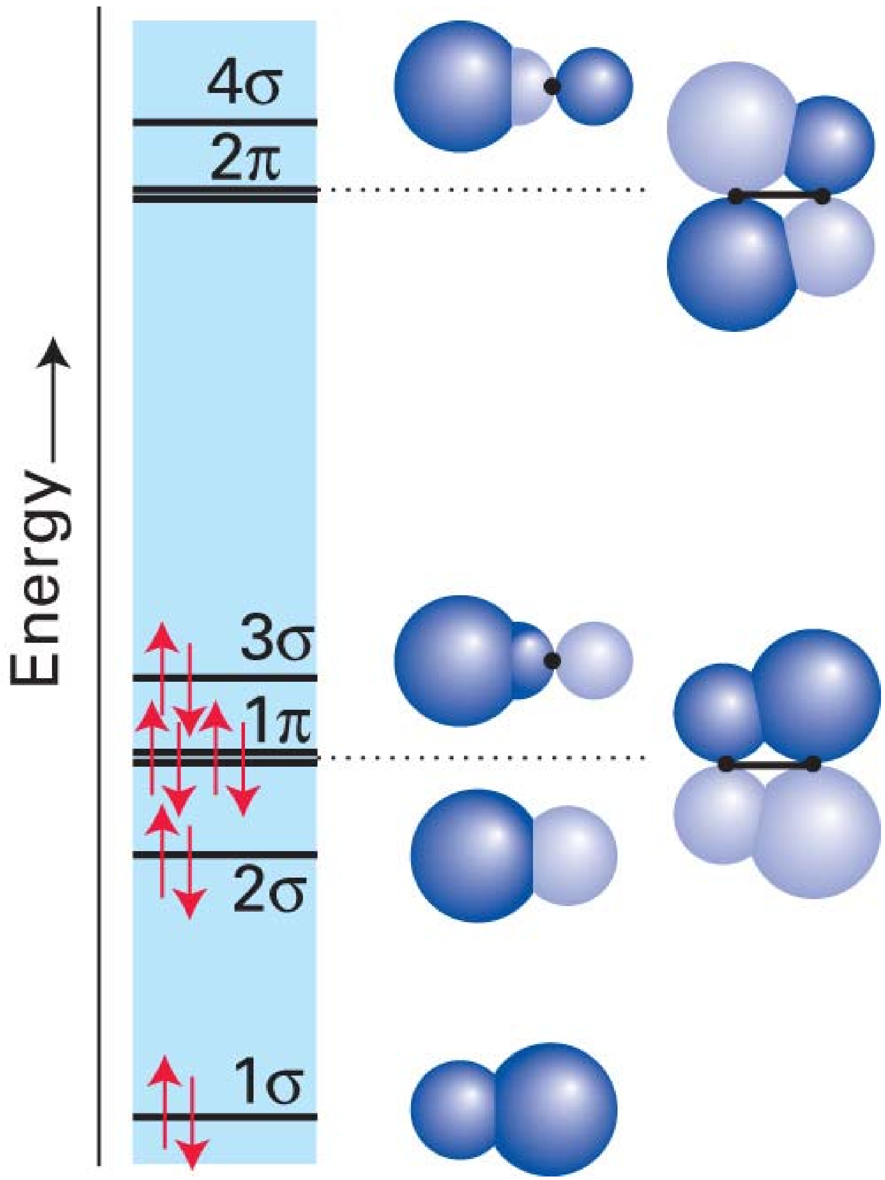
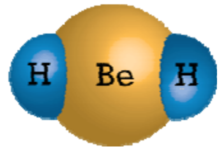
Lecture 17 MO Theory

- ***Delocalization as in benzene***
- ***Delocalization as in Carbon Monoxide and Metal Carbonyls***
- ***Delocalization as in Electron Deficient Molecules***

MO's for CO: the contour plots and significance for Metal Carbonyls

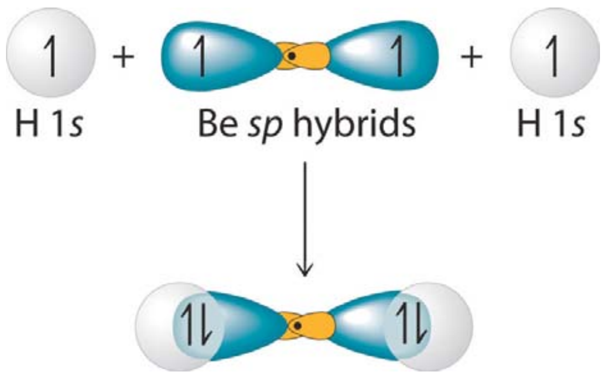


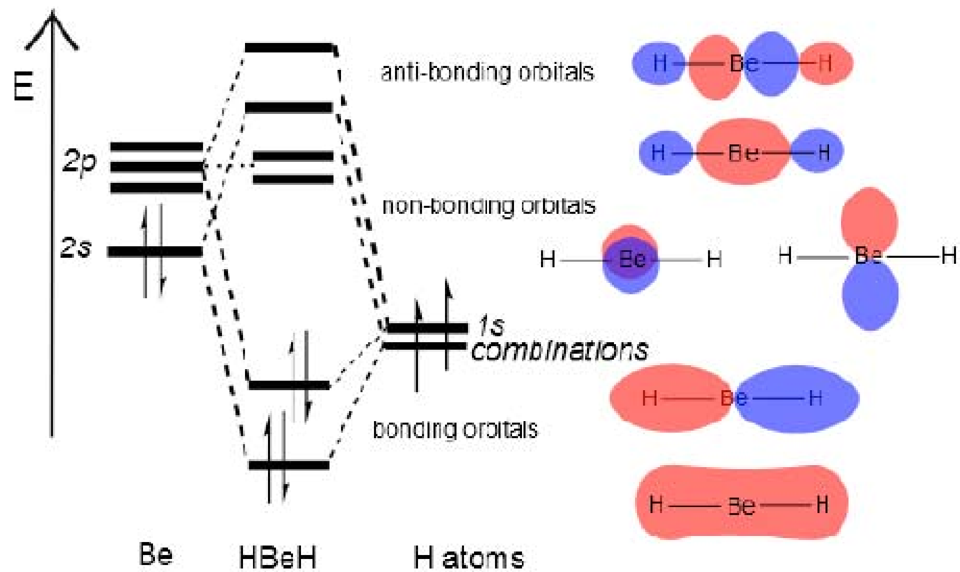
H:Be:H



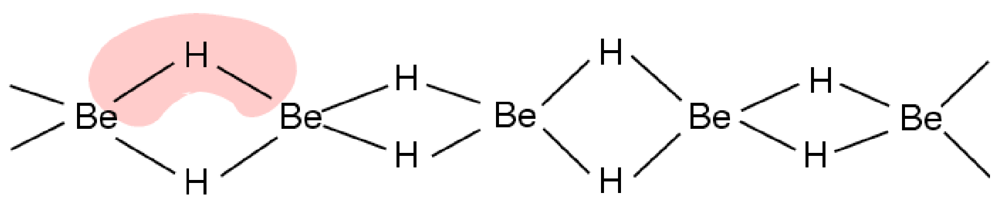
Molecular Orbitals

Localized or Valence Bonds:

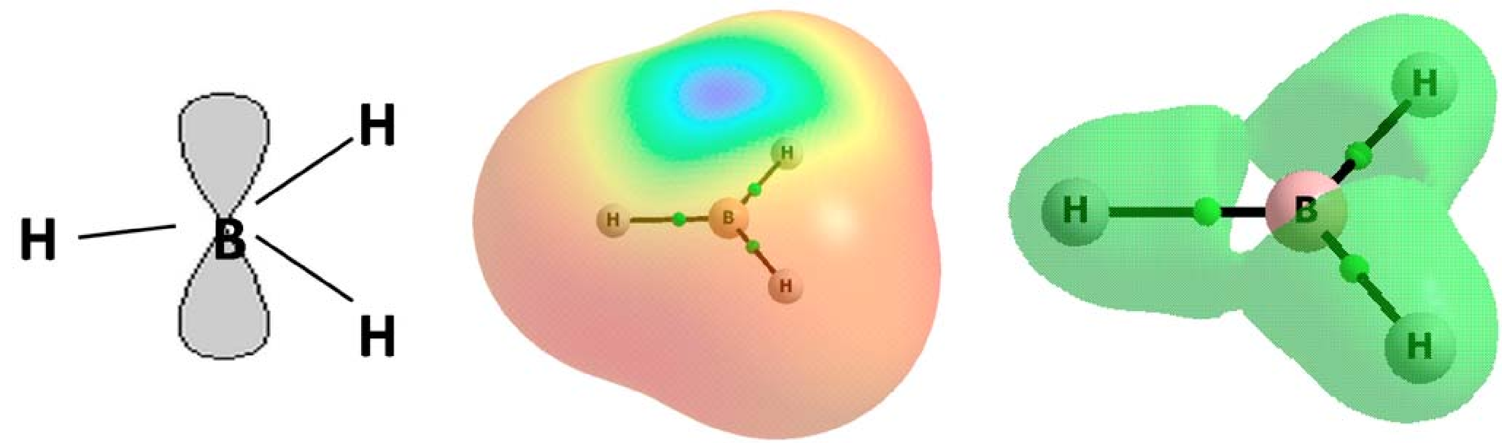




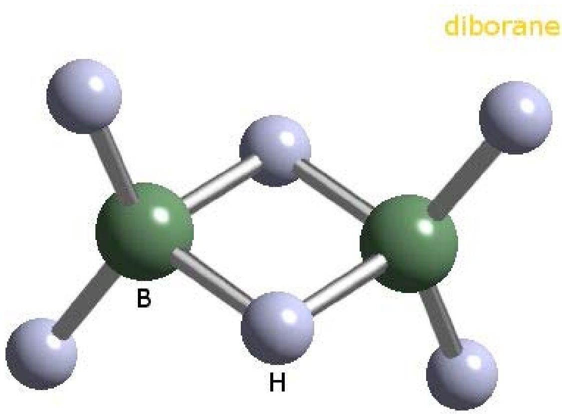
Electron Deficiency leads to aggregation via a bridging hydride

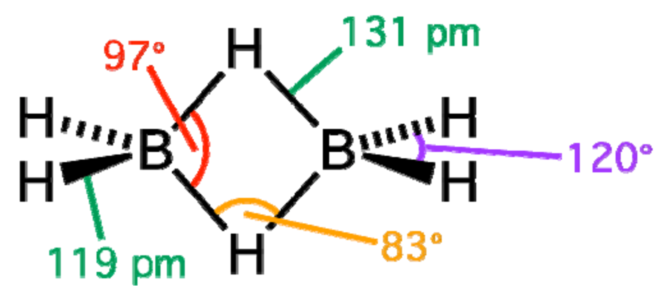


Electrophilic center in BH_3 accounts for its more stable structure as dimer, diborane



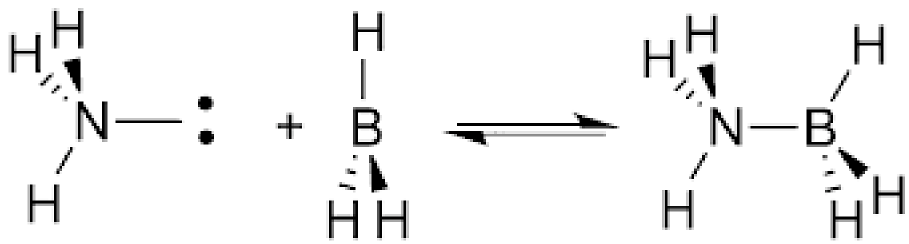
(a) (b) (c)



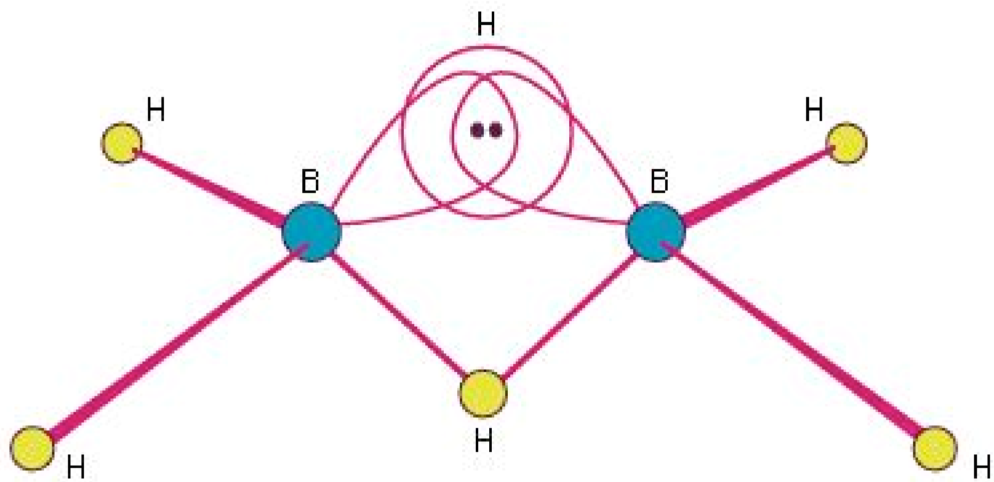


BH_3 dimerizes with 3-centered, 2-electron bond; in diborane, each B considered to be sp^3 hybrid—a quasi tetrahedron.

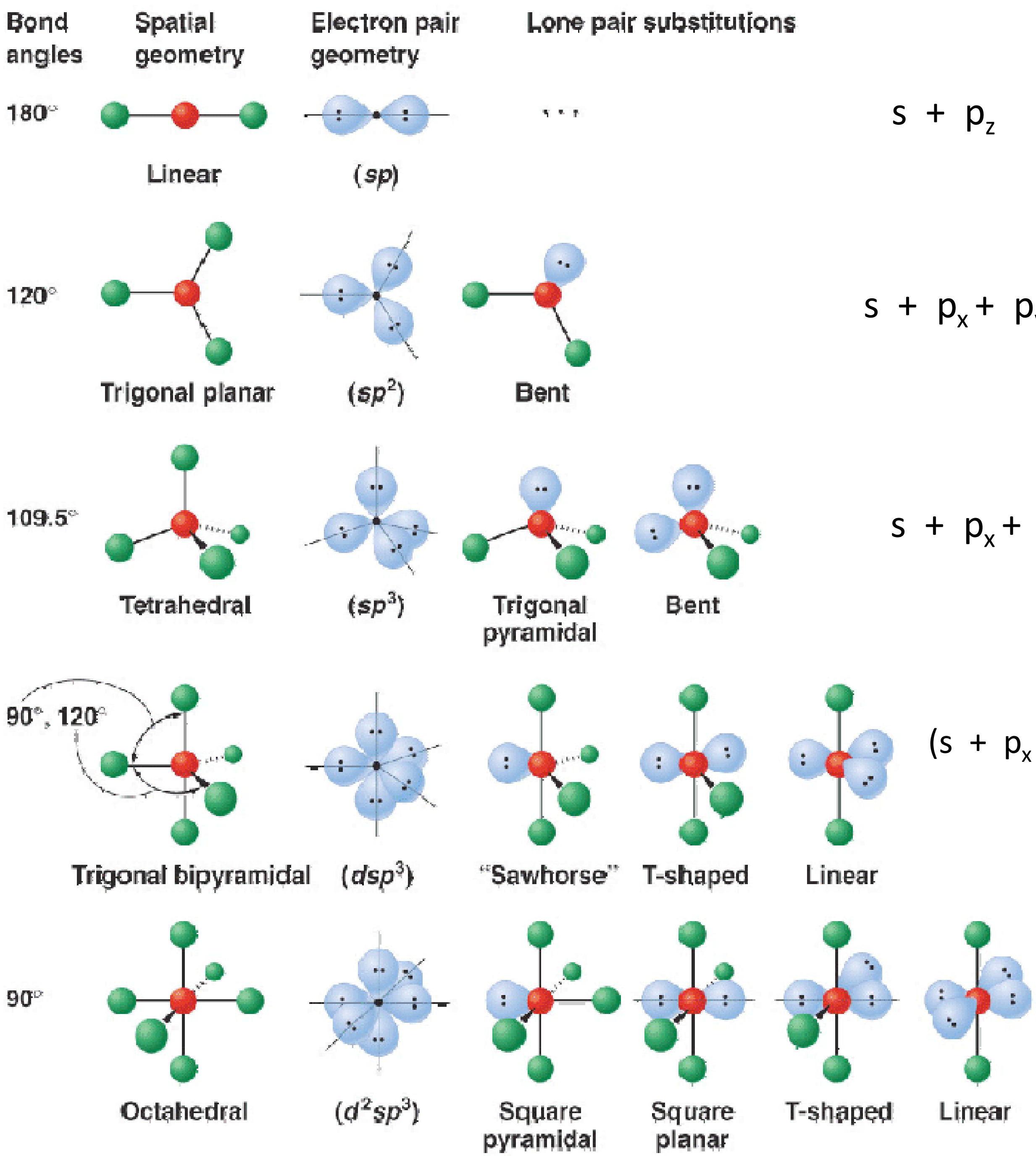
Two types of hydrogens are in diborane, 4 are terminal hydrides and 2 are bridged.



$$K = [NH_3\text{-}BH_3]/([NH_3][BH_3]) \sim 10^{55}$$



Describe Bridge bond by a combination of hybrid orbitals and delocalized MO's.



$s + p_z$

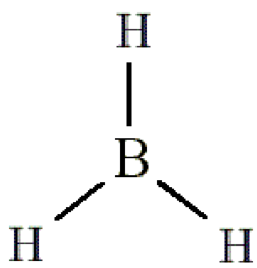
$s + p_x + p_y$

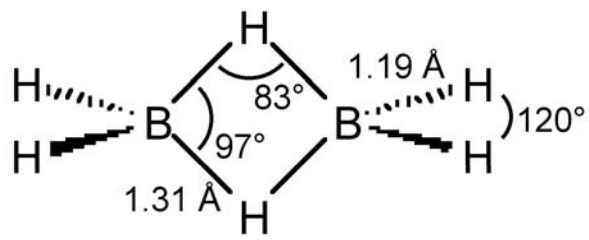
$s + p_x + p_y + p_z$

$(s + p_x + p_y) + (p_z + d_{z^2})$

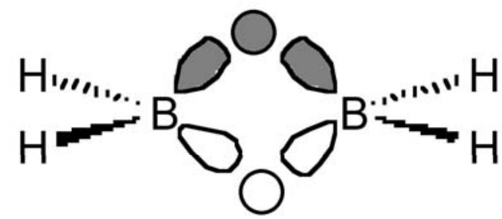
$s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2}$

Lessons from Borane: BH_3 and B_2H_6



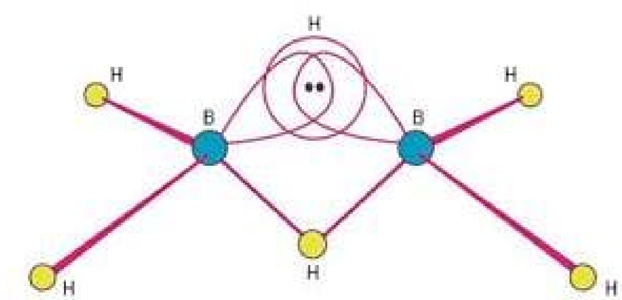


(a)

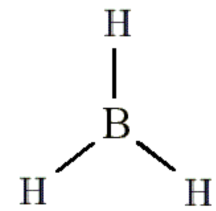


(b)

Terminal hydrides;
Bridging hydrides



Electron Deficient



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)