General Chemistry

Chapter 9

Chap 9 Covalent Bonding: Orbitals

9.1 Hybridization and the Localized Electron Model

Recall:

Localized Electron Model: A molecule is composed of atoms that are bound together by using atomic orbitals to share electron pairs

sp³ hybridization:

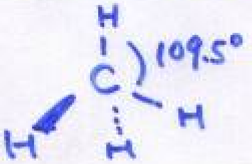
Bonding: involves only the valence orbitals

e.x. CH_4

H: use 1S orbital

C: valence orbitals: 2S, 2p

Recall VSEPR model



S orbital: 球狀

P orbitals: 啞鈴狀

↓ hybridization

sp³ hybridization

(see page 415 Fig 9-3)

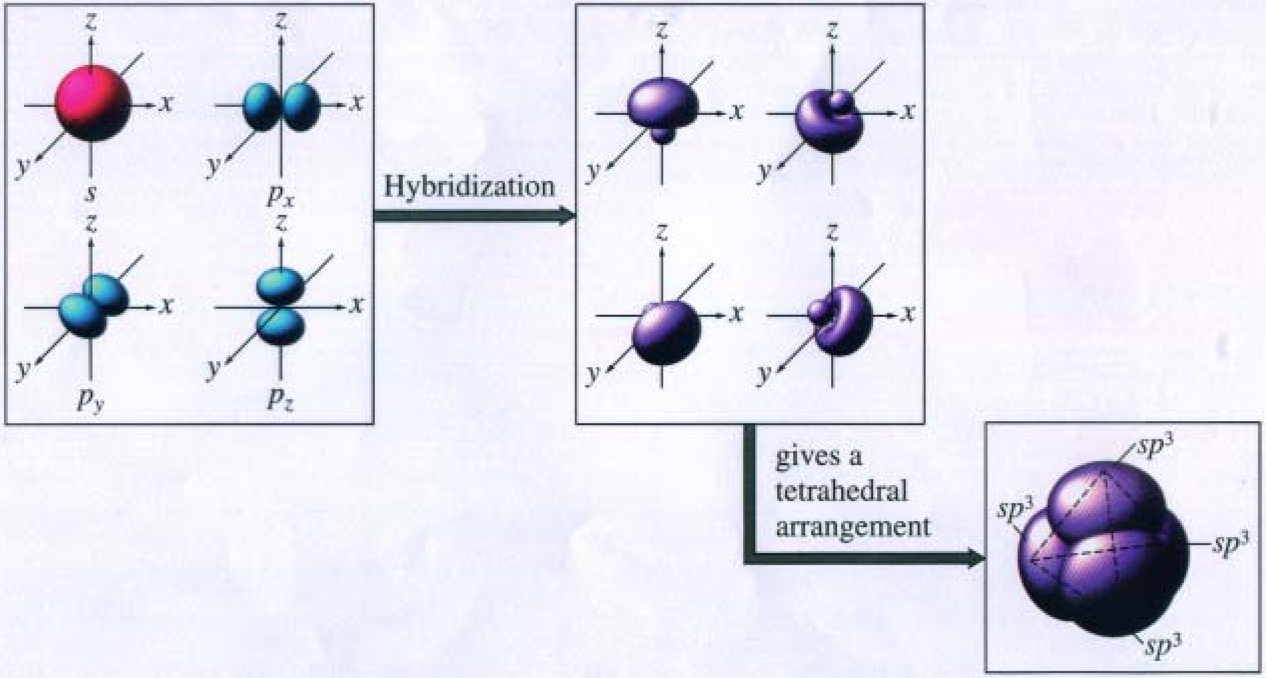


Figure 9.3

The formation of sp^3 hybrid orbitals

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sp^3 hybrid orbitals :

$$\phi_1 = \frac{1}{2}[(s) + (P_x) + (P_y) + (P_z)]$$
$$\phi_2 = \frac{1}{2}[(s) + (P_x) - (P_y) - (P_z)]$$
$$\phi_3 = \frac{1}{2}[(s) - (P_x) + (P_y) - (P_z)]$$
$$\phi_4 = \frac{1}{2}[(s) - (P_x) - (P_y) + (P_z)]$$

(s) : 2s atomic orbital function

(p) : 2p atomic orbital functions

$\frac{1}{2}$: 为了 satisfy boundary condition
(total probability = 1 for each orbital)

$\phi_1, \phi_2, \phi_3, \phi_4$: represents a separate
sp^3 hybrid orbital

如以 energy levels 来表现

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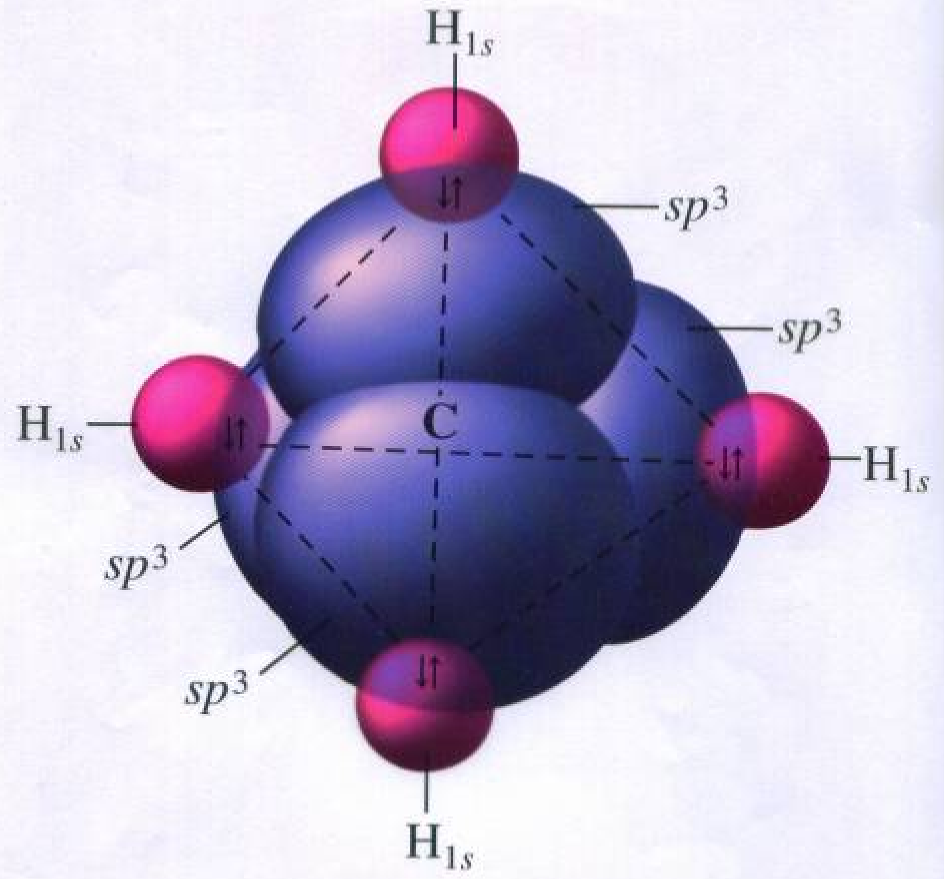


Figure 9.6

The orbitals in CH_4

Whenever a set of equivalent, tetrahedral atomic orbitals is required by an atom, this model assumes that the atom forms a set of sp^3 orbitals; the atom becomes sp^3 hybridized. 9-5

Ex. 9-1 NH$_3$

Sol: the lewis structure of NH$_3$ is

Sp^3 hybridized orbitals (see Fig 9-7

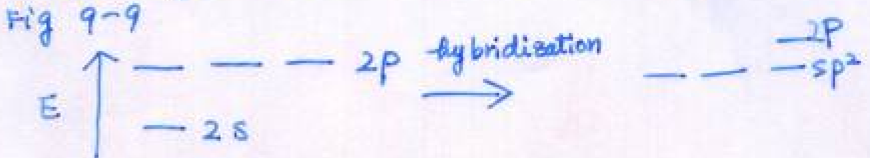
sp^2 Hybridization

C$_2$H$_4$

planar molecule

Sp^2 hybridization ! (see Fig 9-8)

Fig 9-9



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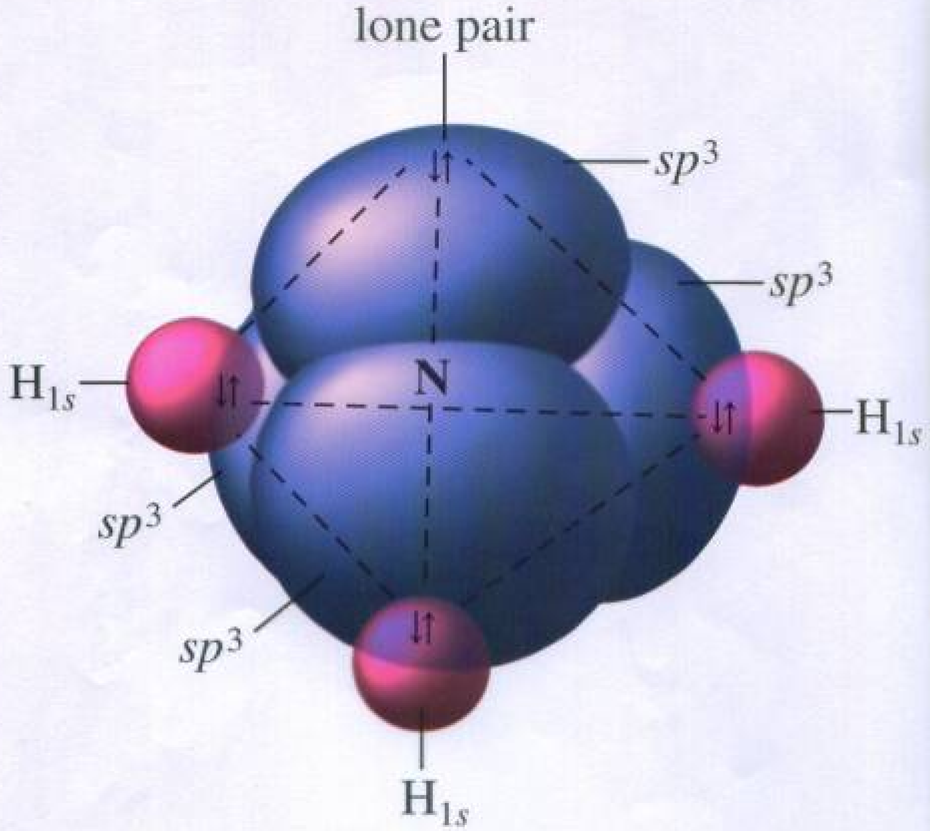

Figure 9.7

The orbitals in NH_3

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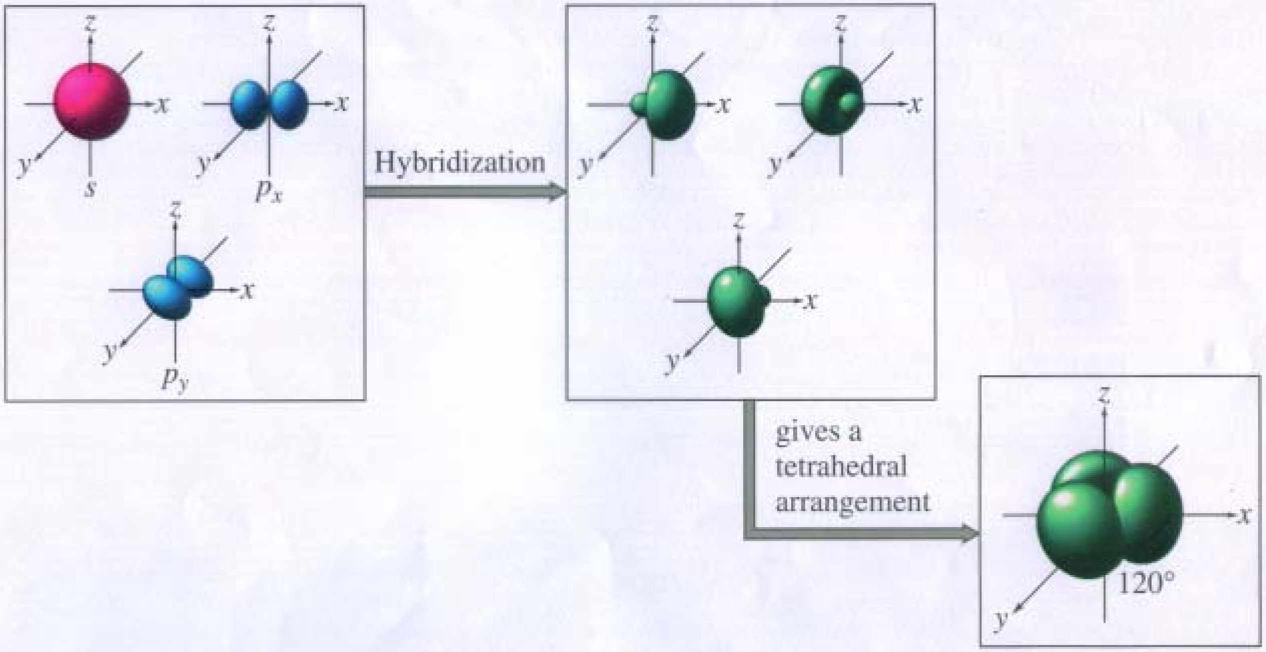

Figure 9.8

The formation of sp^2 hybrid orbitals

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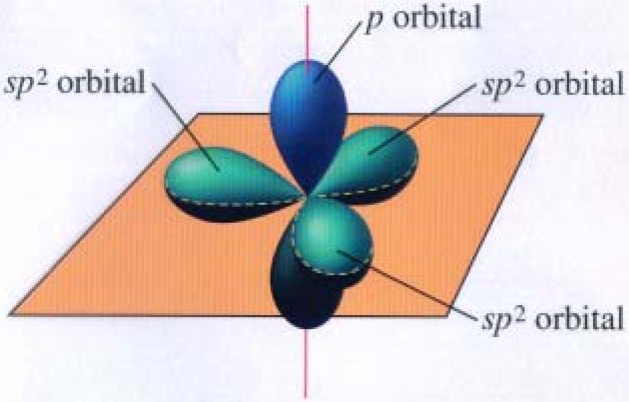

Figure 9.10

An sp^2 hybridized C atom

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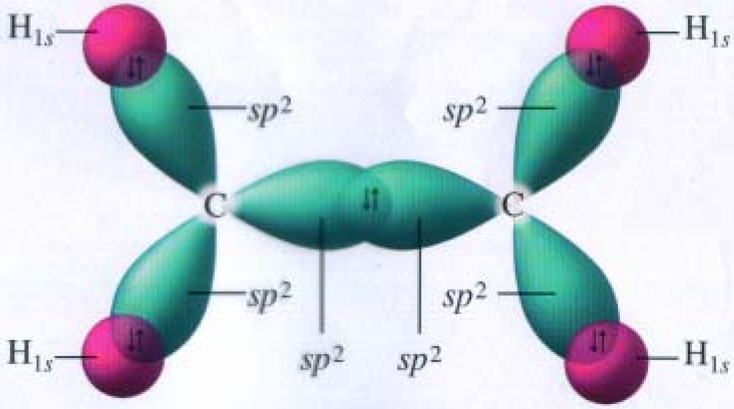

the electron pair is shared in an area centered on a line running between the atoms

: ~~cova~~ sigma bond (σ)

Figure 9.11

Sigma bonding in C_2H_4

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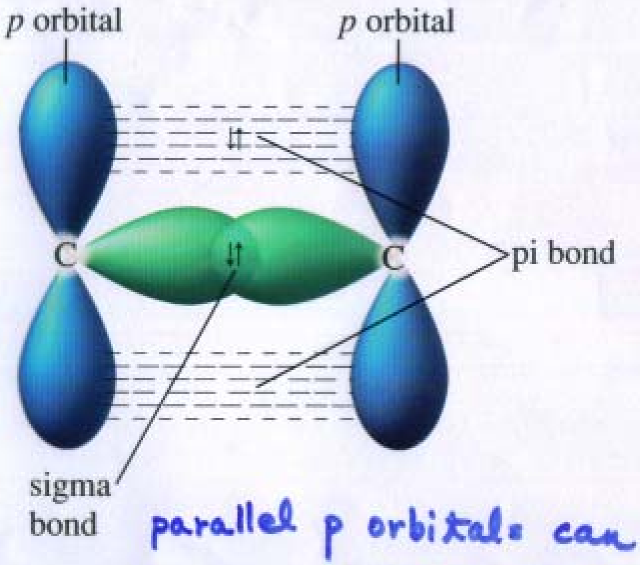

parallel p orbitals can share an electron pair, which occupies the space above and below a line joining the atoms →

to form a pi (π) bond

Figure 9.12

Sigma and pi bonding

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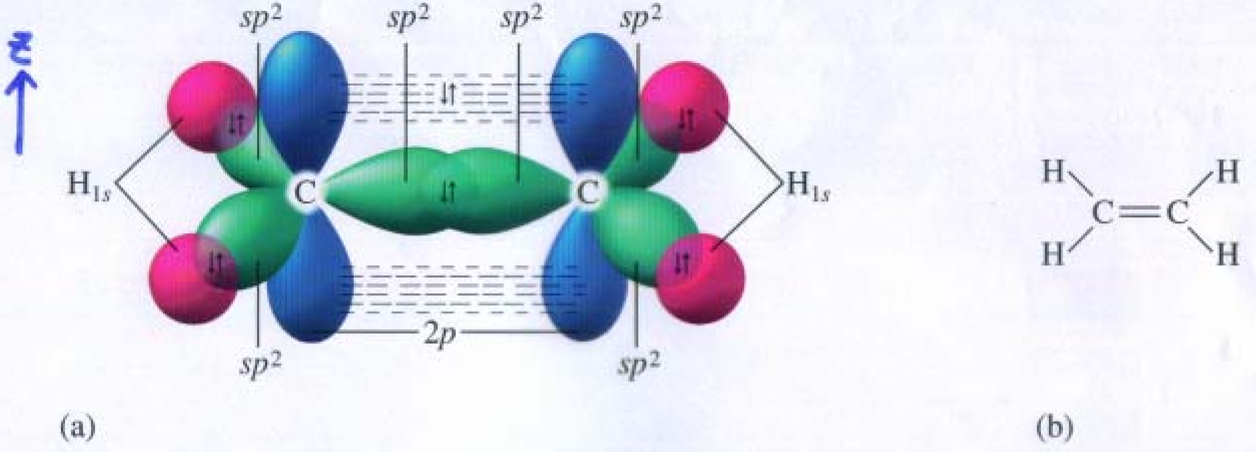

(a)

(b)

Figure 9.13

The orbitals for C_2H_4

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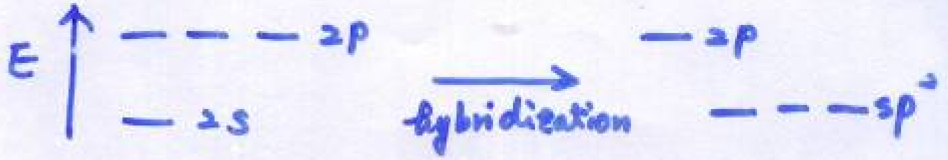

σ bonds: formed from orbitals whose lobes point toward each other.

π bonds: formed from parallel orbitals

(e.g. p_z p_z
(carbon 1) (carbon 2)

A double bond consists of: one σ bond and one π bond

Whenever an atom is surrounded by three effective pairs, a set of sp^2 hybrid orbitals is required.

---

sp Hybridization

CO_2: $:\ddot{O}=C=\ddot{O}:$ 180°

sp hybridization (see Fig 9-14)

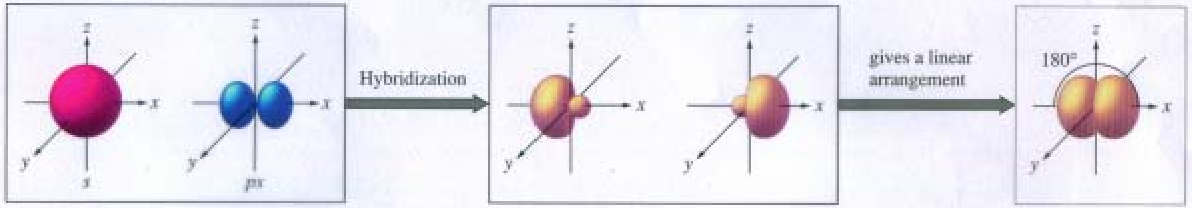

Figure 9.14

The formation of *sp* hybrid orbitals

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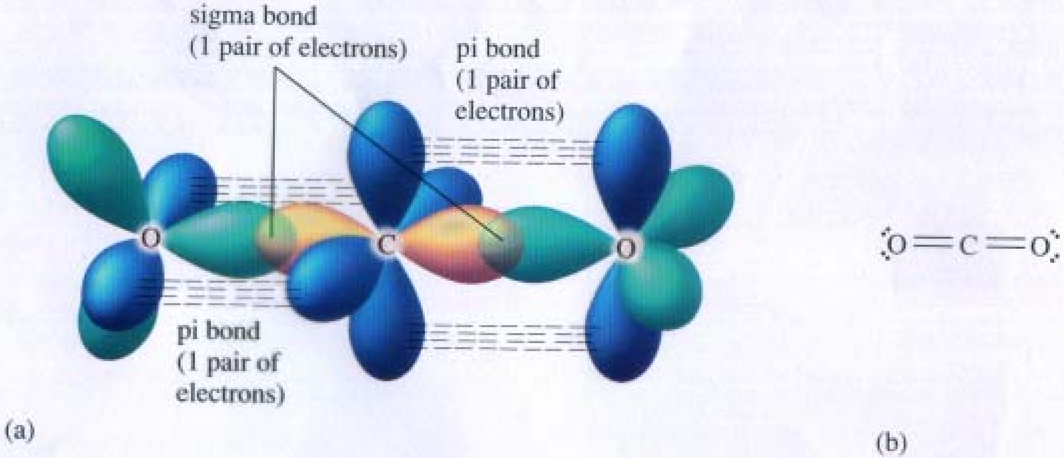

Figure 9.19

The orbitals for CO_2

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Two effective pairs around an atom will always require sp hybridization of that atom

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(Fig 9.14 & 9.15)

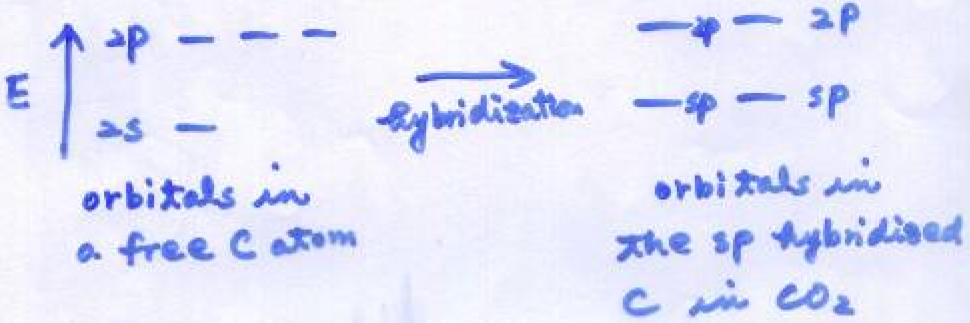

Fig 9.17 & Fig 9.18 & Fig 9.19

Ex. N_2

Sol: $:N \equiv N:$

2 effective pairs (each N atom)

$\downarrow$

sp hybridization

(see fig 9.20)

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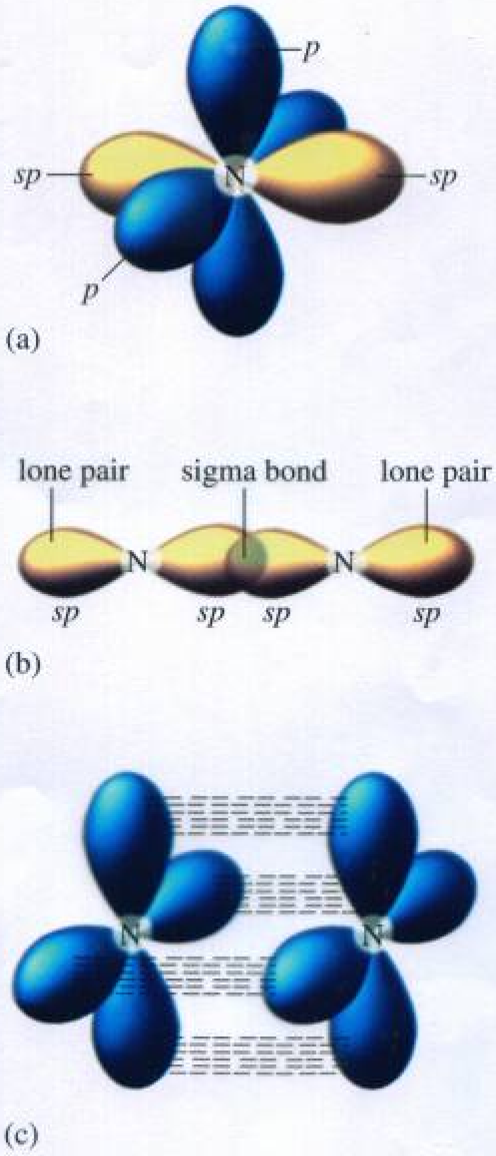
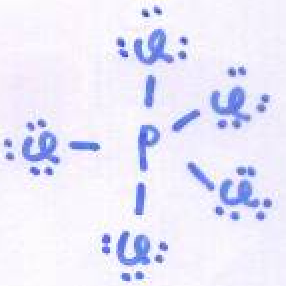


Figure 9.20
The orbitals for N_2

dsp^3 Hybridization

PCl_5 :

Lewis structure



双双金字塔 (trigonal bipyramidal)

see Fig 9.21.

5 P – Cl σ bonds (see Fig. 9-22)

Ex. 9.3

Describe the bonding in the triiodide ion (I_3^-)

Sol: Lewis structure of I_3^-

不符合8偶体

中心 I atom → 5 对 e^- → dsp^3 hybridization

外侧 I atom → 4 对 e^- → sp^3 hybridization

中心 I 的 dsp^3 overlap w/ sp^3 (外圍 I) → σ bon

d^2sp^3 hybridization

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SF_6

Lewis structure :

8面体

octhedra

→ d^2sp^3 hybridization

Ex. 9-4

How is the xenon atom in XeF_4 hybridized?

sol: Lewis structure

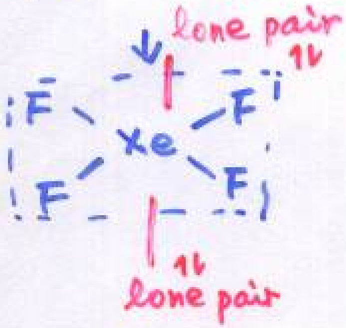
6 pairs of electrons of Xe

↓

octahedral

↓

d^2sp^3 hybridization



⇓

see page 423 Xenon uses 6 d^2sp^3 orbital
to bond to 4 fluorine atoms and to hold 2 lone pai

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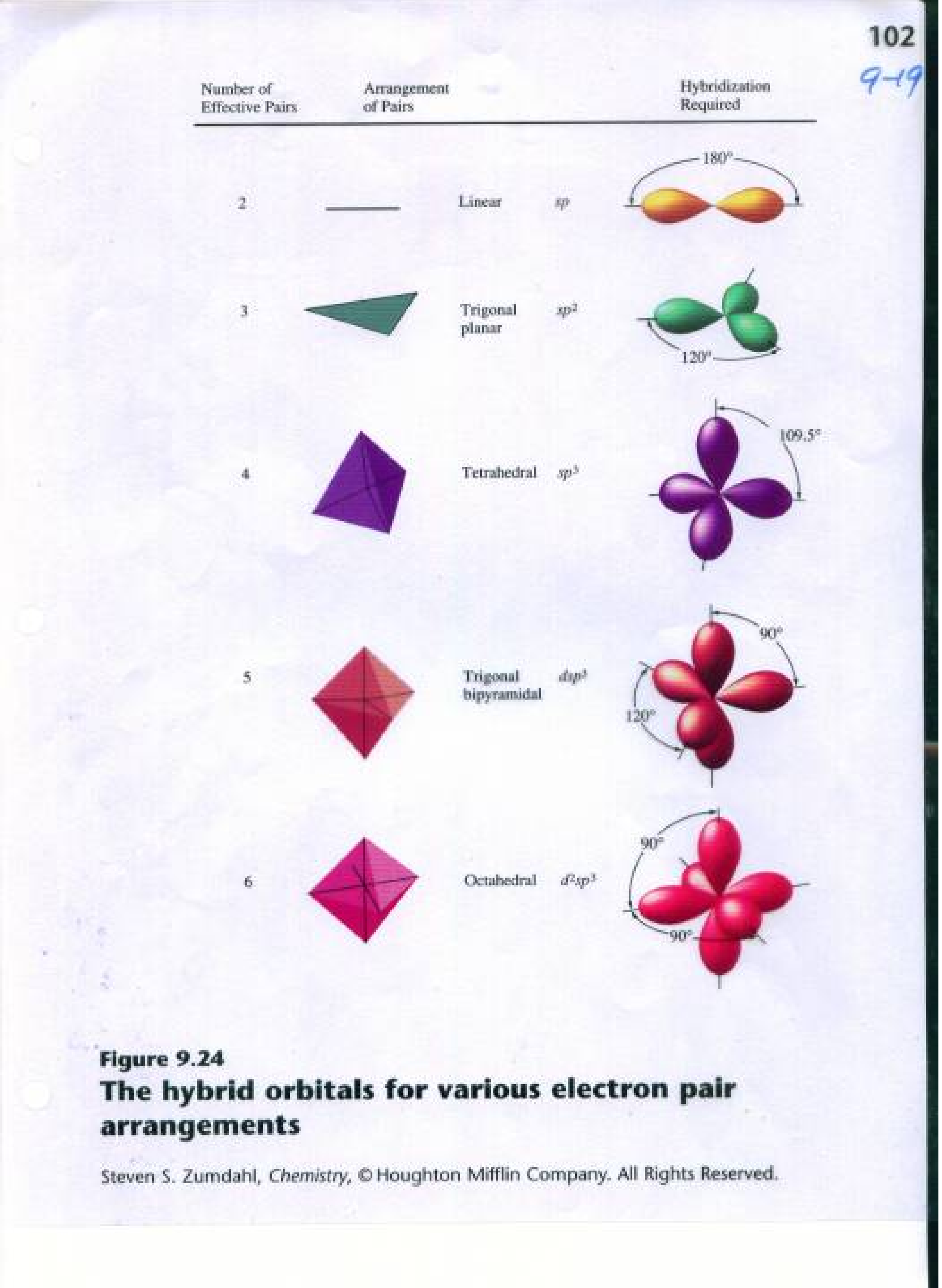

Number of Effective Pairs	Arrangement of Pairs		Hybridization Required
2	Linear	*sp*	
3	Trigonal planar	sp^2	
4	Tetrahedral	sp^3	
5	Trigonal bipyramidal	dsp^3	
6	Octahedral	d^2sp^3	

Figure 9.24
The hybrid orbitals for various electron pair arrangements

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Summary: Describe a molecule w/ the Localized Electron Model

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1. Draw the Lewis structures.
2. Determine the arrangement of electron pairs, using the VSEPR model
3. Specify the hybrid orbitals needed to accommodate the electron pairs

↓

Fig 9.24 (page 424)

Ex. 9-5

For each of the following molecules or ions, describe the molecular structure and predict the hybridization of each atom

a. CO b. BF_4^- c. XeF_2

Sol:

a. CO $:C\equiv O:$

C: 2 effective pairs ∴ sp hybridization

O: " "

C與O間 σ. & π bond (see Figures on p425)

b. BF_4^-

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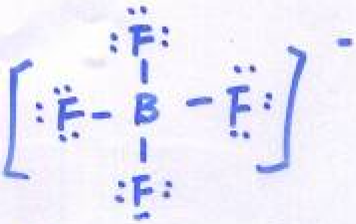
Lewis structure



4 pairs around B

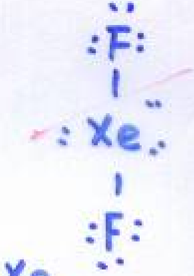
↓

sp^3 hybridization

tetrahedral

c. XeF_2

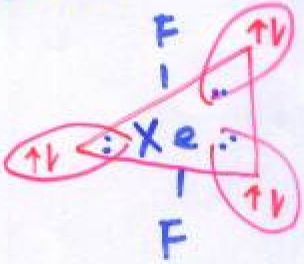
Lewis structure :



5 e pairs around Xe

↓

dsp^3 hybridization



9.2 The Molecular Orbital Model

atomic orbitals : solutions to the quantum mechanical treatment of atoms

molecular orbitals : solutions to the quantum mechanical treatment of molecules
(MOs)

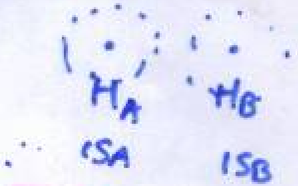
相同性質:

1. 1 orbital → hold 2 e^-
2. orbital 的平方 代表 electron probability

以 H_2 為例

$MO_1 = \frac{1}{\sqrt{2}}(1S_A + 1S_B)$

$MO_2 = \frac{1}{\sqrt{2}}(1S_A - 1S_B)$



See Page 427 9-23

1. electron probability of both M.Os.
is centered along the line passing
through the two nucleii.

MO 1 : the greatest probability
在 中心

M.O.2. : the greatest probability
在 outside the area
between the two nucleii

cylindrically symmetric electron
distribution → sigma (σ) M.O.

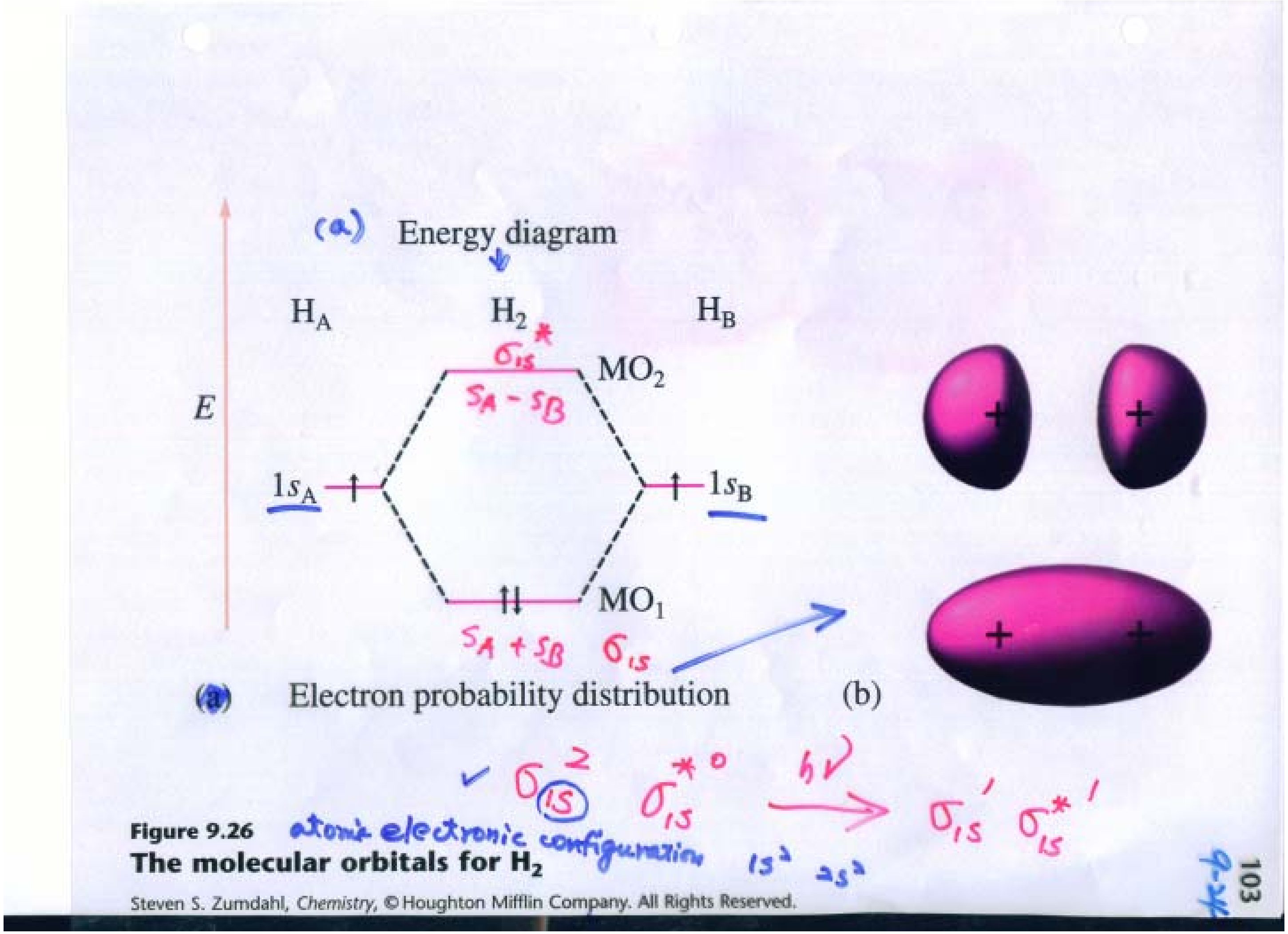
2. In the molecule, only the MOs are
available for occupation by electrons

(The 1s atomic orbitals of the hydrogen
atoms no longer exist !)

a set of new orbitals !!

3. $M.O_1$ is lower in energy than 1s
orbitals of free hydrogen atoms

$M.O_2$ is higher than 1s orbitals



$\checkmark\ \sigma_{\boxed{1s}}^{2}\ \sigma_{1s}^{*0} \xrightarrow{h\nu} \sigma_{1s}^{1}\ \sigma_{1s}^{*1}$

Figure 9.26 atomic electronic configuration $1s^2$ $2s^2$

The molecular orbitals for H_2

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The molecular orbital model

續 p427

3. anti-bonding MO. is higher in energy than the atomic orbitals of which it is composed. favor separating

bonding M.O is lower in energy than the atomic orbitals of which it is composed. favor bonding

4. Fig. 9-26

electrons have the greatest probability of being between the nuclei.

(attracted by both nuclei and lowered in energy)

5. The labels on MOs indicate their symmetry (shapes)

M.O 1 $= \sigma_{1s}$ σ 指 軸对稱

M.O 2 $= \sigma_{1s}^{*}$

6. Molecular electron configurations can be written as the same way as atomic electron configurations.

e.g. H_2. σ_{1s}^{2}

7. Each M.O. can hold 2 electrons 9-26
(w/ opposite spins)

8 The number of MOs = the number of atomic orbitals used to construct them see Fig. 9-27, 9-28

Bond order

the difference between the number of bonding electrons and the number of antibonding electrons, divided by 2

Bond order

$$= \frac{\text{number of bonding electrons} - \#\text{ of antibonding}}{2}$$

Larger bond order ⇒ greater bond strength

e.g. H_2 :

molecular electron configuration: σ_{1s}^2

$\therefore$ Bond order $= \frac{2-0}{2} = 1$

He_2 : $\sigma_{1s}^2 \; \sigma_{1s}^{*2}$

$\therefore$ Bond order $= \frac{2-2}{2} = 0$ (not stable) see Fig 9.28 & 9.29

He_2^+ : $\sigma_{1s}^2 \; \sigma_{1s}^{*1}$

Bond order = $\frac{2-1}{2} = 0.5$ (Bond energy 250 kJ/mol)

H_2^+ : σ_{1s}^1

Bond order = $\frac{1-0}{2} = 0.5$ (255 kJ/mol)

see Fig 9.30, 9.31

§ 9-3 Bonding in Homonuclear Diatomic Molecules

Li : $1s^2 \; 2s^1$

Li_2 :

In order to participate in molecular orbitals atomic orbitals must overlap in space

Only valence orbitals contribute significantly

see Fig 9.33 & 9.34

$\sigma_{2s} \; \sigma_{2s}^*$ ⇐ 2s atomic orbitals

Li_2 : σ_{2s}^2 Bond order = $\frac{2-0}{2} = 1$

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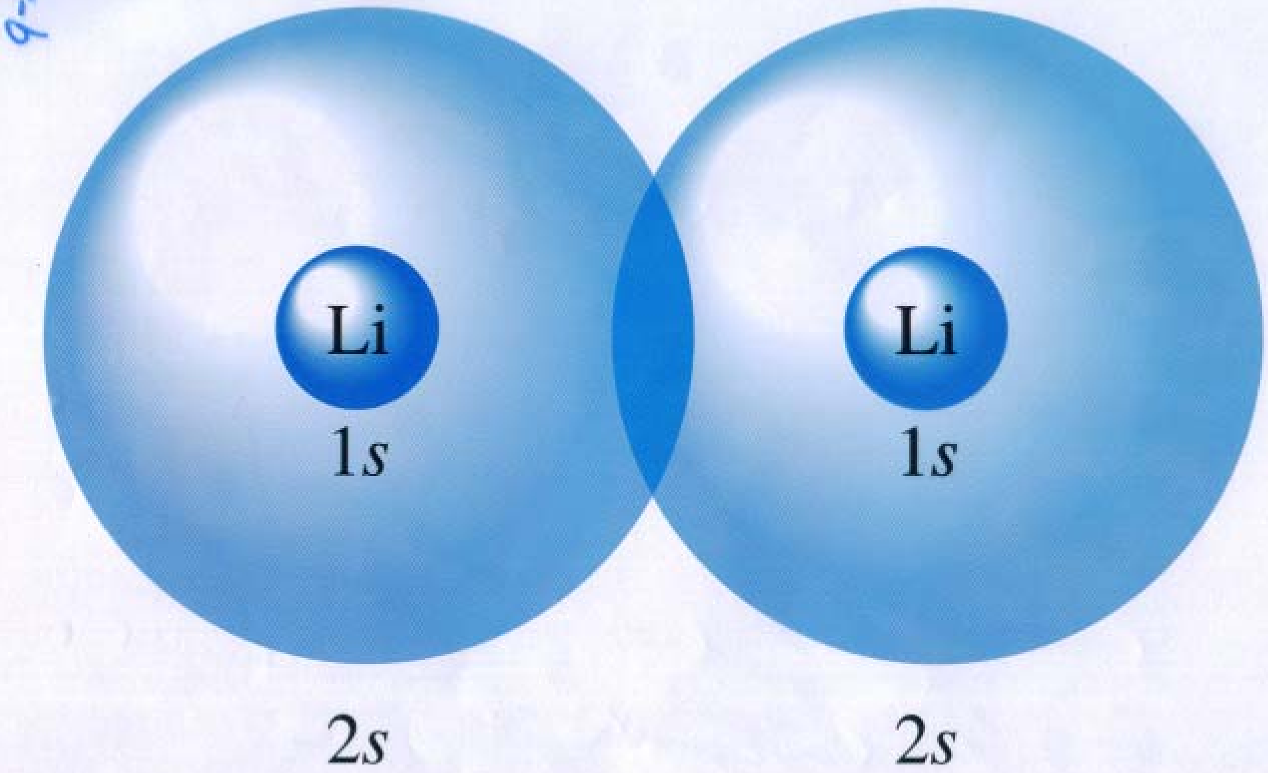

Figure 9.31

Overlap of the 1s and 2s orbitals in Li_2

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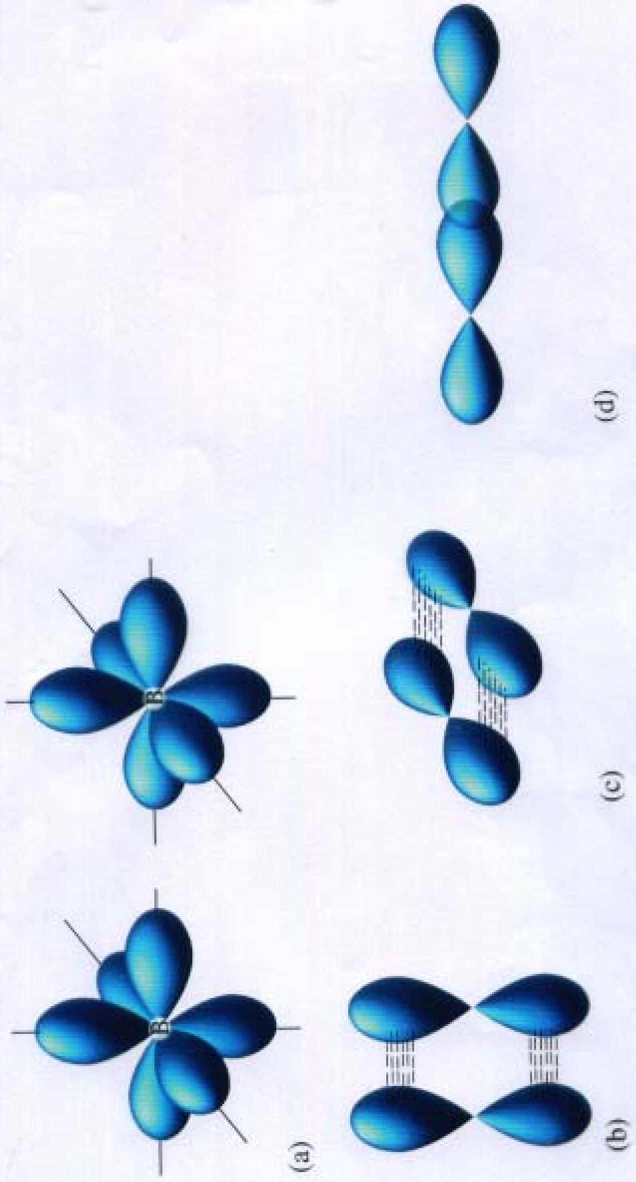
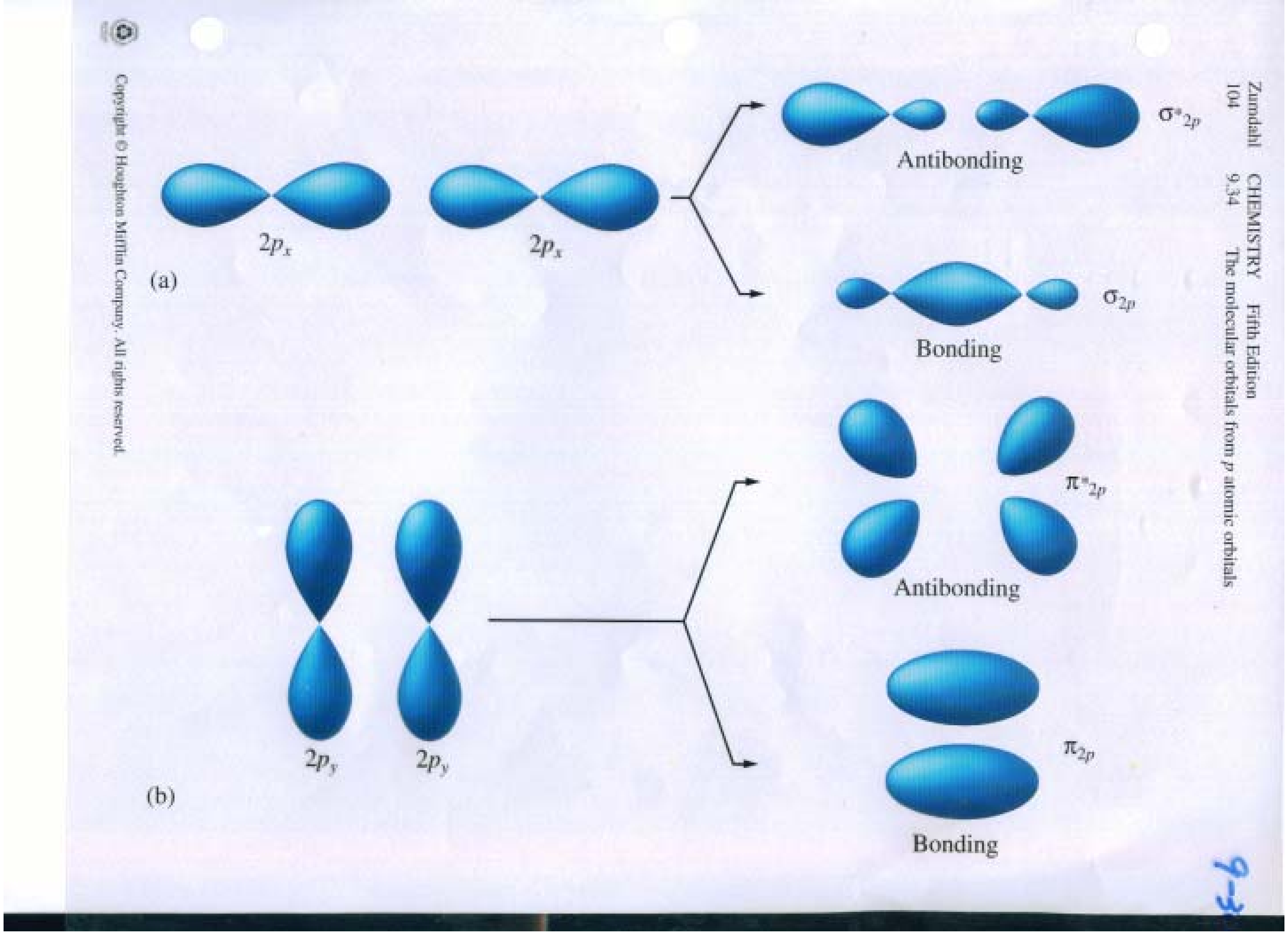
Zumdahl   CHEMISTRY   Fifth Edition
103   9.33   The atomic orbitals in B_2





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104 9.34 The molecular orbitals from p atomic orbitals

Be_2 : $\sigma_{2s}^2 \; \sigma_{2s}^{*2}$

Bond order = $\frac{2-2}{2} = 0$ (not stable)

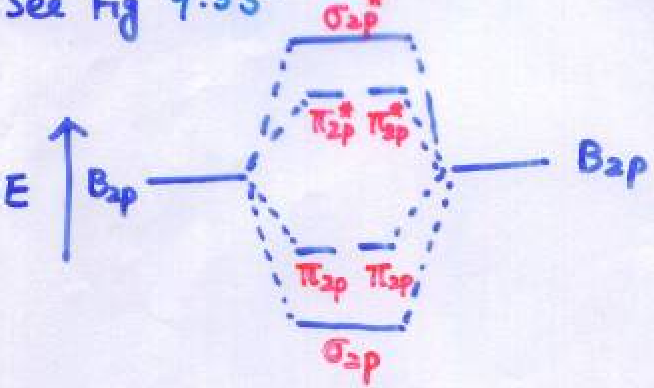
B_2 ?

B : $1s^2 \; 2s^2 \; 2p^1$ (Fig. 9.33 . 9.34)

如果以核為軸 (x軸), 則 $2P_x$ 與 $2P_x$ overlap 會如 Fig 9.33 (a) : σ bonding

$2P_y$ or $2P_z$ 則會形成 : π bonding

See Fig 9.35



B_2 : $\sigma_{2s}^2 \; \sigma_{2s}^{*2} \; \sigma_{2p}^2$

Bond order = $\frac{4-2}{2} = 1$

Fig. 9-36

Paramagnetism (順磁性) • causes the substance to be attracted toward the inducing magnetic field

Diamagnetism (反磁性) • causes the substance to be repelled from the inducing magnetic field.

paramagnetism is associated w/ unpaired electrons

diamagnetism is associated w/ paired electrons

由 Fig 9.36

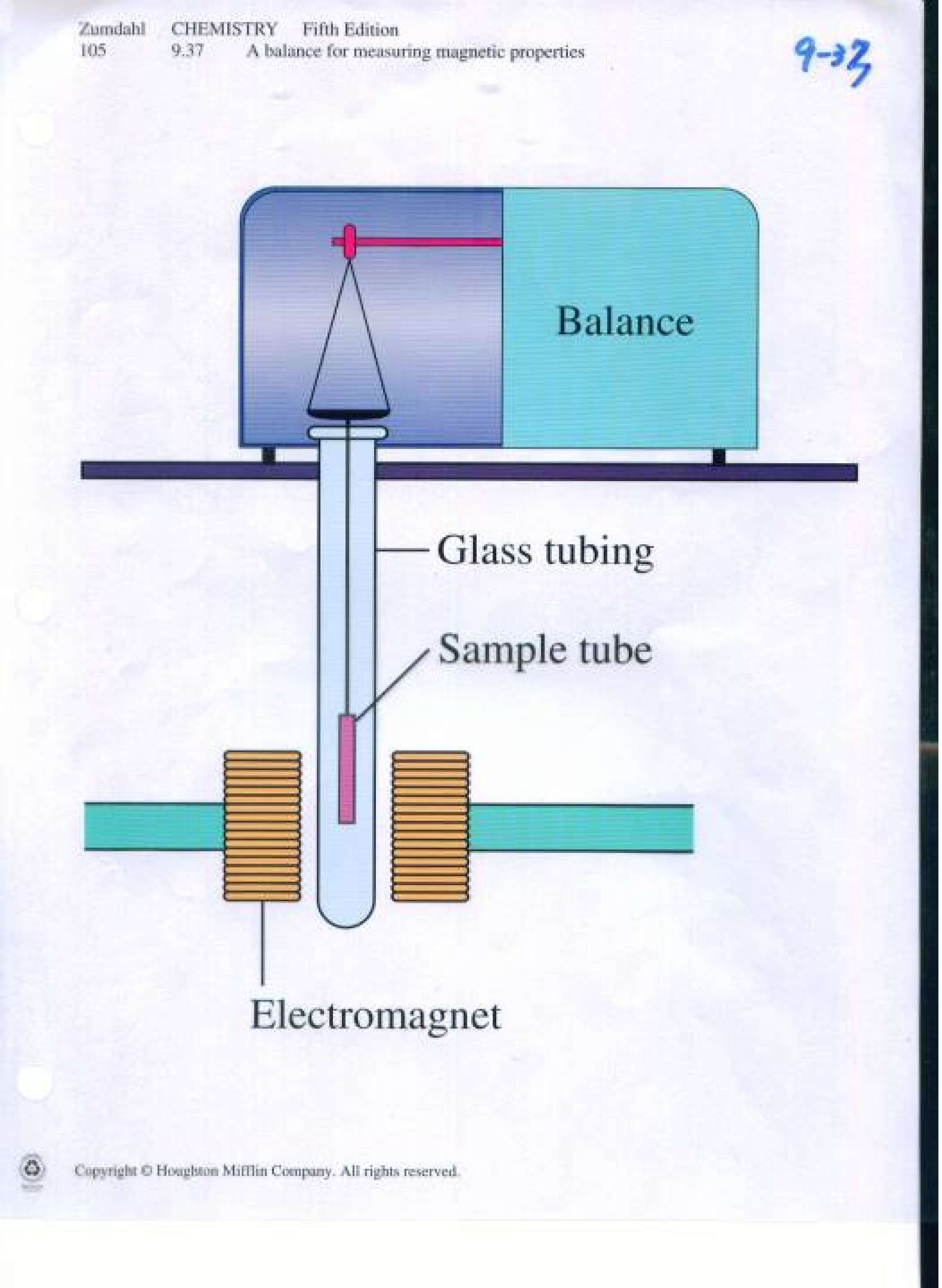
B_2 : 應為 diamagnetic

But, B_2 是 paramagnetic w/ two unpaired electrons

why ?

2S 2p orbital mixing !

molecular orbital energy diagram of B_2, C_2, N_2 不同 ! (see Fig 9.38, 9.39



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105 9.37 A balance for measuring magnetic properties

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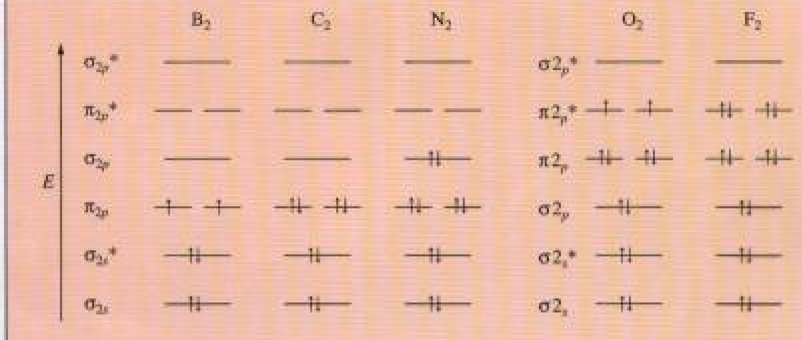

	B$_2$	C$_2$	N$_2$	O$_2$	F$_2$
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

Figure 9.39

Molecular orbital summary of second-row diatomics

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Ex. 9-6 9-35

O_2 : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^2$

O_2^+ $(\pi_{2p}^*)^1$

O_2^- $(\pi_{2p}^*)^3$

Bond order:	Bond energy (KJ/mol)
$O_2 = \frac{8-4}{2} = 2$	495
$O_2^+ = \frac{8-3}{2} = 2.5$	643
$O_2^- = \frac{8-5}{2} = 1.5$	395

Ex. 9.7 use M.O. to predict the bond order and magnetism of

a. Ne_2 b. P_2

Ne_2 : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^4 (\sigma_{2p}^*)^2$

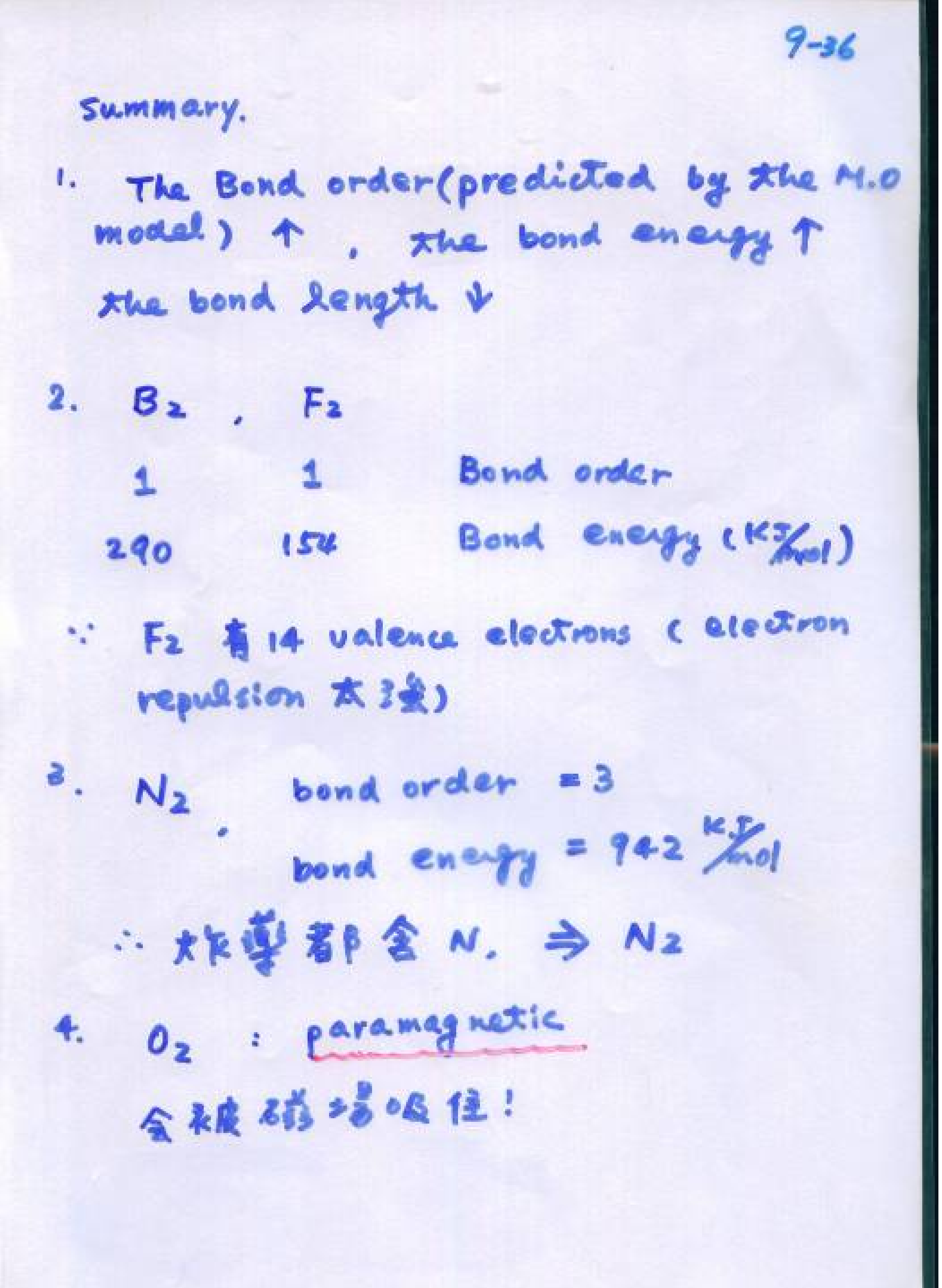
Bond order $= \frac{8-8}{2} = 0$

diamagnetic

P_2 : $(\sigma_{3s})^2 (\sigma_{3s}^*)^2 (\pi_{3p})^4 (\sigma_{3p})^2$

Bond order $= \frac{8-2}{2} = 3$

diamagnetic



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Summary.

1. The Bond order (predicted by the M.O model) ↑ , the bond energy ↑ the bond length ↓

2.

B_2 ,	F_2	
1	1	Bond order
290	154	Bond energy (KJ/mol)

∵ F_2 有 14 valence electrons (electron repulsion 太強)

3. N_2 , bond order = 3
bond energy = 942 KJ/mol

∴ 炸藥都含 N. ⇒ N_2

4. O_2 : paramagnetic
會被磁場吸住!

9-4 Bonding in heteronuclear diatomic molecules 異核雙原子分子

e.x. NO

valence electron = 5 + 6 = 11

Energy level (可以用 N_2)

∴ molecular orbital configuration :

$\sigma_{2s}^2 \ \sigma_{2s}^{*2} \ \pi_{2p}^4 \ \sigma_{2p}^2 \ \pi_{2p}^{*1}$

Bond order = $\frac{8-3}{2}$ = 2.5

paramagnetic

Ex. 9.8

NO^+ and CN^-

NO^+ valence e^- = 10

CN^- valence e^- = 10

configuration 都是 :

$\sigma_{2s}^2 \ \sigma_{2s}^{*2} \ \pi_{2p}^4 \ \sigma_{2p}^2$ ~

Bond order = $\frac{8-2}{2}$ = 3

Diamagnetic

HF molecule

↑ ↖

週期 1 2

与單純同週期異核分子不同

See Fig9-43 & 9-44

H : use 1s atomic orbital

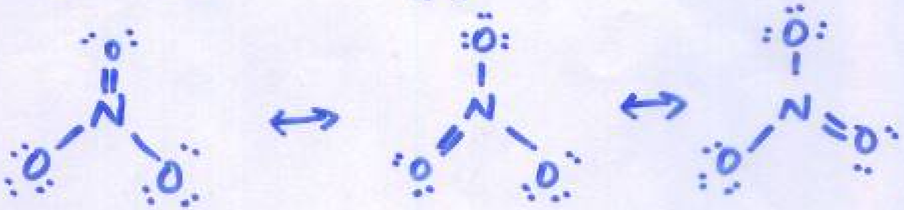
F : use one of 2p orbital

↓

σ and σ^* molecular orbitals

§ 9.5 combining the localized Electron and molecular Orbital models

共振 (resonce) 分子 : O_3 & NO_3^-



a double bond 包括 1 σ bond

1 π bond

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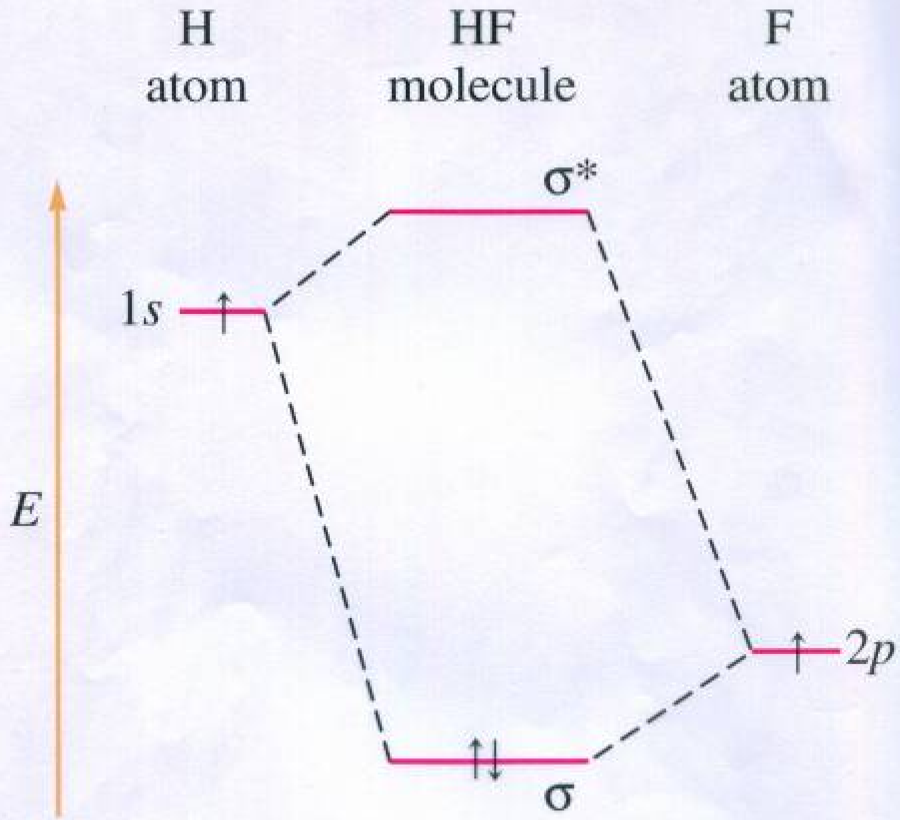

Figure 9.43
The molecular orbital diagram for HF

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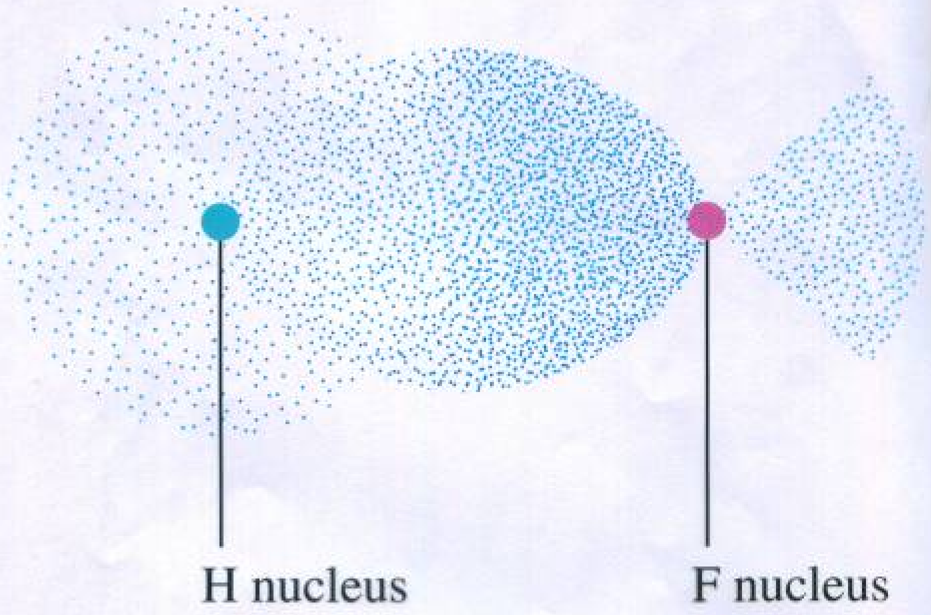


(有較強的負电性)

Figure 9.44

The electron density map for HF

Ideal Bonding model:

use LE model w/ delocalization characteristics of the MO model

Ex. O_3:

中心原子 use sp^2 overlap w/ sp^2 (外圍原子)

But one extra π bonding

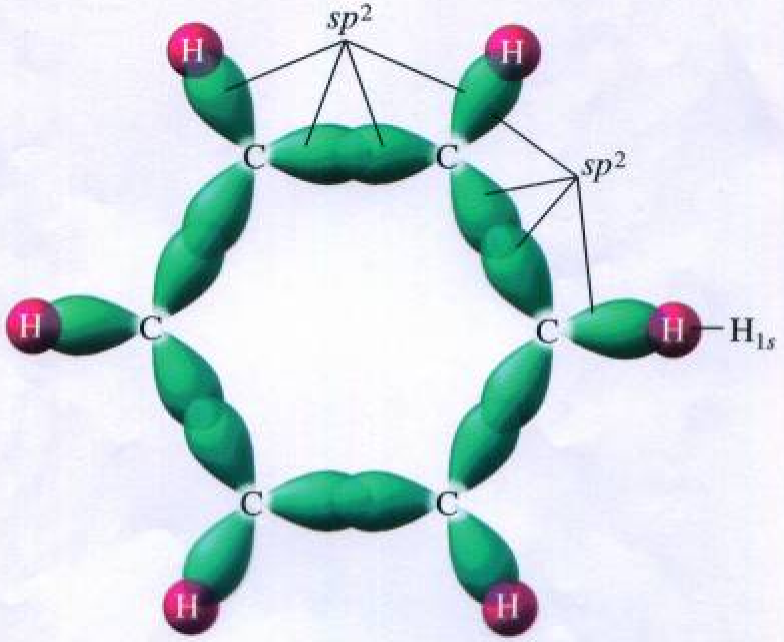
(delocalization between two bonds)

C_6H_6: (see Fig 9-46) LE model

σ bonding: Fig 9-47

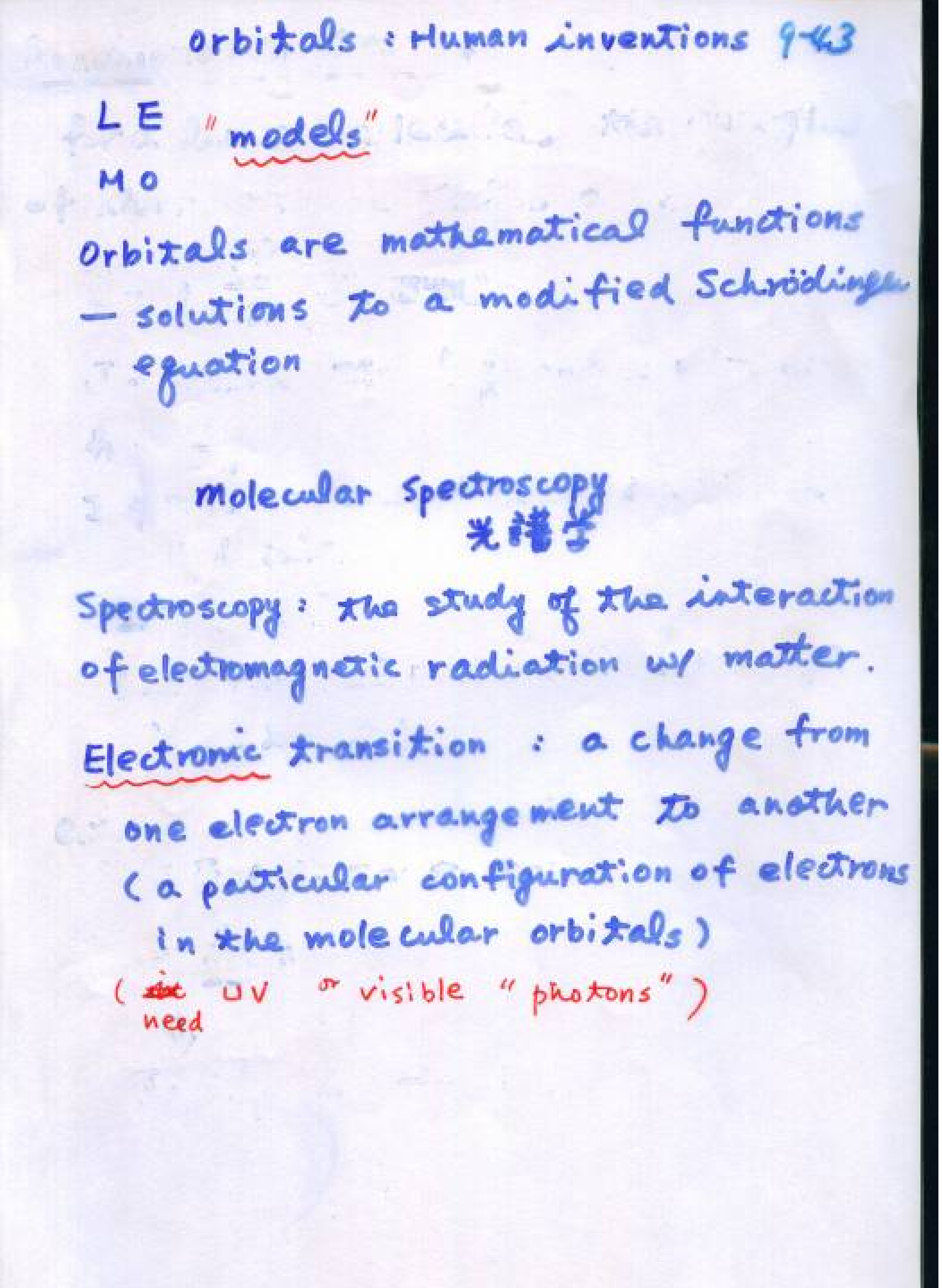
delocalized π bonding: Fig 9-48

9-#2



σ bonding

Figure 9.47
The sigma system for benzene



Orbitals : Human inventions 9-43

LE "models"
MO

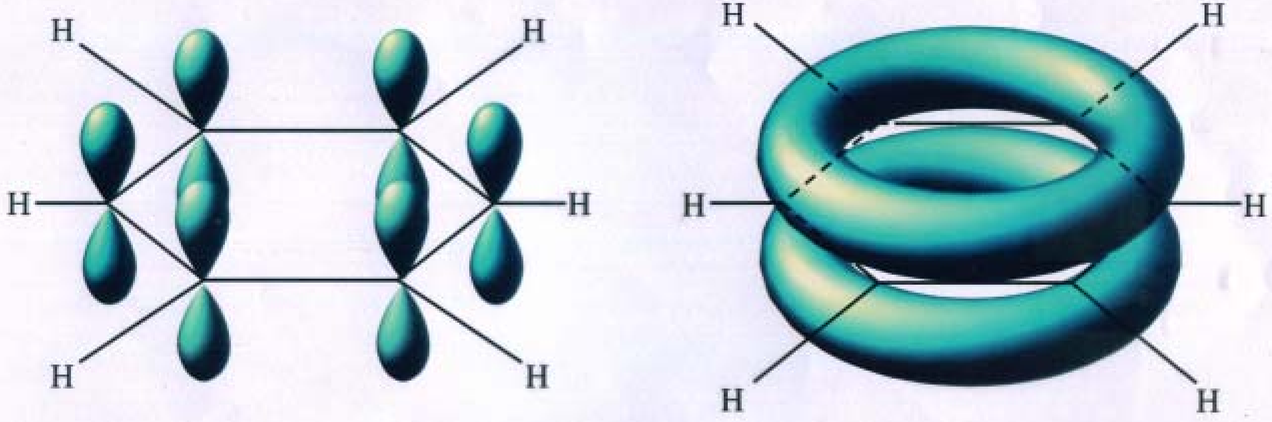
Orbitals are mathematical functions
— solutions to a modified Schrödinger equation

molecular spectroscopy
光譜学

Spectroscopy : the study of the interaction of electromagnetic radiation w/ matter.

Electronic transition : a change from one electron arrangement to another
(a particular configuration of electrons in the molecular orbitals)

(~~[illegible]~~ need UV or visible "photons")



(a) (b)

Figure 9.48

The pi system for benzene

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9-43

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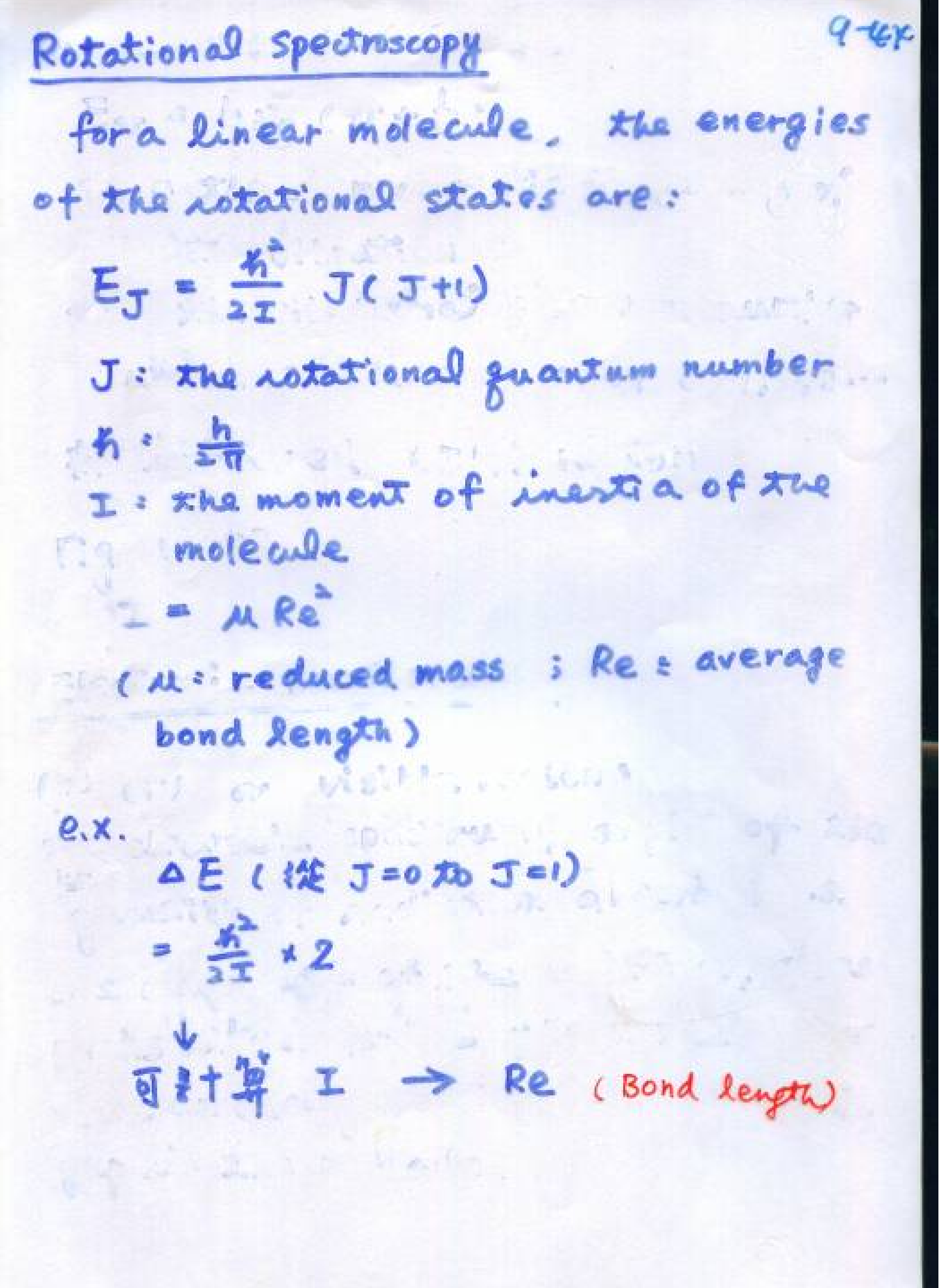


Rotational spectroscopy

9-ex

for a linear molecule, the energies of the rotational states are:

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

J : the rotational quantum number

$\hbar$: $\frac{h}{2\pi}$

I : the moment of inertia of the molecule

$I = \mu Re^2$

(μ : reduced mass ; Re : average bond length)

e.x.

ΔE (從 $J=0$ to $J=1$)

$= \frac{\hbar^2}{2I} \times 2$

$\downarrow$

可計算 I → Re (Bond length)

Vibrational Spectroscopy

$E_v = h\nu_0 (v + \frac{1}{2})$

ν_0 = the characteristic frequency of the vibration

v = the vibrational quantum number which can assume only 0, 1, 2, 3 ...

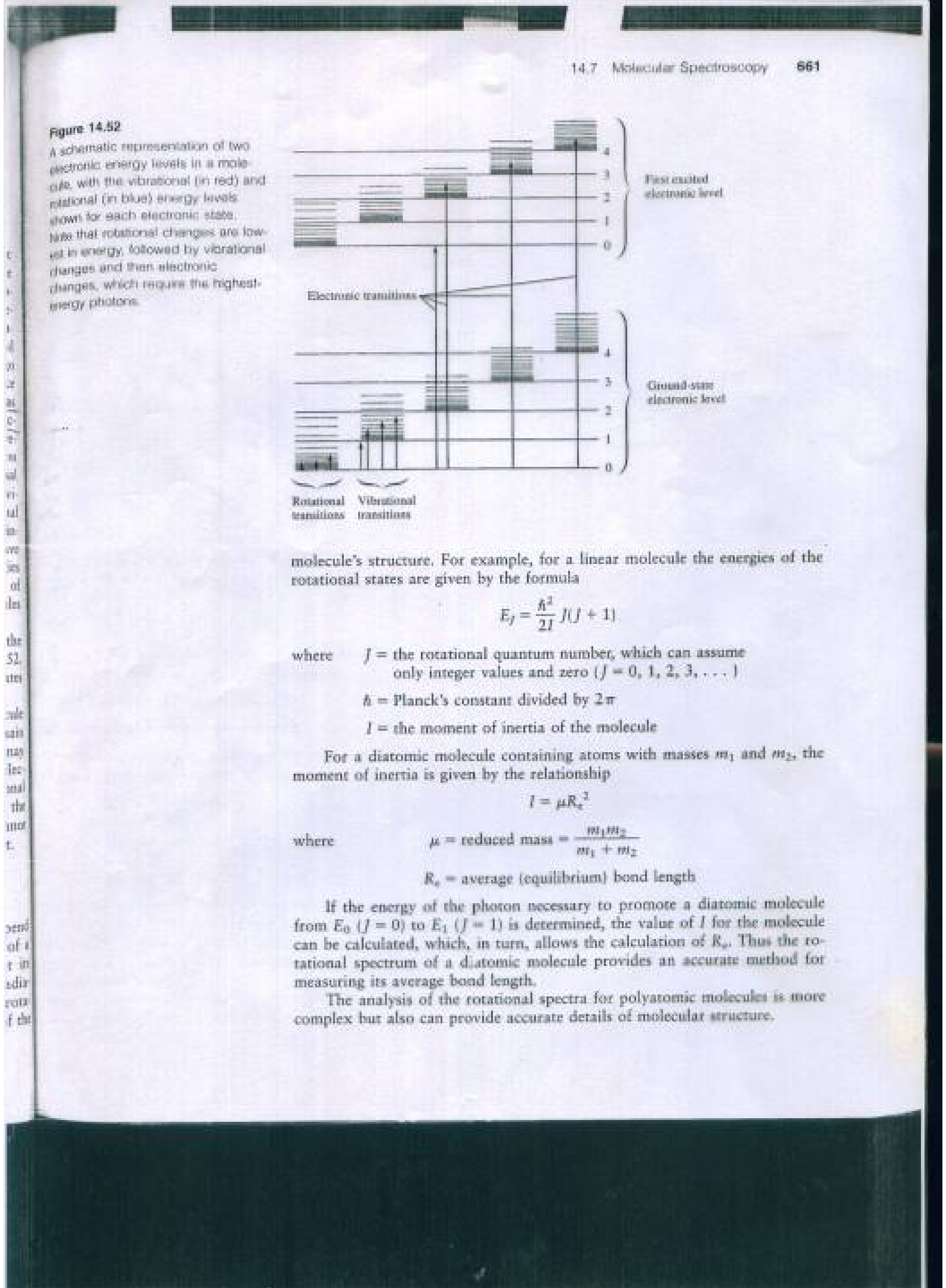
在 infrared (IR) region

Fig 14.53

Electronic spectroscopy

(在 UV or visible region)

the electronic spectrum, a plot of the quantity of radiation absorbed v.s. the wavelength of the radiation, shows peaks at wavelengths where the photons have an energy that matches an energy gap in the molecule.



14.7 Molecular Spectroscopy 661

Figure 14.52
A schematic representation of two electronic energy levels in a molecule, with the vibrational (in red) and rotational (in blue) energy levels shown for each electronic state. Note that rotational changes are lowest in energy, followed by vibrational changes and then electronic changes, which require the highest-energy photons.

molecule's structure. For example, for a linear molecule the energies of the rotational states are given by the formula

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

where J = the rotational quantum number, which can assume only integer values and zero ($J = 0, 1, 2, 3, \ldots$)

$\hbar$ = Planck's constant divided by 2π

I = the moment of inertia of the molecule

For a diatomic molecule containing atoms with masses m_1 and m_2, the moment of inertia is given by the relationship

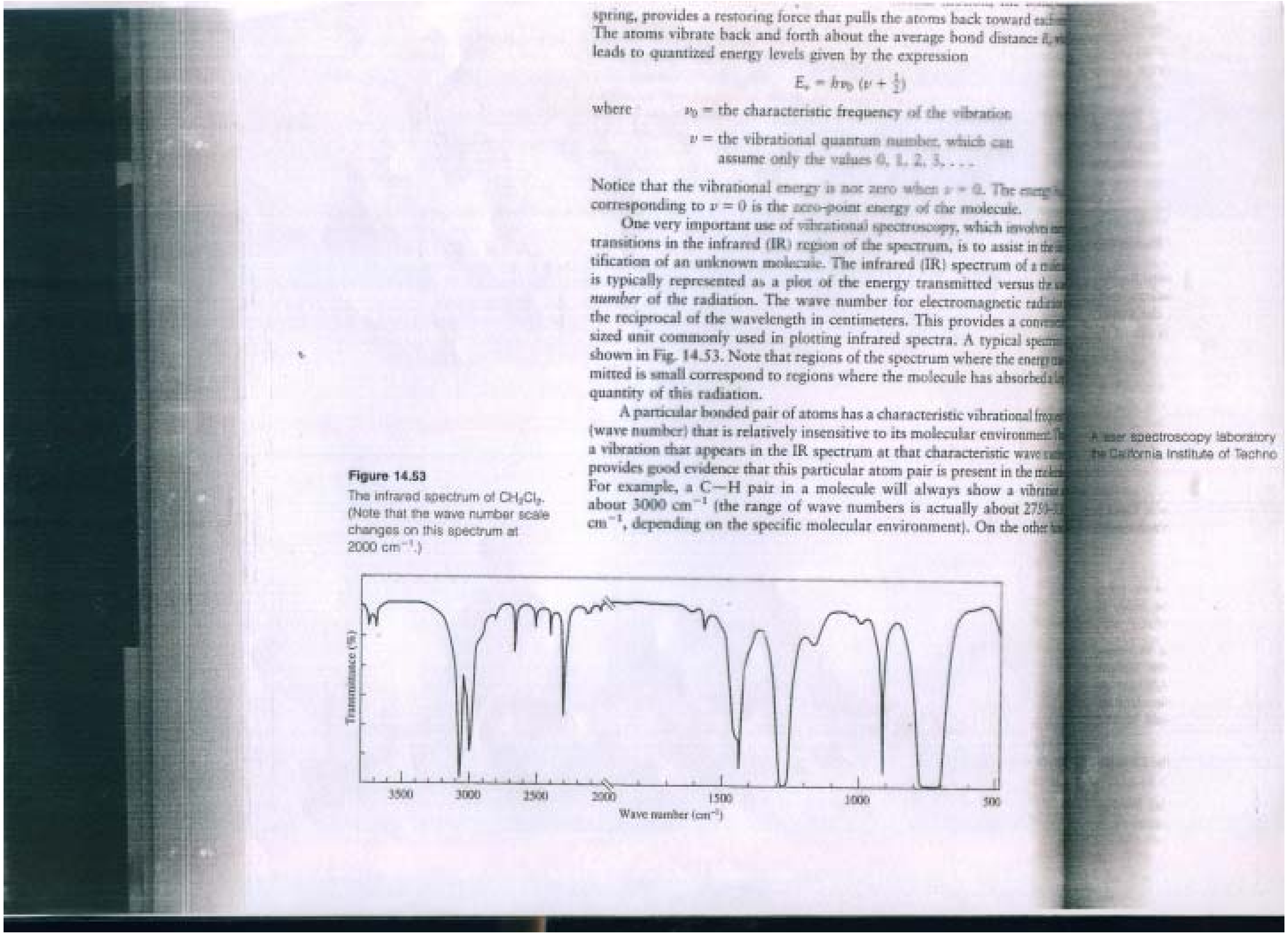
$$I = \mu R_e^2$$

where $\mu = \text{reduced mass} = \frac{m_1 m_2}{m_1 + m_2}$

R_e = average (equilibrium) bond length

If the energy of the photon necessary to promote a diatomic molecule from E_0 ($J = 0$) to E_1 ($J = 1$) is determined, the value of I for the molecule can be calculated, which, in turn, allows the calculation of R_e. Thus the rotational spectrum of a diatomic molecule provides an accurate method for measuring its average bond length.

The analysis of the rotational spectra for polyatomic molecules is more complex but also can provide accurate details of molecular structure.



spring, provides a restoring force that pulls the atoms back toward ea
The atoms vibrate back and forth about the average bond distance R, w
leads to quantized energy levels given by the expression

$$E_v = h\nu_0\,(v + \tfrac{1}{2})$$

where ν_0 = the characteristic frequency of the vibration

v = the vibrational quantum number, which can assume only the values 0, 1, 2, 3, . . .

Notice that the vibrational energy is not zero when $v = 0$. The energ
corresponding to $v = 0$ is the zero-point energy of the molecule.

One very important use of vibrational spectroscopy, which involve
transitions in the infrared (IR) region of the spectrum, is to assist in the
tification of an unknown molecule. The infrared (IR) spectrum of a m
is typically represented as a plot of the energy transmitted versus the
number of the radiation. The wave number for electromagnetic radi
the reciprocal of the wavelength in centimeters. This provides a con
sized unit commonly used in plotting infrared spectra. A typical spe
shown in Fig. 14.53. Note that regions of the spectrum where the energ
mitted is small correspond to regions where the molecule has absorbed a
quantity of this radiation.

A particular bonded pair of atoms has a characteristic vibrational fre
(wave number) that is relatively insensitive to its molecular environment.
a vibration that appears in the IR spectrum at that characteristic wave
provides good evidence that this particular atom pair is present in the mo
For example, a C—H pair in a molecule will always show a vibrat
about 3000 cm^{-1} (the range of wave numbers is actually about 275
cm^{-1}, depending on the specific molecular environment). On the other

A laser spectroscopy laboratory
the California Institute of Techno

Figure 14.53

The infrared spectrum of CH_2Cl_2. (Note that the wave number scale changes on this spectrum at 2000 cm^{-1}.)