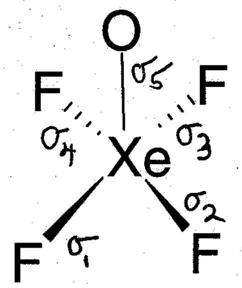
CHEM 721 – INORGANIC STRUCTURE AND BONDING
EXAM 2 – NOVEMBER 6, 2000

NAME KEY

Depicted below is the molecule xenon oxyflouride, $OXeF_4$, which belongs to the C_{4v} symmetry point group.



1. For now, consider only the σ bonding in this molecule. Of the five σ bonding orbitals in this molecule, how many symmetry subsets are present? Which σ bonding orbitals belong to each subset. [15 pts]

2 SUBSETS $(\sigma_1, \sigma_2, \sigma_3, \sigma_4)$ and σ_5

2. Determine the characters for the representations Γ_σ for each symmetry subset. Which irreducible representations are spanned by each Γ_σ? [15 pts]

		E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
σ_5	$\Gamma_\sigma =$	1	1	1	1	1
$(\sigma_1, \sigma_2, \sigma_3, \sigma_4)$	$\Gamma_\sigma =$	4	0	0	2	0

$\Gamma_{\sigma_5} = A_1$ (by inspection of character table)

for $(\sigma_1, \sigma_2, \sigma_3, \sigma_4)$

$a^{A_1} = \frac{1}{8}(4 + 0 + 0 + 2(2) + 0) = \frac{1}{8}(8) = \underline{1}$

$a^{A_2} = \frac{1}{8}(4 + 0 + 0 + 2(-2)) = 0$

$a^{B_1} = \frac{1}{8}(4 + 0 + 0 + 2(+2)) = 1$

$a^{B_2} = \frac{1}{8}(4 + 0 + 0 + 2(-2)) = \frac{1}{8}(4) = 0$

$a^{E} = \frac{1}{8}(2(4) + 0 + 0 + 0 + 0) = \frac{1}{8}(8) = \underline{1}$

$\Gamma_\sigma = A_1 + B_1 + E$

3. Using projection operators, determine the normalized functional forms for each symmetry adapted linear combination of σ orbitals. Show all work. [20 pts]

for σ_5: $P^{A_1}_{(\sigma_5)} \cong \sigma_5 + (\sigma_5+\sigma_5) + \sigma_5 + (\sigma_5+\sigma_5) + (\sigma_5+\sigma_5)$

$\cong 8\sigma_5$

$= \underline{\sigma_5}$

for $(\sigma_1, \sigma_2, \sigma_3, \sigma_4)$

$P^{A_1}_{(\sigma_1)} \cong \sigma_1 + (\sigma_2+\sigma_4) + \sigma_3 + (\sigma_1+\sigma_3) + (\sigma_2+\sigma_4)$

$\cong 2\sigma_1 + 2\sigma_2 + 2\sigma_3 + 2\sigma_4$

$= \underline{\frac{1}{2}(\sigma_1+\sigma_2+\sigma_3+\sigma_4)}$

$P^{B_1}_{(\sigma_1)} \cong \sigma_1 - (\sigma_2+\sigma_4) + \sigma_3 + (\sigma_1+\sigma_3) - (\sigma_2+\sigma_4)$

$\cong 2\sigma_1 + 2\sigma_3 - 2\sigma_2 - 2\sigma_4$

$= \underline{\frac{1}{2}(\sigma_1+\sigma_3-\sigma_2-\sigma_4)}$

$P^{E}_{(\sigma_1)} \cong 2\sigma_1 - 2\sigma_3$

$= \underline{\frac{1}{\sqrt{2}}(\sigma_1-\sigma_3)}$ ← this is just one of 2 solutions

apply symmetry operation to find other partner

$\hat{C}_4\left(\frac{1}{\sqrt{2}}(\sigma_1-\sigma_3)\right) = \underline{\frac{1}{\sqrt{2}}(\sigma_2-\sigma_4)}$ ← this works - it is orthonormal to first solution

4. Determine to which irreducible representation each of the xenon s, p, and d orbitals belong. [15 pts]

s: A_1

p_z: A_1

p_x, p_y: E

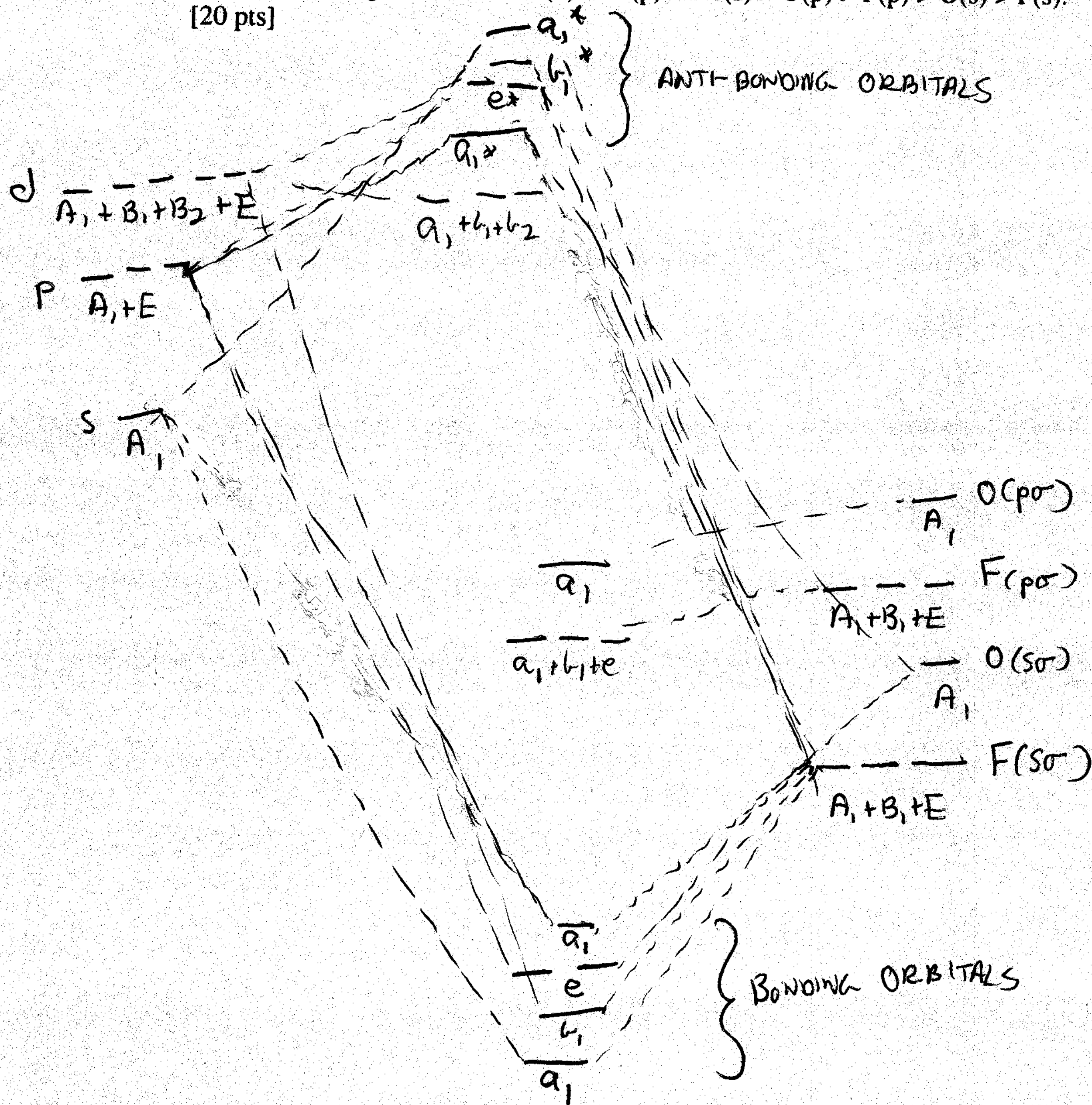
d_{z^2}: A_1

$d_{x^2-y^2}$: B_1

d_{xy}: B_2

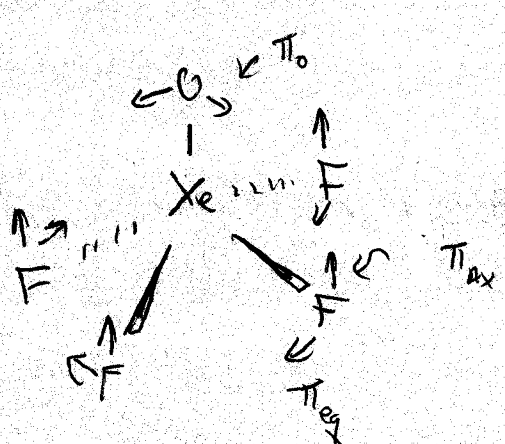
d_{xz}, d_{yz}: E

5. Construct a qualitative MO diagram for $OXeF_4$ showing only σ bonding interactions. Assume the energy of the orbitals from highest (less negative) to lowest(most negative)to be: Xe(d)> Xe(p) > Xe(s) > O(p) > F(p) > O(s) > F(s). [20 pts]



6. Draw a picture of $OXeF_4$ with appropriate vectors denoting the basis for π bonding. How many symmetry subsets exist for π bonding? Calculate the characters for Γ_π for each symmetry subset. (You need not find the irreducible representations that are spanned). [15 pts]

3 SUBSETS: $\pi(O)$, $\pi_{AX}(F)$, $\pi_{RAD}(F)$



	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
$\Gamma_\pi(O)$	2	0	-2	0	0
$\Gamma_{\pi_{AX}}(F)$	4	0	0	2	0
$\Gamma_{\pi_{RAD}}(F)$	4	0	0	-2	0