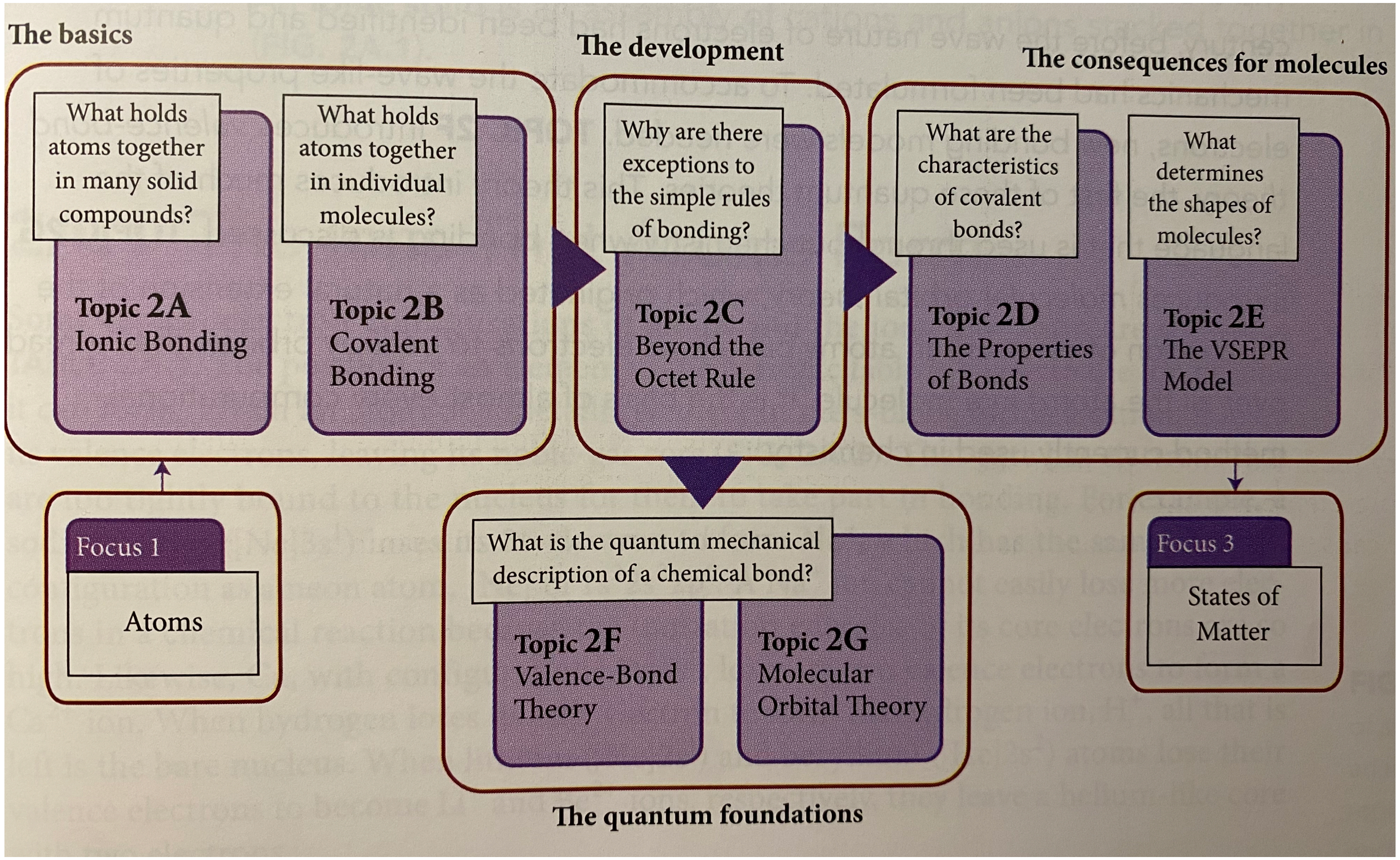
CH-110 Advanced General Chemistry I

Prof. A. Steinauer

angela.steinauer@epfl.ch

Overview Chapter 2 (Focus 2: Bonds Between Atoms)



What is the 3D shape of a molecule?

2E.1 The basic VSEPR model

The method

1. Write the Lewis structure(s). If there are resonance structures, pick *any* one.
2. Count the number of electron pairs (bonding and nonbonding) around the central atom(s). Treat a multiple bond as a *single* unit of high electron density.
3. Identify the *electron arrangement*. Place electron pairs as far apart as possible.
4. Locate the *atoms* and classify the *shape* of the molecule.
5. Optimize *bond angles* for molecules with *lone pairs* on the central atom(s) with the concept in mind that repulsions are in this order:

Lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

2E.2 Molecules with lone pairs on the central atom

The generic VSEPR formula AX_nE_m

A = central atom

X_n = *n* attached atoms

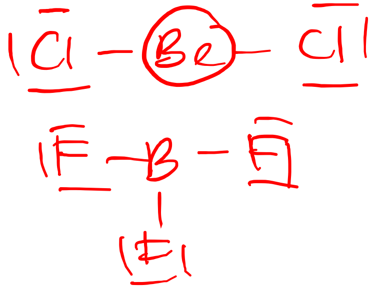
(E_m = *m* lone pairs: see Friday)

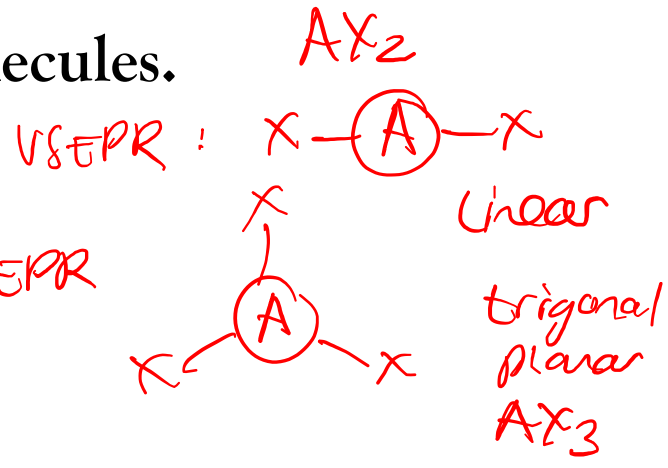
Molecules with the same VSEPR formula have the same electron arrangement and the same shape.

E.g. BF_3 and NO_3^- are examples of AX_3 species.

2E.1 The basic VSEPR model

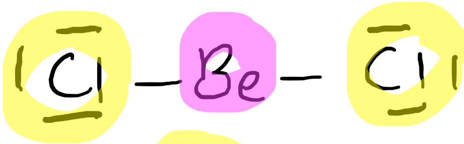
Some examples: predict the shape of these molecules.



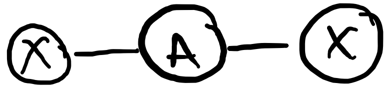


- Beryllium chloride, $BeCl_2$
- Boron trifluoride, BF_3
- Methane, CH_4
- Phosphorous pentachloride, PCl_5
- Sulfur hexafluoride, SF_6
- Carbon dioxide, CO_2
- Carbonate ion, CO_3^{2-}
- Nitrate ion, NO_3^-
- Ethene, C_2H_4

$BeCl_2$:

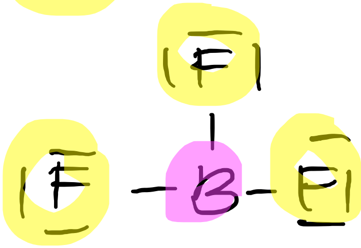


VSEPR: AX_2

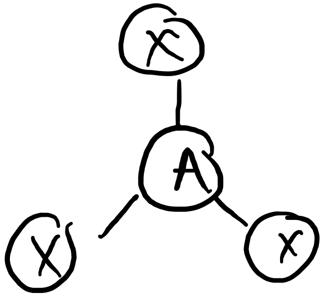


linear

BF_3 :

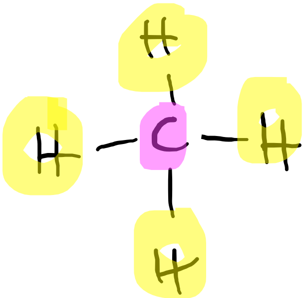


VSEPR: AX_3

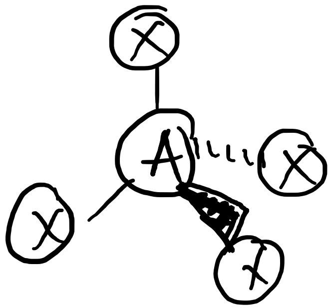


trigonal planar

CH_4 :

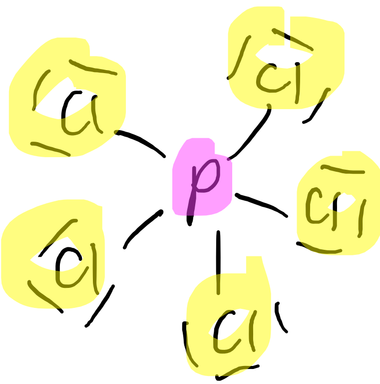


VSEPR: AX_4

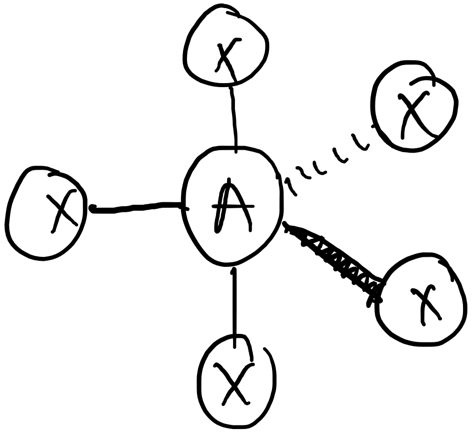


tetrahedral

PCl_5 :

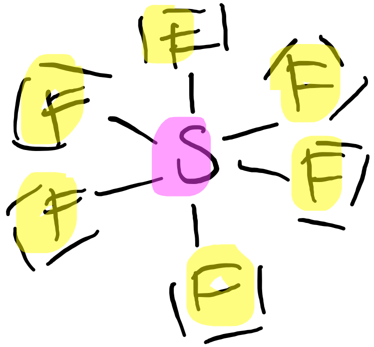


VSEPR AX_5

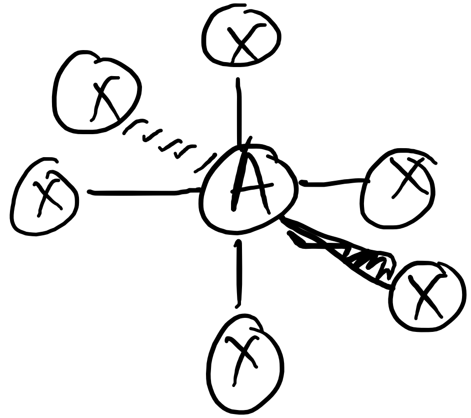


trigonal bipyramidal

SF_6:

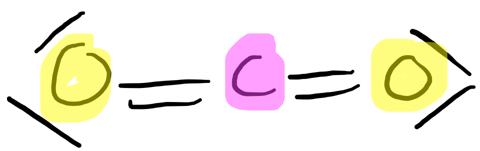


VSEPR: AX_6

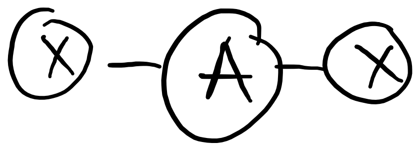


octa-hedral

CO_2:

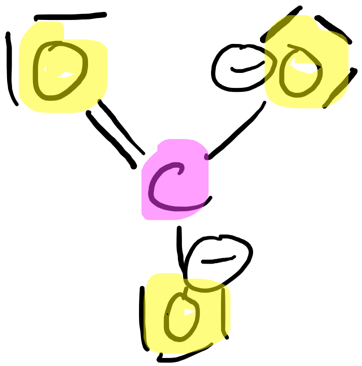


VSEPR: AX_2

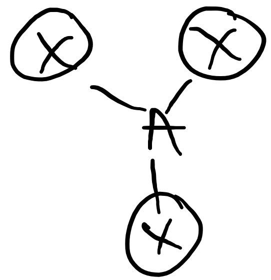


linear

CO_3^{2-}:

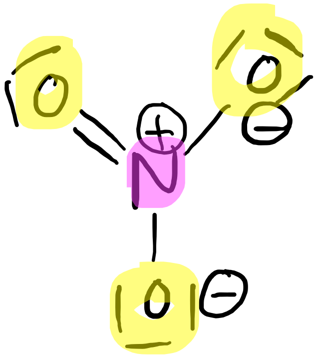


VSEPR: AX_3



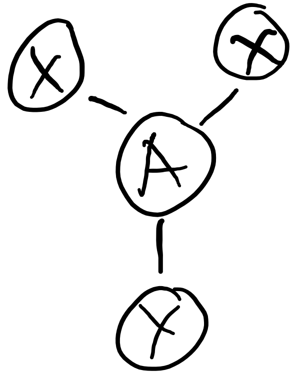
trigonal planar

$NO_3^{\ominus}$:



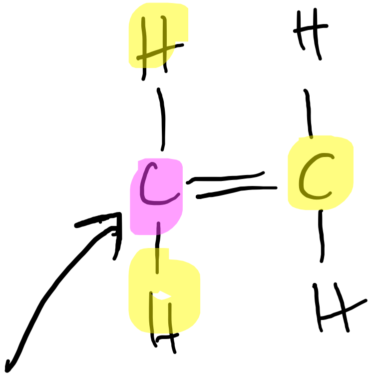
VSEPR:

AX_3



trigonal planar

C_2H_4:

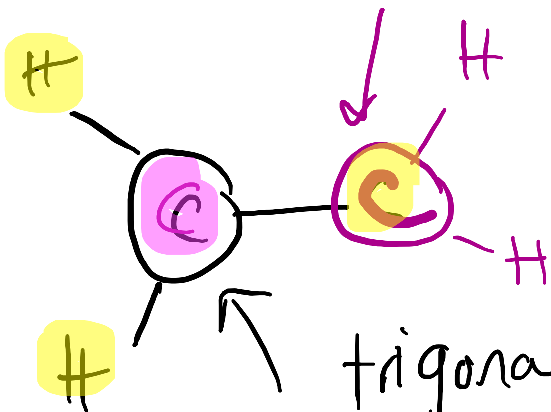


look at each central carbon separately

VSEPR

AX_3

trigonal planar

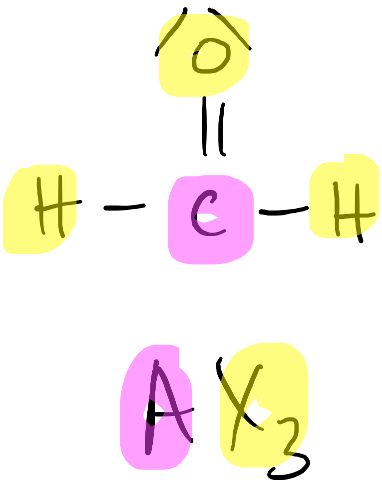


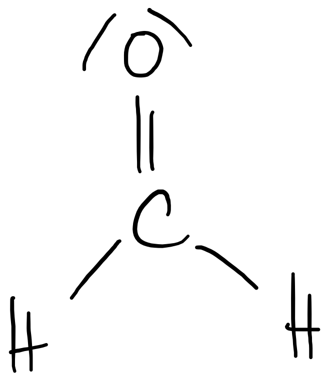
trigonal planar

2E.1 The basic VSEPR model

Example 2E.1

Predict the shape of a methanal molecule (formaldehyde, $H_2C{=}O$).





AX_3

trigonal planar

2E.1 The basic VSEPR model

Summary

According to the VSEPR model, regions of high electron concentration take up positions that maximize their separations; electron pairs in a multiple bond are treated as a single unit. The shape of the molecule is then identified from the relative locations of its atoms.

Molecules with Lone Pairs on the Central Atom

Topic 2E.2

2E.2 Molecules with lone pairs on the central atom

Electron arrangment vs. molecular shape

Rule 3: All regions of high electron concentration, lone pairs and bonds, are included in a description of the electronic arrangement, but **only the positions of atoms are considered when identifying the shape** of a molecule.

A single unpaired electron on a central atom is treated as a region of high electron concentration (= lone pair).

Examples:

Sulfite ion, SO_3^{2-}

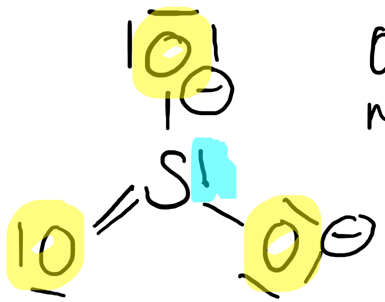
Nitrogen dioxide, NO_2

SO_3^{2-}:

$6 + 3 \cdot 6 + 2$

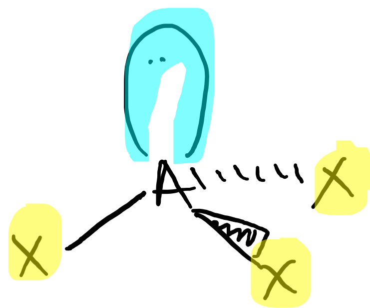
$= 26\ e^{-}$

13 e^{-} pairs



one resonance structure

4 units of e^{-} density: AX_3E



trigonal pyramidal

NO_2:

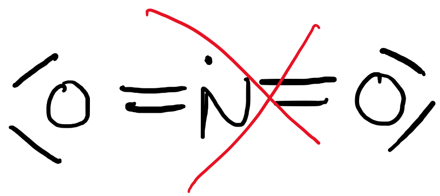
$5 + 2 \cdot 6 = 17\ e^{-}$

↓

odd number

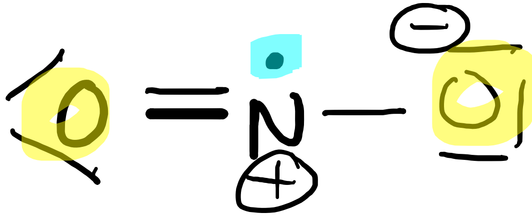
↓

unpaired e^{-}!

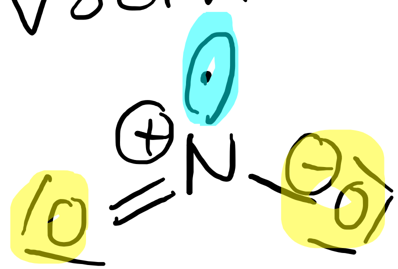


↑

N is in 2nd period, cannot be hypervalent.



VSEPR: AX_2E

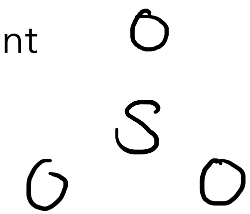


bent

Step by step: Lewis structure of SO_3^{2-}

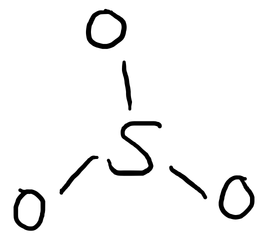
Step 1: Count valence electrons $6 + 3 \cdot 6 + 2 = 26$

Step 2:write down most likely arrangement

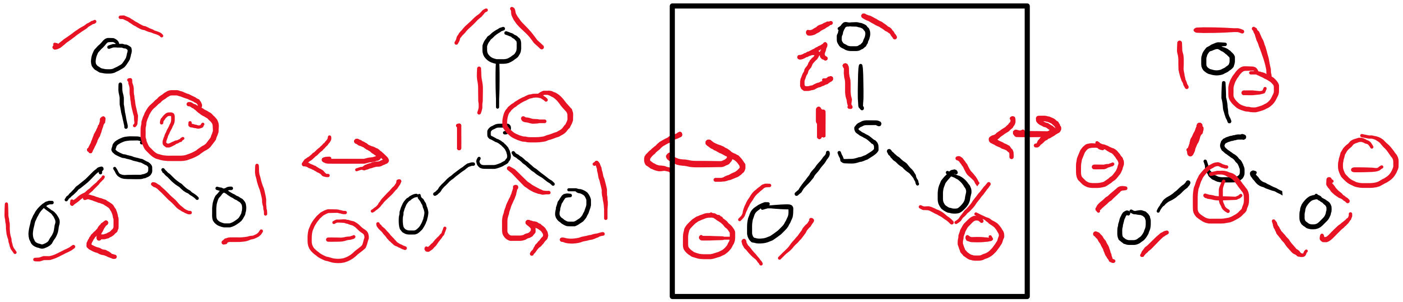


13 e⊖ pairs

Step 3: Place one election pair between each set of bonded atoms



Step 4: Complete octets/duplets $13 - 3$ e⊖ pairs $= 10$ remaining



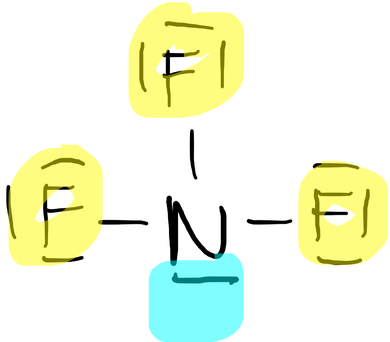
These are all *theoretically* possible resonance structures, the most stable one (boxed) minimizes formal charges and puts the formal charges on the most electronegative atom (oxygen).

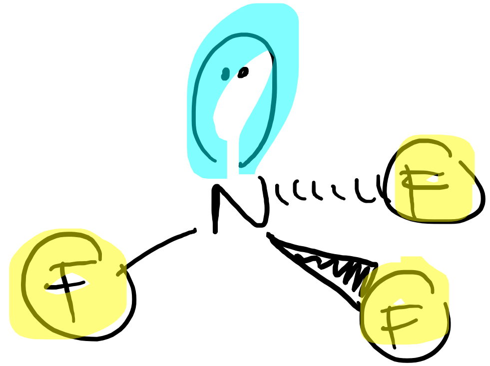
2E.1 The basic VSEPR model

Example 2E.2

Predict the electron arrangement and the shape of a nitrogen trifluoride molecule, NF_3.

VSEPR: AX_3E





2E.2 Molecules with lone pairs on the central atom

VSEPR model refinement

- So far, lone pairs have been treated as equivalent to bonds in their effect on shape. Is that really the case?
- SO_3^{2-} ion is tetrahedral: An O–S–O bond angle of **109.5° expected**
- **Found: 106°**
- Why? Lone pairs have a more repelling effect than electrons in bonds. The lone pairs push the atoms bonded to the central atom closer together. The electron cloud of a lone pair can spread over a larger volume than a bonding pair. The bonding pair is held in place by two atoms, the lone pair only by one.

Rule 4: The strength of repulsions are in the order **lone pair-lone pair** > **lone pair-atom** > **atom-atom**.

- Lowest energy state: lone pairs as far from each other as possible.
- You can expect: in **any AX_3E species, the XAX angle will be less than 109.5°**

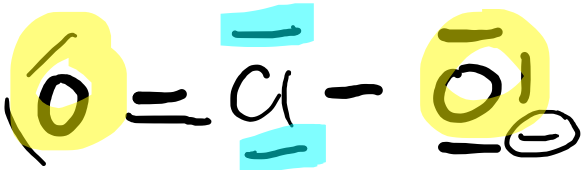
2E.2 Molecules with lone pairs on the central atom

Self-test

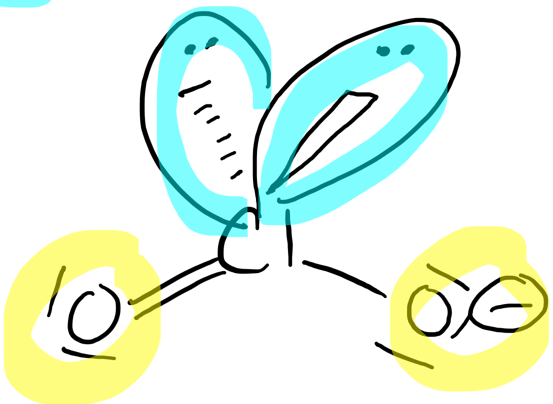
- Give the VSEPR formula of a ClO_2^- ion. Predict its electron arrangement and its shape.

tetrahedral

$7 + 2 \cdot 6 + 1 = 20$ electrons | 10 e^- pairs



AX_2E_2



bent

2E.2 Molecules with lone pairs on the central atom

AX_4E

Rule 4: The strength of repulsions are in the order lone pair-lone pair > lone pair-atom > atom-atom.

Rule 4 allows you to predict the position in which a lone pair will be found.

For example, the electron arrangement in an AX_4E molecule or ion, such as IF_4^+, is trigonal bipyramidal. There are two different possible locations for the lone pair:

a) An axial lone pair

b) An equatorial lone pair

Conclusion: **b) is preferred.**

This shape is known as 'seesaw'.

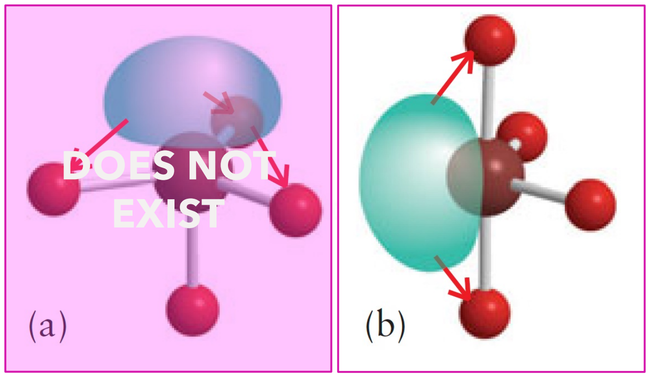
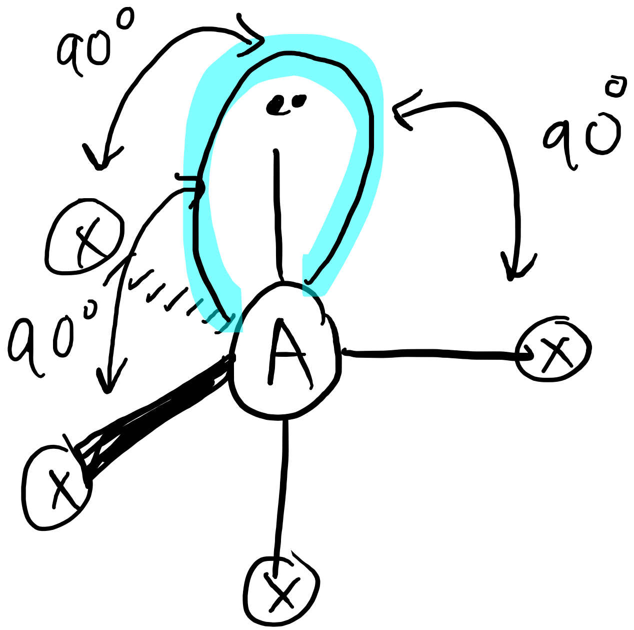


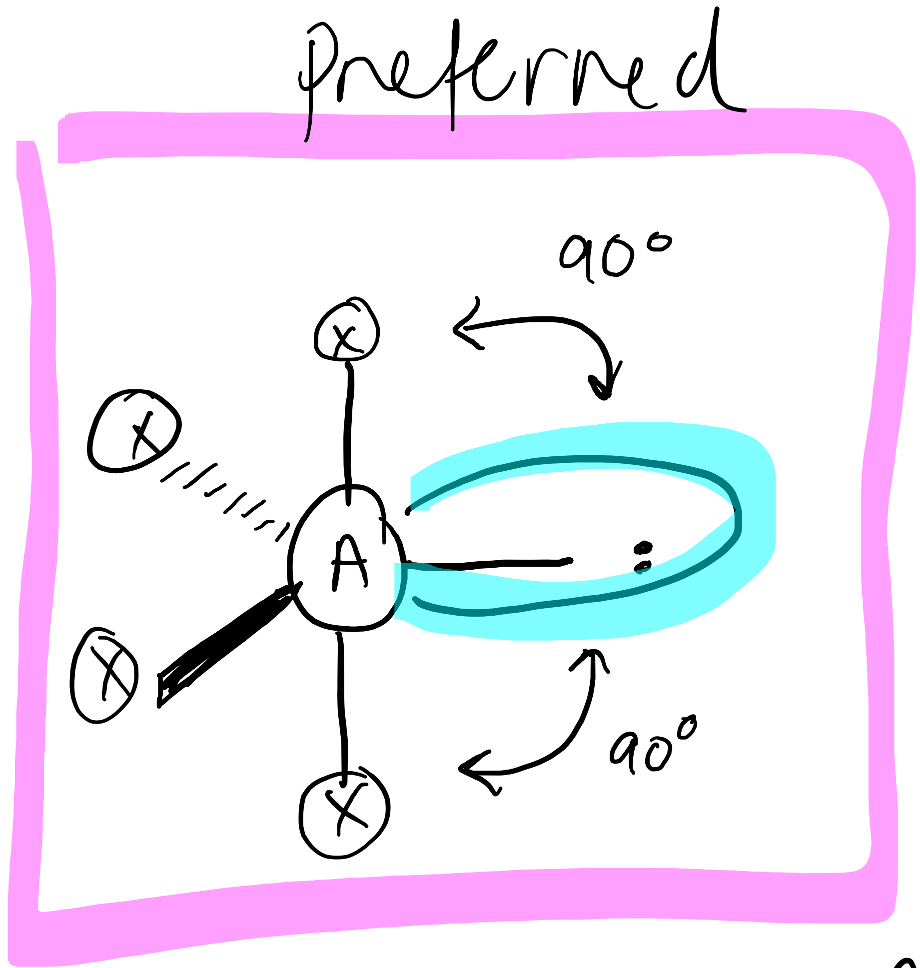
Figure 2E.4

AX_4E:

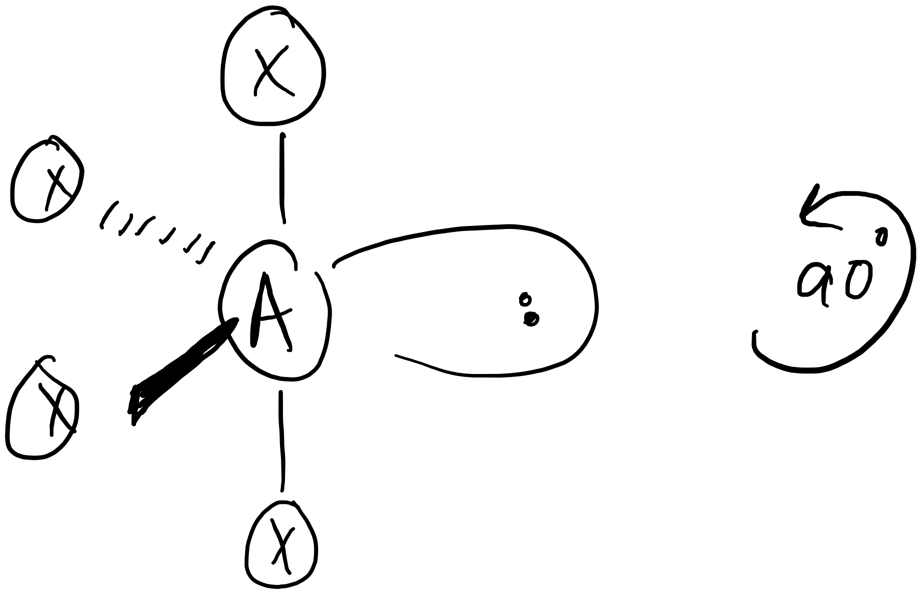


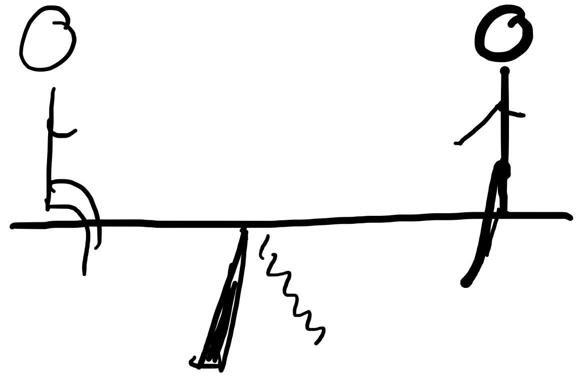
lone pair axial
3 repulsive interactions

vs.



lone pair equatorial
2 repulsive interactions



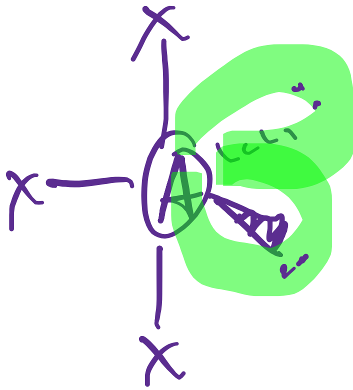


Seesaw

2E.2 Molecules with lone pairs on the central atom

AX_3E_2

- Electron arrangement: trigonal bipyramidal
- Molecular shape: **T-shaped**
- Why? Lone pairs are farthest apart from each other (120°). In the axial case, they would have been at 90° angles from the equatorial positions.



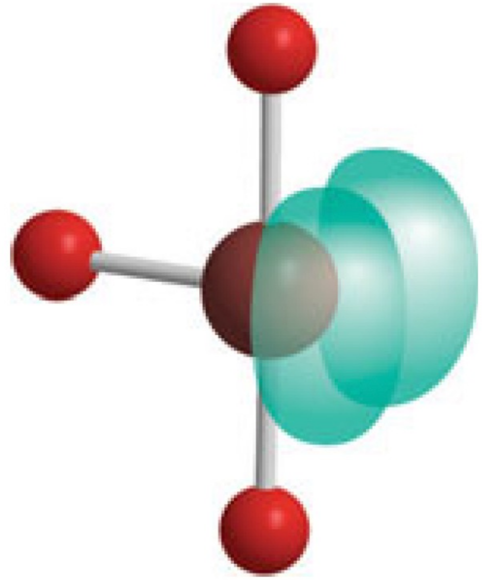
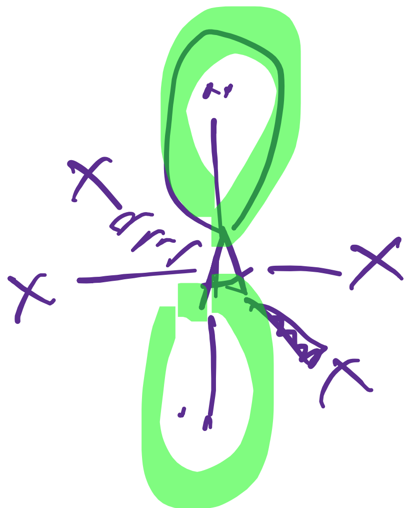


Figure 2E.5

2E.2 Molecules with lone pairs on the central atom

AX_4E_2

- Electron arrangement: octahedral
- Molecular shape: **square planar**
- Why? The two lone pairs are farthest apart when they lie opposite each other.



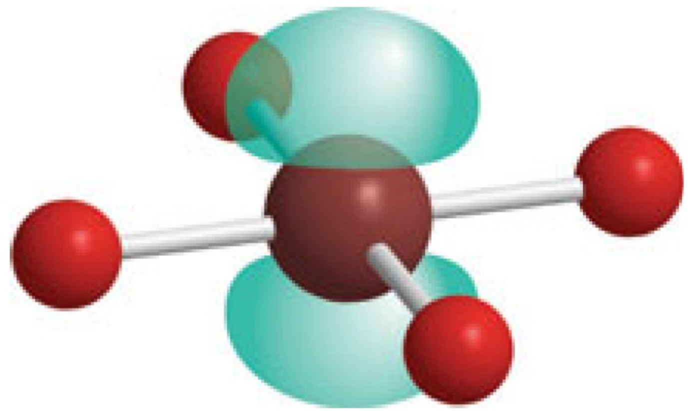


Figure 2E.6

2E.2 Molecules with lone pairs on the central atom

TOOLBOX 3.1 HOW TO USE THE VSEPR MODEL

CONCEPTUAL BASIS

Regions of high electron concentration—bonds and lone pairs attached to a central atom in a molecule—arrange themselves in such a way as to minimize mutual repulsions.

PROCEDURE

The general procedure for predicting the shape of a molecule is as follows:

Step 1 Decide how many atoms and lone pairs are present on the central atom by writing a Lewis structure for the molecule.

Step 2 Identify the electron arrangement, including lone pairs and atoms, and treating a multiple bond as equivalent to a single bond (see Fig. 3.2).

Step 3 Locate the atoms and identify the molecular shape (according to Fig. 3.1). The molecular shape describes only the positions of the atoms, not the lone pairs.

Step 4 Allow the molecule to distort so that lone pairs are as far from one another and from bonding pairs as possible. The repulsions are in the order

$$\text{Lone pair–lone pair} > \text{lone pair–atom} > \text{atom–atom}$$

Example 3.3 shows how this procedure is used.

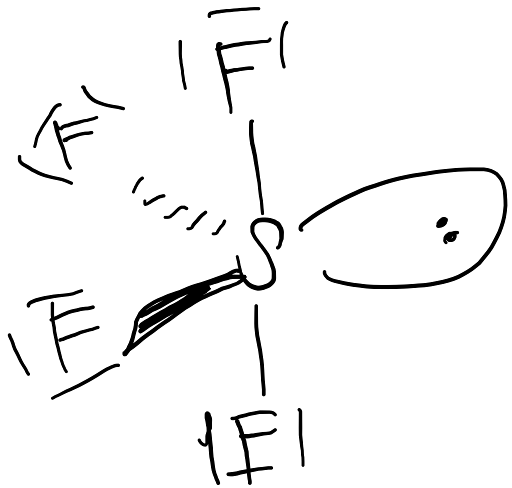
2E.2 Molecules with lone pairs on the central atom

Example 2E.3

$6 + 4 \cdot 7 = 34\ e^{-} \rightarrow 17\ e^{-}p$

Predict the shape of a sulfur tetrafluoride molecule, SF_4.

AX_4E



Shape: Seesaw

2E.2 Molecules with lone pairs on the central atom

Summary

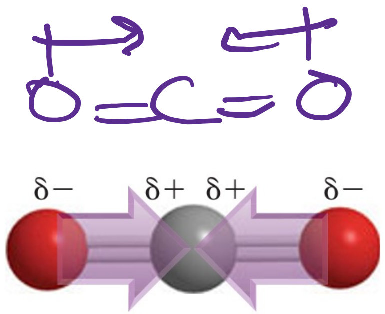
In a molecule that has lone pairs or a single nonbonding electron on the central atom, the valence electrons contribute to the electron arrangement about the central atom, and only bonded atoms are considered in the identification of the shape. Lone pairs distort the shape of a molecule so as to reduce lone pair-lone pair and lone pair-bonding pair repulsions.

Polar Molecules

Topic 2E.3

Definitions of polar molecules

- A diatomic molecule is polar if its bond is polar.
- **Diatomic molecules with two different atoms** are at least **slightly polar**.
- **Homonuclear diatomics** (O_2, N_2, Cl_2, etc.) are **nonpolar** – no dipole moment.
- A polyatomic molecule **can be nonpolar even it its bonds are polar**. Example: CO_2 (two equal C–O dipoles cancel each other).
- The molecular dipole moment is the **vector sum** of all bond dipoles.



2E.3 Polar molecules

A polar molecule has a nonzero dipole moment

- HCl is a polar molecule. Dipole moment is 1.08 D (typical).

TABLE 3.1 Dipole Moments of Selected Molecules

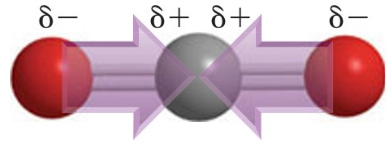
Molecule	Dipole moment (D)	Molecule	Dipole moment (D)
HF	1.91	PH_3	0.58
HCl	1.08	AsH_3	0.20
HBr	0.80	SbH_3	0.12
HI	0.42	O_3	0.53
CO	0.12	CO_2	0
ClF	0.88	BF_3	0
NaCl*	9.00	CH_4	0
CsCl*	10.42	*cis*-CHCl=CHCl	1.90
H_2O	1.85	*trans*-CHCl=CHCl	0
NH_3	1.47		

*For pairs of ions in the gas phase, not the bulk ionic solid.

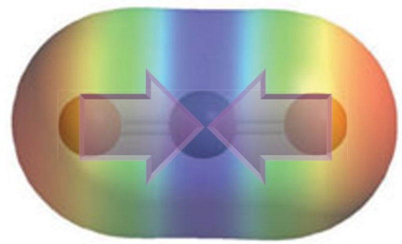
2E.3 Polar molecules

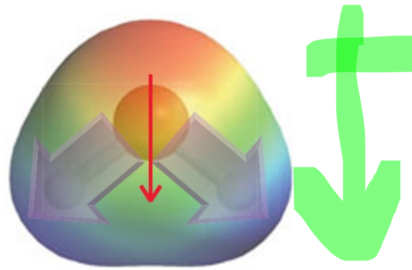
The electrostatic potential surface (the elpot surface)

- Another way to visualize dipole moment
- The net electrostatic potential is calculated at each point on the surface of the molecule and depicted by different colors. **Arrow point from red (neg) to blue (pos).**
- **Blue**: relative positive potential
- **Red**: relative negative potential
- CO_2: nonpolar molecule
- H_2O: polar molecule



26 Carbon dioxide, CO_2



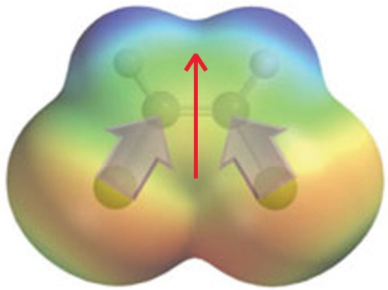


28 Water, H_2O

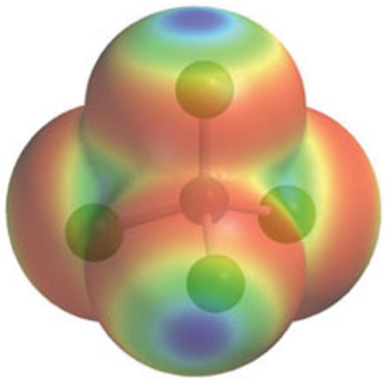
2E.3 Polar molecules

A few more examples

polar



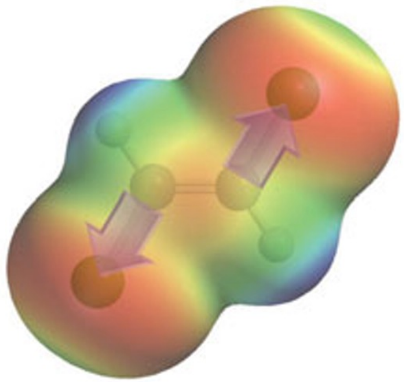
29 *cis*-Dichloroethene, $C_2H_2Cl_2$



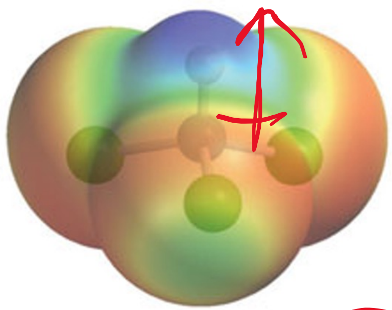
31 Tetrachloromethane, CCl_4

nonpolar

nonpolar



30 *trans*-Dichloroethene, $C_2H_2Cl_2$



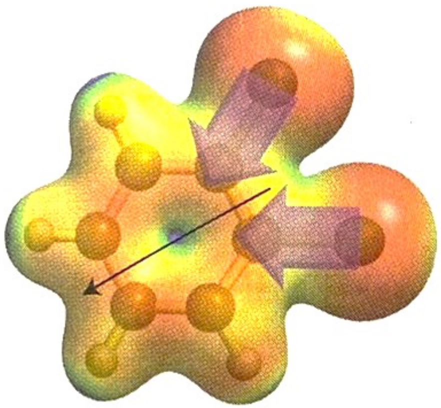
32 Trichloromethane, $CHCl_3$

polar

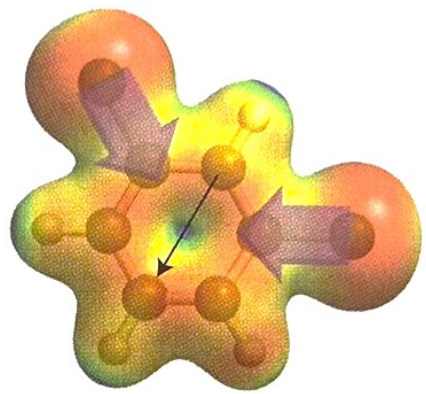
2E.3 Polar molecules

A few more examples

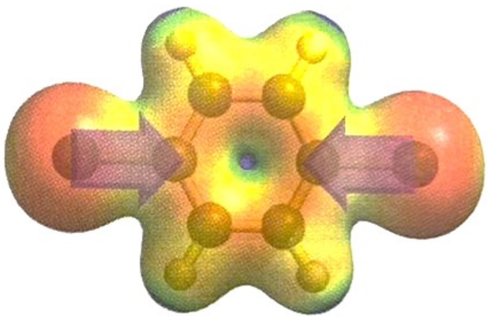
polar > polar nonpolar



31 *o*-Dichlorobenzene, $C_6H_4Cl_2$



32 *m*-Dichlorobenzene, $C_6H_4Cl_2$



33 *p*-Dichlorobenzene, $C_6H_4Cl_2$

2E.3 Polar molecules

Overview of all different VSEPR configurations

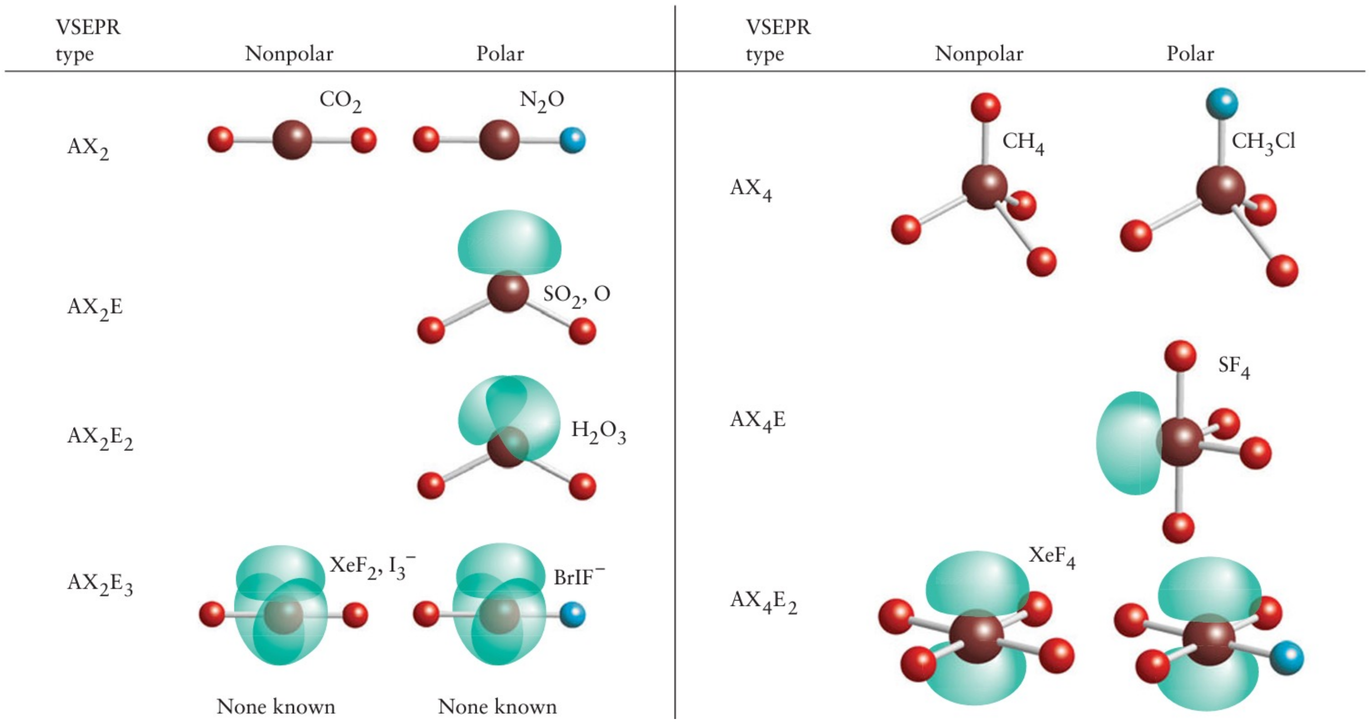


Figure 2E.7 **part 1**

2E.3 Polar molecules

Overview of all different VSEPR configurations

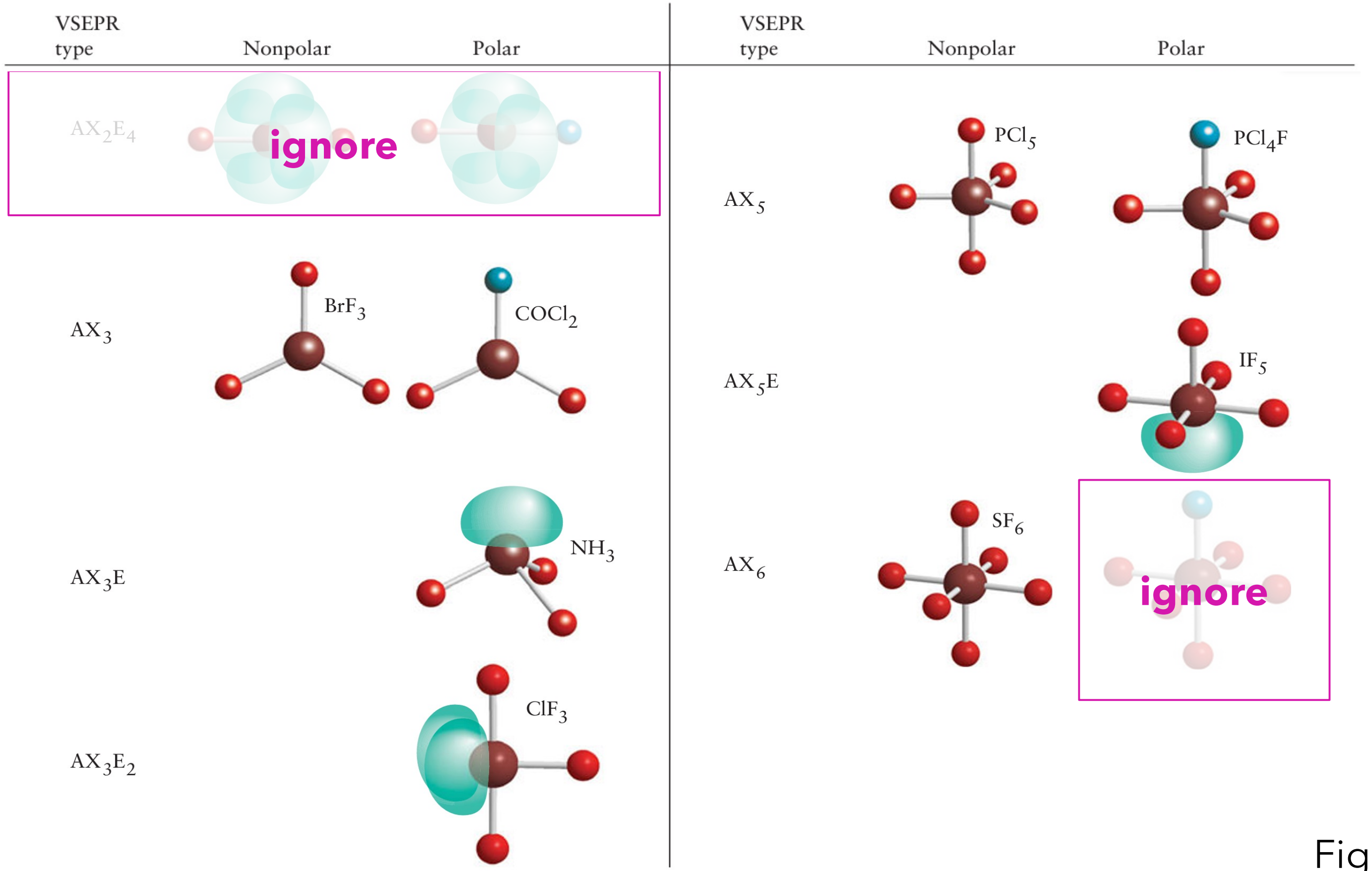


Figure 2E.7 **part 2**