

Some effects of ($2s-2p$) electron promotion in boron

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MS received 28 November 1977

Abstract. The wave function of the promoted (4_p) state of boron of configuration ($1s^2; 2s^1; 2p^2$) obtained as a result of promotion of one electron from $2s$ to $2p$ orbital in the ground state, is calculated. These results indicate that this promotion leads to a 'contraction' of both $2s$ and $2p$ orbitals.

Keywords. Electron promotion; orbital contraction; hybridization.

1. Introduction

After the introduction of the concept of the orbital hybridization by Pauling (1931) a number of detailed studies have been made on the hybridization in carbon (Van Vleck 1933, 1934; Mulliken 1934; Voge 1936, 1948; Moffit 1950). But the hybridization in boron has not been studied in detail. We have taken up a study to investigate the hybridization in boron atom. It is believed that the first step in the process of orbital hybridization in boron, leading to the formation of trigonally hybridized sp^2 orbitals, is the promotion of an electron from the $2s$ -orbital to the $2p$ -orbital in the ground state, generating thereby a 'promoted' state of boron. In this paper some effects of this electron promotion on the radial properties of the $2s$ and $2p$ orbitals of boron are reported.

2. Calculation and results

The ground state of boron has been taken to be the (2_p) state derived from the configuration ($1s^2 2s^2 2p^1$) and the "promoted" state (4_p), from the configuration ($1s^2 2s^1 2p^2$). For both the states variational wave functions constructed from S.T.O. basis set have been used. The ground state wave function used in this work has been taken from the work of Clementi and Raimondi (1963) and that for the "promoted" state has been calculated. The orbital exponents for the $2s$ and $2p$ -orbitals of the "promoted" state have been optimized by minimising the total energy to a convergence limit of 10^{-5} . The inner $1s$ orbital of this state was assumed to be the same as in the ground state. The radial expectation values $\langle r \rangle$, $\langle 1/r \rangle$ for the $2s$ and $2p$ -orbitals as well as their most probable orbital radii, r_{\max} (corresponding to the maxima of the radial distribution functions) for both the ground and the "promoted" state have been calculated and the results are shown in table 1.

Table 1.

	Ground state ($2p$)		Promoted state ($4p$)	
Total energy	-24.49836		-24.41499	
	$2s$	$2p$	$2s$	$2p$
Orbital exponents	1.2881	1.2107	1.3299	1.2350
$\langle r \rangle$	1.9408	2.0649	1.8797	2.0243
r_{\max}	1.5527	1.6519	1.5037	1.6194
$\langle 1/r \rangle$	0.6441	0.6063	0.6649	0.6175

(all quantities are in atomic units)

3. Discussion

From table 1 we see that the ($2s-2p$) electron promotion in boron needs about 0.083 a.u. or 2.2 e.v. of energy. It may be noted that the same process in carbon needs about 4 e.v. Thus the ($2s-2p$) promotion is easier in boron than in carbon. The exponents of the $2s$ -orbital increases from 1.2881 to 1.3299. This, in fact, is to be expected, since the mutual shielding effect of the electrons in $2s$ -orbital in the ground state is eliminated with the promotion of one and hence the remaining one "sees" more of nuclear charge. The exponent of the $2p$ -orbital is also increased from 1.2107 to 1.2350 as a result of promotion. Here the increment is less compared to that in $2s$. This is presumably because of the two opposing factors—the mutual shielding of the two $2p$ -electrons, against the much less shielding provided by the remaining single $2s$ -electron in the promoted state.

The orbital extensions, as measured by the r_{\max} and $\langle r \rangle$ values, of both $2s$ and $2p$ -orbitals are found to be decreased, that is, the orbitals are "contracted" in going from ($2p$) to the ($4p$) state. This contraction can be rationalised on the basis of the increase in the orbital exponents. Following Slater (1964), one can regard the r_{\max} value of the outermost orbital of an atom to be its theoretical atomic radius. Slater's (1964) estimate of the atomic radius of boron is 0.85 Å, while our calculated values are 1.6519 a.u. and 1.619 a.u. i.e. about 0.83 Å and 0.81 Å, for the ground and promoted states respectively; the value for the trigonally hybridized (sp^2)-orbital constructed from the promoted state is calculated to be 0.78 Å. It may be pointed out that Schomaker and Stevenson's (1941) estimation of the covalent radius of boron (0.81 Å) coincides with the $2p$ -orbital radius of the promoted ($4p$) state of boron obtained in this work. The orbital contraction effect, as a result of the promotion of atom, is also observed and commented upon by other workers (Ruedenberg 1962; Politzer 1970; Bhattacharyya *et al* 1975; Weinbaum 1933). Ruedenberg (1962) has shown within the frame work of M.O. theory, that the formation of a molecule from atoms involves "contractive promotion", in which the atomic orbital contracts towards its nucleus, as a necessary step. The preliminary results of our calculation here indicate that orbital contraction may be a necessary step in the V.B.-hybridization theory of molecule formation as well. Further studies are in progress.

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