An *ab initio* Investigation of the Geometry, Bonding and Coupling Constants of BF$_2$

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Comparative calculations, using five different basis sets of contracted Gaussian functions, of the geometry, bonding and hyperfine coupling constants of BF$_2$ are reported. The best calculation, using a near Hartree-Fock atomic basis, predicts a bond angle of 120° and a bond length of 2.50 a.u. ($= 1.32$ Å) for the $X^2 A_1$ ground state. The geometries of three low-lying excited states are also presented.

Key words: Hyperfine coupling – Excited states – BF$_2$

Introduction

For many years *ab initio* calculations on polyatomic open shell species were rather rare, owing to the difficulties often found in achieving convergence in the SCF iterations. This is clearly revealed by an examination of the useful bibliography of Richards, Walker, and Hinkley [1], surveying published work to the end of 1969. Of those few radicals which do appear, almost all are hydrides.

However, interest in the use of *ab initio* calculations to predict the properties of species which are short-lived and difficult to observe has increased recently. The BF$_2$ radical is an ideal case for such treatment, in that it has been definitely characterised spectroscopically, but observations of it have been sparse and very few of its properties are known; even the molecular structure in the ground state is uncertain.

B$_2$F$_4$ is well-known, and the bonding has been interpreted recently by considering it as a dimer of BF$_2$ [2]. There seems however to have been no suggestion that B$_2$F$_4$ will decompose upon heating to give BF$_2$, in a manner analogous to N$_2$F$_4$.

Experimental Observations

The first observation of the BF$_2$ species appears to date from 1967, when an Indian group observed a band emission spectrum in the ultraviolet, after high voltage discharge through gaseous BF$_3$ [3]. Isotopic substitution and analysis of the partially resolved rotational structure suggested the identity of the emitting species as BF$_2$ or BF$_3$. By calculating the separation of the maxima of the P and R bands, and comparing this with experiment, the species was identified as BF$_2$. From a consideration of isotopic substitution on the bending force constant the bond angle was suggested to be around 130°. This deduction however involved

the assumed value of two parameters, which may be responsible for the discrepancy between this prediction and our structure suggested on the basis of ab initio potential energy curves.

Later in the same year Hesser and Dressler [4] reported the observation of a broad emission spectrum obtained after passing a beam of 200-V electrons, modulated at radiofrequency, into low pressure BF_3. This also was attributed to BF_2.

In 1969, the ESR spectrum of the BF_2 radical was reported [5], the signal being obtained after gamma irradiation of BF_3 trapped in a xenon matrix at $4.2\,°K$. It was found to be fairly complex owing to the presence of the two naturally-occurring isotopes of boron, and the anisotropic components of the hyperfine splitting appeared to be partially averaged out by some molecular motion in the matrix.

Interestingly, radiolysis of BF_3 at temperatures between $77°$ and $350\,°K$ by 3 MeV Bremsstrahlung radiation gave no evidence for the formation of BF_2 or BF_2^+, as might have been expected [6].

Previous Calculations

Results have been published both of semi-empirical calculations on BF_2 (CNDO with spin polarization [7], CNDO/2 [8] and three separate INDO calculations [7–9]) and ab initio calculations, using a minimal basis of Slater-type orbitals [10]. Most of these calculations had as their objective the evaluation of the hyperfine coupling constants, and accordingly they are discussed at the appropriate place, later in this report. Pople and Beveridge [8] report bond angle optimisations, having made the assumption of a B–F bond length of $1.30\,Å$ ($= 2.45$ a.u.). Using CNDO/2 they obtained a bond angle of $124.6°$, a dipole moment of -0.05 D, and a bending force constant of $0.62\,mdyn/Å$. With INDO, the respective values are $122.9°$ and $+0.29$ D. (Signs of the dipole moment have been reversed in order to conform to the convention employed here.)

In the only ab initio calculation so far published, McCain and Palke [10] obtain an energy of -222.430 a.u. for the species. They employed however only one geometry in their calculations, that of NO_2, with $R(B–F) = 1.197\,Å$ and $\theta = 134°$, and thus their energy will not be even the best available with the small basis set used.

Nagarajan [11] has estimated the stretching and bending force constants from values of the fundamental spectroscopic frequencies, calculated in turn from the force constants for BF_3. He computes $F(\text{stretch}) = 5.49\,mdyn/Å$, and $F(\theta) = 0.58\,mdyn/Å$.

Calculations Ground State

Calculations were carried out with the programs IBMOL 44 (IBMOL version 4 modified for the IBM 360/44 at the University of St. Andrews) and IBMOL 5 [12]. Both these programs use Roothaan's RHF method.

Like its isoelectronic counterparts NO_2 and CO_2^-, BF_2 is expected to have a $^2A_1$ ground state, and this is confirmed by the present calculations. These have been carried out with five different basis sets of Gaussian orbitals, ranging in size from (5, 2) contracted to $\langle 2, 1\rangle$ – which will be considerably poorer than a minimal

Table 1. Energies and optimised geometries

Basis set	(5, 2)	(7, 3)	(7, 3)	(9, 5)	(11, 7)
Energy (a.u.)	− 221.76857	− 222.96887	−223.28235	− 223.61611	− 223.64617
$R(B–F)$ (a.u.)	2.50	2.635	2.52	2.575	2.495
$\theta°$	120	120	120	117	120

Note: Geometry parameters for the (9, 5) basis have not been fully optimized. Contraction schemes employed were, respectively, $\langle 2, 1\rangle$, $\langle 2, 1\rangle$, $\langle 4, 2\rangle$, $\langle 4, 3\rangle$, and $\langle 6, 4\rangle$.

Slater basis – to an $(11,7) - \langle 6, 4\rangle$ set. The sources from which these basis sets were obtained has been described previously [13]. No attempt was made to include polarization functions in the basis sets.

The geometrical parameters for the species were optimised with each basis, and the results are shown in Table 1. For the two largest basis sets the results re-, present an improvement on the preliminary announcement [13]. All the evidence points to the radical having a bond length of 2.50 a.u., and a bond angle of 120°. This is in reasonable agreement with the angle predicted by INDO calculation of 122.9° [8]. The experimental estimation of the bond angle as 112° [5] used the rather unreliable relationship between the relative p to s character of the singly-occupied orbital and the bond angle.

In the original work [13] it was apparent that the $(7, 3) - \langle 2, 1\rangle$ basis consistently over-estimated bond lengths. It was later suggested [14] that the contraction employed was too restrictive. This was tested by relaxing the contraction to $\langle 4, 2\rangle$; the results of this can be seen in the table, and it is immediately obvious that this does bring about a considerable improvement in the calculated geometry.

The predicted bond length for BF_2 is significantly larger than that found experimentally in BF (2.391 a.u.) and BF_3 (2.447 a.u.).

Ground State Electron Configuration and Orbital Energies

It is known that the eigenvalues obtained using Roothaan's RHF scheme cannot be directly identified with the orbital energies in the sense of Koopmans' theorem. However using the ATMOL system of programs of Hillier and Saunders [15] it is possible to obtain "canonicalized" molecular orbitals, whose eigenvalues do represent the orbital energies. In Table 2 are presented the results of such an ATMOL calculation, together with, for comparison, the eigenvalues obtained from IBMOL-5 calculations using, in the first case the same basis set and geometry, and in the second case (column 3) the best near-Hartree-Fock calculation.

It is immediately apparent that the results obtained using ATMOL and IBMOL are in close agreement, which seems to suggest that even although the eigenvalues resulting from an open-shell calculation using Roothaan's formalism cannot be theoretically justified as representing some physical quantity, there is a *de facto* case for allowing them that significance.

Note in Table 2 the near-degeneracy of the $1b_1$ and $5a_1$ orbitals. The energy of the highest (singly) occupied orbital should represent the first ionization potential of the species. This could of course also be calculated as $(E(\text{radical}) - E(\text{cat-}$

Table 2. Eigenvalues for BF_2 ground state

Program orbital	ATMOL $(7, 3)-\langle 4, 2\rangle$	IBMOL $(7, 3)-\langle 4, 2\rangle$	IBMOL $(11, 7)-\langle 6, 4\rangle$
$1a_1$	-26.36789	-26.36936	-26.34170
$1b_2$	-26.36788	-26.36935	-26.34172
$2a_1$	-7.76450	-7.77590	-7.78757
$3a_1$	-1.65672	-1.66268	-1.67658
$2b_2$	-1.62733	-1.63321	-1.64492
$4a_1$	-0.79851	-0.80440	-0.83387
$3b_2$	-0.73111	-0.74224	-0.77484
$1b_1$	-0.70147	-0.70534	-0.73454
$5a_1$	-0.68756	-0.70438	-0.73452
$1a_2$	-0.64658	-0.64803	-0.67866
$4b_2$	-0.64016	-0.64482	-0.67522
$6a_1$	-0.42333	-0.42333	-0.44529

ion)). In either case this represents the vertical ionization potential, which is expected to be larger than the experimental value, since the ground state of BF_2^+ should be expected to be linear, with a consequent release of energy upon changing the bond angle.

Excited States

Minimal basis set calculations $((5, 2) - \langle 2, 1\rangle)$ have been carried out on three low-lying excited states of the molecule, including the first excited state (A^2B_1) which is expected to be linear. Geometries were optimised using this basis, and the optimised energies and geometries for the various states (together with the comparable calculation on the ground state) are presented in Table 3.

Although obviously the energy calculated with this basis is far from the Hartree-Fock level, it seems probable that the results will have some qualitative significance, as also will the geometries.

Ab initio calculations on isoelectronic NO_2 [16] show the existence of a large family of low-lying excited states. These workers also showed that the first excited state (A^2B_1) is obtained by excitation from the open-shell $6a_1$ orbital to the vacant $2b_1$ orbital, and not by excitation $1b_1 \rightarrow 6a_1$ within the occupied orbitals.

At 120° the energy of the A^2B_1 state is -221.60761. Thus the first excitation $X^2A_1 \rightarrow A^2B_1$ requires 4.4 eV, and consequently the species would not be expected to show an absorption spectrum in the visible range – in contrast to the well-known and stable 23-electron species NO_2. However this excitation energy can be related to the UV emission spectrum reported by two groups [4, 3] who respectively observed a broad emission 2100–3700 Å, and a system of bands 2200–2800 Å. The transition $A^2B_1 \rightarrow X^2A_1$, with a calculated energy difference between the two levels of 0.162 a.u., corresponds to an emission around 2800 Å. This correlation between calculation and observation should not be given too much weight, as it depends upon the numerical difference between two energies known to be only approximate. However it might be mentioned that in their calculation on NO_2 Burnelle, May and Gangi [16] successfully correlated excitation energies obtained with a (5, 2) basis with observed spectral absorptions.

Table 3. Energy and optimised geometry for three excited states

State	Energy	Geometry		Electronic configuration
		R(B–F)	θ	
X^2A_1	−221.76857	2.50	120	...$(1b_1)^2(5a_1)^2(1a_2)^2(4b_2)^2(6a_1)^1$
A^2B_1	−221.64635	2.55	180	...$(1b_1)^2(5a_1)^2(1a_2)^2(4b_2)^2(2b_1)^1$
$^2A_2$	−221.53580	2.79	90	...$(1b_1)^2(5a_1)^2(1a_2)^1(4b_2)^2(6a_1)^2$
$^2B_1$	−221.46425	2.90	99	...$(1b_1)^1(5a_1)^2(1a_2)^2(4b_2)^2(6a_1)^2$

Bonding as Revealed by Mulliken Population Analysis

As the quality of the basis set is improved there is a steady, and often mono-tonic, variation in the parameters evaluated in the population analysis. For this reason only the population analysis of the best wave-function obtained − in this particular case, using the (11, 7) basis − will be considered, as affording the most satisfactory representation of the wave-function.

This seems to suggest that the B–F bond is not strong, but evidence is mount-ing that as the basis set is enlarged and the representation of the polarisation in the bond improves, then the value of some of the parameters evaluated in the Mulliken analysis becomes misleading. This is in accord with the already well-known limitations of the analysis with regard to overlap and atomic charges in polar bonds. Significant contributions to the B–F overlap come from the $4a_1$, $3b_2$, and $1b_1$ orbitals. The single electron in its $6a_1$ orbital is seen to be strongly anti-bonding.

The $1b_1$ orbital has, crudely, the form $0.1\,B(2p_x) + 0.9(F1(2p_x) + F2(2p_x))$ and obviously corresponds to a π bond. This bond contributes roughly 25% to the total overlap population. This figure should be compared with the prediction

Table 4. Population analysis

Basis set	(5, 2) →⟨2, 1⟩	(7, 3) →⟨2, 1⟩	(7, 3) →⟨4, 2⟩	(9, 5) →⟨4, 3⟩	(11, 7) →⟨6, 4⟩
B (GAP)	4.644	4.282	4.255	4.067	4.145
F (GAP)	9.178	9.359	9.373	9.466	9.428
B–F (Overlap)	0.630	0.526	0.548	0.450	0.274
B(2s)[a]	1.014	0.917	0.953	0.903	0.939
(2p$_x$)	0.454	0.317	0.261	0.190	0.192
(2p$_y$)	0.427	0.372	0.409	0.347	0.381
(2p$_z$)	0.749	0.677	0.632	0.628	0.633
F(2s)	1.843	1.902	1.928	1.958	1.964
(2p$_x$)	1.773	1.842	1.870	1.905	1.904
(2p$_y$)	1.751	1.762	1.721	1.749	1.718
(2p$_z$)	1.811	1.854	1.844	1.854	1.841
μ	0.076	0.356	0.389	0.634	0.489

Note: For dipole moment, 1 a.u. = 2.542 D.
      Geometry employed for the (9, 5) basis is not fully optimal

[a] Orbital populations.

Table 5. BF_3 population analysis

Armstrong and Perkins [20]		Schwartz and Allen [21]	Goutier and Burnelle [22]
B (GAP)	3.581	3.612	3.89
F (GAP)	9.473	9.463	9.39
B–F (Overlap)	0.569	0.525	0.67

made by Nelson and Gordy in their original paper [5]: on the basis of the bonding in BCl_3, they predicted both the existence and magnitude of such a bond in the BF_2 species. Their prediction is fully vindicated.

Population analyses of BF_3 calculations have been published by three groups and the results are summarised in Table 5. The existence of a large flow of electrons from the boron into the fluorines is apparent. This would seem to vindicate the population analyses on BF_2, which show a redistribution of charge very similar to that seen in BF_3. This contradicts the conclusion drawn in our preliminary communication [13] from population analyses on the poorer basis set calculations.

Single Electron Properties

From the best wave-function obtained, one-electron properties can be calculated routinely.

Bond polarity in BF_2 is of interest, for the purposes of comparison with BF and BF_3. For the former species, various *ab initio* calculations (by Fraga and Ransil [17], Nesbet [18], and Huo [19]) show the bond to be polarised in the sense $B(\delta-) - F(\delta+)$, with a value for the dipole moment of about 1 D. On considering the variation in dipole moment with bond length, both Huo and Nesbet found that on stretching beyond the experimental bond length the sign of the dipole changed becoming $B(\delta+) - F(\delta-)$. Huo [19] explains this in terms of increasing electron donation by F to the bond as it is shortened. Calculations on BF_3 by Armstrong and Perkins [20] and by Schwartz and Allen [21] show the bonds to be polarised in the sense $B(\delta+) - F(\delta-)$, although obviously there is no net dipole moment in the molecule.

All the calculations reported here predict the dipole to be positive in the sense indicated in Fig. 1. The dipole moment has not been measured for BF or BF_2.

In BF_2 the single electron occupies an orbital in the molecular plane which is a hybrid of $B(2s)$ and $B(2p_z)$ (see Table 6). The calculated populations for the unpaired electron may be compared with various earlier attempts, both semi-empirical and *ab initio*, to account for the observed ESR parameters. Zaucer and Ažman [9] found $\varrho(B) = 0.476$, using the experimental geometry. Most unexpectedly McCain and Palke [10] show the single electron as occupying an orbital with a sizable contribution from the fluorine $2p_z$, together with fluorine $(2s)$ and $(2p_x)$. [Their wave-function: $0.122 B(1s) - 0.799 B(2s) + 0.603 B(2p_z) - 0.028 F(1s) + 0.184 F(2s) - 0.416 F(2p_z) - 0.111 F(2p_x)$.] This calculation employed a minimal Slater basis, and used as geometry the structure of NO_2 ($R = 2.26$ a.u., $\theta = 134°$).
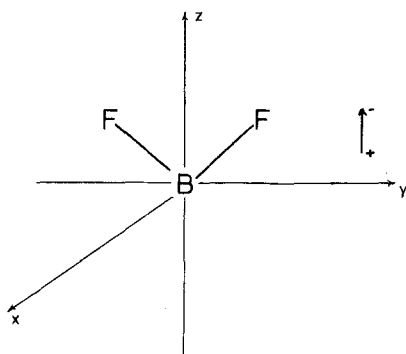
Fig. 1. Definition of coordinate system and direction of dipole moment

Table 6. Boron orbital population of unpaired electron, calculated with various basis sets

Basis Set	(5, 2)	(7, 3)	(7, 3)	(9, 5)	(11, 7)
$B(2s)$	0.41	0.43	0.54	0.52	0.57
$B(2p_z)$	0.40	0.44	0.40	0.44	0.43

Table 7. Electron spin density at each nucleus, calculated with various basis sets

Basis set	(5, 2)	(7, 3)	(7, 3)	(9, 5)	(11, 7)
$\phi(0)B$	0.6687	0.9137	0.5537	0.6243	0.5458
$\phi(0)F$	0.0698	0.0930	0.0906	0.0660	0.0729

It is of considerable interest, as a test of the wave-function, to compare prediction with experiment for the hyperfine coupling constants of radicals. These coupling constants depend on the spin density at the site of any magnetic nuclei in the species. Since the wave-function that we calculate is a linear combination of Gaussian orbitals, which do not in themselves have the correct behaviour at the cusps, a number of Gaussian functions of high exponent have to be superimposed, solely in order to represent with reasonable accuracy the behaviour of the wave-function at the nucleus.

The success or otherwise of this procedure can be tested by looking at the electron spin densities at the nuclei, as calculated with the various basis sets (Table 7). This seems to reveal no general trend in the value of $\phi(0)$ as the basis set is improved.

Taking what are presumably the best values of $\phi(0)$, namely those obtained with the (11, 7) basis, we can calculate isotropic hyperfine coupling constants directly from the relationship

$$a_i = \frac{8\pi}{3} g\beta g_N \beta_N |\phi(0)|^2$$

where β_N is the nuclear magneton, equal to 5.050×10^{-24} erg/G, and g_N is the nuclear g factor. Thus for example, taking g_N for boron as 1.7920, $a_i(B)$

Table 8. Hyperfine coupling constants for BF_2

Method	Experimental [5]	This work	CNDO/SP [7]	INDO [7]	ab initio [10][a]	INDO [9]
a (isotropic) (B)	295.0	279.2	301.5	536.5	270.5	343
a (F)	190.0	109.3	114.1	359.4	285.0	181.4

Note: All values in gauss.

[a] Derived from published values of $\phi(0)$.

(B) $= 285.54 \times 1.7920 \times 0.5458 = 279.2$ G. In Table 8 we compare the experimental values for the isotropic coupling constants in BF_2 with those calculated in this work, together with previously published calculations.

Our calculation is seen to agree well with experiment for the boron coupling, where there is a reasonably large spin density at the nucleus. For fluorine where the agreement is much poorer, the spin density is almost an order of magnitude smaller, and the uncertainty commensurately greater. This observation will be of use in evaluating the reliability of future calculations of hyperfine coupling constants from *ab initio* LCAO–MO wave functions.

Note: After completion of this manuscript there appeared a further *ab initio* study of BF_2 by Rothenberg and Schaefer [23], as part of a study of the first row difluorides. Using a single geometry of $R = 2.45$ a.u., $\theta = 120°$, they obtained energies of -223.5860 with a (9, 5) contracted set, and of -223.6744 a.u. with a (9, 5, 1) contracted set. Many one-electron properties were evaluated.

Since the (9, 5) basis sets used were almost identical, the difference in energy between our work and theirs must be attributed to the slight relaxation in contraction of the $2p$ functions (5 gaussians contracted to 3 functions, as recommended by Dunning [24], as opposed to Rothenberg and Schaefer's two).

From an examination of the d orbital populations Rothenberg and Schaefer conclude that in the series of triatomic difluorides considered, polarization functions are most important in the case of boron. However, a detailed study of SiF_2 [25] has shown the crucial importance of optimising d function exponents before discussing their individual importance as polarisation functions. Such optimisation may produce a change in d orbital population of more than an order of magnitude.

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