THE ELECTRONIC STRUCTURE OF H_3^+

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I. Introduction

Before complete quantum-mechanical treatments of many of the complicated molecules that occur naturally can be given, it is desirable that the simplest molecules should be carefully investigated. Such investigations will show the effect of various simplifying assumptions and will give an idea of the numerical accuracy that is possible. For this purpose the triatomic ion H_3^+ is of some interest, since it is the simplest triatomic molecule, and, having only two electrons, represents the first generalization of the more complete treatments of the diatomic molecule H_2, that have already been given.

The present paper, then, will discuss the structure of H_3^+, following the method of molecular orbitals, as developed by Lennard-Jones, Hund, Mulliken and others. In this method the electrons are fed, one at a time, into the framework provided by the three nuclei, and their mutual interaction is regarded, primarily, as a perturbation between the one orbital and the other. Thus the problem consists, as always in this kind of treatment, of two parts:

(1) The discussion of the individual orbitals, a problem involving only one electron.

(2) The mutual interaction of the orbitals, the effect of which will be to raise the energy above the energies given by (1).

It is interesting to note that the ion has been found in the discharge tube by Aston (1) and Bainbridge (2), though no measurements of its spectrum have been attempted.

II. The types of orbital

The first problem is to consider the shape of the nuclear framework; the ion H_3^+ is so symmetrical in character that only two likely configurations arise—those corresponding to a linear figure or an equilateral triangle. Pending a fuller discussion of this problem, the following reason may be given for choosing, as we do, the triangular model. We are only concerned with two electrons, and thus, in the ground state, only one type of orbital is filled: the two electrons will have the same space wave function but opposed spins. We are to choose that configuration of the nuclei which gives this orbital greatest bonding. If ABC (Fig. 1) is the linear molecule, then the lowest orbital will only represent resonance between

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A–B and B–C; the resonance A–C is too small to make any appreciable contribution to the bonding. But in the triangular model, all three resonances contribute, and we may therefore expect greater bonding. In passing to the neutral molecule H_3, however, a new type of orbital has to be introduced having a node along the dotted line of the figure; this gives a bonding between A–B and B–C but a repulsion A–C; there is thus a definite tendency for this molecule to open out into a flat triangle, or a straight line. When we proceed to heavier molecules and take account of p- and d-binding, the directional effect of the bonds becomes much more important and a 60° bond angle is much less binding than either a 90° or a 180° one. We should expect, therefore, that few, if any, of the heavier triatomic molecules with three equal nuclei would be equilateral. Molecules with only two binding electrons in s-orbitals, such as Li_3^+ or Na_3^+, might be equilateral if they did exist; others would not. This is, indeed, found to be the case with such molecules as O_3 and N_3^-, which appear to be almost straight, and straight, respectively. We shall, therefore, in our discussion of H_3^+, assume that the nuclear framework is an equilateral triangle of side ρ.

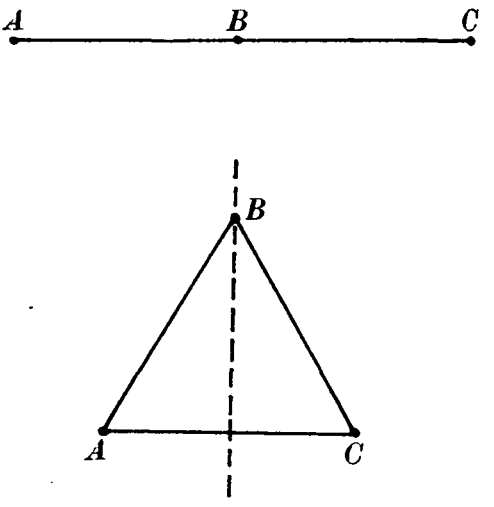


Fig. 1.

Following the usual custom we express the molecular orbitals as linear sums of functions ψ_1, ψ_2, ψ_3 representing an electron in a ground state on nuclei A, B, C respectively, but allowing, if necessary, for a screening constant. The molecular orbital may therefore be written

$$\Psi = \lambda\psi_1 + \mu\psi_2 + \nu\psi_3,$$

where λ, μ, ν have to be determined for each type of orbital. The symmetry of the molecule has been discussed by Lennard-Jones (3) and Mulliken (4) from the standpoint of group theory. By these considerations, or in a straightforward way by use of the perturbation method for degenerate states, it is easily seen that there are two types of orbital, which we shall designate as s- and ω-orbitals. The s-orbital, which is single, is symmetrical in all three nuclei ABC and is given by $\lambda = \mu = \nu = 1$. The ω-orbital, which is double, may be written either as

$$\begin{array}{lll} \text{(A)} & \psi_1 + \omega\psi_2 + \omega^2\psi_3 & \text{or} \quad \text{(B)} \quad \psi_1 - \psi_3 \\ & \psi_1 + \omega^2\psi_2 + \omega\psi_3 & \qquad\qquad\quad \psi_3 - \psi_2 \\ & \omega^3 = 1 & \qquad\qquad\quad \psi_2 - \psi_1 \end{array}$$

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These last three functions are not independent, having zero sum; the first of the three corresponds to a wave function having a line of nodes along the dotted line of Fig. 1. Since a line of nodes generally implies greater energy, we may expect the ω-levels to be much less bonding than the s-levels. It is this which justifies our assumption that H_3^+ consists of two s-orbitals, and is therefore equilateral. In view of the symmetry involved, we shall find it more convenient to use the description (A) rather than (B) and the normalized zero-order wave functions are accordingly:

$$\Psi(s) = (\psi_1 + \psi_2 + \psi_3)/\{3(1+2S)\}^{\frac{1}{2}}, \tag{1}$$

$$\Psi(\omega_+) = (\psi_1 + \omega\psi_2 + \omega^2\psi_3)/\{3(1-S)\}^{\frac{1}{2}}, \tag{2}$$

$$\Psi(\omega_-) = (\psi_1 + \omega^2\psi_2 + \omega\psi_3)/\{3(1-S)\}^{\frac{1}{2}}. \tag{3}$$

where S is the overlap integral $\int \psi_1 \psi_2 d\tau$.

In the "separated-atom" viewpoint of Mulliken(4) all three levels give the same $1s$-atomic levels at infinity, and in the "united-atom" viewpoint the s-wave functions give $1s$-wave functions of the united-atom and the ω-wave functions give a combination of $2p$-levels. This further justifies our hypothesis that the ω-orbital is less bonding than the s-orbital.

There is yet another difference between the two orbitals which is of importance. The component of angular momentum along the axis of the molecule (i.e. perpendicular to the plane of the nuclei) will give the magnetic moment of the molecule, apart from a factor $e/(2mc)$. In this case, if ϕ is an azimuthal angle about the molecular axis, the eigenvalues of the momentum operator $\hbar \dfrac{\partial}{\partial \phi}$ do not correspond with those of the energy operator, and the component of angular momentum is only defined by its mean value

$$\int \Psi^* \times \hbar \frac{\partial}{\partial \phi} \Psi d\tau.$$

The s-orbitals give zero value for this integral, implying no component of angular momentum, and the two ω-orbitals give values

$$\frac{\pm\sqrt{3}\,h}{1-S} \int \psi_1 \frac{\partial \psi_2}{\partial \phi} d\tau,$$

implying that the ω_+ and the ω_- orbitals have equal and opposite non-vanishing magnetic moments. The significance of representation (A) rather than (B) is now apparent. The precise numerical value of this component may be found by integration; it is tedious but without special difficulty. The most important deduction is that, in an electron switch involving a change from s- to ω-type orbitals, radiation will be given out which is circularly polarized when viewed along the axis of the molecule.

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III. Calculation of the orbital energies

We shall, throughout, use atomic units (A.U.) in which the units of mass, length and energy are respectively the electronic mass, the radius of the first Bohr orbit, and twice the energy of the H-atom in its ground state. The Hamiltonian for H_3^+ may now be written

$$H = H(1) + H(2) + 1/r_{12},$$

where $H(1)$ is an operator only affecting the coordinates of electron 1, and is of the form

$$H(1) = -\tfrac{1}{2}\nabla_1^2 - Z(1/r_a + 1/r_b + 1/r_c),$$

Z is the nuclear charge (which we shall later put equal to unity), and r_a, r_b and r_c are the distances of the electron from the nuclei A, B, C respectively. r_{12} is the separation of the two electrons. The individual orbitals are obtained as solutions of the equation

$$(H(1) - E)\Psi(1) = 0.$$

Let us take for our component ψ-functions the normalized atomic wave functions $\psi_1 = \sqrt{\frac{c^3}{\pi}}\, e^{-cr_a}$. "$c$" is so far left undetermined. A better approximation could be obtained by taking, in addition, certain combinations of $2p$-atomic wave functions, but in view of the great added complications this was not considered desirable in a first discussion.

The energy may be expressed as

$$E = \int \Psi^* H \Psi \, d\tau / \int \Psi^* \Psi \, d\tau$$

and, on substituting the values of Ψ given by equations (1) and (3) these reduce to the forms

$$-2E_s = c^2\gamma(t) + Zc\delta(t), \tag{4}$$

$$-2E = c^2\alpha(t) + Zc\beta(t). \tag{5}$$

In these expressions, α, β, γ, δ are all functions of a new variable t, defined as

$$t = c\rho. \tag{6}$$

It is more convenient to work in terms of this variable than with ρ. The actual expressions for α, β, γ, δ need not be written explicitly; they are somewhat lengthy but can all be found by methods similar to those employed by Lennard-Jones(5) and Massey(6).

The simplest assumption to make is that $c = Z$; this is equivalent to the method originally suggested by Pauling(7) and Lennard-Jones(5), and may be called the "perturbation method", since the wave functions used are those of the constituent atoms. The electronic energies have been calculated on this assumption from equations (4) and (5) and are shown dotted in Fig. 2. We may expect this method to break down at small distances where the orbitals must approach more and more to those of the united-atom with central nuclear charge $3Z$, and thus where "c" will itself become appreciably different from Z.

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Accordingly, a variational method has been used, choosing that value of c which makes E a minimum for given ρ, i.e.

$$2c\gamma + c^2\rho\frac{d\gamma}{dt} + Z\delta + Zc\rho\frac{d\delta}{dt} = 0,$$

which may be written

$$\frac{c}{Z} = -\frac{\delta + t\dfrac{d\delta}{dt}}{2\gamma + t\dfrac{d\gamma}{dt}}, \tag{7}$$

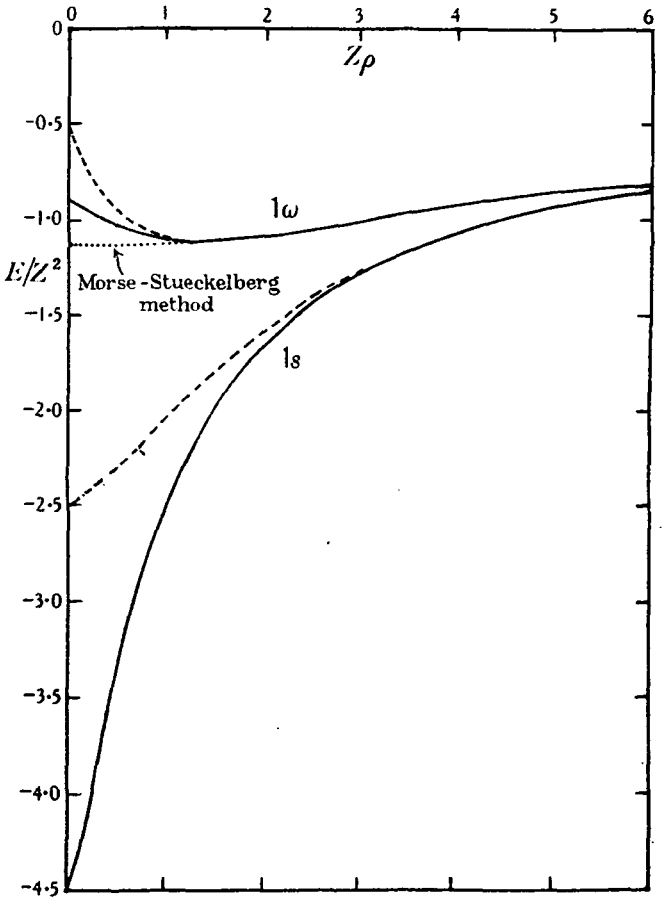


Fig. 2. Energy of single orbitals.
– – – – – Perturbation method. ——— Variation method.

and similarly for the ω-type orbital except that α and β replace γ and δ. The method of treating this equation is to assume some value of t, and then, by evaluating all the functions on the right-hand side of the equation, to determine c/Z. But $t = c\rho$, and hence the value of ρ which corresponds to this value of t can be

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found and the energy can be plotted against the scale of the molecule. These orbital energies are shown by the full curves in Fig. 2. The curves are applicable to any value of Z by a simple change of scale.

As we should expect, the energies obtained by the variational method are lower than those obtained by the simple perturbation method. But the agreement between the two is much closer for the ω-type than for the s-type orbital. In the latter, the difference, at distances comparable with those that occur in practice, is of the order of 5 or 10 volts, whereas in the former it is only about one-tenth of a volt. A precisely similar result has been obtained in some unpublished work of

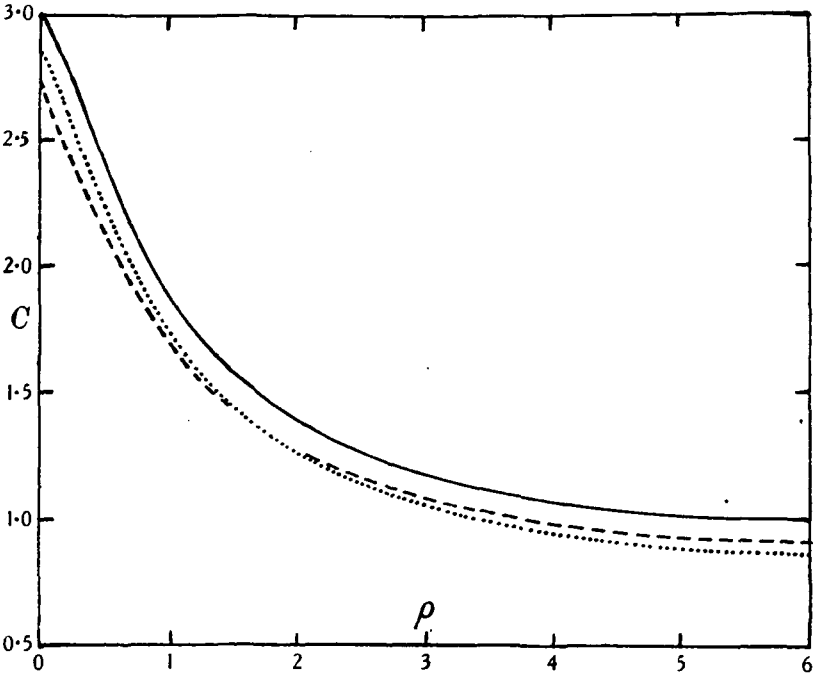


Fig. 3. Variation of parameter c. s-orbitals.
——— No interaction. – – – – – Approx. 4. ····· Approx. 2.

the author in the case of the bonding and anti-bonding orbitals of H_2^+. The conclusion is that the perturbation method is inapplicable for the strongest bonding orbitals, but is more valid for the anti-bonding, or, as in this case, the practically non-bonding ones. From the numerical point of view this is unfortunate, since the labour involved in a variational calculation is far greater than that in a perturbation one.

It is interesting to plot the value of "c" as a function of ρ. The full curve in Fig. 3 shows the values obtained for the s-type orbital and Fig. 4 the corresponding result for the ω-type. It is easy to see from these curves why the per-

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turbation method is a better approximation for the ω-orbitals than for the s-orbitals. The value of c is greatly different from Z in the case of the s-orbitals, whereas, except at very small distances, it does not greatly differ from Z in the ω-orbitals. The ω-type orbital is incorrect at very small distances (below about 1 A.U.) and the curve in this region can be obtained as a perturbation of a $2p$ level of the united-atom by a simple generalization of the method developed by Morse and Stueckelberg (8) for a diatomic molecule, and this extra curve, which joins on quite well to the variational curve already drawn, is also shown in Fig. 2. It is a safe generalization from this, and from similar work for H_2^+, that the simple

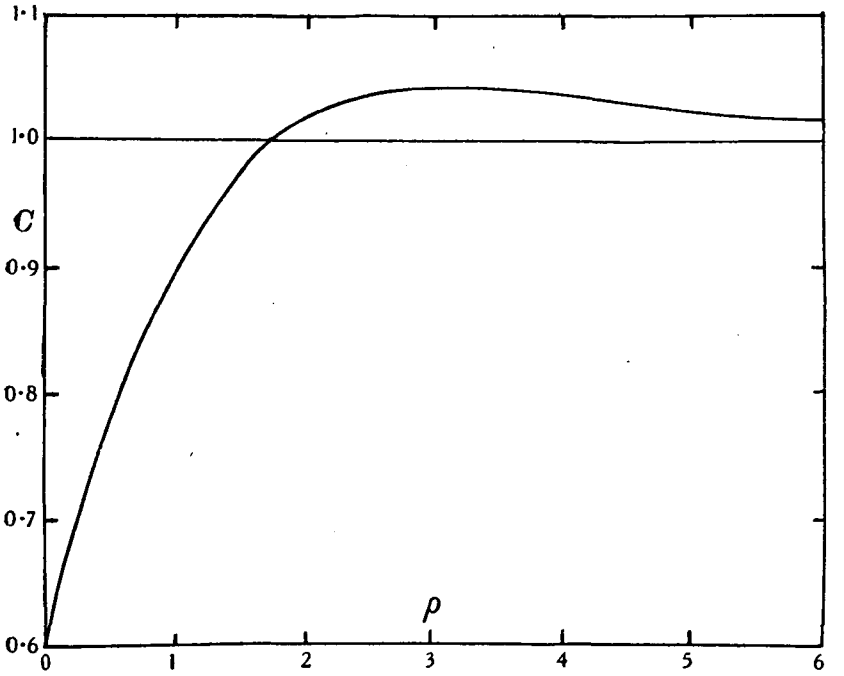


Fig. 4. Variation of parameter c. ω-orbitals.

variational method breaks down at very small distances with all "promoted orbitals", and that it can be supplemented, in this region, very well by a generalized treatment similar to that of Morse and Stueckelberg.

IV. THE ENERGY OF THE GROUND LEVEL OF H_3^+

On adding to the orbital energy just calculated the nuclear Coulomb repulsion energy, it is found that the doubly-ionized molecule H_3^{++} is unstable, in both s- and ω-orbitals. This is not surprising, since the single-electron bond is uncommon and never so strong as the two-electron bond. The actual energy curves are shown in Fig. 5. In connection with the curve for H_3^+ shortly to be obtained, this enables us to estimate the energy needed to eject one of the two electrons in H_3^+ to form

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the unstable ion H_3^{++}. This energy is about 1·5 A.U. of energy which is about 41 volts.

If $\Psi(s.1)$ is the s-orbital for electron 1, then the wave function for H_3^+ can be written $\Psi = \Psi(s.1)\,\Psi(s.2)$.

The spin factor is omitted since it does not affect the energy. The Hamiltonian is $H = H(1) + H(2) + 1/r_{12}$, and the energy can now be written

$$E_s = -c^2\gamma(t) - Zc\delta(t) + \int \frac{\Psi^2(s.1)\,\Psi^2(s.2)}{r_{12}} d\tau_1 d\tau_2.$$

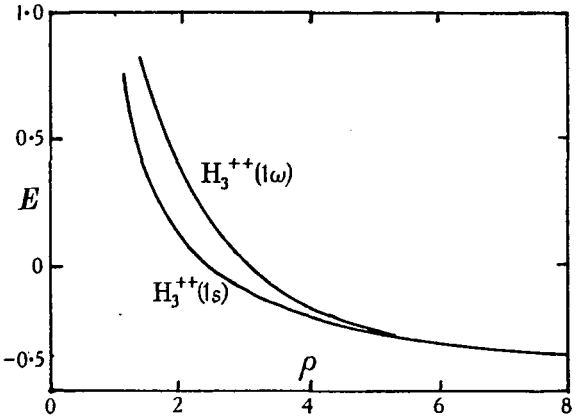


Fig. 5.

The extra energy is the mutual repulsion of the two s-orbitals. Writing for $\Psi(s.1)$ and $\Psi(s.2)$ their complete expressions (1) we can put this extra energy into the form

$$\{(aa.aa) + 2(aa.bb) + 8(aa.ab) + 4(ab.ab) + 4(aa.bc) + 8(ab.ac)\}/3(1+2S)^2. \quad (8)$$

In this notation $(ab.ac) \equiv \int\int \frac{\psi_1(1)\psi_2(1).\psi_1(2)\psi_3(2)}{r_{12}} d\tau_1 d\tau_2,$

and similarly for the others. All these integrals can be expressed as c times a function of t, and we may therefore write equation (8) as follows:

$$E_s = -c^2\gamma(t) - cZ\delta(t) + cf(t). \quad (9)$$

If we are using the perturbation method, the presence of this extra term is not serious; we merely calculate its value with $c = Z$ and hence obtain our expression for the total electronic energy. Using the variational method, however, the presence of the new term $cf(t)$ spoils the earlier analysis which was used to find the appropriate c for each ρ. E is now a minimum with respect to variations of c if

$$-2c\gamma - c^2\rho\frac{d\gamma}{dt} - Z\delta - Zc\rho\frac{d\delta}{dt} + f + c\rho\frac{df}{dt} = 0,$$

i.e. $$c = \left[-Z\left(\delta + t\frac{d\delta}{dt}\right) + \left(f + t\frac{df}{dt}\right)\right] \Big/ \left(2\gamma + t\frac{d\gamma}{dt}\right).$$

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It appears, therefore, that the electron interaction may be allowed for by introducing, instead of Z the true nuclear charge, an effective nuclear charge $Z_{\text{eff.}}$, where

$$Z - Z_{\text{eff.}} = -\left(f + t\frac{df}{dt}\right) \Big/ \left(\delta + t\frac{d\delta}{dt}\right). \tag{10}$$

Starting with any value of t, the equation for c determines c and hence, since $t = c\rho$, the appropriate value of ρ. There are two reasons why the exponent c should be different from the atomic value Z; the first is due to the effect of the nuclei on each other, causing, with the s-orbitals, an increase in c: this is due to the fact that the wave function has to approximate more or less closely to that of the united-atom. The second is due to the interactions of the various orbitals, which, by causing repulsion, make the charge cloud more diffuse, and hence reduce the effective nuclear charge by what is generally called the screening constant. The first of these has no counterpart in atomic spectra; the second gives rise to the well-known rules of Slater (9) and Zener (10). Equation (10) is the counterpart for molecular spectra of the well-known atomic result that the screening of one of the 1s-electrons by the other reduces the effective central charge by 5/16. Equation (10) says that the screening of the one molecular orbital upon the other reduces the effective charge on the nuclei by an amount

$$Z_0 = Z - Z_{\text{eff.}},$$

which, while not constant, is only a function of t and hence is independent of Z. This change of nuclear charge is analogous to the Hartree method of finding a self-consistent field for atoms; in our case the $1/r_{12}$ term is "smoothed out", so that the Hamiltonian becomes

$$\mathrm{H} = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\sum_a 1/r_{1a} + \sum_a 1/r_{2a}\right) + 1/r_{12} = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z_{\text{eff.}}\left(\sum_a 1/r_{1a} + \sum_a 1/r_{2a}\right),$$

and this last form is separable in the two-electron coordinates. At zero separation of the nuclei, the effective nuclear charge changes from $3Z$ to $3Z - 5/16$, and hence Z_0 becomes 5/48. It will be seen later than Z_0 is nearly constant and preserves approximately this value over quite large variations of ρ. From the point of view of the molecular-orbital theory, these two screening effects are quite independent and may be called the screening due to the nuclei and the screening due to the electrons.

Referring back to equation (8), we note that all the integrals except those involving wave functions centred round three different centres of force (viz. $(aa.bc)$ and $(ab.ac)$) can be evaluated by methods similar to those used by Rosen (11) and others. It has always been the custom to neglect these three-centre integrals as being of smaller value than the others. Against this, however, we must put the fact that they occur with a large numerical coefficient which partly compensates for their small value. At large distances they do become vanishingly small, but at small distances they are easily seen to be of the same order of

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magnitude as the other integrals. Their exact values do not seem to be readily expressed in any convenient way, and until this has been done, we must proceed by approximations. In any case, it is evident that with more complicated binding, approximate methods will have to be used. We may accordingly consider four approximations:

Approx. 1. Neglect the $1/r_{12}$ term completely; this will obviously give too low an energy and too small a nuclear separation, but it will be interesting to see what the effect of the electron interaction is.

Approx. 2. Put all the three-centre integrals equal to zero, i.e.

$$(aa.bc) = (ab.ac) = 0.$$

This is still going to give too low an energy and too small an internuclear separation.

Approx. 3. Put all three-centre integrals equal to their largest possible value (viz. $5c/8$). It is soon found that this leads to a hopelessly absurd result, the molecule never having any chance of formation. This approximation has no physical interpretation and we abandon it with the comment that the three-centre integrals cannot be disregarded lightly.

Approx. 4. Put $(aa.bc) = (aa.ba)$ and $(ab.ac) = (ab.ab)$. This hypothesis is intermediate between the two extremes represented by approximations 2 and 3, and gives the correct values at $\rho = 0$ and $\rho = \infty$. It seems probable, pending a more complete discussion of these difficult integrals, that the last approximation is fairly good, the true energy lying very near to the calculated value at moderately small distances, and being a little below the calculated value in the direction of approx. 2 at large separations. We shall refer to these as approximations 1, 2 and 4, relying on 4 for the most probable value.

These three approximations may be treated exactly as the single orbitals were treated in § III; we may use the perturbation method or the variation method. The total energy of the molecule may be found by adding the Coulomb energy of the nuclei $(3/\rho)$ and the resulting curves are shown in Fig. 6.

We may draw the following conclusions from this work:

(*a*) At equilibrium distances, the overlap integral S has the value $\frac{1}{2}$. This is a very pronounced lack of orthogonality and indicates that those approximations in which the wave functions are all assumed orthogonal may be much in error.

(*b*) At equilibrium distances, the exponent c is much greater than unity, implying that the wave function resembles that of the "united-atom" as much as that of the "separated-atoms". Mulliken has already suggested that this may be one condition of firm bonding.

(*c*) Consequent upon this, we find that the simple perturbation calculation is grievously in error; as we should expect, it gives much too high an energy and too large a nuclear separation. This is in excellent agreement with the work of Coolidge and James(12, 13) on the lithium molecule and associated problems;

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these authors find that, in their case too, the perturbation method is inadequate to explain the bonding of Li_2; it looks therefore as though this method will have to be abandoned for all numerical work upon molecular structure.

(*d*) The integrals involving three centres are extremely important; the result of neglecting them completely is about 6 volts in error at the equilibrium point,

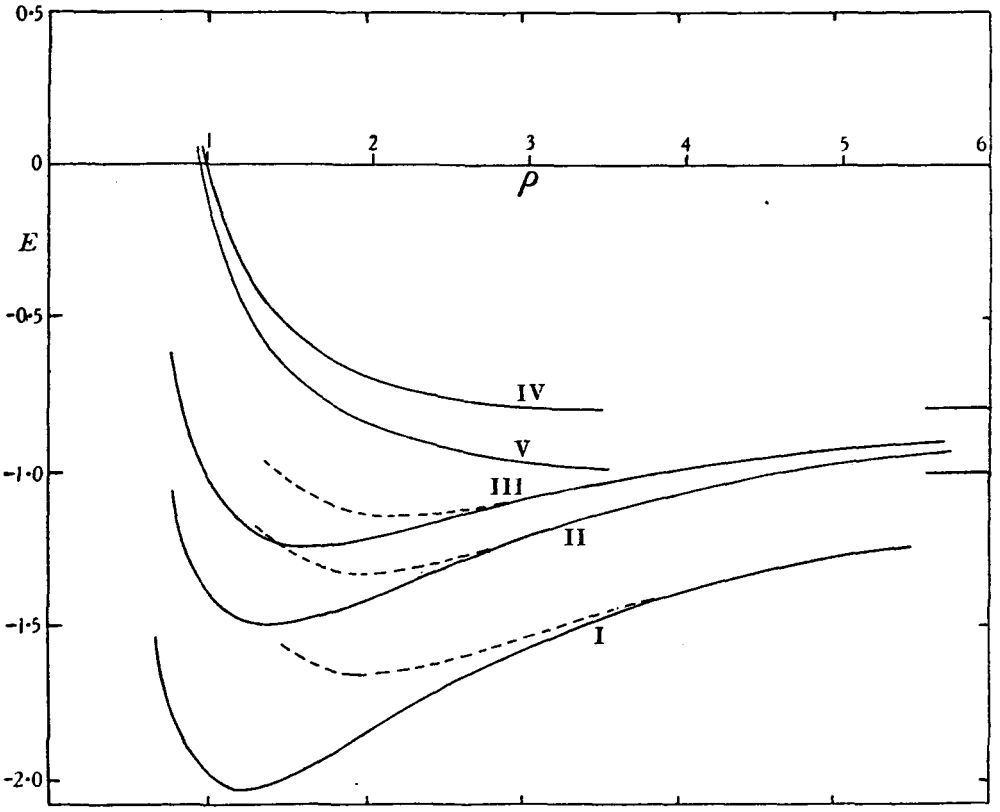


Fig. 6. Energy of H_3^+.

I. Approx. 1. Ground state
II. Approx. 2. ,,
III. Approx. 4. ,,
} full lines, variational method; dotted lines, perturbation method.

IV. Singlet excited state
V. Triplet excited state
} Approx. 4.

whereas the effect of omitting the electron interaction altogether is only about twice this amount. Better numerical methods will have to be developed before it is worth while proceeding further in this type of calculation. This conclusion will always hold for any method where the heat of dissociation is obtained from the total energy, since, except in the case of H_2, this is always a small fraction of

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the total energy and the latter will have to be calculated with great accuracy before any reliable deductions can be made concerning the former.

(*e*) Table I shows the result of fitting Morse functions to all the six curves. If ρ_0 is the equilibrium value of ρ, then the Morse curve is

$$E = E_\infty + D\{e^{-2a(\rho-\rho_0)} - 2e^{-a(\rho-\rho_0)}\}.$$

It is soon shown that if m is the mass of the proton, then the fundamental frequency of "scale-model" vibrations in which only the size and not the shape is altered, is

$$\nu = \frac{a}{\pi}\sqrt{\frac{D}{3m}},$$

and this may be written $\nu = 5902\,\text{cm.}^{-1} \times a\sqrt{D}$,

if a and D are expressed in atomic units. The perturbation curves are always found to be distinctly flatter than the variational ones, and thus the fundamental frequency shows considerable divergence in the two methods. The most likely values for H_3^+ are $\rho_0 = 1{\cdot}61$ A.U. $= 0{\cdot}85$ Å; $\nu_0 = 3170\,\text{cm.}^{-1}$,

and total energy is $-1{\cdot}244$ A.U. $= -33{\cdot}85$ volts.

Taking the energy of $H_2 + H^+$ as $-1{\cdot}17$ A.U. this means that H_3^+ is stable relative to the change

H_3^+ goes to $H_2 + H^+$

by an amount 0·07 A.U. or about 2·0 volts. And it is stable relative to the change

H_3^+ goes to $H + H_2^+$

by an amount 0·14 A.U. or about 4·1 volts.

TABLE I. *Summary of results with* H_3^+. *Ground state*

	Perturbation			Variation		
	ρ_0 A.U.	ν_0 cm.$^{-1}$	Total energy A.U.	ρ_0 A.U.	ν_0 cm.$^{-1}$	Total energy A.U.
Approx. 1	2·017	2780	−1·660	1·244	4080	−2·019
Approx. 2	1·985	2810	−1·330	1·406	3680	−1·493
Approx. 3	2·169	2120	−1·147	1·611	3170	−1·244

(*f*) The relation between c and ρ is shown in full for the three approximations in Fig. 3. Except at very large or very small distances, the curves corresponding to approximations 2 and 4 are nearly identical, and since we may presume that the true value lies between the two, the approximate wave function may be written down with some accuracy.

(*g*) The values of Z_0, the electronic screening constant, as defined by equation (10), are shown in Fig. 7. At distances greater than about $\rho = 6$ A.U. the molecular orbital may break down due to the fact that the molecule will dissociate, not into two H atoms and a proton, but in one of the two ways suggested in (*e*) above, and

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thus the form at infinity of the wave function assumed is wrong. Confirmation is obtained, however, of the result, stated earlier, that in approximation 4 the electronic screening constant differs little from its value (5/48) when $\rho = 0$.

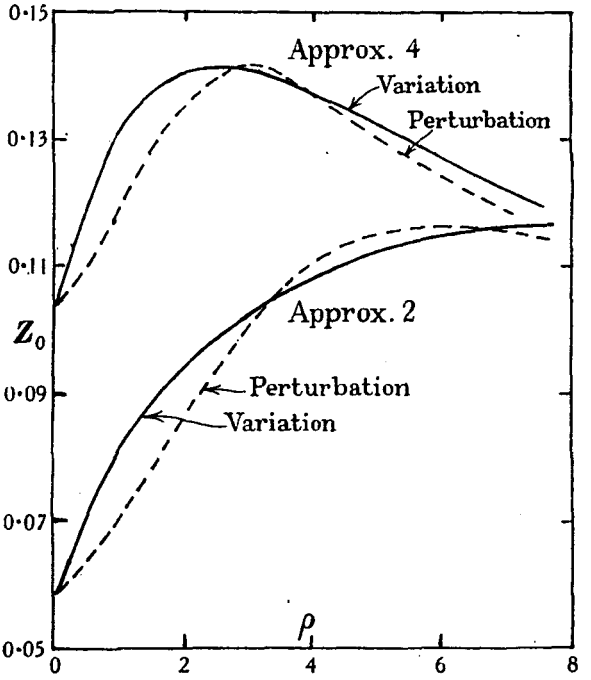


Fig. 7. Screening constant.

V. EXCITED STATES OF H_3^+

The ion H_3^+ might be excited by changing one of the two s-orbitals into an ω-orbital. The configuration $(1s.1\omega)$ gives rise to a singlet and a triplet, whose wave functions are, apart from the spin terms,

$$X_{1,3} = \{\Psi(1)\,\Phi(2) \pm \Phi(1)\,\Psi(2)\} \text{ respectively.}$$

In this function, Ψ is the s-type orbital (1) and Φ is the ω-type orbital (2). The levels are all double due to the choice of configuration $(1s.1\omega_+)$ or $(1s.1\omega_-)$. The energies of these states, calculated in a similar way to the earlier energies, are

$$E_1 = E_s + E_\omega + \int \frac{\Psi^2(1)\,\Phi(2)\,\Phi^\times(2)}{r_{12}}\,d\tau_1 d\tau_2 + \int \frac{\Psi(1)\,\Phi(1)\,\Psi(2)\,\Phi^\times(2)}{r_{12}}\,d\tau_1 d\tau_2,$$

$$E_3 = E_s + E_\omega + \int \frac{\Psi^2(1)\,\Phi(2)\,\Phi^\times(2)}{r_{12}}\,d\tau_1 d\tau_2 - \int \frac{\Psi(1)\,\Phi(1)\,\Psi(2)\,\Phi^\times(2)}{r_{12}}\,d\tau_1 d\tau_2.$$

To a fair approximation, it was found that the interaction energy, in the case of the ground state, depended little upon the exact values of the exponent c, and we

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may therefore evaluate these expressions assuming that this parameter has the same value as in the isolated orbitals. It will indeed be very nearly so, since the interaction between the $1s$- and 1ω-orbitals is much less than that between two $1s$-orbitals, and it is this interaction which causes the exponents to be depressed. The two energies E_1 and E_3 are shown plotted on Fig. 6, and it is seen that they represent unstable states. It is just possible, though very unlikely, that very slight stability might ensue if $2p$ functions were added in the variational equation. The triplet level is lower than the singlet.

Although, as we stated earlier, such a configuration as the one above is unlikely to occur in practice, the three atoms preferring to lie along a straight line than to be at the corners of an equilateral triangle, yet it will be to a state of this nature that transitions would occur from the ground state; there should be a band between the singlet and the ground level; the energy required to produce the excitation is about 0·70 A.U. or 19 volts, with a frequency 152,000 cm.$^{-1}$

VI. The molecule H_3

It is worth while at this stage to examine the possibility of an equilateral configuration for H_3. In view of the fact that the molecule would have two s-type orbitals and one ω-type, it would probably open out into a straight line as suggested by Eyring(14) and Polanyi. But assuming that it does not do this, the wave function can be written down at once and the electron energy is found to be

$$E = 2E_s + E_\omega + \int \frac{\Psi(1)\,\Psi(1)\,\Psi(2)\,\Psi(2)}{r_{12}}\,d\tau_1 d\tau_2 + 2\int \frac{\Psi(1)\,\Psi(1)\,\Phi(2)\,\Phi^\times(2)}{r_{12}}\,d\tau_1 d\tau_2 - \int \frac{\Psi(1)\,\Phi(1)\,\Psi(2)\,\Phi(2)^\times}{r_{12}}\,d\tau_1 d\tau_2,$$

and this may be written

$$E = 2E_s + \int \frac{\Psi(1)\,\Psi(1)\,\Psi(2)\,\Psi(2)}{r_{12}}\,a\tau_1 d\tau_2 + E_\omega + \tfrac{1}{2}\{E_1 - (E_s + E_\omega)\} + \tfrac{3}{2}\{E_3 - (E_s + E_\omega)\}$$

$$= E(H_3^+, \text{ground state}) + \tfrac{1}{2}E_1 + \tfrac{3}{2}E_3 - 2E(H_3^{++}.1s) - E(H_3^{++}.1\omega).$$

On substituting approximate values for these integrals, we find that the total energy of H_3 would have a minimum at about $\rho = 2$ A.U., with total energy $-1{\cdot}41$ A.U. This is unstable with respect to dissociation into three H atoms by about 2–3 volts and might mean that there was a definite life-time for this molecule. Or it might be due to the inadequacy of the method, which certainly must break down at large nuclear separations. In any case, it lends more support to the conclusion already arrived at by Polanyi that the reaction

$$H + H_2(\text{ortho}) \text{ goes to } H_2(\text{para}) + H$$

will take place with the atoms having relative motions along or nearly along a

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common line. The writer hopes in a later paper to discuss this structure more fully.

VII. Comparison with other work

The problem of H_3^+ has been investigated by Massey (6). He only considered what he believed to be the ground state, and used the electron pair method. In this case, one may start with either $H_2 + H^+$ or $H + H_2^+$ and apply the usual perturbation theory. Unfortunately his work has some serious defects:

(1) He does not allow for the modification in screening constant, which, as we have shown, is very important.

(2) He was in error regarding the allowed wave functions.

The wave function for the molecule may be written, on separating out the various motions:

$$\Psi = \psi_{\text{elec.}} \cdot \psi_{\text{elec.spin.}} \cdot \psi_{\text{vibr.}} \cdot \psi_{\text{rot.}} \cdot \psi_{\text{trans.}} \cdot \psi_{\text{nucl.spin.}} \cdot$$

This wave function has to be antisymmetrical in the coordinates of the three nuclei, but only in so far as these coordinates appear in the partial wave functions $\psi_{\text{vibr.}} \cdot \psi_{\text{rot.}} \cdot \psi_{\text{nuc.spin.}} \cdot$ It is true that the coordinates of the nuclei do appear in the expression for $\psi_{\text{elec.}}$, but the distances involved are not distances from nuclei a, b and c, but rather from the points A, B and C, and it is immaterial from the point of view of $\psi_{\text{elec.}}$ whether nuclei a, b and c are at the points A, B and C or at B, C and A respectively. Putting it otherwise, the equation for $\psi_{\text{elec.}}$ is $L(\psi_{\text{elec.}}) = 0$, where L is an operator having the symmetry of an equilateral triangle, and the choice of ψ_{elec} is to be made without reference to whether the nuclei have spins or not. Thus, in effect, Massey disregards the actual ground level of H_3^+ and merely discusses the first excited state. Comparison is therefore difficult between his work and the present, but so far as this can be done it appears that the two methods give similar results.

VIII. Summary

The molecular-orbital method has been applied to a study of H_3^+ in its ground state and excited levels, and the relative importance of the perturbation and variational methods has been considered in some detail, as well as the effect of certain integrals which, in discussions of molecular structure, have often been neglected. It appears that the ion H_3^+ should exist in stable equilateral form with a nuclear distance about 0·85 Å., and that all excited levels are unstable.

Reasons are given for supposing that the molecule H_3 is linear and not triangular.

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