302. *Electron Pairing.*

By J. D. Hopton and J. W. Linnett.

Calculations of the electronic binding energy have shown that, between 0·6 and 1·2 Å, it is only 5—10% greater for H_2 than for H_2^+ despite the fact that two electrons are involved in H_2 and one in H_2^+. This result is discussed in relation to the wide prevalence of the electron-pair bond. In addition it has been shown that for linear symmetrical H_3^+ the best description is in terms of two one-electron bonds.

Over the last fifty years great stress has been placed on the grouping of electrons in pairs in molecules,[1] and it appears that, in the minds of some, there is the belief that the " pairing of electrons " in, for example, the chemical bond provides some special advantage energetically. This impression has been encouraged by the Heitler–London treatment of the bond in the hydrogen molecule [2] and the interpretation of this as a so-called interchange or resonance phenomenon [3] which demands the participation of two electrons. It is the purpose of this paper to examine in some simple cases the degree to which the " pairing of electrons " is important. This is done by studying H_2^+, H_2, and H_3^+. In the first place a comparison is made of the electronic energies of H_2^+ and H_2 as a function of proton–proton separation. In the second, various descriptions of the ground state of linear symmetrical H_3^+ are examined.

The Hydrogen Molecule and Molecule Ion.—For the hydrogen molecule ion, $\omega_e = 2297$ cm.$^{-1}$, $r_e = 1{\cdot}060$, and $D_0 = 2{\cdot}648$ ev.[4] By using also $x_e\omega_e = 62$ cm.$^{-1}$ to obtain D_e, the following Morse expression for the potential energy (in kcal./mole) can be derived:

$$V = 64{\cdot}310\{1 - \exp[-1{\cdot}3238\ (r - r_e)]\}^2, \qquad (1)$$

where r, the proton–proton separation is expressed in Å. The repulsion energy between two protons is given by

$$+331{\cdot}993/r \text{ kcal./mole.} \qquad (2)$$

The energy of a hydrogen atom is

$$-313{\cdot}514 \text{ kcal./g.-atom.} \qquad (3)$$

By combining (1), (2), and (3) it is possible to calculate the decrease in electronic energy, as a function of r, relative to the electronic energy of a proton and a hydrogen atom infinitely separated. The graph of this, which may be called the " electronic binding energy," is shown in the Figure. Because of the approximate nature of the Morse expression, the curve, for small values of r, is uncertain. However, it goes to $-941{\cdot}052$ kcal./mole at $r = 0$ because the energy of He^+ is $-1254{\cdot}566$.

For the hydrogen molecule, $\omega_e = 4395{\cdot}2$ cm.$^{-1}$, $x_e\omega_e = 117{\cdot}9$ cm.$^{-1}$, $r_e = 0{\cdot}7417$ Å, $D_0 = 4{\cdot}476$ ev.[4] This gives for the Morse expression

$$V = 109{\cdot}429\{1 - \exp[-1{\cdot}9421\ (r - r_e)]\}^2. \qquad (4)$$

The energy of two hydrogen atoms is

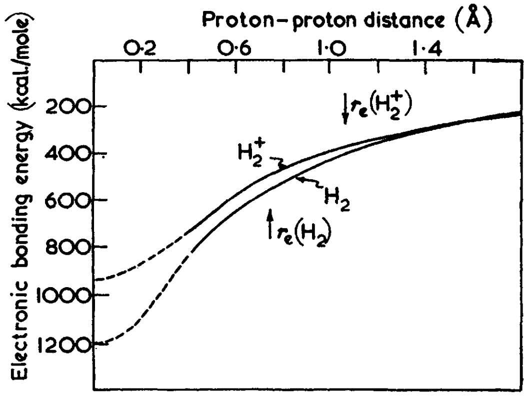
$$-627{\cdot}028 \text{ kcal./g.-atom.} \qquad (5)$$

By combining (4), (2), and (5) the decrease in electronic energy, as a function of r, relative to the electronic energy of two hydrogen atoms can be calculated. This graph, along with the corresponding one for H_2^+, is drawn in the Figure. It goes to $-1194{\cdot}401$ at $r = 0$ because the energy of the helium atom is $-1821{\cdot}429$ kcal./g.-atom.

---

[1] Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762.
[2] Heitler and London, *Z. Phys.*, 1927, **44**, 455.
[3] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1960, p. 25.
[4] Herzberg, " Spectra of Diatomic Molecules," Van Nostrand, New York, 1950.

Before discussing the graphs their reliability must be considered. The Morse expression is only approximate but in the neighbourhood of the equilibrium bond lengths the accuracy is quite good if r_e, ω_e, and D_0 have been used to derive the constants. (In the present cases, D_0 has been converted into D_e by using ω_e and $x_e\omega_e$.) Hence it is possible to be very confident of the curves between 0·6 and 1·2 Å. At shorter distances the approximate course of the curves is known (for instance, they could not cross). At distances greater than 1·2 Å, the position is rather less certain. If the values of (1)—(5) are used the two curves cross at about 1·5 Å, and beyond this the H_2^+ curve is lower than the H_2 curve. However one cannot be sure that this is not a consequence of the approximations involved in using the Morse functions. A more accurate curve could be used for H_2 in place of (4), but the uncertainty regarding H_2^+ for large values of r would remain. It seemed better to restrict consideration to the range 0·6—1·2 Å where the curves are reliable enough for the present purpose. At greater separations all that can yet be said is that the curves for H_2 and H_2^+ are close to one another and it is possible that at large proton–proton separations the lowering of electronic energy is greater for H_2^+ than for H_2. This might repay further study. Finally, it is worth stressing that the curves are not based on approximate wave functions but are essentially " experimental."



Graphs of the electronic binding energy (kcal./mole) of H_2^+ and H_2 as a function of proton–proton separation. The equilibrium bond lengths of H_2^+ and H_2 are also shown.

The most interesting feature of the Figure is that the curves for H_2^+ and H_2 are very close to one another. Between 0·6 and 1·2 Å the electronic binding energy of H_2^+ varies from about 90% to 95% of that of H_2 despite the fact that two electrons are involved in H_2 and one in H_2^+. In both H_2^+ and H_2 the lowering of electronic energy results from a decrease in potential energy, there being in fact an increase in kinetic energy when r is near or smaller than the equilibrium separation (virial theorem).[5] This decrease in potential energy is achieved by an increase in the electron probability in the region between the two nuclei;[6] this concentration is of course limited by the uncertainty principle, or, in other words, by the consequences of the de Broglie effect that an increased restriction of the spread of the electron probability results in an increased kinetic energy. In H_2, a second electron is present. There will be a tendency for it too to be concentrated in the internuclear region. But clearly, because of inter-electron repulsion, each of the two electrons will interfere with the concentration of the other in this region of low potential energy, so that the effect of two cannot be expected to be twice as great as one at the same proton–proton separation. The extent of the mutual interference could hardly be guessed from the above qualitative arguments, but the experimental results show that the increase in electronic binding energy provided by the second electron is only 5—10% in the important region from 1·2 to 0·6 Å. However, though this increase is so surprisingly small, it is of the greatest importance. It means that, if the two protons are brought to a

---

[5] Coulson and Bell, *Trans. Faraday Soc.*, 1945, **41**, 141.

[6] Coulson, " Valence," Oxford Univ. Press, 1961, p. 84.

separation of 1·06 Å (r_e for H_2^+) the electronic binding energy (E_e) for two electrons is greater than for one electron and, moreover, dE_e/dr is also greater. Therefore, r_e is less for H_2 than for H_2^+, and consequently the electronic binding energy of H_2 at its equilibrium separation is about 50% greater than that of H_2^+ at its equilibrium separation. So the stable pair bond is considerably stronger than the single electron bond, though still the electronic binding energy is not twice as great. It is this additional feature which explains why, despite the results summarised in the Figure, the pair bond is so widely prevalent and one-electron bonds comparatively rare, though perhaps bonds containing an odd number of electrons are somewhat more common than is generally supposed.[7]

An important lesson that is suggested by the above result is that the lowering of electronic energy to be expected from the concentration of two electrons in two separate bond regions is likely to be greater than that to be obtained by putting two electrons in the same bond region. To demonstrate and illustrate this point some calculations for linear H_3^+ will be presented.

Ground State of Linear H_3^+.—Hirschfelder, Eyring, and Rosen [8] carried out a considerable number of calculations for linear H_3^+. By use of hydrogen atom 1*s* functions designated by *a*, *b*, and *c* for the three atoms, the wave functions for the singlet states were described in terms of combinations of the following functions:

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

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

$$\psi_3 = \frac{1}{\sqrt{2}}[b(1)b(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

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

The calculated energy for the ground state of the symmetrical linear species is found to be a minimum when the central nucleus is $2a_0$ from the outer ones. The coefficients in the wave function

$$\Psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + C_4\psi_4 \qquad (6)$$

for this condition are $C_1 = 0{\cdot}378$, $C_2 = 0{\cdot}208$, $C_3 = 0{\cdot}203$, and $C_4 = -0{\cdot}100$. This may be described as the " best " function obtainable by using 1*s* hydrogen-like functions.

The object of the present calculations was to discover which of three approximation methods in their simplest form comes closest to the " best " function of Hirschfelder *et al.* These three methods may be described as (i) valence-bond (V.B.), (ii) molecular orbital (M.O.), and (iii) non-pairing (N.P.). They are represented conveniently by the hybrid of (Ia and b) for (i), by formula (II) for (ii), and by formula (III) for (iii) in which each dot represents one electron.

$$\underset{\text{(Ia)}}{\text{H–H H}^+} \qquad \underset{\text{(Ib)}}{\text{H}^+\text{ H–H}} \qquad \underset{\text{(II)}}{\overline{\text{H H H}}} \qquad \underset{\text{(III)}}{\text{H·H·H}}$$

When the spin part is omitted, the formula used to describe (i) is:

$$\begin{aligned}\text{(V.B.)}\ &\{[a(1) + kb(1)][ka(2) + b(2)] + [a(2) + kb(2)][ka(1) + b(1)]\} + \\ &\qquad \{[c(1) + kb(1)][kc(2) + b(2)] + [c(2) + kb(2)][kc(1) + b(1)]\} \\ &\qquad = 2(1 + k^2)\psi_1 + 4\sqrt{2}k\psi_3 + 4k\psi_4.\end{aligned}$$

This wave function is based on that devised by Coulson and Fischer.[9] With $k = 0$, the

---

[7] Linnett, *J. Amer. Chem. Soc.*, 1961, **83**, 2643.

[8] Hirschfelder, Eyring, and Rosen, *J. Chem. Phys.*, 1936, **4**, 130.

[9] Coulson and Fischer, *Phil. Mag.*, 1949, **40**, 386.

Heitler–London formulation is obtained, but as k is increased ionic terms are included. That used for the molecular orbital description (ii) is:

$$(\text{M.O.})\ [a(1) + kb(1) + c(1)][a(2) + kb(2) + c(2)] = 2k\psi_1 + 2\psi_2 + \sqrt{2}k^2\psi_3 + 2\psi_4.$$

It will be seen that each of the above contains one adjustable constant, k. Three functions were tested for the non-pairing approximation (iii), the first of which contained no adjustable constant, and the second and third one adjustable constant each. The functions for these were:

N.P.:

$$\text{A: } [a(1) + b(1)][b(2) + c(2)] + [a(2) + b(2)][b(1) + c(1)] = 2\psi_1 + 2\psi_2 + 2\sqrt{2}\psi_3.$$

$$\text{B: } [a(1) + kb(1)][kb(2) + c(2)] + [a(2) + kb(2)][kb(1) + c(1)] = 2k\psi_1 + 2\psi_2 + 2\sqrt{2}k^2\psi_3.$$

$$\text{C: } [a(1) + kb(1)][b(2) + kc(2)] + [a(2) + kb(2)][b(1) + kc(1)] + [ka(1) + b(1)][kb(2) + c(2)] + [ka(2) + b(2)][kb(1) + c(1)] = 2(1 + k^2)\psi_1 + 4k\psi_2 + 4\sqrt{2}k\psi_3.$$

The form of these will be examined later. In order to test these functions the extent to which they overlapped Hirschfelder, Eyring, and Rosen's function [8] was determined, k being chosen to optimise this. (Overlap $S = \int\Psi\Phi d\tau$, where Ψ is the " best " function and Φ is the function being tested.) Also the " energies " corresponding to the five functions were calculated, the k's being chosen to minimise these, and the amounts by which these energies were greater than that given by the " best " function tabulated. The results are listed in the Table.

Results for overlap (S) and energy [$E - E$(best)] in kcal./mole, together with $k_{\text{max.}}$ for the former and $k_{\text{min.}}$ for the latter and the coefficients in the wave functions.

	Hirschfelder *et al.* " best " function	V.B. (i)	M.O. (ii)	N.P. (iii) A	N.P. (iii) B	N.P. (iii) C
		Overlap				
$k_{\text{max.}}$	—	−0·066	1·87	—	0·895	2·10
C_1	0·378	0·593	0·258	0·253	0·255	0·286
C_2	0·208	0	0·138	0·253	0·285	0·222
C_3	0·203	−0·110	0·341	0·358	0·323	0·314
C_4	−0·100	−0·078	0·138	0	0	0
S	1·0000	0·9825	0·9823	0·9972	0·9978	0·9976
		Energy				
$k_{\text{min.}}$		−0·010	2·15	—	0·904	2·72
C_1	0·378	0·527	0·252	0·253	0·255	0·309
C_2	0·208	0	0·117	0·253	0·283	0·200
C_3	0·203	−0·015	0·384	0·358	0·326	0·283
C_4	−0·100	−0·011	0·117	0	0	0
$E - E$ (best)	0	17	16	3·5	3·2	2·5

The values for the coefficients, C_1, C_2, C_3, and C_4 for the " best " function were obtained from Fig. 3 in the paper by Hirschfelder *et al.*[8] by measuring it as carefully as possible at $R = 2a_0$. Small errors may arise in calculating the overlap from errors in these coefficients, but these would not affect the relative performance of the different methods which is more important to us than the precise achievements of each. Because of inaccuracies in reading the graphs, the calculated energies may be subject to an error of ±1 kcal./mole, but again this would not affect the general conclusion.

The main result to be derived from the Table is that the non-pairing formulation is much better than the valence-bond or molecular-orbital approximation. This is particularly noticeable in the energy results but is also apparent for overlap. Even the non-pairing formula with no adjustable constant is much better than the molecular-orbital and valence-bond approximation. There are two ways in which the non-pairing formula may be modified with an adjustable constant. They are B and C, which may be represented respectively by (IV) and a resonance hybrid of (Va and b). From the overlap criterion there is little to choose between these, though (IV) is slightly better, but from the energy criterion the latter seems better. However, the difference is less marked than was found by Hirst and Linnett [10] for the allyl positive ion. Undoubtedly the interelectron-repulsion and effective-electronegativity effects exert opposing tendencies here. Interelectron repulsion favours structure (IV), but the electronegativity effect favours a higher electron probability in orbital *b* than in *a* or *c*. The latter arises because the central nucleus has two near neighbours whereas the outer nuclei have only one. Hence the electronegativity effect favours forms (Va and b) because, for example, an electron near proton *b* experiences some lowering in its potential energy owing to the presence of protons *a* and *c*.

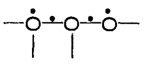
H· H ·H (IV)
H· H· H (Va)
H ·H ·H (Vb)

However, the main result of these calculations for H_3^+ is that the non-pairing formulation is best, so that the feature demonstrated by our consideration of H_2^+ and H_2 is borne out. That is: there is no particular and special energy effect involved in " the pairing of electrons." Therefore, if there are two electrons and two bond regions the best description of the system is as two one-electron bonds.

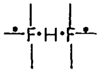
The particular significance of the electron-pair bond appears to reside in the feature that " two electrons are a little better than one," while a third electron could not enter the same region of space effectively because then, of necessity, two of the three electrons would have to have parallel spins, and so, for these two, spin and charge correlation would add to one another in the way that occurs in the $^3\Sigma$ state of H_2, causing it to have a purely repulsive potential-energy curve. The situation in double and triple bonds is, of course, different, in that in systems where they are found there is sufficient space for two, or even three, pairs to occupy separate regions and yet all contribute to bonding.

Recent spectroscopic measurements [11] have shown that Li_2^+ has a larger dissociation energy than Li_2, and that the same is true for Na_2^+ and Na_2, and for K_2^+ and K_2.[12] Theoretical calculations seem to support these experimental results.[13] So these systems, in which one electron provides more binding than two, present additional evidence for the view that there is no special force involved in the pairing of electrons. Also it means that the rather doubtful result obtained earlier, that at proton–proton separations greater than 1·5 Å the electronic binding energy of H_2^+ exceeds that of H_2, may be true. The argument for some further investigation of this is therefore confirmed.

It is proposed to examine other systems in the light of this somewhat modified attitude to the " pairing of electrons." In particular molecules such as the boron hydrides, in which one-electron bonds may provide the best description, will be examined. However,


(VI)


(VII)



(VIII)

it can be stated at once that the results obtained here do support the following formulæ

---

[10] Hirst and Linnett, *J.*, 1962, 1035.
[11] Barrow, Travis, and Wright, *Nature*, 1960, **187**, 141.
[12] Robertson and Barrow, *Proc. Chem. Soc.*, 1961, 329.
[13] James, *J. Chem. Phys.*, 1935, **3**, 9; Faulkner, *ibid.*, 1957, **27**, 369.

for ozone (VI), benzene (VII), and the FHF^- ion (VIII), and others of a similar kind that have been suggested previously.[14]

We thank the Royal Society and Imperial Chemical Industries Limited for providing calculating machines, and Professor H. Hartmann for describing a lecture by one of us as " propaganda against pairing," a remark which encouraged some of the above calculations.

INORGANIC CHEMISTRY LABORATORY, OXFORD. [*Received, November 6th,* 1961.]

---

[14] Ref. 7, and Linnett, *Nature*, 1960, **187**, 859.