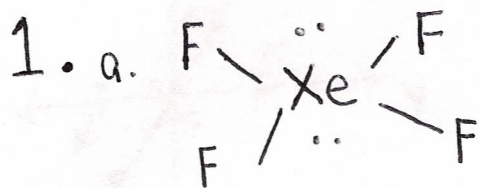


Problem Set 2

1

Chapter 3



Steric #: 6
But have two lone pairs and so the 4 F are in the equatorial position @ 90° from each other.

b. D_{4h}

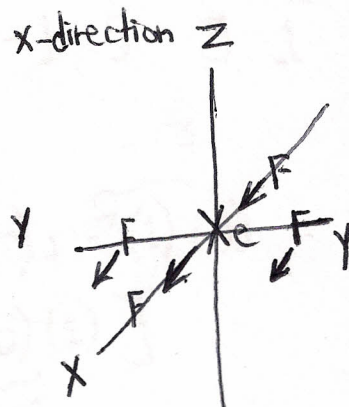
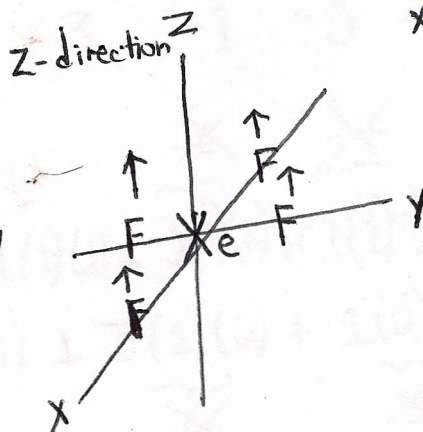
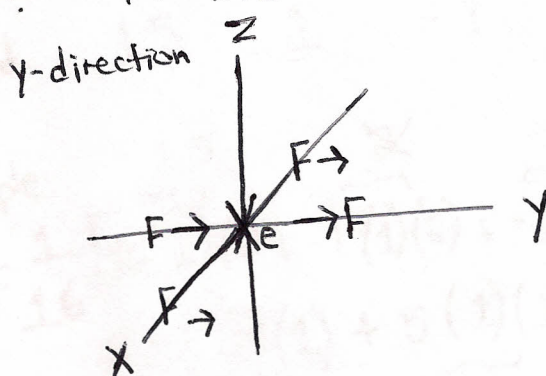
c. Yes, centrosymmetric

d. Not linear

e. $3N = 15$

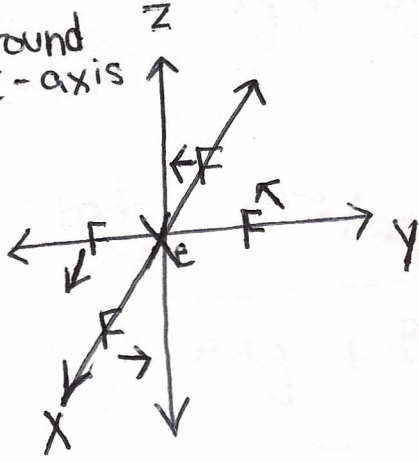
$N = 5$ atoms

f. Translations

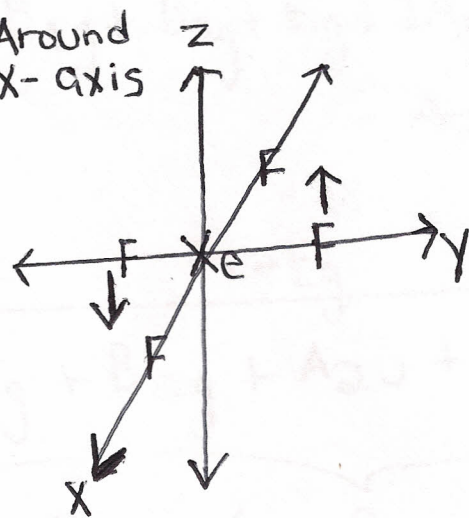


Rotations

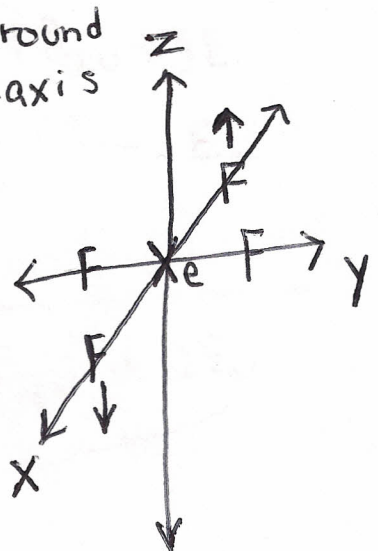
Around Z-axis



Around X-axis



Around y-axis



$9 \cdot 3N - 6 = 15 - 6 = 9$

			same as C_4	along bonds C_2	between bonds C_2	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
h. D_{4h}	E	$2C_4$	C_2	$2C_2$	$2C_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Unmoved	5	1	1	3	1	1	1	5	3	1
Charac. contrib.	3	1	-1	-1	-1	-3	-1	1	1	1
Γ_{red}	15	1	-1	-3	-1	-3	-1	5	3	1

Example

$$N_{A_{1g}} = \frac{1}{16} [\overbrace{15(1)(1)} + \overbrace{1(1)(2)} + \overbrace{-1(1)(1)} + \overbrace{-3(1)(2)} + \overbrace{-1(1)(2)} + \overbrace{-3(1)(1)} + \overbrace{-1(2)(1)} + \overbrace{5(1)(1)} + \overbrace{3(1)(2)} + \overbrace{1(2)(1)}]$$

$$= \frac{16}{16} = 1$$

3N = 15

$$\Gamma_{red} = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$$

-trans - A_{2u} - E_u

-rot

$$\frac{-A_{2g} \qquad -E_g}{A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u}$$

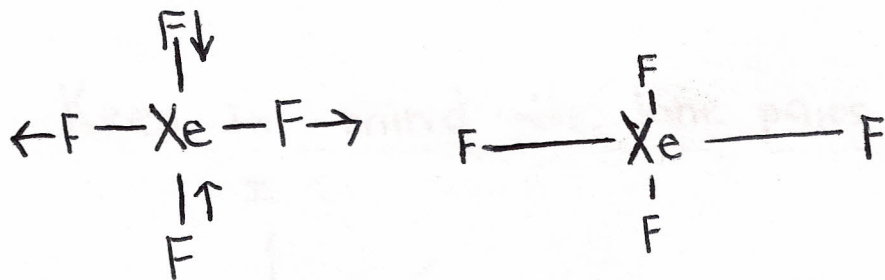
$$3N - 6 = 9$$

i. Because centrosymmetric, mutual exclusivity

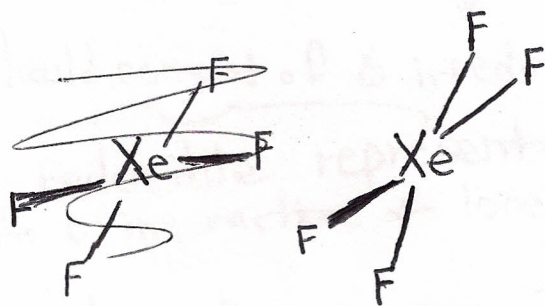
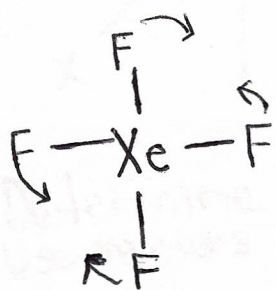
IR active: A_{2u}, E_u

Raman active: A_{1g}, B_{1g}, B_{2g}

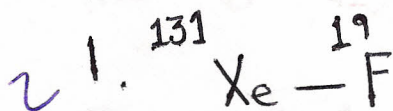
Neither: B_{2u}



E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	σ_d	
1	-1	1	1	-1	1	-1	1	1	-1	B_{2g}^1

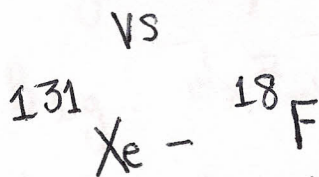


1	-1	1	-1	+1	1	-1	1	-1	+1	B_{2g}
---	----	---	----	----	---	----	---	----	----	----------



$$\mu = \frac{131(19)}{131+19} = 16.59$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

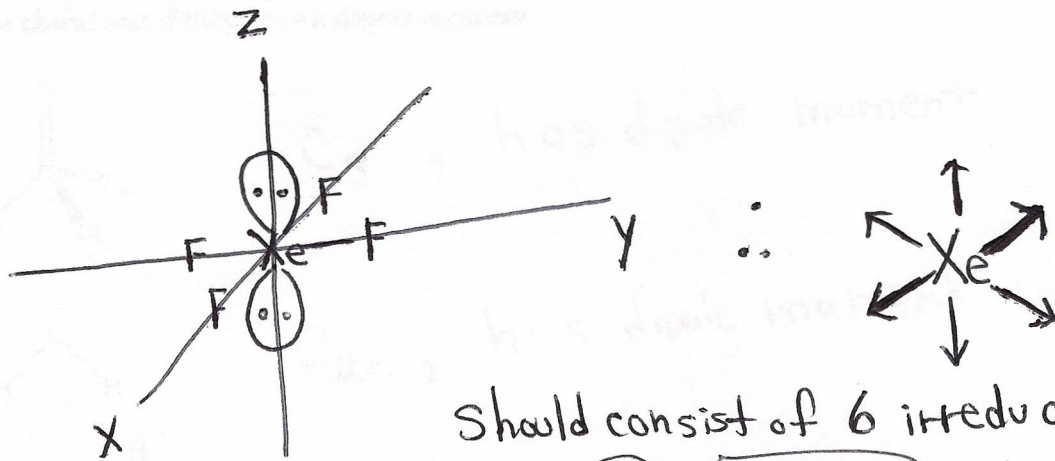


$$\mu = \frac{131(18)}{131+18} = 15.82$$

$\downarrow \mu, \uparrow \bar{\nu}$

\therefore The frequency ($\bar{\nu}$) would increase

2 m. Keep in mind the lone pairs.



Should consist of 6 irreducible reps.

- Determine the reducible representation.
- Use vectors to indicate σ interactions + lone pairs.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{red}	6	2	2	2	0	0	0	4	4	2

$$\Gamma_{red} = 2A_{1g} + B_{1g} + A_{2u} + E_u$$

6 total representations

$$2A_{1g}: s, dz^2$$

$$B_{1g}: dx^2 - y^2$$

$$A_{2u}: p_z$$

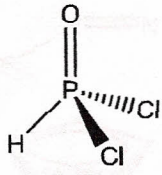
$$E_u: p_x, p_y$$

$$\left. \begin{matrix} d^2 & 3 \\ d & sp \end{matrix} \right\}$$

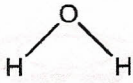
Makes sense b/c octahedral electrical geometry

P.S per structure

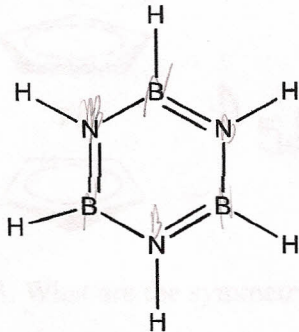
2. Assign the following molecules to their appropriate point groups and identify if they are chiral and if they have a dipole moment.



C_s , has dipole moment



C_{2v} , has dipole moment, achiral



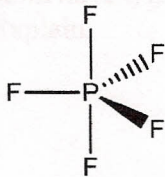
D_{3h}



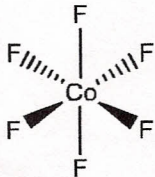
$C_{\infty v}$, has dipole moment



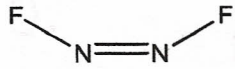
T_d



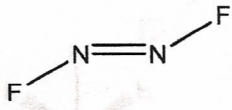
D_{3h}



O_h



C_{2v} , dipole moment



C_{2h}



Fe

D_{5h}

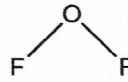


Fe

D_{5d}



3. What are the symmetries of the normal modes of vibration of these molecules?



1 per movement
1 per mass
1 per vis

4. Unlike the water molecule, carbon dioxide has no dipole moment. How is it possible for it to have any of its vibrational modes to be infrared active?

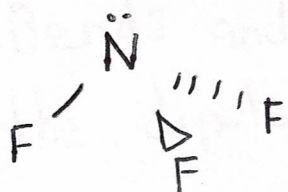
5. Why is it that the O-H band in the IR broadens with H-bonding?

6. In an sp^3d hybridized phosphorus atom in a trigonal bipyramidal molecule, will the atom have a greater electronegativity when bonding through equatorial or axial orbitals? Explain.



3.

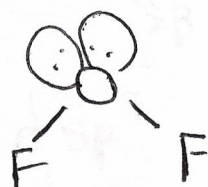
3 entities



$3N = 12$ degrees of freedom

$3N - 6 = 6$ vibrations

C_{3v}	E	$2C_3$	$3\sigma_v$	
Unmoved	4	1	2	
Contrib	3	0	1	
Γ_{red}	12	0	2	$= \overbrace{3A_1 + A_2 + 4E}^{12}$
				$- A_1 \quad - E \quad \Gamma_{trans}$
				$- A_2 - E \quad \Gamma_{rot}$
Γ_{vib}	$2A_1 + 2E$			$\underline{2A_1 + 2E}$
	6 representations			



$3N = 9$ degrees of freedom

$3N - 6 = 3$ normal modes

C_{2v}	E	C_2	σ_v	σ_v'	
Unmoved	3	1	1	3	
cont.	3	-1	1	1	
Γ_{red}	9	-1	1	3	
Γ_{vib}	$3A_1 + A_2 + 2B_1 + 3B_2$				9 degrees

$\Gamma_{vib} = 2A_1 + B_2$ 3 normal modes

$- A_1$ $- B_1$ B_2 Γ_{trans}
 $- A_2$ $- B_1$ $- B_2$ Γ_{rot}

4. Bends and asymmetric stretches change the dipole moment.

5. With H-bonding the length of each O-H bond changes. The vibration thus changes resulting in nonhomogenous frequencies + a broad IR spectrum signal.

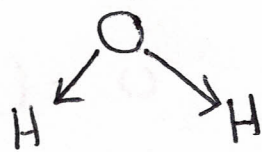
2 6. $\begin{matrix} B \\ \uparrow \\ A \\ \downarrow \\ B \end{matrix}$ } Main contribution: $dz^2 + pz$

$\begin{matrix} & B \\ \swarrow & & \nearrow \\ A & & B \\ \searrow & & \swarrow \\ & B & \end{matrix}$ } Main contribution: s, px, py

dsp^3 but greater s character in equatorial plane. According to Bent's rule, more electronegativity in equatorial plane. The more electronegative substituent will be in the axial position.

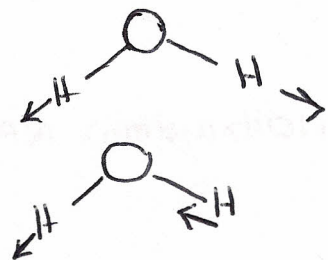
Chapter 5

1 a.

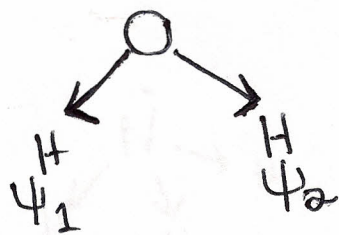


Two bonds \Rightarrow Two stretching vibrations

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_{red}	2	0	0	2
A_1	1	1	1	1
B_2	1	-1	-1	1
	2	0	0	2



b. Projection operator



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Ψ_1	Ψ_1	Ψ_2	Ψ_2	Ψ_1

$$\begin{aligned} \Psi(A_1) &= 1\Psi_1 + 1\Psi_2 + 1\Psi_2 + 1\Psi_1 \\ &= 2\Psi_1 + 2\Psi_2 \end{aligned}$$

$$= \frac{1}{\sqrt{2}} (\Psi_1 + \Psi_2) \text{ in-phase combination}$$

$$\psi(a_2) = 0$$

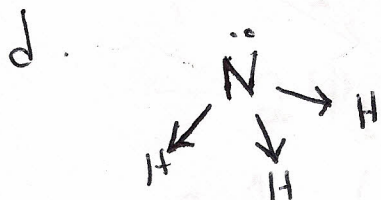
$$\psi(b_1) = 0$$

$$\begin{aligned} \psi(b_2) &= 1\psi_1 + (-1\psi_2) + (-1\psi_2) + (1\psi_1) \\ &= 2\psi_1 - 2\psi_2 \end{aligned}$$

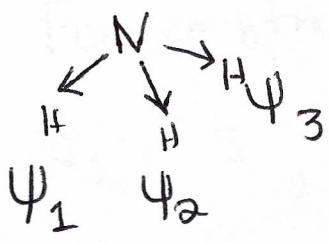
$$= \frac{1}{\sqrt{2}} (\psi_1 - \psi_2) \text{ out of phase combination}$$

c. See your class notes

The higher E a_1 (ψ_3) + the nonbonding b_1 (ψ_4) house the lone pairs.



C_{3v} Γ_{red}	E	2 C_3	3 σ_v
	3	0	1
	1	1	1
	2	-1	0
	+E	3	0

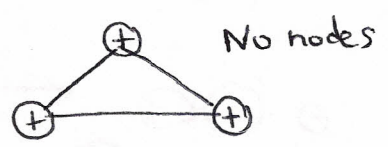


C_{3v}	E	C_3	C_3^2	σ_v^1	σ_v^2	σ_v^3
ψ_1	ψ_1	ψ_2	ψ_3	ψ_1	ψ_3	ψ_2

$$\psi(a_1) = 1\psi_1 + 1\psi_2 + 1\psi_3 + 1\psi_1 + 1\psi_3 + 1\psi_2$$

$$= 2\psi_1 + 2\psi_2 + 2\psi_3$$

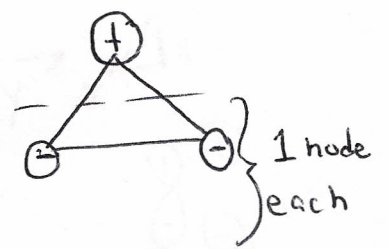
$$\psi(a_1) = \frac{1}{\sqrt{3}} (\psi_1 + \psi_2 + \psi_3)$$



$$\psi(e)_1 = 2\psi_1 + (-1 \times \psi_2) + (-1 \times \psi_3) + 0$$

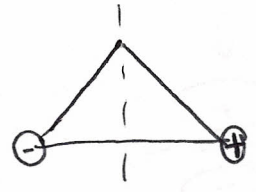
$$= 2\psi_1 - \psi_2 - \psi_3$$

$$= \frac{1}{\sqrt{6}} (2\psi_1 - \psi_2 - \psi_3)$$



Also

$$\psi(e)_2 = \frac{1}{\sqrt{2}} (\psi_2 - \psi_3)$$

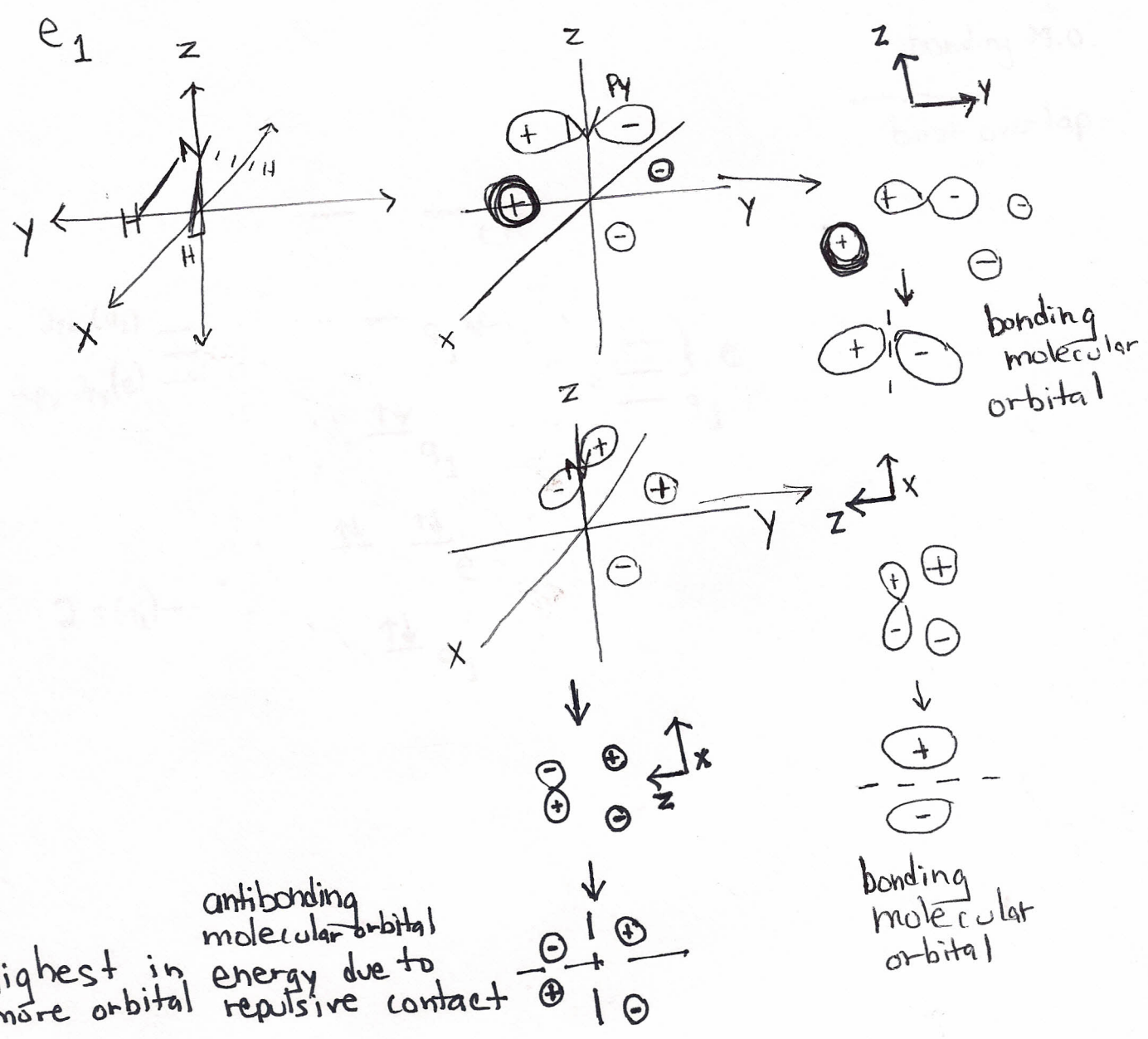


e. For central atom

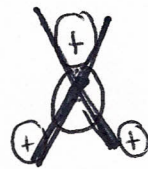
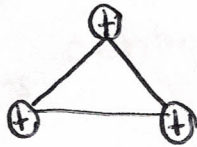
$a_1: s, p_z, \cancel{d_{z^2}}$

$e: p_x, p_y, \cancel{d \text{ orbitals}}$

Symmetry matching



a_1



a_1^*

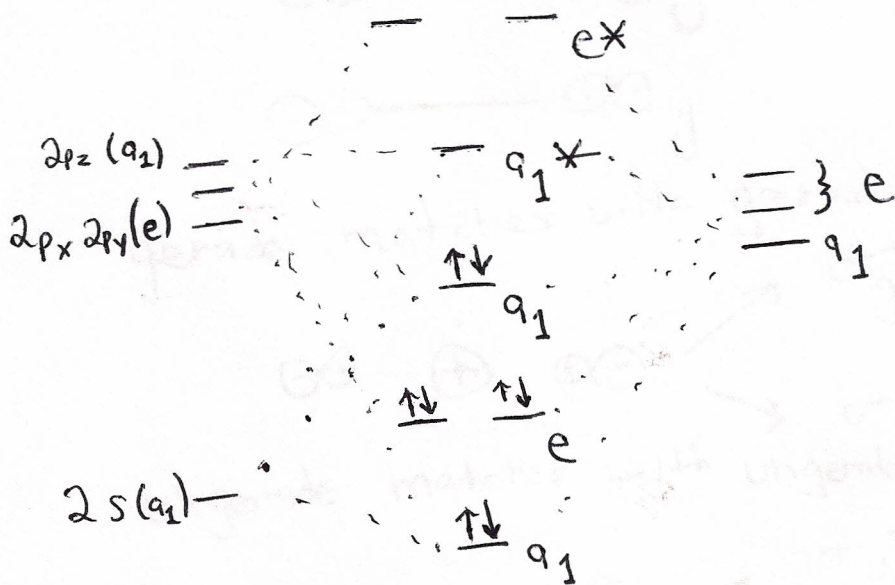


higher E a_1 bonding M.O.



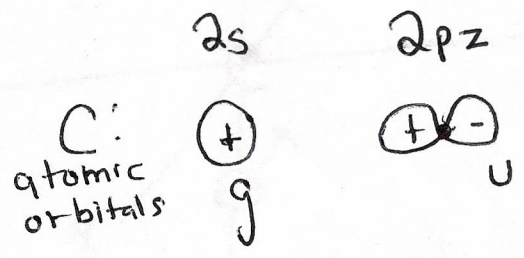
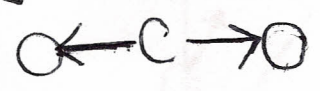
low E a_1 bonding M.O.

best overlap

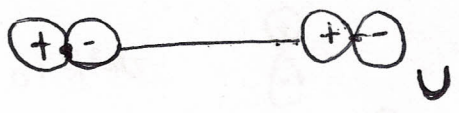


2. $\leftarrow O = C = O \rightarrow$ z-axis

Sigma interactions centrosymmetric



LGO:

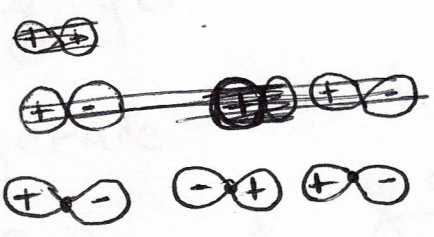


gerade matches with gerade



σ_g^*

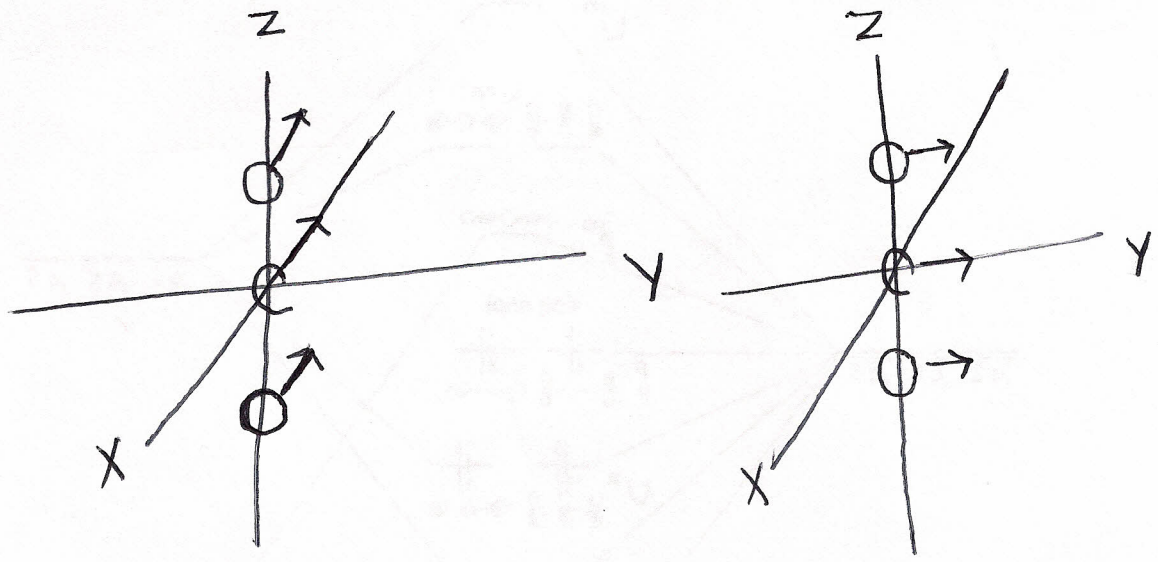
ungerade matches with ungerade



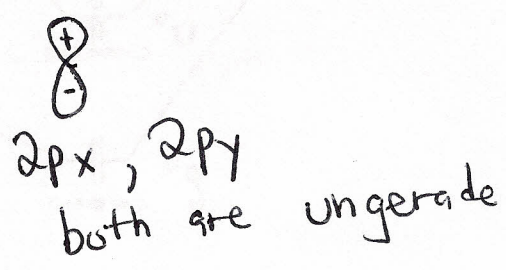
σ_u^*

σ_{eu}

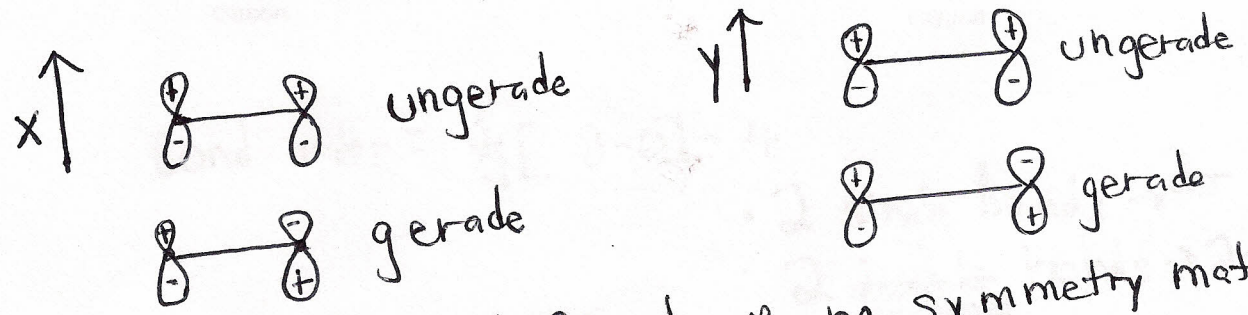
pi interactions



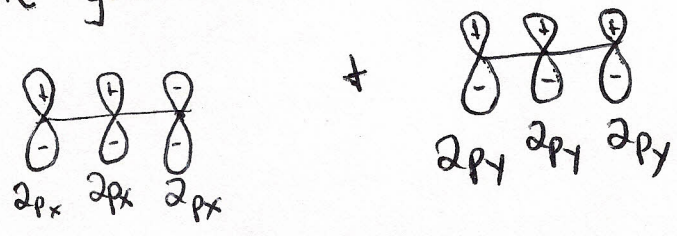
Atomic orbitals:

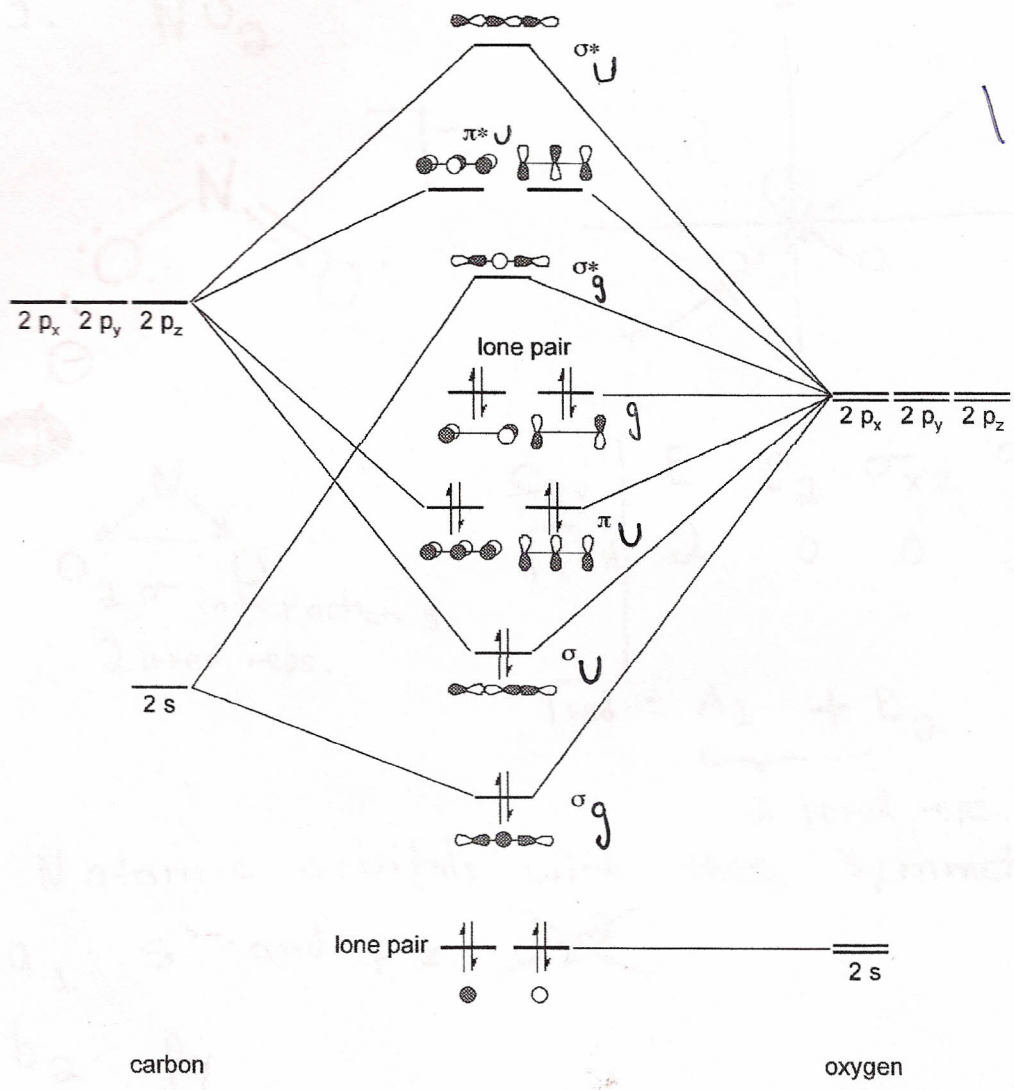


LGOs



The gerade LGOs have no symmetry match. Ungerade matches

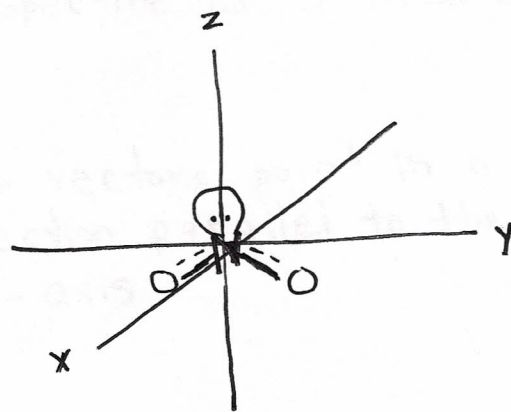
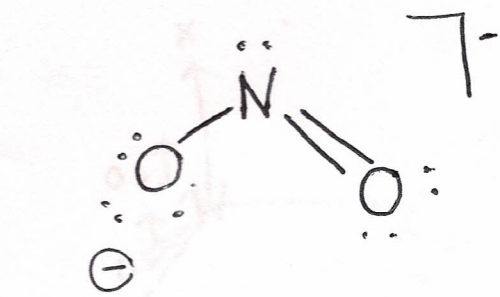




Bond order = $\frac{1}{2} [8 - 0] = 4$

- 2 single bonds → 2σ
- 2 ~~double~~ additional bonds → 2π

3. NO_2^-



a. 2σ interactions
 $\therefore 2$ irred. reps.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Γ_{red}	2	0	0	2

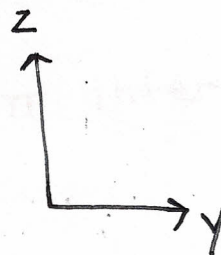
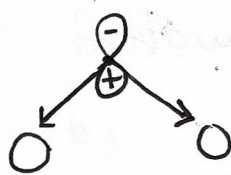
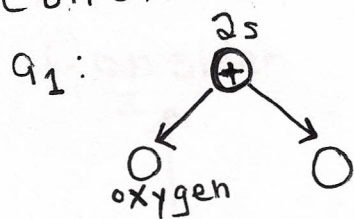
$\Gamma_{\text{red}} = A_1 + B_2$
 2 irred. reps.

Atomic orbitals with these symmetries.

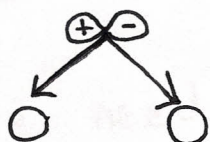
a_1 : s and p_z ~~d_{z^2}~~

b_2 : p_y

Consider the following σ interactions:

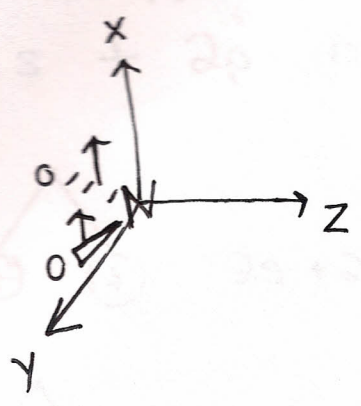


b_2 : $2p_y$



We need LGOs that can interact with these atomic orbitals to form σ interactions.

b. Change your perspective for π interactions



These vectors point in a direction parallel to the x-axis.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Γ_{red}	2	0	0	-2

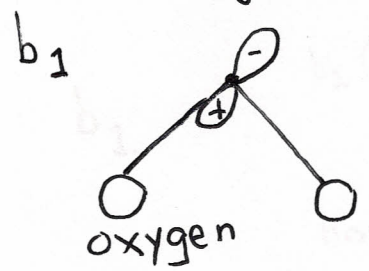
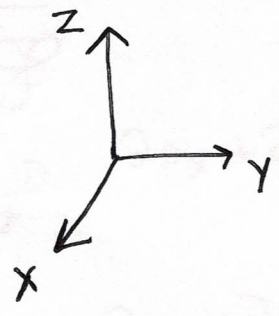
$\Gamma_{red} = A_2 + B_1$

N atomic orbitals with these symmetries.

a_2 : ~~d_{xy}~~

b_1 : p_x , ~~d_{xz}~~

Consider the following π interactions:



We need LGOs that can interact with this atomic orbital to form π interactions.

c/d/e/f

(2)

For LGOs need to consider the linear combination of atomic orbitals of 2s + 2p orbitals

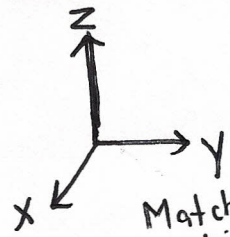


Diagram	Combination	Symmetry	Match with atomic orbital	Possible Type of interaction
	2s + 2s	a ₁	a ₁ (2s) - a ₁ (p _z)	σ
	2s - 2s	b ₂	b ₂ (2p _y)	σ
	2p _y + 2p _y	b ₂	nonbonding	
	2p _y - 2p _y	a ₁	nonbonding	
	2p _z + 2p _z	a ₁	a ₁ (2s) - a ₁ (p _z)	σ
	2p _z - 2p _z	b ₂	b ₂ (2p _y)	σ
	2p _x + 2p _x	b ₁	b ₁ (2p _x)	π
	2p _x - 2p _x	a ₂	nonbonding	

The 'N atomic orbital 2p_z is nonbonding due to mismatch in alignment. (An assumption) But can be included.