Erratum: Ultrasonic Absorption Measurements in Single Crystals of Naphthalene and *p*-Dichlorobenzene

[J. Chem. Phys. **40**, 2538 (1964)]

Seung S. Yun and Robert T. Beyer
Department of Physics, Brown University, Providence, Rhode Island

We have discovered a calculation error in the conversion of the units of the absorption coefficient from decibels/microsecond to nepers/centimeter. The values of the former were multiplied by the velocity of sound in centimeters per microsecond, whereas they should have been divided by this same quantity. As a result, the ordinate values in Fig. 5 (for naphthalene) should be multiplied by $(1/0.33)^2=9.18$ to give the correct values, since the sound velocity in single crystals of naphthalene is 0.33 cm/μsec. Similarly, for the case of *p*-dichlorobenzene, the ordinate values (in Fig. 6) should be multiplied by $(1/0.208)^2=23.1$.

These errors affect the values reported in Tables III and IV. In the first instance, the experimental value of the transition rate κ for naphthalene should be 0.41×10^{10}/sec, and for *p*-dichlorobenzene, 0.33×10^{10}/sec. In Table IV, the absorption coefficient for *p*-dichlorobenzene at 5 MHz should be $0.032/\text{cm}^{-1}$, and for naphthalene, $0.008/\text{cm}^{-1}$.

These errors do not materially affect the discussion of the results given in the original paper, since only order-of-magnitude agreement is obtained with either the correct or the erroneous values. The corrected absorption values are still much smaller than those reported in the literature for benzene and cyclohexane. However, note that the agreement with theory of the corrected experimental transition rate κ for nephthalene is considerably better than that for *p*-dichlorobenzene, (the reverse of the situation in the paper) so that the discussion of the reasons for the relative agreements in the two cases given therein should be taken somewhat less seriously.

On the Bonding Character of First-Row Monohydrides

S. M. Blinder
Department of Chemistry, University of Michigan,
Ann Arbor, Michigan

(Received 12 June 1964)

It has been proposed by Fajans,[1] on empirical and intuitive grounds, that a discontinuous change in bonding type occurs between BH and CH in the series of hydrides LiH to HF. The electronic distribution in LiH, BeH, and BH is characterized by "mononuclear quantization," whereas that in CH, NH, OH, and HF is ascribed "binuclear quantization." The former case might be categorized as ionic bonding between two "mononuclear quanticules" Li^+ and H^-, Be^+ and H^-, etc. The latter case, in view of the bicentric nature of the electronic distribution, is suggestive of covalent bonding.

In this note, the relationship between Fajans' approach (quanticule theory of chemical binding) and molecular-orbital concepts is discussed. It is suggested that the discontinuity in bonding type occurs actually between BeH and BH.

In accordance with the LCAO approximation in its most elementary form, molecular orbitals derive from orbitals of the constituent free atoms. Two opposing AO's of compatible symmetry and comparable orbital energy—say within ±0.2 a.u. (±5 eV)—can interact to give a pair of bicentric MO's, one bonding, the other antibonding. AO's lacking energetically-nearby partners transform into MO's retaining essentially monocentric character. The required first-row atomic orbital energies, taken from the SCF calculations of Clementi *et al.*[2] are listed in Table I.

For LiH, none of the constituent AO's lie in close juxtaposition. The 1σ MO will be almost identical with $1s$ Li while the 2σ will be mostly $1s$ H. The ground state of LiH, with configuration $1\sigma^2 2\sigma^2$, will be best described by the ionic structure Li^+H^-, consistent with the large observed dipole moment.[3]

The case of BeH should be quite similar. Though incipient interaction might be expected between $2s$ Be and $1s$ H, the 3σ MO should be mostly $2s$ Be and the configuration $1\sigma^2 2\sigma^2 3\sigma$ should again be of ionic structure—Be^+H^-.

BH is the most complex of the first-row monohydrides from the standpoint of LCAO theory. The $2s$ level of boron falls almost exactly opposite the $1s$ of hydrogen. These ought to interact strongly to form a pair of bicentric MO's. The 2σ of BH should be predominantly the bonding combination of $2s$ B and $1s$ H. The 3σ MO should, however, contain a significant contribution from the nearby $2p_\sigma$B AO, as well as the antibonding combination of $2s$ B and $1s$ H. 3σ will thus be compounded of antibonding and nonbonding character. Since both 2σ and 3σ are bicentric MO's, the electronic distribution in BH, configuration

Table I. Atomic orbital energies (in atomic units; 1 a.u. = 27.2 eV).

Atom	$1s$	$2s$	$2p$
H	−0.50		
Li	−2.48	−0.20	
Be	−4.73	−0.31	
B	−7.70	−0.49	−0.31
$C(^3P)$	−11.33	−0.71	−0.43
$N(^4S)$	−15.65	−0.95	−0.58
$O(^3P)$	−20.67	−1.24	−0.63
F	−26.38	−1.57	−0.73

$1\sigma^2 2\sigma^2 3\sigma^2$, 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 3σ, BH would belong in the hydridic category. If 3σ were simply the antibonding combination of $2s$ B and $1s$ H, an equivalent orbital transformation[4] could be carried out, retrieving the original AO's by linear combination of 2σ and 3σ. 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 2σ 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 $1s$H so that two bicentric MO's—bonding 3σ and antibonding 4σ—can be formed. The 1π MO, arising from the $2p_\pi$ AO, lies next above the 3σ, so that 4σ 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 3σ 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, 3σ 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 3σ 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.[5] 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 2σ, 3σ, and 4σ 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[5] 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.

---

[1] K. Fajans, J. Chem. Phys. **40**, 1773 (1964); and references cited therein (especially 3 and 4).

[2] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

[3] L. Wharton, L. P. Gold, and W. Klemperer, J. Chem. Phys. **37**, 2149 (1962).

[4] C. A. Coulson, Trans. Faraday Soc. **38**, 433 (1942).

[5] 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

Kasimir Fajans
Department of Chemistry, University of Michigan, Ann Arbor, Michigan

(Received 23 July 1964)

In Letter I the quanticule formulations (Q.F.) $\bar{e}_2B^{3+}H^-$ and $\bar{e}_2Al^{3+}H^-$, 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 discontinuous 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,[1] 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[2] that the formulation $2s^2B^{3+}H^-$ 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 $(BH)^+$.[a]

	BH	Excited states of BH					$(BH)^+$	$(BH)^{+*}$
State	$X, {}^1\Sigma^+$	$A, {}^1\pi$	$B, {}^1\Sigma^+$	$b, {}^3\Sigma^{(-)}$	$C, {}^1\Sigma^+$	$a, {}^3\pi_r$	$X, {}^2\Sigma^+$	$A, {}^2\pi$
r_0	1.2432	1.2390_5	1.2292	1.2270	1.222	1.2005	1.2146	1.2564
Q.F.	$\bar{e}_2B^{3+}H^-$	$\bar{e}^*\bar{e}B^{3+}H^-$		$\bar{e}^* \mid \bar{e}B^{3+}H^-$	$\bar{e}^*\bar{e}B^{3+}H^-$	see text	$\bar{e}B^{3+}H^-$	$\bar{e}B^{3+}(H^-)^*(?)$

[a] * excitation; $\bar{e}^*\bar{e}$, pairing preserved; $\bar{e}^* \mid \bar{e}$, unpairing occurred.