The Electronic States of the BH and CH Radicals

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(Received June 25, 1952)

Introduction

On the electronic states of the BH and CH radicals the electronic terms observed are $^1\Sigma^+$, $^1\Pi$, $^3\Sigma$, $^3\Pi$ and $^2\Pi$, $^2\Delta$, $^2\Sigma^-$, $^1\Sigma^+$,(1) respectively, and their electronic structures were determined by Stehn(2) and King(3) using the semi-empirical approximation. But in their calculations the electronic configurations of the boron and carbon atom were assumed to be only the $(2s)^2(2p)$ and $(2s)^2(2p)^2$ ones, respectively, and the values used for the energy integrals were empirically evaluated from the experimental data. Recently, in the work on the CH_2 radical by Niira and Oohata,(4) the electronic energies of the CH radical were calculated using the method of atomic orbital, considering both the $(2s)^2(2p)^2$ and $(2s)(2p)^3$ electronic configurations of the carbon atom, assuming all atomic orbitals to be orthogonal to each other. The lowest state was found to be the $^4\Sigma^-$. In this paper the electronic energies have been calculated using the method of the atomic orbital. The overlap integrals and all the permutations have been explicitly included for the $2s$ and $2p$ electrons, but no $1s$ electron integrals for the boron atom and the carbon atom have been considered. The electronic configurations of the boron atom are assumed to be both the $(2s)^2(2p)$ and $(2s)(2p)^2$, and of the carbon atom both the $(2s)^2(2p)^2$ and $(2s)(2p)^3$, have been taken into account.

The Basic Wave Functions for the CH Radical

If the calculation of the CH radical is treated as a five electron problem excluding the $1s$ electrons and assuming the $(2s)^2(2p)^2$ and $(2s)(2p)^3$ configurations for the carbon atom, there are eight possible kinds of the electronic orbital wave functions for the entire radical, which are given by the products of atomic orbitals:

$$\left.\begin{aligned}\Phi_1&\equiv(2s)(2s)(2p\sigma)(2p\sigma)(H)\\ \Phi_2&\equiv(2s)(2s)(2p\pi_+)(2p\pi_-)(H)\\ \Phi_3&\equiv(2s)(2s)(2p\sigma)(2p\pi_\pm)(H)\\ \Phi_4&\equiv(2s)(2s)(2p\pi_\pm)(2p\pi_\pm)(H)\end{aligned}\right\}\tag{1}$$

in the s^2p^2 configuration, and

$$\left.\begin{aligned}\Psi_1&\equiv(2s)(2p\sigma)(2p\pi_+)(2p\pi_-)(H)\\ \Psi_2&\equiv(2s)(2p\sigma)(2p\sigma)(2p\pi_\pm)(H)\\ \Psi_3&\equiv(2s)(2p\pi_\pm)(2p\pi_\pm)(2p\pi_\mp)(H)\\ \Psi_4&\equiv(2s)(2p\sigma)(2p\pi_\pm)(2p\pi_\pm)(H)\end{aligned}\right\}\tag{2}$$

in the sp^3 configuration for the carbon atom, where $(2s)$, $(2p\sigma)$ and $(2p\pi_\pm)$ are the $2s$, $2p\sigma$ and $2p\pi_\pm$ atomic orbitals of the carbon atom, respectively, and (H) is the $1s$ orbital of the hydrogen atom.

Since the spatial symmetry of the CH radical belongs to the symmetry group $C_{\infty v}$, and the electronic terms with different multiplicity or symmetry do not interact, the basic wave functions for this radical, which are constructed from (1) and (2) to fit the Pauli principle, can be classified by the irreducible representations of $C_{\infty v}$ (Σ^+, Σ^-, Π and Δ), and they are as follows:

	$^2\Sigma^+$	$^2\Sigma^-$	$^2\Pi$	$^2\Delta$	$^4\Sigma^+$	$^4\Sigma^-$	$^4\Pi$	$^4\Delta$	$^6\Sigma^-$	
Φ_1	1	0	0	0	0	0	0	0	0	
Φ_2	1	1	0	0	0	1	0	0	0	
Φ_3	0	0	2	0	0	0	1	0	0	
Φ_4	0	0	0	1	0	0	0	0	0	(3)
Ψ_1	2	3	0	0	1	3	0	0	1	
Ψ_2	0	0	2	0	0	0	1	0	0	
Ψ_3	0	0	2	0	0	0	1	0	0	
Ψ_4	0	0	0	2	0	0	0	1	0	
Sum	4	4	6	3	1	4	3	1	1	

In this table, it is shown that, for instance, there are three basic wave functions arising from the Φ_2, each belonging to the type of $^2\Sigma^+$, $^2\Sigma^-$ and $^4\Sigma^-$. Thus there are, in all, four basic wave functions belonging to the type of $^2\Sigma^+$, and four, six and three for the types of $^2\Sigma^-$, $^2\Pi$ and $^2\Delta$, respectively, and so on.

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(1) H. Sponer, "Molekülspektren 1, Tabellen", Julius Springer, Berlin, 1935, P. 24.

(2) J. R. Stehn, *J. Chem. Phys.*, **5**, 186 (1937).

(3) G. W. King, *J. Chem. Phys.*, **6**, 378 (1938).

(4) K. Niira and K. Oohata, *J. Phys. Soc. Japan*, **7**, 61 (1952).

The Secular Equations

Using these antisymmetrized basic wave functions, which are linearly independent from each other, a secular equation is obtained for each symmetry type. Since the $1s$ electrons of the carbon atom have been considered to locate in the nucleus, the total Hamiltonian of this system should be given by

$$\boldsymbol{H}=-1/2\sum_{i=1}^{5}\Delta_i+4/R_{CH}-\sum_{i=1}^{5}4/r_{Ci}$$
$$-\sum_{i=1}^{5}1/r_{Hi}+\sum_{\substack{i,j=1\\(i\neq j)}}^{5}1/r_{ij}. \tag{4}$$

Approximately the perturbing term in the present calculation is taken as,

$$\boldsymbol{H}'=4/R_{CH}-4/r_{C5}-\sum_{i=1}^{4}1/r_{Hi}+\sum_{\substack{i,j=1\\(i\neq j)}}^{5}1/r_{ij} \tag{4'}$$

where R_{CH} is the nuclear distance between the carbon and the hydrogen atom. r_{Ci} and r_{Hi} are the distances between the carbon and hydrogen atoms and the i-th electron, and r_{ij} is the distance between the i-th and j-th electrons. In (4′) electrons 1 to 4 are the $2s$ or $2p$ orbitals of the carbon atom and electron 5 is the $1s$ orbital of the hydrogen atom.

Then the secular equations can be set up for the type ${}^4\Sigma^-$; for instance, it can be written as

$$\text{det.}\,|\,H_{ij}-\Delta_{ij}W\,|=0, \tag{5}$$

where

$$H_{11}=\mathfrak{M}^{\Phi_2}-\mathfrak{N}_{ss}^{\Phi_2}-6F_2-2J_{sp}-2N_{\pi\pi}$$
$$+6F_2S^2_{sh}+4L_{s\pi\pi h}S_{sh}$$

$$H_{22}=\mathfrak{M}^{\Psi_1}+\frac{1}{4}\mathfrak{N}_{ss}^{\Psi_1}+\frac{1}{4}\mathfrak{N}_{\sigma\sigma}^{\Psi_1}-12F_2-3J_{sp}$$
$$+\frac{1}{2}N_{\pi\pi}-3F_2S_{sh}^2-\frac{3}{2}F_2S_{\sigma h}^2$$
$$-\frac{1}{2}(L_{s\sigma\sigma h}S_{sh}+L_{\sigma ssh}S_{\sigma h}-K_{s\sigma}S_{sh}S_{\sigma h})$$
$$-L_{s\pi\pi h}S_{sh}-L_{\sigma\pi\pi h}S_{\sigma h}-\frac{1}{2}J_{sp}S_{\sigma h}^2$$

$$H_{33}=\mathfrak{M}^{\Psi_1}-\frac{3}{4}\mathfrak{N}_{ss}^{\Psi_1}-\frac{3}{4}\mathfrak{N}_{\sigma\sigma}^{\Psi_1}-6F_2-J_{sp}$$
$$-\frac{3}{2}N_{\pi\pi}+3F_2S_{sh}^2+\frac{9}{2}F_2S_{\sigma h}^2$$
$$+\frac{3}{2}(L_{s\sigma\sigma h}S_{sh}+L_{\sigma ssh}S_{\sigma h}-K_{s\sigma}S_{sh}S_{\sigma h})$$
$$+L_{s\pi\pi h}S_{sh}+L_{\sigma\pi\pi h}S_{\sigma h}-\frac{1}{2}J_{sp}S_{\sigma h}^2$$

$$H_{44}=\mathfrak{M}^{\Psi_1}-\frac{1}{2}\mathfrak{N}_{ss}^{\Psi_1}-\frac{1}{2}\mathfrak{N}_{\sigma\sigma}^{\Psi_1}-9F_2-2N_{\pi\pi}$$
$$+3F_2S_{sh}^2+3F_2S_{\sigma h}^2$$
$$-(L_{\sigma\sigma sh}S_{sh}+L_{\sigma ssh}S_{\sigma h}-K_{s\sigma}S_{sh}S_{\sigma h})$$
$$+2L_{s\pi\pi h}S_{sh}+2L_{\sigma\pi\pi h}S_{\sigma h}$$

$$H_{12}=\frac{\sqrt{5}}{2}(2L_{\sigma ssh}S_{sh}-K_{s\sigma}S_{sh}^2)-\frac{\sqrt{5}}{2}\mathfrak{N}_{s\sigma}^{\Phi_2\Psi_1}$$
$$+3\sqrt{5}\,F_2S_{sh}S_{\sigma h}+\sqrt{5}\,L_{\sigma\pi\pi h}S_{sh}$$
$$+\sqrt{5}\,J_{sp}S_{sh}S_{\sigma h}$$

$$H_{13}=-\frac{1}{2}(2L_{\sigma ssh}S_{sh}-K_{s\sigma}S_{sh}^2)+\frac{1}{2}\mathfrak{N}_{s\sigma}^{\Phi_2\Psi_1}$$
$$-3F_2S_{sh}S_{\sigma h}-2L_{s\pi\pi h}S_{\sigma h}$$
$$-L_{\sigma\pi\pi h}S_{sh}+J_{sp}S_{sh}S_{\sigma h}$$

$$H_{14}=\sqrt{2}\,\mathfrak{M}_{s\sigma}-\frac{1}{\sqrt{2}}(2L_{\sigma ssh}S_{sh}-K_{s\sigma}S_{sh}^2)$$
$$-\frac{1}{\sqrt{2}}\mathfrak{N}_{s\sigma}^{\Phi_2\Psi_1}+3\sqrt{2}\,F_2S_{sh}S_{\sigma h}$$
$$+\sqrt{2}\,L_{s\pi\pi h}S_{\sigma h}+\sqrt{2}\,L_{\sigma\pi\pi h}S_{sh}$$

$$H_{23}=-\frac{\sqrt{5}}{4}\mathfrak{N}_{ss}^{\Psi_1}-\frac{\sqrt{5}}{4}\mathfrak{N}_{\sigma\sigma}^{\Psi_1}+\frac{\sqrt{5}}{2}N_{\pi\pi}$$
$$+3\sqrt{5}\,F_2S_{sh}^2+3\frac{\sqrt{5}}{2}F_2S_{\sigma h}^2$$
$$+\frac{\sqrt{5}}{2}J_{sp}S_{\sigma h}^2+\frac{\sqrt{5}}{2}(L_{s\sigma\sigma h}S_{sh}+L_{\sigma ssh}S_{\sigma h}$$
$$-K_{s\sigma}S_{sh}S_{\sigma h})$$

$$H_{24}=\frac{\sqrt{5}}{2\sqrt{2}}\mathfrak{N}_{ss}^{\Psi_1}-\frac{\sqrt{5}}{2\sqrt{2}}\mathfrak{N}_{\sigma\sigma}^{\Psi_1}-6\sqrt{\frac{5}{2}}F_2S_{sh}^2$$
$$+3\sqrt{\frac{5}{2}}F_2S_{\sigma h}^2+\sqrt{\frac{5}{2}}J_{sp}S_{\sigma h}^2$$
$$-\sqrt{\frac{5}{2}}L_{s\pi\pi h}S_{sh}+\sqrt{\frac{5}{2}}L_{\sigma\pi\pi h}S_{\sigma h}$$

$$H_{34}=-\frac{1}{2\sqrt{2}}\mathfrak{N}_{ss}^{\Psi_1}+\frac{1}{2\sqrt{2}}\mathfrak{N}_{\sigma\sigma}^{\Psi_1}+3\sqrt{2}\,F_2$$
$$-\sqrt{2}\,J_{sp}-3\frac{1}{\sqrt{2}}F_2S_{\sigma h}^2+\frac{1}{\sqrt{2}}J_{sp}S_{\sigma h}^2$$
$$+\frac{3}{\sqrt{2}}L_{s\pi\pi h}S_{sh}-\frac{3}{\sqrt{2}}L_{\sigma\pi\pi h}S_{\sigma h}$$

$$\Delta_{11}=1-S_{sh}^2$$

$$\Delta_{22}=1+\frac{1}{4}S_{sh}^2+\frac{1}{4}S_{\sigma h}^2$$

$$\Delta_{33}=1-\frac{3}{4}S_{sh}^2-\frac{3}{4}S_{\sigma h}^2$$

$$\Delta_{44}=1-\frac{1}{2}S_{sh}^2-\frac{1}{2}S_{\sigma h}^2$$

$$\Delta_{12}=-\frac{\sqrt{3}}{2}S_{sh}S_{\sigma h}$$

$$\Delta_{13}=\frac{1}{2}S_{sh}S_{\sigma h}$$

$$\Delta_{14}=-\frac{1}{\sqrt{2}}S_{sh}S_{\sigma h}$$

$$\Delta_{23}=-\frac{\sqrt{5}}{4}S_{sh}^2-\frac{\sqrt{5}}{4}S_{\sigma h}^2$$

$$\Delta_{24}=\frac{\sqrt{5}}{2\sqrt{2}}S_{sh}^2-\frac{\sqrt{5}}{2\sqrt{2}}S_{\sigma h}^2$$

$$\Delta_{34}=-\frac{1}{2\sqrt{2}}S_{sh}^2+\frac{1}{2\sqrt{2}}S_{\sigma h}^2$$

Here

$$\left.\begin{aligned}\mathfrak{M}^{\chi}_{\alpha\alpha}&=\int\bar{\chi}\boldsymbol{H}'\chi d\tau\\ \mathfrak{N}^{\chi}_{\alpha\alpha}&=\int P_{\alpha H}\bar{\chi}\boldsymbol{H}'\chi d\tau\end{aligned}\right\}$$

where $P_{\alpha H}$ shows a permutation between the α and H electrons. All the other two-center energy integrals are defined in the table by Kotani and Amemiya⁽⁵⁾, and their values used in this calculation are deduced from the same table, the value of δ being chosen as 1.59 (in the atomic unit) for the carbon atom. The internuclear distance between the carbon atom and the hydrogen atom is taken to be 1.12 A., which is the equilibrium distance in the $^2\Pi$ state. The values of energy integrals are as follows:

$S_{sh}\ =\ 0.5598$
$S_{\sigma h}\ =\ 0.4679$
$M_{ss}\ =11.174$ e. v.
$M_{s\sigma}=\ 3.085$ 〃
$M_{\sigma\sigma}=12.205$ 〃
$M_{\pi\pi}=10.658$ 〃
$N_{ss}\ =\ 4.637$ 〃
$N_{s\sigma}=\ 4.376$ 〃
$N_{\sigma\sigma}=\ 4.742$ 〃
$N_{\pi\pi}=\ 0.664$ 〃

$L_{sssh}\ =7.754$ e. v.
$L_{s\sigma sh}\ =6.076$ 〃
$L_{ss\sigma h}\ =1.313$ 〃
$L_{s\tau\sigma h}=2.335$ 〃
$L_{\sigma s\sigma h}=8.036$ 〃
$L_{\sigma\sigma\sigma h}=6.664$ 〃
$L_{\pi s\pi h}\ =7.613$ 〃
$L_{\pi\pi sh}\ =1.354$ 〃
$L_{\pi\sigma\pi h}=5.782$ 〃
$L_{\pi\pi\sigma h}=0.273$ 〃

$J_{sh}\ =\ 9.750$ e. v.
$J_{\sigma h}\ =\ 7.045$ 〃
$J_{hs}\ =10.618$ 〃
$J_{h\sigma}\ =12.687$ 〃
$K_{ss}\ =12.362$ 〃
$K_{s\sigma}=\ 4.656$ 〃
$K_{\sigma\sigma}=14.672$ 〃
$K_{\pi\pi}=11.199$ 〃
$K_{hh}\ =12.268$ 〃

The values of the one-center energy integrals are deduced from those which are calculated from the Hartree field of carbon atom by Ufford⁽⁶⁾. Accordingly, the energy difference between the states $^3D^0$ and ^3P of the carbon atom is given by

$$W_c(^3D^0)-W_c(^3P)=7.813\text{ e. v.}$$

which is slightly smaller than the observed value⁽⁷⁾ (7.94 e. v.).

The Electronic Energies of the CH Radical

Using these values, the electronic energies W can be computed from the secular equation (5). The resulting energy levels are shown in the middle of Fig. 1, and the energy levels which are obtained from the $(2s)^2(2p)^2$ or $(2s)(2p)^3$ only are shown in the left and the right of Fig. 1., respectively. The electronic energies in this calculation are compared with the values by Niira and Oohata which are calculated assuming all the atomic orbitals to be orthogonal to each other, and with the observed values, in Table 1.

Table 1

The Comparison between the Calculated and the Observed Values of the CH Radical

	Calc. (e. v.) (This work)	Calc.⁽⁴⁾ (e. v.) (Niira-Oohata)	Exp.⁽¹⁾ (e. v.)
$^2\Sigma^+$	+0.83	+0.31	(+0.47)
$^2\Sigma^-$	+0.14	−0.18	(−0.28)
$^2\Delta$	−0.61	−1.14	(−0.60)
$^2\Pi$	−2.87	−2.95	−3.47
$^4\Sigma^-$	−3.60	−3.00	—
$^2\Sigma^+\rightarrow{}^2\Pi$	3.70	3.26	3.94
$^2\Sigma^-\rightarrow{}^2\Pi$	3.01	2.77	3.19
$^2\Delta\rightarrow{}^2\Pi$	2.26	1.81	2.87

The Electronic Energies of the BH Radical

The electronic energies of the BH radical are calculated in a similar manner as in the CH radical, and the resulting energy levels and their comparison with the observed values are shown in Fig. 2 and Table 2. In this

Table 2

The Comparison between the Calculated and the Observed Values of the BH Radical

	Calc. (e. v.)	Exp. (e. v.)
$^1\Pi\rightarrow{}^1\Sigma^+$	2.53	2.86⁽¹⁾
$^3\Sigma\rightarrow{}^3\Pi$	3.08	3.36⁽⁸⁾
$D(^1\Sigma^+)$	4.07	<3.49

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(5) M. Kotani and A. Amemiya, *Proc. Phys. Math. Soc. Japan*, **22** Extra No. 1 (1940).

(6) C. W. Ufford, *Phys. Rev.*, **53**, 568, (1938).

(7) B. Edlen, *Z. f. Phys.* **84**, 746, (1933).

(8) G. M. Almy and R. B. Horsfall, *Phys. Rev.*, **51**, 491 (1937).

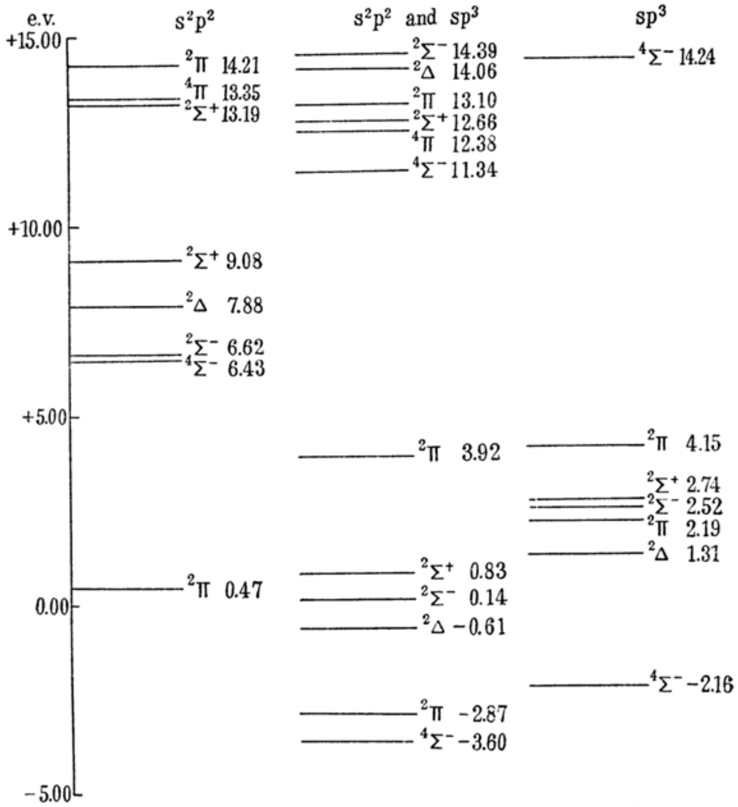

Fig. 1.—The electronic energies of the CH radical. The origin of the energy is chosen to be $C(^3P)+H(^2S)$.

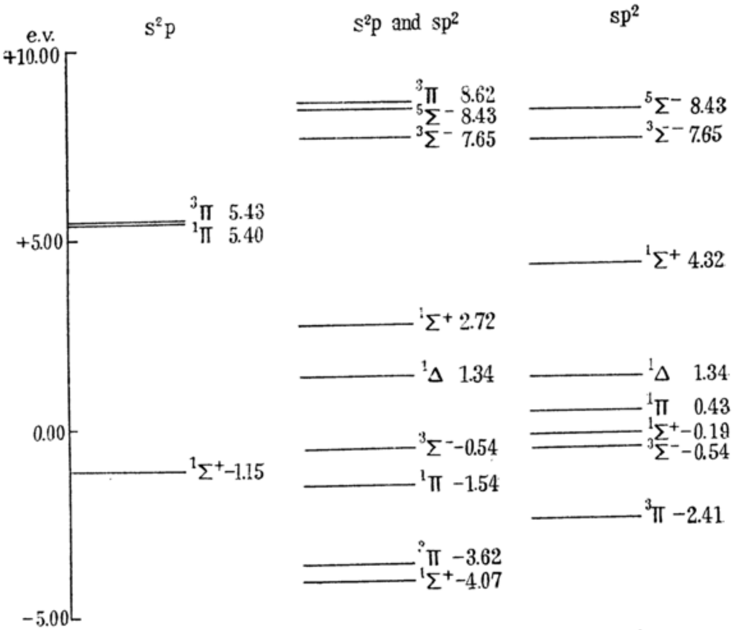

Fig. 2.—The electronic energies of the BH radical. The origin of the energy is chosen to be $B(^2P^0)H(^2S)$.

case the values of the one-center energy integrals are calculated from the functions used in the two-center integrals. The energy difference between the states ^2D and $^2P^0$ of the boron atom is deduced from the spectroscopic data:

$$W_B(^2D)-W_L(^2P^0)=5.932 \text{ e. v.}$$

and the value of δ is chosen as 1.26 for the boron atom. The internuclear distance between the boron atom and the hydrogen atom is taken as 1.226 A. which is the equilibrium distance of the $^1\Sigma^+$ state.

Discussion

These energies obtained in the present calculation can explain satisfactorily the observed values, a consequence of the fact that the electronic configurations of the boron atom have been assumed to be both the $(2s)^2(2p)$ and $(2s)(2p)^2$, and of the carbon atom both the $(2s)^2(2p)^2$ and $(2s)(2p)^3$. Since the overlap integrals and the higher order permutations have been considered, the resulting values become more close to the observed ones than in the case of neglecting the overlap integrals. The lowest state of the CH radical in this calculation is $^4\Sigma^-$, which is not actually observed, but the result is the same as those in the molecular orbital approximation by Mulliken(9) and in the atomic orbital by Niira and Oohata(4). This result is of some interest in comparison with the calculation by Niira and Oohata(4) in which the lowest state of the CH_2 radical is found to be $^3B_1$.

But in the present calculation the electronic configuration of the carbon atom is assumed to be both the $(2s)^2(2p)^2$ and $(2s)(2p)^3$ only and the others are not included. Even if the $(2p)^4$ configuration is added to those, the lowest state of the CH radical is $^4\Sigma^-$ as it is. This is explained as follows: If the $(2p)^4$ electronic configuration for the carbon atom is taken, there are four possible kinds of electronic orbital wave functions for the entire radical, which are given by the products of the atomic orbitals:

$$\left.\begin{aligned}
\chi_1&\equiv(2p\sigma)(2p\sigma)(2p\pi_+)(2p\pi_-)(H)\\
\chi_2&\equiv(2p\pi_+)(2p\pi_+)(2p\pi_-)(2p\pi_-)(H)\\
\chi_3&\equiv(2p\sigma)(2p\pi_\pm)(2p\pi_\pm)(2p\pi_\mp)(H)\\
\chi_4&\equiv(2p\sigma)(2p\sigma)(2p\pi_\pm)(2p\pi_\pm)(H)
\end{aligned}\right\}\quad(6)$$

These wave functions are classified into the symmetry types as

	$^2\Sigma^+$	$^2\Sigma^-$	$^2\Pi$	$^2\Delta$	$^4\Sigma^+$	$^4\Sigma^-$	$^4\Pi$	$^4\Delta$	$^6\Sigma^-$
χ_1	1	1	0	0	0	1	0	0	0
χ_2	1	0	0	0	0	0	0	0	0
χ_3	0	0	2	0	0	0	1	0	0
χ_4	0	0	0	1	0	0	0	0	0
Sum	2	1	2	1	0	1	1	0	0

(7)

Thus including the $(2p)^4$ configuration the numbers of the basic wave functions belonging to the types $^2\Pi$ and $^4\Sigma^-$ increase by two and one, respectively. In the $^4\Sigma^-$, the χ_1 corresponds to the Φ_2 with the replacement of $(2s)$ by $(2p\sigma)$, and so considerably interacts with the Ψ_1 like the Φ_2. Consequently the electronic energy is well stabilized. But in the $^2\Pi$, the χ_3 corresponds to the Ψ_3 with replacement $(2s)$ by $(2p\sigma)$ and then scarcely interacts to the Φ_3 and Ψ_2 like the Ψ_3. (The dissociation energy obtained for the Φ_3 and Ψ_2 is 2.82 e. v., while including the Ψ_3 2.87 e. v. These results show that the energy is stabilized by 0.05 e. v. only.) Thus in the lowest energy of the $^2\Pi$ the Φ_3 and Ψ_2 affect it far more strongly than the Ψ_3 and χ_3; therefore even if the χ_3 is included, it may be improbable that the lowest state of $^2\Pi$ becomes more stable than the $^4\Sigma^-$.

Recently interesting discussions(10)~(14) have been offered as to the dissociation energy and the ground state of the CH radical. In the discussions Glockler has suggested from the regularities of bond energies found in various hydrides, that the dissociaiton energy of the radical 3.47 e. v. (80 kcal.), estimated by Herzberg(15) assuming $^2\Pi$ as the ground state and usually accepted, is too low and that a somewhat larger value of 4.0 e. v. (92.3 kcal.) should be taken.

The results of this work that the ground state is not $^2\Pi$ but $^4\Sigma^-$ and the former lies 0.73 e. v. higher than the latter seem to explain quantitatively Glockler's results: for, if this conclusion is correct, the dissociation energy (for the ground state $^4\Sigma^-$) becomes 0.73 e. v. larger than that for $^2\Pi$ (3.47 e. v.), namely 4.20 e. v., which is in close agreement with Glockler's estimation.

No 1*s* electron integrals of the boron and the carbon atoms have been considered and also the ionic states of the radicals and the

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(9) R. S. Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932).

(10) G. Glockler, *Disc. Farad. Soc.*, No. **10**, 26 (1951).

(11) A. G. Gaydon, ibid., P. 108.

(12) C. A. McDowell and J. W. Warren, ibid., p. 53.

(13) G. Porter, ibid., p. 115.

(14) R. G. W. Norrish, G. Porter and B. A. Thrush, *Nature* **169**, 582 (1952).

(15) G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," 2nd ed. D. Van Nostrand Co. Inc., New York, 1950.

other excited states of the atoms of the radicals are not included. In the excited states of the radicals the effects of these states seem to be fairly large, and so strictly speaking it may be desirable to carry out a calculation including those states.

As the nuclear distances in the present calculation are taken to be the observed values for the ground states, but these are not always equal to the values for the excited states. Accordingly, the electronic energies of these radicals should be calculated changing the nuclear distances.

Summary

The energy levels of the CH and the BH radicals have been calculated by the method of atomic orbitals, taking both s^2p^2 and sp^3 configurations together for the carbon atom and s^2p and sp^2 for the boron atom and including the overlap integrals and the higher order permutations. The values obtained are in excellent agreement with observations.

Acknowledgements are made to Assistant Professors S. Shida and I. Tanaka and Mr. Y. Mori of this Laboratory, and Assistant Professor K. Niira and Mr. K. Oohata of the Laboratory of Physics for their kind discussions and suggestions. The author also expresses his sincere thanks to Dr. G. Glockler (Office of Ordnance Research, Durham), Dr. G. Porter (University of Cambridge, Cambridge) and Dr. A. G. Gaydon (Imperial College, London) for their kind and valuable discussions.

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