

$1\sigma^2 2\sigma^2 3\sigma^2$ , may be described as a binuclear quanticule hence the discontinuity in the hydride series ought to occur between BeH and BH.

It is interesting to note that if not for the mixing of  $2p_\sigma B$  into  $3\sigma$ , BH would belong in the hydridic category. If  $3\sigma$  were simply the antibonding combination of  $2s B$  and  $1s H$ , an equivalent orbital transformation<sup>4</sup> could be carried out, retrieving the original AO's by linear combination of  $2\sigma$  and  $3\sigma$ . An alternative description of the electronic configuration would then be  $1sB^2 2sB^2 1sH^2$ , consistent with binuclear quantization  $B^+H^-$ .

The  $2s$  orbitals of the remaining first-row atoms lie too deep to mix appreciably with the hydrogen  $1s$ . Thus the  $2\sigma$  MO's of the corresponding monohydrides should be monocentric, mainly of lone-pair character. The  $2p_\sigma$  orbital of the heavy atoms now lie within reach of  $1sH$  so that two bicentric MO's—bonding  $3\sigma$  and antibonding  $4\sigma$ —can be formed. The  $1\pi$  MO, arising from the  $2p_\pi$  AO, lies next above the  $3\sigma$ , so that  $4\sigma$  will be unoccupied in the ground states of CH, NH, OH, and HF. The bonding in these four hydrides, due principally to the doubly occupied  $3\sigma$  MO, is thus of covalent type and the "quantization" of the electronic distribution is in the binuclear category.

Since the  $2p$  AO of fluorine is quite far below  $1s H$ ,  $3\sigma$  for HF is expected to be mostly  $2p_\sigma F$ . All the occupied MO's of HF are thus derived from fluorine AO's and the polar structure  $H^+F^-$  is approached. The proton lies,

however, within the compass of the  $3\sigma$  MO (or  $2p_\sigma F$  AO) so that the binuclear characterization is still appropriate.

Analytic self-consistent-field calculations have been carried out on all of the above molecules.<sup>5</sup> The results of these calculations demonstrate, among other things, Nature's disdain for simple models. Still, the above conclusions retain qualitative validity. The  $2s$  and  $2p_\sigma$  AO's mix appreciably in all cases in the  $2\sigma$ ,  $3\sigma$ , and  $4\sigma$  MO's. It might thus be more appropriate to use hybridized AO's in the simple LCAO treatment. More significant, however, the bonding and antibonding characteristics of MO's deduced above seem to be borne out in the SCF calculations by the relative signs of appropriate expansion coefficients.

Ransil's<sup>5</sup> calculations on BH predict a dipole moment of 1.58 D in the sense  $B^-H^+$ , which rather clearly places BH in the second category of hydrides.

The author wishes to acknowledge several discussions with Professor K. Fajans on the theory of chemical bonding.

<sup>1</sup> K. Fajans, *J. Chem. Phys.* **40**, 1773 (1964); and references cited therein (especially 3 and 4).

<sup>2</sup> E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.* **127**, 1618 (1962).

<sup>3</sup> L. Wharton, L. P. Gold, and W. Klemperer, *J. Chem. Phys.* **37**, 2149 (1962).

<sup>4</sup> C. A. Coulson, *Trans. Faraday Soc.* **38**, 433 (1942).

<sup>5</sup> B. J. Ransil, *Rev. Mod. Phys.* **32**, 245 (1960); M. Krauss, *J. Chem. Phys.* **28**, 1021 (1958); and others.

## Discontinuous Change of Binding Type in the Series of Monohydrides.\* II. Place of Discontinuity

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(Received 23 July 1964)

IN Letter I the quanticule formulations (Q.F.)  $\bar{e}_2 B^{3+}H^-$  and  $\bar{e}_2 Al^{3+}H^-$ , initiated with T. Berlin in 1943–1944 (see I, Refs. 3 and 4) were found to be in agreement with some newer spectroscopic data. In addition the Q.F.  $(H^+, C^{4+})\bar{e}_5$  and  $(H^+, Si^{4+})\bar{e}_5$  were reported. Hence it was concluded that the discontinu-

ous change of quantization from two mononuclear quanticules  $M^+H^-$  to one binuclear  $(H^+, X^{n+})\bar{e}_{n-1}$  occurs in the two octaves between the third and fourth groups of the system.

Blinder,<sup>1</sup> using quite different considerations based on MO theory, suggested that the change of bonding type occurs in the first octave between BeH and HB. Therefore, in the present note it is shown in more detail than was done in I which correlations between the binding strengths (B.S.) of various states of BH and  $(BH)^+$  led to the conclusion<sup>2</sup> that the formulation  $2s^2 B^{3+}H^-$  is preferable to  $(H^+, B^{3+})\bar{e}_4$ . A consideration of the relative energies of these two structures follows as a further support for the former one.

The internuclear distance of  $(BH)^+$  (1.2146) is

TABLE I. Internuclear distances (angstroms) for the states of BH and  $(BH)^+$ .<sup>a</sup>

State	BH	Excited states of BH					$(BH)^+$	$(BH)^{++}$
		$A, 1\pi$	$B, 1\Sigma^+$	$b, 3\Sigma^(-)$	$C, 1\Sigma^+$	$a, 3\pi_r$		
$r_0$	1.2432	1.2390 <sub>s</sub>	1.2292	1.2270	1.222	1.2005	1.2146	1.2564
Q.F.	$\bar{e}_2 B^{3+}H^-$	$\bar{e}^* \bar{e} B^{3+}H^-$	$\bar{e}^*   \bar{e} B^{3+}H^-$	$\bar{e}^* \bar{e} B^{3+}H^-$	see text		$\bar{e} B^{3+}H^-$	$\bar{e} B^{3+}(H^-)^*(?)$

<sup>a</sup> \* excitation;  $\bar{e}^* \bar{e}$ , pairing preserved;  $\bar{e}^* | \bar{e}$ , unpairing occurred.

TABLE II. Internal energies (electron volts) of formation of BH and HB from the atoms.

$$\begin{array}{c}
 \begin{array}{c}
 \text{H}^+\text{B}^- \xleftarrow{4',3} \left\{ \begin{array}{c} \text{B}^- \xleftarrow{1'} \text{B} \xrightarrow{1} \text{B}^+ \\ \text{H}^+ \xleftarrow{2'} \text{H} \xrightarrow{2} \text{H}^- \end{array} \right\} \xrightarrow{3,4} \text{B}^+\text{H}^-
 \end{array} \\
 \hline
 x' - 1.7 = x' + 11.58 - 13.60 + 0.3 \quad \left| \quad -8.30 + 0.75 + 11.58 + x = +4.03 + x
 \end{array}$$

smaller, i.e., its B.S. is larger than those of BH (1.2432). Hence an antibinding electron is eliminated in ionization which supports the quantization  $2^2\text{B}^3+\text{H}^-$ . The excited states of the latter are arranged in Table I in the order of increasing B.S. which in all of them, with the exception of  $a, {}^3\pi_r$ , is intermediate between those for the ground states of BH and  $(\text{BH})^+$ . This indicates that one of the  $2^2$  electrons has been excited. Space limitations do not allow going into more detail but for the purpose of the present communication it suffices to state that the strengthening of the binding in the ionized and all known excited states of boron monohydride is not compatible with the structure  $(\text{H}^+, \text{B}^{3+})\bar{e}_4$  most excited states of which would be expected to have a smaller B.S. than the ground state (see I).

The excitation of  $\bar{e}\text{B}^3+\text{H}^-$  does weaken the binding but this does not contradict the given formulation in qualitative respect if one assumes that the change  $\text{H}^- \rightarrow \text{H}^{-*}$  is involved. However, since the increase of  $r$  of 3.4% appears to be rather small, a question mark is placed in Table I next to the formula  $\bar{e}\text{B}^3+(\text{H}^-)^*$ .

It seems that one can feel differently as to the conclusiveness of these correlations vs. those which Blinder bases on MO theory. Thus it is of importance to illuminate the relative stability of the structures BH and HB by comparing their energies. Starting with the free atoms B and H the internal energies of formation of  $\text{B}^+\text{H}^-$  and  $\text{H}^+\text{B}^- = (\text{H}^+, \text{B}^3+)\bar{e}_4$  are estimated in Table II in which the  $+$  sign is used for an exothermic process.

Known are the energies involved in the formation of the free ions  $\text{B}^+$  (1),  $\text{H}^-$  (2),  $\text{B}^-$  (1'),<sup>3,4</sup> and  $\text{H}^+$  (2') as well as the Coulombic term ( $e^2/r_0$ ) (3) involved in the approach of these ions, considered as point charges, up to the equilibrium distance (1.2432 Å) in the molecule. For boron monohydride the correction terms (4 and 4') of the combined energies of repulsion and continuous polarization are uncertain. If one neglects these terms it would result that  $\text{B}^+\text{H}^-$  is  $4.03 - (-1.7) = 5.7$  eV more exothermic, i.e., considerably more stable, than  $\text{H}^+\text{B}^-$ .

If so, one arrives at a reasonable limit of the value of  $x$  knowing that the absolute value of the energy of dissociation of BH into atoms is (in electron volts) smaller than 3.51 (Ref. 9 in I, p. 510). Hence its energy of formation from  $\text{B}^+$  and  $\text{H}^-$  is smaller than 11.06 ( $3.51 + 8.30 - 0.75$ ), which value compared with the Coulombic energy 11.58 gives a lower limit of 4.5% for the repulsive energy.

In order to test whether this simplified thermochemical method leads to the same direction of polarity as

communicated in I for other monohydrides also we shall omit the uncertain correction terms 4 and 4'. It results that the remaining terms are, as expected, more exothermic for LiH (by 8.3 eV), BeH (5.2), and HF (6.5) than for HLi, HBe, and FH, respectively. For the monohydrides of C, N, and O the corresponding differences between  $\text{M}^+\text{H}^-$  and  $\text{H}^+\text{X}^-$  are much smaller (1.85, 0.1,  $-0.73$ , respectively) and that for B (5.7) is much closer to that for Be than for C.

In conclusion it is necessary to mention Blinder's reference to Ransil's SCF calculation of the dipole moment of the boron monohydride molecule. According to extended calculations<sup>5</sup> of this kind the direction of the dipoles and the resulting degrees of polarity are:  $\text{Li}^+\text{H}^-$  (0.77<sub>5</sub>),  $\text{Be}^+\text{H}^-$  (0.04),  $\text{H}^+\text{B}^-$  (0.27<sub>6</sub>),  $\text{H}^+\text{F}^-$  (0.43). This would mean a tremendous increase of the continuous polarization of  $\text{H}^-$  from  $\text{Li}^+$  to  $\bar{e}\text{Be}^{2+}$ , a change of quantization between BeH and HB and a relatively small change from  $(\text{H}^+, \text{B}^3+)\bar{e}_4$  to  $(\text{H}^+, \text{F}^{7+})\bar{e}_8$ . It would be very important to determine experimentally the direction and magnitude of the dipoles of such molecules as beryllium and boron monohydrides.

\* K. Fajans, J. Chem. Phys. **40**, 1773 (1964) (I). In Ref. 5 the name of the journal should be "Chimia." The symbol  $\text{X}^{n+1}$  should be changed at five places to  $\text{X}^{(n+1)+}$ .

<sup>1</sup> S. M. Blinder, J. Chem. Phys. **4004** (1964) (preceding letter).

<sup>2</sup> The conclusions reported in I and here originated in an extended paper which will be published somewhat later. The B.S. is compared on the basis of internuclear distances and force constants mainly from G. Herzberg, Refs. 9 and 10 in I.

<sup>3</sup> B. Edlén, J. Chem. Phys. **33**, 98 (1960).

<sup>4</sup> E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964).

<sup>5</sup> Kind communication by Dr. P. E. Cade and Dr. W. Huo (to be published).

## Notes

### Two-Center Coulomb Integrals\*

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**A**LTHOUGH many specific two-center Coulomb integrals over Slater atomic orbitals have been given in explicit form,<sup>1</sup> there appears to have been no