sigma$ from ${}^2D$ and going into ${}^1D$; $\sigma\pi^3\ {}^3\Pi_i$ from ${}^2P$ (or ${}^2D$) and going into ${}^3P_i$; $\sigma\pi^3\ {}^1\Pi$ from ${}^2P$ and going into ${}^1D$. Of these, ${}^3\Sigma$ and ${}^3\Pi$ have been observed.

For OH, only two stable low levels are predicted: $\sigma^2\pi^3\ {}^2\Pi_i$ from ${}^3P_i$, going over into ${}^2P_i$ of the F atom; and $\sigma\pi^4\ {}^2\Sigma$ from ${}^1S$ and going over into ${}^2P_i$. (The only other possible *two-quantum* state of OH is $2s\sigma 2p\sigma^2 2p\pi^4\ {}^2\Sigma$, from $sp^5\ {}^3P$ and going over into $sp^6\ {}^2S$.) The two predicted levels are found in the familiar ultraviolet OH bands. The prediction that ${}^2\Sigma$ of OH is derived from ${}^1S$ (rather than ${}^1D$) of the O atom is not very well confirmed, since $D-D_0 \sim 1.6$ volts, whereas the corresponding interval (${}^1S-{}^3P$) in the O atom is estimated at 4.2 volts (${}^1S-{}^1D=2.21$ volts, from the green aurora line, but ${}^1D-{}^3P$ is not yet known experimentally; it has, however, been estimated as about 2.0 volts.[20a]). $D-D_0=1.6$ agrees well with (the estimated) ${}^1D-{}^3P=2.0$ volts, so that it may be that ${}^2\Sigma$ of OH is after all derived from ${}^1D$ of the O atom. This would be possible if there is a violation of the $i_{l_\tau}$ conservation rule.[21]

*Selection Rules.* A point which is perhaps worth mentioning in connection with Table I is the absence of any tendency toward a strict selection rule $\Delta l_\tau = \pm 1$. In fact, a large proportion of the transitions there listed have $\Delta l_\tau = 0$; many have $\Delta l_\tau = \pm 1$; none have $|\Delta l_\tau| > 1$.

*London's valence theory.* According to London's valence theory,[22] the possibility of the existence of any molecule in stable form depends on the possibility of the formation of one or more valence bonds when its atoms unite, where a valence bond is said to be formed when two electrons, one from each of two atoms, unite to form a closed shell-of-two. In the union of an M atom and an H atom, for example, two possibilities exist: either no valence bond is formed ($N=0$), or one such bond is formed ($N=1$). Thus in Mg $(\cdots 3s^2\ {}^1S)+\text{H}(1s\ {}^2S)\rightarrow\text{MgH}(\cdots 3s\sigma^2 3p\sigma\ {}^2\Sigma)$, $N=0$, while in $\text{Mg}(\cdots 3s3p\ {}^3P)+\text{H}\rightarrow\text{MgH}(\cdots 3s\sigma^2 3p\pi\ {}^2\Pi)$, or in $\text{Cu}(\cdots 4s\ {}^2S)+\text{H}\rightarrow\text{CuH}(\cdots 4s\sigma^2\ {}^1\Sigma)$, $N=1$. According to London's theory, the valency $V$ of an atom is equal to the number of electrons not yet in closed pairs, and is equal to $(m-1)$, where $m$ is the multiplicity. Thus in the normal H or Cu atom, $V=1$, while in normal Mg, $V=0$. Only in *excited* Mg (triplet states) do we have $V=2$, corresponding to the usual chemical valence. Similar relations exist for nearly all atoms; the maximum $V$ is usually obtained only

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[20a] Cf. J. Kaplan, Phys. Rev. **33**, 638 (1929).

[21] This might occur in the following way. For an $s^2p^4$ O atom in a strong electric field, we have two ${}^1\Sigma$ states, namely, $2s\sigma^2 2p\sigma^2 2p\pi^2$ from ${}^1D$ and $2s\sigma^2 2p\pi^4$ from ${}^1S$. If the $i_{l_\tau}$ conservation rule holds, the former must give with the H electron a $2s\sigma^2 2p\sigma^2 2p\pi^2 3s\sigma$ or similar unstable ${}^2\Sigma$ state, while only the latter can give the $2s\sigma^2 2p\sigma 2p\pi^4$ state which is presumably the observed stable ${}^2\Sigma$ state found in OH. But it may be that the $i_{l_\tau}$ conservation rule is broken here so that the ${}^1\Sigma$ derived from ${}^1D$ takes on the configuration expected for that from ${}^1S$ (and vice versa). Such a breakdown of the $i_{l_\tau}$ ule would be similar to that observed in $F_2$ (cf. R. S. Mulliken, Phys. Rev. **32**, 772 (1928).

[22] F. London, ref. 10, especially Zeits. f. Physik **46**, 455 (1928).

in (moderately) excited states. London's theory involves a translation into quantum theory terms of Lewis' theory of bonding electron pairs.

One might suppose from the theories of Lewis and London that the formation of closed pairs of electrons is the essential or primary cause of stability in the formation of molecules. But it would appear to be more correct to say that the stability of molecular states depends largely on promotion energies,[23] and not at all *intrinsically* on the value of $V$. Low promotion energy probably means high stability, regardless of closed shells. Thus in the case of $O_2$, the normal state $\cdots 3p\pi^2\ {}^3\Sigma$ (cf. Table III of I), is evidently a state of lower energy (as one would expect from the multiplicity) than the as yet undiscovered state $\cdots 3p\pi^2\ {}^1\Delta$, in spite of the fact that in the latter the two $3p\pi$ electrons form a closed shell-of-two, while in the former they do not. For an O atom, we have $V=2$, but in normal $O_2$ only one valency bond is used ($N=1$). But usually it so happens that the lowest stage of promotion for any given pair or set of atoms,—and this stage corresponds ordinarily to the chemically most important lowest state[24] of the molecule,—results *incidentally* in the formation of a molecule containing a maximum of closed shells (cf., e.g., CO or $N_2$ in Table III of I). This is simply because the orbit of lowest energy to which any promoted atomic electron can go is very likely to be the same as that of an electron already

TABLE II. *Valence and stability in diatomic hydrides.* (data from Table I).

| *Atom* | *Atom state* | *Mol. state* | $V$ | $N$ | $r_0$(A.U.) | $D^v$ (volts) | *H orbit* |
|---|---|---|---|---|---|---|---|
| He | $1\ {}^1S$ | ${}^2\Sigma$ | 0 | 0 | (large) | ($\sim$0) | $2p\sigma$ |
| | $2\ {}^3P$ | ${}^2\Pi$ | 2 | 1 | | (Stable) | $1s\sigma$ |
| Be | $2\ {}^1S$ | ${}^2\Sigma$ | 0 | 0 | 1.35 | — | $2p\sigma$ |
| | $2\ {}^3P$ | ${}^2\Pi$ | 2 | 1 | 1.34 | — | $2s\sigma$ |
| Mg | $3\ {}^1S$ | ${}^2\Sigma$ | 0 | 0 | 1.74 | 0.5 | $3p\sigma$ |
| | $3\ {}^3P$ | ${}^2\Pi$ | 2 | 1 | 1.70 | 2.2 | $3s\sigma$ |
| Hg | $6\ {}^1S$ | ${}^2\Sigma$ | 0 | 0 | 1.76 | 0.37 | $6p\sigma$ |
| | $6\ {}^3P$ | ${}^2\Pi$ | 2 | 1 | 1.59 | 2.9 | $6s\sigma$ |
| C | $p^2\ {}^3P$ | ${}^2\Pi$ | 2 | 1 | 1.13 | $D_0$ | $2p\sigma$ |
| | $p^2\ {}^1D$ | ${}^2\Delta$ | 0 | 0 | 1.11 | $D_0$-1.66 | $2p\sigma$ |
| N | $p^3\ {}^4S$ | ${}^3\Sigma$ | 3 | 1 | 1.08 | $D_0$ | $2p\sigma$ |
| | $p^3\ {}^2P$ (or ${}^2D$) | ${}^3\Pi$ | 1 | 0 | 1.08+ | $D_0$-0.11 (or-1.28) | $2p\sigma$ |
| O | $p^4\ {}^3P$ | ${}^2\Pi$ | 2 | 1 | 0.98 | 5.4 | $2p\sigma$ |
| | $p^4\ {}^1S$ (or ${}^1D$) | ${}^2\Sigma$ | 0 | 0 | 1.02 | 3.0 | $2p\sigma$ |

Note. Cf. Table I for data on CuH, AgH, AuH, AlH, for the recorded states of all of which $N=1$.

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[23] Hund discusses this question in a somewhat different way, reaching similar conclusions (ref. 3, p. 789; also, Zeits. f. Elektrochemie **34**, 441, 1928).

[24] In regard to the excited states of $H_2$ derived from $H(1s\ {}^2S)+H(2s\ {}^2S)$, cf. E. A. Hylleras, Zeits. f. Physik **51**, 150 (1928). Of the resulting states, one ${}^3\Sigma$ and one ${}^1\Sigma$ are stable, one ${}^3\Sigma$ and one ${}^1\Sigma$ unstable. Similar results are found for $H\ (1s\ {}^2S)+H(2p\ {}^2P)$: cf. E. C. Kemble and C. Zener, Phys. Rev. **33**, 286 (1929).

present, or formed by promotion, in the other atom. In such cases, the number of electrons in closed shells can be lessened, or the multiplicity increased, only by increased promotion, with resulting decreased stability.

That molecular stability is not essentially determined by the possibility of the formation of new closed electron-pairs is well illustrated by data on the diatomic hydrides (cf. Table II). For the two lowest known states of each of these molecules (but HeH is not yet known experimentally), we find, judging by $r_0$ and $D^v$ data, that there is no *sharp* contrast in stability between states with $N=0$ and those with $N=1$. For the molecules with two outer electrons, the state with $N=1$ is, it is true, the more stable, but this is to be expected because the H electron is here less strongly promoted for $N=1$ than for $N=0$ (cf. Table I). Where the contrast in stability between $N=1$ and $N=0$ is greatest (Hg, He), the difference in promotion energy is greatest (judging by the energy interval ${}^3P-{}^1S$ in the atom,—cf. Table I); where the contrast is least[18a] (Mg, or Be), the difference in promotion energy is least. For the molecules CH, NH, OH, the states with $N=1$ are again the more stable, even though there is here no difference in respect to promotion of the H electron; but the difference in stability can be reasonably explained by the fact that in each case the state with $N=1$ has one more $2p\sigma$, one less $2p\pi$, electron than the state with $N=0$ (cf. Table I); the binding energy is *expected* to be considerably greater for $np\sigma$ than for $np\pi$ electrons (cf. Hund,[3] p. 766–7, also cf. AlH above).

## RELATIONS BETWEEN MULTIPLET SEPARATIONS IN M ATOMS AND MH MOLECULES

*General.*[25] Although the data of Table I are entirely in harmony with a stage 3 Stark effect, they give no good evidence for this as against at least an approach to stage 2 or stage 4. As will now be shown, a study of multiplet separations gives evidence that stage 3 is not *passed* (toward stage 4), but that on the other hand, in cases where it differs from stage 2, it is actually *reached.* Stages 2 and 3 are, of course, identical unless more than one outer electron with $l_\tau>0$ is present.

For *atoms*, multiplet separations depend on quantities of the form $a\sim R\alpha^2Z_i^2Z_a^2/n_a^3\,l_\tau(l_\tau+½)(l_\tau+1)$, where $eZ_i$ is an effective nuclear charge applicable to the innermost part of a penetrating electron orbit (ordinarily $Z_i$ is not much less than $Z$), $Z_a=1$ for a neutral atom, $n_a$ is the effective principal quantum number of the orbit in question, and $R$ and $\alpha$ are familiar constants; $a$ as given by the above expression is in cm$^{-1}$. For atomic ${}^2P$, ${}^3P$, and ${}^4P$ states resulting from one or more (equivalent) $p$ electrons, $\Delta\nu$ (i.e., ${}^2P_{3/2}-{}^2P_{1/2}$, etc.) is proportional to $a$, with a proportionality constant which is a simple fraction (cf. Appendix, Table IV). For the most common

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[25] The relation between the $\Delta\nu$ values for ${}^2\Pi$ and other states of diatomic hydride and other molecules and the $\Delta\nu$ values of corresponding ${}^3P$ and other states of atoms has been discussed previously by E. Hulthén, Nature, Oct. 31, 1925; R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 151 (1926), and especially by R. Mecke, Zeits. f. Physik **36,** 796 (1926); **42,** 419–20 (1927); also R. S. Mulliken, Phys. Rev. **30,** 785 (1927) (${}^2\Pi$ and ${}^2\Delta$ states of CH).

cases ($p\ ^2P$; $sp\ ^3P$; $p^2\ ^3P$; $sp^2\ ^2P$), $\Delta\nu=(3/2)a$, or ($p^5\ ^2P$, $p^4\ ^3P$, etc.), $\Delta\nu=-(3/2)a$; for $p^3\ ^2P$ or $^2D$ etc., $\Delta\nu\sim 0$.

For *molecules*, assuming a *stage 3 Stark effect*, the corresponding relations are, $\Delta\nu=a$ for $\pi\ ^2\Pi$ and $\sigma\pi\ ^3\Pi$, $\Delta\nu=-a$ for $\pi^3\ ^2\Pi$ and $\sigma\pi^3\ ^3\Pi$; for $\pi^2\ ^2\Delta$, $\Delta\nu=0$. $\Delta\nu$ here means $^2\Pi_{3/2}-{}^2\Pi_{1/2}$ or $^3\Pi_2-{}^3\Pi_0$. These relations apply to *rotationless* molecules; in making use of data from actual molecules, certain corrections must be applied (cf. Appendix, p. 747).

Before using these relations for MH molecules, we should consider how the form and value of the function $a$ for the MH molecule are related to the corresponding quantities for the M atom. The $a$ expression for the atom is based on the assumption of an orbit in a central force field. If, as is true for the stage 3 Stark effect, the effect of the H nucleus may be regarded as no greater than a perturbation of this orbit, then the form of the atomic $a$ expression should still hold in the MH molecule, the effect of the perturbation being merely a change in the numercial value of $a$ resulting from changes in $Z_i$ and $n_a$.[26] Accordingly we should consider the effects of an H atom on the values of $Z_i$ and $n_a$ for an outer electron of the M atom. In the cases we are interested in, this is an $np$ electron for which $i_{l_\tau}=1$ in the molecule ($np\pi$). The partial addition of the H electron to the M electron system (cf. p. 737) must produce for the electrons of the latter a *shielding* effect which should cause a small or moderate increase in $n_a$, partly offset, however,—especially if $r_0$ is small,—by the attractive force of the H nucleus. Since $Z_i$ depends essentially on the part of the orbit which is close to the M nucleus and where the force exerted by the H nucleus is relatively small, it should probably be affected by the H atom mainly only indirectly, through $n_a$; a small decrease in $Z_i$ would be expected to result from an increase in $n_a$. Other modifying effects of the H atom on the $a$ expression are probably of small importance.

Thus for a $p\pi$ electron in an MH molecule, assuming a stage 3 Stark effect, we may reasonably expect the quantity $a$ to have a value not far different from, but, because of a small increase in $n_a$, somewhat less than, its value in the M atom. Under these circumstances we expect, for a $\pi^3$ or $\pi\ ^2\Pi$ state of MH derived from a $p^4$ or $p^2$ or $sp\ ^3P$ state of M, $\Delta\nu_{\mathrm{MH}}/\Delta\nu_{\mathrm{M}}=(2/3)(a_{\mathrm{MH}}/a_{\mathrm{M}})$. If $n_a$ is nearly the same for MH as for M, we have $a_{\mathrm{MH}}/a_{\mathrm{M}}\sim 1$ and $\Delta\nu_{\mathrm{MH}}/\Delta\nu_{\mathrm{M}}\sim 2/3$. It should be noted that, because of the form of the $a$ expression, the value of $a$ is very sensitive to changes in $n_a$.

*Discussion of examples.* In Table III, $\Delta\nu$ and $a$ values are given for all hydrides for which data are available. For the present leaving NH out of the discussion, the table is arranged as follows: for each atom (all $^3P$), $\Delta\nu$ and $a_{\mathrm{M}}=(2/3)\Delta\nu$ are given; for each molecule ($^2\Pi$) derived from the given $^3P$ atom (cf. Table I), $a$ is given, assuming $a=|\Delta\nu_{\mathrm{MH}}|$, where $\Delta\nu_{\mathrm{MH}}$ has been corrected to the case of a rotationless molecule. $\Delta\nu_{\mathrm{M}}$ and $\Delta\nu_{\mathrm{MH}}$ are *both positive* in all cases except OH (and NH, which is, however, exceptional in

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[26] In stage 4, $l_\tau$, and the representation of the orbit as a perturbed central orbit, would lose their meaning.

other respects,—see below); in OH they are *both negative*, as expected. The ratio $a_{\mathrm{MH}}/a_{\mathrm{M}}$ is remarkably near unity in all cases, usually somewhat less as predicted, indicating that $n_a$ has been slightly, but only slightly, increased for the outer $p\pi$ electron or electrons in the formation of MH. For CH, NH, and OH, where $r_0$ is especially small (1.0–1.1 A.U.) the ratio is largest; for CaH, where $r_0$ is especially large (2.0 A.U.), the ratio is smallest. This may perhaps be explained as suggested above, as depending on a balance between a shielding effect of the H electron causing increase in $n_a$ and so decrease in $a$, and a compensatory anti-shielding effect of the H nucleus, the latter least for large $r_0$ (CaH).

TABLE III. *Multiplet separations for* M *atoms and* MH *molecules.*

| | *Atom* | | | *Molecule* | | |
|---|---|---|---|---|---|---|
| M | *State* | $\Delta\nu(cm^{-1})$ | $a_{\mathrm{M}}(cm^{-1})$ | *State* | $a_{\mathrm{MH}}(cm^{-1})$ | $a_{\mathrm{MH}}/a_{\mathrm{M}}$ |
| Be | $2s2p\ {}^3P$ | 3.02 | 2.01 | $2s\sigma^2 2p\pi\ {}^2\Pi$ | very small | |
| Mg | $3s3p\ {}^3P$ | 60.6 | 40.4 | $3s\sigma^2 3p\pi\ {}^2\Pi$ | 35 | 0.86 |
| Zn | $4s4p\ {}^3P$ | 578.9 | 385.9 | $4s\sigma^2 4p\pi\ {}^2\Pi$ | 341.1 | 0.885 |
| Cd | $5s5p\ {}^3P$ | 1713 | 1142 | $5s\sigma^2 5p\pi\ {}^2\Pi$ | 1013 | 0.887 |
| Hg | $6s6p\ {}^3P$ | 6398 | 4265 | $6s\sigma^2 6p\pi\ {}^2\Pi$ | 3696 ($n=0$)<br>3741 ($n=1$) | 0.866<br>0.876 |
| Ca | $4s4p\ {}^3P$ | 158.1 | 105.5 | $4s\sigma^2 4p\pi\ {}^2\Pi$ | 79.6 | 0.755 |
| C | $2s^2 2p^2\,{}^3P$ | 42.3 | 28.2 | $2s\sigma^2 2p\sigma^2 2p\pi\ {}^2\Pi$ | 28.4 | 1.01 |
| | $2s2p^4\,{}^4P_i$ | −62 | 46.5 | | | |
| | ${}^2P_i$ | −30 | 30 | | | |
| N | $2s^2 2p^2 3s\ {}^4P$ | 80.5 | 60.3 | $2s\sigma^2 2p\sigma\ 2p\pi^3\,{}^3\Pi_i$ | ∼61 | ∼1 |
| | $4s$ | 118 | 88 | | | |
| | $6s$ | 117 | 88 | | | |
| | $3s\ {}^2P$ | 83.1 | 83.1 | | | |
| | $4s$ | 83 | 83 | | | |
| | $5s$ | 76 | 76 | | | |
| O | $2s^2 2p^4\,{}^3P_i$ | −224 | 149 | $2s\sigma^2 2p\sigma^2 2p\pi^3\,{}^2\Pi_i$ | 137.9 | 0.93 |

*Notes:* Sources of $\Delta\nu$ data for atoms: Mg, Zn, Cd, Hg, Ca, cf. A. Fowler, Report on Series in Line Spectra; Be, cf. W. Grotrian, Graphische Darstellung der Spektren, *I*, p. 182 (J. Springer, 1928); C, Fowler and Selwyn, P. R. S. **118** *A*, 34; N, K. T. Compton and J. C. Boyce, Phys. Rev. **33**, 145 (1929); O, cf. I. S. Bowen and R. A. Millikan, Phys. Rev. **26**, 318 (1925). For $a/\Delta\nu$ ratios used in calculation of $a$ values from $\Delta\nu$ values, cf. Table IV in the Appendix. The $a$ values ($a=|A|$ in all cases, cf. Table IV) for MgH, ZnH, CdH, HgH, and OH have been calculated from data of Hulthén and others (cf. R. S. Mulliken, Phys. Rev. **32**, 388 (1928) and references there cited) by the use of Eqs. (17) and (18). For CH, the value of $a$ ($=A$) was obtained by noting that the observed term form corresponds to $\lambda=+2.00$ in Eq. (14) of the Appendix (cf. note 7 of Table I of Mulliken, Phys. Rev. **32**, 388). In regard to BeH, cf. W. W. Watson, Phys. Rev. **32**, 600 (1928) and M. Petersen, Phys. Rev. **31**, 1130*A* (1928). In the case of NH, the value given is an extrapolation (R. Mecke, Zeits. f. Physik, **42**, 420, 1927) which is probably somewhat less than the true value of $a$.

The interesting case of NH requires special discussion. Here an $s\sigma^2 p\sigma p\pi^3\ {}^3\Pi$ molecule with $|\Delta\nu|\sim 60$[27] is derived from an $s^2p^3\ {}^2D$ (or ${}^2P$) atom with $\Delta\nu=-5$ (or $-1$).[28] The great increase in $|\Delta\nu|$ here, which is quite unlike the uniform 2/3 ratio $\Delta\nu_{\mathrm{MH}}/\Delta\nu_{\mathrm{M}}$ for the cases previously considered, is exactly what one expects theoretically if the coupling of three equivalent $p$ electrons to give a ${}^2D$ or ${}^2P$ atom is completely broken down (stage 3 Stark effect) to give three equivalent $p\pi$ electrons. For according to theory, $\Delta\nu/a\sim 0$ for the ${}^2D$ or ${}^2P$ atom, while for $p\pi^3\ {}^3\Pi$, we expect $\Delta\nu/a=-1$. That $|\Delta\nu|\sim 60$ for NH is in agreement with $a$ for an $s^2p^3$ N atom, as expected if there is *complete* uncoupling of $l_r$'s in NH, cannot be shown directly, because

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[27] Presumably $\Delta\nu\sim-60$, but the available experimental data give only the *magnitude* of $\Delta\nu$.

[28] Cf. K. T. Compton and J. C. Boyce, Phys. Rev. **33**, 145 (1929).

$\Delta\nu/a\sim 0$ for all states derived from the $s^2p^3$ configuration. But a study of data for various nearly related configurations ($sp^4$ and $s^2p^2ns$) gives $a$ values in the neighborhood of 60 (cf. Table III), indicating that this is about the right value of $a$ for the $p$ electrons in $s^2p^3$ in an N atom. Hence we have good evidence that stage 3 is reached in NH, since it is clear that if the $l_r$'s had to any important degree remained coupled as in the N atom, corresponding to stage 2, $\Delta\nu$ in NH would have been nearer zero.

In the CH and OH molecules, the observed $\Delta\nu_{\mathrm{MH}}/\Delta\nu_{\mathrm{M}}\sim 2/3$ is probably no evidence for stage 3 rather than stage 2, since in these cases the uncoupling of the $l_r$'s has no effect on $\Delta\nu$, beyond the factor 2/3. Nevertheless we may reasonably assume, in analogy with NH, that the uncoupling is complete. For the other molecules in Table I, there is no distinction between stages 2 and 3.

In the above we have no strict proof that stage 4 is not reached, since we do not *know* that $a$ would be changed much in the passage from stage 3 to stage 4. It seems unlikely, however, that stage 4 could explain the observed $a_{\mathrm{MH}}/a_{\mathrm{M}}$ ratios.

*$^2\Delta$ state of* CH. In the $^2\Delta$ state of CH (cf. Table I) the observed very narrow inverted $\Delta\nu$[15] is exactly what one would expect, as the writer pointed out in an earlier paper, if the coupling of the two $2p$ electrons in $s^2p^2\ {}^1D$ of carbon is undisturbed in the formation of CH (stage 2). But it is equally compatible with the present formulation $2s\sigma^2 2p\pi^2\ {}^2\Delta$, in which the original coupling has been broken down (stage 3).[29] The observed $\Delta\nu$ should result mainly from the small energy of interaction of the spin of the $2p\sigma$ electron with the $l_r$'s of the $2p\pi$ electrons (cf. ref. 15).

## APPENDIX I. MULTIPLET WIDTHS IN P AND Π STATES

*Atomic multiplets.* For a $^2P$ atom containing, aside from closed shells, only a single $p$ electron ($l=1$) in a penetrating orbit, the energy of magnetic interaction between the $l$ and $s$ vectors is given theoretically by the Landé formula:[30]

$$\gamma=(1/2)a[j(j+1)-l(l+1)-s(s+1)] \tag{1}$$

where (*in cm*$^{-1}$)

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

The doublet separation $\Delta\nu(^2P_{3/2}-{}^2P_{1/2})$, according to Eq. (1), is

$$\Delta\nu=3/2a. \tag{3}$$

For *any* atomic multiplet, if the usual coupling relations exist, the magnetic energy of $(l, s)$ interaction[31] is given by

$$\Gamma=(1/2)A\,[j(j+1)-l(l+1)-s(s+1)]. \tag{4}$$

For $^2P$, $^3P$, $^4P$ states, the total multiplet widths are then as follows:

$$^2P,\ \Delta\nu=(3/2)A;\ {}^3P,\ \Delta\nu=3A;\ {}^4P,\ \Delta\nu=4A \tag{5}$$

Goudsmit[32] has recently discussed the determination of $A$ values for various cases of atoms with more than one outer electron. The results which are of interest for our purposes are given

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[29] The distinction here between stages 2 and 3 is not meaningless in the new quantum mechanics.

[30] A. Landé, Zeits. f. Physik **25**, 46 (1925).

[31] Only the interaction of each $l_r$ with its own $s_r$ is here considered. Other coupling energies here neglected, such as that of the $l_r$ of one electron and the $s_r$ of another, are comparatively small, although not always negligible.

below in table IV,[32] the $A$ values for various electron configurations being expressed in terms of the $a$ value for the $p$ electron or electrons which are present. By the use of Eq. (5), $\Delta\nu$ values are then obtainable for each case in terms of $a$ values.

TABLE IV. *$A$ and $\Delta\nu$ values for $P$ and $\Pi$ states.*

| *State* | *A* | $\Delta\nu$ | *State* | *A* | $\Delta\nu$ | *State* | *A* | $\Delta\nu$ (nuclei fixed) |
|---|---|---|---|---|---|---|---|---|
| $p\ {}^2P$ | $a$ | $(3/2)a$ | $p^4\ {}^3P$ | $-(1/2)a$ | $-(3/2)a$ | $\pi\ {}^2\Pi$ | $a$ | $a$ |
| $sp\ {}^3P$ | $(1/2)a$ | $(3/2)a$ | $sp^4\ {}^2P$ | $-(2/3)a$ | $-a$ | $\sigma\pi\ {}^3\Pi$ | $(1/2)\ a$ | $a$ |
| $p^2\ {}^3P$ | $(1/2)a$ | $(3/2)a$ | $sp^4\ {}^4P$ | $-(1/3)a$ | $-(4/3)a$ | $\pi^3\ {}^2\Pi$ | $-\ a$ | $a$ |
| $sp^2\ {}^2P$ | $(2/3)a$ | $a$ | $p^5\ {}^2P$ | $-a$ | $-(3/2)a$ | $\sigma\pi^3\ {}^3\Pi$ | $-(1/2)a$ | $a$ |
| $sp^2\ {}^4P$ | $(1/3)a$ | $(4/3)a$ | | | | | | |

*Notes:* (1) For any atomic multiplet level, the magnetic energy is given by Eq. (4), for any molecular multiplet level (for fixed nuclei), by Eq. (13). (2) The symbols $p^2$, $p^4$, and $p^5$ stand for two, four, and five equivalent electrons, respectively. (3) The results for the atomic states are, with some exceptions,[32] strictly applicable only if the Russell-Saunders coupling $\{(l_1, l_2, \cdots)(s_1, s_2, \cdots)\} = \{l, s\}$ holds. (4) The results for ${}^2\Pi$ and ${}^3\Pi$ states are strictly applicable only ($a$), for fixed (non-rotating) nuclei, ($b$), if there is no coupling of the $l_\tau$'s; the spins $s$ are ordinarily assumed to give a resultant $s$, as in the Russell-Saunders coupling for atoms, but the results would be unaffected if each $s_\tau$ gave a separate $i_{s_\tau}$.

*Molecular multiplets.* For ${}^2\Pi$ and ${}^3\Pi$ states in which each $l_\tau$ is independently space-quantized with reference to the molecular axis (stage 3 Stark effect), the $\Gamma$ and $\Delta\nu$ relations, for a molecule with nuclei held fixed, can readily be obtained in analogy to the theory of the Paschen-Back effect for atoms. Let us think first of a single $p$ electron in an atom, in a strong magnetic field. Here $l$ and $s$ are separately quantized, giving magnetic quantum numbers $m_l$ and $m_s$, and the relation $\gamma = am_lm_s$ holds for the interaction energy of $l$ and $s$ (cf. Goudsmit, l. c.,[32] p. 952). Now the electrical quantum numbers $i_l$ and $i_s$ in a molecule (strong electric field) are precisely analogous to $m_l$ and $m_s$ of a strong magnetic field.[33] Hence for this case:

$$\pi\ {}^2\Pi:\ \Gamma = Ai_li_s = \gamma = ai_li_s. \tag{6}$$

Putting $i_l = 1$, $i_s = \pm 1/2$ in Eq. (6) and subtracting, one gets

$$\pi\ {}^2\Pi:\ \Delta\nu = a. \tag{7}$$

For the case of a ${}^3\Pi$ state resulting from the presence of a $\sigma$ and a $\pi$ electron, we make use of the general relation (cf. Goudsmit, l. c., Eq. (2))

$$\Gamma = \Sigma\gamma_\tau = \Sigma a_\tau l_\tau s_\tau \overline{\cos (l_\tau, s_\tau)}. \tag{8}$$

For a $\sigma$ electron, $a_\tau = 0$, or $\overline{\cos (l_\tau, s_\tau)} = 0$, or both. Hence $\Gamma = als_1 \overline{\cos (l, s_1)}$, where $a$ and $l$ refer to the $\pi$ electron. The spins $s_1$ and $s_2$, of the $\pi$ and $\sigma$ electrons respectively, are here coupled to give a resultant $s = 1$. Under these circumstances, evaluation of $\overline{\cos (l, s_1)}$, if due account is taken of the meaning of $l$, $s$, and $s_1$ in the new mechanics, gives

$$\Gamma = a[l \cos (i_l, l)][s \cos (s_1, s) \cos (m_s, s)] = ai_li_s/2.$$

That is, if $a$ refers to the $\pi$ electron, we have

$$\sigma\pi\ {}^3\Pi:\ \Gamma = Ai_li_s = (1/2)ai_li_s. \tag{9}$$

Putting $i_l = 1$, $i_s = +1$ and $-1$ in Eq. (9) and subtracting, one gets

$$\sigma\pi\ {}^3\Pi:\ \Delta\nu = a. \tag{10}$$

For a $\pi^3\ {}^2\Pi$ state (cf. I, p. 221), we note first that two of the three $\pi$ electrons must have their $i_{l_\tau}$'s parallel (i.e., say $i_{l_1} = i_{l_2} = \pm 1$). These two electrons must then have their spins anti-parallel, forming a closed shell-of-two (cf. I, p. 192–4), with a net $(l_\tau s_\tau)$ interaction energy

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[32] S. Goudsmit, Phys. Rev. **31**, 946–59 (1928); S. Goudsmit and C. J. Humphreys, Phys. Rev. **31**, 960 (1928). The $A$ and $\Delta\nu$ relations for $P$ states (Table IV below) are not all given explicitly in these papers, but can be readily obtained from results there given. For the simpler cases, the relations have been known for some time.

($\gamma_1+\gamma_2$ in Eq. 8) of zero. We need therefore consider only the ($l_\tau s_\tau$) energy for the third electron. By Eq. 6, this is $\gamma_3=ai_{l_3}i_{s_3}=ai_{l_3}i_s$. Now (cf. I, Fig. 1), on account of the fact that $i_{l_3}$ is opposite to $i_{l_1}$ and $i_{l_2}$, which are both parallel to $i_l(i_l=\sum i_{l_\tau})$, we have $i_{l_3}=-i_l$. Hence,

$$\pi^3\ {}^2\Pi:\ \Gamma=Ai_li_s=-ai_li_s;\ \Delta\nu=-a \tag{11}$$

Making use of the result of the preceding paragraph, and proceeding as for the case of $\sigma\pi\ {}^3\Pi$, it is readily shown that we have

$$\sigma\pi^3\ {}^3\Pi:\ \Gamma=Ai_li_s=-(1/2)ai_li_s;\ \Delta\nu=-a \tag{12}$$

In general, for *any* molecular multiplet,[33] for fixed nuclei,

$$\Gamma=Ai_li_s. \tag{13}$$

*Reduction of molecular $\Delta\nu$ data to the case of fixed nuclei.* In order to obtain, from experimental data, correct $a$ values for multiplet states of real molecules, allowance must be made for the effect of molecular rotation, since Eqs. (6)–(13) apply only for the case of fixed nuclei. Hill and Van Vleck[34] have given formulas for doublet and triplet states in which the sum of the ($l_\tau s_\tau$) magnetic energy and the rotational energy is expressed as a function of the rotational quantum number $j$. For doublet states, the exact energy formula is as follows:

$$E/hc=B[(j+1/2)^2-i_l^2\pm1/2\{4(j+1/2)^2+\lambda(\lambda-4)i_l^2\}^{1/2}]+\cdots. \tag{14}$$

Here $\lambda=A/B$, where $B=h/8\pi^2cI$, and $A$ is the $A$ of Eqs. (6), (11), (13), and Table IV; the upper (+) sign in Eq. (14) refers to $F_2$ levels, the lower (−) to $F_1$ levels.[35].

For large values of $|\lambda|$, corresponding to an approach to Hund's case $a$, expansion of Eq. (14) gives [34] for normal doubtlets ($A>0$),

$$E/hc=\pm(1/2)Ai_l+B[j(j+1)-(i_l\pm1/2)^2+(1/2)\pm\{(j+1/2)^2-i_l^2\}B/Ai_l+\cdots. \tag{15}$$

For inverted doublets ($A<0$), it gives

$$E/hc=\pm(1/2)|A|\,i_l+B[j(j+1)-(i_l\pm1/2)^2+1/2\pm\{(i+1/2)^2-i_l^2\}B/|A|\,i_l+\cdots. \tag{16}$$

In each case the upper sign refers to the $F_2$ levels, the lower to the $F_1$ levels; the $F_2$ levels correspond to ${}^2\Pi_{3/2}$ levels if $A>0$, to ${}^2\Pi_{1/2}$ levels if $A<0$.[15,36]

Expressions corresponding to Eqs. (15) and (16) are also given by Hill and Van Vleck for triplet levels (l. c., p. 261).

If $|\lambda|$ is sufficiently large (say, perhaps, $|\lambda|>6$), Eq. (15) or (16) furnishes a convenient basis for the evaluation of $A$ from experimental data. Considering first the case $A>0$, $i_l=1$, suppose we make the subtraction $F_2(3/2)-F_1(1/2)$, and express the result in terms of $A$ and $B$. In this way we find the relation:

$$A>0:\ A=\{F_2(3/2)-F_1(1/2)\}-B-3B^2/A. \tag{17}$$

Similarly

$$A<0:\ |A|=\{F_2(1/2)-F_1(3/2)\}+B-3B^2/|A|. \tag{18}$$

With the help of Eqs. (17) and (18), $A$ can usually readily be determined, since the interval $F_2(3/2)-F_1(1/2)$ or $F_2(1/2)-F_1(3/2)$ can be obtained directly and accurately as a difference of the wave-numbers of two spectrum lines (cf. the figures in ref. 36), while the value of $B$ is also known with sufficient accuracy from the analysis of the band.

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February 27, 1929.

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[33] Cf. F. Hund, Zeits. f. Physik **36**, 657, 662 (1926); Hund, Linienspektren, p. 76–8, J. Springer, Berlin, 1927.

[34] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 261–2 (1928).

[35] For the definition of $F_1$ and $F_2$ levels in general, cf. ref. 15 and especially ref. 36. For $j=3/2, 5/2, \cdots$, there is an $F_1$ and an $F_2$ level for each $j$ value, but for $j=1/2$ there is only a single level. This is here classified as $F_2(1/2)$ for $\lambda<2$, and as $F_1$ (1/2) for $\lambda>2$ (cf. Fig. 1 of ref. 36, discussion). With this definition, the relations of + and − signs to $F_1$ and $F_2$ in Eqs. (14), (15), (16) are correct as stated in the text. Hill and Van Vleck use a notation which corresponds to calling $F$ (1/2) always $F_2(1/2)$, but if this is done, the use of signs in the equations has to be reversed for $F_2$ (1/2) as compared with other $F_2$ levels.

[36] R. S. Mulliken, Phys. Rev. **32**, 388 (1928).