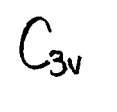
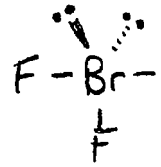
Part C (25 points) **MASTERY QUESTIONS** Answer ONE of the following two questions in the space provided. SHOW ALL YOUR WORK AND WRITE EXPLANATIONS IN COMPLETE SENTENCES.

9. **Answer the following questions for the molecule BrF_3, whose structure is shown below.**

My drawing is wrong! C_{3v}  real geometry is  C_{2v}

a) (6 points) Which orbitals on the F atoms are of correct energy to bond with the central Br atom? Explain briefly.

analogous to NH_3

F	2s −16.1eV	Br	4s −24.1eV
	2p −18.7eV		4p −12.5eV

Only the 2p orbitals on the F atoms are within 10eV of the valence orbitals on Br; therefore, they are the only orbitals that are used in bonding.

b) (7 points) Using the group theoretical approach to bonding, find the irreducible representations for the symmetry adapted linear combinations (SALCs) for the F orbitals that will form sigma (σ) bonds to the central Br.

C_{3v} case

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{p_y}	3	0	1

reduce by inspection: $A_1 + E$

or by reduction formula:

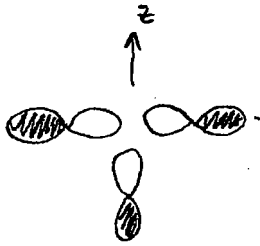
$A_1: \frac{1}{6}[(1)(3)(1)+(2)(0)(1)+3(1)(1)] = 1 \Rightarrow 1A_1$

$A_2: \frac{1}{6}[(1)(3)(1)+(2)(0)(1)+3(1)(-1)] = 0$

$E: \frac{1}{6}[(1)(3)(2)+(2)(0)(-1)+3(1)(0)] = 1 \Rightarrow 1E$

∴ SALCs have A_1 and E symmetries

C_{2v} case



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_{p_y}	3	1	1	3

reduce by inspection: $2A_1 + B_2$

or by reduction formula:

$A_1: \frac{1}{4}[(1)(3)(1)+(1)(1)(1)+(1)(1)(1)+(1)(3)(1)] = 2 \Rightarrow 2A$

$A_2: \frac{1}{4}[(1)(3)(1)+(1)(1)(1)+(1)(1)(-1)+(1)(3)(-1)] = 0$

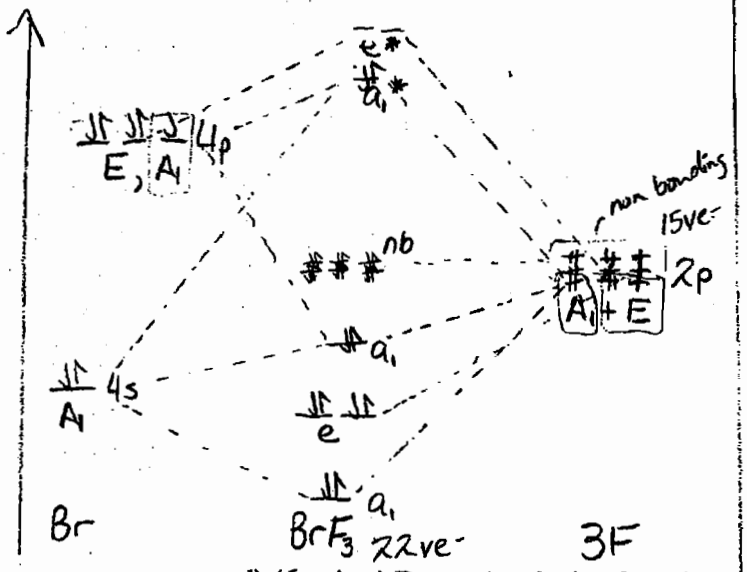
$B_1: \frac{1}{4}[(1)(3)(1)+(1)(1)(-1)+(1)(1)(1)+(1)(3)(-1)] = 0$

$B_2: \frac{1}{4}[(1)(3)(1)+(1)(1)(-1)+(1)(1)(-1)+(1)(3)(1)] = 1 \Rightarrow B_2$

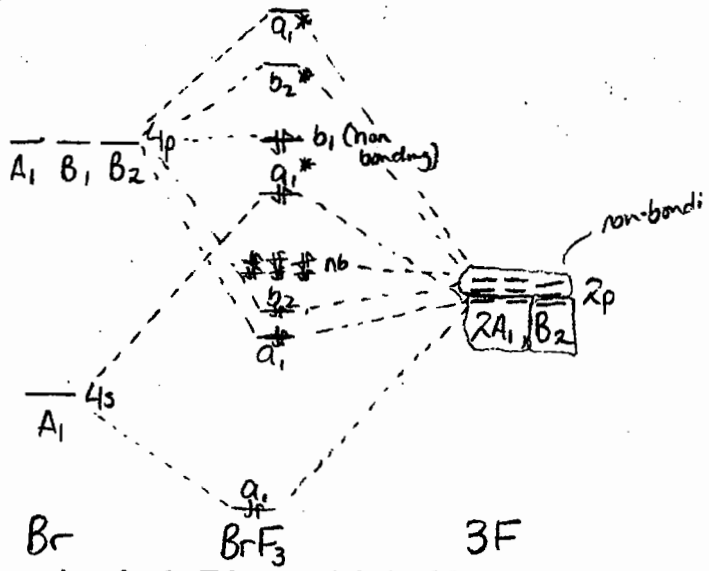
∴ SALCs have $2A_1$ and B_2 symmetry

c) (6 points) Use the SALCs you generated above to construct a qualitative molecular orbital diagram for the sigma (σ) bonds in BrF_3.

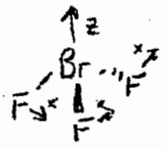
C_{3v} case



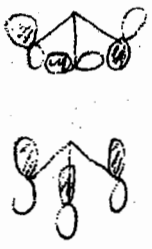
C_{2v} case



d) (6 points) Determine the irreducible representations for the F 2p orbital-derived SALCs that can form pi (π) bonds to the central Br and state which orbitals on the central Br interact with the SALCs.



C_{3v} case



C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{px}	3	0	-1
Γ_{pz}	3	0	1

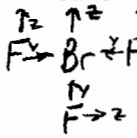
reduce by inspection:

$\Gamma_{px} = A_2 + E$

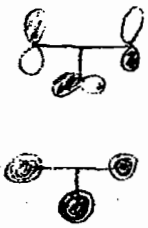
$\Gamma_{pz} = A_1 + E$

} π symmetry SALCs

Br has no remaining 4p orbitals to interact with π SALCs. The Br 4d orbitals ($d_{x^2-y^2}$, d_{xy}) and (d_{xz}, d_{yz}) will interact with the two E symmetry sALCs E_{px} and E_{pz}, respectively. d_{z^2} will interact w/ the A_1 SALC.



C_{2v} case



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_{pz}	3	-1	-1	3
Γ_{px}	3	-1	1	-3

reduce by inspection:

$\Gamma_{pz} = 2B_2 + A_1$

$\Gamma_{px} = 2B_1 + A_2$

One of the B_1 SALCs can interact with the remaining B_1 symmetry Br 4p orbital (p_x). d orbitals on Br can also interact