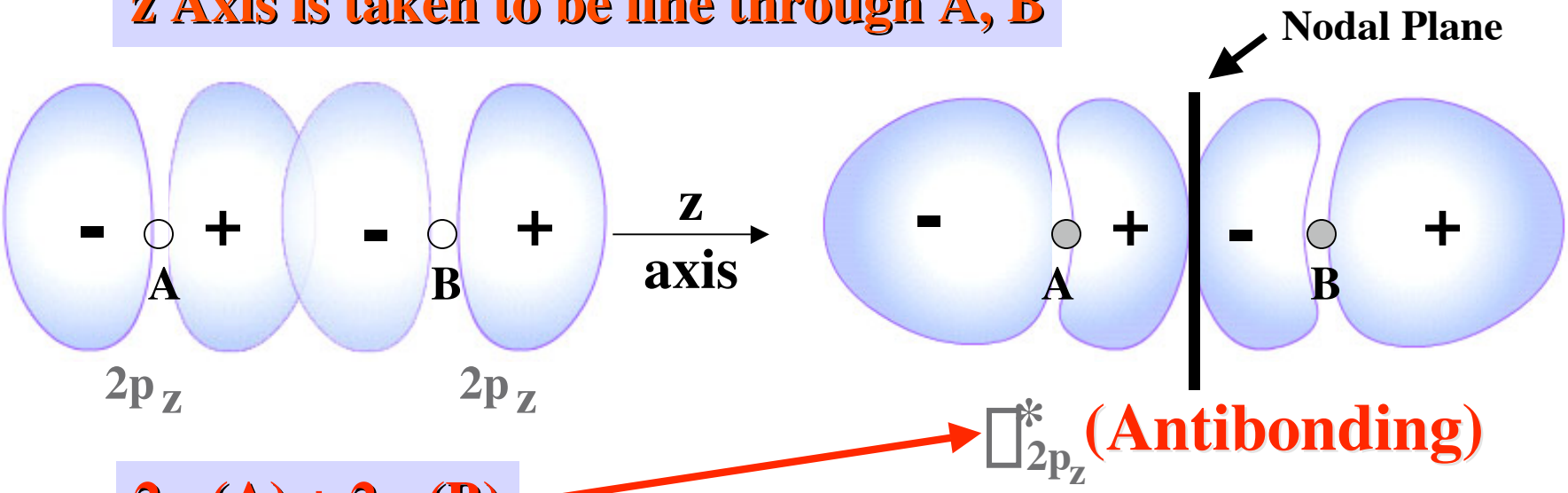
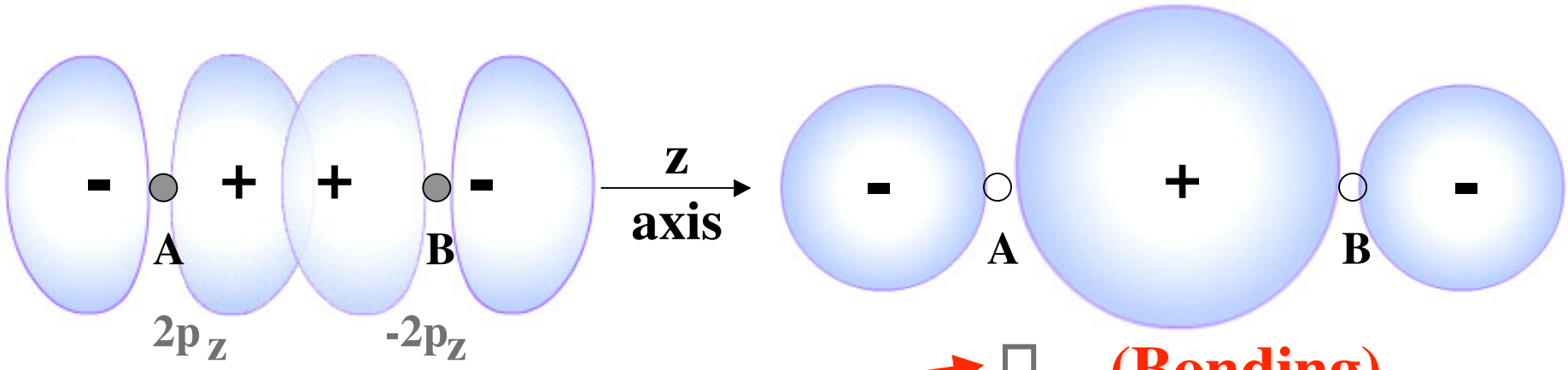
z Axis is taken to be line through A, B



$2p_z(A) + 2p_z(B)$ → $\pi^*_{2p_z}$ (Antibonding)



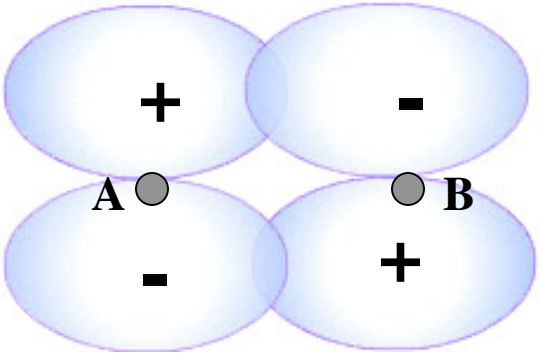
$2p_z(A) - 2p_z(B)$ → π_{2p_z} (Bonding)

Atomic Orbitals of Atoms A,B

Molecular Orbitals

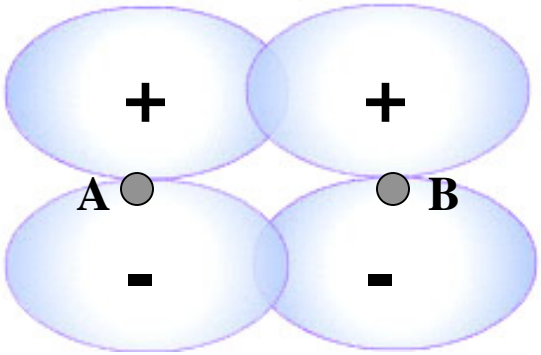
Bonding with 2p Orbitals

Note: orbital is □ to bond (z) axis



$2p_x$ $-2p_x$

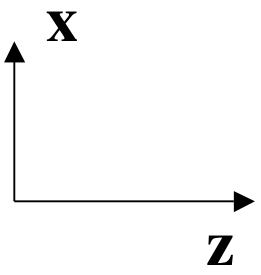
$2p_x(A) - 2p_x(B)$

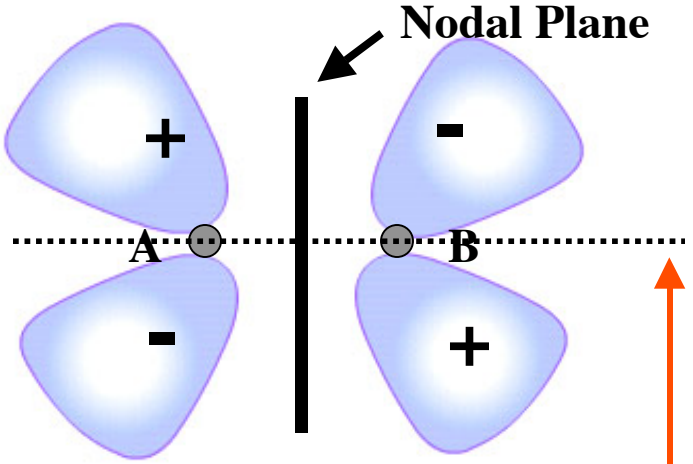


$2p_x$ $2p_x$

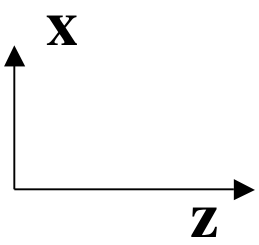
$2p_x(A) + 2p_x(B)$

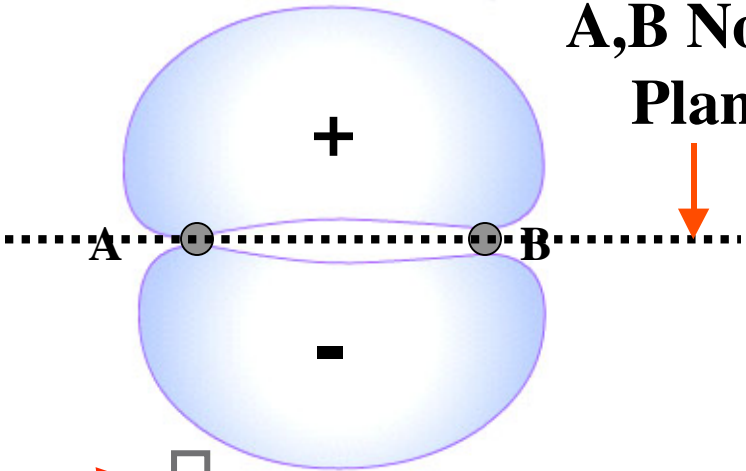
Atomic Orbitals of Atoms A,B





□*$_{2p}$ (antibonding)





A,B Nodal Plane

□$_{2p}$ (bonding)

Molecular Orbitals

Bonding with 2p Orbitals (cont)

Notational Detail

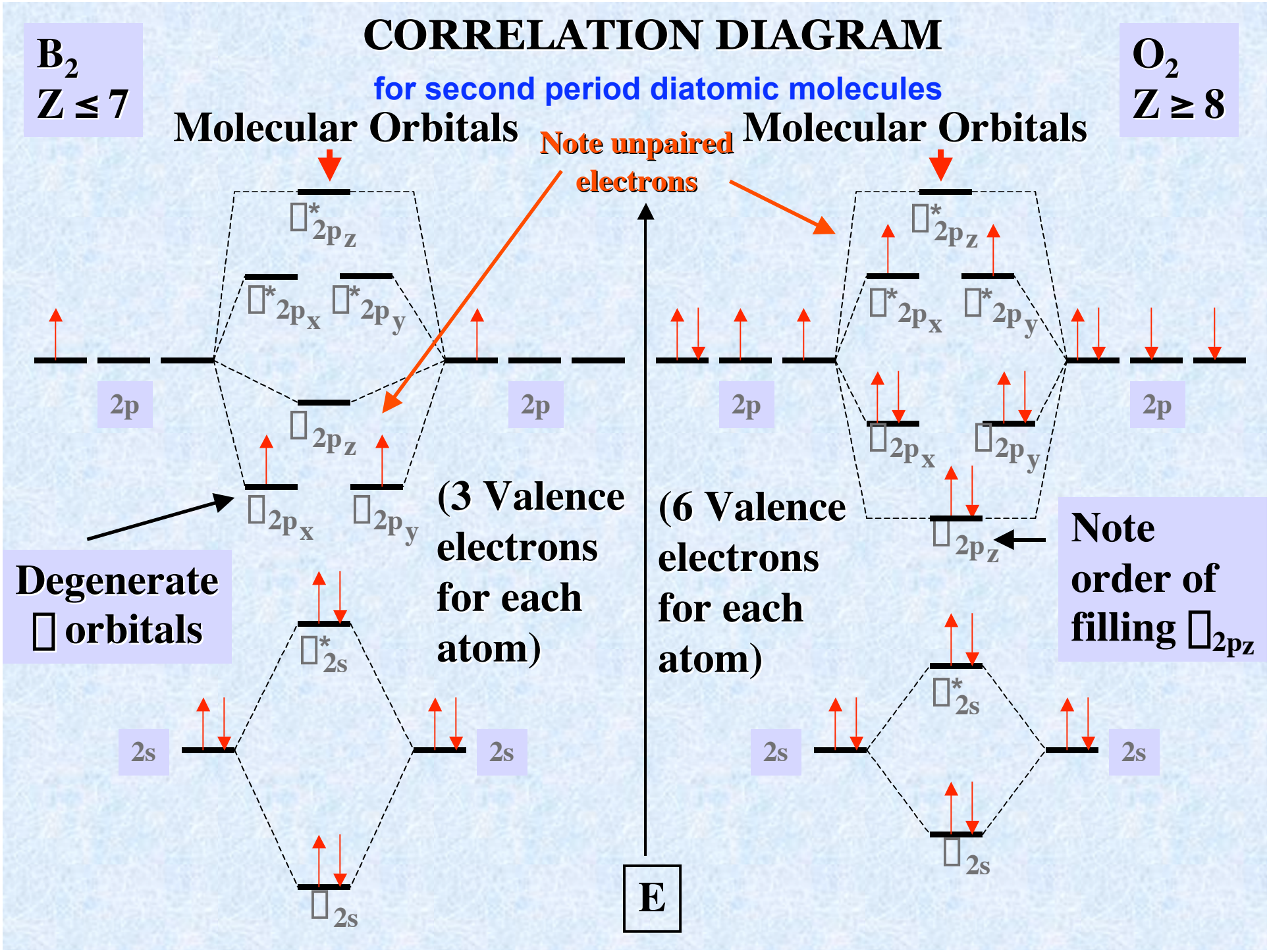
Oxtoby uses two different notations for orbitals in the 4th and 5th editions of the class text:

π_{2pz} in the 4th edition becomes π_{g2pz} in the 5th edition

π_{2pz}^* in the 4th edition becomes π_{u2pz}^* in the 5th edition

π_{2px} in the 4th edition becomes π_{u2px} in the 5th edition

π_{2px}^* in the 4th edition becomes π_{g2px}^* in the 5th edition


CORRELATION DIAGRAM
for second period diatomic molecules
B2
Z ≤ 7
O2
Z ≥ 8
Molecular Orbitals
Molecular Orbitals
Note unpaired electrons
2p
2p
2p
2p
2s
2s
2s
2s
(3 Valence electrons for each atom)
(6 Valence electrons for each atom)
Degenerate π orbitals
Note order of filling π2pz
E

Molecular Orbitals of Homonuclear Diatomic Molecules

Mole-cule	# Valence Electrons	Valence Electron Configuration	Bond Order	Bond Length (Å)	Bond Energy (kJ/mole)
H_2	2	$(\sigma_{1s})^2$	1	0.74	431
He_2	4	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	52	.000008
Li_2	2	$(\sigma_{2s})^2$	1	2.67	105
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	289
C_2	8	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$	2	1.24	599
N_2	10	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p_z})^2$	3	1.10	942
O_2	12	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^2$ ↑ ↑	2	1.21	494
F_2	14	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^4$	1	1.41	154
Ne_2	16	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p_z}^*)^2$	0	-	-

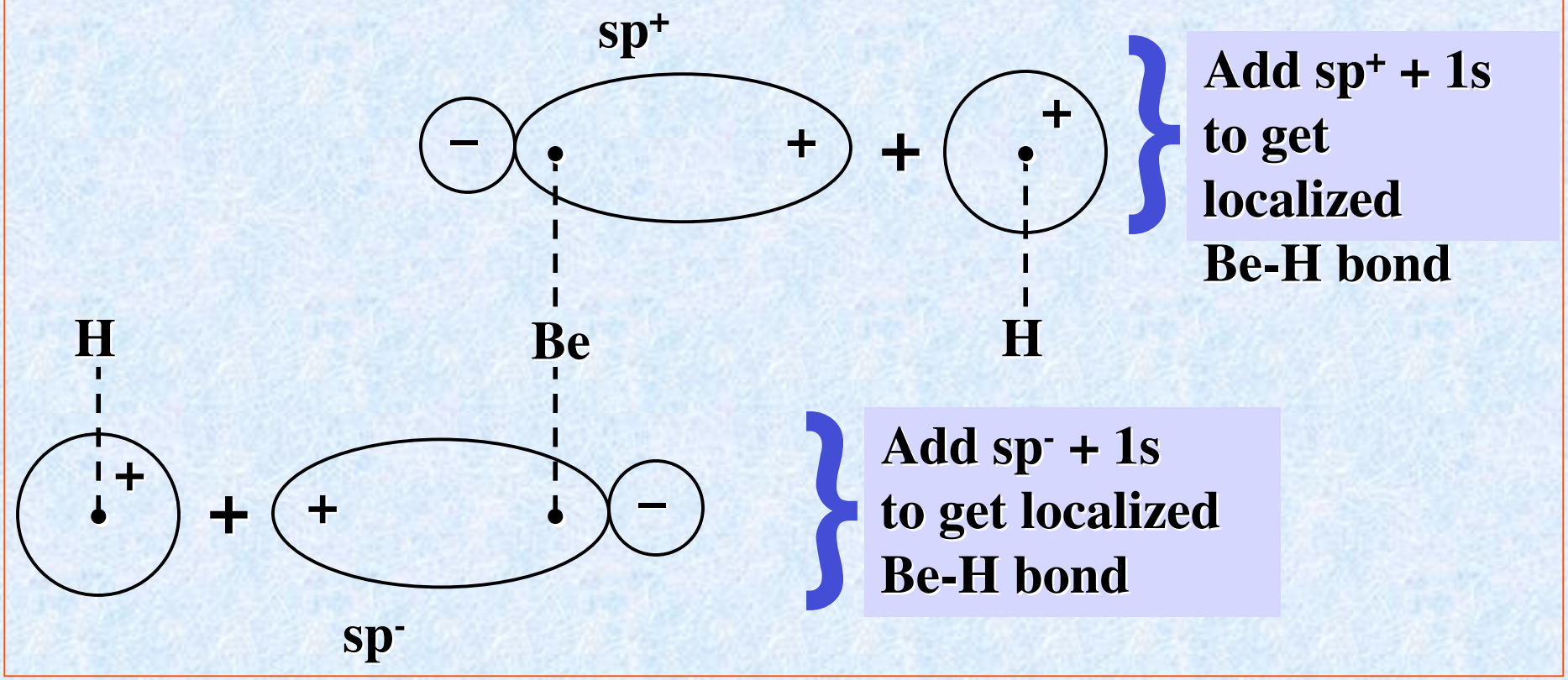
Bonding in Polyatomic Molecules

Basically two ways to approach polyatomics.

First is to use delocalized M.O.'s where e^- are not confined to a single bond (region between 2 atoms) but can wander over 3 or more atoms. We will use this approach later for C bonding.

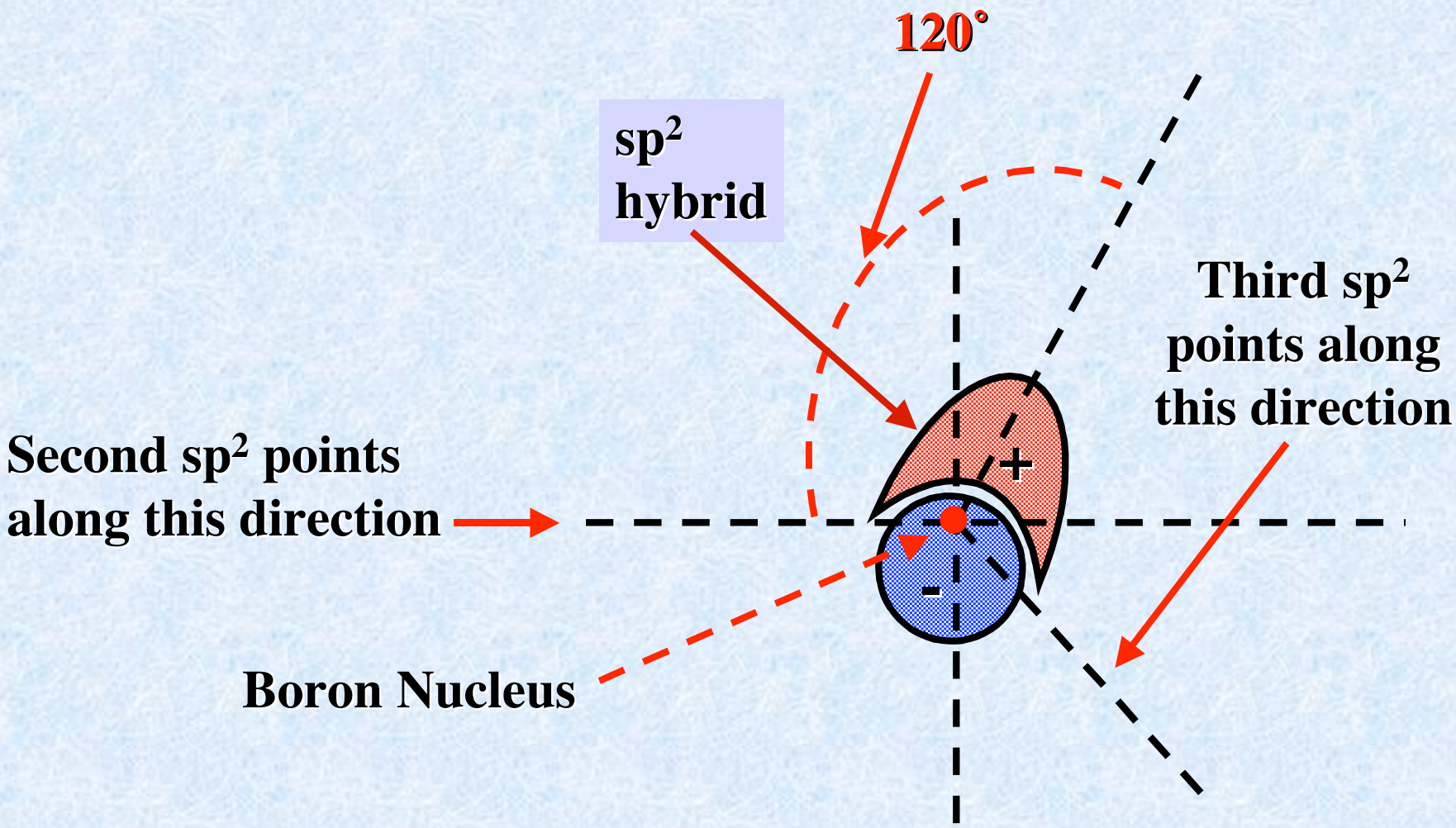
Second is to use hybridization of atomic orbitals and then use these to form localized (usually) bonds.

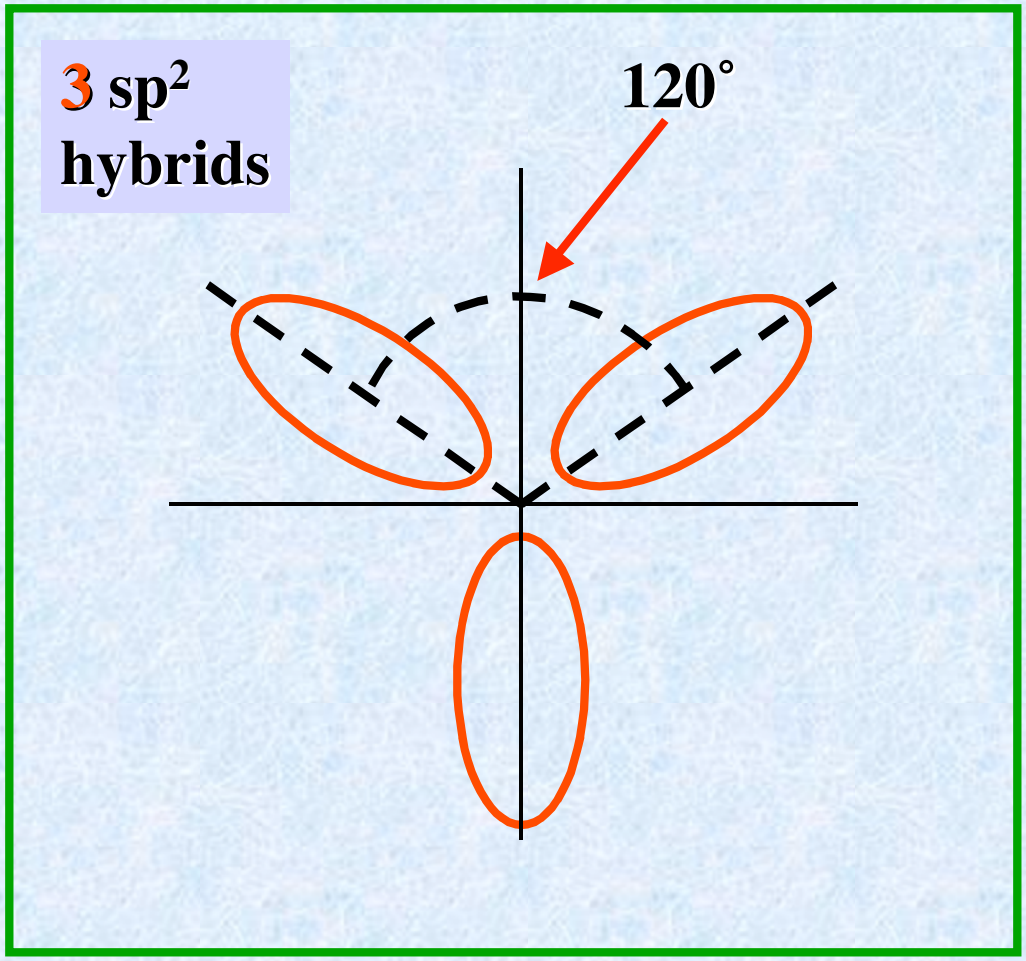
Localized BeH_2 orbitals:



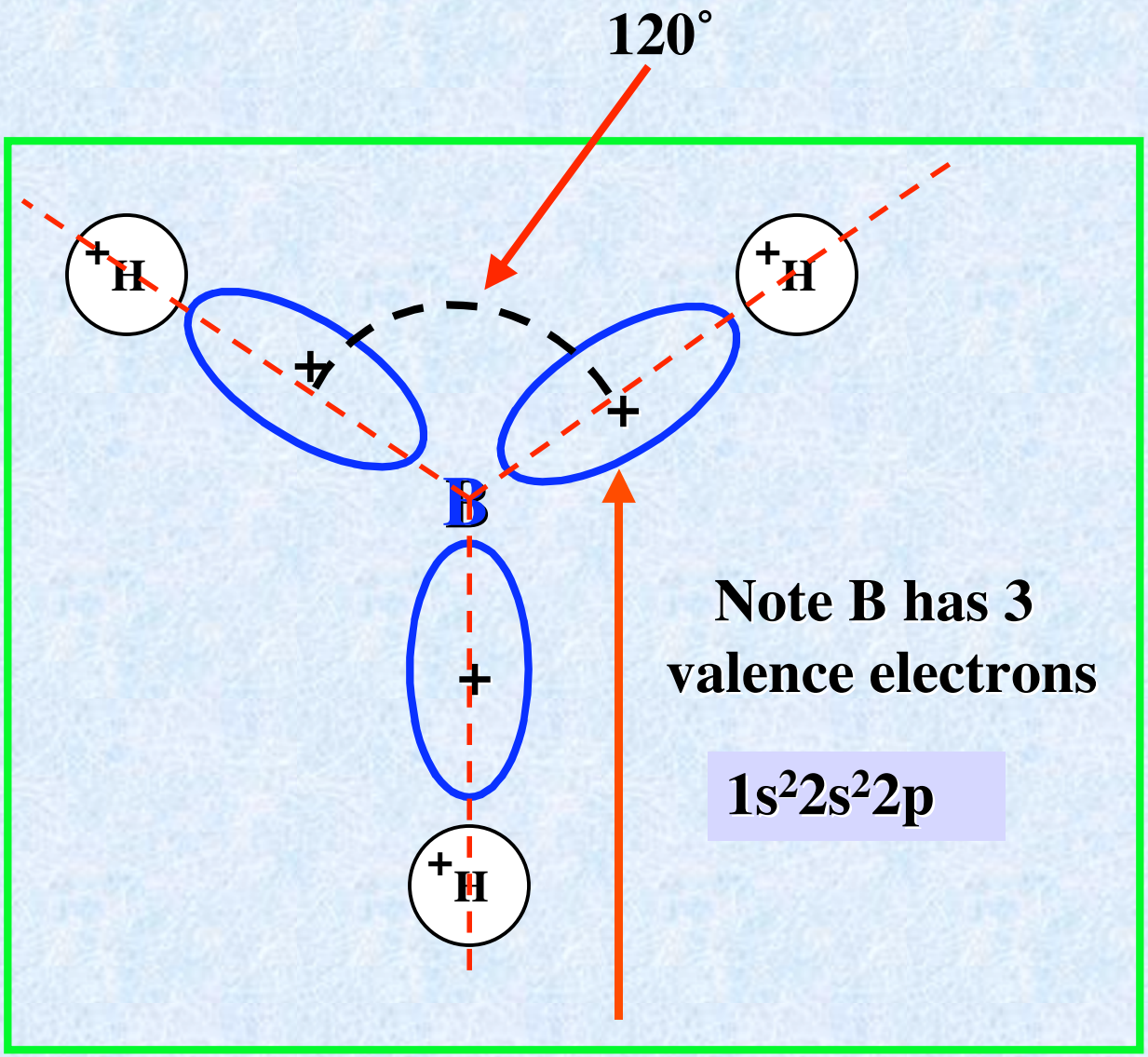
H 1s + (sp^-) **and** **H 1s + (sp^+)**

BH_3 Fragment:




3 sp2 hybrids
120˚

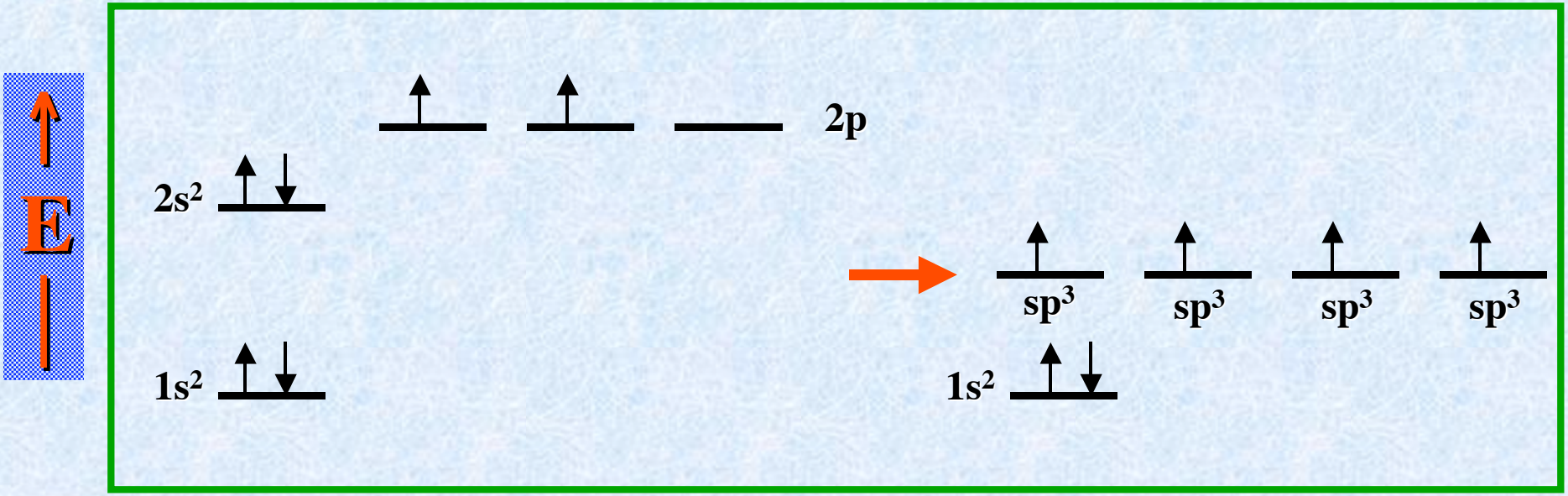
Overlap with H 1s to give 3 B-H bonds in a plane pointing at 120° with respect to each other: BH_3



$2s + 2p_x + 2p_y + 2p_z \equiv sp^3$ gives 4 hybrid orbitals which point to the corners of a tetrahedron. Angle between is 109º28'

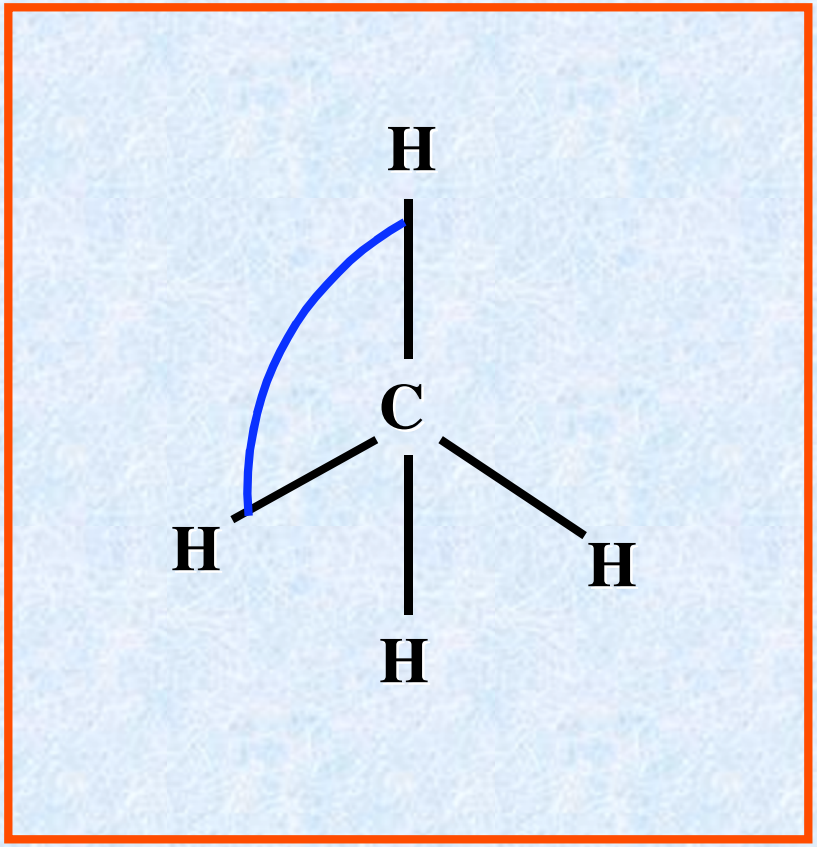
sp^3 [1/4 s, 3/4 p]. Tetrahedral hybrids.

4 H atoms have 4 x 1s 4 valence e^-


E
2p
2s²
1s²
sp³
sp³
sp³
sp³
1s²

Geometry of carbon sp^3/H 1s Bonds in methane (CH_4):

sp^3 hybridization on C leads to 4 bonds. CH_4 is a good example.



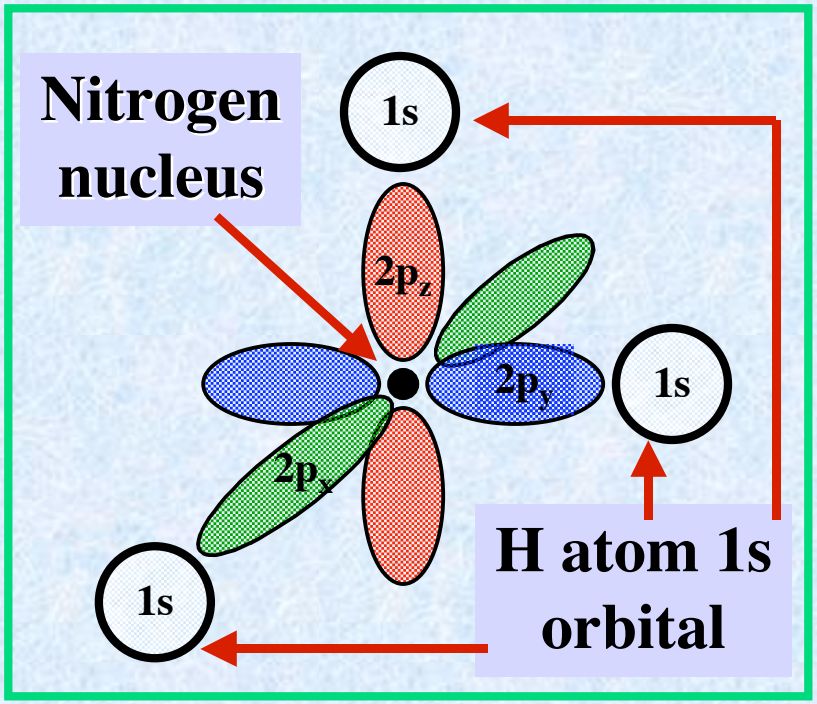
Summary of Hybridization Results

Example	Groups Attached to Center Atom	Hybrid	Geometry
BeH_2	2	sp	linear H-Be-H
BH_3	3	sp^2	trig. plane (120° H-B-H angle)
CH_4	4	sp^3	tetrahedral (109°28' H-C-H angles)

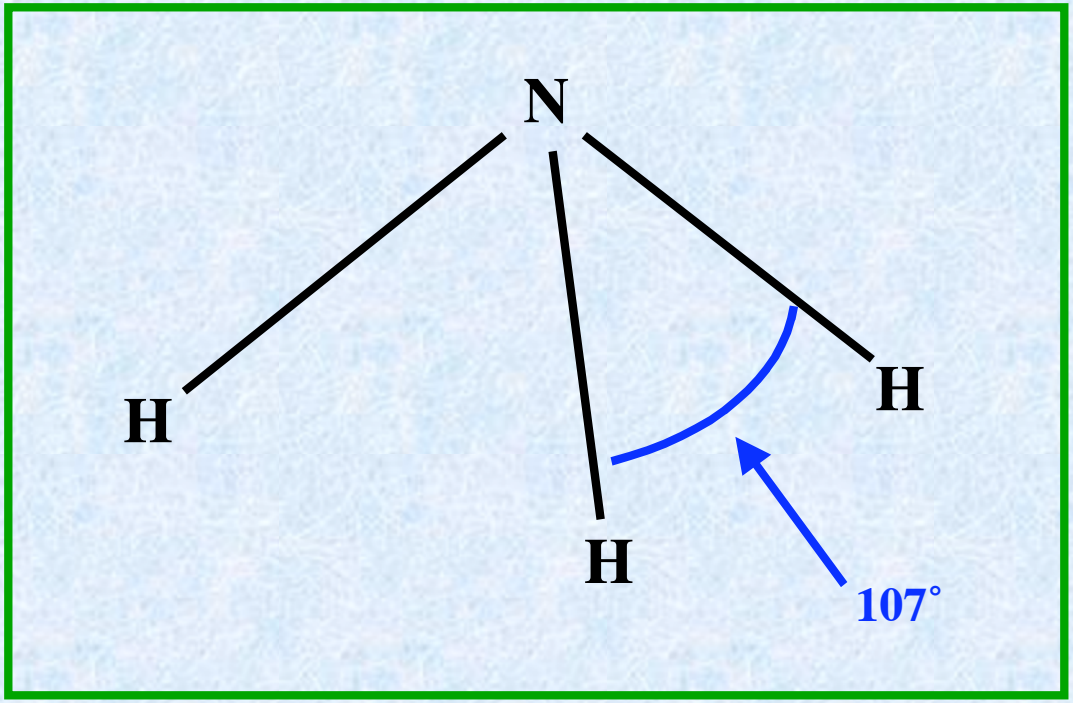
Localized Bonds and Lone Pair Electrons

NH_3 3H, 1s (no choice) N: $1s^2 2s^2 2p^3$

This predicts
90° geometry →



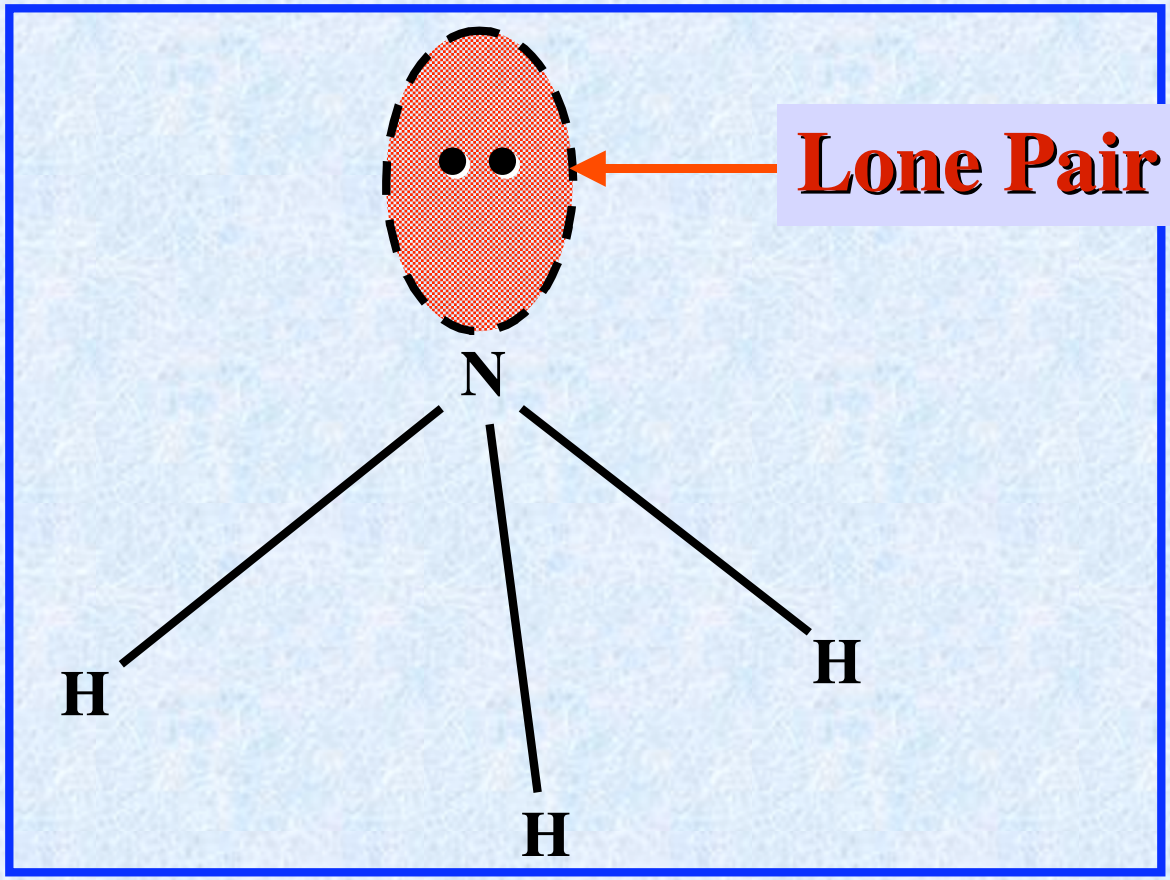
Geometry of NH_3 found to be Trigonal Pyramidal

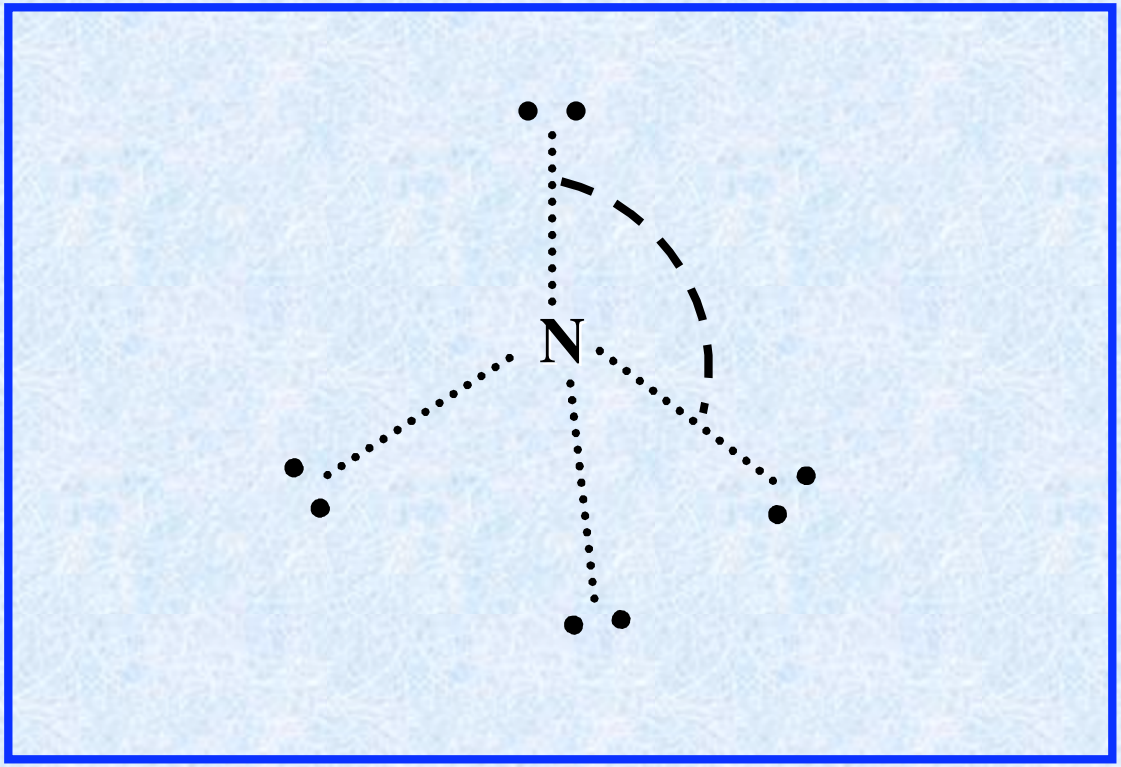


4 N sp^3 orbitals combine with 3 1s H orbitals to give 3 sp^3, 1s M.O.'s leaving one sp^3 hybrid left

Of 5 valence e^- in N, 2 go into one sp^3 orbital, 3 go into other 3 sp^3,s. (combined with H (1s))

One of the driving forces for the tetrahedral configuration is that it puts bonding and lone pair electron groups as far away from each other as possible.


Lone Pair
N
H
H
H



Electron pair repulsion effect is largest for small central atoms like B, N, O.

As go to larger central atoms (e.g. S or metals) frequently find this effect not so large and start to get things closer to pure p orbital bonds (90° structures)

For example, H_2S has H-S-H angle of 92°.

H_2O: 2H 1s ($2e^-$) O $1s^2 2s^2 2p^4$ (6 valence e^-)

4 sp^3 hybrids. Use 2 to make MO bonds with H 1s.

Predicts H-O-H bond of 109º28" - Find 105º