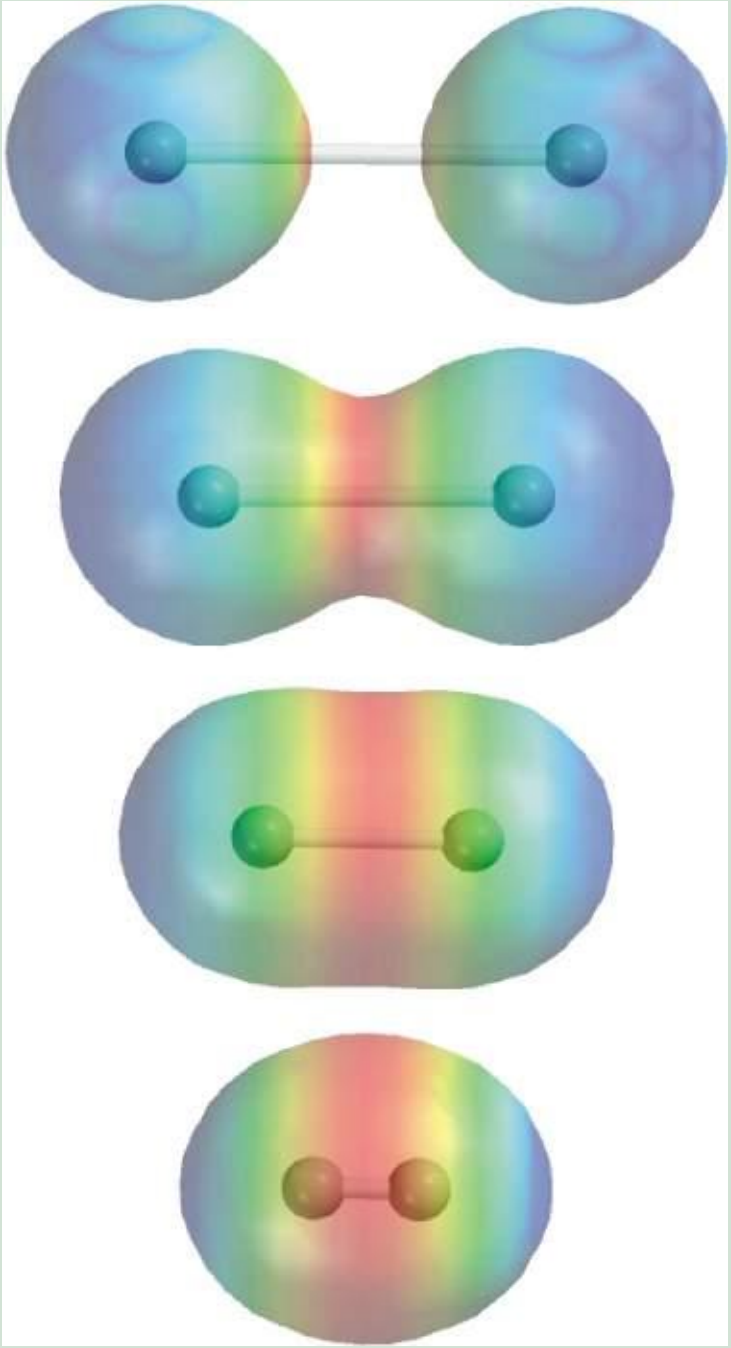
Chapter 7

Covalent Bonding



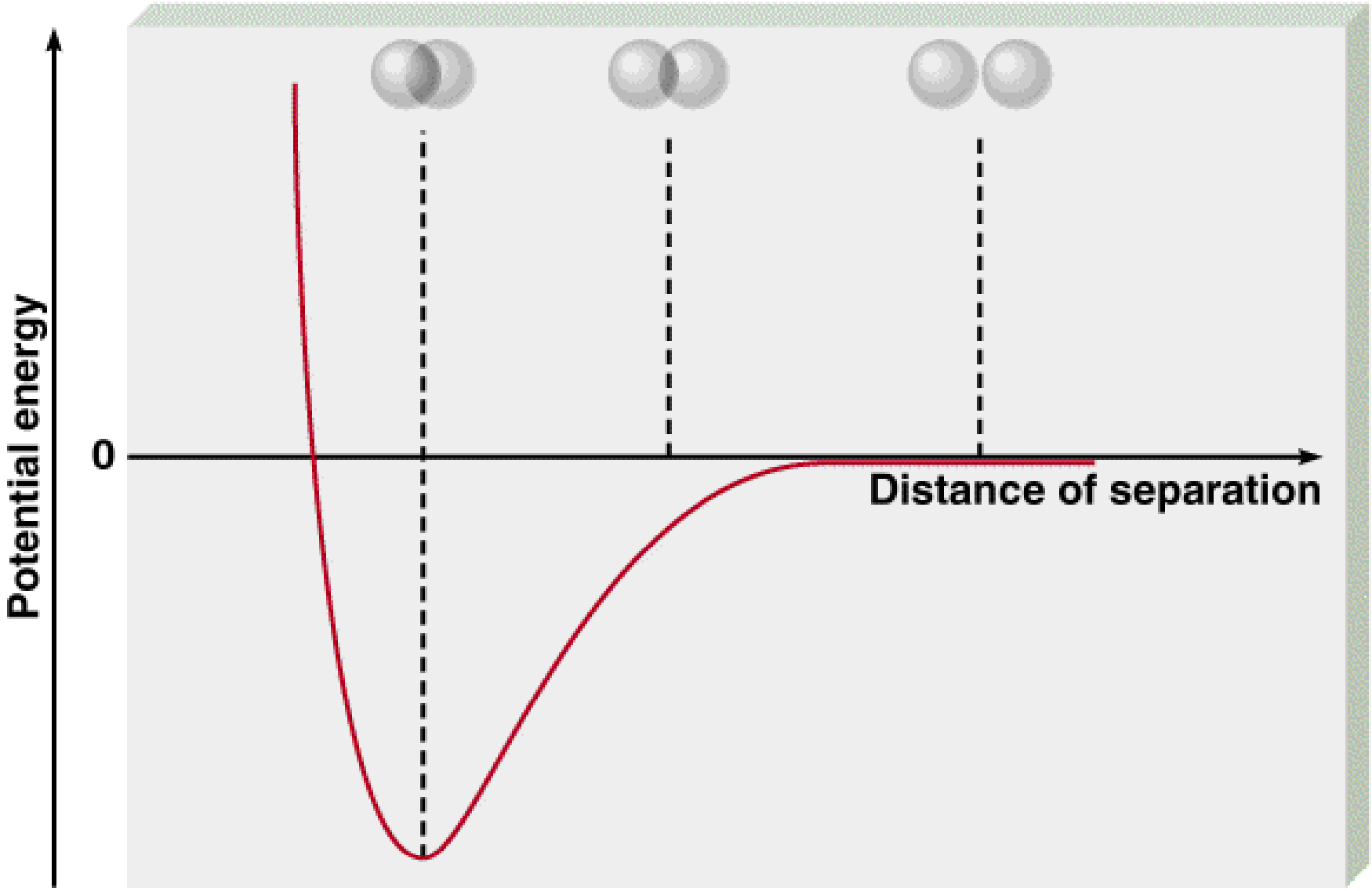
Change in electron density as two hydrogen atoms approach each other.

Energy of two hydrogen atoms as a function of the distance between their nuclei

- Attractive energies between oppositely charged particles (electron-proton) slightly exceed the repulsive energies between particle of like charge (electron-electron, proton- proton)
- (電子與質子間相互吸引力大於電子間與質子間的斥力降低氫分子間靜電能量)

- When two hydrogen atoms cone together to form a molecule, the electrons are spread over the entire volume of the molecule instead of being confined to a particular atom.
- (當兩氫原子結合成分子後，電子是分佈於整個分子體積而不是局限於某一特定原子，將二原子上的1s軌域互相重疊所形成的分子將非常安定。)

Change in Potential Energy of Two H Atoms

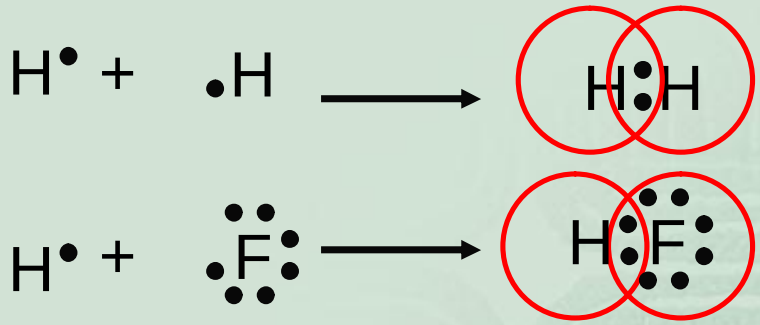


7.1 Lewis Structures; the Octet rule

Lewis pointed out that the electron configuration of the noble gases appears to be a particularly stable one.

Nonmetal atoms, by sharing electrons to form an electron- pair bond , can acquire a stable noble-gas

These structure (without the circles) are referred to as *Lewis structures.*



Using dots to represent electrons; the circles emphasize that the pair of electrons in the covalent bond can be considered to occupy the 1s orbital of either hydrogen atom. in the H_2 molecule has the electronic structure of the noble gas helium. With the electron configuration $1s^{2.}$

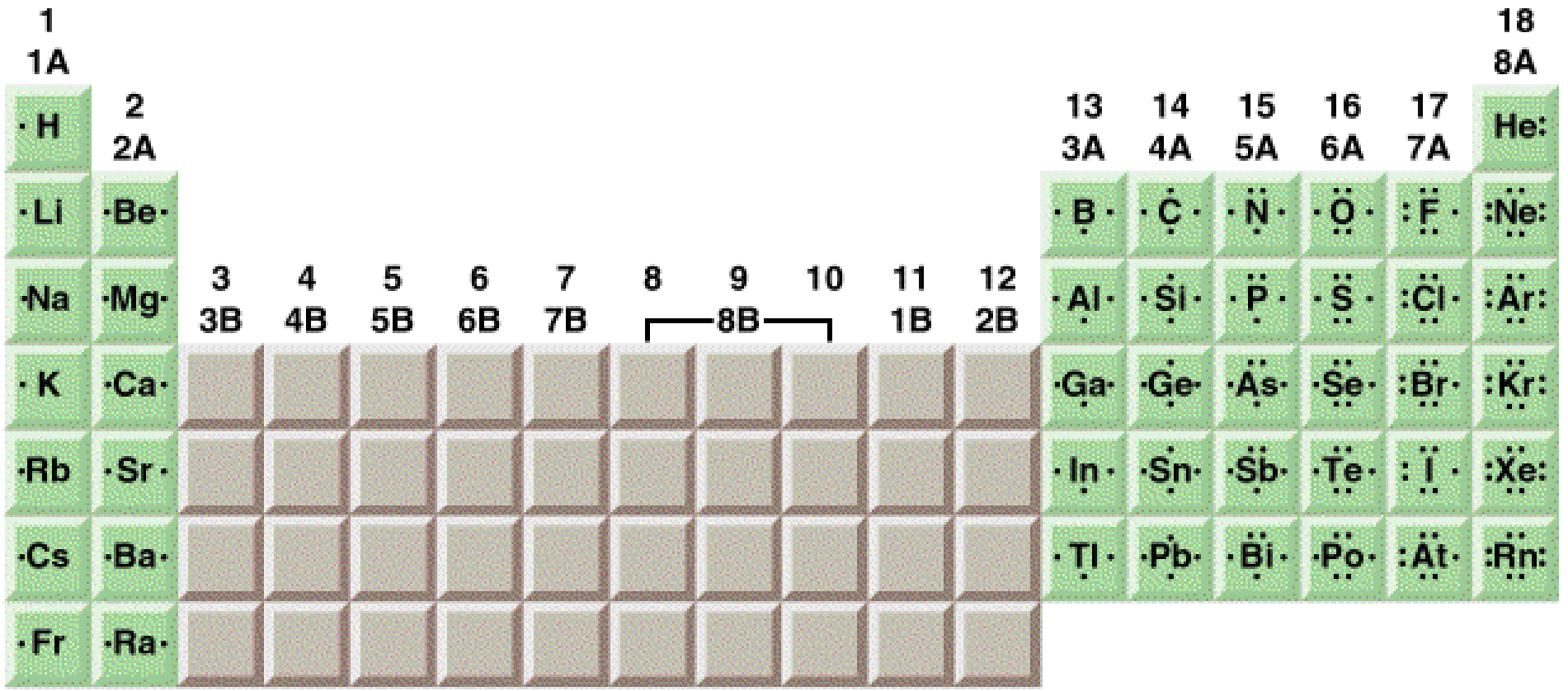
7.1 Lewis Structures; the Octet rule

Valence electrons (價電子)

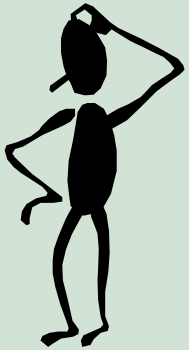
are the outer shell electrons of an atom. The valence electrons are the electrons that participate in chemical bonding

Group	e^- configuration	# of valence e^-
1A	ns^1	1
2A	ns^2	2
3A	ns^2np^1	3
4A	ns^2np^2	4
5A	ns^2np^3	5
6A	ns^2np^4	6
7A	ns^2np^5	7

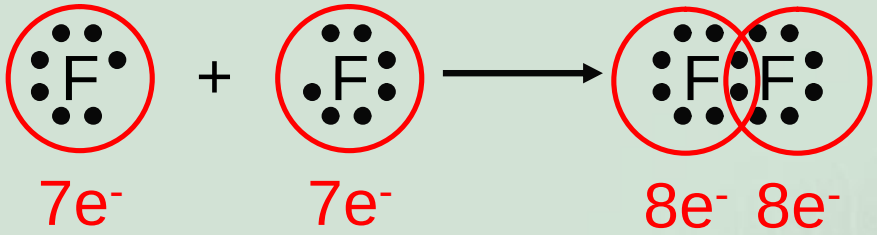
Lewis Dot Symbols



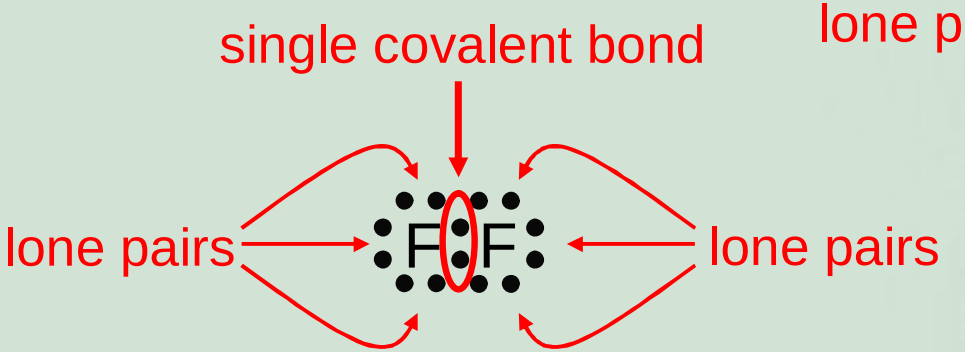
A ***covalent bond*** is a chemical bond in which two or more electrons are shared by two atoms.

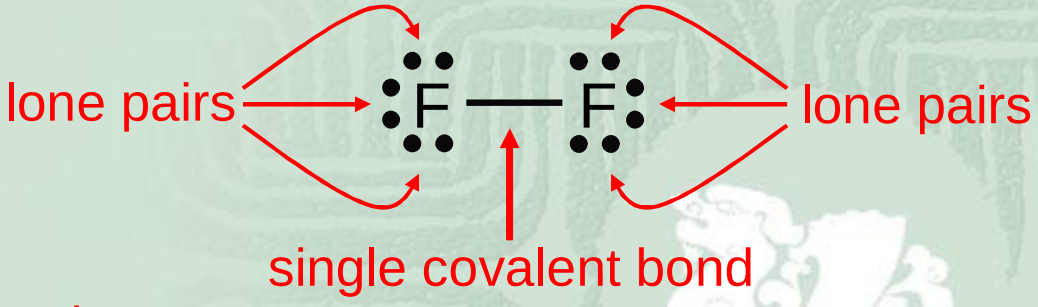


Why should two atoms share electrons?

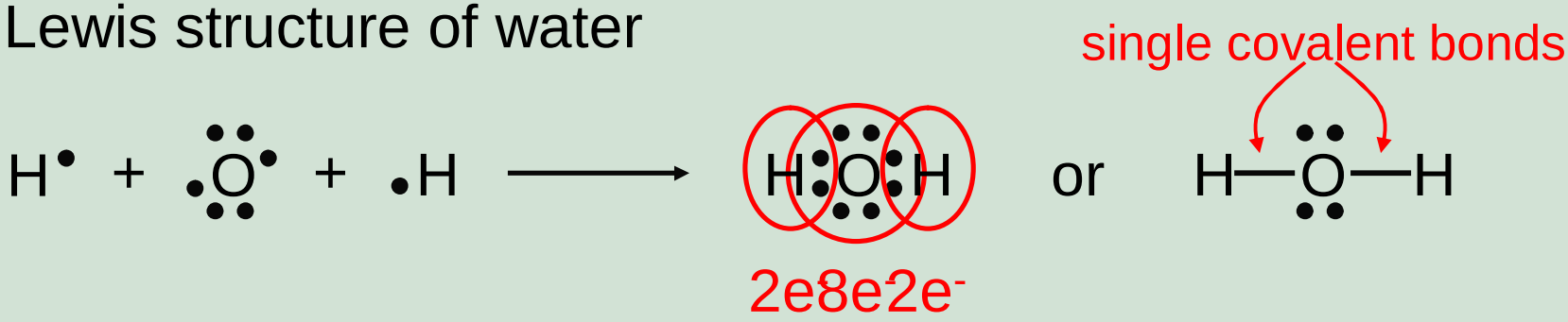


Lewis structure of F_2



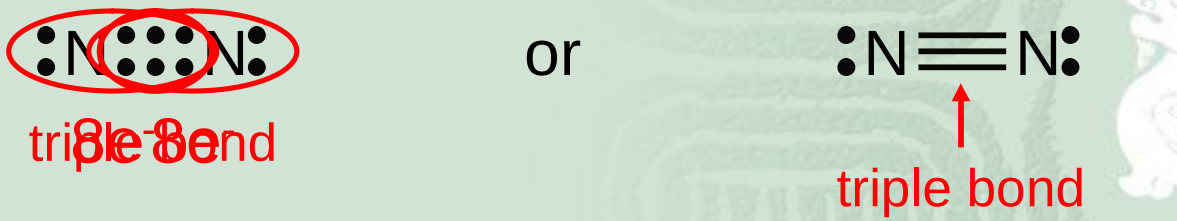


Lewis structure of water



Double bond – two atoms share two pairs of electrons

Triple bond – two atoms share three pairs of electrons



octet rule(八隅律)

- The principle that atoms in covalently bonded species tend to have noble-gas electronic structures.
- (共價鍵原子符合惰性氣體之電子組態。)
- Nonmetals, except for hydrogen, achieve a noble- gas structure by sharing in an octet of electrons (eight).
- (非金屬原子除了氫原子以外藉共用電子獲得如惰性氣體具八個價電子。)

octet rule(八隅律)建議

- 第二週期中元素C, N, O, F都會遵守八隅律，因其價殼軌域只能調節8個電子。
- 第二週期B, Be在其化合物中會有少於8個電子圍繞。這些電子缺少的化合物反應性非常高。
- 第三週期以下的元素通常會滿足八隅體規則，但也可以用其空的d軌域來超過八隅律規律。
- 當要劃出一分子的路易士結構時，首先要滿足該原子之八隅體規則。若在八隅律規則後還有剩餘電子，則將其於置於具有d軌域的元素上。

Writing Lewis Structures p166

1. Count the number of valence electrons計算總價電子數。
2. Draw a skeleton structure for the species, Joining atoms by single bonds.原子之電子參與鍵結形成單鍵劃出化合物結構。
3. Determine the number of valence electrons still available for distribution.

   (依上步驟決定分子內可供使用的電子數，即為總價電子數扣掉鍵結電子數。)

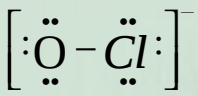
4. Determine the number of valence electrons required to fill out an octet for each atom (except H)

   1. If the number of electrons available is equal to the number required , distribute the available electrons as unshared pairs, satisfying the octet rule for each atom.若步驟3的可供分配電子數與步驟4需求電子數相同時，滿足每個原子符合八隅律下填入未鍵結電子對。
   2. If the number of electrons available is less than the number required , the skeleton structure must be modified by changing single to multiple bonds.若步驟3的可供分配之電子數少於步驟4需求電子數時，則此結構可能含有多重鍵結，多重鍵的形成儘限C, N, O, S等四個原子。

Ex:7.1 Draw Lewis structures of

(a) The Hypochlorite ion,次氯酸鹽離子OCl^-

(1) The number of valence electrons is ,總價電子數

$6 + 7 + 1 = 14$ 

(2) The skeleton structure is [O—Cl] $^-$

(3) 可供分配之電子數 $12 - 2 = 10$

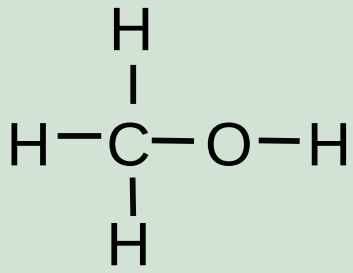
(4) 滿足每一原子符合八隅體所需之電子數

$6 + 6 = 12$

(b) Methanol :CH_4O

(1) valence electrons　$4 + 1\times4 + 6 = 14$

(2) 分子結構



(3) 可供分配之電子數　$14 - 10 = 4$

(4) 滿足每一原子符合八隅體所需之電子數 4

Ex:7.2 Draw Lewis structures of

(a) SO_2

(1) valence electrons $6\times2 + 6 = 18$

(2) 分子結構 [O－S－O]

(3) 可供分配之電子數 $18 - 4 = 14$

(4) 滿足每一原子符合八隅體所需之電子數

$2\times6 + 4 = 16$

(5) 可供分配之電子數少於符合八隅體所需電子數

故有雙鍵

(b) N_2

(1) valence electrons　$2\times5 = 10$

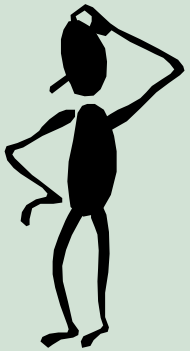
(2) 分子結構 N－N

(3) 可供分配之電子數 $10 - 2 = 8$

(4) 滿足每一原子符合八隅體所需之電子數 12

(5) 可供分配之電子數少於符合八隅體所需電子數故有雙鍵或參鍵。

：N≡N：



Write the Lewis structure of nitrogen trifluoride (NF_3).

Step 1 – N is less electronegative than F, put N in center

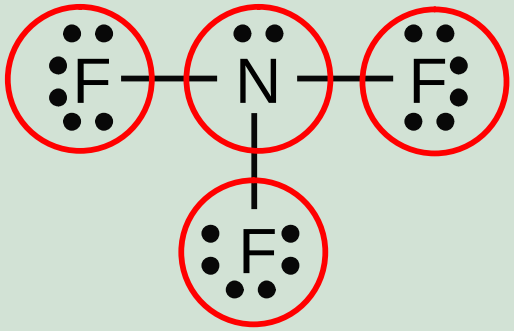
Step 2 – Count valence electrons N - 5 ($2s^2 2p^3$) and F - 7 ($2s^2 2p^5$)

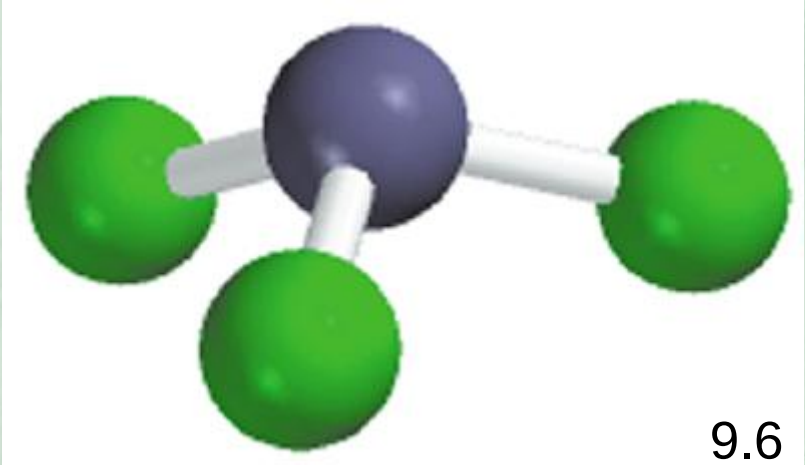
5 + (3 x 7) = 26 valence electrons

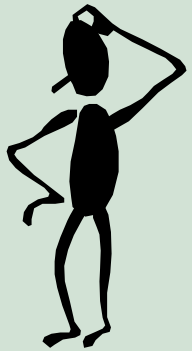
Step 3 – Draw single bonds between N and F atoms and complete octets on N and F atoms.

Step 4 - Check, are # of e^- in structure equal to number of valence e^- ?

3 single bonds (3x2) + 10 lone pairs (10x2) = 26 valence electrons







Write the Lewis structure of the carbonate ion (CO_3^{2-}).

Step 1 – C is less electronegative than O, put C in center

Step 2 – Count valence electrons C - 4 ($2s^2 2p^2$) and O - 6 ($2s^2 2p^4$)
-2 charge – $2e^-$

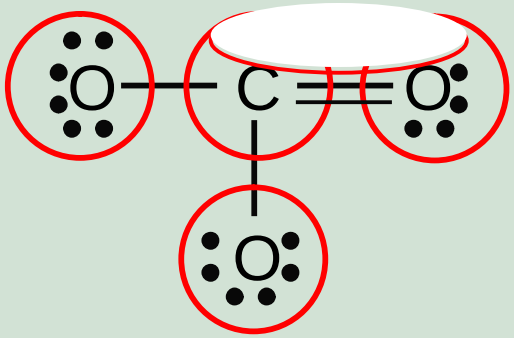
4 + (3 x 6) + 2 = 24 valence electrons

Step 3 – Draw single bonds between C and O atoms and complete octet on C and O atoms.

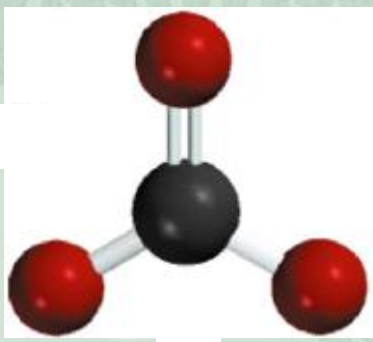
Step 4 - Check, are # of e^- in structure equal to number of valence e^- ?

3 single bonds (3x2) + 10 lone pairs (10x2) = 26 valence electrons

Step 5 - Too many electrons, form double bond and re-check # of e^-



2 single bonds (2x2) = 4
1 double bond = 4
8 lone pairs (8x2) = 16
Total = 24

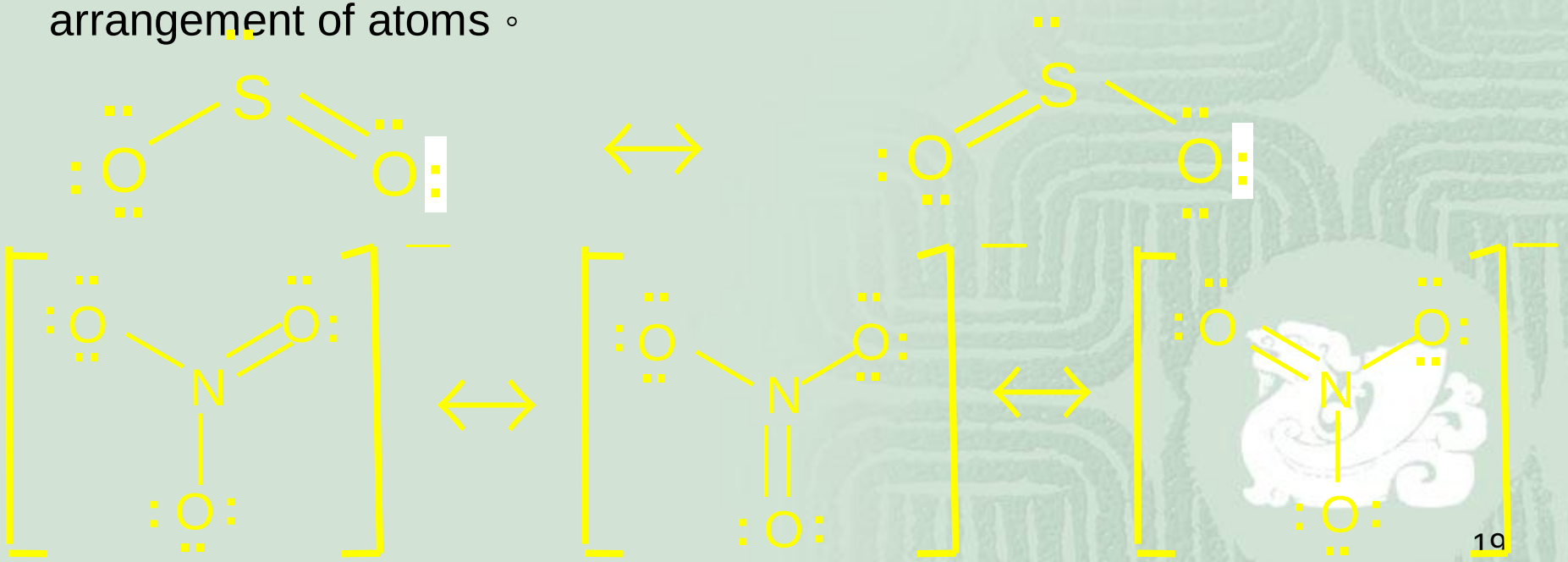


A resonance structure is one of two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure.

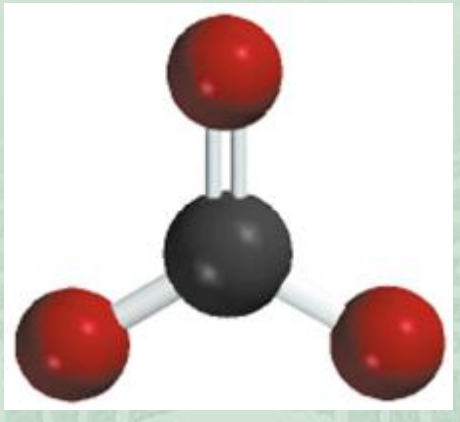
1. Resonance forms do not imply different kinds of molecules with electrons shifting eternally between them.

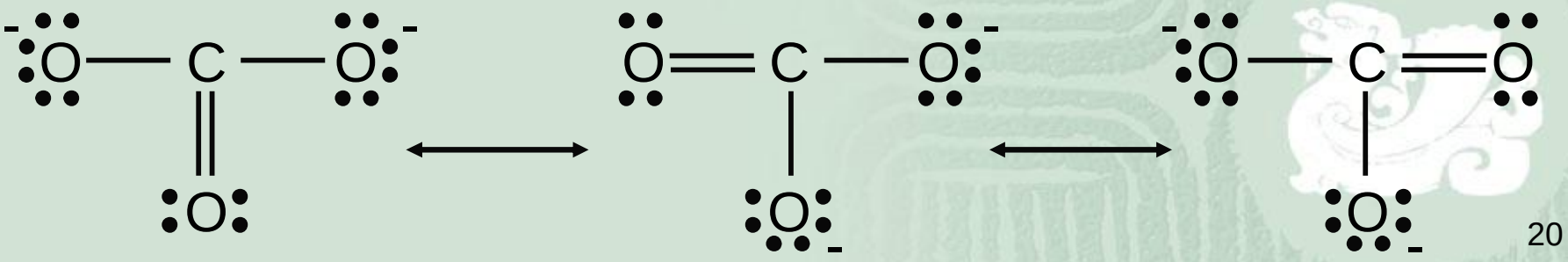
2. Resonace can be anticipated when it is possible to write two or more Lewis structures that are about equally plausible.

3. Resonance forms differ only in the distribution of electrons, not in the arrangement of atoms。



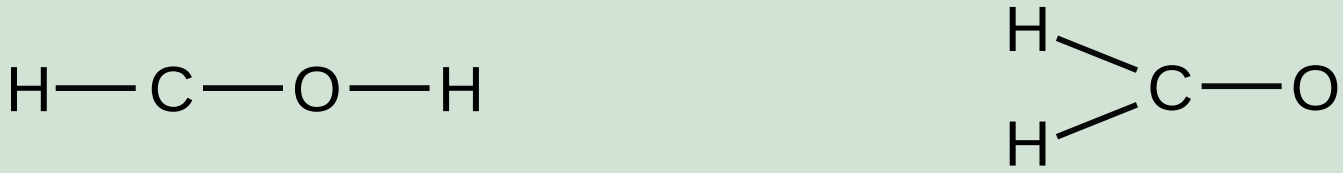
What are the resonance structures of the carbonate (CO_3^{2-}) ion?





Formal Charge

Two possible skeletal structures of formaldehyde (CH_2O)



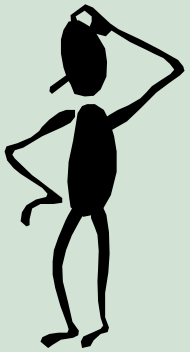
An atom's ***formal charge*** is the difference between the number of valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure. $C_f = X - (Y + Z/2)$

formal charge on an atom in a Lewis structure = total number of valence electrons in the free atom - total number of nonbonding electrons - $\frac{1}{2}$ (total number of bonding electrons)

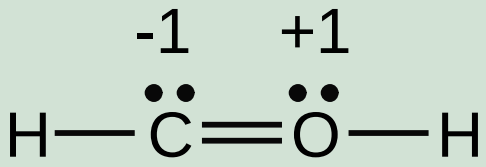
The sum of the formal charges of the atoms in a molecule or ion must equal the charge on the molecule or ion.

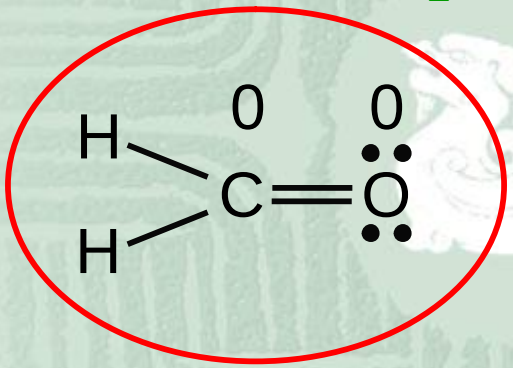
Formal Charge 形式電荷

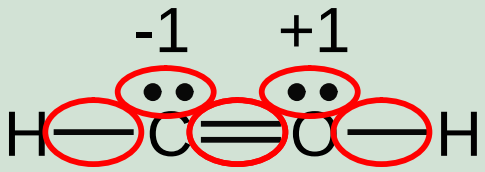
1. 在路易士結構中標示形式電荷，只是有助於瞭解價電子的來龍去脈；形式電荷並不表示真正的電荷。
2. 對於中性分子，所有的原子的形式電荷總和為零；對於離子分子，其形式電荷總和為離子的電荷。
3. Lewis structures 傾向於形式電荷較低者。
4. 當形式電荷的分佈類似時，傾向於將負的形式電荷置於陰電性較高的原子上。



Which is the most likely Lewis structure for CH_2O?







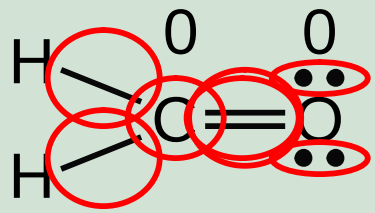
C – 4 e^-
O – 6 e^-
2H – 2x1 e^-
12 e^-

2 single bonds (2x2) = 4
1 double bond = 4
2 lone pairs (2x2) = 4
Total = 12

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

formal charge on C = 4 -2 -½ x 6 = -1

formal charge on O = 6 -2 -½ x 6 = +1



C – 4 e^-
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12 e^-

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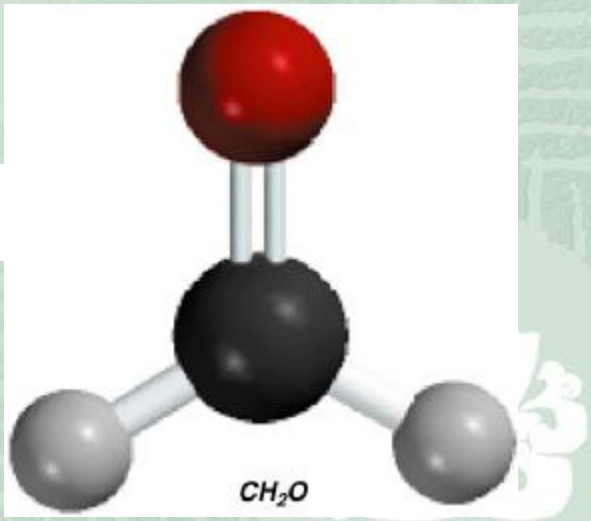
$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

formal charge on C = 4 - 0 - ½ x 8 = 0

formal charge on O = 6 - 4 - ½ x 4 = 0

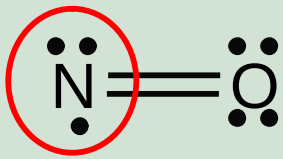


Exceptions to the Octet Rule

Odd-Electron Molecules

NO

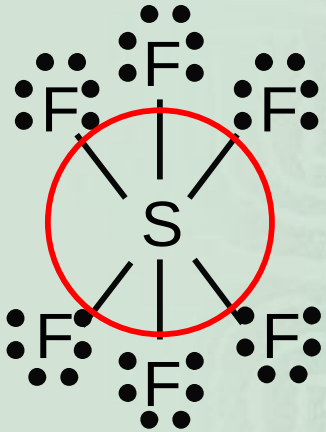
N – $5e^-$
O – $6e^-$
$11e^-$



The Expanded Octet (central atom with principal quantum number n > 2)

SF_6

S – $6e^-$
6F – $42e^-$
$48e^-$



6 single bonds (6x2) = 12
18 lone pairs (18x2) = 36
Total = 48

Exceptions to the Octet Rule

The Incomplete Octet

BeH_2

Be – $2e^-$

2H – $2x1e^-$

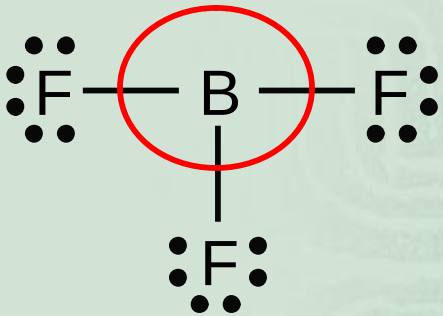
$4e^-$

BF_3

B – $3e^-$

3F – $3x7e^-$

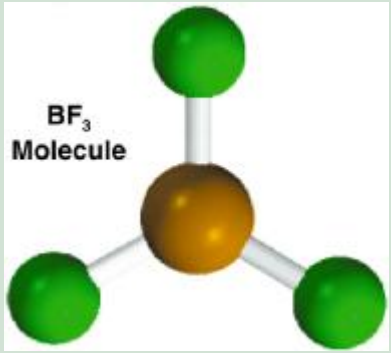
$24e^-$



3 single bonds (3x2) = 6

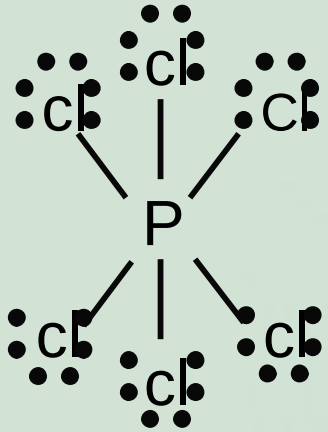
9 lone pairs (9x2) = 18

Total = 24



Exception to the Octet Rule: Expanded Octets

Largest class of molecules to violate the octet rule consists of species in which the central atom is surroundedy more than four pairs of valence electrons.



$7-2$ Molecular Geometry

- The geometry

(1) Diatomic molecule

- Cl_2 Cl-Cl (simply , Two points define a straight line.)

(2) Molecules containing three or more atoms , the geometry is not so obvious . The angles between bonds , called bond angles.

- YX_2
- Linear , bond angle of 180^0 X-Y-X
- Bent , bond angle less than 180^0

7－2 Molecular Geometry

Valence shell electron pair repulsion (VSEPR) model:

The valence electron pairs surrounding an atom repulsion one another. Consequently, the orbitals containing those electron pairs are oriented to be as far apart as possible.

中心原子的電子對配置方式是為了要減少電子對之間的靜電排斥力；不論共用或未共用電子對都會互相排斥，分子中的電子對趨向使斥力減至最小，亦即電子對彼此間距離愈遠愈穩定。

1. 雙鍵及參鍵之間的電子對可視同單鍵
2. 若分子有兩種以上共振結構將VSEPR應用在任何一種即可，且不必顯示形式電荷

Valence shell electron pair repulsion (VSEPR) model:

利用VSEPR模型預測分子結構的規則：

1. 決定該分子之Lewis structure。

2. 對於具有共振結構的分子，任取其中之一來預測分子構造。

3. 計算出中心原子上之電子對的數目。

4. 計算電子對的數目時，每一多重鍵仍視為單鍵結電子對。

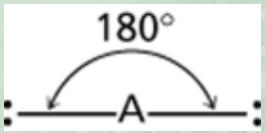
5. 藉由降低電子間的斥力來決定電子對的排列方式，如圖7.5。

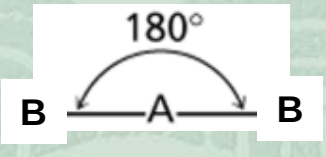
6. 未鍵結電子對比鍵結電子對需要更多的空間。

Valence shell electron pair repulsion (VSEPR) model:

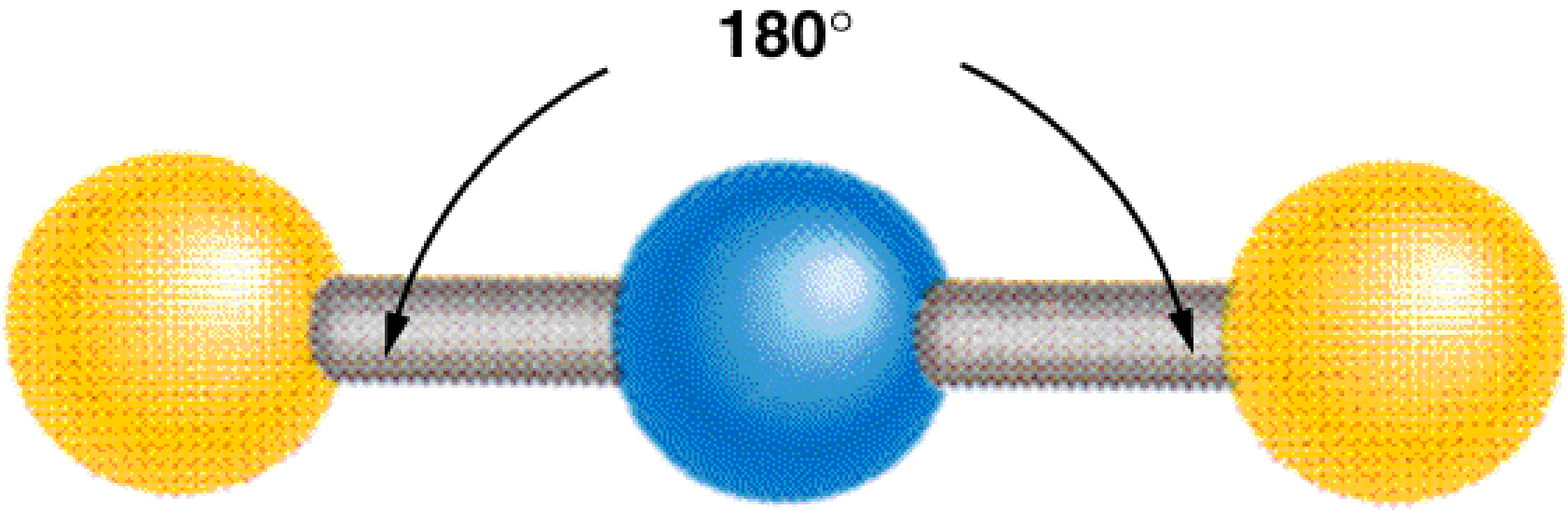
中心原子的電子對配置方式是為了要減少電子對之間的靜電排斥力

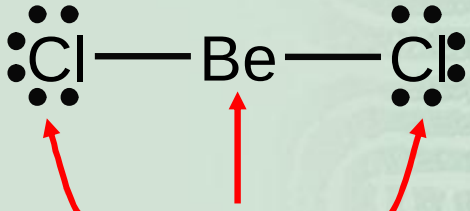
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_2	2	0	linear	linear





Beryllium Chloride

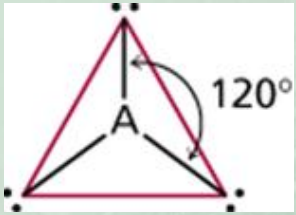
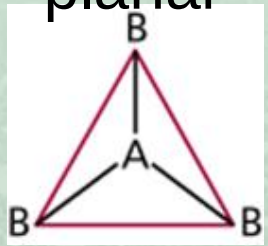




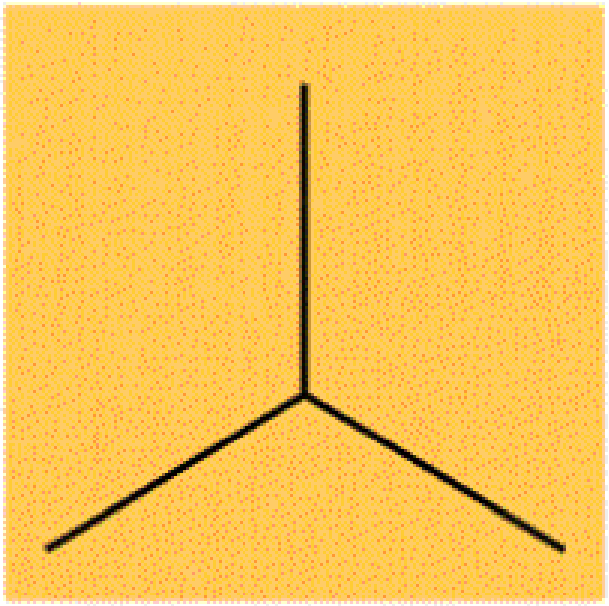
2 atoms bonded to central atom

0 lone pairs on central atom

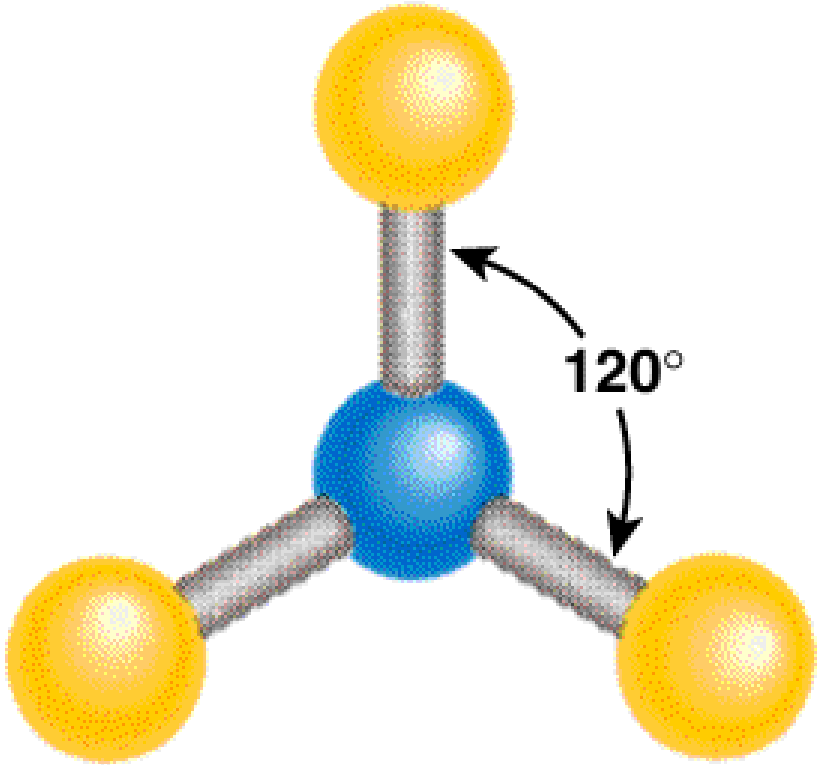
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_2	2	0	linear	linear
AX_3	3	0	triangular planar 	triangular planar 

Boron Trifluoride

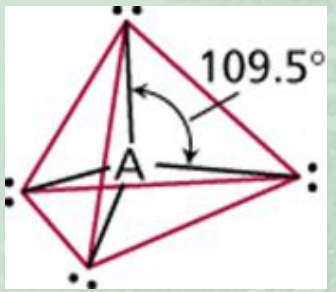


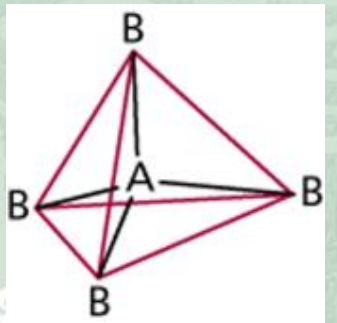
Planar



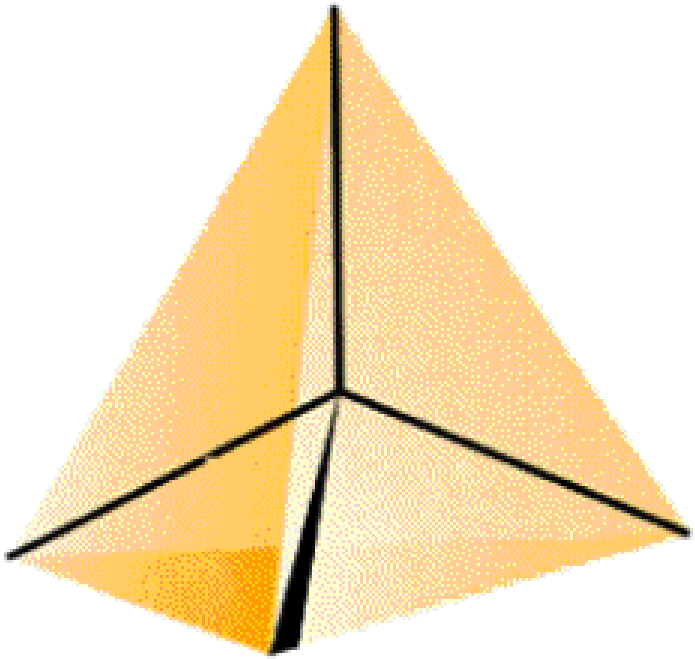
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_2	2	0	linear	linear
AX_3	3	0	trigonal planar	trigonal planar
AX_4	4	0	tetrahedral	tetrahedral

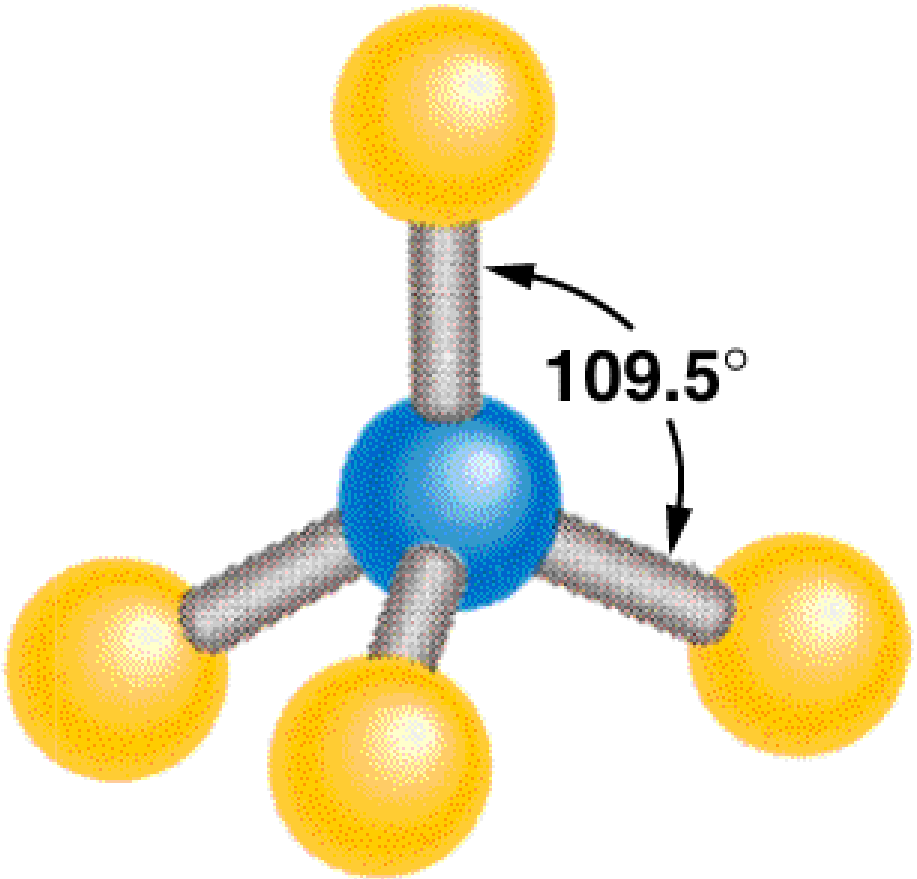




Methane

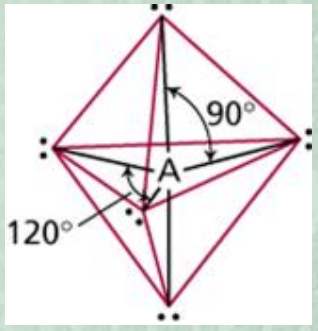


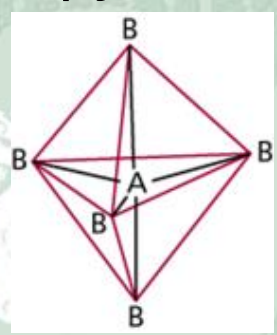
Tetrahedral



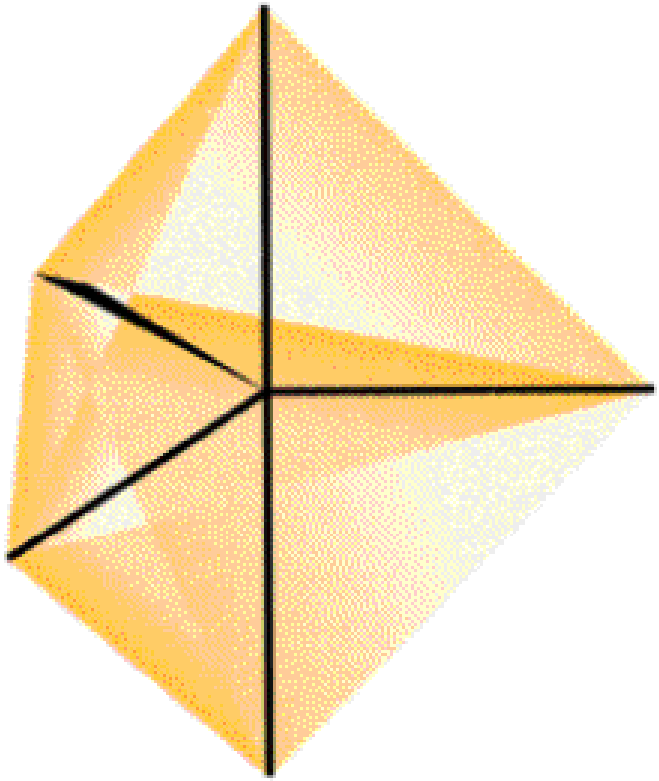
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_2	2	0	linear	linear
AX_3	3	0	trigonal planar	trigonal planar
AX_4	4	0	tetrahedral	tetrahedral
AX_5	5	0	triangular bipyramid	triangular bipyramid

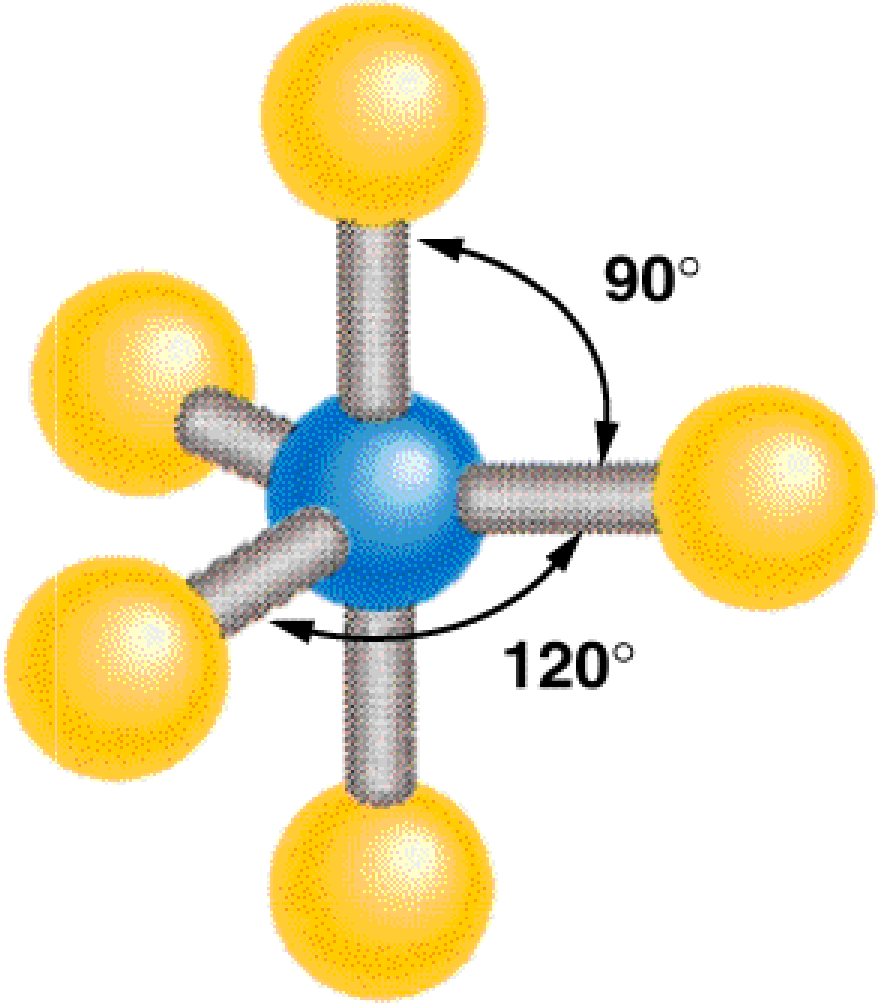




Phosphorus Pentachloride

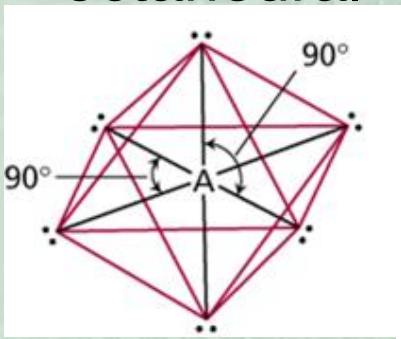


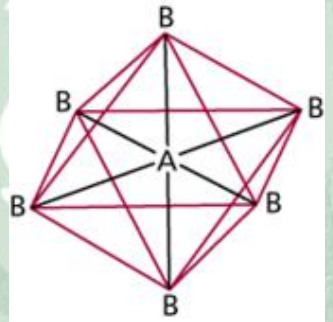
Trigonal bipyramidal



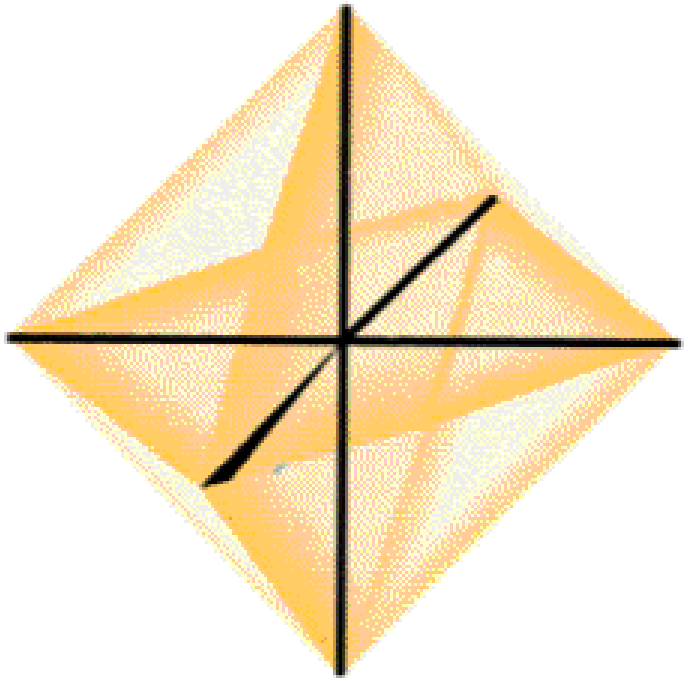
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_2	2	0	linear	linear
AX_3	3	0	trigonal planar	trigonal planar
AX_4	4	0	tetrahedral	tetrahedral
AX_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AX_6	6	0	octahedral	octahedral

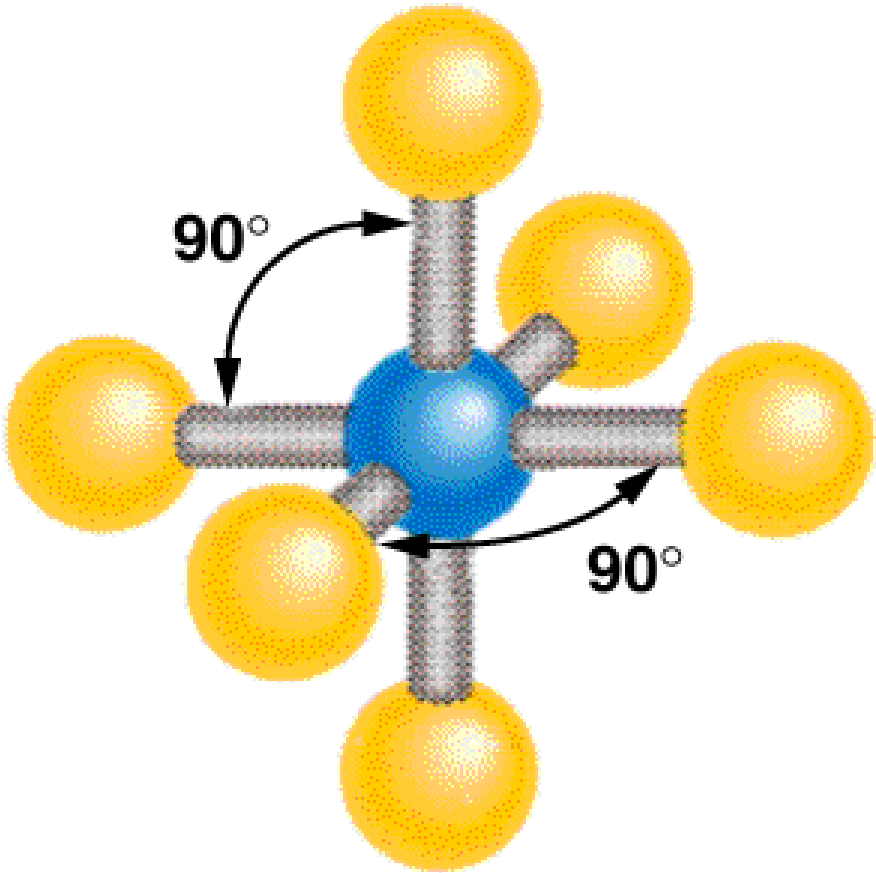




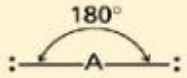
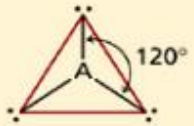
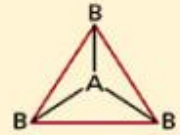
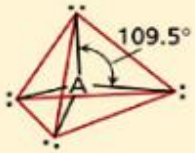
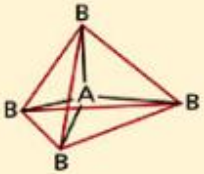
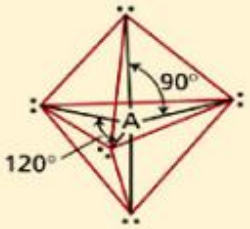
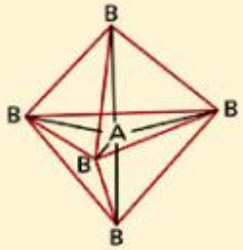
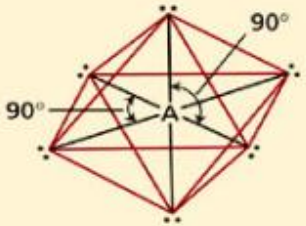
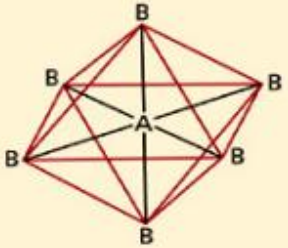
Sulfur Hexafluoride



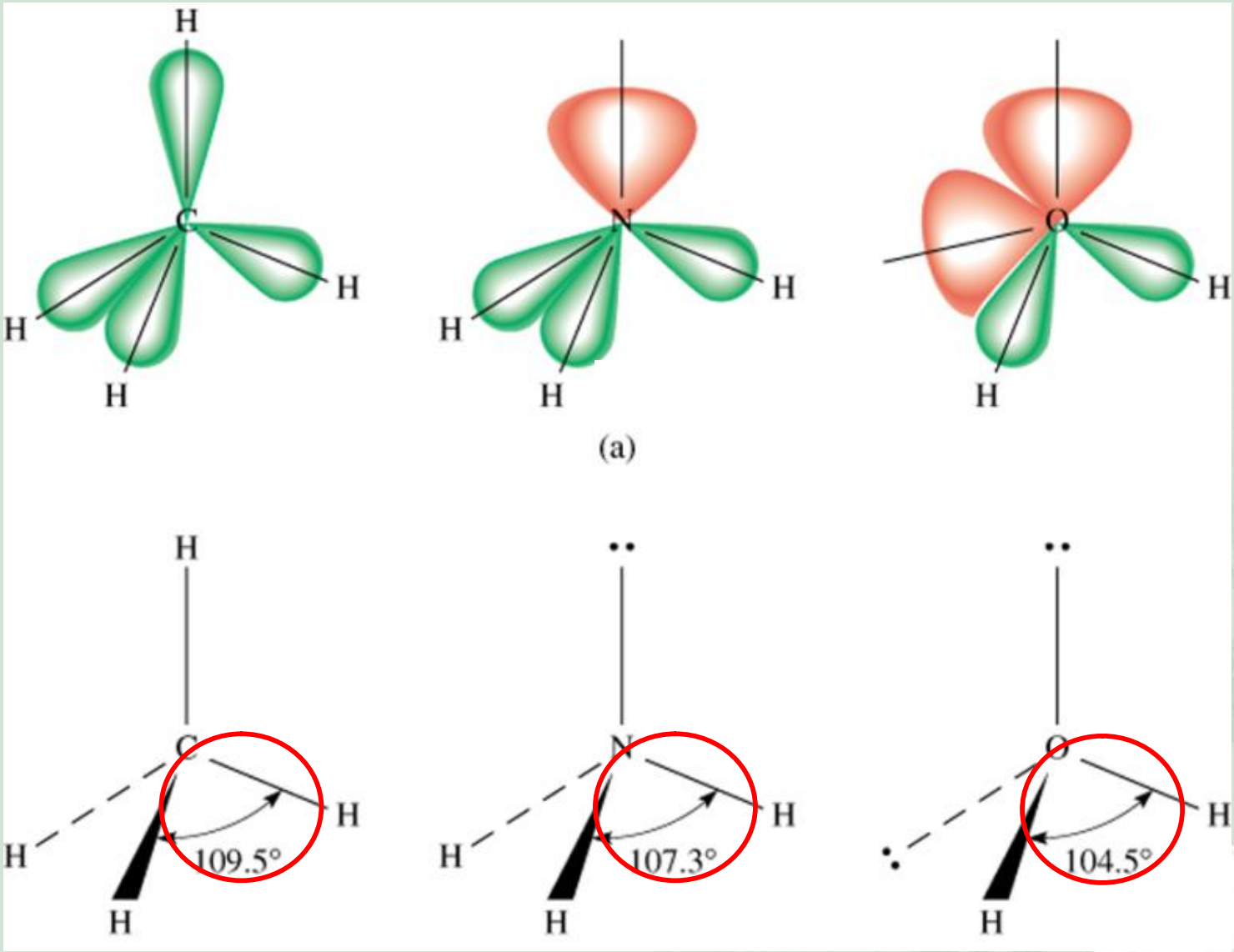
Octahedral



Arrangement of Electron Pairs About a Central Atom (A) in a Molecule and Geometry of Some Simple Molecules and Ions in Which the Central Atom Has No Lone Pairs

Number of Electron Pairs	Arrangement of Electron Pairs*	Molecular Geometry*	Examples
2	 Linear	Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

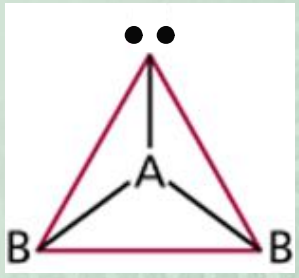
Effect of Unshared Pairs on Molecular geometry

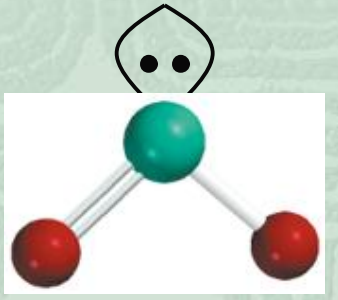


lone-pair vs. lone pair repulsion > lone-pair vs. bonding pair repulsion > bonding-pair vs. bonding pair repulsion

VSEPR

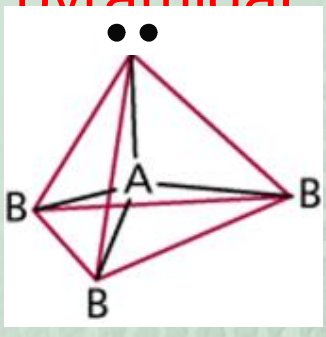
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_3	3	0	triangular planar	triangular planar
AX_2E	2	1	triangular planar	bent

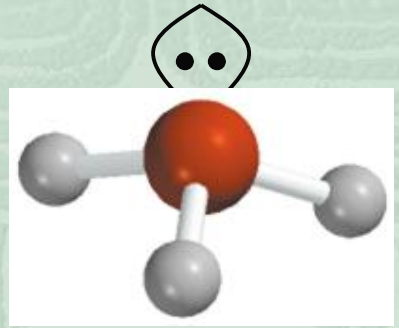




VSEPR

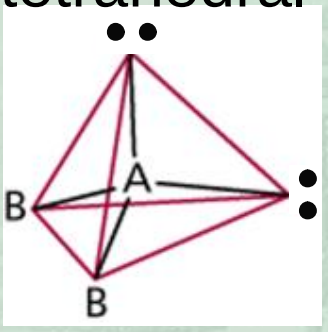
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_4	4	0	tetrahedral	tetrahedral
AX_3E	3	1	triangular pyramidal	triangular pyramidal

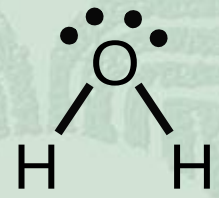




VSEPR

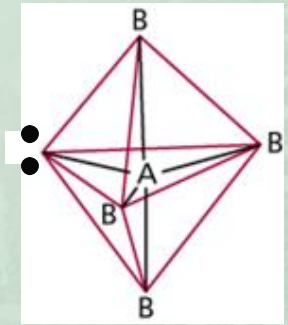
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_4	4	0	tetrahedral	tetrahedral
AX_3E	3	1	tetrahedral	triangular pyramidal
AX_2E_2	2	2	tetrahedral	bent





VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AX_4E	4	1	trigonal bipyramidal	distorted tetrahedron



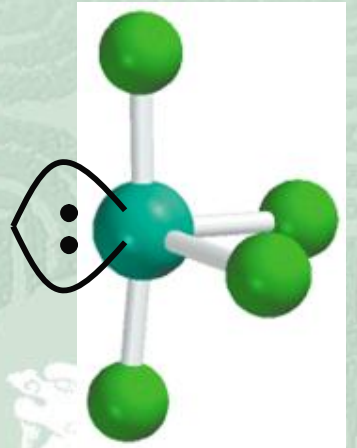
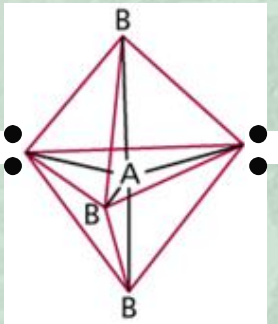
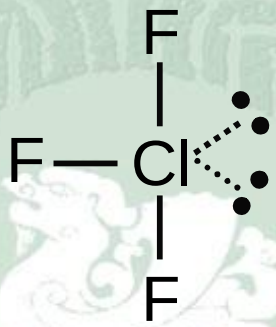


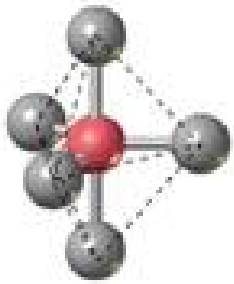
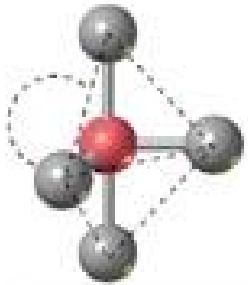
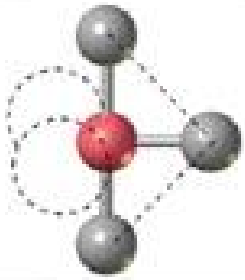
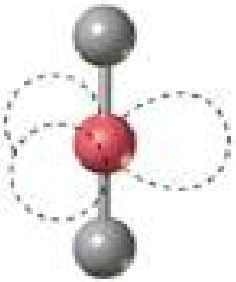
Fig7.8 Molecular geometries for molecules with expanded octets and unshared electron pairs. VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AX_4E	4	1	trigonal bipyramidal	distorted tetrahedron
AX_3E_2	3	2	trigonal bipyramidal	T-shaped



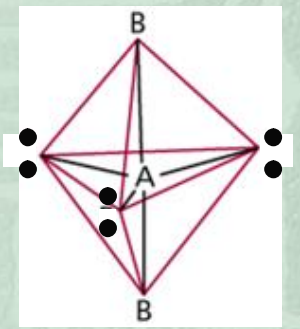


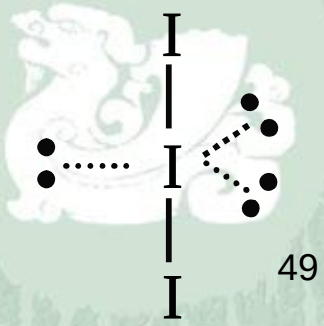
5 ELECTRON PAIRS

Species type	Structure	Description	Example	Bond angles
AX_5		Triangular bipyramidal	PF_5	90°, 120°, 180°
AX_4E		See-saw	SF_4	90°, 120°, 180°
AX_3E_2		T-shaped	ClF_3	90°, 180°
AX_2E_3		Linear	XeF_2	180°

VSEPR

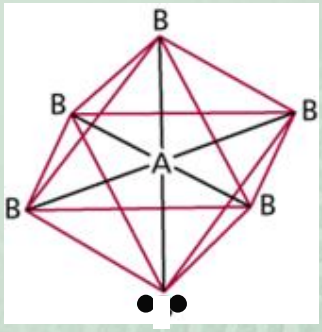
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AX_4E	4	1	trigonal bipyramidal	distorted tetrahedron
AX_3E_2	3	2	trigonal bipyramidal	T-shaped
AX_2E_3	2	3	trigonal bipyramidal	linear





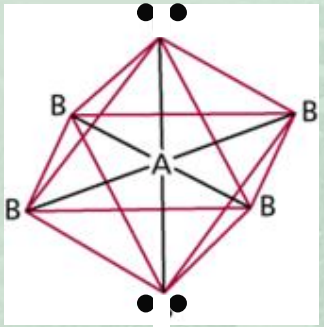
VSEPR

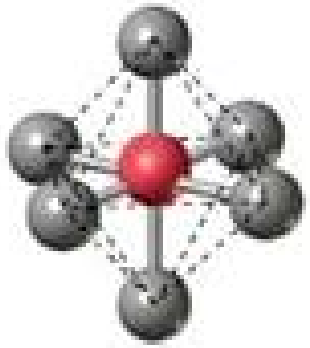
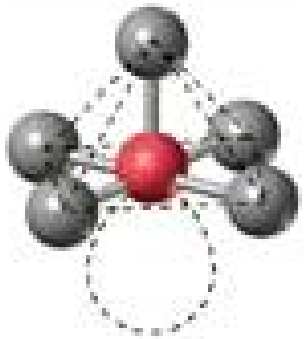
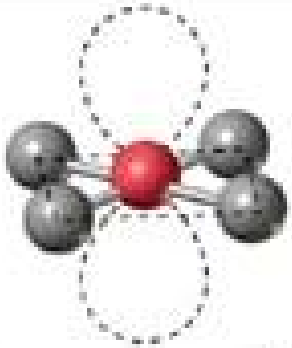
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_6	6	0	octahedral	octahedral
AX_5E	5	1	octahedral	square pyramidal



VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AX_6	6	0	octahedral	octahedral
AX_5E	5	1	octahedral	square pyramidal
AX_4E_2	4	2	octahedral	square planar



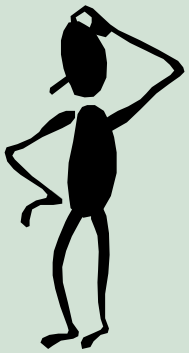
6 ELECTRON PAIRS				
AX_6		Octahedral	SF_6	90°, 180°
AX_5E		Square pyramidal	ClF_5	90°, 180°
AX_4E_2		Square planar	XeF_4	90°, 180°

Geometry of Simple Molecules and Ions in Which the Central Atom Has One or More Lone Pairs

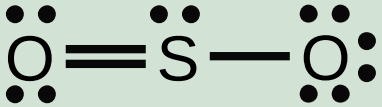
Class of molecule	Total number of electron pairs	Number of bonding pairs	Number of lone pairs	Arrangement of electron pairs*	Geometry	Examples
AB_2E	3	2	1	Trigonal planar	Bent	SO_2
AB_3E	4	3	1	Tetrahedral	Trigonal pyramidal	NH_3
AB_2E_2	4	2	2	Tetrahedral	Bent	H_2O
AB_4E	5	4	1	Trigonal bipyramidal	Distorted tetrahedron (or seesaw)	SF_4
AB_3E_2	5	3	2	Trigonal bipyramidal	T-shaped	ClF_3
AB_2E_3	5	2	3	Trigonal bipyramidal	Linear	I_3^-
AB_5E	6	5	1	Octahedral	Square pyramidal	BrF_5
AB_4E_2	6	4	2	Octahedral	Square planar	XeF_4

Predicting Molecular Geometry

1. Draw Lewis structure for molecule.
2. Count number of lone pairs on the central atom and number of atoms bonded to the central atom.
3. Use VSEPR to predict the geometry of the molecule.

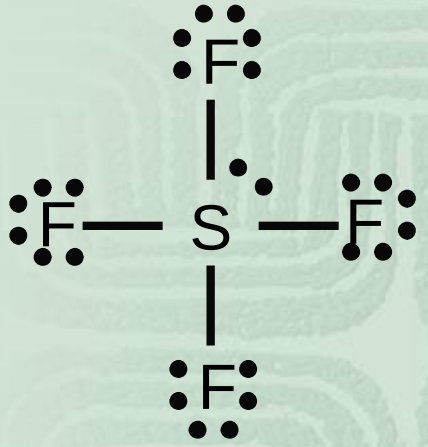


What are the molecular geometries of SO_2 and SF_4?



AX_2E

bent



AX_4E

See- saw

Ex:7.5 Predict the geometry of

(a) NH_4

(b) GeF_2

(c) PF_3

Multiple Bonds

Insofar as molecular geometry is concerned, a multiple bond behaves like a single bond.

the means that the electron pair in a multiple bond must occupy the same region of space as those in a single bond. the extra electron pairs in a multiple bond have no effect on geometry.

EX:7.6 Predict the geometry of the ClO_3^- ion, the NO_3^- ion及N_2O molecule, Which have the Lewis structures?

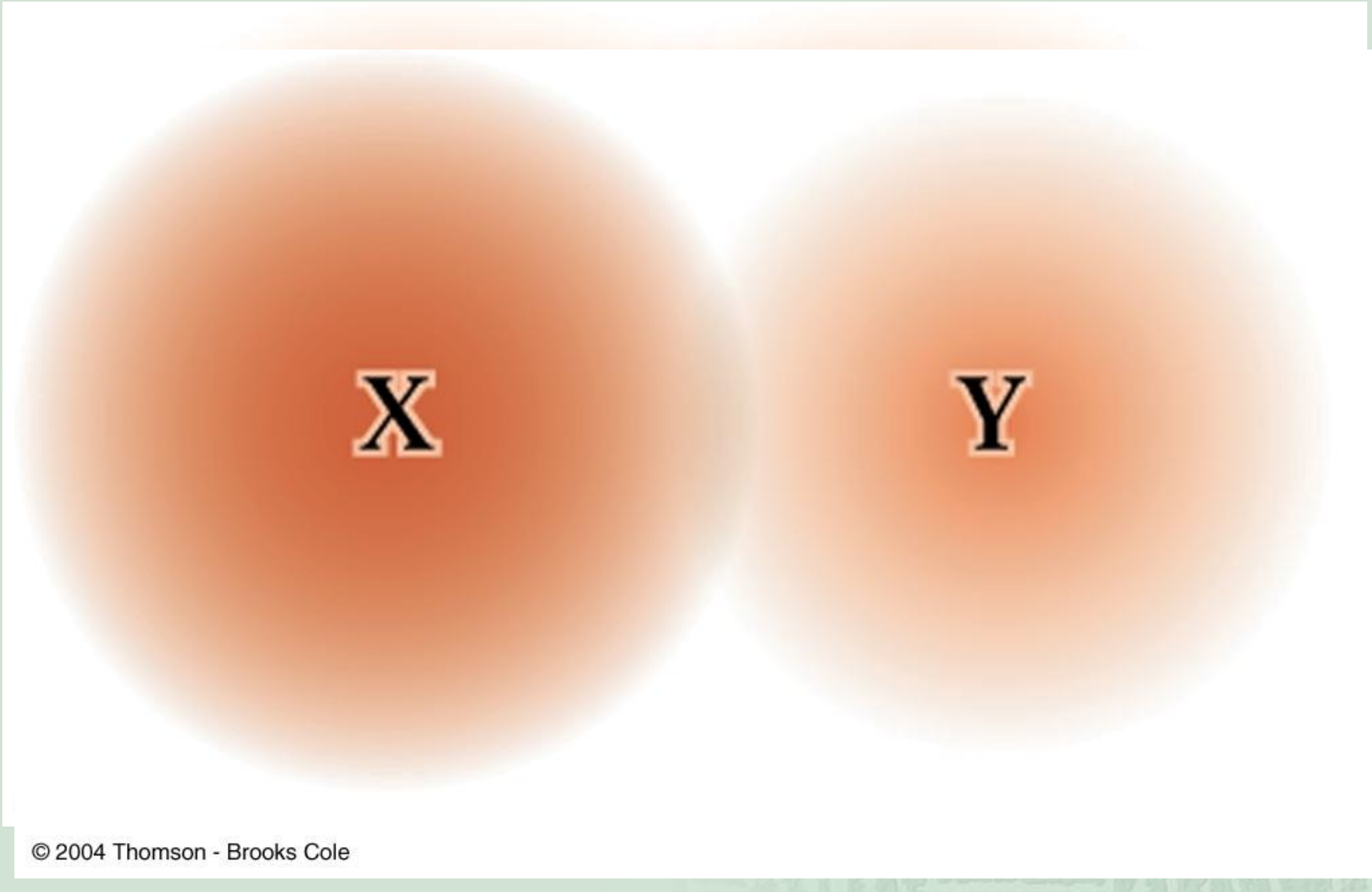
Solution:

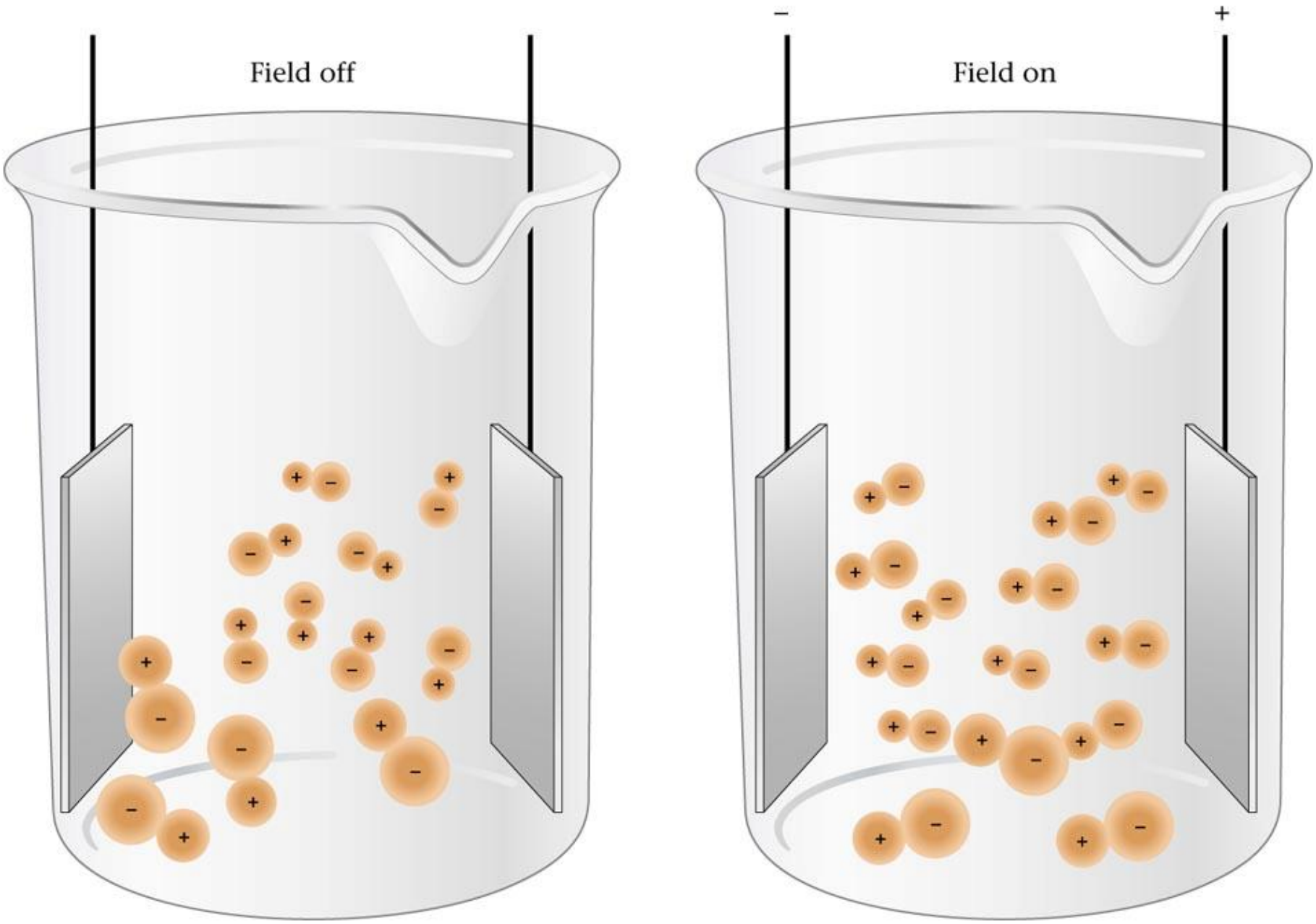
(a) The central atom , Cl, is bonded to three oxygen atoms, it has one unshared pair. The ClO_3^- ion is of the type AX_3E. It is a triangular pyramid

(b) AX_3 It has The geometry of an equilateral triangle,the bond angle is 120^0 .The ion is triangular planar.

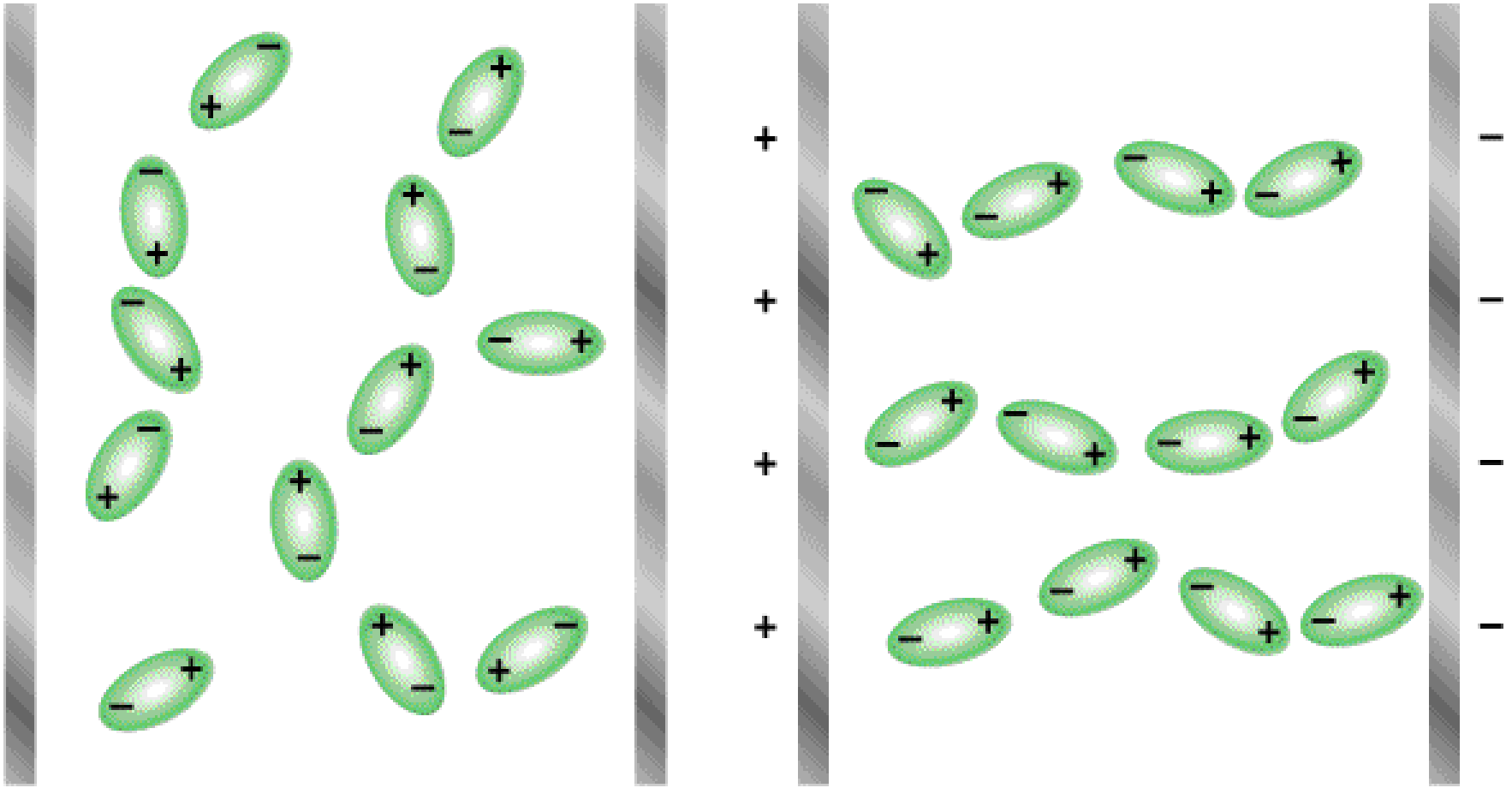
(c) Type AX_2, is linear , with a bond angle of 180^0

7-3 Polarity of Molecules
Polar and Nonpolar covalent Bonds

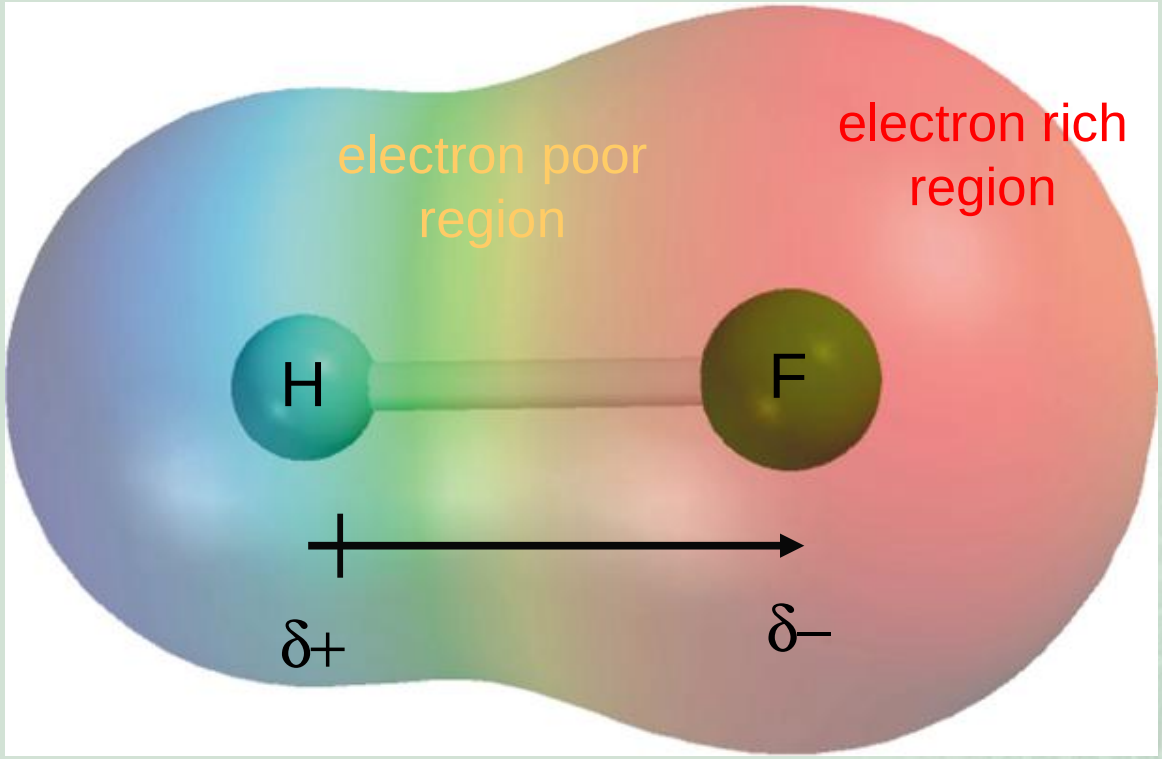




Behavior of Polar Molecules



Dipole Moments–The extent to which molecules tend to orient themselves in an electrical field is a measure.



箭頭代表電子密度高

正號代表電子密度低

從電負度較低者移向電負度較高

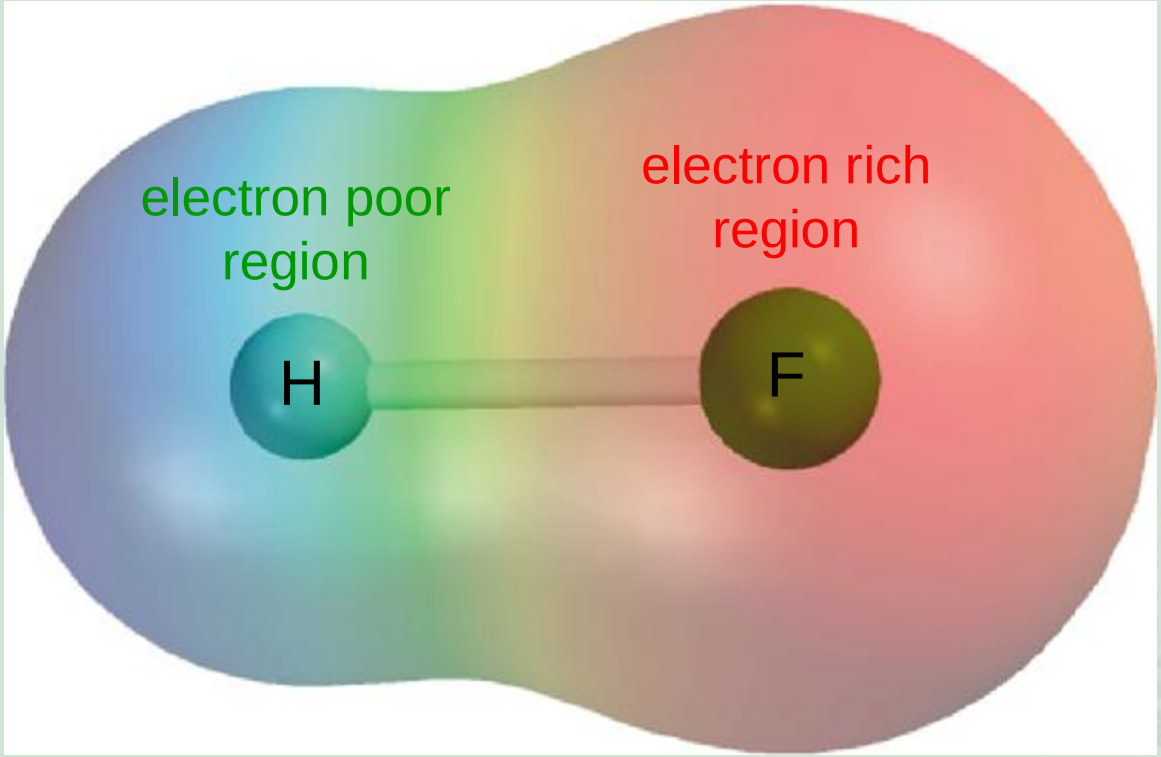
$\mu = Q \times r$

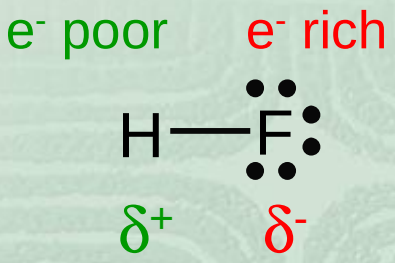
Q is the charge

r is the distance between charges

1 D = 3.36 x 10^{-30} C m

Polar covalent bond or ***polar bond*** is a covalent bond with greater electron density around one of the two atoms

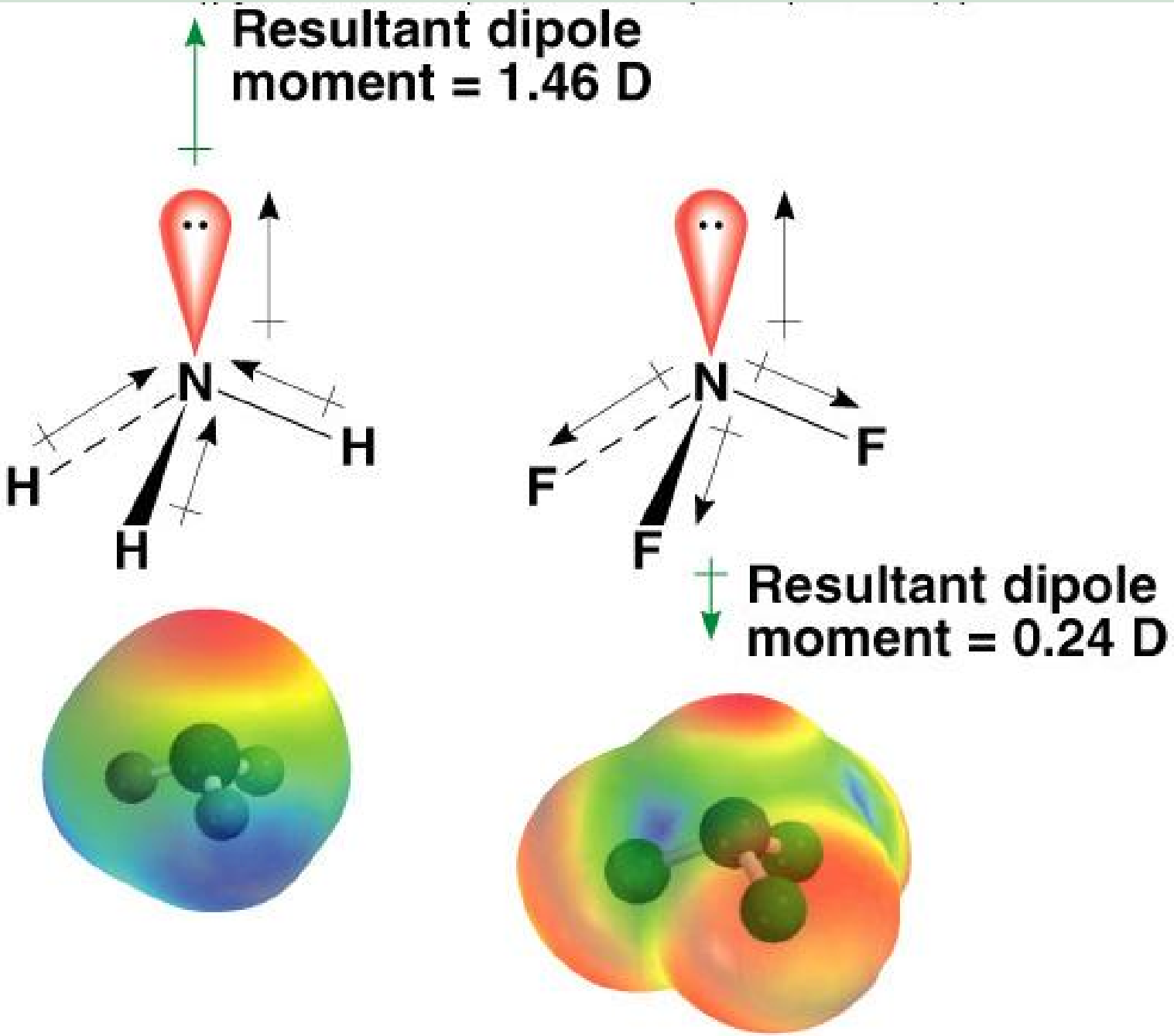


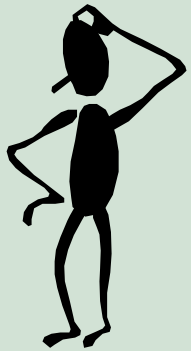


Polar and nonpolar Molecules

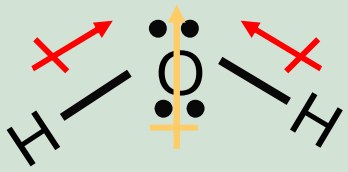
- Bond polarity
- Molecular geometry

- If the polar A-X bonds in a molecule AX_mE_n are arranged symmetrically around the central atom A, the molecule is nonpolar.
- Molecules of the type AX_2(linear),AX_3(triangular planar),and AX_4(tetrahedral)are nonpolar .Ex CO_2, BF_3
- Molecules of the type AX_2E(bent) ,AX_2E_2(bent),and AX_3E (triangular pyramid) are polar. Ex SO_2,H_2O

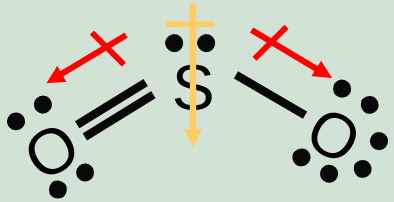

Resultant dipole
moment = 1.46 D
N
H
H
H
N
F
F
F
Resultant dipole
moment = 0.24 D



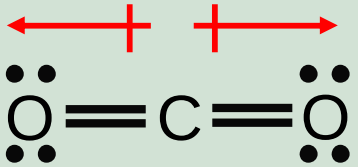
Which of the following molecules have a dipole moment?
H_2O, CO_2, SO_2, and CH_4



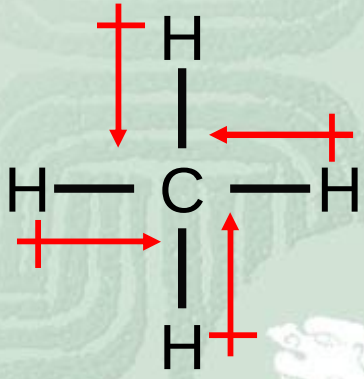
dipole moment
polar molecule



dipole moment
polar molecule

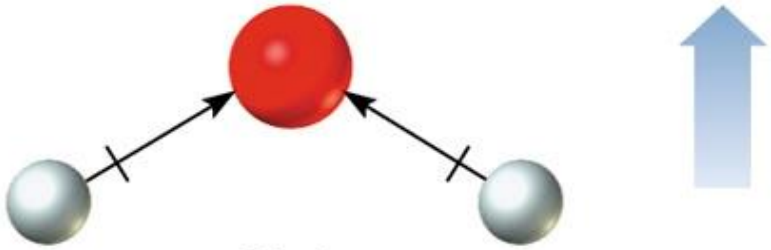


no dipole moment
nonpolar molecule

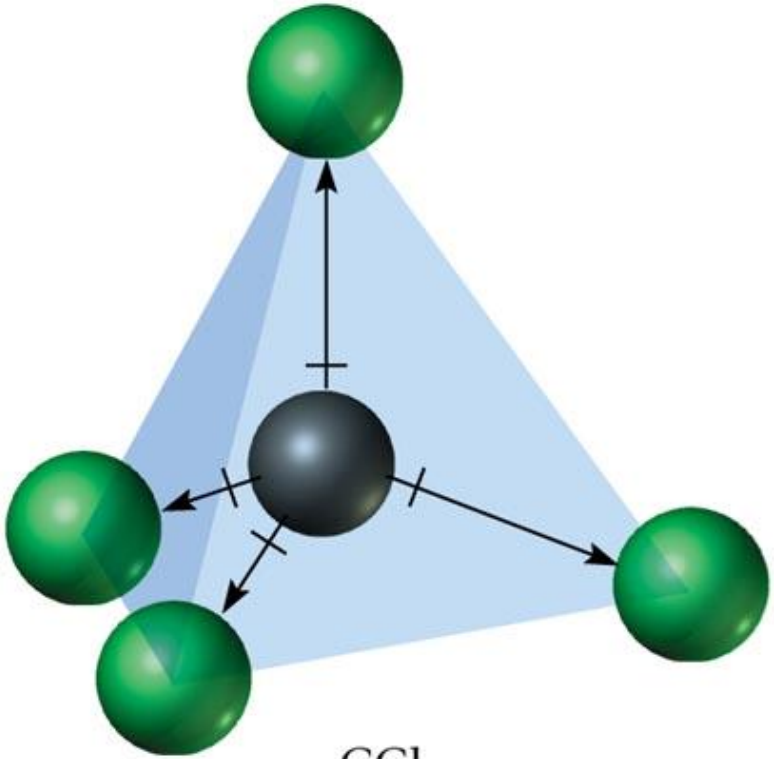


no dipole moment
nonpolar molecule

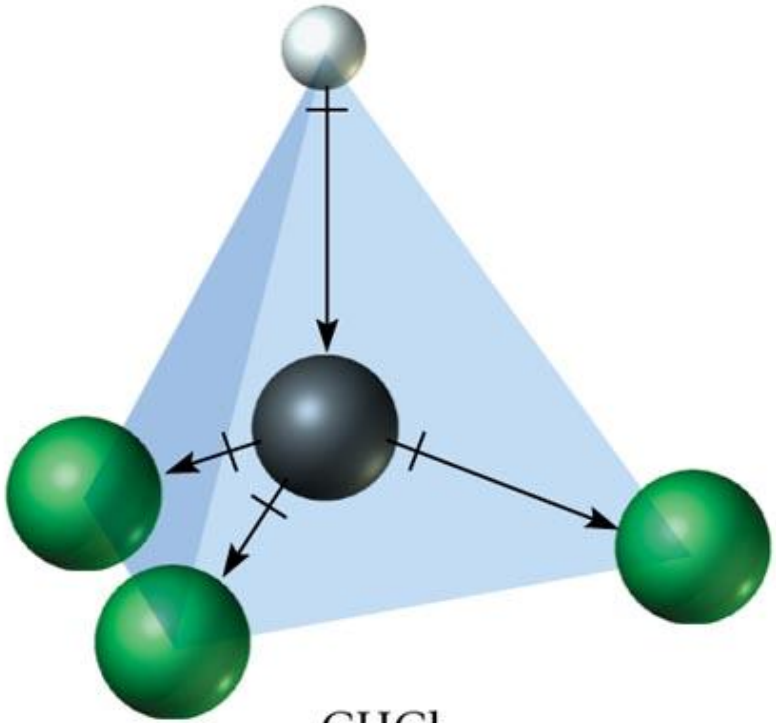
BeF_2



H_2O



CCl_4



$CHCl_3$

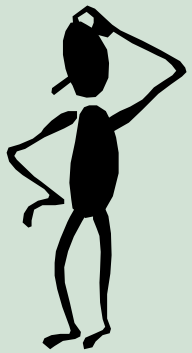
Ex:7.7 Determine whether each of the following is polar or nonpolar?

- SO_2:
- AX_2E It is bent , so it is Ploar
- BF_3

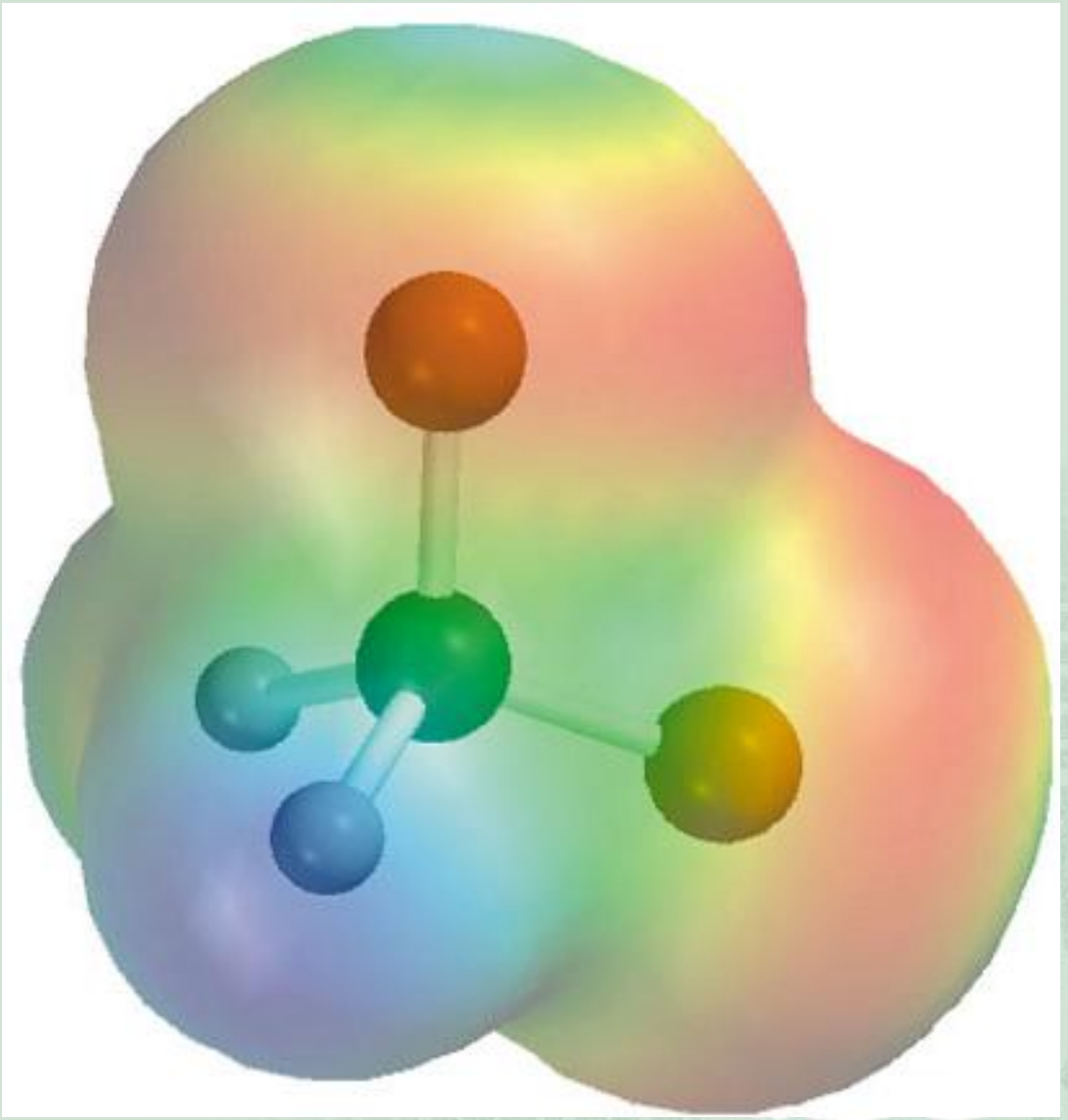
AX_3 It is triangle；It is nonpolar.

CO_2

AX_2 It is a linear ,It is nonpolar



Does CH_2Cl_2 have a dipole moment?



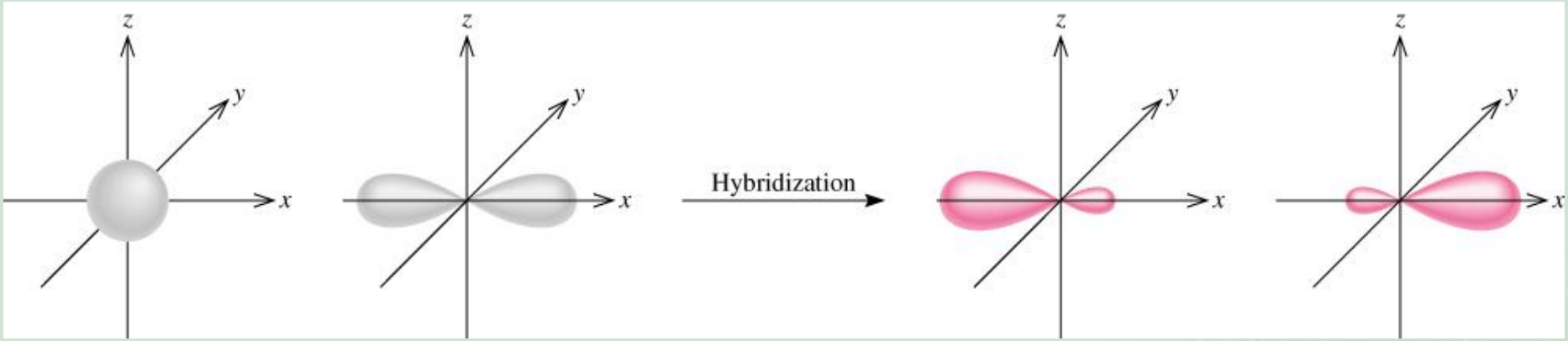
Dipole Moments of Some Polar Molecules

Molecule	Geometry	Dipole Moment (D)
HF	Linear	1.92
HCl	Linear	1.08
HBr	Linear	0.78
HI	Linear	0.38
H_2O	Bent	1.87
H_2S	Bent	1.10
NH_3	Trigonal pyramidal	1.46
SO_2	Bent	1.60

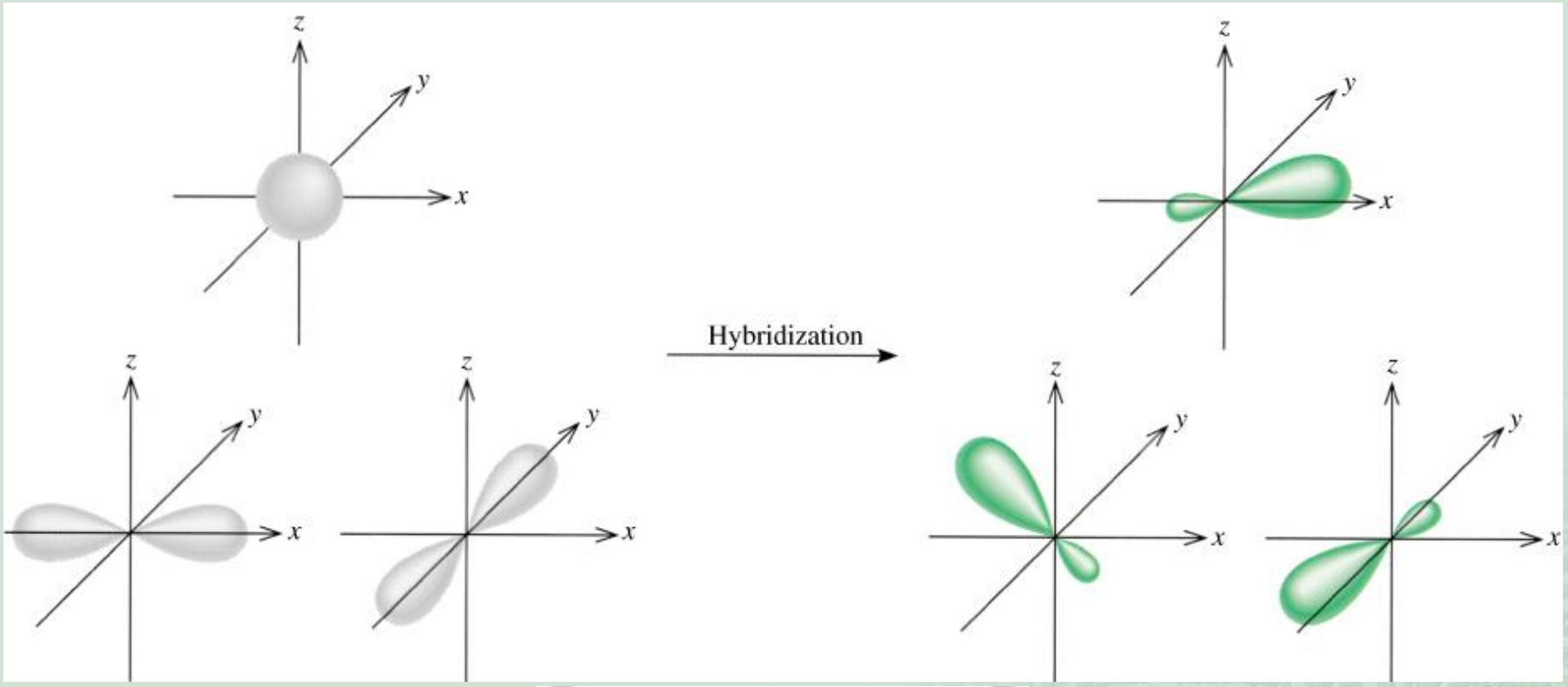
7-4 Atomic orbitals; Hybridization

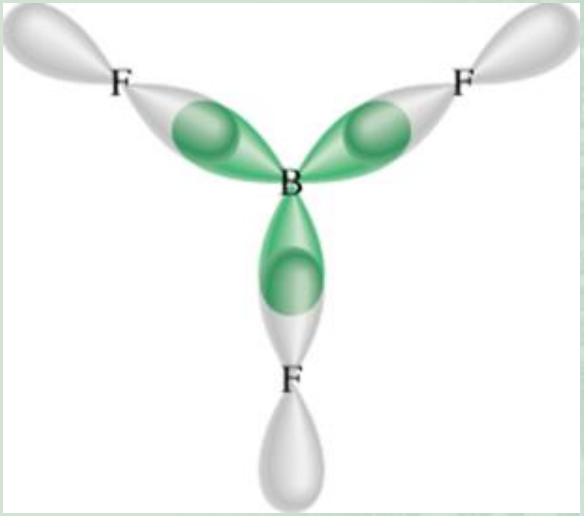
1. Mix at least 2 nonequivalent atomic orbitals (*e.g.* s and p). Hybrid orbitals have very different shape from original atomic orbitals.
2. Number of hybrid orbitals is equal to number of pure atomic orbitals used in the hybridization process.
3. Covalent bonds are formed by:
   a. Overlap of hybrid orbitals with atomic orbitals
   b. Overlap of hybrid orbitals with other hybrid orbitals

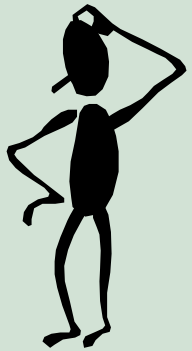
Formation of *sp* Hybrid Orbitals



Formation of sp^2 Hybrid Orbitals





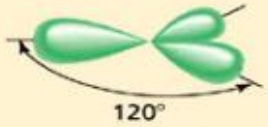
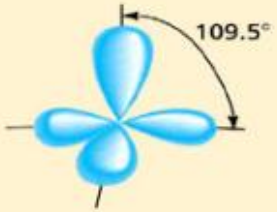
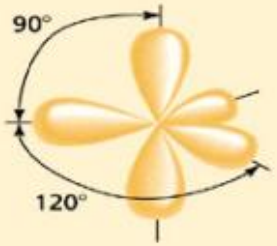
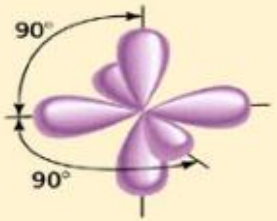


How do I predict the hybridization of the central atom?

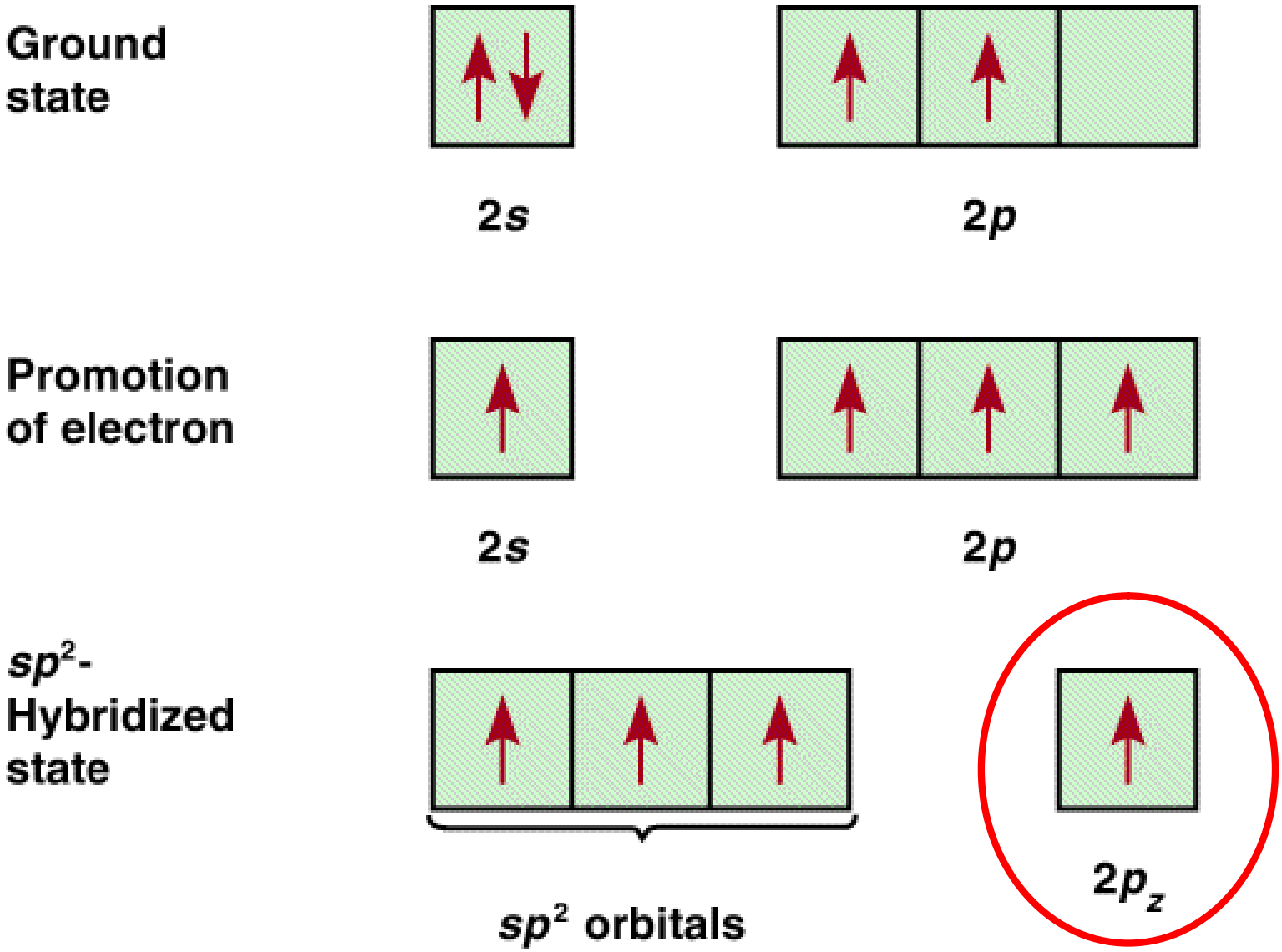
Count the number of lone pairs AND the number of atoms bonded to the central atom

# of Lone Pairs + # of Bonded Atoms	Hybridization	Examples
2	sp	$BeCl_2$
3	sp^2	BF_3
4	sp^3	CH_4, NH_3, H_2O
5	sp^3d	PCl_5
6	sp^3d^2	SF_6

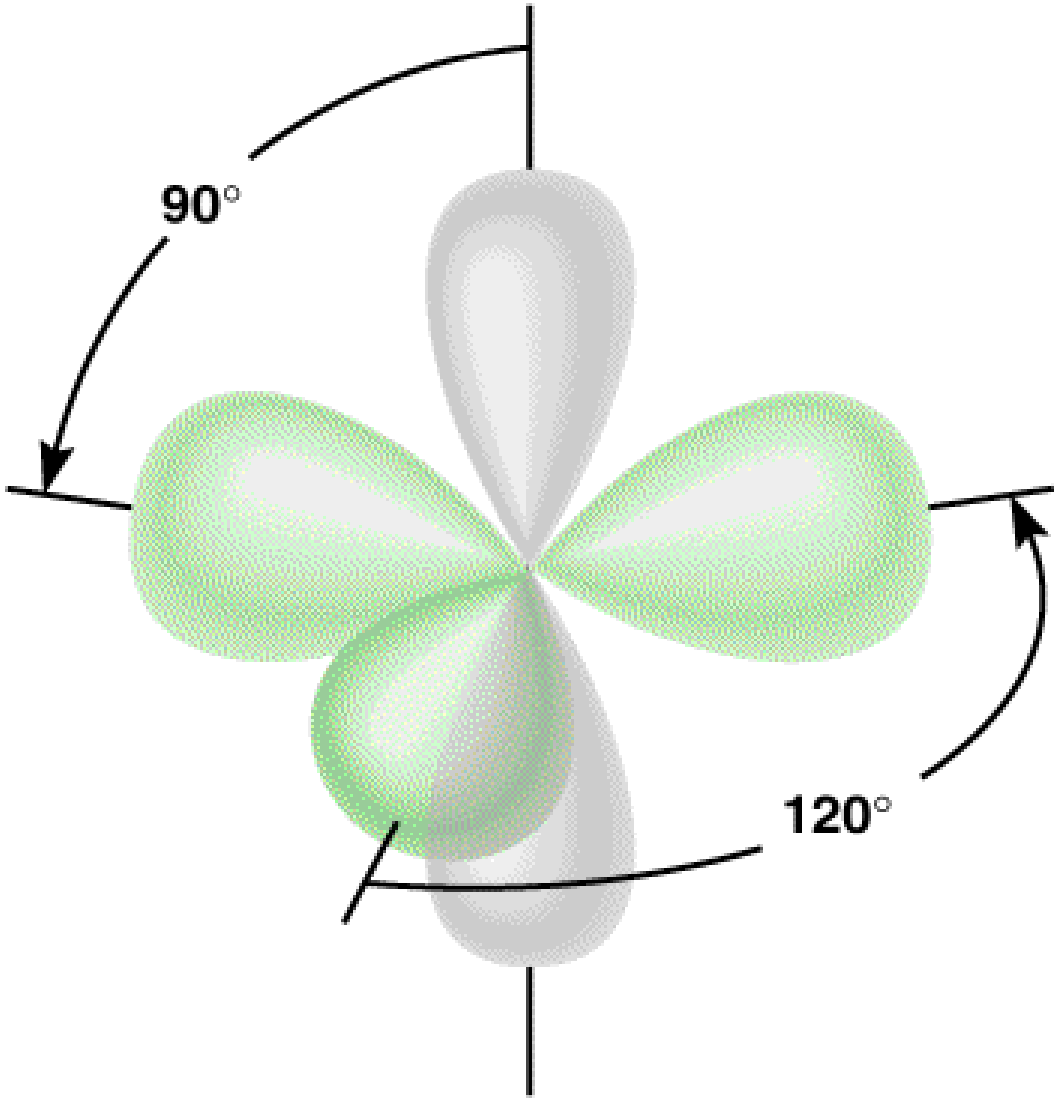
Important Hybrid Orbitals and Their Shapes

Pure Atomic Orbitals of the Central Atom	Hybridization of the Central Atom	Number of Hybrid Orbitals	Shape of Hybrid Orbitals	Examples
s, *p*	*sp*	2	 Linear	$BeCl_2$
s, *p*, *p*	sp^2	3	 Trigonal planar	BF_3
s, *p*, *p*, *p*	sp^3	4	 Tetrahedral	CH_4, NH_4^+
s, *p*, *p*, *p*, *d*	sp^3d	5	 Trigonal bipyramidal	PCl_5
s, *p*, *p*, *p*, *d*, *d*	sp^3d^2	6	 Octahedral	SF_6

sp^2 Hybridization of a Carbon Atom

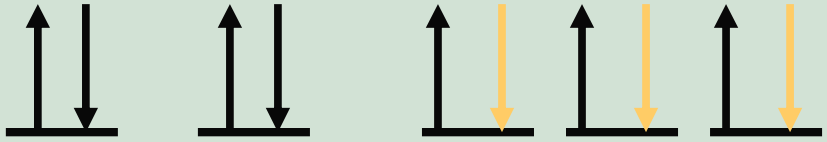


$2p_z$ Orbital Is Perpendicular to the Plane of the Hybrid Orbitals

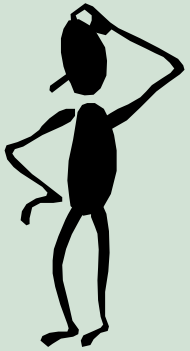


Valence Bond Theory and NH_3

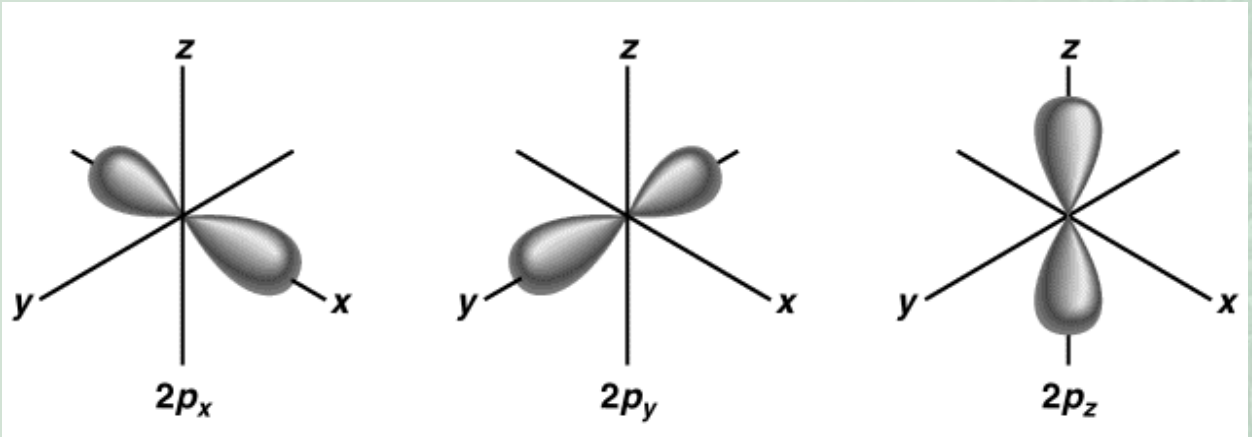
N – $1s^2 2s^2 2p^3$



3 H – $1s^1$



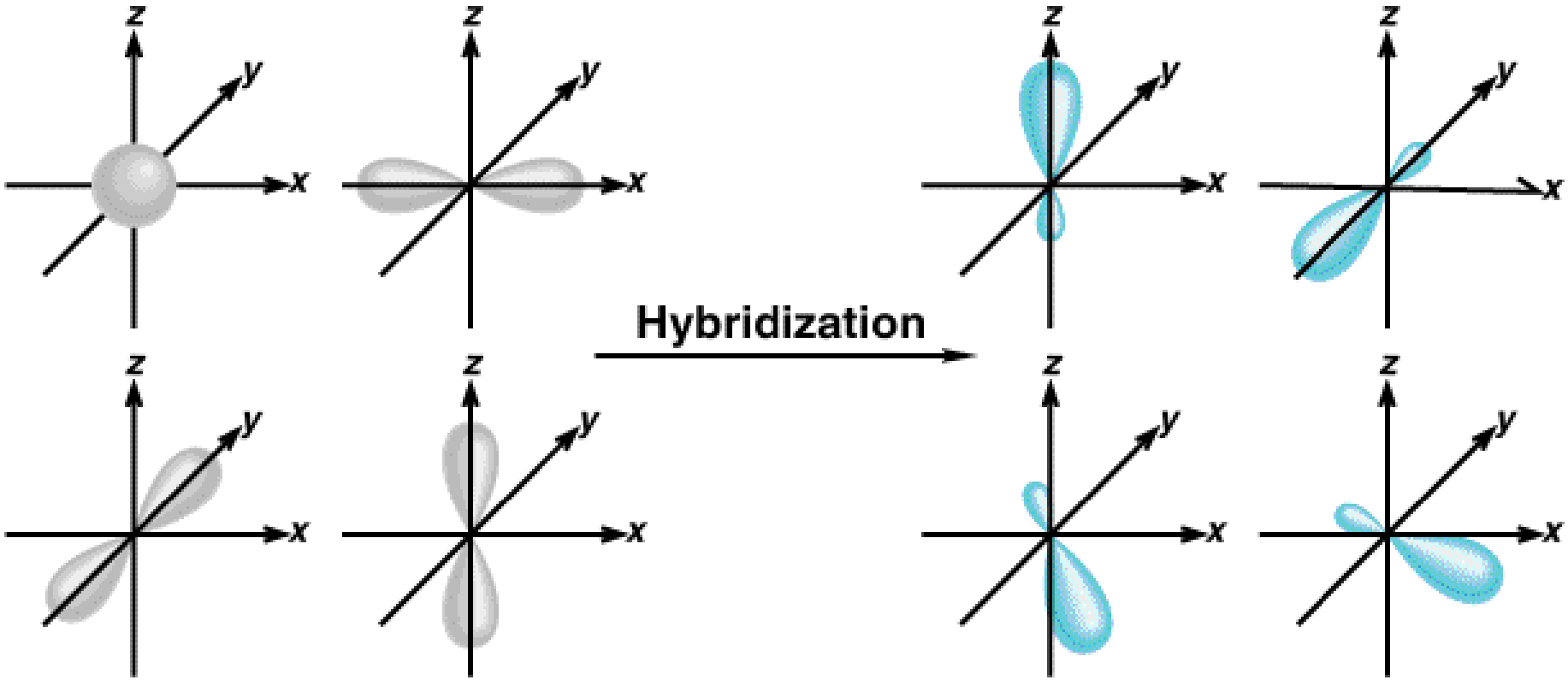
If the bonds form from overlap of 3 2p orbitals on nitrogen with the 1s orbital on each hydrogen atom, what would the molecular geometry of NH_3 be?



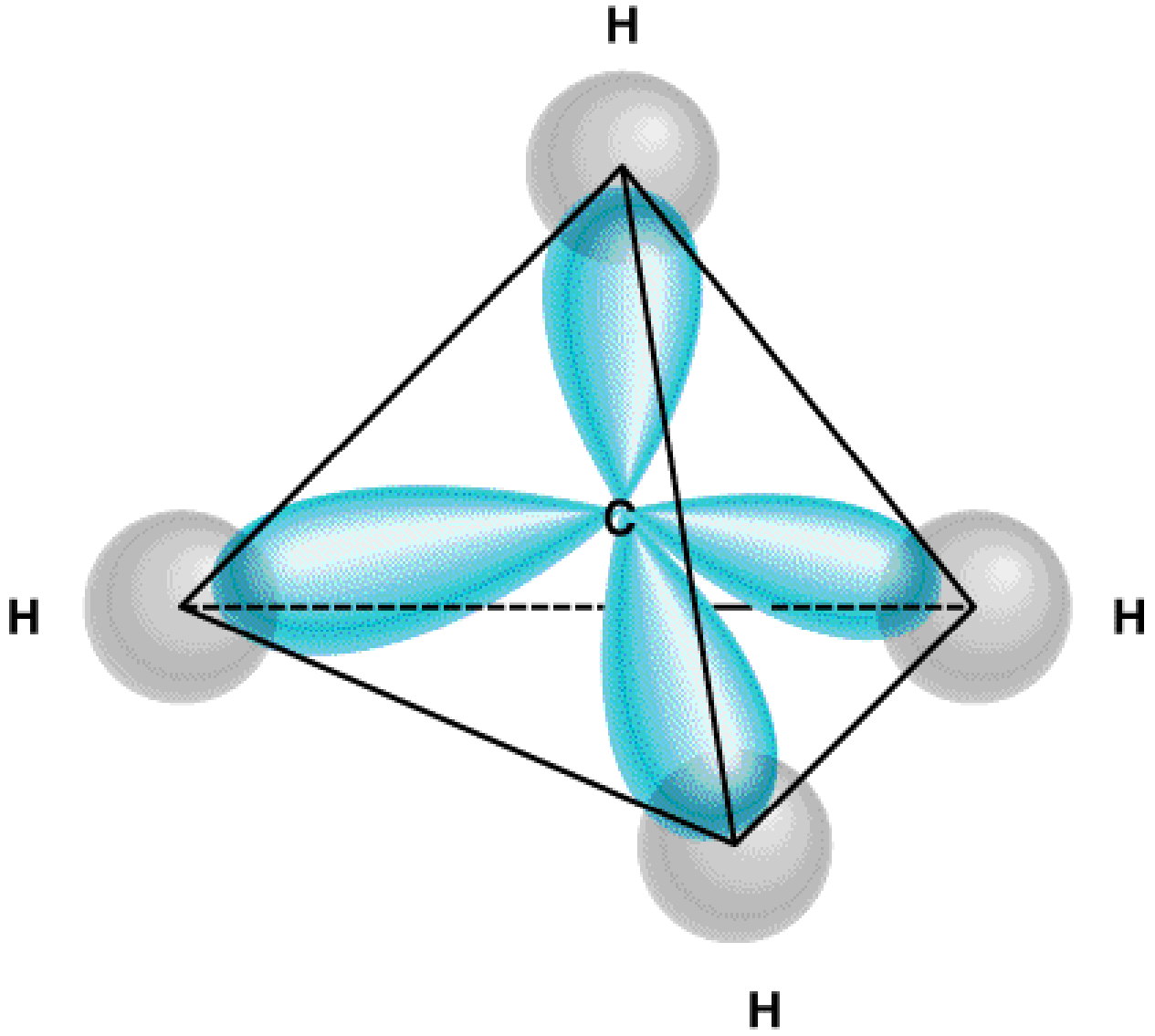
If use the 3 2p orbitals predict 90^0

Actual H-N-H bond angle is 107.3^0

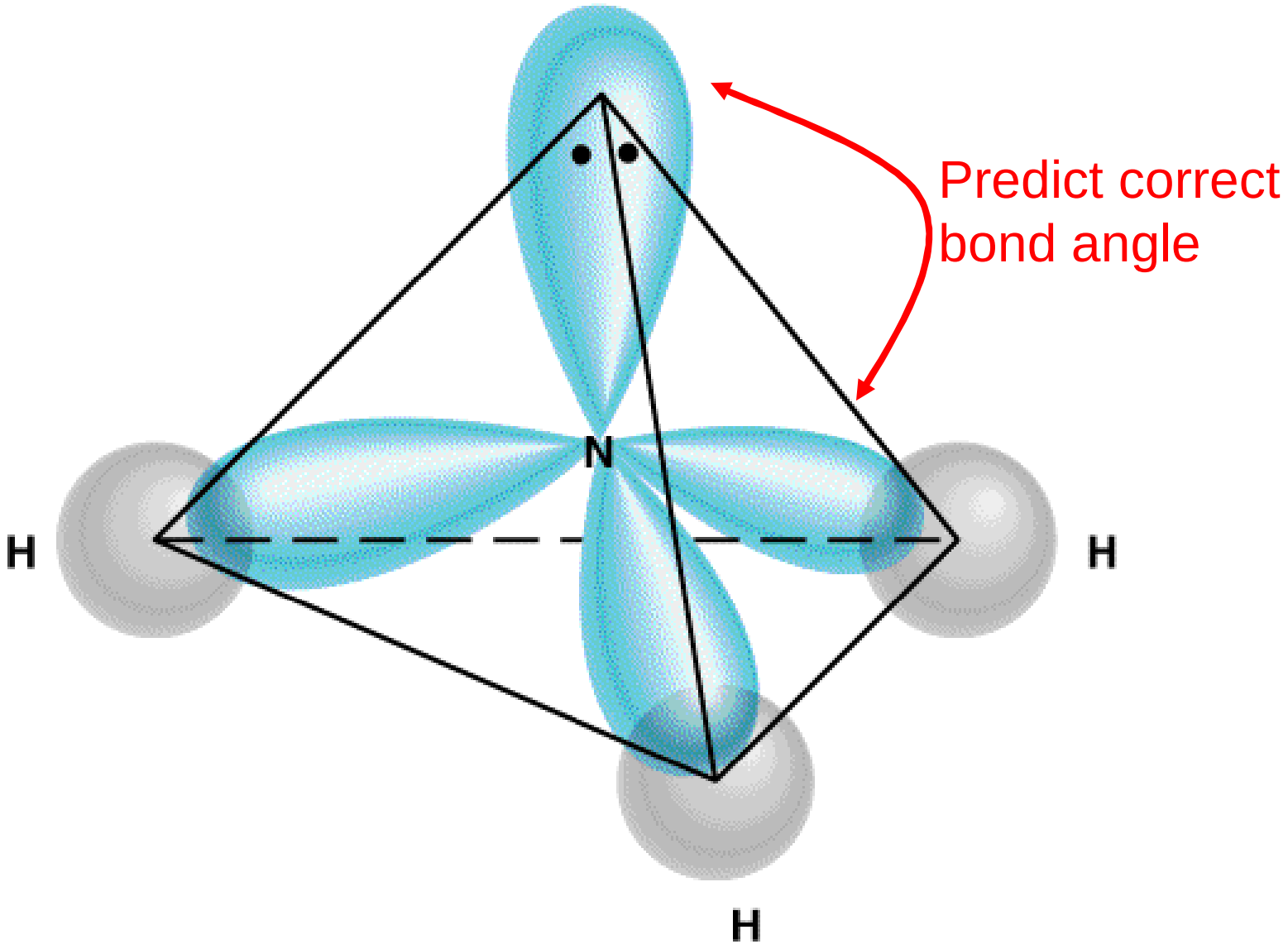
Formation of sp^3 Hybrid Orbitals

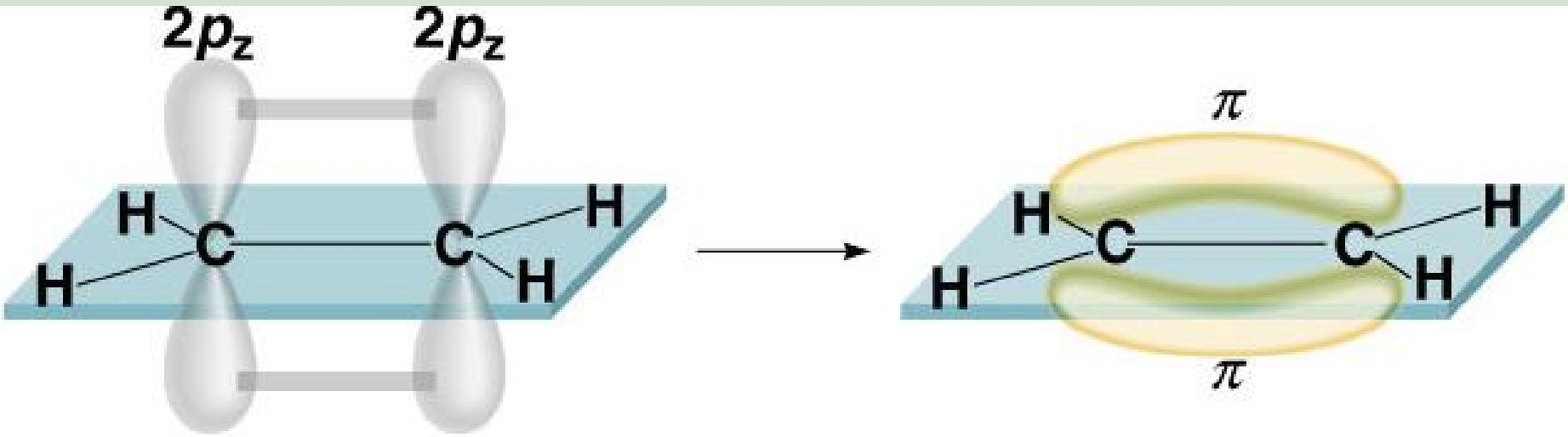


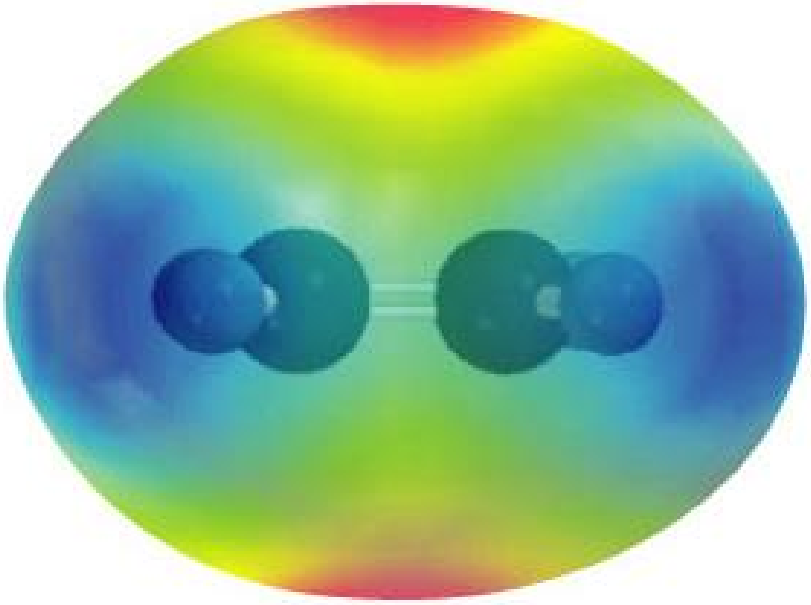
Formation of Covalent Bonds



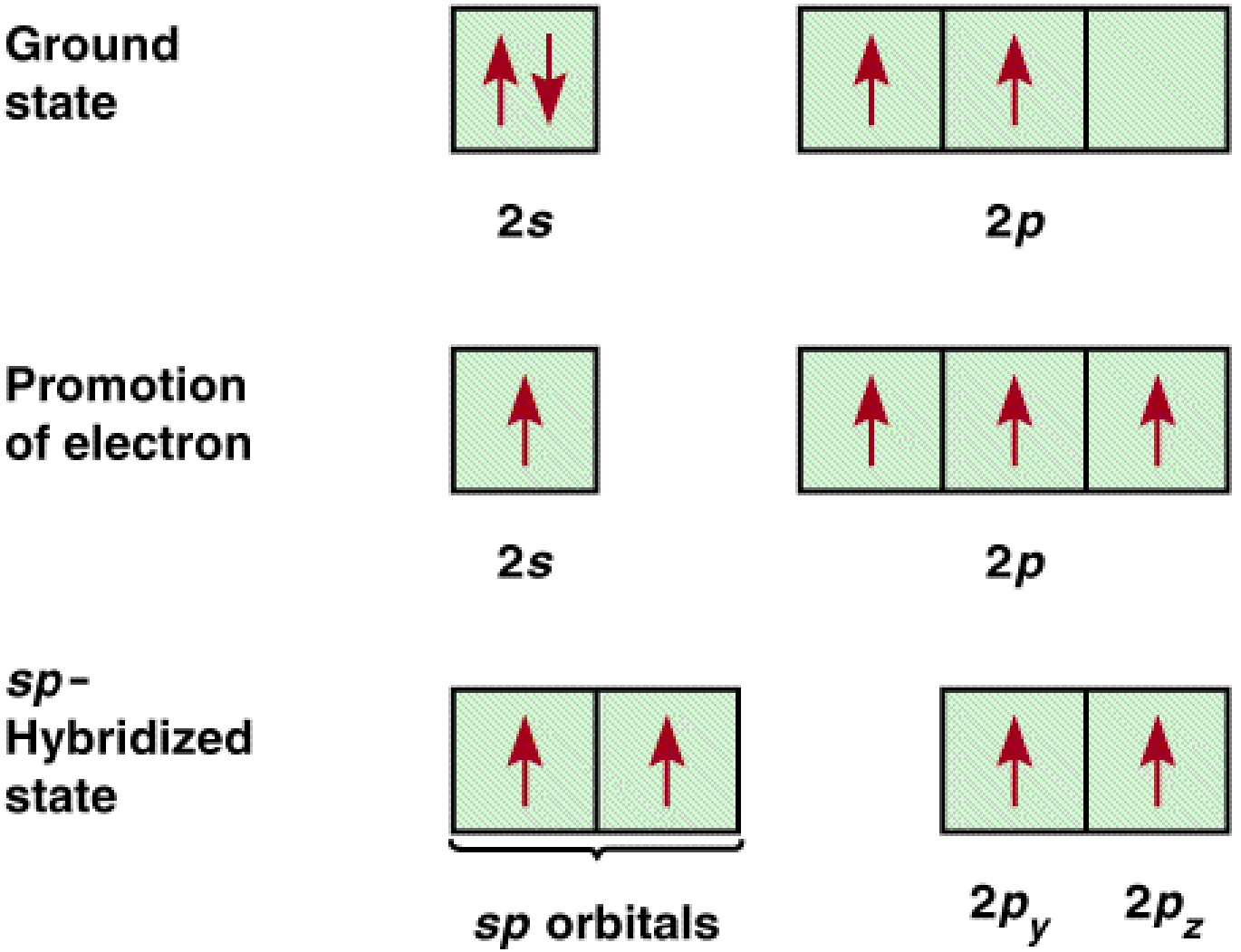
sp^3 – Hybridized N Atom in NH_3

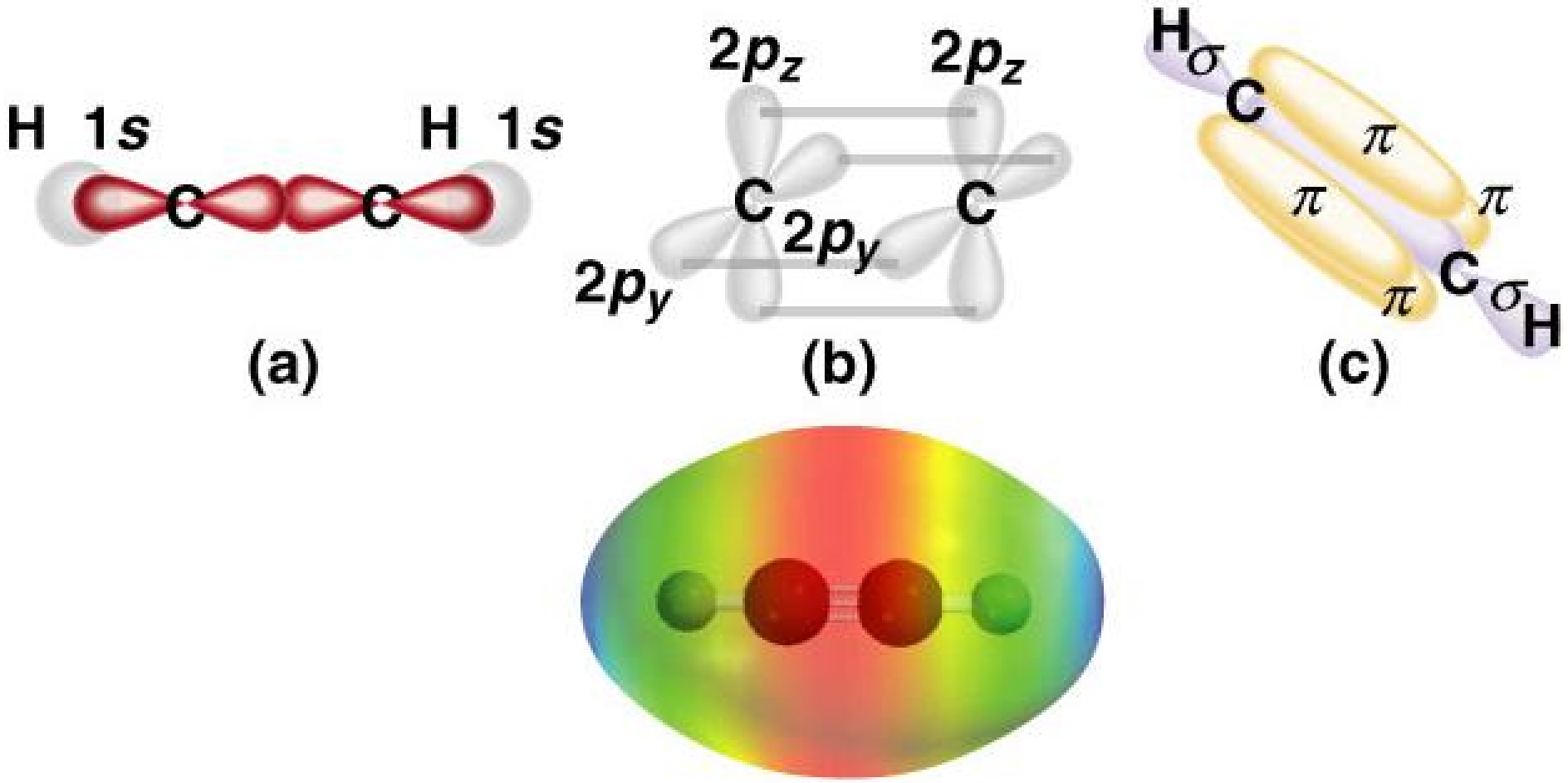



2pz
2pz
H
C
C
H
H
H
H
C
C
H
H
π
π



sp Hybridization of a Carbon Atom




H 1s
H 1s
C
C
(a)
2pz
2pz
C
C
2py
2py
(b)
Hσ
C
π
π
π
π
C
σH
(c)

multiple bond

- Insofar as molecular geometry is concerned , a multiple bond behaves like a single bond.

- The number of terminal atoms ,X, bonded to the central atom , Irrespective of whether the bonds are single , double, or triple.

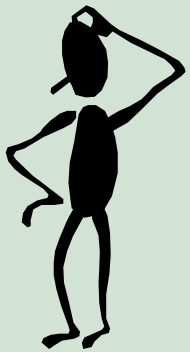
(幾何結構與末端原子數X的多寡有關，不必考慮鍵結是否為單、雙或參鍵。)

- The number of unshared pairs, E ,around the central atom.(圍繞中心原子的未鍵結電子數，亦會影響分子幾合結構。)

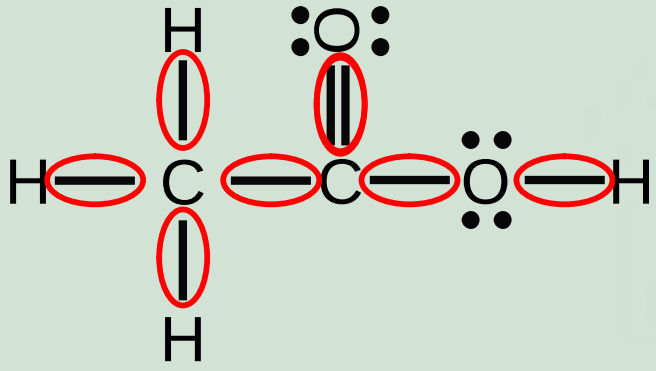
The extra electron pairs in a multiple bond (one pair in a double bond, two pairs in a triple bond) are not located in hybrid orbital.

Sigma (σ) and Pi Bonds (π)

Single bond	1 sigma bond
Double bond	1 sigma bond and 1 pi bond
Triple bond	1 sigma bond and 2 pi bonds



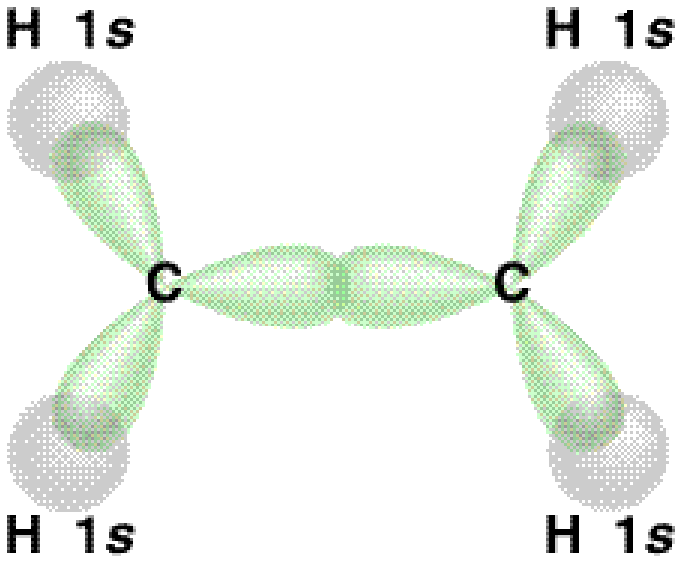
How many σ and π bonds are in the acetic acid (vinegar) molecule CH_3COOH?



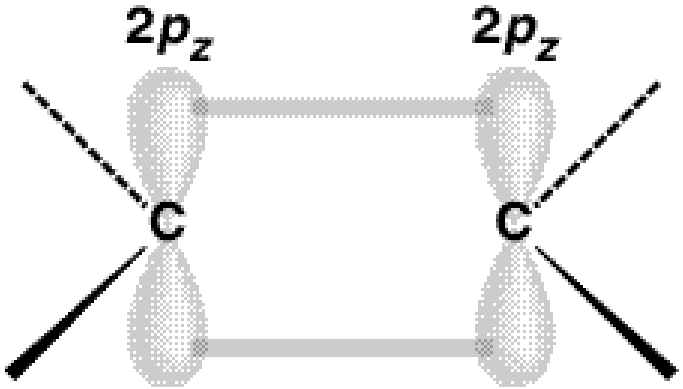
σ bonds = 6 + 1 = 7

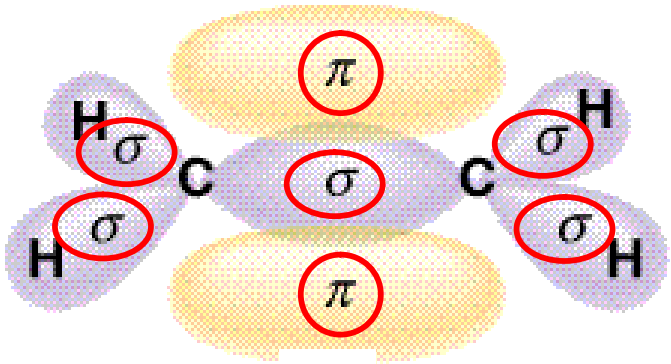
π bonds = 1

Bonding in Ethylene



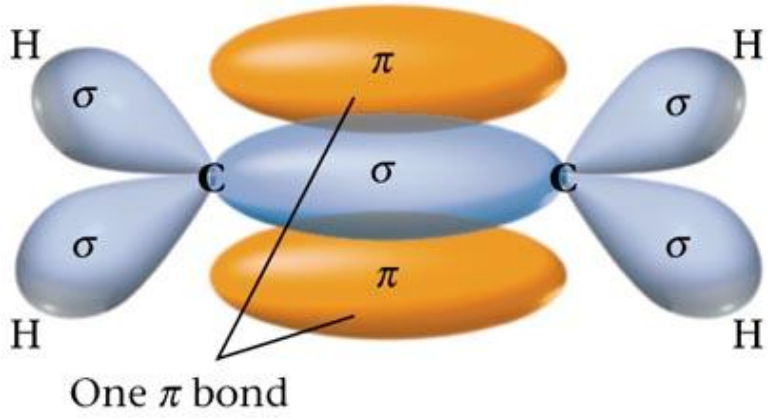
(a)



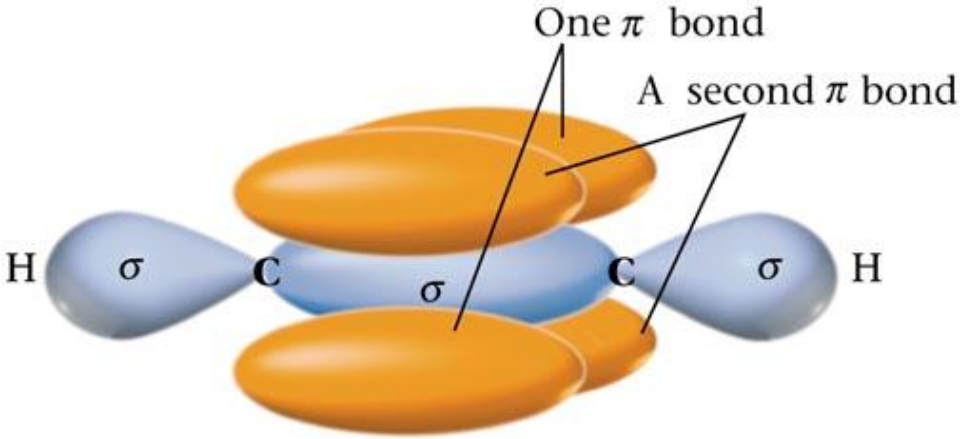


Pi bond (π) – electron density above and below plane of nuclei

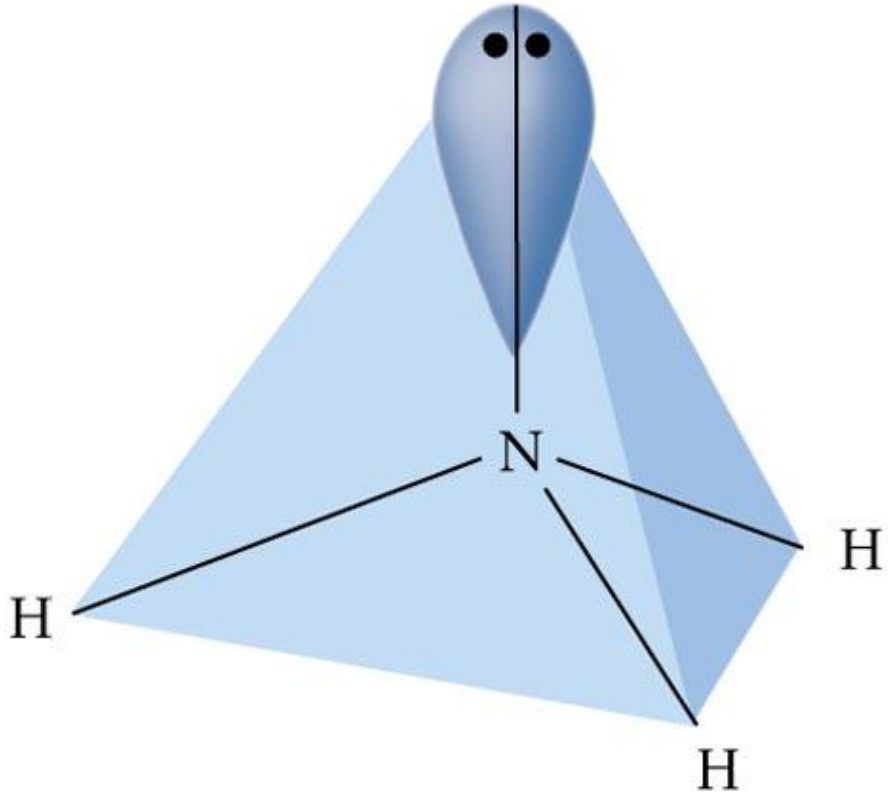
Sigma bond (σ) – electron density between the 2 atoms of the bonding atoms

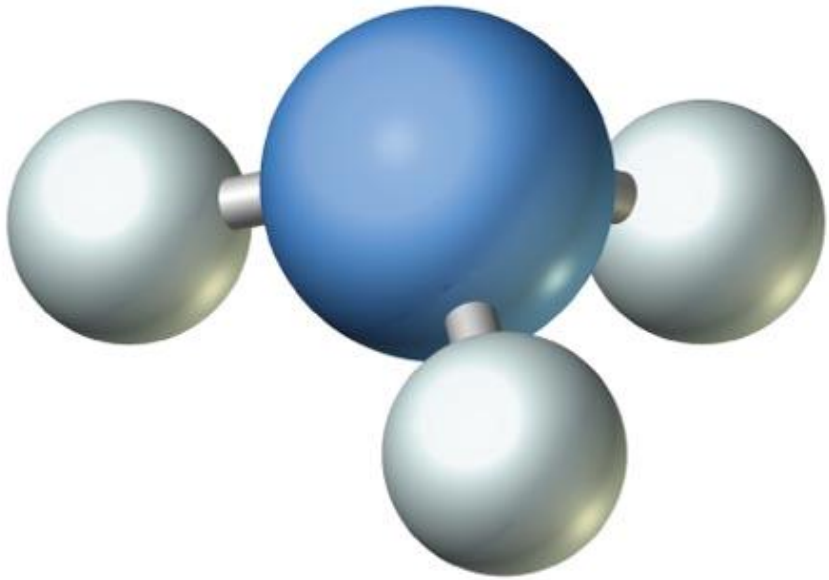


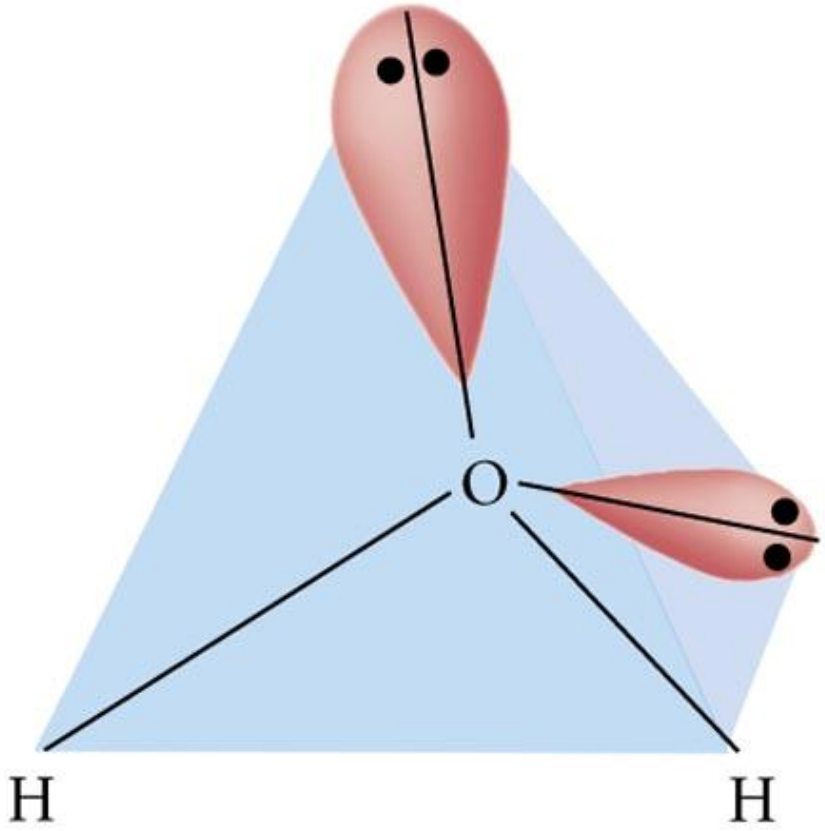
Ethylene

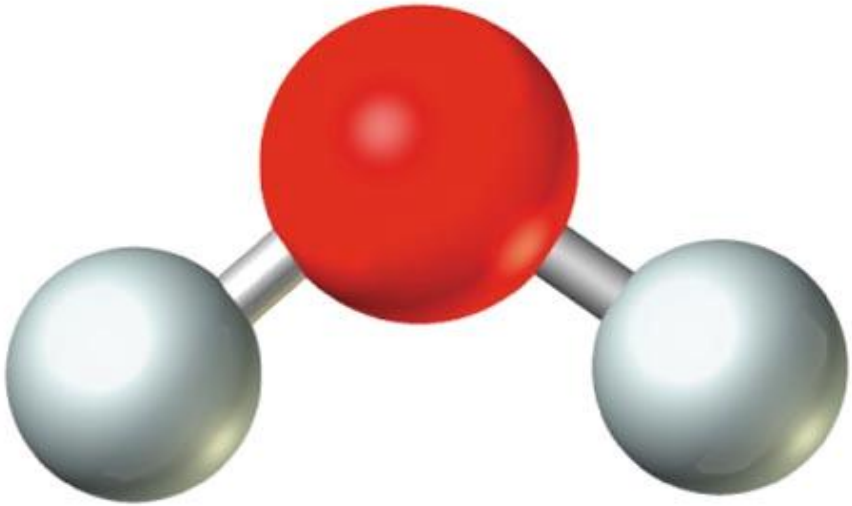


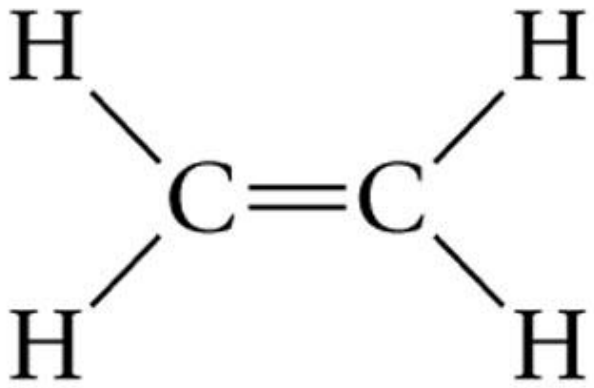
Acetylene

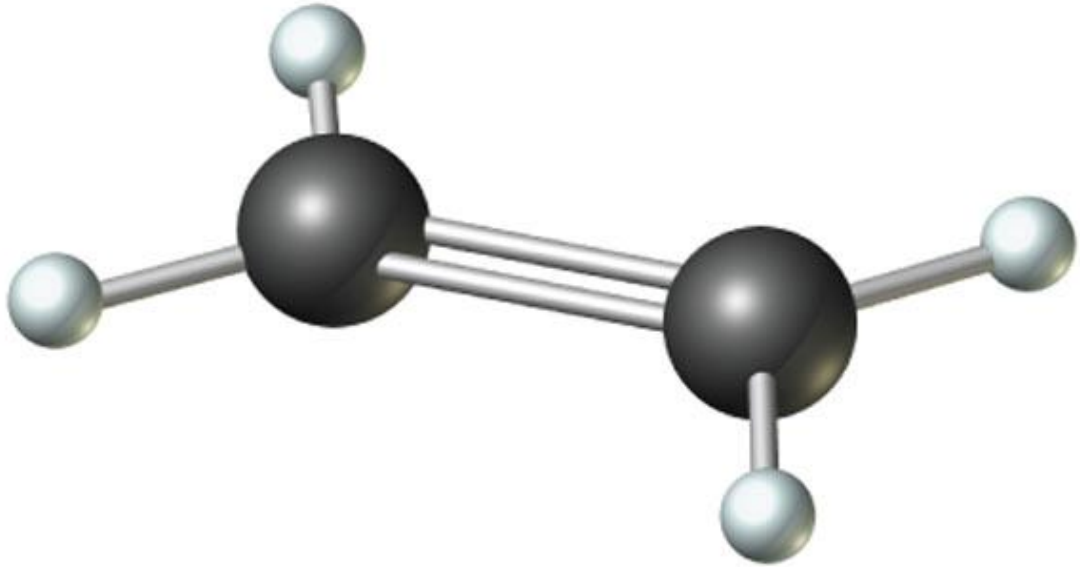




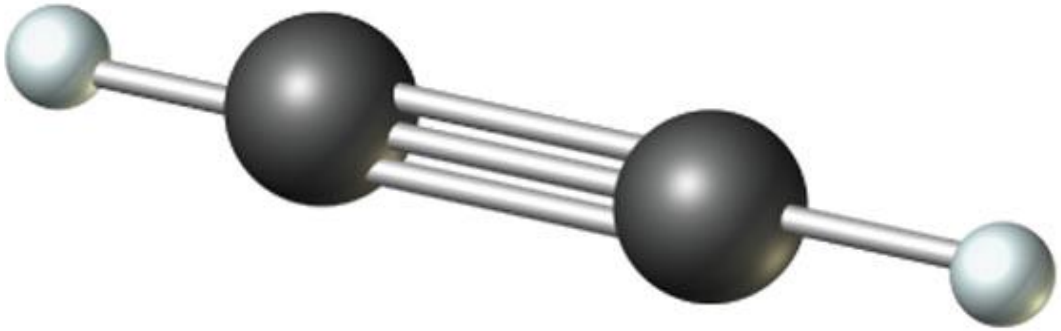


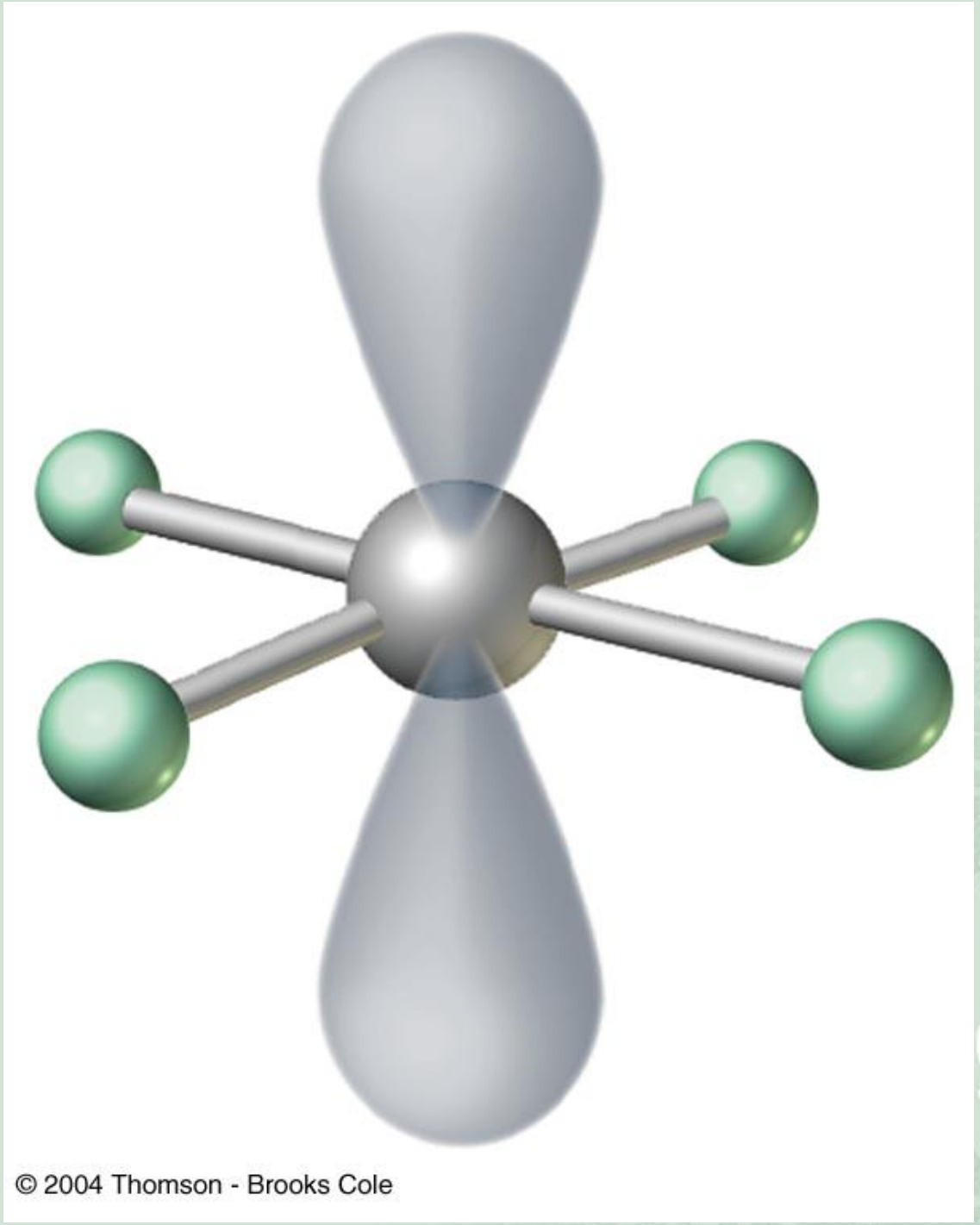




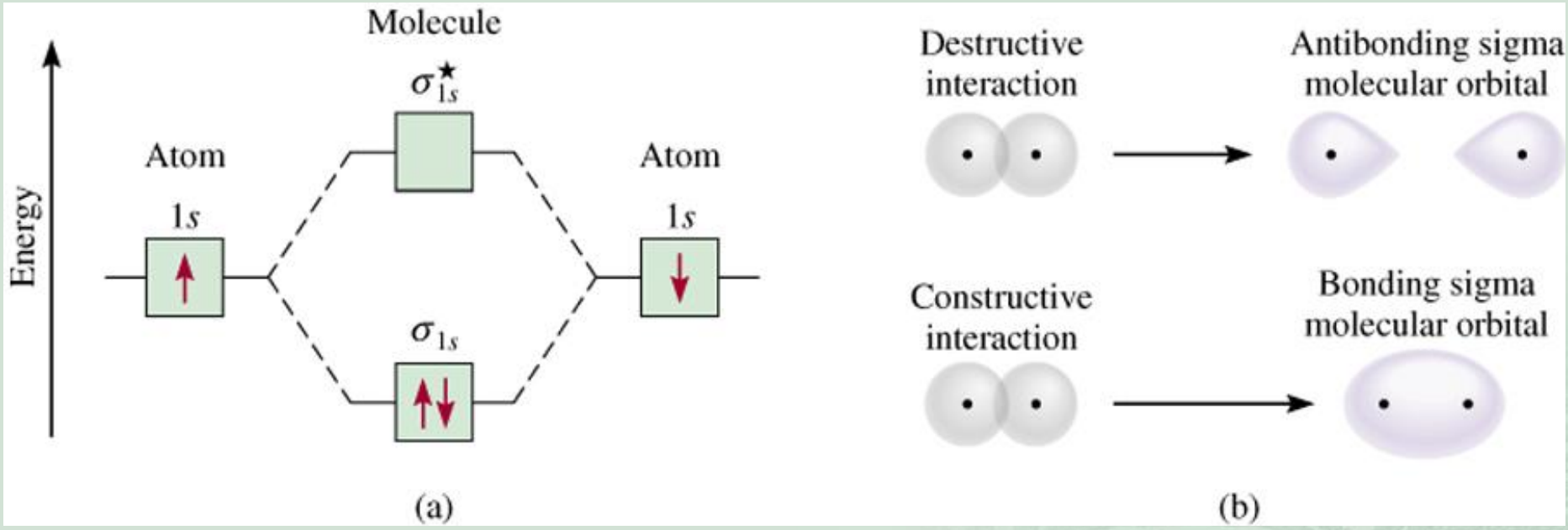


$$H-C\equiv C-H$$



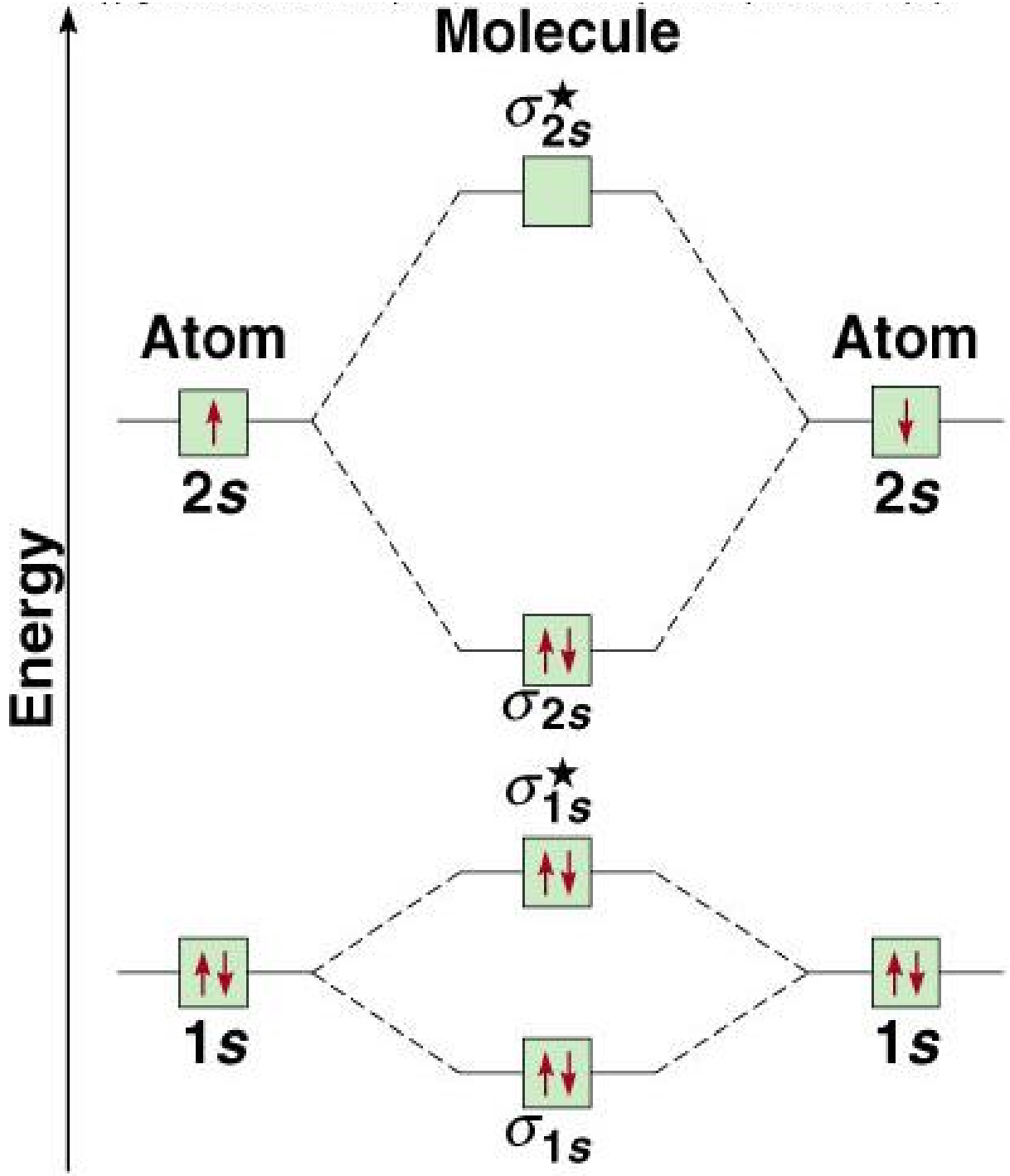


Energy levels of bonding and antibonding **molecular** orbitals in hydrogen (H_2).

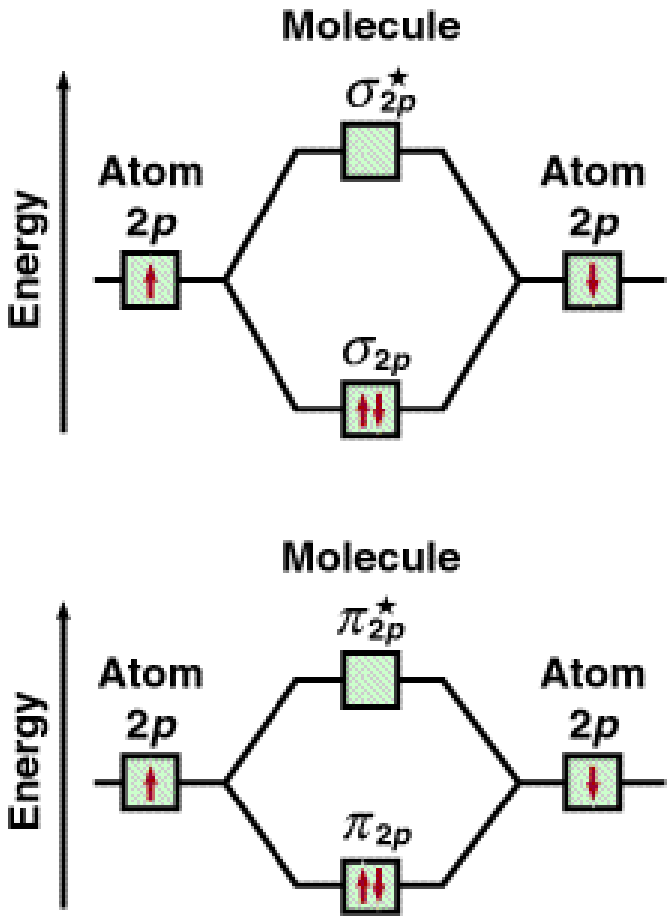


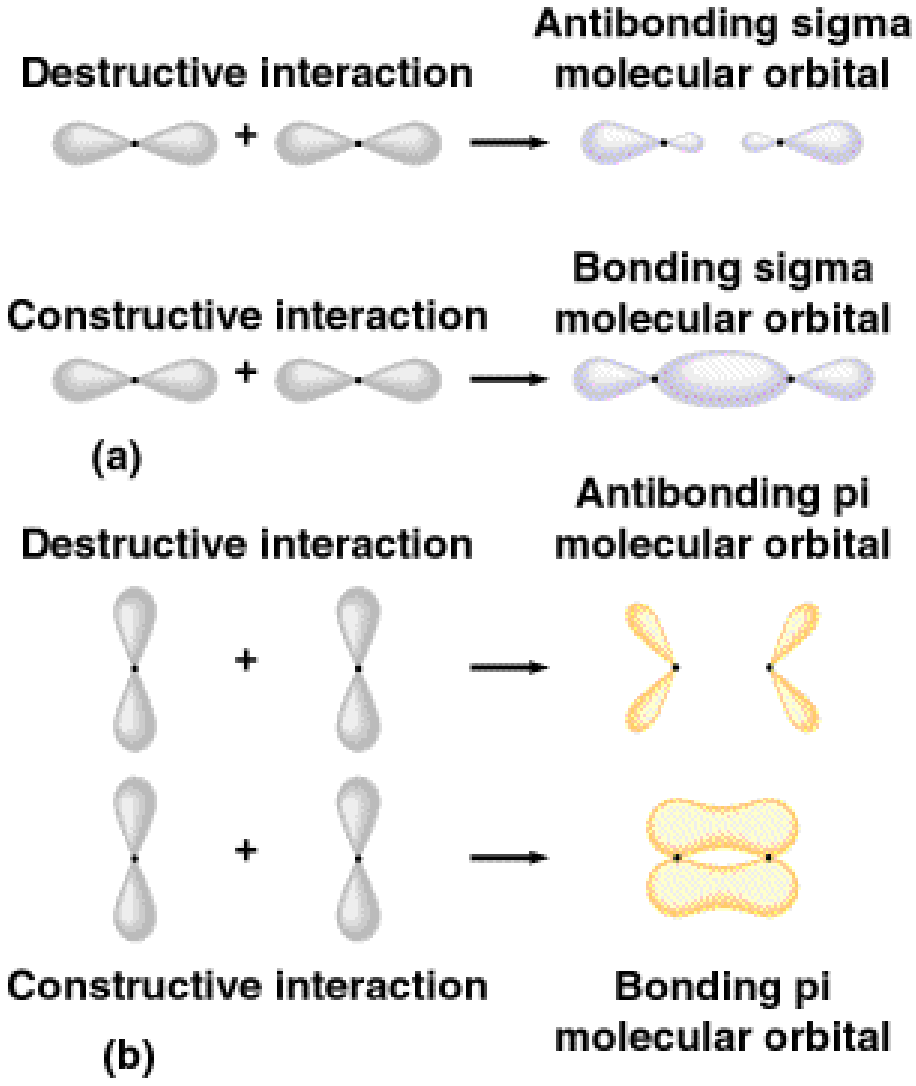
A ***bonding molecular orbital*** has lower energy and greater stability than the atomic orbitals from which it was formed.

An ***antibonding molecular orbital*** has higher energy and lower stability than the atomic orbitals from which it was formed.

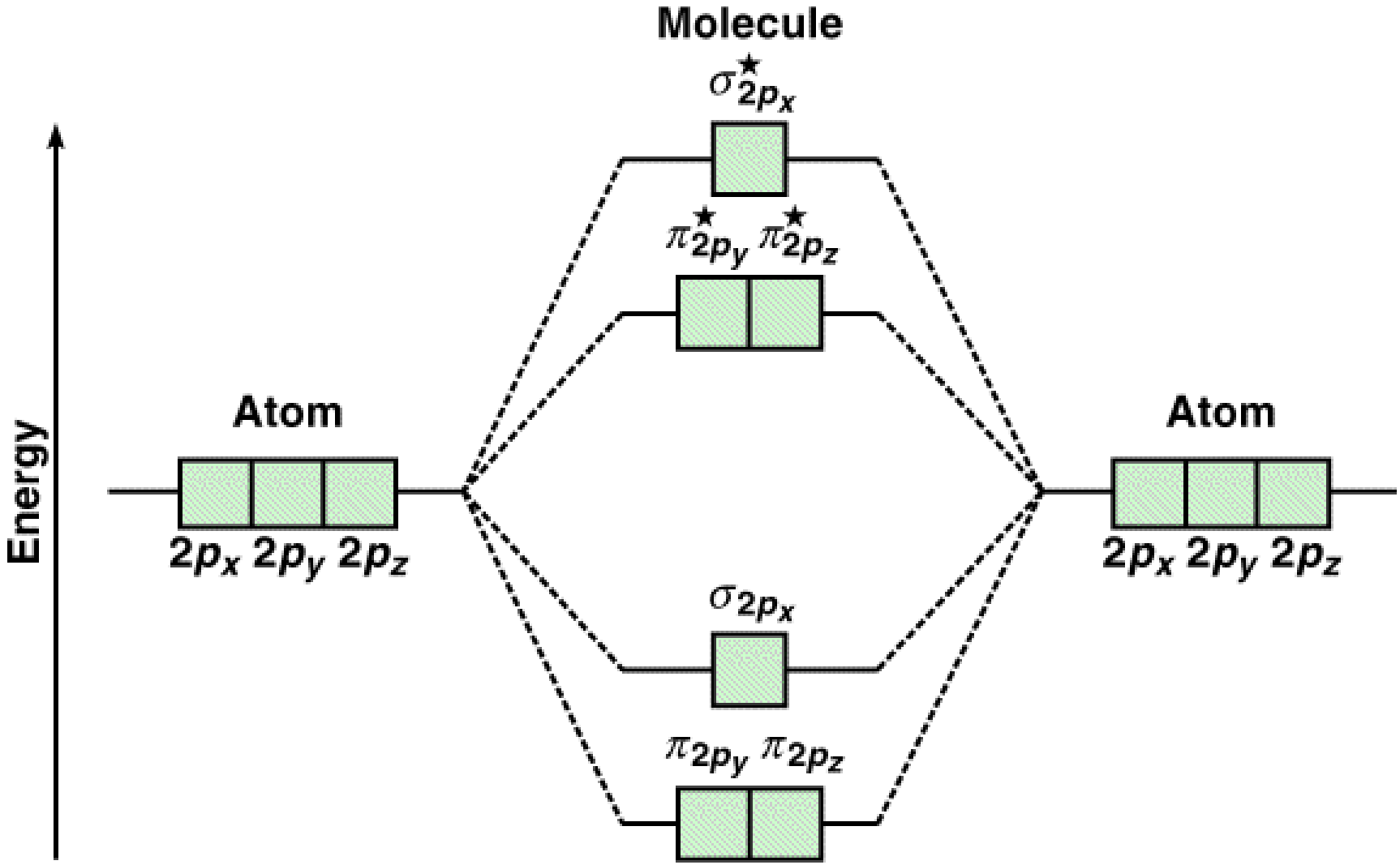

Molecule
$\sigma^{\star}_{2s}$
Atom
Atom
2s
2s
σ_{2s}
$\sigma^{\star}_{1s}$
Energy
1s
1s
σ_{1s}

Two Possible Interactions between Two Equivalent *p* Orbitals and the Corresponding Molecular Orbitals





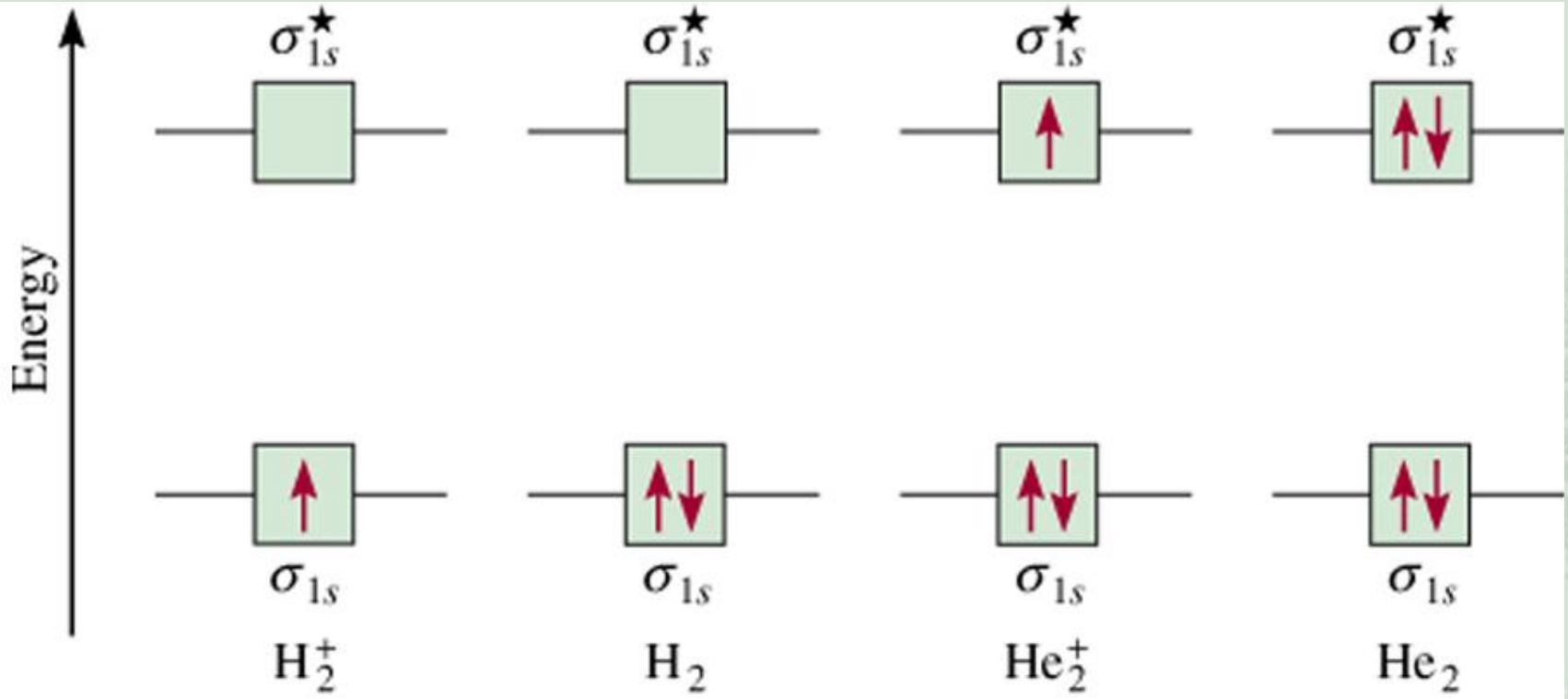
Second-Period Homonuclear Diatomic Molecules Li_2, Be_2, B_2, C_2, and N_2



Molecular Orbital (MO) Configurations

1. The number of molecular orbitals (MOs) formed is always equal to the number of atomic orbitals combined.
2. The more stable the bonding MO, the less stable the corresponding antibonding MO.
3. The filling of MOs proceeds from low to high energies.
4. Each MO can accommodate up to two electrons.
5. Use Hund's rule when adding electrons to MOs of the same energy.
6. The number of electrons in the MOs is equal to the sum of all the electrons on the bonding atoms.

$$\textbf{bond order} = \frac{1}{2}\left(\begin{array}{l}\text{Number of}\\ \text{electrons in}\\ \text{bonding}\\ \text{MOs}\end{array} - \begin{array}{l}\text{Number of}\\ \text{electrons in}\\ \text{antibonding}\\ \text{MOs}\end{array}\right)$$

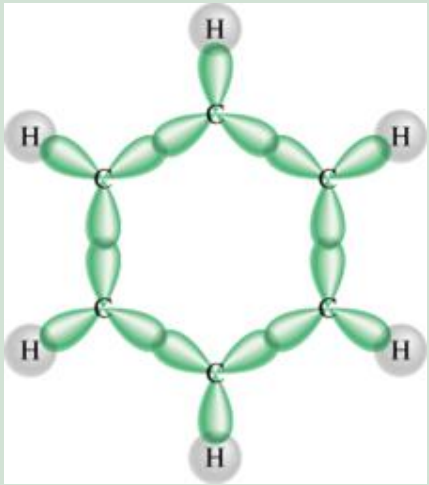


	H_2^+	H_2	He_2^+	He_2
bond order	½	1	½	0

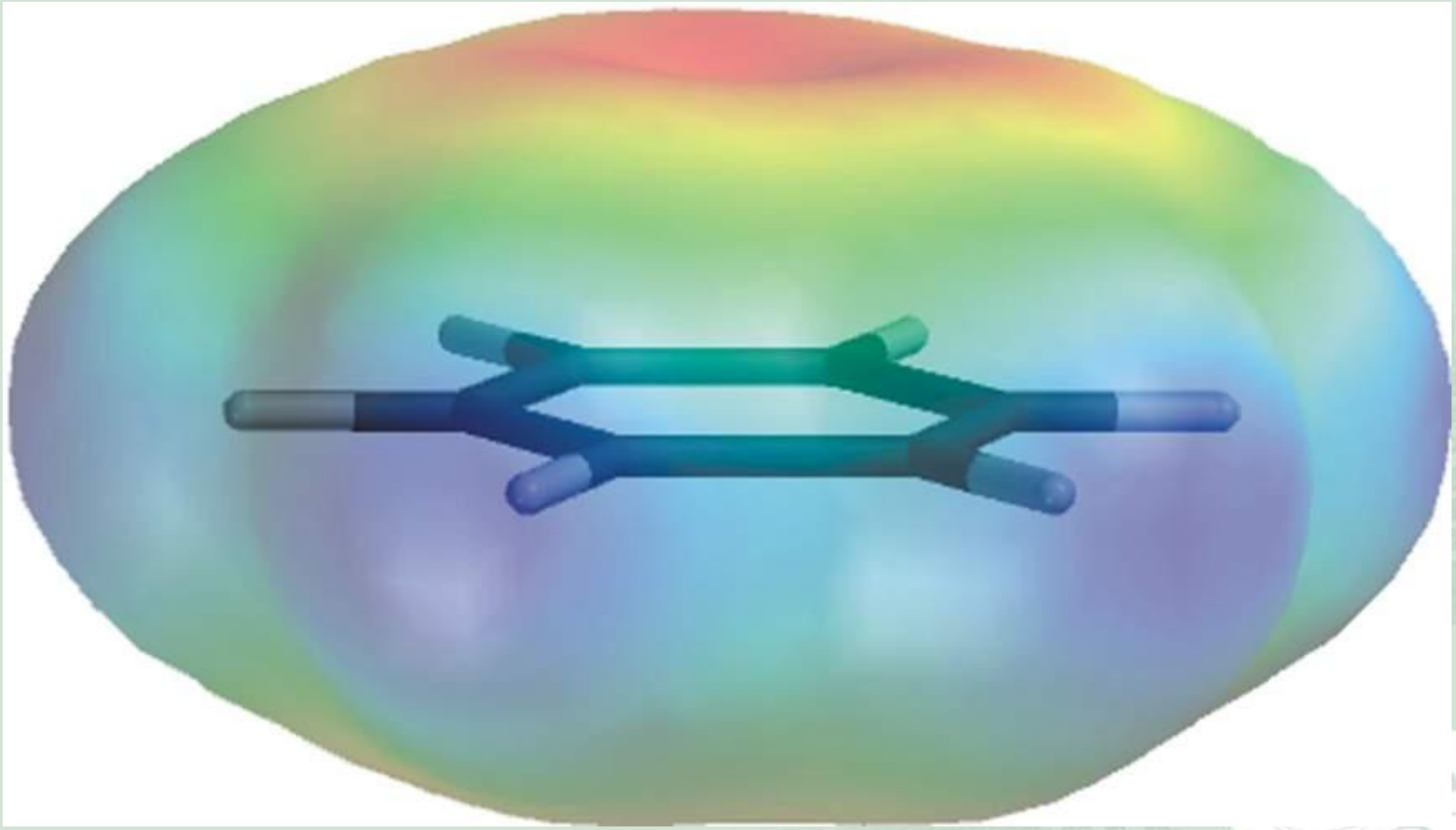
TABLE 10.5 Properties of Homonuclear Diatomic Molecules of the Second-Period Elements*

	Li_2	B_2	C_2	N_2	O_2	F_2	
$\sigma^*_{2p_x}$	☐	☐	☐	☐	☐	☐	$\sigma^*_{2p_x}$
$\pi^*_{2p_y}, \pi^*_{2p_z}$	☐☐	☐☐	☐☐	☐☐	↑↑	↑↓↑↓	$\pi^*_{2p_y}, \pi^*_{2p_z}$
σ_{2p_x}	☐	☐	☐	↑↓	↑↓↑↓	↑↓↑↓	π_{2p_y}, π_{2p_z}
π_{2p_y}, π_{2p_z}	☐☐	↑↑	↑↓↑↓	↑↓↑↓	↑↓	↑↓	σ_{2p_x}
σ^*_{2s}	☐	↑↓	↑↓	↑↓	↑↓	↑↓	σ^*_{2s}
σ_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	σ_{2s}
Bond order	1	1	2	3	2	1	
Bond length (pm)	267	159	131	110	121	142	
Bond energy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9	
Magnetic properties	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	

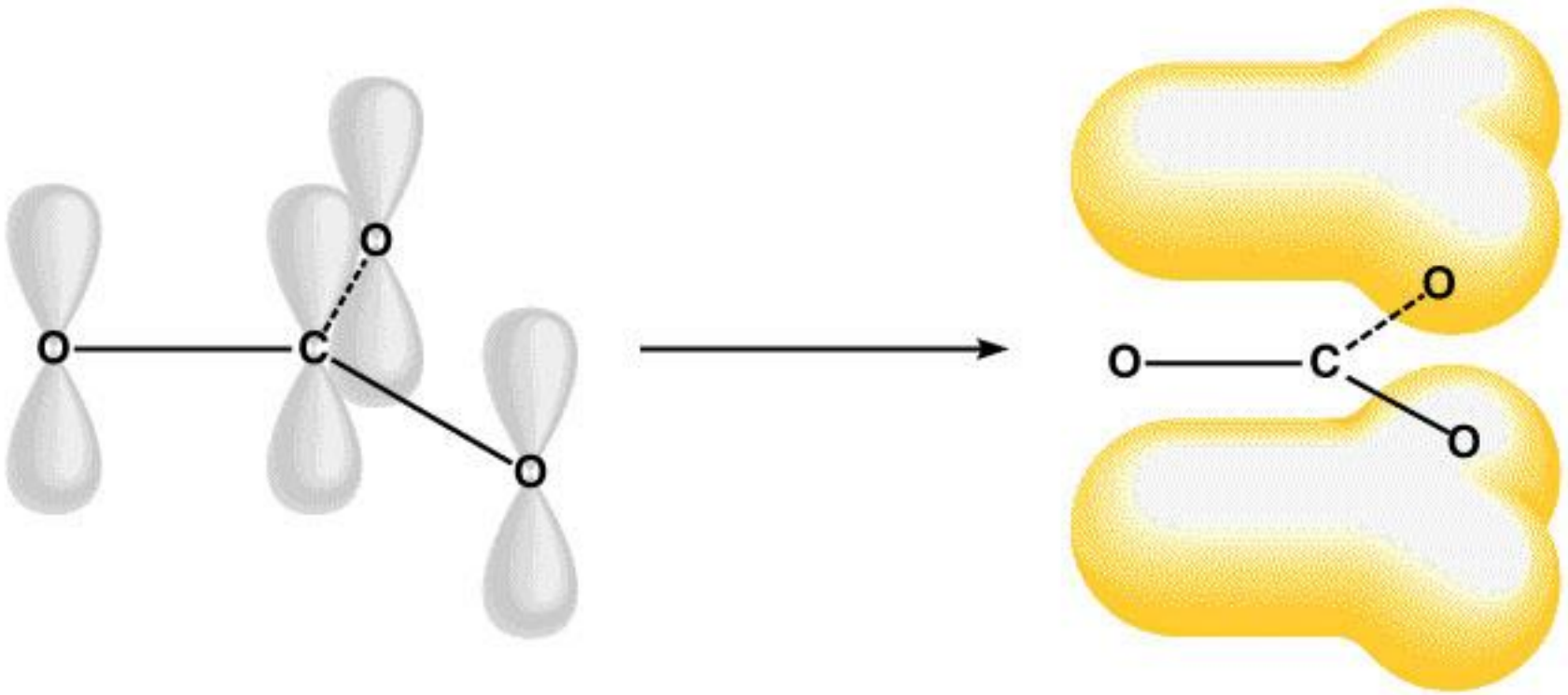
Delocalized molecular orbitals are not confined between two adjacent bonding atoms, but actually extend over three or more atoms.

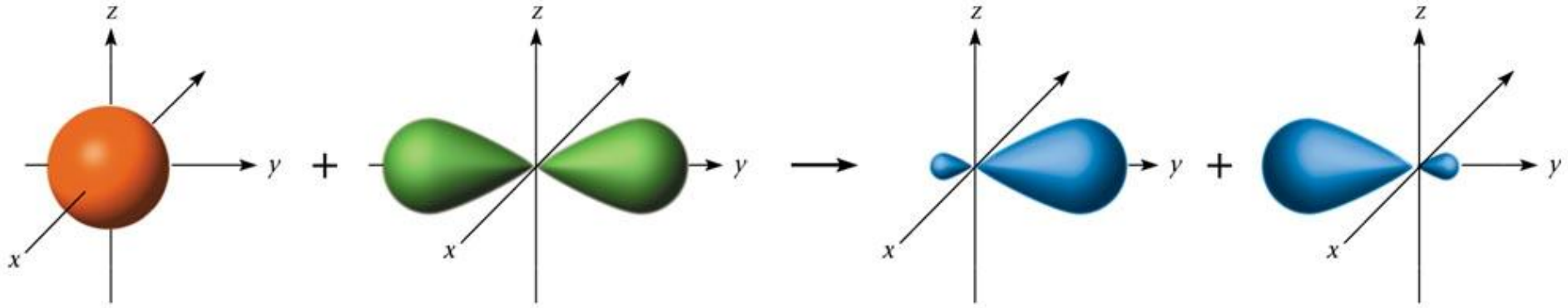


Electron density above and below the plane of the benzene molecule.



Bonding in the Carbonate Ion





s orbital p orbital Two sp orbitals