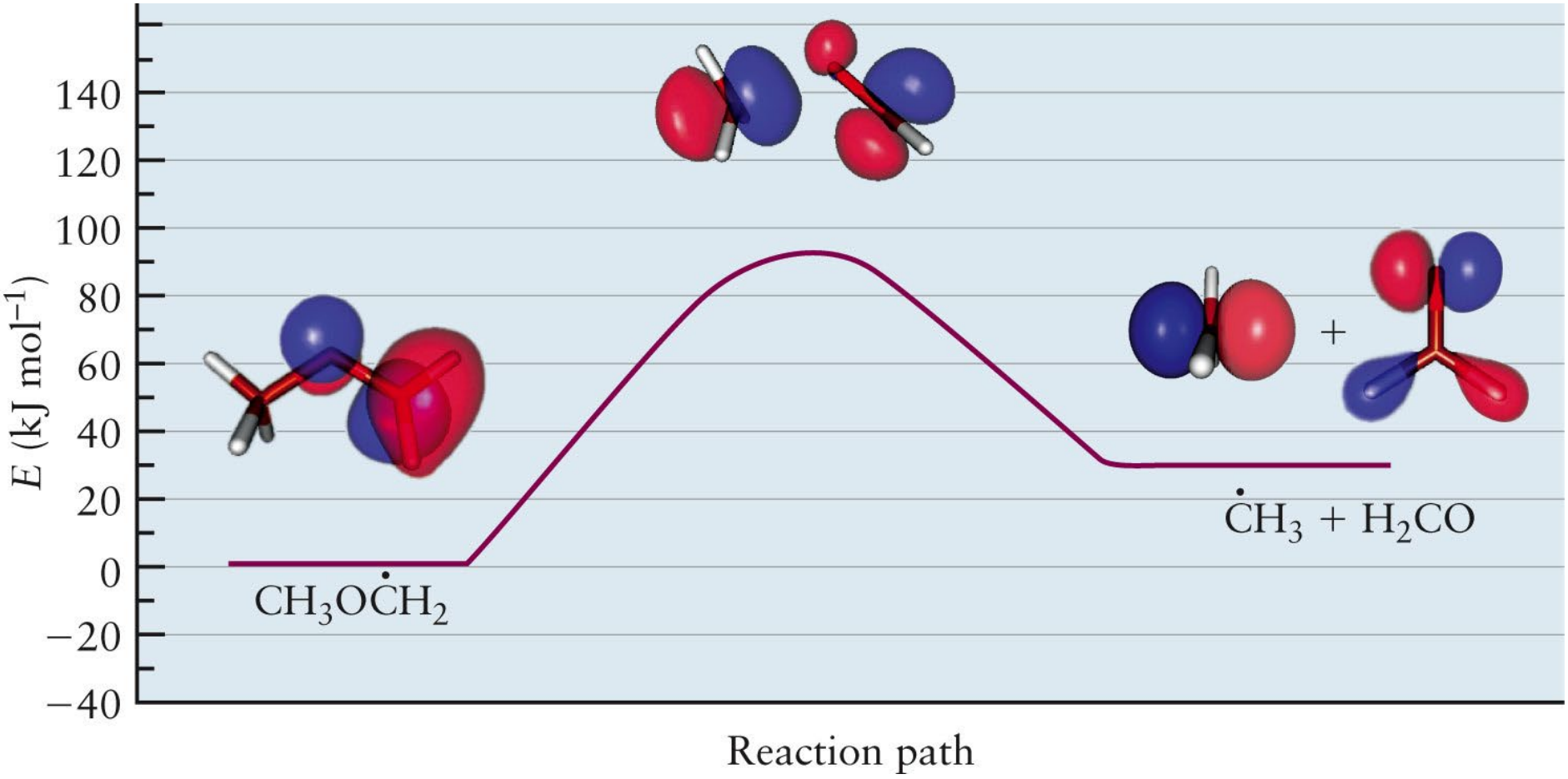
6

CHAPTER

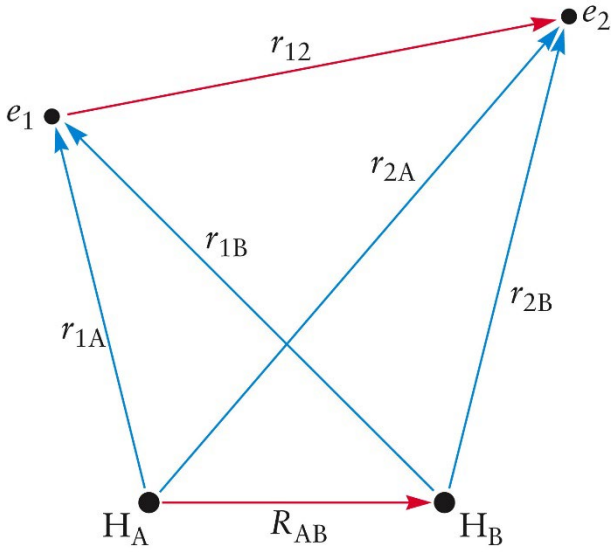
QUANTUM MECHANICS AND MOLECULAR STRUCTURE

KAIST CHEMISTRY



Potential energy diagram for the decomposition of the methyl methoxy radical

6.1 QUANTUM PICTURE OF THE CHEMICAL BOND



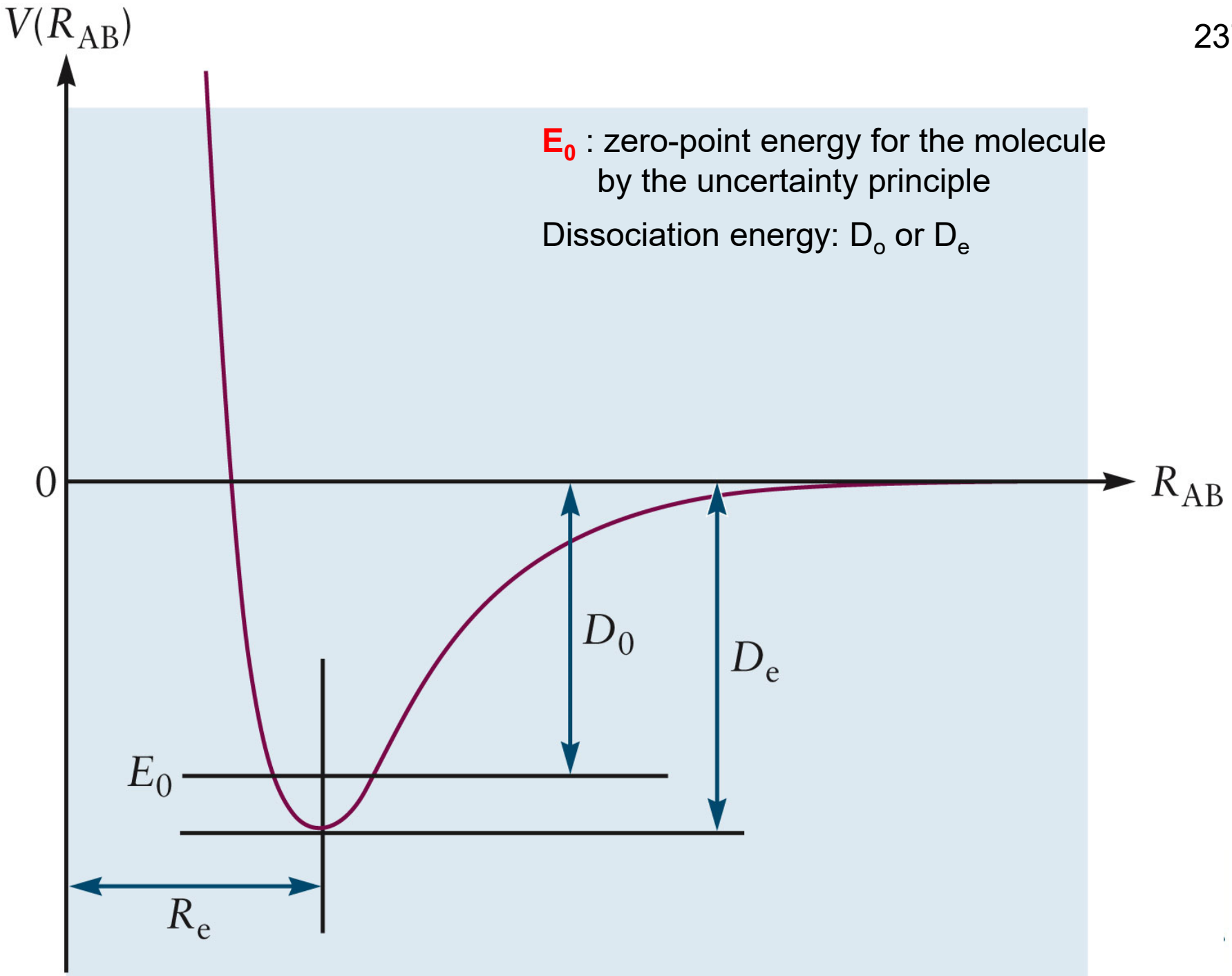
- Specific example of H_2, (in section 3.7)

$$V = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1A}}+\frac{1}{r_{2A}}+\frac{1}{r_{1B}}+\frac{1}{r_{2B}}\right)+\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}}\right)+\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{R_{AB}}\right)$$

$$V = V_{en} + V_{ee} + V_{nn}$$

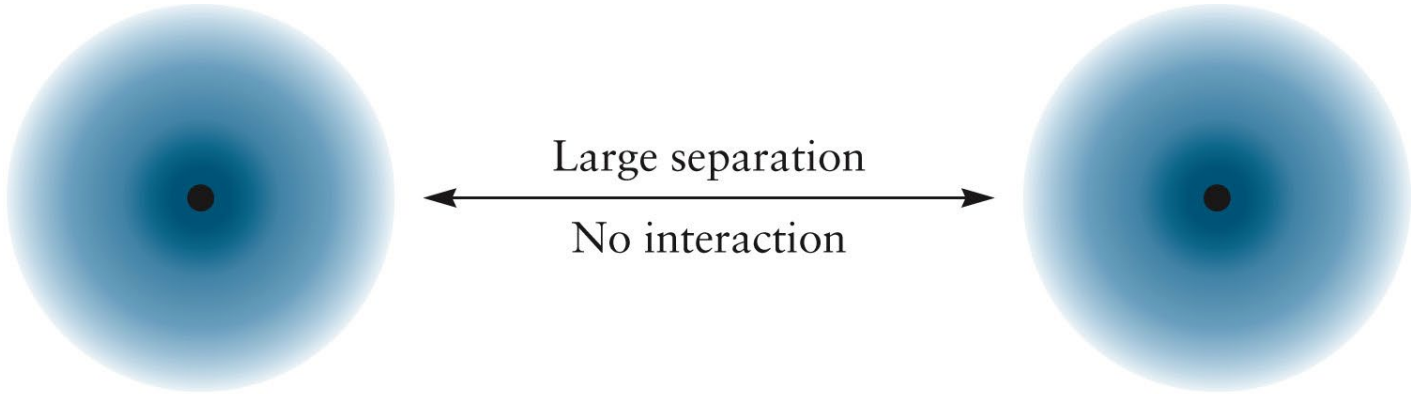
- Using **effective potential energy function**, V_{eff}

  - At large R_{AB}, $V_{eff} \rightarrow 0$, and the atoms do not interact.
  - As R_{AB} decreases, V_{eff} must become negative because of attraction.
  - At very small R_{AB}, V_{eff} must become positive and large as $V_{eff} \rightarrow \infty$.

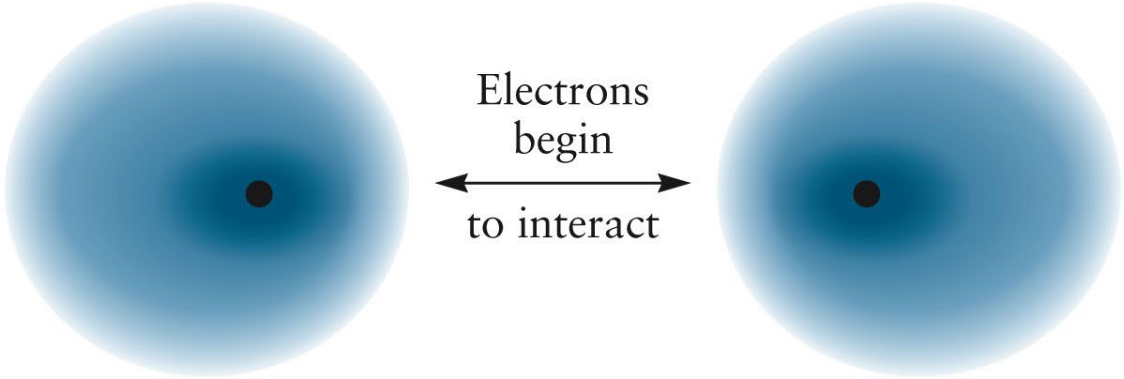


E_0 : zero-point energy for the molecule by the uncertainty principle

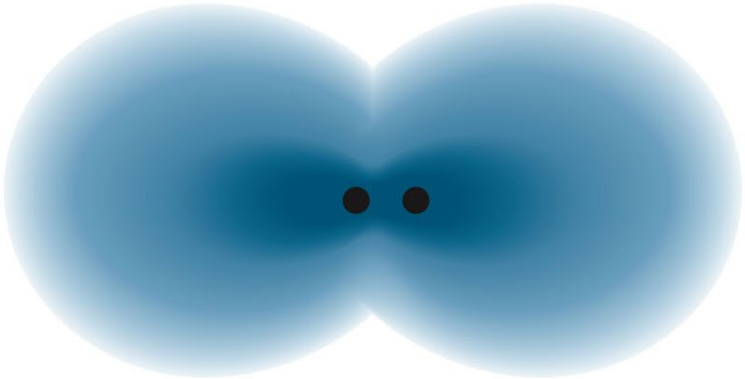
Dissociation energy: D_o or D_e



(a)



(b)



(c)

effective potential
energy function

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**

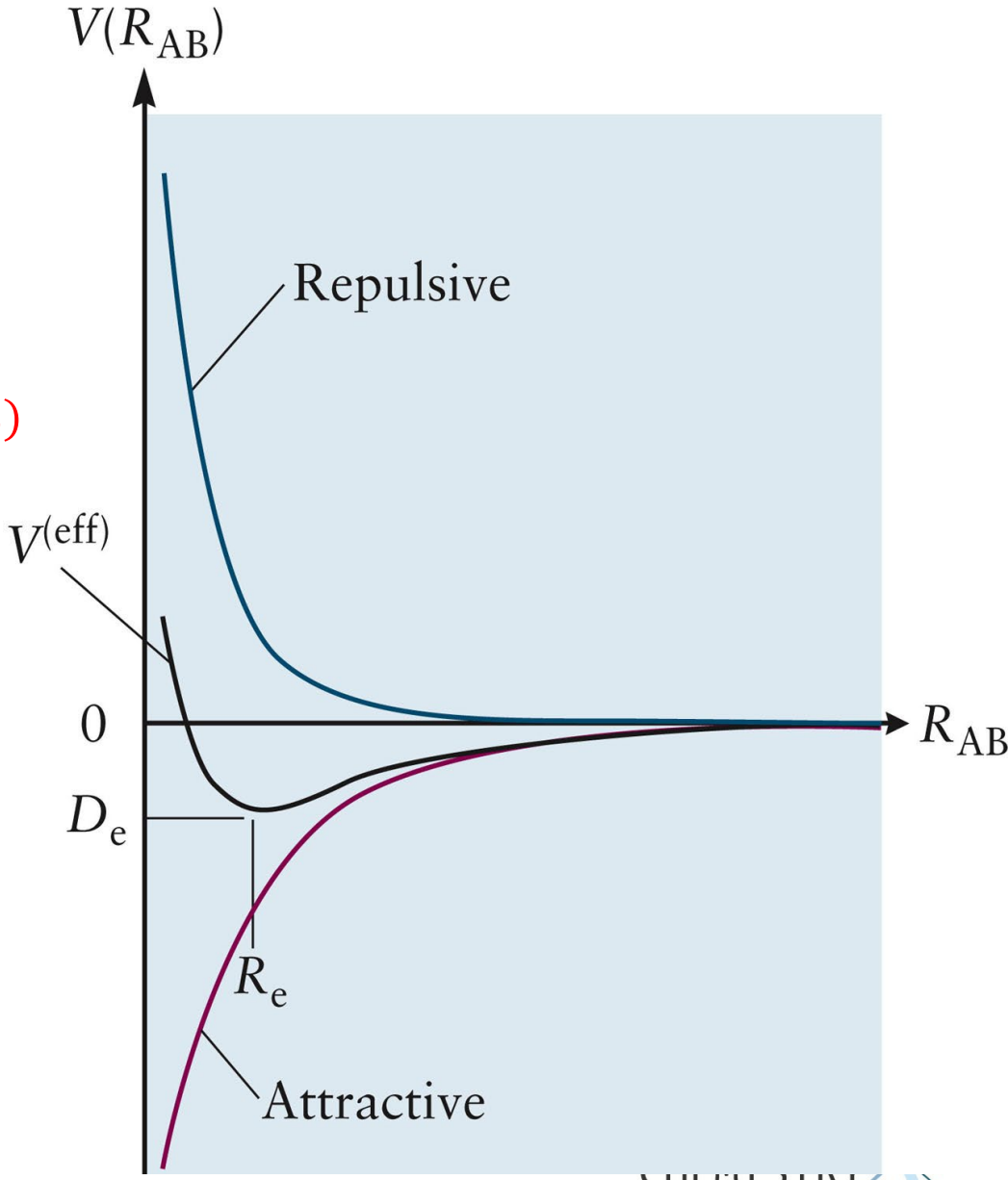
(A) Consider **the nuclei** to be **fixed at a specific set** of positions.
Then solve Schrödinger's equation **for the electrons** moving around and obtain the energy levels and wave functions.
Next, move the nuclei a bit, and repeat the calculation.
Continue this procedure in steps.

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

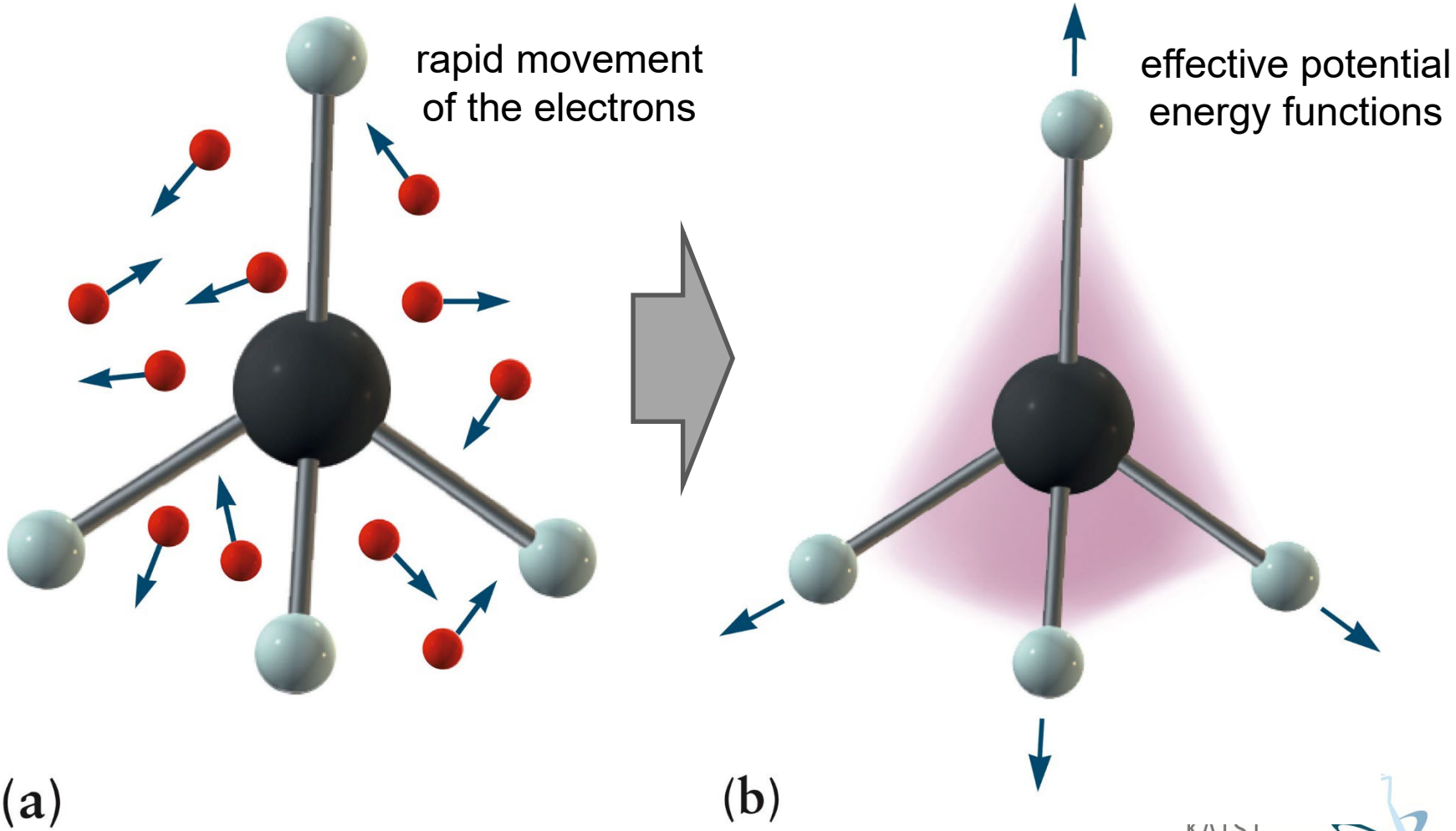
α: the proper set of quantum numbers

(B) Consider the function $E_{\alpha}^{(el)}(R_{AB})$ to be the attractive portion. Add the repulsive interaction to obtain the effective potential energy curve.

$$\boldsymbol{V_{\alpha}^{(eff)}(R_{AB}) = E_{\alpha}^{(el)}(R_{AB}) + V_{nn}(R_{AB})}$$



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

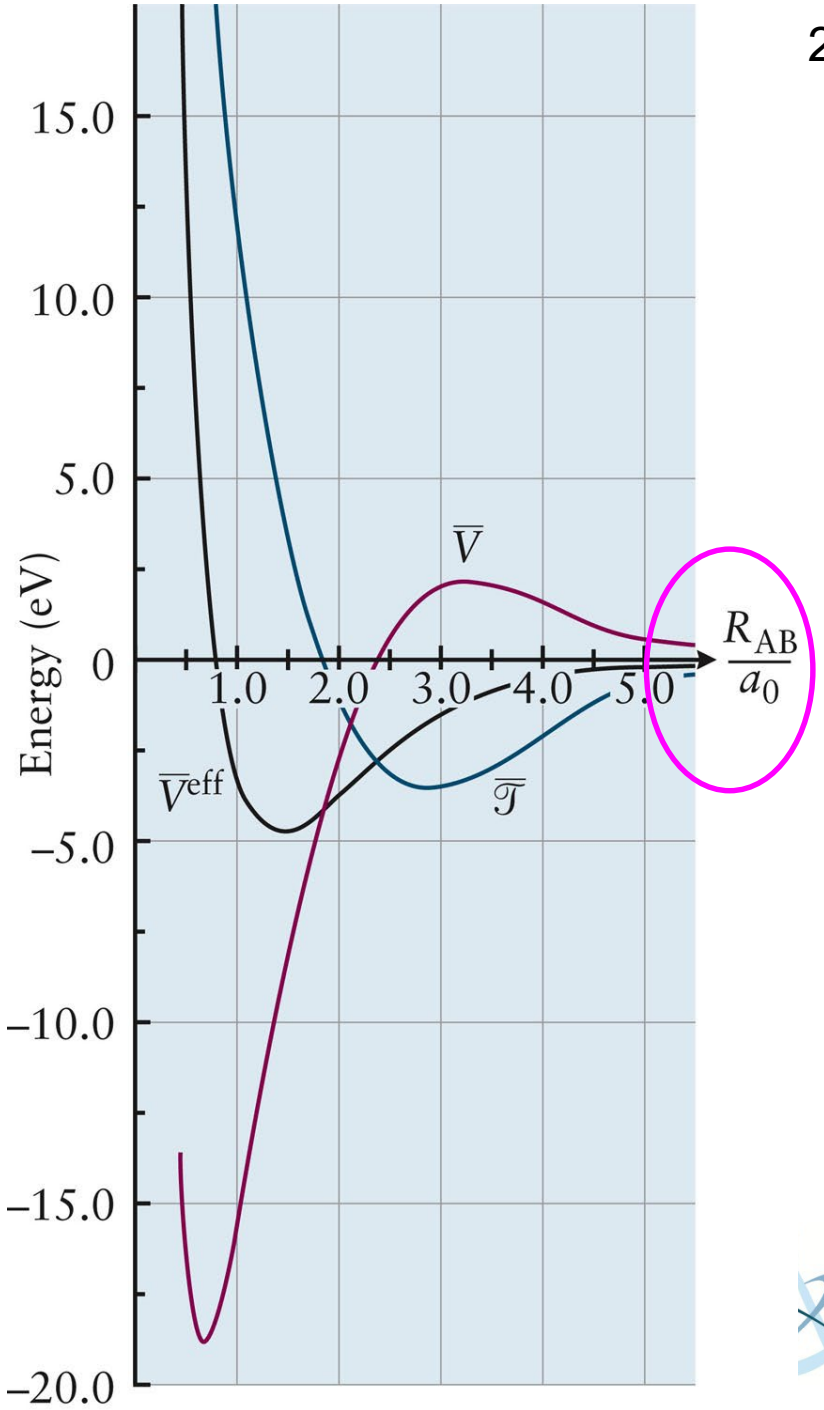


Mechanism of Covalent Bond Formation

The average value of $\boldsymbol{V^{(eff)}(R_{AB})}$,

$$\overline{V}^{(eff)}(R_{AB}) = \overline{T}(R_{AB}) + \overline{V}(R_{AB})$$

- When $R_{AB} \rightarrow \infty$,
  independent H atoms



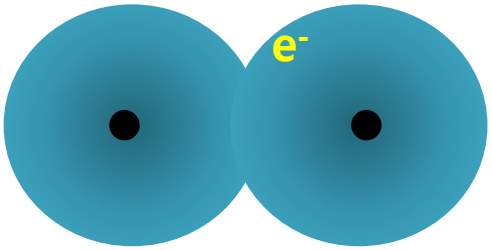
- As the two atoms approach one another,

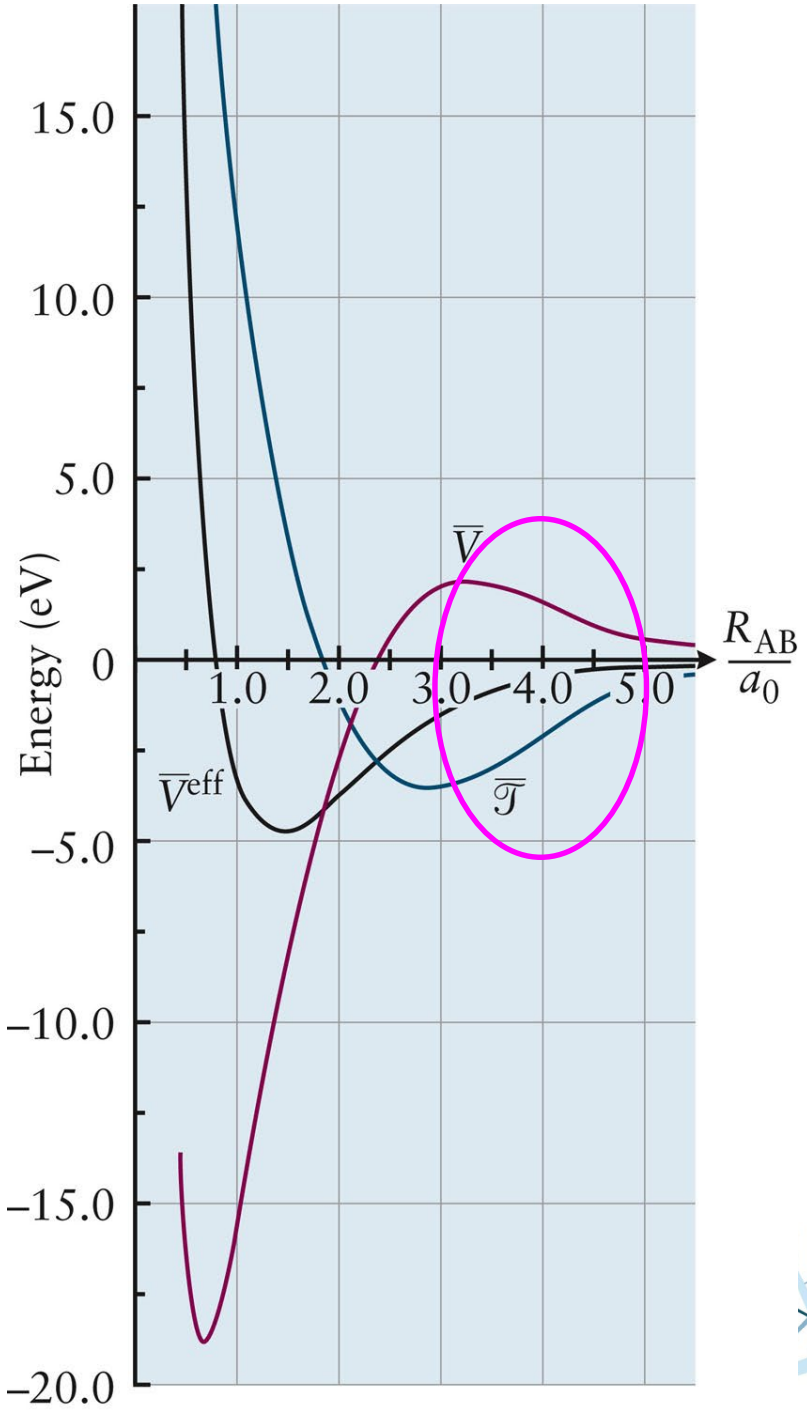
$\overline{V}$ increases;
the Coulomb attraction reduces between each electron and the proton to which it was originally bound .

$\overline{T}$ decreases;
each electron becomes less confined.

(The energy of the particle in a box decrease as the size of the box increases)

➡ **decreasing the $\overline{V}^{(eff)}$**



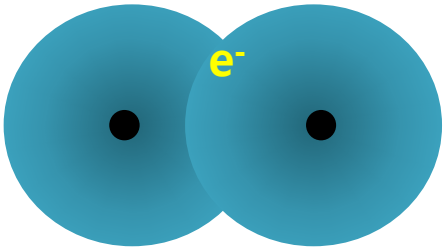


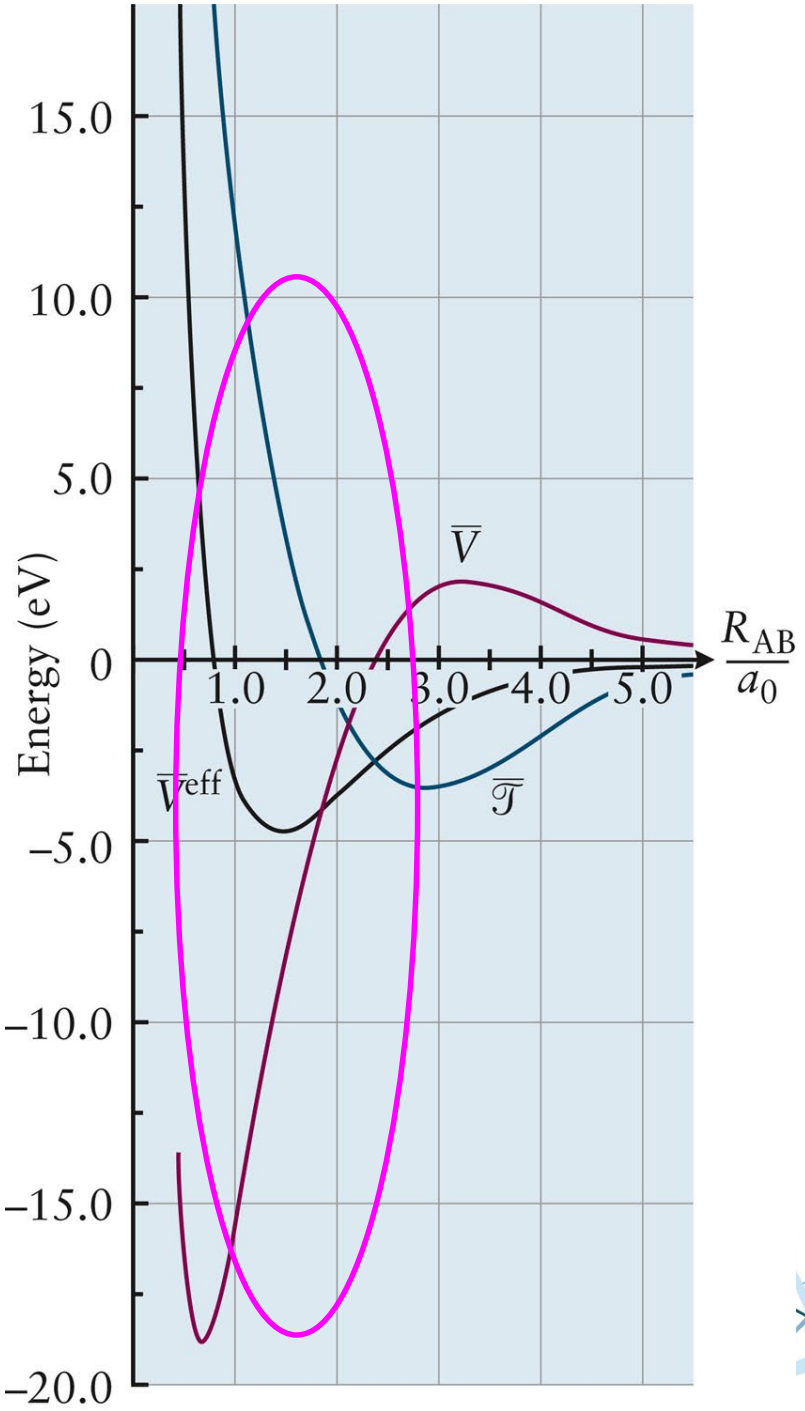
- As bond formation continues,

$\overline{V}$ decreases;
the simultaneous Coulomb attraction of each electron to two protons decreases the average potential energy.

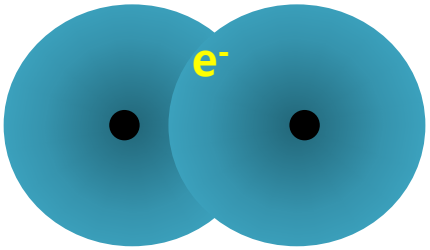
$\overline{T}$ increases;
confinement of the electron to the smaller internuclear region increases its kinetic energy.

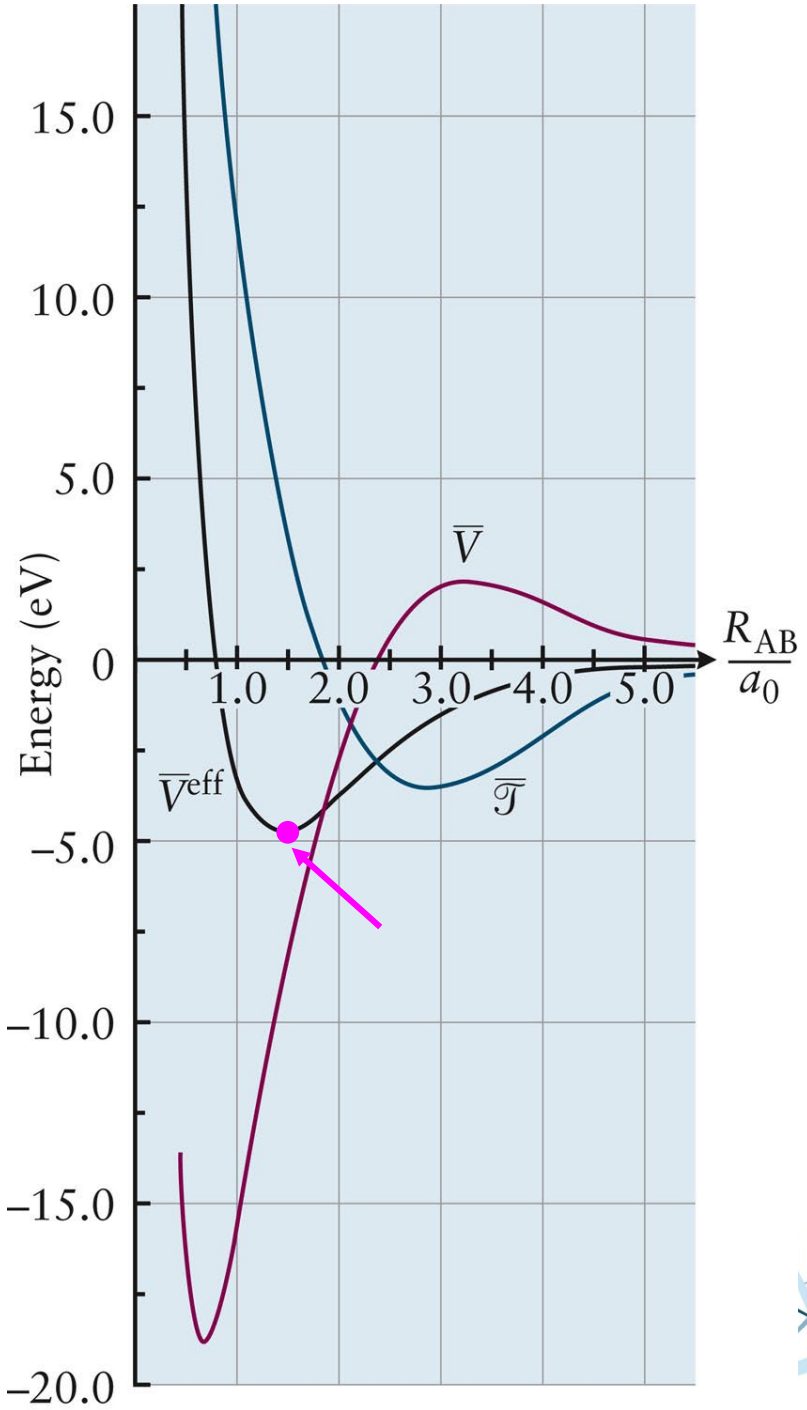
decreasing the $\overline{V}^{(eff)}$



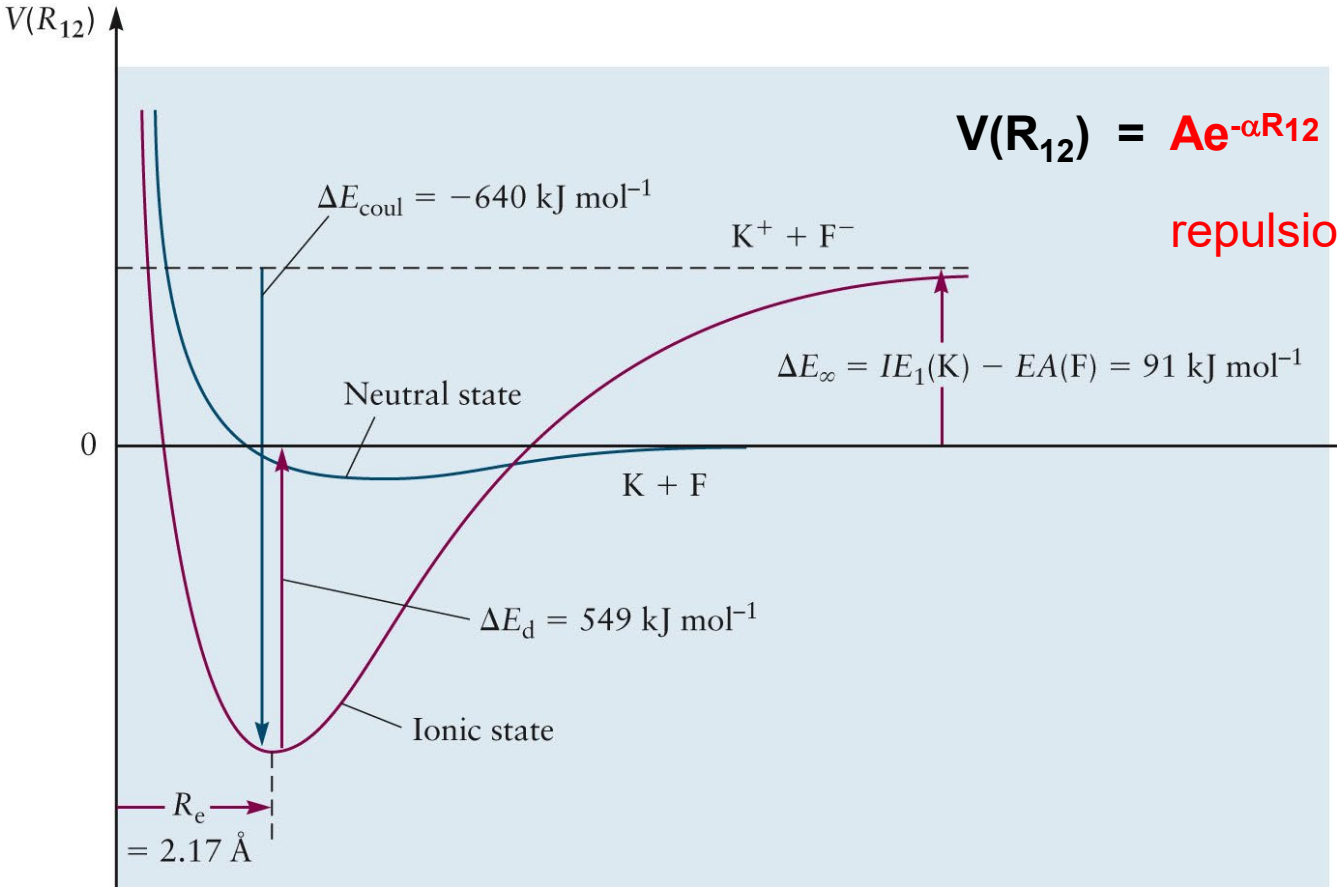


- The minimum in the $\overline{V}^{(eff)}$, and the equilibrium bond length of the molecule, is determined by the competition between the increasing average kinetic energy and the decreasing average potential energy at small values of internuclear separation.





➢ **For the ionic bond**, potential energy alone is essential. (section 3.8)



$$V(R_{12}) = Ae^{-\alpha R12} - B\left(\frac{(e)(-e)}{R_{12}}\right) + \Delta E_\infty$$

repulsion attraction

➢ **For the covalent bond**, the charge distribution and the kinetic energy of the electrons are also important.

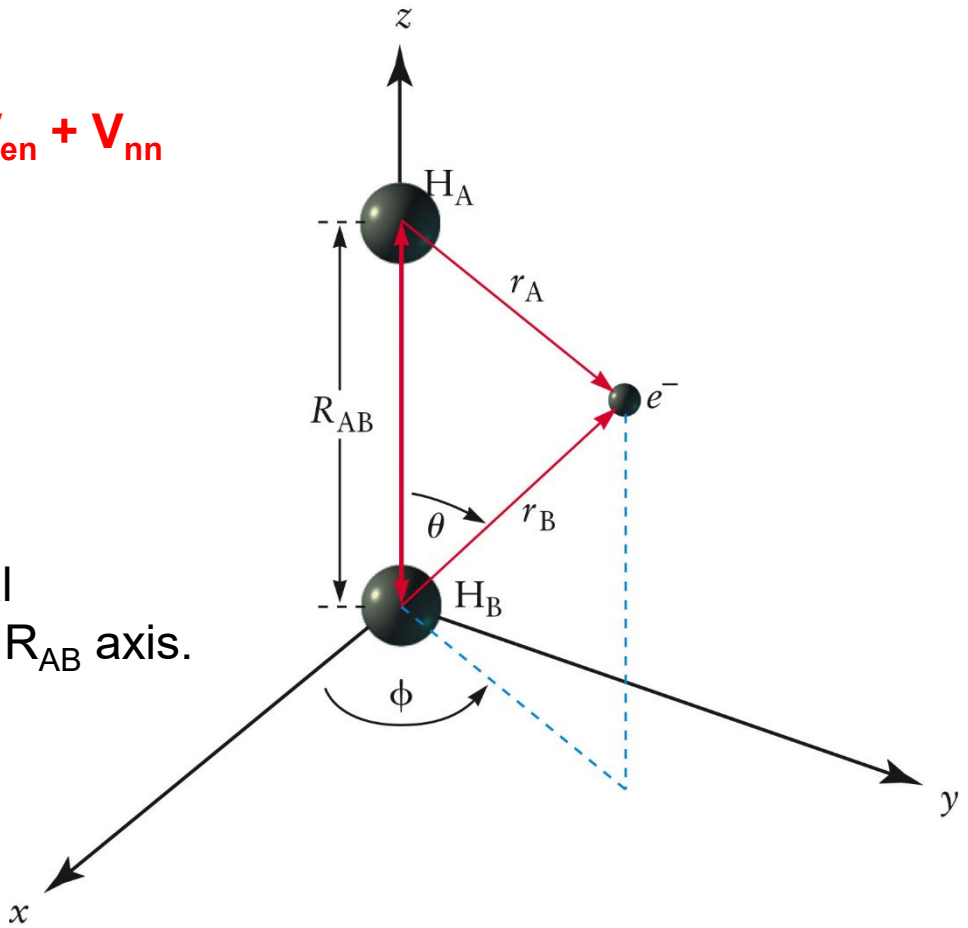
6.2 EXACT MOLECULAR ORBITALS FOR THE SIMPLEST MOLECULE: H_2^+

- **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.



- By the Born-Oppenheimer approximation,

  - R_{AB} : holding at the equilibrium bond length of 1.06 Å

  - $\psi^{el}(r_A, r_B, \phi;\ R_{AB})$: the electronic wave function for the electrons

    Omitting ϕ due to the same potential energy for all values of ϕ

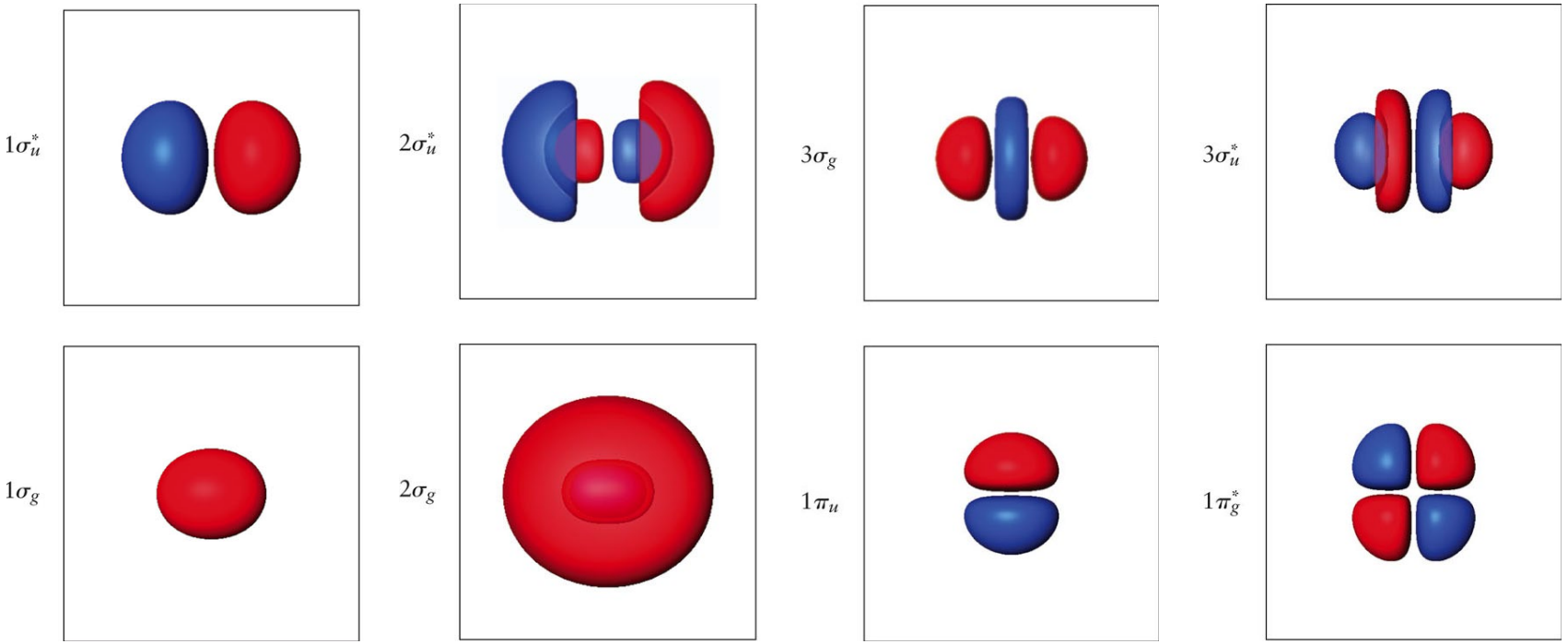
- The solution of the Schrödinger equation:

  - smooth, single-valued, and finite in all regions of space
    to define a probability density function of its square

  - physical boundary conditions
    $\psi^{el} \rightarrow 0$ as $r_A \rightarrow \infty$ and as $r_B \rightarrow \infty$

⇒ Solutions exists when **the total energy and angular momentum are quantized**.

Electronic Wave Functions for H_2^+



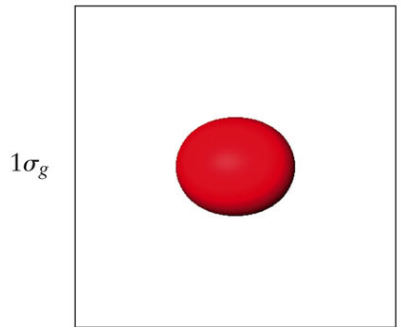
- isosurface comprising the wave function with 0.1 of its maximum value.
- red: + amplitude; blue: - amplitude

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

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

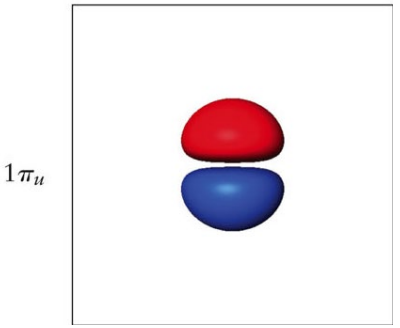
1) **integer**: an index tracking the relative energy of the wave functions of each symmetry type.

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



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



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)

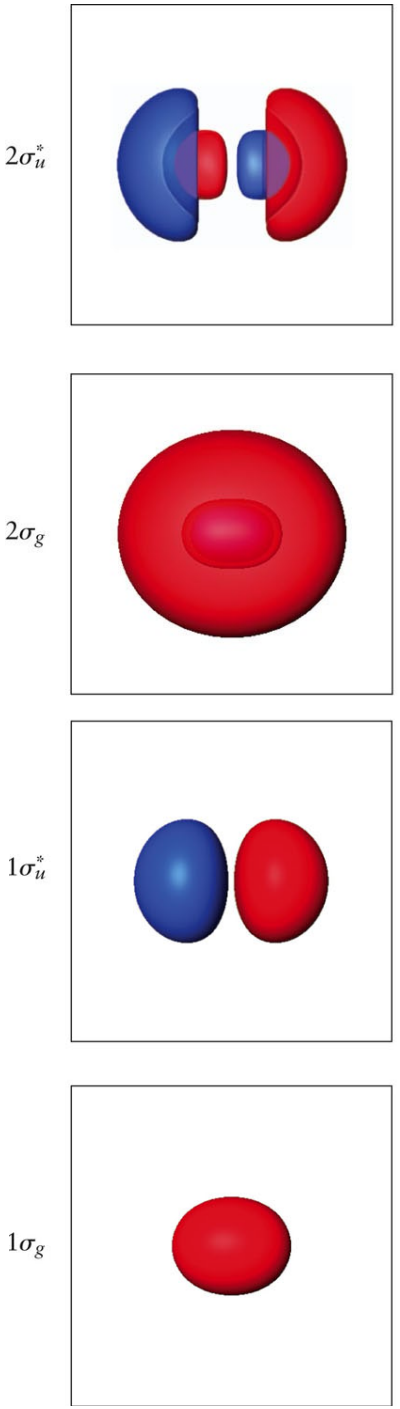
- **g** : symmetric, the same at these points
  gerade

  u : antisymmetric, the opposite at these points
  ungerade

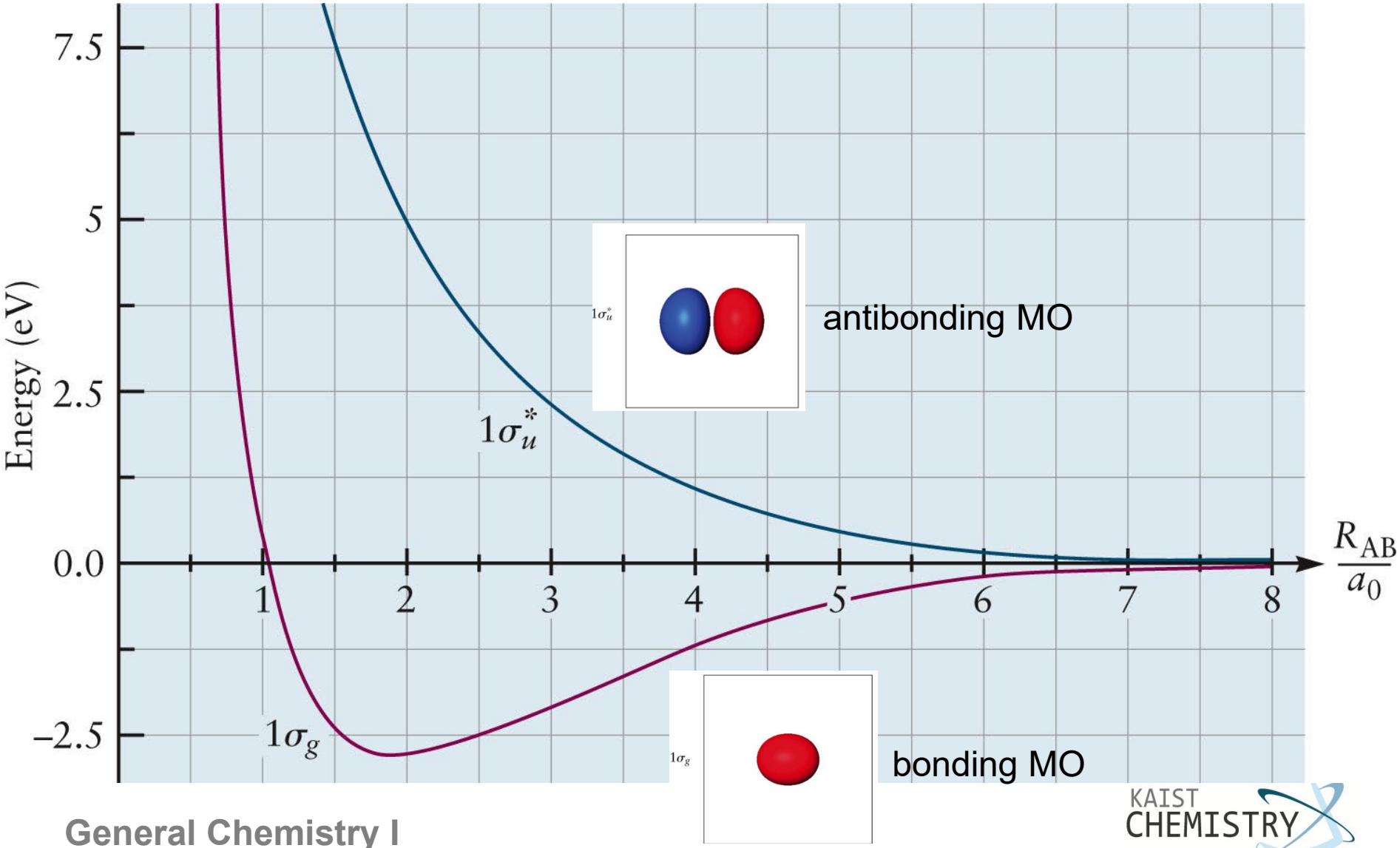
4) * : how the wave function changes when the point of observation is reflected through a plane perpendicular to the internuclear axis

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

  * : changing sign upon reflection



Nature of the Chemical Bond in H_2^+



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

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

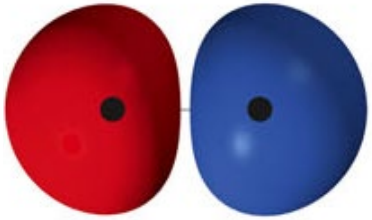
φ: wave function of atomic orbitals

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

- 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

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

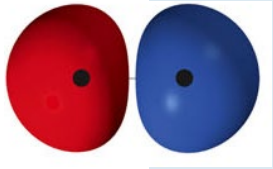
$$\left[\sigma_{u1s}^*\right]^2 = C_u^2\left[\left(\varphi_{1s}^A\right)^2 + \left(\varphi_{1s}^B\right)^2 - 2\varphi_{1s}^A\varphi_{1s}^B\right]$$

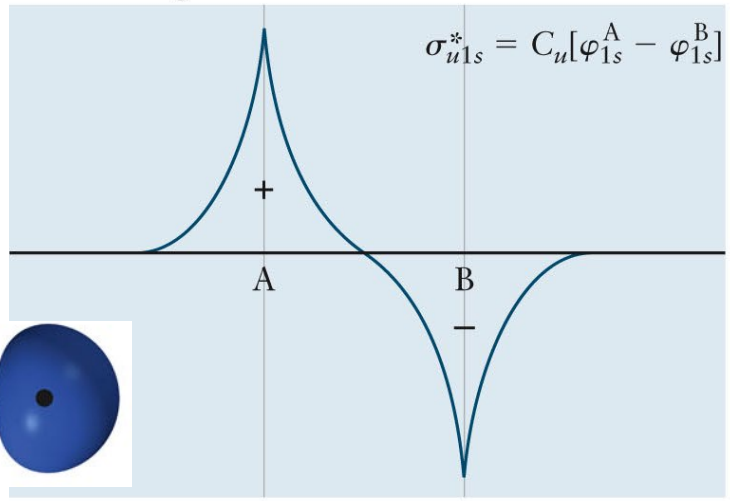
TABLE 6.1

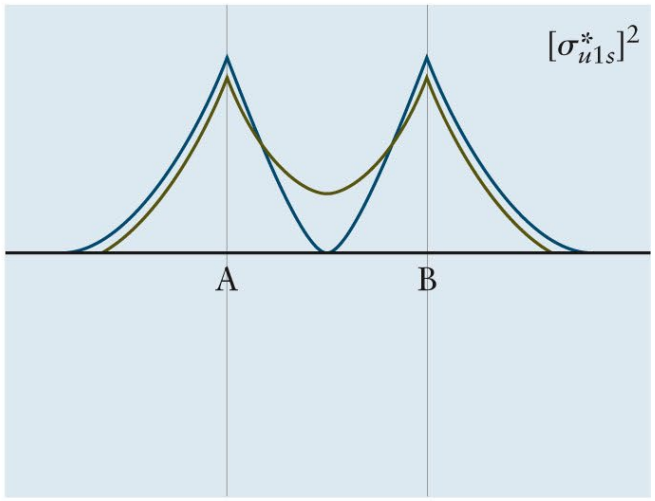
Molecular Orbitals for Homonuclear Diatomic Molecules

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}^*
$1\pi_u$	π_{u2p_x}, π_{u2p_y}
$3\sigma_g$	σ_{g2p_z}
$1\pi_g^*$	$\pi_{g2p_x}^*$, $\pi_{g2p_y}^*$
$3\sigma_u^*$	$\sigma_{u2p_z}^*$

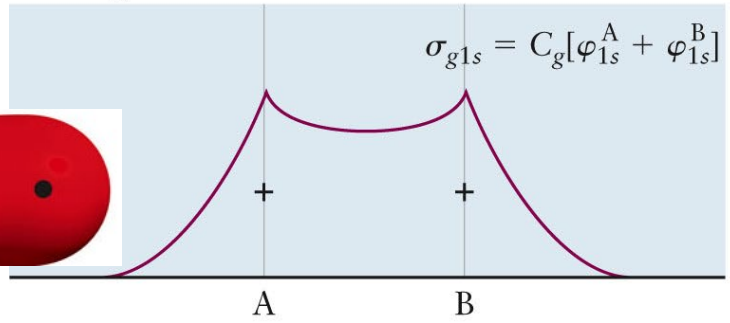
Antibonding

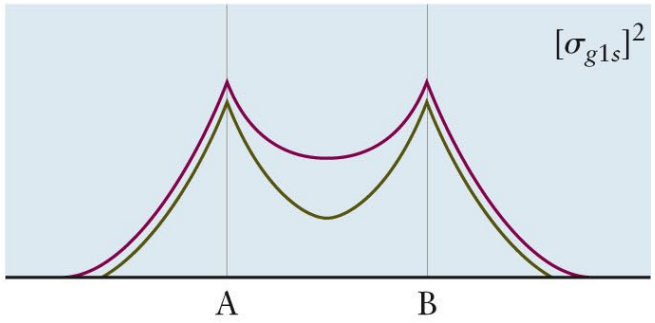




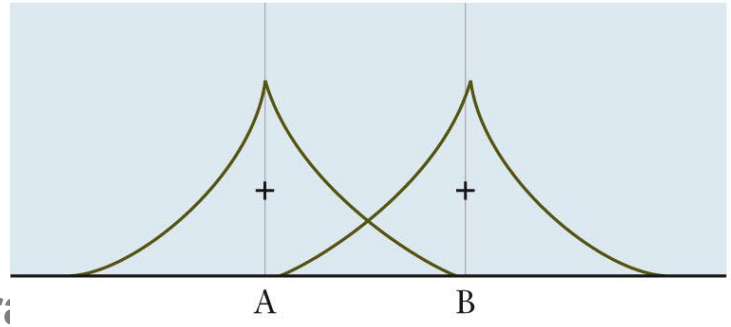


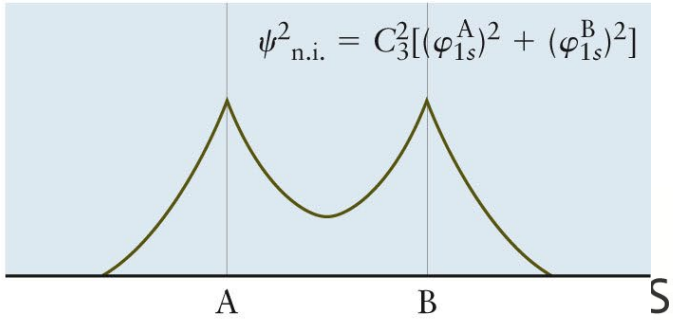
Bonding





Noninteracting

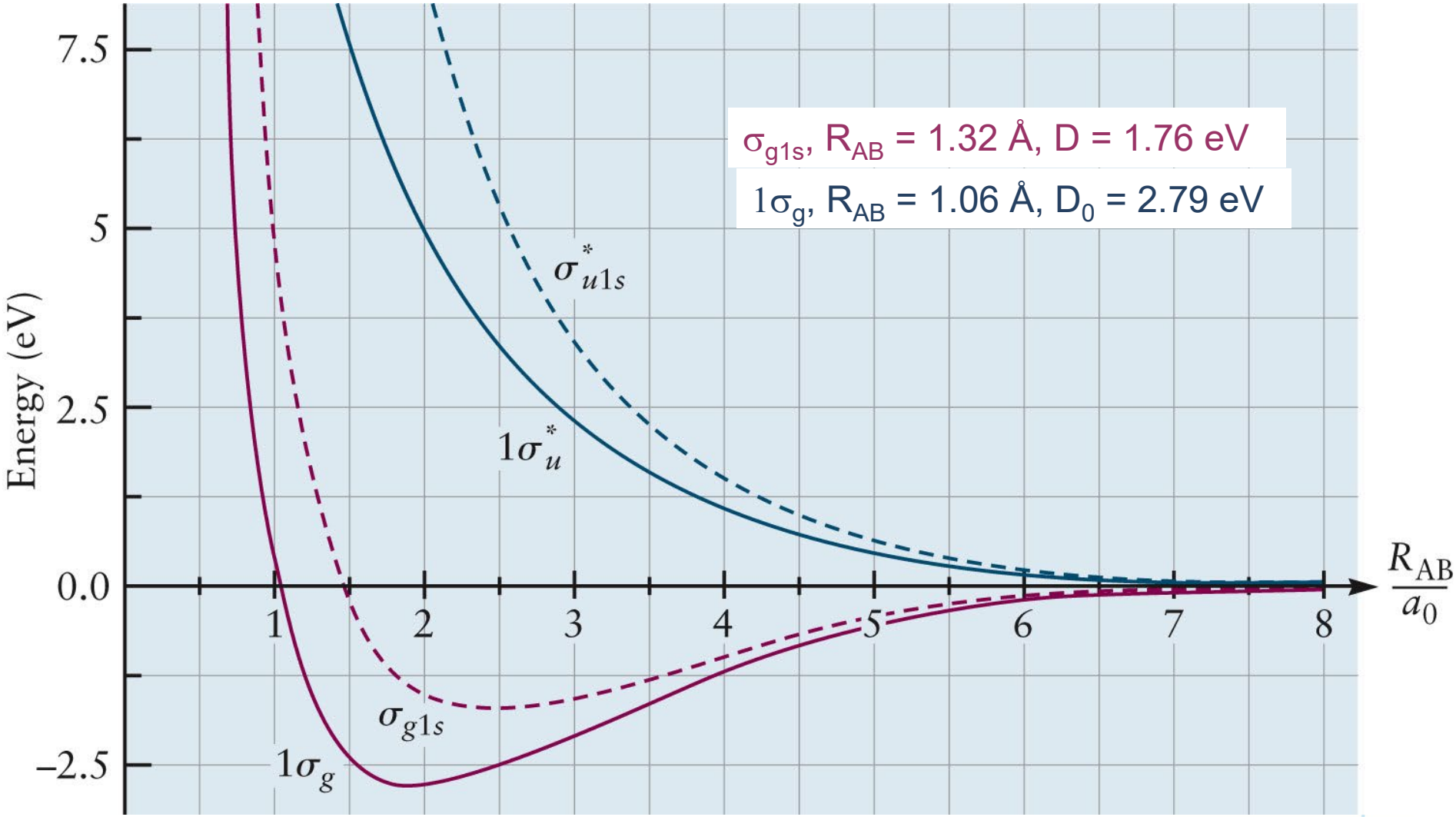




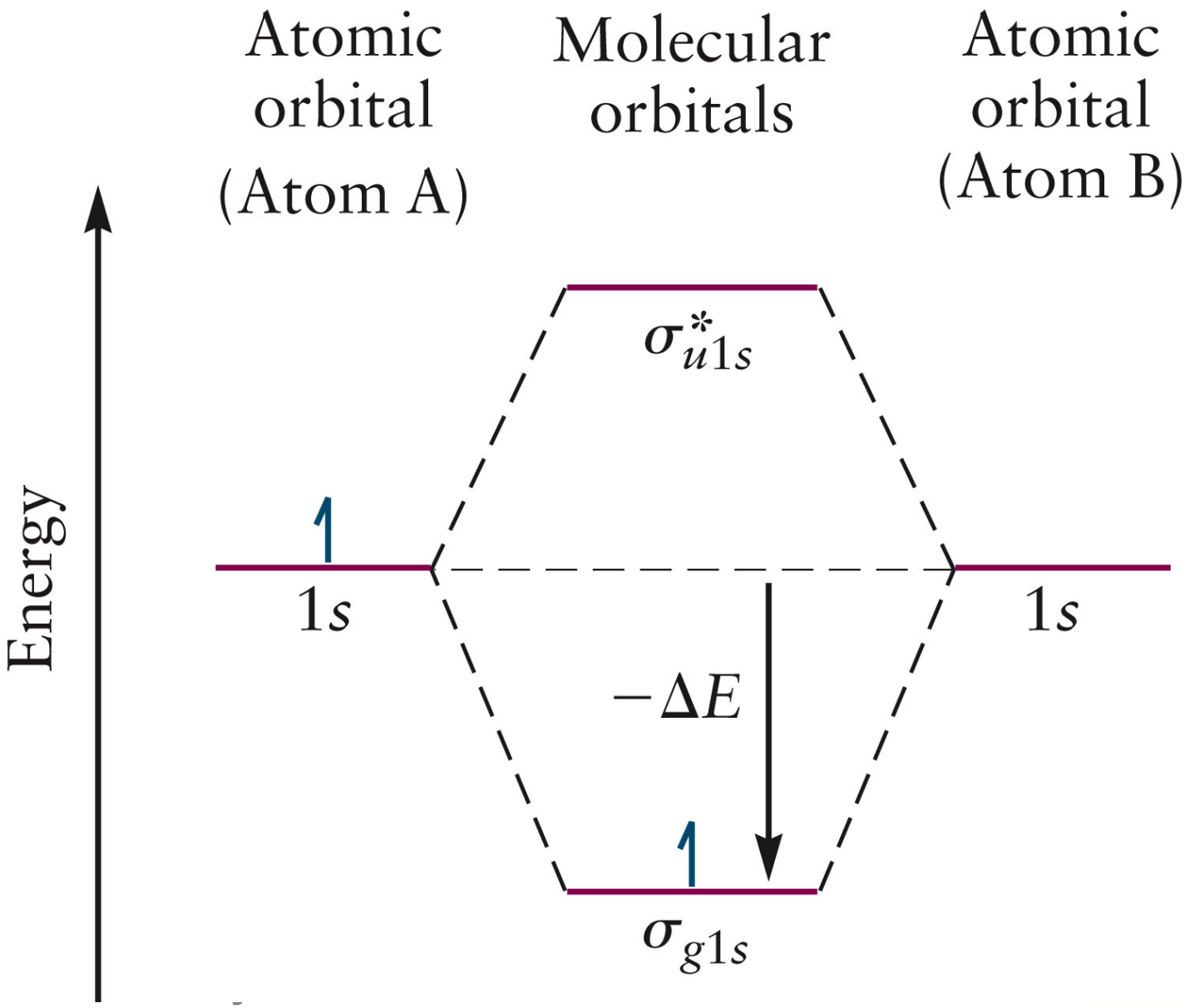
Wave functions

Electron densities

Energy of H_2^+ in the LCAO Approximation



➢ **Correlation diagram**: the energy-level diagram within the LCAO



6.4 HOMONUCLEAR DIATOMIC MOLECULES: FIRST-PERIOD ATOMS

For He_2^+ and He_2,

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

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

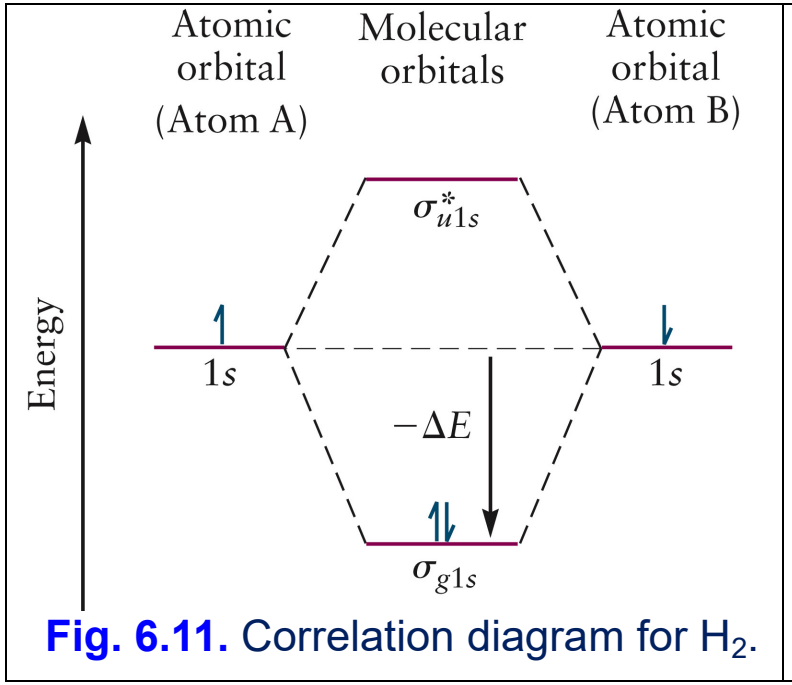


Fig. 6.11. Correlation diagram for H_2.

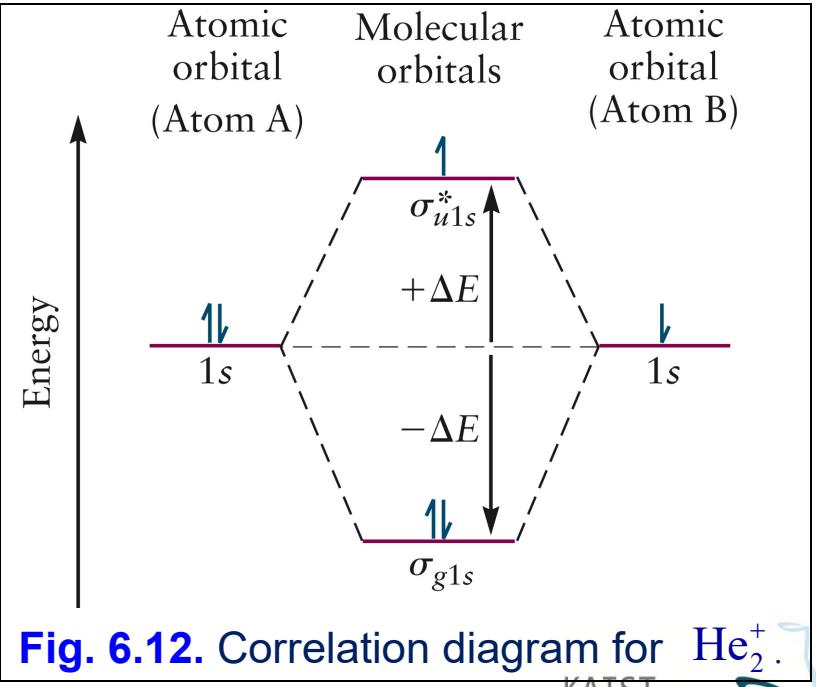
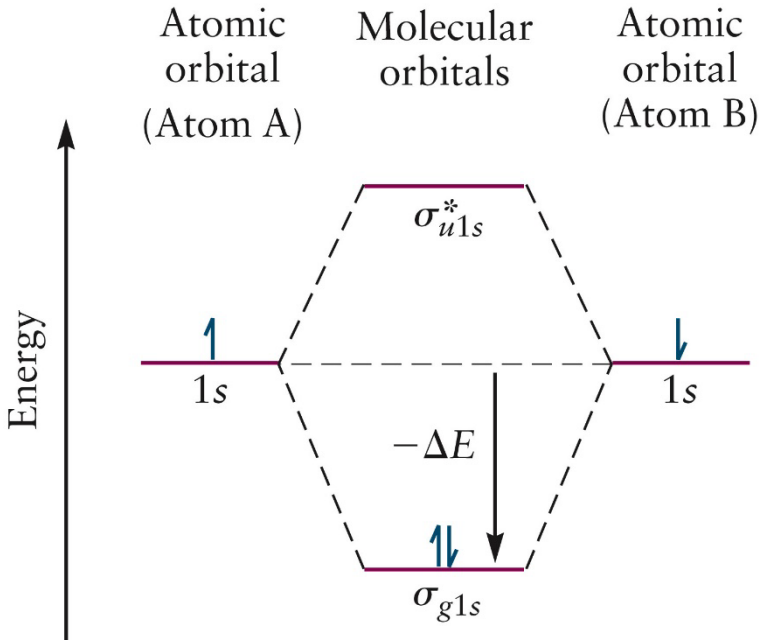


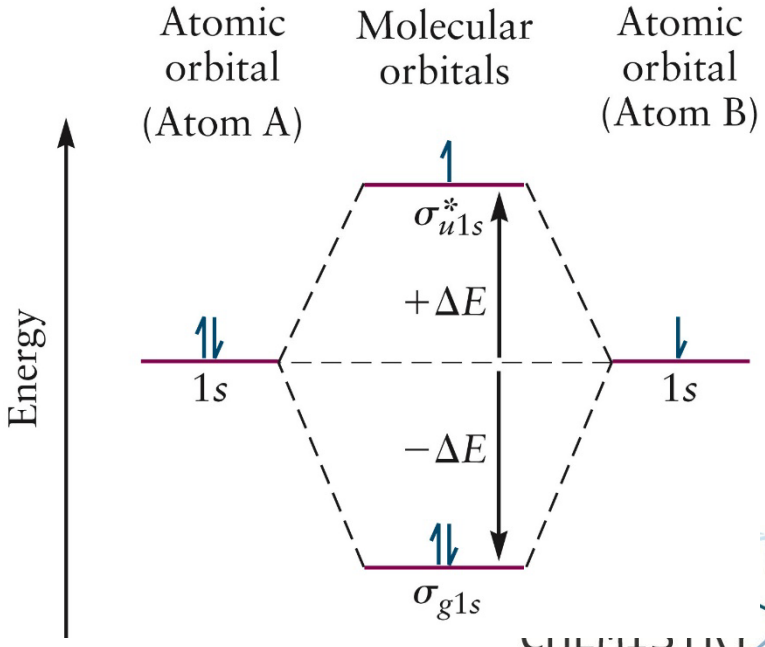
Fig. 6.12. Correlation diagram for He_2^+.

- 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 = $-\Delta E$



❖ 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

6.5 HOMONUCLEAR DIATOMIC MOLECULES: SECOND-PERIOD ATOMS

◆ LCAO-MO approximation

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

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

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

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

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

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

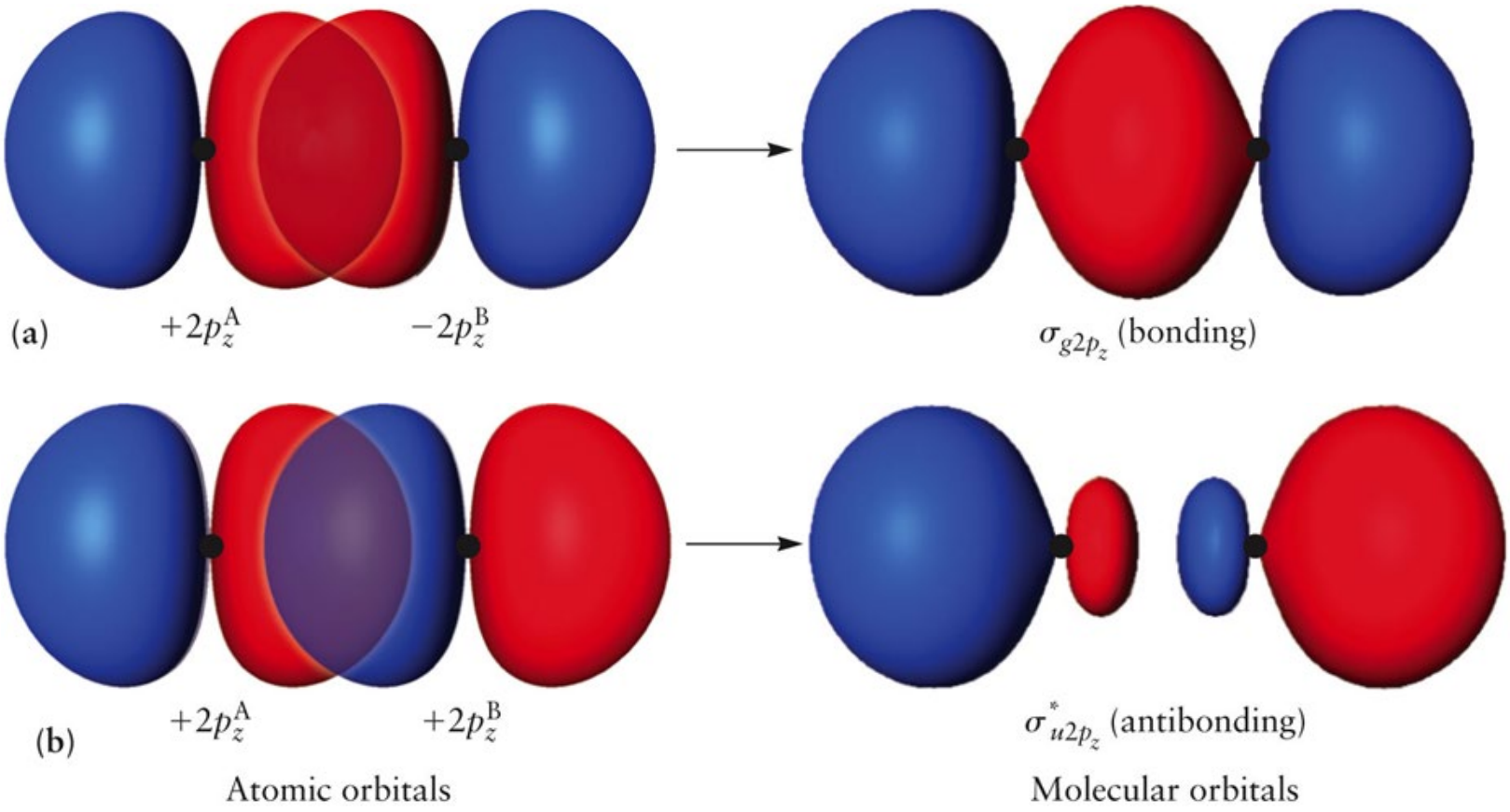


Fig. 6.14. Formation of (a) σ_{g2p_z} bonding and (b) $\sigma^*_{u2p_z}$ antibonding MOs from $2p_z$ orbitals on atoms A and B.

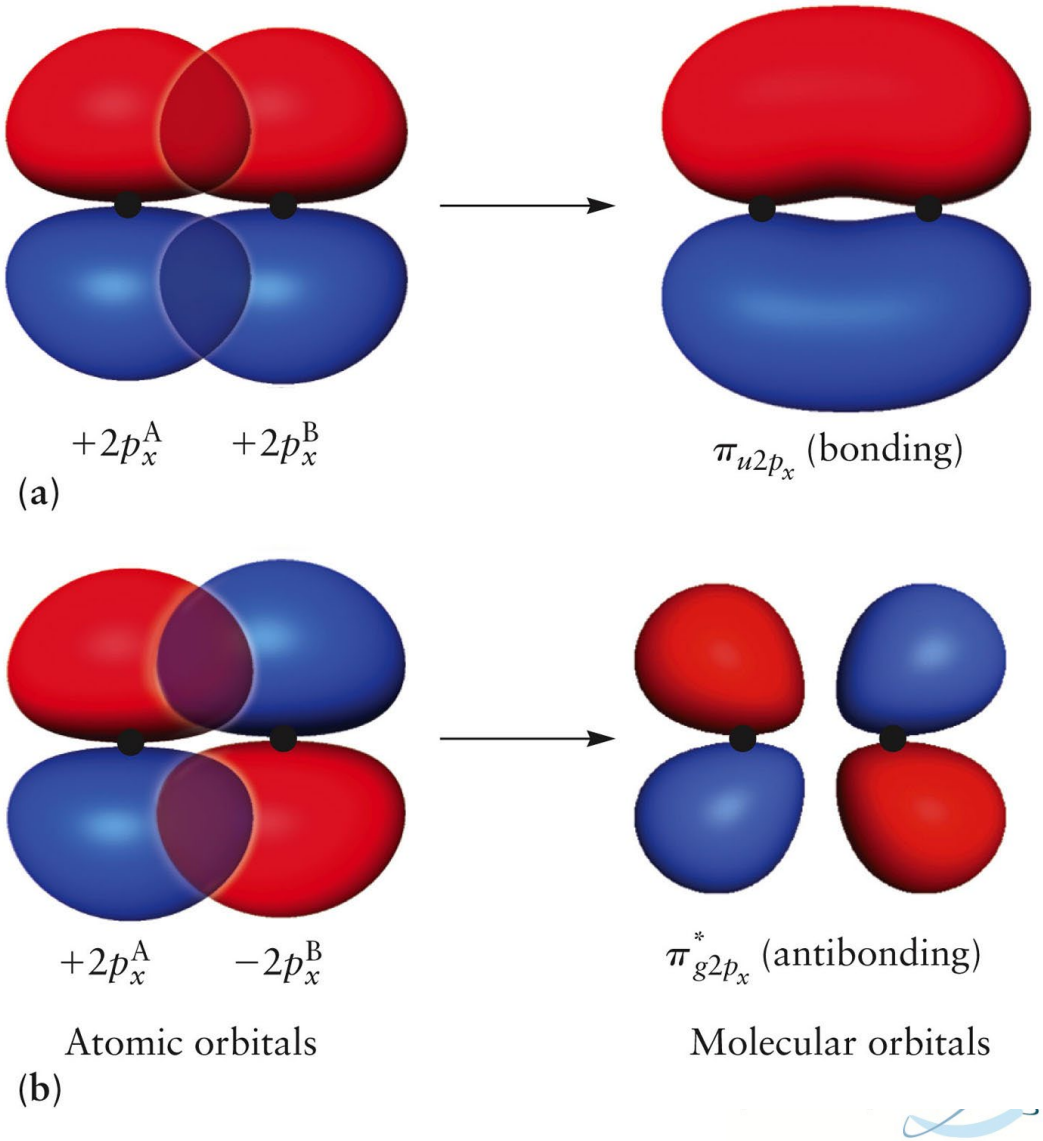
➢ Doubly degenerate π_{2p_x} & π_{u2p_y} MO's

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

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

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

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



➢ 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

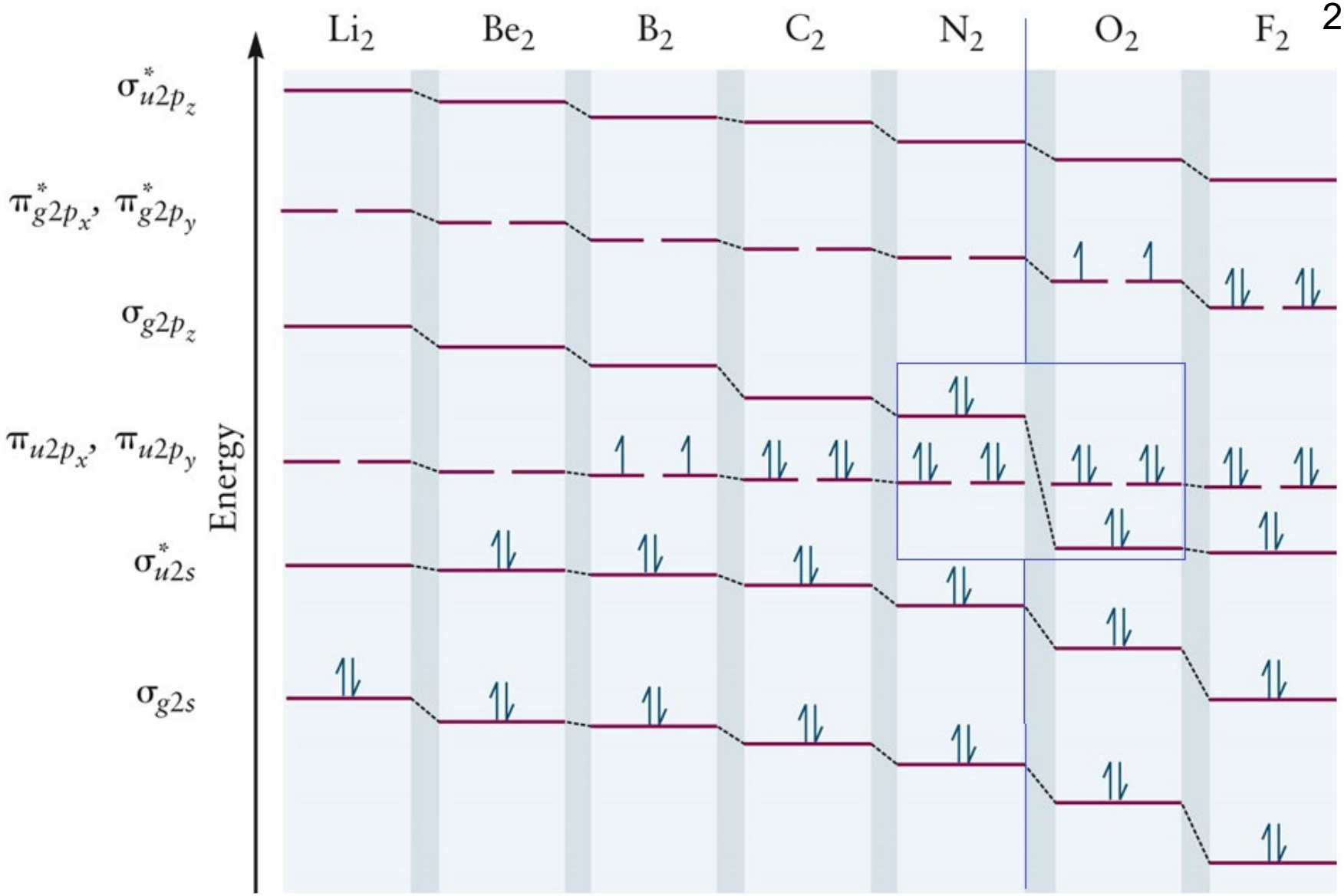


Fig. 6.16. Energy levels for the homonuclear diatomics Li_2 through F_2.

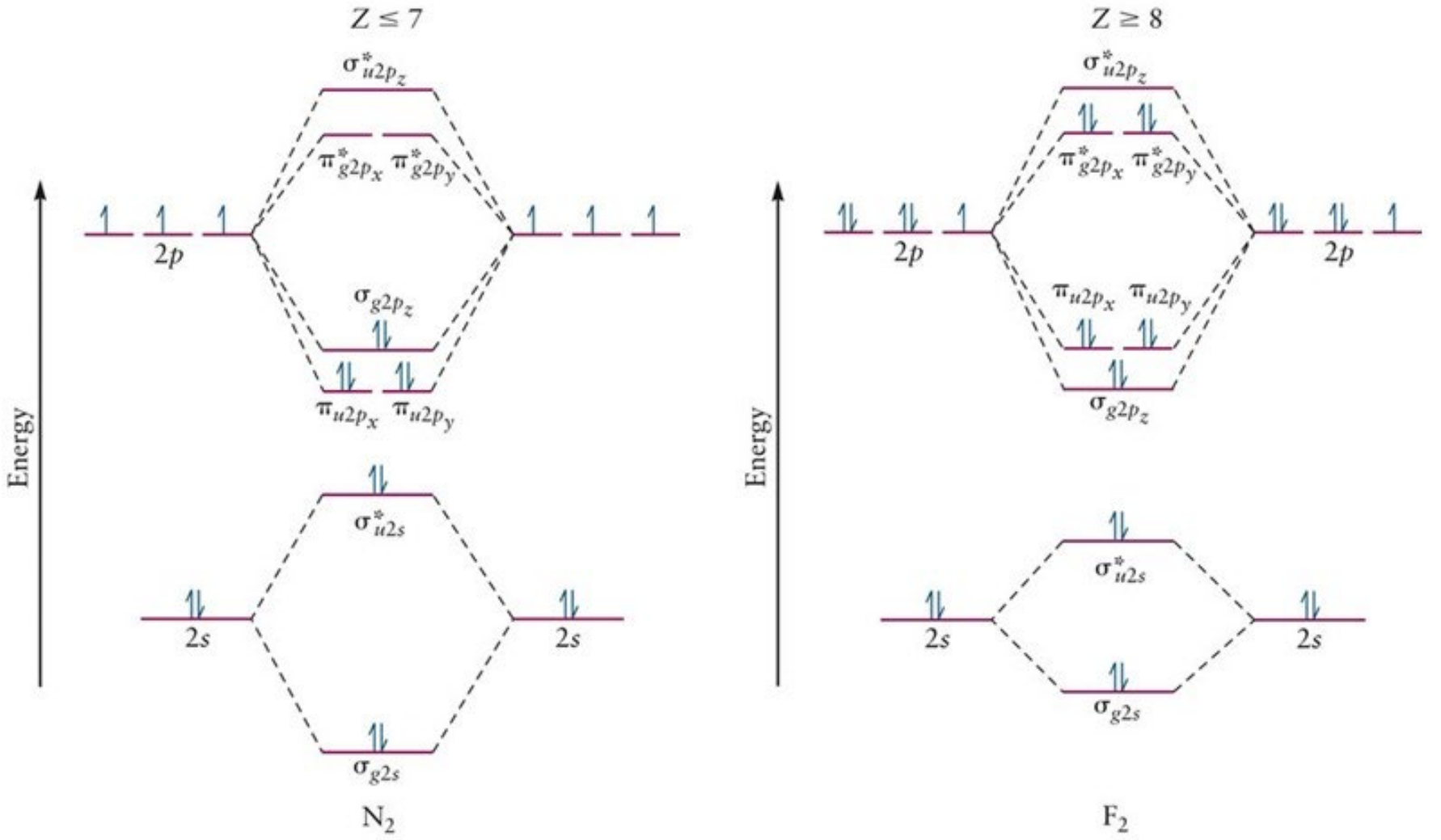
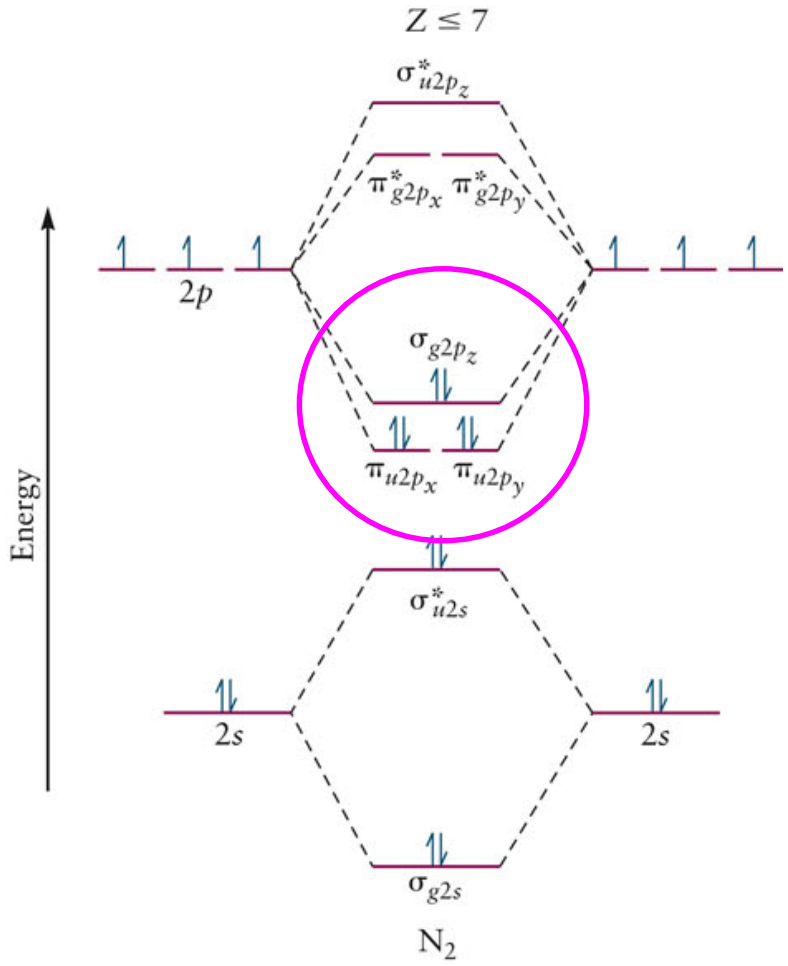
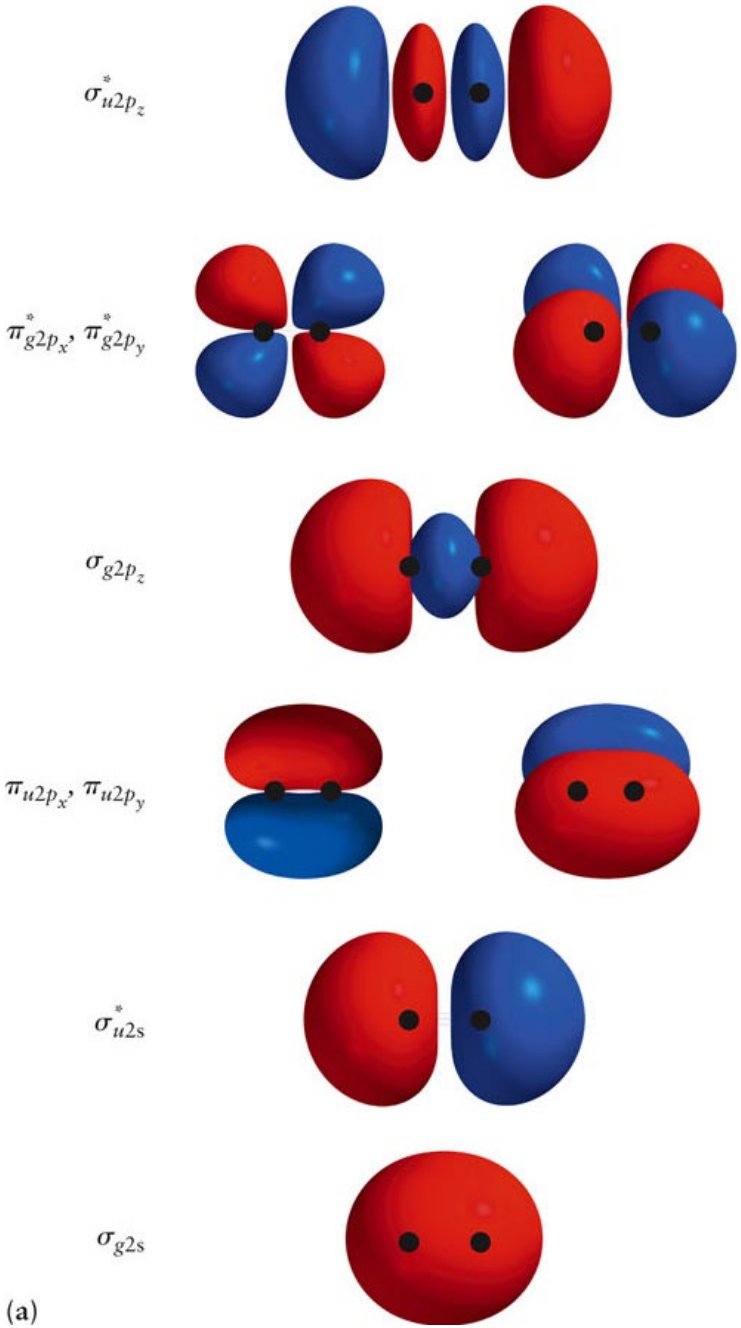
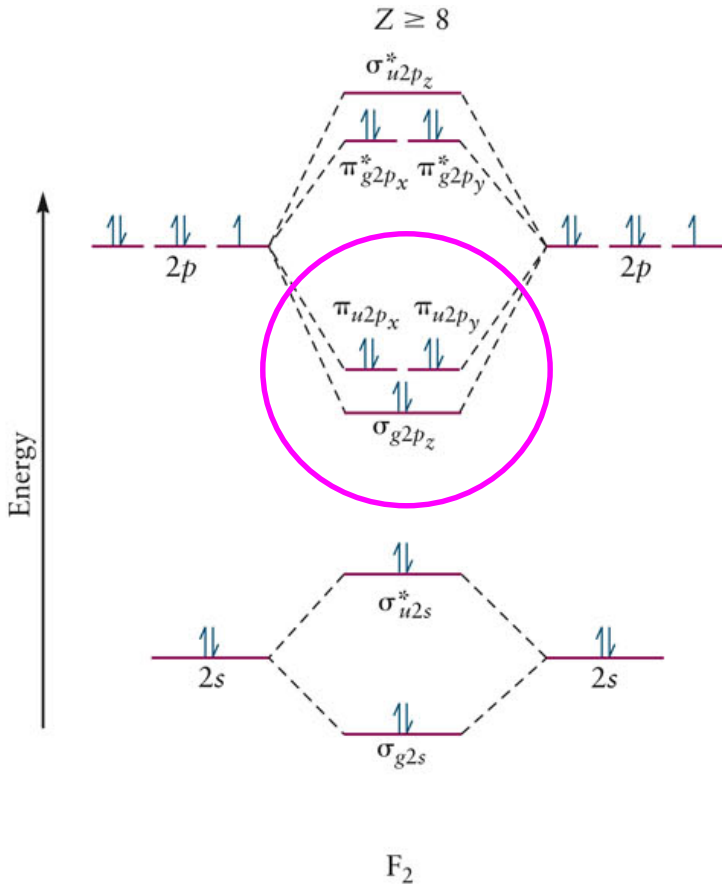
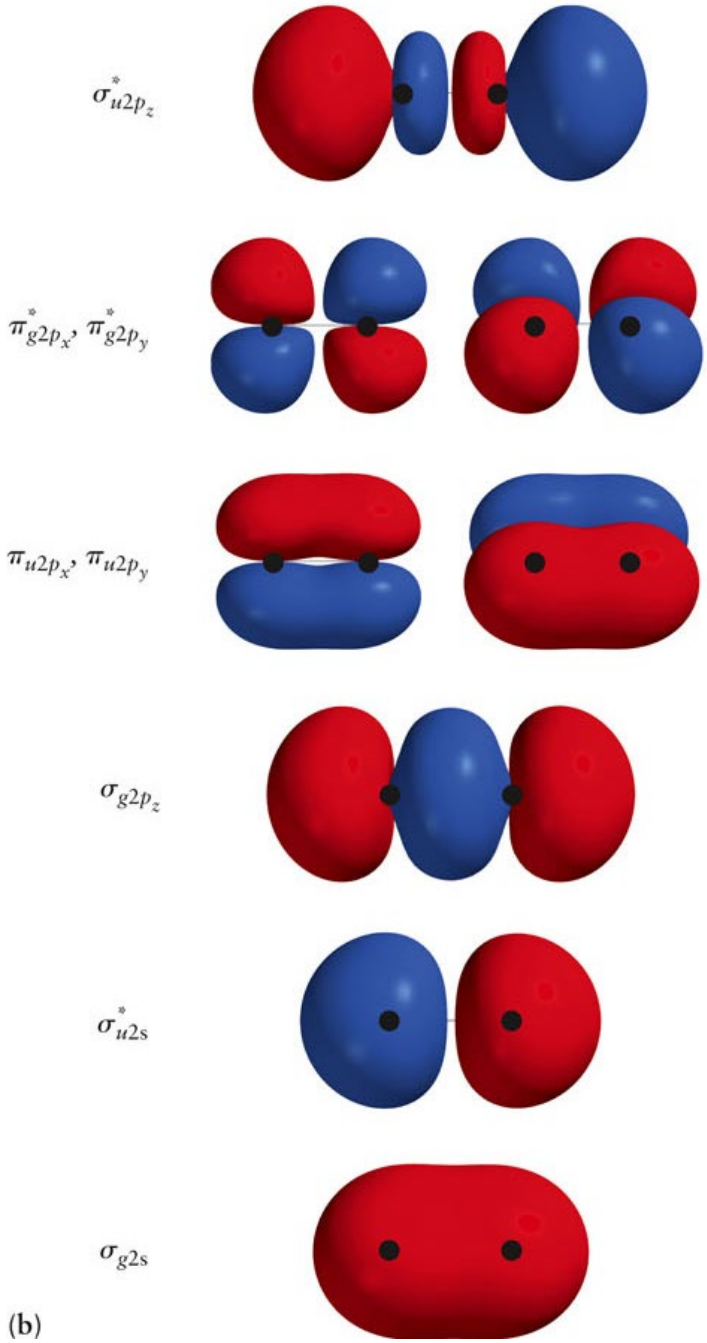


Fig. 6.17. Correlation diagrams for second-period diatomic molecules, N_2 & F_2.


Z ≤ 7
σ*u2pz
π*g2px π*g2py
2p
σg2pz
πu2px πu2py
σ*u2s
2s
2s
σg2s
Energy
N2


σ*u2pz
π*g2px, π*g2py
σg2pz
πu2px, πu2py
σ*u2s
σg2s
(a)


Z ≥ 8
σ*u2pz
π*g2px π*g2py
2p
2p
πu2px πu2py
σg2pz
Energy
σ*u2s
2s
2s
σg2s
F2


σ*u2pz
π*g2px, π*g2py
πu2px, πu2py
σg2pz
σ*u2s
σg2s
(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.

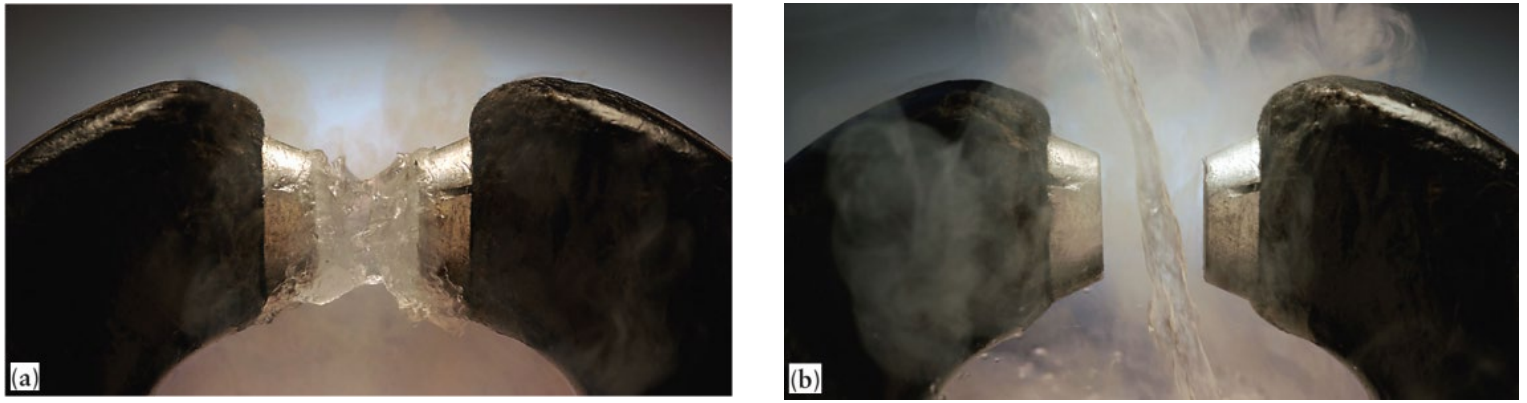


Fig. 6.18. (a) Paramagnetic liquid oxygen, O_2, and (b) diamagnetic liquid nitrogen, N_2, pours straight between the poles of a magnet.

TABLE 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.

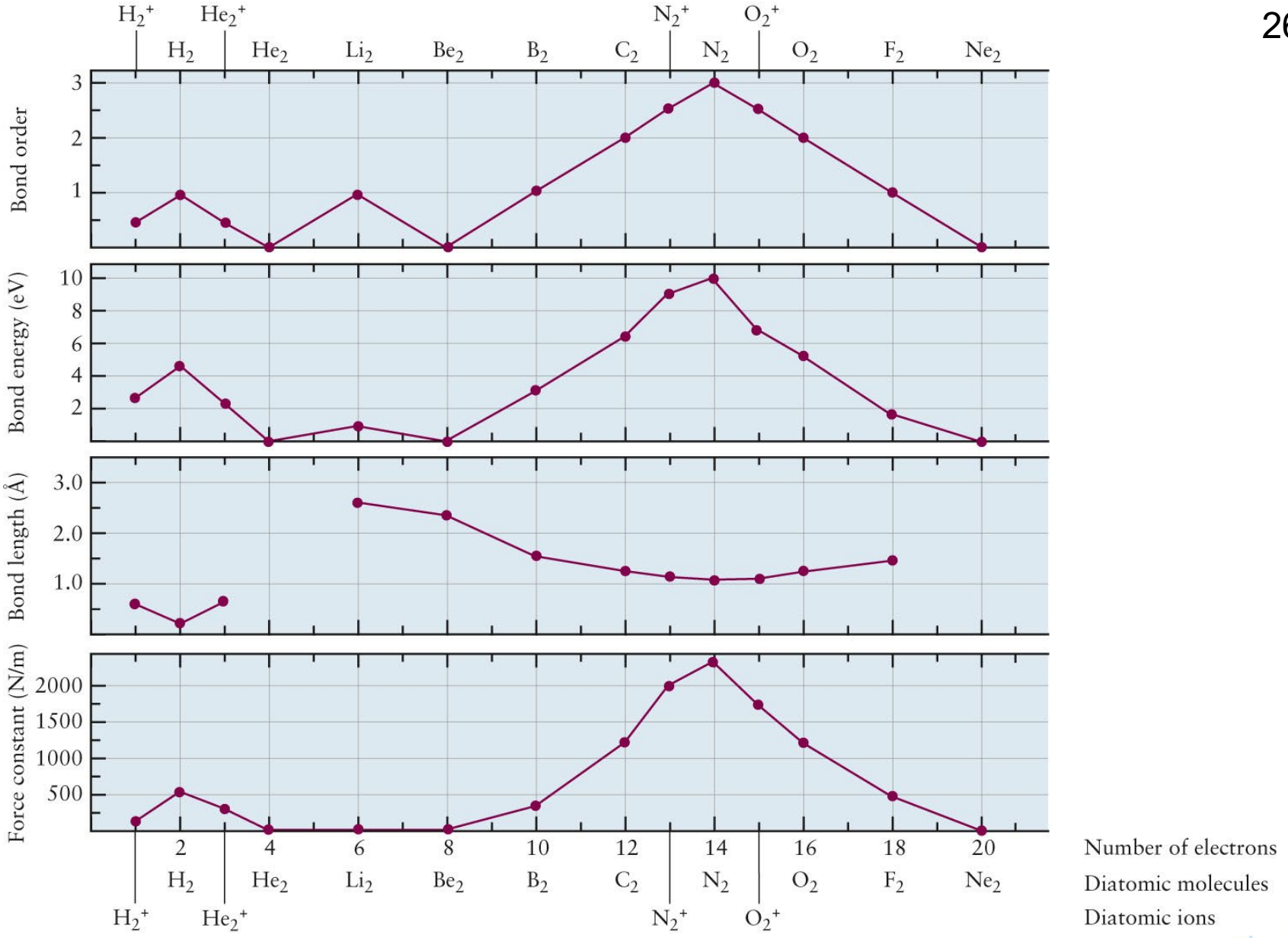


Fig. 6.19. Trends in several properties with the number of valence electrons in the second-row diatomic molecules.

6.6 HETERONUCLEAR DIATOMIC MOLECULES

For the 2s orbitals,

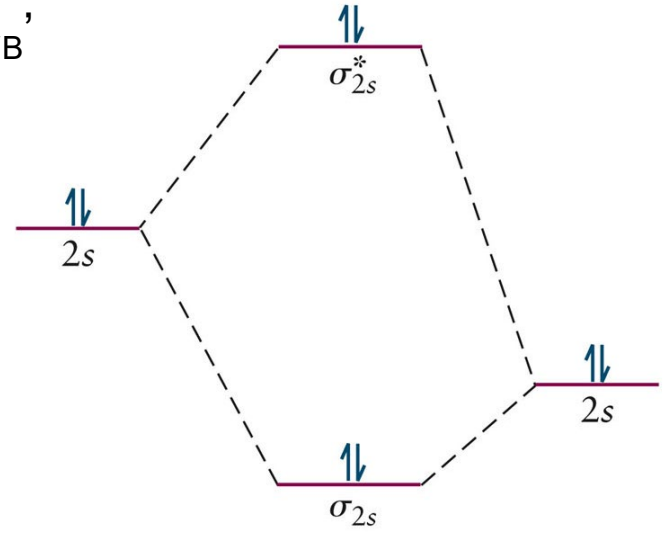
$$\sigma_{2s} = C_A 2s^A + C_B 2s^B \qquad \sigma_{2s}^* = C_A' 2s^A - C_B' 2s^B$$

In the homonuclear case, $C_A = C_B$; $C_A' = C_B'$

If B is more electronegative than A,

$C_B > C_A$ for bonding s MO,

$C_A' > C_B'$ for the higher energy s* MO, closely resembling a $2s^A$ AO



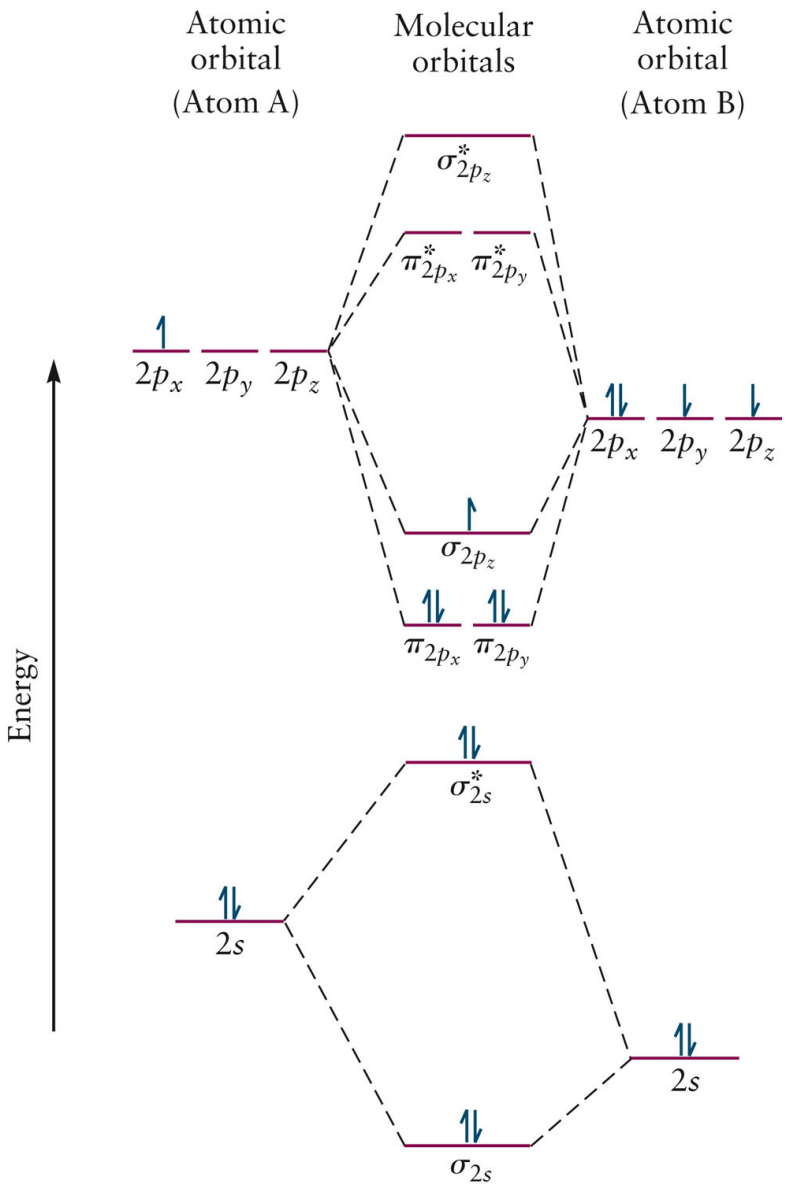
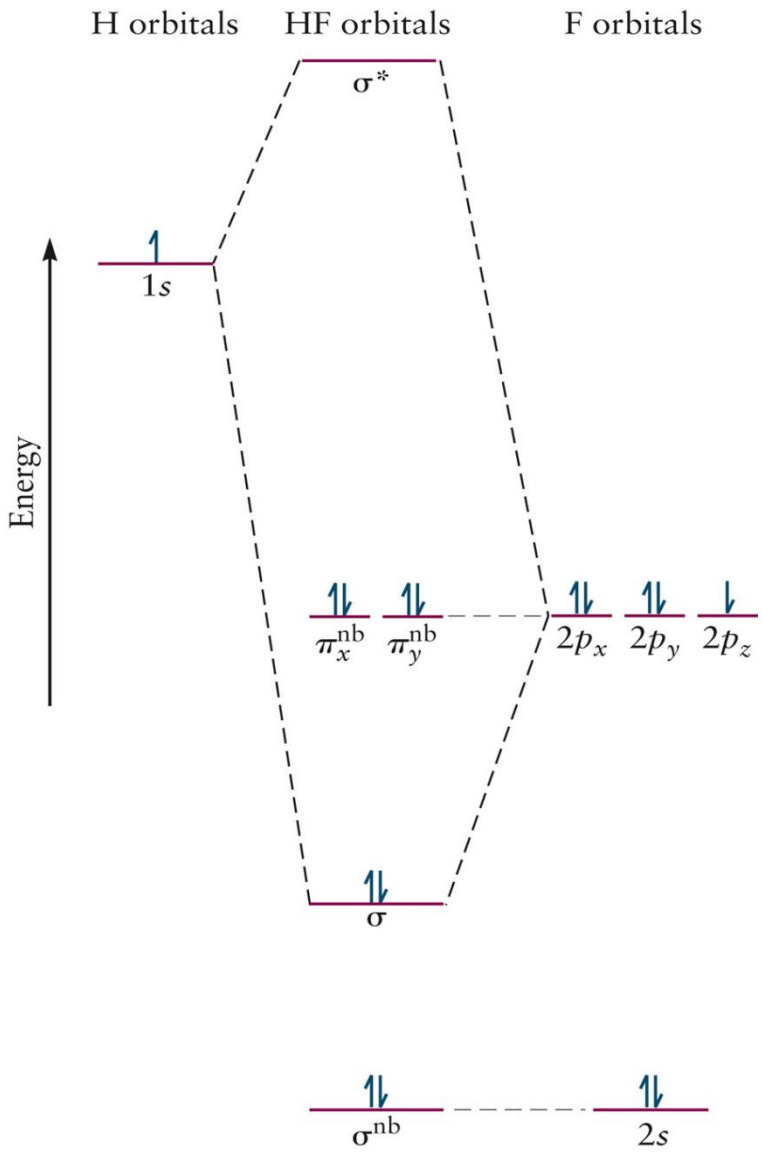


Fig. 6.20. Correlation diagram for heteronuclear diatomic molecules, BO. (O is more electronegative.)



$$\left(\sigma^{nb}\right)^2(\sigma)^2\left(\pi_x^{nb},\pi_y^{nb}\right)^4$$

Fig. 6.22. Correlation diagram for HF. The 2*s*, 2p_x, and 2p_y atomic orbitals of F do not mix with the 1*s* atomic orbital of H, and therefore remain ***nonbonding***.

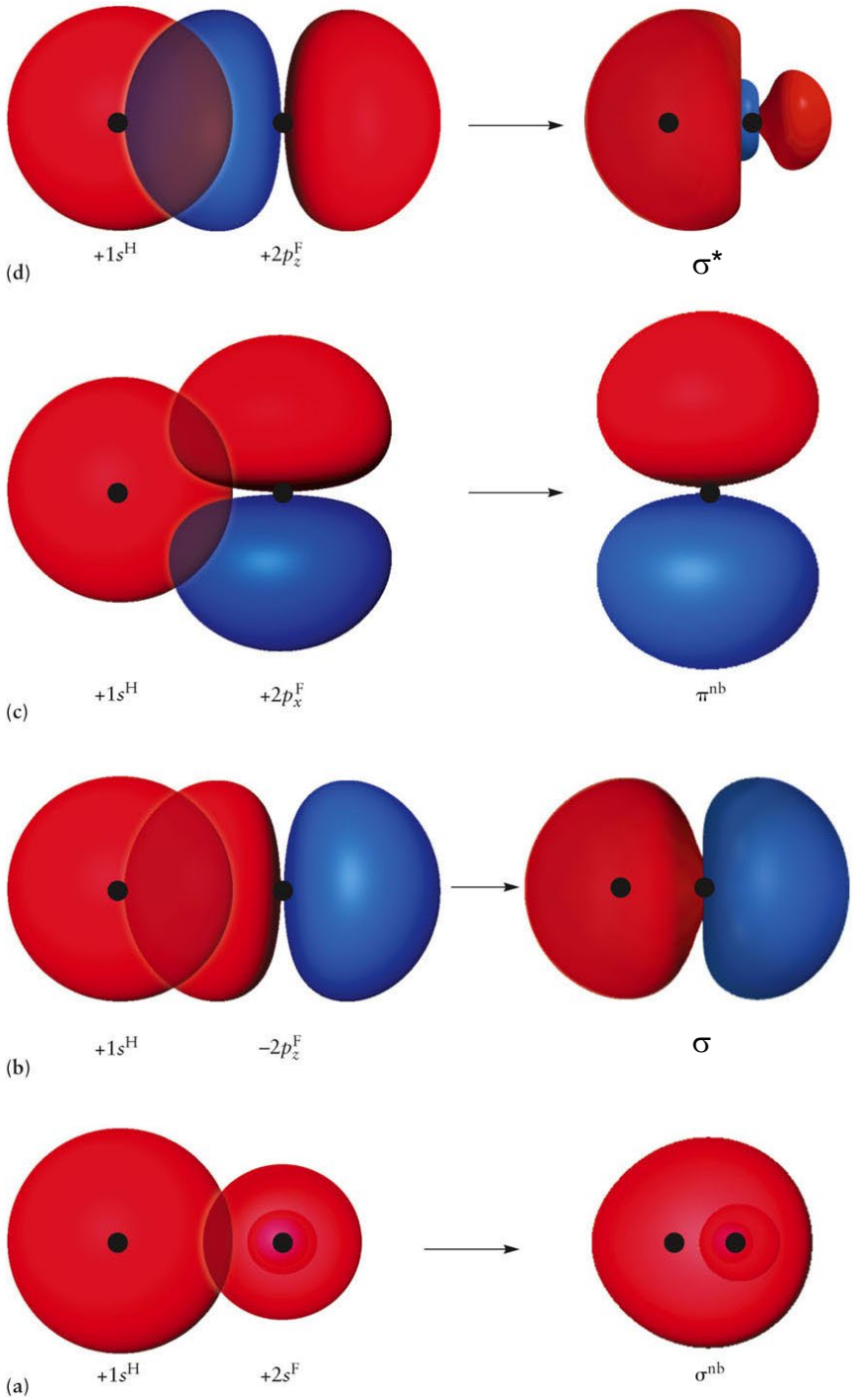


Fig. 6.21. Overlap of atomic orbitals in HF.

6.7 SUMMARY COMMENTS FOR THE LCAO METHOD AND DIATOMIC MOLECULES

The **qualitative LCAO method** easily identifies **the sequence of energy levels for a molecule**, such as trends in bond length and bond energy, but does not give their specific values.

The qualitative energy level diagram is **very useful for interpreting experiments** that involve adsorption and emission of energy such as spectroscopy, ionization by electron removal, and electron attachment.

6

CHAPTER

QUANTUM MECHANICS AND MOLECULAR STRUCTURE

KAIST CHEMISTRY

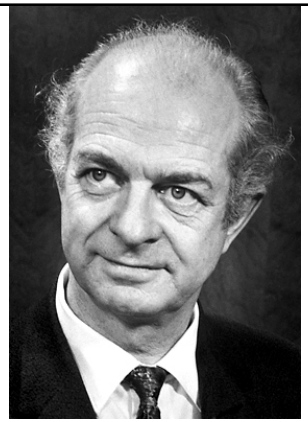
6.8 VALENCE BOND THEORY AND THE ELECTRON PAIR BOND

- 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

Walther Heitler
(DE, 1904-1981)

Fritz London
(DE, 1900-1954)

John C. Slater
(US, 1900-1976)



Linus Pauling
(US,1901-1994)

Nobel Prizes

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

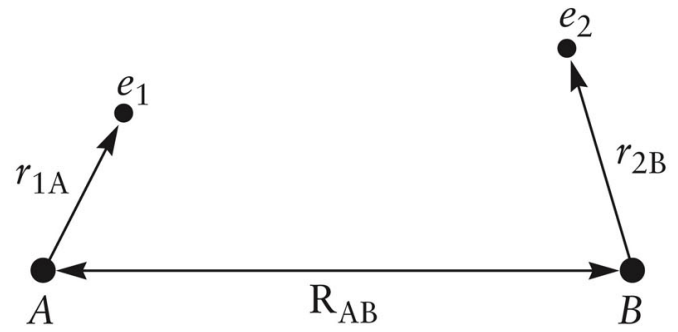
Peace ('62)

➢ 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

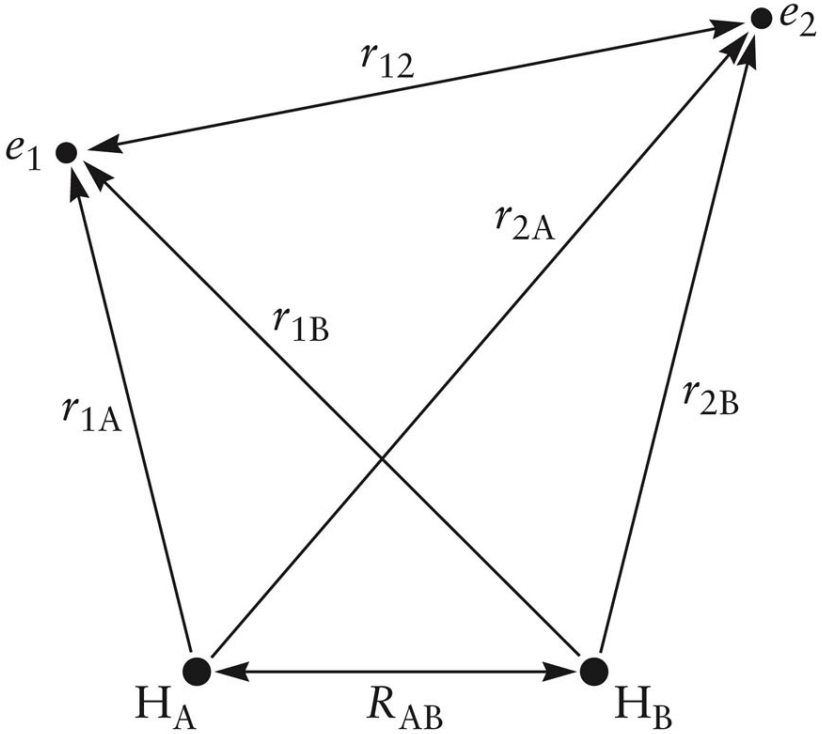


- As the atoms begin to interact strongly,

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

indistinguishable

$$c_1 = \pm c_2$$

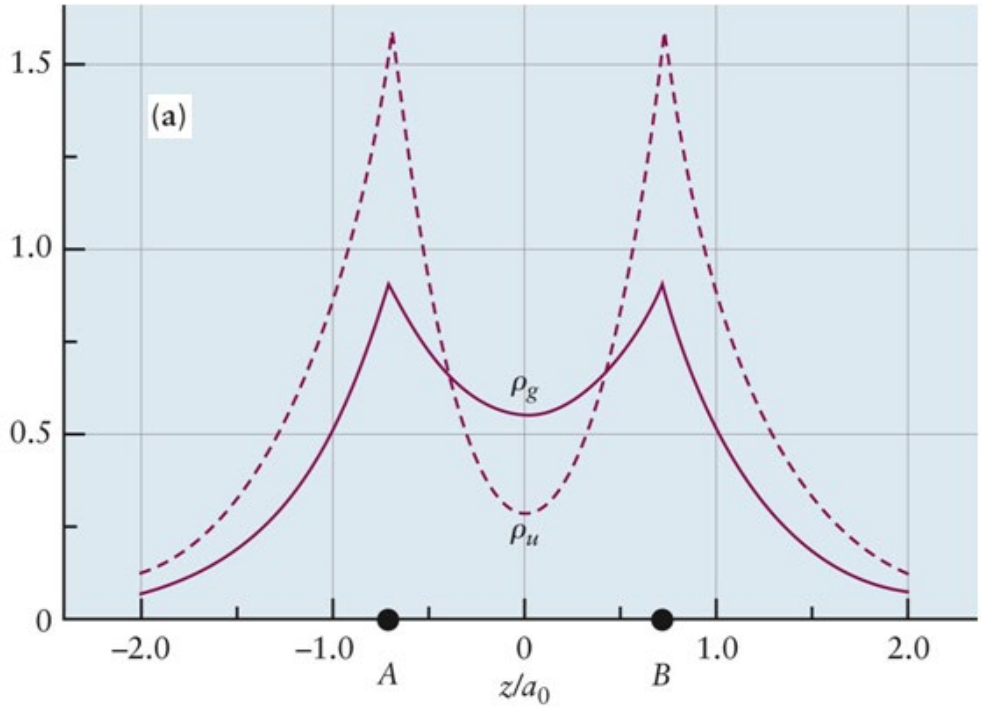


(b)

➢ VB wave function for the single bond in a H_2 molecule

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

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



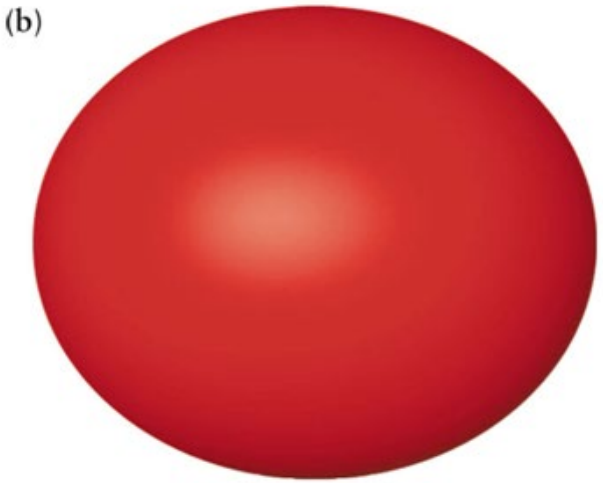
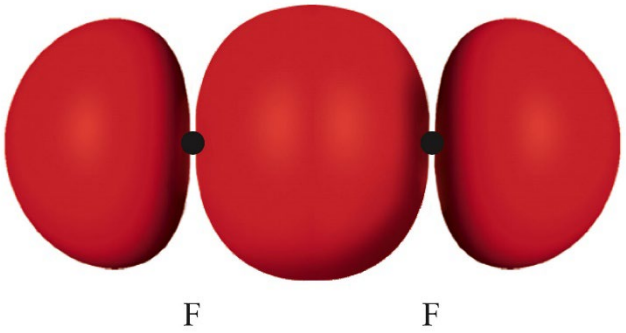


Fig. 6.24. (a) The electron density ρ_g for ψ_g^{el} and ρ_u for ψ_u^{el} in the simple VB model for H_2. (b) Three-dimensional isosurface of the electron density for the ψ_g^{el} wave function in the H_2 σ bond.

- **For F_2 σ bond,**

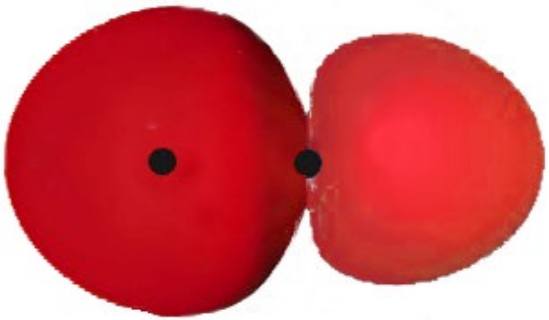
$$\psi_g^{bond} = C_1[2p_z^A(1)2p_z^B(2) + 2p_z^A(2)2p_z^B(1)]$$



Lewis diagram for F_2.

- **For HF σ bond,**

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



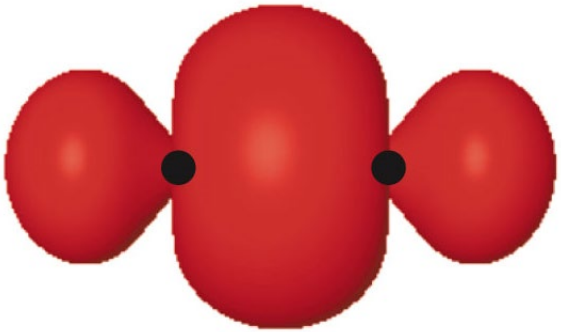
➢ Multiple Bonds

N: $(1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1$

:N: : :N:

Lewis diagram for N_2.

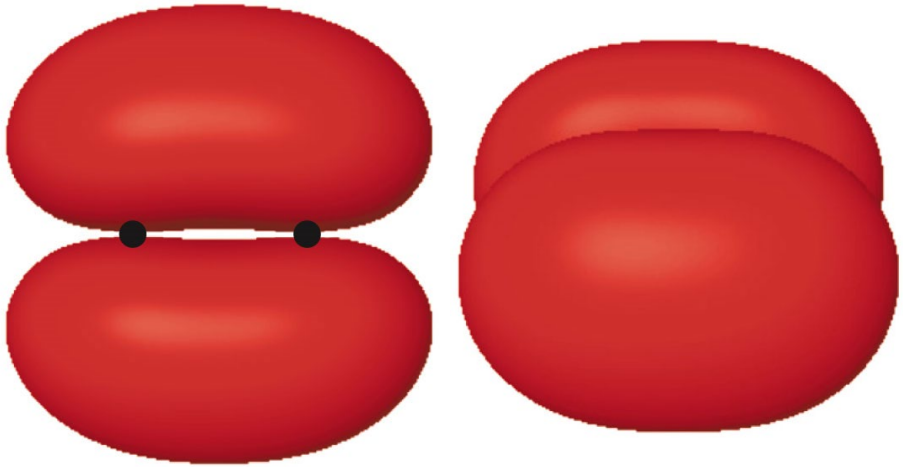
$$\psi_{\sigma}^{bond} = C_1[2p_z^A(1)2p_z^B(2) + 2p_z^A(2)2p_z^B(1)]$$



σ

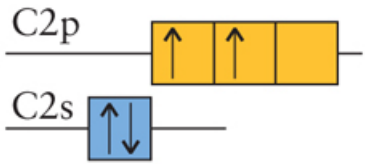
$$\psi_{\pi_x}^{bond}(1,2) = C_1[2p_x^A(1)2p_x^B(2)] + C_1[2p_x^A(2)2p_x^B(1)]$$

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

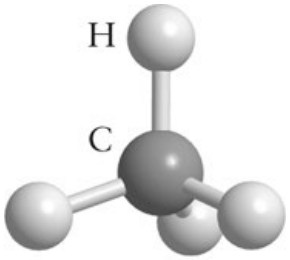


π_x π_y

➢ Polyatomic Molecules



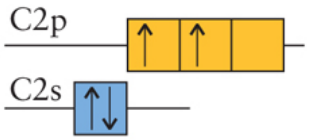
35 Carbon, $[He]2s^2 2p_x^1 2p_y^1$



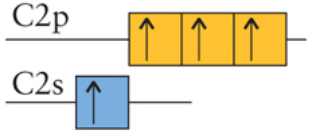
1 Methane, CH_4

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

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**:

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

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 → linear molecule

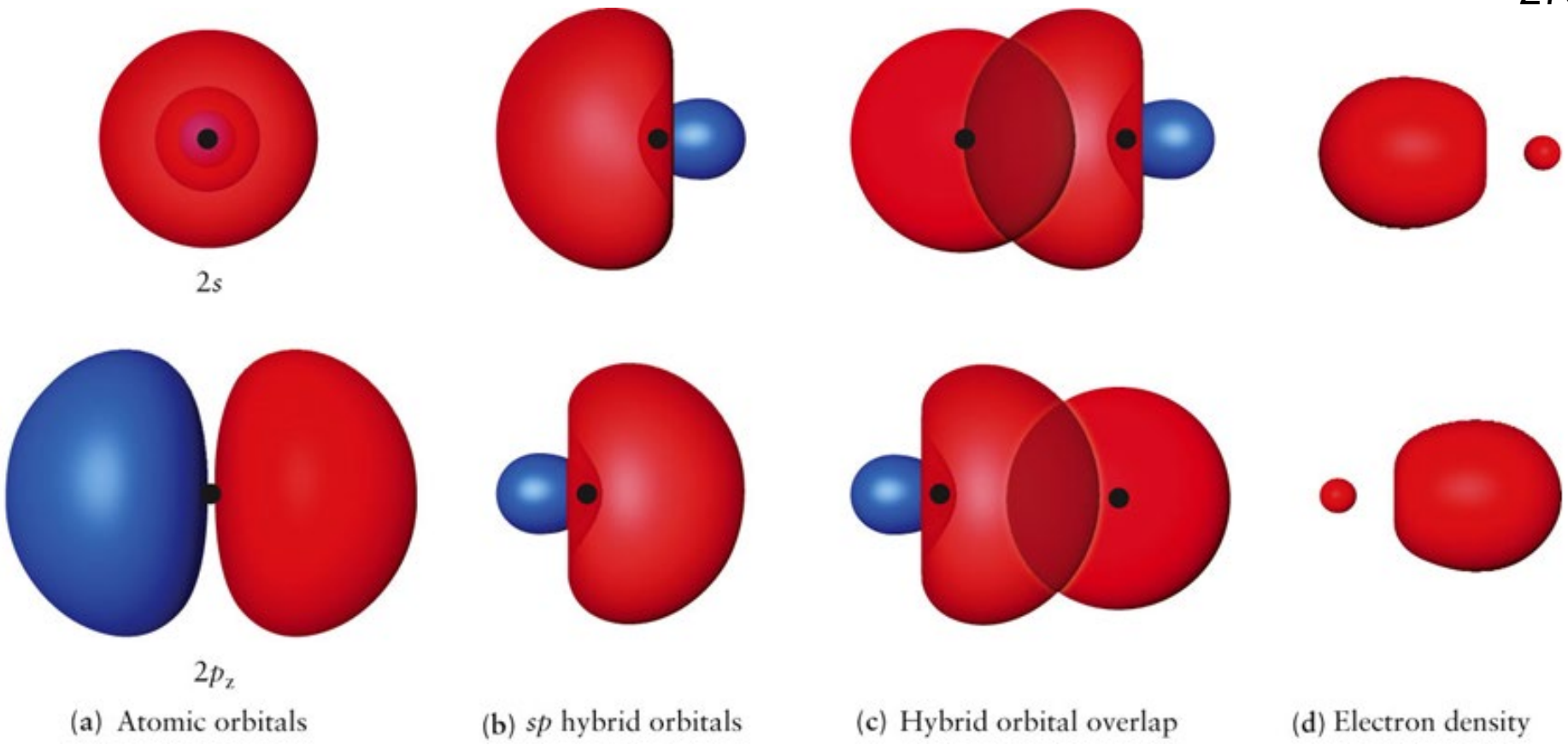


Fig. 6.28. Formation, shapes, and bonding of the *sp* hybrid orbitals in the BeH_2 molecule. (a) The 2*s* and $2p_z$ orbitals of the Be atom. (b) The two *sp* hybrid orbitals formed from the 2*s* and $2p_z$ orbitals on the Be atom. (c) The two σ bonds that form from the overlap of the *sp* hybrid orbitals with the H1*s* orbitals, making tow single bonds in the BeH_2 molecule. (d) Electron density in the two σ bonds.

➢ sp^2-hybridization BH_3

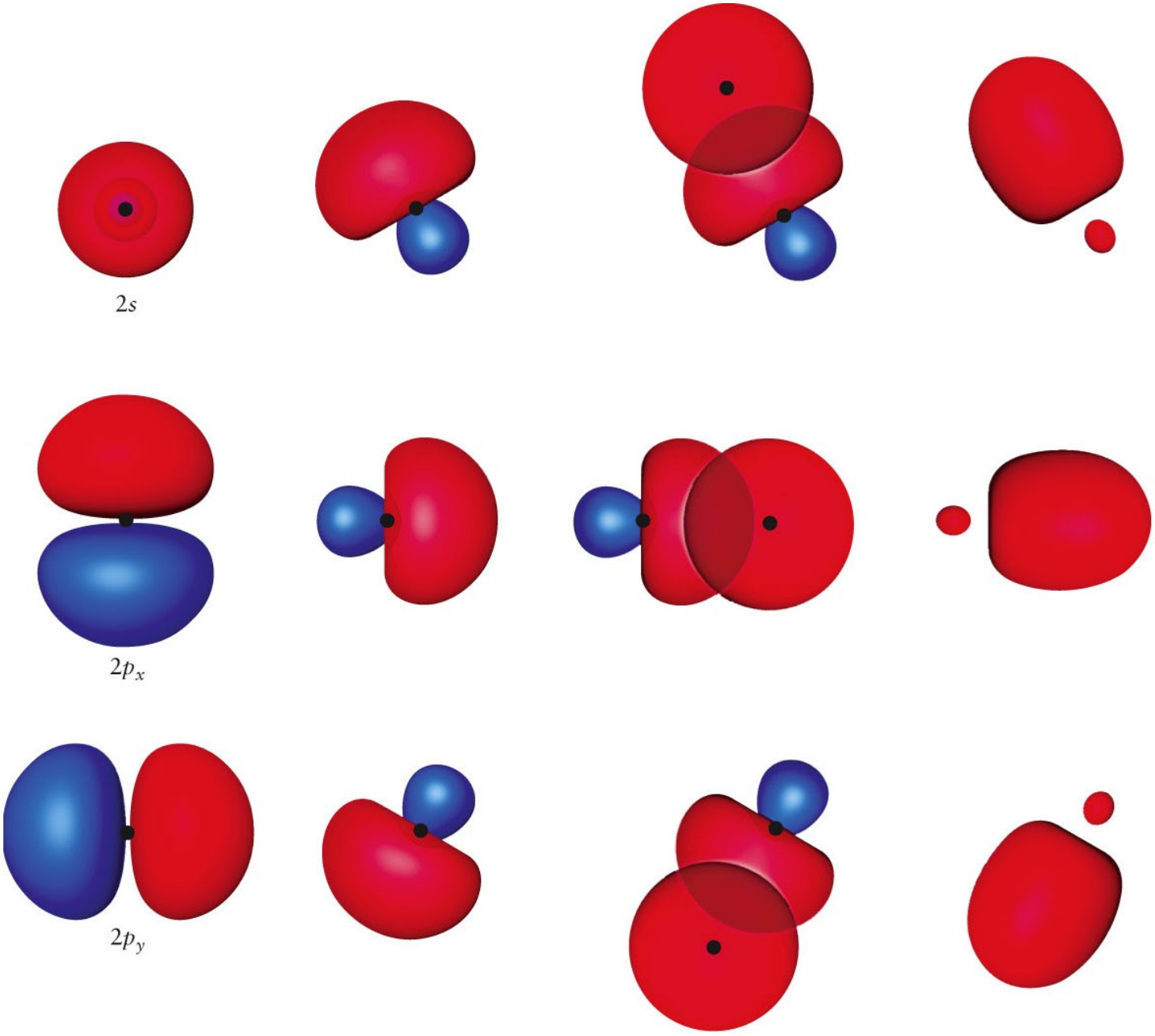
Promotion: B: $(1s)^2(2s)^2(2p_x)^1 \rightarrow$ B: $(1s)^2(2s)^1(2p_x)^1(2p_y)^1$

Three equivalent sp^2 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



(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

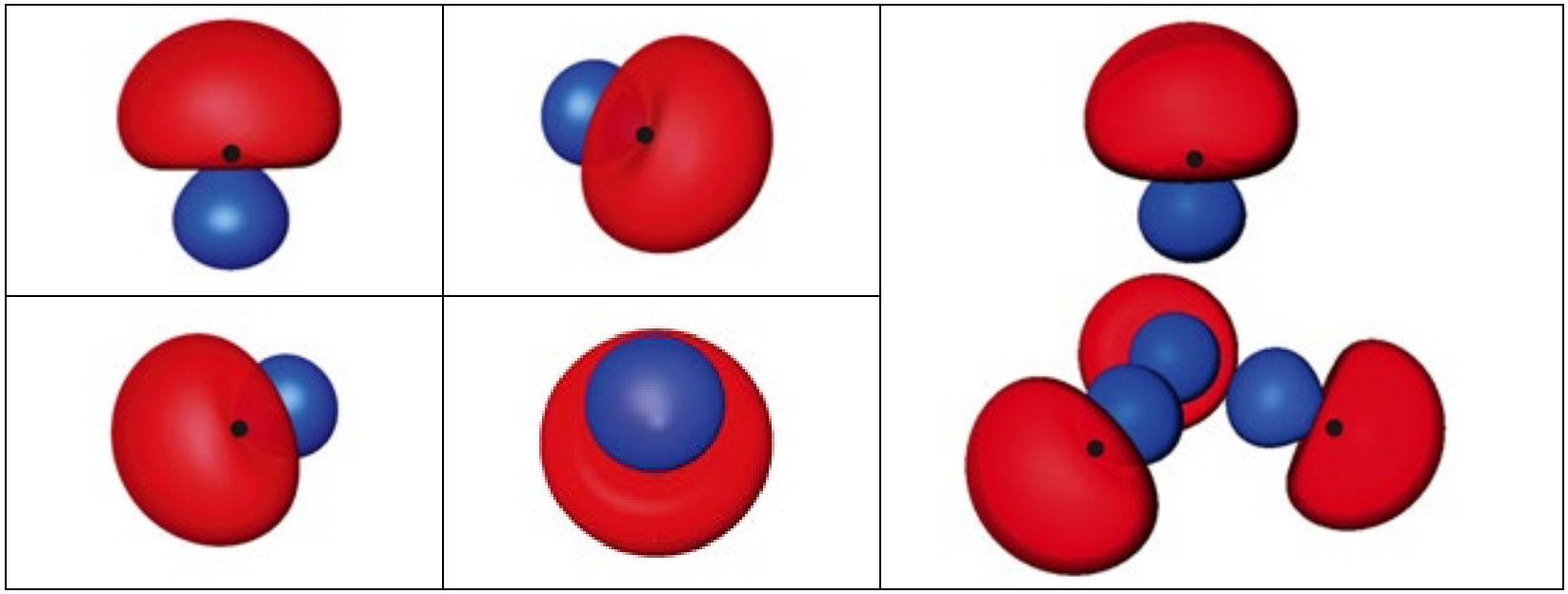


Fig. 6.30. Shapes and relative orientations of the four sp^3 hybrid orbitals in CH_4 pointing at the corners of a tetrahedron with the C atom at its center.

Summary of Hybridization Results

TABLE 6.4

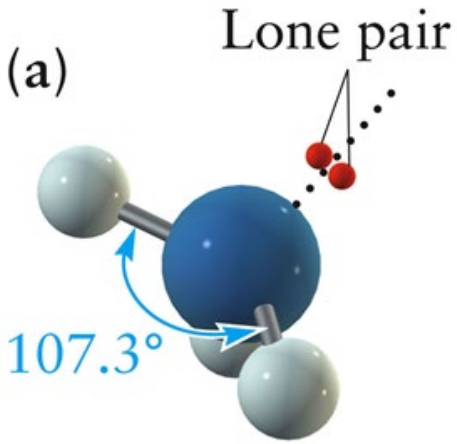
Orbital Hybridization and Molecular Geometry

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

Hybridization and Lone Pairs

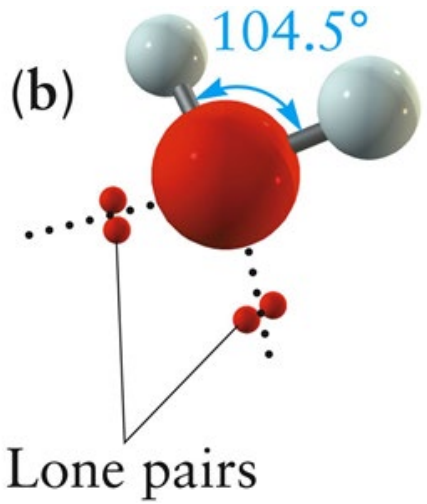
- **NH_3**: sp^3 hybrid orbitals

  trigonal pyramid with three equivalent bonds



- **H_2O**: sp^3 hybrid orbitals

  two lone pairs → the bent or angular structure



➢ 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, $C_2\chi_1$-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): $\sigma(C_1\chi_3$- $C_2\chi_3) + \pi(C_1 2p_z$-$C_2 2p_z)$

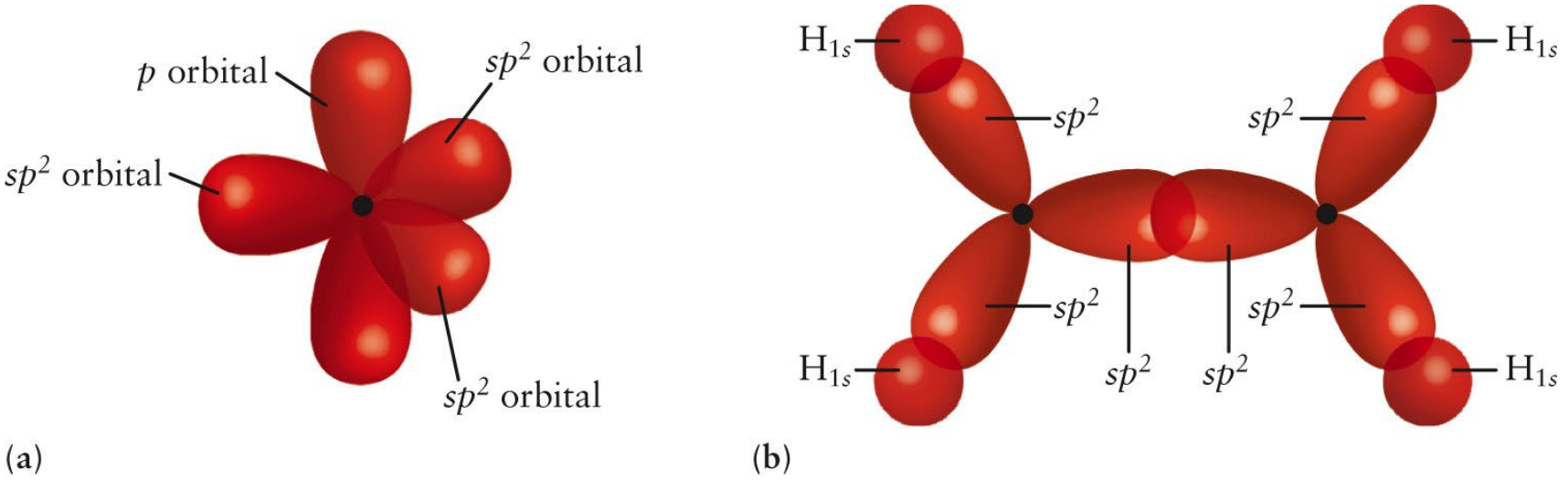


Fig. 6.33. Formation of σ bonds in ethylene.

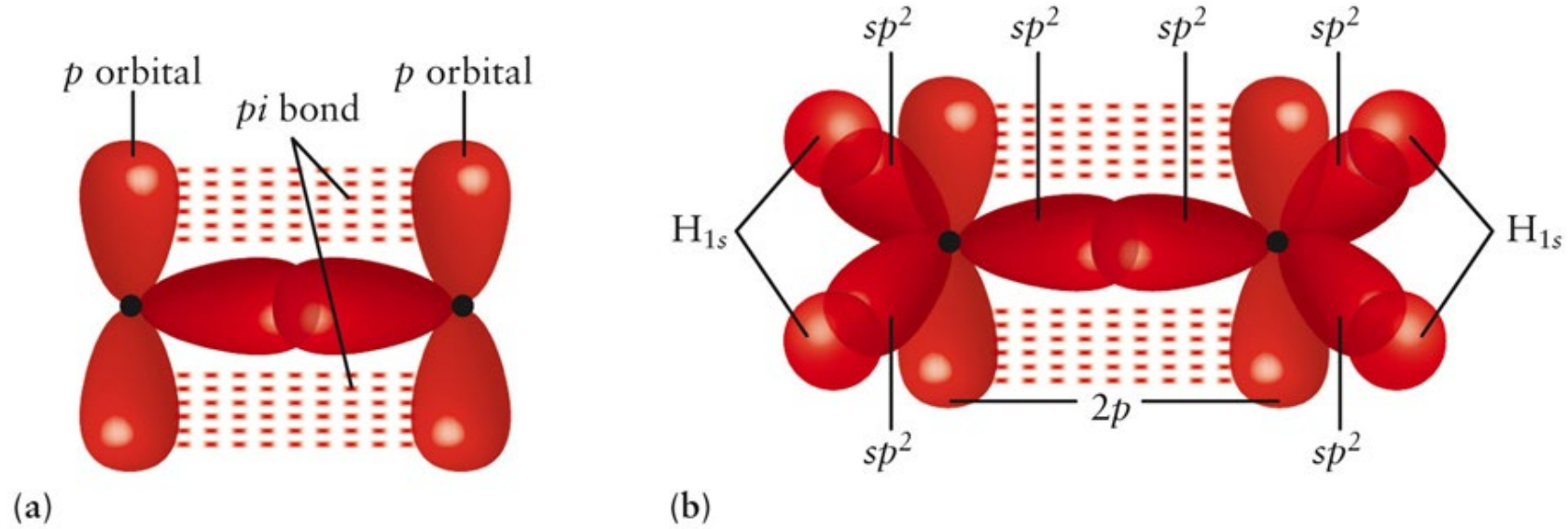


Fig. 6.34. Formation of a π bond in ethylene.

❖ Acetylene, C_2H_2

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 ($C_1 2p_x$-$C_2 2p_x$, $C_1 2p_y$-$C_2 2p_y$)

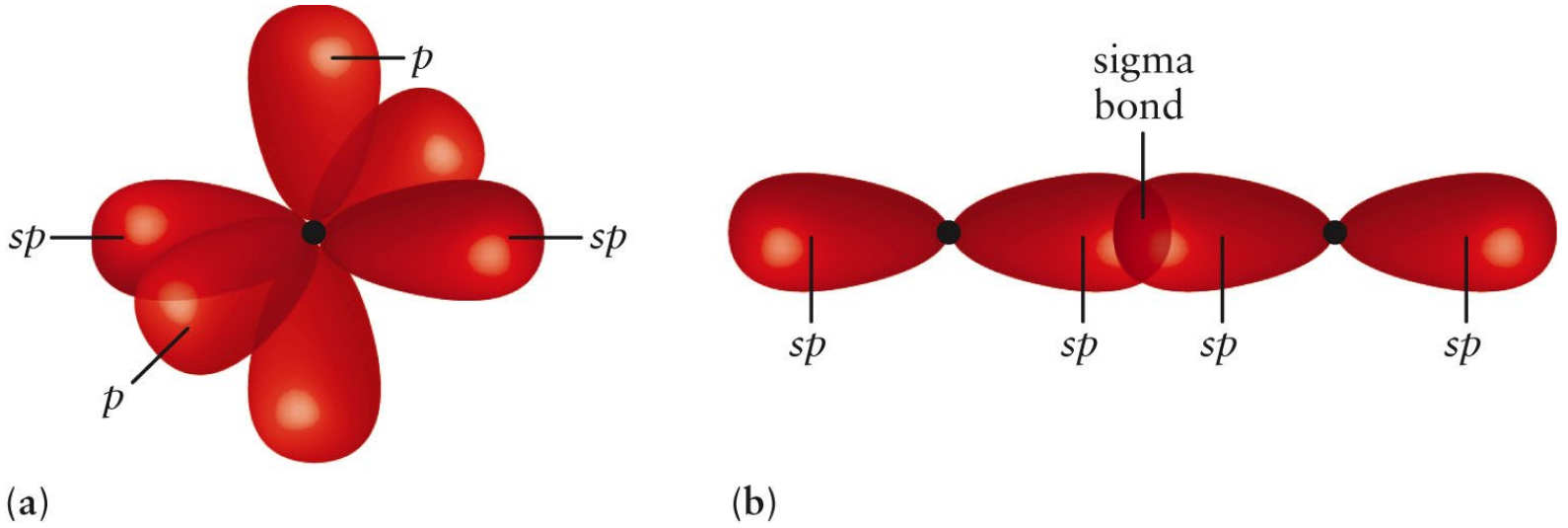


Fig. 6.35. Formation of σ bonds in acetylene.

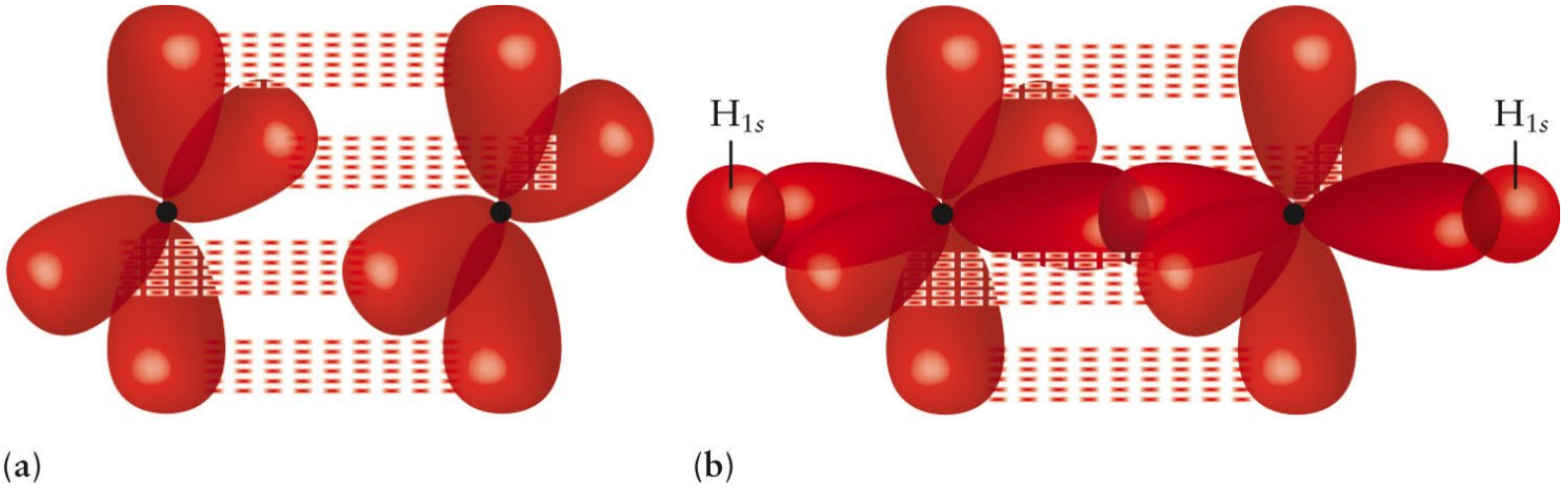


Fig. 6.36. Formation of two π bonds in acetylene.

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.

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 ^{o}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?

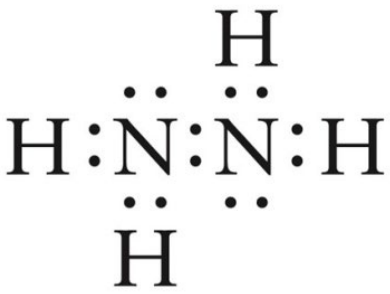
(1) Elemental analysis: N(87.419%), H (12.581%)

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

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

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

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



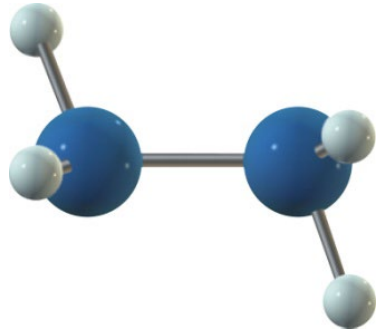
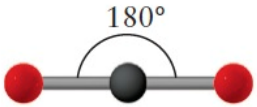
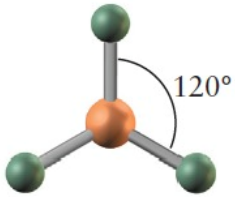
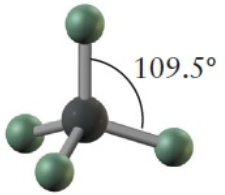


TABLE 6.5

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		BeH_2, CO_2
AX_3	3	0	sp^2	Trigonal planar		BF_3, SO_3
AX_2	3	1	sp^2	Bent		SO_2
AX_4	4	0	sp^3	Tetrahedral		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

The electrostatic potential energy map

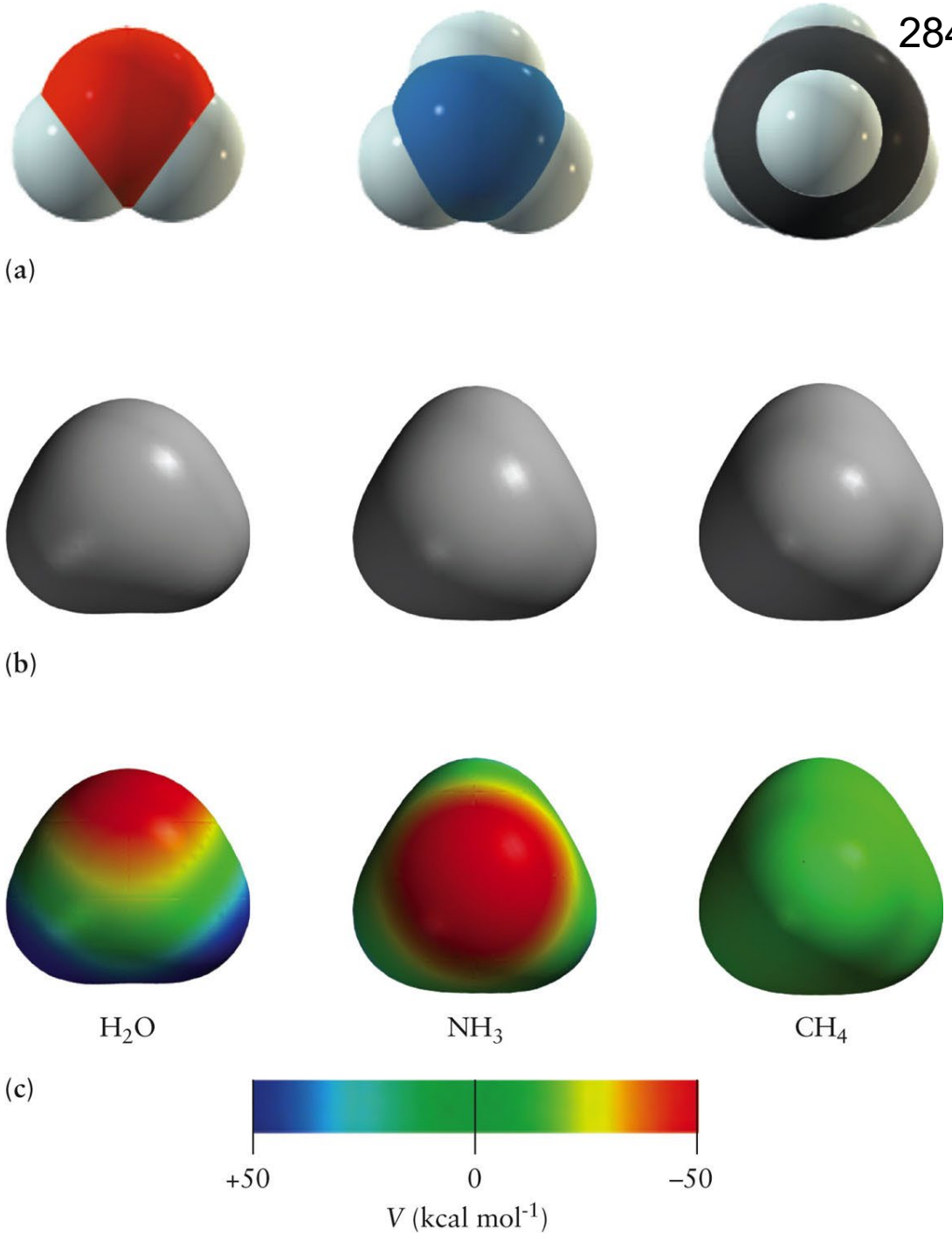


Fig. 6.38. (a) Space-filling models. (b) 0.002 $e/(a_0)^3$ electron density surfaces, and (c) electrostatic potential energy surfaces.

6.11 USING THE LCAO AND VALENCE BOND METHODS TOGETHER

◆ Linear Triatomic Molecules (CO_2, N_2O, NO_2^+)

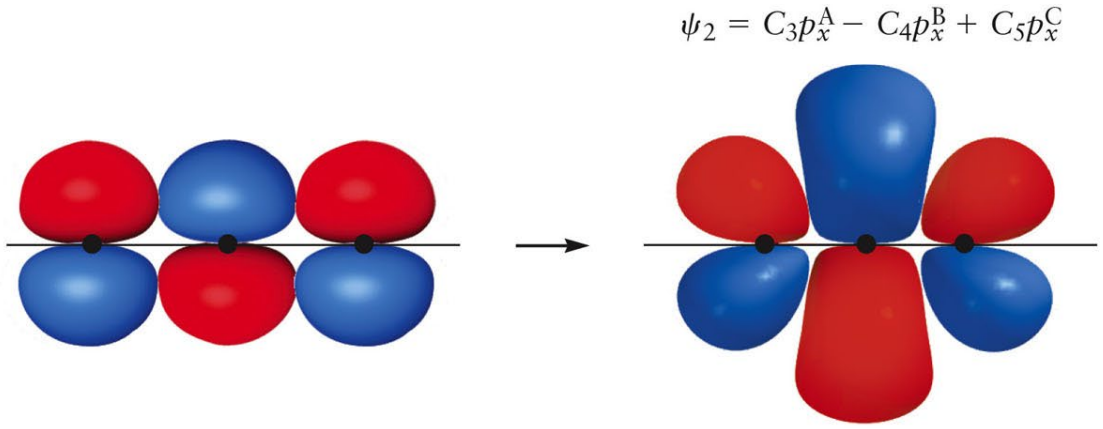
- Central atom → *sp* hybridization from *s* and p_z orbitals

  Two *sp* orbitals form σ bonds with outer atoms

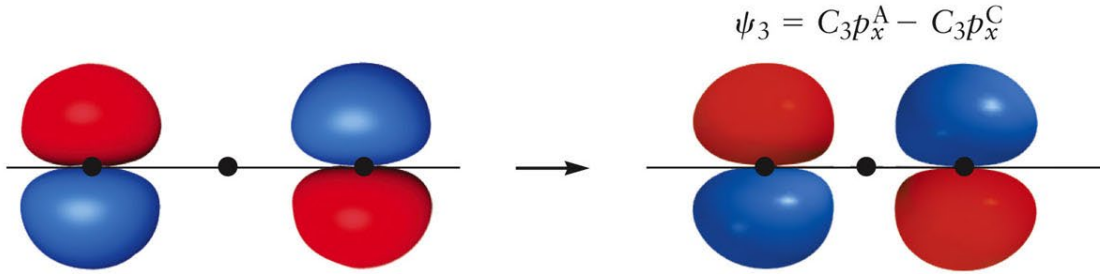
  Remaining p_x and p_y orbitals forms π bond

- σ bonds → p_z orbital (outer) with *sp* hybrid (central)
- π bonds → linear combinations of the p_x (or p_y) orbitals

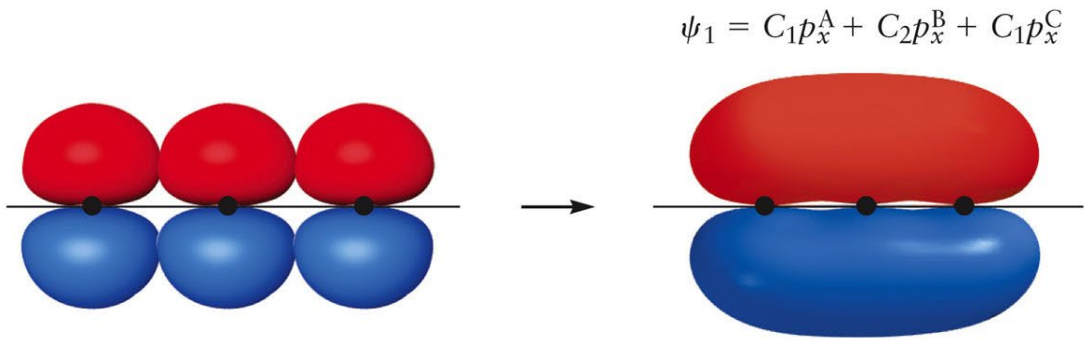
  bonding, antibonding, and nonbonding



(c) π_x^* antibonding

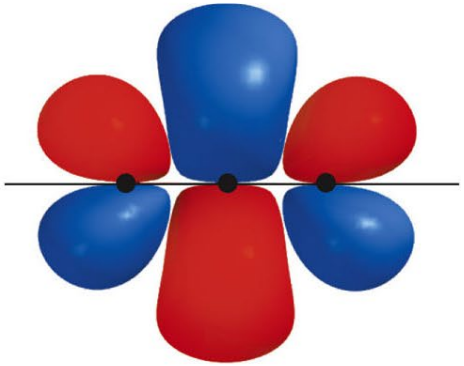


(b) π_x^{nb} nonbonding

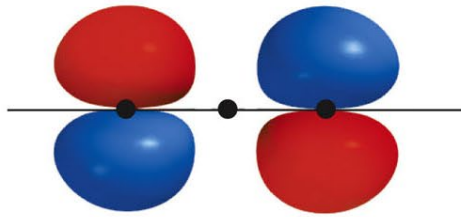


(a) π_x bonding

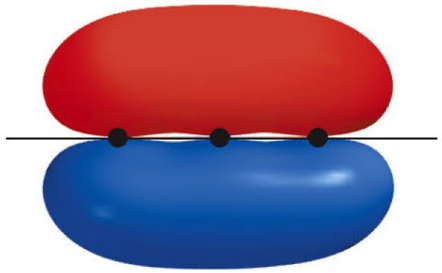
$\psi_2 = C_3p_x^A - C_4p_x^B + C_5p_x^C$

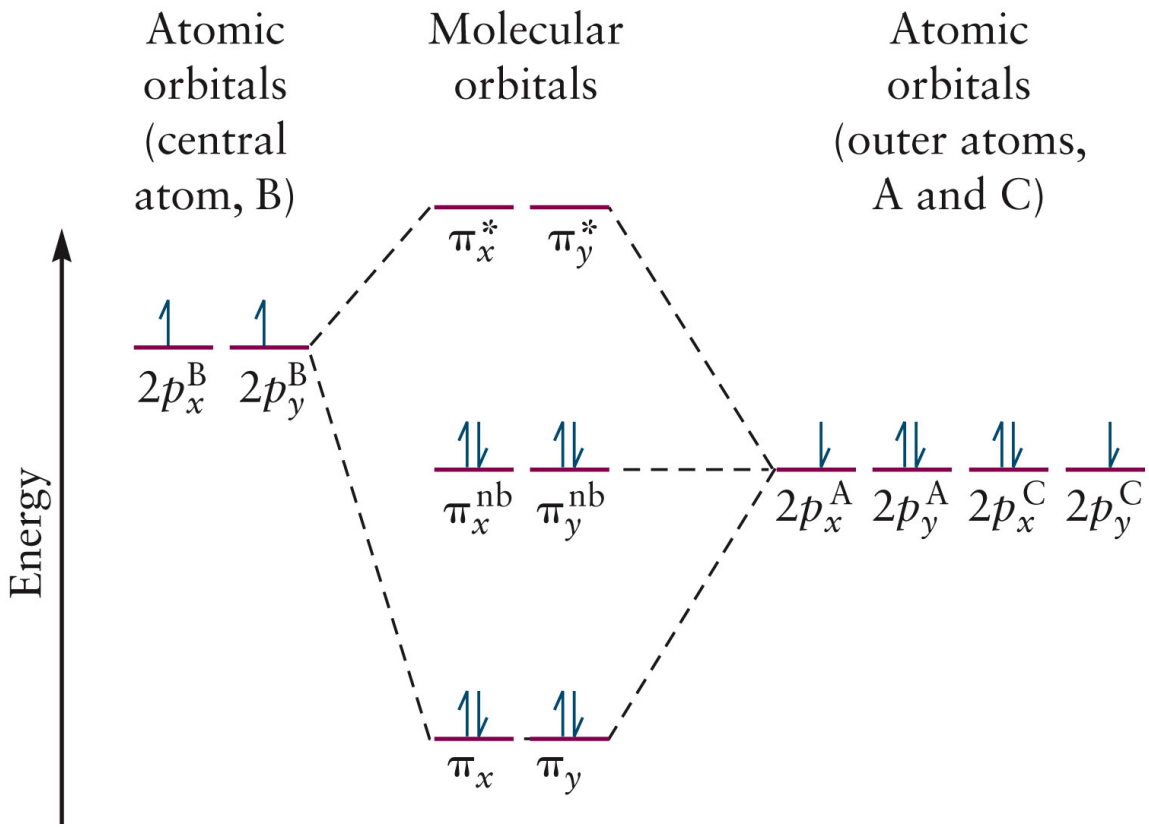


$\psi_3 = C_3p_x^A - C_3p_x^C$



$\psi_1 = C_1p_x^A + C_2p_x^B + C_1p_x^C$





◆ Nonlinear Triatomic Molecules (NO_2, O_3, NF_2, NO_2^-)

- Central atom → sp^2 hybridization from s, p_x, and p_y orbitals

  One of sp^2 orbitals holds a lone pair

  Two of sp^2 orbitals form σ bonds with outer atoms

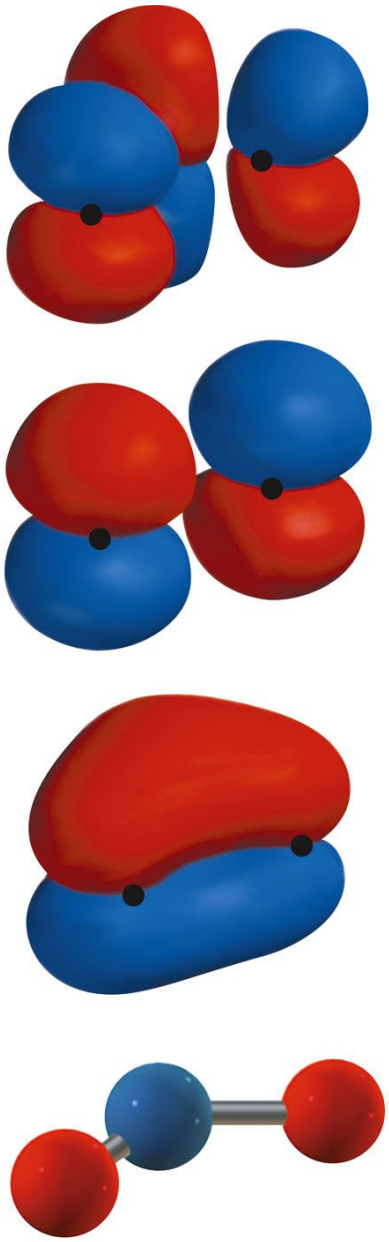
  Remaining p_z orbital forms π bond

- Outer atom

  p orbital pointing toward the central atom forms a σ bond

  p_z orbital forms a π bond with p_z orbitals of other atoms

  Remaining p orbital and s orbital → nonbonding



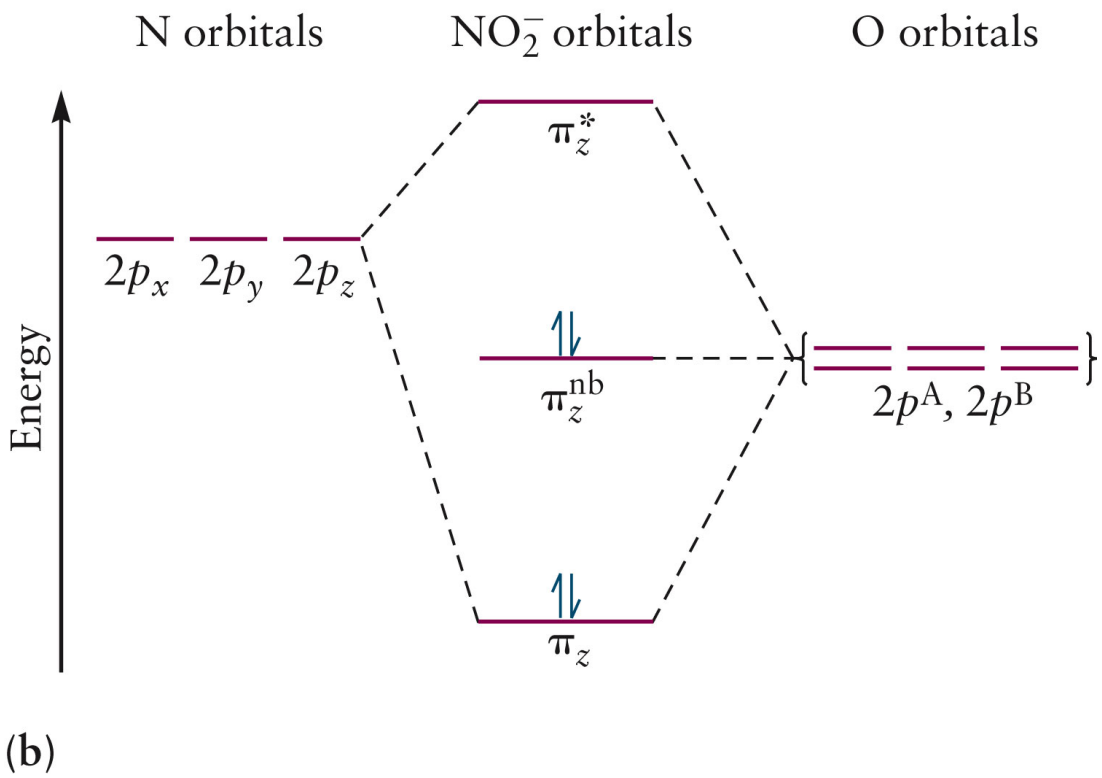


Fig. 6.42. (a) Ball-and-stick model (bottom) and π molecular orbitals for bent triatomic molecule, NO_2^-, with three sp^2 hybrid orbitals on the central N atom that would lie in the plane of the molecule.
(b) Correlation diagram for the π orbitals. There is only one of each of orbitals (π, π^{nb}, π*).

6.12 SUMMARY AND COMPARISON OF THE LCAO AND VALENCE BOND METHODS

- LCAO method for H_2 forming a σ bond:

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

- Molecular electronic wave function in the LCAO approximation:

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

$$\Rightarrow \psi_{MO}^{el} = \left[1s^{A}(1)1s^{B}(2) + 1s^{A}(2)1s^{B}(1) \right] + \left[1s^{A}(1)1s^{A}(2) + 1s^{B}(1)1s^{B}(2) \right]$$

- Molecular electronic wave function in the VB model:

$$\psi_{\mathrm{VB}}^{\mathrm{el}}(r_{1\mathrm{A}}, r_{2\mathrm{B}}) = c_1\varphi_{\mathrm{A}}(r_{1\mathrm{A}})\varphi_{\mathrm{B}}(r_{2\mathrm{B}}) + c_2\varphi_{\mathrm{A}}(r_{2\mathrm{A}})\varphi_{\mathrm{B}}(r_{1\mathrm{B}}) \rightarrow \psi_{\mathrm{VB}}^{\mathrm{el}} = 1s^{\mathrm{A}}(1)1s^{\mathrm{B}}(2) + 1s^{\mathrm{A}}(2)1s^{\mathrm{B}}(1)$$

- Comparison of MO and VB theories:

$$\psi_{MO}^{el} = \underbrace{[1s^A(1)1s^B(2) + 1s^A(2)1s^B(1)]}_{\psi_{VB}^{el}} + \underbrace{[1s^A(1)1s^A(2) + 1s^B(1)1s^B(2)]}_{\psi_{ionic}}$$

purely covalent structure
H–H

mixture of ionic states,
$H_A^- H_B^+$ and $H_A^+ H_B^-$

- Improved VB wavefunction:

$$\psi_{\mathrm{improved}} = \psi_{\mathrm{VB}} + \lambda\psi_{\mathrm{ionic}}$$

TABLE 6.6

Description of Molecular Properties by Introductory Versions of LCAO and VBT

Properties	LCAO	VBT
Diatomics		
Energy levels	Easy	Hard
Excited states	Easy	Hard
Bond shape	Easy	Easy
Electron density	Easy	Hard
Polyatomics		
Energy levels	Impossible	Impossible
Excited states	Impossible	Impossible
Bond angles	Impossible	No prediction
Bond shape	Impossible	No prediction
Electron density	Impossible	Hard