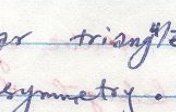
Chapter 4

AB_3 Systems

BORON TRIFLUORIDE BF_3 (From: B. Douglas, p. 154)

Group theory is more needed in more complex molecular structures.

BF_3 is a planar triangular molecule with a D_{3h} symmetry.

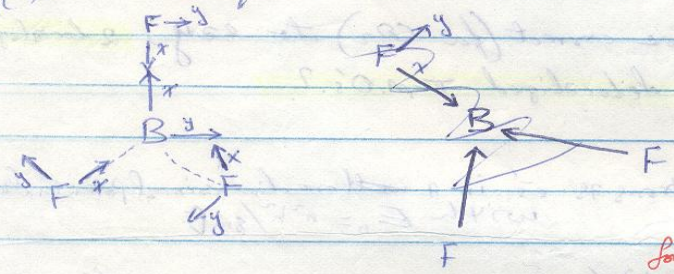


(Other bonding descriptions are also similar, CO_3^{-2}, NO_3^- which are isoelectronic to BF_3.

~~Arbitrarily~~, z-axis is C_3 axis of B,

but for F atoms, z-axes are ~~directed to B~~ parallel to $C_{3(z)}$

((axes must fit with those in character table))



For Boron atom

2s z → a_1'

$2p_z$ z → a_2''

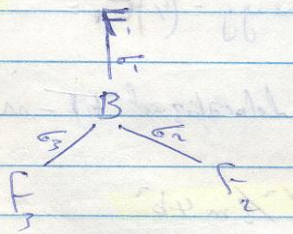
$2p_x$ x → E'

$2p_y$ y → E'

From D_{3h} character table,

Sigma Bonding:

First, construct a basis upon which symmetry operations are to be ~~ppp~~ performed;



(~~See page~~

D_{3h} | for character table, see page (122)

Apply symm. operations of D_{3h} on the basis, σ_1, σ_2 & σ_3

$E \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} 1&0&0 \\ 0&1&0 \\ 0&0&1 \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix}$ $\therefore \chi = 3$

$C_3 \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} 0&1&0 \\ 0&0&1 \\ 1&0&0 \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} \sigma_2 \\ \sigma_3 \\ \sigma_1 \end{pmatrix}$ $\chi = 0$

$C_2^{(1)} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} 1&0&0 \\ 0&0&1 \\ 0&1&0 \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} \sigma_1 \\ \sigma_3 \\ \sigma_2 \end{pmatrix}$ $\chi = 1$

$\vdots$

$\sigma_h \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} 1&0&0 \\ 0&1&0 \\ 0&0&1 \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix}$ $\chi = 3$

$S_3 \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} 0&1&0 \\ 0&0&1 \\ 1&0&0 \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} \sigma_2 \\ \sigma_3 \\ \sigma_1 \end{pmatrix}$ $\chi = 0$

$\sigma_v^{(1)} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} 1&0&0 \\ 0&0&1 \\ 0&1&0 \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = \begin{pmatrix} \sigma_1 \\ \sigma_3 \\ \sigma_2 \end{pmatrix}$ $\chi = 1$

$\vdots$

Or we may find the # of unmoved objects to get the character

D_{3h}	E	C_3	C_2	σ_h	S_3	σ_v
Γ_σ	3	0	1	3	0	1

thus,

thus, a reducible representation is produced for the bases of σ-bonds, thus, it can be reduced into its irreducible representations,

$\therefore \boxed{\Gamma_\sigma = A_1' + E'}$ are the symmetries of the L.G.O's.

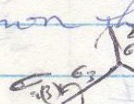
which orbitals of Boron belong to A_1' & E' ??

from D_{3h} character table, we find that (2s (a_1')) and ($2p_x, 2p_y$ (E')) do, with their symmetry labels written.

Then we form the Ligand Group Orbitals, which fit to a_1' & e'.

We use the projection operator method.

on F σ orbital is chosen, and perform every symmetry operation (not only one of each class) on it, and then write down the result. Consider, σ_1;



E C_3 C_3^2 $(C_2)_1$ $(C_2)_2$ $(C_2)_3$ σ_h S_3 S_3^2 σ_v σ_v' σ_v''

$\sigma_1 \rightarrow \sigma_1$ σ_2 σ_3 σ_1 σ_3 σ_2 σ_1 σ_2 σ_3 σ_1 σ_3 σ_2

to find L.C. of F σ orbitals belonging to A_1' representation, multiply each orbital generated by the character of A_1' for the operation used.

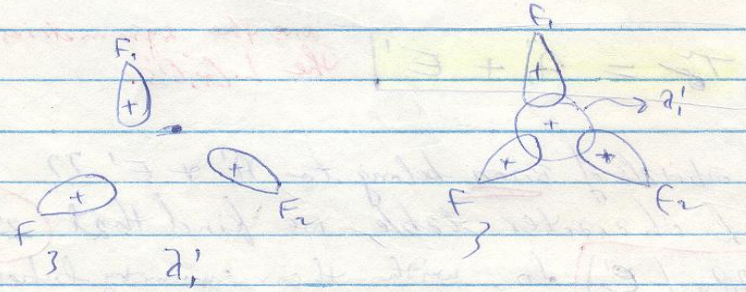
Above are (+1)

& add & then divide by 4 to simplify coefficients;

$$\frac{4}{6}\psi_{a_1'} = 4\sigma_1 + 4\sigma_2 + 4\sigma_3 \equiv \sigma_1 + \sigma_2 + \sigma_3$$

$\therefore$ wavefunction for this F-group orbital is normalized L.C.A.O.

$$\psi_{a_1'} = \frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3)$$



to find the other group orbital e', so we multiply the σ orbitals generated previously by the respective characters for (E') to give:

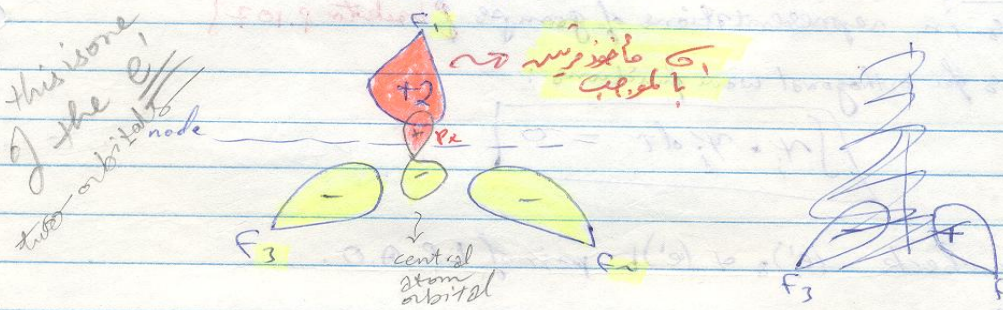
$\chi_{\sigma_{e'}} \Rightarrow +2\sigma_1 - \sigma_2 - \sigma_3 + 0 + 0 + 0 + 2\sigma_1 + \sigma_2 - \sigma_3 + 0 + 0 + 0$

$\chi_{\sigma_{e'}} \Rightarrow 4\sigma_1 - 2\sigma_2 - 2\sigma_3$ or $2\sigma_1 - \sigma_2 - \sigma_3$

and

$\psi_{(\sigma_{e'})_a} = \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3)$ ① this is one of the two e' LGOs

the resulting group orbital has one node



what about the other L.C.A.O. degenerate to this L.C.A.O? it can be found from performance of C_3 & C_3^2 operation on the above L.C.A.O.:

C_3 performing gives: $2\sigma_2 - \sigma_3 - \sigma_1$

C_3^2 " " " : $2\sigma_3 - \sigma_1 - \sigma_2$

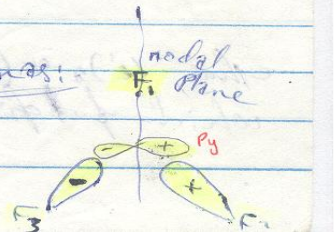
if they are subtracted one from another, then:

$(2\sigma_2 - \sigma_3 - \sigma_1)$

$(-\sigma_2 + 2\sigma_3 - \sigma_1)$

$3\sigma_2 - 3\sigma_3$ or $\sigma_2 - \sigma_3$

$\therefore \psi_{(\sigma_{e'})_b} = \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_3)$ ② draw as:



Orthonormal Wave functions

we must check that the $(\epsilon')_a$ & $(\epsilon')_b$ are basis for E' representation. How ??

A basis set functions must be orthogonal, and normalized if they are orthonormal.

from normalization: $\int \psi^2 d\tau = 1$

orthogonality: scalar product of the functions must be zero.

as in representations of groups {back to p.107}

thus for orthogonal wave functions:

$$\int \psi_i \cdot \psi_j \, d\tau = 0$$

so, to check $(\epsilon')_a$ & $(\epsilon')_b$ pair of L.C.A.O.

$$\int \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3) \cdot \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_3)\, d\tau =$$

$$\frac{1}{\sqrt{12}} \int (2\sigma_1\sigma_2 - 2\sigma_1\sigma_3 - \sigma_2^2 + \sigma_2\sigma_3 - \sigma_3\sigma_2 + \sigma_3^2)\, d\tau$$

But, σ_1, σ_2 & σ_3 are orthonormal atomic wave functions because we start with atomic wave functions that are orthonormal as: $\int \sigma_i \cdot \sigma_j \, d\tau = 0$ (orthogonal), and $\int \sigma_i^2 \, d\tau = 1$ (normalization)

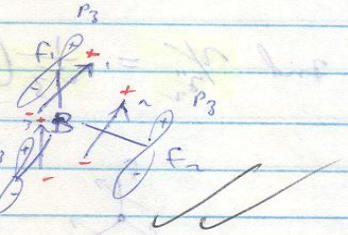
so: $\int \psi_i \psi_j \, d\tau = \frac{1}{\sqrt{12}}[0 - 0 - 1 + 0 - 0 + 1] = 0$

thus, $(\epsilon')_a$ & $(\epsilon')_b$ are an orthonormal pair of functions which fulfill the requirements for E' representation

Pi Bonding

We treat π-bonding similarly

the basis of the three F-atoms are the p_z orbitals, which are perpendicular to molecular plane, thus:



If we perform D_{3h} symm. operations on this basis then:

D_{3h}	E	C_3	C_2	σ_h	S_3	σ_v
Γ_π	3	0	-1	-3	0	1

the Γ_π may be obtained either: i) using matrices or characters
ii) summing the unshifted species

Then, we reduce Γ_π to its irreducible representations using Reduction formula, as:

$$\Gamma_\pi = A_2'' + E''$$

A_2'' goes with (B); E'' → nonbonding,

from D_{3h} character table, we find that from Boron, p_z is belonging to A_2'', thus it is expected to form π-bonds with fluorine atoms, of a_2'' L.G.O.

the e'' group orbitals must be nonbonding, since boron has no orbitals belonging to E''.

Projection Operator method

Thus, the L.C.A.O with a_2'' L.G.O may be found as:

Using all operations on the p_z orbital of one F (π_1) we get:

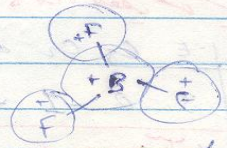
E	C_3	C_3^2	$(C_2)_1$	$(C_2)_2$	$(C_2)_3$	σ_h	S_3	S_3^2	σ_v	σ_v'	σ_v''
$+\pi_1$	$+\pi_2$	$+\pi_3$	$-\pi_1$	$-\pi_3$	$-\pi_2$	$-\pi_1$	$-\pi_2$	$-\pi_3$	$+\pi_1$	$+\pi_3$	$+\pi_2$

If we multiply these by respective characters of B_2'', we get :

$4\pi_1 + 4\pi_2 + 4\pi_3$

or $\pi_1 + \pi_2 + \pi_3$

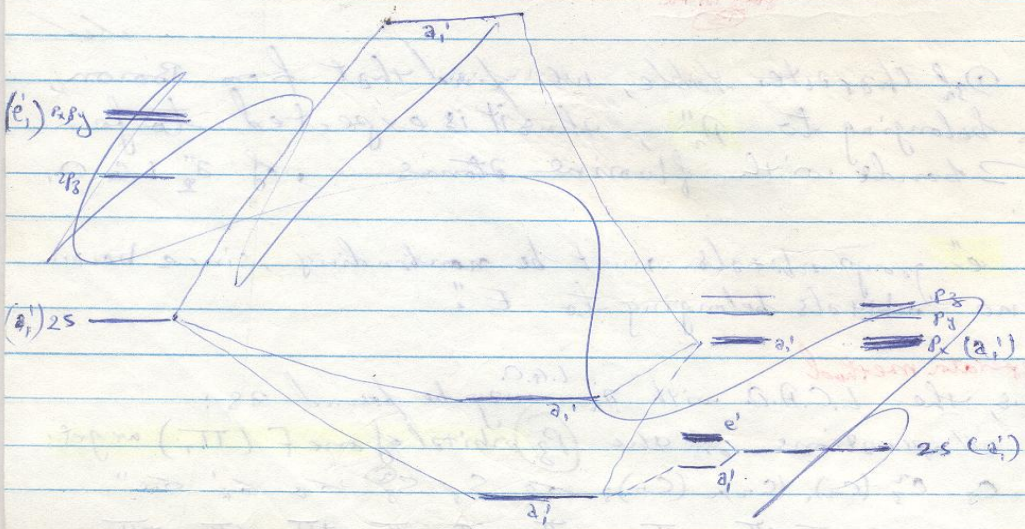
and $\psi_{a_2''} = \frac{1}{\sqrt{3}}(\pi_1 + \pi_2 + \pi_3)$



above view of a_2'' M.O., showing only + lobes

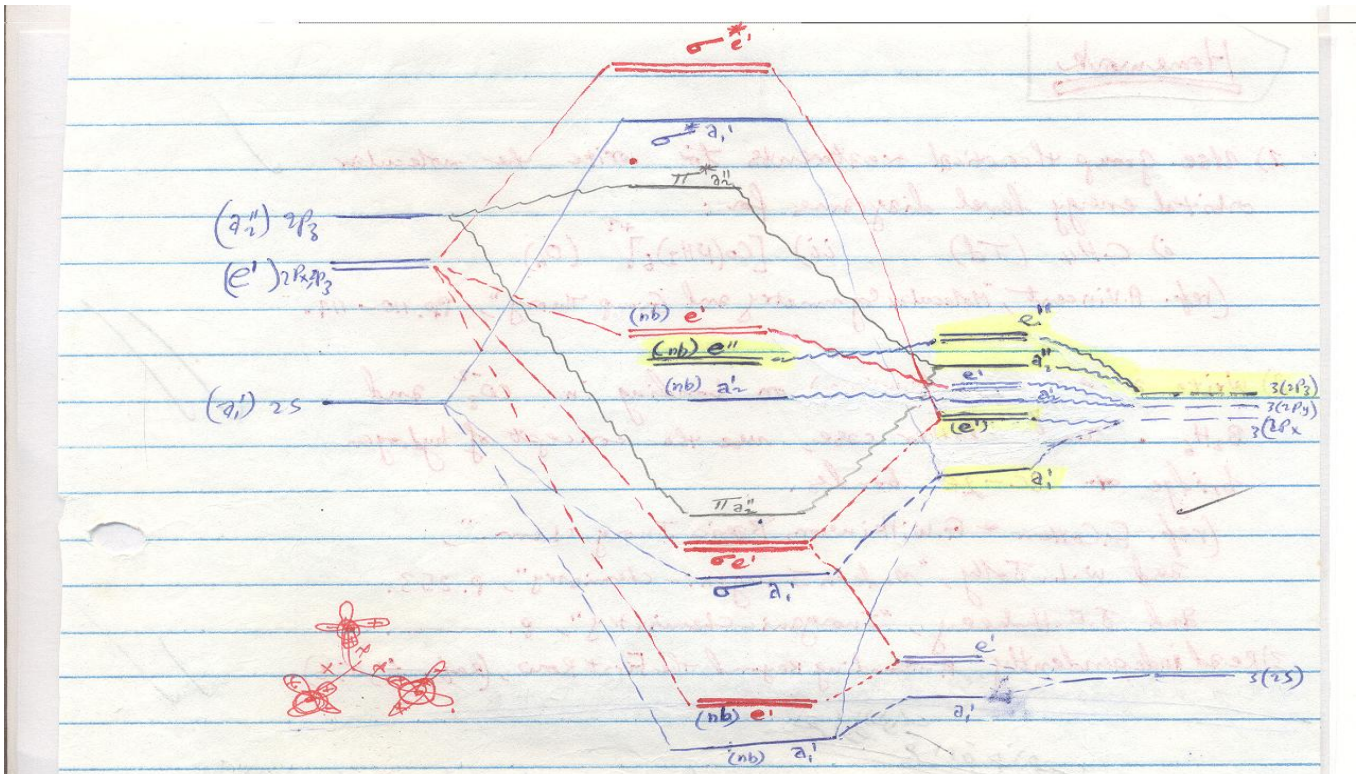
~~do same thing~~

Thus, including, σ, π, (a_2 antibonding, bonding and nonbonding) orbitals, we can construct the M.O. energy level diagram as :



B

3F orbitals



B BF_3 F

Note that

① the figure on page 160 is not clear.

② the 3(2s) orbitals of 3F are giving L.G.Os, as a_1' & e' which go to nonbonding.

③ In each F-atom, the x-axis of the F atom is directed toward Boron atom. the p_x's are split into a_1' and e' $\rightsquigarrow (e')_a + (e')_b$. the a_1' & $e'(e'_{a+b})$ are expected to form $\sigma a_1'$ & $\sigma e'$ bonding (& antibonding) M.Os.

④ 3(2py) of 3F atoms give a_2' & e' which go to nonbonding orbitals.

⑤ e'' of the F ($2p_z$ originally) is nonbonding.

⑥ a_2'' ~~gives~~ (originally from p_z) is forming $\pi_{a_2''}$ & $\pi^*_{a_2''}$.

Homework

1) Use Group theoretical treatments to write the molecular orbital energy level diagrams for:

i) CH_4 (T_d) ii) $[Co(NH_3)_6]^{+3}$ (O_h)

(ref. A. Vincent, "Molecular Symmetry and Group Theory", pp. 110 – 119.

2) Write an essay (qualitative) on bonding in CO_3^{-2} and B_2H_6. In the latter case, use the concept of hydrogen bridge or 3c–2e bonds.

(ref. F. Cotton & G. Wilkinson, "Basic Inorg. chem.",
and W. L. Jolly, "Modern Inorganic chemistry", p. 253.
and J. E. Huheey, "Inorganic Chemistry", p. ——.

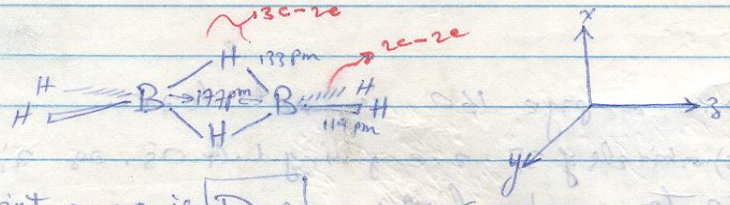
3) Read independently p_i-Bonding beyond the First Row, (Ref. 4, 5, 6)

4) Do independently Diborane D_2H_6

Diborane (((in the bridging orbitals only)))

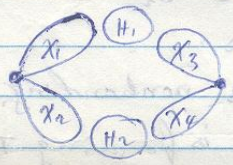
BH_3 exists as a dimer, because it is e⁻-deficient

thus, B_2H_6 is formed as: (note the arrangement



the point group is D_{2h}

directions are arbitrary (no individual main axis),
each boron is tetrahedrally surrounded by 4 H's.
for simplicity use sp^3 boron orbitals



Representations for Boron & Hydrogen Orbitals:

~~perform~~ use orbitals of B and of H (separately) as bases for the reducible representation Γ_S:

D_{3h}	E	$C_2(3)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}
Γ_{Borons}	4	0	0	0	0	0	4	0
Γ_{H_s}	2	0	0	2	0	2	2	0

Reduction gives: $\Gamma_{Borons} = A_g + B_{2g} + B_{1u} + B_{2u}$

$\Gamma_{H_s} = A_g + B_{2u}$

$\therefore$ $B_{2g} + B_{1u}$ of Borons must be nonbonding

Group Orbitals:

We obtain L.C.A.O. for the group orbitals by using the projection operator as:

D_{4h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}
X_1	X_1	X_2	X_4	X_3	X_4	X_3	X_1	X_2
H_1	H_1	H_2	H_2	H_1	H_2	H_1	H_1	H_2

multiplying by the respective characters of the representations involved produces the following L.C.A.O., after normalizing

a_g $\quad 2X_1+2X_2+2X_3+2X_4$ $\quad \therefore \psi_{a_g} = \frac{1}{\sqrt{4}}(X_1+X_2+X_3+X_4)$

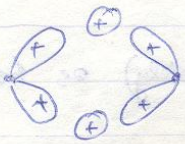
b_{2g} $\quad 2X_1-2X_2-2X_3+2X_4$ $\quad \therefore \psi_{b_{2g}} = \frac{1}{\sqrt{4}}(X_1-X_2-X_3+X_4)$

b_{1u} $\quad 2X_1+2X_2-2X_3-2X_4$ $\quad \therefore \psi_{b_{1u}} = \frac{1}{\sqrt{4}}(X_1+X_2-X_3-X_4)$

b_{2u} $\quad 2X_1-2X_2+2X_3-2X_4$ $\quad \therefore \psi_{b_{2u}} = \frac{1}{\sqrt{4}}(X_1-X_2+X_3-X_4)$

$a_g = 4H_1+4H_2$ $\quad \therefore \psi_{a_g} = \frac{1}{\sqrt{2}}(H_1+H_2)$

b_{2u} $\quad 4H_1-4H_2$ $\quad \therefore \psi_{b_{2u}} = \frac{1}{\sqrt{2}}(H_1-H_2)$



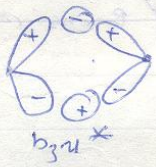
a_g

a_g^*

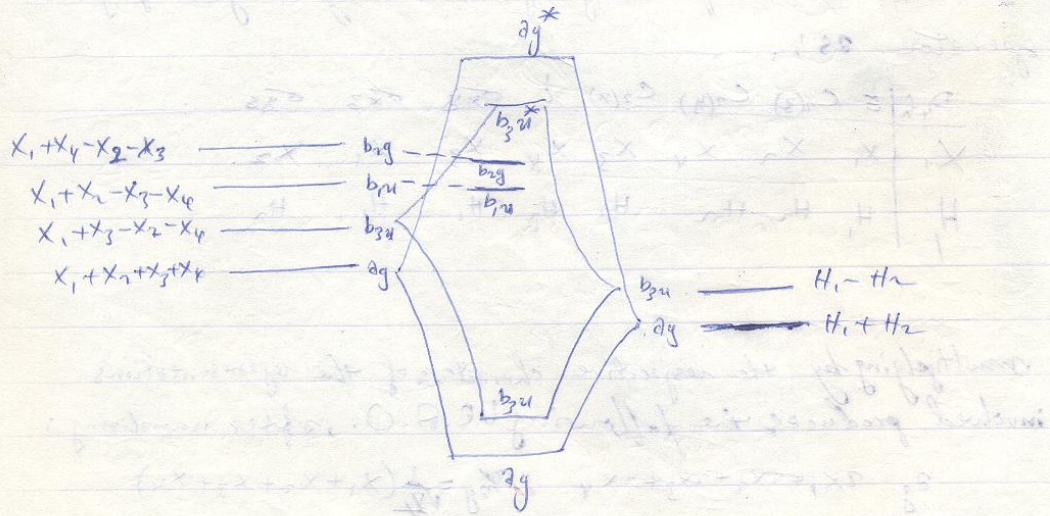
b_{1u}

b_{2g}

b_{3u}



b_{3u}^*



B_2H_6