THE APPLICATION OF THE QUANTUM MECHANICS TO THE STRUCTURE OF THE HYDROGEN MOLECULE AND HYDROGEN MOLECULE-ION AND TO RELATED PROBLEMS

LINUS PAULING

Gates Chemical Laboratory, California Institute of Technology

I. INTRODUCTION

Many attempts were made to derive with the old quantum theory structures for the hydrogen molecule, H_2, and the hydrogen molecule-ion, H_2^+, in agreement with the experimentally observed properties of these substances, in particular their energy contents. These were all unsuccessful, as were similar attempts to derive a satisfactory structure for the helium atom. It became increasingly evident that in these cases the straightforward application of the old quantum theory led to results definitely incompatible with the observed properties of the substances, and that the introduction of variations in the quantum rules was not sufficient to remove the disagreement. (For a summary of these applications see, for example, Van Vleck (1).) This fact was one of those which led to the rejection of the old quantum theory and the origination of the new quantum mechanics. The fundamental principles of the quantum mechanics were proposed by Heisenberg (2) in 1925. The introduction of the matrix algebra (3) led to rapid developments. Many applications of the theory were made, and in every case there was found agreement with experiment. Then the wave equation was discovered by Schrödinger (4), who developed and applied his wave mechanics independently of the previous work. Schrödinger's methods are often considerably simpler than matrix methods of calculation, and since it has been shown (5) that the wave mechanics and the matrix mechanics are mathematically identical, the wave equation is generally used as the starting point in the consideration of the properties of atomic systems, in particular of stationary states.

The physical interpretation of the quantum mechanics and its generalization to include aperiodic phenomena have been the subject of papers by Dirac, Jordan, Heisenberg, and other authors. For our purpose, the calculation of the properties of molecules in stationary states and particularly in the normal state, the consideration of the Schrödinger wave equation alone suffices, and it will not be necessary to discuss the extended theory.

In the following pages, after the introductory consideration of the experimentally determined properties of the hydrogen molecule and molecule-ion, a unified treatment of the application of the quantum mechanics to the structure of these systems is presented. In the course of this treatment a critical discussion will be given the numerous and scattered pertinent publications. It will be seen that in every case the quantum mechanics in contradistinction to the old quantum theory leads to results in agreement with experiment within the limit of error of the calculation. It is of particular significance that the straightforward application of the quantum mechanics results in the unambiguous conclusion that two hydrogen atoms will form a molecule but that two helium atoms will not; for this distinction is characteristically chemical, and its clarification marks the genesis of the science of sub-atomic theoretical chemistry.

II. THE OBSERVED PROPERTIES OF THE HYDROGEN MOLECULE AND MOLECULE-ION

The properties of the hydrogen molecule and molecule-ion which are the most accurately determined and which have also been the subject of theoretical investigation are ionization potentials, heats of dissociation, frequencies of nuclear oscillation, and moments of inertia. The experimental values of all of these quantities are usually obtained from spectroscopic data; substantiation is in some cases provided by other experiments, such as thermochemical measurements, specific heats, etc. A review of the experimental values and comparison with some theoretical results published by Birge (7) has been used as the basis for the following discussion.

The ultraviolet absorption spectrum of hydrogen was analyzed by Dieke and Hopfield (8). They identified the three lowest electronic states, indicated in figure 1 by the symbols *A*, *B*, and *C*, and for each a number of states of oscillation of the nuclei, also shown in the figure. In addition there is a fine-structure of each oscillational state due to rotation of the molecule. A number of these levels were independently obtained by Witmer (9) from the analysis of the Lyman bands. Richardson (10) has analyzed

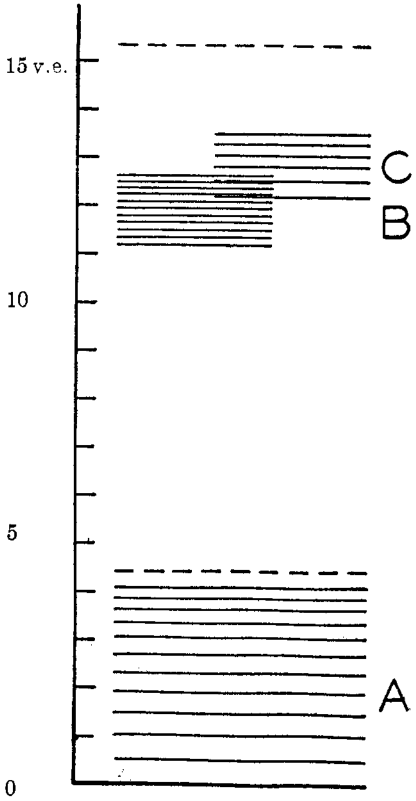

FIG. 1. ENERGY LEVEL DIAGRAM FOR THE THREE LOWEST ELECTRONIC STATES OF THE HYDROGEN MOLECULE, SHOWING SUCCESSIVE OSCILLATIONAL LEVELS

bands in the visible, and on the basis of comparison of the oscillational and rotational fine-structure has identified the lower states of some of these bands with Dieke and Hopfield's *B* and *C* states. The upper levels of Richardson's bands correspond to an electron in successive excited states, and by means of an assumed Rydberg formula Birge has carried out the extrapolation to ionization, and has obtained for the ionization potential of the hydrogen molecule the value

$$I_{H_2} = 15.34 \pm 0.01 \text{ volts}$$

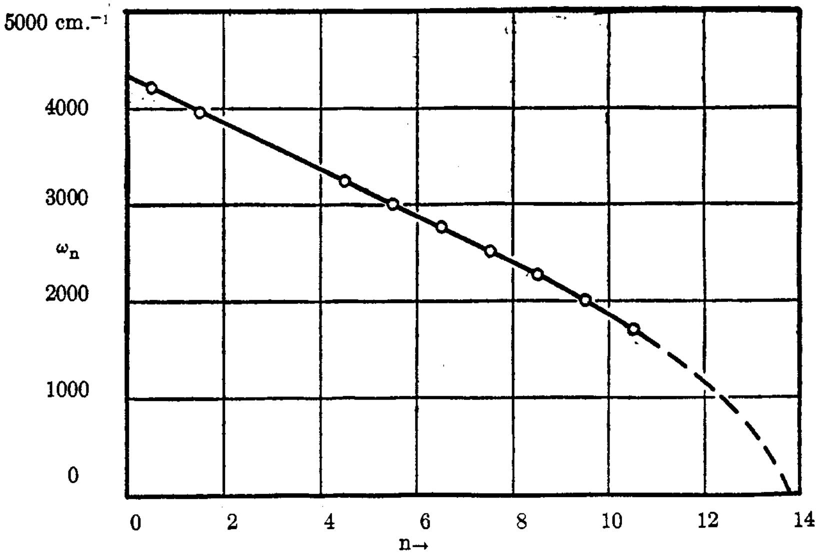

FIG. 2. THE OSCILLATIONAL FREQUENCY FOR THE NORMAL STATE OF THE HYDROGEN MOLECULE AS A FUNCTION OF THE OSCILLATIONAL QUANTUM NUMBER

The area under the curve gives the heat of dissociation

He also states that he has verified this value by means of the heat of dissociation of various excited states of the molecule as obtained by extrapolating the oscillational levels in the way described below.

Ionization by electron impact has been shown (11) to occur at about 16.1 volts. Condon has given the explanation of the discrepancy between this and the band spectrum value in terms of a general phenomenon discovered and interpreted by Franck (12). We shall see later that the equilibrium internuclear distance for H_2 is about 0.75 Å, and for H_2^+, 1.06 Å. When H_2 in the normal state is ionized by electron impact to H_2^+ the nuclei do not have time to move, but are left some distance from their new equilibrium positions. As a result large nuclear oscillations occur, estimated by Condon to correspond to about 1 volt-electron of oscillational energy; and this energy in addition to the ionization energy must be supplied by the impacting electron.

The best experimental value of the heat of dissociation of H_2 is that obtained by Witmer (9) by extrapolating the oscillational levels of the normal state of the molecule to dissociation. The restoring force acting on the two nuclei becomes smaller as the nuclei get farther apart, and as a result the oscillational frequency in successive oscillational states becomes smaller and smaller. For H_2 in the normal state this oscillational frequency

$$\omega_n = \frac{1}{h}\frac{\partial E_n}{\partial n}$$

is represented in figure 2 for values of n, the oscillational quantum number,[1] from 0 to 11. The curve was extrapolated by Witmer as shown by the dotted line; the area under it is equal to the heat of dissociation, and gives

$$D_{H_2} = 4.34 \pm 0.1 \text{ volt-electrons}$$

It is of interest to note that dissociation, represented in figure 1 by the dotted line, is very close to the highest observed oscillational-rotational state. Indeed the oscillational and rotational energy of the highest observed level was 4.10 v.e. (94,600 cal/mole), which must be a lower limit to the heat of dissociation.

The value 4.34 v.e. is equal to 100,000 cal/mole. Thermochemical measurements are in satisfactory agreement with this spectroscopic result. Thus Isnardi's experiments (13) on the thermal conductivity of partially dissociated hydrogen give, with the computational error discovered by Wohl (14) corrected, a

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[1] The true oscillational quantum number has the values 1/2, 3/2, 5/2,... For convenience we shall use in this paper the integers obtained by subtracting ½ from these values, unless specific mention is made of an alternative procedure.

value between 96,765 and 102,257 cal/mole. Langmuir's most recent value from his similar measurements (15) is 97,000 cal/mole.

From the rotational fine-structure of the *A* levels Hori (16) obtained the value

$$I_o = 0.467 \times 10^{-40} \text{ g. cm.}^2$$

for the moment of inertia of the molecule in the normal state, corresponding to an equilibrium internuclear distance

$$r_o = 0.76 \text{ Å}$$

TABLE 1

The properties of the hydrogen molecule

		E_e,cm^{-1}	n^*	ω_0,cm^{-1}	r_0,Å.
1	1^1S(A)	0	0.9396	4264	0.76
2	2^1S(B)	90083	1.7920	1325	1.55
3	2^3P	(94735)	(1.9281)	2390	0.97
4	2^3S	94906.7	1.9337	2593.82	1.08
5	2^1P	(95469)	(1.9526)		
6	C	99086	2.0882	2380	1.06
7	3^3S	111427	2.9261		
8	3^3P	111518.1	2.9365	2306.94	1.136
9	3^1P	111656.8	2.9526	2373.89	
10	4^3P	117169.9	3.9395	2276.45	1.145
11	4^1P	117216.9	3.9526	2325.6(?)	
12	5^3P	119744.2	4.941	2251	1.168
13	6^3P	121130.2	5.942	2229 (?)	1.166
14	7^3P	121961.0	6.942		
15	8^3P	122498.3	7.942		
16	H_2^+	124237		2247	(1.06)

This result is independently verified by Dennison (17) who has recently given a satisfactory theory of the specific heat of hydrogen. The observed specific heat as interpreted by Dennison requires that I_o be equal to 0.464×10^{-40} g. cm.^{2}. The very recent measurements by Cornish and Eastman (18) of the specific heat of hydrogen from the velocity of sound are said to agree very well with Dennison's theory if I_o be given the value of 0.475×10^{-40} g. cm.^{2}.

The oscillational frequency of the nuclei in H_2 in the normal state was calculated by Birge from the measurements of Witmer, Dieke and Hopfield, and Hori to be

$$\omega_{H_2} = 4264 \text{ cm.}^{-1}$$

By extrapolating the observed oscillational frequencies for various excited states of H_2 forming a part of a Rydberg series, Birge obtained for H_2^+ in the normal state the value

$$\omega_{H_2^+} = 2247 \text{ cm.}^{-1}$$

A summary of information regarding various electronic states of the hydrogen molecule is given in table 1, quoted from Birge.

The symbols in the second column represent the electronic state; in particular the first number is the total quantum number of the excited electron. We shall see later that in one case at least the symbol is probably incorrect. The third column gives the wave-number of the lowest oscillational-rotational level, the fourth the effective quantum number, the fifth and sixth the oscillational wave-number and the average internuclear distance for the lowest oscillational-rotational level. The data for H_2^+ were obtained by extrapolation, except r_o, which is Burrau's theoretical value (Section VIa).

The interrelation of these quantities and comparison with theoretical results will be discussed in the following sections of this paper.

III. THE HYDROGEN ATOM

The wave equation representing a conservative Newtonian dynamical system is

$$\Delta\psi + \frac{8\pi^2}{h^2}(W - V(q_k))\,\psi = 0 \qquad (1)$$

with the conditions that ψ, the wave function or eigenfunction, be everywhere continuous, single-valued, and bounded. W and $V(q_k)$ are the energy constant and the potential energy; and the differential operations are with respect to coördinates whose line-element is given by

$$ds^2 = 2T\,(q_k, \dot{q}_k)\,dt^2,$$

in which T is the kinetic energy expressed as a function of the velocities. Only certain functions satisfy these requirements in any given case; to each there corresponds a characteristic value of the energy constant W. For a hydrogen-like atom with fixed nucleus of charge Ze the potential energy is $-\frac{Ze^2}{r}$, and the wave equation is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}\left(W+\frac{Ze^2}{r}\right)\psi = 0 \tag{2}$$

On writing for the eigenfunction

$$\psi_{nlm} = X_{nl}(r)\,Y_{lm}(\vartheta)\,Z_m(\varphi), \tag{3}$$

the wave equation can be resolved into three total differential equations, with the solutions (4) (19)

$$\left.\begin{aligned}
X_{nl}(r) &= \left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\,[(n+l)\,!]^3}\right\}^{\frac{1}{2}} e^{-\frac{\xi}{2}}\,\xi^l\,L^{(2l+1)}_{n+l}(\xi)\\
&\text{with}\\
\xi &= \frac{2Z}{na_0}r,\quad a_0 = \frac{h^2}{4\pi^2 me^2} = 0.529\ \text{Å}.\\
Y_{lm}(\vartheta) &= \left\{(l+\tfrac{1}{2})\frac{(l-m)\,!}{(l+m)\,!}\right\}^{\frac{1}{2}} P_l^m(\cos\vartheta)\\
Z_m(\varphi) &= \frac{1}{\sqrt{2\pi}}\,e^{im\varphi}
\end{aligned}\right\}(4)$$

$L\left({}^{2l+1}_{n+l}\right)(\xi)$ represents the $(2l+1)^{\text{th}}$ derivative of the $(n+l)^{\text{th}}$ Laguerre polynomial (20); and P_l^m $(\cos\vartheta)$ is Ferrers' associated Legendre function of the first kind, of degree l and order m. $Y_{lm}\,Z_m$ thus constitutes a tesseral harmonic (21). The ψ's are in this form orthogonal and normalized, so that they fulfill the conditions

$$\int \psi_{nlm}\,\psi_{n'l'm'}\,d\Omega = \begin{cases}1 \text{ for } n = n',\ l = l',\ m = m'\\ 0 \text{ otherwise}\end{cases} \tag{5}$$

in which $d\Omega$ is the element of volume. The parameter n, the principal quantum number, can assume the values 1, 2, 3, . . . ;

l, the analogue of the azimuthal quantum number, the values 0, 1, 2, . . . n–1; and m, the magnetic quantum number, the values 0, $\pm$ 1, $\pm$ 2, . . . $\pm l$.

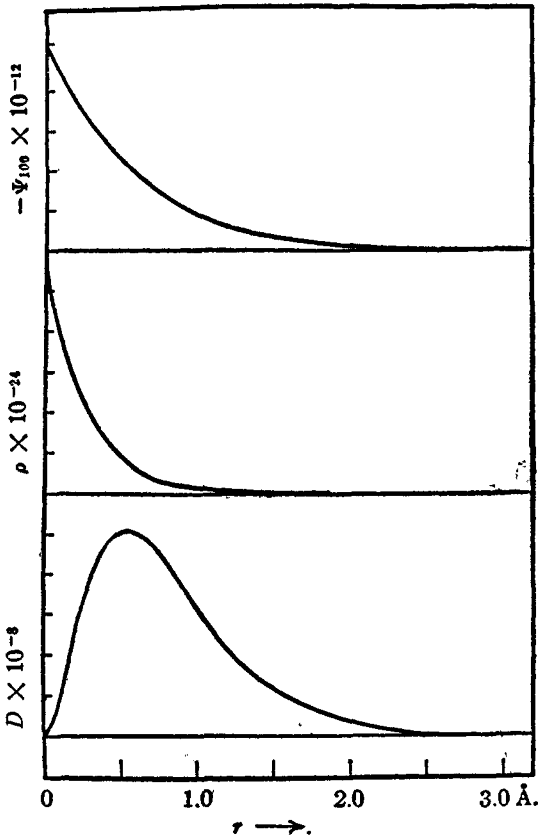

FIG. 3

The eigenfunction ψ_{100}, the electron density $\rho = \psi^2_{100}$, and the electron distribution function $D = 4\pi r^2 \rho$ of the normal hydrogen atom as functions of the distance r from the nucleus.

The normal state of the atom is that with $n = 1, l = 0, m = 0$. The corresponding eigenfunction is

$$\psi_{100} = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{\xi}{2}} \qquad (6)$$

The quantity ψ^2 as a function of the coördinates is interpreted as the probability of the corresponding microscopic state of the system; in this case the probability that the electron occupies a certain position relative to the nucleus. It is seen from equation 6 that in the normal state the hydrogen atom is spherically symmetrical, for ψ_{100} is a function of r alone. The atom is furthermore not bounded, but extends to infinity; the major portion is, however, within a radius of about $2a_o$ or 1Å. In figure 3 are represented the eigenfunction ψ_{100}, the average electron density $\rho = \psi^2_{100}$ and the radial electron distribution $D = 4\pi r^2\rho$ for the normal state of the hydrogen atom.

The energy values correponding to the various stationary states are found from the wave equation to be those deduced originally by Bohr with the old quantum theory; namely,

$$W_{nlm} = -\frac{2\pi^2 m e^4 Z^2}{n^2 h^2} = -\frac{Z^2 e^2}{2 n^2 a_o}. \tag{7}$$

The energy of the normal state of hydrogen is

$$W_H = -\frac{e^2}{2 a_o} = -13.54 \text{ v.e.} \tag{8}$$

I_H, the ionization potential of hydrogen, accordingly is equal to 13.54 volts.

This simplified treatment does not account for the fine-structure of the hydrogen spectrum. It has been shown by Dirac (22) that the assumption that the system conform to the principles of the quantum mechanics and of the theory of relativity leads to results which are to a first approximation equivalent to attributing to each electron a spin; that is, a mechanical moment and a magnetic moment, and to assuming that the spin vector can take either one of two possible orientations in space. The existence of this spin of the electron had been previously deduced by Uhlenbeck and Goudsmit (23) from the empirical study of line spectra. This result is of particular importance for the problems of chemistry.

IV. THE PERTURBATION THEORY OF THE QUANTUM MECHANICS. THE RESONANCE PHENOMENON

The first-order perturbation theory of the quantum mechanics (4, III) is very simple when applied to a non-degenerate state of a system; that is, a state for which only one eigenfunction exists. The energy change W^1 resulting from a perturbation function f is just the quantum mechanics average of f for the state in question; i.e., it is

$$W^1 = \int f \psi^2 \, d\Omega \tag{9}$$

As an example we may calculate the energy of the helium atom in its normal state (24). Neglecting the interaction of the two electrons, each electron is in a hydrogen-like orbit, represented by equation 6; the eigenfunction of the whole atom is then ψ_{100} (1) ψ_{100} (2), where (1) and (2) signify the first and the second electron. The perturbation function is the electronic interaction $\frac{e^2}{r_{12}}$; and the perturbation energy is

$$W^1 = \int\int \frac{e^2}{r_{12}} \psi^2_{100} (1) \, \psi^2_{100} (2) \, d\Omega_1 \, d\Omega_2 \tag{10}$$

in which subscripts refer to the two electrons. This integral has the value $\frac{5}{8} \frac{Ze^2}{a_o}$. The energy of the unperturbed system was (equation 7) $- 2\frac{Z^2e^2}{2a_o} = -108.4$ v.e., giving a total energy of $- \frac{11}{4} \frac{e^2}{a_o}$ or -74.5 v.e. The experimentally determined value is -78.8 v.e. Thus the first-order approximation reduces the discrepancy from 29.6 v.e. to -4.3 v.e. A more accurate theoretical calculation (25) has led to -77.9 v.e.

If the unperturbed system is degenerate, so that several linearly independent eigenfunctions correspond to the same energy value, then a more complicated procedure must be followed. There can always be found a set of eigenfunctions (the zero$^{\text{th}}$ order eigenfunctions) such that for each the perturbation energy is given by equation 9; and the perturbation theory provides the method for finding these eigenfunctions (4, III). This result is of importance for systems containing two or more electrons. Let us consider, for example, an excited helium atom. Neglecting the interaction of the two nuclei the system may be described by saying that the electrons are in two different orbits, represented by the hydrogen-like eigenfunctions ψ and φ, say. The eigenfunction for the atom is, then, $\psi(1)\,\varphi(2)$. But on interchanging the electrons to give $\psi(2)\,\varphi(1)$ the energy of the system is unchanged, so that the system is degenerate. The perturbation theory leads to the result that the correct eigenfunctions are not $\psi(1)\,\varphi(2)$ and $\varphi(1)\,\psi(2)$, but rather

$$\Psi_S = \frac{1}{\sqrt{2}}\{\psi(1)\,\varphi(2) + \varphi(1)\,\psi(2)\} \tag{11a}$$

and

$$\Psi_A = \frac{1}{\sqrt{2}}\{\psi(1)\,\varphi(2) - \varphi(1)\,\psi(2)\} \tag{11b}$$

Ψ_S is said to be symmetric in the coördinates of the two electrons, for interchanging them leaves the eigenfunction unchanged, while Ψ_A is antisymmetric, for interchanging the electrons changes the sign of the eigenfunction.

Substitution of these eigenfunctions in equation 9 leads to the result

$$\begin{aligned} W^1{}_S &= H_{11} + H_{12} \\ W^1{}_A &= H_{11} - H_{12} \end{aligned} \tag{12}$$

with

$$\begin{aligned} H_{11} &= \int\int\int \psi^2(1)\,\varphi^2(2)\,d\Omega_1\,d\Omega_2 \\ H_{12} &= \int\int\int \psi(1)\,\varphi(1)\,\psi(2)\,\varphi(2)\,d\Omega_1\,d\Omega_2. \end{aligned}$$

If the electrons did not change positions; that is, if $\psi(1)\,\varphi(2)$ or $\varphi(1)\,\psi(2)$ were the correct eigenfunction, the perturbation energy would be H_{11} alone. The added or subtracted term H_{12} results from one electron jumping from one orbit (ψ) to the other (φ) at the same time that the other electron makes the reverse jump. For this reason $\pm H_{12}$ is called the interchange or resonance energy. This phenomenon, called the interchange or resonance phenomenon, was discovered by Heisenberg and Dirac (26).

There is no classical analogue of it save the trivial case of the resonance of two similar harmonic oscillators.

The interchange energy of electrons is in general the energy of the non-polar or shared-electron chemical bond.

V. THE PROPERTIES OF MOLECULES ACCORDING TO THE QUANTUM MECHANICS

The procedure to be followed in the theoretical discussion of the structure of molecules has been given by Born and Oppenheimer (27), who applied the perturbation theory (to the fourth order) to a system of nuclei and electrons. They showed that the electronic energy is first to be calculated for various arrangements of the nuclei fixed in space. The stable state will then be that for which the so-calculated electronic energy added to the internuclear energy is a minimum. The nuclei will then undergo oscillations about their equilibrium positions, with the electronic and nuclear energy as the restoring potential; and the molecule as a whole will undergo rotations about axes passing through its center of mass.

The justification was also given for the assumption made originally by Franck (12) that during an electron transition the nuclei retain the configuration characteristic of the initial state.

These results were true for classical mechanics and the old quantum theory, and had been assumed without proof by many people before the work of Born and Oppenheimer was published.

VI. THE HYDROGEN MOLECULE-ION

a. Numerical solution of the wave equation

The system to be considered consists of two nuclei and one electron. For generality let the nuclear charges be Z_Ae and Z_Be. From Born and Oppenheimer's results it is seen that the first step in the determination of the stationary states of the system is the evaluation of the electronic energy with the nuclei fixed an arbitrary distance apart. The wave equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}\left(W + \frac{Z_A e^2}{r_A} + \frac{Z_B e^2}{r_B}\right)\psi = 0 \qquad (13)$$

in which r_A and r_B represent the distance of the electron from nucleus A and nucleus B respectively. If elliptic coördinates ξ, η, and φ, defined by the equations

$$\left.\begin{aligned} \xi &= \frac{r_A + r_B}{r_{AB}} \\ \eta &= \frac{r_A - r_B}{r_{AB}} \\ \varphi &= \cos^{-1} \frac{\mathrm{x}}{\sqrt{\mathrm{x}^2 + \mathrm{y}^2}} \end{aligned}\right\} \quad (14)$$

in which r_{AB} in the internuclear distance, be introduced, the partial differential equation becomes separable into three total differential equations. For introducing

$$\psi = \Xi\,(\xi)\ \mathrm{H}\,(\eta)\ \Phi\,(\varphi), \quad (15)$$

it reduces to

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\varphi^2} = m^2\,\Phi \quad (16a)$$

$$\frac{\mathrm{d}}{\mathrm{d}\xi}\left[(\xi^2 - 1)\,\frac{\mathrm{d}\Xi}{\mathrm{d}\xi}\right] + \left(-\,\lambda\,\xi^2 + 2\,\rho\,\xi + \frac{m^2}{\xi^2 - 1} + \mu\right)\Xi = 0 \quad (16b)$$

$$\text{with}\quad 1 \leqq \xi \leqq \infty$$

and

$$\frac{\mathrm{d}}{\mathrm{d}\eta}\left[(1 - \eta^2)\,\frac{\mathrm{dH}}{\mathrm{d}\eta}\right] + \left(\lambda\eta^2 - 2\,\mathrm{b}\eta + \frac{m^2}{1 - \eta^2} - \mu\right)\mathrm{H} = 0 \quad (16c)$$

$$\text{with}\quad -1 \leqq \eta \leqq +1$$

in which

$$\lambda = -\,\frac{2\,\pi^2\,m\,r_{AB}^2\,W}{h^2} = \rho^2\,\frac{W}{4\,W_H}$$

$$\rho = \frac{r_{AB}\,(Z_A + Z_B)}{2\,a_0}$$

$$\mathrm{b} = \frac{r_{AB}\,(Z_A - Z_B)}{2\,a_0}\,.$$

and m, λ, and μ are undetermined parameters. The solutions of Equation 16a are known; in order that Φ be an eigenfunction m must assume only the values 0, ± 1, ± 2, . . . Similarly in order for Ξ and H to be eigenfunctions λ and μ must assume specific values, with the accompanying determination of the energy constant W as a function of the nuclear separation r_{AB}.

Many efforts have been made to solve these equations analytically, but so far they have all been unsuccessful, and little has been published regarding them. Some unsatisfactory work has been reported by Alexandrow (28). Very recently a short report of a paper read by Wilson before the Royal Society has appeared (29). It is probable, in view of the vigor with which it is being attacked, that the problem will be solved completely before very long.

The problem has already been solved for the normal state of the hydrogen molecule-ion ($Z_A = Z_B = 1$) by the use of numerical methods. A rather complete account of these calculations of Burrau (30) will be given here, since the journal in which they were published is often not available.

The numerical solution of the equations was carried out in the following way. For the lowest state m is equal to 0, and for hydrogen, with $Z_A = Z_B = 1$, b = 0. Introducing new variables $\sigma_\xi = -\frac{1}{\Xi}\frac{d\Xi}{d\xi}$ and $\sigma_\eta = -\frac{1}{H}\frac{dH}{d\eta}$, Equations 16b and 16c become

$$\frac{d\sigma_\xi}{d\xi} = \sigma_\xi^2 - \frac{\lambda\xi^2 - 2(\rho - \sigma_\xi)\xi - \mu}{\xi^2 - 1} \qquad (16b')$$

and

$$\frac{d\sigma_\eta}{d\eta} = \sigma_\eta^2 - \frac{\lambda\eta^2 + 2\sigma_\eta\eta - \mu}{1 - \eta^2}. \qquad (16c')$$

For a given value of λ, σ_η is expanded as a power series satisfying Equation 16c′ about the points $\eta = 0$ and $\eta = 1$ (or -1). It is found that these series coincide at $\eta = 1/2$ only when μ has a certain value. In this way a relation between λ and μ is found.

For each value of μ a similar treatment is given Equation 16b′, resulting in the determination of the corresponding value of ρ, and hence of the relation between W and ρ. The results of the calculation are given in table 2, taken directly from Burrau. The electronic energy is given in the third column. To it must be added the internuclear energy $\frac{e^2}{r_{AB}} = -\frac{2W_H}{\rho}$ (fourth column) to obtain the total energy given in the fifth column.

The relation between W and ρ is shown in figure 4; that for W_{total} in figure 5. It is seen that the equilibrium distance of the nuclei is $\rho = 2.0 \pm 0.1$, or $r_0 = 1.06 \pm 0.05$ Å. The corresponding total energy is $W_{total} = 1.204 \pm 0.002\ W_H$ or -16.30 ± 0.03 v.e. To this there is to be added the oscillational energy $\frac{1}{2}h\omega_0$ of the lowest oscillational state. The frequency ω_0 is obtained from the curvature of the W_{total} curve, and leads to $\frac{1}{2}h\omega_0 = 0.14$ v.e. according to Condon, who corrected an error made by Burrau (Condon's value is reported by Birge (7)). The energy of H_2^+ in the normal state is thus

TABLE 2

Energy of the hydrogen molecule-ion

ρ	λ	$\frac{W}{W_H} = \frac{4\lambda}{\rho^2}$	$\frac{2}{\rho}$	$\frac{W_{total}}{W_H}$
0.0	0.000	4.000	∞	∞
1.0	0.724	2.896	2.000	0.896
1.3	1.119	2.648	1.538	1.110
1.6	1.559	2.436	1.250	1.186
1.8	1.870	2.309	1.111	1.198
2.0	2.204	2.204	1.000	1.204
2.2	2.552	2.109	0.909	1.200
2.4	2.917	2.025	0.833	1.192
2.95	3.995	1.836	0.678	1.158
∞		1.000	0.000	1.000

$$W_{H_2^+} = -16.16 \pm 0.03 \text{ v.e.}$$

It is now possible to check the relation

$$I_{H_2} + I_{H_2^+} = D'_{H_2} + 2\ I_H,$$

in which D'_{H_2} is the dissociation potential of hydrogen. With $I_{H_2} = +15.34$ v. (Section 2), and $I_H = +13.54$ v. This equation leads to

$$D_{H_2} = 4.42 \text{ v.e.} = 102000 \text{ cal/mol.}$$

for the energy of dissociation of the hydrogen molecule. This is within the limit of error equal to the band spectrum value 4.34 ± 0.10 v.e., and is to be accepted as the most accurate determination of the heat of dissociation of hydrogen.

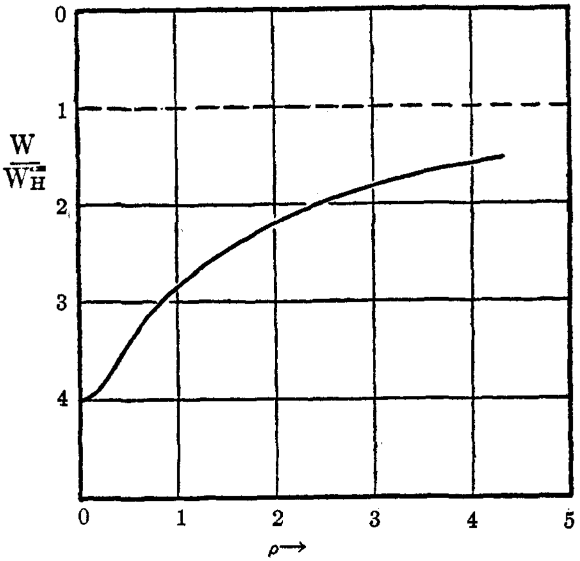

FIG. 4. THE ELECTRONIC ENERGY OF THE HYDROGEN MOLECULE-ION IN THE NORMAL STATE AS A FUNCTION OF THE DISTANCE BETWEEN THE TWO NUCLEI (BURRAU)

The heat of dissociation of H_2^+ into H and H^+ is

$$D_{H_2^+} = W_H - W_{H_2^+} = 2.62 \text{ v.e.}$$

No direct determination of this quantity has been made.

The value 2247 cm^{-1} for ω_0 for H_2^+ obtained by Birge (table 1) leads to $\frac{1}{2}h\omega_0 = 0.141$ v.e., in very good agreement with the theoretical 0.14 v.e.

The average electron density ψ^2 as a function of position was also found by Burrau. For the normal state ψ^2 is represented in figure 6, in which the contour lines pass through points of relative density 1.0, 0.9, 0.8, . . . 0.1. The second curve represents the values of ψ^2 along the line passing through the two nuclei. (ψ^2 is cylindrically symmetrical about this line). It will be seen that the electron is most of the time in the region between the two nuclei, and can be considered as belonging to them both, and forming a bond between them.

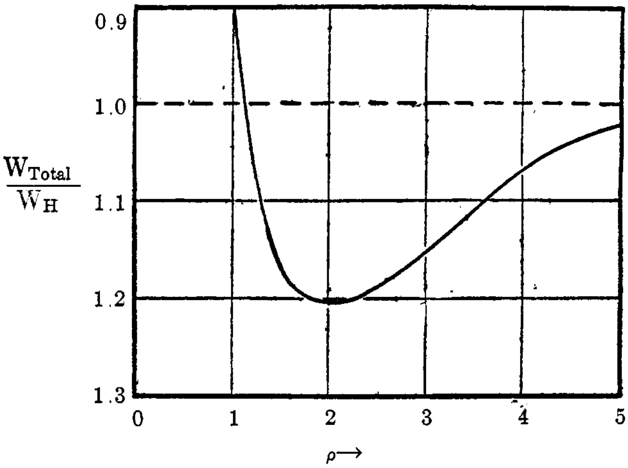

FIG. 5. THE TOTAL ENERGY OF THE HYDROGEN MOLECULE-ION AS A FUNCTION OF ρ (BURRAU)

b. Application of the first-order perturbation theory

Although no new numerical information regarding the hydrogen molecule-ion can be obtained by treating the wave equation by perturbation methods, nevertheless it is of value to do this. For perturbation methods can be applied to many systems for which the wave equation can not be accurately solved, and it is desirable to have some idea of the accuracy of the treatment. This can be gained from a comparison of the results of the perturbation method of the hydrogen molecule-ion and of Burrau's accurate numerical solution. The perturbation treatment assists, moreover, in the physical interpretation of the forces operative in the formation of the ion; for the electronic energy is obtained as the sum of terms each of which can be related without difficulty to a visualisable process of interaction of the nuclei and the electron.

A hydrogen atom and a proton serve as the starting point of the calculation. With the nuclei a distance r_{AB} apart, and with the electron attached to the nucleus A to form a hydrogen atom, the zero$^{\text{th}}$ order eigenfunction is

$$\psi = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{\xi_A}{2}},\ \xi_A = \frac{2\,Z_A}{a_0}\, r_A \tag{17a}$$

and the action of nucleus B on the electron is the perturbation.

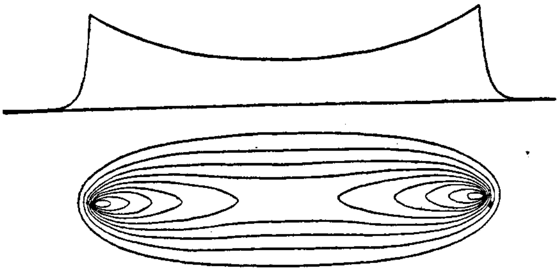

FIG. 6. THE ELECTRON DENSITY ψ^2 FOR THE HYDROGEN MOLECULE-ION IN THE NORMAL STATE (BURRAU)

The contour lines represent in section places of relative density 1.0, 0.9, 0.8, . .0.1. The density at points along a line drawn through the nuclei is given above.

But the configuration with the electron on nucleus B and with the eigenfunction

$$\varphi = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{\xi_B}{2}},\ \xi_B = \frac{2\,Z_B}{a_0}\, r_B \tag{17b}$$

corresponds to the same energy. The unperturbed system is thus degenerate. There is, however, no perturbation function for the system as a whole, for in each case the interaction between the electron and the more distant nucleus produces the perturbation; and accordingly the usual theory for degenerate systems cannot be directly applied. It is instead found that on carrying out the treatment used in the derivation of the ordinary perturbation theory closely similar results are obtained. The correct zero$^{\text{th}}$ order eigenfunctions are linear aggregates of ψ and φ, and are, indeed, symmetric and antisymmetric in the two nuclei; they are

$$\Psi = \frac{1}{\sqrt{2 + 2\,S}}\,(\psi + \varphi) \tag{18a}$$

and

$$\Phi = \frac{1}{\sqrt{2 - 2\,S}}\,(\psi - \varphi) \tag{18b}$$

with

$$S = \int \psi\,\varphi\,\mathrm{d}\Omega = \mathrm{e}^{-\rho}\,(1 + \rho + \tfrac{1}{3}\,\rho^2), \tag{19a}$$

in which

$$\rho = \frac{Z}{a_0}\,r_{AB}, \text{ assuming } Z_A = Z_B = Z.$$

The radicals in the denominators are necessary in order that the new eigenfunctions be normalized. The wave equation (Equation 13) can now be written

$$\Delta\psi + \frac{8\pi^2 m}{h^2}\left(W_{\mathrm{H}} + W^1 + \frac{Z_A\,e^2}{r_A} + \frac{Z_B\,e^2}{r_B}\right)\psi = 0, \tag{20}$$

in which W^1 is the perturbation energy. It is found (see Heitler and London (39) for the detailed treatment of a similar problem) that the perturbation energy for the eigenfunction Ψ is given by the solution of the equation

$$\int \Psi \left\{\Delta\Psi + \frac{8\pi^2 m}{h^2}\left(W_{\mathrm{H}} + W^1 + \frac{Z\,e^2}{r_A} + \frac{Z\,e^2}{r_B}\right)\Psi\right\} \mathrm{d}\Omega = 0 \tag{21}$$

This leads to the result

$$W^1 = -\,e^2\,\frac{I_1 + I_2}{1 + S} \tag{22}$$

in which

$$I_1 = \int \frac{\psi^2}{r_A}\, d\Omega = \frac{Z}{a_0}\left\{\frac{1}{\rho} - e^{-2\rho}\left(1 + \frac{1}{\rho}\right)\right\} \tag{19b}$$

and

$$I_2 = \int \frac{\psi\,\varphi}{r_A}\, d\Omega = \frac{Z}{a_0}\, e^{-\rho}\,(1 + \rho). \tag{19c}$$

The total energy, including the internuclear term, is then

$$W_{\text{Total}} = W_H - e^2\,\frac{I_1 + I_2}{1 + S} + \frac{e^2}{r_{AB}} \tag{23}$$

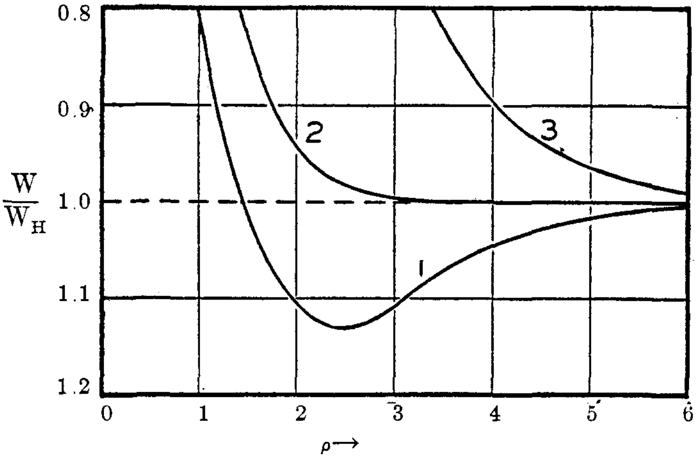

FIG. 7.

Curve 1 represents the total energy of the hydrogen molecule-ion as calculated by the first-order perturbation theory; curve 2, the naïve potential function obtained on neglecting the resonance phenomenon; curve 3, the potential function for the antisymmetric eigenfunction, leading to elastic collision.

In figure 7 is shown the so-calculated total energy W_{total} for H_2^+ as a function of ρ. Comparison with figure 5 shows that the perturbation curve is too high; the force holding the ion together is too small. Equilibrium occurs at $\rho = 2.5$ or $r_0 = 1.32$ Å (correct value, 1.06 Å), and the energy of the ion is then -15.30 v.e. (correct value, -16.30 v.e.).

The eigenfunction Ψ is represented qualitatively by figure 6, but is somewhat more extended, for the contracting influence of the second nucleus has not been taken into account.

It is of interest to calculate the energy corresponding to the single eigenfunction ψ (or φ); i.e., to find the interaction of a proton and a hydrogen atom that would result if the electron were not allowed to jump from one nucleus to the other. For this case

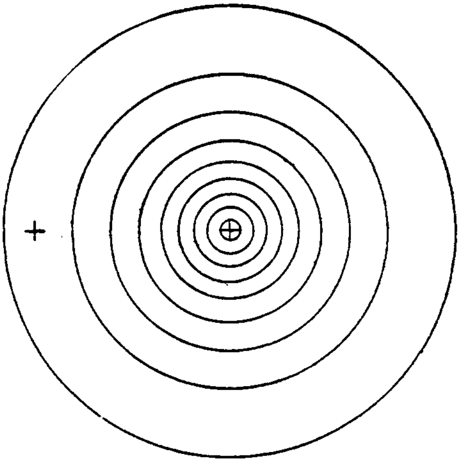

FIG. 8

The contour lines represent points of relative density 1.0, 0.9, 0.8,..0.1 for a hydrogen atom. This figure, with the added proton 1.06 Å from the atom, gives the electron distribution the hydrogen molecule-ion would have (in the zeroth approximation) if the resonance phenomenon did not occur; it is to be compared with figure 6 to show the effect of resonance.

$$W^1 = -e^2 I_1$$

and

$$W_{\text{Total}} = W_{\text{H}} - e^2 I_1 + \frac{e^2}{r_{AB}}. \tag{24}$$

(The perturbation energy is here just the electrostatic energy calculated for the electron distribution given by ψ^2; it is in part this feature of the perturbation theory which led Schrödinger to proclaim that the electron is smeared through space, and which supports the present interpretation of ψ^2 as the probability that the electron will be in the selected region.) This naïve potential is also represented in figure 7. It leads to a repulsive force at all distances. The correct perturbation calculation given in Equation 23 differs from the naïve one in that it involves consideration of the interchange or resonance phenomenon, and leads to an attraction, giving an energy of formation of H_2^+ of about 1.62 v.e. (correct result from Burrau, 2.62 v.e.). We thus see that the fact that the electron can jump from one nucleus to the other—in other words, is shared between the two nuclei— is mainly responsible for the formation of the molecule-ion H_2^+ from H^+ and H. The way the electron distribution is affected by the resonance phenomenon is seen by comparing figure 6 with figure 8, which shows contour lines (of electron density ψ^2) for a hydrogen atom and a proton at the distance $\rho = 2$ (1.06 Å). This comparison is particularly effective in showing that the sharing of the electron between the two nuclei results from the resonance phenomenon.

This resonance energy leads to molecule formation only if the eigenfunction is symmetric in the two nuclei. The perturbation energy for the antisymmetric eigenfunction Φ is

$$W_A^1 = -e^2 \frac{I_1 - I_2}{1 - S}, \tag{25}$$

and the total energy,

$$W_{A\ \mathrm{Total}} = W_{\mathrm{H}} - e^2 \frac{I_1 - I_2}{1 - S} + \frac{e^2}{r_{AB}}, \tag{26}$$

also shown in figure 7, leads to strong repulsion at all distances. This eigenfunction does not, then, give rise to a stable excited state of the hydrogen molecule-ion. Stable excited states will, however, correspond to the symmetric eigenfunctions relating to the various excited states of the hydrogen atom; and in each case (at least until deformation becomes very pronounced) not to the antisymmetric eigenfunctions. This is contrary to the qualitative scheme of levels given by Hund (31), who in a series of papers

(32) has considered the application of the quantum mechanics to molecules in general, with particular reference to molecular spectra.

The above perturbation treatment of the hydrogen molecule-ion has not before been published.

c. The second-order perturbation calculation

An attempt was made by Unsöld (33) to evaluate to the second-order the interaction of a proton and a hydrogen atom. He found, neglecting the resonance phenomenon, that the second-order perturbation energy is given approximately by the expression

$$W^2 = -\frac{9e^2}{4a_0}\left\{\frac{1}{\rho^4} + e^{-2\rho}\left(-\frac{4}{3}\rho + 2 + \frac{4}{3\rho} + \frac{1}{\rho^2} + \frac{2}{\rho^3} + \frac{1}{\rho^4}\right) - e^{-4\rho}\left(1 + \frac{2}{\rho} + \frac{1}{\rho^2}\right) + \frac{8}{3}\rho^2 \mathrm{E_i}(-2\rho)\right\}, \qquad (27)$$

in which $\mathrm{E_i}(-2\rho)$ represents the integral logarithm with the argument -2ρ. This expression is accurate for large values of ρ; for it then reduces to $-\frac{1}{2}\frac{e^2\alpha}{r^4_{AB}}$, in which α, the polarizability of a hydrogen atom, has the value 0.667×10^{-24} deduced from the second-order Stark effect energy (34).

Using this expression and the value given in Equation 24 for the first-order perturbation, Unsöld found that equilibrium would occur at $\rho = 1$, $r_0 = 0.53$ Å; and that the electronic energy of the hydrogen molecule-ion would then be $-1.205\ W_H$, or -16.31 v.e., in exact agreement with Burrau's value. This agreement is, however, misleading, and indeed the calculation is of no significance, for Unsöld neglected to consider the resonance phenomenon, making use instead of the naïve first-order perturbation. We may, however, attempt to rectify this by adding the second-order energy W^2 to the correct first-order energy of Equation 23. When this is done it is found that equilibrium occurs at $\rho = 1.2$, $r_0 = 0.64$ Å, and that the energy then is -17.95 v.e.

The results of Burrau's calculation, of the first-order perturbation treatment, and of the second-order treatment are given in table 3.

It will be seen that the second-order treatment leads to results which deviate more from the correct values than do those given by the first-order treatment alone. This is due in part to the fact that the second-order energy was derived without consideration of the resonance phenomenon, and is probably in error for that reason. The third-order energy is also no doubt appreciable. It can be concluded from table 3 that the first-order perturbation calculation in problems of this type will usually lead to rather good results, and that in general the second-order term need not be evaluated.

TABLE 3

The properties of the hydrogen molecule-ion

	ρ	r_0	$W_{H_2^+}$
Burrau	2.0	1.06Å	−16.30v.e.
First-order	2.5	1.32	−15.30
Second-order	1.2	0.64	−17.95

In dealing with problems of molecular structure it has been customary in the past to introduce the energy of polarization of one atom or ion by another ion in the form $-\frac{1}{2}\frac{e^2\alpha}{r^4_{AB}}$, and to give α the value it possesses in a uniform field. The form of Equation 27 shows that this is not a good representation of the polarization energy, for it gives values which are much too large at small distances. Indeed, if we attach this term to the first-order energy of Equation 23, it is found that the correct equilibrium distance $r_0 = 1.06$ Å results only if α be placed equal to 0.032×10^{-24}, which is only 5 per cent of the true polarizability of hydrogen. This indicates that in general better results will be obtained in the theoretical treatment of the structure of molecules by ignoring polarization completely than by introducing the usual expression for the polarization. As a matter of fact, it has already been pointed out by Fajans (35) that the experimental values of the heat of sublimation of the alkali halides agree better with those calculated by Reis (36), who neglected polarization, than with those of Born and Heisenberg (37), who took it into consideration. As a result of this it is probable that the numerous discussions of molecular structure based on polarization (38) are of only limited significance.

VII. THE HYDROGEN MOLECULE

a. Perturbation treatment of the interaction of two hydrogen atoms

The most satisfactory treatment which has been given the structure of the hydrogen molecule is that of Heitler and London

FIG. 9. DIAGRAMMATIC REPRESENTATION OF THE EIGENFUNCTIONS FOR TWO HYDROGEN ATOMS

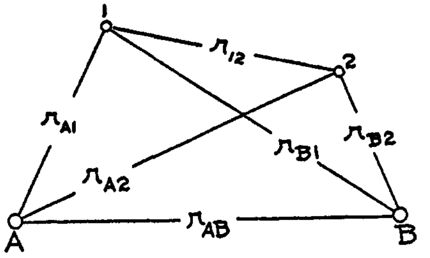

FIG. 10. DIAGRAM SHOWING THE SYMBOLS USED FOR THE VARIOUS INTERNUCLEAR AND INTERELECTRONIC DISTANCES

(39). The system to be treated consists of two nuclei A and B and two electrons 1 and 2. In the unperturbed state two hydrogen atoms are assumed, so that the zero$^{\text{th}}$-order energy is $2W_{\text{H}}$. If the first electron is attached to nucleus A and the second to nucleus B, the zero$^{\text{th}}$-order eigenfunction is $\psi\,(1)\,\varphi\,(2)$, in which ψ and φ are the functions given in Equations 17a and 17b. The state obtained by interchanging the two electrons, $\varphi\,(1)\,\psi(2)$, corresponds to the same zero$^{\text{th}}$-order energy, so that the system is degenerate, and must be treated in a way similar to that applied to the hydrogen molecule-ion in Section VIb.

The wave equation for the hydrogen molecule with fixed nuclei is

$$\Delta_1 \psi + \Delta_2 \psi + \frac{8\pi^2 m}{h^2}\left\{2\,W_{\mathrm{H}} + W^1 + \frac{e^2}{r_{A_1}} + \frac{e^2}{r_{B_1}} + \frac{e^2}{r_{A_2}} + \frac{e^2}{r_{B_2}} - \frac{e^2}{r_{12}} - \frac{e^2}{r_{AB}}\right\}\psi = 0 \qquad (28)$$

in which Δ_1 and Δ_2 represent the second differential operations with respect to the coördinates of the first and the second electron respectively, and the various r's refer to the distances indicated in figure 10. The correct zero$^{\mathrm{th}}$-order eigenfunctions are found by the procedure of Section VIb to be the symmetric

$$\Psi_{\mathrm{H}_2} = \frac{1}{\sqrt{2 + 2\,S^2}}\,\{\psi(1)\,\varphi(2) + \varphi(1)\,\psi(2)\} \qquad (29a)$$

and the antisymmetric

$$\Phi_{\mathrm{H}_2} = \frac{1}{\sqrt{2 - 2\,S^2}}\,\{\psi(1)\,\varphi(2) - \varphi(1)\,\psi(2)\} \qquad (29b)$$

in which S is given by Equation 19a.

In this case, too, molecule formation results from the symmetric eigenfunction. The corresponding perturbation energy W^1 is obtained from an equation of the type of Equation 20 involving Ψ_{H_2} and the wave equation 28. It is

$$W^1 = \frac{e^2}{1 + S^2}\left\{\frac{1 + S^2}{r_{AB}} + I_4 + I_6 - 2\,I_1 - 2\,SI_2\right\} \qquad (30)$$

in which I_1 and I_2 are given by Equations 19b and 19c, and I_4 and I_6 by

$$I_4 = \iint \frac{\psi^2(1)\,\varphi^2(2)}{r_{12}}\,d\Omega_1\,d\Omega_2 = \frac{Z}{a_0}\left\{\frac{1}{\rho} - e^{-2\rho}\left(\frac{1}{\rho} + \frac{11}{8} + \frac{3}{4}\rho + \frac{1}{6}\rho^2\right)\right\} \qquad (19d)$$

and

$$I_6 = \iint \frac{\psi(1)\,\varphi(1)\,\psi(2)\,\varphi(2)}{r_{12}}\,d\Omega_1\,d\Omega_2$$

$$= \frac{Z}{5a_0}\left[- e^{-2\rho}\left(- \frac{25}{8} + \frac{23}{4}\rho + 3\rho^2 + \frac{1}{3}\rho^3\right)\right. \qquad (31)$$

$$\left. + \frac{6}{\rho}\left\{S^2(\gamma + \log \rho) + S'^2\,\mathrm{Ei}(-4\rho) - 2SS'\,\mathrm{Ei}(-2\rho)\right\}\right], \qquad (19e)$$

in which $\gamma = 0.5772$ . . is Euler's constant, and $S' = e^{\rho}(1 - \rho + \frac{1}{3}\rho^2)$.

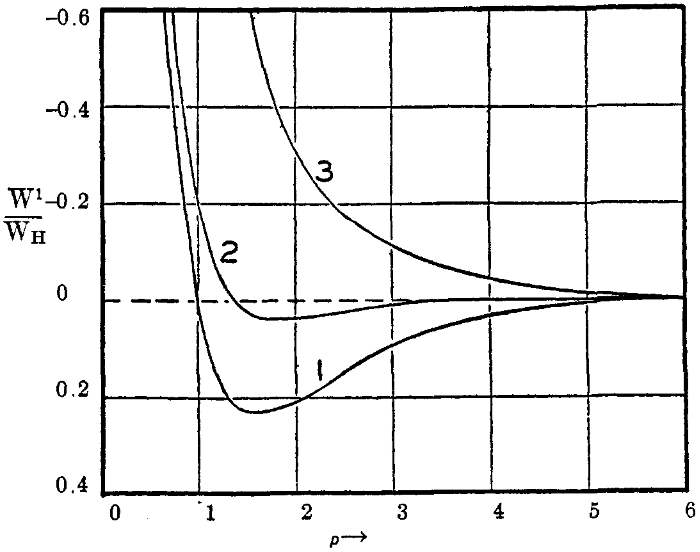

Fig. 11

Curve 1 shows the total energy for the normal state of the hydrogen molecule as given by the first-order perturbation theory; curve 2, the naïve potential function obtained by neglecting the resonance phenomenon; and curve 3, the potential function for the antisymmetric eigenfunction, corresponding to elastic collision.

The energy W^1 depends largely on the integral I_6, for which Heitler and London gave only an approximation. The difficult problem of carrying out this integration was solved by Sugiura (40), whose result is given in Equation 19e. W^1 is shown as a function of ρ in figure 11. It has a minimum at the equilibrium distance $\rho = 1.5$, at which $W^1 = -3.1$ v.e. The comparison of theory and experiment for the hydrogen molecule is shown in table 4. The general agreement is entirely satisfactory in view of the fact that only the first-order perturbation calculation has been made.

It is worthy of mention that the perturbation terms are actually larger than appears from W^1. Thus at $\rho = 1.5$ the term $\frac{e^2}{r_{AB}}$ has the value 18.1 v.e., so that the electronic perturbation energy is −21.3 v.e., which is to be compared with the experimental value −22.5 v.e. It is seen that the electronic perturbation energy is thus in error by only 5 per cent. Furthermore, we saw in Section VIb that the first-order perturbation calculation for the hydrogen molecule-ion gave an energy of dissociation of H_2^+ of 1.62 v.e., which is 1 v.e. smaller than Burrau's correct value. A similar error is to be expected for the hydrogen molecule; and, as a matter of fact, the calculated energy of dissociation is here 1.2 v.e. too small. We are hence justified in the belief that the accurate theoretical treatment of the hydrogen molecule would give results in complete agreement with experiment.

TABLE 4

Properties of the hydrogen molecule

	r_0	I_0	D_{H_2}	ω_0
Calculated....	0.80 Å	0.53×10^{-40} g. cm.^{2}	3.2 v.e.	4800 cm.$^{-1}$
Observed............	0.76	0.48	4.42	4262

By bringing the nuclei into coincidence a helium atom in the normal state is formed; and a value for its energy can be obtained from the expression for the hydrogen molecule by neglecting the internuclear energy and by putting $\rho = 0$. It is found that $W_{He} = -\frac{19}{8} e^2/a_0 = -64.3$ v.e., which lies considerably above the experimental value −78.8 v.e.; the error is in the same direction as that for $D_{H_2^+}$. A similar limiting calculation for the hydrogen molecule-ion gives $W_{He^+} = -3e^2/2a_0 = -40.6$ v.e., instead of the correct value $-4W_H = -54.16$ v.e. Thus for both He and He^+ this perturbation treatment is inaccurate. The treatment gives, however, 64.3 − 40.6 = 23.7 v. for the first ionisation potential of helium, which is in good agreement with the experimental 24.6 v. This agreement was adduced by Suguira as evidence of the accuracy of the perturbation treatment; but it is merely accidental.

If ψ (1) φ (2) or φ (1) ψ (2) alone were to be considered, the perturbation energy would be the electrostatic energy of two nuclei and two electrons distributed according to the probability functions ψ^2 and φ^2; namely,

$$W^1 = e^2 \left\{\frac{1}{r_{AB}} + I_4 - 2\, I_1\right\} = \frac{e^2}{a_0}\, e^{-2\rho} \left(\frac{1}{\rho} + \frac{5}{8} - \frac{3}{4}\rho - \frac{1}{6}\rho^2\right) \quad (31)$$

This, the naïve potential function, is also shown in figure 11. It corresponds to a relatively small attraction, so that the conclusion can be drawn that in the hydrogen molecule the interchange energy of the two electrons is the principal cause of the forces leading to molecule formation.

b. The application to the hydrogen molecule of Burrau's numerical solution for the molecule-ion

If the interaction of the two electrons in the hydrogen molecule were small it could be neglected with respect to the electronic-nuclear interaction. Each electron would then be represented by an H_2^+ eigenfunction, and the electronic energy would be just twice that calculated by Burrau. The interelectronic energy could then be calculated as a perturbation; this would necessitate, however, a knowledge of Burrau's eigenfunctions in a form suitable for integration.

Lacking this knowledge, Condon (41) made use of the following semi-empirical method. The electronic energy of the helium atom is raised from $-4\ e^2/a_0 = -108.32$ v.e. (Burrau's value) to −78.8 v.e. (the experimental value) by the electronic interaction. If it be assumed that the interelectronic energy is to be raised to the same fractional value of the Burrau energy throughout the region corresponding to the normal state of the hydrogen molecule, there is obtained the electronic energy function shown in figure 12. Adding to this the electronic energy e^2/r_{AB}, it is found that equilibrium occurs at $r_0 = 0.73$ Å, with $D_{H_2} = 4.3$ or 4.4 v.e. and $\omega_0 = 7600$ cm.$^{-1}$. These values, except for ω_0, are in excellent agreement with the experimental ones.

This treatment is, however, of less significance than that of the preceding section, for it is more arbitrary and less confidence can be placed in it. In the first place, the interelectronic forces are not small, and it is to be expected that they will cause the electrons to tend to remain on different atoms, as is assumed in the previous treatment of Heitler and London. The assumption that the total electronic energy as calculated by Burrau should be reduced in a constant ratio is, moreover, without justification. It is definitely incorrect for ρ large; for the doubled Burrau energy then approaches the correct value $2W_H$. An assumption which might just as well be made and which is satisfactory both for $\rho = 0$ and for $\rho = \infty$ is that the difference between the doubled Burrau energy and $2W_H$ is to be reduced in a constant ratio; but it leads to the incorrect values $D_{H_2} = 8.0$ v.e. and $r_0 = 0.90$ Å.

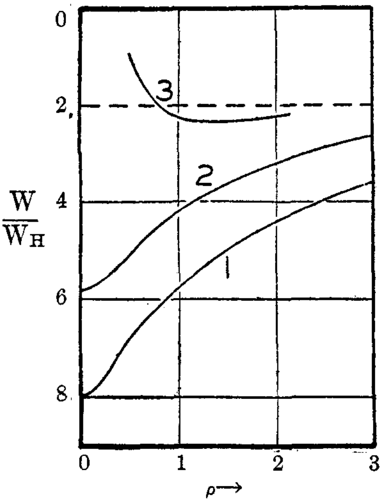

Fig. 12

Curve 1 shows the electronic energy of the hydrogen molecule neglecting interelectronic interaction (from Burrau's solution for the molecule-ion); curve 2, the electronic energy empirically corrected by Condon's method; and curve 3, the total energy of the hydrogen molecule, calculated by Condon's method.

c. The excited states of the hydrogen molecule

Excited states of the hydrogen molecule may be formed from a normal hydrogen atom and a hydrogen atom in various excited states.[2] For these the interelectronic interaction will be small, and the Burrau eigenfunction will represent the molecule in part with considerable accuracy. The properties of the molecule, in particular the equilibrium distance, should then approximate those of the molecule-ion; for the molecule will be essentially a molecule-ion with an added electron in an outer orbit. This is observed in general; the equilibrium distances for all known excited states but one (the second state in table 1) deviate by less than 10 per cent from that for the molecule-ion. It is hence probable that states 3, 4, 5, and 6 are formed from a normal and an excited atom with $n = 2$, and that higher states are similarly formed.

The exceptional state B has a very large equilibrium distance and small oscillational frequency, as has been pointed out by Birge (7). This suggests that the molecule is here not non-polar, but is a polar compound of H^+ and H^-. The electron affinity of hydrogen is probably negative, (about -1 kcal/mole (42)), and it is doubtful that a free negative hydrogen ion in the normal state can exist. The presence of another proton would, however, stabilize the structure, so that a polar hydrogen molecule could be formed. The unperturbed system is again degenerate, for both electrons may be attached to nucleus A or to nucleus B. The zero$^{\text{th}}$-order eigenfunction representing the most stable polar state of the molecule is

$$\frac{1}{\sqrt{2 + 2\,S^2}}\,\{\,\varphi(1)\,\varphi(2) + \psi(1)\,\psi(2)\}. \qquad (32)$$

The first-order perturbation theory in this case does not give good results, since the mutual interaction of two electrons on one nucleus is so large as to greatly deform the eigenfunctions; it leads

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[2] The calculation of the potential function for these states with the use of the method of Heitler and London is being made by Prof. E. C. Kemble (private communication to Dr. J. R. Oppenheimer).

to an equilibrium distance of about 1Å and an energy about 5 v.e. greater than the normal state. There is no energy level of the molecule in this region. The attempt to take into account the effect of deformation has led to the conclusion that both r_0 and the energy should be increased to values compatible with those observed for the first excited state B. Since a polar state is to be expected in this region and since B has properties explicable on this basis but not otherwise, the identification of the two may be made with some certainty.

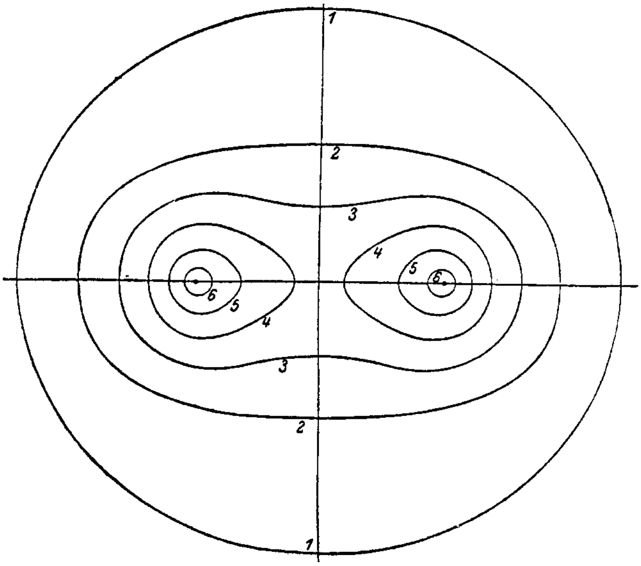

FIG. 13. QUALITATIVE REPRESENTATION BY CONTOURS OF ELECTRON DISTRIBUTION FOR TWO HYDROGEN ATOMS UNITING TO FORM A MOLECULE (LONDON)

We shall next consider whether or not the antisymmetric eigenfunction Φ_{H_2} for two hydrogen atoms (Equation 29b) would lead to an excited state of the hydrogen molecule. The perturbation energy is found to be

$$W^1 = \frac{e^2}{1 - S^2}\left\{\frac{1 - S^2}{r_{AB}} + I_4 - I_6 - 2\,I_1 + 2\,SI_2\right\} \tag{33}$$

This potential differs from that of Equation 30 in that the interchange energy has the opposite sign (and slightly different magnitude). As a result it corresponds to repulsion between the two atoms at all distances, and not to a stable state of the molecule (see figure 11). This result, which had been suggested as a possibility by Hund (31), was proved by Heitler and London. The existence of two potential functions representing the interaction of two normal hydrogen atoms is very remarkable and has, I believe, no classical interpretation. A certain feeling for the phenomenon results from the study of the distribution of the two electrons in the two cases (London, 46). In figure 13, representing the two hydrogen atoms in the process of forming a molecule, it is seen that the electrons tend to assume positions between the two nuclei, and form a bond between them—the shared electron-pair. But if the potential function represents elastic collision (the antisymmetric eigenfunction) the electrons take up positions on the outer sides of the atoms (fig. 14), with the result that the strong internuclear repulsion becomes effective.

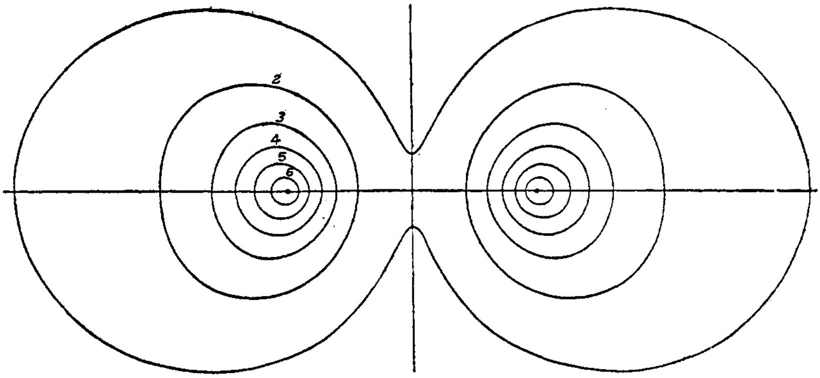

FIG. 14. THE ELECTRON DISTRIBUTION FOR TWO HYDROGEN ATOMS IN ELASTIC COLLISION (LONDON)

VIII. THE PAULI EXCLUSION PRINCIPLE. THE INTERACTION OF TWO HELIUM ATOMS

It was mentioned in Section III that the fine-structure of spectra arises from a phenomenon equivalent to a first approximation to that resulting from a spin of the electron. The spin moment of the electron can assume two orientations in space, which may be represented by spin eigenfunctions α and β. In the foregoing sections discussion has been given only to eigenfunctions referring to the electronic positions. A complete eigenfunction is the product of a positional eigenfunction and a spin eigenfunction, as $\psi\,\alpha$ or $\psi\,\beta$.

The observed structure of the spectra of many-electron atoms is entirely accounted for by the following postulate: *Only eigenfunctions which are antisymmetric in the electrons; that is, change sign when any two electrons are interchanged, correspond to existant states of the system.* This is the quantum mechanics statement (26) of the Pauli exclusion principle (43).

It is equivalent to saying that two electrons cannot occupy the same orbit. Thus there is no antisymmetric eigenfunction composed of $\psi\ (1)\ \alpha\ (1)$ and $\psi\ (2)\ \alpha\ (2)$, and no such state exists (for the helium atom, say). The allowed state is $\frac{1}{\sqrt{2}}\ \{\psi\ (1)\ \alpha\ (1)\ \psi\ (2)\ \beta\ (2) - \psi\ (1)\ \beta\ (1)\ \psi\ (2)\ \alpha\ (2)\}$; that is, in the normal state of the helium atom the two electrons have oppositely directed spins. Other consequences of the exclusion principle, such as that not more than two electrons can occupy the K-shell of an atom, follow directly.

In dealing with systems containing only two electrons we have not been troubled with the exclusion principle, but have accepted both symmetric and antisymmetric positional eigenfunctions; for by multiplying by a spin eigenfunction of the proper symmetry character an antisymmetric total eigenfunction can always be obtained. In the case of two hydrogen atoms there are three symmetric spin eigenfunctions $\alpha\ (1)\ \alpha\ (2)$, $\beta\ (1)\ \beta\ (2)$, and $\frac{1}{\sqrt{2}}\ \{\alpha\ (1)\ \beta\ (2) + \beta\ (1)\ \alpha\ (2)\}$, and one antisymmetric, $\frac{1}{\sqrt{2}}\{\alpha\ (1)\ \beta\ (2) - \beta\ (1)\ \alpha\ (2)\}$. The last is required to make the symmetric positional eigenfunction Ψ_{H_2} of Equation 29a conform to Pauli's principle, and the first three for the antisymmetric Φ_{H_2}. Since the a priori probability of each eigenfunction is the same, there are three chances that two hydrogen atoms will repel each other to one that they will attract.

But if the system contains more than two electrons explicit consideration must be given the spins. This is particularly evident in the problem of the interaction of two helium atoms. There are four individual eigenfunctions $\psi\alpha$, $\psi\beta$, $\varphi\alpha$, and $\varphi\beta$, which are to be occupied by the four electrons. The only eigenfunction allowed by Pauli's principle for the system is

$$\Psi_{\mathrm{He}_2} = a \begin{vmatrix} \psi(1)\,\alpha(1) & \psi(1)\,\beta(1) & \varphi(1)\,\alpha(1) & \varphi(1)\,\beta(1) \\ \psi(2)\,\alpha(2) & \psi(2)\,\beta(2) & \varphi(2)\,\alpha(2) & \varphi(2)\,\beta(2) \\ \psi(3)\,\alpha(3) & \psi(3)\,\beta(3) & \varphi(3)\,\alpha(3) & \varphi(3)\,\beta(3) \\ \psi(4)\,\alpha(4) & \psi(4)\,\beta(4) & \varphi(4)\,\alpha(4) & \varphi(4)\,\beta(4) \end{vmatrix} \tag{34}$$

(a is a factor of such value as to make the eigenfunction normalized.)

It will be seen that this is antisymmetric, for interchanging any two electrons is equivalent to interchanging two rows of the determinant, and hence to changing its sign.

Substitution of this eigenfunction in an expression of the type of Equation 21 permits the evaluation of the perturbation energy W^1, in the course of which use is made of the properties of orthogonality and normalization of the spin eigenfunctions; namely,

$$\left.\begin{array}{c} \int\alpha^2\,d\epsilon = \int\beta^2\,d\epsilon = 1 \\ \int\alpha\,\beta\,d\epsilon = 0. \end{array}\right\} \tag{35}$$

in which ϵ is the variable occurring in the spin eigenfunctions. The value of one further integral is also needed:

$$\begin{aligned} I_5 &= \int\!\!\int \frac{\psi^2(1)\;\psi(2)\;\varphi(2)}{r_{12}}\,d\Omega_1\,d\Omega_2 \\ &= \frac{Z}{a_o}\left\{e^{-\rho}\left(\frac{5}{16\rho}+\frac{1}{8}+\rho\right) - e^{-3\rho}\left(\frac{5}{16\rho}+\frac{1}{8}\right)\right\}. \end{aligned} \tag{19f}$$

The potential function obtained is only approximately correct, for the eigenfunctions are in fact largely perturbed by the interelectronic interaction. There are no forces tending to molecule formation, but instead repulsion at all distances. The van der Waals' attractive force (which is very small for helium) does not appear, and the repulsive force is much larger than the actual one; these discrepancies are no doubt due to the inaccuracy of the calculation.

It is of interest to carry out the evaluation of the naïve potential function obtained from the eigenfunction $\psi(1)\,\alpha(1)\,\psi(2)\,\beta(2)\,\varphi(3)\,\alpha(3)\,\varphi(4)\,\beta(4)$; i.e., with the neglect of the interchange energy of the electrons. This potential leads to a strong attractive force, with the formation of molecules He_2 with about 10,000 or 15,000 cal/mole dissociation energy. The resonance phenomenon is accordingly largely responsible for the very small van der Waals' forces in helium; without it the boiling point of helium would be around room temperature.

IX. OTHER RELATED PROBLEMS. THE EXTENSION OF THE THEORY

The interaction of two alkali metal atoms is to be expected to be similar to that of two hydrogen atoms, for the completed shells of the ions will produce forces similar to the van der Waals' forces of a rare gas. The two valence electrons, combined symmetrically, will then be shared between the two ions, the resonance phenomenon producing a molecule-forming attractive force. This is, in fact, observed in band spectra. The normal state of the Na_2 molecule, for example, has an energy of dissociation of 1 v.e. (44). The first two excited states are similar, as is to be expected; they have dissociation energies of 1.25 and 0.6 v.e. respectively.

In an atom of the second column of the periodic system, such as mercury, the two valence electrons are in the normal state s-electrons, and form a completed sub-group. Two such atoms would hence interact in a way similar to two helium atoms; the attractive forces would be at most very small. This is the case for Hg_2, which in the normal state has an energy of dissociation of only 0.05 v.e. But if one or both of the atoms is excited strong attractive forces can arise; and indeed the excited states of Hg_2 are found to have energies of dissociation of about 1 v.e.

Similarly two Hg^+ ions will attract each other with some force to form the stable Hg_2^{++} ion long recognized by chemists.

The application of the quantum mechanics to the interaction of more complicated atoms, and to the non-polar chemical bond in general, is now being made (45). A discussion of this work can not be given here; it is, however, worthy of mention that qualitative conclusions have been drawn which are completely equivalent to G. N. Lewis's theory of the shared electron pair. The further results which have so far been obtained are promising; and we may look forward with some confidence to the future explanation of chemical valence in general in terms of the Pauli exclusion principle and the Heisenberg-Dirac resonance phenomenon.

NOTE ADDED IN PROOF

Since the submission of this article for publication a number of pertinent papers have appeared.

H. A. Wilson (*Proc. Roy. Soc. London*, A **118,** 635 (1928); see also (29)) states that no functions satisfying the wave equation for the hydrogen molecule-ion and bounded everywhere exist. There are, however, solutions which become logarithmically infinite along the nuclear axis and are bounded elsewhere. These solutions would not be considered eigenfunctions if the usual definition is retained; but would be in case the restriction that the eigenfunction be bounded everywhere were replaced by the restriction that it be quadratically integrable. Wilson has made this assumption, and has found that the so-calculated properties of the hydrogen molecule-ion in the normal state are approximately those given by Burrau. An accurate treatment and the consideration of excited states have not been published.

A treatment of the hydrogen molecule by the Ritz method, applied to helium by Kellner (25), has been reported by S. C. Wang (*Phys. Rev.*, **31,** 579 (1928)). With this method the individual eigenfunctions ψ and φ (equation 29) are taken to be the hydrogen-like eigenfunctions of an atom with atomic number Z differing from unity. The value found for Z is 1.166, and the corresponding constants of the hydrogen molecule in the normal state are

$$r_o = 0.75\ \text{Å},\ I_o = 0.459 \times 10^{-40}\ \text{g. cm.}^2,\ D_{H_2} = 3.76\ \text{v.e.},\ \omega_o = 4900\ \text{cm}^{-1}.$$

Comparison with table 4 shows that these values are in somewhat better agreement with the observed ones than are Sugiura's.

B. N. Finkelstein and G. E. Horowitz (*Z. f. Physik*, **48**, 118 (1928)) have similarly applied the Ritz method to the hydrogen molecule-ion, obtaining the following values:

$$Z = 1.228,\ \rho \cong 2,\ r_o \cong 1.06\ \text{Å},\ W_{H_2^+} = -\ 15.75\ \text{v.e.}$$

These results are better than those given by the perturbation theory (table 3).

F. R. Bichowsky and L. C. Copeland (*J. Am. Chem. Soc.*, **50**, 1315 (1928)) have made a direct determination of the heat of formation of molecular hydrogen, leading to the value $D_{H_2} = 105000 \pm 3500$ cal/mole.

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