

I. Calculation of Energy of H₃ Molecule

J. Hirschfelder, H. Eyring, and N. Rosen

Citation: [The Journal of Chemical Physics](#) **4**, 121 (1936); doi: 10.1063/1.1749798

View online: <http://dx.doi.org/10.1063/1.1749798>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/4/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Gaussian functions in hylleraasCI calculations. I. Ground state energies for H₂, HeH⁺, and H⁺ 3](#)
J. Chem. Phys. **88**, 2091 (1988); 10.1063/1.454090

[Optimized diatomicsinmolecules potential energies for H₃ and H₄](#)
J. Chem. Phys. **65**, 5155 (1976); 10.1063/1.433057

[Manybody perturbation theory applied to molecules: Analysis and correlation energy calculation for Li₂, N₂, and H₃](#)
J. Chem. Phys. **64**, 2641 (1976); 10.1063/1.432518

[Semiempirical Potential Energy Functions. I. The H₂ and H₂ + Diatomic Molecules](#)
J. Chem. Phys. **22**, 1017 (1954); 10.1063/1.1740254

[Calculation of the Energy of H₃ and of H₃ +. III](#)
J. Chem. Phys. **5**, 695 (1937); 10.1063/1.1750101



AIP | Applied Physics
Letters

is pleased to announce **Reuben Collins**
as its new Editor-in-Chief

I. Calculation of Energy of H₃ Molecule

J. HIRSCHFELDER, H. EYRING AND N. ROSEN, *Frick Chemical Laboratory of Princeton University and the Institute for Advanced Study*

(Received November 22, 1935)

The potential energies for linear symmetrical configurations of the triatomic hydrogen molecule have been calculated by the variational method with hydrogen-like 1s atomic orbitals by varying the "effective charge" and the amount of all polar and homopolar states in the eigenfunction. The lowest energies (in kcal./mole = 1/23.06 ev) and corresponding separations between neighboring atoms (in Bohr radii) are given in the table. The activation energies are for the reaction $H + H_2 \rightarrow H_2 + H$, and are

calculated with the same type of approximation for H₂ and H₃. All of the difficult three-center integrals for the repulsions between pairs of electrons were calculated explicitly in ellipsoidal coordinates without the use of infinite series.

	Heitler-London	H.L. plus Polar	Wang	Wang plus Polar	Experiment
$E_{H_3} - 3EH$	-53.11	-60.39	-56.16	-67.09	-103.
r_{H_3}	2.00	2.00	1.89	1.84	
Act. Energy	19.07	13.63	30.68	25.15	7.

INTRODUCTION

THE simplest triatomic systems are those formed from three hydrogen nuclei. The neutral triatomic molecule is of particular interest since it is the intermediate in reactions of the type



and also in the ortho-para hydrogen conversion.

Various approximations for the energy have been considered for H₃. London¹ proposed to use hydrogen atomic orbitals and to neglect all but the diatomic Coulombic and exchange integrals. This led to values for H₃ very much too high as is known by comparison with experiment and certain of the terms neglected are of the same order of magnitude as those which are retained. Coolidge and James² have calculated the energy for a single configuration of the linear symmetric H₃ molecule using hydrogen atomic orbitals to form the lowest homopolar state. Their particular configuration gives an energy more than a half volt higher than they would have obtained for a somewhat larger interatomic distance. A discussion of the criticism of James and Coolidge of the semi-empirical method of calculating activation energies will be given in a forthcoming paper in the light of this work and the results of the method itself.

In the present paper the variational method for the energy is carried through for all the linear

symmetric configurations using hydrogen-like atomic orbitals (of the 1s type) to form the four following eigenfunctions:

- the best homopolar function.
- the best linear combination of polar and homopolar functions.
- the eigenfunction of (a) with the "effective charge" varied to give the lowest energy.
- the eigenfunction of the type in (b) obtained by simultaneous variation of the screening constant and the polar-homopolar composition.

II. THE ENERGY OF THE TRIATOMIC HYDROGEN MOLECULE

All of the integrals used in the calculation of the energy of the triatomic hydrogen molecule are defined and discussed in the appendix. The Hamiltonian operator for the electronic energy is:

$$H = H_A + H_B + H_C + H_D, \quad (2)$$

where

$$H_A = -(\hbar^2/8\pi^2m)[\nabla_1^2 + \nabla_2^2 + \nabla_3^2]$$

= kinetic energy of the electrons,

$$H_B = e^2[r_{ab}^{-1} + r_{ac}^{-1} + r_{bc}^{-1}]$$

= energy of mutual repulsions of nuclei,

$$H_C = -e^2 \sum_{i=1}^3 [r_{ai}^{-1} + r_{bi}^{-1} + r_{ci}^{-1}]$$

= energy of attraction of electrons to the nuclei,

$$H_D = e^2[r_{12}^{-1} + r_{13}^{-1} + r_{23}^{-1}]$$

= energy of mutual repulsions of electrons.

¹ F. London, *Zeits. f. Physik* **46**, 455 (1928); **50**, 24 (1928).

² A. S. Coolidge and H. M. James, *J. Chem. Phys.* **2**, 811 (1934).

Here a , b and c are atoms arranged in the symmetrical linear configuration with b the central atom. The distance between neighboring atoms is Ra_0 ($a_0 = 0.528$ Angstrom, i.e., the radius of the first Bohr orbit for atomic hydrogen). The electrons are denoted by 1, 2, and 3. r_{ij} is the distance between the i th and j th particle. The calculated energy for the molecule is given as:

$$E = \iiint \Psi^* H \Psi d\tau_1 d\tau_2 d\tau_3 / \iiint \Psi^* \Psi d\tau_1 d\tau_2 d\tau_3. \quad (3)$$

By the variational principle E is the actual energy of the molecule when Ψ is really an eigenfunction of H , and E is greater than the lowest energy of the molecule when Ψ is only an approximate eigenfunction. In this treatment we obtain the energy using various types of approximate eigenfunctions built from the $1s$ hydrogenic atomic orbitals:

$$\begin{aligned} a(1) &= (z^3/\pi)^{1/2} e^{-zra_1}, & b(1) &= (z^3/\pi)^{1/2} e^{-zrb_1}, \\ c(1) &= (z^3/\pi)^{1/2} e^{-zrc_1}, \end{aligned} \quad (4)$$

where z is the "effective nuclear charge." These eigenfunctions must be antisymmetric with respect to an interchange of any two electrons because of the Pauli exclusion principle. Without loss of generality they are taken as eigenfunctions for S^2 and S_z , the square and the z component of the total spin, respectively; the lowest energy usually corresponds to the lowest allowed value of S^2 . The fact that H is symmetric with respect to an interchange of atoms a and c , allows the eigenfunctions to be separated into symmetric and antisymmetric functions with respect to this interchange, and the two types of functions are noncombining. In the London approximation, i.e., where the multiple exchange

and overlap integrals are neglected, it is easy to show that the antisymmetric eigenfunctions correspond to the states of lowest energy. This is also found to be the case in the present calculation.

1. The Heitler-London approximation

The simplest form of eigenfunction which we can take for the triatomic hydrogen molecule corresponds to a pure homopolar state with $z=1$. This eigenfunction is the three-atom analog of that used by Heitler and London³ (H.L.) for the normal diatomic hydrogen molecule, and we should expect the energy obtained in this manner for the triatomic molecule to be of the same order of accuracy. There are two eigenfunctions of this type which can be formed: ψ_s is symmetric with respect to an interchange of atoms a and c and corresponds to the bond $a-c$; ψ_1 is antisymmetric in this respect and corresponds to a bond between a and b alternating with a bond between b and c . With the abbreviated notation:

$$\begin{pmatrix} a & b & c \\ \alpha & \beta & \alpha \end{pmatrix} = (3!)^{-1/2} \begin{vmatrix} a(1)\alpha(1) & b(1)\beta(1) & c(1)\alpha(1) \\ a(2)\alpha(2) & b(2)\beta(2) & c(2)\alpha(2) \\ a(3)\alpha(3) & b(3)\beta(3) & c(3)\alpha(3) \end{vmatrix}, \quad (5)$$

where $\alpha(1)$ and $\beta(1)$ are spin functions of electron 1 which are eigenfunctions, respectively, for $S_{z1} = \frac{1}{2}\hbar/2\pi$, $-\frac{1}{2}\hbar/2\pi$.

$$\psi_1 = 2 \begin{pmatrix} a & b & c \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} a & b & c \\ \beta & \alpha & \alpha \end{pmatrix} - \begin{pmatrix} a & b & c \\ \alpha & \alpha & \beta \end{pmatrix}, \quad (6)$$

$$\psi_s = \begin{pmatrix} a & b & c \\ \alpha & \alpha & \beta \end{pmatrix} - \begin{pmatrix} a & b & c \\ \beta & \alpha & \alpha \end{pmatrix}. \quad (7)$$

These correspond to the electronic energies:

$$E_{11} = \frac{\iiint \psi_1 H \psi_1 d\tau_1 d\tau_2 d\tau_3}{\iiint \psi_1 \psi_1 d\tau_1 d\tau_2 d\tau_3} = \frac{a^2 b^2 c^2 + a^2 b c b c - b^2 a c a c - a b b c a c}{1 + I_{00}^2(R) - I_{00}^2(2R) - I_{00}(2R)I_{00}^2(R)}, \quad (8)$$

$$E_{ss} = \frac{\iiint \psi_s H \psi_s d\tau_1 d\tau_2 d\tau_3}{\iiint \psi_s \psi_s d\tau_1 d\tau_2 d\tau_3} = \frac{a^2 b^2 c^2 + b^2 a c a c - a^2 b c b c - a b b c a c}{1 + I_{00}^2(2R) - I_{00}^2(R) - I_{00}(2R)I_{00}^2(R)}, \quad (9)$$

where we have used the notation: $I_{00}(R) = (1/\pi) \int e^{-ra} e^{-rb} d\tau$,

$$a^2 b c b c = (a(1)b(2)c(3) | H | a(1)c(2)b(3)), \quad \text{etc.} \quad (10)$$

These energy components are plotted in Figs. 1 and 2.

The energy of the symmetrical state, ψ_s , is shown in Fig. 3, curve V. It corresponds to a

³ Heitler and London, Zeits. f. Physik **44**, 455 (1927).

strong repulsion between the three hydrogen atoms.

The energy of the state ψ_1 (antisymmetric with respect to a and c) is shown in Fig. 3 as curve I. The energy is less than for the three separated atoms and greater than for a diatomic hydrogen

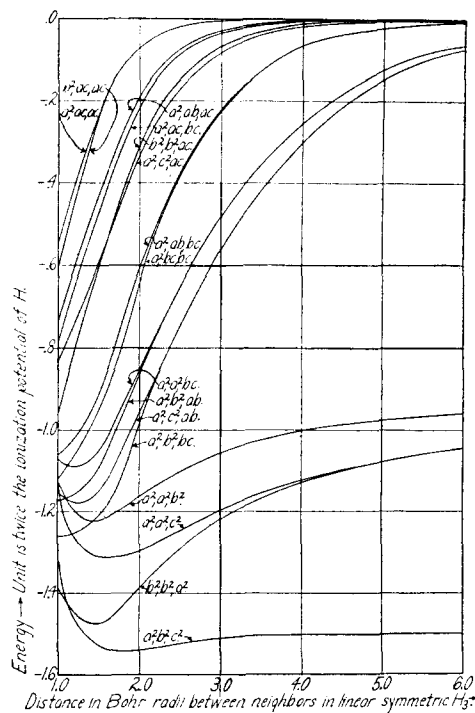


FIG. 1. The energy matrix components for H_3 .

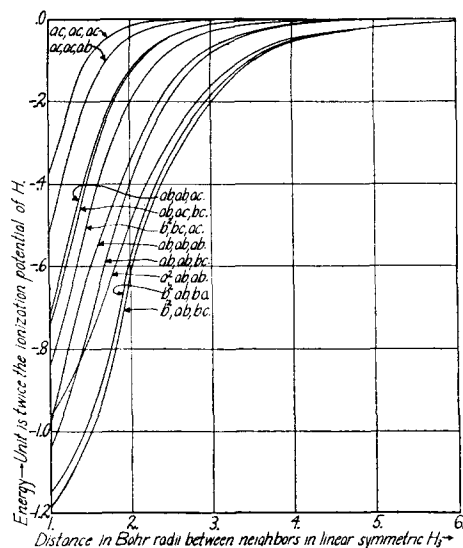


FIG. 2. The energy matrix components for H_3 .

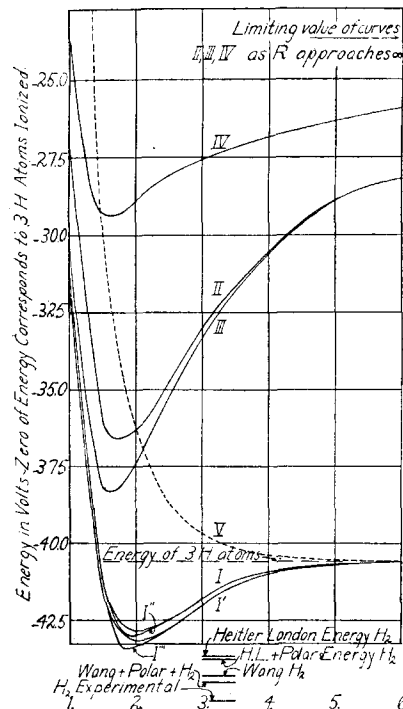


FIG. 3. H to H distance of neighbors in Bohr radii. Potential curves for various states of linear symmetrical H_3 .

molecule and a hydrogen atom. The lowest energy is -53.11 kcal./mole for the separation of $2.0 a_0$ between neighboring atoms. This is to be compared with the energy of the diatomic hydrogen molecule calculated by Heitler and London and Sugiura,⁴ -72.18 kcal./mole. If a linear symmetrical molecule really corresponds to the activated state, then the activation energy for the reaction $H + H_2 \rightarrow H_2 + H$, will be 19.07 kcal./mole by this calculation. However this approximation for the diatomic molecule is 36 kcal. or 1.6 ev higher than the experimental value of -108.6 kcal. Comparing the experimental activation energy (5.5 to 7.3 kcal.),⁵ one sees that the energy obtained here for the triatomic molecule must be about 0.6 ev less accurate than that for the diatomic molecule.

James and Coolidge calculated the energy of the triatomic hydrogen molecule for the single

⁴ Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

⁵ It appears that the zero-point energy in the activated complex is within one or two kcal./mole the same as that for the normal H_2 molecule (6.2 kcal./mole). See A. and L. Farkas, Proc. Roy. Soc. **A152**, 124 (1935); K. Geib and P. Hartek, Zeits. f. physik. Chemie Bodenstein Festband, 849 (1931).

internuclear separation $R = 1.7 a_0$. For this point they obtained the energy of -39.7 kcal./mole which is in good agreement with our value for this separation.

2. Heitler-London plus polar states

A slightly better approximation to the energy of the triatomic hydrogen molecule may be obtained by including the polar states in the eigenfunction. There are three polar states which are antisymmetric with respect to an interchange of a and c and which must be considered. ψ_2 corresponds to two electrons on atom a and one on c alternating with two on c and one on a . ψ_3 corresponds to two electrons on b and one electron alternating between a and c . ψ_4 corresponds to one electron on b and two electrons alternating between a and c :

$$\psi_2 = \begin{pmatrix} a & a & c \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} c & c & a \\ \alpha & \beta & \alpha \end{pmatrix}, \quad (11)$$

$$\Psi = c_1(S_{11})^{-\frac{1}{2}}\psi_1 + c_2(S_{22})^{-\frac{1}{2}}\psi_2 + c_3(S_{33})^{-\frac{1}{2}}\psi_3 + c_4(S_{44})^{-\frac{1}{2}}\psi_4. \quad (15)$$

The c_i are the solutions to the set of linear equations:

$$(S_{11})^{\frac{1}{2}}c_i E = c_1 H_{i1}(S_{11})^{-\frac{1}{2}} + c_2 H_{i2}(S_{22})^{-\frac{1}{2}} + c_3 H_{i3}(S_{33})^{-\frac{1}{2}} + c_4 H_{i4}(S_{44})^{-\frac{1}{2}}, \quad i = 1, 2, 3, 4. \quad (16)$$

The absolute values of the c_i are chosen so that Ψ is normalized to unity. Fig. 4 shows the c_i plotted as functions of the internuclear separation R .

The energy of the pure polar states 2, 3 and 4 are shown by curves II, III and IV, respectively, of Fig. 3. They correspond to much higher energies than the homopolar state. However, these states interact and the best linear combination

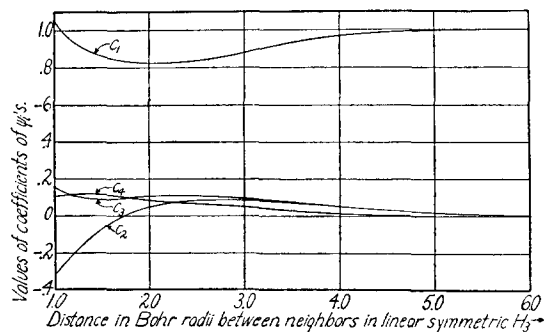


FIG. 4. Coefficients of $\Psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4$. Ψ and ψ_i 's are normalized to unity. ψ_i 's are not orthogonal.

$$\psi_3 = \begin{pmatrix} a & b & b \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} b & b & c \\ \alpha & \beta & \alpha \end{pmatrix}, \quad (12)$$

$$\psi_4 = \begin{pmatrix} b & c & c \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} a & a & b \\ \alpha & \beta & \alpha \end{pmatrix}. \quad (13)$$

The energy components are shown in Figs. 1 and 2. By letting S_{ij} be the matrix components of unity:

$$S_{ij} = \iiint \psi_i \psi_j d\tau_1 d\tau_2 d\tau_3$$

and H_{ij} the matrix components of H :

$$H_{ij} = \iiint \psi_i H \psi_j d\tau_1 d\tau_2 d\tau_3.$$

The energies are given as the roots of the secular equation:

$$|H_{ij} - ES_{ij}| = 0. \quad (14)$$

We are interested only in the lowest root of this equation, the other roots corresponding to higher states of the molecule. The composition of the eigenfunction which leads to the lowest energy value may be written as

of the four gives an energy level which is considerably lower than the homopolar. It is customary to designate such improvement by the term "resonance energy"; its physical significance is the improvement of the faulty charge distribution due to the approximate nature of the original eigenfunctions. The best linear combination is shown as curve I' in Fig. 3. The minimum energy which this type of eigenfunction yields is -60.39 kcal./mole for $R = 2.0 a_0$.

Weinbaum⁶ calculated the energy of the diatomic hydrogen molecule using the same type of eigenfunction, i.e., homopolar plus polar states, and he obtained -74.02 kcal./mole. Comparing the energy of the triatomic molecule with this, one finds that the calculated activation energy for the reaction $H + H_2 \rightarrow H_2 + H$ is (except for zero-point energy) 13.63 kcal./mole. This activation energy is in fair agreement with the experimental value of 5.5 to 7.3 kcal./mole. Unfortunately the eigenfunctions are still too

⁶ S. Weinbaum, J. Chem. Phys. 1, 593 (1933).

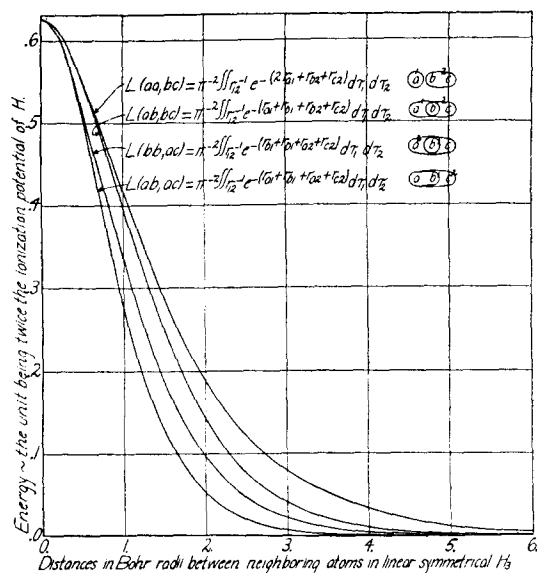


FIG. 5. Potential between pairs of electrons having eigenfunctions involving three centers.

approximate for this agreement to have real

significance, since the absolute value of the energy of the diatomic molecule with which we are comparing the energy of the triatomic molecule is 34 kcal./mole too large.

3. The Wang type of eigenfunction

In the diatomic hydrogen molecule, Wang⁷ obtained a considerable improvement over the Heitler-London energy value by varying the "effective nuclear charge," z , in the atomic orbitals. This same type of variation may be carried out for the triatomic molecule without introducing any new integrals. Our method is similar to that used by Wang and by Coulson.⁸

The overlap integral $I_{00}(R)$ goes into $I_{00}(\rho)$ where $\rho = zR$. The nuclear attraction and electronic repulsion integrals become the same integrals as functions of ρ instead of R except that they are multiplied by z .

The kinetic energy gives rise to three separate integrals:

$$\begin{aligned} \int a(1) \left(-\frac{\hbar^2}{8\pi^2 m} \nabla_1^2 \right) a(1) d\tau_1 &\rightarrow z^2 e^2 / 2a_0, \\ \int b(1) \left(-\frac{\hbar^2}{8\pi^2 m} \nabla_1^2 \right) a(1) d\tau_1 &\rightarrow \left[-\frac{1}{2} z^2 I_{00}(\rho) + z^2 J_{00}(\rho) \right] e^2 / a_0, \\ \int c(1) \left(-\frac{\hbar^2}{8\pi^2 m} \nabla_1^2 \right) a(1) d\tau_1 &\rightarrow \left[-\frac{1}{2} z^2 I_{00}(2\rho) + z^2 J_{00}(2\rho) \right] e^2 / a_0. \end{aligned}$$

By combining the energy components it is easy to show that the energy in units of e^2/a_0 for the pure homopolar state 1 has the form

$$(E)_z = z[(E)_{z=1} + (z-1)A_{11}/S_{11}],$$

where A_{11} is a function of ρ .

Now keeping $zR = \rho$ constant, we can vary z to give the lowest energy:

$$\begin{aligned} (\partial E / \partial z)_\rho = 0 &= (E)_{z=1} + (2z-1)A_{11}/S_{11}, \\ z_{\min} &= -\frac{1}{2}(E)_{z=1}S_{11}/A_{11} + \frac{1}{2}, \\ E_{\min} &= -S_{11}[(E)_{z=1} - A_{11}/S_{11}]^2 / (4A_{11}). \end{aligned}$$

E_{\min} is the lowest energy that may be obtained for a particular value of zR but not necessarily for a particular value of R . However, if ρ is now varied to give the lowest value of E_{\min} , the latter will agree with the lowest possible value of E which can be obtained by varying both R and z .

This process corresponds to the Wang approximation for the diatomic hydrogen molecule. In the diatomic molecule the variation of z led to

an energy of -86.94 kcal./mole which is an improvement of 14.8 kcal./mole over that for $z=1$. In the triatomic molecule this variation leads to an energy of -56.16 kcal./mole (at the point $R=1.889 a_0$ and with $z=1.059$), an improvement of only 3.05 kcal. This is 4.23 kcal./mole worse than for the H.L. plus polar states value. See Fig. 3, curve I'' for the values of E_{\min} . The corresponding activation energy for the $H+H_2 \rightarrow H_2+H$ reaction which we calculate as the difference between diatomic and triatomic energy is then 30.78 kcal./mole.

4. Wang plus polar states approximation

The variation of the "effective nuclear charge," z , was carried out for the eigenfunction in which the polar states are included. The variation of z and of the composition of the eigenfunction was carried out by successive approxima-

⁷ S. C. Wang, Phys. Rev. **31**, 579 (1928).

⁸ C. A. Coulson, Proc. Camb. Phil. Soc. (2) **31**, 244 (1935).

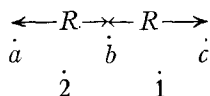
tions. First, the composition of the eigenfunction was taken to be the same as that previously obtained for the H.L. plus polar states approximation; a value of the best z for that composition was then obtained. The composition was then varied for that value of z . This last step improved the energy by only 0.35 kcal./mole at the point $\rho=2.0$; it was therefore deemed unprofitable to go back and readjust z . The energy values are shown as curve I''' in Fig. 3. The value for the Wang plus polar states approximation for the diatomic hydrogen molecule is -92.24 kcal./mole as obtained by Weinbaum. Since the minimum value which we find for the energy of the triatomic hydrogen molecule to this approximation is

-67.09 kcal./mole for $R=1.841 a_0$ and $z=1.087$, the calculated activation energy then becomes 25.15 kcal./mole. This activation energy is 17 kcal./mole larger than the experimental value. This approximation is the best that we can obtain without using more elaborate eigenfunctions and calculating new three-center integrals. It is not surprising that the variation of the screening constant on the three atoms simultaneously gives little improvement in the energy since one would expect that the central and outer atoms really ought to have different screening constants. However, such a treatment would involve the evaluation of additional integrals and has not been attempted here.

APPENDIX

Integrals

The three hydrogen nuclei, a , b , c lie symmetrically on a straight line with a separation of R times the first Bohr radius for atomic hydrogen, a_0 ; and 1 and 2 are electrons.



If the molecular eigenfunctions are compounded from 1s hydrogen-like atomic orbitals each having the same screening constant, all of the troublesome three-center integrals may be carried through directly in terms of ellipsoidal coordinates without resorting to ponderous or slowly converging infinite series. The convenient units $e^2/a_0=27.058$ ev = 623.96 kcal./mole for the energy and $a_0=0.528 \times 10^{-8}$ cm for the length, are used here. The ellipsoidal coordinates are:

$$\lambda_n = (r_{in} + r_{jn})/R',$$

$$\mu_n = (r_{in} - r_{jn})/R',$$

$$\phi_n = \text{azimuthal angle of } n,$$

where i and j are the foci, R' is the distance between them, r_{in} and r_{jn} are the distances of the arbitrary point n to i and j , respectively.

The basic integral in this work is:

$$K(n, ij) = \pi^{-1} \int \int_{\text{all space}} r_{n1}^{-1} \exp(-r_{1i} - r_{1j}) d\tau_1. \quad (17)$$

The integration of $K(n, ij)$ is simple in ellipsoidal coordinates where i and j are foci. It may be obtained as a by-product of Sugiura's calculation of

$$\pi^{-2} \int \int r_{12}^{-1} \exp(-r_{a1} - r_{b1} - r_{a2} - r_{b2}) d\tau_1 d\tau_2.$$

Schuchowsky⁹ and Gordadse¹⁰ have also obtained it.

where:

$$K(n, ij) = [K_0(R', \lambda_n) + \mu_n^2 K_2(R', \lambda_n)], \quad (18)$$

$$K_0(R', \lambda_n) = (4R')^{-1} [3(\lambda_n^2 + 1)D - 6\lambda_n I_{00}(R') + (6\lambda_n - 2R') \exp(-R'\lambda_n)],$$

$$K_2(R', \lambda_n) = 3(4R')^{-1} [-(3\lambda_n^2 - 1)D + 6\lambda_n I_{00}(R') - (6\lambda_n + 2R') \exp(-R'\lambda_n)],$$

$$D = I_{00}(R') [(\log(\lambda_n + 1)/(\lambda_n - 1)) + Ei(-R'(\lambda_n - 1))] - F(R') Ei(-R'(\lambda_n + 1)),$$

$$I_{00}(R') = (\frac{1}{3}R'^2 + R' + 1) \exp(-R'),$$

$$F(R') = (\frac{1}{3}R'^2 - R' + 1) \exp(+R').$$

⁹ A. Schuchowsky, Acta Physicochimica U.S.S.R. 1, 901 (1934).

¹⁰ G. Gordadse, Zeits. f. Physik 96, 542 (1935).

Here $Ei(-x)$ is the integral logarithm, defined by

$$Ei(-x) = - \int_x^{\infty} x^{-1} \exp(-x) dx.$$

Values of $Ei(-x)$ for x greater than 15 were calculated from the asymptotic expansion of $Ei(-x)$. Two special examples of $K(n, ij)$ are the two three-center integrals which arise from the attraction of the electrons to the nuclei. $K(a, bc)$ is $K(n, ij)$ in which $R' = R$, $\mu_n = 1$, $\lambda_n = 3$. $K(b, ac)$ is $K(n, ij)$ in which $R' = 2R$, $\mu_n = 0$, $\lambda_n = 1$.

There are four three-center multiple exchange integrals which arise from the mutual electronic repulsions. We shall consider them in order.

$$1. \quad L(aa, bc) = \pi^{-2} \int \int r_{12}^{-1} \exp(-2r_{a1} - r_{b2} - r_{c2}) d\tau_1 d\tau_2.$$

If we integrate over the coordinates of electron 1, $L(aa, bc) = K(a, bc) - T(a, bc)$,

$$\text{where} \quad T(a, bc) = \pi^{-1} \int (1 + r_{a2}^{-1}) \exp(-2r_{a2} - r_{b2} - r_{c2}) d\tau.$$

By putting this in ellipsoidal coordinates with a and c as foci and integrating over the azimuthal angle ϕ_2 ,

$$T(a, bc) = 2R^3 \int_1^{\infty} \int_{-1}^1 [(\lambda^2 - \mu^2) + R^{-1}(\lambda - \mu)] \exp(-3R\lambda - R\mu - R(\lambda^2 + \mu^2 - 1)^{\frac{1}{2}}) d\mu d\lambda.$$

By making the substitution:

$$t = \mu + (\lambda^2 + \mu^2 - 1)^{\frac{1}{2}},$$

μ is expressible rationally in terms of t :

$$\mu = \frac{1}{2}t - \frac{1}{2}t^{-1}(\lambda^2 - 1).$$

$T(a, bc)$ is now free from radicals:

$$T(a, bc) = \int_1^{\infty} \int_{\lambda-1}^{\lambda+1} [k(\lambda)t^2 + \dots + k'(\lambda)t^{-4}] \exp(-3R\lambda - Rt) dt d\lambda,$$

where $k(\lambda), \dots, k'(\lambda)$ are polynomials. This is readily integrated to give:

$$\begin{aligned} 81T(a, bc) = & (e^{-3R}/16)[131/3R + 1670 + 2256R + 624R^2] - (e^{-5R}/16)[131/3R + 34 + 160R] \\ & - [116/9R + 116/3 + 44R + 16R^2][Ei(-2R) + 2 \log 2]e^{-3R} \\ & + e^{3R}Ei(-8R)[116/9R - 116/3 + 44R - 16R^2]. \end{aligned} \quad (19)$$

$$2. \quad L(bb, ac) = \pi^{-2} \int \int r_{12}^{-1} \exp(-2r_{b1} - r_{a2} - r_{c2}) d\tau_1 d\tau_2.$$

The integration over the first electron coordinates gives: $L(bb, ac) = K(b, ac) - T(b, ac)$,

$$\text{where} \quad T(b, ac) = \pi^{-1} \int (1 + r_{b2}^{-1}) \exp(-2r_{b2} - r_{a2} - r_{c2}) d\tau_2.$$

Again by using the ellipsoidal coordinates with a and c as foci and integrating over ϕ_2 :

$$T(b, ac) = 2R^3 \int_1^\infty \int_1^1 (\lambda^2 - \mu^2) [1 + R^{-1}(\lambda^2 + \mu^2 - 1)^{-\frac{1}{2}}] \exp(-2R\lambda - 2R(\lambda^2 + \mu^2 - 1)^{\frac{1}{2}}) \cdot d\mu d\lambda.$$

The substitution $s = \lambda + (\lambda^2 + \mu^2 - 1)^{\frac{1}{2}}$ enables λ to be expressed rationally in terms of s ,

$$\lambda = \frac{1}{2}s - \frac{1}{2}s^{-1}(\mu^2 - 1),$$

and thereby eliminates radicals from the integral, which may be evaluated directly.

$$105T(b, ac) = 16R^4(7 + 2R^2)[Ei(-2R) - 2Ei(-4R)] + e^{-2R}[16R^5 - 8R^4 + 64R^3 - 40R^2 + 52R + 108 - 51/R] + e^{-4R}[-16R^5 + 4R^4 - 58R^3 + 15.5R^2 - 8.5R + 33.375 + 51/R]. \quad (20)$$

$$3. \quad L(ab, ac) = \pi^{-2} \int \int r_{12}^{-1} \exp(-r_{a1} - r_{c1} - r_{a2} - r_{b2}) d\tau_1 d\tau_2.$$

The integration over the first electron coordinates gives:

$$L(ab, ac) = \pi^{-1} \int K(2, ac) \exp(-r_{a2} - r_{b2}) d\tau_2.$$

By expressing this in ellipsoidal coordinates with foci at a and c and integrating over ϕ_2 ,

$$L(ab, ac) = 2R^3 \int_1^\infty [C_0 K_0(2R, \lambda) + C_2 K_2(2R, \lambda)] d\lambda, \quad (21)$$

where

$$C_0 = \int_{-1}^1 (\lambda^2 - \mu^2) \exp(-R\mu - R(\lambda^2 + \mu^2 - 1)^{\frac{1}{2}}) d\mu,$$

$$C_2 = \int_{-1}^1 (\lambda^2 - \mu^2) \mu^2 \exp(-R\mu - R(\lambda^2 + \mu^2 - 1)^{\frac{1}{2}}) d\mu.$$

The same substitution used in $L(aa, bc)$ makes the integration of C_0 and C_2 possible. The last integration over λ would also be carried through analytically, but the integrand involves so many separate terms that it is much easier to carry through the last integration numerically. C_0 and C_2 as well as $K_0(2R, \lambda)$ and $K_2(2R, \lambda)$ were evaluated for a large number of values of λ for each value of R considered. The final integrand was obtained by accurate curve fitting with functions of the form:

$$f(\lambda) \exp(-2R\lambda) + g(\lambda) \exp(-4R\lambda),$$

where $f(\lambda)$ and $g(\lambda)$ are polynomials. Care was taken that these functions had the proper behavior for large values of λ and that they had no extraneous oscillations. The final integration was carried out with these functions. The values obtained for the integral are probably correct to five figures after the decimal point, in atomic units, i.e., 0.005 kcal.

$$4. \quad L(ab, bc) = \pi^{-2} \int \int r_{12}^{-1} \exp(-r_{a1} - r_{b1} - r_{b2} - r_{c2}) d\tau_1 d\tau_2.$$

After integrating over the coordinates of electron 1,

$$L(ab, bc) = \pi^{-1} \int K(2, ab) \exp(-r_{b2} - r_{c2}) d\tau_2.$$

By integrating over the azimuthal angle and putting this in the ellipsoidal coordinates with a and b as foci.

$$L(ab, bc) = \frac{R^3}{4} \int_1^\infty [M_0 K_0(R, \lambda) + M_2 K_2(R, \lambda)] \exp(-\frac{1}{2} R \lambda) d\lambda, \quad (22)$$

where

$$M_0 = \int_{-1}^1 (\lambda^2 - \mu^2) \exp(\frac{1}{2} R \mu - \frac{1}{2} R (\lambda^2 + \mu^2 - 6\mu\lambda + 8)^{\frac{1}{2}}) d\mu,$$

$$M_2 = \int_{-1}^1 \mu^2 (\lambda^2 - \mu^2) \exp(\frac{1}{2} R \mu - \frac{1}{2} R (\lambda^2 + \mu^2 - 6\mu\lambda + 8)^{\frac{1}{2}}) d\mu.$$

Here the substitution

$$z = 3\lambda - \mu + (\lambda^2 + \mu^2 - 6\mu\lambda + 8)^{\frac{1}{2}}$$

makes μ_2 expressible in terms of z in a rational manner:

$$\mu_2 = -\frac{1}{2}z + 3\lambda + 4z^{-1}(1 - \lambda^2),$$

and the integrations over z may be carried out analytically. The final integration over λ , just as in the case of $L(ab, ac)$, might be carried through analytically but the large number of terms in the integrand at this point makes such a task extremely laborious. The M_0 and M_2 as well as the $K_0(R, \lambda)$ and $K_2(R, \lambda)$ were computed for a large number of values of λ for each value of R considered and the integrand was accurately "curve-fitted." The curve fitting in this case

was much more difficult than in the previous case and it was necessary to fit a number of sections and integrate these separately. The final numerical values for these integrals are probably also correct to five places after the decimal point in atomic units (0.005 kcal./mole). In Fig. 5 the four integrals just discussed are plotted against internuclear separation.

Fig. 8 shows the four three-center integrals as functions of the internuclear separation R . They each approach $5/8$ as R approaches zero. The value of these integrals for ordinary interatomic distances in molecules are of the same order of magnitude as those for two centers although they become comparatively negligible for large separations.

Previous to this work, the three-center multiple exchange integrals have always been treated by expanding $1/r_{12}$ and at least two of the exponential factors in the integrand in terms of a doubly infinite series of spherical harmonics about one of

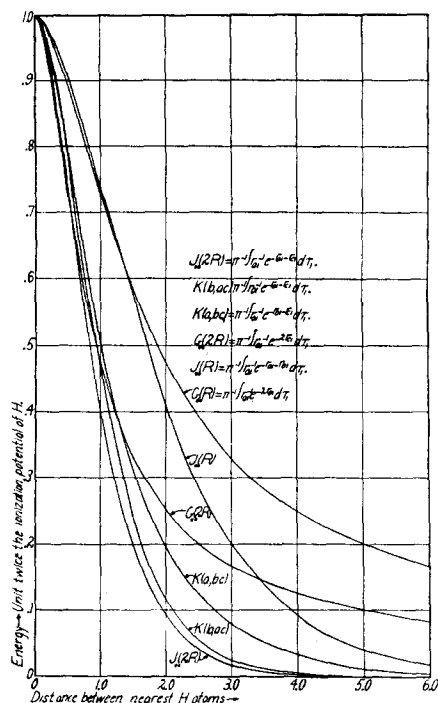


FIG. 6. Some two- and three-center energy integrals.

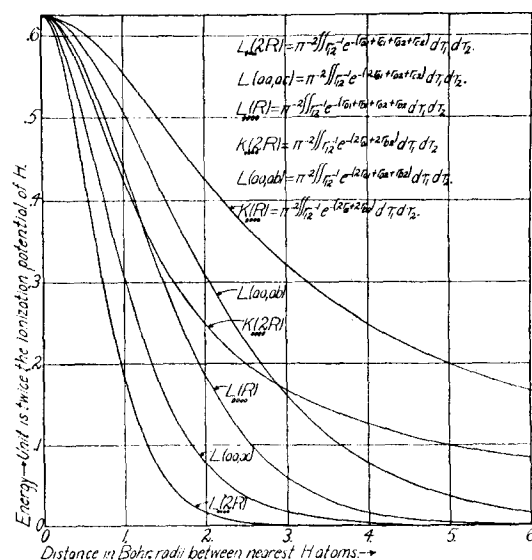


FIG. 7. Some energy integrals.

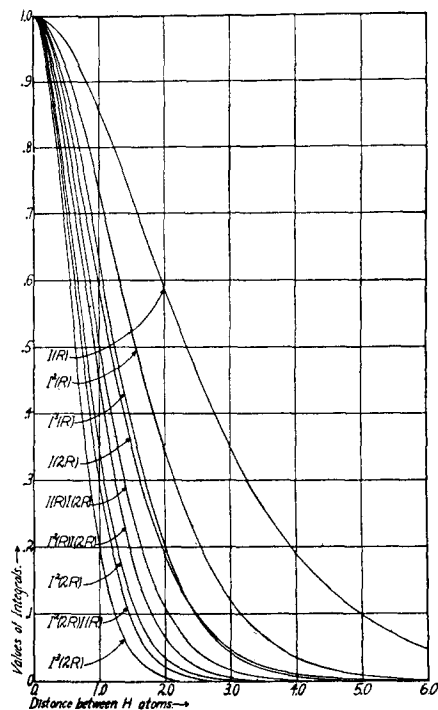


FIG. 8. Normalizing integrals.

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).

FEBRUARY, 1936

JOURNAL OF CHEMICAL PHYSICS

VOLUME 4

II. Calculation of Energy of H_3^+ Ion

J. HIRSCHFELDER, H. EYRING AND N. ROSEN, *Frick Chemistry Laboratory of Princeton University, and the Institute for Advanced Study*

(Received November 22, 1935)

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).