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Joseph O. Hirschfelder

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# The Energy of the Triatomic Hydrogen Molecule and Ion, V.

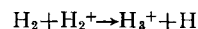
JOSEPH O. HIRSCHFELDER

*Chemistry Department, University of Wisconsin, Madison, Wisconsin*

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In previous papers, the energy of  $H_3$  and of  $H_3^+$  has been obtained by the variational method for linear configurations. In this treatment we are able to evaluate the difficult three center integrals for nonlinear configurations with the aid of the differential analyzer and to compute the energy of  $H_3$  and of  $H_3^+$  as a function of the angle between the nuclei. The excited states as well as the ground states are considered. Direct comparison of calculated energy values for the equilateral triangle show that the molecular orbital approximation is inferior to the method of homopolar bond functions. The triatomic hydrogen molecule has its lowest energy for linear configurations. The angle dependence calculated by the variational method agrees well with that calculated on the basis of the Eyring semi-empirical scheme. By the theorem of Jahn and Teller there could not be a minimum in the energy for the equilateral triangle,

as here the lowest electronic state is doubly degenerate. The triatomic hydrogen ion,  $H_3^+$ , is very stable (when left to itself) and has an energy lower by more than 184. kcal. than two separated hydrogen atoms and a proton. Thus the chemical reaction:



is certainly exothermic by more than 11 kcal. and probably is exothermic by 38 kcal. The triatomic hydrogen ion has a stable configuration corresponding to separation between the nuclei of about 1.79 Å with the nuclei lying intermediate between a right and an equilateral triangle. The vibration frequencies of  $H_3^+$  are estimated but their exact value as well as the exact configuration of the stable state are somewhat in doubt. Two of these frequencies should be infra-red active and susceptible to direct experimental measurement.

## I. INTRODUCTION

THE triatomic hydrogen ion,  $H_3^+$ , is formed in rather large quantities whenever hydrogen gas is ionized; the neutral triatomic hydrogen molecule is the metastable complex formed when a hydrogen atom collides with a hydrogen molecule. The difficulties which arise in the calculation of their energies are met quite generally in molecular quantum mechanics. Throughout this work we have used the variational method and computed some of the difficult integrals on the differential analyzer of the Moore School of Electrical Engineering. A discussion of these integrals is given in the following article. In previous communications<sup>1</sup> the energies were computed for linear configurations of the nuclei. In this paper, we consider the triangular configurations for both the ground and the excited states. A direct comparison of energy levels shows that the molecular orbital approximation is inferior to that of the homopolar bond treatments. This is in accord with the recent work of Coulson<sup>2</sup> on  $H_2$ . The triatomic hydrogen

molecule has its lowest energy for linear configurations and has the same dependence on the bending angle when the variational method is used as is obtained on the Eyring semi-empirical scheme.<sup>3</sup> The triatomic hydrogen ion has its stable configuration intermediate between a right and an equilateral triangle.

## II. THE ENERGY OF $H_3^+$ AND OF $H_3$ IN THE EQUILATERAL TRIANGLE CONFIGURATION

### A. Simplifications due to symmetry

The symmetry of the equilateral triangle simplifies the problem of forming the eigenfunctions for  $H_3^+$  and for  $H_3$ . In this particular configuration the Hamiltonian operator is symmetrical with respect to all of the reflections and rotations whose net result is to interchange the like nuclei:  $a$ ,  $b$ , and  $c$ . These molecules belong to the  $D_{3h}$  symmetry point group<sup>4</sup> and their eigenfunctions

<sup>3</sup> Eyring and Polanyi, *Zeits. f. physik. Chemie* **B12**, 279 (1931); Hirschfelder, Topley and Eyring, *J. Chem. Phys.* **4**, 170 (1936).

<sup>1</sup> Hirschfelder, Eyring and Rosen, *J. Chem. Phys.* **4**, 121 and 130 (1936); Hirschfelder, Diamond and Eyring, *J. Chem. Phys.* **5**, 695 (1937); Stevenson and Hirschfelder, *J. Chem. Phys.* **5**, 933 (1937).

<sup>2</sup> C. A. Coulson, *Proc. Camb. Phil. Soc.* **34**, 204 (1938).

<sup>4</sup> Group theory is the mathematical treatment of symmetry properties. Without it we would obtain the same results but require more work. Some of the most useful references on group theory are: (a) Eugen Wigner, *Gruppentheorie* (Vieweg, 1931). (b) Jenny Rosenthal and G. M. Murphy, *Rev. Mod. Phys.* **8**, 317 (1936). (c) Eyring, Frost and Turkevitch, *J. Chem. Phys.* **1**, 777 (1933). (d) J. E. Lennard-Jones, *Trans. Faraday Soc.* **30**, 70 (1934). (e) Mulliken, *Phys. Rev.* **41**, 49 (1932).

must transform under the various symmetry operations as eigenvectors of the corresponding representations. Here  $D_{3h}$  is the Schönflies notation to indicate that the molecule possesses three vertical and one horizontal symmetry planes. There are altogether twelve operations under which the Hamiltonian remains invariant—six of these consist in pure rotations and reflections about the vertical symmetry plane, the other six involve reflections about the horizontal plane. In this treatment we are limited to a discussion of only those approximate eigenfunctions which can be formed from 1s-hydrogen-like atomic orbitals. Such functions are necessarily symmetrical with respect to a reflection about the nuclear plane and belong to the  $C_{3v}$  subgroup of the  $D_{3h}$ . In order to obtain eigenfunctions with a nodal plane passing through the nuclei it would be necessary to use  $p$ ,  $d$ , ... atomic orbitals. The states which we do not consider for this reason are presumably states of high energy and are therefore relatively unimportant.

There are three classes of eigenfunctions belonging to the  $D_{3h}$  group which are symmetrical with respect to a reflection about the nuclear plane. Any satisfactory function must fall into one of the three Mulliken<sup>4a</sup> classifications:

(1)  $A_1$ . Eigenfunctions of this class are easily recognized because they remain invariant when the coordinates of the nuclei are interchanged.

(2)  $A_2$ . Functions of this class change sign when the coordinates of any two of the nuclei are interchanged.

(3)  $E$ . Unlike the functions of the  $A_1$  and  $A_2$  classes these eigenfunctions do not obey a simple law of transformation. They come in pairs (i.e., the corresponding energy states are doubly degenerate) and are partially converted into one another under the symmetry operations.

In this paper, we form our eigenfunctions as the sum of parameters times products of atomic orbitals. The requirement that these approximate eigenfunctions transform in one of the above three manners, provides very stringent restrictions on the values of these parameters. In other words, group theory enables us *a priori* to partially diagonalize the secular equations.

One-electron eigenfunctions which satisfy the symmetry conditions are termed molecular

orbitals. These can be formed by taking the right linear combinations of the 1s-hydrogen-like atomic orbitals:

$$\begin{aligned} a(1) &= (z^3/\pi)^{1/2} \exp(-zr_{a1}), \\ b(1) &= (z^3/\pi)^{1/2} \exp(-zr_{b1}), \\ c(1) &= (z^3/\pi)^{1/2} \exp(-zr_{c1}). \end{aligned} \quad (1)$$

Here  $r_{a1}$ ,  $r_{b1}$ , and  $r_{c1}$  are the distances of electron 1 to nuclei  $a$ ,  $b$ , and  $c$ , respectively and  $z$  is a parameter which is varied so as to give the lowest energy for the system. In the case of one electron in the field of three protons arranged in an equilateral triangle, i.e.,  $H_3^{++}$ , there are three molecular orbitals which can be formed in this way:

$$A_1 \quad \chi(1) = a(1) + b(1) + c(1), \quad (2)$$

$$E \quad \begin{cases} \varphi_o(1) = a(1) - c(1), \\ \varphi_e(1) = 2b(1) - a(1) - c(1). \end{cases} \quad (3)$$

$$(4)$$

Throughout this paper the subscript  $o$  will indicate that the eigenfunction is antisymmetrical (odd) with respect to a permutation of nuclei  $a$  and  $c$  and the subscript  $e$  will indicate that the function is symmetrical (even) in this sense. The  $\chi(1)$  orbital belongs to the  $A_1$  class since it is symmetrical with respect to an interchange of any of the nuclei. It is often referred to as an  $s$  orbital as it corresponds to a state having no angular momentum for the electron and in this respect it is similar to the  $s$  state of an atom. The  $\varphi_o(1)$  and  $\varphi_e(1)$  belong to the  $E$  class and we shall designate them as  $\omega$  orbitals. Both of these orbitals correspond to states having the same angular momentum but two linear combinations of them will have the electrons revolving in opposite directions. Both states have the same energy. Fig. 1 shows graphically the symmetry of these orbitals. The values of the orbitals are plotted as a function of the angle as we proceed around the circle passing through the three nuclei and having the center of the molecule for its center. The  $s$  orbital has no nodes. The  $\omega$  orbitals have a more complicated structure. It is impossible to form an  $A_2$  orbital out of just one type of atomic function. For the case of just one electron or  $H_3^{++}$  we have only three atomic orbitals at our disposal and these are combined to form the three mutually orthogonal molecular

orbitals. Here there is no ambiguity as to the best linear combinations of atomic orbitals (LCAO); they are equivalent to the molecular orbitals.

## B. The energy of $H_3^+$

The problem of  $H_3^+$  where we have two electrons in the field of trigonal symmetry is more difficult than the one-electron case,  $H_3^{++}$ . The additional complications are caused by the mutual repulsion of the electrons and by the Pauli Exclusion Principle. Coulson<sup>5</sup> studied the triatomic hydrogen ion, and obtained some very interesting qualitative results as to the relative positions of the various energy states, etc. But he was unable to compute the integrals arising from the mutual repulsion of the electrons and make his results quantitative. These integrals are of a very difficult nature and it was only with the aid of the differential analyzer at the Moore School of Electrical Engineering that we were able to evaluate them. A complete discussion of these integrals is given in the following article by C. N. Weygandt and the author. For two electrons, the Pauli exclusion principle divides the states into two divisions. Those having spatial eigenfunctions symmetrical with respect to an interchange of electrons are multiplied by spin functions characteristic of singlets, whereas those spatial eigenfunctions which are antisymmetric with respect to an interchange of electrons are multiplied by triplet spin functions. The spatial eigenfunctions are formed by taking linear combinations of products of either the atomic or of the molecular orbitals. Since there are three atomic orbitals (or three molecular orbitals) there are altogether  $(3 \times 3)$  nine products, or nine mutually orthogonal approximate eigenfunctions which we can form. Three of these functions are for triplets and the other six are for singlets. A little algebra or group theory suffices to further decompose the linear combinations, so that they transform according to the irreducible representations  $A_1$ ,  $E$ , and  $A_2$ . The eigenfunctions for the singlet states are:

$$\psi(^1A_1; s^2) = \chi(1)\chi(2), \quad (5)$$

$$\psi(^1A_1; \omega, \omega) = -\frac{2}{3}\varphi_u(1)\varphi_u(2) - \frac{1}{3}\varphi_o(1)\varphi_o(2), \quad (6)$$

$$\psi_o(^1E; s, \omega) = \chi(1)\varphi_u(2) + \chi(2)\varphi_u(1), \quad (7)$$

$$\psi_o(^1E; \omega, \omega) = \frac{1}{3}\varphi_u(1)\varphi_o(2) + \frac{1}{3}\varphi_u(2)\varphi_o(1), \quad (8)$$

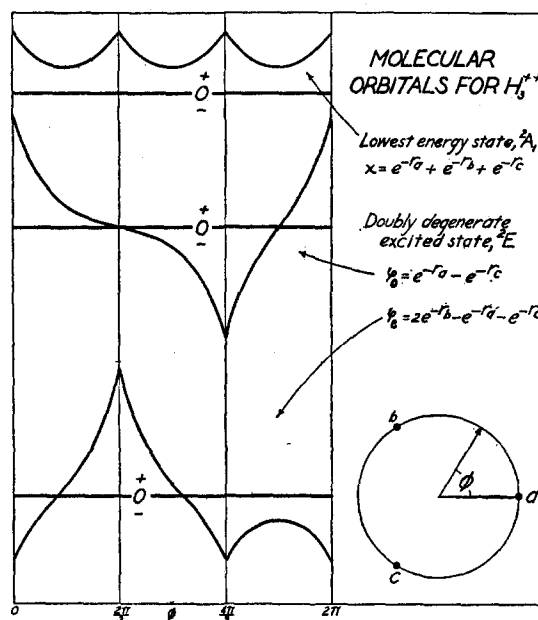


FIG. 1.

$$\psi_o(^1E; s, \omega) = \chi(1)\varphi_o(2) + \chi(2)\varphi_o(1), \quad (9)$$

$$\psi_e(^1E; \omega, \omega) = \frac{2}{3}\varphi_u(1)\varphi_u(2) - \frac{1}{3}\varphi_o(1)\varphi_o(2). \quad (10)$$

The triplet states for  $H_3^+$  are:

$$\begin{aligned} \psi_o(^3E; s, \omega) &= \chi(2)\varphi_u(1) - \chi(1)\varphi_u(2) = 2[a(1)c(2) \\ &\quad - a(2)c(1)] + [a(1)b(2) - a(2)b(1)] \\ &\quad + [b(1)c(2) - c(1)b(2)], \end{aligned} \quad (11)$$

$$\begin{aligned} \psi_e(^3E; s, \omega) &= \frac{1}{3}[\chi(2)\varphi_o(1) - \chi(1)\varphi_o(2)] = [b(1)a(2) \\ &\quad - b(2)a(1)] + [b(1)c(2) - b(2)c(1)], \end{aligned} \quad (12)$$

$$\begin{aligned} \psi_e(^3A_2; \omega, \omega) &= \frac{1}{3}[\varphi_u(1)\varphi_o(2) - \varphi_u(2)\varphi_o(1)] \\ &= [a(1)b(2) - a(2)b(1)] + [c(1)a(2) \\ &\quad - a(1)c(2)] + [b(1)c(2) - c(1)b(2)]. \end{aligned} \quad (13)$$

The three triplet states each have different symmetries and therefore have no matrix components between them. The best eigenfunctions for the singlet states are linear combinations of two molecular orbital functions. Thus the lowest energy state for  $H_3^+$  is a linear combination of  $\psi(^1A_1; s, s)$  and of  $\psi(^1A_1; \omega, \omega)$ . The eigenfunctions for the degenerate  $^1E$  state are a linear combination of  $\psi_u(^1E; s, \omega)$  and of  $\psi_u(^1E; \omega, \omega)$  or of  $\psi_o(^1E; s, \omega)$  and of  $\psi_o(^1E; \omega, \omega)$ . The best energies for these states can be determined by solving second-order secular equations and the best linear combinations (LCAO) can be determined in a similar fashion. However, it has been the practice of many investigators in molecular quantum mechanics to guess what these best linear combinations should be. There are two schools of thought—the molecular orbitalists

<sup>5</sup> C. A. Coulson, Proc. Camb. Phil. Soc. **31**, 244 (1935).

(Hund, Mulliken, Lennard-Jones, etc.) and the homopolarists (Heitler, London, etc.). The former take for their eigenfunctions the functions formed from the lowest orbitals. Thus they would take for the normal state of the  $H_3^+$  ion  $\psi(^1A_1; s, s)$  and neglect the effect of the  $\psi(^1A_1; \omega, \omega)$ . The homopolarists, however, would take that linear combination which does not contain any polar terms, i.e., products such as  $a(1)a(2)$  which connote in a sense that two electrons are revolving about the same nucleus at the same time. The homopolar and polar eigenfunctions may be written as linear combinations of the molecular orbital functions. Thus:

$$\begin{aligned}\psi(^1A_1; \text{homo}) &= \frac{2}{3}\psi(^1A_1; s, s) + \frac{1}{3}\psi(^1A_1; \omega, \omega) \\ &= a(1)b(2) + a(2)b(1) + a(1)c(2) \\ &\quad + a(2)c(1) + b(1)c(2) + b(2)c(1),\end{aligned}\quad (14)$$

$$\begin{aligned}\psi(^1A_1; \text{polar}) &= \frac{1}{3}\psi(^1A_1; s, s) - \frac{1}{3}\psi(^1A_1; \omega, \omega) \\ &= a(1)a(2) + b(1)b(2) + c(1)c(2),\end{aligned}\quad (15)$$

$$\begin{aligned}\psi_o(^1E; \text{homo}) &= \frac{1}{3}\psi_o(^1E; s, \omega) + \frac{2}{3}\psi_o(^1E; \omega, \omega) = a(1)b(2) \\ &\quad + a(2)b(1) - b(1)c(2) - b(2)c(1),\end{aligned}\quad (16)$$

$$\begin{aligned}\psi_o(^1E; \text{polar}) &= \frac{1}{3}\psi_o(^1E; s, \omega) - \frac{1}{3}\psi_o(^1E; \omega, \omega) \\ &= a(1)a(2) - c(1)c(2),\end{aligned}\quad (17)$$

$$\begin{aligned}\psi_e(^1E; \text{homo}) &= \frac{1}{3}\psi_e(^1E; s, \omega) + \frac{2}{3}\psi_e(^1E; \omega, \omega) \\ &= a(1)b(2) + a(2)b(1) + b(1)c(2) \\ &\quad + b(2)c(1) - 2[a(1)c(2) + a(2)c(1)],\end{aligned}\quad (18)$$

$$\begin{aligned}\psi_e(^1E; \text{polar}) &= \frac{1}{3}\psi_e(^1E; s, \omega) - \frac{1}{3}\psi_e(^1E; \omega, \omega) \\ &= 2b(1)b(2) - a(1)a(2) - c(1)c(2).\end{aligned}\quad (19)$$

From the above equations it is clear how we pass from the molecular orbital or Hund-Mulliken description to the homopolar-polar or Heitler-London approach. The real test of these two approximations is the accuracy of the energy levels which they predict. We will compare these energies with those obtained by solving the secular equations and using the best linear combination of atomic orbitals (LCAO).

Having decided upon the approximate eigenfunctions for the various states of the triatomic hydrogen ion, the corresponding energies are calculated by substituting these functions into the expression:

$$E = \frac{\int \int \bar{\Psi} H \Psi d\tau_1 d\tau_2}{\int \int \bar{\Psi} \Psi d\tau_1 d\tau_2}. \quad (20)$$

From the variational principle, it follows that the energies calculated in this manner will be too high. For this reason we vary the effective nuclear charge,  $z$ , and the composition of the

eigenfunctions so as to get as low an energy as possible for a particular state.

When  $z=1$  and the separation between the nuclei is  $R a_0$  (where  $a_0$  is the radius of the first Bohr orbit), the numerator of (20) for each of the states or types of approximations is a linear combination of the six energy components:

$$\begin{aligned}a^2b^2 &= \iint a(1)b(2)Ha(1)b(2)d\tau_1d\tau_2 = (3/R-1) \\ &\quad - 4G(R) + L(aa, bb),\end{aligned}\quad (21)$$

$$\begin{aligned}a^2a^2 &= \iint a(1)a(2)Ha(1)a(2)d\tau_1d\tau_2 = (3/R-1) \\ &\quad - 4G(R) + L(aa, aa),\end{aligned}\quad (22)$$

$$\begin{aligned}a^2bc &= \iint a(1)b(2)Ha(1)c(2)d\tau_1d\tau_2 \\ &= (3/R-1)I(R) - 2I(R)G(R) \\ &\quad - [J(R) + K(a, bc)] + L(aa, bc),\end{aligned}\quad (23)$$

$$\begin{aligned}a^2ab &= \iint a(1)a(2)Ha(1)b(2)d\tau_1d\tau_2 \\ &= (3/R-1)I(R) - 2I(R)G(R) \\ &\quad - [J(R) + K(a, bc)] + L(aa, ab),\end{aligned}\quad (24)$$

$$\begin{aligned}ab ab &= \iint a(1)b(2)Hb(1)a(2)d\tau_1d\tau_2 = (3/R-1)I^2(R) \\ &\quad - 2I(R)[J(R) + K(a, bc)] + L(ab, ab),\end{aligned}\quad (25)$$

$$\begin{aligned}ab ac &= \iint a(1)b(2)Hc(1)a(2)d\tau_1d\tau_2 = (3/R-1)I^2(R) \\ &\quad - 2I(R)[J(R) + K(a, bc)] + L(ab, ac).\end{aligned}\quad (26)$$

Here the unit of energy is  $e^2/a_0 = 627.4$  kcal. per mole. Table I shows the linear combinations of energy components occurring for the various states. The integrals which occur in equations (21) through (26) are defined in the following article and tables of them are given for the convenience of anyone working in molecular quantum mechanics. The integrals

$$\begin{aligned}L(aa, bc) &= \frac{1}{\pi^2} \int \int \frac{1}{r_{12}} \\ &\quad \times \exp(-2r_{a1} - r_{b2} - r_{c2}) d\tau_1 d\tau_2\end{aligned}\quad (27)$$

and

$$\begin{aligned}L(ab, ac) &= \frac{1}{\pi^2} \int \int \frac{1}{r_{12}} \\ &\quad \times \exp(-r_{a1} - r_{b1} - r_{a2} - r_{c2}) d\tau_1 d\tau_2\end{aligned}\quad (28)$$

are the only ones novel to this particular problem and these were evaluated with the aid of the differential analyzer as described in the following article. The denominator of (20) is the same as the numerator when  $a^2b^2$  and  $a^2a^2$  are replaced by 1,  $a^2bc$  and  $a^2ab$  are replaced by  $I(R)$ , and  $ab ab$  and  $ab ac$  are replaced by  $I^2(R)$ .

The variation of the effective nuclear charge,  $z$ , is very simple if at the same time the inter-nuclear separations are changed to  $R a_0/z$ . Then

the energy components in the numerator of (20) become:

$$a^2b^2 = z[(a^2b^2)_{z=1} + (z-1)], \quad (29)$$

$$a^2a^2 = z[(a^2a^2)_{z=1} + (z-1)], \quad (30)$$

$$a^2bc = z[(a^2bc)_{z=1} + (z-1)J(R)], \quad (31)$$

$$a^2ab = z[(a^2ab)_{z=1} + (z-1)J(R)], \quad (32)$$

$$ab\ ab = z[(ab\ ab)_{z=1} + (z-1)(-I^2(R) + 2I(R)J(R))], \quad (33)$$

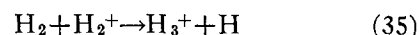
$$ab\ ac = z[(ab\ ac)_{z=1} + (z-1)(-I^2(R) + 2I(R)J(R))]. \quad (34)$$

When the above expressions for the energy components are used, the denominator of Eq. (20) remains the same as for  $z=1$ .

The results of these computations are shown in Fig. 2 and in Table I. The states lie in order of increasing energy:  $^1A_1$ ,  $^3E$ ,  $^1E$ , and  $^3A_2$ . The zero of energy is for two normal H atoms and a proton infinitely far apart. Only the  $^1A_1$  state has a minimum and can correspond to a stable ion in the equilateral configuration. In the other states the nuclei are repelled. In Fig. 2, the energies are given for the LCAO approximation. The black dots correspond to the values of the

energy when  $z=1$ . The fine curves are obtained by varying the value of  $z$ . The heavy curves are then drawn tangent to the fine curves and represent the best energy which we can obtain for these states. The variation of  $z$  results in a considerable improvement of the energy of the stable  $^1A_1$  but has little effect on the excited states.

Using the best linear combination of atomic orbitals and varying  $z$  to get the lowest energy, we find that when the internuclear separation is  $1.79 a_0$  the binding energy of the  $^1A_1$  is more than 184 kcal. This is the energy which would be required to separate the triatomic hydrogen ion into two hydrogen atoms and a proton. Because of the variational principle we know that this value is too small. If we use the correct values for the binding energies of  $H_2$  and of  $H_2^+$  (respectively 108.6 and 64.0 kcal. neglecting zero point energies), the reaction



is exothermic by more than 11.2 kcal. (neglecting zero point energies). A much more probable estimate for this energy of reaction can be obtained by using our binding energy for  $H_3^+$

TABLE I.

A. LOWEST STATE FOR $H_3^+$ ; SINGLET $A_1$ (SYMMETRICAL IN NUCLEI)				
State	$\int \bar{\Psi} H \Psi d\tau$	Energy in kcal. per Mole		
LCAO		$R=2.0 a_0$	$R=2.5 a_0$	$R=3.0 a_0$
		$-115.9, z=1$	$-119.5, z=1$	$-100.9, z=1$
		$-172.6, z=1.37$	$-183.8, z=1.40$	$-153.9, z=1.36$
( $^1A_1$ ; Homo)	$2[a^2b^2 + ab\ ab + 2a^2bc + 2ab\ bc]$	$-115.8, z=1$	$-119.5, z=1$	$-100.5, z=1$
		$-171.6, z=1.36$	$-179.3, z=1.37$	$-147.1, z=1.38$
( $^1A_1$ ; Polar)	$[a^2a^2 + 2ab\ ab]$	$-3.1, z=1$	$+43.5, z=1$	$+106.8, z=1$
		$-16.8, z=1.17$	$+38.9, z=1.10$	$+106.8, z=1$
( $^1A_1$ ; $s, s$ )	$3a^2a^2 + 6a^2b^2 + 12a^2bc + 24a^2ab$	$-100.6, z=1$	$-99.7, z=1$	$-75.0, z=1$
	$+24ab\ ac + 12ab\ ab$	$-157.6, z=1.37$	$-164.6, z=1.48$	$-128.9, z=1.43$
( $^1A_1$ ; $\omega, \omega$ )	$2[a^2b^2 + 2a^2a^2 + 2a^2bc$	$+577.7, z=1$	$+421.8, z=1$	$+333.6, z=1$
	$-8a^2ab + 5ab\ ab - 2ab\ bc]$	$+308.3, z=.50$	$+258.38, z=.60$	$+228.2, z=.66$
B. DOUBLY DEGENERATE EXCITED SINGLET ( $^1E$ ) STATE FOR $H_3^+$				
LCAO		$+238.1, z=1$	$+140.1, z=1$	$+86.83, z=1$
( $^1E$ ; Homo)	$2[a^2b^2 + ab\ ab - a^2bc - ab\ bc]$	$+253.3, z=1$	$+148.9, z=1$	$+91.3, z=1$
( $^1E$ ; Polar)	$a^2a^2 - ab\ ab$	$+341.0, z=1$	$+273.9, z=1$	$+251.0, z=1$
( $^1E$ ; $s, \omega$ )	$2[a^2b^2 + 2a^2a^2 + 2a^2ab - a^2bc$	$+268.9, z=1$	$+189.0, z=1$	$+157.3, z=1$
	$-3ab\ bc - ab\ ab]$			
( $^1E$ ; $\omega, \omega$ )	$[2a^2b^2 + a^2a^2 - 2a^2bc$	$+507.4, z=1$	$+343.4, z=1$	$+250.1, z=1$
	$-4a^2ab + ab\ ab + 2ab\ bc]$			
C. DOUBLY DEGENERATE TRIPLET ( $^3E$ ) STATE FOR $H_3^+$				
( $^3E$ ; $s, \omega$ )	$[a^2b^2 - ab\ ab + a^2bc - ab\ ac]$	$+123.4, z=1$	$+42.5, z=1$	$+7.5, z=1$
D. NONDEGENERATE TRIPLET ( $^3A_2$ ) STATE FOR $H_3^+$				
( $^3A_2$ ; $\omega, \omega$ )	$[a^2b^2 - ab\ ab + 2ab\ bc - 2a^2bc]$	$+436.9, z=1$	$+265.1, z=1$	$+166.5, z=1$

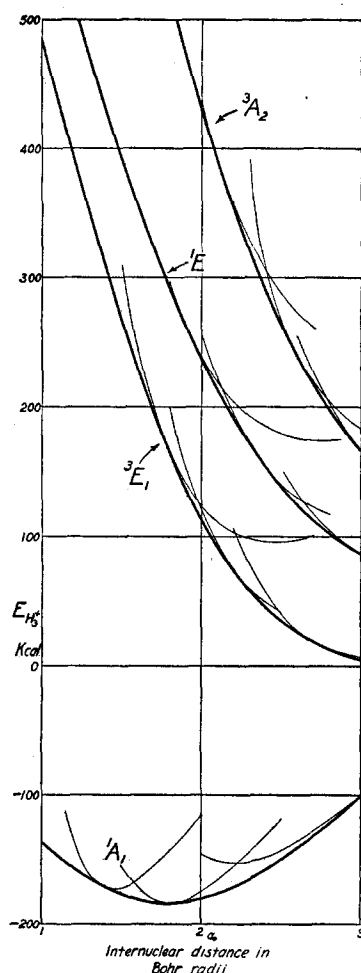


FIG. 2. The energy of  $H_3^+$  in the equilateral triangle configuration as a function of the separation between the nuclei. The zero of energy corresponds to two normal hydrogen atoms and a proton separated by an infinite distance.

together with the binding energies of  $H_2$  and of  $H_2^+$  computed by the same LCAO method (92.2 and 51.9 kcal., respectively). This leads to an exothermic heat of reaction of 39.7 kcal. In any case this reaction is perfectly possible from energy considerations and experimentally<sup>6</sup> it is found to take place with great frequency.

Let us return to a discussion of the relative merits of the homopolar and molecular orbital approximations. For the  $^1A_1$  state at the equilibrium separation corresponding to  $R=2.5(a_0/z)$  the energies are

<sup>6</sup> H. D. Smyth, Rev. Mod. Phys. 3, 347 (1931); Phys. Rev. 4, 452 (1925).

LCAO - 183.8  
Homopolar - 179.3  
Molecular orbital - 164.6

and for the  $^1E$  state for  $R=2.5 a_0$  and  $z=1$ , the energies are:

LCAO + 140.1  
Homopolar + 148.9  
Molecular orbital + 189.0.

It is clear from the above figures that the homopolar approximation is much closer to the best linear combination than is the molecular orbital. The strongest argument in favor of the molecular orbital picture is that the energy of a state formed from the lowest orbitals such as  $\Psi(^1A_1; s, s)$  has a much lower energy than does the excited orbital state  $\Psi(^1E; \omega, \omega)$  and therefore we would expect their interaction to be small. From Table I we see that even though their energy difference is roughly 500 kcal., their interaction lowers the best energy by 19.2 kcal. The reason seems to be that the overlapping of these charge distributions is particularly large when the electrons are close to each other. Thus when  $R=2.5a_0$  and  $z=1$ , the energy of interaction between these states is

$$\frac{\int \int \bar{\Psi}(^1A_1; s, s) H \Psi(^1A_1; \omega, \omega) d\tau}{\left[ \left( \int \Psi^2(^1A_1; s, s) d\tau \right) \left( \int \Psi^2(^1A_1; \omega, \omega) d\tau \right) \right]^{1/2}} = -185 \text{ kcal.} \quad (36)$$

This interaction between the molecular orbital states is zero when the nuclei are very close together and increases as the nuclei are separated. Finally when the nuclei are infinitely far apart the total energy of the  $\Psi(^1A_1; s, s)$  is 104.6 kcal., the energy of the  $\Psi(^1A_1; \omega, \omega)$  is 209.1 kcal., and yet their interaction is strong enough to improve the best energy by 104.6 kcal. So we see that the argument in favor of the molecular orbital picture is not satisfactory in the case of  $H_3^+$  and should be investigated very carefully in other cases. At a first glance we would expect the polar states to give strong interactions with the homopolar, since their energies are close together.

However, the polar states are not orthogonal to the homopolar, i.e.,

$$\int \bar{\Psi}(\text{polar})\Psi(\text{homopolar})d\tau \neq 0,$$

and therefore these energies give us no information as to the strength of the interaction.

Recently, Coulson<sup>2</sup> computed the energy of the normal hydrogen molecule,  $H_2$ , using molecular orbitals. The lowest energy which he was able to calculate on this basis (with a five-term function) was 26.2 kcal. too high and he reached the conclusion that the best possible molecular orbital would have an energy only 0.7 kcal. lower than this. So the best possible molecular orbital would not give as good an approximation to the charge distribution as even the simple homopolar bond function of Wang.<sup>7</sup> This bears out the conclusions of the previous paragraph.

### C. The energy of $H_3$ in the equilateral triangular configuration

The triatomic hydrogen molecule is the intermediate complex in the simplest chemical reactions, i.e., the *ortho-para* hydrogen conversion or the reaction of a deuterium atom with hydrogen. The semi-empirical scheme predicts the energy of this metastable collision complex and therefore it is interesting to see how well the variational calculations agree with these prognostications. The computations of the energy is similar to that for the triatomic ion. No further integrals are required and we obtain the energy of the neutral molecule as a corollary to that for the ion. Again the eigenfunctions must transform according to the three symmetry classes:  $A_1$ ,  $E$ , and  $A_2$ . Since  $H_3$  has three electrons, these eigenfunctions will correspond to both doublet and quartet spin states. The Pauli exclusion principle makes it no longer possible to separate the eigenfunctions for three electrons into a product of a space function times a spin function, but this difficulty is alleviated by the use of Slater determinants. A little consideration shows that there are twenty of these determinants which do not vanish identically, and which can be formed from our three atomic or three molecular orbitals. These correspond to one quartet ( $^4A_2$ ), three doubly degenerate ( $^2E$ ) and two nondegenerate ( $^2A_1$ ,

and  $^2A_2$ ) doublet states. The lowest energy state for  $H_3$  is the doubly degenerate  $^2E$ . Altogether there are six combinations of Slater determinants which have the  $^2E$  symmetry and a spin component of  $(\frac{1}{2})h/2\pi$ . Three of these are symmetric and three antisymmetric with respect to an interchange of the nuclei  $a$  and  $c$ . The symmetric functions do not combine with the antisymmetric ones and this provides a natural division between the degenerate states. In the homopolar-polar description, the states antisymmetric with respect to an interchange of  $a$  and  $c$  are:

$$\Psi_o(^2E; \text{homo}) = 2 \begin{pmatrix} a & b & c \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} a & b & c \\ \beta & \alpha & \alpha \end{pmatrix} - \begin{pmatrix} a & b & c \\ \alpha & \alpha & \beta \end{pmatrix}, \quad (37)$$

$$\begin{aligned} \Psi_o(^2E; \text{polar}_1) = & 2 \begin{pmatrix} a & a & c \\ \alpha & \beta & \alpha \end{pmatrix} - 2 \begin{pmatrix} c & c & a \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} a & a & b \\ \alpha & \beta & \alpha \end{pmatrix} \\ & - \begin{pmatrix} c & c & b \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} b & b & c \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} b & b & a \\ \alpha & \beta & \alpha \end{pmatrix}, \quad (38) \end{aligned}$$

$$\begin{aligned} \Psi_o(^2E; \text{polar}_2) = & 2 \begin{pmatrix} a & a & b \\ \alpha & \beta & \alpha \end{pmatrix} - 2 \begin{pmatrix} c & c & b \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} a & a & c \\ \alpha & \beta & \alpha \end{pmatrix} \\ & - \begin{pmatrix} c & c & a \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} b & b & a \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} b & b & c \\ \alpha & \beta & \alpha \end{pmatrix}. \quad (39) \end{aligned}$$

Here the brackets such as  $\begin{pmatrix} a & b & c \\ \alpha & \beta & \alpha \end{pmatrix}$  represent Slater determinants where the electrons have spacial orbitals as given by the top line and spin functions according to the bottom line.  $\alpha$  is the spin function corresponding to an electron spin in the preferred direction and  $\beta$  corresponds to a spin in the opposite direction. The normal state of the  $H_3$  molecule is made up of a linear combination of two polar and one homopolar state. The lowest value for the energy which we can obtain is for the LCAO approximation and this gives the best linear combination of these three states. As in the case of  $H_3^+$  we should discuss the relative merits of the homopolar and molecular orbital approximations obtained by neglecting the polar states in the former method and by taking a particular linear combination of these states in the second case. The molecular orbital eigenfunction of lowest energy is:

$$\begin{aligned} \Psi_o(^2E; s, s, \omega) = & \begin{pmatrix} \chi & \chi & \varphi_u \\ \alpha & \beta & \alpha \end{pmatrix} = \\ & -\Psi_o(^2E; \text{homopolar}) - 2\Psi_o(^2E; \text{polar}_1). \quad (40) \end{aligned}$$

For the states other than  $^2E$ , there is only one way in which we can form an approximate eigen-

<sup>7</sup> S. C. Wang, Phys. Rev. 31, 579 (1928).



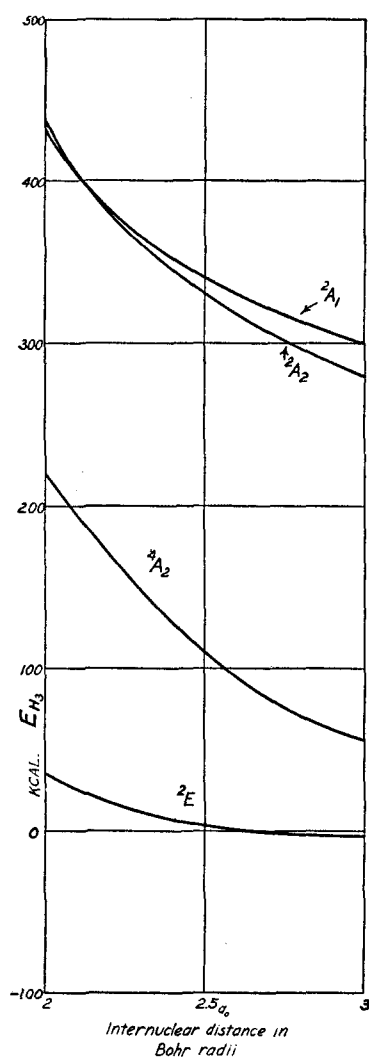


FIG. 3. The energy of  $H_3$  in the equilateral triangle configuration as a function of the distance between the nuclei. The zero of energy corresponds to three normal hydrogen atoms separated infinitely far apart.

function out of atomic orbitals and there is therefore no question as to the proper linear combinations. The eigenfunctions for these states are:

$$\Psi(^2A_2) = \begin{pmatrix} a & a & c \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} c & c & a \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} b & b & a \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} a & a & b \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} c & c & b \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} b & b & c \\ \alpha & \beta & \alpha \end{pmatrix}, \quad (41)$$

$$\Psi(^2A_1) = \begin{pmatrix} a & a & b \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} a & a & c \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} b & b & a \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} b & b & c \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} c & c & a \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} c & c & b \\ \alpha & \beta & \alpha \end{pmatrix}, \quad (42)$$

$$\Psi(^4A_2) = \begin{pmatrix} a & b & c \\ \alpha & \alpha & \alpha \end{pmatrix} = \frac{1}{6} \begin{pmatrix} \chi & \varphi_0 & \varphi_0 \\ \alpha & \alpha & \alpha \end{pmatrix}. \quad (43)$$

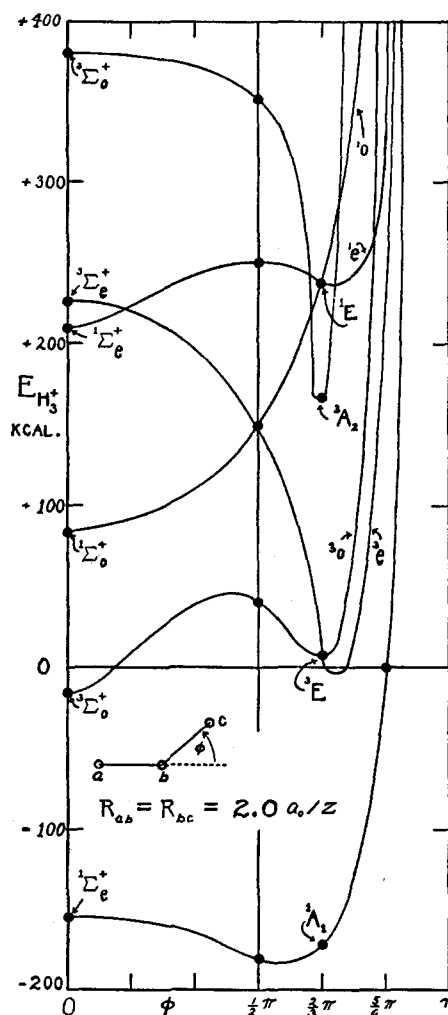
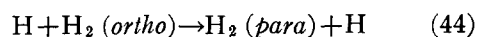


FIG. 4. The energy of  $H_3^+$  ion as a function of the angle between the nuclei. The black dots represent calculated points.

In Fig. 3 we have plotted the energy in kcal. of the various states for  $H_3$  as a function of the internuclear separation,  $R/z$ . The zero of energy is taken to be the energy of three hydrogen atoms separated to infinity. The  $^2E$  has the lowest energy but it has no minimum and therefore corresponds to a repulsion between the three atoms. The energy of the  $H_3$  in the linear configuration is about 80 kcal. lower than for the equilateral triangle. This agrees with the prediction of the semi-empirical scheme and adds additional weight to the assertion that the reaction:



proceeds most often when the hydrogen atom collides with the molecule close to the line of nuclei. The absolute quantitative agreement between the semi-empirical and the LCAO schemes is not so good as might be desired, but the difference in the energies for the equilateral triangular configuration and for the linear is about the same for the two methods of computation ( $101-67=34$  kcal. is the difference in energy of semi-empirical and variational methods for  $H_3$  in a straight line and  $34+4=38$  kcal. is the difference for the equilateral triangle).

For the ground state of  $H_3$ , the homopolar state has an energy between 4 and 12 kcal. higher than the LCAO so that it is not very satisfactory. However, the molecular orbital state has an energy lying between 12 and 60 kcal. higher than the homopolar which shows that this approximation is even worse. The energy of the molecular orbital state is a minimum at  $R=2.5 a_0$ . For larger separations this energy increases rather than decreases and approaches a limiting value of 261.4 kcal. (instead of zero) when the nuclei are separate by an infinite distance.

The  $^4A_2$  lies considerably lower than does the  $^2A_2$  which follows the general rule of spectroscopy that, everything else equal, the state of the greatest multiplicity will have the lowest energy.

The energy of the  $^2A_2$  is almost equal to that of the  $^2A_1$  and in fact, the two levels cross. Because these states have different symmetries such a crossing is permissible.

### III. VARIATION OF THE ENERGY OF $H_3^+$ AND OF $H_3$ WITH THE ANGLE BETWEEN THE NUCLEI

In previous papers<sup>1</sup> we have considered both the energy of the triatomic hydrogen molecule and ion for linear configurations and their force constants for bending from the straight line. With this information at our disposal, it is easy to obtain four terms interpolation formulae for evaluating the difficult three center integrals as functions of the bending angle. These integrals are discussed in the following article. With these integrals we were able to compute the energy of the configurations where  $r_{ab}=r_{bc}=2.0 a_0/z$  and the angle  $abc$  was taken to be  $90^\circ$  (right triangle) and  $151^\circ 3'$  (this angle makes  $r_{ac}=1.0 (a_0/z)$ ). Figs. 4 and 5 show the variation of the energy levels in  $H_3^+$  and  $H_3$  as a function of the angle  $abc$  between the nuclei.

The energy of the ground state of  $H_3^+$  is lower for the right triangle ( $-180$  kcal.) than for the equilateral triangle ( $-173$  kcal.) which indicates that the stable configuration for the  $H_3^+$  lies between the right and the equilateral

TABLE II. Energy  $H_3$  (Equilateral triangle).

$z=1$				
A. LOWEST STATE FOR $H_3$ ; DOUBLY DEGENERATE DOUBLET $^2E$				
State	$\int \bar{\Psi} H \Psi d\tau$	Energy in Kcal. per Mole		
( $^2E$ ; LCAO)		$R=2.0 a_0$	$R=2.5 a_0$	$R=3.0 a_0$
( $^2E$ ; Homo)	$12 [a^2b^2c^2 - ab bc ca]$	+ 38.2	+ 4.2	- 3.2
( $^2E$ ; s, s, w)	$12 [a^2b^2c^2 + 2 a^2a^2b^2 + 6 a^2b^2ac + 2 a^2b^2ab + a^2a^2bc - 2 a^2ab ab - a^2ac ab + a^2bc bc + 2 a^2ab bc - 2 ab bc ca - 8 ab ab ac - 2 ab ab ab]$	+ 50.5	+ 12.6	+ 1.4
		+ 62.5	+ 41.6	+ 61.0
( $^2E$ ; Semi-Empirical, 20% Coulombic)		- 49	- 34	- 20
B. EXCITED DOUBLET STATES FOR $H_3$				
( $^2A_2$ )	$a^2a^2b^2 - a^2ab ab - ab ab ab + a^2b^2ab + b^2ab bc - b^2b^2ac - b^2ac ac + ab bc ca + 2 ab ab ac - 2 a^2ab bc$	+439.2	+330.2	+280.9
( $^2A_1$ )	$a^2a^2b^2 - a^2b^2ab - a^2ab ab + a^2a^2bc - b^2ab bc + ab ab ab + b^2ac ac - ab bc ca + 2 ab ab ac - 2 a^2ab bc$	+434.3	+340.4	+298.2
C. QUARTET STATE FOR $H_3$				
( $^4A_2$ )	$a^2b^2c^2 - 3 a^2bc bc + 2 ab bc ca$	+220.8	+110.4	+ 56.2

triangular configurations. It would be difficult to ascertain the exact angle as the approximation to which these calculations have been made is not sufficiently accurate. Furthermore, we would like to stress the fact that the three center integrals for the right triangle were estimated, not calculated directly so that there is a chance for small error arising from this source. The electron binding is strongest for the equilateral triangle but the energy of nuclear repulsion decreases as the molecule is bent into a straight line. The position of minimum energy is therefore a compromise between these two tendencies.

According to the theorem of Jahn and Teller,<sup>8</sup> we know that the position of lowest energy of the ground state for the neutral triatomic hydrogen molecule cannot correspond to the equilateral triangle. This theorem states that, barring unlikely numerical coincidences, "All non-linear nuclear configurations are unstable for an orbitally degenerate electronic state of a polyatomic molecule." The ground state for  $H_3$  in

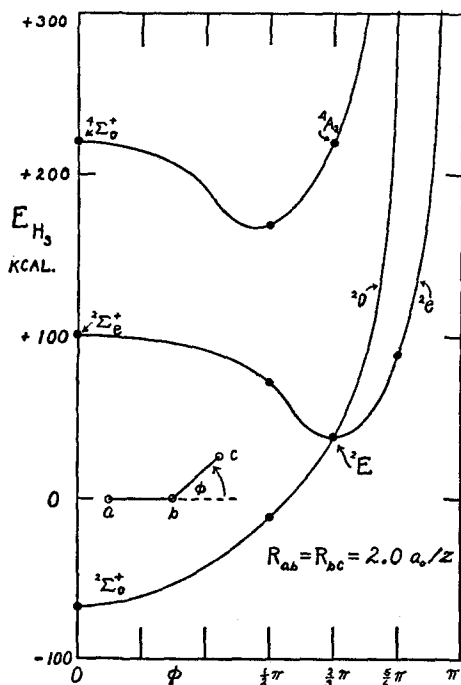


FIG. 5. The energy of the metastable  $H_3$  molecule as a function of the angle between the nuclei. The black dots represent calculated points.

<sup>8</sup> H. A. Jahn and E. Teller, Proc. Roy. Soc. A161, 220 (1937).

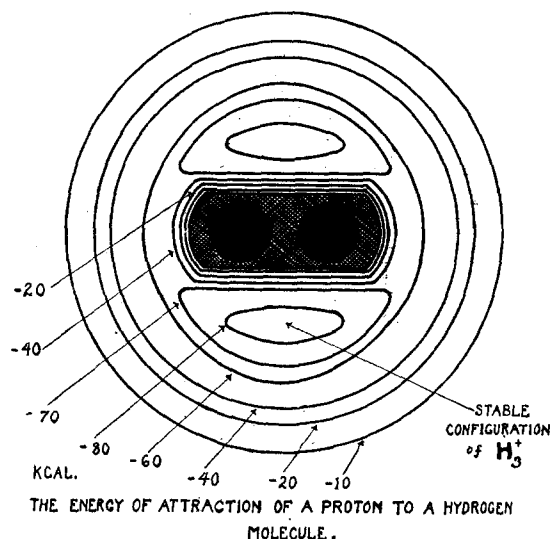


FIG. 6. The energy of attraction of a proton to a hydrogen molecule. The contour lines give the energy of the system when the proton is brought up to a position and the hydrogen molecule is held fixed. The black circles (roughly one Bohr radius in size) outline the location of the hydrogen molecule. The cross-hatched region corresponds to configurations which would be energetically difficult to attain.

the equilateral triangle is the doubly degenerate  $^2E$  and falls into this classification. Fig. 5 shows that indeed the energy for this state decreases as the molecule approaches a straight line and the degeneracy is removed.

When the three nuclei are in a straight line, all of the states given for  $H_3^+$  and for  $H_3$  are either  $\Sigma_g^+$  or  $\Sigma_u^+$ . This does not mean that there are not  $\Pi$  and minus states as well, but only that our method of using  $1s$ -hydrogen-like atomic orbitals cannot lead to the eigenfunctions for these states. Presumably these states would have rather high energies. In all cases for both the ion and the neutral molecule, when an odd and an even state have the same energy for the equilateral triangle, the odd one has the lower energy when  $\phi$  is less than  $2\pi/3$  and the even state has the lower energy when the nuclei  $a$  and  $c$  approach each other. As the nuclei  $a$  and  $c$  come together, the  $H_3^+$  goes into  $HeH^+$  and the  $H_3$  becomes  $HeH$ . The even states become  $\Sigma^+$  and  $\Pi^+$  states for the diatomic molecule with any nodal planes perpendicular to the line of nuclei whilst the *ungerade* become minus states with a nodal plane passing through the line of nuclei. Our calculations indicate that the states with the node perpendicular to the line

of nuclei has a lower energy than the states with the nodal plane passing through the nuclei.

#### IV. PHYSICAL PROPERTIES OF $H_3^+$

##### A. Approach of a proton to a hydrogen molecule

Let us consider the forces which are acting upon a proton as it approaches a hydrogen molecule.<sup>9</sup> Fig. 6 shows the lines of equal potential energy for the system when we keep the two nuclei of the hydrogen molecule (shown as big black circles) fixed at their equilibrium separation, and let the proton explore the field. At large separations, the hydrogen molecule is polarized by the electric charge on the proton and attracted to it with a force whose potential is:

$$E(H_3^+) - E(H_2) = \alpha(H_2)e^2/2R^4 \quad (45)$$

where  $R$  is the separation between the proton and the center of the hydrogen molecule and  $\alpha(H_2)$  is the mean polarizability of  $H_2$ . At large separations the equipotential lines are very nearly circular. At smaller separations (starting with the  $-60$  kcal. contour line) we must use the results of our present computations and take into account the complicated forces of valency as well as the pure electrostatic interactions. We see that for these close separations, the proton is pulled into an energy trough roughly parallel to the line of nuclei. Here it can oscillate rather freely in a long narrow path. The results of our present computations leave the question open as to whether the position of lowest energy is an equilateral triangle, but the best evidence at hand points to a stable configuration lying halfway between the equilateral and the right triangles. If the proton moves even closer to the hydrogen molecule it is repelled. The cross-hatching indicated the region in which the proton is most strongly repelled.

##### B. Vibration frequencies of $H_3^+$

Let us assume for the sake of simplicity that the triatomic hydrogen ion is an equilateral triangle with separations of  $r=1.79\text{\AA}$  between the nuclei. Because of symmetry, the most general expression for the expansion of the

potential energy of the system in powers of the displacements of the nuclei from their equilibrium positions is

$$V = V_0 + (\frac{1}{2})k_1[(\Delta r_{ab})^2 + (\Delta r_{bc})^2 + (\Delta r_{ac})^2] + k_2[\Delta r_{ab}\Delta r_{bc} + \Delta r_{ab}\Delta r_{ac} + \Delta r_{ac}\Delta r_{bc}], \quad (46)$$

where  $k_1$  and  $k_2$  are force constants to be determined from our calculations. In the central-force approximation  $k_2$  is taken to be zero.<sup>10</sup> In order to evaluate the force constants, it is convenient to express the potential energy in terms of the lengthening of two sides,  $\Delta r_{ab}$  and  $\Delta r_{bc}$ , and the change in the angle between them,  $\Delta\phi$ . To do this we substitute the relation

$$\Delta r_{ac} = (\frac{1}{2})(\Delta r_{ab} + \Delta r_{bc}) + \frac{\sqrt{3}}{2}r\Delta\phi \quad (47)$$

into Eq. (46). The potential energy then becomes:

$$V = V_0 + (\frac{1}{2})\left(\frac{5}{4}k_1 + k_2\right)\{(\Delta r_{ab})^2 + (\Delta r_{bc})^2\} + (\frac{1}{2})k_1\frac{3r^2}{4}(\Delta\phi)^2 + (\frac{1}{4}k_1 + 2k_2)\Delta r_{ab}\Delta r_{bc} + ((\frac{1}{2})k_1 + k_2)\frac{\sqrt{3}}{2}r\Delta\phi(\Delta r_{ab} + \Delta r_{bc}). \quad (48)$$

It is interesting to see that in this case of equal masses located in an equilateral triangle, there are no possible choices for the general force constants  $k_1$  and  $k_2$  which would lead to the form of potential energy used by Cross and Van Vleck<sup>11</sup> in which the cross-terms  $\Delta r_{ab}\Delta r_{bc}$  and  $\Delta\phi(\Delta r_{ab} + \Delta r_{bc})$  do not appear. Using our expression (48) for the potential energy in the Routh function as given by Cross and Van Vleck we find that the normal modes of vibration,  $x$ ,  $y$ , and  $z$  are given by the relations:

$$\begin{aligned} \Delta r_{ab} &= x + y + z, \\ \Delta r_{bc} &= x - y + z, \\ \frac{\sqrt{3}}{2}r\Delta\phi &= -3z. \end{aligned} \quad (49)$$

<sup>10</sup> The vibrations of three particles of equal mass located in an equilateral triangle was considered in the central-force approximation by Bhagavantam (Indian J. Phys. 5, 73 (1930)). Radakovic has considered the general problem of three particles in a triangle to this central force approximation (M. Radakovic, Wien Ber. 139, 107 (1930)).

<sup>11</sup> P. C. Cross and J. H. Van Vleck, J. Chem. Phys. 1, 350 (1933).

<sup>9</sup> This was considered in the case of the proton approaching the hydrogen molecule along the line of nuclei in the paper of Hirschfelder, Diamond and Eyring, J. Chem. Phys. 5, 695 (1937).

The normal mode,  $x$ , corresponds to an alternate expansion and contraction of the molecule without distortion. From the group theory point of view the displacement  $x$  is an eigenvector for the  $A_1$  representation of the symmetry group  $C_{3v}$ . The normal modes  $y$  and  $z$  correspond to distortions of the molecule in which one angle remains  $60^\circ$  while one side is lengthened and the other shortened. They belong to the doubly degenerate  $E$  representation. In the special case of the equilateral triangle with equal masses, we see that the normal modes of vibration are independent of the values of the force constants. Substituting  $x$ ,  $y$  and  $z$  into the Routh function, we easily obtain the equations of motion and from them the vibration frequencies:

$$\nu_x = \frac{1}{2\pi} \left( \frac{3(k_1 + k_2)}{m_H} \right)^{\frac{1}{2}}, \quad \nu_y = \nu_z = \frac{1}{2\pi} \left( \frac{3(k_1 - k_2)}{2m_H} \right)^{\frac{1}{2}}. \quad (50)$$

The real test whether or not the  $H_3^+$  ion is an equilateral triangle would be a determination of its vibration spectrum. If  $H_3^+$  has only two fundamental frequencies ( $\nu_x$  and  $\nu_y = \nu_z$ ) it is equilateral. If the degeneracy is removed, it is in some other configuration.

The force constants should be evaluated in the following manner. First set  $\Delta\phi = 0$  and let  $\Delta r_{ab} = \Delta r_{bc} = \Delta r$ . Then  $V = V_0 + (\frac{1}{2})(3k_1 + 6k_2)(\Delta r)^2$ . This variation corresponds to Fig. 2. Second, we keep  $\Delta r_{ab} = \Delta r_{bc} = 0$  and vary  $\Delta\phi$ . In this case,

$$V = V_0 + (\frac{1}{2}) \frac{3r^2}{4} k_1 (\Delta\phi)^2.$$

This variation of the potential energy with the angle is given in Fig. 4. Unfortunately, our calculations of the variation with angle is not sufficiently accurate for this purpose but as closely as we can tell,  $k_2 = 0$  (agreeing with the central force approximation) and  $k_1 = 4.8 \times 10^4$ . From these force constants, it follows that

$$\nu_x = 1550 \text{ cm}^{-1}, \quad \nu_y = \nu_z = 1100 \text{ cm}^{-1} \quad (51)$$

and the zero point energy of  $H_3^+$  is

$$(\frac{1}{2})h\nu_x + (\frac{1}{2})h\nu_y + (\frac{1}{2})h\nu_z = 5.4 \text{ kcal.} \quad (52)$$

The  $z$  and  $y$  modes of vibration should be infra-red active and therefore susceptible to direct experimental observation.

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### Integrals Required for Computing the Energy of $H_3$ and of $H_3^+$

JOSEPH O. HIRSCHFELDER

*Chemistry Department, University of Wisconsin, Madison, Wisconsin*

AND

CORNELIUS N. WEYGANDT

*Moore School of Electrical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania*

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Some of the difficult integrals required for the variational method calculation of the energy of the triatomic hydrogen molecule and positive ion were evaluated with the aid of the differential analyzer. The integral  $\int_0^\pi \exp(-B(1-A \cos \theta)^{\frac{1}{2}}) d\theta$  is tabulated for a complete range of the parameters,  $A$  and  $B$ . The integral  $K(c, ab) = (1/\pi) \int r c^{-1} \exp(-r_a - r_b) dr$  is tabulated for many configurations of the three electrons or nuclei:  $a$ ,  $b$ , and  $c$ . Numerical tables are given of all of the integrals occurring in the Sugiura treatment of the ground state of  $H_2$ . The values of all of the other integrals used in the calculation of the energy of  $H_3$  and of  $H_3^+$  are given. It is expected that these tables will be useful for many problems of molecular quantum mechanics.