Chapter 18 Molecular orbitals and spectroscopy

18.1 Diatomic molecules

18.2 Polyatomic molecules

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18.4 The interaction of light and matter (spectroscopy)

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18.1 Diatomic molecules

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Bonding and antibonding molecular orbitals

Orbital correlation diagrams

MO energies, AO parentage, Bond order

Homonuclear and heteronuclear diatomic molecules

Diamagnetism of N_2 and paramagnetism of O_2

18.1 Diatomic Molecules

Atomic orbitals: orbitals that are localized on single atoms.

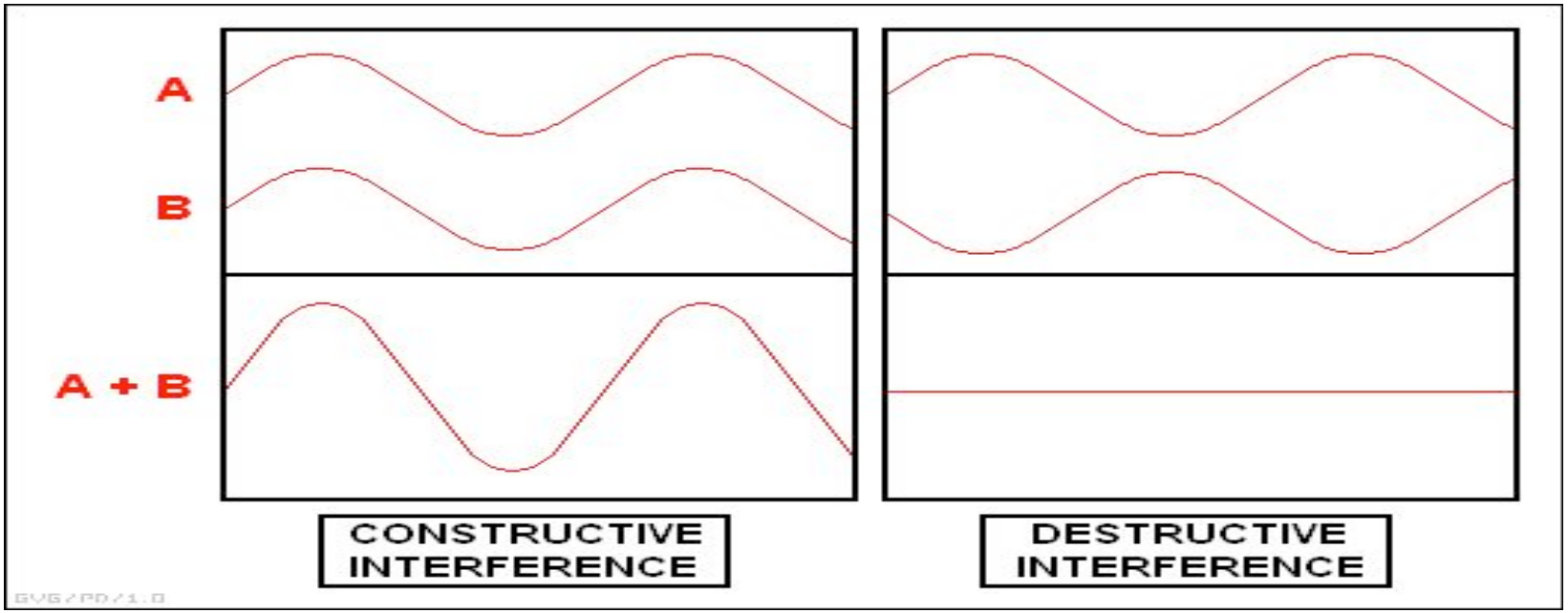
Molecular orbitals: orbitals that span two or more atoms.

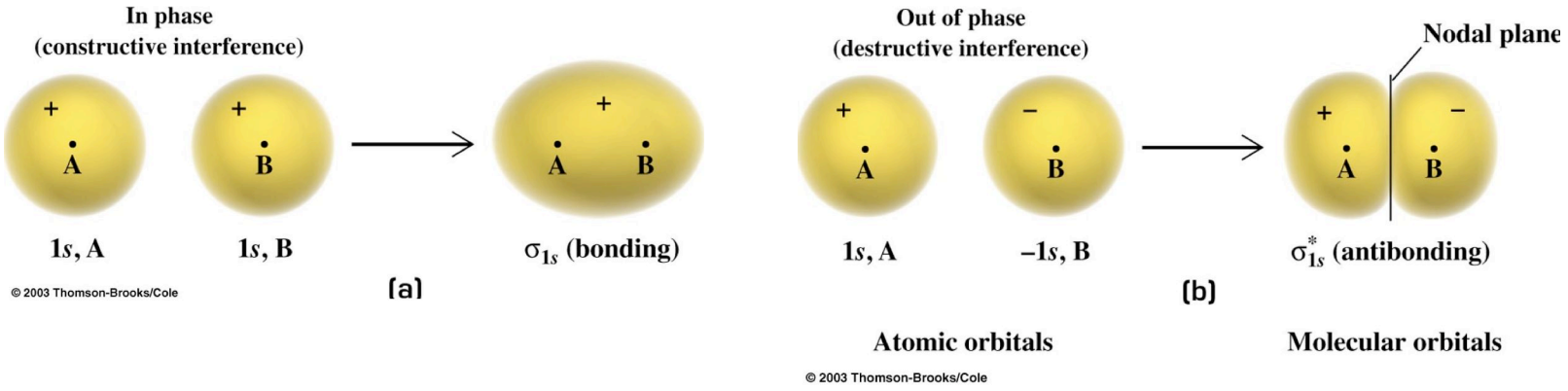
Constructing molecular orbitals (MOs) by overlapping atomic orbitals (AOs)

σ bonds: electron density of MO directed along bond axis

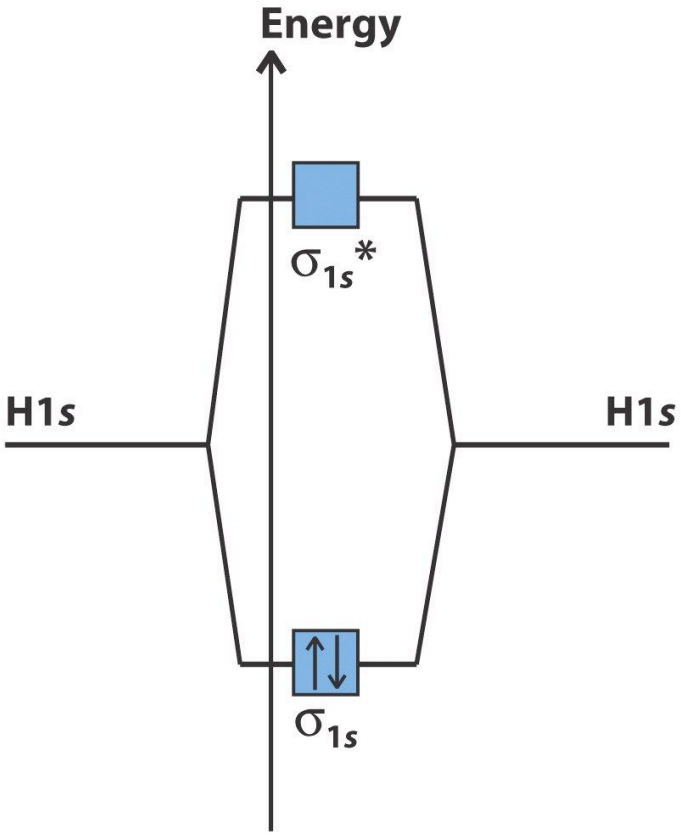
π bonds: electron density of MO has a nodal plane that contains the bond axis

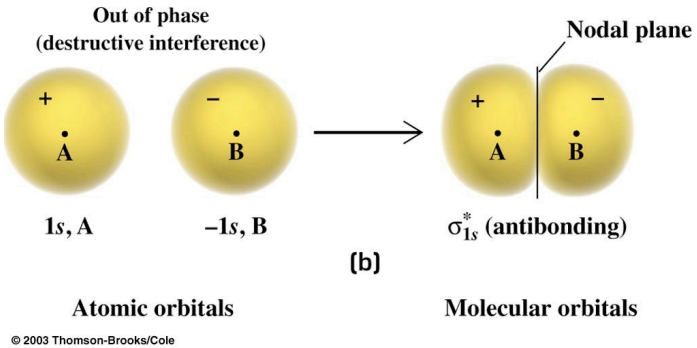
Constructive and destructive interference of waves

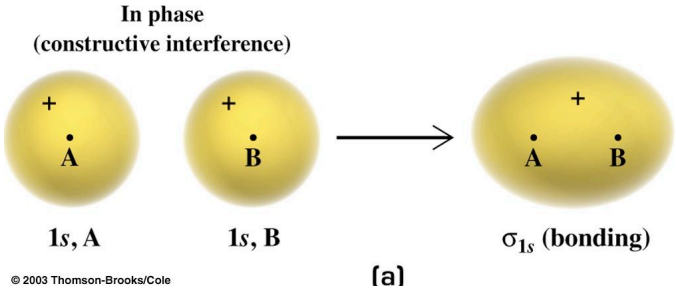




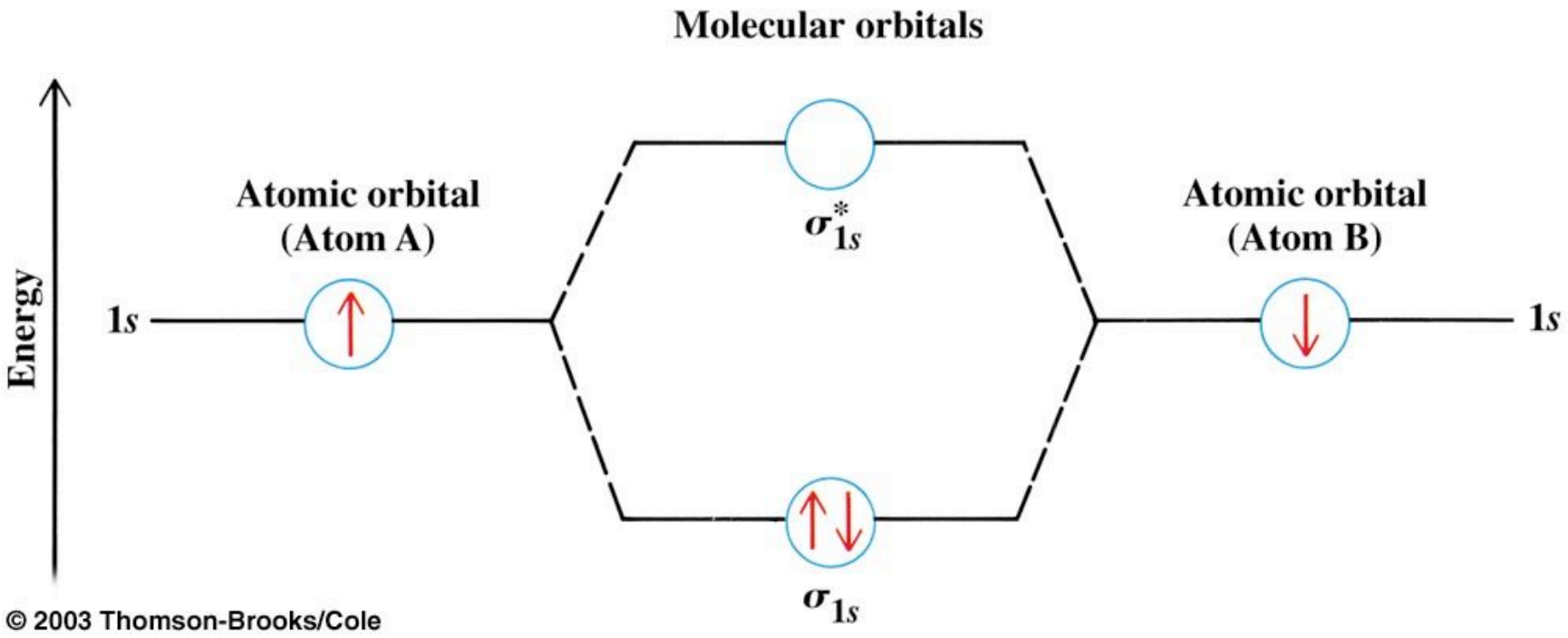
The orbital correlation diagram for overlap of two 1s orbitals







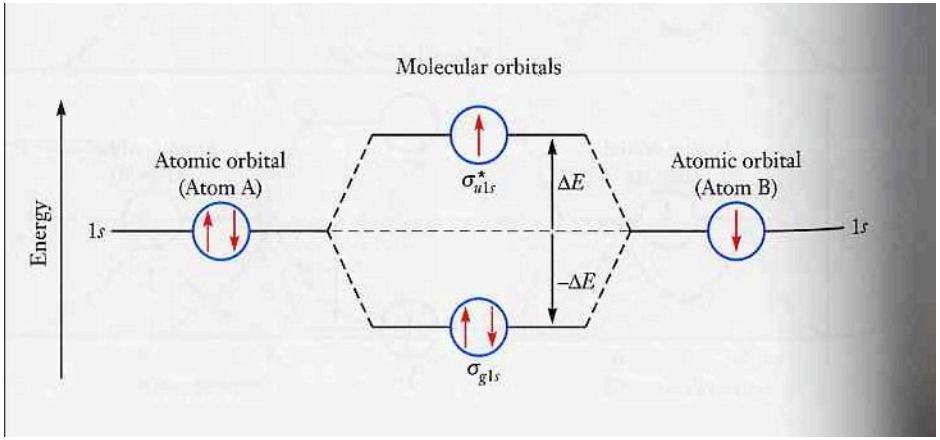
Correlation diagram for the hydrogen molecule, H_2



The electronic configuration of a H_2 molecule is σ_{1s}^2

The subscript ($_{1s}$) tells which AOs are combined, the superscript (^{2}) tells how many electrons are in the MO

What hypothetical diatomic molecules might fit this electron configuration?



Answer: any diatomic with three electrons
Isoelectronic valence = $(\sigma_{1s})^2(\sigma_{1s}{}^*)^1$

Plausible diatomics possessing only combinations of H or He atoms: H_2^-, He_2^+, HHe and the configuration $(\sigma_{1s})^2(\sigma_{1s}{}^*)^1$

Bond order (BO): the net number of bonds, allowing for the cancellation of bonds by anti-bonds

We can deduce molecular stability from BO

BO = 1/2(N - N*) where N = number electrons in bonding orbitals and N* = number of electrons in anti-bonding orbitals

Example: $(\sigma_{1s})^2(\sigma_{1s}^*)^1$

N = 2, N* = 1
BO = 1/2(N - N*) =1/2
Any diatomic molecule with BO > 0 is considered stable relative to the two dissociated atoms.

A shared pair of electrons make a single covalent bond

Electrons in bonding orbitals enhance bonding, electrons in anti-bonding orbitals reduce bonding

Bond order is a measure of the bonding between two atoms: 1/2[(e in bonding MOs) - [(e in anti-bonding MOs)]

TABLE 18–1 Configurations and Bond Orders for First-Row Homonuclear Diatomic Molecules

Species	Electron Configuration	Bond Order	Bond Enthalpy (kJ mol^{-1})	Bond Length (Å)
H_2^+	$(\sigma_{1s})^1$	$\frac{1}{2}$	255	1.06
H_2	$(\sigma_{1s})^2$	1	431	0.74
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	$\frac{1}{2}$	251	1.08
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	Not observed	

What is the bond order of the first electronically excited state of H_2?

The electronic configuration of the first excited state of H_2 is $(\sigma_{1s})^1(\sigma^*_{1s})^1$.

Bond order = 1/2(1 - 1) = 0

Photochemical excitation of H_2 makes it fly apart into 2 H atoms.

Building up the MOs of simple diatomic molecules

Mix atomic orbitals (AOs) of the same or similar energies to form molecular orbitals (MOs)

$2s + 2s = \sigma_{2s} + \sigma_{2s}^*$

$2p_z + 2p_z = \sigma_{2p} + \sigma_{2p}^*$

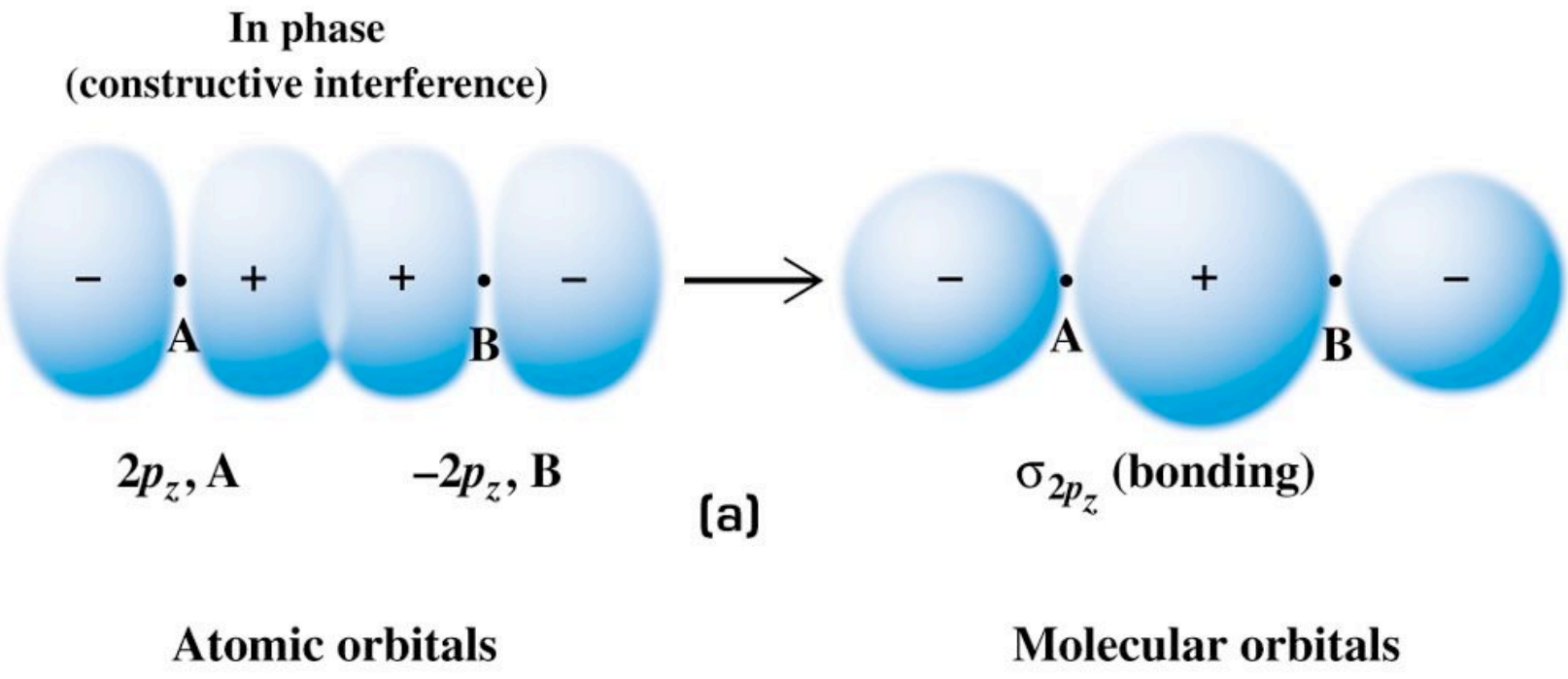
$2p_x + 2p_x = \pi_{2p} + \pi^*_{2p}$

$2p_y + 2p_y = \pi_{2p} + \pi^*_{2p}$

Total of 8 MOs which can hold up to 16 electrons

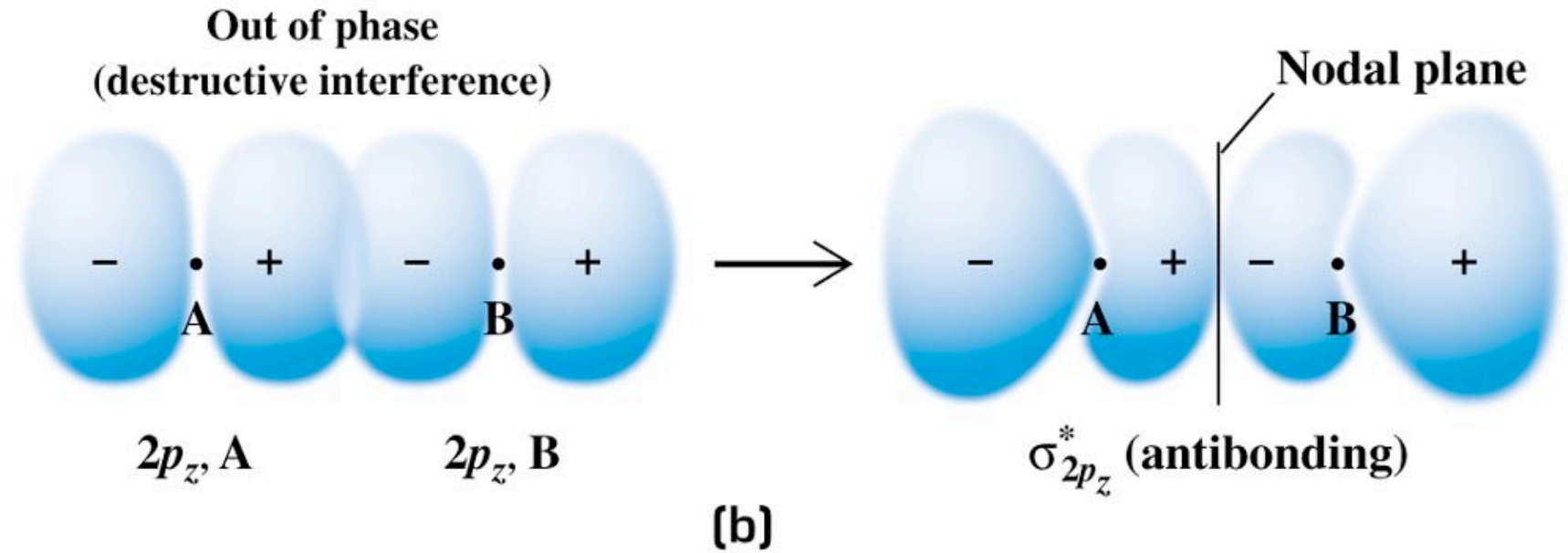
The constructive overlap of two $2p_z$ orbitals on neighboring atoms to produce a σ_{2pz} bonding orbital

$$2p_z + 2p_z = \sigma_{2p} + \sigma_{2p}^*$$



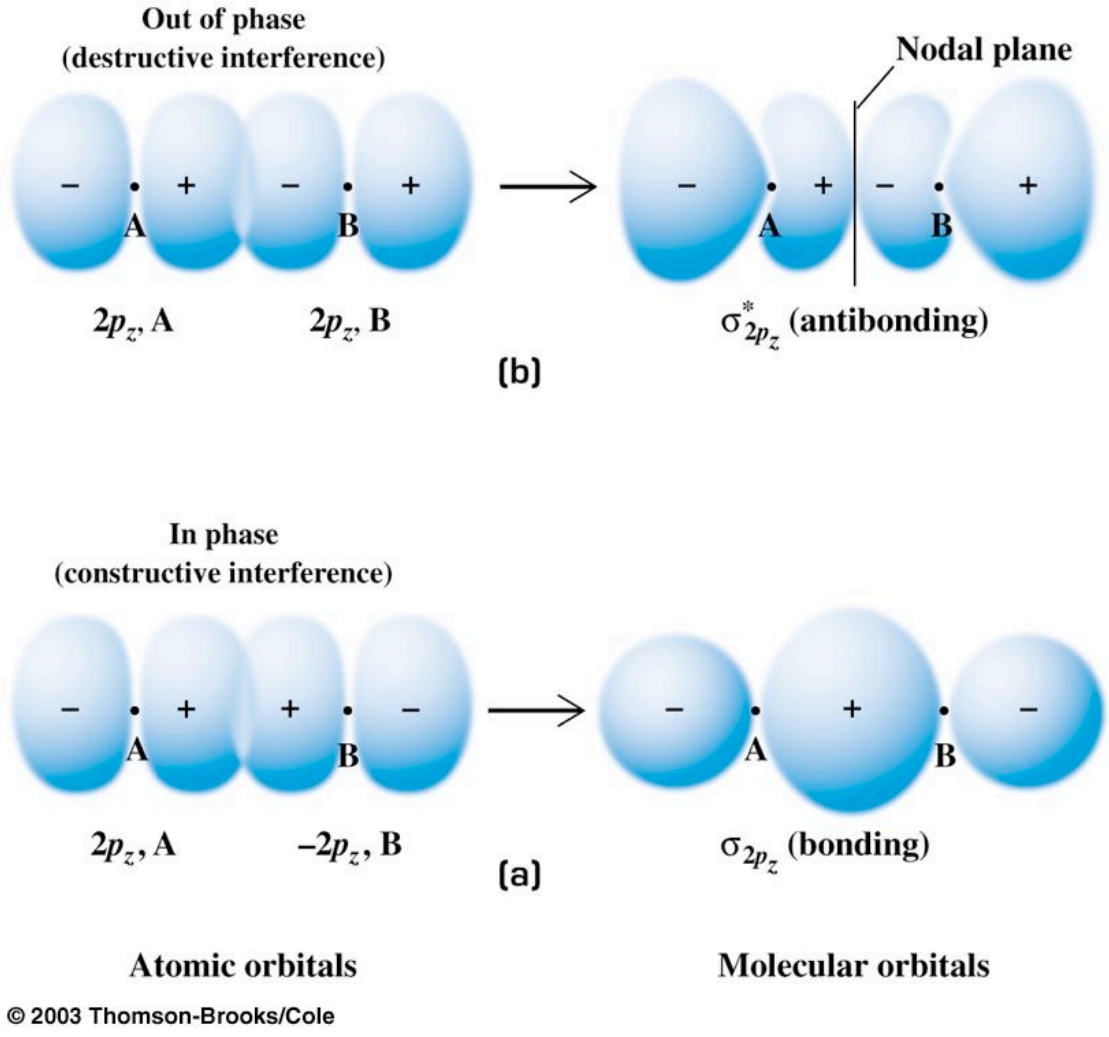
The destructive overlap of two $2p_z$ orbitals on neighboring atoms to produce a σ_{2pz} bonding orbital

$$2p_z + 2p_z \quad = \quad \sigma_{2p} + \sigma_{2p}^*$$



Constructive and destructive overlap of 2 p orbitals to form σ and σ* orbitals

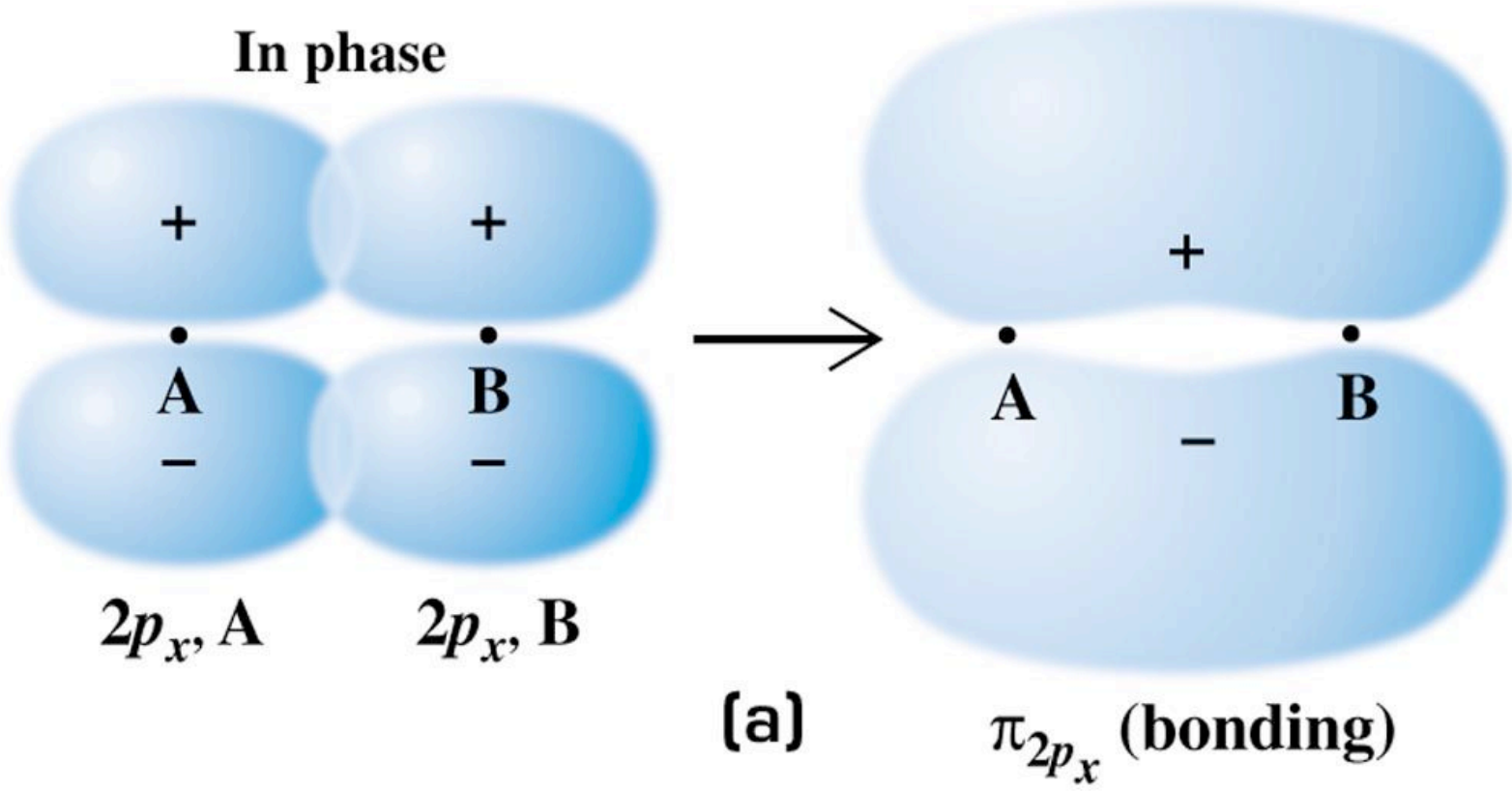
(a) Bonding σ orbital; (b) Antibonding σ* orbital



Overlap along the internuclear axis is termed σ overlap. The resulting orbitals are called σ and σ* orbitals

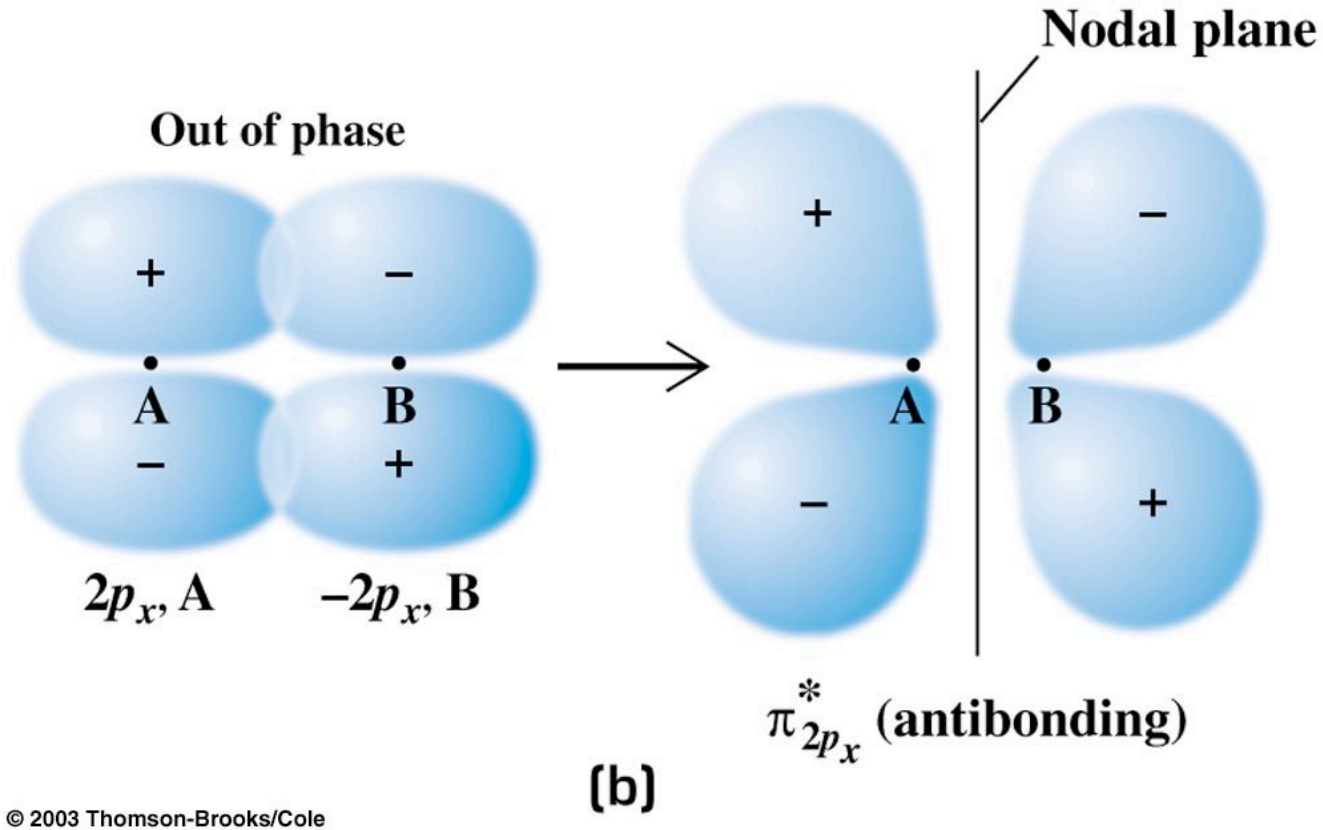
The destructive overlap of two $2p_x$ orbitals on neighboring atoms to produce a π_{2px} bonding orbital

$$2p_x + 2p_x = \pi_{2p} + \pi_{2p}^*$$



The destructive overlap of two $2p_x$ orbitals on neighboring atoms to produce a π_{2px} anti-bonding orbital

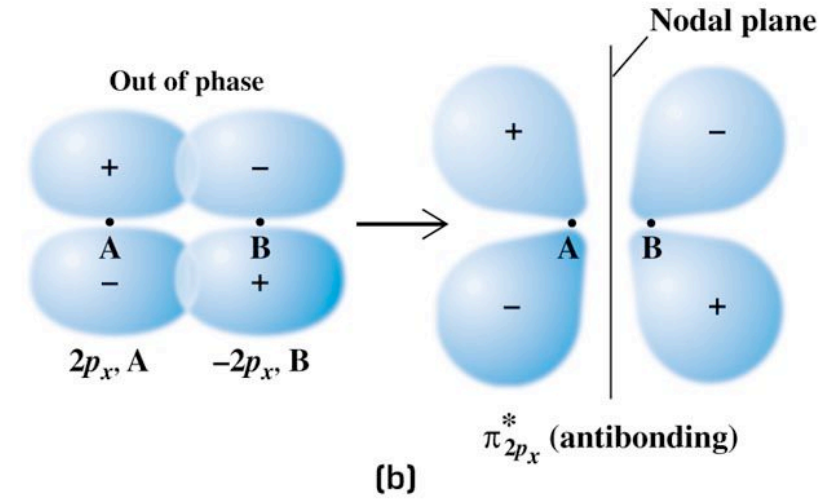
$2p_x + 2p_x = \pi_{2p} + \pi_{2p}^*$

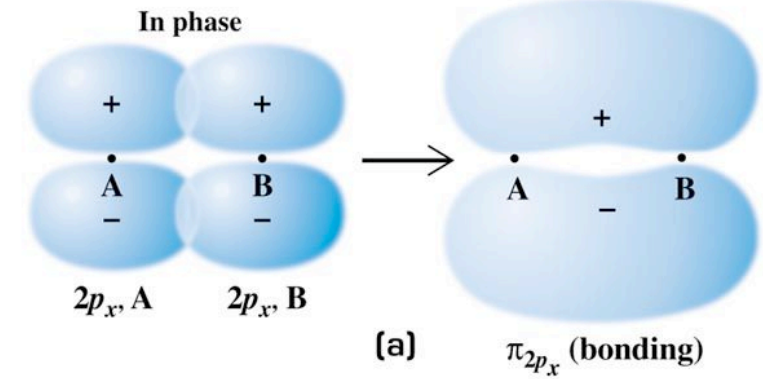


(b)

Constructive and destructive overlap of 2 p orbitals to form π and π* orbitals

(a) Bonding π orbital; (b) Antibonding π* orbital





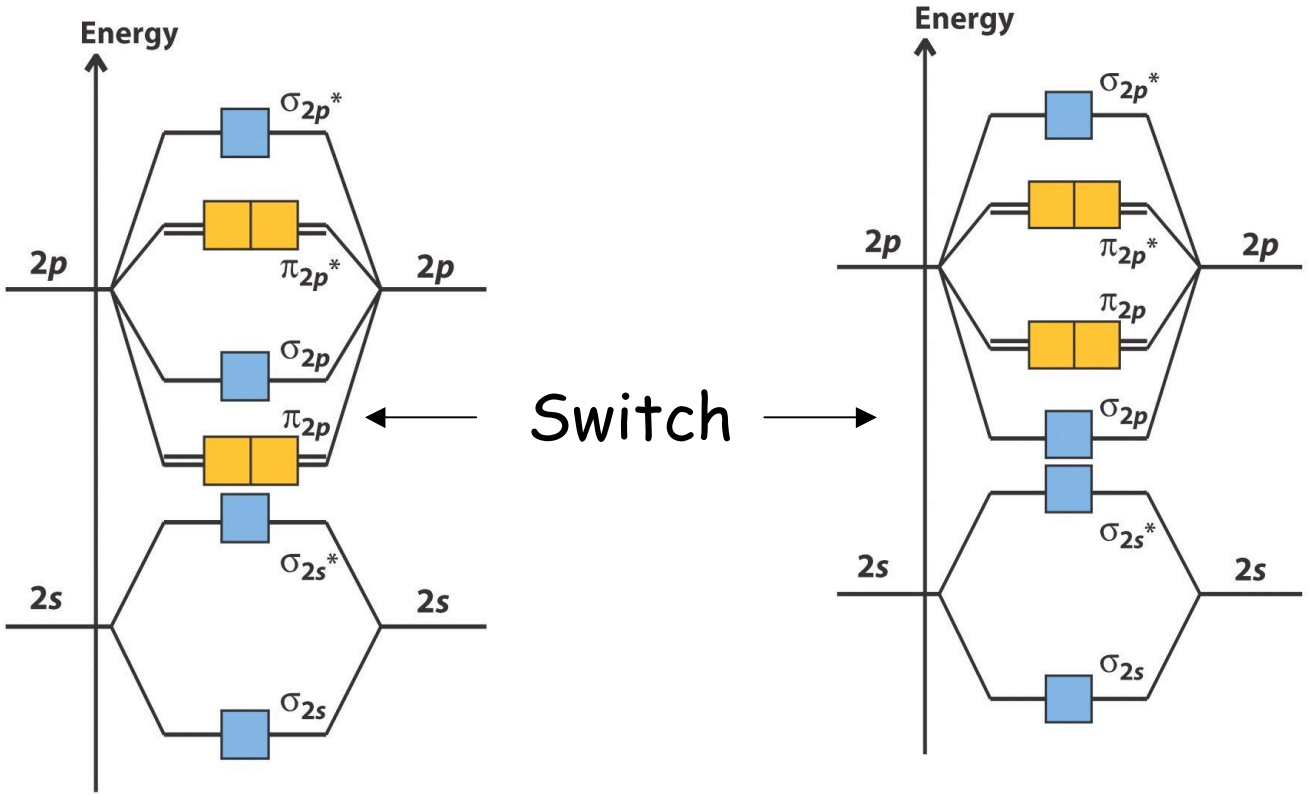
Overlap perpendicular to the internuclear axis is termed π overlap. A nodal plane that contains the bond axis. The resulting orbitals are called π and π* orbitals

Remember: + and - refer to mathematical symbols, not charge

Now we have the orbitals, what are their relative energies?

Orbital energies for the 3Li-^{10}Ne

Note: (1) The energy of the π_{2p} and σ_{2p} orbitals switch energy places between N and O; (2) The electron configuration for any isoelectronic valences is the same



Li, Be, B, C, N

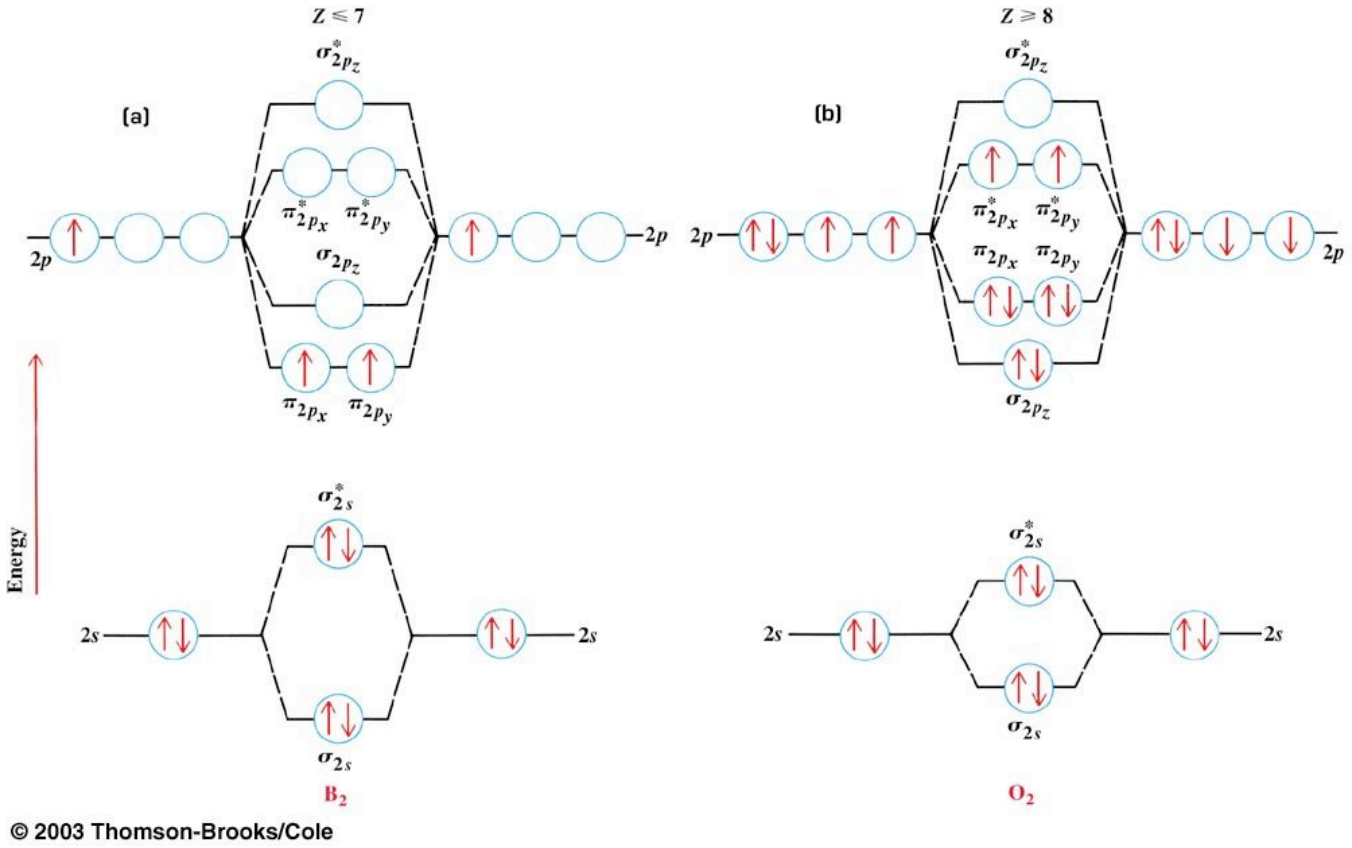
O, F, Ne

Correlation diagrams for B_2 (left) and O_2 (right)

6 VE: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p}\uparrow\uparrow)^2\,(\pi_{2p}^*)^0(\sigma_{2p}^*)^0$

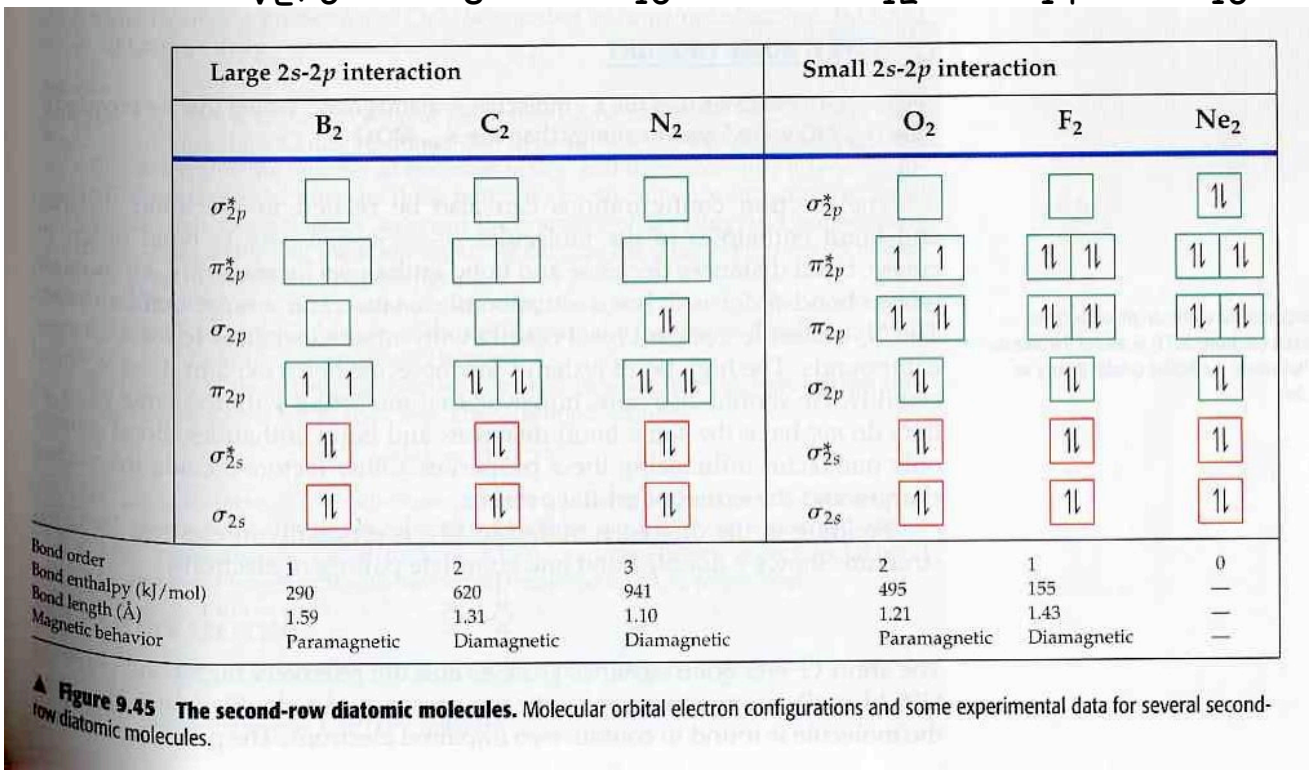
12 VE: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4\,(\pi_{2p}^*\uparrow\uparrow)^2\,(\sigma_{2p}^*)^0$

What are the bond orders? What are the magnetic properties?



Electron configurations for the diatomic molecules: B_2, C_2, N_2, O_2, F_2, Ne_2

VE: 6 8 10 12 14 16

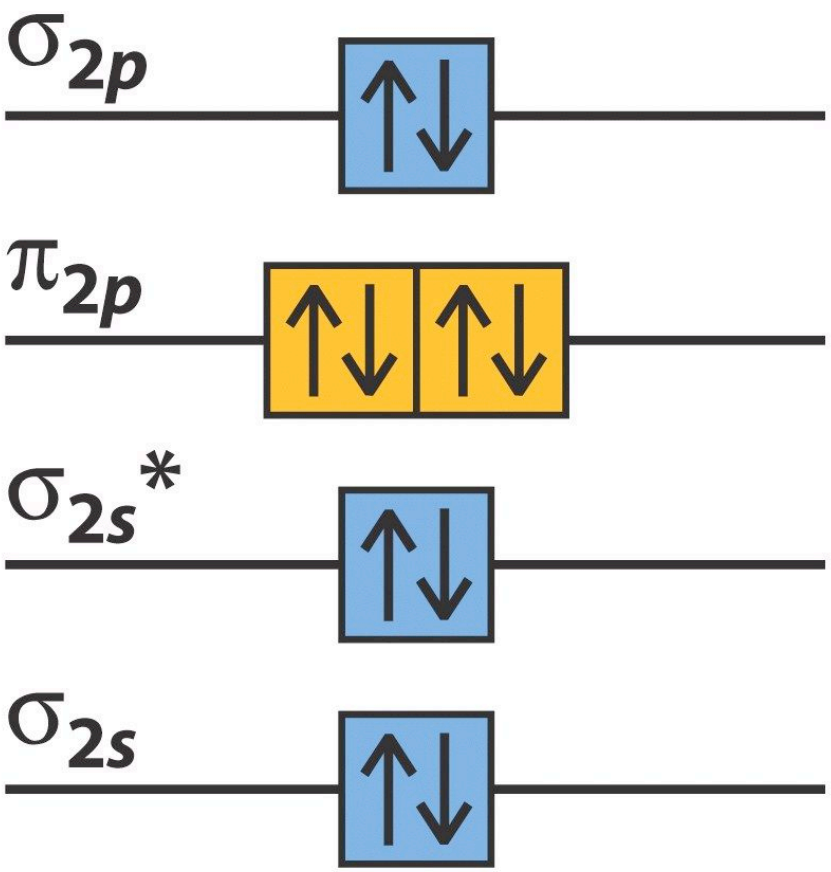


	Large 2s-2p interaction			Small 2s-2p interaction		
	B_2	C_2	N_2	O_2	F_2	Ne_2
σ^*_{2p}						↑↓
π^*_{2p}				↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}			↑↓	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

▲ **Figure 9.45 The second-row diatomic molecules.** Molecular orbital electron configurations and some experimental data for several second-row diatomic molecules.

The molecular orbital electronic configuration of $^{7}N_2$

Group V: Valence electrons = 10. Ignore core electrons



What is the bond order of N_2?

BO = 1/2(N - N*)

N = 8, N* = 2,
N - N* = 6

BO = 1/2(6) = 3

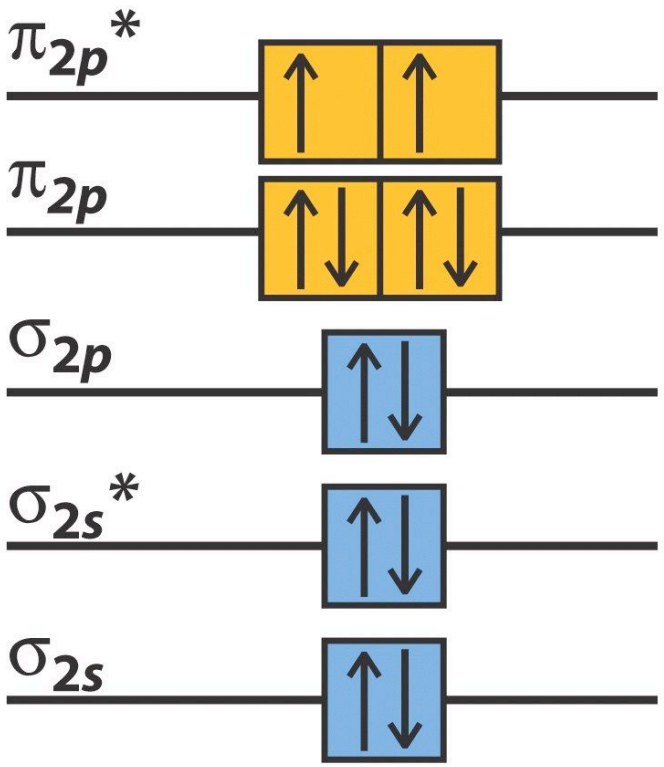
How does the Lewis structure compare to the MO structure?

45 Nitrogen, N_2

:N≡N:

The molecular orbital electronic configuration of $^{8}O_2$

Group VI: Valence electrons = 12. Ignore core electrons



47 Oxygen, O_2

What is the electronic configuration of O_2?

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p}\uparrow\uparrow)^2$

What is the bond order of O_2?

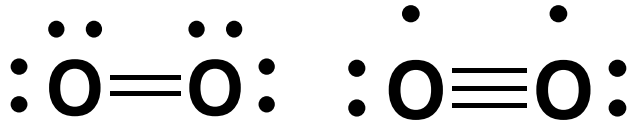
Bond order = 1/2(N - N*)
1/2(8 - 4) = 2

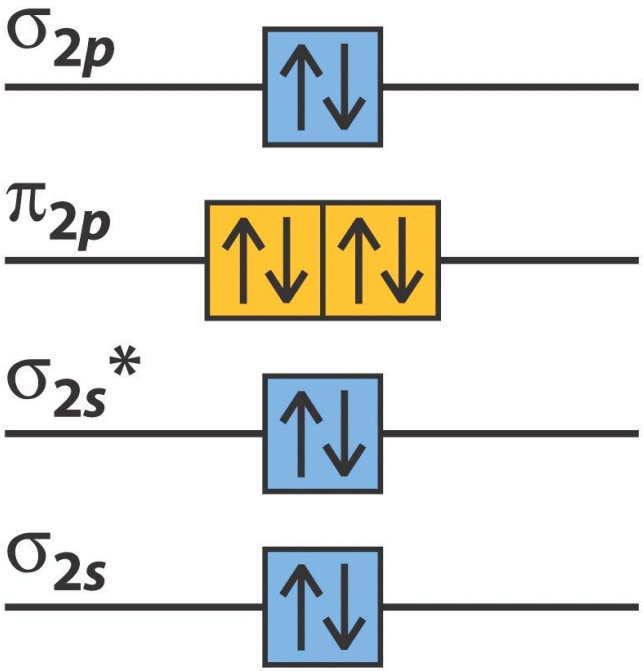
O_2 possesses a net double bond and is paramagnetic

Electron configurations of the valence electrons of N_2 and O_2

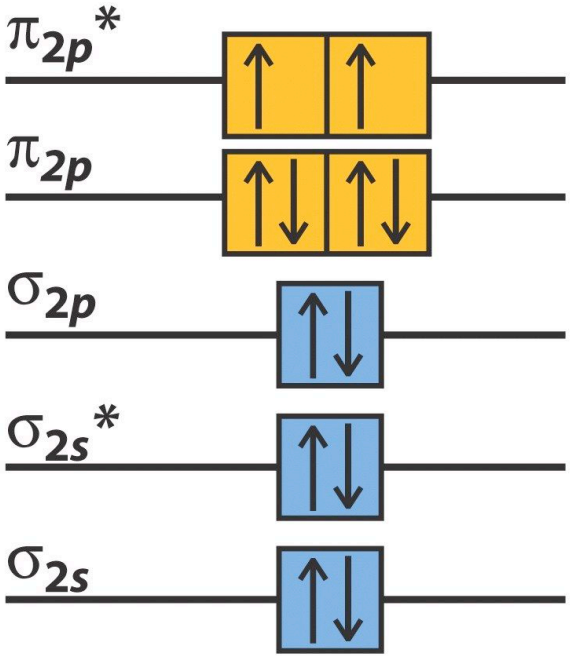
Lewis structure

Lewis structures





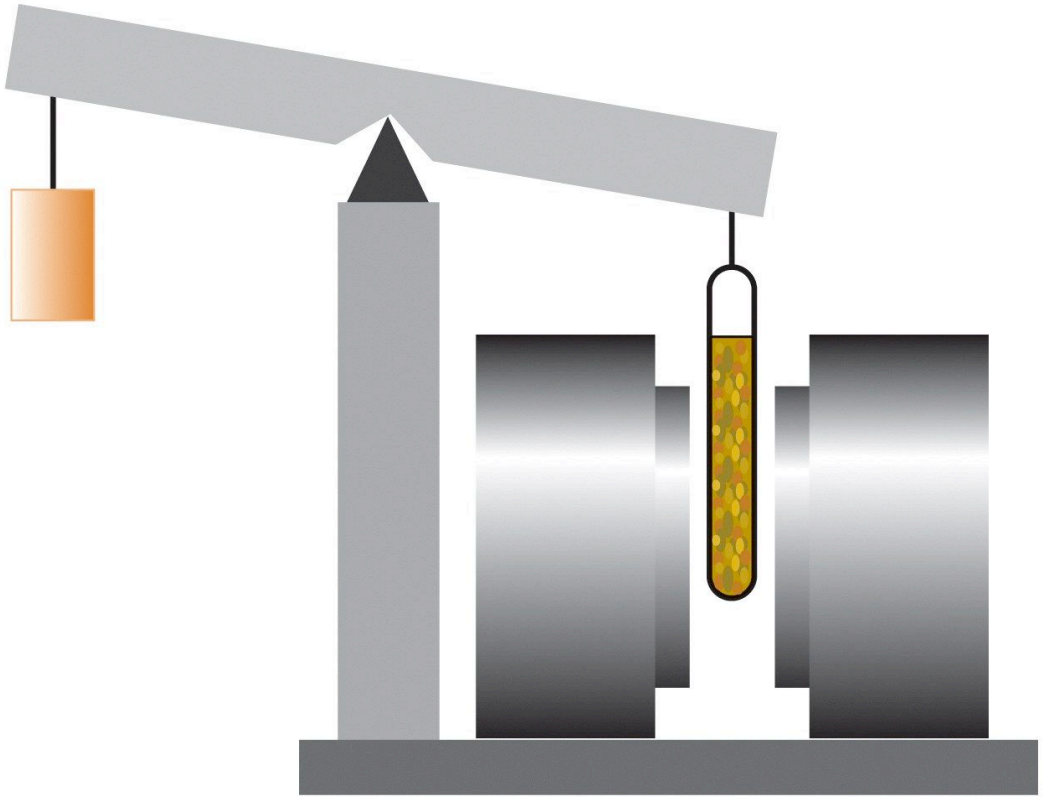
45 Nitrogen, N_2



47 Oxygen, O_2

Paramagnetic: O_2: $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p}\uparrow\uparrow)^2$

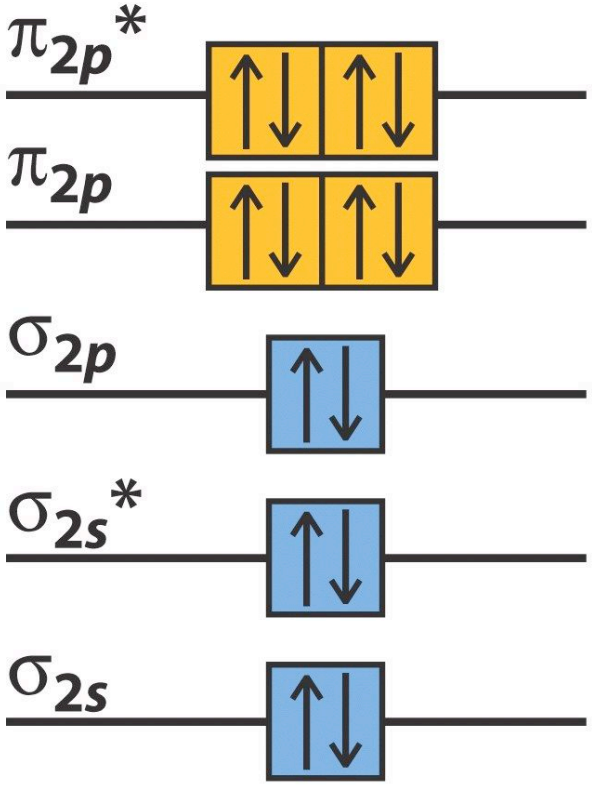
Diamagnetic: N_2: $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4$



O_2 is paramagnetic

The molecular orbital electronic configuration of $^9F_2$

Group VII: Valence electrons = 14



46 Fluorine, F_2

What is the valence electronic configuration of F_2?

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$

What is the bond order of F_2?

BO = 1/2(8 - 6) = 1

F_2 possesses a net single bond

Molecular orbital configurations of homonuclear diatomics

Bond orders, bond lengths and bond energies

TABLE 18–2 Molecular Orbitals of Homonuclear Diatomic Molecules

Species	Number of Valence Electrons	Ground-State Valence-Electron Configuration	Bond Order	Bond Length (Å)	Bond Enthalpy (kJ mol^{-1})
H_2	2	$(\sigma_{2s})^2$	1	0.746	436
He_2	4	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	Not observed	
Li_2	2	$(\sigma_{2s})^2$	1	2.67	106
Be_2	4	$(\sigma_{2s})^2(\sigma_{2s}^*)^2$	0	2.45	9
B_2	6	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2$	1	1.59	297
C_2	8	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$	2	1.24	607
N_2	10	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p_z})^2$	3	1.10	945
O_2	12	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^2$	2	1.21	498
F_2	14	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^4$	1	1.41	158
Ne_2	16	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p_z}^*)^2$	0	Not observed	

The bond orders from MO theory agree with Lewis

18.2 Polyatomic molecules

Valence bond theory and molecular orbital theory

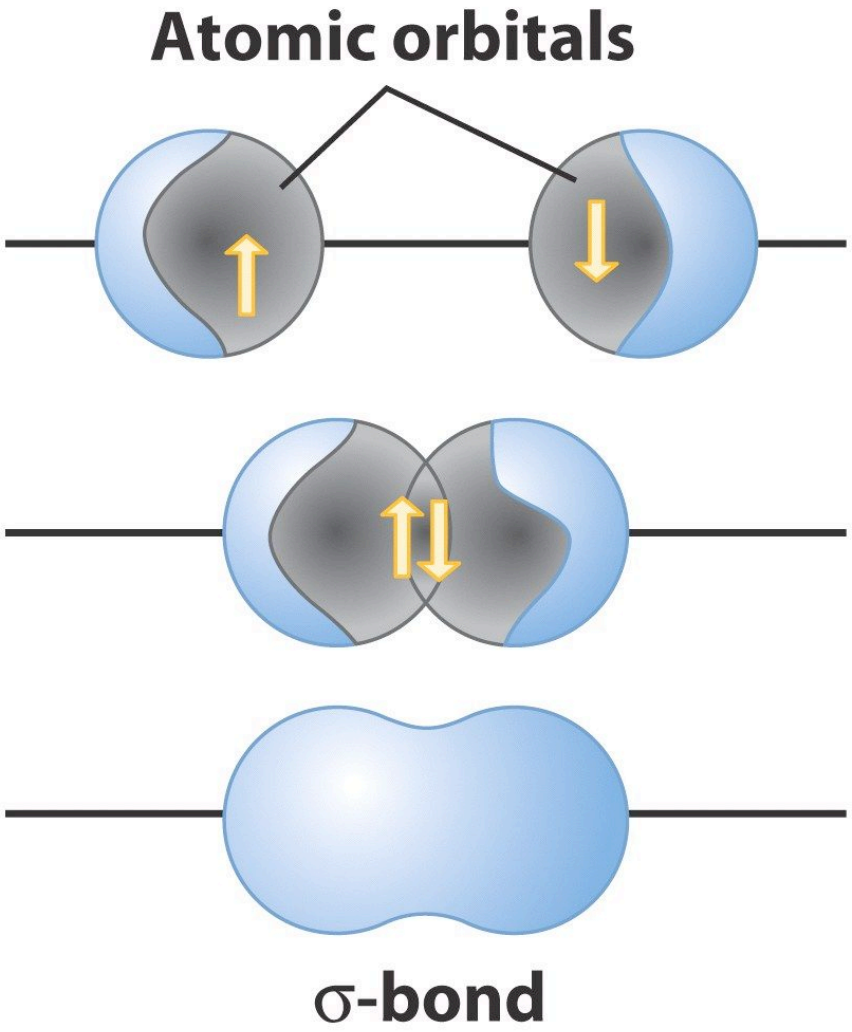
Valence bond theory: localized bonds, like Lewis structures

Hybridization of orbitals to make stronger bonds

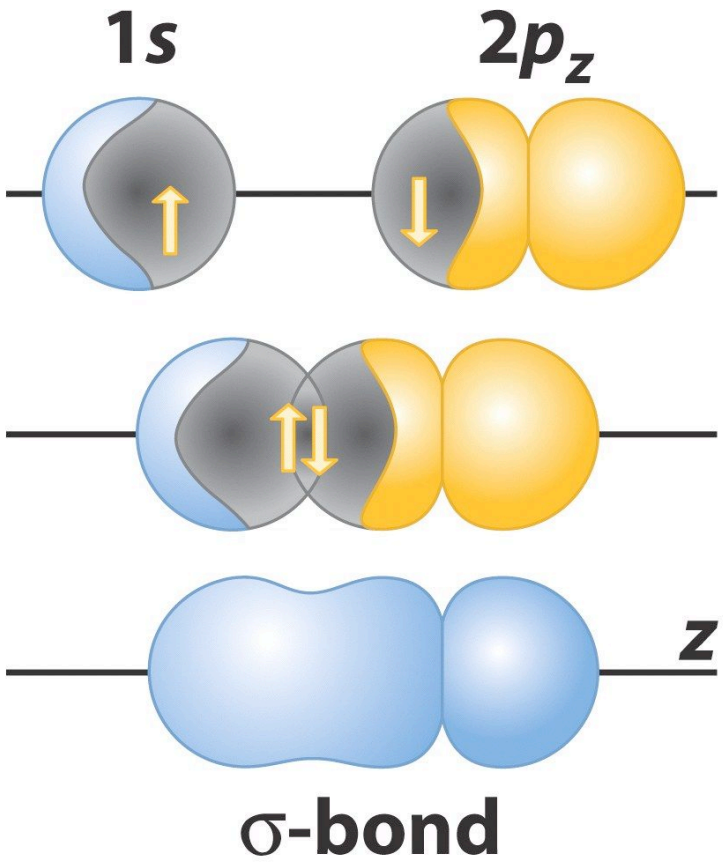
Hybridization and molecular geometry

Hybridization and bond order. Single, double and triple bonds

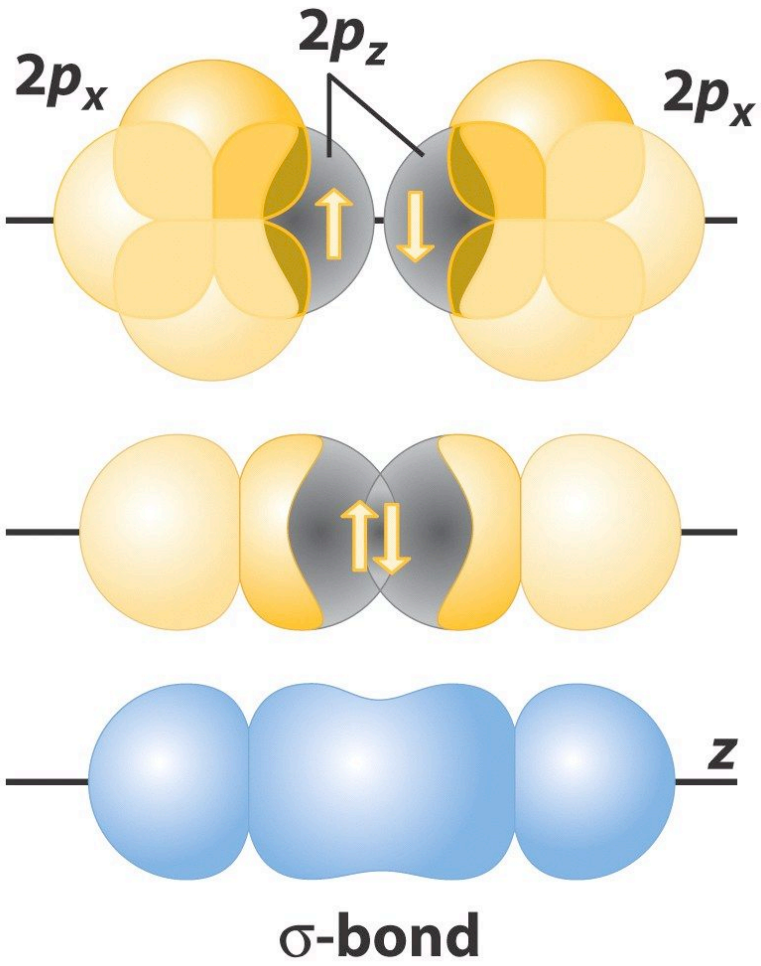
Valence bond: Overlap of two s orbitals to produce a σ bond



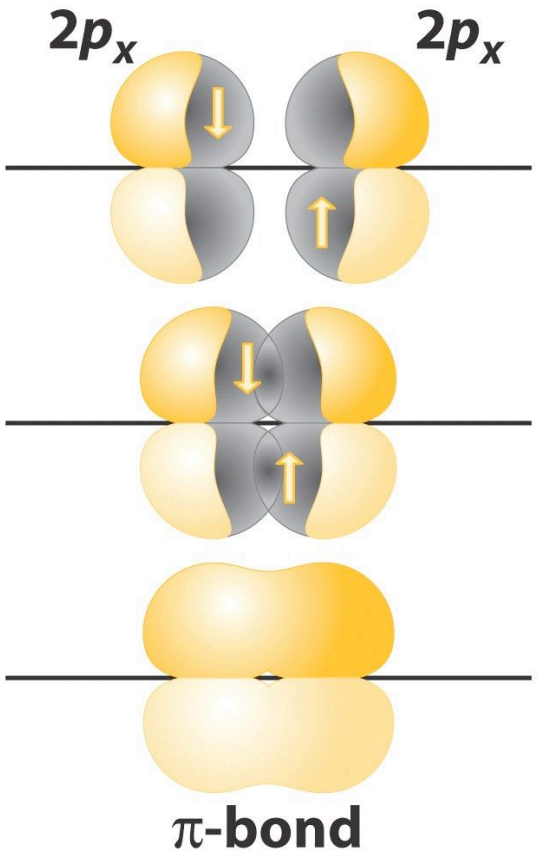
Valence bond: Overlap of an s orbital and a p_z orbital to produce a σ bond



Valence bond: Overlap of two p_z orbitals to produce a σ bond

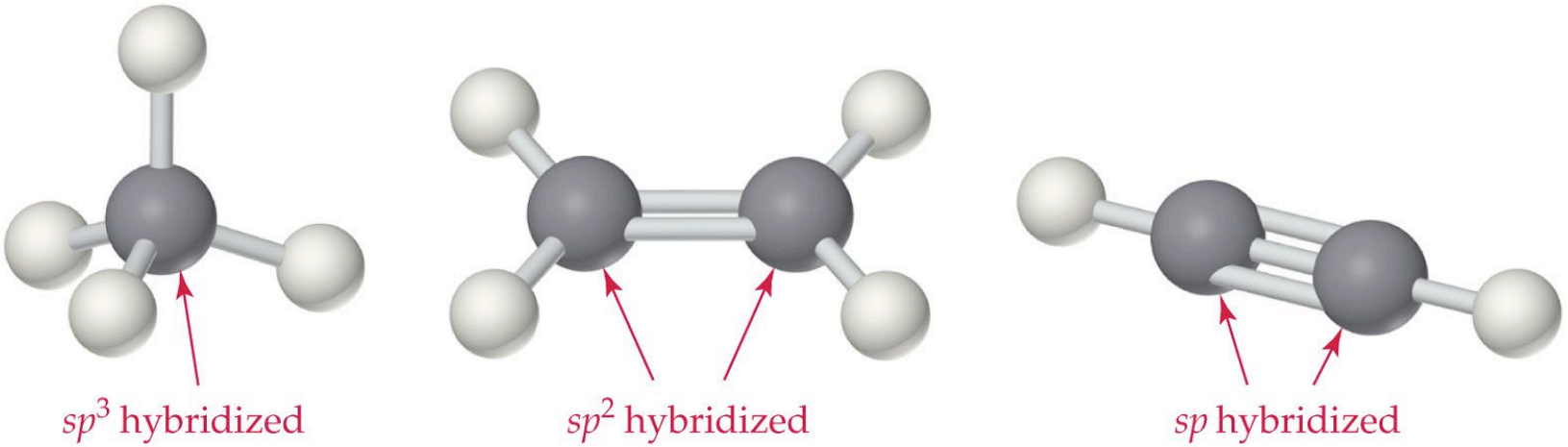


Valence bond: Overlap of two p_x orbitals to produce a π bond

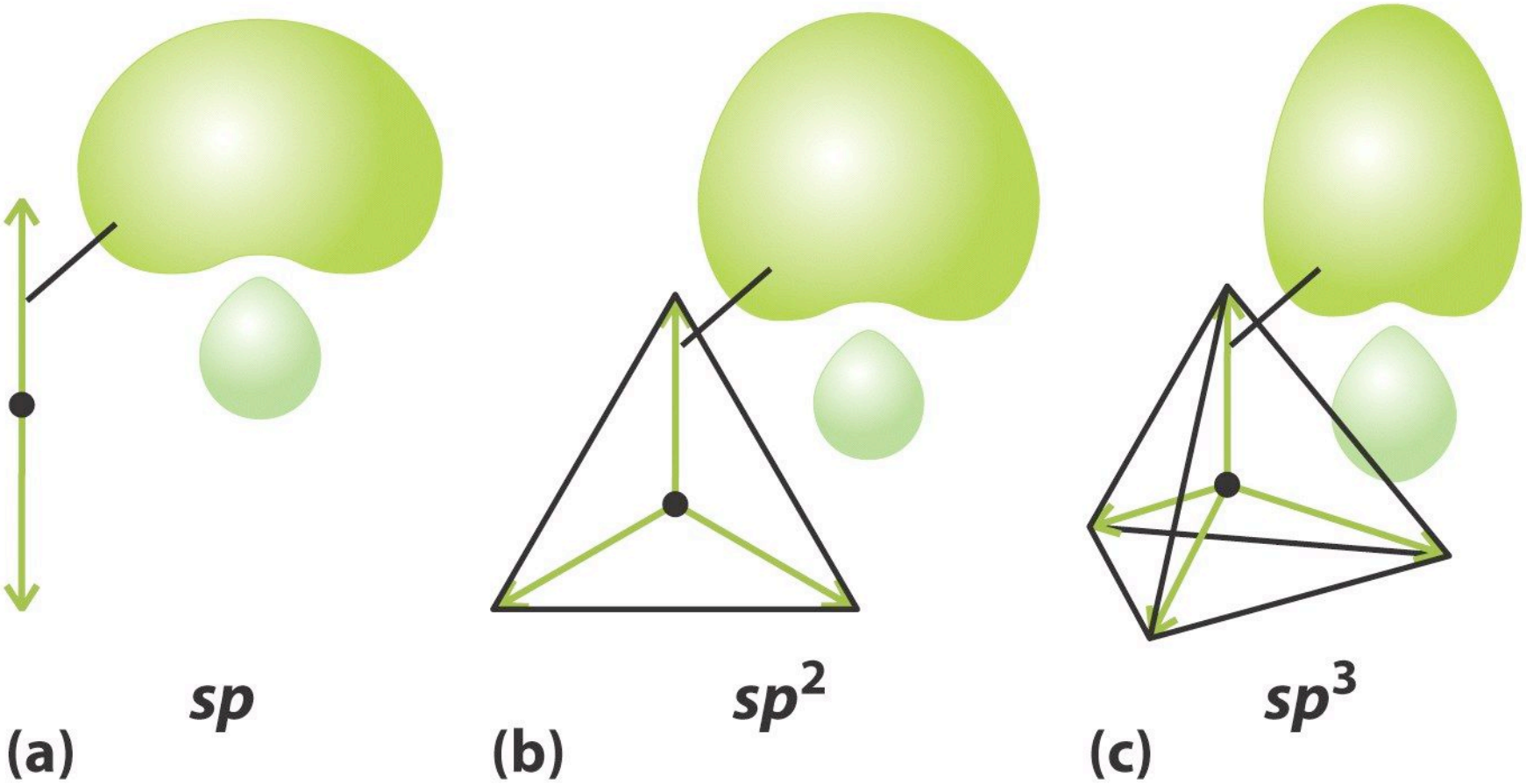


Hybridization

If more than two atoms are involved in a molecule, the shapes of the orbitals must match the shape of the bonds that are needed (trigonal, tetrahedral, etc.). The atomic orbitals do not have these shapes, and must be mixed to achieve the needed shapes

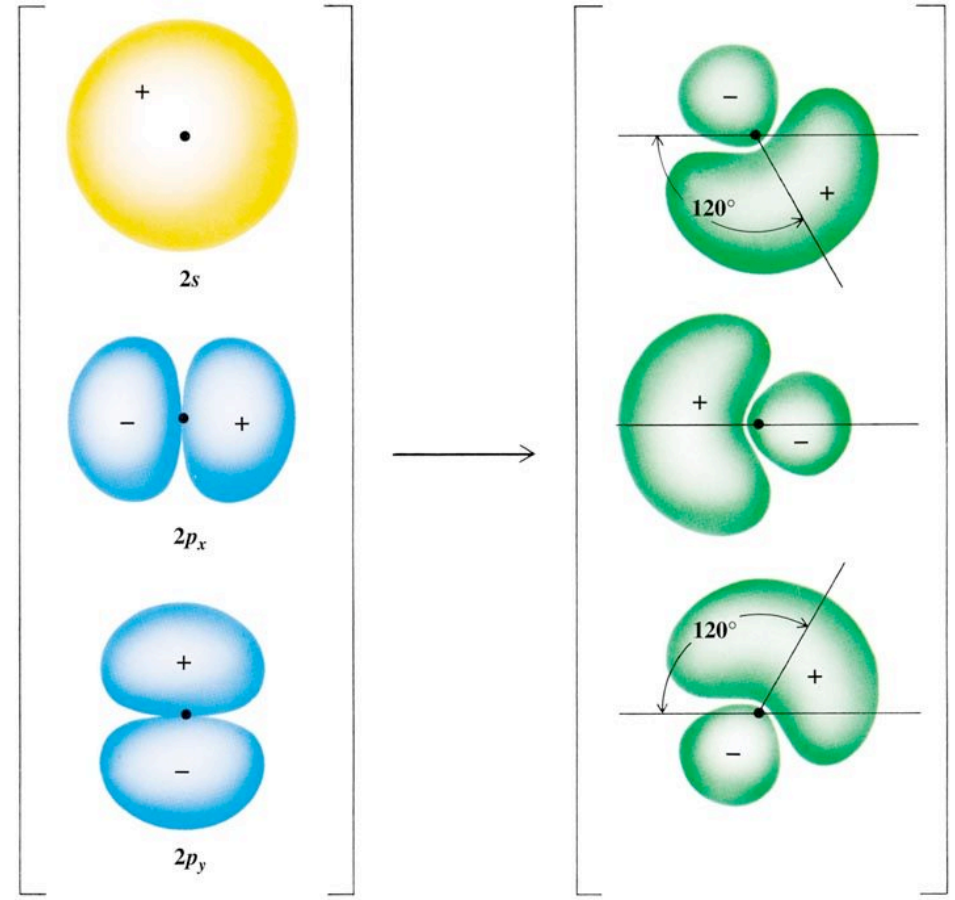


Shapes of hybridized atomic orbitals



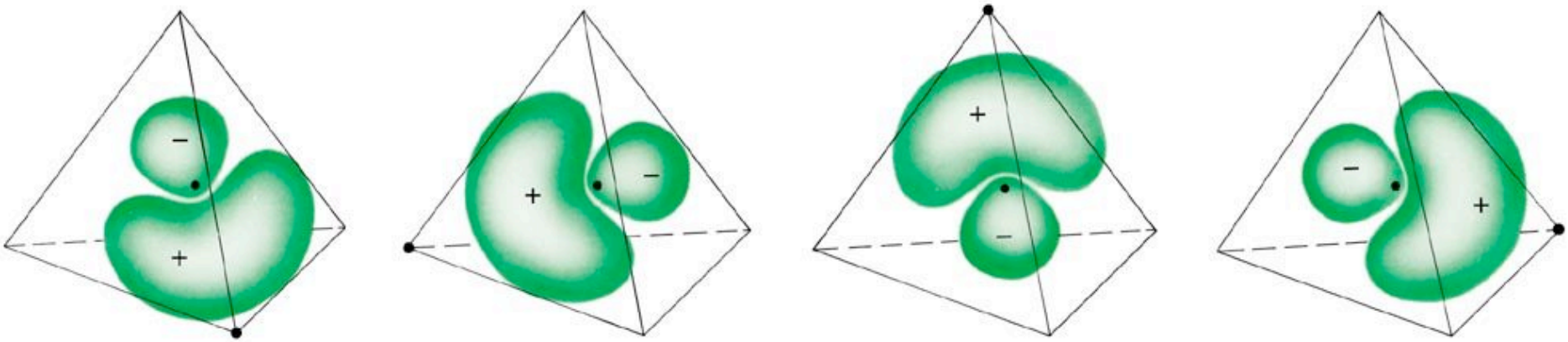
The hybridization of a s orbital and two p orbitals to produce three sp^2 orbitals

Three Atomic orbitals Aos
2s + two 2p



Three hybrid Orbitals HAOs
sp^2

The orientations of four sp^3 orbitals



The hybridization of a s orbital and a p orbital to produce **two** sp hybrid orbitals

2s orbital could be + or -

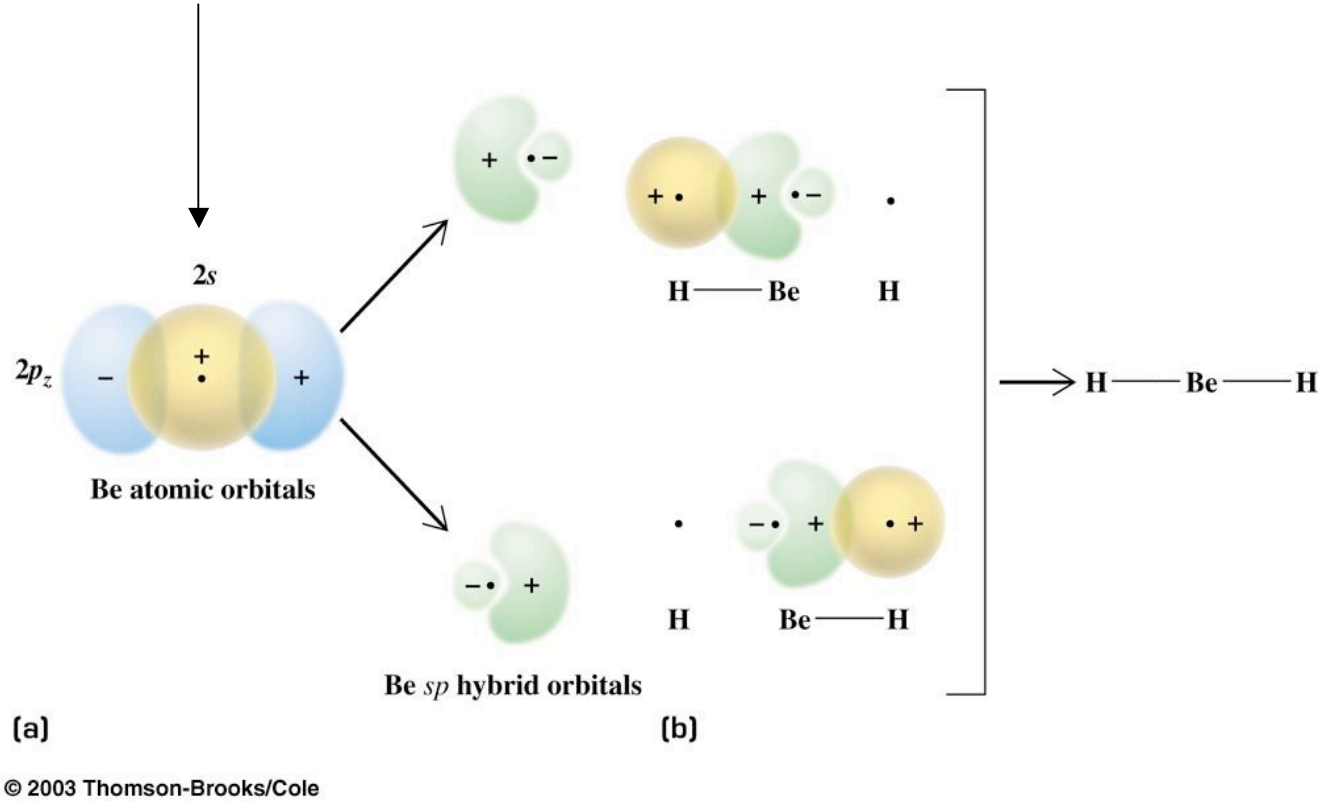


TABLE 3.2 Hybridization and Molecular Shape*

Electron arrangement	Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
linear	2	sp	2
trigonal planar	3	sp^2	3
tetrahedral	4	sp^3	4
trigonal bipyramidal	5	sp^3d	5
octahedral	6	sp^3d^2	6

*Other combinations of *s*-, *p*-, and *d*-orbitals can give rise to the same or different shapes, but these combinations are the most common.