THE TWO QUANTUM EXCITED STATES OF THE HYDROGEN MOLECULE

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Abstract

Theory of two quantum states of H_2 .—There are sixteen possible wave functions for a pair of interacting H atoms which dissociate adiabatically into a normal H atom and a two quantum H atom. These wave functions give rise to eight distinct S states and four distinct P states (the latter are degenerate in the fixed nuclei problem). These states may be divided into four groups of three according to the symmetry of the wave functions with respect to (a) an interchange of electron coordinates, and (b) reflection in the plane which forms the perpendicular bisector of the internuclear axis. The principles of selection for transitions between these various types of electronic state are formulated and compared with the rules of Kronig. A first order perturbation theory computation of the potential energy curves for the P states shows that two of them have the form requisite for the formation of stable molecules. These two may be identified respectively with the C state (upper level for Werner bands) and the 2^3P state reported by Richardson. The agreement between the computed curves and the empirical data is fair.

Valence theory.—The computations show that in the case of the excited states of hydrogen the union of valence electrons to form symmetrical pairs is not the essential feature of molecule formation as London's original valence theory supposed. The rule that molecular formation is contingent on the removal of degeneracy from the wave functions of the interacting atoms seems to have a greater range of applicability than London's rule. The latter is no doubt correct for a great variety of cases, however.

INTRODUCTION

THE potential energy curves for the two sorts of interaction of normal hydrogen atoms have been calculated in first approximation according to the wave mechanics by Heitler and London,¹ Sugiura,² and Wang.³ Heitler and London, whose work was completed by Sugiura, made a conventional application of the Schrödinger perturbation method to the problem, using as unperturbed wave functions those characteristic of the normal hydrogen atom. In the case of large internuclear distances such a first order calculation as theirs is sure to give somewhat too large an energy since the polarization van der Waals forces predominant at large distances are associated with the second and higher order terms in the perturbation theory.⁴ Also in the limiting case where the nuclei are united to form a helium atom the computed energy is much too great at least for that solution of the problem which leads to molecular formation.⁵ This might have been expected since the assumed

¹ W. Heitler and F. London, Zeits. f. Physik 44, 455 (1927).

- ² Y. Sugiura, Zeits. f. Physik 45, 484 (1927).
- ³ S. C. Wang, Phys. Rev. 31, 579 (1928).
- 4 S. C. Wang, Phys. Zeits 28, 663 (1927).

⁵ Sugiura computed the energy in this limiting case and got very good agreement with the observed energy of normal helium. This agreement was due to an error, however, which was called to the attention of the authors by Prof. R. S. Mulliken. The computed energy when corrected is 10 volts too high.

unperturbed wave function in this limiting case is that for two non-repulsive electrons each in the field of a *singly* charged nucleus. This wave function is much more extended in space than the actual wave function and should give an excessively large energy value. In the region of nuclear separations near the normal separation for the molecule, however, the method gives a reasonable first approximation to the potential energy curve for the molecule as determined from the band spectrum.

Dr. Wang's calculation was carried out by the Ritz method and involves a well-chosen, but arbitrary assumption regarding the form of the wave function for the molecule. The polarization forces at large distances are partially included and the approximate wave function for the limiting case of the united atom is that used by Kellner,⁶ so that it is not surprising to find that the method gives values of the molecular constants in better agreement with experiment than those predicted by Heitler, London, and Sugiura.

The present paper reports on an extension of the method of Heitler, London, and Sugiura to the case of certain excited states of the H₂ molecule which dissociate adiabatically into a normal H atom and a two quantum excited H atom. (At the time when the computation was begun we were not familiar with Wang's method and it seems now doubtful whether his method could be carried through with equal success if applied to our problem.) It is to be expected *a priori* that the approximation will be somewhat cruder for these excited states than for the normal molecule, because of the large polarizability of the two quantum H atom and the correspondingly large value of the van der Waals forces which must be neglected. The results are of interest, however, in their qualitative prediction regarding the nature of the different excited states of the molecule and in their bearing on the valence theory of London.⁷

Among the many different electronic levels of H_2 discovered by Richardson and other spectroscopic workers there are five which have been provisionally identified as "two quantum" levels.⁸ Here we use the phrase "two quantum" to characterize molecular states which would dissociate into a normal atom and a two quantum atom if the nuclei were adiabatically separated. At least two of these levels combine freely with the normal state of the H_2 molecule as shown by the absorption measurements of Dieke and Hopfield.⁹ We here adopt the notation of Dieke and Hopfield designating these two states by the symbols *B* and *C*, of which the former refers to the upper level of the Lyman bands and the latter to the upper level for the Werner bands. The normal state is called the *A* level and the system to which the Lyman bands belong is referred to as the *B-A* system.

The recent analysis of the fine structure of the Werner and Lyman bands (corrected as regards the latter series by Kemble and Guillemin¹⁰) makes it

⁶ Kellner, Zeits. f. Physik 44, 91 (1927).

⁷ F. London, Zeits f. Physik 46, 455 (1928); 50, 24 (1928).

⁸ R. T. Birge, Proc. Nat. Acad. Sci. 14, 12 (1928).

⁹ G. H. Dieke and J. J. Hopfield, Phys. Rev. 30, 400 (1927).

¹⁰ E. C. Kemble and Victor Guillemin, Jr., Proc. Nat. Acad. Sci. 14, 782 (1928).

possible to draw approximate potential energy curves for the three electronic states A, B, C. (Cf. Fig. 1.) It also permits us to classify the A and B levels as ¹S type molecular states (without electronic angular momentum) and the C state as a ¹P state.¹¹ The computation described below was begun in the hope of accounting for the striking discrepancy between the potential energy curves for the B and C states. As the B state is very difficult to compute, the



Fig. 1. Experimental and theoretical "potential" energy curves for two quantum states of H_2 . Curves 9, 10, 11, 12 are drawn from the computed values of H_9^0 , H_{10}^{10} , H_{11}^{11} , H_{12}^{12} respectively given in Table I. Curves B and C refer to the B and C states respectively and are based on empirical formulas of the type (38). Curve D is a fragment of the potential energy curve for the 2^3P state as computed from the empirical data of Richardson.

original project has been temporarily abandoned, however, and the authors have contented themselves with an approximate determination of the theoretical curves for the C state and three other states which, as it turns out, are closely related to it.

GENERAL THEORY OF CALCUALTION



It is convenient to measure all distances in terms of the radius r_0 of the Bohr orbit for the normal state of the hydrogen atom and to measure energies in terms of the unit e^2/r_0 which is twice the ionization energy of the normal H atom. On this basis we let a_1 , b_1 , a_2 , b_2 denote the distances of electrons number 1 and number 2 from the nuclei A

¹¹ The singlet character of the C state is deduced from the fact that it combines freely with the normal ¹S state whereas singlet triplet combinations should not occur in so light a molecule.

and B respectively. Let r_{12} be the distance between the electrons and R the distance between the nuclei. Then neglecting the electron spin the wave equation for the hydrogen molecule with fixed nuclei takes the form

$$\nabla_1^2 \psi + \nabla_2^2 \psi + 2 \left[E - \left(\frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{a_1} - \frac{1}{a_2} - \frac{1}{b_1} - \frac{1}{b_2} \right) \right] \psi = 0.$$
 (1)

Following the procedure of Heitler and London we take as our initial set of approximate solutions of (1) the set obtained by multiplying the wave function for a free hydrogen atom successively by the different wave functions characteristic of a free hydrogen atom in one of the two-quantum states. Our "zero" approximations are then much better for large internuclear distances than for small. We denote the wave function for electron 1 on nucleus A in an unperturbed state with quantum numbers (n, l, m) by $\psi_{1^a}(n, l, m)$, that for electron 2 on nucleus B by $\psi_{2^b}(n, l, m)$, etc. Here m is the "magnetic" quantum number giving the orientation in space in the Bohr theory and associated with the azimuthal angle ϕ . It measures the angular momentum along the z axis which we identify with the internuclear axis. As the normal state of the H atom has zero orbital angular momentum, the mvalue for the two-quantum state becomes identical with the orbital electronic angular momentum of the molecule directed along the internuclear axis, i.e. with σ_k (Mulliken's notation). Taking all possible combinations of one electron in the normal one-quantum level and the other in one of the degenerate two-quantum states we obtain the following sixteen possible approximate solutions of (1).

$\psi_1 = \psi_1^a(1)\psi_2^b(2,0,0)$	$\psi_5 = \psi_{2^a}(1)\psi_{1^b}(2,0,0)$
$\psi_2 \!=\! \psi_1{}^a(1) \psi_2{}^b(2,1,0)$	$\psi_6 \!=\! \psi_2{}^a(1) \psi_1{}^b(2,1,0)$
$\psi_3 = \psi_1{}^a(1)\psi_2{}^b(2,1,1)$	$\psi_7 = \psi_2{}^a(1)\psi_1{}^b(2,1,1)$
$\psi_4 = \psi_1^a(1) \psi_2^b(2, 1, -1)$	$\psi_8 = \psi_2^a(1)\psi_1^b(2,1,-1)$
$\psi_9 = \psi_1^{b}(1)\psi_2^{a}(2,0,0)$	$\psi_{13} = \psi_2{}^b(1)\psi_1{}^a(2,0,0)$
$\psi_{10} = \psi_1{}^b(1)\psi_2{}^a(2,1,0)$	$\psi_{14} = \psi_2{}^b(1)\psi_1{}^a(2,1,0)$
$\psi_{11} = \psi_1{}^b(1)\psi_2{}^a(2,1,1)$	$\psi_{15} = \psi_2{}^b(1)\psi_1{}^a(2,1,1)$
$\psi_{12} = \psi_1^{b}(1)\psi_2^{a}(2, 1, -1)$	$\psi_{16} = \psi_2{}^b(1)\psi_1{}^a(2,1,-1)$

Here

$$\psi_1{}^a(1) = \frac{1}{(\pi)^{1/2}} e^{-a_1},$$

$$\psi_1{}^a(2,0,0) = \frac{1}{(8\pi)^{1/2}} \left(1 - \frac{a_1}{2}\right) e^{-a_1/2},$$

$$\psi_1{}^a(2,1,0) = \frac{1}{(32\pi)^{1/2}} a_1 \cos \theta_1{}^a e^{-a_1/2},$$

$$\psi_1{}^a(2,1,1) = \frac{1}{(64\pi)^{1/2}} a_1 \sin \theta_1{}^a e^{i\phi_1 - a_1/2},$$

$$\psi_1{}^a(2,1,-1) = \frac{1}{(64\pi)^{1/2}} a_1 \sin \theta_1{}^a e^{-i\phi_1 - a_1/2},$$

etc. ϕ_1 and ϕ_2 denote the azimuthal angles of the electrons 1 and 2 respectively about the z axis which coincides with the interculear axis and has the direction \overrightarrow{AB} . The angles θ_1^{a} , θ_2^{a} , θ_1^{b} , θ_2^{b} are defined by Fig. 1.

It is convenient to begin a perturbation calculation with approximate solutions of the differential equation which are mutually orthogonal. This condition of orthogonality is not satisfied by the functions $\psi_1, \psi_2, \cdots, \psi_{16}$, but we may readily form from them by linear combination sixteen other approximate solutions which have the same approximate energy value and which are mutually orthogonal. Thus we may take the four functions $\psi_1, \psi_5, \psi_9, \psi_{13}$ and build up from them four others whose symmetry properties insure orthogonality. For example, the combinations

$$u_{S} = \psi_{1} + \psi_{5} = \psi_{1}^{a}(1)\psi_{2}^{b}(2,0,0) + \psi_{2}^{a}(1)\psi_{1}^{b}(2,0,0)$$
$$u_{A} = \psi_{1} - \psi_{5} = \psi_{1}^{a}(1)\psi_{2}^{b}(2,0,0) - \psi_{2}^{a}(1)\psi_{1}^{b}(2,0,0)$$

are respectively symmetric and antisymmetric with respect to an interchange of electronic coordinates, i.e., with respect to the transformation

$$\begin{array}{c} x_{1}', \ y_{1}', \ z_{1}' = x_{2}, \ y_{2}, \ z_{2} \\ x_{2}', \ y_{2}', \ z_{2}' = x_{1}, \ y_{1}, \ z_{1} \end{array} \right\}$$
 (E)

Similarly the combinations

$$\tilde{u}_{S} = \psi_{1} + \psi_{9} = \psi_{1}^{a}(1)\psi_{2}^{b}(2,0,0) + \psi_{1}^{b}(1)\psi_{2}^{a}(2,0,0)$$

$$\tilde{u}_{A} = \psi_{1} - \psi_{9} = \psi_{1}^{a}(1)\psi_{2}^{b}(2,0,0) - \psi_{1}^{b}(1)\psi_{2}^{a}(2,0,0)$$

are respectively symmetric and antisymmetric with respect to the transformation

$$\begin{array}{c} x_{1}', y_{1}', z_{1}' = x_{1}, y_{1}, -z_{1} \\ x_{2}', y_{2}', z_{2}' = x_{2}, y_{2}, -z_{2} \end{array} \right\}$$
 (N)

if the origin is taken at the midpoint of the internuclear axis and the z axis is chosen as stated above. The transformation (N) may be described either as a reflection in the median plane or as an interchange of nuclei with the understanding that the interchange of nuclei does not mean quite the same thing as it does in the free nuclei problem. We introduce the symbols S^{E} , A^{E} to indicate wave functions symmetric and antisymmetric with respect to transformation (E) respectively. S^{N} , A^{N} will be used to indicate the corresponding symmetries with respect to (n). Then clearly the following four approximate solutions of (1) have the symmetries indicated and are mutually orthogonal.¹²

$$\begin{array}{ll} u_1 = g_1(\psi_1 + \psi_5 + \psi_9 + \psi_{13}) & (S^E, S^N) \\ u_2 = g_2(\psi_1 + \psi_5 - \psi_9 - \psi_{13}) & (S^E, A^N) \\ u_3 = g_3(\psi_1 - \psi_5 + \psi_9 - \psi_{13}) & (A^E, S^N) \\ u_4 = g_4(\psi_1 - \psi_5 - \psi_9 + \psi_{13}) & (A^E, A^N) \end{array}$$

Here g_1 , g_2 , g_3 , g_4 are normalizing factors depending only on the parameter R. Similarly we may build up a set of four mutually orthogonal solutions from each of the other three types of two quantum hydrogen atom eigenfunctions. The three additional sets are

$$\begin{split} u_5 &= g_5(\psi_2 + \psi_6 + \psi_{10} + \psi_{14}) & (S^E, A^N) \\ u_6 &= g_6(\psi_2 + \psi_6 - \psi_{10} - \psi_{14}) & (S^E, S^N) \\ u_7 &= g_7(\psi_2 - \psi_6 + \psi_{10} - \psi_{14}) & (A^E, A^N) \\ u_8 &= g_8(\psi_2 - \psi_6 - \psi_{10} + \psi_{14}) & (A^E, S^N) \\ U_9 &= g_9(\psi_3 + \psi_7 + \psi_{11} + \psi_{15}) & (S^E, S^N) \\ U_{10} &= g_{10}(\psi_3 + \psi_7 - \psi_{11} - \psi_{15}) & (S^E, A^N) \\ U_{11} &= g_{11}(\psi_3 - \psi_7 + \psi_{11} - \psi_{15}) & (A^E, S^N) \\ U_{12} &= g_{12}(\psi_3 - \psi_7 - \psi_{11} + \psi_{15}) & (A^E, A^N) \\ U_{13} &= g_{13}(\psi_4 + \psi_8 + \psi_{12} + \psi_{16}) & (S^E, A^N) \\ U_{14} &= g_{14}(\psi_4 + \psi_8 - \psi_{12} - \psi_{16}) & (S^E, A^N) \\ U_{15} &= g_{15}(\psi_4 - \psi_8 + \psi_{12} - \psi_{16}) & (A^E, A^N) \\ U_{16} &= g_{16}(\psi_4 - \psi_8 - \psi_{12} + \psi_{16}) & (A^E, A^N) . \end{split}$$

The symmetry properties of these sixteen functions are shared by the exact solutions of the differential Eq. $(1)^{13}$ and hence these functions are particularly well fitted for use as first approximations. All functions of any one of the four symmetry types are orthogonal to all functions of each of the other types and all functions involving any given value of σ_k are orthogonal to all involving any other value of σ_k . Thus each of the functions, while the only pairs of functions not mutually orthogonal are $(u_1, u_6), (u_2, u_5), (u_3, u_8), (u_4, u_7)$. From each of these pairs one may now form new linear combinations such as

¹³ For example, if $\psi(x_i, y_i, z_i)$ is a solution of (1) substitution shows that

 $\psi^{(1)}(x_i, y_i, z_i) \equiv \psi(x_i, y_i, -z_i)$

¹² The product of any two functions, one of which is symmetric and the other antisymmetric with respect to a coordinate interchange such as (E) or (A), is antisymmetric with respect to the interchange and must therefore integrate to zero if the integral is extended over the region of definition.

is also a solution and has the same eigenvert. Hence either $\psi^{(1)} = \pm \psi$ or $\psi^{(1)}$ and ψ form a degenerate pair of solutions. In the former case ψ is either of the S^N or A^N type and in the latter case, which will occur only as a result of accidental degeneracy, we can form functions of the S^N and A^N type by taking linear combinations of $\psi^{(1)}$ and ψ .

$$U_1 = c_1{}^1u_1 + c_6{}^1u_6$$
$$U_6 = c_1{}^6u_1 + c_6{}^6u_6$$

which are mutual orthogonal and which have unimpaired symmetry. Thus one obtains the required set of sixteen completely orthogonal functions from which to build up the zero approximations to the solution of (1).

We now assume that the wave functions for the two quantum molecular states are of the form

$$\psi = \sum_{\tau=1}^{16} c_{\tau} U_{\tau} + \imath$$

where v is a small correction term orthogonal to U_1, \dots, U_{16} and approaching zero as the internuclear distance R is indefinitely increased. Writing the differential equation in the symbolic form

$$H\psi = E\psi \tag{4}$$

where

$$H = -\frac{1}{2}(\nabla_1{}^2 + \nabla_2{}^2) + \frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{a_1} - \frac{1}{a_2} - \frac{1}{b_1} - \frac{1}{b_2}$$
(5)

and substituting from (3), we obtain

$$\sum_{\tau=1}^{16} c_{\tau} H U_{\tau} = \sum_{\tau=1}^{16} c_{\tau} E U_{\tau} + (E - H) v.$$
(6)

To determine the c's we multiply this equation by U_k^* , the complex conjugate of U_k , and integrate over the entire six dimensional space in which the wave functions are spread out. Let dV denote the element of volume and let $H_{\tau}^{\ k}$ be the integral or matrix element $\int U_k^* H U_{\tau} dV$. The resulting equations then take the form

$$\sum_{\tau=1}^{16} c_{\tau} H_{\tau}{}^{k} = c_{k} E - \int U_{k}^{*} H v dV \qquad k = 1, 2, \cdots, 16.$$
(7)

As v is by hypothesis small, we may neglect the last term in getting a first approximation to a solution of the Eqs. (7) and thus obtain sixteen simultaneous homogeneous equations for the c's. These equations may also be obtained by a procedure which follows closely the standard perturbation method of the Schrödinger theory. The desired approximate energy values are the roots of the secular equation

Fortunately most of the elements in this determinant vanish. For example, all matrix elements $H_{\tau}{}^k$ are zero for which U_k and U_{τ} have different symmetries with respect to either of the transformations (E) or (N), since HU_{τ} has the same symmetry as U_{τ} itself. Thus our wave functions are divided into four equal groups with no matrix components corresponding to combinations between different groups.

Consider next one of these groups such as U_1 , U_5 , U_9 , U_{13} , all members of which have the same symmetry. Matrix elements involving combinations of different members of the group are zero also when the functions U_k and U_τ have different values of σ_k (i.e., different values of *m* for the primary two quantum wave function). It is sufficient to give the proof for the special element

$$H_{\mathfrak{g}^{13}} = \int U_{13}^* H U_{\mathfrak{g}} dV$$

 U_9 is a linear combination of the functions $\psi_3, \psi_7, \psi_{11}, \psi_{15}$. Remembering that $\psi_1^{a}(1), \psi_1^{b}(1), \psi_1^{a}(2), \cdots$, etc. are solutions of the wave equation for a single H atom we may use the relations

$$-\nabla_{1}^{2}\psi_{1}^{a}(1) = 2E_{1} + 2/a_{1}$$

$$-\nabla_{1}^{2}\psi_{1}^{b}(1) = 2E_{1} + 2/b_{1}$$

$$-\nabla_{1}^{2}\psi_{1}^{a}(2) = 2E_{2} + 2/a_{1}$$
(9)

and so on, where E_1 and E_2 are the energies of the normal state and of the first excited state of the hydrogen atom respectively. The sum of E_1 and E_2 is the "unperturbed" energy of the molecule and will be designated by E_0 . Applying the operator H to U_9 we obtain

$$HU_{9} = Hg_{9}[\psi_{1}^{a}(1)\psi_{2}^{b}(2,1,1) + \psi_{2}^{a}(1)\psi_{1}^{b}(2,1,1) + \psi_{1}^{b}(1)\psi_{2}^{a}(2,1,1) + \psi_{2}^{b}(1)\psi_{1}^{a}(2,1,1)]$$

$$= E_{0}U_{9} + \left(\frac{1}{R} + \frac{1}{r_{12}}\right)U_{9} - g_{9}\left(\frac{1}{b_{1}} + \frac{1}{a_{2}}\right)[\psi_{1}^{a}(1)\psi_{2}^{b}(2,1,1) + \psi_{1}^{a}(2,1,1)\psi_{2}^{b}(1)] - g_{9}\left(\frac{1}{b_{2}} + \frac{1}{a_{1}}\right)[\psi_{2}^{a}(1)\psi_{1}^{b}(2,1,1) + \psi_{2}^{a}(2,1,1)\psi_{1}^{b}(1)].$$

$$(10a)$$

Clearly each term of HU_9 like each term in U_9 itself contains either $e^{i\phi_1}$ or $e^{i\phi_2}$ as a factor. Similarly each term in U_{13} contains $e^{-i\phi_1}$ or $e^{-i\phi_2}$. The angles ϕ_1 and ϕ_2 enter into the integrand $U_{13}^*HU_9$ only through these factors and through r_{12} . Changing the independent variables from ϕ_1 and ϕ_2 to

$$\varphi = \varphi_1$$
$$\chi = \varphi_2 - \varphi_1$$

we observe that r_{12} depends only on χ while each term of $U_{13}^*HU_9$ contains one of the three factors

$$e^{-2i\phi_1} = e^{-2i\phi}$$
$$e^{-i(\phi_1 + \phi_2)} = e^{-ix} \times e^{-2i\phi}$$
$$e^{-2i\phi_2} = e^{-2ix} \times e^{-2i\phi}$$

Hence in evaluating H_{θ}^{13} we can factor out the integral $\int_{0}^{2\pi} e^{-2i\phi} d\phi$ which vanishes. The argument is easily extended to show that all matrix elements H_{τ}^{k} vanish if U_{k} and U_{τ} have different values of σ_{k} .

In consequence of the fact that most of the non-diagonal elements of the determinant (8) are zero, the determinant may be resolved into the product of the following factors:

$$\begin{array}{c} (H_{9}^{9}-E) ; \ (H_{10}^{10}-E) ; \ (H_{11}^{11}-E) ; \ (H_{12}^{12}-E) ; \ (H_{13}^{13}-E) ; \\ (H_{14}^{14}-E) ; \ (H_{15}^{15}-E) ; \ (H_{16}^{16}-E) ; \ \left| \begin{array}{c} H_{1}^{1}-E & H_{6}^{1} \\ H_{1}^{6} & H_{6}^{6}-E \end{array} \right| ; \\ \begin{array}{c} H_{2}^{2}-E & H_{5}^{2} \\ H_{2}^{5} & H_{5}^{5}-E \end{array} \right| ; \ \left| \begin{array}{c} H_{3}^{3}-E & H_{3}^{3} \\ H_{3}^{8} & H_{8}^{8}-E \end{array} \right| ; \ \left| \begin{array}{c} H_{4}^{4}-E & K_{7}^{4} \\ H_{4}^{7} & H_{7}^{7}-E \end{array} \right| . \end{array}$$
(11)

Each energy level is obtained by setting one factor equal to zero.

As the functions U_9 , U_{10} , U_{11} , U_{12} differ from the corresponding functions U_{13} , U_{14} , U_{15} , U_{16} respectively only in the sign of the exponent in the factor $e^{\pm i\phi}$, it is clear that

$$H_{9}^{9} = H_{13}^{13}; \quad H_{10}^{10} = H_{14}^{14}; \quad H_{11}^{11} = H_{15}^{15}; \quad H_{12}^{12} = H_{16}^{16}$$

Hence the first eight factors of the set (11) vanish in pairs. The corresponding energy levels are consequently degenerate and the eigenfunctions are indeterminate. Suppose, for example, that

$$H_{9}^{9} - E = H_{13}^{13} - E = 0.$$

Then in (7) all the coefficients c_{τ} must vanish except c_9 and c_{13} which are undetermined except for the normalization condition on

$$\psi = c_9 U_9 + c_{13} U_{13}.$$

These degenerate states are those of the *P* type with $\sigma_k = \pm 1$. The degeneracy is removed when the rotation of the nuclei is taken into account and its removal gives rise to the "sigma-type doubling."¹⁴

By setting any one of the last four factors in the group (11) equal to zero we locate two energy levels of the S type (with $\sigma_k = 0$). Thus there are in all twelve distinguishable energy levels of which four are degenerate and of the P type while the other eight are of the S type. There are two S states and one P state for each of the four types of symmetry. (Of course many of

¹⁴ E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928); R. de L. Kronig, Zeits f. Physik **50**, 347 (1928).

these "states" represent possible collision types for interacting hydrogen atoms which involve an almost purely repulsive force and hence could not yield stable molecules.)

It is well known that in light atoms where the interaction of spin and orbital motion is very slight transitions between singlet and triplet states occur with great infrequency. As the two electron symmetries S^E and A^E correspond to singlet and triplet states respectively (Pauli principle) and as we are dealing with the lightest of molecules, it is clear that jumps between states of different electron symmetry should be negligible.

The principles of selection for symmetrical diatomic molecules have been discussed by Hund ¹⁵ and Kronig¹⁶ using as a basis for argument the complete eigenfunctions for the molecule with free rotating nuclei. Rules governing the transitions between electronic states can be derived even more simply and directly on the basis of the fixed nuclei problem. As the electronic eigenfunction are but little distorted by slow nuclear rotation we may infer that the principles of selection so derived will hold at least approximately when applied to actual molecules.

If we treat the nuclei as fixed, place the origin at a point midway between them and use the internuclear axis as the z axis for a set of spherical coordinates, the expressions for the components of the classical electric moment become

$$P_{x} = \sum_{i} er_{i} \sin \theta_{i} \cos \phi_{i},$$
$$P_{y} = \sum_{i} er_{i} \sin \theta_{i} \sin \phi_{i},$$
$$P_{\bar{z}} = \sum_{i} er_{i} \cos \theta_{i}.$$

The formation of matrices from the three functions P_x , P_y , P_z leads to the following selection rules. (a) When $\Delta \sigma_k$ is zero the matrix elements of P_x and P_y always vanish, while those of P_z are also zero unless the two electronic wave functions concerned have opposite symmetry with respect to the median plane. (b) When $\Delta \sigma_k$ is ± 1 the matrix elements of P_z always vanish, while those of P_x and P_y are zero unless the electronic wave functions have the same symmetry with respect to the median plane. Thus the permitted transitions reduce to the following:

$$A^{N} \longleftrightarrow S^{N} \qquad \text{if} \qquad \Delta \sigma_{k} = 0 ; \qquad (12)$$

$$\left.\begin{array}{c}
S^{N} \longleftrightarrow S\\
A^{N} \longleftrightarrow A^{N}
\end{array}\right\} \quad \text{if} \quad \Delta \sigma_{k} = \pm 1.$$
(13)

¹⁵ F. Hund, Zeits f. Physik **42**, 93 (1927); R. de L. Kronig, Zeits f. Physik **46**, 814 (1928).

¹⁶ Kronig proves only approximate symmetry and approximate anti-symmetry with respect to β , but an examination of the differential equation shows that these symmetry properties are rigorous. This point was brought to the attention of the writers by Professor Kramers.

The method of deriving the above principles of selection may be made rigorous with the aid of the α and β transformations of Kronig. Successive rotational levels for any electronic state of a free molecule have alternating symmetry with respect to the α transformation and with respect to the β transformation. The transformation (N) above is equivalent to the resultant of the α and β transformations. Hence if any rotational state is α -symmetric and also β -symmetric, the associated unperturbed electronic eigenfunction U_{τ} must have the symmetry S^{N} . Conversely if U_{τ} has the symmetry S^{N} , each rotational sublevel will have the same symmetry with respect to the α and β transformations, while if U_{τ} has the symmetry A^{N} , each rotational sublevel will have opposite symmetry with respect to α and β transformations. Consider next a transition for which $\Delta \sigma_k$ vanishes. Then if the jump is to be permitted the upper and lower rotational levels must have the same symmetry with respect to α and opposite symmetry with respect to β . In order to satisfy these conditions simultaneously, it is necessary that in one case the symmetry of the sublevel shall be the same with respect to α as with respect to β , while in the other case the symmetry with respect to α must be opposite to that with respect to β . This leads at once to the principle of selection (12). The rule (13) can be derived in the same way. As every eigenfunction is rigorously symmetrical or antisymmetrical with respect to α and to β ,¹⁶ it is clear that our rules are not affected by the distortion of U_{τ} due to nuclear rotation. Kronig does not call specific attention to the fact that in the case of symmetric molecules the existence of both α and β types of symmetry leads to these principles of selection for electronic levels.

As the normal state of the hydrogen molecule has the symmetry (S^E, S^N) it follows that of the twelve possible two quantum molecular states there is just one of the P type which should combine with the normal state to produce a band system. This state must have the symmetry (S^E, S^N) also and its energy is therefore approximately H_9^9 . This must be the "C" state which forms the upper energy level for the Werner bands.

On the other hand there are two possible molecular levels of the S type having the appropriate symmetry (S^E, A^N) for the production of jumps to and from the normal state. Their energies are the roots of the equation

$$\begin{vmatrix} H_2^2 - E & H_5^2 \\ H_2^5 & H_5^5 - E \end{vmatrix} = 0.$$
(14)

One of these must be the B state which forms the upper level of the A-B system of Dieke and Hopfield to which the Lyman bands belong.

COMPUTATION OF APPROXIMATE ENERGY OF P TYPE STATES

It remains to evaluate the matrix elements H_k and thus to determine the theoretical potential energy curves for the various two quantum electronic states. This we have done for the P type states only. The labor involved in the calculation was considerable and would have been even greater for the S states.

With the aid of Eq. (10c) the following expression for H_{9}^{9} may be derived :

$$H_{9}^{9} = \int U_{9}^{*} H U_{9} dV = E_{0} + R^{-1} + \int U_{9}^{*} U_{9} r_{12}^{-1} dV - g_{9}^{2} \int \left\{ \left[\frac{1}{a_{1}} + \frac{1}{b_{2}} \right] \left[\psi_{2}^{a}(1)\psi_{1}^{b}(2) + \psi_{2}^{a}(2)\psi_{1}^{b}(1) \right] + \left[\frac{1}{a_{2}} + \frac{1}{b_{1}} \right] \left[\psi_{1}^{a}(1)\psi_{2}^{b}(2) + \psi_{1}^{a}(2)\psi_{2}^{b}(1) \right] \right\} \frac{U_{9}^{*}}{g_{9}} dV. \quad (15)$$

Denote the first of the two integrals in the right-hand member of (15) by K and the second by J. The latter may be split into convenient terms if we write U_9 in terms of the primary ψ functions and multiply out. Terms involving the product of two ψ 's with the same subscript but different quantum numbers integrate to zero. For example,

$$\int \left(\frac{1}{a_1} + \frac{1}{b_2}\right) \psi_2^a(1) \psi_1^b(2) \psi_1^{*a}(1) \psi_2^{*b}(2) dV$$

= $\frac{1}{8\pi^2} \int \left(\frac{1}{a_1} + \frac{1}{b_2}\right) \sin \theta_1^b \sin \theta_2^{bb_1} b_2 e^{-[a_1 + a_2 + (b_1 + b_2)/2]} e^{i(\phi_1 - \phi_2)} dV.$ (16)

Here

$dV = a_1^2 \sin \theta_1 da_1 d\theta_1 d\phi_1 a_2^2 \sin \theta_2 da_2 d\theta_2 d\phi_2$

Clearly we can factor out the integral

$$\int_{0}^{2\pi} \int_{0}^{2\pi} e^{i(\phi_1 - \phi_2)} d\phi_1 d\phi_2$$

which vanishes.

A number of the other terms are easily seen to be equivalent and the integral J can be reduced to the form

$$J = 4g_{9^2}(J_1 + J_2) \tag{17}$$

where

$$J_1 = \int \left(\frac{1}{a_1} + \frac{1}{b_2}\right) \psi_1^{b}(1) \psi_1^{*b}(1) \psi_2^{a}(2) \psi_2^{*a}(2) dV$$
(17*a*)

$$J_{2} = \int \left(\frac{1}{a_{2}} + \frac{1}{b_{1}}\right) \psi_{1}{}^{b}(1) \psi_{1}{}^{a}(1) \psi_{2}{}^{a}(2) \psi_{2}{}^{b}(2) dV.$$
(17b)

Similarly K is reducible to the form

$$K = 4g_{\theta^2}(K_1 + K_2 + K_3 + K_4) \tag{18}$$

where

$$K_{1} = \int \frac{\psi_{1}^{b}(1)\psi_{1}^{*}b(1)\psi_{2}^{a}(2)\psi_{2}^{a}(2)}{r_{12}} dV ; \qquad (19a)$$

$$K_{2} = \int \frac{\psi_{1}^{b}(1)\psi_{1}^{*}(1)\psi_{2}^{*}(2)\psi_{2}^{*}b(2)}{r_{12}} dV ; \qquad (19b)$$

$$K_{3} = \int \frac{\psi_{1}^{a}(1) \psi_{1}^{a}(2) \psi_{2}^{b}(2) \psi_{2}^{b}(1)}{r_{12}} dV ; \qquad (19c)$$

$$K_4 = \int \frac{\psi_1^{b}(1) \psi_1^{a}(2) \psi_2^{a}(2) \psi_2^{b}(1)}{r_{12}} dV ; \qquad (19d)$$

Putting these results together and remembering that E_0 is the sum of the energies of a normal H atom and an H atom in a two-quantum state expressed in terms of the unit e^2/a_0 , we have

$$H_{9}^{9} = -5/8 + R^{-1} - 4g_{9}^{2} [J_{1} + J_{2} - (K_{1} + K_{2} + K_{3} + K_{4})]$$
(20)

In the same way we deduce

$$H_{10}^{10} = -5/8 + R^{-1} - 4g_{10}^{2} [J_1 - J_2 - (K_1 - K_2 - K_3 + K_4)]; \qquad (21)$$

$$H_{11}^{11} = -5/8 + R^{-1} - 4g_{11}^2 [J_1 + J_2 - (K_1 + K_2 - K_3 - K_4)]; \qquad (22)$$

$$H_{12}^{12} = -5/8 + R^{-1} - 4g_{12}^{2} [J_1 - J_2 - (K_1 - K_2 + K_3 - K_4)].$$
(23)

Thus the integrals to be evaluated for H_{10}^{10} , H_{11}^{11} , and H_{12}^{12} are the same as those needed for H_{9}^{9} .

The required integrals may be computed most easily by the use of elliptic coordinates. Let us begin with the determination of the normalizing factor g_9 . It is fixed by the condition

$$\int U_{9}^{*}U_{9}dV = g_{9}^{2} \int (\psi_{3}\ddot{\psi}_{3} + \psi_{7}\ddot{\psi}_{7} + \psi_{11}\dot{\psi}_{11} + \psi_{15}\dot{\psi}_{15} + \psi_{3}\dot{\psi}_{7} + \psi_{7}\dot{\psi}_{3} + \psi_{3}\dot{\psi}_{11} + \psi_{11}\dot{\psi}_{3} + \psi_{3}\dot{\psi}_{15} + \psi_{15}\dot{\psi}_{3} + \psi_{7}\dot{\psi}_{11} + \psi_{11}\dot{\psi}_{7} + \psi_{15}\dot{\psi}_{7} + \psi_{7}\dot{\psi}_{15} + \psi_{11}\dot{\psi}_{15} + \psi_{15}\dot{\psi}_{11})dV.$$

As ψ_3 , ψ_7 , ψ_{11} , ψ_{15} are separately normalized we may reduce the above to the form

$$2g_{9^{2}}\left[2+\int (\psi_{3}\psi_{11}+\psi_{7}\psi_{15})dV\right] = 1$$

$$g_{9^{2}} = \frac{1}{4(1+F)}$$
(24)

or

where

$$F = \int \psi_3 \dot{\psi}_{11} dV = \int \psi_7 \dot{\psi}_{15} dV = \int \psi_1^a (1) \dot{\psi}_1^b (1) dV_1 \int \psi_2^a (2) \dot{\psi}_2^b (2) dV_2$$

Introducing the elliptic coordinates

$$\lambda = \frac{a+b}{R} ; \quad \mu = \frac{a-b}{R} ; \quad dV = \frac{R^3(\lambda^2 - \mu^2)}{8} d\lambda d\mu d\phi ,$$

we obtain

$$\int \psi_1{}^a(1) \overset{*}{\psi}{}_1{}^b(1) dV_1 = \frac{R^3}{8\pi} \int_{+1}^{\infty} d\lambda_1 \int_{-1}^{+1} d\mu_1 \int_{0}^{2\pi} d\phi_1(\lambda_1{}^2 - \mu_1{}^2) e^{-\lambda_1 R}$$
$$= e^{-R} (1 + R + R^2/3).$$

Similarly

$$\int \psi_2^{a}(2) \psi_2^{b}(2) dV_2 = \frac{R^5}{16 \times 64} \int_1^{\infty} e^{-R\lambda_2/2} (\lambda_2^2 - 1) d\lambda_2 \int_{-1}^{+1} (\lambda_2^2 - \mu_2^2) (1 - \mu_2^2) d\mu_2$$
$$= e^{-R/2} \left(1 + \frac{R}{2} + \frac{R^2}{10} + \frac{R^3}{120} \right).$$

Finally

$$F = e^{-3R/2} (1 + R + R^2/3) (1 + R/2 + R^2/10 + R^3/120).$$
(25)

The same procedure applied to the other normalizing factor yields

$$g_{11}^2 = g_{9}^2$$
; $g_{12}^2 = g_{10}^2 = \frac{1}{4(1-F)}$ (26)

Inspection of (17a) shows that

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$$J_1 = \int \frac{\psi_1^{b}(1) \overset{*}{\psi}_1^{b}(1)}{a_1} \, dV_1 + \int \frac{\psi_2^{a}(2) \overset{*}{\psi}_2^{a}(2)}{b_2} \, dV_2.$$

Both of these integrals are easily evaluated. We find

$$\begin{split} \int & \frac{\psi_1{}^{b}(1)\bar{\psi}_1{}^{b}(1)}{a_1} dV_1 = \frac{R^2}{2} \int_1^{\infty} d\lambda \int_{-1}^{+1} (\lambda - \mu) e^{-R(\lambda - \mu)} d\mu = \frac{1}{R} - e^{-2R} \left(1 + \frac{1}{R} \right) \\ & \int \frac{\psi_2{}^{a}(2)\bar{\psi}_2{}^{a}(2)}{b_2} dV_2 = \frac{R^4}{8 \times 64} \int_1^{\infty} d\lambda e^{-R\lambda/2} (\lambda^2 - 1) \int_{-1}^{+1} e^{-R\mu/2} (\lambda + \mu) (1 - \mu^2) d\mu \\ & = \frac{1}{R} - \frac{6}{R^3} + \frac{e^{-R}}{4} \left(1 + \frac{8}{R} + \frac{24}{R^2} + \frac{24}{R^3} \right). \end{split}$$

Thus

$$J_1 = \frac{2}{R} - \frac{6}{R^3} + \frac{e^{-R}}{4} \left(1 + \frac{8}{R} + \frac{24}{R^2} + \frac{24}{R^3} \right) - e^{-2R} \left(1 + \frac{1}{R} \right).$$
(27)

The evaluation of J_2 proceeds along lines similar to that of J_1 and presents no features of interest. The result is

$$J_2 = e^{-3R/2} \left[(1+R) \left(1 + \frac{R}{2} + \frac{R^2}{10} + \frac{R^3}{120} \right) + \left(1 + R + \frac{R^2}{3} \right) \left(1 + \frac{R}{2} + \frac{R^2}{12} \right) \right].$$
(28)

 K_1 gives the mutual potential energy of two static charge distributions of density $\psi_1{}^b(1)\dot{\psi}_1{}^b(1)$ and $\psi_2{}^a(2)\dot{\psi}{}^a(2)$ respectively. The first distribution is

spherical and its potential at a point distant b_2 from the nucleus b is easily seen to be

$$4\int_{0}^{b_{2}}\frac{b^{2}e^{-2b}}{b_{2}}db+4\int_{b_{2}}^{\infty}be^{-2b}db=\frac{1}{b_{2}}-e^{-2b_{2}}\left(1+\frac{1}{b_{2}}\right).$$

Multiplying this potential by the density of the second charge distribution and integrating we obtain

$$K_1 = \frac{1}{64\pi} \int \frac{a_2^2 \sin^2 \theta_2^a e^{-a_2}}{b_2} \bigg[1 - e^{-2b_2} (1+b_2) \bigg] dV_2.$$

Transforming to elliptic coordinates and using the relation

$$\sin^2\theta^a = \frac{(\lambda^2 - 1)(1 - \mu^2)}{(\lambda + \mu)^2}$$

one obtains

$$K_{1} = \frac{1}{R} - \frac{6}{R^{3}} - \frac{4}{27} e^{-R} \left(1 + \frac{16}{R} + \frac{112}{3R^{2}} + \frac{112}{3R^{3}} \right) + \frac{1}{27} e^{-2R} \left(1 + \frac{9}{R} + \frac{76}{3R^{2}} + \frac{38}{3R^{3}} \right).$$
(29)

 K_3 may be dealt with in a manner similar to that used in connection with K_1 .

$$K_{3} = \frac{1}{64\pi^{2}} \int \frac{e^{-3/2a_{1}}a_{1}\sin\theta_{1}^{a}e^{-i\phi_{1}}e^{-3/2b_{2}}b_{2}\sin\theta_{2}^{b}e^{i\phi_{2}}}{r_{12}} dV_{1}dV_{2}.$$

The integral is resolved into real and imaginary parts by means of the relation

$$e^{i(\phi_2-\phi_1)} = \cos(\phi_2-\phi_1) + i\sin(\phi_2-\phi_1)$$

As the angles ϕ_1 and ϕ_2 enter the integrand only through r_{12} , which is independent of the sign of $\phi_2 - \phi_1$, and through the exponential $e^{i(\phi_2 - \phi_1)}$, it is evident that the imaginary part of the integral must vanish. Expanding $\cos (\phi_2 - \phi_1)$ into the sum of $\cos \phi_1 \cos \phi_2$ and $\sin \phi_1 \sin \phi_2$ we break K_3 into the sum of the two integrals

$$K_{3}' = \frac{1}{64\pi^{2}} \int \left[\frac{e^{-3b_{1}/2}b_{2}\sin\theta_{2}b\cos\phi_{2}}{r_{12}} \right] \left[e^{-3a_{1}/2}a_{1}\sin\theta_{1}a\cos\phi_{1} \right] dV_{1}dV_{2}$$
$$K_{3}'' = \frac{1}{64\pi^{2}} \int \left[\frac{e^{-3b_{2}/2}b_{2}\sin\theta_{2}b\sin\phi_{2}}{r_{12}} \right] \left[e^{-3a_{1}/2}a_{1}\sin\theta_{1}a\sin\phi_{1} \right] dV_{1}dV_{2}.$$

Let P be the potential at the point b_1 , θ_1^b , ϕ_1 due to the distribution of charge $e^{-2b_2/2}b_2 \sin \theta_2^b \cos \phi_2$. Then

$$K_{3}' = \frac{1}{64\pi^{2}} \int P e^{-3a_{1}/2} a_{1} \sin \theta_{1}^{a} \cos \phi_{1} dV_{1}$$

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As $\sin \theta_2{}^b \cos \phi_2$ is a spherical harmonic of the first order, we have¹⁷

$$P = \frac{4\pi}{3}\sin\theta_1{}^b\cos\phi_1\left\{b_1\int_{b_1}^{\infty}e^{-3b_2/2}b_2db_2 + \frac{1}{b_1{}^2}\int_0^{b_1}e^{-3b_2/2}b_2{}^4db_2\right\}.$$

 K_3' becomes

$$K_{3}' = \frac{1}{36\pi} \int e^{-3a_{1}/2} a_{1} \sin \theta_{1}^{a} \sin \theta_{1}^{b} \cos^{2} \phi_{1} \left\{ \frac{64}{27} b_{1}^{2} - e^{-3b_{1}/2} \left(b_{1} + \frac{8}{3} + \frac{32}{9b_{1}} + \frac{64}{27b_{1}^{2}} \right) \right\} dV_{1}$$

 K_{3}'' is identical with K_{3}' except for the substitution of $\sin^{2} \phi_{1}$ for $\cos^{2} \phi_{1}$ in the integrand. Adding the integrands eliminates ϕ_{1} entirely. Introducing elliptic coordinates, integrating with respect to ϕ_{1} , and making the additional transformation

$$x = \mu$$
; $y = \lambda - \mu$

we obtain

$$K_3 = \frac{R^3}{64} \int_{-1}^{+1} e^{-3Rx/2} (1-x^2) \int_{1-x}^{\infty} F(y) dy,$$

where

$$F(y) = \frac{64}{27R} e^{-3Ry/4} \left(\frac{\alpha}{y^2} + \frac{\beta}{y} + \gamma + y \right) - e^{-3Ry/2} \left\{ \frac{R^2}{8} (\alpha y + \beta y^2 + \gamma y^3 + y^4) + \frac{2R}{3} (\alpha + \beta y + \gamma y^2 + y^3) + \frac{16}{9} \left(\frac{\alpha}{y} + \beta + \gamma y + y^2 \right) + \frac{64}{27R} \left(\frac{\alpha}{y^2} + \frac{\beta}{y} + \gamma + y \right) \right\};$$

and

$$\alpha = 2x(x^2 - 1); \quad \beta = 5x^2 - 1; \quad \gamma = 4x$$

Let $\phi(x)$ be the function

$$\phi(x) = \int_{1-x}^{\infty} F(y) dy.$$

A tedious integration yields

$$\phi(x) = \frac{16}{9} \left(\frac{4\beta}{3} - \alpha\right) \left\{ E_i \left[-\frac{3R(1-x)}{2} \right] - E_i \left[-\frac{3R(1-x)}{4} \right] \right\}$$
$$+ \frac{64}{27R} e^{-3R(1-x)/4} \left(\alpha + \frac{4}{3R} \gamma + \frac{16}{9R^2} + \frac{4(1-x)}{3R} \right)$$

¹⁷ Cf. J. H. Jeans, Electricity and Magnetism, p. 224 Camb. Univ. Press, 1923.

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$$-\frac{2}{3R}e^{-3R/2(1-x)}\left[\left(u_{0}+\frac{2}{3R}u_{1}+\frac{32\alpha}{9}+\frac{8}{9}\frac{u_{2}}{R^{2}}+\frac{16u_{3}}{9R^{3}}+\frac{128}{27R^{4}}\right)\right.\\\left.+\left(u_{1}+\frac{4u_{2}}{3R}+\frac{8u_{3}}{9R^{2}}+\frac{8}{9R^{3}}\right)(1-x)+\left(u_{2}+\frac{2u_{3}}{R}+\frac{2}{3R^{2}}\right)(1-x)^{2}\right.$$

$$\left.+\left(u_{3}+\frac{1}{R}\right)(1-x)^{3}+\frac{3R}{16}(1-x)^{4}\right].$$
(30)

Here Ei(x) is the integral logarithm of x and

$$u_{0} = \frac{2\alpha}{3} + \frac{16\beta}{9} + \frac{64\gamma}{27};$$

$$u_{1} = \frac{\alpha}{8} + \frac{2\beta}{3} + \frac{16\gamma}{9} + \frac{64}{27};$$

$$u_{2} = \frac{\beta}{8} + \frac{2\gamma}{3} + \frac{16}{9};$$

$$u_{3} = \frac{\gamma}{8} + \frac{2}{3}$$

 K_3 is now given by

$$K_3 = \frac{R^3}{72} \int_{-1}^{+1} e^{-3Rx/2} (1-x^2)\phi(x) dx.$$
 (31)

The last quadrature indicated in the above equation has been carried through graphically.

In order to evaluate K_2 and K_4 we have found it necessary to follow Sugiura² in using Neumann's expansion of $1/r_{12}$ in harmonics of $\phi_2 - \phi_1$. This is

$$1/r_{12} = \frac{2}{R} \sum_{\tau=0}^{\infty} \sum_{\nu=0}^{\infty} D_{\tau\nu} P_{\tau\nu} \binom{\lambda_1}{\lambda_2} Q_{\tau\nu} \binom{\lambda_2}{\lambda_1} P_{\tau\nu} (\mu_1) P_{\tau\nu} (\mu_2) \cos \nu (\phi_2 - \phi_1)$$
(32)

where $P_{\tau}{}^{\nu}$ and $Q_{\tau}{}^{\nu}$ are associated Legendre functions of the first and second kind respectively and $D_{\tau\nu}$ is given by

$$D_{\tau\nu} = (-1)^{\nu} \epsilon_{\nu} \frac{2\tau+1}{2} \left(\frac{\Pi(\tau-\nu)}{\Pi(\tau+\nu)} \right)^2, \quad \epsilon_0 = 1 ; \quad \epsilon_1 = \epsilon_2 = \cdots = 2.$$

The upper arguments of $P_{\tau^{\nu}(\lambda_1)}^{\nu}$ and $Q_{\tau^{\nu}(\lambda_1)}^{\nu}$ in (32) apply when $\lambda_2 > \lambda_1$ and the lower arguments when $\lambda_2 < \lambda_1$. Using elliptic coordinates K_2 takes the form

$$K_{2} = \frac{R^{8}}{(128)^{2}\pi^{2}} \int \frac{e^{-(\lambda_{1}R+\lambda_{2}R/2)}}{r_{12}} (\lambda_{2}^{2}-1)(1-\mu_{2}^{2})(\lambda_{1}^{2}-\mu_{1}^{2})(\lambda_{2}^{2}-\mu_{2}^{2})d\lambda_{1}\cdots d\phi_{2} \quad (33)$$

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and as the angles ϕ_1 and ϕ_2 enter the integrand only through the expansion (32) it is clear that integration over these angles will reduce all terms to zero except that for which ν is zero. The corresponding term of (32) is simply

$$\frac{2}{R} \sum_{\tau=0}^{\infty} \left(\frac{2\tau+1}{2}\right) P_{\tau} \binom{\lambda_1}{\lambda_2} Q_{\tau} \binom{\lambda_2}{\lambda_1} P_{\tau}(\mu_1) P_{\tau}(\mu_2).$$

Inserting this term for $1/r_{12}$ in (33) and integrating with respect to μ_1 , we observe that

$$\int_{-1}^{+1} P_{\tau}(\mu_1)(\lambda_1^2 - \mu_1^2) d\mu_1 = 2(\lambda_1^2 - 1/3) \quad \text{if} \quad \tau = 0,$$

= -4/15 if \tau = 2,

and vanishes for all other values of τ . Hence K_2 breaks into two integrals, one for $\tau = 0$, the other for $\tau = 2$. Designating these as $K_2^{(0)}$ and $K_2^{(2)}$ respectively, we have

$$K_{2}^{(0)} = \frac{R^{7}}{32 \times 64} \int P_{0} \binom{\lambda_{1}}{\lambda_{2}} Q_{0} \binom{\lambda_{2}}{\lambda_{1}} P_{0}(\mu_{2}) e^{-(\lambda_{1}R+\lambda_{2}R/2)} (\lambda_{2}^{2}-\mu_{2}^{2})(\lambda_{1}^{2}-\frac{1}{3}) d\lambda_{1} d\lambda_{2} d\mu_{2}$$

$$K_{2}^{(2)} = \frac{-R^{7}}{48 \times 64} \int P_{2} \binom{\lambda_{1}}{\lambda_{2}} Q_{2} \binom{\lambda_{2}}{\lambda_{1}} P_{2}(\mu_{2}) e^{-(\lambda_{1}R+\lambda_{2}R/2)} (\lambda_{2}^{2}-\mu_{2}^{2})(\lambda_{2}^{2}-\mu_{2}^{2}) d\lambda_{1} d\lambda_{2} d\mu_{2}.$$

Inserting the values of the Legendre functions,¹⁸ viz.,

$$P_0(x) = 1 ; P_2(x) = (3x^2 - 1)/2 ; Q_0(x) = ln\left(\frac{x+1}{x-1}\right); Q_2(x) = -3x + \frac{3x^2 - 1}{2} ln\left(\frac{x+1}{x-1}\right),$$

and integrating with respect to μ_2 we obtain

$$K_{2}^{(0)} = \frac{R^7}{24 \times 64} \int_{+1}^{\infty} d\lambda_2 (\lambda_2^2 - 1) (\lambda_2^2 - \frac{1}{5}) e^{-\lambda_2 R/2} \left\{ \int_{\lambda_2}^{\infty} e^{-\lambda_1 R} \ln\left(\frac{\lambda_1 + 1}{\lambda_1 - 1}\right) \left(\lambda_1^2 - \frac{1}{3}\right) d\lambda_1 + \ln\left(\frac{\lambda_2 + 1}{\lambda_2 - 1}\right) \int_{1}^{\lambda_2} e^{-\lambda_1 R} \left(\lambda_1^2 - \frac{1}{3}\right) d\lambda_1 \right\}.$$

Another tedious integration yields

.

$$K_{2}^{(0)} = \frac{1}{24} \left[e^{-R/2} \left\{ Q \left(S \left[C + ln \frac{2R}{3} \right] - S' E_{i}(-2R) \right) + S \left(e^{R} E_{i}(-R) Q' - \left[\frac{2R^{2}}{15} + \frac{31R}{15} + \frac{356}{27} - \frac{262}{27R} \right] \right) \right\}$$

 18 The definition of Q_{τ} underlying the development (32) gives it twice the value now conventional.

$$-e^{R/2}S'Q'Ei(-3R) + e^{-5R/2}S'\left(\frac{83R}{45} - \frac{256}{27} - \frac{46}{27R}\right) -\frac{e^{-3R/2}}{45}\left(R^3 + \frac{12R^2}{3} + \frac{60R}{9} + \frac{120}{27}\right)\right]$$
(34)

where

$$Q = \frac{R^2}{5} + \frac{12R}{5} + 12 + \frac{24}{R}; \qquad S = e^{-R}(1 + R + R^2/3);$$
$$Q' = \frac{R^2}{5} - \frac{12R}{5} + 12 - \frac{24}{R}; \qquad S' = e^{R}(1 - R + R^2/3).$$

C=0.577216= Euler's constant. $K_2^{(2)}$ is reducible to the form

$$K_{2}^{(2)} = \frac{R^{4}}{3840} \int_{1}^{\infty} (\lambda^{2} - 1) \left(\lambda^{2} + \frac{1}{7} \left\{ (3\lambda + R)e^{-3\lambda R/2} - \left(\frac{3\lambda^{2} - 1}{2}\right)e^{-\lambda R/2} \left[S'Ei\{-(\lambda + 1)R\} - SEi\{-(\lambda - 1)R\} - Sln\left(\frac{\lambda + 1}{\lambda - 1}\right) \right] - 3e^{-\lambda R/2}S \right\} d\lambda$$
(35)

The final integration has been performed graphically. $K_2^{(2)}$ turns out to be small compared with $K_2^{(0)}$.

The last integral to be evaluated is

$$K_4 = \frac{1}{64\pi^2} \int \frac{e^{-(b_1 + a_1/2)}}{r_{12}} a_1 \sin \theta_1^a e^{-(b_2 + a_2/2)} a_2 \sin \theta_2^a e^{i(\phi_2 - \phi_1)} dV$$
(36)

Using the expansion (32) again we see that all terms must integrate to zero in which ν differs from unity. We may therefore replace $1/r_{12}$ by

$$-\frac{2}{R}\sum_{\tau=1}^{\infty}(2\tau+1)\left(\frac{\Pi(\tau-1)}{\Pi(\tau+1)}\right)^{2}P_{\tau}^{(1)}\binom{\lambda_{1}}{\lambda_{2}}Q_{\tau}^{(1)}\binom{\lambda_{2}}{\lambda_{1}}P_{\tau}^{(1)}(\mu_{1})P_{\tau}^{(1)}(\mu_{2})\cos(\phi_{2}-\phi_{1})$$

Integrating with respect to ϕ_1 and ϕ_2 and introducing elliptic coordinates in (36) we obtain

$$K_{4} = -\frac{R^{7}}{(64)^{2}} \int d\lambda_{1} d\lambda_{2} d\mu_{1} d\mu_{2} \sum_{\tau} \left\{ \frac{(2\tau+1)}{\tau^{2}(\tau+1)^{2}} e^{-(R/4)(3\lambda_{1}-\mu_{1})} e^{-(R/4)(3\lambda_{2}-\mu_{2})} \right.$$
$$\times P_{\tau}^{(1)} \binom{\lambda_{1}}{\lambda_{2}} Q_{\tau}^{(1)} \binom{\lambda_{2}}{\lambda_{1}} P_{\tau}^{(1)}(\mu_{1}) P_{\tau}^{(1)}(\mu_{2})$$
$$\left. (\lambda_{1}^{2}-1)^{1/2} (1-\mu_{1}^{2})^{1/2} (\lambda_{2}^{2}-1)^{1/2} (1-\mu_{2}^{2})^{1/2} (\lambda_{1}^{2}-\mu_{1}^{2}) (\lambda_{2}^{2}-\mu_{2}^{2}) \right\}.$$

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By means of the relations

$$P_{\tau}^{(1)}(x) = (1-x^2)^{1/2} \frac{d}{dx} P_{\tau}(x) \qquad Q_{\tau}^{(1)}(x) = (1-x^2)^{1/2} \frac{d}{dx} Q_{\tau}(x)$$

we may eliminate all the radical signs. Let $\alpha_{\tau}(R)$ and $\beta_{\tau}(R)$ be defined by

$$\alpha_{\tau}(R) = \int_{-1}^{+1} e^{Rx/4} (1-x^2) \frac{d}{dx} P_{\tau}(x) dx ;$$

$$\beta_{\tau}(R) = \int_{-1}^{+1} e^{Rx/4} x^2 (1-x^2) \frac{d}{dx} P_{\tau}(x) dx .$$

Then K_4 may be thrown into the form

$$K_{4} = \frac{R^{7}}{(64)^{2}} \int_{1}^{\infty} d\lambda_{1} \int_{1}^{\infty} d\lambda_{2} e^{-3R(\lambda_{1}+\lambda_{2})/4} (\lambda_{1}^{2}-1)(\lambda_{2}^{2}-1) \sum_{\tau} \left\{ \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau})(\lambda_{2}^{2}\alpha_{\tau}+\beta_{\tau}) \frac{d}{d\lambda} P_{\tau} \begin{pmatrix} \lambda_{1} \\ \lambda_{2} \end{pmatrix} \right\} d\lambda_{1} \int_{1}^{\infty} d\lambda_{2} e^{-3R(\lambda_{1}+\lambda_{2})/4} (\lambda_{1}^{2}-1)(\lambda_{2}^{2}-1) \sum_{\tau} \left\{ \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau})(\lambda_{2}^{2}\alpha_{\tau}+\beta_{\tau}) \frac{d}{d\lambda} P_{\tau} \begin{pmatrix} \lambda_{1} \\ \lambda_{2} \end{pmatrix} \right\} d\lambda_{1} \int_{1}^{\infty} d\lambda_{2} e^{-3R(\lambda_{1}+\lambda_{2})/4} (\lambda_{1}^{2}-1)(\lambda_{2}^{2}-1) \sum_{\tau} \left\{ \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau})(\lambda_{2}^{2}\alpha_{\tau}+\beta_{\tau}) \frac{d}{d\lambda} P_{\tau} \begin{pmatrix} \lambda_{1} \\ \lambda_{2} \end{pmatrix} \right\} d\lambda_{1} \int_{1}^{\infty} d\lambda_{2} e^{-3R(\lambda_{1}+\lambda_{2})/4} (\lambda_{1}^{2}-1)(\lambda_{2}^{2}-1) \sum_{\tau} \left\{ \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau})(\lambda_{2}^{2}\alpha_{\tau}+\beta_{\tau}) \frac{d}{d\lambda} P_{\tau} \begin{pmatrix} \lambda_{1} \\ \lambda_{2} \end{pmatrix} \right\} d\lambda_{1} \int_{1}^{\infty} d\lambda_{2} e^{-3R(\lambda_{1}+\lambda_{2})/4} (\lambda_{1}^{2}-1)(\lambda_{2}^{2}-1) \sum_{\tau} \left\{ \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau})(\lambda_{2}^{2}\alpha_{\tau}+\beta_{\tau}) \frac{d}{d\lambda} P_{\tau} \begin{pmatrix} \lambda_{1} \\ \lambda_{2} \end{pmatrix} \right\} d\lambda_{1} + \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau}) \left\{ \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau}) \frac{d}{d\lambda} P_{\tau} \begin{pmatrix} \lambda_{1} \\ \lambda_{2} \end{pmatrix} \right\} d\lambda_{1} + \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau}) \left\{ \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau}) \frac{d}{d\lambda} P_{\tau} \begin{pmatrix} \lambda_{1} \\ \lambda_{2} \end{pmatrix} \right\} d\lambda_{1} + \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau}) \left\{ \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau}) + \frac{2\tau+1}{\tau^{2}(\tau+1)^{2}} (\lambda_{1}^{2}\alpha_{\tau} +$$

The integrand is symmetric with respect to the line $\lambda_1 = \lambda_2$ and hence the integral is equal to twice the partial integral over the segment between the lines $\lambda_2 = 1$ and $\lambda_1 = \lambda_1$. By means of the relation

$$(\lambda^2 - 1)\frac{d}{d\lambda}p_{\tau}(\lambda) = \frac{\tau(\tau + 1)}{2\tau + 1} \left[P_{\tau + 1}(\lambda) - P_{\tau - 1}(\lambda) \right]$$

we may then express K_4 in the form

$$K_{4} = -\frac{2R^{7}}{(64)^{2}} \int_{1}^{\infty} d\lambda_{1} \left\{ e^{-3R\lambda_{1}/4} (\lambda_{1}^{2} - 1) \sum_{\tau=1}^{\infty} \frac{(\lambda_{1}^{2}\alpha_{\tau} + \beta_{\tau})}{\tau(\tau+1)} F_{\tau}(\lambda_{1}, R) \frac{d}{d\lambda_{1}} Q_{\tau}(\lambda_{1}) \right\} (37)$$

where

$$F_{\tau}(\lambda_1, R) = \int_{+1}^{\lambda_1} e^{-3R\lambda_2/4} (\lambda_2^2 \alpha_{\tau} + \beta_{\tau}) \left\{ P_{\tau+1}(\lambda_2) - P_{\tau-1}(\lambda_2) \right\} d\lambda_2.$$

The functions $\alpha_{\tau}(R)$, $\beta_{\tau}(R)$, $F_{\tau}(\lambda_1, R)$ have been evaluated analytically but the formulas are somewhat cumbersome and are therefore not reproduced here. The final step of integrating with respect to λ_1 has been performed graphically. Fortunately the series in τ converges rapidly so two terms only need be considered.

RESULTS

We have computed the numerical values of the integrals J_1 , J_2 , K_1 , K_2 , K_3 , K_4 for four different values of the internuclear distance R. The results are given in Table I. The energy values H_9^9 etc. are expressed in volts by means of the reduction factor $e^2/a_0 = 27.08$ volts.

Fig. 1 shows graphically the four computed approximate theoretical potential energy curves together with approximate curves for the C and B

states derived from the experimental band spectrum data. The zero level for the graph is the energy of the dissociated atom pair which lies 16.925 volts below the zero level of Eqs. (20) to (23).

R	g_{9}^{2}	g_{10}^{2}	J_1	J_2	K_1	K_2	K_{3}	K_4
1 2 3 4	0.136 .163 .195 .221	1.529 .534 .348 .288	0.969 .696 .531 .428	0.926 .4945 .224 .091	0.2365 .220 .199 .178	0.204 .123 .063 .028	0.016 .012 .008 .006	0.015 .010 .006 .002
R	· · · · · · · · · · · · · · · · · · ·	$H_{9}{}^{9}$		H_{10}^{10}		H_{11}^{11}		${H_{12}}^{12}$
$\begin{array}{c}1\\2\\3\\4\end{array}$		$2.25-1.06-1.08-0.596(S^{E}, S^{N})$		(volts above 25.26 7.42 2.49 0.812 (S^{E}, A^{N})	<i>E</i> ₀)	$ \begin{array}{c} 1.16 \\ -1.81 \\ -1.68 \\ -0.894 \\ (A^E, S^N) \end{array} $		$25.67.632.651.06(A^{E}, A^{N})$

TABLE I.

The energy of dissociation and the moment of inertia serve to determine ordinate and abscissa R_0 of the minimum point on each of the "empirical" curves while the vibrational frequency and the variation of the moment of inertia with vibrational quantum number may be used to evaluate the second and third derivatives of the potential energy with respect to R at the minimum point.¹⁹ The attractive force between the atoms at large distances should vary as R^{-7} . Hence the best estimate which we can make regarding the form of the actual potential energy curve for any given molecular state is obtained by using a function of the form

$$V(R) = \sum_{n=6}^{5} a_n / R^n \tag{38}$$

¹⁹ The values of the heat of dissociation (indirect calculation) given by Birge⁸ for the Band C states are 3.37 volts and 2.27 volts respectively. These are increased by the equivalent of a half quantum of vibrational energy in passing from the old to the new mechanics. Using 14.5 volts as the energy for $R = \infty$, we obtain in this way

 $V(R_0)_B = 14.5 - 3.45 = 11.05$ volts

 $V(R_0)_C = 14.5 - 2.42 = 12.08$ volts

From the vibrational frequencies given by Birge we compute V

$$''(R_0)_B = 0.919$$

 $V^{\prime\prime}(R_0)_C = 2.98$

Finally $V'''(R_0)$ may be determined from the variation of the constant $B = h/(8\pi^2 IC)$ with the vibrational quantum number. The formula

$$V^{\prime\prime\prime} = V^{\prime\prime} \left[\frac{\omega_0}{2B_0^2} \left(\frac{dB}{dn} \right)_{n=0} - 3 \right] \frac{a_0}{R_0}$$

is to be used. It yields

 $V^{\prime\prime}(R_0)_B = -1.48;$ The equilibrium internuclear distances themselves are $(R_0)_B = 2.45;$

the unit as always being $a_0 = 0.532 \times 10^{-8}$ cm.

 $V^{\prime\prime}(R_0)_C = 6.95.$

$$(R_0)_C = 1.99$$

where the *a*'s are determined to fit the known heat of dissociation and to give the correct values to *V* and its derivatives at the point $R = R_0$. Curves *C* and *B* are graphs of such empirical formulas. A comparison of H_9^9 and C_2 shows that the former is in reasonable harmony with our experimental information. The discrepancy for small values of *R* is not surprising since the approximate wave-functions used must be very inaccurate for the smaller internuclear distances

In addition to B and C there is a 2P level reported by Richardson²⁰ and classified by him as a triplet state. The location of this level has been determined by a Rydberg series into which it fits, there being no known direct combination with the normal state. As the bands associated with this state have not been completely analyzed, the empirical data are somewhat uncertain and we have plotted only a fragment of the empirical potential energy curve (D). Clearly this state is to be correlated with our energy curve for H_{11}^{11} . The agreement is about the same as for the C state.

On the whole the comparison of the H_{θ}^{9} and H_{11}^{11} values with the corresponding experimental data seems to justify the conclusion that all four of the theoretical potential energy curves are qualitatively correct and that the remaining P states $(H_{10}^{10} \text{ and } H_{12}^{12})$ are both of a type which does not lead to the formation of a stable molecule.

These results shed some light on London's theory of non-polar valence.⁷ Two *normal* H atoms can react only in two ways, as Heitler and London have shown. In first approximation the corresponding wave functions in our notation are

$$\psi_{S} = \psi_{1}{}^{a}\psi_{2}{}^{b} + \psi_{2}{}^{a}\psi_{1}{}^{b} \qquad (S^{E}S^{N})$$

$$\psi_{A} = \psi_{1}{}^{a}\psi_{2}{}^{b} - \psi_{2}{}^{a}\psi_{1}{}^{b} \qquad (A^{E}A^{N})$$

Here $\psi_{\rm S}$ is symmetric with respect to both of the transformations (E) and (N) and $\psi_{\rm A}$ is antisymmetric with respect to both. Hybrid symmetries like that of our function U_{10} drop out because both electrons have the same quantum number. Only the symmetric mode of interaction leads to molecular formation and in his first paper on valence theory London infers that symmetry in the coordinates of the valence electron is the characteristic feature of the homopolar bond. This means that when a non-polar molecule is formed by two atoms each of which has a single valence electron a singlet state must result, triplet type interactions leading to repulsion. Our computation and the empirical data show that both singlet and triplet states may lead to the formation of excited molecules, the triplet states being more stable energetically than corresponding singlet states with the same symmetry

²⁰ O. W. Richardson, Proc. Roy. Soc. A114, 643 (1927). Cf. also Birge (Ref. 8 above) and Richardson, Nature 121, 320 (1928).

²¹ It is well known that in atoms with two valence electrons each triplet level lies below the corresponding singlet level. If the singlet-triplet difference always has the same sign for molecules, and if it decreases monatonically as R increases from 0 to infinity, a triplet level must always be more stable than a singlet level similar to it except for electron symmetry.

with respect to the nuclei²¹ (i.e., with respect to the transformation z_1 , $z_2 \rightarrow -z_1, -z_2$). It therefore appears that in the case of hydrogen symmetry in the nuclei has a more important effect on molecular formation than symmetry in the electrons. The reason for this importance is that antisymmetry in the nuclei introduces a "node" including all points for which $z_1 = z_2 = 0$ and leading to an increase in the azimuthal quantum number of one of the electrons in the limit when the nuclei are brought together and the wave function becomes helium-like. This "promotion" and consequent increase in energy for small values of R must tend to produce repulsion and since the removal of degeneracy is generally accompanied by the lifting of half of the sublevels coming from any parent level and a corresponding depression of the remaining sublevels, it is plausible to suppose that the absence of promotion in the case of states with the symmetry S^N should produce attraction and molecular formation. Our conclusion confirms the suggestion made by London in his second paper on valence theory to account for the triplet levels found by Ritschl and Villars in the band spectra of Na_2 and K_2 .

The success of London's theory in describing the facts regarding the *normal* states of molecules must then be due to the fact that in such states the symmetry of the wave function with respect to an interchange of the coordinates of the valence electrons determines the presence or absence of a node between the nuclei. We have made no detailed examination of this question, but surmise that the occurrence of such states as U_{11} above which are antisymmetric in the coordinates of the valence electrons but lack the node between the nuclei is dependent on the fact that two atoms which make up the molecule are identical, but dissociate into different states of excitation.

The B State

It would be natural to infer from our results that in the case of diatomic molecules consisting of identical atoms symmetry in the nuclei is always the crucial element in producing attraction. Such a generalization strikes a snag immediately, however, in the *B* state of the hydrogen molecule which must have the symmetry $S^{E}A^{N}$ to account for its union with the normal state of the molecule to form a band system. From the discussion above it will be clear that both types of symmetry tend to produce repulsion. Nevertheless, the *B* state is actually the most stable energetically of the known two quantum states of H₂.

The most probable explanation of this puzzling situation lies in the fact that the two quantum molecular S states ($\sigma_k = 0$) have in zero approximation an additional type of degeneracy not present in the case of the P states ($\sigma_k = \pm 1$). There are two two quantum molecular S states with the symmetry $S^{\mathbb{F}}A^N$ of the B state. The wave functions in zero approximation are mixtures of U_2 and U_5 and the energy difference given by (14) is $[(H_2^2 - H_5^5)^2 + 4(H_5^2)^2]^{1/2}$. To account for the stability of the B state we must suppose that this energy difference for moderate values of R is quite large compared with the energy differences due to the symmetry in the electrons and in the nuclei.²² The companion state to B with the same symmetry will then be strongly repulsive in type.

An alternative suggestion regarding the B state due to Pauling²³ attributes this energy level to a union of H⁺ and H⁻ ions. In other words, he supposes that the B state does not dissociate adiabatically into a normal H atom and a two quantum H atom, but into H⁺ and H⁻ ions. This hypothesis is compatible with the fact that the B state is of the S type and with its symmetry. It accounts for the fact that the atoms in the B state begin to attract each other at extraordinarily large interatomic distances. The proposal does not recommend itself to us, however, since it leads to a value of the dissociation energy too large for satisfactory agreement with the experimental vibrational energy data. (This fact was first called to our attention by Professor R. S. Mulliken.) The energy of the H⁻ ion is not exactly known and it may be that the ion does not exist. We can hardly go far wrong, however, if we assume that the binding energy of the second electron is zero. In that case the energy of the dissociation products of the B state of the molecule must be three volts higher according to Pauling's hypothesis than according to our own assumption (borrowed from Dieke and Hopfield)⁹, that the B state dissociates adiabatically into a normal atom and a two quantum excited atom. The vibrational energy data extrapolated by Birge⁸ yield 3.41 volts as the energy of dissociation, whereas the value computed on the basis of the second hypothesis above from the more accurately known vibrational data for the normal state is 3.37 volts. It is extremely unlikely that this extrapolation can be in error by the three volts required to make it agree with Pauling's suggestion. Moreover, a consideration of the nodes of the wave function of any molecular state X dissociating into ions suggests that these nodes must be numerous (Cf. as a one dimensional analogy, Hund, Zeits. f. Physik 40, 748, Figs. 3 and 4). If so, X should pass into a high quantum state of He when the nuclei are brought together. Hence the attraction between the atoms at large distances due to the Coulomb forces would soon be counterbalanced with decreasing R by the repulsive action due to multiple promotion of the electrons. It would therefore be difficult to account for such a low energy at intermediate values of R as that associated with the B state.

In view of these facts regarding the B state it appears that neither of the two types of symmetry S^E and S^N is a universal characteristic of the wave functions of stable diatomic molecules. On the other hand there are as yet no definite known exceptions to the less stringent rule that molecular formation always involves the removal of some type of degeneracy characteristic of the atom pair when completely separated. The authors wish to express

$\psi = c_2 U_2 + c_5 U_5$

(A)

²² The choice of the coefficients c_2 and c_5 in the expression for ψ

is readily shown to be that which makes the energy of the resulting state either a maximum or a minimum. Hence, if the variation in the energy integral due to varying the ratio c_2/c_5 is large, one of the two states of type $(S^E A^N)$ will form a stable molecule.

²³ L. Pauling, Chem. Reviews 5, 204 (1928).

their great appreciation for the assistance of Dr. V. Guillemin in checking the computations.*

Note added at reading of proof. Since writing the above paragraphs on the B state we have come to the conclusion that the argument needs modification. If one tries to build up wave-functions for the neutral H₂ molecule from the wave functions of the molecule-ion, it is at once apparent that a suitable combination of the functions for the two lowest ionic terms will yield rough approximations to the lowest energy levels of the polar type of neutral molecule. As one of the molecular ion wave functions to be used has a single node while the other has none, it will be clear that the approximate terms for the polar type neutral molecule will *not* undergo multiple promotion when the nuclei are brought together.

In order to bring this fact into line with the argument regarding the nodes given above, it is necessary to recall Hund's discussion of the possible crossing of terms during the adiabatic variation of a parameter such as the internuclear distance R. (Zeits. f. Physik 40, 751–3, 1927). He observes that we may expect that in many cases an approximate computation will suggest a crossing of terms where a more rigorous treatment would show that the crossing does not actually occur.

The situation will be made clear by the following analytical treatment. Let ψ_1 and ψ_2 be two approximate wave functions with approximate energy values $E_1(R)$ and $E_2(R)$. Let the terms cross at $R = R_1$ and to be specific we assume that E_1 lies above E_2 when $R > R_1$. We shall suppose that $E_1 = \int \psi_1 H \psi_1 dv$ while $E_2 = \int \psi_2 H \psi_2 dv$. If there are no other approximate solutions having energies close to E_1 and E_2 at $R = R_1$, we may assume that in this neighborhood to a close approximation the actual wave functions will be linear combinations of ψ_1 and ψ_2 . Thus we assume

$$\boldsymbol{\psi} = c_1 \boldsymbol{\psi}_1 + c_2 \boldsymbol{\psi}_2 \,. \tag{a}$$

Then by equation (7) above

$$c_1(E_1 - E) + c_2 H_2^1 = 0;$$
 $c_1 H_1^2 + c_2(E_2 - E) = 0.$ (b)

If the energy operator H is real, the conjugate integrals H_{2^1} and H_{1^2} must be equal. Then E is a root of the equation

$$(E_1 - E)(E_2 - E) - (H_2^1)^2 = 0.$$

The two roots are

$$\begin{split} E^{+} &= \frac{E_{1} + E_{2}}{2} + \left[(H_{2}^{1})^{2} + \frac{(E_{2} - E_{1})^{2}}{4} \right]^{1/2} \\ E^{-} &= \frac{E_{1} + E_{2}}{2} - \left[(H_{2}^{1})^{2} + \frac{(E_{2} - E_{1})^{2}}{4} \right]^{1/2} \end{split} \tag{c}$$

* The article by Hylleraas (Zeits. f. Physik **51**, 150, 1928) describing a computation of the two-quantum S states of H_2 came to hand after the present paper was finished. Hylleraas comes to the same conclusion as that reached by us in that he finds that symmetry in the nuclei is more important than symmetry in the electrons in its influence on molecular binding. Unfortunately his computation is, in our opinion, incorrect as he neglects the interaction between the states $\psi(2, 0, 0)$ and $\psi(2, 1, 0)$ (our notation) in molecular formation. Unless this interaction is taken into account, the characteristics of the B state are hardly explicable.

We assume that $H_{2^1}(R)$ is small compared with $E_1(R)$ and $E_2(R)$ in the neighborhood of $R = R_1$. Then equations (c) show that E^+ approximates to E_1 when $R - R_1$ has large positive value, but to E_2 when $R - R_1$ has large negative value. Similarly E^- approximates to E_2 on the one side of $R = R_1$ and to E_1 on the other. If H_{2^1} does not vanish, there is no crossing and the separation of the levels at $R = R_1$ is $2H_{2^1}(R_1)$. If H_{2^1} is rigorously zero, we may, if we like, say that the terms cross. If $H_{2^1}(R_1)$ is very small, the energy level curves for E^+ and E^- will come very close to one another at $R = R_1$ and will bend sharply near this point, but if H_{2^1} is large, the two curves will apparently repel one another when still far apart and the bend near $R = R_1$ will be less abrupt. Finally, if there is no crossing point but the term values E_1 and E_2 merely approach one another at $R = R_1$, the interaction will cause a depression of the lower one and an elevation of the upper one is if due to mutual repulsion.

If $H_{2^{1}}$ does not vanish, the substitution of the value of E^{+} given in (c) into either of the equations (b) leads to the relation

$$c_1^+/_2^+ c = x - (1 + x^2)_2^1$$
 (d)

where $x = (E_2 - E_1)/2H_2^1$. From equation (d) we see that when x is large and positive $(E^+ - E_2 \text{ small}) c_1^+/c_2^+$ is sensibly equal to zero, while if x has a large negative value c_1^+/c_2^+ becomes infinite. More generally, if E^+ or $E^$ differs but little from one of the approximate energy values E_1 and E_2 in a certain range of R values, the actual wave-function will differ but little from the corresponding approximate function. At the apparent crossing point $R = R_1$ each of the rigorous wave functions is composed of equal parts of ψ_1 and ψ_2 .

Although the integral $H_{2^1}(\int \psi^1 H \psi_2 dv)$ always vanishes for two exact solutions of the wave equation which satisfy the boundary conditions, the chance that it will vanish rigorously for two approximate solutions is infinitesimal unless the symmetry of the solutions is different. Hence we conclude that if the approximate term for the polar type of neutral molecule having the symmetry $S^F A^N$ of the *B* state crosses the two approximate two quantum *S* terms of the same symmetry which dissociate into neutral atoms, this crossing will not occur when a more rigorous solution of the problem is worked out. In all probability, therefore, the *B* state would dissociate adiabatically into two neutral atoms. On the other hand, it is also probable that the wave function of the *B* has distinctly polar characteristics which are responsible for the depth of its potential energy minimum. Thus in an important physical sense we are led to accept Pauling's interpretation of the *B* state as one with ionic binding.

The two quantum P states of the molecule, however, would not be similarly affected by polar characteristics since their symmetry would cause the interaction integral with the lowest polar states to vanish (cf. p. 520 above).

This supplementary note originated in a discussion of the term-crossing problem with Professor Slater, to whom we are greatly indebted.

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