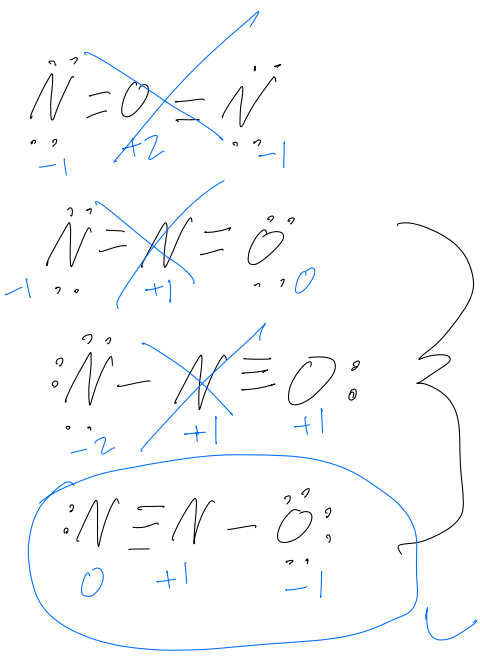
N_2O – 16 e⁻



resonance structures

* preferable to have negative formal charges on more electronegative atoms

O is more electroneg than N

↳ best structure

TABLE 8.8 Some Average Single- and Multiple-Bond Lengths in Picometers (pm)*

Single Bond Lengths

	Group 1A	4A	5A	6A	7A	4A	5A	6A	7A	7A	7A
	H	C	N	O	F	Si	P	S	Cl	Br	I
H	74	110	98	94	92	145	138	132	127	142	161
C		154	147	143	141	194	187	181	176	191	210
N			140	136	134	187	180	174	169	184	203
O				132	130	183	176	170	165	180	199
F					128	181	174	168	163	178	197
Si						234	227	221	216	231	250
P							220	214	209	224	243
S								208	203	218	237
Cl									200	213	232
Br										228	247
I											266

bigger atoms → longer bonds

Multiple Bond Lengths

C=C	134	C≡C	121
C=N	127	C≡N	115
C=O	122	C≡O	113
N=O	115	N≡O	108

bond order = 1 / single → bond order = 2 / double → bond order = 3 / triple

bond length decreases

*1 pm = 10^{-12} m.

ΔH for bond breaking → endothermic

TABLE 8.9 Some Average Bond Dissociation Enthalpies (kJ/mol)*

Single Bonds

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436	413	391	463	565	328	322	347	432	366	299
C		346	305	358	485	—	—	272	339	285	213
N			163	201	283	—	—	—	192	—	—
O				146	—	452	335	—	218	201	201
F					155	565	490	284	253	249	278
Si						222	—	293	381	310	234
P							201	—	326	—	184
S								226	255	—	—
Cl									242	216	208
Br										193	175
I											151

* bond making is exothermic

Multiple Bonds

N═N	418	C═C	610
N≡N	945	C≡C	835
C═N	615	C═O	745
C≡N	887	C≡O	1046
O═O (in O_2)	498		

*Sources of dissociation enthalpies: I. Klotz and R. M. Rosenberg: *Chemical Thermodynamics*, 4th Ed., p. 55, New York, John Wiley, 1994; and J. E. Huheey, E. A. Keiter, and R. L. Keiter: *Inorganic Chemistry* 4th Ed., Table E. 1, New York, Harper-Collins, 1993. See also Lange's *Handbook of Chemistry*, J. A. Dean (ed.), McGraw-Hill Inc., New York.

Table 8-9, p. 389

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

Bonds broken

4 × C–H 4×413 } 2648 kJ
2 × O=O 2×498 }

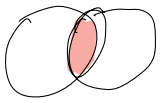
Bonds made

2 × C=O 2×745 } = 3342 kJ
4 × O–H 4×463 }

$\Delta_r H^\circ = -694$ kJ/mol rxn

Valence bond theory → bonding is due to "orbital overlap"

H_2 molecule - 2 H atoms each w/ e^- in 1s



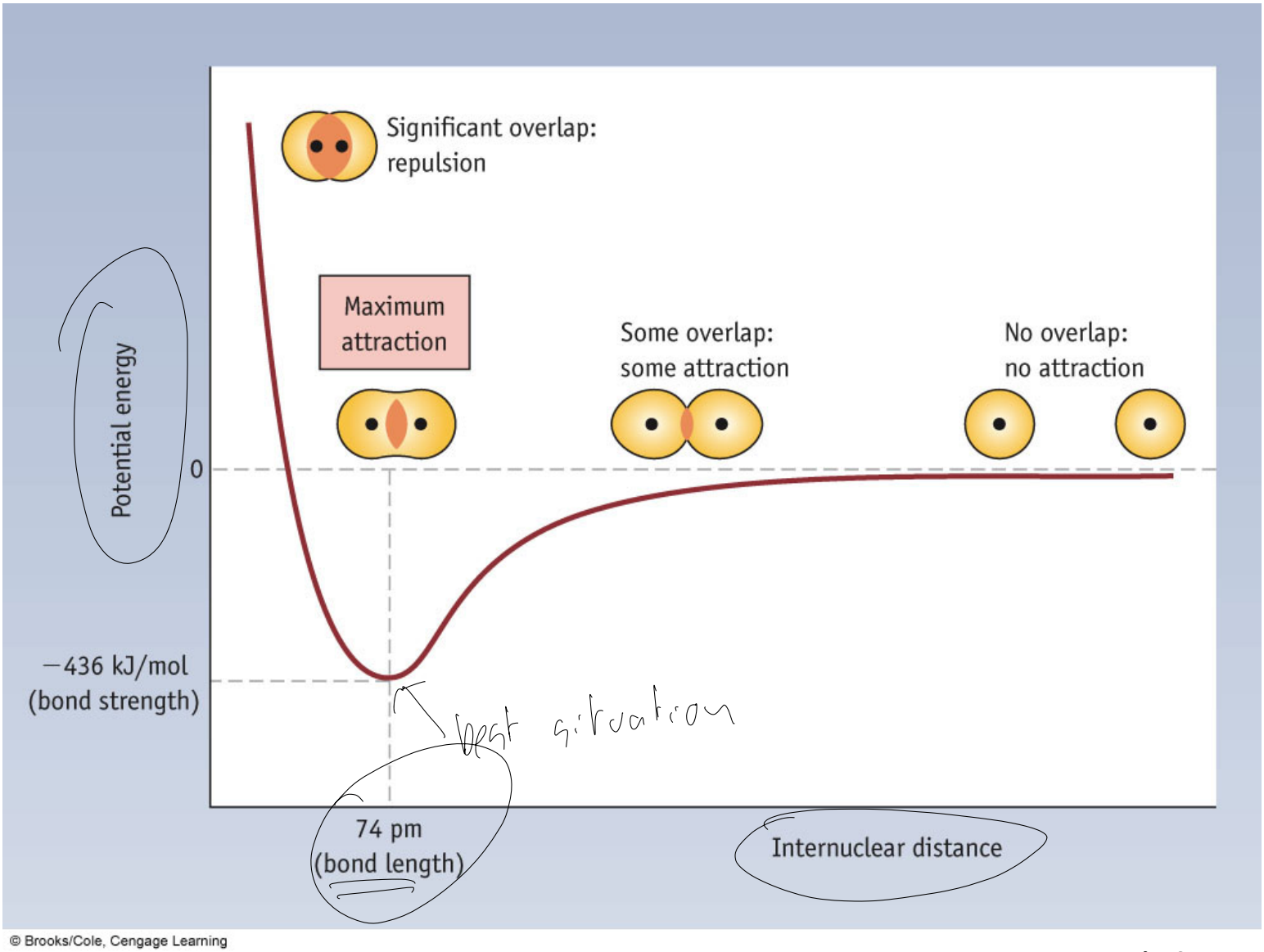


Fig. 9-1, p. 406

Cl_2 molecule

:Cl–Cl: :Cl· ·Cl:

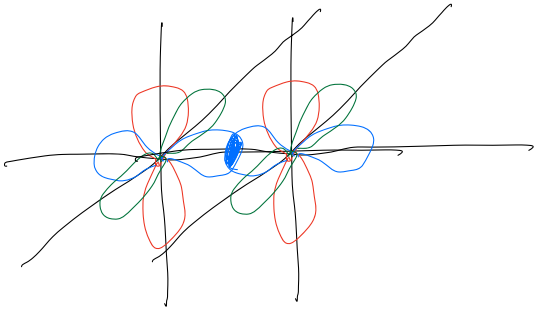
$1s^2 2s^2 2p^6 3s^2 3p^5$

valence

unpaired e⁻ gets shared

↑↓	↑↓	↑↓	↑
3s	3p		

Cl #1 Cl #2



no overlap

↓ bring atoms closer

enhanced electron density at overlap

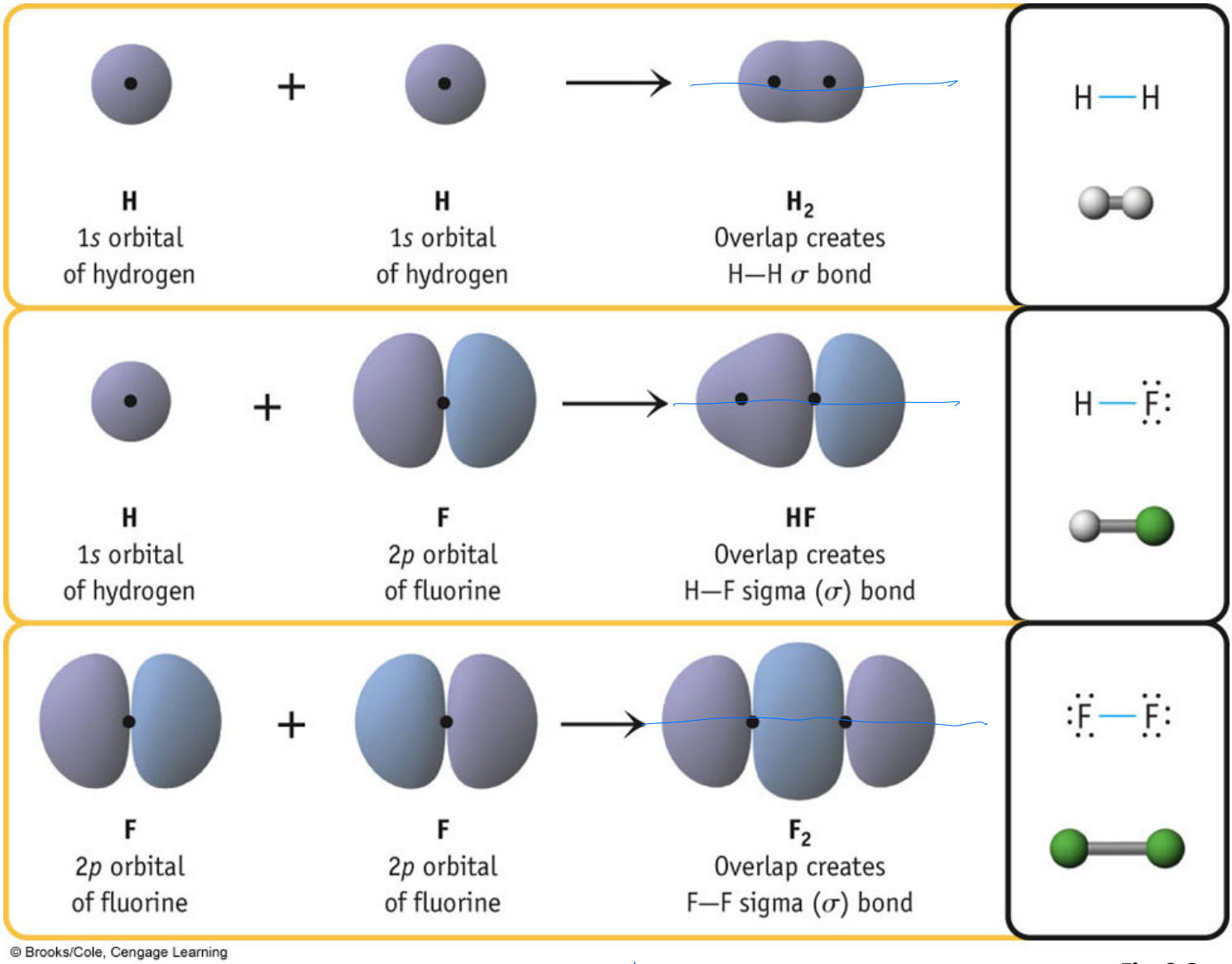


Fig. 9-2, p. 407

bond axis is line connecting nuclei

σ bond is where bond axis "skewers" electron density

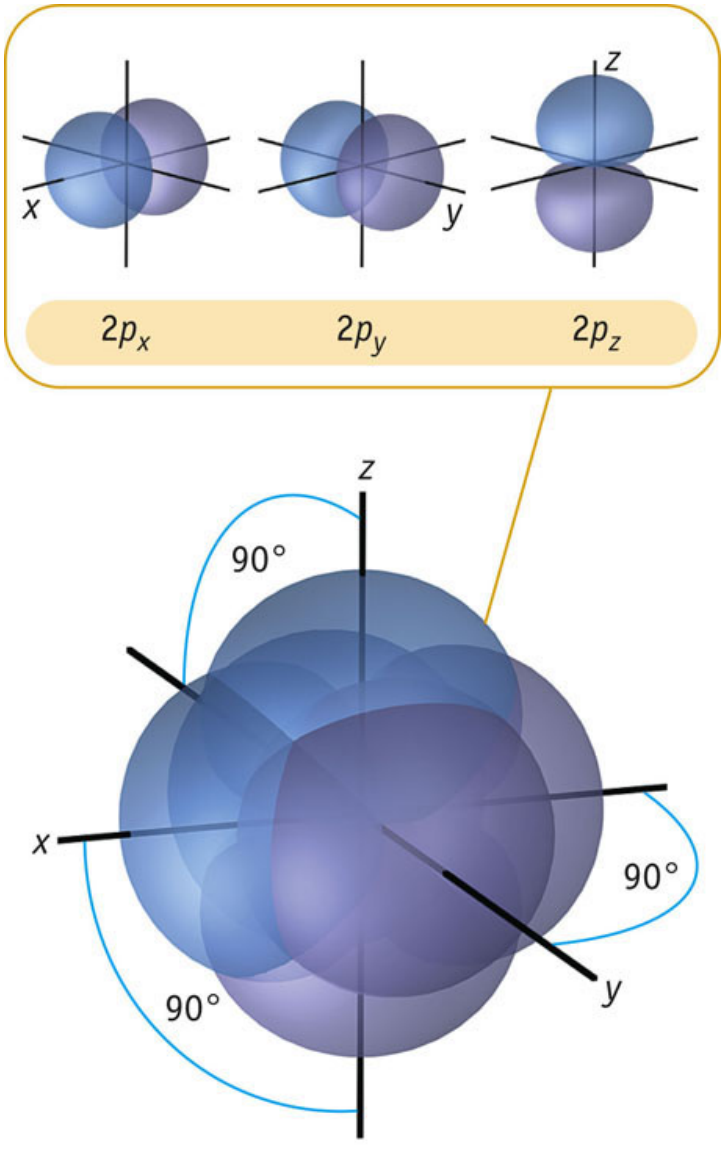
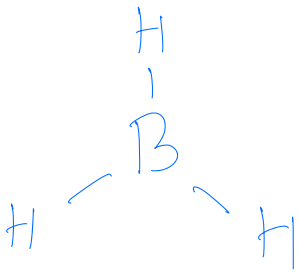


Fig. 9-3, p. 408

BH_3



H has $1e^-$ in 1s

B has $2s^2 2p^1$

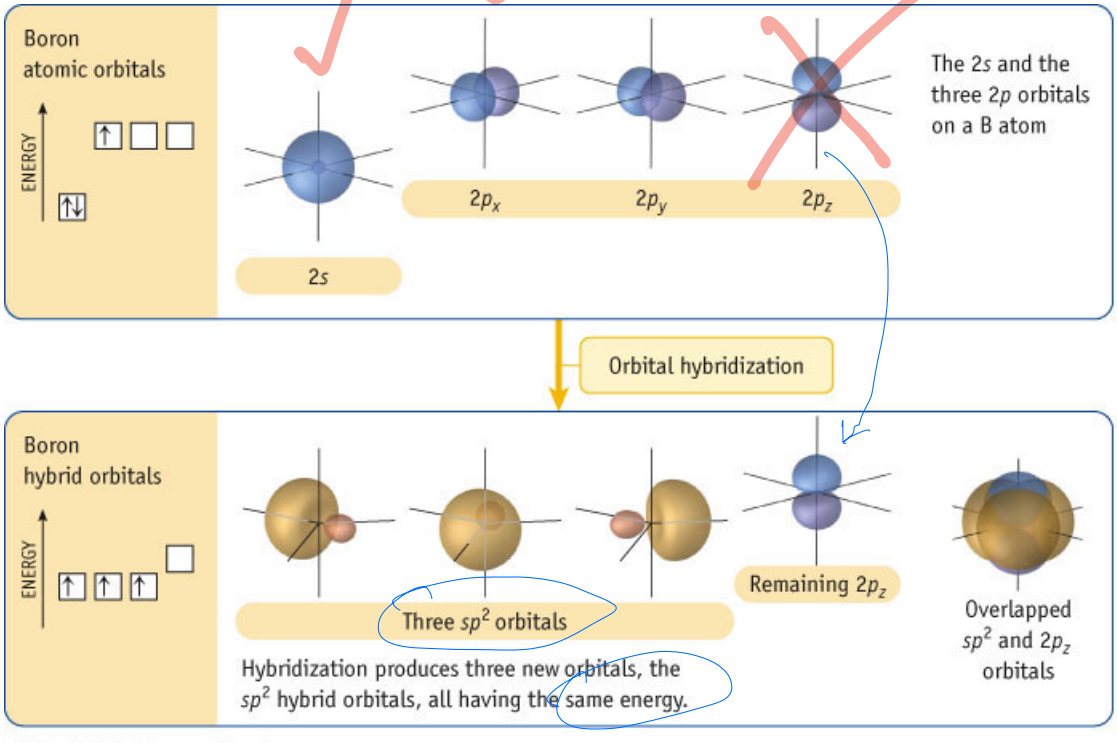
H ↑ — —

geom: trigonal planar

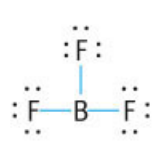
B only has 1 unpaired e^- - how does it make 3 bonds

There are not orbitals on B oriented at 120° from each other - so how do we get trigonal planar

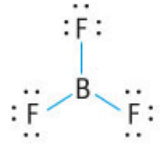
* hybridization - combine original orbitals to create new orbitals with desired characteristics



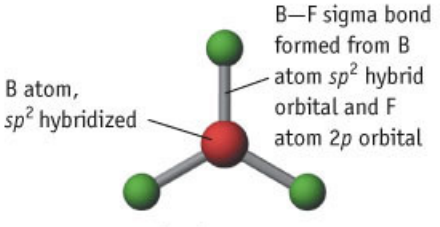
— unhybridized original



Lewis structure



Electron-pair geometry



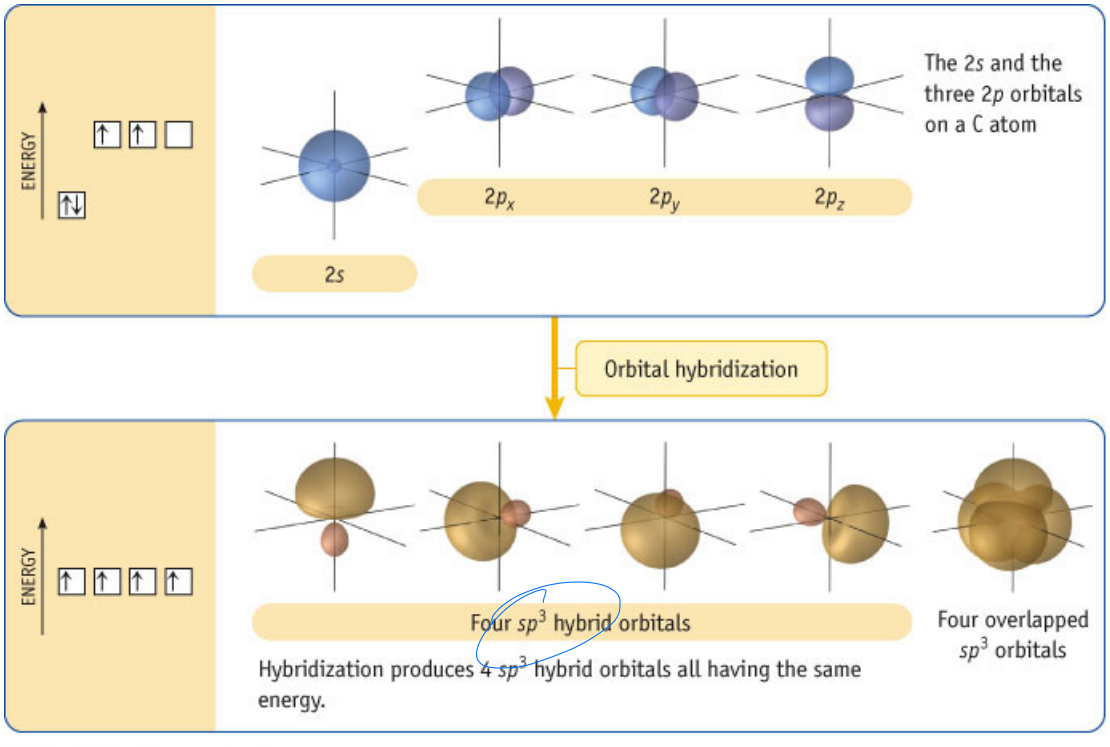
Molecular geometry

combine S, $2p_x$, $2p_y$ to make 3 "sp^2" hybrid orbitals

For BH_3 1s on H overlaps with sp^2 hybrid on B

Fig. 9-8, p. 414

CH4 has same shape – how to get tetrahedral geometry with 90° oriented p-orbitals
→ hybridization



can use all of these orbitals

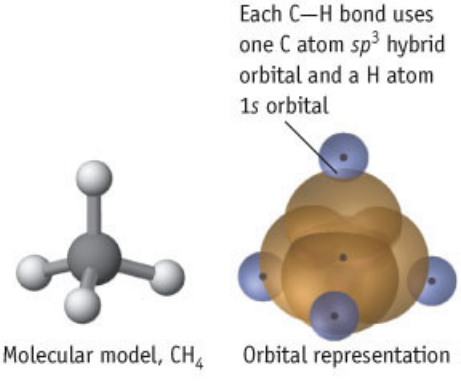
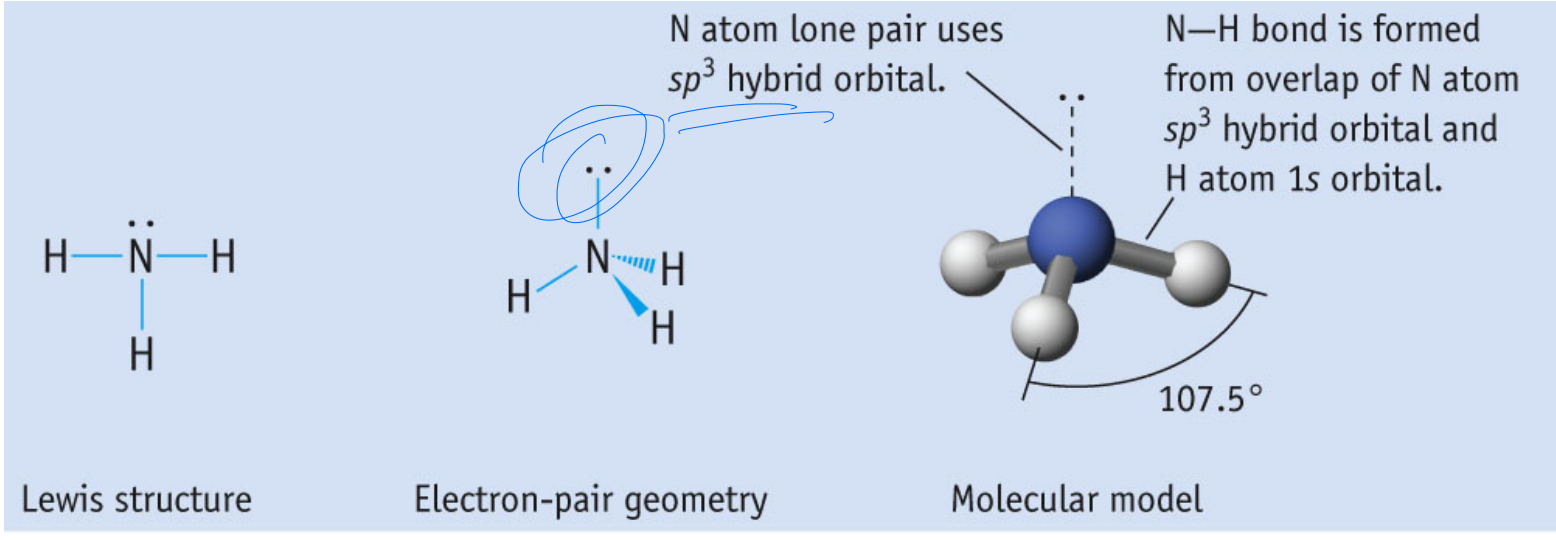


Fig. 9-6, p. 411

electron pair geometry of tetrahedral → due to hybridization



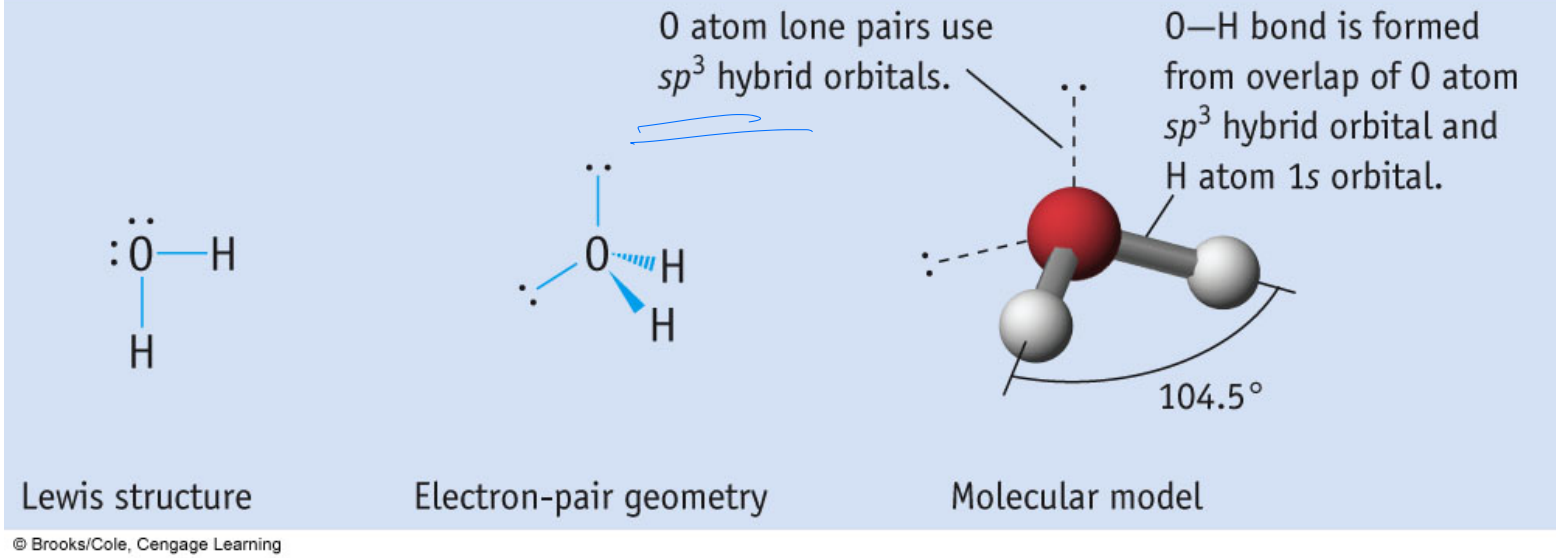


Fig. 9-7, p. 412

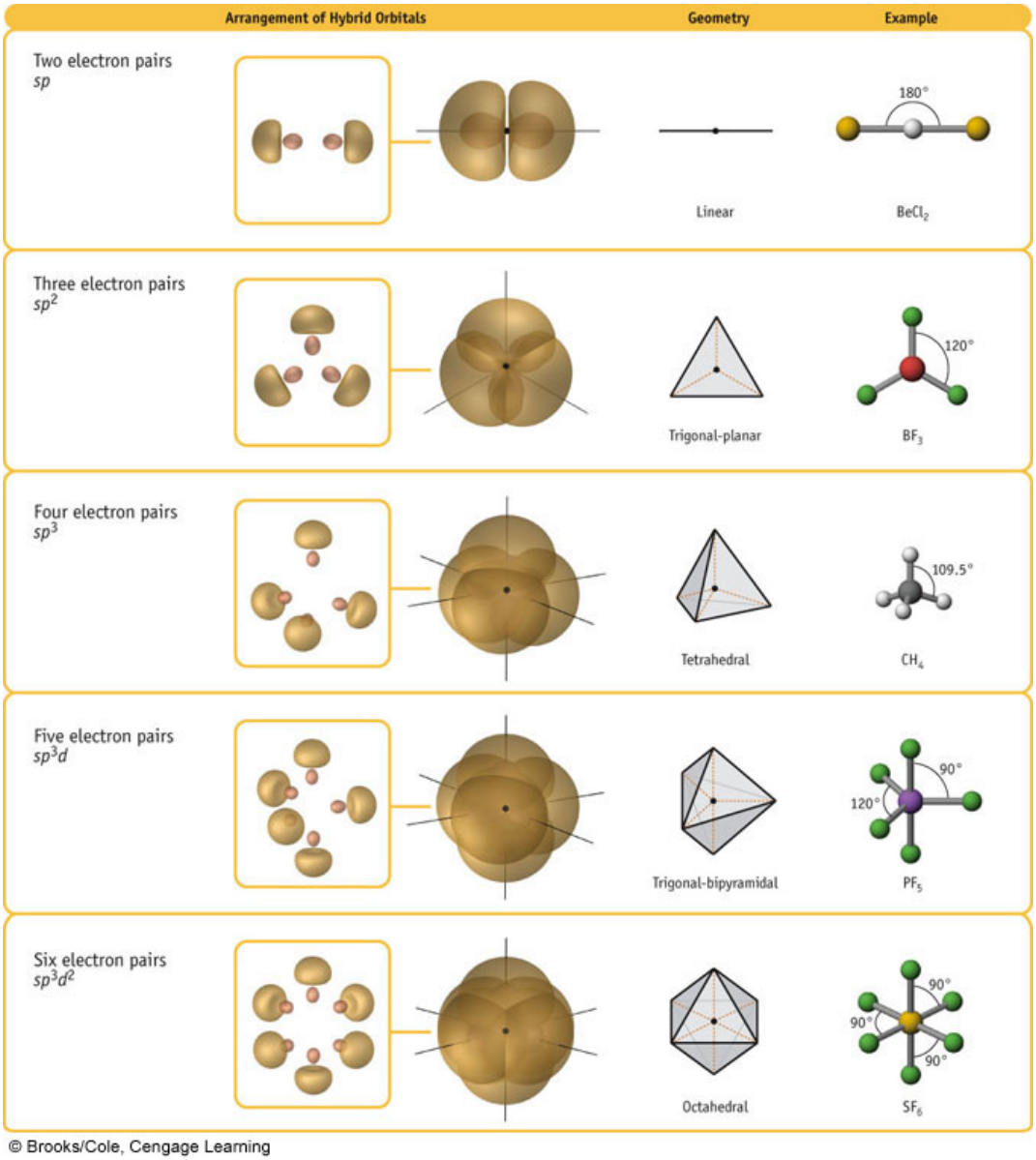


Fig. 9-5, p. 410

C_2H_4

trigonal planar @ C means sp^2 hybridization — one unhybridized p orbital

Lewis

3D

1 σ bond from C sp^2 – C sp^2 overlap

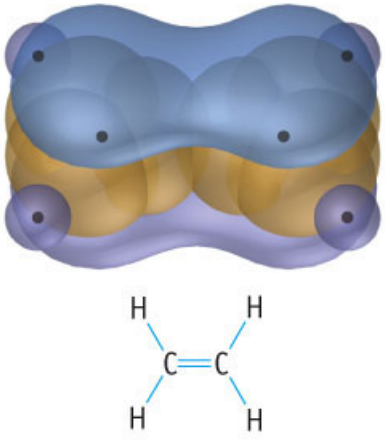
1 π bond from C p – C p overlap

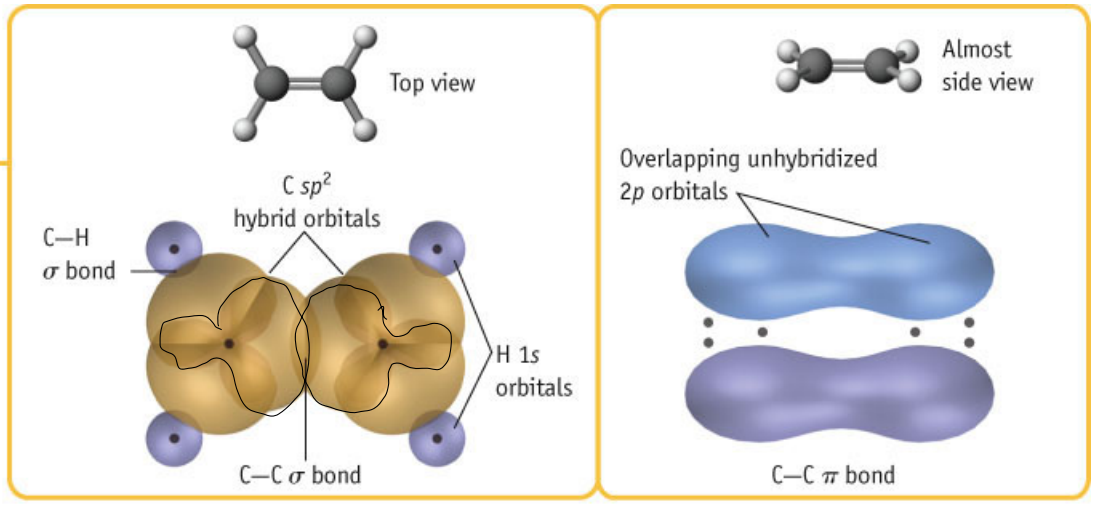
unhyb

p orbitals lean toward each other

π bond – no electron density on bond axis

bond axis





(a) Lewis structure and bonding of ethylene, C_2H_4.

(b) The C—H σ bonds are formed by overlap of C atom sp^2 hybrid orbitals with H atom 1s orbitals. The σ bond between C atoms arises from overlap of sp^2 orbitals.

(c) The carbon–carbon π bond is formed by overlap of an unhybridized 2p orbital on each atom. Note the lack of electron density along the C—C bond axis from this bond.

Fig. 9-10, p. 417

C_2H_2 H–C≡C–H

sp hybridization

σ bond C sp – C sp

2 π bonds C p (unhyb) – C p (unhyb)

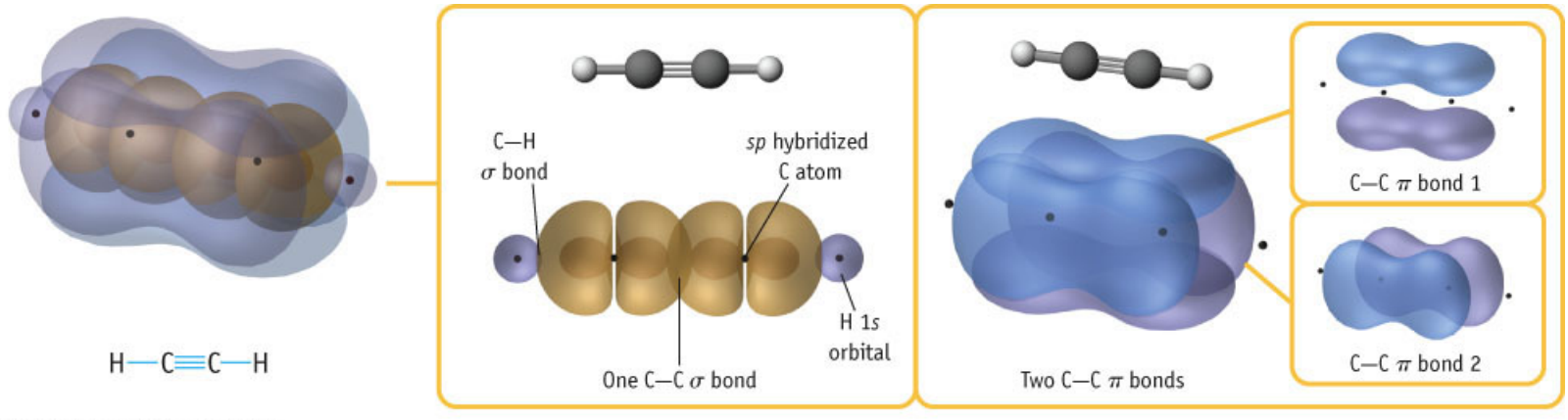
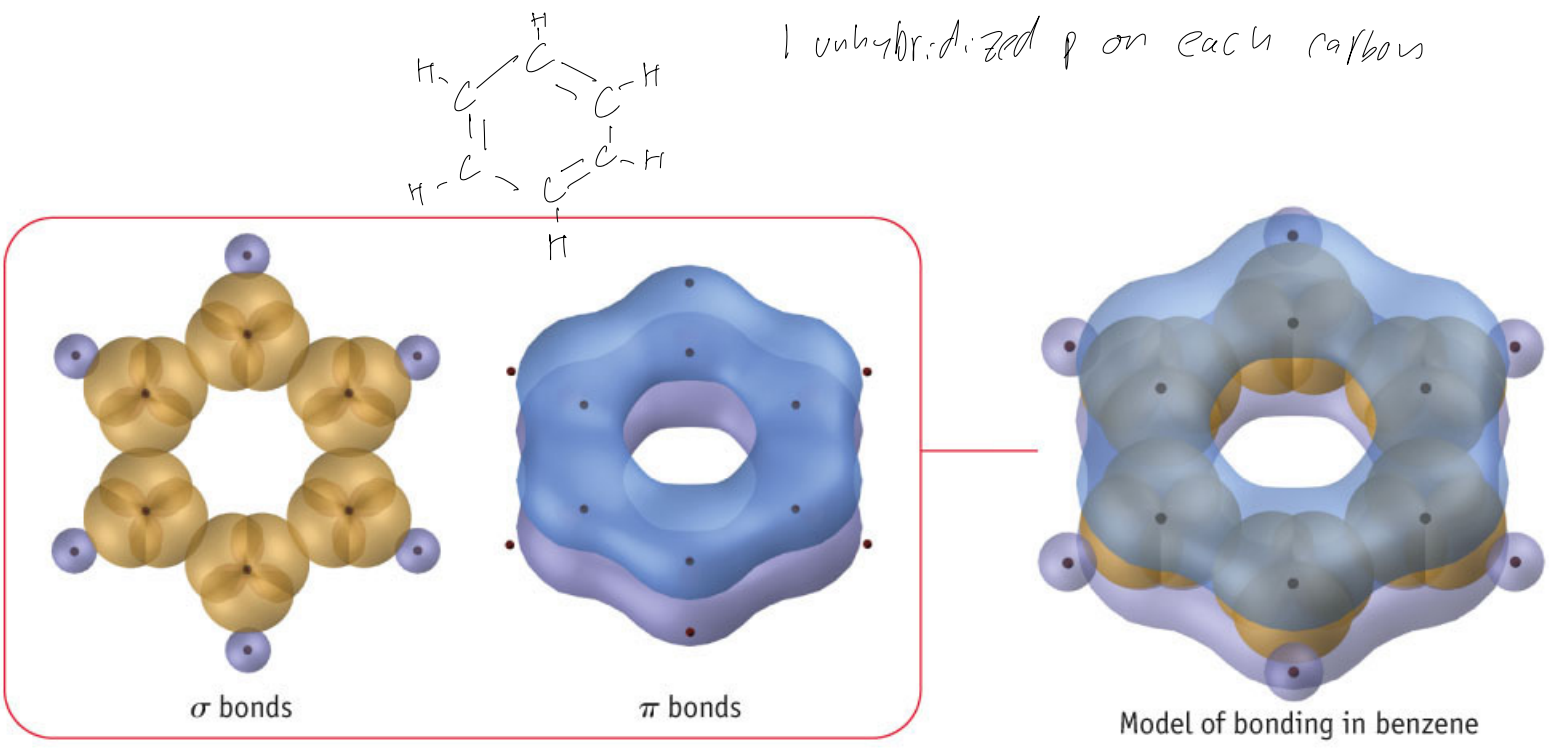


Fig. 9-12, p. 419



σ and π bonding in benzene

Fig. 9-14, p. 422

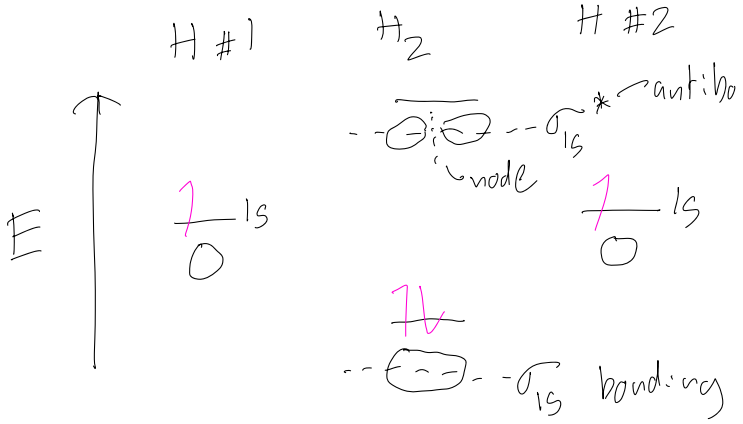
Molecular orbital theory (MOT)

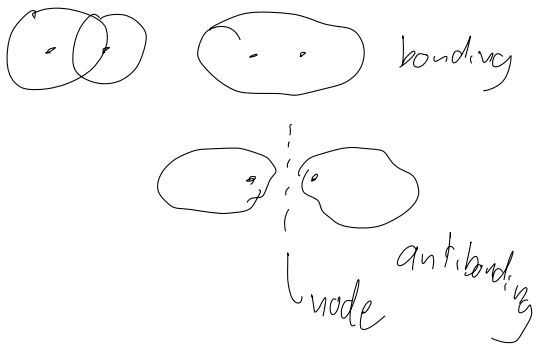
- start with regular unhybridized atomic orbitals (AOs)
- combine to make new orbitals spread out over entire molecule (MOs)

AOs = # MOs

combine 2 AOs → make 2 MOs

one MO will be lower E than AOs "bonding"
one MO will be higher E than AOs "antibonding"

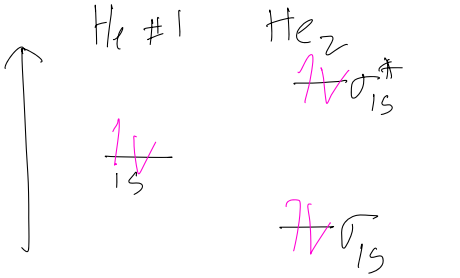




each MO can hold 2 e^-

before – 2 e^- at higher energy
after – 2 e^- at lower energy → this is why they bond

antibonding MO has region of zero electron density btw nuclei



not any net benefit to bonding so they don't bond

$$\text{Bond order} = \frac{\#e^- \text{ in bonding MO} - \#e^- \text{ in antibonding}}{2}$$

He_2^+ has bond order of 0.5

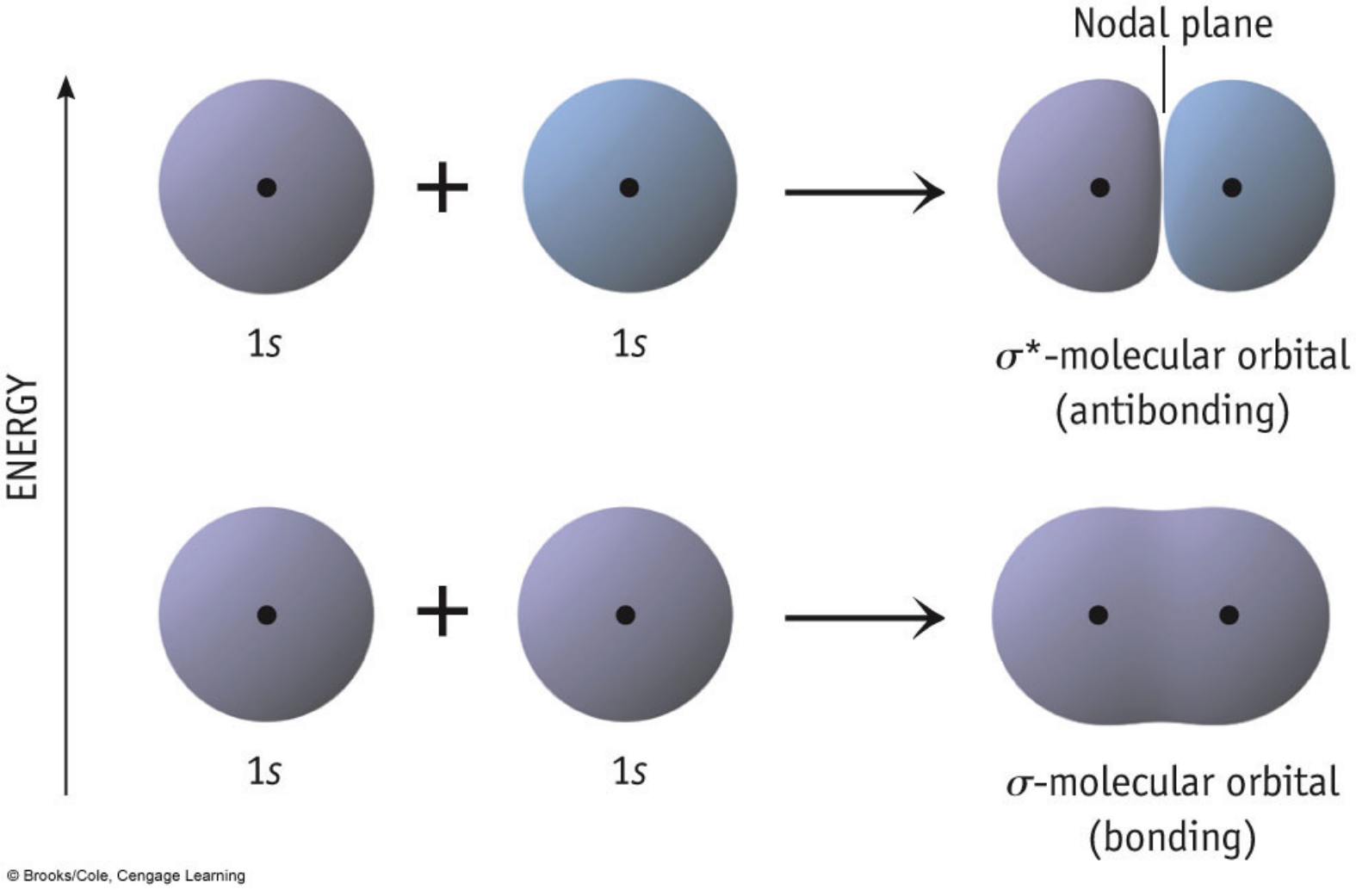


Fig. 9-16, p. 424

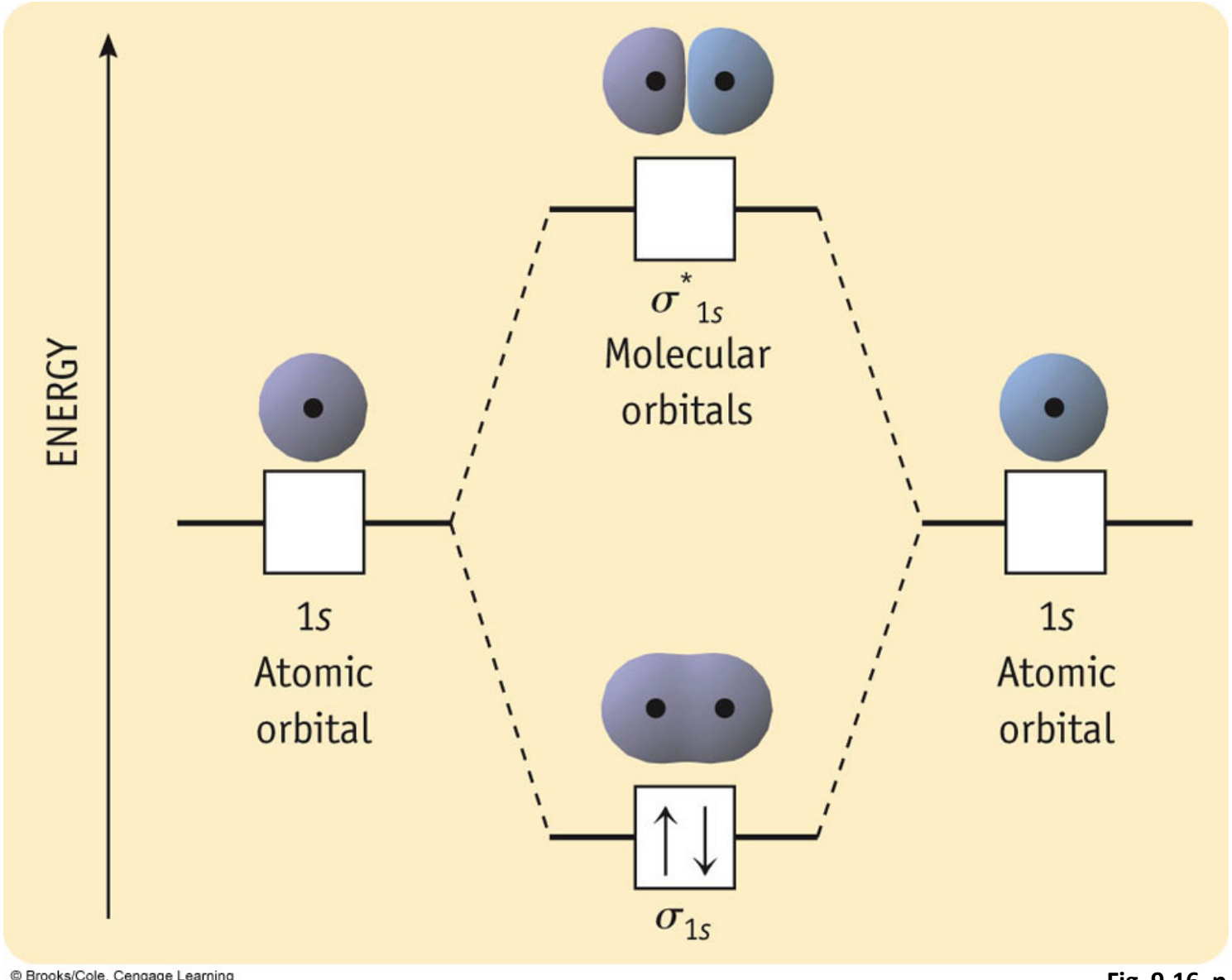


Fig. 9-16, p. 424

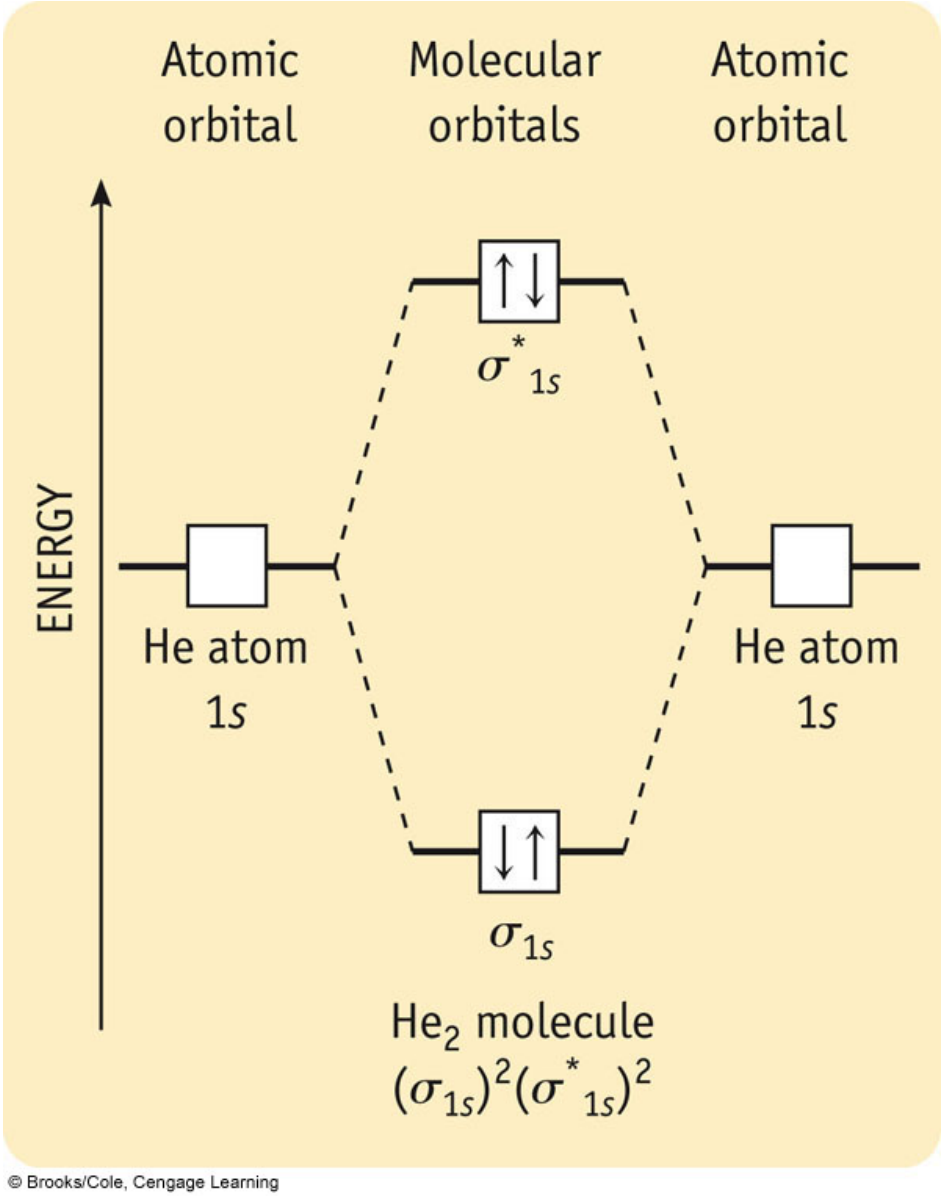


Fig. 9-17, p. 424

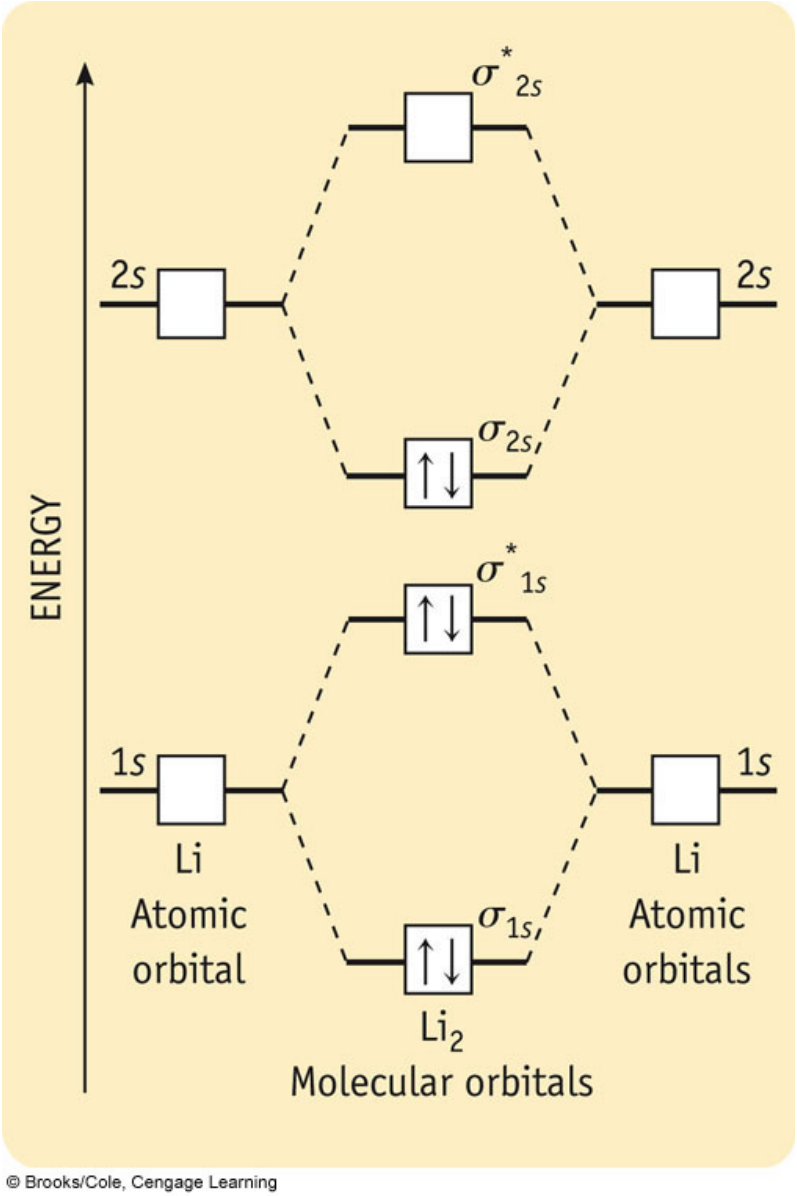
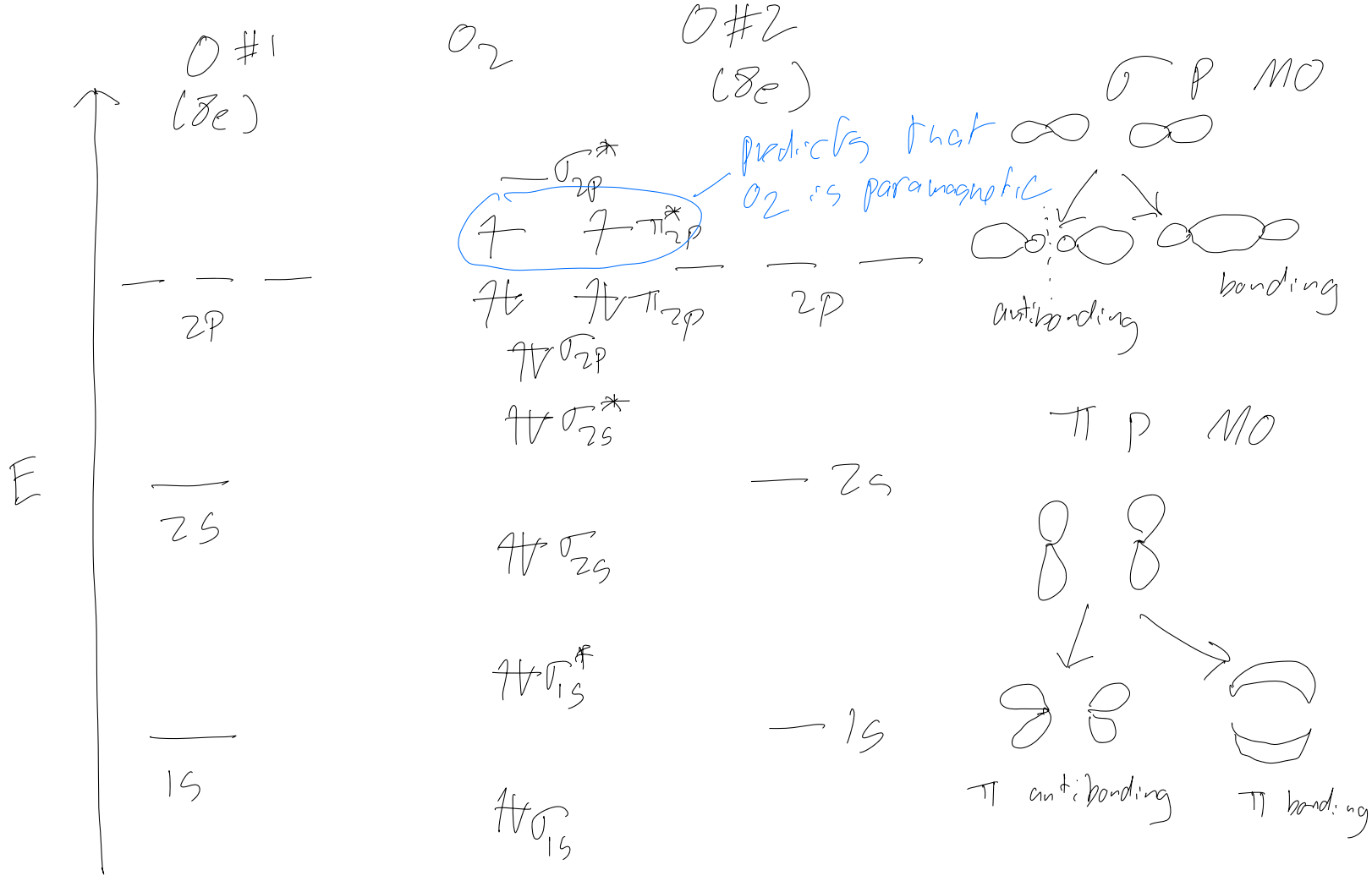


Fig. 9-18, p. 425

O_2 – each atom $1s^2 2s^2 2p^4$



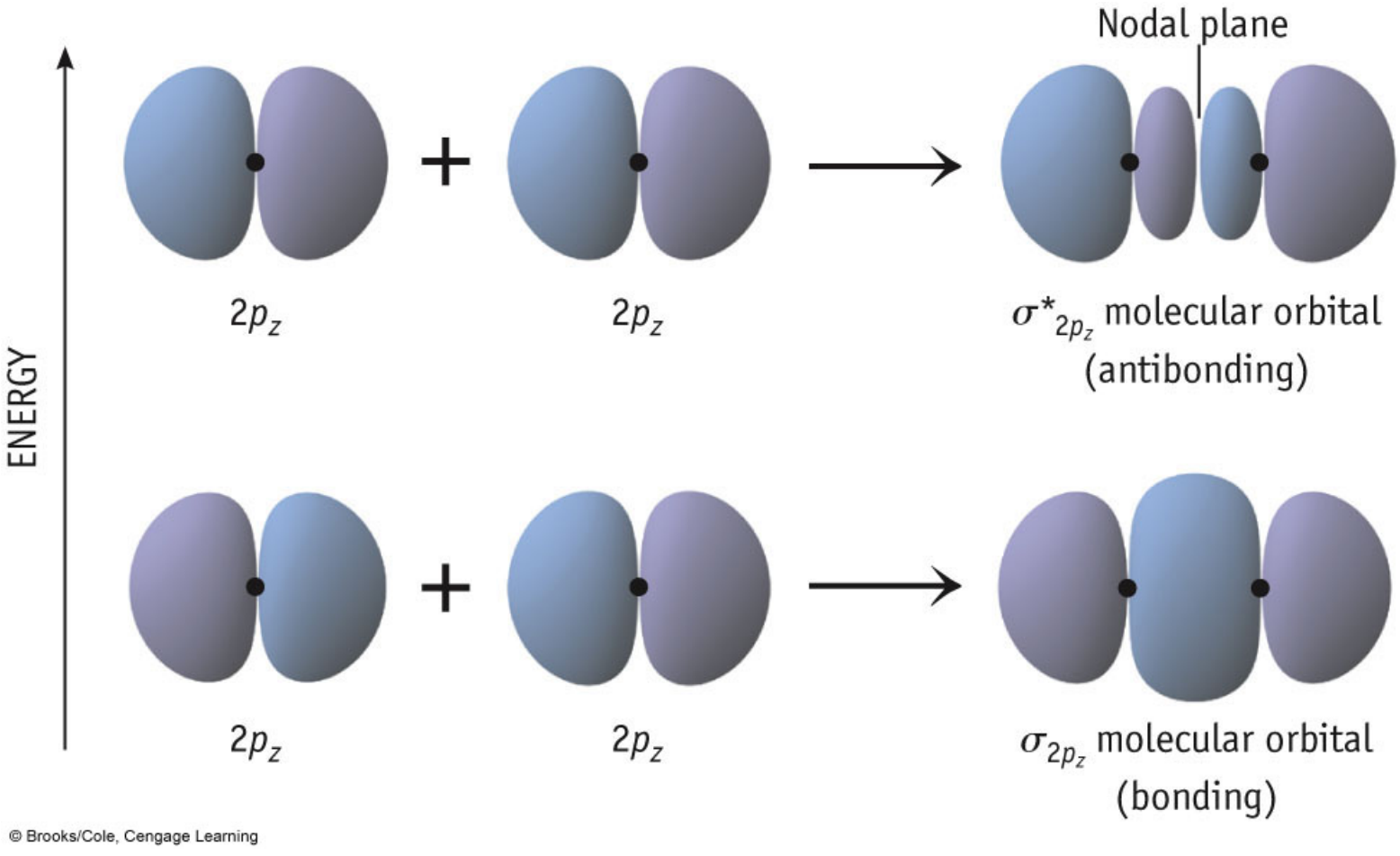


Fig. 9-19, p. 426

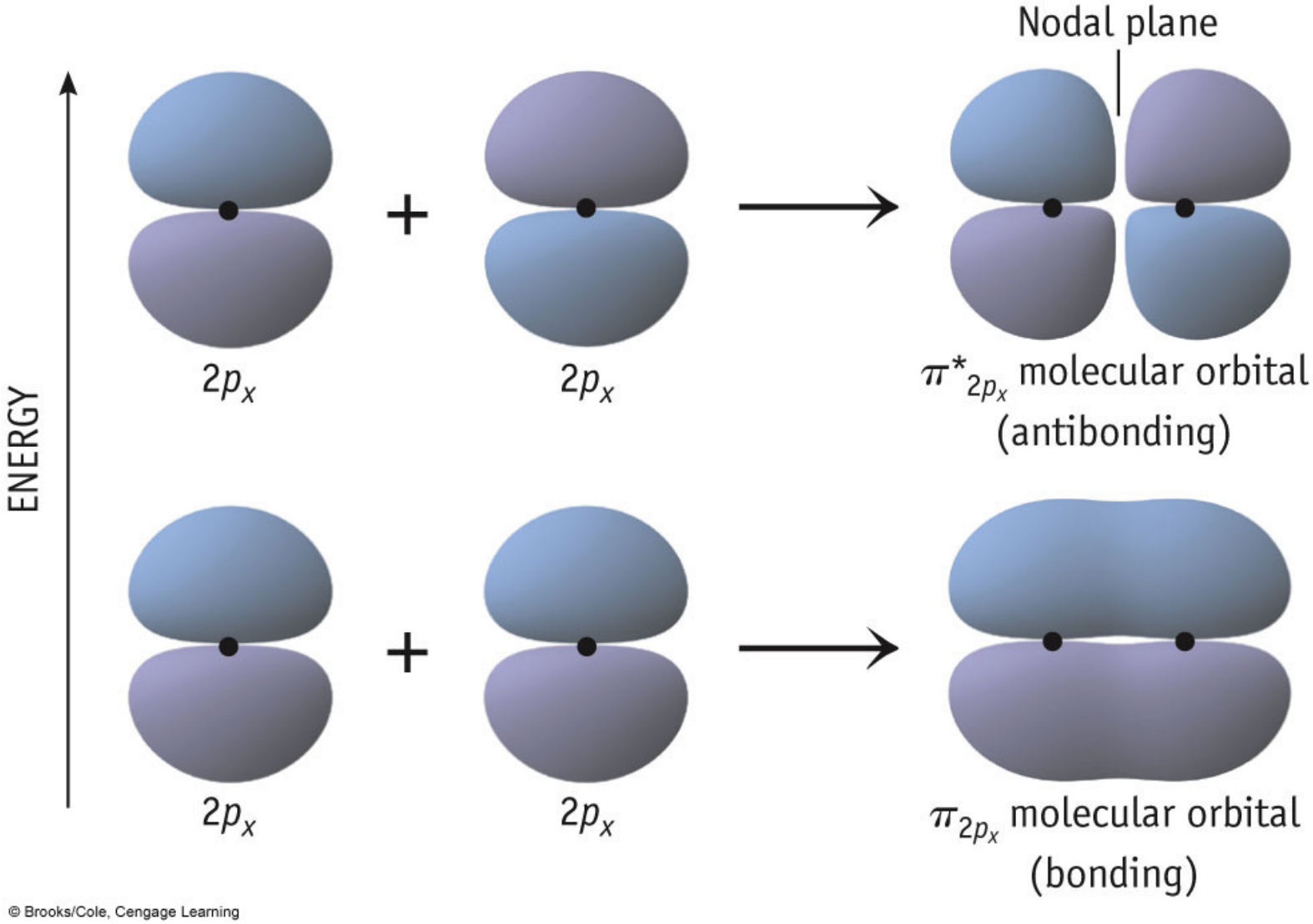


Fig. 9-20, p. 427

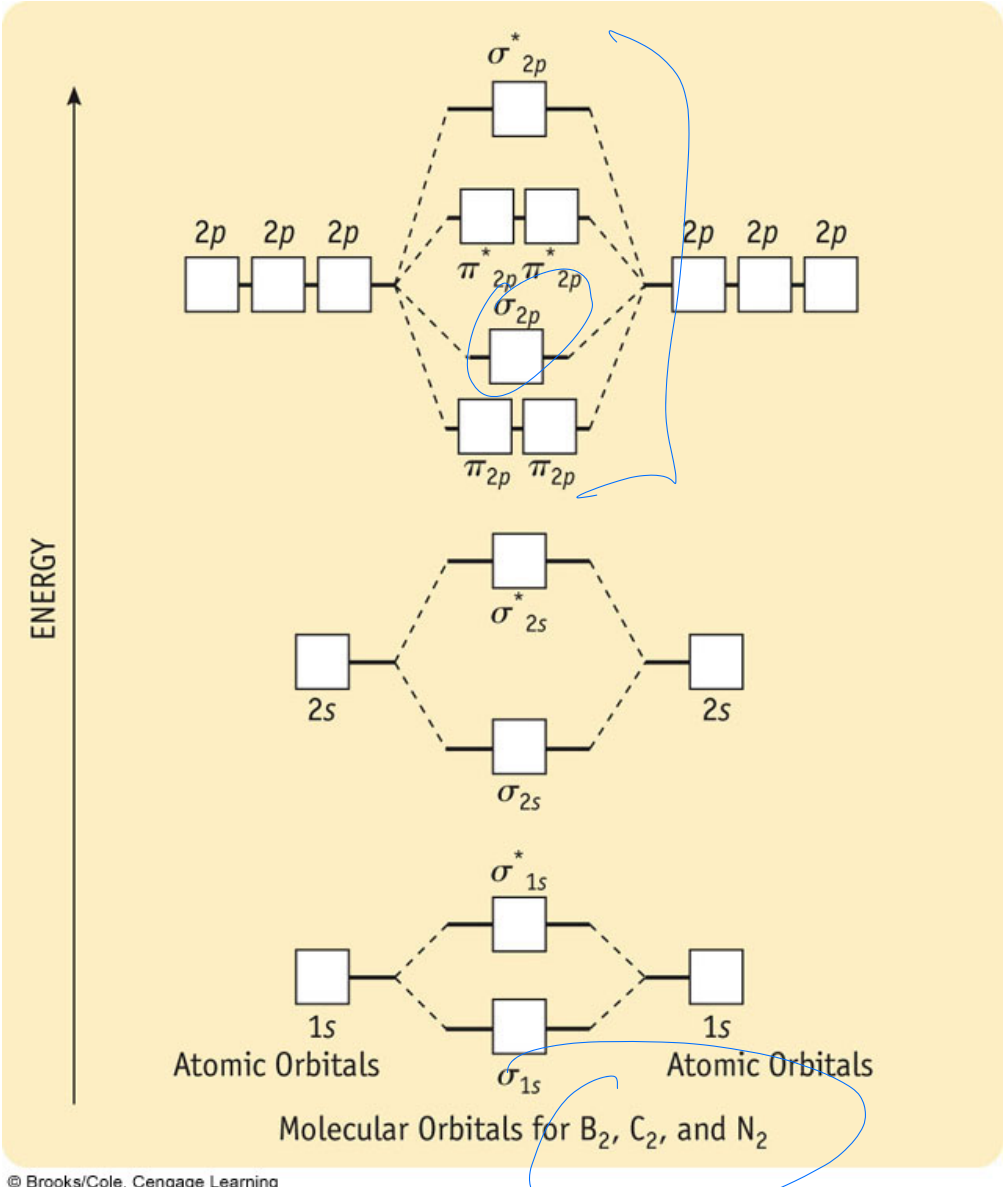


Fig. 9-21a, p. 427

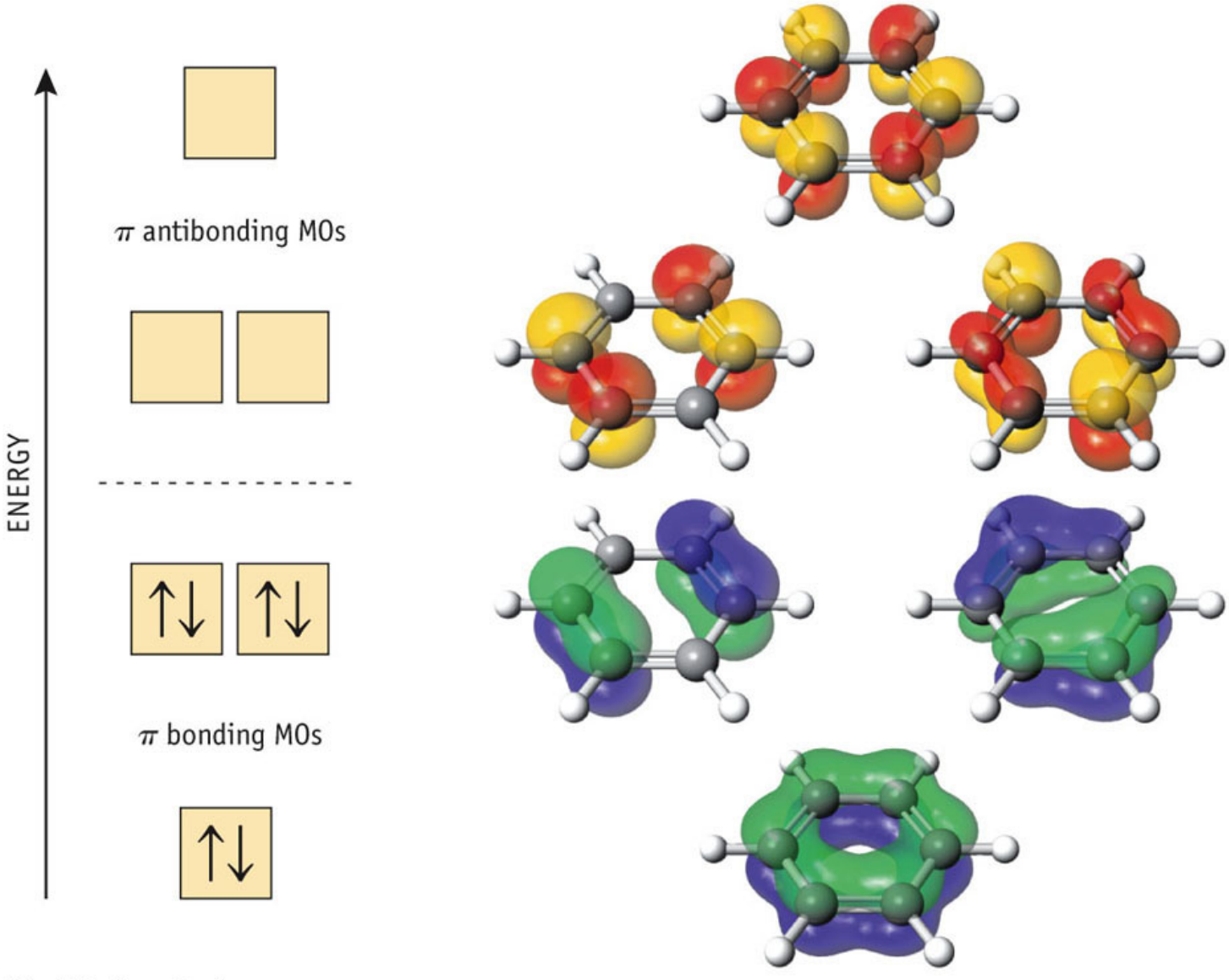


Fig. 9-24, p. 432