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CORRELATION OF ATOMIC J VALUES AND MOLECULAR QUANTUM NUMBERS, WITH APPLICATIONS TO HALOGEN, ALKALINE EARTH HYDRIDE, AND ALKALI MOLECULES

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Abstract

Rules are given for determining the Ω values and symmetry properties of the molecular states obtainable from the union of two atoms with specified J values, assuming case c coupling in the molecule. These are used to determine the correlation of molecular Λ and S values with atomic J values, for cases where there is strong L, S coupling in one or both atoms. The correlation rules are applied to I+I, Hg+H, and Cs+Cs. Difficulties which exist when a similar correlation is attempted in cases where the L, S coupling is weak (e.g. Mg+H, or Na+Na) are discussed. Electron configurations and dissociation products are discussed in some detail in the case of the halogen molecules, and an interpretation is given, in terms of electron configurations, of the analogies and differences between the spectra of the members of homologous series of molecules such as F_2, Cl_2, Br_2, I_2, or Li_2, Na_2, K_2, ...

Statement of the Problem

Wigner and Witmer[1] have given rules for completely determining, in terms of Λ and S values and symmetry properties, the possible molecular states which result from the union of two atoms with specified L and S values $L_1S_1L_2S_2$ and specified symmetry character (even or odd). Most of the results given by these rules can be obtained very simply[2] by assuming negligible L, S couplings in the atoms and determining the possible values of the projections M_{L_1} and M_{L_2} of L_1 and L_2 on the internuclear axis, and from these the possible Λ values ($\Lambda = |M_{L_1}+M_{L_2}|$). The resulting S values are S_1+S_2, S_1+S_2-1, $\cdots$, $|S_1-S_2|$, once for each M_{L_1}, M_{L_2} combination. In the case of two atoms of the same element[2a], in *unlike* states,[3] each molecular state of given M_{L_1}, M_{L_2}, and S occurs twice, there being always one even (g) and one odd (u) state. For like[2a] atoms in the *same* state,[3] the number of molecular states is, however, not doubled. Here a consideration of the way

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[1] E. Wigner and E. E. Witmer, Zeits. f. Physik, **51**, 883 (1928).

[2] The method here indicated was first used by F. Hund. Wigner and Witmer later, by a more rigorous method, cleared up some doubtful points, and determined the symmetry properties of the molecular terms.

[2a] The electron states of a molecule composed of two different isotopes of one element are not quite strictly, but are for all practical purposes, g and u. In respect to the rules given in this paper, different isotopes of an element may be regarded as identical.

[3] "The same state" here means the same set of n's and l's and the same L and S, but not necessarily the same J's or M's. "Unlike states" means here states differing in some way other than in the J's or M's.

in which (in zeroth approximation) the atomic combine to give the molecular wave-functions is required to determine which molecular states are *g* and which are *u*. When $\Lambda=0$, it is necessary to distinguish Σ^+ and Σ^- states. When $\Lambda=0$ results from $M_{L_1}=-M_{L_2}$, there is always one Σ^+ and one Σ^- state, derived from a splitting up of the degenerate pair $+M_{L_1}-M_{L_2}$ and $-M_{L_1}+M_{L_2}$. When $\Lambda=0$ results from $M_{L_1}=M_{L_2}=0$, however, a consideration of the forms of the atomic and molecular wave-functions is required to determine whether the resulting state is Σ^+ or Σ^-. The complete set of rules for all cases is given in convenient form in a recent paper by Hund.[4] These rules are applicable to case *a* or *b* molecular states and hold regardless of whether or not the initial assumption of negligible L, S couplings in the atoms is true.

In cases where the actual L, S couplings are strong, so that atomic states with different J values differ considerably in energy, it is of interest to determine the molecular states capable of being formed from two atoms with specified L, S, *and* J values. For case *a* or *b* molecular states we should like to know to what J values (J_1, J_2) each state of specified Λ and S (and Ω in case *a*) corresponds. The solution of this problem unfortunately cannot be given completely in terms of simple rules like those for the less detailed problem of the correlation of Λ and S with $L_1S_1L_2S_2$. It can, however, be divided into two steps, for the first of which simple rules can be given. These steps are (1) determination of the possible Ω values, assuming case *c* coupling, for each pair of atomic J values (J_1J_2), and (2) correlation of each such state of given Ω with one of the case *a* or *b* states whose Λ and S values are known from the Hund-Wigner-Witmer rules.

The results of the first step are of course directly applicable to case *c* molecular states, where Λ and S lack meaning, for example to certain excited states of the halogen molecules.[5] It should also be noted that molecular states which for r near r_e have case *a* or *b* coupling tend normally to pass through case *c* when r is increased toward dissociation. Similarly, molecular states which have case *c* coupling for $r\sim r_e$ and $>r_e$ tend to go over to case *a* or *b* coupling when r is decreased.

RULES FOR CORRELATION OF Ω VALUES AND ATOMIC J VALUES

The problem of determining the Ω values of the molecular states derived from atoms with given J values is similar to that of the determination of Λ values when atomic L values are given. Most of the results can be obtained very simply, by considering the Ω values resulting from the possible projections M_1 and M_2 of J_1 and J_2 on the internuclear axis. For atoms of *different elements*, the Ω values are determined, if $\Omega>0$, by $\Omega=|M_1+M_2|$. When $\Omega=0$,

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[4] F. Hund, Zeits. f. Physik, **63**, 723, 1930.

[5] R. S. Mulliken, Phys. Rev., **36**, 699 (1930). This article unfortunately contains a number of minor errors, mainly typographical (e.g. use of small π for large Π).

[6] Cf. Ref. 5, p. 702 and ref. 10, for definition and discussion of 0^+ and 0^- states, and nomenclature and selection rules for case *c*.

[7] This is exactly analogous to the fact that when $\Lambda=0$ results from $M_{L_1}=-M_{L_2}$ (cf. text, above), there is always one Σ^+ and one Σ^- state.

we have to distinguish 0^+ and 0^- states.[6] When $\Omega=0$ results from $M_1=-M_2$, there is always one 0^+ and one 0^- state, derived from the degenerate pair $+M_1-M_2$ and $-M_1+M_2$.[7] When $\Omega=0$ results from $M_1=M_2=0$, a consideration of the atomic and molecular wave-functions is required to determine whether the resulting state is 0^+ or 0^-. In the case of two atoms of the *same element*[2a] but in *unlike states*, each molecular state given by the above results is replaced by one even (g) and one odd (u) state.[8] By "unlike states" are here meant atomic states which differ in respect to at least one quantum number, even if only in respect to J or M. (We are using the terms "like" and "unlike" states here in a different sense than in Ref. 3 and in a previous paragraph.) For *like atoms* in the *same state* (i.e. identical in all quantum numbers including M), the number of derived molecular states is the same as in the case of two unlike atoms. The symmetry (g or u) of such states can be determined by means of rules given by Wigner and Witmer.[9] The complete set of rules for the determination of the possible Ω values derivable from two atoms having specified J values can be conveniently expressed as follows:[10]

A. Unlike Atoms

Let $J_1 \geqq J_2$. The possible Ω values are as follows:

$$\begin{array}{r}
J_1+J_2,\ J_1+J_2-1,\cdots,\tfrac{1}{2} \text{ or } 0^+ \\
J_1+J_2-1,\cdots,\tfrac{1}{2} \text{ or } 0^- \\
\cdots \\
\cdots \\
J_1-J_2,\cdots,\tfrac{1}{2} \text{ or } 0^+ \text{ or } 0^-
\end{array}$$

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 in the table of Ω values just given) 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 individual electrons in atoms 1 and 2), is even or odd.

B. Like atoms in states differing in J or in some other quantum number, other than M. The results are the same as under A, except that there is one odd (u) state and one even (g) state in place of each state given under A.

C. Like Atoms in States Alike in all Quantum numbers with the possible

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[8] Cf. Wigner and Witmer, *l. c.* p. 878–9, *B* and *C*.

[9] Cf. Wigner and Witmer, *l. c.* p. 879, *C.* Wigner and Witmer's "positive" and "negative" eigenfunktions are (in the case discussed in p. 879, *C*) respectively "even" and "odd" in the mode of description used here.

[10] The relations given by these rules all follow directly from what has already been said together with what is said in Refs. 8–9, with the exception of (*a*) the rule under *A* for determining the symmetry character of the odd 0 in the case where J_1 and J_2 are both integral, and (*b*) the rule under *C* according to which for 0 states derived from like atoms in the same state, only 0^+_g and 0^-_u, but not 0^+_u or 0^-_g, are possible. These last rules follow indirectly from the results (*l. c.*, pp. 877–883) of Wigner and Witmer. or directly from a consideration of atomic and molecular wave functions.

exception of M. The results are the same as with J_1+J_2 integral under A, except that approximately half the states are even, half odd according to the following schemes (here we write J in place of J_1 and J_2):

(1) J integral (numbers of electrons even in each atom)

$$
\begin{array}{r}
(2J)_g,\ (2J-1)_g,\ (2J-2)_g,\ \cdots,\ (0^+)_g \\
(2J-1)_u,\ (2J-2)_u,\ \cdots,\ (0^-)_u \\
(2J-2)_g,\ \cdots,\ (0^+)_g \\
\cdots \\
\cdots \\
(0^+)_g
\end{array}
$$

(2) J half-integral (number of electrons odd in each atom)

$$
\begin{array}{r}
(2J)_u,\ (2J-1)_u,\ \cdots,\ (0^-)_u \\
(2J-1)_g,\ \cdots,\ (0^+)_g \\
\cdots \\
\cdots \\
(0^+)_g
\end{array}
$$

Correlation of Molecular Λ and S Values with Atomic *J* Values. Discussion of I+I as an Example

Let us now consider, as an example for the correlation of molecular quantum numbers with atomic J values, the union of two identical[2a] halogen atoms, e.g. two I atoms, each in its ^2P normal state ($L_1=L_2=1, S_1=S_2=\frac{1}{2}$, $J_1=\frac{1}{2}$ or $1\frac{1}{2}$, $J_2=\frac{1}{2}$ or $1\frac{1}{2}$). First we must determine the Ω values. If both atoms have $J=1\frac{1}{2}$, we have the following possibilities: (*a*) $M_1=\pm 1\frac{1}{2}$, $M_2=\pm 1\frac{1}{2}$, $\Omega=3_u$, 0_g^+, 0_u^-; (*b*) $M_1=\pm 1\frac{1}{2}$ or $\pm\frac{1}{2}$, $M_2=\pm\frac{1}{2}$ or $\pm 1\frac{1}{2}$, $\Omega=2_u$, 2_g, 1_g, 1_u; (*c*) $M_1=\pm\frac{1}{2}$, $M_2=\pm\frac{1}{2}$, $\Omega=1_u$, 0_g^+, 0_u^-. If one atom has $J=1\frac{1}{2}$, the other $J=\frac{1}{2}$, we get: (*a*) from $J_1=1\frac{1}{2}$, $M_1=\pm 1\frac{1}{2}$, $J_2=\frac{1}{2}$, $M_2=\pm\frac{1}{2}$, and $J_2=1\frac{1}{2}$, $M_2=\pm 1\frac{1}{2}$, $J_1=\frac{1}{2}$, $M_1=\pm\frac{1}{2}$, $\Omega=2_g$, 2_u, 1_g, 1_u; (*b*) from $J_1=1\frac{1}{2}$, $M_1=\pm\frac{1}{2}$, $J_2=\frac{1}{2}$, $M_2=\pm\frac{1}{2}$, and $J_1=\frac{1}{2}$, $M_1=\pm\frac{1}{2}$, $J_2=1\frac{1}{2}$, $M_2=\pm\frac{1}{2}$, $\Omega=1_g$, 1_u, 0_g^+, 0_u^+, 0_g^-, 0_u^-. If both have $J=\frac{1}{2}$, we have $M_1=\pm\frac{1}{2}$, $M_2=\pm\frac{1}{2}$, $\Omega=1_u$, 0_g^+, 0_u^-. (The M's have been written out in detail here in order to help make clear, through an example, the relations of the Ω values and symmetry properties to the M values.) Summarizing, $(1\frac{1}{2}, 1\frac{1}{2})$ gives one each of 3_u, 2_g, 2_u, and 1_g, two each of 1_u, 0_g^+, and 0_u^-; $(1\frac{1}{2}, \frac{1}{2})$ gives one each of 2_g, 2_u, 0_g^+, 0_u^+, 0_g^-, and 0_u^-, two each of 1_g and 1_u; $(\frac{1}{2}, \frac{1}{2})$ gives one each of 1_u, 0_g^+, 0_u^-.

For sufficiently small r values, we expect case *a* or *b* coupling. The correlation between large and small r values can be made (tentatively: cf. last section, on Qualifications and Difficulties) by means of the rules: the lowest 0_g^+ state for large r (case *c*) goes over into the lowest 0_g^+ state for small r (case *a* or *b*), the next lowest 0_g^+ state into the next lowest, and so on, with corresponding rules for each other type of state (2_u, 1_u, 0_u^-, 0_u^+, 1_g, 2_g, 0_g^-). The energy of each individual state as a function of r, for stationary nuclei, may be called a $U(r)$ curve. The rules just given say that no two $U(r)$ curves which belong to the same Ω value and symmetry type can cross; it also implies that any two $U(r)$ curves differing in these respects *may* cross.[11]

In order to apply the rule just given it is necessary to consider what such case *c* designations as 0_g^+, 1_u, and so on, correspond to in cases *a* and *b*. We can best do this by going in the reverse direction. In case *a* states ($^1\Sigma^+$, $^1\Sigma^-$, $^1\Pi$, $^1\Delta$, $\cdots$, $^2\Pi_{\frac{1}{2}}$, $^2\Pi_{1\frac{1}{2}}$, $^2\Delta_{1\frac{1}{2}}$, $^2\Delta_{2\frac{1}{2}}$, $\cdots$, $^3\Pi_0$, $^3\Pi_1$, $^3\Pi_2$, $^3\Delta_1$, $^3\Delta_2$, $^3\Delta_3$, $\cdots$), Ω exists as in case *c*. Hence $^1\Sigma^+$ gives 0^+, $^1\Sigma^-$ gives 0^-, $^1\Pi$ gives 1, $^1\Delta$ gives 2 of case *c*, and so on. $^3\Pi_0$ and all other states with $\Omega=0$ split in case *c* into 0^+ and 0^-.[6] All other states go according to their Ω values. The symmetry property indicated by *g* or *u* is also maintained. Case *b* states with $\Lambda > 0$ can be correlated with case *c* states by first assuming the corresponding case *a* states. Case *b* states with $\Lambda=0$ go over as follows: $^2\Sigma^+$ or $^2\Sigma^-$ gives $\frac{1}{2}$ of case *c*; $^3\Sigma^+$ gives 0^- and 1, $^3\Sigma^-$ gives 0^+ and 1 (cf. Fig. 1); $^4\Sigma^+$ or $^4\Sigma^-$ gives $\frac{1}{2}$ and $1\frac{1}{2}$; $^5\Sigma^+$ gives 0^+, 1, and 2, $^5\Sigma^-$ gives 0^-, 1, and 2 (cf. Fig. 1); and so on.

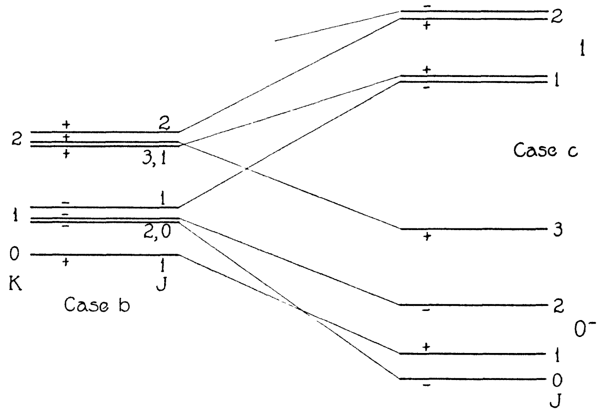

Fig. 1. Correlation of rotational levels of a typical case *b* $^3\Sigma^+$ state with those of the corresponding 0 and 1 states of case *c*. The positive (Wigner-Witmer nomenclature) or even (Kronig nomenclature) rotational levels are marked +, the negative or odd, −. If the case *c* 0 levels lay above instead of below the 1 levels, the correlations would be different, but the 0 state would still be 0^-, since the fact that the one level with $J=0$ in case *b* is a negative (−) level always brings it about that we have a 0^- state in case *c*. To obtain the relations for a case *b* $^3\Sigma^-$ state, which gives a 0^+ and a 1 state in case *c*, it is only necessary to reverse all the signs in Fig. 1. The relations for $^5\Sigma$ and other Σ states follow in a similar manner.

From the rules of Wigner and Witmer for Λ and S values, we know that the following case *a* and *b* states can be formed, using all the combinations $(J_1, J_2) = (1\frac{1}{2}, 1\frac{1}{2})$, $(1\frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2})$, from two normal halogen atoms: $^1\Sigma_g^+$,

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[11] For a general discussion of correlation problems in molecule formation, cf. W. Weizel, Zeits. f. Physik, 59, 320 (1930).

$^3\Pi_u$, $^1\Pi_u$, $^3\Sigma_g^-$, $^1\Delta_g$, $^1\Sigma_g^+$, $^3\Pi_g$, $^1\Pi_g$, $^3\Sigma_u^+$, $^3\Delta_u$, $^3\Sigma_u^+$, $^1\Sigma_u^-$. Let us assume that the order of these states, say for some single definite fairly small value of r, is as just given, i.e. with $^1\Sigma_g^+$ lowest, $^3\Pi_u$ next, and so on. Then according to the correlation rules given above, the lowest $^1\Sigma_g^+$ (small r) becomes 0_g^+ (large r) and gives $^2P_{1\frac{1}{2}} + ^2P_{1\frac{1}{2}}$ on dissociation. For brevity we shall write this $^1\Sigma_g^+$, $0_g{}^+(1\frac{1}{2}, 1\frac{1}{2})$. In a similar manner, we have $^3\Pi_{2u}$, $2_u(1\frac{1}{2}, 1\frac{1}{2})$; $^3\Pi_{1u}$, $1_u(1\frac{1}{2}, 1\frac{1}{2})$; $^3\Pi_{0u}$, $0_u^-(1\frac{1}{2}, 1\frac{1}{2})$ and $0_u^+(1\frac{1}{2}, \frac{1}{2})$; $^1\Pi_u$, $1_u(1\frac{1}{2}, 1\frac{1}{2})$; $^3\Sigma_g^-$, $1_g(1\frac{1}{2}, 1\frac{1}{2})$ and $0_g^+(1\frac{1}{2}, 1\frac{1}{2})$; $^1\Delta_g$, $2_g(1\frac{1}{2}, 1\frac{1}{2})$; $^1\Sigma_g^+$, $0_g^+(1\frac{1}{2}, \frac{1}{2})$; $^3\Pi_{2g}$, $2_g(1\frac{1}{2}, \frac{1}{2})$; $^3\Pi_{1g}$, $1_g(1\frac{1}{2}, \frac{1}{2})$; $^3\Pi_{0g}$, $0_g^-(1\frac{1}{2}, \frac{1}{2})$ and $0_g^+(\frac{1}{2}, \frac{1}{2})$; $^1\Pi_g$, $1_g(1\frac{1}{2}, \frac{1}{2})$; $^3\Sigma_u^+$, $0_u\ (1\frac{1}{2}, 1\frac{1}{2})$ and $1_u(1\frac{1}{2}, \frac{1}{2})$; $^3\Delta_{3u}$, $3_u(1\frac{1}{2}, 1\frac{1}{2})$; $^3\Delta_{2u}$, $2_u(1\frac{1}{2}, \frac{1}{2})$; $^3\Delta_{1u}$, $1_u(1\frac{1}{2}, \frac{1}{2})$; $^3\Sigma_u^+$, $0_u^-(1\frac{1}{2}, \frac{1}{2})$ and $1_u(\frac{1}{2}, \frac{1}{2})$; $^1\Sigma_u^-$, $0_u^-(\frac{1}{2}, \frac{1}{2})$.

A consideration of this example shows that if we assumed a sufficiently different order of molecular levels, the correlation with atomic J values would be more or less altered. For example, if we assumed the order of the molecular levels for small r to be $^1\Sigma_g^+$, $^3\Pi_u$, $^1\Pi_u$, $^1\Sigma_g^+$, $^3\Pi_g$, $^3\Sigma_g^-$, $^1\Delta_g$, etc., then we should have $^1\Sigma_g^+$, $^3\Pi_u$, and $^1\Pi_u$ with correlations just as before but then: $^1\Sigma_g^+$, $0_g^+(1\frac{1}{2}, 1\frac{1}{2}$ instead of $1\frac{1}{2}, \frac{1}{2}$ as before); $^3\Pi_{2g}$, $2_g(1\frac{1}{2}, 1\frac{1}{2}$ instead of $1\frac{1}{2}, \frac{1}{2})$; $^3\Pi_{1g}$, $1_g(1\frac{1}{2}, 1\frac{1}{2}$ instead of $1\frac{1}{2}, \frac{1}{2})$; $^3\Pi_{0g}$, $0_g^-(1\frac{1}{2}, \frac{1}{2}$ as before) and $0_g^+(1\frac{1}{2}, \frac{1}{2}$ instead of $\frac{1}{2}, \frac{1}{2})$; $^3\Sigma_g^-$, $1_g(1\frac{1}{2}, \frac{1}{2}$ instead of $1\frac{1}{2}, 1\frac{1}{2})$ and $0_g^+(\frac{1}{2}, \frac{1}{2}$ instead of $1\frac{1}{2}, 1\frac{1}{2})$; $^1\Delta_g$, $2_g(1\frac{1}{2}, \frac{1}{2}$ instead of $1\frac{1}{2}, 1\frac{1}{2})$. A correct determination of the correlation of molecular Λ and S values with atomic J values therefore evidently depends in an essential manner on a knowledge of the energy order of the molecular levels. This order, however, cannot in general be predicted in advance. Nevertheless it can often be approximately predicted, or in simple cases exactly. Usually we know theoretically that many if not most of the molecular levels given by Wigner and Witmer's Λ and S rules have very high energies for small r values, and have very large r_e values and very small dissociation energies. Predictions of the kind just indicated, combined with an empirical knowledge of part of the levels in question, are often sufficient for practical purposes. Furthermore, there are always one or two "unique levels" for which the J correlation can be given without any knowledge of the energy order of the molecular levels. Unique levels are levels whose Ω and symmetry type occur only once in the list of states derivable from two atoms with given L and S values. In our example, the unique levels are 3_u of case c, which necessarily becomes $^3\Delta_{3u}$ of case a, 0_u^+ which necessarily becomes part of $^3\Pi_{0u}$, and 0_g^- which necessarily becomes part of $^3\Pi_{0g}$.

Fig. 2 illustrates how the foregoing considerations can be applied to the I_2 molecule. (Analogous relations doubtless hold for Br_2, probably also for Cl_2). The normal state of I_2 is in all probability a $^1\Sigma_g^+$ state[5] derived from two iodine atoms each in the ^2P normal state. According to the rules given above it must be derived from two $^2P_{1\frac{1}{2}}$ atoms. The r_e value of the normal state of I_2 (let us call it r_N) is probably small enough so that we have approximately case $a-b$ coupling. As has been shown in a previous paper,[5] the upper state of the visible I_2 absorption bands is in all probability a 0_u^+ state. The r_e value of this state is much larger than r_N and the coupling conditions, for $r \sim r_e$, probably approximate those of case c. If, however, we follow the $U(r)$

curve of this state to smaller r values, we may probably expect nearly case a coupling when $r \sim r_N$ or less. Now this 0_u^+ state is a "unique state" and we know that it must belong to a $^3\Pi_{0u}$ state in case a. But in case a we expect to find $^3\Pi_0$ accompanied by $^3\Pi_1$ and $^3\Pi_2$. In Fig. 2 we have assumed that these three levels form an inverted $^3\Pi$ whose width is of the same order of magnitude as that of the inverted ^2P normal state of the atom. According to the rules given in preceding paragraphs, as well as empirically, the 0_u^+ component of $^3\Pi_{0u}$ is derived from $^2P_{1\frac{1}{2}}+{}^2P_{\frac{1}{2}}$, while the $^3\Pi_2$ and $^3\Pi_1$ levels and the 0_u^- component of the $^3\Pi_0$ are according to our rules derived from two $^2P_{1\frac{1}{2}}$ atoms. (A different correlation would be expected only if the states $^3\Sigma_u^+$ and $^3\Delta_u$ lie below $^3\Pi_u$ for $r = r_N$, an arrangement which is seen to be very improbable when one considers possible electron configurations for the states last mentioned.) The assumption that the $^3\Pi$ state is an inverted $^3\Pi$ with large multiplet spacing is made probable by a consideration of electron configurations (see below). In Fig. 2, $U(r)$ curves are sketched for the normal state and the $^3\Pi_u$ state of I_2, based on the facts and assumptions just discussed and on our experimental knowledge of the normal state and the 0_u^+ state. A study of possible electron configurations indicates that the numerous other molecular

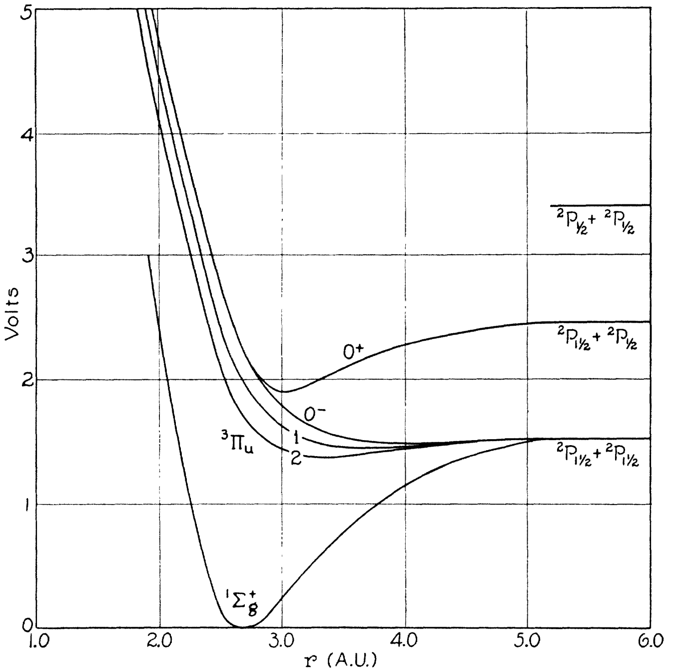

Fig. 2. $U(r)$ curves for $^1\Sigma^+_g$ and 0^+_u states of I_2 drawn to scale according to Morse's function (P. M. Morse, Phys. Rev. **34**, 57, 1929). $U(r)$ curves for the 0^-_u, 1_u, and 2_u components of $^3\Pi_u$ are sketched in a plausible way (cf. text). The numerous other $U(r)$ curves derivable from the normal (^2P) atomic levels probably all correspond to unstable molecular states, and are omitted here. The family of $U(r)$ curves derived from normal atoms is probably crossed by one or more curves of large r_e but large D derived from $F^+ + F^-$ (cf. text).

states derivable from two normal halogen atoms (see above) probably all have larger r_e values and smaller D values than the 0_u^+ state. (To make Fig. 2 complete, the $U(r)$ curves of these states should be added.) To be sure, other states of I_2 are known in addition to ${}^1\Sigma_g^+$ and 0_u^+, including one (state B of Pringsheim and Rosen) which for $r=r_e$ probably lies between ${}^1\Sigma_g^+$ and 0_u^+. Although the data on this state are uncertain[12], they indicate that it has a small or rather small ω_e, hence a large or rather large r_e, but that it has at the same time a large D. These characteristics make it likely that it is derived from two ions $(I^+ + I^-)$.

Before going farther with the theoretical discussion of the correlation of atomic and molecular states, we shall digress in order to consider some other interesting points about the halogen molecules which are brought out or suggested by Fig. 2. If Fig. 2 is correct, one would probably expect to find a strong continuous spectrum resulting from the transition ${}^3\Pi_{1u} \leftarrow {}^1\Sigma_g{}^+$, and probably also weaker continua corresponding to ${}^3\Pi(0_u^-) \leftarrow {}^1\Sigma^+{}_g$ and ${}^3\Pi_{2u} \leftarrow {}^1\Sigma_g^+$. If the arrangement of the $U(r)$ curves for the ${}^3\Pi_u$ levels is correctly shown in Fig. 2, the continua just mentioned should in part overlie the discrete bands of the transition $0_u^+ \leftarrow {}^1\Sigma_g^+$. So far as I know there is, however, no evidence of a strong continuum in this region.

ELECTRON CONFIGURATIONS AND $U(r)$ CURVES IN HALOGEN AND OTHER MOLECULES

By a consideration of electron configurations in connection with the above discussion, a qualitative explanation of the differences between the $0_u^+ \leftarrow {}^1\Sigma_g{}^+$ bands of the four halogens can be given. These differences can be expressed as follows: for the upper level, D increases in the series F_2 to I_2, for the lower level it decreases. The essential thing here is perhaps that the *contrast* between the two states decreases as the quantum numbers of the outer electrons increase.[13] In terms of electron configurations this can be understood as follows. The normal, ${}^1\Sigma_g^+$, state of F_2 has an electron configuration (composed of closed shells) which for definiteness we shall write $1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 3d\sigma^2 3d\pi^4$. (That the four least firmly bound electrons are π electrons is practically certain, although that they are $3d\pi$ is less certain.) The last ten electrons in $F_2(2p\pi^4 3d\sigma^2 3d\pi^4)$ are very probably derived from the ten $2p$ electrons of the two normal F atoms. Of these ten, the $2p\pi$

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[12] State B is observed in absorption, but only at high temperatures (P. Pringsheim and B. Rosen, Zeits. f. Physik, **50**, 1, 1928), as the initial (lower) state of a band system not otherwise known. The upper state of these bands (state D) may be identical (Pringsheim and Rosen, *l.c.*) with the upper state of the ultraviolet absorption bands of I_2, whose lower state is the normal ${}^1\Sigma_g^+$ state (state A). If this last is true, state D must be an odd state (u) and state B, like state A, an even (g) state, since g states combine spectroscopically only with u states. Pringsheim and Rosen's data indicate that state D, like B, has a large r_e and large D, and it seems likely that it also is derived from $I^+ + I^-$.

[13] One should really compare the energies of the ${}^1\Sigma_g^+$ and ${}^3\Pi_u$ states at the same value of r,, instead of at their respective r_e values. One might well, for instance, take $r=r_N$ and project upward from $U(r_e)$ of the ${}^1\Sigma_g^+$ state to the $U(r)$ curves of the ${}^3\Pi_u$ states. When this is done the contrast between F_2 and I_2 becomes very marked, as can be seen by comparing Fig 2. with a corresponding set of curves for F_2.

are unpromoted and the $3d\pi$ are promoted, $2p\pi$ electrons of the atom, while $3d\sigma^2$ represents two promoted $2p\sigma$ atomic electrons. A further stage of promotion is also to be expected for the latter, in which they become probably $4f\sigma$ molecular electrons; these might be looked for in excited states of the molecule. The ${}^3\Pi_u$ state to which our case c 0_u^+ state belongs has very probably a configuration obtained by displacing one of the most loosely-bound electrons ($3d\pi$) to the first available σ orbit, very likely $4f\sigma$; the promoted orbit $3d\pi$ is thus replaced by a more strongly promoted orbit, and D is decreased. Analogous configurations presumably exist in the other halogen molecules; it would be difficult to explain in any other way their great chemical and spectroscopic analogy. For Cl_2 we may reasonably assume $\cdots 3s\sigma^2 4p\sigma^2 3p\pi^4 4d\sigma^2 4d\pi^4$ for the normal state and $\cdots 4d\pi^3 5f\sigma$ for the ${}^3\Pi_u$ state, and for Br_2 and I_2 configurations in which the quantum numbers of the outer electrons are increased by one and by two units respectively. In each case the $p\pi$ electrons are unpromoted atomic p electrons from the outermost shell, the $d\sigma, d\pi$, and $f\sigma$ electrons are promoted electrons from the same source. Now with increase in the principal quantum number of promoted and unpromoted electrons alike, the energy differences between promoted and unpromoted electrons and between different stages of promotion, should evidently decrease steadily. In particular, the energy difference between $nd\pi$ and $(n+1)f\sigma$, and with it the difference in D values between $\cdots nd\pi^4\,{}^1\Sigma$ and $\cdots nd\pi^3(n+1)f\sigma\,{}^3\Pi$, should decrease steadilyas n in creases from 3 in F_2 to 6 in I_2.[13] This seems to explain satisfactorily the characteristics of the halogen levels discussed at the beginning of this paragraph.

Similar analogies and differences are known in other series of homologous molecules, e.g. O_2, S_2, Se_2, Te_2; Li_2, Na_2, K_2, Rb_2, Cs_2; CN, SiN, $\cdots$ BO, AlO $\cdots$. In all such cases, explanations analogous to that just given for the halogens are probably applicable.

FURTHER EXAMPLES

Fig. 3 shows the probable correlation of molecular states of HgH with J values of the Hg atom for the case of $\mathrm{Hg}(\cdots 6s6p, {}^3P)+\mathrm{H}(1s, {}^2S)$, using the rules above discussed. Similar correlations probably hold (but cf. Ref. 16) for CdH and ZnH.

As a further example we may consider the case of two alkali metal atoms with strong L, S coupling, say two Cs atoms, one in its normal (${}^2S$) state, the other in its lowest ${}^2P$ state. For case $a-b$ we get the following states: ${}^3\Pi_u$, ${}^3\Sigma_g^+$, ${}^1\Sigma_u^+$, ${}^1\Sigma_g^+$, ${}^1\Pi_u$, ${}^3\Pi_g$, ${}^3\Sigma_u^+$, ${}^1\Pi_g$. For case c we get 1_g, 1_u, 0_g^+, 0_u^+, 0_g^-, 0_u^-, from ${}^2P_{\frac{1}{2}}+{}^2S$ and 2_g, 2_u, 1_g, 1_u, 1_g, 1_u, 0_g^+, 0_u^+, 0_g^-, 0_u^- from ${}^2P_{1\frac{1}{2}}+{}^2S$. The unique states are 2_g and 2_u, which go over into ${}^3\Pi_{2g}$ and ${}^3\Pi_{2u}$. Experimentally, ${}^1\Sigma_u$ (lower) and ${}^1\Pi_u$ (higher) are known in the case of some of the alkali metal molecules. Assuming, as is probable from a consideration of possible electron configurations, that ${}^3\Pi_{0u}$ and ${}^3\Pi_{1u}$ come below ${}^1\Sigma_u$, we find (e.g. by drawing a diagram like Fig. 3) that ${}^1\Sigma_u$ and ${}^1\Pi_u$ must both be derived from ${}^2P_{1\frac{1}{2}}+{}^2S$ (${}^3\Pi_{0u}$ and ${}^3\Pi_{1u}$ are then derived from ${}^2P_{\frac{1}{2}}+{}^2S$).

QUALIFICATIONS AND DIFFICULTIES

In the preceding discussion, we have been tacitly assuming that crossings of $U(r)$ curves occur only at r values where case c coupling holds. This assumption is implied in the use of the rule given above (p. 1443) for correlating case c with case $a-b$ states; according to this rule, crossings of $U(r)$ curves occur only for states differing in Ω or in symmetry properties (g or u, 0^+ or 0^-). But such an assumption is not general enough.[11] Crossings of $U(r)$

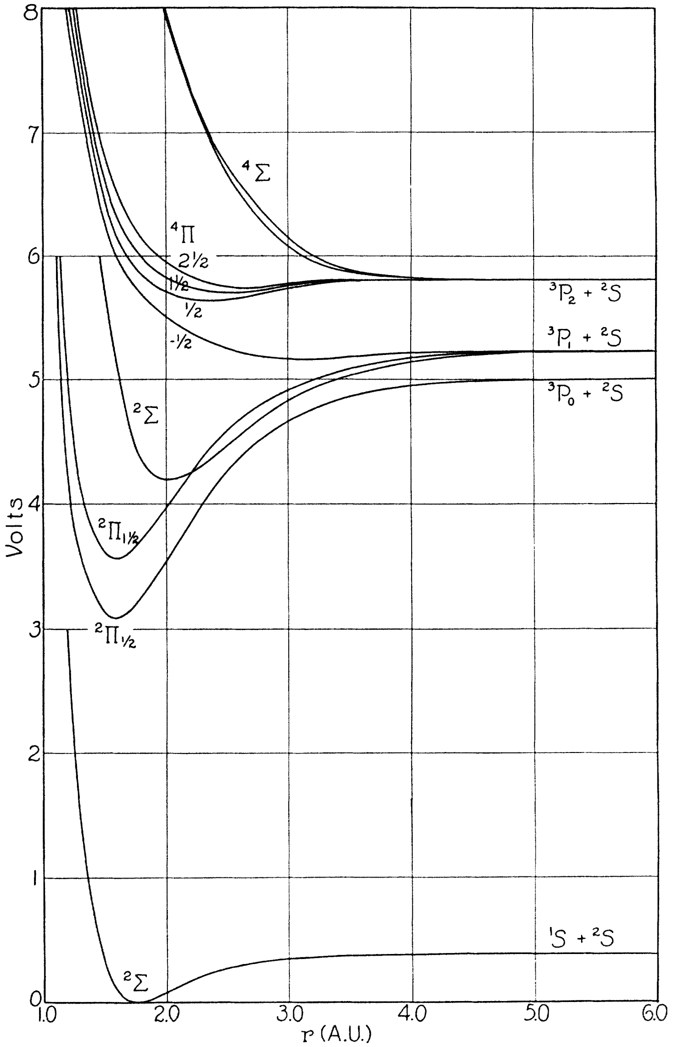

Fig. 3. Correlation of energy levels for separated atoms and molecular distances, for Hg ($\cdots$ $6s^2$, ^1S) plus H ($1s$, ^2S) and for Hg ($\cdots$ $6s\,6p$, ^3P) plus $H(1s, {}^2S)$. The $U(r)$ curves for the $^2\Sigma$ and $^2\Pi$ states are drawn in accordance with Morse's formula, using experimental data on r_e and ν_e values, and using the experimental ω_e and D values of the lower $^2\Sigma$ state. The $^4\Sigma$ and $^4\Pi$ $U(r)$ curves are sketched in a plausible way.

curves may occur or tend to occur at r values where there is case $a-b$ coupling. Here more crossings are possible than in case c, since in case $a-b$ $U(r)$ curves with the same Ω and symmetry properties may cross if they differ in Λ or S. Hence the correlation between atomic J values and molecular states (for $r=r_e$) may in many cases be somewhat different than it would be according to our previous rules. Actually, however, the number of $U(r)$ curves, other than those of "unique states," which tend to cross as r is decreased, hence the number of cases of doubtful correlation, is often small.

In the extreme case of very narrow atomic multiplets (very weak L, S couplings), case a or b molecular coupling exists practically all the way to dissociation, so that our correlation rules fail completely, except for the unique states. Fortunately, however, the correlation with atomic J values lacks importance, if not meaning, in such cases. In intermediate cases, where the atomic multiplets are of small to moderate width,[14] the correlation problem is a complicated one. Considerable departures from our rules may often be expected, but our knowledge of the forces acting between atoms at large distances appears to be as yet insufficient to permit the setting up of better rules, except probably in the special case of the union of two ions, or of an atom and an ion, where the Stark effect probably determines to a first approximation the splitting up of the terms at large r values.[15]

The application of the preceding considerations to the examples discussed above indicates that with decreasing atomic weight of the atoms concerned, the correlations given above (except for "unique states") become less certain. Thus in F+F, the correlations may, for this reason and also perhaps because of a different order of some of the molecular levels, be in part different than in I+I, in Mg+H different than in Hg+H, and in Li+Li or Na+Na different than in Cs+Cs.[16]

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[14] If the L, S couplings are weak in one atom, but strong in the other, we can determine the J correlation in the usual manner for the latter, but not for the former atom. In the special case that the latter atom is in an S state this does not matter (cf. e.g. Hg+H in Fig. 3).

[15] The Stark effect should quickly establish quantum numbers M_1 and M_2 (case c), or M_{L_1} and M_{L_2} (case a or b). The van der Waals forces (cf. R. Eisenschitz and F. London, Zeits. f. Physik, **60,** 491, 1930, and subsequent paper by F. London) may cause some splitting up, but have little if any tendency to give axis-quantization (M_1, M_2, etc.)

[16] Recent data of E. Svensson (Zeit. f. Physik **59**, 349, 1930) suggest that even in CdH the correlations are different than in Hg H, in that the upper ${}^2\Sigma$ state (cf. Fig. 3) may go to ${}^3P_0+{}^2S$ and the ${}^2\Pi_{\frac{1}{2}}$ state to ${}^3P_1-{}^2S$.