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J. Hirschfelder, H. Diamond, and H. Eyring

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Calculation of the Energy of H_3 and of H_3^+ . III

J. HIRSCHFELDER, H. DIAMOND AND H. EYRING
Frick Chemical Laboratory, Princeton, New Jersey

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In previous communications, the energy of the triatomic hydrogen molecule and of the triatomic positive ion was calculated by the variational method for the symmetrical linear configurations. In this paper, these energies are obtained for two unsymmetrical linear configurations using the most general eigenfunction which can be formed out of 1s hydrogen-like atomic orbitals. Two of the four difficult exchange integrals which involve the coordinates of three nuclei are obtained in closed form. For the Wang plus polar states approximation, the activated state for the reaction $H+H_2$ is found to be linear symmetrical whereas the semi-empirical calculations give an unsymmetrical activated state. The complete potential energy surface for three hydrogen atoms on a line is constructed, for this Wang plus polar states approximation. The energy of the triatomic positive ion is likewise lowest for the linear symmetrical. The complete energy surface of H_2+H^+ in a line is constructed and the vibration frequencies computed. The frequency of the linear symmetrical vibration for H_3^+ is 1.4×10^{14} wave no. per sec. and the frequency of the linear unsymmetrical vibration is 1.2×10^{14} .

INTRODUCTION

IN previous communications,^{1,2} the energy of the triatomic hydrogen molecule and of the triatomic positive ion was calculated by the variational method for the symmetrical linear configurations. In this paper, these energies are obtained for two linear unsymmetrical configurations. Using these results, we locate the activated state for the reaction $H+H_2$ as the symmetrical linear configuration, whereas the semi-empirical calculations give an unsymmetrical activated state. The energy for the triatomic positive ion is a minimum for the symmetrical configuration. The linear vibration frequencies are calculated.

I. H_3 , the triatomic hydrogen molecule

The triatomic hydrogen molecule is the metastable molecule which is formed instantaneously in the reaction of a hydrogen (or deuterium) atom with a hydrogen molecule. A knowledge of the energy of this molecule for various configurations of the nuclei is sufficient for the calculation of the absolute rate of the 10 different reactions of either H or D with H_2 *ortho* or *para*, HD, and D_2 *ortho* or *para*.³ The semi-empirical scheme for calculating the energy surfaces gives excellent agreement with the experi-

mentally observed rates of reaction. The justification of this method is still largely empirical so that the present investigation was undertaken to obtain results by means of the rigorous quantum-mechanical variational principle using as complicated an eigenfunction as was consistent with the evaluation of all the integrals. The treatment is restricted to forms for the eigenfunction such that the integrals of the mutual electronic repulsions can be computed. We use here the most general charge distribution which can be made up from hydrogen-like 1s eigenfunctions. This is a linear combination of two homopolar and six polar states.

$$\Psi = a_1\psi_1 + a_2\psi_2 + a_3\psi_3 + a_4\psi_4 + a_5\psi_5 \\ + a_6\psi_6 + a_7\psi_7 + a_8\psi_8.$$

The homopolar states are:

$$\psi_1 = \begin{pmatrix} abc \\ \alpha\beta\alpha \end{pmatrix} - \begin{pmatrix} abc \\ \beta\alpha\alpha \end{pmatrix},$$

corresponding to a valence bond between a and b and

$$\psi_2 = \begin{pmatrix} abc \\ \alpha\beta\alpha \end{pmatrix} - \begin{pmatrix} abc \\ \alpha\alpha\beta \end{pmatrix},$$

corresponding to a valence bond between b and c . Here the quantity in parentheses indicates the usual Slater determinants and α and β are the two eigenfunctions corresponding to the eigenvalues $h/4\pi$ and $-h/4\pi$ for the z components of spin. The third possible homopolar bonding function,

¹ Hirschfelder, Eyring, Rosen, J. Chem. Phys. **4**, 121 (1936).

² Hirschfelder, Eyring, Rosen, J. Chem. Phys. **4**, 130 (1936).

³ Hirschfelder, Eyring, Topley, J. Chem. Phys. **4**, 170 (1936).

i.e., a bond between a and c , is a linear combination of these two and therefore is not considered explicitly. The polar functions are:

$$\begin{aligned}\psi_3 &= \begin{pmatrix} b b c \\ \alpha \beta \alpha \end{pmatrix}, \text{ two electrons on } b, \text{ one on } c \\ \psi_4 &= \begin{pmatrix} b b a \\ \alpha \beta \alpha \end{pmatrix}, \text{ " " " } b, \text{ " " } a \\ \psi_5 &= \begin{pmatrix} a a b \\ \alpha \beta \alpha \end{pmatrix}, \text{ " " " } a, \text{ " " } b \\ \psi_6 &= \begin{pmatrix} c c b \\ \alpha \beta \alpha \end{pmatrix}, \text{ " " " } c, \text{ " " } b \\ \psi_7 &= \begin{pmatrix} a a c \\ \alpha \beta \alpha \end{pmatrix}, \text{ " " " } a, \text{ " " } c \\ \psi_8 &= \begin{pmatrix} c c a \\ \alpha \beta \alpha \end{pmatrix}, \text{ " " " } c, \text{ " " } a\end{aligned}$$

For the symmetrical case previously considered, it was possible to take linear combinations of these states which were either symmetric or anti-symmetric in the nuclei a and c , and since the Hamiltonian in this case was symmetric in these nuclei, the four symmetrical and the four anti-symmetrical combinations were mutually non-combining. For the unsymmetrical linear configurations there is no such simplification and it is necessary to vary the composition of our best eigenfunction by varying the a_1, a_2, \dots, a_8 separately. This corresponds to the Heitler-London plus polar states type of approximation. A better charge distribution is obtained by varying the effective nuclear charge in these eigenfunctions as well as the polar-homopolar composition. This variation of the effective nuclear charge does not involve the evaluation of any further integrals and is carried out readily.

The method of calculation is in every way similar to that which was used⁴ in the case of the linear symmetrical H_3 and H_3^+ . For the Wang plus polar states type of approximation, the best value of the energy E_z for a given value of the screening constant (or effective nuclear charge) z is the solution of the secular equation:

$$|H_{ij} - S_{ij}E_z| = 0.$$

⁴ The method of calculation is explained in considerable detail in the first paper of this series (J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. **4**, 121 (1936)). All of the intermediate steps and numerical data for the linear symmetrical case are given in the Dissertation of J. Hirschfelder, Princeton University (1935). The authors will be glad to furnish on request similar information for this linear unsymmetrical problem.

Here

$$\begin{aligned}H_{ij} &= \int \bar{\psi}_i H \psi_j d\tau, \\ S_{ij} &= \int \bar{\psi}_i \psi_j d\tau,\end{aligned} \quad i, j = 1, 2, \dots, 8,$$

and H is the operator for the sum of the kinetic energy for the electrons, the energy of mutual repulsion of the nuclei, the energy of attraction of the electrons to the nuclei, and the energy of mutual repulsion of the electrons. By solving this secular equation for a number of different values of z , we were able to obtain the best linear combination of the eight different electronic states for the best value of the effective nuclear charge. The integrals, H_{ij} , are the sum of a great many terms which arise from expanding the Slater determinants of the bond eigenfunction, ψ_j , operating on it by the many parts of the Hamiltonian operator, and multiplying this resultant by the Slater determinants of the other eigenfunction, ψ_i . The only terms in these energy integrals which are difficult to evaluate arise from the mutual repulsions of the electrons. These difficult integrals are treated in the appendix. All of the other integrals which appear have been previously considered.^{1, 2}

In this paper, we calculate the energy for two nuclear configurations:

$$r_{ab} = 2.0a_0/z, \quad r_{bc} = 2.5a_0/z \quad (1)$$

and

$$r_{ab} = 1.5a_0/z, \quad r_{bc} = 2.5a_0/z. \quad (2)$$

Here a_0 and z are the Bohr radius and the effective nuclear charge respectively; r_{ab} and r_{bc} are the separations of atoms a to b and b to c , respectively. Table I shows the energies which we obtained for these configurations and compares them with the energies for linear symmetrical configurations previously considered.¹ The Heitler-London and the Wang types of approximations are obtained by considering only the homopolar eigenfunctions. The former corresponds to an effective nuclear charge of unity, the latter to the effective nuclear charge which gives the lowest value for the energy. The best values which we obtain for the energy are computed for the Wang plus polar states approximation. Fig. 1 shows the entire potential energy surface for an H atom

TABLE I. Energy of H_3 (zero of energy for three infinitely separated H atoms).

	H.L.	H.L. PLUS POLAR	WANG	WANG POLAR
Unsymmetrical Configurations				
(1) $r_{ab}=2.0a_0/z$ $r_{bc}=2.5a_0/z$	53.44 kcal.	60.38 kcal.	57.23 ($z=1.066$)	68.68 ($z=1.102$)
(2) $r_{ab}=1.5a_0/z$ $r_{bc}=2.5a_0/z$	54.70	58.45	57.56 ($z=1.0565$)	64.0 ($z=1.10$)
Symmetrical Configurations (previously considered ¹)				
(1) $r_{ab}=2.5a_0/z$ $r_{bc}=2.5a_0/z$	44.06	51.04	47.34 ($z=1.061$)	58.84 ($z=1.097$)
(2) $r_{ab}=2.0a_0/z$ $r_{bc}=2.0a_0/z$	53.11	60.39	56.16 ($z=1.059$)	67.09 ($z=1.087$)
(3) $r_{ab}=1.5a_0/z$ $r_{bc}=1.5a_0/z$	14.99	22.79	14.99 ($z=1.001$)	23.69 ($z=1.034$)
Binding Energy of H_2 (for reference purposes)				
(Sugiura*) $r_{ab}=1.65a_0$	72.18	74.02	86.94 ($z=1.166$)	92.24 ($z=1.193$)
(Wang**) $r_{ab}=1.70a_0$				
(Weinbaum†) $r_{ab}=1.38a_0$				
(Weinbaum†) $r_{ab}=1.42a_0$				

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

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

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

reacting with an H_2 molecule computed for this approximation. The symmetrical configuration $r_{ab}=r_{bc}=1.84a_0=0.97\text{\AA}$ is the activated state. The atoms in the activated state are spread farther apart than in the normal H_2 molecule where $r_{ab}=0.74\text{\AA}$. This expansion is also obtained from semi-empirical calculations. There is one feature of our results which is surprising. The semi-empirical scheme predicts that the activated state will correspond to an unsymmetrical arrangement of the atoms and that the energy will decrease as the atoms go from such an unsymmetrical array to the lowest symmetrical configuration. The calculation of the rates of the reactions will not be essentially changed by this symmetry of the activated configuration. We have a transmission coefficient of unity in the symmetrical case, i.e., all of the molecules reaching the activated state react, but the symmetry number compensates this increase by reducing the number of activated states by a factor of two. When the activated state is unsymmetrical, the transmission coefficient is a half and the symmetry factor is unity. Thus the statistics are not altered. The actual values of the energy which we obtain are not sufficiently accurate, due to the faulty charge distribution, to be used for reaction rate calculations. The frequency of the vibration in which the linear symmetry of the nuclei is preserved is:

$$\nu_s = 9.5 \times 10^{13} \text{ sec.}^{-1}, \quad h\nu_s = 9.0 \text{ kcal.}$$

The activated complex in a chemical reaction is a good example of the resonance phenomenon. The molecules start with one type of bonds in the beginning of the reaction and finish the reaction with another set of bonds. The activated complex corresponds then to a mixture of the two types, the energy is considerably lower for the mixture than it would be for either one separately. As the atoms come closer together the polar states assume greater importance. Thus unsymmetrical activated states possess large dipole

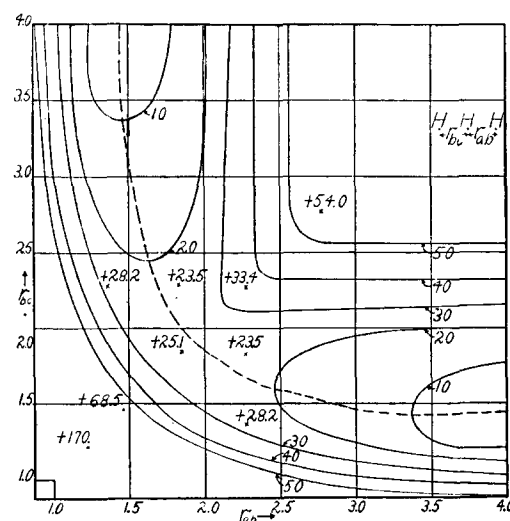


FIG. 1. Energy surface for three hydrogen atoms in a line to the Wang plus polar states approximation. Energies are given in kcal. and distances in Bohr radii.

moments as is exemplified by the polar states in H_3 . A specific example will illustrate this resonance phenomenon. In Fig. 2 the reaction between

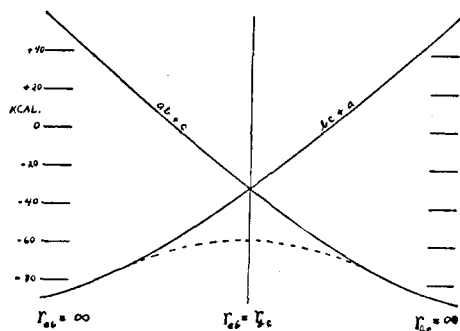


FIG. 2. The energy to the Wang approximation of a deuterium or hydrogen atom, a , approaching a hydrogen molecule, bc . The curves $ab-c$ and $bc-a$ are the energies of the system for the pure bond states. The dotted line is the energy for the best linear combination of the pure bond states.

a D atom, " c ," and the H_2 molecule composed of atoms " a " and " b " is considered using the Wang approximation. The "best" eigenfunction for the molecule composed of three atoms can be written:

$$\Psi = A_{ab}\psi_{ab} + A_{bc}\psi_{bc},$$

where ψ_{ab} and ψ_{bc} are bond eigenfunctions each normalized to unity. When the chemical reaction begins, atom c is far away,

$$\Psi = \psi_{ab}, \quad E = E_{ab}$$

and there is no resonance between the bonds ab and bc . When the atom c has penetrated sufficiently near to a and b , the "best" eigenfunction is the combination of states (1) and (2) which gives the greatest binding energy, i.e., minimum potential energy. This energy is lower than for either of the pure bond states. Thus when

$$r_{ab} = 1.876a_0 \quad \text{and} \quad r_{bc} = 2.345a_0, \\ A_{ab} = .7645 \quad A_{bc} = .3084,$$

$$E = -57.23 \text{ kcal. but } E_{ab} = -48.91 \\ \text{and } E_{bc} = -6.06$$

and when

$$r_{ab} = 1.420a_0 \quad \text{and} \quad r_{bc} = 2.366a_0, \\ A_{ab} = 0.875 \quad A_{bc} = 0.160,$$

$$E = -57.56 \text{ kcal. but } E_{ab} = -54.52 \\ \text{and } E_{bc} = +34.03.$$

Finally when the distance ab is equal to that of bc , $A_{ab} = A_{bc}$. We see that the character of the valence bond in a chemical reaction does not change appreciably until the atoms are very close to the activated state, and it is there that resonance plays an important role.

It is sometimes supposed that states showing a large degree of resonance are necessarily states of low energy. The activated state is an example where the contrary is true since the comparatively pure initial and final bond states have much lower energies. This situation arises in the following way. Bonding is increased if the electrons have many nuclei about which they can circulate since this lowers the zero point energy of the electrons. Acting against this bonding are the mutual repulsions between the electrons and between the nuclei. In general then for a given nuclear configuration resonance lowers the bonding energy but the system will very often sacrifice this resonance and move into a pure bonding state with the full quota of saturated bonds if by so doing it can sufficiently lower the nuclear repulsion.

A further question which one might ask is how sensitive is the binding energy to the screening constant or to the effective nuclear charge, z ,

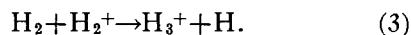
TABLE II. Energy of H_3^+ . (The zero of energy is taken for the two hydrogen atoms and the proton separated infinitely far apart.)

	HEITLER-LONDON PLUS POLAR STATES	WANG PLUS POLAR STATES
Unsymmetrical Configurations		
(1) $r_{ab} = 2.0a_0/z$ $r_{bc} = 2.5a_0/z$	-105.4 kcal.	-151.0 kcal. ($z = 1.32$)
(2) $r_{ab} = 1.5a_0/z$ $r_{bc} = 2.5a_0/z$	-94.0	-129.8 ($z = 1.30$)
Symmetrical Configurations (previously considered ²)		
(1) $r_{ab} = r_{bc} = 2.5a_0/z$	-96.8	-138.1 ($z = 1.30$)
(2) $r_{ab} = r_{bc} = 2.0a_0/z$	-108.6	-155.4 ($z = 1.31$)
(3) $r_{ab} = r_{bc} = 1.5a_0/z$	-78.3	-101.3 ($z = 1.22$)

which is used in the eigenfunctions. When z is very different from its best value, as for example the Heitler-London type of approximation where z is equal to unity, the energy of binding changes rapidly with z ; but when z is in the neighborhood of its best value, a change of 0.02 increases the energy by about 0.2 kcal.

H_3^+ , triatomic positive ion

The triatomic hydrogen positive ion, H_3^+ , is observed in the mass spectrograph when hydrogen gas is ionized at reasonably high pressures.² There is reason to believe that it is formed in three ways:



Experiments tell us no more as to the energy, spectrum, or chemistry of H_3^+ . However, we may use the rigorous quantum mechanical variational principle to calculate the energy for various configurations of the triatomic ion as we did for the triatomic molecule. The energy for symmetrical linear configurations was treated in a previous paper. Unsymmetrical linear configurations are considered here and with them we are able to draw the energy surface either for a hydrogen ion approaching a hydrogen molecule, i.e., reaction (1), or for a hydrogen atom approaching a diatomic hydrogen ion, i.e., reaction (2). The integrals which are necessary for the computations are the same as those for the triatomic molecule and are considered in the appendix. We use for the eigenfunctions the most general linear combination of the three polar and the three homopolar eigenfunctions which can be obtained from hydrogen-like 1s eigenfunctions. The six parameters governing the composition of our eigenfunction are varied simultaneously to give the lowest energy, i.e., Heitler-London plus polar states type of approximation. To obtain an even better charge distribution we vary the effective nuclear charges at the same time as the composition, i.e., Wang plus polar states type of approximation. In the eigenfunctions the polar state with two electrons on the central atom is just as important as the homopolar states. Table II shows the results which we obtained. The energy

for these configurations enables us to calculate the frequency of the linear symmetrical vibration ν_s and the linear unsymmetrical vibration ν_l :

$$\nu_s = 1.4 \times 10^{14}, \quad h\nu_s = 13 \text{ kcal.}$$

$$\nu_l = 1.2 \times 10^{14}, \quad h\nu_l = 12 \text{ kcal.}$$

We can use the polarizabilities, α , of H_2 , H , and H_2^+ to calculate the energy of reactions (1)

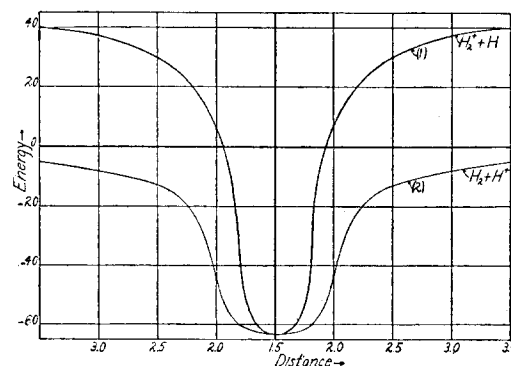


FIG. 3. (1) Energy of an H atom approaching H_2^+ in a line as a function of the separation between the H and the H_2^+ . (2) Energy of a proton approaching H_2 in a line as a function of the distance between the H^+ and the H_2 . Energies are given in kcal. and distances in Bohr radii.

and (2) for large distances. Let us consider reaction (1). The molecule H_2 is polarized by the field of the H and attracted to it with a force whose potential is:

$$E_{H_2+H^+} = -\frac{\alpha_{H_2}e^2}{2R^4}$$

where R is the separation between H^+ and the center of the hydrogen molecule. The experimental mean value for α_{H_2} is $.8 \times 10^{-24} \text{ cm}^3 = 5.4a_0^3$. α_{mean} is used rather than α_{parallel} since the polarizing field of the H^+ is spherical rather than plane for the interesting separations. Fig. 3 shows the energies of $H+H_2^+$ and H_2+H^+ plotted as a function of the separation. For large separations the H_2+H^+ has about 44 kcal. less energy than the H_2^++H . At closer distances, the interaction energy between the ion and the molecule or atom is determined by the polarizabilities. And at the closest distance of approach, $1.5a_0$, the energy of the H_3^+ is the same regardless of whether it originated from H_2^++H or H_2+H^+ . It is surprising that the energy of H_3^+ is nearly equal to the electrostatic energy $\alpha_{H_2}e^2/2R^4$ for the appropriate value of R . This equality is partly

accidental since there are other types of important interactions between H_2 and H^+ . However, we can use this ion-polarization energy to help us draw the contour lines in the energy surface for an H^+ approaching an H_2 molecule, Fig. 4. Here

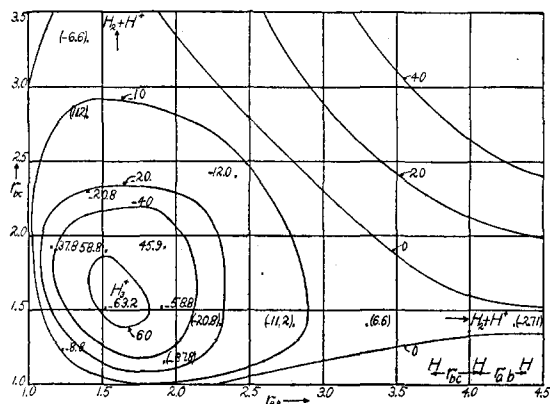


FIG. 4. Energy surface for a system of two hydrogen atoms and a proton. The position of minimum energy corresponds to H_3^+ . Energies are given in kcal. and distances in Bohr radii.

we see that the H^+ is attracted to the H_2 until the nuclei are equally spaced. The equal potential surfaces for the H_3^+ are approximately circular. The numbers given in this figure are the values of the energy which have been calculated to the Wang-plus-polar-states approximation. The numbers given in parentheses are the energies for this ion-polarization attraction. The triatomic molecule corresponds to a symmetrical linear configuration with a minimum of energy for $r_{ab} = r_{bc} = 1.6a_0$. The energy of binding of the two hydrogen atoms and the proton is more than 155 kcal., which is sufficient to make reactions (1) and (2) exothermic and make it probable that (3) takes place without an appreciable activation energy.

The energy surface for an H atom approaching an H_2^+ ion is similar to the case just considered since the energies for the H_3^+ at intermediate and close distances are the same as before. However, the minimum energy for the H_2^+ when the H is far away corresponds to the separation of $2.0a_0$ which is considerably more expanded than the separation in H_2 . Since the binding energy of H_2^+ is only around 60 kcal., the contour lines will be steeper than for the H_2 . The ion-polarization energy in this case is:

$$E_{(H_2^+ + H)} = - \left[\frac{\alpha_H}{2R^4} + \frac{4(\bar{\alpha}_{H_2^+})(\alpha_H)^2 e^2}{R^{10}} \right],$$

where $\bar{\alpha}_{H_2^+} = 2.85a_0^3$ and $\alpha_H = 4.5a_0^3$ are the polarizabilities of H_2 and H , respectively. While this energy is correct for large separations it is not accurate for the smaller internuclear distances.

INTEGRALS

The integrals for the unsymmetrical linear configuration are of the same order of difficulty as those which have already been considered for the symmetrical linear case. There are four integrals arising from the mutual repulsion of two electrons which we shall consider here. Two of these are integrated in closed form. The other two integrals are evaluated numerically. The mathematical treatment of the integrals is not changed in any essential manner by the lack of symmetry with respect to the nuclei.

$$I. L(bb, ac) \quad \begin{array}{ccc} \bullet & r_{ab} & \bullet \\ a & & b \end{array} \quad \begin{array}{ccc} \bullet & r_{bc} & \bullet \\ & & c \end{array}$$

The integral,

$$L(bb, ac) \equiv 1/\pi^2 \int \int (1/r_{12}) e^{-2r_{1b} - r_{2a} - r_{2c}} d\tau_1 d\tau_2$$

is integrated in closed form as for the symmetrical configuration. The integration over the coordinates of electron 1 keeping electron 2 fixed is easily performed. This gives:

$$L(bb, ac) = K(b, ac) - T(b, ac)$$

where

$$K(b, ac) \equiv 1/\pi \int (1/r_b) e^{-r_a - r_c} d\tau,$$

$$T(b, ac) \equiv 1/\pi \int (1 + 1/r_b) e^{-2r_b - r_a - r_c} d\tau.$$

The first integral, $K(b, ac)$, has been previously discussed¹ and offers no difficulty. The second, $T(b, ac)$, can be integrated by introducing the ellipsoidal coordinates with foci at a and at c :

$$\lambda = \frac{r_a + r_c}{r_{ac}}, \quad \mu = \frac{r_a - r_c}{r_{ac}}, \quad \phi$$

The parameter $A = (r_{ab} - r_{bc})/r_{ac}$ is a measure of the asymmetry of the molecule.

$$T(b, ac) = \frac{r_{ac}^3}{4} \int_1^\infty \int_{-1}^1 (\lambda^2 - \mu^2) \left[1 + \frac{2}{r_{ac}(\mu^2 + \lambda^2 - 2A\mu\lambda + A^2 - 1)^{\frac{1}{2}}} \right] \\ \times \exp(-r_{ac}[\lambda + (\mu^2 + \lambda^2 - 2A\mu\lambda + A^2 - 1)^{\frac{1}{2}}]) d\mu d\lambda.$$

The substitution of $X = 2\lambda - 2A\mu + 2(\mu^2 + \lambda^2 - 2A\mu\lambda + (A^2 - 1))^{\frac{1}{2}}$ for λ rationalizes the integral, since

$$\lambda = X/4 + A\mu + [(A^2 - 1)(\mu^2 - 1)]/X^2.$$

There are two limits of integration for X depending on whether A is greater or less than μ . The problem is then resolved into the integration of a large number of simple integrals. We obtain:

$$T(b, ac) = a_1 e^{+(A-2)r_{ac}} + a_2 e^{-(A+2)r_{ac}} + a_3 e^{-r_{ac}} + a_4 e^{-Ar_{ac}} [Ei(-(1-A)r_{ac}) - Ei(-2r_{ac}(1-A)) \\ - Ei(-2r_{ac})] + a_5 e^{+Ar_{ac}} [Ei(-(1+A)r_{ac}) - Ei(-2r_{ac}(1+A)) - Ei(-2r_{ac})],$$

where

$$a_1 = -(1/8)A^{-4}(A^2 - 1)(A^2 - A - 2)r_{ac} + [3/16 + A^{-1} + (15/16)A^{-2} - (5/8)A^{-3} - (5/8)A^{-4}] \\ + r_{ac}^{-1}[-A^{-1} - 3A^{-2} + (57/16)A^{-3} + (31/4)A^{-4} - (15/8)A^{-5} - (15/4)A^{-6}], \\ a_2 = -(1/8)A^{-4}(A^2 - 1)(A^2 + A - 2)r_{ac} + [3/16 - A^{-1} + (15/16)A^{-2} + (5/8)A^{-3} - (5/8)A^{-4}] \\ + r_{ac}^{-1}(A^{-1} - 3A^{-2} - (57/16)A^{-3} + (31/4)A^{-4} + (15/8)A^{-5} - (15/4)A^{-6}), \\ a_3 = -(1/2)A^{-4}(A^2 - 1)r_{ac} + [2 - (9/2)A^{-2} + (5/2)A^{-4}] + r_{ac}^{-1}[6A^{-2} - (31/2)A^{-4} + (15/2)A^{-6}], \\ a_4 = (1/4)A^{-7}(A^2 - 1)[A^3(A^2 - 1)r_{ac}^2 + 2A^2(4A^2 - 3)r_{ac} + 3(7A^2 - 5)(A + r_{ac}^{-1})], \\ a_5 = (1/4)A^{-7}(A^2 - 1)[A^3(A^2 - 1)r_{ac}^2 - 2A^2(4A^2 - 3)r_{ac} + 3(7A^2 - 5)(A - r_{ac}^{-1})].$$

Here $Ei(-X)$ is the integral logarithm,

$$Ei(-X) = - \int_X^\infty (e^{-X}/X) dX,$$

and it is tabulated⁵ in a number of different books. Setting $A=0$, we obtain the value for the symmetrical case which we considered previously. Or setting $A = \pm 1$, which corresponds to coalescence of b and either a or c , $T(b, ac)$ degenerates into a simple two center integral and provides a further check on the validity of our result.

II. $L(aa, bc)$ or $L(cc, ba)$

$$L(aa, bc) \equiv 1/\pi^2 \int \int 1/r_{12} e^{-2r_{a1} - r_{ba} - r_{c2}} d\tau_1 d\tau_2.$$

This integral is somewhat similar to $L(bb, ac)$. We can integrate over the coordinates of electron one and obtain:

$$L(aa, bc) = K(a, bc) - T(a, bc),$$

$$K(a, bc) = 1/\pi \int 1/r_a e^{-r_b - r_c} d\tau,$$

$$T(a, bc) = 1/\pi \int (1 + 1/r_a) e^{-2r_a - r_b - r_c} d\tau,$$

⁵ Cf. Jahnke-Emde, *Funktionentafeln* (Teubner 1933), p. 78.

where again $K(a, bc)$ is an integral considered previously and $T(a, bc)$ is the difficult integral which must be evaluated. Using ellipsoidal coordinates with foci at b and at c and setting $B = 1 + 2(r_{ab}/r_{bc})$

$$T(a, bc) = \frac{r_{bc}^3}{4} \int_1^\infty \int_{-1}^1 (\lambda^2 - \mu^2) \left[1 + \frac{2}{r_{bc}(\lambda^2 + \mu^2 - 2B\mu\lambda + B^2 - 1)^{1/2}} \right] \times \exp(-r_{bc}[\lambda + (\lambda^2 + \mu^2 - 2B\mu\lambda + B^2 - 1)^{1/2}]) d\mu d\lambda.$$

Substituting $X = 2\lambda - 2B\mu + 2(\mu^2 + \lambda^2 - 2B\mu\lambda + B^2 - 1)^{1/2}$ in place of λ , the integrand is rationalized. There is only one range of integration for X and the integrations may be performed without any serious difficulty. We obtain:

$$T(a, bc) = (1/48)[b_1 e^{-Br_{bc}} + b_2 e^{-(B+2)r_{bc}} + b_3 e^{Br_{bc}} Ei(-2(B+1)r_{bc}) + b_4 e^{-Br_{bc}} [Ei(-2r_{bc}) + \log(B+1)]],$$

where

$$\begin{aligned} b_1 &= B^{-3}(2B^5 + 12B^3 - 20B^2 - 6B + 12)r_{bc}^2 + B^{-4}(18B^5 + 24B^4 + 66B^3 - 144B^2 - 36B + 72)r_{bc} \\ &\quad + B^{-5}(9B^5 + 144B^4 + 171B^3 - 372B^2 - 90B + 180) \\ &\quad + B^{-6}(-48B^5 + 144B^4 + 171B^3 - 372B^2 - 90B + 180)r_{bc}^{-1}, \\ b_2 &= B^{-4}(-6B^4 - 6B^3 + 18B^2 + 6B - 12)r_{bc} + B^{-4}(9B^4 - 48B^3 + 45B^2 + 30B - 30) \\ &\quad + B^{-6}(48B^5 - 144B^4 - 171B^3 + 372B^2 + 90B - 180)r_{bc}^{-1}, \\ b_3 &= -12B^{-7}(B^2 - 1)[B^3(B^2 - 1)r_{bc}^2 - 2B^2(4B^2 - 3)r_{bc} + 3(7B^2 - 5)(B - r_{bc}^{-1})], \\ b_4 &= -12B^{-7}(B^2 - 1)[B^3(B^2 - 1)r_{bc}^2 + 2B^2(4B^2 - 3)r_{bc} + 3(7B^2 - 5)(B + r_{bc}^{-1})]. \end{aligned}$$

$T(a, bc)$ reduces to the symmetrical case for $B = 3$ and to the two center integrals corresponding to $r_{ab} = 0$ when $B = 1$.

III. $L(ab, ac)$, $L(ab, bc)$, $L(bc, ac)$

The integrations over the first electronic coordinates may be carried out for these integrals.

$$\begin{aligned} L(ab, ac) &= 1/\pi^2 \int \int 1/r_{12} e^{-r_{a1} - r_{b1} - r_{a2} - r_{c2}} d\tau_1 d\tau_2 \\ &= 1/\pi \int (K(2, ab)) e^{-r_{a2} - r_{c2}} d\tau_2, \\ L(ab, bc) &= 1/\pi^2 \int \int 1/r_{12} e^{-r_{a1} - r_{b1} - r_{b2} - r_{c2}} d\tau_1 d\tau_2 \\ &= 1/\pi \int K(2, ab) e^{-r_{b2} - r_{c2}} d\tau_2. \end{aligned}$$

Here

$$K(2, ab) = \frac{1}{\pi} \int 1/r_{12} e^{-r_{a1} - r_{b1}} d\tau_1$$

is an integral considered previously.¹ Introducing ellipsoidal coordinates at a and at b and setting

$$C = 1 + 2(r_{bc}/r_{ab}):$$

$$L(ab, ac) = \frac{r_{ab}^3}{4} \int_1^\infty \int_{-1}^1 [\lambda^2 - \mu^2] K(2, ab) \exp[-(r_{ab}/2)[\lambda + \mu + (\mu^2 + \lambda^2 - 2C\mu\lambda + C^2 - 1)^{1/2}]] d\mu d\lambda.$$

Also

$$L(ab, bc) = \frac{r_{ab}^3}{4} \int_1^\infty \int_{-1}^1 [\lambda^2 - \mu^2] K(2, ab) \exp [-(r_{ab}/2)[\lambda - \mu + (\mu^2 + \lambda^2 - 2C\mu\lambda + C^2 - 1)^{1/2}]] d\mu d\lambda.$$

Now letting

$$I(\mu, \lambda) = \exp [-(r_{ab}/2)[\lambda + \mu + (\lambda^2 + \mu^2 - 2C\mu\lambda + C^2 - 1)^{1/2}]] (\lambda^2 - \mu^2) K(2, ab).$$

It follows that

$$L(ab, ac) = \frac{r_{ab}^3}{4} \int_{-1}^1 \int_1^\infty I(\mu, \lambda) d\lambda d\mu \quad \text{and} \quad L(ab, bc) = \frac{r_{ab}^3}{4} \int_{-1}^1 e^{\mu r_{ab}} d\mu \int_1^\infty I(\mu, \lambda) d\lambda.$$

The family of integrals, $\int_1^\infty I(\mu, \lambda) d\lambda$, are common to both $L(ab, ac)$ and $L(ab, bc)$. These integrals are obtained in closed form for $\mu = \pm 1$, but for other values it is more tractable to evaluate $I(\mu, \lambda)$ by evaluating the integrand at a whole mesh of points and carry out the integrations numerically. The values of $((\partial/\partial\lambda)I(\mu, \lambda))_{\lambda=1}$ are helpful in curve-fitting the integrand.

The actual numerical integration requires extreme care in order to obtain the desired accuracy. The integrand as a function of λ is divided into a large number of overlapping segments. In each of these segments $I(\mu, \lambda)$ is multiplied by $e^{+a\lambda}$ where a is chosen so as to make $e^{+a\lambda}I(\mu, \lambda)$ as nearly constant as possible throughout the segment. Then $e^{a\lambda}I(\mu, \lambda)$ is curve-fitted by a cubic in λ .

$$e^{a\lambda}I(\mu, \lambda) = b_0 + b_1\lambda + b_2\lambda^2 + b_3\lambda^3.$$

The integration is then performed over a small central part of the segment under consideration.

$$\int_{\lambda_1}^{\lambda_2} I(\mu, \lambda) d\lambda = \int_{\lambda_1}^{\lambda_2} e^{-a\lambda} (b_0 + b_1\lambda + b_2\lambda^2 + b_3\lambda^3) d\lambda,$$

and the result summed over all of the segments.

The integrations over μ are performed in much the same way except in the neighborhood of $\mu = 1$, the integrand has an infinite slope and special precautions taken in order to avoid error in this region.

$L(bc, ac)$ is calculated in the same manner as $L(ab, ac)$ and a second determination of $L(ab, bc)$ is obtained as a by-product. This provides a check on our results since the two values for $L(ab, bc)$ are completely independent. Thus for $r_{ab} = 2.0a_0$, $r_{bc} = 2.5a_0$: $L(ab, bc) = .09678(e^2/a_0)$ and $.09697(e^2/a_0)$ and for $r_{ab} = 1.5a_0$, $r_{bc} = 2.5a_0$: $L(ab, bc) = .128, 13(e^2/a_0)$ and $.12760(e^2/a_0)$. The accuracy in both these cases seems to be considerably better than 1 percent and we can probably trust the energies obtained in this text to about 0.2 kcal.

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