CH-110 Advanced General Chemistry I

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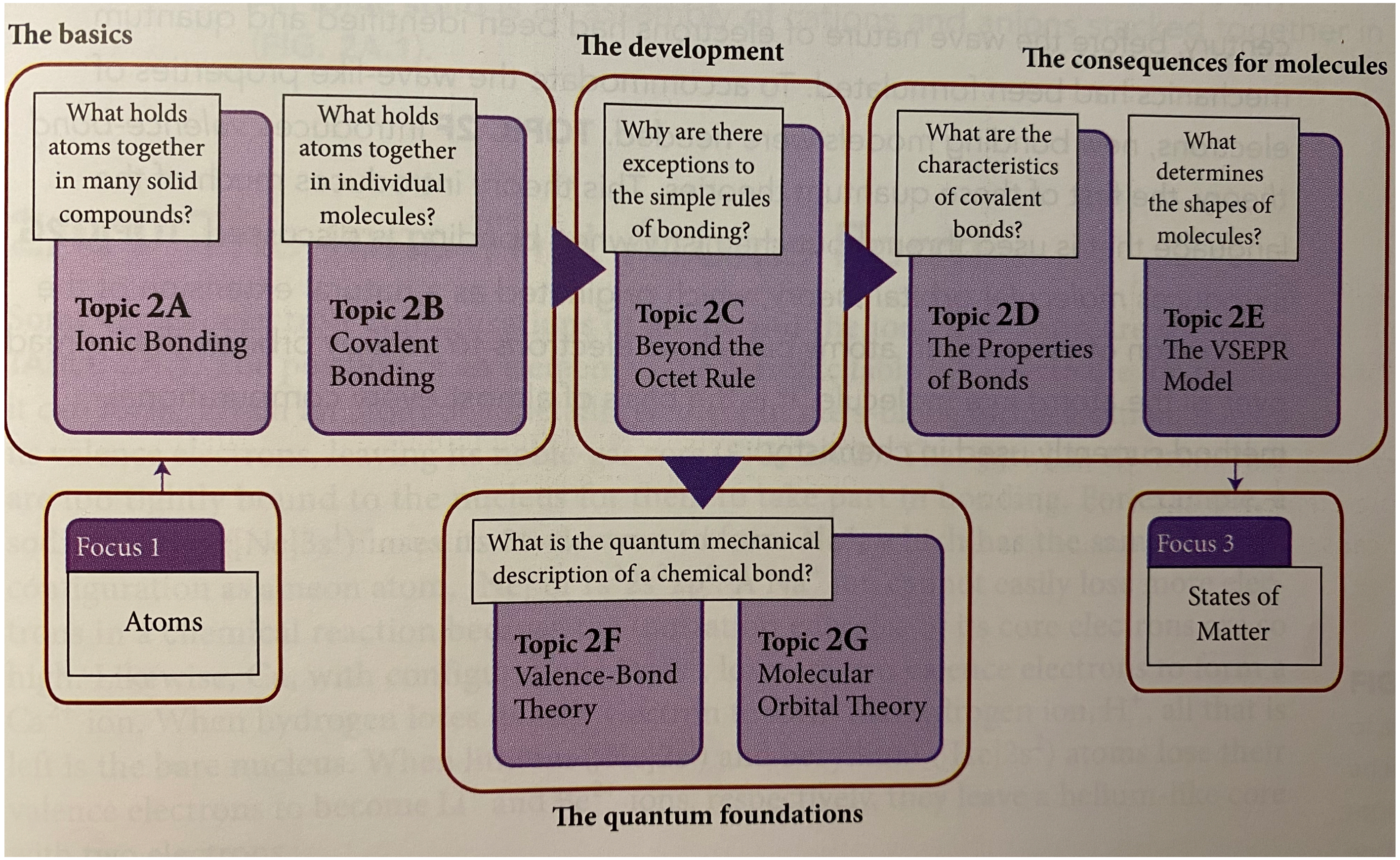
Housekeeping notes

- We decided: mode examen for calculators NOT allowed. Please use a non-programmable calculator.
- Q&A session: class delegate, please come talk to me in the break to find a suitable date and time!

Overview Chapter 2 (Focus 2: Bonds Between Atoms)



The basics

What holds atoms together in many solid compounds?

Topic 2A
Ionic Bonding

What holds atoms together in individual molecules?

Topic 2B
Covalent Bonding

The development

Why are there exceptions to the simple rules of bonding?

Topic 2C
Beyond the Octet Rule

The consequences for molecules

What are the characteristics of covalent bonds?

Topic 2D
The Properties of Bonds

What determines the shapes of molecules?

Topic 2E
The VSEPR Model

Focus 1
Atoms

What is the quantum mechanical description of a chemical bond?

Topic 2F
Valence-Bond Theory

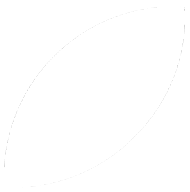
Topic 2G
Molecular Orbital Theory

The quantum foundations

Focus 3
States of Matter

The Properties of Bonds

Topic 2D



Last time: Topic 2D.1 Correcting the covalent model: electronegativity
Last time: Topic 2D.2 Correcting the ionic model: polarizability
Topic 2D.3 Bond strengths
Topic 2D.4 Bond lengths

WHY DO YOU NEED TO KNOW THIS MATERIAL?

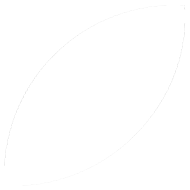
- Properties of bonds vary widely. Variations in bond strength, bond length, and the distribution of electrons in a bond, are used to explain the physical and chemical properties of molecules.

WHAT DO YOU NEED TO KNOW ALREADY?

- Periodic trends (Topic 1F)
- Concept of resonance (Topic 2B)
- Role of electron-pair sharing in covalent bonding (Topic 2B)

Bond Strengths

Topic 2D.3



2D.3 Bond strengths

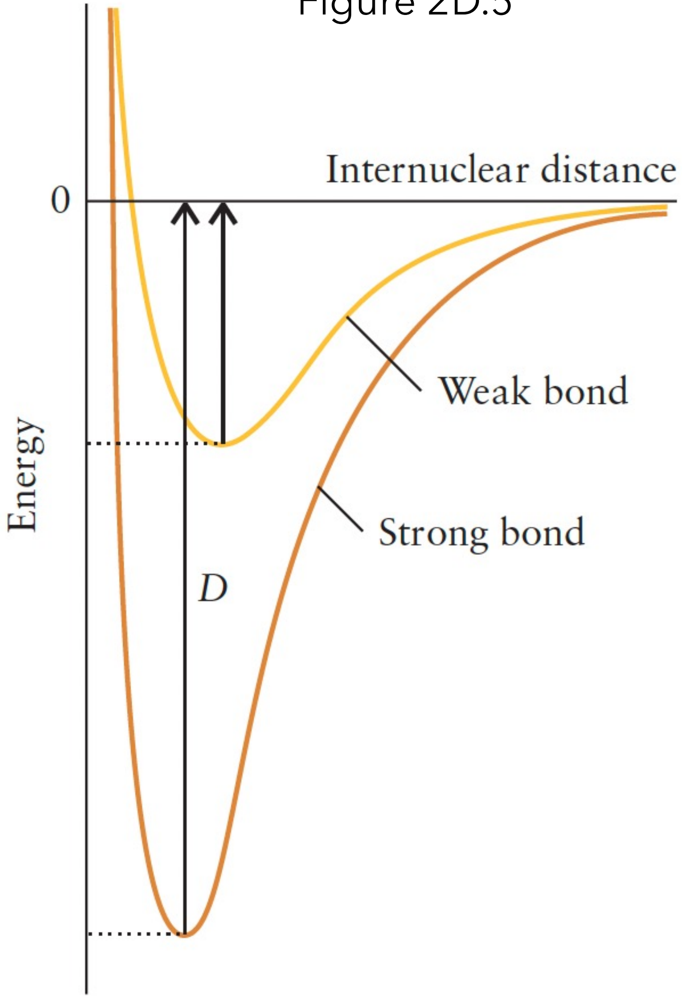
Dissociation energy

- The **strength of a bond** is measured by its **dissociation energy**, *D*, the energy required to separate the bonded atoms completely.
- For these values, upon dissociation, each atom retains one electron (**homolytic**):

$$\mathrm{H{-}Cl(g)} \rightarrow \cdot\,\mathrm{H(g)} + \cdot\,\mathrm{Cl(g)}$$

- Depth of the well indicates (approximately) the strength of bond
- **Strongest known bond** between nonmetals: Carbon monoxide triple bond: C≡O (1062 kJ/mol)
- Weakest bond: iodine in I_2 (139 kJ/mol)

Figure 2D.5



2D.3 Bond strengths

Dissociation energies of diatomic molecules

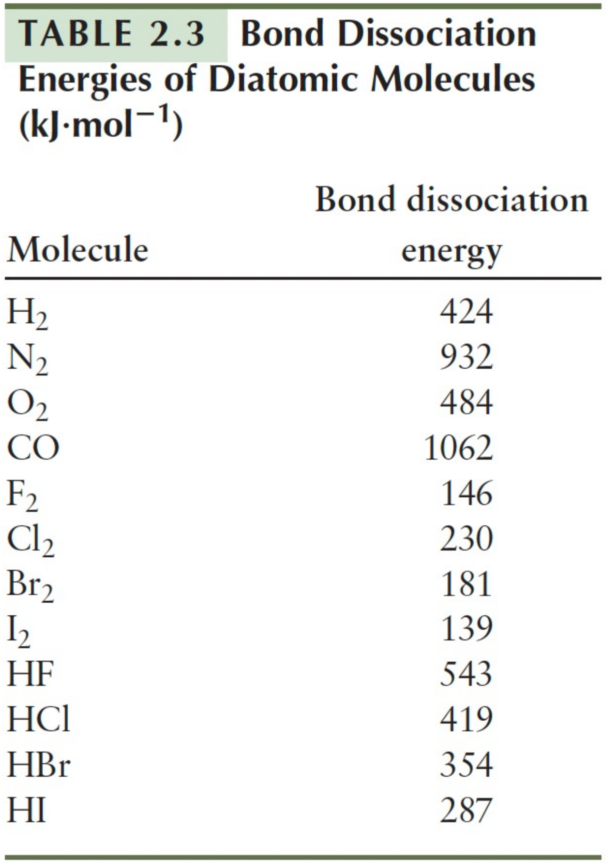


TABLE 2.3 Bond Dissociation Energies of Diatomic Molecules (kJ·mol^{-1})

Molecule	Bond dissociation energy
H_2	424
N_2	932
O_2	484
CO	1062
F_2	146
Cl_2	230
Br_2	181
I_2	139
HF	543
HCl	419
HBr	354
HI	287

TREND (look at Lewis structures) for diatomic molecules:

- $N_2 > O_2 > F_2$: triple > double > single bond:

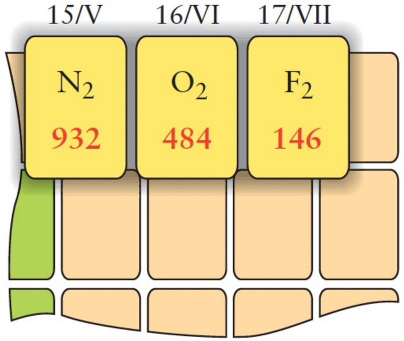


Figure 2D.6

2D.3 Bond strengths

C–C vs. C=C vs. C≡C

- A double bond is not twice as strong as a single bond: One C=C bond (623 kJ/mol) vs. two single C–C bonds (696 kJ/mol)
- One C≡C bond (837 kJ/mol) vs. three single C–C bonds (1044 kJ/mol)
- **Why is there a loss in energy for multiple bonds?** Repulsions between electron pairs in a multiple bond, not quite as effective at bonding as one pair in a single bond

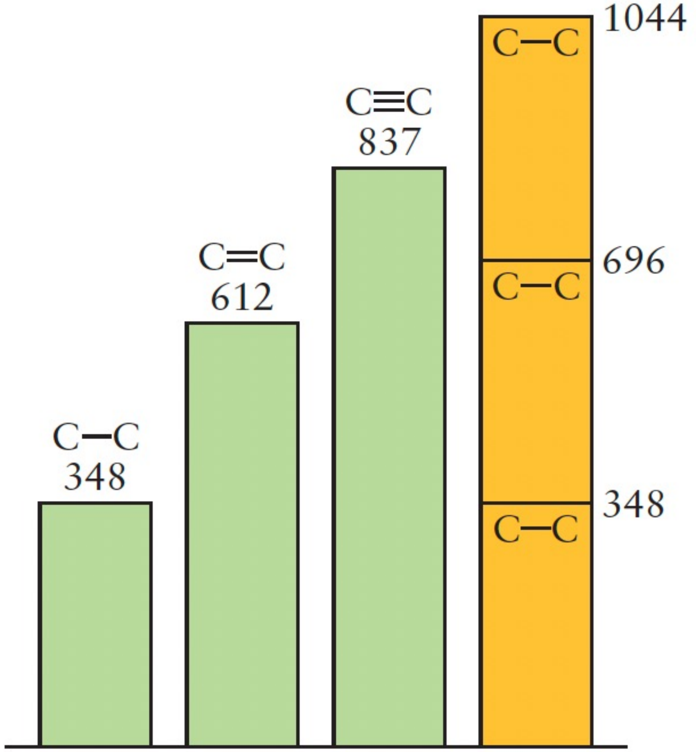


Figure 2D.7

2D.3 Bond strengths

Average bond dissociation energies

- Average for one type of bond, precise bond dissociation energy depends on **context**
- For example, C–H bond could be in methane (CH_4), ethane (C_2H_6) and ethene (C_2H_4)

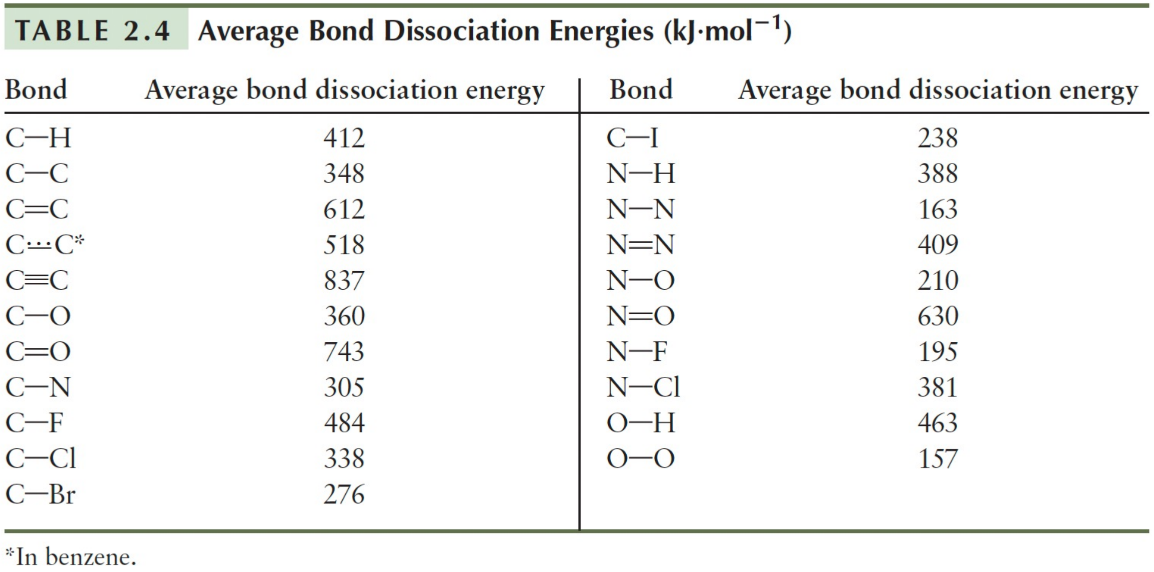


TABLE 2.4 **Average Bond Dissociation Energies (kJ·mol^{-1})**

Bond	Average bond dissociation energy	Bond	Average bond dissociation energy
C—H	412	C—I	238
C—C	348	N—H	388
C=C	612	N—N	163
C⋯C*	518	N=N	409
C≡C	837	N—O	210
C—O	360	N=O	630
C=O	743	N—F	195
C—N	305	N—Cl	381
C—F	484	O—H	463
C—Cl	338	O—O	157
C—Br	276		

*In benzene.

2D.3 Bond strengths

Summary: **Factors that influence bond strength**

- Bond order: C≡C > C=C > C–C
- Resonance: C=C > C–C(benzene) > C–C
- Lone pairs on neighbouring atoms: F-F < H-H
- Atomic radii: HF > HCl > HBr > HI

The smaller the radius, the stronger the bond.

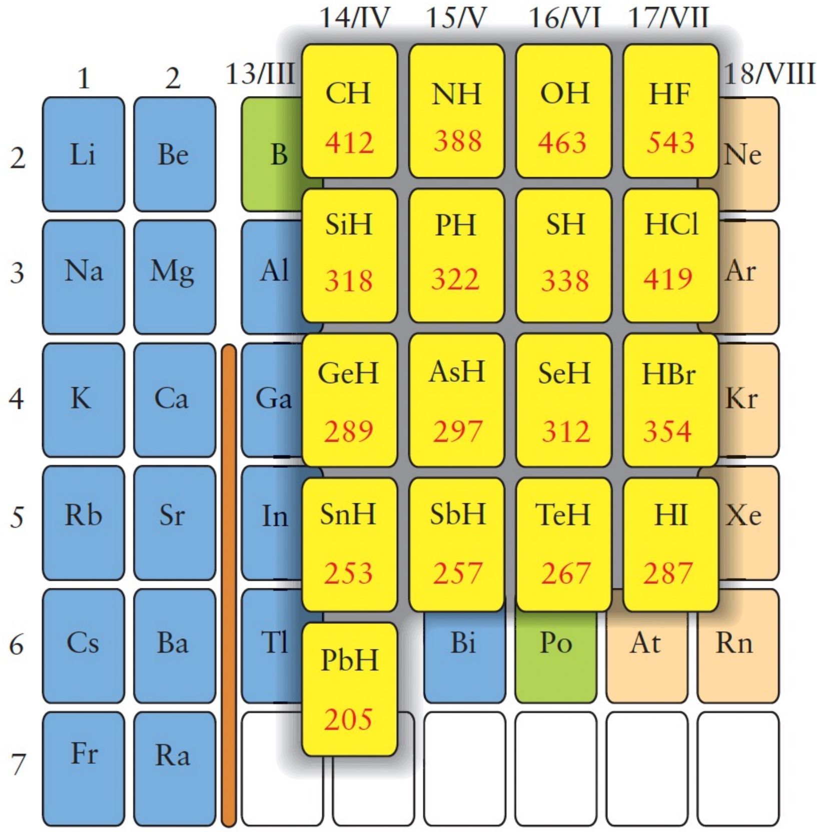


Figure 2D.8

2D.3 Bond strengths

Summary

The strength of a bond between two atoms is measured by its dissociation energy: the greater the dissociation energy, the stronger the bond. Bond strength between the same two atoms increases as the multiplicity of a bond increases, decreases as the number of lone pairs on neighbouring atoms increases, and decreases as the atomic radii increase.

Bond Lengths

Topic 2D.4

2D.4 Bond lengths

Bond length

- **Internuclear distance between the centers of two atoms = bond length**
- Bond lengths affect **size and shape of molecule**
- For example: DNA replication, enzyme binding into active sites
- Determined by spectroscopy or x-ray diffraction

2D.4 Bond lengths

Bond lengths

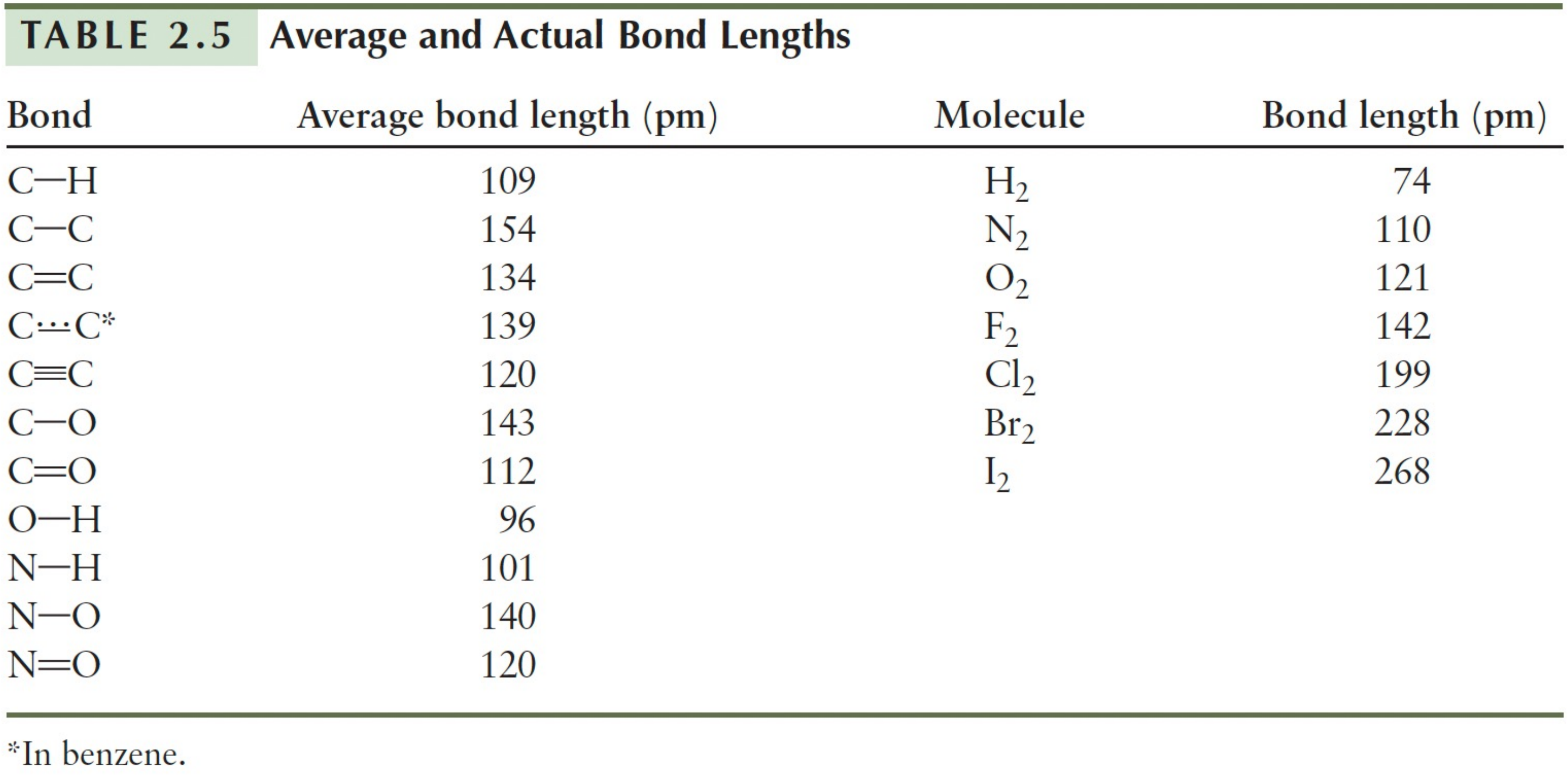


TABLE 2.5 Average and Actual Bond Lengths

Bond	Average bond length (pm)	Molecule	Bond length (pm)
C—H	109	H_2	74
C—C	154	N_2	110
C═C	134	O_2	121
C┄C*	139	F_2	142
C≡C	120	Cl_2	199
C—O	143	Br_2	228
C═O	112	I_2	268
O—H	96		
N—H	101		
N—O	140		
N═O	120		

*In benzene.

2D.4 Bond lengths

Summary: **Factors that influence bond length**

- Bond order: C≡C < C=C < C–C
- Resonance: C=C < C–C(benzene) < C–C
- Lone pairs on neighbouring atoms: F-F > H-H
- Atomic radii: HF < HCl < HBr < HI

The smaller the radius, the shorter the bond (see Figure 2D.9).

These trends are **opposite** of the ones for bond strength.

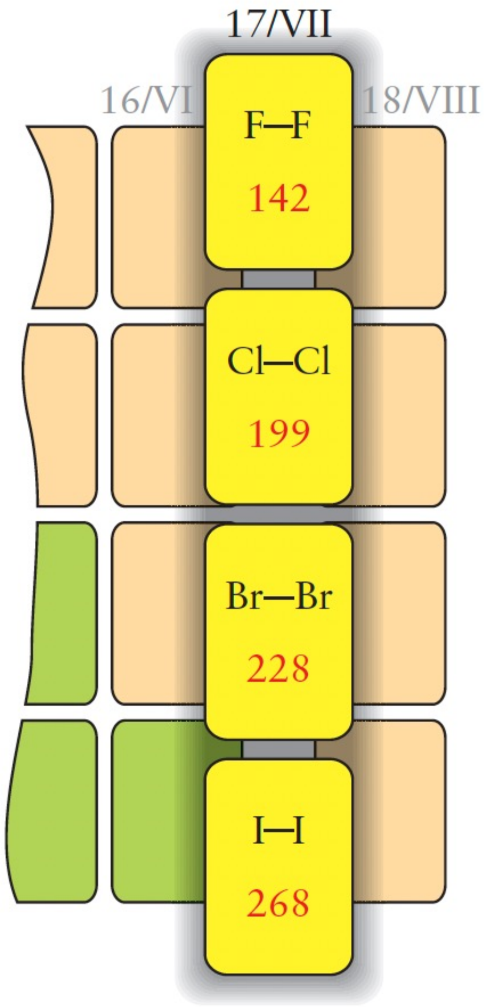


Figure 2D.9

2D.4 Bond lengths

Covalent radius

- **Contribution an atom makes to the length of a covalent bond = covalent radius**
- Measured as half of the distance between the centers (nuclei) of neighboring atoms joined by a covalent bond (*for identical atoms*)
- Covalent radii may be added to estimate bond lengths in molecules
- Tabulated values are averages of radii in polyatomic molecules

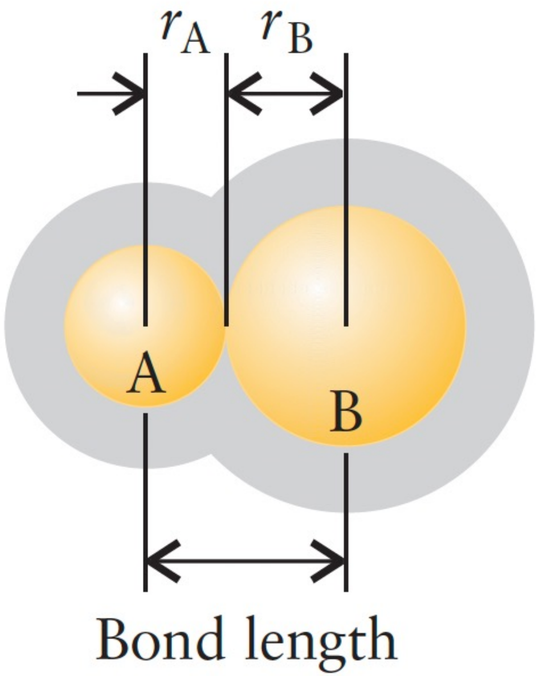
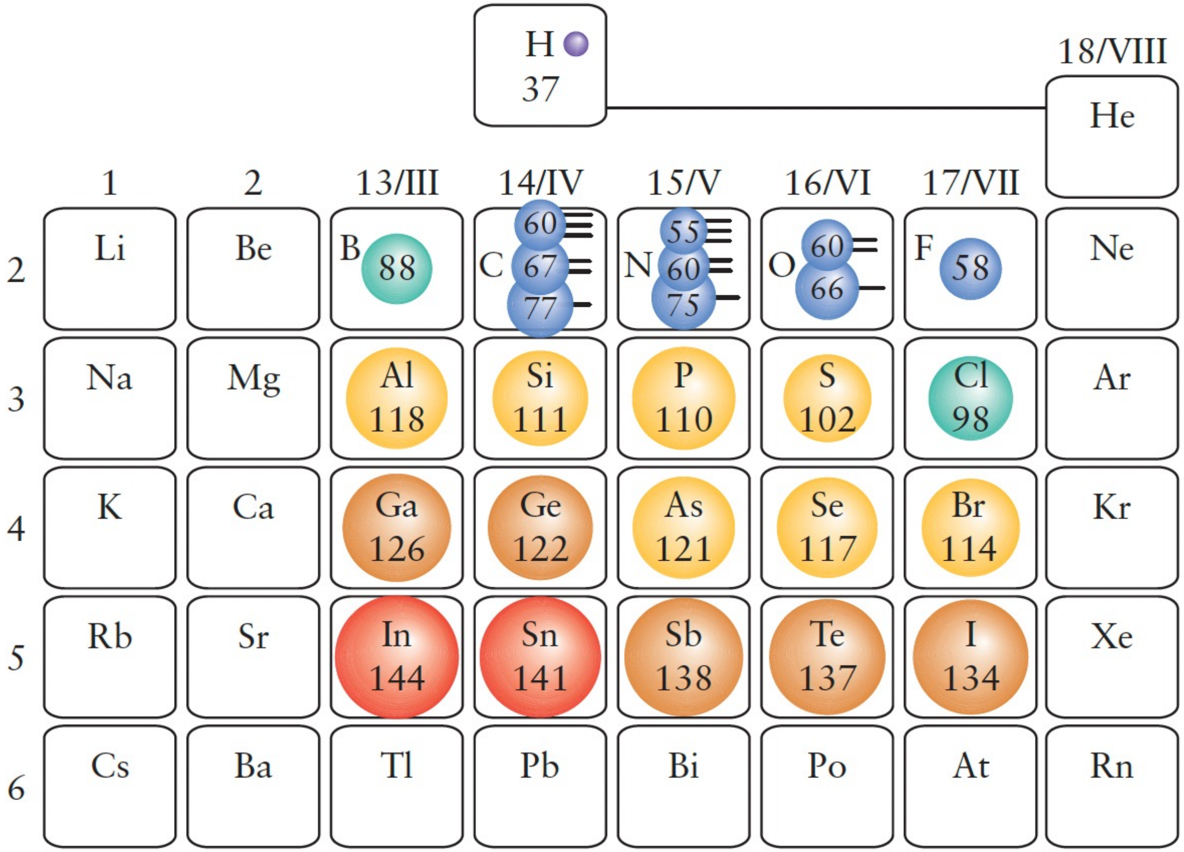


Figure 2D.8

2D.4 Bond lengths

Figure 2D.5

Covalent radii of hydrogen and p-block elements (in pm)



2D.4 Bond lengths

Summary

The covalent radius of an atom is the contribution it makes to the length of a covalent bond; covalent radii are added together to estimate the lengths of bonds in molecules.

The skills you have mastered are the ability to

- Explain the concept of electronegativity and use it to assess whether a bond is polar.
- Explain how resonance is used to improve the description of a covalent bond by introducing ionic character into it.
- Estimate relative ionic or covalent character.
- Explain how the concept of polarizability is used to improve the description of an ionic bond.
- Predict and explain periodic trends in the polarizability of anions and the polarizing power of cations.
- Predict and explain relative bond strengths and bond lengths

Summary: You have learned that the electronegativity of an element enables you to identify which atom in a bond has the greater share of the electron pair. Chemical bonds show a range of character, from completely covalent to completely ionic. You have seen that bond strengths are approximately transferrable between molecules and that atoms make characteristic contributions to the length of bonds.

The VSEPR Model

Topic 2E

2E The VSEPR model

Lead-in

Lewis structures vs. the VSEPR model

Lewis structure	The VSEPR model
Shows **distribution** of valence electrons in bonding pairs (bonds) and lone pairs or unpaired electrons.	The valence electrons about a central atom control the **shape** of a molecule
Shows how atoms are **connected**.	

Topic 2E.1 The basic VSEPR model
Topic 2E.2 Molecules with lone pairs on the central atom
Topic 2E.3 Polar molecules

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- Molecular shape is essential to understand reactivity

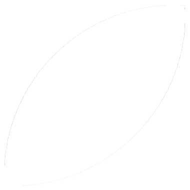
WHAT DO YOU NEED TO KNOW ALREADY?

- Lewis structures (Topic 2B)
- Polar molecules and polar bonds (Topic 2D)

The Basic VSEPR Model

Topic 2E.1

What is the 3D shape of a molecule?



2E.1 The basic VSEPR model

Valence-shell electron-pair repulsion (VSEPR) model

- Focused on understanding of **molecular shape.**
- VSEPR model extends Lewis's theory of bonding by adding rules that account for **bond angles** and **molecular shapes** in terms of **regions of high electron concentration**.

Rule 1: Regions of high electron concentration (bonds and lone pairs on the central atom) repel one another, and, to minimize their repulsions, these regions move **as far apart as possible from each other** while maintaining the same distance from the central atom.

Rule 2: A multiple bond is treated as a single region of high electron concentration.

2E.1 The basic VSEPR model

Valence-shell electron-pair repulsion (VSEPR) model

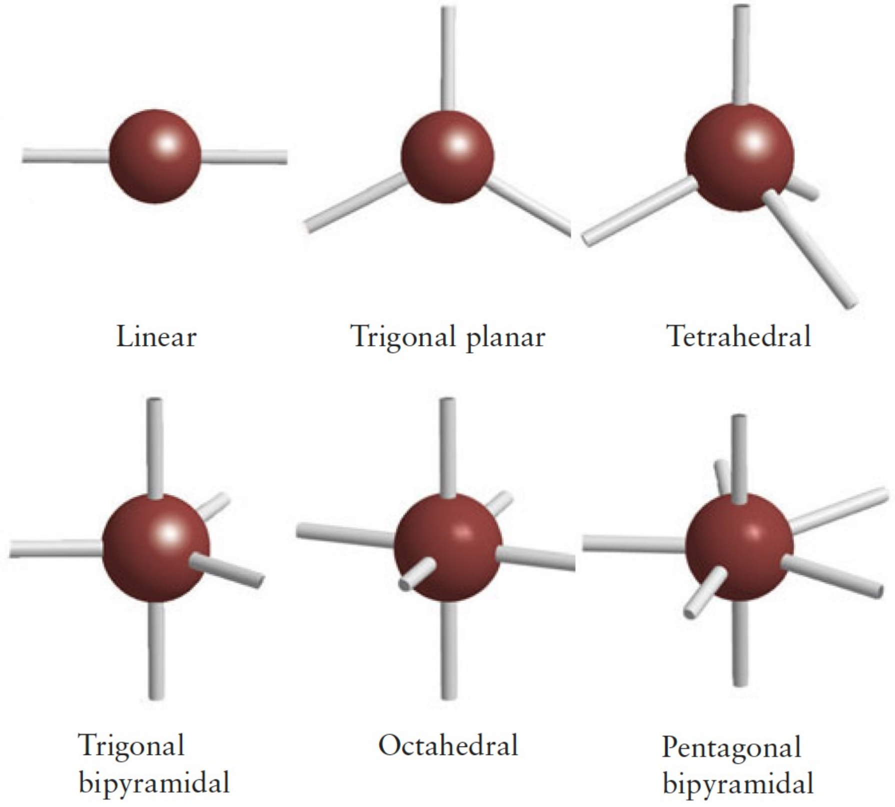
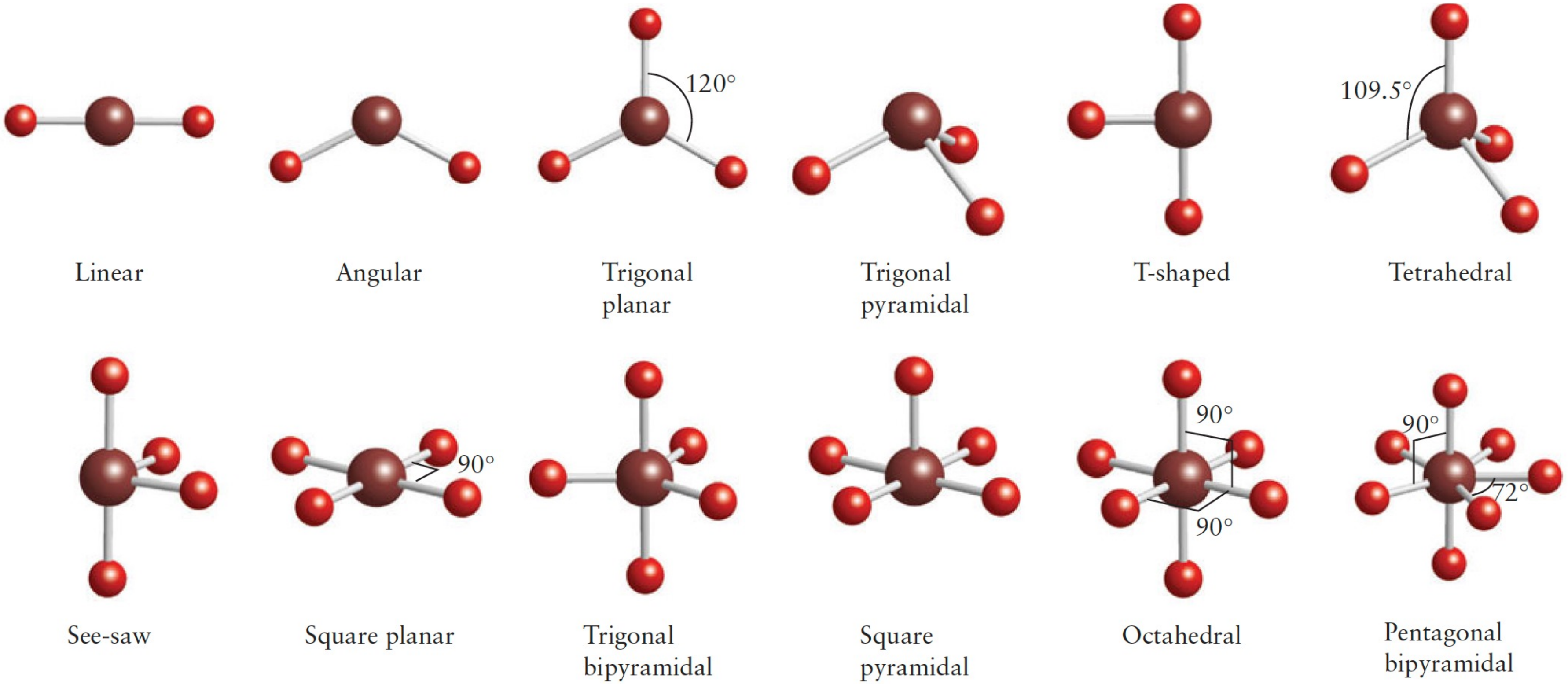


Figure 2E.2

- The positions that two to seven regions of high electron concentration (atoms and lone pairs) take around a central atom.
- **Regions**: straight lines sticking out from the central atom (red).
- Use this diagram to identify the **electron arrangement of a molecule** and then use Fig. 2E.1 to identify the shape of the molecule from the locations of its atoms.

2E.1 The basic VSEPR model

Valence-shell electron-pair repulsion (VSEPR) model



Note: lone pairs are **not** shown in these figures, only atoms.

Figure 2E.1

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:

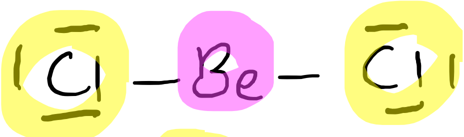
Lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

2E.1 The basic VSEPR model

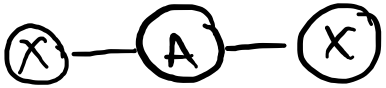
Some examples: predict the shape of these molecules.

- 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

$BeCl_2$:

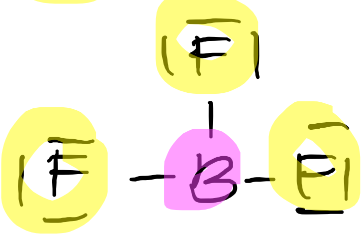


VSEPR: AX_2

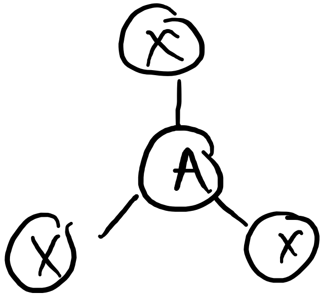


linear

BF_3:

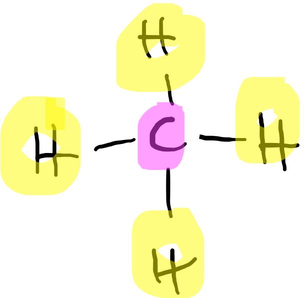


VSEPR: AX_3

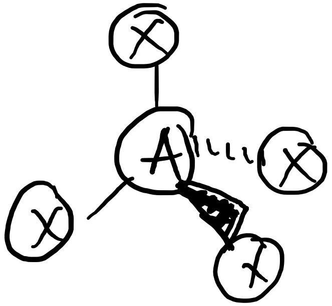


trigonal planar

CH_4:

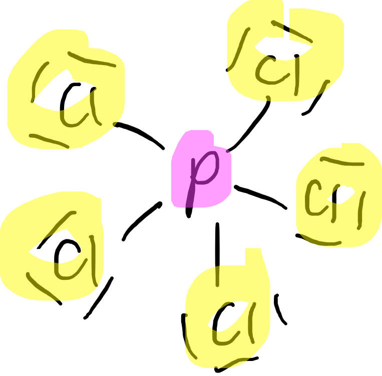


VSEPR: AX_4

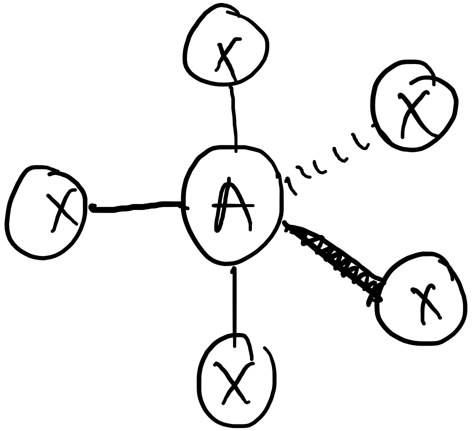


tetrahedral

PCl_5:

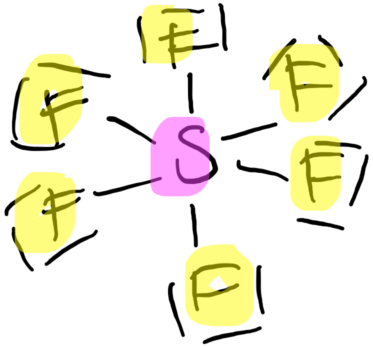


VSEPR AX_5



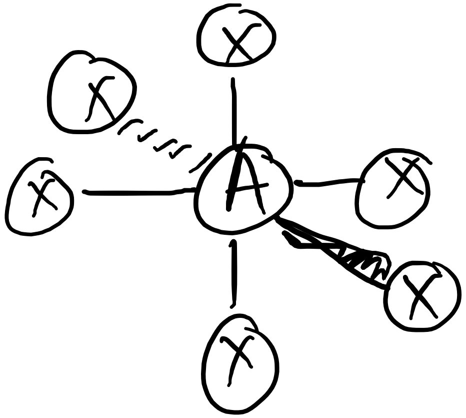
trigonal bipyramidal

SF_6:



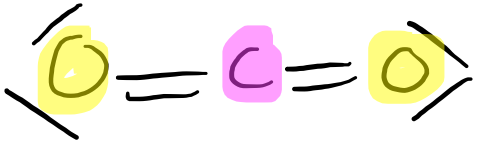
VSEPR:

AX_6



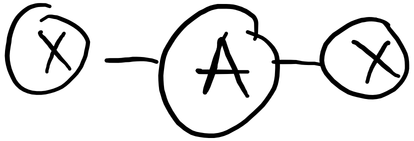
octahedral

CO_2:



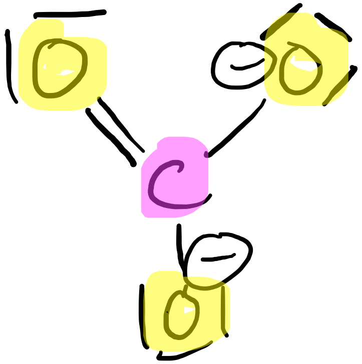
VSEPR:

AX_2



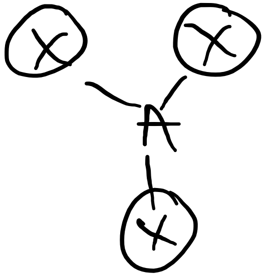
linear

CO_3^{2-}:



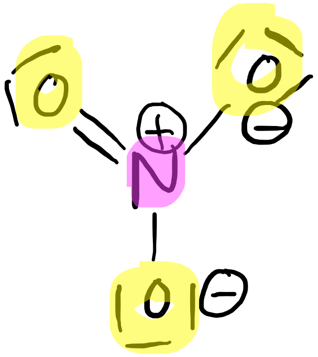
VSEPR:

AX_3



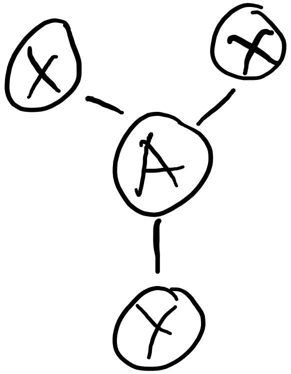
trigonal planar

$NO_3^{\ominus}$:



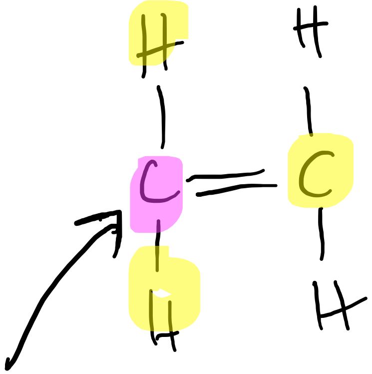
VSEPR:

AX_3



trigonal planar

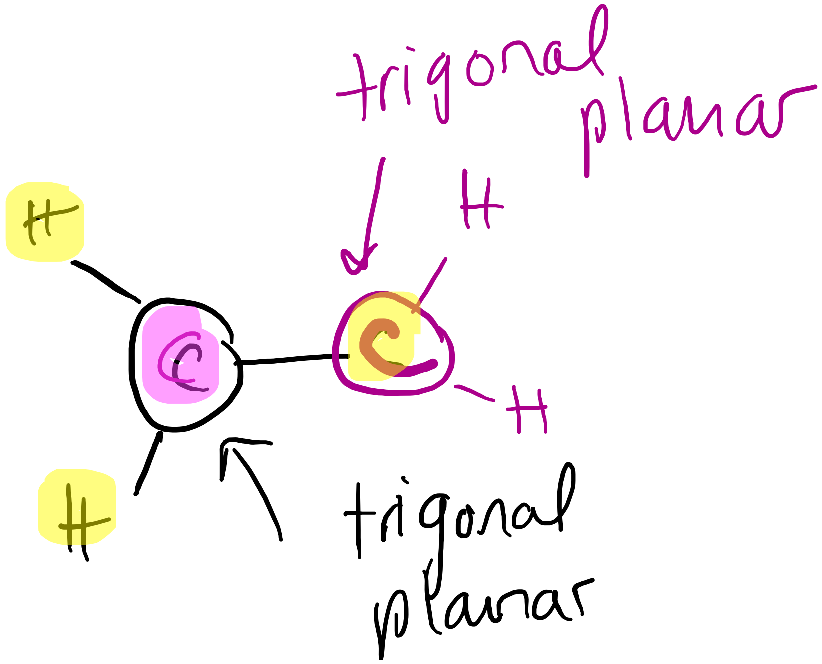
C_2H_4:



look at each central carbon separately

VSEPR

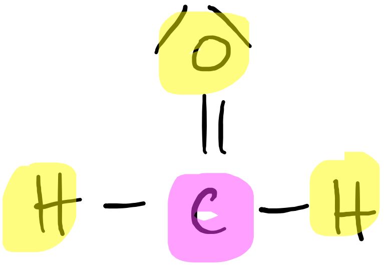
AX_3



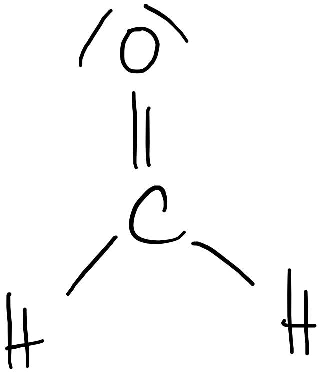
2E.1 The basic VSEPR model

Example 2E.1

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



AX_3



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

The generic VSEPR formula AX_nE_m

A = central atom

X_n = n attached atoms

E_m = m lone pairs

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.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 (blackboard):

Sulfite ion, SO_3^{2-}

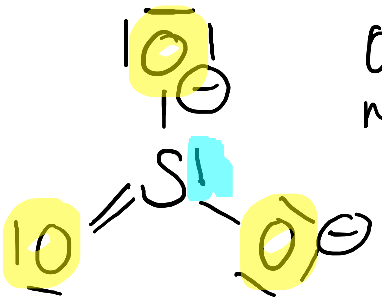
Nitrogen dioxide, NO_2

SO_3^{2-}:

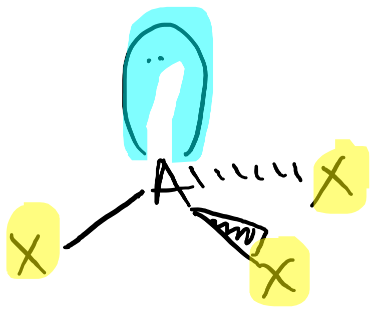
$6+3\cdot6+2$

$= 26\ e^-$

13 e^- pairs



one resonance structure



trigonal pyramidal

4 units of e^- density: $AX_3\bar{E}$

NO_2:

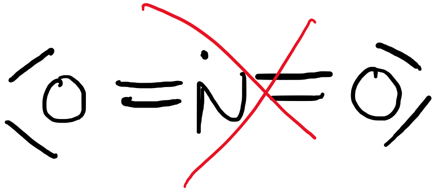
$5+2\cdot6 = 17\ e^-$

↓

odd number

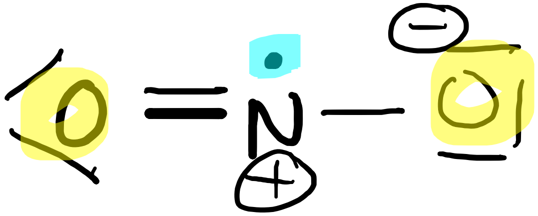
↓

unpaired e^-!

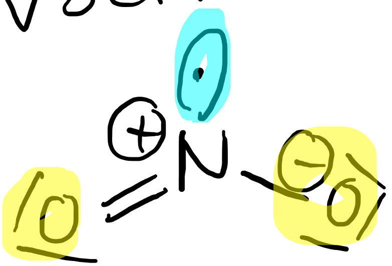


↑

N is in 2nd period, cannot be hypervalent.



VSEPR: $AX_2\bar{E}$



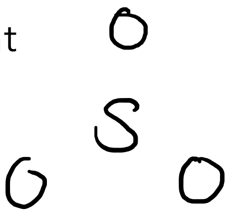
bent

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

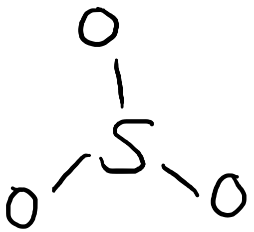
Step 1: Count valence electrons $6 + 3 \cdot 6 + 2 = 26$

13 $e^{\ominus}$ pairs

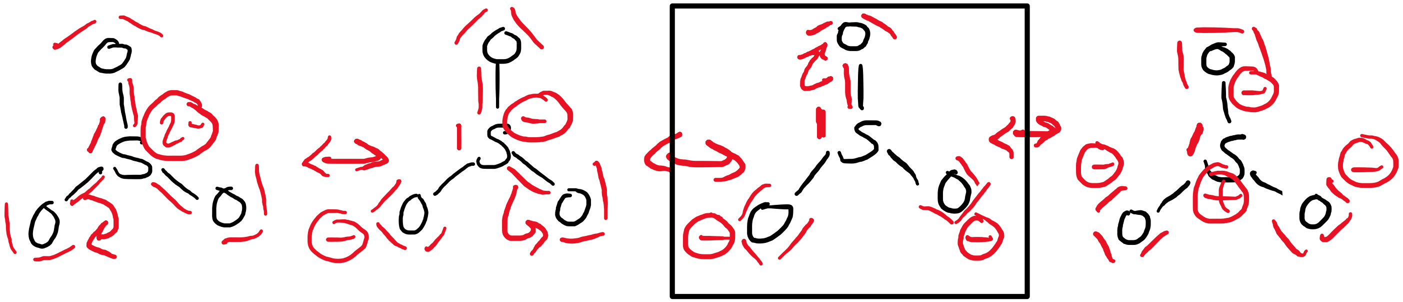
Step 2:write down most likely arrangement



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



Step 4: Complete octets/duplets $13 - 3$ $e^{\ominus}$ pairs $= 10$ remaining



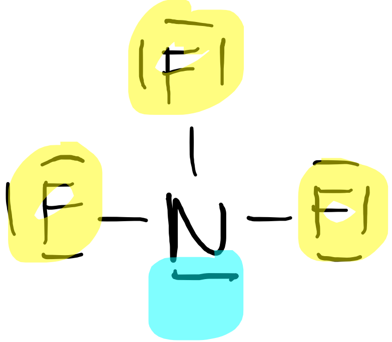
These are all *theoretically* possible resonance structures, the most stable one (boxed) minimizes formal charges and puts the formal charges on the most electronegative atom (oxygen).

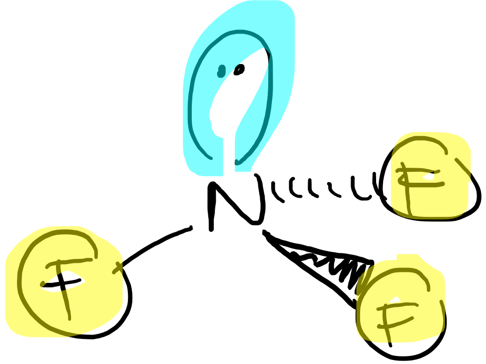
2E.1 The basic VSEPR model

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°**

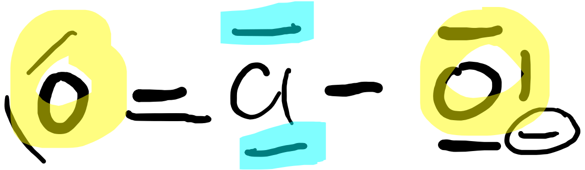
2E.2 Molecules with lone pairs on the central atom

Self-test

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

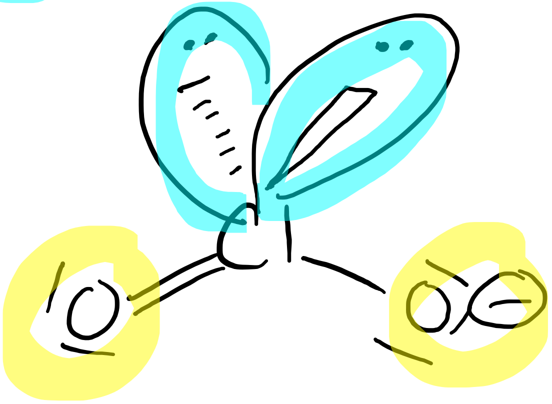
→ tetrahedral

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



→ bent

AX_2E_2



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'.

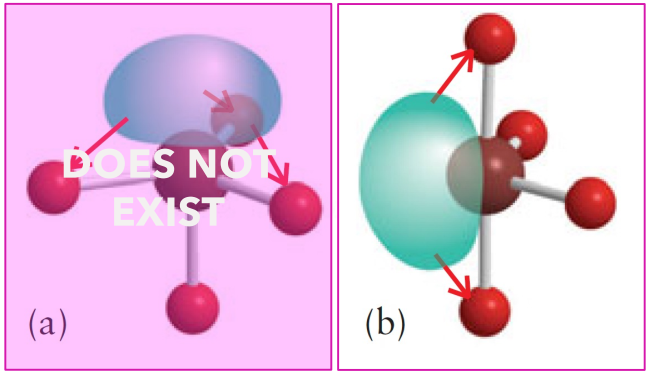
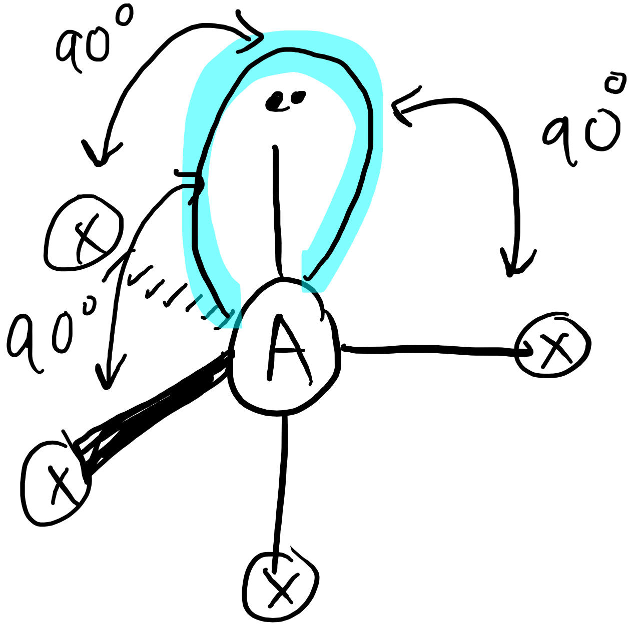


Figure 2E.4

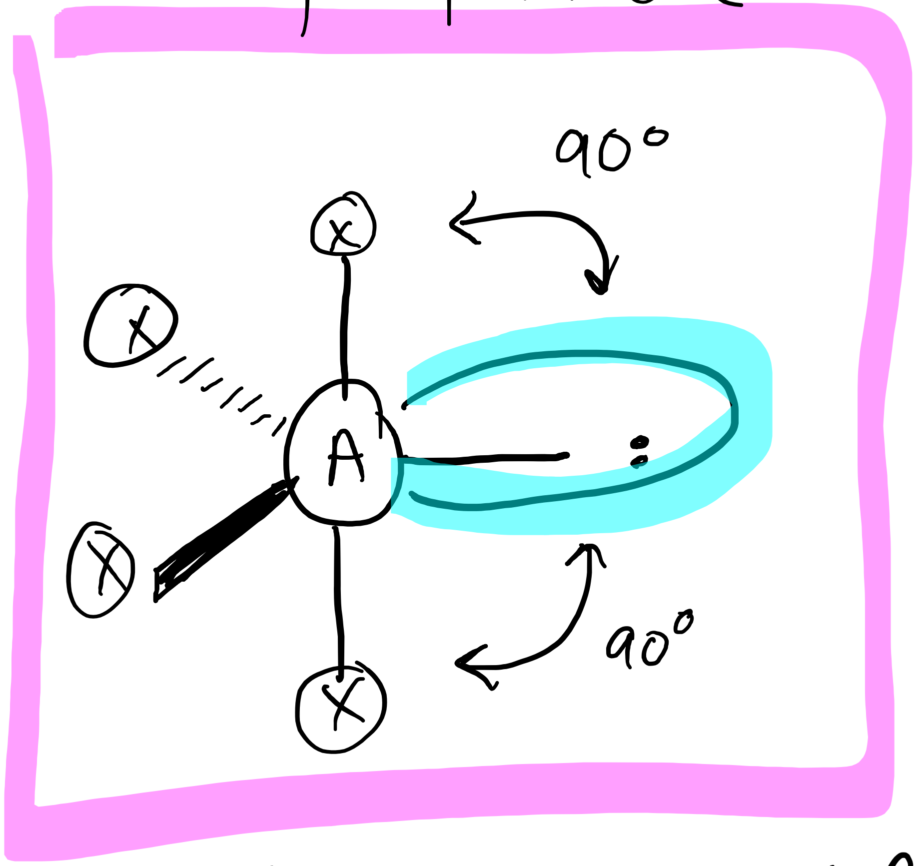
AX$_4$E:



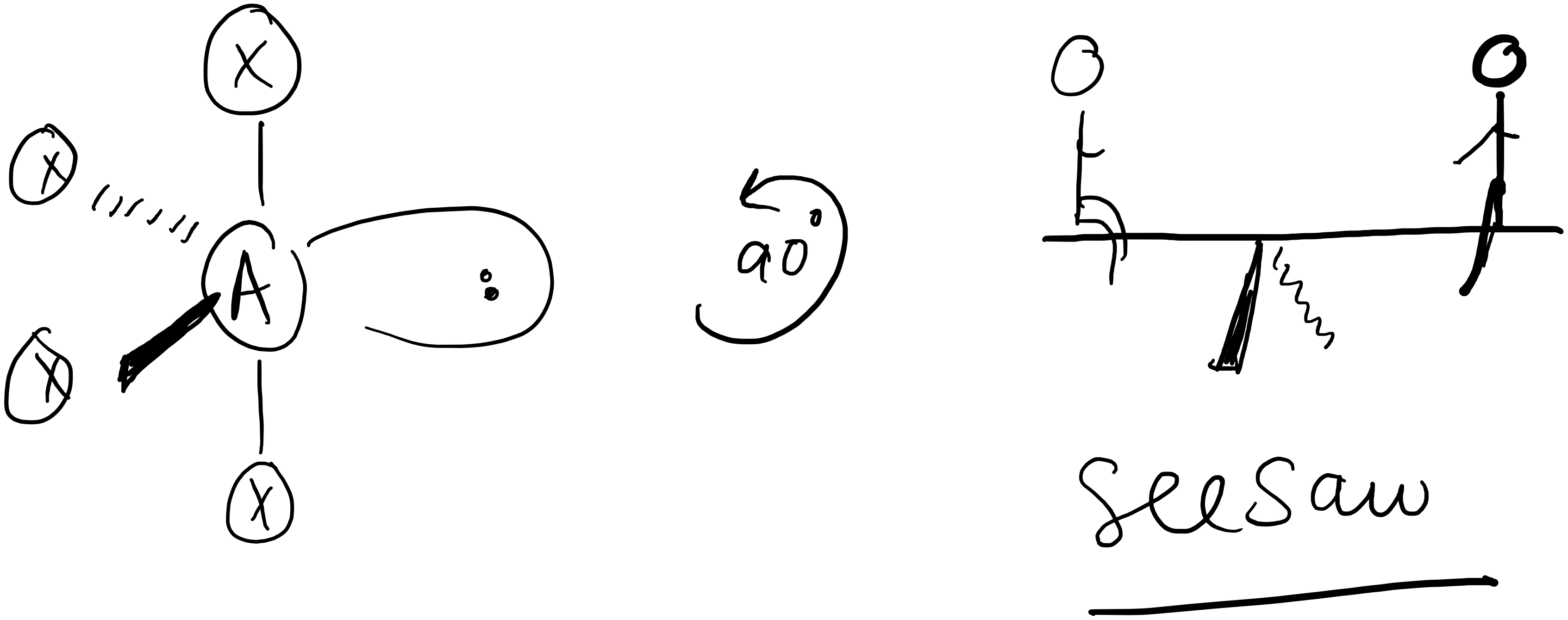
lone pair axial
3 repulsive interactions

vs.

Preferred



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.

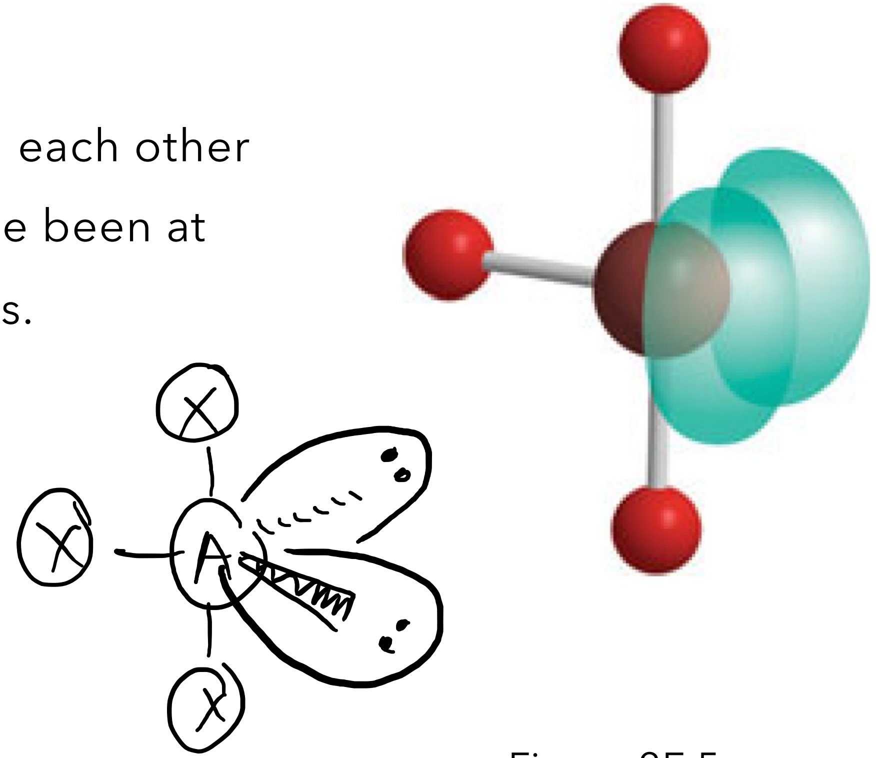


Figure 2E.5

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.

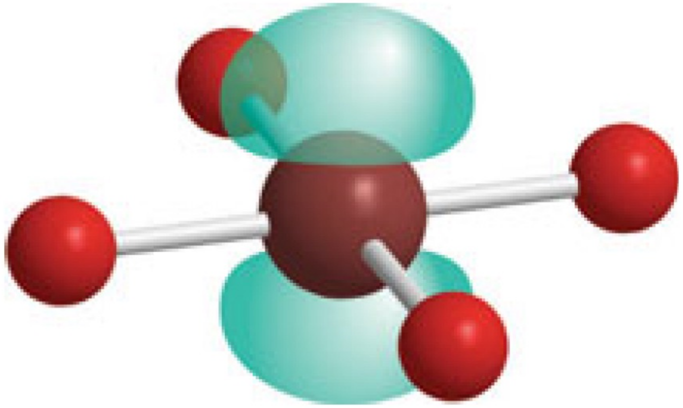
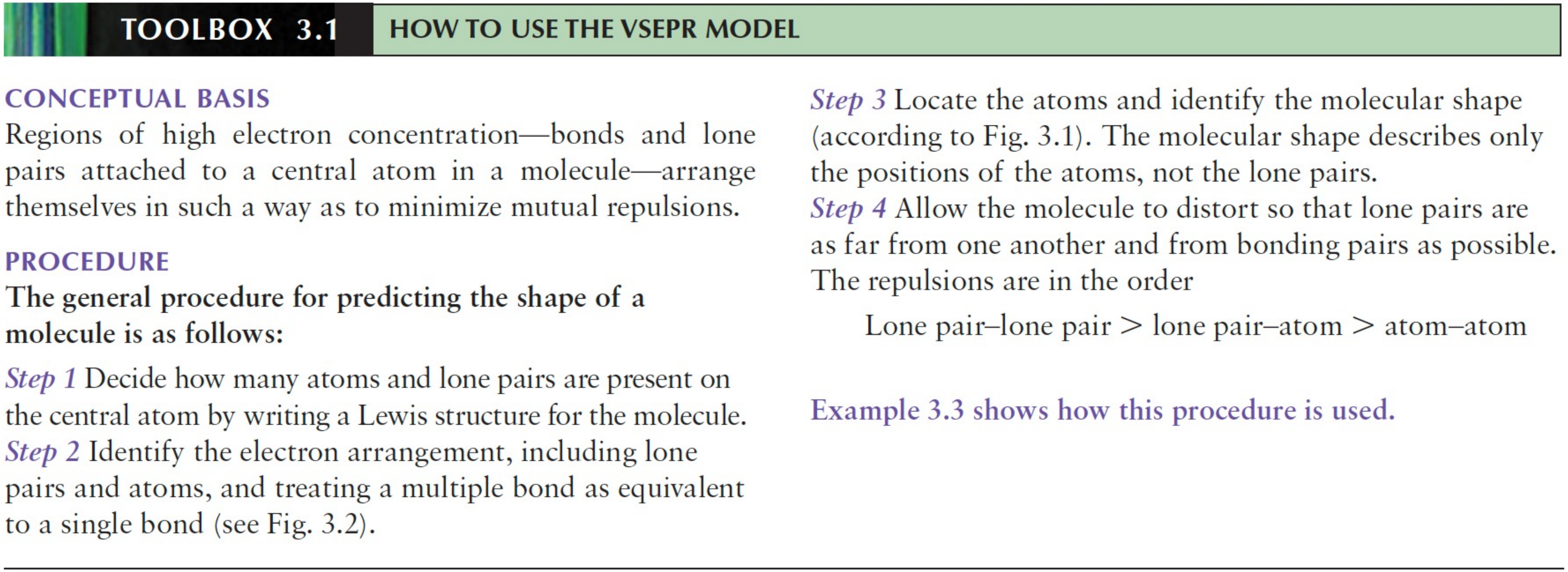


Figure 2E.6

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

Lone pair–lone pair > lone pair–atom > atom–atom

Example 3.3 shows how this procedure is used.

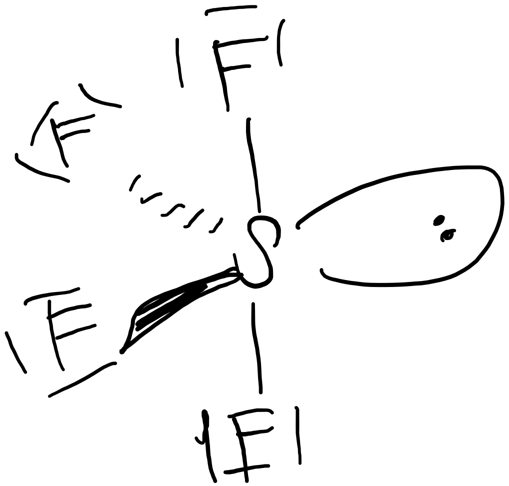
2E.2 Molecules with lone pairs on the central atom

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

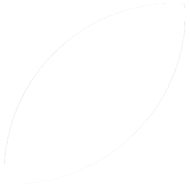
2E.2 Molecules with lone pairs on the central atom

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

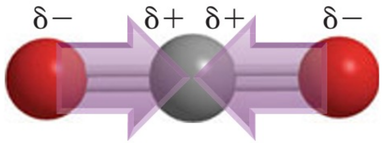
Topic 2E.3



2E.3 Polar molecules

Definitions of polar molecules

- A diatomic molecule is polar if its bond is polar.
- All diatomic molecules composed of two different types of atoms are at least slightly polar.
- A **nonpolar molecules** is molecule that has no electric dipole moment.
- A **homonuclear diatomic molecule** (e.g. O_2, N_2, Cl_2) is nonpolar.
- A polyatomic molecule may be nonpolar even if its bonds are polar. For example: in carbon dioxide, the two C–O dipole moments are equal in magnitude and lie in opposite directions in a planar molecule. The dipole moments cancel each other out.



- **The molecular dipole moment**: is the *vector sum* of bond dipole moments.

2E.3 Polar molecules

A polar molecule has a nonzero dipole moment

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

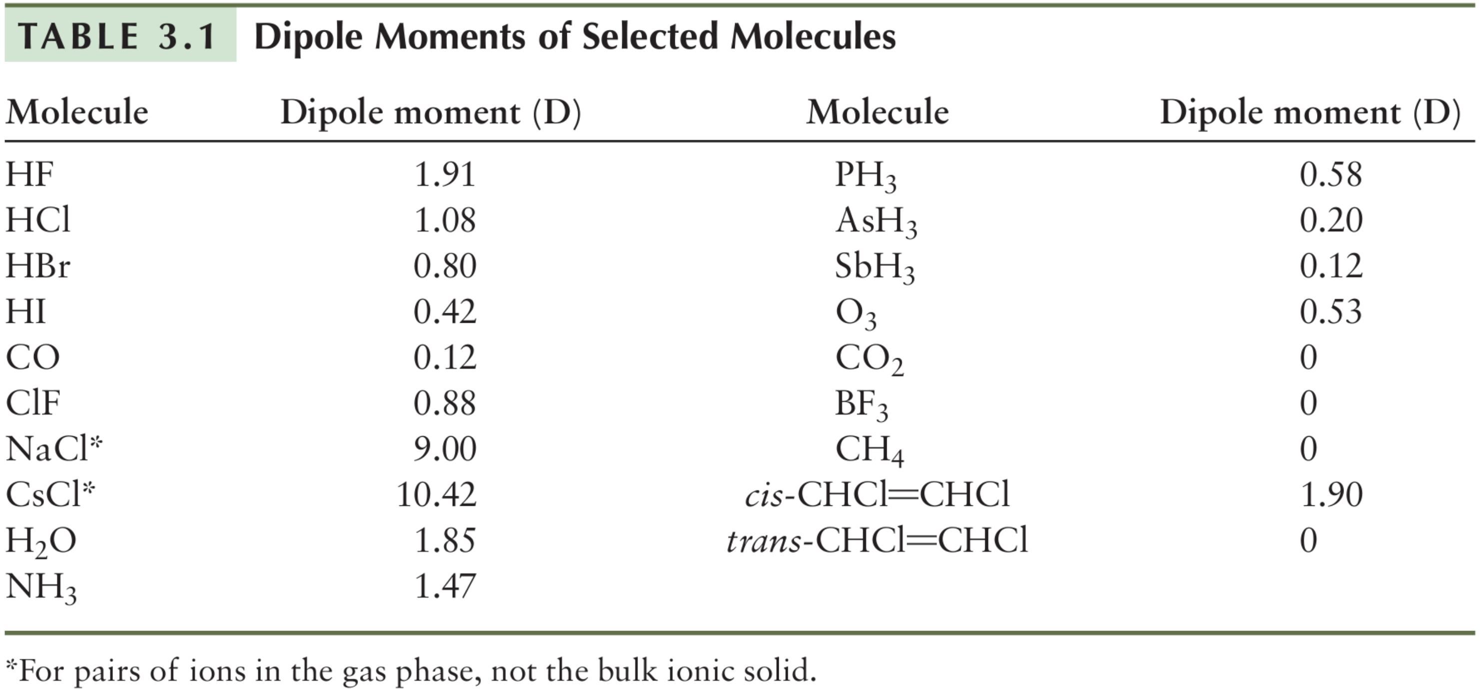


TABLE 3.1 **Dipole Moments of Selected Molecules**

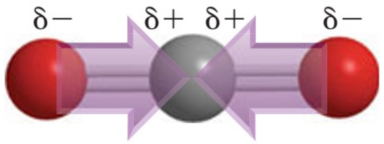
Molecule	Dipole moment (D)	Molecule	Dipole moment (D)
HF	1.91	PH_3	0.58
HCl	1.08	AsH_3	0.20
HBr	0.80	SbH_3	0.12
HI	0.42	O_3	0.53
CO	0.12	CO_2	0
ClF	0.88	BF_3	0
NaCl*	9.00	CH_4	0
CsCl*	10.42	*cis*-CHCl=CHCl	1.90
H_2O	1.85	*trans*-CHCl=CHCl	0
NH_3	1.47		

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

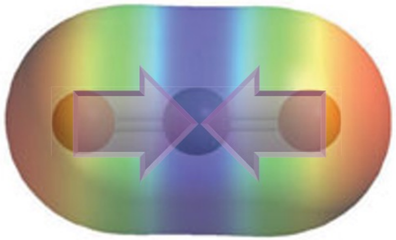
2E.3 Polar molecules

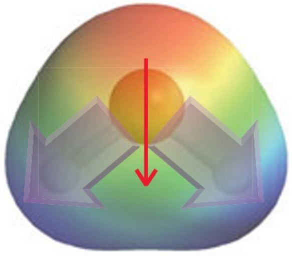
The electrostatic potential surface (the elpot surface)

- 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.
- **Blue**: relative positive potential
- **Red**: relative negative potential
- CO_2: nonpolar molecule
- H_2O: polar molecule



26 Carbon dioxide, CO_2



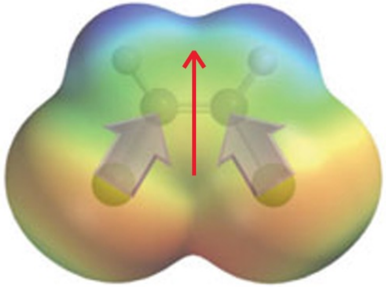


28 Water, H_2O

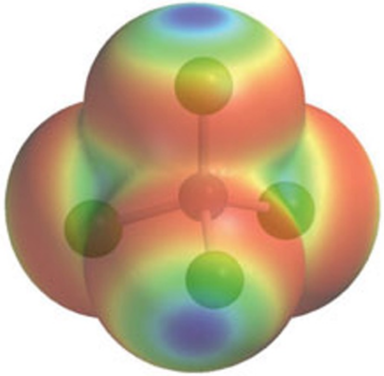
2E.3 Polar molecules

A few more examples

polar



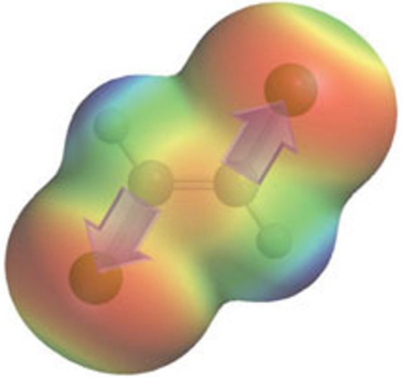
29 *cis*-Dichloroethene, $C_2H_2Cl_2$



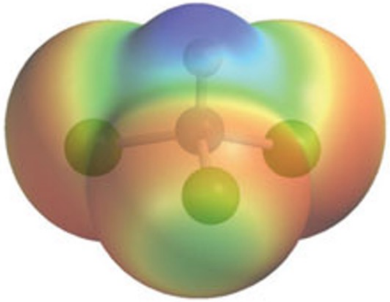
31 Tetrachloromethane, CCl_4

nonpolar

nonpolar



30 *trans*-Dichloroethene, $C_2H_2Cl_2$

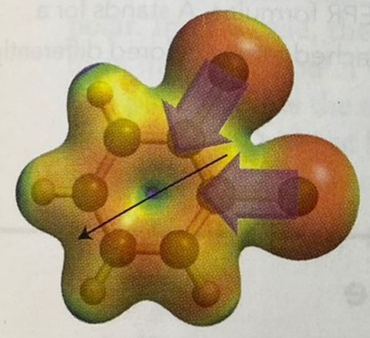


32 Trichloromethane, CH_3Cl

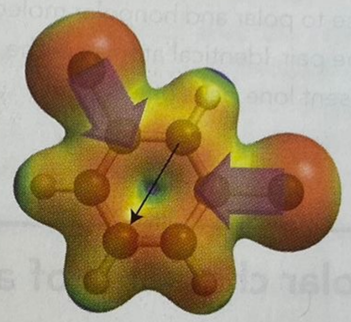
polar

2E.3 Polar molecules

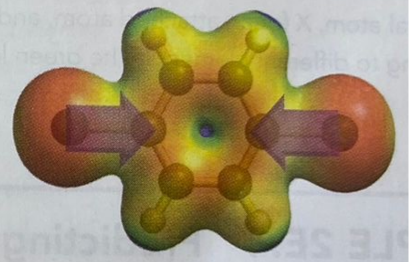
A few more examples



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

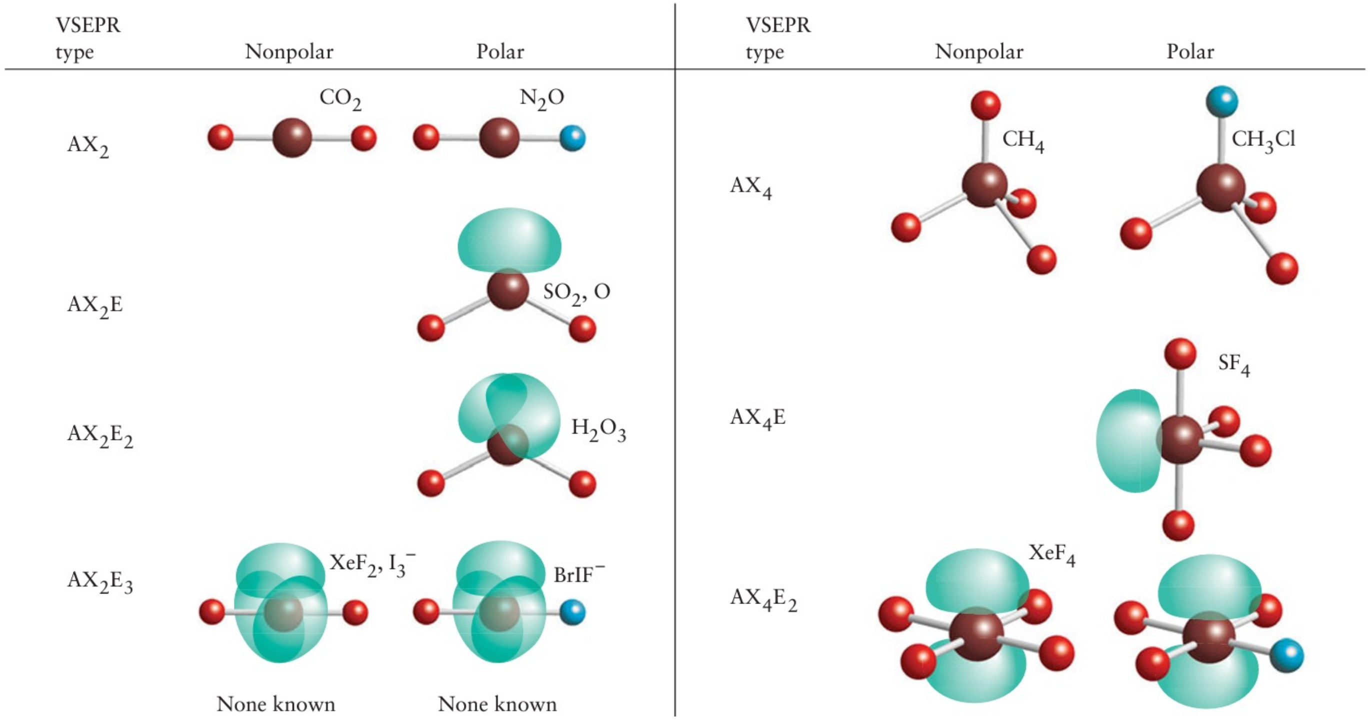


Figure 2E.7 **part 1**

2E.3 Polar molecules

Overview of all different VSEPR configurations

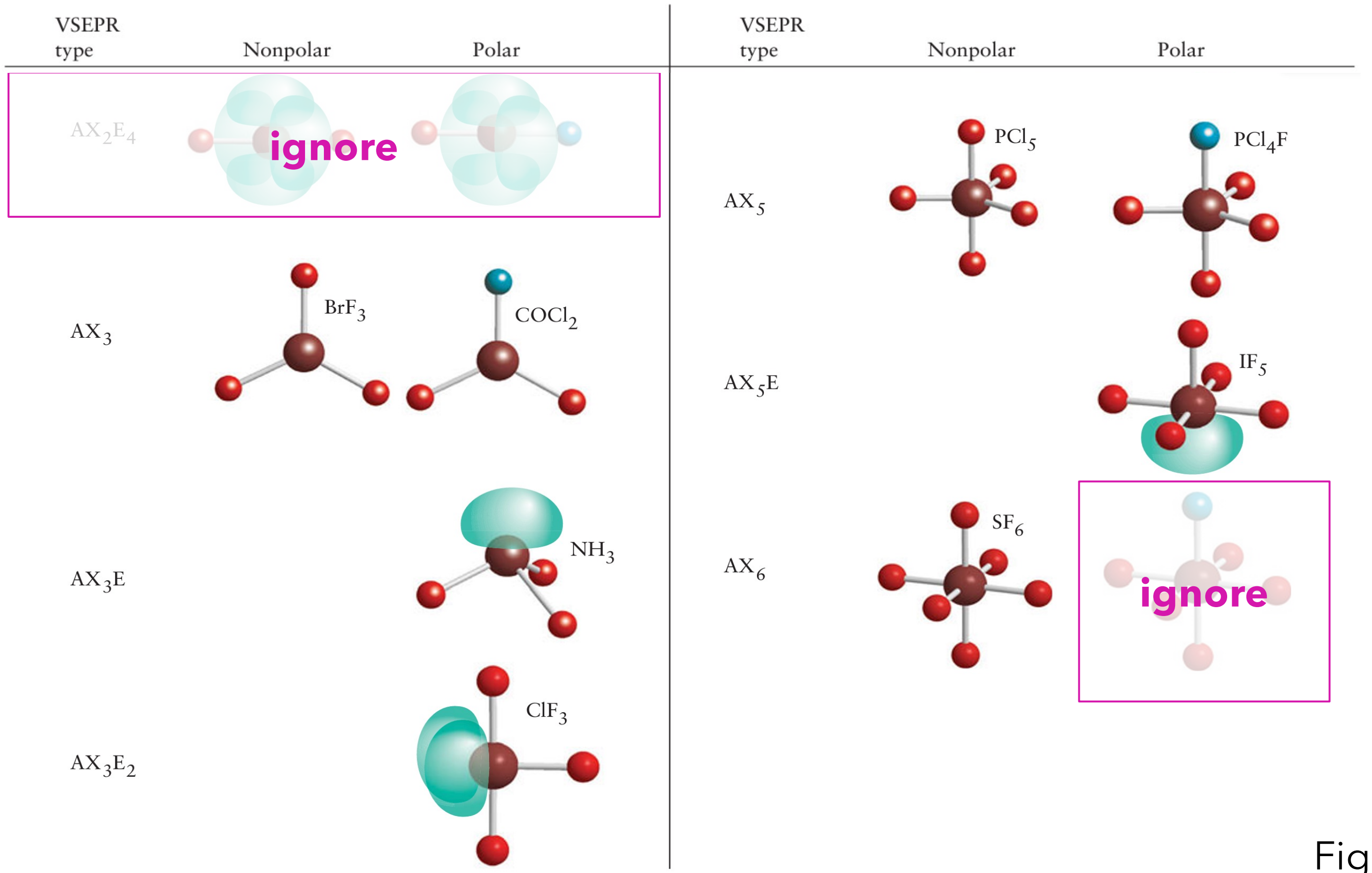


Figure 2E.7 **part 2**

2E.3 Polar molecules

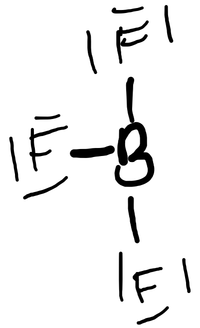
Example 2E.4

$\rightarrow 3+3\cdot 7 = 24\,e^{\ominus}/12\,e^{\ominus}p$

$\rightarrow 3\cdot 6 = 18\,e^{\ominus}/9\,e^{\ominus}p$

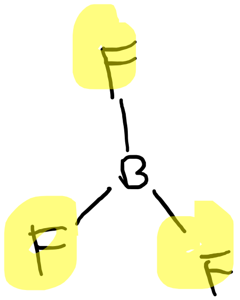
Predict whether (a) a boron trifluoride molecule, BF_3, and (b) an ozone molecule, O_3, are polar.

a)



VSEPR

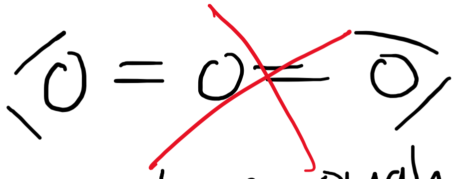
shape



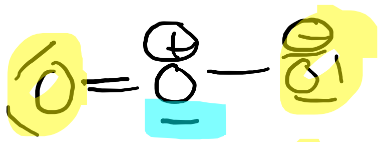
AX_3 : trigonal planar

nonpolar

b)



↳ not enough $e^{\ominus}$ pairs



VSEPR: AX_2E

molecular dipole moment

shape: bent

polar

2E.3 Polar molecules

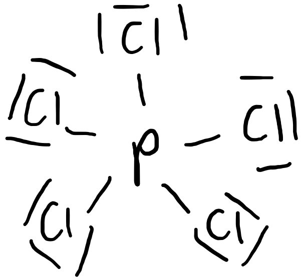
If time allows: **Example 2E.4**

$P\,5 + 5 \cdot 7 = 40\,e^{\ominus} / 20\,e^{\ominus}p$

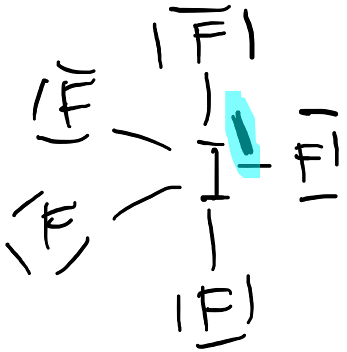
Predict whether (a) PCl_5 and (b) IF_5 are polar or nonpolar.

$\hookrightarrow 7 + 5 \cdot 7 = 42\,e^{\ominus} / 21\,e^{\ominus}p$

a)



b)

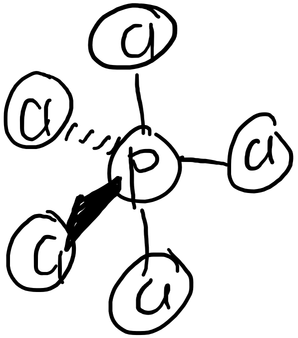


AX_5E

Square pyramidal

polar

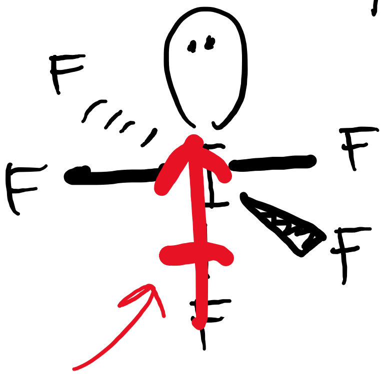
AX_5:



trigonal bipyramidal

nonpolar

molecular dipole moment



2E.3 Polar molecules

Summary

A diatomic molecule is polar if its bond is polar. A polyatomic molecule is polar if it has polar bonds arranged in space in such a way that the dipole moments associated with the bonds do not cancel.

The skills you have mastered are the ability to

- Explain the basis of the VSEPR model of bonding in terms of repulsions between electron pairs.
- Use the VSEPR model to predict the electron arrangement and shape of a molecule or polyatomic ion from its formula.
- Predict the polar character of a molecule.

Summary: The shapes of simple molecules (and the shapes in localized regions of more complex ones) can be predicted by assessing the repulsions between regions of high electron density. You have seen that lone pairs of electrons are more strongly repelling than the electrons in bonds. You have learned that multiple bonds are treated like single bonds when predicting molecular shape and that the shape of a molecule is identified from the localizations of its atoms (not its lone pairs). You have seen that the lone pairs often distort the shape of a molecule in a predictable way. You have also seen how shape plays an important role in determining whether a polyatomic molecule is polar.