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Contract Nonr 3471(00)

Task No. 356-433

TECHNICAL REPORT NO. 7

Calculation of Basic Parameters Necessary for Quantum Chemical Calculations on Boron-Containing Molecules

I. One-Center Electron Repulsion Integral $(pp|pp)_B$

by

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December, 1962

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Calculation of Basic Parameters Necessary for Quantum Chemical Calculations on Boron-Containing Molecules

I. One-Center Electron Repulsion Integral $(pp|pp)_B$

Abstract

A modified one-center electron repulsion integral $(pp|pp)$ for boron which takes into account electron correlation effects has been evaluated by expansion of the energies of the boron atom and its positive and negative ions as a function of spectroscopic term values. The values for $(pp|pp)_B$ calculated from two different pairs of valence states are very close:

$$(pp|pp)_B = 7.094 \text{ ev}$$

$$(pp|pp)_B = 6.976 \text{ ev}$$

It is demonstrated that for boron in certain valence states the Pariser-Parr approximation

$$(pp|pp) = I - A$$

and the more rigorous approximation of Julg

$$(pp|pp) = I - A - \epsilon(I + A)$$

do not hold, because since the electron is put into a formerly empty orbital, an exchange term arises in addition to the Coulomb term.

Calculation of Basic Parameters Necessary for Quantum Chemical Calculations on Boron-Containing Molecules

I. One-Center Electron Repulsion Integral $(pp|pp)_B$

As a part of a general program for quantum chemical calculations on boron-containing molecules, it has been necessary to evaluate modified values for Coulomb repulsion integrals for boron which take into account electron correlation effects. For many other atoms, i.e. carbon, nitrogen, oxygen, the modified value of the one-center electron repulsion integral can be estimated from the Pariser-Parr approximation[1]

$$(pp|pp) = I - A \qquad (1)$$

The one-center electron repulsion integral can also be calculated more exactly by expansion of the energies of the atom and its positive and negative ions as a function of spectroscopic term values. This method has been used by Julg[2] and for the carbon, nitrogen and oxygen, expressions of the form

$$(pp|pp) = I - A - \epsilon(I + A) \qquad (2)$$

are obtained. If the term in ϵ is neglected (ϵ corrects for the fact that the effective nuclear charges are different in the positive ion, the neutral atom and the negative ion), both expressions for $(pp|pp)$ reduce to the same value.

In order to gain some physical insight into the problem for the boron atom, we chose to do the expansion in spectroscopic term

values and, as will be shown later in this article, the expression for $(pp|pp)_B$ turns out not to have the simple form of the expressions for the $(pp|pp)$ of the other atoms. The reason for this is that boron has less than a half-filled shell and we are putting the extra electron into a formerly empty orbital - for this reason, in addition to the Coulomb repulsion term, an exchange term also arises.

Calculations

I.

Valence state energies

B^-	sxyz	$[E_i + 2\alpha + (pp\|pp) - \frac{5}{2}(p\bar{p}\|p\bar{p})](1 - \epsilon)$
B	syz	$E_i + \alpha$
B^+	sz	$E_i(1 + \epsilon)$

$$B^- \quad sxyz \quad = I_s + I_x + I_y + I_z + J_{sx} + J_{sy} + J_{sz} + J_{xy} + J_{xz} + J_{yz}$$
$$- \frac{1}{2}K_{sx} - \frac{1}{2}K_{sy} - \frac{1}{2}K_{sz} - \frac{1}{2}K_{xy} - \frac{1}{2}K_{xy} - \frac{1}{2}K_{xz} - \frac{1}{2}K_{yz}$$

$$B \quad syz \quad = I_s + I_y + I_z + J_{sy} + J_{sz} + J_{yz}$$
$$- \frac{1}{2}K_{sy} - \frac{1}{2}K_{sz} - \frac{1}{2}K_{yz}$$

$$B^{+} \quad sz \quad = I_s + I_z + J_{sz} - \frac{1}{2} K_{sz}$$

$$E_i = I_s + I_z + J_{sz} - \frac{1}{2} K_{sz}$$

$$\alpha = I_y + J_{sy} + J_{yz} - \frac{1}{2} K_{sy} - \frac{1}{2} K_{yz}$$

$$B^{-} = (E_i + 2\alpha + J_{xy} - \frac{1}{2} K_{xy})\ (1 - \epsilon)$$

$$= E_i + 2\alpha + (pp|pp) - \frac{5}{2}(p\bar{p}|p\bar{p})$$

from the relation

$$(pp|pp) - (pp|\bar{p}\bar{p}) = 2(p\bar{p}|p\bar{p})$$

where

$$J_{xx} = (pp|pp)$$

$$J_{xy} = (pp|\bar{p}\bar{p})$$

$$K_{xy} = (p\bar{p}|p\bar{p})$$

$$(B^{-} - B) + (B^{+} - B) = (I - A) = (pp|pp) - \frac{5}{2}(p\bar{p}|p\bar{p}) - \epsilon[2\alpha + (pp|pp) \quad (pp|pp) - \frac{5}{2}(p\bar{p}|p\bar{p})]$$

$$(B - B^{-}) + (B^{+} - B) = -2\alpha - (pp|pp) + \frac{5}{2}(p\bar{p}|p\bar{p})$$

$$\therefore (pp|pp) - \frac{5}{2}(p\bar{p}|p\bar{p}) = I - A - \epsilon(I + A)$$

$$B_{syz} \rightarrow B^{+}_{sz} \qquad I = 8.33 \text{ ev}$$

$$B_{syz} \rightarrow B^{-}_{sxyz} \qquad A = 0.892 \text{ ev}$$

Since the expression for $(pp|pp)$ derived from this valence state also contains $(p\bar{p}|p\bar{p})$ it is necessary to use the evaluation of $(pp|pp)$ and $(p\bar{p}|p\bar{p})$ in terms of ζ (the Slater effective nuclear charge) in order to compare this $(pp|pp)$ with another $(pp|pp)$ derived from a different valence state.

From the formulas of Roothaan.[3]

$$(pp|pp) = 0.391406\ \zeta$$

$$(p\bar{p}|p\bar{p}) = 0.0210938\ \zeta$$

$$0.338811\ \zeta = (8.33 - 1.05) - \epsilon\,(8.33 + 1.05)$$

$$\zeta = 21.486905 - 27.685051\,\epsilon$$

II.

It is necessary to have another expression in ζ and ϵ to evaluate ϵ. This second relation is derived from boron in the following valence states.

B^-	sx^2z	$(E_i + 2\alpha + J_{xx})\,(1 - \epsilon)$
B	sxz	$E_i + \alpha$
B	sz	$E_i\,(1 + \epsilon)$

$$B^- \quad sx^2z = Is + 2\,I_x + I_z + J_{xx} + 2\,J_{sx} + J_{sz} + 2\,J_{xz}$$

$$- K_{sx} - \frac{1}{2} K_{sz} - K_{xz}$$

$$B \quad sxz = I_s + I_x + I_z + J_{sx} + J_{sz} + J_{xz} - \frac{1}{2} K_{sx} - \frac{1}{2} K_{sz} - \frac{1}{2} K_{xz}$$

$$B^+ \quad sz = I_s + I_z + J_{sz} - \frac{1}{2} K_{sz}$$

$$E_i = I_s + I_z + J_{sz} - \frac{1}{2} K_{sz}$$

$$\alpha = I_x + J_{sx} + J_{xz} - \frac{1}{2} K_{sz} - \frac{1}{2} K_{xz}$$

$$(B^- - B) + (B^+ - B) = I - A' = J_{xx} - \epsilon\,(2\alpha + J_{xx})$$

$$(B - B^-) + (B^+ - B) = I + A' = -(J_{xx} + 2\alpha) + \epsilon\lfloor \quad \rfloor$$

Drop Term

to evaluate

$(J_{xx} + 2\alpha)$ to use in

first expression

$$I + A' \cong -(J_{xx} + 2\alpha)$$

$$J_{xx} = I - A' - \epsilon\,(I + A')$$

$$= (8.33 - 0.20) - \epsilon(8.33 + 0.20)$$

$$0.391406\,\zeta = 8.13 - 8.53\,\epsilon$$

$$\zeta = 20.77127 - 21.793227\,\epsilon$$

Equating ζ from the two expressions

$$21.486905 - 27.685051\epsilon = 20.77127 - 21.793227\epsilon$$

$$\epsilon = 0.12146238$$

$$\therefore (pp|pp)_B = 7.094 \text{ ev}$$

III.

There is an alternative method by which to obtain a second relation between ζ and ϵ.

$$B \quad sx^2 \quad E_i + 2\alpha + J_{xx}$$

$$B^+ \quad sx \quad (E_i + \alpha)(1 + \epsilon)$$

$$B^{++} \quad s \quad E_i (1 + 2\epsilon)$$

$$B \quad sx^2 = I_s + 2 I_x + 2 J_{sx} + J_{xx} - K_{sx}$$

$$B^+ \quad sx = I_s + I_x + J_{sx} - \frac{1}{2} K_{sx}$$

$$B^{++} \quad s = I_s$$

$$E_i = I_s$$

$$\alpha = I_x + J_{sx} - \frac{1}{2} K_{sx}$$

$$I_1 = B^+ - B = -\alpha - J_{xx} - \alpha\epsilon$$

$$I_2 = B^{++} - B^{+} = -\alpha \quad -\alpha\epsilon$$

$$I_2 - I_1 = -2\alpha\epsilon \quad + J_{xx} \qquad\qquad -\alpha \cong I_2$$

$$J_{xx} = I_2 - I_1 + 2\alpha\epsilon \quad = I_2 - I_1 - 2\epsilon \; I_2$$

$$J_{xx} = 0.391406 \; \zeta = I_2 - I_1 - 2\epsilon \; I_2$$

$$= 19.399 - 7.276 - 2\epsilon \; (19.399)$$

$$\zeta = 31.16201 - 99.14666\,\epsilon$$

Equating ζ from I and III

$$21.486905 - 27.606851\epsilon \quad = 31.16201 - 99.14666\,\epsilon$$

$$\epsilon = 0.13524085$$

$$(pp|pp)_B = 8.13 - 8.53\,\epsilon \quad = 6.976 \text{ ev}$$

<u>Results</u>

The agreement between the values

$(pp|pp)_B = 7.094$ ev

or $= 6.976$ ev

is quite good, and both are considerably lower than the value $(pp|pp)_B = 13.83$ ev calculated from Slater-type AO's from the closed analytical forms of Roothaan.[3]

ϵ derived from the expansion in spectroscopic term values

0.12146238

or 0.13524085

are both in good agreement with ϵ calculated from Slater's rules

0.1346153.

Acknowledgements

This work was supported by the Chemistry Branch of the Office of Naval Research.

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