

\* NATIONAL RESEARCH FELLOW IN CHEMISTRY.

<sup>1</sup> Warburg, *Berl. Ber.*, p. 746, 1911; p. 216, 1912; p. 872, 1914; *Z. Elektrochem.* 26, 54 (1920); 27, 133 (1921).

<sup>2</sup> Birge and Sponer, *Physic. Rev.*, 28, 259-283 (1926).

<sup>3</sup> Lewis, *J. Amer. Chem. Soc.*, 46, 2027-2032 (1924).

<sup>4</sup> Liveing and Dewar, *Proc. Roy. Soc.*, 46, 222 (1889).

<sup>5</sup> Warburg, *Berl. Ber.*, p. 230, 1915.

---

## THE SHARED-ELECTRON CHEMICAL BOND

BY LINUS PAULING

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated March 7, 1928

With the development of the quantum mechanics it has become evident that the factors mainly responsible for chemical valence are the Pauli exclusion principle and the Heisenberg-Dirac resonance phenomenon. It has been shown<sup>1,2</sup> that in the case of two hydrogen atoms in the normal state brought near each other the eigenfunction which is symmetric in the positional coordinates of the two electrons corresponds to a potential which causes the two atoms to combine to form a molecule. This potential is due mainly to a resonance effect which may be interpreted as involving an interchange in position of the two electrons forming the bond, so that each electron is partially associated with one nucleus and partially with the other. The so-calculated heat of dissociation, moment of inertia, and oscillational frequency<sup>2</sup> of the hydrogen molecule are in approximate agreement with experiment. London<sup>3</sup> has recently suggested that the interchange energy of two electrons, one belonging to each of two atoms, is the energy of the non-polar bond in general. He has shown that an antisymmetric (and hence allowed) eigenfunction symmetric in the coordinates of two electrons can occur only if originally the spin of each electron were not paired with that of another electron in the same atom. The number of electrons with such unpaired spins in an atom is, in the case of Russell-Saunders coupling, equal to  $2s$ , where  $s$  is the resultant spin quantum number, and is closely connected with the multiplicity,  $2s + 1$ , of the spectral term. This is also the number of electrons capable of forming non-polar bonds. The spins of the two electrons forming the bond become paired, so that usually these electrons cannot be effective in forming further bonds.

It may be pointed out that this theory is in simple cases entirely equivalent to G. N. Lewis's successful theory of the shared electron pair, advanced in 1916 on the basis of purely chemical evidence. Lewis's electron

pair consists now of two electrons which are in identical states except that their spins are opposed. If we define the chemical valence of an atom as the sum of its polar valence and the number of its shared electron pairs, the new theory shows that the valence must be always even for elements in the even columns of the periodic system and odd for those in the odd columns. The shared electron structures assigned by Lewis to molecules such as  $H_2$ ,  $F_2$ ,  $Cl_2$ ,  $CH_4$ , etc., are also found for them by London. The quantum mechanics explanation of valence is, moreover, more detailed and correspondingly more powerful than the old picture. For example, it leads to the result that the number of shared bonds possible for an atom of the first row is not greater than four, and for hydrogen not greater than one; for, neglecting spin, there are only four quantum states in the  $L$ -shell and one in the  $K$ -shell.

A number of new results have been obtained in extending and refining London's simple theory, taking into consideration quantitative spectral and thermochemical data. Some of these results are described in the following paragraphs.

It has been found that a sensitive test to determine whether a compound is polar or non-polar is this: If the internuclear equilibrium distance calculated for a polar structure with the aid of the known properties of ions agrees with the value found from experiment, the molecule is polar; the equilibrium distance for a shared electron bond would, on the other hand, be smaller than that calculated. Calculated<sup>4</sup> and observed values of the hydrogen-halogen distances in the hydrogen halides are in agreement only for HF, from which it can be concluded that HF is a polar compound formed from  $H^+$  and  $F^-$  and that, as London had previously stated, HCl, HBr, and HI are probably non-polar. This conclusion regarding HF is further supported by the existence of the hydrogen bond. The structure  $[:\ddot{F}:H:\ddot{F}:]^-$  for the acid fluoride ion and a similar one for  $H_nF_n$  are ruled out by Pauli's principle, if the shared pairs be of London's type. The ionic structure  $:\ddot{F}:^- H^+ :\ddot{F}:^-$ , in which the proton holds the two fluoride ions together by electrostatic forces (including polarization), is, of course, allowed. This conception of the hydrogen bond, requiring the presence of a proton, explains the observation that only atoms of high electron affinity (fluorine, oxygen, and nitrogen) form such bonds.

Compounds of septivalent chlorine probably contain chlorine with a polar valence of +3 and with four shared electron bonds. Thus the perchlorate ion would be formed from  $\cdot\ddot{Cl}\cdot^{+3}$  and  $4\cdot\ddot{O}:^-$  and would have

the structure  $\left[ \begin{array}{ccc} & :\ddot{O}: & \\ :\ddot{O}: & \ddot{Cl}: & :\ddot{O}: \\ & :\ddot{O}: & \end{array} \right]^-$ . This structure is, of course, also possible

for  $\text{FO}_4^-$ , inasmuch as there are positions for four (and only four) unpaired electrons in the  $L$ -shell of fluorine. London assumed that septivalent chlorine had a polar valence of zero and seven shared electron bonds, and pointed out in explanation of the non-existence of valences other than one for fluorine that seven unpaired  $L$ -electrons cannot occur. This simple explanation, however, does not make impossible fluorine with a polar valence of  $+3$  and with four shared bonds; the non-existence of higher valences of fluorine must accordingly instead be explained on energetic considerations, and is connected with its very large ionization potentials.

In the case of some elements of the first row the interchange energy resulting from the formation of shared electron bonds is large enough to change the quantization, destroying the two sub-shells with  $l = 0$  and  $l = 1$  of the  $L$ -shell. Whether this will or will not occur depends largely on the separation of the  $s$ -level ( $l = 0$ ) and the  $p$ -level ( $l = 1$ ) of the atom under consideration; this separation is very much smaller for boron, carbon, and nitrogen than for oxygen and fluorine or their ions, and as a result the quantization can be changed for the first three elements but not for the other two. The changed quantization makes possible the very stable shared electron bonds of the saturated carbon compounds and the relatively stable double bonds of carbon, which are very rare in other atoms, and in particular are not formed by oxygen. This rupture of the  $l$ -quantization also stabilizes structures in which only three electron pairs are attached to one atom, as in molecules containing a triple bond ( $\text{N}_2 = \text{:N:N:}$ ), the carbonate, nitrate, and borate ions ( $\left[ \begin{array}{c} \text{:}\ddot{\text{O}}\text{:C}\text{:}\ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^-$ ,

etc.), the carboxyl group,  $\text{R} : \text{C} \begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}\text{:} \\ \text{H} \end{array}$ , and similar compounds. It has

further been found that as a result of the resonance phenomenon a tetrahedral arrangement of the four bonds of the quadrivalent carbon atom is the stable one.

Electron interactions more complicated than those considered by London also result from the quantum mechanics, and in some cases provide explanations for previously anomalous molecular structures.

It is to be especially emphasized that problems relating to choice among various alternative structures are usually not solved directly by the application of the rules resulting from the quantum mechanics; nevertheless, the interpretation of valence in terms of quantities derived from the consideration of simpler phenomena and susceptible to accurate mathematical investigation by known methods now makes it possible to attack them with a fair assurance of success in many cases.

The detailed account of the material mentioned in this note will be submitted for publication to the *Journal of the American Chemical Society*.

<sup>1</sup> Heitler, W., and London, F., *Z. Phys.*, **44**, 455 (1927).

<sup>2</sup> Y. Sugiura, *Ibid.*, **45**, 484 (1927).

<sup>3</sup> F. London, *Ibid.*, **46**, 455 (1928).

<sup>4</sup> L. Pauling, *Proc. Roy. Soc.*, **A114**, 181 (1927). In this paper it was stated that the consideration of polarization of the anion by the cation would be expected to reduce the calculated values; a number of facts, however, indicate that with ions with the noble gas structure the effect of polarization on the equilibrium distance is small.