

### 195. *Binding in the Hydrogen Molecule and its Ion.*

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The potential-energy curves for  $\text{H}_2^+$  and  $\text{H}_2$  have been obtained, and it is found that, at large internuclear distances, the electronic binding energy is greater for  $\text{H}_2^+$  than for  $\text{H}_2$ . The effect is discussed in terms of coulomb and exchange energies and in terms of the changing average kinetic and potential energies of the electrons in the system. It seems that the binding is less in  $\text{H}_2$  than in  $\text{H}_2^+$ , at large nuclear separations, because interelectron repulsion reduces the transfer of electron probability to the "bond region" between the nuclei.

HOPTON AND LINNETT,<sup>1</sup> using Morse curves for the hydrogen molecule and its ion, concluded that, at large nuclear separations, the electronic binding energy is greater in the ion than in the molecule. Fig. 1 shows the potential energy curves of  $\text{H}_2^+$  and  $\text{H}_2$ . For the former the energies obtained by using the exact solution of the Schrödinger equation are plotted.<sup>2</sup> For the latter, the values determined from spectroscopic data<sup>3</sup> are employed, along with those of Dalgarno and Lynn<sup>4</sup> for larger separations. Fig. 2 shows the corresponding electronic binding energy curves for  $\text{H}_2^+$  and  $\text{H}_2$  (cf. ref. 1). It will be seen that, at large internuclear distances, the electronic energy falls more for  $\text{H}_2^+$  than for  $\text{H}_2$ .

<sup>1</sup> Hopton and Linnett, *J.*, 1962, 1553.

<sup>2</sup> Bates, Ledshaw, and Stewart, *Phil. Trans.*, 1953, *A*, **246**, 215.

<sup>3</sup> Vanderslice and Tobias, *J. Chem. Phys.*, 1961, **35**, 1852; Vanderslice, Mason, Maisch, and Lippincott, *J. Mol. Spectroscopy*, 1959, **3**, 17.

<sup>4</sup> Dalgarno and Lynn, *Proc. Phys. Soc.*, 1956, *A*, **49**, 821.

## DISCUSSION

Calculations have been made for both species at large distances. Coulson<sup>5</sup> obtained the following expression for  $H_2^+$ :

$$E(R) = -2.25/R^4 - 7.5/R^6 - 53.25/R^7 - 121.17/R^8 - 886.5/R^9 - 5378.06/R^{10},$$

while, for  $H_2$ , Pauling and Beach<sup>6</sup> deduced:

$$E(R) = -6.50/R^6 - 124.40/R^8 - 1135.21/R^{10}.$$

The main difference between these arises because, for  $H_2^+$ , the most important term, at large nuclear separations ( $R$ ), results from the polarisation of the hydrogen atom in the

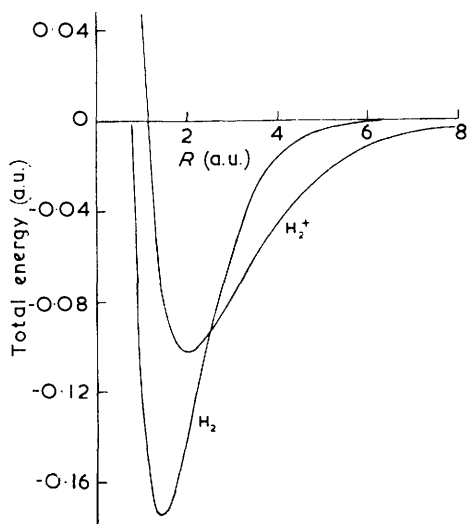


FIG. 1. Potential (or total) energy curves for  $H_2^+$  and  $H_2$ . For energies, 1 a.u. = 27.210 eV; for distances, 1 a.u. = 0.52917 Å.

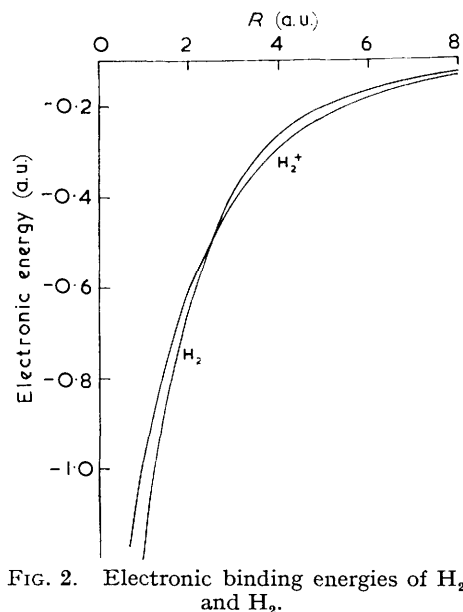


FIG. 2. Electronic binding energies of  $H_2^+$  and  $H_2$ .

field of the proton; for  $H_2$  both particles are atomic and uncharged. At a separation of 6 a.u. the above expressions give, for the energies of  $H_2^+$  and  $H_2$ , 0.002 a.u. and 0.0002 a.u., respectively. The separation of the curves in Fig. 2 at  $R = 6$  a.u. is much greater (0.01 a.u.). This effect is therefore inadequate to explain the difference.

*Coulomb and Exchange Energies.*—Because the potential-energy curves derived from simple wave functions (*e.g.*, Heitler–London,<sup>7</sup> Wang,<sup>8</sup> etc.) predict the observed crossing, a study of these was undertaken. With such functions, the energy can be divided, according to the types of integrals appearing in the expression for the electronic energy, into coulomb and exchange terms. When Finkelstein–Horowitz<sup>9</sup> and Wang-type<sup>8</sup> functions (variable effective nuclear charges) are used for  $H_2^+$  and  $H_2$ , respectively, the coulomb and exchange energies vary with  $R$  as shown in Fig. 3. The exchange-energy

<sup>5</sup> Coulson, *Proc. Roy. Soc. Edinburgh*, 1941–43, **61**, 20.

<sup>6</sup> Pauling and Beach, *Phys. Rev.*, 1935, **47**, 686.

<sup>7</sup> Heitler and London, *Z. Physik*, 1927, **44**, 455.

<sup>8</sup> Wang, *Phys. Rev.*, 1928, **31**, 579.

<sup>9</sup> Finkelstein and Horowitz, *Z. Physik*, 1928, **48**, 118.

curves cross at almost the same internuclear distance as the experimental potential-energy curves. The expressions for the exchange energies are:

$$\begin{aligned} \text{H}_2^+ &: W_{21} - (2 - Z)J_{21} + S_{21}/R \\ \text{H}_2 &: 2S_{21}[W_{21} - (2 - Z)J_{21}] + S_{21}^2/R + K_{21}, \end{aligned}$$

in which

$$\begin{aligned} W_{21} &= \int \psi_B(-\frac{1}{2}\nabla - z/r_A)\psi_A dT \\ J_{21} &= \int (\psi_A\psi_B/r_A) dT \\ S_{21} &= \int \psi_A\psi_B dT \\ K_{21} &= \int \int [\psi_A(1)\psi_B(1)\psi_A(2)\psi_B(2)/r_{12}] dT_1 dT_2 \end{aligned}$$

( $\psi_A$  and  $\psi_B$  are the 1s wave functions on nuclei A and B,  $Z$  is the effective nuclear charge,  $r_A$  is the distance from an electron to nucleus A and  $r_{12}$  is the distance between the electrons

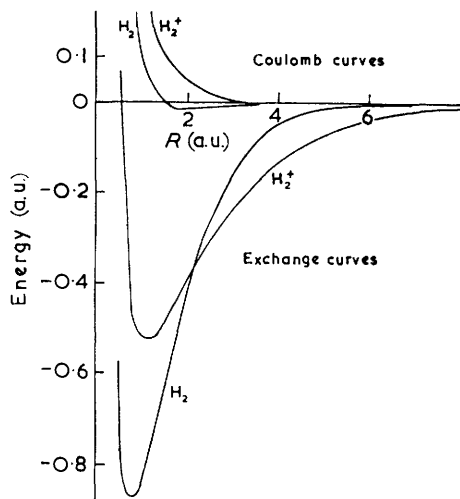


FIG. 3. Coulomb and exchange energies for  $\text{H}_2^+$  and  $\text{H}_2$ , by using the Finkelstein and Horowitz<sup>9</sup> and the Wang<sup>8</sup> function, respectively.

1 and 2). Except for small values of  $R$ , the values of  $S_{21}^2/R$  and  $K_{21}$  are sufficiently close to one another that the energy for  $\text{H}_2$  may be written

$$2S_{21}[W_{21} - (2 - Z)J_{21} + S_{21}/R].$$

In this form, the crossing results from the change in  $S_{21}$  with  $R$ . If  $S_{21}$  is less than one half (large  $R$ ), the exchange energy of  $\text{H}_2^+$  is greater (numerically) than that of  $\text{H}_2$ . If  $S_{21}$  is greater than one half the reverse is true. For  $\text{H}_2$ ,  $S_{21} = 1/2$  at  $R = 2.25$  a.u.; for  $\text{H}_2^+$ ,  $S_{21} = 1/2$  at  $R = 1.9$  a.u. The difference occurs because the "best" effective nuclear charges ( $Z$ ) are different for the molecule and the ion. This provides an analysis of the situation in terms of these simple wave functions, but for more exact treatments the energy does not divide into coulomb and exchange parts. Consequently the variation of electronic potential and kinetic energies with  $R$  will be examined.

*Potential and Kinetic Energies.*—Functions having an effective nuclear charge as a variation parameter obey the virial theorem. Therefore curves for the average kinetic and potential energies can be calculated by using the virial theorem and the Wang, and Finkelstein and Horowitz functions for  $\text{H}_2$  and  $\text{H}_2^+$ . These are shown in Figs. 4a and 4b. The curves that are obtained from experimental data are similar (cf. Coulson and Bell<sup>10</sup>). The point of present interest is that both the potential and kinetic energy curves cross twice,

<sup>10</sup> Coulson and Bell, *Trans. Faraday Soc.*, 1945, **41**, 141.

and, further, the crossing of the curves in Fig. 1 cannot be attributed solely to the one or the other, which is not surprising since  $S_{21}$  appears in the expressions for both the kinetic and potential energies.

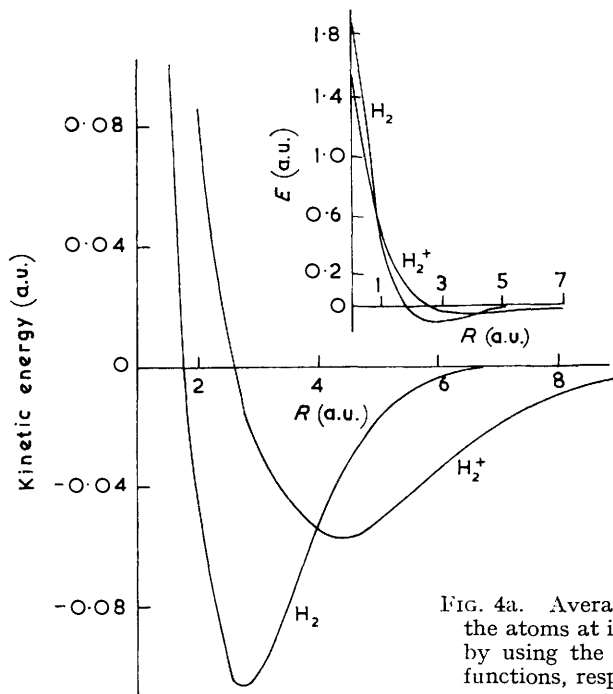


FIG. 4a. Average electronic kinetic energies (relative to the atoms at infinite separation) of  $H_2^+$  and  $H_2$  derived by using the Finkelstein and Horowitz<sup>9</sup> and Wang<sup>8</sup> functions, respectively.

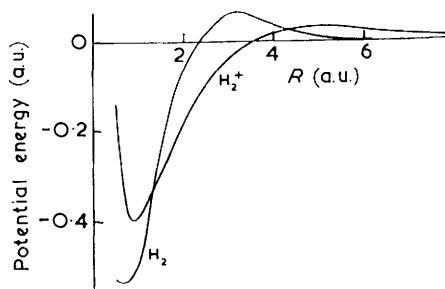


FIG. 4b. Average potential energies (nuclear and electronic, relative to atoms at infinite separation) of  $H_2^+$  and  $H_2$  derived by using the Finkelstein and Horowitz<sup>9</sup> and Wang<sup>8</sup> functions, respectively.

### CONCLUSION

The overlap integral,  $S_{21}$ , can be regarded, with some oversimplification, as providing a means of measuring the enhancement of the chance of finding the electron in the bond region relative to that which would exist if the separate atomic-probability distributions were unaffected by bringing the two nuclei together. For  $H_2^+$ , this enhancement is proportional, for the one electron, to  $S_{21}$ . For  $H_2$  it is, for each, proportional to  $S_{21}^2$ , and, for the two, to twice this. This suggests that, at large values of  $R$ , the transfer of electron probability to the bond region is greater for  $H_2^+$  than for  $H_2$ . A feasible explanation of this is that, in  $H_2$ , the interelectron repulsion largely cancels, for each electron, the attraction of the "other" nucleus which would produce a transfer to the bond region. For  $H_2^+$  no such repulsion exists and so the transfer to the bond region is greater. At large separations this transfer produces a decrease in kinetic energy because the increase in the magnitude of the wave function in the bond region between the nuclei decreases the curvature of the wave function in the regions near the nuclei. This decreases the average kinetic energy because of the high probability of finding the electrons in the *atomic regions*. The increase in the magnitude of the wave function in the bond region takes place even at separations for which the potential energy there is greater than the average potential energy. Consequently the average potential energy is raised. The total energy falls because the decrease in average kinetic energy is greater than the increase in average potential energy. At large distances these effects are greater for  $H_2^+$  than for  $H_2$ , because of the consequences of interelectron repulsion in the latter, as already mentioned.

The above effect is demonstrated by the values of the parameter  $Z$  listed in the Table. This shows that, for  $R$  between 6 and 8 a.u., the effective nuclear charge decreases below

Values of  $Z$ , effective nuclear charge (or scale factor), in the Finkelstein and Horowitz function for  $H_2^+$ , and in the Wang function for  $H_2$ .

$R$ (a.u.) ...	1	2	2.2	2.4	2.5	3	4	5	6	7	8
$Z$ ( $H_2^+$ ) ...	1.538	1.239	1.201	1.168	1.154	1.095	1.028	1.002	0.995	0.9955	0.997
$Z$ ( $H_2$ ) .....	1.286	1.062	1.039	1.022	1.015	0.995	0.992	0.997	0.999	1.000	1.000

unity to a greater extent for  $H_2^+$  than for  $H_2$ . That is, the wave function falls off from the nucleus less sharply, and so the kinetic energy is less. On the other hand, the value of  $Z$  increases above unity at much larger distances for  $H_2^+$  than for  $H_2$ . This is because the dual effect of the two nuclei contracts the wave function towards the internuclear axis to a greater extent for  $H_2^+$  than for  $H_2$ , there being no screening effect of a second electron. This will be true down to very small values of  $R$  (for  $He^+$ ,  $Z = 2$ ; for  $He$   $Z = 1.675$ ). However, at very small values of  $R$ , because there are two electrons, the increase in the average kinetic energy for  $H_2$  is greater than for  $H_2^+$ .

Fig. 4b shows that, at large  $R$ , the average potential energy increases more for  $H_2^+$  than for  $H_2$ . This results from the greater spread of the wave function into the bond region where, for such large values of  $R$ , the potential energy is high. At intermediate values of  $R$ , the potential energy for  $H_2$  is greater than for  $H_2^+$ . This is probably explained most simply as a consequence of electron-electron repulsion. But, at still smaller values of  $R$ , the presence of two electrons results in the average potential energy for  $H_2$  being lower than for  $H_2^+$  (for  $He$ , the total electronic potential energy is lower than for  $He^+$ , though the potential energy "per electron" is greater).

Thus, in very general terms, the curves in Figs. 4a and 4b can be understood, and the surprising features of Figs. 1 and 2, particularly for large value of  $R$ , explained.

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