

7-2: Molecular Geometry 分子幾何結構; 空間立體排列方式

Bond angle 鍵角: the angles between bonds.

Molecular Geometry: base on electron-pair repulsion.

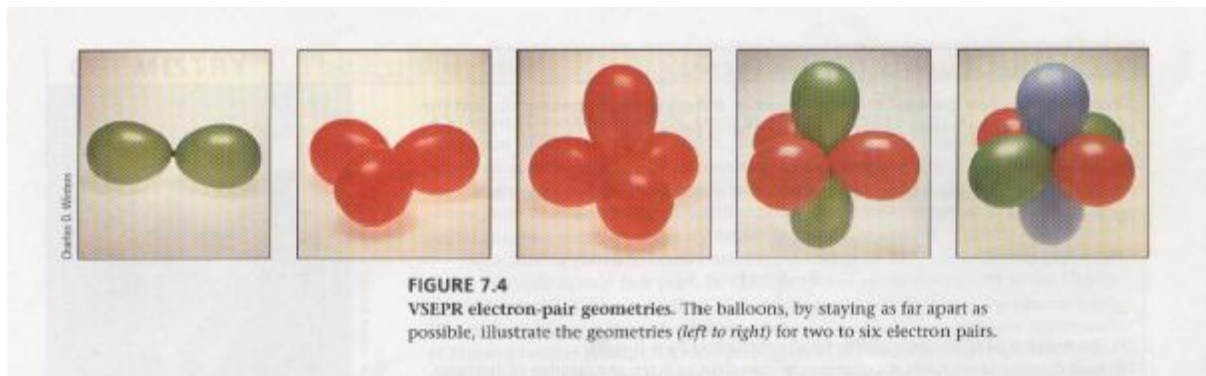


VSEPR model (valence-shell electron-pair repulsion)

By: N.V. Sidgwick, H.M. Powell 1940, R.J. Gillespie and R.S. Nyholm



The valence electron pairs surrounding an atom repel one another. Consequently, the orbitals containing those electron pairs are oriented to be as far apart as possible. ⇒排斥力降至最低.




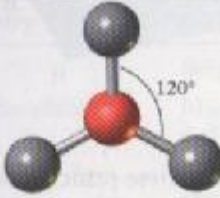
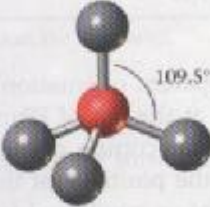
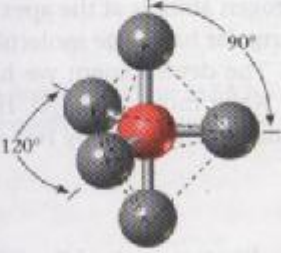
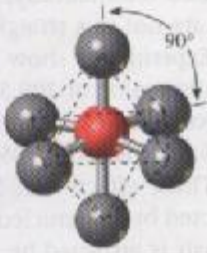
§ Ideal Geometries with two to six electron pairs on the central atom

Central atom: A

Surrounded by from two to six electron pairs.



Fig. 7.5:

Species type	Orientation of electron pairs	Predicted bond angles	Example	Ball and stick model
AX_2	Linear	180°	BeF_2	
AX_3	Triangular planar	120°	BF_3	
AX_4	Tetrahedron	109.5°	CH_4	
AX_5	Triangular bipyramid	90° 120° 180°	PF_5	
AX_6	Octahedron	90° 180°	SF_6	

* central atom 無任何未共用電子對存在

§ Effect of unshared pairs on Molecular Geometry

In many molecules and polyatomic ions, one or more of the electron pairs around the central atom are unshared. :

1. 若全為單鍵 (不含 unshared electron pairs)，則其 electron-pair geometry 與圖 7-5 相似，實際鍵角略小於圖 7-5 之 ideal value.
2. 含一對 or 多對未共用電子對，其 molecular geometry 便大不相同 (Table 7.3).

The positions of the bonded atoms, can be determined experimentally. 而未共用電子對位置卻無法由實驗得知.

↓

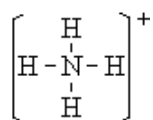
∴無法由分子幾何結構得知未共用電子之位置.

Table 7.3 AX_2 , AX_3 , AX_4 之 Geometries

X : No. of terminal atoms E : unshared pairs

X + E	Type	Ideal bond angles	Molecular geometry	Example
2	AX_2	180°	Linear	BeF_2 , CO_2
3	AX_3	120°	Triangular planar	BeF_3 , SO_3
	AX_2E_1	< 120°	Bent	GeF_2 , SO_2
4	AX_4	109.5°	Tetrahedron 正四面體	CH_4
	AX_3E_1	< 109.5°	Triangular pyramid 三角錐	NH_3
	AX_2E_2	< 109.5°	bent	H_2O

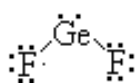
Ex 7-5: Predict the Geometry of



AX_4

鍵角 109.5°

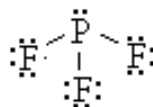
正四面體



AX_2E_1

< 120°

彎曲







AX_3E_1

< 109.5°

三角錐

5 ELECTRON PAIRS

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

6 ELECTRON PAIRS




AX_6		Octahedral	SF_6	$90^\circ, 180^\circ$
AX_5E		Square pyramidal	ClF_5	$90^\circ, 180^\circ$
AX_4E_2		Square planar	XeF_4	$90^\circ, 180^\circ$

FIGURE 7.8

Molecular geometries for molecules with expanded octets and unshared electron pairs. The gray spheres represent terminal atoms (X), and the open ellipses represent unshared electron pairs (E). For example, AX_4E represents a molecule in which the central atom is surrounded by four covalent bonds and one unshared electron pair. **OH!**

§ Multiple Bonds 多重鍵; 對 molecular geometry 無影響

The electron pairs in a multiple bond must occupy the same region of space as those in a single bond. Hence the “extra” electron pairs in a multiple bond have no effect on geometry.

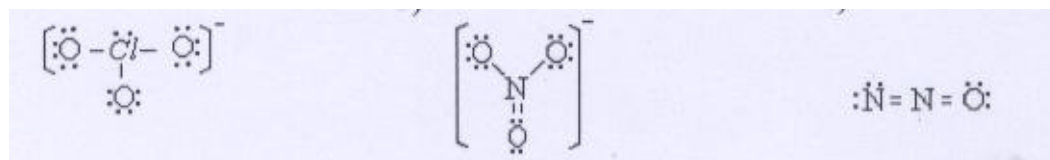


Ex 7-6: Predict the geometries of the ClO_3^- ion, the NO_3^- ion, and the N_2O molecule, Which have the Lewis structure

a)

b)

c)



三角錐

正三角形

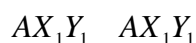
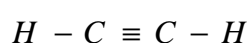
線型

$< 109.5^\circ$

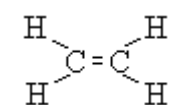
120°

180°

參鍵：



\curvearrowright 180° 線性



$AX_2Y_1 \quad AX_2Y_1$ 鍵角 120° ，正三角形

§7-3: Polarity of molecules

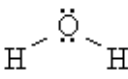
- I Polar: As a result of an **dissymmetrical distribution of electrons**, the bond or molecule contains a positive and a negative pole and is therefore a dipole. 電子對共用不均勻.
- I Nonpolar: A **symmetrical distribution of electrons** leads to a bond or molecule with no positive or negative poles. 電子對共用均勻.

H_2, F_2 nonpolar $\Delta EN = 0$ $m = 0$ $m = q \cdot d$ m : dipole moment; 偶極距
 HF polar $\Delta EN = 1.8$ $m \neq 0$ q : charge
 d : distance

§ Polar and nonpolar covalent bonds

非極性分子：
 AX_2 線性
 AX_3 平面三角形 **X 均為同種原子**
 AX_4 正四面體

BeF_2 F-Be-F AX_2 $m = 0$ 左、右相抵 \therefore 非極性

H_2O  AX_2E_2 彎曲 $m \neq 0$ \therefore 極性

結構不對稱，極性無法相消

CCl_4  AX_4 正四面體 $m = 0$ \therefore 非極性

$CHCl_3$  AX_3Y_1 正四面體 $m \neq 0$ \therefore 極性

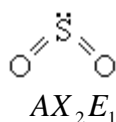
極性判定:

1. bond-polarity
2. molecular geometry

If the polar A-X ($\Delta EN \neq 0$) bonds in a molecule AX_mE_n are arranged symmetrically around the central atom A, the molecule is nonpolar.

Ex 7-7. Determine polar or nonpolar

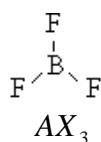
a) SO_2



彎曲 $m \neq 0$

極性

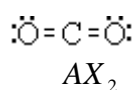
b) BF_3



正三角形 $m = 0$

非極性

c) CO_2



線性 $m = 0$

非極性

• AX_2 CO_2

AX_3 且 X 均為同種原子 nonpolar 例 BF_3

AX_4 CCl_4

若 X 出現不同種原子則為 polar; 例:

$CHCl_3$

• AX_2E SO_2 bent

AX_3E polar 例 NH_3 三角錐

AX_2E_2 H_2O bent

Ex 7-8. For each of the species in column A, choose the description in column B that best applies.

A

B

a) CO_2

e) polar, bent

b) CH_2Cl_2

f) nonpolar, triangular planar

c) XeF_2

g) nonpolar, linear

d) BF_3

h) nonpolar, triangular pyramid

i) polar, tetrahedral

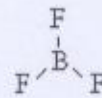
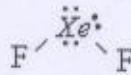
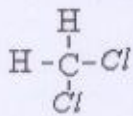
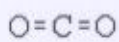
j) polar, triangular pyramid

a) CO_2

b) CH_2Cl_2

c) XeF_2

d) BF_3



$AX_2; m=0$

$AX_2Y_2; m \neq 0$

$AX_2E_3; m=0$

$AX_3; m=0$

linear

正四面體

linear

平面三角形

(g)

(i)

(g)

(f)

→ fig 7.8

§ 7-4. Atomic Orbitals: Hybridization

§ 1930 Linus Pauling: valence bond model

1954 Nobel prize. (chemistry)

1962 Nobel peace prize

↓

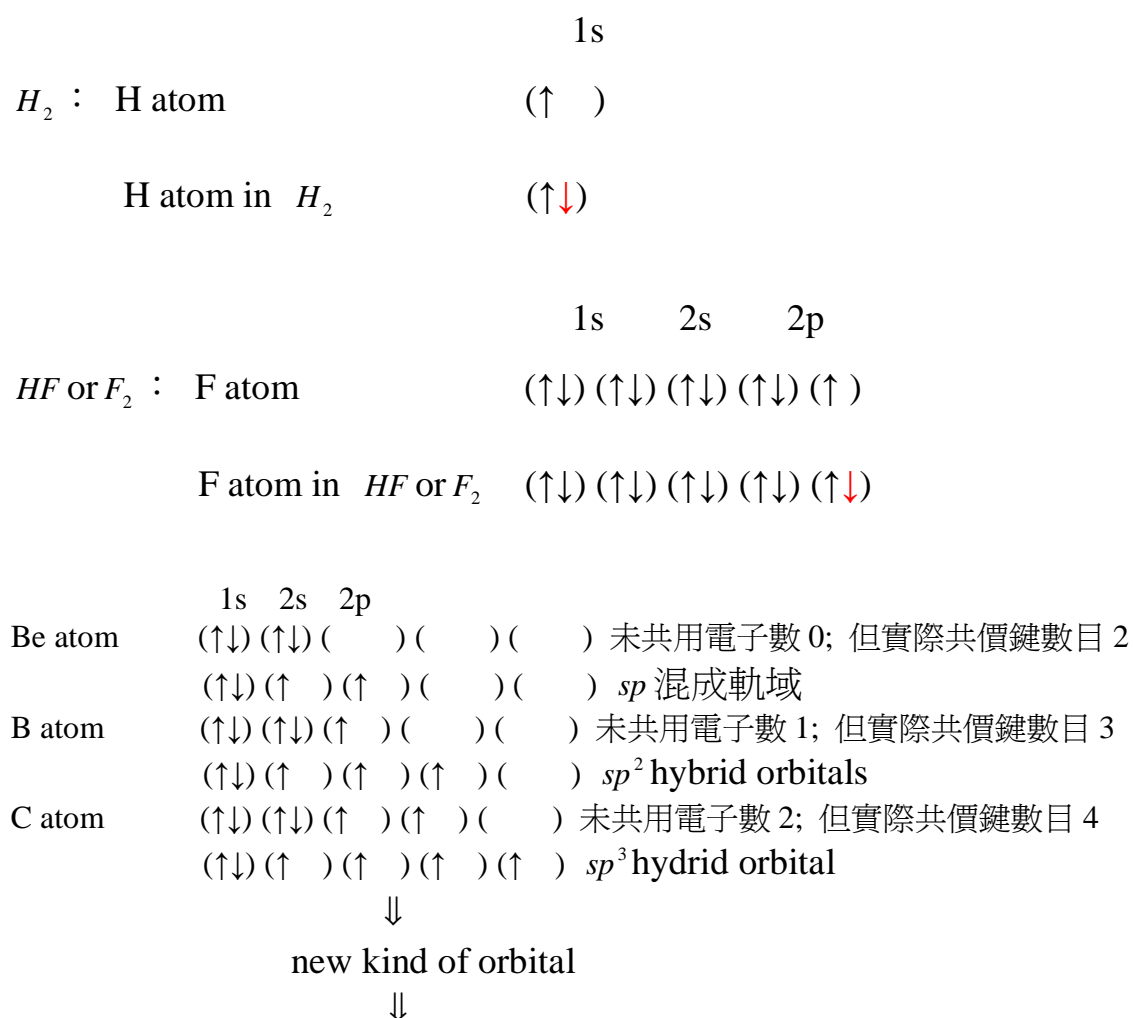
價電子

↓

共用電子對

↓

共價鍵 (一對相反自旋的電子在軌域中)



hybrid orbital 混成軌域

§ Hybrid orbitals : sp , sp^2 , sp^3 , sp^3d , sp^3d^2

1s 2s 2p

BeF_2 中之 Be : $(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\)(\) \Rightarrow$ two sp 混成軌域

s p atomic orbital atomic orbital
1s 2s 2p

BF_3 中之 B $(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\) \Rightarrow$ three sp^2 hybrid orbitals

1s 2s 2p

CH_4 中之 C $(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow) \Rightarrow$ four sp^3 hybrid orbital

unshared as well as shared electron pairs can be located in hybrid orbitals.

Expanded octet : accommodate the extra electron pairs on d orbitals.

PCl_5 :

1 s orbital + 3 p orbitals + **1 d orbitals** \rightarrow sp^3d hybrid orbitals

SF_6 :

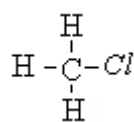
1 s orbital + 3 p orbitals + **2 d orbitals** \rightarrow sp^3d^2 hybrid orbitals

- **the number of hybrid orbitals formed = the number of atomic orbitals mixed.**
- 利用量子力學計算得知之混成較域與 VSEPR 預測結果一致

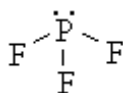
Table 7.4

No. of electron pairs	Atomic orbitals	Hybrid orbitals	Orientation	例
2	1s, 1p	sp	Linear	BeF_2 , CO_2
3	1s, 2p	sp^2	平面三角 形	BeF_3 , SO_3
4	1s, 3p	sp^3	正四面體	CH_4 , NH_3 , H_2O
5	1s, 3p, 1d	sp^3d	雙三角錐	PCl_5 , $:\ddot{Cl}F_3$, $\ddot{S}F_4$
6	1s, 3p, 2d	sp^3d^2	八面體	SF_6 , $\ddot{Cl}F_5$, $\ddot{Xe}F_4$

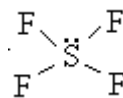
Ex7.9: Give the hybridization of

a) CH_3Cl  AX_3Y sp^3

正四面體

 109.5° b) PH_3  AX_3E sp^3

三角錐

 109.5° c) SF_4  AX_4E fig 7.8 sp^3d

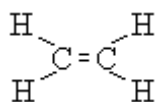
seesaw 蹺蹺板

 $90^\circ; 120^\circ; 180^\circ$

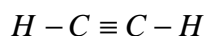
§ Multiple bonds:

The extra electron pairs in a double or triple bond **have no effect** on the geometry of the molecule.

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



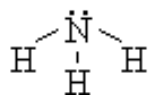
sp^2



sp

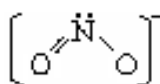
— : hybrid orbital

Ex 7-10: State the hybridization of nitrogen in



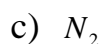
AX_3E_1

sp^3



AX_2E_1

sp^2



$:\text{N} \equiv \text{N}:$

AXE_1

sp

§ Sigma and Pi Bonds

s

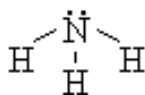
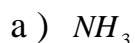
p

Single bond = 1 s bond

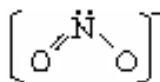
Double bond = 1 s bond + 1 p bond

Triple bond = 1 s bond + 2 p bond

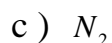
Ex 7-11: Give the number of p bond and s bond in



3 s bond



2 s bond + 1 p bond



$:\text{N} \equiv \text{N}:$

1 s bond + 2 p bond