Chemistry 65.354 Problem Set 3.

1. Draw the symmetry labelled σ- and π-bonding MO scheme for BBr_3.

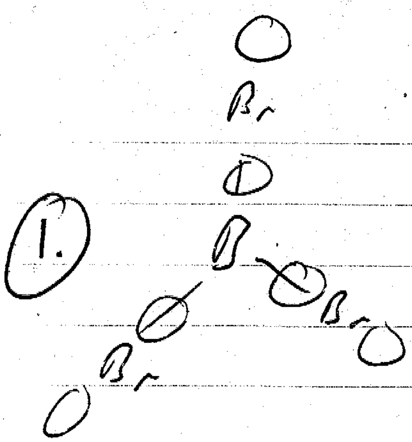
2. Determine the LCAO's of π symmetry for $C_4H_4^{2-}$. The $C_2H_4^{2-}$ dianion is aromatic and is described by the D_{4h} point group. Draw the π-bonding MO scheme (rank the LCAO orbitals according to their relative energies)

3. Draw the symmetry labelled σ-bonding only MO scheme for *cis*-dibromodichloroplatinate(II)

GS. 354

PROB SET 3

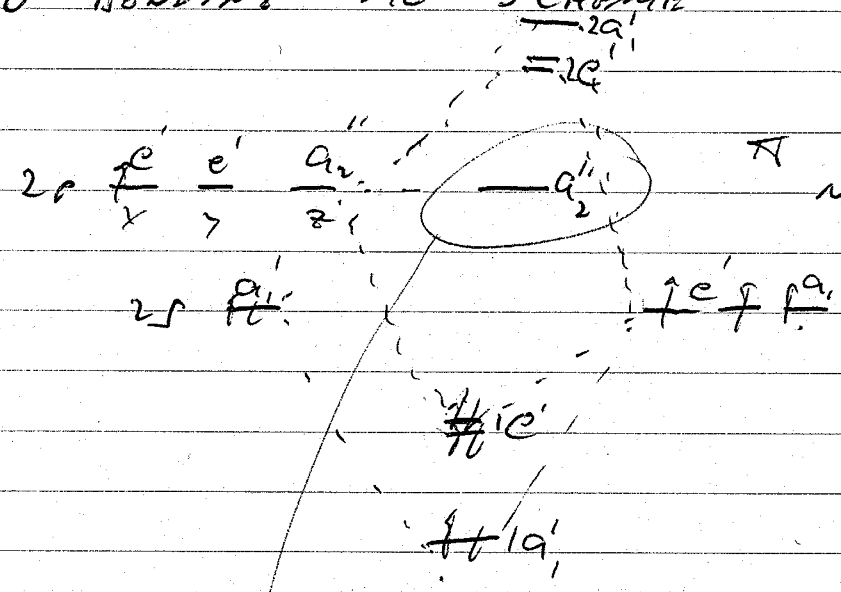
(1.)



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{LCAO\ \sigma\text{-}p}$	3	0	1	3	0	1

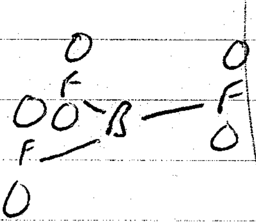
$$\Gamma_{LCAO\ \sigma} = a_1' + e'$$

σ BONDING MO SCHEME



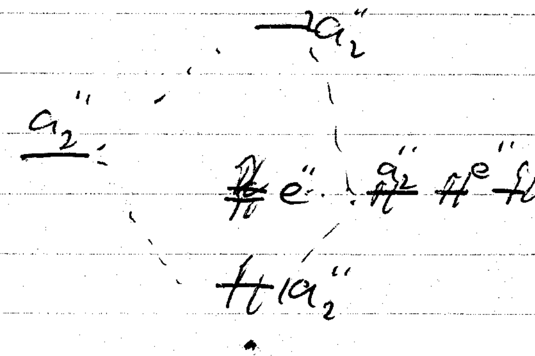
π SYMMETRY SO NON-BONDING IN σ BOND MO SCHEME

π BONDING



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{LCAO\ \pi}$	3	0	-1	-3	0	1

$$\Gamma_{LCAO\ \pi} = a_2'' + e''$$



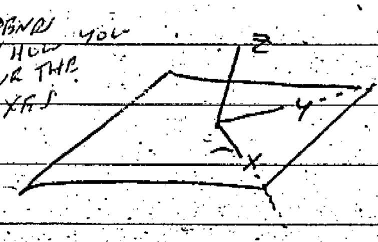
CHEM 354*

ANSWERS TO PROBLEM SET

(2)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{LCAO}	4	0	0	-2	0	0	0	-4	2	0

SMALL LETTERS — OR b_{1u} — DEPENDING ON HOW YOU DEFINE THE AXES



$$\Gamma_{LCAO} = e_g + a_{2u} + b_{2u}$$

	E	C_4^1	C_4^3	C_2
FOR ϕ_a	ϕ_a	ϕ_b	ϕ_d	ϕ_c
ϕ_b	ϕ_b	ϕ_c	ϕ_a	ϕ_d
ϕ_c	ϕ_c	ϕ_d	ϕ_b	ϕ_a
ϕ_d	ϕ_d	ϕ_a	ϕ_c	ϕ_b

→ (THE REST OF THE OPERATIONS ARE REDUNDANT)

NOW MULT. THE LCAO BY THE IRREDUCIBLE REP. OF e_g, a_{2u} OR b_{2u}

a_{2u}

$$\psi = \tfrac{1}{2}(\phi_a + \phi_b + \phi_c + \phi_d)$$

b_{2u} $\psi = \frac{1}{2}(\phi_a - \phi_b + \phi_c - \phi_d)$

e_g

$\psi_1 = 1/\sqrt{2}\,(\phi_a - \phi_c)$

$\psi_2 = 1/\sqrt{2}\,(\phi_b - \phi_d)$

EXTRA

BY SUBTRACTING + ADDING THESE TWO LCAO WE CAN CREATE E_g LCAO'S THAT INVOLVE ALL ATOMIC ORBITALS

ADD $\psi_1 + \psi_2$ + NORMALIZE GET

$$\psi = \frac{1}{2}(\phi_a + \phi_b - \phi_c - \phi_d)$$

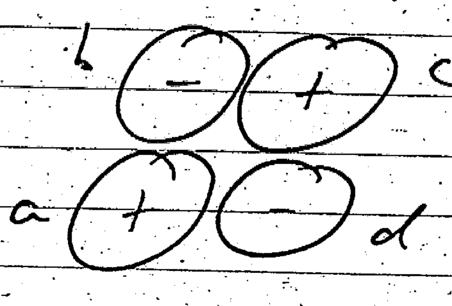
SUBTR. $\psi_1 - \psi_2$

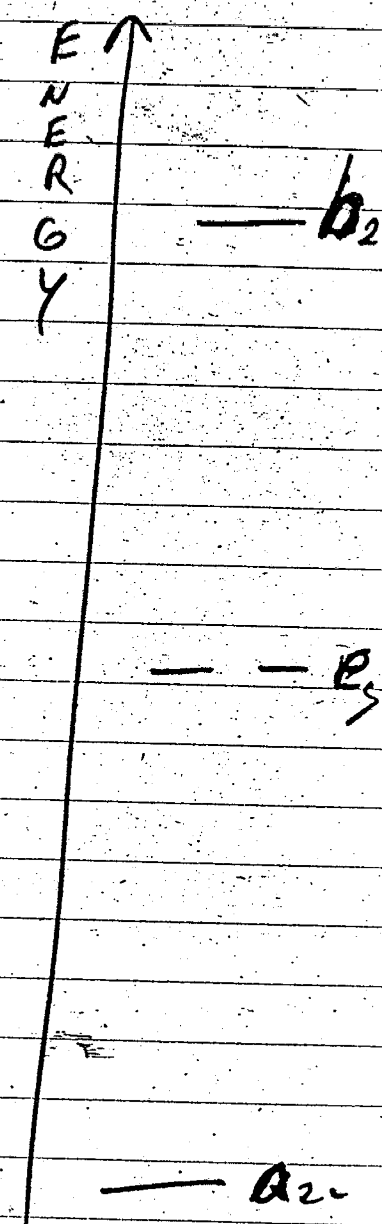
$$= \frac{1}{2}(\phi_a - \phi_b - \phi_c + \phi_d)$$

[redacted]

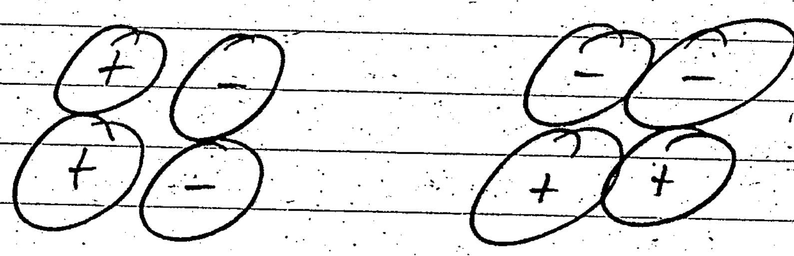
How will these LCAO's look

ANTIBONDING b_{2u}

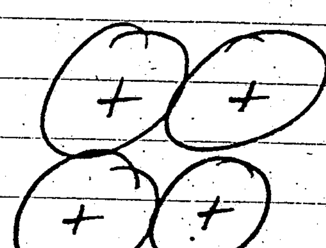




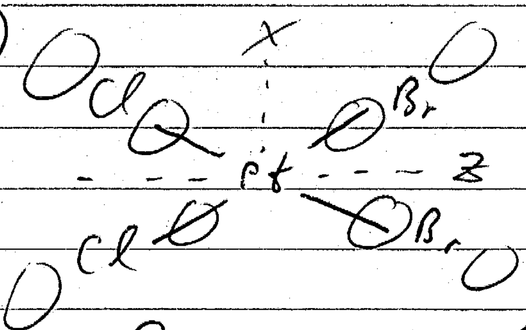
NON BONDING e_g



BONDING a_{2u}



(3.)

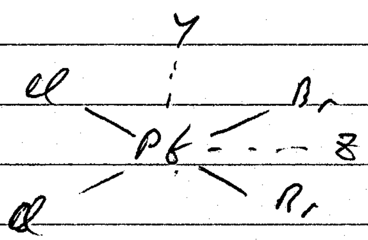


Y AXIS IS ⊥ TO THE PLANE OF THE COMPLEX

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_{LCAO}	4	0	4	0

$$\Gamma_{LCAO\,\sigma} = 2a_1 + 2b_1$$

IF YOU LABELLED DIFFERENTLY

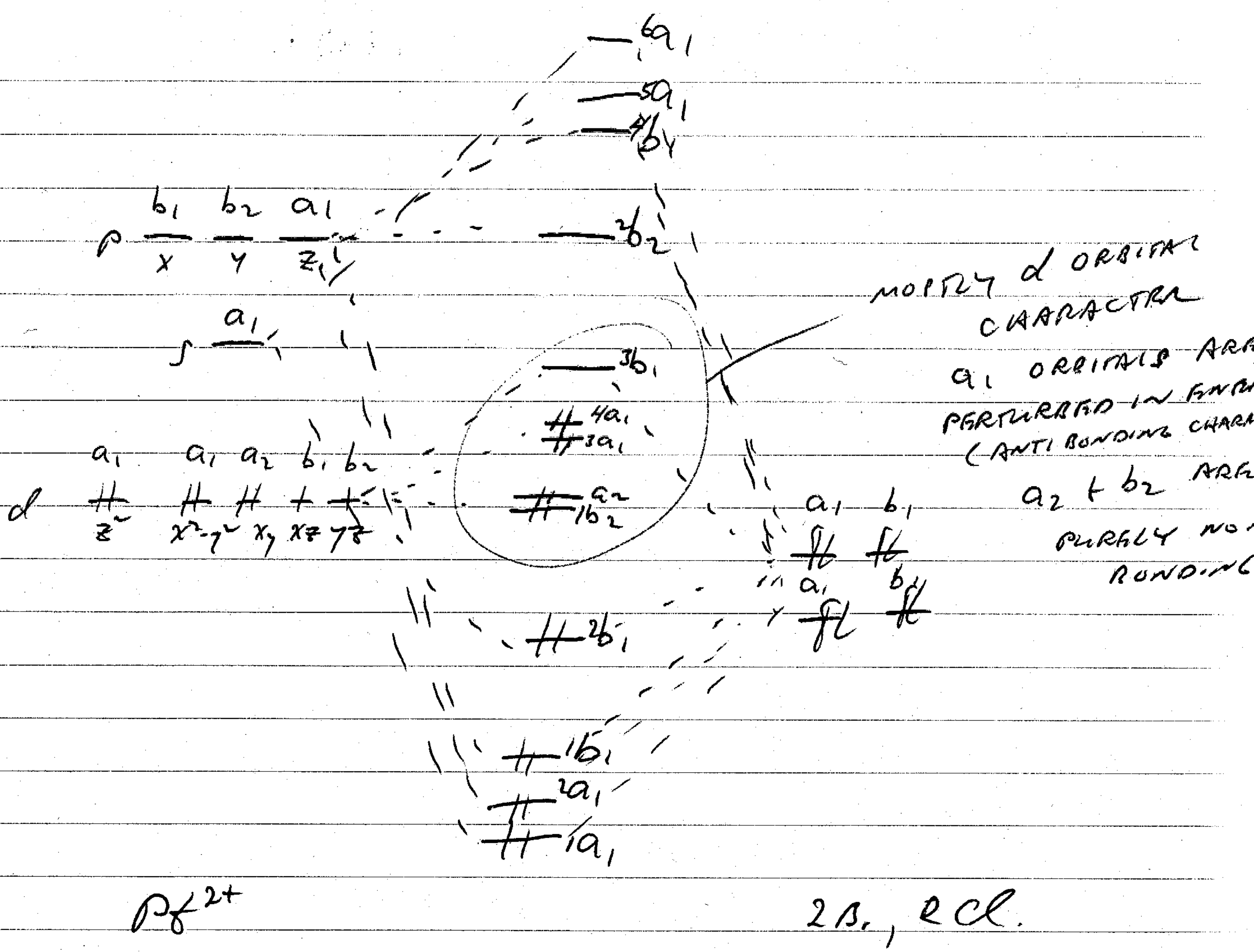


X AXIS IS ⊥ TO THE PLANE OF THE COMPLEX

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_{LCAO}	4	0	0	4

$$\Gamma_{LCAO} = 2a_1 + 2b_2$$

IT DOESN'T MATTER WHICH YOU CHOOSE, SO LONG AS YOU ARE CONSISTANT. I WILL STAY WITH THE TOP AXES SCHEME TO DRAW MY MO SCHEME



MAKE BONDS WITH METAL S + P ORBITALS AND THEN d ORBITALS IF NECESSARY. d ORBITALS WITH THE SAME SYMMETRY AS BONDING ORBITALS WILL HAVE ANTIBONDING CHARACTER MIXED IN ∴ ENERGY ↑