# 6 CHAPTER

QUANTUM MECHANICS AND MOLECULAR STRUCTURE

6.1 Quantum Picture of the Chemical Bond

6.2 Exact Molecular Orbital for the Simplest Molecule: H_2^+

6.3 Molecular Orbital Theory and the Linear Combination of Atomic Orbitals Approximation for H_2^+

6.4 Homonuclear Diatomic Molecules: First-Period Atoms

6.5 Homonuclear Diatomic Molecules: Second-Period Atoms

6.6 Heteronuclear Diatomic Molecules

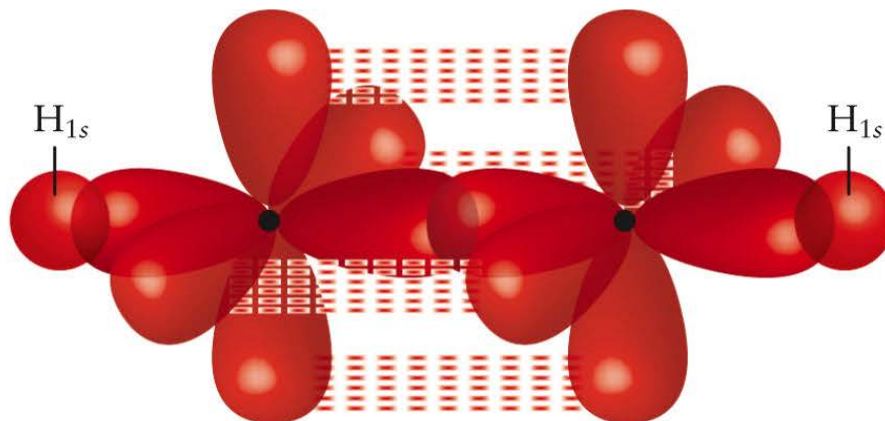**6.7** Summary Comments for the LCAO Method and Diatomic Molecules

General Chemistry I

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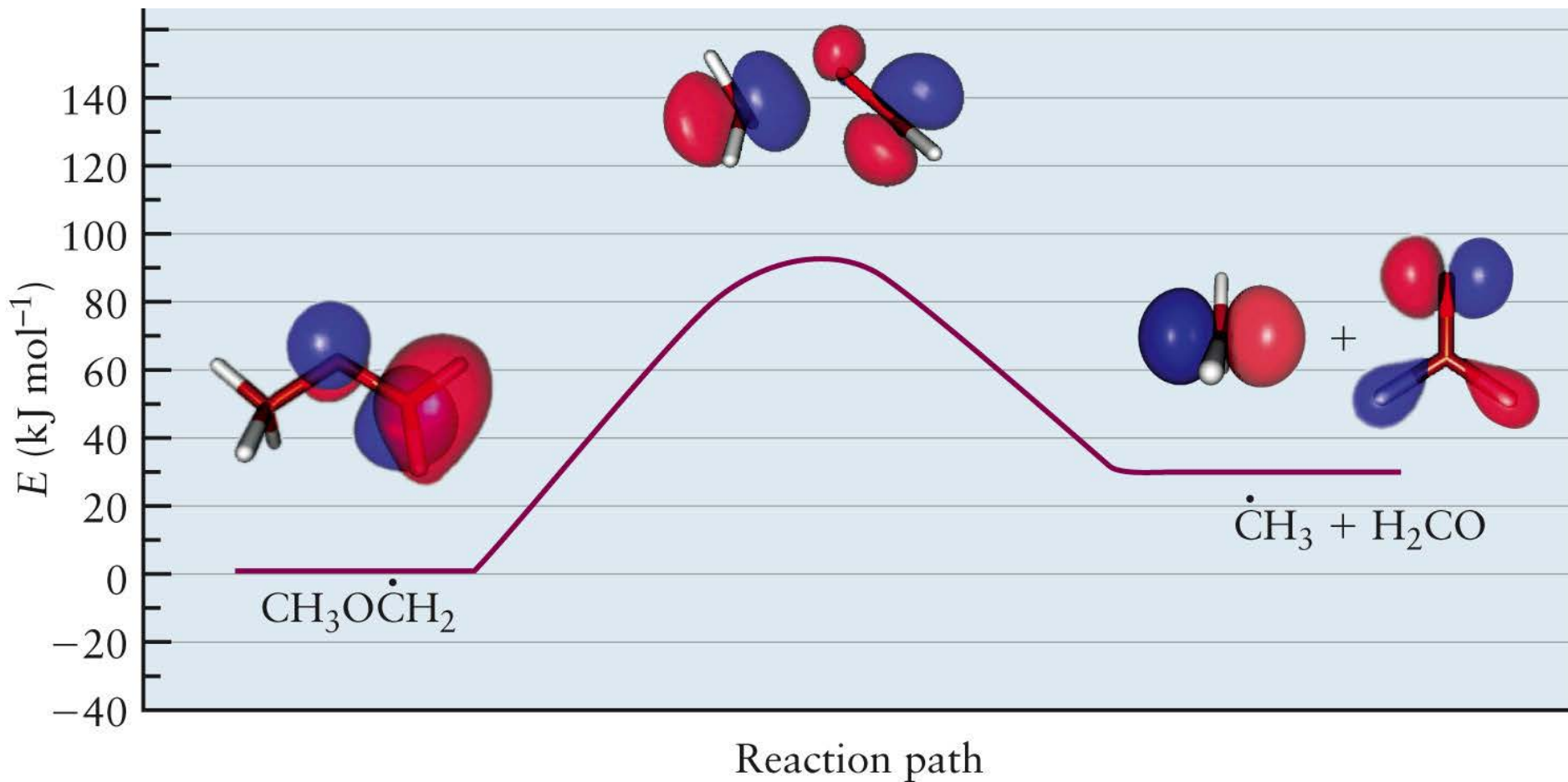
Potential energy diagram for the decomposition of the methyl methoxy radical

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Key question: how can we describe chemical bond in terms of quantum mechanics?

(a)

(b)

H_{1s}

H_{1s}
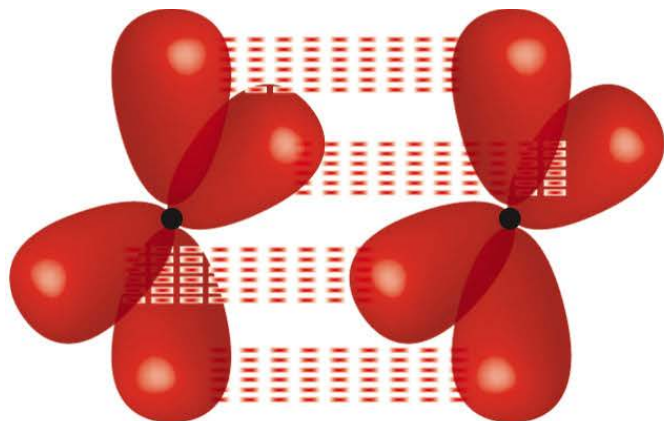
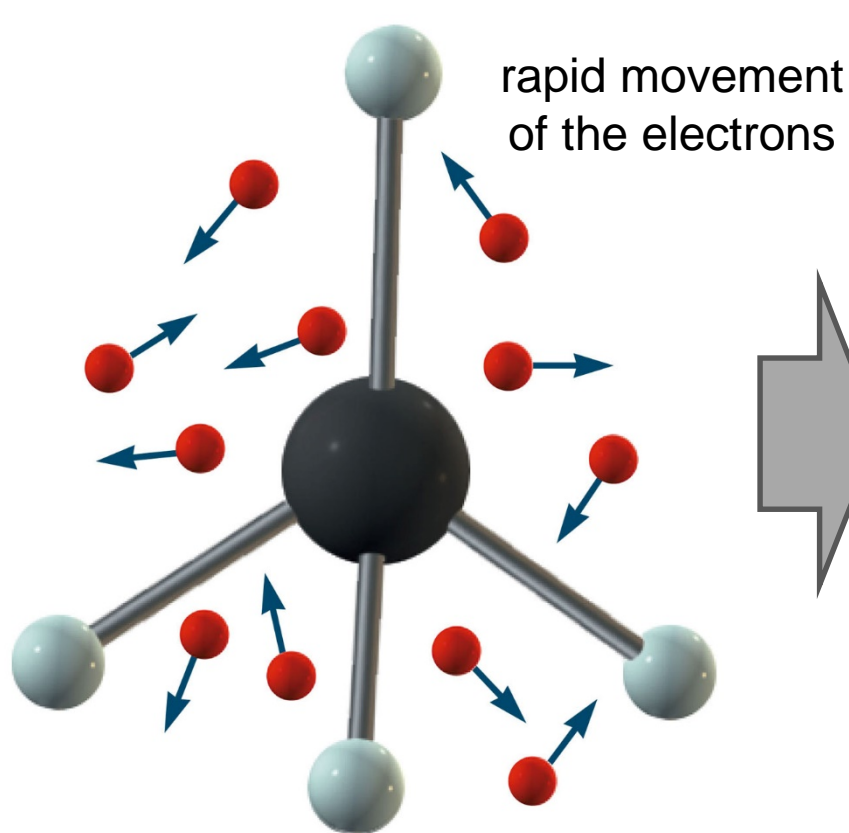# Born-Oppenheimer Approximation: Slow Nuclei, Fast Electrons

- Nuclei are much more massive than the electrons, the nuclei in the molecules will move much more slowly than the electrons.

→ **decoupling of the motions of the nuclei and the electrons**

(A) Consider **the nuclei** to be **fixed at a specific set** of positions.
Then solve Schrödinger's equation **for the electrons** moving around and obtain the energy levels and wave functions.
Next, move the nuclei a bit, and repeat the calculation.
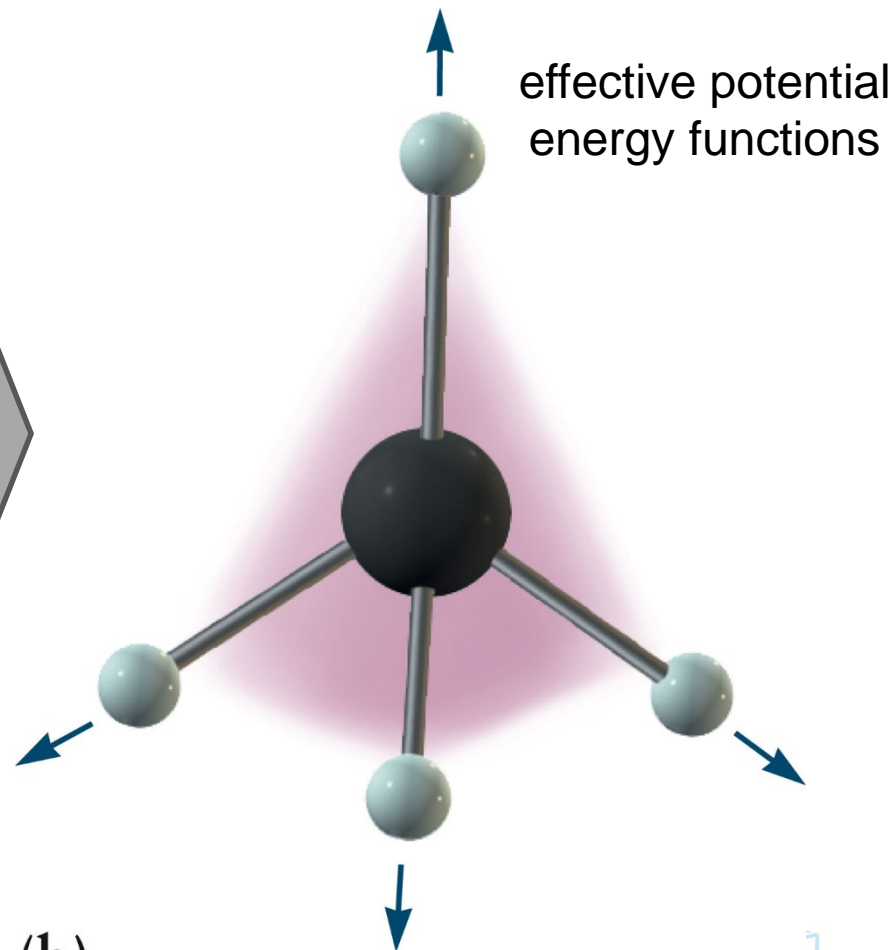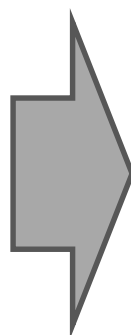Continue this procedure in steps.

Getting each electronic energy $E_\alpha^{(el)}$ to the nuclear coordinates R_{AB}

α: the proper set of quantum numbers

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- Visualizing a group of electrons moving rapidly around the sluggish nuclei, to establish a dynamic distribution of electron density.

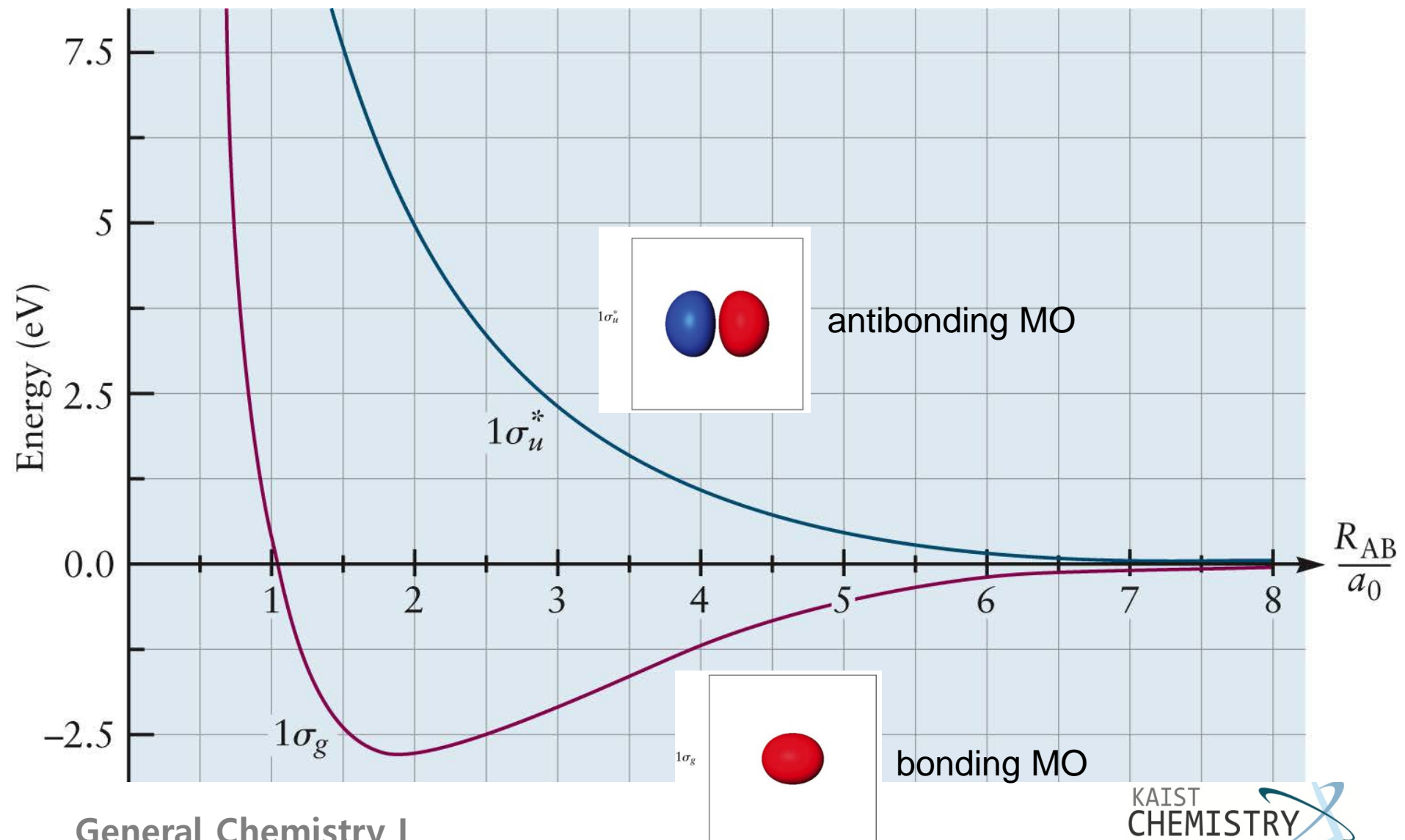rapid movement of the electrons

effective potential energy functions

(a)

(b)

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Nature of the Chemical Bond in H_2^+

antibonding MO

bonding MO

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# 6.2 EXACT MOLECULAR ORBITALS FOR THE SIMPLEST MOLECULE: H_2^+

➤ **H_2^+ ion**: a single electron bound to two protons
   bond length 1.06 Å; bond dissociation energy 2.79 eV = 269 kJ mol^{-1}

$$V = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A}+\frac{1}{r_B}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{R_{AB}}\right) = V_{en} + V_{nn}$$

- For a fixed value of R_{AB},
  the position of the electron:

$(x, y, z) \rightarrow (r_A, r_B, \phi)$

- The potential energy has cylindrical
  (**ellipsoidal**) symmetry around the R_{AB} axis.

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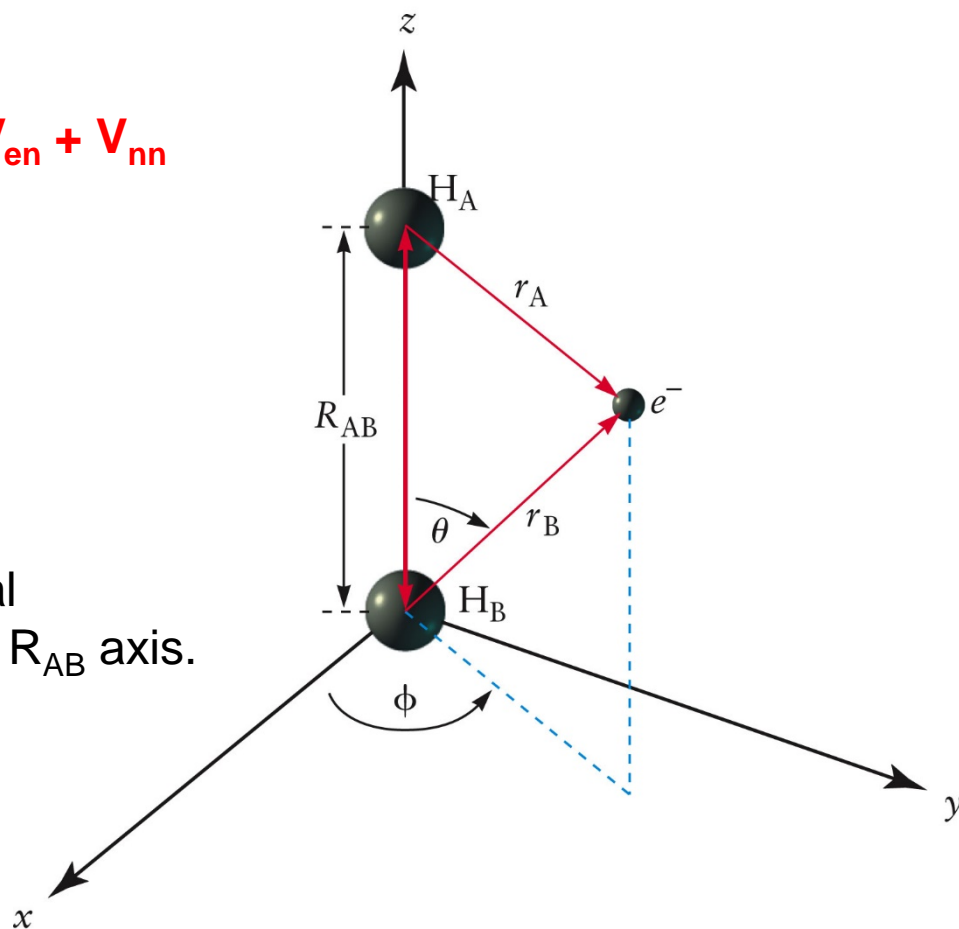
Electronic Wave Functions for H_2^+

$1\sigma_u^*$ $2\sigma_u^*$ $3\sigma_g$ $3\sigma_u^*$

$1\sigma_g$ $2\sigma_g$ $1\pi_u$ $1\pi_g^*$
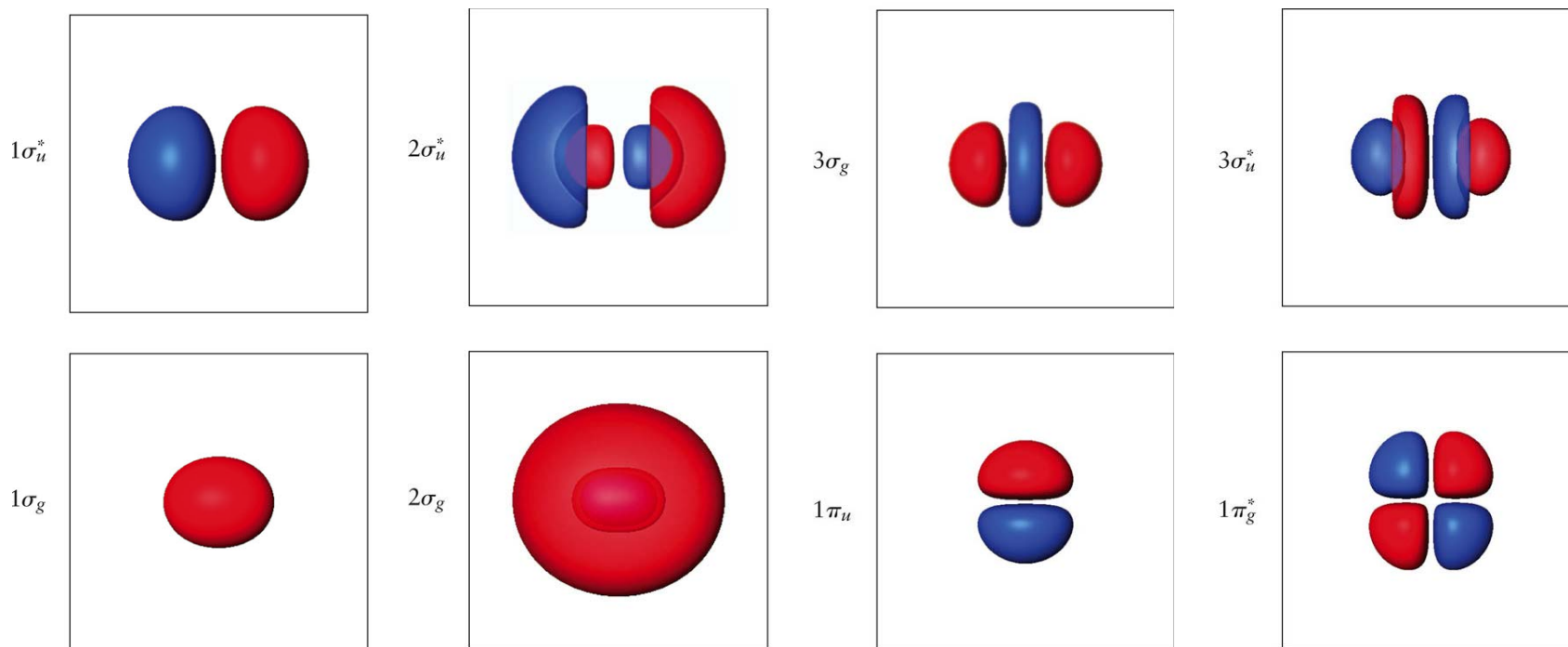
- isosurface comprising the wave function with 0.1 of its maximum value.
- red: + amplitude; blue: - amplitude

- **molecular orbital: each of exact one-electron wave functions**

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- Four labels summarize the energy and the shape of each wave function.

1) **integer**: an index tracking the relative energy
   of the wave functions of each symmetry type.

   i.e.) $1\sigma_g$: the first (the lowest energy) of the
   σ_g wave functions

$1\sigma_g$
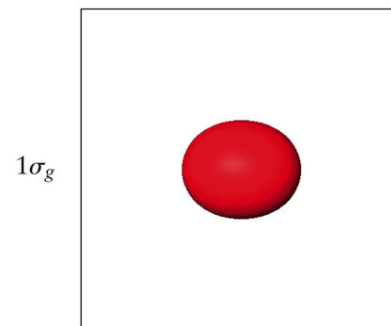
2) **Greek letter**: how the amplitude of the wave
   function is distributed around the internuclear axis.

   - σ : the amplitude with cylindrical symmetry
     around the axis

   - π : the amplitude with a nodal plane that contains
     the internuclear axis

$1\pi_u$
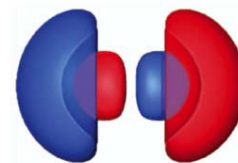
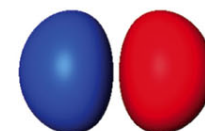**General Chemistry I**

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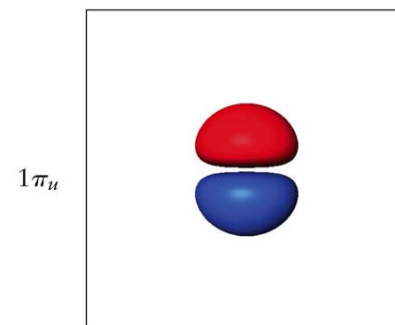
3) **g or u**: how the wave function changes as we invert our point of observation through the center of the molecule
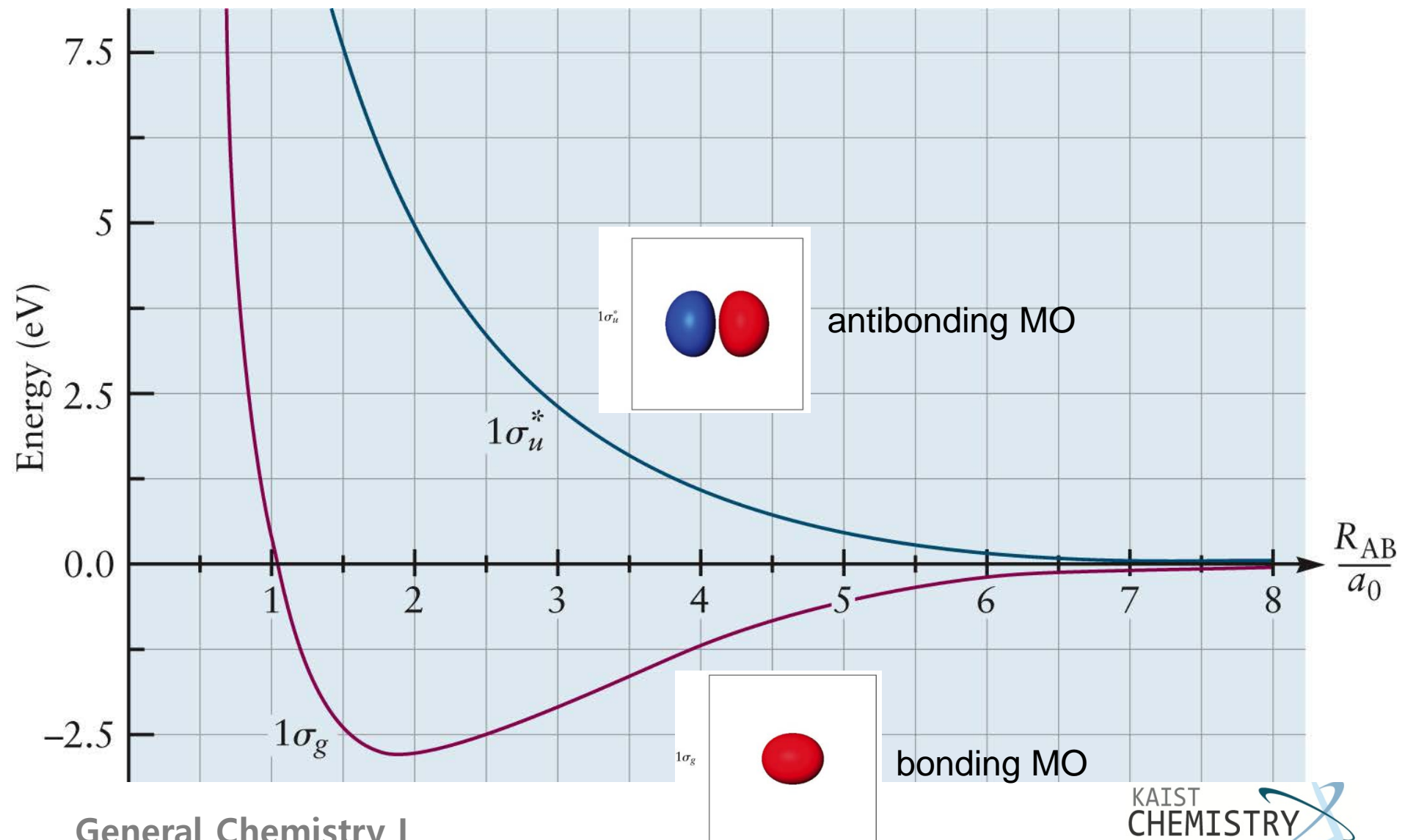
  - the wave function at (x, y, z) and (-x, -y, -z)

  - **g** : symmetric, the same at these points
       gerade

  u : antisymmetric, the opposite at these points
       ungerade

4) ***** : how the wave function changes when the point of observation is reflected through a plane perpendicular to the internuclear axis

  - **no symbol** : no changing sign upon reflection

  ***** : changing sign upon reflection

$2\sigma_u^*$

$2\sigma_g$

$1\sigma_u^*$

$1\sigma_g$

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Nature of the Chemical Bond in H_2^+

antibonding MO

bonding MO

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Summary of the Quantum Picture of Chemical Bonding

1. **The Born-Oppenheimer approximation**: fixing the nuclei position

2. **Molecular orbital**: one-electron wave function,
   its square describes the distribution of electron density

3. **Bonding MO**: increased e density between the nuclei
                   decreased effective potential energy

4. **Antibonding MO**: a node on the internuclear axis
                      high effective potential energy

5. **σ orbital**: cylindrical symmetry; cross-sections perpendicular to the
                 internuclear axis are discs.

6. **π orbital**: a nodal plane containing the internuclear axis

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6.3 MOLECULAR ORBITAL THEORY AND THE LINEAR COMBINATION OF ATOMIC ORBITALS APPROXIMATION FOR H_2^+

➢ **LCAO method**: selecting sums and differences (linear combinations) of atomic orbitals to generate the best approximation to each type of molecular orbital

- The general form for H_2^+

$$\psi_{MO} = C_A(R_{AB})\varphi_{1s}^A \pm C_B(R_{AB})\varphi_{1s}^B$$

ψ: generic wave function

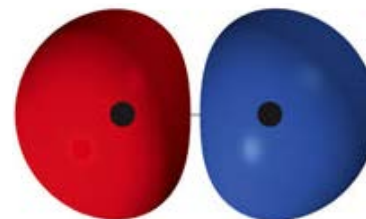φ: wave function of atomic orbitals

The two nuclei are identical, then $C_A = \pm C_B$

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➢ MOs of the σ bonding

$$1\sigma_g \approx \sigma_{g1s} = C_g\left[\varphi_{1s}^A + \varphi_{1s}^B\right]$$

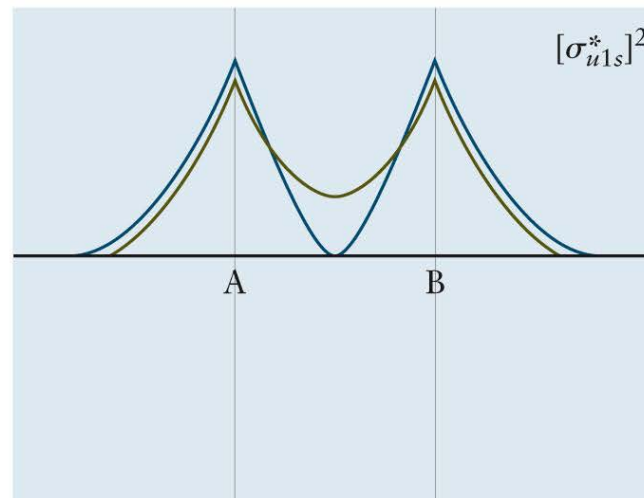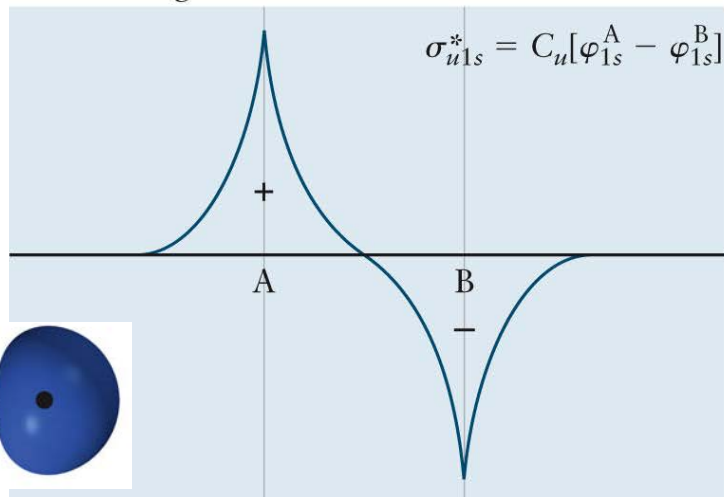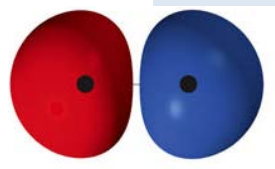$$1\sigma_u^* \approx \sigma_{u1s}^* = C_u\left[\varphi_{1s}^A - \varphi_{1s}^B\right]$$
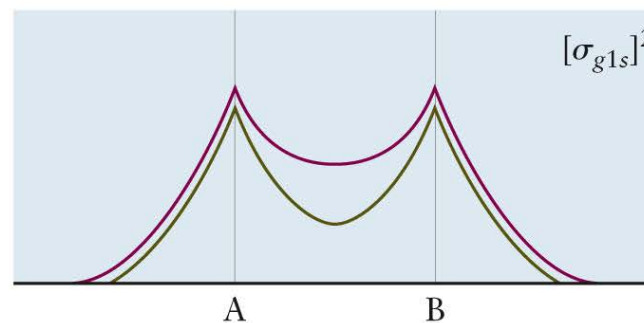
➢ The distribution of electron probability density

$$\left[\sigma_{g1s}\right]^2 = C_g^2\left[\left(\varphi_{1s}^A\right)^2 + \left(\varphi_{1s}^B\right)^2 + 2\varphi_{1s}^A\varphi_{1s}^B\right]$$

$$\left[\sigma_{u1s}^*\right]^2 = C_u^2\left[\left(\varphi_{1s}^A\right)^2 + \left(\varphi_{1s}^B\right)^2 - 2\varphi_{1s}^A\varphi_{1s}^B\right]$$

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Antibonding

$$\sigma^*_{u1s} = C_u[\varphi^A_{1s} - \varphi^B_{1s}]$$

$$[\sigma^*_{u1s}]^2$$

+

A

B

−

A

B

Bonding

$$\sigma_{g1s} = C_g[\varphi^A_{1s} + \varphi^B_{1s}]$$

$$[\sigma_{g1s}]^2$$

+

+

A

B

A

B

Noninteracting

$$\psi^2_{n.i.} = C^2_3[(\varphi^A_{1s})^2 + (\varphi^B_{1s})^2]$$

+

+

A

B

A

B
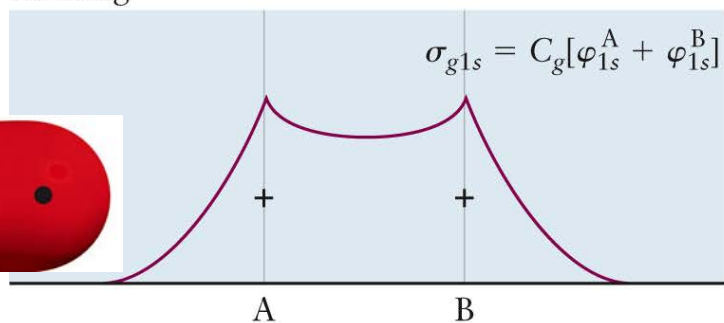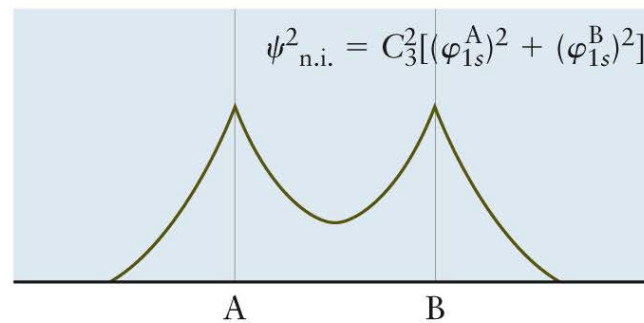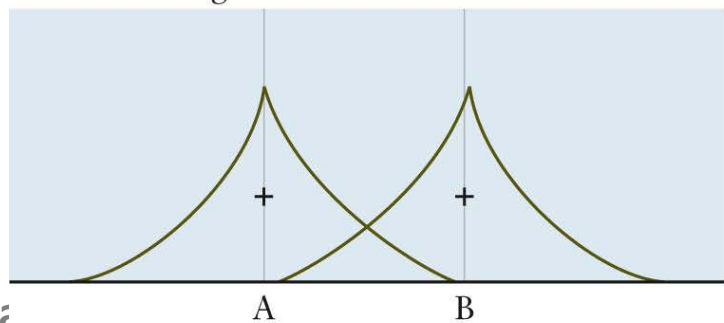
General

Wave functions

Electron densities

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T A B L E 6.1

Molecular Orbitals for Homonuclear Diatomic Molecules

Exact MO Notation	LCAO MO Notation
$1\sigma_g$	σ_{g1s}
$1\sigma_u^*$	σ_{u1s}^*
$2\sigma_g$	σ_{g2s}
$2\sigma_u^*$	σ_{u2s}^*
$1\pi_u$	$\pi_{u2p_x},\ \pi_{u2p_y}$
$3\sigma_g$	σ_{g2p_z}
$1\pi_g^*$	$\pi_{g2p_x}^*,\ \pi_{g2p_y}^*$
$3\sigma_u^*$	$\sigma_{u2p_z}^*$

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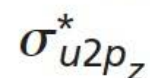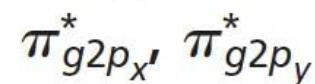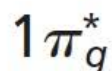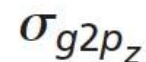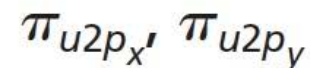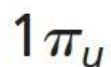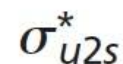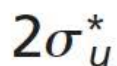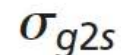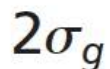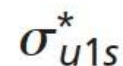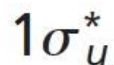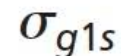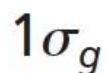
Energy of H_2^+ in the LCAO Approximation

σ_{g1s}, $R_{AB} = 1.32$ Å, D = 1.76 eV

$1\sigma_g$, $R_{AB} = 1.06$ Å, $D_0 = 2.79$ eV

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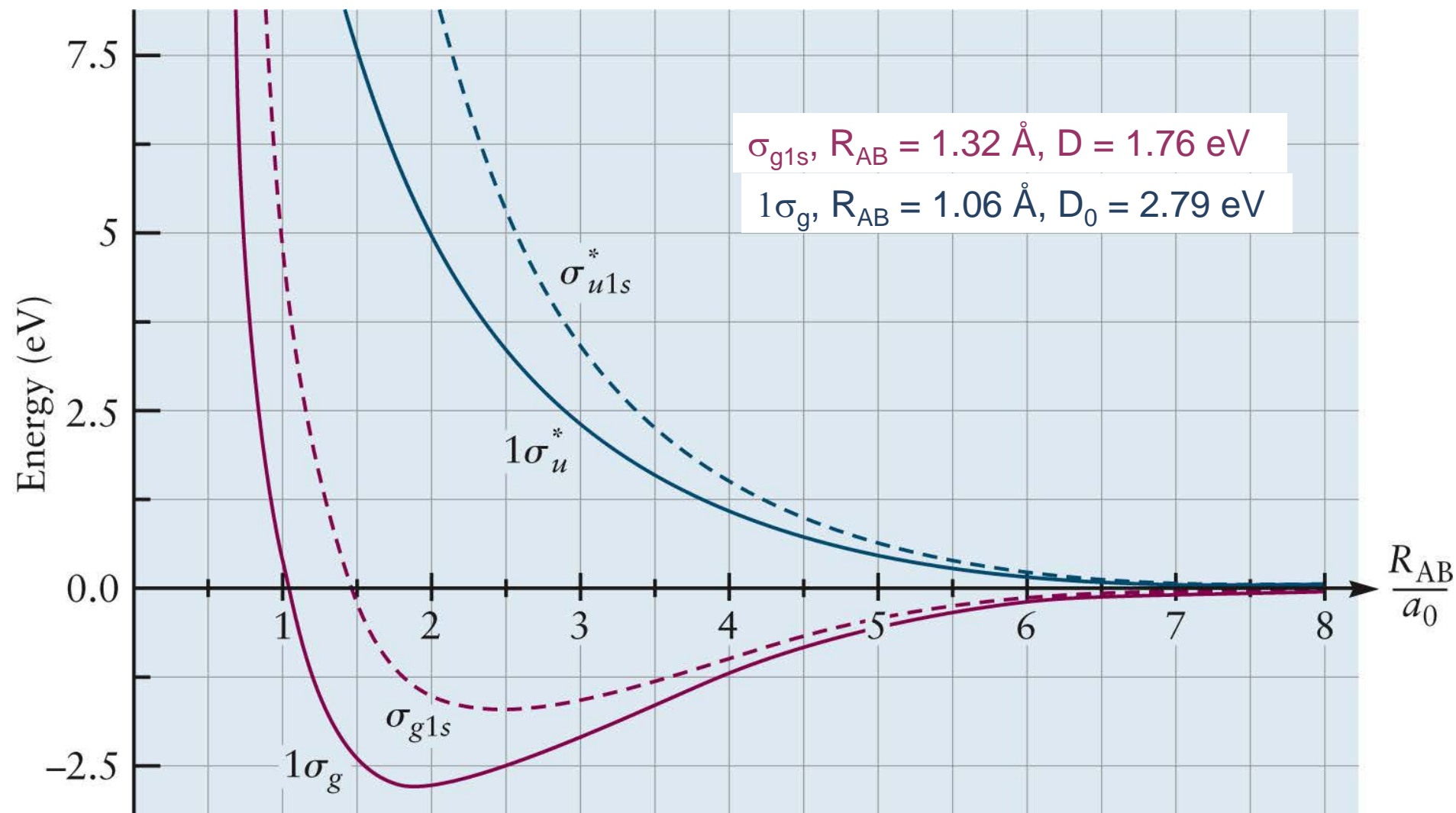
➢ **Correlation diagram**: the energy-level diagram within the LCAO
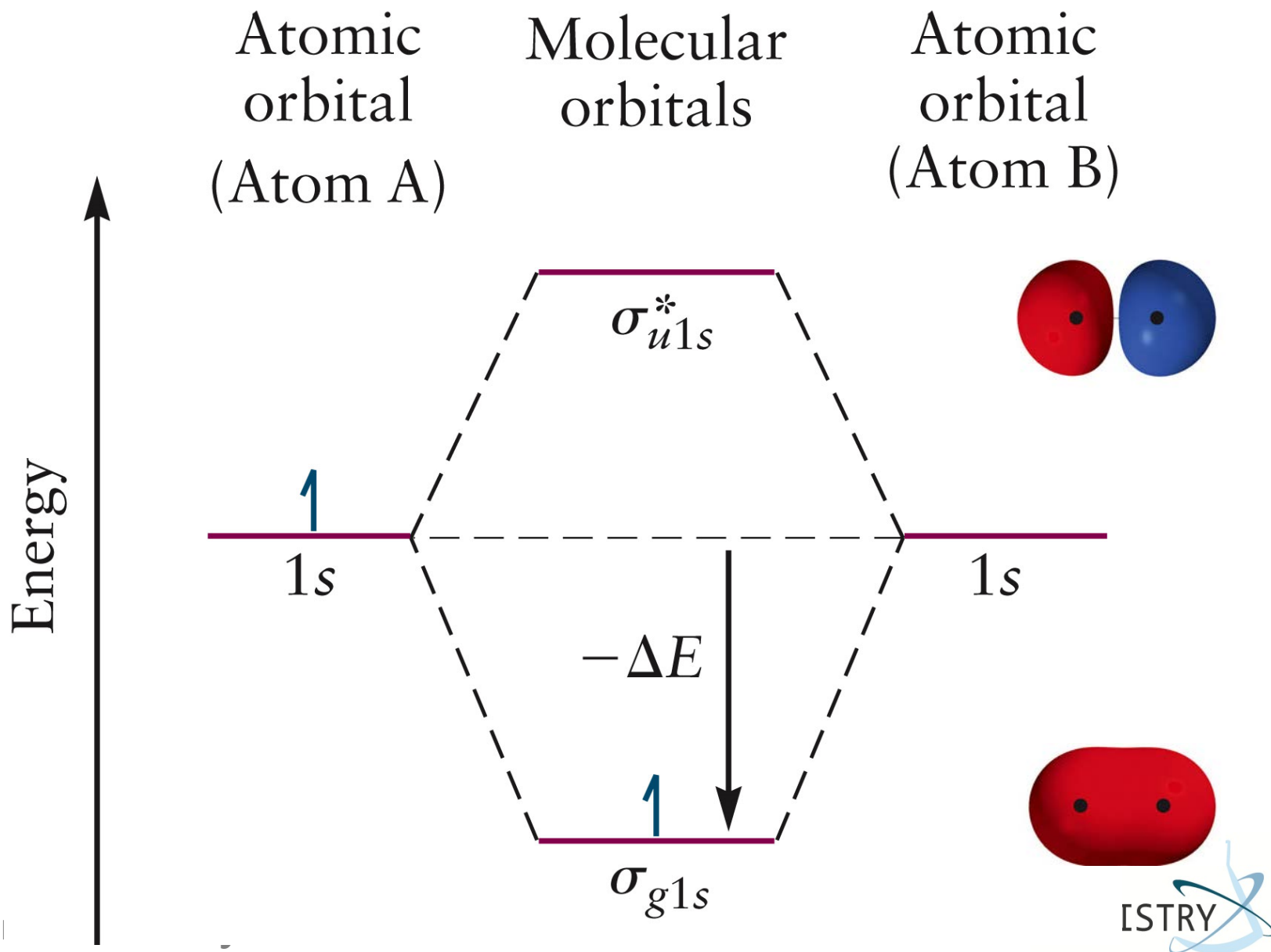
6.4 HOMONUCLEAR DIATOMIC MOLECULES: FIRST-PERIOD ATOMS

For He_2^+ and He_2,

$$\sigma_{g1s} = C_g \left[\psi_{He1s}^A + \psi_{He1s}^B \right] = C_g \left[1s^A + 1s^B \right]$$

$$\sigma_{u1s}^* = C_u \left[\psi_{He1s}^A - \psi_{He1s}^B \right] = C_g \left[1s^A - 1s^B \right]$$

Fig. 6.11. Correlation diagram for H_2.

Fig. 6.12. Correlation diagram for He_2^+.

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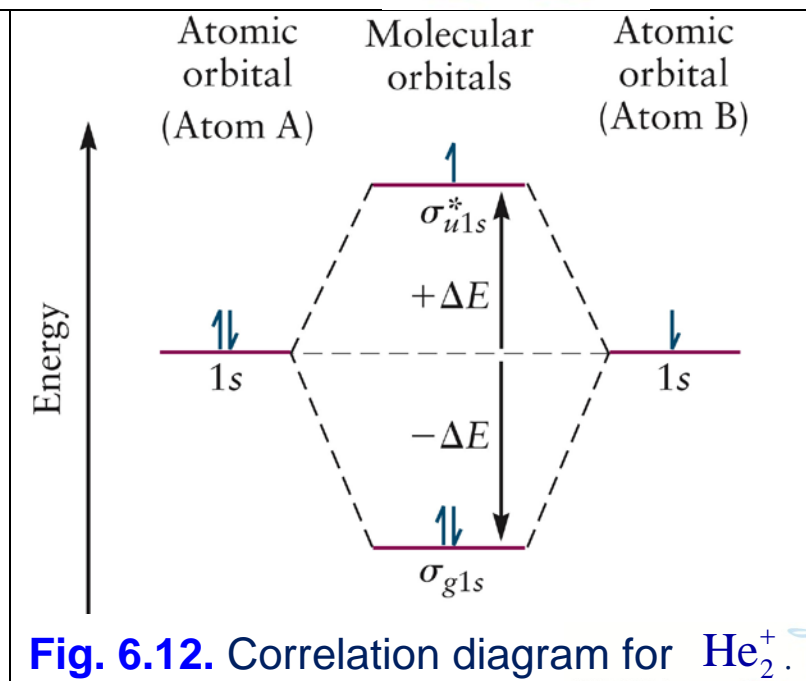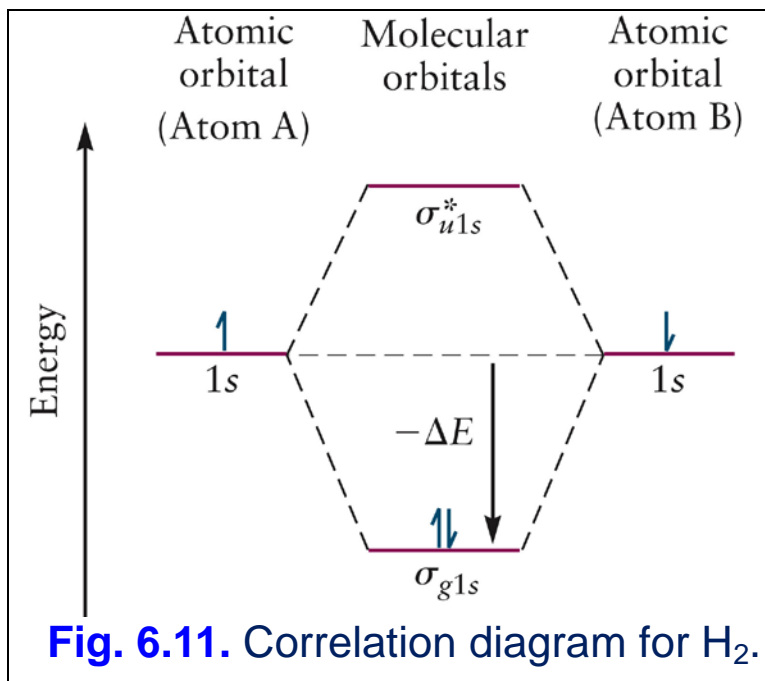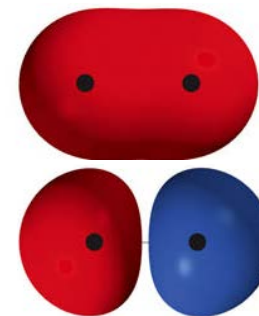
- H$_2$: Stabilization of bonding MO by $2\times(-\Delta E)$ for H$_2$ compared to the noninteracting system.
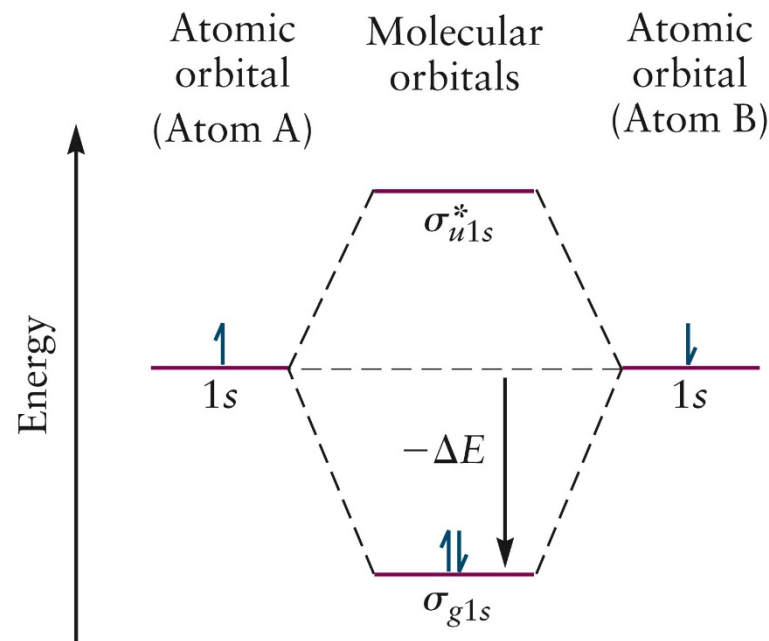
- He$_2^+$: Stabilization of bonding MO by $2\times(-\Delta E)$ compensated by destabilization of antibonding MO by $+\Delta E$.
  ➡ Net stabilization energy = $-\Delta E$

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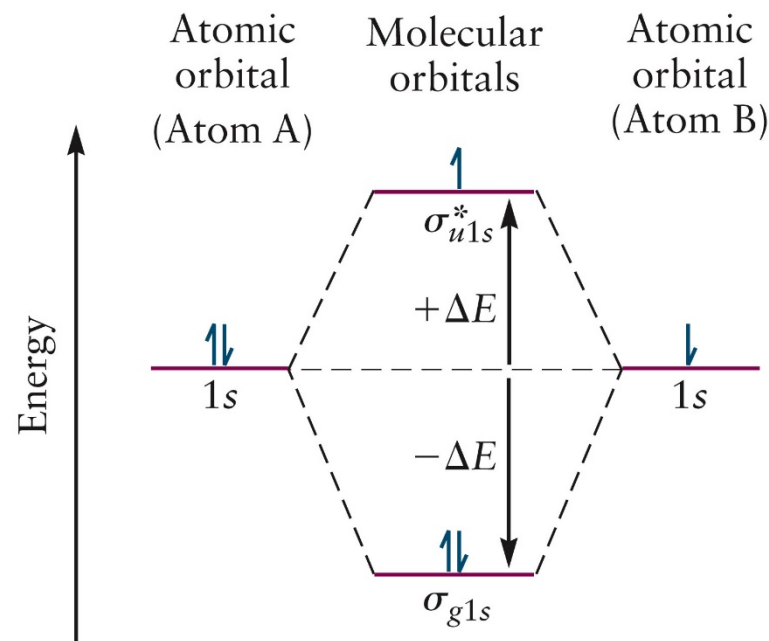
❖ Bond order

Bond order = (1/2) x (number of electrons in bonding MOs
– number of electrons in antibonding MOs)

TABLE 6.2

Electron Configurations and Bond Orders for First-Row Diatomic Molecules

Species	Electron Configuration	Bond Order	Bond Energy $(kJ\ mol^{-1})$	Bond Length $(Å)$
H_2^+	$(\sigma_{g1s})^1$	$\frac{1}{2}$	255	1.06
H_2	$(\sigma_{g1s})^2$	1	431	0.74
He_2^+	$(\sigma_{g1s})^2(\sigma_{u1s}^*)^1$	$\frac{1}{2}$	251	1.08
He_2	$(\sigma_{g1s})^2(\sigma_{u1s}^*)^2$	0	~0	Large

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6.5 HOMONUCLEAR DIATOMIC MOLECULES: SECOND-PERIOD ATOMS

◆ LCAO-MO approximation

➢ Combination of 2*s* AOs to form σ_{g2s} and σ_{u2s}* MOs

$$\sigma_{g2s} = C_g[2s^A + 2s^B]$$

$$\sigma^*_{u2s} = C_u[2s^A - 2s^B]$$

➢ Combination of 2*p*$_z$ AOs to form σ_{g2p_z} and $\sigma^*_{u2p_z}$ MOs

$$\sigma_{g2p_z} = C_g[2p_z^A - 2p_z^B]$$

$$\sigma^*_{u2p_z} = C_u[2p_z^A + 2p_z^B]$$

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(a) $+2p_z^A$ $-2p_z^B$ σ_{g2p_z} (bonding)

(b) $+2p_z^A$ $+2p_z^B$ $\sigma_{u2p_z}^*$ (antibonding)

Atomic orbitals   Molecular orbitals
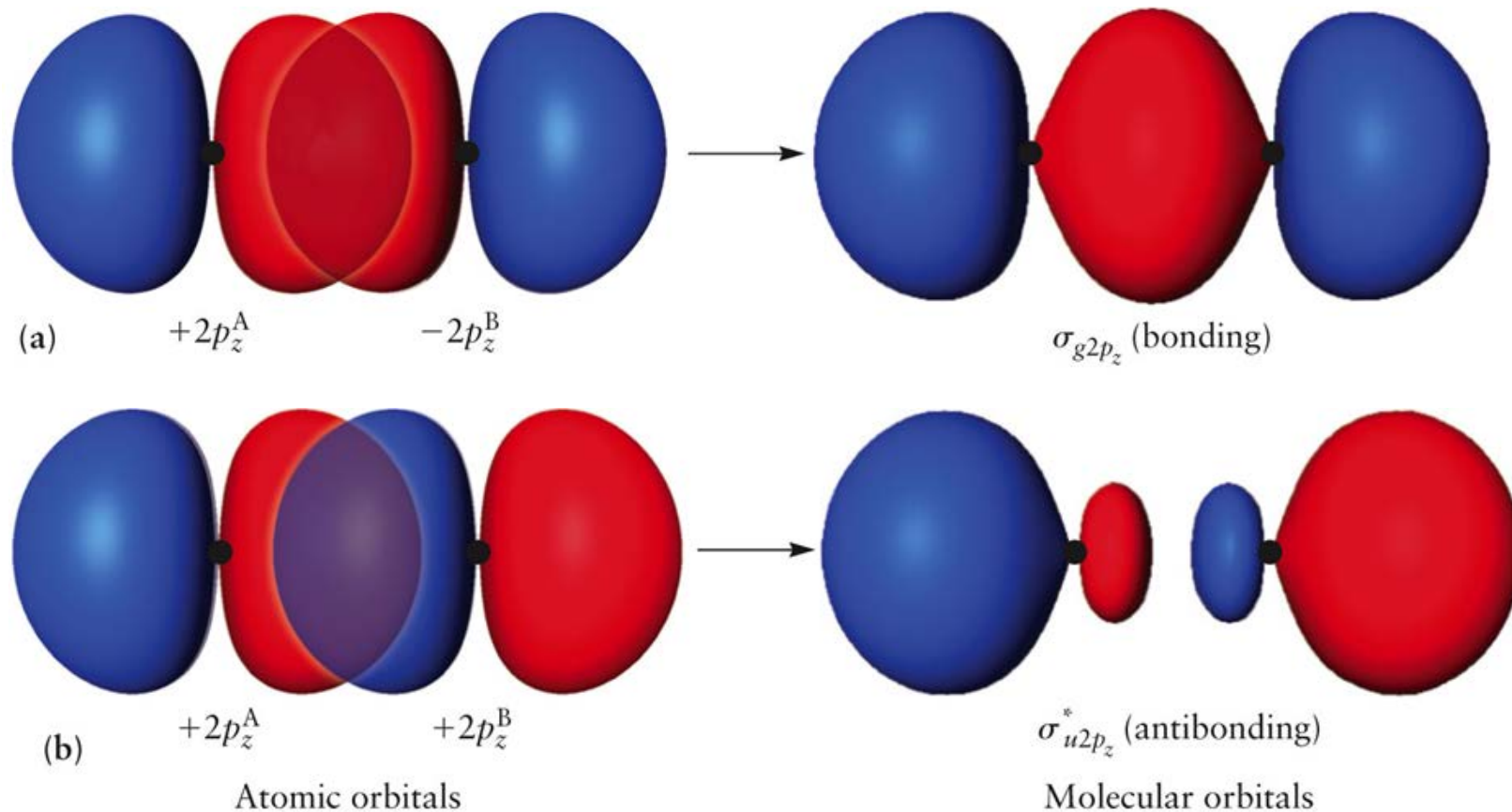
Fig. 6.14. Formation of (a) σ_{g2p_z} bonding and (b) $\sigma_{u2p_z}^*$ antibonding MOs from $2p_z$ orbitals on atoms A and B.

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➢ Doubly degenerate π_{2p_x} & π_{u2p_y} MO's

$$\pi_{u2p_x} = C_u[2p_x^A + 2p_x^B]$$

$$\pi_{g2p_x}^* = C_g[2p_x^A - 2p_x^B]$$

$$\pi_{u2p_y} = C_u[2p_y^A + 2p_y^B]$$

$$\pi_{g2p_y}^* = C_g[2p_y^A - 2p_y^B]$$

$+2p_x^A \qquad +2p_x^B$

(a)

π_{u2p_x} (bonding)

$+2p_x^A \qquad -2p_x^B$

Atomic orbitals

(b)

$\pi_{g2p_x}^*$ (antibonding)

Molecular orbitals

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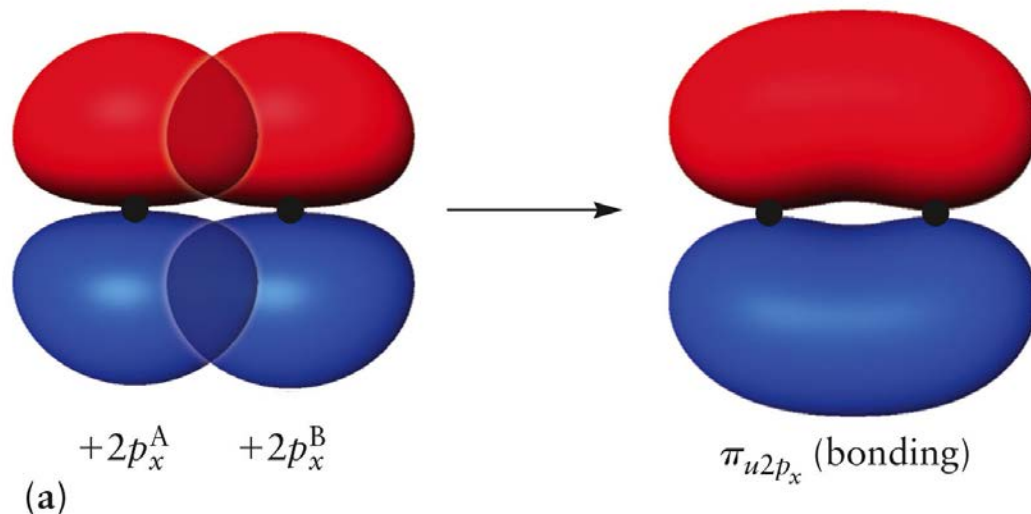
➢ Construction of MOs

1. Two AOs contribute significantly to bond formation only if their atomic energy levels are very close to one another

2. Two AOs on different atoms contribute significantly to bond formation only if they overlap significantly

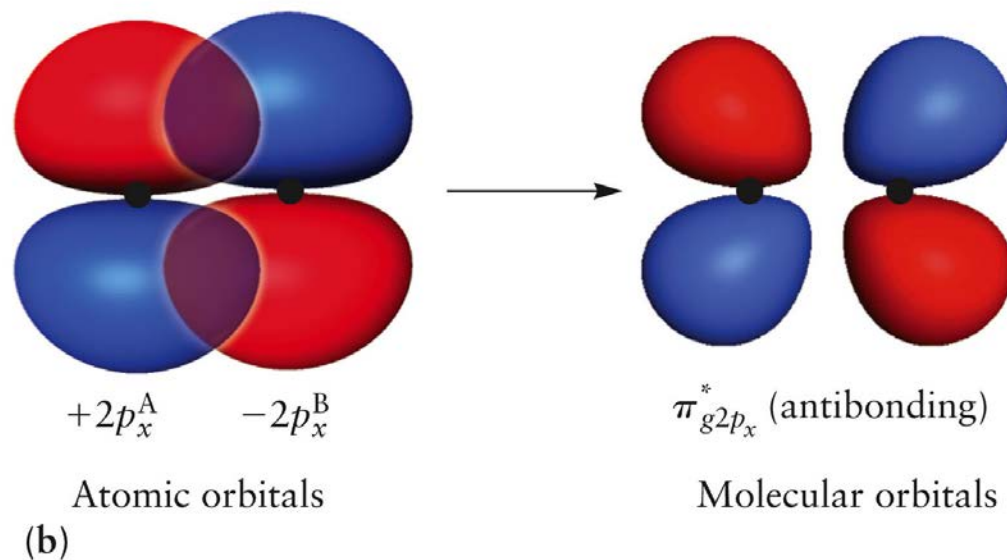➢ Determination of energy ordering

1. Average energy of bonding-antibonding pair of MOs similar to that of original AO's

2. Energy difference between a bonding-antibonding pair becomes large as the overlap of AO's increases

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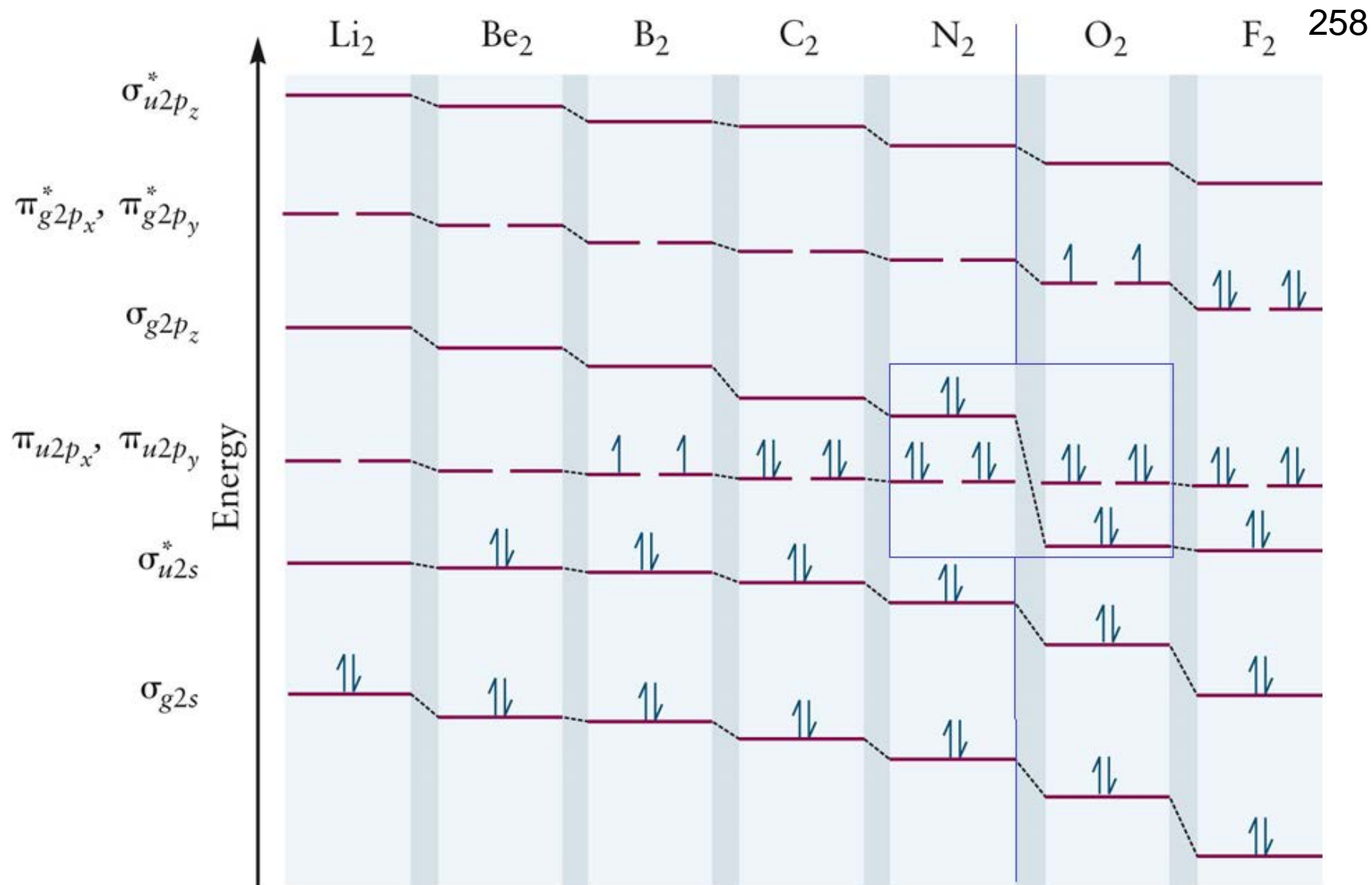
Fig. 6.16. Energy levels for the homonuclear diatomics Li_2 through F_2.

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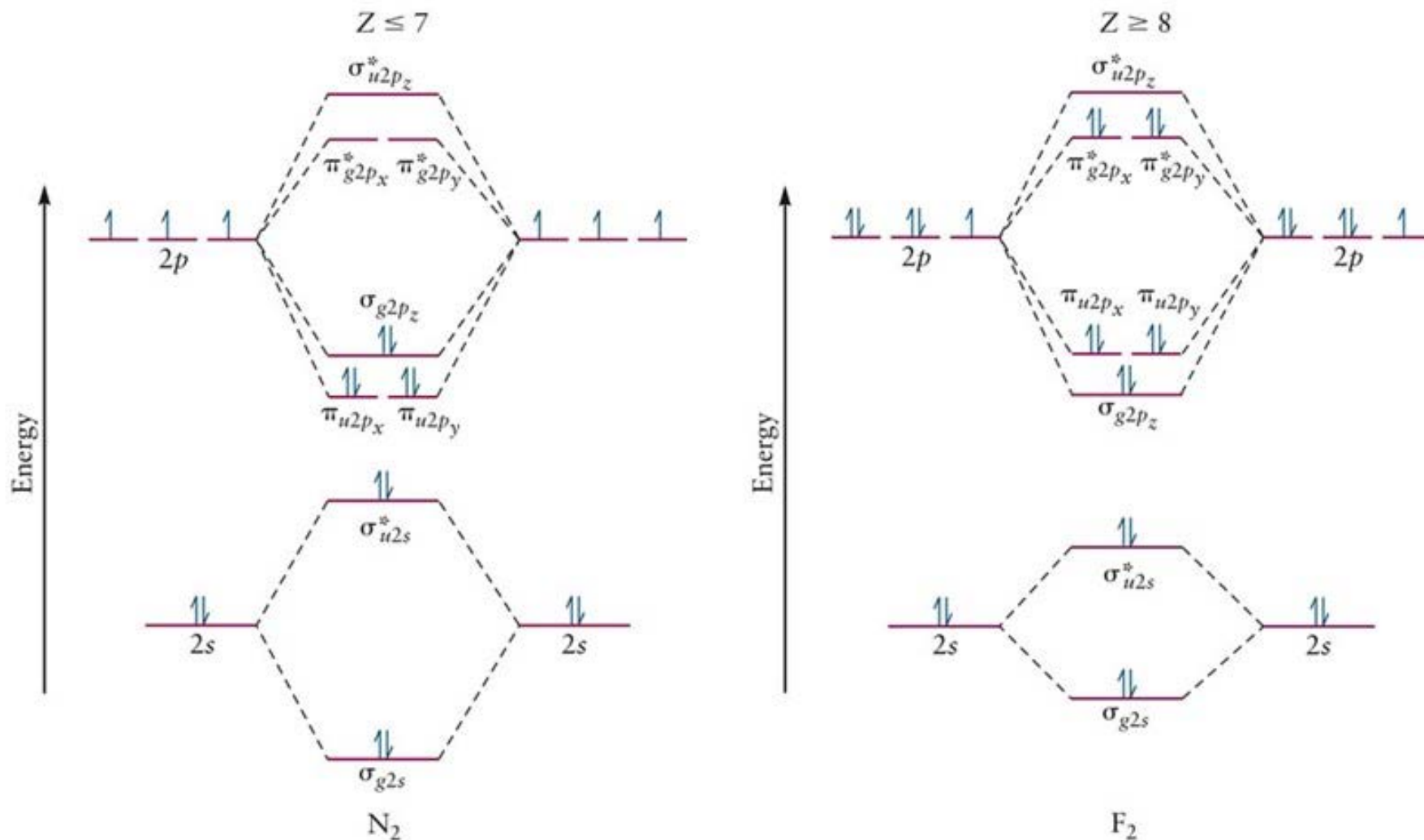
Fig. 6.17. Correlation diagrams for second-period diatomic molecules, N_2 & F_2.

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$Z \leq 7$

$\sigma^*_{u2p_z}$

$\pi^*_{g2p_x}$ $\pi^*_{g2p_y}$

$2p$

σ_{g2p_z}

π_{u2p_x} π_{u2p_y}

σ^*_{u2s}

$2s$ $2s$

σ_{g2s}

N_2

Energy

$\sigma^*_{u2p_z}$

$\pi^*_{g2p_x}, \pi^*_{g2p_y}$

σ_{g2p_z}

π_{u2p_x}, π_{u2p_y}

σ^*_{u2s}

σ_{g2s}

(a)

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$Z \geq 8$

$\sigma^*_{u2p_z}$

$\pi^*_{g2p_x}$ $\pi^*_{g2p_y}$

$2p$ $2p$

π_{u2p_x} π_{u2p_y}

σ_{g2p_z}

Energy

σ^*_{u2s}

$2s$ $2s$

σ_{g2s}

F_2

$\sigma^*_{u2p_z}$

$\pi^*_{g2p_x}$, $\pi^*_{g2p_y}$

π_{u2p_x}, π_{u2p_y}

σ_{g2p_z}

σ^*_{u2s}

σ_{g2s}

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(b)
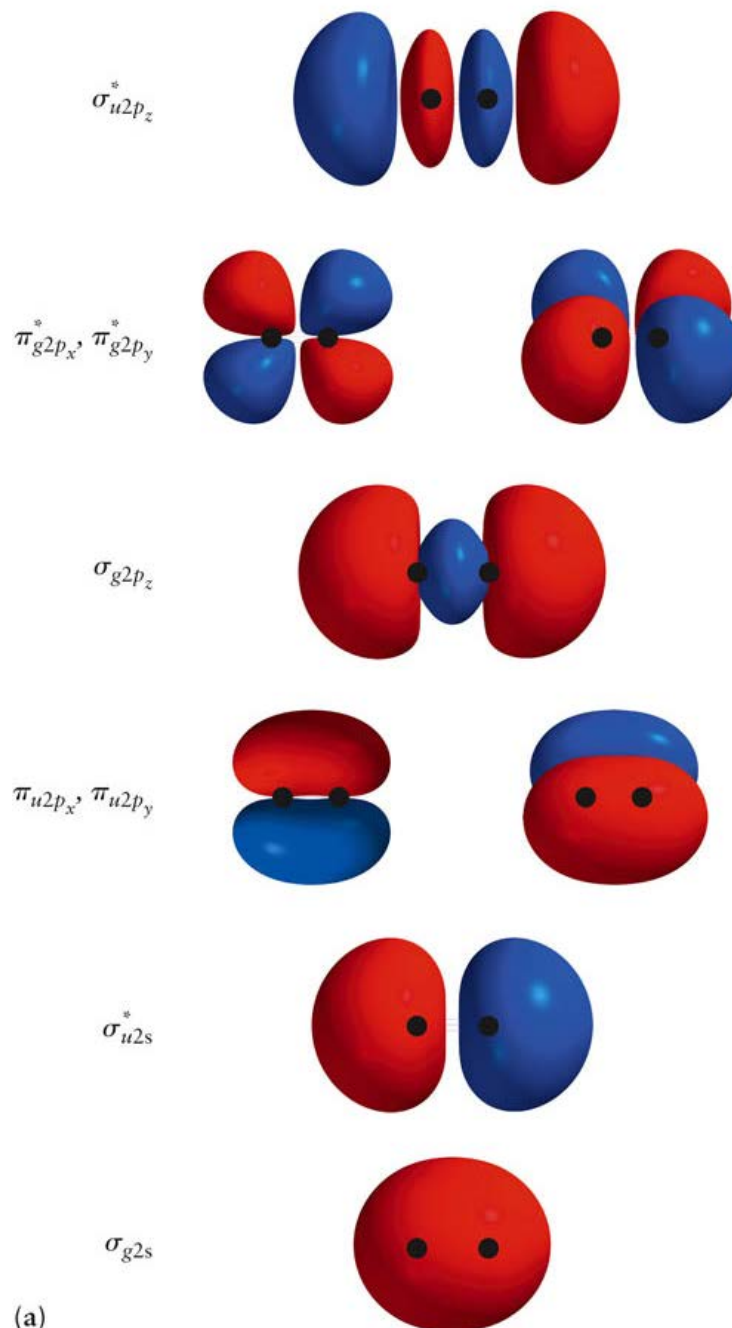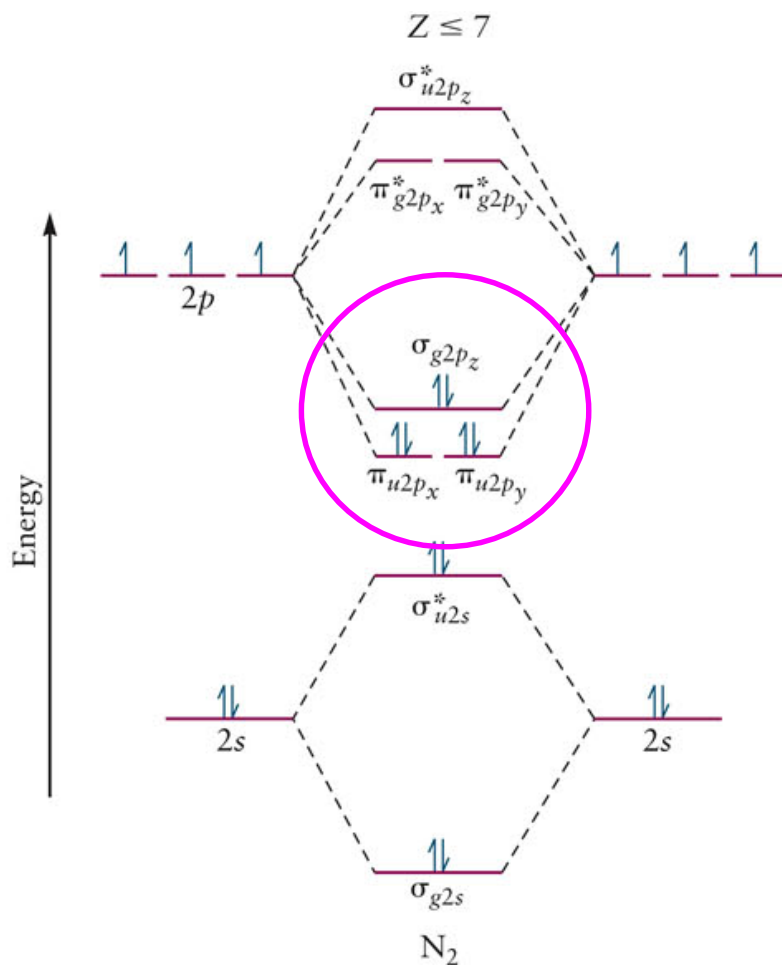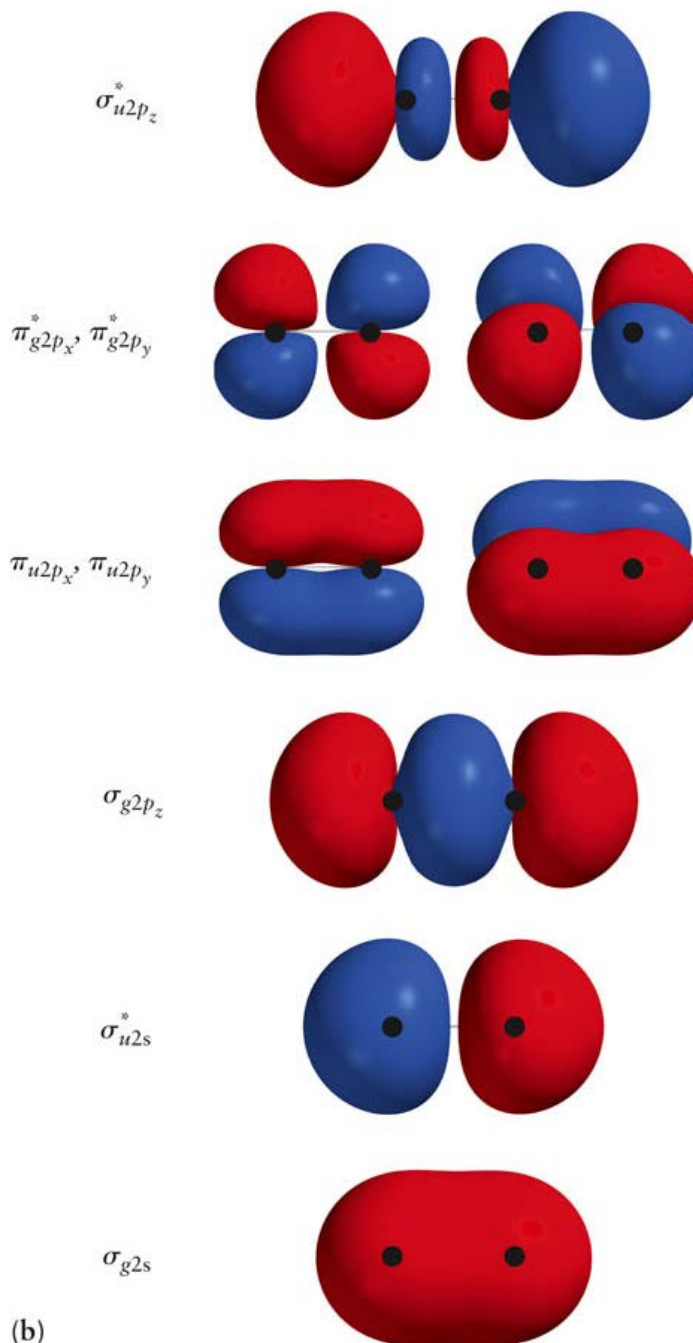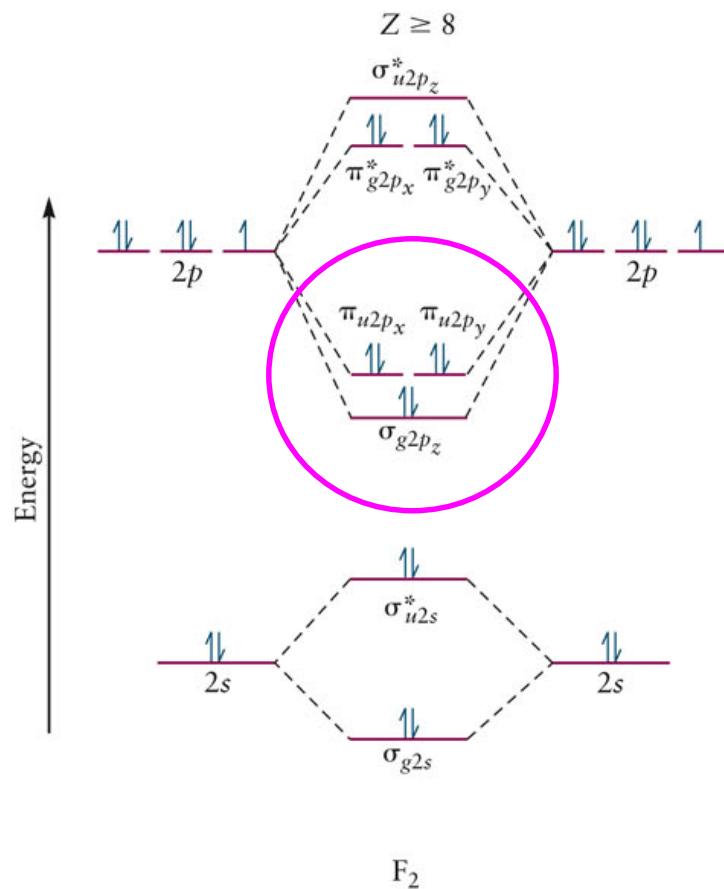
◆ **Cross-over in the correlation diagrams of Li$_2$~N$_2$ and O$_2$~Ne$_2$**

➢ Reversed ordering of energy for Li$_2$ ~ N$_2$

$$\sigma_{g2p_z} > \pi_{u2p_x}(\text{or } \pi_{u2p_y})$$

~ Due to large electron-electron spatial repulsions between electrons in σ_{g2p_z} and σ_{u2s}^* MO's.

➢ Normal ordering of energy for O$_2$, F$_2$, Ne$_2$

$$\sigma_{g2p_z} < \pi_{u2p_x}(\text{or } \pi_{u2p_y})$$

~ As Z increases, the repulsion decreases since electrons in σ_{g2s} and σ_{u2s}^* MO's are drawn more strongly toward the nucleus.
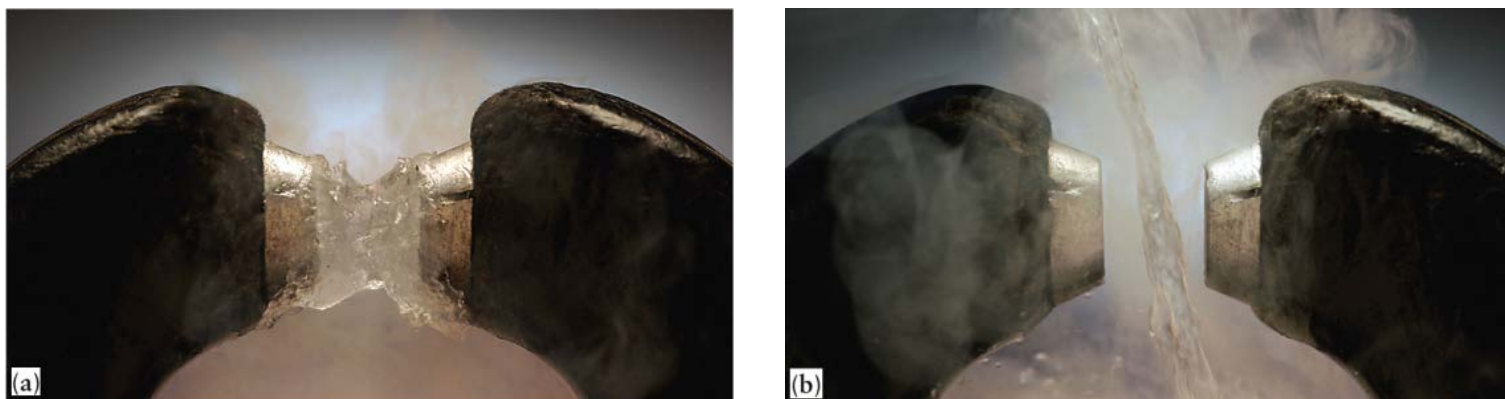
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Fig. 6.18. (a) Paramagnetic liquid oxygen, O_2, and (b) diamagnetic liquid nitrogen, N_2, pours straight between the poles of a magnet.

T A B L E 6.3

Molecular Orbitals of Homonuclear Diatomic Molecules

Species	Number of Valence Electrons	Valence Electron Configuration	Bond Order	Bond Length (Å)	Bond Energy (kJ mol^{-1})
H_2	2	$(\sigma_{g1s})^2$	1	0.74	431
He_2	4	$(\sigma_{g1s})^2(\sigma^*_{u1s})^2$	0		
Li_2	2	$(\sigma_{g2s})^2$	1	2.67	105
Be_2	4	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2$	0	2.45	9
B_2	6	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\pi_{u2p})^2$	1	1.59	289
C_2	8	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\pi_{u2p})^4$	2	1.24	599
N_2	10	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\pi_{u2p})^4(\sigma_{g2p_z})^2$	3	1.10	942
O_2	12	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\sigma_{g2p_z})^2(\pi_{u2p})^4(\pi^*_{g2p})^2$	2	1.21	494
F_2	14	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\sigma_{g2p_z})^2(\pi_{u2p})^4(\pi^*_{g2p})^4$	1	1.41	154
Ne_2	16	$(\sigma_{g2s})^2(\sigma^*_{u2s})^2(\sigma_{g2p_z})^2(\pi_{u2p})^4(\pi^*_{g2p})^4(\sigma^*_{u2p_z})^2$	0		

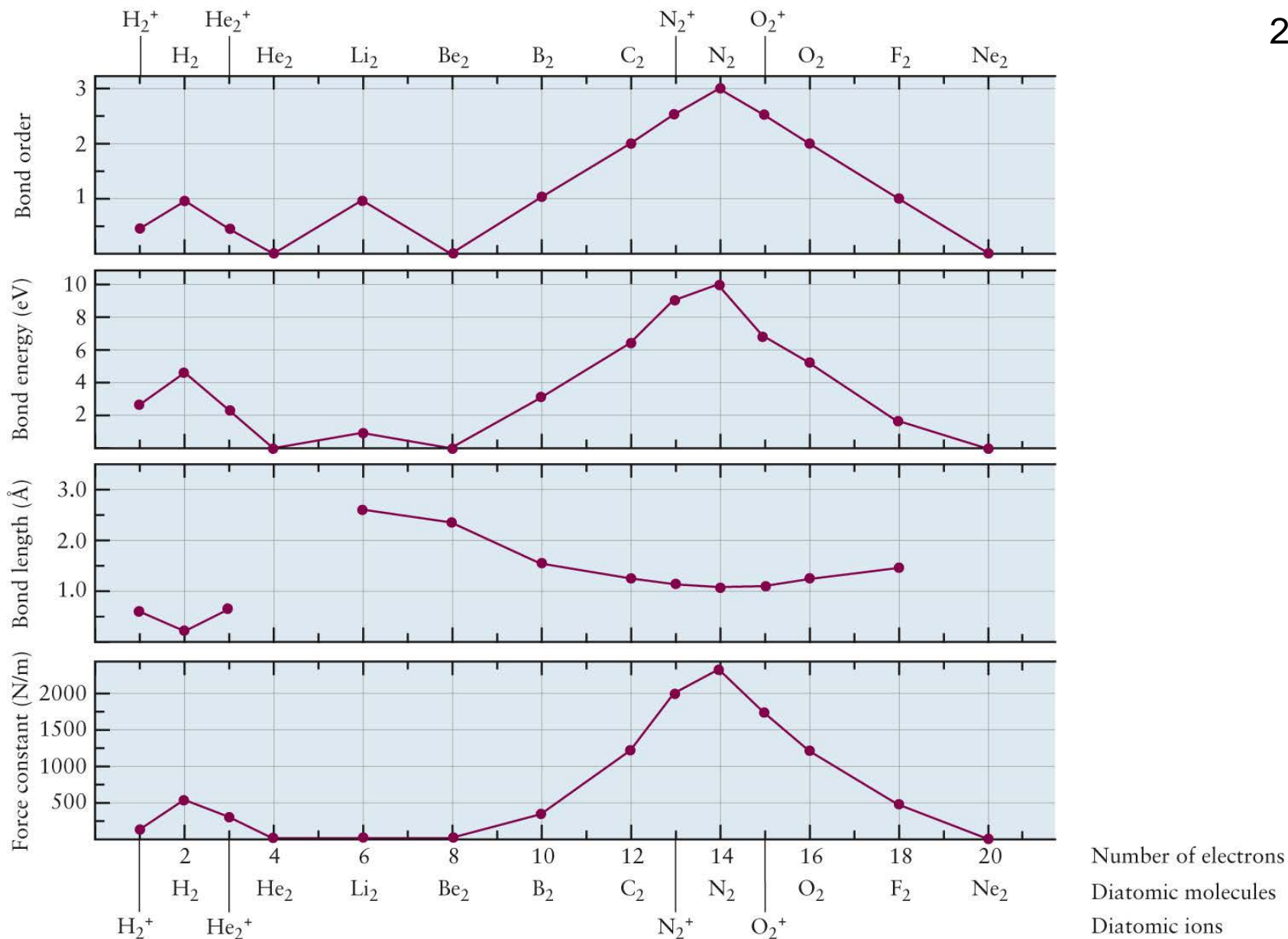π_{u2p} refers to the π orbitals constructed from the $2p_x$ and/or the $2p_y$ orbitals.

Fig. 6.19. Trends in several properties with the number of valence electrons in the second-row diatomic molecules.

6 QUANTUM MECHANICS AND MOLECULAR STRUCTURE

CHAPTER

General Chemistry I

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6.8 VALENCE BOND THEORY AND THE ELECTRON PAIR BOND

➢ Explains the Lewis electron pair model

➢ VB wave function for the bond is a product of two one-electron AOs

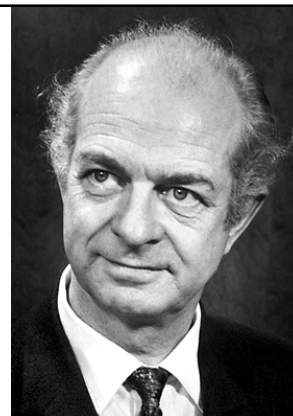➢ Easily describes structure and geometry of bonds in polyatomic molecules

Nobel Prizes

Chemistry ('54) "The Nature of Chemical Bonding"

Peace ('62)

Walther Heitler (DE, 1904-1981)   Fritz London (DE, 1900-1954)   John C. Slater (US, 1900-1976)   Linus Pauling (US,1901-1994)

$$\sigma_{g2s} = C_g[2s^A + 2s^B]$$

$$\sigma_{u2s}^* = C_u[2s^A - 2s^B]$$

➢ **Single Bonds**

- At very large values of R_{AB},

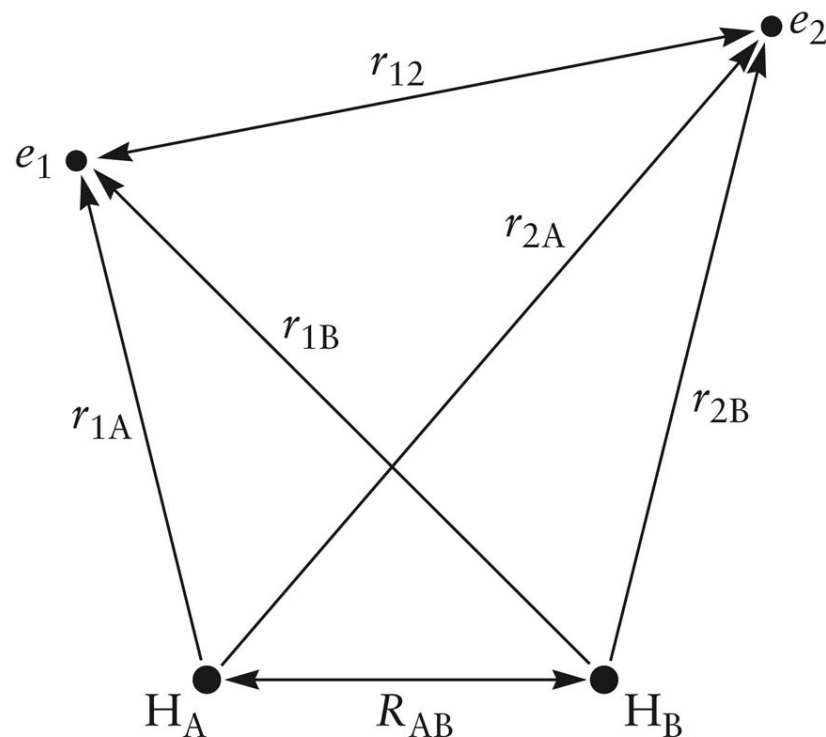$$\psi^{el}(r_{1A}, r_{2B}; R_{AB})$$
$$= c(R_{AB})\varphi^A(r_{1A})\varphi^B(r_{2B})$$

independent atoms

- As the atoms begin to interact strongly,

$$\psi^{el}(r_{1A}, r_{2B}; R_{AB})$$
$$= c_1(R_{AB})\varphi^A(r_{1A})\varphi^B(r_{2B})$$
$$+ c_2(R_{AB})\varphi^A(r_{2A})\varphi^B(r_{1B})$$

indistinguishable

$$c_1 = \pm c_2$$

General Chemistry I

(b)

➢ **VB wave function for the single bond in a H$_2$ molecule**

$$\psi_g^{el} = C_1\left[1s^A(1)1s^B(2) + 1s^A(2)1s^B(1)\right]$$

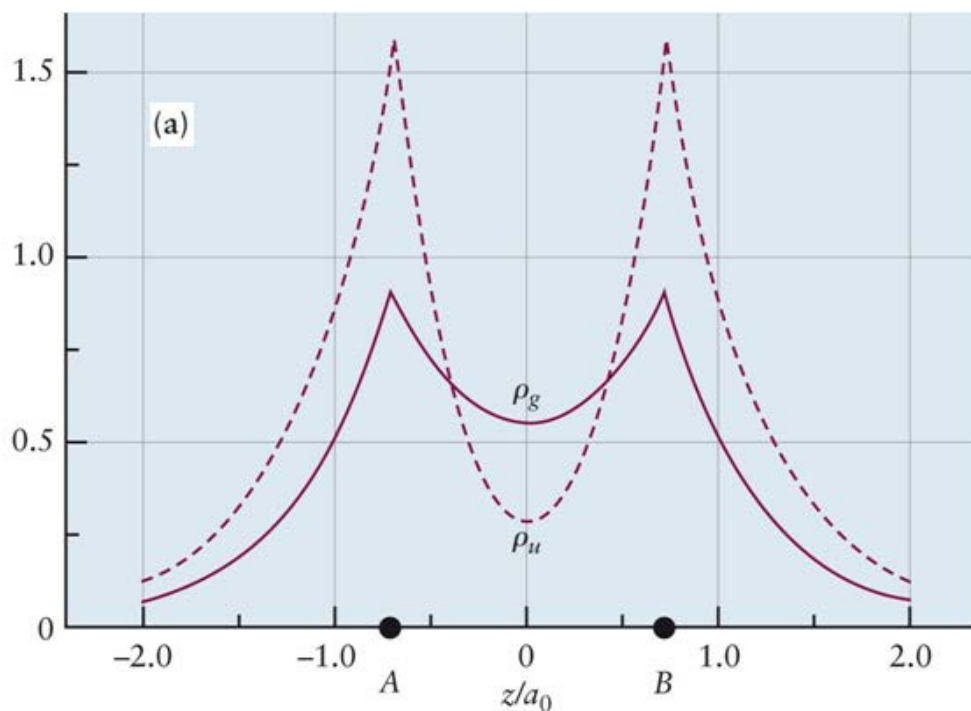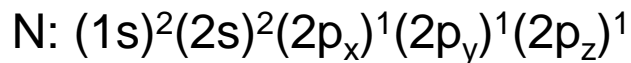$$\psi_u^{el} = C_1\left[1s^A(1)1s^B(2) - 1s^A(2)1s^B(1)\right]$$

Fig. 6.24. (a) The electron density ρ_g for ψ_g^{el} and ρ_u for ψ_u^{el} in the simple VB model for H$_2$. (b) Three-dimensional isosurface of the electron density for the ψ_g^{el} wave function in the H$_2$ σ bond.
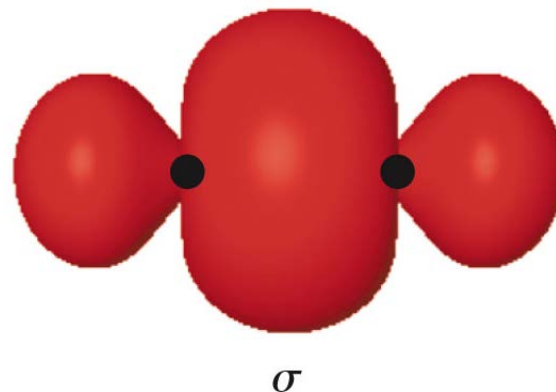
➢ **For F$_2$ σ bond,**

$$\psi_g^{bond} = C_1[2p_z^A(1)2p_z^B(2) + 2p_z^A(2)2p_z^B(1)]$$

F   F

:F̈:F̈:

Lewis diagram for F$_2$.

➢ **For HF σ bond,**

$$\psi^{bond} = C_1[2p_z^F(1)1s^H(2)] + C_2[2p_z^F(2)1s^H(1)]$$

H   F

General Chemistry I

➢ **Multiple Bonds**
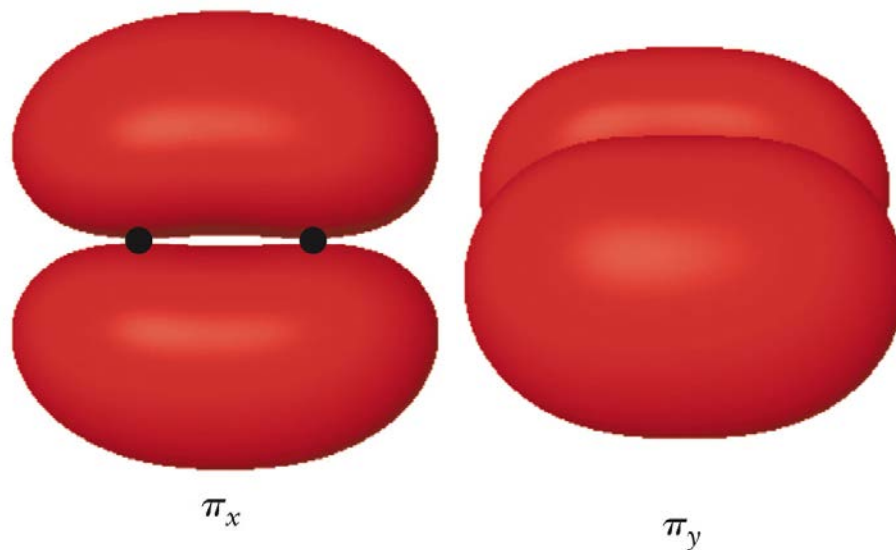
N: $(1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1$

:N:::N:

Lewis diagram for N_2.

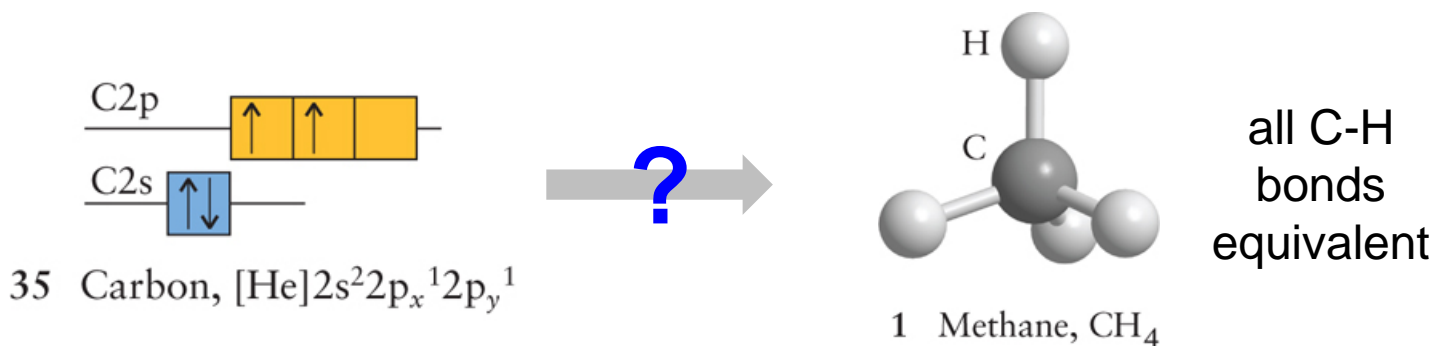$$\psi_\sigma^{bond} = C_1[2p_z^A(1)2p_z^B(2) + 2p_z^A(2)2p_z^B(1)]$$

σ

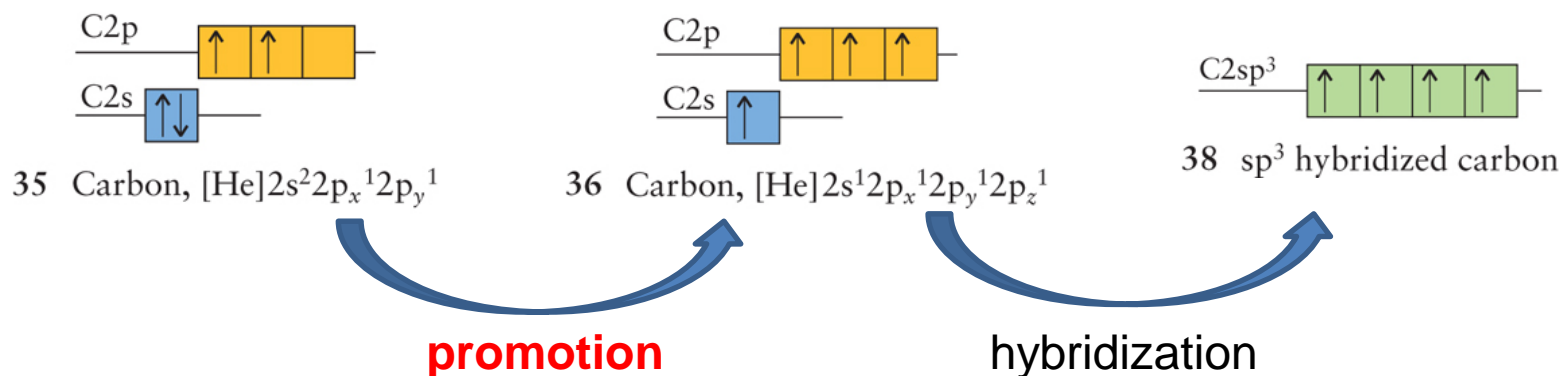$$\psi_{\pi_x}^{bond}(1,2) = C_1[2p_x^A(1)2p_x^B(2)] + C_1[2p_x^A(2)2p_x^B(1)]$$

$$\psi_{\pi_y}^{bond}(1,2) = C_1[2p_y^A(1)2p_y^B(2)] + C_1[2p_y^A(2)2p_y^B(1)]$$

π_x π_y

General Chemistry I

➢ **Polyatomic Molecules**

35 Carbon, [He]$2s^2 2p_x^1 2p_y^1$

1 Methane, CH_4

all C-H bonds equivalent

➢ **Electron promotion**: electron relocated to a higher-energy orbital

35 Carbon, [He]$2s^2 2p_x^1 2p_y^1$

36 Carbon, [He]$2s^1 2p_x^1 2p_y^1 2p_z^1$

38 sp^3 hybridized carbon

promotion   hybridization

General Chemistry I

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6.9 ORBITAL HYBRIDIZATION FOR POLYATOMIC MOLECULES

➢ **sp-hybridization**   BeH$_2$

Promotion: Be: $(1s)^2(2s)^2 \rightarrow$ Be: $(1s)^2(2s)^1(2p_z)^1$

Two equivalent **sp hybrid orbitals**:

$$\chi_1(r) = \frac{1}{\sqrt{2}}\left[2s + 2p_z\right] \text{ and } \chi_2(r) = \frac{1}{\sqrt{2}}\left[2s - 2p_z\right]$$

New electronic configuration, Be: $(1s)^2(\chi_1)^1(\chi_2)^1$

Wave functions for the two bonding pairs of electrons:

$$\psi_{\sigma 1}^{\text{bond}}(1,2) = c_+\left[\chi_1(1)1s^{\text{H}}(2) + \chi_1(2)1s^{\text{H}}(1)\right]$$

$$\psi_{\sigma 2}^{\text{bond}}(3,4) = c_-\left[\chi_2(3)1s^{\text{H}}(4) + \chi_2(4)1s^{\text{H}}(3)\right]$$

A pair of σ bonds at an angle 180° apart $\rightarrow$ linear molecule

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2s

2p$_z$

(a) Atomic orbitals   (b) *sp* hybrid orbitals   (c) Hybrid orbital overlap   (d) Electron density
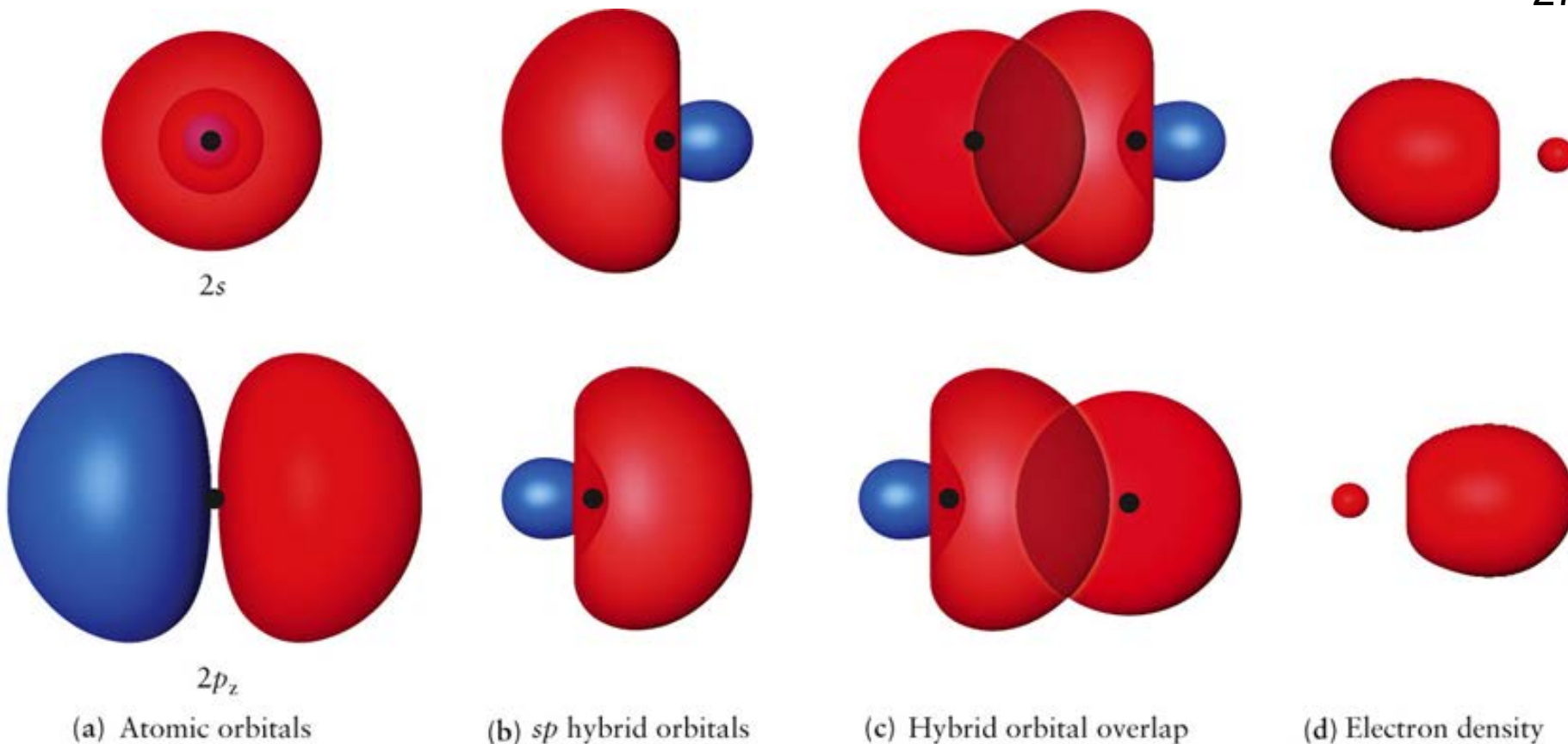
Fig. 6.28. Formation, shapes, and bonding of the *sp* hybrid orbitals in the BeH$_2$ molecule. (a) The 2*s* and 2*p$_z$* orbitals of the Be atom. (b) The two *sp* hybrid orbitals formed from the 2*s* and 2*p$_z$* orbitals on the Be atom. (c) The two σ bonds that form from the overlap of the *sp* hybrid orbitals with the H1*s* orbitals, making tow single bonds in the BeH$_2$ molecule. (d) Electron density in the two σ bonds.

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➢ **_sp²_-hybridization** BH_3

Promotion: B: $(1s)^2(2s)^2(2p_x)^1 \rightarrow$ B: $(1s)^2(2s)^1(2p_x)^1(2p_y)^1$
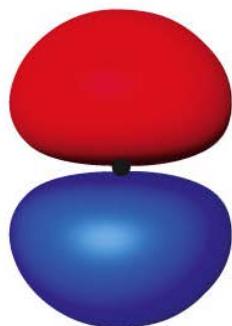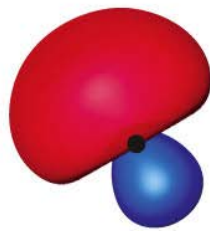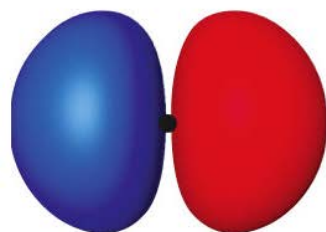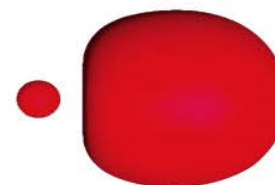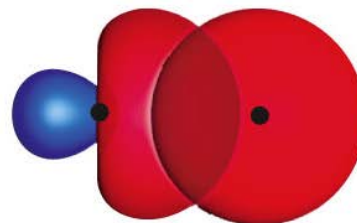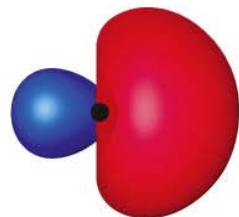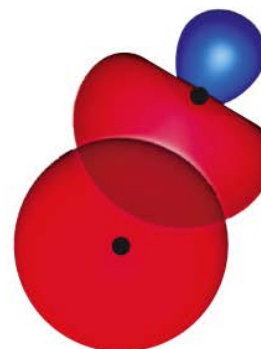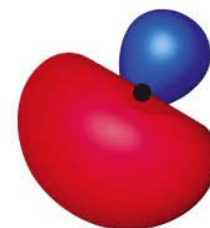
Three equivalent _sp²_ hybrid orbitals:

$$\chi_1(r) = 2s + 2^{1/2}2p_y$$

$$\chi_2(r) = 2s + (3/2)^{1/2}2p_x - (1/2)^{1/2}2p_y$$

$$\chi_3(r) = 2s - (3/2)^{1/2}2p_x - (1/2)^{1/2}2p_y$$

New electronic configuration, B: $(1s)^2(\chi_1)^1(\chi_2)^1(\chi_3)^1$

Three bonds at an angle 120° in a plane → trigonal planar

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Gen (a) Atomic orbitals   (b) sp^2 hybrid orbitals   (c) Hybrid orbital overlap   (d) Electron density

➢ **sp^3-hybridization** CH_4

Promotion: C: $(1s)^2(2s)^2(2p_x)^1(2p_y)^1 \rightarrow$ C: $(1s)^2(2s)^1(2p_x)^1(2p_y)^1(2p_z)^1$

Four equivalent sp^3 hybrid orbitals:

$$\chi_1(r) = \frac{1}{2}\left[2s + 2p_x + 2p_y + 2p_z\right]$$

$$\chi_2(r) = \frac{1}{2}\left[2s - 2p_x - 2p_y + 2p_z\right]$$

$$\chi_3(r) = \frac{1}{2}\left[2s + 2p_x - 2p_y - 2p_z\right]$$

$$\chi_4(r) = \frac{1}{2}\left[2s - 2p_x + 2p_y - 2p_z\right]$$

New electronic configuration, C: $(1s)^2(\chi_1)^1(\chi_2)^1(\chi_3)^1(\chi_4)^1$

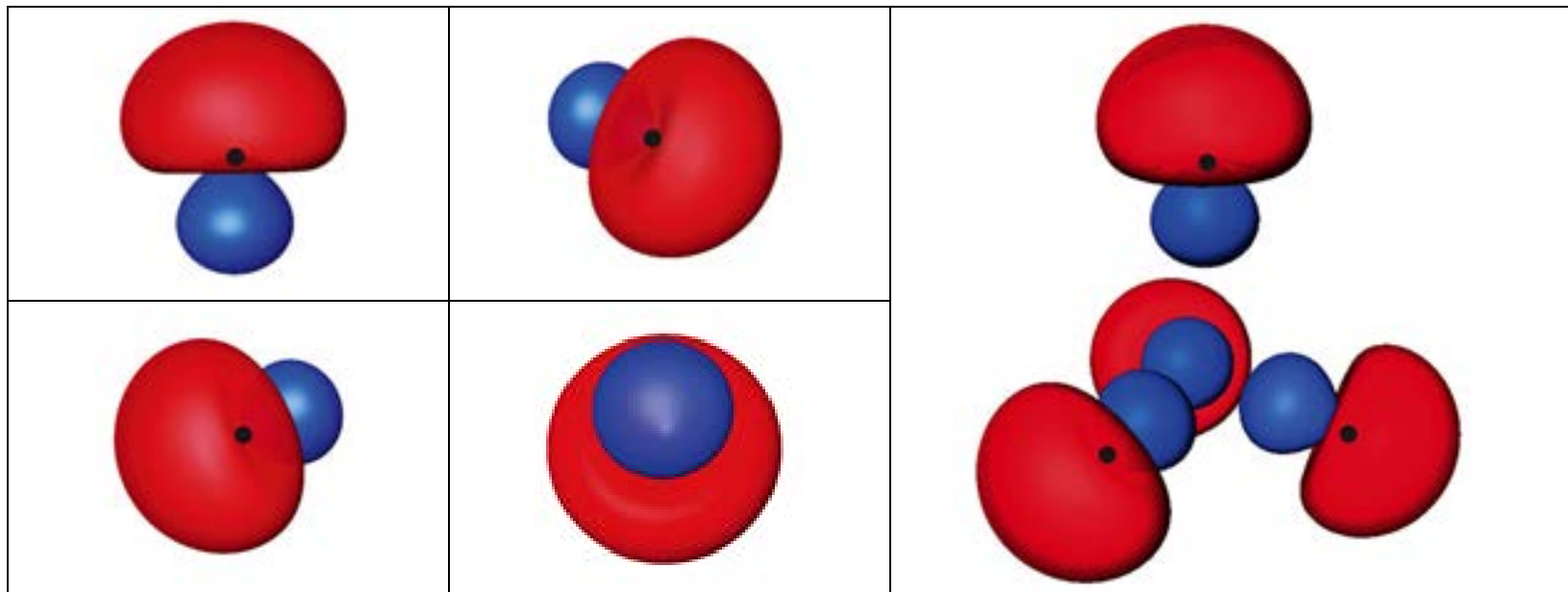Four bonds at an angle 109.5° generating tetrahedral geometry

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Fig. 6.30. Shapes and relative orientations of the four sp^3 hybrid orbitals in CH_4 pointing at the corners of a tetrahedron with the C atom at its center.

General Chemistry I

Summary of Hybridization Results

T A B L E 6.4

Orbital Hybridization and Molecular Geometry

Molecule	Hybrid orbitals on central atom	Molecular geometry	Example
AX_2	sp	Linear	BeH_2
AX_3	sp^2	Trigonal planar	BH_3
AX_4	sp^3	Tetrahedral	CH_4

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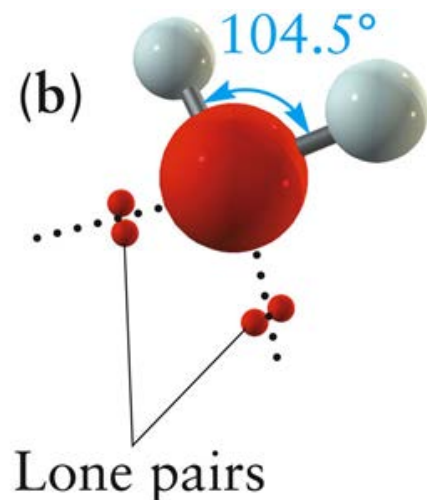# Hybridization and Lone Pairs

➢ **NH$_3$**: sp^3 hybrid orbitals

    trigonal pyramid with three equivalent bonds
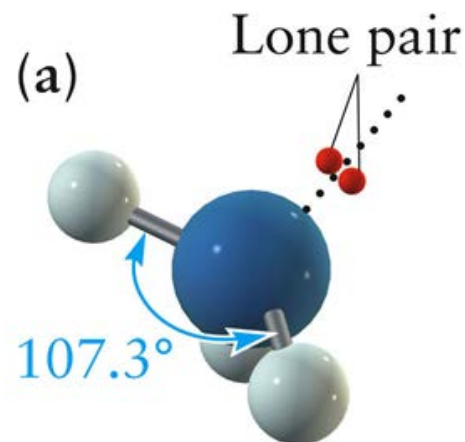
➢ **H$_2$O**: sp^3 hybrid orbitals

    two lone pairs → the bent or angular structure

(a) Lone pair

107.3°

(b) 104.5°

Lone pairs

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➢ **Multiple Bonds in Organic Compounds**

❖ **Ethylene, C_2H_4**

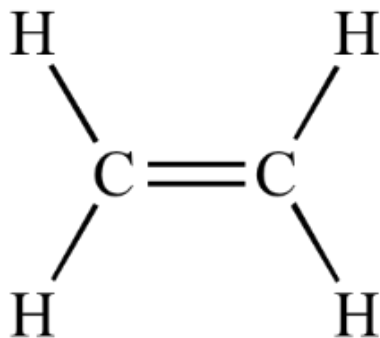Promotion, C: $(1s)^2(2s)^2(2p_x)^1(2p_y)^1 \rightarrow$ C: $(1s)^2(2s)^1(2p_x)^1(2p_y)^1(2p_z)^1$

Formation of three sp^2 hybrid orbitals from the 2s and two 2p orbitals

New electronic configuration, C: $(1s)^2(\chi_1)^1(\chi_2)^1(\chi_3)^1(2p_z)^1$

Five σ bonds: $C_1\chi_1$-H1s, $C_1\chi_2$-H1s, $C_2\chi_1$-H1s, $C_2\chi_2$-H1s, $C_1\chi_3$- $C_2\chi_3$

One π bond: $C_1 2p_z$-$C_2 2p_z$

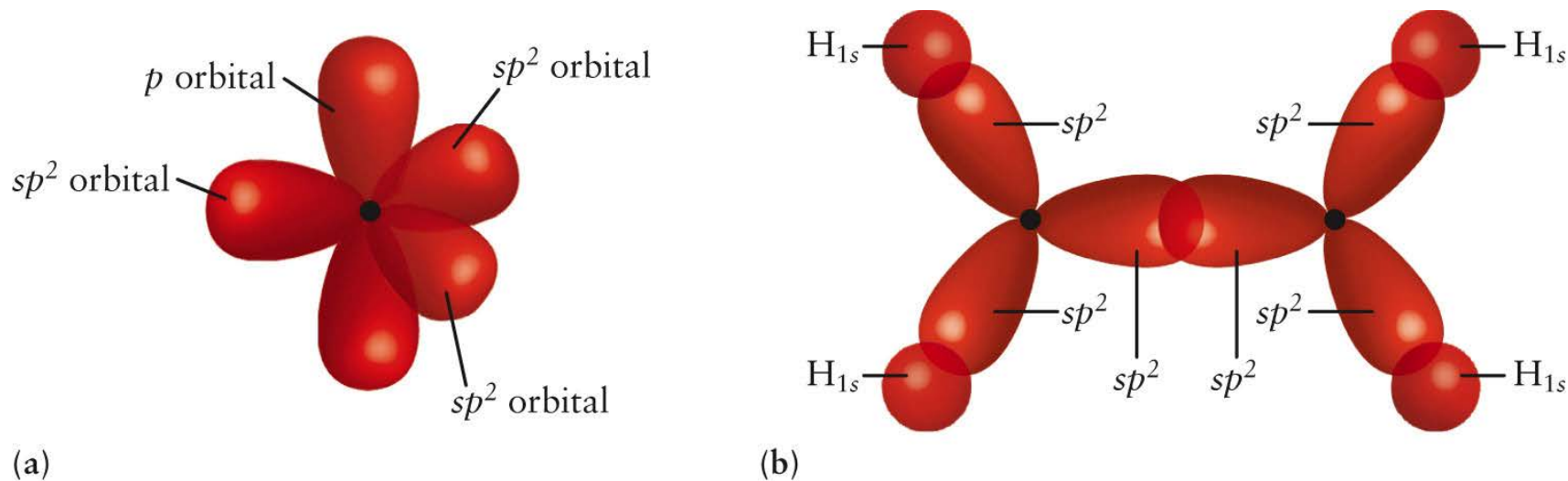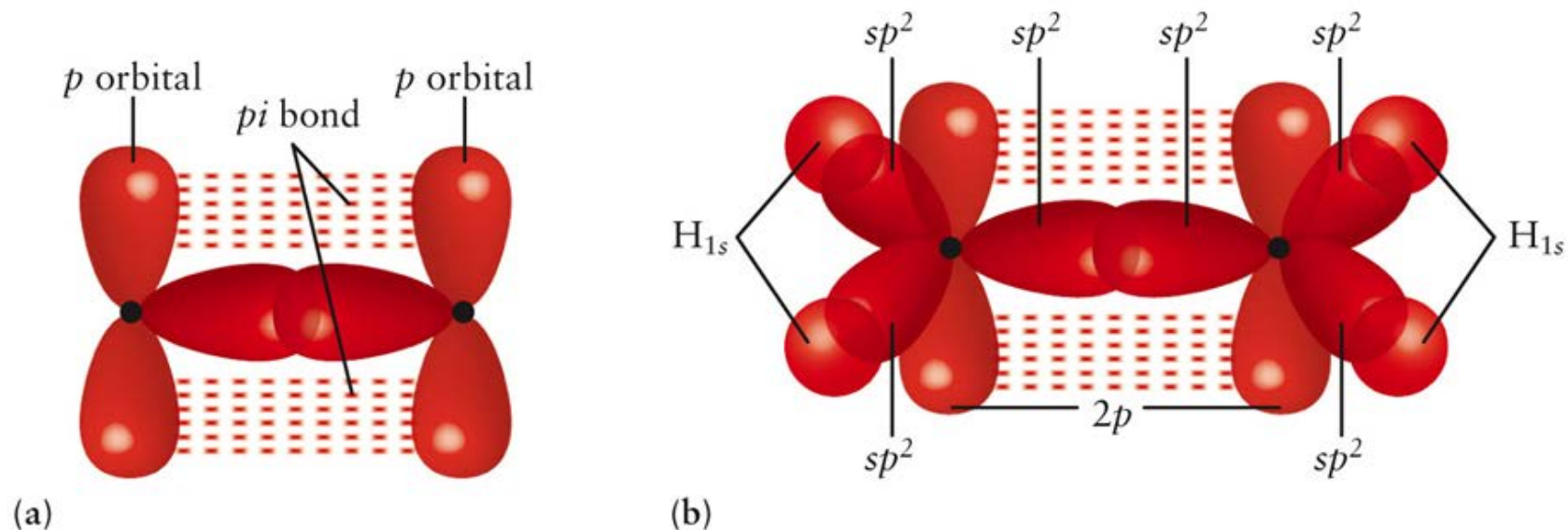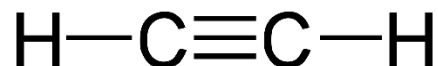One double bond (C=C): $\sigma(C_1\chi_3$- $C_2\chi_3) + \pi(C_1 2p_z$-$C_2 2p_z)$

Fig. 6.33. Formation of σ bonds in ethylene.

General Chem **Fig. 6.34.** Formation of a π bond in ethylene.

❖ **Acetylene, C$_2$H$_2$**   H—C≡C—H

Linear, triple bond, H-C-C bond angles of 180°

Promotion, C: $(1s)^2(2s)^2(2p_x)^1(2p_y)^1 \rightarrow$ C: $(1s)^2(2s)^1(2p_x)^1(2p_y)^1(2p_z)^1$

Formation of two sp hybrid orbitals from the 2s and the 2p$_z$ orbitals

New electronic configuration, C: $(1s)^2(\chi_1)^1(\chi_2)^1(2p_x)^1(2p_y)^1$

Three σ bonds: C$_1\chi_1$-H1s, C$_2\chi_1$-H1s, C$_1\chi_2$- C$_2\chi_2$

Two π bonds: C$_1$2p$_x$-C$_2$2p$_x$, C$_1$2p$_y$-C$_2$2p$_y$

One triple bond : σ (C$_1\chi_2$- C$_2\chi_2$) + π (C$_1$2p$_x$-C$_2$2p$_x$, C$_1$2p$_y$-C$_2$2p$_y$)

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(a)

(b)
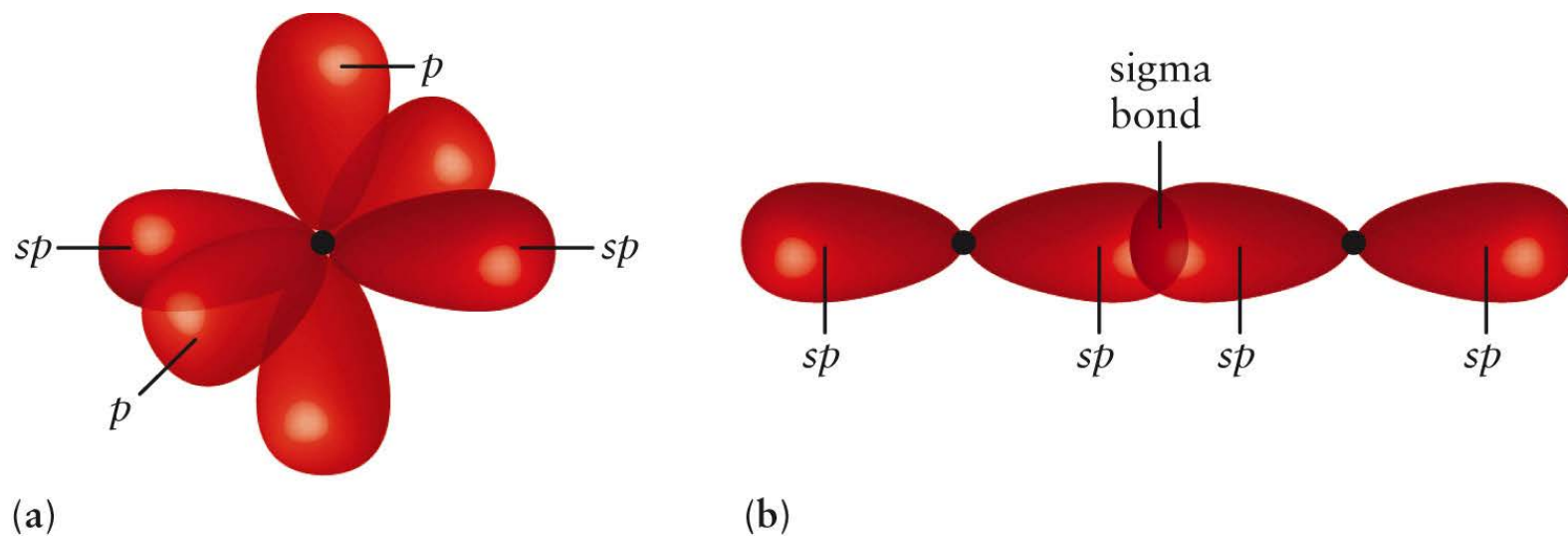
Fig. 6.35. Formation of σ bonds in acetylene.
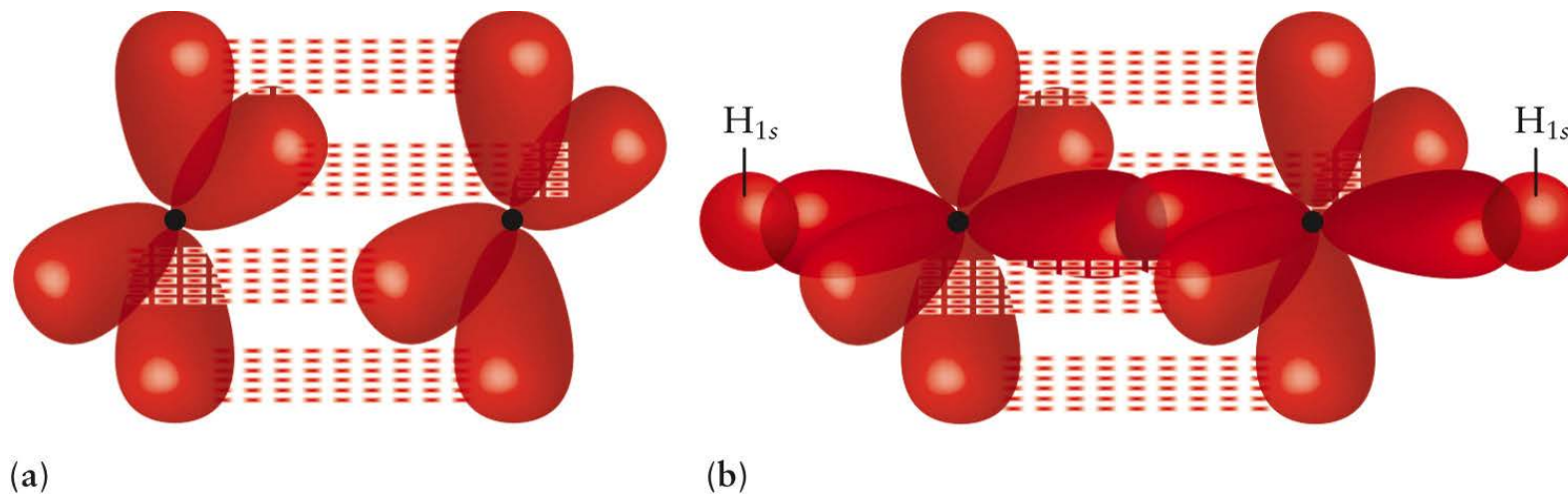

(a)

(b)

General Chem **Fig. 6.36.** Formation of two π bonds in acetylene.

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6.10 PREDICTING MOLECULAR STRUCTURES AND SHAPE

➢ Description of the structure and shape of a molecule

(1) Determine the empirical formula.

(2) Determine the molecular formula.

(3) Determine the structural formula from a Lewis diagram.

(4) Determine the molecular shape from experiments.

(5) Identify the hybridization scheme that best explains

   the shape predicted by VSEPR.

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EXAMPLE 6.4

Hydrizine: Elemental analysis shows its mass per cent composition to be 87.419% nitrogen and 12.581% hydrogen. The density of hydrazine at 1 atm and 25 °C is 1.31 gL⁻¹. Determine the molecular formula for hydrazine. Predict the structure of hydrazine. What is the hybridization of the N atoms?

(1) Elemental analysis: N(87.419%), H (12.581%)

(2) Empirical formula: $NH_2 \rightarrow$ (Molar mass)$_{emp}$

(3) Molar mass calculate from the ideal gas law (with known ρ)

(4) Molar mass / (Molar mass)$_{emp}$ = 2, Molecular formula: N_2H_4

(5) Lewis diagram, steric number (4) $\rightarrow$ sp^3 hybrid orbitals

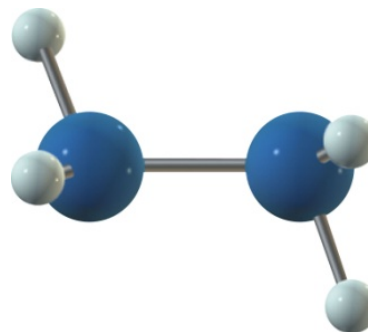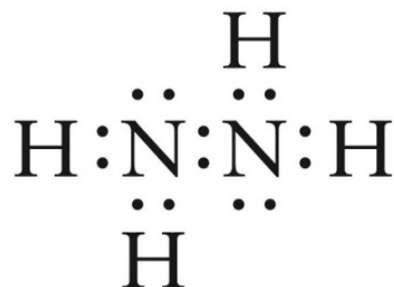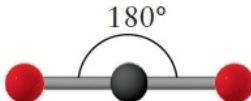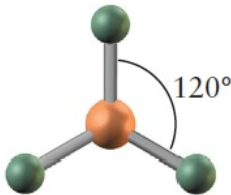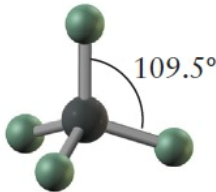**General Chemistry I**

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TABLE 6.5

Molecular Shapes Predicted by the Valence Shell Electron-Pair Repulsion Theory and Rationalized by Orbital Hybridization

Molecule	Steric Number	Number of Lone Pairs	Orbital Hybridization	Predicted Geometry	Image	Example
AX_2	2	0	*sp*	Linear	180°	BeH_2, CO_2
AX_3	3	0	sp^2	Trigonal planar	120°	BF_3, SO_3
AX_2	3	1	sp^2	Bent		SO_2
AX_4	4	0	sp^3	Tetrahedral	109.5°	CF_4, SO_4^{2-}
AX_3	4	1	sp^3	Trigonal pyramidal		NH_3, PF_3, $AsCl_3$
AX_2	4	2	sp^3	Bent		H_2O, H_2S, SF_2

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Key question: how can we describe chemical bond in terms of quantum mechanics?
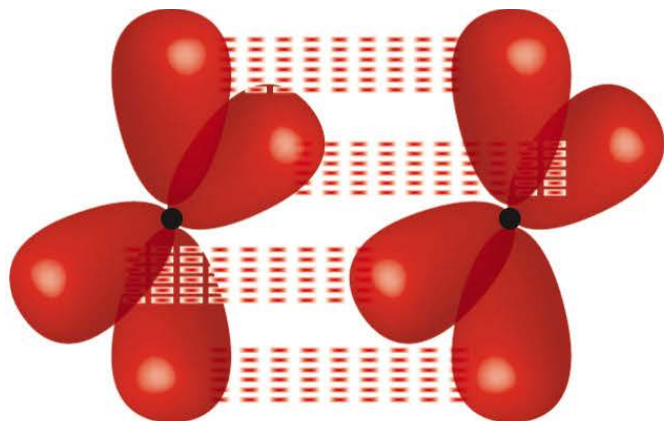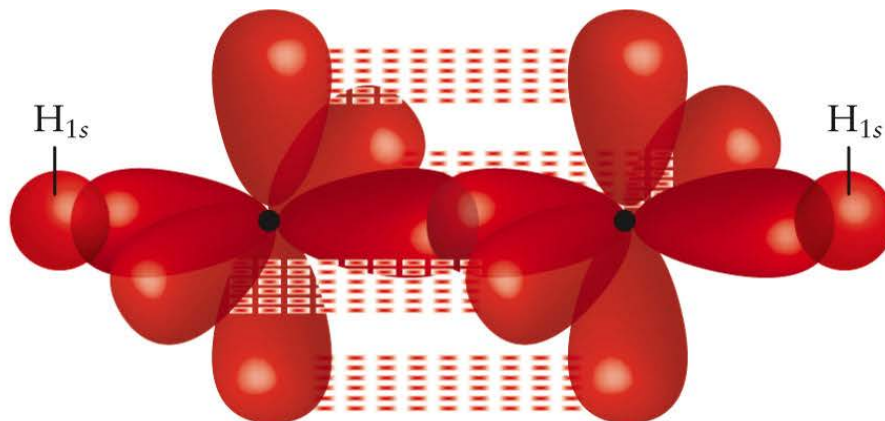
(a)   (b)

Problem Sets

For Chapter 6,

 2, 18, 48, 52, 66, 72

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