

II. Calculation of Energy of H_3^+ Ion

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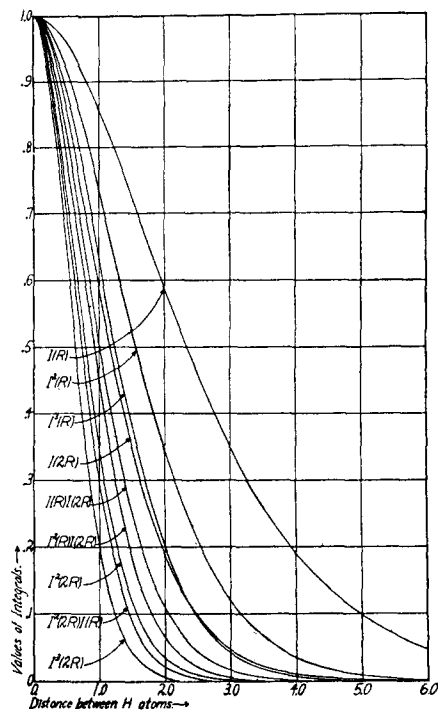


FIG. 8. Normalizing integrals.

the centers.¹¹ The resulting integrations may then

¹¹ A. S. Coolidge, *Phys. Rev.* **42**, 189 (1932), used this method for H_2O . Some work along this line has been done

be carried through by making use of the orthogonality properties of the spherical harmonics. However, the series which must be evaluated, converges slowly except for small internuclear distances and the terms are ponderous. Coolidge and James have used this method for the internuclear separation of $1.7 a_0$ and obtained agreement with our values to within half a kcal./mole for $L(aa, bc)$, $L(bb, ac)$ and $L(ab, bc)$ but their value of $L(ab, ac)$ is some two kcal./mole smaller than ours.

The one- and two-center integrals which occur in this treatment have been previously used for the diatomic hydrogen molecule.¹² The integrals for nuclear attraction are shown in Fig. 6, those for electronic repulsion in Fig. 7. The overlap integrals and all the combinations of them required for H_3 are given in Fig. 8.

We wish to express our appreciation to the American Philosophical Society for financial assistance during the course of this work.

by Hershtenkorn (Diss., M.I.T., June 1932) and by A. A. Frost at Princeton.

¹² See, e.g., N. Rosen, *Phys. Rev.* **38**, 2099 (1931).

II. Calculation of Energy of H_3^+ Ion

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The potential energies for linear symmetrical configurations of H_3^+ have been calculated by the same methods used in the previous paper (I). The energies at the minimum in kcal./mole and the corresponding distances between neighboring atoms in Bohr radii for the various approximations are:

Heitler-London	— 91.92 at 2.00;
H.L. plus polar	— 108.64 at 2.00;

Wang Approx.	— 130.89 at 1.55;
Wang plus polar	— 155.35 at 1.52.

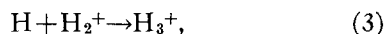
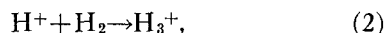
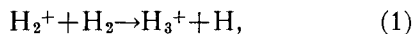
It follows from the use of the variational method that the energy of binding of a proton to H_2 is greater than 46.8 kcal./mole. If we use the same Wang plus polar approximation for H_2 and H_3^+ we obtain for this binding energy 63.11 kcal./mole. The reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ may be exothermal and cannot be more than slightly endothermal.

THERE is experimental evidence that H_3^+ ions are formed whenever H_2 is ionized at any but the lowest pressures.¹ This probably

¹ H. D. Smyth, *Rev. Mod. Phys.* **3**, 347 (1931); *Phys.*

occurs by the following secondary processes:

Rev. **4**, 452 (1925); W. Bleakney, *Phys. Rev.* **40**, 496 (1932); **35**, 1180 (1930); Hogness and Lunn, *Phys. Rev.* **26**, 44 (1925); Brasefield, *Phys. Rev.* **31**, 52 (1928); Dorsch and Kallmann, *Zeits. f. Physik* **53**, 80 (1929).



of which the first is ordinarily the most important. In this paper only the linear symmetric configurations are considered. The calculation of the energy of the triatomic hydrogen ion is then very similar to that of the triatomic hydrogen molecule treated in the paper immediately preceding (I). The same integrals are used and the same types of approximations considered. The lowest energy states for the triatomic hydrogen ion are found to be symmetric with respect to an interchange of atoms a and c in the electronic eigenfunctions as contrasted with the H_3 case.

1. ENERGY OF LOWEST BOND STATE

The simplest type of eigenfunction which we can form from the atomic orbitals considered in paper I corresponds to a bond between the atoms a and b alternating with a bond between b and c .

$$\psi_1 = (2)^{-1} [a(1)b(2) + a(2)b(1) + b(1)c(2) + b(2)c(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)].$$

This state corresponds to the energy:

$$E_{11} = \frac{a^2b^2 + b^2ac + abab + abbc}{1 + I_{00}(2R) + 2I_{00}^2(R)}.$$

Values for the energy components are given in Fig. 1. The energy is shown in Fig. 2 as curve I. The lowest value which we obtained for the energy was -91.92 kcal./mole.

2. HEITLER-LONDON PLUS POLAR STATES TYPE OF EIGENFUNCTION²

The energy for the triatomic hydrogen ion can be considerably improved if we include in the eigenfunction linear combinations of two polar states and two homopolar states so as to get the minimum energy for the combination. The eigenfunctions which can be formed from the atomic orbitals considered, and which are

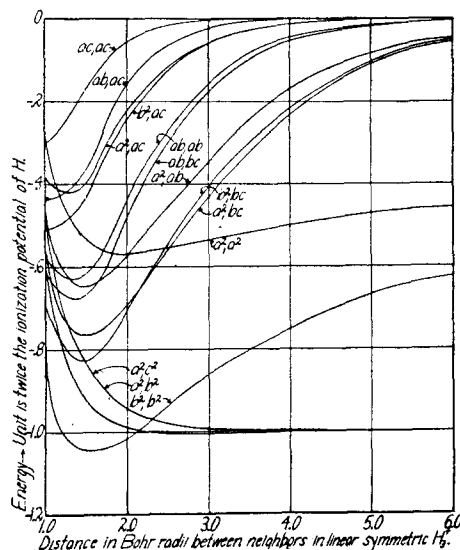


FIG. 1. The energy matrix components for H_3^+ .

symmetrical with respect to an interchange of atoms a and c are: (1) bond eigenfunction between a and b plus a bond eigenfunction between b and c ; (2) bond between a and c ; (3) both electrons on the central atom b ; (4) both electrons alternately on a and then on c .

$$\psi_2 = \frac{1}{2} [a(1)c(2) + c(1)a(2)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)],$$

$$\psi_3 = 2^{-1/2} b(1)b(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)],$$

$$\psi_4 = \frac{1}{2} [a(1)a(2) + c(1)c(2)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)].$$

The calculation of the energy involves the same formal processes as in the equivalent approximation for the triatomic molecule. The energy components are shown in Fig. 1. The energy for the pure states 1, 2, 3 and 4 are shown as curves I, II, III, IV, respectively, in Fig. 2. The energy of the ion is then obtained by the solution of a fourth-order secular equation. The values are shown graphically in Fig. 2 as curve I'. At large internuclear separations there is a strong interaction between the two homopolar states (1) and (2). It is interesting that for distances so large that states ψ_1 and ψ_2 have practically attained their asymptotic energies, their interaction energy H_{12} is still appreciable. At small separations there is a strong interaction between (1) and the polar state (3). Fig. 3 shows the coefficients c_i of the normalized Ψ giving the total normalized eigenfunction of

² Heitler and London, *Zeits. f. Physik* **44**, 455 (1927); S. Weinbaum, *J. Chem. Phys.* **1**, 593 (1933).

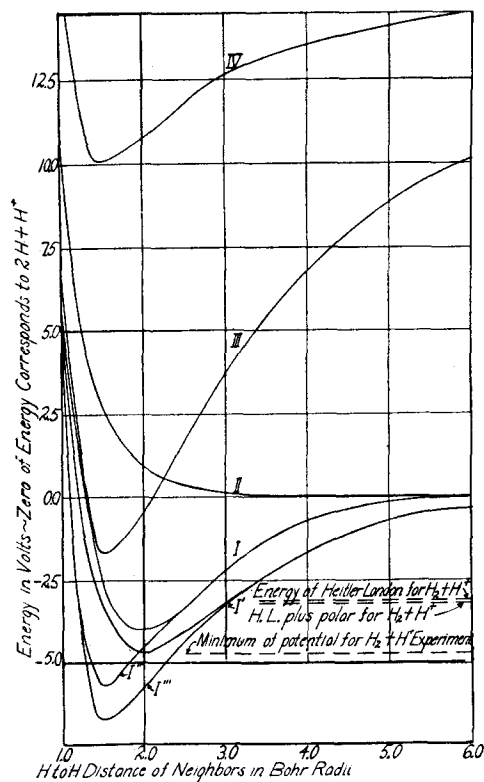


FIG. 2. Potential curves for various states of linear symmetrical H_3^+ .

lowest energy. These c_i are similar to those defined for the triatomic molecule in paper I. The minimum energy that is obtained in this approximation is -108.64 kcal./mole at a separation of $2.0a_0$ between neighboring atoms. The improvement, it will be noticed, is 16.72 kcal./mole over the corresponding value for the lowest homopolar state.

3. WANG TYPE OF EIGENFUNCTION³

It is not difficult to vary the effective nuclear charge in exactly the same manner as for the triatomic hydrogen molecule in paper I. It should be emphasized again that because of the type of variation the value for E is the lowest for a particular value of $\rho = zR$ but not necessarily for any particular value of R except at that point at which it is a minimum for both z and R . Thus it will be noticed in the curve I'' of Fig. 2 which shows this energy as a function of R , that

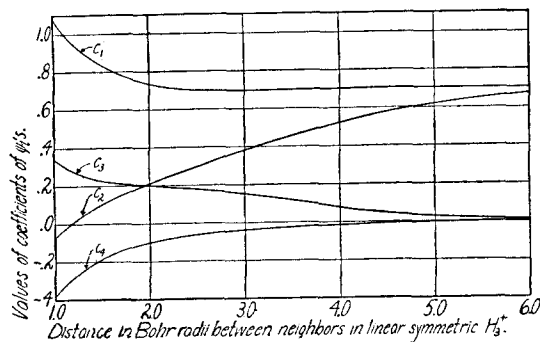


FIG. 3. Coefficients of $\Psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4$. Ψ and the ψ_i 's are normalized to unity. The ψ_i 's are not orthogonal.

this method of varying z led to considerable improvement of the energy for separations near $R=2.0$ which is the most favorable separation when $z=1$. However, curve I'' merges into I' for larger or smaller separations and for these separations this particular way of varying z does not improve the energy. The lowest energy which is obtained in this approximation is -130.89 kcal./mole for the separation $R=1.546a_0$ and $z=1.294$. This is an improvement of 39 kcal./mole over the lowest bond state approximation. It is remarkable that the variation of the effective charge produces such a striking change in this energy when it made so little difference in the energy of the triatomic molecule.

4. WANG PLUS IONIC STATES EIGENFUNCTION

By varying the effective nuclear charge in the H.L. plus polar eigenfunction the energy of the triatomic hydrogen ion is improved considerably. Knowing the composition of this eigenfunction for $z=1$, we may find the energy of the molecule for this same composition as a function of z . The c_i are given in Fig. 3. z is then varied until E has a minimum value for the particular value of $\rho = zR$ considered. This value of E can be improved still further by varying the composition keeping z constant. This variation of the composition improved the result at the energy minimum by 2.87 kcal./mole. The value of the energy as a function of R is shown as curve I''' in Fig. 2. The minimum value of the energy has dropped to -155.35 kcal./mole for the separation of $R=1.525a_0$ which corresponds to $z=1.312$ and

³ S. C. Wang, Phys. Rev. 31, 579 (1928).

$zR=2.0a_0$. This is to be compared with the energy of the normal diatomic molecule calculated in this same manner by Weinbaum,² -92.24 kcal./mole. This calculation gives an energy of binding of a proton to the H_2 of 63.11 kcal./mole. This is very nearly equal to the energy of binding of a proton to a hydrogen atom, i.e., 64.04 kcal./mole. (The zero-point energy is not taken into account in either of these values.) Since the true energy of the diatomic hydrogen molecule is -108.6 kcal./mole instead of the calculated -92.2 , the very smallest amount of binding energy which the triatomic ion could possibly have relative to a hydrogen molecule plus a proton is 46.8 kcal./mole. However, the actual binding energy of the proton to the hydrogen molecule will probably be larger instead of smaller than 63.11 kcal./mole. The reason for this supposition is that our experience with H_3 was that the accuracy for the three-center problem was poorer than that obtained for the two-center case by the corresponding method. In any event, the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ should take place with at most a small amount of kinetic energy, and it is probable (not certain) that it can take place without any relative kinetic energy.

5. REMARKS

From our calculations we find for the linear ion a moment of inertia of 2.15×10^{-40} g cm². If the same distances between neighboring atoms were preserved in the equilateral triangle model, the latter would have two moments of inertia having values of $\frac{1}{2}$ and $\frac{1}{4}$ of the above. It would require an increase of about 40 percent in the distances to double the latter moments of inertia. Allen

and Sandeman⁴ found three band systems in the secondary spectrum of a hydrogen filled Wood's discharge-tube, which they interpret as due to a triatomic hydrogen molecule or ion with a moment of inertia of 1.8×10^{-40} g cm². These bands are enhanced in the arc spectrum and under conditions favorable to the formation of H_3^+ .

The equilateral triangle model for the triatomic hydrogen ion was considered by C. A. Coulson.⁵ However, Coulson did not calculate the three-center multiple exchange integrals, and without them he was not able to place the energy of the molecule within any significant limits. He believed that the triatomic ion would be more stable in the equilateral triangle configuration than in the linear. His argument was based on the fact that the binding energy which two electrons exert on three centers is increased if the configuration is triangular. While this is undoubtedly true, the nuclear repulsions become much larger at the same time. For a separation between neighbors of $1.5a_0$ (which must be nearly the best separation for both cases) the energy of nuclear repulsion is 1040 kcal./mole for the three atoms in a linear symmetrical configuration and 1248 kcal./mole for the equilateral triangle. Thus only if the electronic binding for the triangle exceeds that for the line by over 200 kcal./mole can the former configuration be the more stable. This point requires further investigation.

We wish to express our appreciation to the American Philosophical Society for financial assistance during the course of this work.

⁴ Allen and Sandeman, Proc. Roy. Soc. **A114**, 293 (1927).

⁵ C. A. Coulson, Proc. Camb. Phil. Soc. (2) **31**, 244 (1935).