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The Electronic Structure of Boron Trifluoride

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The electronic structure of boron trifluoride has been calculated *ab initio* by using extended basis sets of Gaussian type atomic orbitals. By variation of the B–F bond length a minimum energy situation was found at 1.306 Å (experimental 1.31 Å). Calculations on the pyramidal (reorganised) form of the molecule led to a reorganisation energy of 34.2 kcal mole^{-1}. The π localisation energy was found to be 50.4 kcal mole^{-1}. Both the latter energy and the π charge distribution are in good agreement with results from a previous Pariser-Parr-Pople calculation. The calculated quantities are used to discuss the energetics of donor-acceptor complex formation.

Die Elektronenstruktur des BF_3-Moleküls wird mit Hilfe einer *ab initio* Rechnung unter Verwendung einer erweiterten GTO-Funktionsbasis ermittelt. Die Variation der Energie bezüglich des B–F-Bindungsabstandes führt zu einem Energieminimum für einen B–F-Abstand von 1,306 Å in guter Übereinstimmung mit dem Experiment (1,31 Å). Dabei erweist sich das planare BF_3-Molekül gegenüber dem pyramidalen um 34,2 Kcal/Mol stabiler. Die π-Elektronen-Lokalisierungsenergie beträgt 50,4 Kcal/Mol. Bezüglich dieser Energie sowie der π-Elektronenladungsverteilung ergibt sich gute Übereinstimmung mit den Resultaten vorangegangener PPP-Rechnungen. Die berechneten Größen werden zur Diskussion der Vorgänge in Donor-Akzeptor-Komplexen herangezogen.

Calcul *ab initio* de la structure électronique due trifluorure de Bore en base étendue d'orbitales atomiques Gaussiennes. La variation des longueurs des liaisons BF donne un minimum à 1.306 Å (valeur expérimentale 1.31 Å). Les calculs de la forme pyramidale (réorganisée) de la molécule donnent une énergie de réorganisation de 34.2 kcal/mole. L'énergie de localisation π vaut 50.4 kcal/mole. Cette dernière valeur, et la distribution de la charge π sont en bon accord avec les résultats d'un calcul antérieur dans le approximations de Pariser-Parr-Pople. Les quantités calculées sont utilisées dans une discussion des caractéristiques énergétiques de la formation de complexes donneur-accepteur.

1. Introduction

Because of its electron acceptor properties boron trifluoride is the progenitor of a large number of coordination compounds and has thus received much attention from chemists [9]. The physical and thermodynamic properties of these have been much studied and discussion, supported by calculation, has centred around the reasons for the weaker acceptor properties of BF_3 in comparison with BCl_3. It has been suggested [2, 4] that the planar-pyramidal reorganisation energy of the molecule is a potent factor affecting the acceptor properties but unfortunately this has heretofore only been calculated as a "vertical" quantity [2]; hence several important features of the reorganisation process *e.g.* change of σ bond strength with B–F bond length and F–B–F angle could not be evaluated. Furthermore the definition of vertical reorganisation necessarily envisages that all the B–F π bond energy is lost on reorganisation, and so takes no account of the residual interactions (which become mixed with the true σ interaction [2]) and which vary depending on the F–B–F angle in the final coordination complex.

Further features of interest in boron trifluoride are (*a*) the charge distribution and (*b*) in the light of recent Extended Hückel [14] calculations on boron halides and CNDO/Gaussian calculations [1] on aminoborane, the symmetry of the highest bonding level *i.e.* whether of σ or π type, and hence where an ionised electron would originate from. In order to throw light on these problems we have calculated the electronic structure of boron trifluoride *ab initio* with extended Gaussian basis sets. This was carried out by using the POLYATOM computational scheme [5] with fixed exponents [6] and two basis sets designated (7,3) and (5,2). (A basis set (m, n) contains m orbitals of s symmetry and n orbitals representing each of $2p_x, 2p_y$, and $2p_z$ per atom.) The calculations were all performed on the Newcastle University IBM 360/67 computer. The B–F bond length was assigned the value 1.31 Å [13] (however see later) and the principal axes on the central atom defined such that the molecule lies in the xy plane with one B–F bond coincident with the x axis.

2. Results and Discussion

1. Energies

The total and individual orbital energies of planar BF_3 are listed in Table 1. In the more extensive basis set a sufficient number of Gaussians were employed such that the total energy approaches the Hartree-Fock limit. The molecular binding energy, *i.e.* the difference between that of the molecule and its constituent atoms is calculated to be 322.8 kcal mole^{-1}.

This quantity however must be corrected for the contribution due to electron correlation. The correction adds a contribution equal to 40.72 kcal mole^{-1} [7] from each new bond formed and hence the modified binding energy is 445 kcal mole^{-1}. This is in satisfactory agreement with the most recently quoted experimental values for this quantity namely 460.5 [8] and 459.5 kcal mole^{-1} [16].

With the exception of the three lowest, the occupied orbitals calculated from the (7,3) basis set are all more stable than those appertaining to the (5,2) basis set. Perhaps the most interesting energy level is the highest bonding orbital which is of σ type and is built from a linear combination of the three fluorine p orbitals which are in the molecular plane and orthogonal to the B–F axes. This orbital lies at -18.24 eV in the absolute energy scale and, if Koopmans' theorem [12] is invoked, correlates with the measured ionisation potential, 15·97 eV [14]. In earlier calculations, essentially by the Pariser-Parr-Pople method [15], of the π electronic structure of BF_3, Armstrong and Perkins [2] calculated a value of 16.0 eV for this quantity and concluded that an ionised electron would be removed from the π type orbitals of the fluorine atoms.

The first vacant orbital is of π type and is composed largely of the boron $2p_z$ atomic level. The electron affinity of the molecule (*i.e.* the energy of this orbital) is $+4.5$ eV. The corresponding value in Ref. [2] is $+2.40$ eV.

Table 1. *The molecular and orbital energies of* BF_3 *(a. u.)*

Basis set	(7,3)	(5,2)
Empty orbitals	0.7848 (e')	2.1365 (a_1')
	0.6757 (a_1')	1.1468 (e')
	0.5435 (a_2'')	1.0373 (a_2'')
	0.3610 (e')	0.5689 (e')
	0.1914 (a_1')	0.4155 (a_1')
	0.1668 (a_2'')	0.2479 (a_2'')
Filled orbitals	− 0.6706 (a_2')	− 0.5708 (a_2')
	− 0.6937 (e'')	− 0.5851 (e'')
	− 0.6993 (e')	− 0.6061 (e')
	− 0.7771 (a_2'')	− 0.6956 (a_2'')
	− 0.8196 (e')	− 0.7226 (e')
	− 0.8663 (a_1')	− 0.7741 (a_1')
	− 1.6866 (e') fluorine s orbital	− 1.6561 (e')
	− 1.7323 (a_1') fluorine s orbital	− 1.6984 (a_1')
	− 7.8379 (a_1') boron inner s orbital	− 7.7614 (a_1')
	− 26.3857 (a_1') fluorine inner s orbitals	− 26.4250 (e')
	− 26.3858 (e') fluorine inner s orbitals	− 26.4251 (a_1')
Electronic energy	−433.657006	−431.001168
Nuclear energy	111.204919	111.204919
Total energy	−322.452087	−319.796249

Table 2. *Gross atomic and overlap populations of boron trifluoride*

Basis set		(7,3)	(5,2)
Boron	s	2.412	2.627
	$2p_x$	0.425	0.531
	$2p_y$	0.425	0.531
	$2p_z$	0.319	0.492
Total		3.581	4.181
Fluorine	s	3.983	3.848
	$2p_x$	1.667	1.698
	$2p_y$	1.929	1.891
	$2p_z$	1.894	1.835
Total		9.473	9.272
B–F	σ	0.455	0.600
	π	0.114	0.138
F–F	σ	−0.040	−0.013
	π	−0.003	−0.001

2. *Charge Distribution*

The gross atomic and overlap electronic population of boron trifluoride is reproduced in Table 2. It is clear that, on bonding, there is a marked flow of electrons from boron to fluorine which produces a net positive charge of 1.419 units on boron. This results from the transfer of 0.579 σ electrons from boron to each fluorine and an overall flow of 0.318 π electrons in the reverse direction.

The latter figure agrees well with the π charge (0.309) predicted by Armstrong and Perkins [2] in the "π only" calculation. It is encouraging that semi-empirical SCF methods may lead to reasonable results for a charge distribution, and adds weight to the same conclusion which was reached in a recent paper [1].

If two electrons are assigned to the boron 1s orbital then the configuration of the second boron quantum level is $2s^{0.412}\,2p_x^{0.425}\,2p_y^{0.425}\,2p_z^{0.318}$. Although the $2p_x$ and $2p_y$ orbitals of boron are equally occupied, the configuration of this element is far from the simple "sp^2 hybrid" pattern which is generally assumed for trigonal boron compounds.

A survey of the bond order components reveals that, as would be expected, the boron-fluorine interactions lead to strong bonding. The F–F components are however slightly antibonding.

3. *Equilibrium* B–F *Bond Length*

The equilibrium B–F bond length was obtained by carrying out a series of calculations with a (5,2) basis set. The resultant energy curve (Fig. 1) exhibits a minimum at a B–F length equal to 1.306 Å. This result is in very good agreement with the experimental value of 1.31 Å [13]. The latter should be larger because of the zero-point energy.

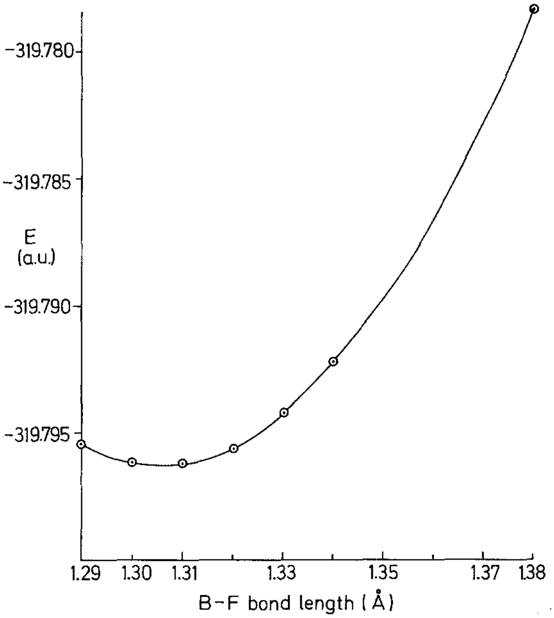

Fig. 1. Variation of the energy of BF_3 with B–F bond length

4. *Reorganisation and π Bond Localisation Energies of Boron Trifluoride*

For boron trifluoride the overall reorganisation process involves a transformation from a planar trigonal to a pyramidal structure in which the interatomic distances increase and the F–B–F angles decrease. The nett energy associated with this process incorporates two terms which are the changes in (*a*) the B–F π

Table 3. *The molecular and orbital energies of the pyramidal and localised models of* BF_3

	Pyramidal BF_3		Localised BF_3	
Basis set	(7,3)	(5,2)	(7,3)	(5,2)
Empty orbitals	0.7175 (a_1)	2.1623 (a_1)	0.7655 (e')	2.1088 (a'_1)
	0.7013 (e)	1.0980 (e)	0.6616 (a'_1)	1.1268 (e')
	0.4910 (a_1)	1.0551 (a_1)	0.5330 (a''_2)	0.9994 (a''_2)
	0.3526 (a_1)	0.5792 (a_1)	0.3604 (e')	0.5721 (e')
	0.3040 (e)	0.4818 (e)	0.1889 (a'_1)	0.4195 (a'_1)
	0.0090 (a_1)	0.1020 (a_1)	$-$ 0.1250 (a''_2)	$-$ 0.0741 (a''_2)
Filled orbitals	$-$ 0.6461 (a_2)	$-$ 0.5479 (a_2)	$-$ 0.6546 (a'_2)	$-$ 0.5363 (a'_2)
	$-$ 0.6586 (e)	$-$ 0.5602 (e)	$-$ 0.6837 (e')	$-$ 0.5731 (e')
	$-$ 0.6808 (e)	$-$ 0.5776 (e)	$-$ 0.7026 (e'')	$-$ 0.5885 (e'')
	$-$ 0.7445 (a_1)	$-$ 0.6611 (a_1)	$-$ 0.7338 (a''_2)	$-$ 0.6047 (a''_2)
	$-$ 0.7885 (e)	$-$ 0.6923 (e)	$-$ 0.8104 (e')	$-$ 0.6973 (e')
	$-$ 0.8520 (a_1)	$-$ 0.7654 (a_1)	$-$ 0.8542 (a'_1)	$-$ 0.7487 (a'_1)
	$-$ 1.6495 (e)	$-$ 1.6203 (e)	$-$ 1.6790 (e')	$-$ 1.6332 (e')
	$-$ 1.7068 (a_1)	$-$ 1.6744 (a_1)	$-$ 1.1248 (a'_1)	$-$ 1.6755 (a'_1)
	$-$ 7.8575 (a_1)	$-$ 7.7820 (a_1)	$-$ 7.8778 (a'_1)	$-$ 7.7998 (a'_1)
	$-$ 26.3648 (e)	$-$ 26.4044 (e)	$-$ 26.3598 (a'_1)	$-$ 26.3668 (a'_1)
	$-$ 26.3649 (a_1)	$-$ 26.4051 (a_1)	$-$ 26.3599 (e')	$-$ 26.3669 (e')
Electronic energy	$-$432.629200	$-$429.956138	$-$433.576497	$-$430.841279
Nuclear energy	110.231701	110.231701	111.204919	111.204919
Total energy	$-$322.397499	$-$319.724437	$-$322.371578	$-$319.636360

energy and (*b*) the B–F σ energy. Although it is obvious that (*a*) will lead to situation of lower stability, the direction of change (*b*) is less clear and indeed cannot be assessed experimentally. This is because in a B–F bond the σ component cannot be dissociated from the π contribution. We can however *calculate* both the overall reorganisation energy and the "vertical" π bond or *localisation* energy, *ab initio* by the POLYATOM method. In the latter calculation the π electrons are artificially restricted to the fluorine atoms and so take no part whatsoever in the bonding. The increase in energy of this "localised" model yields the "vertical" reorganisation energy directly. Further calculations, on localised or non-localised models, in which the bond angles or lengths are varied by degrees yield a complete analysis of the reorganisation process and reveal which factors are the most potent therein.

Table 3 lists the total and orbital energies of both the localised and the pyramidal models of boron trifluoride. In the former the B–F bond length was taken as 1.31 Å whilst for the latter the geometrical parameters were abstracted from data appertaining to the crystal structure of $BF_3 \cdot NH_3$ [11]. The results from the (7,3) basis show, first, that pyramidal BF_3 is less stable than the planar form by 34.2 kcal mole^{-1}. Furthermore (Table 3) the planar localised model is also less stable by 50.4 kcal mole^{-1}. The latter figure is in remarkably good agreement with a value of 56.7 kcal mole^{-1} calculated previously [2]. Since the localisation energy is greater than the total reorganisation energy it is clear that the lengthening and bending of the σ bonds is a factor which helps stabilise the pyramidal form and partially offsets the loss of π energy on reorganisation. The energy recovered in this way amounts to 16.2 kcal mole^{-1}.

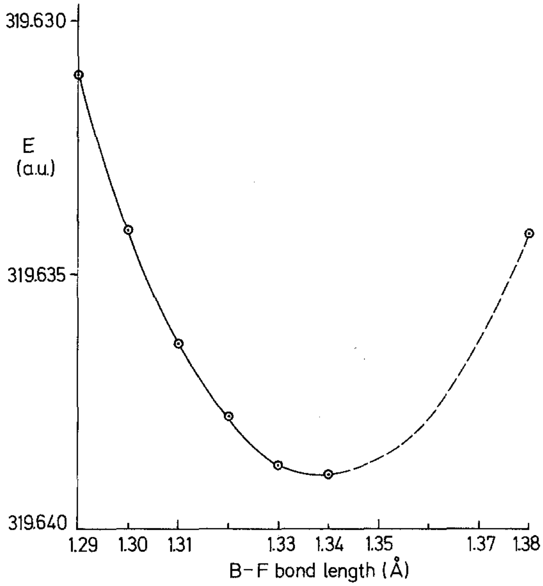

Fig. 2. Variation of energy of BF_3 with B–F bond length (π electrons localised)

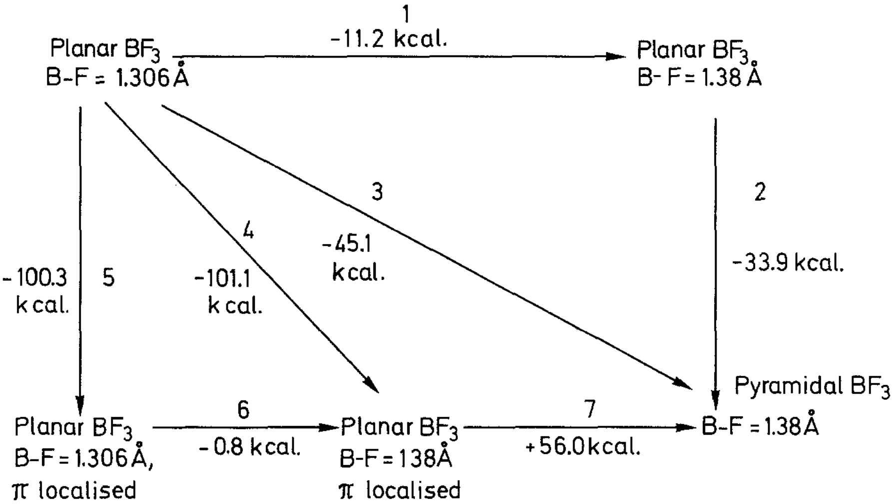

Fig. 3. Thermodynamic cycle for reorganisation of BF_3

It is of some interest to enquire into whether the origin of the gain in σ bonding energy lies in the stretching of the σ bonds or in the decrease in F–B–F angle. In order to throw light on this we carried out a series of calculations on the localised model using the (5,2) basis set and varying the B–F bond distance. The curve produced is shown in Fig. 2 and exhibits a minimum near 1.34 Å. Sufficient information is now available to allow a comprehensive energy cycle to be constructed (Fig. 3) showing a series of hypothetical steps in the reorganisation process. (The energies written into the cycle are all derived from the (5,2) basis set.) Step (1) involves only the stretching of the B–F bond: this results in loss of π bonding energy and, *overall*, a small amount of σ bonding energy. Actually bond stretching at first increases σ bonding energy as is clearly shown by Fig. 2 where for the localised model a gain of 2.2 kcal mole^{-1} results when the B–F bonds increase from 1.31 Å to $\sim$1.34 Å. Further extension however cancels this gain in bonding energy and there is a nett loss of $\sim$0.8 kcal mole^{-1} (stage (6)) at a B–F distance of 1.38 Å. The most important step is number (7) which shows that there is a substantial regain in σ energy on transforming the molecule to the pyramidal form. The gain stems from interaction of the $2p_z$ orbital, which is rendered non-bonding by localisation of the π electrons, with both s and p orbitals on fluorine in the C_{3v} model.

In summary it seems that the important energy contributions on reorganisation of boron trifluoride are firstly loss of π bonding energy and secondly the regain of σ energy from the new $\sigma - \pi$ interactions.

The only other previous *ab initio* calculation of total reorganisation energy was made for borane [3] which, using a comparable (7,3), basis set, yielded a value of 12.5 kcal mole^{-1}. It is interesting to compare the two situations because, for BH_3, σ bonding energy decreases when the pyramidal form is assumed whereas for BF_3, as shown above, there is a decrease in π stabilisation energy coupled with an increase in σ energy for the same process. The overall energy changes are, nevertheless, in the same sense and their relative magnitudes reflect to some extent the difference in the electron acceptor strengths of the two compounds. This is, however, not the only factor governing the thermodynamics of donor-acceptor complex formation because, subsequent to reorganisation, the acceptor moiety must receive as a whole (*i. e.* not the boron atom only) negative charge from the donor. Normally, however, this charge does not amount to one whole electron *e.g.* BH_3 accepts 0.246 electrons from NH_3 in the complex $BH_3 \cdot NH_3$ [3]. The thermodynamics of the donor-acceptor reaction will thus critically depend on the electron affinities of the acceptor molecule. If these parameters are compared for planar and pyramidal BH_3 and BF_3 a surprising effect is revealed: whereas for the planar compound the values are $+1.69$ eV and $+4.54$ eV (Koopmans' theorem [12]) for BH_3 and BF_3 respectively (*i.e.* the compounds repel electrons) the electron affinities of the corresponding *pyramidal* forms are $+0.25$ and $+1.09$ eV. There is thus a dramatic increase in the electron affinity of BF_3 from $+4.54$ to $+0.25$ eV whilst that of BH_3 only increases to $+1,09$ eV.

Hence the limiting situations of reorganisation to a pyramidal form with F–B–F angles of 111° and acceptance by this unit of one whole electron from the donor are associated with the following energy changes.

$$BF_3\,(\text{planar}) \longrightarrow BF_3\,(\text{pyramidal}) \qquad -\Delta H_g = -34.2\ \text{kcal mole}^{-1},$$

$$BF_3\,(\text{pyramidal}) \xrightarrow{+\varepsilon} BF_3^-\,(\text{pyramidal}) \qquad -\Delta H_g = -5.6\ \text{kcal mole}^{-1},$$

$$BH_3\,(\text{planar}) \longrightarrow BH_3\,(\text{pyramidal}) \qquad -\Delta H_g = -12.5\ \text{kcal mole}^{-1},$$

$$BH_3\,(\text{pyramidal}) \xrightarrow{+\varepsilon} BH_3^-\,(\text{pyramidal}) \qquad -\Delta H_g = -25.1\ \text{kcal mole}^{-1}.$$

Thus the overall changes in these processes require 39.8 and 37.6 kcal mole^{-1}. (These energies are of course only correlatable with heats of reaction at the absolute zero since in the calculation no molecular vibrational or rotational energy was included.) The energy which must be supplied for these hypothetical processes is regained in the form of the intrinsic bond dissociation energy of the donor-acceptor bond. If this quantity is assumed to remain constant for a given donor then it is not difficult to understand why the coordination complexes of BH_3 and BF_3 frequently have similar stability. Variations between the two series of adducts are then attributable to subtle factors such as (*a*) bonding interactions between the hydrogen atoms of BH_3 and empty orbitals of the ligand (as in $BH_3 \cdot CO$ [3]) (*b*) steric effects brought about by bulky ligand molecules and (*c*) the degree of transfer of charge from the donor to the BX_3 group.

With respect to complexes with carbon monoxide it is interesting to consider possible reasons for the non-formation of $BF_3 \cdot CO$ at room temperature. If we write a gas-phase cycle with energies abstracted from work on borane carbonyl [3].

$$\begin{tikzcd}
BH_3 \cdot CO \arrow[r, "-\Delta H_D"] & BH_3\text{ (pyramidal)} + CO \arrow[r, "+12.5\text{ kcal.}"] & BH_3\text{ (planar)} + CO \arrow[ll, bend left, "-\Delta H_g + 22.7\text{ kcal.}"]
\end{tikzcd}$$

From this the intrinsic bond dissociation energy $(-\Delta H_D)$ of the B–C bond is 35.2 kcal mole^{-1}. If the cycle is now rewritten with BF_3 substituted for BH_3 and we suppose further that the intrinsic bond dissociation energy of the B–C bond in $BF_3 \cdot CO$ is the same as in $BH_3 \cdot CO$, then the heat of formation of $BF_3 \cdot CO$, $-\Delta H_g$, at the absolute zero is ~ 1 kcal mole^{-1}.

$$\begin{tikzcd}
BF_3 \cdot CO \arrow[r, "-35.2\text{ kcal.}"] & BF_3\text{ (pyramidal)} + CO \arrow[r, "+34.2\text{ kcal.}"] & BF_3\text{ (planar)} + CO \arrow[ll, bend left, "-\Delta H_g\ 1\text{ kcal.}"]
\end{tikzcd}$$

The doubtful assumption here is whether it is correct to assume a constant intrinsic bond dissociation energy for the B–C bond. Greenwood and Wade [10] have shown that, for coordination compounds of Ga and Al halides, the intrinsic N→Ga, N→Al, O→Ga and O→Al bond dissociation energies are remarkably similar for several different ligands and acceptors containing these atoms. Even pronounced steric and electronic effects such as change of ligand from methyl amine to trimethylamine or quinuclidine only affect the intrinsic bond dissociation energy by ~ 10 kcal mole^{-1}. Correction of the value for $-\Delta H_g$ at 0° K to 300° K will increase it to 2–3 kcal mole^{-1} and since the entropy of the association reaction will amount to 10–15 e.u. we have

$$-\Delta G = \sim 2000 - 300\,(\sim 10)$$

i.e. the free energy is zero or negative. This implies that the complex is unstable with respect to dissociation into BF_3 and CO.

Table 4. *Gross atomic and overlap population of the pyramidal and localised models of* BF_3

Basis set		Pyramidal BF_3		Localised BF_3	
		(7,3)	(5,2)	(7,3)	(5,2)
Boron	s	2.447	2.690	2.445	2.666
	$2p_x$	0.410	0.524	0.464	0.579
	$2p_y$	0.410	0.524	0.464	0.579
	$2p_z$	0.292	0.478	0	0
Total		3.559	4.216	3.373	3.824
Fluorine	s	3.989	3.859	3.985	3.848
	$2p_x$	1.720	1.738	1.634	1.664
	$2p_y$	1.940	1.902	1.923	1.879
	$2p_z$	1.832	1.762	2	2
Total		9.481	9.261	9.542	9.391
B–F	σ	0.535	0.699	0.472	0.615
F–F	σ	−0.050	−0.015	0	0

5. The Energy Levels and Electronic Structure of Localised and Pyramidal Boron Trifluoride

With one exception the eigenvalues of pyramidal BF_3 lie higher in the absolute scale than the corresponding levels of the planar compound. This exceptional orbital is of a_1 symmetry and is largely made up the inner s functions of boron.

The electron distribution (Table 4) is similar to that of the planar system although somewhat more polarized.

For the delocalised model the *occupied* orbitals are on the whole less stable than for the delocalised system. One of those violating this generalisation is of e'' type and is a linear combination of the fluorine $2p_\pi$ orbitals. This is as expected since the π electrons have been restricted to these orbitals in the calculation. Similarly the first virtual orbital (here pure boron $2p_z$) becomes more stable than in "normal" BF_3. The electron distribution (Table 4) shows that the σ component of the localised model is stronger than that in the delocalised system.

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