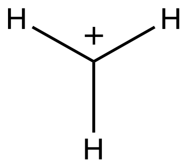
Pauling Electronegativities for Selected Elements

H 2.2						
Li 1.0	Be 1.6	B 1.8	C 2.5	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8						Br 3.0
						I 2.7

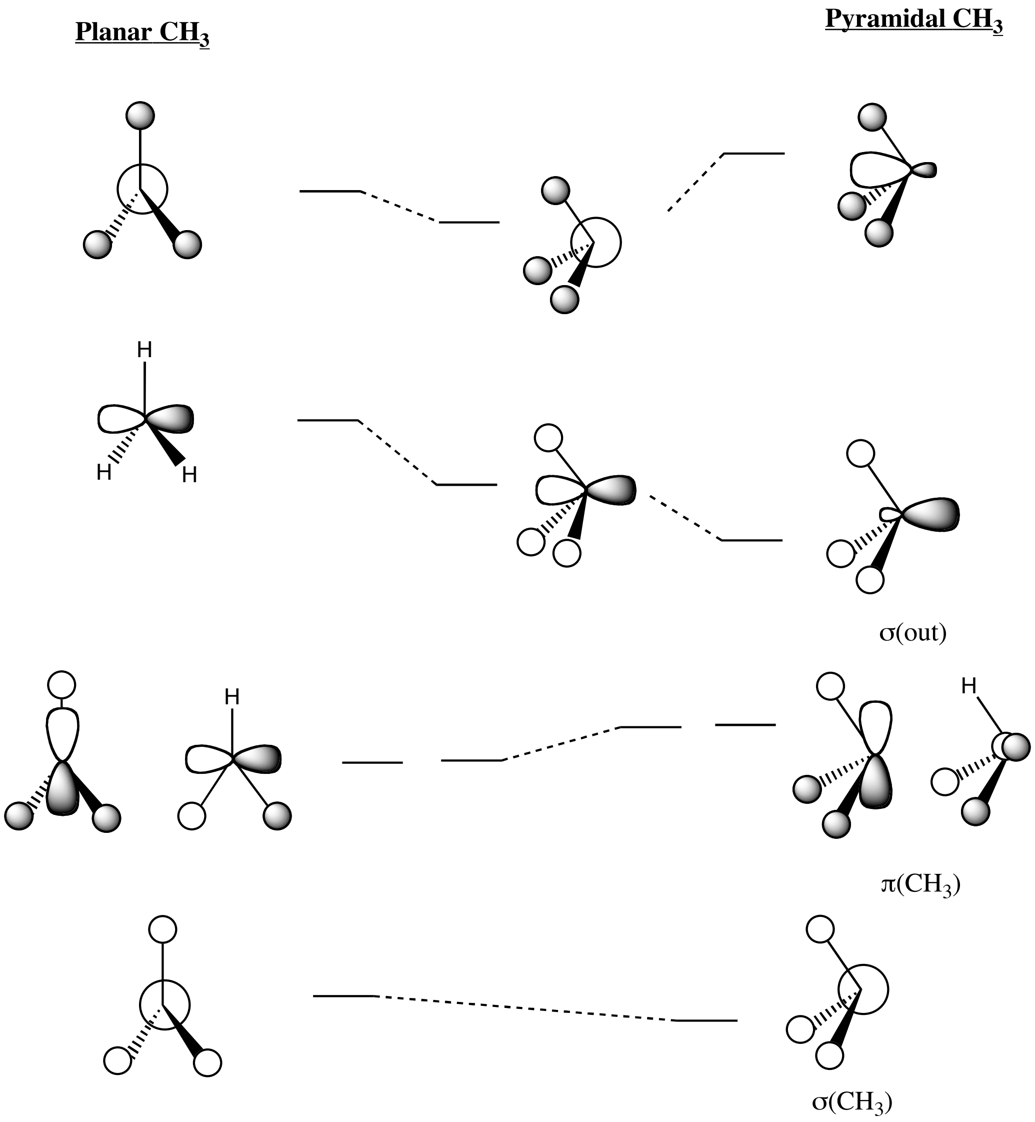


Valence electrons:
3 from H, 3, C. Total=6

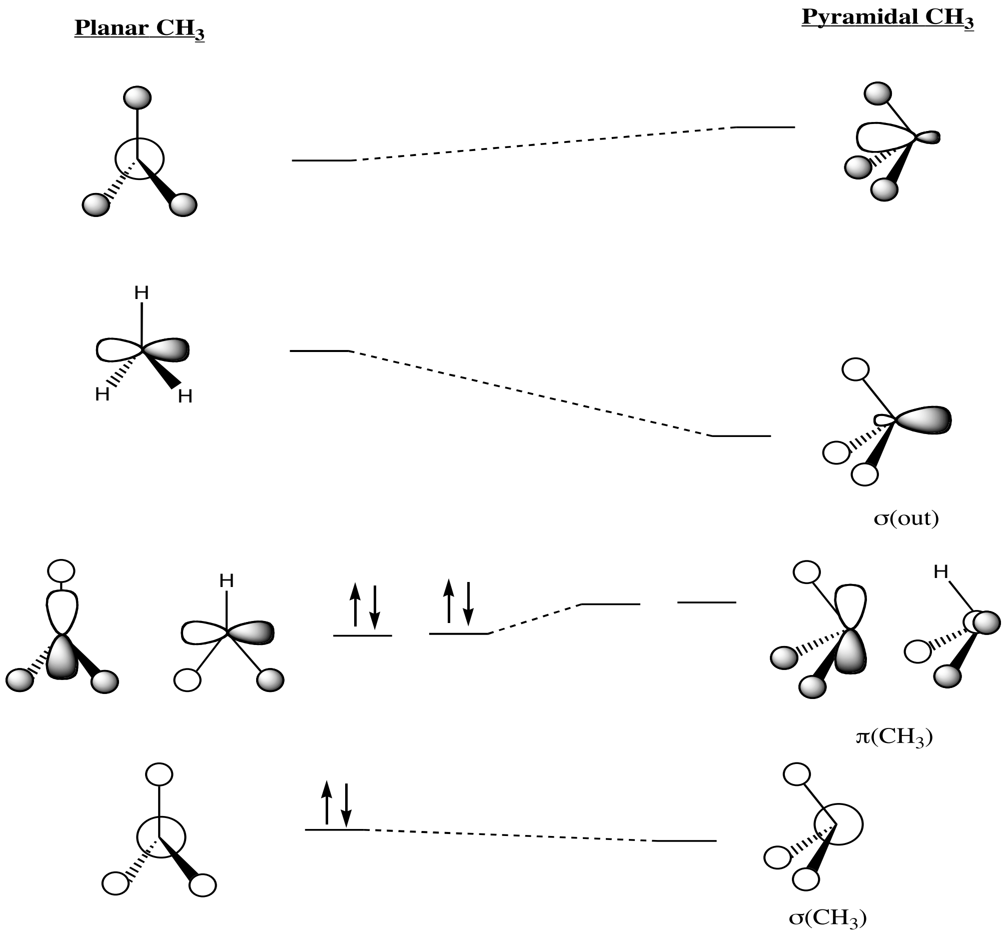
Atomic Orbitals

Energy		MO	C2s	C2px	C2py	C2pz	Hs	Hs	Hs
	↿⇂	Ψ_1	.7915	0	0	0	0.3528	0.3528	0.3528
	↿⇂	Ψ_2	0	.1431	.7466	0	0.0999	0.4012	–0.501
HOMO	↿⇂	Ψ_3	0	.7466	–.1431	0	0.5210	–.3470	–.1740
LUMO	—	Ψ_4	0	0	0	1	0	0	0
	—	Ψ_5	–.6111	0	0	0	0.4570	0.4570	0.4570
	—	Ψ_6	0	.5625	–.3251	0	–.5374	.5377	–0.0003
↓	—	Ψ_7	0	.3251	.5625	0	–.3106	–.3101	.6207

- sign of coefficient simply indicates the sign of the wavefunction (not + or - charge)
- electron density at carbon : $2(.7915)^2 + 2(.1431)^2 + 2(.7466)^2 + 2(.7466)^2 + 2(-.1431)^2 = 3.56$ electrons
- electron density at each H: $2(0.3528)^2 + 2(0.0999)^2 + 2(0.5210)^2 = 0.812$ electron


Planar CH$_3$
Pyramidal CH$_3$
H
H
H
σ(out)
H
H
π(CH$_3$)
σ(CH$_3$)

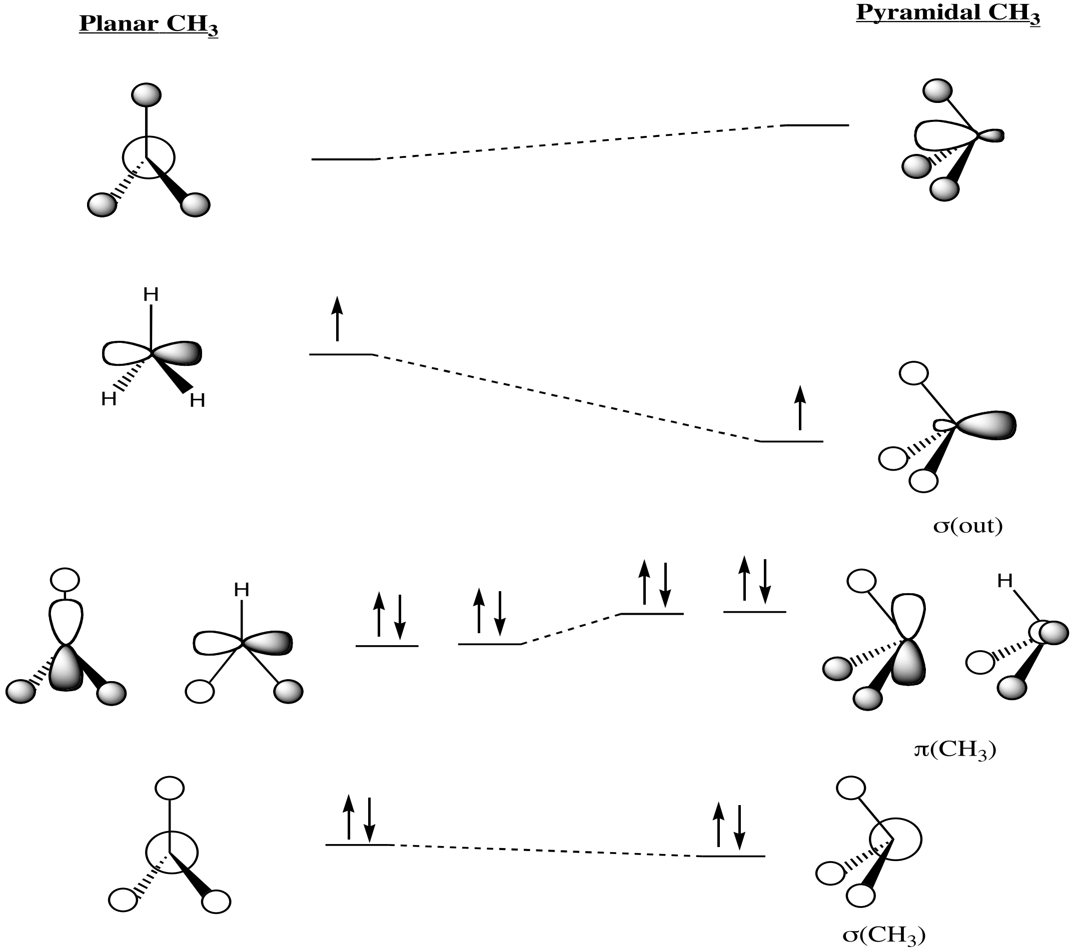
H_3C^+



3 electrons from H
3 valence electrons from C
6 electrons total

planar form is favored because of destabilization of π(CH_3)

$H_3C\bullet$



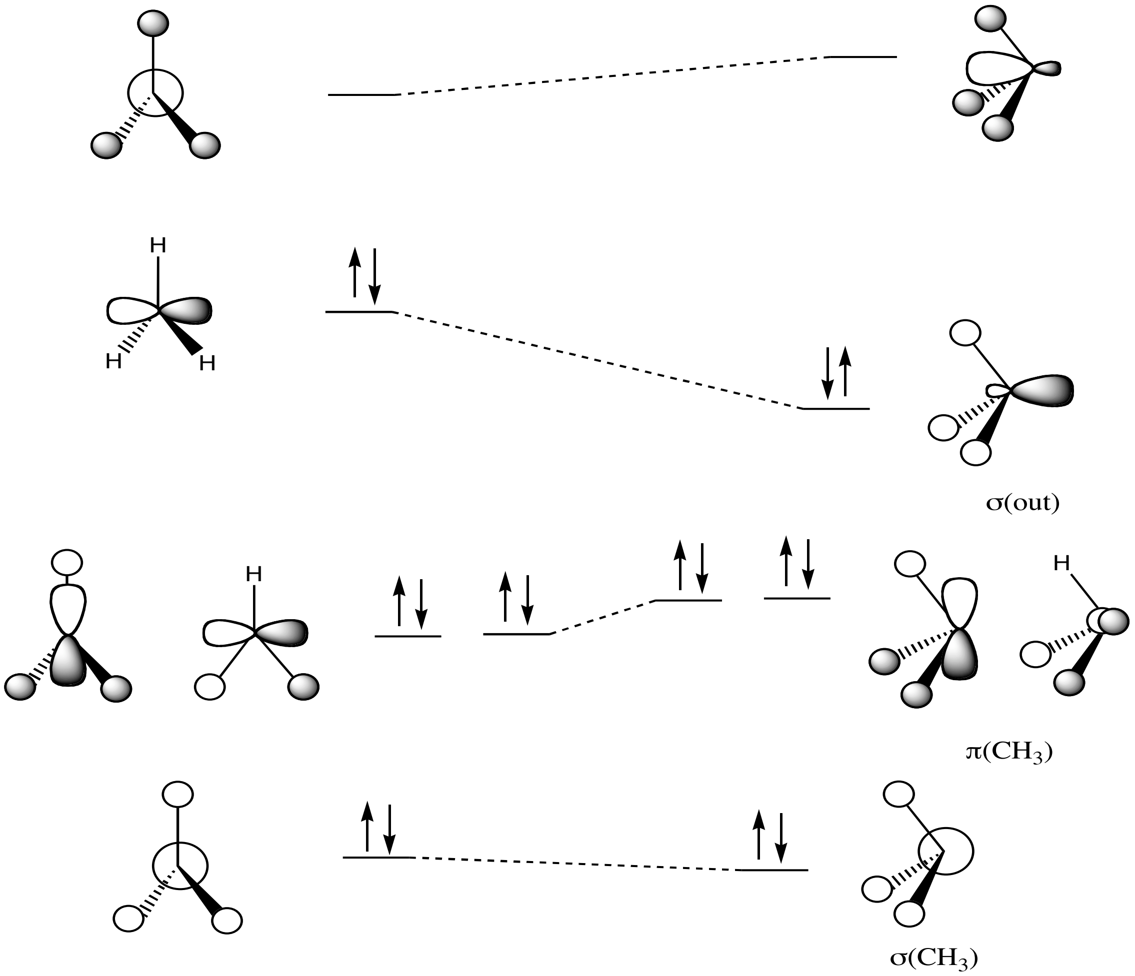
3 electrons from H
4 valence electrons from C
7 electrons total

Stabilization of σ(out) (singly occupied) is offset by destabilization of π(CH_3) (occupied by four electrons)

Methyl radical is planar, but there is a low barrier to pyrimidalization

$H_3C:^-$

Planar CH_3 **Pyramidal CH_3**

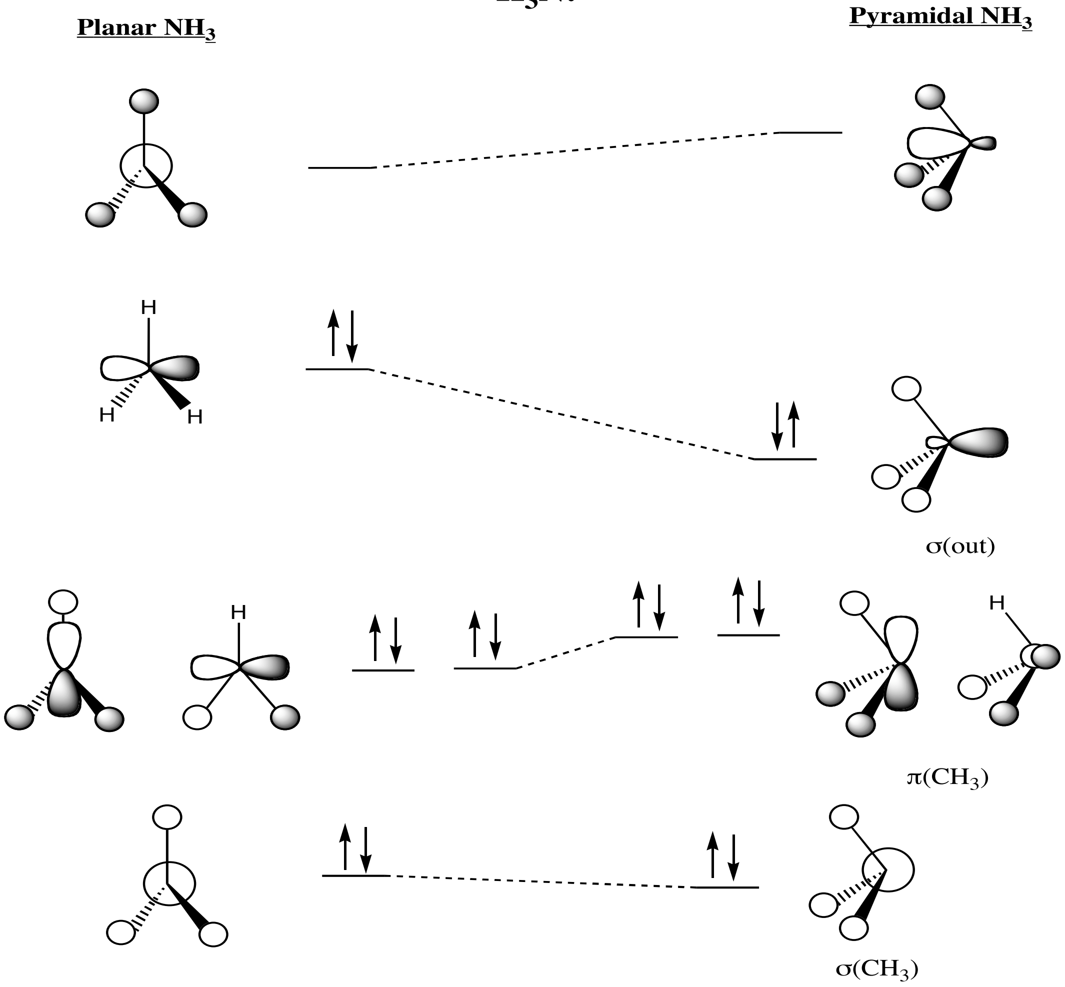


3 electrons from H
5 valence electrons from C
8 electrons total

Methyl anion is pyrimidal!

Stabilization of σ(out) (doubly occupied) offsets destabilization of π(CH_3) (occupied by four electrons)

H_3N:

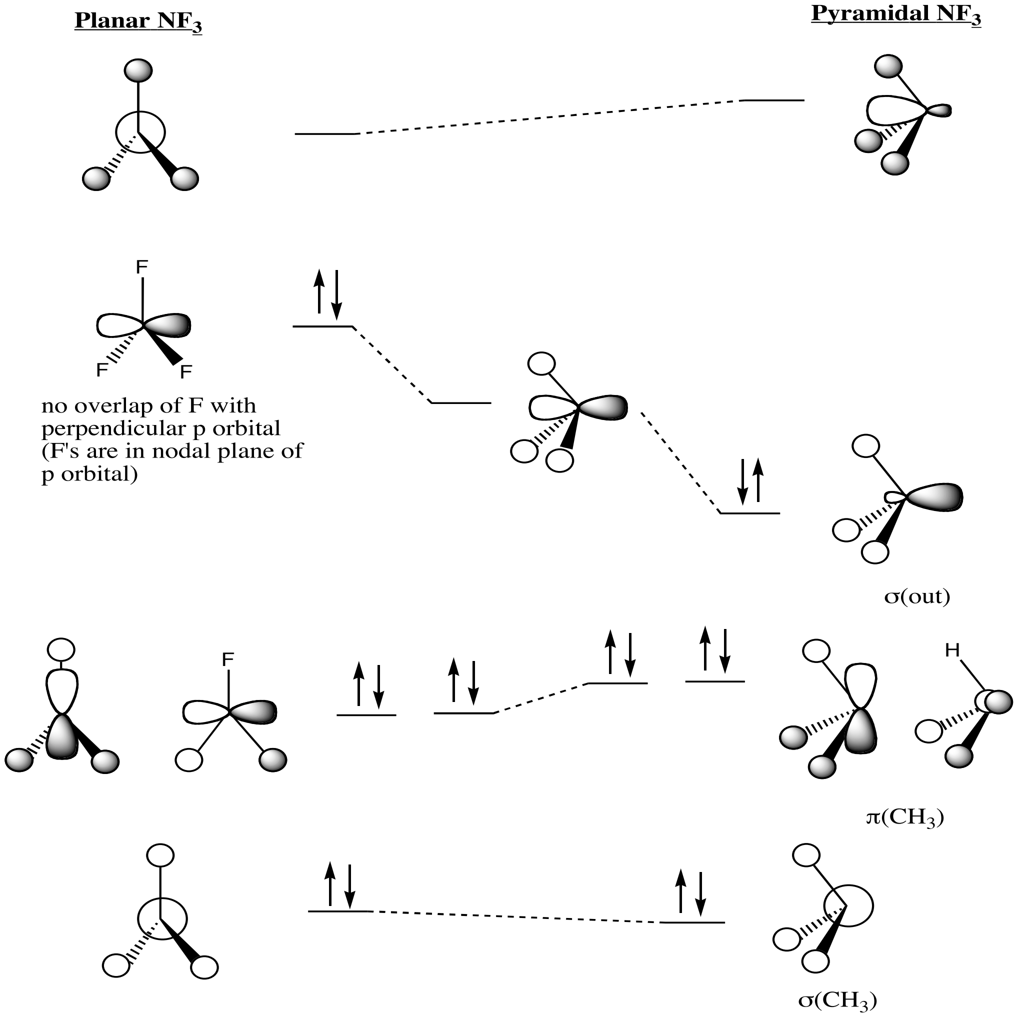


3 electrons from H
5 valence electrons from N
8 electrons total

Stabilization of σ(out) (doubly occupied) offsets destabilization of π(CH_3) (occupied by four electrons)

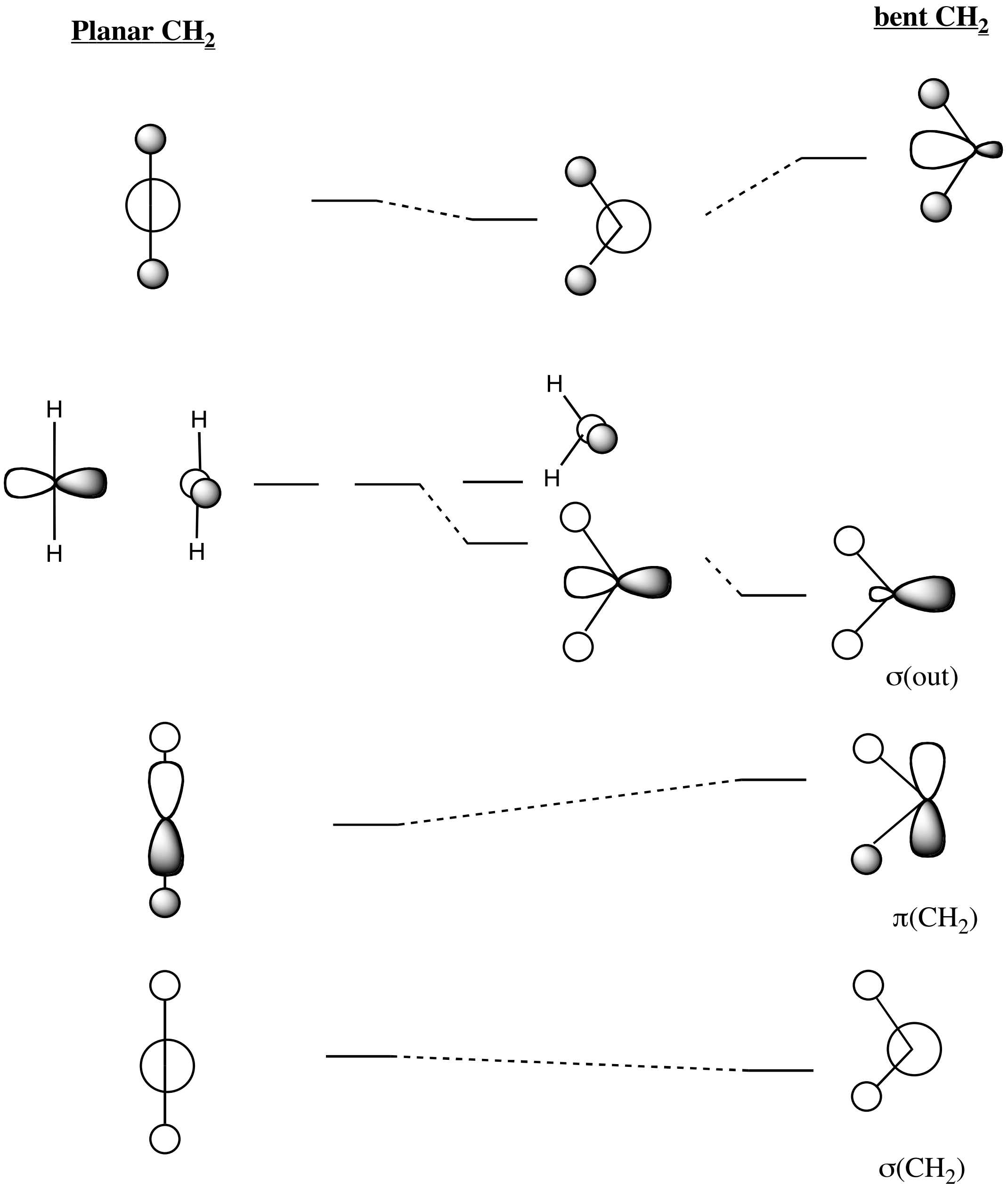
Ammonia is pyrimidal; barrier to inversion (via planar form) is small

F_3N: The effect of electronegative atoms

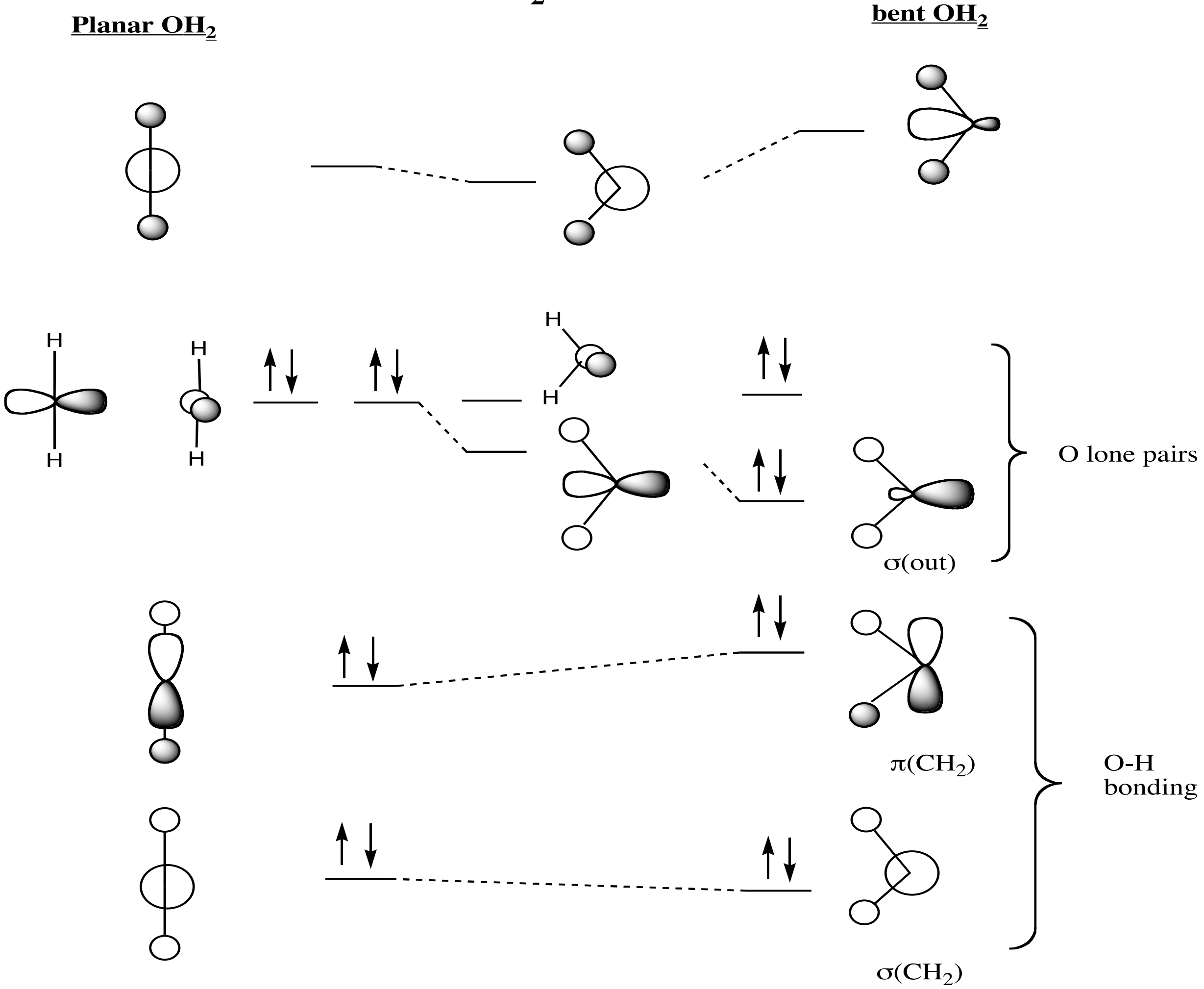


no overlap of F with
perpendicular p orbital
(F's are in nodal plane of
p orbital)

Electronegative elements lower the energy of all orbitals they contribute to:
F_3N is pyrimidal; barrier to inversion (via planar form)
is large


Planar CH_2
bent CH_2
H
H
H
H
H
H
σ(out)
$\pi(CH_2)$
$\sigma(CH_2)$

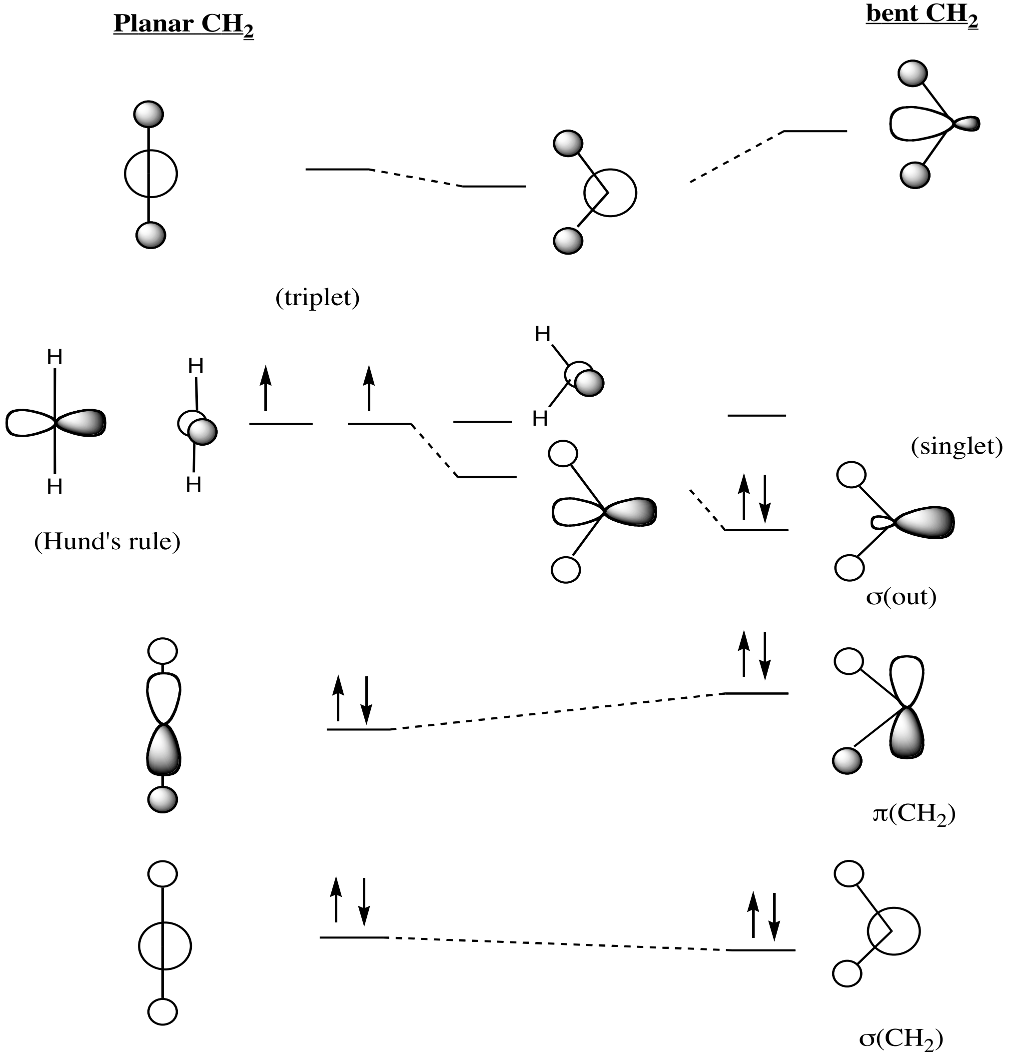
H_2O



2 electrons from H
6 valence electrons from O
8 total electrons

Water is bent because of the stabilization of the pair of electrons in σ(out). Note that the two lone pairs of water occupy non-equivalent orbitals.

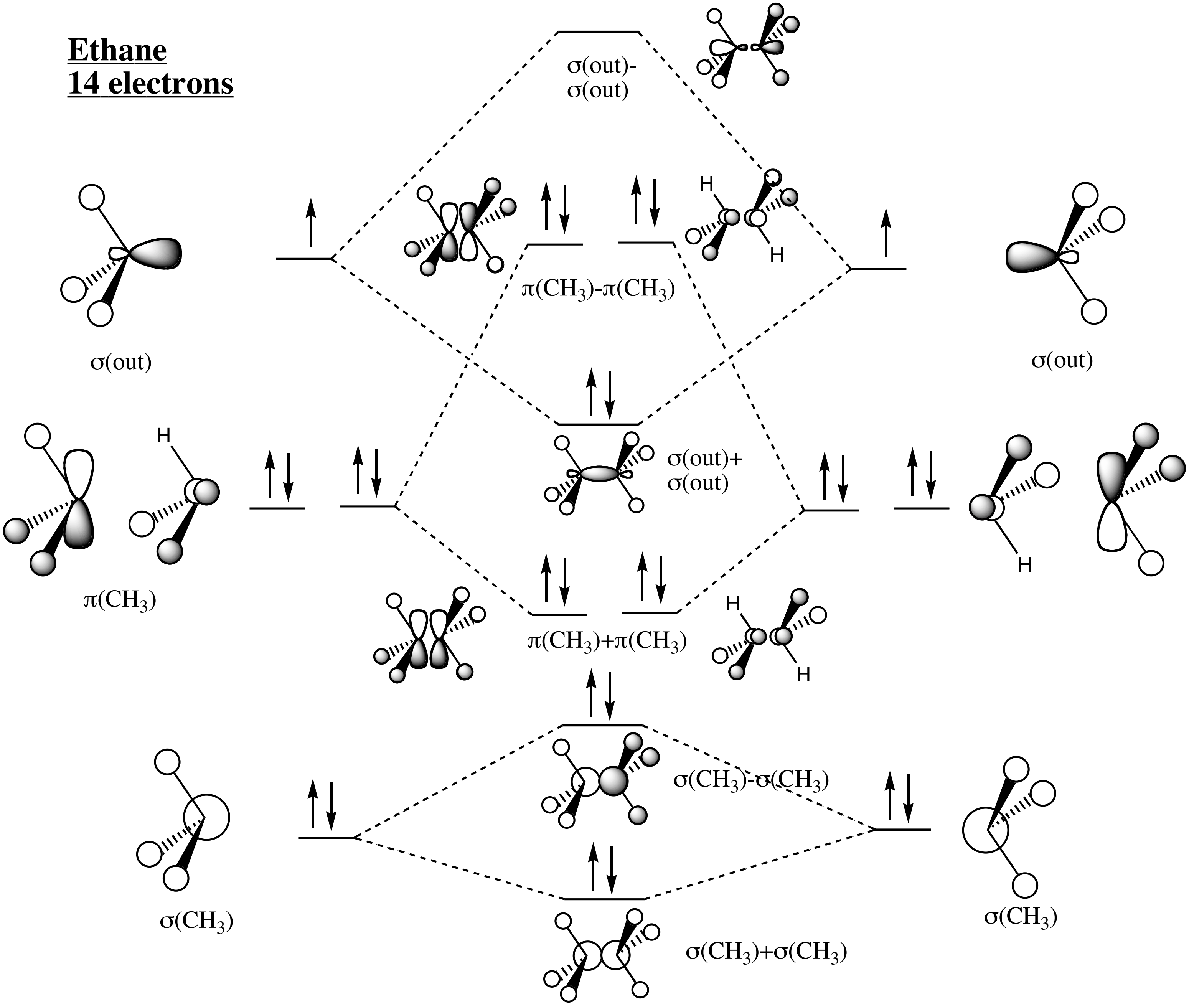
H_2C: (a carbene)



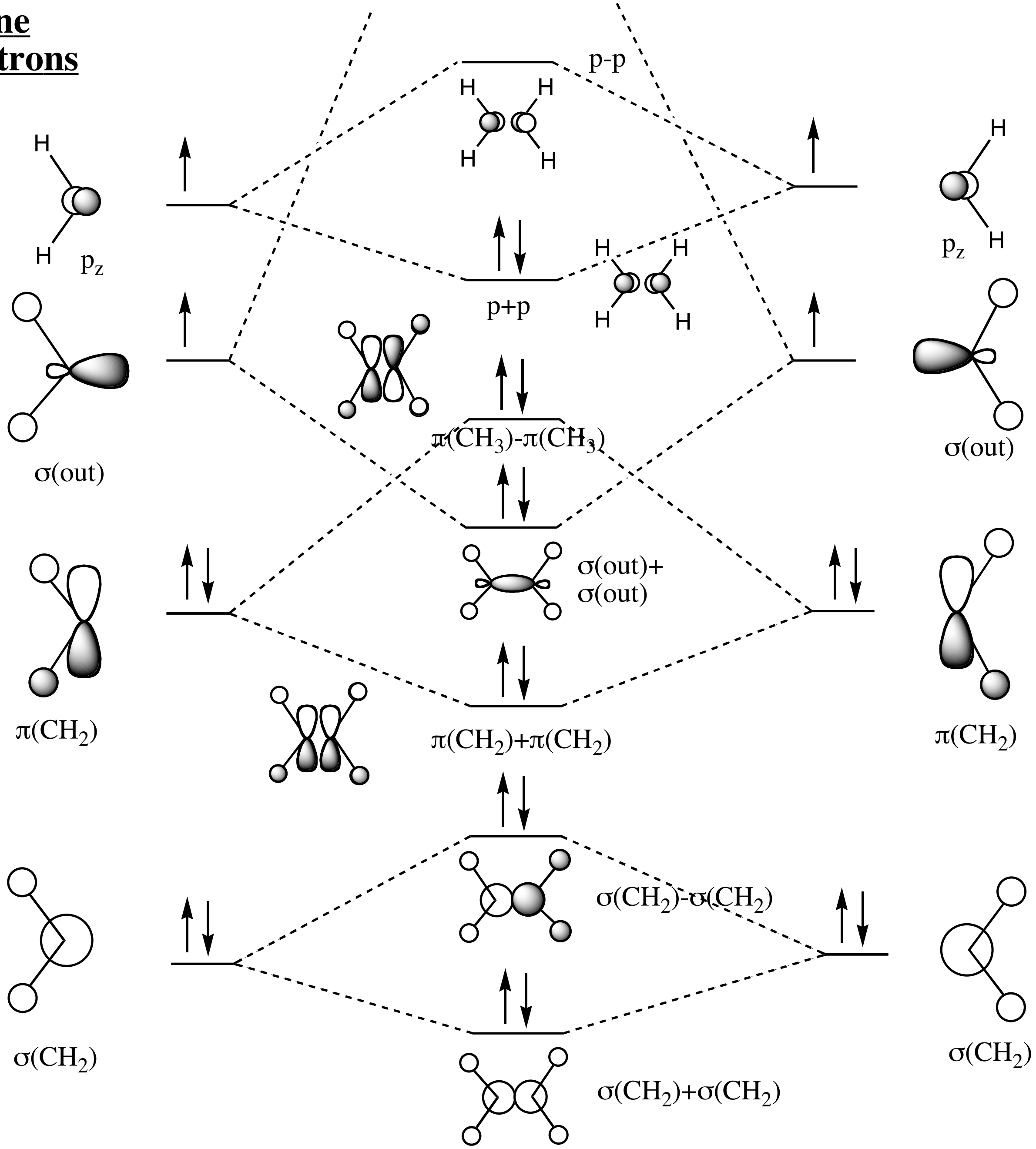
2 electrons from H
4 valence electrons from O
6 total electrons

A carbene can be singlet or triplet ground state depending upon geometry: linear prefers triplet, bent prefers singlet

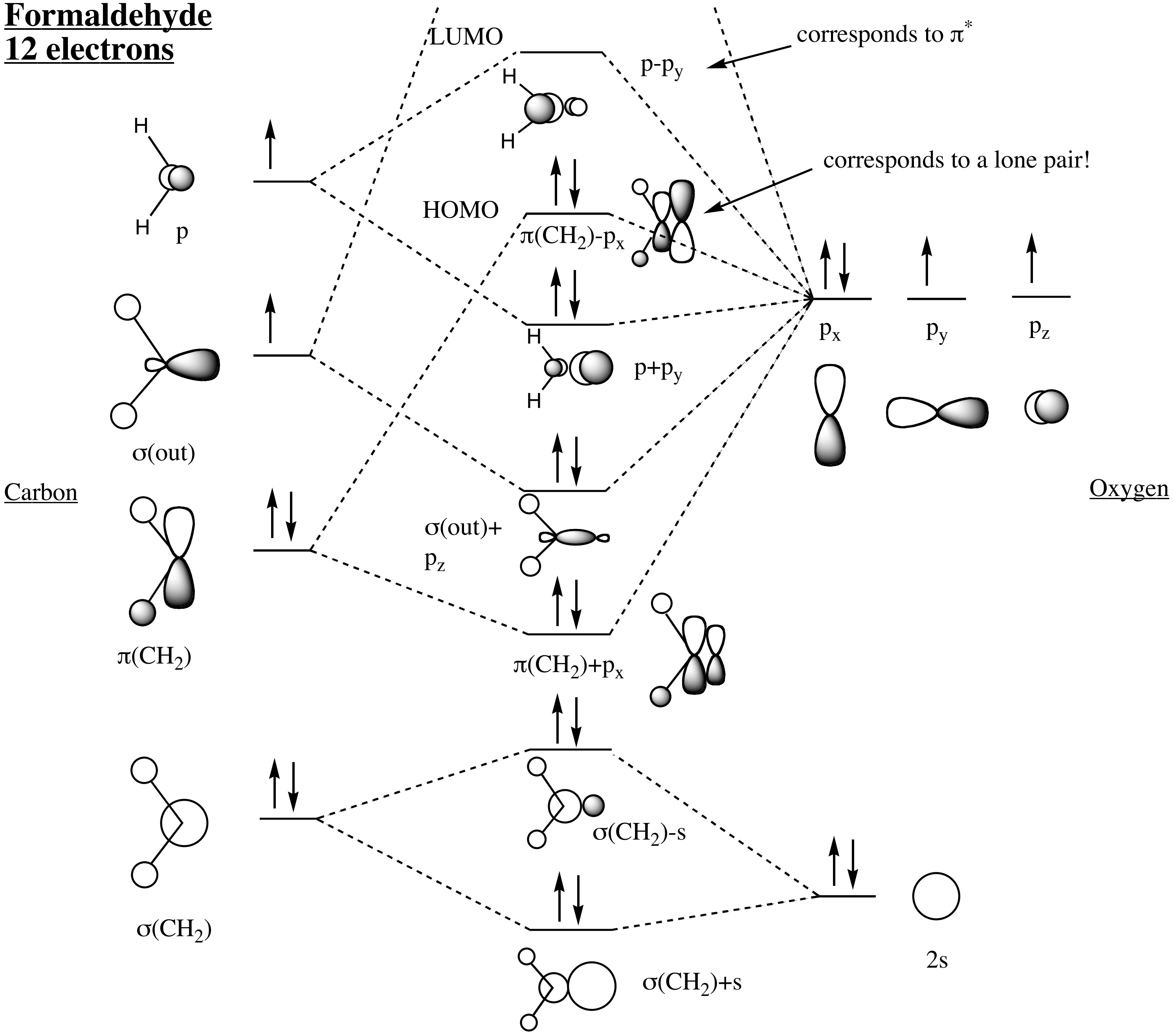
Ethane
14 electrons



Ethylene
12 electrons



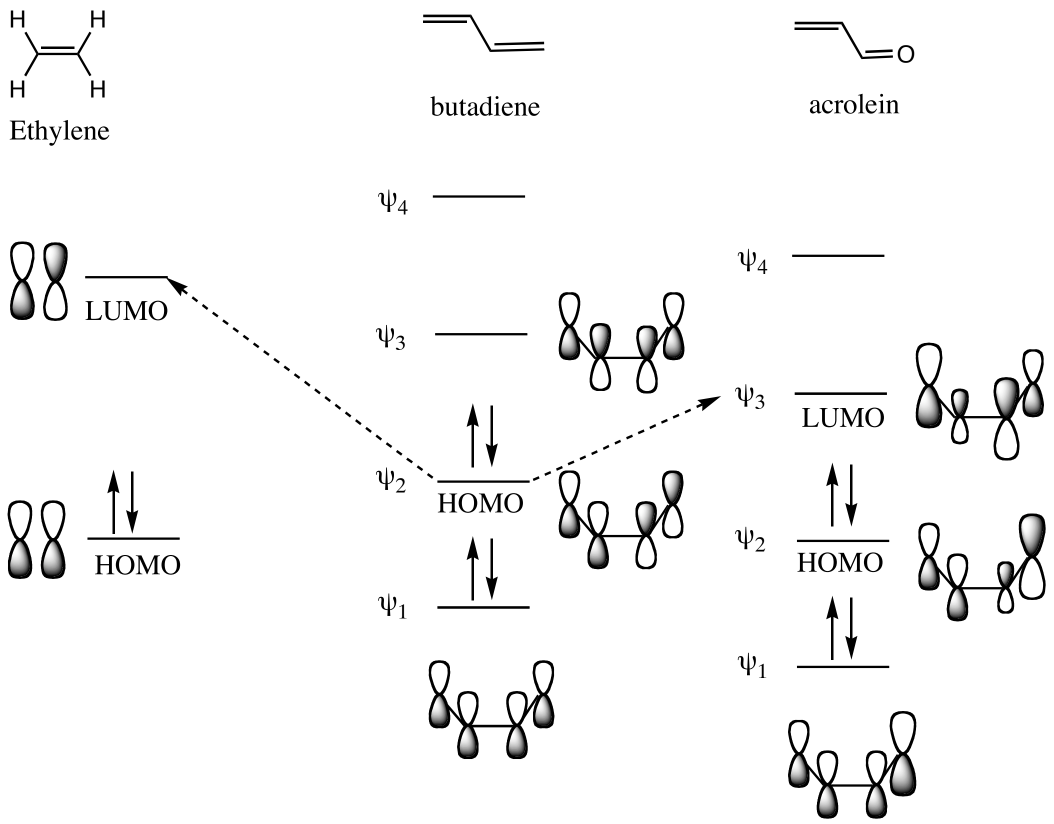
Formaldehyde
12 electrons



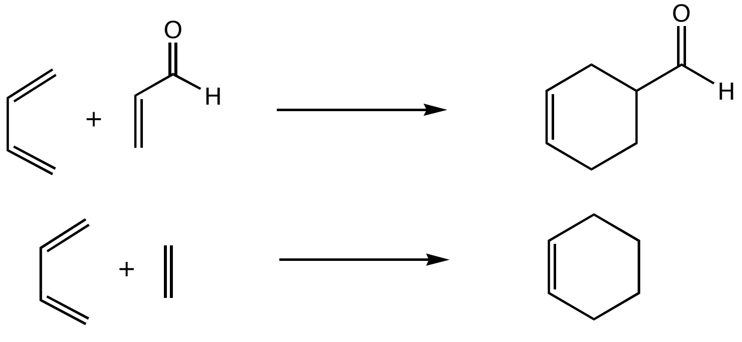
corresponds to π^*

corresponds to a lone pair!

Diels-Alder Reaction

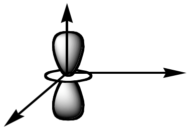


HOMO-LUMO gap smaller for butadiene-acrolein interaction than for butadiene-ethylene interaction

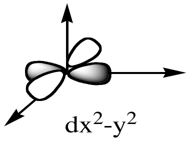


Organometallic Bonding

Sigma bonding orbitals



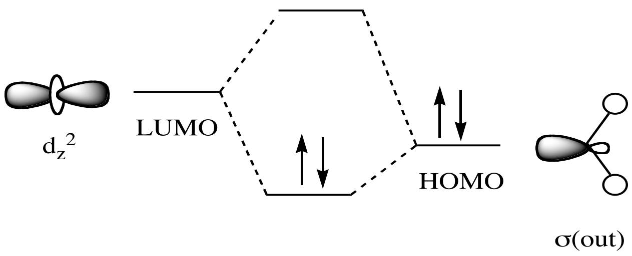
d_{z^2}



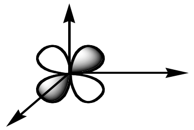
dx^2-y^2

point along bonding axes

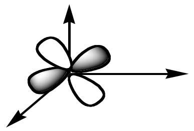
Example



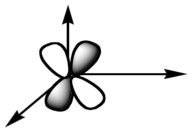
Pi bonding orbitals



dyz

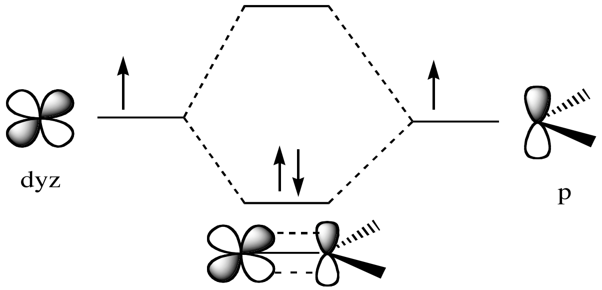


dxy



dxz

Examples



"back-bonding"