Bond order → single bond has BO = 1
triple bond has BO = 3

In O_3 BO = 1.5

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

will correlate w/ atom sizes

As bond order increases, bond length gets smaller

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

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

Table 8-8, p. 387

Bond dissociation enthalpy = ΔH for bond breaking
tells us "strength" of bond

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

When a C-C is broken $\Delta H = 346 \frac{kJ}{mol}$
making a C-C from 2 C atoms
$\Delta H = -346$ kJ/mol

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

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

Break all bonds in reactants
Then form all bonds nec. to make products

Break
4 C-H 4×413
2 O=O 2×498

Make
2 C=O 2×-745
4 O-H 4×-463

2048 kJ

-3742 kJ

$\Delta H = -692$ kJ

Valence Bond Theory
good for molec geometry
"orbital overlap"

Molecular Orbital Theory

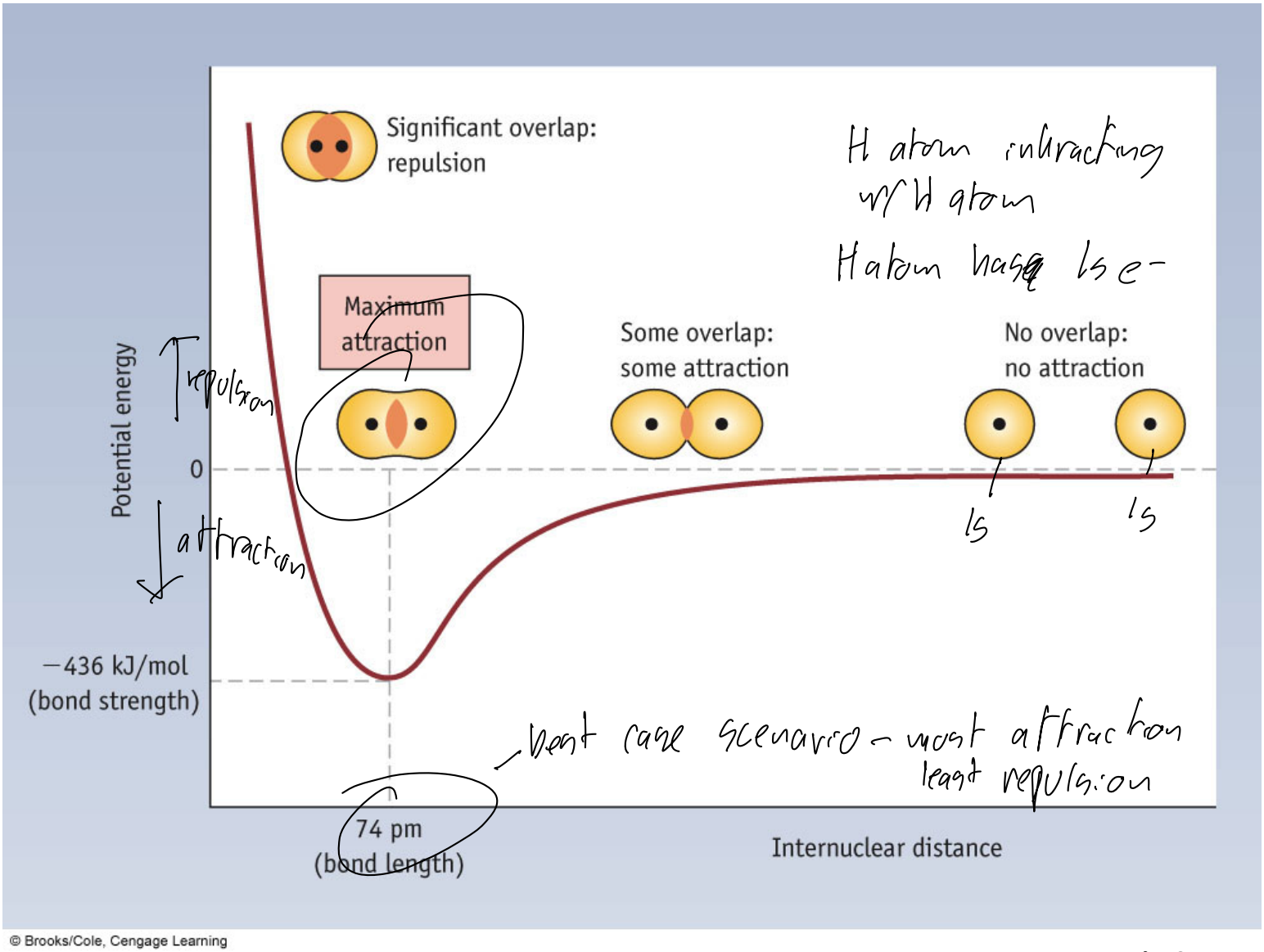
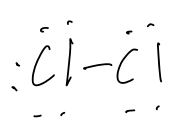


Fig. 9-1, p. 406

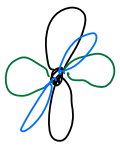
How to think about Cl_2 using valence bond theory

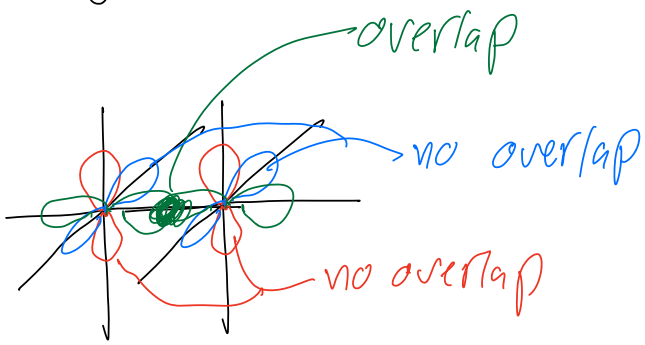
Cl atom - 7 valence electrons



* electron used for bonding is in p-orbitals

*





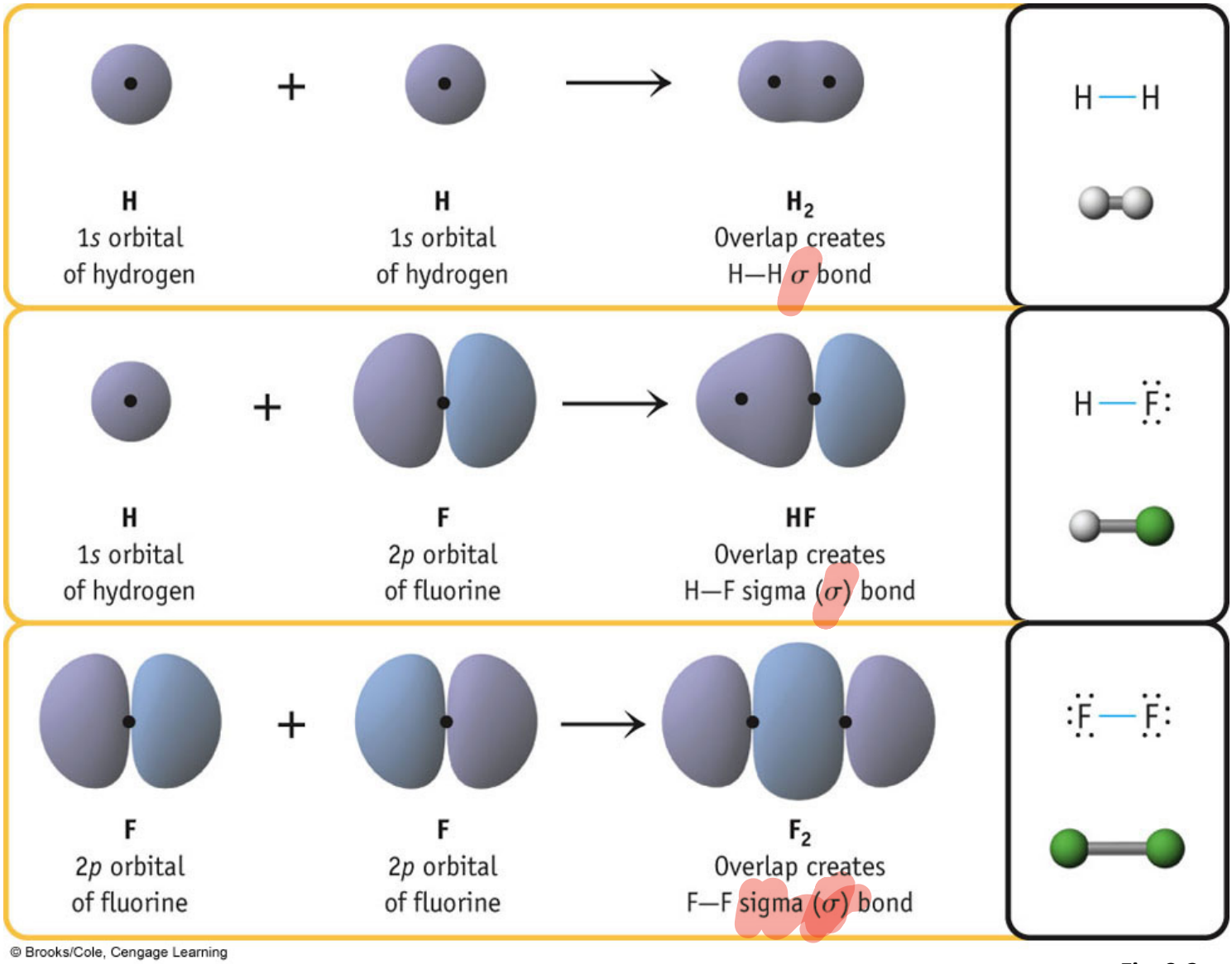


Fig. 9-2, p. 407

Identify bond axis - line between nuclei of atoms

Bond w/ electron density along bond axis is a σ bond

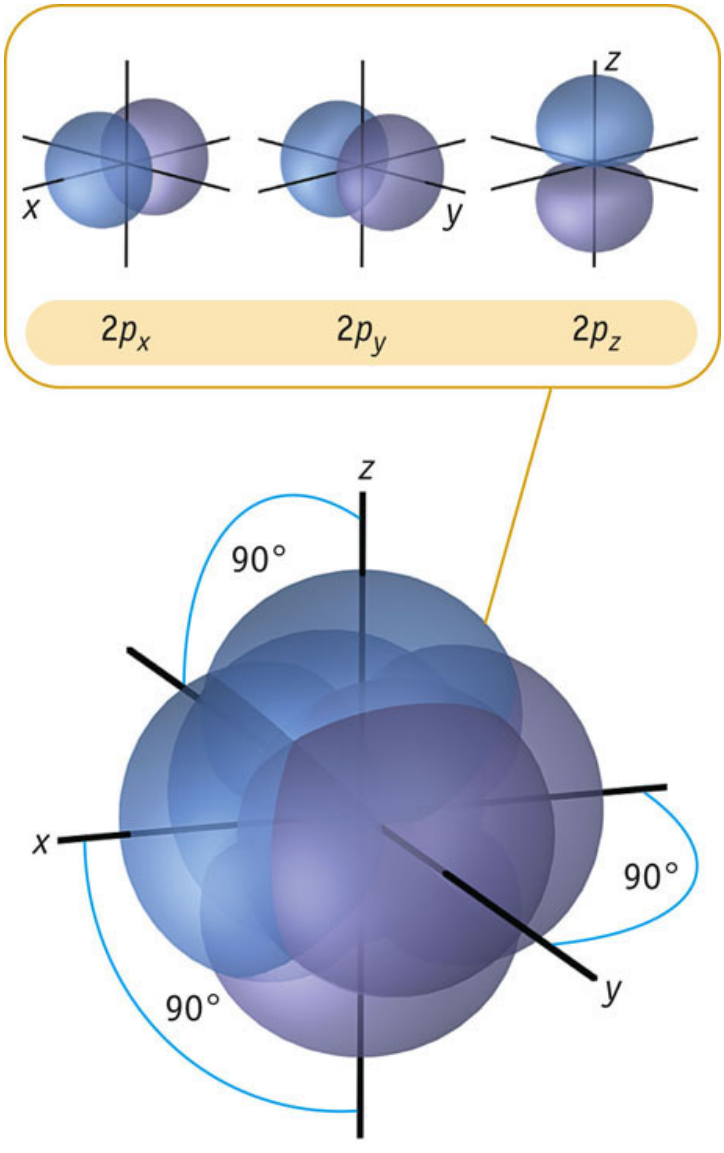
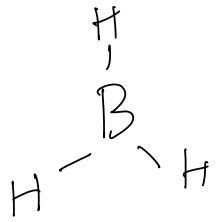


Fig. 9-3, p. 408

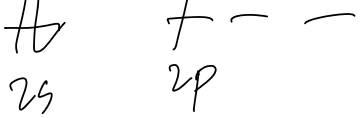
BH_3



want to describe orbital overlap here

H - 1e⁻ in 1s orbital

B - $1s^2 2s^2 2p^1$



For there to be orbital overlaps the B needs orbitals oriented in trigonal planar arrangement

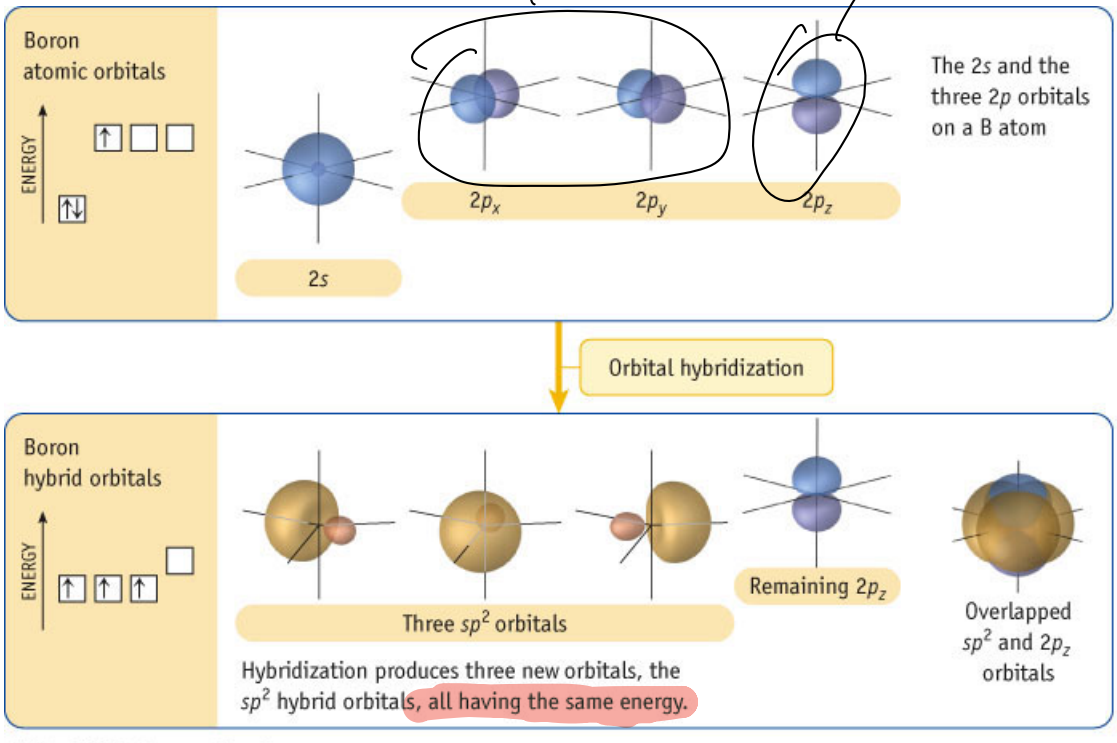
but p orbitals are oriented @ 90° not 120°

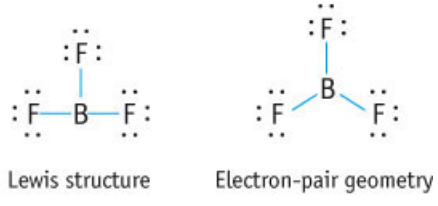
* Hybridization is our solution to this problem

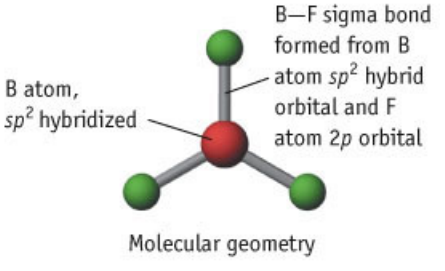
We will combine B orbitals and then make new ones that have useful geometry

in plane of molecule

not in plane of molecule



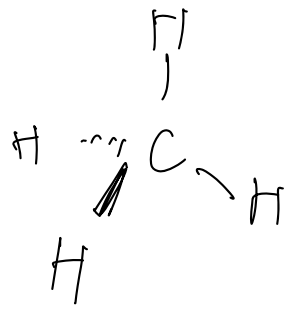


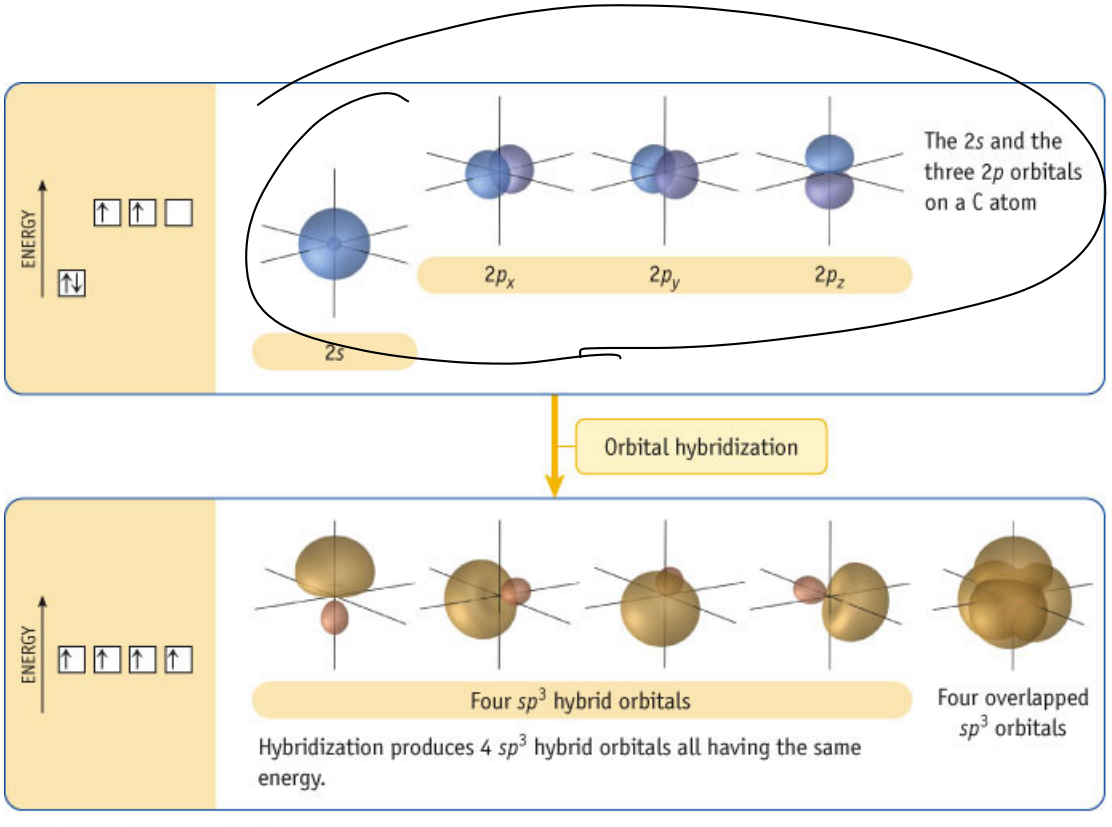


combined 2s, 2p_x, 2p_y to make three sp² hybrid orbitals w/ trigonal planar geometry

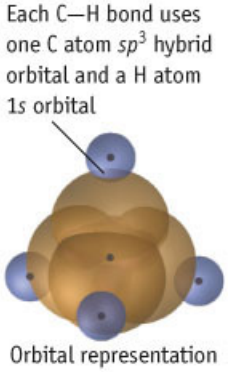
Fig. 9-8, p. 414

tetrahedral





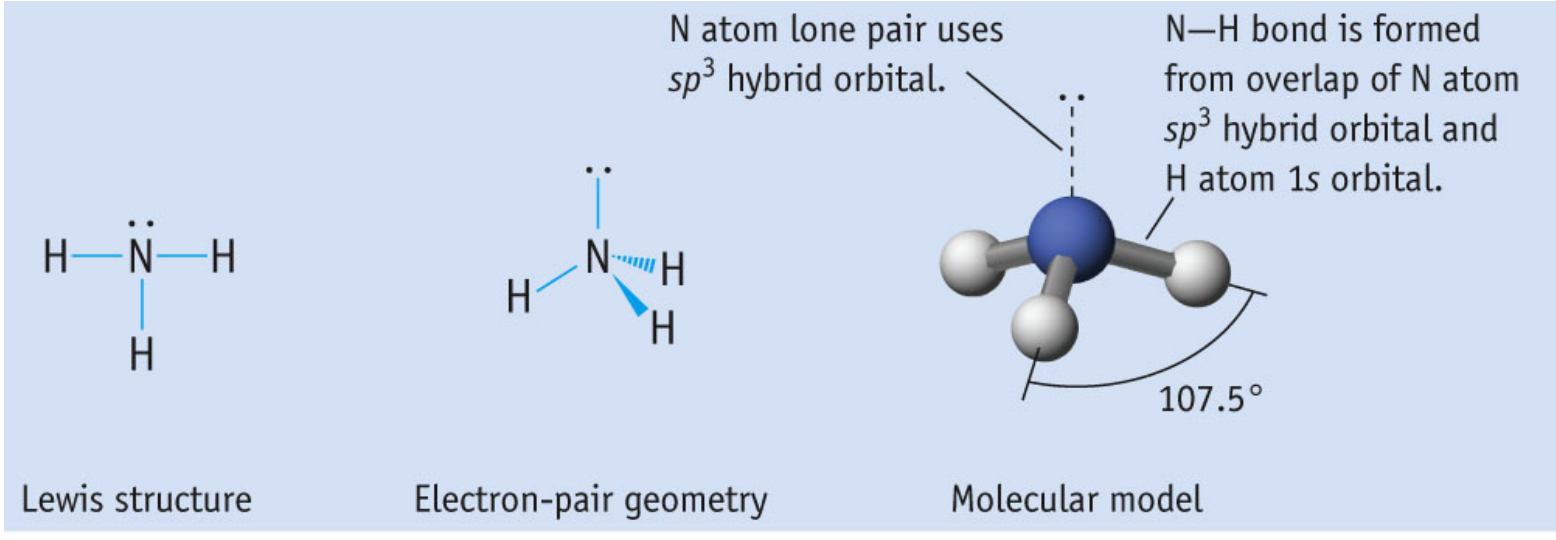
Molecular model, CH_4



Orbital representation

Fig. 9-6, p. 411

tetrahedral e⁻ pair geometry needs sp^3



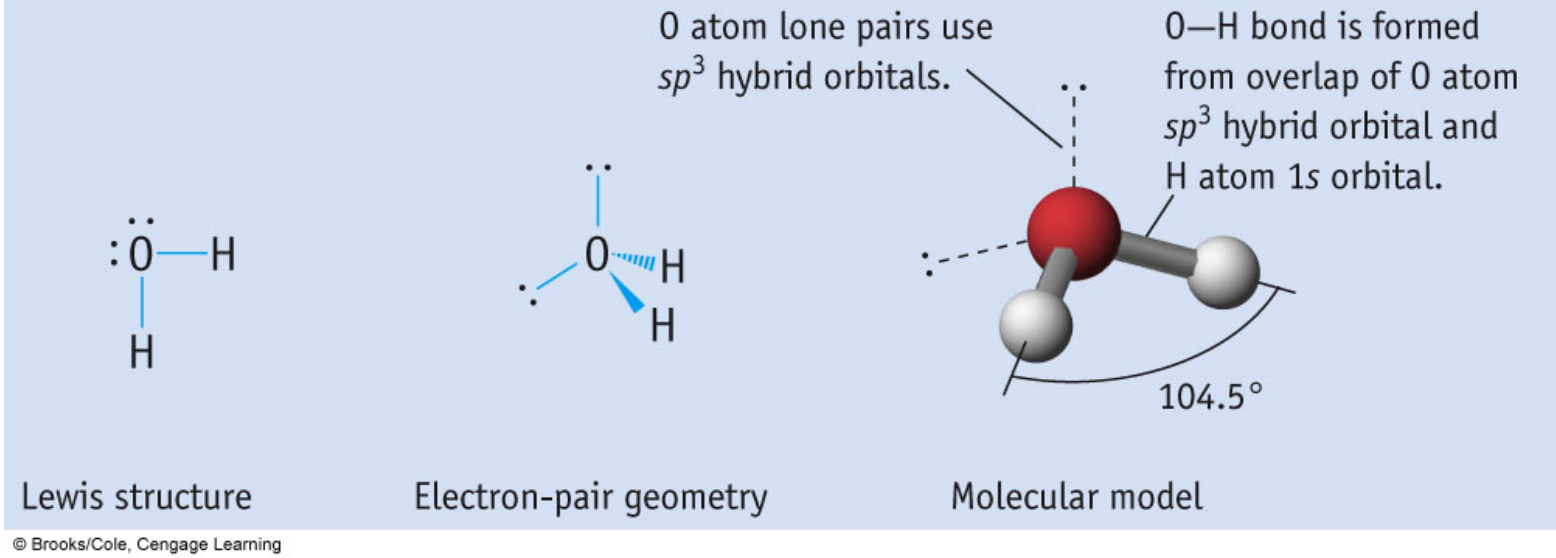


Fig. 9-7, p. 412

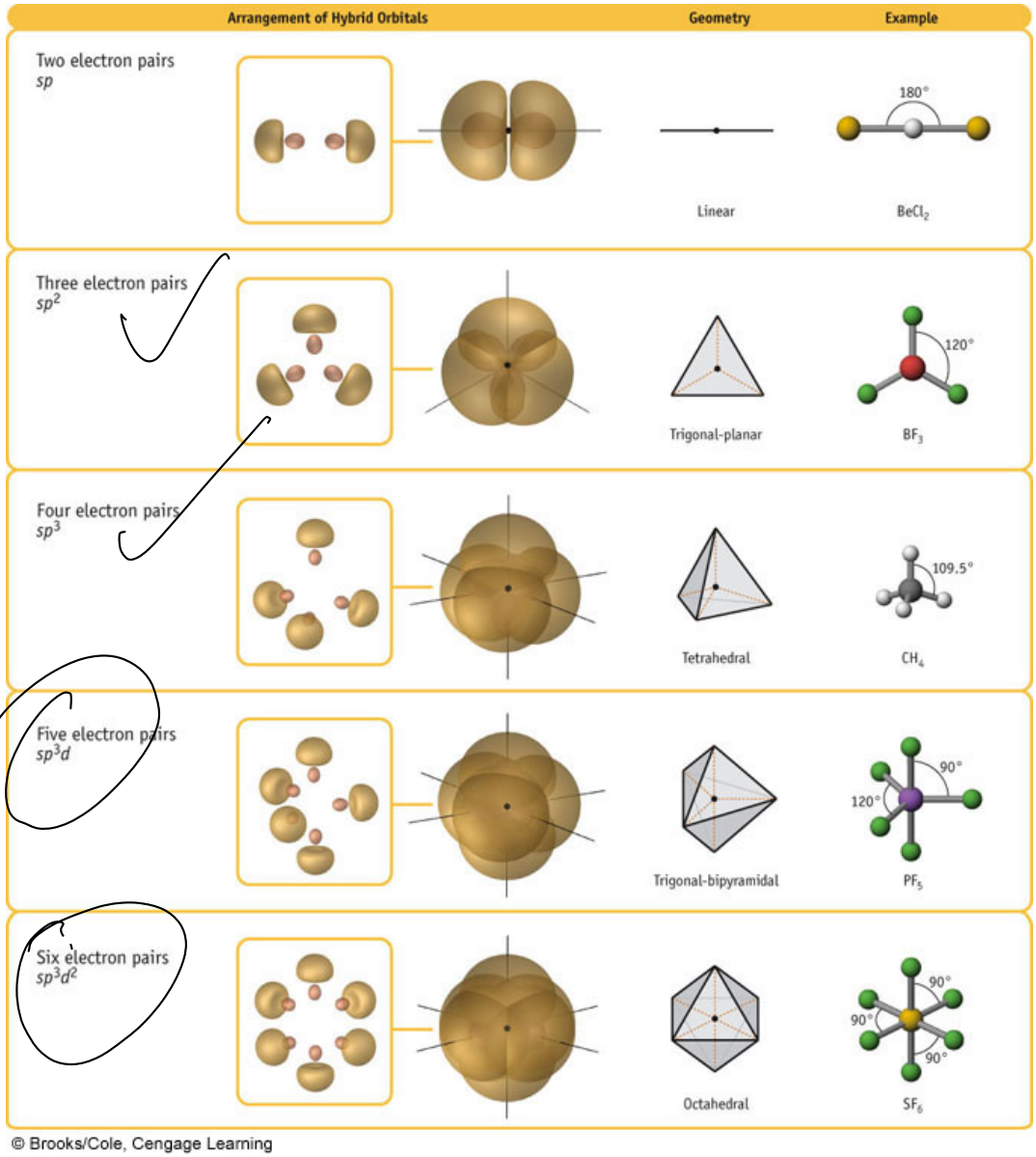


Fig. 9-5, p. 410

C_2H_4

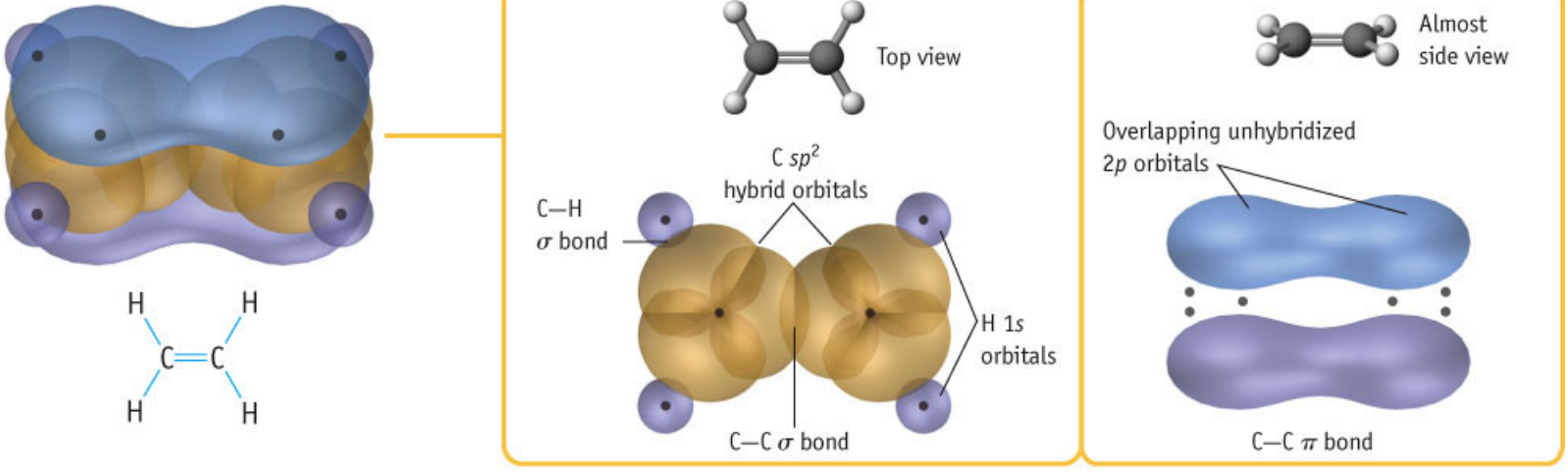
trigonal planar @ C

↓

sp^2 hybridization w/ 1p orbital unhybridized (out of plane)

overlap unhyb p

π bond – no e⁻ density along bond axis



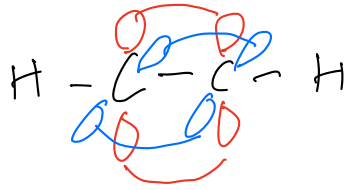
(a) Lewis structure and bonding of ethylene, C_2H_4.

(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 linear geometry



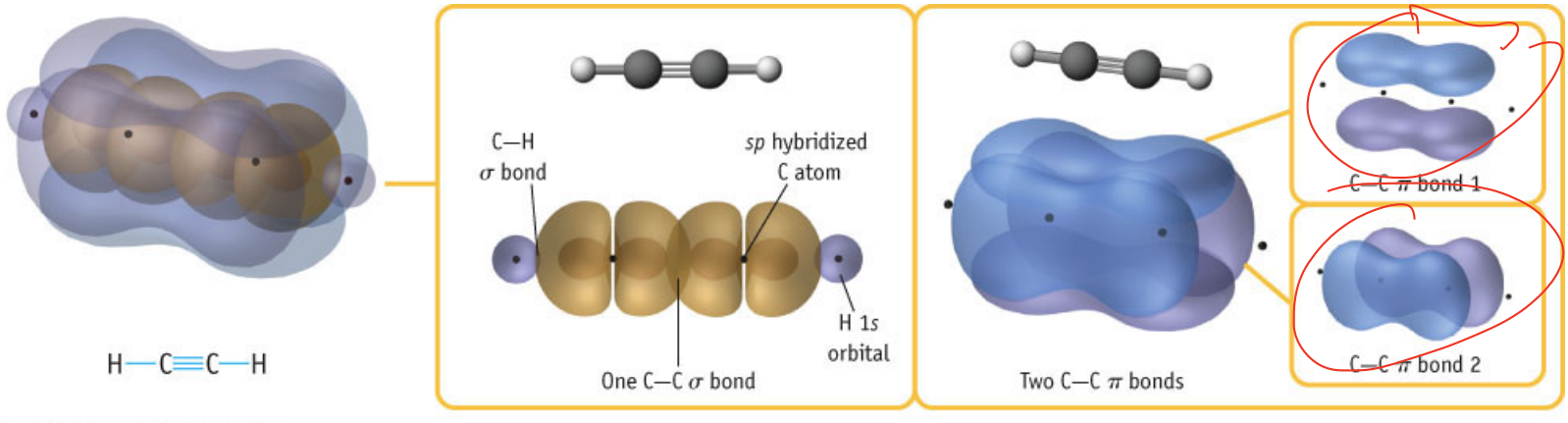
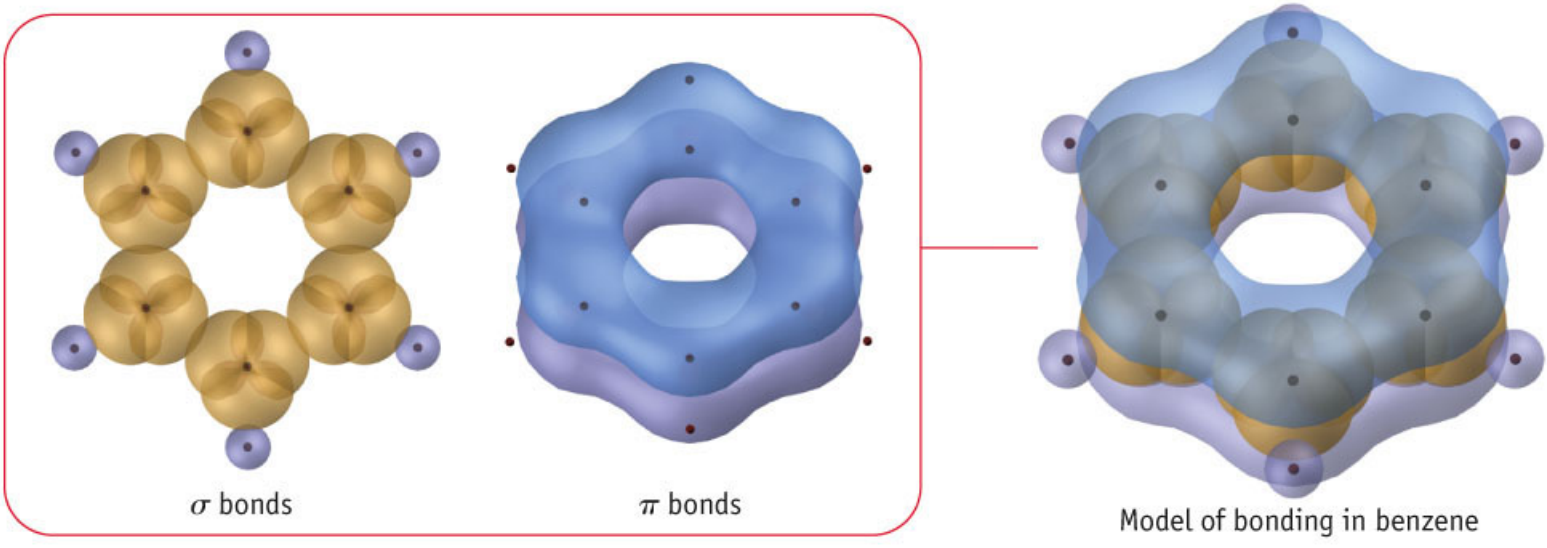


Fig. 9-12, p. 419



σ and π bonding in benzene

Fig. 9-14, p. 422

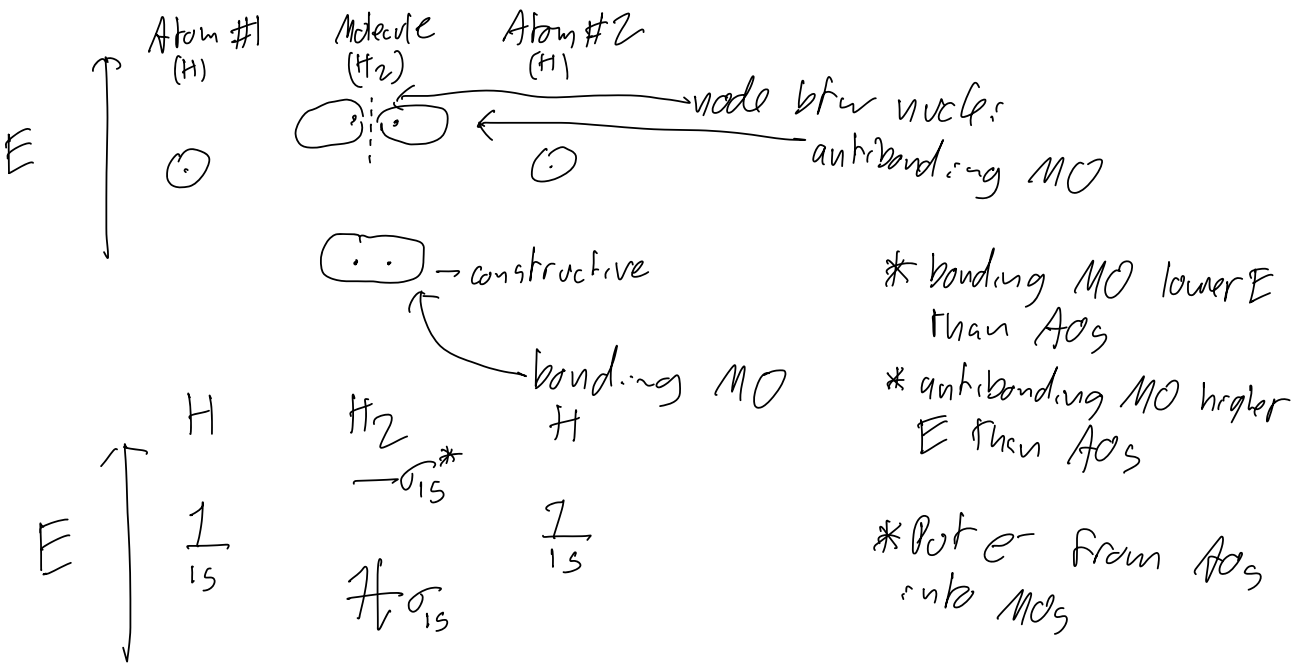
Molecular orbital theory

- start with localized atomic orbitals (regular, unhyb)
- create new orbitals that "belong" to molecule as a whole
- Good for understanding energy levels of electrons in molecules

* # AOs we start with on all atoms = # MOs that we make

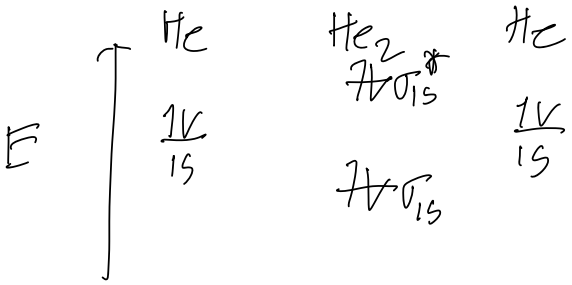
combine AOs "constructively" and "destructively" to make MOs

For H_2 - we start with AOs for each H atom



* bonding MO lower E than AOs
* antibonding MO higher E than AOs
* Put e⁻ from AOs into MOs

Consider He_2



He_2^+

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

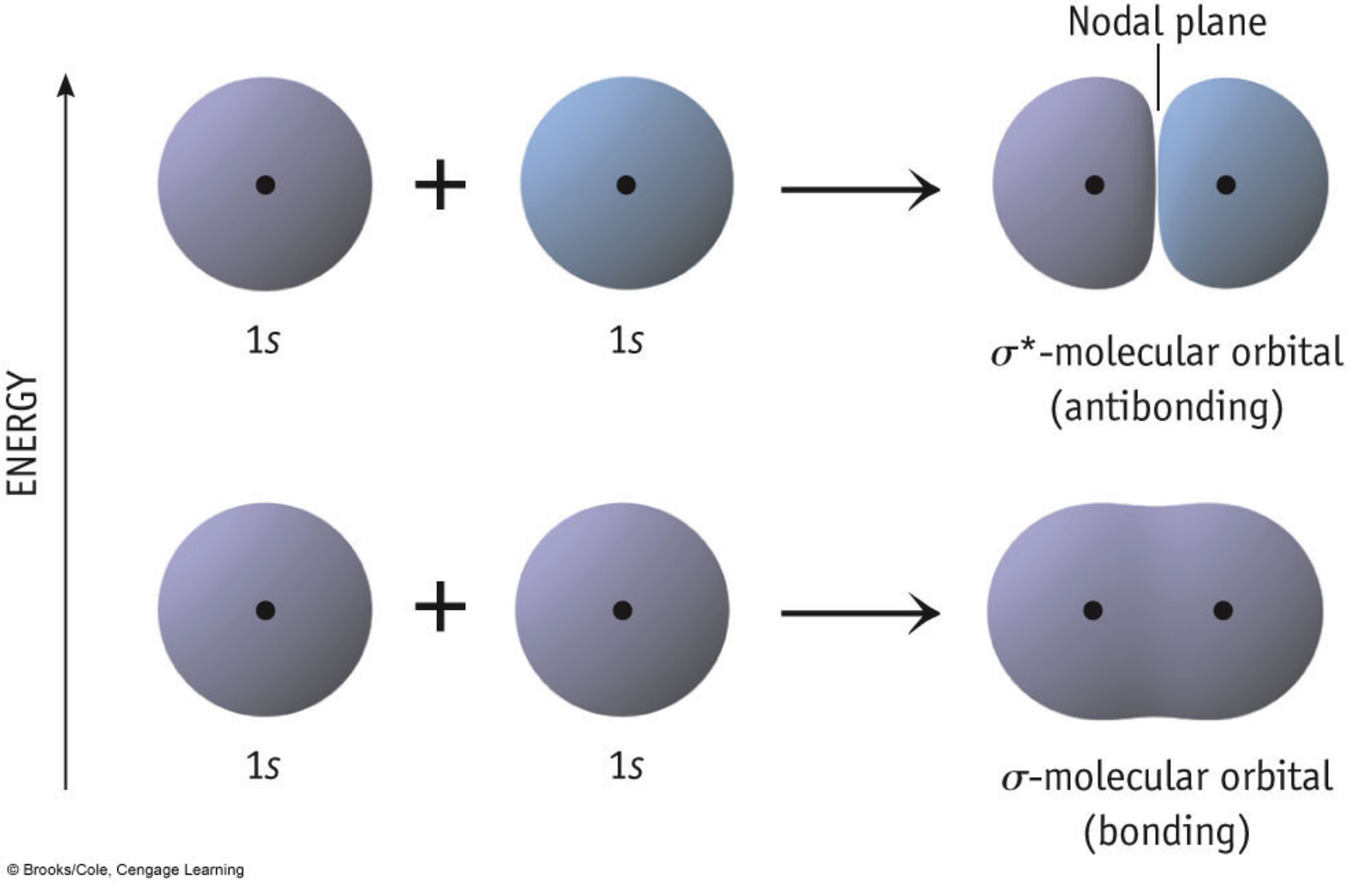
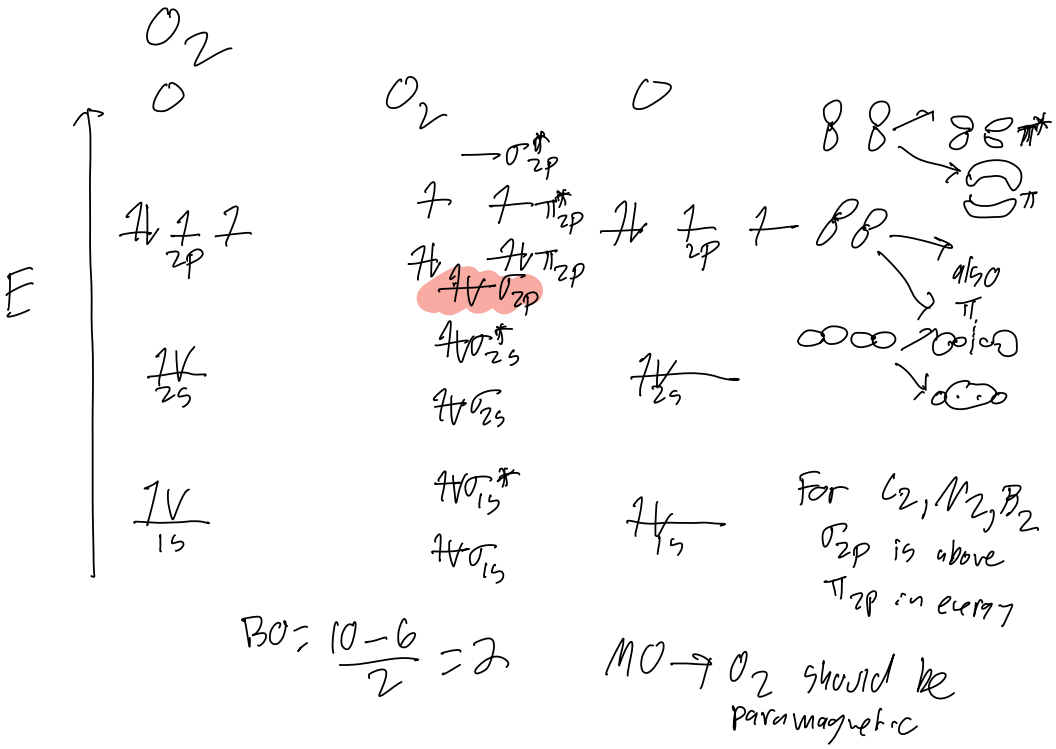


Fig. 9-16, p. 424

When you have a bunch of AOs, make pairs of MOs from pairs of AOs that are similar in energy



BO: $\frac{10-6}{2} = 2$ MO → O_2 should be paramagnetic

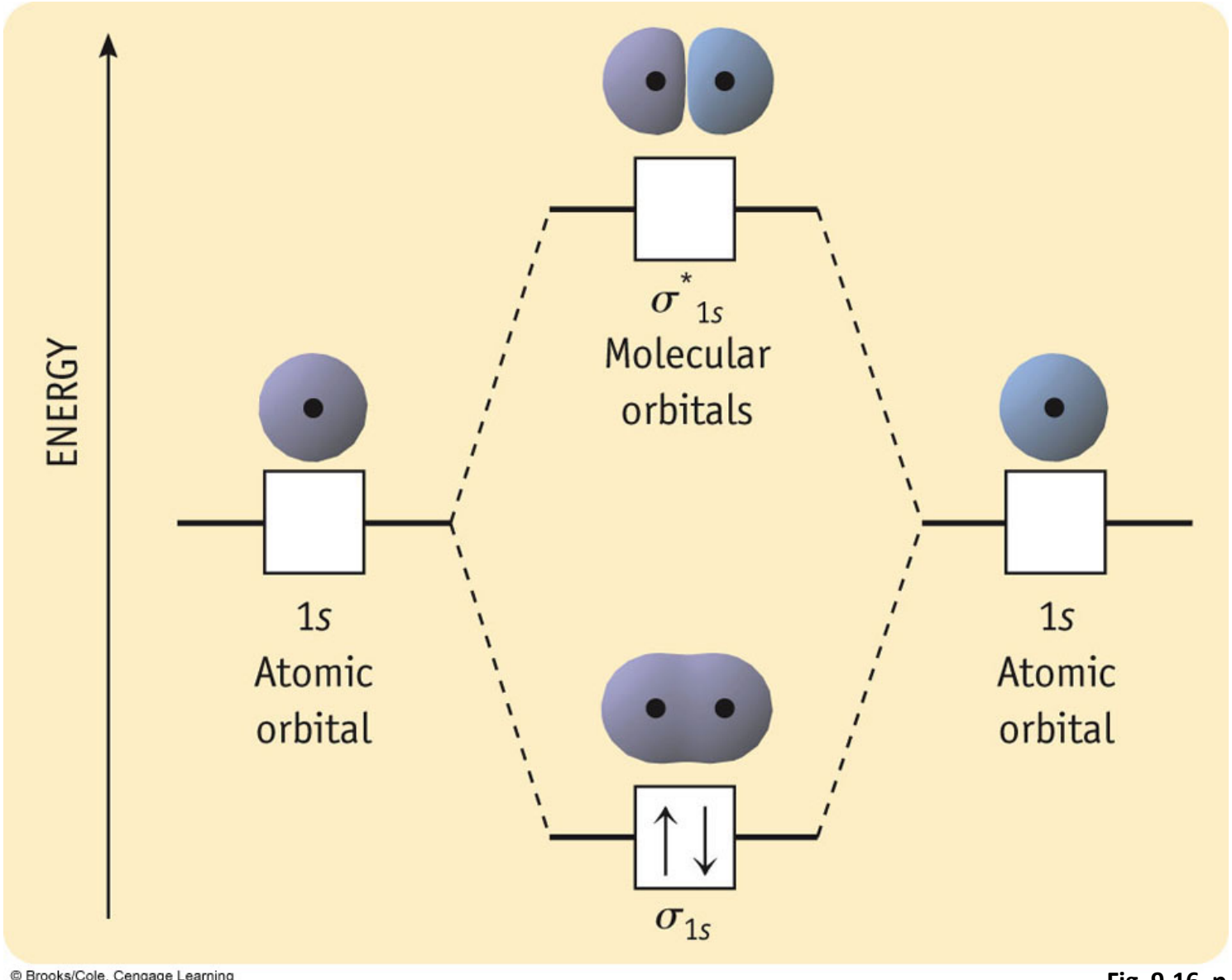


Fig. 9-16, p. 424

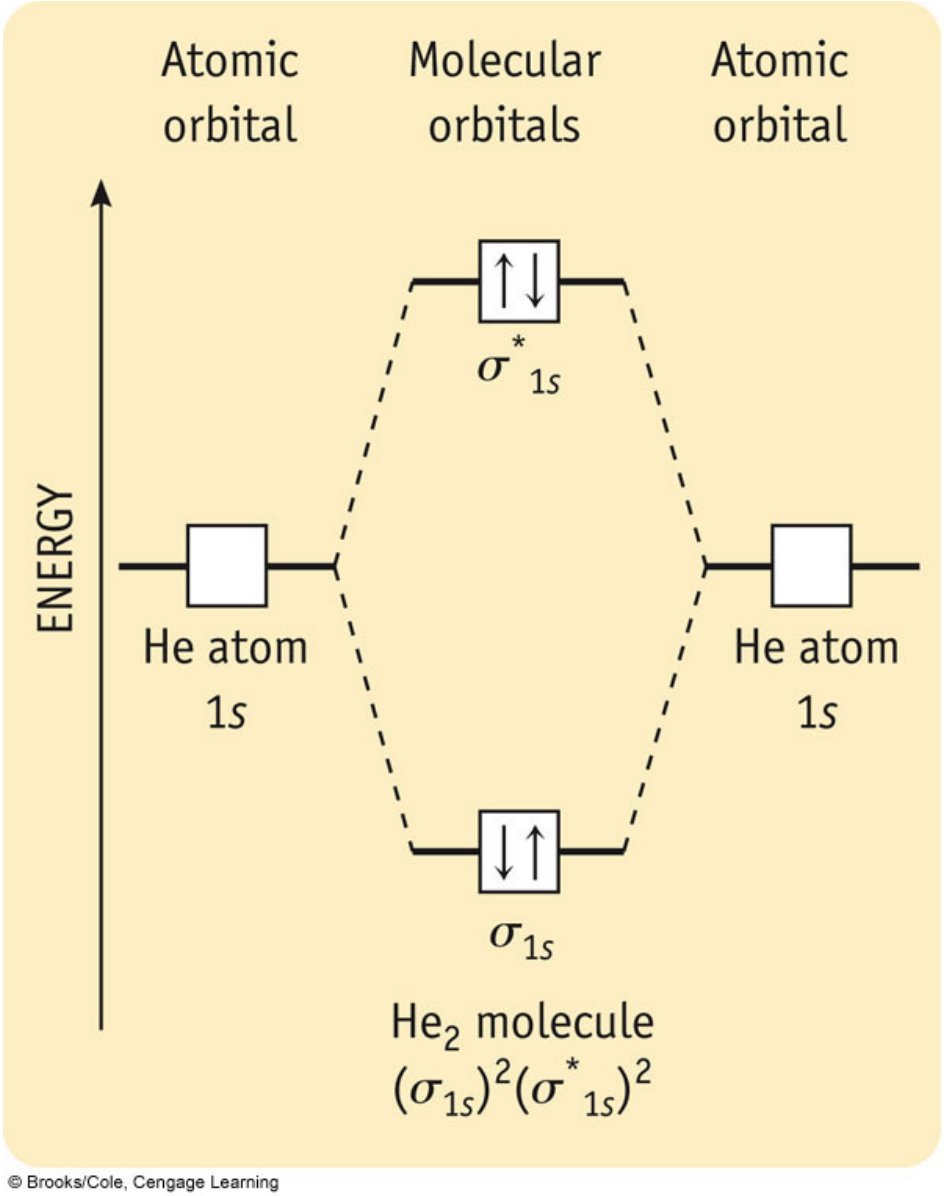


Fig. 9-17, p. 424

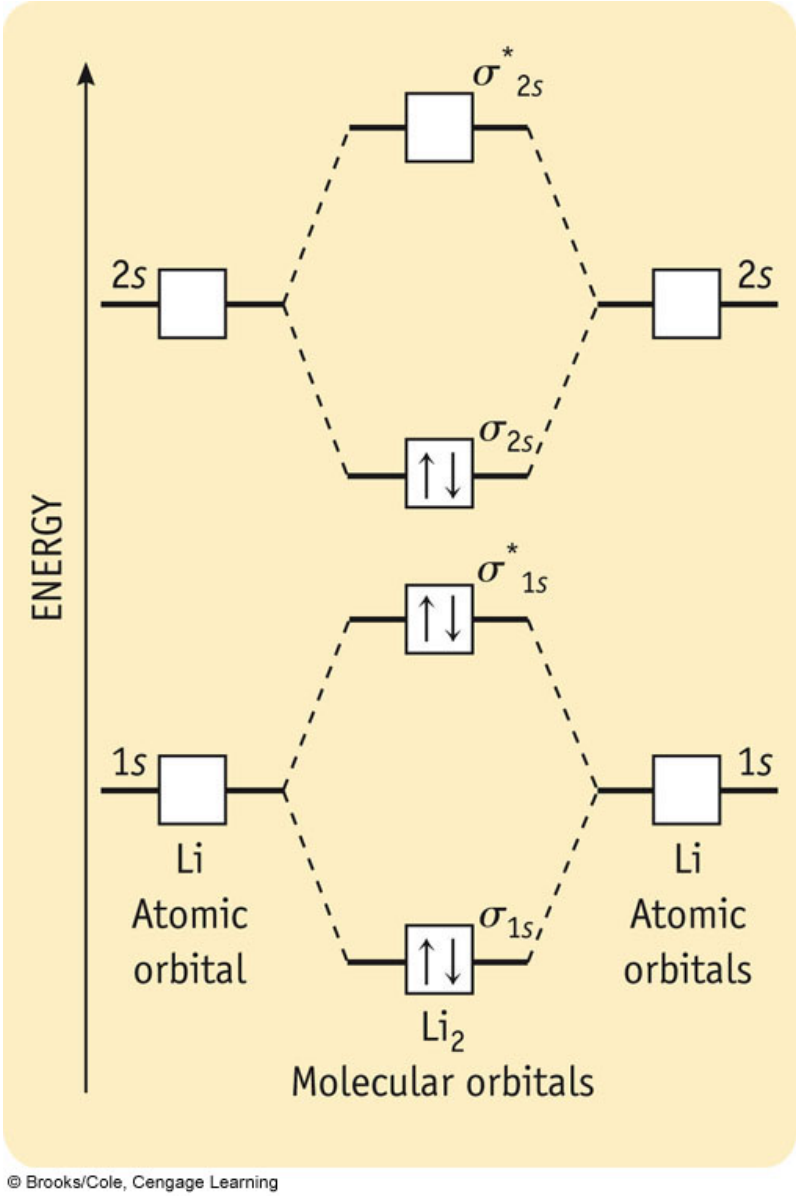


Fig. 9-18, p. 425

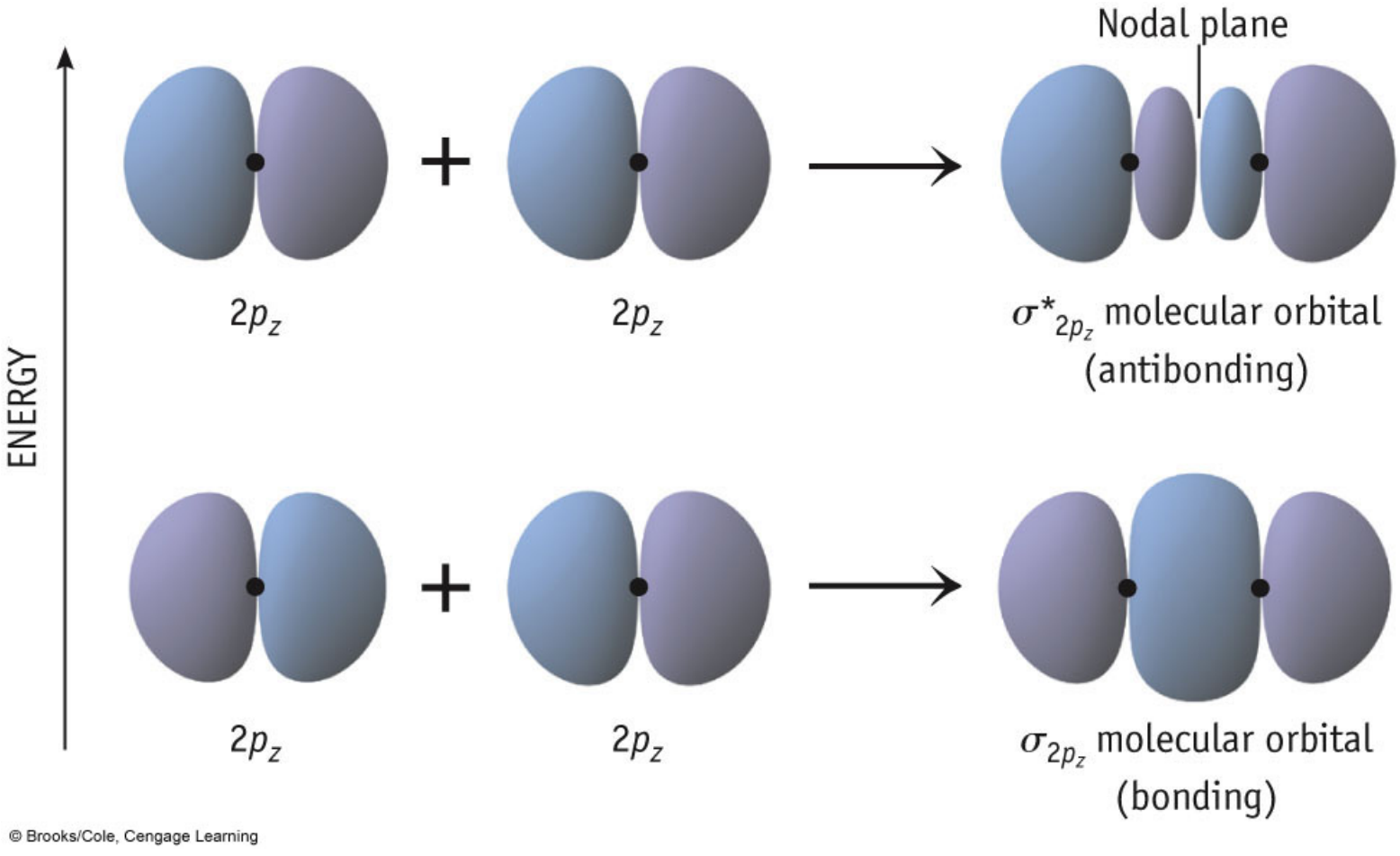


Fig. 9-19, p. 426

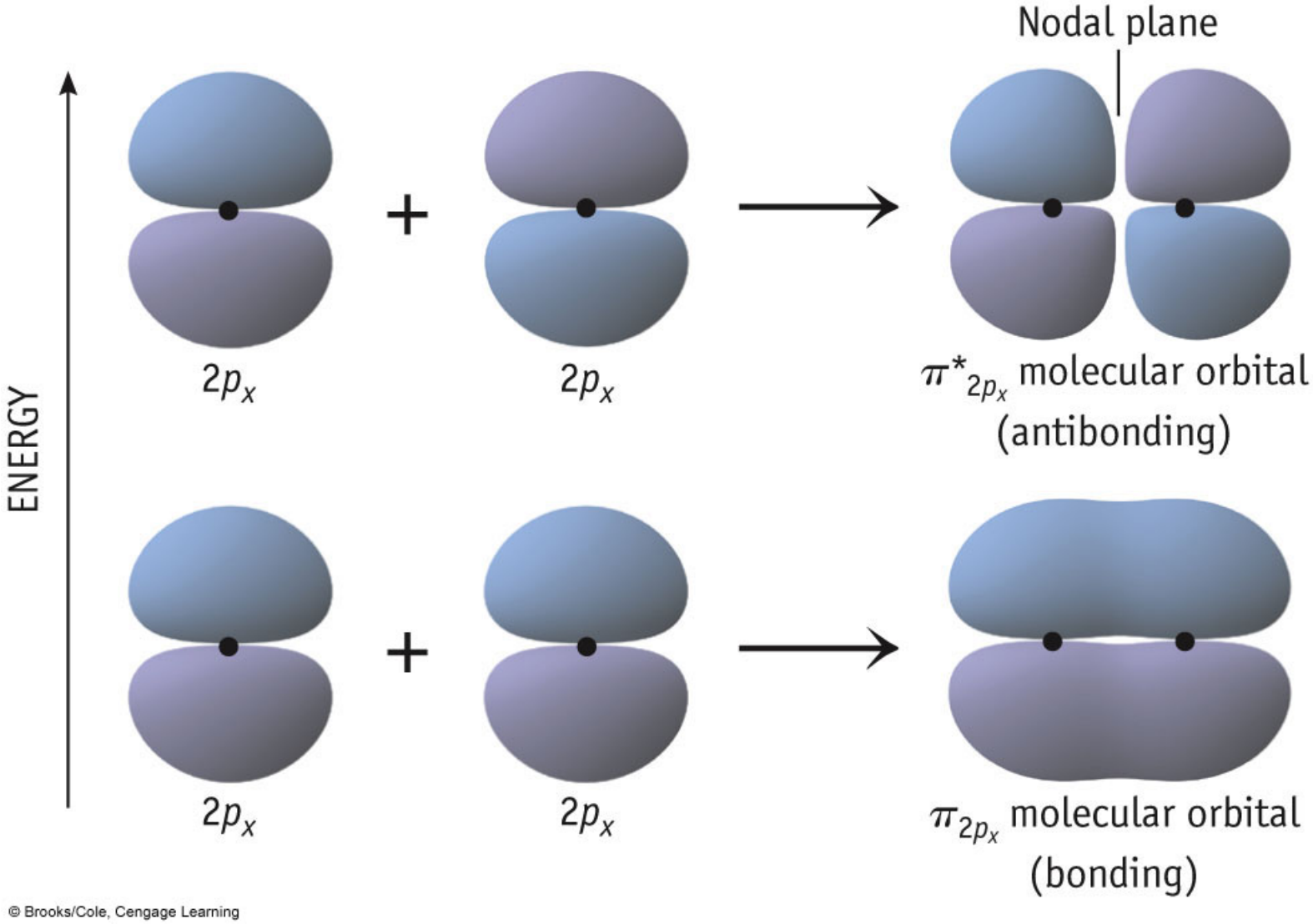


Fig. 9-20, p. 427

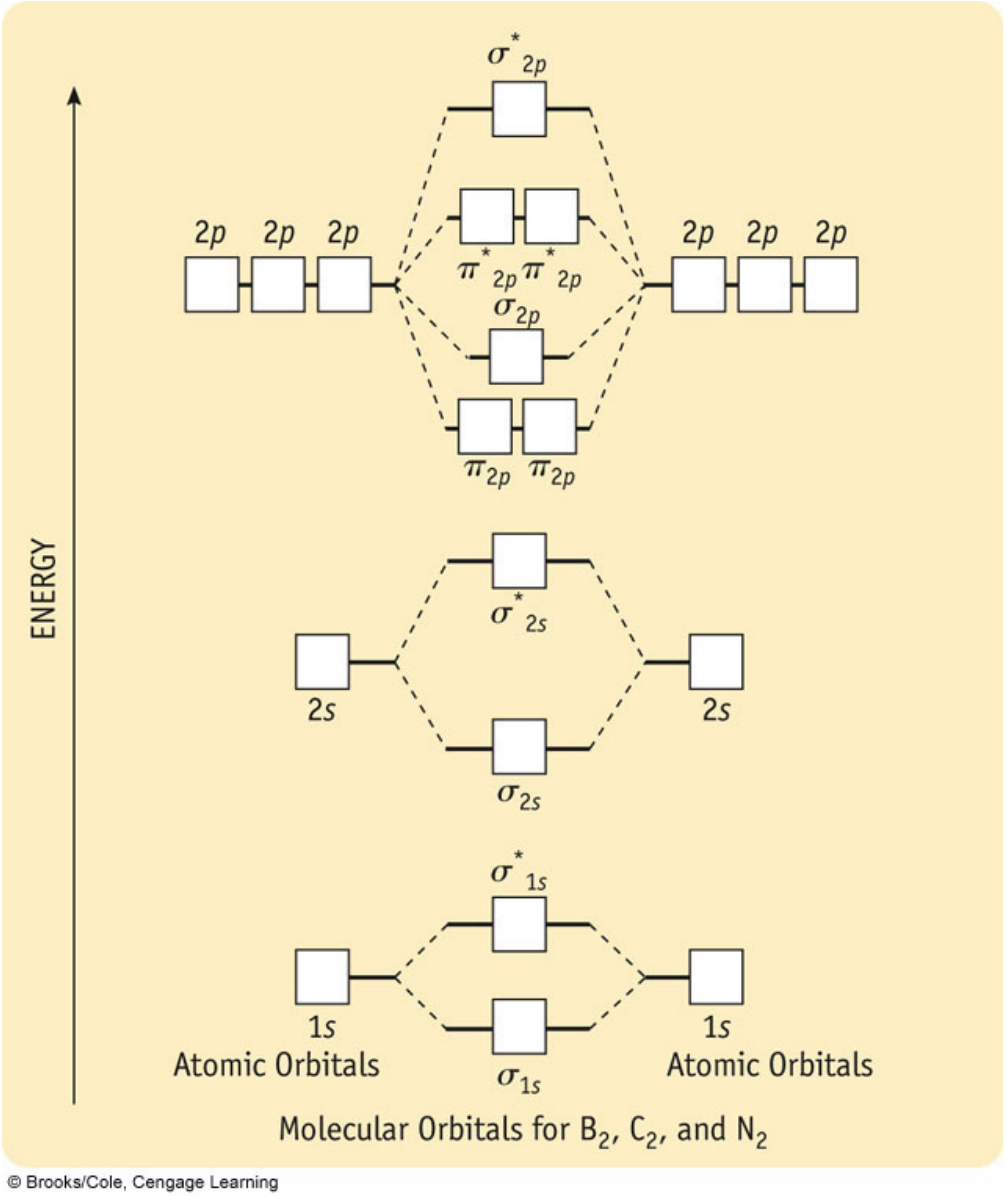


Fig. 9-21a, p. 427

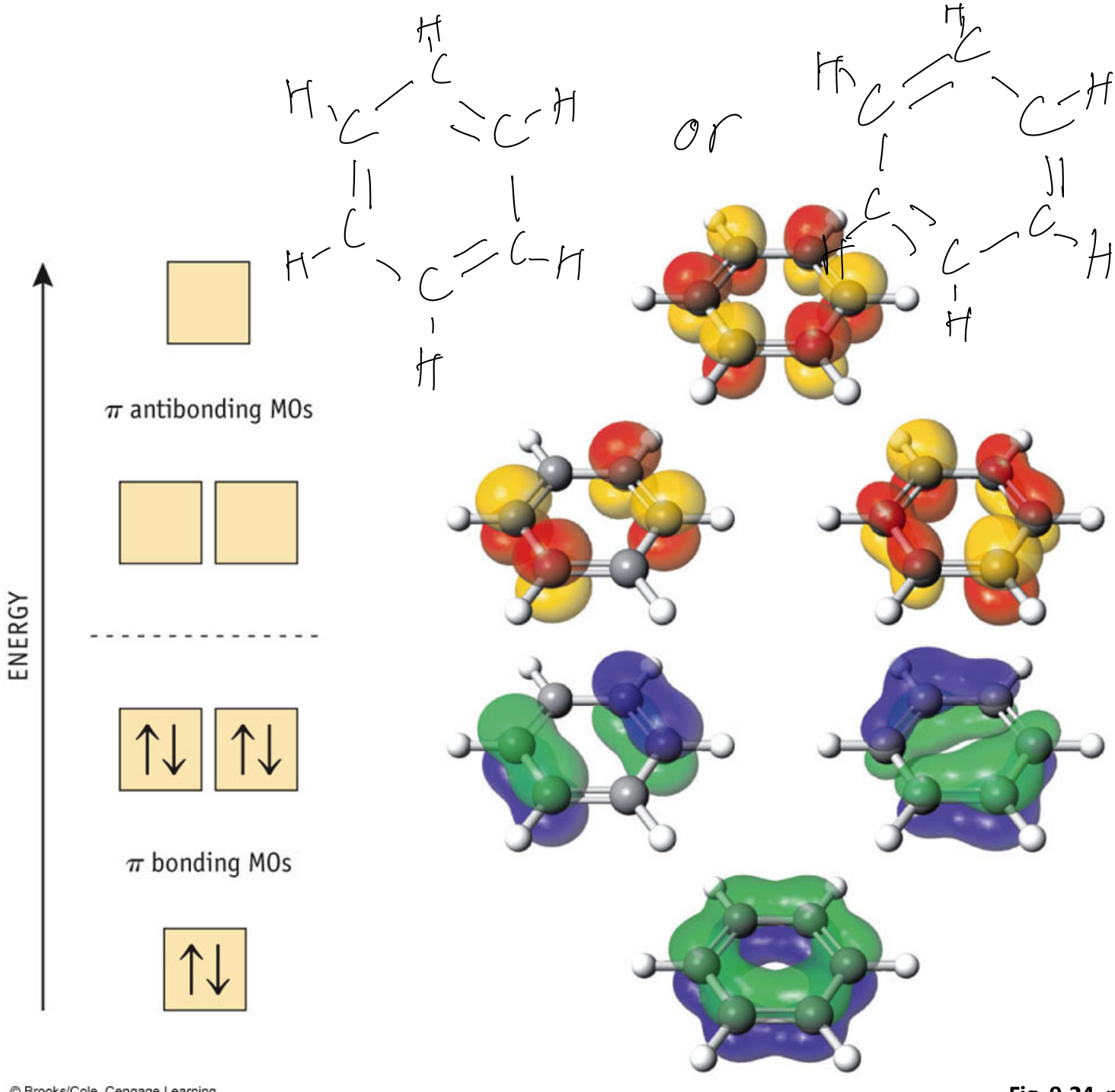


Fig. 9-24, p. 432

Use 6 unhyb p orbitals on 6 C atoms → 6 MOs