Ch. 7 Covalent Bonding

7-1: Lewis structures; The Octet Rule

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Ch.7 Covalent Bonding

Covalent bond:

The forces that hold nonmetal atoms to one another. These bonds consist of an electron pair shared between two atoms.

H:H or H-H

Fig 7.1： H_2 電子密度 ⇒ 實際鍵結方式

電子隨時出現在 2 個 H 原子之間，而非固定出現在某一區域.

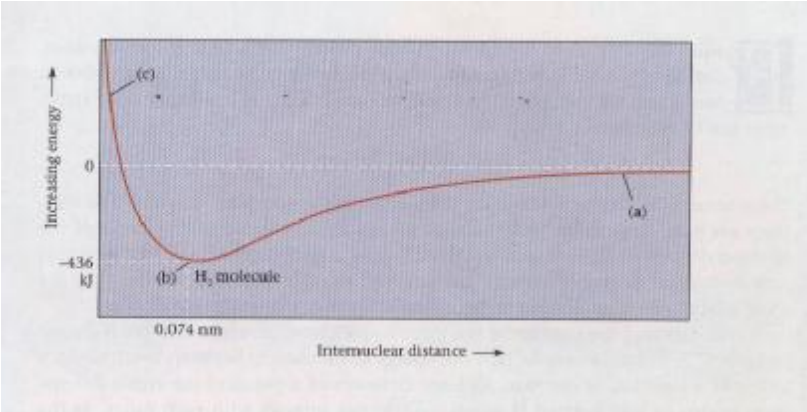
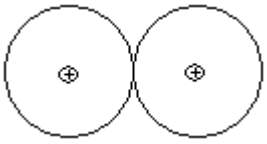


Fig. 7.2: Energy of two hydrogen atoms as a function of the distance between their nuclei.

1.  H_2 ：電子介於 2 個質子間，電子與質子間之吸引力大於電子與電子，質子與質子間之斥力.
2. 二個 H 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原子上.

§ 7–1 Lewis Structures: The Octet rule

Lewis： nonmetal atoms by sharing electrons to form an electron-pair bond, can acquire a stable noble-gas structure.

H· + ·H ⟶ H:H H-H

H· + ·F: ⟶ H:F: H-F:

valence electrons 價電子： ·F: $1s^2\ 2s^2 2p^5$ → outermost electrons; 價電子數: 7.

H:F: F atom surrounded by eight valence electrons

$1s^2\ 2s^2 2p^6$ ⇒ noble gas ⇒ Ne

∴ HF 而非 H_2F; H_3F.
└→安定 └→不安定

Lewis structure：

Only the valence electrons are shown.

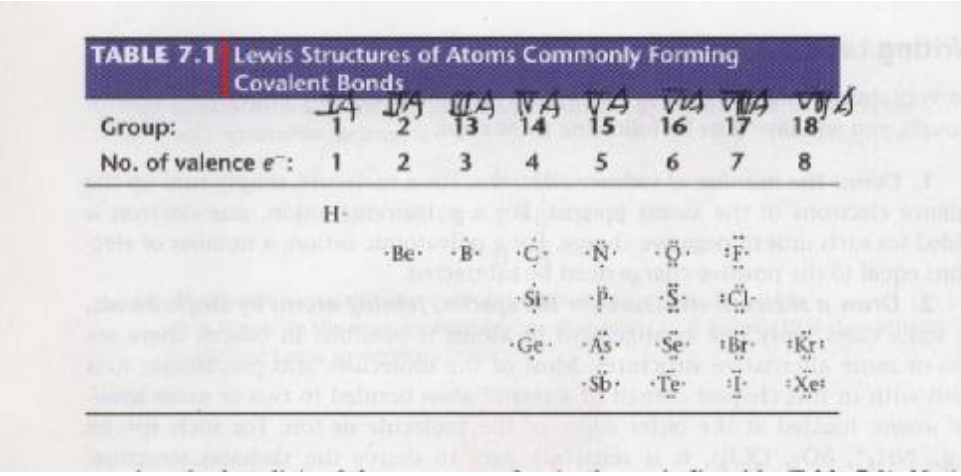


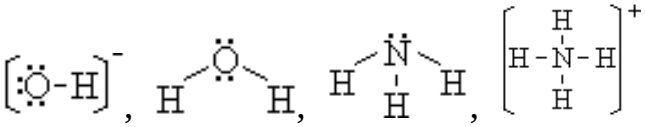
TABLE 7.1 Lewis Structures of Atoms Commonly Forming Covalent Bonds

Group:	1	2	13	14	15	16	17	18
No. of valence e^-:	1	2	3	4	5	6	7	8
	H·							
		·Be·	·B·	·C·	·N·	·O·	·F·	
				·Si·	·P·	·S·	·Cl·	
				·Ge·	·As·	·Se·	·Br·	·Kr·
					·Sb·	·Te·	·I·	·Xe·

In the Lewis structure, there are two kinds of electron pairs.

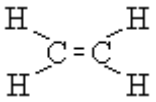
1. A pair of electrons shared between two atoms. ⇒ covalvent bond.
   Shown as a straight line between bonded atoms.
2. Unshared pair of electros owned entirely by one atom. ⇒
   Shown as a pair of dots on that atom.

OH^-, H_2O, NH_3, NH_4^+之 Lewis structure



double bond：atoms share two pairs of electrons.

triple bond：atoms share three pairs of electrons.

C_2H_4  C_2H_2 $H-C\equiv C-H$

Octet rule 八隅體：

Atoms in covalently bonded species tend to have noble-gas electronic structures.

Writing Lewis Structures

1. Count the number of valence electrons
   Anion (陰離子)：一個負電，增加一個價電子數
   Cation (陽離子)：一個正電，減少一個價電子數

2. Draw a skeleton structure for the species, joint atoms by single bonds.

一般多原子化合物中之第一個原子爲 central atom, 與其他原子以單鍵鍵結.

例 NH_4^+ N

SO_2 S 爲 central atom.

CCl_4 C

3. Determine the number of valence electrons still available for distribution, 每一對共用電子對”減 2”

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

   a) 若 step 3 與 step 4 之計算值相同⇒ ok 單鍵結構

   b) 若 step 4 之計算值較 step 3 大 2 ⇒ 結構中含雙鍵

   大 4 ⇒ 含 2 個雙鍵 or 1 個參鍵

Multiple bond formation is pretty limited to the four atoms：C, N, O and S.

Ex 7-1: Draw Lewis structures of

a) OCl^- hypochlorite ion (次氯酸根離子)

b) C_2H_6 ethane

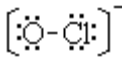
Ans:

a) Step 1 價電子數：6 + 7 + 1 = 14

Step 2 $[O-Cl]^-$

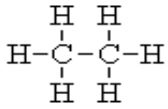
Step 3 可供分配電子數 14 – 1 × 2 = 12

Step 4 滿足八隅體所電子數 6 + 6 = 12

∴ 

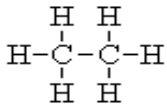
b) Step 1 價電子數 2 × 4 + 6 × 1 = 14

Step2



Step 3 可供分配電子數 14 – 7 × 2 = 0

Step 4 滿足八隅體所需電子數 0 + 0 = 0

∴ 

Ex 7-2: Draw Lewis structures of

a) SO_2 b) N_2

Ans:

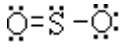
a) Step 1 價電子數 1 × 6 + 2 × 6 = 18

Step 2 $O-S-O$

Step 3 可供分配電子數 18 – 2 × 2 = 14

Step4 滿足八隅體所需電子 6 + 4 + 6 = 16

16 – 14 = 2　　∴ 內含一對雙鍵

∴　 

b) Step 1　價電子數　2 × 5 =10

Step 2　$N - N$

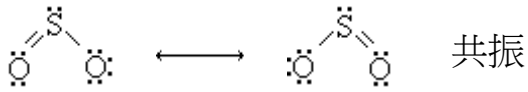
Step 3　可供分配數　10 –　1 × 2　= 8

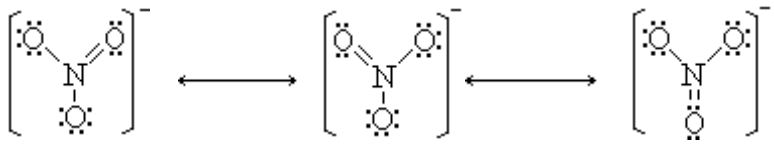
Step 4　滿足八隅體所需電子數　2 × 6 = 12

12 – 8 = 4　　∴ 內含一對參鍵

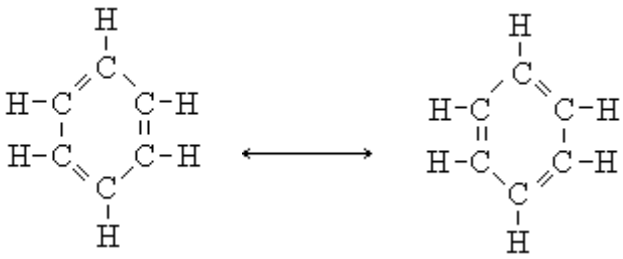
∴　$:N \equiv N:$

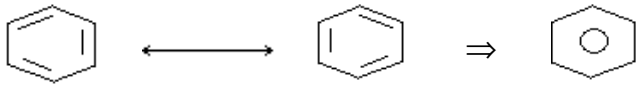
Resonance Forms　共振式

SO_2 ：  　共振

NO_3^- ： 

Benzene：C_6H_6





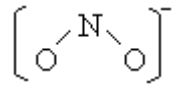
1. 共振式並非不同分子.

2. 共振式是可以劃出2個 or 2個以上 Lewis structure that are about equally plausible.

3. 共振式是電子分布方式不同，而非原子排列不同 (同分異構物).

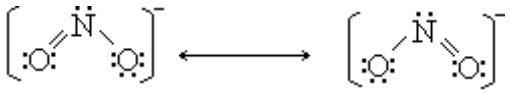
Ex 7.3 Write two resonance structures for the NO_2^- ion.

Step 1 價電子數 $5 + 2 \times 6 + 1 = 18$

Step 2 

Step 3 可供分配之電子數： $18 - 2 \times 2 = 14$

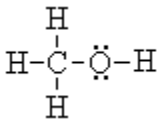
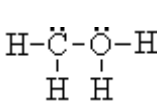
Step 4 滿足八隅體所需之電子數： $4 + 6 \times 2 = 16$ ∴內含一對雙鍵



§ Formal Charge 形式電荷；可用以判定 Lewis structure 正確與否.

Methyl alcohol CH_4O

Lewis structure：

可寫成  或是  但只有一種正確.

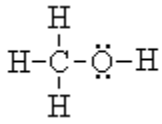
可利用 formal charge 判定何者正確.

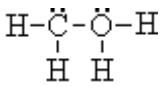
Formal charge (C_f): the difference between the number of valence electrons in the free atom (x) and the number assigned to that atom in Lewis structure (Y + Z/2).

$$C_f = X - (Y + Z/2)$$

X: the number of valence electrons in the free atom, 即所在之 A 族之族數.

Y: the number of unshaired electrons owned by the atom in the Lewis structure.
Z: the number of bonding (shared) electrons owned by the atom in the Lewis structure.





For C： X = 4, Y = 0, Z = 8 For C： X = 4, Y = 2, Z = 6

$C_f = 4 - (0 + {}^{8}\!/_{2}) = 0$ $C_f = 4 - (2 + {}^{6}\!/_{2}) = -1$

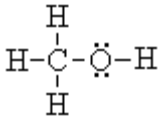
For O： X = 6, Y = 4, Z = 4 For O： X = 6, Y = 2, Z = 6

$C_f = 6 - (4 + {}^{4}\!/_{2}) = 0$ $C_f = 6 - (2 + {}^{6}\!/_{2}) = +1$

如何判定何者正確：

1. formal charge C_f are as close to zero as possible.
2. the negative formal charge is located on the most strongly electronegativity (EN) atom. See P. 156 Table 6-5.

此例中 C：2.5
O：3.5 ⇒ 若C_f出現負值應是 O 而非 C.

∴  爲正確之 Lewis structure

§ Exceptions to the Octet rule：

1. Electron-deficient molecules: 中央原子之外圍電子數 <8

1). Odd electron species (sometimes called free radicals), it is impossible to write Lewis structures.

NO no of valence electrons = 5 + 6 = 11

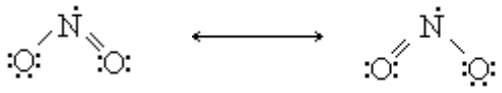
NO_2 no of valence electrons = 5 + 2 × 6 =17

NO ：

 N： $C_f = 5 - (3 + {}^{4}\!/_{2}) = 0$

O： $C_f = 6 - (4 + {}^{4}\!/_{2}) = 0$ ⇒ ok

NO_2 ：



共 17 個電子

N： $C_f = 5 - (1 + \frac{6}{2}) = +1$　N: EN= 3.0

O： $C_f = 6 - (6 + \frac{2}{2}) = -1$　O: EN=3.5

O： $C_f = 6 - (4 + \frac{4}{2}) = 0$

缺電性大者C_f 爲 “－“值 ⇒ ok

2). Central atom violates the octet rule in the sense that it is surrounded by two or three electron pairs rather than four.（central atom is in IIA and IIIA group.）

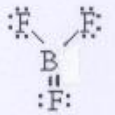
BeF_2 之 Lewis structure： Be: EN= 1.6; F: EN= 4.0

Structure 1　　Structure 2

:F=Be=F: Be： $C_f = 2 - (0 + \frac{8}{2}) = -2$　:F-Be-F: Be： $C_f = 2 - (0 + \frac{4}{2}) = 0$

F： $C_f = 7 - (4 + \frac{4}{2}) = +1$　　F： $C_f = 7 - (6 + \frac{2}{2}) = 0$　ok

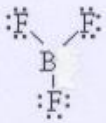
BF_3 之 Lewis structure:　B: EN=2.0



B： $C_f = 3 - (0 + \frac{8}{2}) = -1$

F： $C_f = 7 - (6 + \frac{2}{2}) = 0$

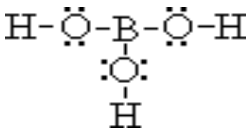
F： $C_f = 7 - (4 + \frac{4}{2}) = +1$



B： $C_f = 3 - (0 + \frac{6}{2}) = 0$

F： $C_f = 7 - (6 + \frac{2}{2}) = 0$　ok

H_3BO_3 boric acid 硼酸



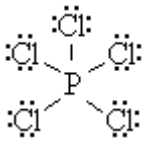
B:　$C_f = 3 - (0 + 6/2) = 0$

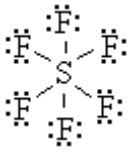
O:　$C_f = 6 - (4 + 4/2) = 0$

H:　$C_f = 1 - (0 + 2/2) = 0$　ok

2. Expanded Octets 中央原子之外圍電子數 > 8

PCl_5： phosphrous pentachloride SF_6： sulfur hexafluoride





中央原子共用超過 4 對共用電子⇒ 不符 Octet rule

此類化合物之：terminal atom 多爲 F，Cl，Br，I 以及少數的 O.

Central atom：第三、四、五週期之 nonmetal

	Group 15	Group 16	Group 17	Group 18
3rd period	**P**	**S**	Cl	
4th period	**As**	**Se**	Br	Kr
5th period	**Sb**	Te	I	**Xe**

4th, 5th period, 6th period elements have d orbitals available for bonding. (3d, 4d and 5d). These are the orbitals in which the extra pairs of electrons are located in those species as PCl_5 and SF_6.
Because there is no 2d sublevel, C, N, and O never form expanded octets.

Distribute the extra electrons (two or four) around the central atom as unshared pairs.

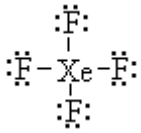
多餘電子對，置於 central atom 旁當做 unshaired electrons. ⇒Ex 7-4.

Ex 7-4: Draw the Lewis structure of XeF_4

Ans: Lewis structure $_{54}Xe$ $_{9}F$

Step 1 價電子數： 8 + 4 × 7 =36

Step 2



Step 3 可供分配之電子數： 36 – 8 = 28

Step 4 滿足八隅體所需之電子： 0 + 4 × 6 = 24

∴ 28 – 24 = 4 多餘電子，而非雙鍵或叁鍵，
多餘電子多以電子對方式置於中央原子上.

⇒